C–H Activation

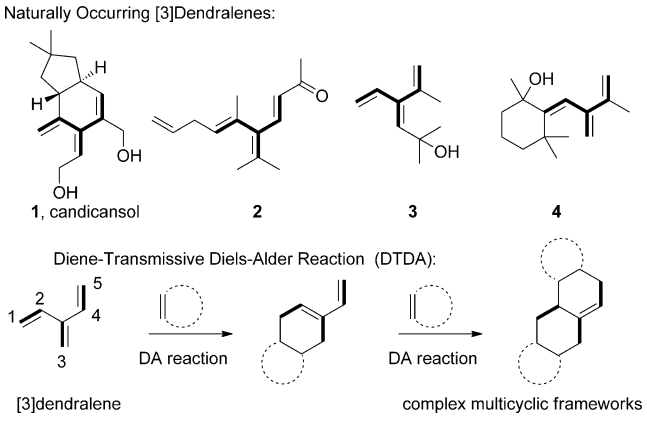
DOI: 10.1002/anie.201306754

[3]Dendralene Synthesis: Rhodium(III)-Catalyzed Alkenyl C–H Activation and Coupling Reaction with Allenyl Carbinol Carbonate**

*Honggen Wang, Bernhard Beiring, Da-Gang Yu, Karl D. Collins, and Frank Glorius**

Dedicated to Professor Henning Hopf

Dendralenes, also known as acyclic cross-conjugated polyenes, have long been neglected as an important class of highly unsaturated hydrocarbons.[1] However, recent years have seen growing interest in dendralene chemistry due to their unique roles in polymer chemistry,[2] theoretical chemistry,[3] and synthetic chemistry.[4] Not surprisingly, [3]dendralenes or cross-conjugated trienes, the simplest dendralenes,[5] have attracted the most attention.[2–4] Their importance has been reflected by their occurrence as a motif in an increasing number of natural products,[6] and, notably, their engagement in diene-transmissive Diels–Alder reactions (DTDA),[7] which facilitate the rapid construction of complex multicyclic frameworks (Scheme 1).[8] So far, there are a handful of procedures available for the synthesis of [3]dendralenes.[9] The drastic conditions typically used and limited substitution patterns call for more straightforward and efficient alternatives.



Scheme 1. [3]Dendralenes in natural products and synthesis.

Over the past few years, Rh^{III}-catalyzed direct C–H functionalization has emerged as a versatile tool to effect various C–C and C–X bond-forming reactions.[10–12] We have recently reported a Rh^{III}-catalyzed allylation of aromatic C–H bonds using allyl carbonates as electrophiles.[13] The reaction was believed to proceed by means of a novel olefin insertion/β-oxygen elimination reaction mechanism (Scheme 2a).[14] Intriguingly, this type of reaction pathway has been rarely exploited in C–H activation reactions. In addition, we developed an oxidative annulation of allenes with *N*-(pivaloyloxy)benzamides in the presence of a Rh^{III} catalyst, wherein the carborhodation of monosubstituted allenes delivered an intermediate in which a C–C bond has been formed at the central carbon atom (Scheme 2b).[15] On the basis of these two reactions, we speculated that the replacement of allyl carbonates with allenyl carbinol carbonates would lead to an analogous allene carborhodation/β-oxygen elimination sequence, providing products that incorporate a valuable diene functionality. Herein, we disclose a Rh^{III}-catalyzed synthesis of [3]dendralenes based on an alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates (Scheme 2c). The reaction was extended to aromatic C–H activation to generate diene-substituted arenes with good efficiency.[16]

