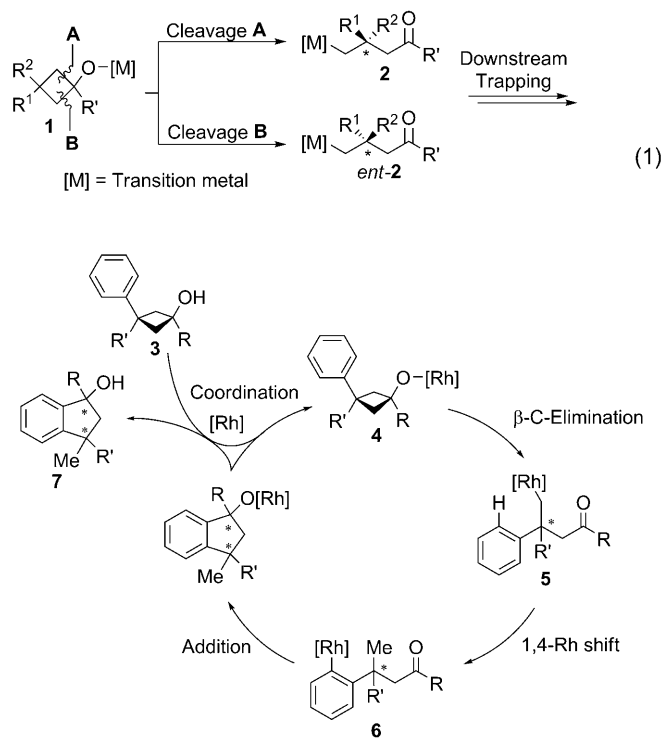


# Enantioselective Synthesis of Indanols from *tert*-Cyclobutanols Using a Rhodium-Catalyzed C–C/C–H Activation Sequence\*\*

Tobias Seiser, Olivia A. Roth, and Nicolai Cramer\*

Reactions involving the selective catalytic functionalization of C–H and C–C bonds by transition-metal complexes have considerable synthetic potential because of their economic and ecological advantages.<sup>[1]</sup> In the presence of palladium or rhodium catalysts, it has been shown that tertiary alcohols can undergo  $\beta$ -carbon eliminations, thus leading to an organometallic species and a ketone in which the formation of the C=O bond is the main driving force for the reaction. Most studies have concentrated on the generation of aryl<sup>[2]</sup> and alkynyl metals<sup>[3]</sup> from simple tertiary alcohols, and in most cases the ketone formed was not incorporated into the product. In stark contrast, the corresponding alkyl metal intermediates that would arise from such reactions have been studied less.<sup>[4,5a,b,e,h]</sup> However, accessing difficult-to-obtain organometallics by activating traditionally unreactive bonds is a promising strategy to omit the use of prefunctionalized reactants. The activation of the strained C–C  $\sigma$ -bond of small rings is a versatile approach to generate such alkyl metal species that are able to undergo further reactions.<sup>[5]</sup> Furthermore, an enantioselective insertion of a chiral metal catalyst into one of the two adjacent C–C bonds (cleavage **A** or **B**) of a symmetrically substituted *tert*-cyclobutanol gives the opportunity for formation of two enantiomeric organometallic species (**2** and *ent*-**2**) having a quaternary stereogenic center [Eq. (1)].<sup>[6]</sup> As such, we have investigated the reactivity of strained tertiary alcohols towards activation by transition metals to capitalize on the alkyl metal species formed for coupled downstream trapping reactions.<sup>[7]</sup> Herein, we report an efficient rhodium(I)-catalyzed activation of *tert*-cyclobutanols that lead to substituted indan-1-ols with high stereocontrol.

