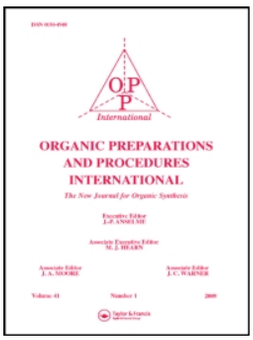


Taylor & Francis
Taylor & Francis Group

Organic Preparations and Procedures International

The New Journal for Organic Synthesis

ISSN: 0030-4948 (Print) 1945-5453 (Online) Journal homepage: http://www.tandfonline.com/loi/uopp20

A Magnetically Recoverable and Reusable Catalyst for Synthesis of 5-Substituted 1*H*-Tetrazoles

Ali Elhampour & Firouzeh Nemati

To cite this article: Ali Elhampour & Firouzeh Nemati (2018) A Magnetically Recoverable and Reusable Catalyst for Synthesis of 5-Substituted 1*H*-Tetrazoles, Organic Preparations and Procedures International, 50:5, 493-501, DOI: 10.1080/00304948.2018.1525673

To link to this article: https://doi.org/10.1080/00304948.2018.1525673

Published online: 04 Jan 2019.

Organic Preparations and Procedures International, 50:493–501, 2018

ISSN: 0030-4948 print / 1945-5453 online
DOI: 10.1080/00304948.2018.1525673

A Magnetically Recoverable and Reusable Catalyst for Synthesis of 5-Substituted 1*H*-Tetrazoles

Ali Elhampour and Firouzeh Nemati

Department of Chemistry, Semnan University, 35131-19111, Semnan, Iran

The nitrile group is valuable in organic synthesis and can be transformed to a variety of functional groups, including thiazoles, oxazolidones, triazoles, and tetrazoles. Moreover, aromatic nitriles constitute a key component of numerous natural products and pharmaceutically important compounds such as dyes and herbicides.[1] Among the different heterocycles generated from benzonitriles, tetrazoles are an increasingly popular functionality with a wide range of applications in the field of medicinal chemistry as metabolically stable surrogates for the related carboxylic acids.[2] Thus, one way to potentiate anti-inflammatory activity is to mimic a carboxylic acid with a tetrazole moiety.[3] Indomethacin and intrazole are interesting examples of anti-arthritis drugs whose carboxylic acid groups may be replaced by tetrazole with no loss of activity. In addition, as the tetrazoles generally offer a more favorable pharmacokinetic profile, they have been widely incorporated into angiotensin II antagonist structures, including losartan and valsartan (*Figure 1*).[4–6]

Aryl nitriles are traditionally synthesized *via* the Rosenmund-von Braun reaction from the corresponding halides or the Sandmeyer reaction from anilines. On the other hand, numerous methods have been developed to insert nitrile groups into molecules.[7–10] Among these methods, substantial research efforts have been developed for the direct transition metal catalyzed transformation of aryl halides to aryl nitriles.[11,12]

Aryl halides are now more attractive as starting materials in lead optimization processes since they can act as precursors for so many reactions. Recently, transition metal-catalyzed cyanation of aryl halides was developed as a useful alternative for the preparation of aryl nitriles. The cyanating agents used were MCN (M = Cu, K, Na, Zn), TMSCN, and $K_4Fe[(CN)_6] \cdot 3H_2O$.[13]

On the other hand, the most adaptable method for the preparation of 5-substituted 1*H*-tetrazoles is *via* [2 + 3] cycloaddition between azides and nitriles.[14] This procedure has advantages but was troubled with such drawbacks as strong Lewis acidity, use of costly or toxic metal organic azides, hydrazoic acid or highly moisture-sensitive reaction conditions. Thus a catalytic method for preparation of tetrazole derivatives is of importance. The most attractive feature of heterogeneous catalysis is the production and convenient separation of large quantities of products with the use of a small amount of catalyst. Recently, several heterogeneous catalytic systems were reported for the syntheses of 5-substituted tetrazoles.[15–22]

Received November 18, 2017; in final form July 31, 2018.
Address correspondence to Firouzeh Nemati, Department of Chemistry, Semnan University, 35131-19111, Semnan, Iran. E-mail: fnemati@semnan.ac.ir.

