DOI: 10.1002/cjoc.201280008

MCM-41-SO_3H as a Highly Efficient Sulfonic Acid Nanoreactor for the Rapid and Green Synthesis of Some Novel Highly Substituted Imidazoles under Solvent-Free Condition

Mahdavinia, Gholam Hossein*,[a] Amani, Ali Mohammad[b] Sepehrian, Hamid[c]

[a] *Department of Chemistry, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran*
[b] *Department of Chemistry, KN Toosi University of Technology, P.O. Box 15875-4416, Tehran, Iran*
[c] *Jaber Ibn Hayan Research Laboratories, AEOI, P.O. Box 11365/8486, Tehran, Iran*

Nanosized MCM-41-SO_3H based on ordered mesoporous silica material with a covalent sulfonic acid group was synthesized and used as acid catalyst for the new, simple, convenient and green synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetra-substituted imidazoles. Also some of synthesis products are new. Echo-friendly protocol, short reaction times, easy and quick isolation of the products and excellent yields are the main advantages of this procedure.

Keywords MCM-41-SO_3H, nanocatalyst, highly substituted imidazoles, solvent-free condition, heterogeneous catalysis, nitrogen heterocycles

Introduction

In recent years more attractive possibilities have been emerged by the development of various new silica materials with ordered structure.[1] One of the best-known examples is MCM-41, which is a structurally well-ordered mesoporous material with a narrow pore size distribution between 1.5 and 10 nm, depending on the surfactant cation and a very high surface area up to 1500 $m^2 \cdot g^{-1}$.[2] It has been proved that Si-MCM-41 lacks Brönsted acid sites and exhibits only weak hydrogen-bonded type sites.[3,4] An additional possibility to develop acidic solids is the modification of the surface of suitable support materials, as the chemical functionalities of these materials can be uniformly modified by covalent anchoring of different organic moieties.[5] While several types of solid sulfonic acids have been created in recent years, there have been only a few reports about their applications as catalyst in chemical transformations. Furthermore, to the best of our knowledge, there is no report on the use of these materials as nanocatalysts in the synthesis of substituted imidazoles. The obtained nanocatalysts were tested for the synthesis of some new substituted imidazoles under solvent-free condition.

Interest in imidazole-containing structures arises from their widespread occurrence in molecules that exhibit significant biological activity such as fungicides, herbicides,[6] plant growth regulators,[7] anti-inflammatory,[8] anti-allergic[9] and analgesic agents.[10] In particular, 4,5-diaryl substituted imidazoles have been identified as potential inhibitors of p38 MAP kinase.[11] Moreover, the synthesis of substituted imidazoles has drawn attention due to these five-membered ring heterocycles, which are present in a wide range of naturally occurring molecules.[12] In the last decade numerous methods have been developed for the synthesis of highly substituted imidazoles by using various catalytic systems including SiO_2/$NaHSO_4$,[13] I_2,[14] heteropolyacid,[15] $HClO_4$-SiO_2,[16] $FeCl_3$-$6H_2O$,[17] *L*-proline,[18] BF_3•SiO_2,[19] WD/SiO_2,[20] SBSSA[21] and DABCO.[22] Also several methods comprise the use of microwave[23,24] and refluxing in SiO_2-H_2SO_4,[25] CH_3COOH,[26] $ZrCl_4$,[27] $NiCl_2$-$6H_2O$/Al_2O_3,[28] CAN,[29] $InCl_3$-$3H_2O$,[30] ionic liquids[31] and ionic liquids in ultrasound irradiation.[32] However, in spite of their potential utility, many of these methods suffer from drawbacks such as relatively low to moderate yield, use of toxic organic solvents, high temperatures and expensive instruments such as microwave and also corrosive reagents. Therefore, the search continues for a better catalyst for the synthesis of substituted imidazoles in terms of operational simplicity, economic viability and environmental care.

