

# Dehydrogenative Carbon–Carbon Bond Formation Using Alkynyloxy Moieties as Hydrogen-Accepting Directing Groups

Yasunori Minami,\* Tatsuro Kodama, and Tamejiro Hiyama\*

**Abstract:** In the presence of a catalyst system consisting of  $\text{Pd}(\text{OAc})_2$ ,  $\text{PCy}_3$ , and  $\text{Zn}(\text{OAc})_2$ , the reaction of alkynyl aryl ethers with bicycloalkenes,  $\alpha,\beta$ -unsaturated esters, or heteroarenes results in the site-selective cleavage of two C–H bonds followed by the formation of C–C bonds. In all cases, the alkynyloxy group acts as a directing group for the activation of an *ortho* C–H bond and as a hydrogen acceptor, thus rendering the use of additives such as an oxidant or base unnecessary.

Cross-dehydrogenative bond-forming reactions are highly attractive methods in the toolbox of synthetic organic chemistry, especially considering their potential in terms of atom and step economy. Representative examples are the cross-dehydrogenative formation of carbon–carbon, carbon–boron, and carbon–silicon bonds.<sup>[1–3]</sup> This concept also enables the custom-tailored construction of a variety of highly functionalized compounds, and the site-selective cleavage of two C–H bonds and the subsequent removal of the eliminated hydrogen atoms are key factors in this context. To trap the emitted hydrogen, several additives, such as olefins or oxidants, have been successfully used, as the release of dihydrogen only meets with difficulty. However, the use of such additives may be problematic from a practical perspective, as they potentially interfere with the dehydrogenative reaction.

Directing groups have been successfully employed for effective site- and regioselective C–H functionalization.<sup>[4]</sup> In one of our previous studies, we demonstrated that alkynyloxy groups ( $-\text{OC}\equiv\text{CR}$ ) are able to act as directing groups for the activation of adjacent C–H bonds, and subsequently engage in addition reactions.<sup>[5]</sup> For example, the reaction with alkynes furnishes chromene derivatives by sequential insertions into *ortho* C–H bonds.<sup>[5a]</sup> On the basis of these results, we expected that the alkynyloxy group might also be able to act as a hydrogen acceptor and enable the cleavage of two C–H bonds, thus facilitating a dehydrogenative carbon–carbon bond-forming reaction. Moreover, this synthetic approach would avoid the use of additives, such as oxidants (e.g.,

benzoquinone) or bases, and the vinyloxy groups resulting from dihydrogenation of the alkynyloxy groups are highly useful functional groups.<sup>[6]</sup> Herein, we report a series of dehydrogenative reactions between alkynyl aryl ethers and bicycloalkenes,  $\alpha,\beta$ -unsaturated esters, or heteroarenes. This approach represents a convenient strategy for additive-free catalytic cross-dehydrogenative C–C bond-forming reactions.

Recently, we reported that the reaction between triisopropylsilyl (TIPS)-substituted *para*-methoxyphenyl ether **1a** and norbornene (**2a**) in the presence of  $[\text{Pd}(\text{PCy}_3)_2]$  (5 mol %) and Zn (5 mol %) proceeds by *ortho* C–H insertion/annulation to afford **4a**.<sup>[5f]</sup> However, when the reaction between **1a** and **2a** was carried out in the presence of  $\text{Pd}(\text{OAc})_2$  (5 mol %),  $\text{PCy}_3$  (10 mol %), and  $\text{Zn}(\text{OAc})_2$  (20 mol %) at 100°C for 24 h, benzocyclobutene **3a** with a *Z*-configured silylethenoxy moiety was obtained in 75% yield, most likely by the cleavage of the *ortho* and *meta* C–H bonds (Table 1, entry 1).<sup>[7–10]</sup> When the amount of **2a** (1.5 equiv) was reduced, **3a** was generated in a similar yield, albeit more slowly with concomitant formation of the *E* isomer **3'a** (entry 2). We also examined other phosphine ligands, such as  $\text{P}^t\text{BuAd}_2$  and XPhos, which also proved to be effective in this reaction. The use of  $\text{P}^t\text{BuAd}_2$  afforded **3a** and **3'a** (91:9) in a combined yield of 80%, whereas the use of XPhos provided **3a** in 86% yield (entries 3 and 4). The absence of  $\text{Zn}(\text{OAc})_2$  resulted in the formation of **3a** in 49% yield, whereas the increased formation of **4a** (27%) suggested that the co-catalyst  $\text{Zn}(\text{OAc})_2$  promotes the generation of **3**. It should be noted that no traces of the corresponding dihydrogenated adduct **5** or ethynyloxy-substituted benzocyclobutene **6** were observed. This observation is consistent with the formation of a four-membered cycle and subsequent dihydrogenation.

