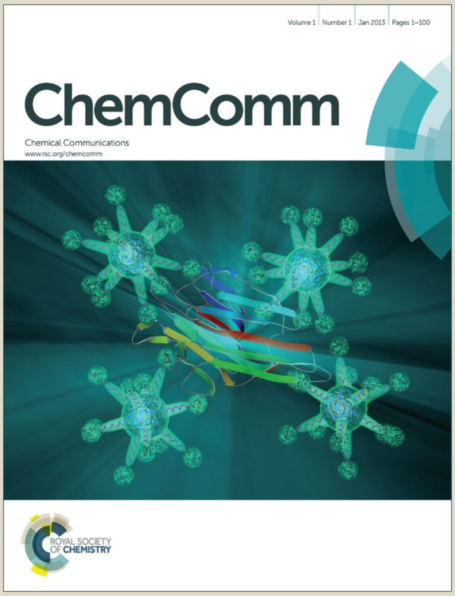
ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Shen, J. Yang, H. Zhao, Y. Feng, L. Zhang and L. Han, *Chem. Commun.*, 2016, DOI: 10.1039/C6CC05428E.



DOI: 10.1039/C6CC05428E

Journal Name

COMMUNICATION

Cu-Catalyzed Hydrophosphorylative Ring Opening of Propargyl Epoxides: Highly Selective Access to 4-Phosphoryl 2,3-Allenols

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

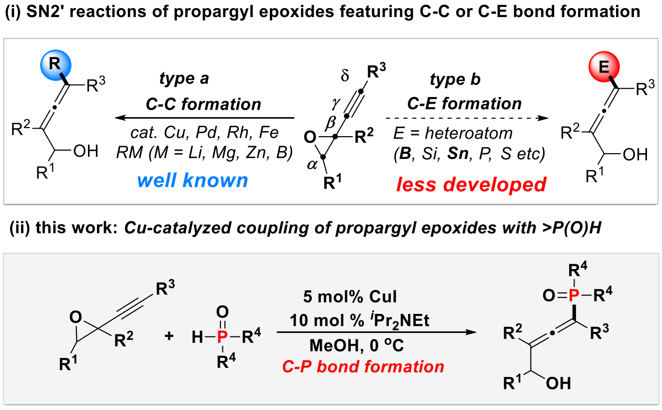
www.rsc.org/

Ruwei Shen,*[a] Jianlin Yang,[a] Haipeng Zhao,[a] Yu Feng,[a] Lixiong Zhang,[a] Li-Biao Han*[b]

A novel CuI-catalyzed cross-couplings of propargyl epoxides with P(O)H compounds is disclosed. The reaction proceeded efficiently under mild conditions to give 4-phosphoryl 2,3-allenols in good to high yields with excellent selectivity. The utility of the products was demonstrated and a plausible mechanism is also proposed.

2,3-Allenols are highly desired building blocks in advanced organic synthesis[1] as they offer expeditious routes to a wide range of useful compounds such as conjugated dienes,[2] 1, 3-enynes,[3] vinyl epoxides,[4] dihydrofurans,[5] furanones[6] and other heterocycles.[7] Among the various synthetic methods, the transition metal catalyzed ring openings (SN2′-type) of propargyl epoxides with organometallic reagents such as Grignard, organolithium, organozinc and organoboron reagents represent one useful and reliable protocol (Scheme 1i, type a).[8-13] Metals including Cu,[9] Pd,[10] Rh[11] and Fe[12] have been found capable of promoting the transformation with efficient C-C bond formation and selectively opening the epoxide ring to give *anti*- or *syn*-configured 2,3-allenols with high selectivity. Furthermore, optically active allenols are also accessible by using chiral propargyl epoxides as substrates[10b, 11, 12] or applying a chiral catalyst[9e] with this strategy.

