

Hydrozirconation of Alkenyloxirane Derivatives: Preparation of Cycloalkylmethanols

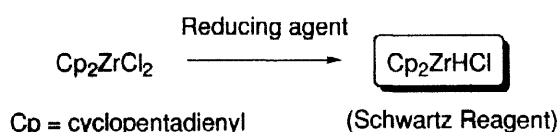
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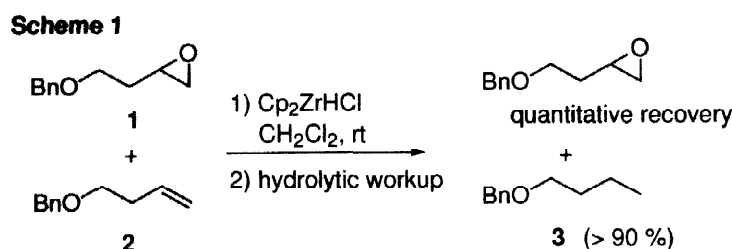
Received 29 September 1997; accepted 7 November 1997

Abstract: Cyclopentyl and cyclopropylmethanol derivatives were efficiently prepared through a chemoselective hydrozirconation reaction of (1-butenyl)oxirane and vinyloxirane with Cp_2ZrHCl . However, the attempted reaction of (1-pentenyl)oxirane or (1-propenyl)oxirane failed to yield cyclohexyl or cyclobutylmethanols. The ring formation was stereospecific and proceeded with the inversion of the configuration at the reacting oxirane carbon. The origin of stereospecificity and the stereoselectivity in the formation of cyclopropylmethanols was presumed by the approach of the Schwartz reagent from the less hindered site of the stable *gauche*-conformer of the vinyloxirane compound in the transition state. (Cyclopropylmethyl)amine derivatives were also prepared by the treatment of vinylaziridine derivatives with Cp_2ZrHCl . © 1997 Elsevier Science Ltd. All rights reserved.

Hydrozirconation of alkenes or alkynes with zirconocenehydrochloride (Cp_2ZrHCl , Schwartz reagent) is the most convenient and the easiest way to create alkyl and/or alkenyl zirconocene compounds. The recent applications of the organozirconocene derivatives, thus generated, to organic synthesis have established their position as convenient organometallics.¹ The Schwartz reagent (Cp_2ZrHCl) can be easily prepared *in situ* or isolated by the reduction of Cp_2ZrCl_2 with the selected hydride reagent; it is even commercially available as moisture-sensitive and photolabile crystals.² We report herein a full account of an efficient formation of cycloalkylmethanol derivatives through the chemoselective hydrozirconation of alkenyloxirane compounds with Cp_2ZrHCl and the following intramolecular nucleophilic cyclization of the oxirane-alkylzirconocene intermediate.³ The application of the present protocol to vinylaziridine derivatives is also described.



The chemoselectivity of the Cp_2ZrHCl reagent in the hydrozirconation reactions of unsaturated compounds which have a Cp_2ZrHCl -susceptible functional group has been well studied, and many procedures have been devised for the chemoselective hydrozirconation of a double or triple bond even in the presence of a carbonyl functionality.⁴ The oxirane ring is usually intolerant to metal hydride reagents, and the reaction of oxirane compounds by Cp_2ZrHCl has also been reported to give alcohols through a regioselective reduction of the oxirane ring.⁵ Since the hydrozirconation of terminal olefin has a very small activation energy and thus is a very facile process (vide infra), it would be interesting to test the tolerance of the oxirane ring in the presence of an olefinic function.



Treatment of a mixture of equimolar amounts of oxirane **1** and olefin **2** with one equiv mol of Cp_2ZrHCl in dichloromethane (CH_2Cl_2) and hydrolytic workup gave a mixture of alkane **3** and the intact starting oxirane **1**, quantitatively. The exclusive reduction of the double bond of **2** indicates that the rate of hydrozirconation to terminal olefin is much faster than the reduction of the oxirane ring. This result also shows that the intermolecular nucleophilic reactivity of the alkyl zirconocene intermediate is very low toward the oxirane compound. It has been reported that the intermolecular reaction of alkylzirconocene with oxirane was accelerated by the addition of a silver salt.^{1c} Based on the chemoselectivity of Cp_2ZrHCl discussed above, we examined the reaction of alkenyloxirane compounds **4** with Cp_2ZrHCl and the following intramolecular cyclization. The results of the reactions are listed in Table 1.

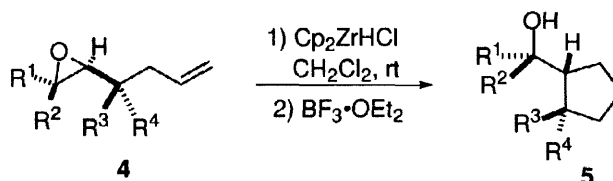


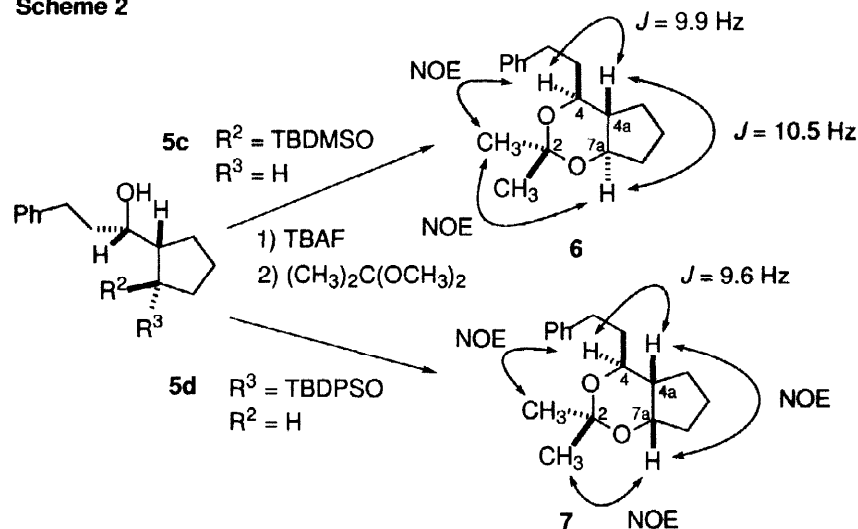
Table 1. Formation of Cyclopentyl Carbinol Derivatives **5**

Entry	Substrate	R ¹	R ²	R ³	R ⁴	Additive ^a	Yield (%) ^b
1	a	H	PhCH_2CH_2	H	H	none	— ^c
2	a	H	PhCH_2CH_2	H	H	AgClO_4	47
3	a	H	PhCH_2CH_2	H	H	$\text{BF}_3 \cdot \text{OEt}_2$	77
4	b	BnOCH_2	H	H	H	$\text{BF}_3 \cdot \text{OEt}_2$	76
5 ^d	c	PhCH_2CH_2	H	TBDMSO	H	$\text{BF}_3 \cdot \text{OEt}_2$	72
6 ^d	d	PhCH_2CH_2	H	H	TBDPSO	$\text{BF}_3 \cdot \text{OEt}_2$	52
7	e	H	H	H	TBDPSO	$\text{BF}_3 \cdot \text{OEt}_2$	50
8	f	H	H	TBDPSO	H	$\text{BF}_3 \cdot \text{OEt}_2$	57

^a Stoichiometric amount. ^b Isolated yield. ^c Saturated oxirane was isolated as a product. ^d **4c,d** were prepared by MCPBA epoxidation of the corresponding allylic alcohol; see the experimental section.