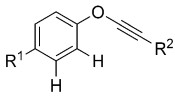
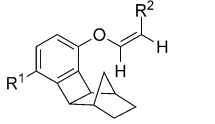
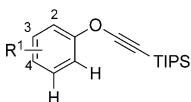
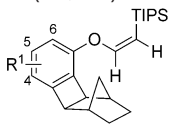
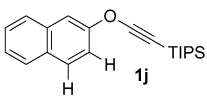
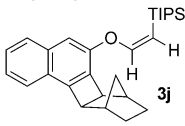
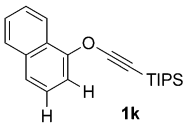
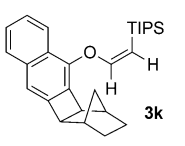
Next, the scope of the twofold C–H cleavage reaction with **2a** using a suitable ligand, namely  $\text{PCy}_3$ ,  $\text{P}^t\text{BuAd}_2$ , or XPhos, was examined, and the results are also summarized in Table 1. In the presence of  $\text{P}^t\text{BuAd}_2$  at a lower concentration of 0.1 M, *tert*-butyldiphenylsilyl (TBDPS)-substituted ethynyl ether **1b** furnished cyclization product **3b** in 82% yield (entry 5).<sup>[11]</sup> Using XPhos, the substrate with a less bulky *tert*-butyldimethylsilyl (TBDMS) group afforded **3c** in lower yield (entry 6). Aryl *tert*-butylalkynyl ether **1d** could also be converted into **3d** in 51% yield in the presence of the XPhos ligand (entry 7). Substrates with a cyclohexyl, methyl, or phenyl group instead of the *tert*-butyl group attached to the ethynyl moiety were not suitable for this reaction.<sup>[12]</sup> These results suggest that a bulky substituent on the ethynyl carbon atom is necessary for effective double C–H cleavage. The presence of *para*-, *meta*-, and *ortho*-substituted aryl groups in the TIPS ethynyloxy moiety did not hamper the reaction (entries 8–12). Silylethynyl 4-biphenyl ether **1i** afforded **3i** in

[\*] Dr. Y. Minami, Prof. Dr. T. Hiyama  
Research and Development Initiative  
Chuo University and JST, ACT-C  
Kasuga, Bunkyo-ku, Tokyo 112-8551 (Japan)  
E-mail: yminami@kc.chuo-u.ac.jp  
thiyama@kc.chuo-u.ac.jp

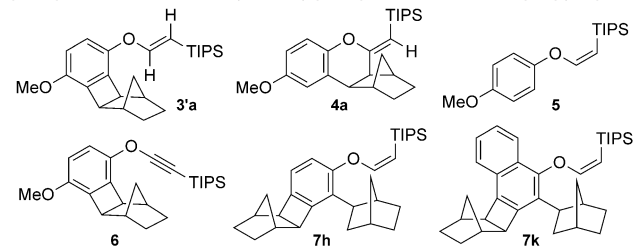
T. Kodama  
Department of Applied Chemistry, Chuo University  
Kasuga, Bunkyo-ku, Tokyo 112-8551 (Japan)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201505789>.

