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Regioswitchable Palladium-Catalyzed Decarboxylative Coupling of 1,3-Dicarbonyl Compounds

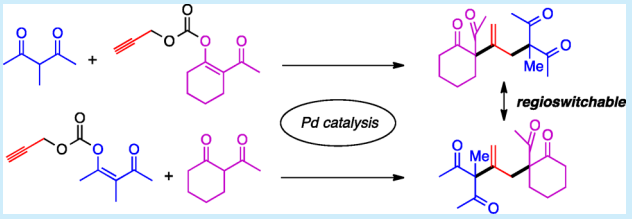
Miles Kenny,[†] Jeppe Christensen,[‡] Simon J. Coles,[‡] and Vilius Franckevičius*[,†]

[†]Department of Chemistry, Lancaster University, Lancaster LA1 4YB, U.K.

[‡]National Crystallography Service, School of Chemistry, University of Southampton, Southampton SO17 1BJ, U.K.

Supporting Information

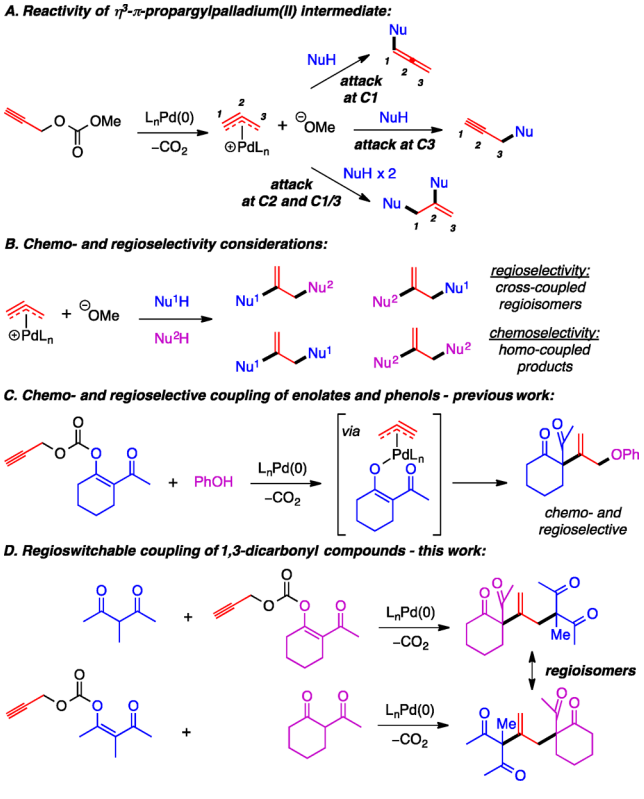
ABSTRACT: A palladium-catalyzed chemo- and regioselective coupling of 1,3-dicarbonyl compounds via an allylic linker has been developed. This reaction, which displays broad substrate scope, forms two C−C bonds and installs two all-carbon quaternary centers. The regioselectivity of the reaction can be predictably controlled by utilizing an enol carbonate of one of the coupling partners.



The palladium(0)-catalyzed alkylation reaction of carbon nucleophiles with allylic electrophiles has over the years matured into a powerful C−C bond-forming tool[1] that enables the stereoselective introduction of congested all-carbon quaternary centers.[2] These processes typically make use of allylic acetates, carbonates, or halides, which undergo oxidative addition to give η^3-π-allylpalladium(II) intermediates. The analogous reaction of palladium(0) with propargylic electrophiles proceeds via η^3-π-propargylpalladium(II) intermediates (Scheme 1A),[3] which exhibit three distinct modes of reactivity.[4] Nucleophilic addition to one of the terminal carbon atoms results in either allenylation or propargylation processes.[5] In addition, with stabilized anions as nucleophiles, η^3-π-propargylpalladium(II) intermediates can undergo sequential double addition,[6] first at the central carbon atom and subsequently at either one of the terminal carbon atoms.[7] The synthetic utility of the latter reactivity mode becomes apparent when two *different* nucleophiles are coupled, rapidly generating complexity in a single operation (Scheme 1B). The challenges associated with this process are control of the chemoselectivity, whereby the formation of homocoupling products is avoided, and control of the regioselectivity, whereby the order of addition of the nucleophiles is controlled. The associated selectivity issues are typically overcome by designing the transformation in such a way that one of the nucleophilic addition steps is intramolecular.[8] In contrast, the regioselective coupling of two different nucleophiles in an intermolecular sense is much more challenging.[9]

