JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

# Asymmetric Allylic C−H Oxidation for the Synthesis of Chromans

Pu-Sheng Wang,[†] Peng Liu,[†] Yu-Jia Zhai,[†] Hua-Chen Lin,[†] Zhi-Yong Han,[†] and Liu-Zhu Gong*[,†,‡]

[†]Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

[‡]Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China

Supporting Information

**ABSTRACT:** An enantioselective intramolecular allylic C−H oxidation to generate optically active chromans has been accomplished under the cooperative catalysis of a palladium complex of chiral phosphoramidite ligand and 2-fluorobenzoic acid. Mechanistic studies suggest that this reaction commences with a Pd-catalyzed allylic C−H activation event and then undergoes asymmetric allylic alkoxylation. The synthetic significance of the method has been embodied by concisely building up a key chiral intermediate to access (+)-diversonol.

Chiral chroman core moiety is widely distributed in numerous naturally occurring compounds, many of which exhibit significant biological properties (Figure 1).[1] For

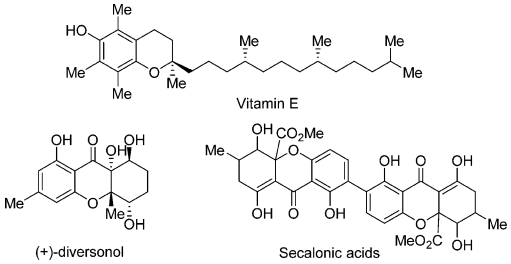
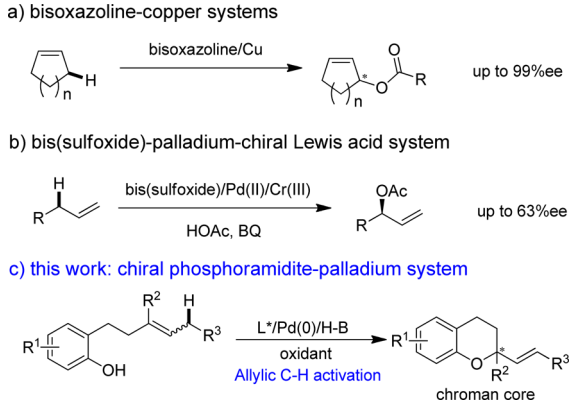



**Figure 1.** Representative natural products bearing chiral chroman core moiety.

example, Vitamin E is a well-known fat-soluble vitamin and important intramembrane antioxidant that prevents the propagation of free radical damage in biological membranes.[2] Another example is tetrahydroxanthenone, which is a fast growing class of mycotoxins with interesting biological activities.[3] Among them is diversonol, which is a fungal metabolite and has been isolated from different fungi such as *Penicillium diversum* and *Microdiplodia sp.*[4] Although the bioactivity of diversonol seems unclear so far, the related dimeric secalonic acids can exhibit antibacterial, cytostatic, and anti-HIV properties.[5] Therefore, the total synthesis of diversonol has continuously drawn the attention of chemical community.[6]

For the synthesis of the chiral chroman motifs, a variety of enantioselective approaches have been described.[7] For years, a great deal of attention has focused on asymmetric synthesis that relies on transition metal-catalyzed Wacker-type[8] or allylic substitution processes.[9] However, the construction of chiral chroman frameworks via direct inert C−H oxidation strategy has not been reported, yet.[10] In the past decade, highly effective allylic C−H oxidation has been established as one of the more appealing synthetic alternatives for fine chemical synthesis, in comparison with conventional procedures.[11] Although a successful application of chiral bisoxazoline/copper complexes in asymmetric allylic C−H oxidation has achieved high levels of enantioselectivity (Scheme 1a), the efficiency of these systems is

**Scheme 1. Asymmetric Allylic C−H Oxidation Reactions**




limited to cyclic olefins.[12] Recently, White and co-workers found that the combined use of a palladium complex and a chiral Lewis acid was able to significantly enhance the efficiency of asymmetric allylic C−H oxidation of terminal olefins, but with a moderate enantioselectivity (Scheme 1b).[13] Soon after the discovery of phosphine ligand promoted Pd-catalyzed allylic C−H alkylations,[14] Trost and co-workers established an asymmetric allylic C−H alkylation by using chiral phosphoramidite ligands to control stereochemistry.[15] Very recently, our group accomplished the first enantioselective $\alpha$-allylation of aldehydes with terminal alkenes by combining chiral counteranion catalysis and Pd-catalyzed allylic C−H activation.[16] Herein, we will present an asymmetric allylic C−H oxidation for asymmetric synthesis of various chromans enabled by cooperative catalysis of chiral palladium complex and achiral Brønsted acid (Scheme 1c), allowing for a concise enantioselective formal synthesis of (+)-diversonol.

