OL | Organic Letters

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

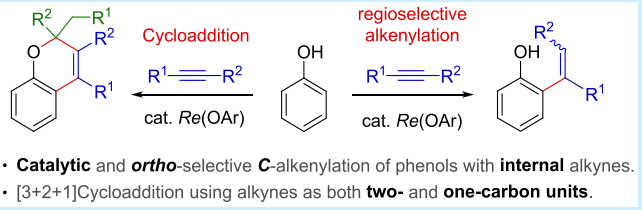
Rhenium-Catalyzed Regioselective *ortho*-Alkenylation and [3 + 2 + 1] Cycloaddition of Phenols with Internal Alkynes

Masahito Murai,* Masaki Yamamoto, and Kazuhiko Takai*

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

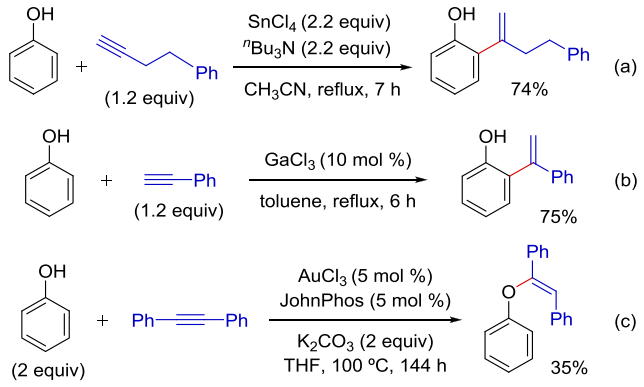
Supporting Information

ABSTRACT: An operationally simple and direct rhenium-catalyzed *ortho*-alkenylation (*C*-alkenylation) of unprotected phenols with alkynes was developed. The protocol provided *ortho*-alkenylphenols exclusively, and formation of *para*- or multiply alkenylated phenols and hydrophenoxylation (*O*-alkenylation) products were not observed. The [3 + 2 + 1] cycloaddition of phenols and two alkynes *via ortho*-alkenylation was also demonstrated, in which the alkynes functioned as both two- and one-carbon units. These reactions proceeded with readily available starting materials under neutral conditions without additional ligands.



Functionalization of inexpensive and abundant phenol derivatives for sustainable production of organic chemicals is an important challenge.[1] Phenols are ubiquitous structural motifs in biologically active compounds, pharmaceuticals, agrochemicals, lignin, and functional materials and are versatile building blocks in organic synthesis.[1b] Thus, development of methods to promote facile and efficient functionalization at specific ring positions is desirable. Among these reactions, additions to alkynes are attractive, because it enables the introduction of synthetically useful phenoxy and double-bond functionalities in the target molecules in an atom-efficient manner. The pioneering work was reported by Yamaguchi using a stoichiometric amount of $SnCl_4$ or $GaCl_3$ (Scheme 1a).[2] However, catalytic *C*-alkenylation of phenols remains limited to protocols involving electronically activated alkynoates,[3b,d] terminal acetylenes,[3a,e,g] or intramolecular cyclizations[3c,f,h] (Scheme 1b). This is because the unprotected phenolic hydroxy group has an acidic proton and usually acts as an oxygen-based nucleophile. Thus, hydrophenoxylation (C−O bond formation) occurs preferentially over C−C bond forming alkenylation of relatively inert C−H bonds (Scheme 1c).[4] Furthermore, functionalization of phenols often results in the formation of regioisomers and overreaction products due to the strong *ortho*-/*para*-orientation of the phenolic hydroxy group.[3]

Scheme 1. Previously Reported Methods for Alkenylation of Phenols



Although the reaction course and resulting addition strongly depend on interactions of phenol and alkyne in the transition state, the directing ability of the phenolic hydroxy group in well-established late transition-metal-catalyzed C−H bond functionalization appears to be relatively weak.[5] We envisioned that rhenium, a group 7 metal located between the early and late transition metals in the periodic table, and therefore possesses both soft and hard Lewis acidity, can alter the manner of addition of the reaction.[6,7] The present work demonstrated the rhenium-catalyzed *ortho*-selective *C*-alkenylation of unprotected phenols with alkynes. The resulting *ortho*-alkenyl phenols, classically synthesized by Claisen rearrangement of allylphenylethers, are useful compounds. The related and rare [3 + 2 + 1] cycloaddition of phenols with two alkynes leading to 2*H*-chromene derivatives is also described.

