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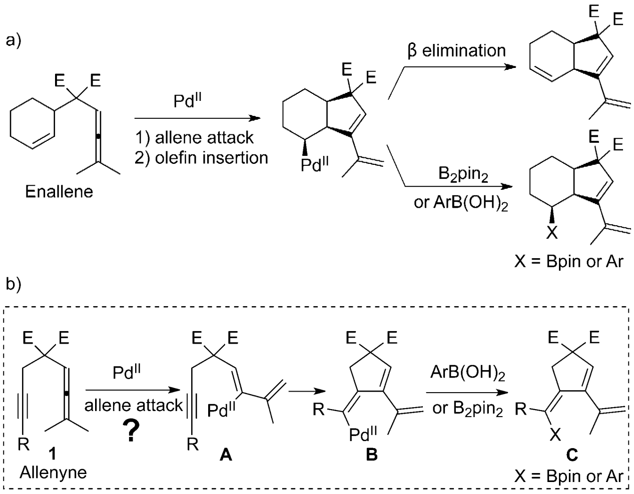
Palladium-Catalyzed Oxidative Arylating Carbocyclization of Allenynes**

*Youqian Deng, Teresa Bartholomeyzik, Andreas K. Å. Persson, Junliang Sun, and Jan-E. Bäckvall**

Transition metal-catalyzed cyclizations of allenynes provide efficient and atom-economical routes to polyunsaturated carbo- and heterocycles.[1–5] In addition to cycloisomerizations[1] and intramolecular Pauson–Khand reactions,[2] cyclizations of allenynes in combination with a second coupling partner have been studied previously. For instance, 1,7-allenynes react under Rh^I catalysis with arylboronic acids to afford arylated bicyclic compounds.[3] Nonoxidative Pd^0-catalyzed carbocyclizations of allenynes in the presence of organoboronic acids[4] or bis(pinacolato)diboron (B_2pin_2)[5] have also been demonstrated.

Much attention has recently been addressed towards an oxidative counterpart of the nonoxidative carbocyclizations,[6] thus allowing for new and different types of catalysts and reaction conditions.[7–10] Our research group has been involved in the development of various oxidative palladium-catalyzed carbocyclizations of en- and dienallenes.[9,10] Very recently, we reported on the palladium-catalyzed oxidative carbocyclization/borylation[10a] and carbocyclization/arylation[10b] of enallenes (Scheme 1 a). To the best of our knowledge, there is no report on the palladium-catalyzed oxidative carbocyclization of allenynes.

With this notion in mind, we envisioned a carbocyclization/arylation or carbocyclization/borylation of allenynes with simple Pd^{II} salts as the catalyst (Scheme 1 b). We hypothesized that interaction of allenynes **1** with Pd^{II} would form intermediate **A** through nucleophilic attack on palladium by the allene.[9,10] Subsequent *cis* insertion of the alkyne into the generated vinyl–palladium bond would give intermediate **B**, which may undergo transmetalation with an arylboronic acid or B_2pin_2 to yield a carbocyclized product **C**. Thus, the challenge involves regeneration of the catalyst, tuning of the reactivity of the allene and alkyne moieties, and control of the stereochemistry. Herein, we describe new patterns of Pd^{II}-catalyzed oxidative carbocyclization of structurally diverse allenynes in the presence of arylboronic acids or B_2pin_2 with *p*-benzoquinone (BQ) as the oxidant.



Scheme 1. a) Oxidative Pd-catalyzed carbocyclization of enallenes[10]. b) Possible pathway for the carbocyclization of allenynes **1** based on our previous studies of enallenes. E = CO_2Me.

In preliminary experiments we observed that treatment of **1a** with $Pd(OAc)_2$ (5 mol %), $PhB(OH)_2$ (1.1 equiv), and BQ (1.1 equiv) in THF at 50 °C gave the phenylated triene product (*Z*)-**2aa** in 60 % yield (determined by NMR spectroscopy; with anisole as the internal standard; see the Supporting Information). In a solvent study, THF was found to be the best solvent for this transformation. Other solvents such as acetone, 1,4-dioxane, methanol, or toluene gave significantly lower yields. An excess of BQ (1.3 equiv) did not improve the yield of the reaction compared to the use of 1.1 equiv. When the amount of phenylboronic acid was increased to 1.3 equiv the yield rose to 67 %. A further increase of the amount of phenylboronic acid (up to 2 equiv) gave no additional improvement. Surprisingly, the yield of (*Z*)-**2aa** could be increased to 75 % simply by decreasing the catalyst loading to 1 mol %. Finally, room temperature (25 °C) was found to be the optimal temperature without loss in yield (Scheme 2). It is interesting to note that in most cases trace amounts of cycloisomerization products **3**, such as **3a**,[11] were also detected in the crude reaction mixture.

