Enantioselective Preparation of 1,3-Cyclohexadiene and 1,4-Cycloheptadiene Derivatives: Synthesis of (+)-Dictyopterene C′

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Starting from optically active 5-trimethylsilyl-2-cyclohexen-1-one derivatives, the title dienes were synthesized by using silicon-mediated 1,4-elimination as a key step. A straightforward synthesis of the unnatural enantiomer of (−)-dictyopterene C′ utilizing the method was also carried out.

Recently, 1,3-cyclohexadienes have attracted considerable attention as useful intermediates for stereo-controlled natural product syntheses using, for instance, intramolecular Diels–Alder reactions[1] and palladium-catalyzed intramolecular 1,4-additions.[2] Though many methods for the preparation of 1,3-cyclohexadienes have been reported,[3] only a limited number of methods for optically active 1,3-cyclohexadiene derivatives are known.[3b] Thus, new and efficient methods for the preparation of optically active types are desirable for enantioselective syntheses.

In connection with our interest in utilizing optically active 5-trimethylsilyl-2-cyclohexen-1-ones **5** in natural-product synthesis,[4] we planned to open a new route to optically active 1,3-cyclohexadienes **1** and 1,4-cycloheptadienes **2** from **5** via the same intermediate **4** by using 1,4-elimination of a trimethylsilyl group and an oxygen moiety intervening a double bond or a cyclopropyl group (Scheme 1).

The preparation of **4** from **5**, which were synthesized by a previously reported method,[5] was envisioned as outlined in Scheme 2.

The reduction of **5** with $NaBH_4$ in the presence (conditions A[6]) or absence (conditions B) of $CeCl_3 \cdot 7H_2O$ was examined (Scheme 3). The results of a series of reductions are summarized in Table 1. The data show that the addition of $CeCl_3 \cdot 7H_2O$ greatly contributes to the diastereoselectivity (Entries 2 and 3).

Since the stereoisomers obtained by the reduction of **5** are chromatographically inseparable, the following Claisen rearrangement of **6** to **7** was examined by using diastereomeric mixtures. Though the Johnson[7] or Ireland[8] protocol resulted in a complex mixture of products, the Eschenmoser method[9] using *N*,*N*-dimethylacetamide dimethyl acetal in refluxing xylene gave the rearranged product **7** in good to high yields (Scheme 4, Table 2).

In the cases of (−)-**7c**, (+)-**7d**, and (+)-**7e**, minor products derived from the trans diastereomers of **6c**—**e** were chromatographically separable.

Iodo-lactonization of **7** in THF–H_2O at room temperature, followed by dehydroiodination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing toluene for 2—4 h, furnished lactone **4** in good to excellent yields (69%-quant, Table 3, Scheme 5). At this stage, a trace amount of contaminated diastereomers of (−)-**4a** and (−)-**4b** was easily removed by recrystallization.

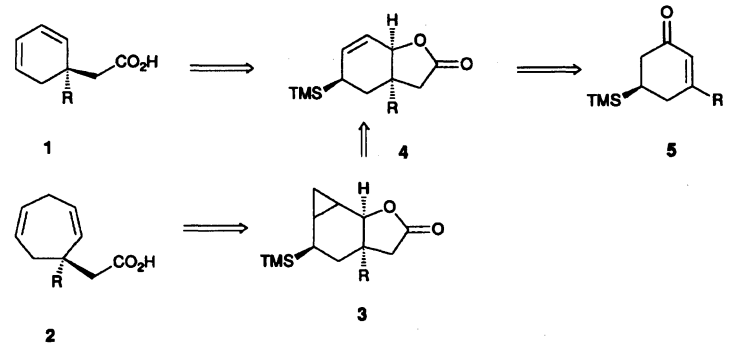
With diastereomerically pure **4a**—**e** on hand, we examined the 1,4-elimination of the trimethylsilyl group and oxygen moiety. A treatment of **4a**—**c** with toluenesulfonic acid in refluxing dichloromethane for 1 h gave the expected 1,3-cyclohexadienes **1** in high yields. Instead of an acid treatment, the exposure of (+)-**4c** to tetrabutylammonium fluoride (TBAF) in THF at room temperature for 0.5 h also gave (+)-**1c** in quantitative yield (Scheme 6, Table 4).

As an extension of the above protocol, we examined the synthesis of the 1,4-cycloheptadiene system via a one carbon ring expansion using a cycloproyl group intervenient 1,4-elimination of silanol.[10] Our initial trial for the cyclopropanation of **4c** by the Simmons-Smith reaction[11] with diethylzinc and diiodomethane resulted in a quantitative formation of the cyclohexadiene derivative **1c**. To stabilize the substrate under the reaction conditions, lactone **4** was converted to the corresponding diol derivative **9** by lithium aluminum hydride reduction. The formation of a small amount of cyclohexadiene derivative was observed under the reduction conditions. The Simmons–Smith reaction of diol **9** proceeded smoothly to give the expected cyclopropane derivative **10** in high yield (Scheme 7). Though the stereochemistry of the cyclopropane ring was not examined, the structure is expected to be as depicted below based on a mechanistic consideration.[12]

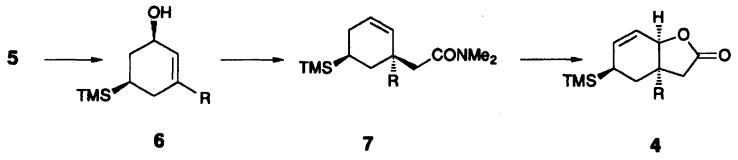
The treatment of **10** with trifluoroacetic acid at room temperature for a short period afforded cycloheptadiene **11** (Scheme 8). When (−)-**10a** (R=H) was used, the yield of (+)-**11a** was not so high as in the case of the reaction from (+)-**10c** to (−)-**11c** (R=Ph). Presumably, one of the reasons for the fair yield is the volatility of the product (−)-**11a**. These two alcohol derivatives of cycloheptadiene were somewhat unstable. When they were left at room temperature gradual decomposition was observed.

