DOI: 10.1002/adsc.201200589

Chiral Tridentate P,N,N Ligands for Highly Enantioselective Copper-Catalyzed Propargylic Amination with both Primary and Secondary Amines as Nucleophiles

Cheng Zhang,[a,b] Ya-Hui Wang,[a] Xin-Hu Hu,[a] Zhuo Zheng,[a] Jie Xu,[a] and Xiang-Ping Hu[a,*]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China
Fax: (+86)-411-8468-4746; e-mail: xiangping@dicp.ac.cn
[b] Graduate University of Chinese Academy of Sciences, Beijing 100039, People's Republic of China

Received: July 6, 2012; Published online: September 28, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200589.

Abstract: Chiral tridentate P,N,N ligands have been demonstrated to be highly efficient for the copper-catalyzed enantioselective propargylic amination of propargylic acetates with both primary and secondary amines as nucleophiles, affording the corresponding propargylic amines in high yields and with excellent enantioselectivities (up to 97% *ee* for secondary amines, and up to 96% *ee* for primary amines). Furthermore, the present catalytic system was also effective for the more challenging aliphatic propargylic acetate substrates.

Keywords: asymmetric catalysis; copper; primary amines; propargylic amination; secondary amines

Propargylic amines are structural units of widespread chemical significance, having been heavily utilized as building blocks for organic synthesis.[1] Among the methods usually employed to generate such scaffolds,[2] catalytic propargylic amination presents an attractive strategy.[3] A seminal report by Murahashi and co-workers sets the stage for an enantioselective Cu-catalyzed propargylic amination.[4] While still in the racemic series at that stage, it was shown that Cu sources promote the amination of propargylic esters smoothly under mild reaction conditions. In 2008, van Maarseveen and Nishibayashi independently reported the asymmetric version of the copper-catalyzed propargylic amination of propargylic acetates. In Nishibayashi's method, a combination of copper(I) triflate with (*R*)-Cl-MeO-biphep **2** was used as the catalyst and only secondary amines worked as suitable nucleophiles,[5] whereas van Maarseveen's method employed a catalyst formed *in situ* from copper(I) iodide and chiral pyridine-2,6-bisoxazoline ligand (pybox) **1** and only primary amines served as efficient nucleophiles.[6] More recent studies on the propargylic amination of aliphatic propargylic esters showed the same result.[7] A comparison of van Maarseveen's and Nishibayashi's protocols disclosed that the major difference between them is the structure of the chiral ligands, a tridentate N ligand (pybox, **1**) and a bidentate P ligand (biphep, **2**) respectively (Figure 1). We therefore

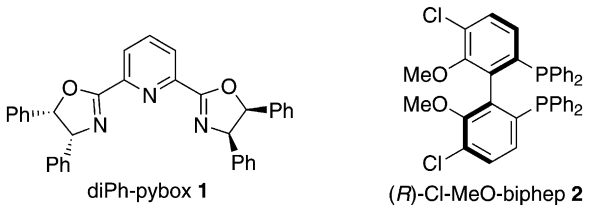


Figure 1. Structures of diPh-pybox **1** and (*R*)-Cl-MeO-biphep **2**.

speculated that the different donor atoms of the ligands used in these two methods may be responsible for their distinct reactivity and enantioselectivity in the Cu-catalyzed propargylic amination with primary and secondary amines as nucleophiles. On the basis of this speculation, we imagine that a chiral ligand bearing the structural feature of both pybox and biphep, such as a tridentate P,N,N ligand, should be efficient for this transformation with both primary and secondary amines as nucleophiles.

Very recently, we have developed a series of chiral P,N,N ligands for highly diastereo- and enantioselective Cu-catalyzed [3+3]cycloaddition of propargylic esters with cyclic enamines, which is believed to proceed *via* the propargylic substitution firstly.[8] We therefore envisioned that these P,N,N ligands should

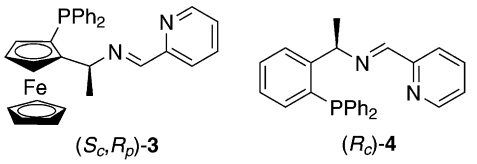


Figure 2. Structures of chiral P,N,N ligands (S_c,R_p)-**3** and (R_c)-**4**.

