The Free Internet Journal for Organic Chemistry

Paper

Archive for Organic Chemistry

Arkivoc **2017**, part iv, 343-352

Appel reagent as novel promoter for the synthesis of polysubstituted imidazoles

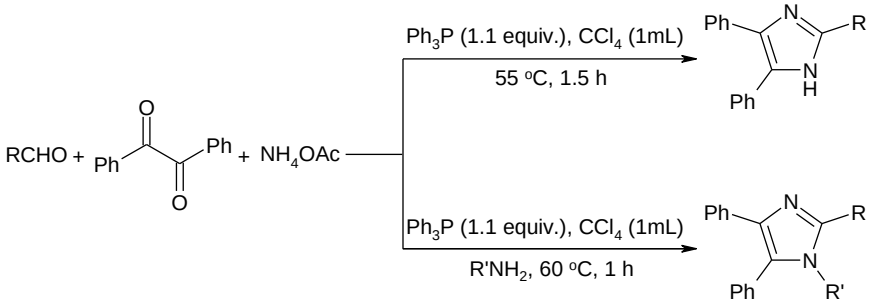
Mehdi Khoshneviszadeh[a] and Mohammad Mahdavi[b]*

[a]*Medicinal&Natural Products Chemistry Research Center, Shiraz University of Medicinal Sciences, Shiraz, Iran*
[b]*Endocrinology and Metabolism Research Center, Endocrinology and Metabolism Clinical Sciences Institute, Tehran University of Medical Sciences, Tehran*
Email: mahdavi_chem@yahoo.com

Received 01-30-2017 **Accepted** 05-06-2017 **Published on line** 06-18-2017

Abstract

We present an efficient method for the synthesis of polysubstituted imidazoles in the presence of Appel reagent (Ph_3P/CCl_4). Tri-substituted imidazoles is synthesized via condensation of aldehydes, benzil and ammonium acetate, and tetra-substituted imidazole is prepared via condensation of aldehydes, benzil, ammonium acetate and primary amines. These protocols allow the simple preparation of the desired products using readily available reagent instead of complex, expensive and toxic reagents under mild reaction conditions in excellent yields.



Keywords: Aldehydes, benzil, ammonium acetate, primary amines, Appel reagent, imidazoles

Introduction

Imidazole and its derivatives are important class of *N*-heterocycles that occupies a significant place in synthetic and medicinal chemistry. These compounds act as organic catalysts,[1] precursors of ionic liquids[2] and carbene ligands,[3] building blocks of complex meaningful molecules and natural products,[4] and ligands in metalloenzymes.[5] The imidazole core exists in many compounds with pharmaceutical and biological activity such as losartan, eprosartan, carnosinemia, histamine, and histidine.[6] The imidazole-containing compounds have also other useful activities such as anthelmintic,[7] antifungal,[8] antiviral activities,[9] antitubercular,[10] antitumor,[11] analgesic,[12] anti-inflammatory,[13] and antibacterial activity.[14]

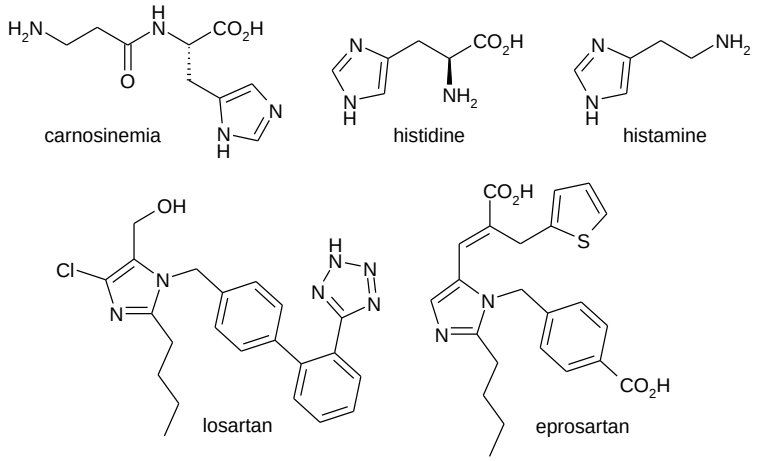


Figure 1. Some examples of pharmaceutical and biological active imidazoles.

