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# Tridentate P,N,N-ligand promoted copper-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters: synthesis of highly functionalized pyrroles†

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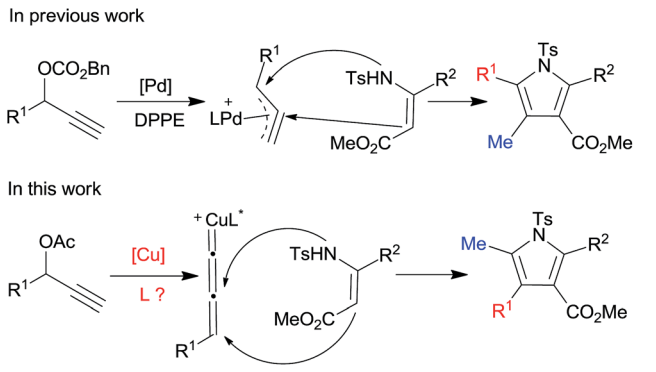
A copper-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters under mild reaction conditions for the construction of highly functionalized pyrroles has been developed. By employment of a newly developed tridentate P,N,N-ligand, a variety of fully substituted pyrroles were achieved in good to high yields.

Pyrroles are one of the most important heterocyclic compounds, which are present in many natural products[1] and synthetic intermediates,[2] and have a broad range of applications in medicinal chemistry,[3] bioorganic chemistry,[4] polymer chemistry[5] and material science.[6] Therefore, great efforts have been devoted to develop efficient methods for the synthesis of pyrroles.[7] The present synthetic methods generally depend on classical condensations such as the Knorr,[8] Paal–Knorr,[9] and Hantzsch reactions.[10] Recently, some more efficient approaches based on transition-metal catalyzed cyclizations[7a,f] and the multicomponent reactions[7d,g] have also been developed. Despite these impressive achievements, the regioselective synthesis of highly functionalized pyrroles with structural diversity, in particular fully substituted pyrroles, remains a challenging and desirable task.[11]

In the past decades, catalytic propargylic transformation has made significant progress.[12] In particular, the cycloadditions of propargylic alcohol derivatives with bis-nucleophiles for the construction of cyclic frameworks have been disclosed. Recently, Yoshida[13] reported a Pd-catalyzed cyclization of propargylic carbonates with β-enamino esters for the synthesis of fully substituted pyrroles (Scheme 1). Considering structural diversity of pyrrole derivatives, further exploration of new strategies for the synthesis of fully substituted pyrroles with different regioselectivities remains in high demand. Based on the recent advances on the copper-catalyzed propargylic transformation for the synthesis of heterocyclic compounds,[14] we envisioned that this methodology should be also a suitable approach for the construction of pyrroles from propargylic esters with β-enamino esters, generating pyrroles with different substitution mode to those with Pd-catalyst due to the different reaction pathway between the Cu- and Pd-catalyzed reaction. As a result, herein we report an efficient and alternative synthesis of highly functionalized pyrroles by a Cu-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters with a new benzylamine-derived P,N,N-ligand.

At the outset of our investigation, the cycloaddition of 1-phenylprop-2-yn-1-yl acetate (**1a**) with (*Z*)-methyl-3-(4-methylphenylsulfonamido)-3-phenylacrylate (**2a**) was chosen as the tested reaction to examine the effect of several commercially available ligands which have proved to be efficient in the Cu-catalyzed reactions. To our disappointment, some diphosphine ligands such as DPPF ($\mathbf{L_1}$), DPPP ($\mathbf{L_2}$) and BINAP ($\mathbf{L_3}$), as well as bidentate nitrogen ligands such as biPy




Scheme 1 Cu-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters for the synthesis of pyrroles.

