Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereocontrolled syntheses of (–)- and (+)-γ-diisoeugenol along with optically active eight stereoisomers of 7,8'-epoxy-8,7'-neolignan

Tatsuaki Takubo, Nao Kikuchi, Hisashi Nishiwaki, Satoshi Yamauchi*

Graduate School of Agriculture, Ehime University, 3-5-7 Tarumi,

Matsuyama, Ehime 790-8566, Japan

Supporting information
Experiment for the syntheses of diol **7**-**13** and 3-*epi*-**13**.

Experimental

General experimental procedures

Melting points (mp) data are uncorrected. Optical rotations were measured on a JASCO P-2100 instrument. NMR data were obtained using a JNM-EX400 spectrometer. EI and FABMS data were measured with a JMS-MS700V spectrometer. The silica gel used was Silica Gel 60N (spherical, neutral, Kanto Chemical, 40-50 μm). The numbering of compounds follows IUPAC rule.

(4*S*)-4-Benzyl-3-[(2*R*,3*S*)-3-(4-benzyloxy-3-methoxyphenyl)-3-hydroxy-2-methylpropanoyl]-2-oxazolidinone 7. A reaction mixture of (*S*)-4-benzyl-3-propanoyl-2-oxazolidinone (18.0 g, 77.2 mmol), $MgCl_2$ (0.74 g, 7.77 mmol), 4-benzyloxy-3-methoxybenzaldhyde (22.4 g, 92.5 mmol), Et_3N (21.5 mL, 0.15 mol), and TMSCl (14.7 mL, 0.12 mol) in EtOAc (50 mL) was stirred at room temperature for 16 h before filtration through silica gel with ether. After concentration of the filtrate, the residue was dissolved in MeOH. To this MeOH solution was added CF_3CO_2H (5 mL), and then the reaction mixture was stirred at room temperature for 5 h. The resulting crystals were filtered and recrystallized from EtOH to give oxazolidinone **7** (25.1 g, 52.8 mmol, 68%) as colorless crystals, mp 151-152 ^{o}C, $[\alpha]^{25}_{D}$ –19 (*c* 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, d, J = 6.8 Hz, CH_3), 2.66 (1H, dd, J = 13.5, 9.4 Hz,

C*H*HPh), 3.10 (1H, d, *J* = 7.5 Hz, O*H*), 3.19 (1H, dd, *J* = 13.5, 3.2 Hz, CH*H*Ph), 3.90 (3H, s, OCH_3), 4.12 (1H, dd, *J* = 9.0, 2.8 Hz, 5-*H*H), 4.16 (1H, dd, *J* = 9.0, 7.6 Hz, 5-H*H*), 4.33 (1H, m, O=C-C*H*-CH_3), 4.67 (1H, m, 4-*H*), 4.74 (1H, dd, *J* = 7.6, 7.5 Hz, ArC*H*OH), 5.13 (2H, s, OCH_2Ph), 6.84 (1H, d, *J* = 8.2 Hz), 6.87 (1H, dd, *J* = 8.2, 1.5 Hz), 7.01 (1H, d, *J* =1.5 Hz), 7.15 (2H, d, *J* = 6.8 Hz), 7.23-7.35 (6H, m), 7.41 (2H, d, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8 (*C*H_3), 37.5 (O=C-*C*-Me), 44.1 (*C*H_2Ph), 55.4 (4-*C*), 55.9 (O*C*H_3), 65.9 (5-*C*), 70.9 (O*C*H_2Ph), 77.2 (Ar*C*OH), 109.9, 113.5, 118.8, 127.1, 127.2, 127.7, 128.4, 128.8, 129.4, 135.1, 135.2, 137.0, 147.8, 149.7, 153.5 (2-*C*), 176.5 (N-(*C*=O)-CCH_3). FABMS 476 $(M+H)^+$. *Anal*. Found: C 70.75%, H 6.44%, N 2.84%; Calcd for $C_{28}H_{29}O_6N$: C 70.72%, H 6.15%, N 2.95%.

ent-**7**. $[\alpha]^{25}_D$ +19 (*c* 0.7, $CHCl_3$), colorless crystals, mp 151-152 ^oC (MeOH).