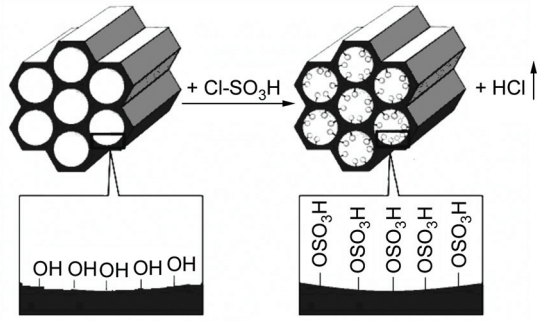
Results and Discussion

The MCM-41 was synthesised according to the previously described method using cetyltrimethylammonium bromide ($C_{16}H_{33}(CH_3)_3N^+Br^-$), as the templating agent.[33] The surfactant template was then removed from the synthesized material by calcination at 540 ℃

* E-mail: hmahdavinia@gmail.com
Received April 2, 2011; accepted October 24, 2011.

for 6 h. Then MCM-41 reacts with chlorosulfonic acid to give a white powder which was named "MCM-41-SO_3H". It is interesting to note that the reaction is easy and clean without any work-up procedure, because HCl gas is evolved from the reaction vessel immediately (Scheme 1).

Scheme 1 Schematic representation for the preparation of MCM-41-SO_3H

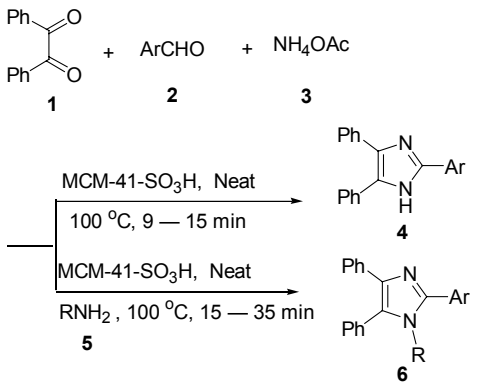


MCM-41-SO_3H nanoreactor was characterized by thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), and acid-base titrations.[34]

In continuation of our work on the development of useful synthetic methodologies toward synthesis of heterocyclic compounds, the catalytic activity of the Brønsted acid nanoreactor MCM-41-SO_3H was tested for the synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetra-substituted imidazoles under solvent-free condition (Scheme 2).

We attempted to find technically simple, high-yielding, solvent-free condition for the synthesis of these compounds. Therefore, we tried to use MCM-41-SO_3H as catalyst in the cyclocondensation of benzil, aldehyde, ammonium acetate and aniline. First of all, the reaction of 4-chlorobenzaldehyde (1 mmol), ammonium acetate (1.2 mmol) and benzil (1 mmol) catalyzed by MCM-41-SO_3H was investigated in different solvents under solvent-free condition, in which the results are shown in Table 1.

Scheme 2 MCM-41-SO_3H catalyzed synthesis of tri and tetra-substituted imidazoles



Initial screening studies confirmed that solvent-free technique is the optimal condition for this reaction. Another important point which could be elicited evidently from these results is that raising the reaction temperature from 60 to 100 ℃ increased the yield and also improved the reaction rates (Table 1, Entries 1—11). Moreover, it is worth mentioning that application of solvents such as H_2O, EtOH and CH_3OH did not lead to better results. Under these conditions, longer reaction times and very low yields can be observed clearly (Table 1, Entries 12—14). Furthermore, one of the most interesting points in this work is due to very large specific surface areas, highly ordered pore systems and moreover, the surface properties (inside the channels) of the modified sulfonic acid nanoreactor (MCM-41-SO_3H) which shows high activity.

Table 1 Synthesis of **4e** using different catalysts and reaction conditions

Entry	Catalyst (g)	Solvent	Temperature/℃	Time/min	Yield/%
1	No catalyst	Solvent free	60	390	—
2	MCM-41-SO_3H (0.01)	Solvent free	60	270	20
3	MCM-41-SO_3H (0.04)	Solvent free	60	210	20
4	MCM-41-SO_3H (0.04)	Solvent free	80	120	40
5	MCM-41-SO_3H (0.005)	Solvent free	90	70	65
6	MCM-41-SO_3H (0.01)	Solvent free	90	50	70
7	MCM-41-SO_3H (0.03)	Solvent free	90	45	70
8	MCM-41-SO_3H (0.04)	Solvent free	90	35	70
9	MCM-41-SO_3H (0.01)	Solvent free	100	30	78
10	MCM-41-SO_3H (0.04)	Solvent free	100	10	92
11	MCM-41-SO_3H (0.1)	Solvent free	100	10	92
12	MCM-41-SO_3H (0.04)	Methanol	Reflux	240	30
13	MCM-41-SO_3H (0.04)	Water	Reflux	270	trace
14	MCM-41-SO_3H (0.04)	Ethanol	Reflux	240	40

