SUPPLEMENTARY MATERIAL

First Asymmetric Synthesis of the Cyclohexanone Subunit of Baconipyrones A and B. Revision of its Structure

Māris Turks, M. Carmen Murcia, Rosario Scopelliti and Pierre Vogel

[*] Prof. Dr. P. Vogel
Laboratory of Glycochemistry and Asymmetric Synthesis, Swiss Federal Institute of Technology (EPFL), BCH, CH-1015 Lausanne-Dorigny, Switzerland
Fax : (+41) 21 693 93 75; e-mail : Pierre.Vogel@epfl.ch
General remarks

Commercial reagents (Fluka, Aldrich) were used without purification. Solvents were distilled prior to use: THF from Na and benzophenone; MeOH from Mg and I₂; DMF and CH₂Cl₂ from CaH₂. Light petroleum ether used refers to the fraction boiling at 40-60°C. Solutions after reactions and extractions were evaporated in a rotatory evaporator under reduced pressure. Liquid/solid flash chromatography (FC): columns of silica gel (0.040-0.63 mm, Merck No.9385 silica gel 60, 240-400 mesh). TLC for reaction monitoring: Merck silica gel 60F₂₅₄ plates; detection by UV light; Pancaldi reagent \([\text{(NH}_4\text{)}_6\text{MoO}_4, \text{Ce(SO}_4\text{)}_2, \text{H}_2\text{SO}_4, \text{H}_2\text{O}]\) or KMnO₄. IR spectra: Perkin-Elmer-1420 spectrometer (ν, cm⁻¹). ¹H NMR spectra: Bruker-ARX-400 spectrometer (400 MHz); δ(H) in ppm relative to the solvent's residual ¹H signal [CHCl₃, δ(H) 7.27; CH₃OD, δ(H) 3.31; C₆H₆, δ(H) 7.3] as internal reference; all ¹H assignments were confirmed by 2D-COSY-45 spectra. ¹³C NMR spectra: same instrument as above (100.6 MHz); δ(C) in ppm relative to solvent's C-signal [CDCl₃, δ(C) 77.0; CD₃OD, δ(C) 49.2; C₆D₆, δ(C) 128.5] as internal reference; coupling constants J in Hz. MS: Nermag R-10-10C, chemical ionization (NH₃) mode m/z (amu) [% relative base peak (100%)], HRMS: Jeol AX-505. Elemental analyses: Ilse Beetz, D-96301 Kronach, Germany.
(+)-(2S,3S,4S,5S,6S)-3-Ethyl-3,5-dihydroxy-2,4,6-trimethylcyclohexan-1-one (1).

Solution of 16 (0.21 g, 0.69 mmol) in methanol (20 mL) containing 10 % Pd/C (50 mg) was stirred under H₂ atmosphere at ambient pressure for 12 h. Suspension was filtered through Celite and evaporated. Yield 0.138 g (quant). A crystal for X-ray diffraction was obtained by crystallization from pentane/dichloromethane (mp. 125°C). White crystals; R_f=0.29 (CH₂Cl₂/MeOH=9:1); [α]$_{589}^{25}$ =+37, (c = 0.03, CHCl₃); IR (KBr): 3400, 2970, 2924, 2881, 1705, 1457, 1385, 1358, 1296, 1179, 1123, 1030; $^1$H-NMR (CDCl₃, 400MHz): 3.9 (ddd, $J$ = 9.3, 5.6, 4.5 Hz, 1H, H-C(5)), 2.87 (dq, $J$ = 7.4, 5.6 Hz, 1H, H-C(6)), 2.76 (q, $J$ = 6.8 Hz, 1H, H-C(2)), 2.10 (bs, 1H, OH), 2.08 (dq, $J$ =6.8, 9.3 Hz, 1H, H-C(4)), 1.70 (dq, $J$ = 14.7, 7.4 Hz, 1H, Ha-C(1’)), 1.53 (dq, $J$ = 14.7, 7.4 Hz, 1H, Hb-C(1’)), 1.32 (bs, 1H, OH), 1.20 (d, $J$ = 7.4 Hz, 3H, CH₃-C(6)), 1.11 (d, $J$ = 6.8 Hz, 3H, CH₃-C(4)), 1.03 (d, $J$ = 6.8 Hz, 3H, CH₃-C(2)), 0.89 (t, $J$ = 7.4 Hz, 3H, H-C(2’)); $^{13}$C-NMR (CDCl₃, 100.6MHz): 214.1, 77.5, 72.8, 49.9, 45.4, 38.3, 29.9, 11.8, 10.8, 8.7, 7.2; Anal. Calcd. for C₁₁H₂₀O₃ (200.27): C 65.97, H 10.07; found C 65.85, H 9.89; MALDI-HRMS Calcd. for C₁₁H₂₀O₃Na⁺ 223.1310; found 223.1312.
H-NMR spectrum of 1:

Mosher’s esters of 1.

General procedure for the preparation of MTPA esters:

To the solution of diol 1 (1 mg) in abs. pyridine (0.5 mL) was added the corresponding α-methoxy-α-trifluoromethylphenylacetyl chloride (2 equiv.) at –20 °C. The mixture was allowed to reach + 20°C and stirred for 2 h. It was then chilled to –20 °C and N,N-dimethylamino ethanol (5 equiv.) was added. The mixture was allowed to warm to +20 °C and stirred for 1 h. It was diluted with Et₂O (30 mL),
washed with aq. sat. solution of CuSO$_4$ (4 x 7 mL), water (10 mL), aq. solution of 2M HCl (4 x 7 mL), aq. sat. solution of NaHCO$_3$ (3 x 5 mL), dried over anh. Na$_2$SO$_4$, filtered and evaporated. All the NMR measurements were done on the crude sample.

(R)-MTPA ester 1A: $^1$H-NMR (CDCl$_3$, 400MHz): 7.53-7.51 (m, 2H, arom), 7.43-7.39 (m, 3H, arom), 5.24 (dd, $J = 8.0, 4.9$ Hz, 1H, H-C(5)), 3.53 (q, $J = 1.2$ Hz, 3H, CH$_3$O-C(2’’)), 3.04 (dq, $J = 6.8, 4.9$ Hz, 1H, H-C(6)), 2.60 (q, $J = 6.8$ Hz, 1H, H-C(2)), 2.25 (dq, $J = 7.4, 6.8$ Hz, 1H, H-C(4)), 1.68 (dq, $J = 14.2, 7.4$ Hz, 1H, Ha-C(1’)), 1.52 (dq, $J = 14.2, 7.4$ Hz, 1H, Hb-C(1’)), 1.07 (d, $J = 7.4$ Hz, 3H, CH$_3$-C(4)), 1.04 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(2)), 0.95 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(6)), 0.84 (t, $J = 7.4$ Hz, 3H, H-C(2’’)); $^{19}$F-NMR (CDCl$_3$+CCl$_3$F, 376.7 MHz): -71.38 (s, CF$_3$-C(2’’)); MALDI-HRMS Calcd. for C$_{21}$H$_{27}$F$_3$O$_5$Na$^+$ 439.1708; found 439.1709.

