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Catalytic asymmetric allylation of aldehydes using the chiral (salen)chromium(III) complexes

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Abstract—The enantioselective addition of allylstannanes to glyoxylates and glyoxals, as well as simple aromatic and aliphatic aldehydes, catalyzed by chiral (salen)Cr(III) complexes, has been studied. The reaction proceeded smoothly for the reactive 2-oxoaldehydes and allyltributyltin in the presence of small amounts (1–2 mol %) of (salen)Cr(III)BF_4 (**1b**) under mild, undemanding conditions. However, in the case of other simple aldehydes, the use of high-pressure conditions is required to obtain good yields. Classic chromium catalyst **1b**, easily prepared from the commercially available chloride complex **1a**, affords homoallylic alcohols usually in good yield and with enantiomeric purity of 50–79% ee. The stereochemical results are rationalized on the basis of the proposed model.
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1. Introduction

The readily available chiral metallosalen complexes are potentially very attractive catalysts, e.g., for reactions catalyzed by Lewis acids. They have already been effectively applied in a variety of reactions,[1] e.g., epoxidation[2] and cyclopropanation[3] of alkenes, epoxide ring opening,[4] Diels–Alder,[5] and Strecker[6] reactions, as well as Michael-type additions,[7] alkylations of tin enolates,[8] and hydrocyanation of aldehydes.[9] One of the most promising and powerful salen-type Lewis acids is chromium(III) complex, well known as efficient enantioselective catalyst for several reactions.[5,8,10] Salen–chromium complexes have also been employed in the allylation of aldehydes in the catalytic Nozaki–Hiyama–Kishi reaction with allylic halides,[11] which is a redox process and requires anhydrous and oxygen-free conditions.

Until now, many efficient methods of enantioselective allylation have been developed which, however, were almost exclusively applied to simple aromatic and aliphatic aldehydes.[12] No efficient catalytic method for the enantioselective allylation of glyoxylates is currently known. This subject was investigated by Mikami et al.[13] with the use of a BINOL–titanium complex (10 mol %) as a catalyst. However, the results obtained were unsatisfactory in terms of both the yield and enantiomeric excess. In the case of reactions of glyoxylates with allyltrimethylsilane or allyltributyltin, the enantiomeric excess values were 30 and 10%, respectively, and the yield did not exceed 40%. Better results were obtained for crotyltin reagents. Of interest was the fact that the same catalytic system, independently used by Keck[14] and Umani-Ronchi[15] for the reaction of simple aliphatic and aromatic aldehydes with allyltributyltin, gave excellent results (the enantiomeric excess value was often above 90%).

The allylation of glyoxylates leads to the corresponding 2-hydroxypent-4-enoates, compounds of significant synthetic interest.[16] Recently, in order to synthesize these compounds and their derivatives in an enantiomerically pure form, diastereoselective methods, widely explored in our group,[17] using chiral auxiliaries attached to the glyoxylate moiety[18] or to the allylating reagents,[19] have been applied. These facts prompted us to search for a catalytic system useful for the enantioselective allylation of glyoxylates using metallosalen complexes. For some allylation reactions carried out under normal conditions, metallosalen complexes cannot be useful due to their relatively low Lewis acidity. In such cases, the problem can be solved by the application of a high-pressure technique.[20]

Recently, we have published two communications concerning catalytic asymmetric allylation of glyoxylates[21] and high-pressure methodology for the reaction with nonactivated aldehydes in the presence of a chromium–salen catalyst (Scheme 1).[22] In this paper, we present in detail the studies on enantioselective addition of allylstannanes to various aldehydes, catalyzed by chiral (salen)Cr(III) complexes

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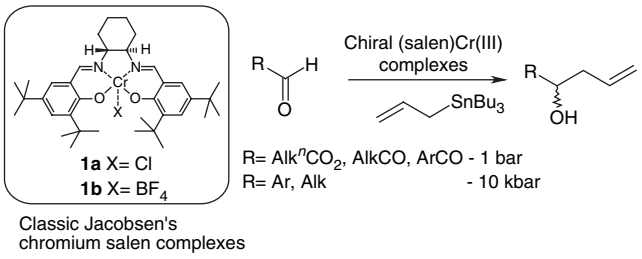
e.g., **1** (Scheme 1). Moreover, we decided to extend the investigation to other active aldehydes such as glyoxals, as well as to other allyltin reagents such as crotylstannanes.



Scheme 1.

2. Results and discussion

2.1. Allylation of activated aldehydes

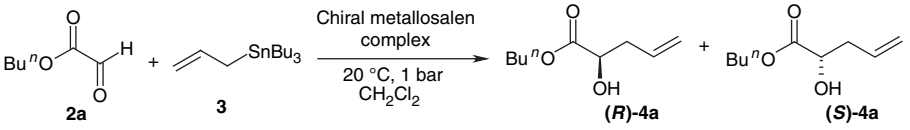
The metallosalen complexes were chosen as candidate chiral Lewis acids. In many cases, they are easily prepared and handled, and stable in the presence of moisture and oxygen. The model reaction was the allylation of *n*-butyl glyoxylate (**2a**) with allyltributyltin (**3**) leading to *n*-butyl 2-hydroxypent-4-enoate (**4a**) (Scheme 2). Subsequent to the preliminary screening of the chiral salen complexes of type **1** (Fig. 1) of the following metals: Ti(IV), VO(IV), Cr(III), Mn(III), Fe(III), Co(II) and (III), Ni(II) and (III), Cu(II) and Al(III), it transpired that the only enantioselectively efficient catalysts were the (salen)chromium(III) complexes **1a–c** (Table 1, entries 1–3). Although the remaining complexes **1d–m** (entries 4–13) did catalyze the allylation, the enantiomeric excess was 10% at best. The commercially available (salen)CrCl complex **1a** (2 mol %) provides the reaction at moderate enantioselectivity (54% ee) and in good yield. However, higher activity and slightly better enantioselectivity (over 60% ee) were observed for the chromium complexes with less coordinating counterions such as BF_4^- (**1b**) and ClO_4^- (**1c**) (entries 2 and 3, respectively) both easily prepared from **1a**.[6]

Table 1. Screening of the metallosalen complexes of type **1** with a classic salen ligand in the reaction of **2a** with **3**[a]

Entry	Catalyst	M	Yield (%)[b]	ee (%)[c]
1	**1a**	CrCl	73	54
2	**1b**	$CrBF_4$	82	61
3	**1c**	$CrClO_4$	90	65
4	**1d**	$TiCl_2$	82	<5
5	**1e**	VO	85	0
6	**1f**	MnCl	80	<5
7	**1g**	FeCl	83	<5
8	**1h**	Co	80	6
9	**1i**	CoCl	79	10
10	**1j**	Ni	66	<5
11	**1k**	$NiBF_4$	79	<5
12	**1l**	Cu	70	<5
13	**1m**	AlCl	78	<5

[a] The reactions were carried out using 1 mmol of *n*-butyl glyoxylate (**2a**), 2 mol % of complex **1**, and 1.1–1.2 mmol of allyltributyltin, in 1 ml of CH_2Cl_2, at 20 °C for 3–4 h.
[b] The yield was determined by GC.
[c] The enantiomeric excess was determined by GC on a capillary chiral β-dex 120 column.

We also tested the applicability of other chromium complexes with modified salen ligands. We studied the effect of the ligand structure with respect to the substituted



Scheme 2. The model reaction.