Our previous work on asymmetric allylic C−H alkylation[16] prompted us to initially apply cooperative catalysis of a palladium complex and a chiral Brønsted acid to the synthesis of the desired

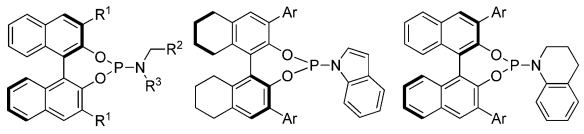
**Received:** February 11, 2015
**Published:** September 24, 2015





DOI: 10.1021/jacs.5b08477
J. Am. Chem. Soc. 2015, 137, 12732−12735

chiral chromans using the substrate **1a** bearing 1,4-diene moiety, however, poor to moderate enantioselectivities were obtained after several trials (Table S1).[17] Alternatively, we decided to employ the combination of palladium complexes of bulky chiral ligands (Figure 2) and Brønsted acids to circumvent the

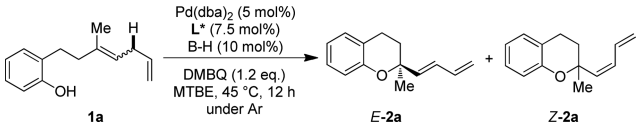


**L1**: $R^1$ = H, $R^2$ = $R^3$ = Ph **L6**: Ar = 3,5-$(CF_3)_2C_6H_3$ **L7**: Ar = 9-anthracenyl
**L2**: $R^1$ = 4-$NO_2C_6H_4$, $R^2$ = $R^3$ = Ph
**L3**: $R^1$ = 4-$NO_2C_6H_4$, $R^2$ = 2-Naphthyl, $R^3$ = Ph
**L4**: $R^1$ = 4-$NO_2C_6H_4$, $R^2$ = 3,5-$(CF_3)_2C_6H_3$, $R^3$ = Ph
**L5**: $R^1$ = 4-$NO_2C_6H_4$, $R^2$ = 3,5-$(CF_3)_2C_6H_3$, $R^3$= 4-$MeOC_6H_4$

**Figure 2.** Chiral phosphoramidite ligands used in this study.

challenge in stereochemical control.[18] Although the use of chiral phosphoric acids still led to unsatisfactory enantioselectivity, an inspiring phenomenon that the counteranions of palladium complexes exerted obvious impact on the catalytic activity was found (Table S1)[17] and thereby prompted us to investigate the effect of achiral Brønsted acid cocatalysts (Table 1, entries 1–4).

