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Novel skeletal rearrangement of hydroindan derivatives into hydroazulenones via an alkoxy radical

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Abstract—A novel construction of hydroazulenones using skeletal rearrangement of epoxy-hydroindan derivatives via alkoxy radical was developed. The reaction was also found to proceed without damage of acetal or olefin group. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

In many cases, a free radical process is useful for C–C bond formation even in the presence of functional groups incompatible with polar reagents.[1] This advantage would also be suitable for ring transformation of a complex molecule without damage to functional groups. We have developed a new radical reaction in which cycloalkanone **1** possessing an acetylenic side chain rearranged to bicyclic ketone **2** (Scheme 1).[2,3] In this transformation, stannylvinyl radical **a** derived from **1** attacked the carbonyl group on the proximate ring. The resulting alkoxy radical **b** was then converted into a tertiary carbon-centered radical **c** through a ring opening. The radical **c** was added to the proximate stannylvinyl group, generating a secondary carbon-centered radical **d**. Finally, the addition of the radical to the carbonyl group followed by ring-opening afforded **2**. The hydroazulenone **2** was successfully converted into diketone **3**, which is a synthetic intermediate of damsinic acid.[2c] One of the key steps in this skeletal rearrangement is the formation of an alkoxy radical, which is alternatively generated by homolytic cleavage of an epoxy ring as shown in the radical sequence of thiocarbonylimidazolide **4** into bicyclo[6.3.0]undecanone **5**.[4,5] We report here a new method for constructing a hydroazulene skeleton, which is present in a wide variety of natural sources, by radical ring transformation of hydroindan epoxides **20**, **21**, **25**, **29**, **33** and **34**.

2. Results and discussion

Scheme 2 shows the preparation of hydroindenes **12**–**14**, which are precursors of hydroindan epoxides. Oxidation of **6**[6] with tetrapropyl-ammonium perruthenate (TPAP) followed by addition of (carbethoxymethylene)triphenylphosphorane gave ester **7**, which was converted into **9** through a sequence of DIBAH reduction and oxidation. Wittig reaction of **9** afforded diene **10**, which was converted into ester **11** upon treatment with MeLi followed by addition of methyl chloroformate in situ.[7] Intramolecular Diels–Alder reaction[8] of **11** was carried out in refluxing toluene to give bicyclodiene **12**. Because of its easy aromatization, **12** was subjected to OsO_4 oxidation[9] or diacetoxylation without purification. Dihydroxylation of **12** with OsO_4 afforded diol **13**. Treatment of **12** with CH_3COOAg/I_2 followed by alkaline hydrolysis gave the diastereomeric diol **14**,[10] whose stereochemistry was determined by X-ray analysis of the corresponding di-bromobenzoate **15** (Fig. 1).

Acetalization of **13** followed by DIBAH reduction gave allyl alcohol **17**, which was treated with *m*-CPBA to give epoxides **18** and **19**. These epoxides were easily separated by column chromatography with silica gel. Epoxides **18** and **19** reacted with thiocarbonyl diimidazole to give **20** and **21**, respectively. On the other hand, silylation of **13** and **14** with TESOTf afforded the corresponding silylethers **22** and **26**. Each compound was converted into thiocarbonyl imidazolide **25** and **29** through a sequence of DIBAH reduction, *m*-CPBA epoxidation and thiocarbonylation. In their epoxidation, addition of $NaHCO_3$ was essential for preventing cleavage of the epoxy ring. DIBAH reduction of diene-ester **12** followed by epoxidation yielded diastereomeric epoxides **31** (more polar) and **32** (less polar), which were separated by column chromatography with silica gel.

Keywords: radical; skeletal rearrangement; hydroindan; hydroazulenone.
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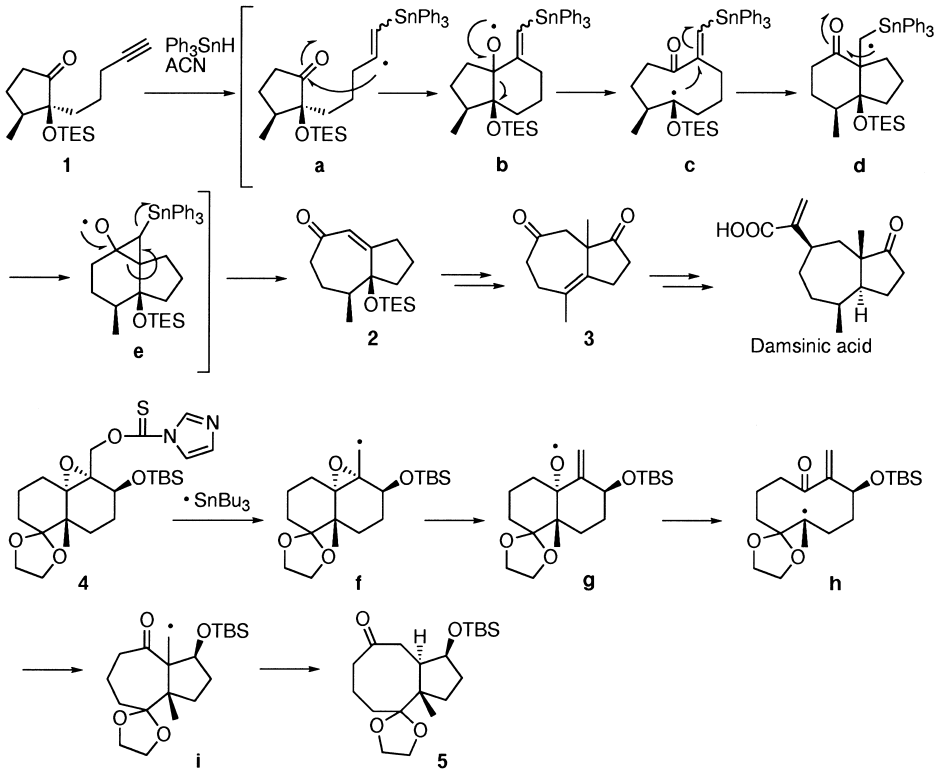
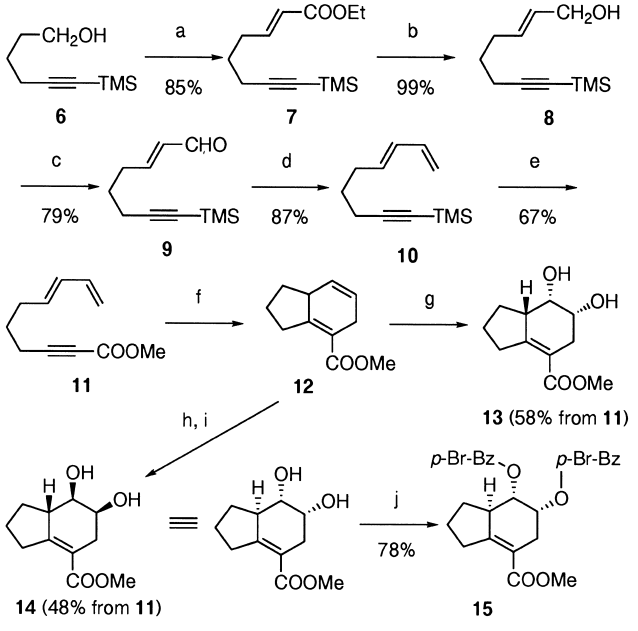


Scheme 1.

Stereochemistries of these compounds could not be determined. Epoxides were converted into the corresponding thiocarbonyl imidazolides **33** and **34**[11] (Scheme 3)

The relative configuration of epoxides **18**, **24** and **28** was determined by the combination of chemical conversion and NOE experiments. Treatment of epoxide **18** with diethylaluminium 2,2,6,6-tetramethylpiperidide (DATMP)[12] gave diol **35**. On the other hand, ring opening of **24** and **28** was performed by using $TsOH{\cdot}H_2O$ to give diol **37** and **39**. Diols



Scheme 2. *Reagents*: (a) (1) TPAP, NMO, MS4Å (2) $Ph_3P{=}CHCOOEt$; (b) DIBAH, −78°C; (c) TPAP, NMO, MS4Å; (d) $Ph_3P{=}CH_2$; (e) MeLi, ClCOOMe, −30°C; (f) reflux to toluene; (g) OsO_4, NMO, *t*-BuOH, H_2O, −20°C; (h) (1) CH_3COOAg, I_2, AcOH (2) AcOH, H_2O, reflux; (i) KOH; (j) *p*-bromobenzoyl chloride, DMAP, pyridine.

