Headline Articles

Asymmetric Hydrosilylation of 1-Alkenes Catalyzed by Palladium–MOP

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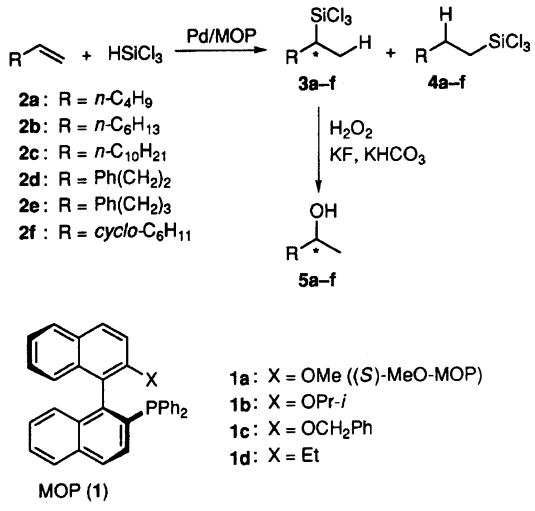
Asymmetric hydrosilylation of simple terminal alkenes ($RCH{=}CH_2$) with trichlorosilane at 40 °C in the presence of 1×10^{-3} or 1×10^{-4} molar amounts of palladium catalyst prepared in situ from [PdCl(η^3-C_3H_5)]$_2$ and (*S*)-2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl ((*S*)-MeO-MOP) proceeded with unusual regioselectivity and with high enantioselectivity to give high yields of 2-(trichlorosilyl)alkanes together with a minor amount of 1-(trichlorosilyl)alkanes. Optically active alcohols, $RCH(OH)CH_3$, were obtained by oxidation of the carbon–silicon bond. Regioselectivities for forming 2-silylalkanes over 1-silylalkanes and enantiomeric purities of alcohols are as follows: R=*n*-C_4H_9: 89/11, 94% ee (*R*). R=*n*-C_6H_{13}: 93/7 95% ee (*R*). R=*n*-$C_{10}H_{21}$: 94/6, 95% ee (*R*). R=$PhCH_2CH_2$: 81/19, 97% ee (*S*). R=$PhCH_2CH_2CH_2$: 80/20, 92% ee (*R*). R=*cyclo*-C_6H_{11}: 66/34, 96% ee (*R*). A similar hydrosilylation of 1-alkenes, 4-pentenyl benzoate and 1,5-heptadiene gave corresponding 2-alkanols of 90% ee and 87% ee, respectively, the ester carbonyl and the internal double bond remaining intact.

Hydrometallation reaction of olefins is one of the most useful functional group manipulations in organic synthesis, and asymmetric hydrometallation constitutes a powerful strategy for the synthesis of a variety of optically active compounds.[1] In particular, among the asymmetric hydrometallations, those catalyzed by chiral transition metal complexes are attractive for synthetic organic chemists.[2] Although the catalytic asymmetric functionalization of olefins has been reported in palladium-catalyzed hydrosilylation[3] and rhodium-catalyzed hydroboration,[4] the olefinic substrates are limited to styrenes, 1,3-dienes, and norbornene derivatives.[5—7] We report here the first successful conversion of terminal olefins into optically active secondary alcohols.[8] This is realized by palladium-catalyzed asymmetric hydrosilylation in the presence of a new chiral monodentate phosphine ligand (MOP, **1**)[9,10] (Scheme 1), followed by oxidation of the carbon–silicon bond.



Scheme 1.

Results and Discussion

Hydrosilylation of 1-Hexene and 1-Octene Catalyzed by Palladium–Phosphine Complexes. It is well-documented[11] that the hydrosilylation of ter-

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Table 1. Hydrosilylation of 1-Hexene (**2a**) and 1-Octene (**2b**) Catalyzed by Palladium–Phosphine Complexes[a)]

Entry	Alkene	Ligand[b)]	Temp °C	Time h	Yield[c)] %	Ratio (**3**/**4**)[d)]
1	1-Octene (**2b**)	dppb[e)]	80	24	0	—
2	1-Octene (**2b**)	chiraphos[f)]	80	24	0	—
3	1-Octene (**2b**)	BINAP[g)]	80	24	0	—
4	1-Octene (**2b**)	PPh_3	40	24	7	7/93
5	1-Hexene (**2a**)	PPh_3	40	24	12	9/91
6	1-Hexene (**2a**)	PPh_3	100	12	26	9/91
7	1-Hexene (**2a**)	$PC_6F_5Ph_2$	100	12	20	15/85
8	1-Hexene (**2a**)	P(*o*-Tol)$_3$	100	12	10	25/75[h)]
9	1-Hexene (**2a**)	MeO-MOP (**1a**)	40	24	91	89/11
10	1-Octene (**2b**)	MeO-MOP (**1a**)	40	24	83	93/7

a) All reactions were run in the presence of 0.001—0.01 molar amount of palladium–phosphine complex generated in situ by mixing $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and phosphine ligand without solvent. b) The molar ratio of Pd/P=1/2. c) Isolated yield by distillation. d) Determined by GC and ^{1}H NMR analysis. e) 1,4-Bis(diphenylphosphino)butane. f) 2,3-Bis(diphenylphosphino)butane. g) 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl. h) A trace of other regioisomers were detected.

Table 2. Catalytic Asymmetric Hydrosilylation of 1-Octene (**2b**)[a)]

Entry	Ligand (X in **1**)	Yield[b)] of hydrosilylation	Ratio[c)] of **3b**/**4b**	ee %[d)] (configuration)[e)]
1	**1a** (OMe)	83	93/7	95 (*R*)
2[f)]	**1a** (OMe)	97	87/13	94 (*R*)
3[g)]	**1a** (OMe)	97	88/12	91 (*R*)
4[h)]	**1a** (OMe)	93	89/11	86 (*R*)
5	**1b** (OPr-*i*)	88	90/10	91 (*R*)
6	**1c** (OCH_2Ph)	85	80/20	95 (*R*)
7	**1d** (Et)	80	90/10	93 (*R*)

a) All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and ligand MOP ((*S*)-**1a**, (*S*)-**1b**, (*S*)-**1c**, or (*R*)-**1d**) at 40 °C for 24 h. The molar ratio of **2b**/$HSiCl_3$/Pd/**1** is 1.0/1.2/0.001/0.002 unless otherwise noted. b) Isolated yield of a mixture of **3b** and **4b** by distillation. c) Determined by GLC or ^{1}H NMR analysis. d) Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate (**6b**) with a chiral column (see text). e) The absolute configuration was determined to be (*R*) by measurement of the specific rotation of the alcohol **5b** (94% ee (Entry 2); $[\alpha]_D^{25}$ −10.3 (*c* 5.59, EtOH)). The literature rotation for optically pure (*S*)-**5b** is $[\alpha]_D$ +9.79 (EtOH) (Ref. 20). f) Reaction with 1×10^{-4} molar amount of the catalyst for 72 h. g) Molar ratio of P/Pd is 1/1. h) Reaction at 60 °C for 16 h.