**Table 1. Optimization of Reaction Conditions**[a]



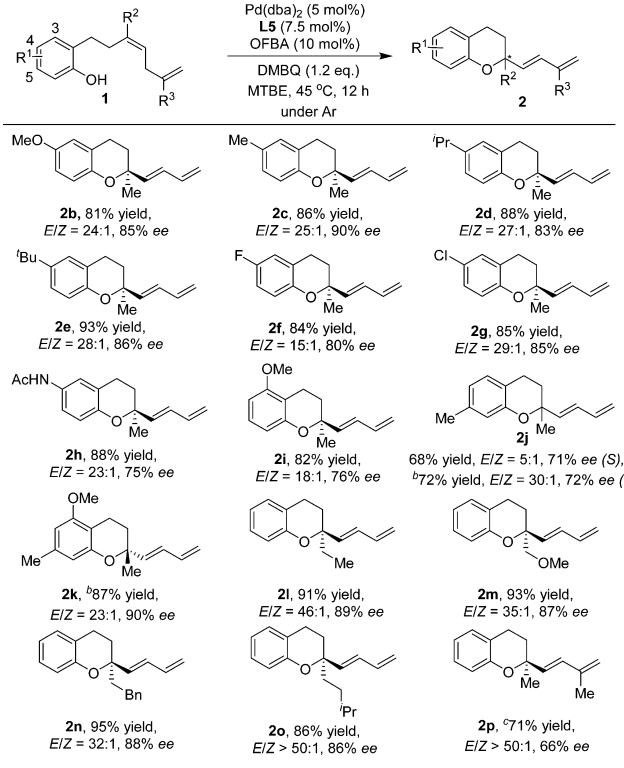

| entry | 1 | L* | B–H | yield (%)[b] | $E/Z$[b] | *ee* (%)[c] |
|---|---|---|---|---|---|---|
| 1 | **1a** | **L1** | $(PhO)_2PO_2H$ | 6 | 4:1 | 0 |
| 2 | **1a** | **L1** | AcOH | 44 | 20:1 | 18 |
| 3 | **1a** | **L1** | BzOH | 26 | 36:1 | 7 |
| 4 | **1a** | **L1** | OFBA | 59 | 20:1 | 21 |
| 5 | **1a** | **L2** | OFBA | 97 | 18:1 | 84 |
| 6 | **1a** | **L3** | OFBA | 95 | 16:1 | 83 |
| 7 | **1a** | **L4** | OFBA | 94 | 16:1 | 85 |
| 8 | **1a** | **L5** | OFBA | 95(92[d]) | 16:1 | 87 |
| 9 | *E*-**1a** | **L5** | OFBA | 90[d] | 7:1 | 85 |
| 10 | *Z*-**1a** | **L5** | OFBA | 87[d] | 20:1 | 88 |
| 11 | *Z*-**1a** | **L5** | | 70[d] | 28:1 | 48 |
| 12 | *Z*-**1a** | | OFBA | trace | | |

[a]Reaction conditions: **1a** (0.1 mmol, $E/Z$ = 1:1.2), $Pd(dba)_2$ (5 mol %), **L** (7.5 mol %), B–H (10 mol %), DMBQ (1.2 equiv), MTBE (1 mL), 45 °C, 12 h, under Ar. [b]Based on $^1$H NMR analysis of the crude reaction mixture using benzyl benzoate as an internal standard. [c]Determined by HPLC. [d]Isolated yield. OFBA = 2-fluorobenzoic acid. MTBE = methyl *tert*-butyl ether. DMBQ = 2,6-dimethyl-1,4-benzoquinone.

To our delight, the use of 2-fluorobenzoic acid as the organic cocatalyst was able to promote the efficiency and enantioselectivity of the reaction (entry 4). Then, various chiral BINOL derived phosphoramidites **L2**–**5** were evaluated. It was identified that the introduction of highly electron-deficient 4-nitrobenzyl substitution to 3,3′-positions of the BINOL moiety was able to greatly enhance the enantioselectivity (entry 5). Fine tuning of amine moiety on phosphoramidite ligands found that the presence of sterically less demanding and more electronically deficient substituents on the benzyl group were beneficial to the control of enantioselectivity (entries 6–8). The highest enantioselectivity was obtained upon using a chiral phosphoramidite ligand incorporated with an electronically rich aryl substituent on amine moiety (entry 8). Interestingly, the olefin geometry of the substrate showed obvious impact on the reaction. In comparison with *E*-isomer, *Z*-isomer underwent the allylic alkoxylation with higher $E/Z$ selectivity and slightly enhanced enantioselectivity (entries 9–10), which to some extent implied the proposed allylic substitution process, as the Wacker-type approach should give thermodynamically controlled similar $E/Z$ selectivity via $\beta$-H elimination event, basically unconnected with the olefin geometry after the initial nucleopalladation,[19] while $E/Z$ selectivity of the allylic alkoxylation showed obvious correlation with the olefin geometry.[9b] Although the reaction was also able to proceed smoothly in the absence of 2-fluorobenzoic acid (OFBA), a much diminished enantioselectivity was obtained (entry 11), implying that the Brønsted acid played an important role in the control of stereoselectivity. Notably, the absence of phosphoramidite ligand **L5** was unable to give the desired product **2a** with nearly quantitative recovery of **1a** (entry 12), which further demonstrated that this Pd-catalyzed allylic C–H oxidation process was dramatically accelerated by the Brønsted acid and phosphoramidite ligand.