To demonstrate the applicability of the above-mentioned protocol, we examined the synthesis of (+)-dictyopterene C′, (+)-**13** (Scheme 9).

(*R*)-(−)-Dictyopterene C′ isolated from the Hawai-



Scheme 1.

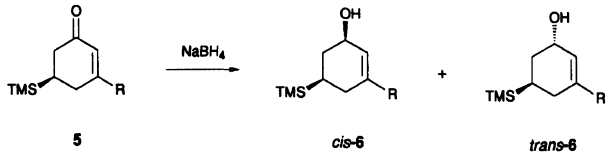


Scheme 2.

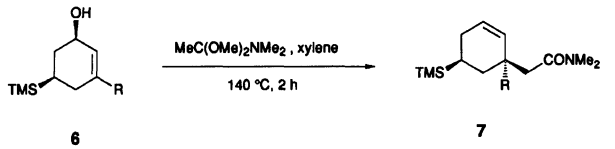
Table 1. Reduction of **5** with $NaBH_4$

Entry	Enone	R	Conditions[b]	Yield **6**/%	Ratio (*cis*/*trans*)
1	(−)-**5a**	H	A	Quant	≥20/1[c]
2	(+)-**5b**[a]	Me	A	90	≥20/1[c]
3	(+)-**5b**[a]	Me	B	Quant	6/1
4	(+)-**5c**[a]	Ph	A	Quant	≥20/1[c]
5	(−)-**5d**	*p*-Tol	B	91	10/1
6	(−)-**5e**	*p*-$MeOC_6H_4$	B	89	10/1

a) The absolute structures of **1b**—**8b** and **1c**—**11c** are antipodal to the depicted structures. b) Conditions A; reduction was carried out in the presence of $CeCl_3 \cdot 7H_2O$ in EtOH–H_2O at −20 °C. Conditions B; reduction was carried out in MeOH at 0 °C. c) A trace amount of *trans* isomer was detected by ^{13}C NMR.



Scheme 3.



Scheme 4.

Table 2. The Claisen Rearrangement of **6**

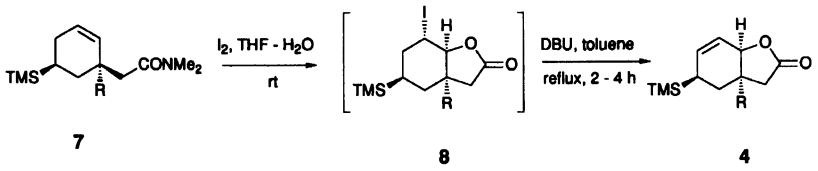
Entry	**6**	R	Product	Yield/%
1	(+)-**6a**	H	(+)-**7a**	90
2	(−)-**6b**	Me	(−)-**7b**	70
3	(−)-**6c**	Ph	(−)-**7c**	72
4	(+)-**6d**	*p*-Tol	(+)-**7d**	70
5	(+)-**6e**	*p*-$MeOC_6H_4$	(+)-**7e**	77

Table 3. Synthesis of Lactone **4**

Entry	Product	R	Yield/%
1	(−)-**4a**	H	85
2	(−)-**4b**	Me	75
3	(+)-**4c**	Ph	77
4	(+)-**4d**	*p*-Tol	69
5	(+)-**4e**	*p*-$MeOC_6H_4$	Quant

ian seaweeds *Dictyopteris plagiogramma* (Montagne) Vickers and *Daustralis* Sonder[13] is the sperm attractant of female gametes of the North Atlantic phaeophyte *Dictyota dichotoma*.[14] Known enantioselective syntheses of the cycloheptadiene compound are based on a Cope rearrangement of a divinylcyclopropane derivative.[15]

Tosylation of alcohol (+)-**11a** with excess toluenesulfonyl chloride gave (−)-**12** in 78% yield. The reaction of (−)-**12** with ethylmagnesium bromide (1.2 equiv) in the presence of Li_2CuCl_4 (0.2 equiv) under the reported reaction conditions[16] gave a disappointing result (<14%). The use of a large excess (20 equiv) of the Grignard reagent and 1 equivalent of Li_2CuCl_4 in THF gave (+)-**13** $[[\alpha]_D^{15}$ +15.12° (*c* 0.44, $CHCl_3$), lit, for (−)-**13**: $[\alpha]_D^{22}$ −12.12° (*c* 7.32, $CHCl_3$),[13] $[\alpha]_D^{25}$

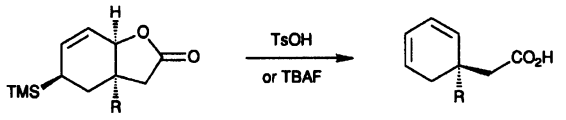


7 8 4

Scheme 5.

Table 4. Synthesis of Cyclohexadiene-1-acetic Acid **1**

Entry	R	Reagent	(equiv)	Product		$[\alpha]_D$	Yield/%
1	H	TsOH	(1.0)	(−)-**1a**	−158.9°	(*c* 1.0, EtOH)	74
2	Me	TsOH	(1.0)	(+)-**1b**	+74.9°	(*c* 0.9, $CHCl_3$)	92
3	Ph	TsOH	(1.0)	(+)-**1c**	+76.2°	(*c* 1.0, $CHCl_3$)	Quant
4	Ph	TBAF	(1.0)	(+)-**1c**	+73.2°	(*c* 1.2, $CHCl_3$)	Quant



4 1

Scheme 6.

