Regio-, Diastereo-, and Enantioselective Synthesis of *vic*-Diols via α-Silyl Ketones According to the SAMP/RAMP Hydrazone Method

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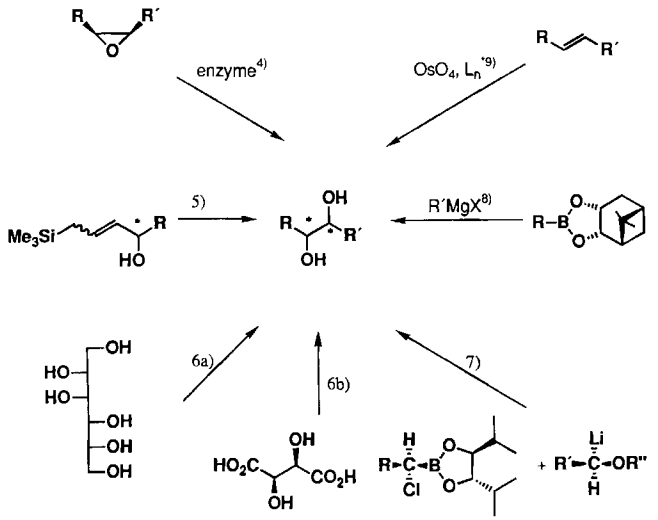
α-Silylated ketones **5** or **10** of high enantiomeric purity (ee ≥ 90%) are easily available by silylation or silylation/alkylation of ketones **1** or **6**, resp., according to the SAMP/RAMP hydrazone method. Reduction of **5** or **10** with L-selectride®, followed by oxidative cleavage of the C–Si bond, leads to *vic*-diols **11**–**13** with high diastereoselectivity (de ≥ 90%) and without racemization. The stereoselectivity of the reduction depends on the structure of the α-silyl ketones **5** or **10**, the reducing reagents, and the solvents used.

Asymmetric synthesis of *vic*-diols has recently received considerable attention, because *vic*-diols are common structural features of many natural products[1], useful chiral building blocks in the synthesis of biologically active compounds[2], and valuable intermediates in a variety of synthetic transformations[3].

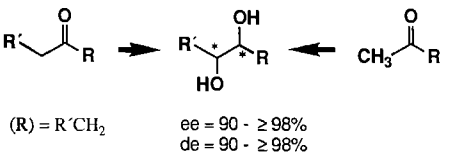
These approaches have been carried out by enantioselective ring opening by epoxide hydrase[4], ring opening by diastereoselective epoxidation of chiral allylic alcohols[5], "chiral pool" syntheses from natural products[6] including diastereoselective 1,2-additions of organometallics to α-alkoxy aldehydes[6c], stereospecific coupling of chiral boronic esters with chiral lithio esters followed by hydrolysis[7], homologation of alkylboronates followed by hydrolysis[8], and asymmetric osmylation of olefins with chiral amines as ligands[9]. On the other hand, stereoselective reductions to form *vic*-diols have also been described based on diastereoselective reduction of α-hydroxy ketones[10], but little attention has been paid to enantioselective syntheses of *vic*-diols by enantio- and diastereoselective reductions, although in the realm of aliphatic ketones efficient techniques[11] are now at hand to selectively introduce stereocenters on acyclic carbon chains[12]. Therefore, the development of still more versatile and effective diastereo- and enantioselective syntheses of *vic*-diols is of considerable interest.

In continuation of our efforts to further explore the utility of the SAMP/RAMP hydrazone method[13], we now report on a convenient synthesis of *vic*-diols with high regio-, diastereo- and enantioselectivity.

Scheme 1



Scheme 2



Enantioselective Synthesis of α-Silyl Ketones 5 and 10

α-Silyl Ketones **5** and **10** were synthesized from symmetrical dialkyl ketones **1** or unsymmetrical methyl alkyl ketones **6** according to Schemes 3 and 4.

Symmetrical dialkyl ketones **1**, after conversion into their corresponding SAMP hydrazones (*S*)-**2**, are metalated with lithium diisopropylamide and then α-*C*-silylated with isopropoxydimethylsilyl chloride. The α-silylated SAMP hydrazones **3** (de ≧ 90%) thus obtained are cleaved oxidatively and free of racemization with ozone affording, after chromatographic separation of (*S*)-**4** (recycling of the chiral auxiliary), the α-silyl ketones (*R*)-**5** of high enantiomeric purity

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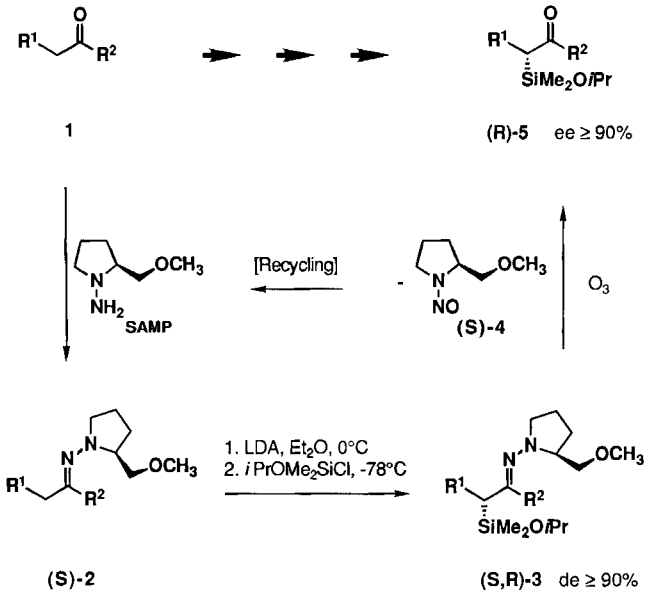
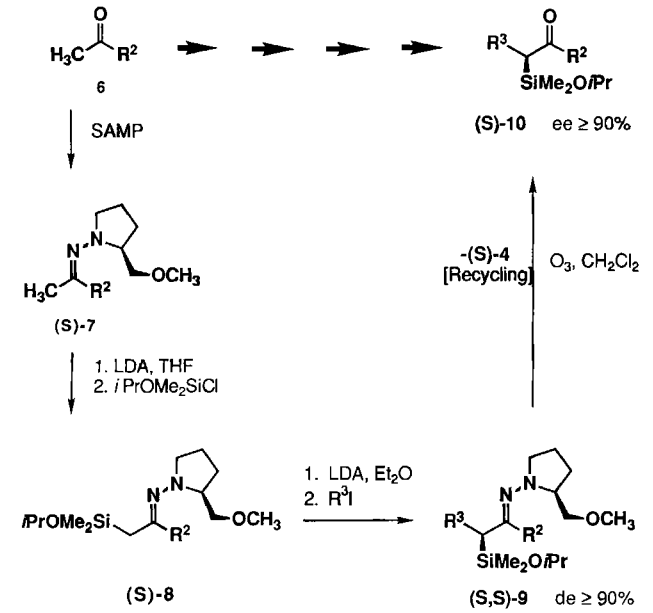
(ee ≧ 90%) in good chemical yields of 53–79% (Scheme 3, Table 1).

Scheme 3. Enantioselective synthesis of α-silyl ketones **5**



On the other hand, methyl alkyl ketones **6** are converted enantioselectively into the unsymmetrical α-silyl ketones (*S*)-**10** by metallation/α-silylation of the SAMP hydrazones (*S*)-**7** and subsequent alkylation of α-silyl SAMP hydrazones (*S*)-**8** with alkyl iodides according to our SAMP/RAMP hydrazone method (ee ≧ 90%, chemical yields: 47–72%, Scheme 4, Table 2).

