AN EFFICIENT ASYMMETRIC ALDOL REACTION OF 4-TRIMETHYLSILOXY-6-METHYLENE-1,3-DIOXINES BY CHIRAL BINAPHTHOL-TITANIUM COMPLEX CATALYSIS[1]

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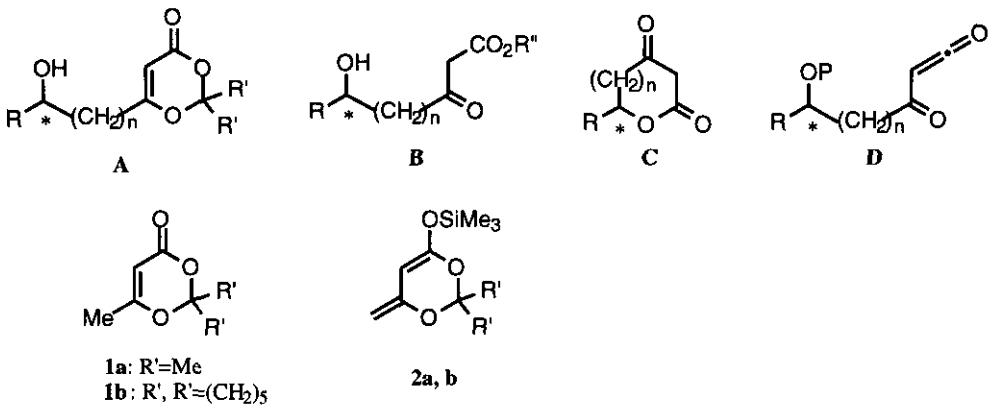
Abstract--The asymmetric aldol reaction of 4-trimethylsiloxy-6-methylene-1,3-dioxines or the 6-ethylidene analogue with achiral aldehydes proceeds in a highly enantioselective manner under chiral binaphthol-titanium complex catalysis to afford 6-substituted 1,3-dioxin-4-ones which serve as chemical equivalents of δ-hydroxy-β-keto esters, potential chiral building blocks. An explanation for the stereoselectivity is also presented.

INTRODUCTION

Previously, we have reported enantioselective syntheses of 1,3-dioxin-4-ones having hydroxylated alkyl group at the 6-position (**A**) by means of asymmetric reduction,[2] kinetic resolution,[3,4] and asymmetric aldol reaction of 4-trimethylsiloxy-6-methylene-1,3-dioxines (**2**) with chiral aldehydes under an achiral catalyst[5] or with achiral aldehydes under a chiral calatyst.[6] Due to the ready manupilation of the 1,3-dioxin-4-one ring (**A**) to β-keto ester (**B**), β-keto lactone (**C**), or acylketene (**D**), these chiral dioxinones have been efficiently used for enantioselective synthesis of biologically active compounds.[2~8] Among the above synthetic methods for dioxinones with chiral 2-hydroxyalkyl group at the 6-position (**A** : n = 1), the asymmetric aldol reaction of **2** [readily obtained from the 6-methyldioxinone (**1**)] by chiral catalysts is the most powerful though the enantioselectivity was lower than those in the other methods. Thus, our attention was focused on improvement of the enantiocontrol in this aldol reaction. This paper reports the successful results including diastereocontrol in the reaction of a 6-ethylidenedioxine.



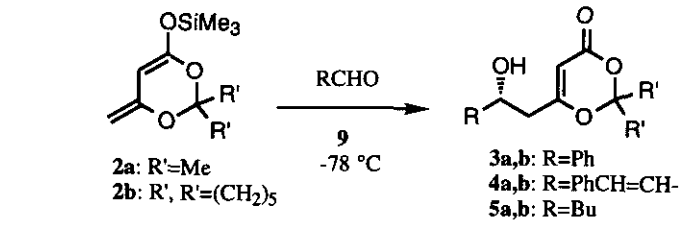
Scheme 1

RESULTS AND DISCUSSION

As reported previously, the aldol reaction of **2a** with a variety of aldehydes proceeds enantioselectively under chiral borane catalysts to give the product (**3a**).[6] Among several chiral boranes including tryptophan-derived catalyst,[9] chiral tartaric acid-derived acylborane (**6**)[10] gave the best result [enantiomeric excess (ee): 62~76%], though 50% molar amount of **6** to **2** had to be used for satisfactory chemical yields due to the slow catalytic cycle. Titanium complexes with chiral ligands have been successfully used as catalyst in a variety of asymmetric addition reactions including aldol reaction.[11] Thus, the aldol reaction of **2** under titanium complex with chiral binaphthol (*R*-**7**) was examined.

