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Stereocontrolled Formation of Three Contiguous Stereogenic Centers by Free Radical Cyclization – Synthesis of (+)-Iridomyrmecin and (–)-Isoiridomyrmecin – Formal Synthesis of δ-Skythantine

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Dedicated to Professor Horst Kunz on the occasion of his 65th birthday

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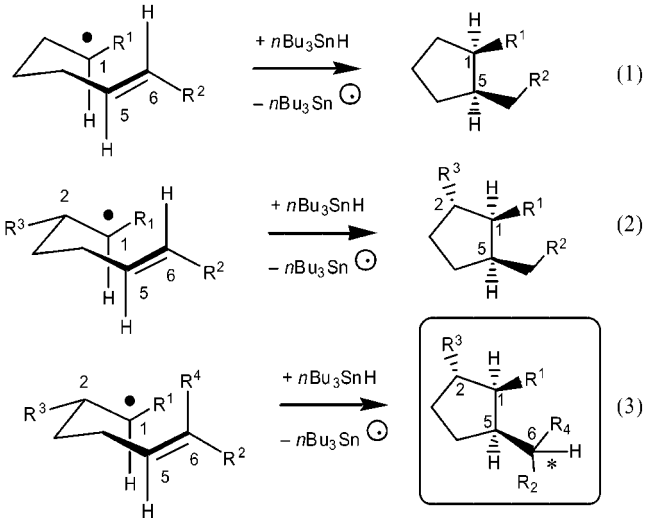
A synthesis of (+)-iridomyrmecin (**1**), a naturally occurring insecticide with antibiotic properties, via free radical cyclization is described. In this key step, three contiguous stereogenic centers are generated with a high level of stereocontrol.

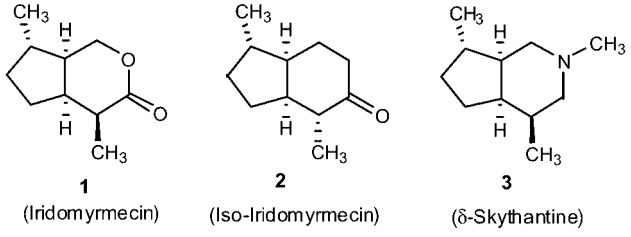
Introduction

5-Hexenyl radicals normally cyclize via a 5-*exo*-*trig*[1] mode.[2] With respect to the stereochemical outcome three cases may be distinguished (Scheme 1). In the first case, Scheme 1, Equation (1), the cyclization of 1-substituted 5-hexenyl radicals is described. It leads preferentially to 1,5-*cis*-disubstituted cyclopentanes, according to the Beckwith transition state model.[3] This model postulates an early transition state, which resembles a "chair-like" cyclohexane ring with substituents in *pseudo*-equatorial rather than *pseudo*-axial[4] positions.



Scheme 1.

In the second case Equation (2), we have a stereogenic center at C-2. The substituent at C-2 leads to a high 1,2-*trans* induction[5] whereas the relative *cis*-configuration of C-2 and C-5 is maintained. In the third case, Equation (3), a 5,6-trisubstituted double bond with defined *E*/*Z*-geometry is attacked by the free radical. The 1,2-*trans* and 1,5-*cis* inductions should remain. However, the question arises if there is any stereocontrol with respect to the third prostereogenic center (C-6). In extension of previous work on radical cyclizations[6] we decided to take this as an issue for own research and chose the synthesis[7] of enantiomerically pure (+)-iridomyrmecin (**1**),[8] a naturally occurring cyclic monoterpene with insecticidal and antibiotic properties[9] as a suitable target. *En route*, *iso*-iridomyrmecin (**2**)[10] and the iridoalkaloid δ-skythantine (**3**)[11] (structures **1**–**3**) were also aimed for.



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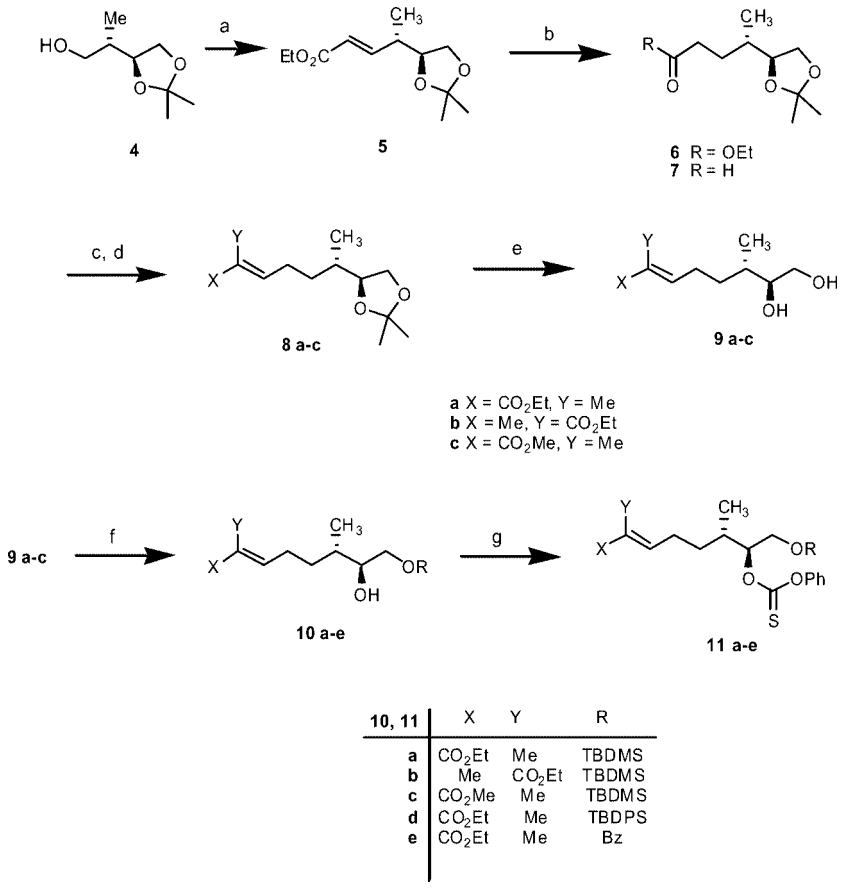
Results and Discussion

Results: Our synthesis (Scheme 2) started with the known[12] alcohol **4**, which was converted into aldehyde **7** via some routine steps. The stereoselectivity of the ensuing Wittig reaction of **7** to the enoates **8a**–**c** proved to be highly solvent dependent. Thus, the olefination in diethyl ether proceeded *E*-selectively and furnished esters **8a** (*E*/*Z* = 97:3) and **8c** (*E*/*Z* = 90:10). When isolated and reacted in methanol, aldehyde **7** afforded an 80:20 ratio of **8a**/**b**. This mixture was separated chromatographically and provided sufficient quantities of the (*Z*)-ester **8b**. After removal of the acetonide diols **9a**–**c** were obtained, which were silylated or benzoylated selectively at the primary hydroxy group to furnish the monoprotected derivatives **10a**–**e**. Treatment with PhOC(S)Cl gave thiocarbonates **11a**–**e** in almost quantitative yields.

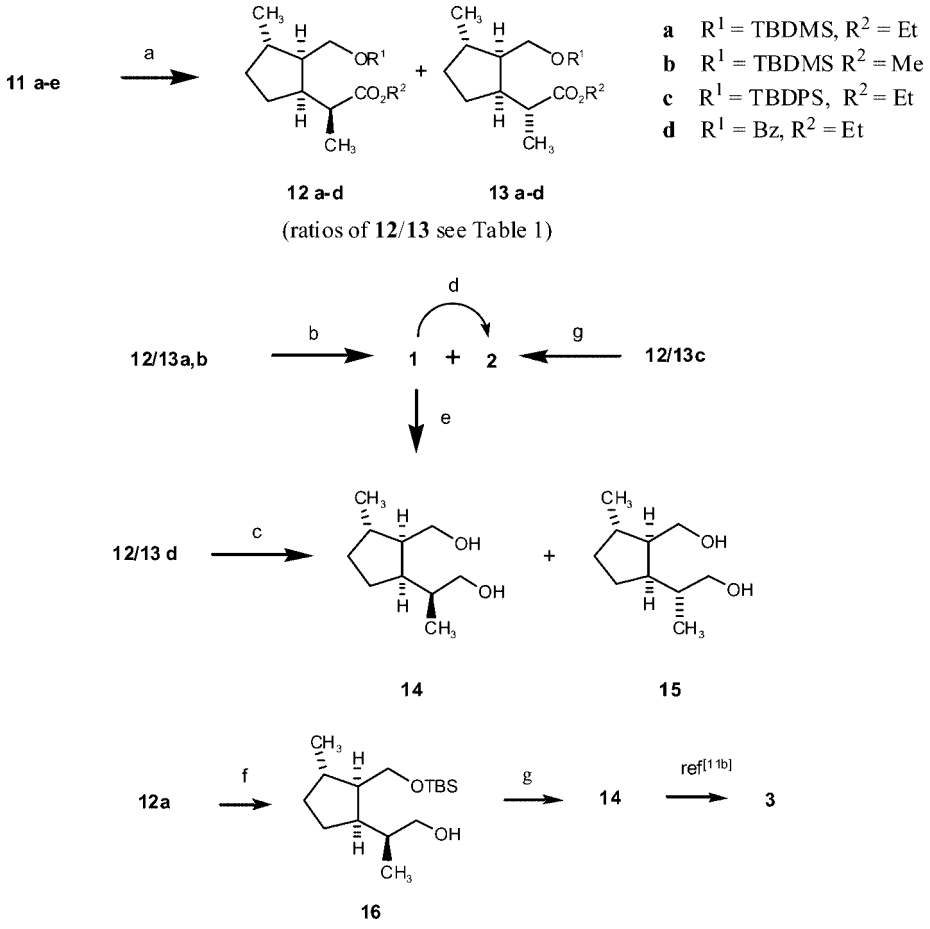
The free radical cyclization of **11a**–**e** was carried out with tributyltin hydride and catalytic amounts of AIBN at 80–90 °C in a 0.02 M toluene solution (Scheme 3, Table 1).[13] Two main diastereomers **12** and **13** were obtained, sometimes along with minor amounts of other diastereomers.

