Absolute Stereochemistry of Amphidinolide C

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Experimental Procedure

General Methods. FABMS spectra were recorded using p-nitrobenzyl alcohol as matrix in positive mode. 1 H, 13 C, and 2D NMR spectra were recorded on a 600 MHz spectrometer at 300 K using 2.5 mm micro cells for CDCl₃ (Shigemi Co. Ltd.). HETLOC experiments were obtained with the pulse sequence proposed by Woolborn and Leibfritz¹ with composite pulses for broadband constant rotations (bandwidth ± 0.60). The duration of the trim pulse, the delay in the BIRD pulse, and the constant time for J_{CH} evaluation were 2.5, 300, and 3.57 msec, respectively. The MLEV17 spin-lock period was set to 30 ms for $^{2.3}J_{\text{C,H}}$. For 256 t_1 increments, 256 transients with 16 dummy scans were accumulated in 1K data points. Zero-filling to 1K for F_1 and multiplication with squared cosine-bell windows shifted in both dimensions were performed prior to 2D Fourier transformation. The measuring time was ca. 48 h. Cultivation and isolation were described previously.³

Bis-(*S*)-MTPA Ester (3a) of 7,8-Isopropylidene Derivative (2). To a CH₂Cl₂ solution (20 μL) of 7,8-isopropylidene derivative (2, 0.3 mg) of amphidinolide C (1) was added 4-dimethylaminopyridine (20 μg), triethylamine (2 μL), and (*R*)-(-)-MTPACl (1 μL) at room temperature, and stirring was continued for 6 h. After addition of *N*,*N*-dimethyl-1,3-propanediamine (1 μL) and evaporation of solvent, the residue was passed through a silica gel column (hexane/acetone, 4:1) to afford the bis-(*S*)-MTPA ester (3a, 0.2 mg) of 2. 3a: colorless oil; ¹H NMR (Table S1); FABMS m/z 1209 (M+Na)⁺; HRFABMS m/z 1209.5320 [calcd for C₆₄H₈₀O₁₄F₆Na (M+Na)⁺, 1209.5351].

Bis-(R)-MTPA Ester (3b) of 7,8-Isopropylidene Derivative (2). 7,8-Isopropylidene derivative (2, 0.4 mg) was treated with (S)-(+)-MTPACl (1.5 μ L) by the

¹ Wollborn, U.; Leibfritz, D. J. Magn. Reson. **1992**, 98, 142-146.

² Shaka, A. J.; Pines, A. J. Magn. Reson. **1987**, 71, 495-503.

³ Kobayashi, J.; Kubota, T.; Endo, T.; Tsuda, M. J. Org. Chem. **2001**, 66, 134-142.

same procedure as described above to afford the bis-(R)-MTPA ester (**3b**, 0.3 mg) of **2**. **3b:** colorless oil; ¹H NMR (Table S1); FABMS m/z 1209 (M+Na)⁺; HRFABMS m/z 1209.5310 [calcd for $C_{64}H_{80}O_{14}F_6Na$ (M+Na)⁺, 1209.5351].

Oxidative Degradation of Amphidinolide C (1). Amphidinolide C (1, 0.4 mg) was dissolved in CH₂Cl₂ (50 µL) and treated with 0.95M solution of DIBAL in toluene (15 μL, 14 μmol) at -78 °C for 1 h. The reaction mixture was partitioned between EtOAc (200 μL x 3) and 1M phosphate buffer (100 μL). The organic phase was evaporated in vacuo to afford a crude residue. To a solution of the residue in THF/1M phosphate buffer (1:1, 50 µL) was added NaIO₄ (1.0 mg), and the mixture was stirred at 0 °C for 1 h. After evaporation, the reaction mixture was extracted with MeOH (150 µL x 3) and the extract was concentrated to 50 µL in vacuo. NaBH₄ (1.0 mg) was added to the solution, and stirring was continued at 0 °C for 30 min. The mixture was evaporated, and then partitioned between EtOAc (200 µL x 3) and 1M phosphate buffer (100 µL). The organic phase was evaporated, and the residue was dissolved in 1% DMAP solution in CH₂Cl₂ (20 μ L). To the mixture were added Et₃N (2 μ L) and (R)-(-)-MTPACl (2 μ L), and stirring was continued at room temperature for 24 h. After addition of N,N-dimethyl-1,3propanediamine (2 µL), the solvent was evaporated in vacuo. The residue was passed through a silica gel column (hexane/acetone, 5:1) and purified by C₁₈ HPLC (Wakosil-II 5C18 RS, Wako Pure Chemical Ind., Ltd., 4.6 x 250 mm; eluent CH₃CN/H₂O, 90:10; flow rate, 1.0 mL/min; UV detection at 254 nm) to give compound 4a (0.08 mg, t_R 7.2 min) as colorless oil; ¹H NMR (C_6D_6) δ 0.57 (3H, d, J = 6.9 Hz), 0.92 (1H, m), 1.34 (1H, m), 1.44 (1H, m), 1.52 (1H, m), 1.64 (1H, m), 3.18 (1H, m), 3.44 (3H, s), 3.51 (3H, s), 3.83 (1H, m), 3.97 (1H, dd, J=11.2 and 5.6 Hz), 4.06 (1H, dd, J=11.2 and 3.7 m)Hz), 4.27 (1H, m), 4.38 (1H, m), $7.05 \sim 7.17$ (6H, m), and $7.69 \sim 7.78$ (4H, m); FABMS m/z 593 (M+H)⁺; HRFABMS 593.1965 [calcd for $C_{28}H_{31}O_{7}F_{6}$ (M+H)⁺,

593.1974].

