ORGANIC LETTERS

2012
Vol. 14, No. 16
4114–4117

{1,6}-Transannular Catalytic Asymmetric Gosteli–Claisen Rearrangement

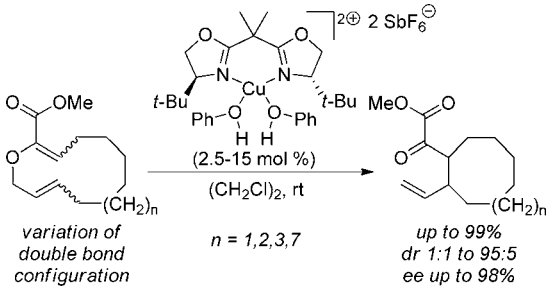
Tobias Jaschinski and Martin Hiersemann*

Fakultät Chemie, Technische Universität Dortmund, 44227 Dortmund, Germany

martin.hiersemann@udo.edu

Received June 27, 2012

ABSTRACT



The first uncatalyzed and [Cu(R-box)L_2](SbF_6)$_2$-catalyzed {1,6}-transannular Gosteli–Claisen rearrangement of cyclic 2-alkoxycarbonyl-substituted allyl vinyl ethers to afford medium- and large-sized carbacycles is disclosed.

Major progress has been made during the past decade in the development of catalytic asymmetric Claisen rearrangements.[1] Carrying the established procedures to application in target-oriented synthesis provides an efficient means to identify new challenges.

(+)-Xeniolide F (**I**) is a member of the xenicane family of diterpenes of marine origin (Figure 1).[2] In connection with an ongoing research enterprise toward the synthesis of (+)-xeniolide F,[3,4] a retrosynthesis was proposed that hinges on the success of a {1,6}-transannular catalytic asymmetric Gosteli–Claisen rearrangement ({1,6}-TCAGC).[5] The prospect of a single step construction of the critical stereogenic carbon atoms C2 and C10 (xenicane numbering) as well as the strained nine-membered carbacycle with predictable catalyst-induced diastereoselectivity lured us to consider the development of this unprecedented variation of the catalytic asymmetric Gosteli–Claisen rearrangement.[6]

Considering the relatively thin experimental basis,[6] we decided to embark on a model study to explore the

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(2) Anta, C.; Gonzalez, N.; Santafe, G.; Rodriguez, J.; Jimenez, C. *J. Nat. Prod.* **2002**, *65*, 766–768.

(3) Pollex, A.; Hiersemann, M. *Org. Lett.* **2005**, *7*, 5705–5708.

(4) For total synthesis of xenicane diterpenoids, see: (a) Renneberg, D.; Pfander, H.; Leumann, C. J. *J. Org. Chem.* **2000**, *65*, 9069–9079. (b) Mushti, C. S.; Kim, J.-H.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 14050–14052. (c) Larionov, O. V.; Corey, E. J. *J. Am. Chem. Soc.* **2008**, *130*, 2954–2955. (d) Hamel, C.; Prusov, E. V.; Gertsch, J.; Schweizer, W. B.; Altmann, K.-H. *Angew. Chem.* **2008**, *120*, 10235–10239. (e) Williams, D. R.; Walsh, M. J.; Miller, N. A. *J. Am. Chem. Soc.* **2009**, *131*, 9038–9045.

(5) For previous application of the CAGC in target-oriented synthesis, see: (a) Gille, A.; Hiersemann, M. *Org. Lett.* **2010**, *12*, 5258–5261. (b) Körner, M.; Hiersemann, M. *Org. Lett.* **2007**, *9*, 4979–4982. (c) Stiasni, N.; Hiersemann, M. *Synlett* **2009**, 2133–2136.