In particular, the cyclization of **11a**,**b** proved to be highly stereoselective. In this step three new stereogenic centers were generated to form two diastereomers **12/13a** in a ratio of 82:14. Although this mixture could be easily separated by analytical HPLC, this was difficult on a preparative scale. However, on desilylation the **12/13a**–**c** mixtures spontaneously lactonized to an easily separable mixture of **1** and **2**. On treatment with base, **1** was epimerized into the thermodynamically more stable epimer **2**.[8b] By contrast, the mixture of **12/13d** was reduced to the diols **14/15**, which could also be separated chromatographically. To exclude any artefacts that might have resulted from working with mixtures, a small quantity of pure **12a** was procured by preparative HPLC, reduced to **16** and desilylated to **14** which was identical with the material prepared from **12/13d**. Alternatively, **14** was obtained from the LAH reduction of **1**. The analytical data of our compounds **1**[9b] and **2**[9b] were in full agreement with those reported in the literature. The conversion of diol **14** into alkaloid **3** has already been described.[11b]



10, 11	X	Y	R
a	CO_2Et	Me	TBDMS
b	Me	CO_2Et	TBDMS
c	CO_2Me	Me	TBDMS
d	CO_2Et	Me	TBDPS
e	CO_2Et	Me	Bz

Scheme 2. Reagents and conditions: a) DMSO, oxalyl chloride, CH_2Cl_2, –78 °C; Et_3N; $Ph_3P{=}CHCO_2Et$, CH_2Cl_2/EtOH, 92%; b) H_2 (1 bar), Raney-Ni, room temp., 12 h, EtOH, 96%. c) DIBAL-H, diethyl ether/toluene, –78 °C; d) **8a**: $Ph_3P{=}CMeCO_2Et$, diethyl ether/EtOH; *E*/*Z* = 97:3, 72% over 2 steps; **8b**: $Ph_3P{=}CMeCO_2Et$, MeOH; (*E*/*Z* = 4:1, 68% over 2 steps)); **8c**: $Ph_3P{=}CMeCO_2Me$, diethyl ether/EtOH; *E*/*Z* = 9:1, 69% over 2 steps; e) TFA, H_2O, EtOH (**9a**: 98%; **9b**: 95%; **9c**: 96%). f) **10a-c**: *t*$BuMe_2SiCl$, imidazole, DMF, 79–82%; **10d**: *t*$BuPh_2SiCl$, imidazole, DMF, 82%; **10e**: BzCl, DMAP, pyridine, 78%; g) **11a-e**: PhOCSCl, DMAP, pyridine, CH_2Cl_2, 92–97%.



Scheme 3. Reagents and conditions: a) nBu$_3$SnH, AIBN, toluene, 80–90 °C, 12 h, 75–85%; b) TFA, H_2O, CH_2Cl_2, 91%; c) $LiAlH_4$, diethyl ether, 82–86%; d) NaOMe, MeOH, 12 h, 85%; e) $LiAlH_4$, diethyl ether, 87%; f) DIBAL-H, diethyl ether/n-hexane, –40 °C, 87%; g) nBu$_4$NF, THF, 86%.

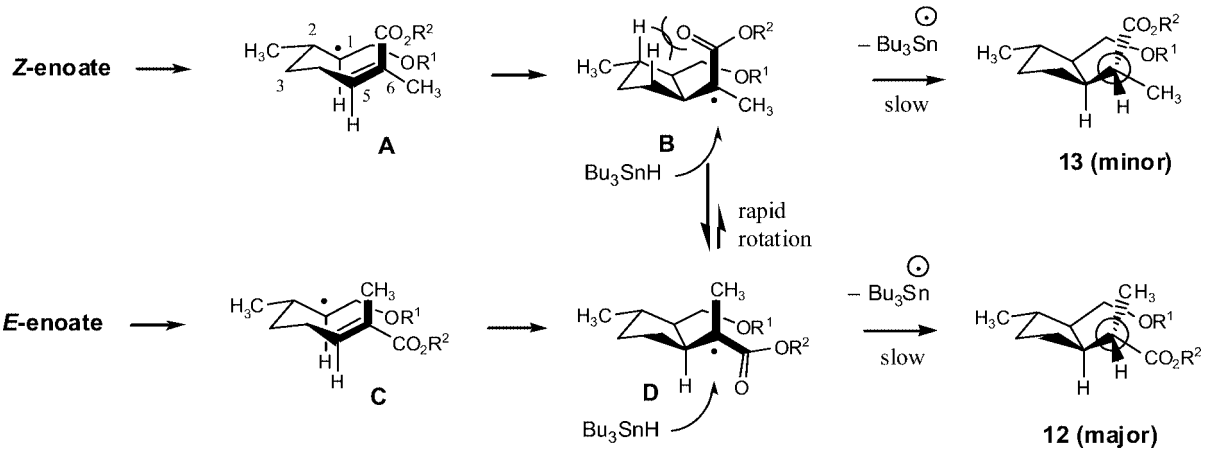
Table 1. Diastereomeric ratios and overall yields of the radical cyclization of **11a**–**e**.

11	R^1	R^2	**12/13**/other diastereomers	Overall yield [%]
a (*E*)	TBDMS	Et	82:14 <4	75
b (*Z*)	TBDMS	Et	82:14 <4	75
c (*E*)	TBDMS	Me	67:28 <5	75
d (*E*)	TBDPS	Et	54:34:12	80
e (*E*)	Bz	Et	60:23:17	85

Discussion

For clarity, we restrict our mechanistic rationalization (Scheme 4) to the stereoselective cases **11a** and **b**. We apply Beckwith's model and assume that the radicals **A** and **C**, which are formed from the (*Z*)-and (*E*)-enoates, adopt chair like conformations with the C-2-methyl group in a pseudo-equatorial position. In this geometry 1,5-cyclization occurs to form the new radicals **B** and **D**, which may rotate freely around the 5,6-axis. Due to the allylic 1,3-strain[14] exerted by the ester carbonyl, the *transoid* conformer **D** is more stable than the *cisoid* conformer **B**. As the "backside" of the radicals is shielded by the *cis*-CH_2OR^1 moiety, it may be assumed that the hydrogen donor selectively attacks from the "frontside" to give the final products **12a** and **13a**. *E*- and *Z*-enoates **11a** and **b** give the same ratio of **12a/13a**, which indicates that the equilibration of **B** and **D** is fast compared to the hydrogen transfer. This appears plausible as the rotation is a reaction of first order and the hydrogen transfer one of second order. Thus, the ratio of **12a/13a** to a first approximation reflects the equilibrium composition of **D/B**. The diminished selectivity of **11c** may be attributed to a lower preference for conformer **D**, due to the smaller size of the OMe group. The remaining two examples **11d** and **e** are more complex. Obviously, conformations other than **B** and **D** are also involved, so that more than two diastereomers result from the cyclization.

In conclusion, we have described the free radical cyclization of acyclic chirally C-2-substituted 1-hexenyl radicals. Three contiguous stereogenic centers are formed with varying stereocontrol. In the best case, only two diastereomers out of eight are produced in a ratio of 82:14. The cyclopentane derivatives thus formed were readily converted into the natural products **1**, **2** and, via a formal synthesis, also into **3**.



Scheme 4.

Experimental Section

General Methods: NMR spectra were measured either on a Bruker AC 250 spectrometer in $CDCl_3$ with TMS as an internal standard unless noted otherwise. IR spectra were recorded on a Perkin–Elmer IR 580 B infrared spectrometer or a Nicolet FTIR-Interferometer system 5 SXC using KBr pellets. Mass spectra were measured on a Varian MAT 711 (EI). The elemental analyses were determined on a Perkin–Elmer 2400 CHN Elemental Analyser. Optical rotations were obtained in $CHCl_3$, unless stated otherwise, with a Perkin–Elmer 241 polarimeter. Melting points are uncorrected. HPLC separations were performed on Nucleosil 50 with particle sizes 5 μm (analytical) and 7 μm (preparative), with RI and UV detection. Preparative column chromatography was performed on silica gel Merck 60 (0.063–0.04 mm). All reactions were carried out under an argon atmosphere in purified solvents with magnetic stirring and were controlled with TLC plates (Merck 5554).