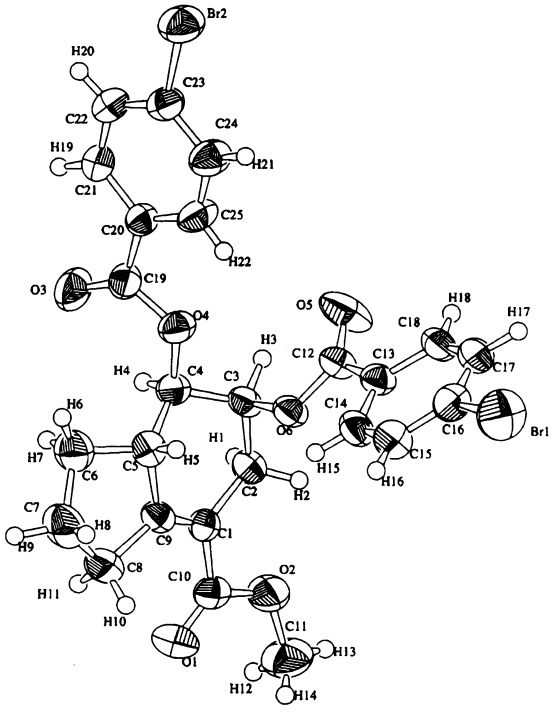
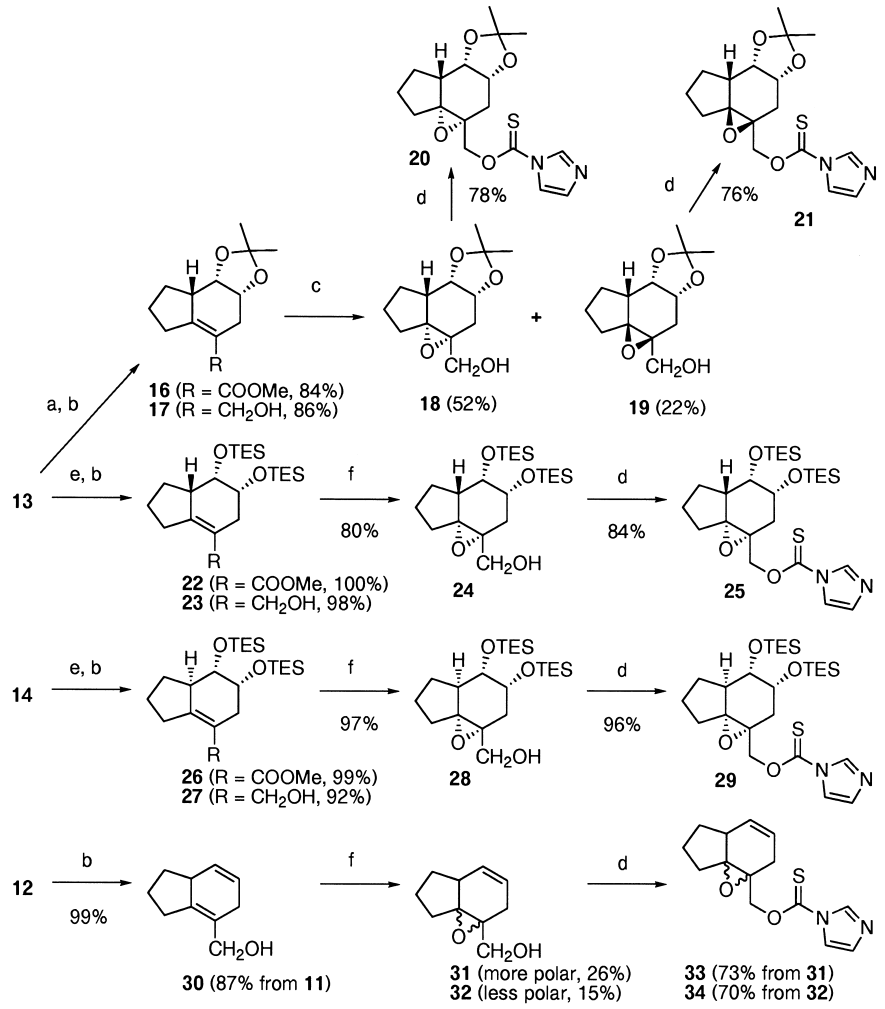
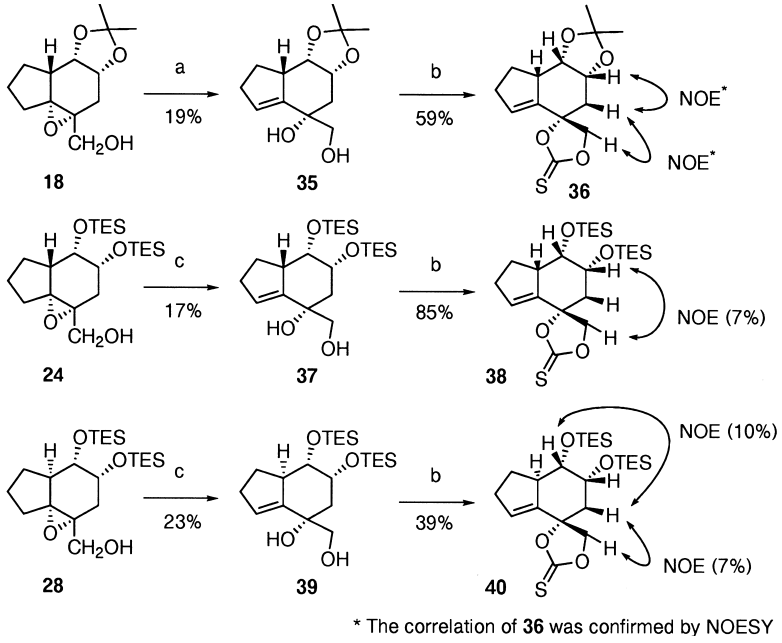


Figure 1. X-Ray structure of **15**.

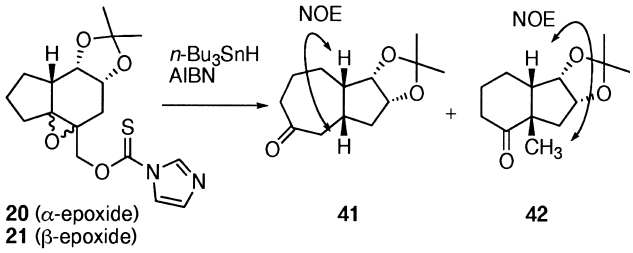


Scheme 3. *Reagents*: (a) PPTS, 2,2-dimethoxypropane; (b) DIBAH, −78°C; (c) *m*-CPBA, −20°C; (d) thiocarbonyl diimidazole, reflux in 1,2-dichloroethane; (e) TESOTf, 2,6-lutidine, −15°C; (f) MCPBA, $NaHCO_3$, −20°C.



Scheme 4. *Reagents*: (a) DATMP; (b) thiocarbonyl diimidazole, reflux in 1,2-dichloroethane; (c) $TsOH{\cdot}H_2O$.

Table 1.



Run	Sub.	Method	Solvents	Temperature (°C)	Time (min)	Yield (%)	
						41	**42**
1	**20**	A	Benzene	80	30	Trace	28
2	**20**	B	Benzene	80	50	20	Trace
3	**20**	A	Toluene	110	40	25	25
4	**20**	B	Toluene	110	60	60	21
5	**21**	A	Toluene	110	30	26	23
6	**21**	B	Toluene	110	60	56	9

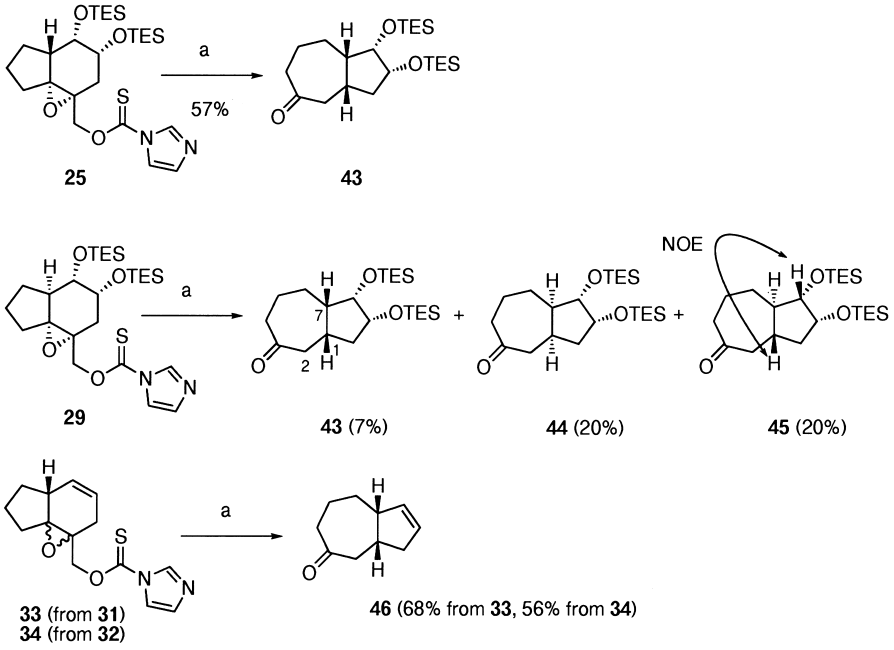
Method A. A solution of a substrate, AIBN and *n*-Bu_3SnH in a solvent was refluxed. *Method B*. To a refluxing solution of a substrate in benzene or toluene was slowly added a solution of AIBN and *n*-Bu_3SnH in benzene or toluene by using a syringe pump. The resulting mixture was further refluxed.

35, **37** and **39** were converted into **36**, **38** and **40**, whose ^1H NMR spectra showed NOE correlations as shown in Scheme 4.

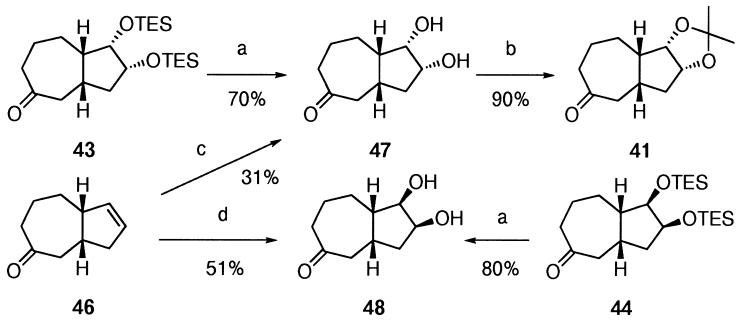
The result of radical reaction of **20** and **21** is summarized in Table 1. When a mixture of **20**, *n*-Bu_3SnH and AIBN in benzene was heated at 80°C, there was almost no formation of the desired hydroazulenone **41**. However, α-methylhydroindanone **42** was obtained in 28% yield. Formation of **41** was achieved by increasing the reaction temperature. Treatment of **20** with *n*-Bu_3SnH and AIBN in toluene at 110°C produced **41** (25%) and **42** (25%). Furthermore, when a solution of *n*-Bu_3SnH and AIBN in toluene was added slowly to a heating solution of **20** in toluene, the yield of **41** was drastically improved (60%). By this procedure, another epoxide **21** was also converted into **41** in 56% yield along with **42**. Stereochemistries of **41** and **42** were determined by NOE correlations as shown in Table 1.

