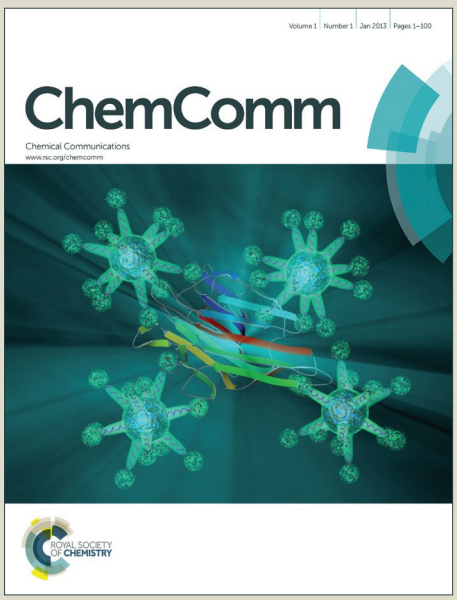
ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Shen, B. Luo, J. Yang, L. Zhang and L. Han, *Chem. Commun.*, 2016, DOI: 10.1039/C6CC02563C.



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

View Article Online
DOI: 10.1039/C6CC02563C

Journal Name

COMMUNICATION

Convenient Synthesis of Allenylphosphoryl Compounds *via* Cu-Catalysed Couplings of P(O)H Compounds with Propargyl Acetates

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

DOI: 10.1039/x0xx00000x

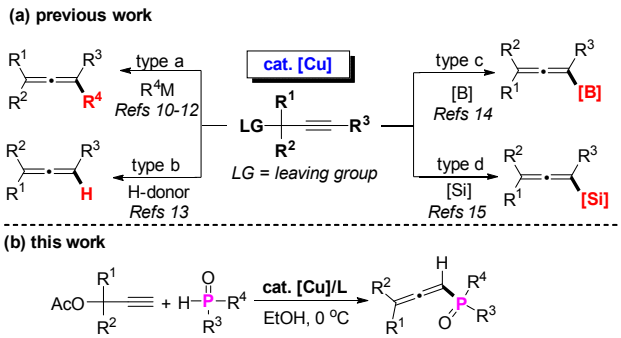
www.rsc.org/

Ruwei Shen,*[a] Bing Luo,[a] Jianlin Yang,[a] Lixiong Zhang,[a] Li-Biao Han*[b]

A novel Cu-catalysed substitution reaction of propargyl acetates with P(O)H compounds is developed to afford allenylphosphoryl compounds via C-P bond coupling in high yields under mild conditions. A plausible mechanism involving the nucleophilic interception of the Cu-allenylidene intermediates is proposed.

Allene and its derivatives constitute a special class of organic compounds and have received tremendous attention in recent years.[1] Among them, phosphorylated allenes including allenyl phosphonates, phosphinates and phosphine oxides are versatile synthetic intermediates which display a lot of applications in organic synthesis.[2-7] For example, these compounds could undergo facile and selective additions with electrophiles or nucleophiles to afford stereodefined functional olefins,[2,3] and the transition metal-catalyzed asymmetric additions enable the synthesis of valuable chiral phosphorus compounds.[4] Allenyl phosphonates and phosphinates are also valuable precursors to access phosphorus heterocycles of pharmaceutical interest.[5] In addition, some phosphorylated allenes participate smoothly in Diels–Alder and related cyclizations to generate other structurally sophisticated organophosphorus compounds.[6,7] On contrast to their valuable utility, very few methods are known for their synthesis.[8] A traditional method to make them is the Horner-Mark [2,3]-rearrangement reaction discovered in early 1960s.[8a] This reaction while still intensively used today unfortunately suffers from hash conditions, low yields, limited scopes and the use of highly toxic phosphorous chlorides.