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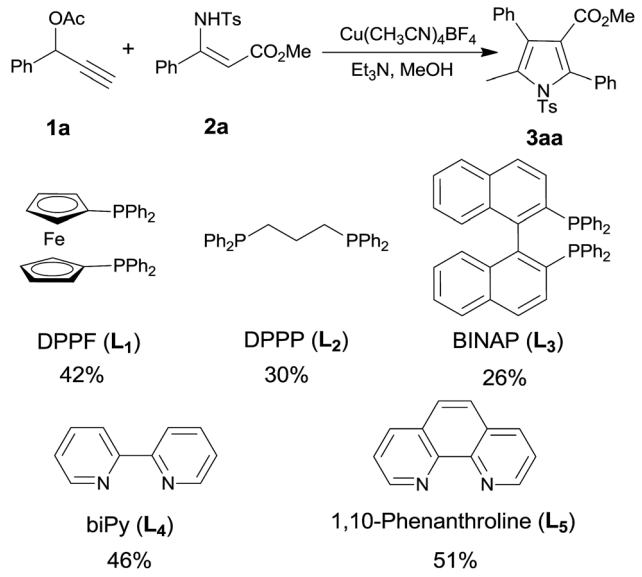
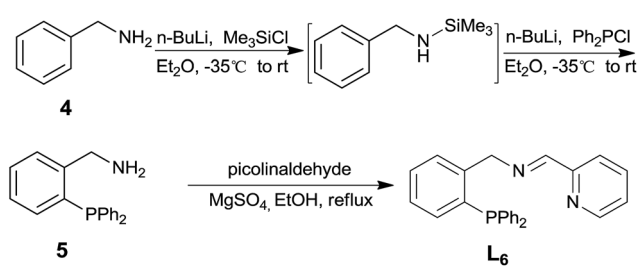



Scheme 2 Ligands evaluated for the Cu-catalyzed [3 + 2] cycloaddition.

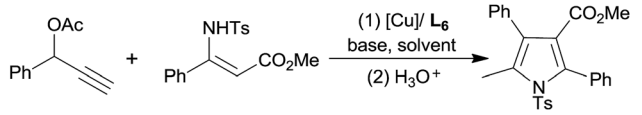
($\mathbf{L_4}$) and 1,10-phenanthroline ($\mathbf{L_5}$), all gave low to moderate yield of the corresponding [3 + 2] cycloaddition product **3aa** (Scheme 2). Recently, we have developed a series of chiral P,N,N-ligands which showed excellent diastereo- and enantioselectivities in the Cu-catalyzed asymmetric propargylic substitution,[15] decarboxylative propargylic substitution[16] and [3 + 3] cycloaddition reactions.[17] In particular, we have reported an example of highly enantioselective synthesis of optically active 2,3-dihydrofurans by Cu-catalyzed [3 + 2] cycloaddition of propargylic esters with β-ketoesters with chiral P,N,N-ligand.[18] The distinct structure of tridentate chelates generating from the complexion of P,N,N-ligands to copper should be responsible to high reactivity and enantioselectivity observed in the copper-catalyzed propargylic transformation.[16a,17] Due to excellent performance of P,N,N-ligands in the Cu-catalyzed propargylic transformation, we envisioned that this tridentate P,N,N-ligand type should be also efficient to the Cu-catalyzed [3 + 2] cycloaddition of propargylic esters **1** with β-enamino esters **2** for the synthesis of pyrroles. Considering the high cost and the difficult synthesis of chiral P,N,N-ligand, a structurally similar and nonchiral P,N,N-ligand $\mathbf{L_6}$ was then designed for this reaction.

The new P,N,N-ligand $\mathbf{L_6}$ was prepared from readily available and cheap benzylamine **4** *via* a concise procedure as outlined in Scheme 3. In the first step, benzylamine **4** was treated with *n*-BuLi and TMSCl to give a sily-protected benzylamine intermediate, which was further lithiated and *ortho*-phosphinated with $Ph_2PCl$ to give 2-(diphenylphosphino) benzylamine **5** in 56% overall yield. Condensation of **5** with 2-pyridinecarboxaldehyde in the presence of $MgSO_4$ gave the desired P,N,N-ligand $\mathbf{L_6}$ in 89% yield.