Next, radical skeletal rearrangement of two epimeric hydroindans **25** and **29** with silyloxy groups was carried out (Scheme 5). Treatment of **25** with *n*-Bu_3SnH in refluxing toluene gave **43** in 57% yield. On the other hand, the reaction of **29** afforded **44** and **45** along with a small amount of **43**. Hydroazulenone **46** having a double bond was obtained from both epoxides **33** and **34** in good yield. The double bond was also found to be compatible with these reaction conditions.

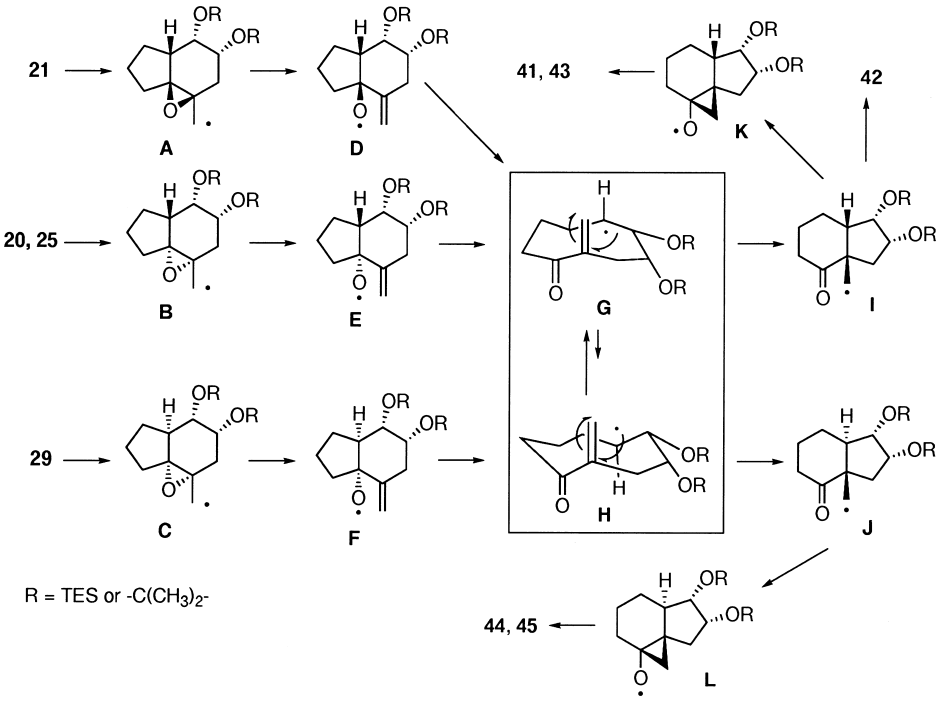
Identification of **43**, **44** and **46** was carried out by chemical



Scheme 5. *Conditions*: (a) *n*-Bu_3SnH, AIBN, toluene, 110°C, slow addition using a syringe pump.



Scheme 6. *Reagents*: (a) TBAF; (b) PPTS, 2,2-dimethoxypropane; (c) (1) CH_3COOAg, I_2, AcOH (2) KOH; (d) QsO_4, NMO, *t*-BuOH, H_2O, −20°C.



Scheme 7.

conversion (Scheme 6). Desilylation of **43** followed by acetalization gave **41**, whose structure had already been determined. Enone **46** was subjected to oxidation with CH_3COOAg/I_2 and subsequent alkaline hydrolysis, and the resulting compound was identical to diol **47**. On the other hand, OsO_4 oxidation of **46** yielded **48**, which was also obtained by desilylation of **44**. Compound **45** was found to be a *trans*-ring isomer by confirming the NOE correlation as shown in Scheme 5.

Scheme 7 shows a possible mechanism of the radical skeletal rearrangement. Homolytic cleavage of epoxy rings of methyl radicals **A**–**C** gives the corresponding alkoxy radicals **D**–**F**. Nine-membered cyclic radical **G** is formed by β-cleavage of **D** or **E**. On the other hand, β-cleavage of **F** affords a nine-membered cyclic radical **H**. Interconversion between **G** and **H** should be possible, but the rate of interconversion would be very slow. Radical **G** or **H** undertakes ring formation to form **I** or **J**, respectively. At a higher temperature, methyl radicals **I** and **J** are converted into **K** and **L**, which undertake ring expansion to give the corresponding hydroazulenone compounds, while at lower temperature, methyl radical **I** traps hydride to produce hydroindanone **42**. The interconversion between **G** and **H** contributes to the stereochemistries of the products.

In conclusion, we have developed a new method for the formation of hydroazulene compounds. The reaction was found to proceed without damage to the acetal, silyl ether and olefin groups. This reaction would be applicable to various compounds possessing incompatible functional groups with polar reagents.

3. Experimental

3.1. General methods

Melting points were measured using a Yanaco micro melting point apparatus and were uncorrected. NMR spectra were recorded on a JEOL JNM-GX270 spectrometer or a JEOL JNM-ECP 500 FT-NMR with tetramethylsilane as

internal standard. Abbreviations are as follows: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad. The electron impact mass spectra (EI-MS) were measured using a Hitachi-M-2000 mass spectrometer, and IR spectra were measured using a JASCO FT-IR7000 or a JASCO A-102 IR spectrophotometer. Reactions were followed by thin-layer chromatography (TLC) on Silica gel 60 F_{254}-precoated TLC plates. Silica gel used on column chromatography was Silica gel 60 (Merck, 70–230 or 230–400 mesh).

3.1.1. Ethyl (2*E*)-8-trimethylsilyloct-2-en-7-ynoate (7). To a mixture of **6** (36.0 g, 212 mmol), molecular sieves 4 Å (80.0 g) and CH_2Cl_2 (1 l) was added *N*-methylmorpholine *N*-oxide (NMO, 35.0 g, 299 mmol) and tetrapropylammonium perruthenate (TPAP, 2.00 g, 5.69 mmol) at room temperature. After being stirred for 1 h, (carbethoxymethylene)triphenylphosphorane (83.0 g, 238 mmol) was added to the mixture. After 1.5 h, the reaction mixture was diluted with ether and filtered through a celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (15/1) to give **7** (43.0 g, 181 mmol, 85%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.94 (1H, dt, J=15.7, 7.0 Hz), 5.84 (1H, dt, J=15.7, 1.5 Hz), 4.18 (2H, q, J=7.1 Hz), 2.36–2.26 (2H, m), 2.26 (2H, t, J=7.0 Hz), 1.68 (2H, quintet, J=7.0 Hz), 1.28 (3H, t, J=7.1 Hz), 0.16 (9H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.4, 147.9, 121.9, 106.2, 85.2, 60.1, 30.9, 26.8, 19.2, 14.2, 0.0 (×3). IR (neat) 2180, 1710, 1650 cm^{-1}. EI-MS m/z 238 (M^+). HR-MS m/z 238.1382 (Calcd for $C_{13}H_{22}O_2Si$: 238.1388).

3.1.2. (2*E*)-8-Trimethylsilyloct-2-en-7-yn-1-ol (8). To a solution of **7** (8.70 g, 36.6 mmol) in hexane (200 ml) was added dropwise DIBAH (0.95 M in hexane, 84 ml, 79.8 mmol) at −78°C under an argon atmosphere. After being stirred for 30 min, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was filtered through a celite pad. The filtrate was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (5/1) to give **8** (7.09 g, 36.2 mmol, 99%) as a pale yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.70–5.65 (2H, m), 4.09 (2H, br), 2.23 (2H, t, J=7.1 Hz), 2.20–2.11 (2H, m), 1.61 (2H, quintet, J=7.1 Hz), 1.38 (1H, br), 0.0 (9H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 131.9, 129.7, 106.9, 84.7, 63.6, 31.0, 27.8, 19.1, 0.0 (×3). IR (neat) 3320, 2275 cm^{-1}. EI-MS m/z 196 (M^+). HR-MS m/z 196.1297 (Calcd for $C_{11}H_{20}OSi$: 196.1282).

3.1.3. (2*E*)-8-Trimethylsilyloct-2-en-7-ynal (9). To a mixture of **8** (1.73 g, 8.83 mmol), molecular sieves 4 Å (4 g) and CH_2Cl_2 (40 ml) was added NMO (1.35 g, 11.5 mmol), and TPAP (150 mg, 0.427 mmol) at room temperature. After being stirred for 1.5 h, the reaction mixture was diluted with ether and filtered through a celite pad. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (15/1) to give **9** (1.35 g, 6.96 mmol, 79%) as a pale yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.52 (1H, d, J=7.8 Hz), 6.86 (1H, dt, J=15.6, 6.8 Hz), 6.15 (1H, ddt, J=15.6, 7.8, 1.6 Hz), 2.47 (2H, m), 2.30 (2H, t, J=7.1 Hz), 1.74 (2H, quintet, J=7.1 Hz), 0.15 (9H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 193.7, 157.3, 133.3, 105.8, 85.6, 31.4, 26.6, 19.1, 0.0 (×3). IR (neat) 2700, 2160, 1680, 1630 cm^{-1}. EI-MS m/z 194 (M^+). HR-MS m/z 194.1145 (Calcd for $C_{11}H_{18}OSi$: 194.1126).

3.1.4. (6*E*)-1-Trimethylsilylnona-6,8-dien-1-yne (10). To a suspension of methyltriphenylphosphonium bromide (95.0 g, 266 mmol) in THF (900 ml) was added dropwise *n*-BuLi (1.64 M in hexane, 163 ml, 267 mmol) at −20°C under an argon atmosphere. After being stirred for 30 min, a solution of **9** (21.0 g, 108 mmol) in THF (150 ml) was added to the mixture at −20°C. After 30 min, the reaction mixture was quenched with H_2O at 0°C and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with pentane/ether (20/1) to give **10** (18.0 g, 93.8 mmol, 87%) as a yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.30 (1H, dt, J=16.9, 10.3 Hz), 6.07 (1H, dd, J=15.1, 10.3 Hz), 5.68 (1H, dt, J=15.1, 7.1 Hz), 5.10 (1H, d, J=16.9 Hz), 4.93 (1H, d, J=10.3 Hz), 2.27–2.14 (4H, m), 1.62 (2H, quintet, J=7.1 Hz), 0.15 (9H, s). Signals at 6.07, 5.10 and 4.93 ppm show also small couplings. ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.0, 133.9, 131.6, 115.0, 107.0, 84.6, 31.3, 27.9, 19.1, 0.0 (×3). IR (neat) 2200, 1640, 1600 cm^{-1}. EI-MS m/z 192 (M^+). HR-MS m/z 192.1303 (Calcd for $C_{12}H_{20}Si$: 192.1333).