On the other hand, the Cu-catalysed nucleophilic substitution of propargylic alcohol derivatives is one of the most popular well-developed methods to access allenes.[9] For example, the Cu-catalyzed substitutions of propargyl derivatives with organometallic reagents such as organolithium[10a] or Grignard reagents,[10b-10d] were known as early as 1970s and are still frequently used today.[11] Particularly, the introduction of organoborates as C-nucleophiles by Sawamura and Lalic independently has enabled the synthesis of optically active allenes with excellent chirality transfer from chiral propargylic phosphates.[12] In these reactions, new C-C bonds are formed (Scheme 1a, type a). In the presence of hydrogen donors such as hydrosilanes instead, various di- or tri-substituted allenes are accessible with the formation of C-H bonds (Scheme 1a, type b).[13] Furthermore, recent studies also show that heteroatom-substituted allenes can be synthesized based on this strategy. For example, Ito and Sawamura[14] have reported a Cu(O-*t*-Bu)-Xanphos catalysed substitution of propargylic carbonates with B_2Pin_2 to afford allenylboron compounds (Scheme 1a, type c). Oestreich et al[15] realized a CuCN-catalysed propargylic substitution with silicon nucleophiles to afford silylallenes (Scheme 1a, type d). Despite of these excellent contributions, to our knowledge, there is no example on Cu-catalysed propargylic substitution involving a phosphorus nucleophile. Such a transformation is however a very promising synthetic method towards allenylphosphoryl compounds. Here we present the first highly efficient Cu-catalysed substitutions of propargyl acetates with P(O)H compounds to afford a diverse collection of phosphorylated allenes in high yields under mild conditions (Scheme 1b).[16]



Scheme 1 Cu-catalyzed propargylic substitutions to produce allenes.

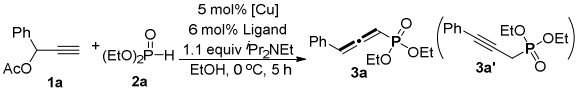
Our study began with the reaction of 1-phenylpropargyl acetate (**1a**) with diethyl phosphonate (**2a**) as model substrates.

[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

View Article Online
DOI: 10.1039/C6CC02563C

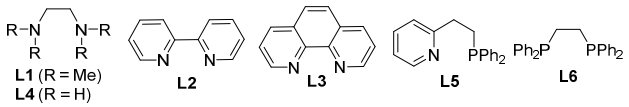
Table 1 Typical optimization results on the reaction[a]



run	[Cu]	ligand	yield% (**3a**/**3a'**)[b]	run	[Cu]	ligand	yield% (**3a**/**3a'**)[b]
1	**CuI**	**L1**	**95 (98/2)**	7	CuBr	L1	91 (97/3)
2	CuI	L2	16[c]	8	CuCl	L1	91 (98/2)
3	CuI	L3	8[c]	9	$CuPF_6(MeCN)_4$	L1	93 (96/4)
4	CuI	L4	NR	10	$Cu(OAc)_2$	L1	84 (98/2)
5	CuI	L5	5[c]	11	$CuCl_2 \cdot 2H_2O$	L1	86 (95/5)
6	CuI	L6	trace[c]	12	$CoCl_2$, $FeCl_3$, etc	L1	NR

[a]Conditions: **1** (0.24 mmol), **2** (0.2 mmol), [Cu] (5 mol%), Ligand (6 mol%), $^iPr_2NEt$ (0.22mmol) in EtOH (2 mL), 0 °C. [b]Yields and ratio based on ^{31}P NMR. [c]**3a** only.

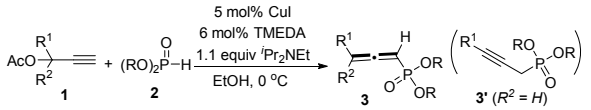
structures of the ligands L1-L6

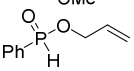


Typical optimization results are shown in Table 1. When **1a** and **2a** were treated with 5 mol% of CuI and 6 mol% of TMEDA (**L1**) in the presence of 1.1 equiv of $^iPr_2NEt$ in EtOH at 0 °C for 5 h, the reaction gave diethyl (3-phenylpropa-1,2-dien-1-yl)phosphonate (**3a**) and the allene-alkyne isomer **3a'** in 95% yield with a selectivity up to 98/2 (run 1). The efficiency of the reaction is critically depended on the ligand. Bidentate N,N-ligands such as bpy (**L2**), 1,10-Phen (**L3**) and ethylenediamine (**L4**), N,P-ligand 2-(2-(diphenylphosphino) ethyl)pyridine (**L5**) and P,P-ligand dppe (**L6**) were all proved to be less effective (runs 2-6). The Cu source has little effect. CuBr, CuCl and $Cu(MeCN)_4PF_6$ are all good catalysts, giving **3a** with comparable yields and selectivity (runs 7-9). Divalent copper salts $Cu(OAc)_2$ and $CuCl_2 \cdot 2H_2O$ were also competent to catalyse the reaction, albeit giving **3a** in somewhat lower yields (runs 10 and 11). However, other metal salts such as $CoCl_2$, $FeCl_3$, $RuCl_3$ and $Pd(OAc)_2$ showed no reactivity. The high efficiency of the reaction also depends on the use of a protic solvent as THF, DCM, DMF and MeCN all gave **3a** in low yields (For details, see Table S1 in ESI).