Ethyl (4*S*,5*S*,2*E*)-5,6-Isopropylidene-4-methylhexenoate (5): Oxalyl chloride (1.06 mL, 12.4 mmol) in dichloromethane (30 mL) was treated at –78 °C with DMSO (1.2 mL, 16.5 mmol) in dichloromethane (3 mL). After 15 min alcohol **4** (1.32 g, 8.24 mmol) in dichloromethane (12 mL) was added dropwise. After 20 min triethylamine (5.7 mL, 41.2 mmol) was added. After 20 min the mixture was warmed to 0 °C and stirred for additional 20 min. Water and ether were added, the organic phase was separated washed with brine, dried with magnesium sulfate and concentrated under reduced pressure to give crude aldehyde which was diluted with THF (50 mL) and treated with (ethoxycarbonylmethylene)triphenylphosphorane (4.92 g, 16 mmol) at room temp. for 12 h. The solvent was evaporated and the residue was diluted with diethyl ether to remove the phosphane oxide by crystallization. The mother liquor was chromatographed (hexane/ethyl acetate, 3:1) to give pure ester **5** (1.63 g, 92%) as a colorless oil. B.p. (3 Torr) 75–80 °C. $[\alpha]_D^{20}$ = –18.9 (*c* = 2.6, $CHCl_3$). ^{1}H NMR: δ = 6.97 (dd, *J* = 16.2 Hz, *J* = 7.6 Hz, 1 H), 5.87 (dd, *J* = 16.2 Hz, *J* = 1.6 Hz, 1 H), 4.20 (q, *J* = 7.3 Hz, 2 H), 4.02 (m_c, 2 H), 3.64 (m, 1 H), 2.50 (m_c, *J* = 7.6 Hz, *J* = 6.8 Hz, *J* = 1.6 Hz, 1 H), 1.42 (s, 3 H), 1.36 (s, 3 H), 1.31 (t, *J* = 7.3 Hz, 3 H), 1.06 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR: δ = 166.27, 149.55, 121.58, 109.16, 78.51, 67.32, 60.09, 39.72, 26.37, 25.29, 15.07, 14.11 ppm. IR: $\tilde{\nu}_{max}$ = 1720 (s), 1650 (m) cm^{-1}. MS: *m*/*z* = 213 (20.4%, $[M - CH_3]^+$), 183 (3.9%, $[M - C_2H_5O]^+$), 153 (3.6%, $[M - H_2O - 2CH_3]^+$), 125 (15.2%, $[M - C_2H_5O - 2CH_3 - CO]^+$), 101 (100.0%, $[C_5H_9O_2]^+$), 72 (16.9%, $[C_4H_8O]^+$), 43 (62.9%, $[C_2H_3O]^+$). $C_{12}H_{20}O_4$ (228.29): calcd. C 63.14, H 8.83; found C 62.82, H 8.77.

Ethyl (4*S*,5*S*)-5,6-Isopropylidene-4-methylhexanoate (6): A solution of **5** (7.0 g, 30.7 mmol) in ethanol (50 mL) was hydrogenated over Raney-Ni (pH 7–8, 0.5–1.0 g) at 1 bar for 5 h. Filtration over Celite and evaporation gave **6** as a colorless oil (6.75 g, 96%). $[\alpha]_D^{20}$ = +4.2 (*c* = 1.9, $CHCl_3$). ^{1}H NMR: δ = 4.13 (q, *J* = 7.3 Hz, 2 H), 4.00 (dd, *J* = 7.8 Hz, *J* = 6.2 Hz, 1 H), 3.85 (ddd, *J* = 7.8 Hz, *J* = 6.2 Hz, *J* = 5.4 Hz, 1 H), 3.60 (t, *J* = 7.8, *J* = 6.2 Hz, 1 H), 2.38 (m, 2 H), 1.95 (m_c, 1 H), 1.64 (m_c, 1 H), 1.49 (m, 1 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.27 (t, *J* = 7.3 Hz, 3 H), 0.86 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR: δ = 173.51, 108.67, 80.06, 67.64, 60.06, 36.13, 31.88, 28.59, 26.54, 25.46, 14.94, 14.12 ppm. IR: $\tilde{\nu}_{max}$ = 1730 (s) cm^{-1}. MS: *m*/*z* = 215 (60.0%, $[M - CH_3]^+$), 185 (24.2%, $[M - C_2H_5O]^+$), 155 (61.1%, $[M - C_2H_5O - 2CH_3]^+$), 127 (34.9%, $[M - C_2H_5O - 2CH_3 - CO]^+$), 109 (32.6%), 101 (54.5%, $[C_5H_9O_2]^+$), 81 (50.9%), 72 (57.2%, $[C_4H_8O]^+$), 43 (100.0%, $[C_2H_3O]^+$). $C_{12}H_{22}O_4$ (230.31): calcd. C 62.58, H 9.63; found C 62.37, H 9.48.

Ethyl (2*E*,6*S*,7*S*)- and Ethyl (2*Z*,6*S*,7*S*)-7,8-Isopropylidenedioxy-2,6-dimethyl-2-octenoate (8a,b): To a stirred solution of ethyl ester **6** (5.60 g, 24.32 mmol) in diethyl ether (330 mL) a 1.3 M solution of DIBAH in toluene (18.70 mL, 24.32 mmol) was added slowly at –78 °C and stirred for 3 h at the same temperature. The mixture was quenched with ethanol (10 mL), and the resulting aldehyde **7** was treated *in situ* with (ethoxycarbonylmethyliden)triphenylphosphorane solvated in ethanol (20 mL), stirred for 12 h and quenched with some water. The solution was concentrated and diluted with diethyl ether/water. The organic layer was washed with water and brine, dried ($MgSO_4$) and the solvents evaporated. Chromatography on silica (hexane/ethyl acetate, 3:1) gave a 97:3 mixture of **8a/b** (4.73 g, 72%). When isolating aldehyde **7** and performing the olefination in methanol at 0 °C, a 80:20 mixture of **8a/b** was obtained, which was separated by HPLC (ethyl acetate/hexanes, 8:92) to give **8a** (3.54 g, 54%) and **8b** (930 mg, 14%) as colorless oils.

8a: $[\alpha]_D^{20}$ = +0.7 (*c* = 2.0, $CHCl_3$). ^{1}H NMR: δ = 6.76 (dt, *J* = 7.3 Hz, *J* = 1.3 Hz, 1 H), 4.19 (q, *J* = 7.3 Hz, 2 H), 4.00 (dd, *J* = 7.5 Hz, *J* = 5.8 Hz, 1 H), 3.85 (ddd, *J* = 7.5 Hz, *J* = 5.8 Hz, *J* = 5.0 Hz, 1 H), 3.60 (t, *J* = 7.5 Hz, 1 H), 2.38–2.09 (m, 2 H), 1.86 (d, *J* = 1.3 Hz, 3 H), 1.83–1.58 (m, 2 H), 1.42 (s, 3 H), 1.40 (s, 3 H), 1.37–1.22 (m, 1 H), 1.31 (t, *J* = 7.3 Hz, 3 H), 0.88 (d, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.07, 141.90, 127.77, 108.65, 80.11, 67.64, 60.26, 36.20, 32.08, 26.60, 25.89, 25.51, 14.91, 14.20, 12.24 ppm. IR: $\tilde{\nu}_{max}$ = 1710 (s), 1650 (w) cm^{-1}. MS: *m*/*z* = 270 (13.2%, $[M]^+$), 255 (42.3%, $[M - CH_3]^+$), 212 (17.5%, $[M - CH_3 - C_2H_3O]^+$), 167 (36.6%, $[M - CH_3 - C_2H_3O - C_2H_5O]^+$), 149 (18.6%), 140 (19.36%), 121 (73.0%), 113 (14.9%), 101 (61.1%,

$[C_5H_9O_2]^+$), 93 (31.6%), 81 (11.7%), 72 (53.9%, $[C_4H_8O]^+$), 55 (25.5%), 43 (100.0%, $[C_2H_3O]^+$). $C_{15}H_{26}O_4$ (270.37): calcd. C 66.64, H 9.69; found C 66.13, H 9.60.

8b: $[\alpha]_D^{20}$ = +8.8 (*c* = 2.2, $CHCl_3$). ^1H NMR: δ = 5.92 (m_c, *J* = 1.8 Hz, 1 H), 4.20 (q, *J* = 7.3 Hz, 2 H), 4.00 (dd, *J* = 7.5 Hz, *J* = 5.8 Hz, 1 H), 3.87 (ddd, *J* = 7.5 Hz, *J* = 5.8 Hz, *J* = 5.0 Hz, 1 H), 3.60 (t, *J* = 7.5 Hz, 1 H), 2.62–2.37 (m, 2 H), 1.89 (d, *J* = 1.8 Hz, 3 H), 1.78–1.56 (m, 2 H), 1.43 (s, 3 H), 1.40 (s, 3 H), 1.36 (t, *J* = 7.3 Hz, 3 H), 1.31–1.15 (m, 1 H), 0.86 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR: δ = 167.86, 142.60, 127.08, 108.46, 79.97, 67.43, 59.85, 36.14, 32.73, 26.70, 26.52, 25.44, 20.50, 14.61, 14.14 ppm. IR $\tilde{\nu}_{max}$ = 1715 (s), 1650 (w) cm^{-1}. MS: *m/z* = 270 (15.0%, $[M]^+$), 255 (41.3%, $[M - CH_3]^+$), 212 (19.7%, $[M - CH_3 - C_2H_3O]^+$), 167 (44.0%, $[M - CH_3 - C_2H_3O - C_2H_5O]^+$), 149 (52.7%), 140 (21.6%), 121 (71.9%), 101 (85.6%, $[C_5H_9O_2]^+$), 93 (28.0%), 72 (64.1%, $[C_4H_8O]^+$), 55 (26.0%), 43 (100.0%, $[C_2H_3O]^+$). $C_{15}H_{26}O_4$ (270.37): calcd. C 66.64, H 9.69; found C 66.28, H 9.62.

Methyl (2*E*,6*S*,7*S*)-7,8-Dihydroxy-2,6-dimethyl-2-octenoate (8c): 8c (4.45 g, 69%, *E*/*Z* = 9:1) was prepared from **6** (5.80 g, 25.2 mmol) as described for the preparation of **8a**. $[\alpha]_D^{20}$ = +2.0 (*c* = 2.2, $CHCl_3$). ^1H NMR: δ = 6.76 (m_c, *J* = 1.5 Hz, 1 H), 4.00 (dd, *J* = 7.5 Hz, *J* = 5.8 Hz, 1 H), 3.84 (ddd, *J* = 7.5 Hz, *J* = 5.0 Hz, 1 H), 3.73 (s, 3 H), 3.58 (t, *J* = 7.5 Hz, 1 H), 2.37–2.08 (m, 2 H), 1.84 (d, *J* = 1.5 Hz, 3 H), 1.81–1.57 (m, 2 H), 1.40 (s, 3 H), 1.35 (s, 3 H), 1.28 (m, 1 H), 0.88 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.51, 142.28, 127.47, 108.64, 80.10, 67.64, 51.54, 36.15, 32.05, 26.60, 25.88, 25.49, 14.92, 12.26 ppm. IR: $\tilde{\nu}_{max}$ = 1715 (s), 1650 (w) cm^{-1}. $C_{14}H_{24}O_4$ (256.34): calcd. C 65.60, H 9.44; found C 65.39, H 9.17.

