# Asymmetric Hetero-Diels−Alder Reactions Catalyzed by Chiral (Salen)Chromium(III) Complexes

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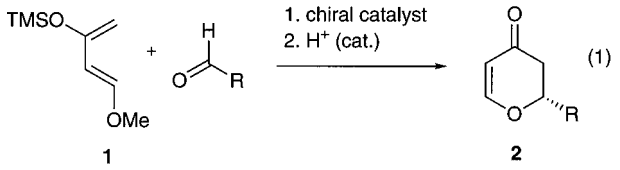
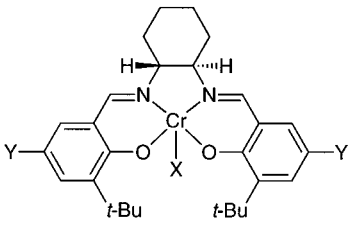
## Introduction

The formal hetero-Diels−Alder reaction between 1-methoxy-3-[(trimethylsilyl)oxy]-1,3-butadiene (**1**, "Danishefsky's diene") and aldehydes provides useful access to dihydropyranones (**2**, eq 1), a class of compounds with




**1** **2**

extensive utility in organic synthesis.[1] Recently, several groups have reported enantioselective catalytic versions of this reaction.[2] In most cases, these condensations have been shown not to involve a formal cycloaddition reaction but rather to proceed via a Mukaiyama aldol condensation followed by cyclization under the influence of acid catalysis to generate **2**.[2a,b] Recently we have found that chiral chromium- and cobalt-containing salen complexes catalyze the highly enantioselective reaction of nucleophiles with epoxides.[3] In an effort to ascertain whether other classes of nucleophile−electrophile reactions are promoted by such catalysts, we evaluated a series of chiral (salen)metal complexes for the hetero-Diels−Alder reaction shown in eq 1, and identified that (salen)Cr(III)-Cl complex **3** does indeed catalyze the reaction. Optimi-




(*R,R*) - **3**: X = Cl, Y = *t*-Bu
**4**: X = $N_3$, Y = *t*-Bu
**5**: X = F, Y = *t*-Bu
**6**: X = $BF_4$ **a**: Y = *t*-Bu
**b**: Y = OMe

zation of the catalyst and reaction conditions has led to the development of a protocol for this synthetically important transformation that requires only 2 mol % of readily available chiral catalyst and affords **2** with good enantioselectivity.

## Results and Discussion

Several parameters were found to influence the rate and enantioselectivity of the condensation reaction. Reactions performed in noncoordinating ethereal solvents such as $Et_2O$ and TBME afforded the dihydropyranone in the highest yield and enantioselectivity. The reaction of **1** with benzaldehyde in the presence of 2 mol % (*R,R*)-**3** at room temperature yielded (*R*)-**2a** in 96% isolated yield and 56% ee.[4] With an initial substrate concentration of 1.0 M, the reaction required 8 h to attain >90% conversion. At 5-fold higher concentration the reaction was complete in 4 h with a slight increase in enantioselectivity (60% ee). A further increase to 64% ee was obtained with 68% isolated yield in reactions carried out at −30 °C, although substantially longer reaction times were also required (70% conversion of **1** after 24 h with $[\mathbf{1}]_0 = 5$ M).

The identity of the catalyst counterion was also revealed to be a critical parameter for the attainment of high enantioselectivity. For example, azide complex **4** displayed significantly higher enantioselectivity (81% ee) and yield (86%) at −30 °C relative to chloride catalyst **3** in the model reaction with benzaldehyde. Catalyst **5**, bearing the more electronegative fluoride counterion, afforded even higher enantioselectivity (86% ee) but lower product yield (56%). Catalysts bearing less coordinating counterions [X = $BF_4$, $PF_6$, $B(Ar_f)_4$ ($Ar_f$ = 3,5-$C_6H_3(CF_3)_2$)] proved to be much less reactive and less enantioselective. However, the addition of oven-dried powdered 4 Å molecular sieves to reactions with these catalysts led to increased yield and enantioselectivities in each case with the best result obtained with the tetrafluoroborate catalyst **6a**, which afforded **2a** in 87% ee and 85% isolated yield at −30 °C (Table 1, entry a). A brief screen of substitution of the salicylidene component of the salen ligand showed that catalyst **6a**, derived from the commercially available *tert*-butyl-substituted salen ligand, was the most effective, although the methoxy-substituted catalyst **6b** conferred measurably higher enantioselectivity and yield in select cases (entries e and f).