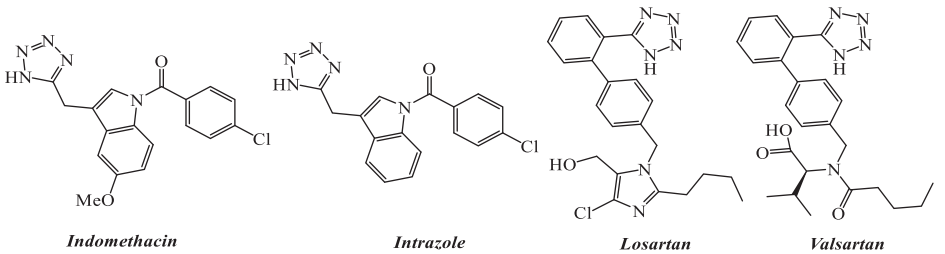


Figure 1. Bioactive tetrazole moieties.

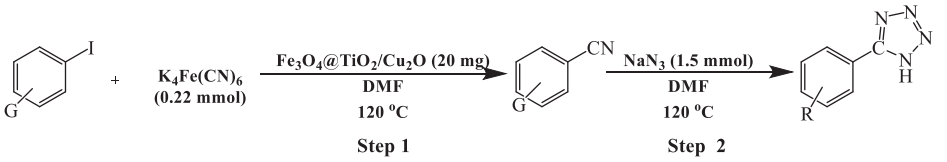
In the past decade, magnetic nanoparticles (MNPs) have become a useful group of heterogeneous catalysts because they have high surface area, unique magnetic properties and high catalytic activity.[23,24] Importantly, the easy separation of magnetic nanoparticles is simple, economical, and an attractive alternative to filtration or centrifugation because it prevents loss of catalyst and enhances reusability, making the catalyst cost-effective and promising for industrial applications.[25] However, MNPs suffer from drawbacks, including the tendency to aggregation in the reaction mixture.[26] To solve this problem, MNPs are coated by using suitable stabilizing materials such as silica, titanium dioxide, polymers or zeolites.[27–30]

Titanium dioxide (TiO_2) nanoparticles have enjoyed widespread application.[31] However, one of the major disadvantages of TiO_2 nanoparticles is the inconvenience of recycling these catalysts. Filtration or centrifugation may lead to catalyst loss and energy consumption. A strategy developed to solve this issue is coating the magnetic nanoparticle core with a TiO_2 insulation layer to avoid an unfavorable heterojunction. In terms of convenience, TiO_2-based catalysts are cheap, easy to prepare, and are insoluble in all organic solvents. Among various TiO_2-based heterogeneous catalysts, Fe_3O_4 cores within shells of TiO_2 have the merits of low cost, ease of preparation and can be recycled.[32–35] They are easy to recover by simply applying a magnetic field.

Recently, we have used a type of magnetic nano-Fe_3O_4 as an easily separable catalyst in different organic reactions.[35–40] In continuation of our interest, we have studied the application of the magnetic Fe_3O_4 core and TiO_2 shell with microcrystals of Cu_2O for the regioselective synthesis of 1,4-disubstituated 1,2,3-triazoles, *via* the click reaction and A^3 and KA^2 coupling reaction. We have previously described our rationale for using TiO_2 and Cu_2O together.[35,36] We now report a new process for the cyanation of aryl iodides to the corresponding aryl nitriles and synthesis of 5-substituted 1-*H*-tetrazoles using nano-Fe_3O_4@TiO_2/Cu_2O core-shell magnetic composites as a safe, environmentally benign, and inexpensive catalyst (*Scheme 1*).

The reaction was carried out in two steps in one pot, including: 1) preparation of aryl nitriles and 2) synthesis of 5-substituted 1*H*-tetrazoles. In an effort to develop better reaction conditions in the first step, loading of catalyst and different solvents were screened for the synthesis of benzonitrile from the reaction of phenyl iodide and $K_4[Fe(CN)_6] \cdot 3H_2O$ as a template reaction (Step 1, *Scheme 1*). The results of the optimization of the reaction conditions are summarized in *Table 1*. Solvents, temperatures and reaction times were studied.

The data suggested that an excellent yield was obtained in DMF as the solvent at 120 °C by applying 20 mg of nano magnetic Fe_3O_4@TiO_2/Cu_2O core-shell composite and a 1:0.22 molar ratio of aryl iodide: $K_4[Fe(CN)_6] \cdot 3H_2O$ (*Table 1, entry 3*). Notably,



One Pot Process

Scheme 1.