(4*S*)-4-Benzyl-3-[(2*R*,3*S*)-3-(4-benzyloxy-3-methoxyphenyl)-2-methyl-3-(triisopropylsilyloxy)propanoyl]-2-oxazolidinone 8. To an ice-cooled solution of benzyl alcohol **7** (13.2 g, 27.8 mmol) and 2,6-lutidine (7.80 mL, 67.3 mol) in CH_2Cl_2 (20 mL) was added TIPSOTf (8.97 mL, 33.4 mmol). After the reaction solution was stirred at room temperature for 1 h, sat. aq. $NaHCO_3$ was added. The organic solution was separated, washed with sat. aq. $CuSO_4$ and sat. aq. $NaHCO_3$, dried (Na_2SO_4), and concentrated. The residue was recrystallized from *iso*-Pr_2O

to give silyl ether **8** (16.3 g, 25.8 mmol, 93%) as colorless crystals, mp 93-94 °C; $[\alpha]^{25}_{D}$ –54 (*c* 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38-0.99 (21H, m, TIPS), 0.86 (3H, d, *J* = 7.0 Hz, CH_3), 2.64 (1H, dd, *J* = 13.2, 10.8 Hz, 4-C*H*HPh), 3.52 (1H, dd, *J* = 13.2, 3.2 Hz, 4-CH*H*Ph), 3.90 (3H, s, OCH_3), 4.13 (2H, d, *J* = 5.2 Hz, 5-CH_2), 4.32 (1H, m, O=C-C*H*-CH_3), 4.65 (1H, m, 4-H), 5.04 (1H, d, *J* = 8.8 Hz, ArC*H*OTIPS), 5.13 (2H, s, OCH_2Ph), 6.80 (2H, d, *J* = 0.8 Hz), 7.06 (1H, s), 7.24-7.29 (4H, m), 7.32-7.36 (4H, m), 7.42-7.43 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6 (TIPS), 14.6 (CH_3), 18.0 (TIPS), 18.1 (TIPS), 38.3 (O=C-*C*-Me), 46.2 (4-C), 55.8 (OCH_3), 56.0 (4-C), 65.9 (5-C), 71.1 (OCH_2Ph), 77.6 (ArCOH), 111.0, 113.4, 120.2, 127.3, 127.4, 127.8, 128.5, 129.0, 129.3, 135.7, 135.9, 137.1, 147.9, 149.7, 153.3 (2-C), 175.8 (N-(*C*=O)-CCH_3); FABMS 632 $(M+H)^+$. *Anal*. Found: C 70.31%, H 8.07%, N 2.06%; Calcd for $C_{37}H_{49}O_6NSi$: C70.33%, H 7.82%, N2.22%.

ent-**8**. $[\alpha]^{25}_{D}$ +53 (*c* 0.8, $CHCl_3$), colorless crystals, mp 96-98 °C (*iso*-Pr_2O)

(2*S*,3*S*)-3-(4-Benzyloxy-3-methoxyphenyl)-2-methyl-3-(triisopropylsilyloxy)-1-propanol 9. To a solution of oxazolidinone **8** (16.3 g, 25.7 mmol) and MeOH (8 mL) in THF (50 mL) was added a suspension of $LiBH_4$ (0.16 mol) in THF (100 mL). After stirring at room temperature for 1 h, sat. aq. NH_4Cl was added. The organic solution was separated and dried (Na_2SO_4). Concentration followed by silica gel