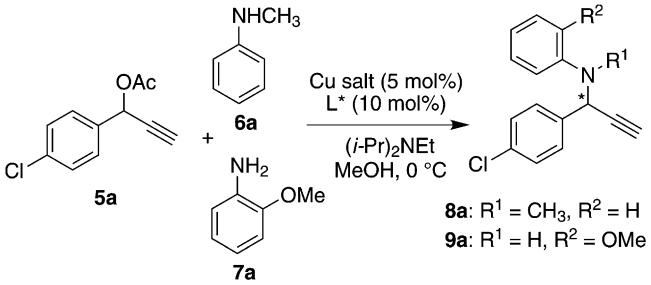
be also efficient to the Cu-catalyzed propargylic amination of propargylic esters. As a result, herein we present our studies on the application of chiral tridentate P,N,N ligands (S_c,R_p)-**3** and (R_c)-**4** (Figure 2) for the copper-catalyzed propargylic amination of various aliphatic and aromatic propargylic acetates with both primary and secondary amines as nucleophiles, in which excellent performance was achieved.

To test our speculation, chiral P,N,N ligands (S_c,R_p)-**3** and (R_c)-**4** were then subjected to the Cu-catalyzed propargylic amination of 1-(4-chlorophenyl)-2-propynyl acetate **5a** with both *N*-methylaniline **6a** and *o*-anisidine **7a**, and some representative results are summarized in Table 1.

The reaction was performed in methanol at 0 °C for 12 h in the presence of N,N-diisopropylethylamine and a catalytic amount of $Cu(OTf)_2$ (5 mol%). To our delight, planar-chiral ferrocenyl ligand (S_c,R_p)-**3** displayed excellent enantioselectivity (95% *ee*) with good yield (87%) for the secondary amine, *N*-methylaniline **6a** (entry 1), and good enantioselectivity (80% *ee*) with moderate yield (71%) for the primary amine, *o*-anisidine **7a** (entry 2). In comparison with (S_c,R_p)-**3**, its phenyl analogue (R_c)-**4** showed lower enantioselectivities with both *N*-methylaniline **6a** and *o*-anisidine **7a** as nucleophiles (entries 3 and 4). Since the result for the amination of **5a** with primary amine **7a** was not so satisfactory with the $Cu(OTf)_2$/(S_c,R_p)-**3** catalytic system, the search for an appropriate Cu source was then performed. After a careful survey of copper salts in the propargylic amination of **5a** with *o*-anisidine **7a** (entries 5-10), CuCl was identified as the best Cu source, affording the corresponding propargylic amine **9a** in 88% yield and with 93% *ee* (entry10). CuCl is also highly effective for the propargylic amination of **5a** with *N*-methylaniline **6a**, giving the substituted product **8a** in 89% yield and with 95% *ee*, comparable to that obtained with $Cu(OTf)_2$ (entry 11 *vs.* entry 1). These results demonstrate that P,N,N ligand (S_c,R_p)-**3** is a promising ligand scaffold for the Cu-catalyzed amination of propargylic esters with both primary and secondary amines as nucleophiles.

With the optimal CuCl/(S_c,R_p)-**3** catalytic system, we first examined the substrate scope of the propargylic amination of propargylic esters **5** with secondary amines **6**. As shown in Table 2, a wide range of 1-aryl-

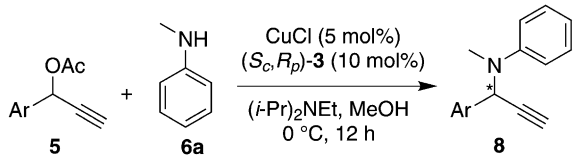
Table 1. Influence of ligand and Cu precursor on the reaction.[a]



Entry	Nu	[Cu]	L*	Yield [%][b]	*ee* [%][c]
1	**6a**	$Cu(OTf)_2$	**3**	87	95
2	**7a**	$Cu(OTf)_2$	**3**	71	80
3	**6a**	$Cu(OTf)_2$	**4**	41	85
4	**7a**	$Cu(OTf)_2$	**4**	83	72
5	**7a**	$Cu(OAc)_2{\cdot}H_2O$	**3**	81	84
6	**7a**	$CuF_2{\cdot}2H_2O$	**3**	58	91
7	**7a**	$Cu(OTf){\cdot}(C_6H_6)_{0.5}$	**3**	87	92
8	**7a**	CuI	**3**	31	79
9	**7a**	$Cu(CH_3CN)_4ClO_4$	**3**	91	89
10	**7a**	CuCl	**3**	88	93
11	**6a**	CuCl	**3**	89	95

