C–H Activation

DOI: 10.1002/anie.201005215

Enantioselective Rhodium-Catalyzed Allylic C–H Activation for the Addition to Conjugated Dienes**

*Qian Li and Zhi-Xiang Yu**

Transition-metal-catalyzed C–H activation has the potential to streamline organic synthesis because it can provide novel disconnections in the retrosynthetic analysis of a target molecule.[1,2] A synthetically useful C–H activation method should be diastereoselective and more importantly, enantioselective, if one or more stereocenter is generated in this process. Although significant progress has been made in transition-metal-catalyzed C–H activation reactions, the progress of enantioselective C–H activation and subsequent C–C bond formations through metal insertion[3] has lagged behind.[4] Several impressive examples in this area have emerged. For example, the research groups of Mikami,[5] Murai,[6] and Bergman and Ellman[7] have all reported pioneering work on the enantioselective coupling reactions of vinylic and aromatic C–H bonds with alkenes.[8] Enantioselective hydroacylation reactions of alkenes and ketones through the cleavage of an acyl C–H bond have also been reported.[9] Yu and co-workers have developed an elegant palladium(II)-catalyzed enantioselective coupling reaction of aromatic C–H bonds with boronic acids and styrenes using a desymmetrization strategy.[10a,b] By using a similar approach, Albicker and Cramer achieved enantioselective palladium-catalyzed direct arylations.[10c] Despite these notable advances in the enantioselective sp^2 C–H activation reactions, the enantioselective sp^3 C–H activation/C–C bond formation through the intermediate formation of carbon–metal bonds remains elusive.[11–15] The lack of progress may be attributed to the limited methods for sp^3 C–H activation, the harsh reaction conditions required for the cleavage of an sp^3 C–H bond, and the paucity of ligands available for enantioselective C–H activations. One example of an enantioselective sp^3 C–H activation/C–C bond formation came from Yu and co-workers, who reported a palladium(II)-catalyzed pyridine-directed reaction that occurred with a promising 37% *ee*.[10a] For enantioselective allylic C–H oxidations, White and co-workers[16a,b] achieved a 63% *ee* for the palladium(II)-catalyzed allylic oxygenation of terminal olefins.[16c–g] Even though it is challenging to achieve asymmetric sp^3 C–H activation with high enantioselectivity, considering its synthetic importance, continuous endeavors to meet such a challenge are required.

Recently, our research group has developed a conjugated-diene-assisted, rhodium-catalyzed addition of allylic C–H bonds to conjugated dienes to furnish multifunctional tetrahydropyrrole, tetrahydrofuran, and cyclopentane compounds. The two new stereogenic centers in the final products had good to excellent diastereoselectivity (see the reaction shown in Table 1).[17] We were eager to develop an asymmetric version of this allylic C–H activation/C–C bond formation reaction, which would provide efficient and easy access to the multifunctional chiral tetrahydropyrrole, tetrahydrofuran, and cyclopentane compounds. The two challenges for this enantioselective reaction are the asymmetric allylic C–H activation/C–C bond formation, and the asymmetric synthesis of a quaternary carbon center, which has been a longstanding challenge in organic synthesis.[18] Herein, we report the first example of a highly enantioselective allylic C–H activation/C–C bond formation reaction through metal insertion.[3] We show that the present reaction provides an easy route to the asymmetric synthesis of two adjacent sp^3 carbon centers, one of which is a quaternary carbon center.