The generality of the reaction was then examined. As shown in Table 2, a series of 1-arylpropargyl acetates bearing either electron-donating or electron-withdrawing group at the aryl ring could be used to afford the corresponding products in high yields with high selectivity. Functional groups such as alkoxy, fluoro, chloro and bromo substituents on the aryl rings were tolerated (runs 3-8). The steric hindrance of substituents on the phenyls did not have a strong influence. Thus, substrates **1c** and **1g** bearing *ortho* substituents on the phenyls reacted smoothly to give the desired products selectively in high yields (runs 4 and 8). The 1-deuterated substrate **1a**-d_γ gave the deuterated **3a**-d_γ in 90% yield with a selectivity of 98% (run 2). The reaction of 1-styrylpropargyl acetate (**1h**) also proceeded smoothly to give a vinylallenyl product **3h** in high yield with 95% selectivity (run 9). The disubstituted propargyl acetates **1i** and **1j** performed exquisitely well to give **3i** and **3j** almost in

Table 2 Cu-catalysed synthesis of allenyl phosphonates and phosphinates **3**[a]



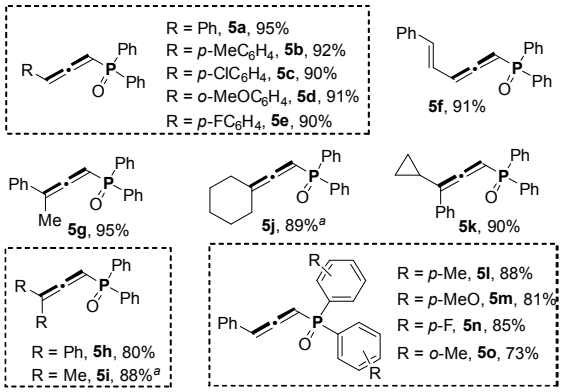
run	**1** (R^1, R^2)	**2**	t (h)	**3**, yield% (**3**/**3'**)[b]
1	**1a** (Ph, H)	**2a** (R = Et)	5	**3a**, 91 (98/2)
2	**1a** (Ph, D)[c]	**2a**	5	**3a**-*d*, 90 (98/2)[c]
3	**1b** (*p*-MeC_6H_4, H)	**2a**	5	**3b**, 91 (98/2)
4	**1c** (*o*-$MeOC_6H_4$, H)	**2a**	5	**3c**, 90 (99/1)
5	**1d** (*m*-BrC_6H_4, H)	**2a**	5	**3d**, 85 (97/3)
6	**1e** (*p*-ClC_6H_4, H)	**2a**	5	**3e**, 88 (97/3)
7	**1f** (*p*-FC_6H_4, H)	**2a**	4	**3f**, 89 (96/4)
8	**1g** (*o*-BrC_6H_4, H)	**2a**	4	**3g**, 80 (96/4)
9	**1h** (cinnamyl, H)	**2a**	4	**3h**, 81 (95/5)
10	**1i** (Ph, Me)	**2a**	2	**3i**, 99
11	**1j** (Ph, Ph)	**2a**	2	**3j**, 98
12	**1k** (Me, Me)	**2a**	24	**3k**, 80
13	**1l** (-$(CH)_5$-)	**2a**	24	**3l**, 88
14	**1m** (Ph,)	**2b** (R = Me)	2	**3m**, 84
15	**1a**	**2b**	5	**3n**, 89 (>99/1)
16	**1a**	**2c** (R = ^nBu)	5	**3o**, 80 (97/3)
17	**1a**	**2d** 	2	**3p**, 92[d]
18	**1a**	**2e** 	2	**3q**, 90[e]