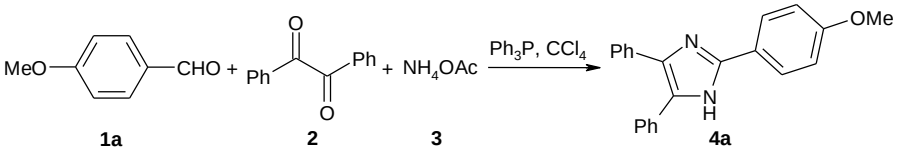
Although the broad variety of synthetic routes have been reported to synthesize imidazole derivatives,[15, 16] there are few protocols for preparation of polysubstituted imidazoles. The well-known route for preparation of polysubstituted imidazoles is one-pot reaction between aldehydes, benzil, ammonium acetate and primary amines catalyzed by various catalysts such as $FeCl_3·6H_2O$,[17] silica gel/$NaHSO_4$,[18] PPA–SiO_2,[19] $BF_3·SiO_2$,20 silica gel or HY zeolite,[21] heteropolyacids,[22] HOAc,[23] L-proline,[24] $InCl_3·3H_2O$,[25] nanocrystalline sulfated zirconia,[26] 1,4-diazabicyclo[2,2,2]octane (DABCO),[27] $K_5CoW_{12}O_{40}·3H_2O$,[28] alumina,[29] ionic liquids,[30] $HClO_4$–SiO_2,[31] silica-bonded propylpiperazine *N*-sulfamic acid,32 and $Zr(acac)_4$.[33] However, some of these methods involve the use of toxic and expensive catalysts or media, and have notable disadvantages such as harsh reaction conditions, long reaction times, and moderate yields. Therefore, the development of novel and efficient approaches to generate polysubstituted imidazoles is still desirable.

Due to the chemical and pharmacological significance of imidazoles, we sought to develop a one-pot protocol for the efficient formation of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles through the addition reaction between aldehydes, benzil, ammonium acetate and primary amines in the presence of Ph_3P and CCl_4 which known as the Appel reagent. Although, the Appel reagent converts an alcohol into the corresponding alkyl halide, we believed that this reagent can be promoted the synthesis of the desired imidazoles.

Results and Discussion

To synthesize the 2,4,5-trisubstituted imidazoles, the reaction between 4-methoxybenzaldehyde **1a**, benzil **2** and ammonium acetate **3**, as a model reaction, was investigated in the presence of various amounts of Ph_3P and CCl_4, at different temperatures. As shown in table 1, the best yield of tri-substituted imidazole **4a** was obtained in the presence of 1.1 equiv. of Ph_3P at 55 °C in 1 mL of CCl_4 as reactive solvent after 1.5 h (Table 1, entry 9, 95%). In addition, we examined the reaction in various additional solvents such as $CHCl_3$, CH_2Cl_2, toluene, DMF, THF, DMSO, and it was found that although the reaction led to approximately acceptable yields in these solvents, the addition of these solvents did not give the better yield of product (Table 1, entries 10–15).

Table 1 Optimization of three-component synthesis of 2,4,5-trisubstituted imidazole **4a** in the presence of Appel reagent[a]



1a **2** **3** **4a**

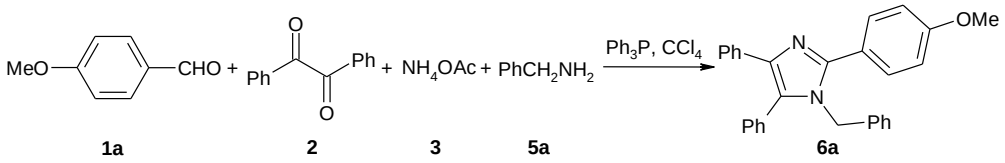
Entry	Ph_3P	CCl_4	Temp. °C	Solvent	Time (h)	Yield of **4a** (%)[b]
1	0.2 equiv.	0.2 equiv.	r.t	–	8	No reaction
2	0.2 equiv.	0.2 equiv.	40	–	8	12
3	0.2 equiv.	0.2 equiv.	50	–	8	22
4	0.2 equiv.	0.2 equiv.	55	–	8	25
5	0.5 equiv.	0.5 equiv.	55	–	8	36
6	1.0 equiv.	1.0 equiv.	55	–	8	60
7	1.1 equiv.	1.1 equiv.	55	–	8	65
8	1.1 equiv.	1.2 equiv.	55	–	4	67
9	1.1 equiv.	1 mL	55	–	1.5	95
10	1.1 equiv.	1 mL	55	CH_2Cl_2	1.5	70
11	1.1 equiv.	1 mL	55	$CHCl_3$	1.5	75
12	1.1 equiv.	1 mL	55	DMSO	1.5	73
13	1.1 equiv.	1 mL	55	DMF	1.5	65
14	1.1 equiv.	1 mL	55	THF	1.5	62
15	1.1 equiv.	1 mL	55	Toluene	1.5	68

[a] reaction conditions: use of 4-methoxybenzaldehyde (1 mmol), benzil (1 mmol), ammonium acetate (2.5 mmol), and appropriate amount of Ph_3P and CCl_4; additional solvent (3 mL); related temperature and time.
[b] Isolated yield.

