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Pd(II)-Catalyzed Enantioselective Synthesis of P-Stereogenic Phosphinamides via Desymmetric C−H Arylation

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Supporting Information

ABSTRACT: We present the enantioselective synthesis of P-stereogenic phosphinamides through Pd-catalyzed desymmetric ortho C−H arylation of diarylphosphinamides with boronic esters. The method represents the first example of the synthesis of P-stereogenic phosphorus compounds via the desymmetric C−H functionalization strategy. The reaction proceeded efficiently with a wide array of reaction partners to afford the P-stereogenic phosphinamides in up to 74% yield and 98% ee. The efficiency was further demonstrated by gram scale syntheses. Moreover, the flexible conversion of the P-stereogenic phosphinamides into various types of P-stereogenic phosphorus derivatives was also elaborated. Thus, the protocol provides a novel tool for the efficient and versatile synthesis of P-stereogenic compounds.

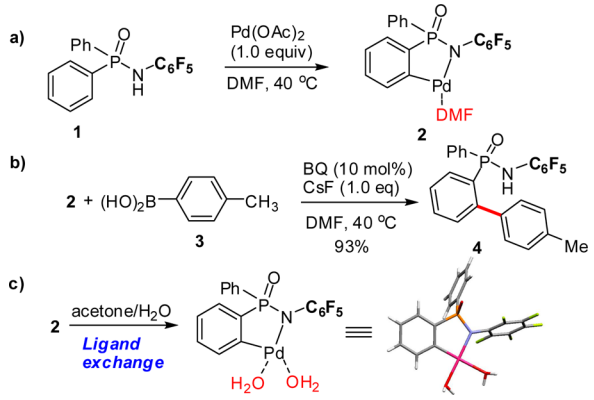
In recent decades, comprehensive studies have revealed the importance of chiral phosphorus compounds in asymmetric synthesis both as ligands in metal-catalyzed reactions[1] and as organocatalysts.[2] However, the majority of these studies focused on axial, planar, spiro, or carbon-centered chiral phosphorus derivatives.[1,2] Although P-stereogenic compounds have shown prominent chiral induction stemming from chirality proximate to the catalytic center,[3] their wide application has been severely restricted because of the lack of efficient synthetic methods. Conventional approaches for their preparation include resolution,[3a,4] chiral-auxiliary-based approaches,[4,5] and enantioselective lithiation−trapping of phosphine−boranes or related analogues.[6] Recently, transition metal (TM)-catalyzed asymmetric cross-couplings of aryl halides with secondary phosphines,[7] hydrophosphination of electron-deficient olefins,[8] alkylation of secondary phosphines with alkyl halides,[9] addition reactions of secondary phosphines and benzoquinone,[10] and ring-closing metathesis of olefins[11] have also been reported. Despite these important advances, the scope and efficiency of most of the approaches await further improvements. More to the point, some types of potentially useful P-stereogenic compounds are still inaccessible.

Intense interest in chiral BINOL- and spirocycle-based phosphoramide Brønsted acid-catalyzed asymmetric reactions has recently been observed.[2] Such catalysts have the advantage of catalyzing a broad range of transformations through various activation modes such as Brønsted acidity, hydrogen bonding, ion pairing, and metal phosphates.[2e] Stimulated by these prominent results, one may certainly consider the catalytic properties of the corresponding P-stereogenic derivatives such as phosphoramides and phosphinamides, but to the best of our knowledge, such derivatives have never been investigated because of the paucity of suitable synthetic methods, although amino-group-directed ortho lithiation is a potential option.[6b,g]

Thus, the exploration of a conceptually new protocol for the synthesis of P-stereogenic phosphoramides or phosphinamides is of prime importance in view of their wide potential applications. On the basis of our recent work on the BINOL-based chiral-phosphoramide-catalyzed asymmetric reaction of indol-2-yl carbinols[12] and TM-catalyzed C−H functionalization,[13] we became interested in developing a method for the synthesis of P-stereogenic phosphoramides or phosphinamides and investigating their applications in asymmetric synthesis. As the first step directed toward these goals, we report the successful enantioselective synthesis of P-stereogenic phosphinamides through a desymmetric C−H arylation strategy.