(S)-MTPA ester 1B: $^1$H-NMR (CDCl$_3$, 400MHz): 7.51-7.49 (m, 2H, arom), 7.42-7.39 (m, 3H, arom), 5.24 (dd, $J = 6.2, 4.3$ Hz, 1H, H-C(5)), 3.53 (q, $J = 1.2$ Hz, 3H, CH$_3$O-C(2’’)), 3.03 (dq, $J = 6.8, 4.3$ Hz, 1H, H-C(6)), 2.51 (q, $J = 6.8$ Hz, 1H, H-C(2)), 2.18 (quint, $J = 6.8$ Hz, 1H, H-C(4)), 1.64 (dq, $J = 15.4, 7.4$ Hz, 1H, Ha-C(1’)), 1.48 (dq, $J = 15.4, 7.4$ Hz, 1H, Hb-C(1’)), 1.10 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(4)), 1.03 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(2)), 1.02 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(6)), 0.76 (t, $J = 7.4$ Hz, 3H, H-C(2’’)); $^{19}$F-NMR (CDCl$_3$+CCl$_3$F, 376.7 MHz): -71.15 (s, CF$_3$-C(2’’)); MALDI-HRMS Calcd. for C$_{21}$H$_{27}$F$_3$O$_5$Na$^+$ 439.1708; found 439.1703.
$^{19}$F-NMR spectrum of 1A and 1B:

\textit{ee: 97\%}

X-ray structure of 1:

\footnotesize

\[\text{Crystallographic data for 1 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-245521.}\]
(-)-(2S,3R,4S,5S,6S)-3-Ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''S)-1''-phenylethoxy)cyclohexan-1-one (2).

To the solution of 11 (0.25 g, 0.67 mmol, 1 equiv.) in CH$_2$Cl$_2$ (5 mL) was added a solution of TMSI (18.1 µL, 0.13 mmol, 0.2 equiv.) in CH$_2$Cl$_2$ (0.7 mL) at –78 °C. The reaction mixture was stirred at –78 °C overnight and poured into a sat. aq. solution of NaHCO$_3$. The aqueous phase was extracted with CH$_2$Cl$_2$. The combined organic layers were washed with brine, dried (anh. Na$_2$SO$_4$) and evaporated in vacuo. FC (light petroleum ether/EtOAc=9:1) afforded 36.1 mg (17.8 %) of 2, and 109 mg (53.5 %) of 16.

The same procedure was applied when TMSOTf was used as Lewis acid. Data for 2: colorless oil, [α]$_{25}^{20}$ = -40, (c = 0.31, CHCl$_3$); IR(film): 3415, 2927, 1719, 1642, 1453; $^1$H-NMR (CDCl$_3$), 400 MHz): 7.35-7.28 (m, 5H, arom), 4.42 (q, J = 6.8 Hz, 1H, H-C(1'')), 3.35 (dd, J = 9.9, 5.2 Hz, 1H, H-C(5)), 2.96 (dq, J = 7.4, 5.5 Hz, 1H, H-C(6)), 2.70 (q, J = 6.8 Hz, 1H, H-C(2)), 2.09 (dq, J = 9.9, 6.8 Hz, 1H, H-C(4)), 1.66 (m, 1H, Ha-C(1')), 1.53 (m, 1H, Hb-C(1')), 1.50 (d, J = 6.2 Hz, 3H, H-C(2'')), 1.20 (d, J = 7.4 Hz, 3H, CH$_3$-C(6)), 0.92 (d, J = 7.2 Hz, 3H, CH$_3$-C(2')), 0.85 (d, J = 6.9 Hz, 3H, CH$_3$-C(4)), 0.79 (t, J = 7.4 Hz, 3H, H-C(2')); $^{13}$C-NMR (CDCl$_3$), 100.6 MHz): 213.6, 142.7, 128.3, 127.7, 127.1, 82.6, 75.9, 74.6, 46.3, 46.1, 37.5, 28.4, 23.7, 12.4, 11.2, 8.7, 7.6; Anal. Calcd. for C$_{19}$H$_{28}$O$_3$: C 74.96, H 9.27; found C 74.98, H 9.22; MALDI-HRMS Cald. for C$_{19}$H$_{28}$O$_3$Na$^+$ 327.1936; found 327.1904.

$^2$ For data for 16 see procedure with Bu$_3$SnOMe.
NOESYs observed for 2:

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\begin{align*}
(\pm)-(2RS,3RS,4SR,5RS,6SR)-3\text{-Ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''SR)-1''-phenylethoxy)cyclohexan-1-one (3) and (\pm)-(2RS,3SR,4SR,5RS,6SR)-3\text{-ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''SR)-1''-phenylethoxy)cyclohexan-1-one (4).}
\end{align*}
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**Procedure A.** To the solution of crude (±)-27 (62.0 mg, 0.148 mmol, 1 equiv) in CH\(_2\)Cl\(_2\) (5 mL) was added BF\(_3\)OEt\(_2\) (37 µL, 0.296 mmol, 2 equiv) at –78 °C. The reaction mixture was stirred at –78 °C for 15 min. and then poured into sat. aq. solution of NaHCO\(_3\). 1M solution of TBAF in THF (0.15 mL, 0.15 mmol, 1 equiv.) was added and stirring was continued for 1h at +20 °C. The aqueous phase was extracted with EtOAc (3 x 7 mL). The combined organic layers were washed with brine, dried (anh. Na\(_2\)SO\(_4\)) and evaporated *in vacuo.* FC (light petroleum ether/EtOAc=85:15) afforded 30.4 mg (67.5 %) of 3 and 3.5 mg (7.5 %) of 4.

**Procedure B.** To the solution of crude (±)-27 (0.21 g, 0.50 mmol, 1 equiv) in THF (10 mL) was added 1M TBAF solution in THF (0.5 mL, 0.50 mmol, 1 equiv) at –15 °C. The reaction mixture was stirred at –15 °C for 15 min., quenched with MeOH/aq. sat. NH\(_4\)Cl=1 :1 (2 mL) and evaporated at room temperature. The solid residue was
directly purified by FC (hexane/EtOAc=8:2) affording 92.0 mg (60%) of 3 and 18.3 mg (12%) of 4.