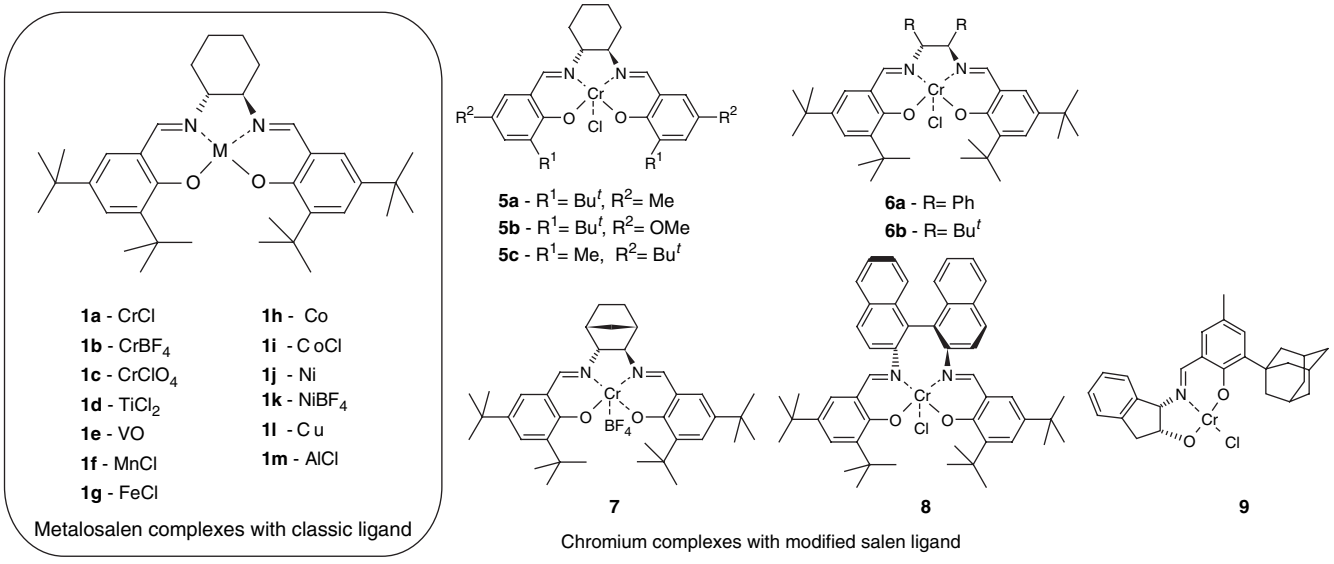


Figure 1. The metallosalen complexes used in this work.

Table 2. The reaction of **2a** with **3** catalyzed by chromium(III) complexes with modified salen ligands[a]

Entry	Catalyst	Yield (%)[b]	ee (%)[c]
1	**1a**	73	54
2	**5a**	82	55
3	**5b**	85	49
4	**5c**	75	29
5	**6a**	70	44
6	**6b**	52	21[d]
7	**7**	70	<5
8	**8**	65	<5
9	**9**	49	7

[a] The reactions were carried out using 1 mmol of *n*-butyl glyoxylate (**2a**), 2 mol % of chromium complex, and 1.1–1.2 mmol of allyltributyltin, in 1 ml of CH_2Cl_2, at 20 °C for 3–4 h.
[b] The yield was determined by GC.
[c] The enantiomeric excess was determined by GC on a capillary chiral β-dex 120 column.
[d] Opposite sense of asymmetric induction.

salicylidene and diamine (Table 2). When the R^1 substituent being *tert*-butyl was conserved, and the R^2 substituent was replaced by smaller groups such as methyl and methoxyl, the asymmetric induction remained similar (entries 1–3). A more significant decrease in induction was observed for replacing *tert*-butyl with methyl as an R^1 substituent (entry 4).

We investigated the chromium complexes with diamines other than 1,2-diaminocyclohexane, but the enantioselectivities obtained were lower (entries 5–9). Only the complex derived from 1,2-diphenylethylenediamine **6a** produced results similar to **1a** (entry 5). For the complex **6b**, reversed and lower enantioselectivity was observed (entry 6). This is a consequence of the altered conformation of the complex, since two *tert*-butyl groups of the amine, for steric reasons, cannot occupy both the pseudodiequatorial positions. The complex with 1,1′-binaphthyl-2,2′-diamine (**8**) gave practically no induction (entry 8); it likely adopts the cis-β configuration,[23] departing structurally from the complexes of type **1**, which typically adopt the trans conformation. In the context of the works of Jacobsen concerning the tridentate chromium(III) complex **9**,[24] we tested its performance in the model reaction. The results however, were unsatisfactory, and the enantiomeric excess of product **4a** was not greater than 10% (entry 9).

As already mentioned, (salen)chromium complexes have been applied to the enantioselective allylation reactions of simple aldehydes using allyl halides, via the Nozaki–Hiyama–Kishi reaction.[11] We examined this procedure for the allylation of glyoxylates, but in our hands the results were at best unsatisfactory.

We studied the influence of the enantiomeric purity of the catalyst **1b** on the enantioselectivity of the model reaction (Fig. 2, Scheme 2).[25] Linear correlation between enantiomeric purity of the catalyst and the enantioselectivity of the allylation reaction was found.

Next we tested different simple allylating reagents in the reaction of glyoxylate **2a**, e.g., allyltrimethylsilane. The chromium complex **1b** turned out to be too weak a Lewis acid to efficiently catalyze the reaction with allyltrimethylsilane, even under high-pressure conditions (10 kbar). We isolated

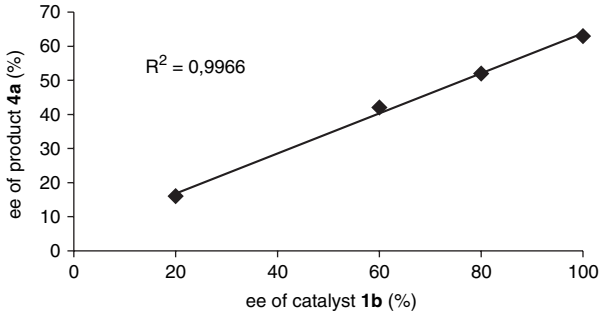


Figure 2. Absence of nonlinear effects in the reaction of **2a** with **3** catalyzed by **1b**.

the product **4a** in low yield (<40%), and enantioselectivity was within the range of 30–40% ee. The use of other tin allylating reagents did not improve the enantiomeric excess. Allyltrimethyltin gives practically the same results as allyltributyltin, being much more toxic owing to its volatility. When allyltriphenyltin was used, the enantioselectivity decreased to 46% ee. The reaction proceeded most rapidly for tetraallyltin, but the enantiomeric excesses obtained did not exceed 13%. Therefore, further studies were performed with commercially available allyltributyltin.

The natural consequence of the above studies was to optimize the reaction conditions. We investigated several factors such as concentration of reagents, solvent, temperature, and additives (Table 3).

Neither the presence of 4 Å molecular sieves (cf. entries 1 and 2 in Table 2) nor glyoxylate concentration (cf. entries 1 and 3) had considerable influence on the results of the model reaction in CH_2Cl_2. Moreover, the rate of addition of the allylating agent, based on a 1 mmol scale, and the amount of catalyst (2 mol % and more), seemed to have no influence on enantiomeric excess (cf. entries 1 and 4).