While this methodology has met with considerable success to offer access to a variety of 2,3-allenols via the formation of C-C bonds based on the use of carbon-nucleophiles (Scheme 1i, Type a), very few examples are known on similar catalytic reactions with heteroatomic counterparts although such a type of transformations is very promising as synthetic methods to afford various 4-functionalized 2,3-allenols via the formation of C-heteroatom bonds (Scheme 1i, type b).[14, 15] A relevant example, to our knowledge, was first described by Szabó in a detailed study on the palladium-catalyzed substitutions of propargyl substrates with dimetallic reagents in 2005, in which several 4-stannyl 2,3-allenols were obtained.[14a] Recently the same group also investigated the Cu/Pd-catalyzed borylation of propargyl epoxides and related compounds with B_2pin_2,[14b, 14c] and a selective production of 4-borylated 2,3-allenol is achieved using $CuI-P(1\text{-}nap)_3$ as the catalyst.[14b] We are currently engaged in a joint project geared towards efficient synthesis of useful organophosphorus compounds via new catalytic transformations of the easily available P(O)H compounds.[16] Recently we have developed an efficient Cu-catalyzed coupling of propargyl acetates with P(O)H compounds proceeding via a unique nucleophilic interception of Cu-allenylidene intermediates by phosphorus nucleophiles to afford allenylphosphoryl compounds in high yields under mild conditions.[16a] In this paper we wish to communicate a new highly selective and atom-economic ring-opening of propargyl epoxides by P(O)H compounds catalyzed by a simple copper salt.[17] This reaction ultimately leads to a novel class of useful 4-phosphoryl 2,3-allenol derivatives in high yields (Scheme 1ii).



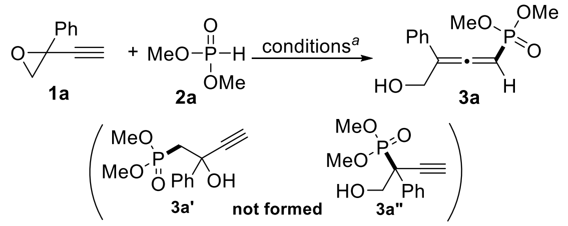
Scheme 1 TM-catalyzed SN2′-type reaction of propargyl epoxides to produce allenols.

We began our study by examining the reaction of 2-ethynyl-2-phenyloxirane (**1a**) and dimethyl phosphonate (**2a**) with the treatment of a catalytic amount of Cu(1) species (Table 1). While the possible competition reactions, e.g., the potential direct attacks of the nucleophile to the epoxide ring, were firstly concerned, we were pleased to observe that the reaction gave

---

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing Tech University, Nanjing 210009, China. E-mail: shenrw@njtech.edu.cn
[b] National Institute of Advanced Industrial Science & Technology (AIST), Tsukuba, Ibaraki, 305-8565, Japan. E-mail: libiao-han@aist.go.jp
Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data of the products. See DOI: 10.1039/x0xx00000x

Table 1 Optimization data on reaction conditions [a]



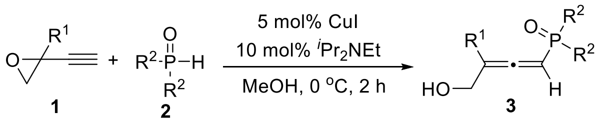
entry	[Cu]	ligand	solvent	yield (%)[b]
1	CuI	TMEDA	MeOH	79[c]
2	CuI	2,2'-bpy	MeOH	74[c]
3	CuI	1,10-Phen	MeOH	90
4	CuI	dppe	MeOH	92
5	**CuI**	**-[d]**	**MeOH**	**92**
6	CuCl	-[d]	MeOH	89
7	CuBr	-[d]	MeOH	83
8	Cu(OAc)$_2$	-[d]	MeOH	83
9	-[e]	-[d]	MeOH	0
10	CuI	-[d]	MeOH	0[f]
11	CuI	-[d]	THF	40
12	CuI	-[d]	MeCN	48
13	CuI	-[d]	DCM	24
14	CuI	-[d]	DMF	0
15	CuI	-[d]	Toluene	trace