We found $Re_2(CO)_{10}$ was effective for the alkenylation of phenol with 1-phenyl-1-propyne in chlorobenzene (2 M) at 160 °C. 2-Alkenylphenol **1a** was obtained in 89% yield as a mixture of two stereoisomers, and the major stereoisomer had the *Z* configuration as determined by NOE studies. The formation of regioisomers was not observed at all. The reaction can be conducted even on 5 mmol scale (see eq S1 in the Supporting Information). Note that the use of $GaCl_3$, which was reported to promote alkenylation with terminal alkynes as shown in Scheme

Received: April 5, 2019

DOI: 10.1021/acs.orglett.9b01214
Org. Lett. XXXX, XXX, XXX−XXX

1c,[3d,e] failed to provide **1a**. Using $Re_2(CO)_{10}$ as a catalyst, the scope of the *ortho*-selective alkenylation was examined (Figure 1).[8] Electron-rich 4-methoxyphenol reacted smoothly with 1-

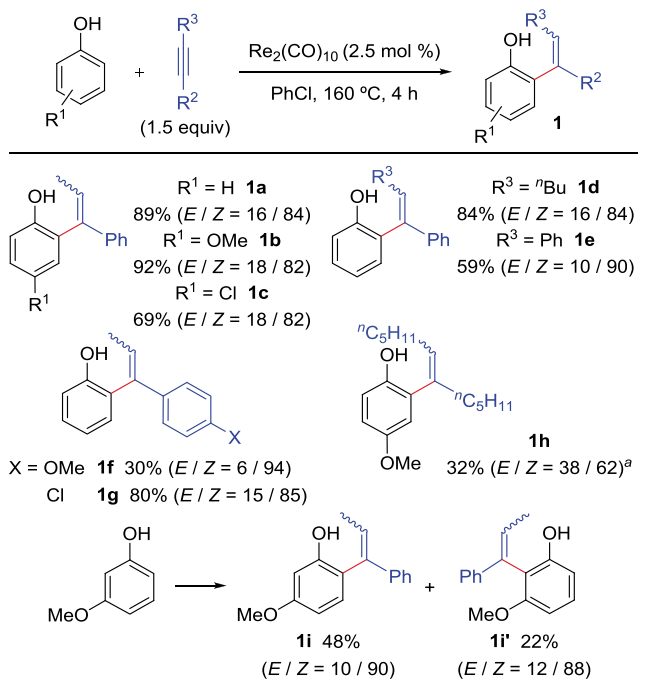


Figure 1. Rhenium-catalyzed regioselective alkenylation of phenol derivatives. Maximum yields are 95% as noted in ref 8. Stereoselectivity was determined by ^{1}H NMR. [a] 200 °C, 24 h.

phenyl-1-propyne to furnish **1b** in 92% yield. Despite the electronic nature of the substituents, alkenylation occur selectively at the position *ortho* to the phenolic hydroxy group, and the potentially coordinating methoxy group did not disturb the site selectivity.[9] Although the chloro group of 4-chlorophenol was well-tolerated and provided **1c**, substitution of these electron-withdrawing groups decreased reaction efficiency. Olefination of electron-poor 4-trifluoromethylphenol did not proceed, indicating that the current olefination reaction can be classified as electrophilic functionalization. Note that the reactivity trend was completely different from that of the classic Friedel–Crafts type electrophilic functionalization, in which multiple functionalizations and/or functionalization at the *para* position usually occur as competitive side reactions. The electronic effect of substituents on the alkyne also affected reaction efficiency. Although **1d** was obtained in 84% yield by reaction with 1-phenyl-1-hexyne, olefination with more sterically hindered diphenylacetylene was sluggish and furnished **1e** in moderate yield. The electron-rich methoxy group substituted arylalkyne provided the corresponding adduct **1f** in low yield due to competitive oligomerization of the alkyne under the reaction conditions. In contrast, alkenylation with relatively electron-poor 1-(4-chloropheny)-1-propyne gave the expected **1g** in 80% yield. Olefination with aliphatic alkynes, such as 6-dodecyne, was sluggish, and the corresponding adduct **1h** was obtained in low yield, even when heated at high temperature for a long period. When 3-methoxyphenol was used, formation of a regioisomeric mixture of the desired *ortho*-alkenylphenol was observed in a 69/31 ratio in favor of the sterically less hindered **1i**. Unfortunately, terminal alkynes oligomerized under the current reaction conditions, and did not provide the corresponding alkenylated products.[10]

