# ASYMMETRIC ALDOL REACTION: A HIGHLY <u>ERYTHRO</u>-SELECTIVE ALDOL REACTION BETWEEN TRICARBONYL(O-TRIMETHYLSILYLBENZALDEHYDE DERIVATIVE)-CHROMIUM(0) COMPLEXES AND CYCLIC SILYL ENOL ETHERS<sup>1</sup>

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Summary: Reaction of  $(\pm)$ -chromium(0)-complexes **4e-g** with **5-7** gave the <u>erythro</u> isomers in a highly selective manner. This aldol reaction was successfully applied to the asymmetric one. The absolute configuration was determined by X-ray analysis of (-)-<u>erythro</u>-**8e**.

#### Introduction

Tricarbonyl( $\eta^6$ -arene)chromium(0) complexes<sup>2</sup> have been found to be able to stabilize their benzylic cations as well as anions.<sup>3</sup> This useful benzylic activation ability was successfully applied for a carbon-carbon bond formation at the benzylic positions of the tricarbonyl(arene)chromium complexes. In particular, Reetz<sup>4</sup> and Uemura<sup>5</sup> have independently achieved a stereoselective carbon-carbon construction via the tricarbonylchromiumstabilized benzylic cation intermediates. Another synthetically significant feature of the tricarbonyl(arene)chromium complexes<sup>2</sup> is that they have an inherently high  $\pi$ -facial selectivity<sup>6</sup> with respect to the arene ring. The tricarbonyl(arene)chromium complexes interfere the approach of reagents from the face of the arene occupied by the tricarbonylchromium group and allow reagents attack predominantly from the face opposite to the tricarbonylchromium moiety. These steric directing effects coupled with benzylic activation ability of the tricarbonyl(arene)chromium complex have been utilized for the stereospecific functionalization $^{2,7}$  at the benzylic positions.

We were interested in application of these synthetically attractive properties to the stereoselective aldol reaction,<sup>8</sup> especially for asymmetric one. We envisioned that the benzylic cation species would be derived from the corresponding tricarbonyl(benzaldehyde derivative)chromium(0) complex in the presence of Lewis acid (Mukaiyama

3007



condition).<sup>8c</sup> This benzylic cation intermediate should be captured by the

silyl enol ether <u>via</u> the non-chelated acyclic transition state rather than the cyclic one. The former would lead to the formation of an <u>erythro</u> product<sup>8</sup> regardless of the geometry of the starting silyl enol ethers. The approach of the silyl enol ether to the benzylic cation thus generated would take place from the face opposite to the tricarbonylchromium group.<sup>2,3,6,7</sup> If the optically pure chromium(0)<sup>9</sup> complex is taken as a starting material, the reaction will give an optically active <u>erythro</u>aldol. On the basis of the above consideration, we initiated our program for the development of new type of asymmetric aldol reaction. In this paper, we present details of our investigation of the <u>erythro</u>-selective asymmetric aldol reaction between tricarbonyl(<u>o</u>-trimethylsilylbenzaldehyde derivative)chromium complexes and cyclic silyl enol ethers.

# Results and Discussion Aldol Reaction of Racemic Tricarbonyl(o-substituted-benzaldehyde)chromium(0) Complexes with Cyclic Silyl Enol Ethers

Taking into account an asymmetric aldol reaction, we employed <u>ortho</u>substituted benzaldehyde-chromium(0) complexes **4** as starting complexes. The chromium(0) complexes **4a-c** were prepared according to the literature.<sup>10</sup> Other chromium(0) complexes **4d-g** were synthesized by conventional means (Scheme 1). For instance, <u>o</u>-ethyl- and <u>o</u>-trimethylsilyl (TMS) benzaldehyde (**1d**,e)<sup>11</sup> were treated with ethylene glycol in the presence of <u>p</u>-toluenesulfonic acid (<u>p</u>-TsOH) to give the corresponding acetals **2d**,e in 81 and 98% yields, respectively. Chromium complexation of 2d,e was realized by heating of 2d,e with chromium hexacarbonyl in <u>n</u>-heptane/di-<u>n</u>-butylether (2/1) at 130°C to afford 3d,e (54 and 82%, respectively). The formation of complexes 3d,e was easily elucidated by the high field shift<sup>2</sup> of aromatic ring protons in their <sup>1</sup>H NMR spectra. Hydrolysis of the acetals 3d,e with 10% hydrochloric acid in refluxing



### Scheme 1

acetone furnished the tricarbonyl( $\underline{o}$ -ethylbenzaldehyde)chromium and the tricarbonyl( $\underline{o}$ -TMS-benzaldehyde)chromium complexes (**4d**,**e**) in 69 and 89% yields, respectively. Compounds **4f**,**g** were also prepared by the same method.

We initially investigated the aldol reaction between racemic 4 and cyclic silyl enol ethers, since these cyclic silyl enol ethers ( $\underline{E}$ -enol ether) are readily available and free from contamination of  $\underline{Z}$ -enol ether. Thus, the aldol reaction of the tricarbonyl( $\underline{O}$ -methoxybenzaldehyde)chromium complex (4b)<sup>10</sup> with the six-membered cyclic enol ether 6 was examined. We thought the oxygen atom of the formyl group in 4b would face opposite to the methoxy group because of the

electronic effect of the <u>ortho</u> methoxy  $group^{2,9}$  in **4b**. Actually, the aldol reaction was carried out in methylene chloride at -78°C in the presence of BF<sub>3</sub>·OEt<sub>2</sub><sup>8c</sup> for 2h. The crude condensation products **9b** were subsequently decomplexed with CAN<sup>12</sup> in methanol at 0°C to yield the aldol products **12b** and **15b** in 89% yield. A careful analysis of <sup>1</sup>H NMR spectrum of the products<sup>13</sup> revealed that this mixture was made up of the <u>erythro</u> isomer **12b** and the <u>threo</u> isomer **15b** in a ratio of 69 to 31. The similar treatment of **4b** with 1-trimethylsilyloxycyclopentene (5) provided a mixture of **11b** and **14b** nonselectively (<u>erythro/threo</u>=50/50) in 84% yield. Silyl enol ethers **5**, **6** were also condensed with the <u>ortho</u>-unsubstituted tricarbonyl(benzaldehyde)chromium complex (**4a**) to leave the corresponding aldol products in a nonstereoselective manner as shown in Table I. Disappointingly these results were in disagreement with our prediction,



## Scheme 2

3010

although moderate <u>erythro</u>-selectivity was observed in the reaction of **4b** with **6** 

At this point, we noted that the tricarbonyl(o-TMS-benzaldehyde)chromium complex (4e) is as an ideal substrate to achieve stereoselective aldol reaction, because (i) the TMS group can be easily removed from the aldol product with fluoride anion to produce the parent benzene ring and (ii) the silyl group is known to be capable of making the pentacoordinated species<sup>14</sup> by neighboring group participation. The aldehyde group in 4e, therefore, would be fixed in a conformation where the aldehyde oxygen is forced to face the TMS group by coordination. This assumption was tested by the reaction of 4e with 6. Treatment of 4e with 6 at -78°C in the presence of the Lewis acid,<sup>15</sup> followed by decomplexation with CAN<sup>12</sup> produced a mixture of 12e and 15e in 70% yield in a ratio of 90 to 10. The erythro selectivity<sup>16</sup> was greatly improved as compared to the case of 4b. This result encouraged us to continue the examination of the aldol reaction of 4e with other silyl enol ethers. Similar treatment of 4e with the five-membered enol ether 5 furnished the condensation products in a highly erythro-selective manner (61%: 11e/14e=96/4). The seven-membered enol ether 7, on exposure to 4e, gave 13e exclusively in 75% yield. No three isomer 16e could be virtually detected in the <sup>1</sup>H NMR spectrum. The chromium(0) complex 4f, which has an electron-releasing group at the para position of the aldehyde moiety, was submitted to the reaction with cyclic silyl enol ethers 5-7 to afford the corresponding erythro isomers in a highly stereoselective manner (five- and six-membered) or exclusively (seven-membered). Similarly, a highly erythro-selective reaction was achieved irrespective of the ring size of the silyl enol ether in the case of 4g bearing the chloro substituent at the para position. The reactivity was not affected by the electronic property of the benzene ring. It seems that the seven-membered silyl enol ether 7 is the best nucleophile for this aldol reaction from a stereoselective consideration. We next investigated the aldol reaction of the o-methyl<sup>10</sup> and o-ethylbenzaldehydechromium (0) complexes (4c,d) with the seven-membered silyl enol ether 7. The o-methyl derivative 4c exhibited a fairly good selectivity (erythro/threo=86/14). Changing the ortho substituent from the methyl to the ethyl group brought about a great improvement of the selectivity producing the erythro isomer 13d exclusively in 84% yield. The results obtained were summarized in Table I.

In order to confirm whether the chromium complexation of benzaldehyde derivatives is mandatory for this <u>erythro</u>-selective reaction, several control experiments were performed. An uncomplexed <u>o</u>-TMS-benzaldehyde (1e), for example, produced the aldol condensation products 11e-16e when

entry	aldehyde	R <sup>1</sup>	R <sup>2</sup>	enol ether	product <sup>a</sup>	yield <sup>b</sup> %
1	4a	н	н	5	11a:14a=66:34	87
2	4a	Н	н	6	12a:15a=47:53	91
3	4a	н	н	7	13a:16a=49:51	81
4	4b	OMe	Н	5	11b:14b=50:50	84
5	<b>4</b> b	OMe	н	6	12b:15b=69:31	89
6	4c	Me	н	7	13c:16c=86:14	78
7	4d	Et	н	7	13d:16d=>98:2 <sup>C</sup>	84
8	4e	TMS	H	5	11e:14e=96:4	61
9	4e	TMS	Н	б	12e:15e=90:10	70
10	4e	TMS	н	7	13e:16e=>98:2 <sup>C</sup>	75
11	4f	TMS	OMe	5	11f:14f=93:7	95
12	4f	TMS	OMe	6	12f:15f=97:3	70
13	<b>4f</b>	TMS	OMe	7	13f:16f=>98:2 <sup>C</sup>	86
14	4g	TMS	Cl	5	11g:14g=95:5	69
15	4g	TMS	Cl	6	12g:15g=92:8	72
16	<b>4</b> g	TMS	Cl	7	13g:16g=95:5	94