In continuous, we examined the reaction of 4-methoxybenzaldehyde **1a**, benzil **2**, ammonium acetate **3**, and benzylamine **5a** in the presence of various amount of Ph_3P and CCl_4 under several reaction conditions to generate 1,2,4,5-tetrasubstituted imidazole **6a**. As shown in table 2, the best yield of tetra-substituted imidazole **6a** was obtained in the presence of 1.1 equiv. of Ph_3P at 60 °C in 1 mL of CCl_4 as reactive solvent

after 1 h (Table 2, entry 8, 92%). Also, we found that the addition of various solvents such as $CHCl_3$, CH_2Cl_2, toluene, DMF, THF, DMSO in the reaction mixture, did not lead to better yield of product (Table 2, entries 9–14).

Table 2 Optimization of four-component synthesis of 1,2,4,5-tetrasubstituted imidazole **6a** in the presence of Appel reagent[a]



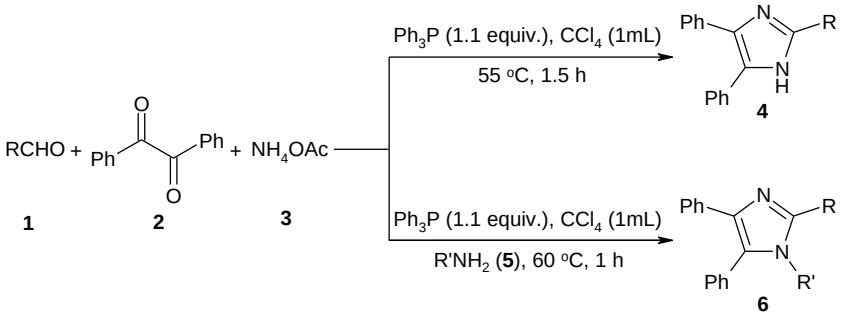
Entry	Ph_3P	CCl_4	Temp. °C	Solvent	Time (h)	Yield of **6a** (%)[b]
1	0.2 equiv.	0.2 equiv.	r.t	–	8	No reaction
2	0.2 equiv.	0.2 equiv.	55	–	8	20
3	0.2 equiv.	0.2 equiv.	60	–	8	26
4	0.5 equiv.	0.5 equiv.	60	–	8	33
5	1.0 equiv.	1.0 equiv.	60	–	8	54
6	1.1 equiv.	1.1 equiv.	60	–	8	62
7	1.1 equiv.	1.2 equiv.	60	–	6	67
8	1.1 equiv.	1 mL	60	–	1	92
9	1.1 equiv.	1 mL	60	CH_2Cl_2	1	63
10	1.1 equiv.	1 mL	60	$CHCl_3$	1	70
11	1.1 equiv.	1 mL	60	DMSO	1	67
12	1.1 equiv.	1 mL	60	DMF	1	58
13	1.1 equiv.	1 mL	60	THF	1	60
14	1.1 equiv.	1 mL	60	Toluene	1	65

[a] reaction conditions: use of 4-methoxybenzaldehyde (1 mmol), benzil (1 mmol), ammonium acetate (1.2 mmol), benzylamine (1 mmol), and appropriate amount of Ph_3P and CCl_4; additional solvent (3 mL); related temperature and time.

[b] Isolated yield.

In order to show the generality and scope of these new protocols, the reactions were performed using various aldehydes **1** and primary amines **5** in the presence of 1.1 equiv. Ph_3P in 1mL CCl_4 at convenient temperatures to produce the corresponding polysubstituted imidazoles **4** and **6** (Table 3).

