RSC Advances

PAPER

Cite this: *RSC Adv.*, 2014, **4**, 8612

An efficient and recyclable heterogeneous catalytic system for the synthesis of 1,2,4-triazoles using air as the oxidant†

Xu Meng, Chaoying Yu and Peiqing Zhao*

Received 26th November 2013
Accepted 17th January 2014

DOI: 10.1039/c3ra47029f

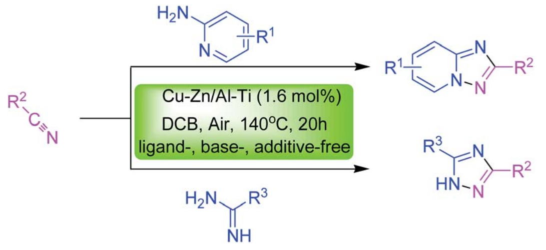
www.rsc.org/advances

Copper–zinc supported on Al_2O_3–TiO_2 was found as a simple and efficient heterogeneous catalyst for the oxidative synthesis of 1,2,4-triazole derivatives using air as the green oxidant under ligand-, base- and additive-free conditions. The heterogeneous reactions carried out smoothly with a large range of substrates, including NO_2-, vinyl-, pyrimidine- and imidazole-contained starting materials, and provided corresponding triazoles in moderate to excellent yields with low catalyst loading (1.6 mol%). Furthermore, the catalyst can be simply recycled many times without significant loss in catalytic activity.

Introduction

Although significant advances have been brought in homogeneous catalysis in decades, this knowledge has not largely been applied in an industrial environment and industrial processes still employ heterogeneous catalysts.[1] Nevertheless, heterogeneous catalysis is widely employed in industrial processes because it has economic advantages and combats practical issues, such as catalyst handing, recyclability and the separation of catalyst from the products.[2–6] More importantly, heterogeneous catalysis meets the requirements of green sustainable chemistry due to the use of unrecoverable metal- and ligand-free reaction conditions.[2–5] Therefore, the development of economic and environmentally friendly heterogeneous catalytic systems is highly desirable.

The 1,2,4-triazole derivatives are valuable structural motifs present in a variety of functionalized molecules which have applied into organocatalysis and material science.[6] Moreover, they are a significant class of heterocycles with broad utilities in the pharmaceutical industry because of their biological activities.[7] Commonly, the 1,2,4-triazole derivatives are prepared *via* multistep intramolecular condensations of *N*-acylamidorazones that are obtained from carboxylic acid derivatives and hydrazines.[8] With the development of transition-metal-catalysis, the synthesis of 1,2,4-triazoles turns to be more efficient, simple, atom-economic and environmentally friendly. The first transition-metal-catalytic synthesis of 1,2,4-triazoles using readily available starting materials was discovered by Nagasawa's group, although the homogeneous catalytic system suffers the use of additional ligand, base, additive and alternative solvents as the change of substrates.[9] Most recently, Fu's group developed a Cu-catalyzed sequential method of synthesis of 1,2,4-triazole from amidines.[10] In the course of investigating novel activity of heterogeneous catalysts in our research group,[4a,11] we envisioned a heterogeneous catalytic system for single-step synthesis of 1,2,4-triazoles from readily available starting materials using a simple solid-supported catalyst, which can be a complement to the previous methods.



Scheme 1 Heterogeneous Cu–Zn/Al–Ti-catalyzed cyclization.

Here we describe the heterogeneous oxidative catalytic synthesis of 1,2,4-triazole derivatives *via* addition-oxidative cyclizations from 2-aminopyridines and nitriles using solid-supported CuO_x–ZnO/Al_2O_3–TiO_2[12] (Cu–Zn/Al–Ti) as the catalyst (Scheme 1). The catalytic system is ligand-, base-, additive-free, and can tolerate a large range of functional groups as well as successfully employs air as the oxidant. More importantly, Cu–Zn/Al–Ti is likely to be heterogeneous in nature and can recycle many times without losing of activity.

