Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 15 (2004) 3189–3194

The enantioselective Diels–Alder reaction of 1-methoxybuta-1,3-diene with *n*-butyl glyoxylate catalyzed by the (salen)Cr(III)Cl and Co(II) complexes

Piotr Kwiatkowski,[a] Monika Asztemborska[b] and Janusz Jurczak[a,c,*]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*
[b]*Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland*
[c]*Department of Chemistry, Warsaw University, 02-093 Warsaw, Poland*

Received 26 June 2004; accepted 16 August 2004

Abstract—Commercially available (salen)Cr(III)Cl **4c** and (salen)Co(II) **5a** complexes were found to promote [4+2]cycloaddition of 1-methoxybuta-1,3-diene **1** to *n*-butyl glyoxylate **2**, affording 6-substituted 2-methoxy-5,6-dihydro-2*H*-pyrans **3** in good yield and with enantioselectivites of 70–90% ee. The catalyst **5a** was also effective in the reaction of Danishefsky's diene **6**, piperylene **8** and 2,3-dimethylbuta-1,3-diene **10** with glyoxylate **2**, however enantioselectivities were lower.

1. Introduction

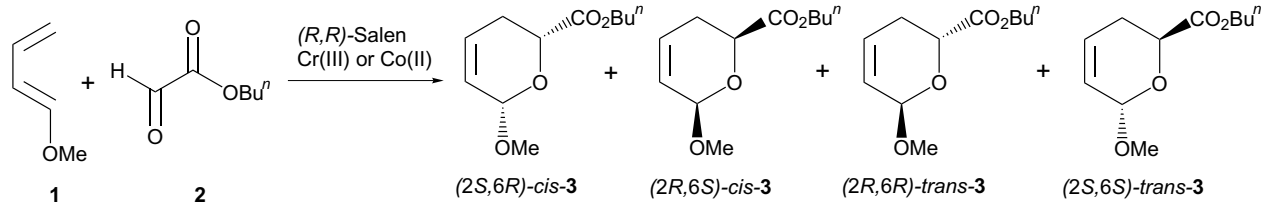
The hetero-Diels–Alder (HDA) reaction of 1,3-dienes with carbonyl compounds is a very useful method to construct the dihydropyran derivatives, which are important precursors from the synthetic point of view.[1] The enantioselective version of this reaction has been intensively investigated since 1990.[2] In most cases, the reactions of simple aldehydes with the Danishefsky's diene in the presence of chiral catalysts were studied. Among other catalysts, salen–chromium(III) complexes, applied for this reaction for the first time by Jacobsen et al.[3] turned out to be quite versatile in hetero [4+2]cycloadditions and some other reactions.[4] We have also performed studies using this catalyst for reactions of simple nonactivated dienes such as buta-1,3-diene, 2,3-dimethylbuta-1,3-diene and cyclohexa-1,3-diene with alkyl glyoxylates[5] as well as highly activated 1-methoxybuta-1,3-diene **1** to the same heterodienophiles.[6]

In parallel, we focused our attention on both cationic and neutral salen cobalt complexes, well known as excellent catalysts for kinetic resolution of epoxides.[7] We have proven recently that these complexes were also active in the high-pressure Friedel–Crafts reaction, to give enantioselectivities of up to 76% ee.[8] Examples of use of salen–cobalt(II) and –cobalt(III) complexes in the hetero-Diels–Alder reaction are rather rare in the literature. The (salen)cobalt(II) complex was used by Wu and co-workers[9] for the first time in HDA reaction between chiral activated dienes and alkyl glyoxylates. The other examples concern the use of the optically active β-ketoiminato-cobalt(II) and (III) complexes by Yamada and co-workers[10] for the reaction of aromatic aldehydes with the Danishefsky's diene.