Our initial idea originated from a very recent study of Pd-catalyzed racemic C−H arylation,[13b] wherein we found that phosphinamide **1** and $Pd(OAc)_2$ can form the stable palladacycle **2** in DMF (Scheme 1a). The reaction of **2** with boronic acid **3** proceeds smoothly to deliver *o*-arylphosphinamide **4** in excellent yield (Scheme 1b). Crystallization of **2** from an acetone/H_2O solvent system revealed that the DMF in **2** was displaced by two molecules of H_2O (Scheme 1c). The coordination of a DMF

Scheme 1. Palladacycle 2 and Control Experiment[13b]



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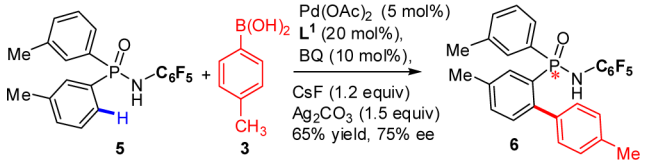
molecule and the ease of ligand exchange of **2** attracted our attention because, conceptually, a P-stereogenic phosphinamide should be generated if an appropriate DMF-like chiral ligand could be used in place of H_2O to exchange with the DMF in the reaction system.

Thus, a variety of amino acid derivatives were selected to evaluate the reaction conditions. Our first consideration in using amino acids as chiral ligands is that such compounds are structurally similar to DMF, and their efficiency in the asymmetric synthesis of C-centered chiral compounds has been demonstrated by Yu.[14] As expected, by screening an array of amino acid derivatives and carefully tuning bases, oxidants, and additives on the basis of the procedure for the racemic arylation,[13b] we found that the arylation of phosphinamide **5** with boronic acid **3** in the presence of Boc-L-phenylalanine (Boc-L-Phe-OH, $\mathbf{L^1}$) could afford the desired P-stereogenic phosphinamide **6** in 65% yield with 75% ee with $Pd(OAc)_2$ as the catalyst, Ag_2CO_3 as the oxidant, benzoquinone (BQ) as an additive, and CsF as the base (Scheme 2). Although further

Scheme 2. Initial Result of Enantioselective C−H Arylation

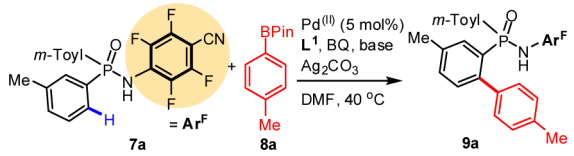


exhaustive optimization of the reaction parameters to improve the enantioselectivity proved to be futile, the preliminary result was encouraging in terms of yield and enantioselectivity.

At this juncture, our attention was shifted to the effect of the directing group of the phosphinamide substrate and the nature of the boron compound. An orthogonal evaluation of various phosphinamides and boron compounds showed phosphinamide **7a** bearing a 2,3,5,6-tetrafluoro-4-cyanophenylamino ($\mathbf{Ar^F}$) directing group and boronic acid pinacol ester **8a** to be a promising combination of reaction partners, affording the desired product **9a** in 59% yield with 93% ee in the presence of $\mathbf{L^1}$ (Table 1, entry 1). Interestingly, the addition of ca. 40 equiv of H_2O in anhydrous DMF was also crucial to improve both the yield and the chiral induction (entry 1 vs 2), although the critical role of H_2O deserves a detailed clarification. We then screened an array of Pd catalysts and bases (Table 1). Among a variety of conditions examined, $Pd(OAc)_2$ and Li_2CO_3 or $NaHCO_3$ were found to be the optimal catalyst and base, respectively, giving **9a** in over 60% yield with up to 96% ee (entries 5 and 8). The results, together those of Yu on amide-group-directed C−H activation for the synthesis of C-stereogenic molecules,[14d] indicate that the electron-deficient polyfluorophenyl group may act as a powerful substituent in enantioselective C−H activation.