Results and discussion

Our initial addition-oxidative cyclizations of 2-aminopyridine and benzonitrile were carried out by using 1,2-dichlorobenzene

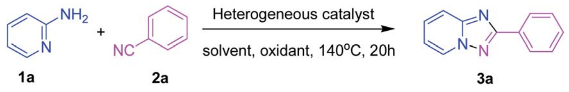
---

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R China. E-mail: zhaopq@licp.cas.cn; Fax: +96 931 8277008; Tel: +86 931 4968688

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra47029f

(DCB) as the solvent, air as the oxidant at 140 °C for 20 h to optimize the catalytic system (Table 1). Firstly, it was found using mono-metal solid-supported catalyst, such as Cu/Al–Ti, Zn/Al–Ti, Ru/Al–Ti and Pt/Al–Ti, did not give any desired product (Table 1, entries 1–4). Pleasingly, the reaction provided desired product of 52% yield, when Cu–Zn/Al–Ti (0.4 mol%, Cu = 3.25 wt%, Zn = 3.40 wt%) was used as the heterogeneous catalyst (Table 1, entry 5). Obviously, the cyclization has a relatively high reaction energy barrier since the reaction failed if the reaction temperature was decreased (Table 1, entry 5). To better the yield of reaction, we tried to use other green oxidants although the optimization confirmed air was the best and most economic green oxidant (Table 1, entries 5–7). Subsequently, the blank experiment was performed by only using support Al_2O_3–TiO_2 as the catalyst, which gave us a result that Al_2O_3–TiO_2 did not efficiently catalyze the reaction at all (Table 1, entry 8). Furthermore, the other bimetallic solid-supported catalysts did not make the reaction perform smoothly (Table 1, entries 9 and 10). In an attempt to increase the yield of reaction, we proposed a variety of solvents to enhance reactivity of reaction system, including polar, nonpolar, protic solvents and H_2O, and the results showed that polar organic solvent DCB was the best choice (Table 1, entries 11–20). Finally, the examination of the catalyst loading bettered the yield of the reaction significantly. Consequently, when the loading of catalyst enhanced to 1.6 mol%, the yield of reaction arrived at 83% (Table 1, entries 21 and 22). However, keeping increasing the catalyst loading did not better the reaction anymore.

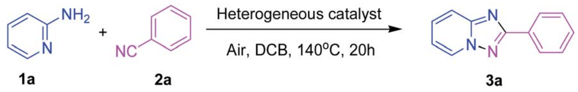
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (0.5 mol%)	Oxidant	Solvent	Isolated yield (%)
1	Cu/Al–Ti	Air	DCB	Trace
2	Zn/Al–Ti	Air	DCB	0
3	Ru/Al–Ti	Air	DCB	0
4	Pt/Al–Ti	Air	DCB	0
5	Cu–Zn/Al–Ti	Air	DCB	52 (0[b])
6	Cu–Zn/Al–Ti	O_2 (1 atm)	DCB	57
7[c]	Cu–Zn/Al–Ti	H_2O_2	DCB	<5
8	Al–Ti	Air	DCB	Trace
9	Cu–Fe/Al–Ti	Air	DCB	0
10	Cu–Ni/Al–Ti	Air	DCB	0
11	Cu–Zn/Al–Ti	Air	DMSO	8
12	Cu–Zn/Al–Ti	Air	CH_3NO_2	0
13	Cu–Zn/Al–Ti	Air	AcOH	10
14	Cu–Zn/Al–Ti	Air	*o*-Xylene	0
15	Cu–Zn/Al–Ti	Air	Dioxane	0
16	Cu–Zn/Al–Ti	Air	DMF	Trace
17	Cu–Zn/Al–Ti	Air	Pyridine	0
18	Cu–Zn/Al–Ti	Air	EtOAc	0
19	Cu–Zn/Al–Ti	Air	EtOH	0
20	Cu–Zn/Al–Ti	Air	H_2O	10
21	Cu–Zn/Al–Ti	Air	DCB	75[d]
22	Cu–Zn/Al–Ti	Air	DCB	83[e] (80[f])

[a] Reaction Conditions: benzonitrile (0.6 mmol), 2-aminopyridine (0.72 mmol), catalyst (6 mg, 0.4 mol%), DCB (0.6 mL), 140 °C, 20 h, air. [b] At 80 °C. [c] Using 0.06 mL H_2O_2 (30%) as oxidant. [d] Increasing the amount of catalyst to 15 mg, 1 mol%. [e] Increasing the amount of catalyst to 24 mg, 1.6 mol%. [f] Using 60 mg, 4 mol% catalyst.