In the present work we turned our attention to [4+2]cycloaddition of 1-methoxybuta-1,3-diene **1** to *n*-butyl glyoxylate **2**, leading to 2-methoxy-5,6-dihydro-2*H*-pyran-6-carboxylic esters **3** (Scheme 1), important precursors for the synthesis of many natural products, for example, modified carbohydrates[11] and other biologically active substances, such as compactin and mevinolin.[12] The literature describes several examples of enantioselective reactions of diene **1** with alkyl glyoxylates, mainly using BINOL–titanium(IV) complexes.[13] Recently, Jacobsen et al.[14] reported a highly diastereo- and enantioselective reaction of diene **1** with nonactivated aldehydes, using a chiral tridentate Cr(III) complex as a catalyst.

* Corresponding author. Tel.: +48 22 6320578; fax: +48 22 6326681; e-mail: jurczak@icho.edu.pl

0957-4166/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2004.08.002



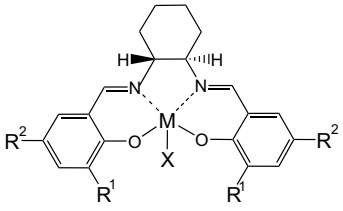
Scheme 1.

2. Results and discussion

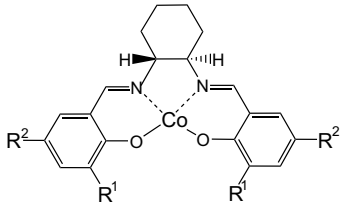
Taking into account our previous studies using chiral auxiliaries,[12c,15] we resolved to search for a chiral salen-type catalyst effective for the reaction of alkyl glyoxylates with 1-methoxybuta-1,3-diene **1**, and requiring no complicated protocols. We have succeeded using the commercially available (salen)Cr(III)Cl **4c** and (salen)-Co(II) **5a** complexes (Fig. 1).

At the beginning of our studies we decided to use (salen)$CrBF_4$ complex **4a** for the reaction of diene **1** with glyoxylate **2**. However, complex **4a**, which previously worked very well in the reactions of Danishefsky's diene and simple aldehydes,[3] turned out to be very poor in terms of both yield and enantiomeric excess (Table 1, entry 1). The major reaction product was the *trans*-diastereomer, and the *cis:trans* ratio was dependent on the reaction time. Adding the catalyst **4a** to the *cis*-cycloadduct **3** resulted in isomerization to the *trans*-diastereomer. In the case of cationic cobalt complex **4b**, with the same counterion, *cis*-diastereoselectivity was improved, whereas the enantioselectivity was still low (entry 2).

Application of the less-active chromium–chloride complex **4c** caused a significant improvement of the yield, diastereoselectivity, as well as enantioselectivity (entry 3). The product was obtained in a good yield along with *endo*-selectivity, and the major *cis*-cycloadduct was formed with 70% ee. These results confirm that the complex **4a** having a less-coordinated counterion BF_4^- is much more active and acidic than the chloride complex **4c**, causing a partial polymerization of diene **1**, which explains why the yield in this case is low. When we used



4a M= Cr, X=BF_4, R^1=R^2=Bu^t
4b M= Co, X=BF_4, R^1=R^2=Bu^t
4c M= Cr, X=Cl, R^1=R^2=Bu^t
4d M= Co, X=Cl, R^1=R^2=Bu^t
4e M= Cr, X=Cl, R^1=Bu^t, R^2=Me
4f M= Cr, X=Cl, R^1=Bu^t, R^2=OMe
4g M= Cr, X=Cl, R^1=Me, R^2=Bu^t



5a R^1=R^2=Bu^t
5b R^1=Bu^t, R^2=Me
5c R^1=Bu^t, R^2=OMe
5d R^1=Bu^t, R^2=Br
5e R^1=Bu^t, R^2=NO_2
5f R^1=Bu^t, R^2=H
5g R^1=Pr^i, R^2=H
5h R^1=Me, R^2=Bu^t

Figure 1. (Salen)Cr(III), Co(II) and (III) complexes.