Table 3 The synthesis of polysubstituted imidazoles **4**[a] and **6**[b] in the presence of Appel reagent[a]



Product	R	R’	Yield (%)[c]	Mp (°C)	Lit. mp (°C)
4a	4-$MeOC_6H_4$	–	95	229–230	228–230[26]
4b	2-$MeOC_6H_4$	–	92	205–207	204–206[34]
4c	4-$(Me)_2NC_6H_4$	–	90	257–259	256–259[24]
4d	4-OHC_6H_4	–	93	233–234	234–236[35]
4e	2-OHC_6H_4	–	91	204–206	202–205[24]
4f	Ph	–	95	275	274–276[26]
4g	4-MeC_6H_4	–	94	233–234	232–234[26]
4h	4-BrC_6H_4	–	93	255–257	254–256[26]
4i	4-ClC_6H_4	–	94	260–261	260–262[26]
4j	4-$NO_2C_6H_4$	–	97	234–236	234–236[26]
4k	3-$NO_2C_6H_4$	–	92	308–310	308–309[36]
4l	2-$NO_2C_6H_4$	–	94	231	230–231[24]
6a	4-$MeOC_6H_4$	Bn	92	163–165	162–164[37]
6b	4-$MeOC_6H_4$	4-MeC_6H_4	92	177–178	176–178[38]
6c	4-OHC_6H_4	Bn	94	135	134–135[31]
6d	Ph	Ph	96	215–216	214–216[36]
6e	Ph	Bn	95	164–165	162–164[39]
6f	4-MeC_6H_4	Ph	93	181–183	182–184[21]
6g	4-MeC_6H_4	Bn	93	157–158	156–158[40]
6h	4-MeC_6H_4	4-MeC_6H_4	90	190–192	188–191[18]
6i	3-$NO_2C_6H_4$	Bn	91	150–151	
6j	4-BrC_6H_4	Bn	94	172–173	170–172[31]
6k	4-ClC_6H_4	Bn	91	160–161	160–162[37]
6l	3-ClC_6H_4	Bn	91	144–145	144–146[18]
6m	2-ClC_6H_4	Bn	94	141	140–141[31]
6n	4-$NO_2C_6H_4$	4-MeC_6H_4	96	220–222	219–220[18]
6o	3-$NO_2C_6H_4$	4-MeC_6H_4	90	148–150	149–151[18]

[a] Reaction conditions: aldehydes (1 mmol), benzil (1 mmol), ammonium acetate (2.5 mmol), Ph_3P (1.1 mmol), CCl_4 (1 mL); 55 °C; 1.5 h.

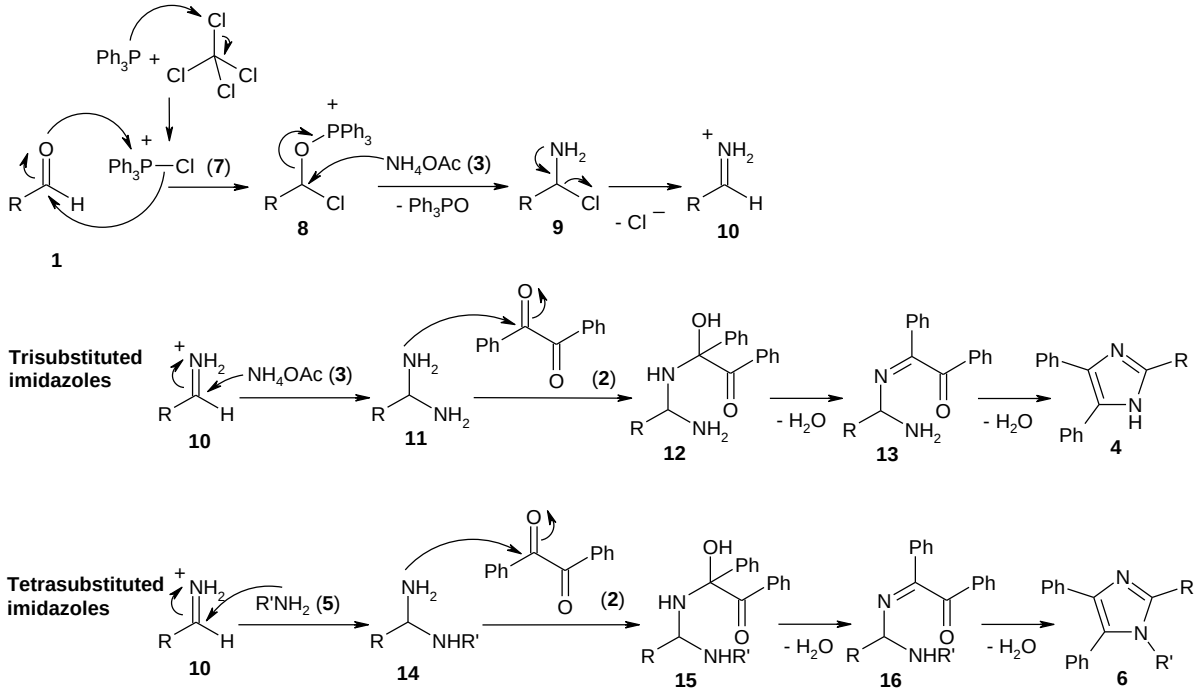
[b] Reaction conditions: aldehydes (1 mmol), benzil (1 mmol), ammonium acetate (1.2 mmol), primary amines (1 mmol), Ph_3P (1.1 mmol), CCl_4 (1 mL); 60 °C; 1 h.

