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Palladium-Catalyzed Oxidative Domino Carbocyclization–Carbonylation–Alkynylation of Enallenes

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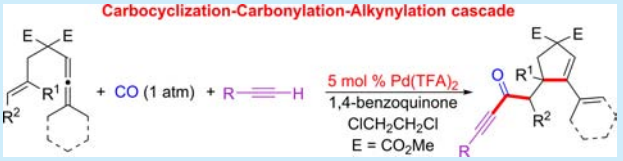
Supporting Information

ABSTRACT: An oxidative carbocyclization–carbonylation–alkynylation reaction cascade has been developed using catalytic amounts of palladium(II) salts. The domino reaction proceeds efficiently, giving the corresponding ynones in good to excellent yields under operationally simple conditions. A wide range of aromatic and aliphatic terminal alkynes with various functional groups are tolerated under the reaction conditions.

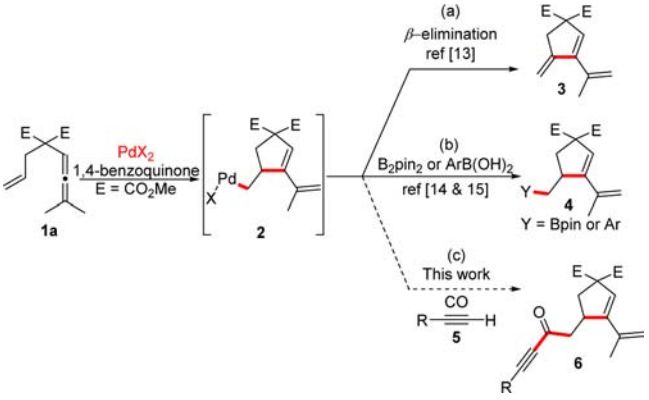


Carbocyclization reactions constitute an important class of transformations for the construction of carbocyclic and heterocyclic frameworks.[1] This field has been dominated by palladium catalysts involving developments in both oxidative and nonoxidative types of systems.[2] While there are many advances in this field, development of cascade or domino reactions in oxidative palladium-catalyzed carbocyclizations has received much less attention.[3] Cascade reactions in which multiple bond-forming events occur in one pot have several advantages including high atom and step economy and constitute a topic of great interest.[4]

Also, palladium-catalyzed carbonylation reactions using carbon monoxide are becoming increasingly important for the synthesis of carbonyl derivatives, which are valuable intermediates in the manufacturing of dyes, pharmaceuticals, and agrochemicals.[5] Carbonylation reactions taking place under oxidative conditions have been studied as a powerful tool for the synthesis of carbonylated compounds.[6] Typically an alcohol or an amine will be used as the nucleophile in these carbonylation reactions. Quenching of the acylpalladium(II) species with a carbon nucleophile such as a terminal alkyne, resulting in the synthesis of an ynone unit, are relatively scarce.[7] High reaction temperatures and high pressures of carbon monoxide are generally required for the selective carbonylative Sonogashira reaction. Several reports were published in recent years for the successful synthesis of ynones.[8] Ynones are key building blocks for the synthesis of various heterocycles such as pyrimidines,[9] pyrazoles,[10] oximes,[11] and others. They are also valuable precursors for the preparation of a wide variety of biologically active molecules and synthetic intermediates.

Development of palladium-catalyzed oxidative carbocyclization reactions has been one of the prime interests in our group for the formation of various carbo- and heterocycles.[12] Along these lines, we have previously reported palladium-catalyzed carbocyclization reactions of enallenes, dienallenes, and allenynes. In the presence of catalytic amounts of Pd(II) salts, enallene **1a** undergoes carbocyclization to give the intermediate **2** (Scheme 1). In the absence of any coupling partner, this intermediate leads to triene **3** after β-elimination

Scheme 1. Palladium-Catalyzed Oxidative Carbocyclization Reactions



(Path a).[13] More recently, the synthetic potential of these carbocyclization reactions has been extended to borylation[14] and arylations (Path b).[15] Attempts to trap the alkylpalladium(II) species with other organometallic reagents and pronucleophiles have not been successful. Based on our previous work and the importance of ynones, we envisioned a carbocyclization–carbonylative Sonogashira reaction cascade of enallenes **1** and terminal alkynes **5** in the presence of carbon monoxide (Path c).[16] To our knowledge, carbonylative Sonogashira reaction as a last step of the insertion cascade of a carbocyclization reaction was never reported.

