DOI: 10.1002/cjoc.201700007

Copper(II) Acetylacetonate: An Efficient Catalyst for Huisgen-Click Reaction for Synthesis of 1,2,3-Triazoles in Water

Yuqin Jiang,[a] Xingfeng Li,[a] Xiyong Li,[b] Yamin Sun,[b] Yaru Zhao,[a] Shuhong Jia,[a] Niu Guo,[a] Guiqing Xu,*[,a] and Weiwei Zhang*[,a]

[a] *Henan Engineering Laboratory of Chemical Pharmaceuticals & Biomedical Materials, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China*

[b] *Weihai Ocean Vocational College, Weihai, Shandong 264300, China*

An efficient and green copper(II) acetylacetonate-catalyzed protocol for the Huisgen-click reaction in water at 100 ℃ has been established. The protocol was not only suitable for the reaction between organic azides and alkynes, but also suitable for one-pot three-component reaction among alkyl halides, NaN_3 and alkynes.

Keywords copper(II) acetylacetonate, Huisgen-click reaction, water, alkynes , one-pot

Introduction

1,4-Disubstituted 1,2,3-triazoles are important N-heterocyclic compounds, which have also been widely applied in industrial applications such as material science,[1] polymer chemistry,[2] pharmaceutical synthesis[3] and biological conjugation.[4] In addition, 1,2,3-triazoles are important privileged scaffolds and basic skeletons with a broad spectrum of biological activities, such as anti-tumour,[5] anti-viral,[6] antiallergic,[7] fungicidal,[7b] anti-HIV[8] activities and so on. The classical method for synthesis of 1,2,3-triazoles is the thermal Huisgen reaction between the terminal alkynes and azides, which has been considered as one of the important reactions for synthesis of five-member nitrogen heterocycles in organic chemistry.[9-11]

Since the Huisgen-click reaction catalyzed by copper(I) species for regioselective synthesis of 1,4-disubstituted 1,2,3-triazoles was independently discovered by the groups of Sharpless[12] and Meldal,[13] a kind of copper catalytic systems were developed for the Huisgen-click reaction, including copper(I) salts and their complexes,[14] copper(II) salt using appropriate reducing agents[12,15,16] and metallic copper.[17] Considering the instability of simple copper(I) species, Cu(II) species were also applied for the Huisgen-click reaction, such as copper(II) complexes,[18] nanocrystalline copper oxide(II),[19] copper(II) on supports.[20-24] In addition, benign solvents are also the crucial factor for environmentally and friendly sustainable chemical processes.[25] The Huisgen-click reactions have been successfully carried out in green solvents, such as $scCO_2$,[26] ionic liquids,[27] water[28] and so on. Therefore, water is still the preferred benign and suitable solvent for the Huisgen-click reaction.

Copper(II) acetylacetonate [$Cu(acac)_2$] complexes have been widely used in organic chemistry as efficient catalysts for C－X (X＝C, N, P) bond formation,[29] asymmetric sulfoxidation,[30] C－H or C－C cleavage,[31] synthesis of (*E*)-*β*-chloro-enesulfonamides,[32] substituted ketones[33] and sulfur-containing triazoles.[34] In most cases mentioned above, $Cu(acac)_2$ was used as a homogeneous catalytic system. For a recyclable protocol, efforts were put to make $Cu(acac)_2$ as an heterogeneous recyclable catalytic system by immobilizing on supports, such as active carbon,[35] mesoporous silica,[36] caly,[37] ionic liquids,[38] core-shell structured Fe_3O_4@SiO_2[39] and so on. It is worthy mentioning that $Cu(acac)_2$ has poor solubility in water, which is the preferred green solvent for organic transformation and would make $Cu(acac)_2$ act as heterogeneous catalysts. To the best of our knowledge, $Cu(acac)_2$ has not been used lonely as the catalyst for the Huisgn-click reaction in water. In continuation with our previous works on the Cu(II) species-catalyzed Huisgen-click reaction,[26c,28j] the main work described in this paper shows a green and efficient protocol using $Cu(acac)_2$ as the catalyst for Huisgen-click reaction in water at 100 ℃ without any bases or ligands at a relatively low catalyst loading (0.2 mol%).

* E-mail: zhangweiwei@htu.edu.cn; Tel.: 0086-0373-3326335; Fax: 0086-0373-3326335
Received January 10, 2017; accepted February 22, 2017; published online XXXX, 2017.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201700007 or from the author.

Experimental

General procedure for cycloaddition reaction between alkynes and azides

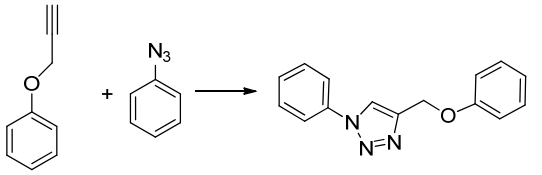
Alkyne (1.0 mmol), azide (1.0 mmol), and copper(II) acetylacetonate (0.002 mmol) were dissolved (or suspended) in deionized water (2.0 mL). The mixture was reacted at 100 ℃ and monitored by TLC until the starting materials disappeared. After the completion of the reaction, the resulting solution was extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed to give the corresponding triazoles, which were purified by column chromatography (petroleum ether/ethyl acetate, V∶V=6∶1).