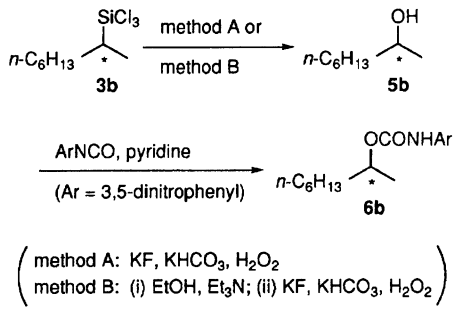
minal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikov selectivity leading to 1-silylalkanes. In specialized cases, a palladium complex catalyzes hydrosilylation of 1-alkenes to give 2-silylated products. Thus, for examples, the palladium-catalyzed hydrosilylations of styrenes and 3,3,3-trifluoropropene give 1-phenyl-1-silylethane[7c)] and 1,1,1-trifluoro-2-silylpropane,[12)] respectively.[13)] However, rather surprisingly, only a little attention has been paid to the use of palladium catalysts for the hydrosilylation of simple 1-alkenes,[14)] in spite of their frequent use for the reaction of 1,3-dienes and styrenes.[11)] Provided that the hydrosilylation of simple 1-alkenes proceeds with regioselectivity in giving 2-silylated products which contain a new stereogenic carbon center, there will be some possibility of the catalytic asymmetric functionalization of 1-alkenes. In order to develop a catalyst which possesses high catalytic activity, high regioselectivity in giving 2-silylalkanes, and high enantioselectivity, we examined several types of palladium–phosphine catalysts for the reaction of 1-hexene (**2a**) or 1-octene (**2b**) with trichlorosilane (Table 1). It was found that palladium complexes coordinated with chelating bis(phosphino) compounds: 1,4-bis(diphenylphosphino)butane (dppb), 2,3-bis(diphenylphosphino)butane (chiraphos),[15)] or 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP),[16)] did not catalyze the hydrosilylation at all even at 80 °C (Entries 1, 2, and 3 in Table 1). On the other hand, the reaction took place at 40 °C with triphenylphosphine as a ligand, though the chemical yields of silylalkane are low (Entries 4 and 5). Thus, the reac-

Table 3. Selected Bond Distances (Å) and Angles (deg) for *trans*-$[PdCl_2\{(R)\text{-MeO-MOP}\}_2]\cdot Et_2O$

Distances (Å)			
Pd–Cl(1)	2.299(2)	P(1)–C(28)	1.834(9)
Pd–Cl(2)	2.284(3)	C(2)–C(11)	1.49(1)
Pd–P(1)	2.344(2)	P(2)–C(34)	1.839(8)
Pd–P(2)	2.339(2)	P(2)–C(55)	1.826(9)
P(1)–C(1)	1.827(8)	P(2)–C(61)	1.840(8)
P(1)–C(22)	1.81(1)	C(35)–C(44)	1.51(1)
Angles (degree)			
Cl(1)–Pd–P(1)	93.60(8)	C(34)–P(2)–C(55)	112.0(4)
Cl(1)–Pd–P(2)	86.44(7)	C(34)–P(2)–C(61)	99.2(3)
Cl(2)–Pd–P(1)	87.25(8)	C(55)–P(2)–C(61)	105.3(4)
Cl(2)–Pd–P(2)	93.05(8)	P(1)–C(1)–C(2)	128.4(7)
P(1)–Pd–P(2)	174.95(8)	P(1)–C(1)–C(10)	112.1(5)
Cl(1)–Pd–Cl(2)	176.00(9)	P(1)–C(22)–C(27)	118.0(7)
Pd–P(1)–C(1)	111.7(3)	P(1)–C(28)–C(29)	120.9(6)
Pd–P(1)–C(22)	113.5(3)	P(2)–C(34)–C(35)	128.2(7)
Pd–P(1)–C(28)	113.7(2)	P(2)–C(34)–C(43)	111.3(6)
C(1)–P(1)–C(22)	111.5(4)	P(2)–C(55)–C(60)	118.5(6)
C(1)–P(1)–C(28)	101.2(4)	P(2)–C(61)–C(62)	119.9(7)
C(22)–P(1)–C(28)	104.3(4)	C(1)–C(2)–C(11)	123.6(7)
Pd–P(2)–C(34)	114.3(3)	C(2)–C(11)–C(12)	120.1(8)
Pd–P(2)–C(55)	112.9(2)	C(34)–C(35)–C(44)	124.3(7)
Pd–P(2)–C(61)	112.0(2)	C(35)–C(44)–C(45)	121.2(7)

tion in the presence of 0.001 molar amount of a palladium-triphenylphosphine catalyst (P/Pd=2/1) at 40 °C for 24 h gave 12% yield of the hydrosilylation products consisting of 2-(trichlorosilyl)hexane (**3a**) and 1-(trichlorosilyl)hexane (**4a**) in a ratio of 9/91 (Entry 5), the hydrosilylation being accompanied by isomerization of 1-hexene into internal olefins. The regioselectivity forming 2-silylalkane **3a** was increased to some extent by use of sterically more bulky monophosphine ligands, pentafluorophenyl(diphenyl)phosphine and tris(2-methylphenyl)phosphine giving **3a** with 15 and 25% regioselectivity, respectively, though the chemical yields were still low (Entries 7 and 8). It is reasonable to expect that a monodentate phosphine ligand generates a palladium catalyst that is more active for the hydrosilylation than a chelating bis(phosphino) ligand. Divalent palladium complexes are known to have sixteen electron square planar structures.[17] The monodentate phosphine ligand can allow the palladium to form intermediate $PdH(SiCl_3)L(CH_2{=}CHR)$ (L=monophosphine) that offers a coordination site for the activation of olefin and hydrosilane,[3f] while an unfavored five-coordinated species is required with bis(phosphino) ligands for the activation. Studies on the effects of monodentate phosphine ligands on the catalytic activity and the regioselectivity for forming 1-silylalkane or 2-silylalkane revealed that (*S*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MeO-MOP, **1a**)[10] is a unique ligand for the hydrosilylation, its palladium complex exhibiting both high catalytic activity and high unusual regioselectivity in forming 2-silylalkanes, and high enantioselectivity in addition. The predominant formation of 2-silylalkanes **3** from aliphatic 1-alkenes **2** has never been observed with any transition-metal catalysts.[11] For example, the reaction of 1-hexene (**2a**) with trichlorosilane in the presence of 0.001 molar amount of palladium–MOP complex, which was generated in situ by mixing di-μ-chlorobis(η^3-allylpalladium) and 4 molar amounts of (*S*)-MeO-MOP, at 40 °C was completed in 24 h to give high yield of 2-(trichlorosilyl)hexane (**3a**), the ratio of **3a** to its 1-silyl isomer **4a** being 89 to 11 (Entry 9). Similarly, the hydrosilylation of 1-octene (**2b**) with the palladium–MOP catalyst gave 2-silyloctane (**3b**) with 93% regioselectivity (Entry 10).