Similar to most cascade reactions, the main problem for the intended project is the competing kinetics between several possible reaction pathways.[4] Insertion of carbon monoxide into the C–Pd bond of **2** should be fast enough so that the competing β-elimination to give **3** is avoided. Also, direct reaction of **2** with the terminal alkyne to give a noncarbonylative coupling product (cf., **4** Y = alkyne) is expected

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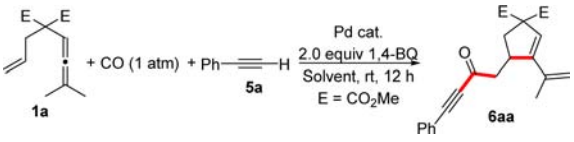
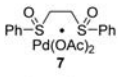
to be slower than carbonylation. The other challenge would be to control the hampering reactivity of terminal alkynes to undergo homocoupling under the oxidative conditions.[17]

Enallene **1a** and phenylacetylene **5a** were chosen as the coupling partners for the optimization of the reaction cascade. Under 1 atm of carbon monoxide, various solvents were screened using 5 mol % of $Pd(OAc)_2$ as the catalyst and 2.0 equiv of 1,4-benzoquinone (1,4-BQ) as the oxidant (Table 1).

Table 1. Optimization of Conditions for the Oxidative Carbocyclization Reaction[a]



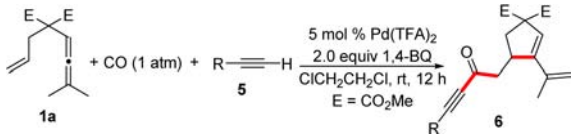
entry	Pd-cat.	mol %	solvent	yield (%)[b]
1	$Pd(OAc)_2$	5	THF	22
2	$Pd(OAc)_2$	5	toluene	6
3	$Pd(OAc)_2$	5	acetone	16
4	$Pd(OAc)_2$	5	$ClCH_2CH_2Cl$	35 (29[d])
5	$Pd(OAc)_2$	10	$ClCH_2CH_2Cl$	64[c]
6	$Pd(acac)_2$	5	$ClCH_2CH_2Cl$	-
7	$PdCl_2$	5	$ClCH_2CH_2Cl$	-
8	 7	5	$ClCH_2CH_2Cl$	13
9	**$Pd(TFA)_2$**	**5**	**$ClCH_2CH_2Cl$**	**92 (85[c])**
10	$Pd(TFA)_2$	5	THF	5
11	$Pd(TFA)_2$	5	toluene	69
12	$Pd(TFA)_2$	5	CH_3CN	17
13	$Pd(TFA)_2$	2	$ClCH_2CH_2Cl$	87[d]

[a]General: 1.0 equiv of **1a** (0.13 mmol), 2.0 equiv of phenylacetylene **5a**, and 2.0 equiv of 1,4-BQ (1,4-benzoquinone) in 1.0 mL of solvent at rt for 12 h. [b]Yield was determined by ^1H NMR spectroscopy using mesitylene as the internal standard. [c]Yield of the isolated product after column chromatography. [d]Reaction was run for 36 h.

We were pleased to find that the reaction cascade proceeded cleanly at rt in $ClCH_2CH_2Cl$ after 12 h, giving the product **6aa** in 35% NMR yield along with the remaining starting material **1a** (entry 4). The reaction furnished selectively ynone **6aa**, and no β-elimination product **3** was observed in the ^1H NMR spectrum of the crude reaction mixture. The whole process involves the formation of three carbon−carbon bonds in a domino fashion. The use of 10 mol % of $Pd(OAc)_2$ and a prolonged reaction time (36 h) gave **6aa** in 64% yield (entry 5). To improve the yields, other palladium salts were tested for the reaction (entries 6−9). While $PdCl_2$ and $Pd(acac)_2$ led to no reaction, 1,2-bis(phenylsulfinyl)ethanepalladium(II) diacetate **7** afforded **6aa** in only 13% yield. Interestingly, the use of 5 mol % of $Pd(TFA)_2$ (TFA = trifluoroacetate) in place of $Pd(OAc)_2$ in $ClCH_2CH_2Cl$ dramatically improved the conversion and gave **6aa** in 92% yield (85% isolated yield). The combination of catalytic amounts of $Pd(TFA)_2$ and $ClCH_2CH_2Cl$ as solvent was found to be essential for the success of the reaction, as other solvents such as THF, toluene, and acetonitrile with 5 mol % $Pd(TFA)_2$ led to lower yields (entries 10−12). It should be noted that the cascade reaction can be carried out with 2 mol % of $Pd(TFA)_2$ as the catalyst; in this case a longer reaction time (36 h) was required (entry 13).