Table 1
Effects of Amount of Catalyst, Duration of Reaction and Solvent on the Yield of Benzonitrile Prepared from $K_4[Fe(CN)_6] \cdot 3H_2O$ and Aryl Iodidea

Entry	Fe_3O_4@TiO_2/Cu_2O (g)	Condition/ Temp	Time (h)	Yieldb (%)
1	0.020	DMF / r.t	6	Trace
2	0.020	DMF / 100°C	3	60
3	**0.020**	**DMF / 120°C**	**3**	**90**
4	0.020	DMF/ 130°C	3	90
5	0.030	DMF / 120°C	3	90
6	0.010	DMF / 120°C	3	71
7	0.020	H_2O / Reflux	5	11
8	0.020	DMSO / 120°C	3	75
9	0.020	Toluene / 120°C	3	47
10	0.020	Solvent free/120°C	3	42
11	–	DMF / 120°C	5	n.r.
11	0.020	DMF / r.t	6	Trace
12	Fe_3O_4@TiO_2(0.02 g)	DMF / 120°C	3	40
13	Fe_3O_4/Cu_2O(0.02 g)	DMF / 120°C	3	76

[a]Reaction condition: Iodobenzene (1 equiv.), $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.22 equiv.), Solvent (2 mL).
[b]Isolated yield.

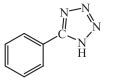
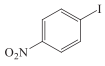
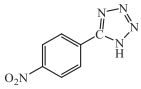
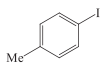
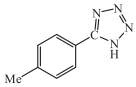
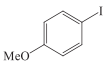
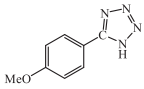
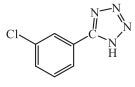
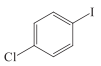
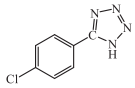
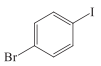
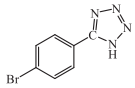
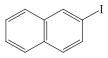
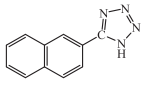
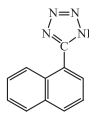
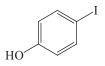
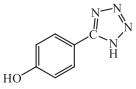
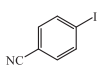
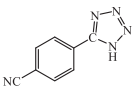
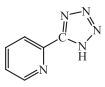
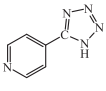
the reaction proceeds smoothly to completion and the corresponding products were obtained with high purity. We then investigated the reaction between the formed benzonitrile with sodium azide to provide the 5-substituted 1*H*-tetrazole in one pot. The best results were obtained by using a 1:1.5 ratio of benzonitrile and sodium azide after 5h.

Using our optimized conditions, we next explored the diversity and limitations of substrates as well as the efficiency of our catalysts for the one-pot reaction to prepare 5-substituted 1*H*-tetrazoles. The results are summarized in *Table 2*. The aryl iodides included aromatic and heteroaromatic compounds. Yields were uniformly good and not particulary sensitive to iodide structure.

Notably, *o*-iodo naphthalene and *m*-iodo naphthalene also reacted smoothly and gave the corresponding products in good yield (*Table 2, entries 8* and *9*). It is interesting to note that heteroaromatic iodides such as *o*-iodo pyridine and *p*-iodo pyridine are compatible in the tetrazole synthesis (*Table 2, entries 12* and *13*). This study reveals

Table 2

Synthesis of 5-Substituted 1*H*-Tetrazoles from Aryl Iodide with $K_4[Fe(CN)_6].3H_2O$ and Sodium Azide Catalyzed by Nano Magnetic Fe_3O_4@TiO_2/Cu_2O (Scheme 1)[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]	Mp (°C) found	Mp (°C) Lit
1			8	90	213-215	214-215[8]
2			7	91	218-219	220-22[8]
3			10	85	249-251	247-249[8]
4			12	84	230–232	231-233[41]
5			8	88	138-140	137–139[42]
6			8	81	251-253	251-252[8]
7			8	88	267-268	268-269[8]
8			9	81	205–207	204-206[43]
9			10	78	265-267	264–267[43]
10			9	89	235	233-234[8]
11			7	77	257-259	258–260[44]
12			8	85	210-213	211-212[45]
13			9	89	256-258	254-255[46]

[a]Reaction conditions: a mixture of Aryl iodide (1equiv.) (or its 2-Iodo pyridine and 4-Iodo pyridine), $K_4[Fe(CN)_6] \cdot 3H_2O$ (0.22 equiv.), Sodium azide (1.5 equiv.) and Nano magnetic Fe_3O_4@TiO_2/Cu_2O (20 mg) was heated in 2 mL of DMF at 120 °C.