3.1.5. Methyl (7*E*)-deca-7,9-dien-2-ynoate (11). To a solution of **10** (3.40 g, 17.7 mmol) in THF (70 ml) was added dropwise MeLi (1.06 M in ether, 33 ml, 35.0 mmol) at 0°C under an argon atmosphere. After being stirred for 1.5 h, the resulting mixture was added dropwise to a solution of methyl chloroformate (7 ml, 90.6 mmol) in THF (70 ml) at −30°C under an argon atmosphere. After 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with pentane/ether (20/1) to give **11** (2.10 g, 11.8 mmol, 67%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.30 (1H, dt, J=16.9, 10.3 Hz), 6.09 (1H, dd, J=15.1, 10.3 Hz), 5.64 (1H, dt, J=15.1, 7.0 Hz), 5.12 (1H, d, J=16.9 Hz), 4.99 (1H, d, J=10.3 Hz), 3.76 (3H, s), 2.35 (2H, t, J=7.0 Hz), 2.21 (2H, q, J=7.0 Hz), 1.69 (2H, quintet, J=7.0 Hz). Signals at 6.09, 5.12 and 4.99 ppm show also small couplings. ^{13}C NMR (68 MHz, $CDCl_3$) δ 154.4, 137.1, 132.9, 132.5, 115.4, 89.5, 73.4, 52.7, 31.6, 27.2, 18.2. IR (neat) 2200, 1700, 1640, 1580 cm^{-1}. EI-MS m/z 178 (M^+). HR-MS m/z 178.0994 (Calcd for $C_{11}H_{14}O_2$: 178.0993).

3.1.6. (4*RS*,5*SR*,6*SR*)-4,5-Dihydroxy-2-methoxycarbonylbicyclo[4.3.0]non-1-ene (13). A solution of **11** (1.00 g, 5.62 mmol) in toluene (600 ml) was refluxed for 2.5 h under an argon atmosphere. The reaction mixture was cooled to room temperature and concentrated under reduced pressure to give crude **12** (990 mg, 99%) as a colorless oil. To a solution of crude **12** (990 mg) in *tert*-BuOH (5 ml), H_2O (5 ml) and acetone (20 ml) was added NMO (977 mg, 8.34 mmol) and OsO_4 (283 mg, 1.11 mmol) at

−20°C under an argon atmosphere. After being stirred for 30 min, the reaction mixture was quenched with saturated aqueous Na_2SO_3 and extracted with AcOEt. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (2/1) to give **13** (691 mg, 3.26 mmol, 58% from **11**) as white crystals. Mp 131.5–132.5°C (EtOH). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.12–4.06 (1H, m), 3.99–3.87 (1H, m), 3.71 (3H, s), 2.92–2.50 (4H, m), 2.39–2.23 (1H, m), 2.00–1.80 (2H, m), 1.99 (1H, d, J=6.8 Hz), 1.87 (1H, d, J=6.4 Hz), 1.75–1.53 (2H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.3, 157.0, 118.1, 70.1, 69.2, 51.2, 49.0, 32.2, 30.3, 26.7, 24.2. IR ($CHCl_3$) 3400, 1700, 1660 cm^{-1}. EI-MS m/z 212 (M^+). HR-MS m/z 212.1029 (Calcd for $C_{11}H_{16}O_4$: 212.1048). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.20; H, 7.68.

3.1.7. (4*SR*,5*RS*,6*SR*)-4,5-Dihydroxy-2-methoxycarbonylbicyclo[4.3.0]non-1-ene (14). Crude **12** (645 mg), which was obtained from **11** (650 mg, 3.65 mmol), was solvated in AcOH (20 ml). To the solution was added I_2 (974 mg, 3.83 mmol) and AgOAc (1.37 g, 8.21 mmol) at room temperature. After being stirred for 3 h, aqueous AcOH (H_2O/AcOH 1/25, 6 ml) was added to the reaction mixture. After being refluxed for 2 h, NaCl (2 g) was added to the reaction mixture at 0°C and the resulting mixture was filtered. The filtrate was concentrated under reduced pressure. The residue was solvated in methanol and 10% KOH (10 ml) was added to the resulting mixture. After 24 h, since the reaction did not proceed completely, KOH (2.0 g, 35.7 mmol) was added to the mixture. After 10 min, the mixture was concentrated under reduced pressure and extracted with AcOEt. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (1/1) to give **14** (370 mg, 1.75 mmol, 48%, from **11**) as white crystals. Mp 101–102°C (AcOEt/$CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.16 (1H, dd, J=5.9, 2.4 Hz), 3.72 (3H, s), 3.49 (1H, dd, J=9.8, 2.4 Hz), 2.98–2.58 (5H, m), 2.30–2.17 (3H, m), 1.99–1.85 (1H, m), 1.72–1.50 (1H, m), 1.33–1.14 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.5, 158.1, 117.1, 74.5, 68.8, 51.2, 45.2, 34.1, 32.8, 30.5, 23.9. IR ($CHCl_3$) 3450, 1702, 1653 cm^{-1}. EI-MS m/z 212 (M^+), 194, 135. HR-MS m/z 212.1058 (Calcd for $C_{11}H_{16}O_4$: 212.1048). Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.51; H, 7.79.

3.1.8. (4*RS*,5*SR*,6*RS*)-4,5-Di(4-bromobenzoyloxy)-2-methoxycarbonylbicyclo[4.3.0]non-1-ene (15). To a solution of **14** (38.9 mg, 0.183 mmol) in pyridine (1 ml) was added *p*-bromobenzoyl chloride (242 mg, 1.10 mmol) and dimethylaminopyridine (DMAP, 134 mg, 1.10 mmol) at room temperature under an argon atmosphere. After being stirred for 1.5 h, the reaction mixture was quenched with 5% HCl at 0°C and extracted with ether. The extract was washed with brine and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (10/1) to give **15** (82.2 mg, 0.142 mmol, 78%) as a white solid. Recrystallization from benzene afforded **15** as colorless prisms. Mp 150–151°C (benzene). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.86 (2H, d, J=8.8 Hz), 7.79 (2H, d, J=8.6 Hz), 7.59 (2H, d, J=8.6 Hz), 7.52 (2H, d, J=8.8 Hz), 5.88–5.80 (1H, m), 5.11 (1H, dd, J=10.5, 2.4 Hz), 3.75 (3H, s), 3.16–2.73 (5H, m), 2.21–2.07 (1H, m), 1.79–1.56 (1H, m), 1.44–1.24 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 166.9, 165.2, 165.0, 157.7, 131.8, 131.7, 131.1 (×2), 129.0, 128.7, 128.3 (×2), 117.4, 75.2, 69.2, 51.4, 43.7, 32.7, 32.3, 30.7, 23.8. IR ($CHCl_3$) 1721, 1657 cm^{-1}. EI-MS m/z 547 (M^+−OMe). Anal. Calcd for $C_{25}H_{22}Br_2O_6$: C, 51.93; H, 3.83. Found: C, 52.08; H, 3.86. Crystal data, M=578.25; monoclinic; $P2_1/c$(#14); a=11.491(2) Å, b=17.496(2) Å, c=11.981(2) Å, V=2403.6(6) Å^3; Z=4; μ(Mo Kα)=34.21 cm^{-1}; F_{000}=1160.00; D_c=1.598 g/cm^3; crystal dimensions: 0.20×0.20×0.20 mm^3. A total of 5978 reflections were collected using the ω–2θ scan technique to a maximum 2θ value of 55°, and 2803 reflections with $I>3.00\sigma(I)$ were used in the structure determination. Final R and Rw values were 0.052 and 0.097, respectively. The maximum and minimum peaks in the difference map were 0.37 and −0.39 e$^-$/Å^3, respectively.

3.1.9. (4*RS*,5*SR*,6*SR*)-4,5-Isopropylidenedioxy-2-methoxycarbonylbicyclo[4.3.0]non-1-ene (16). To a solution of **13** (123 mg, 0.580 mmol) in dry acetone (4 ml) was added 2,2-dimethoxypropane (0.36 ml, 2.96 mmol) and PPTS (30 mg, 0.119 mmol) under an argon atmosphere at room temperature. After being stirred for 3 h, the reaction mixture was quenched with triethylamine (0.1 ml) and the solvent was removed under reduced pressure. The residue was extracted with ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (10/1) to give **16** (123 mg, 0.488 mmol, 84%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.60 (1H, ddd, J=7.3, 3.4, 1.9 Hz), 4.52 (1H, dd, J=7.3, 4.2 Hz), 3.74 (3H, s), 3.05 (1H, dd, J=15.9, 1.9 Hz), 3.02–2.87 (1H, m), 2.70–2.51 (1H, m), 2.28–2.16 (1H, m), 2.01–1.77 (4H, m), 1.71–1.52 (1H, m), 1.29 (3H, s), 1.24 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.3, 161.6, 118.4, 107.8, 75.5, 74.9, 51.1, 45.7, 33.8, 28.9, 26.9, 26.2, 26.0, 24.2. IR (neat) 1700, 1640 cm^{-1}. EI-MS m/z 252 (M^+). HR-MS m/z 252.1337 (Calcd for $C_{14}H_{20}O_4$: 252.1360).