During these studies, selective formation of 2*H*-chromene derivatives **2** *via* alkenylation of phenols proceeded by simply increasing the reaction time and amount of alkene.[11] In contrast to the usual reactivity of alkynes as two-carbon annulation partners in the $[n + n' + 2]$ cycloaddition,[12] this represents a rare example of [3 + 2 + 1] cycloaddition using alkynes as both two- and one-carbon units (Figure 2, left).[13] Reaction of phenols with

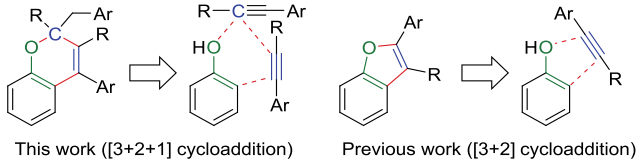


Figure 2. Novel reactivity of phenols toward internal alkynes.

alkynes was previously reported for the synthesis of benzofurans by formal [3 + 2] cycloaddition *via* hydrophenoxylation to alkynes (Figure 2, right).[14] Arylalkynes were used in these studies, resulting in selective attack by the oxygen atom of phenol on the aryl-group-substituted carbon atom of the alkyne. In the current study, the regioselectivity of the addition was the opposite, with the carbon atom of the phenoxy ring attacking the aryl group-substituted carbon atom of the alkyne.

Since the 2*H*-chromene skeleton is a common structural motif in biologically active compounds and optoelectronic materials, the generality of the current novel approach by [3 + 2 + 1] cycloaddition was examined briefly (Figure 3).[8,11] Cyclo-

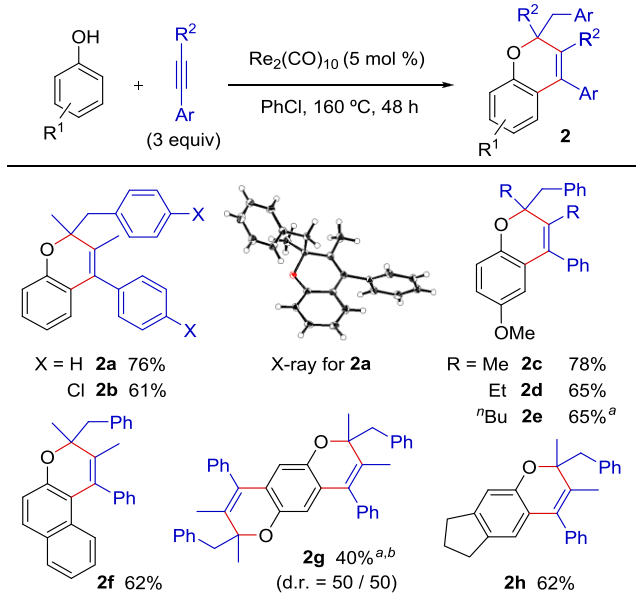


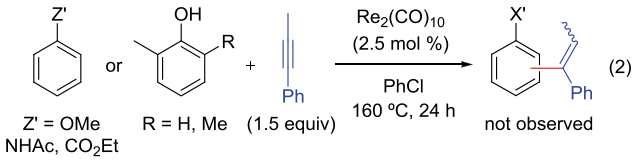
Figure 3. [3 + 2 + 1] Cycloaddition reaction of phenol with internal alkynes. The maximum yields are 90% as noted in ref 8. [a] $Re_2(CO)_{10}$ (10 mol %) or [b] alkyne (6 equiv) was used.

