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A Sequenced Radical Reaction—A Novel Stereocontrolled Route to Angularly Disubstituted *cis*-Decalins

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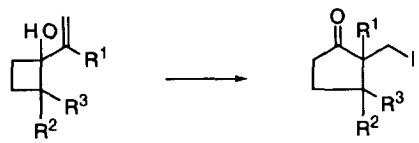
Abstract: The complete stereocontrolled synthesis of angularly disubstituted *cis*-decalins based on the sequenced radical ring expansion and cyclization process of α-iodomethylcyclopentanones **1** and **6** is described and the stereochemical outcome of this radical reaction is also discussed. The compounds **2–5** and **7–13** thus prepared could be versatile intermediates for the synthesis of biologically important compounds. Copyright © 1996 Elsevier Science Ltd

During the course of our efforts[1] toward the development of synthetic methodology using small ring compounds as a cornerstone, we have succeeded[2] in providing a versatile method for the synthesis of neopentyl type halogenated cyclopentanoid **B** *via* olefinic cyclobutanone **A** (Chart 1).

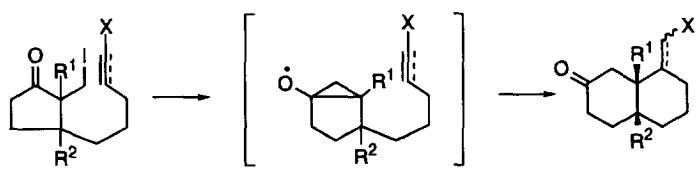
Chart 1



A **B**

In the present contribution, we wish to report the powerful function of **B** as a synthon for valuable compounds. Thereby, the radical reaction[3] of olefinic cyclopentanone **C** proceeds in a sequenced manner *via* cyclopropyl alkoxy radical **D** to afford stereoselectively angularly disubstituted *cis*-decalin **E** (Chart 2).

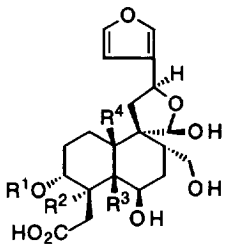
Chart 2



C **D** **E**

The compound **E** thus prepared constitutes basic framework of many types of biologically important compounds[4] including neo-clerodane diterpenes musabalbisianes **A**, **B** and **C** (I–III)[5] isolated from the seed of *Musa balbisiana* which show amoebicidal activity *in vitro* (Figure 1).

