Tetrahedron Letters 52 (2011) 3565–3569

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

$CuFe_2O_4$ nanoparticles: a magnetically recoverable and reusable catalyst for the synthesis of 5-substituted 1*H*-tetrazoles

B. Sreedhar *, A. Suresh Kumar, Divya Yada

Inorganic and Physical Chemistry Division, Indian Institute of Chemical Technology (Council of Scientific and Industrial Research), Hyderabad 500 607, India

ARTICLE INFO

Article history:
Received 16 March 2011
Revised 21 April 2011
Accepted 24 April 2011
Available online 10 May 2011

Keywords:
[2+3] Cycloaddition
Aryl nitriles
$CuFe_2O_4$ nanoparticles
5-Substituted 1*H*-tetrazoles

ABSTRACT

An efficient and economical protocol for the synthesis of 5-substituted 1*H*-tetrazoles from various nitriles and sodium azide is described using magnetically recoverable and reusable $CuFe_2O_4$ nanoparticles. A wide variety of aryl nitriles underwent [2+3] cycloaddition under mild reaction conditions to afford tetrazoles in good to excellent yields. The catalyst was magnetically separated and reused five times without significant loss of catalytic activity.

1. Introduction

Tetrazoles are an increasingly popular functionality with wide ranging applications.[1] Interest in tetrazole chemistry over the past few years has been increasing rapidly, mainly as a result of the role played by this heterocyclic functionality in medicinal chemistry as these offer a more favorable pharmacokinetic profile and a metabolically stable surrogate for carboxylic acid functionalities.[2] In particular, by the widespread incorporation of the tetrazole functionality into angiotensin II antagonist structures (sartans, Fig. 1), several methods have been reported in literature during the past few years for the synthesis of tetrazoles.[3]

This functionality has also been frequently used as lipophilic spacers, ligands, precursors of a variety of nitrogen containing heterocycles in coordination chemistry[4,5] and in material sciences including photography, information recording systems, and explosives.[6]

In general, the most direct and versatile method of the synthesis of 5-substituted 1*H*-tetrazoles is [2+3] the cycloaddition between nitriles and azides. A plethora of synthetic protocols and variations on this general theme have been reported in the literature.[6] In the majority of cases, sodium azide (NaN_3) has been used as an inorganic azide source in combination with an ammonium halide as the additive employing dipolar aprotic solvents.[6,7] In some instances, Brønsted[8] or Lewis acids,[9] or stoichiometric amounts of Zn(II) salts[10] have been reported as suitable additives to afford the desired azide–nitrile addition process. As an alternative to inorganic azide salts, trimethylsilyl,[11] trialkyl tin[12] and organoaluminum azides[13] have been introduced as comparatively safe azide sources (sometimes prepared in situ), which have the added benefit of being soluble in organic solvents under homogeneous conditions. Unfortunately, with very few exceptions, all of these methods require long reaction times (several hours to days) in combination with high reaction temperatures.

Heterogeneous catalysis is particularly attractive as it allows the production and ready separation of large quantities of products with the use of a small amount of catalyst. Recently, several heterogeneous catalytic systems were reported using, for example, nanocrystalline ZnO,[14a] Zn/Al hydrotalcite,[14b] Zn hydroxyapatite[14c] and Cu_2O,[15] tungstate salts[16] as catalysts. Very recently, Zheng Xu et al. have reported the synthesis of 5-substituted 1*H*-tetrazoles using mesoporous ZnS nanospheres.[17]

In recent years, magnetic nanoparticles have emerged as a useful group of heterogeneous catalysts due to their numerous applications in synthesis and catalysis.[18] Separation of magnetic nanoparticles is simple, economical, and an attractive alternative to filtration or centrifugation as it prevents loss of catalyst and enhances reusability, making the catalyst cost-effective and promising for industrial applications.

As a part of our research program directed toward the utility of magnetic nanoparticles,[19] in the present study, we exploit magnetically separable $CuFe_2O_4$ nanoparticles[20] for the synthesis of 5-substituted 1*H*-tetrazoles from a wide variety of organic nitriles with sodium azide (Scheme 1).