Inspired by palladium-catalyzed decarboxylative allylic alkylation processes,[10] which enable the regiospecific formation of enolates under mild and neutral reaction conditions,[11] we recently disclosed the first palladium-catalyzed chemo- and regioselective coupling of enolates and phenols via an η^3-π-propargylpalladium(II) intermediate (Scheme 1C).[12] In this approach, the regioselectivity is governed by the tight association of the η^3-π-propargylpalladium(II) intermediate with the enolate. Given the recent drive by the pharmaceutical industry to find new methodologies that facilitate the synthesis of sp^3-rich molecules,[13] we envisaged that a similar strategy could facilitate the chemo- and regioselective coupling of two

Scheme 1. Reactivity Modes of Propargylic Compounds with Nucleophiles



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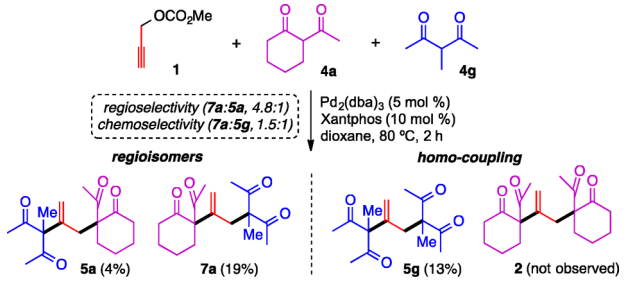
1,3-dicarbonyl compounds, resulting in the formation of two C−C bonds and two quaternary all-carbon centers in a single operation (Scheme 1D). In particular, we postulated that both regioisomers of the product could be predictably accessed by judiciously subjecting one of the coupling partners to the reaction as the enol carbonate. Herein we report a regioswitchable palladium-catalyzed decarboxylative coupling reaction of 1,3-dicarbonyl compounds via an allylic linker, thus resulting in the formation of two new C−C bonds and the installation of two quaternary all-carbon centers.

At the outset, the intermolecular coupling reaction of two 1,3-diketone nucleophiles **4a** and **4g** in the presence of propargylic carbonate **1** in equimolar amounts was investigated (Scheme 2). Of the four possible products, three were obtained

Scheme 2. Selectivity Issues in Intermolecular Coupling of Carbon Nucleophiles

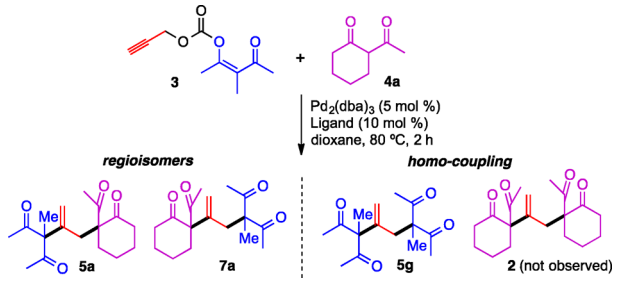


with moderate regioselectivity, low chemoselectivity, and poor yield. Specifically, regioisomers **7a** and **5a** were obtained in a 4.8:1 ratio in 19% and 4% yield, respectively, in addition to significant quantities of the undesired homocoupling product **5g**, which was formed in 13% yield. These results show that the direct coupling of two similar partners leads to significant homocoupling, whereas the sense of regioselectivity of heterocoupling is difficult to predict. In addition, this process does not allow for efficient access to both regioisomers. Therefore, we reasoned that the use of one of the coupling partners as the enol carbonate could bestow predictable regiocontrol and increased efficiency on the transformation.