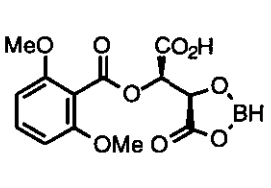
Mikami *et al.* have reported a highly enantioselective aldol reaction of silyl enol ethers under the catalysis of chiral binaphthol-derived titanium dichloride (**8**).[12] Under this catalyst, the reaction of **2a** with benzaldehyde at -78 ℃ to room temperature gave the product (**3a**) in very low chemical and optical yields. However, the diisopropoxide catalyst (**9** : 20% mol)[13] prepared *in situ* from *R*-**7** and titanium tetraisopropoxide in the presence of Molecular Sieves 4A[14] gave good results as shown in Table 1. In the reaction of **2a** with benzaldehyde, the highest asymmetric induction (ee 88%) was observed in THF (Entries 1~3). The reaction of **2a** with cinnamaldehyde in THF gave the poor result, while the reaction with pentanal gave **5a** with the highest ee (92%). The absolute configuration of **3a~d** was determined by comparison of the specific rotations with those of authentic samples,[6] and the ee was determined by hplc analysis with chiral columns (Scheme 2, Table 1).

When the spirodioxine (**2b**) was used for this asymmetric aldol reaction, both the chemical and optical yields were improved except for the reaction with pentanal (Table 2).



2a: R'=Me
2b: R', R'=$(CH_2)_5$

3a,b: R=Ph
4a,b: R=PhCH=CH-
5a,b: R=Bu



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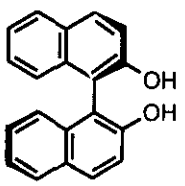
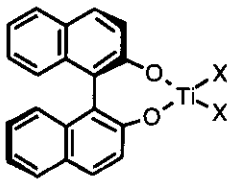


R-**7**



8: X=Cl
9: X=O*iso*-Pr

Scheme 2

Table 1. Asymmetric Aldol Reaction of 2a

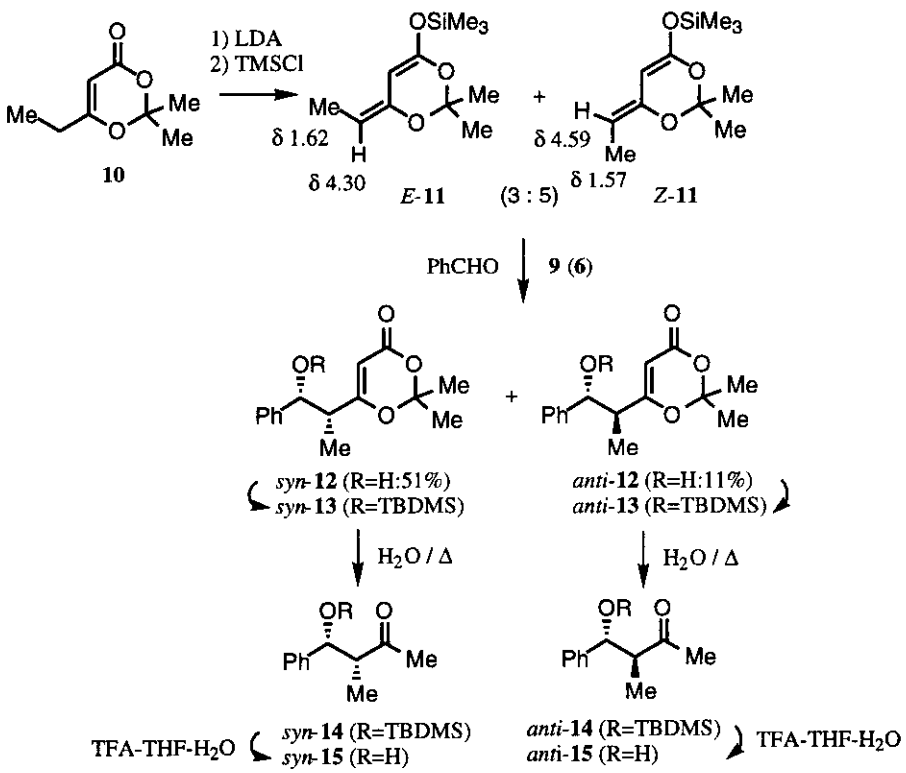
Entry	Aldehyde	Solvent	No.	Yield (%)	ee (%)	$[\alpha]_D$ ($CHCl_3$)
1	PhCHO	THF	**3a**	38	88	+37.3 °
2	"	EtCN	"	23	75	
3	"	CH_2Cl_2	"	10	50	
4	*trans*-PhCH=CHCHO	THF	**4a**	32	33	+2.4 °
5	BuCHO	"	**5a**	55	92	+19.8 °