Table 1. Results of the reaction of *n*-butyl glyoxylate **2** with diene **1** catalyzed by salen–chromium and cobalt complexes[a]

Entry	Catalyst (mol%)		Solvent	Temperature (°C)	Time (h)	Yield (%)	*cis:trans*-**3**	Ee for *cis*-**3** (%)
1	**4a**	2	Toluene	20	3	43	28:72	24[b]
2	**4b**	2	Toluene	20	3	42	59:41	32
3	**4c**	2	Toluene	20	3	80	86:14	70
4	**4d**	2	Toluene	20	3	50	78:22	56
5	**4c**	2	Toluene	−20	24	50	85:15	80
6	**4c**	2	*t*-BuOMe	20	3	83	74:26	70
7	**4c**	2	CH_2Cl_2	20	3	78	72:28	62
8	**5a**	2	Toluene	20	3	75	87:13	80[b]
9	**5a**	10	Toluene	20	4	80	89:11	82
10	**5a**	5	Toluene	20	3	76	87:13	80
11	**5a**	1	Toluene	20	4	70	87:13	80
12	**5a**	0.5	Toluene	20	15	70	81:19	68
13	**5a**	2	Toluene	−10	15	65	90:10	90
14	**5a**	2	*t*-BuOMe	20	3	62	86:14	82
15	**5a**	2	CH_2Cl_2	20	3	85	80:20	70
16	**5a**	2	No solvent	20	3	72	84:16	82

[a] The reactions were carried out with 1 mmol of **2**, 1.2 mmol of **1** in 2 mL of solvent.
[b] For *trans*-**3** enantioselectivity was 16% ee (entry 1) and 12% ee (entry 8).

cobalt–chloride complex **4d**, stereoselectivities also increased (56% ee, entry 4) as compared with **4b**, although not as good as in the case of **4c**. Next we optimized the reaction catalyzed by **4c**. Lowering the temperature to −20 °C increased the enantiomeric excess to 80% (entry 5). Replacement of toluene by Bu^{t}OMe or CH_2Cl_2 decreased the diastereoselectivity and enantioselectivity (entries 3, 6 and 7, respectively).

We also found that, compared to the cobalt(III) complexes **4b** and **4d**, the commercially available salen–cobalt(II) complex **5a** (Fig. 1) is much more effective as a catalyst in the HDA reaction of 1-methoxybuta-1,3-diene **1** with *n*-butyl glyoxylate **2**, leading under mild conditions almost exclusively to the *cis*-cycloadduct **3** in 75% overall yield along with good 80% enantiomeric excess (entry 8). The minor *trans*-isomer was formed with much lower enantioselectivity.

Next, we attempted to optimize the reaction of diene **1** with glyoxylate **2** using the (salen)Co(II) complex **5a**. Variation of the catalyst concentration in the range of 1–10 mol% influences neither enantio- nor diastereoselectivity (entries 8–11). Concentrations below 1 mol% give generally worse results (entry 12). This is probably due to partial oxidation of the catalyst. A decrease in temperature increases enantioselectivity up to 90% ee (entry 13). The reaction is stereochemically efficient in CH_2Cl_2 (up to 70% ee, entry 15) but better enantiomeric excesses (up to 82%) were obtained in toluene and Bu^t-OMe (entries 8 and 14, respectively).

Variation of the concentration of glyoxylate **2** in the range of 0.2–2.0 mol/L has no significant effect on the enantioselectivity of the process. The reaction can be carried out even without solvent, but still with high enantioselectivity (entry 16).

The enantioselectivity of the minor *trans*-**3** isomer was in the range of 0–40% ee and it was irreproducible. We have also tested two other glyoxylates. The results (de and ee) were very similar for ethyl glyoxylate, and somewhat worse for *iso*-propyl glyoxylate, as compared with *n*-butyl glyoxylate.

