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DIANANE-Cr^{III}-salen Complexes as Highly Enantioselective Catalysts for Hetero-Diels–Alder Reactions of Aldehydes with Dienes

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A new type of chromium-salen complex bearing DIANANE (*endo*,*endo*-2,5-diaminonorbornane) as chiral backbone has been synthesized and applied to the hetero-Diels–Alder reaction of Danishefsky's diene with various aldehydes. The reactions afford the corresponding 2-substituted 2,3-dihydro-4*H*-pyran-4-ones in high yields and enantioselectivities (up to 96 % *ee*). The effect of different counteranions of the complex on reactivity as well as enantioselectivity has been investigated. Besides Danishefsky's diene, reaction of the less reactive 1-methoxybutadiene with benzaldehyde and ethyl glyoxylate can be effected by the chromium catalysts as well.

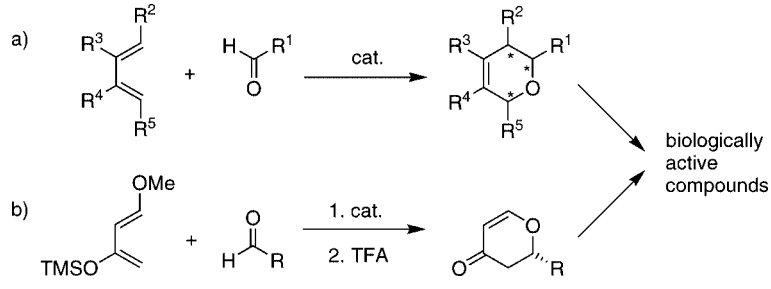
Introduction

The asymmetric hetero-Diels–Alder (HDA) cycloaddition of dienes with aldehydes is a powerful and well-investigated reaction in organic synthesis. In principle, up to three new stereocenters can be formed in a single step (see Scheme 1, equation a).

The chiral pyran derivatives generated by this reaction are versatile building blocks for the synthesis of many biologically active compounds including, for example, carbohydrates,[1] pheromones,[2] antitumor agents,[3] and sesquiterpenoids.[4]

Since the discovery by Danishefsky et al.[5a] that Lewis acids catalyze the hetero-Diels–Alder reaction between aldehydes and electron-rich dienes such as 1-methoxy-3-(trimethylsilyloxy)butadiene (Danishefsky's diene; see Scheme 1, equation b), a variety of chiral Lewis acid catalysts have been developed.[5b,6–17] It has been shown that different metal centers like Co^{II},[18,19] Cu^{II},[20,21] Rh^{II},[9,22] B^{III},[23] Al^{III},[6,24,25] Cr^{III},[7,10,11,26] Eu^{III},[27] Yb^{III},[28,29] Mn^{IV},[10,26] and Ti^{IV}[15,30,31] in combination with chiral ligands containing carboxamidate,[9] BINOL,[31–33] 3,3′-disubstituted BINOL,[6,12,24] salen,[7,10,19,26,34] bisoxazoline,[21,31,33,35] and triflylamide[29] catalyze the HDA cycloaddition. In this context, the catalysts developed by Ding et al.[12,13,36] and Jacobsen et al.[7,8,11,17] deserve special mention (Zn and Cr complexes, respectively) as enantioselectivities of up to 99% have been obtained for the cycloaddition of benzaldehyde to Danishefsky's diene.

While many catalytic systems give good yields and enantioselectivities in the enantioselective version of the HDA reaction of Danishefsky's diene with aldehydes, only a few methods for the [4+2] cycloaddition of less-electron-rich dienes with aldehydes have been developed so far. This reaction requires strong Lewis acid catalysts that can activate the aldehyde but which do not promote side reactions, for example polymerization of sensitive dienes such as 1-methoxybuta-1,3-diene. Very good results in the cycloaddition of 1-methoxybuta-1,3-diene derivatives with glyoxylates have been obtained by the method developed by Mi-



Scheme 1. HDA reaction of dienes with aldehydes (equation a) and of Danishefsky's diene with aldehydes (equation b).

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kami et al.[37] using the BINOL-Ti complex (*ee* up to 96%). However, at least 10 mol-% of the catalyst is necessary and the method requires substantial technical experience, as reported by Kalesse et al.[38] Excellent diastereo- and enantioselectivities in the reaction of several less reactive dienes (compared to Danishefsky's diene) with nonactivated aldehydes have been reported by Jacobsen et al. employing a Cr^{III} complex with a chiral tridentate Schiff-base ligand as catalyst.[8]

As far as salen ligands are concerned, substantial effort has been invested to varying the steric and electronic properties of the salicylic aldehyde moiety, whereas the influence of the diamine has been much less investigated. We decided to replace the usually employed 1,2-diamines like cyclohexanediamine by a 1,4-diamine with the aim of investigating how an increase in the N–N distance influences the reactivity and selectivity of the corresponding metal–salen complexes (Figure 1). Recently, we reported an effective enantioselective synthesis of DIANANE (**1**), which is a new chiral 1,4-diamine, and its corresponding salen ligand **2**.[39] Furthermore, the latter ligand has become commercially available. In this paper, we describe the synthesis of chiral Cr^{III}-salen complexes **3** bearing the DIANANE backbone and their use as catalysts for the asymmetric HDA reaction of dienes with aldehydes.