General procedure for one-pot three-component 1,3-dipolar cycloaddition catalyzed by copper(II) acetylacetonate in water

Alkyne (1.0 mmol), sodium azide (1.2 mmol), alkyl halide (1.0 mmol), and copper(II) acetylacetonate (0.02 mmol) were dissolved (or suspended) in deionized water (2.0 mL). The mixture reacted at 100 ℃ and was monitored by TLC until the starting materials disappeared. After the completion of the reaction, the resulting solution was extracted with ethyl acetate. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed to give the corresponding triazoles, which were purified by column chromatography (petroleum ether/ethyl acetate, V∶V=6∶1).

Results and Discussion

Our investigation began with an effort to optimize the reaction temperature for the model reaction using phenyl azide and propargyl phenyl ether as the starting materials (Eq. 1). The reaction conditions were settled as follows: phenyl azide (1.0 mmol), propargyl phenyl ether (1.0 mmol), $Cu(acac)_2$ (20 mol%) and water (2.0 mL). The model reaction was carried out at 25, 40, 50, 80 and 100 ℃ for 30 min. As shown in Figure 1, the obtained yields of the model reaction increased greatly with the temperature range from 25 to 50 ℃ and kept almost the same with the temperature range from 50 to 100 ℃. The obtained yields of the model reaction at 25 and 40 ℃ were only 5% and 40% respectively. While at 50 ℃, the obtained yield of the model reaction was 91%, which indicated that the reaction temperature has a great effect on the model reaction. And elevating the reaction temperature to 80 or 100 ℃, the obtained yields of the model reaction were almost the same as that obtained at 50 ℃. Therefore, 50 ℃ was selected as the temperature for the model reaction.



(1)

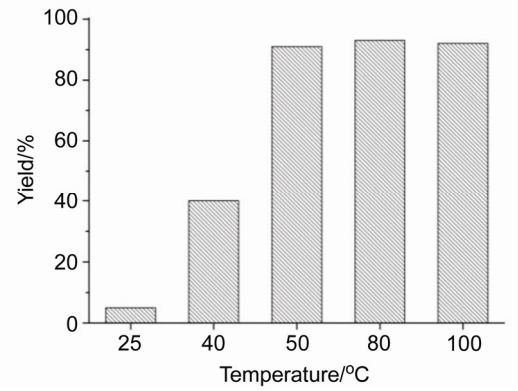


Figure 1 Effects of reaction temperature on the model reaction.

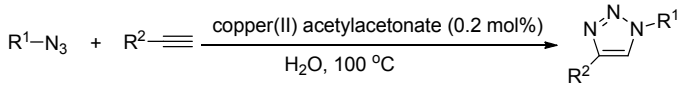
To investigate the influence of the catalyst loading on the cycloaddition, the model reaction was performed at 50 ℃ catalyzed by different amounts of $Cu(acac)_2$. As shown in Table 1 (Entries 1, 2), the model reaction could still finish in 30 min, when catalyzed by 10 mol% or 5 mol% $Cu(acac)_2$ with almost the same yields as that when catalyzed by 20 mol% $Cu(acac)_2$. However, a further decrease of the loading of $Cu(acac)_2$ (Entries 3—6) led to a long reaction time. The reaction time was 120 min when catalyzed by 2 mol% $Cu(acac)_2$, which was four times that when catalyzed by 5 mol% $Cu(acac)_2$. When catalyzed by 1 mol%, 0.5 mol%, and 0.2 mol% $Cu(acac)_2$, the corresponding reaction time was 240, 270 and 360 min, respectively. It is worthy mentioning that although the longest reaction time was taken when catalyzed by 0.2 mol% $Cu(acac)_2$, it was the enough catalyst loading for completing the model reaction. According to our previous works on the Cu(II) catalyzed Huisgen-click reaction,[28j] elevating the reaction temperature is a direct way to short reaction time. To improve the efficiency of 0.2 mol% $Cu(acac)_2$ on the model reaction, the reaction temperature was increased to 80 and 100 ℃. It is uplifting that the reaction time was 90 min for 80 ℃ (Entry 7) and 50 min for 100 ℃ (Entry 8). Therefore, the optimized conditions are as follows: $Cu(acac)_2$ (0.2 mol%) as the catalyst, water (2.0 mL) as the solvent, and 100 ℃ as the reaction temperature.