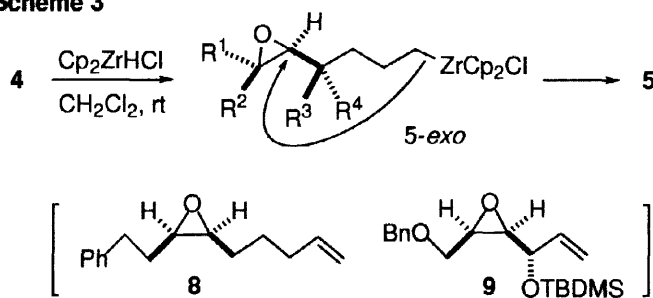
Without the use of an additive, the sole event observed was the reduction of the double bond of **4a** and the cyclization did not take place (entry 1). The intramolecular nucleophilic attack of the alkylzirconocene intermediate to the oxirane ring was accelerated by adding a silver salt or $\text{BF}_3 \cdot \text{OEt}_2$. Although we must await the precise reactive species of zirconocene compound in these reactions, the role of the additives could involve both the activation of oxirane ring and the formation of cationic species of zirconocene compound. Among the silver salts examined, a modest amount of the product was isolated by the addition of AgClO_4 (entry 2).⁶ The yield of the product was improved by the addition of a stoichiometric amount of $\text{BF}_3 \cdot \text{OEt}_2$. The reactions of diastereomeric alkenyloxiranes (**4c,d**) which possess a chiral center at the aliphatic chain gave diastereomeric products **5c,d** respectively (entries 5 and 6). No other diastereomers were isolated from the reaction mixtures. The structures of **5c,d** were confirmed by the conversion to acetonides **6** and **7**, respectively, and the following analysis of coupling constants and the NOE of the diagnostic hydrogens of the acetonides **6** and **7** as described in Scheme 2. The acetonide **6** showed clear NOE correlations between one of two methyl groups and two hydrogens at 4 and 7a positions. The diastereomeric acetonide **7** showed the distinctive NOE correlations for both of the methyl groups – one methyl group correlates with hydrogen at position 4 and the other methyl group correlates with angular hydrogen at position 7a. In acetonide **7**, a further obvious correlation between two hydrogens at 4a and 7a positions was also observed in the NOESY spectrum. The NOE data and the coupling constants unambiguously indicate the stereostructure of **6** and **7**, and confirmed the structures of **5c** and **5d**.

Scheme 2



The stereospecific formation of **5c,d** indicates that the mode of the intramolecular cyclization of alkylzirconocene to the oxirane ring proceeds through an inversion of the configuration at the reacting oxirane center as the ring opening of the Lewis acid-activated oxirane by nucleophiles. In all cases examined, the 5-*exo* cyclization mode to oxirane has been observed and no six-membered ring formation based on the 6-*endo* cyclization was observed. The attempted reaction of alkenyloxiranes **8** and **9** with Cp₂ZrHCl failed to yield six- or four-membered ring compounds (Scheme 3).

Scheme 3



During our efforts for the chemoselective hydrosilylation and the following cyclization of alkenyloxiranes, vinyloxirane **10**, which has no methylene tether, was found to give cyclopropylmethanol derivatives **11** in good yields. It is worth mentioning that, in the reactions of **10**, the intramolecular cyclization to **11** efficiently proceeds without using any additives (Scheme 4). The direct formation of cyclopropylmethanol **11** by the reaction of **10** with Cp_2ZrHCl is considered to be a result of the kinetically favored formation of the cyclopropyl ring.⁷ The results are listed in Table 2.

Scheme 4

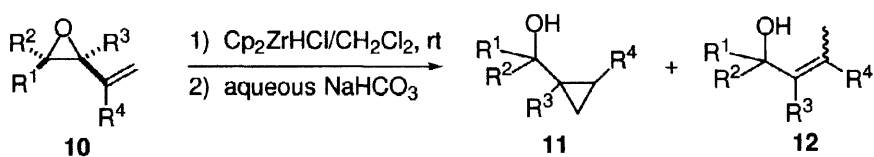
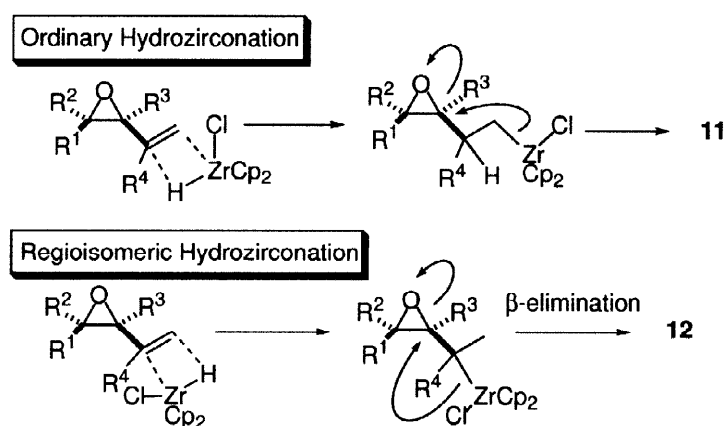


Table 2. Reactions of Vinyl Oxiranes 10

Entry	Substrates	R ¹	R ²	R ³	R ⁴	Yields (%) ^a	
						11	12
1	<i>cis</i> -10a	PhCH ₂ CH ₂	H	H	H	72	18 (Z only)
2	<i>trans</i> -10a	H	PhCH ₂ CH ₂	H	H	59	15 (Z only)
3	10b	BnOCH ₂	H	H	H	52	22 <i>E/Z</i> = 1/7.3 ^b
4	10c	H	PhCH ₂ CH ₂	CH ₃	H	76	2 <i>E/Z</i> = 1/1.9
5	10d	Ph	H	H	H	75	11 <i>E/Z</i> = 1/2.0
6	10e	H	Ph	CH ₃	H	70	5 <i>E/Z</i> = 1/5.1
7	<i>cis</i> -10f	PhCH ₂ CH ₂	H	H	CH ₃	98	—
8	<i>trans</i> -10f	H	PhCH ₂ CH ₂	H	CH ₃	75	—

^a Isolated yield. ^b Ratio has been determined by ¹H NMR.

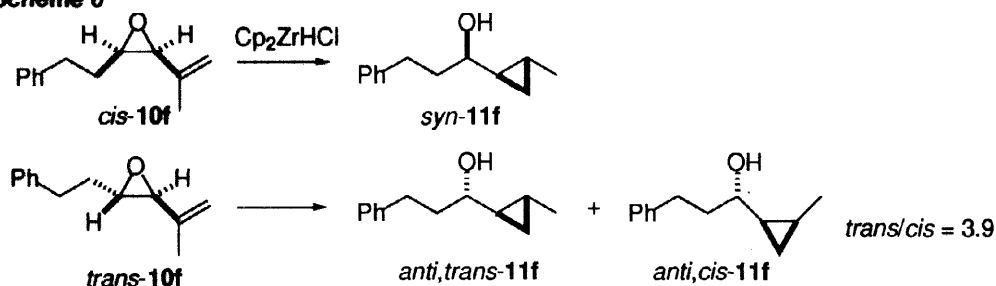
In the reactions of 10a~f (R₄ = H), allylic alcohol 12 was isolated as a by-product (entries 1~6). The formation of the by-products 12 is considered to be a result of the regioisomeric hydrozirconation product of vinyl oxiranes since the regioisomeric hydrozirconation results in the facile β-elimination of the carbon-oxygen bond to give allylic alcohol 12 as a side-product (Scheme 5). It has been reported that the hydrozirconation of olefins gives the terminal zirconocene compound under the thermodynamically equilibrated conditions, and the regioselectivity is affected by the presence of an oxygen function at the allylic position or an aromatic ring under the kinetic conditions.⁸ Thus, in the reactions of 10a~e (entries 1 ~ 6, Table 2), it is considered that the epoxide function causes the regioisomeric hydrozirconation followed by β-elimination to give allylic alcohols 12 under the kinetic conditions or the equilibrium nature of hydrozirconation might responsible for giving allylic alcohols 12 through the β-elimination of the less favored internal zirconocene isomer under the thermodynamic conditions (Scheme 5).⁹ Thus, the nonexistence of 12 as a side-product in the reaction of 10f indicates the perfect regiocontrol in the hydrozirconation of *cis*- and *trans*-10f, in which a methyl substituent on the double bond strongly forces the zirconation to the terminal position.