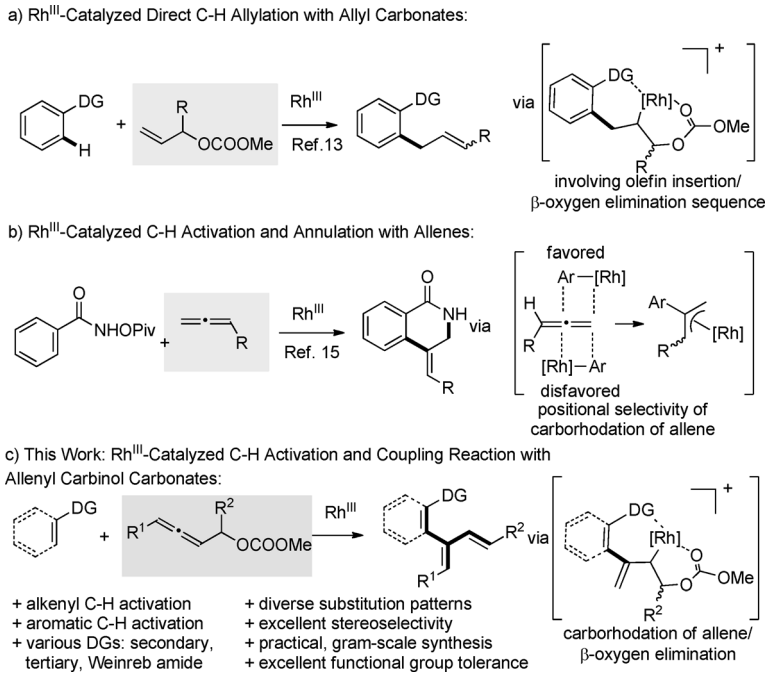
We focused our efforts on alkenyl C–H functionalization due to the high value of cross-conjugated triene products and the intrinsic challenges in their synthesis. We initiated our study by examining the reaction of cinnamamide **5a** with branched 1-methyl-substituted allenyl carbinol carbonate **6a**. To our delight, we found that the reaction proceeded smoothly in the presence of $[Cp^*Rh(MeCN)_3](SbF_6)_2$ (5.0 mol%) and PivOH (0.5 equiv) in CH_2Cl_2 at 60°C, giving 5-substituted [3]dendralene **7aa** in 79% yield as a single stereoisomer [Eq. (1)].[17] Furthermore, the reaction was found to be scalable and practical as 71% yield was obtained when the reaction was performed at a 5-mmol scale without the exclusion of air and moisture.[18] It is worth mentioning that acrylamides represent an important and readily accessible class of building blocks.

The scope of the reaction was then explored.[19] As shown in Table 1, a variety of acrylamides and coupling partners with different functional groups and substitution patterns were examined. Cinnamamides **5b** and **5c** bearing OMe and CF_3 groups, respectively, gave the corresponding [3]dendralene

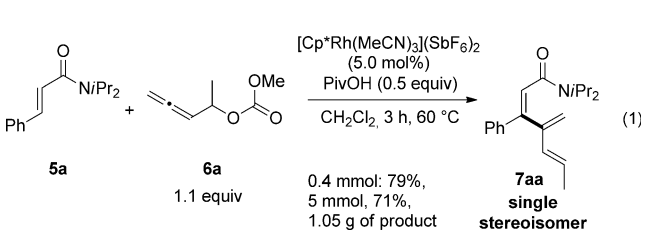
[*] Dr. H. Wang, B. Beiring, Dr. D.-G. Yu, Dr. K. D. Collins, Prof. Dr. F. Glorius
Universität Münster, Organisch-Chemisches Institut
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: glorius@uni-muenster.de
Homepage: http://www.uni-muenster.de/Chemie.oc/glorius/index.html

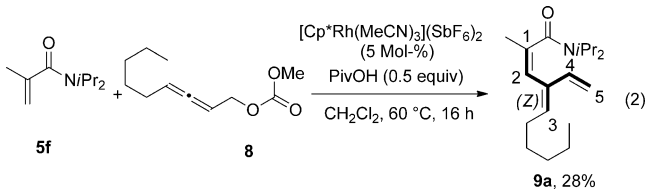
[**] We thank N. Kuhl, N. Schröder, C. Nimphius, C. Weitkamp, and D. Dietrich for experimental support. This work was supported by the European Research Council under auspices of the European Community's Seventh Framework Program (FP7 2007–2013/ERC grant agreement no. 25936) and by the Alexander von Humboldt Foundation (D.-G.Y.). The research of F.G. has been supported by the Alfried Krupp Prize for Young University Teachers of the Alfried Krupp von Bohlen und Halbach Foundation.

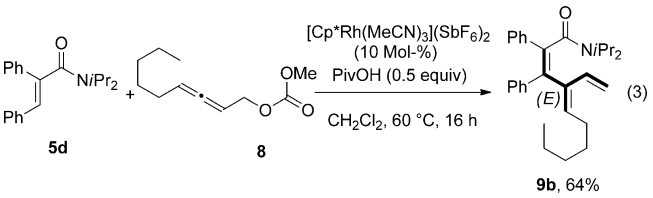
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306754.



Scheme 2. Rational design on Rh^{III}-catalyzed diene incorporation. DG = directing group, Piv = pivaloyl.







products **7ba** and **7ca** in good yields. Interestingly, whereas cinnamamide **5d** with a 2-phenyl substitutent showed excellent reactivity, 2-methyl cinnamamide **5e** reacted much more slowly, providing **7ea** in comparatively much lower yield. However, 2-methacrylamide **5f** was a good substrate for this transformation, though only a moderate yield was obtained due to decomposition of the product **7fa**. We would like to highlight two examples: the 3-bromo-substituted acrylamide **5g** underwent smooth reaction to give **7ga** in 78% yield. The bromo substituent provides a valuable and reliable handle for further transformations. Fumaric acid derivative **5h**, representing a highly electron-deficient alkene, also gave the product without difficulty. Gratifyingly, the reaction was not limited to substrates with tertiary amide directing groups. For instance, secondary *N*-*n*-butyl (**5i**) and *N*-methyl (**5j**) amides reacted with comparable efficiency. Importantly, it was found that Weinreb amide **5k** also gave a reasonable yield, thus expanding opportunities for functional group manipulation.