Initially, in an effort to develop better reaction conditions, different solvents were screened for the preparation of 5-substituted 1*H*-tetrazole from the reaction of benzonitrile with sodium azide in

* Corresponding author. Tel.: +91 40 27193510; fax: +91 40 27160921.
E-mail address: sreedharb@iict.res.in (B. Sreedhar).

0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.04.094

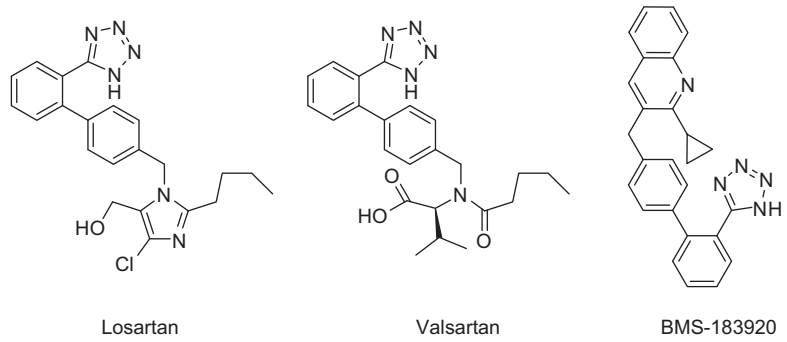
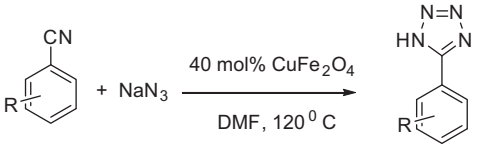


Figure 1. Sartans.



Scheme 1. Magnetically separable $CuFe_2O_4$ catalyzed synthesis of 5-substituted 1*H*-tetrazoles.

the presence of 40 mol % of $CuFe_2O_4$ and the results are summarized in Table 1. Among the different solvents screened DMF gave the product in good yield at 120 °C and DMSO also was equally effective at 130 °C (Table 1, entries 1–2). Other solvents, such as NMP and toluene gave the desired products in low yield (Table 1, entries 3–4). However, only a trace amount of the product was formed in THF and water (Table 1, entries 5–6). On the other hand, no product was formed when the reaction was carried out in the absence of catalyst.

Under the optimized reaction conditions, we chose a variety of structurally divergent benzonitriles to understand the scope and generality of the $CuFe_2O_4$ promoted [2+3] cycloaddition reaction to form 5-substituted 1*H*-tetrazoles and the results are presented in Table 2. Unsubstituted as well as benzonitriles with electron-donating substituents at both para and meta positions reacted well and gave the corresponding products in good to excellent yields (Table 2, entries 1–4). Further, the reaction was extended to di- and tri- substituted benzonitriles, 3,5-dimethoxybenzonitrile, piperonyl benzonitrile and 3,4,5-trimethoxybenzonitrile, respectively, to generate tetrazoles in moderate to excellent yields (Table 2, entries 5–7). 2-cyanonaphthalene and different halogen substituted benzonitriles, such as 4-chlorobenzonitrile, 3-chlorobenzonitrile, 4-bromobenzonitrile and 3-bromobenzonitrile reacted smoothly and gave the desired products in decent yields (Table 2, entries 8–12). Furthermore, the reaction was equally effective with benzonitriles having substituted electron-withdrawing groups and gave the expected tetrazoles in good yields (Table 2, entries 13 and 14). On the other hand, when 4-phenyl substituted benzonitriles, 2,2-dimethyl-2*H*-chromene-6-carbonitrile and thiophene-3-carbonitrile were used, the product was formed in moderate yield (Table 2, entries 15–18). Unfortunately the present method is not amenable for aliphatic nitriles.