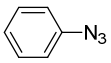
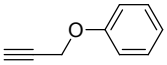
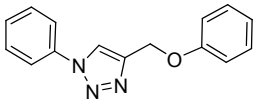
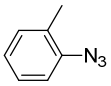
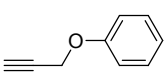
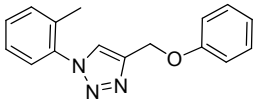
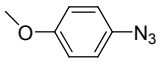
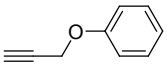
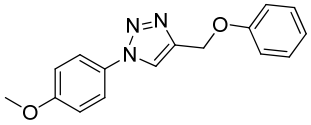
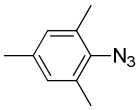
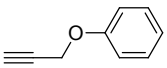
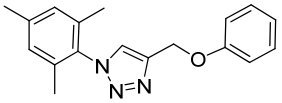
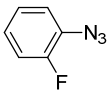
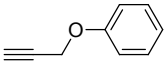
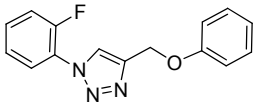
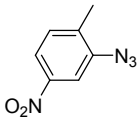
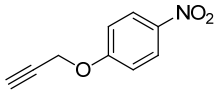
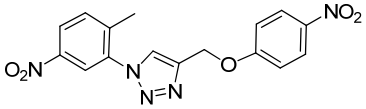
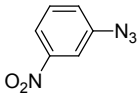
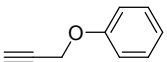
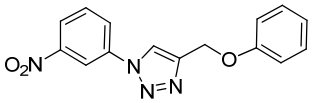
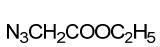
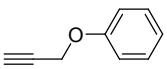
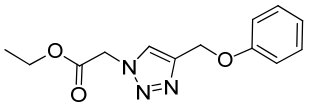
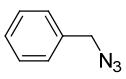
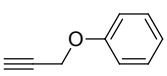
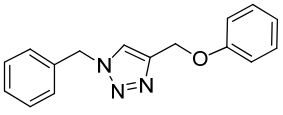
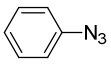
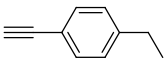
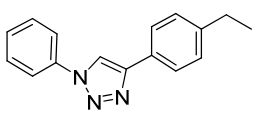
Table 1 Effects of catalyst loading on the model reaction

Entry	Catalyst loading/mol%	Temp./℃	Time/min	Yield/%
1	10	50	30	94
2	5	50	30	93
3	2	50	120	92
4	1	50	240	91
5	0.5	50	270	92
6	0.2	50	360	91
7	0.2	80	90	93
8	0.2	100	50	92

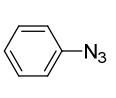
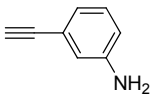
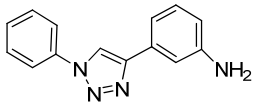
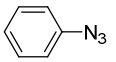
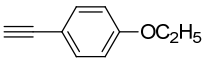
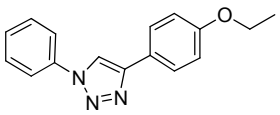
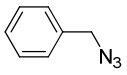
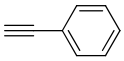
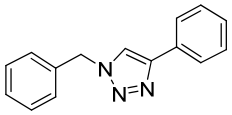
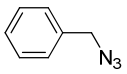
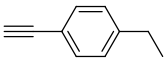
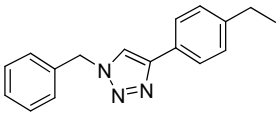
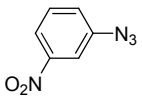
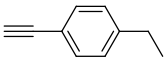
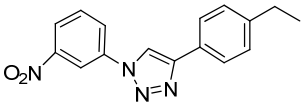
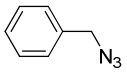
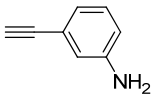
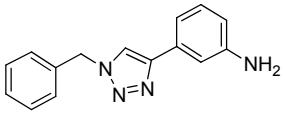
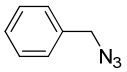
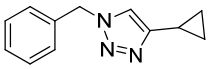
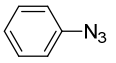
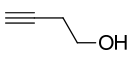
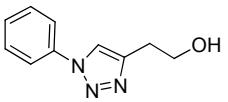
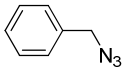
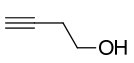
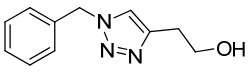
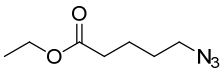
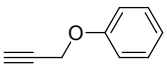
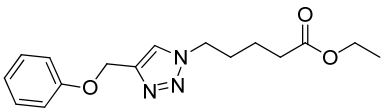
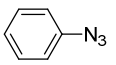
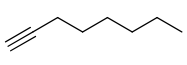
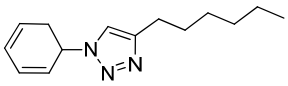
With the optimized reaction conditions established, the scope of this reaction was then evaluated with respect to various substituted terminal alkynes and azides. As shown in Table 2, these transformations displayed high functional group tolerance and proved to be a general method for the synthesis of 1,4-disubstituted 1,2,3-triazoles. Terminal alkynes with ethyl, ethoxyl and amino groups on the arene or aliphatic alkynes gave the corresponding 1,2,3-triazoles in good to excellent yields. And the reactions worked well not only with aryl azides, but also with alkyl azides. It was also found that the substituents (electron withdrawing, electron rich and heterocycle) do not have any peculiar effects, as most of the reactions were completed within 20 — 200 min. However, aliphatic azide (ethyl 2-azidoacetate) and aliphatic alkyne (1-octyne) took a relatively longer reaction time for the formation of triazoles (Table 2, Entry 8 and Entry 21).