addition of phenol with 1-phenyl- or (4-chlorophenyl)-1-propyne gave **2a** and **2b**, respectively, in moderate to good yield. The structure of **2a** was determined unambiguously by single-crystal X-ray crystallography (see Figure S2 in the Supporting Information for details). Substitution of the methoxy group did not affect the reactivity and yielded the corresponding 2*H*-chromene derivatives **2c**, **2d**, or **2e**. 2-Naphthol was also a

DOI: 10.1021/acs.orglett.9b01214
Org. Lett. XXXX, XXX, XXX−XXX

suitable substrate to afford benzo[*f*]chromene **2f** *via* regioselective *C*-alkenylation at the most electron-rich 1-position without the formation of other regioisomers. Twofold [3 + 2 + 1] cycloaddition with hydroquinone, which is susceptible to oxidation, provided **2g** as a mixture of two diastereomers. Cyclopentane-fused tricycle **2h**, a potentially useful building block for constructing biologically active compounds and functional materials,[15] was obtained through regioselective alkenylation at the least sterically hindered position of the phenol ring.

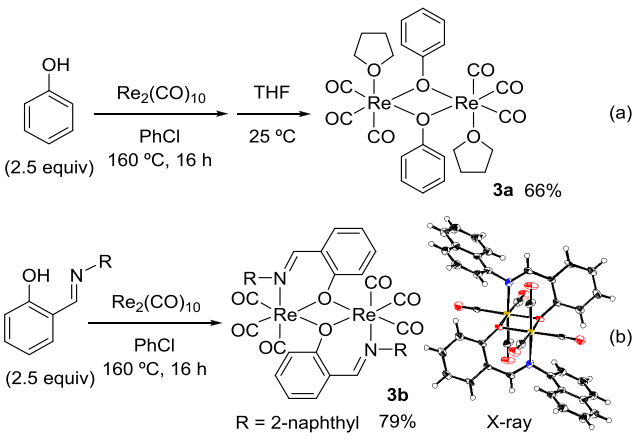
The current alkenylation proceeded selectively at the *ortho* position to provide only monoalkenylated products. The use of anisole, acetanilide, and ethyl benzoate, which are common substrates for regioselective functionalization based on C−H bond activation, in place of phenol did not afford any alkenylation products, but resulted in the recovery of the aromatic starting materials (eq 2). Furthermore, sterically



hindered phenol derivatives with a methyl group at the *ortho* position also prevented the alkenylation reaction at any position, indicating that interaction of the phenoxy oxygen atom with the rhenium center is key for the current transformation.

As expected, the phenoxy-bridged rhenium carbonyl dimer, $[Re(OPh)(CO)_3(thf)]_2$ **4a**, was obtained exclusively by reaction of $Re_2(CO)_{10}$ with phenol, followed by treatment with THF to stabilize the resulting complex (Scheme 2a). The

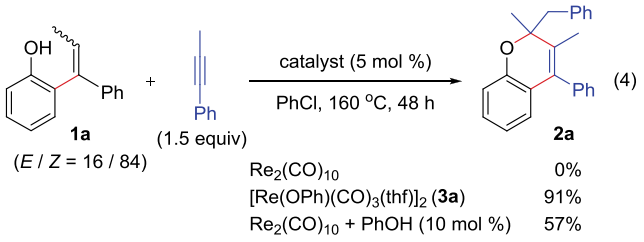
Scheme 2. Synthesis and X-ray Crystal Structure (Yellow, Re; Blue, N; Red, O) of $[Re(OAr)(CO)_3(thf)_n]_2$ Complexes 3[a]



[a]Solvent atoms were omitted from the ORTEP drawing for clarity.

structure was tentatively assigned by the results of NMR and elemental analysis (see SI for details).[16] A structurally characterizable single crystal of the (*μ*-phenoxo)rhenium complex **3b** was obtained using 2-iminophenol as a substrate (Scheme 2b). The ORTEP drawing clearly showed an aryloxy ligand-bridged dinuclear rhenium structure stabilized by coordination of nitrogen atoms of the imino groups at the apical position (see also Figure S3 in the Supporting Information). The isolated **3a** was confirmed to perform well as a catalyst for the current alkenylation.