Scheme 4. Enantioselective synthesis of α-silyl ketones **10**



The absolute configuration at the α-position of the ketones **5** is opposite to that of ketones **10**. The signs of the optical rotations of ketones **5** and **10** reasonably coincide

Table 1. α-Silyl ketones **5** synthesized from symmetrical dialkyl ketones **1** by enantioselective silylation via SAMP hydrazones **2**

	R^1	R^2	Yield[a][%]	$[\alpha]_D^{22}$ (c, C_6H_6)	ee [%]	Config.
5a	CH_3	C_2H_5	79	+132.3 (1.9)	≥ 90	(R)
5b[b]	CH_3	C_2H_5	65	-132.2 (5.0)	≥ 98	(S)
5c	C_2H_5	n-C_3H_7	69	+ 35.8 (2.3)		(R)
5d	n-C_3H_7	n-C_4H_9	53	+ 59.7 (1.3)		(R)

[a] Yields of **5** based on SAMP hydrazones **2**. — [b] RAMP was used instead of SAMP as the chiral auxiliary.

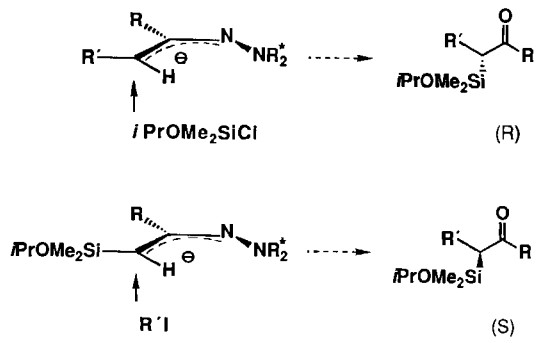
Table 2. α-Silyl ketones **10** synthesized from methyl alkyl ketones **6** by silylation/alkylation via SAMP hydrazones **7**

	R^2	R^3	Yield[a] [%]	$[\alpha]_D^{22}$ (c, C_6H_6)	ee [%]	Config.
10a	CH_3	CH_3	48	- 175.7 (0.9)	≥ 98	(S)
10b	CH_3	C_2H_5	47	- 147.8 (2.5)	≥ 95	(S)
10c	C_2H_5	CH_3	72	- 132.0 (3.1)	≥ 90	(S)
10d	C_2H_5	n-C_6H_{13}	61	- 73.5 (2.6)		(S)
10e	n-C_6H_{13}	CH_3	66	-133.3 (1.8)	≥ 98	(S)

[a] Yields of **10** based on SAMP hydrazones **7**.

with those of literature data[13c]. The above results support the previously postulated mechanism for electrophilic substitutions via SAMP/RAMP hydrazones[13] and thus the absolute configuration at the α-position of ketones **5** is (*R*), and that of ketones **10** is (*S*). The stereoselectivities in the preparation of α-silyl ketones **5** and **10** may be explained by the transition states shown in Scheme 5.

Scheme 5



The optical antipodes to the α-silyl ketones **5** and **10** are obtained in the same way by simply replacing SAMP by the enantiomeric RAMP. The diastereomeric excess of α-silylated SAMP hydrazones **3** or **9** can be deduced from the enantiomeric excess of α-silyl ketones **5** or **10**, respectively, as subsequent ozonolysis is free of reacemization[13c]. The enantiomeric excess of **5** or **10** is determined by ^{1}H-NMR shift experiments with Eu(hfc)$_3$ or may be deduced from the

enantiomeric excess of the *vic*-diols **11**–**13**, as subsequent transformations are free of racemization. The racemic compounds *rac*-**5** are prepared via the *N,N*-dimethylhydrazones for comparison.

Asymmetric Reduction of α-Silyl Ketones 5 or 10

The results of the reduction of a model compound, (2*R*)-(+)-2-(isopropoxydimethylsilyl)-3-pentanone (**5a**), with various types of metal hydride complexes are summarized in Table 3. α-Silyl ketone **5a** is easily converted into *vic*-diol **11a** by reduction followed by oxidative cleavage of the C–Si bond according to Tamao's method[14], which proceeds with retention of configuration. The enantiomeric excess in α-silyl ketones **5** or **10** and *vic*-diols **11**–**13** is in good agreement (see Table 1, 2 and 4). The diastereomeric excess and *syn*-/*anti*-configuration of the *vic*-diols **11**–**13** is determined by ^{13}C- and ^{1}H-NMR spectroscopy and by comparison with authentic samples prepared from (*E*/*Z*)-alkenes by the *cis*-hydroxylation method of Brutscher et al.[15].

Table 3. Hydride reduction of **5a**

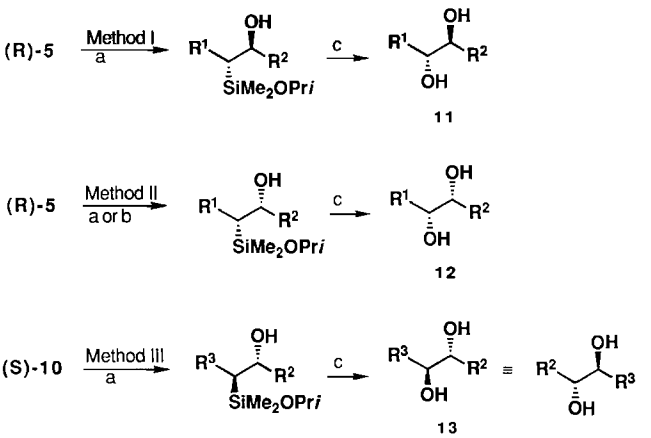
Entry	Reducing agent	Solvent	Conc. 5a mol/l	Temp. [°C]	Reaction time [h]	Config. main product	de [%]	Yield [%][a]
1	L-Selectride®[b]	Et_2O	0.09	-78	3	anti	75	69
2		THF	0.09	-78	3	syn	50	28
3		THF	0.10	0	4	anti	50	48
4		n-pentane	0.09	-78	3	anti	60	69
5		toluene	0.09	-78	3	anti	80	78
6		toluene	0.04	-90	4	anti	65	56
7		toluene	0.32	-78	6	anti	95	10
8		toluene	0.20	-78	7	anti	94	63
9	9-BBN	THF	0.09	0	2	syn	70	56
10	LAH	THF	0.09	-78	10[c]	syn	6	56
11		CH_2Cl_2	0.09	-78	10[c]	anti	29	69
12	DIBAL	Et_2O	0.09	-78	10[c]	syn	70	42
13	L-Selectride® +$SnCl_4$	toluene	0.09	-78	3	-	-	0
14		Et_2O	0.09	-78	3	syn	98	19
15		Et_2O	0.06	-78	6	syn	98	19
16	L-Selectride® +$TiCl_4$	Et_2O	0.09	-78	3	anti	25	19
17	L-Selectride® +$BF_3{\cdot}Et_2O$	Et_2O	0.09	-78	3	syn	72	69

[a] Chemical yield of *vic*-diol **11a** based on α-silyl ketone **5a**. – [b] Lithium tri-*sec*-butylhydridoborate. – [c] After the reaction at –78°C for 10 h, the reaction mixture was kept at room temp. for 24 h.

