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.

(4S)-4-Benzyl-3-[(2R,3S)-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-methoxybenzaldehyde (22.4 g, 92.5 mmol), Et$_3$N (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$_3$CO$_2$H (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 °C, [α]$^{25}_{D}$ −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$_2$HPh), 3.10 (1H, d, $J = 7.5$ Hz, O$H$), 3.19 (1H, dd, $J = 13.5$, 3.2 Hz, CHHPh), 3.90 (3H, s, OCH$_3$), 4.12 (1H, dd, $J = 9.0$, 2.8 Hz, 5-HH), 4.16 (1H, dd, $J = 9.0$, 7.6 Hz, 5-HH), 4.33 (1H, m, O=C-CH-CH$_3$), 4.67 (1H, m, 4-H), 4.74 (1H, dd, $J = 7.6$, 7.5 Hz, ArCHOH), 5.13 (2H, s, OCH$_2$Ph), 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$_3$) $\delta$ 14.8 (C$_3$H$_3$), 37.5 (O=C-CH-CH$_3$), 44.1 (CH$_2$Ph), 55.4 (4-C), 55.9 (OCH$_3$), 65.9 (5-C), 70.9 (OCH$_2$Ph), 77.2 (ArCOH), 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$_6$N: 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 °C (MeOH).

(4S)-4-Benzyl-3-[(2R,3S)-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$_2$Cl$_2$ (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$_2$SO$_4$), and concentrated. The residue was recrystallized from iso-Pr$_2$O.
to give silyl ether 8 (16.3 g, 25.8 mmol, 93%) as colorless crystals, mp 93-94 °C; \([\alpha]_D^{25} = -54 (c 0.8, \text{CHCl}_3)\).  \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 0.38-0.99 (21\text{H, m, TIPS}), 0.86 (3\text{H, d, } J = 7.0 \text{ Hz, CH}_3), 2.64 (1\text{H, dd, } J = 13.2, 10.8 \text{ Hz, } 4-\text{CHHPh}), 3.52 (1\text{H, dd, } J = 13.2, 3.2 \text{ Hz, } 4-\text{CHHPh}), 3.90 (3\text{H, s, OCH}_3), 4.13 (2\text{H, d, } J = 5.2 \text{ Hz, 5-CH}_2), 4.32 (1\text{H, m, O=C-CH-CH}_3), 4.65 (1\text{H, m, 4-H}), 5.04 (1\text{H, d, } J = 8.8 \text{ Hz, ArCHOTIPS}), 5.13 (2\text{H, s, OCH}_2\text{Ph}), 6.80 (2\text{H, d, } J = 0.8 \text{ Hz}), 7.06 (1\text{H, s}), 7.24-7.29 (4\text{H, m}), 7.32-7.36 (4\text{H, m}), 7.42-7.43 (2\text{H, m}).  \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 12.6 \text{ (TIPS), 14.6 (CH}_3\text{), 18.0 (TIPS), 18.1 (TIPS), 38.3 (O=C-C-Me), 46.2 (4-C), 55.8 (OCH}_3\text{), 56.0 (4-C), 65.9 (5-C), 71.1 (OCH}_2\text{Ph), 77.6 (ArCOH), 111.0, 113.4, 120.2, 127.3, 127.4, 127.8, 128.5, 129.0, 129.3, 135.7, 135.9, 137.1, 147.9, 149.7, 153.3 (2-C), 175.8 (N-(C=O)-CCH}_3); \text{FABMS 632 (M+H)}^+\).  Anal. Found: C 70.31%, H 8.07%, N 2.06%; Calcd for C\(_{37}\)H\(_{49}\)O\(_6\)NSi: C 70.33%, H 7.82%, N 2.22%.

\(\text{ent-8. } \ [\alpha]_D^{25} +53 (c 0.8, \text{CHCl}_3), \text{colorless crystals, mp 96-98 °C (iso-Pr}_2\text{O)}\)

\((2S,3S)-3-(4-\text{Benzyloxy-3-methoxyphenyl)-2-methyl-3-(triisopropylsilyloxy)-1-propanol 9.}\) 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\(_4\)Cl was added. The organic solution was separated and dried (Na\(_2\)SO\(_4\)). Concentration followed by silica gel
column chromatography (5% EtOAc/toluene) gave alcohol 9 (11.2 g, 24.4 mmol, 95%) as a colorless oil, \( \left[ \alpha \right]^{25}_{D} -86 \) (c 0.8, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) \( \delta 0.77 \) (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$_2$Ph), 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$_3$) \( \delta 12.5 \) (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$_2$Ph), 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$_4$Si: C 70.70%, H 9.23%.