The reaction also shows broad substrate scope in terms of the allenyl carbinol carbonate partner. Thus, unsubstituted (R^5 = H) and alkyl- (R^5 = alkyl) and aryl-substituted (R^5 = Ph) allenyl carbinol carbonates **6** all delivered the corresponding products in good yields. In some cases, deactivation of catalyst was observed. To ensure high conversion, a second batch of catalyst and **6** was added. In all cases, excellent stereoselectivities (>20:1) were observed.

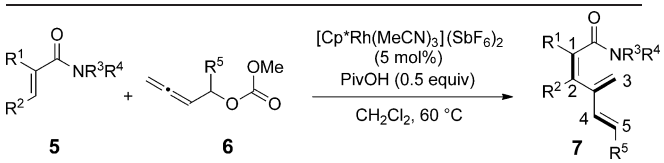
Realizing the current method was limited to the synthesis of 5-substituted [3]dendralenes, we reasoned that the use of linear substituted allenyl carbinol carbonates might provide 3-substituted [3]dendralenes, thus leading to more diverse products. As expected, the reaction of α-substituted **5f** with **8** gave the desired **9a** in 28% yield, with complete *Z* selectivity at the newly formed double bond [Eq. (2)]. Surprisingly, the reaction of α,β-disubstituted acrylamide **5d** gave a higher yield (64%), but with complete reversal of stereoselectivity—an *E* isomer was formed instead [Eq. (3); vide infra for rationale of stereoselectivity].

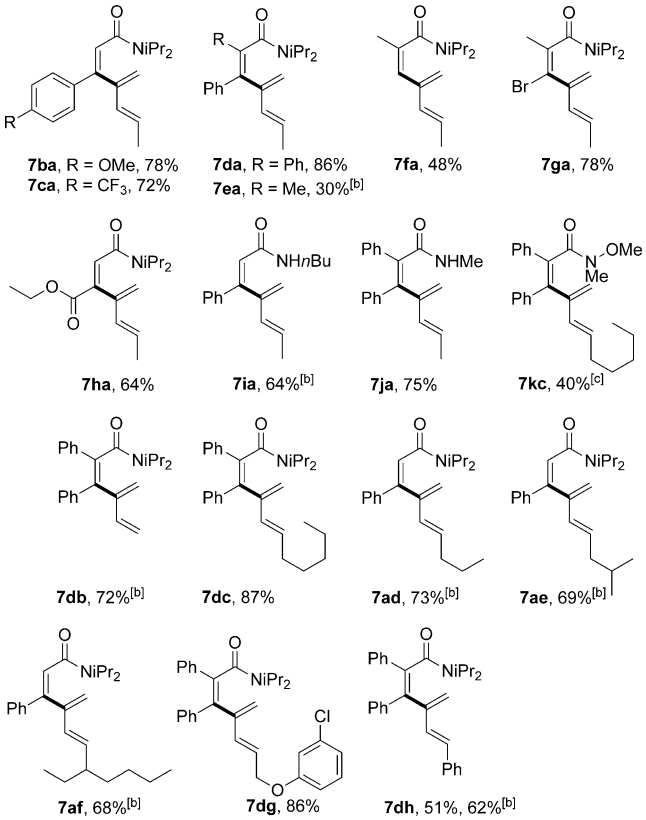
We also sought to investigate the C–H functionalization on aromatic rings. The reaction was demonstrated to be a reliable method to introduce diene functionality to benzamides **10** under modified reaction conditions with 15 mol% $Cu(OAc)_2$ as an additive (Table 2).[12t] $Cu(OAc)_2$ might serve as an oxidant to regenerate the active Rh^{III} catalyst, which is deactivated by an unproductive pathway. Many functional groups, including ester, trifluoromethyl, formyl, methoxy, chloro, and bromo groups, were well tolerated. The use of less hindered *N*,*N*-diethylbenzamide (**10b**) or *N*,*N*-dimethylbenzamide (**10c**) also assured a good yield.

Finally, to demonstrate the synthetic utility of the [3]dendralene product, Diels–Alder reactions with different dienophiles were conducted (Scheme 3). The reaction of **7aa** with *N*-methylmaleimide (**12**) resulted in the formation of cyclohexene **13** in 81% yield, with a diastereoselectivity of 8:1. The reaction takes place exclusively at the less sterically hindered, electron-rich diene moiety. Analogously, the use of dimethyl acetylenedicarboxylate (**14**) furnished the cyclohexadiene **15** in good yields.