Preparation of 9a–c: To a solution of **8a** (4.00 g, 14.79 mmol) in ethanol (200 mL) TFA (8 mL) and water (4 mL) were added dropwise and stirred for 2 d at room temp. The mixture was concentrated and chromatographed (hexane/ethyl acetate, 1:2). Recovered starting material **8a** was recycled to give pure diol **9a** (3.33 g, 98%) as a colorless oil. **9b** (1.05 g) was prepared from **8b** (1.30 g) as described for the preparation of **9a** (yield: 95%). **9c** (3.13 g) was prepared from **8c** (3.86 g) as described for the preparation of **9a** (yield: 96%).

Ethyl (2*E*,6*S*,7*S*)-7,8-Dihydroxy-2,6-dimethyl-2-octenoate (9a): $[\alpha]_D^{20}$ = –8.8 (*c* = 2.0, $CHCl_3$). ^1H NMR: δ = 6.75 (dt, *J* = 7.0 Hz, *J* = 1.4 Hz, 1 H), 4.18 (q, *J* = 7.3 Hz, 2 H), 3.84 (s, 2 H, OH), 3.71 (m, 1 H), 3.51 (m, 2 H), 2.24 (m_c, 1 H), 2.16 (m_c, 1 H), 1.79 (d, *J* = 1.4 Hz, 3 H), 1.79–1.53 (m, 2 H), 1.37–1.21 (m, 1 H), 1.30 (t, *J* = 7.3 Hz, 3 H), 0.92 (d, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.30, 142.10, 127.67, 75.84, 64.26, 60.38, 35.61, 31.10, 25.93, 14.96, 14.10, 12.16 ppm. IR: $\tilde{\nu}_{max}$ = 3405 (s), 1711 (s), 1648 (w) cm^{-1}. MS: *m/z* = 230 (3.4%, $[M]^+$), 212 (1.2%, $[M - H_2O]^+$),199 (5.2%, $[M - CH_2OH]^+$), 184 (40.7%, $[M - CH_2OH - CH_3]^+$), 167 (14.4%, $[M - H_2O–C_2H_5O]^+$), 153 (61.3%, $[M - H_2O - C_2H_5O - CH_2OH]^+$), 140 (23.1%), 121 (27.8%), 112 (42.4%), 95 (64.1%), 82 (36.0%), 67 (41.5%), 55 (78.1%), 43 (100.0%, $[C_2H_3O]^+$). $C_{12}H_{22}O_4$ (230.31): calcd. C 62.58, H 9.63; found C 62.36, H 9.45. HRMS calcd. for $[C_{12}H_{22}O_4]^+$: 230.15181, found 230.15172.

Ethyl (2*Z*,6*S*,7*S*)-7,8-Dihydroxy-2,6-dimethyl-2-octenoate (9b): $[\alpha]_D^{20}$ = –11.9 (*c* = 2.3, $CHCl_3$). ^1H NMR: δ = 5.85 (dt, *J* = 7.8 Hz, *J* = 1.5 Hz, 1 H), 4.10 (q, *J* = 7.3 Hz, 2 H), 3.94 (s, 2 H, OH), 3.60 (m, 1 H), 3.41 (m, 2 H), 2.44 (m, 1 H), 2.31 (m_c, 1 H), 1.80 (d, *J* = 1.5 Hz, 3 H), 1.54 (m, 2 H), 1.30–1.13 (m, 1 H), 1.22 (t, *J* = 7.3 Hz, 3 H), 0.80 (d, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.60, 142.95, 127.07, 75.74, 64.24, 60.01, 35.52, 31.86, 26.56, 20.42, 14.99, 14.07 ppm. IR: $\tilde{\nu}_{max}$ = 3391 (s), 1714 (s), 1645 (m) cm^{-1}. MS: *m/z* = 230 (1.6%, $[M]^+$), 212 (1.1%, $[M - H]^+$),199 (11.9%), 184 (43.4%, $[M - CH_2OH - CH_3]^+$), 167 (21.4%, $[M - H_2O - C_2H_5O]^+$), 153 (70.8%, $[M - H_2O - C_2H_5O - CH_2OH]^+$), 140 (24.4%), 128 (43.1%), 112 (53.0%), 95 (74.2%), 81 (33.2%), 67 (47.6%), 55 (100.0%), 43 (99.4%, $[C_2H_3O]^+$). HRMS calcd. for $[C_{12}H_{22}O_4]^+$: 230.15181, found 230.15172. $C_{12}H_{22}O_4$ (230.31): calcd. C 62.58, H 9.63; found C 62.29, H 9.53.

Methyl (2*E*,6*S*,7*S*)-7,8-Dihydroxy-2,6-dimethyl-2-octenoate (9c): $[\alpha]_D^{20}$ = –10.0 (*c* = 2.3, $CHCl_3$). ^1H NMR: δ = 6.74 (dt, *J* = 6.8 Hz, *J* = 1.1 Hz, 1 H), 3.92 (s, 2 H), 3.73 (s, 3 H), 3.68 (m, 1 H), 3.51 (m, 2 H), 2.25 (m_c, 2 H), 2.16 (m_c, 1 H), 1.84 (d, *J* = 1.1 Hz, 3 H), 1.71 (m, 1 H); 1.63 (m, 1 H), 1.31 (m_c, 1 H), 0.92 (d, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.63, 142.43, 127.43, 75.85, 64.22, 51.61, 35.58, 31.08, 25.91, 14.94, 12.20 ppm. IR: $\tilde{\nu}_{max}$ = 3391 (s), 1714 (s), 1649 (m) cm^{-1}. MS: *m/z* = 216 (1.6%, $[M]^+$), 198 (11.9%, $[M - CH_2OH]^+$), 184 (43.4%, $[M - CH_2OH - CH_3]^+$), 153 (70.8%, $[M - H_2O - C_2H_5O - CH_2OH]^+$), 126 (43.1%), 111 (53.0%), 97 (74.2%), 95 (65.2%) 81 (24.2%), 67 (33.5%), 55 (100.0%). HRMS calcd. for $[C_{11}H_{20}O_4]^+$: 216.13616, found 216.13613. $C_{11}H_{20}O_4$ (216.28): calcd. C 61.09, H 9.32; found C 61.36, H 9.49.

Preparation of 10a–d: To a stirred solution of **9a** (4.61 g, 20.20 mmol) and imidazole (2.73 g, 40.03 mmol) in DMF (250 mL) *t*BuSiMe$_2$Cl (3.02 g, 20.20 mmol) in DMF (50 mL) was added slowly at –12 °C and stirred for 6 h at 0 °C and for 12 h at room temp. The mixture was quenched with cold water, concentrated, diluted with diethyl ether/water, and extracted with diethyl ether. The organic layer was washed with water and brine, dried ($MgSO_4$) and the solvents evaporated. Chromatography (hexane/ethyl acetate, 3:1) gave **10a** (5.58 g, 81%) as a colorless oil. **10b** (1.29 g) was prepared from **9b** (1.05 g) as described for the preparation of **10a** (yield: 82%). **10c** (1.93 g) was prepared from **9c** (1.60 g) as described for the preparation of **10a** (yield: 82%). **10d** (1.00 g) was prepared with *t*BuSiPh$_2$Cl from **9c** (600 mg) as described for the preparation of **10a** (yield 82%).

Ethyl (2*E*,6*S*,7*S*)-8-*tert*-Butyldimethylsiloxy-7-hydroxy-2,6-dimethyl-2-octenoate (10a): $[\alpha]_D^{20}$ = –2.6 (*c* = 2.0, $CHCl_3$). ^1H NMR: δ = 6.68 (dt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1 H), 4.08 (q, *J* = 7.3 Hz, 2 H), 3.60 (m_c, 1 H), 3.43 (m_c, 1 H), 3.29 (m, 1 H), 2.52 (s_{br}, 1 H, OH), 2.28–1.97 (m, 2 H), 1.76 (d, *J* = 1.3 Hz, 3 H), 1.66 (m, 1 H), 1.52 (m, 1 H), 1.26 (m, 1 H), 1.21 (t, *J* = 7.3 Hz, 3 H), 0.84 (s, 9 H), 0.84 (d, *J* = 7.0 Hz, 3 H), 0.02 (s, 6 H) ppm. ^{13}C NMR: δ = 168.02, 142.04, 127.61, 75.23, 64.99, 60.16, 35.26, 31.19, 26.00, 25.73, 18.11, 15.07, 14.15, 12.16, –5.50, –5.56 ppm. IR: $\tilde{\nu}_{max}$ = 3520 (m), 1710 (s), 1650 (w) cm^{-1}. MS: *m/z* = 344 (1.8%, $[M]^+$), 299 (2.2%, $[M - C_2H_5O]^+$), 287 (5.1%, $[M - C_4H_9]^+$), 269 (2.9%, $[M - C_2H_5O - 2CH_3]^+$), 257 (7.2%, $[M - C_4H_9 - 2CH_3]^+$), 241 (22.2%, $[M - C_2H_5O - 2CH_3 - CO]^+$), 211 (11.4%), 149 (22.8%), 121 (39.3%), 105 (34.5%), 93 (19.3%), 75 (100.0%). HRMS calcd. for $[C_{18}H_{36}O_4Si]^+$: 344.23829, found 344.23834; calcd. for $[C_{16}H_{31}O_3Si]^+$: 299.20425, found 299.20423. $C_{18}H_{36}O_4Si$ (344.57): calcd. C 62.74, H 10.53; found C 62.52, H 10.43.