3.1.10. (4*RS*,5*SR*,6*SR*)-2-Hydroxymethyl-4,5-isopropylidenedioxybicyclo[4.3.0]non-1-ene (17). To a solution of **16** (97.5 mg, 0.387 mmol) in toluene (3 ml) was added dropwise DIBAH (1.02 M in toluene, 0.85 ml, 0.867 mmol) under an argon atmosphere at −78°C. After being stirred for 30 min, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (1/1) to give **17** (74.9 mg, 0.334 mmol, 86%) as white crystals. Mp 89.5–90.5°C (EtOH). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.55 (1H, ddd, J=7.3, 2.9, 2.0 Hz), 4.49 (1H, dd, J=7.3, 3.9 Hz), 4.18 (1H, br d, J=9.0 Hz), 4.02 (1H, br d, J=9.0 Hz), 2.50 (1H, dd, J=15.4, 2.0 Hz), 2.32 (2H, br), 2.13 (1H, br), 2.00–1.75 (4H, m), 1.71–1.44 (2H, m), 1.30 (3H, s), 1.28 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 141.9, 124.7, 107.5, 76.5, 75.0, 63.0, 42.4, 30.6,

29.2, 27.4, 26.4, 25.9, 24.2. IR ($CHCl_3$) 3450, 1680 cm^{-1}. EI-MS *m/z*: 224 (M^+). HR-MS *m/z* 224.1384 (Calcd for $C_{13}H_{20}O_3$: 224.1411). Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.58; H, 9.24.

3.1.11. (1*RS*,2*RS*,4*RS*,5*SR*,6*RS*)-1,2-Epoxy-2-hydroxymethyl-4,5-isopropylidenedioxybicyclo[4.3.0]nonane (18) and (1*SR*,2*SR*,4*RS*,5*SR*,6*RS*)-1,2-epoxy-2-hydroxymethyl-4,5-isopropylidenedioxybicyclo[4.3.0]nonane (19). To a solution of **17** (90.0 mg, 0.402 mmol) in CH_2Cl_2 (12 ml) was added *m*-CPBA (70%, 148 mg, 0.600 mmol) under an argon atmosphere at −20°C. After being stirred for 2.5 h, the reaction mixture was warmed to −5°C, then quenched with saturated aqueous Na_2SO_3 and extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (1/1) to give **18** (49.6 mg, 0.207 mmol, 52%) as white crystals and **19** (20.8 mg, 0.0867 mmol, 22%) as a colorless oil. **18**: mp 76.0–77.0°C (AcOEt/hexane). ^1H NMR (270 MHz, $CDCl_3$) δ 4.45–4.36 (2H, m), 3.78–3.65 (2H, m), 2.44 (1H, d, *J*=15.8 Hz), 2.20–1.50 (9H, m), 1.51 (3H, s), 1.27 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 108.0, 71.7, 71.5, 69.0, 64.4, 61.4, 41.5, 28.4, 27.8, 26.4, 25.9, 23.4, 22.6. IR ($CHCl_3$) 3300 cm^{-1}. EI-MS *m/z* 240 (M^+). HR-MS *m/z* 240.1348 (Calcd for $C_{13}H_{20}O_{4:}$ 240.1360). Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.65; H, 8.50. **19**: ^1H NMR (270 MHz, $CDCl_3$) δ 4.47–4.43 (1H, m), 4.35 (1H, dd, *J*=7.3, 3.7 Hz), 3.78 (1H, dd, *J*=11.2, 4.8 Hz), 3.57 (1H, dd, *J*=11.2, 5.9 Hz), 2.65–2.50 (1H, m), 2.51 (1H, dd, *J*=15.6, 2.4 Hz), 2.10–1.60 (7H, m), 1.50 (1H, dd, *J*=15.6, 3.1 Hz), 1.44 (3H, s), 1.32 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 107.1, 75.5, 73.8, 71.2, 64.7, 60.5, 43.4, 32.6, 30.1, 26.8, 25.9, 25.6, 23.1. IR (neat): 3200 cm^{-1}. EI-MS *m/z* 240 (M^+). HR-MS *m/z* 240.1370 (Calcd for $C_{13}H_{20}O_{4:}$ 240.1360).

3.1.12. (1*RS*,2*RS*,4*RS*,5*SR*,6*RS*)-1,2-Epoxy-2-imidazoylthiocarbonyloxymethyl-4,5-isopropylidenedioxybicyclo[4.3.0]nonane (20). To a solution of **18** (49.0 mg, 0.204 mmol) in 1,2-dichloroethane (1.5 ml) was added 1,1′-thiocarbonyldiimdazole (90%, 81.0 mg, 0.410 mmol). After being refluxed for 20 min, the reaction was quenched with saturated aqueous Na_2SO_3 at room temperature and extracted with CH_2Cl_2. Combined extracts were treated with cold 1 N HCl, washed saturated aqueous $NaHCO_3$, brine and dried ($MgSO_4$). The solvent was removed under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (2/1) to give **20** (56.0 mg, 0.160 mmol, 78%) as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$) δ 8.36 (1H, br s), 7.65 (1H, t, *J*=1.5 Hz), 7.06 (1H, dd, *J*=1.5, 0.7 Hz), 4.80 (1H, d, *J*=12.0 Hz), 4.62 (1H, d, *J*=12.0 Hz), 4.47–4.37 (2H, m), 2.47 (1H, d, *J*=15.6 Hz), 2.19–1.57 (8H, m), 1.52 (3H, s), 1.27 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.9, 136.9, 131.0, 117.9, 108.3, 75.1, 71.6, 71.1, 68.6, 58.2, 41.3, 29.1, 27.6, 26.4, 25.9, 23.5, 22.5. IR ($CHCl_3$) 1280, 1000 cm^{-1}. EI-MS *m/z* 350 (M^+), 335, 147. HR-MS *m/z* 350.1328 (Calcd for $C_{17}H_{22}O_4N_2S$: 350.1299).

3.1.13. (1*SR*,2*SR*,4*RS*,5*SR*,6*RS*)-1,2-Epoxy-2-imidazoylthiocarbonyloxymethyl-4,5-isopropylidenedioxybicyclo[4.3.0]nonane (21). According to the preparation of **20**, **19** (132 mg, 0.550 mmol) was converted into **21** (146 mg, 76%) as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$) δ 8.41 (1H, br s), 7.70 (1H, br s), 7.05 (1H, br s), 4.95 (1H, dd, *J*=11.7, 1.5 Hz), 4.51 (1H, br d, *J*=11.7 Hz), 4.48–4.44 (1H, m), 4.41–4.34 (1H, m), 2.57 (1H, br d, *J*=15.6 Hz), 2.14–1.70 (8H, m), 1.40 (3H, s), 1.30 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 184.1, 136.9, 130.8, 118.0, 107.0, 76.4, 75.1, 73.9, 70.3, 58.2, 43.3, 31.9, 30.4, 26.7, 26.3, 25.7, 23.2. IR (neat) 1200, 980 cm^{-1}. EI-MS *m/z* 350 (M^+), 335, 223. HR-MS *m/z* 350.1326 (Calcd for $C_{17}H_{22}O_4N_2S$: 350.1299).

3.1.14. (4*RS*,5*SR*,6*SR*)-2-Methoxycarbonyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-1-ene (22). To a solution of **13** (154 mg, 0.726 mmol) and 2,6-lutidine (0.45 ml, 3.86 mmol) in CH_2Cl_2 (12 ml) was added TESOTf (0.65 ml, 2.9 mmol) at −15°C under an argon atmosphere. After being stirred for 10 min, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (15/1) to give **22** (319 mg, 0.725 mmol, 100%) as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$) δ 3.98 (1H, dd, *J*=2.6, 1.7 Hz), 3.76 (1H, td, *J*=8.6, 1.7 Hz), 3.73 (3H, s), 2.85–2.35 (5H, m), 1.90–1.45 (4H, m), 0.97 (9H, t, *J*=7.4 Hz), 0.93 (9H, t, *J*=7.4 Hz), 0.62 (12H, q, *J*=7.4 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.7, 157.6, 118.5, 71.7, 71.2, 51.0, 50.6, 32.2, 30.7, 27.0, 24.3, 7.0 (×3), 6.9 (×3), 5.2 (×3), 5.0 (×3). IR (neat) 1710, 1660 cm^{-1}. EI-MS *m/z* 440 (M^+). HR-MS *m/z* 440.2793 (Calcd for $C_{23}H_{44}O_4Si_2$: 440.2776).

3.1.15. (4*RS*,5*SR*,6*SR*)-2-Hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-1-ene (23). According to the preparation of **17**, **22** (61.9 mg, 0.141 mmol) was converted into **23** (56.7 mg, 0.138 mmol, 98%) as white crystals. Mp 56.0–57.0°C (AcOEt/hexane). ^1H NMR (270 MHz, $CDCl_3$) δ 4.04 (2H, br), 3.99–3.95 (1H, m), 3.87–3.77 (1H, m), 2.40–2.08 (5H, m), 1.84–1.45 (5H, m), 0.97 (9H, t, *J*=8.1 Hz), 0.93 (9H, t, *J*=8.1 Hz), 0.68–0.56 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 137.5, 125.1, 72.2, 71.8, 63.7, 48.0, 31.8, 27.24, 27.16, 24.2, 7.0 (×3), 6.9 (×3), 5.3 (×3), 4.9 (×3). IR ($CHCl_3$) 3550 cm^{-1}. EI-MS *m/z*: 412 (M^+). HR-MS *m/z*: 412.2839 (Calcd for $C_{22}H_{44}O_3Si_2$: 412.2827). Anal. Calcd for $C_{22}H_{44}O_3Si_2$: C, 64.05; H, 10.75. Found: C, 63.65; H, 10.74.

