J Nanostruct 11(2): 286-296, Spring 2021

RESEARCH PAPER

Facile and Benign Synthesis of Mono- and Di-substituted Benzimidazoles by using SnO_2 Nanoparticles Catalyst

*Effat Samiei paghaleh [1], Seyed Mohammad Vahdat[1,] *, and Mehdi Hatami [2]*

[1] *Department of Chemistry, Ayatollah Amoli Branch, Islamic Azad University, Amol, Iran*

[2] *Polymer Research Laboratory, University of Bonab, Bonab, Iran*

ARTICLE INFO

Article History:
Received 28 October 2020
Accepted 13 March 2021
Published 01 April 2021

Keywords:
1,2-Disubstituted benzimidazoles
1,2-Phenylenediamine
2-Substituted benzimidazoles
SnO_2 nanoparticles

ABSTRACT

SnO_2 nanoparticles was establish to catalyze efficiently a cyclo-condensation of 1,2-phenylenediamine with aldehydes in ethanol solvent at room temperature to provide the mono- and di-substituted benzimidazole derivatives in appropriate yields and short reaction time. Moreover, we used SnO_2 nanoparticles as an easily available, less expensive and probable under environmentally friendly conditions catalyst in this technique. Therefore, this process presented significant advantageous including purification of target products by non-chromatographic procedure, low catalytic amount, simple efficient, application of recyclability and reusability of the catalyst, green and appropriate for the synthesis of a wide range of mono- and di-substituted benzimidazole derivatives. Furthermore, water was the only by-products, which added to its desirability. Benzimidazole derivatives have various range of pharmacological activities.SnO_2 nanoparticles is a noteworthy material due to its properties for instance high degree of transparency in the visible spectrum, strong thermal stability in air, low operating temperature and strong physical and chemical interaction with adsorbed species.

How to cite this article
Samiei paghaleh E, Vahdat M, Hatami M. Facile and Benign Synthesis of Mono- and Di-substituted Benzimidazoles by using SnO_2 Nanoparticles Catalyst. J Nanostruct, 2021; 11(2):286-296. DOI: 10.22052/JNS.2021.02.009

INTRODUCTION

The design of environmentally friendly catalysts could be advantages in green chemistry. Since the progress of catalysts, heterogeneous catalysts have been received specific attention because of particular benefits like comfort of separation[1-5]. Among the numerous kinds of heterogeneous catalysis systems, scientists have attentive typically on nanoscale particles due to their informal operational process, effective catalytic activity, reusability, high stability, huge surface area and superb functionalization ability[6-10]. Metal nano-catalysis has developed as an efficient approach for the syntheses of various molecules, and its use in numerous transformations as a heterogeneous catalyst is significant [11].

Imidazole derivatives, one of the most substantial heterocyclic compounds, have been establish in many natural products [12-14] and broadly used in functional materials [15-18]. Especially, they have appropriate pharmacological activities [19-21] for example anti-tumor [22, 23], anti-plasmodium [24], anti-bacterial[25-27], anti-fungal[28-30] and anti-inflammatory[31, 32]. Furthermore, they have worthy photo physical properties [33, 34] and are applied as ligands in metal catalyzed reactions [35-37]. Various synthetic processes and catalysts have been known for the synthesis of imidazoles because of the worth of this type of compounds such as $[MIMPS]_3PW_{12}O_{40}$ and $[TEAPS]_3PW_{12}O_{40}$

* *Corresponding Author Email: vahdat_mohammad@yahoo.com*

[38], alumina-methane sulfonic acid[39], copper nanoparticles on activated carbon[40], MCM-41[41], glycerol as green solvent[42], scolecite [43], oxone [44], activated carbon [45], SDS [46] and [2,6-DMPy-NO_2]C(NO_2)$_3$ [47].

In our continuous attempt to progress approaches for the synthesis of heterocyclic compounds and ongoing study on the metal nano oxide catalyst [48-54], herein, we report an efficient and benign process for the synthesis of the 2-substituted benzimidazoles and 1,2-disubstituted benzimidazoles via the cyclo-condensation reaction between 1,2-phenylenediamine and aldehydes by using 1 mol% catalytic amount of SnO_2 nanoparticles in ethanol solvent at room temperature.

MATERIALS AND METHODS

General procedure for the synthesis of 2-substituted benzimidazoles(3) and 1,2-disubstituted benzimidazoles(4) by using SnO_2 nanoparticles

According to Fig. 1, SnO_2 nanoparticles (1mol%) was added to a ethanolicsolution (2 mL) of 1,2-phenylenediamine (1 mmol; 0.108 g) and aldehydes(1mmol for the synthesis of 3 and 2 mmol for the synthesis of 4) at room temperature for the appropriate period of time as showed in Table 2. The progress of the reaction was checked by TLC (n-hexane/ethyl acetate; 5:2). After end of the reaction, the reaction mixture was heated in ethanol. SnO_2 nanoparticles was filtered (the product was soluble in hot ethanol and the catalyst was insoluble). The corresponding products 3 and 4 were attained via simple filtering and recrystallized from ethanol.

General procedure for the synthesis of 2,2'-Bis-1H-benzimidazole (10) by using SnO_2 nanoparticles

To a ethanolic solution (2 mL) of 1,2-phenylenediamine (2mmol; 0.216 g) and oxalic acid (1 mmol; 0.09 g; 0.05 mL), SnO_2 nanoparticles (1 mol%) was added. The mixture solution was stirred at room temperature for 24 hours. The progress of the reaction was observed by TLC (n-hexane/ethyl acetate; 5:2). After completion of the reaction, the reaction mixture was heated in ethanol. SnO_2 nanoparticles was filtered and the corresponding product 10 was achieved via simple filtering and recrystallized from ethanol.

Selected characterization data for the products

2-(4-Nitrophenyl)-1H-benzo[d]imidazole (Table 2, 3a): Dark orange solid, M.p.: 319-321 °C; Yield: 98%; FT-IR (KBr)(υ_{max}, cm^{-1}): 3482, 1598, 1513, 1438, 1336, 1106, 856; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} = 13.28 (s, 1H, –NH), 8.40-8.44 (dd, 4H, J_1= 16.0 Hz and J_2= 8.0 Hz, Ar–H), 7.72-7.74(d, 1H, J=8.0 Hz, Ar–H), 7.58-7.60 (d, 1H, J=8.0 Hz, Ar–H), 7.25-7.29 (dd, 2H, J_1= 16.0 Hz and J_2= 8.0 Hz, Ar–H).