[b]Isolated yield.

that the nano magnetic Fe_3O_4@TiO_2/Cu_2O core-shell composite is an efficient catalyst for both aromatic and heterocyclic tetrazole synthesis from aryl iodide derivatives.

The reusability of the catalyst is one of the most important benefits. In a typical experiment, after the reaction was completed, the nano magnetic catalyst was isolated from the reaction mixture by an external magnet in the work-up stage, washed with acetone, distilled water and ethanol, respectively, and then dried in a desiccator and subjected to the next run. The Fe_3O_4@TiO_2/Cu_2O magnetic composite was reused for five cycles with steady activity. Moreover, there was little decrease in the yield of the corresponding product indicating high potency of the catalyst (Run 1, 90%, Run 2, 89%, Run 3, 87%, Run 4, 86%, Run 5, 85%).

In summary, a very useful procedure for the preparation of 5-substituted 1*H*-tetrazoles was developed using magnetically separable nanoparticle Fe_3O_4@TiO_2/Cu_2O core-shell composite as a heterogeneous catalyst. The important benefits of this methodology are high yields, an easy procedure and simple recovery and reusability of the catalyst.

Experimental Section

All reagents were purchased from Merck and Aldrich and used without further purification. The progress of the reactions was monitored by TLC on commercial aluminum-backed plates of silica gel 60 F254, visualized using ultraviolet light. Melting points were determined using an Electrothermal 9100 and were uncorrected. FT-IR spectra were obtained with potassium bromide pellets in the range of 400–4000 cm-1 using a Shimadzu 8400s spectrometer.

NMR spectra were obtained on a Bruker Avance 400 spectrometer (^{1}H NMR at 400 and 250 Hz, ^{13}C NMR at 100 and 62.9 Hz) in $CDCl_3$ or DMSO using TMS as an internal standard. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Nano magnetic-Fe_3O_4@TiO_2/Cu_2O core-shell composite was prepared and characterized according to our previous report.[35] The model reaction was also carried out in the presence of Fe_3O_4@TiO_2 and Fe_3O_4/Cu_2O as catalyst, and lower yield of the corresponding product was obtained (*Table 1, entries 12 and 13*).

Preparation of nano-Fe_3O_4

The Fe_3O_4 nanoparticles were prepared in accordance with our earlier report.[37]

Preparation of nano-Fe_3O_4@TiO_2

Nano-Fe_3O_4@TiO_2 was synthesized according to a previously reported method,[42] subjected to modification. The above prepared nano-magnetic Fe_3O_4 particles were dispersed in a mixture of absolute ethanol and acetonitrile (250 mL/90 mL). This mixture was sonicated for 15 min, and then 1.5 mL of NH_4OH solution (25 wt.%) was added. After continuous mechanical stirring for 30 min, 3 mL (8 mmol) of tetrabutyl titanate (TBOT), dissolved in 20 mL of absolute ethanol was added drop-wise to the above suspension, under continuous mechanical stirring at 30 °C. The reaction mixture was further stirred for 1.5 h to obtain Fe_3O_4@TiO_2 core/shell nanoparticles. Magnetic separation

was used for collection of nanoparticles. After that, they were washed three times with absolute ethanol.

