Complexation of Vinylcyclopropanes with Zirconocene−1-butene Complex: Application to the Stereocontrolled Synthesis of Steroidal Side Chains

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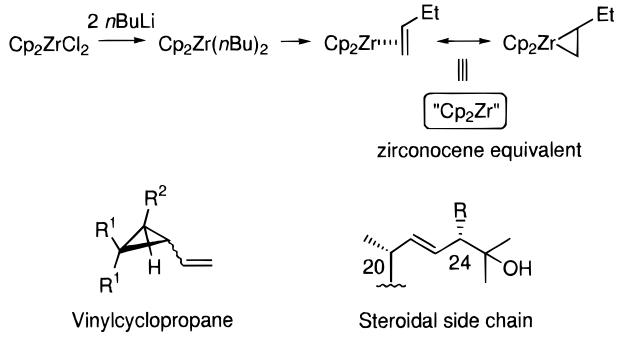
Reactions of vinylcyclopropane derivatives with a zirconocene−1-butene complex ("Cp_2Zr") caused regioselective cleavage of the cyclopropyl bond to give η^3 π-allylic and/or η^1 σ-allylic complexes. The regioselectivity of the bond cleavage and the formation of a η^3 π-allylic or η^1 σ-allylic complex depend on the bulkiness of the substituents on the cyclopropyl group and the presence of leaving functionality. A catalytic use of "Cp_2Zr" in the presence of excess Grignard reagent also caused a ring opening of the vinylcyclopropane derivatives with the same sense of regiochemical selectivity. The reaction of the thermally equilibrated "Cp_2Zr"−propenylcyclopropane complex with acetone indicated the possibility for the synthesis of the steroidal side chain in either natural or unnatural forms. The synthetic utility of the present "Cp_2Zr"−vinylcyclopropane chemistry was ascertained by the stereocontrolled preparation of the C-20, C-24 dimethylated steroidal side chain which is identical to the active metabolite of vitamin D_2.

Introduction

Transition metal-mediated transformations of organic molecules is a major and important discipline in modern organic chemistry, and a large number of new synthetic works committed to transition metal complexes have been reported. Recent progress in synthetic chemistry using early-transition metal complexes, especially organozirconocene derivatives, reveals a wide-ranging possibilities for organic synthesis.[1] In our search for new reactions, we have been devoting much time to synthetic use of a zirconocene−1-butene complex,[2] which can be generated *in situ* from zirconocene dichloride (Cp_2ZrCl_2) and *n*-butyllithium in an aprotic solvent according to the procedure developed by Negishi *et al.*[3] The zirconocene−1-butene complex is known to undergo a ligand exchange with external unsaturation to give a new zirconocene complex by releasing the 1-butene ligand. Therefore, the zirconocene−1-butene complex can be regarded as a zirconocene itself and is often termed a zirconocene equivalent, which is abbreviated to "Cp_2Zr". Since the discovery of a very practical method[3] to generate "Cp_2Zr", the chemistry of the zirconocene complex has quickly developed and been applied to the preparation of many types of organic molecules, including complex natural products.[4] Herein, we report a full account of vinylcyclopropane reactions with "Cp_2Zr" and the application of "Cp_2Zr"−vinylcyclopropane chemistry to stereocontrolled preparations of steroidal side chains.[5]



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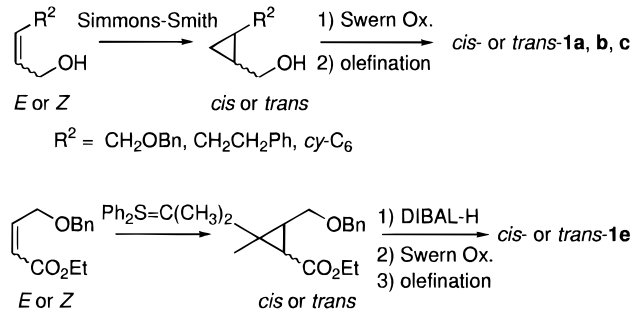
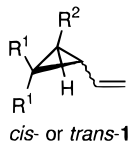
Scheme 1



Vinylcyclopropane is often used as a favorable molecule for the study of complexations with transition metals and a number of examples using various transition metals have been reported.[6] It is considered significant to examine the reactivity of vinylcyclopropane derivatives toward "Cp_2Zr". As model compounds, we selected *cis* and/or *trans* substituted vinylcyclopropane derivatives **1a**−**e** which were easily prepared by the sequences shown in Scheme 1.



	R^1	R^2
a	H	CH_2OBn
b	H	CH_2CH_2Ph
c	H	*cy*-C_6
d[a]	CH_3	H
e	CH_3	CH_2OBn

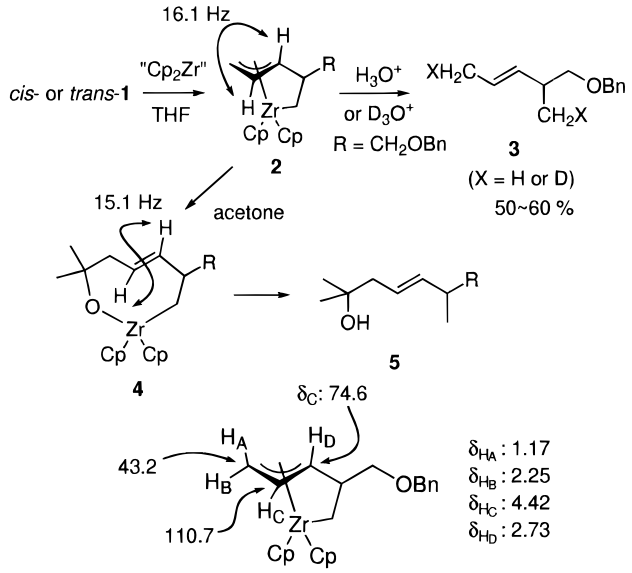
[a] see ref 7.

Results and Discussion

Treatment of *cis*- or *trans*-**1a** with "Cp_2Zr" (see the Experimental Section) in tetrahydrofuran (THF), or toluene, followed by acidic (1 M HCl) workup of the reaction mixture, yielded ring-opened compounds **3** (50%) (Scheme 2). Since the reaction of the cyclopropyl compound which has no vinyl group ended in recovery of the starting material under the same reaction conditions, the double bond is an essential factor in bringing about the ring opening of **1a** with "Cp_2Zr". In the reaction of **1a**, addition of 10% deuterium chloride in deuterium oxide to the reaction mixture revealed an efficient incorporation of the two deuteriums, one by one, into each methyl group of **3** (X = D) (60% yield). Adding acetone to the reaction mixture of **1a** and "Cp_2Zr" followed by concentration of the mixture yielded an eight-membered oxazirconacyclic compound **4** (R = CH_2OBn) containing an *E*-double bond (J = 15.1 Hz) in the ring (Scheme 2). The oxazirconacyclic compound **4** was quantitatively converted to **5** by the addition of 1 M HCl.