Detailed studies on the asymmetric hydrosilylation were performed for 1-octene (**2b**) under various conditions. The representative results are summarized in Table 2. The catalytic activity of palladium–MOP is so high as to catalyze the hydrosilylation with only 1×10^{-4} molar amount of the catalyst (Entry 2 in Table 2). The resulting silyloctanes **3b** and **4b** were transformed into the corresponding alcohols directly or



Scheme 2.

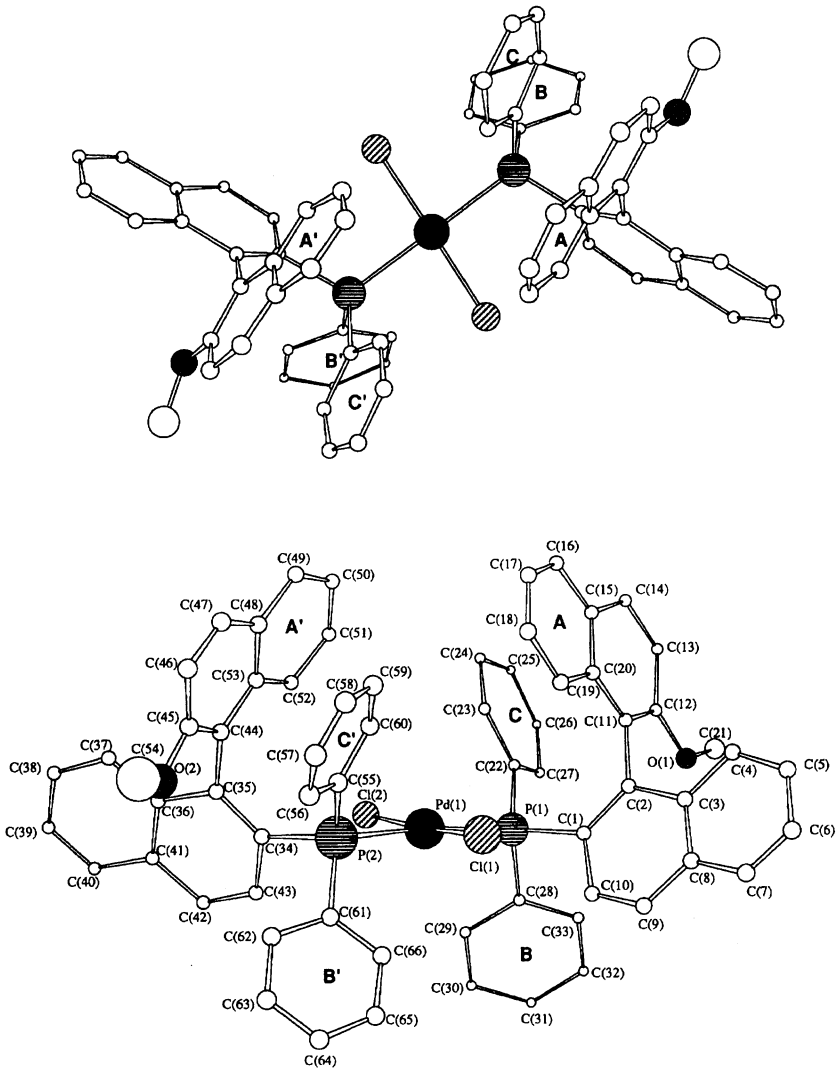


Fig. 1. Molecular structure and atom numbering scheme for *trans*-$[PdCl_2\{(R)\text{-MeO-MOP}\}_2]\cdot Et_2O$. Ether molecule is omitted for simplicity.

Table 4. Asymmetric Synthesis of 2-Alkanols through Asymmetric Hydrosilylation of 1-Alkenes Catalyzed by Palladium–(*S*)-MeO-MOP (**1a**)[a)]

Entry	1-Alkene (**2**)	Reaction conditions	Yield[b)] of hydrosilylation (%)	Ratio[c)] of **3**/**4**	Yield[d)] of **5** (%)	% ee[e)] (config.)	$[\alpha]_D$ (solvent)[f)]
1	n-$C_4H_9CH{=}CH_2$ (**2a**)	40 °C, 24 h	91	89/11	70	94 (*R*)	−12.3 (*c* 5.06, EtOH)[g)]
2	n-$C_{10}H_{21}CH{=}CH_2$ (**2c**)	40 °C, 72 h	90	94/6	75	95 (*R*)	−8.0 (*c* 8.10, EtOH)[g)]
3	$Ph(CH_2)_2CH{=}CH_2$ (**2d**)	40 °C, 24 h	90	81/19	68	97 (*S*)	+16.7 (*c* 2.40, $CHCl_3$)[g)]
4[h)]	$Ph(CH_2)_3CH{=}CH_2$ (**2e**)	30 °C, 60 h	81	80/20	69	92 (*R*)	−7.8 (*c* 0.72, $CHCl_3$)[g)]
5	*cyclo*-$C_6H_{11}CH{=}CH_2$ (**2f**)	40 °C, 24 h	100	66/34	45[i)]	96 (*R*)	−7.8 (*c* 3.10, Et_2O)[i,j)]