The scope of boronic acids was studied using allenyne **1a** (Scheme 3). The electronic properties of the arylboronic acid had little effect on the reaction. Phenylboronic acids with alkyl substituents in the *para* or *meta* position reacted smoothly under the standard conditions to give the products (**2ab**, **2ac**, and **2ae**) in 73–79 % yield. Sterically demanding

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[*] Dr. Y. Deng, T. Bartholomeyzik, A. K. Å. Persson, Prof. Dr. J.-E. Bäckvall
Department of Organic Chemistry, Arrhenius Laboratory
Stockholm University, 10691 Stockholm (Sweden)
E-mail: jeb@organ.su.se
Prof. Dr. J. Sun
Structural Chemistry and Berzelii Centre EXSELENT on Porous Materials, Stockholm University (Sweden)

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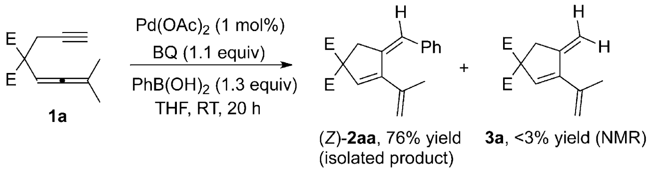
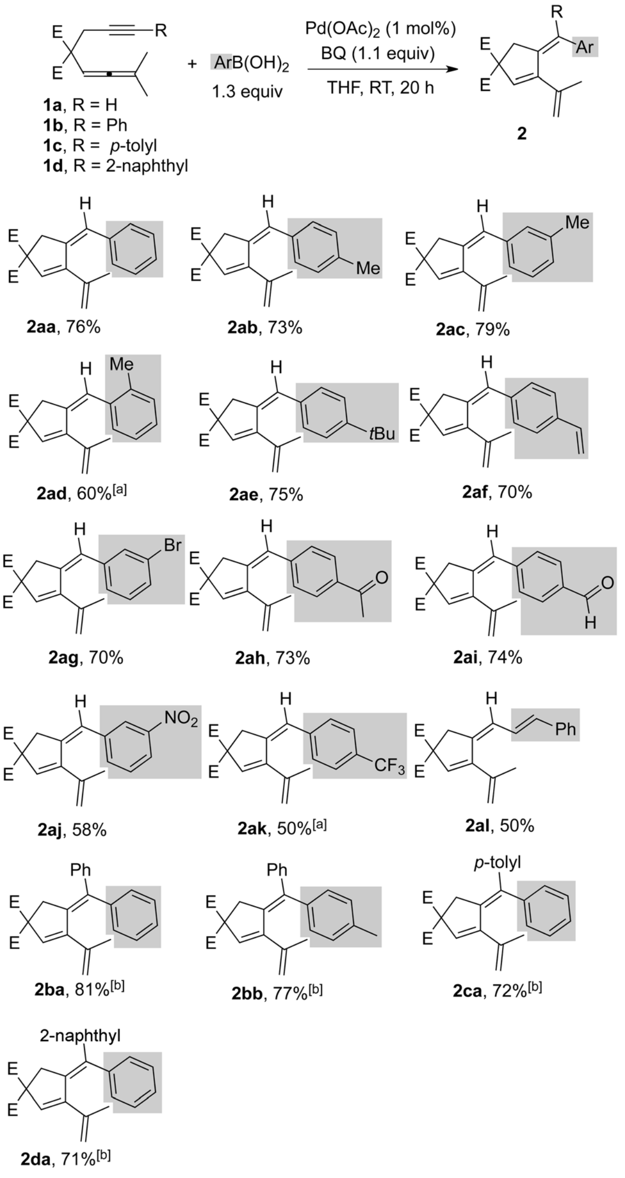


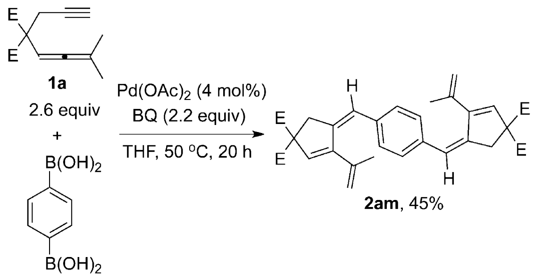
Scheme 2. Oxidative phenylating carbocyclization of allenyne **1a**. E = $\mathrm{CO_2Me}$.