Results of the reactions of vinylcyclopropane derivatives with "Cp_2Zr" are listed in Table 1. Reactions with *cis*-isomers generally give higher yields of the products

Scheme 2



^{1}H and ^{13}C NMR chemical shifts (ppm) of **2a**

Table 1. Reaction Products of Vinylcyclopropanes with "Cp_2Zr" and Carbonyls

entry	starting material	carbonyl	product	yield (%)
1	*cis*-**1a**	acetone	**5a**	86
2	*trans*-**1a**			48
3	*cis*-**1b**		**5b**	84
4	*trans*-**1b**			45
5	*cis*-**1c**		**5c**	93
6	*trans*-**1c**[a]			80
7	**1d**	PhCHO	**7**	41
8	*cis*-**1e**		**10**	80
9	*trans*-**1e**			26

[a] *trans*/*cis* = 7.6.

than reactions with *trans*-isomers (entries 1, 3, 5, and 8). In all cases examined, a regioselective cyclopropyl bond-scission with "Cp_2Zr" occurred at the less sterically crowding cyclopropyl bond. The presence of an oxygen functionality which is able to coordinate to zirconium metal does not affect the regioselectivity of the cyclopropyl bond cleavage (entries 1, 2, 8, and 9).

The incorporation of two deuteriums into **3** (X = D), the formation of **5**, and the NMR spectrum of the eight-membered oxazirconacycle **4** suggest the formation of an η^3 π-allylic zirconocene complex **2** in the reaction of **1** with "Cp_2Zr" (Scheme 2). Although we could not obtain a clear NMR spectrum of **2a** due to its diastereomeric and/or unstable nature, the η^3 π-allylic structures of **2a** was confirmed by characteristic ^{1}H- and ^{13}C-chemical shifts of the η^3 π-allylic portion (Scheme 2).[8] The dimethyl η^3 π-allylic zirconocene complex **6** which is generated from **1d** showed a clearer NMR spectrum than **2a** (Scheme 3). *E*-Stereochemistry of η^3 π-allylic complexes **2a**, **6** was deduced by coupling constants (J = 16.1 and 16.9 Hz, respectively) between two vinyl protons (Schemes 2 and 3). In the reaction of **1e**, the initially formed η^3 π-allylic complex **8** is converted to the σ-allylic complex **9** through a facile β-elimination of the benzyloxy group.[2a] The structure of the zirconocene intermediate **9** was confirmed to be *E* σ-allylic complex ($J_{olefinic}$ = 15.3 Hz) from

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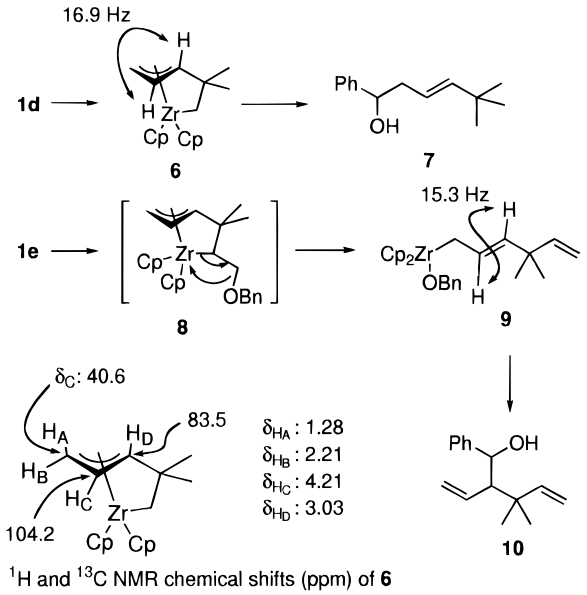
Scheme 3



^{1}H and ^{13}C NMR chemical shifts (ppm) of **6**

NMR data (Scheme 3).[2h] The reactions of **6** and **9** with benzaldehyde showed formations of homoallylic alcohol **7** and **10** in 41% and 80% yields, respectively (entries 7 and 8, Table 1). In the reaction of **1e** with "Cp_2Zr", the *gem*-dimethyl group is considered bulky enough to force cleavage of the (benzyloxy)methyl-substituted σ-bond of the cyclopropyl ring. The regioselective bond scission of substituted vinylcyclopropane with "Cp_2Zr" indicates the influence of substituent bulkiness on the cyclopropyl ring. The observation that the *cis*-isomer of **1** generally gives a higher yield of the product than the *trans*-isomer might be a reflection of the steric effect during complexation. An experiment which was essentially the same was independently reported by Whitby's group.[8] They suggested the possibility that the participation of the preferable conformation **A** over **B** of the zirconacyclopropane intermediate **11** forms the *E*-stereochemical η^3 π-allylic complex (Figure 1).

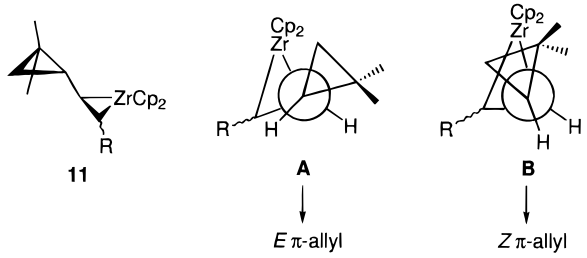
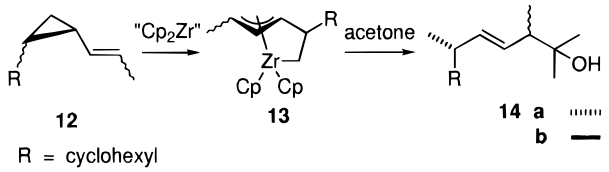


Figure 1. Whitby's proposal for the formation of the π-allylic zirconocene complex.[8]

Complexation of *cis*- or *trans*-(1-propenyl)cyclopropane derivatives **12** (a mixture of *E*/*Z* olefinic isomers) with "Cp_2Zr", followed by treatment with acetone, gave **14** as a diastereomeric mixture (Scheme 4). As expected from the results of the reactions of "Cp_2Zr" with vinylcyclopropane derivatives **1**, the *cis*-substituted isomer *cis*-**12** gave a much higher yield of diastereomeric products **14** (63−85%) than the *trans*-**12** (<10%). The diastereomeric ratio of **14**, while disappointing, was suggested to be dependent on the olefinic geometry of the starting material *cis*-**12** (Scheme 4). Thus, according to Whitby's proposal,[8] the geometrical and diastereomeric mixture of complexes **13** was converted to the thermodynamically

Scheme 4



	yield of **14**	**14a** : **14b**
cis-**12** *Z*/*E* = 2.8	85 %	1 : 1
cis-**12** *Z*/*E* = 1	63 %	2 : 1
cis-**12** *Z*/*E* = 2.8	50 %	**14a** only[a]
trans-**12** *Z*/*E* = 2.3	<10%	

[a] Thermal equilibrium conditions (70 °C, 12 h).

stable complex (*E*,*E*)-**13** by equilibrium through the assumed σ-allylic zirconocene species (**15**, **16**, and **17**) (Figure 2). Heating of π-complexes **13** at 70 °C for 12 h and the subsequent reaction with acetone gave a single diastereomer **14a** in 50% yield. The 1,4-relative configuration of the dimethyl groups in product **14a** was confirmed to be (1*R**,4*R**)-configuration with X-ray analysis of the 3,5-dinitrobenzoate of **14a**.[9] The selective formation of (1*R**,4*R**)-dimethyl compound **14a** as a single product can be explained as a result of the reaction between the thermodynamically stable σ-allylic zirconocene **18** and acetone through a six-membered chair-form cyclic transition state which is considered the most favorable energetically (Figure 3). In the reaction of the equilibrated (70 °C, 12 h) π-complexes **13** with acetone, the lowered yield (50%) and the exclusive formation of **14a** compared to those (85% yield, **14a**:**14b** = 1:1) under nonequilibrium conditions might indicate a possibility for selective decomposition of the thermodynamically unstable zirconocene complex, which leads to **14b**, during the thermal equilibration process.