Ethyl (4R,6R)-7-Benzyloxy-6-hydroxy-4-methyl-2-heptenoate (8). To a solution of (4*R*,6*R*)-6-hydroxymethyl-4-methyl-γ-butyrolactone (**7**, 5.35 g, 24.3 mmol) in CH₂Cl₂ (100 mL) was added 1.1 M hexane solution of DIBAL (25 mL, 27.5 mmol) at -78 °C, and the mixture was stirred for 30 min. After addition of MeOH (3 mL) and saturated aqueous potassium sodium tartrate (100 mL), the mixture was allowed to warm to room temperature, and stirred vigorously for 1 h. The reaction mixture was extracted with EtOAc, and the organic phase was washed with H₂O and then brine, dried with MgSO₄, and evaporated in vacuo to give a crude acetal compound (5.13 g, 23.1 mmol, 95 %). To a solution of the crude acetal compound (5.08 g) in benzene (100 mL) was added (ethoxycarbonylmethylene)triphenylphosphorane (11.5 g, 33.0 mmol), and stirring was continued at 80 °C for 20 h. After evaporation of the solvent, the residue was subjected to silica gel column chromatography (hexane/EtOAc, 6:1) to afford compound 8 (6.30 g, 21.6 mmol, 94 %) as colorless oil; $[\alpha]_D^{20}$ -15° (c 1.0, CHCl₃); IR (neat) v_{max} 3479, 2930, 1717, and 1652 cm⁻¹; ¹H NMR (CDCl₃) δ 1.07 (3H, d, J = 6.2 Hz), 1.28 (3H, t, J = 7.1 Hz), 1.34 (1H, m), 1.62 (1H, m), 2.55 (1H, m), 3.31 (1H, dd, J = 9.4 and 7.5 Hz), 3.48 (1H, dd, J = 9.4 and 3.1 Hz), 3.87 (1H, m), 4.17 (2H, q, J = 7.1 Hz), 4.54 (2H, s), 5.77(1H, dd, J = 15.7 and 1.0 Hz), 6.91 (1H, dd, J = 15.7 and 7.5 Hz), and 7.26 ~ 7.37 (5H, m); 13 C NMR (CDCl₃) δ 14.2 (q), 18.5 (q), 32.6 (d), 38.8 (t), 60.2 (t), 67.8 (d), 73.3 (t), 74.5 (t), 119.4 (d), 127.7 (2C, d), 127.8 (d), 128.4 (2C, d), 137.7 (s), 154.2 (d), and 166.8 (s); FABMS m/z 297 (M+H)⁺; HRFABMS m/z 297.1764 [calcd for $C_{17}H_{25}O_4$ $(M+H)^+$, 297.1753].

(2'S,3'R,5'R)-2-(5'-Benzyloxymethyl-3'-methyl-tetrahydrofuran-2'-yl)-ethanol (9). To a solution of compound 8 (6.25 g, 21.4 mmol) in THF (100 mL) was added 1 M THF solution of TBAF (31 mL, 31 mmol), and the mixture was stirred at room

temperature for 30 min. After evaporation of the solvent, the residue was subjected to silica gel column chromatography (hexane/EtOAc, 6:1) to give a tetrahydrofuran compound (5.88 g, 20.1 mmol, 94 %). To a solution of this tetrahydrofuran (5.83 g, 20.0 mmol) in CH₂Cl₂ was added 1.01 M hexane solution of DIBAL (60 mL, 61 mmol) at -78 °C, and the mixture was stirred for 90 min. After addition of MeOH (3 mL) and saturated aqueous potassium sodium tartrate (100 mL), the mixture was allowed to warm to room temperature, and stirred vigorously for 1 h. The reaction mixture was extracted with EtOAc, and the organic phase was washed with H₂O and then brine, dried with MgSO₄, and evaporated in vacuo to afford compound 9 (4.53 g, 18.1 mmol, 91 %) as colorless oil; $[\alpha]_D^{20}$ -7.8° (c 1.0, CHCl₃); IR (neat) v_{max} 3419, 2929, 1455, and 1115 cm⁻¹; ¹H NMR (CDCl₃) δ 1.00 (3H, d, J = 6.6 Hz), 1.34 (1H, m), 1.65 (1H, m), 1.85 (1H, m), 1.92 (1H, m), 2.13 (1H, m), 3.47 (2H, m), 3.58 (1H, m), 3.78 (2H, m), 4.20 (1H, m), 4.55 (1H, d, J = 10.6 Hz), 4.58 (1H, d, J = 10.6 Hz), and 7.25 ~ 7.35 (5H, m); ¹³C NMR $(CDCl_3)$ δ 16.0 (q), 35.3 (t), 37.2 (t), 39.8 (d), 61.5 (t), 72.8 (t), 73.2 (t), 77.3 (d), 85.3 (d), 127.5 (d), 127.5 (2C, d), 128.3 (2C, d), and 138.2 (s); FABMS m/z 251 (M+H)⁺; HRFABMS m/z 251.1660 [calcd for $C_{15}H_{23}O_3$ (M+H)⁺, 251.1647].

Synthetic 4a. To a solution of compound **9** (5 mg, 20 μmol) in EtOH (1 mL) was added 10% Pd/C (1 mg), and stirring was continued under H_2 atmosphere at room temperature for 4 h. After filtration of insoluble materials and then evaporation, the residue was dissolved in 1% DMAP solution in CH_2Cl_2 (100 μL). To the mixture were added Et_3N (10 μL) and (R)-(-)-MTPACl (7 μL), and stirring was continued at room temperature for 24 h. After addition of N,N-dimethyl-1,3-propanediamine (10 μL) and evaporation of the solvent, the residue was subjected to C_{18} HPLC (Wakosil-II 5C18 RS, 4.6 x 250 mm; eluent CH_3CN/H_2O , 85:15; flow rate, 1.0 mL/min; UV detection at 254 nm) to give a bis-(S)-MTPA ester (**4a**, 9.5 mg, 16 μmol, 80 %, t_R 7.8 min) as colorless

oil; $[\alpha]_D^{20}$ -53° (*c* 0.3, CHCl₃); IR (neat) v_{max} 1749, 1272, and 1169 cm⁻¹; ¹H NMR (C_6D_6) δ 0.57 (3H, d, J = 6.9 Hz), 0.92 (1H, m), 1.34 (1H, m), 1.44 (1H, m), 1.52 (1H, m), 1.64 (1H, m), 3.18 (1H, m), 3.44 (3H, s), 3.51 (3H, s), 3.83 (1H, m), 3.97 (1H, dd, J=11.2 and 5.6 Hz), 4.06 (1H, dd, J=11.2 and 3.7 Hz), 4.27 (1H, m), 4.38 (1H, m), 7.05 \sim 7.17 (6H, m), and 7.69 \sim 7.78 (4H, m); FABMS m/z 593 (M+H)⁺; HRFABMS 593.1965 [calcd for $C_{28}H_{31}O_7F_6$ (M+H)⁺, 593.1974].

Synthetic 4b. Compound **9** (5 mg, 20 μmol) was treated with (*S*)-(+)-MTPACl (0.5 μL) by the same procedure as described above to afford a (*R*)-(+)-MTPA ester (**4b**, mg, 17 μmol, 85 % t_R 8.0 min) as colorless oil; $[\alpha]_D^{20}$ +24° (c 0.3, CHCl₃); IR (neat) ν_{max} 1749, 1271, and 1168 cm⁻¹; ¹H NMR (C_6D_6) δ 0.57 (3H, d, J = 6.9 Hz), 0.77 (1H, m), 1.30 (1H, m), 1.38 (1H, m), 1.50 (1H, m), 1.64 (1H, m), 3.17 (1H, m), 3.47 (3H, s), 3.55 (3H, s), 3.77 ~ 3.84 (2H, m), 4.13 (1H, dd, J = 11.8 and 7.5 Hz), 4.24 (1H, m), 4.39 (1H, m), 7.05 ~ 7.18 (6H, m), and 7.69 ~ 7.81 (4H, m); FABMS m/z 593 (M+H)⁺; HRFABMS 593.1936 [calcd for $C_{28}H_{31}O_7F_6$ (M+H)⁺, 593.1974].