The anticipated reaction pathway is initiated by the formation of a rhodium alkoxide species **4** from the alcohol **3** (Scheme 1). A selective insertion into one of the enantiotopic C–C  $\sigma$ -bonds of the cyclobutane ring should form the primary alkyl rhodium species **5**. This intermediate bears a quaternary carbon in the  $\alpha$  position, therefore blocking  $\beta$ -



**Scheme 1.** Proposed catalytic cycle for the formation of indanol **7**.

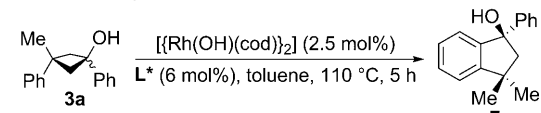
hydride elimination. If undesired pathways, for example, proto-demetalation or other intermolecular reactions, are slow we speculate on the possibility of relaying the metal through a 1,4-rhodium shift<sup>[3g,8]</sup> to access the more stable aryl rhodium intermediate **6**. Such species would be predisposed to add in an intramolecular fashion to the carbonyl group<sup>[9]</sup> to furnish indanol **7**.

A selective process would require the identification of ligands that would not only promote the initial  $\beta$ -carbon elimination in an enantioselective fashion, but also control the facial selectivity of the carbonyl addition step to selectively form one of the possible diastereomers. In this respect, we initially turned our attention to substrates with  $R' = \text{Me}$ , thus allowing sole optimization of the selectivity of the carbonyl addition. In an initial experiment, 1,3-diphenyl-3-methyl-cyclobutanol (**3a**) was heated at reflux in toluene in the presence of  $[\text{Rh}(\text{OH})(\text{cod})]_2$  (2.5 mol %) and (*R*)-binap (**L1**, 6 mol %). These reaction conditions efficiently promoted the formation of the expected indanol **7a** as the only detectable product in 92 % yield and with an *ee* value of 64 % (Table 1, entry 1). A brief survey of chiral phosphine ligands (Table 1, entries 2–5) revealed that the josiphos ligand family (Table 1, entries 6–11) was particularly suited for this

[\*] T. Seiser, O. A. Roth, Dr. N. Cramer  
Laboratory of Organic Chemistry, ETH Zurich  
Wolfgang-Pauli-Strasse 10, HCI H 304, 8093 Zurich (Switzerland)  
Fax: (+41) 44-632-1328  
http://www.cramer.ethz.ch  
E-mail: nicolai.cramer@org.chem.ethz.ch

[\*\*] We thank the Swiss National Foundation (21-119750.01), Solvias AG for the Josiphos ligands and Umicore AG & Co. KG for rhodium salts and Prof. Dr. E. M. Carreira for generous support. The Fonds der Chemischen Industrie is acknowledged for a Liebig Fellowship (N.C.) and a Kekulé Fellowship (T.S.).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.200903189>.

**Table 1:** Selected optimization studies.<sup>[a]</sup>


**L2** (Ar = Ph, R = H)  
**L3** (Ar = DTBM, R = H)  
**L4** (Ar = Ph, R = F)

**L5**

**L6** (Ar = Ph, R = *t*Bu)  
**L7** (Ar = Ph, R = Cy)  
**L8** (Ar = 4-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, R = *t*Bu)  
**L9** (Ar = DMM, R = *t*Bu)

| Entry             | L*                             | Yield [%] <sup>[b]</sup> | ee [%] <sup>[c]</sup> |
|-------------------|--------------------------------|--------------------------|-----------------------|
| 1                 | <b>L1</b> (( <i>R</i> )-binap) | 92                       | 64 ( <i>R</i> )       |
| 2                 | <b>L2</b>                      | 99                       | 76 ( <i>R</i> )       |
| 3                 | <b>L3</b>                      | 99                       | 24 ( <i>R</i> )       |
| 4                 | <b>L4</b>                      | 99                       | 89 ( <i>R</i> )       |
| 5 <sup>[d]</sup>  | <b>L5</b>                      | 86                       | 82 ( <i>R</i> )       |
| 6                 | <b>L6</b>                      | 85                       | 92 ( <i>R</i> )       |
| 7                 | <b>L7</b>                      | 84                       | 81 ( <i>R</i> )       |
| 8                 | <b>L8</b>                      | 94                       | 96 ( <i>R</i> )       |
| 9                 | <b>L9</b>                      | 91                       | 92 ( <i>R</i> )       |
| 10 <sup>[e]</sup> | <b>L8</b>                      | 99                       | 84 ( <i>R</i> )       |
| 11 <sup>[f]</sup> | <b>L8</b>                      | 96                       | 92 ( <i>R</i> )       |