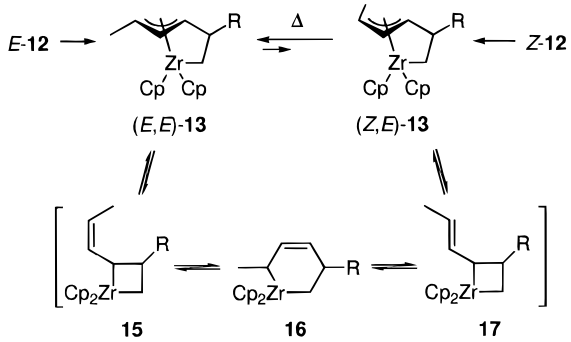


Figure 2. Thermal isomerization of allylic zirconocene species.

The catalytic use of Cp_2ZrCl_2 or its optically active derivative has become a very challenging task in modern chemical synthesis.[10] The bond scission of vinylcyclopropane derivatives **1a** was also carried out with a

(9) Crystals for X-ray analysis were prepared by the reaction of **19a** with 3,5-dinitrobenzoyl chloride in the presence of DMAP in pyridine, and the crystals were recrystallized from hexane−ethyl acetate, mp 83−86 °C. Cu Kα radiation (n = 1.54178 Å). Crystal data: empirical formula $C_{22}H_{30}N_2O_6$; monoclinic; space group $p2_1$(no. 14); a = 6.321(4) Å, b = 9.721(6) Å, c = 37.452(3) Å, β = 92.66(2)°, V = 2298(1) Å^3, Z = 4, D = 1.209 g/cm^3. A total of 3032 unique reflections were collected. The final R factor was 0.064. The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

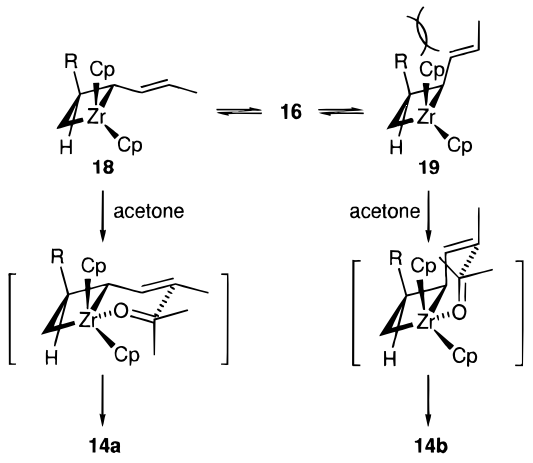
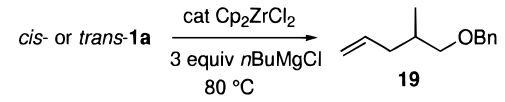


Figure 3. Transition state model for the reaction of the thermally stable complex with acetone.

Table 2. Ring Opening of Vinylcyclopropanes with Catalytic "Cp_2Zr"



entry	vinylcyclopropane	Cp_2ZrCl_2 (mol %)	reaction time (h)	yield (%)
1	*cis*-**1a**	10	8	30
2	*cis*-**1a**	30	0.3	56
3	*trans*-**1a**	30	0.3	38

catalytic amount of Cp_2ZrCl_2 (10−30 mol %) and *n*-butylmagnesium chloride (3 mol equiv) in THF or toluene; however, yields of product **19** (38−56%) were low (Table 2). Addition 10% DCl−D_2O to the reaction mixture gave a monodeuterated compound of **19** (X = D). These results support the formation of a "Cp_2Zr" catalytic cycle. Under catalytic conditions, formation of olefinic compound **19**, which is an isomer of **3**, and the incorporation of monodeuterium into the methyl group of **19** suggest Grignard reagent **20** is generated during the course of the catalytic reaction (Figure 4).

To apply "Cp_2Zr"-vinylcyclopropane chemistry, we attempted stereocontrolled construction of the steroidal side chain, which is identical to the active vitamin D_2 metabolite.[11] The present "Cp_2Zr"−vinylcyclopropane chemistry also indicates the possibility of preparing the side

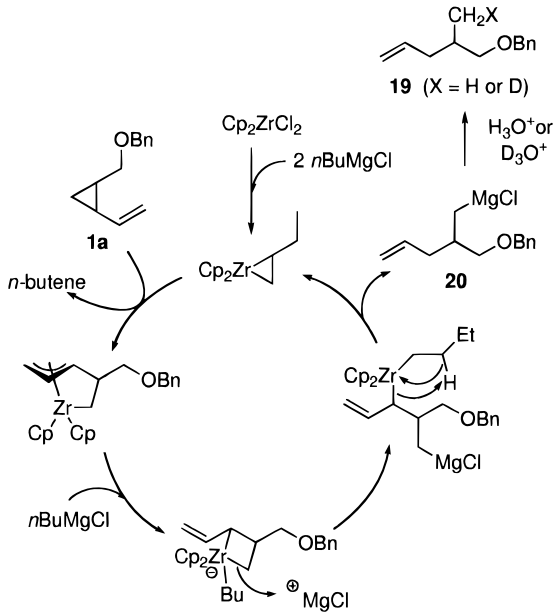
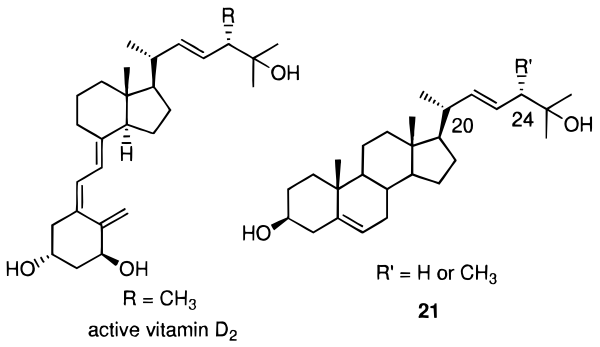


Figure 4. A catalytic cycle for the ring opening of **1a** with "Cp_2Zr".

chain analog for steroids because the carbon−zirconium bond is easily converted to a carbon−oxygen or halogen bond.[1] The construction of the steroidal side chain has attracted much attention not only from a biological view point, but also in the stereocontrolled synthesis of the acyclic system. Although a number of methods have been reported for stereocontrolled construction of the side chain of active vitamin D_2 metabolite, to our knowledge, there are no reports about the simultaneous construction of two methyl groups at C-20 and C-24 positions in a stereocontrolled manner.[12] To synthesis the steroidal side chain, steroid **21**[13] was chosen as the target.