Pentakis-(S)-MTPA Ester (5a) of Linear Methyl Ester of Amphidinolide C (1). To a solution of amphidinolide C (1, 0.5 mg) in MeOH (30 μL) was added K_2CO_3 (0.14 mg), and the mixture was stirred at 4 °C for 50 h. After filtration and evaporation *in vacuo*, the residue was subjected to C_{18} HPLC (Develosil ODS-HG-5, Nomura Chemical Co., Ltd., 10 x 250 mm; eluent, CH_3CN/H_2O , 65:35; flow rate, 2.5 mL/min; UV detection at 240 nm) to give other two linear methyl esters (0.23 mg, t_R 12.0 min; 0.18 mg, t_R 13.2 min) and a mixture of two methyl esters (0.22 mg, t_R 12.8 min). To the linear methyl ester (0.10 mg) eluted at 12.0 min, which was dissolved in 1 % DMAP solution in CH_2Cl_2 (15 μL), were added Et_3N (1 μL) and (R)-(-)-MTPACl (0.5 μL), and stirring was continued at room temperature for 6 h. After addition of N,N-dimethyl-1,3-propanediamine (0.5 μL), the reaction mixture was partitioned between CH_2Cl_2 (50 μL x

3) and 1M phosphate buffer (50 μ L). The combined organic layer was evaporated in vacuo, and the residue was purified by C₁₈ HPLC (Develosil ODS-HG-5, 10 x 250 mm; eluent, CH₃CN/H₂O, 95:5; flow rate, 2.5 mL/min; UV detection at 240 nm) to afford a pentakis-(*R*)-MTPA ester (**5a**, 0.08 mg, t_R 12.4 min); ¹H NMR (Table S2); ESIMS m/z 1849 (M+Na)⁺; HRESIMS m/z 1849.6499 [calcd for C₉₂H₁₀₁O₂₁F₁₅Na (M+Na)⁺, 1849.6494].

Pentakis-(R)-MTPA Ester (5b) of Linear Methyl Ester of Amphidinolide C (1). The linear methyl ester (0.10 mg, t_R 12.0 min) of amphidinolide C (1) was treated with (S)-(+)-MTPACl (0.5 μ L) by the same procedure as described above to afford the pentakis-(R)-MTPA ester (5b, 0.08 mg, t_R 13.2 min); ¹H NMR (Table S2); ESIMS m/z 1849 (M+Na)⁺; HRESIMS m/z 1849.6489 [calcd for $C_{92}H_{101}O_{21}F_{15}Na$ (M+Na)⁺, 1849.6494].

Baeyer-Villiger Reaction of Amphidinolide C (1). To a solution of amphidinolide C (1, 0.5 mg) in CH₂Cl₂ (80 μL) was added TFPA prepared by adding trifluoroacetic anhydride (124 μL) to a 30 % aqueous H₂O₂ (22 μL) in CH₂Cl₂ (134 μL) was at 0 °C, and stirring was continued at room temperature for 7 days. After evaporation, to the reaction mixture were added THF (50 μL) and LiAlH₄ (5 mg), and the mixture was stirred at room temperature for 6 h. The solvent was evaporated, the residue was extracted with EtOAc (200 μL x 3), and the extract was concentrated in vacuo. The residue was dissolved in CH₂Cl₂ (50 μL), and Et₃N (3.5 μL), DMAP (5.6 mg), and (*S*)-(+)-MTPACl (6.2 μL) were added to the mixture, and stirring was continued at room temperature for 14 h. After addition of *N*,*N*-dimethyl-1,3-propanediamine (4 μL), the solvent was evaporated *in vacuo*. The residue was passed through a silica gel column (hexane/acetone, 8:1) and then purified by C₁₈ HPLC (Wakosil-II 5C18 AR, 10 x 250 mm; eluent, CH₃CN/H₂O, 75:25; flow rate, 2.5 mL/min; UV detection at 240 nm) to

afford a bis-(R)-MTPA ester **6a** (0.02 mg, t_R 11.7 min). **6a:** ¹H NMR (CDCl₃) δ 1.34 (3H, d, J = 6.3 Hz, H₃-39), 1.97 (2H, m, H₂-17), 3.54 (3H, s, OCH₃), 3.56 (3H, s, OCH₃), 4.15 (1H, m, H-18), 4.23 (1H, m, H-18), 5.17 (1H, m, H-16), 7.36 ~ 7.44 (6H, m, Ph), and 7.50 (4H, m, Ph); FABMS m/z 523 (M+H)⁺; HRFABMS m/z 523.1561 [calcd for $C_{24}H_{25}O_6F_6$ (M+H)⁺, 523.1555].

R-MTPA Ester (6a) of (S)-(+)-1,3-Butanediol. Colorless oil; [α]_D+66° (c 1.0, CHCl₃); IR (neat) v_{max} 1749, 1271, and 1169 cm⁻¹; ¹H NMR (CDCl₃) δ 1.34 (3H, d, J = 6.3 Hz), 1.97 (2H, m), 3.54 (3H, s), 3.56 (3H, s), 4.15 (1H, m), 4.23 (1H, m), 5.17 (1H, m), 7.36 ~ 7.44 (6H, m), and 7.50 (4H, m); FABMS 523 (M+H)⁺; HRFABMS m/z 523.1563 [calcd for $C_{24}H_{25}O_6F_6$ (M+H)⁺, 523.1555].

R-MTPA Ester (6b) of (R)-(+)-1,3-Butanediol. Colorless oil; $[\alpha]_D$ +21° (*c* 1.0, CHCl₃); IR (neat) ν_{max} 1749, 1271, and 1169 cm⁻¹; ¹H NMR (CDCl₃) δ 1.28 (3H, d, J = 6.2 Hz), 2.00 (2H, m), 3.51 (3H, s), 3.55 (3H, s), 4.28 (1H, m), 4.37 (1H, m), 5.16 (1H, m), 7.39 (6H, m), and 7.49 (4H, m); FABMS 523 (M+H)⁺; HRFABMS m/z 523.1559 [calcd for $C_{24}H_{25}O_6F_6$ (M+H)⁺, 523.1555].

Figure S1. NOESY spectrum of amphidinolide C (1) in CDCl₃.