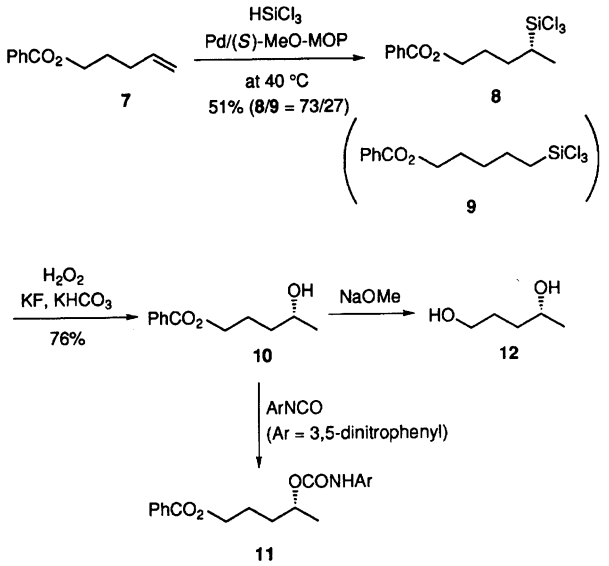
a) All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing $[PdCl(\eta^3\text{-}C_3H_5)]_2$ and ligand (*S*)-MeO-MOP (**1a**). The molar ratio of **2**/$HSiCl_3$/Pd/**1a** is 1.0/1.2/0.001/0.002 unless otherwise noted. b) Isolated yield of a mixture of **3** and **4** by distillation. c) Determined by GLC or ^1H NMR analysis of **3** (and **4**). d) Isolated yield of regioisomerically pure alcohol **5**. e) Determined by HPLC analysis of 3,5-dinitrophenylcarbamate **6** with a chiral stationary phase column (Sumichiral OA-1100). f) The literature rotations for optically pure alcohols **5** are shown in the Experimental Section. g) Rotation at 25 °C. h) The hydrosilylation was carried out in THF. The initial concentration of **2e** was 1.0 mol dm^{-3}. i) Contaminated with 5% of 2-cyclohexylethanol. j) Rotation at 20 °C.

by way of (triethoxysilyl)octanes by oxidative cleavage of silyl-carbon bond with hydrogen peroxide in the presence of potassium fluoride according to the procedure reported by Tamao (Scheme 2).[18)] The isomerically pure 2-octanol (**5b**) was isolated by removal of a small amount of 1-octanol resulting from **4b** by the preferen-

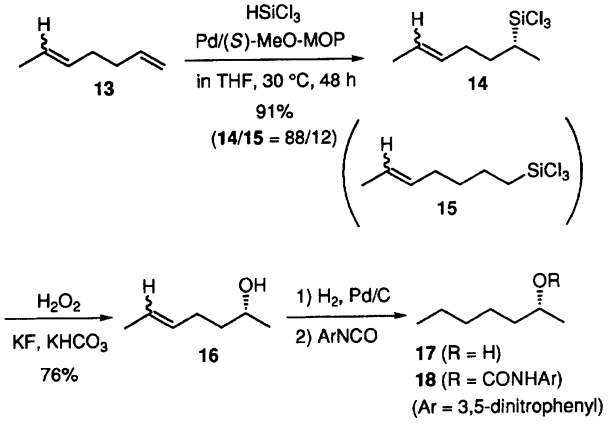
tial complexation with calcium chloride[19] in 71% yield. The absolute configuration of 2-octanol (**5b**) thus obtained was determined by measurement of its specific rotation ($[\alpha]_D^{25} -10.3$ (c 0.51, ethanol)) to be (R)[20] and the enantiomeric purity of **5b** was determined to be 94% ee by HPLC analysis of 3,5-dinitrophenylcarbamate **6b**, which was readily derived from **5b** by treatment with 3,5-dinitrophenyl isocyanate, using a chiral stationary phase column (Sumichiral OA-1100, hexane/1,2-dichloroethane/ethanol=100/20/1). Use of two molar amounts of (S)-MeO-MOP to [PdCl(η^3-C_3H_5)]$_2$ gave almost the same result as above (Entry 3), indicating that the key intermediate (PdH($SiCl_3$)L-(CH_2=CHR)) contains one molecule of MOP ligand.[3f] The high selectivity was also observed with MOP ligands, **1b**, **1c**, and **1d**, which have other substituents than methoxy at C2′ position. Thus, the hydrosilylation in the presence of the palladium–MOP complexes substituted with isopropoxy or benzyloxy group proceeded at 40 °C to give 2-silyloctane **3b** (>91% ee) with over 80% regioselectivity (Entries 5 and 6), suggesting that the steric bulkiness of the C2′-substituents has little influence on the present asymmetric hydrosilylation. The presence of an alkoxy group at the C2′ position is not essential for the high selectivity. Replacement of the methoxy group at the C2′ position by an alkyl group did not affect the selectivity (Entry 7). The lack of influence of the C2′ substituents on the stereoselectivity may be ascribed to how the MOP ligand coordinates to palladium (vide infra).

X-Ray Structure of [$PdCl_2$\{(R)-MeO-MOP\}$_2$]. In order to gain structural information on a palladium species coordinated with the MOP ligand, the crystal structure of [$PdCl_2$\{(R)-MeO-MOP\}$_2$] was studied by X-ray diffraction. Selected bond lengths and angles are listed in Table 3 and the molecular structure is shown in Fig. 1. The complex has a square-planer geometry with two phosphorus atoms and two chlorine atoms, where the MOP ligand coordinates to palladium with the phosphorus atom as a monodentate ligand. The phosphorus atoms or chlorine atoms are trans to each other. It should be noted that the naphthyl ring having a methoxy group plays an important role in construction of the chiral surroundings of the palladium. Thus, the naphthyl ring A (A′) extrudes toward the vicinity of palladium, while the methoxy group is located in the opposite side to palladium. The conformation of the naphthyl group where the C2′ substituent is far away from the palladium center explains the high stereoselectivity observed in the asymmetric hydrosilylation, irrespective of the C2′ substituents on the MOP ligand. The phenyls B (B′) and C (C′) are situated below and above the plane around the palladium atom. These structural features are very different from those commonly observed in complexes coordinated with chiral bidentate bis(phosphino) ligands such as BINAP.[21]

Asymmetric Hydrosilylation of Various Olefins Catalyzed by Palladium–MOP. The representative results obtained for the asymmetric synthesis of several 2-alkanols **5** through the hydrosilylation of terminal olefins **2** are summarized in Table 4. All the olefins, 1-hexene (**2a**), 1-dodecene (**2c**), 4-phenyl-1-butene (**2d**), 5-phenyl-1-pentene (**2e**), and vinylcyclohexane (**2f**) were transformed efficiently into the corresponding optically active alcohols **5**, with the enantioselectivity ranging between 92 and 97% ee, by the catalytic hydrosilylation-oxidation procedure. The selectivity attained here is highest for the enantioface selection of simple terminal olefins. Thus, the hydrosilylation of 1-hexene (**2a**) and 1-dodecene (**2c**) took place with the palladium–MOP catalyst to give high yields of 2-silylalkanes with around 90% regioselectivity (Entries 1 and 2). The silylalkanes were transformed into the corresponding alcohols by the oxidation in good yields. The enantiomeric purities were 94% ee for 2-hexanol (**5a**) and 95% ee for 2-dodecanol (**5c**). Phenyl-substituted 1-alkenes, 4-phenyl-1-butene (**2d**) and 5-phenyl-1-pentene (**2e**), were also successfully converted into



Scheme 3.