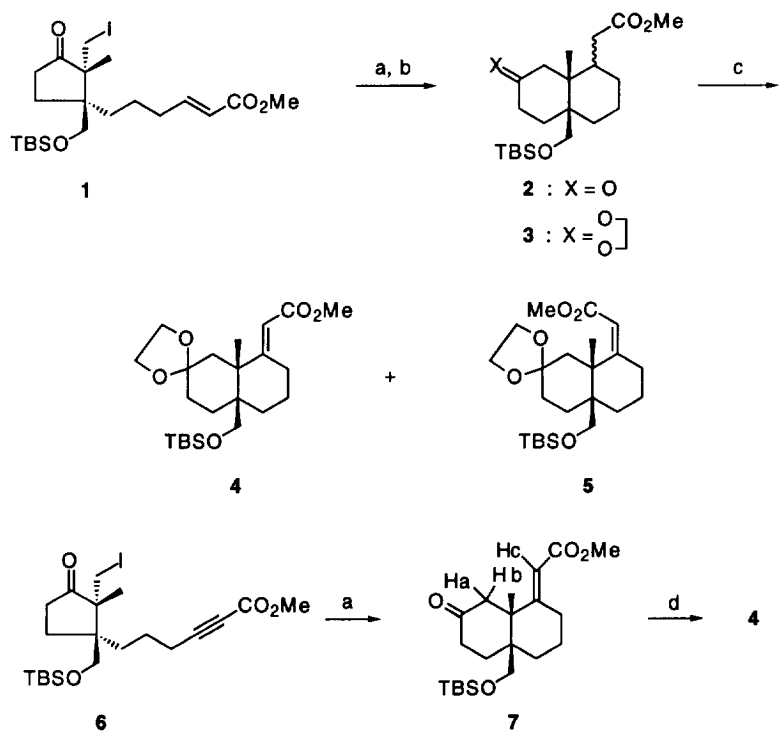
Figure 1



	R^1	R^2	R^3	R^4
I	H	CO_2H	CHO	CHO
II	H	CHO	CO_2H	CH_2OH
III	Ang	CH_2OH	CH_2OH	CH_2OH

The sequenced reaction of **1**[2] proceeded effectively under radical conditions to give the *cis*-decalin **2** as 1:1 mixture of diastereomers in 97% yield. Then ketal **3** derived (85%) from **2** was converted to the easily separable mixture (1:4) of *E* (**4**) and *Z* (**5**) unsaturated esters in 67% yield by phenylselenylation-oxidative elimination sequences. The acetylenic iodide **6**[2] was also transformed into the *cis*-decalin **7** selectively in 85% yield under the same conditions for **1**. On ketalization, **7** furnished the ketal **4** (66%) identical with that described above (Scheme 1).

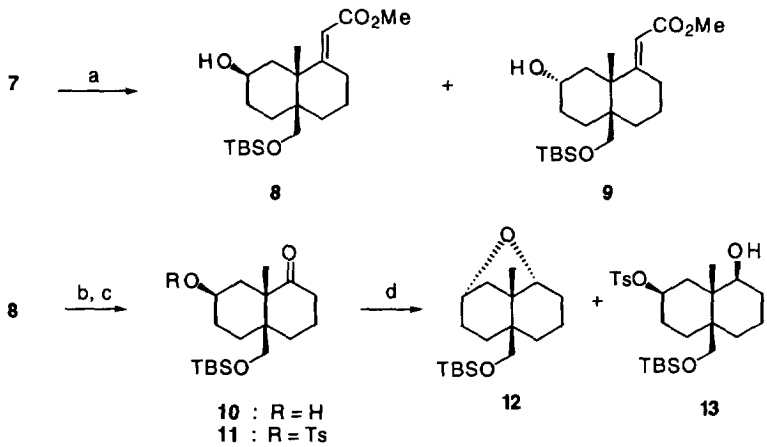
Scheme 1



[a]Steps: (a) $^nBu_3SnH$, AIBN, benzene, reflux, 5 h; (b) $HOCH_2CH_2OH$, *p*-TsOH, benzene,reflux, 9 h; (c) (1) LDA, PhSeBr, THF, –78 °C, 4.5 h; (2) 30% H_2O_2, $NaHCO_3$, THF, rt, 2 h; (d) $HOCH_2CH_2OH$, PPTs, benzene, reflux, 14 h.

In the NMR (500 MHz) spectrum of **7**, the definite nOe between Ha and Hb [2.21 and 2.82 ppm (each 1H, each d, J = 15.0 Hz)], and Hc [5.68 ppm (1H, s)] was observed confirming its *E*-geometry. The *cis* ring juncture of **7** was determined unambiguously giving the suitably functionalized *cis*-decalins for further elaboration as follows. Reduction of the ketone **7** afforded the alcohols **8** and **9** (4:1) in 69% yield and **8** was then subjected to ozonolysis to give the keto alcohol **10** (55%). Finally, the tosylate **11** derived (81%) from **10** was reduced to furnish the tricyclic compound **12** (59%) together with the alcohol **13** (38%). The formation of **12** shows definitely the *cis* ring juncture of **7** (Scheme 2).