Scheme 3 Procedure for the synthesis of P,N,N-ligand $\mathbf{L_6}$.

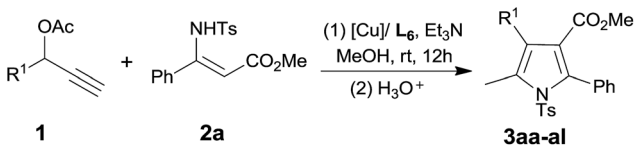
Table 1 Optimization of the reaction conditions[a]




| Entry | [Cu] | Base | Solvent | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $Cu(CH_3CN)_4BF_4$ | $Et_3N$ | MeOH | 84 |
| 2 | $Cu(OAc)_2 \cdot H_2O$ | $Et_3N$ | MeOH | 70 |
| 3 | $Cu(OTf)_2$ | $Et_3N$ | MeOH | 87 |
| 4 | CuI | $Et_3N$ | MeOH | 47 |
| 5 | $Cu(OTf)_2$ | None | MeOH | NR |
| 6 | $Cu(OTf)_2$ | i-$Pr_2NEt$ | MeOH | 78 |
| 7 | $Cu(OTf)_2$ | DBU | MeOH | 69 |
| 8 | $Cu(OTf)_2$ | $Et_3N$ | $CH_2Cl_2$ | 24 |
| 9 | $Cu(OTf)_2$ | $Et_3N$ | Toluene | —[c] |
| 10 | $Cu(OTf)_2$ | $Et_3N$ | $Et_2O$ | —[c] |

[a] The reaction was carried out with **1a** (0.36 mmol), **2a** (0.3 mmol), [Cu] (0.015 mmol, 5 mol%), $\mathbf{L_6}$ (0.0165 mmol, 5.5 mol%) and base (0.36 mmol) in 3 mL of solvent at room temperature for 12 h. [b] Yield of isolated product. [c] Trace reaction detected by TLC.

Table 2 Substrate scope of propargylic esters **1**[a]

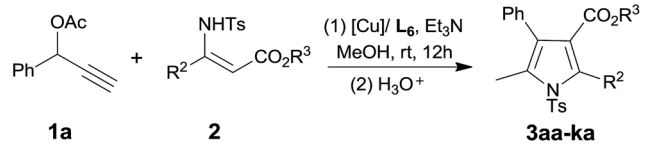



| Entry | **1** ($R^1$) | Product | Yield[b] (%) |
|---|---|---|---|
| 1 | **1a** ($C_6H_5$) | **3aa** | 87 |
| 2 | **1b** (2-$ClC_6H_4$) | **3ab** | 72 |
| 3 | **1c** (3-$ClC_6H_4$) | **3ac** | 82 |
| 4 | **1d** (4-$ClC_6H_4$) | **3ad** | 88 |
| 5 | **1e** (4-$FC_6H_4$) | **3ae** | 90 |
| 6 | **1f** (4-$BrC_6H_4$) | **3af** | 86 |
| 7 | **1g** (4-$OMeC_6H_4$) | **3ag** | 85 |
| 8 | **1h** (4-$MeC_6H_4$) | **3ah** | 83 |
| 9 | **1i** (2-naphthyl) | **3ai** | 82 |
| 10 | **1j** (2-thienyl) | **3aj** | 80 |
| 11 | **1k** ($C_6H_5CH{=}CH$) | **3ak** | 88 |
| 12[c] | **1l′** (Me) | **3al** | 70 |

[a] The reaction was carried out with **1** (0.36 mmol), **2a** (0.3 mmol), $Cu(OTf)_2$ (0.015 mmol, 5 mol%), $\mathbf{L_6}$ (0.0165 mmol, 5.5 mol%), and $Et_3N$ (0.36 mmol) in 3 mL of MeOH at room temperature for 12 h. [b] Yield of isolated product. [c] The pentafluorobenzoate was used instead of the corresponding acetate and the reaction was conducted at reflux temperature for 24 hours.