After optimization of the reaction condition for the synthesis of 2,4,5-triarylimidazoles **4a**—**4h** (Scheme 2, Table 2), the scope and generality of the catalytic role of MCM-41-SO_3H was examined by selecting a four component synthesis of 1,2,4,5-tetraarylimidazoles **6a**—**6l**. As expected, excellent yields of product were obtained under solvent-free condition with 0.04 g of MCM-41-SO_3H (Scheme 2, Table 3).

The scope and generality of the above process is illustrated with respect to the reactions of different aromatic primary amines and a wide range of aromatic aldehydes. Most importantly, it can be observed from Tables 2 and 3 that aromatic aldehydes carrying either electron-donating or electron-withdrawing groups did not show much difference and reacted very well, giving excellent yields.

We then continued our study to examine the reusability and recoverability of the catalyst as an additional important factor in the field of heterogonous nanocatalysts. To achieve this, the model reaction of 4-chlorobenzaldehyde (1 mmol), ammonium acetate (1.2 mmol) and benzil (1 mmol) was carried out in the presence of MCM-41-SO_3H (40 mg). After completion of the reaction, the MCM-41-SO_3H could be recovered as specified in the experimental section, the results of which are given in Table 4. These results showed a good recoverability and reusability of MCM-41-SO_3H for the synthesis of product **4e**. It can clearly be seen that even after four runs, the recovery percentage is high (Table 4).

The plausible mechanism for the synthesis of substituted imidazoles in the presence of MCM-41-SO_3H involves the initial formation of diamine intermediate (A). Intermediate (A), in the presence of MCM-41-SO_3H, cyclocondenses with benzil to form imidazol-5-ol intermediate (C), which in turn changes to substituted imidazoles by elimination of water (Scheme 3).

Conclusions

In conclusion, in comparison to the available synthetic methods for the synthesis of substituted imidazoles, we have developed a simple and highly efficient practical method for the one-pot synthesis of the title compounds using the MCM-41-SO_3H. The yields of products are very good and the use of toxic solvents is avoided. Using of MCM-41-SO_3H for synthesis of

Table 2 Preparation of trisubstituted imidazoles catalyzed by MCM-41-SO_3H under solvent free condition (Scheme 2)

Entry	Ar	Product	Time/min	Yield/%	m.p./℃	
					Found	Reported
1	4-$PhCH_2O$-C_6H_4	**4a**	15	92	232—233	—
2	4-MeCONH-C_6H_4	**4b**	9	70	289—290	—
3	3-Indol	**4c**	12	95	290—291	—
4	C_6H_5	**4d**	10	92	276—277	274—275[35]
5	4-Cl-C_6H_4	**4e**	10	92	264—265	261—263[35]
6	4-NO_2-C_6H_4	**4f**	15	85	196—197	196[27]
7	4-CN-C_6H_4	**4g**	10	95	236—237	232—235[36]
8	3-NO_2-C_6H_4	**4h**	14	90	196—197	196[27]
9	4-CHO-C_6H_4	**4i**	12	90	240—242	232—235[14]

Table 3 Preparation of tetrasubstituted imidazoles catalyzed by MCM-41-SO_3H under solvent free condition (Scheme 2)

Entry	Ar	R	Product	Time/min	Yield/%	M.p./℃	
						Found	Reported
1	4-CN-C_6H_4	Ph	**6a**	30	87	197—198	—
2	4-$PhCH_2O$-C_6H_4	Ph	**6b**	30	88	235—236	—
3	3-Indol	Ph	**6c**	20	98	247—249	—
4	C_6H_5	Ph	**6d**	25	91	224—225	221[14]
5	4-Cl-C_6H_4	Ph	**6e**	20	90	152—154	149—151[14]
6	4-NO_2-C_6H_4	Ph	**6f**	25	85	250—252	244—246[14]
7	4-Me-C_6H_4	Ph	**6g**	25	85	180—182	185—188[19]
8	4-MeO-C_6H_4	Ph	**6h**	25	98	172—174	184—185[14]
9	4-HO-C_6H_4	Ph	**6i**	15	89	279—281	280—281[14]
10	4-Cl-C_6H_4	$PhCH_2$	**6j**	20	92	162—165	162—165[19]
11	4-Me-C_6H_4	$PhCH_2$	**6k**	25	85	165—167	165—166[19]
12	4-MeO-C_6H_4	$PhCH_2$	**6l**	25	85	160—161	157—160[16]