Scheme 5

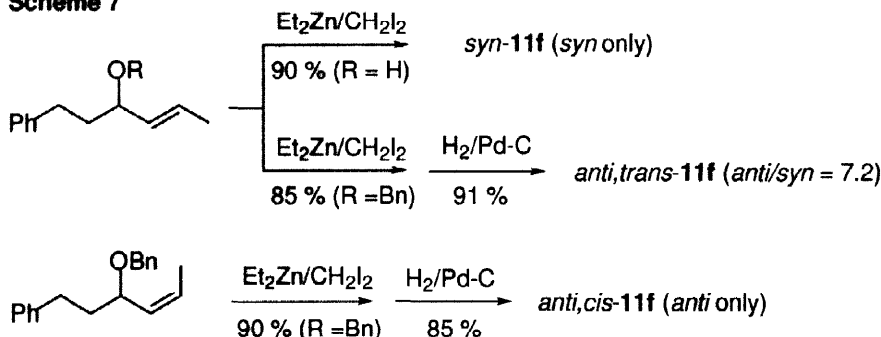
More importantly, *cis*-10f and *trans*-10f gave stereospecifically *syn*-11f and *anti*-11f, respectively. On the stereoselectivity of the substituents on the cyclopropyl ring, in the formation of *syn*-11f from *cis*-10f shows a perfect *trans* stereoselectivity, while in the formation of *anti*-11f from *trans*-10f, poor *trans* selectivity (3.9) was observed (Scheme 6). The stereochemistry of the products 11f was confirmed by

comparing with the authentic samples prepared by the well-established diastereoselective Simmons-Smith reaction of the allylic alcohol derivatives (Scheme 7).¹⁰

Scheme 6



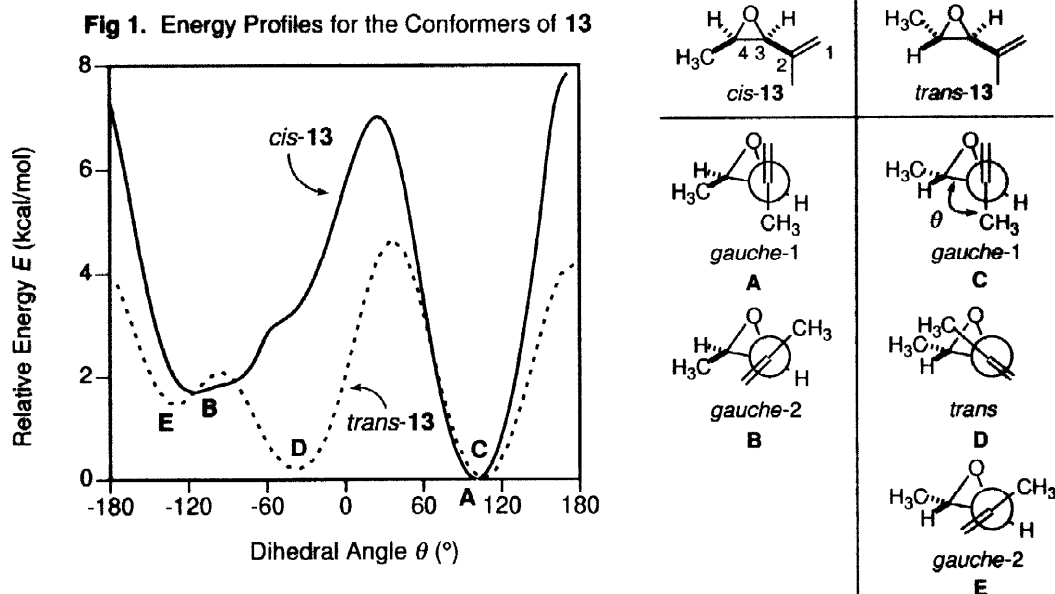
Scheme 7



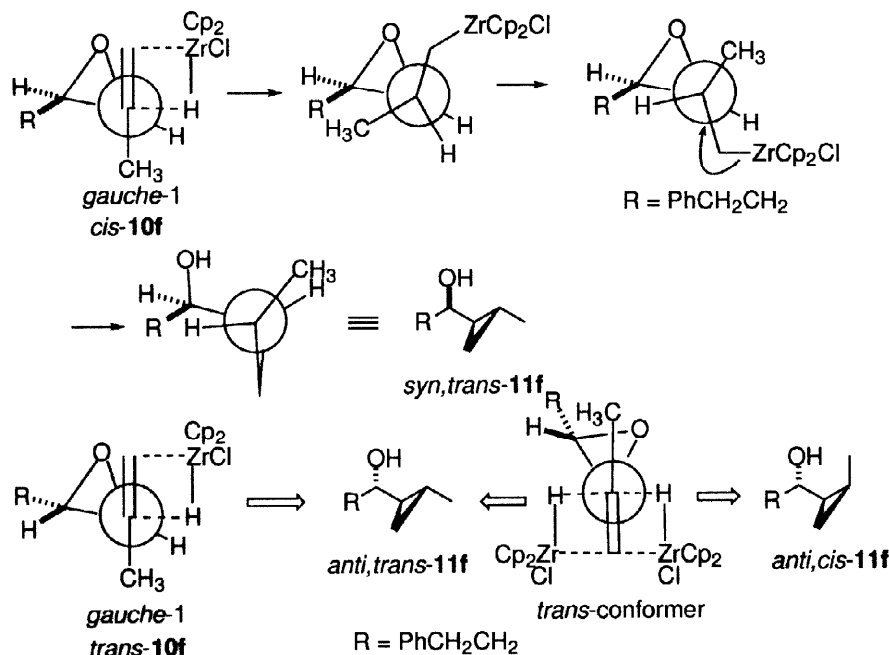
The stereospecific formation (*syn*- or *anti*-) of cyclopropylmethanols **11f** indicates that the cyclopropane formation from the hydrozirconated intermediate proceeds through an inversion of the configuration at the reacting oxirane carbon as described in the formations of **5**. The *trans*- or *cis*-stereoselectivity of substituents in the cyclopropyl ring is related to the diastereoselectivity of the hydrozirconation process to vinyl oxiranes **10f**.¹¹ Thus, the diastereoselectivity of the hydrozirconation for *cis*-**10f** is 100% and that for the *trans*-**10f** is about 80%. Although the actual molecularity of Cp_2ZrHCl in an organic solvent is not clear,^{1a} it has been theoretically suggested that the transition state for the hydrozirconation of olefin with Cp_2ZrHCl is reactant-like and has a very low activation energy.¹² Because of the early transition state, factors that influence the ground state conformation of **10f** would also be expected to influence the transition state in the hydrozirconation reaction.¹³

Energy calculation of each conformer of model compounds *cis*-**13** and *trans*-**13** was performed by *ab initio* calculation using 6-31G⁺ by rotating a vinyl group around an axis through a C₂-C₃ single bond of **13** by 10 degrees. Survey of the energy profile of each isomer indicates the presence of two energy minima for *cis*-**13** and three energy minima for *trans*-**13**, respectively (Fig 1). Of the two energy minima of *cis*-**13**, the lower energy minimum is estimated to be *gauche*-1 conformer **A**, which is 1.7 kcal/mol more stable than *gauche*-2 conformer **B**. In the *trans*-**13**, *gauche*-1 conformer **C** is estimated to be more stable than *trans* and *gauche*-2 conformers (**D** and **E**) by 0.2 and 1.47 kcal/mol, respectively.¹⁴ Thus, conformer **A** for *cis*-**13** and conformers **C/D** for *trans*-**13** would be the important conformers for the transition state of the hydrozirconation to *cis*- and *trans*-vinyl oxiranes **13**, respectively. According to the data of the conformational analyses for the model compounds **13**, we postulated the analogous conformers of *cis*- and *trans*-**10f** in the transition state of hydrozirconation, respectively. Taking into consideration the steric effect during the approach of the Cp_2ZrHCl to the more accessible conformers in the transition state and the inversion of the configuration at the reacting site of the oxirane ring, the exclusive formation of *syn,trans*-**11f** from *cis*-**10f** can be rationalized by the approach of Cp_2ZrHCl from the sterically less crowded site of *gauche*-1 conformer of *cis*-**10f** and the subsequent cyclopropane ring formation as shown in Scheme 8. In the reaction of *trans*-**10f**, one of the two energetically compatible isomers, *gauche*-1 conformer, would be expected to give a *trans*-compound (*anti,trans*-**11f**) by the approach of Cp_2ZrHCl from the less sterically

crowded site and the subsequent cyclization. The other isomer, *trans*-conformer, would be considered to yield *cis*- and *trans*-isomers (*anti,cis*-11f and *anti,trans*-11f, respectively) because of the sterically comparable approach of Cp_2ZrHCl from both sides of the *trans*-conformer of *trans*-10f in the transition state. Although the prediction of the hydrozirconation diastereoselectivity discussed in the present paper is based on the argument of the vinyloxirane ground state, the early transition state – reactant-like transition state – implied in the hydrozirconation makes the present discussion of vinyloxiranes reasonable.¹³

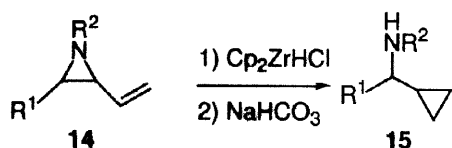


Scheme 8



As in the reaction of vinyloxirane derivatives **10**, the conversion of vinylaziridine derivatives **14** with Cp_2ZrHCl to (cyclopropylmethyl)amine **15** was also effected in good yields (Scheme 9). The substituent of the aziridine nitrogen was restricted to an alkyl or benzyl group since the reaction of *N*-Ts vinylaziridine with Cp_2ZrHCl failed to yield the cyclopropyl compound.

