OL | Organic Letters

pubs.acs.org/OrgLett Letter

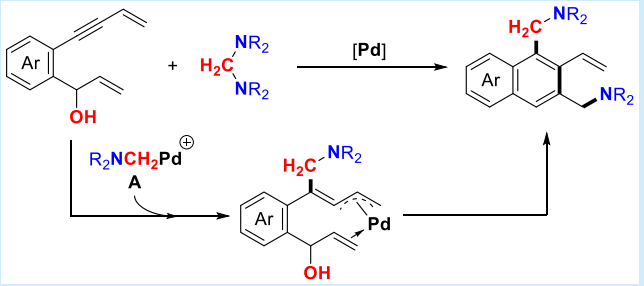
Palladium-Catalyzed Chemoselective Aminomethylative Cyclization and Aromatizing Allylic Amination: Access to Functionalized Naphthalenes

Bangkui Yu, Houjian Yu, and Hanmin Huang*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c03365 Read Online

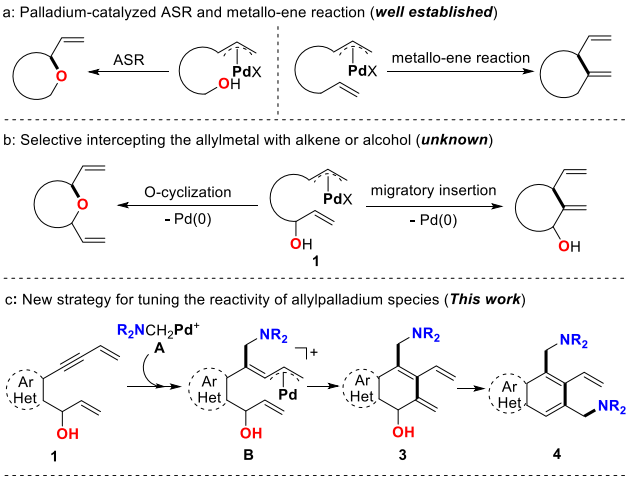
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A palladium-catalyzed chemoselective aminomethylative cyclization and aromatizing allylic amination of enyne-tethered allylic alcohols with aminals is described. Under the reaction conditions, the cationic vinyl allylpalladium species undergoes selective migratory insertion of alkenes rather than reductive elimination with nucleophiles. This strategy provides an efficient and unique approach to the construction of functionalized naphthalenes, which are important building blocks in synthetic organic chemistry. Mechanistic studies have revealed that the selective sequential migratory insertion of enyne and alkene is crucial for the cyclization.



Palladium-catalyzed allylic substitution reactions (ASRs) pioneered by Tsuji and Trost have been widely applied in organic chemistry.[1] Many classes of carbon-centered nucleophiles and heteroatom-centered nucleophiles can be employed to intercept the key allylpalladium intermediates via reductive elimination.[2] Oppolzer has discovered that the allylpalladium species could also be intercepted by adjoining olefins through migratory insertion (Scheme 1a).[3] Such a transformation has found widespread use in constructing five- or six-membered carbocycles and heterocycles.[4] However, when both active heteroatom-centered nucleophiles and olefin moieties are present in such an allylpalladium intermediate, the corresponding cyclization reaction would become intricate as it is hard to control the active allylmetal species to be selectively intercepted by the alkenes through migratory insertion (Scheme 1b). Herein, we describe an approach for facilitating the palladium capture of the alkene and enabling the allylpalladium species to be selectively intercepted by alkenes via enhancing the electrophilicity of the palladium center of the allylpalladium species.