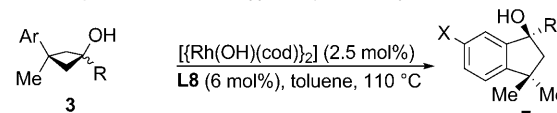
[a] Reaction conditions: **3a** (0.1 mmol; mixture of *cis/trans* isomers),<sup>[10]</sup> toluene (0.20 M). [b] Yield of isolated product **7a**. [c] Determined by HPLC on a chiral stationary phase. [d] **L5** (12 mol%) and [Rh(OAc)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>]<sub>2</sub> (2.5 mol%). [e] Cs<sub>2</sub>CO<sub>3</sub> (1.1 equiv); [f] [Rh(OH)(cod)]<sub>2</sub> (0.25 mol%) and **L8** (0.6 mol%), xylenes (1.0 M), 120 °C, 12 h. binap = 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl, cod = 1,5-cyclooctadiene, Cy = cyclohexyl, DMM = 3,5-dimethyl-4-methoxyphenyl, DTBM = 3,5-di-*tert*-butyl-4-methoxyphenyl.

task. Steric and electronic fine-tuning led to the identification of **L8**, bearing electron-poor aryl groups on the phosphorous atom of the ferrocene backbone, as the best performer and afforded **7a** in 94 % yield and 96 % *ee* (Table 1, entry 8). With only a minor decrease of the *ee* value (92 % *ee*; Table 1, entry 11), the catalyst loading could be lowered from 5 to 0.5 mol% rhodium. Bases such as cesium carbonate significantly increased the reaction rates, however, at the expense of lower selectivity (Table 1, entry 10).

The scope of the rhodium-catalyzed rearrangement was examined with the optimized reaction conditions (Table 2). In general, different aromatic tertiary cyclobutanols were afforded the corresponding indanols in good yields and high selectivities (Table 2, entries 1–6). This selectivity was maintained for substrates with small alkyl substituents (Table 2, entries 7 and 8) as well as for those with sterically more demanding isopropyl or *tert*-butyl substituents (Table 2, entries 9–11).

The absolute configuration of the *para*-chlorophenyl derivative **7k** was established to be *R* by X-ray crystallographic analysis.<sup>[11]</sup>

We next turned our attention to substrates where R' ≠ Me (Table 3). However, exposure of **3i** to the aforementioned optimized reaction conditions resulted in a 1.2:1 mixture of

**Table 2:** Scope of the rhodium(I)-catalyzed C–C/C–H activation.<sup>[a]</sup>


| Entry | <b>3</b>  | R                                  | <b>7(X)</b>    | Yield [%] <sup>[b]</sup> | ee [%] <sup>[c]</sup> |
|-------|-----------|------------------------------------|----------------|--------------------------|-----------------------|
| 1     | <b>3a</b> | Ph                                 | <b>7a</b> (H)  | 94                       | 96 ( <i>R</i> )       |
| 2     | <b>3b</b> | 4-ClC <sub>6</sub> H <sub>4</sub>  | <b>7b</b> (H)  | 87                       | 96 ( <i>R</i> )       |
| 3     | <b>3c</b> | 4-MeOC <sub>6</sub> H <sub>4</sub> | <b>7c</b> (H)  | 88                       | 94 ( <i>R</i> )       |
| 4     | <b>3d</b> | 1-naphth                           | <b>7d</b> (H)  | 79                       | 88 ( <i>R</i> )       |
| 5     | <b>3e</b> | 2-naphth                           | <b>7e</b> (H)  | 98                       | 94 ( <i>R</i> )       |
| 6     | <b>3f</b> | ( <i>E</i> )-styryl                | <b>7f</b> (H)  | 75                       | 91 ( <i>R</i> )       |
| 7     | <b>3g</b> | Me                                 | <b>7g</b> (H)  | 96                       | 90 ( <i>S</i> )       |
| 8     | <b>3h</b> | <i>n</i> Bu                        | <b>7h</b> (H)  | 95                       | 93 ( <i>S</i> )       |
| 9     | <b>3i</b> | <i>i</i> Pr                        | <b>7i</b> (H)  | 88                       | 91 ( <i>R</i> )       |
| 10    | <b>3j</b> | <i>t</i> Bu                        | <b>7j</b> (H)  | 99                       | 94 ( <i>R</i> )       |
| 11    | <b>3k</b> | <i>t</i> Bu                        | <b>7k</b> (Cl) | 99                       | 90 ( <i>R</i> )       |