The reaction proceeded best at room temperature. Enhancing temperature to the boiling point of CH_2Cl_2 increased the reaction rate with an insignificant sacrifice in enantioselectivity (cf. entries 4 and 5). Surprisingly, lowering the temperature resulted in a drop in enantioselectivity to 36% ee (entries 6 and 7).

Out of the investigated solvents, $MeNO_2$ appeared to be the most efficient in terms of the enantiomeric excess (70% ee, entry 8). The allylation reactions are efficiently catalyzed even by minor amounts of the catalyst **1b** (0.2 mol %) yet accompanied by a decrease in enantioselectivity to 62% ee (entry 9). Of interest is the fact that the reaction proceeded well without any solvent (entry 10), which is a definite advantage of this procedure.

A slight improvement in enantioselectivity was observed for reactions conducted in the presence of amines or PPh_3 in CH_2Cl_2 (from 61 to 68% ee in the case of lutidine, cf. entries 1 and 11). This can be explained by additional coordination of the catalyst–aldehyde complex by the molecule of amine, which probably slightly deforms its structure. Beneficial effect of coordination of additional ligands on the reaction enantioselectivity is well known in the literature.[26] What is

Table 3. Results of the enantioselective reaction of *n*-butyl glyoxylate (**2a**) with allyltributyltin catalyzed by the complex **1b** under various reaction conditions[a]

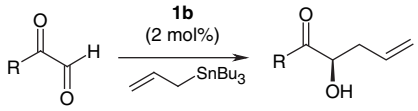
Entry	Mol % of the catalyst **1b**	Additives	Solvent	Concn of **2a** (mol/l)	*T* (°C)	Time (h)	Yield (%)[b]	ee (%)[c]
1	2		CH_2Cl_2	1	20	3	82	61
2	2	4 Å MS	CH_2Cl_2	1	20	1	82	62
3	2		CH_2Cl_2	0.1	20	5	81	61
4	5		CH_2Cl_2	1	20	1	80	61
5	5		CH_2Cl_2	1	40	0.25	77	58
6	5		CH_2Cl_2	1	5	24	78	51
7	5		CH_2Cl_2	1	−78→−20	24	76	36
8	2		$MeNO_2$	1	20	3	79	70
9	0.2		$MeNO_2$	2	20	24	61	62
10	2		No solvent		5→20	5	90	65
11	2	2,6-Lutidine (2.5 mol %)	CH_2Cl_2	1	20	4	80	68
12	2	2,6-Lutidine (2.5 mol %)	$MeNO_2$	1	20	3	80	70

[a] The reactions were carried out using 1 mmol of *n*-butyl glyoxylate (**2a**) and 1.2 mmol of allyltributyltin.
[b] The yield was determined by GC.
[c] The enantiomeric excess was determined by GC on a capillary chiral β-dex 120 column.

more, Katsuki gave an example of the use of achiral salen complex coordinated by a chiral amine, as a catalyst in enantioselective epoxidation of olefins.[27] In contrast, the addition of lutidine to the reaction performed in $MeNO_2$ caused no change (entry 12).

We also performed allylations using the glyoxylates (R=OPr^i, OBu^t, and OBn) other than **2a**. This methodology was extended to other active 2-oxoaldehydes such as glyoxals (**2e–i**, R=Bu^n, Pr^i, Bu^t, Ph, and furyl) (Table 4). With respect to enantioselectivity, the results for alkyl glyoxylates (**2b–d**) and alkyl glyoxals (**2e–g**) were quite similar to those obtained for *n*-butyl glyoxylate and ranged from 61 to 77% ee. Of the alkyl glyoxylates, the highest enantiomeric excess was obtained for **2c** having the bulky *tert*-butyl group (entry 5). In contrast, for alkyl glyoxals **2e–g**, the best results were obtained for **2e**, which contained an *n*-alkyl substituent. However, a drop in enantioselectivity was observed for arylglyoxals **2h–i**. As regards the solvent, the change of CH_2Cl_2 for $MeNO_2$ had virtually no influence for alkyl glyoxals, but it was crucial in the case of arylglyoxals **2h–i**. Much better enantioselectivity was observed when the reaction was conducted in $MeNO_2$ (cf. entries 14–17).

Table 4. Enantioselective allylation of 2-oxoaldehydes catalyzed by **1b**[a]



2a-i **4a-i**

Entry	Aldehyde	R	Solvent	Yield (%)[b]	ee (%)[c]
1	**2a**	OBu^n	CH_2Cl_2	80	61
2	**2a**	OBu^n	$MeNO_2$	78	70
3	**2b**	OPr^i	CH_2Cl_2	78	66
4	**2b**	OPr^i	$MeNO_2$	74	73
5	**2c**	OBu^t	CH_2Cl_2	76	76
6	**2c**	OBu^t	$MeNO_2$	65	73
7	**2d**	OBn	CH_2Cl_2	84	61
8	**2e**	Bu^n	CH_2Cl_2	81	75
9	**2e**	Bu^n	$MeNO_2$	70	77
10	**2f**	Pr^i	CH_2Cl_2	71	67
11	**2f**	Pr^i	$MeNO_2$	65	67
12	**2g**	Bu^t	CH_2Cl_2	82	65
13	**2g**	Bu^t	$MeNO_2$	80	66
14	**2h**	Ph	CH_2Cl_2	78	14
15	**2h**	Ph	$MeNO_2$	74	36
16	**2i**	Furyl	CH_2Cl_2	75	15
17	**2i**	Furyl	$MeNO_2$	70	40

[a] The reactions were carried out using 1 mmol of 2-oxoaldehyde, 2 mol % of **1b**, and 1.1–1.2 mmol of allyltributyltin, in 1 ml of solvent, at 20 °C for 3–4 h.
[b] Isolated yield.
[c] The enantiomeric excess was determined by GC on a capillary chiral β-dex 120 column.

Complex **1b** catalyzed also the addition of allyltributyltin to active ketones, e.g., methyl pyruvate, in good yield but, unfortunately, with practically no enantioselectivity.

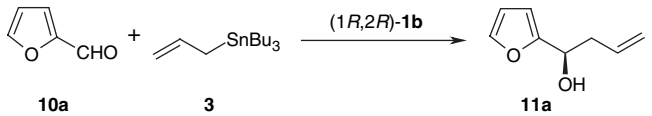
The absolute configuration of products **4a–d** derived from glyoxylates was determined by correlation with 1,2-pentanediol[17a] obtained via hydrogenation followed by $LiAlH_4$ reduction. In all cases where the chromium complexes (1*R*,2*R*)-**1b**, **5a–c**, and (1*R*,2*R*)-**6a** were used (with the exception of (1*R*,2*R*)-**6b**), the allylation product had the (*R*)-configuration.

2.2. Allylation of nonactivated aldehydes

The next stage of our study was an attempt to use salen–chromium complexes for allylation of simple aromatic and aliphatic aldehydes. As a model allylation, we chose the reaction of furfural (**10a**) with allyltributyltin in dichloromethane. Under the conditions similar to the ones used for glyoxylates and in the presence of **1b**, the reaction was very slow (Table 5, entry 1), leading, after three days, to the expected product with 56% ee, in a yield of ca. 10%. Unfortunately, the (salen)Cr(III) complexes are rather weak Lewis acids compared to the typical catalysts used for these reactions.[12] We tried to optimize the reaction conditions, e.g., by increasing temperature to 60 °C, but this change did not improve the yield satisfactorily, even when the reaction was carried out without any solvent. Addition of molecular sieves raised the yield to 46%, but the results were still unsatisfactory (entry 2). We concluded therefore that in the case of simple aldehydes and allyltributyltin, in the presence of **1b**, this reaction was apparently ineffective under ambient conditions.