After obtaining the optimized conditions for the cascade carbocyclization−carbonylation−alkynylation, we tested the scope of the different terminal alkynes for the reaction using **1a** as the substrate. As can be seen from Table 2, under operationally simple reaction conditions various substituted phenylacetylenes reacted with **1a** to provide the corresponding cyclized ynones **6aa**−**6ah** in good to high isolated yields (entries 1−8). Both electron-donating and -withdrawing groups were compatible with the reaction conditions. The reaction was found not to be sensitive to the presence of electronically and sterically different substituents on the aromatic ring. Interestingly, the reaction of **1a** with 1,3-diethynylbenzene **5h**, which has two terminal alkyne units, selectively gave monoalkynylation product **6ah**, and the second alkyne group stayed intact during the reaction (entry 8). Aliphatic acyclic and cyclic terminal alkynes also reacted smoothly in the reaction to generate the corresponding products in good yields (entries 9−14). Notably, bromo and chloro substituents were also compatible with the reaction conditions (entries 10 and 11). The use of enynes as terminal alkynes afforded the corresponding products **6am** and **6an** in 94% and 79% yields, respectively (entries 13 and 14). Gratifyingly, the reaction can be extended to trimethylsilylacetylene to give the TMS-protected alkyne **6ao** (81% yield), which after desilylation can be used for further functionalization (entry 15).

Table 2. Scope of the Terminal Alkynes for the Carbonylative Alkynylation[a]



entry	R	product	yield (%)[b]
1	Ph	**6aa**	85
2	4-Me-C_6H_4	**6ab**	83
3	4-(*n*-pent)-C_6H_4	**6ac**	82
4	4-MeO-C_6H_4	**6ad**	87
5	2-MeO-C_6H_4	**6ae**	84
6	4-F-C_6H_4	**6af**	73
7	4-CF_3-C_6H_4	**6ag**	79
8	3-ethynyl-C_6H_4	**6ah**	72
9	*n*-butyl	**6ai**	67
10	2-bromoethyl	**6aj**	54
11	3-chloropropyl	**6ak**	69
12	cyclopentyl	**6al**	75
13	2-propenyl	**6am**	94
14	1-cyclohexenyl	**6an**	79
15	TMS	**6ao**	81[c]

[a]General: 0.13 mmol of **1a**, 5 mol % $Pd(TFA)_2$, 2.0 equiv of 1,4-BQ (1,4-benzoquinone), and 2.0 equiv of terminal alkyne in 1.0 mL of solvent. [b]Yield of isolated product after column chromatography. [c]4.0 equiv of TMS-acetylene were used.

Subsequently, we tested the scope of the enallenes for the cascade reaction using phenylacetylene **5a** as the terminal alkyne (Table 3). Under standard conditions, differently substituted enallenes **1** served as useful substrates for the formation of cyclic enynes **6** in good yields. Substrates in which

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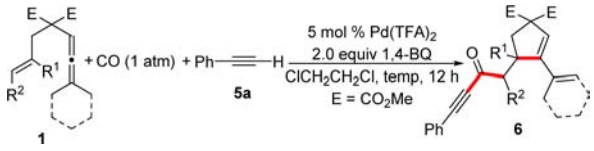
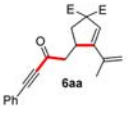
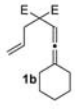
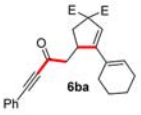
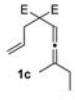
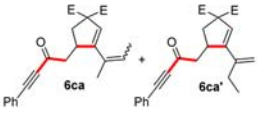
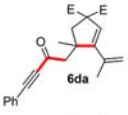
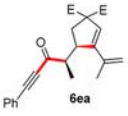
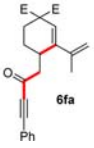
Table 3. Scope of Different Enallenes for the Cascade Reaction[a]