Table	I.	Aldol	Reaction of	<b>f</b>	Chromiu	1m (0)-	-Complex	ed	Benzaldehydes	4	with
			Cyc]	lic	Silyl	Enol	Ethers	5-7	1		

<sup>a</sup>Ratio was determined by 400-MHz <sup>1</sup>H NMR spectra. <sup>b</sup>Yields of products isolated, after decomplexation, by chromatography. <sup>C</sup>No <u>threo</u> isomer (16) could be virtually detected by <sup>1</sup>H NMR spectra.

entry	aldehyde	R <sup>1</sup>	R <sup>2</sup>	enol ether	product <sup>a</sup>	yield <sup>b</sup> %
1	1a	н	Н	6	12a:15a=36:64	70
2	1b	OMe	н	6	12b:15b=46:54	73
3	1c	Me	н	7	13c:15c=48:52	88
4	1d	Et	н	7	13d:16d=67:33	67
5	1e	TMS	н	5	11e:14e=62:38	63
6	1e	TMS	н	6	12e:15e=69:31	60
7	1e	TMS	н	7	13e:16e=67:33	74

Table II. Aldol Reaction of Benzaldehydes 1 with Cyclic Silyl Enol Ethers 5-7

<sup>a</sup>Ratio was determined by 400-MHz <sup>1</sup>H NMR spectra. <sup>b</sup>Yields of products isolated by chromatography.

treated with cyclic silyl enol ethers 5-7. The <u>erythro</u> selectivity was much lower than the case of **4e**, although the moderate selectivity was constantly obtained. The results of other control experiments were summarized in Table II.<sup>17</sup>



Figure 1

Table I and II suggest that the role of the chromium(0) complexation is essential to attain the high <u>erythro</u> selectivity. We previously proposed an acyclic transition state<sup>1</sup> ( $A_1$  and  $A_2$ ) involving a pentacoordinated intermediate to explain the high diastereoselectivity as shown in Figure 1. However, the high <u>erythro</u> selectivity obtained in the cases of 4c and 4d can not be rationalized in terms of the above explanation because the <u>o</u>-methyl or <u>o</u>-ethyl derivatives can not form the pentacoordinated species in the transition states. An alternative explanation for this <u>erythro</u>selective aldol reaction is based on that the selectivity is dependent on the degree of the steric bulkiness of the <u>ortho</u> substituents in the chromium(0) complex 4. In order to get more conclusive information about the reaction mechanism, our next endeavor was focused on an asymmetric aldol reaction by using optically pure chromium(0) complexes.

Before describing the asymmetric aldol reaction, some other results should be mentioned. The benzylic proton of the aldol condensation products 8-10 were completely obscured by the high field-shifted aromatic protons in their <sup>1</sup>H NMR spectra. No information was available about the stereochemical relationship between the diastereotopic center on the aromatic ring caused by complexation and the aliphatic stereogenic centers. The pure <u>erythro</u>-8f was acetylated under usual condition to give the acetylated derivative 17, <sup>1</sup>H NMR spectrum of which revealed the down field-shifted benzylic proton at 6.22 ppm as a doublet (J= 2.4 Hz). <sup>1</sup>H NMR spectrum consideration indicated that 17 (and <u>erythro</u>-8f) was made up of a single isomer with respect to the stereogenic center on the aromatic ring, although the stereochemical relationship was not apparent from the spectral evidence. Decomplexation of 17 with CAN<sup>12</sup> afforded 18, which was identical with the authentic sample derived from 11f. On the other hand, desilylation of 8e (<u>erythro/threo=96/4</u>) with tetrabutylammonium fluoride (TBAF) in THF at -78°C, followed by treatment with CAN yielded a mixture of 11a and 14a in a ratio of 72 to 28. When the



Scheme 3

pure erythro-8e was exposed to the same condition described above, a mixture of 11a and 14a (11a/14a=86/14) was obtained again. Unfortunately isomerization of the erythro isomer to the threo isomer occurred during desilylation. Isomerization with TBAF, however, is indeed not a serious drawback, since the TMS group on the chromium-complexed benzene ring of the compounds could be easily removed by TBAF without isomerization at the benzylic position<sup>18</sup> after transformation of these aldol products to the compounds having no  $\beta$ -hydroxy carbonyl moiety. This isomerization with TBAF is understandable because an equilibrium between the erythro and the threo isomers was already reported in the TBAF catalyzed aldol reaction<sup>19</sup> of silyl enol ethers with carbonyl compounds.

# Asymmetric Aldol Reaction of (+)- and (-)-Tricarbonyl(<u>o</u>-TMS-benzaldehyde)chromium Complexes with Cyclic Silyl Enol Ethers

Optical resolution of racemic 4e into (+)- and (-)-4e was carried out by the following sequences.<sup>10</sup> Racemic 4e was treated with (S)-(-)-5( $\alpha$ phenylethyl)semioxamazide<sup>20</sup> in refluxing benzene in the presence of <u>p</u>-TsOH to give the (+)-semioxamazone  $19[(+)-19, [\alpha]_D^{25} + 596^{\circ}(\underline{c}, 0.52, CHCl_3)]$ and the (-)-semioxamazone  $19[(-)-19, [\alpha]_D^{25}-657^\circ$  (c, 0.51, CHCl<sub>3</sub>)] in 37 and 37% yields, respectively, after chromatographic separation. Exposure of (+)-19 to 60% sulfuric acid in refluxing benzene effected hydrolysis to produce (+)-4e  $[\alpha]_{D}^{25}$  + 149°( $\underline{c}$ , 0.50, CHCl<sub>3</sub>), lit.<sup>18</sup>  $[\alpha]_{D}^{20}$  +146° ( $\underline{c}$ , 0.10, CHCl<sub>3</sub>)] in 81 % yield. Similar hydrolysis of (-)-19 afforded (-)-4e [[ $\alpha$ ]<sup>25</sup><sub>D</sub>  $-153^{\circ}$  (c, 0.48, CHCl<sub>3</sub>), lit.<sup>18</sup> [ $\alpha$ ]<sup>18</sup><sub>D</sub> -154° (c, 1, CHCl<sub>3</sub>)] in 73% yield. The absolute configuration of (+)- and (-)-4e was tentatively assigned as depicted in Scheme 4 according to an empirical rule for assignment of metallocene configuration from its rotation sign, 9,21 and was eventually confirmed by an X-ray crystallographic analysis (vide infra). During studies on this program, Davies and Goodfellow<sup>18,22</sup> recently reported a synthesis of racemic 4e and its optical resolution into (+)- and (-)-4e via the imine derivatives derived from L-valinol. Optically pure (+)- and (-)- tricarbonyl(o-TMS-benzaldehyde)chromium complexes (4e) being in hand, we next investigated an asymmetric aldol reaction of (+)and (-)-4e with cyclic silvl enol ethers 5-7.

The optically pure (+)-4e was treated with 5 in methylene chloride at -78°C in the presence of the Lewis acid<sup>8C</sup> to give the (-)-<u>erythro</u>-8e, which was subsequently decomplexed with CAN<sup>12</sup> to leave the crude reaction mixture. Chromatography of the crude material provided (-)-11e  $[[\alpha]_D^{20}-84^\circ$  (<u>c</u>, 0.20, CHCl<sub>3</sub>)] in 65% yield. On the other hand, an enantiomeric isomer,



(-)-4e produced an antipode, (+)-11e  $[[\alpha]_{D}^{19} + 89^{\circ} (\underline{c}, 0.34, CHCl_{3})]$  in 69% yield on treatment with 5. Optical purity of these condensation products [(+)- and (-)-11e] was determined to be >98% enantiomeric excess (ee) for each isomer by <sup>1</sup>H NMR spectra using a sift reagent, tris[3-(trifluoromethylhydroxymethylene-d-camphorato]europium (III) [Eu(tfc)]. The six- and seven-membered silyl enol ethers 6, 7 also reacted with (+)- and (-)-4e to furnish the corresponding erythro isomers in a highly enantioselective manner. Chemical and optical yields were summarized in Table III. Satisfactorily high optical yields (90 - >98% ee) were achieved in all cases. In order to establish the absolute configuration of the aldol condensation products, we undertook an X-ray crystallographic analysis of (-)-erythro-8e, obtained from the reaction of (+)-4e with 5. It has become apparent that the absolute configuration of two aliphatic carbon chiral centers were (S),(S) as shown in Figure 2. Thus, the absolute configuration of (-)-11e-13e was established to be (S),(S), while that of (+)-11e-13e to be (R),(R). Furthermore, an X-ray analysis unambiguously established the absolute configuration of (+)- and (-)-4e, predicted earlier on the basis of analogy with the literature precedent.9,21

entry	aldehyde	enol ether	product	$[\alpha]_{D}^{a}$	ee <sup>b</sup> %	yield % <sup>C</sup>	
1	(+)-4e	5	(-)-11e	-84°(c, 0.20)	>98d	65	
2	(+)- <b>4e</b>	6	(-)-12e	-54°(c, 0.40)	90	71	
3	(+)- <b>4e</b>	7	(-)-13e	-85°(c, 0.95)	95	98	
4	(-)- <b>4e</b>	5	(+)-11e	+89°(c, 0.34)	>98 <sup>d</sup>	69	
5	(-)- <b>4e</b>	6	(+)-12e	+57°(c, 0.42)	90	70	
6	(-)- <b>4e</b>	7	(+)-13e	+83°(c, 0.91)	96	91	

Table III. Aldol Reaction of (+)- and (-)-4e with Cyclic Silyl Enol Ethers 5-7

<sup>a</sup>Measured in  $CHCl_3$ . <sup>b</sup>Optical yields were determined by 400-MHz <sup>1</sup>H NMR spectra in the presence of  $Eu(tfc)_3$ . <sup>C</sup>Isolated by chromatography. <sup>d</sup>No enantiomeric isomer could be virtually detected by <sup>1</sup>H NMR spectra.