The scope of the asymmetric condensation of **1** with aldehydes proved to be quite broad (Table 1). Although enantioselectivity in excess of 90% was achieved only in one case (entry b), several of the dihydropyranone products could be recrystallized to enantiomeric purity (entries d−g). The simplicity of the experimental procedure and the ready accessibility of the catalysts thus renders this an experimentally attractive method for the preparation of enantioenriched dihydropyranone derivatives.

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(4) The absolute stereochemistry was assigned by comparison of the optical rotation with literature values (ref 2a,b).

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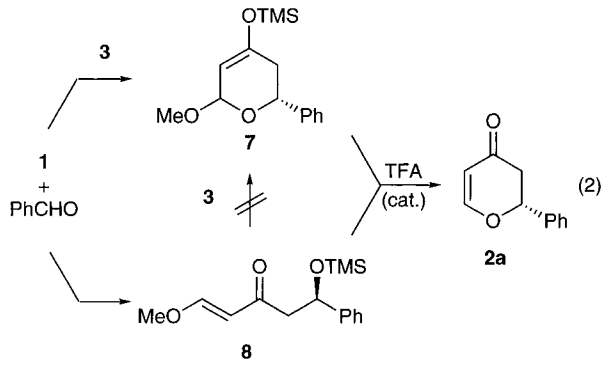
**Table 1. Asymmetric Hetero-Diels−Alder Reactions of Diene 1 Catalyzed by 6a and 6b[a]**

| | | | cat. **6a** | | cat. **6b** | |
|---|---|---|---|---|---|---|
| entry | R | temp (°C) | ee (%)[b] | yield (%)[c] | ee (%)[b] | yield (%)[c] |
| a | Ph | −30 | 87 | 85 | 65 | 98 |
| b | $C_6H_{11}$ | −20 | 93 | 71 | 85 | 76 |
| c | *n*-$C_5H_{11}$ | −40 | 83 | 86 | 62 | 85 |
| d | 2-furyl | −10 | 76 (99) | 89 (63) | 68 | 80 |
| e | (*E*)-PhCH=CH | 0 | 70 | 65 | 73 (99) | 96 (64) |
| f | *p*-$BrC_6H_4CH_2OCH_2$ | −30 | 79 | 67 | 84 (99)[d] | 94 (70)[d] |
| g | *o*-$ClC_6H_4CO_2CH_2$ | −20 | 83 (99)[d] | 92 (67)[d] | 72 | 86 |

[a] Unless noted otherwise, all reactions were run at 5.0 M in TBME using 2 mol % catalyst, 1.0 mmol of aldehyde, 1.0 mmol of diene **1**, and 300 mg of oven-dried 4 Å molecular sieves for 24 h. [b] Enantiomeric excesses in parentheses were obtained after recrystallization (see Experimental). [c] Yields in parentheses refer to recrystallized yields. [d] Reactions were run on 10.0 mmol scale.

An important question arises regarding the mechanism of the (salen)Cr-catalyzed condensation of **1** with aldehydes. A Mukaiyama aldol condensation mechanism has been identified in the highly effective asymmetric versions of this reaction developed by Keck and by Corey, whereas a concerted [4 + 2] cycloaddition pathway was indicated in the Eu(hfc)$_3$-catalyzed reaction reported by Danishefsky.[5] In the present (salen)Cr catalytic system, the $^1$H NMR spectrum of the crude reaction product of **1** with benzaldehyde catalyzed by complex **3** revealed the exclusive presence of cycloadduct **7** (eq 2). To test the




possible intermediacy of a Mukaiyama aldol condensation adduct, silyl ether **8** was synthesized independently[6] and subjected to the conditions of the Cr(salen)-catalyzed condensation reaction. However, no detectable cyclization of **8** to **7** was observed after exposure to 2 mol % of catalyst **3** for 6 h at room temperature. These results point toward a concerted [4 + 2] mechanism for the (salen)Cr catalysts and thus extend the scope of enantioselective reactions catalyzed by these complexes to the important arena of cycloaddition chemistry.

## Experimental Section

**Preparation of (*R,R*)-6a.** To a solution of (*R,R*)-**3** (632 mg, 1.00 mmol) in TBME (10 mL) was added $AgBF_4$ (195 mg, 1.00 mmol). The reaction flask was wrapped with aluminum foil and stirred at rt for 5 h, after which it was filtered through Celite and washed with TBME. Evaporation of the solvent gave 680 mg (0.99 mmol, 99%) of a brown solid, which was used without further purification: IR (KBr, cm$^{-1}$) 2952, 1621, 1534, 1436, 1392, 1361, 1319, 1255, 1171, 1062; exact mass (FAB) calcd for $C_{36}H_{52}N_2O_4Cr$ [M − $BF_4$]$^+$ 596.3434, found 596.3450.