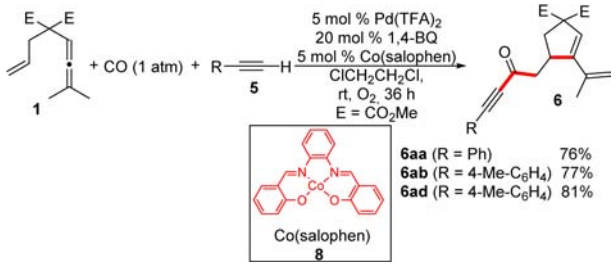
entry	enallene	product	temp (°C)	yield (%)[b]
1			rt	85
2			40	76
3			40	88[c]
4			80	73
5			50	53[d]
6			rt - 80	0

[a]General: 0.13 mmol of **1**, 5 mol % $Pd(TFA)_2$, 2.0 equiv of 1,4-BQ (1,4-benzoquinone), and 2.0 equiv of phenylacetylene **5a** in 1.0 mL of $ClCH_2CH_2Cl$. [b]Yield of isolated product after column chromatography. [c](*Z*/*E*) = 8:1 and **6ca**/**6ca′** = 2:1. [d]10 mol % $Pd(TFA)_2$ was used instead of 5 mol %.

the dimethyl groups of the allene unit were replaced with either a pentamethylene or methylethyl unit required a slight increase in temperature to 40 °C for a clean reaction to give **6ba** and **6ca** (entries 2 and 3). Enallene **1d** having a methyl substitution on the olefin unit underwent the cascade carbocyclization−carbonylation−alkynylation to afford ynone **6da** having an all-carbon quaternary center in 73% yield at 80 °C (entry 4). For the substrate **1e** with a substituent on the terminal position of the alkene, we were pleased to find after optimization that 10 mol % of $Pd(TFA)_2$ at 50 °C led predominantly to cyclized product **6ea** (entry 5).[18] Reaction with substrate **1f** shed light on the importance of the position of alkene and allene units for the coordination. While 1,5-enallenes are found to be good substrates at rt for the cascade reaction, a 1,6-enallene such as **1f** did not give any product even at high temperatures (entry 6).

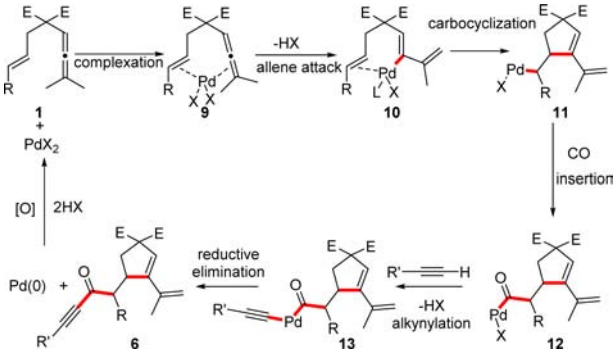
Aerobic oxidative carbocyclization reactions proceeding using molecular oxygen as the stoichiometric oxidant have gained considerable attention in recent years, as these processes are inexpensive and environmental friendly and produce water as the only byproduct.[19] Direct reoxidation of the reduced metal catalyst with molecular oxygen is often a slow and difficult process because of the high kinetic barrier for the reoxidation. To circumvent high pressures of O_2, biomimetic procedures in which the high kinetic barrier will be divided into several smaller units by using electron-transfer mediators (ETMs) were previously used in our group for various transformations.[20] A balloon consisting of approximately equal amounts of CO and O_2 was used along with 20 mol % of BQ and 5 mol % Co(salophen) **8** as ETMs for the reaction at rt (Scheme 2). These optimized conditions worked well for the cascade reaction to give the products **6aa**−**6ad** in good yields after 36 h.

Scheme 2. Palladium-Catalyzed Cascade Carbonylation−Alkynylation under Biomimetic Conditions



A possible mechanism for the palladium-catalyzed oxidative cascade carbocyclization−carbonylation−alkynylation is depicted in Scheme 3 based on previous studies in our group.

Scheme 3. Proposed Mechanism



In the first step, palladium forms a π-complex with both the allene and alkene units. Attack of the allene moiety on Pd(II) generates **10**, which undergoes carbocyclization to provide **11**. Insertion of carbon monoxide onto the Pd−C bond of **11** takes place to give the acylpalladium(II) species **12**. Subsequent transfer of an alkynyl moiety leads to the formation of intermediate **13**. Reductive elimination from **13** affords the product **6** and Pd(0), which can be oxidized back to Pd(II) by the oxidant.