Table 2. Asymmetric Aldol Reaction of 2b

Entry	Aldehyde	No.	Yield (%)	ee (%)	$[\alpha]_D$ ($CHCl_3$)
1	PhCHO	**3b**	93	92	+28.7 °
2	*trans*-PhCH=CHCHO	**4b**	58	79	+3.2 °
3	BuCHO	**5b**	37	76	+13.9 °

Silylation of 6-ethyl-2,2-dimethyldioxinone (**10**) gave the 6-ethylidenedioxine (**11**) as a mixture of *E- and Z*-isomers (*E*:*Z*=3:5). The configuration was assigned based on the ^{1}H-nmr data. Due to the deshielding effect of the ring C=C double bond, the methyl proton at the methylene group of *E*-**11** appeared at a lower field than that of *Z*-**11**, whereas the vinyl proton of *Z*-**11** appeared at a lower field than that of *E*-**11**. The aldol reaction of

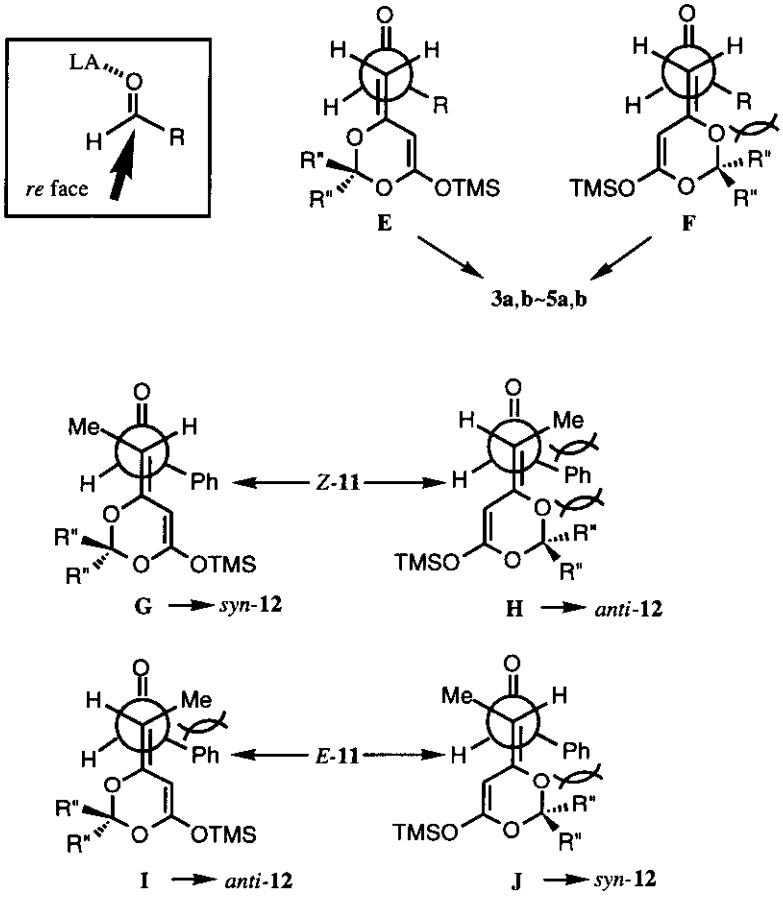
this mixture with benzaldehyde under the catalyst (**9**) proceeded in a highly stereocontrolled manner. The major diastereoisomer (*syn*-**12**) was obtained in 51% yield as an enantiomerically pure compound together with *anti*-**12** (11% yield; ee, 26%). When this reaction was conducted under catalysis of the chiral borane (**6**),[6] *syn*-**12** (25% yield; ee 80%) and *anti*-**12** (75% yield; ee 63%) were obtained. The stereostructure of *syn*-**12** and *anti*-**12** was confirmed by their conversion to the known compounds *syn*-**15**[15] and *anti*-**15**[16] by the method as illustrated in Scheme 3.