Table 2 The examination of other supports for the heterogeneous system[a]



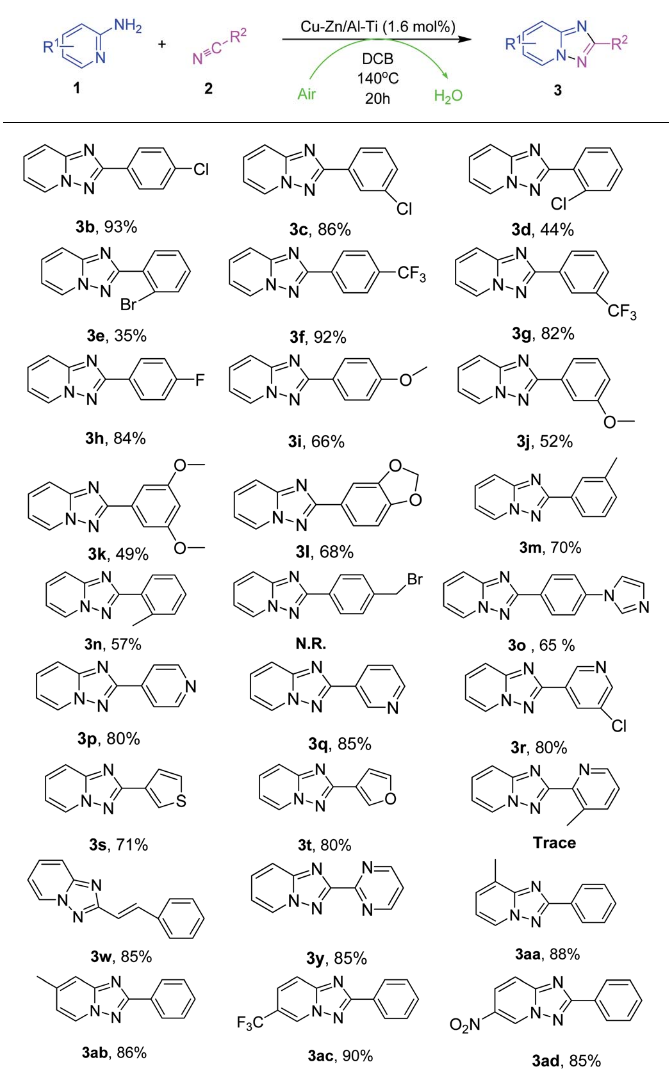
Entry	Catalyst (1.6 mol%)	Isolated yield (%)
1	Cu–Zn/Al–Ti	83
2	Cu–Zn/CeO_2	51
3[b]	Cu–Zn/ATP	15
4[c]	Cu–Zn/MWCNT	75
5	Cu–Zn/nano-r-Al_2O_3	21
6	Cu–Zn/nano-TiO_2	25
7	Cu–Zn/nano-ZrO_2	12

[a] Reaction Conditions: benzonitrile (0.6 mmol), 2-aminopyridine (0.72 mmol), catalyst (24 mg, 1.6 mol%), 140 °C, 20 h, air. [b] ATP = Attapulgite. [c] MWCNT = Multi-wall carbon nanotube.

On the other hand, the supports we investigated could affect reactivity of the catalyst obviously (Table 2). In Table 2, we loaded Cu–Zn on various solid supports (CeO, ATP, charcoal, nano-r-Al_2O_3, nano-TiO_2 and nano-ZrO_2) and performed the cyclization under the established reaction conditions. As a consequence, all heterogeneous catalysts could catalyze the reaction to some extent and Cu–Zn/Al–Ti was proved to be the most efficient heterogeneous catalyst among them (Table 2).