A putative reaction pathway was proposed. The C–H activation is assisted by the amide directing group and PivOH

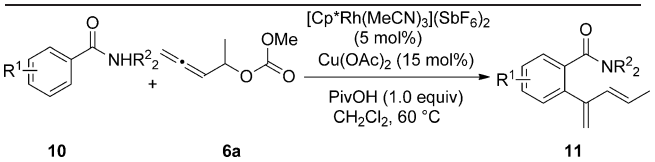
Table 1: Reaction scope.[a]

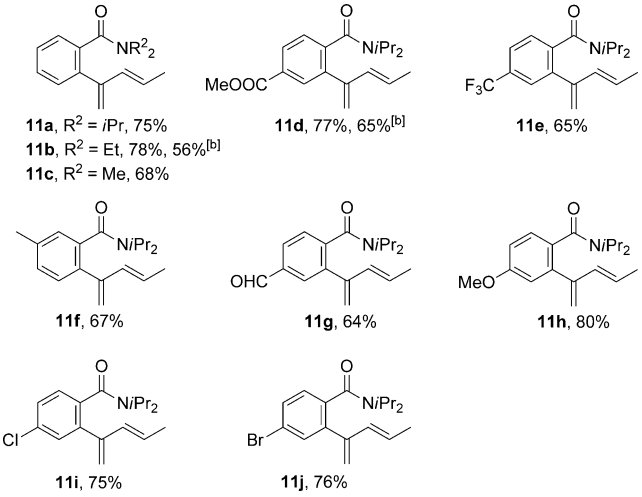




[a] Reaction conditions: **5** (0.4 mmol), **6** (0.44 mmol), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5.0 mol%), PivOH (0.5 equiv), CH_2Cl_2 (2 mL), 60°C, 2-24 h, yields of isolated products. [b] A second batch of [Cp*Rh(CH$_3$CN)$_3$](SbF$_6$)$_2$ (5 mol%) and **6** (0.44 mmol) was used. [c] 40°C.

Table 2: Reaction scope.[a]

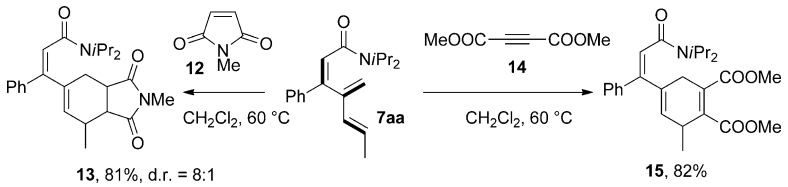




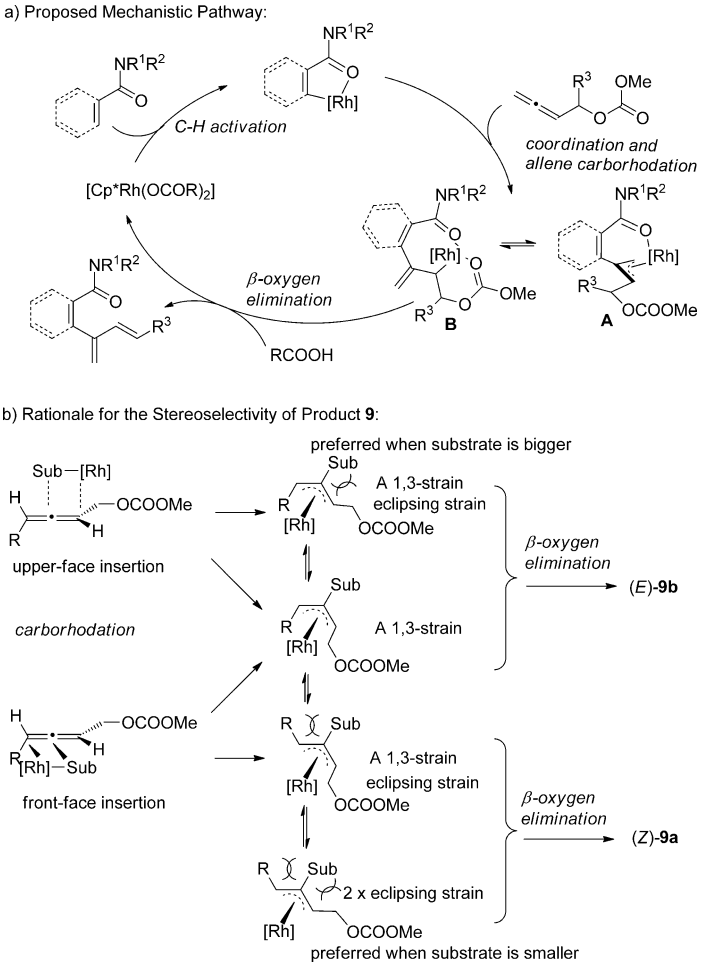
[a] Reaction conditions: **10** (0.4 mmol), **6a** (0.8 mmol), [Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$ (5.0 mol%), Cu(OAc)$_2$ (15 mol%), PivOH (1.0 equiv), CH_2Cl_2 (2 mL), 60°C, 3–24 h, yield of isolated product. [b] Without Cu(OAc)$_2$, **6a** (0.48 mmol) was used.