An X-ray analysis of  $(-)-\underline{erythro}-8e$  gave some information about the reaction mechanism. Chromium complexation with arene should control the  $\pi$ -facial selectivity with respect to the benzene ring, where a nucleophile

must approach the electrophilic center from the face opposite to the one occupied by the chromium moiety. As will be discussed shortly (vide <u>infra</u>), there are two possible preferred conformation of (+)-4e to be considered: one is a conformer (A) in which the oxygen atom of the aldehyde is coordinated with the vicinal TMS group forming the fivemembered ring (see Figure 1), the other is the one (B) where the oxygen atom of the formyl moiety is directed far from the TMS group in order to avoid an unfavorable nonbonding interaction. If silyl enol ethers likely approach the aldehyde from the face away from the chromium complex through an acyclic transition state, the conformer A should give the aldol condensation product with (R),(R) configuration, whereas the conformer B must produce the (S),(S)-isomer upon treatment with silyl enol ethers. Reaction of (+)-4e actually afforded (-)-11e with (S),(S) configuration.







Therefore, it would be appropriate to conclude that this <u>erythro</u>selective aldol reaction proceeded <u>via</u> the conformer B rather than the pentacoordinated conformer A. Coordination of the aldehyde with Lewis acid under the Mukaiyama condition might drastically increase the bulkiness of oxygen functionality and result in the predominance of the conformer B. Similar Lewis acid coordinated mechanism<sup>18,22</sup> was proposed for the stereoselective addition of alkyl metals to **4e** pre-treated with magnesium bromide. An X-ray analysis of <u>erythro</u>-**8e** also suggests that the chromium(0) complex **4e** has the preferred conformation in which one of three methyl groups in the TMS moiety orients almost perpendicularly to the benzene ring to release the interference with the formyl group.

As indicated in Table I, highly preferential formation of the erythro isomer over the three isomer was observed only when the ortho substituent was TMS or ethyl group, and changing to methyl group caused a slight decrease of the erythro selectivity. The ortho methoxy group (compound 4b) could not attain a high diastereoselectivity, neither the hydrogen (compound 4a). Although the reaction mechanism is so far not clear, these observation in combination with the result of an X-ray analysis of (-)erythro-8e may tentatively suggest the following explanation: there are six staggered transition states in which silyl enol ethers approach the aldehyde from the face away from the chromium complex through conformer B as depicted in Figure 3. Among these transition states, transition states  $B_1$  and  $B_4$  may be favorable on the basis of consideration of the nonbonding interaction between the bulky ortho TMS group and the substituent on the double bond of silyl enol ethers. However, transition state  ${\tt B}_{\tt A}$  has a serious interaction between the trimethylsilyloxy group on the double bond and the aromatic proton (Ha) in comparison with the case of transition state  $B_1$ . Difference for the selectivity between the ortho methyl (4c) and the ortho TMS or ethyl group (4e or 4d) may reflect the difference of bulkiness.

#### Conclusion

Optically pure (+)- and (-)-tricarbonyl(<u>o</u>-TMS-benzaldehyde)chromium(0) complexes (4e) are easily available from racemic 4e by a conventional resolution method. A highly diastereo- and enantioselective aldol reaction of these chiral complexes with cyclic silyl enol ethers has been developed. In addition, an explanation was given to understand the <u>erythro</u>-selectivity, where the bulky <u>ortho</u> substituents of the formyl group played the most important role to govern the stereoselectivity. We

3020

are currently undertaking more detailed investigation from the mechanistic point of view as well as application of this asymmetric reaction to other substrates.

### **Experimental Section**

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. Infrared (IR) spectra were measured with a JASCO A-102 spectrometer, mass spectra (MS) with a Hitachi M-80 mass spectrometer, optical rotation with a JASCO DIP-181 digital polarimeter, and <sup>1</sup>H NMR spectra with JEOL JNM-GX 400 spectrometer in CDCl<sub>3</sub> using tetramethylsilane as an internal standard. Silica gel (silica gel 60, 230-400 mesh, Nacalai Tesque) was used for chromatography. Organic extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>.

**Preparation of 2-Phenyl-1,3-dioxolane (2).** A mixture of the benzaldehyde (1, 1 eq.) and ethylene glycol (1.2 eq.) in benzene was refluxed by using Dean-Stark apparatus in the presence of p-TsOH (3 mol%) for 7 h. The reaction mixture was diluted with AcOEt and then washed with sat. NaHCO<sub>3</sub> solution and brine. The AcOEt solution was dried and concentrated to leave the residual oil, which was purified by chromatography with n-hexane/AcOEt (100/5) to afford **2**.

**2-(2-Ethylphenyl)-1,3-dioxolane (2d).** The acetal **2d** (219 mg, 85%) was obtained as colorless oil from **1d** (194 mg, 1.40 mmol) and ethylene glycol (128 mg, 2.10 mmol): <sup>1</sup>H NMR  $\delta$  7.91-7.00 (4H, m, aromatic H), 6.01 (1H, s, Benzylic H), 4.25-3.89 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 2.78 (2H, g, <u>J</u>=7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.17 (3H, t, <u>J</u>=7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>); MS, <u>m/z</u> (%) 178 (M<sup>+</sup>, 100), 177 (67), 149 (80), 133 (100). Anal. Calcd for C<sub>11</sub>H<sub>14</sub>O<sub>2</sub>: C, 74.13; H, 4.36. Found: C, 74.23; H, 8.23.

**2-(2-Trimethylsilylphenyl)**-1,3-dioxolane (2e). The acetal 2e (3.05 g, 98%) was obtained as colorless oil from 1e (2.40 g, 13.5 mmol) and ethylene glycol (1.01 g, 16.3 mmol): <sup>1</sup>H NMR  $\delta$ 7.72-7.21 (4H, m, aromatic H), 5.97 (1H, s, benzylic H), 4.27-3.90 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 0.35 (9H, s, TMS); MS, <u>m/z</u> (%) 222 (M<sup>+</sup>, 1), 221 (2), 207 (38), 163 (100).

2-(4-Methoxy-2-trimethylsilylphenyl)-1,3-dioxolane (2f). The acetal 2f (459 mg, 89%) was obtained as colorless oil from 1f (426 mg, 2.05 mmol) and ethylene glycol (156 mg, 2.46 mmol): <sup>1</sup>H NMR & 7.94-6.84 (3H, m, aromatic H), 5.93 (1H, s, benzylic H), 4.30-3.94 (4H, m,  $OCH_2CH_2O$ ), 3.81 (3H, s, OMe), 0.34 (9H, s, TMS); MS, m/z (%) 252 (M<sup>+</sup>, 19), 237 (23), 193 (100). High resolution mass, calcd for  $C_{13}H_{20}O_3Si$ : 252.1180. Found: 252.1178.

**2-(4-Chloro-2-trimethylsilylphenyl)-1,3-dioxolane (2g).** The acetal **2g** (662 mg, 99%) was obtained as colorless oil from **1g** (555 mg, 2.61 mmol) and ethylene glycol (194 mg, 3.13 mmol): <sup>1</sup>H NMR  $\delta$  7.65-7.28 (3H, m, aromatic H), 5.93 (1H, s, benzylic H), 4.25-3.90 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 0.35 (9H, s, TMS); MS, <u>m/z</u> (%) 252 (M<sup>+</sup>+2, 2), 256 (M<sup>+</sup>, 5), 241 (100), 199 (99), 193 (93). Anal. Calcd for C<sub>12</sub>H<sub>17</sub>ClO<sub>2</sub>Si: C, 56.13; H, 6.67. Found: C, 56.20; H, 7.03.

Complexation of 2 with Chromium Hexacarbonyl. A mixture of 2-phenyl-1,3dioxolane (2, 1 eq.) and  $Cr(CO)_6$  (1.2 eq.) in <u>n</u>-heptane/<u>n</u>-Bu<sub>2</sub>O (2/1) was refluxed under nitrogen atmosphere for 48 h. The solvent was evaporated off and the residue was chromatographed with <u>n</u>-hexane/AcOEt (100/10) to afford 3.

**Tricarbonyl**[ $\eta^{6}$ -2-(2-ethylphenyl)-1,3-dioxolane]chromium(0)(3d). The chromium complex 3d (889 mg, 54%) was prepared as yellow plates from 2d (938 mg, 5.30 mmol) and Cr(CO)<sub>6</sub> (1.41 g, 6.40 mmol): mp 97-100°C (<u>n</u>-hexane); <sup>1</sup>H NMR  $\delta$  6.04-5.05 (5H, m, aromatic and benzylic H), 4.21-3.96 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 2.96-2.25 (2H, m, C<u>H<sub>2</sub>CH<sub>3</sub></u>), 1.26 (3H, t, <u>J</u>=7.6 Hz, CH<sub>2</sub>C<u>H<sub>3</sub></u>); IR (CHCl<sub>3</sub>) 1975, 1900 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 314 (M<sup>+</sup>, 45), 230 (100). Anal. Calcd for C<sub>14</sub>H<sub>14</sub>CrO<sub>5</sub>: C, 53.55; H, 4.49. Found: C, 53.69; H, 4.61.

**Tricarbonyl**[ $\eta^{6}$ -2-(2-trimethylsilylphenyl)-1,3-dioxolane]chromium(0) (3e). The chromium complex 3e (1.54 g, 82%) was prepared as yellow oil from 2e (1.16 g, 5.23 mmol) and Cr(CO)<sub>6</sub> (1.38 g, 6.27 mmol): <sup>1</sup>H NMR  $\delta$  5.70 (1H, s, benzylic H), 5.60-5.07 (4H, m, aromatic H), 4.16-3.97 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 0.38 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1960, 1870 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 358 (M<sup>+</sup>, 38), 275 (29), 274 (100), 163 (70). Anal. Calcd for C<sub>15</sub>H<sub>18</sub>CrO<sub>5</sub>Si: C, 50.27; H, 5.06. Found: C, 50.60; H, 5.27.

**Tricarbonyl**[ $\eta^{6}$ -2-(4-methoxy-2-trimethylsilylphenyl)-1,3dioxolane]chromium(0) (3f). The chromium complex 3f (376 mg, 74%) was prepared as yellow oil from 2f (330 mg, 1.31 mmol) and Cr(CO)<sub>6</sub> (346 mg, 1.57 mmol): <sup>1</sup>H NMR $\delta$  5.96-5.04 (4H, m, aromatic and benzylic H), 4.28-3.88 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>O), 3.69 (3H, s, OMe), 0.41 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1965, 1885 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 388 (M<sup>+</sup>, 31), 304 (76), 193 (100). High resolution mass, calcd for C<sub>16</sub>H<sub>20</sub>CrO<sub>6</sub>Si: 388.0433. Found: 388.0439.