With the optimized conditions established we explored the scope of the reaction (Table 3). Electron-poor and electron-neutral benzonitriles could react with 2-aminopyridine successfully and gave excellent yields, while electron-rich benzonitriles offered relatively low yields of 1,2,4-trizaoles (Table 3, b–n). Generally, the steric hindrance of the substrates could low the yields of the reactions and the reaction did not even work when 3-methyl-2-aminopyridine was used as the substrate (Table 3, d, e and n). Unfortunately, the reaction failed to give the desired product when 4-(bromomethyl)benzonitrile was used as the substrate. Notably, imidazole-subtituted benzonitrile also could react with 2-aminopryridine very well and gave high yield of 1,2,4,-triazole which is important structure in medicine intermediate (Table 3, o).[13] Delightfully, the reactions performed very smoothly when the heterocyclic nitriles were employed as substrates and offered good yields of products, such as substituted cyanopyridines, cyanofuran and cyanothiophene (Table 3, p–t), although sterically hindered cyanopyridine failed the reaction. Interestingly, the heterogeneous system not only beard aryl nitriles, but also tolerated vinyl nitrile and provided single E-isomer product in excellent yield of 85% (Table 3, w). Impressively, the heterogeneous catalytic system also could tolerate cyanopyrimidine as the substrate and provided very good yield of 1,2,4-triazole (Table 3, y), which offer a simple way to synthesize pyrimidine-substituted triazole. However, benzonitriles substituted by certain sensitive

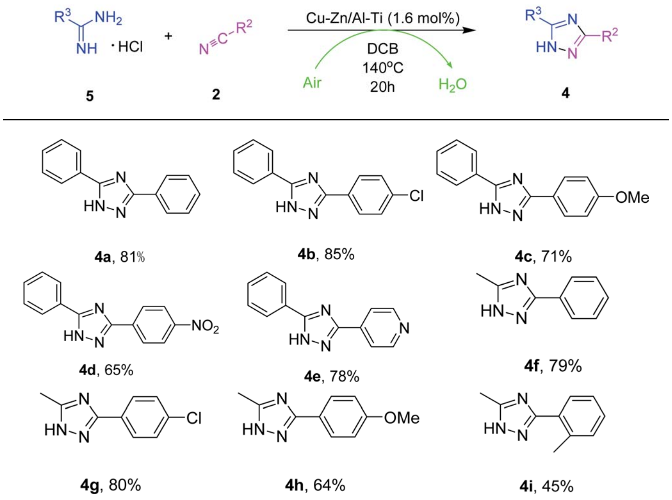
Table 3 The scope of the cyclization between 2-aminopyridine and nitriles[a]



3b, 93%
3c, 86%
3d, 44%
3e, 35%
3f, 92%
3g, 82%
3h, 84%
3i, 66%
3j, 52%
3k, 49%
3l, 68%
3m, 70%
3n, 57%
N.R.
3o , 65 %
3p, 80%
3q, 85%
3r, 80%
3s, 71%
3t, 80%
Trace
3w, 85%
3y, 85%
3aa, 88%
3ab, 86%
3ac, 90%
3ad, 85%

[a] Reaction Conditions: benzonitrile (0.6 mmol), 2-aminopyridine (0.72 mmol), Cu–Zn/Al–Ti (24 mg, 1.6 mol%), DCB (0.6 mL), 140 °C, 20 h, air, isolated yields.