Complex **3a** also catalyzed the conversion of 2-alkenylphenol **1a** to 2*H*-chromenes **2a**, which demonstrated that **1** was an intermediate for formation of **2** (eq 4). Unexpectedly, this [5 + 1] cycloaddition did not proceed when only $Re_2(CO)_{10}$ was used as the catalyst, and addition of a catalytic amount of phenol was required. The (*μ*-phenoxo)rhenium complex **3a** prepared *in situ* by reaction of $Re_2(CO)_{10}$ and PhOH demonstrated catalytic performance. These results clearly show that the real catalyst was an aryloxyrhenium species, and phenol derivatives having substituents at the 2-position did not work as precursors as shown in eq 2 due to steric hindrance. While the exact role of the phenoxy ligand was not clear, it was indispensable for the current alkenylation and cycloaddition, and no reaction occurred with $[ReBr(CO)_3(thf)]_2$ as a catalyst.



Based on these results, the proposed reaction mechanism for formation of 2-alkenylphenol **1a** and 2*H*-chromene **2a** is shown in Figure 4, which exemplifies the reaction of phenol with 1-

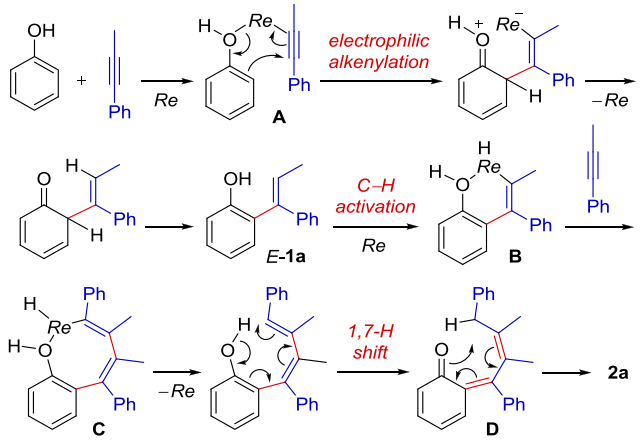


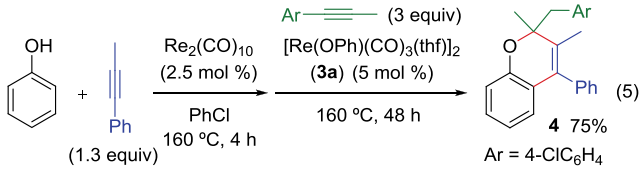
Figure 4. Proposed reaction mechanism (*Re* = $Re(OPh)(CO)_3$).

phenyl-1-propyne. First, nucleophilic attack of phenol occurred site selectively at the position *ortho* to the phenolic hydroxy group, which was assisted by coordination of both the phenol and alkyne to the rhenium centers in intermediate **A**.[17,18] Only rhenium catalysts exhibited activity toward the current *ortho*-alkenylation, likely due to the unique soft and hard Lewis acid nature of rhenium, a metal between the early and late transition metals in the periodic table.[6] Thus, low-valent rhenium carbonyl complexes could activate both the soft carbon−carbon triple bonds of alkynes and the hard oxygen atoms of phenol at the same time, to promote the addition reaction. Subsequent protonation and isomerization initially furnished *E*-**1a**, which was rapidly isomerized via a 1,5-H shift to a mixture of two stereoisomers *E*- and *Z*-**1a**. Then, phenolic hydroxy-group-directed C(sp^2)−H bond activation in the *E*-configuration,[5,19]

DOI: 10.1021/acs.orglett.9b01214
Org. Lett. XXXX, XXX, XXX−XXX

followed by insertion of an alkyne, resulted in the eight-membered ring oxarhenacycle intermediate **C**. The terminal alkenyl carbon of **1a** selectively attacked the methyl-group-substituted carbon atom of an alkyne, which proceeded via a C−H activation/insertion mechanism, not a Friedel−Crafts-type electrophilic alkenylation mechanism. Reductive elimination then afforded 2-dienylphenol intermediates, which finally converted into 2*H*-chromene **2a** via a 1,7-H shift followed by oxa-6π-electrocyclization of *ortho*-quinone methide intermediate **D**.[20,21]

Three-component coupling of phenol and two different alkynes via [3 + 2 + 1] cycloaddition was examined to demonstrate the utility of the present 2*H*-chromene synthesis. The expected multiple-substituted chromene derivative **4** was obtained in 75% yield by sequential treatment of two different alkynes (eq 5). Addition of a catalytic amount of (μ-phenoxo) rhenium complex **3a** along with treatment of the second alkyne greatly promoted the formation of 2*H*-chromene.