Under the optimized conditions, we next explored the generality of the asymmetric allylic C–H oxidation reaction (Scheme 2). The installation of different substituents on the benzene ring was nicely tolerated, giving rise to the desired chiral chromans **2** in high yields, excellent $E/Z$ selectivity, and with moderate to good levels of enantioselectivities. Either electron donating or withdrawing substituent at 4-position of the benzene

**Scheme 2. Substrate Scope**[a]




[a]Reaction conditions: **1** (0.1 mmol), $Pd(dba)_2$ (5 mol %), **L5** (7.5 mol %), OFBA (10 mol %), DMBQ (1.2 equiv), MTBE (1.0 mL), 45 °C, 12 h, under Ar. [b]**L6** was used instead of **L5**. [c]**L7** was used instead of **L5**.

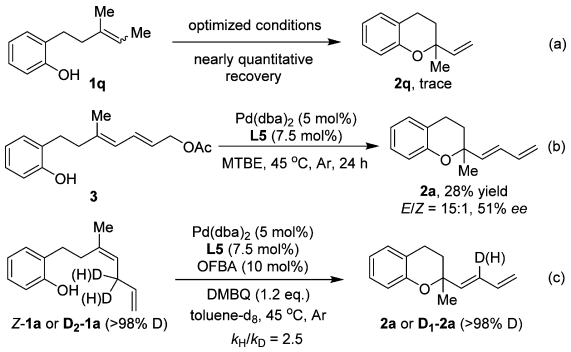


DOI: 10.1021/jacs.5b08477
J. Am. Chem. Soc. 2015, 137, 12732–12735

ring led to the generation of chromans **2b–g** with good performance, except for 4-acetamide substituted substrate **1h**, which gave slightly lower enantioselectivity. Especially, the reaction was highly sensitive to the substitution pattern on the benzene ring, as shown in **1i–j**. As such, the installation of a substituent at either 3- or 5-position led to much diminished *E*/*Z* selectivity and enantioselectivity. To our delight, the *E*/*Z* selectivity could be improved to 30:1 with slightly improved enantioselectivity by using ligand **L6** to replace **L5** in the case of **1j**. Notably, **1k** was also able to participate in a clean reaction with ligand **L6** to give excellent *E*/*Z* selectivity and enantioselectivity. Moreover, the presence of bulkier alkyl group adjacent to the internal alkenes (**1l–o**) was also compatible with the optimal reaction conditions, delivering the desired products in good yields and with high enantioselectivities. However, the presence of a substituent at the terminal double bond (**1p**) led to a much slower reaction under the optimized conditions, while enhanced results could be obtained by replacing ligand **L5** with ligand **L7**.

Then, a series of parallel reactions (Scheme 3) were conducted to identify the allylic C–H activation pathway. The control

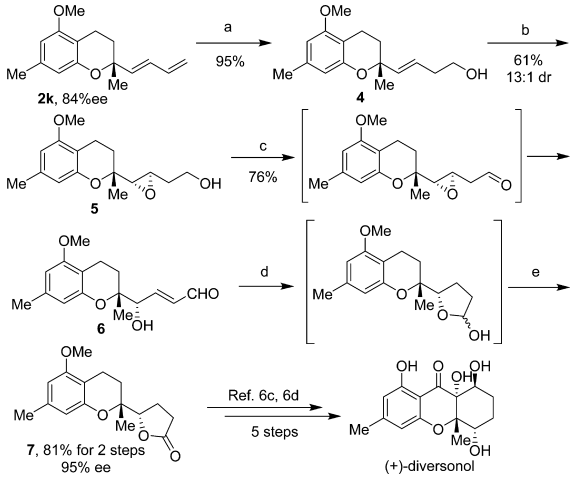
**Scheme 3. Experiments for Mechanistic Studies**




reaction using 2-(3-methylpent-3-en-1-yl)phenol (**1q**) under the optimized conditions (Scheme 3a) failed to afford the desired product, and the starting material was nearly quantitatively recovered, implying that the Wacker-type reaction is impossible to occur and might thereby be ruled out as a pathway. In contrast, a typical Pd-catalyzed allylic alkoxylation of **3** in the presence of ligand **L5** resulted in 15:1 *E*/*Z* selectivity (Scheme 3b), relatively close to the results observed for the reaction of **1a** (Table 1). More importantly, a significant intramolecular kinetic isotope effect (KIE, $k_H/k_D = 2.5$) was observed for the reaction of $\mathbf{D_2}$**-1a** (Scheme 3c),[17] which revealed that the allylic C–H cleavage was the rate-determining step. All of these results aggregately suggest that the allylic C–H activation process to generate $\pi$-allyl palladium species turns out to be the initial step of the reaction, rather than a Wacker-type pathway.[8]