Scheme 3 Plausible mechanism for the formation of substituted imidazoles

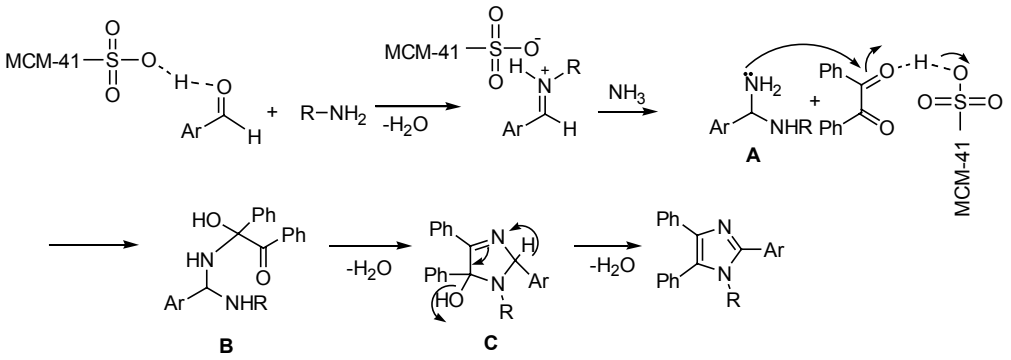


Table 4 The recycling of MCM-41-SO_3H in synthesis of **4e**

Entry	Time/min	Yield/%
1	10	92
2	10	92
3	10	85
4	10	83

highly substituted imidazoles and also synthesis of some novel substituted imidazoles under mild conditions is the most important aspect of this study. Simple work-up and a high degree of MCM-41-SO_3H reusability are the other interesting points of the developed procedure. We expect to find more applications for this catalytic system in organic synthesis.

Experimental

Synthesis and functionalization of MCM-41-SO_3H

MCM-41 was modified using a 100 mL suction flask equipped with a constant pressure dropping funnel containing chlorosulfonic acid (0.466 g, 0.004 mol) and a gas inlet tube for conducting HCl gas over an adsorbing solution. Into it was charged 1.20 g of MCM-41 and chlorosulfonic acid was then added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately. After completion of addition the mixture was shaken for 30 min, and the white solid (MCM-41-SO_3H) was obtained (1.52 g).[34]

General experimental procedure for the preparation of 2,4,5-triarylimidazole 4a—4h

A mixture of benzil (1 mmol), aldehyde (1 mmol) ammonium acetate (1.2 mmol) and MCM-41-SO_3H (0.04 g), were heated at 100 ℃ with stirring for 9—15 min. After completion of reaction (monitored by TLC) the mixture was cooled to room temperature and 20 mL chloroform/methanol (1∶1) was added. The catalyst was filtered off and the solids were washed with acetone (10 mL). The combined acetone solution was then concentrated in vacuum to afford crude product. The crystalline pure product was obtained by further recrystalization from 9∶1 acetone-water solution (Scheme 2).

General procedure for the synthesis of tetrasubstituted imidazoles 6a—6l

A mixture of benzil (1 mmol), aldehyde (1 mmol), ammonium acetate (1.2 mmol), aromatic amine (1 mmol) and MCM-41-SO_3H (0.04 g), was heated at 100 ℃ with stirring for 15—30 min. After completion of the reaction, same work-up procedure was followed in the synthesis of 2,4,5-triarylimidazoles (Scheme 2).