Scheme 9



Substrate	R ¹	R ²	Yield (%) ^a
a	H	Bn	86
b^b	CH ₃	Bn	71
c^c	PhCH ₂ CH ₂	cyC ₆ H ₁₁	82

^a Isolated yield. ^b *cis*-Isomer. ^c A mixture of *cis*- and *trans*-isomers.

The procedure described in this article provides for an alternative possibility for the synthesis of a cycloalkylmethanol or (cycloalkylmethyl)amine from an oxiranyl or aziridino olefin through a hydrozirconation procedure. Especially, the very facile, highly stereospecific and selective formation of the substituted cyclopropylmethanol which is normally prepared by the diastereo- or enantioselective Simmons-Smith cyclopropanation¹⁰ of allylic alcohols, has opened a new possibility in organic synthesis.

Acknowledgment. Partial financial support from the Ministry of Education, Science and Culture of Japan [Grant-in-aid for Scientific Research] (No. 08672447).

Experimental Section

All nonaqueous reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions. Tetrahydrofuran (THF), diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl. Dichloromethane (CH₂Cl₂) was distilled from calcium hydride. Zirconocenylhydrochloride (Cp₂ZrHCl) was prepared by the method of Buchwald.^{2a,b} Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. NMR spectra were measured at 300 or 400 MHz for ¹H and 75.5 or 100.6 MHz for ¹³C. Fuji silycia silica gel BW-80S (60 – 200 mesh) was used for column chromatography and prepacked column CPS-223L-1 (Kusano Kagaku Kikai Works Co., Japan) was used for medium-pressure liquid chromatography (MPLC).

***cis*-2-(3-Butenyl)-3-(2-phenylethyl)oxirane (4a).** To a solution of (*Z*)-8-phenyl-1,5-octadiene (257 mg, 1.38 mmol) in CH₂Cl₂ cooled to 0 °C was added 3-chloroperoxybenzoic acid (70%, 340 mg, 1.38 mmol), and the resulting mixture was stirred for 2 h at 0 °C. The mixture was poured into aqueous Na₂SO₃ and extracted with Et₂O. The organic extracts were washed with NaHCO₃ and brine, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 10 : 1) gave **4a** (225 mg, 81%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.46 – 1.66 (m, 2 H), 1.81 – 1.89 (m, 2 H), 2.09 – 2.30 (m, 2 H), 2.70 – 3.01 (m, 4 H), 4.98 – 5.09 (m, 2 H), 5.83 (tdd, *J* = 6.0, 10.2, 17.1 Hz, 1 H), 7.18 – 7.33 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 27.2, 29.8, 30.7, 32.8, 56.6, 56.9, 115.2, 126.0, 128.40, 128.44, 137.6, 141.3; EIMS *m/z* 202 (*M*⁺); HRMS Calcd for C₁₄H₁₈O: 202.1358. Found: 202.1350.

***trans*-2-[(Benzyloxy)methyl]-3-(3-butenyl)oxirane (4b).** Experimental procedure was the same as the procedure described for **4a** (36% yield). ¹H NMR (300 MHz, CDCl₃) δ 1.61 – 1.75 (m, 2 H), 2.12 – 2.31 (m, 2 H), 2.84 – 2.88 (m, 1 H), 2.95 – 2.99 (m, 1 H), 3.47 (dd, *J* = 5.6, 11.4 Hz, 1 H), 3.72 (dd, *J* = 3.3, 11.4 Hz, 1 H), 4.55 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.98 – 5.10 (m, 2 H), 5.83 (tdd, *J* = 6.6, 10.2, 17.1 Hz, 1 H), 7.26 – 7.36 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 30.1, 31.0, 55.5, 57.1, 70.3, 73.2, 115.2, 127.7, 128.4, 137.5, 137.9; CIMS *m/z* 219 (*M*⁺ + 1).

(2*S, 3*R**)-2-[(1*S**)-(*tert*-Butyldimethylsilyl)oxy]-3-butenyl}-3-(2-phenylethyl)-oxirane (4c).** i) To a solution of (*E*)-8-phenyl-1,5-octadien-4-ol (1.37 g, 6.8 mmol) in CH₂Cl₂ (30 ml) cooled to 0 °C was added 3-chloroperoxybenzoic acid (70%, 1.67 g, 6.8 mmol), and the resulting mixture was stirred for 2.5 h at 0 °C. The mixture was poured into aqueous Na₂SO₃ and extracted with Et₂O. The organic extracts were washed with NaHCO₃ and brine, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 6 : 1 → 4 : 1 → 3 : 1) followed by MPLC (hexane : EtOAc = 5 : 1) gave (1*S**)-1-[(2*R**, 3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-

buten-1-ol (more polar, 719 mg, 49%) and (1*R**)-1-[(2*R**,3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-buten-1-ol (less polar, 406 mg, 27%).

(1*S**)-1-[(2*R**,3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-buten-1-ol: ¹H NMR (400 MHz, CDCl₃) δ 1.86–1.92 (m, 2 H), 1.94 (bs, 1 H), 2.28–2.37 (m, 2 H), 2.69–2.85 (m, 3 H), 2.96 (dt, *J* = 2.3, 5.8 Hz, 4 H), 3.50–3.55 (m, 1 H), 5.12–5.17 (m, 2 H), 5.81 (tdd, *J* = 7.1, 10.2, 17.0 Hz, 1 H), 7.19–7.30 (m, 5 H); ¹³C NMR (100.6 MHz, CDCl₃) δ 32.1, 33.3, 39.0, 56.0, 61.3, 70.0, 118.3, 126.1, 128.3, 128.5, 133.5, 141.0; IR (neat) ν 3443 (br), 2928, 1454 cm⁻¹; CIMS *m/z* 219 (*M*⁺ + 1).

(1*R**)-1-[(2*R**,3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-buten-1-ol: ¹H NMR (400 MHz, CDCl₃) δ 1.85–1.95 (m, 3 H), 2.21–2.36 (m, 2 H), 2.70–2.87 (m, 3 H), 3.03 (dt, *J* = 2.2, 5.8 Hz, 1 H), 3.76 (m, 1 H), 5.12–5.17 (m, 2 H), 5.83 (tdd, *J* = 7.1, 10.2, 17.0 Hz, 1 H), 7.19–7.35 (m, 5 H); ¹³C NMR (100.6 MHz, CDCl₃) δ 32.2, 33.2, 38.0, 54.9, 60.6, 68.3, 118.1, 126.1, 128.3, 128.5, 133.6, 141.0; IR (neat) ν 3445 (br), 2928, 2361 cm⁻¹; CIMS *m/z* 219 (*M*⁺ + 1).

ii) To a solution of (1*S**)-1-[(2*R**,3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-buten-1-ol (390 mg, 1.79 mmol) in *N,N*-dimethylformamide (DMF, 5 ml) cooled to 0 °C were added imidazole (243 mg, 3.57 mmol) and *tert*-butylchlorodimethylsilane (404 mg, 2.68 mmol), and the resulting mixture was stirred for 12 h at room temperature. The mixture was poured into HCl (1 M) and extracted with Et₂O. The organic extracts were washed with water, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 20 : 1 → 15 : 1) gave **4c** (594 mg, quant) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.90 (s, 9 H), 1.83–1.90 (m, 2 H), 2.23–2.27 (m, 2 H), 2.67–2.86 (m, 4 H), 3.35 (dt, *J* = 6.4, 6.4 Hz, 1 H), 5.04–5.10 (m, 2 H), 5.79 (tdd, *J* = 7.2, 10.2, 17.0 Hz, 1 H), 7.18–7.32 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ -4.9, -4.4, 18.2, 25.8, 32.2, 33.5, 39.7, 56.0, 62.2, 73.6, 117.3, 126.0, 128.3, 128.5, 134.2, 141.1; CIMS *m/z* 333 (*M*⁺ + 1); Anal. Calcd for C₂₀H₃₂O₂Si: C, 72.23; H, 9.70. Found: C, 71.95; H, 9.69.