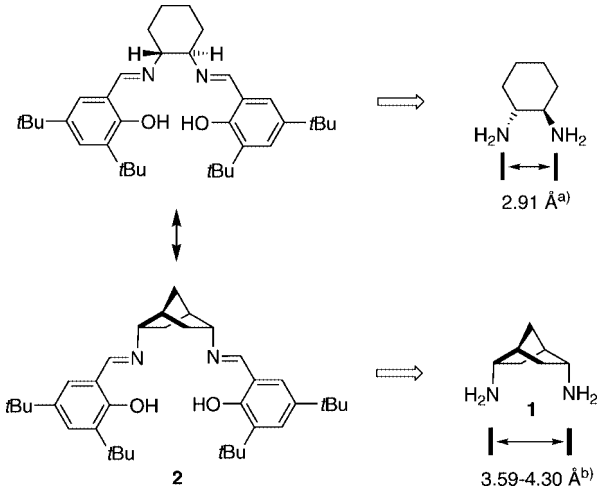


Figure 1. Salen ligands derived from *trans*-1,2-diaminocyclohexane and DIANANE, and the corresponding N–N distances. a) N–N distance in the ligand derived from 3,5-di-*tert*-butylsalicylic aldehyde[40]. b) N–N distances in various differently substituted salen ligands[39,41]

Results and Discussion

Preparation of the Chromium-Salen Complexes

The salen ligand **2** (Figure 1) was prepared according to our previous publication.[39] The corresponding Cr^{III}-salen complex **3a** (Figure 2) was synthesized following the procedure of Jacobsen et al.[7] with the exception that triethylamine had to be added in order to effect quantitative complex formation. First, the Cr^{II}-salen complex was formed by adding excess $CrCl_2$ to a solution of the deprotonated salen ligand **2** in thf under inert atmosphere and stirring for 12 h at room temperature. The Cr^{III} complex could be isolated in 78% yield by subsequent oxidation in air for 12 h, followed by an aqueous work-up. The perchlorate (**3b**), tosylate (**3c**), and tetrafluoroborate (**3d**) salts were obtained from the chloride **3a** upon treatment with the different silver salts in *tert*-butyl methyl ether (mtbe). Complex **3e** bearing BPh_4^- as counteranion was synthesized from **3b** upon reaction with $NaBPh_4$.

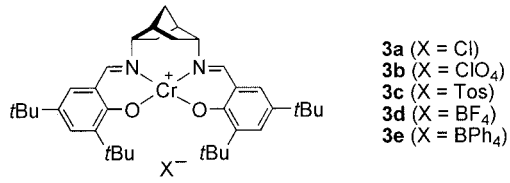
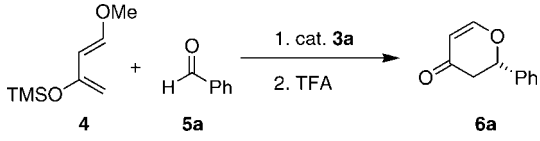


Figure 2. DIANANE-Cr^{III}-salen complexes **3a**–**e** bearing different counteranions.

Catalytic Asymmetric HDA Reaction of Danishefsky's Diene with Benzaldehyde

We first employed the chiral Cr^{III}-salen **3a** to optimize the reaction conditions for the HDA between Danishefsky's diene (**4**) and benzaldehyde (**5a**) [Equation (1)].



(1)

First, the influence of water and air on the course of the reaction was studied. It was found that conversion and yield were higher when the HDA cycloaddition was conducted under an inert atmosphere in the presence of molecular sieves (Δ up to 13%). Of the various solvents employed, mtbe turned out to be the best one with respect to catalytic activity and enantioselectivity. The effect of catalyst loading is summarized in Table 1.

Table 1. Effect of catalyst loading on the reaction of diene **4** with benzaldehyde (**5a**).[a]

Entry	Cat. loading [mol-%]	Conv.[b,c] [%]	Yield[c] [%]	*ee*[d] [%]
1	8	91	87	92
2	4	90	80	92
3	2	61	42	91
4	1	32	19	85
5	0.5	32	13	76

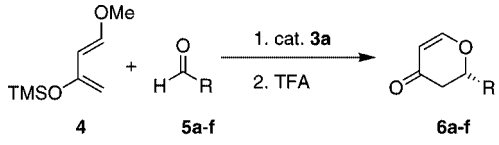
[a] All reactions were performed in mtbe in the presence of dry 3-Å molecular sieves at –21 °C; reaction time: 28 h. [b] Based on the aldehyde. [c] Determined by capillary GC using Ph_2O as internal standard. [d] Determined by capillary GC.

Optimal conditions were found at a catalyst loading of 4 mol-%, where a high yield of product was obtained (entry 2, conv. 90%, yield: 80%) after 28 h. The (*S*)-(+)-

enantiomer of the HDA product **6a** was formed with an enantiomeric excess of 92%. A lower catalyst loading or further lowering of the temperature retards the cycloaddition. At higher temperatures, faster conversion but lower enantiomeric excess was observed.

This initial success prompted us to apply the optimized reaction conditions of Table 1 (entry 2) to the asymmetric HDA of **4** with a number of other aldehydes **5**. The results are summarized in Table 2.

Table 2. Asymmetric HDA of different aldehydes **5a**–**f** with diene **4** employing catalyst **3a**.[a]



4 **5a-f** **6a-f**

5,6a: R = Ph; **5,6b**: R = *n*-hexyl; **5,6c**: R = *c*-hexyl; **5,6d**: R = 2-furyl; **5,6e**: R = *trans*-β-styryl; **5,6f**: R = CO_2Et.