Tricarbonyl[ $\eta^6$ -2-(4-chloro-2-trimethylsilylphenyl)-1,3dioxolane]chromium(0) (3g). The chromium complex 3g (176 mg, 42%) was prepared as yellow oil from 2g (274 mg, 1.07 mmol) and Cr(CO)<sub>6</sub> (282 mg, 1.28 mmol): <sup>1</sup>H NMR  $\delta$  5.99-5.29 (4H, m, aromatic and benzylic H), 4.20-3.90 (4H, m,  $OCH_2CH_2O$ ), 0.35 (9H, s, TMS); IR ( $CHCl_3$ ) 1970, 1890 cm-1; MS, m/z(%) 394 ( $M^++2$ , 16), 392 ( $M^+$ , 37), 310 (41), 309 (30), 308 (100). Anal. Calcd for  $C_{15}H_{17}Clcro_5Si$ : C, 45.86; H, 4.36. Found: C, 45.69, H, 4.47.

Hydrolysis of 3 with Hydrochloric Acid. 10% Hydrochloric acid (3 ml) was added to the solution of 3 in acetone under nitrogen atmosphere at room temperature. After stirring for 3 h, AcOEt was added to the reaction mixture and the AcOEt layer was separated. The AcOEt layer was washed with sat. NaHCO<sub>3</sub> solution, water, and brine, dried, and concentrated to dryness. Chromatography of the residue with <u>n</u>-hexane/AcOEt (100/5) gave 4.

**Tricarbonyl**( $\eta^{6}$ -2-ethylbenzaldehyde)chromium(0) (4d). Hydrolysis of 3d (270 mg, 0.86 mmol) with 10% HCl solution produced 4d (160 mg, 69%) as red needles: mp 51-52°C (<u>n</u>-hexane); <sup>1</sup>H NMR  $\delta$  9.78 (1H, s, CHO), 6.14-4.85 (4H, m, aromatic H), 3.34-2.16 (2H, m, CH<sub>2</sub>CH<sub>3</sub>), 1.31 (3H, t, <u>J</u>=7.6 Hz, CH<sub>2</sub>CH<sub>3</sub>); IR (CHCl<sub>3</sub>) 1990, 1920, 1685 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 270 (M<sup>+</sup>, 29), 186 (100). High resolution mass, calcd for C<sub>12</sub>H<sub>10</sub>CrO<sub>4</sub>: 269.9983. Found: 269.9975.

**Tricarbonyl**( $\eta^{6}$ -2-trimethylsilylbenzaldehyde)chromium(0) (4e). Hydrolysis of 3e (180 mg, 0.50 mmol) with 10% HCl solution produced 4e (140 mg, 89%) as red oil: <sup>1</sup>H NMR  $\delta$  9.72 (1H, s, CHO), 5.84-5.08 (4H, m, aromatic H), 0.41 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1980, 1900, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 314 (M<sup>+</sup>, 19), 230 (64), 163 (100). Anal. Calcd for C<sub>13</sub>H<sub>14</sub>CrO<sub>4</sub>Si: C, 49.67; H, 4.49. Found: C, 49.65; H, 4.52.

**Tricarbonyl**( $\eta^{6}$ -4-methoxy-2-trimethylsilylbenzaldehyde)chromium-(0) (4f). Hydrolysis of 3f (356 mg, 0.92 mmol) with 10% HCl solution produced 4f (323 mg, 93%) as red needles: mp 71-71.5°C (<u>n</u>-hexane); <sup>1</sup>H NMR $\delta$ 9.57 (1H, s, CHO), 6.14-5.08 (3H, m, aromatic H), 3.78 (3H, s, OMe), 0.44 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1960, 1900, 1670 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 344 (M<sup>+</sup>, 18), 260 (62), 193 (100). High resolution mass, calcd for C<sub>14</sub>H<sub>16</sub>Cr0<sub>5</sub>Si: 344.0170. Found: 344.0103.

**Tricarbonyl**( $\eta^6$ -4-chloro-2-trimethylsilylbenzaldehyde)chromium-(0) (4g). Hydrolysis of 3g (340 mg, 0.87 mmol) with 10% HCl solution produced 4g (158 mg, 52%) as red needles: mp 72-73°C (<u>n</u>-hexane); <sup>1</sup>H NMR $\delta$ 9.61 (1H, s, CHO), 6.02-5.39 (3H, m, aromatic H), 0.45 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1975, 1920, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 350 (M<sup>+</sup>+2, 9),348 (M<sup>+</sup>, 21), 266 (36), 264 (86), 197 (100). Anal. Calcd for C<sub>13</sub>H<sub>13</sub>ClCrO<sub>4</sub>Si: C, 44.74; H, 3.76. Found: C, 33.93; H, 3.90.

General Procedure for the Aldol Reaction of 4 with Silyl Enol Ethers 5-7. To a solution of the aldehyde (4, 1.0 eq.) and silyl enol ether(1.2-3 eq.) in  $CH_2Cl_2$  (1 ml/0.1 mmol) was slowly added  $BF_3$   $OEt_2$  (1.2-4 eq.) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at the same temperature for <u>ca</u>. 30 min and then quenched by addition of sat. NH<sub>4</sub>Cl solution. The reaction mixture was diluted with MeOH (4 ml), to which CAN (3 eq.) was added portionwise at 0°C. After stirring for an additional hour,  $CH_2Cl_2$  (5 ml) was added to the reaction mixture and washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with  $CH_2Cl_2/AcOEt$  afforded the aldol product.

 $(S^*, S^*)$  - and  $(S^*, R^*)$  -2-Hydroxyphenylmethyl-1-cyclopentanone (11a and 14a). The aldehyde 4a (44 mg, 0.18 mmol) and 5 (57 mg, 0.37 mmol) were treated with BF<sub>3</sub>·OEt<sub>2</sub> (0.73 mmol) and then with CAN (301 mg, 0.55 mmol) to furnish a mixture of 11a and 14a (30 mg, 87%): <sup>1</sup>H NMR  $\delta$  7.40 (5H, s, aromatic H), 5.30 (66/100H, d, <u>J</u>=2.9 Hz, benzylic H), 4.71 (34/100H, d, <u>J</u>=9.0 Hz, benzylic H), 2.62-1.58 (7H, m, aliphatic H); IR (CHCl<sub>3</sub>) 3400, 1710 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 190 (M<sup>+</sup>, 8), 172 (41), 107 (84), 84 (100).

 $(S^*, S^*)$ - and  $(S^*, R^*)$ -2-Hydroxyphenylmethyl-1-cyclohexanone (12a and 15a). The aldehyde 4a (80 mg, 0.33 mmol) and 6 (67 mg, 0.39 mmol) were treated with BF<sub>3</sub>·OEt<sub>2</sub> (0.40 mmol) and then with CAN (543 mg, 0.99 mmol) to furnish a mixture of 12a and 15a (61 mg, 91%): <sup>1</sup>H NMR § 7.40-7.19 (5H, m, aromatic H), 5.37 (47/100H, d, J=2.7 Hz, benzylic H), 4.78 (53/100H, d, J=8.8 Hz, benzylic H), 2.56-1.09 (9H, m, aliphatic H); IR (CHCl<sub>3</sub>) 3400, 1690 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 204 (M<sup>+</sup>, 3), 186 (33), 185 (26), 106 (100), 105 (96). High resolution mass, calcd for C<sub>13</sub>H<sub>16</sub>O<sub>2</sub>: 204.1148. Found: 204.1115.

 $(S^*, S^*)$ -and  $(S^*, R^*)$ -2-Hydroxyphenylmethyl-1-cycloheptanone (13a and 16a). The aldehyde 4a (33 mg, 0.14 mmol) and 7 (31 mg, 0.17 mmol) were treated with BF<sub>3</sub>·OEt<sub>2</sub> (0.17 mmol) and then with CAN (227 mg, 0.41 mmol) to furnish a mixture of 13a and 16a (24 mg, 81%): <sup>1</sup>H NMR  $\delta$  7.76-7.00 (5H, m, aromatic H), 5.17 (49/100H, d, <u>J</u>=2.5 Hz, benzylic H), 4.80 (51/100H, d, <u>J</u>=8.3 Hz, benzylic H), 2.61-1.33 (11H, m, aliphatic H); IR (CHCl<sub>3</sub>) 3400, 1670 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 218 (M<sup>+</sup>, 6), 200 (47), 175 (19), 112 (100). High resolution mass, calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: 218.1305. Found: 218.1304.

 $(S^*, S^*)$ -and  $(S^*, R^*)$ -2-Hydroxy(2-methoxyphenyl)methyl-1-cyclopentanone (11b and 14b). The aldehyde 4b (55 mg, 0.20 mmol) and 5 (38 mg, 0.24 mmol) were treated with BF<sub>3</sub>·OEt<sub>2</sub> (0.24 mmol) and then with CAN (333 mg, 0.61 mmol) to give a mixture of 11b and 14b (38 mg, 84%): <sup>1</sup>H NMR  $\delta$  7.52-6.71 (4H, m, aromatic H), 5.59 (50/100H, d, <u>J</u>=2.2 Hz, benzylic H), 5.18 (50/100H, d, <u>J</u>=9.0 Hz, benzylic H), 3.80 (3H, s, OMe), 2.75-1.39 (7H, m, aliphatic H); IR (CHCl<sub>3</sub>) 3450, 1720 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 220 (M<sup>+</sup>, 3), 137 (100), 107 (23). High resolution mass, calcd for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: 220.1099. Found: 220.1111.

 $(S^*, S^*)$ -and  $(S^*, R^*)$ -2-Hydroxy(2-methoxyphenyl)methyl-1-cyclohexanone (12b and 15b). The aldehyde 4b (58 mg, 0.21 mmol) and 6 (47 mg, 0.28 mmol) were treated with BF<sub>3</sub>·OEt<sub>2</sub> (0.26 mmol) and then with CAN (350 mg, 0.64 mmol) to give a mixture of 12b and 15b (45 mg, 89%): <sup>1</sup>H NMR  $\delta$ 7.556.77 (4H, m, aromatic H), 5.63 (69/100H, d, <u>J</u>=2.4 Hz, benzylic H), 5.26 (31/100H, d, <u>J</u>=8.5 Hz, benzylic H), 3.80 (3H, OMe), 3.33-1.32 (9H, m, aliphatic H); IR (CHCl<sub>3</sub>) 3550, 1690 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 234 (M<sup>+</sup>, 5), 216 (4), 137 (100). High resolution mass, calcd for  $C_{14}H_{18}O_3$ : 234.1255. Found: 234.1259.