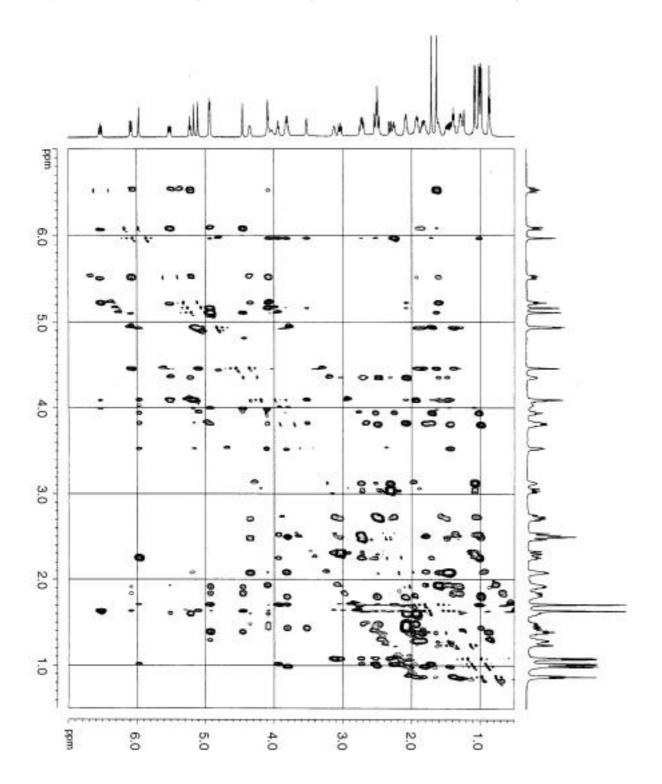
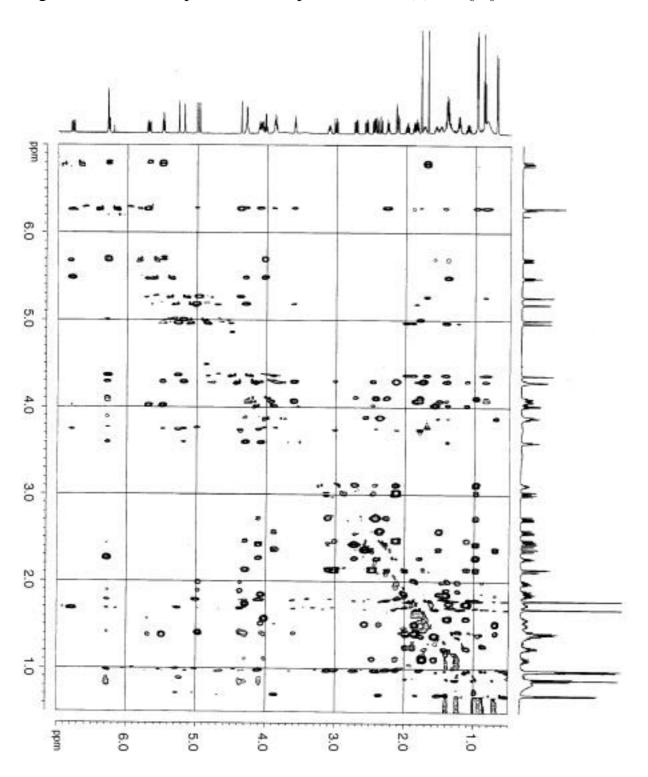
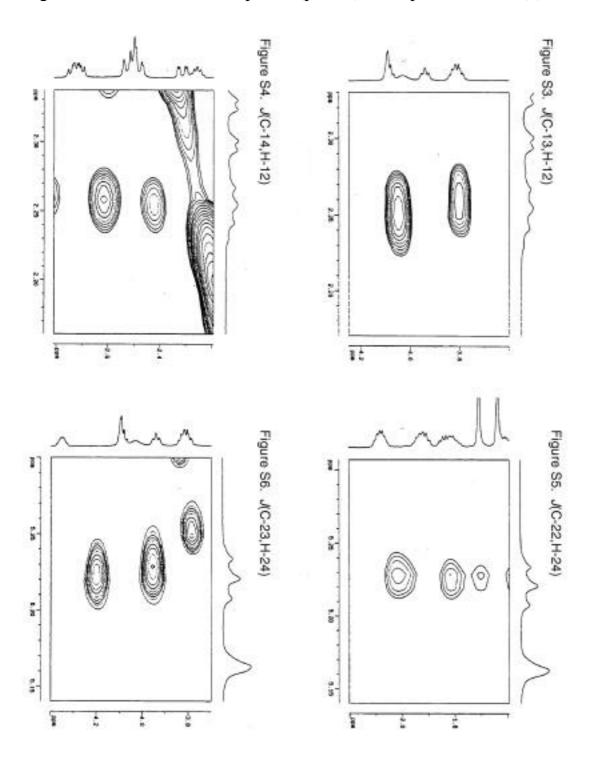


Figure S2. NOESY spectrum of amphidinolide C (1) in C_6D_6 .



Figures S3 ~ S6. HETLOC spectra (partial) of amphidinolide C (1) in $CDCl_3$.



Figures S7 and S8. HETLOC spectra (partial) of amphidinolide C (1) in CDCl₃.

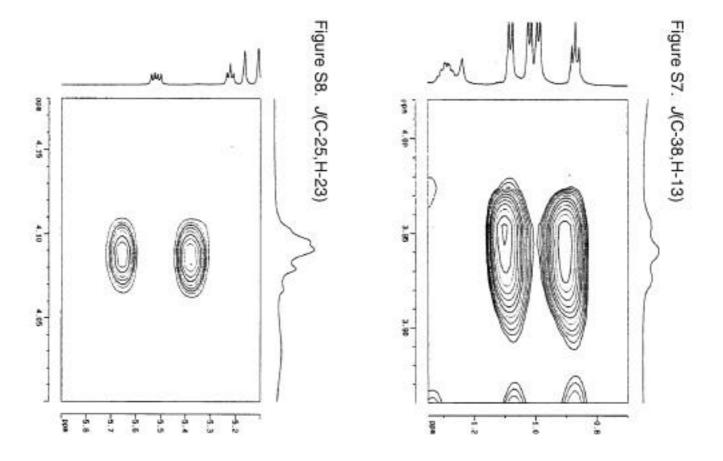


Figure S9. ¹H NMR spectrum of 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**) in CDCl₃.

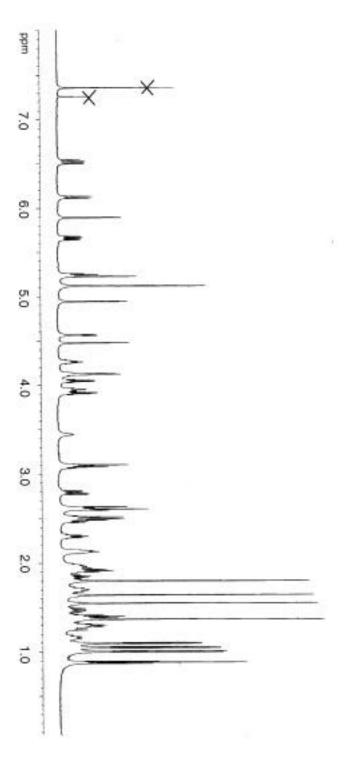


Figure S10. NOESY spectrum of 7,8-*O*-isopropylidene derivative (2) of amphidinolide C (1) in CDCl₃.