Ethyl (2*Z*,6*S*,7*S*)-8-*tert*-Butyldimethylsiloxy-7-hydroxy-2,6-dimethyl-2-octenoate (10b): $[\alpha]_D^{20}$ = +5.3 (*c* = 2.1, $CHCl_3$). ^1H NMR: δ = 5.92 (dt, *J* = 7.3 Hz, *J* = 1.6 Hz, 1 H), 4.18 (q, *J* = 7.3 Hz, 2 H), 3.69 (dd, *J* = 8.6 Hz, *J* = 6.5 Hz, 1 H), 3.46 (m_c, *J* = 8.6 Hz, 1 H), 3.41 (m, 1 H), 2.62 (s, 1 H, OH), 2.58–2.36 (m, 2 H), 1.88 (d, *J* = 1.6 Hz, 3 H), 1.72 (m_c, 1 H), 1.60 (m, 1 H), 1.30 (t, *J* = 7.3 Hz, 3 H), 1.24 (m, 1 H), 0.92 (s, 9 H), 0.89 (d, *J* = 7.0 Hz, 3 H), 0.09 (s, 6 H) ppm. ^{13}C NMR: δ = 167.93, 142.93, 126.96, 75.16, 64.95, 59.86, 35.27, 31.95, 26.81, 25.73, 20.48, 18.11, 14.93, 14.13, –5.49, –5.56 ppm. IR: $\tilde{\nu}_{max}$ = 3314 (w), 1716 (s), 1646 (w) cm^{-1}. MS: *m/z* = 344 (1.1%, $[M]^+$), 299 (3.2%, $[M - C_2H_5O]^+$), 287 (9.3%, $[M - C_4H_9]^+$), 269 (4.2%, $[M - C_2H_5O - 2CH_3]^+$), 257

(6.3%, $[M - C_4H_9 - 2CH_3]^+$), 241 (22.1%, $[M - C_2H_5O - 2CH_3 - CO]^+$), 223 (15.5%), 211 (13.8%), 149 (61.8%), 121 (70.5%), 105 (30.2%), 93 (22.5%), 75 (100.0%). HRMS calcd. for $[C_{18}H_{36}O_4Si]^+$: 344.23829, found 344.23817; calcd. for $[C_{16}H_{31}O_3Si]^+$: 299.20425, found 299.20320; calcd. for $[C_{14}H_{27}O_4Si]^+$: 287.16786, found 287.16758. $C_{18}H_{36}O_4Si$ (344.57): calcd. C 62.74, H 10.53; found C 62.62, H 10.38.

Methyl (2*E*,6*S*,7*S*)-8-*tert*-Butyldimethylsiloxy-7-hydroxy-2,6-dimethyl-2-octenoate (10c): $[\alpha]_D^{20} = -1.3$ (c = 1.7, $CHCl_3$). ^1H NMR: δ = 6.68 (dt, J = 7.3 Hz, J = 1.1 Hz, 1 H), 3.64 (s, 3 H), 3.60 (m_c, 1 H), 3.37 (m_c, 1 H), 3.33 (m, 1 H), 2.48 (s_{br}, 1 H, OH) 2.16 (m_c, 1 H), 2.08 (m_c, 1 H), 1.76 (d, J = 1.1 Hz, 3 H), 1.65 (m_c, 1 H), 1.52 (m_c, 1 H), 1.30–1.15 (m, 2 H), 0.83 (s, 9 H), 0.81 (d, J = 7.0 Hz, 3 H), 0.01 (s, 6 H) ppm. ^{13}C NMR: δ = 168.76, 142.54, 127.62, 75.37, 65.10, 51.59, 35.40, 31.35, 26.11, 25.85, 18.24, 15.16, 12.23, –5.36, –5.43 ppm. IR: $\tilde{\nu}_{max}$ = 3511 (w), 1717 (s), 1649 (w) cm^{-1}. MS: m/z = 330 (5.5%, $[M]^+$), 299 (4.2%, $[M - CH_3O]^+$), 273 (10.5%, $[M - C_4H_9]^+$), 255 (5.1%), 241 (37.5%), 223 (14.0%), 149 (22.8%), 121 (39.3%), 105 (34.5%), 93 (19.3%), 75 (100.0%). HRMS calcd. for $[C_{17}H_{34}O_4]^+$: 330.22264, found 330.22328. $C_{17}H_{34}O_4Si$ (330.54): calcd. C 61.77, H 10.37; found C 63.02, H 10.47.

Ethyl (2*E*,6*S*,7*S*)-8-*tert*-Butyldiphenylsiloxy-7-hydroxy-2,6-dimethyl-2-octenoate (10d): ^1H NMR: δ = 7.63 (m, 4 H), 7.37 (m, 6 H), 6.67 (dt, J = 7.6 Hz, J = 1.4 Hz, 1 H), 4.16 (q, J = 7.3 Hz, 2 H), 3.58 (m, 3 H), 2.36 (m, 1 H), 2.13 (m, 2 H), 1.80 (d, J = 1.4 Hz, 3 H), 1.56 (m, 2 H), 1.28 (t, J = 7.3 Hz, 3 H), 1.06 (s, 9 H), 1.04 (m, 1 H), 0.89 (d, J = 6.2 Hz, 3 H) ppm; MS (EI, 80eV): m/z = 423 (0.2%, $[M - C_2H_5O]^+$), 411 (2.0%, $[M - C_4H_9]^+$), 393 (1.4%), 365 (13.3%), 333 (34.6%), 287 (10.9%), 299 (10.1%), 199 (100.0%, $[C_{12}H_{11}OSi]^+$), 181 (14.6%), 149 (17.7%), 135 (17.6%), 121 (34.1%), 77 (15.9%, $[C_6H_5]^+$). $C_{26}H_{40}O_4Si$ (444.70): calcd. C 70.22, H 9.07; found C 71.20, H 8.83.

Preparation of 10e: A solution of diol **9a** (1.50 g, 6.94 mmol) and pyridine (1.68 mL, 3 equiv.) in CH_2Cl_2 (21 mL) was treated with DMAP (200 mg, 1.63 mmol) and benzoic acid chloride (0.81 mL, 6.94 mmol) at –12 °C, stirred for 2 h at 0 °C and 1–2 h at room temp., quenched with a saturated aqueous solution of NH_4Cl, extracted with diethyl ether, washed with water, brine, dried ($MgSO_4$) and chromatographed (hexane/ethyl acetate, 3:1) to give colorless liquid benzoate **10e** (1.73 g, 78%).

Ethyl (2*E*,6*S*,7*S*)-8-Benzoyloxy-7-hydroxy-2,6-dimethyl-2-octenoate (10e): $[\alpha]_D^{20} = -3.9$ (c = 0.6, $CHCl_3$). ^1H NMR: δ = 8.02 (d, J = 7.3 Hz, 2 H), 7.56 (t, J = 7.3 Hz, 1 H), 7.42 (t, J = 7.3 Hz, 2 H), 6.74 (dt, J = 7.6 Hz, J = 1.6 Hz, 1 H), 4.47 (dd, J = 11.3 Hz, J = 3.5 Hz, 1 H), 4.28 (dd, J = 11.3 Hz, J = 7.3 Hz, 1 H), 4.16 (q, J = 7.3 Hz, 2 H), 3.80 (m_c, 1 H), 2.39–2.09 (m, 3 H), 2.52 (s, 1 H, OH), 1.85 (d, J = 1.6 Hz, 3 H), 1.75 (m, 2 H), 1.41 (m_c, 1 H), 1.29 (t, J = 7.3 Hz, 3 H), 1.02 (d, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR: δ = 168.12, 166.77, 141.77, 133.07, 129.55, 128.32, 127.89, 73.68, 67.51, 60.32, 35.97, 30.92, 26.02, 15.15, 14.16, 12.25 ppm. IR: $\tilde{\nu}_{max}$ = 3485 (m), 1718 (s), 1710 (s), 1647 (w) cm^{-1}. MS: m/z = 334 (1.6%, $[M]^+$), 316 (0.84%, $[M - H_2O]^+$), 288 ($[M - H - C_2H_5O]^+$), 212 ($[M - C_6H_5 - C_2H_5O]^+$), 176, 166 ($[M - PhCO - C_2H_5O - H_2O]^+$), 153, 121 ($[PhCO_2]^+$), 105 ($[PhCO]^+$), 77 ($[Ph]^+$). HRMS calcd. for $[C_{19}H_{26}O_5]^+$: 334.17803, found 334.17818; calcd. for $[C_{17}H_{20}O_4]^+$: 288.13616, found 288.13599. $C_{19}H_{26}O_5$ (344.42): calcd. C 66.26, H 7.61; found C 66.42, H 7.59.

Preparation of Thiocarbonates 11a–e: A solution of alcohol **10a** (3.05 g, 8.85 mmol) and pyridine (2.15 mL, 26.55 mmol) in 18 mL CH_2Cl_2 was treated with DMAP (200 mg, 1.63 mmol) and PhOC(S)Cl (2.98 mL, 22.13 mmol) at 0 °C, stirred for 12 h at room temp., quenched with water, extracted with diethyl ether, washed with sat. aqueous NH_4Cl, water, brine, dried ($MgSO_4$), concentrated under reduced pressure and chromatographed (hexane/ethyl acetate, 10:1) to give thiocarbonate **11a** (4.04 g, 95%). Analogously, **11b–e** were prepared in 92–97% yield.