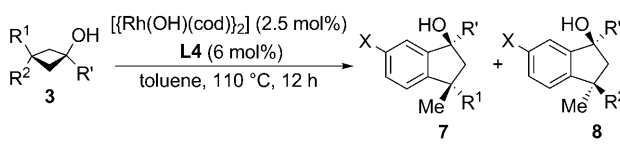
[a] Reaction conditions: **3** (0.1 mmol), toluene (0.20 M), 5–12 h. [b] Yield of isolated product **7**. [c] Determined by HPLC on a chiral stationary phase and the absolute configuration was assigned by analogy with **7k**. naphth = naphthalene.

the two diastereomers **7i** and **8m** (Table 3, entry 1). Dehydration of the indanol to the indene revealed that the initial C–C cleavage step—responsible for the configuration of the quaternary stereocenter—had proceeded almost with no selectivity. Gratifyingly, the difluorophos ligand (**L4**) induced useful selectivities in both stereodetermining steps, resulting in an overall excellent *ee* value of 99 % and a good diastereomeric ratio of 20:1 (Table 3, entry 2). The corresponding *trans*-configured cyclobutanol **3m** provided the diastereomer **8m** with the opposite configuration at C3 with comparable *ee* and d.r. values (Table 3, entry 3). The scope of the reaction was explored with diverse cyclobutanols having aromatic and heteroaromatic substituents. By being exposed to this second set of conditions, the cyclobutanols furnished the rearranged products in excellent yields as well as diastereo- and enantioselectivities (Table 3, entries 3–13). The 6-aza-indanols **7t** and **8u** were selectively formed over the corresponding indanols (Table 3, entry 10 (2:1) and entry 11 (8:1)), thus suggesting that electron-poor aromatic compounds preferentially participate in the 1,4-rhodium shift. Nevertheless, electron-rich heteroaromatic substituents, like a thiophene group, are well suited for the reaction (Table 3, entries 12 and 13).

A cyclobutanol substrate with identical aryl groups in the 3-position (**3x**) offers the possibility to explore the feasibility of an enantioselective version of the 1,4-rhodium shift (Scheme 2). Indeed, synthetically useful selectivities were observed with the difluorophos ligand **L8** and **8x** was formed in 96 % yield, 92 % *ee*, and with 4.5:1 d.r. Further screening revealed that the Taniaphos ligand **L10** is unique in preferentially providing the opposite diastereomer **7x** (9:1 d.r.), however, only as a racemate.

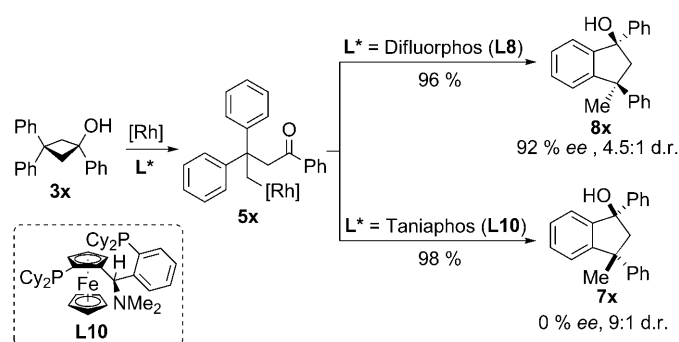
In conclusion, we have demonstrated an efficient protocol for the activation of *tert*-cyclobutanols through an enantioselective rhodium(I)-catalyzed insertion into the C–C σ-bond leading to alkyl rhodium species. These reactive intermedi-