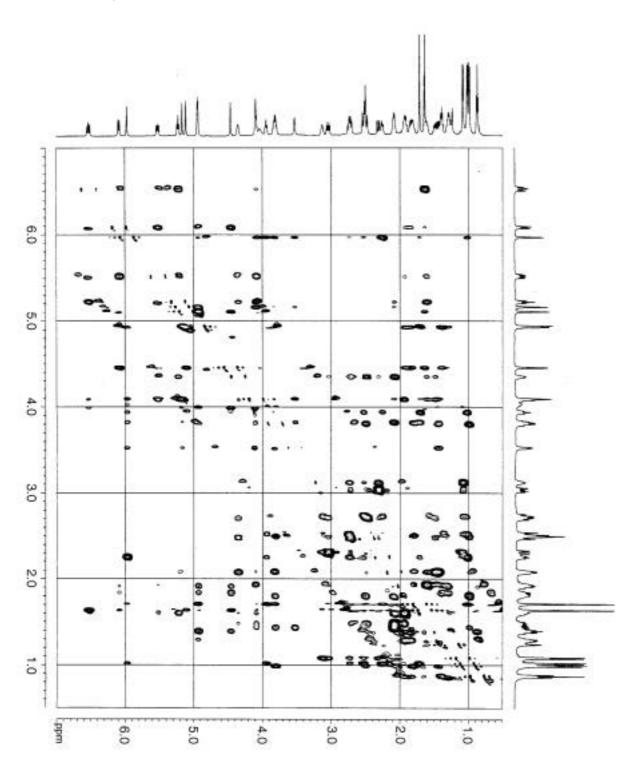


Figure S11. ¹H NMR spectrum of (S)-MTPA esters (3a) of the 7,8-O-isopropylidene derivative (2) of amphidinolide C (1) in CDCl₃.

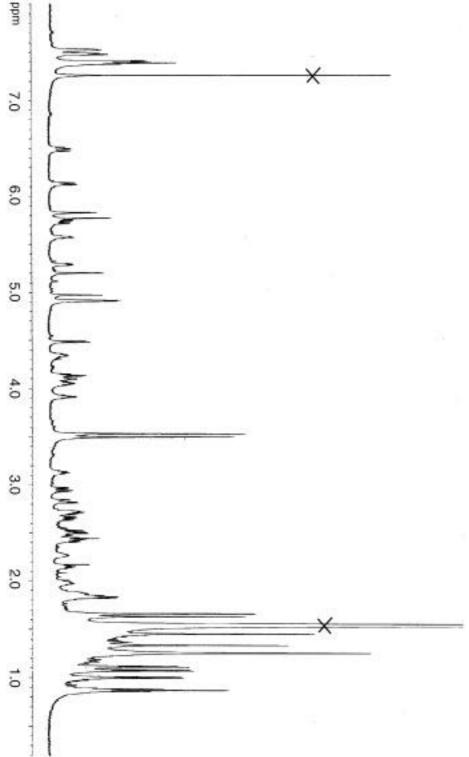


Figure S12. ¹H NMR spectrum of (R)-MTPA esters (**3b**) of the 7,8-O-isopropylidene derivative (**2**) of amphidinolide C (**1**) in CDCl₃.

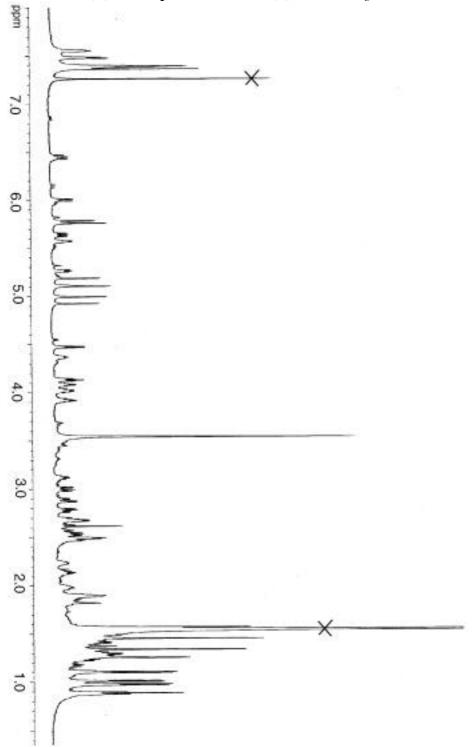


Figure S13. 1 H NMR spectrum of bis-(S)-MTPA ester (**4a**) of C-1–C-7 segment derived from amphidinolide C (**1**) in C_6D_6 .

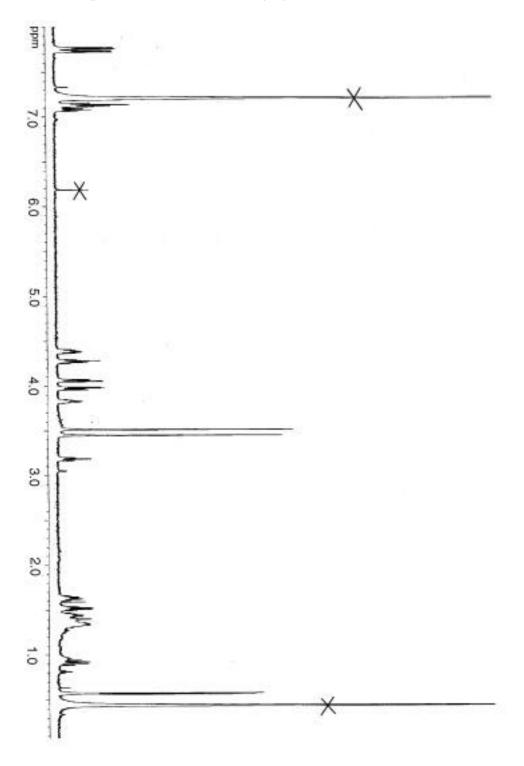


Figure S14. 1 H NMR spectrum of synthetic bis-(S)-MTPA ester (4a) of C-1-C-7 segment in C_6D_6 .

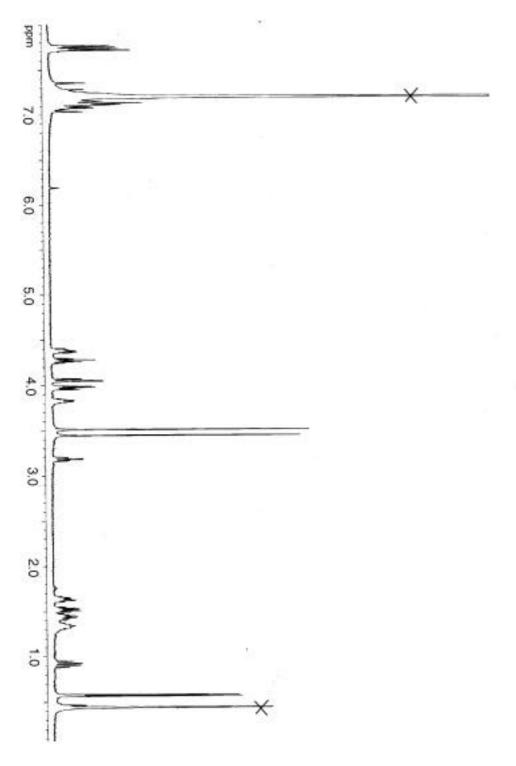


Figure S15. 1 H NMR spectrum of synthetic bis-(R)-MTPA ester (**4b**) of C-1-C-7 segment in C_6D_6 .