Finally, we attempted to apply this new method to the enantioselective synthesis of (+)-diversonol (Scheme 4). It is noteworthy that the more easily accessible *E*/*Z*-isomeric mixture of **1k** was able to undergo a scale-up reaction to give **2k** in a high yield and with synthetically useful enantioselectivity in the presence of 2 mol % of chiral palladium complex.[17] Regioselective hydroboration of **2k** with 9-borabicyclo[3.3.1]-nonane (9-BBN) and followed by an oxidation with hydrogen peroxide in the presence of sodium hydroxide was able to give homoallylic alcohol **4** in an almost perfect yield. After various conditions were examined for the diastereoselective epoxidation of **4**, a modified Onaka's Zr(O$^t$Bu)$_4$–DIPT–TBHP system was

**Scheme 4. Asymmetric Formal Synthesis of (+)-Diversonol**[a]




[a]Reaction conditions: (a) 9-BBN (2.0 equiv), THF, rt, 12 h, then NaOH, $H_2O_2$. (b) Zr(O$^t$Bu)$_4$ (0.5 equiv), D-(−)-DIPT (0.6 equiv), TBHP (2.0 equiv), DCM, 0 °C, 12 h. (c) $SO_3$·Py (6.0 equiv), $Et_3N$ (10 equiv), DMSO (40 equiv), DCM, 0 °C, 1 h. (d) Pd/C (5 mol %), $H_2$, EtOAc, rt, 1 h. (e) PCC (2.0 equiv), DCM, rt, 1 h.

found to give satisfactory diastereomeric ratio of 13:1.[20] The conversion of **5** to $\gamma$-hydroxyl unsaturated aldehyde **6** was established by $\beta$-elimination reaction of the corresponding epoxide aldehyde intermediate[21] under the standard Parikh–Doering oxidation conditions.[22] The hydrogenation of **6** catalyzed by Pd/C under $H_2$ atmosphere gave rise to the corresponding hemiacetal intermediate, which was oxidized by PCC to furnish the chroman lactone **7** with 95% *ee*, which was actually a key intermediate for the total synthesis of (+)-diversonol by following procedures reported by Nicolaou[6c] and Bräse.[6d] All of the spectroscopic data of the synthetic chroman lactone **7** was in complete agreement with those reported previously.[6d,17]

In conclusion, an enantioselective intramolecular allylic C–H oxidation reaction has been established under the cooperative catalysis of a chiral palladium complex and 2-fluorobenzoic acid, allowing for an efficient synthesis of chromans in high yields and with high levels of enantioselectivity. Mechanistic studies suggest that the reaction proceeds via an initial counteranion-assisted Pd-catalyzed allylic C–H activation and followed by an allylic alkoxylation, rather than a formal Wacker-type cyclization. More significantly, this method has provided a new efficient synthetic route to the key chiral intermediate for the synthesis of (+)-diversonol.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b08477.

Complete experimental procedures (PDF)
Characterization data for the prepared compounds (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

*gonglz@ustc.edu.cn

### Notes

The authors declare no competing financial interest.



DOI: 10.1021/jacs.5b08477
J. Am. Chem. Soc. 2015, 137, 12732–12735

## ■ ACKNOWLEDGMENTS

We are grateful for financial support from MOST (973 project 2015CB856600), NSFC (21232007, 21302177), and the Fundamental Research Funds for the Central Universities (WK2060190041).