column chromatography (5% EtOAc/toluene) gave alcohol **9** (11.2 g, 24.4 mmol, 95%) as a colorless oil, $[\alpha]^{25}_{D}$ –86 (*c* 0.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (3H, d, *J* = 7.0 Hz, CH_3), 0.95-1.01 (21H, m, TIPS), 2.00 (1H, m, OH), 2.70 (1H, m, 2-H), 3.62 (2H, br s, 1-H), 3.87 (3H, s, OCH_3), 4.70 (1H, d, *J* = 6.8 Hz, 3-H), 5.13 (2H, s, OCH_2Ph), 6.73 (1H, dd, *J* = 8.2, 1.8 Hz), 6.80 (1H, d, *J* = 8.2 Hz), 6.94 (1H, d, *J* = 1.8 Hz), 7.30 (1H, m), 7.35 (2H, dd, *J* = 8.0, 7.3 Hz), 7.43 (2H, br d, *J* = 7.3Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5 (TIPS), 13.4 (CH_3), 17.9 (TIPS), 18.1 (TIPS), 43.7 (2-C), 55.9 (OCH_3), 66.4 (1-C), 71.1 (OCH_2Ph), 79.8 (3-C), 110.6, 113.4, 119.4, 127.4, 127.8, 128.5, 136.7, 137.2, 147.4, 149.4. FABMS 459 (M^++H). *Anal*. Found: C 70.83%, H 9.33%; Calcd for $C_{27}H_{42}O_4Si$: C 70.70%, H 9.23%.

ent-**9**. colorless oil, $[\alpha]^{25}_{D}$ +84 (*c* 0.9, $CHCl_3$)

(2*R*,3*S*)-3-(4-Benzyloxy-3-methoxyphenyl)-2-methyl-3-(triisopropylsilyloxy)propanal 10. A reaction mixture of alcohol **9** (6.43 g, 14.0 mmol), PCC (3.60 g, 16.7 mmol), and MS 4A (1 g) in CH_2Cl_2 (80 mL) was stirred at 0 ^{o}C for 16 h before addition of ether. After filtration, the filtrate was concentrated. The residue was applied to silica gel column chromatography (10% EtOAc/hexane) to give aldehyde **10** (4.45 g, 9.74 mmol, 70%) as a colorless oil, $[\alpha]^{25}_{D}$ –66 (*c* 2.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, d, *J* = 6.9 Hz, CH_3), 0.93-1.04 (21H, m, TIPS), 2.73 (1H, m, 2-CH), 3.88 (3H, s, OCH_3), 4.92 (1H, d, *J* = 7.5 Hz, 3-

CH), 5.13 (2H, s, OCH_2Ph), 6.72 (1H, dd, J = 8.2, 1.9 Hz), 6.81 (1H, d, J = 8.2 Hz), 6.92 (1H, d, J = 1.9 Hz), 7.29 (1H, m), 7.36 (2H, dd, J = 7.5, 7.1 Hz), 7.43 (2H, d, J = 7.1 Hz), 9.82 (1H, d, J = 2.7 Hz, CHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5 (CH_3), 12.4 (TIPS), 17.9 (TIPS), 18.0 (TIPS), 55.1 (2-C), 55.9 (OCH_3), 71.0 (OCH_2Ph), 76.3 (3-C), 110.1, 113.3, 119.2, 127.3, 127.8, 128.5, 135.4, 137.0, 147.7, 149.5, 204.5 (CHO); FABMS 457 $(M+H)^+$. *Anal*. Found: C 71.22%, H 8.95%; Calcd for $C_{27}H_{40}O_4Si$: C 71.01%, H 8.83%.

ent-**10**. colorless oil, $[\alpha]^{25}_D$ +67 (*c* 1.1, $CHCl_3$)