Table 3 Substrate scope of β-enamino esters 2[a]



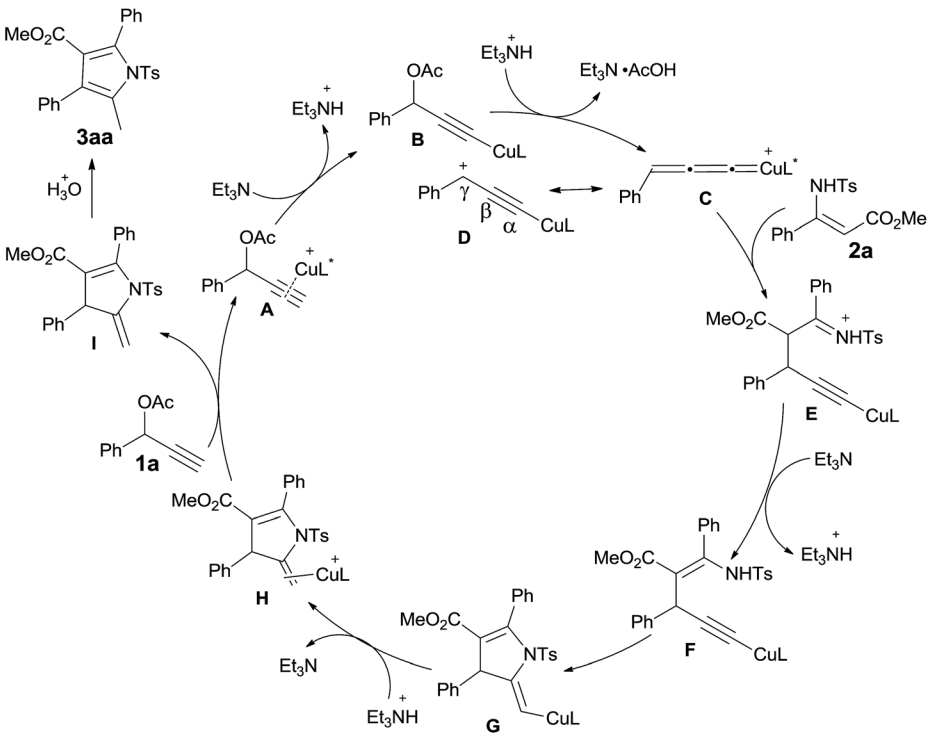

1a 2 3aa-ka

| Entry | 2 ($R^2$, $R^3$) | Product | Yield[b] (%) |
|---|---|---|---|
| 1 | **2a** ($R^2 = C_6H_5$, $R^3$ = Me) | **3aa** | 87 |
| 2 | **2b** ($R^2$ = 4-Me$C_6H_4$, $R^3$ = Me) | **3ba** | 80 |
| 3 | **2c** ($R^2$ = 4-F$C_6H_4$, $R^3$ = Me) | **3ca** | 85 |
| 4 | **2d** ($R^2$ = 4-Br$C_6H_4$, $R^3$ = Me) | **3da** | 83 |
| 5 | **2e** ($R^2$ = 4-Cl$C_6H_4$, $R^3$ = Me) | **3ea** | 86 |
| 6 | **2f** ($R^2$ = 3-Cl$C_6H_4$, $R^3$ = Me) | **3fa** | 88 |
| 7 | **2g** ($R^2$ = 2-Cl$C_6H_4$, $R^3$ = Me) | **3ga** | 74 |
| 8 | **2h** ($R^2$ = 6-OMe-2-naphthyl, $R^3$ = Me) | **3ha** | 80 |
| 9 | **2i** ($R^2$ = Me, $R^3$ = Me) | **3ia** | 82 |
| 10 | **2j** ($R^2 = C_6H_5$, $R^3$ = Et) | **3ja** | 88 |
| 11 | **2k** ($R^2$ = Me, $R^3$ = Et) | **3ka** | 85 |
| 12[c] | **2l** ($R^2 = C_6H_5$, $R^3$ = Me) | | NR |