−15.50° (*c* 1.74, $CHCl_3$)[15a)]] in 55% yield, which was identical with the reported natural compound, except for the sign of $[\alpha]_D$.

Experimental

The specific rotation was measured on a Horiba SEPA-200 in $CHCl_3$. IR was recorded on a Hitachi 260-50. ^1H and ^{13}C NMR were recorded on a JEOL JNM-EX270 in $CDCl_3$.

(−)-(1*R*,5*R*)-5-Trimethylsilyl-2-cyclohexen-1-ol (−)-6a. To a solution of (−)-**5a** (2.62 g, 15.6 mmol) in EtOH (110 ml)–H_2O (120 ml) was added a solution of $CeCl_3 \cdot 7H_2O$ (6.36 g, 17.1 mmol) in H_2O (30 mL) at room temperature; the mixture was cooled to −15 °C. After the addition of $NaBH_4$ (0.68 g, 18 mmol), the reaction mixture was stirred at that temperature for 0.5 h. Acetone and brine were added to the mixture. Extraction with ether and purification by silica-gel column chromatography (hexane : AcOEt=10 : 1) gave (−)-**6a** (2.58 g, 100%) containing a trace amount of diastereoisomer. Oil: $[\alpha]_D^{25}$ −34.75° (*c* 0.975). ^1H NMR δ=0.03 (9H, s), 0.93—0.98 (1H, m), 1.20 (1H, dt, *J*=9.9 and 12.2 Hz), 1.78—2.08 (1H, br s), 1.86—1.90 (2H, m), 2.05 (1H, dd, *J*=5.3 and 11.5 Hz), 4.09—4.15 (1H, br s) 5.68 (1H, d, *J*=10.2 Hz), 5.81 (1H, dt, *J*=2.2 and 10.2 Hz); ^{13}C NMR δ=−3.8, 20.2, 25.7, 33.3, 68.2, 129.9, 131.6; IR (neat) 3320 cm^{-1} (OH). Found: C, 63.15; H, 10.82%. Calcd for $C_9H_{18}OSi$: C, 63.46; H, 10.65%.

(+)-(1*S*,5*S*)-3-Methyl-5-trimethylsilyl-2-cyclohexen-1-ol (+)-6b. Oil: $[\alpha]_D^{20}$ +68.93° (*c* 1.6). ^1H NMR δ=−0.01 (9H, s), 0.92 (1H, ddt, *J*=5.6, 13.9, and 8.6 Hz), 1.10 (1H, ddd, *J*=9.6, 11.9, and 13.9 Hz), 1.62—1.75 (1H, br s), 1.68 (3H, s), 1.79 (2H, d, *J*=8.6 Hz), 2.10 (1H, ddd, *J*=0.3, 5.6, and 11.9 Hz), 4.14—4.27 (1H, s), 5.40 (1H, br d, *J*=1.6 Hz); ^{13}C NMR δ=−3.8, 20.4, 23.2, 30.7, 33.4, 68.9, 126.0, 137.9; IR (neat) 3320 cm^{-1} (OH). Found: C, 64.88, H, 11.18%. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.94%.

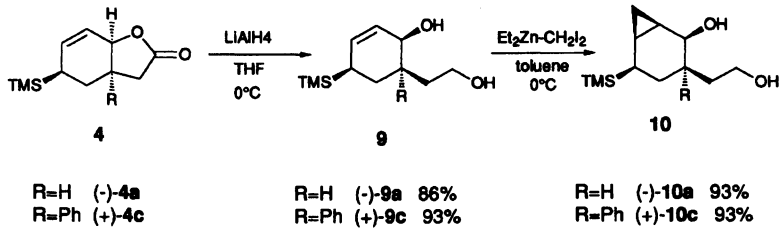
(−)-(1*S*,5*S*)-3-Phenyl-5-trimethylsilyl-2-cyclohexen-1-ol (−)-6c. Oil: $[\alpha]_D^{19.5}$ −76.59° (*c* 0.9). ^1H NMR δ=0.04 (9H, s), 1.04 (1H, dddd, *J*=2.0, 5.9, 10.9, and 13.9 Hz), 1.24 (1H, ddd, *J*=1.3, 5.9, and 12.2 Hz), 2.30—2.42 (1H, m), 2.70 (1H, dddd, *J*=2.3, 3.9, 10.9, and 17.5 Hz), 4.48 (1H, br s), 6.06 (1H, br s), 7.22—7.42 (5H, m); ^{13}C NMR δ=−3.7, 20.5, 28.2, 33.2, 69.2, 125.4, 127.3, 128.3, 128.3, 139.9, 141.3; IR (neat) 3310 cm^{-1} (OH). Found: C, 72.83; H, 9.38%. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00%.

(−)-(1*R*,5*R*)-3-(*p*-Tolyl)-5-trimethylsilyl-2-cyclohexen-1-ol (−)-6d. Mp 81.0—81.5 °C (hexanne); $[\alpha]_D^{16}$ −83.07° (*c* 0.8). ^1H NMR δ=0.04 (9H, s), 1.03 (1H, dddd, *J*=2.0, 5.6, 11.2, and 13.9 Hz), 1.22 (1H, ddd, *J*=9.9, 12.2, and 13.9 Hz), 1.66 (1H, br s), 2.09—2.19 (1H, m), 2.21—2.34 (2H, m), 2.34 (3H, s), 4.38 (1H, br s), 6.02 (1H, d, *J*=1.0 Hz), 7.12 (2H, d, *J*=7.9 Hz), 7.26 (2H, d, *J*=7.9 Hz); ^{13}C NMR δ=−3.7, 20.4, 21.1, 28.1, 33.2, 69.2, 125.2, 127.6, 129.0, 137.0, 138.4, 139.5; IR (KBr) 3290 cm^{-1} (OH). Found: C, 73.49; H, 9.55%. Calcd for $C_{16}H_{24}OSi$: C, 73.78; H, 9.29%.