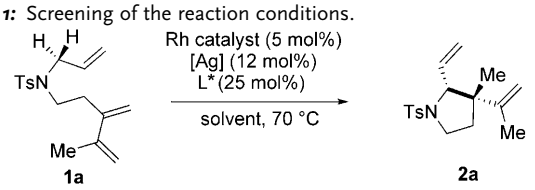
Our study began with the identification of an effective chiral ligand for the target reaction (Table 1). We found that chelating diphosphines such as binap inhibited the reaction, therefore we focused our effort on screening the monodentate ligands. Chiral phosphoramidites,[19] which are a class of easily accessible and highly modulable ligands, were tested. Fortunately, the application of phosphoramidite ligand **A** under our previous reaction conditions gave a high yield and a promising *ee* value (Table 1, entry 1). This encouraging result led us to further optimize the reaction conditions. We observed that changing the silver source from $AbSbF_6$ to AgOTf improved the enantioselectivity (entry 2). Better enantioselectivity was obtained when DME or benzene were used as the solvent (entries 3 and 4, respectively) compared with DCE (entry 2), although the reaction in benzene was slower. The use of $[\{Rh(coe)_2Cl\}_2]$ as a catalyst precursor provided a faster reaction rate (entry 5), presumably as a result of the faster dissociation of the coe ligand from the catalyst precursor. Next, we tested a variety of phosphoramidite ligands. A slight increase of the steric bulk on the nitrogen center improved the *ee* value, for example, phosphoramidites bearing diethyl amine (**B**), diisopropyl amine (**C**), piperidine (**D**), and morpholine (**E**) gave 90%, 89%, 87%, and 90% *ee*, respec-

[*] Q. Li, Prof. Dr. Z.-X. Yu
Beijing National Laboratory of Molecular Sciences (BNLMS)
Key Laboratory of Bioorganic Chemistry and Molecular Engineering
College of Chemistry, Peking University, Beijing, 100871 (China)
Fax: (+86) 10-6275-1708
E-mail: yuzx@pku.edu.cn

[**] We thank the National Natural Science Foundation of China (20825205–National Science Fund for Distinguished Young Scholars, 20772007, 20672005) and the Ministry of Science and Technology (2011CB808603 and 2010CB833203–National Basic Research Programs of China-973 Programs) for financial support. We also thank Prof. Norio Miyaura (Hokkaido University), Prof. Qi-Lin Zhou (Nankai University), and Prof. Shu-Li You (SIOC) for sending us the chiral ligands.

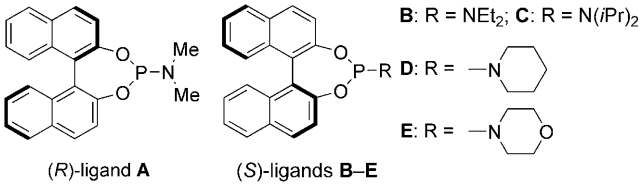
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005215.

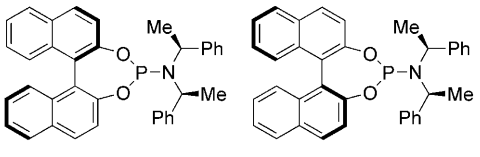
Table 1: Screening of the reaction conditions.

