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Palladium-Catalyzed Three-Component Reaction of 3-(Tri-*n*-butylstannyl)allyl Acetates, Aldehydes, and Triorganoboranes: An Alternative to the Carbonyl Allylation Using α,γ-Substituted Allylic Tin Reagents

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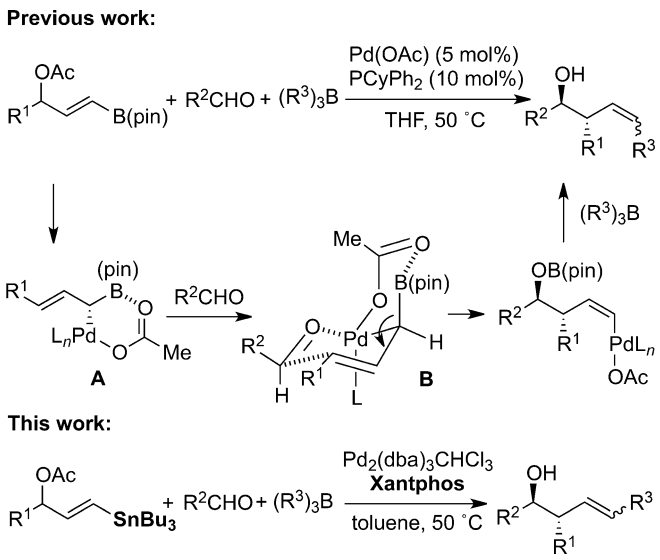
Abstract: A three-component reaction of 3-(tri-*n*-butylstannyl)allyl acetates, aldehydes, and triorganoboranes in the presence of a palladium-Xantphos catalyst system predominately gave (*E*)-*anti*-homoallylic alcohols with high diastereoselectivity and good to high levels of alkene stereocontrol. An efficient chirality transfer was observed when an enantioenriched substrate was employed. The reaction was initiated by the formation of an allylic *gem*-palladium/stannyl intermediate, which subsequently underwent allylation of the aldehyde by an allyltributyltin followed by a coupling reaction of the *in-situ*-generated (*E*)-vinylpalladium acetate with the triorganoborane.

Keywords: allylation; allylic tin compounds; homoallylic alcohols; palladium; three-component reaction

The stereoselective synthesis of homoallylic alcohols is of great synthetic interest because they are found in natural compounds as a ubiquitous structure.[1] In addition, they are considered versatile building blocks for the synthesis of natural products[2] and useful intermediates for the synthesis of complex molecules.[3] The diastereoselective allylation of aldehydes with γ-alkyl-substituted allylic tin(IV) reagents is one of the most reliable and important methods for this purpose.[4] This reaction is usually performed in the presence of a Lewis acid or a Brønsted acid because allylic tin(IV) reagents are not sufficiently reactive toward aldehydes under mild conditions. As a result, the corresponding *syn*-homoallylic alcohols are usually obtained. Interestingly, Baba and Yasuda reported that the allyl tin(II) species generated *in situ* from allylic tin(IV) species and $SnCl_2$ react with both ketones and aldehydes in acetonitrile as a solvent, without any external activation.[5] This reaction has been proposed to proceed *via* a cyclic transition state because of the strong affinity between the tin(II) atom and the carbonyl oxygen atom. Thus, *anti*-homoallylic alcohols are obtained as the major product with good to high stereoselectivity. Furthermore, Oestreich and coworkers have contributed a substantial advance in this area. They developed a method for the facile synthesis of α-chiral γ-substituted allylic tin(IV) reagents and applied it to enantiospecific and diastereoselective thermal- and Lewis acid-promoted carbonyl allylations.[6] Despite these advances, the synthesis of (*E*)-*anti*-homoallylic alcohols using allylic tin reagents and aldehydes remains a formidable challenge.

We recently reported the palladium-catalyzed three-component reaction of 3-(pinacolatoboryl)allyl acetates, aldehydes, and triorganoboranes; this reaction provides access to and extensive alkene stereocontrol of a wide variety of functionalized (*Z*)-*anti*-homoallylic alcohols (Scheme 1).[7] The reaction is proposed to proceed through a putative *cis*-decalin-like transition state **B**, wherein the palladium atom behaves as a Lewis acid and an acetoxy group on the palladium atom acts as a Lewis base to intramolecularly activate allylboronates.