To check the reusability of the catalyst, as can be seen from Table 3, the reaction was performed with benzonitrile and NaN_3 under the optimized reaction conditions. The catalyst was separated from the reaction mixture by applying external magnetic field and reused five times without significant loss of catalytic activity. Atomic absorption spectroscopy (AAS) was employed to determine the copper content of $CuFe_2O_4$ nanoparticles, and it was found to be 27.32%. The leaching of the metal after the third cycle was determined by AAS and was found to be negligible. (0.048%)

In conclusion we have developed a simple and efficient method for the synthesis of 5-substituted 1*H*-tetrazoles using magnetically separable $CuFe_2O_4$ nanoparticles as the catalyst under mild reaction conditions. This catalyst has been used to generate a diverse range of 5-substituted 1*H*-tetrazoles of using different nitriles in good to excellent yields. Furthermore, the catalyst is magnetically separable and eliminates the requirement of catalyst filtration after completion of the reaction, which is an additional sustainable attribute of this protocol.

Table 1
Screening of various solvents for the reaction of benzonitrile with sodium azide[a]

Entry	Solvent	Temp °C	Yield[b] (%)
1	DMF	120	0[c], 82
2	DMSO	130	80
3	NMP	80	28
4	Toluene	110	35
5	THF	65	Trace
6	Water	100	Trace

[a] Reaction conditions: benzonitrile (1 mmol), NaN_3 (1.5 mmol), $CuFe_2O_4$ (40 mol %) in DMF (5 mL) at 120 °C for 12 h.
[b] Yield of isolated products.
[c] Reaction without catalyst.

2. Spectroscopic data for the unknown products

2.1. 5-(Benzo[1,3]dioxol-5yl)-1*H*-tetrazole (Table 1, entry 5)

White solid. Mp: 250–252 °C. IR (KBr): 3448, 3065, 2895, 1852, 1576, 1459, 1254, 1043, 925, 818, 745 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$ + DMSO): δ 6.07 (s, 2H), 6.92 (d, 1H, J = 8.3 Hz), 7.54(d, 1H, J = 1.5 Hz), 7.66 (dd, 1H, J = 1.5 Hz, 8.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 100.9, 106.5, 108.0, 117.3, 121.0, 147.5, 149.0, 154.9. EI-MS (m/z): 190 (M^+).

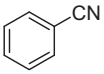
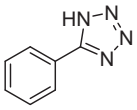
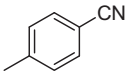
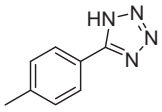
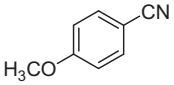
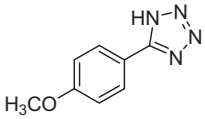
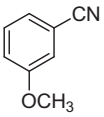
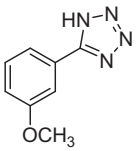
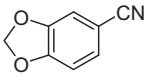
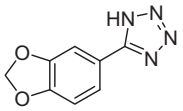
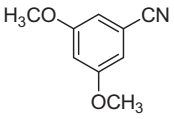
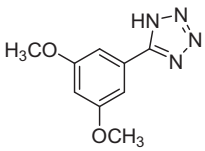
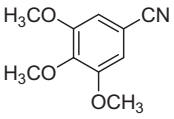
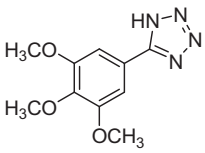
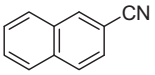
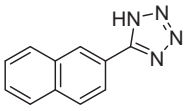
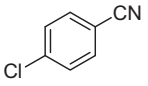
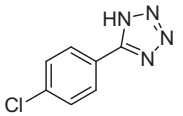
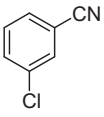
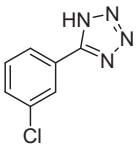
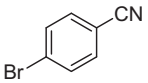
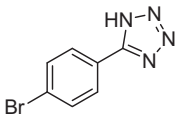
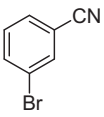
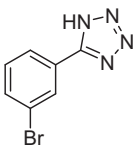
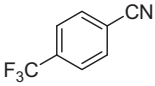
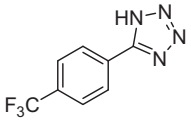
2.2. 5-(3,5-Dimethoxyphenyl)-1*H*-tetrazole (Table 1, entry 6)