Scheme 3. Pd$^{\mathrm{II}}$-catalyzed oxidative arylating carbocyclization of **1a**–**1d**. E = $\mathrm{CO_2Me}$. [a] $\mathrm{Pd(OAc)_2}$ (2 mol%), 50 °C. [b] $\mathrm{Pd(OAc)_2}$ (5 mol%), reflux.

(*ortho*-methylphenyl)boronic acid required elevated temperature (50 °C) and increased catalyst loading (2 mol% of $\mathrm{Pd(OAc)_2}$) for full conversion and acceptable yield (**2ad**). Notably, the procedure tolerated a range of functional groups as phenyl substituents, including vinyl and bromo groups (**2af** and **2ag**, respectively), which are useful for further functionalization. Acetyl and formyl groups were also well tolerated under the reaction conditions (**2ah** and **2ai**, respectively). Nitro- or trifluoromethyl-substituted electron-deficient arylboronic acids reacted slower and afforded the corresponding products **2aj** and **2ak** in 58 and 50% yield, respectively. It is worth noting that (*E*)-styrylboronic acid was a good reaction partner as well (affording **2al**). Furthermore, benzene-1,4-diboronic acid reacted smoothly with **1a** to afford product **2am** (Scheme 4).

We also investigated the aryl-substituted alkynes **1b–d** (Scheme 3). Despite the higher steric hindrance, these substrates reacted smoothly when using 5 mol% of $\mathrm{Pd(OAc)_2}$ in refluxing THF to afford the corresponding arylated products in good to high yields. The configuration of the cross-conjugated triene products **2bb** (*Z*) and **2da** (*E*) was established by NOESY ^{1}H NMR measurements.

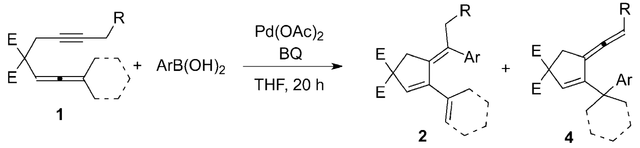


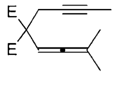
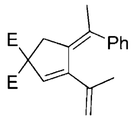
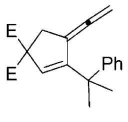
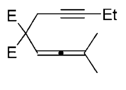
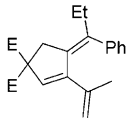
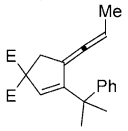
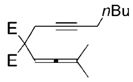
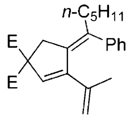
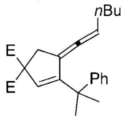
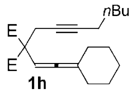
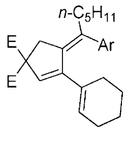
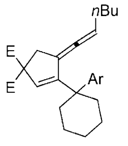
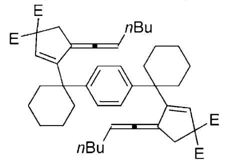
Scheme 4. Carbocyclization of **1a** with benzene-1,4-diboronic acid. E = $\mathrm{CO_2Me}$.

By altering the substituent on the alkyne from H or aryl groups to alkyl groups, new products were obtained (Table 1). Substrate **1e** with a methyl group (R = H, Table 1) on the triple bond afforded the expected triene product **2ea** in 50% yield along with the unexpected vinylallene product **4ea** in 17% yield. Interestingly, reaction of allenyne **1f** having an ethyl group on the triple bond proceeded with reversed selectivity affording the vinylallene product **4fa** as the major product in 65% yield, while the amount of triene (**2fa**) decreased to 10%. Pentyl-substituted substrate **1g** displayed a similar selectivity. When both methyl groups on the terminal carbon atom of the allene moiety of **1g** were replaced by pentamethylene (forming the cyclohexylidene group of **1h**), the reaction gave the vinylallene product **4ha** in 67% yield together with only trace amounts of triene product **2ha**. Furthermore, it was found that the scope with respect to the arylboronic acid coupling partner was broad. Arylboronic acids with alkyl or vinyl substituents reacted smoothly under the standard conditions (products **4hb** and **4hc** or **4hd**). Halogen substituents at the *meta* or *para* position, including sensitive aryl iodides which would serve as further functional handles, were compatible with the reaction conditions (**4he**–**4hh**).