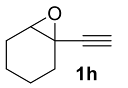
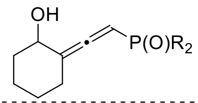
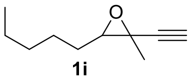
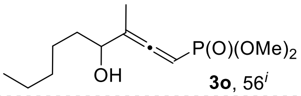
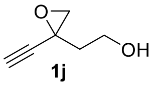
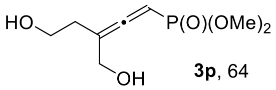
[a] Conditions: 1 (0.36 mmol), 2 (0.3 mmol), copper salt (5 mol%), Ligand (6 mol%) if added, ^{i}Pr$_2$NEt(10 mol%) in a solvent (2 mL), 0 ^{o}C, 2 h. [b] Isolated yields. [c] Unidentified byproducts were obtained (weight < 10 mg). [d] No ligand. [e] No catalyst. [f] ^{i}Pr$_2$NEt was not added.

3a in 79% yield with an excellent regioselectivity in the presence of 5 mol% of CuI and 6 mol% of TMEDA with 10 mol% of ^{i}Pr$_2$NEt at a first attempt (entry 1). A small amount of unidentified byproducts were also obtained, yet we reasoned that these identities should result from the transformations of **1a** only, but not the epoxide-opening of **1a** by possible attack of the nucleophile **2a**, as the ^{31}P NMR spectroscopy of the crude mixture clearly show only one peak at ca. 17.5 ppm assigned to be **3a**. The formation of the possible byproducts **3a'** or **3a''** was totally not observed. Subsequent screening of the ligands shows that the use of 1,10-Phen or dppe gave improved yields (90-92%, entries 3 and 4). Surprisingly, a blank experiment reveals that CuI alone also catalyzed the reaction, and cleanly gave the product in high yield without loss of the reaction efficiency (entry 5). Similar unidentified byproducts were undetected by TLC. The reaction could also be catalyzed by other copper salts. Thus, CuCl gave **3a** in 89% yield, while CuBr and Cu(OAc)$_2$ both gave **3a** in 83% yield (entries 6-8). However, no reaction took place in the absence of a copper salt or the amine base (entries 9 and 10). Finally it is worth noting that the reaction is critically dependent on the solvent and MeOH is the best. THF, DCM and MeCN all gave **3a** in low yields (entries 11-13). **3a** was not formed in DMF and only a trace amount was detected in toluene (entries 14 and 15).

With the optimal conditions, the scope of the reaction was briefly explored. As shown in Table 2, a series of propargyl epoxides bearing substituted phenyl groups reacted smoothly with **2a** affording the corresponding products in high yields. Chloro, bromo, trifluoromethyl and phenyl substituents are tolerated (entries 2-5). The reaction was also successfully performed with **1g** bearing a steric hindering *tert*-butyl, giving **3f** in 95% yield with no variation of reaction efficiency (entry 6). In addition to **2a**, diethyl phosphonate **2b** also reacted with **1a** to give **3g** in good yield (entry 7). Probably due to the steric effect, the reaction of dibutyl phosphonate **2c** produced the coresponding product **3i** in a lower yield while the reaction of diisopropyl phosphonate **2d** did not give the desired product (entries 8 and 9). On the other hand, diphenylphosphine oxide **2e** is a suitable substrate for the reaction. As examplified in entries 10-12, the reactions of **2e** with **1a**, **1c** or **1g** produced the corresponding products **3j-3l** in good to high yields. To obtain some information on the stereochemistry of the reaction, propargyl epoxide **1h** was prepared. It was observed that the reaction of **1h** with **2a** produced **3m** in 77% yield with a *dr* value of 56/44 (entry 13). The reaction of **1h** with **2e** demonstrated a slightly good diastereoselectivity, affording **3n** with a *dr* value of 75/25 (entry 14). The disubstituted propargyl epoxide **1i** also gave a mixture of stereoisomers (entry 15). Finally, the substrate **1j** bearing a free hydroxyl group is also examined, which afforded the expected product **3p** in a modest yield (entry 16).