 $(S^*, S^*)$  - and  $(S^*, R^*)$  -2-Hydroxy(2-methylphenyl)methyl-1-cycloheptanone (13c and 16c). A mixture of 13c and 16c (36 mg, 78%) was obtained from 4c (50 mg, 0,20 mmol) and 7 (73 mg, 0.32 mmol): <sup>1</sup>H NMR § 7.60-7.03 (4H, m, aromatic H), 5.37 (86/100H, d, <u>J</u>=2.7 Hz, benzylic H), 5.16 (14/100H, d, <u>J</u>=9.0 Hz, benzylic H), 2.85-1.07 (11H, m, aliphatic H), 2.29 (3x86/100H, s, Me), 2.16 (3x14/100H, s, Me); IR (CHCl<sub>3</sub>) 3450, 1690 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 232 (M<sup>+</sup>, 10), 112 (100). High resolution mass, calcd for C<sub>15</sub>H<sub>20</sub>O<sub>2</sub>: 232.1463. Found: 232.1481.

 $(S^*, S^*) - 2 - (2 - Ethylphenyl)hydroxymethyl - 1 - cycloheptanone (13d). The aldol$ product 13d (42 mg, 84%) was obtained from 4d (55 mg, 0.20 mmol) and 7 $(60 mg, 0.26 mmol): <sup>1</sup>H NMR <math>\delta$  7.52-7.20 (4H, m, aromatic H), 5.42 (1H, d,  $\underline{J}=2.5$  Hz, benzylic H), 2.80-1.20 (13H, m, aliphatic H and CH<sub>2</sub>CH<sub>3</sub>), 1.26 (3H, t,  $\underline{J}=7.6$  Hz, CH<sub>2</sub>CH<sub>3</sub>; IR (CHCl<sub>3</sub>) 3550, 1700 cm<sup>-1</sup>; MS,  $\underline{m/z}$  (%) 246 (M<sup>+</sup>, 9), 112 (100). High resolution mass, calcd for C<sub>16</sub>H<sub>22</sub>O<sub>2</sub>: 246.1618. Found: 246.1631.

 $(S^*, S^*)$  - and  $(S^*, R^*)$  -2-Hydroxy(2-trimethylsilylphenyl)methyl-1cyclopentanone (11e and 14e). A mixture of 11e and 14e (30 mg, 61%) was obtained from 4e (58 mg, 0.19 mmol) and 5 (58 mg, 0.37 mmol): <sup>1</sup>H NMR  $\delta$ 7.65-7.15 (4H, m, aromatic H), 5.59 (96/100H, d, J=1.5 Hz, benzylic H), 4.91 (4/100H, d, J=9.8 Hz, benzylic H), 2.40-1.80 (7H, m, aliphatic H), 0.29 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3450, 1720 cm<sup>-1</sup>; MS, m/z (%) 262 (M<sup>+</sup>, 0.3), 247 (25), 164 (35), 163 (100). Pure 11e was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 122-123°C. High resolution mass, calcd for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>Si: 262.1388. Found: 262.1410.

 $(S^*, S^*)$  - and  $(S^*, R^*)$  -2-Hydroxy(2-trimethylsilylphenyl)methyl-1cyclohexanone (12e and 15e). A mixture of 12e and 15e (35 mg, 70%) was obtained from 4e (56 mg, 0.18 mmol) and 6 (61 mg, 0.36 mmol): <sup>1</sup>H NMR  $\delta$ 7.60-7.21 (4H, m, aromatic H), 5.62 (90/100H, d, <u>J</u>=2.0 Hz, benzylic H), 5.11 (10/100H, d, <u>J</u>=9.3 Hz, benzylic H), 2.61-1.40 (9H, m, aliphatic H), 0.29 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3400, 1690 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 276 (M<sup>+</sup>, 0.3), 164 (15), 163 (100), 98 (32). Pure 12e was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 58-59°C. High resolution mass, calcd for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>Si: 276.1545. Found: 276.1550.

 $(S^*, S^*) \sim 2$ -Hydroxy(2-trimethylsilylphenyl)methyl-1-cycloheptanone (13e). The aldol product 13e (40 mg, 75%) was obtained from 4e (58 mg, 0.19 mmol) and 7 (68 mg, 0.37 mmol) as colorless oil : <sup>1</sup>H NMR  $\delta$  7.65-7.14 (4H, m, aromatic H), 5.38 (1H, d,  $\underline{J}=2.7$  Hz, benzylic H), 2.97-1.09 (11H, m, aliphatic H), 0.33 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3450, 1670 cm<sup>-1</sup>; MS,  $\underline{m/z}$  (%) 290 (M<sup>+</sup>, 3), 275 (9), 199 (18), 163 (100). High resolution mass, calcd for  $C_{17}H_{26}O_2Si$ : 290.1700. Found: 290.1701.

 $(S^*,S^*)$ - and  $(S^*,R^*)$ -2-Hydroxy-(4-methoxy-2-trimethylsilylphenyl)methyl-1-cyclopentanone (11f and 14f). A mixture of 11f and 14f (40 mg, 95%) was obtained from 4f (50 mg, 0.14 mmol) and 5 (45 mg, 0.29 mmol): <sup>1</sup>H NMR  $\delta$  7.60-6.80 (3H, m, aromatic H), 5.54 (93/100H, d, <u>J</u>=1.0 Hz, benzylic H), 4.86 (7/100H, d, <u>J</u>=9.8 Hz, benzylic H), 3.80 (3H, s, OMe), 2.49-1.47 (7H, m, aliphatic H), 0.35 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3300, 1715 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 292 (M<sup>+</sup>, 6), 223 (15), 194 (73), 193 (100). Pure 11f was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 124-126°C. High resolution mass, calcd for C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>Si: 292.1494. Found: 292.1496.

 $(S^*,S^*)$  - and  $(S^*,R^*)$  - 2-Hydroxy(4-methoxy-2-trimethylsilylphenyl)methyl-1-cyclohexanone (12f and 15f). A mixture of 12f and 15f (39 mg, 70%) was obtained from 4f (62 mg, 0.18 mmol) and 6 (61 mg, 0.34 mmol): <sup>1</sup>H NMR  $\delta$  7.51-6.81 (3H, m, aromatic H), 5.56 (97/100H, d, <u>J</u>=2.2 Hz, benzylic H), 5.06 (3/100H, d, <u>J</u>=9.3 Hz, benzylic H), 3.81 (3H, s, OMe), 2.60-1.41 (9H, m, aliphatic H), 0.29 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3500, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 306 (M<sup>+</sup>, 4), 273 (5), 209 (29), 193 (100). Pure 12f was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 109-110°C. High resolution mass, calcd for C<sub>17</sub>H<sub>26</sub>O<sub>3</sub>Si: 306.1650. Found: 306.1654.

 $(S^*, S^*)$ -2-Hydroxy(4-methoxy-2trimethylsilylphenyl)methyl-1cycloheptanone (13f). The aldol product 13f (42 mg, 86%) was obtained from 4f (52 mg, 0.15 mmol) and 7 (55 mg, 0.30 mmol) as colorless oil: <sup>1</sup>H NMR  $\delta$  7.57-6.80 (3H, m, aromatic H), 5.31 (1H, d, <u>J</u>=3.4 Hz, benzylic H), 3.80 (3H, s, OMe), 2.95-1.08 (11H, m, aliphatic H), 0.33 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3500, 1670 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 320 (M<sup>+</sup>, 2), 209 (32), 194 (55), 193 (100). High resolution mass, calcd for C<sub>18</sub>H<sub>28</sub>O<sub>3</sub>Si: 320.1807. Found: 320.1819.

 $(S^*, S^*)$ - and  $(S^*, R^*)$ -2-(4-Chloro-2-trimethylsilylphenyl)hydroxy-methyl-1-cyclopentanone (11g and 14g). A mixture of 11g and 14g (21 mg, 69%) was obtained from 4g (36 mg, 0.10 mmol) and 5 (32 mg, 0.21 mmol): <sup>1</sup>H NMR  $\delta$ 7.59-7.25 (3H, m, aromatic H), 5.55 (95/100H, d, J=1.5 Hz, benzylic H), 4.88 (5/100H, d, J=9.5 Hz, benzylic H), 2.47-1.50 (7H, m, aliphatic H), 0.36 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3400, 1720 cm<sup>-1</sup>; MS, m/z (%) 298 (M<sup>+</sup>+2, 0.1), 296 (M<sup>+</sup>, 0.2), 199 (42), 197 (100). Pure 11g was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 122-124°C. High resolution mass, calcd for C<sub>15</sub>H<sub>21</sub>ClO<sub>2</sub>Si: 296.0998. Found: 296.1007.  $(S^*, S^*)-(S^*, R^*)-2-(4-Chloro-2-trimethylsilylphenyl)hydroxy-methyl-1$ cyclohexanone (12g and 15g). A mixture of 12g and 15g (32 mg, 72%) was $obtained from 4g (50 mg, 0.14 mmol) and 6 (49 mg, 0.29 mmol): <sup>1</sup>H NMR <math>\delta$ 7.51-7.34 (3H, m, aromatic H), 5.58 (92/100H, d, <u>J</u>=2.0 Hz, benzylic H), 5.07 (8/100H, d, <u>J</u>=9.5 Hz, benzylic H), 2.56-1.09 (9H, m, aliphatic H), 0.30 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3550, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 312 (M<sup>+</sup>+2, 0.1), 310 (M<sup>+</sup>, 0.4), 199 (36), 197 (100). Pure 12g was obtained by recrystallization from <u>n</u>-hexane/Et<sub>2</sub>O as colorless needles, mp 140.5-141.5°C. High resolution mass, calcd for C<sub>16</sub>H<sub>23</sub>ClO<sub>2</sub>Si: 310.1153. Found: 310.1143.

 $(S^*, S^*)-(S^*, R^*)-2-(4-Chloro-2-trimethylsilylphenyl)hydroxy-methyl-1$ cycloheptanone (13g and 16g). A mixture of 13g and 16g

(34 mg, 94%) was obtained from **4g** (39 mg, 0.11 mmol) and **7** (41 mg, 0.22 mmol): <sup>1</sup>H NMR § 7.57-7.23 (3H, m, aromatic H), 5.34 (95/100H, d, <u>J</u>=2.2 Hz, benzylic H), 5.12 (5/100H, d, <u>J</u>=9.3 Hz, benzylic H), 2.86-0.76 (11H, m, aliphatic H), 0.33 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3450, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 326 (M<sup>+</sup>+2, 0.4), 324 (M<sup>+</sup>, 1), 199 (72), 198 (30), 197 (100). High resolution mass, calcd for  $C_{17}H_{25}ClO_2Si$ : 324.1311. Found: 324.1313.