We envisioned that if the acetoxy group on the palladium atom can intramolecularly activate a tributyltin group instead of a pinacolatoboryl group in intermediate **A**, the *in-situ*-formed allyltributyltin would react with an aldehyde to form an *E*-vinylpalladium intermediate. Because the tributyltin group is significantly more bulky than a pinacolatoboryl group, it would prefer to be at the equatorial position rather than the axial position. Furthermore, its coupling with



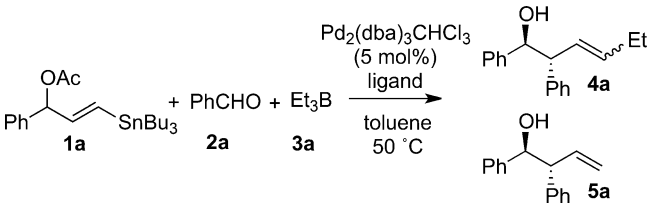
Scheme 1. Palladium-catalyzed three component reactions *via* allylic *gem*-palladium/boryl and stannyl intermediates.

triorganoboranes would provide a useful alternative approach to the synthesis of (*E*)-*anti*-homoallylic alcohols that cannot be accessed by allylation of aldehydes with allylic tributyltins. Herein we report the three-component reaction of 3-(tri-*n*-butylstannyl)allyl acetates, aldehydes, and triorganoboranes by a palladium-Xantphos[8] catalyst system that predominantly furnishes (*E*)-*anti*-homoallylic alcohols.

Initially, we chose the reaction of **1a**, benzaldehyde (**2a**), and triethylborane (**3a**) as a model and began optimization studies by evaluating various ligands in conjunction with $Pd_2(dba)_3CHCl_3$ (Table 1). Monodentate phosphines such as PPh_3 and $P(n\text{-}Bu)_3$ gave **4a** in 26% and 53% isolated yields, respectively, with moderate to good *E*/*Z* ratios (entries 1 and 2). However, a substantial amount of **5a** was obtained. Among the bisphosphines tested, Xantphos exhibited the best results in terms of both alkene stereocontrol and chemical yield of **4a** (entries 3–7). Eventually, we observed that lowering the catalyst loading led to **4a** with a high level of alkene stereocontrol (entry 8). However, further reducing the catalyst loading did not give comparable results in terms of the *E*/*Z* ratio of the product (entry 9). Furthermore, use of THF as a solvent reduced the chemical yield of **4a** (entry 10). In all cases, excellent diastereoselectivity was observed.

Having determined the optimal conditions, we subsequently explored the reaction scope of various aldehydes using **1a** and **3a** (Table 2). Electron-neutral and electron-deficient aromatic aldehydes underwent the three-component reaction to produce **4b**–**4d** in good yields with good to high levels of alkene stereocontrol. When *p*-formylbenzonitrile was employed, 3 equivalents of Et_3B were required to promote the

Table 1. Optimization of the reaction conditions.[a]



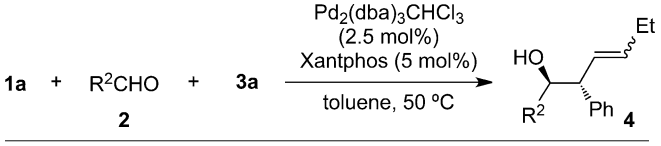
Entry	Ligand [mol%]	Time [h]	**4a** [%][b]	*E*/*Z*[c]	**5a** [%][b]
1	$P(Cy)Ph_2$ (20)	3	26	4.5/1	52
2	$P(n\text{-}Bu)_3$ (20)	5	53	6/1	11
3	BINAP (10)	12	2	1.6/1	0
4	DPPF (10)	12	12	6/1	0
5	DPPPent (10)	1.5	43	5/1	0
6	DPEphos (10)	1.5	61	6/1	0
7	Xantphos (10)	0.5	77	7.5/1	0
8[d]	Xantphos (5)	0.5	77	11/1	0
9[e]	Xantphos (2.5)	0.5	78	8/1	0
10[f]	Xantphos (5)	0.5	58	6/1	0

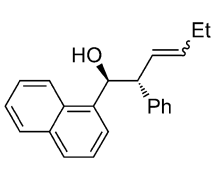
[a] *Conditions:* **1a** (0.5 mmol), **2a** (1.2 mmol), **3a** (1.2 mmol), $Pd_2(dba)_3CHCl_3$ (0.025 mmol), and ligand [BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, DPPF = 1,1′-bis(di-phenylphosphino)ferrocene, DPEphos = bis(2-diphenylphosphinophenyl) ether, Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene] in toluene (2 mL) at 50 °C.
[b] Yield of the isolated product.
[c] Determined by NMR analysis.
[d] $Pd_2(dba)_3CHCl_3$ (1.25×10^{-2} mmol) was used.
[e] $Pd_2(dba)_3CHCl_3$ (6.25×10^{-3} mmol) was used.
[f] THF was used as a solvent.