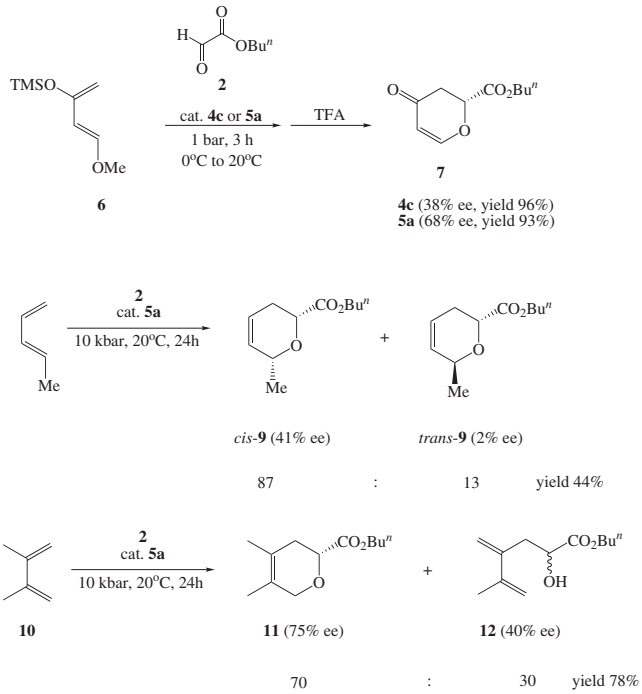
We have also studied the effect of the ligand structure with respect to substituted salicylidene moieties (Table 2). The electronic effect predominates distinctly, whereas the steric one is rather negligible. One can generalize that if R^1 and R^2 are either alkyl or stronger electron-donor (e.g., OMe) substituents the diastereoselectivity is at a level of 83:17 to 89:11 whereas enantioselectivity ranges from 70% to 82% (Table 2). If the aromatic ring bears the strongly electron-withdrawing nitro group (entry 9), the catalyst activity increases, and the diastereoselectivity changes its direction, however enantioselectivity dropped. The induction was also lower when we used the catalyst with chiral 1,2-diphenylethylenediamine instead of 1,2-diaminocyclohexane. A comparison of influence of chromium(III)Cl (entries 1–4) with cobalt(II) (entries 5–7 and 12) catalysts on the asymmetric induction shows that the latter complexes are slightly better then the former ones.

Table 2. Influence of the ligand structure in the chromium(III) and cobalt(II) catalysts on cycloaddition of **1** and **2**[a]

Entry	Catalyst	Yield [%]	*cis*:*trans*-**3**	Ee for *cis*-**3**
1	**4c**	80	86:14	70
2	**4e**	76	87:13	76
3	**4f**	81	84:16	74
4	**4g**	61	80:20	47
5	**5a**	75	87:13	80
6	**5b**	73	88:12	80
7	**5c**	67	87:13	82
8	**5d**	78	75:25	76
9	**5e**[b]	90	38:62	54
10	**5f**	69	85:15	78
11	**5g**	71	89:11	76
12	**5h**[b]	55	83:17	82

[a] The reactions were carried out using 1 mmol of **2**, 1.2 mmol of **1** and 2 mol% of cobalt(II) or chromium(III)Cl complexes in 2 mL of toluene at 20 °C for 3 h.
[b] Dissolution of the catalyst was incomplete.

We have also checked the complexes **4c** and **5a** in the reaction of *n*-butyl glyoxylate **2** with Danishefsky's diene **6** (Scheme 2), resulting in synthetically important dihydropyranone **7**.[16] However, in this case the reaction proceeds with lower enantioselectivity (up to 68% ee for **5a**) as compared with diene **1** (Scheme 1 and Table 1, entries 3 and 8). We then carried out the reaction catalyzed by the cobalt complex **5a** using piperylene **8** as 1,3-diene of moderate activity. Under atmospheric-pressure conditions the [4+2]cycloadducts **9** were formed in a 10% yield only. So, we decided to apply the high-pressure conditions for this reaction giving the expected products **9** in a 44% yield, good diastereoselectivity (87:13) and rather low enantioselectivity (41% ee for *cis*-**9**, Scheme 2). Similar enantioselectivities (up to 52% ee) were observed for the active 1-alkyl-3-silyloxy-1,3-dienes.[9b]



Scheme 2. Conditions: reactions were carried out using 1 mmol of **2**, 1.2–1.5 mmol of diene, 2 mol% of catalyst in 2 mL of toluene.