Scheme 4.

the corresponding optically active 2-alkanols, **5d** (97% ee) and **5e** (92% ee), in good chemical yields by the hydrosilylation–oxidation sequence (Entries 3 and 4). The regioselectivity in forming 2-silylalkanes is surprisingly high[11] for the terminal olefins **2a**—**d** which are substituted with primary alkyl groups on the double bond. Lower regioselectivity was observed with vinylcyclohexane (**2f**) which is substituted with a sterically bulky group (Entry 5).

It was found that an ester group remains intact under the conditions of the present asymmetric hydrosilylation. Thus, 4-pentenyl benzoate (**7**) underwent the hydrosilylation with trichlorosilane in the presence of the palladium–MOP catalyst to give 51% yield of hydrosilylation products consisting of 4-silylpentyl benzoate (**8**) and 5-silyl isomer **9** in a ratio of 73 to 27 (Scheme 3). The branch isomer **8** was oxidized into the corresponding alcohol **10** in 76% yield. The enantiomeric purity was determined by HPLC analysis of carbamate ester **11** to be 90% ee, and the absolute configuration was determined to be (*R*) by measurement of the specific rotation of diol **12**,[22] which was obtained by hydrolysis of the benzoate group of **10**.

The chemoselectivities of the present hydrosilylation on a terminal and on an internal carbon–carbon double bond were examined. It turned out that *cis*- or *trans*-2-octene does not undergo hydrosilylation under the standard conditions (at 40 °C, 24 h), the starting 2-octene being recovered without isomerization of the double bond. The hydrosilylation of 1,5-heptadiene (**13**), which contains both internal and terminal carbon–carbon double bonds and is a 9/1 mixture of geometrical isomers, took place at 30 °C to give 91% yield of silylation products **14** and **15**, where the internal double bond did not undergo the hydrosilylation or olefin isomerization at all. Oxidative cleavage of the carbon–silicon bond with hydrogen peroxide gave 76% yield of (*R*)-5-hepten-2-ol (**16**) (Scheme 4). The absolute configuration (*R*) was assigned by the correlation with known (*R*)-2-heptanol (**17**)[20] and the enantiomeric purity determined by the HPLC analysis of carbamate **18** was 87% ee. The results obtained in the asymmetric hydrosilylation of **7** and **13** demonstrate that the present catalysis is highly chemoselective to transform terminal olefins selectively in the presence of internal olefin or ester carbonyl into the corresponding 2-silylalkanes without loss of the high regioselectivity or the high enantioselectivity.

Experimental

General. ^{1}H NMR spectra were measured on a JEOL JNM-EX270 spectrometer in $CDCl_3$. Chemical shifts of ^{1}H NMR are reported in δ ppm referred to tetramethylsilane as an internal standard. Optical rotations were measured on a JASCO DIP-370 polarimeter. Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. The purity of all compounds was judged to be $\geq$95% by ^{1}H NMR spectral determination.

Palladium-Catalyzed Asymmetric Hydrosilylation of 1-Alkenes. Typical Procedure: To a mixture of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.92 mg, 0.0025 mmol), (*S*)-MeO-MOP (4.68 mg, 0.01 mmol), and 1-octene (**2b**) (560 mg, 5.0 mmol) was added trichlorosilane (745 mg, 5.5 mmol) at 0 °C. The reaction mixture was stirred at 40 °C for 24 h. GC analysis and ^{1}H NMR study on the crude mixture indicated that the ratio of 2-(trichlorosilyl)octane (**3b**)/1-(trichlorosilyl)octane (**4b**) was 93/7. The crude mixture was purified by bulb-to-bulb distillation under reduced pressure to give 1.03 g of a mixture of **3b** and **4b** (83%). ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, br t, J=6.7 Hz), 1.18 (2.8H, d, J=5.9 Hz), 1.21—1.60 (10.3H, m), 1.71—1.81 (0.9H, m). Since complete separation of 2-silyloctane **3b** from the regioisomer **4b** was difficult, major regioisomer was isolated and fully characterized in known alcohol **5b**.

Asymmetric hydrosilylation of 1-hexene (**2a**), 1-dodecene (**2c**), 4-phenyl-1-butene (**2d**), 5-phenyl-1-pentene (**2e**), and vinylcyclohexane (**2f**) was carried out in essentially the same manner as that of **2b**. The reaction conditions and the results are summarized in Table 4. ^{1}H NMR data for the hydrosilylation products are shown below.

(Trichlorosilyl)hexanes (3a/4a=89/11): δ=0.92 (3H, br t, J=6.7 Hz), 1.18 (2.7H, d, J=5.9 Hz), 1.20—1.58 (6.4H, m), 1.71—1.81 (0.9H, m).

(Trichlorosilyl)dodecanes (3c/4c=94/6): δ=0.90 (3H, br t, J=6.8 Hz), 1.20 (2.8H, d, J=6.2 Hz), 1.20—1.70 (18.3H, m), 1.71—1.80 (0.9H, m).

1- Phenyl(trichlorosilyl)butanes (3d/4d=81/19): δ=1.2 (2.4H, d (overlapped), J=6 Hz), 1.2—1.9 (2.8H, m), 1.9—2.2 (0.8H, m), 2.4—3.0 (2H, m), 7.1—7.5 (5H, m).

1- Phenyl(trichlorosilyl)pentanes (3e/4e=80/20): δ=1.19 (2.4H, d, J=6.6 Hz), 1.36—1.86 (5.6H, m), 2.59—2.70 (2H, m), 7.16—7.32 (5H, m).

Cyclohexyl(trichlorosilyl)ethanes (3f/4f=66/34): δ=0.88—1.84 (13H, m), 1.18 (2.0H, d (overlapped), J=7.3 Hz).

Oxidation of (Trichlorosilyl)alkanes.[18] Typical Procedure:

Method A: To a suspension of KF (1.44 g, 24.9 mmol) and $KHCO_3$ (5.00 g, 50.0 mmol) in 200 ml of THF/MeOH was added (trichlorosilyl)octanes (1.03 g, 4.15 mmol) which contains **3b** and **4b** in a ratio of 87/13. To the suspension was added 4.15 ml of 30% H_2O_2 at ambient temperature. Then the reaction mixture was vigorously stirred for 12 h. To this reaction mixture was added 5 g of $Na_2S_2O_3\cdot5H_2O$ and then entire mixture was stirred for 1 h. The mixture was filtered through a Celite plug, and the filter cake was rinsed with Et_2O. The filtrate was concentrated in vacuo and the resulting residue was dissolved in CH_2Cl_2. After drying over $MgSO_4$, organic solvent was removed in vacuo to give 485 mg of crude alcohol.