[c] Isolated yields.

All the reactions reached to completion within 1.5 h for 2,4,5-trisubstituted imidazoles **4** and 1 h for 1,2,4,5-tetrasubstituted imidazoles **6**. ^{1}H NMR analysis of the reaction mixtures clearly indicated formation of the polysubstituted imidazoles **4** and **6** in excellent yields.

The structures of the polysubstituted imidazoles **4** and **6** were deduced by melting point determination and from ^{1}H and ^{13}C NMR spectral data.

A proposed mechanism for the formation of the polysubstituted imidazoles **4** and **6** is depicted in Scheme 1. On the basis of the Appel reaction,[41] the treatment of triphenylphosphine with carbon tetrachloride leads to form phosphonium ion **7**, that reacts with aldehydes **1** to form the oxyphosphonium intermediates **8**. The generation of the oxyphosphonium intermediates **8** promotes the nucleophilic addition of ammonium acetate **3** via removal of triphenylphosphine oxide and chloride anion to generate the iminium ions **10**. The addition of another ammonium acetate on the iminium ions **10** gives the intermediates **11**. Then, the condensation of intermediates **11** with benzil **2** produces trisubstituted imidazoles **4** by removal of 2 water molecules. In similar pathway, the addition of primary amines **5** onto iminium ions **10** forms intermediates **14** which produces tetrasubstituted imidazol **6** via condensation with benzil.



Scheme 1. Proposed mechanism.

Conclusions

In conclusion, we have developed a one-pot and multicomponent reaction between aldehydes, benzil, ammonium acetate and primary amines in the presence of Ph_3P and CCl_4 which known as Appel reagent. The reactions were carried out under mild reaction conditions and without the use of very high temprature, and complex, toxic and expensive reagents to prepare the polysubstituted imidazoles which are of potential synthetic and pharmacological interest. Use of simple materials, relatively short reaction times, and high yield of the products are the other advantages of our protocol. We believe that the success in this process could

open the door to the design of diverse reactions and the generation of interesting organic compounds based on treatment of carbonyl groups with Appel reagent.

Experimental Section

Ammonium acetate, benzil, aldehydes, primary amines, triphenylphosphine and carbon tetrachloride were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Progress of the reactions was monitored by thin layer chromatography (TLC). Melting points were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C NMR spectra were measured with a Bruker DRX-300 (at 300 and 75 MHz) spectrometer using $CDCl_3$ solvent with TMS as an internal standard. Chromatography columns were prepared from Merck silica gel 230-240 meshes.

General procedure for the preparation of 2,4,5-trisubstituted imidazoles 4, exemplified on 4a. A mixture of 4-methoxybenzaldehyde (0.136 g, 1 mmol), benzil (0.210 g, 1 mmol), ammonium acetate (0.192 g, 2.5 mmol) and Ph_3P (0.280 g, 1.1 mmol) in CCl_4 (1mL) was stirred for 1.5 h at 55 ºC. After completion of the reaction, the solvent was removed and the residue was purified by column chromatography using *n*-hexane–EtOAc (3:1) as eluent. The solvent was removed to afford the product **4a** as white solid.

The spectral data of some 2,4,5-trisubstituted imidazoles **4** are given next.

2-(4-Methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (4a) Yield. 0.31 g, 95%; m.p = 229–230 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (3H, s, OCH_3), 7.04 (2H, d, *J* 8.1 Hz, 2 CH), 7.15–7.53 (10H, m, 10 CH), 7.97 (2H, d, *J* 8.1 Hz, 2 CH), 12.61 (1H, br s, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.14, 114.17, 123.55, 126.83, 127.72, 128.38, 129.01, 131.64, 135.75, 137.19, 146.11, 159.80.

2-(2-Hydroxyphenyl)-4,5-diphenyl-1*H*-imidazole (4e). Yield 0.28 g, 91%; m.p = 204–206 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.97 (1H, d, *J* 7.6 Hz, CH), 7.14 (1H, d, *J* 7.6 Hz, CH), 7.29–7.62 (11H, m, 11 CH), 7.65 (1H, t, *J* 7.6 Hz, CH), 9.40 (1H, br s, OH), 12.90 (1H, br s, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.42, 116.79, 118.01, 122.08, 126.43, 127.12, 127.40, 128.11, 129.46, 144.72, 156.37.

