Synlett Á. Magyar, Z. Hell Letter

One-Pot Three-Component Synthesis of 2,4,5-Triaryl-1*H*-imidazoles in the Presence of a Molecular Sieve Supported Titanium Catalyst under Mild Basic Conditions

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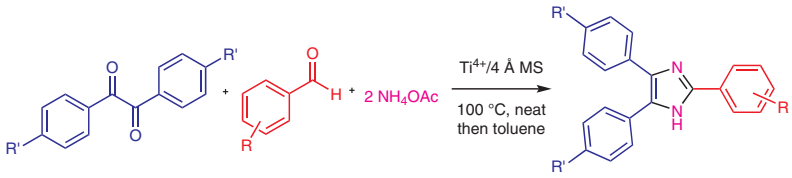


R = H, halogen, methyl, methoxy, OH

15 examples
58–86% yield

Received: 16.08.2018
Accepted after revision: 09.11.2018
Published online: 30.11.2018
DOI: 10.1055/s-0037-1611155; Art ID: st-2018-d0693-l

Abstract A series of 2,4,5-trisubstituted-imidazoles has been synthesized with good to excellent yields by the one-pot condensation reaction of 1,2-dicarbonyl compounds, benzaldehydes, and ammonium acetate in the presence of 4 Å molecular sieves modified with titanium(IV) as an efficient heterogeneous catalyst. The catalyst could be recovered easily and reused without significant loss of activity.

Keywords 2,4,5-triaryl-1*H*-imidazoles, multicomponent reactions, titanium, 4 Å molecular sieves, heterogeneous catalysis

Imidazole and its derivatives represent a highly important class of *N*-heterocycles that are the subject of intensive current research due to their wide range of pharmacological and biological properties.[1] The potential and wide range of application of the imidazole pharmacophore may be attributed to its hydrogen bond donor–acceptor ability, as well as its high affinity for metals, which are present in many protein active sites (e.g., Zn, Fe, Mg).[2] Substituted imidazoles have been demonstrated to be inhibitors of B-Raf kinase,[3] glucagon receptors,[4] and p38 MAP kinase,[5] or to act as antibacterial,[6] antifungal,[7] anti-inflammatory,[8] antitumor agents,[9] pesticides,[10] and plant-growth regulators.[11] Recent advances in green chemistry and organometallic catalysis have extended the utilization of imidazoles as ionic liquids[12] and *N*-heterocyclic carbenes.[13] They are also central components of existing drugs such as losartan, irbesartan,[14] and trifenagrel[15].

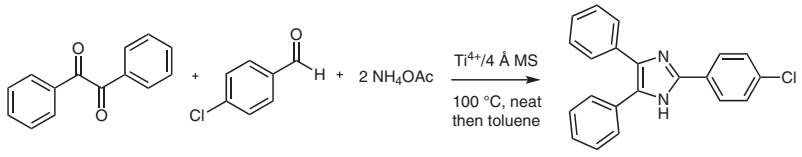
Multicomponent reactions (MCRs) have been the focus of much interest in recent years. They are one-pot processes starting from three or more components and can provide complex molecular structures with shortened reaction times, increased yields, and less side products compared to conventional reaction strategies. Therefore, it is not surprising, that the elaboration of new MCRs and the development of known multicomponent reactions are areas of considerable current interest.

Several methods have been reported in the literature for the synthesis of polysubstituted imidazoles. 2,4,5-Trisubstituted imidazoles are generally synthesized by the three-component cyclocondensation of a 1,2-diketone, α-hydroxyketone, or α-ketomonoxime with an aldehyde and ammonium acetate, under the influence of acidic catalysts such as silica sulfuric acid,[16] acetic acid,[17] $TiCl_4/SiO_2$,[18] $InCl_3·3H_2O$,[19] $UO_2(NO_3)_2·6H_2O$ supported on acidic alumina,[20] ceric ammonium nitrate (CAN),[21] ionic liquids,[22] and microwave irradiation.[23]

Many of the synthetic methods for imidazole synthesis suffer from one or more disadvantages, such as harsh reaction conditions,[17] tedious workup procedure,[17] and application of hazardous and expensive catalysts and/or reagents.[18–21] Thus the development of a simpler method requiring milder conditions is synthetically significant.

Our research group works on the elaboration of new heterogeneous catalytic methods for the preparation of organic compounds using supported metal catalysts. During this work, several supported metal catalysts were used with good to excellent yields in different organic syntheses, for example 4 Å molecular sieves supported copper,[24] lanthanum,[25] titanium,[26] and zinc catalysts.[27] In this communication we report a method for the one-pot three-component synthesis of 2,4,5-triaryl-1*H*-imidazoles promoted by a heterogeneous, 4 Å molecular sieve supported titanium catalyst.