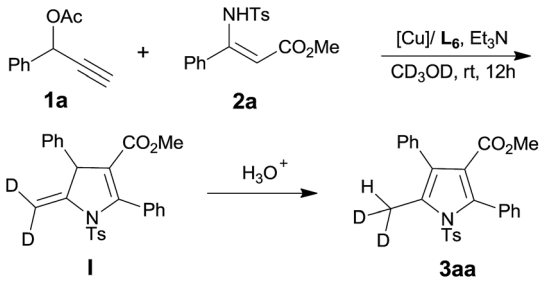
[a] The reaction was carried out with **1a** (0.36 mmol), **2** (0.3 mmol), $Cu(OTf)_2$ (0.015 mmol, 5 mol%), $\mathbf{L_6}$ (0.0165 mmol, 5.5 mol%) and $Et_3N$ (0.36 mmol) in 3 mL of MeOH at room temperature for 12 h. [b] Yield of isolated product. [c] Substrate **2l** ((*Z*)-methyl-3-amino-3-phenylacrylate) without tosyl group was used.

With this newly developed ligand $\mathbf{L_6}$ in hand, we then investigated its efficiency in the Cu-catalyzed [3 + 2] cycloaddition (Table 1). As expected, good result of 84% yield was obtained with ligand $\mathbf{L_6}$ (entry 1). Next investigation of Cu salts modified with $\mathbf{L_6}$ showed that except for CuI, all of the Cu salts, including $Cu(OTf)_2$ and $Cu(OAc)_2$, displayed good performance (entries 2–4). Among them, $Cu(OTf)_2$ proved to be the best choice, which gave the corresponding product in 87% yield (entry 3). The addition of a base proved to be crucial to this reaction since none of the desired product was observed in its absence (entry 5). $Et_3N$ provided better result than i-$Pr_2NEt$ and DBU (entries 3, 6 and 7). Solvent also highly affected the reaction. Of the solvents that we tested, MeOH was the only suitable one, and few reactions occurred in $CH_2Cl_2$, toluene and $Et_2O$ (entries 3, 8–10). Thus, the optimal reaction condition was identified as follow: $Cu(OTf)_2$ (5 mol%), ligand $\mathbf{L_6}$ (5.5 mol%), $Et_3N$ (1.2 eq.) in MeOH at room temperature for 12 h.

Having established the optimized conditions, we first examined the scope and limitation of the reaction with respect to propargylic esters **1**. As shown in Table 2, a wide range of propargylic esters reacted with β-enamino esters **2a** to give the corresponding fully substituted pyrroles in high yields. It appeared that the position of the substituent on the phenyl ring had important effect on the reaction. Thus, substrates with an *ortho*-chloro group on the phenyl ring gave lower yield in comparison with its *meta*- or *para*-chloro substituted analogues (entries 2–4). Both electron-withdrawing (F, Cl, Br) and -donating substituents (OMe, Me) at the *para*-position of the phenyl ring were tolerated in this transformation (entries 4–8). In addition, 2-naphthyl substrate **1i** proved to be suitable for this reaction (entry 9). Meanwhile a heteroaromatic propargylic ester **1j** was also efficient, giving the cycloaddition product in 80% yield (entry 10). Furthermore, the vinyl substrate **1k** also worked smoothly to give the desired product in 88% yield (entry




Scheme 4 Proposed mechanism.




Scheme 5 Isotopic labeling experiments using $CD_3OD$ as solvent.