Scheme 1. Cyclization of Allylpalladium Species with Adjoining Alkenes or a Nucleophile



We envisioned that tuning the electronic nature of the metal center of the allylpalladium species could facilitate it to undergo alkene insertion. Previous pioneering studies have established that the insertion of alkene into the M−C bonds of metal complexes containing more electrophilic metal centers is faster than those into M−C bonds of complexes containing more electron-rich metal centers.[5] In this context, it would be expected that the migratory insertion of alkene incurred by the π-allylpalladium could be facilitated by the electron-deficient allylic ligands. Recently, our research group has established a highly chemo- and regioselective 1,4-aminomethylamination of 1,3-enynes with aminals to afford allenic 1,5-diamines,[6] in which the cationic vinyl π-allylpalladium species was generated as a key intermediate.[7] The vinyl allylic ligand possessing stronger electron acceptability than alkyl ones could render the

Received: October 8, 2020

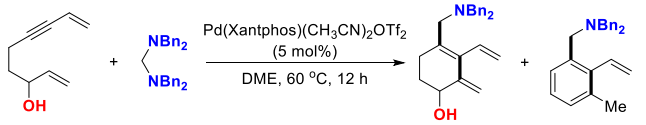
https://dx.doi.org/10.1021/acs.orglett.0c03365
Org. Lett. XXXX, XXX, XXX−XXX

coordinated palladium center more electrophilic to capture the alkene to undergo migratory insertion with the corresponding allylpalladium species.

Fascinated and inspired by this unique feature, we envisioned that cationic vinyl π-allylpalladium species **B** generated from enyne-tethered allylic alcohols **1** via migratory insertion of enyne into the C−Pd bond of cationic palladium complex **A** should favor the alkene insertion to exclusively furnish the metallo-ene reaction (Scheme 1c).

To test the viability of the cascade reaction, substrate **1a** was subjected to 5 mol % $Pd(Xantphos)(CH_3CN)_2OTf_2$ and aminal **2a** at 80 °C in THF (Scheme 2). Gratifyingly, the

Scheme 2. Initial Result for the Aminomethylative Cyclization via Sequential Alkyne and Alkene Insertion



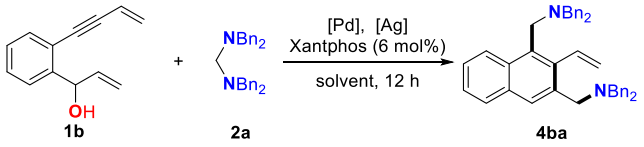
corresponding cyclization product was formed in 76% yield along with **4aa**, which might be generated from **3aa** via C−O bond cleavage and aromatization. The O-trapping product arising from reductive elimination with -OH was not detected.

Inspired by this initial result, we envisioned that if benzene-tethered enyne-allylic alcohol were subjected to the reaction condition, the subsequent dehydration−aromatization reaction would be favored to give the corresponding functionalized naphthalenes.[8]

To verify the feasibility of the proposed cascade reaction, we began our investigation with the reaction between 1-[2-(but-3-en-1-yn-1-yl)phenyl]prop-2-en-1-ol (**1b**) and *N,N,N′,N′*-tetrabenzylmethanediamine (**2a**) in CH_2Cl_2 at 80 °C with $Pd(CH_3CN)_2Cl_2$ as a catalyst precursor and AgOTf as an additive. To our surprise, an unexpected functionalized naphthalene **4ba** with two amine moieties was obtained in 57% yield when Xantphos served as the ligand (Table 1, entry 1). Product **4ba** could be viewed as incorporating one molecule of aminal into the naphthalene skeleton. Inspired by this promising result, we next sought to improve the efficiency of the cascade cyclization and substituted reaction. Screening of the solvent demonstrated that the corresponding naphthalene product **4ba** could be obtained in 81% yield with THF as the solvent (Table 1, entries 1−5). Subsequently, several other palladium catalyst precursors were examined, and it was found that almost no desired product was observed with $Pd(OAc)_2$ or $Pd_2(dba)_3$ as the palladium source (Table 1, entries 6−8). However, the reaction performed well in the presence of a catalytic amount of AgOTf or HOTf with $Pd_2(dba)_3$ as the palladium source (Table 1, entries 9 and 10), indicating the importance of TfO^- as a counteranion for cationic palladium species and that the Pd(0) was involved in the reaction presented here. As expected, almost the same yield (83%) of **4ba** was gained when cationic palladium Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ was utilized as the catalyst (Table 1, entry 11). In addition, the decrease in reaction temperature has diminished the reactivity (Table 1, entry 12). The yield of **4ba** was not improved further by slightly adjusting the ratio of starting materials (Table 1, entry 13).