Method B: To a mixture of 5 ml of EtOH, 10 ml of Et_3N, and 700 ml of pentane was added 6.2 g of (trichlorosilyl)octanes (**3b/4b**=87/13) (25 mmol) at room temperature with vigorous stirring. The resulting white suspension was stirred for 16 h, and then filtered through a Celite plug. The filtrate was concentrated in vacuo to give a colorless oil. This oil was distilled (bulb-to-bulb) to give 6.7 g of a mixture of 2-(triethoxysilyl)octane and 1-(triethoxysilyl)-octane. To a suspension of KF (5.8 g, 100.0 mmol) and $KHCO_3$ (10.0 g, 100 mmol) in 1.20 dm^3 of MeOH–THF

(1/1) was added the mixture of (triethoxysilyl)octanes (6.7 g, 24.2 mmol) at 0 °C. To the mixture was added 25 ml of 30% H_2O_2 at 0 °C; the entire mixture was stirred vigorously at room temperature for 16 h. Powdered $Na_2S_2O_3 \cdot 5H_2O$ (30.0 g) was added to quench an excess of H_2O_2, and then the reaction mixture was filtered through a Celite plug. The filtrate was concentrated in vacuo and the resulting residue was dissolved in CH_2Cl_2. After drying over $MgSO_4$, organic solvent was removed in vacuo to give 2.95 g of crude alcohol.

Purification of (*R*)-2-Octanol (5b). To a solution of 3.3 g of the crude octanol (2-octanol/1-octanol=87/13) (25.3 mmol) in 100 ml of hexane was added 20 ml of EtOH and 2.8 g of powdered $CaCl_2$. The mixture was stirred vigorously at room temperature for 16 h. The mixture was filtered through a Celite plug and the filter cake was rinsed with pentane. The combined filtrate was concentrated in vacuo and then distilled to give 2.50 g of 2-octanol (71% from (trichlorosilyl)octanes (**3b**/**4b**=87/13)). $[\alpha]_D^{25}$ −10.3 (*c* 0.51, ethanol).

By the same procedures used for the oxidation of a mixture of **3b** and **4b** and the purification of **5b** mentioned above, the (trichlorosilyl)alkanes obtained by the asymmetric hydrosilylation were converted into optically active 2-alkanols: **5a**, **5c**, **5d**, **5e**, and **5f**. The isolated yields of the purified 2-alkanols and their specific rotations are summarized in Table 4. The literature rotations for optically pure (*S*)-**5a**,[20] (*S*)-**5b**,[20] (*S*)-**5c**,[20] (*S*)-**5d**,[23] (*S*)-**5e**,[24] and (*S*)-**5f**[25] are $[\alpha]_D$ +12.70 (EtOH), $[\alpha]_D$ +7.94 (EtOH), $[\alpha]_D$ +17.2 (chloroform), $[\alpha]_D^{20}$ +8.63 (chloroform), and $[\alpha]_D^{20}$ +8.43 (Et_2O), respectively.

***trans*-[PdCl$_2${(*R*)-MeO-MOP}$_2$]·Et$_2$O:** (*R*)-**1a** (14 mg, 0.03 mmol) and $[PdCl_2(CH_3CN)_2]$ (3.9 mg, 0.015 mmol) were dissolved in 1 ml of benzene, and the solution was concentrated in vacuo to give orange-yellow solid. A solution of the crude solid in 0.5 ml of CH_2Cl_2 was placed in a small open bottle (2 ml). This bottle was placed in a reagent bottle (30 ml) which contains ether (3 ml). After 5 d, dispersion of the solvents gave *trans*-[PdCl$_2${(*R*)-MeO-MOP}$_2$]·Et$_2$O as orange-yellow crystals (12 mg, 67%). The crystals contain one molecule of ether as a crystal solvent. Found: C, 70.90; H, 4.99; Cl, 5.89%. Calcd for $C_{70}H_{60}O_3Cl_2P_2Pd$: C, 70.74; H, 5.09; Cl, 5.97%.

X-Ray Diffraction Study of *trans*-[PdCl$_2${(*R*)-MeO-MOP}$_2$]·Et$_2$O: A single crystal (0.30×0.20×0.15 mm) of the palladium complex *trans*-[PdCl$_2${(*R*)-MeO-MOP}$_2$]·Et$_2$O obtained above was sealed in a glass capillary tube. Intensity data were collected on an Enraf–Nonius CAD4 diffractometer. The cell dimensions suggested a monoclinic cell, and systematic absences in the diffractometer data indicated the space group $P2_1$. Diffraction data were collected in the range $2.0 < 2\theta < 50.0°$ using the $\omega/2\theta$ scan technique at a scan rate of 2—7 ° min^{-1} in ω. Three standard reflections, monitored by every 60 reflection measurements, showed no significant variation in the intensities during the data collection. The data were corrected for Lorenz and polarization effects. Stronger reflections (3886) were classified as observed ($I > 3\sigma(I)$); these were used for the solution and refinement of the trial structure. Calculations were performed on a VAX Station 4000/60 with the MolEN Package provided by Enraf–Nonius. The scattering factors were taken from "International Tables for X-Ray Crystallography".[26] The palladium atom was located from a Patterson map, and other non-hydrogen atoms were found by subsequent difference Fourier syntheses. Hydrogen atoms were not located. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized in least squares was $\sum w(|F_o|-|F_c|)^2$ ($w=1/[\sigma^2(F_o)]$). The final R index was 0.040 (R_w=0.051, S=1.47). $R=\sum||F_o|-|F_c||/\sum|F_o|$, $R_w=[\sum w(|F_o|-|F_o|)^2/\sum w|F_o|^2]^{1/2}$, and $S=[\sum w(|F_o|-|F_c|)^2/(N_o-N_p)]^{1/2}$, where N_o is the number of observed data and N_p is the number of parameters varied. Crystal data and details of data collection and refinement are summarized in Table 5. Positional parameters are listed in Table 6.