**Preparation of (*R,R*)-6b.** Under a nitrogen atmosphere, $CrCl_2$ (86 mg, 0.70 mmol) was added to (*R,R*)-2,2′-[(1,2-cyclohexanediyl)bis(nitrilomethylidyne)]bis[4-methoxy-6-(1,1-dimethylethyl)phenol][7] (ligand of **6b**, 285 mg, 0.580 mmol) in dry, degassed THF (10 mL). The resulting mixture was stirred under nitrogen for 3 h, at which time the flask was opened to air and allowed to stir for an additional 16 h at room temperature. The solution was diluted with TBME and rinsed with saturated $NH_4Cl$ (5 × 50 mL) and saturated NaCl (1 × 50 mL). The organic phase was separated, dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The resulting residue was dissolved in TBME (7 mL) and treated with solid $AgBF_4$ (105 mg, 0.537 mmol). The reaction flask was wrapped with aluminum foil and stirred at rt for 5 h. The resulting mixture was filtered through Celite. Solvent removal by rotary evaporation afforded 328 mg (0.520 mmol, 90%) of **6b** as a brown solid which was used without further purification: IR (KBr, cm$^{-1}$) 2949, 1623, 1546, 1459, 1422, 1345, 1313, 1175, 1062, 821; exact mass (FAB) calcd for $C_{30}H_{40}N_2O_4Cr$ [M − $BF_4$]$^+$ 544.2393, found 544.2394.

**Preparation of (*R,R*)-5.** To a solution of (*R,R*)-**6a** (684 mg, 1.00 mmol) in acetonitrile (10 mL) was added NaF (84 mg, 2.00 mmol). The reaction mixture was stirred at room temperature for 24 h, solvent was removed by rotary evaporation, and the residue was suspended in TBME and washed three times with water. The organic phase was dried, filtered through Celite, and evaporated to give 568 mg (0.92 mmol, 92%) of **5** as a brown solid which was used without further purification: IR (KBr, cm$^{-1}$) 2954, 1623, 1533, 1463, 1436, 1392, 1361, 1321, 1256, 1170, 1083, 837; exact mass (FAB) calcd for $C_{36}H_{52}N_2O_4Cr$ [M − F]$^+$ 596.3434, found 596.3423.

**Representative Procedure for the Hetero-Diels−Alder Reaction of 1 with Aldehydes. (*R*)-2-Phenyl-2,3-dihydro-4*H*-pyran-4-one (2a).** A 10 mL oven-dried flask equipped with a stir bar was charged with (*R,R*)-**6a** (13 mg, 0.02 mmol) and 0.3 g of oven-dried powdered 4 Å molecular sieves. The flask was sealed with a rubber septum and purged with $N_2$. The catalyst was dissolved in TBME (200 μL), and benzaldehyde (100 μL, 1.0 mmol) was added via syringe at rt. The reaction was then cooled to −30 °C followed by the addition of 1-methoxy-3-[(trimethylsilyl)oxy]butadiene (**1**) (195 μL, 1.0 mmol). The mixture was allowed to stir at − 30 °C for 24 h, at which time it was removed from the bath, diluted with 2 mL of $CH_2Cl_2$, and treated with a drop of TFA. After stirring 10 min at rt, the reaction was concentrated in vacuo and the crude residue was purified by flash chromatography (7:3 hexanes:EtOAc) to yield **2a**[8] (151 mg, 0.85 mmol, 85% yield) as a clear oil. The isolated material was determined to be in 87% ee by chiral GC analysis (Cyclodex-B, 155 °C, 20 min, isothermal, $t_R$(minor) = 15.4 min, $t_R$(major) = 15.7 min). [α]$^{26}_D$ −96° (*c* 0.58, $CH_2Cl_2$); lit[2b] −83° for 82% ee material (*c* 0.5, $CHCl_3$).