General Procedure for the Aldol Reaction of Benzaldehydes (1) with Silyl enol ethers 5-7. To a solution of benzaldehydes (1)(0.55 mmol) and silyl enol ethers 5-7 (0.66 mmol, 1.2 eq.) in  $CH_2Cl_2$  (1 ml/0.1 mmol) was added  $BF_3 \cdot OEt_2$  (0.66 mmol, 1.2 eq.) at -78°C. After stirring for 10-30 min, sat.  $NH_4Cl$  solution was added to the reaction mixture. Work-up and chromatography of the residue with  $CH_2Cl_2/AcOEt$  gave the aldol products. The results were summarized in Table II. The benzylic proton of 16d, 16e, and 16f appeared at  $\delta$  5.20 (J= 9.3 Hz), 5.17 (J=9.3 Hz), and 5.12 (J=9.5 Hz), respectively.

 $(S^*,S^*)$ -Tricarbonyl[ $\eta^6$ -2-acetoxy(4-methoxy-2-trimethylsilylphenyl)methyl-1-cyclopentanone]chromium(0) (17). The aldol products 8f, derived from 4f (67 mg, 0.20 mmol) and 5 (61 mg, 0.39 mmol), was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 ml). Acetic anhydride (3 drops) and N,N,dimethylaminopyridine (DMAP)(120 mg, 0.98 mmol) were added to the CH<sub>2</sub>Cl<sub>2</sub> solution. After standing for 2 h at room temperature, the CH<sub>2</sub>Cl<sub>2</sub> solution was washed with sat. NaHCO<sub>3</sub> solution, water, and brine, dried, and concentrated to dryness. Chromatography of the residue with <u>n</u>hexane/CH<sub>2</sub>Cl<sub>2</sub> (1/1) provided 17 (36 mg, 40% overall yield from 4f) as yellow needles: mp 165-168°C (MeOH); <sup>1</sup>H NMR  $\delta$  6.22 (1H, d, <u>J</u>=2.4 Hz, benzylic H), 5.58 (1H, d, <u>J</u>=7.0 Hz, aromatic H), 5.17 (1H, dd, <u>J</u>=7.0 and 2.4 Hz, aromatic H), 4.93 (1H, d, <u>J</u>=2.4 Hz, aromatic H), 3.70 (3H, s, OMe), 2.50-1.52 (7H, m, aliphatic H), 2.06 (3H, s, OAc), 0.50 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1950, 1860, 1730 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 470 (M<sup>+</sup>, 5), 386 (40), 326 (100). High resolution mass, calcd for  $C_{21}H_{26}CrO_7Si$ : 470.0851. Found: 470.0862.

 $(s^*, s^*)$ -2-Acetoxy(4-methoxy-2-trimethylsilylphenyl)methyl-1cyclopentanone (18). To a solution of 17 (18 mg, 0.04 mmol) in MeOH/CH<sub>2</sub>Cl<sub>2</sub> (5 ml/3 ml) was added portionwise CAN (62 mg, 0.11 mmol) at 0°C. After stirring for 1 h, the reaction mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (5 ml) and washed with water and brine, dried, and concentrated to leave the residue which was chromatographed with CH<sub>2</sub>Cl<sub>2</sub> to afford 18 (12 mg, 97%) as colorless needles: mp 101-103°C (hexane/Et<sub>2</sub>O); <sup>1</sup>H NMR  $\delta$  7.28 (1H, d, J=8.8 Hz, aromatic H), 7.05 (1H, d, J=2.7 Hz, aromatic H), 6.85 (1H, dd, J=8.8 and 2.7 Hz, aromatic H), 6.38 (1H, d, J=2.0 Hz, benzylic H), 3.79 (3H, s, OMe), 2.63-1.82 (7H, m, aliphatic H), 2.00 (3H, s, OAC), 0.41 (9H, s, TMS); IR (CHCl<sub>3</sub>) 1720 cm<sup>-1</sup>; MS, m/z (%) 334 (M<sup>+</sup>, 13), 260 (22), 259 (100), 193 (99). High resolution mass, calcd for C<sub>18</sub>H<sub>26</sub>O<sub>4</sub>Si: 334.1598. Found: 334.1591. THe acetyl derivative 18 was also derived from 11f by acetylation with acetic anhydride and DMAP in 65% overall yield from **4f**.

Removal of TMS group in the Aldol Product. The aldol condensation of 4e (61 mg, 0.19 mmol) with 5 (57 mg, 0.37 mmol) produced 8e (erythro/threo=96/4), which was subsequently treated with TBAF (0.21 ml of 1 M solution in THF, 0.21 mmol) in THF (5 ml) at  $-20^{\circ}$ C for 3 min. The reaction mixture was then diluted with MeOH (5 ml) and CAN (317 mg, 0.58 mmol) was added portionwise to the MeOH solution at 0°C. Stirring was continued for 1 h. A usual work-up gave the residue which was chromatographed with CH<sub>2</sub>Cl<sub>2</sub>/AcOEt (100/5) to give a mixture of 11a and 14a (28 mg, 75%) in a ratio of 72 to 28. The structure of 11a was identified by comparison with the authentic specimen.<sup>23</sup> Pure erythro-8e afforded under the similar condition a mixture of 11a and 14a (86/14).

Conversion of Racemic-4e into (+)- and (-)- Semioxamazones. A solution of (+)-4e (442 mg, 1.35 mmol) and (S)-(-)5-( $\alpha$ -phenylethyl)semioxamazide (278 mg, 1.35 mmol) in benzene (20 ml) was heated under reflux in the presence of p-TsOH·H<sub>2</sub>O (17 mg, 0.09 mmol) for 1 h. After cooling, AcOEt (20 ml) was added to the benzene solution and the organic solution was washed with sat. NaHCO<sub>3</sub>, water, and brine, dried, and concentrated to dryness. Chromatography of the residue with <u>n</u>-hexane/AcOEt (100/40) gave (+)-19 (251 mg, 37%) and (-)-19 (251 mg, 37%). (+)-19: yellow needles, mp 135-141°C (<u>n</u>-hexane/Et<sub>2</sub>O);  $[\alpha]_D^{25}$ +596°(<u>c</u>, 0.52, CHCl<sub>3</sub>); <sup>1</sup>H NMR $\delta$  10.33 (1H, s, NH), 8.44 (1H, s, CH=N), 7.71 (1H, d, <u>J</u>=7.8 Hz, NH), 7.34 (5H, s, aromatic H), 6.01-4.93 (5H, m, aromatic and benzylic H), 1.60 (3H, d, <u>J</u>=7.0 Hz, CHC<u>H<sub>3</sub></u>), 0.41 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3400, 3320, 1975, 1900, 1680 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 503 (M<sup>+</sup>, 5), 420 (25), 419 (65), 162 (91), 105 (100). Anal. Calcd for C<sub>23</sub>H<sub>25</sub>CrN<sub>3</sub>O<sub>5</sub>Si: C, 54.86; H, 5.00; N, 8.34. Found:

C, 54.60; H, 5.07; N, 8.21. (-)-19: yellow needles, mp 93-98°C (<u>n</u>-hexane/Et<sub>2</sub>O);  $[\alpha]_D^{25}$  -657°(<u>c</u>, 0.51, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$ 10.32 (1H, s, NH), 8.48 (1H, s, CH=N), 7.71 (1H, d, <u>J</u>=9.0 Hz, NH), 7.34 (5H, s, aromatic H), 5.98-4.92 (5H, m, aromatic and benzylic H), 1.60 (3H, d, <u>J</u>=7.0 Hz, CHC<u>H<sub>3</sub></u>), 0.42 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3400, 3330, 1980, 1910, 1685 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 503 (M<sup>+</sup>, 1), 420 (34), 419 (87), 162 (100), 105 (76). Anal. Calcd for  $C_{23}H_{25}CrN_{3}O_{5}Si:$  C, 54.86; H, 5.00; N, 8.34. Found: C, 54.74; H, 5.09; N, 8.66.

Hydrolysis of (+)- and (-)- Semioxamazones [(+)-19 and (-)-19]. A solution of (+)-19 (151 mg, 0.30 mmol) and 60% H<sub>2</sub>SO<sub>4</sub> solution (3 ml) in benzene (8 ml) was refluxed for 12 h under nitrogen atmosphere. The benzene solution was diluted with AcOEt (15 ml) and the organic solution was washed with sat. NaHCO<sub>3</sub> solution, water, and brine, dried, and concentrated to dryness. Chromatography of the residue with <u>n</u>-hexane/AcOEt (100/5) afforded (+)-4e (76 mg, 81%) as red oil:  $[\alpha]_D^{25}$  +149°( $\underline{c}$ , 0.50, CHCl<sub>3</sub>), lit<sup>18</sup>  $[\alpha]_D^{20}$  +146°( $\underline{c}$ , 0.10, CHCl<sub>3</sub>). (-)-4e (115 mg, 73%) was obtained from (-)-19 (251 mg, 0.50 mmol) as red oil:  $[\alpha]_D^{25}$  -153°( $\underline{c}$ , 0.48, CHCl<sub>3</sub>), lit<sup>18</sup>  $[\alpha]_D^{16}$  -154 ( $\underline{c}$ , 1, CHCl<sub>3</sub>).

(5,S)-(-)-8e. The aldehyde, (+)-4e (57 mg, 0.18 mmol) was treated with 5 (56 mg, 0.36 mmol) under the similar condition (without exposure to CAN) described for racemic-4e to provide the crude aldol product. Careful chromatography of the residue gave (S,S)-(-)-8e (47 mg, 66%) as yellow plates: mp 162-164°C (MeOH);  $[\alpha]_D^{18}$  -48°(<u>c</u>, 0.17, CHCl<sub>3</sub>); <sup>1</sup>H NMR  $\delta$  5.78-5.00 (5H, m, aromatic and benzylic H), 2.50-1.51 (7H, m, aliphatic H), 0.41 (9H, s, TMS); IR (CHCl<sub>3</sub>) 3400, 1970, 1900, 1740 cm<sup>-1</sup>; MS, <u>m/z</u> (%) 398 (M<sup>+</sup>, 1), 314 (24), 230 (50), 163 (100). Anal. Calcd for C<sub>18</sub>H<sub>22</sub>CrO<sub>5</sub>Si: C, 54.26; H, 5.57. Found: C, 53.99; H, 5.74.