**Table 3:** Scope of the diastereoselective reaction.<sup>[a]</sup>



| Entry            | 3  | R <sup>1</sup>                    | R <sup>2</sup>                    | R'  | Major product <sup>[b]</sup> (X) | 7/8 <sup>[c]</sup> | Yield [%] <sup>[d]</sup> | ee [%] <sup>[e]</sup> |
|------------------|----|-----------------------------------|-----------------------------------|-----|----------------------------------|--------------------|--------------------------|-----------------------|
| 1 <sup>[f]</sup> | 3l | Ph                                | Et                                | nBu | 7l (H)                           | 1.2:1              | 94                       | 97                    |
| 2                | 3l | Ph                                | Et                                | nBu | 7l (H)                           | 20:1               | 95                       | 99                    |
| 3                | 3m | Et                                | Ph                                | nBu | 8m (H)                           | 1:10               | 98                       | 99                    |
| 4 <sup>[g]</sup> | 3n | Ph                                | CH <sub>2</sub> OBn               | Ph  | 7n (H)                           | > 20:1             | 97                       | 97                    |
| 5 <sup>[g]</sup> | 3o | CH <sub>2</sub> OBn               | Ph                                | Ph  | 8o (H)                           | 1:12               | 91                       | 97                    |
| 6                | 3p | 4-ClC <sub>6</sub> H <sub>4</sub> | CO <sub>2</sub> Me                | Ph  | 7p (Cl)                          | 9:1                | 90                       | 99                    |
| 7                | 3q | CO <sub>2</sub> Me                | 4-ClC <sub>6</sub> H <sub>4</sub> | Ph  | 8q (Cl)                          | 1:4.5              | 90                       | 99                    |
| 8                | 3r | 4-ClC <sub>6</sub> H <sub>4</sub> | nBu                               | Et  | 7r (Cl)                          | 20:1               | 93                       | 96                    |
| 9                | 3s | nBu                               | 4-ClC <sub>6</sub> H <sub>4</sub> | Et  | 8s (Cl)                          | 1:6                | 95                       | 99                    |
| 10               | 3t |                                   | Ph                                | Et  | 7t                               | 10:1               | 74 <sup>[h]</sup>        | 96                    |
| 11               | 3u | Ph                                |                                   | Et  | 8u                               | 1:6                | 63 <sup>[i]</sup>        | 99                    |
| 12               | 3v |                                   | Et                                | nBu | 7v                               | 3:1                | 90                       | 99                    |
| 13               | 3w | Et                                |                                   | nBu | 8w                               | 1:15               | 65                       | 96                    |

[a] Reaction conditions: **3** (0.1 mmol), toluene (0.20 mL). [b] Configuration assigned by analogy with **7k** and diagnostic nOe interactions. [c] Determined by <sup>1</sup>H NMR spectroscopy of the crude reaction mixture. [d] Yield of isolated product **7**. [e] Determined by HPLC on a chiral stationary phase. [f] **L8** (6.0 mol%). [g] **L2** (6.0 mol%). [h] 9% of the indanol was formed. [i] 32% of the indanol was formed. Bn = benzyl.



**Scheme 2.** Probing an enantioselective 1,4-rhodium shift. Reaction conditions: **3x** (0.1 mmol),  $[\text{Rh}(\text{OH})(\text{cod})_2]$  (2.5 mol%), **L\*** (6.0 mol%), toluene (0.20 mL), 110 °C, 12 h.

ates lead (presumably by a C–H activation pathway) to aryl rhodium species that ultimately give access to highly substituted indanol derivatives in an enantio- and diastereose-

lective manner. Studies focusing on related activation/relaying modes and on an expansion of the reaction manifold are ongoing.