(2*S**,3*R**)-2-[[[(1*R**)-1-(*tert*-Butyldiphenylsilyl)oxy]-3-butenyl]-3-(2-phenylethyl)oxirane (**4d**). To a solution of (1*R**)-1-[(2*R**,3*R**)-3-(2-phenylethyl)oxiran-2-yl]-3-buten-1-ol (301 mg, 1.38 mmol) in DMF (5 ml) cooled to 0 °C were added imidazole (188 mg, 2.76 mmol) and *tert*-butylchlorodiphenylsilane (0.54 ml, 2.08 mmol), and the resulting mixture was stirred for 12 h at room temperature. The mixture was poured into HCl (1 M) and extracted with Et₂O. The organic extracts were washed with water, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : Et₂O = 20 : 1 → 10 : 1) gave **4d** (433 mg, 69%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.06 (s, 9 H), 1.41–1.53 (m, 1 H), 1.61–1.72 (m, 1 H), 2.28–2.41 (m, 3 H), 2.46–2.67 (m, 2 H), 2.76 (dd, *J* = 1.6, 6.5 Hz, 1 H), 3.47 (dt, *J* = 5.7, 5.7 Hz, 1 H), 5.06–5.11 (m, 2 H), 5.84–5.97 (m, 1 H), 7.09–7.47 (m, 11 H), 7.63–7.71 (m, 4 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 19.3, 26.9, 32.0, 33.2, 39.7, 57.4, 60.1, 72.7, 117.6, 125.9, 127.56, 127.62, 128.3, 128.4, 129.7, 129.8, 133.5, 133.7, 133.8, 135.9, 141.2; CIMS *m/z* 457 (*M*⁺ + 1); Anal. Calcd for C₃₀H₃₆O₂Si: C, 78.90; H, 7.95. Found: C, 78.84; H, 8.19.

(2*R**)-[[[(1*S**)-1-(*tert*-Butyldiphenylsilyl)oxy]-3-butenyl]oxirane (**4e**). Experimental procedure was the same as the procedure described in literature.¹⁵ [α]_D²⁷ = +37.4 ° (*c* = 1.16, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 1.16 (s, 9 H), 2.15 (dd, *J* = 2.7, 5.2 Hz, 1 H), 2.29–2.44 (m, 2 H), 2.47 (dd, *J* = 3.9, 5.2 Hz, 1 H), 2.91 (ddd, *J* = 2.7, 3.9, 6.1 Hz, 1 H), 3.48 (dt, *J* = 6.1, 5.5 Hz, 1 H), 5.05–5.11 (m, 2 H), 5.82–5.96 (m, 1 H), 7.35–7.47 (m, 6 H), 7.66–7.72 (m, 4 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 19.4, 26.9, 39.8, 46.2, 53.9, 72.8, 117.6, 127.5, 127.6, 129.7, 129.8, 133.7, 135.9; CIMS *m/z* 353 (*M*⁺ + 1).

(2*R**)-[[[(1*R**)-1-(*tert*-Butyldiphenylsilyl)oxy]-3-butenyl]oxirane (**4f**). Experimental procedure was the same as the procedure described for **4e**. [α]_D²⁷ = -17.8 ° (*c* = 1.57, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 1.10 (s, 9 H), 2.17–2.37 (m, 2 H), 2.48 (dd, *J* = 2.7, 4.9 Hz, 1 H), 2.72 (dd, *J* = 4.1, 4.9 Hz, 1 H), 3.07 (ddd, *J* = 2.7, 4.1, 6.5 Hz, 1 H), 3.43 (ddd, *J* = 5.2, 6.5, 6.5 Hz, 1 H), 4.92–4.99 (m, 2 H), 5.71 (tdd, *J* = 7.2, 10.6, 16.5 Hz, 1 H), 7.35–7.46 (m, 6 H), 7.70–7.74 (m, 4 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 19.4, 27.0, 39.5, 44.9, 55.3, 74.6, 117.5, 127.4, 127.5, 129.6, 133.6, 135.9; CIMS *m/z* 353 (*M*⁺ + 1).

General Procedure for the Formation of Cyclopentylmethanols. To a suspension of zirconocenehydrochloride (96 mg, 0.37 mmol) in CH₂Cl₂ (3 ml) was added a solution of **4a** (50 mg, 0.25

mmol) in CH_2Cl_2 (3 ml), and the resulting mixture was stirred for 30 min at room temperature in the dark. While cooling to 0 °C, boron trifluoride etherate ($\text{BF}_3 \cdot \text{OEt}_2$, freshly distilled, 0.03 ml, 0.25 mmol) was added and the mixture was stirred for 2 h at room temperature. After quenching with aqueous NaHCO_3 , the mixture was extracted with Et_2O . The organic extracts were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 15 : 1 $\rightarrow$ 10 : 1) gave **5a** (39 mg, 77%) as a colorless oil. **1-Cyclopentyl-3-phenyl-1-propanol (5a)**: ^1H NMR (300 MHz, CDCl_3) δ 1.16–1.26 (m, 1 H), 1.28–1.40 (m, 1 H), 1.44 (bs, 1 H), 1.47–1.98 (m, 9 H), 2.68 (ddd, J = 6.7, 9.7, 13.7 Hz, 1 H), 2.86 (ddd, J = 5.2, 9.9, 13.7 Hz, 1 H), 3.40–3.47 (m, 1 H), 7.17–7.32 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 25.6, 25.7, 28.6, 29.1, 32.2, 37.9, 46.5, 75.4, 125.7, 128.35, 128.42, 142.4; IR (neat) ν 3373 (br), 2949, 2866 cm^{-1} ; EIMS m/z 204 (M^+); Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 82.30; H, 9.87. Found: C, 82.00; H, 10.16.

2-(Benzyloxy)-1-cyclopentyl-1-ethanol (5b). ^1H NMR (300 MHz, CDCl_3) δ 1.16–1.23 (m, 1 H), 1.40–1.65 (m, 6 H), 1.77–1.93 (m, 2 H), 2.44 (bd, J = 3.1 Hz, 1 H), 3.36 (dd, J = 7.9, 9.4 Hz, 1 H), 3.55–3.65 (m, 2 H), 4.56 (s, 2 H), 7.26–7.39 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 25.4, 25.6, 28.8, 28.9, 42.5, 73.3, 74.0, 74.5, 127.66, 127.71, 128.4, 138.0; IR (neat) ν 3448 (br), 2951, 2865 cm^{-1} ; EIMS m/z 220 (M^+); HRMS Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2$: 220.1463. Found: 220.1457.

{(1S,2S)-2-[(*tert*-Butyldiphenylsilyl)oxy]cyclopentyl} methanol (5e). $[\alpha]_{\text{D}}^{27} = +17.9^\circ$ (c = 0.75, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 1.08 (s, 9 H), 1.29–1.76 (m, 6 H), 2.00–2.11 (m, 1 H), 2.45 (t, J = 6.0 Hz, 1 H), 3.69–3.85 (m, 2 H), 4.40 (dt, J = 5.5, 5.5 Hz, 1 H), 7.36–7.48 (m, 6 H), 7.67–7.72 (m, 4 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 19.2, 21.5, 25.7, 27.0, 34.4, 45.5, 63.6, 77.6, 127.6, 127.7, 129.8, 133.4, 134.1, 135.8, 135.9.

{(1S,2R)-2-[(*tert*-Butyldiphenylsilyl)oxy]cyclopentyl} methanol (5f). $[\alpha]_{\text{D}}^{27} = -11.9^\circ$ (c = 0.91, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 1.06 (s, 9 H), 1.12–1.27 (m, 2 H), 1.41–1.90 (m, 5 H), 2.01–2.12 (m, 1 H), 3.35 (bd, J = 5.3 Hz, 2 H), 4.02 (dt, J = 5.5, 5.5 Hz, 1 H), 7.35–7.46 (m, 6 H), 7.66–7.71 (m, 4 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 19.1, 21.8, 25.9, 27.0, 34.7, 50.4, 65.0, 77.6, 127.5, 127.6, 129.6, 129.7, 134.2, 134.4, 135.8. The title compound was converted to the known material, (1R,2S)-2-(hydroxymethyl)cyclopentan-1-ol: $[\alpha]_{\text{D}}^{25} = -22.7^\circ$ (c = 0.73, CHCl_3) {lit.¹⁶ $[\alpha]_{\text{D}}^{23} = -13.7^\circ$ (c = 1.0, CHCl_3)}.