Ethyl (2*E*,6S,7S)-8-*tert*-Butyldimethylsiloxy-2,6-dimethyl-7-[(phenoxythiocarbonyl)oxy]-2-octenoate (11a): $[\alpha]_D^{20} = -13.8$ (c = 1.6, $CHCl_3$). ^1H NMR: δ = 7.52 (m_c, 2 H, *m*-aryl-H), 7.40 (m_c, 1 H, *p*-aryl-H), 7.20 (m_c, 2 H, *o*-aryl-H), 6.87 (dt, J = 7.6 Hz, J = 1.4 Hz, 1 H, 3-H), 5.41 (m_c, 1 H, 7-H), 4.30 (q, J = 7.3 Hz, 2 H, ethyl CH_2), 4.01 (m, 2 H, 8-H), 2.49–2.18 (m, 3 H), 1.97 (d, J = 1.4 Hz, 3 H, 2-Me), 1.88–1.73 (m, 1 H), 1.57–1.45 (m, 1 H), 1.42 (t, 3 H, J = 7.3 Hz, 3 H, ethyl-Me), 1.04 (d, J = 7.0 Hz, 3 H, 6-Me), 1.04 (s, 9 H, *t*Bu), 0.24 (s, 6 H, $SiMe_2$) ppm. ^{13}C NMR: δ = 195.04, 168.09, 153.34, 141.46, 129.41, 128.09, 126.40, 121.93, 88.81, 61.38, 60.37, 33.24, 30.96, 26.05, 25.78, 18.18, 15.16, 14.26, 12.36, –5.44 ppm. IR: $\tilde{\nu}_{max}$ = 1711 (s), 1650 (w), 1201 (s) cm^{-1}. MS: m/z = 423 (1.5%, $[M - C_4H_9]^+$), 326 (7.2%, $[M - C_7H_5O_2S - H]^+$), 281 (2.8%, $[M - C_7H_5O_2S - H - C_2H_5O]^+$), 269 (46.2%, $[M - C_7H_5O_2S - H - C_4H_9]^+$), 211 (32.2%, $[M - C_7H_5O_2S - H - SitBuMe_2]^+$), 151 (22.4%, $[M - C_7H_5O_2S - H - SitBuMe_2 - C_2H_5O - CH_3]^+$), 121 (33.0%), 89 (28.6%), 73 (100.0%). HRMS calcd. for $[C_{21}H_{31}O_5SSi]^+$: 423.16615, found 423.16600; calcd. for $[C_{18}H_{34}O_3Si]^+$: 326.22772, found 326.22775; calcd. for $[C_{14}H_{25}O_3Si]^+$: 269.15730, found 269.15729. $C_{25}H_{40}O_5SSi$ (480.75): calcd. C 62.45, H 8.39; found C 62.42, H 8.10.

Ethyl (2*Z*,6*S*,7*S*)-8-*tert*-Butyldimethylsiloxy-2,6-dimethyl-7-[(phenoxythiocarbonyl)oxy]-2-octenoate (11b): $[\alpha]_D^{20} = -7.9$ (c = 1.4, $CHCl_3$). ^1H NMR: δ = 7.39 (m, 2 H, *m*-aryl), 7.25 (m, 1 H, *p*-aryl), 7.08 (m, 2 H, *o*-aryl), 5.91 (dt, J = 6.8 Hz, J = 1.6 Hz, 1 H, 3-H), 5.28 (m_c, 1 H, 7 H), 4.20 (q, J = 7.3 Hz, 2 H, ethyl CH_2), 3.89 (ddd, J = 11.3 Hz, J = 5.4 Hz, J = 3.8 Hz, 2 H, 8-H), 2.53 (m, 2 H), 2.12 (m, 1 H), 1.90 (d, J = 1.6 Hz, 3 H, 2-Me), 1.66 (m, 1 H), 1.34 (m, 1 H), 1.32 (t, J = 7.3 Hz, 3 H, ethyl-Me), 1.02 (d, J = 7.0 Hz, 3 H, 6-Me), 0.93 (s, 9 H, *t*Bu), 0.11 (s, 6 H, $SiMe_2$) ppm. ^{13}C NMR: δ = 195.08, 168.01, 153.35, 142.22, 129.40, 127.55, 126.38, 121.97, 89.10, 61.36, 60.06, 33.29, 31.75, 26.97, 25.80, 20.72, 18.18, 14.99, 14.31, –5.43 ppm. IR: $\tilde{\nu}_{max}$ = 1715 (s), 1647 (w), 1202 (s) cm^{-1}. MS: m/z = 23 (1.4%, $[M - C_4H_9]^+$), 326 (8.3%, $[M - C_7H_5O_2S - H]^+$), 303 (2.7%), 281 (4.2%, $[M - C_7H_5O_2S - H - C_2H_5O]^+$), 269 (76.6%, $[M - C_7H_5O_2S - H - C_4H_5]^+$), 223 (27.9%), 211 (35.5%, $[M - C_7H_5O_2S - H - SitBuMe_2]^+$), 195 (18.4%), 185 (10.4%), 149 (39.1%), 121 (40.4%), 89 (27.1%), 73 (100.0%, $[C_6H_5]^+$). HRMS calcd. for $[C_{21}H_{31}O_5SSi]^+$: 423.16615, found 423.16680. $C_{25}H_{40}O_5SSi$ (480.75): calcd. C 62.45, H 8.39; found C 62.73, H 8.00.

Methyl (2*E*,6*S*,7*S*)-8-*tert*-Butyldimethylsiloxy-2,6-dimethyl-7-[(phenoxythiocarbonyl)oxy]-2-octenoate (11c): $[\alpha]_D^{20} = -14.7$ (c = 1.5, $CHCl_3$). ^1H NMR: δ = 7.36–6.93 (m, 5 H, aryl), 6.64 (dt, J = 7.3 Hz, J = 1.0 Hz, 1 H, 3-H), 5.18 (m_c, 1 H, 7-H), 3.78 (m, 2 H, 8-H), 3.61 (s, 3 H, OMe), 2.28–1.98 (m, 3 H), 1.76 (d, J = 1.0 Hz, 3 H, 2-Me), 1.58 (m_c, 1 H), 1.28 (m, 1 H), 0.93 (d, J = 7.0 Hz, 3 H, 6-Me), 0.84 (s, 9 H, *t*Bu), 0.20 (s, 6 H, $SiMe_2$) ppm. ^{13}C NMR: δ = 194.90, 168.35, 153.23, 141.71, 129.29, 127.69, 126.28, 121.81, 88.64, 61.26, 51.50, 33.08, 30.81, 25.89, 25.68, 18.06,15.06, 12.28, –5.55 ppm. IR: $\tilde{\nu}_{max}$ = 1715 (s), 1651 (w), 1202 (s) cm^{-1}. MS: m/z = 451 (0.1%, $[M–CH_3]^+$), 423 (0.3%), 409 (4.4%, $[M - C_4H_9]^+$), 312 (19.5%, $[M - C_7H_5O_2S - H]^+$), 255 (100.0%, $[M - C_7H_5O_2S - H - C_4H_9]^+$), 223 (28.7%, $[M - C_7H_5O_2S - H - CH_3O - CO - 2CH_3]^+$), 211 (64.6%), 185 (15.1%), 151 (32.3%), 121 (25.8%), 89 (39.1%), 73 (82.2%). $C_{24}H_{38}O_5SSi$ (466.72): calcd. C 61.76, H 8.20; found C 61.99, H 8.05.

Ethyl (2*E*,6*S*,7*S*)-8-*tert*-Butyldiphenylsiloxy-2,6-dimethyl-7-[(phenoxythiocarbonyl)oxy]-2-octenoate (11d): ^1H NMR: δ = 7.68 (m, 4

H), 7.39–7.12 (m, 9 H), 7.04 (m, 2 H), 6.72 (dt, J = 7.6 Hz, J = 1.2 Hz, 1 H, 3-H), 5.52 (m_c, 1 H, 7-H), 4.18 (q, J = 7.3 Hz, 2 H, ethyl CH_2), 3.85 (m, 2 H, 8-H), 2.25 (m, 2 H), 2.09 (m, 1 H), 1.90 (d, J = 1.2 Hz, 3 H, 2-Me), 1.61 (m, 1 H), 1.36 (m, 1 H), 1.30 (t, J = 7.3 Hz, 3 H, ethyl-Me), 1.08 (s, 9 H, *t*Bu), 1.00 (d, J = 7.0 Hz, 3 H, 6-Me) ppm. ^{13}C NMR: δ = 195.23, 168.18, 153.39, 141.32, 135.62, 135.58, 133.04, 129.80, 129.43, 127.77, 126.43, 121.97, 87.65, 62.40, 60.43, 33.41, 31.54, 26.73, 26.30, 19.18, 14.50, 14.29, 12.42 ppm. IR: $\tilde{\nu}_{max}$ = 1709 (s), 1650 (w), 1202 (s) cm^{-1}. MS: m/z = 547 (3.4%, $[M - C_4H_9]^+$), 450 (4.7%, $[M - H - C_7H_5O_2S]^+$), 393 (76.8%, $[M - H - C_7H_5O_2S - C_4H_9]^+$), 335 (31.7%), 275 (41.9%), 227 (21.6%), 199 (59.3%, $[C_{12}H_{11}OSi]^+$), 135 (48.7%), 109 (49.6%), 77 (100.0%, $[C_6H_5]^+$). $C_{35}H_{44}O_5SSi$ (604.89): calcd. C 69.50, H 7.33; found C 69.45, H 7.10.