[a] Conditions: **1** (0.24 mmol), **2** (0.2 mmol), CuI (5 mol%), TMEDA (6 mol%) and $^iPr_2NEt$ (0.22 mmol) in EtOH (2 mL). [b]Isolated Yield; Ratios of **3**/**3'** based on ^{31}P NMR. [c]D%>99%. [d]dr=3.2/1. [e]dr=2.9/1.

quantitative yields (runs 10 and 11). As compared to aryl-substituted propargyl acetates, the reactions of alkyl-substituted substrates **1k** and **1l** proceeded slowly affording **3k** and **3j** in 80% and 88% yields in 24 h (runs12 and 13). The reaction of a cyclopropanyl substrate **1m** also efficiently gave the expected products **3m** in 84% yields, in which the cyclopropane-opening products were not formed (run 14). In addition to **2a**, dimethyl phosphonate (**2b**) and dibutyl phosphonate (**2c**) also reacted smoothly to give the products selectively in high yields (runs 14-16). Moreover, H-phosphinates are also applicable. For example, H-phosphinate **2d** reacted with **1a** producing allenylphosphinate **3p** in 92% yield (run 17). The reaction also shows a moderate stereoselectivity as **3p** was obtained as a 3.2:1 diastereoisomer mixture. A similar result was also observed from the reaction of **1a** with **2e** that bears an allyloxyl group (run 18).

Further, the present method is also applicable to the synthesis of allenylphosphine oxides. As shown in Scheme 2, **5a**-**5k** were successfully obtained in high yields with excellent selectivity from the reactions of diphenylphosphine oxide (**4a**) with the corresponding propargyl acetates. Typical diarylphosphine oxides bearing electron-donating and electron-withdrawing substitutes on the phenyl rings are also successful substrates to produce the expected products **5l**-**5n** in high yields. In addition, a more steric hindering substrate bearing *o*-tolyl groups also gave the expected product **5o** in good yields. Here it should be

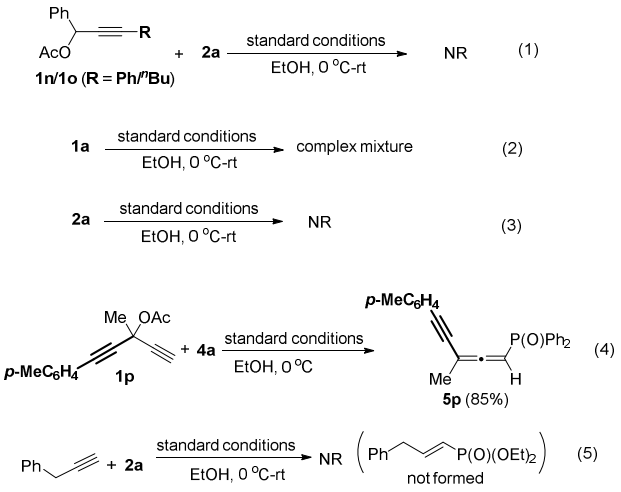
View Article Online
DOI: 10.1039/C6CC02563C



Scheme 2 Cu-catalysed synthesis of allenyl phosphine oxides (conditions for **5a**-**5h**, **5k**-**5o**: 0 °C, 2h; conditions for **5i** and **5j**: 0 °C-rt, 12 h. Isolated yields are given.)

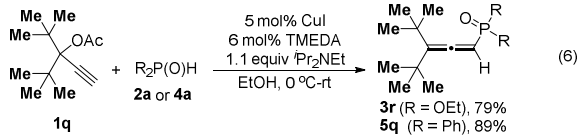
noted that these secondary phosphine oxides are readily available from reactions of diethyl phosphonate with the corresponding Grignard reagents.[17] Thus, a diversity of P(O) functionalities could be easily incorporated into the allenic frameworks with the present method.