Data of 3: colorless oil, Rf=0.26 (light petroleum ether/EtOAc=8:2); IR (film): 3450, 2982, 2921, 2885, 1711, 1493, 1461, 1384, 1279, 1118; 1H-NMR (CDCl3, 400MHz): 7.33-7.31 (m, 4H, arom), 7.28-7.24 (m, 1H, arom), 4.53 (q, J = 6.4 Hz, 1H, H-C(1”)), 3.48 (dd, J = 11.5, 5.1 Hz, 1H, H-C(5)), 2.61-2.52 (m, 2H, H-C(2), H-C(6)), 2.48 (dq, J = 7.0, 5.1 Hz, 1H, H-C(4)), 1.62 (dq, J = 14.5, 7.0 Hz, 1H, Ha-C(1’)), 1.57 (dq, J = 14.5, 7.0 Hz, 1H, Hb-C(1’)), 1.50 (d, J = 6.4 Hz, 3H, H-C(2’’)), 1.17 (d, J = 7.0 Hz, 3H, CH3-C(4)), 0.99 (t, J = 7.0 Hz, 3H, H-C(2’’)), 0.98, 0.96 (2d, J = 7.0 Hz, 2 x 3H, CH3-C(2), CH3-C(6)); 13C-NMR (CDCl3, 100.6MHz): 210.1, 143.2, 128.4, 127.8, 126.9, 78.5, 77.8, 75.1, 48.4, 46.6, 37.0, 30.3, 24.3, 11.0, 9.3, 7.0, 6.8; Anal. Calcd. for C19H28O3 (304.42): C 74.96, H 9.27; found C 74.86, H 9.29; MALDI-HRMS Calcd. for C19H28O3Na+ 327.1936; found 327.1920.

Data of 4: colorless oil, Rf=0.17 (light petroleum ether/EtOAc=8:2); IR (film): 3520, 2975, 2933, 2879, 1709, 1495, 1455, 1378, 1284, 1120; 1H-NMR (CDCl3, 400MHz): 7.37-7.27 (m, 5H, arom), 4.56 (q, J = 6.7 Hz, 1H, H-C(1”)), 2.99 (dd, J = 10.6, 4.8 Hz, 1H, H-C(5)), 2.88 (q, J = 6.7 Hz, 1H, H-C(2)), 2.61 (dq, J = 7.0, 4.8 Hz, 1H, H-C(4)), 2.57 (dq, J = 10.7, 6.7 Hz, 1H, H-C(6)), 1.51 (d, J = 6.7 Hz, 3H, H-C(2’’)), 1.46-1.39 (m, 1H, Ha-C(1’’)), 1.29 (d, J = 7.0 Hz, 3H, CH3-C(4)), 1.02 (d, J = 6.4 Hz, 3H, CH3-C(6)), 1.01 (d, J = 6.7 Hz, 3H, CH3-C(2)), 0.76-0.68 (m, 4H, Hb-C(1’’), H-C(2’’)). 13C-NMR (CDCl3, 100.6MHz): 209.6, 142.8, 128.5, 128.0, 126.9, 76.3, 75.8, 74.6, 50.3, 46.3, 35.6, 26.8, 24.5, 11.5, 7.8, 7.1, 6.1; Anal. Calcd. for C19H28O3 (304.42): C 74.96, H 9.27; found C 74.98, H 9.43; MALDI-HRMS Calcd. for C19H28O3K+ 343.1676; found 343.1675.
The relative configuration of 3 was assigned from the X-ray diffraction studies of its deprotected form 3a.  

(±)-(2RS,3RS,4SR,5RS,6SR)-3-Ethyl-3,5-dihydroxy-2,4,6-trimethylcyclohexan-1-one (3a).  

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\text{O} \quad \text{OH} \\
\downarrow \\
\text{OH} \\
\downarrow \\
1\, 2 \, 3 \, 4 \, 5 \, 6 \, 1' \, 2' \\
\]

Solution of 3 (90 mg, 0.30 mmol) in methanol (10 mL) containing 10 % Pd/C (20 mg) was stirred under H₂ atmosphere at ambient pressure for 12 h. The suspension was filtered through a pad of Celite and evaporated. Yield: 59 mg (quant). A crystal for X-ray diffraction was obtained by crystallization from pentane/dichloromethane (mp. 172 °C). White crystals; IR (KBr): 3360, 2997, 2975, 2906, 1712, 1454, 1324, 1280, 1149, 1031; ¹H-NMR (CDCl₃, 400MHz): 3.96 (ddd, \(J = 11.1, 4.9, 5.5\) Hz, 1H, H-C(5)), 2.62 (dq, \(J = 6.8, 1.2\) Hz, 1H, H-C(2)), 2.54 (dq, \(J = 11.7, 6.3\) Hz, 1H, H-C(6)), 2.34 (dq, \(J = 7.4, 4.9\) Hz, 1H, H-C(4)), 1.71 (d, \(J = 5.5\) Hz, 1H, OH), 1.63 (dq, \(J = 14.8, 6.8\) Hz, 1H, Ha-C(1’)), 1.59 (dq, \(J = 14.8, 6.8\) Hz, 1H, Hb-C(1’)), 1.19 (s, 1H, OH), 1.16 (d, \(J = 6.8\) Hz, 3H, CH₃-C(6)), 1.15 (d, \(J = 7.4\) Hz, 3H, CH₃-C(4)), 1.03 (d, \(J = 6.8\) Hz, 3H, CH₃-C(2)), 0.97 (t, \(J = 7.4\) Hz, 3H, H-C(2’)); ¹³C-NMR (CDCl₃, 100.6MHz): 209.7, 78.7, 73.9, 48.2, 47.6, 30.1, 10.7, 8.7, 8.7, 7.0, 6.7; Anal. Calcd.

for C₇₁H₂₀O₃ (200.27): C 65.97, H 10.07; found C 65.83, H 10.00; MALDI-HRMS Calcd. for C₁₁H₂₀O₃Na⁺ 223.1310; found 223.1390.
X-ray structure of 3a:\(^3\):

NOESY's observed for 4:

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\begin{align*}
\text{J(H4,H5)} &= 4.8 \text{ Hz} \\
\text{J(H5,H6)} &= 10.6 \text{ Hz}
\end{align*}
\]

\((\pm)-(2RS,3SR,4SR,5RS,6SR)-3\text{-Ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''SR)-1’’-phenylethoxy)cyclohexan-1-one (4) and (±)-(2SR,3SR,4SR,5RS,6SR)-3-ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''SR)-1’’-phenylethoxy)cyclohexan-1-one (5).}

To the solution of crude \((\pm)-27\) (0.267 g, 95 % purity, 0.608 mmol, 1 equiv) in CH\(_2\)Cl\(_2\) (20 mL) was added 1M TBAF solution in THF (0.61 mL, 0.608 mmol, 1 equiv) at –78 °C. The reaction mixture was stirred at –50 °C for 2 h. and quenched with aq. sat. NH\(_4\)Cl (20 mL). The aqueous phase was extracted with EtOAc (3 x 10