With the optimal reaction conditions in hand, the generality of this palladium-catalyzed cascade process was investigated.

Table 1. Optimization of the Reaction Conditions[a]

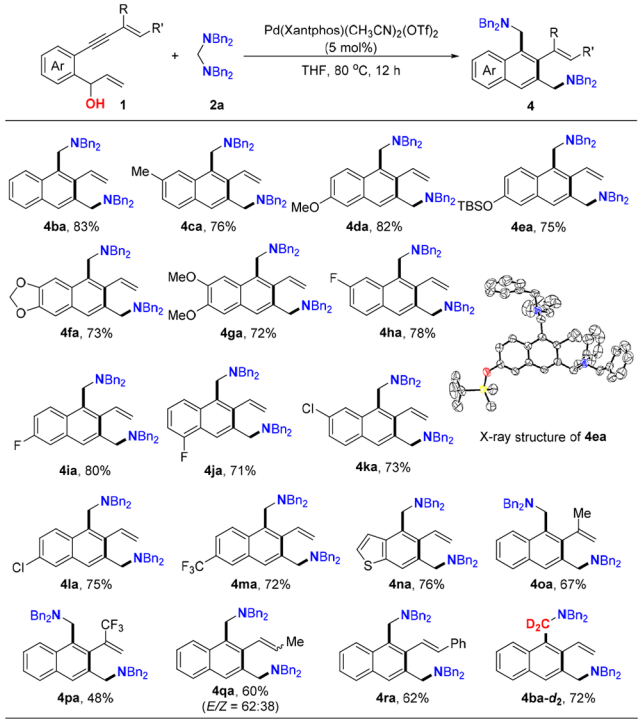


entry	catalyst	additive	solvent	yield (%)[b]
1	$Pd(CH_3CN)_2Cl_2$	AgOTf	DCM	57
2	$Pd(CH_3CN)_2Cl_2$	AgOTf	THF	81
3	$Pd(CH_3CN)_2Cl_2$	AgOTf	TBME	40
4	$Pd(CH_3CN)_2Cl_2$	AgOTf	dioxane	57
5	$Pd(CH_3CN)_2Cl_2$	AgOTf	CH_3CN	60
6	$[Pd(allyl)Cl]_2$	AgOTf	THF	76
7	$Pd(OAc)_2$	–	THF	trace
8	$Pd_2(dba)_3$	–	THF	0
9	$Pd_2(dba)_3$	AgOTf	THF	68
10	$Pd_2(dba)_3$	HOTf	THF	62
11	Pd(Xantphos)$(CH_3CN)_2(OTf)_2$	–	THF	83
12[c]	Pd(Xantphos)$(CH_3CN)_2(OTf)_2$	–	THF	58
13[d]	Pd(Xantphos)$(CH_3CN)_2(OTf)_2$	–	THF	82

[a]Reaction conditions: **1b** (0.3 mmol), **2a** (0.36 mmol), Pd (5 mol %), Ag (10 mol %), Xantphos (6 mol %), solvent (1.0 mL), 80 °C, 12 h. [b]Isolated yield. [c]At 60 °C. [d]**1b** (0.36 mmol), **2a** (0.30 mmol).