In summary, we have developed an operationally simple protocol for the palladium-catalyzed oxidative carbocyclization followed by the carbonylative Sonogashira reaction of enallenes. The reaction proceeds under ambient conditions of temperature and pressure (rt and 1 atm of carbon monoxide) using 5 mol % of $Pd(TFA)_2$ in $ClCH_2CH_2Cl$ in the absence of any ligands. Good to excellent yields were obtained for various aliphatic, aromatic, and silyl-protected terminal alkynes to provide the corresponding ynones. Three new carbon−carbon bonds are formed in an efficient manner, and a high degree of molecular complexity was achieved during the cascade

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carbocyclization−carbonylation−alkynylation reaction. Further evaluation of scope and limitation of this transformation and mechanistic studies are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and full characterization details including ^{1}H, ^{13}C NMR and HRMS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donovan, R. J. *Chem. Rev.* **1996**, *96*, 635. (b) Méndez, M.; Echavarren, A. M. *Eur. J. Org. Chem.* **2002**, 15. (c) Negishi, E.-I.; Copéret, C.; Ma, S.; Liou, S. Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365. (d) Trost, B. M.; Dean Toste, F.; Pinkerton, A. B. *Chem. Rev.* **2001**, *101*, 2067. (e) Aubert, C.; Buisine, O.; Malacria, M. *Chem. Rev.* **2002**, *102*, 813. (f) Aubert, C.; Fensterbank, L.; Gandon, V.; Malacria, M. *Top. Organomet. Chem.* **2006**, *19*, 259. (g) Zhang, D. H.; Zhang, Z.; Shi, M. *Chem. Commun.* **2012**, *48*, 10271. (h) Aubert, C.; Fensterbank, L.; Garcia, P.; Malacria, M.; Simonneau, A. *Chem. Rev.* **2011**, *111*, 1954.

(2) (a) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (b) Dénès, F.; Perez-Luna, A.; Chemla, F. *Chem. Rev.* **2010**, *110*, 2366. (c) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215. (d) Deng, Y.; Persson, A. K. Å.; Bäckvall, J.-E. *Chem.—Eur. J.* **2012**, *18*, 11498.

(3) (a) Müller, T. J. J. *Metal Catalyzed Cascade Reactions*, Vol. *19*; Springer-Verlag: Berlin, 2006. (b) Vlaar, T.; Ruijter, E.; Orru, R. V. A. *Adv. Synth. Catal.* **2011**, *353*, 809.

(4) (a) Tietze, L. F., Brasche, G., Gericke, K., Eds. *Domino Reactions in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 2006. (b) Nicolaou, K. C.; Edmonds, D. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7134. (c) Nicolaou, K. C.; Chen, J. S. *Chem. Soc. Rev.* **2009**, *38*, 2993.

(5) (a) El Ali, B.; Alper, H. *Synlett* **2000**, 161. (b) Trzeciak, A. M.; Ziolkowski, J. J. *Coord. Chem. Rev.* **2005**, *249*, 2308. (c) Morimoto, T.; Kakiuchi, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5580. (d) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *1*, 28. (e) Brennführer, A.; Neumann, H.; Beller, M. *ChemCatChem* **2009**, *1*, 28. (f) Grigg, R.; Mutton, S. P. *Tetrahedron* **2010**, *66*, 5515. (g) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402. (h) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (i) Wu, X. F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (j) Gadge, S. T.; Bhanage, B. M. *RSC Adv.* **2014**, *4*, 10367.

(6) (a) Gabriele, B.; Salerno, G.; Costa, M. *Top. Organomet. Chem.* **2006**, *18*, 239. (b) Gabriele, B.; Salerno, G.; Costa, M. *Synlett* **2004**, 2468. (c) Gabriele, B.; Salerno, G.; Costa, M.; Chiusoli, G. P. *J. Organomet. Chem.* **2003**, *687*, 219. (d) Liu, Q.; Zhang, A.; Lei, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 10788. (e) Gabriele, B.; Mancuso, R.; Salerno, G. *Eur. J. Org. Chem.* **2012**, 6825. (f) Wu, X. F.; Neumann, H.; Beller, M. *ChemSusChem* **2013**, *6*, 229.