Ethyl (2*E*,6*S*,7*S*)-8-Benzoyloxy-2,6-dimethyl-7-[(phenoxythiocarbonyl)oxy]-2-octenoate (11e): $[\alpha]_D^{20}$ = –4.6 (c = 1.2, $CHCl_3$). ^{1}H NMR: δ = 8.02 (m_c, 2 H, aryl-H), 7.53 (m, 1 H, aryl-H), 7.38 (m_c, 4 H, aryl-H), 7.24 (m_c, 1 H, aryl-H), 7.01 (m_c, 2 H, aryl-H), 6.72 (dt, J = 7.3 Hz, J = 3 Hz, 1 H, 3-H), 5.68 (dt, J = 7.3 Hz, J = 3.0 Hz, 1 H, 7-H), 4.69 (dd, J = 12.3 Hz, J = 3.0 Hz, 1 H, 8-H), 4.50 (dd, J = 12.3 Hz, J = 7.3 Hz, 1 H, 8-H), 4.16 (q, J = 7.3 Hz, 2 H, ethyl CH_2), 2.41–2.09 (m, 3 H), 1.87 (d, J = 1.3 Hz, 3 H, 2-Me), 1.74 (m_c, 1 H), 1.47 (m, 1 H), 1.29 (t, J = 7.3 Hz, 3 H, ethyl-Me), 1.12 (d, J = 7.0 Hz, 3 H, 6-Me) ppm. ^{13}C NMR: δ = 194.76, 167.74, 165.93, 153.12, 140.80, 133.03, 129.55, 129.43, 129.27, 128.23, 126.34, 121.63, 85.28, 63.12, 60.22, 33.84, 30.93, 25.67, 14.87, 14.08, 12.24 ppm. IR: $\tilde{\nu}_{max}$ = 1724 (s), 1710 (s), 1649 (w), 1202 (s) cm^{-1}. MS: m/z = 470 (0.6%, $[M]^+$), 425 (3.9%, $[M - C_2H_5O]^+$), 316 (20.1%, $[M - C_7H_5O_2S - H]^+$), 194 (31.7%, $[M - C_7H_5O_2S - H - C_6H_5 - C_2H_5O]^+$), 149 (30.5%), 121 (69.6%, $[PhCO_2]^+$), 105 (100.0%, $[C_7H_5O]^+$), 93 (38.6%, $[C_6H_5O]^+$), 77 (65.4%, $[C_6H_5]^+$). HRMS calcd. for $[C_{26}H_{30}O_6S]^+$: 470.17631, found 470.17635; calcd. for $[C_{24}H_{25}O_5S]^+$: 425.14227, found 425.14226. $C_{26}H_{30}O_6S$ (470.58): calcd. C 66.36, H 6.43; found C 66.48, H 6.27.

Free Radical Cyclization of 11a–e to give 12/13a–d. Typical Procedure: For ensuring quantitative conversion, an excess of the stannane was applied. Thus, to a stirred solution of 1 mmol nBu$_3$SnH and 0.05 mmol AIBN in toluene (50 mL) a solution of 1 mmol **11a**–**e**, 2 mmol nBu$_3$SnH and 0.05 mmol AIBN in toluene (1–3 mL) was added slowly during 12 h at 80–90 °C. The mixture was stirred for 2–4 h at 90 °C, evaporated and purified by chromatography (hexane/ethyl acetate, 10:1) to give a mixture of diastereomers. The diastereomeric ratio was determined by HPLC and ^{1}H NMR spectroscopy. A preparative separation of the diastereomers was not possible in all cases. Overall yields and ratios of **12/13a**–**d** see Table 1.

(1*S*,2*R*,3*S*)-2-(*tert*-Butyldimethylsiloxymethyl)-1-[(1*S*)-1-(ethoxycarbonyl)ethyl]-3-methylcyclopentane (12a): ^{1}H NMR: δ = 4.10 (q, J = 7.0 Hz, 2 H, ethyl CH_2), 3.53 (m_c, 1 H, 8-H), 3.40 (dd, J = 10.0 Hz, J = 7.3 Hz, 1 H, 8-H), 2.44 (m, 1 H), 2.04 (m, 1 H), 1.84 (m, 1 H), 1.74–1.04 (m_c, 5 H), 1.23 (t, J = 7.0 Hz, 3 H, ethyl CH_2), 0.93 (d, J = 6.8 Hz, 3 H, 3-Me), 0.92 (s, 9 H, *t*Bu), 0.88 (d, J = 7.0 Hz, 3 H, 1-Me), 0.30 (s, 6 H, $SiMe_2$) ppm. ^{13}C NMR: δ = 177.11, 62.91, 59.90, 49.11, 45.19, 40.36, 35.89, 32.53, 29.68, 25.87, 22.68, 22.49, 17.22, 14.22, –5.52 ppm. $C_{18}H_{38}O_3Si$ (330.59): calcd. C 65.40, H 11.59; found C 65.62, H 11.79.

(1*S*,2*R*,3*S*)-2-(*tert*-Butyldiphenylsiloxymethyl)-1-[(1*S*)-1-(ethoxycarbonyl)ethyl]-3-methylcyclopentane (12c): ^{1}H NMR: δ = 7.64 (m, 4 H, aryl-H), 7.37 (m, 6 H, aryl-H), 4.07 (q, J = 6.8 Hz, 2 H, ethyl CH_2), 3.60 (dd, J = 9.8 Hz, J = 5.0 Hz, 1 H, 8-H), 3.41 (dd, J = 9.8 Hz, J = 7.5 Hz, 1 H, 8-H), 2.32 (m_c, 1 H), 2.17 (m_c, 1 H), 2.04 (m_c, 1 H), 1.84 (m_c, 1 H), 1.76 (m_c, 1 H), 1.57 (m, 1 H), 1.32 (m, 1 H), 1.22 (t, J = 6.8 Hz, 3 H, ethyl-Me), 1.11 (m, 1 H), 1.06 (s, 9 H, *t*Bu), 1.04 (d, J = 7.0 Hz, 3 H, 1-Me), 1.00 (d, J = 7.0 Hz, 3 H, 3-Me) ppm. ^{13}C NMR: δ = 176.92, 135.62, 133.87, 129.58, 127.62, 63.60, 59.90, 53.77, 49.30, 45.08, 40.32, 32.44, 29.71, 26.86, 22.52, 19.18, 17.00, 14.21 ppm. IR: $\tilde{\nu}_{max}$ = 1960 (w), 1890 (w), 1825 (w), 1730 (s) cm^{-1}. MS: m/z = 437 (0.4%, $[M - CH_3]^+$), 407 (7.3%, $[M - C_2H_5O]^+$), 395 (100.0%, $[M - C_4H_9]^+$), 349 (4.5%, $[M - C_4H_9 - C_2H_5O - H]^+$), 289 (9.1%), 227 (18.5%), 199 (28.2%, $[C_{12}H_{11}OSi]^+$), 183 (17.2%), 139 (13.2%), 123 (13.0%), 95 (19.6%). $C_{28}H_{40}O_3Si$ (452.71): calcd. C 74.29, H 8.91; found C 73.82, H 8.86.

(1*S*,2*R*,3*S*)-2-(*tert*-Butyldiphenylsiloxymethyl)-1-[(1*R*)-1-(ethoxycarbonyl)ethyl]-3-methylcyclopentane (13c): ^{1}H NMR: δ = 7.64 (m, 4 H), 7.36 (m, 6 H), 4.06 (q, J = 7.3 Hz, 2 H), 3.85 (m, 2 H), 2.42 (m_c, 1 H), 2.19 (m_c, 1 H), 2.01–1.57 (m, 4 H), 1.44 (m, 1 H), 1.28 (m, 1 H), 1.23 (t, J = 7.3 Hz, 3 H), 1.08 (d, J = 7.0 Hz, 3 H), 1.05 (s, 9 H), 0.98 (d, J = 6.8 Hz, 3 H). $C_{28}H_{40}O_3Si$ (452.71): calcd. C 74.29, H 8.91; found C 74.35, H 8.76.

(1S,2R,3S)-2-(Benzoyloxymethyl)-1-[(1*S*)-1-(ethoxycarbonyl)ethyl]-3-methylcyclopentane (12d): ^{1}H NMR: δ = 8.00 (d, J = 7.0 Hz, 2 H, *o*-aryl), 7.53 (t, J = 7.1 Hz, 1 H, *p*-aryl), 7.41 (t, J = 7.0 Hz, 2 H, *m*-aryl), 4.40 (dd, J = 11.9 Hz, J = 5.4 Hz, 1 H, 8-H), 4.25 (d, J = 11.9 Hz, 1 H, 8-H), 4.11 (q, J = 7.5 Hz, 2 H, ethyl CH2), 2.48 (m, 1 H), 2.21 (m, 1 H), 2.08 (m_c, 1 H), 1.97 (m, 1 H), 1.72 (m, 1 H), 1.48 (m, 1 H), 1.28 (d, J = 7.0 Hz, 3 H, 1-Me), 1.21 (t, J = 7.5 Hz, 3 H, ethyl-Me), 1.17 (m, 1 H), 1.08 (d, J = 7.0 Hz, 3 H, 3-Me). $C_{19}H_{26}O_4$ (318.42): calcd. C 71.67, H 8.23; found C 71.39, H 8.18.

Formation of 1 and 2: The mixture of silyl ethers **12/13a**–**b** (1 mmol) in CH_2Cl_2 (20 mL) was treated dropwise with TFA (1 mL) and water (1 mL) at –12 °C and stirred for 12 h at room temp. The mixture was diluted with CH_2Cl_2 (40 mL) and water (10 mL). The organic layer was washed with water and brine, dried ($MgSO_4$) and the solvents evaporated. Chromatography (hexane/ethyl acetate, 3:1) gave a mixture of diastereomers, which were separated by HPLC (2% 2-propanol/hexane) to give **1** and **2**. Sublimation and recrystallization from hexane afforded colorless needles. The mixture of TBDPS ethers **12/13c** (0.40 g, 0.88 mmol) in THF (4.4 mL) was stirred with a 1.1 M solution of TBAF in THF (1.46 mL, 1.33 mmol) for 12 h at room temp. Workup and purification were the same as above (yield 95%).