(4S*,4aS*,7aR*)-2,2-dimethyl-4-(2-phenylethyl)perhydrocyclopenta[d][1,3]-dioxine (6). To a solution of cyclopentylmethanol **5c** (50 mg, 0.15 mmol) in THF (2 ml) was added tetrabutylammonium fluoride (1.0 M in THF, 0.3 ml, 0.30 mmol), and the resulting mixture was stirred for 12 h at room temperature. The mixture was poured into water and extracted with EtOAc . The organic extracts were dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. The crude oil was dissolved in DMF (3 ml) and the solution was treated with 2,2-dimethoxypropane (2 ml) and *p*-toluenesulfonic acid (catalytic). After being stirred for 24 h at room temperature, the mixture was poured into aqueous NaHCO_3 and extracted with Et_2O . The organic extracts were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 10 : 1) gave acetone **6** (33 mg, 86%, 2 steps) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.01–1.17 (m, 1 H), 1.24–1.37 (m, 1 H), 1.41–1.74 (m, 4 H), 1.45 (s, 3 H), 1.48 (s, 3 H), 1.75–1.82 (m, 2 H), 1.87–1.95 (m, 1 H), 2.66 (td, J = 8.2, 13.6 Hz, 1 H), 2.80 (td, J = 7.4, 13.6 Hz, 1 H), 3.52 (ddd, J = 6.8, 10.5, 10.5 Hz, 1 H), 3.61 (td, J = 5.8, 9.9 Hz, 1 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 18.4, 20.4, 22.4, 29.1, 30.1, 31.1, 36.4, 47.3, 75.0, 75.5, 99.8, 125.7, 128.2, 128.6, 142.3; EIMS m/z 260 (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: C, 78.42; H, 9.29. Found: C, 78.18; H, 9.52.

(4S*,4aS*,7aS*)-2,2-dimethyl-4-(2-phenylethyl)perhydrocyclopenta[d][1,3]dioxine (7). The title compound was derived from product **5d** as the procedure described for **6**. ^1H NMR (300 MHz, CDCl_3) δ 1.24–1.31 (m, 1 H), 1.33 (s, 3 H), 1.40 (s, 3 H), 1.41–1.51 (m, 1 H), 1.56–1.92 (m, 6 H), 1.92–2.02 (m, 1 H), 2.60 (ddd, J = 7.1, 9.3, 14.0 Hz, 1 H), 2.87 (ddd, J = 5.2, 9.5, 14.0 Hz, 1 H), 3.34 (ddd, J = 3.2, 9.6, 9.6 Hz, 1 H), 4.23 (dt, J = 2.8, 6.3 Hz, 1 H), 7.15–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 24.3, 24.4, 25.4, 28.9, 32.1, 33.9, 36.4, 47.8, 71.6, 72.4, 99.5, 125.7, 128.3, 128.4, 142.3; EIMS m/z 260 (M^+); Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: C, 78.42; H, 9.29. Found: C, 78.02; H, 9.49.

Preparation of vinyloxiranes 10a ~ f

Compounds *cis*-/*trans*-10a, 10c, 10d, 10e and *cis*-10f were known compounds.¹⁷

***cis*-2-[(Benzyloxy)methyl]-3-vinyloxirane (10b).** To a suspension of methyltriphenylphosphonium bromide (5.5 g, 15.4 mmol) in THF (30 ml) cooled to 0 °C was added butyllithium (1.54 M in hexane, 10.0 ml, 15.4 mmol), and the resulting mixture was stirred for 1 h at 0 °C. A solution of *cis*-3-[(benzyloxy)methyl]-2-oxiranecarbaldehyde¹⁸ (1.97 g, 10.2 mmol) in THF (10 ml) was added at 0 °C and the mixture was stirred at room temperature for 12 h. After quenching with aqueous NH₄Cl, the mixture was extracted with Et₂O. The organic extracts were washed with brine, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 20 : 1 → 15 : 1) gave **10b** (362 mg, 19%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 3.36 (ddd, *J* = 4.4, 4.4, 6.3 Hz, 1 H), 3.49 (dd, *J* = 4.4, 6.9 Hz, 1 H), 3.57 (dd, *J* = 6.3, 11.3 Hz, 1 H), 3.68 (dd, *J* = 4.4, 11.3 Hz, 1 H), 4.54 (d, *J* = 11.8 Hz, 1 H), 4.63 (d, *J* = 11.8 Hz, 1 H), 5.33–5.37 (m, 1 H), 5.46–5.52 (m, 1 H), 5.68 (ddd, *J* = 6.9, 10.4, 17.0 Hz, 1 H), 7.26–7.36 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 56.1, 56.8, 67.9, 73.2, 120.9, 127.8, 128.4, 131.8, 137.8; CIMS *m/z* 191 (*M*⁺ + 1); Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.64; H, 7.38.

***trans*-2-isopropenyl-3-(2-phenylethyl)oxirane (*trans*-10f).** To a mixture of methyltriphenylphosphonium bromide (3.10 g, 8.7 mmol) and *N,N*-diisopropylamine (1.3 ml, 9.9 mmol) in THF (20 ml) cooled to –23 °C was added butyllithium (1.47 M in hexane, 5.9 ml, 8.7 mmol), and the resulting mixture was stirred for 1 h at –23 °C. After additional stirring for 1 h at 0 °C, a solution of *trans*-1-[3-(2-phenylethyl)-2-oxiranyl]-1-ethanone (1.16 g, 6.1 mmol) in THF (5 ml) was added at 0 °C and the mixture was stirred at 0 °C for 1 h, and then stirred at room temperature for 1 h. After quenching with aqueous NH₄Cl, the mixture was extracted with Et₂O. The organic extracts were washed with brine, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 30 : 1 → 20 : 1) gave ***trans*-10f** (565 mg, 58%) as a colorless oil. ¹H NMR (300 MHz, CDCl₃) δ 1.60 (s, 3 H), 1.82–1.99 (m, 2 H), 2.69–2.87 (m, 2 H), 2.92 (ddd, *J* = 2.1, 5.7, 5.7 Hz, 1 H), 3.08 (d, *J* = 2.1 Hz, 1 H), 4.94–4.96 (m, 1 H), 5.06 (s, 1 H), 7.18–7.32 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 16.9, 32.2, 33.9, 57.8, 60.9, 113.8, 126.0, 128.35, 128.44, 141.2, 141.4; EIMS *m/z* 188 (*M*⁺); HRMS Calcd for C₁₃H₁₆O: 188.1207. Found: 188.1201.

General Procedure for the Hydrozirconation of Vinyloxiranes 10. To a suspension of zirconocenehydrochloride (222 mg, 0.86 mmol) in CH₂Cl₂ (3 ml) was added a solution of **10a** (100 mg, 0.57 mmol) in CH₂Cl₂ (3 ml), and the resulting mixture was stirred for 2 h at room temperature in the dark. After quenching with aqueous NaHCO₃ at 0 °C, the mixture was extracted with Et₂O. The organic extracts were washed with brine, dried (MgSO₄), filtered, and concentrated *in vacuo* to give a crude oil. Passing through a very short silica gel column (hexane : EtOAc = 5 : 1 → 3 : 1) gave a mixture of **11a** and **12a** (91 mg, 90%). The samples for analytical data were further purified by MPLC (hexane : Et₂O = 3 : 1). **1-Cyclopropyl-3-phenyl-1-propanol (11a):** ¹H NMR (300 MHz, CDCl₃) δ 0.17–0.31 (m, 2 H), 0.46–0.59 (m, 2 H), 0.89–1.01 (m, 1 H), 1.57 (bs, 1 H), 1.90–1.97 (m, 2 H), 2.68–2.93 (m, 3 H), 7.15–7.32 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 2.6, 2.7, 18.0, 32.0, 38.7, 76.2, 125.7, 128.3, 128.4, 142.2; IR (neat) ν 3385 (br), 1042, 700 cm^{–1}; EIMS *m/z* 176 (*M*⁺); HRMS Calcd for C₁₂H₁₆O: 176.1201. Found: 176.1200. **(*Z*)-1-Phenyl-4-hexen-3-ol (12a):** ¹H NMR (300 MHz, CDCl₃) δ 1.40 (bs, 1 H), 1.65 (dd, *J* = 1.7, 6.8 Hz, 3 H), 1.71–1.83 (m, 1 H), 1.88–2.00 (m, 1 H), 2.61–2.77 (m, 2 H), 4.46–4.53 (m, 1 H), 5.46 (qdd, *J* = 1.7, 8.8, 10.9 Hz, 1 H), 5.56–5.66 (m, 1 H), 7.16–7.31 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 13.4, 31.7, 38.9, 66.8, 125.8, 126.7, 128.3, 128.4, 133.2, 141.9; IR (neat) ν 3359 (br), 2924, 699 cm^{–1}; EIMS *m/z* 176 (*M*⁺); HRMS Calcd for C₁₂H₁₆O: 176.1201. Found: 176.1211.