1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1H-benzo[d]imidazole (Table 2, 4a): Dark orange solid, M.p.: 195-197°C; Yield: 98%; FT-IR (KBr)(υ_{max}, cm^{-1}): 3104, 1594, 1515, 1342, 1103, 964; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} = 8.56 (s, 2H, –CH_2), 8.32-8.34 (dd, 4H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H), 8.06-8.08 (dd, 4H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H), 7.36-7.38(dd, 2H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H), 7.24-7.26 (dd, 2H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H).

1H,1'H-2,2'-bibenzo[d]imidazole (Fig. 3, 10): Orange solid, M.p.: 250°C; Yield: 85%; FT-IR (KBr) (υ_{max}, cm^{-1}): 3423, 3344, 3187, 1554, 1315, 1155, 742; ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} = 6.57-6.61 (dd, 4H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H), 6.46-6.50 (dd, 4H, J_1= 16.0 Hz and J_2= 8.0 Hz, Ar–H), 5.71 (brs, 2H, –NH); ^{1}H NMR (400 MHz, D_2O): δ_{ppm} = 6.58-6.60 (dd, 4H, J_1= 8.0 Hz and J_2= 4.0 Hz,

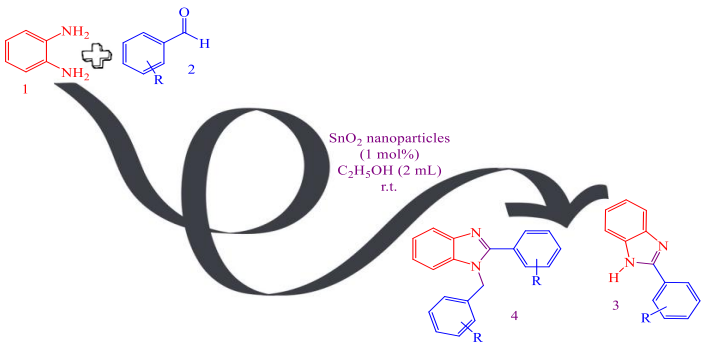


Fig. 1. SnO_2 nanoparticles catalyzed the synthesis of mono- and di-substituted benzimidazoles.

Ar–H), 6.46-6.48 (dd, 4H, J_1= 8.0 Hz and J_2= 4.0 Hz, Ar–H);^{13}C NMR (100 MHz, DMSO-d_6): δ_{ppm} = 163.1, 134.2, 118.9, 116.2.

RESULTS AND DISCUSSION

Characterization of SnO_2 nanoparticles

SnO_2 nanoparticles was purchased from commercial centers and then characterized by X-ray diffraction patterns (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) analyses (Figs. 2-5) [50, 55] and EDS spectra (Fig. 6).

For study of the crystal structure of the SnO_2 nanoparticles, the XRD pattern was attained (Fig. 2). The crystalline peaks at diffraction angles indicate the structure of SnO_2 nanoparticles (JCPDS card no. 41-1445), and are showed by Miller indices in the spectrum. All the diffraction peaks prove the tetragonal structure of SnO_2 nanoparticles. The average crystallite size was calculated to be 65 nm. Also, no peaks of impurities are identified, signifying that the SnO_2 nanoparticles are pure and good crystallized.

The sizes, morphology, and uniformity of the SnO_2 nanoparticlesare obviously showed in the SEM images (Fig. 3). This figure describes that the SnO_2 nanoparticles have a homogeneous size distribution and grain have spherical in shape. The SEM images display approximately uniform and spherical nanoparticles with sizes about 65 nm.

Surface morphology of the SnO_2 nanoparticles was characterized by TEM images (Fig. 4). It was showed an approximately spherical shape of the particle size ranged from 60 to 65 nm which was in worthy agreement with that calculated from XRD and SEM analyses.

The morphology and size of the recycled SnO_2 nanoparticles was studied by SEM images, and (Fig. 5) shows that the dimensions of recycled SnO_2 nanoparticles is between 85 and 90 nm. According to SEM images of recycled SnO_2 nanoparticles, its structure is stable.

The presence of Sn and O were confirmed by EDS analysis from nanoparticle (Fig. 6).

Application of SnO_2 nanoparticles for the synthesis of mono- and di-substituted benzimidazoles

To investigation the effect of catalyst loading on the synthesis of corresponding mono- and di-substituted benzimidazoles, the reaction of 1,2-phenylenediamine and 4-nitrobenzaldehyde was selected as a model in ethanol at room temperature (Table 1). To prove the requirement of SnO_2 nanoparticles as a catalyst for the synthesis of 3a and 4a, we studied the model reaction in the absence of catalyst. The results display obviously that SnO_2 nanoparticles is an effective catalyst for this synthesis and without the catalyst the

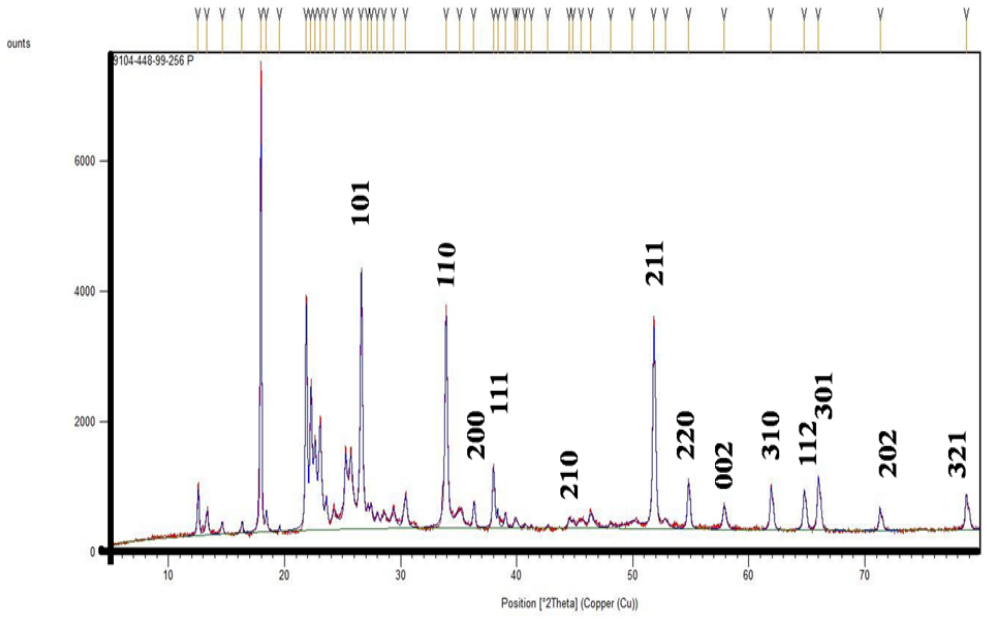


Fig. 2. XRD pattern of SnO_2 nanoparticle.