Spectral data of unknown compounds

2-(4-(Benzyloxyphenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4a) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 5.15 (s, CH_2, 2H), 7.13 (d, J=8.7 Hz, 2H), 7.20—7.58 (m, 15H), 8.04 (d, J=8.7 Hz, 2H), 12.54 (1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 69.3, 114.9, 123.4, 126.4, 126.7, 127.1, 127.3, 127.6, 127.7, 127.9, 128.1, 128.3, 128.4, 128.6, 131.2, 135.3, 136.8, 136.9, 145.6, 158.5; IR (KBr) ν_{max}: 3404, 3060, 1609, 1600 cm^{-1}; MS *m*/*z* (%): 77 (23.5), 91 (79), 152 (8.5), 165 (23), 283 (30), 311 (100), 402 (72) [M^+]. Anal. calcd for $C_{28}H_{22}N_2O$: C 83.56, H 5.51, N 6.96; found C 83.60, H 5.49, N 7.02.

2-(4-Acetamidophenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4b) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.06 (s, 3H, CH_3), 7.20—7.31 (m, 3H), 7.26—7.31 (m, 2H), 7.36—7.54 (m, 7H), 7.66 (d, J=8.7 Hz, 2H), 7.99 (d, J=8.7 Hz, 2H), 10.00 (1H, NH), 12.54 (1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 24.1, 118.9, 125.1, 125.7, 126.4, 127.0, 127.6, 127.8, 128.1, 128.4, 128.6, 131.1, 135.2, 136.9, 139.4, 145.5, 168.3; IR (KBr) ν_{max}: 3627, 3049, 1668, 1602, 1549 cm^{-1}; MS *m*/*z* (%): 77 (8.5), 165 (36.5), 311 (45.7), 353 (100) [M^+]. Anal. calcd for $C_{23}H_{19}N_3O$: C 78.16, H 5.42, N 11.89; found C 78.15, H 5.41, N 11.87.

3-(4,5-Diphenyl-1*H*-imidazol-2-yl)-1*H*-indole (Table 2, 4c) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.12—7.23 (m, 3H), 7.53 (d, J=7.1 Hz, 2H), 7.64 (d, J=7.1 Hz, 2H), 8.00 (d, J=7.1 Hz, 1H), 8.49 (dd, J=7.1, 6.8 Hz, 1H), 11.40 (1H, NH), 12.3 (1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 106.8, 111.6, 119.7, 121.5, 121.8, 123.8, 125.1, 125.7, 126.1, 126.9, 127.4, 128.2, 128.7, 131.6, 135.8, 136.0, 136.3, 143.7; IR (KBr) ν_{max}: 34.14, 3056, 1622, 1599 cm^{-1}; MS *m*/*z* (%): 77 (8.5), 101 (7.0), 128 (10.0), 204 (5.4), 231 (14.7), 335 (100) [M^+]. Anal. calcd for $C_{23}H_{17}N_3$: C 82.36, H 5.11, N 12.53; found C

82.33, H 5.14, N 12.48.

2,4,5-Triphenyl-1*H*-imidazole (Table 2, 4d) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.27—8.10 (m, 15H), 12.69 (1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 122.5, 127.0, 128.7, 129.2, 136.4.

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4e) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.21—8.10 (m, 14H), 12.77 (sbr, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 126.6, 126.8, 127.0, 127.8, 128.2, 128.4, 128.5, 128.6, 128.7, 129.1, 130.1, 132.7, 134.9, 137.2, 144.4.

2-(4-Nitrophenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4f) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.40—7.64 (m, 10H), 7.92 (d, J=8.0 Hz, 2H), 8.50 (d, J=8.0 Hz, 2H), 12.30 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 118.7, 122.5, 124.2, 125.4, 126.3, 126.8, 127.6, 127.8, 128.4, 129.7, 130.6, 131.5, 142.9, 148.7.

2-(4-Cyanophenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4g) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.31 (d, J=8.2 Hz, 2H), 7.51—7.86 (m, 10H), 7.89 (d, J=8.2 Hz, 2H), 11.85 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 110.3, 116.1, 122.4, 124.2, 124.9, 125.9, 126.4, 127.8, 127.9, 128.2, 129.7, 130.6, 131.5, 142.9, 147.9.