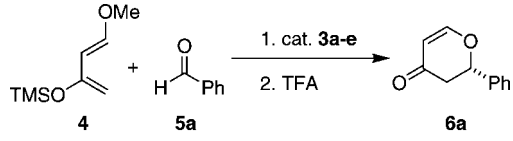
Entry	**5**	*T* [°C]	*t* [h]	Conv.[b] [%]	Yield[c] [%]	*ee*[d] [%]
1	**5a**	–21 to –24	28	91	80	92 (92)
			68	92	84	95 (95)
2	**5b**	–12	24	96	85	90 (90)
		–16	24	58	46	93 (93)
3	**5c**	–12	43	85	32	96 (96)
4	**5d**	–12	20	97	93	90 (98)
		–16	23	98	72	84 (98)
5	**5e**	5 to 10	68[e]	87	54	79 (79)
6	**5f**	–35 to –26	69[f]	100	45	61 (67)

[a] All reactions were performed in mtbe in the presence of dry 3-Å molecular sieves using 4 mol-% of catalyst. [b] Determined by capillary GC using Ph_2O as internal standard, based on the aldehyde. [c] Yield of isolated products. [d] Determined by capillary GC, values in brackets are the *ee* values of the isolated products after column chromatography; for **6d** (entry 4), the value in brackets resulted from additional crystallization. [e] 22 h at 5 °C and 46 h at 10 °C. [f] 18 h at –35 °C and 51 h at –26 °C.

Aromatic as well as aliphatic aldehydes could be activated by the chiral Lewis acid **3a** such that they underwent cycloaddition with diene **4** in an asymmetric way. The expected dihydropyranones **6a**–**f** could be obtained in moderate to good yields and, in most cases, excellent enantioselectivities (>90% *ee*). In particular, besides benzaldehyde **5a** (entry 1), the aliphatic aldehydes heptanal (**5b**) and cyclohexylcarbaldehyde (**5c**) as well as furfural (**5d**) also reacted with Danishefsky's diene to afford the corresponding dihydropyranones **6a**–**d** with high *ee* (93%, 96%, and 90% *ee*, respectively; see entries 2–4) after acidic workup. In the case of **5d**, the HDA product crystallized readily after purification by column chromatography. This single crystallization resulted in a significantly enhanced enantiomeric excess (98% *ee*, entry 4). *trans*-Cinnamic aldehyde (**5e**), which is an α,β-unsaturated aldehyde, underwent cycloaddition relatively sluggishly. Therefore, the reaction temperature had to be raised to 10 °C (entry 5), whereupon it provides the dihydropyranone **6e** in moderate yield and enantioselectivity (54% yield, 79% *ee*, entry 5). A somewhat lower enantioselectivity was obtained with the electron-poor aldehyde **5f** (67% *ee*, entry 6), which could be isolated in a moderate yield of 45%. Unfortunately, pivalaldehyde, pyrrol-2-carbaldehyde, and pyridine-2-carbaldehyde, which were tested during these studies as well, did not show any reactivity towards **4**. For pyridine-2-carbaldehyde, this observation may be explained by its coordinating ability towards transition metal catalysts in general, which results in deactivation of the chromium complex **3a**.

In order to investigate the effect of the counteranion on the activity and selectivity of the catalyst, we synthesized the chromium complexes **3b**–**e** from complex **3a** by anion exchange. The performance of these complexes in the asymmetric HDA cycloaddition of **4** with **5a** is summarized in Table 3.

Table 3. Effect of the catalyst counterion on the asymmetric HDA of benzaldehyde with diene **4**.[a]



4 **5a** **6a**

Entry	Catalyst	Conv.[b,c] [%]	Yield[c] [%]	*ee*[d] [%]
1	**3a**	62	61	95
2	**3b**	55	13	94
3	**3c**	14	3	90
4	**3d**	70	5	50
5	**3e**	39	19	87

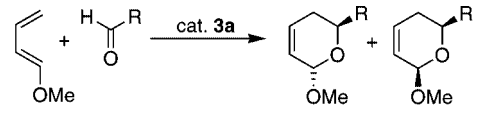
[a] All reactions were performed at –24 °C in mtbe in the presence of dry 3-Å molecular sieves using 4 mol-% of catalyst **2a**; reaction time: 24 h. [b] Based on the aldehyde. [c] Determined by capillary GC using Ph_2O as internal standard. [d] Determined by capillary GC.

From Jacobsen's work it is known that Cr^{III}-salen complexes bearing less coordinating counterions such as BF_4^- and $B(Ar)_4^-$ are less reactive and less enantioselective than complexes with strongly coordinating anions.[4] Of our Cr^{III}-salen complexes **3a**–**e** tested in the HDA cycloaddition, only **3a** shows satisfactory results in terms of yield and enantioselectivity. With complexes **3b**–**e**, either the conversion was very low (Table 3, entries 3 and 5) or the selectivity for HDA cyclization was poor due to side reactions (Table 3, entries 2 and 4). Catalysts **3d** and **3e**, which bear less coordinating counterions, proved to be less enantioselective than the catalysts bearing more strongly coordinating anions (**3a**–**c**). This is in accordance with the findings by Jacobsen and co-workers.[7]

Next, the suitability of catalyst **3a** for the HDA of 1-methoxybuta-1,3-diene (**7**), a diene of lower electron density, with benzaldehyde (**5a**) and ethyl glyoxylate (**5f**) was investigated; the results are summarized in Table 4.

