Organic LETTERS

Letter

pubs.acs.org/OrgLett

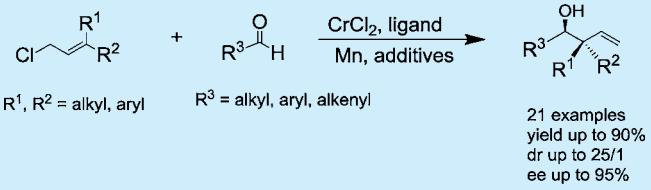
Enantioselective Synthesis of Quaternary Stereocenters via Chromium Catalysis

Yang Xiong and Guozhu Zhang*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

Supporting Information

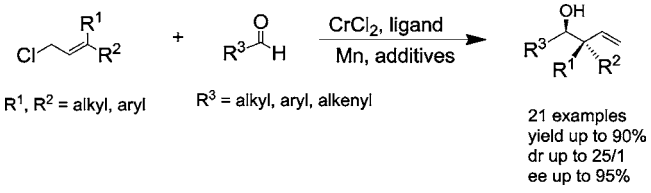
ABSTRACT: Asymmetric allylation of aldehydes with γ-disubstituted allyl halides has been achieved in the presence of a sulfonamide/oxazoline chromium complex. A variety of synthetically useful α-homoallylic alcohols with two consecutive stereogenic centers, including one quaternary carbon, can be accessed in a highly diastereoselective and enantioselective manner.



Catalytic and enantioselective construction of quaternary stereocenters constitutes an important topic because of the wide occurrence of this motif in biologically active molecules.[1] Sustained interest has been directed into this very challenging research area.[2] Thanks to the efforts of different research groups, quite a few efficient strategies have been developed, such as asymmetric Claisen rearrangement,[3] intermolecular cycloaddition and intramolecular cyclization reactions,[4] S_N2'-type allylic substitution of 3,3′-disubstituted allyl electrophiles,[5] enantioseletive conjugate additions on prochiral β,β-disubstituted enones and other related electrophiles,[6] asymmetric alkylation of α-monosubstituted ketones, nitriles, and esters,[7] transition-metal-catalyzed asymmetric insertion reactions including Heck-type addition,[8] dearomative addition reactions,[9] etc. Carbonyl allylation with allylmetal reagents represents a significant transformation in organic synthesis, as the resulting homoallylic alcohols serve as important building blocks leading to polypropionate-derived natural products, carbohydrates, and other polyhydroxylated compounds.[10] A quaternary stereocenter could be generated when a 3,3′-disubstituted allylmetal reagent was employed. However, for asymmetric versions, only a few elegant methods using allyl boronates,[11] allyl silicate reagents[12] and iridium-catalyzed coupling of alcohols with vinyl epoxide[13] have been reported. Given the broad existence and diverse application of homoallylic alcohols, methods to construct this important motif under mild reaction conditions from facile starting materials are still highly desired.

3,3′-Disubstituted allyl halides are readily available stock chemicals and are easy to prepare. Direct use of them as carbonyl allylation reagents to generate quaternary stereogenic centers has been investigated in chromium catalysis[14] and indium catalysis.[15] However, constructing enantioenriched quaternary stereocenters by the above-mentioned methods still remains an unmet challenge. In line with our continuing interest in chromium-catalyzed coupling of functionalized organohalides with aldehydes,[16] herein we report our preliminary results on chromium-catalyzed enantioselective carbonyl allylation with 3,3′-disubstituted allyl halides (Scheme 1). Besides the high degree of *anti* diastereoselectivity and enantioselectivity, the highlights of this reaction also include the following: (1) sulfonamide/oxazolines developed by Kishi were the most effective chiral ligands (Figure 1);[17] (2) this reaction exhibits broad functional group compatibility and mild reaction conditions; (3) 3,3′-disubstituted allylic halides can be directly used as starting materials, and two substituents can be freely functionalized; (4) the utility of this protocol was demonstrated