(Scheme 4a). Allene coordination followed by regioselective carborhodation leads to a π-allyl rhodium(III) complex **A**, which is in equilibrium with the η^1-allyl rhodium(III) complex **B**. A subsequent formal β-oxygen elimination delivers the final product and regenerates the Rh^{III} catalyst.[20] The stereoselectivity in the 3-substituted [3]dendralene products **8** deserves some explanation (Scheme 4b). Four different Rh^{III} complexes could be possibly formed after the carborhodation. Within these complexes, allylic 1,3-strain and eclipsing strain are pronounced. With a sterically hindered substrate, eclipsing strain dominates, and the *E* isomer forms selectively. In contrast, allylic 1,3-strain becomes more pronounced when a less bulky substrate was used. As a result, the *Z* isomer was observed.[21]

In conclusion, we have developed a Rh^{III}-catalyzed alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates. This method provides a novel and straightforward synthesis of [3]dendralenes. A variety of [3]dendralenes with diverse substitution patterns are accessible with good efficiency. In addition, the reaction is highly stereoselective and compatible with different directing groups and numerous functional groups. We also demonstrated that the title reaction is robust, practical, and scalable. The method was successfully extended to the synthesis of diene-substituted arenes. We expect this new method to complement existing methodology and find its application in [3]dendralene chemistry.



Scheme 3. Diels–Alder reaction of [3]dendralene **7aa**.



Scheme 4. Mechanistic hypothesis and rationale for the stereoselective formation of product **9**. Sub = Substrate

Received: August 1, 2013
Published online: ■■ ■■, ■■■■

Keywords: [3]dendralenes · C–C coupling · C–H activation · dienes · trienes

[1] Reviews: a) H. Hopf in *Classics in Hydrocarbon Chemistry*: *Syntheses*, *Concepts*, *Perspectives*, Wiley-VCH, Weinheim, **2000**; b) H. Hopf, *Angew. Chem.* **2001**, *113*, 727; *Angew. Chem. Int. Ed.* **2001**, *40*, 705; c) H. Hopf, *Nature* **2009**, *460*, 183; d) H. Hopf, M. S. Sherburn, *Angew. Chem.* **2012**, *124*, 2346; *Angew. Chem. Int. Ed.* **2012**, *51*, 2298.

[2] a) W. J. Bailey, J. Economy, M. E. Hermes, *J. Org. Chem.* **1962**, *27*, 3295; b) R. C. Blume, U.S. Pat. 3,860,669, **1973**; c) C. D. Diakoumakos, J. A. Mikroyannidis, *J. Appl. Polym. Sci.* **1994**, *53*, 201.

[3] U. Fleischer, W. Kutzelnigg, P. Lazzeretti, V. Muhlenkamp, *J. Am. Chem. Soc.* **1994**, *116*, 5298.

[4] a) L. Stehling, G. Wilke, *Angew. Chem.* **1988**, *100*, 575; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 571; b) M. Wehbe, Y. Lepage, *Bull. Soc. Chim. Fr.* **1988**, 1027; c) A. D. Payne, A. C. Willis, M. S. Sherburn, *J. Am. Chem. Soc.* **2005**, *127*, 12188; d) H. Pellissier, *Tetrahedron* **2005**, *61*, 6479; e) A. J. Frontier, C. Collison, *Tetrahedron* **2005**, *61*, 7577; f) M. A. Tius, *Eur. J. Org. Chem.* **2005**, 2193; g) G. Bojase, A. D. Payne, A. C. Willis, M. S. Sherburn, *Angew. Chem.* **2008**, *120*, 924; *Angew. Chem. Int. Ed.* **2008**, *47*, 910; h) C. J. Rieder, K. J. Winberg, F. G. West, *J. Am. Chem. Soc.* **2009**, *131*, 7504; i) W. Li, M. Shi, Y. Li, *Chem. Eur. J.* **2009**, *15*, 8852; j) H. Hopf, S. Yildizhan, *Eur. J. Org. Chem.* **2011**, 2029; k) G. Bojase, T. V. Nguyen, A. D. Payne, A. C. Willis, M. S. Sherburn, *Chem. Sci.* **2011**, *2*, 229; l) N. J. Green, A. L. Lawrence, G. Bojase, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2013**, *125*, 8491; *Angew. Chem. Int. Ed.* **2013**, *52*, 8333.