Next, we systematically inspected the effect of the amino acid derivative on this reaction using $Pd(OAc)_2$ as the catalyst and Li_2CO_3 as the base (Table 2). A general observation is that for an array of Boc-protected amino acids $\mathbf{L^1}$–$\mathbf{L^8}$, the yield and enantioselectivity are less affected by the steric and electronic nature of the R group. In most cases **9a** could be obtained in ca. 60% yield with a high enantioselectivity of over 90% ee, with Boc-Tyr(^{t}Bu)-OH ($\mathbf{L^3}$) giving the best results in terms of yield (64%) and enantioselectivity (94% ee). These results provide an important advantage for flexibly choosing the chiral ligand within a broad window. Nevertheless, we still found that precise tuning of the steric nature of the R group is important as shown by a

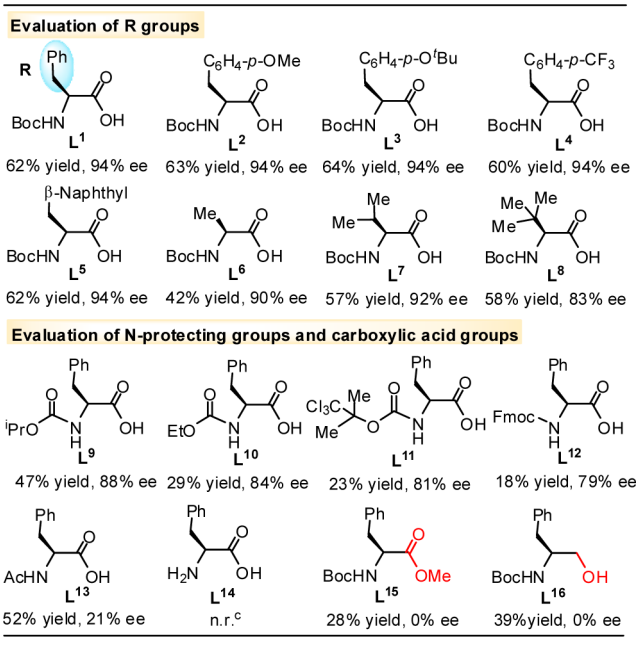
Table 1. Effect of the Palladium Catalyst and Base[a]



entry	catalyst	base	yield (%)[b]	ee (%)[c]
1	$Pd(OAc)_2$	Na_2CO_3	59	93
2[d]	$Pd(OAc)_2$	Na_2CO_3	18	80
3	$PdCl_2$	Na_2CO_3	51	92
4	$Pd(O_2CCF_3)_2$	Na_2CO_3	25	86
5	**$Pd(OAc)_2$**	**Li_2CO_3**	**62**	**94**
6	$Pd(OAc)_2$	K_2CO_3	n.r.[e]	–
7	$Pd(OAc)_2$	Cs_2CO_3	n.r.	–
8	**$Pd(OAc)_2$**	**$NaHCO_3$**	**60**	**96**
9	$Pd(OAc)_2$	CsF	trace	–

[a]Reaction conditions: **7a** (0.2 mmol), **8a** (0.4 mmol), Pd catalyst (5 mol %), $\mathbf{L^1}$ (20 mol %), BQ (0.5 equiv), base (3.0 equiv), Ag_2CO_3 (1.5 equiv), and H_2O (40.0 equiv) in 2 mL of anhydrous DMF at 40 °C under air, unless otherwise noted. [b]Isolated yields. [c]Determined by chiral HPLC analysis on an AD-H column. [d]No H_2O. [e]No reaction.

Table 2. Evaluation of Chiral Ligands[a,b]



[a]Reaction conditions: **7a** (0.2 mmol), **8a** (0.4 mmol), $Pd(OAc)_2$ (5 mol %), ligand (20 mol %), BQ (0.5 equiv), Li_2CO_3 (3.0 equiv), Ag_2CO_3 (1.5 equiv), and H_2O (40.0 equiv) in 2 mL of anhydrous DMF at 40 °C under air. [b]Shown are isolated yields and ee values determined by chiral HPLC analysis on a CD-H column. [c]No reaction.

comparison of Boc-Ala-OH ($\mathbf{L^6}$), Boc-Val-OH ($\mathbf{L^7}$), and Boc-*tert*-Leu-OH ($\mathbf{L^8}$). Both the smallest ($\mathbf{L^6}$) and the largest ($\mathbf{L^8}$) offered results inferior to that obtained with the middle-sized $\mathbf{L^7}$. The ee value for the large $\mathbf{L^8}$ decreased even to 83%.