In the literature, acidic catalysts have mainly been used for the one-pot three-component preparation of 2,4,5-triaryl-1*H*-imidazoles. There is an example for the use of a titanium compound, $TiCl_4/SiO_2$ as catalyst for this cyclization, which is also acidic in nature. Our Ti^{4+}/4 Å MS catalyst is slightly basic in the bulk phase (pH = 7.35). As this catalyst



1a 2e 3 4e

Scheme 1 Ti^{4+}/4 Å MS catalyzed synthesis of **4e**

was used successfully for the THP protection of alcohols, which is an acid-catalyzed conversion,[26] we examined the reaction of benzil, different aromatic aldehydes, and ammonium acetate as nitrogen source in the presence of this catalyst.

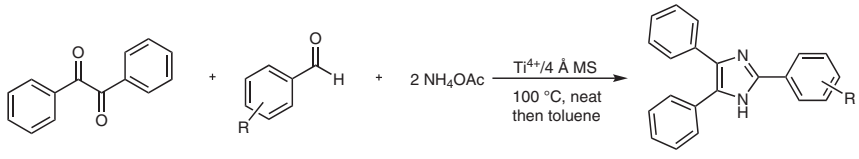
Initially, we reacted benzil, 4-chlorobenzaldehyde, and ammonium acetate (in 10 mol% excess) without solvent, at 100 °C (Scheme 1). After 1 h, the reaction mixture solidified, thus a small quantity of toluene had to be added. After 10 h, TLC analysis of the reaction mixture showed that the benzil had been completely consumed. After the workup, the desired product was obtained in 80% yield. When toluene was added at the outset of the reaction, the yield decreased significantly.

We examined the reaction using a range of aldehydes. As the later addition of toluene gave a better result in our initial study, we used these reaction conditions (neat for 1 h, then 1 mL toluene, 100 °C, 10 h) throughout. The results are summarized in Table 1.

Substituted aromatic aldehydes reacted with benzil and ammonium acetate in the presence of the Ti^{4+}/4 Å MS catalyst to give the corresponding 2,4,5-trisubstituted imidazoles in good yields. In the reaction of 2-methoxybenzaldehyde (**2j**, Table 1, entry **10**), based on the TLC analysis of the reaction mixture, several products were obtained. Although the desired product was present, it could not be purified even after two attempts at recrystallization from ethanol. Among the other products, only the intermediate diamine (Scheme 2, compound **A**) could be identified.

We also examined the reaction with 2-nitro-, 3-nitro-, 4-nitro-, and *p*-dimethylaminobenzaldehyde, but in these cases, no products were formed according to TLC analysis and only intermediates could be detected. As an example for aliphatic aldehydes, we examined the reaction of butanal, but due to its lower boiling point we had to reduce the reaction temperature significantly (80 °C). Under these conditions no product was formed and only the intermedi-

Table 1 Synthesis of 2,4,5-Trisubstituted Imidazoles Catalyzed by Ti^{4+}/4 Å MS[a]

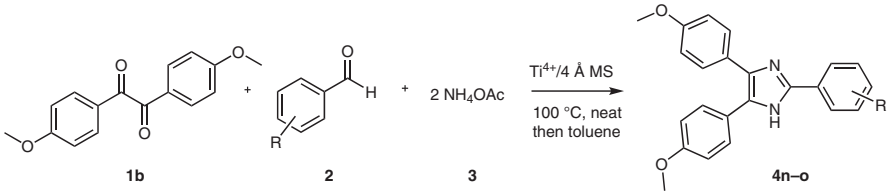


1a 2 3 4a–m

Entry	R	Product	Yield (%)[b]
1	H	**4a**	81
2	3-Br	**4b**	77
3	4-Br	**4c**	85
4	2-Cl	**4d**	78
5	4-Cl	**4e**	80
6	2-F	**4f**	73
7	2-Me	**4g**	84
8	3-Me	**4h**	58
9	4-Me	**4i**	65
10	2-MeO	**4j**	–
11	3-MeO	**4k**	73
12	4-MeO	**4l**	86
13	2-OH	**4m**	67

[a] Reaction conditions: 1 mmol benzil, 1 mmol benzaldehyde, 2.2 mmol ammonium acetate, 0.1 g catalyst, neat for 1 h, then 1 mL toluene, 100 °C, 10 h.
[a] Isolated yield.