[5] A. T. Blomquist, J. A. Verdol, *J. Am. Chem. Soc.* **1955**, *77*, 81.

[6] a) A. Arnone, R. Cardillo, V. Dimodugno, G. Nasini, *J. Chem. Soc. Perkin Trans. 1* **1989**, 1995; b) J. Wang, Z. Hu, J. Feng, Z. Su, X. Zhang, *Xibei Zhiwu Xuebao* **2008**, *28*, 1239; c) D. H. E. Tattje, R. Bos, A. P. Bruins, *Planta Med.* **1980**, *38*, 79; d) M. Manzoor-i-Khuda, M. Rahman, M. Yusaf, J. U. Chowdhury, M. A. Wahab, *Bangladesh J. Sci. Ind. Res.* **1987**, *22*, 152.

[7] O. Tsuge, E. Wada, S. Kanemasa, *Chem. Lett.* **1983**, *12*, 1525.

[8] a) W. J. Bailey, C. H. Cunov, L. Nicholas, *J. Am. Chem. Soc.* **1955**, *77*, 2787; b) S. Kanemasa, H. Sakoh, E. Wada, O. Tsuge, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3312; c) S. Kanemasa, H. Sakoh, E. Wada, O. Tsuge, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1869; d) S. Woo, S. Legoupy, S. Parra, G. F. Alex, *Org. Lett.* **1999**, *1*, 1013; e) A. Melekhov, P. Forgione, S. Legoupy, A. G. Fallis, *Org. Lett.* **2000**, *2*, 2793; f) M. D. Clay, D. Riber, A. G. Fallis, *Can. J. Chem.* **2005**, *83*, 559; g) T. A. Bradford, A. D. Payne, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *J. Org. Chem.* **2010**, *75*, 491.

[9] Some recent examples: a) M. Arisawa, T. Sugihara, M. Yamaguchi, *Chem. Commun.* **1998**, 2615; b) H.-M. Chang, C.-H. Cheng, *J. Org. Chem.* **2000**, *65*, 1767; c) K. M. Brummond, H. Chen, P. Sill, L. You, *J. Am. Chem. Soc.* **2002**, *124*, 15186; d) C. S. Chin, H. Lee, H. Park, M. Kim, *Organometallics* **2002**, *21*, 3889; e) B. Kang, D.-H. Kim, Y. Do, S. Chang, *Org. Lett.* **2003**, *5*, 3041; f) M. Shi, L.-X. Shao, *Synlett* **2004**, 0807; g) S. Bräse, H. Wertal, D. Frank, D. Vidović, A. de Meijere, *Eur. J. Org. Chem.* **2005**, 4167; h) T. A. Bradford, A. D. Payne, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Org. Lett.* **2007**, *9*, 4861; i) N. A. Miller, A. C. Willis, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2007**, *119*, 955; *Angew. Chem. Int. Ed.* **2007**, *46*, 937; j) H. L. Shimp, A. Hare, M. McLaughlin, G. C. Micalizio, *Tetrahedron* **2008**, *64*, 3437; k) A. D. Payne, G. Bojase, M. N. Paddon-Row, M. S. Sherburn, *Angew. Chem.* **2009**, *121*, 4930; *Angew. Chem. Int. Ed.* **2009**, *48*, 4836; l) S. Kim, D. Seomoon, P. H. Lee, *Chem. Commun.* **2009**, 1873; m) K. Beydoun, H.-J. Zhang, B. Sundararaju, B. Demerseman, M. Achard, Z. Xi, C. Bruneau, *Chem. Commun.* **2009**, 6580; n) R. Singh, S. K. Ghosh, *Chem. Commun.* **2011**, *47*, 10809; o) H. Toombs-Ruane, E. L. Pearson, M. N. Paddon-Row, M. S. Sherburn, *Chem. Commun.* **2012**, *48*, 6639.

[10] For recent reviews on C–H activation: a) T. Newhouse, P. S. Baran, *Angew. Chem.* **2011**, *123*, 3422; *Angew. Chem. Int. Ed.* **2011**, *50*, 3362; b) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315; c) L. McMurray, F. O'Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; d) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; e) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem.* **2012**, *124*, 10382; *Angew. Chem. Int. Ed.* **2012**, *51*, 10236; f) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; g) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; h) K. M. Engle, T.-S. Mei, M. Wasa, J.-Q. Yu, *Acc. Chem. Res.* **2012**, *45*, 788; i) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; j) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293; k) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068; l) J.