reaction, giving **4e** in 53% yield; however, the *E*/*Z* ratio of **4e** decreased. The reaction also tolerated methoxy-substituted benzaldehydes to afford **4f**–**4h** in good yields, but the *E*/*Z* ratio of **4g** was moderate. Although *m*-hydroxybenzaldehyde afforded **4i** in only 30% yield, this reaction was performed without prior protection of the hydroxy group. Moreover, we investigated the reaction of heterocyclic aldehydes such as thienyl and furyl aldehydes and observed that the reactions of 3- and 2-thienyl aldehydes proceeded smoothly to produce **4j** and **4k**, respectively, in high yields with moderate to good levels of alkene stereocontrol. The reaction of furfural also afforded **4l**, but the *E* selectivity was moderate. Furthermore, aliphatic aldehydes participated in the three-component reaction to afford the corresponding products **4m**–**4p** as mixtures of *E*- and *Z*-isomers in 54–82% yields with *E*/*Z* ratios from 5/1 to 6.9/1. Excellent diastereoselectivities were observed for all aldehydes examined.

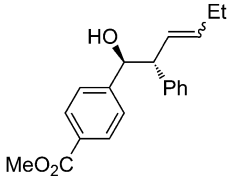
We then examined the substrate scope (Table 3). 1-Naphthyl-substituted substrate gave **6a** in 73% yield with an *E*/*Z* ratio of 13/1. The present palladium-Xantphos catalyst system was compatible with electronically diverse substituents such as methoxy, methoxycarbonyl, and bromo groups on the aromatic

Table 2. Reaction scope of aldehydes.[a]

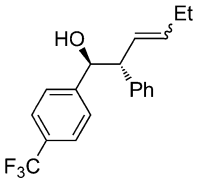




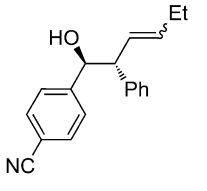
4b: 68%, *E*/*Z* = 8.2/1



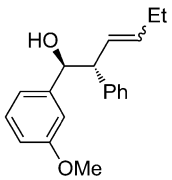
4c: 71%, *E*/*Z* = 12/1



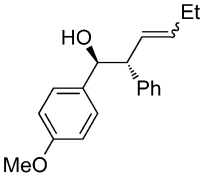
4d: 62%, *E*/*Z* = 12/1



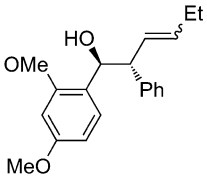
4e: 53%, *E*/*Z* = 6.5/1[b]



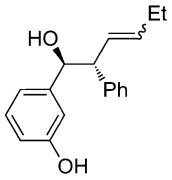
4f: 72%, *E*/*Z* = 9.6/1



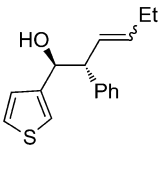
4g: 74%, *E*/*Z* = 5.5/1



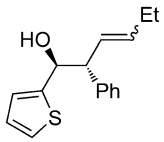
4h: 70%, *E*/*Z* = 7.2/1



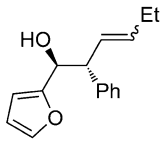
4i: 30%, *E*/*Z* = 7.1/1[b]