Scheme 2

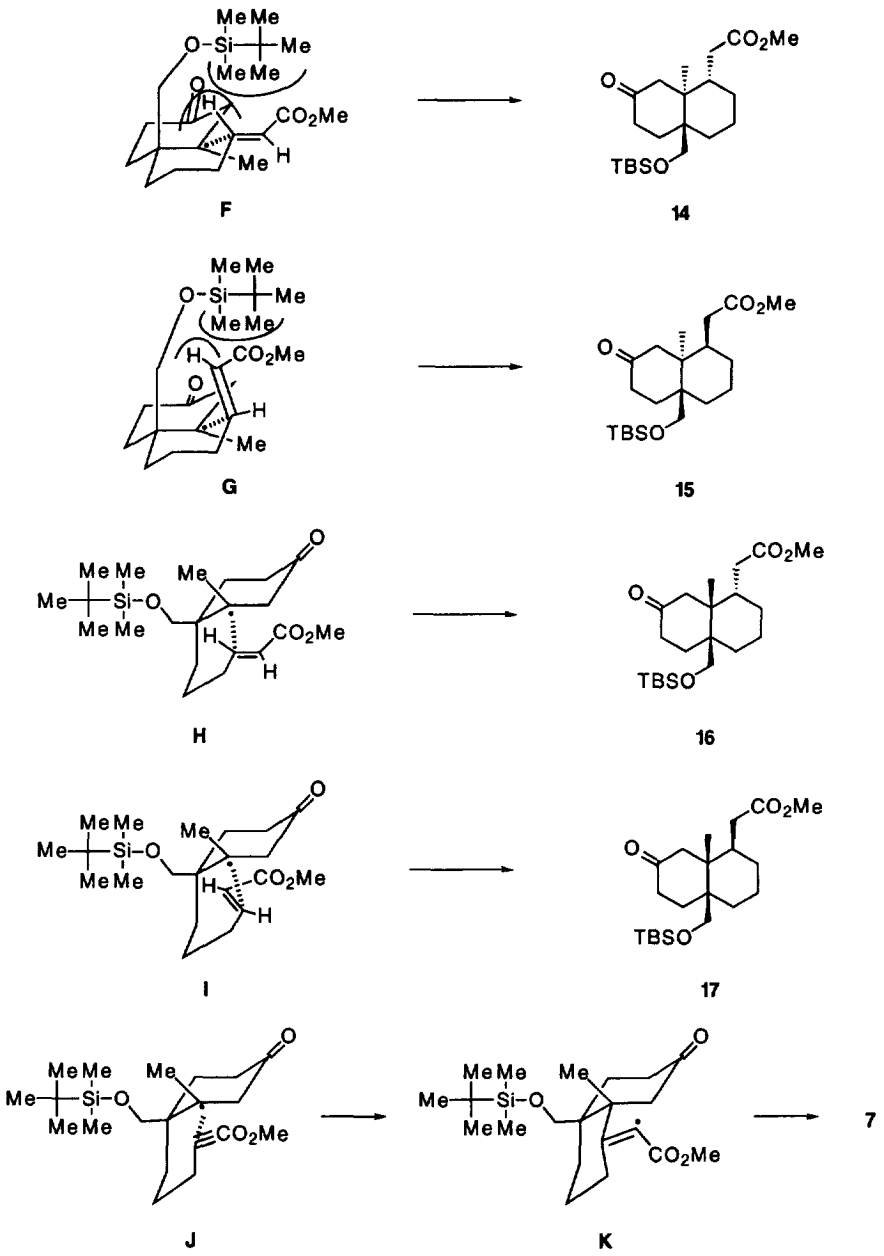


[a]Steps: (a) $NaBH_4$, MeOH-CH_2Cl_2, 0 °C, 15 min; (b) O_3, CH_2Cl_2, –78 °C, 3 h then Me_2S; (c) *p*-TsCl, pyridine, DMAP, 0 °C, 24 h; (d) $NaBH_4$, MeOH-CH_2Cl_2, 0 °C, 3 h.

The stereochemical outcomes in these tandem radical reactions could be rationalized as follows. Of the four possible radical intermediates **F–I** derived from **1** *via* cyclopropyl alkoxy radical (**D**), **F** and **G** leading to *trans-syn*[6] **14** and *trans-anti* **15** respectively have considerable steric congestions between siloxymethyl and unsaturated ester groups and thus, are unfavorable intermediates. In contrast to these, **H** and **I** leading to *cis-anti* **16** and *cis-syn* **17** respectively have not such serious steric congestions and could be favorable intermediates. By the analogous argument, the thermodynamically more favorable radical **K** with *E* configuration in unsaturated ester, formed by cyclization of the sterically more favorable radical **J** which is derived from **6**, could give *cis*-decalin **7** (Chart 3).