(6) Knight has reported an uncatalyzed {1,6}-transannular Ireland–Claisen rearrangement of a 13- and 15-membered lactone containing an *E*-configured allyl ether double bond. In the event, the rearrangement products were isolated as mixtures of diastereomers (*trans*/*cis* = 56:44 and 68:32), presumably due to the intermediacy of double bond isomeric silyl ketene acetals. The rearrangement of the corresponding 15-membered lactone featuring a *Z*-configured allyl ether double bond delivered the 11-membered rearrangement product as a mixture of diastereomers (*trans*/*cis* = 34:66); see: (a) Cameron, A. G.; Knight, D. W. *Tetrahedron Lett.* **1982**, *23*, 5455–5458. (b) Cameron, A. G.; Knight, D. W. *J. Chem. Soc., Perkin Trans. 1* **1986**, 161–167.

10.1021/ol3017676
Published on Web 08/03/2012

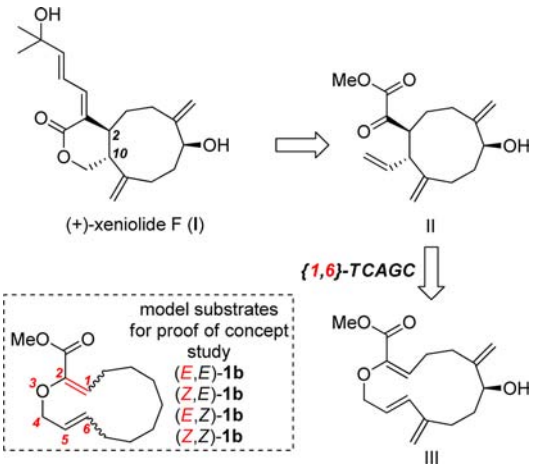
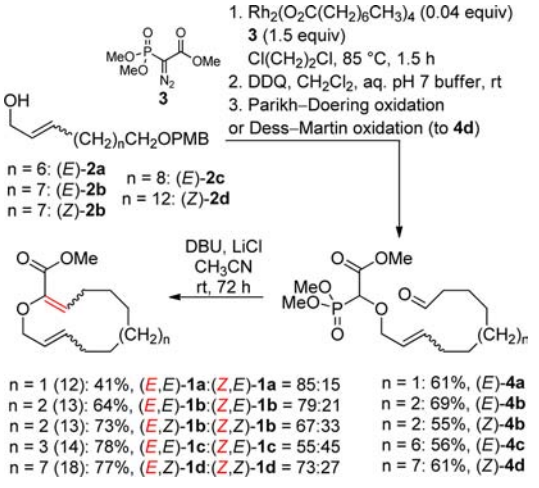


Figure 1. Retrosynthesis of xeniolide F and design of a proof of concept study for a {1,6}-TCAGC.

synthetic access to cyclic 2-alkoxycarbonyl-substituted allyl vinyl ethers (**1**) as well as the stereoselectivity of the uncatalyzed and catalyzed {1,6}-transannular Gosteli–Claisen rearrangement ({1,6}-TGC). For that purpose, we synthesized the four double bond isomers of the 13-membered **1b** and, in order to gain insights into the influence of the ring size on reactivity and stereoselectivity, the 12-membered **1a**, the 14-membered **1c**, and the 18-membered **1d** (Scheme 1).

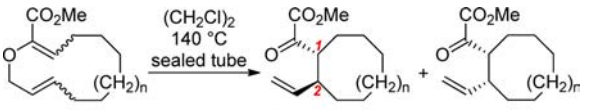
The synthesis of **1a**–**d** commenced from the allylic alcohols **2a**–**d**[7] and proceeded via a sequence consisting of Rh(I)-catalyzed OH insertion,[8] deprotection,[9] and oxidation[10,11] to afford the aldehydes **4a**–**d** (Scheme 1). Subsequent intramolecular Horner–Wadsworth–Emmons reaction furnished **1a**–**d** as mixtures of double bond isomers which were separated by preparative HPLC.[12,13]