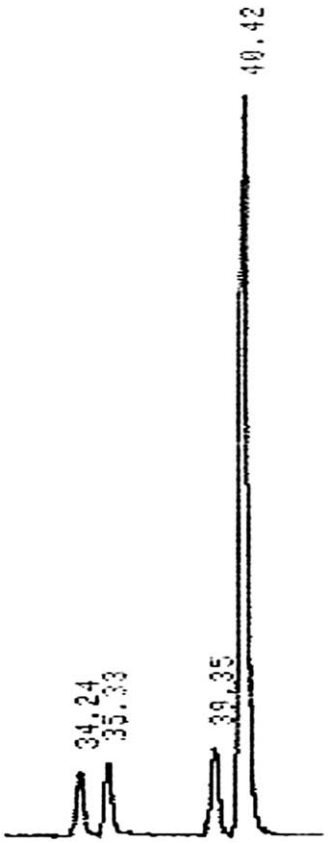
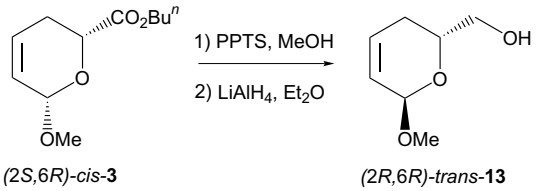


Figure 2. Typical chromatogram of a mixture of [4+2]cycloadducts **3** (Table 1, entry 8).

When 2,3-dimethylbuta-1,3-diene **10** was reacted with glyoxylate **2**, the enantioselectivity for the [4 + 2]cycloadduct **11** was 75% ee. These results suggest that the presence of an alkyl substituent at the 1-position of the diene reduces the enantioselectivity of the process.

The ratio of four stereoisomeric [4+2]cycloadducts **3** obtained (Scheme 1) was measured applying gas chromatography method with the use of chiral columns (cf. Experimental). A typical chromatogram is shown in Figure 2.

The absolute configuration of [4+2]cycloaducts **3** were determined by chemical correlation with alcohol **13** (Scheme 3). A mixture of products **3** were isomerized using PPTS in MeOH to give *trans*-**3**, which was reduced to the appropriate alcohol mixture and its specific rotation was determined.[17] In all cases, when chromium(III)Cl (1*R*,2*R*)-**4c**, **4e**–**g** and cobalt (1*R*,2*R*)-**5a**–**h** complexes were used, we observed predomination of the (2*S*,6*R*)-*cis*-**3** [4+2]cycloadduct.



Scheme 3. Chemical correlation.

3. Conclusion

Summing up, we found that the (salen)Cr(III) **4** and (salen)Co(II) **5** complexes perform well as chiral catalysts in the enantioselective Diels–Alder reaction of 1-methoxybuta-1,3-diene with *n*-butyl glyoxylate, affording 2-methoxy-5,6-dihydro-2*H*-pyran-6-carboxylic acid *n*-butyl ester **3**, important precursor for the synthesis of many natural products. This reaction proceeds efficiently at low loading of **4c** and **5a** complexes under undemanding conditions, using the reagent grade solvents, in the yield of 50–80%, and with the stereoselectivities in the range of 70–80% de and 70–90% ee. The complex **5a** affords somewhat better enantioselectivities than the analogous complexes (salen)Cr(III)Cl **4c**, while the *endo*/*exo* selectivities are practically the same.

4. Experimental

4.1. General

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, toluene, *t*-BuOMe, hexane, AcOEt) were distilled prior to use. All reported NMR spectra were recorded with a Varian Gemini spectrometer at 200 (^{1}H NMR) and 50 (^{13}C NMR) MHz in $CDCl_3$. Chemical shifts of ^{1}H NMR are reported as δ values relative to TMS peak defined at $\delta = 0.00$. Chemical shifts of ^{13}C NMR are reported as δ values relative to $CDCl_3$ peak defined at $\delta = 77.1$. Flash chromatography was performed on silica gel (Kieselgel 60, 200–400 mesh). Optical rotations were recorded using a JASCO DIP-360 polarimeter.