Scheme 1. Catalytic and Asymmetric Construction of Quaternary Stereocenters



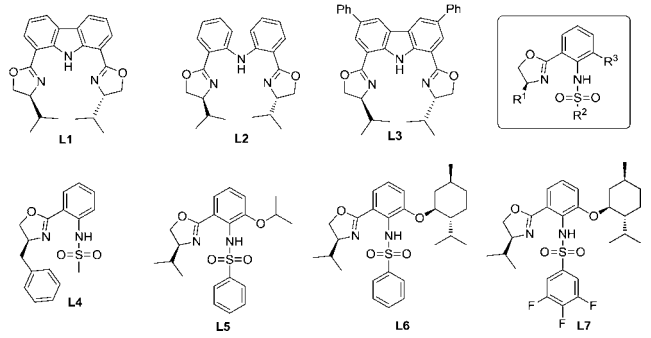


Figure 1. Tested ligands.

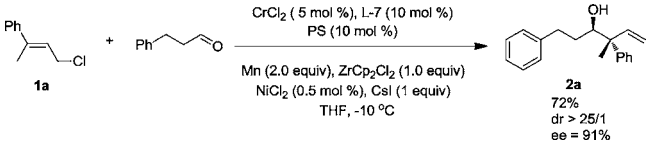
Received: August 24, 2016
Published: September 13, 2016

DOI: 10.1021/acs.orglett.6b02540
Org. Lett. 2016, 18, 5094−5097

in the formal asymmetric synthesis of an enantiomer of the serotonin antagonist LY426945 and an enantioselective synthesis of (+)-bakuchiol.

At the beginning, the reaction between dihydrocinnamaldehyde and easily accessible (*E*)-(4-chlorobut-2-en-2-yl)benzene (**1a**) was chosen as the model reaction. With **L1** as the chiral ligand,[16] the desired product **2a** was obtained in 70% yield with about 50% ee as a single diastereomer. However, extensive ligand screening and conditions optimization centered on the carbazole-based bisoxazoline ligands led to no further improvement in enantioselectivity.[18] Diphenylamine bis(oxazoline) **L2** was also examined, and 30% ee was observed.[19] Known **L3** was also tested, and **2a** was obtained in 67% yield with 45% ee (Table 1, entry 4). The effects of chiral ligands on the reaction

Table 1. Optimization of the Reaction Conditions



entry[a]	deviation from the standard conditions	yield (%)[b]	ee (%)[c]
1	none	72	91
2	**L1**	65	50
3	**L2**	65	30
4	**L3**	67	45
5	**L4**	69	7
6	**L5**	66	55
7	**L6**	70	55
8	rt instead of −10 °C	70	83
9	5% $CrCl_2$, 7% **L7**	78	85
10	$CrCl_3$[d,e]	64	86
11	without $NiCl_2$	50	81
12	without CsI	49	72
13	TMSCl instead of $ZrCp_2Cl_2$	60	83
14	1 mmol of aldehyde	70	91

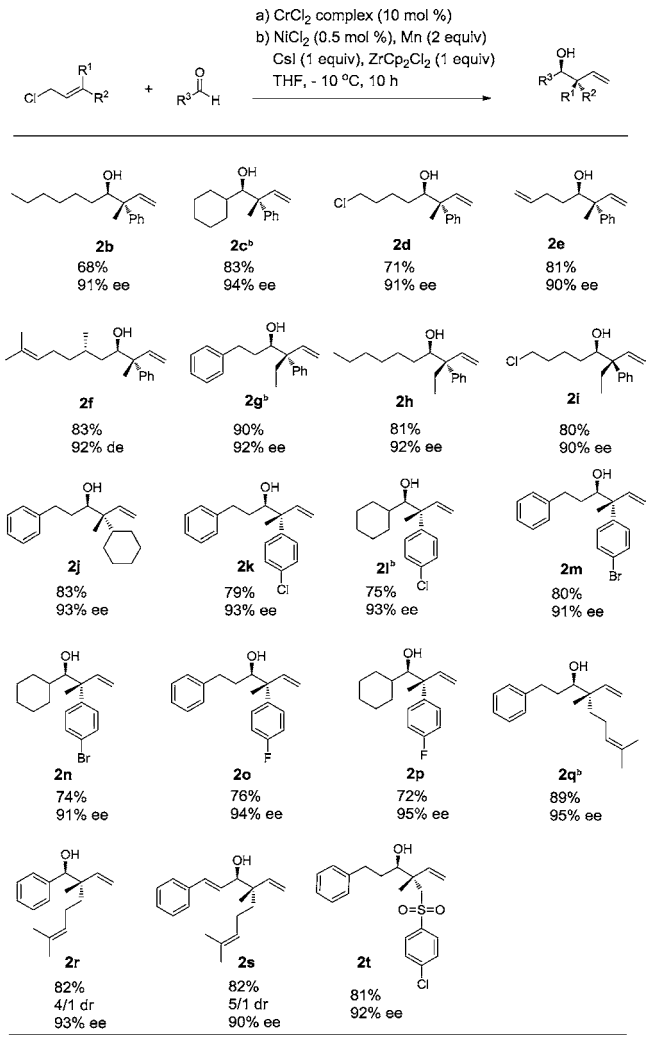
[a]The reactions were carried out on a 0.2 mmol scale, unless noted otherwise. [b]Isolated yields. [c]Determined by chiral HPLC analysis; the product configuration was assigned by comparison with a reported example. [d]1 equiv of Mn was added for the complex formation. [e]Complexation took 8 h.