With **5a** and **7** as substrates, a slow reaction could be effected by catalyst **3a**. After 64 h reaction time, an aldehyde conversion of 35% was obtained and the product was isolated in 11% yield as a mixture of diastereomers. The *cis*

Table 4. HDA of 1-methoxybuta-1,3-diene (**7**) with **5a** and **5f** employing catalyst **3a**.[a]



7 5a 5f 8a 9a 8b 9b

5a: R = Ph; **5f**: R = CO_2Et; **8a,b**: R = Ph; **9a,b**: R = CO_2Et

5	*T* [°C]	*t* [h]	Conv.[b] [%]	Yield **8**–**9**[c] [%]	*dr* *trans*:*cis*	*ee*[d] **8a/9a** [%]	*ee*[d] **8b/9b** [%]
5a	55 to 65	64[e]	35	11	5:95	14	75
5f	–21 to –16	69[f]	64	45	25:75	17	90

[a] All reactions were performed in mtbe in the presence of dry 3-Å molecular sieves. With **5a** 6 mol-% of catalyst was employed, whereas with **5f** 4 mol-% was employed. [b] Determined by capillary GC using Ph_2O as internal standard, based on the aldehyde. [c] Yield of isolated products. [d] Determined by capillary GC. [e] 41 h at 55 °C and 23 h at 65 °C. [f] 45 h at –21 °C and 24 h at –16 °C.

diastereomer **8b** was formed in large excess with respect to the *trans* diastereomer **8a** (dr 95:5). The former was obtained with an enantiomeric excess of 75%, while the minor *trans* diastereomer was obtained with 14% *ee*. Moderate conversion and yield were obtained after 69 h in the cycloaddition of **5f** and **7** in the presence of catalyst **3a**. In this reaction, a mixture of diastereomers **9a** (*trans*) and **9b** (*cis*) was formed in a ratio of 25:75. The minor *trans* product was obtained with an *ee* of 17% and the predominant *cis* product with an *ee* of 90%. The observation that the *cis* product **9b** is formed in excess is in accordance with the findings of Jurczak et al.,[42] who employed several Cr^{III}-salen ligands developed by Jacobsen for the HDA cycloaddition of **7** with *n*-butyl glyoxylate. The maximum enantiomeric excess obtained in the latter study for the *cis* diastereomer was 80%, with C_2-symmetrical salen ligands. With our catalytic system, we obtained somewhat higher enantioselectivity in a comparable reaction.

The catalytic results using our Cr^{III}-salen complexes are complementary to those using chiral Cr^{III}-porphyrins, which were studied in our laboratory.[43] While the Cr^{III}-salen complexes bearing DIANANE as backbone (reported in this paper) produce the *cis*-diastereomer **8b** in excess, the Cr^{III}-porphyrins give predominant access to the *trans* diastereomer **8a**.

Conclusions

We have shown that the readily available Cr^{III}-salen catalyst **3a** performs excellently in a number of HDA cycloadditions of Danishefsky's diene **4** with various aldehydes, affording enantiomeric excesses of greater than 90%. Besides **4**, less reactive 1-methoxybuta-1,3-diene (**7**) also shows reactivity towards the electronically diverse aldehydes **5a** and **5f**, producing the *cis* diastereomers **8b** and **9b** in high excess (up to 95:5 *dr*) and moderate to high enantioselectivity (up to 90% *ee*).

Experimental Section

General: All reactions were performed in oven-dried glassware under argon in a glove box, or using standard Schlenk techniques. Molecular sieves were activated prior to use by heating in vacuo. Solvents were dried and distilled using standard techniques. The aldehydes were freshly distilled prior to use. 1-Methoxy-3-(trimethylsilyloxy)-1,3-butadiene (Danishefsky's diene, **4**) was purchased from Fluka (≥95%) or Aldrich (90%, distilled prior to use). 1-Methoxybuta-1,3-diene was purchased from Fluka (50% solution in toluene) and used without further purification. The ligand **2** is commercially available from TCI (Tokyo Chemical Industries). NMR spectra were recorded with a Bruker AC 300 instrument. The IR measurements were performed with a Perkin–Elmer Paragon 1000 spectrometer. ESI mass spectra were recorded with a Finnigan MAT 900 spectrometer, and GC mass spectra with a Hewlett–Packard HP 6890 gas chromatograph with an HP 5973 mass selective detector. Capillary GC data were obtained with a Hewlett–Packard HP 6890 gas chromatograph with a Chirasil-Dex column (25 m). The signs of optical rotation were determined with a Perkin–Elmer polarimeter 343plus.