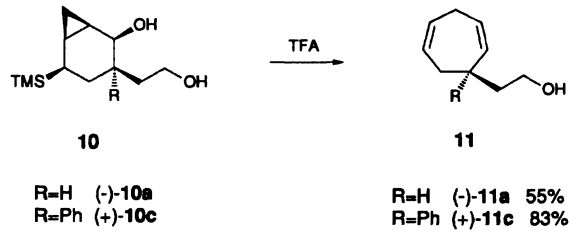
(−)-(1*S*,5*S*)-3-(*p*-Methoxyphenyl)-5-trimethylsilyl-2-cyclohexen-1-ol (−)-6e. Mp 119.5—120 °C (hexane); $[\alpha]_D^{19}$ −84.5° (*c* 1.5). ^1H NMR δ=0.04 (9H, s,), 1.04 (1H, dddd, *J*=2.0, 5.9, 10.9, and 13.9 Hz), 1.20 (1H, ddd, *J*=9.9, 12.2, and 13.9 Hz), 1.67 (1H, s), 2.12 (1H, ddd, *J*=1.7, 5.9, and 12.2 Hz), 2.22—2.32 (2H, m), 3.81 (3H, s), 4.44 (1H, m), 5.98 (1H, s), 6.86 (2H, d, *J*=8.9 Hz), 7.35 (2H, d, *J*=8.9 Hz); ^{13}C NMR δ=−3.7, 20.5, 28.2, 33.2, 55.3, 69.3, 113.6, 126.4, 126.8, 133.8, 139.0, 158.9; IR (KBr) 3325 cm^{-1} (OH). Found: C, 69.73; H, 9.10%. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75%.

(+)-(1*S*,5*S*)-*N*,*N*-Dimethyl-5-trimethylsilyl-2-cyclohexene-1-acetamide (+)-7a. Under an Ar atmosphere, a solution of (−)-**6a** (1.25 g, 7.34 mmol) and *N*,*N*-dimethylacetamide dimethyl acetal (stabilized with 10% MeOH, 1.66 g, 11.25 mmol) in dry xylene (11.5 mL) was gradually heated up to 140 °C and then refluxed for 2 h, with removal of the methanol formed. After being cooled to a room temperature, the reaction mixture was directly separated by silica-gel column chromatography (hexane : AcOEt=4 : 1) to give (+)-**7a** (1.60 g, 90%).

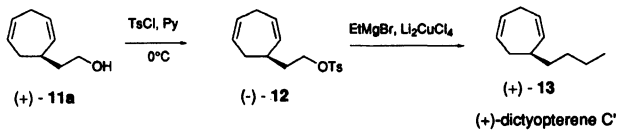
Oil: $[\alpha]_D^{22}$ +0.41° (*c* 1.2). ^1H NMR δ=−0.03 (9H, s), 0.89—1.01 (2H, m), 1.79—2.06 (3H, m), 2.39 (2H, d, *J*=7.4 Hz), 2.61—2.75 (1H, m), 3.01 (3H, s), 3.05 (3H, s) 5.61 (1H, d, *J*=10.2 Hz), 5.81 (1H, ddt, *J*=4.6, 10.2, and 2.3 Hz); ^{13}C NMR δ=−3.7, 21.3, 25.9, 30.8, 33.9, 35.4, 37.4, 39.9,



Scheme 7.



Scheme 8.



Scheme 9.

128.4, 131.2, 206.8; IR (neat) 1640 cm^{-1} (C=O). Found: C, 65.07; H, 10.44; N, 5.61%. Calcd for $C_{13}H_{25}ONSi$: C, 65.21; H, 10.53; N, 5.85%.

(−)-(1*R*,5*R*)-*N*,*N*-Dimethyl-1-methyl-5-trimethylsilyl-2-cyclohexene-1-acetamide (−)-7b. Oil: $[\alpha]_D^{24}$ −21.91° (*c* 0.9). ^1H NMR δ=−0.01 (9H, s), 1.00 (1H, dddd, J=2.3, 5.3, 11.6, and 16.8 Hz), 1.13 (3H, s), 1.75—1.86 (3H, m), 1.96 (1H, dt, J=17.2 and 4.0 Hz), 2.27 (1H, d, J=14.2 Hz), 2.95 (3H, s), 5.32—5.74 (1H, m); ^{13}C NMR δ=−3.7, 17.3, 25.9, 26.4, 35.1, 35.4, 36.9, 37.4, 38.3, 45.2, 126.5, 135.4, 171.4; IR (neat) 1640 cm^{-1} (C=O). Found: C, 66.18; H, 10.71; N, 5.53%. Calcd for $C_{14}H_{27}ONSi$: C, 66.34; H, 10.74: N, 5.53%.

(−)-(1*S*,5*R*)-*N*,*N*-Dimethyl-1-phenyl-5-trimethylsilyl-2-cyclohexene-1-acetamide (−)-7c. Mp 88 °C (hexane); $[\alpha]_D^{21.5}$ −44.91° (*c* 1.2). ^1H NMR δ=0.10 (9H, s), 0.65—0.79 (1H, m), 1.78 (1H, d, J=13.2 Hz), 1.85—2.06 (2H, m), 2.37 (1H, d, J=13.2 Hz), 2.71 (1H, d, J=14.5 Hz), 2.76 (3H, s), 2.82 (1H, d, J=14.5 Hz), 2.90 (3H, s), 6.95 (1H, ddd, J=3.0, 4.0, and 10.2 Hz), 6.36 (1H, dq, J=2.0 and 10.2 Hz), 7.32—7.45 (5H, m); ^{13}C NMR δ=−3.8, 17.0, 26.4, 35.3, 36.8, 37.7, 42.6, 45.6, 125.7, 127.0, 128.0, 128.8, 133.1, 147.2, 170.6; IR (KBr) 1650 cm^{-1} (C=O). Found: C, 72.56; H, 9.28; N, 4.40%. Calcd for $C_{19}H_{29}ONSi$: C, 72.32, H, 9.26; N, 4.44%.