Table 2 Synthesis of triazoles using $Cu(acac)_2$ as the catalyst[a]



Entry	Azide	Alkyne	Product	Time/min	Yield[b]/%
1				50	93
2				90	89
3				75	91
4				100	84
5				120	86
6				80	84
7				50	90
8				180	83
9				30	90
10				20	89

Continued

Entry	Azide	Alkyne	Product	Time/min	Yield[b]/%
11				30	93
12				60	88
13				90	90
14				40	89
15				60	87
16				120	83
17				90	85
18				100	83
19				120	82
20				130	82
21				200	84

[a] Reaction conditions: terminal alkyne (1.0 mmol), azide (1.0 mmol), $Cu(acac)_2$ (0.2 mol%), H_2O (2 mL), 100 ℃. [b] Isolated yields.

Furthermore, we have also developed an experimentally convenient one-pot, regioselective protocol for synthesis of 1,2,3-triazoles from alkyl halides, NaN_3, and alkynes. It is worthy mentioning that the catalyst loading needed for three-component ont-pot reaction is 2 mol%. Therefore the optimized conditions are as follows: terminal alkyne (1.0 mmol), sodium azide (1.2 mmol), alkyl halide (1.0 mmol), $Cu(acac)_2$ (2 mol%), H_2O (2.0 mL) and 100 ℃. As shown in Table 3, the corresponding 1,4-disubstituded 1,2,3-triazoles could be obtained in good to excellent yields under such conditions.

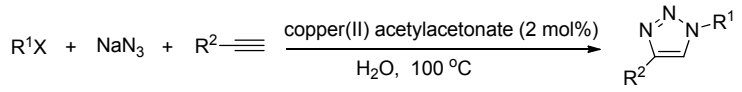
The catalytic mechanism of copper(II) for Huisgen-click reaction has been proposed according to the previous reports.[19,23,28n,28j] As for reaction between the azides and alkynes, it seems that the Cu(II) has been reduced by alkynes to Cu(I),[28n] which is the true catalyst. As for three-component 1,3-dipolar cycloaddition, copper(II) acetylacetonate might be reduced by sodium azide to give the needed catalysis of Cu(I).[23,28j]

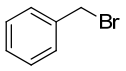
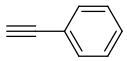
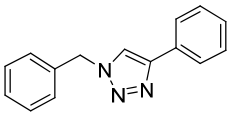
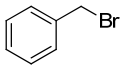
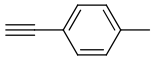
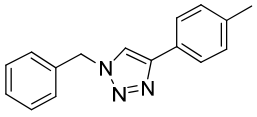
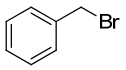
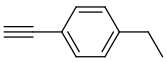
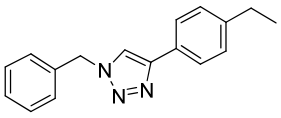
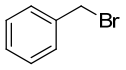
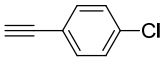
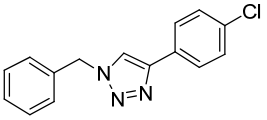
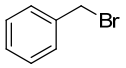
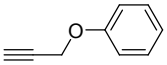
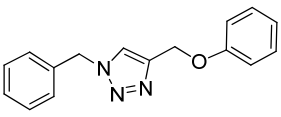
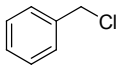
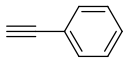
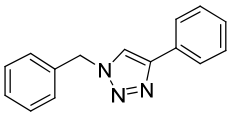
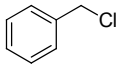
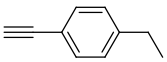
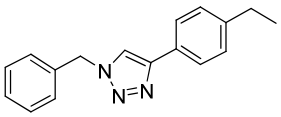
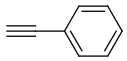
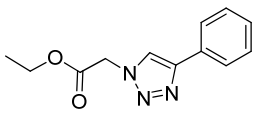
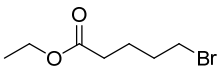
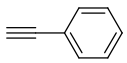
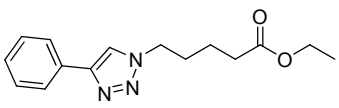
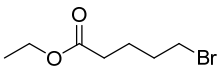
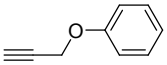
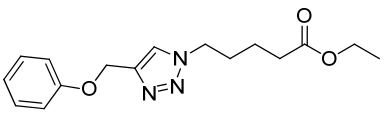
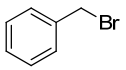
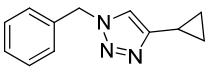
Conclusions

In summary, we presented a simple protocol for the Huisgen click reaction using $Cu(acac)_2$ as the catalyst in water at 100 ℃. The protocol was also proved to be

CHINESE JOURNAL OF CHEMISTRY

Table 3 One-pot synthesis of triazoles from alkyl halides, NaN_3 and alkynes[a]



Entry	R^1X	R^2—≡	Product	Time/min	Yield[b]/%
1				70	89
2				60	90
3				45	88
4				90	84
5				200	80
6				100	90
7				75	88
8	$EtOOCCH_2Cl$			180	86
9				160	81
10				210	82
11				150	80

[a] Reaction conditions:. terminal alkyne (1.0 mmol), sodium azide (1.2 mmol), alkyl halide (1.0 mmol), $Cu(acac)_2$ (2 mol%), H_2O (2.0 mL) and 100 ℃. [b] Isolated yields.

suitable for one-pot three-component reactions among alkyl halides, NaN_3 and alkynes.