Acceptable stereoselectivities (de ≧ 80%) are attained with L-selectride® (lithium tri-*sec*-butylhydridoborate) in toluene at –78°C (entries 5, 7, and 8). Stereoselectivities increase with increasing concentration of substrate **5a**, but it takes a long time for the reduction as carried out by Brown et al.[11] (entries 5, 6, 7, and 8). The yield of *vic*-diol **11a** depends on the reaction time (entries 7 and 8). Different stereoselectivities are observed depending on temperature (compare entries 2 with 3), solvent (compare entries 10 with 11), reducing agent (entries 1–12), and addition of salts or catalysts (entries 13–17). Not all reasons for the observed stereoselectivity changes are understood in detail presently. The reduction of α-silyl ketone **5a** (concentration 0.2 M) with L-selectride® in toluene at –78°C for 7 h gave the *anti*-isomer **11a** with high diastereoselectivity (de ≧ 94%) and in 63% yield (entry 8). The corresponding *syn*-isomer **12c** is obtained by addition of $SnCl_4$ to the reaction mixture using diethyl ether instead of toluene as a solvent (entries 14 and 15).

Encouraged by these results (entries 8 and 14), we applied those reaction conditions to a series of representative α-silyl ketones **5** and **10**. The results are summarized in Table 4.

Scheme 6



a: L-Selectride®, toluene, -78°C
b: L-Selectride®, diethyl ether, $SnCl_4$, -78°C
c: KF, $KHCO_3$, 30% H_2O_2 aqueous solution / MeOH-THF
Method I a: $R^1 = CH_3$ or $R^2 = CH_3, C_2H_5$
Method II a: $R^1 \neq CH_3, R^2 \neq CH_3, C_2H_5$
Method IIb: $R^1 = CH_3$ or $R^2 = CH_3, C_2H_5$
Method IIIa: $R^3 = CH_3$ or $R^2 = CH_3, C_2H_5$

When the reduction of **5a** was carried out on a large scale, the chemical yield of **11a** in Table 4 (entry 1) was lower than that of entry 8 in Table 3, but this is a small matter. The reductions of **5a, 10b, 10c, 10d**, and **10e** with L-selectride® in toluene at –78°C for 7 h gave *anti*-isomers (entries 1, 2, 5, 8, and 9), but those of **5c** and **5d** under the same conditions gave *syn*-isomers (entries 6 and 7). When the reduction of **5a** was carried out in the presence of $SnCl_4$ in diethyl ether as a solvent, **12c**, the *syn*-isomer of **11a**, is obtained (entry 3). The enantiomer (**11d** or **13e**) of **11a** (entry 1) is obtained in the same way by simply replacing SAMP by the enantiomeric RAMP (entry 4) or using method IIIa (entry 5).

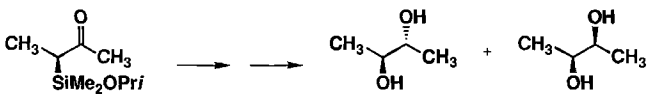
The absolute configurations of the *vic*-diols **11**–**13** were also defined experimentally. From the reduction of (*S*)-**10a** according to method Ia, the *meso* compound (*anti*-isomer) **13j** was isolated along with a small amount of (2*S*,3*S*)-(+)-butane-2,3-diol (*syn*-isomer) (**14j**), whose optical rotation was in agreement with that of an authentic sample (see experimental section).

Table 4. Regio-, diastereo-, and enantioselective synthesis of *vic*-diols **11**–**13**

Entry	Compound	R′	R	Starting material[a] (Method)	Yield[b] [%]	$[\alpha]_D^{22}$ (c, $CHCl_3$)	ee[c] [%]	de [%]	Config.
1	**11a**	R^1=CH_3	R^2=C_2H_5	**5a** (Ia)	56	-14.0 (0.6)	≥ 90[A,B]	≥ 98	(2R,3S)
2	**13b**	R^2=CH_3	R^3=C_2H_5	**10b** (IIIa)	52	-14.2 (2.1)	≥ 95[B]	≥ 98	(2R,3S)
3	**12c**	R^1=CH_3	R^2=C_2H_5	**5a** (IIb)	14	+4.5 (1.0)	≥ 90[A,B]	≥ 98	(2R,3R)
4	**11d**	R^1=C_2H_5	R^2=CH_3	**5b**[d] (Ia)	58	+13.9 (0.7)	≥ 98[A,B]	≥ 98	(2S,3R)
5	**13e**	R^2=C_2H_5	R^3=CH_3	**10c** (IIIa)	52	+13.2 (1.7)	≥ 90[A,B]	≥ 98	(2S,3R)
6	**12f**	R^1=C_2H_5	R^2=n-C_3H_7	**5c** (IIa)	47	+19.2 (0.6)		≥ 95[A,e]	(3R,4R)
7	**12g**	R^1=n-C_3H_7	R^2=n-C_4H_9	**5d** (IIa)	48	+26.0 (0.5)		≥ 95[B,e]	(4R,5R)
8	**13h**	R^2=C_2H_5	R^3=n-C_6H_{13}	**10d** (IIIa)	24	-5.0 (0.3)		≥ 98[C,e]	(3R,4S)
9	**13i**	R^2=n-C_6H_{13}	R^3=CH_3	**10e** (IIIa)	53	+6.0 (0.5)	≥ 98[A]	≥ 98	(2S,3R)
10	**12k**[f]	R^1=C_2H_5	R^2=C_2H_5	- -	-	+22.7 (2.5, H_2O)	-	-	(3R,4R)

[a] α-Silyl ketones **5** or **10**. — [b] Chemical yields of pure *vic*-diols **11**–**13** based on α-silyl ketones **5** or **10**. — [c] Enantiomeric excesses are determined by ^{1}H-NMR shift experiments[A] of α-silyl ketones [Eu(hfc)$_3$] and/or GLC analysis[B] of the bis-Mosher esters of *vic*-diols on a 25 m XE-60-(*S*)-Val-*S*-α-PEA capillary column. — [d] RAMP was used instead of SAMP as the chiral auxiliary. — [e] These values were obtained after separation of the minor diastereomer by two column chromatographies. The first isolated products showed de ≥ 75%[A], de ≥ 70%[B], and de ≥ 70%[C], respectively. — [f] Literature data[6a].

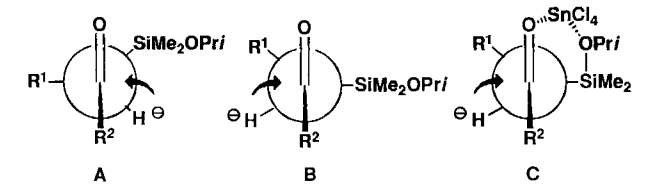
Scheme 7



The absolute configurations of **12f** and **12g** were determined by a comparison of the optical rotation of these compounds with that of **12k** reported by Cope et al.[6a] (entries 6, 7, and 10 in Table 4).

To explain the observed stereochemistry of the *vic*-diols **11**–**13**, we propose the transition state models **A**–**C**.

Scheme 8. Transion states **A**–**C**



The *anti* selectivity obtained with methods Ia and IIIa may be due to considerable steric repulsion between R^2 and the very large isopropoxydimethylsilyl group leading to a conformation depicted in transition state **A**. However, when longer carbon chains are present, repulsion between R^1 and R^2 is increased, and the addition of hydride may be explained using the Felkin-Anh model[16] (transition state **B**). The Lewis acid-mediated reduction can also be explained according to the Felkin-Anh model[16] (transition state **C**). A six-membered chelate including Sn directs attack by hydride towards the side opposite to the silyl group.