Table 2 Application of 4,4′-dimethoxybenzil in the Ti^{4+}/4 Å MS Catalyzed Synthesis of 2,4,5-Trisubstituted Imidazoles[a]



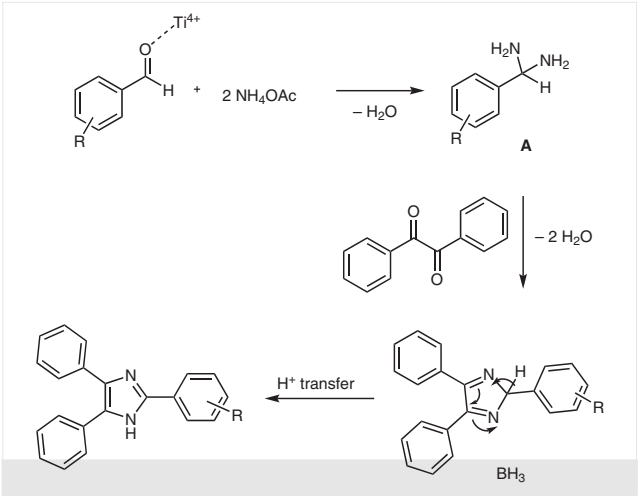
Entry	R	Product	Yield (%)[b]
1	H	**4n**	25
2	4-Br	**4o**	15

[a] Reaction conditions: 1 mmol 4,4′-dimethoxybenzil, 1 mmol benzaldehyde, 2.2 mmol ammonium acetate, 0.1 g catalyst, neat for 1 h, then 1 mL toluene, 100 °C, 10 h.
[b] Conversion determined by ^{1}H NMR spectroscopy.

ates could be detected. This temperature perhaps was not high enough for the cyclization. In the reactions of *trans*-cinnamaldehyde and 3-phenylpropionaldehyde complex mixtures were obtained. With heteroaryl aldehydes (furfural, thiophene-2-carbaldehyde, and *N*-methyl-2-pyrrolecarboxaldehyde) the product could be detected by TLC analysis of the reaction mixture but, probably due to the polymerization of the aldehydes, their isolation was unsuccessful.

To investigate the scope of the reaction further, we applied 4,4′-dimethoxybenzil instead of benzil in the synthesis. In these cases, the starting material was not consumed after 10 h and further heating (20 h) resulted in substantial decomposition. The results are summarized in Table 2.

According to the reported mechanisms,[19,20] we propose a plausible pathway for the formation of the 2,4,5-triaryl-1*H*-imidazole derivatives (Scheme 2). Although the bulk phase of the Ti^{4+}/4 Å molecular sieve catalyst is slightly basic, the titanium is located on the surface of the support, forming acidic sites.[26] These areas of the catalyst might facilitate the reaction steps through the coordination of the heteroatoms in the transition states. The reaction is proposed to proceed through diamine intermediate **A**, which may form by the activation of the carbonyl oxygen of the aldehyde by the Ti^{4+} cation, and subsequent condensation with two molecules of ammonia. In the following step, intermediate **A** condenses with the carbonyl carbons of the 1,2-diketone followed by dehydration to afford the imino intermediate **B**, which rearranges to the desired trisubstituted imidazole.



Scheme 2 Possible mechanism of the reaction

The lower reactivity of 4,4′-dimethoxybenzil might be explained with the possibility of the formation of a complex between the titanium ion and the methoxy group instead of the carbonyl oxygen or the lower electrophilicity of the carbonyls.

The workup of the reaction mixtures was very simple; the catalyst was filtered off and washed with acetone. The crude product obtained after the evaporation of the filtrate was then recrystallized from ethanol. The reusability of the catalyst was examined in the reaction of benzil, 4-chlorobenzaldehyde, and ammonium acetate. After a 10 h reflux, the reaction mixture was worked up as described above, then the catalyst was heated at ca. 150 °C for 1 h. It was reused in three more runs without a notable decrease in its activity. The isolated yields for the three successive runs were 80%, 78%, 77%, respectively, clearly demonstrating the practical recyclability of this catalyst.

In conclusion, titanium(IV) on a 4 Å molecular sieve support has proved to be an effective catalyst for the one-pot, three component synthesis of 2,4,5-triaryl-1*H*-imidazoles under mild, slightly basic conditions,[28–31] which is almost unprecedented in the literature. The catalyst can be prepared readily and can be reused maintaining its activity.

Funding Information

Á. M. is grateful to the József Varga Foundation for financial support.