**Table 1:** Pd-catalyzed dehydrogenative cleavage of two C–H bonds.<sup>[a]</sup>

$\text{R}^1\text{---}\text{C}_6\text{H}_4\text{---}\text{O---C}\equiv\text{C---R}^2 + \text{2a} \xrightarrow[\text{toluene, 100 }^\circ\text{C}]{\text{Pd(OAc)}_2 \text{ (5 mol\%)} \\ \text{ligand (10 mol\%)} \\ \text{Zn(OAc)}_2 \text{ (20 mol\%)}}$				
Entry	Ligand	1 (R <sup>1</sup> , R <sup>2</sup> )	Time [h]	3 (R <sup>1</sup> , R <sup>2</sup> ) Yield [%] <sup>[b]</sup>
1	PCy <sub>3</sub>		24	 75
2 <sup>[c]</sup>	PCy <sub>3</sub>	<b>1a</b> (OMe, TIPS)	60	<b>3a</b> (OMe, TIPS) (69) <sup>[d]</sup>
3	PBuAd <sub>2</sub>	<b>1a</b>	24	<b>3a</b> (80) <sup>[e]</sup>
4	XPhos	<b>1a</b>	24	<b>3a</b> 86
5	PBuAd <sub>2</sub>	<b>1b</b> (OMe, TBDPS)	15	<b>3b</b> (OMe, TBDPS) 82
6	XPhos	<b>1c</b> (OMe, TBDMS)	13	<b>3c</b> (OMe, TBDMS) 40
7	XPhos	<b>1d</b> (Me, <i>t</i> Bu)	46	<b>3d</b> (Me, <i>t</i> Bu) 51
8	XPhos		21	 82
9	PCy <sub>3</sub>	<b>1f</b> (3-Me)	11	<b>3f</b> (5-Me) 71
10	XPhos	<b>1g</b> (2-Me)	11	<b>3g</b> (6-Me) 40
11	XPhos	<b>1h</b> (H)	8	<b>3h</b> (H) 47 <sup>[f]</sup>
12	XPhos	<b>1l</b> (4-Ph)	11	<b>3l</b> (4-Ph) 78
13	PCy <sub>3</sub>		12	 79
14	XPhos		17	 70 <sup>[g]</sup>

[a] Unless otherwise noted, a mixture of **1** (1 equiv), **2a** (5 equiv), Pd(OAc)<sub>2</sub> (5 mol%), ligand (10 mol%), Zn(OAc)<sub>2</sub> (20 mol%), and toluene (1 M for entries 1–4 and 8–14, 0.1 M for entries 5–7) was heated to 100°C. [b] Yield of isolated product. [c] **2a** (1.5 equiv). [d] Combined NMR yield of **3a** and **3'a** (67:33). [e] Combined NMR yield of **3a** and **3'a** (85:15). [f] **7h** was formed in 32% yield. [g] **7k** was formed in 10% yield. PBuAd<sub>2</sub> = *n*-butyldi-1-adamantylphosphine, XPhos = 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl.



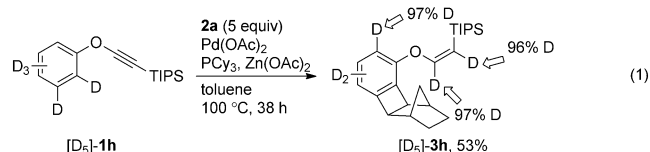
78% yield (entry 12); the molecular structure of **3i** was confirmed by single-crystal X-ray diffraction.<sup>[13]</sup> The 2- and 1-naphthyl-substituted TIPS-protected ethynyl ethers **1j** and **1k** provided the corresponding cyclic products **3j** and **3k** (entries 13 and 14). Substrates **1h** and **1k**, with an unsubstituted 4-position, also generated the side products **7h** and **7k**.

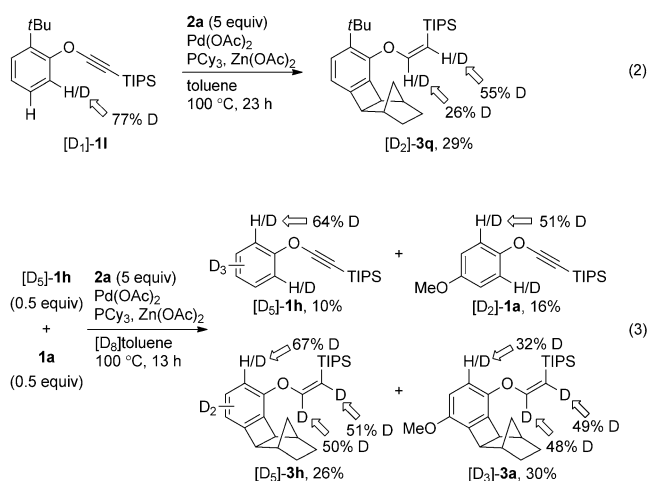
Subsequently, a variety of bicyclic alkenes were subjected to the double C–H functionalization reaction with **1j** (Table 2). In these cases, only the PCy<sub>3</sub> ligand was effective, whereas XPhos afforded the desired products in reduced yields or not at all. The reaction with norbornadiene (**2b**) provided monoannulated **3l** in 56% yield, whereas the cyclopentadiene dimer **2c** afforded **3m** in 78% yield. The presence of functional groups, such as esters or acid anhydrides, or benzannulated systems did not interfere with the reaction, and the desired products **3n–3p** were obtained in good yields.