Table 4 The scope of the cyclization between amidines and nitriles[a]



4a, 81%
4b, 85%
4c, 71%
4d, 65%
4e, 78%
4f, 79%
4g, 80%
4h, 64%
4i, 45%

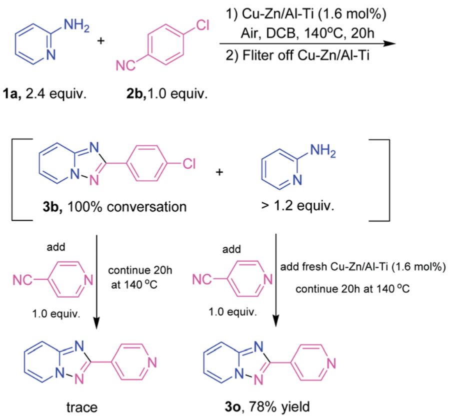
[a] Reaction Conditions: benzonitrile (0.6 mmol), 2-aminopyridine (0.72 mmol), Cu–Zn/Al–Ti (24 mg, 1.6 mol%), DCB (0.6 mL), 140 °C, 20 h, air, isolated yields.

functional groups, shcu as –NH_2, –OH and –COOH, could not be applied into this reaction.

Next, 2-aminopyridines with substituted groups were examined under our heterogeneous catalytic system. In general, 2-aminopyridines with electron-donating and electron-withdrawing groups could react with benzonitrile successfully and gave 1,2,4-triazoles in good yields (Table 3, aa–ad). Especially, nitro-substituted 2-aminopyridine could be tolerated in this reaction, which can provide an efficient method to synthesis nitro-substituted 1,2,4-triazoles (3ad) as a complement to previous methods.

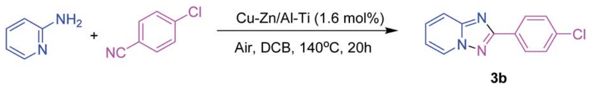
To our delight, application of this heterogeneous catalytic system can be employed to synthesize 1*H*-1,2,4-triazoles without changing the standard reaction conditions (Table 4). Specifically, electron-poor benzotriles brought better yields than electron-rich ones did and steric hindrance of substrates led to low yields of the products. In terms of amidines, not only aryl amidine but also alkyl amidine could be employed to synthesize 1*H*-1,2,4-triazoles under the heterogeneous catalytic system successfully. Importantly, nitro-substituted benzonitrile, the sensitive substrate for the previous synthetic methods,[9] can be employed into this catalytic system (Table 4, d).

To confirm this procedure catalyzed by Cu–Zn/Al–Ti is unambiguously heterogeneous in nature, an additional experiment was carried out (Scheme 2). After filtering a totally converted reaction mixture (4-Cl-benzonitrile as a substrate) to remove the catalyst, 1.0 equiv. of a different aryl nitrile was added as an additional substrate to the filtrate, then the filtrate was treated with the remaining amount of 2-aminopyridine (>1.2 equiv.). Therefore, only trace amount of another triazole **3o** was discovered, while 78% yield of **3o** would be obtained, if the fresh Cu–Zn/Al–Ti was added to the filtrate.



Scheme 2 The test of heterogeneous system.

Table 5 Recycling of the Cu–Zn/Al–Ti catalyst[a]



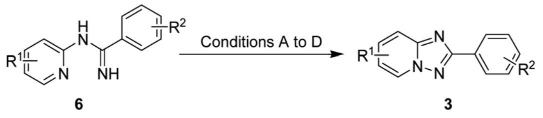
Cycle	1	2	3	4	5
Isolated yield of 3b (%)	92	91	91	88	85

[a] Reaction conditions: 2-aminopyridine (0.72 mmol), 4-Cl-benzonitrile (0.6 mmol), Cu–Zn/Al–Ti (24 mg, 1.6 mol%), DCB (0.6 mL), 140 °C, air, 20 h.

For the practical applications of such heterogeneous system, the lifetime of the catalyst and its level of reusability are key factors. To testify this issue, we performed a set of experiments of 2-aminopyridine and 4-chlorobenzonitrile using the Cu–Zn/Al–Ti catalyst under the standard reaction conditions (Table 5). After the completion of the first reaction, the reaction mixture was filtered and the catalyst was washed by EtOAc and water, then it was dried at 100 °C for 2 h for being subjected to the next run of the same reaction process. After five cycles, the recovered catalyst remained highly catalytic reactivity and the desired product was obtained above 85% yield (Table 5, entry 5). Thus, the Cu–Zn/Al–Ti catalyst could be used at least 5 times without any significant change in its activity.