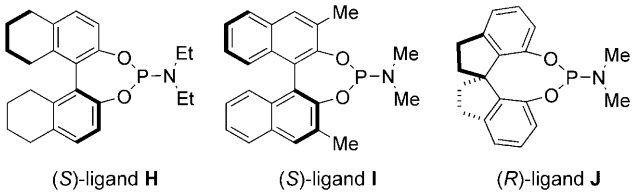


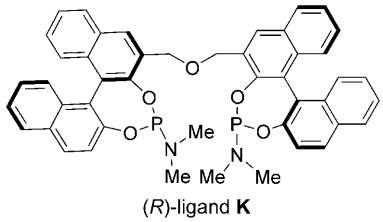
Entry	[Rh]	L*	[Ag]	Solvent	*t* [h]	Yield [%][a]	*ee* [%][b]
1	$[\{Rh(cod)Cl\}_2]$	**A**	$AgSbF_6$	DCE	20	95	58 (2*S*,3*R*)
2	$[\{Rh(cod)Cl\}_2]$	**A**	AgOTf	DCE	12	85	70 (2*S*,3*R*)
3	$[\{Rh(cod)Cl\}_2]$	**A**	AgOTf	DME	11	87	80 (2*S*,3*R*)
4	$[\{Rh(cod)Cl\}_2]$	**A**	AgOTf	benzene	40	86	80 (2*S*,3*R*)
5	$[\{Rh(coe)_2Cl\}_2]$	**A**	AgOTf	DME	8	87	80 (2*S*,3*R*)
6	$[\{Rh(coe)_2Cl\}_2]$	**B**	AgOTf	DME	11	90	90 (2*R*,3*S*)
7	$[\{Rh(coe)_2Cl\}_2]$	**C**	AgOTf	DME	11	90	89 (2*R*, 3*S*)
8	$[\{Rh(coe)_2Cl\}_2]$	**D**	AgOTf	DME	11	90	87 (2*R*,3*S*)
9	$[\{Rh(coe)_2Cl\}_2]$	**E**	AgOTf	DME	11	90	90 (2*R*,3*S*)
10	$[\{Rh(coe)_2Cl\}_2]$	**F**	AgOTf	DME	24	<5	ND
11	$[\{Rh(coe)_2Cl\}_2]$	**G**	AgOTf	DME	24	<5	ND
12	$[\{Rh(coe)_2Cl\}_2]$	**H**	AgOTf	DME	11	91	87 (2*R*, 3*S*)
13	$[\{Rh(coe)_2Cl\}_2]$	**I**	AgOTf	DME	11	90	70 (2*R*,3*S*)
14	$[\{Rh(coe)_2Cl\}_2]$	**J**	AgOTf	DME	36	83	14 (2*R*,3*S*)
15	$[\{Rh(coe)_2Cl\}_2]$	**K**	AgOTf	DME	48	57	77 (2*S*,3*R*)
16[c]	$[\{Rh(coe)_2Cl\}_2]$	**B**	AgOTf	DME	27	90	89 (2*R*,3*S*)
17[d]	$[\{Rh(coe)_2Cl\}_2]$	**B**	AgOTf	DME	36	53	90 (2*R*,3*S*)

[a] Yield of isolated product. [b] The *ee* values were determined by HPLC on a chiral stationary phase. Sense of induction is indicated in parentheses. [c] 1.5 mol% of $[\{Rh(coe)_2Cl\}_2]$, 7.5 mol% of L*, and 3.6 mol% of [Ag]. [d] 1 mol% of $[\{Rh(coe)_2Cl\}_2]$, 5 mol% of L*, and 2.4 mol% of [Ag]. cod = cyclooctadiene, coe = cyclooctene, DCE = 1,2-dichloroethane, DME = 1,2-dimethoxyethane, ND = not determined, Tf = trifluoromethanesulfonyl.