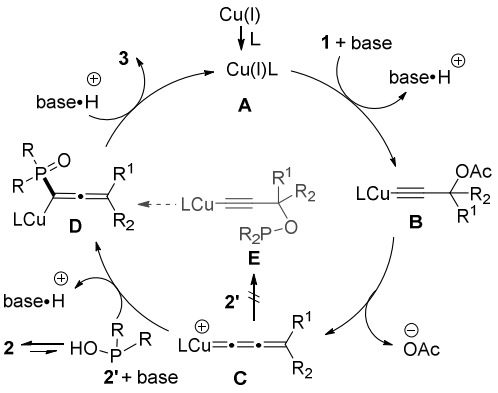
To gain some insight into the reaction mechanism, several control experiments were performed. In contrast to terminal akynes used, we found that internal propargyl acetates **1n** and **1o** are inactive under the catalytic conditions (eq. 1), indicative of the necessity of an active C_{sp}-H bond for the propargylic substrates. We deduced that a copper-alkynide intermediate that is readily formed from terminal alkynes with copper complexes under basic conditions may be crucial. Probably due to the decomposition of these Cu-intermediates, **1a** was also quickly consumed to give an unidentifiable mixture in the absence of the nucleophile **2a** (eq. 2), nevertheless **2a** was inert and fully recovered under the same conditions (eq. 3). Furthermore, a clean transformation of a bis-alkynyl substrate **1p** into the yne-allenyl compound **5p** in 85% yield was observed while the possible isomer with the phosphors functionality attached to the internal triple bonds was not formed (eq. 4). In addition, the treatment of a simple alkyne with **2a** under identical conditions



did not afford an alkenylphosphonate product (eq. 5), suggesting that an addition of a possible Cu-phosphido species to the C-C triple bond may not take place under the conditions. The Cu-catalysed substitutions of propargyl substrates to afford substituted allenes via an addition-elimination mechanism is well known.[9] Nevertheless, such a mechanism may be less possible for our reaction accordingly.

Alternatively, a process as depicted in Scheme 3 was proposed to rationalize the observed results based on the known Cu-catalysed propargylic substitutions of terminal propargyl acetates with N- and C-nucleophiles which involves Cu-allenylidene species as key intermediates.[18] In the presence of a base, the active Cu(I) species **A**[19] generated from the reaction of the copper salt with TMEDA first reacts with the propargyl acetate **1** to produce the copper acetylide complex **B**. Loss of an ester group from **B** would form a Cu-allenylidene complex **C**.[17b] The nucleophilic reaction of **C** with **2** would then produce an allenylcopper intermediate **D**, protonation of which gives the product and regenerate the catalyst (Scheme 3).[20,21] A route involving propargylic substitution to form phosphinite or phosphite intermediate **E** followed by 2,3-rearrangement could be excluded since the reactions of **1q** wherein the propargyl carbon is covered by two highly sterically crowded *tert*-butyls, also took place smoothly to give the products in high yields (eq 6). With respect to this mechanism, the unique selectivity to form allenyl product is notable as catalytic reactions involving Cu-allenylidenes with other nucleophiles reported thus far all give propargyl products.[18] Detailed mechanistic investigations is however still needed to elucidate this unusuality.





Scheme 3 A tentative mechanism

Conclusions

In summary, we have disclosed a new Cu-catalyzed reaction to produce allenylphosphoryl compounds from propargyl acetates with P(O)H compounds. The reaction utilizes a simple

View Article Online
DOI: 10.1039/C6CC02563C

and cheap catalyst, takes place under mild conditions in an environmentally benign solvent and has a broad scope. Further mechanistic investigations and applications of the method are currently underway and will be reported soon.

Financial support from the National Natural Science Foundation of China (21302095), Research Fund for the Doctoral Program of Higher Education of China (20133221120003), Jiangsu Provincial NSFC (BK20130924), and Foundation of Jiangsu Educational Committee of China (13KJB150019) 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) H. Guo, R. Qian, Y. Guo and S. Ma, *J. Org. Chem.,* 2008, **73**, 7934; (b) G. He, C. Fu and S. Ma, *Tetrahedron,* 2009, **65**, 8035; (c) G. He, H. Guo, R. Qian, Y. Guo, C. Fu and S. Ma, *Tetrahedron,* 2009, **65**, 4877.