(*R*)-4-(Trichlorosilyl)pentyl Benzoate (8). The same procedure as employed for the preparation of **3b** was followed with 4-pentenyl benzoate (**7**) (748 mg, 3.9 mmol), trichlorosilane (677 mg, 5.0 mmol), $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (0.80 mg, 2.1 μmol), and (*S*)-MeO-MOP (4.30 mg, 9.18 μmol) to give a mixture of 4-(trichlorosilyl)pentyl benzoate (**8**) and 5-(trichlorosilyl)pentyl benzoate (**9**) in a ratio of 73/27 (51% yield). ^{1}H NMR δ=1.24 (2.2H, d, J=6.9 Hz), 1.41—2.00 (5.8H, m), 4.31—4.36 (2H, m), 7.42—7.60 (3H, m), 8.02—8.05 (2H, m).

(*R*)-5-Benzoyloxy-2-pentanol (10). The same procedure as employed for the preparation of **5b** was followed with (trichlorosilyl)pentyl benzoate (**8**/**9**=69/31) (345 mg, 0.95 mmol), KF (353 mg, 6.08 mmol), $KHCO_3$ (960 mg, 9.60 mmol), and 1.0 ml of 30% H_2O_2 in 100 ml of THF/MeOH (1/1) to give 215 mg of a mixture of **10** and 5-benzoyloxy-1-

Table 5. Crystal Data and Details of the Structure Determination for *trans*-[PdCl$_2${(*R*)-MeO-MOP}$_2$]·Et$_2$O

Formula	$C_{66}H_{50}Cl_2O_2P_2Pd \cdot C_4H_{10}O$
Formula weight	1188.51
Crystal size, mm	0.30×0.20×0.15
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	14.015(1)
b/Å	18.259(1)
c/Å	12.743(1)
β/deg	114.23(1)
V/Å^3	2973.6
Z	2
d_{calc}/g cm^{-3}	1.33
μ(Mo $K\alpha$)/cm^{-1}	4.96
F(000)	1228
Radiation	Mo $K\alpha$ (λ=0.71073 Å)
Monochromator	Graphite
Maximum 2θ/deg	50.0
Scan type	ω–2θ
Scan width/deg	0.9+0.15 tan θ
Scan rate/deg min^{-1}	2—7 (in ω)
Temperature/K	298
No. of reflections measured	5409
No. of observed reflections	3886 with $I>3\sigma(I)$
No. of parameters refined	678
R	0.040
R_w	0.051
S	1.47
Max and min peak/e Å^{-3}	0.56, −0.09

Table 6. Positional and Equivalent Isotropic Thermal Parameters for *trans*-[$PdCl_2$\{(*R*)-MeO-MOP\}$_2$]·Et_2O

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
Pd	0.42798(4)	0.0	0.23866(4)	2.882(9)	C(33)	0.6043(7)	−0.2050(6)	0.4691(7)	5.3(2)
Cl(1)	0.3764(2)	0.0516(1)	0.3716(2)	4.01(5)	C(34)	0.2614(6)	0.0360(5)	−0.0504(6)	3.3(2)
Cl(2)	0.4844(2)	−0.0436(1)	0.1059(2)	4.13(5)	C(35)	0.2661(6)	0.0843(5)	−0.1284(6)	3.6(2)
P(1)	0.5686(2)	−0.0630(1)	0.3782(2)	3.13(5)	C(36)	0.2444(6)	0.0583(6)	−0.2435(7)	4.2(2)
P(2)	0.2786(2)	0.0538(1)	0.0983(2)	3.06(4)	C(37)	0.2459(7)	0.1049(7)	−0.3303(7)	5.7(3)
O(1)	0.8416(4)	−0.0712(4)	0.6783(5)	5.3(2)	C(38)	0.2254(8)	0.0776(8)	−0.4390(8)	7.6(3)
O(2)	0.1122(5)	0.1878(4)	−0.1954(6)	6.4(2)	C(39)	0.2007(8)	0.0066(9)	−0.4665(7)	7.6(3)
C(1)	0.5792(6)	−0.0443(5)	0.5235(6)	3.3(2)	C(40)	0.1986(7)	−0.0412(7)	−0.3855(8)	6.5(3)
C(2)	0.6532(5)	−0.0027(6)	0.6084(5)	3.2(1)	C(41)	0.2222(6)	−0.0175(5)	−0.2699(6)	4.3(2)
C(3)	0.6452(5)	0.0035(6)	0.7185(6)	3.7(2)	C(42)	0.2252(6)	−0.0657(5)	−0.1830(7)	4.3(2)
C(4)	0.7183(7)	0.0443(6)	0.8095(7)	4.9(2)	C(43)	0.2439(6)	−0.0407(5)	−0.0783(7)	4.0(2)
C(5)	0.7097(9)	0.0466(7)	0.9166(8)	6.7(3)	C(44)	0.2908(6)	0.1645(5)	−0.1047(6)	3.6(2)
C(6)	0.6325(7)	0.0126(7)	0.9320(7)	6.3(3)	C(45)	0.2144(7)	0.2161(6)	−0.1435(7)	4.7(2)
C(7)	0.5570(7)	−0.0242(6)	0.8449(7)	5.2(2)	C(46)	0.2354(8)	0.2928(6)	−0.1300(8)	5.5(3)
C(8)	0.5621(6)	−0.0298(5)	0.7363(6)	4.0(2)	C(47)	0.3344(8)	0.3134(6)	−0.0757(8)	5.8(3)
C(9)	0.4867(6)	−0.0687(6)	0.6458(7)	4.4(2)	C(48)	0.4163(7)	0.2650(5)	−0.0279(7)	4.6(2)
C(10)	0.4959(6)	−0.0770(5)	0.5443(6)	3.8(2)	C(49)	0.5195(9)	0.2870(6)	0.0352(9)	6.5(3)
C(11)	0.7436(6)	0.0326(5)	0.5958(6)	3.5(2)	C(50)	0.6013(8)	0.2386(7)	0.0858(9)	6.7(3)
C(12)	0.8380(5)	−0.0019(7)	0.6349(6)	4.4(2)	C(51)	0.5794(8)	0.1636(6)	0.0681(9)	5.9(3)
C(13)	0.9274(7)	0.0320(6)	0.6307(8)	5.6(3)	C(52)	0.4791(7)	0.1400(5)	0.0016(8)	4.9(2)
C(14)	0.9199(7)	0.0993(7)	0.5871(9)	6.3(3)	C(53)	0.3931(6)	0.1885(5)	−0.0464(6)	3.6(2)
C(15)	0.8201(8)	0.1390(6)	0.5457(9)	6.1(3)	C(54)	0.0318(9)	0.2395(8)	−0.212(1)	9.2(4)
C(16)	0.8089(9)	0.2101(7)	0.495(1)	8.9(4)	C(55)	0.2669(6)	0.1510(5)	0.1242(6)	3.5(2)
C(17)	0.7173(9)	0.2444(8)	0.460(1)	11.0(5)	C(56)	0.1694(7)	0.1851(6)	0.0924(8)	5.0(2)
C(18)	0.6310(9)	0.2117(7)	0.460(1)	8.5(4)	C(57)	0.1651(8)	0.2578(6)	0.1231(9)	6.1(3)
C(19)	0.6412(8)	0.1423(6)	0.5086(9)	5.9(3)	C(58)	0.2518(9)	0.2966(6)	0.1759(9)	6.6(3)
C(20)	0.7340(6)	0.1047(5)	0.5509(7)	4.2(2)	C(59)	0.3497(8)	0.2633(5)	0.2076(8)	5.4(3)
C(21)	0.9343(8)	−0.1123(7)	0.711(1)	7.5(3)	C(60)	0.3571(6)	0.1908(5)	0.1824(7)	3.9(2)
C(22)	0.6917(6)	−0.0480(6)	0.3672(7)	4.3(2)	C(61)	0.1575(5)	0.0116(5)	0.0932(6)	3.6(2)
C(23)	0.7682(7)	−0.1021(7)	0.3926(8)	5.7(3)	C(62)	0.0655(6)	0.0162(5)	−0.0071(7)	4.6(2)
C(24)	0.8617(7)	−0.0900(8)	0.3788(9)	7.5(3)	C(63)	−0.0248(7)	−0.0188(7)	−0.0128(9)	6.3(3)
C(25)	0.8788(7)	−0.028(1)	0.335(1)	11.2(6)	C(64)	−0.0239(8)	−0.0577(7)	0.078(1)	7.1(3)
C(26)	0.8033(8)	0.0263(8)	0.3032(9)	8.6(4)	C(65)	0.0642(7)	−0.0614(7)	0.1751(8)	6.2(3)
C(27)	0.7061(7)	0.0182(6)	0.3227(7)	5.7(3)	C(66)	0.1541(7)	−0.0282(6)	0.1848(7)	4.8(2)
C(28)	0.5527(6)	−0.1628(5)	0.3710(6)	3.7(2)	O(101)	0.901(1)	0.221(1)	0.091(1)	9.1(5)
C(29)	0.4956(7)	−0.1973(5)	0.2682(8)	4.6(2)	C(101)	0.914(2)	0.196(2)	0.176(2)	8.6(7)
C(30)	0.4886(8)	−0.2737(6)	0.2620(9)	6.0(3)	C(102)	0.149(2)	0.735(2)	−0.000(2)	9.9(8)
C(31)	0.5377(8)	−0.3148(6)	0.3583(9)	6.9(3)	C(103)	0.172(2)	0.771(2)	0.084(2)	8.8(7)
C(32)	0.5966(8)	−0.2803(6)	0.4617(9)	6.4(3)	C(104)	0.984(3)	0.164(2)	0.246(3)	11(1)