In contrast, the nature of the N-protecting group has a dramatic effect on the reaction (Table 2). When the N-protecting group was changed from Boc in $\mathbf{L^1}$ to ^{i}PrOCO ($\mathbf{L^9}$), EtOCO ($\mathbf{L^{10}}$), TcBoc ($\mathbf{L^{11}}$), and ultimately Fmoc ($\mathbf{L^{12}}$), both the yield and enantioselectivity gradually decreased, although good enantioselectivity was still maintained (79–88%). Surprisingly, however, when the protecting group was replaced by an acyl

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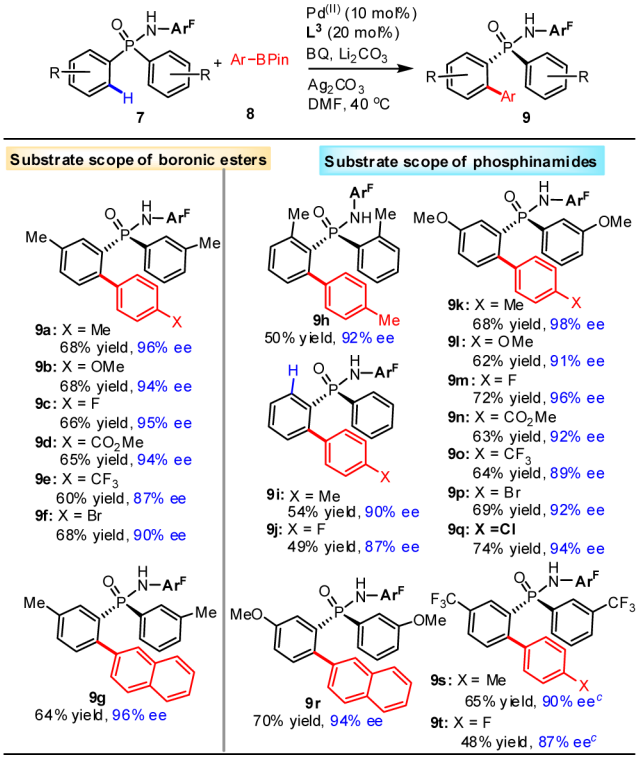
group (L^{13}), only poor enantioselectivity (21% ee) was observed, and the reaction was entirely suppressed when the unprotected amino acid was used (L^{14}). These results suggest that the presence of a carbamate moiety in the ligand is of crucial importance to induce good enantioselectivity. Finally, the carboxylic acid group also plays a vital role in the reaction since the enantioinduction was completely lost when the carboxylic acid functionality was blocked by esterification (L^{15}) or conversion into a hydroxyl group (L^{16}).

Having defined the optimal ligand L^3, we explored the loading of $Pd(OAc)_2$ catalyst, the ratio of catalyst to L^3, and the effect of the atmosphere with the aim of further improving the reaction efficiency. While significant improvement was not observed, the use of a combination of 10 mol % catalyst and 20 mol % L^3 did slightly increase the efficiency, affording **9a** in 68% yield with 96% ee under an air atmosphere. Identical yields and enantioselectivities were obtained when the reaction was performed under nitrogen and oxygen. Altogether, it was found that the optimized conditions for the asymmetric synthesis of P-stereogenic phosphinamides via desymmetric C−H arylation are 10 mol % $Pd(OAc)_2$, 20 mol % L^3, 0.5 equiv of BQ, 1.5 equiv of Ag_2CO_3, 3.0 equiv of Li_2CO_3, and 40.0 equiv of H_2O in anhydrous DMF at 40 °C under an air atmosphere. These conditions could be reliably employed for large-scale synthesis with consistent yields and enantioselectivities (vide infra).

Having established robust conditions, we investigated the substrate scope of the protocol (Table 3). The reaction of a variety of boronic esters decorated by either weak (**9a**) or strong electron-donating groups (**9b**) or various electron-withdrawing groups (**9c**−**f**) proceeded smoothly with phosphinamide **7a** to give the P-stereogenic phosphinamides in good yields (60−68%) with high to excellent enantioselectivities (87−96% ee). A variety of functional groups such as ether (**9b**), fluoro (**9c**), ester (**9d**), trifluoromethyl (**9e**), and bromo (**9f**) were well-tolerated, and a ring-fused nucleophile was also compatible, giving **9g** in 64% yield with 96% ee.