(3*R*,4*S*,5*S*)-5-(4-Benzyloxy-3-methoxyphenyl)-4-methyl-5-triisopropylsilyloxy-1-penten-3-ol 11 and (3*S*,4*S*,5*S*)-5-(4-benzyloxy-3-methoxyphenyl)-4-methyl-5-triisopropylsilyloxy-1-penten-3-ol 3-*epi*-**11**. To an ice-cooled solution of vinylmagnesium bromide (17.5 mL, 1 M in THF, 17.5 mmol) in THF (20 mL) was added a solution of aldehyde **10** (4.00 g, 8.76 mmol) in THF (10 mL). The reaction solution was stirred at room temperature for 1 h before additions of sat. aq. NH_4Cl and EtOAc. The organic solution was separated, dried (Na_2SO_4), and concentrated. The residue was applied to silica gel column chromatography (EtOAc/hexane = 1/8) to give allyl alcohol 3-*epi*-**11** (0.61 g, 1.26 mmol, 14%) as a colorless oil and **11** (2.06 g, 4.25 mmol, 49%) as a colorless oil. 3-*epi*-**11**: $[\alpha]^{25}_D$ –31 (*c* 1.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (3H, d, J = 7.1 Hz, CH_3), 0.87-1.10 (21H, m, TIPS), 1.70 (1H, br. s, OH),

2.05 (1H, m, 4-H), 3.89 (3H, s, OCH_3), 4.80 (1H, m, 3-H), 4.92 (1H, d, J = 3.6 Hz, 5-H), 5.07-5.16 (2H, overlapped, 1-CH_2), 5.14 (2H, s, OCH_2Ph), 5.77 (1H, ddd, J = 17.1, 10.1, 7.1 Hz, 2-CH), 6.76 (1H, dd, J = 8.2, 1.8 Hz), 6.84 (1H, d, J = 8.2 Hz), 7.04 (1H, d, J = 1.8 Hz), 7.30 (1H, m), 7.36 (2H, dd, J = 7.0, 7.0 Hz), 7.44 (2H, d, J = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.1 (TIPS), 13.8 (CH_3), 17.9 (TIPS), 44.5 (4-C), 56.0 (OCH_3), 71.0 (OCH_2Ph), 75.2 (3-C), 80.3 (5-C), 111.1, 113.1, 116.1 (1-C), 119.8, 127.4, 127.8, 128.4, 133.5 (2-C), 137.1, 139.8, 147.4, 149.1. FABMS: 485 $(M+H)^+$. HRMS (FAB): calculated $C_{29}H_{45}O_4Si$: 485.3086, found: 485.3083. **11**: $[\alpha]^{25}_D$ –39 (*c* 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, d, J = 7.2 Hz, CH_3), 0.95-1.02 (21H, m, TIPS), 1.79 (1H, m, 4-H), 3.10 (1H, d, J = 3.1 Hz, OH), 3.88 (3H, s, OCH_3), 4.52 (1H, m, 3-H), 4.85 (1H, d, J = 5.4 Hz, 5-H), 5.12 (1H, ddd, J = 10.4, 1.8, 1.8 Hz, 1-C*H*H), 5.14 (2H, s, OCH_2Ph), 5.24 (1H, ddd, J = 17.3, 1.8, 1.8 Hz, 1-CH*H*), 5.79 (1H, ddd, J = 17.3, 10.4, 5.4 Hz, 2-H), 6.75 (1H, dd, J = 8.2, 1.8 Hz), 6.82 (1H, d, J = 8.2 Hz), 6.94 (1H, d, J = 1.8 Hz), 7.29 (1H, m), 7.35 (2H, dd, J = 7.7, 7.0 Hz), 7.43 (2H, d, J = 7.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.9 (CH_3), 12.6 (TIPS), 18.0 (TIPS), 45.7 (4-C), 55.9 (OCH_3), 71.1 (OCH_2Ph), 71.4 (3-C), 79.4 (5-C), 110.1, 113.5, 114.3 (1-C), 118.9, 127.3, 127.8, 128.4, 136.9 (2-C), 137.1, 139.8, 147.3, 149.3. FABMS: 485 $(M+H)^+$. *Anal*. Found: C 71.77%, H 9.08%; Calcd for $C_{29}H_{44}O_4Si$: C 71.85%, H 9.15%.

ent-3-*epi*-**11**. colorless oil, $[\alpha]^{25}_{D}$ +36 (*c* 1.3, $CHCl_3$)

ent-**11**. colorless oil, $[\alpha]^{25}_{D}$ +40 (*c* 1.0, $CHCl_3$)