Acknowledgement

This work was financially supported by the Key Scientific and Technological Project of Henan Province (Nos. 152102210285 and 152102310312), the Innovative Talents Program of Henan Province (Nos. 164100510015 and 174100510025), the Production-Learning-Research Cooperation Project of Henan Province (Nos. 122107000014, 142107000081 and 122107000014), the Foundation of Henan Educational Committee (Nos. 14A350005 and 16A350015), the

Scientific Research Foundation for Doctors (No. qd16106) and the Youth Foundation (No. 2016QK09) of Henan Normal University.

References

[1] Lutz, J. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018.

[2] (a) Evans, R. A. *Aust. J. Chem.* **2007**, *60*, 384; (b) Johnson, J. A.; Koberstein, J. T.; Finn, M. G.; Turro, N. J. *Macromol. Rapid Commun.* **2008**, *29*, 1052; (c) Zhang, W.-W.; Jiang, W.-W.; Zhang, D.-L.; Bai, G.-Y.; Lou, P.-X.; Hu, Z.-G. *Polym. Chem.* **2015**, *6*, 2274.

[3] (a) Pinna, G. A.; Curzu, M. M.; Sechi, M.; Chelucci, G.; Maciocco, E. *Farmaco* **1999**, *54*, 542; (b) Murineddu, G.; Loriga, G.; Gavini, E.; Peanna, A. T.; Mule, A. C.; Pinna, G. A. *Arch. Pharm.* **2001**, *334*, 393.

[4] (a) Link, A. J.; Tirrell, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 11164; (b) Wang, Q.; Chan, T. R.; Hilgraf, R.; Fokin, V. V.; Sharpless, K. B.; Finn, M. G. *J. Am. Chem. Soc.* **2003**, *125*, 3192; (c) Lutz, J. F.; Zarafshani, Z. *Adv. Drug Delivery Rev.* **2008**, *60*, 958.

[5] (a) Grana, G. *J. Surg. Oncol.* **2006**, *93*, 585; (b) Chao, S.; Oh, S.; Um, Y.; Jung, J. H.; Ham, J.; Shin, W. S.; Lee, S. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 382; (c) Zhang, J.-J.; Garrossian, M.; Gardner, D.; Garrossian, A.; Chang, Y. T.; Kim, Y. K.; Chang, C. W. T. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 1359; (d) Odlo, K.; Hentzen, J.; dit Chabert, J. F.; Ducki, S.; Gani, O. A. B. S. M.; Sylte, I.; Skerede, M.; Fløenes, V. A.; Hansen, T. V. *Bioorg. Med. Chem.* **2008**, *16*, 4829.

[6] Palhagen, S.; Canger, R.; Henriksen, O.; van Parys, J. A.; Riviere, M. E.; Karolchyk, M. A. *Epilepsy Res.* **2001**, *43*, 115.

[7] (a) Buckle, D. R.; Rockell, C. J. M.; Smith, H.; Spicer, B. A. *J. Med. Chem.* **1986**, *29*, 2262; (b) Fung-Tomc, J. C.; Huczko, E.; Minassian, B.; Bonner, D. P. *Antimicrob. Agents Chemother.* **1998**, *42*, 313.

[8] (a) Alvarez, R.; Velazquez, S.; Sanfelix, A.; Aquaro, S.; Declercq, E.; Perno, C. F.; Karlsson, A.; Balzarini, J.; Camarasa, M. J. *J. Med. Chem.* **1994**, *37*, 4185; (b) da Silva, F. D.; de Souza, M. C. B. V.; Frugulhetti, I. I. P.; Castro, H. C.; Souza, S. L. D.; de Souza, T. M. L.; Rodrigues, D. Q.; Souza, A. M. T.; Abreu, P. A.; Passamani, F.; Rodrigues, C. R.; Ferreira, V. F. *Eur. J. Med. Chem.* **2009**, *44*, 373.

[9] Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*, Vol. 1, Ed.: Padwa, A., Wiley, New York, **1984**, p. 1.