are summarized in the Supporting Information. Then we tested the modified sulfonamide/oxazoline ligand **L5**.[17] To our delight, a slight increase in enantioselectivity was observed, and **2a** was obtained in 70% yield with 55% ee (Table 1, entry 6).[20] Attention was then directed toward the optimization of sulfonamide ligands. A modified synthetic route was developed to prepare a series of sulfonamide ligands bearing different substitutions with varying size and electron-inductive ability.[21] Isopropyl as the R^1 substituent was identified as the substitution of choice. Further ligand screening studies revealed that the enantioselectivity increased as the bulkiness of the substituent R^3 was enhanced. Menthol was determined to be the optimal substituent. Fixing R^1 as isopropyl and R^3 as menthol, we then turned our attention to R^2. Eventually, ligand **L7** with a 2,3,4-trifluorobenzenesulfonyl group was the most effective, affording **2a** in 75% yield with 91% ee.

The impact of various deviations from the standard reaction conditions was also evaluated. Solvent screening revealed that THF gave the best results. The presence of a tiny amount of $NiCl_2$ is critical to the efficiency of the coupling reaction, as the yield of **2a** decreased under conditions without this component. Cheaper and easier-to-handle $CrCl_3$ could also be directly used (87% yield, 86% ee; Table 1, entry 10). In this case, the complexation step required the addition of 1 equiv of Mn metal. CsI exhibited an enhancing effect on the coupling rate and enantioselectivity. Similar to LiCl, CsI is likely to facilitate the formation of the allyl species and its transmetalation to the chiral chromium complex. Both TMSCl[22] and $ZrCp_2Cl_2$[23] have been previously used as dissociating reagents; in this case, TMSCl had slightly lower efficiency (Table 1, entry 13). Notably, the reaction scale could be increased to 1 mmol with maintenance of the efficiency (Table 1, entry 14).

This highly enantioselective synthesis of **2a** could also be expanded to reactions with a broad range of aldehydes, and high enantioselectivity (90−95% ee) was obtained (Scheme 2). Coupling of **1a** with representative aliphatic aldehydes, including cyclohexyl carboxaldehyde and heptaldehyde, proceeded smoothly, and the corresponding homoallylic alcohols **2b** and **2c** were isolated in high yields with excellent

Scheme 2. Scope Studies[a]



[a]All of the reactions carried out on a 0.2 mmol scale under the standard conditions. Ligand **L7** was used. Generally over 15/1 *anti* diastereoselectivity was observed. The product configuration was assigned by comparison with a reported examples.[12e,f,26b] [b]Reactions carried out at 1 mmol scale.