11). For the aliphatic substrate, the pentafluorobenzoate **1l′** (but-3-yn-2-yl pentafluorobenzoate) should be used instead of the corresponding acetate in order to achieve acceptable yield (entry 12).

The scope of β-enamino esters **2** was subsequently examined after the investigating of propargylic esters, and the results are summarized in Table 3. Good performance was observed for aryl β-enamino esters with both electron-donating and -withdrawing groups at the *para* or *meta* position (entries 2–6). The substrate **2g** with 2-Cl substituent resulted in the decreased yield presumably due to the steric hindrance (entry 7). 6-OMe-2-naphthyl substrate **2h** also worked well, giving the cycloaddition product in 80% yield (entry 8). Pleasingly, the aliphatic substituted β-enamino ester **2i** was also suitable for this reaction (entry 9). Meanwhile, the ethyl ester substrates turned out to be tolerated in this transformation (entries 10 and 11). However, no desired product was obtained when the substrate **2l** ((*Z*)-methyl-3-amino-3-phenylacrylate) without tosyl group was employed in the reaction (entry 12), probably due to the weaker acidity of hydrogen at the nitrogen atom.

We proposed the plausible mechanism for the formation of **3aa** as shown in Scheme 4. In the first step, the Cu complex formed a π-complex **A** with propargylic acetate **1a**.[19] Deprotonation with $Et_3N$ gave Cu-acetylide complex **B**. Loss of an acetyl group from **B** formed Cu-allenylidene complex **C**, where the Cu-acetylide complex **D** bearing a cationic γ-carbon exists as a resonance structure.[20] Nucleophilic attack of **2a** at the $C_\gamma$ atom of **C** gave the corresponding Cu-acetylide complex **E**. Then, intramolecular nucleophilic attack of N at the $C_\beta$ atom of **F** would at last afford the 2,3-dihydropyrrole **I** bearing an exocyclic double bond at the 2-position. The structure of compound **I** was confirmed by X-ray analysis.[21] Isomerization of 2,3-dihydropyrrole **I** gave the corresponding pyrrole **3aa**. Isotopic labeling experiments using $CD_3OD$ as solvent (Scheme 5) also confirmed the above conclusion.

## Conclusions

In conclusion, a new nonchiral P,N,N-ligand has been synthesized from benzylamine *via* a concise procedure and successfully applied to the Cu-catalyzed [3 + 2] cycloaddition of propargylic esters with β-enamino esters. Under the optimized condition, a wide range of substitution patterns at the propargylic esters and β-enamino esters were well tolerated to the reaction, providing the corresponding fully substituted pyrroles in good to high yields. The present work provides an efficient and alternative access to the highly functionalized pyrroles.