\(^3\) Crystallographic data for 3a have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-245520.
mL). The combined organic layers were washed with brine, dried (anh. Na₂SO₄) and evaporated *in vacuo*. FC (hexane/EtOAc=80:20) afforded 109 mg (59 %) of 4 and 31 mg (17 %) of 5. Data for 5: colorless oil, Rₛ=0.36 (hexane/EtOAc=8:2); IR (film): 3482, 2972, 2941, 2883, 1715, 1495, 1376, 1332, 1208, 1084, 1036; ¹H-NMR (CDCl₃, 400MHz): 7.36-7.27 (m, 5H, arom), 4.51 (q, J = 6.4 Hz, 1H, H-C(1’’)), 3.97 (s, 1H, OH), 3.76 (t, J = 2.2 Hz, 1H, H-C(5)), 2.71 (q, J = 6.7 Hz, 1H, H-C(2)), 2.59 (dq, J = 7.4, 2.2 Hz, 1H, H-C(6)), 2.32 (dq, J = 7.0, 2.2 Hz, 1H, H-C(4)), 1.62 (dq, J = 15.0, 7.4 Hz, 1H, Ha-C(1’)), 1.56 (dq, J = 15.0, 7.4 Hz, 1H, Hb-C(1’)), 1.43 (d, J = 6.1 Hz, 3H, H-C(2’’)), 1.26 (d, J = 7.0 Hz, 3H, CH₃-C(4)), 1.07 (d, J = 7.7 Hz, 3H, CH₃-C(6)), 1.06 (d, J = 6.7 Hz, 3H, CH₃-C(2)), 0.85 (t, J = 7.4 Hz, 3H, H-C(2’’)). ¹³C-NMR (CDCl₃, 100.6MHz): 214.2, 142.7, 128.6, 128.0, 126.3, 87.8, 81.0, 79.1, 50.0, 46.3, 33.5, 28.6, 22.7, 16.5, 11.9, 8.5, 6.7; Anal. Calcd. for C₁₉H₂₈O₃ (304.42): C 74.96, H 9.27; found C 74.79, H 9.19; MALDI-HRMS Calcd. for C₁₉H₂₈O₃K⁺ 343.1676; found 343.1665.

NOESYs observed for 5:

![NOESYs observed for 5](image)
(−)-(4S,6S)-4,6-Dimethyl-5-hydroxynonan-3,7-dione (6).

To a solution of enantiomerically enriched, crude 27 (70 mg, 95% purity, 0.176 mmol) in MeOH (2 mL) was added water (0.5 mL) and sat. aq. solution of NH₄Cl (0.2 mL). The suspension so-obtained was heated in a closed ampoule under microwave irradiation (130°C, 5 min.). Reaction mixture was diluted with brine (10 mL) and extracted with CH₂Cl₂ (4 x 10 mL). The combined organic layers were dried (anh. Na₂SO₄) and evaporated in vacuo. FC (hexane/EtOAc=95:5) afforded 22 mg (41%) of 31 and 23 mg (43%) of a mixture of cyclic products. Data for 31: colorless oil, Rf=0.37 (light petroleum ether/EtOAc=9:1); H-NMR (CDCl₃, 400MHz): 7.35-7.25 (m, 5H, arom), 4.50 (q, J = 6.2 Hz, 1H, H-C(1’)), 4.04 (dd, J = 6.8, 4.3 Hz, 1H, H-C(5)), 2.89 (dq, J = 7.4, 6.8 Hz, 1H, H*-C(4)), 2.59 (dq, J = 18.5, 7.4 Hz, 1H, Ha*-C(2)), 2.56 (m, 1H, H*-C(6)), 2.47 (dq, J = 18.5, 7.4 Hz, 1H, Hb*-C(2)), 2.29 (dq, J = 18.5, 7.4 Hz, 1H, Ha*-C(8)), 2.22 (dq, J = 18.5, 7.4 Hz, 1H, Hb*-C(8)), 1.32 (d, J = 6.2 Hz, 3H, H-C(2’)), 1.06 (d, J = 7.4 Hz, 3H, CH₃*-C(4)), 1.05 (t, J = 7.4 Hz, 3H, H*-C(1)), 0.98 (d, J = 7.4 Hz, 3H, CH₃*-C(6)), 0.87 (t, J = 7.4 Hz, 3H, H*-C(9)); C-NMR (CDCl₃, 100.6MHz): 213.9, 213.2, 143.5, 128.4, 127.7, 126.6, 79.3, 77.4, 48.7, 48.0, 36.9, 34.9, 23.7, 23.3, 12.9, 12.2, 7.6; exchangeable assignments; MALDI-HRMS Calcd. for C₁₉H₂₇O₃Na⁺ 327.1936; found 327.1939.

A solution of 31 (22 mg, 0.072 mmol) in methanol (5 mL) containing 10 % Pd/C (5 mg) was stirred under H₂ atmosphere at ambient pressure for 12 h. The suspension was filtered through Cellite and evaporated in vacuo. The residue was filtrated through a small silica gel pad with CH₂Cl₂/MeOH=9:1 and evaporated in vacuo.
Yield 14.5 mg (quant). Colorless oil, R<sub>f</sub>=0.44 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH=95:5); [α]<sup>25</sup><sub>589</sub> = -15.8, (c =0.9, CHCl<sub>3</sub>); ¹H-NMR (CDCl<sub>3</sub>, 400MHz): 4.04 (ddd, J = 8.0, 4.5, 3.8 Hz, 1H, H-C(5)), 3.24 (d, J = 4.5 Hz, 1H, OH), 2.69 (dq, J = 8.0, 7.0 Hz, 1H, H*-C(4)), 2.66 (dq, J = 7.0, 3.8 Hz, 1H, CH<sub>3</sub>*-C(6)), 1.05 (t, J = 7.0 Hz, 3H, H*-C(1)), 1.045 (d, J = 7.0 Hz, 3H, CH<sub>3</sub>*-C(6)), 1.04 (t, J = 7.0 Hz, 3H, H*-C(9)); ¹³C-NMR (CDCl<sub>3</sub>, 100.6MHz): 215.7, 215.6, 73.5, 47.5, 47.3, 36.3, 34.9, 13.9, 10.1, 7.6, 7.4; *- exchangeable assignments; MALDI-HRMS Calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>Na<sup>+</sup> 223.1310; found 223.1309. 

(-)-(1Z,2S,3R,4S)-1-Ethylidene-2,4-dimethyl-5-oxo-3-((1''S)-1-phenylethoxy)-heptyl isobutyrate (11) and (-)-(1Z,2S,3R,4R)-1-ethylidene-2,4-dimethyl-5-oxo-3-((1''S)-1-phenylethoxy)heptyl isobutyrate (12).