Pleasingly, the coupling of propargyl enol carbonate **3** with 1,3-diketone **4a** with Xantphos as the ligand for palladium in 1,4-dioxane as the solvent proceeded with complete regioselectivity and moderate chemoselectivity (Table 1, entry 1), predictably affording **5a** as the major product in good yield. A similar result was obtained with palladium tetrakis(triphenylphosphine) as the catalyst (entry 2). Finally, the best product yields were obtained when the large-bite-angle ligands dppf and DPEphos were used (entries 3 and 4), with DPEphos providing product **5a** with complete regioselectivity, good chemoselectivity, and excellent yield. It is worthy of note that the reaction in other solvents, such as toluene, dichloromethane, DMF and acetonitrile, resulted in significant erosion in both the selectivity and yield of **5a** (see the Supporting Information).

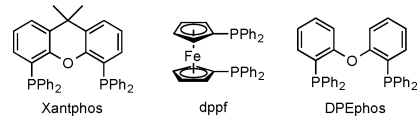
After the optimal ligand for palladium was identified, the reaction scope was investigated by testing the coupling of linear propargyl enol carbonate **3** with a range of 1,3-dicarbonyl compounds **4** (Scheme 3). Specifically, all of the products were obtained with complete regioselectivity. Cyclohexanone-based 1,3-diketones as external coupling partners provided products **5a** and **5b** in high yields. Acyclic diketones also took part in regioselective coupling, giving rise to **5c−f** in good yields.

Table 1. Ligand Screen

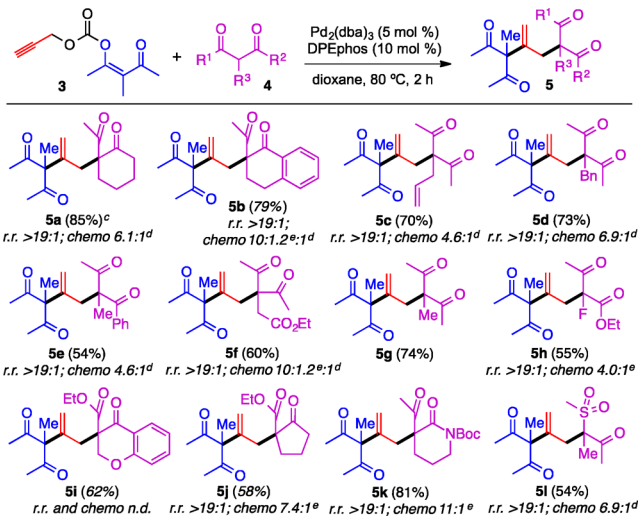


		selectivity[a]		
entry	ligand	regio (**5a**:**7a**)	chemo (**5a**:**5g**)	yield of **5a** (%)[b]
1	Xantphos	>19:1	5.8:1	56
2	PPh_3[c]	>19:1	5.9:1	59
3	dppf	>19:1	6.4:1	73
4	**DPEphos**	**>19:1**	**6.1:1**	**85**

[a]Determined by ^{1}H NMR analysis of the crude product mixtures. [b]Yields of isolated **5a**. [c]$[Pd(PPh_3)_4]$ was used in place of $[Pd_2(dba)_3]$.



Scheme 3. 1,3-Dicarbonyl Scope[a,b,c]



[a]Reaction stoichiometry: 0.24 mmol of **3** and **4**; concn = 0.16 M. [b]Regioselectivity (r.r.) and chemoselectivity (chemo) ratios were determined by ^{1}H NMR analysis of the crude product mixtures. n.d. = not determined due to overlapping signals. [c]Yields of isolated **5** are shown. [d]Refers to homocoupling of **3**. [e]Refers to homocoupling of **4**.

Unsurprisingly, the use of 3-methyl-2,4-pentanedione (**4g**) as the nucleophile afforded homocoupled **5g**. *β*-Keto esters as nucleophiles, both acyclic and cyclic, gave products **5h−j** in good yields. Finally, the incorporation of a *β*-keto lactam and *β*-keto sulfone was also successful, providing the respective coupled products **5k** and **5l**.