It is obvious that the diastereoselective introduction of the cyclopropyl ring into a steroidal side chain is crucial to a stereocontrolled construction of the 20,24-dimethyl side chain with our present "Cp_2Zr"−vinylcyclopropane chemistry. The diastereoselective Simmons−Smith cyclopropanation[14] (10 equiv of diethyl zinc and 10 equiv of diiodomethane in toluene at −30 °C) of *Z*-allylic alcohol **23** which can be prepared from aldehyde **22**[15] gave an inseparable mixture of **24** and **25** in a ratio of 78:22 in 84% yield (Scheme 5). Separation of the diastereomeric mixture was carried out at the final stage of preparing **21** and **28** (*vide infra*). The Simmons−Smith reaction in the presence of 1 equiv of L-dibutyl tartrate in THF gave **24** as the major isomer at more than 94% de in 87% yield.[16] The stereochemistry of **24** as the major isomer was confirmed by converting the mixture to the known

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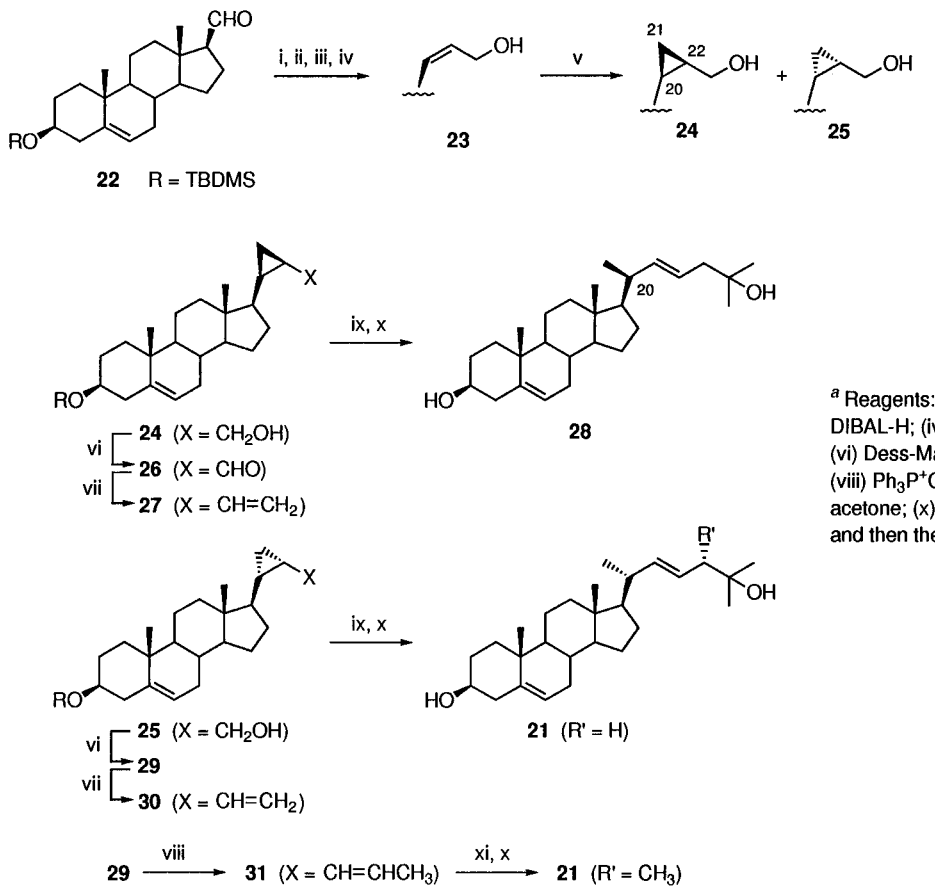
Scheme 5



additive	ratio (**24** : **25**)	yield (%)
none	78 : 22	84
L- tartrate	> 97 : 3	87
D- tartrate	27 : 73	76
Charette's dioxaborolane	11 : 89	90

[a] Reagents: (i) Ph_3P, CBr_4, Zn; (ii) *n*BuLi, ClCOOEt; (iii) DIBAL-H; (iv) H_2, Pd-$BaSO_4$, quinoline; (v) CH_2I_2, Et_2Zn; (vi) Dess-Martin periodinane; (vii) $Ph_3P^+CH_3\ Br^-$, *n*BuLi; (viii) $Ph_3P^+CH_2CH_3\ Br^-$, *n*BuLi; (ix) "Cp_2Zr", and then acetone; (x) aqueous HF, CH_3CN/toluene; (xi) "Cp_2Zr", and then thermal isomerization (70 °C, 12 h), acetone.

25-OH, C-20 *epi* steroid **28**[12v] (60% based on the calculated amount of **27**) via compounds **26** and **27** by (i) the Dess-Martin oxidation of **24**, (ii) Wittig olefination of **26** ($Ph_3P^+CH_3Br^-$/*n*BuLi), (iii) "Cp_2Zr" complexation of **27** followed by the addition of acetone, (iv) deprotection and separation of the diastereomer. In order to prepare a steroid, which has a natural configuration at C-20, the requisite introduction of the cyclopropyl ring into **23** was carried out by the Simmons−Smith reaction in the presence of D-diisopropyl tartrate (2−3 equiv) as a stereocontrolling agent to give **24** and **25** in a 27:73 ratio in 76−83% yield. The improved ratio of **25** (**24:25** = 11:89) was obtained by Charette's enantioselective Simmons−Smith cyclopropanation[17] of **23** using a chiral dioxaborolane ligand derived from (*R*,*R*)-(+)-*N*,*N*,*N*′,*N*′-tetramethyltartaric acid diamide. Configuration of the cyclopropyl ring of **25** was confirmed by converting the mixture to the C-20 naturally configured steroid **21** (R′ = H)[12v] (47% yield based on the calculated amount of **30**) in the same way as the preparation of **28**. To prepare **21**, compound **25** (**24:25** = 27:73) was oxidized with the Dess-Martin reagent to aldehyde and the subsequent Wittig olefination ($Ph_3P^+CH_2CH_3Br^-$/*n*BuLi) to give **31** as an *E*/*Z* mixture (*E*:*Z* = 22:78). Heating (70 °C, 12 h) the "Cp_2Zr" complex generated from **31** in THF, followed by the reaction with acetone, and deprotection, gave **21** (R′ = CH_3). All of the synthesized steroids (**28**, **21** R′ = H, R′ = CH_3) were identical in every respect to the reported spectral data in the literature.[12v,13]

In summary, an efficient complexation of vinylcyclopropane derivatives with a stoichiometric amount of "Cp_2Zr" was established to give zirconocene complexes through a regioselective ring-opening of the vinylcyclopropane derivative. The regioselective cleavage of the cyclopropyl bond and the formation of η^3 π-allylic complex and/or η^1 σ-allylic complex depend upon the bulkiness of the substituents on the cyclopropyl ring. With a catalytic amount of "Cp_2Zr" and 3 equiv of Grignard reagent, the same sense of regioselective cleavage of vinylcyclopropane

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was observed. Extension of this chemistry to the stereocontrolled preparation of the steroidal side chain in natural and/or unnatural form showed a high possibility of constructing the analog of the steroidal side chain.

Experimental Section

All nonaqueous reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions. Tetrahydrofuran (THF), diethyl ether (Et_2O), and dimethoxyethane (DME) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) and toluene were distilled from calcium hydride. NMR spectra were measured at 300 and 400 MHz for ^1H and 75.5 or 100.6 MHz for ^{13}C. Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. *n*-Butyllithium was purchased from Aldrich Chemical Co. as a 1.6 M solution in hexane. Fuji silysia silica gel BW80S was used for column chromatography, and prepacked columns CPS-223L-1 (Kusano Kagaku Kikai Works Co., Japan) were used for medium pressure liquid chromatography (MPLC).