The reaction also works well for an array of diarylphosphinamides. The ortho-substituted substrate gave the product **9h** in 50% yield with 92% ee. The somewhat decreased yield of **9h** compared with the meta-substituted analogues **9a**−**g** is presumably due to steric hindrance by the *o*-Me group. The unsubstituted substrate also afforded the products in moderately high yields with high enantioselectivities (**9i** and **9j**). For such substrates, small amounts of diarylated byproducts (<10%) were isolated. A phosphinamide modified with a strong electron-donating OMe group reacted very smoothly with a wide range of boronic esters to produce the corresponding P-stereogenic products in good yields of up to 74% as well as excellent enantioselectivities of up to 98% ee (**9k**−**r**). The conditions were also compatible with a wide range of functional groups. More to the point, the reaction could be performed on a large scale with consistent efficiency, as exemplified by the synthesis of **9k** on a gram scale (70−72% yield, 97−98% ee) and **9q** on a 0.5 g scale (72% yield, 95% ee). Finally, the arylation of substrates bearing an electron-withdrawing CF_3 group was sluggish at 40 °C, but satisfactory results were obtained at 70 °C (**9s** and **9t**). Of note, only monoarylated products were produced with the ortho- or meta-substituted substrates under the optimized conditions. The absolute configuration of **9k** was *S* as determined by X-ray crystallography (Figure 1), and those of the other products were assigned by analogy.

Table 3. Evaluation of the Substrate Scope[a,b]



[a]Reaction conditions: **7** (0.2 mmol), **8** (0.4 mmol), $Pd(OAc)_2$ (10 mol %), L^3 (20 mol %), BQ (0.5 equiv), Li_2CO_3 (3.0 equiv), Ag_2CO_3 (1.5 equiv), and H_2O (40.0 equiv) in 2 mL of anhydrous DMF at 40 °C under air. [b]Shown are isolated yields and ee values determined by chiral HPLC analysis. [c]The reaction was carried out at 70 °C.

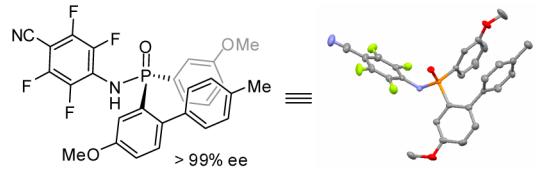


Figure 1. Absolute configuration of **9k**.

Finally, to further demonstrate the utility of this methodology, the conversion of the P-stereogenic phosphinamides into other types of potentially useful P-chiral phosphorus derivatives was elaborated using **9k** (Scheme 3). Treatment of **9k** (97% ee) with Lawesson's reagent afforded thiophosphinamide **10** in high yield and enantiomeric purity (95% ee).[15] On the other hand, while methanolysis of **9k** with HCl proved to be sluggish,[6g] TfOH was effective and afforded methyl phosphinate **11** in 62% yield. Most significantly, only a negligible decrease in enantiomeric excess (from 98% to 97% ee) was observed under the unoptimized conditions. Subsequently, the conversion of **11** into P-stereogenic phosphine oxide **12** proceeded uneventfully under the effect of MeLi (71% yield, 94.3% ee).[5b] Finally, reduction of **12** with $LiAlH_4$ according to a known procedure[16] gave P-stereogenic phosphine **13** in high yield (70%) with slightly reduced chirality (92.3% ee).

In summary, we have developed an unprecedented protocol that realizes the asymmetric synthesis of conventionally inaccessible P-stereogenic phosphinamides via Pd-catalyzed desymmetric C−H arylation. The importance of this protocol was further exemplified by the conversion of a chiral

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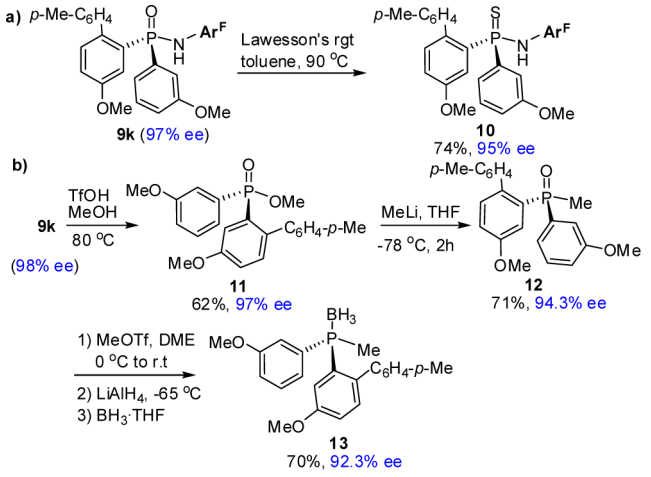
Scheme 3. Derivatization of Phosphinamides



phosphinamide into several other types of potentially useful P-stereogenic derivatives. As a result, the protocol should open a new avenue for the versatile synthesis of P-stereogenic compounds with potential applications in catalysis. The practical applications of these different types of P-stereogenic compounds in asymmetric reactions are currently under study.