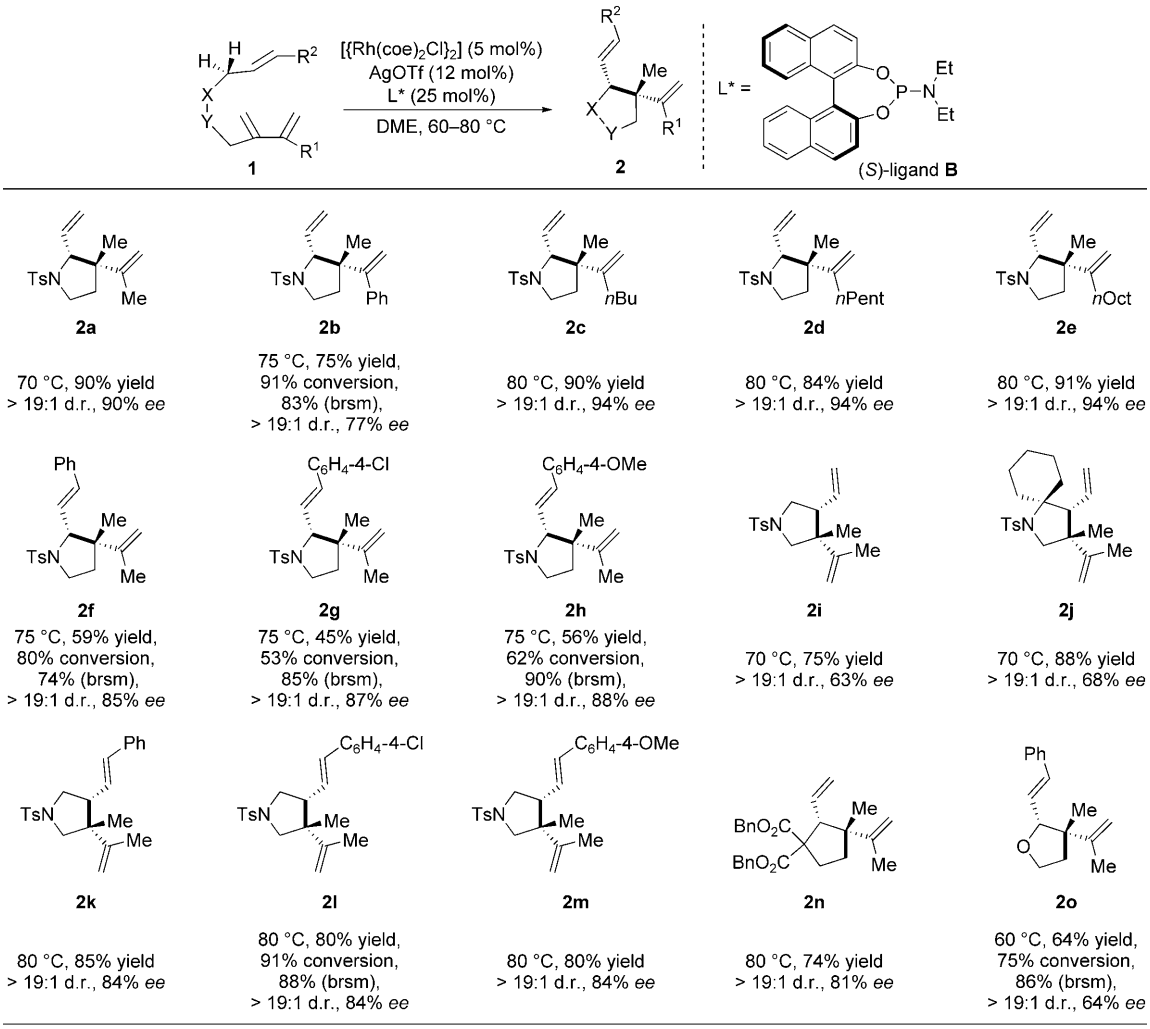




tively (entries 6–9). However, any further increase of the steric bulk on the ligands (**F** and **G**) resulted in negligible yields; this result is probably due to the inhibition of their complexation with the catalyst (entries 10 and 11). Phosphoramidite ligand **H** with an octahydrodinaphthyl group and ligand **I** with a substituent on the binaphthyl scaffold gave high yields but slightly lower enantioselectivities (entries 12 and 13, respectively). Zhou's spiro phosphoramidite ligand **J** was less effective for the enantioinduction in our reaction (entry 14).[20] When using Miyaura's ligand **K** (entry 15) a similar enantioselectivity was achieved as with ligand **A**, but a longer reaction time was required and the yield was lower.[21]

We also examined the catalytic reaction of **1a** using lower rhodium loadings (entries 16 and 17). Pleasingly, when the loading of $[\{Rh(coe)_2Cl\}_2]$ was lowered to 1.5 mol%, an excellent yield and *ee* value were obtained after a prolonged reaction time (27 h). The same enantioselectivity was achieved when the catalyst loading was lowered to 1.0 mol%, although the reaction time was extended to 36 hours. To achieve a practical reaction time, we found that 5 mol% of $[\{Rh(coe)_2Cl\}_2]$, 12 mol% of AgOTf, 25 mol% of ligand **B**, and DME were the optimal conditions.