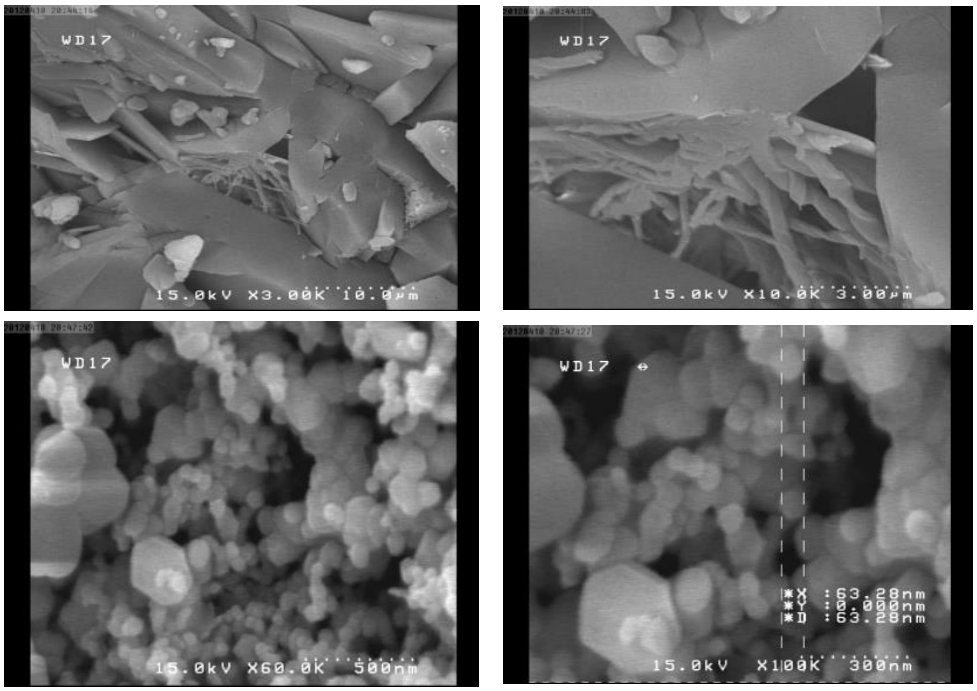


Fig. 3. SEM analysis of SnO_2 nanoparticle.

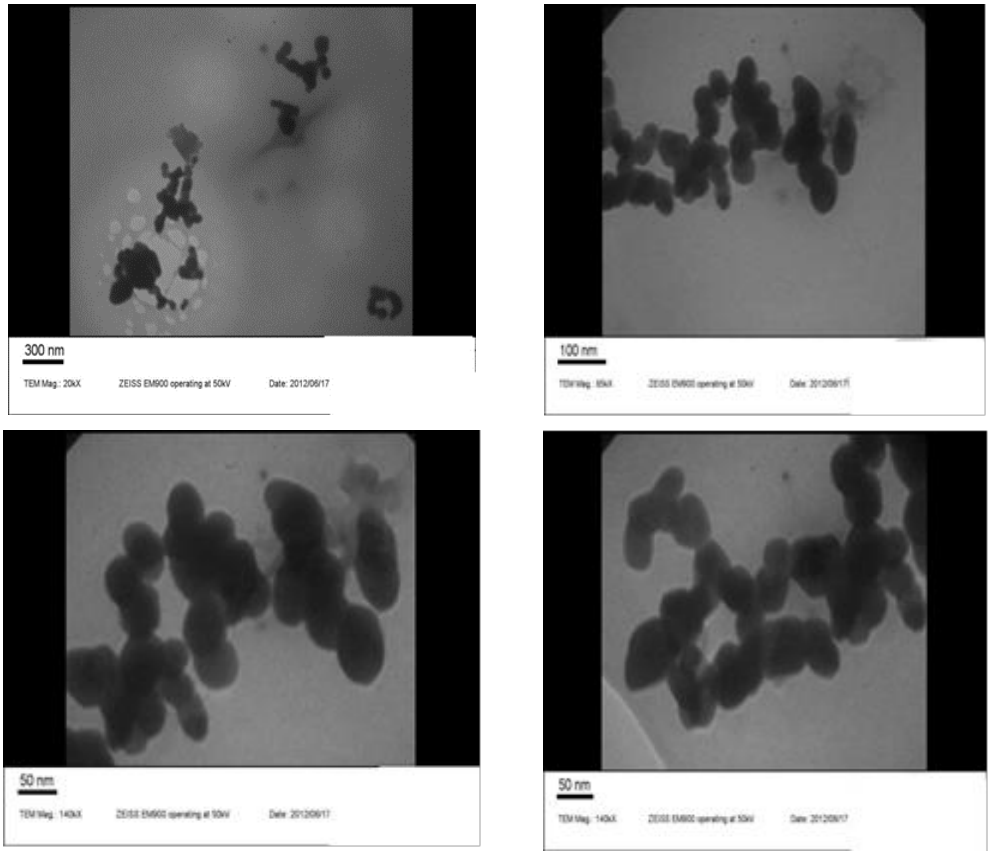


Fig. 4. TEM analysis of SnO_2 nanoparticle.