(*E*)-2-[(Benzyloxy)methyl]-3-pentene (3, X = H). To a solution of zirconocene dichloride (403 mg, 1.38 mmol) in THF (3 mL) cooled to −78 °C was added dropwise *n*BuLi (1.41 M in hexane, 2.0 mL, 2.82 mmol), and the resulting solution was stirred for 1 h at −78 °C. A solution of **1a** (200 mg, 1.06 mmol) in THF (3 mL) was added, and the reaction mixture was warmed to room temperature. After stirring for 5 h, the mixture was quenched with aqueous HCl (1 M) while cooling to 0 °C and extracted with Et_2O. The organic extracts were washed with water, $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude oil. Purification by column chromatography (hexane:EtOAc = 20:1) followed by MPLC (hexane:EtOAc = 100:1) yielded **3** (X = H) (97 mg, 48%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, J = 6.8 Hz, 3 H), 1.67 (d, J = 6.0 Hz, 3 H), 2.41 − 2.50 (m, 1 H), 3.26 (dd, J = 7.1, 9.1 Hz, 1 H), 3.35 (dd, J = 6.4, 9.1 Hz, 1 H), 4.52 (s, 2 H), 5.33−5.56 (m, 2 H), 7.26−7.35 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.3, 18.1, 36.9, 72.9, 75.5, 124.6, 127.4, 127.5, 128.3, 133.9; EIMS m/z 190 (M^+); HRMS calcd for $C_{13}H_{18}O$: 190.1358, found: 190.1360.

(*E*)-1-(Benzyloxy)-2-methyl-*d*-3-pentene-5-*d* (3, X = D). The reaction mixture, which was obtained by the procedure as described for compound **3** (X = H), was quenched with DCl/D_2O (10%) while cooling to 0 °C. Extraction and purification by column chromatography yielded **3** (X = D) (90 mg, 59%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.00−1.05 (m, 2 H), 1.64−1.69 (m, 2 H), 2.41−2.50 (m, 1 H), 3.27 (dd, J = 7.1, 9.1 Hz, 1 H), 3.36 (dd, J = 6.4, 9.1 Hz, 1 H), 4.53 (s, 2 H), 5.37−5.54 (m, 2 H), 7.26−7.38 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.0 (t), 17.8 (t), 36.8, 72.9, 75.5, 124.6, 127.4, 127.5, 128.3, 133.9, 138.7; EIMS m/z 192 (M^+); HRMS calcd for $C_{13}H_{16}D_2O$: 192.1483, found: 192.1485.

Oxazirconacycle 4 (R = CH_2OBn). To a solution of zirconocene dichloride (322 mg, 1.10 mmol) in THF (3 mL) cooled to −78 °C was added dropwise *n*BuLi (1.56 M in hexane, 1.4 mL, 2.18 mmol), and the resulting solution was stirred for 1 h at −78 °C. A solution of vinylcyclopropane **1a** (1.00 mmol) in THF (3 mL) was added, and the reaction mixture was warmed to room temperature. After 6 h, acetone (0.15 mL, 2.04 mmol) was added dropwise while cooling to 0 °C, and the mixture was stirred for 3 h at room temperature. The solvent was then concentrated to dryness in vacuo, and the residue was dissolved in benzene-d_6 (2 mL). ^1H NMR (400 MHz, C_6D_6) δ 0.59 (dd, J = 2.8, 12.2 Hz, 1 H), 0.98 (s, 3 H), 1.05 (s, 3 H), 1.25 (t, J = 12.2 Hz, 1 H), 1.71 (t, J = 11.5 Hz, 1 H), 2.09 (dd, J = 3.8, 11.5 Hz, 1 H), 2.93−3.00 (m, 1 H), 3.48 (dd, J = 8.0, 9.1 Hz, 1 H), 3.57 (dd, J = 5.4, 9.1 Hz, 1 H), 4.62 (s, 1 H), 4.86 (dd, J = 10.1, 15.1 Hz, 1 H), 5.21 (ddd, J = 3.8, 11.5, 15.1 Hz, 1 H), 5.73 (s, 5 H), 5.76 (s, 5 H), 7.15−7.50 (m, 5 H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 30.1, 32.2, 36.2, 46.2, 47.7, 73.0, 79.5, 79.8, 109.7, 110.7, 122.8, 123.4, 127.8, 128.5, 140.1, 143.5.

(*E*)-7-(Benzyloxy)-2,6-dimethyl-4-hepten-2-ol (5a). To a solution of zirconocene dichloride (403 mg, 1.38 mmol) in THF (3 mL) cooled to −78 °C was added dropwise *n*BuLi (1.55 M in hexane, 1.8 mL, 2.79 mmol), and the resulting solution was stirred for 1 h at −78 °C. A solution of **1a** (200 mg, 1.06 mmol) in THF (3 mL) was added and the reaction mixture was warmed to room temperature. After 3 h, acetone (0.16 mL, 2.18 mmol) was added dropwise while cooling to 0 °C, and the mixture was stirred for 5 h at room temperature. The mixture was quenched with aqueous HCl (1 M) while cooling on an ice bath and extracted with Et_2O. The organic extracts were washed with water, $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude oil. Purification by column chromatography (hexane:EtOAc = 20:1 → 5:1) yielded **5a** (228 mg, 86%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, J = 6.7 Hz, 3 H), 1.19 (s, 3 H), 1.20 (s, 3 H), 1.63 (bs, 1 H), 2.17 (d, J = 6.7 Hz, 2 H), 2.47 − 2.57 (m, 1 H), 3.31 (dd, J = 6.7, 8.9 Hz, 1 H), 3.35 (dd, J = 6.7, 8.9 Hz, 1 H), 4.51 (s, 2 H), 5.47 (dd, J = 6.7, 15.5 Hz, 1 H), 5.54 (ddd, J = 6.7, 15.5, 15.5 Hz, 1 H), 7.26−7.36 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.2, 28.9, 29.1, 37.1, 46.9, 70.2, 72.9, 75.2, 125.2, 127.5, 127.6, 128.3, 137.7, 138.5; IR (neat) ν 3393 (br), 2969, 1096 cm^{-1}; EIMS m/z 230 ($M^+ - H_2O$). Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.64; H, 9.66.

(*E*)-2,6-Dimethyl-8-phenyl-4-octen-2-ol (5b). Experimental procedure was same as the procedure described for **5a**. ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, J = 6.7 Hz, 3 H), 1.22 (s, 6 H), 1.48 (bs, 1 H), 1.57−1.62 (m, 2 H), 2.15−2.22 (m, 1 H), 2.19 (d, J = 6.2 Hz, 2 H), 2.53−2.66 (m, 2 H), 5.40−5.46 (m, 1 H), 5.49 (dd, J = 6.5, 15.3 Hz, 1 H), 7.15−7.29 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 20.9, 29.1, 33.8, 36.6, 38.8, 47.0, 70.5, 81.2, 124.1, 125.6, 128.3, 128.4, 140.7, 142.7; IR (neat) ν 3382 (br), 2968, 699 cm^{-1}; EIMS m/z 217 ($M^+ - CH_3$). Anal. Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.35; H, 10.60.