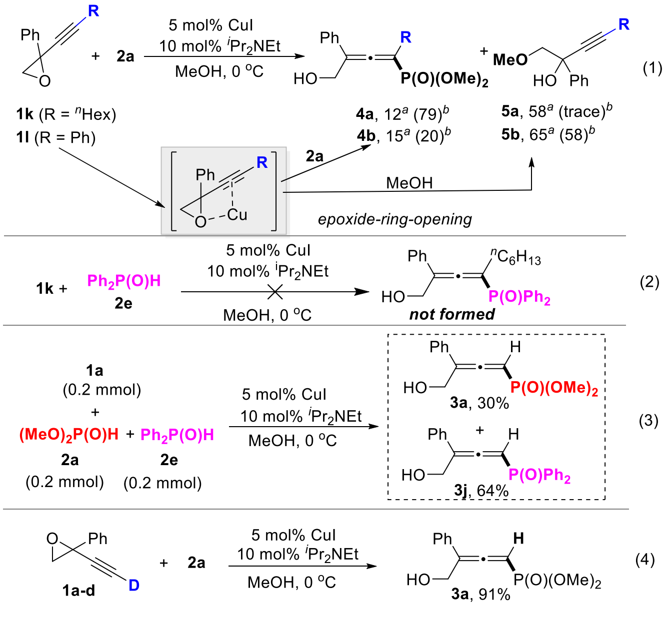
Table 2 Cu-catalyzed synthesis of 4-phosphoryl 2,3-allenols [a]



entry	**1** (R^1)	**2** (R^2)	**3**, yield (%)[b]
1	**1a** (Ph)	**2a** (R^2 = OMe)	**3a**, 92 (90)[c]
2	**1b** (p-ClC$_6$H$_4$)	**2a**	**3b**, 99
3	**1c** (p-BrC$_6$H$_4$)	**2a**	**3c**, 94
4	**1d** (p-CF$_3$C$_6$H$_4$)	**2a**	**3d**, 84
5	**1f** (p-PhC$_6$H$_4$)	**2a**	**3e**, 91
6	**1g** (^{t}Bu)	**2a**	**3f**, 95
7	**1a**	**2b** (R^2 = OEt)	**3g**, 89[d]
8	**1a**	**2c** (R^2 = O^{n}Bu)	**3h**, 66[e]
9	**1a**	**2d** (R^2 = O^{i}Pr)	**3i**, 0
10	**1a**	**2e** (R^2 = Ph)	**3j**, 89[f]
11	**1c**	**2e**	**3k** 88[f]
12	**1g**	**2e**	**3l**, 68
13	 **1h**	**2a** 	**3m**, 77[g]
14		**2e**	**3n**, 72[h]
15	 **1i**	**2a** 	**3o**, 56[i]
16	 **1j**	**2a** 	**3p**, 64

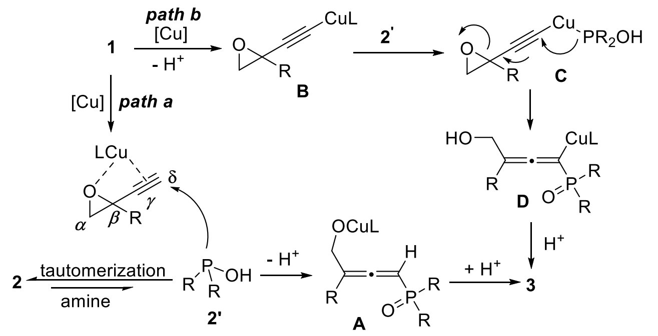
[a] Conditions: 1 (0.36 mmol), 2 (0.3 mmol), CuI (5 mol%), ^{i}Pr$_2$NEt (0.03 mmol) in MeOH (2 mL). [b] Isolated Yield. [c] The reaction was conducted on 1 mmol scale based on 2a. [d] EtOH as a solvent. [e] 6 mol% of dppe was added. [f] Reactions were performed on 0.6 mmol scale based on 2e. [g] dr: 56/44. [h] dr: 75/25, determined from its esterified derivative with HOAc (see ESI). [i] dr: 55/45.