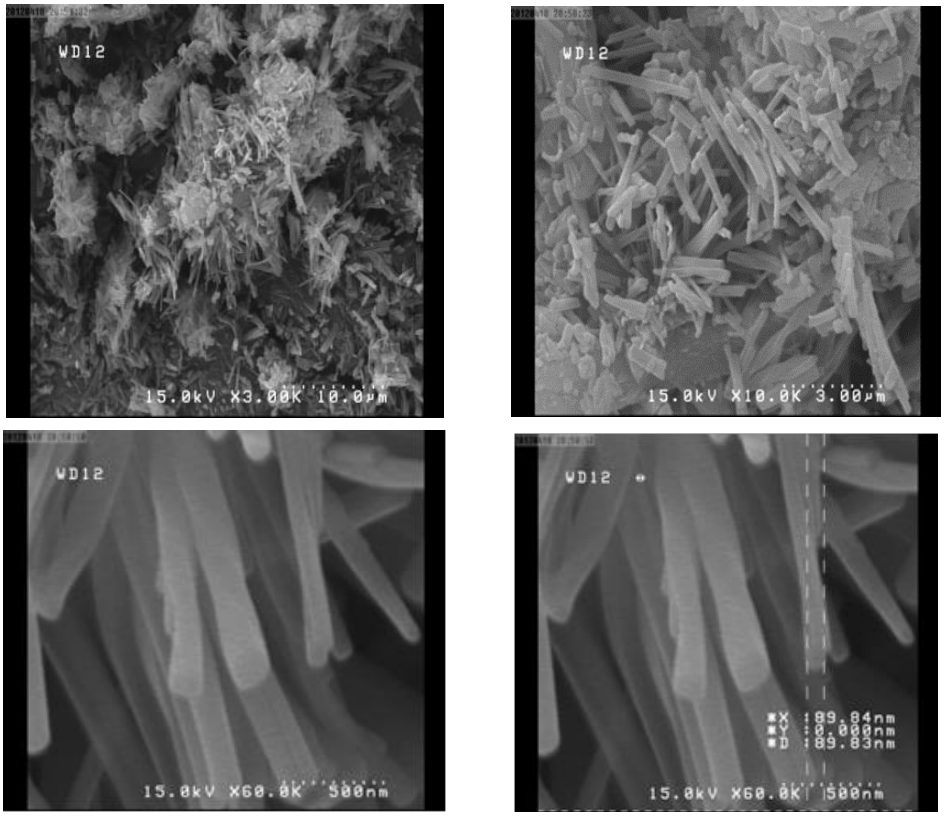


Fig. 5. SEM analysis of recycled SnO_2 nanoparticle.

reaction did not occur, even after 60 minutes. As showed in Table 1, the best results have been attained with 1 mol% of SnO_2 nanoparticles (Table 1, entry 2).Extending the reaction time did not improve the yield. Nonetheless, the yield was shrinking when the catalyst loading was decreased to 0.5 mol% (Table 1, entry 1), while the yield remained unaffected when the catalyst loading was increased to 5 mol% (Table 1, entries 3 and 4).

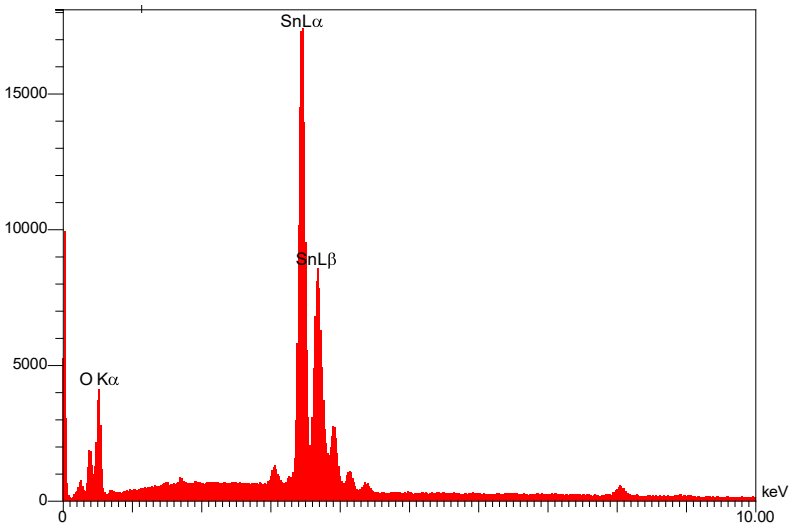
We subsequent ready an investigation on the effect of solvents in the synthesis of 3a and 4a. The model reaction was performed at room temperature by using 1 mol% catalytic amount of SnO_2 nanoparticles. As a general rule, nonpolar solvents for example dichloromethane, ethyl acetate and toluene led to low yields (Table 1, entries 7-9). The optimum result was detected when the reaction was carried out in ethanol (Table 1, entry 2).

The third significant part that could be stimulated from these results is that increasing the reaction temperature from room temperature stepwise to reflux condition did not improve the yields of 3a and 4a. Thus, the best temperature was room temperature.

The optimum yield of the chosen products 3a and 4a were attained by perform the reaction with 1:1 of 1,2-phenylenediamine and 4-nitrobenzaldehyde (for the synthesis of mono-substituted benzimidazoles) and 1:2 of 1,2-phenylenediamine and 4-nitrobenzaldehyde (for the synthesis of di-substituted benzimidazoles) by using 1 mol% catalytic amount of SnO_2 nanoparticles at room temperature in ethanol solvent.

The recoverability and reusability of the catalyst was studied in model reaction. After end of the reaction, hot ethanol was added to the reaction mixture and filtered to separate the catalyst. The separated catalyst was applied for additional runs. The activity of the catalyst did not display any substantialdecrease even after three runs. The structure of recycled catalyst was studied by SEM analysis and the results displayed that the catalyst is stable (Fig. S4).

Following, we investigated the scope of this



Quantitative Results

Elt	Line	Int	Error	K	Kr	W%	A%	ZAF	Formula	Ox%	Pk/Bg
O	Ka	506.9	350.9113	0.1096	0.0712	35.60	80.40	0.2000		0.00	356.43
Sn	La	3461.4	123.2157	0.8904	0.5788	64.40	19.60	0.8987		0.00	124.14
				1.0000	0.6500	100.00	100.00			0.00	

Fig. 6. EDS analysis of SnO_2 nanoparticle.

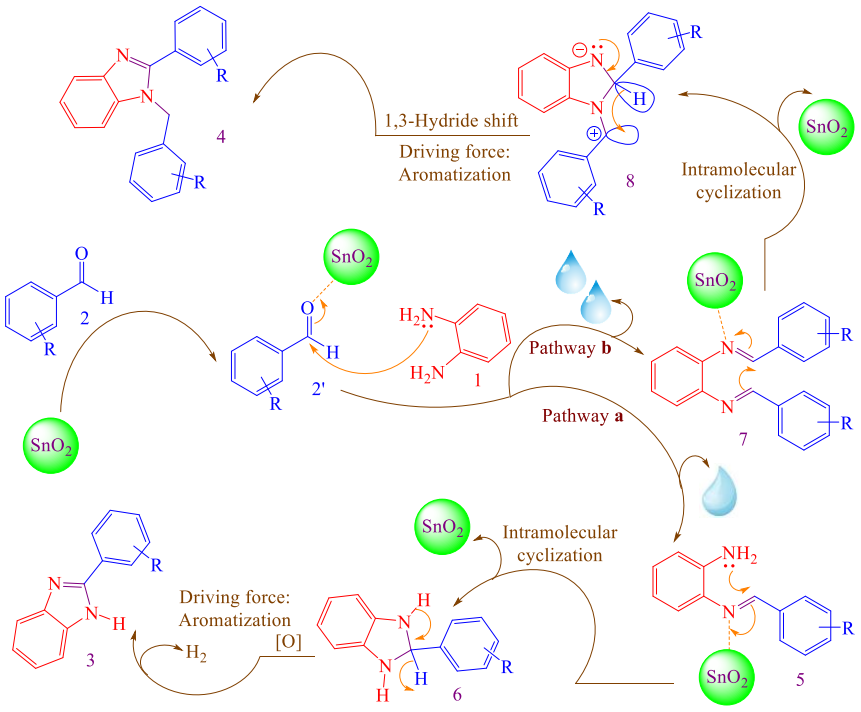
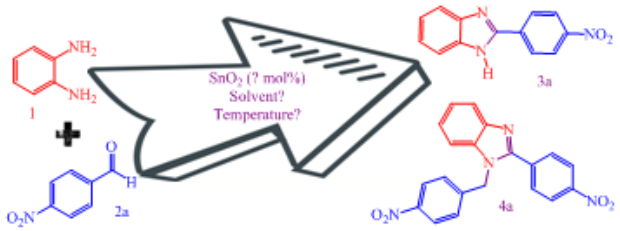