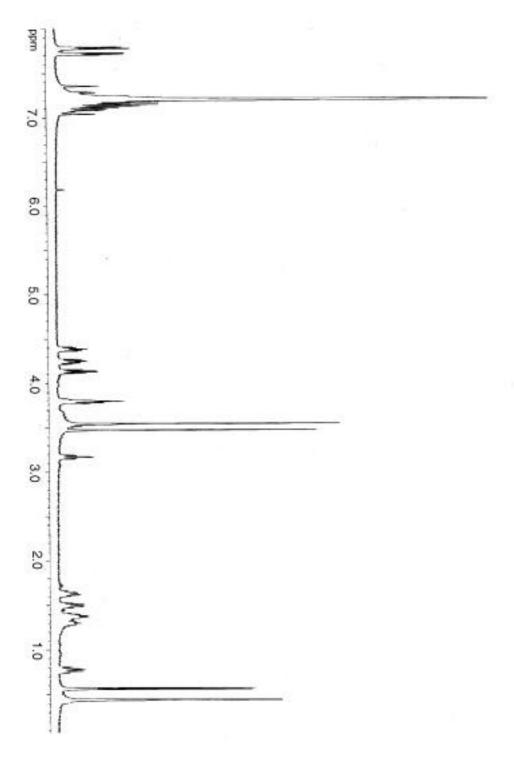


Figure S16. 1 H NMR spectrum of the pentakis-(S)-MTPA esters (**5a**) of the linear methyl ester of amphidinolide C (**1**) in CDCl₃.

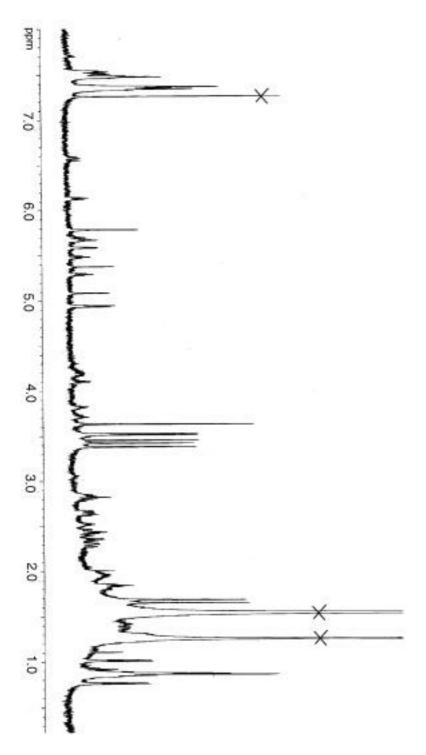


Figure S17. 1 H NMR spectrum of the pentakis-(R)-MTPA esters ($\mathbf{5b}$) of the linear methyl ester of amphidinolide C ($\mathbf{1}$) in CDCl₃.

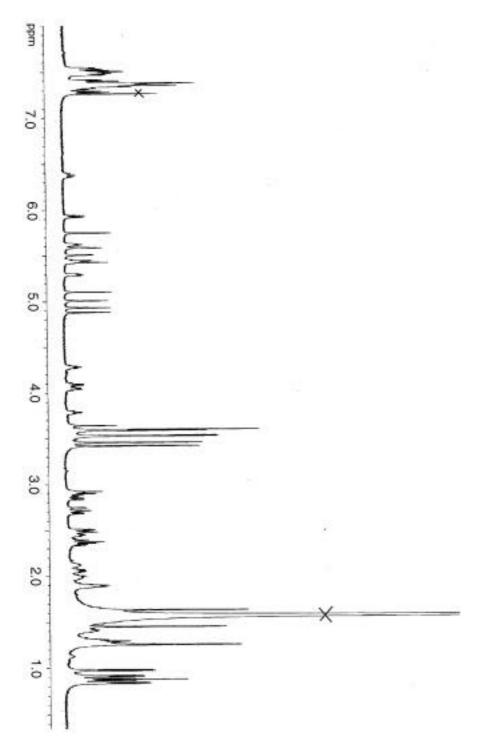


Figure S18. ¹H NMR spectrum of bis-(R)-MTPA ester (6a) of C-16–C-18 segment derived from amphidinolide C (1) in CDCl₃.

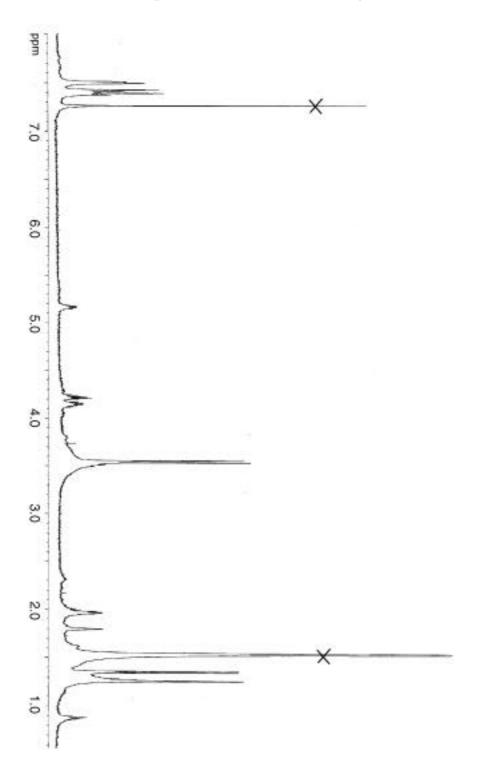


Figure S19. 1 H NMR spectrum of bis-(R)-MTPA ester (**6a**) of (S)-1,3-butanediol in CDCl₃.

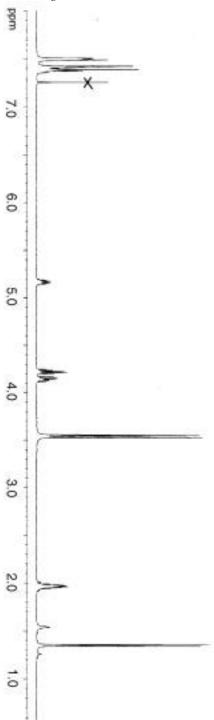


Figure S20. ¹H NMR spectrum of bis-(R)-MTPA ester (6b) of (R)-1,3-butanediol in CDCl₃.