Synthesis of the Catalyst 3a: Triethylamine (345 μL, 2.48 mmol) was added to a solution of the salen ligand **2** (448 mg, 0.8 mmol) in absolute and degassed thf (20 mL). After stirring for half an hour at room temperature, $CrCl_2$ (108 mg, 0.88 mmol) was added. After several minutes, the reaction mixture turned from yellow to brown. Stirring was continued at room temperature for 12 h with exclusion of air. The flask was then opened to air and allowed to stir for an additional 12 h. The solution was diluted with mtbe (90 mL) and washed with saturated NH_4Cl solution (3 × 50 mL) and saturated NaCl solution (3 × 50 mL). The organic suspension was dried with Na_2SO_4 and then decanted from the drying agent. Complex **3a** was then isolated by filtration as a brown solid. After drying in vacuo, the chromium complex **3a** was obtained in 78% yield (400 mg). IR (KBr): $\tilde{\nu}$ = 3610, 3420, 2953, 2869, 1613, 1548, 1534, 1415, 1359, 1323, 1258, 1202, 1189, 1172, 1036, 841, 784, 747, 520, 487 cm^{-1}. UV/Vis: λ_{max} = 403.0 nm. MS (ESI, CH_2Cl_2/MeOH): *m*/*z* (%) 642.40 [$M^+(^{54}Cr)$ – Cl + MeOH], 641.40 [$M^+(^{53}Cr)$ – Cl + MeOH], 640.40 (100) [$M^+(^{52}Cr)$ – Cl + MeOH], 638.36 [$M^+(^{50}Cr)$ – Cl + MeOH], 610.38 [$M^+(^{54}Cr)$ – Cl], 609.37 [$M^+(^{53}Cr)$ – Cl], 608.36 [$M^+(^{52}Cr)$ – Cl], 606.36 [$M^+(^{50}Cr)$ – Cl]; exact mass (ESI) calculated for $C_{37}H_{52}CrN_2O_2$ [M – Cl]$^+$: 608.343; found 608.342.

Representative Procedure for the Synthesis of Complexes 3b,c,d: The corresponding silver salt (1 equiv.) was added to a solution of the chromium complex **3a** in absolute mtbe and the heterogeneous mixture was stirred for one day at room temperature in the dark. The reaction mixture was then filtered through celite and the solvent was removed in vacuo.

Synthesis of Complex 3b: Complex **3b** was obtained in a yield of 77% from 78.0 μmol of complex **3a** and 1 equiv. of $AgClO_4$ in mtbe (12 mL). MS (ESI_{pos}, CH_2Cl_2/MeOH): *m*/*z* (%) 643.33, 642.35 [$M^+(^{54}Cr)$ – ClO_4 + MeOH], 641.36 [$M^+(^{53}Cr)$ – ClO_4 + MeOH], 640.35 (100) [$M^+(^{52}Cr)$ – ClO_4 + MeOH], 638.36 [$M^+(^{50}Cr)$ – ClO_4 + MeOH], 610.34 [$M^+(^{54}Cr)$ – ClO_4], 609.32 [$M^+(^{53}Cr)$ – ClO_4], 608.33 [$M^+(^{52}Cr)$ – ClO_4]. MS (ESI_{neg}, CH_2Cl_2/MeOH): *m*/*z* (%)

101.15 [ClO_4, (^{37}Cl)], 99.17 (100) [ClO_4, (^{35}Cl)]; exact mass (ESI) calculated for $C_{37}H_{52}CrN_2O_2$ [M – ClO_4]$^+$: 608.343; found 608.344.

Synthesis of Complex 3c: Complex **3c** was obtained in a yield of 92% from 77.6 μmol of complex **3a** and 1 equiv. of AgTos in mtbe (12 mL). MS (ESI_{pos}, CH_2Cl_2/MeOH): *m/z* (%) 643.32, 642.31 [M$^+$(^{54}Cr) – Tos + MeOH], 641.31 [M$^+$(^{53}Cr) – Tos + MeOH], 640.31 (100) [M$^+$(^{52}Cr) – Tos + MeOH], 638.31 [M$^+$(^{50}Cr) – Tos + MeOH], 611.31, 610.31 [M$^+$(^{54}Cr) – Tos], 609.31 [M$^+$(^{53}Cr) – Tos], 608.31 [M$^+$(^{52}Cr) – Tos], 606.31 [M$^+$(^{50}Cr) – Tos]. MS (ESI_{neg}, CH_2Cl_2/MeOH): *m/z* (%) 173.22 [Tos (^{34}S)], 171.16 (100) [Tos (^{32}S)], 121.24 [Tos (^{32}S) – C_4H_2]; exact mass (ESI) calculated for $C_{37}H_{52}CrN_2O_2$ [M – Tos]$^+$: 608.343; found 608.344.

Synthesis of Complex 3d: Complex **3d** was obtained in a yield of 76% from 383 μmol of complex **3a** and 1 equiv. of $AgBF_4$ in mtbe (50 mL). MS (ESI_{pos}, CH_2Cl_2/MeOH): *m/z* (%) 643.33, 642.35 [M$^+$(^{54}Cr) – BF_4 + MeOH], 641.36 [M$^+$(^{53}Cr) – BF_4 + MeOH], 640.35 [M$^+$(^{52}Cr) – BF_4 + MeOH], 638.36 [M$^+$(^{50}Cr) – BF_4 + MeOH], 610.34 [M$^+$(^{54}Cr) – BF_4], 609.32 [M$^+$(^{53}Cr) – BF_4], 608.33 [M$^+$(^{52}Cr) – BF_4], 606.31 [M$^+$(^{50}Cr) – BF_4]; exact mass (ESI) calculated for $C_{37}H_{52}CrN_2O_2$ [M – BF_4]$^+$: 608.343; found 608.344.