We finally succeeded when high-pressure conditions (ca. 10 kbar) were applied.[20] More than 20 years ago, Yamamoto et al.[28] had found that allylic stannanes reacted with

Table 5. Results of the model reaction of furfural (**10a**) with allyltributyltin[a]



10a **3** **11a**

Entry	Catalyst	Mol % of catalyst	Concentration of **2a** (mol/L)	Pressure (bar)	Solvent	Time (h)	Yield (%)[b]	ee (%)[c]
1	**1b**	2	1.4	1	CH_2Cl_2	72	10	56
2	**1b**	2+4 Å MS	1.4	1	CH_2Cl_2	72	46	58
3	**1b**	2	0.5	7000	CH_2Cl_2	24	71	62
4	**1b**	2	0.5	10,000	CH_2Cl_2	24	91	67
5	**1b**	2+4 Å MS	0.5	10,000	CH_2Cl_2	24	95	52
6	no cat.	—	0.5	10,000	CH_2Cl_2	24	17	0
7	**1b**	5	0.5	10,000	CH_2Cl_2	24	94	68
8	**1b**	1	0.5	10,000	CH_2Cl_2	24	82	64
9	**1b**	0.5	0.5	10,000	CH_2Cl_2	24	69	61
10	**1b**	2	1.0	10,000	CH_2Cl_2	24	94	68
11	**1b**	1	1.5	10,000	CH_2Cl_2	24	89	67
12	**1b**	2	0.5	10,000	$CHCl_3$	24	91	66
13	**1b**	2	0.5	10,000	$(CH_2Cl)_2$	24	84	67
14	**1b**	2	0.5	10,000	$^{i}PrNO_2$	24	56	71
15	**1a**	2	0.5	10,000	CH_2Cl_2	24	67	66
16	**6a**	2	0.5	10,000	CH_2Cl_2	24	81	20
17[d]	**1b**	2	0.5	10,000	CH_2Cl_2	24	92	60

[a] High-pressure reactions were carried out in 2 ml Teflon ampoule using 1.1 equiv of allyltributyltin at 20 °C.
[b] The yield was determined by GC.
[c] The enantiomeric excess was determined by GC on capillary chiral β-dex 120 column.
[d] Instead of allyltributyltin, 1.1 equiv of allyltrimethyltin was used.

aldehydes at room temperature under high-pressure (10 kbar) without any catalyst. This procedure is a mild method for the allylation of aldehydes, which may be useful for preparation of the labile, thermally unstable, and acid-sensitive compounds. To the best of our knowledge, this high-pressure methodology has not been used for enantioselective allylation. Nonetheless, there are in the literature[29] some examples of diastereoselective allylation of chiral aldehydes, e.g., α-amino aldehydes.

Not only did high-pressure accelerate the reaction rate, but also increased the enantioselectivity from 56 to 67% ee (Table 5, entries 1, 3, and 4); the best results were achieved under a pressure of 10 kbar. Unfortunately, addition of molecular sieves to the reaction mixture under high-pressure conditions reduced the enantiomeric excess (entry 5). Unlike in numerous other enantioselective procedures, a catalyst concentration of 2 mol % proved to be sufficient in this method for effective allylation of furfural to afford the expected homoallylic alcohols in high yield of ca. 90% (e.g., entry 4). To compare, an analogous reaction, performed without any catalyst, proceeded with considerably lower yield (entry 6). This means that the (salen)$CrBF_4$ complexes, although rather weak Lewis acids, have a strong influence on the rate of the investigated reaction conducted under high-pressure conditions.

We continued our research with an attempt to optimize the reaction conditions at 10 kbar. We investigated several factors such as the amount of the catalyst, solvents, additives, and concentration of the aldehyde. The amount of the catalyst in the range of 0.5–5 mol % slightly influenced enantioselectivity (cf. entries 4 and 7–9). What is very promising in this method is that even 0.5 mol % of **1b** gave quite good results (entry 9). Allylation proceeded, without lowering enantiomeric excess, at a higher concentration of the aldehyde (entry 10), even when the 2 ml Teflon ampoule (cf. Section 4) was filled with 3 mmol of **10a**, 1 mol % of **1b**, 1 ml of allyltributyltin, and filled up with CH_2Cl_2 (entry 11). The possibility of using concentrated reaction mixtures is a great advantage in view of the limitation of the volume of high-pressure chambers (the average volume is 50 ml). Unfortunately, the reaction did not work well without solvent for furfural and other aldehydes insoluble in allyltributyltin.

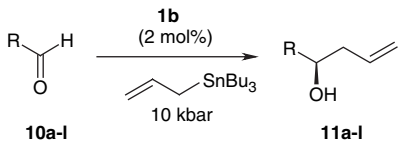
Of the solvents examined besides CH_2Cl_2, also $CHCl_3$, 1,2-dichloroethane, CH_2Cl_2/hexane (1:1), and $^{i}PrNO_2$ proved useful (e.g., entries 12–14). The latter gave the highest enantiomeric excess, but the yield was lower.

We also tested the applicability of two other chromium complexes for this reaction. The commercially available complex **1a**, bearing the chloride counterion, catalyzed the reaction practically with the same enantioselectivity (cf. entries 4 and 15), but in lower yield. We also investigated the chromium chloride complex **6a** having another widely used chiral 1,2-diamine, i.e., 1,2-diphenylethylenediamine, though the enantioselectivity decreased markedly (entry 16). The more reactive allyltrimethyltin in a non-catalyzed reaction[28] could also be used instead of allyltributyltin, although the enantiomeric excess was slightly lower (entry 17).

The next step was an endeavor to show the usefulness of the high-pressure method in reactions using other aldehydes. Table 6 summarizes the results achieved for the reactions of a wide variety of aromatic and aliphatic aldehydes with 1.1 equiv of allyltributyltin, in the presence of 2 mol % of catalyst **1b**.

The enantiomeric excesses obtained for aromatic aldehydes **10a–f** ranged from 55 to 68% ee and the yields exceeded

Table 6. High-pressure enantioselective allylation of aryl and alkyl aldehydes catalyzed by (1*R*,2*R*)-**1b**[a]



10a-l **11a-l**

Entry	Aldehyde	R	Yield (%)[b]	ee (%)[c]
1	**10a**	Furyl	89	67 (*R*)
2	**10b**	5-Methylfuryl	79	61
3	**10c**	Ph	82	55 (*R*)
4	**10d**	4-ClC_6H_4	81	60
5	**10e**	2-ClC_6H_4	85	68
6	**10f**	4-$O_2NC_6H_4$	83	68
7	**10g**	*n*-C_4H_9	52	75 (*S*)
8	**10h**	Pr^i	86	68
9	**10i**	*c*-C_6H_{11}	82	79 (*R*)
10	**10j**	Bu^t	70	35
11	**10k**	PhCH=CH	84	65 (*R*)
12	**10l**	Ph_3COCH_2	86	53 (*R*)

[a] Conditions: 1 mmol of the aldehyde, 2 mol % of (1*R*,2*R*)-(salen)$CrBF_4$ (**1b**), 1.1 mmol of allyltributyltin in CH_2Cl_2 in 2 ml Teflon ampoule; 10 kbar at 20 °C for 24 h.
[b] Isolated yield.
[c] The enantiomeric excess was determined by GC on a capillary chiral β-dex 120 column.