Because the enolate generated in situ following decarboxylation is regioselectively alkenylated and the externally added partner is allylated, we next investigated the scope of reversing the regioselectivity by reacting the propargyl enol carbonates of a range of 1,3-dicarbonyl compounds in the presence of 3-methyl-2,4-pentanedione (**4g**) as the external nucleophile

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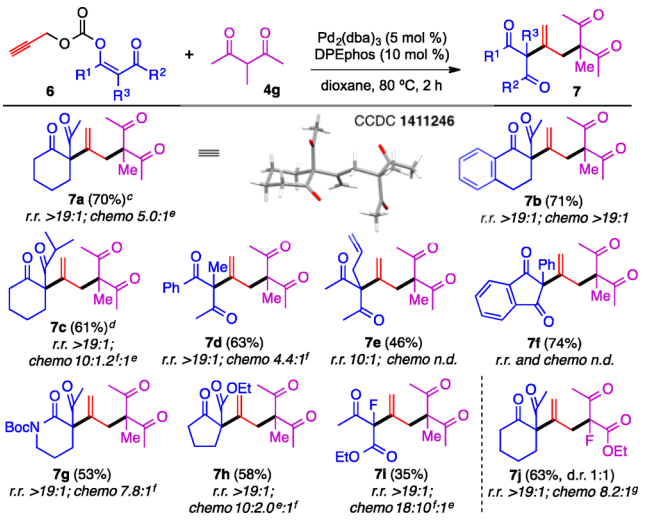
(Scheme 4). In this context, both cyclic and acyclic 1,3-diketones led to the predictable formation of products **7a**–**f**, in

Scheme 4. Carbonate Scope[a,b,c]



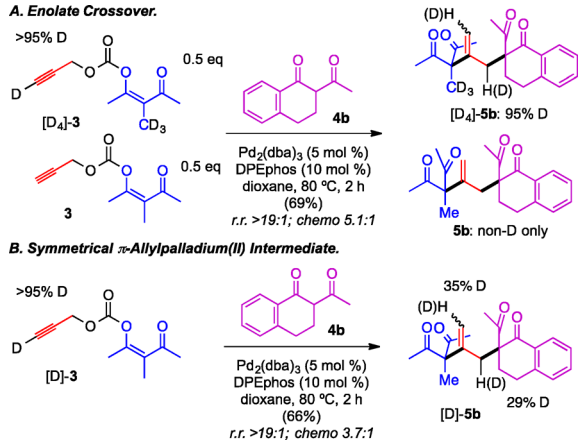
[a]Reaction stoichiometry: 0.24 mmol of **6** and **4g**; concn = 0.16 M. [b]Regioselectivity (r.r.) and chemoselectivity (chemo) ratios were determined by ^{1}H NMR analysis of the crude product mixtures. n.d. = not determined due to overlapping signals. [c]Yields of isolated **7** are shown. [d]The reaction was run for 4 h. [e]Refers to homocoupling of **4g**. [f]Refers to homocoupling of **6**. [g]Refers to homocoupling of β-keto ester **4h**.

which the original enol carbonate substrate had been alkenylated. Although the structures of the products were readily identifiable by long-range HMBC correlations, we obtained an X-ray crystal structure of **7a** to confirm the sense of regioselectivity of the reaction.[14] In the case of a β-keto lactam and a β-keto ester, both were alkenylated successfully (**7g** and **7h**). However, the use of a carbonate of a fluorinated β-keto ester gave the corresponding product **7i** in low chemoselectivity and yield. Finally, when the coupling reaction led to the installation of two stereogenic centers, such as in **7j**, the yield of product was high, but a mixture of diastereoisomers was obtained.

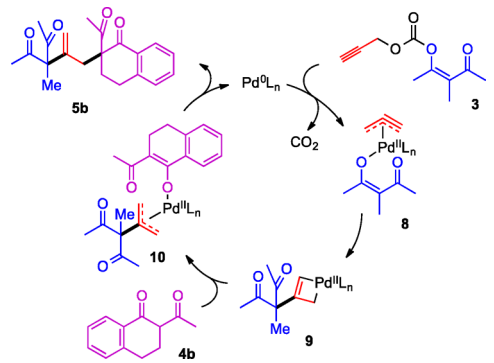
To rationalize the high regioselectivity of these reactions, an enolate crossover experiment using equimolar amounts of [D_4]-**3** and nondeuterated **3** in the presence of 1,3-diketone **4b** as the external nucleophile was performed (Scheme 5A); the reaction afforded [D_4]-**5b** and nondeuterated **5b** as the only products, as determined by mass spectrometry. The absence of enolate crossover strongly suggests a tight association of the η^3-π-propargylpalladium(II) complex with the enolate following decarboxylation. The intermediacy of an η^3-π-allylpalladium(II) complex, which participates in the second nucleophilic addition, was supported by the scrambling of the deuterium label in [D]-**5b** when carbonate [D]-**3** was coupled with 1,3-diketone **4b** (Scheme 5B).