[a] *Reaction conditions:* Cu salts (0.015 mmol), ligand (0.03 mmol), **5a** (0.3 mmol), *N*-methylaniline (**6a**) or *o*-anisidine (**7a**) (0.36 mmol), and $(i\text{-Pr})_2$NEt (0.36 mmol) were stirred in 2 mL of methanol at 0 °C for 12 h (for **6a**) or 24 h (for **7a**).
[b] Isolated yield after column chromatography.
[c] Determined by HPLC on a chiral column.

Table 2. Cu-Catalyzed asymmetric propargylic amination with *N*-methylaniline (**6a**): scope of aromatic propargylic acetates (**5**).[a]



Entry	Substrate (**5**: Ar)	Product (**8**)	Yield [%][b]	*ee* [%][c]
1	**5a**: 4-ClC_6H_4	**8a**	89	95
2	**5b**: 3-ClC_6H_4	**8b**	86	97
3	**5c**: 2-ClC_6H_4	**8c**	87	96
4	**5d**: Ph	**8d**	86	95
5	**5e**: 4-FC_6H_4	**8e**	90	97
6	**5f**: 4-BrC_6H_4	**8f**	90	96
7	**5g**: 4-$CF_3C_6H_4$	**8g**	88	96
8	**5h**: 4-MeC_6H_4	**8h**	84	92
9	**5i**: 2-naphthyl	**8i**	86	94
10	**5j**: 2-furyl	**8j**	88	91

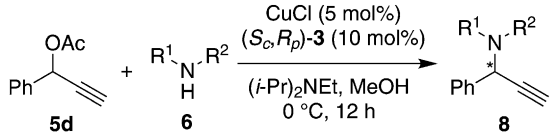
[a] *Reaction conditions:* CuCl (0.015 mmol), (S_c,R_p)-**3** (0.03 mmol), **5** (0.3 mmol), *N*-methylaniline **6a** (0.36 mmol), and $(i\text{-Pr})_2$NEt (0.36 mmol) were stirred in 2 mL of methanol at 0 °C for 12 h.
[b] Isolated yield.
[c] Determined by HPLC on a chiral column.

2-propynyl acetates with varying electronic demands were successfully reacted with *N*-methylaniline **6a**, giving the corresponding proparylamines **8a–j** in good yields (84–90%) and with excellent enantioselectivities (91–97% *ee*) (entries 1–10). The reaction had a high tolerance to the substitution pattern on the phenyl ring of the substrates. Thus, all of chloro-substituted substrates **5a–c** gave similar results (entries 1–3). The electronic property of the substituent in the *para*-position of the phenyl ring had little effect in the reactivity (84–90% yield) and enantioselectivity (91–97% *ee*) (entries 4–8).

We also examined the effect of the substituent on the phenyl ring of aromatic secondary amines with regard to the reactivity and enantioselectivity, and the results are summarized in Table 3. The results indicated that the substitution pattern and electronic property had little effect on the reactivity and enantioselectivity. All of *N*-methyl aromatic amines **6a–h** reacted with 1-phenyl-2-propynyl acetate **5d** in excellent enantioselectivities and yields (entries 1–8). The propargylic amination of 1-phenyl-2-propynyl acetate **5d** with secondary dialkylamine **6i** was also investigated under the same reaction conditions as those with aromatic amines except that a longer reaction time (24 h) was required, affording the corresponding propargylic amine **8r** in high yield (87%) and with excellent enantioselectivity (95% *ee*) (entry 9). However, when cyclic amines **6j** and **6k** were used as nucleophiles, the results were very poor. By replacing CuCl with $CuOTf\cdot(C_6H_6)_{0.5}$, propargylic amines **8s** and **8t** were formed in good yields and with excellent *ee* values (entries 10 and 11).