2-(3-Nitrophenyl)-4,5-diphenyl-1*H*-imidazole (4k). Yield 0.31 g, 92%; m.p = 308–310 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.58 (10H, m, 10 CH), 7.82 (1H, t, *J* 8.1 Hz, CH), 8.54 (1H, d, *J* 8.1 Hz, CH), 9.02 (1H, t, *J* 1.8 Hz, CH), 9.46 (1H, d, *J* 8.1 Hz, CH), 13.13 (1H, br s, NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 119.43, 122.58, 127.05, 128.41, 128.74, 130.47, 131.23, 131.90, 143.38, 148.32.

General Procedure for the Preparation of 1,2,4,5-tetrasubstituted imidazoles 6, Exemplified on 6a: A mixture of 4-methoxybenzaldehyde (0.136 g, 1 mmol), benzil (0.210 g, 1 mmol) ammonium acetate (0.092 g, 1.2 mmol), benzylamine (0.107 g, 1 mmol) and Ph_3P (0.280 g, 1.1 mmol) in CCl_4 (1mL) was stirred for 1 h at 60 ºC. After completion of the reaction, the solvent was removed and the residue was purified by column chromatography using *n*-hexane–EtOAc (4:1) as eluent. The solvent was removed to afford the pure product **6a** as pale yellow solid.

The spectral data of some 1,2,4,5-tetrasubstituted imidazoles **6** are given next.

1-Benzyl-2-(4-methoxyphenyl)-4,5-diphenyl-1*H*-imidazole (6a) Yield 0.38 g, 92%; mp = 163–165 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (3H, s, OCH_3), 5.09 (2H, s, CH_2Ph), 6.84–7.06 (3H, m, 3 CH), 7.07 (2H, d, *J* 8.0 Hz, 2 CH), 7.08–7.56 (12H, m, 12 CH), 7.92 (2H, d, *J* 8.0 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.12, 54.31, 112.89, 122.38, 125.00, 125.17, 125.65, 126.25, 127.02, 127.52, 127.54, 128.00, 128.67, 129.47, 130.01, 130.16, 133.53, 136.60, 136.81, 146.92, 159.06.

1,4,5-Triphenyl-2-*p*-tolyl-1*H*-imidazole (6f) Yield 0.36 g, 93%; mp = 181–183 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.30 (3H, s, CH_3), 7.11 (2H, d, *J* 7.9 Hz, 2 CH), 7.19 (1H, t, *J* 7.5 Hz, CH), 7.24–7.31 (12H, m, 12 CH), 7.35 (2H, d, *J* 7.5 Hz, 2 CH), 7.54 (2H, d, *J* 7.9 Hz, 2 CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.56, 127.18, 128.45, 129.03, 129.06, 129.24, 129.52, 129.60, 129.66, 123.24, 131.35, 132.02, 132.17, 135.36, 137.65, 137.76, 138.58, 147.08.
1-Benzyl-2-(3-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (6i) Yield 0.39 g, 91%; mp = 150–151 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (2H, s, CH_2Ph), 6.84–7.12 (5H, m, 5 CH), 7.20 (2H, d, *J* 7.5 Hz, 2CH), 7.23–7.54 (6H, m, 6 CH), 7.59 (1H, t, *J* 7.9 Hz, CH), 7.70 (2H, t, *J* 7.5 Hz, 2CH), 8.10 (1H, d, *J* 7.9 Hz, CH), 8.29 (1H, d, *J* 7.9 Hz, CH), 8.59 (1H, s, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 47.38, 122.35, 122.62, 124.70, 125.70, 125.65, 126.73, 127.21, 127.87, 128.06, 128.58, 129.43, 129.98, 130.27, 131.63, 133.05, 133.50, 135.86, 144.33, 147.17.
1-(4-Methylphenyl)-2-(3-nitrophenyl)-4,5-diphenyl-1*H*-imidazole (6o) Yield 0.39 g, 90%; mp = 148–150 ºC. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (3H, s, CH_3), 6.87–7.39 (14H, m, 14 CH), 7.54 (1H, t, *J* 8.0 Hz, CH), 8.16 (1H, d, *J* 8.0 Hz, CH), 8.30 (1H, d, *J* 8.0 Hz, CH), 8.55 (1H, s, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.17, 122.67, 123.50, 127.00, 127.31, 127.96, 128.22, 128.85, 129.05, 131.01, 131.90, 132.27, 133.64, 134.37, 138.68, 139.12, 144.36, 147.98.