2-(3-Nitrophenyl)-4,5-diphenyl-1*H*-imidazole (Table 2, 4h) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.35—7.52 (m, 10H), 7.81 (d, J=8.0 Hz, 1H), 8.23 (d, J=7.8 Hz, 1H), 8.53 (d, J=7.5 Hz, 1H), 8.59 (s, 1H), 13.10 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 119.4, 122.6, 127.1, 128.4, 128.7, 130.4, 131.2, 131.8, 143.4, 148.4.

2-(4-Cyanophenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6a) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.18—7.35 (m, 9H), 7.51—7.56 (m, 6H), 7.92 (d, J=8.0 Hz, 2H), 8.25 (d, J=8.0 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 118.9, 125.5, 126.4, 127.1 128.2, 128.5, 128.6, 128.7, 129.3, 129.6, 131.0, 132,1, 132.7, 134.0, 134.2, 136.2, 143.7; IR (KBr) ν_{max}: 3060, 2225, 1608, 1490 cm^{-1}; MS m/z (%): 77 (35.5), 89 (19.0), 165 (194.1), 190 (15.0), 267 (8.0), 297 (10.0), 321 (27.0), 397 (100) [M$^+$]. Anal. calcd for $C_{28}H_{19}N_3$: C 84.61, H 4.82, N 10.57; found C 84.59, H 4.87, N 10.51.

2-(4-(Benzyloxy)phenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6b) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 5.15 (s, 2H, CH_2), 7.12 (d, J=8.5 Hz, 2H), 7.11—7.55 (m, 20H), 8.01 (d, J=8.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 69.3, 115.0, 123.4, 126.4, 126.7, 127.1, 127.7, 127.8, 128.2, 128.3, 128.5, 128.6, 129.2, 131.2, 135.3, 136.8, 136.9, 145.6, 158.5; IR (KBr) ν_{max}: 3054, 1578 cm^{-1}; MS m/z (%): 77 (35), 91 (91), 165 (64), 283 (16), 296(26), 311 (100), 387 (38), 402 (36.5), 478 (13) [M$^+$]. Anal. calcd for $C_{34}H_{26}N_2O$: C 85.33, H 5.48, N 5.85; found C 85.26, H 5.53, N 5.86.

3-(1,4,5-Triphenyl-1*H*-imidazol-2-yl)-1*H*-indole (Table 3, 6c) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.20 (s, 1H), 7.16—7.18 (m, 3H), 7.24—7.28 (m, 7H), 7.38—7.42 (m, 6H), 7.57—7.60 (d, J=7.5 Hz, 2H), 8.58 (s, 1H), 11.16 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 105.7, 111.1, 119.9, 121.8, 122.1, 123.4, 126.1, 128.3, 128.4, 129.0, 129.1, 129.4, 129.5, 130.8, 131.2, 134.9, 135.5, 136.2, 137.1, 143.5; IR (KBr) ν_{max}: 3419, 1603, 1570 cm^{-1}; MS m/z (%): 77(35), 165 (71), 206 (15.5), 297 (7.7), 353 (4), 410 (63.5), 411 (100) [M$^+$]. Anal. calcd for $C_{29}H_{21}N_3$: C 84.64, H 5.14, N 10.21; found C 84.65, H 5.12, N 10.21.

1,2,4,5-Tetraphenyl-1*H*-imidazole (Table 3, 6d) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.17—7.39 (m, 20H).

2-(4-Chlorophenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6e) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.30—7.60 (m, 15H), 7.69 (d, J=8.2 Hz, 2H), 7.97 (d, J=8.4 Hz, 2H).

2-(4-Nitrophenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6f) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.60—7.10 (m, 17H), 8.12 (d, J=8.7 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 123.4, 124.0, 124.2, 127.0, 127.9, 128.2, 128.5, 128.6, 128.7, 128.8, 128.9, 129.2, 129.3, 129.4, 129.5, 129.9, 131.0, 131.8, 133.8, 136.5, 136.6, 140.1, 144.2, 147.1.

2-(4-Methylphenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6g) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.85 (s, 3H, CH_3), 7.12 (d, J=8.2 Hz, 2H), 7.27—7.36 (m, 15H), 7.46 (d, J=7.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 21.3, 126.5, 127.4, 127.6, 127.8, 128.1, 128.2, 128.4, 128.8, 128.9, 130.6, 130.7, 131.1, 134.5, 137.2, 138.1, 147.1.