3 (a) K. C. K. Swamy, E. Balaraman and N. S. Kumar, *Tetrahedron,* 2006, **62**, 10152; (b) M. Chakravarty and K. C. K. Swamy, *Synthesis* 2007, 3171; (c) S. E. Denmark, J. E. Marlin and G. Rajendra, *J. Org. Chem.,* 2013, **78**, 66; (d) Y.-Z. Chen, L. Zhang, A.-M. Lu, F. Yang and L. Wu, *J. Org. Chem.*, 2015, **80**, 673; (e) J. K. E. T. Berton, T. S. A. Heugebaert, W. Debrouwer and C. V. Stevens, *Org. Lett.*, 2016, **18**, 208.

4 (a) T. Nishimura, S. Hirabayashi, Y. Yasuhara and T. Hayashi, *J. Am. Chem. Soc.,* 2006, **128**, 2556; (c) T. Kawamoto, S. Hirabayashi, X.-X. Guo, T. Nishimura and T. Hayashi, *Chem. Commun.* **2009**, 3528.

5 (a) F. Yu, X. Lian and S. Ma, *Org. Lett.,* 2007, **9**, 1703; (b) F. Yu, X. Lian, J. Zhao, Y. Yu and Ma, S. *J. Org. Chem.,* 2009, **74**, 1130; (c) P. Li, Z.-J. Liu, J.-T. Liu, *Tetrahedron,* 2010, **66**, 9729; (d) N. Xin and S. Ma, *Eur. J. Org. Chem.* 2012, 3806.

6 (a) C. Mukai, M. Ohta, H. Yamashita and S. Kitagaki, *J. Org. Chem*., 2004, **69**, 6867; (b) S. Kitagaki, Y. Okumara and C. Mukai, *Tetrahedron,* 2006, **62**, 10311; (c) Y. Gu, T. Hama and G. B. Hammond, *Chem. Commun.,* 2000, 395.

7 (a) K. V. Sajna and K. C. K. Swamy, *J. Org. Chem.,* 2012, **77**, 8712; (b) V. K. Brel, V. K. Belsky, A. I. Stash, V. E. Zavodnik and P. J. Stang, *Eur. J. Org. Chem.,* 2005, 512; (c) K. V. Sajna and K. C. K. Swamy, *J. Org. Chem.,* 2012, **77**, 5345; (d) M. Chakravarty and K. C. Swamy, *J. Org. Chem.,* 2006, **71**, 9128; (e) M. Pavan, M. Chakravarty and K. C. Swamy, *Eur. J. Org. Chem.*, 2009, 5927; (f) K. C. Swamy, M. Chakravarty, N. N. Kumar and K. V. Sajna, *Eur. J. Org. Chem.*, 2008, 4500.

8 (a) V. Mark, *Tetrahedron Lett.,* 1962, 281; (b) A. P. Boisselle and N. A. Meinhardt, *J. Org. Chem.,* 1962, **27**, 1828; (c) M. Kalek, T. Johansson, M. Jezowska and J. Stawinski, *Org. Lett.,* 2010, **12**, 4702; (d) C. Santelli-Rouvier, L. Toupet and M. Santelli, *J. Org. Chem.*, 1997, **62**, 9039.

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

10 (a) P. R. Ortiz de Montellano, *J. Chem. Soc., Chem. Commun.*, 1973, 709; (b) C. Cahiez, A. Alexakis and J. F. Normant, *Synthesis,* 1978, 528; (c) G. Tadema, P. Vermeer, J. Meijer and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, 1976, **95**, 66; (d) A. Alexakis, A. Commercon, J. Villiéras and J. F. Normant, *Tetrahedron Lett.,* 1976, **17**, 2313; For other organometallic reagents, see: (e) F. Bertozzi, P. Crotti, F. Macchia, M. Pineschi, A. Arnold and B. L. Feringa, Tetrahedron Lett., 1999, 40, 4893; (f) M. Kotora, Y. Noguchi and T. Takahashi, *Collect. Czech. Chem. Commun.*, 1999, **64**, 1119; (g) Z. Duan, T. Nishimoto, M. Ogasawara and T. Takahashi, *Synthesis,* 2005, 2055;

11 Selected examples: (a) J. Li, C. Zhou, C. Fu and S. Ma, *Tetrahedron,* 2009, **65**, 3695; (b) J. Li, W. Kong, C. Fu and S. Ma, *J. Org. Chem.,* 2009, **74**, 5104. (c) C. Bucuroaia, U. Groth, T. Huhn and M. Klinge, *Eur. J. Org. Chem.,* 2009, 3605; (d) A. Nakatani, K. Hirano, T. Satoh and M. Miura, *Org. Lett.*, 2012, **14**, 2586; (e) H. Li, D. Müller, L. Guénée and A. Alexakis, *Org. Lett.,* 2012, **14**, 5880; (f) H. Li, D. Grassi, L Guénée, T. Bürgi and A. Alexakis, *Chem. -Eur. J.,* 2004, **20**, 16694.