The 0.5 M solution of Tf<sub>2</sub>NH in CH<sub>2</sub>Cl<sub>2</sub> (9.3 mL, 4.65 mmol, 0.25 equiv.) was diluted with toluene (40 mL). Sulfur dioxide (40 mL) was condensed at –196 °C. The mixture was stirred at –78 °C for 20 min. The solution of diene 7a (5.36 g, 1.6 mmol, 1 equiv.) and 3-trimethylsilyloxy pent-3-ene (10.8 mL, 55.8 mmol, 3 equiv.) in toluene (6 mL) was added slowly dropwise at –80 °C under vigorous stirring and Ar atmosphere. The reaction mixture was stirred for 36 h at –80 °C. Sulfur dioxide was evaporated at –78 °C (0.1 mbar) for 5 h, then at room temperature for 1 h. The residual solution (~30 mL) was diluted with MeCN (50 mL) and transferred into a suspension of Pd(OAc)<sub>2</sub> (0.45 g, 1.86 mmol, 0.1 eq.), Ph<sub>3</sub>P (0.49 g, 1.86 mmol, 0.1 eq.), K<sub>2</sub>CO<sub>3</sub> (1.60 g, 11.5

mmol, 0.62 eq.) in MeCN (70 mL). Isopropanol (50 mL) was added and the mixture was heated under reflux for 20 min, cooled to 20 °C and partitioned between aq. solution of NaHCO₃ and EtOAc. The aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with aq. solution of NaHCO₃, brine, dried (MgSO₄) and evaporated in vacuo. The residue was purified by FC (light petroleum ether/EtOAc=98/2). Yield 4.66 g (67 %) of 11 and 0.9 g (13 %) of 12. Data for 11: colorless oil; Rₛ=0.4 (PE/EA=9/1); [α]²⁵ₐ₅₈₉ = -18, (c =0.5, CHCl₃); IR (film): 2966, 2879, 1756, 1612, 1460, 1383, 1135; ¹H-NMR (CDCl₃, 400MHz): 7.32-7.24 (m, 5H, arom), 5.21 (q, J = 6.8 Hz, 1H, H-C(1’)), 4.44 (q, J = 6.8 Hz, 1H, H-C(1’’)), 3.77 (t, J = 5.5 Hz, 1H, H-C(3)), 2.69 (dq, J = 5.5, 6.8 Hz, 1H, H-C(2)), 2.64 (m, 2H, H-C(4), (CH₃)₂CHCOO-C(1)), 2.19 (dq, AB-syst, J = 17.9, 7.4 Hz, 1H, H-C(6)), 2.09 (dq, AB-syst, J = 17.9, 7.4 Hz, 1H, Hb-C(6)), 1.45 (dd, J = 6.8, 1.2 Hz, 3H, H-(C2’)), 1.37 (d, J = 7.4 Hz, 3H, H-C(2’’)), 1.22 (d, J = 6.8 Hz, 6H, (CH₃)₂CHCOO-C(1)), 1.10 (d, J = 7.4 Hz, 3H, CH₃-C(2)), 0.99 (d, J = 6.8 Hz, 3H, CH₃-C(4)) 0.82 (t, J = 7.4 Hz, 3H, H-C(7)); ¹³C-NMR (CDCl₃, 100.6MHz): 213.0, 174.1, 149.6, 143.6, 128.3, 127.5, 126.8, 112.5, 76.9, 76.7, 47.8, 40.9, 34.2, 33.9, 23.6, 19.2, 19.1, 13.3, 12.5, 10.9, 7.7; Anal. Calcd. for C₂₃H₃₄O₄ (374.51): C 73.76, H 9.15; found C 73.77, H 9.09; MALDI-HRMS Calcd. for C₂₃H₃₄O₄Na⁺ 397.2355; found 397.2345.

Data for 12: colorless oil; Rₛ=0.45 (PE/EA=9/1); [α]²⁵ₐ₅₈₉ = -46, (c = 1.7, CHCl₃); IR (film): 2973, 2936, 2877, 1746, 1715, 1455, 1373, 1238, 1140, 1082; ¹H-NMR (CDCl₃, 400MHz): 7.33-7.18 (m, 5H, arom), 5.21 (dq, J = 6.8, 1.2 Hz, 1H, H-C(1’)), 4.40 (q, J = 6.8 Hz, 1H, H-C(1’’)), 3.60 (dd, J = 8.0, 4.3 Hz, 1H, H-C(3)), 2.84-2.79 (m, 1H, H-C(2)), 2.77 (quint, J = 7.4 Hz, 1H, H-C(4)), 2.56 (sept., J = 6.8 Hz, 1H, (CH₃)₂CHCOO-C(1)), 2.41 (dq, AB-syst, J = 17.8, 7.4 Hz, 1H, Ha-C(6)), 2.28 (dq,
AB-syst, $J = 17.8$, 7.4 Hz, 1H, Hb-C(6)), 1.46 (dd, $J = 6.8$, 1.2 Hz, 3H, H-(C2’)), 1.34 (d, $J = 6.2$ Hz, 3H, H-C(2’)), 1.17 (d, $J = 6.8$ Hz, 6H, (CH$_3$)$_2$CHCOO-C(1)), 1.13 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(2)), 0.90 (t, $J = 7.4$ Hz, 3H, H-C(7)), 0.88 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(4)); $^{13}$C-NMR (CDCl$_3$, 100.6MHz): 213.9, 174.5, 149.9, 143.3, 128.3, 127.5, 126.6, 111.5, 79.2, 76.4, 47.8, 38.7, 36.4, 40.9, 34.2, 24.1, 19.0, 13.6, 12.3, 7.5 ; Anal. Calcd. for C$_{23}$H$_{34}$O$_4$ (374.51): C 73.76, H 9.15; found C 73.80, H 9.05; MALDI-HRMS Calcd. for C$_{23}$H$_{34}$O$_4$Na$^+$ 397.2355; found 397.2359.

(+)-(1Z,2S,3R,4S)-1-Ethylidene-2,4-dimethyl-5-oxo-3-hydroxyhept-1-yl isobutyrate (13).

A solution of 11 (0.163 g, 0.435 mmol, 1 equiv) in CH$_2$Cl$_2$ (1 mL) was added at –78 °C to a TiCl$_4$ (1M in CH$_2$Cl$_2$, 0.87 mL, 0.87 mmol, 2 equiv.) solution in CH$_2$Cl$_2$ (45 mL). The reaction mixture was stirred at –78 °C for 2 h and then poured into sat. aq. NaHCO$_3$. The aqueous phase was extracted with CH$_2$Cl$_2$ (4 x 10 mL). The combined organic layers were washed with brine, dried (anh. Na$_2$SO$_4$) and evaporated in vacuo. FC (light petroleum ether/EtOAc=85:15) afforded 97 mg (82%) of 13, colorless oil, $R_f$=0.18 (light petroleum ether/EtOAc=9:1); $[a]^25_{	ext{D}}$ = +19, (c =0.6, CHCl$_3$); IR (film): 3507, 2973, 2938, 2878, 1731, 1715, 1462, 1385, 1385, 1245, 1148, 1063; $^1$H-NMR (CDCl$_3$, 400MHz): 5.29 (q, $J = 7.0$ Hz, 1H, H-C(1’)), 3.70 (dt, $J = 9.6$, 3.2 Hz, 1H, H-C(3)), 3.16 (d, $J = 3.2$ Hz, 1H, OH), 2.75 (sept, $J = 7.0$ Hz, 1H, (CH$_3$)$_2$CHCOO-C(1)), 2.54 (m, 3H, H-C(6), H-C(2)), 2.38 (dq, $J = 9.0$, 7.0 Hz, 1H, H-C(4)), 1.47 (d, $J = 7.0$ Hz, H-C(2’)), 1.29, 1.28 (2d, $J = 7.0$ Hz, 6H, (CH$_3$)$_2$CHCOO-C(1)), 1.13 (d, $J = 7.0$ Hz, 3H, CH$_3$-C(2)), 1.05 (t, d, $J = 7.0$ Hz, H-C(7)), 1.01 (d, $J = 7.0$ Hz, 3H, CH$_3$-
C(4)); $^{13}$C-NMR (CDCl$_3$, 100.6MHz): 213.9, 176.2, 148.6, 114.6, 71.9, 47.8, 43.6, 34.2, 33.7, 19.3, 19.2, 14.6, 10.9, 8.6, 7.8; Anal. Calcd. for C$_{15}$H$_{26}$O$_4$ (270.40): C 66.64, H 9.69; found C 66.66, H 9.73; MALDI-HRMS Calcd. for C$_{15}$H$_{26}$O$_4$Na$^+$ 293.1729, found 293.1765.