We next investigated the generality of the enantioselective allylic C–H activation reaction of ene-2-dienes (Scheme 1). A phenyl substituent at the internal position of the conjugated diene decreased the *ee* value, whereas a butyl group at the same position gave a slightly improved *ee* value of 94% (**2b** and **2c**, respectively; Scheme 1). However, increasing the length of the alkyl substituent at the internal position did not give a higher enantioselectivity (**2d** and **2e**). The catalytic system was also applicable to internal allylic C–H bonds. For example, the reactions of substrates that have aryl groups at the terminal position proceeded with lower yields but without any erosion of enantioselectivity (**2f**–**2h**). Significantly, the enantioselective reactions were not limited to allylic C–H bonds which are adjacent to a nitrogen atom, as demonstrated by the successful reactions of homoallylic substrates to give products **2i**–**2m**. However, the enantioselectivity decreased when the unsubstituted homoallylic substrate was used. We synthesized the spiro substrate to increase the conformational rigidity in the hope that this would improve the enantioselectivity of the reaction. Unfortunately, the *ee* value achieved was 68%, although the reaction yield was increased to 88% (**2j**). Interestingly, in contrast to aryl-substituted allylic substrates that gave **2f**–**2h** as products in low yields, aryl substituents on the homoallylic substrates did not affect the reaction yields and maintained the high enantioselectivity (**2k**–**2m**). In addition to the nitrogen-tethered substrates, the carbon- and oxygen-tethered substrates also reacted efficiently and gave products **2n** and **2o**, respectively, with good to high enantiocontrol. Importantly, for all the substrates tested the reactions proceeded diastereoselectively resulting in the *cis* products. Thus, this process provides a facile method to synthesize substituted tetrahydropyrrole, tetrahydrofuran, and cyclopentane compounds with excellent diastereoselectivity and good to high enantioselectivity. The absolute configuration of product **2f** was determined by X-ray crystallographic analysis (Figure 1).[22] Additionally, we performed a nonlinear effect study of the



Scheme 1. Scope of the asymmetric allylic C–H activation/addition to conjugated dienes. The reaction time of each substrate is indicated in the Supporting Information. The yields reported are for the isolated products. The major enantiomer is shown. The diastereoselectivity was determined by ^{1}H NMR spectroscopy. The *ee* values were determined by HPLC on a chiral stationary phase. The absolute configuration of **2 f** was determined by X-ray crystallography and the absolute configuration of the other products was determined by analogy to **2 f**. Bn = Benzyl, brsm = based on the recovered starting material, Ts = *p*-toluenesulfonyl.

reaction of **1 a** using ligand **B**. It turned out that there is no nonlinear effect in our asymmetric allylic C–H activation reaction, thus suggesting that there is one chiral phosphoramidite group coordinated to the rhodium center in the stereodetermining step (see the Supporting Information for details).

In summary, we have developed a highly enantioselective rhodium-catalyzed allylic C–H activation/addition to conjugated dienes. The asymmetric synthesis of tetrahydropyrrole, tetrahydrofuran, and cyclopentane compounds that contain two adjacent sp^3 carbon centers, one of which is a quaternary carbon center, was achieved. Investigations into the mechanism and additional applications of this novel method in organic synthesis are currently underway.

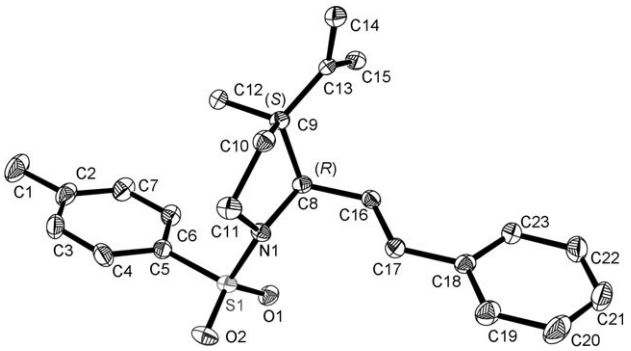


Figure 1. Ortep drawing of **2 f**. Hydrogen atoms are omitted for clarity and ellipsoids are drawn at 50% probability.