DOI: 10.1021/acs.orglett.6b02540
Org. Lett. 2016, 18, 5094−5097

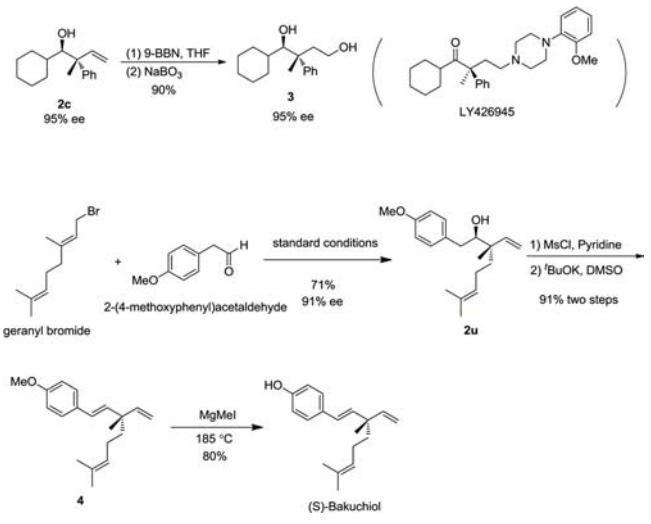
enantiomeric excess (91% and 94% ee). Substrates with a chloro group and a terminal C−C double bond reacted well, giving **2d** and **2e** in good yields with high ee. The naturally occurring aldehyde (−)-citronellal, bearing a chiral methyl group β to the carbonyl group, exhibited negligible catalyst−substrate mismatching profile, as the reaction of (−)-citronellal worked well, giving product **2f** as a single diastereomer in 82% yield with (+)90% ee. Attempts to modify the substituents on the allyl chloride turned out to be successful. Substrates with slightly increased bulkiness resulting from changing the methyl group to an ethyl group reacted equally well with three aliphatic aldehydes, giving products **2g−I** in good yields of 79−81% with excellent ee (>90%).

The reaction of a substrate bearing two aliphatic substituents (one methyl and one cyclohexyl) worked slightly better than **1a**, leading to product **2j** in 83% isolated yield with 93% ee. The phenyl group at the γ-position could be freely halogenated with Cl, Br, and F without compromising the reaction efficiency in terms of yield and ee, as products **2k−p** were isolated in moderate to good yields with decent ee ranging from 91% to 95%. To our delight, commercially available geranyl bromide could serve as a suitable substrate for this reaction as well; an even higher enantioselectivity was obtained with dihydrocinnamaldehyde, as the corresponding product **2q** was isolated in 76% yield with 95% ee. Notably, this allylation protocol could be applied to aryl aldehydes and α,β-unsaturated aldehydes to produce the corresponding **2r** and **2s** in moderate to good yields with good enantiomeric excess (90−93% ee) and slightly decreased diastereoselectivity (5/1 and 4/1, respectively). Furthermore, a sulfonyl function could be tolerated, giving the highly functionalized product **2t** in 81% yield with 92% ee.

It is worth mentioning that in our attempt to make another pair of diastereomers by the coupling of (*Z*)-geranyl bromide with dihydrocinnamaldehyde, a significant erosion of the diastereoselectivity was observed, presumably due to the *Z*/*E* isomerization, in which the undesired *E* configuration is more favored in the transition state.

To demonstrate the synthetic potential of our methodology, two short transformations were carried out (Scheme 3). One of the allylation products, **2c** (95% ee), underwent hydroboration and oxidation smoothly to deliver a 90% yield of diol **3**, which is the enantiomer of an advanced intermediate in the synthesis of the serotonin antagonist LY426945.[24] The reaction of commercially available 2-(4-methoxyphenyl)acetaldehyde with geranyl bromide proceeded smoothly to give product **2u** in good yield with 91% ee. **2u** was converted into dehydroxylated **4** via a two-step sequence. The final demethylation of **4** with MgMeI furnished the natural product (*S*)-bakuchiol, which belongs to a family of monoterpene phenols occurring in the traditional Chinese medicinal plant *Psoralea corylifolia L.*[25] Many of these natural product members and derivatives display a variety of biological activities and are currently the subject of active investigations.[26]

Scheme 3. Synthetic Utilities of α,α-Disubstituted Homoallylic Alcohols



In summary, we have established an efficient method to construct two consecutive stereogenic centers, including one quaternary carbon, through chromium-catalyzed asymmetric allylation of aldehydes with γ-disubstituted allyl halides. Key features include readily available allylation reagents, convenient execution and mild reaction conditions, broad functional group tolerance, and high levels of diastereoselectivity and excellent enantioselectivity. The synthetic value was demonstrated in two short transformations. We positively believe that this protocol will find applications in the enantioselective synthesis of pharmaceutical compounds and natural products containing quaternary stereocenters.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02540.