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(28) ^{1}H NMR and ^{13}C NMR spectra were made on a BRUKER Avance-300 instrument using TMS as an internal standard in DMSO-d_6. Melting points were determined on SETARAM DSC 92 apparatus, where the initial temperature was 25 °C, followed by programming at 10 °C/min up to 300 °C under nitrogen atmosphere. All compounds and solvents were purchased from Merck Hungary Ltd.
(29) The catalyst was prepared according to the method described in ref. 26. Samples were heated at 120 °C for 1 h before the reaction. Figure 1 shows the SEM image of the catalyst. The characteristic cuboctahedron shape of the molecular sieve support can be seen, the particles are well defined both in shape and size, and the titanium is evenly distributed on the surface of the support.

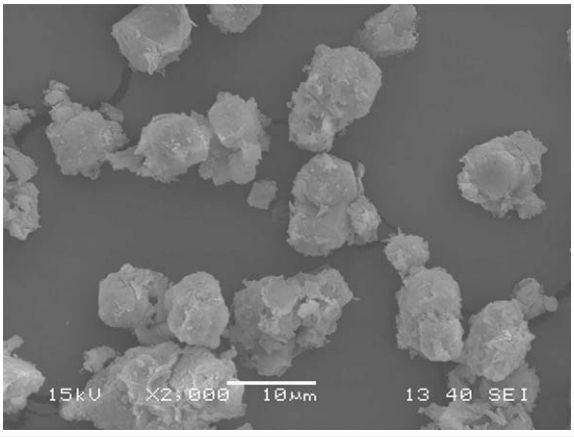

Figure 1

(30) **General Procedure for the One-Pot Synthesis of 2,4,5-Triaryl-1*H*-imidazoles**
A mixture of benzil (1 mmol, 0.21 g), aldehyde (1 mmol), ammonium acetate (2.2 mmol, 0.17 g), and Ti^{4+}/4A (0.1 g) was stirred in a 10 mL flask at 100 °C. After 1 h toluene (1 mL) was added because the precipitated product impeded stirring of the melt. The stirring was continued, and progress of the reaction was monitored by TLC. After completion (10 h), the mixture was cooled to room temperature, diluted with acetone (10 mL), any solid was filtered off, and the filtrate was evaporated. The product was purified by recrystallization from ethanol.
(31) **2,4,5-Triphenyl-1*H*-imidazole (4a)**
White solid, mp 278 °C (lit.: 274–276 °C[20]). ^{1}H NMR (300 MHz): δ = 7.22–7.57 (m, 13 H), 8.09 (d, 2 H), 12.70 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 125.20, 126.53, 127.09, 127.79, 128.20, 128.26, 128.47, 128.69, 130.36, 131.10, 135.19, 137.12, 145.52 ppm.
2-(2-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (4b)
White solid, mp 197 °C (lit.: 196–198 °C[32]). ^{1}H NMR (300 MHz): δ = 7.28–7.51 (m, 10 H), 7.55 (d, 2 H), 7.61 (t, 1 H), 7.81 (t, 1 H), 12.65 (b rs, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 126.51, 127.13, 127.68, 127.99, 128.15, 128.62, 130.01, 130.15, 130.87, 131.48,

131.55, 135.08, 136.86, 143.35 ppm.

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (4c)

White solid, mp 264 °C (lit.: 261–262 °C[19]). ^{1}H NMR (300 MHz): δ = 7.23–7.56 (m, 12 H), 8.11 (d, 2 H), 12.79 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 126.56, 126.80, 127.03, 127.83, 128.16, 128.39, 128.63, 128.73, 129.17, 130.89, 132.71, 134.97, 137.27, 144.38 ppm.

2-(3-Bromophenyl)-4,5-diphenyl-1*H*-imidazole (4d)

White solid, mp 306 °C (lit.: 301–303 °C[18]). ^{1}H NMR (300 MHz): δ = 7.24–7.57 (m, 13 H), 8.10 (d, 1 H), 8.32 (s, 1 H), 12.84 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 121.93, 123.81, 126,49, 126,89, 127.29, 127.71, 128.01, 128.17, 128.45, 130.57, 130.72, 132.27, 134.68, 137.19, 143.64 ppm.

2-(4-Bromophenyl)-4,5-diphenyl-1*H*-imidazole (4e)

White solid, mp 260 °C (lit.: 252–254 °C[16]) ppm. ^{1}H NMR (300 MHz): δ = 7.21–7.53 (m, 10 H), 7.68 (d, 2 H), 8.05 (d, 2 H), 12.83 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 121.90, 126.63, 126.98, 127.62, 127.97, 128.19, 128.69, 129.10, 129.52, 129.71, 130.06, 132.18, 144.99 ppm.