First, the substrate scope with respect to the enyne-tethered allylic alcohols was examined, and the results are summarized in Scheme 3. A series of enyne-tethered allylic alcohols bearing

Scheme 3. Substrate Scope of Enyne-Tethered Allylic Alcohols[a]



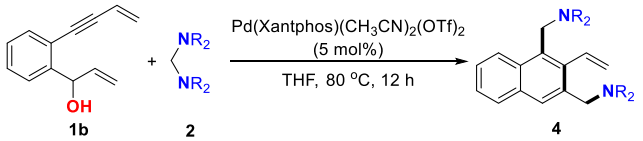
[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.36 mmol), Pd(Xantphos)-$(CH_3CN)_2(OTf)_2$ (5 mol %), THF (1.0 mL), 80 °C, 12 h. Isolated yield.

https://dx.doi.org/10.1021/acs.orglett.0c03365
Org. Lett. XXXX, XXX, XXX−XXX

different substituents in the phenyl ring reacted smoothly with aminal **2a**, leading to the corresponding products in moderate to good yields (**4ba**−**4ma**). There is no essential correlation between reactivity and the electronic properties of substituents on the phenyl ring, as both electron-donating substituents (CH_3, TBSO, and OCH_3) and electron-withdrawing groups (F, Cl, and CF_3) gave their corresponding naphthalene derivatives in good yields. Moreover, for substrates with disubstituents on the aryl ring, including the dimethoxy and methylenedioxy-substituted enyne-tethered allylic alcohols, the reactions proceeded well to deliver the desired products **4fa** and **4ga**, respectively, in good yields. Notably, similar results were obtained regardless of the substitution pattern of the substituents on the aryl ring (**4ha**−**4ja**). In addition, the thiophene-containing substrate was also compatible with this reaction, generating the corresponding thianaphthene **4na** in 76% yield. To our delight, the reaction could be extended to enyne-tethered allylic alcohols with methyl and trifluoromethyl functional groups attached at the β position of the alkene moiety, producing the desired products in moderate to good yields (**4oa** and **4pa**). The enyne-tethered allylic alcohols with substituents at the alkene terminus were also tolerated in this reaction system to afford the corresponding products in good yields (**4qa** and **4ra**). In addition, the benzyl-deuterated naphthalene derivative could be obtained with good yield and high selectivity from deuterated aminal under standard reaction conditions (**4ba**-d_2).

Next, we explored the scope of aminals for the synthesis of functionalized naphthalene derivatives. As shown in Table 2, a

Table 2. Substrate Scope of Aminals[a]



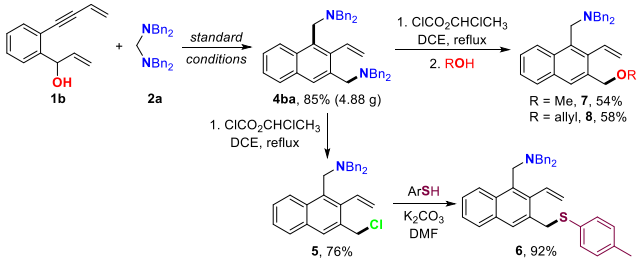
entry	R	4	yield (%)
1	$C_6H_5CH_2$-	**4ba**	83
2	4-Me$C_6H_4CH_2$-	**4bb**	73
3	4-*t*-Bu-$C_6H_4CH_2$-	**4bc**	70
4	4-F$C_6H_4CH_2$-	**4bd**	73
5	2-F$C_6H_4CH_2$-	**4be**	77
6	3-F$C_6H_4CH_2$-	**4bf**	65
7	4-Cl$C_6H_4CH_2$-	**4bg**	79
8	2-Cl$C_6H_4CH_2$-	**4bh**	77
9	4-Br$C_6H_4CH_2$-	**4bi**	41
10	4-$CF_3C_6H_4CH_2$-	**4bj**	66
11	(*S*)-*N*-benzyl-*N*-1-phenylethyl	**4bk**	74
12	-$CH_2CH_2OCH_2CH_2$-	**4bl**	60

[a]Reaction conditions: **1b** (0.3 mmol), **2** (0.36 mmol), Pd(Xantphos)-$(CH_3CN)_2(OTf)_2$ (5 mol %), THF (1.0 mL), 80 °C, 12 h. Isolated yield.

variety of aminals derived from dibenzylamines containing different substituents performed well to give the corresponding products in moderate to good yields (**4ba**−**4bj**). Either electron-donating (CH_3 and *t*-Bu) or electron-withdrawing (F, Cl, Br, and CF_3) groups on the phenyl moiety of aminals were tolerated well. Meanwhile, aminal derived from a chiral benzylamine gave the corresponding product (**4bk**) in 74% yield. Moreover, aminal prepared from alicyclic amines, such as morpholine, could give the corresponding functionalized naphthalene **4bl** in decent yield.