Synthesis of Complex 3e: $NaBPh_4$ (5 equiv.) was added to a solution of complex **3b** (78.0 μmol) in mtbe (12 mL) and the heterogeneous mixture was stirred at room temperature for one day. Further mtbe (60 mL) was then added and the reaction mixture was washed with water (3×40 mL). The organic phase was dried with Na_2SO_4, and the solvent was removed in vacuo. Complex **3e** was isolated as a brown solid in 98% yield. MS (ESI_{pos}, CH_2Cl_2/MeOH): *m/z* (%) 643.49, 642.47 [M$^+$(^{54}Cr) – BPh_4 + MeOH], 641.47 [M$^+$(^{53}Cr) – BPh_4 + MeOH], 640.46 [M$^+$(^{52}Cr) – BPh_4 + MeOH], 638.47 [M$^+$(^{50}Cr) – BPh_4 + MeOH], 611.46, 610.46 [M$^+$(^{54}Cr) – BPh_4], 609.45 [M$^+$(^{53}Cr) – BPh_4], 608.45 (100) [M$^+$(^{52}Cr) – BPh_4], 606.45 [M$^+$(^{50}Cr) – BPh_4], 367.35, 366.35, 365.35, 364.35. MS (ESI_{neg}, CH_2Cl_2/MeOH): *m/z* 321.18, 320.21 [BPh_4, (^{11}B, ^{13}C)], 319.18 [BPh_4, (^{11}B)], 318.19 [BPh_4, (^{10}B)]; exact mass (ESI) calculated for $C_{37}H_{52}CrN_2O_2$ [M – BPh_4]$^+$: 608.343; found 608.344.

Representative Procedure for the HDA Reaction of Danishefsky's Diene (4) with Aldehydes 5 Catalyzed by Complexes 3: Aldehyde **5** (0.25 mmol) and diphenyl ether (19.8 μL, 0.125 mmol, GC standard) were dissolved in absolute mtbe (0.3 mL) and cooled to the temperature specified in the tables. Molecular sieves (3 Å) and a catalytic amount of the chromium complex (4 mol-%, unless otherwise stated) were then added and the reaction was started by adding Danishefsky's diene (**4**; 0.3 mmol). For quenching the reaction, 5 drops of triflic acid were added and the mixture was stirred for half an hour. Samples were taken before the reaction was started and after the reaction was stopped, and analyzed by chiral GC. The HDA products were purified by column chromatography of the reaction mixture after washing with water. The enantiomeric excess of the chromatographically pure products was measured again by capillary GC.

(*S*)-(+)-2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (6a): Column chromatography (*n*-hexane/Et_2O, 3:1) afforded **6a** as a clear oil. The chromatographed material had 92% *ee* (reaction at –21 °C) and 95% *ee* (reaction at –24 °C). Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 170 °C, isothermal]: t_R(major) = 11.1, t_R(minor) = 11.7 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 9.77 min; *m/z* 174 [M$^+$], 156, 128, 104 (100%), 78, 51. IR (film): $\tilde{\nu}$ = 3058, 3027, 2925, 1719, 1664, 1598, 1576, 1494, 1449, 1330, 1176, 977, 758, 698, 553 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.48 (dd, J_1 = 6.1, J_2 = 0.7 Hz, 1 H), 7.41–7.35 (m, 5 H), 5.51 (dd, J_1 = 6.1, J_2 = 1.3 Hz, 1 H), 5.41 (dd, J_1 = 14.4, J_2 = 3.5 Hz, 1 H), 2.89 (dd, J_1 = 16.8, J_2 = 14.4 Hz, 1 H), 2.64 (ddd, J_1 = 16.8, J_2 = 3.5, J_3 = 1.3 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 192.4 (s), 163.4 (d), 137.6 (s), 128.8 (d), 128.7 (d), 126.0 (d), 107.2 (d), 81.0 (d), 43.1 ppm (t). The absolute configuration of the major enantiomer was assigned as (+)-*S* based on comparison of the measured optical rotation with the literature value.[7]

(*R*)-(+)-2-Hexyl-2,3-dihydro-4*H*-pyran-4-one (6b): Column chromatography (*n*-hexane/Et_2O, 3:1) afforded **6b** as a clear oil. The chromatographed material had 90% *ee* (reaction at –12 °C) and 93% *ee* (reaction at –16 °C). Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 150 °C (16 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(major) = 23.9, t_R(minor) = 24.5 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 9.87 min; *m/z* 182 [M$^+$], 167, 153, 139, 124, 111, 97, 84, 71 (100%), 55. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34 (d, J = 6.0 Hz, 1 H), 5.39 (d, J = 6.0 Hz, 1 H), 4.43–4.33 (m, 1 H), 2.56–2.43 (m, 2 H), 1.86–1.74 (m, 1 H), 1.67–1.57 (m, 1 H), 1.46–1.23 (m, 8 H), 0.87 (t, J = 6.4 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 192.8 (s), 163.6 (d), 106.9 (d), 79.6 (d), 41.8 (t), 34.4 (t), 31.6 (t), 29.0 (t), 24.7 (t), 22.5 (t), 14.0 ppm (q). The absolute configuration of the major enantiomer was assigned as (+)-*R* by analogy to compounds **6a** and **6c**–**e**.

(*S*)-(+)-2-Cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (6c): Column chromatography (*n*-hexane/Et_2O, 3:1) afforded **6c** as a clear oil. The chromatographed material had 96% *ee*. Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 160 °C (39 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(major) = 25.3, t_R(minor) = 26.3 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 10.47 min; *m/z* 180 [M$^+$], 162, 151, 136, 122, 110, 95, 81 (100%), 67, 55. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36 (d, J = 5.9 Hz, 1 H), 5.38 (d, J = 5.9 Hz, 1 H), 4.15 (ddd, J_1 = 14.3, J_2 = 5.6, J_3 = 3.3 Hz, 1 H), 2.54 (dd, J_1 = 16.7, J_2 = 14.3 Hz, 1 H), 2.38 (dd, J_1 = 16.7, J_2 = 3.3 Hz, 1 H), 1.95–1.55 (m, 6 H), 1.35–0.94 (m, 5 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 193.8 (s), 164.0 (d), 106.7 (d), 83.6 (d), 41.4 (d), 39.0 (t), 28.2 (t), 28.0 (t), 26.2 (t), 25.9 (t), 25.8 ppm (t). The absolute configuration of the excess enantiomer was assigned as (+)-*S* based on comparison of the measured optical rotation with the literature value.[7]