(+)-(1*R*,5*S*)-*N*,*N*-Dimethyl-1-(*p*-tolyl)-5-trimethylsilyl-2-cyclohexene-1-acetamide (+)-7d. Mp 79.5—80 °C (hexane); $[\alpha]_D^{15}$ +64.12° (*c* 0.7). ^1H NMR δ=0.10 (9H, s), 0.65—0.82 (1H, m), 1.75 (1H, t, J=13.2 Hz), 1.95—2.10 (2H, m), 2.25—2.38 (1H, m), 2.40 (3H, s), 2.70 (1H, d, J=14.2 Hz), 2.74 (3H, s), 2.77 (1H, d, J=14.2 Hz), 2.89 (3H, s), 5.95—6.05 (1H, m), 6.31 (1H, d, J=8.6 Hz), 7.15—7.35 (4H, m); ^{13}C NMR δ=−3.8, 17.0, 20.9, 26.4, 35.4, 36.6, 37.7, 42.2, 46.7, 126.8, 128.7, 133.3, 135.0, 144.2, 170.7; IR (KBr) 1635 cm^{-1} (C=O). Found: C, 72.90; H, 9.21; N, 4.21%. Calcd for $C_{20}H_{31}ONSi$: C, 72.89; H, 9.48; N, 4.25%.

(+)-(1*R*,5*S*)-*N*,*N*-Dimethyl-1-(*p*-methoxyphenyl)-5-trimethylsilyl-2-cyclohexene-1-acetamide (+)-7e. Mp 96.0—96.5 °C (hexane); $[\alpha]_D^{18}$ +76.56° (*c* 0.8). ^1H NMR δ=0.09 (9H, s), 0.65—0.77 (1H, m), 1.76 (1H, t, 13.2 Hz), 1.96—2.02 (2H, m), 2.31 (1H, d, J=13.2 Hz), 2.77 (3H, s), 2.79 (1H, d, J=14.2 Hz), 2.86 (1H, d, J=14.2 Hz), 2.90 (3H, s), 3.88 (3H, s), 6.01 (1H, dt, J=3.3 and 10.2 Hz), 6.31 (1H, dq, J=10.2 and 1.7 Hz), 6.84 (2H, d, J=6.6 Hz), 7.22 (2H, d, J=6.6 Hz); ^{13}C NMR δ=−3.8, 16.9, 26.4, 35.3, 36.9, 37.7, 42.0, 45.7, 55.1, 113.3, 128.0, 128.6, 133.4, 139.2, 157.4, 170.7; IR (KBr) 1620 cm^{-1} (C=O). Found: C, 69.26; H, 8.97; N, 4.01%. Calcd for $C_{20}H_{31}O_2NSi$:C, 69.52; H, 9.04; N, 4.05%.

(−)-(3a*S*,5*R*,7a*S*)-3a,4,5,7a-Tetrahydro-5-trimethylsilyl-2(3*H*)-benzofuranone (−)-4a. To a solution of (+)-**7a** (1.56 g, 6.51 mmol) in THF (35 mL)–H_2O (30 mL) was added iodine (6.71 g, 26.44 mmol); the mixture was stirred at room temperature for 24 h. After the addition of aq. Na_2SO_3, the mixture was extracted with Et_2O and the solvent was removed under reduced pressure. To a toluene (65 mL) solution of the residue was added DBU (2.94 mL, 19.55 mmol); the mixture was refluxed for 2 h. Extraction with Et_2O and purification by silica-gel column chromatography (hexane : AcOEt=8 : 1) gave (−)-**4a** (1.18 g, 86%). Mp 92.0—92.5 °C (hexane); $[\alpha]_D^{15}$ −15.22° (*c* 1.2). ^1H NMR δ=0.02 (9H, s), 1.14 (1H, q, J=13.2 Hz), 1.45—1.55 (1H, m), 1.70 (1H, dt, J=13.2 and 4.6 Hz), 2.27 (1H, d, J=17.2 Hz), 2.37 (1H, ddt, J=7.6, 13.2, and 5.0 Hz), 2.86 (1H, dd, J=7.6 and 17.2 Hz), 4.72 (1H, br t, J=5.0 Hz), 5.95 (1H, ddd, J=3.0, 5.0, and 9.9 Hz), 6.13 (1H, d, J=9.9 Hz); ^{13}C NMR δ=−3.6, 25.3, 25.5, 34.6, 37.0, 75.5, 121.5, 136.6, 176.8; IR (KBr) 1760 cm^{-1} (C=O). Found: C, 62.66; H, 8.83%. Calcd for $C_{11}H_{18}O_2Si$: C, 62.81; H, 8.63%.

(−)-(3a*R*,5*R*,7a*S*)-3a,4,5,7a-Tetrahydro-3a-methyl-5-trimethylsilyl-2(3*H*)-benzofuranone (−)-4b. Mp 149.5 °C (hexane); $[\alpha]_D^{19}$ −38.89° (*c* 0.7). ^1H NMR δ=0.03 (9H, s), 1.09 (3H, s), 1.31—1.46 (2H, m), 1.57—1.60 (1H, m), 2.32 (1H, d, J=17.2 Hz), 2.67 (1H, d, J=17.2 Hz), 4.31 (1H, d, J=4.6 Hz), 5.58 (1H, ddd, J=3.0, 5.0, and 9.9 Hz), 6.07 (1H, d, J=9.9 Hz); ^{13}C NMR δ=−3.6, 20.3, 23.1, 30.5, 36.8, 44.7, 80.4, 119.8, 135.8, 176.3; IR (KBr) 1760 cm^{-1} (C=O). Found: C, 63.98; H, 9.06%. Calcd for $C_{12}H_{20}O_2Si$: C, 64.23; H, 8.99%.