Fig. 7. Suggested mechanism for the synthesis of 2-substituted benzimidazoles3 and 1,2-disubstituted benzimidazoles4 catalyzed by SnO_2 nanoparticles.

Table 1. Evaluation of catalytic amount and solvent in the synthesis of target molecules 3a and 4a.



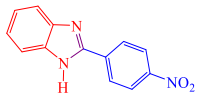
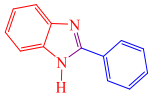
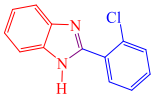
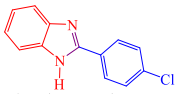
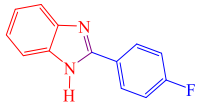
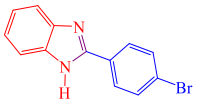
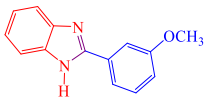
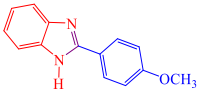
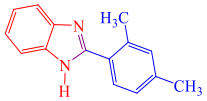
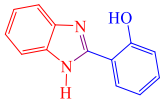
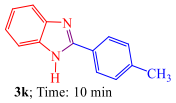
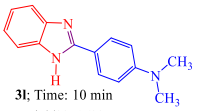
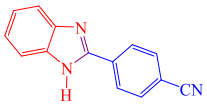
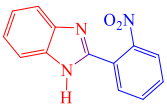
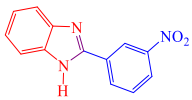
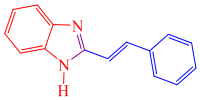
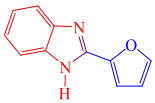
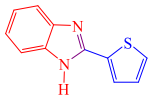
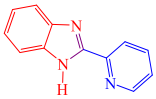
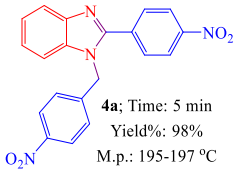
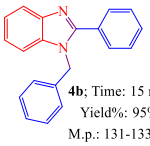
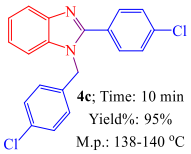
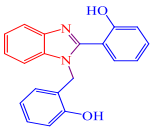
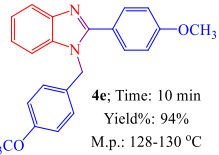
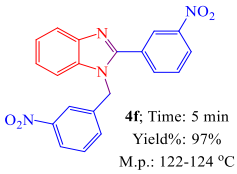
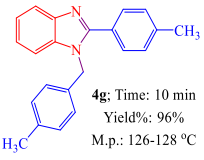
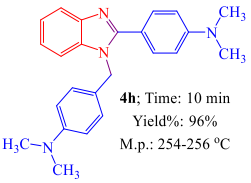
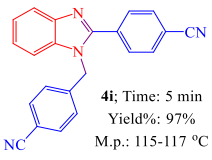
Entry	Solvent	Catalytic amount (mol%)	**3a**[a]		**4a**[b]	
			Time (min)	Yield (%)[c]	Time (min)	Yield (%)[c]
1	C_2H_5OH	0.5	5	90	5	90
2	C_2H_5OH	1	5	98	5	98
3	C_2H_5OH	2	5	98	5	98
4	C_2H_5OH	5	5	98	5	98
5	H_2O	1	45	92	45	80
6	CH_3CN	1	40	94	45	81
7	CH_2Cl_2	1	50	88	50	76
8	Ethyl acetate	1	45	85	50	74
9	Toluene	1	50	80	50	70

:eaction condition: [a]4-nitrobenzaldehyde (1 mmol; 0.151 g), 1,2-phenylenediamine (1 mmol; 0.108 g); [b]4-nitrobenzaldehyde (2 mmol; 0.302 :), 1,2-phenylenediamine (1 mmol; 0.108 g);[c] Isolated yield.

reaction (Table 2). As assessed, this reaction progressed effortlessly and the chosen products were attained in appropriate yields. A series of aldehydes with either electron-releasing or electron-withdrawing groups attaching to aromatic ring were studied. The substitution groups on the aromatic ring had no clear effect on the yield. We also investigated reaction of aromatic heterocyclic aldehydes with 1,2-phenylenediamine and the desired products were achieved in good yields.

The proposed mechanism for the synthesis of title compounds 3 and 4were showed in Fig. 7 (pathway a andb)[56, 57]. Initially, SnO_2 nanoparticles activates the carbonyl group of aldehyde 2 to provide intermediate 2'. In pathway a, the nucleophilic attack of 1,2-phenylenediamine 1 on the intermediate 2' to afford intermediates 5 via elimination of one molecule of water. In the next step, intramolecular cyclization of intermediate 5 via nucleophilic attack of amine group on the imine band to give intermediate 6 which aromatized through air oxidation to 2-substituted benzimidazoles3. In pathway b, the nucleophilic attack of 1,2-phenylenediamine 1 on the two molecule of intermediate 2' to give intermediates 7 via elimination of two molecule of water. At that time, intramolecular cyclization of intermediate 7 to provide intermediate 8 which

Table 2. Synthesis of 2-substituted benzimidazoles3and 1,2-disubstituted benzimidazoles4catalyzed by SnO_2 nanoparticles.[a-c]