It is well known that the reduction of α-substituted ketones with L-selectride® affords *syn*-alcohols, whilst reduction with $Zn(BH_4)_2$ gives rise to *anti* products by the chelate rule[17]. The improvement of the *anti* selectivity by the modification of the substrate is an attractive alternative[18], which, when combined with the SAMP/RAMP hydrazone method should allow to enantioselectively synthesize a wide variety of *vic*-diols with relative and absolute configuration of choice.

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Experimental

NMR: Solvent $CDCl_3$, tetramethylsilane as internal standard, Varian EM 390 or VXR D 300 spectrometers. — IR: Beckman Acculab 4 or Perkin-Elmer FT IR 1750. — GC: Siemens Sichromat 2 or Sichromat 3 instrument connected with a Shimadzu Chromatopack C-R3A [detector: FID; carrier gas: N_2; 25-m XE-60-(*S*)-Val-*S*-α-PEA capillary column]. — Optical rotations: Perkin-Elmer polarimeter P 241.

Isopropoxydimethylsilyl chloride was prepared from dichlorodimethylsilane and absol. isopropyl alcohol by the method of Jakoubková et al.[19]; L-selectride® (1 M solution in THF), 9-BBN® (0.5 M solution in THF), and DIBAL (1 M solution in CH_2Cl_2) were obtained from Aldrich.

Merck silica gel (mesh 70–230 or 230–400) was used for column chromatography. Solvents were purified by standard methods.

General Procedure for the Preparation of the SAMP/RAMP Hydrazones **2**: 3-Pentanone (**1a**) (R^1 = CH_3, R^2 = C_2H_5) (5.4 g, 62.5 mmol) was added dropwise at 0°C to (*S*)-1-amino-2-(methoxyme-

thyl)pyrrolidine (SAMP) (6.5 g, 50 mmol) and stirred at 60°C for ca. 12 h. The mixture was poured into dichloromethane/water (4:1, 150 ml). The organic layer was separated, dried with Na_2SO_4, and concentrated in vacuo. Distillation of the residue under reduced pressure gave the SAMP hydrazone **2a** ($R^1 = CH_3$, $R^2 = C_2H_5$).

Table 5. Preparation of the SAMP hydrazones (*S*)-**2** and (*S*)-**7**

	From ketones	R^1	R^2	Yield [%]	B.p. [°C/Torr]	$[\alpha]_D^{22}$ (neat) (ref.[13a])
(S)-2a	**1a**	CH_3	C_2H_5	94	61/0.05	+222(+223)
(S)-2b	**1b**	C_2H_5	n-C_3H_7	96	94/0.05	+195(+204)
(S)-2c	**1c**	n-C_3H_7	n-C_4H_9	75	108/0.07	+175(+175)
(S)-7a	**6a**	-	CH_3	89	75/8	+305(+306)
(S)-7b	**6b**	-	C_2H_5	98	85/5	+281(+289)
(S)-7c	**6c**	-	n-C_6H_{13}	90	110/0.07	+217

Preparation of (R)-α-Silyl Ketone SAMP Hydrazones **3**: A solution of *n*-butyllithium in *n*-hexane (6.5 ml of 1.6 N *n*-butyllithium solution) was added dropwise with a syringe to a solution of diisopropylamine (1.5 ml, 10.7 mmol) in absol. diethyl ether (30 ml) under argon at 0°C and stirred for 15 min to generate a solution of lithium diisopropylamide (10.5 mmol). A solution of 3-pentanone SAMP hydrazone (**2a**) ($R^1 = CH_3$, $R^2 = C_2H_5$) (2.0 g, 10 mmol) in absol. diethyl ether (30 ml) was added dropwise to a stirred solution of the lithium diisopropylamide (10.5 mmol) at 0°C. After 4 h the mixture was cooled to −78°C and treated at once with isopropoxydimethylsilyl chloride (1.53 g, 10 mmol). After further stirring for 1 h, the mixture was allowed to warm up to room temp. within 10 h and was then poured into 50 ml of water and extracted three times with 50 ml of diethyl ether. The combined extracts were dried with $MgSO_4$ and concentrated by evaporation. Subsequent bulb-to-bulb distillation afforded (2*R*)-2-(isopropoxydimethylsilyl)-3-pentanone SAMP hydrazone (**3a**) ($R^1 = CH_3$, $R^2 = C_2H_5$), 2.55 g (81%), colorless oil, b.p. 230°C (bath)/0.12 Torr, $[\alpha]_D^{22} = +98.3$ ($c = 3.44$, benzene). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 3H, $SiCH_3$), 0.13 (s, 3H, $SiCH_3$), 0.90 (d, $J = 6.7$ Hz, 3H, CH_3), 1.09 (t, $J = 7.4$ Hz, 3H, CH_3), 1.16 (d, $J = 6.1$ Hz, 3H, $OCHCH_3$), 1.20 (d, $J = 6.1$ Hz, 3H, $OCHCH_3$), 1.58−2.45 (m, 6H, 2 × ring CH_2 and CH_2CH_3), 2.89−3.44 (m, 6H, CH_2OCH_3, NH, NCH_2, and CH), 3.32 (s, 3H, OCH_3), 4.01 (q of q, $J = 6.1/6.1$ Hz, 1H, $OCHMe_2$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.1 (SiMe), −2.0 (SiMe), 11.9 (C-5), 12.3 (C-1), 22.0 (C-4′), 25.8 ($OCHMe_2$), 27.0 (C-4), 27.5 (C-3′), 28.8 (C-2), 54.7 (C-5′), 59.0 (OCH_3), 65.1 (OCH), 66.2 (C-2′), 76.3 (CH_2OCH_3), 172.8 (C-3). − IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2940 and 2880 ($-CH_2-$, CH_3), 1645 and 1615 (C=N), 1460 ($-CH_2-$, CH_3), 1380 (d, *i*Pr), 1130 (OCH_3).

$C_{16}H_{34}N_2O_2Si$ (314.6) Calcd. C 61.10 H 10.89 N 8.90
Found C 61.24 H 11.00 N 9.10

(3R)-(+)-3-Isopropoxydimethylsilyl)-4-heptanone SAMP Hydrazone (**3b**) ($R^1 = C_2H_5$, $R^2 = n$-C_3H_7): Yield 85%, colorless oil, b.p. 160°C (bath)/0.07 Torr, $[\alpha]_D^{22} = +83.3$ ($c = 2.15$, benzene). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.90 (t, $J = 7.4$ Hz, 3H, CH_3), 0.95 (t, $J = 7.4$, 3H, CH_3), 1.16 (d, $J = 6.1$ Hz, 6H, $OCHMe_2$), 1.35−2.50 (m, 10H, 2 × ring CH_2, 3 × CH_2), 2.96−3.61 (m, 5H, CH_2OCH_3, NCH_2, NCH), 3.33 (s, 3H, OCH_3), 4.06 (q of q, $J = 6.1/6.1$ Hz, 1H, $OCHMe_2$), 5.03 (t, $J = 7.4$ Hz, 1H, CH−Si). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.8 (SiMe), 14.3 (C-7), 15.0 (C-1), 20.9 (C-6), 21.2 (C-2), 22.0 (C-4′), 25.8 ($CHMe_2$), 28.5 (C-3′), 32.4 (C-5), 54.2 (C-5′), 59.1 (OCH_3), 64.5 (C-2′), 65.1 (OCH), 76.3 (CH_2OCH_3), 76.4 (C-3), 171.4 (C-4). − IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2940 and 2880 ($-CH_2-$, CH_3), 1645 and 1615 (C=N), 1460 ($-CH_2-$, CH_3), 1380 (d, *i*Pr), 1130 (OCH_3).