(-)-(2$^S$,3$^S$,4$^S$,5$^S$,6$^S$)-3-Ethyl-3-hydroxy-2,4,6-trimethyl-3-((1''$S$)-1''-phenylethoxy)cyclohexan-1-one (16).

A mixture of 11 (0.16 g, 0.43 mmol, 1 equiv.) and tributyltin methoxide (0.49 mL, 1.71 mmol, 4 equiv.) was heated to +70 °C for 12 h under vacuum (0.1 Torr). The reaction mixture was diluted with ether (30 mL) and poured into a sat. aq. solution of KF (30 mL). After stirring at 20 °C for 1 h, the layers were separated and the aqueous phase was extracted with ether (3 x 10 mL). The combined organic layer was washed with aq. NaCl, dried (Na$_2$SO$_4$) and evaporated in vacuo. The residue was purified by FC (light petroleum ether/EtOAc=9:1) providing 0.112 g (86 %) of 16, colorless oil; $R_f=0.14$ (light petroleum ether/EtOAc=9:1); $[a]_{589}^{25} = -75$, (c = 1.05, CHCl$_3$); IR (film): 3405, 2984, 1713, 1695, 1455; $^1$H-NMR (CDCl$_3$, 400MHz): 7.35-7.24 (m, 5H, arom), 4.44 (q, $J = 6.8$ Hz, 1H, H-C(1'')), 3.46 (dd, $J = 9.9$, 5.6 Hz, 1H, H-C(5)), 3.03 (dq, $J = 7.4$, 5.5 Hz, 1H, H-C(6)), 2.78 (q, $J = 6.8$ Hz, 1H, H-C(2)), 2.13 (dq, $J = 9.9$, 6.8 Hz, 1H, H-C(4)), 1.60 (dq, $J = 14.2$, 7.4 Hz, 1H, Ha-C(1'')), 1.47 (d, $J = 6.2$ Hz, 3H, H-C(2'')), 1.46 (dq, $J = 14.2$, 7.4 Hz, 1H, Hb-C(1'')), 1.24 (d, $J = 7.4$ Hz, 3H, CH$_3$-C(6)), 0.98 (d, $J = 6.9$ Hz, 3H, CH$_3$-C(2)), 0.93 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(4)), 0.83 (t, $J = 7.4$ Hz, 3H, H-C(2')); $^{13}$C-NMR (CDCl$_3$, 100.6MHz): 213.8, 143.1, 128.5, 127.8,
To the solution of diol 1 (10 mg, 0.05 mmol) in abs. pyridine (1.0 mL) was added (-)-camphanic chloride (22 mg, 0.10 mmol, 2 equiv.) at –20 °C. The mixture was allowed to reach + 20°C and was stirred for 3 more h. It was diluted with Et₂O (40 mL), washed with aq. sat. solution of CuSO₄ (4 x 10 mL), water (10 mL), aq. sat. solution of NaHCO₃ (3 x 10 mL), dried over (Na₂SO₄) and evaporated. FC (CH₂Cl₂/MeOH=97:3) afforded 19 mg of 17(quant). Crystals for X-ray diffraction studies were obtained by crystallization from pentane/CH₂Cl₂ (mp. 158 °C). White crystals [α]_25^25 = -11, (c = 0.16, CHCl₃); IR (KBr): 3472, 2969, 2950, 1769, 1715, 1652, 1558, 1457, 1396, 1272, 1167, 1103; ¹H-NMR (CDCl₃, 400MHz): 5.22 (dd, J = 8.3, 5.2 Hz, 1H, H-C(5')), 3.09 (dq, J = 7.0, 5.2 Hz, 1H, H-C(6')), 2.71 (q, J = 7.1, Hz, 1H, H-C(2')), 2.41 (ddd, J = 13.6, 10.5, 4.3 Hz, 1H, Ha-C(6)), 2.29 (dq, J = 8.3, 6.8 Hz, 1H, H-C(4')), 2.03 (ddd, J = 13.7, 9.6, 4.6 Hz, Hb-C(6)), 1.99-1.91 (m, 1H, Ha-C(5)), 1.77-1.69 (m, 1H, Hb-C(5)), 1.70 (dq, J = 15.1, 7.5 Hz, 1H, Ha-C(1'')), 1.55 (dq, J = 15.1, 7.5 Hz, 1H, Hb-C(1'')), 1.16 (d, J = 7.1 Hz, 3H, CH₃-C(2')), 1.13, 1.08 (2s, 6H, 2xCH₃-C(7)), 1.07 (2d, J = 7.0 Hz, 6H, CH₃-C(4')), CH₃-C(6')), 1.00 (s,
3H, CH$_3$-C(4)), 0.89 (t, $J = 7.5$ Hz, 3H, H-C(2’’)); $^{13}$C-NMR (CDCl$_3$, 100.6MHz): 211.4, 178.3, 166.9, 91.1, 78.5, 76.9, 54.9, 54.2, 45.9, 45.8, 37.1, 31.1, 30.8, 29.0, 16.9, 16.8, 12.5, 11.2, 9.8, 8.8, 7.3; Anal. Calcd. for C$_{21}$H$_{32}$O$_6$ (380.48): C 66.29, H 8.48; found C 66.20, H 8.31; MALDI-HRMS Calcd. for C$_{21}$H$_{32}$O$_6$Na$^+$ 403.2097; found 403.2091.

X-ray structure of 17$^5$:

(-)-(1$R$,2$R$,3$R$,4$R$,5$R$,6$R$)-1-Ethyl-2,4,6-trimethyl-5-((1’’$S$)-1’’-phenylethoxy) cyclohexane-1,3-diol (19).