Enantiomeric excess of products was determined by gas chromatography performed using a Hewlett–Packard GC unit equipped with a capillary chiral column β-dex 120 (permethyl-β-cyclodextrin, 30 m × 0.25 mm I.D. Supelco, Bellefonte, USA). Chromatography conditions: carrier gas—argon, 100 kPa; injection temp 200 °C; detector temp 250 °C.

4.1.1. Materials. 1-Methoxy-1,3-butadiene **1**, (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride **4c** (dried before use) and (*R*,*R*)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) **5a**, and dienes **6**, **8**, **10** were purchased from Aldrich. Other chromium(III) **4e**–**g** and cobalt(II) **5b**–**h** salen complexes were prepared according to known procedures, starting from apropriate salen ligand and $CrCl_2$ or $Co(OAc)_2$ salts.[18] Salen ligands were synthesized according to the method described by Larrow and Jacobsen.[19] *n*-Butyl glyoxylate **2** was prepared by oxidative cleavage of di-*n*-butyl tartrate, using $NaIO_4$ in water.[20] Finally, compound **2** was distilled in the presence of P_2O_5.

4.2. General procedure for the catalytic [4+2]-cycloaddition

To a solution of an appropriate salen catalyst (usually 2 mol%) in toluene (2 mL), freshly distilled *n*-butyl gly-

oxylate **2** (130 mg, 1 mmol) was added. After 10 min, 1-methoxybuta-1,3-diene **1** (125 μL, 1.2 mmol) was added in one portion to the solution, and a mixture was stirred for 3 h at room temperature. After evaporation the residue was subjected for silica gel column chromatography using hexane/AcOEt 9:1→8:2 as an eluent. In case of the reaction of Danishefsky's diene **6** with glyoxylate **2**, after stirring a reaction mixture for 3 h trifluoroacetic acid was added. Then the mixture was quenched by addition of saturated aqueous $NaHCO_3$, extracted with ethyl ether and dried over $MgSO_4$. After evaporation of solvents the residue was chromatographed on a silica gel column using hexane/AcOEt 9:1→6:4.

4.3. General procedure for the high-pressure [4+2]-cycloaddition[21]

In a 2 ml Teflon ampoule were placed (salen)Co **5a** (12.1 mg, 2 mol%), solution of *n*-butyl glyoxylate (**2**) (130 mg, 1 mmol) in toluene, 1.5 equiv of diene **8** or **10** and the ampoule was filled with toluene and placed in a high-pressure vessel, and pressure was slowly increased to 10 kbar at 20 °C. After stabilization of pressure, the reaction mixture was kept under these conditions for 24 h. After decompression, the mixture was subjected to column chromatography.

4.4. Analytical data

4.4.1. *cis-n*-Butyl 2-methoxy-5,6-dihydro-2*H*-pyran-6-carboxylate *cis*-3. ^{1}H NMR: δ = 6.08–5.98 (m, 1H), 5.73–5.65 (m, 1H), 5.07–5.03 (m, 1H), 4.41–4.35 (m, 1H), 4.19 (t, J = 6.7 Hz, 1H), 4.14 (t, J = 6.7 Hz, 1H), 3.50 (s, 3H), 2.57–2.24 (m, 2H), 1.74–1.59 (m, 2H), 1.49–1.31 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR: δ = 170.8 (C), 127.7 (CH), 126.2 (CH), 97.2 (CH), 69.6 (CH_3), 64.9 (CH_2), 55.5 (CH), 30.5 (CH_2), 26.1 (CH_2), 19.0 (CH_2), 13.6 (CH_3); HRMS (M+Na)$^+$ calcd for $C_{11}H_{18}O_4Na$ 237.1103, found 237.1108; GC (column β-dex 120): T = 140 °C, t_R[(2*R*,6*S*)-**3**] = 39.3 min, t_R[(2*S*,6*R*)-**3**] = 40.4 min; bp 109 °C/3 Torr.