To further demonstrate the scope and flexibility of the present CuCl/(S_c,R_p)-**3** catalytic system, we investigated the catalytic asymmetric propargylic amination using aromatic primary amines as nucleophiles, and the results are summarized in Table 4. The results disclosed that the substitution pattern of the substituent on the phenyl ring displayed some influence on the enantioselectivity (entries 1–3). Thus, 4-Cl and 3-Cl substituted substrates **5a** and **5b** proceeded smoothly at 0 °C to give the corresponding amines in high enantioselectivities (entries 1 and 2), whereas the reaction of 1-(2-chlorophenyl)-1-propynyl acetate **5c** with *o*-anisidine **7a** should be performed at lower temperature (−20 °C) to obtain a satisfactory enantio-

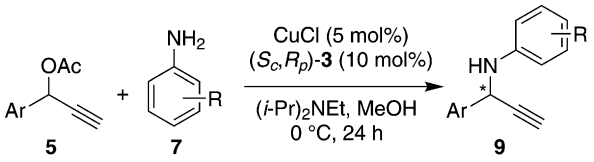
Table 3. Cu-Catalyzed asymmetric propargylic amination of 1-phenyl-2-propynyl acetate (**5d**): scope of secondary amines (**6**).[a]



Entry	Amine (**6**: R^1, R^2)	Product (**8**)	Yield [%][b]	*ee* [%][c]
1	**6a**: Ph, CH_3	**8d**	86	95
2	**6b**: 2-$MeOC_6H_4$, CH_3	**8k**	82	93
3	**6c**: 3-$MeOC_6H_4$, CH_3	**8l**	86	94
4	**6d**: 4-$MeOC_6H_4$, CH_3	**8m**	91	95
5	**6e**: 4-FC_6H_4, CH_3	**8n**	89	95
6	**6f**: 4-ClC_6H_4, CH_3	**8o**	92	93
7	**6g**: 4-BrC_6H_4, CH_3	**8p**	91	94
8	**6h**: 4-MeC_6H_4, CH_3	**8q**	84	92
9[d]	**6i**: Et, Et	**8r**	87	95
10[e]	**6j**: piperidine	**8s**	77	91
11[e]	**6k**: morpholine	**8t**	67	87

[a] *Reaction conditions:* CuCl (0.015 mmol), (S_c,R_p)-**3** (0.03 mmol), **5** (0.3 mmol), secondary amine **6** (0.36 mmol), and (*i*-Pr)$_2$NEt (0.36 mmol) were stirred in 2 mL of methanol at 0 °C for 12 h.
[b] Isolated yield.
[c] Determined by HPLC on a chiral column.
[d] Reaction time: 24 h.
[e] $CuOTf\cdot(C_6H_6)_{0.5}$ was used instead of CuCl.

Table 4. Cu-Catalyzed asymmetric propargylic amination of aromatic propargylic acetates (**5**) with primary amines (**7**).[a]



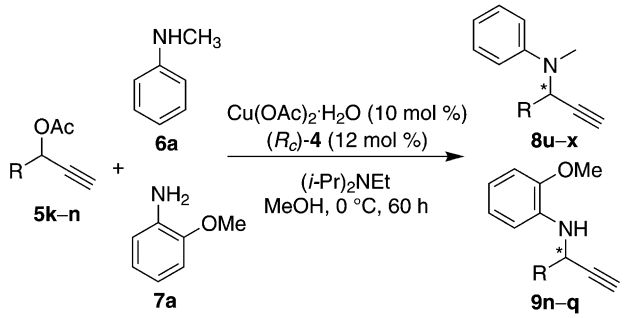
Entry	Substrate (**5**: Ar)	Amine (**7**: R)	**9**	Yield [%][b]	*ee* [%][c]
1	**5a**: 4-ClC_6H_4	**7a**: 2-OMe	**9a**	88	93
2	**5b**: 3-ClC_6H_4	**7a**: 2-OMe	**9b**	86	96
3[d]	**5c**: 2-ClC_6H_4	**7a**: 2-OMe	**9c**	76	93
4	**5d**: Ph	**7a**: 2-OMe	**9d**	89	93
5	**5e**: 4-FC_6H_4	**7a**: 2-OMe	**9e**	88	93
6	**5f**: 4-BrC_6H_4	**7a**: 2-OMe	**9f**	90	94
7	**5g**: 4-$CF_3C_6H_4$	**7a**: 2-OMe	**9g**	85	96
8	**5h**: 4-$CH_3C_6H_4$	**7a**: 2-OMe	**9h**	84	90
9	**5i**: 2-naphthyl	**7a**: 2-OMe	**9i**	86	91
10[d]	**5j**: 2-furyl	**7a**: 2-OMe	**9j**	92	89
11[d]	**5d**: Ph	**7b**: 3-OMe	**9k**	86	92
12[d]	**5d**: Ph	**7c**: 4-OMe	**9l**	80	90
13[d]	**5d**: Ph	**7d**: H	**9m**	85	90