12 $\rightarrow$ 18: Same procedure as for synthesis of 16 using 12 instead of 11. Yield of 18: 84%. Data for 18: colorless oil; $R_f$=0.38 (light petroleum ether/EtOAc=8:2); $^1$H-NMR (CDCl$_3$, 400MHz): 7.35-7.25 (m, 5H, arom), 4.46 (q, $J = 6.4$ Hz, 1H, H-C(1’’)), 3.90 (dd, $J = 6.4$, 5.1 Hz, 1H, H-C(5)), 2.95 (dq, $J =7.0$, 6.4 Hz, 1H, H-C(6)), 2.85 (q, $J =$

$^5$ Crystallographic data for 17 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-245648.
7.0 Hz, 1H, H-C(2)), 2.11 (dq, $J = 7.0$, 5.1 Hz, 1H, H-C(4)), 1.68-1.55 (m, 2H, H-C(1′)), 1.44 (d, $J = 6.4$ Hz, 3H, H-C(2′′)), 1.29 (d, $J = 7.0$ Hz, 3H, CH₃-C(6)), 1.03 (d, $J = 7.0$ Hz, 3H, CH₃-C(2)), 1.02 (d, $J = 7.0$ Hz, 3H, CH₃-C(4)), 0.85 (t, $J = 7.5$ Hz, 3H, H-C(2′)). Anal. Calcd. for C₁₉H₂₈O₃ (304.42): C 74.96, H 9.27; found C 74.64, H 9.41; MALDI-HRMS Calcd. for C₁₉H₂₈O₃Na⁺ 327.1936; found 327.1972.

To a solution of 18 (0.21 g, 0.69 mmol, 1 equiv.) in THF (5 mL) was added solution of L-selectride in THF (1M, 2.8 mL, 2.76 mmol, 4 equiv.) at –78 °C. The reaction mixture was stirred for 24 h at –78 °C and quenched by sequential addition of MeOH (3 mL), sat. aq. solution of NaHCO₃ (18 mL) and 30% aq. H₂O₂ (6 mL). The formed suspension was stirred at 0 °C for 3 h. The excess of H₂O₂ was decomposed by a sat. aq. solution of Na₂S₂O₃. The aqueous phase was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with sat. aq. solution of Na₂S₂O₃, brine, dried (Na₂SO₄) and evaporated. FC (CH₂Cl₂/EtOAc=9:1) provided 0.17 g (80 %) of 19. Crystals for X-ray diffraction were obtained by crystallization from pentane (mp. 110 °C). White crystals, Rf=0.27 (CH₂Cl₂/EtOAc=9:1); [α]_25^25 = -77, (c = 0.1, CHCl₃);

IR (KBr): 3261, 2970, 2912, 1454, 1383, 1283, 1103, 1088; $^1$H-NMR (CDCl₃, 400MHz, 333K): 7.38-7.30, 7.27-7.22 (2m, 5H, arom), 4.58 (q, $J = 6.8$ Hz, 1H, H-C(1′′)), 3.48 (t, $J = 5.1$ Hz, 1H, H-C(5)), 3.66 (bs, 1H, H-C(3)), 2.94 (bs, 1H, OH), 2.43-2.36 (m, 1H, H-C(4)), 2.05 (bs, 1H, OH), 1.96 (dq, $J = 7.7$, 5.6 Hz, 1H, H-C(6)), 1.87 (dq, $J = 7.1$, 3.1 Hz, H-C(2)), 1.66 (dq, $J = 14.8$, 7.4 Hz, 1H, Ha-C(1′)), 1.47 (d, $J = 6.2$ Hz, 3H, H-C(2′′)), 1.39 (dq, $J = 14.8$, 7.4 Hz, 1H, Hb-C(1′)), 1.10 (d, $J = 6.8$ Hz, 3H, CH₃-C(4)), 1.08 (d, $J = 7.4$ Hz, 3H, CH₃-C(2)), 0.90 (d, $J = 7.4$ Hz, 3H, CH₃-C(6)), 0.82 (t, $J = 7.4$ Hz, 3H, H-C(2′)); $^{13}$C-NMR (CDCl₃, 100.6 MHz, 333K): 145.2, 128.3, 127.3, 126.4, 82.9, 79.5, 75.4, 72.1, 41.6, 40.4, 32.7, 29.5, 24.3, 13.6, 11.6,
11.2, 5.8. Anal. Calcd. for C_{19}H_{30}O_{3} (306.44): C 74.47, H 9.87; found C 74.67, H 10.00; MALDI-HRMS Calcd. for C_{19}H_{30}O_{3}Na^{+} 329.2093; found 329.2098.

**Mosher’s esters of 19:**

Same procedure as for preparing Mosher’s esters from 1, using 19 as starting material.

**(R)-MTPA ester 19A:** IR (film): 3423, 2954, 2925, 2853, 1736, 1652, 1634, 1558, 1458, 1378, 1261; \(^1\)H-NMR (CDCl\(_3\), 400MHz, 333 K): 7.57-7.55 (m, 2H, arom), 7.42-7.40 (m, 3H, arom), 7.32-7.23 (m, 5H, arom), 5.16 (dd, \(J = 6.2, 3.7\) Hz, 1H, H-C(1)), 4.38 (q, \(J = 6.2\) Hz, 1H, H-C(1’’)), 3.62 (t, \(J = 4.3\) Hz, 1H, H-C(5)), 3.52 (s, 3H, CH\(_3\)O-C(2’)); 19F-NMR (CDCl\(_3\)+CCl\(_3\)F, 376.7 MHz, 333 K): -71.48 (s, CF\(_3\)-C(2’)); MALDI-HRMS Calcd. for C\(_{29}\)H\(_{37}\)F\(_3\)O\(_5\)Na\(^+\) 545.2491; found 545.2498.

**(S)-MTPA ester 19B:** IR (film): 3444, 2956, 2924, 2853, 1743, 1652, 1558, 1456, 1377, 1260; \(^1\)H-NMR (CDCl\(_3\), 400MHz, 333 K): 7.55-7.53 (m, 2H, arom), 7.40-7.38 (m, 3H, arom), 7.35-7.25 (m, 5H, arom), 5.10 (dd, \(J = 6.8, 3.7\) Hz, 1H, H-C(1)), 4.48 (q, \(J = 6.2\) Hz, 1H, H-C(1’’)), 3.74 (t, \(J = 4.3\) Hz, 1H, H-C(5)), 3.46 (s, 3H, CH\(_3\)O-C(2’)); 19F-NMR (CDCl\(_3\)+CCl\(_3\)F, 376.7 MHz, 333 K): -71.48 (s, CF\(_3\)-C(2’)); MALDI-HRMS Calcd. for C\(_{29}\)H\(_{37}\)F\(_3\)O\(_5\)Na\(^+\) 545.2491; found 545.2498.
H-C(2′′)), 0.76 (d, J = 7.4 Hz, 3H, CH₃-C(4)), 0.75 (d, J = 6.8 Hz, 3H, CH₃-C(6));

¹⁹F-NMR (CDCl₃+CCl₃F, 376.7 MHz, 333 K): -71.48 (s, CF₃-C(2′)); MALDI-HRMS
Calcd. for C₂₉H₃₇F₃O₅Na⁺ 545.2491; found 545.2409.

Signals of 19A and 19B in ¹⁹F-NMR spectrum were superposed; therefore MeO-
signals in the ¹H-NMR spectrum were used for the determination of the ee.