4.4.2. *trans-n*-Butyl 2-methoxy-5,6-dihydro-2*H*-pyran-6-carboxylate *trans*-3. ^{1}H NMR: δ = 6.06–5.97 (m, 1H), 5.80–5.72 (m, 1H), 5.00–4.97 (m, 1H), 4.53–4.45 (m, 1H), 4.20 (t, J = 6.7 Hz, 1H), 4.19 (t, J = 6.7 Hz, 1H), 3.46 (s, 3H), 2.35–2.27 (m, 2H), 1.73–1.59 (m, 2H), 1.48–1.30 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR: δ = 171.2 (C), 127.6 (CH), 125.4 (CH), 95.8 (CH), 65.7 (CH_3), 64.9 (CH_2), 55.5 (CH), 30.5 (CH_2), 27.4 (CH_2), 19.0 (CH_2), 13.6 (CH_3); HRMS (M+Na)$^+$ calcd for $C_{11}H_{18}O_4Na$ 237.1103, found 237.1018; GC (column β-dex 120): T = 140 °C, t_R[(2*S*,6*S*)-**3**] = 34.2 min, t_R[(2*R*,6*R*)-**3**] = 35.3 min.

4.4.3. *cis-n*-Butyl 6-methyl-3,6-dihydro-2*H*-pyran-2-carboxylate *cis*-9. ^{1}H NMR: δ = 5.86–5.74 (m, 1H), 5.71–5.59 (m, 1H), 4.44–4.15 (m, 2H), 4.19 (t, J = 6.8 Hz, 2H), 2.39–2.20 (m, 2H), 1.73–1.58 (m, 2H), 1.47–1.25 (m, 2H), 1.31 (d, J = 6.6 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ = 171.4 (C), 131.4 (CH), 123.1 (CH), 73.0 (CH), 71.7 (CH), 64.9 (CH_2), 30.7 (CH_2), 28.1 (CH_2), 21.2 (CH_3), 19.1 (CH_2), 13.8 (CH_3); GC (column β-dex 120): T = 130 °C, t_{R1} = 32.0 min, t_{R2} = 32.7 min.

The NMR data of compounds **7**, **11** and **12** are in agreement with those described in the literature.[5,16d]

Chromatographic parameters of enantioseparation of other investigated compounds determined by GC on β-dex 120 column: **7** (T = 150 °C, t_{R1} = 45.2 min, t_{R2} = 46.2 min); *trans*-**9** (T = 130 °C, t_{R1} = 29.2 min, t_{R2} = 30.8 min); **11** (T = 130 °C, t_{R1} = 29.7 min, t_{R2} = 30.2 min); **12** (T = 130 °C, t_{R1} = 22.6 min, t_{R2} = 23.0 min).

4.5. Chemical correlation

A mixture of products *cis:trans*-**3** 87:13 (Table 1, entry 8) obtained in the presence of (*R*,*R*)-**5a** complex, was isomerized in the presence of pyridinium *p*-toluene sulfonate (PPTS) in methanol for 2 days. The resulting mixture of *cis:trans*-**3** 6:94 was evaporated and the residue was subjected for reduction with $LiAlH_4$. After usual work-up, a post-reaction mixture was dried over $MgSO_4$ and after concentration, the residue was chromatographed on a silica gel column using hexane/AcOEt 9:1→6:4, yield 71%. $[\alpha]_D^{20} = +54$ (*c* 1.21, benzene), lit.[17] for (2*S*,6*S*)-**13**: $[\alpha]_D^{20} = -79.2$ (*c* 1.5, benzene).