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## Notes and references

1 H. Fan, J. Peng, M. T. Hamann and J.-F. Hu, *Chem. Rev.*, 2008, **108**, 264.
2 B. A. Trofimov, L. N. Sobenina, A. P. Demenev and A. I. Mikhaleva, *Chem. Rev.*, 2004, **104**, 2481.
3 A. Aiello, M. D'Esposito, E. Fattorusso, M. Menna, W. E. G. Müller, S. Perović-Ottstadt and H. C. Schröder, *Bioorg. Med. Chem.*, 2006, **14**, 17.
4 A. Fürstner, *Angew. Chem., Int. Ed.*, 2003, **42**, 3582.
5 P. S. Sharma, A. Pietrzyk-Le, F. D'Souza and W. Kutner, *Anal. Bioanal. Chem.*, 2012, **402**, 3177.
6 (*a*) S. J. Higgins, *Chem. Soc. Rev.*, 1997, **26**, 247; (*b*) P. Novák, K. Müller, K. S. V. Santhanam and O. Hass, *Chem. Rev.*, 1997, **97**, 207.
7 For reviews, see: (*a*) I. Nakamura and Y. Yamamoto, *Chem. Rev.*, 2004, **104**, 2127; (*b*) C. Schmuck and D. Rupprecht, *Synthesis*, 2007, 3095; (*c*) N. Ono, *Heterocycles*, 2008, **75**, 243; (*d*) V. Estévez, M. Villacampa and J. C. Menéndez, *Chem. Soc. Rev.*, 2010, **39**, 4402; (*e*) W. Jia-Jie, Y. Zhu and Z.-P. Zhan, *Asian J. Org. Chem.*, 2012, **1**, 108; (*f*) A. V. Gulevich, A. S. Dudnik, N. Chernyak and V. Gevorgyan, *Chem. Rev.*, 2013, **113**, 3084; (*g*) P. K. Maji, R. U. Islam and S. K. Bera, *Heterocycles*, 2014, **89**, 869.
8 L. Knorr, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 1635.
9 C. Paal, *Ber. Dtsch. Chem. Ges.*, 1885, **18**, 367.
10 A. Hantzsch, *Ber. Dtsch. Chem. Ges.*, 1890, **23**, 1474.
11 For selected examples for the synthesis of highly functionalized pyrroles, see: (*a*) O. A. Attanasi, G. Favi, F. Mantellini, G. Moscatelli and S. Santeusanio, *J. Org. Chem.*, 2011, **76**, 2860; (*b*) A. Palmieri, S. Gabrielli, C. Cimarelli and R. Ballini, *Green Chem.*, 2011, **13**, 3333; (*c*) Z.-H. Guan, L. Li, Z.-H. Ren and M.-N. Zhao, *Green Chem.*, 2011, **13**, 1664; (*d*) D. Dhara, K. S. Gayen, S. Khamarui, P. Pandit, S. Ghosh and D. K. Maiti, *J. Org. Chem.*, 2012, **77**, 10441; (*e*) R. Suresh, S. Muthusubramanian, M. Nagaraja and G. Manickam, *Tetrahedron Lett.*, 2013, **54**, 1779; (*f*) Y. Lian, T. Huber, K. D. Hesp, R. G. Bergman and J. A. Ellman, *Angew. Chem., Int. Ed.*, 2013, **52**, 629; (*g*) D. R. Magar, Y.-J. Ke and K. Chen, *Asian J. Org. Chem.*, 2013, **2**, 330; (*h*) N. Bhunia and B. Das, *Synthesis*, 2013, **45**, 1045; (*i*) S. Karamthulla, S. Pal, M. N. Khan and L. H. Choudhury, *Synlett*, 2014, **25**, 1926; (*j*) Y. Li, J. Shi, Z. Wu, X. Wang, X. Wu, J. Gu, H. Bu and H. Ma, *Tetrahedron*, 2014, **70**, 2472; (*k*) H. Mehrabi, M. Anary-Abbasinejad and F. Mirhashemi, *Tetrahedron Lett.*, 2014,

 

**55**, 4310; (*l*) K. Lida, T. Miura, J. Ando and S. Saito, *Org. Lett.*, 2013, **15**, 1436; (*m*) D. Srimani, Y. Ben-David and D. Milstein, *Angew. Chem., Int. Ed.*, 2013, **52**, 4012; (*n*) S. Michlik and R. Kempe, *Nat. Chem.*, 2013, **5**, 149; (*o*) D. Forberg, J. Obenauf, M. Friedrich, S.-M. Hühne, W. Mader, G. Motz and R. Kempe, *Catal. Sci. Technol.*, 2014, **4**, 4188.

12 For reviews in catalytic propargylic transformation, see: (*a*) N. Ljungdahl and N. Kann, *Angew. Chem., Int. Ed.*, 2009, **48**, 642; (*b*) R. J. Detz, H. Hiemstra and J. H. van Maarseveen, *Eur. J. Org. Chem.*, 2009, 6263; (*c*) Y. Miyake, S. Uemura and Y. Nishibayashi, *ChemCatChem*, 2009, **1**, 342; (*d*) C.-H. Ding and X.-L. Hou, *Chem. Rev.*, 2011, **111**, 1914; (*e*) Y. Nishibayashi, *Synthesis*, 2012, **44**, 489; (*f*) E. B. Bauer, *Synthesis*, 2012, **44**, 1131; (*g*) D.-Y. Zhang and X.-P. Hu, *Tetrahedron Lett.*, 2015, **56**, 283; (*h*) X.-H. Hu, Z.-T. Liu, L. Shao and X.-P. Hu, *Synthesis*, 2015, **47**, 913.