The synthetic versatility of this catalytic protocol was demonstrated through large-scale reaction and functional group transformations of the resulting naphthalene derivatives (Scheme 4). When the model reaction of enyne-tethered allylic

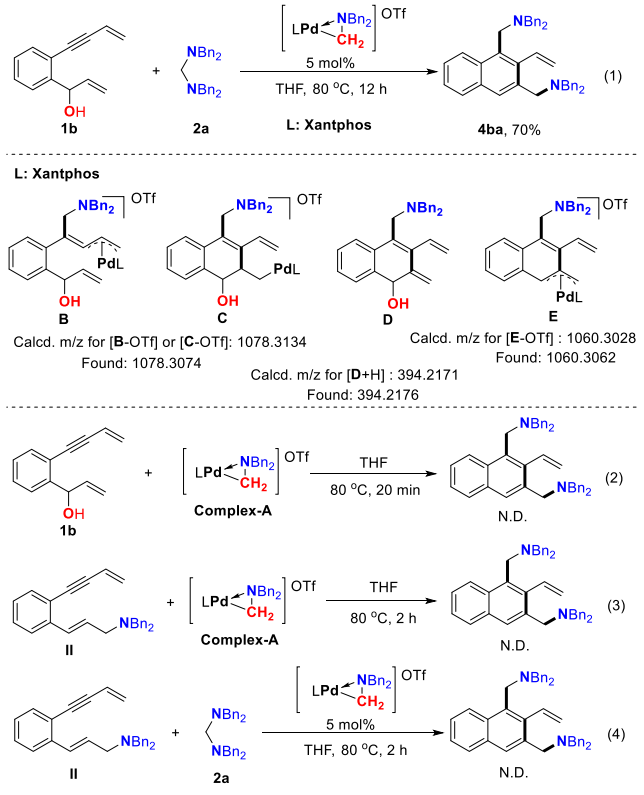
Scheme 4. Transformations of Product 4ba



alcohols **1b** and aminal **2a** was performed on a 10 mmol scale in the presence of 5 mol % catalyst, the corresponding product **4ba** was obtained in 85% yield (4.88 g). The C−N bond in compound **4ba** could be selectively cleaved with $ClCO_2CHClCH_3$ to form chlorinated product **5** [the structure of product **5** was determined by the comparison of the ^{1}H NMR spectra of products **4ba**, **4ba**-d_2, and **5** (for details, see the Supporting Information)].[9] Further nucleophilic attack by *p*-toluenethiol afforded the corresponding thioether **6** in 92% yield.[10] In addition, alkoxylated products **7** and **8** could also be obtained via a one-pot, two-step cascade reaction without separation of benzyl chloride **5**.

To gain insights into the possible mechanism of this process, several control experiments were conducted (Scheme 5). First,