A range of aryl substituents with varying electronic properties was tolerated, from electron-rich methoxy to electron-deficient formyl and nitro groups (products **4hi**, **4hj**, and **4hk**, respectively). Even benzene-1,4-diboronic acid worked and afforded bis(vinylallene) product **4hl**. It is worth

Table 1: Pd^{II}-catalyzed oxidative arylating carbocyclization of **1e**–**1h**.[a]

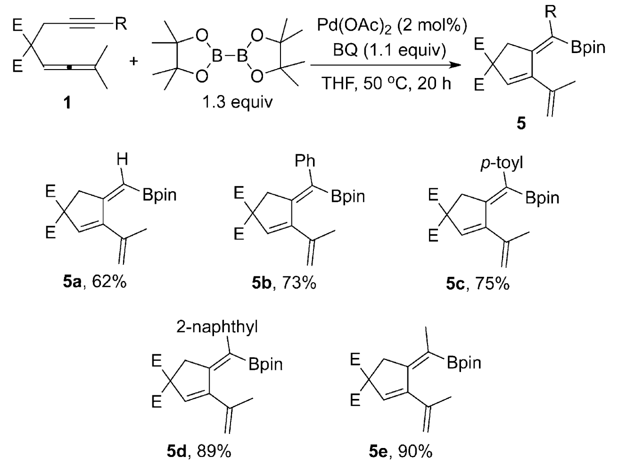


Entry	Allenyne	Boronic acid	Products, Yields [%]	
1	 **1e**	$PhB(OH)_2$	 **2ea**, 50	 **4ea**, 17
2	 **1f**	$PhB(OH)_2$	 **2fa**, 10	 **4fa**, 65
3	 **1g**	$PhB(OH)_2$	 **2ga**, 9	 **4ga**, 67
	 **1h**	$ArB(OH)_2$		
4	**1h**	Ar = Ph	**2ha**, < 2	**4ha**, 67
5	**1h**	Ar = p-MeC_6H_4	**2hb**, 2	**4hb**, 68
6	**1h**	Ar = p-$tBuC_6H_4$	**2hc**, 3	**4hc**, 69
7	**1h**	Ar = p-$(CH_2{=}CH)$-C_6H_4	**2hd**, < 2	**4hd**, 60
8[b]	**1h**	Ar = p-IC_6H_4	**2he**, 2	**4he**, 60
9	**1h**	Ar = p-BrC_6H_4	**2hf**, < 2	**4hf**, 72
10	**1h**	Ar = m-BrC_6H_4	**2hg**, < 2	**4hg**, 73
11	**1h**	Ar = p-ClC_6H_4	**2hh**, < 2	**4hh**, 62
12	**1h**	Ar = m-$OMeC_6H_4$	**2hi**, 3	**4hi**, 75
13	**1h**	Ar = p-$CHOC_6H_4$	**2hj**, < 2	**4hj**, 85
14	**1h**	Ar = m-$NO_2C_6H_4$	**2hk**, < 2	**4hk**, 80
15[c]		Ar = p-$B(OH)_2C_6H_4$	 **4hl**, 50	

[a] E = CO_2Me. Conditions unless otherwise noted: $Pd(OAc)_2$ (1 mol%), boronic acid (1.3 equiv), BQ (1.1 equiv), room temperature. [b] $Pd(OAc)_2$ (5 mol%), boronic acid (2 equiv). [c] Benzene-1,4-diboronic acid, **1h** (2.6 equiv), $Pd(OAc)_2$ (2 mol%), BQ (2.2 equiv), 50 °C.

noting that the Pd^{II}-catalyzed oxidative carbocyclization provides an efficient route to cyclic vinylallene derivatives, known to be versatile precursors of hydrindenones[12] and retinoids.[13]

Organoboronates, a synthetically useful class of compounds, can be used for the construction of C–C bonds, for example through Suzuki–Miyaura cross-coupling reactions.[14] Thus, after realization of the arylation, we turned our attention to the borylation of allenynes (Scheme 5). By increasing the catalyst loading to 2 mol% the reaction of **1a** with B_2pin_2 at 50 °C gave complete conversion affording the borylated product **5a** in 62% yield. Aryl-substituted substrates **1b**, **1c**, and **1d** could also successfully be used to give borylated products **5b** (73%), **5c** (75%), and **5d** (89%), respectively. Surprisingly, the borylation of methyl-substituted substrate **1e** afforded the triene product **5e** selectively in 90% yield with < 2% of allenic products analogous to **4**. We believe that the mechanism of this borylation reaction involves the pathway depicted in Scheme 1b. The configuration of the C–C double bond in these triene products was further established by X-ray diffraction studies of **5b** and **5e**.[15] It is interesting to note that the borylation in the oxidative reactions only occurs at the alkyne in contrast to the corresponding nonoxidative reactions, where borylation occurred at the allene.[5]

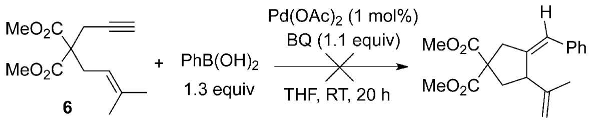


Scheme 5. Pd^{II}-catalyzed oxidative borylating carbocyclization of allenynes **1**. E = CO_2Me.