(4*R*,5*S*)-5-(4-Benzyloxy-3-methoxyphenyl)-4-methyl-5-(triisopropylsilyloxy)-1-penten-3-one 12. A reaction mixture of **11** (1.00 g, 2.06 mmol), PDC (0.94 g, 2.50 mmol), and MS 4A (0.3 g) in CH_2Cl_2 (20 mL) was stirred at room temperature for 16 h before filtration. Concentration of the filtrate, followed by silica gel column chromatography (EtOAc/hexane = 1/9) gave ketone **12** (0.65 g, 1.35 mmol, 66%) as a colorless oil; $[\alpha]^{25}_{D}$ –88 (*c* 1.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (3H, d, *J* = 7.0 Hz, CH_3), 0.88-1.10 (21H, m, TIPS), 3.21 (1H, m, 4-H), 3.89 (3H, s, OCH_3), 4.90 (1H, d, *J* = 8.6 Hz, 5-H), 5.14 (2H, s, OCH_2Ph), 5.81 (1H, d, *J* = 10.6 Hz, 1-C*H*H), 6.30 (1H, d, *J* = 17.4 Hz, 1-CH*H*), 6.49 (1H, dd, *J* = 17.4, 10.6 Hz, 2-H), 6.75 (1H, d, *J* = 8.2 Hz), 6.81 (1H, d, *J* = 8.1 Hz), 6.92 (1H, s), 7.29 (1H, dd, *J* = 7.2, 7.2 Hz), 7.35 (2H, dd, *J* = 7.5, 7.2 Hz), 7.43 (2H, d, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4 (TIPS), 13.9 (CH_3), 17.9 (TIPS), 51.7 (4-C), 55.9 (OCH_3), 71.0 (OCH_2Ph), 77.7 (5-C), 110.4, 113.3, 119.6, 127.3, 127.8, 128.0, 128.4, 136.1, 136.98, 137.04, 147.6, 149.4, 203.5 (C=O); FABMS 483 $(M+H)^+$. HRMS (FAB): calculated $C_{29}H_{43}O_4Si$: 483.2930, found: 483.2922

ent-**12**. colorless oil, $[\alpha]^{25}_{D}$ +87 (*c* 0.9, $CHCl_3$)

Reduction of ketone 12. Method A: To a solution of ketone **12** (0.30 g, 0.62 mmol) in MeOH (5 mL) and THF (5 mL) was added

$CeCl_3 \cdot 7H_2O$ (0.31 g, 0.83 mmol) and $NaBH_4$ (27 mg, 0.71 mmol) at –60 °C, and then the reaction mixture was warmed to 0 °C. After stirring at 0 °C for 30 min, sat. aq. NH_4Cl and $CHCl_3$ were added. The organic solution was separated and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (EtOAc/hexane = 1/8) gave alcohol 3-*epi*-**11** (0.11 g, 0.23 mmol, 37%) and **11** (0.14 g, 0.29 mmol, 47%). Method B: To a solution of **12** (0.35 g, 0.73 mmol) in toluene (10 mL) was added DIBAL-H (1.50 mL, 1.0 M in toluene, 1.50 mmol) at –75 °C. After the reaction solution was stirred at –75 °C for 2 h, 1 M aq. HCl and EtOAc were added. The organic solution was separated, washed with sat. aq. $NaHCO_3$ and brine, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (EtOAc/hexane = 1/8) gave alcohol 3-*epi*-**11** (0.19 g, 0.39 mmol, 54%) and **11** (29 mg, 0.060 mmol, 8%).