At the current stage, internal propargyl epoxides are not well applicable in the reaction. However, experimental results on these substrates are informative for a mechanism consideration (Scheme 2). As shown in eq. 1, the reaction of **1k** with **2a** catalyzed by CuI gave **4a** only in 12% yield. The major product is 1-methoxy-2-phenyldec-3-yn-2-ol (**5a**), arising from an epoxide-ring opening reaction by MeOH probably due to the dual activation of both the epoxide ring and the triple bonds by a Cu(I) species. A similar result was also obtained from **1l** bearing a phenyl group at the terminal of the alkyne. Interestingly, the yield of **4a** could be improved to 79% by adding dppe as a ligand and with a molar ratio of **2a**/**1k** to 2/1, yet **1l** failed to give a better result under identical conditions. These results suggest that the two competative pathways (SN_2' by P(O)H *vs* SN_2 by MeOH) are very sensitive to the electronic property of the alkynyl moiety for nonterminal substrates. On the other hand, the P(O)H partner also appears crucial for a successful transformation of internal propargyl epoxides into allenols as the reaction of **2e** with **1k** did not give the desired product (eq. 2). In contrast, a control experiment by performing the reaction of **2a**, **2e** and **1a** with equivalent molar ratio gave **3a** and **3j** in 30% and 64% yield, indicating that **2e** is however more reactive than **2a** in reactions of terminal propargyl epoxides (eq. 3). These results indicate that different mechanisms may operate in the SN_2' reactions of terminal and nonterminal substrates. Finally, almost no deuterium incorporation was observed at the C1 position in the hydrophosphorylative ring-opening product of **1a-d** (eq. 4).[18] The H/D exchange may indicate the involvement of a Cu-alkynide intermediate in the reaction.[19]



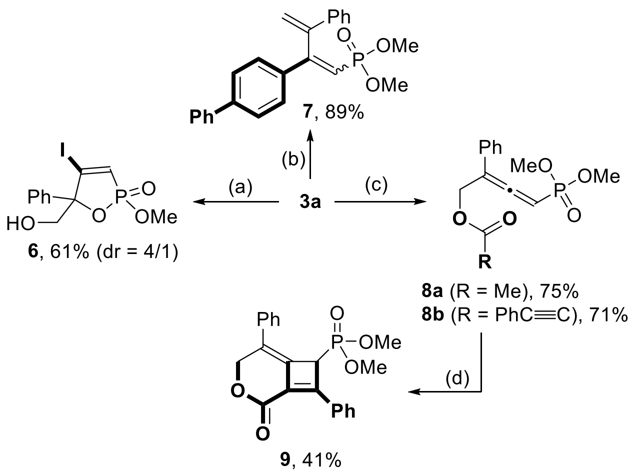
Scheme 2 Reactivity of internal vs terminal propargyl epoxides. ^{a}Conditions: 1i or 1j (0.36 mmol), 2a (0.3 mmol), CuI (5 mol%), $^iPr_2NEt$ (0.03 mmol) in MeOH (2 mL). ^{b}Conditions: 1i or 1j (0.3 mmol), 2a (0.6 mmol), CuI (5 mol%), dppe (6 mol%), $^iPr_2NEt$ (0.03 mmol) in MeOH (2 mL).

A plausible mechanism is proposed in Scheme 3. Dual coordination of Cu(1) complex to both the alkyne and epoxide in **1** may induce the nucleophilic attack of **2'** (tautomer form of **2**) to the δ-position of the propargyl epoxide to form a Cu-alkoxide intermediate **A**. Protonation of **A** then gives the product (path a). Considering the facility of the reactions for terminal propargyl epoxides, another mechanism may also operate, and probably as a major path (path b). The terminal substrate **1** first reacts with Cu(I) salt to form a Cu-acetylide intermediate **B**. The coordination of **2'** to the Cu center via ligand exchange results in the formation of intermediate **C**. An epoxide-ring opening and C-P bond formation sequence then takes place to give Cu-allenyl intermediate **D**, protodemetalation of which gives the product and regenerates the catalyst.