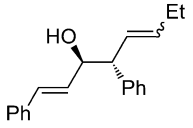
4j: 82%, *E*/*Z* = 7.3/1



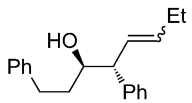
4k: 82%, *E*/*Z* = 5.3/1



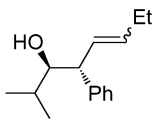
4l: 60%, *E*/*Z* = 4.3/1



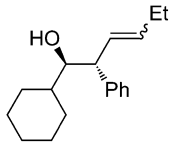
4m: 54%, *E*/*Z* = 6.9/1



4n: 55%, *E*/*Z* = 5.3/1



4o: 55%, *E*/*Z* = 6.3/1



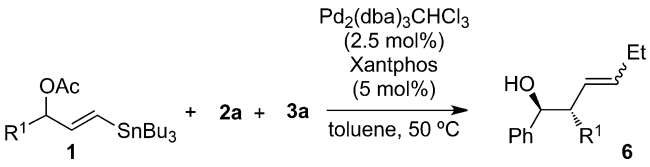
4p: 82%, *E*/*Z* = 5/1

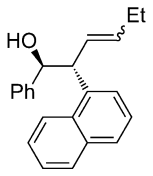
[a] *Conditions:* **1a** (0.5 mmol), **2** (1.2 mmol), **3a** (1.2 mmol), $Pd_2(dba)_3CHCl_3$ (0.0125 mmol), and Xantphos (0.025 mmol) in toluene (2 mL) at 50 °C.
[b] 3 equivalents of Et_3B were used.

ring, giving **6b–6e** in 73–89% yields with *E*/*Z* ratios ranging from 6.4/1 to 7.7/1. Notably, the *m*-bromophenyl-substituted substrate was compatible with the reaction conditions, whereas the C–Br bond remained intact, providing an opportunity for further functionalization. The heteroaryl-substituted substrates were also amenable to reaction, giving **6f–6h** in 55–76% yields as mixtures of *E*- and *Z*-isomers in ratios ranging from 4/1 to 5.2/1.

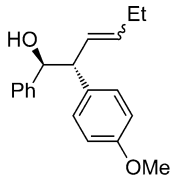
To further probe the scope of this process, diverse tri-*n*-alkylboranes prepared from the corresponding alkenes with $BH_3{\cdot}SMe_2$ were surveyed (Table 4). The

Table 3. Substrate scope.[a]

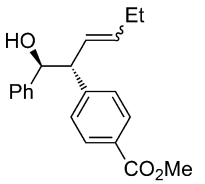




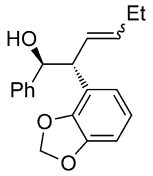
6a: 73%, *E*/*Z* = 13/1



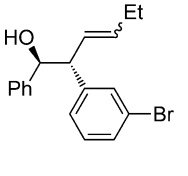
6b: 77%, *E*/*Z* = 7.3/1



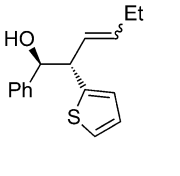
6c: 89%, *E*/*Z* = 6.5/1



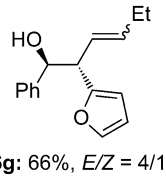
6d: 87%, *E*/*Z* = 6.4/1



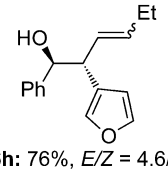
6e: 73%, *E*/*Z* = 7.7/1



6f: 55%, *E*/*Z* = 5.2/1



6g: 66%, *E*/*Z* = 4/1

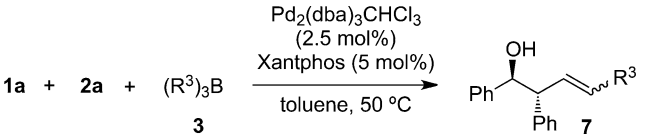


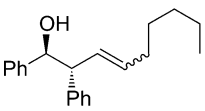
6h: 76%, *E*/*Z* = 4.6/1

[a] *Conditions:* **1** (0.5 mmol), **2a** (1.2 mmol), **3a** (1.2 mmol), $Pd_2(dba)_3CHCl_3$ (0.0125 mmol), and Xantphos (0.025 mmol) in toluene (2 mL) at 50 °C.

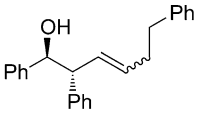
scope with respect to the tri-*n*-alkylboranes was broad to produce **7a–7c** in good yields with high levels of *E*/*Z* stereo- and diastereoselectivity. In addition, a cyclohexyl group was introduced into the alkene of the homoallylic alcohol product, albeit in moderate yield,

Table 4. Reaction scope of triorganoboranes.[a]