Received: August 20, 2010
Revised: December 14, 2010
Published online: ■■ ■■, ■■■■

Keywords: asymmetric synthesis · C–H activation · conjugated diene · enantioselectivity · rhodium

[1] a) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; c) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077; d) X. Chen, K. M. Engle, D. H. Wang, J.-Q. Yu, *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem. Int. Ed.* **2009**, *48*, 5094; e) A. A. Kulkarni, O. Daugulis, *Synthesis* **2009**, 4087; f) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem.* **2009**, *121*, 9976; *Angew. Chem. Int. Ed.* **2009**, *48*, 9792; g) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; h) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; i) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.* **2010**, *46*, 677; j) R. Jazzar, H. Julien, A. Renaudat, J. Sofack-Kreutzer, O. Baudoin, *Chem. Eur. J.* **2010**, *16*, 2654.

[2] a) J. A. Johnson, N. Li, D. Sames, *J. Am. Chem. Soc.* **2002**, *124*, 6900; b) P. S. Baran, E. J. Corey, *J. Am. Chem. Soc.* **2002**, *124*, 7904; c) A. Hinman, J. Du Bois, *J. Am. Chem. Soc.* **2003**, *125*, 11510; d) S. J. O'Malley, K. L. Tan, A. Watzke, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2005**, *127*, 13496; e) H. M. L. Davies, X. Dai, M. S. Long, *J. Am. Chem. Soc.* **2006**, *128*, 2485; f) U. K. Tambar, D. C. Ebner, B. M. Stoltz, *J. Am. Chem. Soc.* **2006**, *128*, 11752; g) E. M. Beck, R. Hatley, M. J. Gaunt, *Angew. Chem.* **2008**, *120*, 3046; *Angew. Chem. Int. Ed.* **2008**, *47*, 3004; h) K. Chen, P. S. Baran, *Nature* **2009**, *459*, 824; i) M. S. Chen, M. C. White, *Science* **2007**, *318*, 783; j) E. M. Stang, M. C. White, *Nat. Chem.* **2009**, *1*, 547; k) K. Godula, D. Sames, *Science* **2006**, *312*, 67.

[3] For a discussion of the term "C–H activation", see: a) B. Sezen, D. Sames in *Handbook of C–H Transformations* (Eds.: G. Dyker), Wiley-VCH, Weinheim, **2005**; for selected reviews, see: b) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826; c) R. G. Bergman, *Nature* **2007**, *446*, 391; d) S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180; e) R. H. Crabtree, *Chem. Rev.* **1985**, *85*, 245.

[4] For a review of stereoselective C–H functionalization, see: a) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242; for a highlight on the enantioselective palladium-catalyzed direct alkylation and olefination reaction of simple arenes, see: b) H. M. Peng, L.-X. Dai, S.-L. You, *Angew. Chem.* **2010**, *122*, 5962; *Angew. Chem. Int. Ed.* **2010**, *49*, 5826.

[5] K. Mikami, M. Hatano, M. Terada, *Chem. Lett.* **1999**, *1*, 55.

[6] a) N. Fujii, F. Kakiuchi, A. Yamada, N. Chatani, S. Murai, *Chem. Lett.* **1997**, *26*, 425; b) F. Kakiuchi, P. Le Gendre, A. Yamada, H. Ohtaki, S. Murai, *Tetrahedron: Asymmetry* **2000**, *11*, 2647.

[7] a) R. K. Thalji, J. A. Ellman, R. G. Bergman, *J. Am. Chem. Soc.* **2004**, *126*, 7192; b) H. Harada, R. K. Thalji, R. G. Bergman, J. A. Ellman, *J. Org. Chem.* **2008**, *73*, 6772; c) A. S. Tsai, R. M. Wilson, H. Harada, R. G. Bergman, J. A. Ellman, *Chem. Commun.* **2009**, 3910; d) R. M. Wilson, R. K. Thalji, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2006**, *8*, 1745.