Experimental procedures and characterization data for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: guozhuzhang@sioc.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to NSFC-21421091, the "Thousand Plan" Youth Program, and the State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. We thank Professor Yoshito Kishi (Harvard University) for valuable suggestions.

■ REFERENCES

(1) (a) *Quaternary Stereocenters: Challenges and Solutions for Organic Synthesis*; Christoffers, J., Baro, A., Eds.; Wiley-VCH: Weinheim, Germany, 2005. (b) Douglas, C. J.; Overman, L. E. *Proc. Natl. Acad. Sci. U. S. A.* **2004**, *101*, 5363. (c) Denissova, I.; Barriault, L. *Tetrahedron* **2003**, *59*, 10105. (d) Christoffers, J.; Mann, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4591. (e) Corey, E. J.; Guzman-Perez, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 388. (f) Fuji, K. *Chem. Rev.* **1993**, *93*, 2037.

(2) Selected reviews: (a) Liu, Y.; Han, S.-J.; Liu, W.- B.; Stoltz, B. M. *Acc. Chem. Res.* **2015**, *48*, 740. (b) Quasdorf, K. W.; Overman, L. E. *Nature* **2014**, *516*, 181. (c) Das, J. P.; Marek, I. *Chem. Commun.* **2011**, *47*, 4593. (d) Shimizu, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5998. (e) Wang, B.; Tu, Y. Q. *Acc. Chem. Res.* **2011**, *44*, 1207. (f) Hawner, C.; Alexakis, A. *Chem. Commun.* **2010**, *46*, 7295. (g) Jautze, S.; Peters, R. *Synthesis* **2010**, *2010*, 365. (h) Bella, M.; Gasperi, T. *Synthesis* **2009**,

DOI: 10.1021/acs.orglett.6b02540
Org. Lett. 2016, 18, 5094−5097

2009, 1583. (i) Cozzi, P. G.; Hilgraf, R.; Zimmermann, N. *Eur. J. Org. Chem.* **2007**, *2007*, 5969. (j) Mohr, J. T.; Stoltz, B. M. *Chem. - Asian J.* **2007**, *2*, 1476. (k) Trost, B. M.; Jiang, C. *Synthesis* **2006**, 369.

(3) (a) Tan, J.; Cheon, C.-H.; Yamamoto, H. *Angew. Chem., Int. Ed.* **2012**, *51*, 8264. (b) Linton, E. C.; Kozlowski, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 16162. (c) Castro, A. M. M. *Chem. Rev.* **2004**, *104*, 2939.

(4) (a) Jiang, X.- X.; Wang, R. *Chem. Rev.* **2013**, *113*, 5515. (b) Chen, X.-H.; Wei, Q.; Luo, S.-W.; Xiao, H.; Gong, L.-Z. *J. Am. Chem. Soc.* **2009**, *131*, 13819. (c) Corey, E. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2100. (d) Wilson, R. M.; Jen, W. S.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 11616. (e) Corey, E. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1650. (f) Kagan, H.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007.

(5) Selected examples: (a) Grassi, D.; Alexakis, A. *Adv. Synth. Catal.* **2015**, *357*, 3171. (b) Magrez, M.; Le Guen, Y.; Baslé, O.; Crévisy, C.; Mauduit, M. *Chem. - Eur. J.* **2013**, *19*, 1199. (c) Gao, F.; Carr, J. L.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6613. (d) Luchaco-Cullis, C. A.; Mizutani, H.; Murphy, K. E.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1456.