Thus, we could provide an efficient pathway to disubstituted *cis*-decalins which could be potential intermediates for the synthesis of biologically important compounds, although the general and detailed aspects of this sequenced reaction are still remained to be studied thoroughly.

Chart 3



Experimental Section

General Procedure: All reactions were carried out under positive atmosphere of dry N_2 unless indicated otherwise. Solvents were freshly distilled prior to use: THF and Et_2O were distilled from sodium

benzophenone, and DMSO, DMF, CH_2Cl_2, and Et_3N were distilled from CaH_2 and kept over 4 Å molecular sieves. The phrase "residue upon workup" refers to the residue obtained when the organic layer was separated and dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. Silica gel column chromatography was carried out with Wako gel C-200, while Merck Kieselgel 60 Art. 9385 was used for flash chromatography.

(1*R, 6*S**)-6-*t*-Butyldimethylsiloxymethyl-2-methoxycarbonylmethyl-1-methylbicyclo[4.4.0]decan-9-one (2).** A solution of the iodide **1** (93 mg, 0.183 mmol), *n*-Bu_3SnH (0.06 mL, 0.22 mmol), and a catalytic amount of 2,2'-azobisisobutyronitrile (AIBN) in benzene (36 mL) was refluxed for 5 h. The residue upon evaporation of the solvent was chromatographed on silica gel with hexane–AcOEt (96:4 v/v) as eluant to give the *cis*-decalin **2** (68.2 mg, 97%) as a colorless oil: IR (neat) 1740, 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (1.5H, s), 0.05 (3H, s), 0.07 (1.5H, s), 0.84 (1.5H, s), 0.87 (4.5H, s), 0.88 (4.5H, s), 0.90 (1.5H, s), 1.10–2.79 (15H, m), 3.37 and 3.95 (each 0.5H, each d, J = 9.9 Hz), 3.46 and 3.93 (each 0.5H, each d, J = 10.3 Hz), 3.65 (1.5H, s), 3.66 (1.5H, s); MS (EI) m/z 325 (M^+ –57); HRMS calcd for $C_{17}H_{29}O_4Si$ 325.1835, found 325.1821.

(1*R,6*S**)-6-*t*-Butyldimethylsiloxymethyl-2-methoxycarbonylmethyl-1-methylbicyclo-[4.4.0]decan-9-one Ethylene Acetal (3).** A solution of ketone **2** (1.84 g, 4.8 mmol), ethylene glycol (1.34 mL, 24 mmol), and catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in benzene (35 mL) was refluxed for 9 h using a Dean-Stark trap to remove water. The reaction mixture was washed with saturated aqueous $NaHCO_3$ and NaCl successively. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (96:4 v/v) as eluant to give the acetal **3** (1.75 g, 85%) as a colorless oil: IR (neat) 1740 cm^{-1}: ^1H NMR (300 MHz, $CDCl_3$) δ 0.02 (1.5H, s), 0.03 (3H, s) 0.69 (1.5H, s), 0.85 (1.5H, s), 0.88 (9H, s), 1.00 (1.5H, s), 1.03–2.12 (13.5H, m), 2.35–2.48 (1H, m), 2.73–2.84 (0.5H, m), 3.25–3.33 (1H, m), 3.65 (1.5H, s), 3.67 (1.5H, s), 3.78 (0.5H, d, J = 9.2 Hz), 3.82–4.01 (4.5H, m); MS (EI) m/z 426 (M^+); HRMS calcd for $C_{23}H_{42}O_5Si$ 426.2802, found 426.2782.