White solid. Mp: 204–206 °C. IR (KBr): 3091, 2970, 2843, 1730, 1603, 1553, 1474, 1285, 1206, 1062, 837, 742, 538 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + DMSO): δ 3.86 (s, 6H,), 6.55 (t, 1H J = 2.2 Hz), 7.21 (d, 2H, J = 2.2 Hz).^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 54.8, 102.6, 104.4, 125.4, 155.4, 160.5. ESI-MS (m/z): 207 (M+H).

2.3. 5-(3,4,5-Trimethoxyphenyl)-1*H*-tetrazole (Table 1, entry 7)

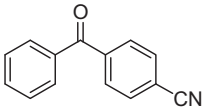
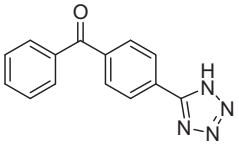
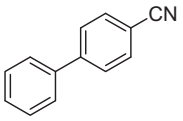
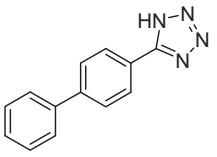
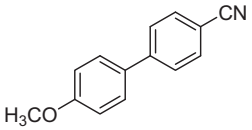
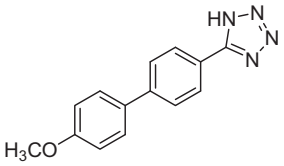
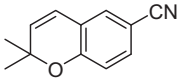
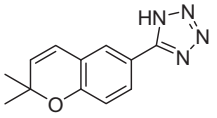
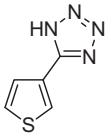
White solid. Mp: 202–203 °C . IR (KBr): 3442, 3184, 2977, 1594, 1503, 1467, 1252, 1125, 999, 855, 751 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$ + DMSO): δ 3.81 (s, 3H,), 3.92 (s, 6H), 7.35 (s, 2H)^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 55.1, 59.6, 103.4, 118.5, 138.9, 152.5, 154.6. ESI-MS (m/z): 237 (M+H).

Table 2
Magnetically separable $CuFe_2O_4$ catalyzed preparation of 5-substituted 1*H*-tetrazoles[a]

Entry	Substrate	Product	Yield (%)	Melting point (°C)
1			82	213–214 (215–216)[10]
2			85	250–251 (248–249)[21]
3			90	231–233 (231–232)[22]
4			88	157–159 (158–160)[11]
5			73	250–252
6			80	204–206
7			93	202–203
8			78	204–206 (205–207)[10]
9			89	250–252 (252–253)[23]
10			87	138–139 (139–140)[8a]
11			90	267–269 (268–269)[7a]
12			86	155–156 (154–155)[23a]
13			80	220–222 (218–219)[24]

(*continued on next page*)

Table 2 (*continued*)

Entry	Substrate	Product	Yield (%)	Melting point (°C)
14			78	197–199
15[b]			70	247–249
16[b]			72	238–240
17			70	196–198 (195–197)[11a]
18			68	245–247 (244–246)[25]

[a] Reaction conditions: aryl nitrile (1 mmol), NaN_3 (1.5 mmol), $CuFe_2O_4$ (40 mol %) in DMF (3 mL) at 120 °C for 12 h.[26]
[b] Reaction carried out at 130 °C for 20 h.

Table 3
Recovery and reuse of CuFe204 catalyst for the reaction between benzonitrile and sodium azide[a]

Yield(%)					Average yield (%)
First	Second	Third	Fourth	Fifth	
82	80	80	78	75	79

[a] Reaction conditions: benzonitrile (1 mmol), NaN_3 (1.5 mmol), $CuFe_20_4$ (40 mol %) in DMF (5 mL) at 120 °C for 12 h.