Scheme 5. Control Experiments



https://dx.doi.org/10.1021/acs.orglett.0c03365
Org. Lett. XXXX, XXX, XXX−XXX

the catalytic reaction with Pd(Xantphos)(CH_2NBn_2)OTf (complex **A**)[11] as a catalyst was conducted, and the desired product **4ba** could be exclusively obtained in 70% yield, which indicated that complex **A** was most likely involved in this reaction. HRMS analysis of the reaction mixture showed a peak at m/z 1078.3074, which corresponded to the mass of $[\mathbf{B} - \mathrm{OTf}]^+$ or $[\mathbf{C} - \mathrm{OTf}]^+$. Another peak at m/z 1060.3062 was also detected, which was assigned to the mass of $[\mathbf{E} - \mathrm{OTf}]^+$. Intermediate **D** was also observed as the peak at m/z 1078.3074 was detected. These results supported that tentative intermediates **B** (or **C**), **D**, and **E** might be involved in the catalytic cycle of this transformation. Moreover, the stoichiometric reaction of **1b** and complex **A** was also conducted under the standard reaction conditions. Although no product **4ba** was observed, the HRMS analysis demonstrated that tentative intermediates **B** or **C** and **E** were also produced. In addition, to rule out the possibility that the reaction is initiated by the oxidative addition of allyl alcohol **1b** with Pd(0) to form intermediate **II**, the catalytic reaction and stoichiometric reaction with intermediate **II** and palladium complex **A** were carried out and we found that no desired product was detected. The results presented above excluded the possibility that the reaction goes through intermediate **II** (for details, see the Supporting Information).

On the basis of the results presented above and our previous work,[12] a plausible reaction mechanism was proposed (Figure 1). The reaction was initiated by the formation of cyclo-

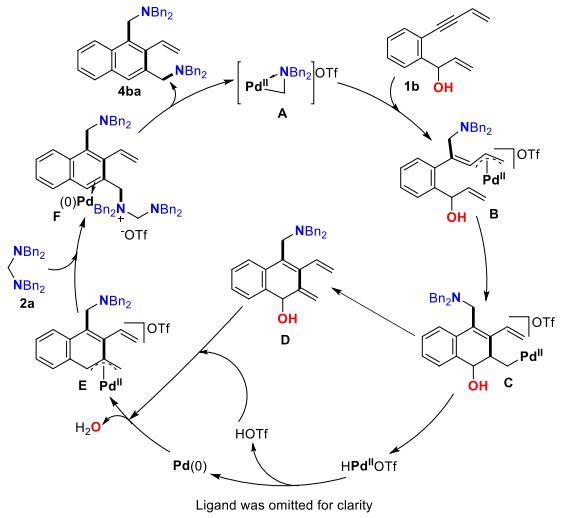


Figure 1. Proposed catalytic cycle.

palladated complex **A**. First, the triple bond of enyne-tethered allylic alcohols **1a** coordinates to the palladium center and then forms allylpalladium complex **B** by migratory insertion of the triple bond into the C−Pd bond of complex **A**. Subsequently, intramolecular migratory insertion of the double bond takes place to give alkylpalladium complex **C**, which is followed by β-hydride elimination to deliver intermediate **D** as well as HPdOTf. Reductive elimination of the palladium hydride species gives Pd(0), which undergoes oxidative addition with intermediate **D** to afford π-allylpalladium complex **E** aided by HOTf. Intermediate **E** is then intercepted by an aminal to form intermediate **F** via reductive elimination. Finally, the oxidative addition of intermediate **F** to Pd(0) delivers the desired product **4ba** together with regenerating active palladium complex **A** for the next catalytic cycle.

In summary, we have disclosed a strategy to facilitate π-allylpalladium species to be exclusively intercepted by alkene via enhancing the electrophilicity of the metal center, which realized the first metallo-ene-type cyclization with an O-centered nucleophile containing allylpalladium species. This method has enabled a palladium-catalyzed chemoselective aminomethylative cyclization and aromatizing allylic amination of enyne-tethered allylic alcohols with aminals via C−N and C−O bond activation. A wide range of functionalized naphthalenes have been obtained in good yields, which provides a versatile platform for the design of drugs and functional materials. Further investigation will be focused on the application of this strategy to many other palladium-catalyzed aminomethylation-aromatizing cyclization reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03365.

Experimental procedures and characterization data (PDF)

Accession Codes

CCDC 2032165 contains 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 Author

Hanmin Huang − *Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China; Center for Excellence in Molecular Synthesis of CAS, Hefei 230026, P. R. China;* orcid.org/0000-0002-0108-6542; Email: hanmin@ustc.edu.cn

Authors

Bangkui Yu − *Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China*

Houjian Yu − *Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c03365

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Natural Science Foundation of China (21672199, 21790333, 21925111, and 21702197).