**ent-9.** colorless oil, \( \left[ \alpha \right]^{25}_{D} +84 \) (c 0.9, CHCl$_3$)

**(2R,3S)-3-(4-Benzylxyo-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$_2$Cl$_2$ (80 mL) was stirred at 0 °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, \( \left[ \alpha \right]^{25}_{D} -66 \) (c 2.4, CHCl$_3$). $^1$H NMR (400 MHz, CDCl$_3$) \( \delta 0.88 \) (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, OCH₂Ph), 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). ¹³C NMR (100 MHz, CDCl₃) δ 10.5 (CH₃), 12.4 (TIPS), 17.9 (TIPS), 18.0 (TIPS), 55.1 (2-C), 55.9 (OCH₃), 71.0 (OCH₂Ph), 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 C₂₇H₄₀O₄Si: C 71.01%, H 8.83%.

ent-10. colorless oil, [α]²⁵_D +67 (c 1.1, CHCl₃)

(3R,4S,5S)-5-(4-Benzyloxy-3-methoxyphenyl)-4-methyl-5-triisopropylsilyloxy-1-penten-3-ol 11 and (3S,4S,5S)-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. NH₄Cl and EtOAc. The organic solution was separated, dried (Na₂SO₄), 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: [α]²⁵_D −31 (c 1.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 0.67 (3H, d, J = 7.1 Hz, CH₃), 0.87-1.10 (21H, m, TIPS), 1.70 (1H, br. s, OH),
2.05 (1H, m, 4-H), 3.89 (3H, s, OCH₃), 4.80 (1H, m, 3-H), 4.92 (1H, d, J = 3.6 Hz, 5-H), 5.07-5.16 (2H, overlapped, 1-CH₂), 5.14 (2H, s, OCH₂Ph), 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). ¹³C NMR (100 MHz, CDCl₃) δ 12.1 (TIPS), 13.8 (CH₃), 17.9 (TIPS), 44.5 (4-C), 56.0 (OCH₃), 71.0 (OCH₂Ph), 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 C₂₉H₄₅O₄Si: 485.3086, found: 485.3083.  ¹¹¹: [α]²⁵D −39 (c 1.5, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 0.89 (3H, d, J = 7.2 Hz, CH₃), 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, OCH₃), 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-CH/H), 5.14 (2H, s, OCH₂Ph), 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). ¹³C NMR (100 MHz, CDCl₃) δ 10.9 (CH₃), 12.6 (TIPS), 18.0 (TIPS), 45.7 (4-C), 55.9 (OCH₃), 71.1 (OCH₂Ph), 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 C₂₉H₄₄O₄Si: 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$_3$)

(4R,5S)-5-(4-Benzylxylo-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$_2$Cl$_2$ (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$_3$) $\delta$

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$_2$Ph), 5.81 (1H, d, $J = 10.6$ Hz, 1-CHH), 6.30 (1H, d, $J = 17.4$ Hz, 1-CHH), 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$_3$) $\delta$ 12.4 (TIPS), 13.9 (CH$_3$), 17.9 (TIPS), 51.7 (4-C), 55.9 (OCH$_3$), 71.0 (OCH$_2$Ph), 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$_4$Si: 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
CeCl₃·7H₂O (0.31 g, 0.83 mmol) and NaBH₄ (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. NH₄Cl and CHCl₃ were added. The organic solution was separated and dried (Na₂SO₄). 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. NaHCO₃ and brine, and dried (Na₂SO₄). 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%).

(3S,4S,5S)-5-(4-Benzylxy)-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-Bu₄NF (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. CuSO₄ were added. The organic solution was separated, washed with sat. aq. NaHCO₃, and dried (Na₂SO₄). 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, [α]²⁵_D +3 (c1.0, CHCl₃). ¹H NMR (400
MHz, CDCl$_3$) $\delta$ 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$_2$Ph), 5.16 (1H, dd, $J = 10.3, 1.5$ Hz, 1-CHH), 5.24 (1H, d, $J = 17.0$ Hz, 1-CHH), 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$_3$) $\delta$ 13.6 (CH$_3$), 44.4 (4-C), 55.9 (OCH$_3$), 70.9 (OCH$_2$Ph), 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 °C; $[\alpha]^{25}_D$ −3 (c 0.5, CHCl$_3$).

(3R,4S,5S)-5-(4-Benzxyloxy-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$_3$) $\delta$ 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$_2$Ph), 5.20 (1H, ddd, $J = 10.6, 1.5, 1.5$ Hz, 1-CHH), 5.27 (1H, ddd, $J = 17.3, 1.5, 1.5$ Hz, 1-CHH), 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$_3$) $\delta$ 12.4 (CH$_3$), 44.0 (4-C), 55.9 (OCH$_3$), 71.0 (OCH$_2$Ph), 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$_3$)