In light of the deuterium-labeling studies, we propose a reaction mechanism in which the palladium(0) catalyst undergoes oxidative addition to carbonate **3** to give intermediate **8** following decarboxylation (Scheme 6). Because the palladium metal center is likely to be strongly associated with the enolate in **8** (see above, Scheme 5), we believe that the intramolecular inner-sphere mode of addition of the enolate to the central carbon atom of the η^3-π-propargylpalladium(II)

Scheme 5. Deuterium-Labeling Experiments



Scheme 6. Proposed Catalytic Cycle



species in the next step determines the high regioselectivity of the reaction. However, this observation is at variance with the outer-sphere mechanism proposed for the addition of stabilized nucleophiles to η^3-π-allylpalladium(II) intermediates.[15] Although the involvement of a palladacyclobutene intermediate **9** following nucleophilic addition has been previously suggested,[8b,m,16] the lack of experimental evidence for its existence intimates that nucleophilic addition of the enolate in **8** is followed by immediate protonation by the external nucleophile **4b** in a synchronous manner to give **10**.[17] In the final step, the resulting η^3-π-allylpalladium(II) complex in **10** undergoes nucleophilic addition by the second enolate coupling partner, affording product **5b** with complete regiocontrol and regenerating the palladium(0) catalyst.

In summary, a regio- and chemoselective decarboxylative palladium-catalyzed coupling of two carbon nucleophiles is disclosed, a transformation that generates two C–C bonds and two all-carbon quaternary centers in a single operation. The reaction is predictably regioswitchable, providing access to either of the two regioisomers of product depending on the choice of the propargyl enol carbonate substrate. We are now exploring avenues of accessing these products in an enantioselective manner.

■ ASSOCIATED CONTENT

Supporting Information

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Full experimental procedures, characterization data, and HRMS and ^{1}H and ^{13}C NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: v.franckevicius@lancaster.ac.uk.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Tsuji, J.; Takahashi, H.; Morikawa, M. *Tetrahedron Lett.* **1965**, *6*, 4387. (b) Atkins, K. E.; Walker, W. E.; Manyik, R. M. *Tetrahedron Lett.* **1970**, *11*, 3821. (c) Hata, G.; Takahashi, K.; Miyake, A. *J. Chem. Soc. D* **1970**, 1392. (d) Trost, B. M.; Fullerton, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 292. (e) Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649.

(2) For reviews in the area, see: (a) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (b) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. (c) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195. (d) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203. (e) Trost, B. M. *Chem. Pharm. Bull.* **2002**, *50*, 1. (f) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921. (g) Trost, B. M. *J. Org. Chem.* **2004**, *69*, 5813. (h) Trost, B. M.; Fandrick, D. R. *Aldrichimica Acta* **2007**, *40*, 59. (i) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258. (j) Trost, B. M. *Org. Process Res. Dev.* **2012**, *16*, 185. (k) Hong, A. Y.; Stoltz, B. M. *Eur. J. Org. Chem.* **2013**, *2013*, 2745. (l) Oliver, S.; Evans, P. A. *Synthesis* **2013**, *45*, 3179. (m) Zhuo, C.-X.; Zheng, C.; You, S.-L. *Acc. Chem. Res.* **2014**, *47*, 2558.

(3) Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 1938.

(4) (a) Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1996**, *34*, 2589. (b) Ma, S. M. *Eur. J. Org. Chem.* **2004**, *2004*, 1175.