3.1.16. (1*RS*,2*RS*,4*RS*,5*SR*,6*RS*)-1,2-Epoxy-2-hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]nonane (24). To a mixture of **23** (33.6 mg, 81.6 μmol) and $NaHCO_3$ (20.3 mg, 0.242 mmol) in CH_2Cl_2 (18 ml) was added *m*-CPBA (70%, 30.0 mg, 0.122 mmol) under an argon atmosphere at −20°C. After being stirred for 1 h, the reaction mixture was warmed to room temperature and then was quenched with saturated aqueous Na_2SO_3. The mixture was extracted with CH_2Cl_2. Combined extracts were washed with brine and dried ($MgSO_4$). The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (5/1) to give **24** (28.0 mg, 65.4 μmol, 80%) as a colorless oil. ^1H NMR (270 MHz, $CDCl_3$) δ 3.91 (2H, br, *J*=2.1 Hz), 3.70–3.60 (3H, m), 2.10 (1H, dd, *J*=14.5, 10.8 Hz), 2.02–1.50 (8H, m), 0.96 (18H, t,

J=8.0 Hz), 0.61 (12H, q, J=8.0 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 71.7, 71.6, 71.4, 65.1, 62.1, 45.6, 31.9, 27.8, 23.7, 21.0, 7.0 (×3), 6.8 (×3), 5.1 (×3), 4.8 (×3). IR (neat) 3400 cm^{-1}. EI-MS m/z 428 (M^+). HR-MS m/z 428.2798 (Calcd for $C_{22}H_{44}O_4Si_2$: 428.2776).

3.1.17. (1*RS*,2*RS*,4*RS*,5*SR*,6*RS*)-1,2-Epoxy-2-imidazolylthiocarbonyloxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]nonane (25). According to the preparation of **20**, **24** (116 mg, 0.271 mmol) was converted into **25** (122 mg, 0.228 mmol, 84%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.36 (1H, br s), 7.65 (1H, t, J=1.4 Hz), 7.06 (1H, br), 4.81 (1H, d, J=11.7 Hz), 4.53 (1H, d, J=11.7 Hz), 3.94 (1H, br), 3.69 (1H, ddd, J=10.7, 6.8, 2.2 Hz), 2.21 (1H, dd, J=14.4, 10.7 Hz), 2.10–1.50 (8H, m), 0.96 (9H, t, J=8.1 Hz), 0.95 (9H, t, J=7.6 Hz) 0.66–0.54 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 184.0, 136.8, 130.9, 117.8, 76.1, 71.4, 71.1, 58.6, 53.3, 45.3, 31.8, 27.7, 23.7, 20.8, 6.9 (×3), 6.6 (×3), 5.1 (×3), 4.7 (×3). IR (neat) 1280, 1000 cm^{-1}. EI-MS m/z 538 (M^+), 509, 480, 382. HR-MS m/z 538.2712 (Calcd for $C_{26}H_{46}N_2O_4SSi_2$: 538.2714).

3.1.18. (4*RS*,5*SR*,6*RS*)-2-Methoxycarbonyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-1-ene (26). According to the preparation of **22**, **14** (240 mg, 1.13 mmol) was converted into **26** (493 mg, 1.12 mmol, 99%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.01 (1H, dd, J=2.9, 2.0 Hz), 3.70 (3H, s), 3.39 (1H, dd, J=9.8, 2.0 Hz), 2.96–2.55 (3H, m), 2.51–2.45 (2H, m), 2.18–2.06 (1H, m), 1.91–1.78 (1H, m), 1.67–1.44 (1H, m), 1.22–1.00 (1H, m), 1.00–0.90 (18H, m), 0.65–0.46 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 167.9, 159.8, 116.9, 75.8, 70.7, 51.0, 45.6, 36.3, 33.0, 31.1, 23.8, 6.9 (×3), 6.8 (×3), 6.4 (×3), 5.0 (×3). IR (neat) 1719, 1655 cm^{-1}. EI-MS m/z 440 (M^+), 411. HR-MS m/z 440.2792 (Calcd for $C_{23}H_{44}O_4Si_2$: 440.2776).

3.1.19. (4*RS*,5*SR*,6*RS*)-2-Hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-1-ene (27). According to the preparation of **17**, **26** (719 mg, 1.63 mmol) was converted into **27** (618 mg, 1.50 mmol, 92%) as white crystals. Mp 68.0–69.0°C (AcOEt/hexane). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.15–3.96 (3H, m), 3.36 (1H, dd, J=9.9, 2.0 Hz), 2.59 (1H, br), 2.47–2.17 (5H, m), 2.13–2.01 (1H, m), 1.83–1.73 (1H, m), 1.64–1.43 (1H, m), 1.17–1.01 (1H, m), 1.00–0.92 (18H, m), 0.61 (12H, q, J=8.4 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 139.7, 123.2, 76.5, 71.3, 63.6, 43.3, 37.1, 31.7, 28.0, 23.7, 7.0 (×6), 5.1 (×6). IR ($CHCl_3$) 3454 cm^{-1}. EI-MS m/z 412 (M^+), 383. HR-MS m/z 412.2805 (Calcd for $C_{22}H_{44}O_3Si_2$: 412.2827). Anal. Calcd for $C_{22}H_{44}O_3Si_2$: C, 64.05; H, 10.75. Found: C, 63.75; H, 11.19.

3.1.20. (1*RS*,2*RS*,4*RS*,5*SR*,6*SR*)-1,2-Epoxy-2-hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]nonane (28). According to the preparation of **24**, **27** (618 mg, 1.50 mmol) was converted into **28** (624 mg, 1.46 mmol, 97%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.87–3.80 (1H, m), 3.58 (2H, br), 3.30 (1H, dd, J=9.5, 2.0 Hz), 2.52–2.38 (1H, m), 2.22 (1H, dd, J=15.8, 2.0 Hz), 2.21–2.08 (1H, m), 1.98–1.58 (6H, m), 1.33–1.15 (1H, m), 0.96 (18H, t, J=7.8 Hz), 0.65–0.54 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 76.8, 71.6, 70.7, 65.4, 62.1, 43.3, 34.3, 32.4, 31.6, 24.4, 7.4 (×6), 5.5 (×6). IR (neat) 3450 cm^{-1}. EI-MS m/z 428 (M^+), 399, 381. HR-MS m/z 428.2752 (Calcd for $C_{22}H_{44}O_4Si_2$:428.2776).

3.1.21. (1*RS*,2*RS*,4*RS*,5*SR*,6*SR*)-1,2-Epoxy-2-imidazolylthiocarbonyloxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]nonane (29). According to the preparation of **20**, **28** (500 mg, 1.17 mmol) was converted into **29** (605 mg, 1.12 mmol, 96%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.34 (1H, br), 7.63 (1H, t, J=1.7 Hz), 7.07 (1H, dd, J=1.7, 1.0 Hz), 4.71 (1H, d, J=11.7 Hz), 4.46 (1H, d, J=11.7 Hz), 3.90–3.83 (1H, m), 3.33 (1H, dd, J=9.8, 2.0 Hz), 2.58–2.45 (1H, m), 2.31 (1H, dd, J=15.8, 3.0 Hz), 2.28–2.15 (1H, m), 1.93 (1H, dd, J=15.8, 4.2 Hz) 1.95–1.58 (4H, m), 1.38–1.16 (1H, m), 0.97 (18H, t, J=7.8 Hz), 0.67–0.54 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.9, 136.7, 131.0, 117.8, 76.5, 76.1, 70.7, 69.9, 58.5, 42.5, 34.1, 32.0, 31.1, 24.0, 6.94 (×3), 6.88 (×3), 5.1 (×6). IR (neat) 1232, 998 cm^{-1}. EI-MS m/z 509 (M^+-Et). HR-MS m/z 509.2338 (Calcd for $C_{24}H_{41}N_2O_4SSi_2$: 509.2323).

3.1.22. 2-Hydroxymethylbicyclo[4.3.0]nona-1,4-diene (30). DIBAH reduction of the crude **12**, which was prepared by Diels–Alder reaction of **11** (586 mg, 3.29 mmol), was carried out according to the preparation of **17** to give **30** (429 mg, 2.86 mmol, 87% from **11**) as a wax. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.87–5.74 (2H, m), 4.11 (2H, s), 2.96–2.86 (1H, m), 2.72 (2H, br), 2.36 (2H, br t, J=7.5 Hz), 2.16–1.96 (2H, m), 1.85–1.56 (2H, m), 1.26–1.07 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 139.5, 128.0, 125.1, 124.5, 63.2, 41.6, 32.3, 28.4, 26.6, 23.1. IR (neat) 3300, 1640 cm^{-1}. EI-MS m/z 149 (M^+−H), 130. HR-MS m/z 149.0946 (Calcd for $C_{10}H_{13}O$: 149.0966).

3.1.23. 1,2-Epoxy-2-hydroxymethylbicyclo[4.3.0]non-4-enes (31 and 32). According to the epoxidation of **23**, **30** (1.20 g, 8.00 mmol) was converted into **31** (340 mg, 2.05 mmol, 26%, more polar) and **32** (194 mg, 1.17 mmol, 15%, less polar) as colorless oils. **31**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.55 (1H, br d, J=10.2 Hz), 5.49–5.40 (1H, m), 3.77 (1H, dd, J=12.1, 6.1 Hz), 3.68 (1H, dd, J=12.1, 4.4 Hz), 2.73–2.54 (2H, m), 2.46–2.29 (2H, m), 2.12–1.82 (3H, m), 1.75–1.58 (2H, m), 1.55–1.40 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 125.7, 122.9, 72.9, 64.4, 53.3, 41.1, 27.7, 27.3, 26.9, 20.7. IR (neat) 3450 cm^{-1}. EI-MS m/z 166 (M^+), 83. HR-MS m/z 166.1010 (Calcd for $C_{10}H_{14}O_2$: 166.0993). **32**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.66–5.57 (1H, m), 5.54–5.44 (1H, m), 3.69 (2H, d, J=5.4 Hz), 2.69–2.55 (1H, m), 2.52–2.46 (2H, m), 2.33 (1H, t, J=5.7 Hz), 2.14–1.75 (5H, m), 1.37–1.18 (1H, m). ^{13}C NMR ($CDCl_3$) δ 125.4, 121.4, 69.9, 64.7, 61.9, 41.1, 31.5, 27.3, 27.1, 23.4. IR ($CHCl_3$): 3400, 1660 cm^{-1}. EI-MS m/z 166 (M^+), 83. HR-MS m/z 166.0992 (Calcd for $C_{10}H_{14}O_2$: 166.0993).