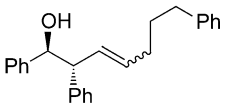




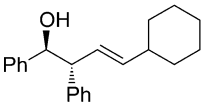
7a: 74%, *E*/*Z* = 12/1



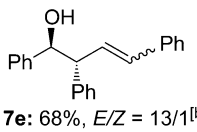
7b: 73%, *E*/*Z* = 14/1



7c: 65%, *E*/*Z* = 14/1



7d: 18%

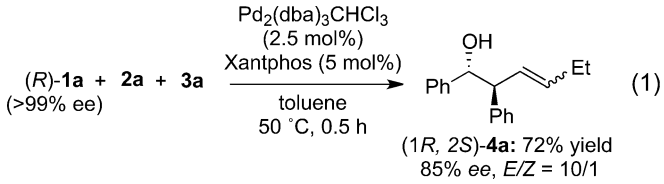


7e: 68%, *E*/*Z* = 13/1[b]

[a] *Conditions:* **1a** (0.5 mmol), **2a** (1.2 mmol), **3** (1.5 mmol), $Pd_2(dba)_3CHCl_3$ (0.0125 mmol), and Xantphos (0.025 mmol) in toluene (2 mL) at 50 °C.
[b] 2.4 equivalents of Ph_3B were used.

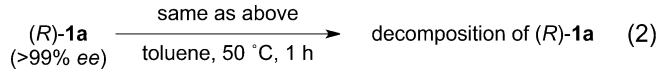
through the use of tricyclohexylborane. Furthermore, a commercially available triphenylborane fruitfully underwent a cross-coupling reaction to afford **7e** in 68% yield with an *E*/*Z* ratio of 13/1 and excellent diastereoselectivity. In another attempt to use *B*-alkyl-9-BBN and alkyl boronate esters, no conversion was observed.

To expand the scope of the reaction from a synthetic viewpoint, we conducted a chirality transfer experiment using (*R*)-**1a** under the optimized reaction conditions. As observed in our previous work,[7] a similar efficient chirality transfer was achieved, resulting in **4a** in 72% yield and 85% *ee* [Eq. (1)]. The incomplete



chirality transfer may be explained by a redox transmetalation process.[9] Importantly, the absolute configuration of **4a** differed from that of the product in our previous work. The absolute stereochemical assignment of **4a** was determined to be (1*R*, 2*S*) by transformation into known diols,[10] and the relative stereochemistry of **4a** was reconfirmed as the *anti*-isomer by single-crystal X-ray diffraction analysis (Figure 1).[11]

To better understand the racemization process, we treated (*R*)-**1a** with a catalytic amount of $Pd_2(dba)_3CHCl_3$ (2.5 mol%) and Xantphos (5 mol%) in toluene at 50 °C for 1 h [Eq. (2)]. However, decomposition of (*R*)-**1a** was observed and 1,6-diphenyl-1,3,5-hexatriene was instead produced in 29% yield by the dimerization of the palladium-complexed 3-phenyl-2-propenylcarbene.[12,13]



A catalytic mechanism based on the aforementioned results is proposed in Scheme 2. The palladium-Xantphos complex reacts with **1** to initially form a π-allylpalladium intermediate **C**.[14] The oxygen atom of an acetoxy group in **C** coordinates intramolecularly to the tributyltin group, leading to σ-allylpalladium intermediate **C′**.[12] Accordingly, the palladium atom in the σ-allylpalladium instead of the tin atom in the tributyltin group functions as a Lewis acid to form a putative *trans*-decalin-like cyclic transition state **D**. The nucleophilic allylation of an aldehyde by an allyltributyltin then generates (*E*)-vinylpalladium acetate intermediate **E**. Subsequent transmetalation

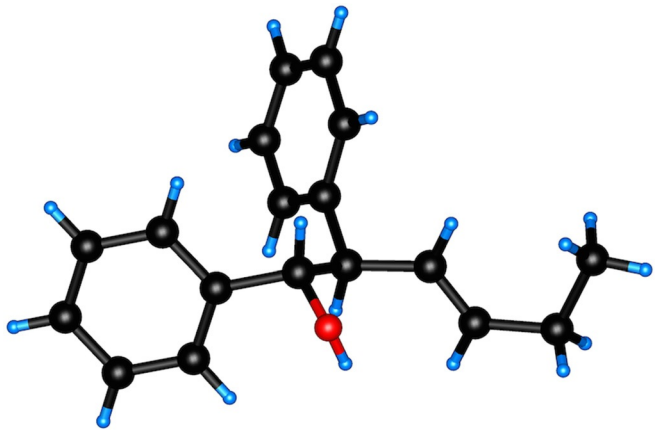
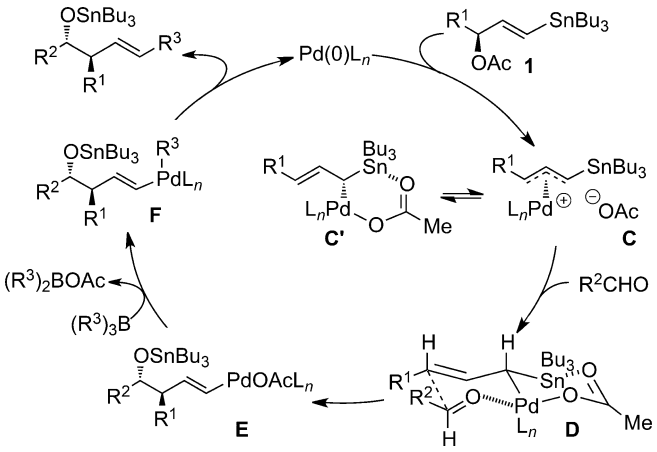