(*E*)-6-Cyclohexyl-2-methyl-4-hepten-2-ol (5c). Experimental procedure was same as the procedure described for **5a**. ^1H NMR (400 MHz, $CDCl_3$) δ 0.92−0.97 (m, 2 H), 0.96 (d, J = 6.9 Hz, 3 H), 1.08−1.24 (m, 4 H), 1.20 (s, 6 H), 1.50 (bs, 1 H), 1.62−1.73 (m, 5 H), 1.92−2.00 (m, 1 H), 2.16 (d, J = 6.0 Hz, 2 H), 5.38 (dt, J = 6.0, 15.3 Hz, 1 H), 5.43 (dd, J = 6.9, 15.3 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 17.9, 26.6, 26.7, 29.1, 30.4, 30.5, 42.6, 43.1, 47.0, 70.4, 124.0, 140.0; IR (neat) ν 3373 (br), 2925, 2852 cm^{-1}; EIMS m/z 195 ($M^+ - CH_3$). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.54; H, 12.33.

(*E*)-η^3-π-Allylzirconocene 6. Sample was prepared as in the case of **4** except for the addition of acetone. ^1H NMR (400 MHz, C_6D_6) δ −0.94 (d, J = 10.0 Hz, 1 H), −0.81 (d, J = 10.0 Hz, 1 H), 1.00 (s, 3 H), 1.28 (dd, J = 4.5, 14.2 Hz, 1 H), 1.37 (s, 3 H), 2.21 (dd, J = 4.5, 7.7 Hz, 1 H), 3.03 (d, J = 16.9 Hz, 1 H), 4.21 (ddd, J = 7.7, 14.2, 16.9 Hz, 1 H), 5.19 (s, 5 H), 5.27 (s, 5 H); ^{13}C NMR (100.6 MHz, C_6D_6) δ −14.8, 26.1, 33.4, 37.2, 40.6, 83.5, 104.0, 104.2, 104.5.

(*E*)-5,5-Dimethyl-1-phenyl-3-hexen-1-ol (7). ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 9 H), 2.08 (bs, 1 H), 2.38−2.49 (m, 2 H), 4.68 (dd, J = 4.9, 7.8 Hz, 1 H), 5.32 (ddd, J = 6.6, 7.7, 15.6 Hz, 1 H), 5.59 (dt, J = 1.2, 15.6 Hz, 1 H), 7.25−7.36 (m, 5 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 29.6, 33.1, 42.9, 73.5, 120.0, 125.8, 127.3, 128.3, 144.0, 146.3; IR (neat) ν 3421 (br), 2960, 701 cm^{-1}; EIMS m/z 204 (M^+); HRMS calcd for $C_{14}H_{20}O$: 204.1514, found: 204.1499.

(*E*)-η^1-σ-allylzirconocene 9. Sample was prepared as in the case of **6**. ^1H NMR (400 MHz, C_6D_6) δ 1.31 (s, 6 H), 1.96 (dd, J = 1.2, 8.5 Hz, 2 H), 4.88 (s, 2 H), 5.04 (dd, J = 1.6, 10.5 Hz, 1 H), 5.17 (dd, J = 1.6, 17.4 Hz, 1 H), 5.21 (dt, J = 1.2, 15.3 Hz, 1 H), 5.78 (s, 10 H), 5.91 (dt, J = 8.5, 15.3 Hz, 1 H), 6.11 (dd, J = 10.5, 17.4 Hz, 1 H), 7.16−7.31 (m, 5 H); ^{13}C NMR (100.6 MHz, C_6D_6) δ 28.4, 39.3, 44.2, 75.7, 109.3, 111.2, 111.7, 126.5, 127.1, 128.5, 134.9, 143.3, 149.5.

3,3-Dimethyl-1-phenyl-2-vinyl-4-penten-1-ol (10). Mp 37.3−39.0 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (s, 3 H), 1.14 (s, 3 H), 1.99 (d, J = 3.5 Hz, 1 H), 2.06 (dd, J = 2.2, 10.2 Hz, 1 H), 4.67 (dd, J = 2.2, 17.2 Hz, 1 H), 5.08−5.14 (m, 4 H), 5.93 (dt, J = 10.2 Hz, 1 H), 6.04 (dd, J = 10.5, 17.9 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 25.0, 26.6, 39.2, 61.9, 73.2, 112.0, 119.6, 125.8, 126.7, 127.7, 133.0, 144.6, 147.3; IR (KBr) ν 3358 (br), 2965, 918 cm^{-1}; EIMS m/z 107 ($M^+ - H_2O - C_7H_7$). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 82.92; H, 9.40.

(3*R,6*R**)-(*E*)-6-Cyclohexyl-2,3-dimethyl-4-hepten-2-ol (14a).** To a solution of zirconocene dichloride (380 mg, 1.30 mmol) in THF (3 mL) cooled to −78 °C was added dropwise *n*BuLi (1.64 M in hexane, 1.6 mL, 2.62 mmol), and the resulting solution was stirred for 1 h at −78 °C. A solution of *cis*-**12** (*Z*/*E* = 2.8, 164 mg, 1.00 mmol) in THF (3 mL) was added, and the reaction mixture was warmed to room temperature. After stirring for 5 h, the mixture was heated to reflux at 70 °C for 12 h. Acetone (0.15 mL, 2.04 mmol) was added dropwise while cooling to 0 °C, and the mixture was stirred for 5 h at room temperature. The mixture was quenched with aqueous HCl (1 M) while cooling on an ice bath and extracted with Et_2O. The organic extracts were washed with water, $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude oil. Purification by column chromatography (hexane:EtOAc = 10:1 → 3:1) yielded alcohol **14a** (112 mg, 50%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85−1.02 (m, 2 H), 0.95 (d, J = 6.9 Hz, 3 H), 1.01 (d, J = 6.9 Hz, 3 H), 1.05−1.22 (m, 4 H), 1.13 (s, 3 H), 1.17 (s, 3 H), 1.57−1.73 (m, 6 H), 1.93 (m, 1 H), 2.14 (dq, J = 6.9, 8.5 Hz, 1 H), 5.28 (dd, J = 8.5, 15.4 Hz, 1 H), 5.41 (dd, J = 7.9, 15.4 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9, 17.9, 26.3, 26.6, 26.7, 27.0, 30.4, 30.5, 42.5, 43.1, 48.4, 72.3, 130.4, 137.6; IR (neat) ν 3431 (br), 2927, 2853 cm^{-1}; EIMS m/z 209 ($M^+ - CH_3$). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 79.90; H, 12.58.