 **3a**; Time: 5 min Yield%: 98% M.p.: 319-321 °C	 **3b**; Time: 15 min Yield%: 93% M.p.: 291-293 °C	 **3c**; Time: 10 min Yield%: 94% M.p.: 234-235 °C	 **3d**; Time: 10 min Yield%: 95% M.p.: 290-292 °C
 **3e**; Time: 10 min Yield%: 95% M.p.: 245-247 °C	 **3f**; Time: 10 min Yield%: 94% M.p.: 262-264 °C	 **3g**; Time: 10 min Yield%: 94% M.p.: 206-208 °C	 **3h**; Time: 10 min Yield%: 95% M.p.: 223-225 °C
 **3i**; Time: 15 min Yield%: 95% M.p.: 250-255 °C	 **3j**; Time: 20 min Yield%: 90% M.p.: 244-246 °C	 **3k**; Time: 10 min Yield%: 95% M.p.: 268-270 °C	 **3l**; Time: 10 min Yield%: 96% M.p.: 235-237 °C
 **3m**; Time: 5 min Yield%: 97% M.p.: 257-259 °C	 **3n**; Time: 10 min Yield%: 93% M.p.: 261-263 °C	 **3o**; Time: 5 min Yield%: 97% M.p.: 204-206 °C	 **3p**; Time: 15 min Yield%: 94% M.p.: 201-203 °C
 **3q**; Time: 10 min Yield%: 95% M.p.: 284-286 °C	 **3r**; Time: 10 min Yield%: 95% M.p.: 325-327 °C	 **3s**; Time: 10 min Yield%: 96% M.p.: 216-218 °C	 **4a**; Time: 5 min Yield%: 98% M.p.: 195-197 °C
 **4b**; Time: 15 min Yield%: 95% M.p.: 131-133 °C	 **4c**; Time: 10 min Yield%: 95% M.p.: 138-140 °C	 **4d**; Time: 15 min Yield%: 91% M.p.: 207-209 °C	 **4e**; Time: 10 min Yield%: 94% M.p.: 128-130 °C
 **4f**; Time: 5 min Yield%: 97% M.p.: 122-124 °C	 **4g**; Time: 10 min Yield%: 96% M.p.: 126-128 °C	 **4h**; Time: 10 min Yield%: 96% M.p.: 254-256 °C	 **4i**; Time: 5 min Yield%: 97% M.p.: 115-117 °C

Reaction condition: [a] aldehyde (1 mmol), 1,2-phenylenediamine (1 mmol; 0.108 g), ethanol (2 mL), r.t.; [b] aldehyde (2 mmol), 1,2-phenylenediamine (1 mmol; 0.108 g), ethanol (2 mL), r.t.; [c] Isolated yield.

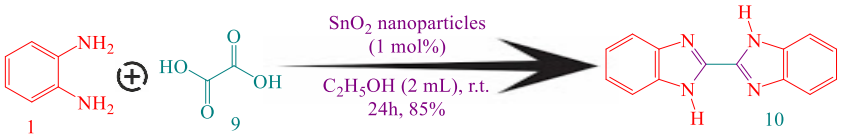


Fig. 8. Synthesis of 1H,1'H-2,2'-bibenzo[d]imidazole 10 catalyzed by SnO_2 nanoparticles.

aromatized via 1,3-hydide shift to 1,2-disubstituted benzimidazoles4.

In other work, for investigation of catalytic activity of SnO_2 nanoparticles, the synthesis of 1H,1'H-2,2'-bibenzo[d]imidazole10was performedvia the reaction between 1,2-phenylenediamine1and oxalic acid 9 by using 1 mol% SnO_2 nanoparticles in ethanol at room temperature.

CONCLUSION

In summary, we have described an efficacious approach for the facile and appropriate synthesis of 2-substituted benzimidazoles and 1,2-disubstituted benzimidazolesin a cyclo-condensation reaction between 1,2-phenylenediamine and aldehydes by using 1 mol% catalytic amount of SnO_2 nanoparticles under mild conditions. Application of informal reaction conditions, isolation and purification makes this process very interesting from a cost-effective viewpoint.

ACKNOWLEDGEMENTS

The authors are thankful for the facilities provided to carry out research in chemistry research laboratory at Ayatollah Amoli Branch, Islamic Azad University.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES

1. Zeng T, Chen W-W, Cirtiu CM, Moores A, Song G, Li C-J. Fe3O4 nanoparticles: a robust and magnetically recoverable catalyst for three-component coupling of aldehyde, alkyne and amine. Green Chemistry. 2010;12(4):570.
2. Mojtahedi MM, Saeed Abaee M, Alishiri T. Superparamagnetic iron oxide as an efficient catalyst for the one-pot, solvent-free synthesis of α-aminonitriles. Tetrahedron Letters. 2009;50(20):2322-5.
3. Patil RD, Adimurthy S. Copper-Catalyzed Aerobic Oxidation of Amines to Imines under Neat Conditions with Low Catalyst Loading. Advanced Synthesis & Catalysis. 2011;353(10):1695-700.
4. Maleki A. An Efficient Magnetic Heterogeneous Nanocatalyst for the Synthesis of Pyrazinoporphyrazine Macrocycles. Polycyclic Aromatic Compounds. 2016;38(5):402-9.
5. Tamoradi T, Ghorbani-Choghamarani A, Ghadermazi M. CoFe2O4@glycine-M (M= Pr, Tb and Yb): Three green, novel, efficient and magnetically-recoverable nanocatalysts for synthesis of 5-substituted 1H–tetrazoles and oxidation of sulfides in green condition. Solid State Sciences. 2019;88:81-94.
6. Maleki B, Baghayeri M, Ghanei-Motlagh M, Mohammadi Zonoz F, Amiri A, Hajizadeh F, et al. Polyamidoamine dendrimer functionalized iron oxide nanoparticles for simultaneous electrochemical detection of Pb2+ and Cd2+ ions in environmental waters. Measurement. 2019;140:81-8.
7. Baskar G, Aiswarya R. Trends in catalytic production of biodiesel from various feedstocks. Renewable and Sustainable Energy Reviews. 2016;57:496-504.
8. Madhuvilakku R, Piraman S. Biodiesel synthesis by TiO2–ZnO mixed oxide nanocatalyst catalyzed palm oil transesterification process. Bioresource Technology. 2013;150:55-9.
9. Ambat I, Srivastava V, Sillanpää M. Recent advancement in biodiesel production methodologies using various feedstock: A review. Renewable and Sustainable Energy Reviews. 2018;90:356-69.
10. Lin C, Wei W, Hu YH. Catalytic behavior of graphene oxide for cement hydration process. Journal of Physics and Chemistry of Solids. 2016;89:128-33.
11. Chen K, Fan W, Huang C, Qiu X. Enhanced stability and catalytic activity of bismuth nanoparticles by modified with porous silica. Journal of Physics and Chemistry of Solids. 2017;110:9-14.
12. Luca LD. Naturally Occurring and Synthetic Imidazoles: Their Chemistry and Their Biological Activities. Current Medicinal Chemistry. 2006;13(1):1-23.
13. Xiong F, Chen X-X, Chen F-E. An improved asymmetric total synthesis of (+)-biotin via the enantioselective desymmetrization of a meso-cyclic anhydride mediated by cinchona alkaloid-based sulfonamide. Tetrahedron: Asymmetry. 2010;21(6):665-9.
14. Roué M, Domart-Coulon I, Ereskovsky A, Djediat C, Perez T, Bourguet-Kondracki M-L. Cellular Localization of Clathridimine, an Antimicrobial 2-Aminoimidazole Alkaloid Produced by the Mediterranean Calcareous Sponge Clathrina clathrus. Journal of Natural Products. 2010;73(7):1277-82.
15. Asensio JA, Gómez-Romero P. Recent Developments on Proton Conduc-ting Poly(2,5-benzimidazole) (ABPBI) Membranes for High Temperature Poly-mer Electrolyte Membrane Fuel Cells. Fuel Cells. 2005;5(3):336-43.
16. Singh N, Jang DO. Benzimidazole-Based Tripodal Receptor: Highly Selective Fluorescent Chemosensor for Iodide in Aqueous Solution. Organic Letters. 2007;9(10):1991-4.
17. Kwon JE, Park S, Park SY. Realizing Molecular Pixel System for Full-Color Fluorescence Reproduction: RGB-Emitting Molecular Mixture Free from Energy Transfer Crosstalk. Journal of the American Chemical Society. 2013;135(30):11239-46.