Preparation of nano-Fe_3O_4@TiO_2/Cu_2O Core-Shell Magnetic Composite

Four types of composites with different molar ratio of Fe_3O_4@TiO_2:Cu_2O were synthesized. Here we describe the most favorable ratio. Nano-Fe_3O_4@TiO_2 (0.036-0.324 g) was dispersed in 80 mL of deionized water. 5 mL of (0.1 mol/L) $CuCl_2$ solution was added to the aqueous Fe_3O_4@TiO_2 and sonicated for 15 min. Then, 1.8 mL of (1.0 mol/L) NaOH solution was added dropwise under ultrasonic radiation. The resulting solution turned light blue instantly, indicating the formation of $Cu(OH)_2$. Eventually, 12 mL of $NH_2OH{\cdot}HCl$ (0.1 mol/L) was immediately injected over 5 sec. into the solution. The solution was kept in the water bath for 1 h and centrifuged for 3 min. Then the solution was decanted as much as possible. After the liquid was decanted, the precipitate was washed with 6 mL of a 1:1 volume ratio of water and ethanol three times. The nano-Fe_3O_4@TiO_2/Cu_2O was collected as a brown solid which could be stored in a tight vessel for several months without any changes in color and activity. We found that the most appropriate ratio of nano-Fe_3O_4@TiO_2:Cu_2O was 80:20%.[36] Therefore, the optimal weight ratio of Fe_3O_4@TiO_2:Cu_2O 8:2 was selected for this methodology.

General Procedure for Synthesis of 5-Phenyl-1H-tetrazole (entry 1)

Nano-Fe_3O_4@TiO_2/Cu_2O (20 mg) and $K_4[Fe(CN)_6]{\cdot}3H_2O$ (0.09 g, 0.22 mmol), was added to a solution of aryl iodide (1 mmol) in distilled DMF (2 mL) and the reaction mixture was stirred under heating at 120 °C for the appropriate time to obtain the nitrile compound. To the nitrile compound generated *in situ* was added sodium azide (*Safety Note: Sodium azide is highly toxic. All workers should be thoroughly familiar with its safe use before attempting experiments and proper personal protective gear must be used.* 0.1g, 1.5 mmol) and the reaction was continued until the complete conversion of the nitrile to the tetrazole during 5 hours. After the completion of the reaction (as monitored by TLC, 75:25 ethyl acetate: *n*-hexane), the catalyst was easily separated out from the reaction mixture by using an external magnet, washed with acetone, dried in the oven and re-used for a consecutive run under the same reaction conditions. After the separation of the catalyst the crude material was then taken up in ethyl acetate and washed with HCl (5 N) and the layers separated. The combined organic layers were then washed with water and concentrated to obtain the crude product. The crude product was purified by short column chromatography to obtain the pure products in high yield (see *Tables 1* and *2*). All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.

Spectral Data of Selected Products

5-Phenyl-1H-tetrazole (*Table 2, entry 1*): White powder, m.p. 213-215 °C; ^{1}H-NMR (400 MHz, DMSO)*:* δ 7.92 (s, 2H), 7.68 (s, 3H), ^{13}C-NMR (100 MHz, DMSO): δ 155.0, 134.6, 130.3, 128.6, 126.6.

5-(4-Nitrophenyl)-1H-tetrazole (*Table 2, entry 2*): Yellow solid, m.p. 218-219 °C; ^{1}H-NMR (400 MHz, DMSO): δ 8.39 (d, 2H, *J* 8.8, Ar-H), 8.30 (d, 2H, *J* 8.4, Ar-H), ^{13}C-NMR (100 MHz, DMSO): δ 149.51, 131.08, 129.13, 127.66.

5-(4-Methylphenyl)-1H-tetrazole (*Table 2, entry 3*): White solid, m.p. 249-251 °C. ^{1}H NMR (250 MHz, DMSO): δ 7.90 (d, 2H, *J* 7.5 Hz, ArH), 7.37 (d, 2H, *J* 7.6 Hz, ArH), 2.35 (s, 3H, CH_3).

5-(3-Chlorophenyl)-1H-tetrazole (*Table 2, entry 5*): White solid, m.p. 138-140 °C; ^{1}H NMR (250 MHz, DMSO): δ 7.99, (s, 1H), 7.96 (d, 1H, *J* 7.6, Ar-H), 7.55 (m, 2H). ^{13}C NMR (62.9 MHz, DMSO): δ 154.6, 133.9, 131.1, 130.7, 126.4, 126.2, 125.4.

5-(4-Chlorophenyl)-1H-tetrazole (*Table 2, entry 6*): White powder, m.p. 251-253 °C; ^{1}H-NMR (400 MHz, DMSO): δ 8.09 (d, 2H, *J* 8.8, Ar-H); 7.61 (d, 2H, *J* 8.4, Ar-H).