In conclusion, a facile and practical method for *ortho*-alkenylation of phenols with complete site selectivity and regioselectivity was achieved using a rhenium catalyst. In contrast to classic Friedel−Crafts electrophilic functionalization (proceeding with *ortho*- and *para*-orientation to yield a mixture of mono- and multisubstituted adducts), reaction occurred selectively at the position *ortho* to the phenolic hydroxy group, providing selectively monoalkenylated phenols. Although a high temperature was required, these reactions proceeded with readily available starting materials under neutral conditions without additional ligands. These reaction schemes offer new insights into the reactivity of phenols and expand their potential as a readily available inexpensive chemical feedstock for synthesis of biologically active molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01214.

Experimental procedures, spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1873674 and 1873676 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: masahito.murai@okayama-u.ac.jp.
*E-mail: ktakai@cc.okayama-u.ac.jp.

ORCID

Masahito Murai: 0000-0002-9694-123X
Kazuhiko Takai: 0000-0002-2572-0851

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by a Grant-in-Aid for Scientific Research (No. 18H03911) from MEXT, Japan.

■ REFERENCES

(1) (a) Tyman, J. H. P. *Synthetic and Natural Phenols*; Elsevier: 1996. (b) Yamaguchi, M. In *The Chemistry of Phenols*; Rappoport, Z., Ed.; John Wiley & Sons, Ltd.: Chichester, 2003; pp 661−712.

(2) (a) Yamaguchi, M.; Hayashi, A.; Hirama, M. *J. Am. Chem. Soc.* **1995**, *117*, 1151. (b) Yamaguchi, M.; Arisawa, M.; Kido, Y.; Hirama, M. *Chem. Commun.* **1997**, 1663. (c) Yamaguchi, M. *Pure Appl. Chem.* **1998**, *70*, 1091.

(3) For catalytic C-alkenylation of unprotected phenol derivatives, see: (a) Kobayashi, K.; Yamaguchi, M. *Org. Lett.* **2001**, *3*, 241. (b) Trost, B. M.; Toste, F. D.; Greenman, K. Atom Economy. *J. Am. Chem. Soc.* **2003**, *125*, 4518. (c) Nevado, C.; Echavarren, A. M. *Chem. - Eur. J.* **2005**, *11*, 3155. (d) Yadav, J. S.; Subba Reddy, B. V.; Gupta, M. K.; Dash, U.; Pandey, S. K. *Synlett* **2007**, *2007*, 809. (e) Yadav, J. S.; Subba Reddy, B. V.; Sengupta, S.; Biswas, S. K. *Synthesis* **2009**, *2009*, 1301. (f) Arcadi, A.; Blesi, F.; Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Marinelli, F. *Org. Biomol. Chem.* **2012**, *10*, 9700. (g) Rao, V. K.; Shelke, G. M.; Tiwari, R.; Parang, K.; Kumar, A. *Org. Lett.* **2013**, *15*, 2190. (h) Nemoto, T.; Matsuo, N.; Hamada, Y. *Adv. Synth. Catal.* **2014**, *356*, 2417.

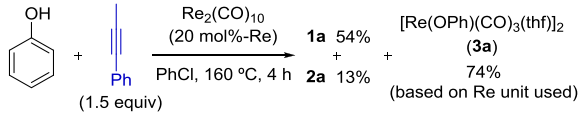
(4) (a) Camacho, D. H.; Saito, S.; Yamamoto, Y. *Tetrahedron Lett.* **2002**, *43*, 1085. (b) Kuram, M. R.; Bhanuchandra, M.; Sahoo, A. K. *J. Org. Chem.* **2010**, *75*, 2247. (c) Oonishi, Y.; Gómez-Suárez, A.; Martin, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 9767.