3.1.24. Imidazolylthiocarbonylation of 31. According to the preparation of **20**, **31** (91.9 mg, 0.554 mmol) was converted into **33** (112 mg, 0.406 mmol, 73%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.37 (1H, s), 7.64 (1H, br s), 7.05 (1H, br s), 5.64 (1H, br d, J=10.2 Hz), 5.56–5.45 (1H, m), 4.99 (1H, d, J=11.7 Hz), 4.65 (1H, d, J=11.7 Hz), 2.71 (1H, dd, J=16.1, 5.9 Hz), 2.60–2.42 (2H, m),

2.25–2.10 (1H, m), 2.10–1.90 (2H, m), 1.89–1.69 (2H, m), 1.66–1.47 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 183.8, 136.7, 130.9, 126.2, 122.2, 117.7, 74.9, 72.3, 60.6, 41.0, 28.4, 27.4, 27.1, 20.8. IR ($CHCl_3$) 1225, 1000 cm^{-1}. EI-MS *m/z* 276 (M^+), 149. HR-MS *m/z* 276.0914 (Calcd for $C_{14}H_{16}N_2O_2S$: 276.0932).

3.1.25. Imidazolylthiocarbonylation of 32. According to the preparation of **20**, **32** (100 mg, 0.602 mmol) was converted into **34** (117 mg, 0.424 mmol, 70%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.35 (1H, br s), 7.64 (1H, br s), 7.06 (1H, br s), 5.71–5.62 (1H, m), 5.54–5.45 (1H, m), 4.78 (1H, d, *J*=11.7 Hz), 4.59 (1H, d, *J*=11.7 Hz), 2.75–2.54 (3H, m), 2.14–2.02 (1H, m), 1.92–1.74 (4H, m), 1.36–1.32 (1H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 184.1, 137.1, 131.3, 125.8, 120.9, 118.1, 76.5, 69.8, 58.9, 41.0, 31.8, 27.6, 27.5, 23.6. IR (neat) 1220, 985 cm^{-1}. EI-MS *m/z* 276 (M^+), 149, 131. HR-MS *m/z* 276.0913 (Calcd for $C_{14}H_{16}N_2O_2S$: 276.0932).

3.1.26. Conversion of 18 into 36. To a solution of 2,2,6,6-tetramethylpiperidine (0.22 ml, 1.30 mmol) in benzene (1.5 ml) was added dropwise *n*-BuLi (1.63 M in hexane, 0.8 ml, 1.30 mmol) under an argon atmosphere at 0°C. After being stirred for 15 min, a solution of diethylaluminiumchloride (0.95 M in hexane, 1.38 ml, 1.31 mmol) was added dropwise to the mixture at the same temperature. After 30 min, a solution of **18** (80.0 mg, 0.333 mmol) in benzene (1.5 ml) was added to the mixture at the same temperature. After 1 h, the reaction was quenched with 1 N HCl and was extracted with ether. The extract was washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to give **35**, which was solvated in 1,2-dichloroethane (0.5 ml). To the solution was added 1,1′-thiocarbonyldiimidazole (90%, 25.0 mg, 0.126 mmol). After being refluxed for 1 h, the reaction mixture was quenched with saturated aqueous Na_2SO_3 at room temperature and extracted with CH_2Cl_2. The extract was treated with cold 1 N HCl, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (1/1) to give **36** (10.6 mg, 37.6 μmol, 11% from **18**) as a colorless oil. ^{1}H NMR (benzene-d_6) δ 5.69 (1H, br), 3.85–3.65 (2H, m), 3.54–3.52 (1H, m), 3.26–3.20 (1H, m), 2.30–1.50 (6H, m), 1.44 (3H, s), 1.16 (3H, s), 1.06–0.88 (1H, m). ^{13}C NMR (benzene-d_6) δ 191.6, 138.5, 130.4, 109.0, 85.9, 77.8, 75.3, 72.8, 45.0, 36.2, 32.9, 27.0, 25.2, 25.0. IR ($CHCl_3$) 1310, 1120 cm^{-1}. EI-MS *m/z* 282 (M^+), 267. HR-MS *m/z* 282.0933 (Calcd for $C_{14}H_{18}O_4$: 282.0925).

3.1.27. (2*SR*,4*RS*,5*SR*,6*SR*)-2-Hydroxy-2-hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-9-ene (37). To a solution of **24** (110 mg, 0.257 mmol) in CH_2Cl_2 (20 ml) was added *p*-TsOH·H_2O (9 mg) under an argon atmosphere at 0°C. After being stirred for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with brine and dried over $MgSO_4$. The residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (10/1) to give **37** (19.0 mg, 44.4 μmol, 17%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.69 (1H, br), 3.78 (1H, br), 3.63 (1H, ddd, *J*=11.7, 4.4, 2.0 Hz), 3.56–3.42 (2H, m), 2.67–2.55 (1H, m), 2.45–2.21 (2H, m), 2.10 (1H, br), 1.99–1.77 (5H, m), 0.96 (9H, t, *J*=8.0 Hz), 0.94 (9H, t, *J*=8.0 Hz), 0.67–0.56 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 143.4, 126.0, 74.4, 73.9, 71.5, 66.8, 48.4, 38.4, 31.7, 24.4, 7.0 (×3), 6.8 (×3), 5.3 (×3), 4.8 (×3). IR ($CHCl_3$) 1522 cm^{-1}. EI-MS *m/z* 381 (M^+−Et, H_2O). HR-MS *m/z* 381.2282 (Calcd for $C_{20}H_{37}O_3Si_2$: 381.2279).

3.1.28. Thiocarbonylation of 37. According to the preparation of **36** from **35**, **37** (169 mg, 0.395 mmol) was converted into **38** (158 mg, 85%) as white crystals. Mp 51.0–52.0°C (AcOEt/hexane). ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.80 (1H, br), 4.37 (2H, s), 3.81 (1H, br), 3.54 (1H, ddd, *J*=12.0, 3.7, 2.0 Hz), 2.64–2.55 (1H, m), 2.54 (1H, t, *J*=12.0 Hz), 2.49–2.24 (2H, m), 1.97 (2H, q, *J*=7.6 Hz), 1.79 (1H, dd, *J*=12.0, 3.9 Hz), 0.96 (9H, t, *J*=8.0 Hz), 0.93 (9H, t, *J*=8.0 Hz), 0.62 (12H, q, *J*=8.0 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.2, 136.5, 126.9, 87.8, 78.0, 73.4, 71.1, 47.9, 37.9, 31.9, 24.1, 6.8 (×3), 6.7 (×3), 5.2 (×3), 4.6 (×3). IR ($CHCl_3$) 1230, 990 cm^{-1}. EI-MS *m/z* 470 (M^+), 427, 398. HR-MS *m/z* 470.2313 (Calcd for $C_{23}H_{42}O_4SSi_2$: 470.2340). Anal. Calcd for $C_{23}H_{42}O_4SSi_2$: C, 58.70; H, 8.99. Found: C, 58.34; H, 9.07.

3.1.29. (2*SR*,4*RS*,5*SR*,6*RS*)-2-Hydroxy-2-hydroxymethyl-4,5-bis(triethylsilyloxy)bicyclo[4.3.0]non-9-ene (39). According to the preparation of **37**, **28** (124 mg, 0.290 mmol) was converted into **39** (28.6 mg, 0.0668 mmol, 23%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.57 (1H, br), 5.16 (1H, s, (OH)), 4.13 (1H, br), 3.82 (1H, d, *J*=11.0 Hz), 3.58–3.46 (1H, m), 3.24 (2H, s), 2.40–2.07 (4H, m), 1.69–1.50 (2H, m), 1.47 (1H, dd, *J*=14.4, 1.7 Hz), 0.99 (9H, t, *J*=7.6 Hz), 0.97 (9H, t, *J*=7.6 Hz), 0.73–0.59 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 144.9, 123.6, 79.7, 74.4, 70.5, 67.8, 45.3, 38.9, 31.5, 27.8, 7.0 (×3), 6.8 (×3), 5.2 (×3), 4.9 (×3). IR (neat) 3480 cm^{-1}. EI-MS *m/z* 399 (M^+−Et), 381. HR-MS *m/z* 399.2384 (Calcd for $C_{20}H_{39}O_4Si_2$: 399.2385).

3.1.30. Thiocarbonylation of 39. According to the preparation of **36**, **39** (19.5 mg, 0.0456 mmol) was converted into **40** (8.30 mg, 39%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.90 (1H, br), 4.77 (1H, d, *J*=8.9 Hz), 4.20 (1H, d, *J*=8.9 Hz), 4.02 (1H, br), 3.39 (1H, m), 3.20 (1H, dd, *J*=10.4, 2.5 Hz), 2.43–2.17 (4H, m), 1.71 (1H, dd, *J*=15.3, 2.4 Hz), 1.58 (1H, m), 1.00 (9H, t, *J*=8.4 Hz), 0.97 (9H, t, *J*=8.4 Hz), 0.77–0.57 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 191.5, 140.0, 130.5, 85.5, 78.6, 75.7, 70.9, 44.8, 42.0, 31.3, 28.3, 7.00 (×3), 6.97 (×3), 5.2 (×3), 5.1 (×3). IR ($CHCl_3$) 1218, 1050 cm^{-1}. EI-MS *m/z* 441 (M^+−Et). HR-MS *m/z* 441.1948 (Calcd for $C_{21}H_{37}O_4S_1Si_2$: 441.1950).