**(*R*)-2-Cyclohexyl-2,3-dihydro-4*H*-pyran-4-one (2b).** The crude product mixture was purified by flash chromatography (7:3 hexanes:EtOAc) to afford **2b** in 71% yield (128 mg, 0.71 mmol) as a clear oil. The chromatographed material was determined to be in 93% ee by chiral GC analysis (Cyclodex-B, 150 °C, isothermal, $t_R$(minor) = 18.7 min, $t_R$(major) = 19.3 min). [α]$^{26}_D$ −157° (*c* 1.03, $CH_2Cl_2$); lit[2b] −159° for 76% ee material (*c* 0.5, $CHCl_3$); IR (thin film, cm$^{-1}$) 3498, 2927, 2856, 1677, 1595, 1450, 1408, 1276, 1225, 1038, 992, 910, 794; $^1$H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, 2H, *J* = 6.0 Hz), 5.38 (dd, 1H, *J* = 1.0 and 6.0 Hz), 4.16 (ddd, 1H, *J* = 3.3, 5.6 and 14.5 Hz), 2.54 (dd, 1H, *J* = 14.5 and 16.7 Hz), 2.38 (ddd, 1H, *J* = 1.0, 3.3 and 16.7 Hz), 1.64−1.81 (m, 6H), 1.00−1.27 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz) δ 193.3, 163.6, 106.9, 83.6, 41.4, 39.2, 28.2, 26.3, 25.9, 25.8; exact mass (EI) calcd for $C_{11}H_{16}O_2$ [M]$^+$ 180.1150, found 180.1150. The absolute stereochemistry was assigned as (−)-*R* based on comparison of the measured rotation with the literature value.[2b]

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**(*R*)-2-Pentyl-2,3-dihydro-4*H*-pyran-4-one (2c).** Product **2c** was obtained in 86% yield (145 mg, 0.86 mmol) as a clear oil after purification by flash chromatography (8:2 hexanes:EtOAc) and in 83% ee by chiral GC analysis (Cyclodex-B, 120 °C, 21 min, 1 °C/min to 130 °C, $t_R$(minor) = 24.5 min, $t_R$(major) = 25.2 min): $[\alpha]^{26}_D$ −106° (*c* 0.500, $CH_2Cl_2$); IR (thin film, $cm^{-1}$) 2933, 1680, 1596, 1407, 1272, 1230, 1039, 897, 791; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.36 (d, 2H, *J* = 6.0 Hz), 5.40 (dd, 1H, *J* = 1.1 and 6.0 Hz), 4.36−4.43 (m, 1H), 2.52 (dd, 1H, *J* = 13.4 and 16.7 Hz), 2.42 (dt, 1H, *J* = 2.8 and 12.8 Hz), 1.79−1.83 (m, 1H), 1.64−1.68 (m, 1H), 1.29−1.48 (m, 6H), 0.89 (t, 3H, *J* = 7.0 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 192.8, 163.3, 106.9, 79.6, 41.8, 34.3, 31.4, 24.4, 22.5, 13.9; exact mass (EI) calcd for $C_{10}H_{16}O_2$ $[M]^+$ 168.1150, found 168.1144. The absolute stereochemistry was assigned as (−)-*R* by analogy to compounds **2a**,**b**,**d**.

**(*R*)-2-(2-Furyl)-2,3-dihydro-4*H*-pyran-4-one (2d).** The crude product mixture was purified by flash chromatography (7:3 hexanes:EtOAc) to yield **2d**[5a] in 89% yield (146 mg, 0.89 mmol) as a clear oil which solidified upon standing. The chromatographed material was determined to be 76% ee by chiral GC analysis (Cyclodex-B, 130 °C, isothermal, $t_R$(minor) = 20.5 min, $t_R$(major) = 21.1 min). A single recrystallization from 1:2 $Et_2O$:hexanes yielded 103 mg (63%) of white needlelike crystals in 99% ee by GC analysis. $[\alpha]^{26}_D$ −357° (*c* 0.805, $CH_2Cl_2$); lit[2b] −255° for 67% ee material (*c* 0.5, $CHCl_3$).

**(*R*)-2-(*E*)-Styryl-2,3-dihydro-4*H*-pyran-4-one (2e).** The crude residue obtained from the reaction was purified by flash chromatography (7:3 hexanes:EtOAc) to afford **2e**[8] in 96% yield (191 mg, 0.96 mmol) as a clear oil which solidified after standing. The isolated material was determined to have 84% ee by chiral HPLC analysis (Chiralcel OD, 9:1 hexanes:IPA, 1.5 mL/min, $t_R$(minor) = 11.2 min, $t_R$(major) = 26.7 min). Recrystallization from a minimal amount of 4:1 $Et_2O$:hexanes at 0 °C yielded 128 mg (64%) of opaque needlelike crystals in 99% ee by HPLC analysis: $[\alpha]^{26}_D$ −215° (*c* 0.36, $CH_2Cl_2$). The absolute stereochemistry was assigned as (−)-*R* by analogy to compounds **2a**,**b**,**d**.