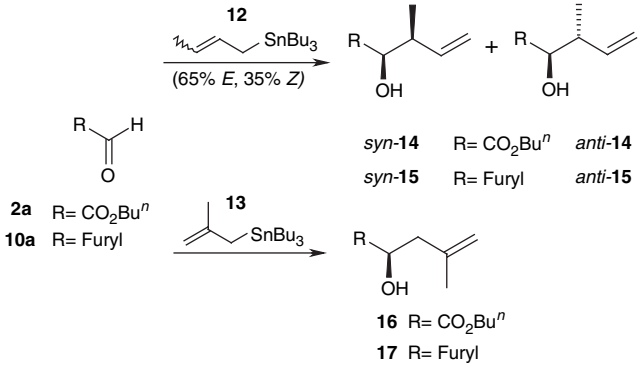
79%. This methodology also worked well for aliphatic aldehydes (e.g., **10g–i**), although the yields were sometimes less satisfactory. The lowest enantiomeric excess was obtained for the bulky pivalaldehyde **10j** (entry 10); it seems that the catalyst **1b** does not perform well for sterically demanding aldehydes such as pivalaldehyde. Allylation of α,β-unsaturated cinnamaldehyde **10k** (entry 11) and the glycolaldehyde derivative **10l** (entry 12) also proceeded in good yield and at moderate enantiomeric excess (65 and 53%, respectively).

2.3. Methyl-substituted allylating reagents

In our investigations, we also used other substituted allylating reagents such as crotyltributyltin **12** (as an *E*/*Z* mixture, 65:35) and methallyltributyltin **13**. In the case of **12** in the reaction with *n*-butyl glyoxylate, *syn*-**14** was formed as a main product with enantioselectivity of up to 75% ee (Table 7, entries 1–3). The results concerning the enantioselectivity for the *syn*-adduct were very similar to those obtained for simple allylations (Table 3). The minor *anti* product (23–29%) was isolated with a low enantioselectivity of up to 40% ee. Our results for crotylation were similar to those obtained by Mikami.[13]

When the allylating reagent was used in excess (2 equiv), a slight increase in diastereoselectivity was observed. The unreacted tin compound was investigated in the post-reaction mixture. It appeared that the contents of the *Z* isomer rose from 35 to 55%. This means that the *E*-isomer is more reactive. When less than the stoichiometric amount of the allylating reagent was used (**2a**:**12**=2:1), the diastereoselectivity slightly decreased to 66:34. Regardless of the amount of the allylating reagent (*E*/*Z*=65:35), the enantiomeric excesses for the *syn*-**14** product were similar. In the case of high-pressure crotylation of furfural (entry 4), the selectivities were similar to those obtained for *n*-butyl glyoxalate.

Table 7. Allylation of **2a** or **10a** with **12** and **13** catalyzed by **1b**[a]



Entry	Aldehyde	Allyl reagent	Solvent	Pressure (bar)	Yield (%)[b]	*syn* (ee (%))/ *anti* (ee (%))[c]
1	**2a**	**12**	CH_2Cl_2	1	69	71 (70)/29 (24)
2	**2a**	**12**	$MeNO_2$	1	62	72 (71)/28 (25)
3	**2a**	**12**	No solvent	1	70	77 (75)/23 (40)
4	**10a**	**12**	CH_2Cl_2	10,000	75	70 (68)/30 (43)
5	**2a**	**13**	CH_2Cl_2	1	80	(37)
6	**2a**	**13**	$MeNO_2$	1	79	(38)
7	**10a**	**13**	CH_2Cl_2	10,000	82	(23)

[a] The reactions were carried out using 1 mmol of aldehyde, 2 mol % of **1b**, and 1.5 mmol of **12** or **13**, in 1 ml of solvent, at 20 °C for 3–4 h under 1 bar and 24 h under 10 kbar.
[b] Isolated yield.
[c] The enantiomeric excesses were determined by GC on a capillary chiral β-dex 120 column.

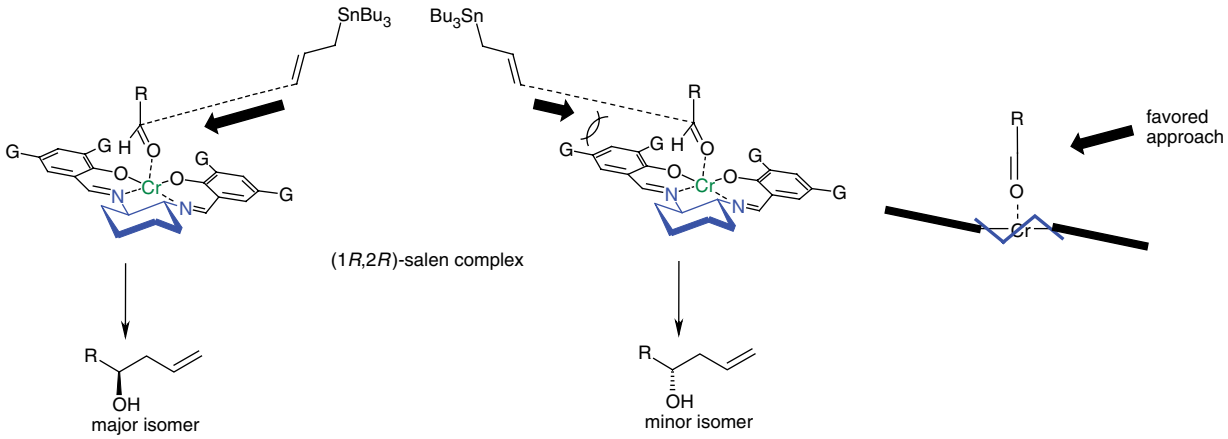
In spite of good yield, the enantioselectivity was much lower for methallyltributyltin (**13**) (up to 38%, entries 5–7). It seems that the allylating reagents containing any substituents (e.g., Me) at the β-position are poor in the studied reactions.

2.4. The stereochemical model

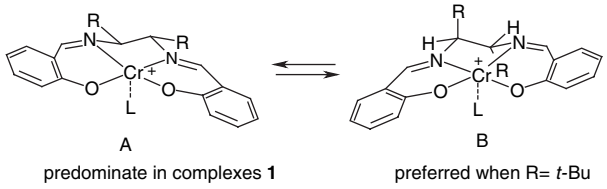
Rationalization of our results obtained in this work can be based on the stereochemical model shown in Scheme 3.

Our model originates from two sources: (i) from the conformational analysis of metallosalen complexes and their influence on the asymmetric induction of catalytic epoxidation of olefins presented by Katsuki et al.[27,30] and (ii) from the X-ray analysis of classic (salen)Co(III)SbF_6 complex modified by two molecules of benzaldehyde in the axial positions, published recently by Rawal et al.[31]

The crucial conclusion given by Katsuki et al. concerns the nonplanar, usually stepped conformation of the complex. To prove this assumption they presented some experiments in which it was shown that achiral complex modified by a chiral axial ligand (e.g., chiral amine or *N*-oxide) is able to catalyze epoxidation of an olefin in an enantioselective manner.[27] The chiral additive shifts the equilibrium to one of the enantiomeric conformers of the achiral complex (Scheme 4, in this case R=H, L=chiral ligand). They also synthesized a chiral complex bearing a 1,2-diamine moiety with a carboxylate group, which coordinates to the metal center, reversing the conformation of the catalyst, as well as the sense of asymmetric induction.[30] These experiments as well as some crystal structures of metallosalen complexes confirm the origin of asymmetric induction.