Scheme 1. Synthesis of Cyclic Allyl Vinyl Ethers



With the requisite cyclic allyl vinyl ethers **1a**–**d** in hand, the unprecedented {1,6}-TGC was investigated first (Table 1). Previous experimental[14] and computational[15] studies on the uncatalyzed Gosteli–Claisen rearrangement of acyclic allyl vinyl ethers established high yields and nearly perfect diastereoselectivities due to a pronounced preference for a chairlike transition state (TS) structure irrespective of the allyl vinyl ether double bond configuration. The 18-membered (*E*,*Z*)- and (*Z*,*Z*)-**1d**, selected to mimic the transition to the acyclic case, upon heating, underwent the {1,6}-TGC in excellent yield and diastereoselectivity (entries 1 and 2). In the event, and in accordance with a pronounced preference for a chairlike TS structure, (*E*,*Z*)-**1d** provided (±)-*cis*-**5d** (99%, dr = 95:5) whereas (*Z*,*Z*)-**1d** preferentially afforded (±)-*trans*-**5d** (99%, dr = 93:7). The {1,6}-TGC of the 12-, 13-, or 14-membered (*E*,*E*)-**1a**–**c** provided the cycloalkanes (±)-*trans*-**5a**–**c** in very good yields and diastereoselectivities (entries 3, 4, and 5);[16] notably, a significantly increased reaction time at 140 °C was required to ensure complete conversion of (*E*,*E*)-**1b**,**c**. Subjecting (*Z*,*E*)- or (*E*,*Z*)-**1b** to identical conditions provided (±)-*cis*-**5b** in a slightly diminished yield but still with useful diastereoselectivities (entries 6 and 7). Notably, only miniscule amounts of (±)-*cis*-**5b** were isolated after prolonged heating of (*Z*,*Z*)-**1b** at 140 °C, attesting to the reluctance of (*Z*,*Z*)-**1b** to undergo the {1,6}-TGC (entry 8). More forcing conditions (μw, 210 °C) led to a faster formation of (±)-*cis*-**5b** via a boat-like TS structure and with concurrent decomposition of the starting material (entry 9).

Table 1. Uncatalyzed {1,6}-Transannular Gosteli–Claisen Rearrangement[a]



entry	ring size	substrate	time (h)	yield (%)[b]	dr[c]
1	18→14	(*E*,*Z*)-**1d**	24	99	5:95
2	18→14	(*Z*,*Z*)-**1d**	24	99	93:7
3	12→8	(*E*,*E*)-**1a**	24	98	88:12
4	13→9	(*E*,*E*)-**1b**	94	92	94:6
5	14→10	(*E*,*E*)-**1c**	94	99	87:13
6	13→9	(*Z*,*E*)-**1b**	94	74	11:89
7	13→9	(*E*,*Z*)-**1b**	94	76[d]	8:92
8	13→9	(*Z*,*Z*)-**1b**	94	6[e]	<5:95
9	13→9	(*Z*,*Z*)-**1b**	31[f]	37[g]	5:95

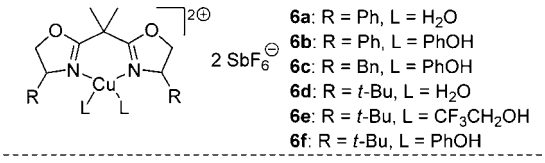
[a] Experiments conducted with 0.08 mmol of **1a**–**c** and 0.06 mmol of **1d**. [b] Isolated yield after purification by chromatography. [c] *trans*-**5**/*cis*-**5**, ratio determined by NMR; relative configuration assigned by NOE experiments. See Supporting Information for details. [d] With 8% of (*E*,*Z*)-**1b** recovered. Complete consumption of (*E*,*Z*)-**1b** after 168 h: 74%, dr = 8:92. [e] With 92% of (*Z*,*Z*)-**1b** recovered. [f] 210 °C by microwave irradiation. [g] With 50% of (*Z*,*Z*)-**1b** recovered and contaminated with [1,3]-rearrangement product.

(7) For the synthesis of **2a**–**d**, see the Supporting Information.