a) $B_{eq}=(4/3)\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

pentanol. The mixture was separated by preparative TLC on silica gel (eluent; hexane/EtOAc=5/1) to give 123 mg of isomerically pure **10** (62%). ^{1}H NMR δ=1.24 (3H, d, J=6.1 Hz), 1.41 (1H, br s), 1.61 (2H, br q, J=7.3 Hz), 1.80—1.96 (2H, m), 3.89 (1H, br q, J=6.1 Hz), 4.36 (2H, t, J=6.6 Hz), 7.44 (2H, t, J=7.6 Hz), 7.56 (1H, t, J=7.3 Hz), 8.04 (2H, d, J=7.9 Hz).

(*R*)-1,4-Pentandiol (12).[22] A solution of **10** (60 mg, 0.29 mmol) and NaOMe (11 mg, 0.20 mmol) in 3 ml of methanol was stirred at room temperature for 10 h. To the reaction mixture was added 11 mg of NH_4Cl; then the entire mixture was concentrated in vacuo. The residue was chromatographed on silica gel (eluent; EtOAc only) to give 21 mg of **12** (69%). $[\alpha]_D^{16}$ −11.7 (*c* 1.0, EtOH); ^{1}H NMR δ=1.18 (3H, d, J=6.3 Hz), 1.50—1.72 (4H, m), 2.95 (2H, br s), 3.55—3.88 (3H, m).

(*R*)-6-(Trichlorosilyl)-2-heptene (14). The same procedure as employed for the preparation of **3b** was followed with 1,5-heptadiene (**13**) (385 mg, 4.0 mmol), trichlorosilane (677 mg, 5.0 mmol), [$PdCl(\eta^3$-$C_3H_5)]_2$ (3.65 mg, 0.01 mmol), and (*S*)-MeO-MOP (18.7 mg, 0.04 mmol) in 1 ml of THF to give a mixture of 6-(trichlorosilyl)-2-heptene (**14**) and 7-(trichlorosilyl)-2-heptene (**15**) (1.05 g) in a ratio of 88/12 in 91% yield. ^{1}H NMR δ=1.17 (2.6H, d, J=6.6 Hz), 1.23—2.23 (5.4H, m), 1.66 (3H, br d (overlapped), J=5.6 Hz), 5.35—5.51 (2H, m).

(*R*)-5-Hepten-2-ol (16). The same procedure as employed for the preparation of **5b** was followed with trichlorosilyl-2-heptenes (**14**/**15**=88/12) (463 mg, 2.0 mmol), KF (580 mg, 10.0 mmol), $KHCO_3$ (2.0 g, 20.0 mmol), and 2.0 ml of 30% H_2O_2 in 100 ml of THF/MeOH (1/1) to give 207 mg of a mixture of **16** and 5-hepten-1-ol. The mixture was separated by column chromatography on silica gel (eluent; hexane/EtOAc=5/1) to give 174 mg of **16** (76%). ^{1}H NMR δ=1.19 (2.7H, d, J=6.1 Hz), 1.25 (0.3H, d, J=6.4 Hz), 1.37—1.57 (3H, m), 1.65 (3H, br d, J=4.3 Hz), 2.04—2.14 (2H, m), 3.81 (1H, br d, J=6.1 Hz), 5.40—5.48 (2H, m).

(*R*)-2-Heptanol (17).[20] To a suspension of 20 mg of 10% Pd/C in 1 ml of EtOAc was added **17** (100 mg, 0.88 mmol) at room temperature under H_2 atmosphere and the mixture was stirred for 3 h. The reaction mixture was filtered through a Celite plug and the filter cake was rinsed with Et_2O. The combined filtrate was concentrated in vacuo to give crude alcohol as colorless oil. The residual oil was distilled (bulb-to-bulb) to give 97 mg of **17** (95%). $[\alpha]_D^{25}$ −9.6 (*c* 0.9, EtOH).

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