(6) Selected examples: (a) Gao, J.-R.; Wu, H.; Xiang, B.; Yu, W.-B.; Han, L.; Jia, Y.-X. *J. Am. Chem. Soc.* **2013**, *135*, 2983. (b) Kikushima, K.; Holder, J. C.; Gatti, M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2011**, *133*, 6902. (c) Shintani, R.; Duan, W.-L.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628. (d) Schulz, S. R.; Blechert, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3966. (e) Hird, A. W.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 14988. (f) d'Augustin, M.; Palais, L.; Alexakis, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1376.

(7) Selected examples: (a) Turnbull, B. W. H.; Evans, P. A. *J. Am. Chem. Soc.* **2015**, *137*, 6156. (b) Zhou, H.; Zhang, L.; Xu, C.-M.; Luo, S.-Z. *Angew. Chem., Int. Ed.* **2015**, *54*, 12645. (c) Wang, P.-S.; Lin, H.-C.; Zhai, Y.-J.; Han, Z.-Y.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2014**, *53*, 12218. (d) Zhu, Y.; Zhang, L.; Luo, S.-Z. *J. Am. Chem. Soc.* **2014**, *136*, 14642. (e) Holder, J. C.; Zou, L.; Marziale, A. N.; Liu, P.; Lan, Y.; Gatti, M.; Kikushima, K.; Houk, K. N.; Stoltz, B. M. *J. Am. Chem. Soc.* **2013**, *135*, 14996. (f) Seto, M.; Roizen, J. L.; Stoltz, B. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6873.

(8) Selected examples: (a) Mei, T.-S.; P atel, H. H.; Sigman, M. S. *Nature* **2014**, *508*, 340. (b) Xu, T.; Ko, H. M.; Savage, N. A.; Dong, G. *J. Am. Chem. Soc.* **2012**, *134*, 20005.

(9) Selected examples: (a) Wu, Q.-F.; He, H.; Liu, W.-B.; You, S.-L. *J. Am. Chem. Soc.* **2010**, *132*, 11418. (a) Trost, B. M.; Quancard, J. *J. Am. Chem. Soc.* **2006**, *128*, 6314. (b) García-Fortanet, J.; Kessler, F.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6676.

(10) Chemler, S. R.; Roush, W. R. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VCH: Weinheim, Germany, 2000; p 403.

(11) (a) Alam, R.; Vollgraff, T.; Eriksson, L.; Szabó, K. J. *J. Am. Chem. Soc.* **2015**, *137*, 11262. (b) Chen, J. L. Y.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2014**, *53*, 10992. (c) Potter, B.; Szymaniak, A. A.; Edelstein, E. K.; Morken, J. P. *J. Am. Chem. Soc.* **2014**, *136*, 17918. (d) Silverio, D. L.; Torker, S.; Pilyugina, T.; Vieira, E. M.; Snapper, M. L.; Haeffner, F.; Hoveyda, A. H. *Nature* **2013**, *494*, 216. (e) Meng, F.; Jang, H.; Jung, B.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2013**, *52*, 5046. (f) Ferris, G. E.; Hong, K.; Roundtree, I. A.; Morken, J. P. *J. Am. Chem. Soc.* **2013**, *135*, 2501. (g) Shi, S.-L.; Xu, L.-W.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 6638. (h) Ogasawara, M.; Okada, A.; Subbarayan, V.; Sörgel, S.; Takahashi, T. *Org. Lett.* **2010**, *12*, 5736. (i) Ito, H.; Okura, T.; Matsuura, K.; Sawamura, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 560. (j) Barnett, D. S.; Moquist, P. N.; Schaus, S. E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8679. (k) Lou, S.; Moquist, P. N.; Schaus, S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660. (l) Canales, E.; Hernandez, E.; Soderquist, J. A. *J. Am. Chem. Soc.* **2006**, *128*, 8712. (m) Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8910. (n) Kennedy, J. W. J.; Hall, D. G. *J. Am. Chem. Soc.* **2002**, *124*, 898.

(12) (a) Denmark, S. R.; Fu, J.; Lawler, M. J. *J. Org. Chem.* **2006**, *71*, 1523. (b) Denmark, S. R.; Fu, J.; Coe, D. M.; Su, X.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **2006**, *71*, 1513. (c) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2003**, *125*, 2208. (d) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763. (e) Denmark, S. E.; Fu, J. *Org. Lett.* **2002**, *4*, 1951. (f) Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2001**, *123*, 9488.