[8] For related studies, see: a) K. Tsuchikama, Y. Kuwata, Y. Tahara, Y. Yoshinami, T. Shibata, *Org. Lett.* **2007**, *9*, 3097; b) K. Tsuchikama, M. Kasagawa, Y. Hashimoto, K. Endo, T. Shibata, *J. Organomet. Chem.* **2008**, *693*, 3939.

[9] a) B. Bosnich, X. Wang, *Organometallics* **1994**, *13*, 4131; b) K. Mikami, M. Hatano, M. Terada, *Chem. Lett.* **1999**, *28*, 55; c) R. W. Barnhart, X. Wang, P. Noheda, S. H. Bergens, J. Whelan, B. Bosnich, *J. Am. Chem. Soc.* **1994**, *116*, 1821; d) M. M. Coulter, P. K. Dornan, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 6932; e) Y. Shibata, K. Tanaka, *J. Am. Chem. Soc.* **2009**, *131*, 12552; f) Z. Shen, H. A. Khan, V. M. Dong, *J. Am. Chem. Soc.* **2008**, *130*, 2916; g) D. H. T. Phan, B. Kim, V. M. Dong, *J. Am. Chem. Soc.* **2009**, *131*, 15608.

[10] a) B.-F. Shi, N. Maugel, Y.-H. Zhang, J.-Q. Yu, *Angew. Chem.* **2008**, *120*, 4839; *Angew. Chem. Int. Ed.* **2008**, *47*, 4761; b) B.-F. Shi, Y.-H. Zhang, J. K. Lam, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 460; for a palladium(0)-catalyzed enantioselective arylation, see: c) M. R. Albicker, N. Cramer, *Angew. Chem.* **2009**, *121*, 9303; *Angew. Chem. Int. Ed.* **2009**, *48*, 9139.

[11] For reviews on enantioselective C–H activation by means of carbene and nitrene insertions, see: a) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417; b) P. Müller, C. Fruit, *Chem. Rev.* **2003**, *103*, 2905; c) M. P. Doyle, R. Duffy, M. Ratnikov, L. Zhou, *Chem. Rev.* **2010**, *110*, 704.

[12] For enantioselective C–H oxidation/C–C bond formation, see: a) Z. Li, C.-J. Li, *Org. Lett.* **2004**, *6*, 4997; b) N. Sasamoto, C. Dubs, Y. Hamashima, M. Sodeoka, *J. Am. Chem. Soc.* **2006**, *128*, 14010; c) F. Benfatti, M. G. Capdevila, L. Zoli, E. Benedetto, P. G. Cozzi, *Chem. Commun.* **2009**, 5919; d) C. Guo, J. Song, S.-W. Luo, L.-Z. Gong, *Angew. Chem.* **2010**, *122*, 5690; *Angew. Chem. Int. Ed.* **2010**, *49*, 5558.

[13] For enantioselective hydride transfer/C–C bond formation, see: a) S. Murarka, I. Deb, C. Zhang, D. Seidel, *J. Am. Chem. Soc.* **2009**, *131*, 13226; b) Y. K. Kang, S. M. Kim, D. Y. Kim, *J. Am. Chem. Soc.* **2010**, *132*, 11847.

[14] For a formal allylic C–H functionalization, see: H. Du, W. Yuan, B. Zhao, Y. Shi, *J. Am. Chem. Soc.* **2007**, *129*, 7496.

[15] For a formal asymmetric palladium-catalyzed C–H arylation of carboxylic esters, see: A. Renaudat, L. Jean-Gérard, R. Jazzar, C. E. Kefalidis, E. Clot, O. Baudoin, *Angew. Chem.* **2010**, *122*, 7419; *Angew. Chem. Int. Ed.* **2010**, *49*, 7261.