2-(2-Fluorophenyl)-4,5-diphenyl-1*H*-imidazole (4f)

White solid, mp 208 °C (lit.: 205.5–206 °C[33]). ^{1}H NMR (300 MHz): δ = 7.23–7.55 (m, 13 H), 8.00 (t, 1 H), 12.56 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 116.66, 116.82, 119.21, 125.18, 125.21, 127.08, 127.69, 128.33, 128.69, 129.04, 130.14, 130.91, 131.37, 135.49, 137.71, 141.34, 158.35, 160.33 ppm.

4,5-Diphenyl-2-(2-methylphenyl)-1*H*-imidazole (4g)

White solid, mp 253 °C (lit.: 252 °C[33]). ^{1}H NMR (300 MHz): δ = 2.65 (s, 3 H), 7.21 (t, 1 H), 7.29–7.37 (m, 6 H), 7.43 (t, 2 H), 7.52 (d, 2 H), 7.56 (d, 2 H), 7.72 (t, 1 H), 12.49 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 21.63, 126.21, 126.88, 127.52, 127.96, 128.12, 128.67, 128.72, 128.84, 129.13, 129.21, 130.49, 131.59, 135.89, 136.77, 137.11, 146.61 ppm.

4,5-Diphenyl-2-(3-methylphenyl)-1*H*-imidazole (4h)

White solid, mp 299 °C (lit.: 296–298 °C[20]). ^{1}H NMR (300 MHz): δ = 2.39 (s, 3 H), 7.20–7.55 (m, 12 H), 7.88 (d, 1 H), 7.94 (s, 1 H), 12.64 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 21.62, 122.88, 126.25, 127.00, 127.58, 128.24, 128.68, 128.92, 129.14, 129.43, 130.03, 130.11, 130.78, 131.61, 135.72, 137.54, 138.31, 146.11 ppm.

4,5-Diphenyl-2-(4-methylphenyl)-1*H*-imidazole (4i)

White solid, mp 239 °C (lit.: 230–233 °C[18]). ^{1}H NMR (300 MHz): δ = 2.35 (s, 3 H), 7.22 (t, 1 H), 7.29 (t, 4 H), 7.37 (t, 1 H), 7.44 (t, 2 H), 7.50 (d, 2 H), 7.56 (d, 2 H), 7.98 (d, 2 H), 12.60 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 21.40, 125.67, 126.95, 127.56, 128.20, 128.43, 128.66, 128.91, 129.13, 129.74, 131.66, 135.76, 137.42, 138.16, 146.16 ppm.

4,5-Diphenyl-2-(3-methoxyphenyl)-1*H*-imidazole (4k)

White solid, mp 266 °C (lit.: 259–262 °C[18]). ^{1}H NMR (300 MHz): δ = 3.84 (s, 3 H), 6.95 (d, 1 H), 7.26–7.57 (m, 11 H), 7.68–7.71 (m, 2 H), 12.70 (br s, 1 H) ppm. ^{13}C NMR (300 MHz): δ = 55.72, 110.7, 114.72, 118.13, 127.02, 127.57, 128.31, 128.69, 128.99, 129.16, 130.0, 130.11, 130.31, 131.59, 132.15, 135.64, 136.04, 137.58, 145.86, 160.06 ppm.

4,5-Diphenyl.2-(4-methoxyphenyl)-1*H*-imidazole (4l)

White solid, mp 228.5 °C (lit.: 228–231 °C[18]). ^{1}H NMR (300 MHz): δ = 3.82 (s, 3 H), 7.05 (d, 2 H), 7.21 (t, 1 H), 7.29 (t, 2 H), 7.36 (t, 1 H), 7.44 (t, 2 H), 7.50 (d, 2 H), 7.55 (d, 2 H), 7.79 (s, 2 H), 8.03 (d, 2 H), 12.51 (br s, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 55.21, 114.09, 123.14, 126.39, 126.69, 127.04, 127.60, 128.14, 128.35, 128.62, 131.24, 135.33, 136.76, 145.62, 159.41 ppm.

4-(4,5-Diphenyl-1*H*-imidazol-2-yl)-phenol (4m)

Light-yellow solid, mp 214 °C (lit.: 215 °C[34]). ^{1}H NMR (300 MHz): δ = 6.94–7.01 (m, 2 H), 7.28 (t, 2 H), 7.30–7.49 (m, 5 H), 7.54 (d, 4 H), 8.06 (d, 1 H), 13.02 (br s, 1 H). ^{13}C NMR (75 MHz): δ = 112.88, 116.82, 118.84, 124.94, 128.62, 130.06, 145.87, 156.70 ppm.

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