(5) For selected examples, see: (a) Tsuji, J.; Sugiura, T.; Yuhara, M.; Minami, I. *J. Chem. Soc., Chem. Commun.* **1986**, 922. (b) Tamaru, Y.; Goto, S.; Tanaka, A.; Shimizu, M.; Kimura, M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 878. (c) Yoshida, M.; Ueda, H.; Ihara, M. *Tetrahedron Lett.* **2005**, *46*, 6705. (d) Behenna, D. C.; Mohr, J. T.; Sherden, N. H.; Marinescu, S. C.; Harned, A. M.; Tani, K.; Seto, M.; Ma, S.; Novak, Z.; Krout, M. R.; McFadden, R. M.; Roizen, J. L.; Enquist, J. A.; White, D. E.; Levine, S. R.; Petrova, K. V.; Iwashita, A.; Virgil, S. C.; Stoltz, B. M. *Chem. - Eur. J.* **2011**, *17*, 14199.

(6) For reviews in the area, see: (a) Guo, L.-N.; Duan, X.-H.; Liang, Y.-M. *Acc. Chem. Res.* **2011**, *44*, 111. (b) Yoshida, M. *Chem. Pharm. Bull.* **2012**, *60*, 285. (c) Yoshida, M. *Heterocycles* **2013**, *87*, 1835.

(7) (a) Tsuji, J.; Watanabe, H.; Minami, I.; Shimizu, I. *J. Am. Chem. Soc.* **1985**, *107*, 2196. (b) Geng, L.; Lu, X. *Tetrahedron Lett.* **1990**, *31*, 111. (c) Labrosse, J. R.; Lhoste, P.; Sinou, D. *Tetrahedron Lett.* **1999**, *40*, 9025. (d) Labrosse, J. R.; Lhoste, P.; Sinou, D. *Org. Lett.* **2000**, *2*, 527. (e) Labrosse, J. R.; Lhoste, P.; Sinou, D. *J. Org. Chem.* **2001**, *66*, 6634. (f) Zong, K. W.; Abboud, K. A.; Reynolds, J. R. *Tetrahedron Lett.* **2004**, *45*, 4973. (g) Dominczak, N.; Damez, C.; Rhers, B.; Labrosse, J.-R.; Lhoste, P.; Kryczka, B.; Sinou, D. *Tetrahedron* **2005**, *61*, 2589. (h) Cacchi, S.; Fabrizi, G.; Filisti, E.; Goggiamani, A.; Iazzetti, A.; Maurone, L. *Org. Biomol. Chem.* **2012**, *10*, 4699.

(8) (a) Minami, I.; Yuhara, M.; Watanabe, H.; Tsuji, J. *J. Organomet. Chem.* **1987**, *334*, 225. (b) Yoshida, M.; Fujita, M.; Ihara, M. *Org. Lett.* **2003**, *5*, 3325. (c) Duan, X.-H.; Liu, X.-Y.; Guo, L.-N.; Liao, M.-C.; Liu, W.-M.; Liang, Y.-M. *J. Org. Chem.* **2005**, *70*, 6980. (d) Ambrogio, I.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2006**, *8*, 2083. (e) Duan, X.-H.; Guo, L.-N.; Bi, H.-P.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2006**, *8*, 5777. (f) Ohno, H.; Okano, A.; Kosaka, S.; Tsukamoto, K.; Ohata, M.; Ishihara, K.; Maeda, H.; Tanaka, T.; Fujii, N. *Org. Lett.* **2008**, *10*, 1171. (g) Yoshida, M.; Higuchi, M.; Shishido, K. *Tetrahedron Lett.* **2008**, *49*, 1678. (h) Yoshida, M.; Higuchi, M.; Shishido, K. *Org. Lett.* **2009**, *11*, 4752. (i) Yoshida, M.; Higuchi, M.; Shishido, K. *Tetrahedron* **2010**, *66*, 2675. (j) Yoshida, M.; Sugimura, C.; Shishido, K. *Org. Lett.* **2011**, *13*, 3482. (k) Yoshida, M.; Ohno, S.; Shishido, K. *Chem. - Eur. J.* **2012**, *18*, 1604. (l) Yoshida, M.; Sugimura, C. *Tetrahedron Lett.* **2013**, *54*, 2082. (m) Nemoto, T.; Zhao, Z. D.; Yokosaka, T.; Suzuki, Y.; Wu, R.; Hamada, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 2217. (n) Iwata, A.; Inuki, S.; Oishi, S.; Fujii, N.; Ohno, H. *Chem. Commun.* **2014**, *50*, 298. (o) Montgomery, T. D.; Nibbs, A. E.; Zhu, Y.; Rawal, V. H. *Org. Lett.* **2014**, *16*, 3480. (p) Gao, R.-D.; Liu, C.; Dai, L.-X.; Zhang, W.; You, S.-L. *Org. Lett.* **2014**, *16*, 3919. (q) Nibbs, A. E.; Montgomery, T. D.; Zhu, Y.; Rawal, V. H. *J. Org. Chem.* **2015**, *80*, 4928.