(*S*)-(+)-2-(2-Furyl)-2,3-dihydro-4*H*-pyran-4-one (6d): Column chromatography (*n*-hexane/Et_2O, 3:1) gave **6d** as a colorless solid. The enantiomeric excess before work-up ranged from 84 to 90% (depending on the reaction temperature). The chromatographed material had 98% *ee* after additional recrystallization. M.p. 70 °C; chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 150 °C (16 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(major) = 21.3, t_R(minor) = 22.0 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 8.81 min; *m/z* 164 [M$^+$], 146, 134, 122, 108, 94 (100%), 81, 66, 55. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.45 (dd, J_1 = 1.5, J_2 = 0.9 Hz, 1 H), 7.35 (d, J = 6.2 Hz, 1 H), 6.43 (dd, J_1 = 3.3, J_2 = 0.5 Hz, 1 H), 6.38 (dd, J_1 = 3.3, J_2 = 1.8 Hz, 1 H), 5.50–5.42 (m, 2 H), 3.07 (dd, J_1 = 16.9, J_2 = 12.8 Hz, 1 H), 2.71 (dd, J_1 = 16.9, J_2 = 4.1 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 191.4 (s), 162.5 (d), 149.9 (s), 143.6 (d), 110.5 (d), 109.7 (d), 107.3 (d), 73.5 (d), 39.8 ppm (t). The absolute configuration of the excess enantiomer was assigned as (+)-*S* based on comparison of the measured optical rotation with the literature value.[7]

(*S*)-(+)-2-[(*E*)-Styryl]-2,3-dihydro-4*H*-pyran-4-one (6e): Column chromatography (*n*-hexane/Et_2O, 3:1) afforded **6e** as a clear oil. The chromatographed material had 79% *ee*. Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 160

°C (65 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(major) = 69.4, t_R(minor) = 71.9 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 13.43 min; *m*/*z* 200 [M$^+$], 185, 171, 153, 129 (100%), 115, 91, 77, 51. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.47–7.24 (m, 6 H), 6.71 (dd, J_1 = 16.0, J_2 = 0.9 Hz, 1 H), 6.28 (dd, J_1 = 16.0, J_2 = 6.6 Hz, 1 H), 5.45 (dd, J_1 = 6.1, J_2 = 1.0 Hz, 1 H), 5.10–5.02 (m, 1 H), 2.72 (dd, J_1 = 16.8, J_2 = 12.6 Hz, 1 H), 2.60 (ddd, J_1 = 16.8, J_2 = 4.2, J_3 = 1.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 190.7 (s), 162.9 (d), 135.6 (s), 133.8 (d), 128.7 (d), 128.5 (d), 126.8 (d), 125.0 (d), 107.3 (d), 79.7 (d), 42.0 ppm (t). The absolute configuration of the excess enantiomer was assigned as (+)-*S* based on comparison of the measured optical rotation with the literature value.[7]

Ethyl (*S*)-3,4-Dihydro-4-oxo-2*H*-pyran-2-carboxylate (6f): Column chromatography (*n*-hexane/Et_2O, 2:1) afforded **6f** as a slightly yellow oil. The chromatographed material had 67% *ee*. Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 160 (24 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(major) = 15.6, t_R(minor) = 15.8 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 8.52; *m*/*z* 170 [M$^+$], 154, 142, 125, 113, 101, 97 (100%), 85, 73, 55. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.37 (d, *J* = 6.1 Hz, 1 H), 5.45 (d, *J* = 6.1 Hz, 1 H), 4.98 (t, *J* = 7.8 Hz, 1 H), 4.25 (q, J = 7.1 Hz, 2 H), 2.83 (d, *J* = 7.8 Hz, 2 H), 1.28 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 189.4 (s), 187.0 (s), 161.7 (d), 107.9 (d), 76.1 (d), 62.2 (t), 38.3 (t), 14.0 ppm (q). The absolute configuration of the excess enantiomer was assigned as (+)-*S* based on comparison of the measured optical rotation with the literature value.[16]

Procedure for the HDA Reaction of 1-Methoxybuta-1,3-diene (7) with Benzaldehyde (5a) Using Catalyst 3a: Benzaldehyde (25.4 μL, 0.25 mmol) and diphenyl ether (19.8 μL, 0.125 mmol, GC standard) were dissolved in 0.25 mL of absolute mtbe and warmed to 55 °C. Molecular sieves (3 Å) and the chromium complex **3a** (9.75 mg, 15.0 μmol, 6 mol-%) were added and the reaction was started by adding 1-methoxybuta-1,3-diene (**7**; 30.2 μL, 0.3 mmol). After 41 h, the temperature was raised to 65 °C and the reaction was stirred for another 23 h. Samples were taken before the reaction was started and just before the reaction mixture was purified and analyzed by chiral GC. The HDA product was purified by column chromatography (silica gel, *n*-hexane/Et_2O, 3:1) to afford a clear oil. The enantiomeric excess of both diastereomers was measured by capillary GC.