Scheme 3. The stereochemical model.



Scheme 4. Equilibrium of conformational isomers of *trans*-(salen)Cr(III) complexes.

In turn, the Rawal proposal based on the crystal structure[31] pointed out that the aldehyde molecules are not oriented perpendicularly to the complex plane, which is slightly deformed, and the aldehyde hydrogen is located close to the oxygen atoms in the complex, as shown in Scheme 3. Therefore, the approach of the allylating reagent to the complexed aldehyde should occur from the outer side. The direction of asymmetric induction we observed is in a good agreement with the proposed stereochemical model. When the salen–chromium complexes based on 1,2-diaminocyclohexane (**1a**, **1b**) and 1,2-diphenylethylenediamine (**6a**) of (*R*,*R*)-configuration were used, the same direction of the asymmetric induction was obtained, and the major product formed was most usually the homoallylic alcohol having the (*R*)-configuration.

A reversion of the product configuration and a decrease in enantioselection (Table 2, entry 6) were observed when using the complex **6b** based on (1*R*,2*R*)-1,2-di-*tert*-butyletylenediamine, the ligand having the same sense of chirality as the ones discussed above. This is caused by the change in the conformation of the complex (Scheme 4). The reason is that the *tert*-butyl groups at the 1,2-positions cannot adopt the pseudoequatorial orientation because of steric reasons, and the predominating conformer B promotes formation of the second enantiomer. Both our observations and the X-ray structure of this complex[32] support the proposed stereochemical model.

3. Conclusion

Summing up, we have developed a novel method for the enantioselective allylation of aldehydes with tin allylating reagents, catalyzed by chromium–salen complexes. The reaction is highly reproducible and not very sensitive to external factors such as oxygen or moisture and requires only 1–2 mol % of the catalyst. The yields are good, although the enantioselectivites at this stage of our studies are moderate (usually 50–79% ee). For active aldehydes such as glyoxylates and glyoxals, the allylation works well under ambient conditions even with no solvents and on large scale. Allylation of simple aromatic and aliphatic aldehydes requires application of a high-pressure technique.

4. Experimental

4.1. General remarks

All reported NMR spectra were recorded in $CDCl_3$ using a Varian Gemini spectrometer at 200 MHz (^{1}H NMR) and 50 MHz (^{13}C NMR). Chemical shifts of ^{1}H NMR are reported as δ values relative to TMS peak defined at δ=0.00. Chemical shifts of ^{13}C NMR are reported as δ values relative to $CDCl_3$ peak defined at δ=77.0. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; dt, doublet of triplets; m, multiplet. High resolution mass spectra (HRMS) were recorded on a AMD 604 or Mariner PE Biosystems unit using the EI or ESI technique, respectively. Optical rotations were measured using a JASCO DIP-360 polarimeter. Analytical TLC was carried out on commercial plates coated with 0.25 mm of Merck Kieselgel 60. Preparative flash silica chromatography was performed using Merck Kieselgel 60 (230–400 mesh). Enantiomeric excesses of the products were determined using GC and HPLC techniques. GC analyses were carried out on Trace 2000 GC (Thermo Finnigan) apparatus equipped with a flame ionization detector (FID) and a chiral capillary β-dex 120 column (permethyl-β-cyclodextrin, 30 m×0.25 mm I.D. Supelco, Bellefonte, USA) employing nitrogen as a carrier gas. Data were collected under the following conditions: pressure of nitrogen—100 kPa, injector temperature—200 °C, detector temperature—250 °C. The oven temperature varied according to types of products (vide infra). HPLC analyses were performed on chromatograph fitted with the diode array detector (DAD) and Chiracel OD-H column eluted with 4% *iso*-propanol in hexane.

4.2. Materials

All commercially available chemicals were used as received unless otherwise noted. Reagent-grade solvents were dried and distilled prior to use. (*R*,*R*)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride (**1a**) was purchased from Aldrich and used for the preparation of catalysts **1b** and **1c**.[5a] Remaining chromium(III) complexes (**5**–**8**) and salen complexes of other metals (**1d**–**m**) were prepared according to the known procedures, starting from appropriate salen ligand and metal salt.[4a,33] The salen ligands were synthesized according to the method described by Jacobsen et al.[34]

n-Butyl (**2a**) and *iso*-propyl (**2b**) glyoxylates were prepared by oxidative cleavage of the appropriate tartrate esters using $NaIO_4$ in water,[35] and *tert*-butyl glyoxylate (**2c**) was prepared by ozonolysis of di-*tert*-butyl fumarate.[36] The glyoxylates **2a**–**c** were distilled in the presence of P_2O_5 prior to use. Benzyl glyoxylate (**2d**) was prepared using $Pb(OAc)_4$ in CH_2Cl_2. Distillation of **2d** in the presence of P_2O_5 leads to decomposition. The alkyl glyoxals were prepared from hexanal, isovaleraldehyde, and pinacolone by oxidation with SeO_2/H_2O in boiling MeOH[37] and arylglyoxylates from acetophenone and acetylfuran in boiling dioxane.[38] The allyltributyltin reagents were prepared from bis(tributyltin)oxide and the appropriate allyl Grignard reagent according to the known procedure.[39] Allyltributyltin (**3**) can be purchased from Aldrich.

4.3. General procedure for the allylation of activated aldehydes

To a solution of metallosalen complex (usually 2 mol %) in appropriate solvent (usually 1 ml), 2-oxoaldehyde (**2**) (1 mmol) was added. After 10 min, allyltributyltin (**3**) (365 mg, 1.1 mmol) was dropped into the solution, and stirred at room temperature. After 3–4 h the reaction mixture was diluted with wet Et_2O, dried and after concentration subjected to chromatography using hexane/AcOEt 9:1→8:2 as an eluent.

4.4. General procedure for the high-pressure allylation

The 2-ml Teflon ampoule was charged with (salen)$CrBF_4$ **1b** (usually 13.7 mg, 2 mol %), ca. 1 ml of the solvent (usually CH_2Cl_2), followed by the aldehyde (usually 1 mmol) and allyltributyltin (1.1 equiv). Finally, the ampoule was filled up with solvent, closed, and placed in a high-pressure chamber, and the pressure was slowly increased to 10 kbar at 20 °C. After stabilization of the pressure, the reaction mixture was kept under these conditions for 24 h. After decompression, the reaction mixture was diluted with wet Et_2O, and dried over $MgSO_4$. After evaporation of solvents, the residue was chromatographed on a silica gel column using hexane/AcOEt as an eluent.

4.4.1. *n*-Butyl 2-hydroxypent-4-enoate (4a). $[\alpha]_D^{25}$ +2.0 (*c* 5.01, $CHCl_3$, 61% ee, major (*R*)-**4a**); bp 64–65 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.94 (t, *J*=7.3 Hz, 3H), 1.30–1.48 (m, 2H), 1.58–1.72 (m, 2H), 2.36–2.66 (m, 2H), 2.84 (d, *J*=5.9 Hz, 1H), 4.13–4.31 (m, 3H), 5.11–5.21 (m, 2H), 5.71–5.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.6 (CH_3), 19.0 (CH_2), 30.5 (CH_2), 38.7 (CH_2), 65.6 (CH_2), 69.9 (CH), 118.7 (CH_2), 132.5 (CH), 174.5 (C); IR (film) 3475, 2962, 1737, 1642, 1466, 1210, 1086, 918 cm^{-1}; HRMS calcd for $C_9H_{16}O_3$: 172.1099, found: 172.1104; GC: *T*=120 °C, $t_{R(R)\text{-}\mathbf{4a}}$=13.6 min, $t_{R(S)\text{-}\mathbf{4a}}$=14.1 min, or analyzed as a trifluoroacetate, *T*=100 °C, $t_{R(R)\text{-}\mathbf{4c}}$=14.3 min, $t_{R(S)\text{-}\mathbf{4c}}$=14.6 min.