(7) (a) Kobayashi, T.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1981**, 333. (b) Tanaka, M.; Kobayashi, T.; Sakakura, T. *Nippon Kagaku Kaishi* **1985**, 537; *Chem. Abstr.* **1986**, *104*, 129561d. (c) Delaude, L.; Masdeu, A. M.; Alper, H. *Synthesis* **1994**, 1149.

(8) (a) Mohamed Ahmed, M. S.; Mori, A. *Org. Lett.* **2003**, *5*, 3057. (b) Liang, B.; Huang, M.; You, Z.; Xiong, Z.; Lu, K.; Fathi, R.; Chen, J.; Yang, Z. *J. Org. Chem.* **2005**, *70*, 6097. (c) Liu, J.; Chen, J.; Xia, C. *J. Catal.* **2008**, *253*, 50. (d) Liu, J.; Peng, X.; Sun, W.; Zhao, Y.; Xia, C. *Org. Lett.* **2008**, *10*, 3933. (e) Tambade, P. J.; Patil, Y. P.; Nandurkur, N. S.; Bhanage, B. M. *Synlett* **2008**, 886. (f) Fusano, A.; Fukuyama, T.; Nishitani, S.; Inouye, T.; Ryu, I. *Org. Lett.* **2010**, *12*, 2410. (g) Park, A.; Park, K.; Kim, Y.; Lee, S. *Org. Lett.* **2011**, *13*, 944. (h) Wu, X.-F.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 11142. (i) Wu, X.-F.; Sundararaju, B.; Neumann, H.; Dixneuf, P. H.; Beller, M. *Chem.—Eur. J.* **2011**, *17*, 106. (j) Kim, W.; Park, K.; Park, A.; Choe, J.; Lee, S. *Org. Lett.* **2013**, *15*, 1654.

(9) (a) Karpov, A. S.; Merkul, E.; Rominger, F.; Müller, T. J. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6951. (b) Bannwarth, P.; Valleix, A.; Grée, R. *J. Org. Chem.* **2009**, *74*, 4646.

(10) Mohamed Ahmed, M. S.; Kobayashi, K.; Mori, A. *Org. Lett.* **2005**, *7*, 4487.

(11) She, Z.; Niu, D.; Chen, L.; Gunawan, M. A.; Shanja, X.; hersh, W. H.; Chen, Y. *J. Org. Chem.* **2012**, *77*, 3627.

(12) (a) Piera, J.; Persson, A.; Caldentey, X.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2007**, *129*, 14120. (b) Johnston, E. V.; Karlsson, E. A.; Lindberg, S. A.; Åkermark, B.; Bäckvall, J.-E. *Chem.—Eur. J.* **2009**, *15*, 6799. (c) Persson, A. K. Å.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2010**, *49*, 4624. (d) Deng, Y.; Bartholomeyzik, T.; Persson, A. K. Å.; Sun, J.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2012**, *51*, 2703. (e) Deng, Y.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2013**, *52*, 3217. (f) Deng, Y.; Bartholomeyzik, T.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2013**, *52*, 6283. (g) Volla, C. M. R.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2013**, *52*, 14209.

(13) (a) Franzén, J.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2003**, *125*, 6056. (b) Piera, J.; Närhi, K.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2006**, *118*, 6914.

(14) Persson, A. K. Å.; Jiang, T.; Johnson, M. T.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2011**, *50*, 6155.

(15) Jiang, T.; Persson, A. K. Å.; Bäckvall, J.-E. *Org. Lett.* **2011**, *13*, 5838.

(16) For the carbocyclization−carbonylation reaction of allenynes, see: Volla, C. M. R.; Mazuela, J.; Bäckvall, J.-E. *Chem.—Eur. J.* **2014**, *20*, 7608.

(17) Li, J.-H.; Liang, Y.; Xie, Y.-X. *J. Org. Chem.* **2005**, *70*, 4393.

(18) The stereochemistry for **6ea** was reported based on a *syn*-carbopalladation mechanism, and the stereochemical assignment was described in the Supporting Information.

(19) For a review on biomimetic oxidation reactions, see: Piera, J.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2008**, *47*, 3506.

(20) Bäckvall, J.-E.; Hopkins, R. B.; Grennberg, H.; Mader, M.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 5160.