2-(4-Methoxyphenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6h) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.73 (s, 3H, OCH_3), 6.84 (d, J=8.3 Hz, 2H), 7.21—7.37 (m, 15H), 7.55 (d, J=7.5 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 55.2, 113.9, 123.3, 125.9, 126.2, 126.7, 127.2, 127.9, 128.5, 128.7, 129.0, 129.7, 130.3, 130.9, 131.0, 134.5, 137.6, 147.9, 159.9.

2-(4-Hydroxyphenyl)-1,4,5-triphenyl-1*H*-imidazole (Table 3, 6i) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 6.84—7.50 (m, 17H), 7.75 (d, J=8.4 Hz, 2H), 8.37 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 123.2, 123.9, 124.3, 127.1, 127.3, 127.4, 127.7, 128.1, 128.5, 128.8, 129.1, 129.4, 129.6, 130.1, 131.0, 132.1, 134.0, 136.2, 136.9, 139.2, 144.4, 158.1.

1-Benzyl-2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (Table 3, 6j) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 5.11 (s, 2H, CH_2), 6.97—7.98 (m, 19H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 48.1, 125.5, 126.0, 126.5, 127.2, 128.1, 128.4, 128.5, 128.9, 129.5, 130.1, 130.2, 130.4, 130.6, 133.8, 134.9.

1-Benzyl-2-(4-methylphenyl)-4,5-diphenyl-1*H*-imidazole (Table 3, 6k) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.45 (s, 3H, CH_3), 5.09 (s, 2H, CH_2), 6.80 (d, J=4.2 Hz, 2H), 7.12—7.33 (m, 13H), 7.57 (d, J=7.5 Hz, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 21.3, 48.2, 125.9, 126.2, 126.7, 127.2, 128.0, 128.5, 128.7, 128.9, 129.2, 129.8, 131.0, 131.1, 134.5, 137.6, 137.9, 138.8, 148.2.

1-Benzyl-2-(4-methoxylphenyl)-4,5-diphenyl-1*H*-imidazole (Table 3, 6l) ^{1}H NMR (300 MHz, DMSO-d_6) δ: 3.81 (s, 3H, OCH_3), 5.08 (s, 2H, CH_2),

6.80—6.92 (m, 4H), 7.12—7.31 (m, 11H), 7.58 (d, J= 7.8 Hz, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ: 48.1, 55.2, 113.9, 123.3, 125.9, 126.2, 126.7, 127.2, 127.9, 128.5, 128.7, 129.0, 129.7, 130.3, 130.9, 131.0, 134.5, 137.6, 147.9, 159.9

References

[1] Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

[2] Zhang, W.; Pauly, T. R.; Pinnavaia, T. J. *Chem. Mater.* **1997**, *9*, 2491.

[3] Galarneau, A.; Desplantier-Giscard, D.; Di Renzo, F.; Fajula, F. *Catal. Today* **2001**, *68*, 191.

[4] Gusev, V. Y.; Feng, X.; Bu, Z.; Haller, G. L.; O'Brien, J. A. *J. Phys. Chem.* **1996**, *100*, 1985.

[5] Hoffmann, F.; Cornelius, M.; Morell, J.; Fröba, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.

[6] Maier, T.; Schmierer, R.; Bauer, K.; Bieringer, H.; Buerstell, H.; Sachse, B. *US 4820335* **1989** [*Chem. Abstr.* **1989**, *111*, 19494].

[7] Schmierer, R.; Mildenberger, H.; Buerstell, H. *US 4786312* **1988**, [*Chem. Abstr.* **1988**, *108*, 37838].

[8] Misono, M. *Chem. Commun.* **2001**, 1141.

[9] Black, J. W.; Durant, G. J.; Emmett, J. C.; Ganellin, C. R. *Nature* **1974**, *248*, 65.

[10] Ucucu, U.; Karaburun, N. G.; Iskdag, I. *Il Farmaco* **2001**, *56*, 285.

[11] Murry, J. A. *Curr. Opin. Drug Discov. Dev.* **2003**, *6*, 945.

[12] Ho, J. Z.; Hohareb, R. M.; Ahn, J. H.; Sim, T. B.; Rapoport, H. *J. Org. Chem.* **2003**, *68*, 109.