(9) Nishioka, N.; Koizumi, T. *Tetrahedron Lett.* **2011**, *52*, 3662.

(10) For reviews in the area, see: (a) Tunge, J. A.; Burger, E. C. *Eur. J. Org. Chem.* **2005**, *2005*, 1715. (b) Mohr, J. T.; Stoltz, B. M. *Chem. - Asian J.* **2007**, *2*, 1476. (c) Weaver, J. D.; Recio, A., III; Grenning, A. J.; Tunge, J. A. *Chem. Rev.* **2011**, *111*, 1846.

(11) For selected examples, see: (a) Shimizu, I.; Yamada, T.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 3199. (b) Tsuda, T.; Chujo, Y.; Nishi, S.; Tawara, K.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6381. (c) Burger, E. C.; Tunge, J. A. *Org. Lett.* **2004**, *6*, 4113. (d) Behenna, D. C.; Stoltz, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 15044. (e) Trost, B. M.; Xu, J. Y. *J. Am. Chem. Soc.* **2005**, *127*, 2846. (f) Nakamura, M.; Hajra, L.; Endo, K.; Nakamura, E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7248. (g) Kuwano, R.; Ishida, N.; Murakami, M. *Chem. Commun.* **2005**, 3951. (h) Trost, B. M.; Xu, J.; Reichle, M. *J. Am. Chem. Soc.* **2007**, *129*, 282. (i) Weaver, J. D.; Ka, B. J.; Morris, D. K.; Thompson, W.; Tunge, J. A. *J. Am. Chem. Soc.* **2010**, *132*, 12179. (j) Franckevičius, V.; Cuthbertson, J. D.; Pickworth, M.; Pugh, D. S.; Taylor, R. J. K. *Org. Lett.* **2011**, *13*, 4264. (k) Trost, B. M.; Schäffner, B.; Osipov, M.; Wilton, D. A. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 3548. (l) Behenna, D. C.; Liu, Y.; Yurino, T.; Kim, J.; White, D. E.; Virgil, S. C.; Stoltz, B. M. *Nat. Chem.* **2012**, *4*, 130. (m) Arseniyadis, S.; Fournier, J.; Thangavelu, S.; Lozano, O.; Prevost, S.; Archambeau, A.; Menozzi, C.; Cossy, J. *Synlett* **2013**, *24*, 2350. (n) Ariyarathna, Y.; Tunge, J. A. *Org. Biomol. Chem.* **2014**, *12*, 8386. (o) Korch, K. M.; Eidamshaus, C.; Behenna, D. C.; Nam, S.; Horne, D.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2015**, *54*, 179. (p) Yang, M. H.; Orsi, D. L.; Altman, R. A. *Angew. Chem., Int. Ed.* **2015**, *54*, 2361.

(12) Schröder, S. P.; Taylor, N. J.; Jackson, P.; Franckevičius, V. *Org. Lett.* **2013**, *15*, 3778.

(13) (a) Lovering, F.; Bikker, J.; Humblet, C. *J. Med. Chem.* **2009**, *52*, 6752. (b) Nadin, A.; Hattotuwagama, C.; Churcher, I. *Angew. Chem., Int. Ed.* **2012**, *51*, 1114.

(14) X-ray data for **7a** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1411246) and can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

(15) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416.

(16) (a) Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722. (b) Ohno, H.; Hamaguchi, H.; Ohata, M.; Kosaka, S.; Tanaka, T. *J. Am. Chem. Soc.* **2004**, *126*, 8744. (c) Horino, Y.; Homura, N.; Inoue, K.; Yoshikawa, S. *Adv. Synth. Catal.* **2012**, *354*, 828.

(17) Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164.

(18) Coles, S. J.; Gale, P. A. *Chem. Sci.* **2012**, *3*, 683.

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