(1*R,6*S**)-6-*t*-Butyldimethylsiloxymethyl-2-[(*E* and *Z*)-methoxycarbonylmethylene]-1-methylbicyclo[4.4.0]decan-9-one Ethylene Acetals (4) and (5).** To a stirred solution of lithium diisopropylamide (LDA)[prepared from diisopropylamine (0.03 mL, 0.23 mmol) and *n*-BuLi (0.15 mL of 1.5 mol solution in hexane, 0.23 mmol)] in THF (1 mL) was added a solution of the acetal **3** (63.8 mg, 0.15 mmol) in THF (1 mL) at –78 °C and stirring was continued for 40 min at the same temperature. The reaction mixture was treated with a solution of phenylselenyl bromide (42.5 mg, 0.18 mmol) in THF (1 mL), stirred for 4.5 h at the same temperature, then treated with saturated aqueous NH_4Cl solution, and extracted with Et_2O. The combined extracts were washed with saturated aqueous NaCl solution. To a solution of the residue upon workup in THF (1 mL) were added $NaHCO_3$ (101 mg, 1.2 mmol) and H_2O_2 (0.17 mL of 30% w/v aqueous solution, 1.5 mmol) at 0 °C and stirring was continued for 2 h at room temperature. The reaction mixture was treated with water and extracted with Et_2O. The combined extracts were washed with saturated aqueous NaCl solution. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (98:2 v/v) as eluant to give the (*E*)-ester **4** (9 mg, 14%) as colorless plates from the first fraction and the (*Z*)-ester **5** (33.6 mg, 53%) as a colorless oil from the second fraction.

4: mp 56–57 °C (from hexane); IR ($CHCl_3$) 1710, 1630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ –0.04 (3H, s), –0.03 (3H, s), 0.83 (9H, s), 1.15 (3H, s), 1.42–1.88 (10H, m), 2.08 –2.19 (1H, m), 2.26 (1H, d, J = 14.0 Hz), 3.22 and 3.43 (each 1H, each d, J = 9.8 Hz), 3.66 (3H, s), 3.73–3.97 (4H, m), 5.72 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.6, –5.5, 18.2, 20.3, 21.7, 25.1, 25.8, 29.4, 30.4, 41.9, 34.1, 44.4, 50.9, 63.6, 64.5, 66.0, 109.2, 113.9, 167.7, 167.9; MS (EI) m/z 424 (M^+); HRMS calcd for $C_{23}H_{40}O_5Si$ 424.2645, found 424.2652.
5: IR (neat) 1710, 1640 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ –0.02 (3H, s), –0.01 (3H, s), 0.84 (9H, s), 1.20 (3H, s), 1.41–2.04 (9H, m), 2.04–2.12 (1H, m), 2.19 (1H, d, J = 14.0 Hz), 2.38–2.49 (1H, m), 3.25 and 3.56 (each 1H, each d, J = 9.8 Hz), 3.67 (3H, s), 3.79–3.98 (4H, m), 5.59 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.5, –5.4, 18.3, 19.6, 21.9, 25.9, 26.0, 28.8, 30.4, 35.4, 41.5, 41.9, 44.2, 51.6, 63.7, 64.5, 65.8, 109.2, 117.0, 153.2, 170.0; MS (EI) m/z 424 (M^+); HRMS calcd for $C_{23}H_{40}O_5Si$ 424.2645, found 424.2621.

(1*R,6*S**)-6-*t*-Butyldimethylsiloxymethyl-2-[(*E*)-methoxycarbonylmethylene]-1-methyl-bicyclo[4.4.0]decan-9-one (7).** A solution of the iodide **6** (415 mg, 0.82 mmol), *n*-Bu_3SnH (0.264 mL, 0.983 mmol) and a catalytic amount of AIBN in benzene (200 mL) was refluxed for 2 h. The residue upon evaporation of the solvent was chromatographed on silica gel with hexane–AcOEt (97:3 v/v) as eluant to give the keto ester **7** (265 mg, 85%) as a colorless oil: IR (neat) 1720, 1710, 1630 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.03 (6H, s), 0.87 (9H, s), 1.11 (3H, s), 1.21–1.95 (6H, m), 2.21 and 2.82 (each 1H, each d, J = 15.0 Hz), 2.39 (2H, t, J = 7.0 Hz), 2.91–3.05 (2H, m), 3.55 and 3.62 (each 1H, each d, J = 9.9 Hz), 3.67 (3H, s), 5.68 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ –5.6, –5.4, 18.2, 21.8, 25.1, 25.9, 26.7, 28.1, 30.4, 37.7, 42.3, 47.4, 50.0, 51.1, 66.5, 114.5, 165.0, 167.3, 210.9; MS (EI) m/z 323 (M^+ –57); HRMS calcd for $C_{17}H_{27}O_4Si$ 323.1679, found 323.1642. Anal. Calcd for $C_{21}H_{36}O_4Si$; C, 66.27; H, 9.53. Found: C, 66.25; H, 9.28.