[a] *Reaction conditions:* CuCl (0.015 mmol), (S_c,R_p)-**3** (0.03 mmol), **5** (0.3 mmol), primary amine **7** (0.36 mmol), and (*i*-Pr)$_2$NEt (0.36 mmol) were stirred in 2 mL of methanol at 0 °C for 24 h.
[b] Isolated yield after column chromatography.
[c] Determined by HPLC on a chiral column.
[d] The reaction was performed at −20 °C using **5** (0.3 mmol) and primary amine **7** (0.6 mmol) and (*i*-Pr)$_2$NEt (1.2 mmol) for 48 h.

selectivity (entry 3). As was observed in the reaction with *N*-methylaniline, the electronic property of the substituent on the phenyl ring of the substrates had little effect on the reactivity and enantioselectivity. All of 4-substituted 1-phenyl-2-propynyl acetates **5a** and **5e–h** reacted smoothly with *o*-anisidine **7a** to give the corresponding amines in high yields (84–90%) and with high enantioselectivities (90–96% *ee*) (entries 1 and 5–8). Similar results to those with *o*-anisidine **7a** were obtained when *m*-anisidine **7b**, *p*-anisidine **7c** and aniline **7d** were used as nucleophiles (entries 11–13).

The success of the CuCl/(S_c,R_p)-**3** catalytic system in the propargylic amination of aromatic propargylic acetates prompted us to investigate its application in more challenging substrates, aliphatic propargylic actetates (Table 5). Under a catalyst loadings of 10 mol% and performing the reaction at room temperature for 60 h, the reaction of the simplest aliphatic propargyl acetate, but-3-yn-2-yl acetate **5k** with secondary amine **6a** proceeded smoothly, providing the corresponding propargylic amine **8u** in high yield (84% yield) and with excellent enantioselectivity

Table 5. Cu-Catalyzed asymmetric propargylic amination of aliphatic propargylic acetates.[a]



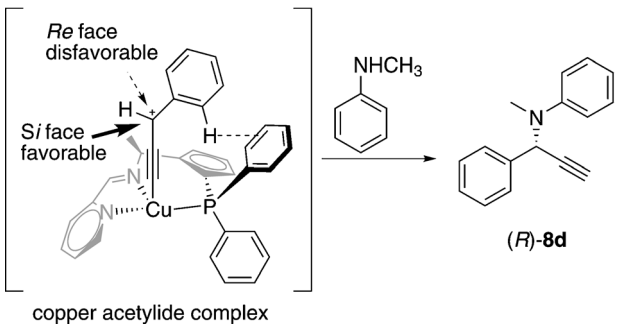
Entry	Substrate (**5**: R)	Nu	Product	Yield [%][b]	*ee* [%][c]
1[d]	**5k**: Me	**6a**	**8u**	84	95
2[d]	**5k**: Me	**7a**	**9n**	–	–
3[e]	**5k**: Me	**7a**	**9n**	84	87
4[e]	**5l**: *n*-Pr	**7a**	**9o**	82	79
5	**5l**: *n*-Pr	**6a**	**8v**	76	91
6	**5m**: Cy	**7a**	**9p**	52	81
7	**5m**: Cy	**6a**	**8w**	69	93
8	**5n**: benzyl	**7a**	**9q**	45	78
9[f]	**5n**: benzyl	**6a**	**8x**	76	86

[a] *Reaction conditions:* $Cu(OAc)_2·H_2O$ (0.03 mmol), (R_c)-**4** (0.036 mmol), **5k–n** (0.3 mmol), amine (0.6 mmol), and $(i\text{-Pr})_2NEt$ (1.2 mmol) were stirred in 2 mL of methanol at 0 °C for 60 h, unless otherwise specified.
[b] Isolated yield after column chromatography.
[c] Determined by HPLC on a chiral column.
[d] The reaction was performed at room temperature using CuCl/(R_c,S_p)-**3** as the catalyst.
[e] A combination of $Cu(OAc)_2·H_2O$ and (R_c,S_p)-**3** was used.
[f] The reaction was carried out at room temperature.