(R,R)-(+)-8e. the aldol product, (R,R)-(+)-8e (29 mg, 65%), $[\alpha]_D^{18}$  +53°( $\underline{c}$ , 0.19, CHCl<sub>3</sub>) was obtained from (-)-4e (35 mg, 0.11 mmol).

X-Ray Crystallographic Analysis of (S,S)-(-)-8e. Cell constant:  $C_{18}H_{22}O_5SiCr$ , orthorhombic, space group  $P2_12_12_1$ , Z=4, a=10.704 (2), b=16.313 (2), c=8.555 (2)Å, v=1912.4(9)Å<sup>3</sup>, Dc=1.384 g/cm<sup>3</sup>,  $\mu = (M_0K)=6.67$ cm<sup>-1</sup>. The final R-value was 0.040. Bond distances and bond angles were summarized in Table IV and V. The absolute configuration was determined by Bijoveti anomalous-dispersion method based on the observed and calculated structure factors of 26 Friedel pairs.

atom	atom	distance	3	atom	atom	dista	nce
Cr	C <sub>1</sub>	2.231 (6	5)	0 <sub>4</sub>	C <sub>17</sub>	1.135	(8)
Cr	C2	2.176 (7	7)	0 <sub>5</sub>	с <sub>18</sub>	1.149	(8)
Cr	c3	2.214 (7	7)	с <sub>1</sub>	c2	1.444	(8)
Cr	C4	2.210 (7	7)	C <sub>1</sub>	C6	1.430	(8)
Cr	с <sub>5</sub>	2.221 (6	5)	C2	с <sub>з</sub>	1.379	(9)
Cr	с <sub>б</sub>	2.228 (6	5)	c3	C <sub>4</sub>	1.40	(1)
Cr	C <sub>16</sub>	1.835 (8	3)	C <sub>4</sub>	c <sub>5</sub>	1.395	(8)
Cr	C <sub>17</sub>	1.849 (7	7)	C <sub>5</sub>	C <sub>6</sub>	1.418	(8)
Cr	C <sub>18</sub>	1.852 (8	3)	C <sub>6</sub>	C <sub>7</sub>	1.514	(8)
Si	C <sub>1</sub>	1.901 (6	5)	C <sub>7</sub>	C <sub>8</sub>	1.527	(8)
Si	c <sub>13</sub>	1.862 (8	3)	c <sub>8</sub>	C <sub>9</sub>	1.536	(8)
Si	c <sub>14</sub>	1.861 (9	))	C <sub>8</sub>	C <sub>12</sub>	1.535	(8)
Si	C <sub>15</sub>	1.85 (1	)	C <sub>9</sub>	C <sub>10</sub>	1.50	(1)
0 <sub>1</sub>	с <sub>7</sub>	1.413 (7	7)	C <sub>10</sub>	C <sub>11</sub>	1.53	(1)
0 <sub>2</sub>	Сg	1.208 (7	7)	C <sub>11</sub>	C <sub>12</sub>	1.52	(1)
0 <sub>3</sub>	<sup>C</sup> 16	1.159 (8	3)				
0 <sub>1</sub>	<sup>H</sup> 10	0.67 (7	7)	C <sub>12</sub>	H121	1.00	(5)
с <sub>2</sub>	H <sub>2</sub>	0.92 (5	5)	C <sub>12</sub>	H <sub>122</sub>	0.89	(5)
c3	H <sub>3</sub>	0.81 (5	5)	C <sub>13</sub>	H <sub>131</sub>	0.91	(7)
C <sub>4</sub>	H <sub>4</sub>	0.81 (7	7)	C <sub>13</sub>	H <sub>132</sub>	0.95	(8)
с <sub>5</sub>	H <sub>5</sub>	0.95 (6	5)	C <sub>13</sub>	<sup>H</sup> 133	0.93	(8)
с <sub>7</sub>	<sup>H</sup> 7	0.99 (5	5)	C <sub>14</sub>	<sup>H</sup> 141	0.90	(9)
с <sub>8</sub>	<sup>н</sup> 8	0.89 (6	5)	C <sub>14</sub>	<sup>H</sup> 142	0.99	(6)
C <sub>10</sub>	<sup>H</sup> 101	0.94 (7	7)	C <sub>14</sub>	<sup>H</sup> 143	0.79	(7)
C <sub>10</sub>	<sup>H</sup> 102	0.72 (6	5)	C <sub>15</sub>	<sup>H</sup> 151	0.93	(8)
c <sub>11</sub>	H <sub>111</sub>	0.89 (6	5)	C <sub>15</sub>	H <sub>152</sub>	0.8	(1)
C <sub>11</sub>	<sup>H</sup> 112	1.16 (7	")	C <sub>15</sub>	<sup>H</sup> 153	1.0	(1)

Table IV. Bond Distances (in Å) of (-)-Erythro-8e with Estimated Standard Deviations in Parentheses

			Deviations				
atom	atom	atom	angle	atom	atom	atom	angle
с <sub>1</sub>	CR <sub>1</sub>	c <sub>2</sub>	38.2 (2)	C4	CR <sub>1</sub>	с <sub>18</sub>	130.9 (3)
c <sub>1</sub>	CR <sub>1</sub>	c <sub>3</sub>	68.1 (2)	с <sub>5</sub>	CR <sub>1</sub>	с <sub>б</sub>	37.2 (2)
C1	CR <sub>1</sub>	C4	80.6 (2)	с <sub>5</sub>	CR <sub>1</sub>	C <sub>16</sub>	162.3 (3)
с <sub>1</sub>	CR <sub>1</sub>	с <sub>5</sub>	67.7 (2)	с <sub>5</sub>	CR <sub>1</sub>	C <sub>17</sub>	106.8 (3)
с <sub>1</sub>	CR <sub>1</sub>	C <sub>6</sub>	37.4 (2)	с <sub>5</sub>	CR <sub>1</sub>	C <sub>18</sub>	99.8 (3)
с <sub>1</sub>	CR <sub>1</sub>	C <sub>16</sub>	94.9 (3)	с <sub>6</sub>	CR <sub>1</sub>	C <sub>16</sub>	128.0 (3)
с <sub>1</sub>	CR <sub>1</sub>	C <sub>17</sub>	164.9 (3)	с <sub>б</sub>	CR <sub>1</sub>	C <sub>17</sub>	142.4 (3)
с <sub>1</sub>	CR <sub>1</sub>	с <sub>18</sub>	106.2 (3)	c <sub>6</sub>	CR <sub>1</sub>	C <sub>18</sub>	89.0 (3)
с <sub>2</sub>	CR <sub>1</sub>	c3	36.6 (2)	C <sub>16</sub>	cr <sub>1</sub>	C <sub>17</sub>	89.4 (3)
c <sub>2</sub>	CR1	с <sub>4</sub>	66.5 (3)	c <sub>16</sub>	CR <sub>1</sub>	c <sub>18</sub>	87.5 (3)
с <sub>2</sub>	CR1	с <sub>5</sub>	78.2 (2)	C <sub>17</sub>	CR <sub>1</sub>	C <sub>18</sub>	88.5 (3)
с <sub>2</sub>	CR <sub>1</sub>	с <sub>б</sub>	66.8 (2)	с <sub>1</sub>	si <sub>1</sub>	C <sub>13</sub>	112.3 (4)
c <sub>2</sub>	CR <sub>1</sub>	C <sub>16</sub>	86.2 (3)	c <sub>1</sub>	SI1	C <sub>14</sub>	107.0 (3)
с <sub>2</sub>	CR <sub>1</sub>	C <sub>17</sub>	128.0 (3)	c <sub>1</sub>	si <sub>1</sub>	C <sub>15</sub>	111.5 (4)
c <sub>2</sub>	CR <sub>1</sub>	C <sub>18</sub>	142.8 (3)	с <sub>13</sub>	si <sub>1</sub>	C <sub>14</sub>	107.3 (5)
c3	CR <sub>1</sub>	C4	37.0 (2)	C <sub>13</sub>	si <sub>1</sub>	c <sub>15</sub>	108.9 (6)
c3	CR <sub>1</sub>	c <sub>5</sub>	66.1 (3)	C <sub>14</sub>	si <sub>1</sub>	C <sub>15</sub>	109.6 (6)
c3	CR1	с <sub>6</sub>	78.8 (2)	CR <sub>1</sub>	с <sub>1</sub>	si <sub>1</sub>	125.9 (3)
c3	CR1	<sup>C</sup> 16	105.6 (3)	CR <sub>1</sub>	с <sub>1</sub>	c2	68.8 (4)
c3	CR <sub>1</sub>	C <sub>17</sub>	96.7 (3)	CR <sub>1</sub>	с <sub>1</sub>	с <sub>б</sub>	71.2 (3)
c3	CR1	с <sub>18</sub>	165.8 (3)	si <sub>1</sub>	c <sub>1</sub>	c2	118.1 (4)
C <sub>4</sub>	CR <sub>1</sub>	c <sub>5</sub>	36.7 (2)	si <sub>1</sub>	с <sub>1</sub>	с <sub>б</sub>	126.8 (4)
C <sub>4</sub>	CR <sub>1</sub>	c <sub>6</sub>	66.9 (2)	C <sub>2</sub>	c <sub>1</sub>	с <sub>6</sub>	115.1 (5)
C4	CR <sub>1</sub>	C <sub>16</sub>	141.2 (3)	CR <sub>1</sub>	с <sub>2</sub>	c <sub>1</sub>	72.9 (3)
C4	CR <sub>1</sub>	C <sub>17</sub>	87.0 (3)	CR <sub>1</sub>	$c_2$	C3	73.2 (4)

01

01

с<sub>6</sub>

C7

C7

C9

0<sub>2</sub>

02

с<sub>8</sub>

C7

C7

C7

с<sub>8</sub>

С8

C<sub>8</sub>

с<sub>9</sub>

C9

Cg

c<sub>6</sub>

с8

C<sub>8</sub>

c9

C<sub>12</sub>

C<sub>12</sub>

c<sub>8</sub>

C<sub>10</sub>

C<sub>10</sub>

111.7 (5)