(*E*)-Ethylene Acetal 4 from the Ketone 7. A solution of the ketone **7** (265 mg, 0.696 mmol), ethylene glycol (0.194 mL, 3.48 mmol), and a catalytic amount of PPTs in benzene (5 mL) was refluxed for 14 h using a Dean-Stark trap to remove water. The reaction mixture was washed with saturated aqueous $NaHCO_3$ and NaCl solution successively. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (96:4 v/v) as eluant to give the acetal **4** (194 mg, 66%) as colorless plates which was identical with the sample described above in all aspects including mixed melting point test.

[(1*R,6*S**,9*R**)- and (1*R**,6*S**,9*S**)]-6-*t*-Butyldimethylsiloxymethyl-2-[(*E*)-methoxycarbonylmethylene]-1-methylbicyclo[4.4.0]decan-9-ols (8 and 9).** To a solution of the ketone **7** (636 mg, 1.67 mmol) in MeOH–CH_2Cl_2 (1:1) (3 mL) was added portionwise $NaBH_4$ (63.3 mg, 1.67 mmol) at 0 °C and stirring was continued for 15 min at the same temperature. The reaction mixture was treated with water and extracted with CH_2Cl_2. The combined extracts were washed with saturated aqueous NaCl solution. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (91:9 v/v) as eluant to give the decanol **8** (442 mg, 69%) as a colorless oil from the first fraction and then the decanol **9** (110 mg, 17%) as a colorless oil from the second fraction.

8: IR (neat) 3400, 1720, 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.03 (6H, s), 0.88 (9H, s), 1.07 (3H, s), 1.40–1.70 (10H, m), 1.77–1.80 (1H, m), 2.04 and 2.08 (each 1H, each d, J = 1.5 Hz), 3.44 and 3.79 (each 1H, each d, J = 9.5 Hz), 3.68 (3H, s), 3.98 (1H, m), 5.79 (1H, s); MS (EI) m/z 382 (M^+); HRMS calcd for $C_{21}H_{38}O_4Si$ 382.2537, found 382.2512.
9: IR (neat) 3400, 1730, 1630 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ –0.01 (6H, s), 0.85 (9H, s), 1.11 (3H, s), 1.24–2.14 (10H, m), 1.85–1.95 (1H, m), 2.09–2.19 (2H, m), 3.19 and 3.44 (each 1H, each d, J = 9.9 Hz), 3.69 (3H, s), 3.89 (1H, m), 5.70 (1H, s); MS (EI) m/z 325 (M^+ –57); HRMS calcd for $C_{17}H_{29}O_4Si$ 325.1833, found 325.1879.

(1*S, 6*S**, 9*R**)-6-*t*-Butyldimethylsiloxymethyl-9-hydroxy-1-methylbicyclo[4.4.0]-decan-2-one (10)**. A solution of the alcohol **8** (89.1 mg, 0.233 mmol) in CH_2Cl_2 (40 mL) was treated with ozone at –78 °C until the starting material disappeared (3 h). The reaction mixture was treated with Me_2S (0.2 mL, 2.86 mmol) at the same temperature and the temperature was raised to room temperature. The resulting mixture was diluted with CH_2Cl_2 and washed with saturated aqueous NaCl solution. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (90:10 v/v) as eluant to give the ketone **10** (41.8 mg, 55%) as a colorless oil: IR (neat) 3400, 1700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.06 (6H, s), 0.90 (9H, s), 1.09 (3H, s), 1.18–1.88 (10H, m), 2.26 (2H, m), 2.50 (1H, m), 3.52 and 3.75 (each 1H, each d, J = 9.2 Hz), 3.82 (1H, m); MS (EI) m/z 269 (M^+ –57); HRMS calcd for $C_{14}H_{25}O_3Si$ 269.1571, found 269.1564.