(3*R,6*R**)-(*E*)-6-Cyclohexyl-2,3-dimethyl-2-[(3,5-dinitrobenzoyl)oxy]-4-heptene.** To a solution of alcohol **14a** (32 mg, 0.14 mmol) and 4-(dimethylamino)pyridine (1 mg) in dry pyridine (3 mL) was added slowly 3,5-dinitrobenzoyl chloride (49 mg, 0.21 mmol), and the resulting mixture was heated at 50 °C for 24 h. After being quenched with water, the mixture was extracted with CH_2Cl_2, and the organic extracts were washed with aqueous HCl (10%), distilled water, and $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid. Purification by column chromatography (hexane:EtOAc = 20:1 → 10:1) followed by recrystallized (hexane−EtOAc) yielded benzoate (47 mg, 79%) as colorless crystals. Mp 83.1−86.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (d, J = 6.9 Hz, 3 H), 0.82−0.89 (m, 2 H), 1.05−1.16 (m, 5 H), 1.10 (d, J = 6.9 Hz, 3 H), 1.56−1.67 (m, 4 H), 1.59 (s, 3 H), 1.61 (s, 3 H), 1.89 (m, 1 H), 2.97 (dq, J = 6.9, 8.0 Hz, 1 H), 5.29 (dd, J = 8.2, 15.4 Hz, 1 H), 5.43 (dd, J = 8.0, 15.4 Hz, 1 H), 9.07 (d, J = 2.1 Hz, 2 H), 9.19 (t, J = 2.1 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 15.9, 17.7, 23.4, 23.6, 26.58, 26.64, 30.39, 30.44, 42.5, 43.0, 45.3, 89.0, 121.9, 129.0, 129.2, 135.8, 135.5, 148.5, 161.2; IR (KBr) ν 1714, 1542, 1346 cm^{-1}; CIMS m/z 417 ($M^+ - 1$). Anal. Calcd for $C_{22}H_{30}N_2O_6$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.06; H, 7.31; N, 6.63.

1-(Benzyloxy)-2-methyl-4-pentene (19, X = H). To a solution of **1a** and zirconocene dichloride (44 mg, 30 mol %) in THF (3 mL) cooled to 0 °C was added dropwise *n*BuMgCl (0.90 M in THF, 1.7 mL, 1.53 mmol), and the resulting solution was heated to reflux for 20 min. The reaction mixture was quenched with aqueous HCl (1 M) while cooling to 0 °C and extracted with Et_2O. The organic extracts were washed with water, $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude oil. Purification by column chromatography (hexane:EtOAc = 30:1) yielded **19** (X = H) (53 mg, 56%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (d, J = 6.5 Hz, 3 H), 1.82−1.98 (m, 2 H), 2.18−2.28 (m, 1 H), 3.28 (dd, J = 6.0, 9.0 Hz, 1 H), 3.35 (dd, J = 6.3, 9.0 Hz, 1 H), 4.51 (s, 2 H), 4.99−5.05 (m, 2 H), 5.79 (ddt, J = 7.0, 10.1, 17.1 Hz, 1 H), 7.26−7.36 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.8, 33.4, 38.1, 73.0, 75.3, 115.9, 127.4, 127.5, 128.3, 137.0, 138.8; EIMS m/z 190 (M^+); HRMS calcd for $C_{13}H_{18}O$: 190.1358, found: 190.1344.

1-(Benzyloxy)-2-methyl-*d*-4-pentene (19, X = D). The reaction mixture, which was obtained by the procedure as described for compound **19** (X = H), was quenched with DCl/D_2O (10%) while cooling to 0 °C. Extraction and purification by column chromatography yielded **19** (X = D) (32%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91−0.95 (m, 2 H), 1.83−1.98 (m, 2 H), 2.19−2.28 (m, 1 H), 3.28 (dd, J = 6.0, 9.0 Hz, 1 H), 3.34 (dd, J = 6.1, 9.0 Hz, 1 H), 4.51 (s, 2 H), 4.99−5.05 (m, 2 H), 5.79 (ddt, J = 6.9, 10.2, 17.0 Hz, 1 H), 7.26−7.36 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 16.5 (t), 33.3, 38.0, 73.0, 75.3, 115.9, 127.4, 127.5, 128.3, 137.0, 138.8; EIMS m/z 191 (M^+); HRMS calcd for $C_{13}H_{17}DO$: 191.1420, found: 191.1422.

Cyclopropanation of 23. By Tartrate Addition. To a solution of **23** (200 mg, 0.45 mmol) in toluene cooled to −30 °C were added a solution of (+)-L-dibutyl tartrate (118 mg, 0.45 mmol) in toluene (5 mL) and diethylzinc (1.0 M solution in hexane, 4.5 mL, 4.5 mmol), and the resulting mixture was stirred for 15 min at −30 °C. While cooling to −30 °C, diiodomethane (0.36 mL, 4.5 mmol) was added, and the mixture was stirred for 6 h at −30 °C. The mixture was quenched with aqueous HCl (1 M) on an ice bath and extracted with toluene. 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 solid. Purification by column chromatography (toluene:EtOAc = 10:1) yielded an inseparable mixture of **24** and **25** (187 mg, 91%, **24:25** = 97:3 ratio). The same procedure in the presence of 2−3 equiv of (−)-D-diisopropyl tartrate instead of (+)-L-dibutyl tartrate gave α-cyclopropanemethanol **25** as a major product (**24:25** = 27:73) in 76−83% yield.

By Charette's Method.[17] To a mixture of dioxaborolane (134 mg, 0.5 mmol), **23** (200 mg, 0.45 mmol), and molecular sieves (4 Å) (20 mg) in CH_2Cl_2 (3 mL) cooled to −15 °C was added the previously prepared solution of $Zn(CH_2I)_2$·DME complex (2.25 mmol in 3 mL of CH_2Cl_2), and the resulting mixture was stirred at −15 °C for 6 h. The mixture was then quenched with aqueous NH_4Cl, and the layers were separated. The aqueous layer was extracted with toluene, and the combined organic extracts were stirred vigorously for 12 h with aqueous KOH (5 M). The layers were separated, and the organic layer was washed with aqueous HCl (1 M), $NaHCO_3$, water and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid. Purification by column chromatography (toluene:EtOAc = 10:1) yielded **24** and **25** (186 mg, 90%, **24:25** = 11:89, inseparable mixture) as a white solid. **Cyclopropanemethanol 24:** ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.06 (dd, J = 5.5, 9.9 Hz, 1 H), 0.02−0.06 (m, 1 H), 0.05 (s, 6 H), 0.72 (s, 3 H), 0.89 (s, 9 H), 1.01 (s, 3 H), 3.33−3.40 (m, 1 H), 3.42−3.53 (m, 1 H), 3.78−3.84 (m, 1 H), 5.31−5.32 (m, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ −4.6, 7.5, 13.0, 16.2, 18.3, 19.0, 19.5, 20.9, 24.4, 25.9, 28.8, 31.9, 32.1, 36.7, 37.4, 38.1, 42.1, 42.8, 50.1, 50.4, 56.1, 63.8, 72.6, 121.0, 141.6.

Cyclopropanemethanol 25: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.74 (s, 3 H), 0.89 (s, 9 H), 1.01 (s, 3 H), 3.42−3.53 (m, 1 H), 3.57−3.61 (m, 1 H), 5.31−5.32 (m, 1 H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ −4.6, 8.2, 13.0, 16.1, 16.2, 18.3, 19.5, 20.8, 24.8, 25.9, 28.8, 31.9, 32.0, 32.1, 36.7, 37.4, 38.4, 42.8, 43.0, 50.2, 50.6, 63.4, 72.6, 121.1, 141.6.