Scheme 3 A plausible mechanism

Notably, the resulted products are very attractive synthetic building blocks due to the versatile reactivity of the dense functionalities. Some representative transformations of **3a** are presented in Scheme 4. Thus, the electrophilic cyclization of **3a** with I_2 gave the phosphorus cycle **6** in 61% yield. **3a** also successfully coupled with 4-biphenylboronic acid upon a Pd catalyst to afford the phosphoryl 1,3-dienes **7** in 89% yield with excellent stereoselectivity.[20] In addition, **3a** also readily reacts with carboxylic acids to give the esterified products **8**. Particularly, the reaction of **3a** with 3-phenylpropiolic acid afforded the ester-tethered alkyne-allene product **8b**, a valuable precursor for complex ring synthesis via cyclization reaction[21] as exemplified by compound **9**.



Scheme 4 Synthetic transformations of 3a (Conditions: (a) I_2 (2.0 equiv), CH_2Cl_2, rt, overnight. (b) 4-biphenylboronic acid (2.0 equiv), 5 mol% $PdCl_2(Ph_3P)_2$, H_2O, reflux, 3 h. (c) RCO_2H (1.1 equiv), DCC (1.1 equiv), DMAP (5 mol%), CH_2Cl_2, 0 °C. (d) Tol, 110 °C, 48 h)

Conclusions

In summary, we have disclosed an efficient Cu-catalyzed atom-economic ring-opening of propargyl epoxides with P(O)H compounds to afford a new class of 4-phosphoryl 2,3-allenols. The reactions proceed under mild conditions and give the products highly selectively in good to high yields. Further investigations into the reaction scope, stereochemistry and target-oriented synthesis of phosphorus compounds via the transformations of the densely functionalized products are underway and will be reported in due course. Financial support from the National Natural Science Foundation of China (21302095), Research Fund for the Doctoral Program of Higher Education of China (20133221120003) and Jiangsu Provincial NSFC (BK20130924) is acknowledged.

Notes and references

1 Selected reviews on allene chemistry: (a) B. Alcaide, P. Almendros, Eds. '*Progress in allene chemistry*' Special issue, *Chem. Soc. Rev.*, 2014, **43**, 2879-3206; (b) S. Yu, S. Ma, *Angew. Chem. Int. Ed.*, 2013, **51**, 13074; (c) S. Ma, *Chem. Rev.*, 2005, **105**, 2829; (d) A. Hoffmann-Röder and N. Krause, *Angew. Chem. Int. Ed.*, 2004, **43**, 1196.

2 (a) S. Webster, P. C. Young, G. Barker, G. M. Rosair and A.-L. Lee, *J. Org. Chem*., 2015, **80**, 1703; (b) L. Wu, H. Huang, Y. Liang and P. Cheng, *J. Org. Chem.*, 2014, **79**, 11264; (c) B. Alcaide, P. Almendros, A. Luna, N. Prieto, *J. Org. Chem.*, 2012, **77**, 11388; (d) S. Ma, Z. Gu, *J. Am. Chem. Soc.*, 2005, **127**, 6182.

3 (a) B. Alcaide, P. Almendros, T. M. del Campoa, *Org. Biomol. Chem*., 2012, **10**, 7603; (b) Y. Deng, X. Jin, C. Fu and S. Ma, *Org. Lett.*, 2009, **11**, 2169; (c) Y. Choe and P. H. Lee, *Org. Lett.*, 2009, **11**, 1445.

4 (a) R. W. Friesen and M. Blouin, *J. Org. Chem.*, 1993, **58,** 1653; (b) S. Ma and S. Zhao, *J. Am. Chem. Soc.*, 1999, **121**, 7943.