A part of ¹H-NMR spectrum of 19A and 19B: ee: 97%

X-ray structure of 19:

Crystallographic data for 19 have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-245522.
To a solution of 11 (4.0 g, 10.7 mmol, 1 equiv.) in CH$_2$Cl$_2$ (60 mL) at −20 °C was added NEt$_3$ (3.0 mL, 21.4 mmol, 2 equiv.) followed by TESOTf (2.9 mL, 12.8 mmol, 1.2 equiv.). The reaction mixture was allowed to reach + 20 °C in 2 h. Cold pentane (300 mL (-50 °C)) was added and the resulting suspension was filtered through a small silica gel pad (suspended in pentane containing 2 % of NEt$_3$). The organic phase was sequentially washed with 15 % aq. solution of citric acid (3 x 70 mL), sat. aq. solution of NaHCO$_3$ (3 x 50 mL), brine (2 x 50 mL), dried (anh. Na$_2$SO$_4$) and evaporated in vacuo. The resulted oil was dried under reduced pressure (0.06 Torr, 24 h). Yield 5.23 g (quant.), colorless oil. $^1$H-NMR (CDCl$_3$, 400MHz): 7.33-7.18 (m, 5H, arom), 5.23 (q, $J = 6.8$ Hz, 1H, H-C(1’)), 4.50 (q, $J = 6.8$ Hz, 1H, H-C(1’’)), 4.33 (q, $J = 7.4$ Hz, 1H, H-C(6)), 3.77 (dd, $J = 8.0$, 3.7 Hz, 1H, H-C(3)), 2.71 (sept, $J = 7.4$ Hz, 1H, (CH$_3$)$_2$CHCOO-C(1)), 2.60 (quint, $J = 7.4$ Hz, 1H, H-C(2)), 1.47 (d, $J = 6.8$ Hz, 3H, H-C(2’’)), 1.34 (dd, $J = 6.8$, 1.2 Hz, 3H, H-C(2’)), 1.31-1.28 (m, 9H, H-C(7), (CH$_3$)$_2$CHCOO-C(1)), 1.04 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(2)), 0.98 (t, $J = 8.0$ Hz, 9H, TES), 0.91 (d, $J = 6.8$ Hz, 3H, CH$_3$-C(4)), 0.62 (q, $J = 8.0$ Hz, 6H, TES); $^{13}$C-NMR (CDCl$_3$, 100.6MHz): 174.7, 152.8, 149.9, 145.2, 127.8, 126.8, 126.3, 111.9, 102.4, 77.4, 76.9, 42.1, 41.1, 34.3, 23.2, 19.3, 14.3, 11.8, 11.0, 6.9, 6.5, 5.7; MALDI-HRMS Calcd. for C$_{29}$H$_{48}$O$_4$SiNa$^+$ 511.3220; found 511.3225.
(7Z,4S,5S,6S)-4,6-Dimethyl-5-((1'S,1-phenylethoxy)-7-((triethylsilyl)oxy) non-7-en-3-one (27).

Solution of crude 26 (1.0 g, 2.0 mmol, 1 equiv.) in Et₂O (8 mL) was added at −78 °C to a solution of MeLiLiBr (2 M, 4.0 mL, 8.0 mmol, 4 equiv.) in Et₂O (8 mL). The reaction mixture was stirred at −78 °C overnight and afterwards poured slowly into sat. aq. solution of NH₄Cl (50 mL). The aqueous phase was extracted with Et₂O (3 x 20 mL), washed brine, dried (anh. Na₂SO₄) and evaporated in vacuo. The resulting oil was dried under reduced pressure (0.06 Torr, 24 h) and used without further purification. Yield 0.77 g (90%), colorless oil, Rf=0.49 (light petroleum ether/EtOAc=95:5); ¹H-NMR (CDCl₃, 400MHz): 7.33-7.18 (m, 5H, arom), 4.48 (q, J = 6.4 Hz, 1H, H-C(1')), 4.31 (dq, J = 6.4, 1.3 Hz, 1H, H-C(8)), 3.77 (dd, J = 9.0, 3.2 Hz, 1H, H-C(5)), 2.89 (dq, J = 9.0, 7.0 Hz, 1H, H-C(6)), 2.69 (dq, J = 18.6, 7.0 Hz, 1H, Ha-C(2)), 2.50 (dq, J = 18.6, 7.0 Hz, 1H, Hb-C(2)), 2.15 (m, 1H, H-C(4)), 1.32 (dd, J = 6.4, 1.3 Hz, 3H, H-C(9)), 1.16 (d, J = 7.0 Hz, 3H, H-C(2'))), 1.06 (t, J = 7.0 Hz, 3H, H-C(1)), 1.00 (d, J = 7.0 Hz, 3H, CH₃-C(6)), 0.99 (t, J = 8.3 Hz, 9H, TES), 0.91 (d, J = 7.0 Hz, 3H, CH₃-C(4)), 0.66 (q, J = 8.3 Hz, 6H, TES); ¹³C-NMR (CDCl₃, 100.6MHz): 214.9, 152.2, 145.4, 127.9, 126.6, 125.9, 103.0, 79.1, 77.3, 48.3, 41.4, 38.0, 22.8, 13.9, 11.3, 11.1, 7.5, 7.0, 6.5; MALDI-HRMS Calcd. for C₂₅H₄₂O₃SiNa⁺ 441.2801; found 441.2809.

Synthesis of $11^7$, was complete starting from advanced intermediate $6$ as shown in the Scheme bellow:

![Scheme 3](image)

The relative configuration of $8$ was assigned by NOE experiments and coupling constant analysis as follows:

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The relative configuration of 10 was not discussed neither in the text of the publication, nor in supporting information.

Moreover, last step in the sequence (10 → 11) was carried out as follows:

\[(2R^*, 3R^*, 4R^*, 5R^*, 6R^*)-3-(ethyl)-3',5-(dihydroxy)-2,4,6-trimethylcyclohexan-1-one, 11.\] To a solution of 10 (9 mg, 0.04 mmol) in CH\(_3\)CN (1 ml) at rt were added NaI (1 mg, 0.007 mmol) and CeCl\(_3\) ⋅ 7H\(_2\)O (27.9 mg, 0.07 mmol). The reaction was warmed to 65°C and stirred for 3h. After cooling to rt, the mixture was quenched with a 0.5N HCl solution. The aqueous layer was extracted with ether and dried over MgSO\(_4\). After removal of the solvent in vacuo, purification by chromatography eluting with hexanes/ethyl acetate (2:1) gave 6.4 mg of 11 (87%) as a colorless oil. \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.90 (t, 3 H, \(J = 5.0\) Hz), 0.98 (d, 3 H, \(J = 4.2\) Hz),

Under the above conditions, isomerization at positions α to the carbonyl function are possible. Any proofs related to the relative configuration of 11 are missing.

When 1\(^8\) (page 3 of this Supp. Inform.) prepared according to our method was submitted to identical conditions (CeCl\(_3\) ⋅ 7H\(_2\)O / NaI / MeCN / 65 °C / 3h) 1 was completely transformed into undefined products, including products of degradation.

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\(^8\) Numeration corresponds to this report.