Figure 1. X-ray crystallographic structure of **4a**.



Scheme 2. Proposed reaction mechanism.

of **E** with a triorganoborane followed by the reductive elimination of a vinylpalladium intermediate **F** gives (*E*)-*anti*-homoallylic alcohols. This mechanism reasonably explains the stereochemistry observed in the chiral transfer reaction [Eq. (1)]. On the other hand, β-hydride elimination from **F** followed by reductive elimination of the resulting palladium hydride intermediate leads to product **5a**. Another reaction mechanism is plausible, where a tin-substituted σ-allyl(R^3)palladium intermediate is formed *via* transmetalation of **C′** with $(R^3)_3B$, which then undergoes nucleophilic allylation of an aldehyde by an allyltributyltin through a cyclic transition state to produce **F**. However, the Lewis acidity of the palladium atom in the formation of a σ-allyl(R^3)palladium intermediate would become weaker. Moreover, the allylation of an aldehyde may proceed from a σ-allyl(R^3)palladium rather than an allyltributyltin.[10,15–17]

In summary, we have developed a three-component reaction of 3-(tri-*n*-butylstannyl)allyl acetates, aldehydes, and triorganoboranes by a palladium-Xantphos

catalyst system, which provides facile access into (*E*)-*anti*-homoallylic alcohols. The present method not only allows the introduction of *n*-alkyl, *sec*-alkyl, and aryl groups into the alkene of the homoallylic alcohols but also gives access to effective control of the (*E*)-geometry at the double bond. Interestingly, the present reaction proceeds through a σ-allylpalladium-controlled cyclic transition state. Further investigations along these lines are currently underway in our laboratories.

Experimental Section

Typical Procedure for Palladium-Catalyzed Three-Component Reaction; Synthesis of 4a

A 10-mL two-neck round-bottom flask was charged with $Pd_2(dba)_3CHCl_3$ (12.9 mg, 0.0125 mmol), Xantphos (14.5 mg, 0.025 mmol), and toluene (1 mL). The mixture was stirred at room temperature for 0.5 h. A solution of **1a** (232.6 mg, 0.5 mmol) and benzaldehyde (**2a**) (123 μL, 1.2 mmol) in toluene (1 mL) and Et_3B (**3a**) (1.2 mmol, 1.0 M hexane solution) were then successively added. The reaction mixture was stirred at 50 °C for 0.5 h. Upon completion of the reaction, the reaction mixture was diluted with EtOAc (20 mL) and washed with saturated NH_4Cl (2 × 20 mL) and brine (2 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by silica gel chromatography (R_f 0.45, EtOAc/hexane = 1/4) to give **4a** as a yellow oil; yield: 97.2 mg (77%).

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References

[1] a) G. Y. Fang, V. K. Aggarwal, *Angew. Chem.* **2007**, *119*, 363–366; *Angew. Chem. Int. Ed.* **2007**, *46*, 359–362; b) P. R. Lassen, D. M. Skytte, L. Hemmingsen, S. F. Nielsen, T. B. Freedman, L. A. Nafie, S. B. Christensen, *J. Nat. Prod.* **2005**, *68*, 1603–1609; c) S. Suzuki, T. Umezawa, M. Shimada, *J. Chem. Soc. Perkin Trans. 1* **2001**, 3252–3252.

[2] a) J. Lee, J. S. Panek, *J. Org. Chem.* **2015**, *80*, 2959–2971; b) T. Neubauer, C. Kammerer-Pentierz, T. Bach, *Chem. Commun.* **2012**, *48*, 11629–11631; c) E. de Lemos, F.-H. Porée, A. Commerçon, J.-F. Betzer, A. Ange Pancrazi, J. Ardisson, *Angew. Chem.* **2007**, *119*, 1949–1953; *Angew. Chem. Int. Ed.* **2007**, *46*, 1917–1921.