Preparations of 27, 30. To a solution of a mixture of **24** and **25** (**24:25** = 97:3 or 11:89) (133 mg, 0.29 mmol) in CH_2Cl_2 (10 mL) cooled to 0 °C was added Dess−Martin periodinane (185 mg, 0.44 mmol), and the resulting mixture was stirred for 2 h at 0 °C. The mixture was quenched with $Na_2S_2O_3$ and extracted with toluene. The organic extracts were washed with $NaHCO_3$ and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid **26** or **29** (ca. 120 mg). To a suspension of methyltriphenylphosphonium bromide (156 mg, 0.44 mmol) in THF (5 mL) cooled to 0 °C was added *n*BuLi (1.43 M, 0.31 mL, 0.44 mmol), and the resulting mixture was stirred for 1 h at 0 °C. A solution of crude aldehyde **26** or **29** (50 mg, 0.11 mmol) in THF (5 mL) was added via a cannula, and the mixture was stirred for additional 12 h at room temperature. The mixture was quenched with NH_4Cl and extracted with toluene. The organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid. Purification by column chromatography (toluene) yielded vinylcyclopropane **27** or **30** (48 mg, 96%) as a white solid. **Vinylcyclopropane 27:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.14−0.19 (m, 1 H), 0.71 (s, 3 H), 0.89 (s, 9 H), 1.00 (s, 3 H), 3.42−3.53 (m, 1 H), 4.90 (dd, J = 2.0, 10.2 Hz, 1 H), 5.04 (dd, J = 2.0, 17.0 Hz, 1 H), 5.31−5.32 (m, 1 H), 5.58 (ddd, J = 8.9, 10.2, 17.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −4.6, 10.8, 13.0, 18.3, 19.3, 19.5, 20.4, 20.8, 24.6, 26.0, 28.6, 32.0, 32.1, 36.7, 37.4, 38.5, 42.5, 42.8, 50.0,

50.5, 56.2, 72.6, 112.7, 121.1, 140.0, 141.6. **Vinylcyclopropane 30:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.33 (dd, J = 5.0, 9.3 Hz, 1 H), 0.73 (s, 3 H), 0.89 (s, 9 H), 1.02 (s, 3 H), 3.43−3.54 (m, 1 H), 4.94 (dd, J = 2.1, 10.2 Hz, 1 H), 5.08 (dd, J = 2.1, 17.0 Hz, 1 H), 5.31−5.32 (m, 1 H), 5.61 (ddd, J = 8.5, 10.2, 17.0 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ −4.6, 11.7, 13.0, 17.6, 18.3, 19.1, 19.5, 20.8, 24.7, 25.9, 27.9, 31.9, 32.0, 32.1, 36.7, 37.4, 38.4, 42.8, 50.6, 50.9, 55.9, 72.6, 113.6, 121.1, 138.8, 141.6. Anal. Calcd for $C_{30}H_{50}OSi$: C, 79.23; H, 11.08. Found: C, 79.01; H, 10.86 (as a mixture of **29** and **32**).

Preparation of 31. To a suspension of ethyltriphenylphosphonium bromide (163 mg, 0.44 mmol) in THF (5 mL) cooled to 0 °C was added *n*BuLi (1.43 M, 0.31 mL, 0.44 mmol), and the resulting mixture was stirred for 1 h at 0 °C. A solution of crude aldehyde **27** (50 mg, 0.11 mmol, **26:29** = 27:73) in THF (5 mL) was added, and the mixture was stirred for 12 h at room temperature. The mixture was quenched with NH_4Cl and extracted with toluene. The organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid. Purification by column chromatography (toluene) yielded (1-propenyl)cyclopropane (51 mg, 99%, *E:Z* = 22:78, inseparable mixture) as a white solid. **(*Z*)-31:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.21 (dd, J = 5.2, 9.7 Hz, 1 H), 0.73 (s, 3 H), 0.89 (s, 9 H), 1.01 (s, 3 H), 1.71 (dd, J = 1.6, 6.8 Hz, 3 H), 3.43−3.53 (m, 1 H), 5.10 (ddq, J = 1.6, 9.1, 10.6 Hz, 1 H), 5.31−5.32 (m, 1 H), 5.37−5.55 (m, 1 H); the characteristic ^{13}C NMR signals (75.5 MHz, $CDCl_3$) δ 121.1, 124.2, 130.7. Anal. Calcd for $C_{31}H_{52}OSi$: C, 79.42; H, 11.18. Found: C, 79.23; H, 11.10 (as an *E*/*Z* mixture). The characteristic ^{1}H NMR signals of (*E*)-**31**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (dd, J = 1.6, 6.4 Hz, 3 H), 5.22 (ddq, J = 1.6, 8.5, 15.2 hz, 1 H).

Preparation of Steroids 28, 21. Steroid 28. Compound **27** (32 mg, 0.07 mmol) was treated with "Cp_2Zr" and acetone as described for **5a** to give acetone-adduct (25 mg, 68%). To a solution of acetone-adduct (19 mg, 0.03 mmol) in toluene (1 mL) and CH_3CN (1 mL) cooled to 0 °C was added dropwise aqueous HF (46%, 0.11 mL), and the resulting mixture was stirred for 2 h at room temperature. The mixture was diluted with toluene and water, separated, and extracted with toluene. The organic extracts were washed with water, dried ($MgSO_4$), filtered, and concentrated in vacuo to give a crude solid. Purification by column chromatography (toluene:EtOAc = 5:1) followed by recrystallization (MeOH) yielded pure **28** (12 mg, 60% yield from the calculated amount of **27**) as a white solid. The NMR spectra of the synthesized product **28** was identical to the authentic sample: mp 204.5−207.1 °C, $[\alpha]^{27}_D$ = −54.48° (*c* 0.41, $CHCl_3$) {lit.[12v] mp 205−205.5 °C, $[\alpha]_D$ = −54.35° (*c* 0.471, $CHCl_3$)}.

Steroid 21 (R′ = H). The experimental procedure was the same as that described for the preparation of **28**. The major isomeric mixture of vinylcyclopropane **30** (15 mg, 0.03 mmol, **27:30** = 27:73) was treated with "Cp_2Zr" followed by acetone to give acetone-adduct. The adduct was deprotected by HF−CH_3CN−toluene, and the resulting crude solid was purified and recrystallized (MeOH) to give pure **21** (R′ = H) (5 mg, 47% yield from the calculated amount of **32**). The synthesized material **21** (R′ = H) was identical to an authentic sample: mp 175.0−177.3 °C, $[\alpha]^{28}_D$ = −51.42° (*c* 0.35, $CHCl_3$) {lit.[12v] mp 178.0−178.5 °C, $[\alpha]_D$ = −51.38° (*c* 0.253, $CHCl_3$)}.

Steroid 21 (R′ = CH_3). The experimental procedure was the same as that described for the preparation of **14a**. The *E*/*Z* mixture of (1-propenyl)cyclopropane **31** (11 mg, 0.02 mmol) was treated with "Cp_2Zr" followed by thermal isomerization and the addition of acetone to give acetone-adduct (6 mg, 45%). The adduct was deprotected by HF−CH_3CN−toluene, and the resulting crude solid was purified and recrystallized (MeOH) to give pure **21** (R′ = CH_3). The synthesized material **21** (R′ = CH_3) was identical to an authentic sample: mp 166.6−168.0 °C, $[\alpha]^{30}_D$ = −92.86° (*c* 0.11, $CHCl_3$) (lit.[13] mp 168.5−169.5 °C).

Supporting Information Available: Procedures and characterization data of the intermediates for **1**, **12**, and **23**, copies of ^{1}H and ^{13}C NMR spectra for all new compounds without elementary analysis data and synthesized steroids **(21, 28)**, and an ORTEP drawing for 3,5-dinitrobenzoate of **14a** (64 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; seen any current masthead page for ordering information.

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