Representative synthetic applications for compounds such as **3j** are shown in Scheme 1. For example, acid hydrolysis of **3j** with a catalytic amount of HCl furnished 2-naphthol derivative **8** in 72% yield.<sup>[14]</sup> When a stoichiometric amount of HCl was used, sequential deprotection and cyclization of **8** with an in situ generated aldehyde furnished 18*H*-dibenzo[*a,j*]xanthene **9**.<sup>[15]</sup>

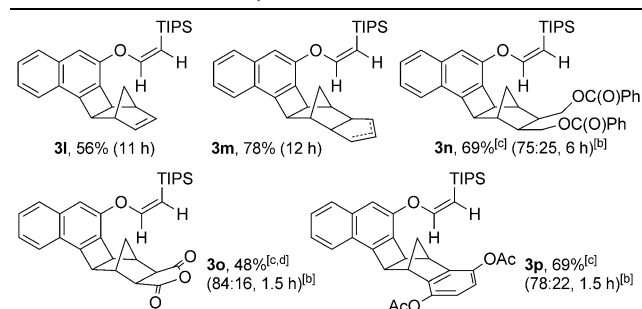
To elucidate the mechanism for the formation of **3**, deuterium-labeling experiments were carried out. As evident from <sup>1</sup>H NMR analysis, the reaction between deuterated [D<sub>5</sub>]-**1h** and **2a** in toluene in the presence of Pd(OAc)<sub>2</sub>/PCy<sub>3</sub>/Zn(OAc)<sub>2</sub> resulted in the formation of [D<sub>5</sub>]-**3h**, demonstrating that the deuterium atoms originally located at the *ortho* and *meta* positions selectively shifted to the silylthynyl group [Eq. (1)].<sup>[16]</sup> The reaction between [D<sub>1</sub>]-**1l**, which is deuterated only at the *ortho* position, provided [D<sub>2</sub>]-**3q**, with the deuterium atoms equally distributed over both vinyl carbon atoms [Eq. (2)]. A competition experiment between [D<sub>5</sub>]-**1h** and **1a** revealed that the three deuterium atoms from the 2-, 3-, and 6-positions in [D<sub>5</sub>]-**1h** migrated to the vinyl moieties and the 6-position in both [D<sub>5</sub>]-**3h** and [D<sub>1</sub>]-**3a**. Furthermore, H/D scrambling was observed at the *ortho* positions in the two recovered substrates [Eq. (3)].<sup>[17]</sup> These results suggest that cleavage of the *ortho* C–H bond should be reversible at an early stage and be followed by an irreversible *meta* C–H bond cleavage by a concerted metalation/deprotonation (CMD) pathway to form the aryl palladium complexes and acetic acid,<sup>[10,18]</sup> delivering the hydrogen atoms to each alkynyl carbon atom (for a proposed reaction mechanism, see the Supporting Information).

Having successfully established a dehydrogenative reaction system, we applied it to cross-dehydrogenative reactions involving other alkenes and heteroarenes. The reaction between **1j** and 1,4-epoxy-1,4-dihydronaphthalene (**10**)<sup>[19]</sup> using catalytic amounts of Pd(OAc)<sub>2</sub>, PCy<sub>3</sub>, and Zn(OAc)<sub>2</sub> at 100°C for 5 h afforded

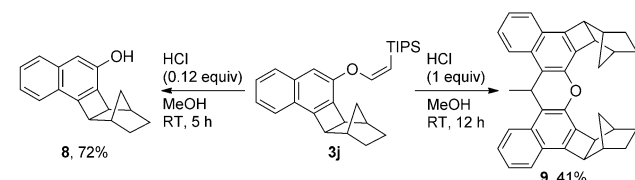




**Table 2:** Variation of the bicycloalkene.<sup>[a]</sup>



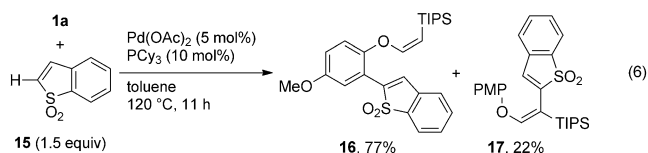
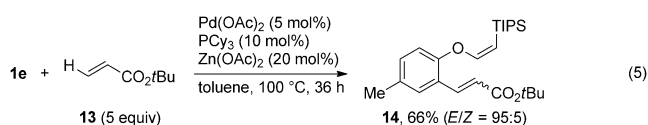
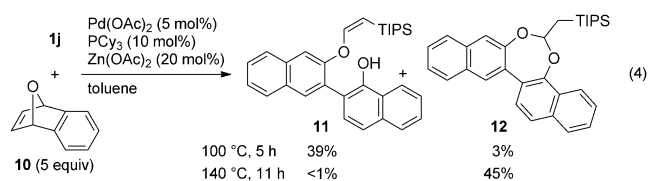
[a] Unless otherwise noted, a mixture of **1j** (1 equiv), **2** (1.5 equiv), Pd(OAc)<sub>2</sub> (5 mol %), PCy<sub>3</sub> (10 mol %), Zn(OAc)<sub>2</sub> (20 mol %), and toluene (1 M) was heated to 100 °C. Yields of isolated products are given. [b] Z/E ratio. [c] 140 °C. [d] Yield determined by NMR spectroscopy.