2-(Benzyloxy)-1-cyclopropyl-1-ethanol (11b): ¹H NMR (300 MHz, CDCl₃) δ 0.17–0.25 (m, 1 H), 0.34–0.60 (m, 3 H), 0.87 (tdt, *J* = 4.9, 8.2, 8.2 Hz, 1 H), 2.37 (bs, 1 H), 3.09–3.16 (m, 1 H), 3.48 (dd, *J* = 8.0, 9.6 Hz, 1 H), 3.64 (dd, *J* = 3.0, 9.6 Hz, 1 H), 4.58 (s, 2 H), 7.26–7.39 (m, 5 H); ¹³C NMR (75.5 MHz, CDCl₃) δ 1.8, 2.5, 13.5, 73.3, 74.3, 75.1, 127.70, 127.74, 128.4, 138.0; IR (neat) ν 3423 (br), 1114, 1087 cm^{–1}; EIMS *m/z* 192 (*M*⁺); Anal. Calcd for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 74.74; H, 8.43.

1-(1-Methylcyclopropyl)-3-phenyl-1-propanol (11c): ¹H NMR (300 MHz, CDCl₃) δ 0.29

–0.40 (m, 4 H), 1.06 (s, 3 H), 1.50 (bs, 1 H), 1.80–1.98 (m, 2 H), 2.66 (ddd, $J = 7.1, 9.4, 13.9$ Hz, 1 H), 2.77–2.89 (m, 2 H), 7.16–7.32 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.2, 12.0, 17.2, 20.7, 32.6, 35.8, 78.4, 125.7, 128.3, 142.2; IR (neat) ν 3423 (br), 2953, 1042 cm^{-1} ; EIMS m/z 190 (M^+); HRMS Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: 190.1358. Found: 190.1359.

(Z)-4-Methyl-1-phenyl-4-hexen-3-ol (Z-12c): ^1H NMR (300 MHz, CDCl_3) δ 1.35–1.37 (m, 1 H), 1.57 (dd, $J = 1.5, 7.0$ Hz, 3 H), 1.72 (s, 3 H), 1.74–1.84 (m, 1 H), 1.99 (dddd, $J = 6.0, 7.6, 9.6, 13.5$ Hz, 1 H), 2.60 (ddd, $J = 6.2, 9.6, 13.9$ Hz, 1 H), 2.70 (ddd, $J = 6.0, 10.0, 13.9$ Hz, 1 H), 4.59–4.65 (m, 1 H), 5.32–5.40 (m, 1 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 12.9, 17.3, 32.0, 36.3, 68.7, 122.1, 125.8, 128.3, 137.0, 141.9; IR (neat) ν 3368 (br), 2942, 1454 cm^{-1} ; EIMS m/z 190 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.95; H, 9.43.

(E)-4-Methyl-1-phenyl-4-hexen-3-ol (E-12c): ^1H NMR (300 MHz, CDCl_3) δ 1.40 (m, 1 H), 1.62 (s, 3 H), 1.63 (d, $J = 5.2$ Hz, 3 H), 1.77–1.95 (m, 2 H), 2.53–2.73 (m, 2 H), 4.03 (ddd, $J = 3.4, 6.7, 6.7$ Hz, 1 H), 5.48–5.50 (m, 1 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 10.9, 13.1, 32.2, 36.4, 77.4, 121.2, 125.7, 128.3, 128.4, 137.7, 142.1; IR (neat) ν 3358 (br), 2937, 1454 cm^{-1} ; EIMS m/z 190 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.82; H, 9.44.

(1-Methylcyclopropyl)(phenyl)methanol (11e): ^1H NMR (300 MHz, CDCl_3) δ 0.35–0.46 (m, 2 H), 0.59–0.65 (m, 1 H), 0.69–0.75 (m, 1 H), 0.95 (s, 3 H), 1.89 (bs, 1 H), 4.19 (s, 1 H), 7.25–7.41 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 11.1, 11.5, 18.3, 21.8, 79.8, 126.2, 127.2, 128.0, 142.5; IR (neat) ν 3400 (br), 1026, 700 cm^{-1} ; EIMS m/z 162 (M^+); HRMS Calcd for $\text{C}_{11}\text{H}_{14}\text{O}$: 162.1045. Found: 162.1051.

Compounds **12b**, **11d**, **12d** and **12e** were known compounds.¹⁹

Simmons-Smith Cyclopropanation

(1R*)-1-[(1R*,2R*)-2-methylcyclopropyl]-3-phenylpropan-1-ol (syn-11f). To a solution of (*E*)-1-phenyl-4-hexen-3-ol (350 mg, 2.0 mmol) in CH_2Cl_2 cooled to -10°C were added diethylzinc (1.0 M solution in hexane, 10.0 ml, 10.0 mmol) and diiodomethane (0.8 ml, 10.0 mmol), and the resulting mixture was stirred for 3 h while warming gradually to room temperature. After quenching with aqueous NH_4Cl on an ice bath, the mixture was diluted with Et_2O and 10% HCl followed by extracting with Et_2O . The organic extracts were washed with Na_2SO_3 , NaHCO_3 and brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : $\text{EtOAc} = 10 : 1 \rightarrow 5 : 1$) gave **syn-11f** (341 mg, 90%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.24–0.30 (m, 1 H), 0.42–0.48 (m, 1 H), 0.58–0.69 (m, 2 H), 1.05 (d, $J = 5.6$ Hz, 3 H), 1.54 (bs, 1 H), 1.86–2.02 (m, 2 H), 2.67–2.86 (m, 2 H), 2.89–2.96 (m, 1 H), 7.16–7.32 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 10.9, 11.1, 18.3, 26.9, 32.1, 38.9, 75.7, 125.7, 128.3, 124.2; IR (neat) ν 3374 (br), 2948, 2927 cm^{-1} ; EIMS m/z 190 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.81; H, 9.50.

(1S*)-1-[(1R*,2R*)-2-methylcyclopropyl]-3-phenylpropan-1-ol (anti,trans-11f). Cyclopropanation of (*E*)-4-(benzyloxy)-6-phenyl-2-hexene, which was the same as the procedure described for **syn-11f**, gave crude cyclopropane derivative in 85% yield. To a solution of the crude oil (150 mg) in methanol (1 ml) was added a catalytic amount of 10% Pd-C, and the resulting mixture was stirred vigorously under hydrogen atmosphere. After 3 days, the mixture was filtered and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : $\text{EtOAc} = 10 : 1 \rightarrow 5 : 1$) gave **anti,trans-11f** (*anti/syn* = 7.2, 93 mg, 91%) as a colorless oil. The analytical sample was purified by MPLC (CHCl_3 : $\text{Et}_2\text{O} = 15 : 1$). ^1H NMR (300 MHz, CDCl_3) δ 0.25–0.31 (m, 1 H), 0.33–0.39 (m, 1 H), 0.62–0.76 (m, 2 H), 1.06 (d, $J = 5.8$ Hz, 3 H), 1.51 (bs, 1 H), 1.85–1.93 (m, 2 H), 2.66–2.86 (m, 2 H), 2.92–2.98 (m, 1 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 10.7, 11.1, 18.7, 26.6, 32.0, 38.6, 75.7, 125.7, 128.30, 128.35, 142.3; IR (neat) ν 3387 (br), 2949, 2926 cm^{-1} ; EIMS m/z 190 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.79; H, 9.56.

(1S*)-1-[(1R*,2S*)-2-methylcyclopropyl]-3-phenylpropan-1-ol (anti,cis-11f). Experimental procedure was the same as the procedure described for **anti,trans-11f** (77% yield, 2 steps). ^1H NMR (300 MHz, CDCl_3) δ 0.01–0.06 (m, 1 H), 0.69–0.75 (m, 1 H), 0.87–1.00 (m, 2 H), 1.01 (d, $J = 5.4$ Hz, 3 H), 1.53 (bs, 1 H), 1.88–1.99 (m, 2 H), 2.67–2.77 (m, 1 H), 2.87 (ddd, $J = 6.3, 9.1, 13.8$ Hz, 1 H), 3.18–3.26 (m, 1 H), 7.16–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 10.3, 10.6,

13.8, 23.0, 31.9, 39.5, 72.0, 125.7, 128.3, 128.4, 142.3; IR (neat) ν 3386 (br), 2361, 1041 cm^{-1} ; EIMS m/z 190 (M^+); Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}$: C, 82.06; H, 9.53. Found: C, 81.71; H, 9.55.