2.4. Phenyl-[4-(1*H*-tetrazol-5-yl)-phenyl]-methanone (Table 2, entry 14)

White solid. Mp: 197–199 °C . IR (KBr) : 3014, 2857, 1657, 1563, 1435, 1277, 1156, 1054, 926, 865, 696, 657 cm^{-1}.1H NMR (300 MHz, $CDCl_3$ + DMSO): δ 7.47–7.56 (m, 2H), 7.63 (t, 1H, J = 7.4 Hz), 7.78 (d, 2H, J = 8.3 Hz), 7.91 (d, 2H, J = 8.3 Hz), 8.24 (d, 2H, J = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 126.2, 127.6, 129.0, 129.7, 132.0, 136.1, 138.4, 155.4, 194.7. ESI-MS (m/z): 251 (M+H).

2.5. 5-(Biphenyl-4-yl)-1*H*-tetrazole (Table 2, entry 15)

White solid. Mp: 247–249 °C . IR (KBr): 3440, 2924, 2855, 1708, 1612, 1424, 1158, 1057, 992, 846, 743, 693 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO): δ, 7.31-7.40 (m, 1H). 7.40–7.50 (m, 2H), 7.63 (d, 1H, J = 8.1 Hz) 7.75 (d, 2H, J = 8.3 Hz), 8.15 (d, 2H, J = 8.3 Hz).^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 121.9, 125.4, 126.0, 126.1, 126.4, 127.4, 138.0, 141.6, 154.6, 160.6. ESI-MS (m/z): 223 (M+H).

2.6. 5-(4-Methoxy-biphenyl-4-yl)-1*H*-tetrazole (Table 2, entry 16)

White solid. Mp: 238–240 °C. IR (KBr): 3468, 3010, 2924, 2853, 1606, 1493, 1247, 1175, 1032, 824, 753, 523 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO): δ 3.85 (s, 3H), 6.96 (d, 2H, J = 7.6 Hz), 7.56 (d, 1H, J = 7.6 Hz), 7.69 (d, 2H, J = 7.4 Hz), 8.11 (d, 2H, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO): δ 53.8, 112.9, 121.2, 125.5, 126.2, 126.5, 130.4, 141.5, 155.2, 158.2. ESI-MS (m/z): 253 (M+H).

Acknowledgments

ASK thanks the university grant commission for the award of Senior Research Fellowship and Council of Scientific and Industrial Research, New Delhi for the financial support.

References and notes

1. (a) Herr, R. J. *Bioorg. Med. Chem.* **2002**, *10*, 3379; (b) Butler, R. N. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; 4, p 621.
2. (a) Myznikov, L. V.; Hrabalek, A.; Koldobskii, G. I. *Chem. Heterocycl. Compd.* **2007**, *43*, 1.
3. (a) Wittenberger, S. J.; Donner, B. G. *J. Org. Chem.* **1993**, *58*, 4139; (b) Duncia, J. V.; Pierce, M. E.; Santella, J. B., III *J. Org. Chem.* **1991**, *56*, 2395; (c) Smith, R. D.; Duncia, J. V.; Lee, R. J.; Christ, D. D.; Chiu, A. T.; Carini, D. J.; Herblin, W. F.; Timmermans, P. B. M. W. M.; Wexler, R. R. *Methods Neurosci.* **1993**, *13*, 258; (d) Chiu, A. T.; Duncia, J. V.; McCall, D. E.; Wong, P. C.; Price, W. A., Jr.; Thoolen, M. J. M. C.; Carini, D. J.; Johnson, A. L.; Timmermans, P. B. M. W. M. *J. Pharmacol. Exp. Ther.* **1989**, *250*, 867; (e) Buehlmayer, P.; Criscione, L.; Fuhrer, W.; Furet, P.; De Gasparo, M.; Stutz, S.; Whitebread, S. *J. Med. Chem.* **1991**, *34*, 3105.
4. Huisgen, R.; Sauer, J.; Sturn, H. J.; Markgraf, J. H. *Chem. Ber.* **1960**, *93*, 2106.
5. Moderhack, D. J. *Prakt. Chem.* **1988**, *340*, 687.