(+)-(3a*R*,5*R*,7a*S*)-3a,4,5,7a-Tetrahydro-3a-phenyl-5-trimethylsilyl-2(3*H*)-benzofuranone (+)-4c. Mp 81.5—82.0 °C (hexane); $[\alpha]_D^{17}$ +5.34 °C (*c* 1.0). ^1H NMR δ=0.03 (9H, s), 1.12—1.18 (1H, m), 1.66 (1H, t, J=14.2 Hz), 1.73 (1H, dd, J=2.3 and 14.2 Hz), 2.89 (1H, d, J=17.2), 2.99 (1H, d, J=17.2 Hz) 4.95 (1H, d, J=13.3 Hz), 6.16—

6.26 (2H, m), 7.14—7.38 (5H, m); ^{13}C NMR δ=−3.6, 22.8, 33.4, 44.3, 44.9, 77.9, 121.3, 125.8, 127.0, 128.6; IR (KBr) 1775 cm^{-1} (C=O). Found: C, 71.23; H, 7.84%. Calcd for $C_{17}H_{22}O_2Si$: C, 71.28; H, 7.74%.

(+)-(3a*R*,5*R*,7a*S*)-3a,4,5,7a-Tetrahydro-3a-(*p*-tolyl)-5-trimethylsilyl-2(3*H*)-benzofuranone (+)-4d. Mp 104—105 °C (hexane); $[\alpha]_D^{17}$+2.43° (*c* 0.7). ^{1}H NMR δ=0.03 (9H, s), 1.17—1.21 (1H, m), 1.61—1.74 (2H, m), 2.37 (3H, s), 2.86 (1H, d, *J*=16.8 Hz), 2.99 (1H, d, *J*=16.8 Hz), 4.92—4.94 (1H, m), 6.14—6.25 (2H, m), 7.04 (2H, d, *J*=8.3 Hz), 7.14 (2H, d, *J*=8.3 Hz); ^{13}C NMR δ=−3.5, 21.0, 22.9, 33.4, 44.5, 44.6, 121.3, 125.8, 129.3, 136.7, 137.8, 139.4, 175.4; IR (KBr) 1775 cm^{-1} (C=O). Found: C, 71.88; H, 8.22%. Calcd for $C_{18}H_{24}O_2Si$: C, 71.95; H, 8.05%.

(+)-(3a*S*,5*S*,7a*R*)-3a,4,5,7a-Tetrahydro-3a-(*p*-methoxyphenyl)-5-trimethylsilyl-2(3*H*)-benzofuranone (+)-4e. Mp 95.0—95.5 °C (hexane); $[\alpha]_D^{24}$ +7.22° (*c* 0.4). ^{1}H NMR δ=0.03 (9H, s), 1.14—1.23 (1H, m), 1.60—1.74 (2H, m), 2.84 (1H, d, *J*=17.2 Hz), 2.96 (1H, d, *J*=17.2 Hz), 3.83 (3H, s), 4.90 (1H, dd, *J*=1.0 and 4.3 Hz), 6.13—6.24 (2H, m), 6.88 (2H, d, *J*=8.9 Hz), 7.07 (2H, d, *J*=8.9 Hz); ^{13}C NMR δ=−3.5, 14.2, 22.9, 33.4, 44.6, 55.2, 60.4, 78.2, 113.9, 121.3, 127.0, 134.4, 137.8, 175.4; IR (KBr) 1760 cm^{-1} (C=O). Found: C, 67.99, H, 7.93%. Calcd for $C_{18}H_{24}O_3Si$: C, 68.31; H, 7.64%.

(+)-(*R*)-1-Phenyl-2,4-cyclohexadiene-1-acetic Acid (+)-1c. A solution of (−)-**4c** (127 mg, 0.45 mmol) and *p*-toluenesulfonic acid (76.6 mg, 0.45 mmol) in dichloromethane (5 mL) was refluxed for 1 h. After usual workup, purification by silica-gel column chromatography (hexane : AcOEt=1 : 3) gave (+)-**1c** (96 mg, quant). Mp 84 °C (hexane); $[\alpha]_D^{19}$ +84.84° (*c* 1.1). ^{1}H NMR δ=2.48 (1H, ddd, *J*=1.7, 4.6, and 17.5 Hz), 2.60 (1H, ddd, *J*=2.0, 4.0, and 17.5 Hz), 2.76 (1H, d, *J*=16.8 Hz), 2.92 (1H, d, *J*=16.8 Hz), 5.74 (1H, ddd, *J*=4.0, 4.6, and 6.0 Hz), 5.82—5.97 (1H, m), 6.06 (1H, dd, *J*=6.0 and 9.6 Hz), 6.15 (1H, d, *J*=9.6 Hz), 7.17—7.38 (5H, m); ^{13}C NMR δ=37.1, 40.5, 43.1, 128.3, 124.2, 125.1, 126.0, 126.4, 128.2, 133.0, 145.9, 177.6; IR (KBr) 1710 cm^{-1} (C=O). Found: C, 78.86; H, 6.74%. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59%.

(−)-(*R*)-2,4-Cyclohexadiene-1-acetic Acid (−)-1a. Oil: $[\alpha]_D^{15.5}$ −158.95° (*c* 1.0, EtOH). ^{1}H NMR δ=2.00—2.12 (1H, m), 2.32—2.46 (3H, m), 2.68—2.81 (1H, m), 5.71—5.80 (2H, m), 5.88—5.97 (2H, m), 10.83 (1H, br s); ^{13}C NMR δ=28.1, 29.4, 38.1, 124.0, 124.7, 125.2, 129.1, 179.0; IR (neat) 1710 cm^{-1} (C=O).