Scheme 3

The stereochemical outcome in these aldol reactions under the catalyst (**9**) is well rationalized as follows. The *si* face of aldehydes is shielded by coordination with the chiral Lewis acid (**9**). Thus, siloxydioxines (**2a,b**) react at the *re* face of aldehydes through the transition assembly **E** which is sterically more favorable than the another assembly **F** to afford **3a,b~5a,b**. The preferential formation of *syn*-**12** with high ee from the mixture of *E*-**11** and *Z*-**11**(*E*:*Z* =3:5) is explained similarly. *Z*-**11** reacts with benzaldehyde through **G** to give *syn*-**12**. The alternative assembly **H** which may lead to *anti*-**12** is the most unfavorable due to the steric reason. On the

other hand, both of the assemblies **I** and **J** from *E*-**11** have steric repulsion. Thus, *E*-**11** reacts from *si* face of the aldehyde to some extent resulting in the low ee of *anti*-**12**. Presumably, *E*-**11** also affords *syn*-**12** through **J** resulting in the high chemical yield of *syn*-**12** (Scheme 4).



Scheme 4

In conclusion, the asymmetric aldol reaction of silylated dioxinones by chiral binaphthol-titanium complex catalysis provided a highly enantiocontrolled method for introduction of 2-hydroxylated alkyl group at the 6-position of dioxinones. The products, some of which could be obtained as enantiomerically pure crystals,[6] serve as potential chiral building blocks due to their ready manipulation to **B** to **D**.[2~6]

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EXPERIMENTAL

All melting points were determined on Yanagimoto micro-hot stage and are uncorrected. Optical rotations were measured with a JASCO DIP-340 digital polarimeter. Ir spectra were mesured on a JASCO A-102 spectrophotometer and ^{1}H-nmr spectra were recorded on a JEOL JNM-PMX 60 SI or JEOL JNM-GX 500 spectrometer with tetramethylsilane as an internal standard; the abbreviations of signal patterns are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. High-resolution mass spectra were recorded on a JEOL JMS-DX-303 or JMS-AX-500 spectrometer. Wakogel (C-200) and Merck Kieselgel 60 F 254 were employed for column and preparative thin layer chromatographies (ptlc), respectively. The ratios of solvent mixtures for chromatography are shown as volume/volume.

6-Ethylidene-2,2-dimethyl-4-trimethylsiloxy-1,3-dioxine (11): *n*-BuLi (1.6 *M* solution in hexane, 80 ml, 128 mmol) was added to a solution of diisopropylamine (12.9 g, 128 mmol) in dry THF (100 ml) at -20 °C under Ar atmosphere. After stirring for 30 min, the solution was cooled to -78 °C. The compound (**10**, 10.0 g, 64.1 mmol)[17] was added dropwise to this solution. The mixture was stirred for 45 min and then trimethylchlorosilane (20.3 ml, 160 mmol) was added dropwise. After stirring for 2 h, the reaction mixture was permitted to warm to room temperature, and the solvent was evaporated *in vacuo*. The residue was distilled in vacuum to give **11** (12.7 g, 87%). bp 50 °C / 0.1 mmHg. Ir ($CHCl_3$): 1683, 1642 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.27 (9H, s, $SiMe_3$), 1.51 (6H x 5/8, s, Me_3), 1.54 (6H x 3/8, s, Me_3), 1.57 (3H x 5/8, d, J = 7.0 Hz, Me), 1.61 (3H x 3/8, d, J = 7.0 Hz, Me), 4.30 (1H x 3/8, q, J = 7.0 Hz, =C*H*Me), 4.56 (1H x 3/8, s, =CH), 4.59 (1H x 5/8, q, J = 7.0 Hz, =C*H*Me), 4.76 (1H x 5/8, s, =CH). High-resolution ms *m/z* Calcd for $C_{11}H_{20}O_3Si$ (M^+): 228.1181. Found: 228.1182.