## Experimental Section

1,3-Diphenyl-3-methyl-cyclobutanol (**3a**, 23.8 mg, 0.10 mmol),  $[\text{Rh}(\text{cod})(\text{OH})_2]$  (1.14 mg, 2.50  $\mu\text{mol}$ ) and (*R,S*)-Josiphos (**L8**, 4.07 mg, 6.00  $\mu\text{mol}$ ) were weighed into an oven dried vial equipped with a magnetic stirrer. The vial was then sealed with a rubber septum and flushed with nitrogen. After the addition of dry toluene (0.4 mL), the reaction mixture was degassed by three freeze-pump-thaw cycles, stirred for 10 min at 23 °C and subsequently immersed into a preheated oil bath (110 °C) for 5 h. After conversion was complete (as evident by TLC), the reaction mixture was cooled to 23 °C and directly purified by column chromatography on silica gel (pentane/EtOAc 13:1,  $R_f$  = 0.42) to give indanol (*R*)-**7a** (22.4 mg, 94 % yield, 96 % ee) as a colorless oil.

Received: June 12, 2009

Published online: July 16, 2009

**Keywords:** asymmetric catalysis · C–C activation · C–H activation · indanols · rhodium

- [1] Reviews on C–H bond functionalization: a) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808–1822; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698–1712; b) F. Kakiuchi, S. Murai, *Top. Organomet. Chem.* **1999**, *3*, 47–79; c) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731–1770; d) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826–834; e) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211–241; f) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077–1101; g) F. Kakiuchi, *Top. Organomet. Chem.* **2008**, *24*, 1–33; h) I. V. Seregin, V. Gevorgyan, *Chem. Soc. Rev.* **2007**, *36*, 1173–1193; i) J. C. Lewis, R. G. Bergman, J. A. Ellman, *Acc. Chem. Res.* **2008**, *41*, 1013–1025; j) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013–3039; reviews on C–C bond activation: k) B. Rybtchinski, D. Milstein, *Angew. Chem.* **1999**, *111*, 918–932; *Angew. Chem. Int. Ed.* **1999**, *38*, 870–883; l) M. Murakami, Y. Ito, *Top. Organomet. Chem.* **1999**, *3*, 97–129; m) C.-H. Jun, C. W. Moon, D.-Y. Lee, *Chem. Eur. J.* **2002**, *8*, 2423–2428; n) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759–1792; o) C.-H. Jun, *Chem. Soc. Rev.* **2004**, *33*, 610–618; p) T. Satoh, M. Miura, *Top. Organomet. Chem.* **2005**, *14*, 1–20; q) T. Seiser, N. Cramer, *Org. Biomol. Chem.* **2009**, *7*, 2835–2840.

- [2] a) Y. Terao, H. Wakui, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2001**, *123*, 10407–10408; b) Y. Terao, H. Wakui, M. Nomoto, T. Satoh, M. Miura, M. Nomura, *J. Org. Chem.* **2003**,