(+)-(*S*)-1-Methyl-2,4-cyclohexadiene-1-acetic Acid (+)-1b. Oil: $[\alpha]_D^{14}$ +74.91° (*c* 0.9). ^{1}H NMR δ=1.17 (3H, s), 2.13 (1H, dd, *J*=2.7 and 17.5 Hz), 2.15 (1H, dd, *J*=2.0 and 17.5 Hz), 2.31 (1H, d, *J*=14.9 Hz), 2.44 (1H, d, *J*=14.9 Hz), 2.31—2.44 (2H, m), 5.60—5.68 (1H, m), 5.72—5.80 (1H, m), 5.82—5.98 (2H, m), 11.35 (1H, br s); ^{13}C NMR δ=25.4, 33.2, 35.6, 43.4, 123.0, 123.4, 125.3, 134.7, 178.1; IR (neat) 1710 cm^{-1} (C=O).

(−)-(1*S*,4*R*,6*S*)-6-(2-Hydroxyethyl)-4-trimethylsilyl-2-cyclohexen-1-ol (−)-9a. To a cooled (0 °C) solution of (−)-**4a** (219 mg, 1.04 mmol) in dry ether (10 mL) was added $LiAlH_4$ (43.4 mg, 1.14 mmol). After 0.5 h, aqueous NH_4Cl was added and the mixture was filtered through a short pad of celite. Extraction with ether and purification by silica-gel column chromatography (hexane : AcOEt=1 : 1) gave (−)-**9a** (189.5 mg, 85%). Mp 92—93 °C (toluene); $[\alpha]_D^{16}$ −98.97° (*c* 1.1). ^{1}H NMR δ=−0.09 (9H, s), 1.32 (2H, t, *J*=13.0 Hz), 1.40—1.95 (4H, m), 1.95—2.75 (2H, br s), 3.68—3.81 (2H, m), 4.08 (1H, br s), 5.83—5.92 (2H, m); ^{13}C NMR δ=−3.5, 23.9, 27.6, 34.9, 37.9, 60.9, 65.1, 126.9, 133.0; IR (KBr) 3315 and 3230 cm^{-1} (OH). Found: C, 61.78; H, 10.33%. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.34%.

(+)-(1*R*,4*S*,6*R*)-6-(2-Hydroxyethyl)-6-phenyl-4-trimethylsilyl-2-cyclohexen-1-ol (+)-9c. Mp 109.5—110 °C (hexane); $[\alpha]_D^{16}$ +102.61° (*c* 1.0). ^{1}H NMR δ=−0.02 (9H, s), 1.09—1.13 (1H, m), 1.75—1.80 (1H, m), 1.84 (2H, d, *J*=8.9 Hz), 2.24 (1H, ddd, *J*=4.3, 9.2, and 13.5 Hz), 2.66 (1H, br s), 3.44 (1H, ddd, *J*=3.3, 9.2, and 12.5 Hz), 3.55 (1H, dt, *J*=4.3 and 12.5 Hz), 4.73 (1H, d, *J*=5.6 Hz), 5.71 (1H, dd, *J*=2.0 and 9.9 Hz), 5.99 (1H, ddd, *J*=3.0, 5.6, and 9.6 Hz), 7.18—7.35 (5H, m); ^{13}C NMR δ=−3.5, 24.4, 30.9, 42.4, 44.3, 59.3, 66.0, 125.6, 125.7, 127.0, 127.8, 133.4, 143.6; IR (KBr) 3400 cm^{-1} (OH). Found: C, 70.32; H, 8.94%. Calcd for $C_{17}H_{26}O_2Si$: C, 70.29; H, 9.02%.

(−)-(1*R*,2*S*,3*S*,5*R*,6*S*)-3-(2-Hydroxyethyl)-5-trimethylsilylbicyclo[4.1.0]heptan-2-ol (−)-10a. To a cooled (0 °C) solution of (−)-**9a** (124 mg, 0.58 mmol) in dry toluene (28 mL) were added diethylzinc (1.0 M solution in hexane, 2.8 mL) and diiodomethane (191.5 μL 2.30 mmol). After being stirred at that temperature for 2 h, the mixture was filtered through a short pad of silica gel. Purification by silica-gel column chromatography (hexane : AcOEt=1 : 1) gave (−)-**10a** (122 mg, 92%). Mp 78.5 °C (toluene); $[\alpha]_D^{20}$ −28.45° (*c* 0.7). ^{1}H NMR δ=0.00 (9H, s), 0.42—0.49 (2H, m), 0.94—1.20 (3H, m), 1.15—1.43 (2H, m), 1.44—1.75 (3H, m), 1.98 (2H, br s), 3.69 (1H, ddd, *J*=4.3, 7.6, and 17.8 Hz), 3.78 (1H, ddd, *J*=4.3, 6.3, and 17.8 Hz), 4.28 (1H, dd, *J*=4.3 and 8.3 Hz); ^{13}C NMR δ=−2.9, 2.1, 13.4, 15.4, 21.4, 23.1, 34.5, 40.3, 60.8, 65.2; IR (KBr) 3325 and 3380 cm^{-1} (OH). Found: C, 62.92; H, 10.63%. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%.