$C_{18}H_{38}N_2O_2Si$ (342.1) Calcd. C 63.11 H 11.18 N 8.18
Found C 63.24 H 11.18 N 8.17

(4R)-(+)-4-(Isopropoxydimethylsilyl)-5-nonanone SAMP Hydrazone (**3c**) ($R^1 = n$-C_3H_7, $R^2 = n$-C_4H_9): Yield 70%, colorless oil, b.p. 180°C (bath)/0.07 Torr, $[\alpha]_D^{22} = +90.1$ ($c = 1.34$, benzene). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 3H, $SiCH_3$), 0.15 (s, 3H, $SiCH_3$), 0.91 (t, $J = 6.9$ Hz, 6H, CH_3), 1.16 (d, $J = 6.1$ Hz, 6H, $CHMe_2$), 1.27−2.43 (m, 14H, 2 × ring CH_2, 5 × CH_2), 2.99−3.61 (m, 5H, CH_2OMe, NCH, NCH_2), 3.32 (s, 3H, OCH_3), 4.06 (q of q, $J = 6.1/6.1$ Hz, 1H, $OCHMe_2$), 5.03 (t, $J = 7.6$ Hz, 1H, CHSi). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.5 (SiMe), 14.0 (C-9), 14.1 (C-1), 22.0 (C-4′), 23.0 (C-8), 23.5 (C-2), 25.8 ($CHMe_2$), 28.5 (C-3′), 29.7 (C-7), 30.2 (C-3), 34.3 (C-6), 36.0 (C-4), 54.2 (C-5′), 59.1 (OCH_3), 64.4 (OCH), 65.5 (C-2′), 76.3 (CH_2OCH_3), 172.0 (C-5). − IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 and 2870 ($-CH_2-$, CH_3), 1640 and 1615 (C=N), 1460 ($-CH_2-$, CH_3), 1380 (d, *i*Pr), 1130 (OCH_3).

$C_{20}H_{42}N_2O_2Si$ (370.7) Calcd. C 64.81 H 11.42 N 7.65
Found C 64.77 H 11.80 N 7.52

Preparation of (S)-α-Silyl Ketone SAMP Hydrazones **9**: A solution of *n*-butyllithium in *n*-hexane (6.5 ml of 1.6 N *n*-butyllithium solution) was added dropwise with a syringe to a solution of diisopropylamine (1.5 ml, 10.7 mmol) in absol. THF (30 ml) under argon at 0°C. The mixture was stirred for 15 min to generate a solution of lithium diisopropylamide (10.5 mmol). A solution of SAMP hydrazone **7b** ($R^2 = C_2H_5$) (1.8 g, 10 mmol) in absol. THF (30 ml) was added dropwise to a stirred solution of the lithium diisopropylamide (10.5 mmol) at 0°C. After 4 h, the mixture was cooled to −78°C and treated at once with isopropoxydimethylsilyl chloride (1.53 g, 10 mmol). After further stirring for 1 h, the mixture was allowed to warm up to room temp. within 10 h and was then evaporated in vacuo. Petroleum ether (150 ml) was added to the residue. The extract was evaporated in vacuo, and the residue was used in the following alkylation without further purification. − To the solution of the above prepared α-silyl SAMP hydrazone **8b** ($R^2 = C_2H_5$) (ca. 10 mmol) in absol. diethyl ether (60 ml), a solution of *n*-butyllithium in *n*-hexane (6.5 ml of 1.6 N *n*-butyllithium solution) was added dropwise with a syringe under argon at 0°C. After 4 h the mixture was cooled to −78°C and treated at once with diisopropylamine (1.5 ml, 10.7 mmol). After 15 min methyl iodide (1.4 g, 10 mmol) was added to the mixture. After further stirring for 1 h, the mixture was allowed to reach room temp. within 10 h and was then poured into 50 ml of water and extracted three times with 50 ml of diethyl ether. The combined extracts were dried with $MgSO_4$ and concentrated by evaporation. The residue **9b** ($R^2 = C_2H_5$) was used in the following ozonolysis without further purification.

Ozonolysis of α-Silyl Ketone Hydrazones **3** *and* **9**: A typical example of the procedure is described. Hydrazone **3a** ($R^1 = CH_3$, $R^2 = C_2H_5$) (3.2 g, 10 mmol) was taken up in 50 ml of dichloromethane, and the solution was cooled to −78°C. Ozone was then passed through the solution until complete oxidative cleavage of the hydrazone (TLC monitoring). After removal of excess ozone by passing argon through the solution and evaporation to dryness, the product was separated from the nitrosamine by silica-gel column chromatography (eluant: diethyl ether/petroleum ether 1:20. TLC monitoring: diethyl ether/petroleum ether 1:4, nitrosamine **4**: R_f = 0.3, α-silyl ketones: $R_f \geq 0.8$).

(2R)-(+)-2-(Isopropoxydimethylsilyl)-3-pentanone (**5a**): Yield 79%, pale yellow oil, $[\alpha]_D^{22} = +132.3$ ($c = 1.85$, benzene), ee ≧

90% (from ^{1}H-NMR shift experiment). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.12 (s, 3H, SiMe), 0.18 (s, 3H, SiMe), 1.03 (t, J = 7.2 Hz, 3H, CH_3), 1.13 and 1.17 (2 d, J = 6.0 Hz, each 3H, $CHMe_2$), 1.14 (d, J = 7.1 Hz, 3H, CH_3), 2.38 (m, 1H, CHCO), 2.55 (q, J = 7.2 Hz, 2H, $COCH_2$), 4.02 (q of q, J = 6.0/6.0 Hz, 1H, $CHMe_2$). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.3 (SiMe), –2.7 (SiMe), 7.9 (C-5), 10.5 (C-1), 25.7 ($CHMe_2$), 36.7 (C-4), 41.7 (C-2), 65.6 ($CHMe_2$), 213.0 (C-3). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 and 2870 (–CH_2–, CH_3), 1730 (CO), 1460 (–CH_2–, CH_3), 1375 (d, *i*Pr).

$C_{10}H_{22}O_2Si$ (202.4) Calcd. C 59.35 H 10.96
Found C 58.76 H 11.39

(2S)-(–)-2-(Isopropoxydimethylsilyl)-3-pentanone (**5b**): RAMP was used instead of SAMP as the chiral auxiliary. Yield 65% (from RAMP hydrazone). $[\alpha]_D^{22}$ = –132.2 (c = 5.02, benzene). ee ≧ 98% (from ^{1}H-NMR shift experiment).

10c: Yield 72% (from SAMP hydrazone). $[\alpha]_D^{22}$ = –132.0 (c = 3.13, benzene), ee ≧ 90% (from ^{1}H-NMR shift experiment).