Yamaguchi, A. D. Yamaguchi, K. Itami, *Angew. Chem.* **2012**, *124*, 9092; *Angew. Chem. Int. Ed.* **2012**, *51*, 8960; m) C. Zhu, R. Wang, J. R. Falck, *Chem. Asian J.* **2012**, *7*, 1502; n) P. B. Arockiam, C. Bruneau, P. H. Dixneuf, *Chem. Rev.* **2012**, *112*, 5879; o) J. Wencel-Delord, F. Glorius, *Nat. Chem.* **2013**, *5*, 369; p) J. Wencel-Delord, T. Dröge, F. Liu, F. Glorius, *Chem. Soc. Rev.* **2011**, *40*, 4740.

[11] For recent reviews on Rh^{III}-catalyzed C–H activation, see: a) G. Song, F. Wang, X. Li, *Chem. Soc. Rev.* **2012**, *41*, 3651; b) T. Satoh, M. Miura, *Chem. Eur. J.* **2010**, *16*, 11212; c) F. W. Patureau, J. Wencel-Delord, F. Glorius, *Aldrichimica Acta* **2012**, *45*, 31; d) S. Chiba, *Chem. Lett.* **2012**, *41*, 1554.

[12] Selected recent Rh^{III}-catalyzed C–H activations: a) K. Morimoto, M. Itoh, K. Hirano, T. Satoh, Y. Shibata, K. Tanaka, M. Miura, *Angew. Chem.* **2012**, *124*, 5455; *Angew. Chem. Int. Ed.* **2012**, *51*, 5359; b) Y. Unoh, Y. Hashimoto, D. Takeda, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2013**, *15*, 3258; c) K. Shin, S. Y. Baek, S. Chang, *Angew. Chem.* **2013**, *125*, 8189; *Angew. Chem. Int. Ed.* **2013**, *52*, 8031; d) Y. Lian, T. Huber, K. D. Hesp, R. G. Bergman, J. A. Ellman, *Angew. Chem.* **2013**, *125*, 657; *Angew. Chem. Int. Ed.* **2013**, *52*, 629; e) T. K. Hyster, K. E. Ruhl, T. Rovis, *J. Am. Chem. Soc.* **2013**, *135*, 5364; f) T. K. Hyster, L. Knörr, T. R. Ward, T. Rovis, *Science* **2012**, *338*, 500; g) B. Ye, N. Cramer, *Science* **2012**, *338*, 504; h) D.-S. Kim, J.-W. Park, C.-H. Jun, *Chem. Commun.* **2012**, *48*, 11334; i) J. Dong, Z. Long, F. Song, N. Wu, Q. Guo, J. Lan, J. You, *Angew. Chem.* **2013**, *125*, 608; *Angew. Chem. Int. Ed.* **2013**, *52*, 580; j) B.-J. Li, H.-Y. Wang, Q.-L. Zhu, Z.-J. Shi, *Angew. Chem.* **2012**, *124*, 4014; *Angew. Chem. Int. Ed.* **2012**, *51*, 3948; k) N. Guimond, S. I. Gorelsky, K. Fagnou, *J. Am. Chem. Soc.* **2011**, *133*, 6449; l) X. Xu, Y. Liu, C.-M. Park, *Angew. Chem.* **2012**, *124*, 9506; *Angew. Chem. Int. Ed.* **2012**, *51*, 9372; m) J. Jayakumar, K. Parthasarathy, C.-H. Cheng, *Angew. Chem.* **2012**, *124*, 201; *Angew. Chem. Int. Ed.* **2012**, *51*, 197; n) W.-W. Chan, S.-F. Lo, Z. Zhou, W.-Y. Yu, *J. Am. Chem. Soc.* **2012**, *134*, 13565; o) C. Wang, H. Chen, Z. Wang, J. Chen, Y. Huang, *Angew. Chem.* **2012**, *124*, 7354; *Angew. Chem. Int. Ed.* **2012**, *51*, 7242; p) X. Li, S. Yu, F. Wang, B. Wan, X. Yu, *Angew. Chem.* **2013**, *125*, 2637; *Angew. Chem. Int. Ed.* **2013**, *52*, 2577; q) J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem.* **2012**, *124*, 2290; *Angew. Chem. Int. Ed.* **2012**, *51*, 2247; r) J. Wencel-Delord, C. Nimphius, H. Wang, F. Glorius, *Angew. Chem.* **2012**, *124*, 13175; *Angew. Chem. Int. Ed.* **2012**, *51*, 13001; s) N. Schröder, J. Wencel-Delord, F. Glorius, *J. Am. Chem. Soc.* **2012**, *134*, 8298; t) H. Wang, C. Grohmann, C. Nimphius, F. Glorius, *J. Am. Chem. Soc.* **2012**, *134*, 19592; u) Z. Shi, C. Grohmann, F. Glorius, *Angew. Chem.* **2013**, *125*, 5503; *Angew. Chem. Int. Ed.* **2013**, *52*, 5393; v) D.-G. Yu, M. Suri, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 8802; w) Z. Shi, D. C. Koester, M. Boultadakis-Arapinis, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 12204; x) B. Liu, Y. Fan, Y. Gao, C. Sun, C. Xu, J. Zhu, *J. Am. Chem. Soc.* **2013**, *135*, 468; y) T. J. Gong, B. Xiao, W.-M. Cheng, W. Su, J. Xu, Z.-J. Liu, L. Liu, Y. Fu, *J. Am. Chem. Soc.* **2013**, *135*, 10630.