■ ASSOCIATED CONTENT

Supporting Information

Procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

‖Z.-J.D. and J.G. contributed equally.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (b) Wei, Y.; Shi, M. *Acc. Chem. Res.* **2010**, *43*, 1005. (c) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Claver, C.; Pàmies, O.; Diéguez, M. *Chem. Rev.* **2011**, *111*, 2077. (d) Xie, J.-H.; Zhu, S.-F.; Zhou, Q.-L. *Chem. Soc. Rev.* **2012**, *41*, 4126. (e) Xie, J.-H.; Zhou, Q.-L. *Acta Chim. Sin.* **2014**, *72*, 778.

(2) (a) You, S.-L.; Cai, Q.; Zeng, M. *Chem. Soc. Rev.* **2009**, *38*, 2190. (b) Mahlau, M.; List, B. *Angew. Chem., Int. Ed.* **2013**, *52*, 518. (c) Brak, K.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **2013**, *52*, 534. (d) Phipps, R. J.; Hamilton, G. L.; Toste, F. D. *Nat. Chem.* **2012**, *4*, 603. (e) Parmar, D.; Sugiono, E.; Raja, S.; Rueping, M. *Chem. Rev.* **2014**, *114*, 9047.

(3) (a) Crépy, K. V. L.; Imamoto, T. *Top. Curr. Chem.* **2003**, *229*, 1. (b) Imamoto, T.; Sugita, K.; Yoshida, K. *J. Am. Chem. Soc.* **2005**, *127*, 11934. (c) Tang, W.; Patel, N. D.; Xu, G.; Xu, X.; Savoie, J.; Ma, S.; Hao, M.-H.; Keshipeddy, S.; Capacci, A. G.; Wei, X.; Zhang, Y.; Gao, J. J.; Li, W.; Rodriguez, S.; Lu, B. Z.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2012**, *14*, 2258. (d) Luo, R.; Liao, J.; Xie, L.; Tang, W.; Chan, A. S. *Chem. Commun.* **2013**, *49*, 9959. (e) Liu, G.; Liu, X.; Cai, Z.; Jiao, G.; Xu, G.; Tang, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 4235. (f) Xu, G.; Fu, W.; Liu, G.; Senanayake, C. H.; Tang, W. *J. Am. Chem. Soc.* **2014**, *136*, 570.

(4) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375.

(5) (a) Adams, H.; Collins, R. C.; Jones, S.; Warner, C. J. A. *Org. Lett.* **2011**, *13*, 6576. (b) Han, Z. S.; Goyal, N.; Herbage, M. A.; Sieber, J. D.; Qu, B.; Xu, Y.; Li, Z.; Reeves, J. T.; Desrosiers, J.-N.; Ma, S.; Grinberg, N.; Lee, H.; Mangunurn, H. P. R.; Zhang, Y.; Krishnamurthy, D.; Lu, B. Z.; Song, J. J.; Wang, G.; Senanayake, C. H. *J. Am. Chem. Soc.* **2013**, *135*, 2474. (c) Berger, O.; Montchamp, J.-L. *Angew. Chem., Int. Ed.* **2013**, *52*, 11377. (d) Gwon, D.; Lee, D.; Kim, J.; Park, S.; Chang, S. *Chem.—Eur. J.* **2014**, *20*, 12421.

(6) (a) Bergin, E.; O'Connor, C. T.; Robinson, S. B.; McGarrigle, E. M.; O'Mahony, C. P.; Gilheany, D. G. *J. Am. Chem. Soc.* **2007**, *129*, 9566. (b) Popovici, C.; Oña-Burgos, P.; Fernández, I.; Roces, L.; García-Granda, S.; Iglesias, M. J.; Ortiz, F. L. *Org. Lett.* **2010**, *12*, 428. (c) Granander, J.; Secci, F.; Canipa, S. J.; O'Brien, P.; Kelly, B. *J. Org. Chem.* **2011**, *76*, 4794. (d) Gammon, J. J.; Gessner, V. H.; Barker, G. R.; Granander, J.; Whitwood, A. C.; Strohmann, C.; O'Brien, P.; Kelly, B. *J. Am. Chem. Soc.* **2010**, *132*, 13922. (e) Gatineau, D.; Giordano, L.; Buono, G. *J. Am. Chem. Soc.* **2011**, *133*, 10728. (f) Bayardon, J.; Laureano, H.; Diemer, V.; Dutartre, M.; Das, U.; Rousselin, Y.; Henry, J.-C.; Colobert, F.; Leroux, F. R.; Jugé, S. *J. Org. Chem.* **2012**, *77*, 5759. (g) Casimiro, M.; Roces, L.; García-Granda, S.; Iglesias, M. J.; Ortiz, F. L. *Org. Lett.* **2013**, *15*, 2378.