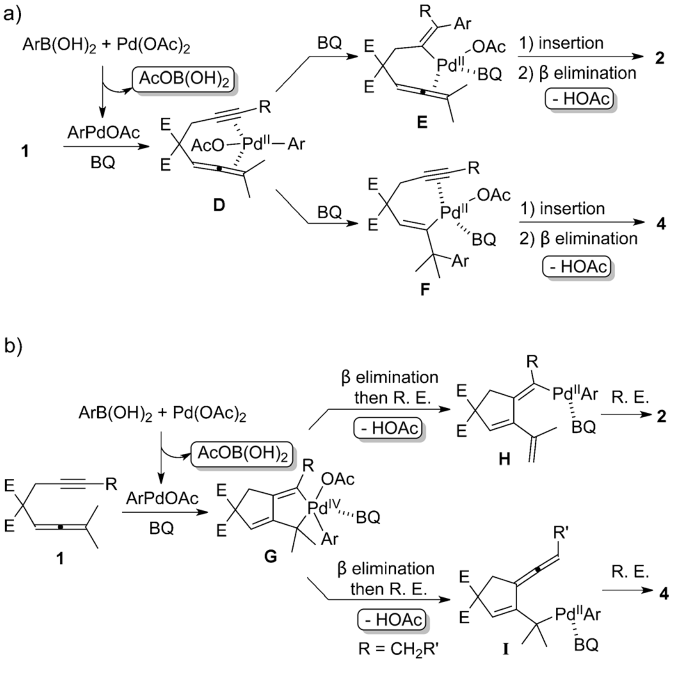
To gain further insight into the mechanism some control experiments were carried out (for details see the Supporting Information). When a mixture of stoichiometric amounts of **1a**, $Pd(OAc)_2$, and $PhB(OH)_2$ was monitored by ^1H NMR spectroscopy, only trace amounts of **2aa** were observed, the ratio of **2aa**/**1a** being 1/222 after 1.5 h. After addition of 10 mol% of BQ this ratio was dramatically increased to 1/2.8 within 1 h. After 14 h the starting material was fully consumed. This result clearly indicates that BQ plays an important role as a ligand in addition to its role as an oxidant for the reaction.[16]

Moreover, when enyne **6** was used, no carbocyclization was observed under the standard conditions (Scheme 6).[17] This shows that the allene moiety is crucial for the oxidative transformation.

Although formation of triene product **2** in principle can be explained by the mechanism outlined in Scheme 1b, the formation of vinylallene product **4** cannot. The reaction giving **2** and **4** should begin with the formation of ArPdOAc[18] from $ArB(OH)_2$ and $Pd(OAc)_2$.[19] Insertion of the alkyne into the Ar–Pd bond[20] in **D** can generate **E** (Scheme 7a). In the next



Scheme 6. Reaction of enyne **6** with phenylboronic acid.



Scheme 7. Proposed mechanisms for the palladium-catalyzed oxidative arylating carbocyclization of allenyne **1**. R.E. = reductive elimination.

step, the allene can insert into the new Pd–C bond. Subsequent β elimination would give **2**. Alternatively, insertion of the allene into the Ar–Pd bond in **D** would give **F**. Insertion of the alkyne into the vinyl–Pd bond in **F** and subsequent β elimination would produce **4**.[21]

The formation of **2** and **4** can also be explained by the cyclopalladation mechanism proposed in Scheme 7b. First, interaction of allenyne **1** and ArPdOAc in the presence of BQ would form pallada(IV)cyclopentene intermediate **G** regioselectively.[4a,22,23] This dicyclopentene-fused intermediate **G** may be kinetically preferred. β Hydride elimination involving one of the *gem*-dimethyl groups and loss of HOAc would give intermediate **H**, which on reductive elimination would give cross-conjugated triene **2**. The alternative β hydride elimination followed by reductive elimination of HOAc would generate allene intermediate **I**,[21] which after subsequent reductive elimination would give vinylallene **4**.