[13] a) H. Wang, N. Schröder, F. Glorius, *Angew. Chem.* **2013**, *125*, 5495; *Angew. Chem. Int. Ed.* **2013**, *52*, 5386.

[14] For examples in Rh^{I} chemistry, see: a) M. Murakami, H. Igawa, *Helv. Chim. Acta* **2002**, *85*, 4182; b) T. Miura, M. Shimada, S.-Y. Ku, T. Tamai, M. Murakami, *Angew. Chem.* **2007**, *119*, 7231; *Angew. Chem. Int. Ed.* **2007**, *46*, 7101; c) N. Sakiyama, K. Noguchi, K. Tanaka, *Angew. Chem.* **2012**, *124*, 6078; *Angew. Chem. Int. Ed.* **2012**, *51*, 5976.

[15] a) H. Wang, F. Glorius, *Angew. Chem.* **2012**, *124*, 7430; *Angew. Chem. Int. Ed.* **2012**, *51*, 7318; b) R. Zeng, J. Ye, C. Fu, S. Ma, *Adv. Synth. Catal.* **2013**, *355*, 1963.

[16] For selected 1,3-diene synthesis: a) A. L. Hansen, J.-P. Ebran, M. Ahlquist, P.-O. Norrby, T. Skydstrup, *Angew. Chem.* **2006**, *118*, 3427; *Angew. Chem. Int. Ed.* **2006**, *45*, 3349; b) S. E. Denmark, *J. Am. Chem. Soc.* **1999**, *121*, 5821; c) T. Kurahashi, H. Shinokubo, A. Osuka, *Angew. Chem.* **2006**, *118*, 6484; *Angew. Chem. Int. Ed.* **2006**, *45*, 6336; d) Y. Nakao, A. Yada, S. Ebata, T. Hiyama, *J. Am. Chem. Soc.* **2007**, *129*, 2428.

[17] No product was detected when the Rh^{III} catalyst was not added.

[18] A catalyst loading of 7.5 mol% was used to drive the reaction to higher conversion. See the Supporting Information for details.

[19] We screened for robustness (see the Supporting Information for details); a) K. D. Collins, F. Glorius, *Nat. Chem.* **2013**, *5*, 597; b) K. D. Collins, F. Glorius, *Tetrahedron* **2013**, *69*, 7817; c) N. Kuhl, N. Schröder, J. Wencel-Delord, F. Glorius, *Org. Lett.* **2013**, *15*, 3860.

[20] a) A. S. Tsai, M. Brasse, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2011**, *13*, 540; b) C. Feng, D. Feng, T.-P. Loh, *Org. Lett.* **2013**, *15*, 3670; c) Z. Qi, X. Li, *Angew. Chem.* **2013**, *125*, 9165; *Angew. Chem. Int. Ed.* **2013**, *52*, 8995.

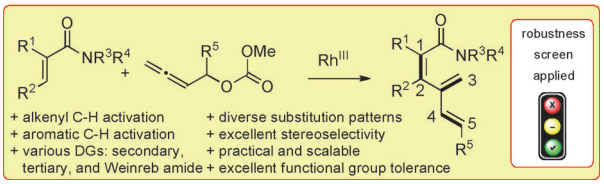
[21] a) R. Hoffmann, *Chem. Rev.* **1989**, *89*, 1841.

Communications

C–H Activation

H. Wang, B. Beiring, D.-G. Yu,
K. D. Collins, F. Glorius* ____ ▮▮▮▮–▮▮▮▮

[3]Dendralene Synthesis: Rhodium(III)-Catalyzed Alkenyl C–H Activation and Coupling Reaction with Allenyl Carbinol Carbonate



[3]DendrAl(l)ene! A new synthesis of [3]dendralenes is based on a Rh^{III}-catalyzed alkenyl C–H activation and coupling reaction with allenyl carbinol carbonates (see scheme; DG = directing group). A variety of [3]dendralenes with diverse substitution patterns are accessible with good efficiency. The reaction is highly stereoselective and compatible with different directing groups and numerous functional groups.