12 (a) H. Ohmiya, U. Yokobori, Y. Makida and M. Sawamura, *Org. Lett.,* 2011, **13**, 6312; (b) M. Yang, N. Yokokawa, H. Ohmiya, M. Sawamura, *Org. Lett.,* 2012, **14**, 816; (c) U. Yokobori, H. Ohmiya and M. Sawamura, *Organometallics*, 2012, **31**, 7909; (d) M. R. Uehling, S. T. Marionni and G. Lalic, *Org. Lett.,* 2012, **14**, 362.

13 (a) C. Deutsch, B. H. Lipshutz and N. Krause, *Angew. Chem., Int. Ed.,* 2007, **46**, 1650; (b) C. Deutsch, B. H. Lipshutz and N. Krause, *Org. Lett.,* 2009, **11**, 5010; (c) C. Zhong, Y. Sasaki, H. Ito and M. Sawamura, *Chem. Commun.,* 2009, 5850; (d) H. Reeker, P.-O. Norrby and N. Krause, *Organometallics*, 2012, **31**, 8024.

14 H. Ito, Y. Sasaki and M. Sawamura, *J. Am. Chem. Soc.,* 2008, **130**, 15774; (c) A. Nakatani, K. Hirano, T. Satoh and M. Miura, *Org. Lett.,* 2012, **14**, 2586.

15 (a) D. J. Vyas, C. K. Hazra and M. Oestreich, *Org. Lett.,* 2011, **13**, 4462; (b) C. K. Hazra and M. Oestreich, *Org. Lett.,* 2012, **14**, 4010.

16 The Cu-catalyzed reactions of alkynes and P(O)H compounds for the synthesis of unsaturated alkynyl and alkenyl phosphoryl compounds were known: (a) Y. Gao, G. Wang, L. Chen, P. Xu, Y. Zhao, Y. Zhou and L.-B. Han, *J. Am. Chem. Soc.,* 2009, **131**, 7956; (b) M. Niu, H. Fu, Y. Jiang and Y. Zhao, *Chem. Commun.,* 2007, 272; (c) E. Bernoud, C. Alayrac, O. Delacroix and A.-C. Gaumont, *Chem. Commun.*, 2011, **47**, 3239; (d) I. G. Trostyanskaya and I.P. Beletskaya, *Tetrahedron,* 2014, **70**, 2556.

17 (a) H.R. Hays, *J. Org. Chem.*, 1968, **33**, 3690; (b) M. J. P. Harger, S. Westlake, *Tetrahedron*, 1982, **38**, 1511.

18 Selected examples: (a) Y. Imada, M. Yuasa, I. Nakamura and S.-I. Murahashi, *J. Org. Chem.,* 1994, **59**, 2282; (b) G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake and Y. Nishibayashi, *J. Am. Chem. Soc.,* 2010, **132**, 10592; (c) R. J. Detz, Z. Abiri, R. Le Griel, H. Hiemstra and J. H. van Maarseveen, *Chem. –Eur. J.,* 2011, **17**, 5921; (d) 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.

19 M. F. Garbauskas, D. A. Haitko and J. S. Kasper, *J. Crystal. Spectro. Res.* 1986, **16**, 729.

20 The reactions conducted in CH_3OD (D%>99.5%) afforded the α-deuterated phosphorylated allenes.

21 When *N*-methylaniline was used as nucleophile instead of **2a** under identical conditions, propargylic substitution product (*N*-methyl-*N*-(1-phenylprop-2-yn-1-yl)aniline) was formed in 89% yield, in agreement to the catalytic propargylic amination via Cu-allenylidene intermediates (Refs. 18a-18c).