When 1 equiv of Pd(OAc)$_2$ and 1 equiv of PhB(OH)$_2$ were mixed with of 4-phenyl-1-butyne, 1-phenyl-1-butyne, or 4-octyne in [D$_8$]THF, ^{1}H NMR monitoring showed that all three alkynes undergo facile arylpalladation, however in the order 4-phenyl-1-butyne > 4-octyne > 1-phenyl-1-butyne. To explain the observed ratio between **2** and **4** the mechanism in Scheme 7a would require that insertion of alkyne into Pd–Ar in **D** is slower for R = Ethyl or *n*-Pentyl than for R = phenyl. The order of rates of the alkynes in the control experiment therefore does not seem to support mechanism (a).

In the lower pathway in Scheme 7a, the β elimination from the vinyl–Pd intermediate formed from **F** (through insertion) should be slow.[21a] In the control experiment above, where 4-octyne readily inserted into Ar–Pd, we observed no β elimination to give allene, not even under the conditions of the catalytic reaction at 50 °C for 20 h.

We also carried out experiments with a large excess of PhB(OH)$_2$ or a large excess of a 1:1 mixture of PhB(OH)$_2$ and B$_2$pin$_2$. With mechanism (a) one would expect some diarylation or arylation–borylation product, whereas with mechanism (b) only monoarylation or monoborylation is expected. Reaction of **1e** with 3.0 equiv of PhB(OH)$_2$ or 1.3 equiv of PhB(OH)$_2$ and 1.3 equiv of B$_2$pin$_2$ in the presence of 5 mol % of Pd(OAc)$_2$ and 1.1 equiv of BQ gave no detectable amounts of diarylation or arylation–borylation product. This observation is better explained by mechanism (b).

In conclusion, we have developed an unprecedented Pd^{II}-catalyzed oxidative arylating or borylating carbocyclization of allenynes, which provides access to trienes and vinylallenes not accessible with other metals. We propose that the borylating carbocyclization proceeds through allene attack on Pd^{II} whereas arylating carbocyclization may involve arylpalladation of a triple/double bond or formation of a pallada(IV)cyclopentene intermediate. Structural differences in the starting material will determine whether trienes **2** or vinylallenes **4** are formed. Further studies on the scope, mechanism, and synthetic application of these reactions are underway in our laboratory.

Experimental Section

Typical experimental procedure for the palladium-catalyzed oxidative arylating carbocyclization of allenyne **1**: To a mixture of PhB(OH)$_2$ (32.0 mg, 0.26 mmol), BQ (24.0 mg, 0.22 mmol), and Pd(OAc)$_2$ (0.5 mg, 0.002 mmol) were added **1a** (47.5 mg, 0.20 mmol) and THF (1 mL) at room temperature (RT). The reaction was stirred at RT for 20 h. After the reaction was complete as monitored by TLC, evaporation and column chromatography on silica gel (pentane/ethyl acetate = 30/1) afforded (*Z*)-**2aa** (47.7 mg, 76 %) as a liquid; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.20$–7.11 (m, 5 H), 6.53 (s, 1 H), 6.19 (s, 1 H), 4.93–4.91 (m, 1 H), 4.73–4.71 (m, 1 H), 3.77 (s, 6 H), 3.37 (d, $J = 1.6$ Hz, 2 H), 1.40–1.38 ppm (m, 3 H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 170.7$, 149.7, 140.0, 139.9, 137.2, 134.2, 129.1, 127.3, 126.6, 122.5, 115.8, 62.5, 52.9, 42.7, 21.4 ppm; HR-MS (ESI): calc. for $C_{19}H_{20}NaO_4$ $[M+Na]^+$: 335.1254; found: 335.1258.

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[1] For a review on the transition metal-catalyzed cycloisomerization of allenynes, see: C. Aubert, L. Fensterbank, P. Garcia, M. Malacria, A. Simonneau, *Chem. Rev.* **2011**, *111*, 1954, and references therein.

[2] For Pauson–Khand reactions of allenynes, see: a) J. L. Kent, H. Wan, K. M. Brummond, *Tetrahedron Lett.* **1995**, *36*, 2407; b) K. M. Brummond, H. Wan, *Tetrahedron Lett.* **1998**, *39*, 931;

c) K. M. Brummond, H. Wan, J. L. Kent, *J. Org. Chem.* **1998**, *63*, 6535; d) K. M. Brummond, H. Chen, K. D. Fisher, A. D. Kerekes, B. Rickards, P. C. Sill, S. J. Geib, *Org. Lett.* **2002**, *4*, 1931; e) B. Alcaide, P. Almendros, C. Aragoncillo, *Chem. Eur. J.* **2002**, *8*, 1719; f) T. Shibata, S. Kadowaki, M. Hirase, K. Takagi, *Synlett* **2003**, 573; g) K. M. Brummond, D. Gao, *Org. Lett.* **2003**, *5*, 3491; h) C. Mukai, I. Nomura, S. Kitagaki, *J. Org. Chem.* **2003**, *68*, 1376.