5-(4-Hydroxyphenyl)-1H-tetrazole (*Table 2, entry 10*): White powder, m.p. 235 °C; ^{1}H-NMR (400 MHz, DMSO): δ 10.11 (s broad, OH); 7.58 (d, 2H, *J* 8.4, Ar-H); 6.91 (d, 2H, *J* 8.4, Ar-H); ^{13}C-NMR (100 MHz, DMSO): δ 159.8; 153.2; 128.8; 117.4; 116.1.

4-(1H-Tetrazol-5-yl)-benzonitrile (*Table 2, entry 11*): White solid, m.p. 257-259 °C. ^{1}H NMR (250 MHz, DMSO): δ 8.19 (d, 2H, *J* 8.6, Ar-H), 8.06 (d, 2H, *J* 7.1, Ar-H). ^{13}C NMR (62.9 MHz, DMSO): δ 162.2, 155.2, 133.17, 128.7, 127.6, 118.1, 113.3.

2-(1H-Tetrazol-5-yl)pyridine (*Table 2, entry 12*): White solid, m.p. 210-213 °C; ^{1}H-NMR (400 MHz, DMSO): δ 8.63 (s, 1H); 8.20 (d, 1H, *J* 8.4 Ar-H); 8.07 (s, 1H); 7.75 (s, 1H).

4-(1H-Tetrazol-5-yl)pyridine (*Table 2, entry 13*): White solid, m.p. 256-258 °C; ^{1}H NMR (250 MHz, DMSO): δ 8.77 (d, 2H, *J* 6.5, Ar-H), 8.10 (d, 2H, *J* 6.0, Ar-H), ^{13}C NMR (62.9 MHz, DMSO): δ 165.7, 149.9, 133.8, 121.3, 120.9.

Acknowledgments

The authors gratefully acknowledge The Research Council of Semnan University Science and Technology Park and the Vice-chancellor for Education and Postgraduates for financial support of this work.

ORCID

Firouzeh Nemati http://orcid.org/0000-0002-9446-8936

References

1. I. K. Khanna, R. M. Weier, Y. Yu, X. D. Xu, F. J. Koszyk, P. W. Collins, C. M. Koboldt, A. W. Veenhuizen, W. E. Perkins, J. J. Casler, J. L. Masferrer, Y. Y. Zhang, S. A. Gregory, K. Seibert and P. C. Isakson, *J. Med. Chem.*, **40**, 1634 (1997).

2. U. Yapuri, S. Palle, O. Gudaparthi, S. R. Narahari, D. K. Rawat, Kh. Mukkanti and J. Vantikommu, *Tetrahedron Lett.*, **54**, 4732 (2013).