**(*R*)-2-{[(4-Bromophenyl)methoxy]methyl}-2,3-dihydro-4*H*-pyran-4-one (2f).** Using 2.29 g (10.0 mmol) of [(4-bromophenyl)methoxy]acetaldehyde,[9] the crude residue from the reaction was purified by flash chromatography (7:3 hexanes:EtOAc) to yield **2f** (2.81 g, 9.39 mmol, 94% yield) as a clear oil, which solidified upon standing, in 84% ee by chiral HPLC analysis (Chiralcel OD, 9:1 hexanes:IPA, 1 mL/min, $t_R$(minor) = 11.3 min, $t_R$(major) = 12.8 min). Recrystallization from a minimal amount of $Et_2O$ at 0 °C yielded 2.09 g (70%) of opaque cube like crystals in 99% ee by HPLC analysis: $[\alpha]^{26}_D$ −112° (*c* 1.74, $CHCl_3$); IR (KBr, $cm^{-1}$) 2852, 1674, 1662, 1590, 1487, 1410, 1291, 1227, 1129, 1093, 1041, 890, 786; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.48 (d, 2H, *J* = 8.3 Hz), 7.37 (d, 1H, *J* = 6.0 Hz), 7.21 (d, 2H, *J* = 8.3 Hz), 5.42 (d, 1H, *J* = 6.0 Hz), 4.56−4.62 (m, 3H), 3.66−3.74 (m, 2H), 2.74 (dd, 1H, *J* = 14.2 and 16.8 Hz), 2.40 (dd, 1H, *J* = 3.4 and 16.8 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 192.3, 162.8, 136.5, 131,6, 129.3, 121.8, 107.2, 107.1, 78.2, 72.8, 70.8, 38.3; exact mass (CI) calcd for $C_{13}H_{17}BrNO_3$ $[M + NH_4]^+$ 314.0392, found 314.0390. The absolute stereochemistry was assigned as (−)-*R* by analogy to compounds **2a**,**b**,**d**.

**(*R*)-2-{[(2-Chlorobenzoyl)oxy]methyl}-2,3-dihydro-4*H*-pyran-4-one (2g).** Using 1.99 g (10.0 mmol) of [(2-chlorobenzoyl)oxy]acetaldehyde,[10] the crude residue from the reaction was purified by flash chromatography (7:3 hexanes:EtOAc) to yield **2g** (2.44 g, 9.20 mmol, 92% yield) as a clear oil which solidified upon standing. The chromatographed material was determined to have 83% ee by chiral HPLC analysis (Chiralcel OD, 9:1 hexanes:IPA, 1 mL/min, $t_R$(minor) = 20.6 min, $t_R$(major) = 23.4 min). Recrystallization from a minimal amount of $Et_2O$ at 0 °C yielded 1.78 g (67%) of opaque white crystals that were 99% ee by HPLC analysis: $[\alpha]^{26}_D$ −144° (*c* 0.508, $CHCl_3$); IR (KBr, $cm^{-1}$) 3068, 2958, 1740, 1681, 1592, 1407, 1298, 1270, 1215, 1141, 1123, 1055, 1041, 1028, 977, 872, 799; $^1$H NMR ($CDCl_3$, 400 MHz) $\delta$ 7.84 (d, 2H, *J* = 6.0 Hz), 7.2−7.5 (m, 4H), 5.45 (dd, 1H, *J* = 0.9 and 6.0 Hz), 4.76 (m, 1H), 4.60 (dd, 1H, *J* = 3.4 and 12.2 Hz), 4.53 (dd, 1H, *J* = 5.6 and 12.2 Hz) 2.78 (dd, 1H, *J* = 14.0 and 17.6 Hz), 2.53 (ddd, 1H, *J* = 0.9, 3.6 and 17.6 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz) $\delta$ 190.9, 165.0, 162.5, 133.8, 133.0, 131.6, 131.2, 129.1, 126.6, 107.3, 76.6, 65.2, 38.2; exact mass (CI) calcd for $C_{13}H_{11}ClO_4$ $[M]^+$ 266.0346, found 266.0346. The absolute stereochemistry was assigned as (−)-*R* by analogy to compounds **2a**,**b**,**d**.

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**Supporting Information Available:** Chromatographic analyses of racemic and enantiomerically enriched dihydropyranones, and copies of $^1$H NMR spectra of **2a**−**g**, **7**, **8**, and **8** in the presence of (*R*,*R*)-**3** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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