1-Benzyl-2-vinylaziridine (14a). To a suspension of methyltriphenylphosphonium bromide (6.7 g, 18.7 mmol) in THF (40 ml) cooled to 0 °C was added potassium bis(trimethylsilyl)amide (0.5 M in toluene, 34.6 ml, 17.3 mmol), and the resulting mixture was stirred for 1 h at 0 °C. A solution of 1-benzyl-2-aziridinecarbaldehyde (2.32 g, 14.4 mmol) in THF (10 ml) was added at 0 °C and the mixture was stirred at room temperature for 12 h. After quenching with aqueous NH_4Cl , the mixture was extracted with EtOAc. The organic extracts were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 20 : 1 $\rightarrow$ 5 : 1) gave **14a** (773 mg, 34%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 1.55 (d, J = 6.4 Hz, 1 H), 1.77 (d, J = 3.4 Hz, 1 H), 1.92 – 1.96 (m, 1 H), 3.41 (d, J = 13.7 Hz, 1 H), 3.44 (d, J = 13.7 Hz, 1 H), 5.03 (dd, J = 1.3, 10.3 Hz, 1 H), 5.23 (dd, J = 1.3, 17.3 Hz, 1 H), 5.52 (ddd, J = 7.8, 10.3, 17.3 Hz, 1 H), 7.16 – 7.28 (m, 5 H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 35.3, 41.4, 64.4, 116.3, 126.9, 127.8, 128.3, 138.2, 139.0; EIMS m/z 159 (M^+); HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{N}$: 159.1048. Found: 159.1040.

cis-1-Benzyl-2-methyl-3-vinylaziridine (14b). Experimental procedure was the same as the procedure described for **14a** (81% yield). ^1H NMR (400 MHz, CDCl_3) δ 1.18 (d, J = 5.7 Hz, 3 H), 1.76 – 1.82 (m, 1 H), 2.05 – 2.08 (m, 1 H), 3.57 (s, 2 H), 5.20 (dd, J = 1.5, 10.5 Hz, 1 H), 5.33 (dd, J = 1.5, 17.2 Hz, 1 H), 5.70 (ddd, J = 7.7, 10.5, 17.2 Hz, 1 H), 7.23 – 7.35 (m, 5 H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 13.7, 41.0, 45.9, 64.3, 117.6, 126.8, 127.6, 128.3, 135.1, 139.3; EIMS m/z 158 ($\text{M}^+ - \text{CH}_3$); HRMS Calcd for $\text{C}_{11}\text{H}_{12}\text{N}$ ($\text{M}^+ - \text{CH}_3$): 158.0970. Found: 158.0971.

1-Cyclohexyl-2-(2-phenylethyl)-3-vinylaziridine (14c). To a mixture of allyl chloride (0.8 ml, 9.8 mmol) and diethylaluminum chloride (0.95 M in hexane, 19.6 ml, 20.6 mmol) cooled to –78 °C was added a solution of lithium 2,2,6,6-tetramethylpiperidide in THF [prepared from 2,2,6,6-tetramethylpiperidine (1.72 ml, 10.2 mmol), butyllithium (1.41 M in hexane, 6.92 ml, 9.8 mmol) and THF (15 ml)], and the resulting mixture was stirred at –78 °C for 1 h. A solution of *N*-cyclohexyl-*N*-(3-phenylpropylidene)amine (1.0 g, 4.6 mmol) in THF (5 ml) was added and the mixture was warmed to room temperature over 12 h. While cooling to 0 °C, the mixture was quenched with 10% KOH (10 ml) and filtered through Celite followed by separation. The organic extracts were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (hexane : EtOAc = 10 : 1 $\rightarrow$ 5 : 1) gave **14c** (inseparable *cis/trans* mixture, 427 mg, 36%). The characteristic NMR signals for the major isomer: ^1H NMR (400 MHz, CDCl_3) δ 2.32 (dd, J = 3.0, 9.4 Hz, 1 H), 2.68 (ddd, J = 6.2, 9.7, 13.8 Hz, 1 H), 2.81 (ddd, J = 5.9, 9.9, 13.8 Hz, 1 H), 5.21 (dd, J = 1.6, 10.2 Hz, 1 H), 5.34 (dd, J = 1.6, 17.0 Hz, 1 H), 5.74 (ddd, J = 9.8, 10.2, 17.0 Hz, 1H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 24.7, 25.1, 26.0, 32.5, 33.5, 33.9, 35.0, 45.1, 45.3, 60.5, 118.8, 125.7, 128.28, 128.34, 133.9, 141.9.

***N*-Benzyl-*N*-cyclopropylmethylamine (15a).** To a suspension of zirconocenehydrochloride (243 mg, 0.94 mmol) in CH_2Cl_2 (3 ml) was added a solution of **14a** (100 mg, 0.63 mmol) in CH_2Cl_2 (3 ml), and the resulting mixture was stirred for 30 min at room temperature in the dark. The mixture was refluxed at 50 °C for 2h and then cooled to room temperature. After quenching with aqueous NaHCO_3 at 0 °C, the mixture was extracted with Et_2O . The organic extracts were washed with brine, dried (MgSO_4), filtered, and concentrated *in vacuo* to give a crude oil. Purification by column chromatography (EtOAc : methanol = 10 : 1 $\rightarrow$ 5 : 1) gave **15a** (91 mg, 90%) as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 0.08 – 0.13 (m, 2 H), 0.45 – 0.51 (m, 2 H), 0.93 – 1.06 (m, 1 H), 2.11 (bs, 1 H), 2.50 (d, J = 6.9 Hz, 2 H), 3.83 (s, 2 H), 7.23 – 7.34 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 3.4, 11.1, 53.7, 54.3, 126.9, 128.2, 128.4, 140.1; IR (neat) ν 3318 (br), 3003, 1454 cm^{-1} ; EIMS m/z 161 (M^+); HRMS Calcd for $\text{C}_{11}\text{H}_{15}\text{N}$: 161.1205. Found: 161.1201.

***N*-Benzyl-*N*-(1-cyclopropylethyl)amine (15b).** Experimental procedure was the same as the procedure described for **15a** (71% yield). ^1H NMR (300 MHz, CDCl_3) δ 0.02 – 0.10 (m, 1 H), 0.12 – 0.20 (m, 1 H), 0.39 – 0.56 (m, 2 H), 0.72 – 0.83 (m, 1 H), 1.19 (d, J = 6.3 Hz, 3 H), 1.67 (bs, 1 H), 1.90 (qd, J = 6.3, 8.8 Hz, 1 H), 3.83 (d, J = 13.2 Hz, 1 H), 3.85 (d, J = 13.2 Hz, 1 H), 7.22 – 7.33 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 1.9, 4.4, 17.9, 20.5, 51.7, 58.3, 126.7, 128.0, 128.4, 140.8; IR (neat) ν 3318 (br), 2967, 1454 cm^{-1} ; EIMS m/z 175 ($\text{M}^+ - \text{CH}_3$); HRMS Calcd for $\text{C}_{11}\text{H}_{14}\text{N}$ ($\text{M}^+ - \text{CH}_3$):

160.1126. Found: 160.1132.

N-Cyclohexyl-N-(1-cyclopropyl-3-phenylpropyl)amine (15c). The title compound was obtained from **14c** in 82% yield without refluxing by the procedure described for hydrozirconation of vinyloxiranes. ^1H NMR (300 MHz, CDCl_3) δ 0.10–0.20 (m, 2 H), 0.47–0.56 (m, 2 H), 0.71–0.83 (m, 1 H), 0.89–1.32 (m, 6 H), 1.59–1.62 (m, 1 H), 1.69–1.74 (m, 2 H), 1.80–1.97 (m, 5 H), 2.50–2.60 (m, 1 H), 2.63–2.85 (m, 2 H), 7.15–7.31 (m, 5 H); ^{13}C NMR (75.5 MHz, CDCl_3) δ 3.1, 3.6, 17.0, 25.3, 25.4, 26.2, 32.2, 34.2, 34.6, 37.6, 53.5, 59.1, 125.6, 128.3, 142.9; IR (neat) ν 2926, 2852, 1452 cm^{-1} ; EIMS m/z 257 (M^+); HRMS Calcd for $\text{C}_{18}\text{H}_{27}\text{N}$: 257.2144. Found: 257.2138.

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