18. Jeżewski A, Hammann T, Cywiński PJ, Gryko DT. Optical Behavior of Substituted 4-(2′-Hydroxyphenyl)imidazoles. The Journal of Physical Chemistry B. 2015;119(6):2507-14.
19. Dietrich J, Gokhale V, Wang X, Hurley LH, Flynn GA. Application of a novel [3+2] cycloaddition reaction to prepare substituted imidazoles and their use in the design of potent DFG-out allosteric B-Raf inhibitors. Bioorganic & Medicinal Chemistry. 2010;18(1):292-304.
20. Jin CH, Krishnaiah M, Sreenu D, Subrahmanyam VB, Rao KS, Lee HJ, et al. Discovery of N-((4-([1,2,4]Triazolo[1,5-a]pyridin-6-yl)-5-(6-methylpyridin-2-yl)-1H-imidazol-2-yl)methyl)-2-fluoroaniline (EW-7197): A Highly Potent, Selective, and Orally Bioavailable Inhibitor of TGF-β Type I Receptor Kinase as Cancer Immunotherapeutic/Antifibrotic Agent. Journal of Medicinal Chemistry. 2014;57(10):4213-38.
21. Zhang L, Peng X-M, Damu GLV, Geng R-X, Zhou C-H. Comprehensive Review in Current Developments of Imidazole-Based Medicinal Chemistry. Medicinal Research Reviews. 2013;34(2):340-437.
22. Atwell GJ, Fan J-Y, Tan K, Denny WA. DNA-Directed Alkylating Agents. 7. Synthesis, DNA Interaction, and Antitumor Activity of Bis(hydroxymethyl)- and Bis(carbamate)-Substituted Pyrrolizines and Imidazoles. Journal of Medicinal Chemistry. 1998;41(24):4744-54.
23. Al-Raqa SY, ElSharief AMS, Khalil SME, Al-Amri AM. Synthesis of some novel imidazolidine derivatives and their metal complexes with biological and antitumor activity. Heteroatom Chemistry. 2006;17(7):634-47.
24. Vlahakis JZ, Lazar C, Crandall IE, Szarek WA. Anti-Plasmodium activity of imidazolium and triazolium salts. Bioorganic & Medicinal Chemistry. 2010;18(16):6184-96.
25. Vijesh AM, Isloor AM, Telkar S, Peethambar SK, Rai S, Isloor N. Synthesis, characterization and antimicrobial studies of some new pyrazole incorporated imidazole derivatives. European Journal of Medicinal Chemistry. 2011;46(8):3531-6.
26. Choi JY, Plummer MS, Starr J, Desbonnet CR, Soutter HH, Chang J, et al. Structure Guided Development of Novel Thymidine Mimetics targeting Pseudomonas aeruginosa Thymidylate Kinase: from Hit to Lead Generation. Worldwide Protein Data Bank; 2012.
27. Yurttas L, Duran M, Demirayak S, Gencer HK, Tunali Y. ChemInform Abstract: Synthesis and Initial Biological Evaluation of Substituted 1-Phenylamino-2-thio-4,5-dimethyl-1H-imidazole Derivatives. ChemInform. 2014;45(18):no-no.
28. Sennequier N, Wolan D, Stuehr DJ. Antifungal Imidazoles Block Assembly of Inducible NO Synthase into an Active Dimer. Journal of Biological Chemistry. 1999;274(2):930-8.
29. Koga H, Nanjoh Y, Makimura K, Tsuboi R. In vitroantifungal activities of luliconazole, a new topical imidazole. Medical Mycology. 2009;47(6):640-7.
30. Röhrig UF, Majjigapu SR, Chambon M, Bron S, Pilotte L, Colau D, et al. Detailed analysis and follow-up studies of a high-throughput screening for indoleamine 2,3-dioxygenase 1 (IDO1) inhibitors. European Journal of Medicinal Chemistry. 2014;84:284-301.
31.Lee JC, Laydon JT, Mcdonnell PC. A protein kinase involved in the regulation of inflammatory cytokine biosynthesis. Nature, 1994; 372:739-746.
32. Adams JL, Boehm JC, Gallagher TF, Kassis S, Webb EF, Hall R, et al. Pyrimidinylimidazole inhibitors of p38: cyclic N-1 imidazole substituents enhance p38 kinase inhibition and oral activity. Bioorganic & Medicinal Chemistry Letters. 2001;11(21):2867-70.
33. Zhang Q, Luo L, Xu H, Hu Z, Brommesson C, Wu J, et al. Design, synthesis, linear and nonlinear photophysical properties of novel pyrimidine-based imidazole derivatives. New Journal of Chemistry. 2016;40(4):3456-63.
34. Wächtler M, Maiuri M, Brida D, Popp J, Rau S, Cerullo G, et al. Utilizing Ancillary Ligands to Optimize the Photophysical Properties of 4H-Imidazole Ruthenium Dyes. ChemPhysChem. 2013;14(13):2973-83.
35. Bhalla R, Helliwell M, Garner CD. Synthesis and Coordination Chemistry of the Bis(imidazole) Ligand, Bis(1-methyl-4,5-diphenylimidaz-2-oyl)(benzyloxy)methane. Inorganic Chemistry. 1997;36(14):2944-9.
36. Mohr P, Scheler W, Schumann H, Muller K. Ligand-Protein Interactions in Imidazole and 1,2,4-Triazole Complexes of Methaemoglobin from Chironomus plumosus. European Journal of Biochemistry. 1967;3(2):158-63.
37. Erden Ib, Demirhan N, Avcıata U. Synthesis and Characterization of a New Imidazole Ligand and its Complexes with Cobalt(II), Nickel(II) and Copper(II). Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry. 2006;36(7):559-62.
38. Vahdat S, Baghery S. A Green and Efficient Protocol for the Synthesis of Quinoxaline, Benzoxazole and Benzimidazole Derivatives Using Heteropolyanion-Based Ionic Liquids: As a Recyclable Solid Catalyst. Combinatorial Chemistry & High Throughput Screening. 2013;16(8):618-27.
39. Niknam K, Fatehi-Raviz A. Synthesis of 2-substituted benzimidazoles and bis-benzimidazoles by microwave in the presence of alumina-methanesulfonic acid. Journal of the Iranian Chemical Society. 2007;4(4):438-43.
40. Sharghi H, Khalifeh R, Mansouri SG, Aberi M, Eskandari MM. Simple, Efficient, and Applicable Route for Synthesis of 2-Aryl(Heteroaryl)-Benzimidazoles at Room Temperature Using Copper Nanoparticles on Activated Carbon as a Reusable Heterogeneous Catalyst. Catalysis Letters. 2011;141(12):1845-50.
41. Heravi MM, Baghernejad B, Oskooie HA, Malakooti R. Mesoporous Molecular Sieve MCM-41 as a Novel and Efficient Catalyst to Synthesis of 2-Substituted Benzimidazoles. Journal of the Chinese Chemical Society. 2008;55(5):1129-32.
42. Bachhav HM, Bhagat SB, Telvekar VN. Efficient protocol for the synthesis of quinoxaline, benzoxazole and benzimidazole derivatives using glycerol as green solvent. Tetrahedron Letters. 2011;52(43):5697-701.
43. Gadekar LS, Arbad BR, Lande MK. Eco-friendly synthesis of benzimidazole derivatives using solid acid scolecite catalyst. Chinese Chemical Letters. 2010;21(9):1053-6.
44. Beaulieu PL, Hache B, von Moos E. A Practical Oxone®-Mediated, High-Throughput, Solution-Phase Synthesis of Benzimidazoles from 1,2-Phenylenediamines and Aldehydes and Its Application to Preparative Scale Synthesis. ChemInform. 2003;34(50).
45. Kawashita Y, Nakamichi N, Kawabata H, Hayashi M. Direct and Practical Synthesis of 2-Arylbenzoxazoles Promoted by Activated Carbon. Organic Letters. 2003;5(20):3713-5.
46. Bahrami K, Khodaei MM, Nejati A. Synthesis of 1,2-disubstituted benzimidazoles, 2-substituted benzimidazoles and 2-substituted benzothiazoles in SDS micelles. Green Chemistry. 2010;12(7):1237.
47. Zolfigol MA, Khazaei A, Alaie S, Baghery S, Maleki F, Bayat