(95% *ee*) (entry 1). However, the reaction of **5k** with primary amine **7a** gave very low conversion under the same condition (entry 2). Replacing CuCl with $Cu(OAc)_2·H_2O$ significantly promoted the reaction rate, leading to 84% yield and 87% *ee* (entry 3). With this $Cu(OAc)_2·H_2O$/(S_c,R_p)-**3** catalytic system, *n*-Pr-substituted substrate **5l** reacted with primary amine **7a** in 82% yield and 79% *ee* (entry 4). For the reaction of *n*-Pr-substituted substrate **5l** with secondary amine **6a**, however, a combination of $Cu(OAc)_2·H_2O$ and (R_c)-**4** proved to be the suitable catalyst, giving the propargylamine **8v** in 91% *ee* (entry 5). The $Cu(OAc)_2·H_2O$/(R_c)-**4** catalytic system showed good enantioselectivities for the reaction of cyclohexyl- and benzyl-substituted substrates **5m** and **5n** with both primary and secondary amines as nucleophiles (entries 6–9). The results suggested that the reactions of aliphatic propargylic acetates with secondary amine **6a** usually afforded higher yield and better enantioselectivity than those with primary amine **7a**.

Based on the crystal structure of the CuCl/(R_c,S_p)-**3** complex[8] and the observed absolute stereochemistry of the major enantiomer, we proposed a preliminary model for the enantioinduction (Scheme 1). An edge-to-face aromatic interaction makes a phenyl group of the substrate close to a phenyl group of the ligand in the copper acetylide complex.[7b,c] As a result, the attack of the γ-carbon atom by a nucleophile amine happened favorably from the *Si* face to form (*R*)-product while the *Re* face was hampered due to the steric hindrance of the ligand.

In conclusion, we have demonstrated that chiral tridentate P,N,N ligands, (S_c,R_p)-**3** and (R_c)-**4**, were highly efficient for the Cu-catalyzed asymmetric propargylic amination of propargylic acetates with various amines. The unique feature of the present CuCl/(S_c,R_p)-**3** catalytic system lies in its significant activity and selectivity in the use of both primary and secondary amines as nucleophiles for the catalytic propargylic amination. With secondary amines as nucleophiles, a series of 1-aryl-2-propynyl acetates was converted into the corresponding amines with excellent enantioselectivities (91–97% *ee*). Primary aromatic



Scheme 1. Proposed model for enantioinduction. A CpFe group in the ligand has been omitted for clarity.

amines were also suitable nucleophiles, leading to the corresponding propargylic amines in high yields and excellent enantioselectivities (up to 96% *ee*). Aliphatic propargylic acetates turned out to serve well as the substrate for this process, providing good to excellent enantioselectivities (up to 95% *ee*). To the best of our knowledge, the present Cu/P,N,N ligand catalytic system represents the first example with which both primary and secondary amines can be used as efficient nucleophiles for the highly enantioselective catalytic propargylic amination of both aliphatic and aromatic propargylic acetates.

Experimental Section

General Experimental Procedure

CuCl (1.5 mg, 0.015 mmol) and (S_c,R_p)-**3** (15.1 mg, 0.03 mmol) were stirred in 1 mL of anhydrous methanol under a nitrogen atmosphere for 1 h. The mixture was cooled to 0 °C, and then a solution of propargylic acetate **5** (0.3 mmol), amine **6** or **7** (0.36 mmol) and *N*,*N*-diisopropylethylamine (0.36 mmol) in 1 mL of anhydrous MeOH was added. The reaction mixture was kept at 0 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by the silica gel column chromatography with petroleum and ethyl acetate as eluent. The enantiomeric excess was determined by HPLC on a chiral column.

Acknowledgements

Support for this research from Dalian Institute of Chemical Physics (CAS) is gratefully acknowledged.

References

[1] P. Aschwanden, E. M. Carreira, in: *Acetylene Chemistry: Chemistry, Biology and Material Science* (Eds: F. Diederich, P. J. Stang, R. R. Tykwinski), Wiley-VCH, Weinheim, **2005**, pp 101–138.