3. R. J. Herr, *Bioorg. Med. Chem.*, **10**, 3379 (2002).

4. J. Clayden, N. Greeves, S. Warren and P. Wothers, *Organic Chemistry*, p. 1169, Oxford University Press: New York, 2001.
5. R. R. Wexler, W. J. Greenlee, J. D. Irvin and M. R. Goldberg, *J. Med. Chem*., **39**, 625 (1996).
6. B. Schmidt and B. Schieffer, *J. Med. Chem*., **46**, 2261 (2003).
7. S. Kumar, S. Dubey, N. Saxena and S. K. Awasthi, *Tetrahedron Lett*., **55**, 6034 (2014).
8. G. A. Meshram, S. S. Deshpande, P. A. Wagh and V. A. Vala, *Tetrahedron Lett*., **55**, 3557 (2014).
9. S. Kumar, A. Kumar, A. Agarwal and S. K. Awasthi, *RSC Adv*., **5**, 21651 (2015).
10. S. M. Sajadi and M. Maham, *Org. Chem*., **11**, 136 (2014).
11. M. Alterman and A. Hallberg, *J. Org. Chem*., **65**, 7984 (2000).
12. B. Akhlaghinia and S. Rezazadeh, *J. Braz. Chem. Soc*., **23**, 2197 (2012).
13. S.-L. Zhang and L. Huang, *Org. Biomol. Chem*., **13**, 9963 (2015).
14. M. Tajbakhsh, H. Alinezhad, M. Nasrollahzadeh and T. A. Kamali, *Monatsh. Chem*., **147**, 2135 (2016).
15. G. Qi and Y. Dai, *Chin. Chem. Lett*., **21**, 1029 (2010).
16. L. Lang, B. Li, W. Liu, L. Jiang, Z. Xu and G. Yin, *Chem. Commun*., **46**, 448 (2010).
17. M. Nasrollahzadeh, D. Habibi, Z. Shahkarami and Y. Bayat, *Tetrahedron*, **65**, 10715 (2009).
18. S. M. Sajadi, M. Nader and Sh. Babadoust, *J. Nat. Sci. Res*., **1**, 1 (2011).
19. M. Esmaeilpour, J. Javidi and S. Zahmatkesh, *Appl. Organomet. Chem*., **30**, 897 (2016).
20. M. Kazemnejadi and A. R. Sardarian, *RSC Adv*., **6**, 91999 (2016).
21. M. Esmaeilpour, J. Javidi, F. N. Dodeji and M. M. Abarghoui, *J. Mol. Catl. A. Chem*., **393**, 18 (2014).
22. F. Dehghani, A. R. Sardarian and M. Esmaeilpour, *J. Organomet. Chem*., **743**, 87 (2013).
23. B. H. Zhang, L. X. Shi, S. J. Liu and R. X. Guo, *J. Heterocycl. Chem*., **52**, 1234 (2014).
24. D. Wang and D. Astruc, *Chem. Rev*., **114**, 6949 (2014).
25. M. B. Gawande, Y. Monga, R. Zboril and R. K. Sharma, *Coord. Chem. Rev*., **288**, 118 (2015).
26. R. Hudson, Y. Feng, R. S. Varma and A. Moores, *Green Chem*., **16**, 4493 (2014).
27. P. Hu, J. V. Morabito and C. K. Tsung, *ACS Catal*., **4**, 4409 (2014).
28. R. B. Nasir Baig and R. S. Varma, *Chem. Commun*., **49**, 752 (2013).
29. R. B. Nasir Baig and R. S. Varma, *Green Chem*., **15**, 398 (2013).
30. R. Luque, B. Baruwati and R. S. Varma, *Green Chem*., **12**, 1540 (2010).
31. S. P. Pujari, L. Scheres, A. T. M. Marcelis and H. Zuilhof, *Angew. Chem. Int. Ed*., **53**, 6322 (2014).
32. F. Nemati, A. Elhampour, H. Farrokhi and M. Bagheri Natanzi, *Catal. Commun*., **66**, 15 (2015).

33. Y. Zhu, J. Shen, K. Zhou, C. Chen, X. Yang and C. Li, *J. Phys. Chem. C*., **115**, 1614 (2011).

34. J. Ge, T. Huynh, Y. Hu and Y. Yin, *Nano Lett*., **8**, 931 (2008).

35. F. Nemati, M. M. Heravi and A. Elhampour, *RSC Adv*., **5**, 775 (2015).

36. A. Elhampour and N. Nemati, *J. Chin. Chem. Soc*., **63**, 653 (2016).

37. F. Nemati, M. M. Heravi and R. Saeedirad, *Chin. J. Catal*., **33**, 1825 (2012).

38. F. Nemati and R. Saeedirad, *Chin. Chem. Lett*., ***24***, 370 (2013).

39. F. Nemati, M. Golmohammadi Afkham and A. Elhampour, *Green Chem. Lett. Rev*., **7**, 79 (2014).

40. F. Nemati, A. Elhampour and S. Zulfaghari, *Phosphorus Sulfur Silicon Relat. Elem*., **190**, 1692 (2015).

41. F. Niu, Y. Jiang and W. Song, *Nano Res*., ***3***, 757 (2010).

42. W. Hu, B. Liu, Q. Wang, Y. Liu, Y. Liu, P. Jing, S. Yu, L. Liua and J. Zhang, *Chem. Commun*., **49**, 7596 (2013).

43. B. Sreedhar, A. S. Kumar and D. Yada, *Tetrahedron Lett*., **52**, 3565 (2011).

44. V. Rama, K. Kanagaraj and K. Pitchumani, *J. Org. Chem*., **76**, 9090 (2011).

45. M. Esmaeilpour, J. Javidi, F. Nowroozi Dodeji and M. Mokhtari Abarghoui, *J. Mol. Catal. A: Chem*., **393**, 18 (2014).

46. A. I. Azath, P. Suresh and K. Pitchumani, *New J. Chem*., **36**, 2334 (2012).