[3] a) S. Hayashi, K. Hirao, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 12650–12651; b) H. Huang, J. S. Panek, *J. Am. Chem. Soc.* **2000**, *122*, 9836–9837.

[4] For selected reviews, see: a) Y. Yamamoto, N. Asao, *Chem. Rev.* **1993**, *93*, 2207–2293; b) Y. Nishiguchi, A. Takuwa, Y. Naruta, K. Maruyama, *Tetrahedron* **1993**, *49*, 7395–7426; c) J. A. Marshall, *Chem. Rev.* **2000**, *100*, 3163–3185; d) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763–2793; e) G. Zanoni, A. Pontiroli, A. Marchetti, G. Vidari, *Eur. J. Org. Chem.* **2007**, 3599–3611.

[5] a) M. Yasuda, Y. Sugawa, A. Yamamoto, I. Shibata, A. Baba, *Tetrahedron Lett.* **1996**, *37*, 5951–5954; b) M. Yasuda, K. Hirata, M. Nishino, A. Yamamoto, A. Baba, *J. Am. Chem. Soc.* **2002**, *124*, 13442–13447; c) M. Yasuda, T. Azuma, K. Tsuruwa, S. A. Babu, A. Baba, *Tetrahedron Lett.* **2009**, *50*, 3209–3212; d) M. Yasuda, T. Azuma, K. Tsuruwa, S. A. Babu, A. Baba, *Tetrahedron* **2009**, *65*, 9569–9574.

[6] a) E. S. Schmidtmann, M. Oestreich, *Angew. Chem.* **2009**, *121*, 4705–4709; *Angew. Chem. Int. Ed.* **2009**, *48*, 4634–4638; b) D. J. Vyas, R. Frohlich, M. Oestreich, *J. Org. Chem.* **2010**, *75*, 6720–6723.

[7] Y. Horino, A. Aimono, H. Abe, *Org. Lett.* **2015**, *17*, 2824–2827.

[8] a) M. Kranenburg, Y. E. M. van der Burgt, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* **1995**, *14*, 3081–3089; b) P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741–2769.

[9] a) P. B. Mackenzie, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1985**, *107*, 2046–2054; b) H. Kurosawa, S. Ogoshi, N. Chatani, Y. Kawasaki, S. Murai, I. Ikeda, *Chem. Lett.* **1990**, 1745–1748; c) J.-E. Bäckvall, K. L. Granberg, A. Heumann, *Isr. J. Chem.* **1991**, *31*, 17–24; d) K. L. Granberg, J.-E. Bäckvall, *J. Am. Chem. Soc.* **1992**, *114*, 6858–6863; e) C. Amatore, S. Gamez, A. Jutand, G. Meyer, M. Moreno-Mañas, L. Morral, R. Pleixats, *Chem. Eur. J.* **2000**, *6*, 3372–3376; f) C. Amatore, A. Jutand, L. Mensah, G. Meyer, J.-C. Fiaud, J. Y. Legros, *Eur. J. Org. Chem.* **2006**, 1185–1192; g) G. Blessley, P. Holden, M. Walker, J. M. Brown, V. Gouverneur, *Org. Lett.* **2012**, *14*, 2754–2757; h) H. L. Amanda, J. P. Morken, *Org. Lett.* **2014**, *16*, 2096–2099.

[10] See the Supporting Information for details.

[11] CCDC 1419321 contains 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.

[12] V. É. Trépanier, E. Fillion, *Organometallics* **2007**, *26*, 30–32.

[13] a) M. P. Doyle, M. Yan, *J. Org. Chem.* **2002**, *67*, 602–604; b) T. Mesganaw, G. Y. J. Im, N. K. Garg, *J. Org. Chem.* **2013**, *78*, 3391–3393; c) Y. Horino, Y. Takahashi, K. Koketsu, H. Abe, K. Tsuge, *Org. Lett.* **2014**, *16*, 3184–3187; d) Y. Horino, Y. Takahashi, R. Kobayashi, H. Abe, *Eur. J. Org. Chem.* **2014**, 7818–7822.

[14] T. Oshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya, K. Mashima, *J. Am. Chem. Soc.* **2009**, *131*, 14317–14328.