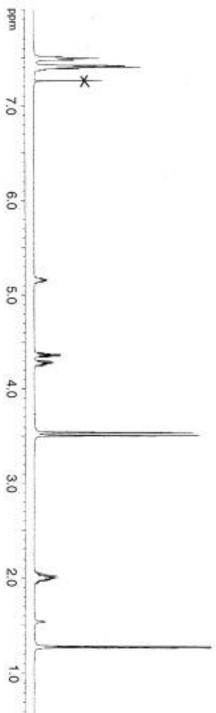


Table S1. 1 H NMR data of bis-(S)- and bis-(R)-MTPA esters ($\mathbf{3a}$ and $\mathbf{3b}$, respectively) of the 7,8-O-isopropylidene derivative ($\mathbf{2}$) of amphidinolide C ($\mathbf{1}$)

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						21			
2a 2.533 dd, 14.0, 8.1 2.555 dd 14.1, 7.8 2b 2.487 dd 14.0, 4.9 2.586 dd 14.1, 5.2 3 3.913 dt 4.9, 8.1 3.918 m 7.8, 5.2 4 1.863 m 1.882 m 5a 2.150 dt 11.8, 6.5 2.138 dt 12.3, 6.7 5b 1.175 m 1.172 dt 12.3, 10.1 6 6 4.052 dt 5.7, 9.0 4.019 dt 5.6, 8.9 7 4.137 dd 8.3, 6.9 4.131 dd 8.2, 7.1 10 5.829 s 5.787 s 12 2.722 m 2.683 m 12 2.722 m 2.683 m 13 5.576 dt 7.5, 4.8 5.573 dt 6.3, 5.2 14 2.651 dd 15.9, 7.5 2.779 dd 16.4, 5.6	nositn	δ	3a m	Нz	δ	3b	Н7		
2b									
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23	22a	1.981	m		1.990	m			
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25	23	4.099	dt	4.3, 7.3	4.081	dt	4.5, 7.3		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24	5.290	dd	7.5, 3.9	5.266	dd	7.8, 4.5		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25	5.736	dd	15.5, 7.5	5.639	dd	15.3, 7.8		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26	6.493	dd	15.5, 10.8	6.451	dd	15.3, 10.8		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27	6.130	d	10.8	6.003	d	10.8		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5.772	S		5.762	S			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1.835^{a}	m		1.902^{a}	m			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1.373^{a}	m		1.410^{a}	m			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			m			m			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0.870^{b}		7.3	0.886^{b}		7.4		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	35	1.001^{b}			1.013^{b}	d			
36b 4.971 s 4.925 s 37 1.630^b s 1.576^b s 38 1.116^b d 7.1 0.979^b d 7.1									
$\begin{array}{cccccccccccccccccccccccccccccccccccc$									
38 1.116^b d 7.1 0.979^b d 7.1									
				7.1			7.1		
39 1.0/5° d /.1 1.10/° d /.1	39	1.075^{b}	d	7.1	1.107^{b}	d	7.1		
$40 1.660^b s 1.544^b s$									

41a	4.916 s	5.104 s
41b	4.907 s	4.995 s
CH_3-1	1.453^{b} s	1.454^{b} s
CH_3^3-2	1.335^{b} s	1.338^{b} s
Ph	$7.36 \sim 7.54^{c}$ m	$7.34 \sim 7.58^{c}$ m
OCH_3-1	3.529^b s	3.541^b s
OCH_3^3 -2	3.495^b s	3.541^{b} s

^a2H. ^b3H. ^c10H.

Table S2. ¹H NMR data of pentakis-(*S*)- and pentakis-(*R*)-MTPA esters (**5a** and **5b**, respectively) of the linear methyl ester of amphidinolide C (**1**).