(13) (a) Feng, J.; Garza, V. J.; Krische, M. J. *J. Am. Chem. Soc.* **2014**, *136*, 8911. Related studies: (b) Zbieg, J. R.; Moran, J.; Krische, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 10582. (c) Sam, B.; Luong, T.; Krische, M. J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5465.

(14) Takai, K. Organochromium Reagents. In *Comprehensive Organic Synthesis*, 2nd ed.; Elsevier: Amsterdam, 2014; Vol. *1*, pp 159−203.

(15) Shen, Z.-L.; Wang, S.-Y.; Chok, Y.-K.; Xu, Y.-H.; Loh, T.-P. *Chem. Rev.* **2013**, *113*, 271−401 and references therein.

(16) (a) Tian, Q.; Zhang, G. *Synthesis* **2016**, DOI: 10.1055/s-0036-1589457. (b) Tian, Q.; Bai, J.; Chen, B.; Zhang, G. *Org. Lett.* **2016**, *18*, 1828. (c) Chen, W.; Yang, Q.; Zhou, T.; Tian, Q.; Zhang, G. *Org. Lett.* **2015**, *17*, 5236.

(17) (a) Guo, H. B.; Dong, C. G.; Kim, D. S.; Urabe, D.; Wang, J. S.; Kim, J. T.; Liu, X.; Sasaki, T.; Kishi, Y. *J. Am. Chem. Soc.* **2009**, *131*, 15387. (b) Choi, H.-w.; Demeke, D.; Kang, F.-A.; Kishi, Y.; Nakajima, K.; Nowak, P.; Wan, Z.-K.; Xie, C. *Pure Appl. Chem.* **2003**, *75*, 1. (c) Chen, C.; Tagami, K.; Kishi, Y. *J. Org. Chem.* **1995**, *60*, 5386.

(18) (a) Inoue, M.; Suzuki, T.; Kinoshita, A.; Nakada, M. *Chem. Rec.* **2008**, *8*, 169. (b) Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc.* **2003**, *125*, 1140. (c) Suzuki, T.; Kinoshita, A.; Kawada, H.; Nakada, M. *Synlett* **2003**, *4*, 570.

(19) (a) McManus, H. A.; Cozzi, P. G.; Guiry, P. J. *Adv. Synth. Catal.* **2006**, *348*, 551. (b) Hargaden, G. C.; McManus, H. A.; Cozzi, P. G.; Guiry, P. J. *Org. Biomol. Chem.* **2007**, *5*, 763.

(20) (a) Zhang, Z. Y.; Huang, J.; Ma, B.; Kishi, Y. *Org. Lett.* **2008**, *10*, 3073. (b) Kurosu, M.; Lin, M.-H.; Kishi, Y. *J. Am. Chem. Soc.* **2004**, *126*, 12248.

(21) See the Supporting Information for the modified synthesis of sulfonamide/oxazoline ligands.

(22) (a) Fürstner, A.; Wuchrer, M. *Chem. - Eur. J.* **2006**, *12*, 76. (b) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 2533. (c) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349.

(23) Namba, K.; Kishi, Y. *Org. Lett.* **2004**, *6*, 5031.

(24) Denmark, S. E.; Fu, J. *Org. Lett.* **2002**, *4*, 1951.

(25) Xu, Q.-Q.; Zhao, Q.; Shan, G.-S.; Yang, X.-C.; Shi, Q.-Y.; Lei, X. *Tetrahedron* **2013**, *69*, 10739.

(26) (a) Huang, M.-Y.; Chen, L.; Li, R.; Jia, X.; Hong, R. *Chin. J. Chem.* **2014**, *32*, 715 and references therein. An elegant asymmetric synthesis of bakuchiol: (b) Gao, F.; McGrath, K. P.; Lee, Y.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2010**, *132*, 14315.

DOI: 10.1021/acs.orglett.6b02540
Org. Lett. 2016, 18, 5094−5097