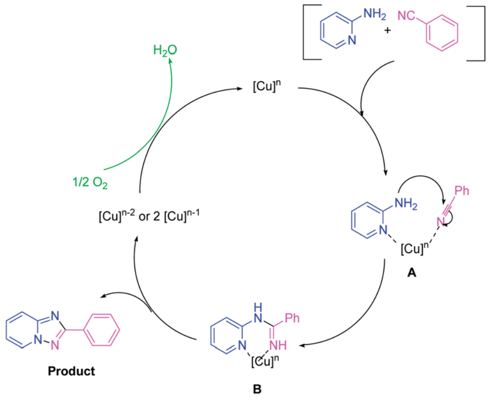
When the mechanism of this reaction was investigated, we proposed the amidine **6** formed from 2-aminopyridine and nitrile, would be the intermediate.[9,14,15] We used amidine **6** as the starting materials to perform the cyclization under the heterogeneous catalytic system (Scheme 3). The results showed the cyclization could happen smoothly and gave higher yield of 88% (Scheme 3A), while the desired product could also be obtained by using Cu/Al–Ti catalyst in moderate yield (Scheme 3B). Moreover, the cyclization achieved efficiently and provided higher yields of products by using other substituted benzonitriles under Cu–Zn/Al–Ti-catalyzed conditions (Scheme 3C and D). Therefore, it is hypothesized that the zinc probably assists the initial amidine formation step.[9] Additional, due to the high energy barrier of the oxidative cyclization, zinc probably plays a role of electron-transfer mediate for decreasing the energy barrier between the reduced transition-metal and oxidant, thereby increasing the efficiency of the reaction and making air as the efficient oxidant.[16]

According to our observed results and a number of related literatures involving oxidative C–N/N–N formation,[9,17] it is plausible that the nucleophilic attack of 2-aminopyridine on the nitrile promoted by copper happens firstly by forming coordinated intermediate **A** probably (Scheme 4). Next, intermediate **A** might provide cyclic intermediate **B** after amino attacks the carbon of cyano and proton-transfer process. Then, the intramolecular oxidative cyclization takes place induced by copper, which gave the desired 1,2,4-triazole and reduced copper species. Finally, the reduced copper species was oxidized by oxygen of air to give active copper species for finishing the catalytic cycle of the reaction.



A: Standard reaction conditions; R^1= Ph, R^2= Ph, 88% yield
B: Cu/Al-Ti (1.6 mol%), DCB, Air, 140 °C, 20h; R^1= Ph, R^2= Ph, 68% yield
C: Standard reaction conditions; R^1= Ph, R^2= 4-Cl-Ph, 95% yield
D: Standard reaction conditions; R^1= Ph, R^2= 4-OMe-Ph, 78% yield

Scheme 3 The direct cyclization of amidine **6**.



Scheme 4 The proposed mechanism of the reaction.

Conclusions

In summary, we have described an efficient and simple heterogeneously catalyzed addition-oxidative cyclization between 2-aminopyridines or amidines and nitriles *via* C–N/N–N bond-formation using air as the green oxidant. The heterogeneous catalytic system is ligand-, base- and additive-free, which tolerate a large range of substrates, including heterocycles, $-NO_2$, vinyl, pyrimidine and imidazole groups. The catalytic system also can be applied into the synthesis of 1,2,4-triazoles directly from *N*-(pyridin-2-yl)benzamidines. Furthermore, the Cu–Zn/Al–Ti catalyst can recycle many times without losing activity, which provides the potential for practical applications.

Experimental

General

All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (230–400 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. ^1H NMR and ^{13}C NMR (300 or 400 and 75 or 100 MHz respectively) spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin–spin coupling constants (J) are given in Hz.