(3*S*,4*S*,5*S*)-5-(4-Benzyloxy-3-methoxyphenyl)-4-methyl-1-pentene-3,5-diol 3-*epi*-**13**. To a solution of silyl ether 3-*epi*-**11** (1.50 g, 3.09 mmol) in THF (10 mL) was added a solution of *n*-Bu_4NF (3.50 mL, 1 M in THF, 3.50 mmol). After the reaction solution was stirred at room temperature for 1 h, EtOAc and sat. aq. $CuSO_4$ were added. The organic solution was separated, washed with sat. aq. $NaHCO_3$, and dried (Na_2SO_4). Concentration followed by silica gel column chromatography (EtOAc/hexane = 2/3) gave diol 3-*epi*-**13** (0.92 g, 2.80 mmol, 91%) as colorless crystals, mp 65-66 °C, $[\alpha]^{25}_D$ +3 (*c*1.0, $CHCl_3$). ^1H NMR (400

MHz, $CDCl_3$) δ 0.49 (3H, d, J = 6.9 Hz, CH_3), 1.87 (1H, m, 4-H), 3.86-4.00 (2H, br, OH), 3.87 (3H, s, OCH_3), 4.09 (1H, dd, J = 7.9, 7.9 Hz, 3-H), 4.42 (1H, d, J = 9.2 Hz, 5-H), 5.12 (2H, s, OCH_2Ph), 5.16 (1H, dd, J = 10.3, 1.5 Hz, 1-C*H*H), 5.24 (1H, d, J = 17.0 Hz, 1-CH*H*), 5.85 (1H, ddd, J = 17.0, 10.3, 7.9 Hz, 2-H), 6.73 (1H, dd, J = 8.1, 1.8 Hz), 6.80 (1H, d, J = 8.1 H), 6.90 (1H, d, J = 1.8 Hz), 7.28 (1H, m), 7.35 (2H, dd, J = 7.2, 7.2 Hz), 7.42 (2H, d, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6 (CH_3), 44.4 (4-C), 55.9 (OCH_3), 70.9 (OCH_2Ph), 79.0 (3-C), 80.2 (5-C), 110.1, 113.3, 116.7 (1-C), 119.5, 127.2, 127.7, 128.4, 136.3 (2-C), 137.0, 139.2, 147.6, 149.6. FABMS 329 $(M+H)^+$. HRMS (FAB): calculated $C_{20}H_{25}O_4$: 329.1753, found: 329.1749.

ent-3-*epi*-**13**. colorless crystals, mp 75-77 ^{o}C; $[\alpha]^{25}_D$ −3 (*c* 0.5, $CHCl_3$).

(3*R*,4*S*,5*S*)-5-(4-Benzyloxy-3-methoxyphenyl)-4-methyl-1-pentene-3,5-diol 13. 95% yield from silyl ether **11**. colorless oil, $[\alpha]^{25}_D$ +1.8 (*c*1.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 (3H, d, J = 7.2 Hz, CH_3), 2.02 (1H, m, 4-H), 3.50 (2H, br. s, OH), 3.86 (3H, s, OCH_3), 4.31 (1H, m, 3-H), 4.50 (1H, d, J = 8.3 Hz, 5-H), 5.12 (2H, s, OCH_2Ph), 5.20 (1H, ddd, J = 10.6, 1.5, 1.5 Hz, 1-C*H*H), 5.27 (1H, ddd, J = 17.3, 1.5, 1.5 Hz, 1-CH*H*), 5.93 (1H, ddd, J = 17.3, 10.6, 5.5 Hz, 2-H), 6.73 (1H, dd, J = 8.2, 1.9 Hz), 6.81 (1H, d, J = 8.2 Hz), 6.88 (1H, d, J = 1.9 Hz), 7.28 (1H, m), 7.35 (2H, dd J = 7.6, 7.6 Hz), 7.42 (2H, d, J = 7.6 Hz). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 12.4 (CH_3), 44.0 (4-C), 55.9 (OCH_3), 71.0 (OCH_2Ph), 74.9 (3-C), 77.6 (5-C), 109.9, 113.5, 115.5 (1-C), 118.8, 127.2, 127.7, 128.4, 136.7 (2-C), 137.0, 137.9, 147.5, 149.5. FABMS 329 $(M+H)^+$. *Anal*. Found: C 73.36%, H 7.43%; Calcd for $C_{20}H_{24}O_4$: C 73.15%, H 7.37%.

ent-**13**. colorless oil, $[\alpha]^{25}_D$ −2.3 (*c*1.2, $CHCl_3$)