(3R)-(+)-3-(Isopropoxydimethylsilyl)-4-heptanone (**5c**): Yield 69% (from SAMP hydrazone), pale yellow oil, $[\alpha]_D^{22}$ = +35.8 (c = 2.29, benzene). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 3H, SiMe), 0.16 (s, 3H, SiMe), 0.92 (t, J = 7.4 Hz, 3H, CH_3), 0.92 (t, J = 7.4 Hz, 3H, CH_3), 1.16 and 1.17 (2 d, each J = 6.1 Hz, each 3H, $CHMe_2$), 1.53–1.72 (m, 4H, CH_3CH_2), 2.46–2.57 (m, 2H, $COCH_2$), 4.11 (q of q, J = 6.1/6.1 Hz, 1H, $CHMe_2$), 4.12 (t, J = 6.0 Hz, 1H, COCH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.1 (SiMe), 9.4 (C-7), 13.8 (C-1), 25.7 ($CHMe_2$), 27.7 (C-2 and -6), 39.5 (C-5), 65.1 ($CHMe_2$), 79.3 (C-3), 213.2 (C-4). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 and 2870 (–CH_2–, CH_3), 1730 (CO), 1460 (–CH_2–, CH_3), 1375 (d, *i*Pr).

$C_{12}H_{26}O_2Si$ (230.4) Calcd. C 62.55 H 11.37
Found C 62.72 H 11.07

(4R)-(+)-4-(Isopropoxydimethylsilyl)-5-nonanone (**5d**): Yield 53% (from SAMP hydrazone), pale yellow oil, $[\alpha]_D^{22}$ = +59.7 (c = 1.34, benzene). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 3H, SiMe), 0.16 (s, 3H, SiMe), 0.90 (t, J = 7.4 Hz, 6H, CH_3), 1.16 (d, J = 6.1 Hz, 6H, $CHMe_2$), 1.31 (m, 4H, CH_3CH_2), 1.50–1.63 (m, 4H, $C_2H_5CH_2$), 2.39 (t, J = 7.4 Hz, 2H, $COCH_2$), 4.00 (q of q, J = 6.1/6.1 Hz, 1H, $CHMe_2$), 4.07–4.19 (m, 1H, COCH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.8 (SiMe), –2.1 (SiMe), 13.9 (C-1 and -9), 22.4 (C-2 and -8), 26.0 ($OCHMe_2$), 28.6 (C-7), 36.8 (C-3), 42.6 (C-6), 49.3 (C-4), 65.6 ($OCHMe_2$), 212.0 (C-5). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 and 2870 (–CH_2–, CH_3), 1720 (CO), 1460 (–CH_2–, CH_3), 1380 (d, *i*Pr).

$C_{14}H_{30}O_2Si$ (258.5) Calcd. C 65.05 H 11.70
Found C 65.30 H 11.56

(3S)-(–)-3-(Isopropoxydimethylsilyl)-2-butanone (**10a**): Yield 48% (from SAMP hydrazone), colorless oil, $[\alpha]_D^{22}$ = –175.7 (c = 0.85, benzene), ee ≧ 98% (from ^{1}H-NMR shift experiment). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.14 (s, 3H, SiMe), 0.20 (s, 3H, SiMe), 1.14 (d, J = 7.1 Hz, 3H, CH_3), 1.15 and 1.18 (each d, each J = 6.1 Hz, each 3H, $CHMe_2$), 2.16 (s, 3H, $COCH_3$), 2.52 (q, J = 7.1 Hz, 1H, COCH), 4.03 (q of q, J = 6.1/6.1 Hz, 1H, $CHMe_2$). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.3 (SiMe), –2.3 (SiMe), 10.4 (C-4), 25.7 ($CHMe_2$), 31.1 (C-1), 43.1 (C-3), 65.7 ($OCHMe_2$), 212.0 (C-2). – IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2930 and 2880 (–CH_2–, CH_3), 1690 (CO), 1460 (–CH_2–, CH_3), 1380 (d, *i*Pr).

$C_9H_{20}O_2Si$ (188.3) Calcd. C 57.39 H 10.70
Found C 56.20 H 10.68

(3S)-(–)-3-(Isopropoxydimethylsilyl)-2-pentanone (**10b**): Yield 47% (from SAMP hydrazone), pale yellow oil, $[\alpha]_D^{22}$ = –147.8 (c = 2.54, benzene), ee ≧ 95% (from the GLC analysis of the bis-Mosher ester of *vic*-diol **13b**). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 3H, SiMe), 0.18 (s, 3h, SiMe), 0.89 (t, J = 7.2 Hz, 3H, CH_3), 1.14 and 1.16 (2 d, each J = 6.1 Hz, each 3H, $CHMe_2$), 1.39–1.51 (m, 1H, CH_3CH_2) and 1.85–2.00 (m, 1H, CH_3CH_2), 2.14 (s, 3H, CH_3), 2.44 (dd, J = 2.9/11.3 Hz, 1H, CHCO), 4.01 (q of q, J = 6.1/6.1 Hz, 1H, $CHMe_2$). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.8 (SiMe), –2.1 (SiMe), 15.1 (C-5), 19.7 (C-4), 25.7 ($CHMe_2$), 32.3 (C-1), 52.6 (C-3), 65.6 ($OCHMe_2$), 210.2 (C-2). – IR (neat): $\tilde{\nu}$ = 2970 cm^{-1}, 2930, 2870 (–CH_2–, CH_3), 1690 (CO), 1460 (–CH_2–, CH_3), 1380 (d, *i*Pr).

(4S)-(–)-4-(Isopropoxydimethylsilyl)-3-decanone (**10d**): Yield 61% (from SAMP hydrazone), pale yellow oil, $[\alpha]_D^{22}$ = –73.5 (c = 2.55, benzene). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.11 (s, 3H, SiMe), 0.17 (s, 3H, SiMe), 0.86 (t, J = 7.0 Hz, 3H, CH_3), 1.02 (t, J = 7.4 Hz, 3H, CH_3), 1.12–1.17 (2 d, each J = 6.1 Hz, each 3H, $CHMe_2$), 1.20–1.99 (m, 10H, CH_2), 2.26–2.58 (m, 3H, COCH and $COCH_2$), 3.99 (q of q, J = 6.1/6.1 Hz, 1H, $OCHMe_2$). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –2.8 (SiMe), –2.1 (SiMe), 7.9 (C-1), 14.1 (C-10), 22.7 (C-9), 25.7 ($OCHMe_2$), 26.4 (C-8), 29.1 (C-7), 30.6 (C-6), 31.7 (C-5), 38.0 (C-2), 49.2 (C-4), 65.6 ($OCHMe_2$), 212.7 (C-3). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2920 and 2850 (–CH_2–, CH_3), 1715 (CO), 1460 (–CH_2–, CH_3), 1380 (d, *i*Pr).