Y, et al. Experimental and theoretical approving of anomeric based oxidation in the preparation of 2-sbstituted benz-(imida, oxa and othia)-zoles using [2,6-DMPy-NO2] C(NO2)3 as a novel nano molten salt catalyst. RSC Advances. 2016;6(63):58667-79.
48. Vahdat SM, Raz SG, Baghery S. Application of nano SnO2 as a green and recyclable catalyst for the synthesis of 2-aryl or alkylbenzoxazole derivatives under ambient temperature. Journal of Chemical Sciences. 2014;126(3):579-85.
49.Vahdat SM, Chekin F, Hatami M, Khavarpour M, Baghery S, Roshan-Kouhi Z. Synthesis of polyhydroquinoline derivatives via a four-compone. Chin J Catal, 2013; 34:758-763.
50. Zolfigol MA, Baghery S, Moosavi-Zare AR, Vahdat SM, Alinezhad H, Norouzi M. Design of 1-methylimidazolium tricyanomethanide as the first nanostructured molten salt and its catalytic application in the condensation reaction of various aromatic aldehydes, amides and β-naphthol compared with tin dioxide nanoparticles. RSC Advances. 2015;5(56):45027-37.
51. Zolfigol MA, Baghery S, Moosavi-Zare AR, Vahdat SM. Synthesis and characterization of new 1-(α-aminoalkyl)-2-naphthols using pyrazine-1,4-diium trinitromethanide {[1,4-DHPyrazine][C(NO2)3]2} as a novel nano-structured molten salt and catalyst in compared with Ag–TiO2 nano composite. Journal of Molecular Catalysis A: Chemical. 2015;409:216-26.
52. Maleki B, Baghayeri M, Vahdat SM, Mohammadzadeh A, Akhoondi S. Ag@TiO2 nanocomposite; synthesis, characterization and its application as a novel and recyclable catalyst for the one-pot synthesis of benzoxazole derivatives in aqueous media. RSC Advances. 2015;5(58):46545-51.
53. Chekin F, Vahdat SM, Asadi MJ. Green synthesis and characterization of cobalt oxide nanoparticles and its electrocatalytic behavior. Russian Journal of Applied Chemistry. 2016;89(5):816-22.
54. Yazdani S, Hatami M, Vahdat SM. The chemistry concerned with the sonochemical-assisted synthesis of CeO$_{2}$/poly(amic acid) nanocomposites. TURKISH JOURNAL OF CHEMISTRY. 2014;38:388-401.
55. Zhang H, Hu C, He X, Hong L, Du G, Zhang Y. Pt support of multidimensional active sites and radial channels formed by SnO2 flower-like crystals for methanol and ethanol oxidation. Journal of Power Sources. 2011;196(10):4499-505.
56. Azarifar D, Pirhayati M, Maleki B, Sanginabadi M, Yami N. Acetic acid-promoted condensation of o-phenylenediamine with aldehydes into 2-aryl-1-(arylmethyl)-1H-benzimidazoles under microwave irradiation. Journal of the Serbian Chemical Society. 2010;75(9):1181-9.
57. Chen G-F, Dong X-Y. Facile and Selective Synthesis of 2-Substituted Benzimidazoles Catalyzed by FeCl3/ Al2O3. E-Journal of Chemistry. 2012;9(1):289-93.