Acknowledgements

This study was supported by the Research Council of Tehran University of Medicinal Sciences (TUMS) and Iran National Science Foundation (INSF).

References

1. Li, Y.; Giulionatti, M.; Houghten, R. A. *Org. Lett.* **2010**, *12*, 2250–2253, and references therein. https://doi.org/10.1021/ol100596p
2. Dupont, J.; de Souza, R. F.; Suarez, P. A. *Chem. Rev.* **2002**, *102*, 3667–3692. https://doi.org/10.1021/cr010338r
3. Hahn, F. E.; Jahnke, M. C. *Angew. Chem.* **2008**, *120*, 3166–3216. https://doi.org/10.1002/ange.200703883
4. Ueda, S.; Su, M.; Buchwald, S. L. *J. Am. Chem. Soc.* **2012**, *134*, 700–706, and references therein. https://doi.org/10.1021/ja2102373
5. Holm, R. H.; Kennepohl, P.; Solomon, E. I. *Chem. Rev.* **1996**, *96*, 2239–2314. https://doi.org/10.1021/cr9500390
6. Boersma, C.; Atthobari, J.; Gansevoort, R. T.; de Jong, P. E.; de Zeeuw, D.; Annemans, L. J.; Postma, M. J. *Pharmacoeconomics* **2006**, *24*, 523–535. https://doi.org/10.2165/00019053-200624060-00001
7. Dutta, S. *Acta Pharm.* **2010**, *60*, 229–235. https://doi.org/10.2478/v10007-010-0011-1
8. Dahiya, R. *Sci. Pharm.* **2008**, *76*, 217–239. https://doi.org/10.3797/scipharm.0803-04
9. Cheng, J.; Xie, J.; Luo, X. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 267–269. https://doi.org/10.1016/j.bmcl.2004.10.087

10. Narayanan, S.; Vangapandu, S.; Jain, R. *Bioorg. Med. Chem. Lett.* **2001**, *11*, 1133–1136. https://doi.org/10.1016/S0960-894X(01)00154-8
11. Wang, L.; Woods, K. W.; Li, Q.; Barr, K. J.; McCroskey, R. W.; Hannick, S. M.; Gherke, L.; Credo, R. B.; Hui, Y. H.; Marsh, K.; Warner, R. *J. Med. Chem.* **2002**, *45*, 1697–1711. https://doi.org/10.1021/jm010523x
12. Sondhi, S. M.; Jain, S.; Dinodia, M.; Kumar, A. *Med. Chem.* **2008**, *4*, 146–154, and references therein. https://doi.org/10.2174/157340608783789194
13. Li, Q.; Hu, Q.; Wang, X.; Zong, Y.; Zhao, L.; Xing, J.; Zhou, J.; Zhang, H. *Chem. Biol. Drug Des.* **2015**, *86*, 509–516. https://doi.org/10.1111/cbdd.12513
14. Matysiak, J.; Niewiadomy, A.; Krajewska-Kułak, E.; Mącik-Niewiadomy, G. *Il Farmaco* **2003**, *58*, 455–461. https://doi.org/10.1016/S0014-827X(03)00046-6
15. Gribble, G. W.; Joule, J. A.; Gilchrist, T. L. *Progress in heterocyclic chemistry*; Elsevier: Oxford, 2001-2005, and references therein.
16. Zhu, Y.; Li, C.; Zhang, J.; She, M.; Sun, W.; Wan, K.; Wang, Y.; Yin, B.; Liu, P.; Li, J. *Org. Lett.* **2015**, *17*, 3872–3875, and references therein. https://doi.org/10.1021/acs.orglett.5b01854
17. Heravi, M. M.; Derikvand, F.; Haghighi, M. *Monatsh. Chem.* **2008**, *139*, 31–33. https://doi.org/10.1007/s00706-007-0736-9
18. Karimi, A. R.; Alimohammadi, Z.; Azizian, J.; Mohammadi, A. A.; Mohammadizadeh, M. R. *Catal. Commun.* **2006**, *7*, 728–732. https://doi.org/10.1016/j.catcom.2006.04.004
19. Montazeri, N.; Pourshamsian, K.; Khoddadi, M.; Khoddadi, K. *Orient. J. Chem.* **2011**, *27*, 1023–1027.
20. Sadeghi, B.; Mirjalili, B. B. F.; Hashemi, M. M. *Tetrahedron Lett.* **2008**, *49*, 2575–2577. https://doi.org/10.1016/j.tetlet.2008.02.100
21. Balalaie, S.; Arabanian, A. *Green Chem.* **2000**, *2*, 274–276. https://doi.org/10.1039/b006201o
22. Heravi, M. M.; Derikvand, F.; Bamoharram, F. F. *J. Mol. Catal. A Chem.* **2007**, *263*, 112–114. https://doi.org/10.1016/j.molcata.2006.08.048
23. Schubert, H.; Stodolka, H. *J. Prakt. Chem.* **1963**, *22*, 130–139. https://doi.org/10.1002/prac.19630220303
24. Samai, S.; Nandi, G. C.; Singh, P.; Singh, M. S. *Tetrahedron* **2009**, *65*, 10155–10161. https://doi.org/10.1016/j.tet.2009.10.019
25. Kidwai, M.; Mothsra, P.; Bansal, V.; Somvanshi, R. K.; Ethayathulla, A. S.; Dey, S.; Singh, T. P. *J. Mol. Catal. A Chem.* **2007**, *265*, 177–182. https://doi.org/10.1016/j.molcata.2006.10.009
26. Teimouri, A.; Chermahini, A. N. *J. Mol. Catal. A Chem.* **2011**, *346*, 39–45. https://doi.org/10.1016/j.molcata.2011.06.007
27. Murthy, S. N.; Madhav, B.; Nageswar, Y. V. D. *Tetrahedron Lett*. **2010**, *51*, 5252–5257. https://doi.org/10.1016/j.tetlet.2010.07.128
28. Nagarapu, L.; Apuri, S.; Kantevari, S. *J. Mol. Catal. A Chem.* **2007**, *266*, 104–108. https://doi.org/10.1016/j.molcata.2006.10.056
29. Usyatinsky, A. Y.; Khmelnitsky, Y. L. *Tetrahedron Lett*. **2000**, *41*, 5031–5034. https://doi.org/10.1016/S0040-4039(00)00771-1