[13] Karimi, A. R.; Alimohammadi, Z.; Azizian, J.; Mohammadi, A. A.; Mohmmadizadeh, M. R. *Catal. Commun.* **2006**, *7*, 728.

[14] Kidwai, M.; Mothsra, P.; Bansal, V.; Somvanshi, R. K.; Ethayathulla, A. S.; Dey, S.; Singh, T. P. *J. Mol. Catal. A: Chem.* **2007**, *265*, 177.

[15] Heravi, M. M.; Derikvand, F.; Bamoharram, F. F. *J. Mol. Catal. A: Chem.* **2007**, *263*, 112.

[16] Kantevari, S.; Vuppalapati, S. V. N.; Biradar, D. O.; Nagarapu, L. *J. Mol. Catal. A: Chem.* **2007**, *266*, 109.

[17] Heravi, M. M.; Derikvand, F.; Haghighi, M. *Monatsh. Chem.* **2008**, *139*, 31

[18] Samai, S.; Nandi, G. C.; Singh, P.; Singh, M. S. *Tetrahedron* **2009**, *65*, 10155.

[19] Sadeghi, B.; Mirjalili, B. B. F.; Hashemi, M. M. *Tetrahedron Lett.* **2008**, *49*, 2575.

[20] Karimi, A. R.; Alimohammadi, Z.; Amini, M. M. *Mol. Divers.* **2009**, doi:10.1007/s11030-009-9197-x.

[21] Niknam, K.; Mohammadizadeh, M. R.; Mirzaee, S.; Saberi, D. *Chin. J. Chem.* **2010**, *28*, 663.

[22] Murthy, S. N.; Madhav, B.; Nageswar, Y. V. D. *Tetrahedron Lett.* **2010**, *51*, 5252.

[23] Oskooie, H. A.; Alimohammadi, Z.; Heravi, M. M. *Heteroatom. Chem.* **2006**, *17*, 699.

[24] Zhou, J.-F.; Gong, G.-X.; Sun, X.-J.; Zhu, Y.-L. *Synth. Commun.* **2010**, *40*, 1134.

[25] Shaabani, A.; Rahmati, A.; Farhangi, E.; Badri, Z. *Catal. Commun.* **2007**, *8*, 1149.

[26] Wang, J.; Mason, R.; Derveer, D. V.; Feng, K.; Bu, X. R. *J. Org. Chem.* **2003**, *68*, 5415.

[27] Sharma, G. V. M.; Jyothi, Y.; Lakshmi, P. S. *Synth. Commun.* **2006**, *36*, 2991.

[28] Heravi, M. M.; Bakhtiari, K.; Oskooie, H. A.; Taheri, S. *J. Mol. Catal. A: Chem.* **2007**, *263*, 279.

[29] Sangshetti, J. N.; Kokare, N. D.; Kotharkara, S. A.; Shinde, D. B. *J. Chem. Sci.* **2008**, *5*, 463.

[30] Sharma, S. D.; Hazarika, P.; Konwar, D. *Tetrahedron Lett.* **2008**, *49*, 2216.

[31] Siddiqui, S. A.; Narkhede, U. C.; Palimkar, S. S.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. *Tetrahedron* **2005**, *61*, 3539.

[32] Zang, H.; Su, Q.; Mo, Y.; Cheng, B.-W.; Jun, S. *Ultrason. Sonochem.* **2010**, *17*, 749.

[33] Sayari, A. H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2920.

[34] (a) Rostamizadeh, S.; Amani, M. A.; Mahdavinia, G. H.; Amiri, G.; Sepehrian, H. *Ultrason. Sonochem.* **2010**, *17*, 306; (b) Rostamizadeh, S.; Amani, M. A.; Mahdavinia, G. H.; Sepehrian, H.; Ebrahimi, S. *Synthesis* **2010**, 1356.

[35] Khodaei, M. M.; Bahrami, K.; Kavianinia, I. *J. Chin. Chem. Soc.* **2007**, *54*, 829.

[36] Zhao, N.; Wang, Y.-L.; Wang, J.-Y. *J. Chin. Chem. Soc.* **2005**, *52*, 535.

(E1104021 Zhao, X.)