3.2. General procedure of radical rearrangement

Under an argon atmosphere, a solution of *n*-Bu_3SnH (2 equiv.) and AIBN (0.13 equiv.) in benzene or toluene was added slowly to a refluxing solution of substrate in benzene or toluene by using a syringe pump. After being refluxed for adequate time, the reaction mixture was cooled to room temperature and the solvent was removed under reduced pressure. The residue was purified by column

chromatography on silica gel eluted with hexane/AcOEt to give bicyclo[5.3.0]decanones and bicyclo[4.3.0]nonanones.

3.2.1. (1*RS*,7*SR*,8*SR*,9*RS*)-8,9-Isopropylidenedioxybicyclo[5.3.0]decan-3-one (41). Colorless oil. Compound **41** was obtained as a mixture with an undetected minor product. The ratio was found to be ca. 4: 1 based on ^{1}H NMR. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.66 (1H, td, J=6.0, 1.0 Hz), 4.58 (1H, t, J=6.0 Hz), 3.15 (1H, t, J=14.0 Hz), 2.55 (1H, ddd, J=15.6, 7.6, 5.5 Hz), 2.43 (1H, ddd, J=15.6, 7.9, 6.1 Hz), 2.31–2.24 (2H, m), 2.14–2.04 (2H, m), 2.03–1.95 (2H, m), 1.94–1.85 (1H, m), 1.80 (1H, d, J=14.3 Hz), 1.70–1.55 (1H, m), 1.50 (3H, s), 1.305 (3H, s). Observable signals for minor product: 4.60 (1H, t, J=5.8 Hz), 4.54 (1H, t, J=5.8 Hz), 2.63 (1H, dd, J=16.5, 2.7 Hz), 2.50 (1H, dd, J=11.6, 2.5 Hz), 1.45 (3H, s), 1.297 (3H, s). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.4, 110.0, 83.7, 80.8, 47.2, 45.4, 44.0, 38.8, 37.6, 26.2, 25.0, 23.3, 21.4. IR (neat) 1690 cm^{-1}. EI-MS m/z 224 (M^+), 209, 149. HR-MS m/z 224.1395 (Calcd for $C_{13}H_{20}O_3$: 224.1411).

3.2.2. (1*SR*,6*SR*,7*SR*,8*RS*)-7,8-Isopropylidenedioxy-1-methylbicyclo[4.3.0]nonan-2-one (42). Colorless oil. ^{1}H NMR (270 MHz, benzene-d_6) δ 4.22 (1H, t, J=6.4 Hz), 4.16 (1H, t, J=6.4 Hz), 3.10 (1H, d, J=13.9 Hz), 2.54–2.10 (3H, m), 1.74–1.47 (3H, m), 1.43 (3H, s), 1.40–1.32 (1H, m), 1.13 (3H, s), 0.95 (1H, dd, J=14.3, 6.4 Hz), 0.85 (3H, s). ^{13}C NMR (68 MHz, benzene-d_6) δ 210.8, 111.2, 85.6, 80.3, 54.2, 51.3, 42.2, 37.9, 26.3, 26.2, 25.0, 24.6, 22.4. IR (neat) 1700 cm^{-1}. EI-MS m/z 209 (M^+-Me), 149, 109, 93. HR-MS m/z 209.1149 (Calcd for $C_{12}H_{17}O_3$: 209.1177).

3.2.3. (1*RS*,7*SR*,8*SR*,9*RS*)-8,9-Bis(triethylsilyloxy)bicyclo[5.3.0]decan-3-one (43). Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.91–3.82 (2H, m), 2.68 (1H, t, J=13.2 Hz), 2.62–2.50 (1H, m), 2.40–2.13 (3H, m), 2.08–1.70 (5H, m), 1.60–1.35 (2H, m), 0.96 (9H, t, J=8.3 Hz), 0.95 (9H, t, J=8.3 Hz), 0.68–0.54 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.8, 78.7, 74.7, 48.0, 44.1, 43.9, 38.4, 33.4, 24.2, 23.1, 7.0 (×3), 6.8 (×3), 5.2 (×3), 4.8 (×3). IR (neat) 1700 cm^{-1}. EI-MS m/z 412 (M^+), 325, 217. HR-MS m/z 412.2856 (Calcd for $C_{22}H_{44}O_3Si_2$: 412.2827).

3.2.4. (1*SR*,7*RS*,8*SR*,9*RS*)-8,9-Bis(triethylsilyloxy)bicyclo[5.3.0]decan-3-one (44). Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.98 (1H, br), 3.54 (1H, dd, J=8.8, 3.4 Hz), 2.67–2.49 (2H, m), 2.42–2.10 (3H, m), 2.39 (1H, t, J=13.7 Hz), 2.03–1.83 (3H, m), 1.63–1.39 (2H, m), 1.30–1.18 (1H, m), 0.97 (9H, t, J=8.0 Hz), 0.96 (9H, t, J=7.6 Hz), 0.67–0.55 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.2, 80.8, 74.5, 46.7, 44.8, 44.2, 38.7, 32.7, 27.2, 23.6, 7.0 (×6), 5.1 (×3), 5.0 (×3). IR ($CHCl_3$) 1700 cm^{-1}. EI-MS m/z 383 (M^+-Et), 251, 217. HR-MS m/z 383.2413 (Calcd for $C_{20}H_{39}O_3Si_2$: 383.2436).

3.2.5. (1*RS*,7*RS*,8*SR*,9*RS*)-8,9-Bis(triethylsilyloxy)bicyclo[5.3.0]decan-3-one (45). Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.95 (1H, td, J=4.0, 2.2 Hz), 3.43 (1H, dd, J=9.3, 4.0 Hz), 2.64–2.40 (3H, m), 2.37 (1H, dd, J=17.6, 11.5 Hz), 2.20–1.68 (4H, m), 1.64–1.46 (1H, m), 1.34–1.07 (3H, m), 0.97 (9H, t, J=8.3), 0.96 (9H, t, J=7.8 Hz), 0.67–0.54 (12H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 214.1, 80.2, 73.6, 50.7, 50.6, 43.9, 38.2, 34.8, 33.0, 25.5, 7.6 (×3), 7.0 (×3), 5.4 (×3), 5.1 (×3). IR (neat) 1696 cm^{-1}. EI-MS m/z 383 (M^+-Et), 280, 217. HR-MS m/z 383.2415 (Calcd for $C_{20}H_{39}O_3Si_2$: 383.2436).

3.2.6. *cis*-Bicyclo[5.3.0]decan-8-ene-3-one (46). Colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.67–5.62 (1H, m), 5.53–5.52 (1H, m), 2.84 (1H, br), 2.73–2.22 (6H, m), 2.18–2.00 (1H, m), 1.95–1.75 (2H, m), 1.65–1.50 (2H, m), 1.43–1.09 (4H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.1, 134.6, 128.6, 48.9, 45.8, 44.5, 39.8, 36.0, 29.1, 22.7. IR (neat) 1700, 1670 cm^{-1}. EI-MS m/z 150 (M^+), 101. HR-MS m/z 150.1036 (Calcd for $C_{10}H_{14}O$: 150.1044).

3.2.7. (1*RS*,7*SR*,8*SR*,9*RS*)-8,9-Dihydroxybicyclo[5.3.0]decan-3-one (47) (desilylation of 43). To a solution of **43** (4.8 mg, 11.7 μmol) in dry THF (0.1 ml) was added TBAF (1 M solution in THF, 25 μl, 25 μmol) at 0°C under an argon atmosphere. After being stirred for 2 h, the reaction mixture was quenched with H_2O, extracted with ether, washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with silica gel eluted with hexane/AcOEt (1/10) to give **47** (1.5 mg, 8.15 μmol, 70%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.10 (1H, ddd, J=10.7, 6.6, 4.1 Hz), 3.94 (1H, t, J=4.1 Hz), 2.70 (1H, dd, J=13.6, 11.7 Hz), 2.62–1.88 (11H, m), 1.60–1.40 (2H, m). ^{13}C NMR (68 MHz, $CDCl_3$) δ 213.2, 77.2, 73.5, 47.3, 44.3, 44.2, 38.6, 33.9, 23.6, 23.2. IR ($CHCl_3$) 1698 cm^{-1}. EI-MS m/z 184 (M^+), 166, 125. HR-MS m/z 184.1068 (Calcd for $C_{10}H_{16}O_3$: 184.1099).

3.2.8. (1*RS*,7*SR*,8*RS*,9*SR*)-8,9-Dihdroxybicyclo[5.3.0]decan-3-one (48) (desilylation of 44). According to the preparation of **47** from **43**, **44** (20.0 mg, 48.5 μmol) was converted into **48** (7.1 mg, 38.6 μmol, 80%) as a colorless oil. ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.11 (1H, td, J=4.0, 1.5 Hz), 3.74 (1H, dd, J=8.3, 4.0 Hz), 2.75–2.50 (2H, m), 2.47–2.29 (4H, m), 2.20–1.88 (5H, m), 1.68–1.53 (2H, m), 1.42 (1H, ddd, J=13.7, 8.8, 4.0 Hz). ^{13}C NMR (68 MHz, $CDCl_3$) δ 212.8, 79.9, 72.9, 46.4, 46.2, 44.1, 38.1, 33.5, 27.4, 23.2. IR ($CHCl_3$) 1690 cm^{-1}. EI-MS m/z 184 (M^+), 166. HR-MS m/z 184.1106 (Calcd for $C_{10}H_{16}O_3$: 184.1099).

3.2.9. Conversion of 47 into 41. According to the preparation of **16** from **13**, **47** (7.5 mg, 40.8 μmol) was converted into **41** (8.2 mg, 36.8 μmol, 90%).

3.2.10. Conversion of 46 into 47. According to the preparation of **14** from **12**, **46** (20.0 mg, 0.133 mmol) was converted into **47** (7.5 mg, 40.8 μmol, 31%).

3.2.11. Conversion of 46 into 48. According to the preparation of **13** from **12**, **46** (8.4 mg, 56.0 μmol) was converted into **48** (5.2 mg, 28.3 μmol, 51%).

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