5 (a) D. A. Mundal, K. E. Lutz and R. J. Thomson, *J. Am. Chem. Soc.*, 2012, **134**, 5782; (b) T. Sun, C. Deutsch and N. Krause, *Org. Biomol. Chem.*, 2012, **10**, 5965; (c) Y. Deng, Y. Yu, S. Ma, *J. Org. Chem.*, 2008, **73**, 585; (d) B. Alcaide, P. Almendros and R. Rodríguez-Acebes, *Chem. Eur. J.*, 2005, **11**, 5708; (e) B. Alcaide, P. Almendros, T. M. del Campo, M. C. Redondo and I. Fernández, *Chem. Eur. J.*, 2011, **17**, 15005; (f) B. Alcaide, P. Almendros, A. Luna and E. Soriano, *J. Org. Chem.*, 2015, **80**, 7050.

6 (a) X. Chen, X. Jiang, Y. Yu and S. Ma, *J. Org. Chem.*, 2008, **73**, 8960; (b) S. Li, B. Miao, W. Yuan and Ma, S. *Org. Lett.*, 2013, **15**, 977; (c) E. Yoneda, T. Kaneko, S.-W. Zhang, K. Onitsuka and S. Takahashi, *Org. Lett.*, 2000, **2**, 441.

7 Selected examples: (a) W. Kong, C. Fu and Ma, S. *Chem. Comm.*, 2009, 4572; (b) Q. Li, X. Jiang, C. Fu and S. Ma, *Org. Lett.*, 2011, **13**, 466; (c) Y. Qiu, C. Fu, X. Zhang and S. Ma, *Chem. Eur. J.*, 2014, **20**, 10314; (d) Y. He, X. Zhang and X. Fan, *Chem. Commun.*, 2015, **51**, 16263; (e) B. Alcaide, P. Almendros, J. M. Alonso, I. Fernández and S. Khodabakhshi *Adv. Synth. Catal.*, 2014, **356**, 1370.

8 For reviews on allene synthesis, see: (a) S. Yu and S. Ma, *Chem. Commun.*, 2011, **47**, 5384; (b) R. K. Neff and D. E. Frantz, *ACS catal.*, 2014, **4**, 519.

9 Cu-catalyzed reactions of propargyl epoxides with Grignard reagents: (a) A. Alexakis, I. Marek, P. Mangeney and J. F. Normant, *Tetrahedron*, 1991, **47**, 1677; (b) A. Alexakis, I. Marek, P. Mangeney and J. F. Normant, *Tetrahedron Lett.*, 1989, **30**, 2387; (b) C. Spino and S. Frechette, *Tetrahedron Lett.*, 2000, **41**, 8033; (c) C. Deutsch, A. Hoffmann-Röder, A. Domke and N. Krause, *Synlett.*, 2007, **5**, 737; (d) Cu-catalyzed reactions of propargyl epoxides with organolithium reagents: A. Alexakis, I. Marek, P. Mangeney and J. F. Normant, *Tetrahedron Lett.*, 1989, **30**, 2391. (e) Cu-catalyzed reactions of propargyl epoxides with organozinc reagents: F. Bertozzi, P. Crotti, F. Macchia, M. Pineschi, A. Arnold and B. L. Feringa, *Tetrahedron Lett.*, 1999, **40**, 4893.

10 (a) Pd-catalyzed reactions of propargyl epoxides with organozinc reagents: H. Kleijn, J. Meijer, G. C. Overbeek and P. Vermeer, *Rec. Trav. Chim. Pays-Bas*, 1982, **101**, 97; (b) Pd-catalyzed reactions of propargyl epoxides with alkynylcopper: M. Yoshida, M. Hayashi and K. Shishido, *Org. Lett.*, 2007, **9**, 1643; (c) Pd-catalyzed reactions of propargyl epoxides with organoborons: M. Yoshida, H. Ueda and M. Ihara, *Tetrahedron Lett.*, 2005, **46**, 6705.