positn. δ _H m Hz δ _H m Hz 2a 2.446 m 2.503 m 2b 2.346 m 2.353 dd 14.5, 8.5 3 3.714 m 3.788 dt 4.4, 9.0 4 1.812 m 1.904 m 5a 1.959 m 2.061 dt 12.3, 7.2 5b 1.227 m 1.305 m 6 3.826 m 4.048 dt 5.6, 8.9 7 5.293 dd 6.6, 5.4 5.293 dd 7.4, 3.9 8 8 5.88 d 5.4 5.507 d 3.9 3.9 10 5.785 s 5.587 s 12 2.522 m 2.460 m 13 5.668 m 5.621 m 14 2.833 m 2.858 d 18.0, 8.5 14b 2.653 m<			5a			5b			
2a 2.446 m 2.503 m 2b 2.346 m 2.353 dd 14.5, 8.5 3 3.714 m 2.383 dd 4.4, 9.0 4 1.812 m 1.904 m 5a 1.959 m 2.061 dt 12.3, 7.2 5b 1.227 m 1.305 m 6 3.826 m 4.048 dt 5.6, 8.9 7 5.293 dd 6.6, 5.4 5.293 dd 7.4, 3.9 8 5.588 d 5.4 5.507 d 3.9 10 5.785 s 5.587 s 1.2 2.522 m 2.460 m 13 5.668 m 5.621 m 1.44 2.833 m 2.2858 dd 18.0, 8.5 14a 2.843 m 2.920 m 17a 2.815 m 2.920 m 17a <t< th=""><th>positn.</th><th>δ_{H}</th><th></th><th>Hz</th><th>δ_{H}</th><th></th><th>Hz</th><th></th><th></th></t<>	positn.	δ_{H}		Hz	δ_{H}		Hz		
2b			m			m			
3 3.714 m 3.788 dt 4.4, 9.0 4 1.812 m 1.904 m 5a 1.959 m 2.061 dt 12.3, 7.2 5b 1.227 m 1.305 m 6 3.826 m 4.048 dt 5.6, 8.9 7 5.293 dd 6.6, 5.4 5.293 dd 7.4, 3.9 8 5.588 d 5.4 5.507 d 3.9 10 5.785 s 5.587 s 12 2.522 m 2.460 m 13 5.668 m 5.621 m 14a 2.833 m 2.888 dd 18.0, 8.5 14b 2.653 m 2.733 dd 16.4, 3.9 16 2.843 m 2.2928 m 17a 2.815 m 2.920 m 17b 2.279 m 2.386 m 19a 2.640 m 2.2697 dd 15.6, 6.6 19b 2.412 m 2.499 m 20 4.184 m 4.282 dt 14.3, 6.1 21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.932 m 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 4.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s 31 1.841" m 1.900" m 32 1.377" m 1.409" m 33 1.283" m 1.900" m 34 0.875" t 7.3 0.879" t 7.4 35 0.867" d 6.5 0.978" d 6.4 36a 5.379 s 4.931 s 36b 5.086 s 4.880 s 37 1.684" s 1.631" s 38 1.016" d 6.9 0.840" d 6.8 39 0.764" d 6.9 0.915" d 6.7							14.5, 8.5		
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6 3.826 m							,		
7							5.6, 8.9		
8 5.588 d 5.4 5.07 d 3.9 10 5.785 s 5.587 s 12 2.522 m 2.460 m 13 5.668 m 5.621 m 14a 2.833 m 2.858 dd 18.0, 8.5 14b 2.653 m 2.733 dd 16.4, 3.9 16 2.843 m 2.928 m 17a 2.815 m 2.920 m 17b 2.279 m 2.386 m 19a 2.640 m 2.697 dd 15.6, 6.6 19b 2.412 m 2.499 m 20 4.184 m 4.282 dt 14.3, 6.1 21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.932 m 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 4.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s 31 1.841a m 1.900a m 32 1.377a m 1.409a m 33 1.283a m 1.299a m 34 0.875b t 7.3 0.879b t 7.4 35 0.867b d 6.5 0.978b d 6.4 36a 5.379 s 4.931 s 36b 5.086 s 4.880 s 37 1.684b s 1.631b s 38 1.016b d 6.9 0.840b d 6.8 39 0.764b d 6.9 0.840b d 6.8 30 0.764b d 6.9 0.840b d 6.7	7	5.293		6.6, 5.4	5.293				
12	8	5.588	d			d			
12	10	5.785	S		5.587	S			
13		2.522	m		2.460				
14b 2.653 m 2.733 dd 16.4, 3.9 16 2.843 m 2.928 m 17a 2.815 m 2.920 m 17b 2.279 m 2.386 m 19a 2.640 m 2.697 dd 15.6, 6.6 19b 2.412 m 2.499 m 20 4.184 m 4.282 dt 14.3, 6.1 21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 4.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s		5.668	m		5.621	m			
16 2.843 m 2.928 m 17a 2.815 m 2.920 m 17b 2.279 m 2.386 m 19a 2.640 m 2.697 dd 15.6, 6.6 19b 2.412 m 2.499 m 20 4.184 m 4.282 dt 14.3, 6.1 21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.932 m 1.996 m 22a 1.932 m 1.643 m 23 4.105 dt 4.5, 7.2 4.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 29 5.785 s 5.747 s 31 1.841a m 1.900a m	14a	2.833	m		2.858	dd	18.0, 8.5		
17a	14b	2.653	m		2.733	dd	16.4, 3.9		
17b	16	2.843	m		2.928	m			
19a 2.640 m 2.697 dd 15.6, 6.6 19b 2.412 m 2.499 m 20 4.184 m 4.282 dt 14.3, 6.1 21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.932 m 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 d.099 dt 4.4, 7.2 24 5.484 t 7.2 d.099 dt 4.4, 7.2 24 5.484 t 7.2 d.099 dt 4.4, 7.2 26 6.573 dd 15.0, 10.5 d.377 dd 14.2, 10.5 27 6.132 d 10.5 d.05 d.05 d.05 d.05 d.05 d.05 d.05 d	17a	2.815	m		2.920	m			
19b	17b	2.279	m		2.386	m			
20	19a	2.640	m		2.697	dd	15.6, 6.6		
21a 1.984 m 2.131 m 21b 1.423 m 1.507 m 22a 1.932 m 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 d.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s 31 1.841a m 1.900a m 32 1.377a m 1.409a m 33 1.283a m 1.299a m 34 0.875b t 7.3 0.879b t 7.4 35 0.867b d 6.5 0.978b d 6.4 36a 5.379 s 4.931 s 36b 5.086 s 4.880 s 37 1.684b s 1.631b s 38 1.016b d 6.9 0.840b d 6.8 39 0.764b d 6.9 0.915b d 6.7	19b	2.412	m		2.499	m			
21b	20	4.184	m		4.282	dt	14.3, 6.1		
22a 1.932 m 1.996 m 22b 1.586 m 1.643 m 23 4.105 dt 4.5, 7.2 4.099 dt 4.4, 7.2 24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s 31 1.841° m 1.900° m 32 1.377° m 1.409° m 33 1.283° m 1.299° m 34 0.875° t 7.3 0.879° t 7.4 35 0.867° d 6.5 0.978° d 6.4 36a 5.379 s 4.880 s 37 1.684° s 1.631° s 38 1.016°	21a	1.984	m		2.131	m			
22b	21b	1.423	m		1.507	m			
23	22a	1.932	m		1.996	m			
24 5.484 t 7.2 5.444 m 25 5.683 dd 15.0, 7.8 5.436 m 26 6.573 dd 15.0, 10.5 6.377 dd 14.2, 10.5 27 6.132 d 10.5 5.927 d 10.5 29 5.785 s 5.747 s 31 1.841a m 1.900a m 32 1.377a m 1.409a m 33 1.283a m 1.299a m 34 0.875b t 7.3 0.879b t 7.4 35 0.867b d 6.5 0.978b d 6.4 36a 5.379 s 4.931 s 36b 5.086 s 4.880 s 37 1.684b s 1.631b s 38 1.016b d 6.9 0.840b d 6.8 39 0.764b d 6.9 0.915b d 6.7	22b	1.586	m		1.643	m			
25	23	4.105	dt	4.5, 7.2	4.099	dt	4.4, 7.2		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24	5.484	t	7.2	5.444	m			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	25	5.683	dd	15.0, 7.8	5.436	m			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	26	6.573	dd	15.0, 10.5	6.377	dd	14.2, 10.5		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	27	6.132	d	10.5	5.927	d	10.5		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5.785	S		5.747	S			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	31	1.841^{a}	m		1.900^{a}	m			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	32	1.377^{a}	m		1.409^{a}	m			
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			m			m			
$36a$ 5.379 s 4.931 s $36b$ 5.086 s 4.880 s 37 1.684^b s 1.631^b s 38 1.016^b d 6.9 0.840^b d 6.8 39 0.764^b d 6.9 0.915^b d 6.7	34	0.875^{b}	t	7.3		t	7.4		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	35	0.867^{b}	d	6.5	0.978^{b}	d	6.4		
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5.379	S			S			
38 1.016^b d 6.9 0.840^b d 6.8 39 0.764^b d 6.9 0.915^b d 6.7	36b	5.086	S			S			
39 0.764^b d 6.9 0.915^b d 6.7			S		1.631^{b}	S			
			d			d	6.8		
40 1.651^b s 1.449^b s	39			6.9		d	6.7		
	40	1.651^{b}	S		1.449^{b}	S			

41a	4.946 s		5.103 s	
41b	4.934 s		5.006 s	
1-OCH ₃	3.632^{b} s		3.598^{b} s	
Ph	$7.30 \sim 7.56^{c}$	m	$7.27 \sim 7.56^{c}$	m
OCH_3-1	3.381^{b} s		3.420^{b} s	
OCH_3-2			3.457^{b} s	
OCH_3-3			3.527^{b} s	
OCH_3^3 -4			3.534^{b} s	
OCH_3-5	3.526^{b} s		3.588^{b} s	

^а2H. ^ь3H. ^с25H.