4.4.2. *iso*-Propyl 2-hydroxypent-4-enoate (4b). Bp 78–80 °C/14 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.27 (d, *J*=6.2 Hz, 3H), 1.28 (d, *J*=6.2 Hz, 3H), 2.35–2.65 (m, 2H), 2.86 (d, *J*=5.9 Hz, 1H), 4.17–4.26 (m, 1H), 5.10 (sept, *J*=6.2 Hz, 1H), 5.10–5.20 (m, 2H), 5.70–5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=21.7 (CH_3), 21.8 (CH_3), 38.7 (CH_2), 69.6 (CH), 69.9 (CH), 118.6 (CH_2), 132.5 (CH), 174.0 (C); IR (film) 3474, 2982, 1732, 1642, 1467, 1219, 1107, 916 cm^{-1}; HRMS calcd for $C_8H_{14}O_3Na$: 181.0835, found: 181.0821; GC: *T*=110 °C, $t_{R(R)\text{-}\mathbf{4b}}$=9.6 min, $t_{R(S)\text{-}\mathbf{4b}}$=9.8 min, or analyzed as a trifluoroacetate, *T*=90 °C, $t_{R(R)\text{-}\mathbf{4c}}$=8.2 min, $t_{R(S)\text{-}\mathbf{4c}}$=8.4 min.

4.4.3. *tert*-Butyl 2-hydroxypent-4-enoate (4c). ^{1}H NMR ($CDCl_3$) δ=1.49 (s, 9H), 2.33–2.62 (m, 2H), 2.88 (d, *J*=5.9 Hz, 1H), 4.14 (dt, *J*=5.9, 4.8 Hz, 1H), 5.09–5.21 (m, 2H), 5.71–5.92 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=28.0 (3×CH_3), 38.8 (CH_2), 69.9 (CH), 82.5 (C), 118.4 (CH_2), 132.6 (CH), 173.7 (C); IR (film) 3477, 2960, 2932, 1739, 1642, 1464, 1370, 1289, 1159, 1108, 843 cm^{-1}; HRMS calcd for $C_9H_{16}O_3Na$: 195.0997, found: 195.1016; GC: *T*=120 °C, $t_{R(S)\text{-}\mathbf{4c}}$=8.2 min, $t_{R(R)\text{-}\mathbf{4c}}$=8.5 min, or analyzed as a trifluoroacetate, *T*=80 °C, $t_{R(R)\text{-}\mathbf{4c}}$=14.5 min, $t_{R(S)\text{-}\mathbf{4c}}$=15.0 min.

4.4.4. Benzyl 2-hydroxypent-4-enoate (4d). ^{1}H NMR ($CDCl_3$) δ=2.38–2.50 (m, 1H), 2.52–2.67 (m, 1H), 2.84 (d, *J*=6.0 Hz, 1H), 4.28–4.37 (m, 1H), 5.06–5.18 (m, 2H), 5.22 (s, 2H), 5.69–5.89 (m, 1H), 7.35–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=38.6 (CH_2), 67.4 (CH_2), 70.0 (CH), 118.8 (CH_2), 128.4 (2×CH), 128.6 (CH), 128.7 (2×CH), 132.3 (CH), 135.1 (C), 174.2 (C); IR (film) 3464, 3068, 2951, 1738, 1642, 1456, 1214, 1199, 1134, 1083, 919, 698 cm^{-1}; HRMS calcd for $C_{12}H_{14}O_3Na$: 229.0841, found: 229.0813; GC: analyzed as a isopropylidene derivative of pent-4-ene-1,2-diol; hydroxyester **4d** was reduced by $LiAlH_4$ followed by protection with acetone in the presence of TsOH, *T*=90 °C, $t_{R(R)}$=7.3 min, $t_{R(S)}$=7.5 min.

4.4.5. Chemical correlation of 4a–d with (*R*)-1,2-pentanediol. A mixture of *n*-butyl 2-hydroxypent-4-enoate (**4a**) (350 mg, 2 mmol) (obtained in the reaction catalyzed by (1*R*,2*R*)-**1b**), Pd/C (50 mg) in MeOH (20 ml) was stirred under H_2 for 12 h. After that time the catalyst was filtered off through a short pad of Celite and the filtrate concentrated to yield 354 mg (quant.) of *n*-butyl 2-hydroxy-pentanoate. The crude product was dissolved in THF (2 ml) and added to the stirred suspension of $LiAlH_4$ (90 mg, 2.4 mmol) in THF (5 ml). Then the mixture was refluxed for 2 h, cooled to rt, and the excess of $LiAlH_4$ was decomposed with 10% water in THF and aqueous NaOH. The resulting mixture was extracted with Et_2O (3×15 ml), washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and concentrated. The product was purified by flash chromatography to give 133 mg (1.3 mmol, 64%) of the colorless oil. $[\alpha]_D^{22}$ +11.4

(*c* 2.8, EtOH, 61% ee), lit.[17a]: $[\alpha]_D^{20}$ −15.5 (*c* 0.81, EtOH) for (*S*)-isomer.

4.4.6. 4-Hydroxynon-1-en-5-one (4e). ^{1}H NMR ($CDCl_3$) δ=0.92 (t, *J*=7.2 Hz, 3H), 1.24–1.42 (m, 2H), 1.54–1.68 (m, 2H), 2.30–2.42 (m, 1H), 2.43–2.52 (m, 2H), 2.56–2.70 (m, 1H), 3.52 (d, *J*=5.1 Hz, 1H), 4.21–4.29 (m, 1H), 5.09–5.20 (m, 2H), 5.68–5.89 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.8 (CH_2), 22.3 (CH_2), 25.5 (CH_2), 37.9 (CH_2), 38.2 (CH_2), 75.8 (CH), 118.4 (CH_2), 132.5 (CH), 211.5 (C); IR (film) 3425, 2960, 1714, 1404, 1181, 920 cm^{-1}; HRMS calcd for $C_9H_{16}O_2$: 156.1150, found: 156.1141; GC: *T*=130 °C, t_{R1}=9.4 min, t_{R2}=9.8 min.

4.4.7. 4-Hydroxy-2-methylhept-6-en-3-one (4f). ^{1}H NMR ($CDCl_3$) δ=1.13 (dd, *J*=6.8, 6.8 Hz, 6H), 2.29–2.45 (m, 1H), 2.56–2.70 (m, 1H), 2.84 (sept, *J*=6.8 Hz, 1H), 3.51 (d, *J*=5.4 Hz, 1H), 4.42 (ddd, *J*=6.4, 5.4, 4.7 Hz, 1H), 5.09–5.20 (m, 2H), 5.68–5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=16.9 (CH_3), 19.1 (CH_3), 35.8 (CH), 37.9 (CH_2), 73.9 (CH), 118.0 (CH_2), 132.3 (CH), 214.9 (C); IR (film) 3464, 2971, 1710, 1627, 1468, 1385, 1024, 920 cm^{-1}; HRMS calcd for $C_8H_{14}O_2$: 142.0994, found: 142.0995; *T*=120 °C, t_{R1}=9.1 min, t_{R2}=9.4 min.