107.8 (5)

109.5 (5)

111.4 (5)

117.5 (5)

103.6 (5)

124.9 (6)

126.8 (6)

108.2 (6)

Table	v.	Bond	Angles	(°)	of	( - ) -EI	rythro-8e	with	Estimated	Standard
			Γ	evi	atic	ons in	Parenthes	ses		

\_\_\_\_ с<sub>1</sub> с<sub>1</sub>  $C_1$  $c_1$ с<sub>1</sub> с<sub>1</sub> с<sub>1</sub> с<sub>1</sub> с<sub>2</sub> c<sub>2</sub> с<sub>2</sub> с<sub>2</sub> c<sub>2</sub> с<sub>2</sub> c<sub>2</sub> c3 c3 c3 c3 c3 c<sub>3</sub> c<sub>4</sub> с<sub>4</sub> C4 с<sub>4</sub> с<sub>1</sub>

с<sub>2</sub>

C<sub>3</sub>

c3

C<sub>3</sub>

C4

C<sub>4</sub>

с<sub>4</sub>

с<sub>5</sub>

с<sub>5</sub>

CR1

 $CR_1$ 

 $C_2$ 

 $CR_1$ 

CR<sub>1</sub>

c3

CR1

CR1

C3

c<sub>2</sub>

с<sub>4</sub>

C<sub>4</sub>

c3

с<sub>5</sub>

с<sub>5</sub>

с<sub>4</sub>

C<sub>6</sub>

123.7 (6)

70.2 (4)

71.4 (4)

119.6 (6)

71.6 (4)

72.1 (4)

119.6 (7)

71.3 (4)

71.7 (3)

atom	atom	atom	angl	e	atom	atom	atom	angl	e
с <sub>4</sub>	с <sub>5</sub>	с <sub>6</sub>	121.0	(5)	و٢	C <sub>10</sub>	C <sub>11</sub>	105.7	(6)
CR <sub>1</sub>	с <sub>б</sub>	c1	71.4	(3)	c <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub>	103.3	(6)
CR <sub>1</sub>	с <sub>6</sub>	с <sub>5</sub>	71.1	(4)	c <sub>8</sub>	c <sub>12</sub>	c <sub>11</sub>	104.1	(6)
cr <sub>1</sub>	с <sub>6</sub>	C7	133.3	(4)	CR <sub>1</sub>	C <sub>16</sub>	03	177.9	(7)
с <sub>1</sub>	с <sub>6</sub>	с <sub>5</sub>	121.0	(5)	CR <sub>1</sub>	C <sub>17</sub>	0 <sub>4</sub>	177.4	(7)
с <sub>1</sub>	c <sub>6</sub>	с <sub>7</sub>	121.9	(5)	CR <sub>1</sub>	с <sub>18</sub>	0 <sub>5</sub>	178.5	(7)
с <sub>5</sub>	с <sub>6</sub>	с <sub>7</sub>	117.0	(5)					
с <sub>7</sub>	01	<sup>H</sup> 10	113	(7)	C4	с <sub>5</sub>	<sup>H</sup> 5	124	(3)
CR <sub>1</sub>	с <sub>2</sub>	<sup>H</sup> 2	130	(3)	с <sub>6</sub>	с <sub>5</sub>	<sup>H</sup> 5	115	(3)
с <sub>1</sub>	c2	<sup>H</sup> 2	116	(3)	0 <sub>1</sub>	с <sub>7</sub>	H <sub>7</sub>	113	(3)
c3	с <sub>2</sub>	<sup>H</sup> 2	120	(3)	с <sub>б</sub>	с <sub>7</sub>	H <sub>7</sub>	110	(3)
CR <sub>1</sub>	c3	H <sub>3</sub>	125	(4)	с <sub>8</sub>	с <sub>7</sub>	H <sub>7</sub>	105	(3)
с <sub>2</sub>	c3	н <sub>3</sub>	127	(4)	с <sub>7</sub>	с <sub>8</sub>	<sup>H</sup> 8	102	(4)
с <sub>4</sub>	c3	н <sub>3</sub>	113	(4)	c <sub>9</sub>	с <sub>8</sub>	<sup>H</sup> 8	110	(4)
CR <sub>1</sub>	C <sub>4</sub>	<sup>H</sup> 4	135	(6)	<sup>C</sup> 12	с <sub>8</sub>	<sup>H</sup> 8	112	(4)
c3	C4	H <sub>4</sub>	119	(6)	c <sub>9</sub>	c <sub>10</sub>	<sup>H</sup> 101	102	(5)
с <sub>5</sub>	C4	H <sub>4</sub>	121	(6)	c <sub>9</sub>	c <sub>10</sub>	<sup>H</sup> 102	115	(6)
CR <sub>1</sub>	с <sub>5</sub>	н <sub>5</sub>	128	(3)	C <sub>11</sub>	C <sub>10</sub>	H101	111	(5)
c <sub>11</sub>	c <sub>10</sub>	<sup>H</sup> 102	115	(6)	<sup>H</sup> 131	с <sub>13</sub>	<sup>H</sup> 132	96	(7)
<sup>H</sup> 101	c <sub>10</sub>	<sup>H</sup> 102	107	(7)	<sup>H</sup> 131	C <sub>13</sub>	H <sub>133</sub>	96	(7)
<sup>C</sup> 10	c <sub>11</sub>	<sup>H</sup> 111	105	(4)	<sup>H</sup> 132	с <sub>13</sub>	<sup>H</sup> 133	105	(7)
c <sub>10</sub>	c <sub>11</sub>	<sup>H</sup> 112	113	(4)	si <sub>1</sub>	<sup>C</sup> 14	<sup>H</sup> 141	109	(6)
c <sub>12</sub>	c <sub>11</sub>	H111	104	(4)	SI1	<sup>C</sup> 14	<sup>H</sup> 142	111	(3)
C <sub>12</sub>	c <sub>11</sub>	<sup>H</sup> 112	112	(3)	SI1	C <sub>14</sub>	<sup>H</sup> 143	129	(5)
<sup>H</sup> 111	C <sub>11</sub>	<sup>H</sup> 112	118	(5)	<sup>H</sup> 141	C <sub>14</sub>	<sup>H</sup> 142	97	(7)
с <sub>8</sub>	<sup>C</sup> 12	<sup>H</sup> 121	111	(3)	<sup>H</sup> 141	<sup>C</sup> 14	<sup>H</sup> 143	80	(7)
с <sub>8</sub>	c <sub>12</sub>	<sup>H</sup> 122	110	(3)	<sup>H</sup> 142	c <sub>14</sub>	<sup>H</sup> 143	117	(6)
C <sub>11</sub>	c <sub>12</sub>	<sup>H</sup> 121	115	(4)	SI1	c <sub>15</sub>	<sup>H</sup> 151	95	(5)
C <sub>11</sub>	<sup>C</sup> 12	<sup>H</sup> 122	106	(3)	si <sub>1</sub>	C <sub>15</sub>	<sup>H</sup> 152	116	(9)
<sup>H</sup> 121	c <sub>12</sub>	<sup>H</sup> 122	111	(5)	SI1	C <sub>15</sub>	<sup>H</sup> 153	111	(7)
SI1	с <sub>13</sub>	<sup>H</sup> 131	117	(5)	<sup>H</sup> 151	°15	<sup>H</sup> 152	121	(10)
si <sub>1</sub>	c <sub>13</sub>	<sup>H</sup> 132	123	(5)	<sup>H</sup> 151	с <sub>15</sub>	<sup>H</sup> 153	103	(8)
si <sub>1</sub>	с <sub>13</sub>	<sup>H</sup> 133	116	(6)	<sup>H</sup> 152	C <sub>15</sub>	<sup>H</sup> 153	110	(10)

Table V. (Continued)

Asymmetric Aldol Reaction. Asymmetric aldol reactions were carried out as described for the racemates.

(S,S)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cyclopentanone [(-)-11e]. The aldol product, (-)-11e (24 mg, 65%) was obtained from (+)-4e (44 mg, 0.14 mmol) after careful chromatography: colorless needles, mp 80-81°C (hexane/Et<sub>2</sub>O);  $[\alpha]_D^{20} - 84^{\circ}(\underline{c}, 0.20, CHCl_3)(>98\%$  ee).

(R,R)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cyclopentanone [(+)-11e]. The aldol product, (+)-11e (20 mg, 69%) was obtained from (-)-4e (35 mg, 0.11 mmol) after careful chromatography: colorless needles, mp 80-81°C (hexane/Et<sub>2</sub>O);  $[\alpha]_D^{19}$  +89°( $\underline{C}$ , 0.34, CHCl<sub>3</sub>)(>98% ee).

(S,S)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cyclohexanone [(-)-12e]. The aldol product, (-)-12e (20 mg, 71%) was obtained from (+)-4e (32 mg, 0.10 mmol) after careful chromatography: colorless needles, mp 51-53°C (hexane/Et<sub>2</sub>O);  $[\alpha]_D^{18}$ -54°( $\underline{c}$ , 0.40, CHCl<sub>3</sub>)(90% ee).

(R,R)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cyclohexanone [(+)-12e]. The aldol product, (+)-12e (21 mg, 70%) was obtained from (-)-4e (33 mg, 0.10 mmol) after careful chromatography: colorless needles, mp 51-53°C (hexane/Et<sub>2</sub>0);  $[\alpha]_{D}^{19}$ +57°( $\underline{c}$ , 0.42, CHCl<sub>3</sub>)(90% ee).

(S,S)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cycloheptanone [(-)-13e]. The aldol product , (-)-13e (56 mg, 98%) was obtained from (+)-4e (62 mg, 0.20 mmol) after careful chromatography:  $[\alpha]_D^{25}$  -85°( $\underline{c}$ , 0.95, CHCl<sub>3</sub>)(95% ee).

(R,R)-2-Hydroxy(2-trimethylsilylphenyl)methyl-1-cycloheptanone [(+)-13e]. The aldol product, (+)-13e (46 mg, 91%) was obtained from (-)-4e (55 mg, 0.17 mmol) after careful chromatography:  $[\alpha]_D^{25}$ +83°( $\underline{c}$ , 0.91, CHCl<sub>3</sub>)(96% ee).

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