$C_{15}H_{32}O_2Si$ (272.5) Calcd. C 66.11 H 11.84
Found C 66.21 H 11.76

(2S)-(–)-2-(Isopropoxydimethylsilyl)-3-nonanone (**10e**): Yield 66% (from SAMP hydrazone), pale yellow oil, $[\alpha]_D^{22}$ = –133.3 (c = 1.77, benzene), ee ≧ 98% (from ^{1}H-NMR shift experiment). – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.12 (s, 3H, SiMe), 0.18 (s, 3H, SiMe), 0.88 (t, J = 6.7 Hz, 3H, CH_3), 1.13 (d, J = 6.7 Hz, 3H, CH_3), 1.14 and 1.17 (2 d, each J = 6.1 Hz, each 3H, $CHMe_2$), 1.23–1.34 (m, 6H, CH_2), 1.48–1.61 (m, 2H, $COCH_2CH_2$), 2.31–2.57 (m, 3H, COCH and $COCH_2$), 4.02 (q of q, J = 6.1 Hz and 6.1 Hz, 1H, $CHMe_2$). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –3.2 (SiMe), –2.3 (SiMe), 10.5 (C-1), 14.1 (C-9), 22.5 (C-8), 25.7 (C-7), 25.8 ($CHMe_2$), 29.0 (C-6), 31.7 (C-5), 42.0 (C-2), 43.8 (C-4), 65.6 ($OCHMe_2$), 212.0 (C-3). – IR (neat): $\tilde{\nu}$ = 2960 cm^{-1}, 2930 and 2870 (–CH_2–, CH_3), 1715 (CO), 1460 (–CH_2–, CH_3), 1380 (d, *i*Pr).

Preparation of vic-Diols **11, 12, 13**

Reduction of α-Silyl Ketones **5** *or* **10**: A typical example of the procedure is described. A solution of **5a** (R^1 = CH_3, R^2 = C_2H_5) (2.0 g, 9.9 mmol) in absol. toluene (50 ml) was placed in a flame-dried 250 ml round-bottom flask and cooled to –78 °C. A solution of L-selectride® in THF (11.9 ml of 1 M lithium tri-*sec*-butylhydridoborate solution) was added with a syringe through the septum. The mixture was magnetically stirred under argon at –78 °C for 7 h. After the mixture was quenched with 3 ml of MeOH, saturated NaCl solution (30 ml) was added, and the organic layer was separated from the aqueous suspension. The aqueous layer was extracted three times with diethyl ether (60 ml × 3). The combined organic layers were dried with $MgSO_4$ and concentrated by evaporation. The residue was used in the following oxidative cleavage reaction of the C–Si bond without purification.

When we carried out the reduction using L-selectride® in the presence of an equivalent amount of $SnCl_4$, we used diethyl ether instead of toluene as solvent.

Oxidative Cleavage of the C–Si Bond: The residue obtained by the reduction of α-silyl ketone **5a** (R^1 = CH_3, R^2 = C_2H_5) (2.0 g, 9.9 mmol) was added to a mixture of MeOH (25 ml), THF (25 ml), $KHCO_3$ (3.0 g, 29.7 mmol; 3 eq), KF (1.7 g, 29.7 mmol; 3 eq), and 30% H_2O_2 aqueous solution (8.9 ml, c.a. 89 mmol; 9 eq). The mixture was stirred at room temp. for 12 h. For the purpose of decom-

position of the remaining H_2O_2, well-ground $Na_2S_2O_3 \cdot 5\ H_2O$ (ca. 7.5 g; 12 eq) was added to the reaction mixture at 0°C, then the mixture was stirred at room temp. for 30 min. The mixture was diluted with CH_2Cl_2 (c.a. 50 ml) and filtered with celite. The filtrate was concentrated in vacuo and the residue diluted again with CH_2Cl_2 (150 ml). The dried solution (Na_2SO_4) was evaporated in vacuo. The residue was subjected to column chromatography on silica gel with petroleum ether/diethyl ether (gradient) as eluant.

(2R,3S)-(−)-2,3-Pentanediol (**11a**): Yield 56%, colorless oil, $[\alpha]_D^{22} = -14.0$ (c = 0.61, $CHCl_3$), de ≧ 98% (from ^1H, ^{13}C NMR, and GLC analysis of the bis-Mosher derivative). ee ≧ 90% (from GLC analysis of the bis-Mosher derivative and ^1H-NMR shift experiment of **5a**). Column chromatography (petroleum ether/diethyl ether 2:1−0:1), TLC (R_f = 0.35, diethyl ether). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98 (t, J = 7.6 Hz, 3H, CH_3), 1.13 (d, J = 6.7 Hz, 3H, CH_3), 1.38−1.49 (m, 2H, CH_2), 3.15 (s, 2H, OH), 3.49−3.56 [m, 1H, C*H*(C_2H_5)OH], 3.79 [d of q, J = 3.0/6.7 Hz, 1H, C*H*(CH_3)OH]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.5 (C-5), 16.4 (C-1), 24.8 (C-4), 70.3 (C-2), 76.5 (C-3). − IR (neat): $\tilde{\nu}$ = 3600−3150 cm^{-1} (br, OH), 2970, 2930 and 2880 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1080 (OH).

$C_5H_{12}O_2$ (104.2) Calcd. C 57.66 H 11.62
Found C 57.12 H 11.86

13b: Yield 52%, colorless oil, $[\alpha]_D^{22} = -14.2$ (c = 2.13, $CHCl_3$), de ≧ 98% (from ^1H, ^{13}C NMR and GLC analysis of bis-Mosher derivative). ee ≧ 95% (from GLC analysis of bis-Mosher derivative).

(2R,3R)-(+)-2,3-Pentanediol (**12c**): Yield 14%, colorless oil, $[\alpha]_D^{22} = +4.5$ (c = 1.00, $CHCl_3$), de ≧ 98% (from ^1H, ^{13}C NMR shift experiment of **5a** and GLC analysis of the bis-Mosher derivative). Column chromatography (petroleum ether/diethyl ether 2:1−0:1), TLC (R_f = 0.38, diethyl ether). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.6 Hz, 3H, CH_3), 1.18 (d, J = 6.4 Hz, 3H, CH_3), 1.33−1.47 (m, 1H, CH_2), 1.51−1.64 (m, 1H, CH_2), 2.91 (s, 2H, OH), 3.22−3.29 [m, 1H, C*H*(C_2H_5)OH], 3.60 [d of q, J = 6.4/6.4 Hz, 1H, C*H*(CH_3)OH]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.9 (C-5), 19.5 (C-1), 26.2 (C-4), 70.6 (C-2), 77.6 (C-3). − IR (neat): $\tilde{\nu}$ = 3550−3150 cm^{-1} (br, OH), 2970, 2930 and 2870 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1070 (OH).

$C_5H_{12}O_2$ (104.2) Calcd. C 57.66 H 11.62
Found C 57.17 H 11.80

(2S,3R)-(+)-2,3-Pentanediol (**11d**): Yield 58%, colorless oil, $[\alpha]_D^{22} = +13.9$ (c = 0.7, $CHCl_3$), de ≧ 98% (from ^1H, ^{13}C NMR and GLC analysis of the bis-Mosher derivative), ee ≧ 98% (from ^1H-NMR shift experiment and GLC analysis of the bis-Mosher derivative).

$C_5H_{12}O_2$ (104.2) Calcd. C 57.66 H 11.62
Found C 57.46 H 11.83

13e: Yield 52%, colorless oil, $[\alpha]_D^{22} = +13.2$ (c = 1.65, $CHCl_3$), de ≧ 98% (from ^1H, ^{13}C NMR and GLC analysis of the bis-Mosher derivative), ee ≧ 90 (from ^1H-NMR shift experiment of **10c** and GLC analysis of the bis-Mosher derivative).