4.4.8. 4-Hydroxy-2,2-dimethylhept-6-en-3-one (4g). ^{1}H NMR ($CDCl_3$) δ=1.22 (s, 9H), 2.18–2.34 (m, 1H), 2.50–2.64 (m, 1H), 3.22 (d, *J*=8.1 Hz, 1H), 4.59 (ddd, *J*=8.1, 7.1, 3.8 Hz, 1H), 5.08–5.19 (m, 2H), 5.69–5.90 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=26.7 (3×CH_3), 39.2 (CH_2), 42.8 (C), 71.8 (CH), 118.3 (CH_2), 132.8 (CH), 216.9 (C); IR (film) 3462, 2969, 1704, 1480, 1053, 971, 917 cm^{-1}; HRMS calcd for $C_9H_{16}O_2$: 156.1150, found: 156.1143; GC: *T*=120 °C, t_{R1}=8.3 min, t_{R2}=8.6 min.

4.4.9. 2-Hydroxy-1-phenylpent-4-en-1-one (4h). ^{1}H NMR ($CDCl_3$) δ=2.28–2.43 (m, 1H), 2.61–2.75 (m, 1H), 3.74 (d, *J*=6.6 Hz, 1H), 4.96–5.12 (m, 2H), 5.17 (dt, *J*=6.6, 4.1 Hz, 1H), 5.70–5.91 (m, 1H), 7.46–7.68 (m, 3H), 7.88–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=40.0 (CH_2), 72.6 (CH), 118.4 (CH_2), 128.5 (2×CH), 128.9 (2×CH), 132.4 (CH), 133.7 (C), 134.0 (CH), 201.2 (C); IR (film) 3458, 2921, 1682, 1598, 1450, 1263, 1073, 963, 691 cm^{-1}; HRMS calcd for $C_{11}H_{12}O_2$: 176.0837, found: 176.0841; enantiomeric excess determined by HPLC (Chiracel OD-H column, hexane/*i*-PrOH, 96:4, flow rate 1.0 ml/min, λ=240 nm) t_{R1}=7.7 min, t_{R2}=9.2 min.

4.4.10. 1-(Furan-2-yl)-2-hydroxypent-4-en-1-one (4i). ^{1}H NMR ($CDCl_3$) δ=2.40–2.56 (m, 1H), 2.65–2.79 (m, 1H), 3.50 (d, *J*=6.8 Hz, 1H), 4.92 (dt, *J*=6.8, 4.1 Hz, 1H), 5.03–5.14 (m, 2H), 5.72–5.93 (m, 1H), 6.61 (dd, *J*=3.6, 1.7 Hz, 1H), 7.34 (dd, *J*=3.6, 0.6 Hz, 1H), 7.66 (dd, *J*=1.7, 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=39.7 (CH_2), 72.9 (CH), 112.6 (CH), 118.5 (CH_2), 119.0 (CH), 132.5 (CH), 147.1 (CH), 150.2 (C), 189.6 (C); IR (film) 3448, 2953, 1726, 1660, 1437, 1279, 1171, 986 cm^{-1}; HRMS calcd for $C_9H_{10}O_3$: 166.0630, found: 166.0622; GC: *T*=130 °C, t_{R1}=16.5 min, t_{R2}=17.3 min.

4.4.11. *n*-Butyl 2-hydroxy-4-methylpent-4-enoate (16). ^{1}H NMR ($CDCl_3$) δ=0.95 (t, *J*=7.2 Hz, 3H), 1.30–1.49 (m, 2H), 1.58–1.73 (m, 2H), 1.80 (br s, 3H), 2.30–2.43 (m, 1H), 2.48–2.59 (m, 1H), 2.77 (d, *J*=5.8 Hz, 1H), 4.19 (t, *J*=6.6 Hz, 2H), 4.28–4.38 (m, 1H), 4.80–491 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=13.6 (CH_3), 19.0 (CH_2), 22.5 (CH_3), 30.6 (CH_2), 42.7 (CH_2), 65.5 (CH_2), 69.1 (CH), 113.9 (CH_2), 140.9 (C), 174.8 (C); IR (film) 3483, 2961, 1735, 1649, 1458, 1202, 1102, 893 cm^{-1}; HRMS calcd for $C_{10}H_{18}O_3$: 186.1256, found: 186.1261; GC: analyzed as a trifluoroacetate, *T*=100 °C, t_{R1}=20.0 min, t_{R2}=20.6 min.

Homoallylic alcohols **11a–l**, **14**, **15**, and **17** are known and their NMR data are in agreement with those described in literature. In some cases the absolute configuration of the obtained homoallylic alcohols (**11a**, **11c**, **11i**, **11k**, and **11l**) was confirmed via measurement of optical rotation and comparison with literature data.

The enantiomeric excesses of the investigated homoallyl alcohols **11a–l** were determined by GC employing a capillary chiral β-dex 120 column, either directly or after derivatization. Alcohol **11k** was analyzed directly, **11a**, **11b**, **11d**, **11e**, **11f**, **11g**, **11h**, and **11j** as their *O*-trimethylsilyl derivatives, **11c** as an acetate, **11i** as a trifluoroacetate and **11l** as an isopropylidene derivative of pent-4-ene-1,2-diol.

Chromatographic parameters of enantioseparation of homoallylic alcohols or their derivatives are given in Table 8.

Table 8. Chromatographic parameters of enantioseparation of homoallylic alcohols **11a–l**

Compound	R	OPG	*T* (°C)	t_{R1} (min)	t_{R2} (min)
11a	Furyl	OTMS	85	18.6 (*R*)	19.1 (*S*)
11b	5-Methylfuryl	OTMS	90	24.6	25.2
11c	Ph	OAc	110	36.7 (*S*)	37.2 (*R*)
11d	4-ClC_6H_4	OTMS	125	25.6	26.3
11e	2-ClC_6H_4	OTMS	110	26.8	27.5
11f	4-$O_2NC_6H_4$	OTMS	150	40.7	41.7
11g	*n*-C_4H_9	OTMS	75	12.4	12.7
11h	Pr^i	OTMS	75	6.9	7.2
11i	*c*-C_6H_{11}	O_2CCF_3	85	27.7 (*S*)	28.3 (*R*)
11j	Bu^t	OTMS	80	9.2	9.8
11k	PhCH=CH	OH	155	27.5 (*R*)	28.2 (*S*)
11l	Ph_3COCH_2	[a]	90	7.3 (*R*)	7.5 (*S*)

[a] Analyzed as a isopropylidene derivative of pent-4-ene-1,2-diol.

Chromatographic parameters of enantioseparation of methyl-substituted homoallylic alcohols:

14[13]—analyzed as a isopropylidene derivative of 3-methylpent-4-ene-1,2-diol: *T*=80 °C, $t_{R1(syn)}$=17.9 min, $t_{R2(syn)}$=18.3 min, $t_{R1(anti)}$=19.2 min, $t_{R2(anti)}$=20.0 min.
15—analyzed as a *O*-allylated alcohol: *T*=80 °C, $t_{R1(syn)}$=41.3 min, $t_{R2(syn)}$=41.9 min, $t_{R1(anti)}$=44.9 min, $t_{R2(anti)}$=45.9 min.
17—analyzed as an OTMS protected alcohol: *T*=90 °C, t_{R1}=22.4 min, t_{R2}=23.1 min.

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