13 M. Yoshida and C. Sugimura, *Tetrahedron Lett.*, 2013, **54**, 2082.

14 (*a*) Z.-P. Zhan, S.-P. Wang, X.-B. Cai, H.-J. Liu, J.-L. Yu and Y.-Y. Cui, *Adv. Synth. Catal.*, 2007, **349**, 2097; (*b*) Y.-M. Pan, S.-Y. Zhao, W.-H. Ji and Z.-P. Zhan, *J. Comb. Chem.*, 2009, **11**, 103; (*c*) G. Hattori, Y. Miyake and Y. Nishibayashi, *ChemCatChem*, 2010, **2**, 155; (*d*) M. Lin, Q.-Z. Chen, Y. Zhu, X.-L. Chen, J.-J. Cai, Y.-M. Pan and Z.-P. Zhan, *Synlett*, 2011, 1179; (*e*) W. Shao, H. Li, C. Liu, C.-J. Liu and S.-L. You, *Angew. Chem., Int. Ed.*, 2015, **54**, 7684–7687; (*f*) D.-Y. Zhang, L. Shao, J. Xu and X.-P. Hu, *ACS Catal.*, 2015, **5**, 5026.

15 (*a*) C. Zhang, Y.-H. Wang, X.-H. Hu, Z. Zheng, J. Xu and X.-P. Hu, *Adv. Synth. Catal.*, 2012, **354**, 2854; (*b*) F.-Z. Han, F.-L. Zhu, Y.-H. Wang, Y. Zou, X.-H. Hu, S. Chen and X.-P. Hu, *Org. Lett.*, 2014, **16**, 588; (*c*) D.-Y. Zhang, F.-L. Zhu, Y.-H. Wang, X.-H. Hu, S. Chen, C.-J. Hou and X.-P. Hu, *Chem. Commun.*, 2014, **50**, 14459; (*d*) F. Zhu and X.-P. Hu, *Chin. J. Catal.*, 2015, **36**, 86.

16 (*a*) F.-L. Zhu, Y. Zou, D.-Y. Zhang, Y.-H. Wang, X.-H. Hu, S. Chen, J. Xu and X.-P. Hu, *Angew. Chem., Int. Ed.*, 2014, **53**, 1410; (*b*) Y. Zou, F.-L. Zhu, Z.-C. Duan, Y.-H. Wang, D.-Y. Zhang, Z. Cao, Z. Zheng and X.-P. Hu, *Tetrahedron Lett.*, 2014, **55**, 2033; (*c*) F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, X.-H. Hu, S. Chen, C.-J. Hou, J. Xu and X.-P. Hu, *Adv. Synth. Catal.*, 2014, **356**, 3231.

17 C. Zhang, X.-H. Hu, Y.-H. Wang, Z. Zheng, J. Xu and X.-P. Hu, *J. Am. Chem. Soc.*, 2012, **134**, 9585.

18 F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, J. Xu and X.-P. Hu, *Angew. Chem., Int. Ed.*, 2014, **53**, 10223.

19 F. Himo, T. Lovell, R. Hilgraf, V. V. Rostovtsev, L. Noodleman, K. B. Sharpless and V. V. Fokin, *J. Am. Chem. Soc.*, 2005, **127**, 210.

20 Y. Imada, M. Yuasa, I. Nakamura and S.-I. Murahashi, *J. Org. Chem.*, 1994, **59**, 2282.

21 ESI†