6. (a) Ostrovskii, V. A.; Pevzner, M. S.; Kofmna, T. P.; Shcherbinin, M. B.; Tselinskii, I. V. *Targets Heterocycl. Syst.* **1999**, *3*, 467; (b) Koldobskii, G. I.; Ostrovskii, V. A. *Usp. Khim.* **1994**, *63*, 847.
7. (a) Finnegan, W. G.; Henry, R. A.; Lofquist, R. *J. Am. Chem. Soc.* **1958**, *80*, 3908; (b) Lieber, E.; Enkoji, T. *J. Org. Chem.* **1961**, *26*, 4472; (c) Bernstein, P. R.; Vacek, E. P. *Synthesis* **1987**, 1133; (d) Koguro, K.; Oga, T.; Mitsui, S.; Orita, R. *Synthesis* **1998**, 910; (e) Jursic, B. S.; Leblanc, B. W. *J. Heterocycl. Chem.* **1998**, *35*, 405; (f) Alterman, M.; Hallberg, A. *J. Org. Chem.* **2000**, *65*, 7984; (g) Shie, J. J.; Fang, J. M. *J. Org. Chem.* **2007**, *72*, 3141; (h) Roh, J.; Artamonova, T. V.; Vavrova, K.; Koldobskii, G. I.; Hrabalek, A. *Synthesis* **2009**, 2175; (i) Schmidt, B.; Meid, D.; Kieser, D. *Tetrahedron* **2007**, *63*, 492.
8. (a) Herbst, R. M.; Wilson, K. R. *J. Org. Chem.* **1957**, *22*, 1142; (b) Mihina, J. S.; Herbst, R. M. *J. Org. Chem.* **1950**, *15*, 1082.
9. (a) Kumar, A.; Narayanan, R.; Shechter, H. *J. Org. Chem.* **1996**, *61*, 4462; (b) Venkateshwarlu, G.; Premalatha, A.; Rajanna, K. C.; Saiprakash, P. K. *Synth. Commun.* **2009**, *39*, 4479; (c) Venkateshwarlu, G.; Rajanna, K. C.; Saiprakash, P. K. *Synth. Commun.* **2009**, *39*, 426.
10. (a) Demko, Z. P.; Sharpless, K. B. *J. Org. Chem.* **2001**, *66*, 7945; (b) Himo, F.; Demko, Z. P.; Noodleman, L.; Sharpless, K. B. *J. Am. Chem. Soc.* **2003**, *125*, 9983; (c) Shie, J. J.; Fang, J. M. *J. Org. Chem.* **2003**, *68*, 1158; (d) Myznikov, L. V.; Roh, J.; Artamonava, T. V.; Hrabalek, A.; Koldobskii, G. I. *Russ. J. Org. Chem.* **2007**, *43*, 765; (e) Zhu, Y.; Ren, Y.; Cai, C. *Helv. Chim. Acta* **2009**, *92*, 171.
11. (a) Huff, B. E.; Staszak, M. A. *Tetrahedron Lett.* **1993**, *34*, 8011; (b) Wittenberger, S. J.; Donner, B. G. *J. Org. Chem.* **1993**, *58*, 4139; (c) Amantini, D.; Belaggia, R.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2004**, *69*, 2896; (d) Bliznets, I. V.; Vasil'ev, A. A.; Shorshnev, S. V.; Stepanov, A. E.; Lukyanov, S. M. *Tetrahedron Lett.* **2004**, *45*, 2571; (e) Bonnamour, J.; Bolm, C. *Chem. Eur. J.* **2009**, *15*, 4543.
12. (a) McMurray, J. S.; Khabashesku, O.; Britwistle, J. S.; Wang, W. *Tetrahedron Lett.* **2000**, *41*, 6555; (b) Rival, Y.; Wermuth, C. G. *Synth. Commun.* **2000**, *30*, 1587; (c) Duncia, J. V.; Pierce, M. E.; Santella, J. B. *J. Org. Chem.* **1991**, *56*, 2395; (d) Curran, D. P.; Hadida, S.; Kim, S. Y. *Tetrahedron* **1999**, *55*, 8997.
13. (a) Arnold, C.; Thatcher, D. N. *J. Org. Chem.* **1969**, *34*, 1141; (b) Aureggi, V.; Sedelmeier, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8440.