(8) Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811–10843.

We next turned our attention to the envisioned {1,6}-TCAGC using the 13-membered (*E*,*E*)-**1b** for the purpose of catalyst optimization (Table 2). (*R*,*R*)-**6a** and (*S*,*S*)-**6d**, members of the copper(II)bis(oxazoline) family of chelating C_2-symmetric Lewis acids,[17] are known catalysts for the catalytic asymmetric Gosteli–Claisen rearrangement (CAGC) at ambient temperature. Additionally, the stereodifferentiating substituents (R) and the ligands (L) were varied to modulate selectivity and reactivity; selected examples are summarized in Table 2. (*R*,*R*)-**6a** (R = Ph, L = H_2O) proved to be an effective catalyst for a rt {1,6}-TCAGC providing *trans*-**5b** in high yields and diastereoselectives (dr = 92:8) but offered only low enantioselectivities (13% ee) (entry 1). (*R*,*R*)-**6b** (R = Ph, L = PhOH) demonstrated faster conversion but otherwise did not bias the stereoselectivity (entry 2). An increase in enantioselectivity (70% ee) was obtained with (*R*,*R*)-**6c** (R = Bn, L = PhOH) but at the expense of a slightly lower diastereoselectivity (dr = 87:13) (entry 3).[18] For the known (*S*,*S*)-**6d** (R = *t*-Bu, L = H_2O), the enantioselectivity eventually reached synthetically useful levels (>98% ee) (entry 4). Subsequent experiments using the previously unreported (*S*,*S*)-**6e** (R = *t*-Bu, L = CF_3CH_2OH) or (*S*,*S*)-**6f** (R = *t*-Bu, L = PhOH) resulted in comparable enantioselectivities but increased turnover (entries 5 and 6). It was then found possible to reduce the catalyst loading to 5 mol % for (*S*,*S*)-**6f** by prolonging the reaction time (entry 7). The increase in enantioselectivity (>98% ee) observed with the catalysts (*S*,*S*)-**6d**,**e**,**f** (R = *t*-Bu) was accompanied by a significantly diminshed diastereoselectivity (dr = 83:17). A subtle dependence of diastereoselectivity on the ring size was observed when 12-membered (*E*,*E*)-**1a** and 14-membered (*E*,*E*)-**1c** were subjected to the standard protocol using (*S*,*S*)-**6f** as the catalyst. In detail, using either 15 or 2.5 mol % of (*S*,*S*)-**6f**, the {1,6}-TCAGC of (*E*,*E*)-**1a** provided the 8-membered **5a** with low diastereoselectivity, but excellent enantioselectivity (dr = 62:38, >97% ee) (entry 8); (*E*,*E*)-**1c** underwent the enantioselective {1,6}-TCAGC to afford the 10-membered **5c** without any noticeable diastereoselectivity (dr = 51:49, > 98% ee) (entries 9 and 10).

Table 2. {1,6}-TCAGC of (*E*,*E*)-**1a**: Variation of Catalyst Structure[a]



entry	substrate	catalyst	time (h)	yield (%)[b]	dr[c]	ee (%)[d]
1	(*E*,*E*)-**1b**	(*R*,*R*)-**6a**	5	97[e]	92:8	13
2	(*E*,*E*)-**1b**	(*R*,*R*)-**6b**	1.5	92	92:8	13
3	(*E*,*E*)-**1b**	(*R*,*R*)-**6c**	1.5	70	87:13	70[f]
4	(*E*,*E*)-**1b**	(*S*,*S*)-**6d**	72	90[g]	83:17	>98
5	(*E*,*E*)-**1b**	(*S*,*S*)-**6e**	18	87	83:17	>98
6	(*E*,*E*)-**1b**	(*S*,*S*)-**6f**	18	87	83:17	>98
7[h]	(*E*,*E*)-**1b**	(*S*,*S*)-**6f**	26	86	83:17	>98
8[i]	(*E*,*E*)-**1a**	(*S*,*S*)-**6f**	2	98	62:38	>97
9	(*E*,*E*)-**1c**	(*S*,*S*)-**6f**	18	95	51:49	>98
10[j]	(*E*,*E*)-**1c**	(*S*,*S*)-**6f**	48	86	51:49	>98