(3R,4R)-(+)-3,4-Heptanediol (**12f**): Yield 47%, colorless oil, $[\alpha]_D^{22} = +19.2$ (c = 0.59, $CHCl_3$), de ≧ 95%, but the first isolated product showed de ≧ 75% (from ^1H, ^{13}C NMR spectra). Column chromatography (petroleum ether/diethyl ether 3:1−1:1), TLC (R_f = 0.49, petroleum ether/diethyl ether 1:2). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, J = 6.7 Hz, 3H, CH_3), 0.98 (t, J = 7.4 Hz, 3H, CH_3), 1.35−1.65 (m, 6H, CH_2), 2.69 (s, 2H, OH), 3.29−3.35 (m, 1H, C*H*OH), 3.38−3.46 [m, 1H, C*H*(C_2H_5)OH]; cf. (*erythro*-): 3.47−3.55 (m, 1H, C*H*OH), 3.58−3.65 [m, 1H, C*H*(C_2H_5)OH]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.0 (C-1), 14.1 (C-7), 18.9 (C-6), 26.4 (C-2), 35.8 (C-5), 73.9 (C-4), 75.9 (C-3); cf. (*erythro*-): 10.5 (C-1), 14.1 (C-7), 19.2 (C-6), 24.2 (C-2), 33.3 (C-5), 74.2 (C-2), 76.3 (C-3). − IR (neat): $\tilde{\nu}$ = 3550−3200 cm^{-1} (br, OH), 2960, 2930 and 2870 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1070 (OH).

$C_7H_{16}O_2$ (132.2) Calcd. C 63.59 H 12.20
Found C 63.80 H 12.01

(4R,5R)-(+)-4,5-Nonanediol (**12g**): Yield 48%, colorless oil, $[\alpha]_D^{22} = +26.2$ (c = 0.52, $CHCl_3$), de ≧ 95%, but the first isolated product showed de ≧ 70% (from ^1H, ^{13}C NMR spectra). Column chromatography (petroleum ether/diethyl ether 3:1−1:1), TLC (R_f = 0.42, petrolcum ether/diethyl ether 1:2). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 3H, CH_3), 0.94 (t, J = 7.1 Hz, 3H, CH_3), 1.28−1.56 (m, 10H, CH_2), 2.74 (s, 2H, OH), 3.40 (m, 2H, C*H*OH); cf. (*erythro*-): 3.59 (m, 2H, C*H*OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-9), 18.9 (C-2), 22.8 (C-8), 27.9 (C-7), 33.3 (C-6), 35.8 (C-3), 74.3 (C-5), 74.6 (C-4); cf. (*erythro*-): 14.1 (C-9), 14.1 (C-1), 19.3 (C-2), 22.8 (C-8), 28.3 (C-7), 30.9 (C-6), 33.3 (C-3), 74.5 (C-5), 74.8 (C-4). − IR (neat): $\tilde{\nu}$ = 3550−3200 cm^{-1} (br. OH), 2960, 2930 and 2870 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1070 (OH).

$C_9H_{20}O_2$ (160.3) Calcd. C 67.45 H 12.58
Found C 67.02 H 12.85

(3R,4S)-(−)-3,4-Decanediol (**13h**): Yield 24%, m.p. 85°C, colorless powder, $[\alpha]_D^{22} = -4.8$ (c = 0.30, $CHCl_3$), de ≧ 98%, but the first isolated product showed de ≧ 70% (from ^{13}C-NMR spectrum). Column chromatography (petroleum ether/diethyl ether 3:1−1:1), TLC (R_f = 0.70, diethyl ether). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.7 Hz, 3H, CH_3), 1.00 (t, J = 7.4 Hz, 3H, CH_3), 1.23−1.59 (m, 12H, CH_2), 1.84 (s, 2H, OH), 3.52 (m, 1H, C*H*OH), 3.60 [m, 1H, C*H*(C_2H_5)OH]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4 (C-1), 14.1 (C-10), 22.6 (C-9), 24.2 (C-2), 26.0 (C-8), 29.4 (C-7), 31.3 (C-6), 31.8 (C-5), 74.5 (C-4), 76.2 (C-3). − IR ($CHCl_3$): $\tilde{\nu}$ = 3400−3150 cm^{-1} (br, OH), 2960, 2920 and 2850 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1070 (OH).

$C_{10}H_{22}O_2$ (174.3) Calcd. C 68.91 H 12.73
Found C 68.47 H 12.49

(2S,3R)-(+)-2,3-Nonanediol (**13i**): Yield 53%, m.p. 53°C, colorless powder, $[\alpha]_D^{22} = +6.0$ (c = 0.52, $CHCl_3$), de ≧ 98% (from ^{13}C-NMR spectrum), ee ≧ 98% (from ^1H-NMR shift experiment of α-silyl ketone **10e**). Column chromatography (petroleum ether/diethyl ether 2:1−1:1), TLC (R_f = 0.20, petroleum ether/diethyl ether 1:2). − ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.7 Hz, 3H, CH_3), 1.15 (d, J = 6.4 Hz, 3H, CH_3), 1.26−1.49 (m, 10H, CH_2), 2.00 (s, 2H, OH), 3.62 (m, 1H, C*H*OH), 3.79 [d of q, J = 3.2/6.4 Hz, 1H, CH(CH_3)OH]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1 (C-9), 16.7 (C-1), 22.6 (C-8), 26.0 (C-7), 29.4 (C-6), 31.8 (C-5), 31.9 (C-4), 70.5 (C-2), 70.5 (C-3). − IR ($CHCl_3$): $\tilde{\nu}$ = 3500−3150 cm^{-1} (br, OH), 2960, 2920 and 2850 (−CH_2−, CH_3), 1460 and 1380 (−CH_2−, CH_3), 1070 (OH).

$C_9H_{20}O_2$ (160.3) Calcd. C 67.45 H 12.58
Found C 67.02 H 12.81

(2S,3R)-Butane-2,3-diol (**13j**): Yield 49% (from SAMP hydrazone), colorless oil, de ≧ 98% (from ^1H, ^{13}C NMR spectra), ee ≧ 98% (^1H-NMR shift experiment of α-silyl ketone **10a**). Column chromatography (petroleum ether/diethyl ether 2:1−0:1), TLC (R_f = 0.27, diethyl ether). − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, J = 6.4 Hz, 6H, CH_3), 1.93 (s, 2H, OH), 3.80 (m, 2H, C*H*OH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.0 (C-1 and -4), 70.9 (C-2 and -3). − IR (neat): $\tilde{\nu}$ = 3550−3200 cm^{-1} (br, OH),

2980, 2930 and 2870 ($-CH_2-$, CH_3), 1460 and 1380 ($-CH_2-$, CH_3), 1080 (OH).

$C_4H_{10}O_2$ (90.1) Calcd. C 53.31 H 11.19
Found C 53.35 H 11.08

(2S,3S)-(+)-Butane-2,3-diol (**14j**) (byproduct): Mixture of **13j** and **14j** (9:4), colorless oil, $[\alpha]_D^{22} = +6.0$ ($c = 1.00$, $CHCl_3$). Theoretical optical rotation for **14j**: $[\alpha]_D^{22} = 6/[4/(4 + 9)] = 19.5$ [authentic sample fo **14j**: $[\alpha]_D^{22} = +20.0$ ($c = 0.64$, $CHCl_3$)]. – ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.17$ (d, $J = 6.0$ Hz, 6H, CH_3), 2.99 (s, 2H, OH), 3.51 (m, 2H, C*H*OH). – ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 19.3$ (C-1 and -4), 75.2 (C-2 and -3).

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