[16] a) D. J. Covell, M. C. White, *Angew. Chem.* **2008**, *120*, 6548; *Angew. Chem. Int. Ed.* **2008**, *47*, 6448; for selected non-asymmetric allylic C–H activation, see: b) M. S. Chen, M. C. White, *J. Am. Chem. Soc.* **2004**, *126*, 1346; c) S. Lin, C.-X. Song, G.-X. Cai, W.-H. Wang, Z.-J. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 12901; d) G. Liu, G. Yin, L. Wu, *Angew. Chem.* **2008**, *120*, 4811; *Angew. Chem. Int. Ed.* **2008**, *47*, 4733; e) B. M. Trost, F. D. Toste, *J. Am. Chem. Soc.* **1999**, *121*, 9728; f) A. Ajamian, J. L. Gleason, *Org. Lett.* **2003**, *5*, 2409; g) K. M. Brummond, H. Chen, B. Mitasev, A. D. Casarez, *Org. Lett.* **2004**, *6*, 2161; h) W. Li, W. Yuan, M. Shi, E. Hernandez, G. Li, *Org. Lett.* **2010**, *12*, 64.

[17] a) Q. Li, Z.-X. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 4542; addition and correction: b) Q. Li, Z.-X. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 6862.

[18] a) K. Fuji, *Chem. Rev.* **1993**, *93*, 2037; b) C. J. Douglas, L. E. Overman, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 5363; c) B. M. Trost, D. C. Jiang, *Synthesis* **2006**, 369.

[19] J. F. Teichert, B. L. Feringa, *Angew. Chem.* **2010**, *122*, 2538; *Angew. Chem. Int. Ed.* **2010**, *49*, 2486.

[20] a) J.-H. Xie, Q.-L. Zhou, *Acc. Chem. Res.* **2008**, *41*, 581; b) G.-H. Hou, J.-H. Xie, P.-C. Yan, Q.-L. Zhou, *J. Am. Chem. Soc.* **2009**, *131*, 1366; c) Y. Yang, S.-F. Zhu, C.-Y. Zhou, Q.-L. Zhou, *J. Am. Chem. Soc.* **2008**, *130*, 14052.

[21] a) K. Kurihara, N. Sugishita, K. Oshita, D. Piao, Y. Yamamoto, N. Miyaura, *J. Organomet. Chem.* **2007**, *692*, 428; b) K. Kurihara, Y. Yamamoto, N. Miyaura, *Tetrahedron Lett.* **2009**, *50*, 3158; c) K. Kurihara, Y. Yamamoto, N. Miyaura, *Adv. Synth. Catal.* **2009**, *351*, 260; d) Y. Yamamoto, K. Kurihara, N. Miyaura, *Angew. Chem.* **2009**, *121*, 4478; *Angew. Chem. Int. Ed.* **2009**, *48*, 4414.

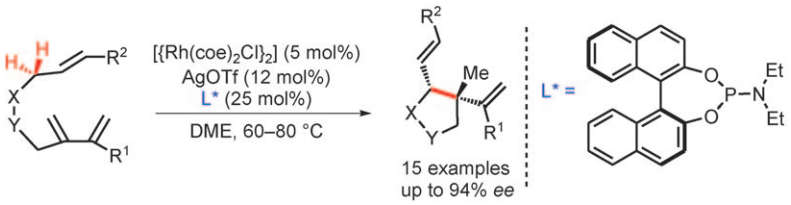
[22] CCDC 789812 (**2 f**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Communications

C–H Activation

Q. Li, Z.-X. Yu* _____ ■■■–■■■

Enantioselective Rhodium-Catalyzed Allylic C–H Activation for the Addition to Conjugated Dienes



Easy and efficient: By applying the title transformation, two adjacent sp^3 stereogenic centers, one of which is a quaternary carbon center, can be easily formed. This asymmetric reaction provides easy and efficient access to multifunctionalized tetrahydropyrrole, tetrahydrofuran, and cyclopentane compounds (see scheme; coe = cyclooctene, DME = 1,2-dimethoxyethane, Tf = trifluoromethanesulfonyl).