[a] Experiments conducted with 0.08 mmol (*E*,*E*)-**1a**–**c** in 1,2-dichloroethane at ambient temperature. Catalysts prepared as described in the Supporting Information. [b] Isolated yield after purification by chromatography. [c] *trans*-**5**/*cis*-**5**, ratio determined by NMR. [d] ee for the major diastereomer determined by chiral HPLC. The absolute configuration was assigned based on the accepted TS model for the CAGC. [e] 39% yield after 1.5 h with 56% of (*E*,*E*)-**1b** recovered. [f] In favor of the (1*S*,2*R*)-*trans*-**5b** diastereomer. [g] 66% yield after 18 h with 33% of (*E*,*E*)-**1b** recovered. [h] 0.05 equiv of (*S*,*S*)-**6f**. [i] Identical outcome using 0.025 equiv of (*S*,*S*)-**6f** after 18 h. [j] 0.05 equiv of (*S*,*S*)-**6f**.

We next studied the influence of the double bond configuration on the chemo- and diastereoselectivity of the {1,6}-TCAGC (Table 3). In general, the difference between the 13-membered (*E*,*E*)-**1b** and its double bond isomers was substantial; in particular, varying reactivities, diastereoselectivities, and the formation of the inseparable byproduct **7** were observed. In detail, attempts to catalyze the {1,6}-TCAGC of (*Z*,*E*)-**1b** using (*S*,*S*)-**6d** (R = *t*-Bu, L = H_2O) led to a miniscule conversion, even after 3 days, and the formation of a 1:1 mixture of diastereomers (entry 1). A faster conversion to a nearly 1:1:1 mixture of diastereomers and **7** was observed using (*S*,*S*)-**6e** (R = *t*-Bu, L = CF_3CH_2OH) or (*S*,*S*)-**6f** (R = *t*-Bu, L = PhOH) (entries 2 and 3). Somewhat surprinsingly in light of the results from the {1,6}-TGC (Table 1, entry 7), using 15 or even 30 mol % of (*S*,*S*)-**6f**, (*E*,*Z*)-**1b** was reluctant to undergo the {1,6}-TCAGC and only small amounts of a roughly 1:1 mixture of *cis*- and *trans*-**5b** contaminated with traces of **7** were obtained (entry 4). In contrast, attempts to realize the {1,6}-TCAGC of (*Z*,*Z*)-**1b** led to the expected low conversion via a boat-like TS structure to afford *cis*-**5b** and the formation of **7** via the nonconcerted pathway (entry 5).

(9) Oikawa, Y.; Yoshioka, T.; Yonemitsu, O. *Tetrahedron Lett*. **1982**, *23*, 885–888.

(10) Parikh, J. R.; Doering, W. v. E. *J. Am. Chem. Soc*. **1967**, *89*, 5505–5507.

(11) Dess, D. B.; Martin, J. C. *J. Org. Chem*. **1983**, *48*, 4155–4156.

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(13) Assignment of the double bond configuration by NOE experiments; see Supporting Information for details.

(14) Rehbein, J.; Leick, S.; Hiersemann, M. *J. Org. Chem*. **2009**, *74*, 1531–1540.

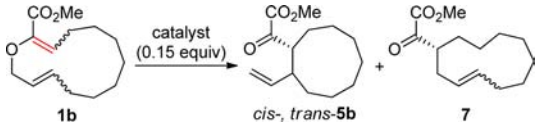
(15) Rehbein, J.; Hiersemann, M. *J. Org. Chem*. **2009**, *74*, 4336–4342.