[2] For reviews, see: a) P. G. Cozzi, R. Hilgraf, N. Zimmermann, *Eur. J. Org. Chem.* **2004**, 4095–4105; b) C.-M. Wei, Z.-G. Li, C.-J. Li, *Synlett* **2004**, 1472–1483; c) L. Zani, C. Bolm, *Chem. Commun.* **2006**, 4263–4275; d) G. Blay, A. Monleon, J. R. Pedro, *Curr. Org. Chem.* **2009**, *13*, 1498–1539; e) B. M. Trost, A. H. Weiss, *Adv. Synth. Catal.* **2009**, *351*, 963–983; f) C.-J. Li, *Acc. Chem. Res.* **2010**, *43*, 581–590. For recent examples, see: g) G. Huang, J. Yang, X. Zhang, *Chem. Commun.* **2011**, *47*, 5587–5589; h) T. Zeng, L. Yang, R. Hudson, G. Song, A. R. Moores, C.-J. Li, *Org. Lett.* **2011**, *13*, 442–445; i) E. G. Klauber, C. K. De, T. K. Shah, D. Seidel, *J. Am. Chem. Soc.* **2010**, *132*, 13624–13626; j) F. Peng, Z. Shao, A. S. C. Chan, *Tetrahedron: Asymmetry* **2010**, *21*, 465–468; k) S. Nakamura, M. Ohara, Y. Nakamura, N. Shibata, T. Toru, *Chem. Eur. J.* **2010**, *16*, 2360–2362; l) P. de Armas, D. Tejedor, F. Garcia-Tellado, *Angew. Chem.* **2010**, *122*, 1029–1032; *Angew. Chem. Int. Ed.* **2010**, *49*, 1013–1016; m) B.-L. Chen, B. Wang, G.-Q. Lin, *J. Org. Chem.* **2010**, *75*, 941–944; n) T. Sugiishi, A. Kimura, H. Nakamura, *J. Am. Chem. Soc.* **2010**, *132*, 5332–5333; o) S. Zhu, W. Yan, B. Mao, X. Jiang, R. Wang, *J. Org. Chem.* **2009**, *74*, 6980–6985.

[3] For reviews, see: a) N. Ljungdahl, N. Kann, *Angew. Chem.* **2009**, *121*, 652–654; *Angew. Chem. Int. Ed.* **2009**, *48*, 642–644; b) R. J. Detz, H. Hiemstra, J. H. Maarseveen, *Eur. J. Org. Chem.* **2009**, 6263–6276; c) Y. Miyake, S. Uemura, Y. Nishibayashi, *ChemCatChem* **2009**, *1*, 342–356.

[4] Y. Imada, M. Yuasa, I. Nakamura, S.-I. Murahashi, *J. Org. Chem.* **1994**, *59*, 2282–2284.

[5] G. Hattori, H. Matsuzawa, Y. Miyake, Y. Nishibayashi, *Angew. Chem.* **2008**, *120*, 3841–3843; *Angew. Chem. Int. Ed.* **2008**, *47*, 3781–3783.

[6] R. J. Detz, M. M. E. Delville, H. Hiemstra, J. H. Maarseveen, *Angew. Chem.* **2008**, *120*, 3837–3840; *Angew. Chem. Int. Ed.* **2008**, *47*, 3777–3780.

[7] a) G. Hattori, A. Yoshida, Y. Miyake, Y. Nishibayashi, *J. Org. Chem.* **2009**, *74*, 7603–7607; b) G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake, Y. Nishibayashi, *J. Am. Chem. Soc.* **2010**, *132*, 10592–10608; c) G. Hattori, Y. Miyake, Y. Nishibayashi, *ChemCatChem* **2010**, *2*, 155–158; d) A. Yoshida, G. Hattori, Y. Miyake, Y. Nishibayashi, *Org. Lett.* **2011**, *13*, 2460–2463; e) R. J. Detz, Z. Abiri, R. Griel, H. Hiemstra, J. H. Maarseveen, *Chem. Eur. J.* **2011**, *17*, 5921–5930.

[8] C. Zhang, X.-H. Hu, Y.-H. Wang, Z. Zheng, J. Xu, X.-P. Hu, *J. Am. Chem. Soc.* **2012**, *134*, 9585–9588.