(7) (a) Harvey, J. S.; Gouverneur, V. *Chem. Commun.* **2010**, *46*, 7477. (b) Blank, N. F.; Moncarz, J. R.; Brunker, T. J.; Scriban, C.; Anderson, B. J.; Amir, O.; Glueck, D. S.; Zakharov, L. N.; Golen, J. A.; Incarvito, C. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **2007**, *129*, 6847. (c) Chan, V. S.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 15122. (d) Anderson, B. J.; Guino-o, M. A.; Glueck, D. S.; Golen, J. A.; DiPasquale, A. G.; Liable-Sands, L. M.; Rheingold, A. L. *Org. Lett.* **2008**, *10*, 4425.

(8) Join, B.; Mimeau, D.; Delacroix, O.; Gaumont, A.-C. *Chem. Commun.* **2006**, 3249.

(9) (a) Chan, V. S.; Stewart, I. C.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 2786. (b) Scriban, C.; Glueck, D. S. *J. Am. Chem. Soc.* **2006**, *128*, 2788. (c) Chan, V. S.; Chiu, M.; Bergman, R. G.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 6021.

(10) Huang, Y.; Li, Y.; Leung, P.-H.; Hayashi, T. *J. Am. Chem. Soc.* **2014**, *136*, 4865.

(11) Harvey, J. S.; Malcolmson, S. J.; Dunne, K. S.; Meek, S. J.; Thompson, A. L.; Schrock, R. R.; Hoveyda, A. H.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2009**, *48*, 762.

(12) Qi, S.; Liu, C.-Y.; Ding, J.-Y.; Han, F.-S. *Chem. Commun.* **2014**, *50*, 8605.

(13) (a) Xu, H.; Liu, P.-T.; Li, Y.-H.; Han, F.-S. *Org. Lett.* **2013**, *15*, 3354. (b) Guan, J.; Wu, G.-J.; Han, F.-S. *Chem.—Eur. J.* **2014**, *20*, 3301. (c) Wu, G.-J.; Guan, J.; Han, F.-S.; Zhao, Y.-L. *ChemCatChem* **2014**, *6*, 1589. (d) Du, Z.-J.; Gao, L.-X.; Lin, Y.-J.; Han, F.-S. *ChemCatChem* **2014**, *6*, 123.

(14) (a) Sokolov, V. I.; Troitskaya, L. L.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *182*, 537. (b) Shi, B.-F.; Maugel, N.; Zhang, Y.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 4882. (c) Shi, B.-F.; Zhang, Y.-H.; Lam, J.-K.; Wang, D.-H.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 460. (d) Wasa, M.; Engle, K. M.; Lin, D. W.; Yoo, E. J.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 19598. (e) Musaev, D. G.; Kaledin, A.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc.* **2012**, *134*, 1690. (f) Chu, L.; Wang, X.-C.; Moore, C. E.; Rheingold, A. L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 16344. (g) Cheng, X.-F.; Li, Y.; Su, Y.-M.; Yin, F.; Wang, J.-Y.; Sheng, J.; Vora, H. U.; Wang, X.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2013**, *135*, 1236. (h) Zhang, Y.; Wu, Q.; Cui, S. *Chem. Sci.* **2014**, *5*, 297. (i) Xiao, K.-J.; Lin, D. W.; Miura, M.; Zhu, R.-Y.; Gong, W.; Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 8138.

(15) Mikołajczyk, M.; Łuczak, J.; Kiełbasiński, P.; Colonna, S. *Tetrahedron: Asymmetry* **2009**, *20*, 1948.

(16) Imamoto, T.; Kikuchi, S.-i.; Miura, T.; Wada, Y. *Org. Lett.* **2001**, *3*, 87.

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