30. Zang, H.; Su, Q.; Mo, Y.; Cheng, B. W.; Jun, S. *Ultrason. Sonochem.* **2010**, *17*, 749–751. https://doi.org/10.1016/j.ultsonch.2010.01.015
31. Kantevari, S.; Vuppalapati, S. V.; Biradar, D. O.; Nagarapu, L. *J. Mol. Catal. A Chem.* **2007**, *266*, 109–113. https://doi.org/10.1016/j.molcata.2006.10.048
32. Niknam, K.; Deris, A.; Naeimi, F.; Majleci, F. *Tetrahedron Lett.* **2011**, *52*, 4642–4645. https://doi.org/10.1016/j.tetlet.2011.06.105
33. Hasaninejad, A.; Zare, A.; Shekouhy, M.; Ameri Rad, J. *J. Comb. Chem.* **2010**, *12*, 844–849. https://doi.org/10.1021/cc100097m
34. Karami, B.; Dehghani, F. M.; Eskandari, K. *Croat. Chem. Acta*, **2012**, *85*, 147-153. https://doi.org/10.5562/cca1979
35. Banothu, J.; Gali, R.; Velpula, R.; Bavantula, R. *Arab. J. Chem.*, **2013**. http://dx.doi.org/10.1016/j.arabjc.2013.10.022.
36. Wang, L. M.; Wang, Y. H.; Tian, H.; Yao, Y. F.; Shao, J. H.; Liu, B. *J. Fluorine Chem.* **2006**, *127*, 1570–1573. https://doi.org/10.1016/j.jfluchem.2006.08.005
37. Mohammadi, A.; Keshvari, H.; Sandaroos, R.; Maleki, B.; Rouhi, H.; Moradi, H.; Sepehr, Z.; Damavandi, S. *Appl. Catal. A.* **2012**, *429*, 73-78. https://doi.org/10.1016/j.apcata.2012.04.011
38. Ray, S.; Das, P.; Bhaumik, A.; Dutta, A.; Mukhopadhyay, C. *Appl. Catal., A.* **2013**, *458*, 183–195. https://doi.org/10.1016/j.apcata.2013.03.024
39. Reddy, P. P.; Mukkanti, K.; Purandhar, K. *Rasayan J. Chem.* **2010**, *3*, 335–340.
40. Karimi, A. R.; Alimohammadi, Z.; Amini, M. M. *Mol. Div.* **2010**, *14*, 635–641. https://doi.org/10.1007/s11030-009-9197-x
41. Appel, R. *Angew. Chem. Int. Ed.* **1975**, *14*, 801-811. https://doi.org/10.1002/anie.197508011