General procedure for the synthesis of CuO_x–ZnO/Al_2O_3–TiO_2

Support Al_2O_3–TiO_2 powder (8 g) was added to a 250 mL round-bottom flask. A solution of $Cu(NO_3)_2$–$3H_2O$ (1.205 g) and $Zn(NO_3)_2$–$6H_2O$ (1.462 g) in deionized water (100 mL) was added to Al_2O_3–TiO_2 powder, and additional deionized water (50 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3 h at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 90 °C for more than 2 h. Subsequently, the white powder was dried into an oven under the condition of increasing the temperature from 25 °C to 110 °C within 1 h and keeping the temperature for another 5 h. Finally, the dried white powder was calcined under the condition of increasing the temperature from 25 °C to 350 °C within 1 h and keeping the temperature for 2 more hours to get the catalyst Cu (3.25 wt%)–Zn(3.40 wt%)/Al–Ti. For the catalyst characterization, see ESI.†

General procedure for Cu–Zn/Al–Ti-catalyzed cyclization

Cu–Zn/Al–Ti (24 mg, 1.6 mol%), 2-aminopyridine (0.72 mmol), benzonitrile (0.6 mmol) and DCB (0.6 mL) were added to a flask with a bar. The flask was stirred at 140 °C for indicated time under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 3/2 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by ^1H and ^{13}C NMR spectroscopic analysis.

Notes and references

1 (*a*) H. U. Blaser and E. Schmidt, *Asymmetric Catalysis on Industrial Scale*, Wiley-VCH, Weinheim, 2004; (*b*) R. A. Sheldon and H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2001.

2 A. Thayer, *Chem. Eng. News*, 2005, **83**, 55.

3 Review on heterogeneous palladium-catalyzed couplings: L. Yin and J. Liebscher, *Chem. Rev.*, 2007, **107**, 133.

4 For the selected papers on the application of solid-supported heterogeneous catalysts see: (*a*) X. Meng, X. Xu, T. Gao and B. Chen, *Eur. J. Org. Chem.*, 2010, 5409; (*b*) R. B. N. Baig and R. S. Varma, *Green Chem.*, 2013, **15**, 1838; (*c*) D. D. Tang, K. D. Collins and F. Glorius, *J. Am. Chem. Soc.*, 2013, **135**, 7450; (*d*) C. Liu, X. Rao, Y. Zhang, X. Li, J. Qiu and Z. Jin, *Eur. J. Org. Chem.*, 2013, 4345.

5 For the selected reviews on the application of nanocatalysts, see: (*a*) E. Gross, J. H.-C. Liu, F. D. Toste and G. A. Somorjai, *Nat. Chem.*, 2012, **4**, 947; (*b*) V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara and J.-M. Basset, *Chem. Rev.*, 2011, **111**, 3036; (*c*) K. V. S. Ranganath and F. Glorius, *Catal. Sci. Technol.*, 2011, **1**, 13; (*d*) A. Schätz, O. Reiser and W. J. Stark, *Chem. – Eur. J.*, 2010, **16**, 8950.

6 (*a*) R. Sarges, H. R. Howard, R. G. Browne, L. A. Lebel, P. A. Seymour and B. K. Koe, *J. Med. Chem.*, 1990, **33**, 2240; (*b*) B. K. Trivedi and R. F. bruns, *J. Med. Chem.*, 1988, **31**, 1011; (*c*) K. Makino, G. Sakata and K. Morimoto, *Heterocycles*, 1985, **23**, 2025.

7 (*a*) D. R. Armour, D. A. Baxter, J. S. Bryans, K. N. Dack, P. S. Johnson, R. A. Lewthwaite, J. Newman, D. J. Rawson and T. Ryckmans, WO 2004037809, 2004, Chem. Abstr., 2004, **140**, 370921; (*b*) J.-C. Pascal and D. Carniato, EP 1099695, 2001, *Chem. Abstr.*, 2001, **134**, 353312.