## ■ REFERENCES

(1) (a) Reddy, K. A.; Lohray, B. B.; Bhushan, V.; Reddy, A. S.; Rao Mamidi, N. V.; Reddy, P. P.; Saibaba, V.; Reddy, N. J.; Suryaprakash, A.; Misra, P.; Vikramadithyan, R. K.; Rajagopalan, R. *J. Med. Chem.* **1999**, *42*, 3265. (b) Koufaki, M.; Detsi, A.; Theodorou, E.; Kiziridi, C.; Calogeropoulou, T.; Vassilopoulos, A.; Kourounakis, A. P.; Rekka, E.; Kourounakis, P. N.; Gaitanaki, C.; Papazafiri, P. *Bioorg. Med. Chem.* **2004**, *12*, 4835. (c) Fukunaga-Takenaka, R.; Shirai, Y.; Yagi, K.; Adachi, N.; Sakai, N.; Merino, E.; Merida, I.; Saito, N. *Genes Cells* **2005**, *10*, 311. (d) Koufaki, M.; Theodorou, E.; Galaris, D.; Nousis, L.; Katsanou, E. S.; Alexis, M. N. *J. Med. Chem.* **2006**, *49*, 300. (e) Yang, J.; Liu, G.-Y.; Lu, D.-L.; Dai, F.; Qian, Y.-P.; Jin, X.-L.; Zhou, B. *Chem. - Eur. J.* **2010**, *16*, 12808.

(2) (a) Bowry, V. W.; Stocker, R. *J. Am. Chem. Soc.* **1993**, *115*, 6029. (b) Weber, C.; Podda, M.; Rallis, M.; Thiele, J. J.; Traber, M. G.; Packer, L. *Free Radical Biol. Med.* **1997**, *22*, 761.

(3) (a) Hayes, A. W. *Clin. Toxicol.* **1980**, *17*, 45. (b) Lesch, B.; Brase, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 115. (c) Rezanka, T.; Sigler, K. *J. Nat. Prod.* **2007**, *70*, 1487. (d) Zhang, Y.; Song, Z.; Hao, J.; Qiu, S.; Xu, Z. *Fitoterapia* **2010**, *81*, 595.

(4) Turner, W. B. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1621.

(5) (a) Franck, B.; Gottschalk, E. M.; Ohnsorge, U.; Baumann, G. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 441. (b) Howard, C. C.; Johnston, Ra *J. Chem. Soc., Perkin Trans. 1* **1973**, 2440. (c) Andersen, R.; Buchi, G.; Kobbe, B.; Demain, A. L. *J. Org. Chem.* **1977**, *42*, 352. (d) Kurobane, I.; Iwahashi, S.; Fukuda, A. *Drugs Exp. Clin. Res.* **1987**, *13*, 339. (e) El-Elimat, T.; Raja, H.; Oberlies, N. H. *Planta Med.* **2013**, *79*, 849.

(6) (a) Nising, C. F.; Ohnemuller, U. K.; Bräse, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 307. (b) Gerard, E. M. C.; Bräse, S. *Chem. - Eur. J.* **2008**, *14*, 8086. (c) Nicolaou, K. C.; Li, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 6579. (d) Brohmer, M. C.; Bourcet, E.; Nieger, M.; Brase, S. *Chem. - Eur. J.* **2011**, *17*, 13706. (e) Siddiqui, I. N.; Zahoor, A.; Hussain, H.; Ahmed, I.; Ahmad, V. U.; Padula, D.; Draeger, S.; Schulz, B.; Meier, K.; Steinert, M.; Kurtan, T.; Florke, U.; Pescitelli, G.; Krohn, K. *J. Nat. Prod.* **2011**, *74*, 365. (f) Tietze, L. F.; Jackenkroll, S.; Raith, C.; Spiegl, D. A.; Reiner, J. R.; Ochoa Campos, M. C. *Chem. - Eur. J.* **2013**, *19*, 4876. (g) Sudhakar, G.; Bayya, S.; Kadam, V. D.; Nanubolu, J. B. *Org. Biomol. Chem.* **2014**, *12*, 5601.

(7) (a) Shen, H. C. *Tetrahedron* **2009**, *65*, 3931. (b) Nibbs, A. E.; Scheidt, K. A. *Eur. J. Org. Chem.* **2012**, *2012*, 449.