- 68, 5236–5243; c) Y. Terao, M. Nomoto, T. Satoh, M. Miura, M. Nomura, *J. Org. Chem.* **2004**, *69*, 6942–6944; d) H. Wakui, S. Kawasaki, T. Satoh, M. Miura, M. Nomura, *J. Am. Chem. Soc.* **2004**, *126*, 8658–8659; e) T. Nishimura, T. Katoh, T. Hayashi, *Angew. Chem.* **2007**, *119*, 5025–5027; *Angew. Chem. Int. Ed.* **2007**, *46*, 4937–4939; f) T. Uto, M. Shimizu, K. Ueura, H. Tsurugi, T. Satoh, M. Miura, *J. Org. Chem.* **2008**, *73*, 298–300.
- [3] a) H.-F. Chow, C.-W. Wan, K.-H. Low, Y.-Y. Yeung, *J. Org. Chem.* **2001**, *66*, 1910–1913; b) C.-K. Choi, J.-W. Hong, I. Tomita, T. Endo, *Bull. Korean Chem. Soc.* **2002**, *23*, 112–118; c) T. Nishimura, H. Araki, Y. Maeda, S. Uemura, *Org. Lett.* **2003**, *5*, 2997–2999; d) A. Funayama, T. Satoh, M. Miura, *J. Am. Chem. Soc.* **2005**, *127*, 15354–15355; e) A. Horitake, H. Tsurugi, A. Funayama, T. Satoh, M. Miura, *Org. Lett.* **2007**, *9*, 2231–2233; f) T. Nishimura, T. Katoh, K. Takatsu, R. Shintani, T. Hayashi, *J. Am. Chem. Soc.* **2007**, *129*, 14158–14159; g) R. Shintani, K. Takatsu, T. Katoh, T. Nishimura, T. Hayashi, *Angew. Chem.* **2008**, *120*, 1469–1471; *Angew. Chem. Int. Ed.* **2008**, *47*, 1447–1449.
- [4] Examples for retroallylation of homoallylic tertiary alcohols: a) T. Kondo, K. Kodoi, E. Nishinaga, T. Okada, Y. Morisaki, Y. Watanabe, T.-A. Mitsudo, *J. Am. Chem. Soc.* **1998**, *120*, 5587–5588; b) D. Necas, M. Tursky, M. Kotora, *J. Am. Chem. Soc.* **2004**, *126*, 10222–10223; c) S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2006**, *128*, 2210–2211; d) M. Iwasaki, S. Hayashi, K. Hirano, H. Yorimitsu, K. Oshima, *J. Am. Chem. Soc.* **2007**, *129*, 4463–4469; e) R. Shintani, K. Takatsu, T. Hayashi, *Org. Lett.* **2008**, *10*, 1191–1193.
- [5] For examples, see: a) T. Nishimura, K. Ohe, S. Uemura, *J. Am. Chem. Soc.* **1999**, *121*, 2645–2646; b) T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **1999**, *121*, 11010–11011; c) R. C. Larock, C. K. Reddy, *Org. Lett.* **2000**, *2*, 3325–3327; d) M. Murakami, T. Itahashi, Y. Ito, *J. Am. Chem. Soc.* **2002**, *124*, 13976–13977; e) T. Nishimura, Y. Nishiguchi, Y. Maeda, S. Uemura, *J. Org. Chem.* **2004**, *69*, 5342–5347; f) T. Matsuda, M. Makino, M. Murakami, *Angew. Chem.* **2005**, *117*, 4684–4687; *Angew. Chem. Int. Ed.* **2005**, *44*, 4608–4611; g) M. Murakami, S. Ashida, T. Matsuda, *J. Am. Chem. Soc.* **2006**, *128*, 2166–2167; h) M. Murakami, S. Ashida, T. Matsuda, *Tetrahedron* **2006**, *62*, 7540–7546; i) M. Murakami, M. Makino, S. Ashida, T. Matsuda, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1315–1321.
- [6] a) T. Nishimura, S. Matsumura, Y. Maeda, S. Uemura, *Chem. Commun.* **2002**, 50–51; b) S. Matsumura, Y. Maeda, T. Nishimura, S. Uemura, *J. Am. Chem. Soc.* **2003**, *125*, 8862–8869; c) T. Matsuda, M. Shigeno, M. Makino, M. Murakami, *Org. Lett.* **2006**, *8*, 3379–3381; d) T. Matsuda, M. Shigeno, M. Murakami, *J. Am. Chem. Soc.* **2007**, *129*, 12086–12087; e) C. Winter, N. Krause, *Angew. Chem.* **2009**, *121*, 2497–2499; *Angew. Chem. Int. Ed.* **2009**, *48*, 2460–2462.
- [7] T. Seiser, N. Cramer, *Angew. Chem.* **2008**, *120*, 9435–9438; *Angew. Chem. Int. Ed.* **2008**, *47*, 9294–9297.
- [8] Review: a) S. Ma, Z. Gu, *Angew. Chem.* **2005**, *117*, 7680–7685; *Angew. Chem. Int. Ed.* **2005**, *44*, 7512–7517; recent examples: b) T. Miura, T. Sasaki, H. Nakazawa, M. Murakami, *J. Am. Chem. Soc.* **2005**, *127*, 1390–1391; c) T. Matsuda, M. Shigeno, M. Murakami, *J. Am. Chem. Soc.* **2007**, *129*, 12086–12087.
- [9] For a related palladium-catalyzed intramolecular addition to ketones, see: G. Liu, X. Lu, *J. Am. Chem. Soc.* **2006**, *128*, 16504–16505.
- [10] Pure *cis* and *trans* isomers gave identical yields and selectivities.
- [11] See the Supporting Information for details.