11 Rh-catalyzed reactions of propargyl epoxides with organoborons: (a) T. Miura, M. Shimada, S.-Y. Ku, T. Tamai and M. Murakami, *Angew. Chem., Int. Ed.*, 2007, **46**, 7101; (b) T. Miura, M. Shimada, P. de Mendoza, C.Deutsch, N. Krause and Murakami, M. *J. Org. Chem.*, 2009, **74**, 6050.

12 Fe-catalyzed reactions of propargyl epoxides with Grignard reagents: A. Füurstner and M. Méndez, *Angew. Chem., Int. Ed.*, 2003, **42**, 5355.

13 Selected examples of other methods: (a) M. Inoue and Nakada, M. *Angew. Chem., Int. Ed.*, 2006, **45**, 252; (b) G. Xia and H. Yamamoto, *J. Am. Chem. Soc.*, 2007, **129**, 496; (c) J. Ye, W. Fan and S. Ma, *Chem. Eur. J.*, 2013, **19**, 716; (d) X. Huang, T. Cao, Y. Han, X. Jiang, W. Lin, J. Zhang and S. Ma, *Chem. Commun.*, 2015, **51**, 6956; (e) A. Roy, B. A. Bhat and S. D. Lepore, *Org. Lett.*, 2015, **17**, 900; (f) J. Park, S. H. Kim and P. H. Lee, *Org. Lett.*, 2008, **10**, 5067; (g) A. D. Mundal; E. K. Lutz and J. R. Thomson, *J. Am. Chem. Soc.*, 2012, **134**, 5782; (h) H. Luo and S. Ma, *Eur. J. Org. Chem.*, 2013, 3041.

14 (a) J. Kjellgren, H. Sundén and K. J. Szabó, *J. Am. Chem. Soc.*, 2005, **127**, 1787; (b) J. Zhao and K. J. Szabó, *Angew. Chem., Int. Ed.*, 2016, **55**, 1502; (c) T. S. N. Zhao, Y. Yang, T. Lessing and K. J. Szabó, *J. Am. Chem. Soc.*, 2014, **136**, 7563.

15 4-Silyl 2,3-allenol has been synthesized via the addition of $R_3SiAlEt_2$ to propargyl epoxide by the Trost group: B. M. Trost and J. M. Tour, *J. Org. Chem*. 1989, **54**, 484.

16 (a) R. Shen, B. Luo, J. Yang, L. Zhang and L.-B Han, *Chem. Comm.*, 2016, **52**, 6541; (b) J. Yang, T. Chen and L. -B. Han, *J. Am. Chem. Soc.*, 2015, **137**, 1782; (c) Early work, see: Q. Xu and L.-B. Han, *J. Organometallic Chem.* 2011, **696**, 130.

17 For a recent review on Cu-catalyzed C-P forming reactions, see: H. Zhang, X.-Y. Zhang, D.-Q. Dong and Z.-L. Wang, *RSC Adv*., 2015, **5**, 52824.

18 The reaction of **1a** and **2a** performed in CH_3OD afforded the C1-deuterated **3a** in 91% yield (see ESI).

19 When **1a** was treated under the catalytic conditions in the absence of **2a**, a complex mixture was formed probably due to the decomposition of the Cu-alkynide intermediate. For a review on Cu-alkyne and -alkynides, see: H. Lang, A. Jakob and B. Milde, *Organometallics*, 2012, **31**, 7661.

20 M. Yoshida, T. Gotou and M. Ihara, *Chem. Commun.*, **2004**, 1124. The configuration of the C-C double bonds in **7** has not been determined. We reason that the reaction proceeds with high stereoselectivity since the NMR data of **7** indicate that only one of the stereoisomers was formed (see ESI).

21 (a) M. S. Shepard and E. M. Carreira, *J. Am. Chem. Soc.*, 1997, **119**, 2597; (b) T. Gillmann, T. Hülsen, W. Massa and S. Wocadlo, *Synlett*, 1995, 1257; (c) A. Padwa, H. Lipka, S. H. Watterson and S. S. Murphree, *J. Org. Chem.*, 2003, **68**, 6238.