■ REFERENCES

(1) For selected reviews of the Tsuji−Trost reaction, see: (a) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395−422. (b) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921−2943. (c) Trost, B. M.; Machacek, M. R.; Aponick, A. *Acc. Chem. Res.* **2006**, *39*, 747−

760. (d) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258−297. (e) Sundararaju, B.; Achard, M.; Bruneau, C. *Chem. Soc. Rev.* **2012**, *41*, 4467−4483. (f) Haydl, A. M.; Breit, B.; Liang, T.; Krische, M. J. *Angew. Chem., Int. Ed.* **2017**, *56*, 11312−11325. (g) Noreen, S.; Fawad Zahoor, A.; Ahmad, S.; Shahzadi, I.; Irfan, A.; Faiz, S. *Curr. Org. Chem.* **2019**, *23*, 1168−1213.

(2) For selected examples of allylic substitution reactions, see: (a) Jellerichs, B. G.; Kong, J.-R.; Krische, M. J. *J. Am. Chem. Soc.* **2003**, *125*, 7758−7759. (b) Kinoshita, H.; Shinokubo, H.; Oshima, K. *Org. Lett.* **2004**, *6*, 4085−4088. (c) Nemoto, T.; Matsumoto, T.; Masuda, T.; Hitomi, T.; Hatano, K.; Hamada, Y. *J. Am. Chem. Soc.* **2004**, *126*, 3690−3691. (d) Mohr, J. T.; Behenna, D. C.; Harned, A. M.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6924−6927. (e) Ibrahem, I.; Córdova, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1952−1956. (f) Bravo-Altamirano, K.; Montchamp, J.-L. *Org. Lett.* **2006**, *8*, 4169−4171. (g) Behenna, D. C.; Liu, Y.; Yurino, T.; Kim, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M. *Nat. Chem.* **2012**, *4*, 130−133. (h) Li, Y.-X.; Xuan, Q.-Q.; Liu, L.; Wang, D.; Chen, Y.-J.; Li, C.-J. *J. Am. Chem. Soc.* **2013**, *135*, 12536−12539.

(3) For selected reviews of the metallo-ene reaction, see: (a) Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. *5*, Chapter 1.2. (b) Oppolzer, W. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. *12*, Chapter 8.3. (c) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 38−52. (d) Oppolzer, W. *Pure Appl. Chem.* **1990**, *62*, 1941−1948. (e) Heumann, A.; Reglier, M. *Tetrahedron* **1995**, *51*, 975−1015. (f) Yadav, S.; Ramasastry, S. S. V. *Chem. - Asian J.* **2020**, *15*, 2764−2774.

(4) For selected examples of metallo-ene reaction, see: (a) Oppolzer, W.; Pitteloud, R.; Strauss, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 6476−6477. (b) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781−1783. (c) Gomez-Bengoa, E.; Cuerva, J. M.; Echavarren, A. M.; Martorell, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 767−769. (d) Tsukada, N.; Sugawara, S.; Inoue, Y. *Org. Lett.* **2000**, *2*, 655−657. (e) Michelet, V.; Galland, J.-C.; Charruault, L.; Savignac, M.; Genet, J.-P. *Org. Lett.* **2001**, *3*, 2065−2067. (f) Campana, A. G.; Bazdi, B.; Fuentes, N.; Robles, R.; Cuerva, J. M.; Oltra, J. E.; Porcel, S.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 7515−7519. (g) Liang, H.; Yan, F.; Dong, X.; Liu, Q.; Wei, X.; Liu, S.; Dong, Y.; Liu, H. *Chem. Commun.* **2017**, *53*, 3138−3141. (h) Bankar, S. K.; Singh, B.; Tung, P.; Ramasastry, S. S. V. *Angew. Chem., Int. Ed.* **2018**, *57*, 1678−1682. (i) Yadav, S.; Hazra, R.; Singh, A.; Ramasastry, S. S. V. *Org. Lett.* **2019**, *21*, 2983−2987. (j) Singh, B.; Bankar, S. K.; Kumar, K.; Ramasastry, S. S. V. *Chem. Sci.* **2020**, *11*, 4948−4953.