(5) The type of catalytic C−H bond functionalization possible for unprotected phenol derivatives is limited. 2-Arylphenols were used as substrates in most reactions. For representative examples, see: (a) Miura, M.; Tsuda, T.; Satoh, T.; Nomura, M. *Chem. Lett.* **1997**, *26*, 1103. (b) Dorta, R.; Togni, A. *Chem. Commun.* **2003**, 760. (c) Xiao, B.; Gong, T.-J.; Liu, Z.-J.; Liu, J.-H.; Luo, D.-F.; Xu, J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 9250. (d) Seoane, A.; Casanova, N.; Quiñones, N.; Mascareñas, J. L.; Gulías, M. *J. Am. Chem. Soc.* **2014**, *136*, 7607. (e) Yu, Z.; Ma, B.; Chen, M.; Wu, H.-H.; Liu, L.; Zhang, J. *J. Am. Chem. Soc.* **2014**, *136*, 6904.

(6) For reviews, see: (a) Kuninobu, Y.; Takai, K. *Chem. Rev.* **2011**, *111*, 1938. (b) Mao, G.; Huang, Q.; Wang, C. *Eur. J. Org. Chem.* **2017**, *2017*, 3549. For our recent contribution, see: (c) Hori, S.; Murai, M.; Takai, K. *J. Am. Chem. Soc.* **2015**, *137*, 1452. (d) Nakagiri, T.; Murai, M.; Takai, K. *Org. Lett.* **2015**, *17*, 3346. (e) Murai, M.; Uemura, E.; Hori, S.; Takai, K. *Angew. Chem., Int. Ed.* **2017**, *56*, 5862. (f) Murai, M.; Uemura, E.; Takai, K. *ACS Catal.* **2018**, *8*, 5454. (g) Murai, M.; Ogita, T.; Takai, K. *Chem. Commun.* **2019**, *55*, 2332.

(7) For rhenium-catalyzed *ortho* selective alkylation of phenols, see: (a) Kuninobu, Y.; Matsuki, T.; Takai, K. *J. Am. Chem. Soc.* **2009**, *131*, 9914. (b) Kuninobu, Y.; Yamamoto, M.; Nishi, M.; Yamamoto, T.; Matsuki, T.; Murai, M.; Takai, K. *Org. Synth.* **2017**, *94*, 280.

(8) For alkenylation under the conditions shown below, a 74% yield of $[Re(OPh)(CO)_3(thf)]_2$ **3a** was obtained based on the $Re_2(CO)_{10}$ employed. This result suggested that 2 equiv of phenol derivatives relative to $Re_2(CO)_{10}$ were consumed for the formation of (μ-phenoxo) rhenium complex **3a**, and did not participate in the catalytic alkenylation.



DOI: 10.1021/acs.orglett.9b01214
Org. Lett. XXXX, XXX, XXX−XXX

(9) (a) Oyamada, J.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 10720. (b) Oyamada, J.; Hou, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 12828.

(10) Phenol derivatives having amino and cyano groups failed to provide alkenylated products in the reaction with 1-phenyl-1-propyne. Addition of amines, such as triethylamine, DABCO, and pyridine, decreased the yield of **1a**. See ref 6f for the effect of amines in the rhenium-catalyzed transformation.

(11) Functionalized 2*H*-chromenes are important targets in organic synthesis. See: (a) Ferreira, S. B.; da Silva, F. de C.; Pinto, A. C.; Gonzaga, D. T. G.; Ferreira, V. F. *J. Heterocycl. Chem.* **2009**, *46*, 1080. (b) Pratap, R.; Ram, V. *Chem. Rev.* **2014**, *114*, 10476. (c) Majumdar, N.; Paul, N. D.; Mandal, S.; de Bruin, B.; Wulff, W. D. *ACS Catal.* **2015**, *5*, 2329. (d) Graham, T. J. A.; Doyle, A. G. *Org. Lett.* **2012**, *14*, 1616 and references cited therein .