(1*S, 6*S**,9*R**)-6-*t*-Butyldimethylsiloxymethyl-1-methyl-9-*p*-toluenesulfonyl-oxybicyclo-[4.4.0]decan-2-one (11)**. To a solution of the ketone **10** (46.7 mg, 0.143 mmol) and a catalytic amount of dimethylaminopyridine (DMAP) in pyridine (2 mL) was added portionwise *p*-toluenesulfonyl chloride (136 mg, 0.715 mmol) at 0 °C and stirring was continued for 24 h at room temperature. The reaction mixture was diluted with water and extracted with Et_2O. The combined extracts were washed successively with 10% HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl solution. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (95:5 v/v) as eluant to give the tosylate **11** (53.3 mg, 81%) as a colorless oil: IR (neat), 1700, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.88 (9H, s), 1.02 (3H, s), 1.34–1.88 (10H, m), 2.44 (3H, s), 2.10–2.25 (2H, m), 3.47 and 3.68 (each 1H, each d, J = 9.5 Hz), 4.63 (1H, m), 7.35 and 7.85 (each 2H, each d, J = 8.2 Hz); MS (EI) m/z 251 (M^+ –229); HRMS calcd for $C_{14}H_{23}O_2Si$ 251.1466, found 251.1460.

(1*S,2*R**,6*S**,9*S**)-6-*t*-Butyldimethylsiloxymethyl-2,9-epoxy-1-methylbicyclo-[4.4.0]-decane (12) and (1*S**,2*S**,6*S**,9*R**)-6-*t*-Butyldimethylsiloxymethyl-1-methyl-9-*p*-toluene-sulfonyloxybicyclo[4.4.0]decan-2-ol (13)**. To a solution of the tosylate **11** (27.1 mg, 0.056 mmol) in MeOH–CH_2Cl_2 (1:1) (2 mL) was added portionwise $NaBH_4$ (2.13 mg, 0.056 mmol) at 0 °C and stirring was continued for 3 h at the same temperature. The reaction mixture was treated with water and extracted with CH_2Cl_2. The combined extracts were washed with saturated aqueous NaCl solution. The residue upon workup was chromatographed on silica gel with hexane–AcOEt (93:7 v/v) as eluant to give the ether **12** (10.4 mg, 59%) as a colorless oil and with hexane–AcOEt (90:10 v/v) as eluant to give the alcohol **13** (10.4 mg, 38%) as a colorless oil.

12: IR (neat) 1130 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (6H, s), 0.91 (9H, s), 1.01 (3H, s), 1.07–2.19 (12H, m), 3.09 and 3.55 (each 1H, each d, J = 9.5 Hz), 3.46 (1H, m), 4.22 (1H, m); MS (EI) m/z 310 (M^+); HRMS calcd for $C_{18}H_{34}O_2Si$ 310.2326, found 310.2354.

13: IR (neat) 3400, 1600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.01 (6H, s), 0.76 (3H, s), 0.86 (9H, s), 1.25–1.90 (12H, m), 2.00–2.08 (1H, m), 2.44 (3H, s), 3.26 and 3.73 (each 1H, each d, J = 9.5 Hz), 3.78 (1H, m), 4.73 (1H, m), 7.33 and 7.80 (each 2H, each d, J = 8.4 Hz); MS (EI) m/z 253 (M^+ –229); HRMS calcd for $C_{14}H_{25}O_2Si$ 253.1622, found 253.1629.

References and Notes

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6. *Trans-syn* refers to ring juncture and relative configuration of methyl and methoxycarbonymethyl groups respectively.

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