[3] T. Miura, K. Ueda, Y. Takahashi, M. Murakami, *Chem. Commun.* **2008**, 5366.

[4] a) C. H. Oh, D. I. Park, S. H. Jung, V. R. Reddy, A. K. Gupta, Y. M. Kim, *Synlett* **2005**, 2092; b) A. K. Gupta, C. Y. Rhim, C. H. Oh, *Tetrahedron Lett.* **2005**, *46*, 2247.

[5] V. Pardo-Rodríguez, J. Marco-Martínez, E. Buñuel, D. J. Cárdenas, *Org. Lett.* **2009**, *11*, 4548.

[6] For selected reviews on carbocyclization reactions, see: a) I. Ojima, M. Tzamarioudaki, Z. Li, R. J. Donovan, *Chem. Rev.* **1996**, *96*, 635; b) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.* **2007**, *107*, 5318; c) F. Dénès, A. Pérez-Luna, F. Chemla, *Chem. Rev.* **2010**, *110*, 2366; d) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215.

[7] For selected recent oxidative C–C bond forming reactions, see: a) K. S. Yoo, C. H. Yoon, K. W. Jung, *J. Am. Chem. Soc.* **2006**, *128*, 16384; b) J. Lindh, P. Enquist, Å. Pilotti, P. Nilsson, M. Larhed, *J. Org. Chem.* **2007**, *72*, 7957; c) J. H. Delcamp, A. P. Brucks, M. C. White, *J. Am. Chem. Soc.* **2008**, *130*, 11270; d) T. Jensen, P. Fristrup, *Chem. Eur. J.* **2009**, *15*, 9632; e) L. Liao, M. S. Sigman, *J. Am. Chem. Soc.* **2010**, *132*, 10209; f) E. W. Werner, M. S. Sigman, *J. Am. Chem. Soc.* **2010**, *132*, 13981.

[8] For selected recent oxidative carbocyclization reactions, see: a) T. Pei, X. Wang, R. A. Widenhoefer, *J. Am. Chem. Soc.* **2003**, *125*, 648; b) E. M. Ferreira, B. M. Stoltz, *J. Am. Chem. Soc.* **2003**, *125*, 9578; c) H. Zhang, E. M. Ferreira, B. M. Stoltz, *Angew. Chem.* **2004**, *116*, 6270; *Angew. Chem. Int. Ed.* **2004**, *43*, 6144; d) A. Kong, X. Han, X. Lu, *Org. Lett.* **2006**, *8*, 1339.

[9] a) J. Löfstedt, J. Franzén, J.-E. Bäckvall, *J. Org. Chem.* **2001**, *66*, 8015; b) J. Franzén, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2003**, *125*, 6056; c) J. Piera, K. Närhi, J.-E. Bäckvall, *Angew. Chem.* **2006**, *118*, 7068; *Angew. Chem. Int. Ed.* **2006**, *45*, 6914; d) J. Piera, A. Persson, X. Caldentey, J.-E. Bäckvall, *J. Am. Chem. Soc.* **2007**, *129*, 14120; e) E. V. Johnston, E. A. Karlsson, S. A. Lindberg, B. Åkermark, J.-E. Bäckvall, *Chem. Eur. J.* **2009**, *15*, 6799; f) A. K. Å. Persson, J.-E. Bäckvall, *Angew. Chem.* **2010**, *122*, 4728; *Angew. Chem. Int. Ed.* **2010**, *49*, 4624; g) for a DFT calculation of the allene attack on Pd^{II}, see: E. A. Karlsson, J.-E. Bäckvall, *Chem. Eur. J.* **2008**, *14*, 9175.

[10] a) A. K. Å. Persson, T. Jiang, M. T. Johnson, J.-E. Bäckvall, *Angew. Chem.* **2011**, *123*, 6279; *Angew. Chem. Int. Ed.* **2011**, *50*, 6155; b) T. Jiang, A. K. Å. Persson, J.-E. Bäckvall, *Org. Lett.* **2011**, *13*, 5838.

[11] P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk, F. D. Toste, *J. Am. Chem. Soc.* **2008**, *130*, 4517.

[12] a) M. Bertrand, J.-P. Dulcère, J. Grimaldi, M. Malacria, *C. R. Seances Acad. Sci. Ser. C* **1974**, *279*, 805; b) Y.-K. Wu, F. G. West, *J. Org. Chem.* **2010**, *75*, 5410.