[15] Recent studies on palladium-catalyzed enantioselective allylation of aldehydes via σ-allylethylpalladium intermediates, see: a) G. Zanoni, S. Gladiali, A. Marchetti, P. Piccinini, I. Tredici, G. Vidari, *Angew. Chem.* **2004**, *116*, 864–867; *Angew. Chem. Int. Ed.* **2004**, *43*, 846–849; b) S.-F. Zhu, Y. Yang, L.-X. Wang, B. Liu, Q.-L. Zhou,

Org. Lett. **2005**, *7*, 2333–2335; c) G. P. Howell, A. J. Minnaard, B. L. Feringa, *Org. Biomol. Chem.* **2006**, *4*, 1278–1283; d) O. Onomura, N. Fujimura, T. Oda, Y. Matsumura, Y. Demizu, *Heterocycles* **2008**, *76*, 177–182; e) W. Wang, T. Zhang, M. Shi, *Organometallics* **2009**, *28*, 2640–2642; f) X.-C. Qiao, S.-F. Zhu, W.-Q. Chen, Q.-L. Zhou, *Tetrahedron: Asymmetry* **2010**, *21*, 1216–1220; g) J.-J. Jiang, D. Wang, W.-F. Wang, Z.-L. Yuan, M.-X. Zhao, F.-J. Wang, M. Shi, *Tetrahedron: Asymmetry* **2010**, *21*, 2050–2054; h) S.-F. Zhu, X.-Q. Qiao, Y.-Z. Zhang, L.-X. Wang, Q.-L. Zhou, *Chem. Sci.* **2011**, *2*, 1135–1140; i) M. Yus, J. C. González-Gómez, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774–7854.

[16] σ-Allylpalladium species are known to react with CO_2, see: a) M. Shi, K. M. Nicholas, *J. Am. Chem. Soc.* **1997**, *119*, 5057–5085; b) R. Johansson, O. F. Wendt, *Dalton Trans.* **2007**, 488–492; c) D. P. Hruszkewycz, J. Wu, N. Hazari, C. D. Incarvito, *J. Am. Chem. Soc.* **2011**, *133*, 3280–3283; d) J. Wu, N. Hazari, *Chem. Commun.* **2011**, *47*, 1069–1071; e) T. Hung, P. W. Jolly, G. Wilke, *J. Organomet. Chem.* **1980**, *190*, C5-C7; f) J. Wu, J. C. Green, N. Hazari, D. P. Hruszkewycz, C. D. Incarvito, T. J. Schmeier, *Organometallics* **2010**, *29*, 6369–6376; g) J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2008**, *130*, 15254–15255; h) J. Takaya, K. Sasano, N. Iwasawa, *Org. Lett.* **2011**, *13*, 1698–1701; i) J. Takaya, N. Iwasawa, *Organometallics* **2009**, *28*, 6636–6638; j) H.-W. Suh, L. M. Guard, N. Hazari, *Chem. Sci.* **2014**, *5*, 3859–3872; k) N. Selander, K. J. Szabó, *Chem. Rev.* **2011**, *111*, 2048–2076; l) T. Mita, Y. Higuchi, Y. Sato, *Chem. Eur. J.* **2015**, *21*, 16391–16394.

[17] For other examples of allylation reactions by nucleophilic σ-allylpalladium intermediates, see: a) H. Kurosawa, A. Urabe, *Chem. Lett.* **1985**, 1839–1840; b) H. Kurosawa, S. Ogoshi, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973–981; c) H. Nakamura, H. Iwama, Y. Yamamoto, *J. Am. Chem. Soc.* **1996**, *118*, 6641–6647; d) H. Nakamura, K. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1998**, *120*, 4242–4243; e) R. A. Fernandes, A. Stimac, Y. Yamamoto, *J. Am. Chem. Soc.* **2003**, *125*, 14133–14139; f) N. Solin, J. Kjellgre, K. J. Szabó, *Angew. Chem.* **2003**, *115*, 3784–3786; *Angew. Chem. Int. Ed.* **2003**, *42*, 3656–3658; g) N. Solin, J. Kjellgren, K. J. Szabó, *J. Am. Chem. Soc.* **2004**, *126*, 7026–7033; h) N. T. Barczak, R. E. Grote, E. R. Jarvo, *Organometallics* **2007**, *26*, 4863–4865; i) M. B. Shaghafi, B. L. Kohn, E. R. Jarvo, *Org. Lett.* **2008**, *10*, 4743–4746.