General Procedure for the Binaphthol-Titanium Complex-Catalyzed Asymmetric Aldol Reaction of the Siloxydioxine (2a,b) with Aldehyde: A mixture of (*R*)-(+)-1,1'-bi-2-naphthol (*R*-**7**, 28 mg, 0.1 mmol), titanium tetraisopropoxide (28.4 mg, 0.1 mmol), and Molecular Sieves 4A (500 mg) in THF (1 ml) was stirred for 1 h at room temperature under an Ar atmosphere. The mixture was cooled to -78 ℃ and the compound (**2a**[6,18] or **2b**[6], 0.60 mmol) and an aldehyde (0.5 mmol) were added simultaneously to the

mixture *via* syringes over 30 min period. The whole was stirred for 1 h at -78 °C and then allowed to warm to room temperature. After stirring for 9 h at that temperature, the whole was poured into saturated $NaHCO_3$ solution. After vigorous stirring for 30 min, the product was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by silica gel column chromatography to give the product (**3~5a** or **3~5b**) whose ir and ^{1}H-nmr data are identical with those of the reported data.[6] The yield, specific rotation (measured at 20~24 °C), and ee are shown in Tables 1 and 2. The ee was determined by hplc analysis with chiral columns (CHIRALCEL OD for **3a~5a**, **3b**, and **4b**; CHIRALCEL OJ for **5b**) using a mixture of hexane and isopropanol (7:3 ~ 98:2) as an eluent. Recrystallization of **4b** gave an enantiomerically pure sample.[6]

(1'*R*,2'*R*)-6-(2-Hydroxy-1-methyl-2-phenylethyl)-2,2-dimethyl-1,3-dioxin-4-one (*syn*-12) and (1'*R*,2'*S*)-6-(2-Hydroxy-1-methyl-2-phenylethyl)-2,2-dimethyl-1,3-dioxin-4-one (*anti*-12): a) A mixture of *R*-**7** (28 mg, 0.1 mmol), titanium tetraisopropoxide (28.4 mg, 0.1 mmol), and Molecular Sieves 4A (500 mg) in THF (1 ml) was stirred for 1 h at room temperature under an Ar atmosphere. The reaction mixture was cooled to -78 °C and the compound (**11**, 136 mg, 0.60 mmol) and benzaldehyde (53 mg, 0.5 mmol) were added simultaneously to the mixture *via* syringes over 30 min period. The whole was stirred for 1 h at -78 °C and then allowed to warm to room temperature. After stirring for 9 h at that temperature, the whole was poured into saturated $NaHCO_3$. After vigorous stirring for 30 min at that temperature, the product was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The residue was purified by silica gel column chromatography to give the product as a diastereomixture. Then the diastereoisomers were separated by Lobar column with a mixture of benzene and ethyl acetate (10:1) to give *syn*-**12** (63.2 mg, 51% yield) and *anti*-**12** (14.1 mg, 11% yield). The ee of *syn*-**12** was higher than 99% and that of *anti*-**12** was 26% based on hplc analysis [CHIRALCEL OD, hexane-isopropanol (95:5)]. Recrystallization of *syn*-**12** from Et_2O gave an enantiomerically pure sample.

b) Following the reported procedure,[6] the compound (**11**, 134 mg, 0.6 mmol) was reacted with benzaldehyde (53 mg, 0.5 mmol) under the catalyst (**6**, 100 mol%) at -78 °C for 1 h in CH_2Cl_2 (2 ml). Diluted (10%) HCl was added to the reaction mixture and the whole was allowed to warm up to room temperature with stirring. The product was extracted with CH_2Cl_2, dried over $MgSO_4$, and purified as in a) to give *anti*-**12** (93 mg, 75% yield, ee 63%) and *syn*-**12** (31 mg, 25% yield, ee 80%). Recrystallization of *anti*-**12** from Et_2O gave an enantiomerically pure sample. *syn*-**12**: mp 112 ~ 113°C. $[\alpha]_D^{22}$ -12.7 ° (*c* 1.07, $CHCl_3$). Ir ($CHCl_3$): 1721, 1635 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ:1.20 (3H, d, J = 7.0 Hz, C_1'-Me), 1.70 (6H , s, C_6-Me_3), 2.73~2.96 (1H, m,