(4a*S*)-4*t*,4a*r*,7*c*,7a*c*-4,7-Dimethylhexahydrocyclopenta[*c*]pyran-3-one [(+)-Iridomyrmecin (1)]: $[\alpha]_D^{25}$ = +211 (c = 1.0, CCl_4); [ref.[9b] $[\alpha]_D^{17}$ = +205 (c = 0.22, CCl_4)], m.p. 60–61 °C (ref.[9b] 59–60 °C). ^{1}H NMR: δ = 4.27 (dd, J = 11.7 Hz, J = 3.7 Hz, 1 H, 8-H), 4.16 (d, J = 11.7 Hz, 1 H, 8-H), 2.71 (quint, J = 6.8 Hz, 1 H, 2-H), 2.60 (m_c, 1 H, 3-H), 1.96–1.73 (m, 4 H, 4-H, 5-H, 6-H, 7-H), 1.16 (d, J = 6.8 Hz, 3 H, 2-Me), 1.06 (d, J = 6.8 Hz, 3 H, 6-Me), 1.02 (m, 2 H, 4-H, 5-H) ppm; ^{1}HNMR (270 MHz, [D$_6$]acetone): δ = 4.36 (dd, J = 11.3 Hz, J = 3.5 Hz, 1 H), 4.12 (d, J = 11.3 Hz, 1 H), 2.85 (quint, J = 6.8 Hz, 1 H), 2.66 (m_c, 1 H), 1.92 (m, 1 H), 1.88–1.68 (m, 3 H), 1.07 (d, J = 6.3 Hz, 3 H), 1.04 (d, J = 6.8 Hz, 3 H), 0.92 (m, 2 H). ^{1}H NMR ([D$_6$]benzene): δ = 3.63 (d, J = 11.3 Hz, 1 H), 3.48 (dd, J = 11.3 Hz, J = 3.8 Hz, 1 H), 1.92 (quint, J = 6.5 Hz, 1 H), 1.83 (m_c, 1 H), 1.55 (m_c, 1 H), 1.48–1.20 (m, 3 H), 1.02 (d, J = 6.0 Hz, 3 H), 0.88 (m_c, 1 H), 0.71 (d, J = 6.8 Hz, 3 H), 0.62 (m_c, 1 H) ppm. ^{13}C NMR: δ = 175.87, 67.86, 45.68, 43.31, 38.00, 37.27, 34.20, 29.73, 18.31, 12.64 ppm. ^{13}C NMR ([D$_6$]acetone): δ = 176.14, 67.85, 45.43, 41.11, 37.84, 37.21, 34.10, 29.74, 18.29, 12.65 ppm. IR: $\tilde{\nu}_{max}$ = 1730 (s) cm^{-1}. MS: m/z = 168 (8.8%, $[M]^+$), 153 (0.7%, $[M - CH_3]^+$), 150 (2.1%), 138 (1.2%, $[M\text{-}2CH_3]^+$), 123 (1.4%), 109 (46.8%, $[M - CO_2 - CH_3]^+$), 95 (100.0%), 81 (54.9%), 67 (66.7%), 55 (24.9%). HRMS calcd. for $[C_{10}H_{16}O_2]^+$: 168.11503,

found 168.11505. $C_{10}H_{16}O_2$ (168.24): calcd. C 71.39, H 9.59; found C 71.08, H 9.48.

(–)-Isoiridomyrmecin (2): $[\alpha]_D^{20}$ = –62.4 (*c* = 0.7, CCl_4), ref.[9b] $[\alpha]_D^{19}$ = –64 (*c* = 1, CCl_4); m.p. 58–59 °C (ref.[9b] 57.5–58 °C). ^{1}H NMR: δ = 4.35 (dd, *J* = 11.6 Hz, *J* = 6.2 Hz, 1 H, 8-H), 3.96 (t, *J* = 11.6 Hz, 1 H, 8-H), 2.36 (m, 1 H, 6-H), 2.12 (m, 1 H, 4-H), 2.04 (m_c, 2 H, 5-H, 7-H), 1.90 (m, 1 H, 3-H), 1.66 (m, 1 H, 2-H), 1.29 (m, 2 H, 4-H, 5-H), 1.20 (d, *J* = 7.0 Hz, 3 H, 6-Me), 1.06 (d, *J* = 7.0 Hz, 3 H, 2-Me) ppm. ^{13}C NMR: δ = 176.24, 69.34, 45.28, 43.16, 39.01, 38.22, 35.61, 33.03, 19.08, 13.89 ppm. IR: $\tilde{\nu}_{max}$ = 1731 (s) cm^{-1}. MS: *m*/*z* = 168 (38.8%, $[M]^+$), 109 (52.4%, $[M - CO_2 - CH_3]^+$), 95 (100.0%), 81 (88.0%), 67 (81.1%), 55 (34.1%), 41 (64.2%, $[C_3H_5]^+$). HRMS calcd. for $[C_{10}H_{16}O_2]^+$: 168.11503, found 168.11518. $C_{10}H_{16}O_2$ (168.24): calcd. C 71.39, H 9.59; found C 71.12, H 9.52.

Diols 14/15: The mixture of benzoates **12/13d** (0.53 g 1.66 mmol) in diethyl ether (30 mL) was treated with LAH (0.13 g, 3.33 mmol) at –12 °C and stirred for 3 h at 0 °C. The mixture was quenched with a sat. aq. NH_4Cl, diluted with CH_2Cl_2, filtered, dried ($MgSO_4$) and the solvents evaporated. Chromatography (hexane/ethyl acetate, 1:2) gave a mixture of diastereomers **14/15** (0.25 g, 1.45 mmol), from which **14** was isolated by HPLC (5% 2-propanol/hexane).

(1*R*,2*R*,3*S*)-2-(Hydroxymethyl)-1-[(1*S*)-2-hydroxy-1-methylethyl]-3-methylcyclopentane (14): ^{1}H NMR: δ = 3.68 (ddd, *J* = 10.8 Hz, *J* = 5.1 Hz, *J* = 4.1 Hz, 2 H), 3.37 (m, 2 H), 2.16–1.88 (m, 3 H), 1.76 (m, 2 H), 1.56 (m_c, 1 H), 1.37–1.07 (m, 3 H), 1.05 (d, *J* = 6.5 Hz, 3 H), 1.01 (d, *J* = 7.3 Hz, 3 H), 0.88 (m, 1 H) ppm. ^{13}C NMR: δ = 67.60, 62.59, 50.08, 44.23, 36.05, 35.19, 31.87, 28.88, 22.77, 16.76 ppm. IR: $\tilde{\nu}_{max}$ = 3460 (m) cm^{-1}. MS: *m*/*z* = 169 (37.0%), 153 (100.0%, $[M - H_2O - H]^+$), 139 (34.8%), 123 (65.7%), 95 (88.5%), 91 (65.3%), 81 (54.7%), 68 (32.5%), 55 (43.7%), 43 (70.0%). $C_{10}H_{20}O_2$ (172.27): calcd. C 69.72, H 11.70; found C 69.90, H 11.66.

(1*R*,2*R*,3*S*)-2-(*tert*-Butyldimethylsiloxymethyl)-1-[(1*S*)-2-hydroxy-1-methylethyl]-3-methylcyclopentane (16): Ester **12a** (1.10 g, 3.35 mmol) in diethyl ether (80 mL) was treated dropwise with DIBAL-H (0.98 M *in* hexane, 7.52 mL, 7.37 mmol) at –40 °C and stirred for 1 h at –40 °C and for another 2 h at –10 °C. Workup with sat.aq. NH_4Cl and chromatography (hexane/ethyl acetate, 3:1) furnished **16** (820 mg, 86%) as a colorless oil. $[\alpha]_D^{20}$ = –13.3 (*c* = 1.8, $CHCl_3$). ^{1}H NMR: δ = 3.64 (ddd, *J* = 10.3 Hz, *J* = 4.8 Hz, *J* = 4.0 Hz, 2 H), 3.39 (ddd, *J* = 14.8 Hz, *J* = 7.5 Hz, *J* = 5.0 Hz, 2 H), 2.09 (m_c, 1 H), 1.92 (m, 1 H), 1.79–1.64 (m, 3 H), 1.60 (m, 1 H), 1.35 (m,1 H), 1.28 (m, 1 H), 1.13 (m, 1 H), 1.05 (d, *J* = 6.8 Hz, 3 H), 1.00 (d, *J* = 7.3 Hz, 3 H), 0.91 (s, 9 H), 0.06 (s, 6 H) ppm. ^{13}C NMR: δ = 67.67, 62.79, 49.57, 44.23, 35.83, 35.17, 32.53, 29.21, 25.77, 22.69, 18.11, 16.79, –5.53 ppm. IR: $\tilde{\nu}_{max}$ = 3349 (m) cm^{-1}. MS: *m*/*z* = 271 (0.1%, $[M - CH_3]^+$), 255 (0.1%, $[M - CH_2OH]^+$), 229 (0.9%, $[M - C_4H_9]^+$), 211 (1.6%), 183 (1.5%), 137 (100.0%), 105 (50.5%), 95 (71.9%), 81 (79.2%), 75 (95.7%). HRMS calcd. for $[C_{15}H_{31}O_2Si]^+$: 271.20933, found 271.20879. $C_{16}H_{34}O_2$ (286.54): calcd. C 67.07, H 11.96; found C 67.23, H 12.21. Treatment of **16** (750 mg, 2.62 mmol) in THF (20 mL) with solid TBAF (5 mmol) at room temp. for 12 h delivered **14** after aqueous workup and chromatography (hexane/ethyl acetate, 1:1) (380 mg, 85%) as a colorless oil. The analytical data matched with those described above.

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