(8) (a) Tietze, L. F.; Stecker, F.; Zinngrebe, J.; Sommer, K. M. *Chem. - Eur. J.* **2006**, *12*, 8770. (b) Tietze, L. F.; Zinngrebe, J.; Spiegl, D. A.; Stecker, F. *Heterocycles* **2007**, *74*, 473. (c) Hua, Q. L.; Li, C.; Wang, X. F.; Lu, L. Q.; Chen, J. R.; Xiao, W. J. *ACS Catal.* **2011**, *1*, 221. (d) Liu, Q. C.; Wen, K.; Zhang, Z. F.; Wu, Z. X.; Zhang, Y. J.; Zhang, W. B. *Tetrahedron* **2012**, *68*, 5209.

(9) (a) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 9074. (b) Trost, B. M.; Shen, H. C.; Dong, L.; Surivet, J. P.; Sylvain, C. *J. Am. Chem. Soc.* **2004**, *126*, 11966. (c) Uria, U.; Vila, C.; Lin, M. Y.; Rueping, M. *Chem. - Eur. J.* **2014**, *20*, 13913.

(10) (a) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (b) Jensen, T.; Fristrup, P. *Chem. - Eur. J.* **2009**, *15*, 9632. (c) Liu, G.; Wu, Y. *Top. Curr. Chem.* **2009**, *292*, 195. (d) Engelin, C. J.; Fristrup, P. *Molecules* **2011**, *16*, 951. (e) Li, B.-J.; Shi, Z.-J. *Chem. Soc. Rev.* **2012**, *41*, 5588. (f) Kumar, R.; Van der Eycken, E. V. *Chem. Soc. Rev.* **2013**, *42*, 1121. (g) Nakamura, A.; Nakada, M. *Synthesis* **2013**, *45*, 1421. (h) Chen, K.; Zhang, P.; Wang, Y.; Li, H. *Green Chem.* **2014**, *16*, 2344. (i) Liron, F.; Oble, J.; Lorion, M. M.; Poli, G. *Eur. J. Org. Chem.* **2014**, *2014*, 5863. (j) Zheng, C.; You, S.-L. *RSC Adv.* **2014**, *4*, 6173.

(11) (a) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346. (b) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970. (c) Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 15076. (d) Li, Z. P.; Li, C. J. *J. Am. Chem. Soc.* **2006**, *128*, 56. (e) Vermeulen, N. A.; Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 11323. (f) Huang, D. S.; Wang, H. N.; Xue, F. Z.; Shi, Y. *J. Org. Chem.* **2011**, *76*, 7269. (g) Ammann, S. E.; Rice, G. T.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 10834. (h) Osberger, T. J.; White, M. C. *J. Am. Chem. Soc.* **2014**, *136*, 11176. (i) Wang, P.-S.; Lin, H.-C.; Zhou, X.-L.; Gong, L.-Z. *Org. Lett.* **2014**, *16*, 3332.

(12) Andrus, M. B.; Zhou, Z. N. *J. Am. Chem. Soc.* **2002**, *124*, 8806.

(13) Covell, D. J.; White, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 6448.

(14) Trost, B. M.; Hansmann, M. M.; Thaisrivongs, D. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4950.

(15) (a) Trost, B. M.; Thaisrivongs, D. A.; Donckele, E. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 1523. For applications of chiral phosphoramidite ligand in asymmetric allylic C−H amination, see: (b) Du, H.; Zhao, B.; Shi, Y. *J. Am. Chem. Soc.* **2008**, *130*, 8590.

(16) Wang, P.-S.; Lin, H.-C.; Zhai, Y.-J.; Han, Z.-Y.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 12218.

(17) See the Supporting Information for details.

(18) Tao, Z.-L.; Zhang, W.-Q.; Chen, D.-F.; Adele, A.; Gong, L.-Z. *J. Am. Chem. Soc.* **2013**, *135*, 9255.

(19) McDonald, R. I.; Liu, G.; Stahl, S. S. *Chem. Rev.* **2011**, *111*, 2981.

(20) Okachi, T.; Murai, N.; Onaka, M. *Org. Lett.* **2003**, *5*, 85.

(21) Chakraborty, T. K.; Purkait, S.; Das, S. *Tetrahedron* **2003**, *59*, 9127.

(22) Parikh, J. R.; Doering, W. V. E. *J. Am. Chem. Soc.* **1967**, *89*, 5505.



DOI: 10.1021/jacs.5b08477
*J. Am. Chem. Soc.* 2015, 137, 12732−12735