2-Methoxy-6-phenyl-5,6-dihydro-2*H*-pyran (8): The purified material consisted of a 5:95 mixture of the diastereomers **8a** (*trans*) and **8b** (*cis*). The minor, *trans* diastereomer **8a** had 14% *ee* and the major, *cis* diastereomer **8b** had 75% *ee*. Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 170 °C (16 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(**8a**, minor) = 15.4, t_R(**8a**, major) = 15.5 min; t_R(**8b**, major) = 16.1, t_R(**8b**, minor) = 16.3 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 9.67 min (*trans*, minor); *m*/*z* 159, 145, 131, 117 (100%), 105, 91, 84, 77, 69, 59, 51; t_R = 9.89 min (*cis*, major); *m*/*z* 159, 144, 129, 104, 84 (100%), 69, 51.

8a: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.17 (m, 5 H), 6.08–5.98 (m, 1 H), 5.77 (dtd, J_1 = 10.5, J_2 = 2.8, J_3 = 1.5 Hz, 1 H), 4.96–4.94 (m, 1 H), 4.84 (dd, J_1 = 11.0, J_2 = 4.2 Hz, 1 H), 3.38 (s, 3 H), 2.36–2.12 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.3 (s), 129.1 (d), 128.5 (d), 127.6 (d), 126.2 (d), 125.5 (d), 96.4 (d), 68.4 (d), 55.3 (q), 32.2 ppm (t).

8b: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.40–7.17 (m, 5 H), 6.08–5.98 (m, 1 H), 5.67 (dtd, J_1 = 10.2, J_2 = 1.3 Hz, 1 H), 5.24–5.19 (m, 1 H), 4.72 (dd, J_1 = 9.9, J_2 = 4.0 Hz, 1 H), 3.47 (s, 3 H), 2.36–2.12 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.5 (s), 129.6 (d), 128.4 (d), 128.3 (d), 127.5 (d), 125.7 (d), 99.2 (d), 74.0 (d), 55.2 (q), 32.9 ppm (t).

Procedure for the HDA Reaction of 1-Methoxybuta-1,3-diene (7) with Ethyl Glyoxylate (5f) Using Catalyst 3a: A 50% solution of **5f** in toluene (49.56 μL, 0.25 mmol) and diphenyl ether (19.8 μL, 0.125 mmol, GC standard) was added to absolute mtbe (0.25 mL) and cooled to –21 °C. Molecular sieves (3 Å) and chromium complex **3a** (6.5 mg, 10.0 μmol, 4 mol-%) were added and the reaction was started by adding 1-methoxybuta-1,3-diene (**7**; 30.2 μL, 0.3 mmol). Samples were taken before the reaction was started and when the reaction was stopped and analyzed by chiral GC. The HDA product (diastereomeric mixture) was purified by column chromatography (silica gel, *n*-hexane/Et_2O, 2:1) to afford a colorless oil. The enantiomeric excess of both diastereomers was measured by capillary GC.

Ethyl 2-Methoxy-5,6-dihydro-2*H*-pyran-6-carboxylate (9): The purified material consisted of a 25:75 mixture of the diastereomers **9a** (*trans*) and **9b** (*cis*). The minor, *trans* diastereomer **9a** had 17% *ee* and the major, *cis* diastereomer **9b** had 90% *ee*. Chiral GC analysis [WCOT-FS CP-Chirasil-Dex CB, 90 °C (7 min), 15 °C min^{-1}, 160 °C (24 min), 15 °C min^{-1}, 180 °C (2 min)]: t_R(**9a**, minor) = 12.8, t_R (**9a**, major) = 13.0 min; t_R(**9b**, major) = 13.5, t_R (**9b**, minor) = 13.7 min. GC-MS [HP5-MS, 100 °C (5 min), 20 °C min^{-1}, 200 °C (15 min), 20 °C min^{-1}, 280 °C (10 min)]: t_R = 8.0 min (*trans*, minor), t_R(*cis*, major) = 8.18 min; *m*/*z* 185 [M$^+$ – 1], 171, 155, 140, 127, 113, 99, 81 (100%), 71, 53.

9a: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.04–5.99 (m, 1 H), 5.74 (ddd, J_1 = 10.1, J_2 = 4.8, J_3 = 2.6 Hz, 1 H), 4.99–4.96 (m, 1 H), 4.47 (dd, J_1 = 8.7, J_2 = 6.8 Hz, 1 H), 4.28–4.17 (m, 2 H, superimposed by signals of the *cis*-product), 3.44 (s, 3 H), 2.52–2.42 (m, 2 H), 1.41–1.23 (m, 3 H, superimposed by signals of the *cis*-product) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 127.6 (d), 125.4 (d), 95.9 (d), 65.8 (d), 61.2 (t), 55.6 (q), 26.0 (t), 14.2 ppm (q).

9b: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.04–5.99 (m, 1 H), 5.67 (ddd, J_1 = 10.3, J_2 = 4.0, J_3 = 2.0 Hz, 1 H), 5.02–5.00 (m, 1 H), 4.35 (dd, J_1 = 6.6, J_2 = 5.4 Hz, 1 H), 4.28–4.17 (m, 2 H, superimposed by signals of the *trans*-product), 3.48 (s, 3 H), 2.36–2.26 (m, 2 H), 1.41–1.23 (m, 3 H, superimposed by signals of the *trans*-product) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 127.7 (d), 126.1 (d), 97.2 (d), 69.6 (d), 61.1 (t), 55.6 (q), 27.5 (t), 14.1 ppm (q).

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