(+)-(1*S*,2*S*,3*R*,5*S*,6*R*)-3-(2-Hydroxyethyl)-3-phenyl-5-trimethylsilylbicyclo[4.1.0]heptan-2-ol (+)-10c. Mp 125.5—126 °C (hexane); $[\alpha]_D^{15}$ +59.47° (*c* 0.7). ^{1}H NMR δ=−0.06 (9H, s), 0.42—0.53 (2H, m), 0.62 (1H, dt, *J*=4.6 and 13.5 Hz), 0.74—0.85 (1H, m), 1.24—1.52 (3H, m), 1.71 (1H, dt, *J*=3.0 and 10.6 Hz), 2.05—2.17 (1H, m), 2.22 (1H, br s), 2.78 (1H, br s), 3.35 (1H, dd, *J*=1.7 and 8.6 Hz), 7.17—7.57 (5H, m); ^{13}C NMR δ=−2.9, 1.9, 12.8, 14.4, 16.8, 28.6, 41.7, 44.1, 59.5, 65.3, 125.6, 127.3, 128.3, 144.4; IR (KBr) 3440 and 3350 cm^{-1} (OH). Found: C, 71.36; H, 9.49%. Calcd for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27%.

(+)-(*S*)-2,5-Cycloheptadiene-1-ethanol (+)-11a. Trifluoroacetic acid (4 mL) was added to (−)-**10a** (119 mg, 0.52 mmol). After a homogeneous solution was obtained, volatiles were removed under reduced pressure. Purification of the residue by silica-gel column chromatography (hexane : AcOEt=1 : 5) gave (+)-**11a** (39.5 mg, 55%). Oil: $[\alpha]_D^{14}$ +3.79° (*c* 0.7). ^{1}H NMR δ=1.56—1.76 (3H, m), 2.05—2.19 (1H, m), 2.20—2.33 (1H, m), 2.64—2.73 (1H, m), 2.75 (1H, dt, *J*=5.0 and 19.1 Hz), 3.00 (1H, d, *J*=19.1 Hz), 3.71 (2H, t, *J*=7.0 Hz), 5.56—5.75 (4H, m); ^{13}C NMR δ=28.4, 32.8, 39.0, 61.0, 128.1, 128.3, 129.5, 135.7; IR (neat) 3320 cm^{-1} (OH).

(−)-(*S*)-1-Phenyl-2,5-cycloheptadiene-1-ethanol (−)-11c. Oil: $[\alpha]_D^{14}$ −4.93° (*c* 0.8). ^{1}H NMR δ=2.03 (1H, ddd, *J*=6.3, 8.6, and 14.5 Hz), 2.12 (1H, ddd, *J*=6.3, 8.6, and 14.5 Hz), 2.56 (1H, dd, *J*=6.9 and 14.2 Hz), 2.65—

2.94 (3H, m), 3.03 (1H, br s), 3.55—3.71 (2H, m), 5.48—5.84 (4H, m), 7.14—7.77 (5H, m); ^{13}C NMR δ=28.5, 39.1, 45.2, 45.8, 59.9, 125.9, 126.6, 127.6, 128.2, 128.6, 130.2, 136.7, 146.7; IR (neat) 3300 cm^{-1} (OH).

(−)-(*S*)-6-[2-(*p*-Tolylsulfonyloxy)ethyl]-1,4-cycloheptadiene (−)-12. To a cooled (0 °C) solution of (+)-**11a** (431 mg, 3.12 mmol) in pyridine (20 mL) was added *p*-toluenesulfonyl chloride (1190 mg, 6.24 mmol) under an Ar atmosphere. After being stirred for 10 h, the reaction mixture was worked up in the usual manner. Purification of the product by silica-gel column chromatography (hexane : AcOEt=10 : 1) gave (−)-**12** (711 mg, 78%). Oil: $[\alpha]_D^{14}$ −7.12° (*c* 0.9). ^{1}H NMR δ=1.72 (1H, tt, *J*=6.6 and 7.3 Hz), 1.97—2.06 (1H, m), 2.15—2.29 (1H, m), 2.45 (3H, s), 2.51—2.72 (2H, m), 2.86—2.97 (1H, m), 4.08 (1H, dt, *J*=2.0 and 6.6 Hz), 5.44 (1H, ddd, *J*=2.0, 5.0, and 11.3 Hz), 5.56—5.67 (3H, m), 7.35 (2H, d, *J*=8.6 Hz), 7.89 (2H, d, *J*=8.6 Hz); ^{13}C NMR δ=21.7, 28.5, 32.2, 33.5, 34.7, 68.8, 127.9, 128.5, 128.7, 128.8, 129.8, 133.1, 134.2, 144.7; IR (neat) 1360 cm^{-1} (OSO_2).

(+)-(6*S*)-6-Butyl-1,4-cycloheptadiene [(+)-Dictyopterene C'] (+)-13. To a cooled (−78 °C) solution of (−)-**12** (286.4 mg, 0.98 mmol) in dry THF (5.0 mL) were added a THF solution (5.0 mL) of Li_2CuCl_4 (0.98 mmol) and EtMgBr (21.6 mmol). The mixture was allowed to warm to 0 °C over a period of 0.5 h. Direct separation of the reaction mixture by silica-gel column chromatography (hexane) followed by TLC (pentane) gave (+)-**13** (80.6 mg, 55%). Oil: $[\alpha]_D^{16}$ +15.12° (*c* 0.4). ^{1}H NMR δ=0.86—0.91 (3H, m), 1.20—1.40 (6H, m), 2.02—2.16 (1H, m), 2.16—2.29 (1H, m), 2.37—2.54 (1H, m), 2.69 (1H, dt, *J*=1.7 and 18.8 Hz), 2.96 (1H, d, *J*=18.8 Hz), 5.51—5.77 (4H, m); ^{13}C NMR δ=14.1, 22.9, 28.4, 29.5, 32.9, 36.1, 37.2, 127.3, 128.1, 129.9, 136.9: IR (neat) 1625 cm^{-1} (C=C). The above spectral data are in good agreement with those of natural one.

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