(16) Funk has reported the uncatalyzed {1,6}-transannular Ireland–Claisen rearrangement of an 11-membered lactone containing an *E*-configured double bond. In the event, the 7-membered rearrangement product was isolated as a mixture of diastereomers (*trans*/*cis* = 59:41); see: Abelman, M. M.; Funk, R. L.; Munger, J. D. *J. Am. Chem. Soc*. **1982**, *104*, 4030–4032.

(17) Desimoni, G.; Faita, G.; Jørgensen, K. A. *Chem. Rev*. **2011**, *111*, PR284–PR437.

(18) The intriguing reversal in enantioface differentiation by going from **6a** (R = Ph) to **6c** (R = Bn) or **6d** (R = *tert*-Bu) is documented in the literature; see: (a) Johanssen, M.; Jørgensen, K. A. *J. Org. Chem*. **1995**, *60*, 5757–5762 (HDA reaction). (b) Evans, D. A.; Rovis, T.; Kozlowski, M. C.; Downey, C. W.; Tedrow, J. S. *J. Am. Chem. Soc*. **2000**, *122*, 9134–9142 (Mukaiyama–Michael reaction), and ref 1m (Gosteli–Claisen rearrangement).

Table 3. {1,6}-TCAGC of **1b**: Variation of Double Bond Configuration and Catalyst Structure[a]



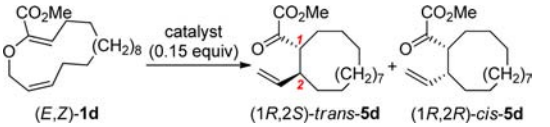
entry	substrate	catalyst	time (h)	yield (%)[b]	ratio[c]
1	(*Z*,*E*)-**1b**	(*S*,*S*)-**6d**	72	8[d]	32:35:33
2	(*Z*,*E*)-**1b**	(*S*,*S*)-**6e**	18	69	34:36:30
3	(*Z*,*E*)-**1b**	(*S*,*S*)-**6f**	18	65	33:36:31
4	(*E*,*Z*)-**1b**	(*S*,*S*)-**6f**	18	7[e]	52:39:9
5	(*Z*,*Z*)-**1b**	(*S*,*S*)-**6f**	18	12[f]	0:57:43

[a] Experiments conducted with 0.08 mmol of **1b** in 1,2-dichloroethane at ambient temperature. Catalyst prepared as described in the Supporting Information. Formation of product mixtures prevented ee determination. [b] Isolated yield after purification by chromatography. [c] *trans*-**5b**/*cis*-**5b**/**7**, product ratio determined by NMR. [d] With 70% of (*Z*,*E*)-**1b** recovered. [e] With 70% of (*E*,*Z*)-**1b** recovered. 0.3 equiv of (*S*,*S*)-**6f**: 10% yield with 71% of (*E*,*Z*)-**1b** recovered. [f] With 76% of (*Z*,*Z*)-**1b** recovered.

Intrigued by the notable difference in reactivity of the 13-membered (*E*,*Z*)-**1b** in the uncatalyzed or catalyzed {1,6}-TGC (Table 1, entry 7 vs Table 3, entry 4), we studied the {1,6}-TCAGC of the 18-membered (*E*,*Z*)-**1d** to compare ring size effects on reactivity and selectivity (Table 4). In general, our experiments demonstrate the propensity of (*E*,*Z*)-**1d** to undergo the {1,6}-TCAGC via a chairlike TS structure to afford *cis*-**5d** in excellent yield and diastereoselectivity. In detail, when using (*R*,*R*)-**6b** (R = Ph, L = PhOH) *cis*-**5d** was obtained in excellent yield (99%) and diastereoselectivity (dr = 95:5) but only modest enantioselectivity (44% ee) (entry 1). Switching to (*S*,*S*)-**6d** (R = *t*-Bu, L = H_2O) had the expected beneficial effect on the enantioselectivity (>98% ee) without affecting yield or diastereoselectivity (entry 2). With the same level of selectivity, an improved rate of conversion was again obtained with (*S*,*S*)-**6e** (R = *t*-Bu, L = CF_3CH_2OH) and (*S*,*S*)-**6f** (R = *t*-Bu, L = PhOH) (entries 3 and 4); notably, while maintaining the outcome, (*S*,*S*)-**6f** loading could be optimized to 2.5 mol % (entry 5). Finally, we studied the {1,6}-TCAGC of (*Z*,*Z*)-**1d** using our standard protocol with 15 mol % (*S*,*S*)-**6f** (entry 6). In the event, and in expected contrast to the result of the {1,6}-TCAGC of the 13-membered (*Z*,*Z*)-**1b** (Table 3, entry 5), we observed the high-yielding (99%) formation of *trans*-**5d** in moderate diastereoselectivity (dr = 86:14).