$C_{1'}$-H), 4.86 (1H, d, J = 6.0 Hz, $C_{2'}$-H), 5.37 (1H, s, C_3-H), 7.73 (5H, s, phenyl). Ms *m/z*: 263 (M^++1). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.54; H, 6.94. *anti*-**12**: mp 117 ~ 118.5 °C. $[\alpha]_D^{22}$ -103.9 ° (*c* 1.06, $CHCl_3$). Ir ($CHCl_3$): 1721, 1635 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.92 (3H, d, J = 6.0 Hz, $C_{1'}$-Me), 1.72 (6H , s, C_6-Me_3), 2.22~2.95 (1H, m, $C_{1'}$-H), 4.67 (1H, d, J = 9.0 Hz, $C_{2'}$-H), 5.38 (1H, s, C_3-H), 7.39 (5H, s, phenyl). Ms *m/z*: 263 (M^++1). *Anal.* Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.52; H, 7.03.

(1'*R*,2'*R*)-6-(2-*tert*-Butyldimethylsiloxy-1-methyl-2-phenylethyl)-2,2-dimethyl-1,3-dioxin-4-one (*syn*-13): *tert*-Butyldimethylchlorosilane (30 mg, 0.2 mmol) and imidazole (10.2 mg, 0.2 mmol) were added to a solution of *syn*-**12** (26.1 mg, 0.1 mmol) in DMF (1 ml) under ice-cooling. The whole was stirred at room temperature for 1 day. Ice water was added to the mixture and the whole was extracted with Et_2O. The organic layer was dried over $MgSO_4$, and the solvent was evaporated off *in vacuo*. The residue was purified by ptlc [hexane-AcOEt (5:1)] to give *syn*-**13** (33.6 mg, 89% yield) as a colorless oil. $[\alpha]_D^{20}$ +13.9 ° (*c* 1.68, $CHCl_3$). Ir ($CHCl_3$): 1727, 1638 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.27 (6H, s, $SiMe_2$), 1.14 (9H , s, *tert*-Bu), 1.41 (3H, d, J = 7.0 Hz, $C_{1'}$-Me), 1.83 (6H, s, C_2-H), 2.53-3.03 (1H, m, $C_{1'}$-H), 5.01 (1H, d, J = 7.0 Hz, $C_{2'}$-H), 5.35 (1H, s, C_5-H), 7.52 (5H, s, phenyl). High-resolution ms *m/z* Calcd for $C_{21}H_{33}O_4Si(M^+)$: 377.2148. Found: 377.2140.

(3*R*,4*R*)-4-*tert*-Butyldimethylsiloxy-3-methyl-4-phenylbutan-2-one (*syn*-14): A solution of *syn*-**13** (33.6 mg, 0.089 mmol) and H_2O (0.1 ml) in toluene (1 ml) was refluxed for 2 h. The solvent was evaporated *in vacuo*, and the residue was purified by ptlc [hexane-AcOEt (5:1)] to give *syn*-**14** (27.1 mg, 74% yield) as a colorless oil. $[\alpha]_D^{20}$ +12.9 ° (*c* 1.07, $CHCl_3$). Ir ($CHCl_3$): 1714, 1265 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.25 (6H, s, $SiMe_2$), 1.01 (9H , s, *tert*-Bu), 1.39 (3H, d, J = 7.0 Hz, C_3-Me), 2.13(3H, s, C_1-Me), 2.83-3.40 (1H, m, C_3-H), 5.07 (1H, d, J = 7.0 Hz, C_4-H), 7.50 (5H, s, phenyl). High-resolution ms *m/z* Calcd for $C_{13}H_{19}O_2Si$ (M^+-*tert*-Bu): 235.1154. Found: 235.1150.