**Scheme 1.** Acid hydrolysis of **3j** with HCl.

the desired product **11** in 39% yield [Eq. (4)].<sup>[20]</sup> Conversely, when the reaction was carried out at 140 °C for 11 h, seven-membered dioxepin **12** was formed in 45% yield.<sup>[21]</sup> Subsequently, we examined the reaction with *tert*-butyl acrylate (**13**) and successfully obtained *ortho*-alkenylated *Z*-alkenoxy arene **14** in 66% yield [*E/Z* = 95:5;<sup>[22]</sup> Eq. (5)]. The bulky *tert*-butyl group in **13** was an important factor for the success of the alkenylation; *n*-butyl acrylate, acrylonitrile, or styrene only afforded traces of the corresponding *ortho*-alkenylated products under these conditions. Finally, we focused on the development of dehydrogenative cross-coupling reactions between two aromatic compounds to establish aryl–aryl bond-forming reactions. Therefore, we examined the reaction of **1a** and benzothiophene dioxide (**15**), which resulted in the

formation of *ortho*-arylated *Z*-alkenoxy arene **16** in 77% yield, together with the C–H *anti* addition product **17** in 22% yield in the presence of Pd(OAc)<sub>2</sub> and PCy<sub>3</sub> [Eq. (6)]. In this case, the absence of Zn(OAc)<sub>2</sub> was beneficial for the formation of **16**. However, the mechanistic details of the formation of both **16** and **17** still remain unclear at present.



In conclusion, we have described a series of dehydrogenative C–C bond-forming reactions involving alkynoxy groups. In the presence of Pd(OAc)<sub>2</sub>, a suitable phosphine ligand, and Zn(OAc)<sub>2</sub>, the reaction between alkynyl aryl ethers and bicycloalkenes resulted in the formation of vinyl-oxy benzocyclobutenes. Deuterium-labeling experiments demonstrated that the hydrogen atoms originally attached to the *ortho* and *meta* positions of the alkynyl aryl ethers are cleaved and transferred onto the vinyl carbon atoms. This catalytic reaction system can be applied to a variety of dehydrogenative reactions, for example, with 1,4-epoxy-1,4-dihydronaphthalene, *tert*-butyl acrylate, and benzothiophene dioxide, to form the corresponding products after C–C bond formation. The present reaction system, which induces a site-selective C–H bond cleavage, allows an additive-free dehydrogenative process, which is applicable to various alkenes and heteroarenes and generates desirable vinyloxy groups. Our current efforts are directed towards the further development of such dehydrogenative bond-forming reactions and towards a better understanding of the underlying reaction mechanisms.

## Acknowledgements

This work has been supported financially by Grants in-Aid for Scientific Research (S) (21225005 to T.H.) and Young Scientists (B) (25870747 to Y.M.) from the JSPS. Y.M. would also like to acknowledge the Asahi Glass Foundation.

**Keywords:** alkynes · annulation · C–C coupling · C–H activation · palladium

**How to cite:** *Angew. Chem. Int. Ed.* **2015**, *54*, 11813–11816  
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- [11] The low concentrations are necessary for high yields of **3b**, **3c**, and **3d**.
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- [13] CCDC 1400670 (**3i**), 1400671 (**7k**), and 1400672 (**12**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
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- [16] A kinetic isotope effect was not observed for the formation of **3h**, suggesting that the rate-determining step does not involve the hydrogen atoms in the *ortho* and *meta* positions.
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- [22] Alkenylated product **14** could not be isolated cleanly because of inseparable impurities. Therefore, the structure of **14** was eventually determined after hydrolysis of **14**. See the Supporting Information for experimental details.

Received: June 23, 2015

Revised: July 18, 2015

Published online: August 14, 2015