In summary, we have revealed the first uncatalyzed and [Cu(R-box)L_2]$(SbF_6)_2$-catalyzed {1,6}-transannular Gosteli–Claisen rearrangement. This includes the development of a robust and scalable synthesis of cyclic 2-alkoxycarbonyl-substituted allyl vinyl ethers. Catalyst structure (R, L) and the ring size as well as double bond configuration of the cyclic allyl vinyl ether substrates are determinants for the efficiency of the {1,6}-TGC. Considering their prevalence in asymmetric catalysis, our finding of a notable modulation of the activity of the [Cu(R-box)L_2]$(SbF_6)_2$ catalyst system by variation of L (H_2O < CF_3CH_2OH or PhOH) could be of general utility. We expect that the disclosed {1,6}-TGC (92%, dr = 94:6) or {1,6}-TCAGC (87%, dr = 83:17, >98% ee) of (*E*,*E*)-**1b** will guide our way to (+)-xeniolide F. Enforcing the chair/boat TS hierarchy in catalyzed transannular Claisen rearrangement serves as an ample challenge in future catalyst development.[1]

Table 4. {1,6}-TCAGC: Variation of Ring Size and Catalyst Structure[a]



entry	catalyst	substrate	time (h)	yield[b] (%)	dr[c]	ee[d] (%)
1	(*R*,*R*)-**6b**	(*E*,*Z*)-**1d**	0.5	99	5:95	44
2	(*S*,*S*)-**6d**	(*E*,*Z*)-**1d**	18	99[e]	5:95	>98
3	(*S*,*S*)-**6e**	(*E*,*Z*)-**1d**	4	99	5:95	>98
4	(*S*,*S*)-**6f**	(*E*,*Z*)-**1d**	4	99	5:95	>98
5[f]	(*S*,*S*)-**6f**	(*E*,*Z*)-**1d**	18	99	5:95	>98
6	(*S*,*S*)-**6f**	(*Z*,*Z*)-**1d**	7.5[g]	99	86:14[h]	–[i]

[a] Experiments conducted with 0.06 mmol of **1d** in 1,2-dichloroethane at ambient temperature. Catalysts prepared as described in the Supporting Information. [b] Isolated yield after purification by chromatography. [c] *trans*-**5d**/*cis*-**5d**, ratio determined by NMR. [d] Determined by chiral HPLC. [e] 77% yield after 4 h with 22% of (*E*,*Z*)-**1d** recovered. [f] 0.025 equiv of (*S*,*S*)-**6f**. [g] 94% yield after 4 h with 6% of (*Z*,*Z*)-**1d** recovered. [h] (1*S*,2*R*)-*trans*-**5d**/(1*S*,2*S*)-*cis*-**5d**. [i] Inconclusive ee determination.

Acknowledgment. Financial support by the Technische Universität Dortmund and generous donations of $Rh_2(O_2C(CH_2)_6CH_3)_4$ by Umicore as well as L-*tert*-leucin by Evonik Degussa GmbH is gratefully acknowledged.

Supporting Information Available. Text, tables, and figures giving experimental procedures, spectral and analytical data, and ^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.