(3*R*,4*R*)-4-Hydroxy-3-methyl-4-phenylbutan-2-one (*syn*-15): A mixture of trifluoroacetic acid (0.1 ml), THF (0.5 ml), H_2O (0.5 ml), and *syn*-**14** (21.7 mg, 0.07 mmol) was stirred at room temperature for 3 h. Ice-water was added to the mixture and the whole was extracted with CH_2Cl_2. The organic layer was washed with H_2O and dried over $MgSO_4$. The solvent was evaporated *in vacuo*. The residue was purified by ptlc [hexane-AcOEt (5:1)] to give *syn*-**15** (6.2 mg, 50% yield) as a colorless oil. $[\alpha]_D^{22}$ +40.6 ° (*c* 0.36, $CHCl_3$)

[lit.,[15] $[\alpha]_D^{22}$ -33.3 °(*c* 1, $CHCl_3$), 65% ee]. ^{1}H-Nmr ($CDCl_3$) δ: 1.07 (3H, d, *J* = 6.4 Hz, C_3-Me), 2.10 (3H, s, acetyl-Me), 2.62-2.87 (1H, m, C_3-H), 5.03 (1H, d, *J* = 4.0 Hz, C_4-H), 7.13 (5H, s, phenyl). High-resolution ms *m/z* Calcd for $C_{11}H_{14}O_2$ (M^+): 178.0994. Found: 178.0975.

(1'*R*,2'*S*)-6-(2-*tert*-Butyldimethylsiloxy-1-methyl-2-phenylethyl)-2,2-dimethyl-1,3-dioxin-4-one (*anti*-13): Following the procedure given for preparation of *syn*-**13**, *anti*-**12** (26.1 mg, 0.1 mmol) was silylated to give *anti*-**13** (34.7 mg, 92% yield) as a colorless oil. $[\alpha]_D^{19}$ +114.2 °(*c* 1.61, $CHCl_3$). Ir ($CHCl_3$): 1725, 1640 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.31 (6H, s, $SiMe_2$), 1.18 (9H , s, *tert*-Bu), 1.14 (3H, d, *J* = 8.0 Hz, $C_{1'}$-Me), 1.97 (6H, s, C_2-H), 2.75~3.15 (1H, m, $C_{1'}$-H), 4.95 (1H, d, *J* = 7.0 Hz, $C_{2'}$-H), 5.61 (1H, s, C_5-H), 7.63 (5H, s, phenyl). High-resolution ms *m/z* Calcd for $C_{21}H_{33}O_4Si$ (M^+): 377.2148. Found: 377.2137.

(3*R*,4*S*)-4-*tert*-Butyldimethylsiloxy-3-methyl-4-phenylbutan-2-one (*anti*-14): Following the procedure given for preparation of *syn*-**14**, *anti*-**13** (16.1 mg, 0.040 mmol) was hydrolyzed to give *anti*-**14** (8.1 mg, 69% yield) as a colorless oil. $[\alpha]_D^{19}$ +108.2 °(*c* 0.81, $CHCl_3$). Ir ($CHCl_3$): 1717, 1268 cm^{-1}. ^{1}H-Nmr ($CDCl_3$) δ: 0.33 (6H, s, $SiMe_2$), 1.13 (9H , s, *tert*-Bu), 1.07 (3H, d, *J* = 10.0 Hz, C_3-Me), 2.58(3H, s, C_1-Me), 3.00-3.46 (1H, m, C_3-H), 5.00 (1H, d, *J* = 10.0 Hz, C_4-H), 7.64 (5H, s, phenyl). High-resolution ms *m/z* Calcd for $C_{13}H_{19}O_2Si$ (M^+-*tert*-Bu): 235.1154. Found: 235.1136.

(3*R*,4*S*)-4-Hydroxy-3-methyl-4-phenylbutan-2-one (*anti*-15): Following the procedure given for preparation of *syn*-**15**, *anti*-**14** (8.1 mg, 0.03 mmol) was desilylated to give *anti*-**15** (2.1 mg, 40% yield) as a colorless oil. $[\alpha]_D^{19}$ +44.8 °(*c* 0.21, $CHCl_3$) [lit.,[16] $[\alpha]_D^{20}$ +47.9 °($CHCl_3$)]. ^{1}H-Nmr ($CDCl_3$) δ: 0.946 (3H, d, *J* = 7.4 Hz, C_3-Me), 2.233 (3H, s, acetyl-Me), 2.933 (1H, dq, *J* = 8.6, 7.4 Hz, C_3-H), 7.452 (1H, d, *J* = 8.6 Hz, C_4-H), 7.263 (5H, s, phenyl).

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