[10] For recent reviews about Huisgen reaction, see: (a) Jalani, H. B.; Karagöz, A. Ç.; Tsogoeva, S. B. *Synthesis* **2017**, *49*, 29; (b) Wang, C.; Ikhlef, D.; Kahlal, S.; Saillard, J. Y. *Coord. Chem. Rev.* **2016**, *316*, 1; (c) Castro, V.; Rodríguez, H.; Albericio, F. *ACS Comb. Sci.* **2016**, *18*, 1; (d) Chassaing, S.; Bénéteau, V.; Pale, P. *Catal. Sci. Technol.* **2016**, *6*, 923; (e) Ötvös, S. B.; Fülöp, F. *Catal. Sci. Technol.* **2015**, *5*, 4926; (f) Haldón, E.; Nicasio, M. C.; Pérez, P. J. *Org. Biomol. Chem.* **2015**, *13*, 9528; (g) Kumar, K. A. *Int. J. Chem. Tech. Res.* **2013**, *5*, 3032.

[11] For recent examples about Huisgen reaction, see: (a) González-Olvera, R.; Urquiza-Castro, C. I.; Negrón-Silva, G. E.; Ángeles-Beltrán, D.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Lara, V. H.; Santillan, R.; Morales-Serna, J. A. *RSC Adv.* **2016**, *6*, 63660; (b) Koganei, H.; Tachikawa, S.; El-Zaria, M. E.; Nakamura, H. *New J. Chem.* **2015**, *39*, 6388; (c) Shaygan Nia, A.; Rana, S.; Döhler, D.; Jirsa, F.; Meister, A.; Guadagno, L.; Koslowski, E.; Bron, M.; Binder, W. *Chem. Eur. J.* **2015**, *21*, 10763; (d) Slimi, R.; Kalhor-Monfared, S.; Plancq, B.; Girard, C. *Tetrahedron Lett.* **2015**, *56*, 4339; (e) Diz, P.; Pernas, P.; El Maatougui, A.; Tubio, C. R.; Azuaje, J.; Sotelo, E.; Guitian, F.; Gil, A.; Coelho, A. *Appl. Catal., A* **2015**, *502*, 86; (f) Jayaramulu, K.; Suresh, V. M.; Maji, T. K. *Dalton Trans.* **2015**, *44*, 83; (g) Saravanan, N.; Arthanareeswari, M.; Kamaraj, P.; Sivakumar, B. *Res. Chem. Intermed.* **2015**, *41*, 5379; (h) Mekhzoum, M. E. M.; Benzeid, H.; Qaiss, A. E. K.; Essassi, E. M.; Bouhfid, R. *Catal. Lett.* **2016**, *146*, 136.

[12] Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596.

[13] Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057.

[14] (a) Díez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2008**, *47*, 8881; (b) Díez-González, S.; Stevens, E. D.; Nolan, S. P. *Chem. Commun.* **2008**, 4747; (c) Gruijters, B. W. T.; Broeren, M. A. C.; van Delft, F. L.; Sijbesma, R. P.; Hermkens, P. H. H.; Rutjes, F. P. J. T. *Org. Lett.* **2006**, *8*, 3163; (d) Ozcubukcu, S.; Ozkal, E.; Jimeno, C.; Pericàs, M. A. *Org. Lett.* **2009**, *11*, 4680; (e) Garciá-Álvarez, J.; Díez, J.; Gimeno, J. *Green Chem.* **2010**, *12*, 2127; (f) Li, L.; Lopes, P. S.; Rosa, V.; Figueira, C. A.; Lemos, M. A.; Duarte, M. T.; Aviles, T.; Gomes, P. T. *Dalton Trans.* **2012**, *41*, 5144; (g) Lal, S.; McNally, J.; White, A. J. P.; Díez-González, S. *Organometallics* **2011**, *30*, 6225; (h) Islam, R. U.; Taher, A.; Choudhary, M.; Witcomb, M. J.; Mallick, K. *Dalton Trans.* **2015**, *44*, 1341; (i) Jayaramulu, K.; Suresh, V. M.; Maji, T. K. *Dalton Trans.* **2015**, *44*, 83.

[15] Camp, C.; Dorbes, S.; Picard, C.; Benoist, E. *Tetrahedron Lett.* **2008**, *49*, 1979.

[16] (a) Pathigoolla, A.; Pola, R. P.; Sureshan, K. M. *Appl. Catal. A-Gen.* **2013**, *453*, 151; (b) Kumar, A. S.; Datta, K. K. R.; Rao, T. S.; Raghavan, K. V.; Eswaramoorthy, M.; Reddy, B. V. S. *J. Nanosci. Nanotechnol.* **2013**, *13*, 3136.

[17] (a) Pachon, L. D.; Maarseveen, J. H.; Rothenberg, G. *Adv. Synth. Catal.* **2005**, *347*, 811; (b) Molteni, G.; Bianchi, C. L.; Marinoni, G.; Santo, N.; Ponti, A. *New J. Chem.* **2006**, *30*, 1137; (c) Park, I. S.; Kwon, M. S.; Kim, Y.; Lee, J. S.; Park, J. *Org. Lett.* **2008**, *10*, 497; (d) Kaur, S.; Bhalla, V.; Kumar, M. *Chem. Commun.* **2015**, 526.

[18] Song, Y. J.; Yoo, C.; Hong, J. T.; Kim, S. J.; Son, S. U.; Jang, H. Y. *Bull. Korean Chem. Soc.* **2008**, *29*, 1561.