8 (*a*) J. Balsells, L. DiMichele, J. Liu, M. Kubryk, K. Hansen and J. D. Armstrong, *Org. Lett.*, 2005, **7**, 1039; (*b*) M. J. Stocks, D. R. Cheshire and R. Reynold, *Org. Lett.*, 2004, **6**, 2969; (*c*) S. D. Larsen and B. A. DiPaolo, *Org. Lett.*, 2001, **3**, 3341.

9 S. Ueda and H. Nagasawa, *J. Am. Chem. Soc.*, 2009, **131**, 15080.

10 H. Xu, Y. Jiang and H. Fu, *Synlett*, 2013, **24**, 125.

11 (*a*) J. Liu, C. Yu, P. Zhao and G. Chen, *Appl. Surf. Sci.*, 2012, **258**, 9096; (*b*) C. Yu, P. Zhao, G. Chen and H. Bin, *Appl. Surf. Sci.*, 2011, **257**, 7727.

12 For the selected papers on the properties of Al_2O_3–TiO_2 and relative solid-supported catalyst see: (*a*) Y. Saih, M. Nagata, T. Funamoto, Y. Masuyama and K. Segawa, *Appl. Catal., A*, 2005, **295**, 11; (*b*) K. Segawa, M. Katsuta and F. Kameda, *Catal. Today*, 1996, **29**, 215; (*c*) C. Pophal, F. Kameda, K. Hoshino, S. Yoshinaka and K. Segawa, *Catal. Today*, 1997, **39**, 21; (*d*) S. Yoshinaka and K. Segawa, *Catal. Today*, 1998, **45**, 293; (*e*) K. Segawa, K. Takahashi and S. Satoh, *Catal. Today*, 2000, **63**, 123; (*f*) K. Takahashi, Y. Saih and K. Segawa, *Stud. Surf. Sci. Catal.*, 2002, **145**, 311; (*g*) Y. Saih and K. Segawa, *Catal. Today*, 2003, **186**, 61; (*h*) Y. Saih and K. Segawa, *Catal. Surv. Asia*, 2003, **7**, 235; (*i*) A. Duan, R. Li, G. Jiang, J. Gao, Z. Zhao, G. Wan, D. Zhang, W. Huang and K. H. Chung, *Catal. Today*, 2009, **140**, 187.

13 (*a*) P. N. Craig, in *ComprehensiVe Medicinal Chemistry*, ed. C. J. Drayton, Pergamon Press, New York, 1991, vol. 8; (*b*) P. Cozzi, G. Carganico, D. Fusar, M. Grossoni, M. Menichincheri, V. Pinciroli, R. Tonani, F. Vaghi and P. Salvati, *J. Med. Chem.*, 1993, **36**, 2964.

14 G. Rousselet, P. Capdevielle and M. Maumy, *Tetrahedron Lett.*, 1993, **34**, 6395.

15 (*a*) J. Wang, F. Xu, T. Cai and Q. Shen, *Org. Lett.*, 2008, **10**, 445; (*b*) F. Xu, J. Sun and Q. Shen, *Tetrahedron Lett.*, 2002, **43**, 1867.

16 For the selected papers on the applications of electron-transfer mediates in oxidative reactions see: (*a*) J. Piera and J.-E. Bäckvall, *Angew. Chem., Int. Ed.*, 2008, **47**, 3506; (*b*) B. P. Babu, X. Meng and J.-E. Bäckvall, *Chem. – Eur. J.*, 2013, **19**, 4140; (*c*) X. Meng, C. Li, B. Han, T. Wang and B. Chen, *Tetrahedron*, 2010, **66**, 3029; (*d*) T. Oishi, K. Yamaguchi and N. Mizuno, *ACS Catal.*, 2011, **1**, 1351.

17 (*a*) O. Prakash, H. K. Gujral, N. Rani and S. P. Singh, *Synth. Commun.*, 2000, **30**, 417; (*b*) G. Jones and D. R. Sliskovic, *J. Chem. Soc., Perkin Trans. 1*, 1982, **4**, 967; (*c*) S. Mineo, S. Kawamura and K. Nakagawa, *Synth. Commun.*, 1976, **6**, 69.