(12) (a) Varela, J. A.; Saá, C. *Chem. Rev.* **2003**, *103*, 3787. (b) Domínguez, G.; Pérez-Castells, J. *Chem. Soc. Rev.* **2011**, *40*, 3430. (c) Broere, D. L. J.; Ruijter, E. *Synthesis* **2012**, *44*, 2639. (d) Tanaka, K., Ed. *Transition-Metal-Mediated Aromatic Ring Construction*; John Wiley & Sons: Hoboken, NJ, 2013.

(13) For an [*n* + 1] cycloaddition using internal alkynes as one-carbon components, see: (a) Villeneuve, K.; Tam, W. *Organometallics* **2006**, *25*, 843. (b) Burns, D. J.; Lam, H. W. *Angew. Chem., Int. Ed.* **2014**, *53*, 9931. (c) Yan, H.; Wang, H.; Li, X.; Xin, X.; Wang, C.; Wan, B. *Angew. Chem., Int. Ed.* **2015**, *54*, 10613. (d) Hong, S. Y.; Jeong, J.; Chang, S. *Angew. Chem., Int. Ed.* **2017**, *56*, 2408. (e) Wang, C.-Q.; Ye, L.; Feng, C.; Loh, T.-P. *J. Am. Chem. Soc.* **2017**, *139*, 1762.

(14) (a) Kuram, M. R.; Bhanuchandra, M.; Sahoo, A. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 4607. (b) Zeng, W.; Wu, W.; Jiang, H.; Huang, L.; Sun, Y.; Chen, Z.; Li, X. *Chem. Commun.* **2013**, *49*, 6611. (c) Zhu, R.; Wei, J.; Shi, Z. *Chem. Sci.* **2013**, *4*, 3706.

(15) (a) Kuck, D. *Chem. Rev.* **2006**, *106*, 4885. (b) Aitken, D. J.; Eijsberg, H.; Frongia, A.; Ollivier, J.; Piras, P. P. *Synthesis* **2013**, *46*, 1. (c) Chen, J.-R.; Hu, X.-Q.; Lu, L.-Q.; Xiao, W.-J. *Chem. Rev.* **2015**, *115*, 5301.

(16) Since all attempts to obtain the exact molecular weight of $[Re(OPh)(CO)_3(thf)]_n$ (**3a**) by mass spectrometry failed, the number of rhenium nuclei was unclear. A tentative structure for the dimer is shown in Scheme 2. The catalyst loading in this study was calculated based on the number of rhenium units.

(17) Because formation of *para*-alkenylated phenols was not observed in the current transformation, intermolecular nucleophilic attack of phenols to alkynes without proceeding through intermediate **A** in Figure 4 can be ruled out.

(18) A possible alternative mechanism for alkenylation via C−H bond activation of phenol followed by addition of rhenium hydride species via a stepwise radical rebound mechanism cannot be ruled out completely. See: Lehnherr, D.; Wang, X.; Peng, F.; Reibarkh, M.; Weisel, M.; Maloney, K. M. *Organometallics* **2019**, *38*, 103.

(19) Although a concerted metalation/deprotonation mechanism is proposed for formation of intermediate **B** by C−H activation in Figure 4, an alternative route *via* dearomatization/rearomatization (see eq S2 in the SI) cannot be ruled out.

(20) Oxacycles formation via a 1,7-H shift followed by oxa-6π-electrocyclization is rare. See: (a) Parker, K. A.; Mindt, T. L. *Org. Lett.* **2001**, *3*, 3875. (b) Ramachary, D. B.; Narayana, V. V.; Ramakumar, K. *Eur. J. Org. Chem.* **2008**, *2008*, 3907. For reviews on the synthesis of chromene derivatives via electrocyclization of *ortho*-quinone methide intermediates, see: (c) Beaudry, C. M.; Malerich, J. P.; Trauner, D. *Chem. Rev.* **2005**, *105*, 4757. (d) Ferreira, S. B.; da Silva, F. C.; Pinto, A. C.; Gonzaga, D. T. G.; Ferreira, V. F. *J. Heterocycl. Chem.* **2009**, *46*, 1080.

(21) An alternative mechanism for oxacycle formation *via* the following rhenium-catalyzed 6-*exo*-*dig* cyclization cannot be ruled out (see eq S3 in the SI).

DOI: 10.1021/acs.orglett.9b01214
Org. Lett. XXXX, XXX, XXX−XXX