[19] Brotherton, W. S.; Michaels, H. A.; Simmons, J. T.; Clark, R. J.; Dalal, N. S.; Zhu, L. *Org. Lett.* **2009**, *11*, 4954.

[20] Masuyama, Y.; Yoshikawa, K.; Suzuki, N.; Hara, K.; Fukuoka, A. *Tetrahedron Lett.* **2011**, *52*, 6916.

[21] Namitharan, K.; Kumarraja, M.; Pitchumani, K. *Chem. Eur. J.* **2009**, *15*, 2755.

[22] Reddy, K. R.; Rajgopal, K.; Kantam, M. L. *Catal. Lett.* **2007**, *114*, 36.

[23] Mohammed, S.; Padala, A. K.; Dar, B. A.; Singh, B.; Sreedhar, B.; Vishwakarma, R. A.; Bharate, S. B. *Tetrahedron* **2012**, *68*, 8156.

[24] Guha, P. M.; Phan, H.; Kinyon, J. S.; Brotherton, W. S.; Sreenath, K.; Simmons, J. T.; Wang, Z.-X.; Clark, R. J.; Dalal, N. S.; Shatruk, M.; Zhu, L. *Inorg. Chem.* **2012**, *51*, 3465.

[25] (a) Clark, J. H. *Green Chem.* **1999**, *1*, 1; (b) Sheldon, A. R. *Green Chem.* **2005**, *7*, 267; (c) Song, C. E.; Lee, S. G. *Chem. Rev.* **2002**, *102*, 3495; (d) Serrano, E.; Linares, N.; Garcia, M. J.; Berenguer, J. R. *ChemCatChem* **2013**, *5*, 844; (e) Trakhtenberg, S.; Warner, J. C. *Chem. Rev.* **2007**, *107*, 2174; (f) Mason, B. P.; Price, K. E.; Steinbacher, J. L.; Bogdan, A. R.; McQuade, D. T. *Chem. Rev.* **2007**, *107*, 2300; (g) Descorme, C.; Gallezot, P.; Geantet, C.; George, C. *ChemCatChem* **2012**, *4*, 1897.

[26] (a) Grignard, B.; Schmeits, S.; Riva, R.; Detrembleur, C.; Lecomte, P.; Jérŏme, C. *Green Chem.* **2009**, *11*, 1525; (b) Grignard, B.; Calberg, C.; Jérŏme, C.; Detrembleur, C. *J. Supercrit. Fluid.* **2010**, *53*, 151; (c) Zhang, W.-W.; He, X.; Ren, B.-Q.; Jiang, Y.-Q.; Hu, Z.-G. *Tetrahedron Lett.* **2015**, *56*, 2472; (d) Jiang, Y.-Q.; Li, X.-F.; Yao, M.-H.; Dong, W.-P.; Li, X.; Cao, X.-H.; Xu, G.-Q.; Li, W. *CN 105688999A*, **2016** [*Chem. Abstr.* **2016**, *165*, 169660].

[27] (a) Ahmady, A. Z.; Heidarizadeh, F.; Keshavarz, M. *Synth. Commun.* **2013**, *43*, 2100; (b) Marra, A.; Vecchi, A.; Chiappe, C.; Melai, B.; Dondoni, A. *J. Org. Chem.* **2008**, *73*, 2458; (c) Yan, J.-C.; Wang, L. *Synthesis* **2010**, 447; (d) Zhao, Y.-B.; Yan, Z.-Y.; Liang, Y.-M. *Tetrahedron Lett.* **2006**, *47*, 1545; (e) Zhong, P.; Guo, S.-R. *Chin. J. Chem.* **2004**, *22*, 1183.

[28] (a) Alonso, F.; Moglie, Y.; Radivoy, G. *Acc. Chem. Res.* **2015**, *48*, 2516; (b) Purohit, V. B.; Karad, S. C.; Patel, K. H.; Raval, D. K. *RSC Adv.* **2014**, *4*, 46002; (c) Jiang, Y.-Q.; Kong, D.-Y.; Zhao, J.-L.; Qi, Q.-H.; Li, W.; Xu, G.-Q. *RSC Adv.* **2014**, *4*, 1010; (d) Roy, S.; Chat-