(5) For a leading review of migratory insertion, see: (a) Cavell, K. J. *Coord. Chem. Rev.* **1996**, *155*, 209−243. For selective reports of migratory insertion, see: (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888−899. (c) Tye, J. W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 14703−14712. (d) Hanley, P. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 15661−15673. (e) Xie, Y.; Hu, J.; Xie, P.; Qian, B.; Huang, H. *J. Am. Chem. Soc.* **2013**, *135*, 18327−18330.

(6) Zhang, Y.; Yu, B.; Gao, B.; Zhang, T.; Huang, H. *Org. Lett.* **2019**, *21*, 535−539.

(7) (a) Nishimura, T.; Makino, H.; Nagaosa, M.; Hayashi, T. *J. Am. Chem. Soc.* **2010**, *132*, 12865−12867. (b) Wang, M.; Liu, Z.-L.; Zhang, X.; Tian, P.-P.; Xu, Y.-H.; Loh, T.-P. *J. Am. Chem. Soc.* **2015**, *137*, 14830−14833.

(8) (a) Bringmann, G.; Ochse, M.; Schupp, O.; Tasler, S. In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Falk, H., Kirby, G. W., Moore, R. E., Tamm, C., Eds.; Springer: New York, 2001; Vol. *82*, p 1. (b) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267−1300. (c) Dai, J.; Liu, Y.; Zhou, Y.-D.; Nagle, D. G. *J. Nat. Prod.* **2007**, *70*, 1824−1826. (d) Reddy, R. A.; Baumeister, U.; Keith, C.; Tschierske, C. *J. Mater. Chem.* **2007**, *17*, 62−75. (e) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452−483. (f) Shibasaki, M.; Matsunaga, S. BINOL. In *Privileged Chiral Ligands and Catalysts*; Zhou, Q.-L., Ed.; Wiley: New York, 2011; pp 295−332. (g) Jiang, W.; Li, Y.; Wang, Z.-H. *Acc. Chem. Res.* **2014**, *47*, 3135−3147. (h) Guo, Y.-R.; Cao, Q.-D.; Hong, Z.-S.; Tan, Y.-Y.; Chen, S.-D.; Jin, H.-J.; Tan, K.-S.; Wang, D.-Y.; Yan, Y. *Military Med. Res.* **2020**, *7*, 11.

(9) Olofson, R. A.; Martz, J. T.; Senet, J.-P.; Piteau, M.; Malfroot, T. *J. Org. Chem.* **1984**, *49*, 2081−2082.

(10) Yu, M.; Xie, Y.; Xie, C.; Zhang, Y. *Org. Lett.* **2012**, *14*, 2164−2167.

(11) Xie, Y.; Hu, J.; Wang, Y.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 20613−20616.

(12) (a) Hu, J.; Xie, Y.; Huang, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 7272−7276. (b) Qin, G.; Li, L.; Li, J.; Huang, H. *J. Am. Chem. Soc.* **2015**, *137*, 12490−12493. (c) Liu, Y.; Xie, Y.; Wang, H.; Huang, H. *J. Am. Chem. Soc.* **2016**, *138*, 4314−4317. (d) Li, L.; Liu, P.; Su, Y.; Huang, H. *Org. Lett.* **2016**, *18*, 5736−5739. (e) Li, L.; Zhou, X.; Yu, B.; Huang, H. *Org. Lett.* **2017**, *19*, 4600−4603. (f) Qi, X.; Liu, S.; Lan, Y. *Organometallics* **2016**, *35*, 1582−1585. (g) Qiao, C.; Chen, A.; Gao, B.; Liu, Y.; Huang, H. *Chin. J. Chem.* **2018**, *36*, 929−933.

https://dx.doi.org/10.1021/acs.orglett.0c03365
Org. Lett. XXXX, XXX, XXX−XXX