[13] W. H. Okamura, *Acc. Chem. Res.* **1983**, *16*, 81.

[14] a) A. Suzuki, N. Miyaura, *Chem. Rev.* **1995**, *95*, 2451; b) N. Miyaura, *Top. Curr. Chem.* **2002**, *219*, 248; c) N. Miyaura in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**, pp. 41–123.

[15] See the Supporting Information for the crystal data of **5b** and **5e**. CCDC 845597 and 845598 (**5b** and **5e**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] a) J. S. Temple, M. Riediker, J. Schwartz, *J. Am. Chem. Soc.* **1982**, *104*, 1310; b) J.-E. Bäckvall, S. E. Byström, R. E. Nordberg, *J. Org. Chem.* **1984**, *49*, 4619; c) J.-E. Bäckvall, R. E. Nordberg, D. Wilhelm, *J. Am. Chem. Soc.* **1985**, *107*, 6892; d) K. J. Szabó, *Organometallics* **1998**, *17*, 1677; e) A. C. Albéniz, P. Espinet, B. Martín-Ruiz, *Chem. Eur. J.* **2001**, *7*, 2481; f) M. S. Chen, N. Prabagaran, N. A. Labenz, M. C. White, *J. Am. Chem. Soc.* **2005**, *127*, 6970; g) X. Chen, J.-J. Li, X.-S. Hao, C. E. Goodhue, J.-Q. Yu, *J. Am. Chem. Soc.* **2006**, *128*, 78; h) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904; i) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 9651; j) M. Pérez-Rodríguez, A. A. C. Braga, M. Garcia-Melchor, M. H. Pérez-Temprano, J. A. Casares, G. Ujaque, A. R. de Lera, R. Álvarez, F. Maseras, P. Espinet, *J. Am. Chem. Soc.* **2009**, *131*, 3650.

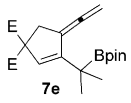
[17] For the palladium-catalyzed nonoxidative borylating cyclization of enynes, see: J. Marco-Martínez, V. López-Carrillo, E. Buñuel, R. Simancas, D. J. Cárdenas, *J. Am. Chem. Soc.* **2007**, *129*, 1874.

[18] H. A. Dieck, R. F. Heck, *J. Org. Chem.* **1975**, *40*, 1083.

[19] The reaction of **1** in the presence of $PhB(OH)_2$ does not seem to involve allene attack according to Scheme 1b. This was indicated by a dramatic shift of the product in the B_2pin_2 borylation reaction of **1e** in Scheme 5 from **5e** to **7e** (**7e**:**5e** = 4:1), when a catalytic amount of $PhB(OH)_2$ (20 mol%) was present. The presence of 20 mol% of *p*-tolSO_3H led to exclusive formation of **7e** (**7e**:**5e** > 15:1).

[20] C. Zhou, R. C. Larock, *J. Org. Chem.* **2006**, *71*, 3184.

[21] For reactions involving β-H elimination in vinyl palladium intermediates to give an allene, see: a) S. Pivsa-Art, T. Satoh, M. Miura, M. Nomura, *Chem. Lett.* **1997**, 823; b) R. C. Larock, Q. Tian, A. A. Pletnev, *J. Am. Chem. Soc.* **1999**, *121*, 3238; c) E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7280.



7e

[22] a) For the cycloisomerization of enynes involving a proposed pallada(IV)cyclopentene intermediate, see: B. M. Trost, M. Lautens, *J. Am. Chem. Soc.* **1985**, *107*, 1781; b) for the Pauson–Khand type reaction of enynes involving a proposed pallada(IV)cyclopentene intermediate, see: Y. Tang, L. Deng, Y. Zhang, G. Dong, J. Chen, Z. Yang, *Org. Lett.* **2005**, *7*, 1657; c) DFT-based theoretical study of this Pauson–Khand type reaction, see: Y. Lan, L. Deng, J. Liu, C. Wang, O. Wiest, Z. Yang, Y.-D. Wu, *J. Org. Chem.* **2009**, *74*, 5049.

[23] For recent reviews on Pd^{IV} catalysis, see: a) K. Muñiz, *Angew. Chem.* **2009**, *121*, 9576; *Angew. Chem. Int. Ed.* **2009**, *48*, 9412; b) L.-M. Xu, B.-J. Li, Z. Yang, Z.-J. Shi, *Chem. Soc. Rev.* **2010**, *39*, 712; c) P. Sehnal, R. J. K. Taylor, I. J. S. Fairlamb, *Chem. Rev.* **2010**, *110*, 824.