References

1. Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15–23.
2. For a review, see: Jørgensen, K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 3558–3588.
3. Schaus, S. E.; Brånalt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 403–405.
4. For a review of applications of (salen)Cr complexes in asymmetric catalysis, see: Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Chem. Commun.* **2002**, 919–927.
5. Kwiatkowski, P.; Asztemborska, M.; Caille, J.-C.; Jurczak, J. *Adv. Synth. Catal.* **2003**, 506–509.
6. Kwiatkowski, P.; Asztemborska, M.; Jurczak, J. *Synlett*, **2004**, 1755–1758.
7. (a) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936–938; (b) Jacobsen, E. N.; Kakiuchi, F.; Konsler, R. G.; Larrow, J. F.; Tokunaga, M. *Tetrahedron Lett.* **1997**, *38*, 773–776.
8. Kwiatkowski, P.; Wojaczynska, E.; Jurczak, J. *Tetrahedron: Asymmetry* **2003**, *14*, 3643–3645.
9. (a) Hu, Y.-J.; Huang, X.-D.; Yao, Z.-J.; Wu, Y.-L. *J. Org. Chem.* **1998**, *63*, 2456–2461; (b) Li, L.-S.; Wu, Y.; Hu, Y.-J.; Xia, L.-J.; Wu, Y.-L. *Tetrahedron: Asymmetry* **1998**, *9*, 2271–2277.
10. (a) Yamada, T.; Kezuka, S.; Mita, T.; Ikeno, T. *Heterocycles* **2000**, *52*, 1041–1045; (b) Kezuka, S.; Mita, T.; Ohtsuki, N.; Ikeno, T.; Yamada, T. *Chem. Lett.* **2000**, 824–825.
11. (a) Konowal, A.; Jurczak, J.; Zamojski, A. *Tetrahedron* **1976**, *32*, 2957–2959; (b) Golebiowski, A.; Jurczak, J. *Synlett* **1993**, 241–245; (c) Jurczak, J. In *Total Synthesis of Amino Sugars in Preparative Carbohydrate Chemistry*; Hanessian, S., Ed.; Marcel Dekker: New York, 1997; pp 595–614.
12. (a) Rosen, T.; Heathcock, C. H. *Tetrahedron* **1986**, *42*, 4909–4951; (b) Bauer, T.; Kozak, J.; Chapuis, C.; Jurczak,

J. *J. Chem. Soc., Chem. Commun.* **1990**, 1178–1179; (c) Bauer, T.; Chapuis, C.; Jezewski, A.; Kozak, J.; Jurczak, J. *Tetrahedron: Asymmetry* **1996**, *7*, 1391–1404.
13. (a) Quimpere, M.; Jankowski, K. *J. Chem. Soc., Chem. Commun.* **1987**, 676–677; (b) Terada, M.; Mikami, K.; Nakai, T. *Tetrahedron Lett.* **1991**, *32*, 935–938; (c) Quitschalle, M.; Christmann, M.; Bhatt, U.; Kalesse, M. *Tetrahedron Lett.* **2001**, *42*, 1263–1265.
14. Dossetter, A. G.; Jamison, T. F.; Jacobsen, E. N. *Angew. Chem., Int. Ed.* **1999**, *38*, 2398–2400.
15. Bauer, T.; Chapuis, C.; Kozak, J.; Jurczak, J. *Helv. Chim. Acta* **1989**, *72*, 482–486.
16. (a) Motoyama, Y.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1994**, 1563–1564; (b) Ghosh, A. K.; Mathivanan, P.; Cappiello, J.; Krishnan, K. *Tetrahedron: Asymmetry* **1996**, *7*, 2165–2168; (c) Matsukawa, S.; Mikami, K. *Tetrahedron: Asymmetry* **1997**, *8*, 815–816; (d) Motoyama, Y.; Koga, Y.; Nishiyama, H. *Tetrahedron* **2001**, *57*, 853–860.
17. Bauer, T.; Jezewski, A.; Jurczak, J. *Tetrahedron: Asymmetry* **1996**, *7*, 1405–1412.
18. (a) Martínez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5897–5898; (b) Leung, W.-H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Reng, S.-M. *J. Chem. Soc., Dalton Trans.* **1996**, 1229–1236.
19. Larrow, J. F.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 1939–1942.
20. Atkinson, C. M.; Brown, C. W.; Simpson, J. C. E. *J. Chem. Soc.* **1956**, 26–30.
21. Jurczak, J.; Chmielewski, M.; Filipek, S. *Synthesis* **1979**, 41–42.