terjee, T.; Pramanik, M.; Roy, A. S.; Bhaumik, A.; Islam, S. M. *J. Mol. Catal. A-Chem.* **2014**, *386*, 78; (e) Kaboudin, B.; Mostafalua, R.; Yokomatsub, T. *Green Chem.* **2013**, *15*, 2266; (f) Deraedt, C.; Pinaud, N.; Astruc, D. *J. Am. Chem. Soc.* **2014**, *136*, 12092; (g) Radatz, C. S.; Soares, L. A.; Vieira, E. R.; Alves, D.; Russowsky, D.; Schneider, P. H. *New J. Chem.* **2014**, *38*, 1410; (h) Baig, R. B. N.; Varma, R. S. *Green Chem.* **2013**, *15*, 1839; (i) Shao, C.-W.; Zhu, R.; Luo, S.; Zhang, Q.; Wang, X.-Y.; Hu, Y.-F. *Tetrahedron Lett.* **2011**, *52*, 3782; (j) Jiang, Y.-Q.; Kong, D.-Y.; Zhao, J.-L.; Zhang, W.-W.; Xu, W.-J.; Li, W.; Xu, G.-Q. *Tetrahedron Lett.* **2014**, *55*, 2410; (k) Zhang, Z.-F.; Dong, C.-M.; Yang, C.-H.; Hu, D.; Long, J.; Wang, L.; Li, H.; Chen, Y.; Kong, D.-L. *Adv. Synth. Catal.* **2010**, *352*, 1600; (l) Wang, K.; Bi, X.-H.; Xing, S.-X.; Liao, P.-Q.; Fang, Z.-X.; Meng, X.-Y.; Zhang, Q.; Liu, Q.; Ji, Y. *Green Chem.* **2011**, *13*, 562; (m) Reddy, K. R.; Rajgopal, K.; Kantam, M. L. *Synlett* **2006**, 957; (n) Wang, Y.; Liu, J.-H.; Xia, C.-G. *Adv. Synth. Catal.* **2011**, *353*, 1534; (o) Masuyama, Y.; Yoshikawa, K.; Suzuki, N.; Hara, K.; Fukuoka, A. *Tetrahedron Lett.* **2011**, *52*, 6916; (p) Zhang, W.-W.; Ren, B.-Q.; Jiang, Y.-Q.; Hu, Z.-G. *RSC Adv.* **2015**, *5*, 12043; (q) Tasca, E.; Sorella, G. L.; Sperni, L.; Strukul, G.; Scarso, A. *Green Chem.* **2015**, *17*, 1414; (r) Jiang, Y.-Q.; Zhang, P.; Li, X.-J.; Li, W.; Xu, G.-Q. *Z. Naturforsch. B* **2012**, *67b*, 226.

[29] (a) Monnier, F.; Turtaut, F.; Duroure, L.; Taillefer, M. *Org. Lett.* **2008**, *10*, 3203; (b) Huang, H.; Jiang, H.-L.; Chen, K.-X.; Liu, H. *J. Org. Chem.* **2008**, *73*, 9061; (c) Xu, Z.-W.; Yu, X.-Q.; Feng, X.-J.; Bao, M. *J. Org. Chem.* **2011**, *76*, 6901; (d) Shen, Y.; Chen, J.-X.; Liu, M.-C.; Ding, J.-C.; Gao, W.-X.; Huang, X.-B.; Wu, H.-Y. *Chem. Commun.* **2014**, *50*, 4292.

[30] O'Mahony, G. E.; Ford, A.; Maguire, A. R. *J. Org. Chem.* **2012**, *77*, 3288.

[31] (a) Xie, P.; Wang, Z.-Q.; Deng, G.-B.; Song, R.-J.; Xia, J.-D.; Hu, M.; Li, J.-H. *Adv. Synth. Catal.* **2013**, *355*, 2257; (b) Kang, Y. W.; Cho, Y. J.; Ko, K. Y.; Jang, H. Y. *Catal. Sci. Technol.* **2015**, *5*, 3931.

[32] Liu, X.-Y.; Gao, P.; Shen, Y.-W.; Liang, Y.-M. *Adv. Synth. Catal.* **2011**, *353*, 3157.

[33] (a) Yi, N.-N.; Zhang, H.; Xu, C.-H.; Deng, W.; Wang, R.-J.; Peng, D.-M.; Zeng, Z.-B.; Xiang, J.-N. *Org. Lett.* **2016**, *18*, 1780; (b) Luo, Q.; Liu, C.-M.; Tong, J.-J.; Shao, Y.; Shan, W.-Y.; Wang, H.-H.; Zheng, H.; Cheng, J.; Wan, X.-B. *J. Org. Chem.* **2016**, *81*, 3103.

[34] Shen, T.; Huang, X.-Q.; Liang, Y.-F.; Jiao, N. *Org. Lett.* **2015**, *17*, 6186.

[35] (a) Silva, A. R.; Martins, M.; Freitas, M. M. A.; Figueiredo, J. L.; Freire, C.; de Castro, B. *Eur. J. Inorg. Chem.* **2004**, 2027; (b) Silva, A. R.; Figueiredo, J. L.; Freire, C.; de Castro, B. *Catal. Today* **2005**, *102*, 154.

[36] Silva, A. R.; Wilson, K.; Whitwood, A. C.; Clark, J. H.; Freire, C. *Eur. J. Inorg. Chem.* **2006**, 1275.

[37] Pereira, C.; Patricio, S.; Silva, A. R.; Magalhaes, A. L.; Carvalho, A. P.; Pires, J.; Freire, C. *J. Colloid Interface Sci.* **2007**, *316*, 570.

[38] Jain, S. L.; Joseph, J. K.; Sain, B. *Catal. Lett.* **2007**, *115*, 52.

[39] Sun, J.; Yu, G.-L.; Liu, L.-L.; Li, Z.-F.; Kan, Q.-B.; Huo, Q.-S.; Guan, J.-Q. *Catal. Sci. Technol.* **2014**, *4*, 1246.

(Zhao, C.)