14. (a) Kantam, M. L.; Shiva Kumar, K. B.; Sridhar, C. *Adv. Synth. Catal.* **2005**, *347*, 1212; (b) Kantam, M. L.; Shiva Kumar, K. B.; Raja, K. P. *J. Mol. Catal. A: Chem.* **2006**, *247*, 186; (c) Kantam, M. L.; Balasubrahmanyam, V.; Shiva Kumar, K. B. *Synth. Commun.* **2006**, *36*, 1809.
15. Jin, T.; Kitahara, F.; Kamijo, S.; Yamamoto, Y. *Tetrahedron Lett.* **2008**, *49*, 2824.
16. He, J.; Li, B.; Chen, F.; Xu, Z.; Yin, G. *J. Mol. Catal. A: Chem.* **2009**, *304*, 135–138.
17. Lang, L.; Li, B.; Liu, W.; Jiang, Li.; Xu, Z.; Yin, G. *Chem. Commun.* **2010**, *46*, 448.
18. (a) Abu-Reziq, R.; Alper, H.; Wang, D.; Post, M. L. *J. Am. Chem. Soc.* **2006**, *128*, 5279; (b) Zang, D.-H.; Li, G.-D.; Li, J.-X.; Chen, J.-S. *Chem. Commun.* **2008**, *29*, 3414; (c) Shokouhimehr, M.; Piao, Y.; Kim, J.; Jang, Y.; Hyeon, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 7039; (d) Lu, A.-H.; Salabas, E. L.; Schuth, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1222.
19. Sreedhar, B.; Kumar, A. S.; Reddy, P. S. *Tetrahedron Lett.* **2010**, *51*, 1891.
20. Magnetic $CuFe_2O_4$ nanoparticles were prepared according to literature Nedkov, I.; Vandenberghe, R. E.; Marinova, Ts.; Thailhades, Ph.; Merodiiska, T.; Avramova, I. *Appl. Surf. Sci.* **2006**, *253*, 2589.
21. (a) Richard, N. B.; Victor, C. G. *J. Chem. Soc., Perkin Trans. 1* **1981**, *66*, 390; (b) Butler, R. N.; McEvoy, T. M. *J. Chem. Soc., Perkin Trans. 2* **1978**, *66*, 1087.
22. Demko, Z. P.; Sharpless, K. B. *Org. Lett.* **2002**, *4*, 2525–2527.
23. (a) Kaczmarek, J.; Smagowski, H.; Grzonka, Z. *J. Chem. Soc., Perkin Trans. 2* **1979**, *12*, 1670; (b) Ciarkowski, J.; Kaczmarek, J.; Grzonka, Z. *Org. Magn. Res.* **1979**, *12*, 631.
24. Markgraf, J. H.; Brown, S. H.; Kaplinsky, M. W.; Peterson, R. G. *J. Org. Chem.* **1964**, *29*, 2629.
25. Elpern, B.; Nachod, F. C. *J. Am. Chem. Soc.* **1950**, *72*, 3379.
26. *Typical procedure for the synthesis of 5-Substituted 1H-Tetrazoles:* A mixture of nitrile (1 mmol), sodium azide (1.5 mmol), catalyst (40 mol%) and DMF (3 mL) was taken in a round-bottomed flask and stirred at 120 °C temperature for 12 h. After completion of the reaction the catalyst was separated from the reaction mixture with an external magnet and reaction mixture was treated with ethyl acetate (30 mL) and 5 N HCl (20 mL). The resultant organic layer was separated and the aqueous layer was again extracted with ethyl acetate (20 mL). The combined organic layers were washed with water, concentrated, and the crude material was chromatographed on silica gel (Hexane-EtoAc, 1:1) to afford the pure product.