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 $CDCl_3$ (Shigemi Co. Ltd.). HETLOC experiments were obtained with the pulse sequence proposed by Woolborn and Leibfritz[1] with composite pulses for broadband constant rotations (bandwidth ±0.60).[2] 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 $^{2,3}J_{C,H}$. 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 CH_2Cl_2 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; ^{1}H NMR (Table S1); FABMS *m/z* 1209 $(M+Na)^+$; HRFABMS *m/z* 1209.5320 [calcd for $C_{64}H_{80}O_{14}F_6Na$ $(M+Na)^+$, 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 μL) 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; ^{1}H 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 CH_2Cl_2 (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 $NaIO_4$ (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. $NaBH_4$ (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 CH_2Cl_2 (20 μL). To the mixture were added Et_3N (2 μL) and (*R*)-(-)-MTPACl (2 μL), and stirring was continued at room temperature for 24 h. After addition of *N*,*N*-dimethyl-1,3-propanediamine (2 μL), the solvent was evaporated in vacuo. The residue was passed through a silica gel column (hexane/acetone, 5:1) and purified by C_{18} HPLC (Wakosil-II 5C18 RS, Wako Pure Chemical Ind., Ltd., 4.6 x 250 mm; eluent CH_3CN/H_2O, 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; ^{1}H 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 ~ 7.17 (6H, m), and 7.69 ~ 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].

Ethyl (4*R*,6*R*)-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 CH_2Cl_2 (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 H_2O and then brine, dried with $MgSO_4$, 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, $CHCl_3$); IR (neat) ν_{max} 3479, 2930, 1717, and 1652 cm^{-1}; ^1H NMR ($CDCl_3$) 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 ($CDCl_3$) 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 CH_2Cl_2 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 H_2O and then brine, dried with $MgSO_4$, 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, $CHCl_3$); IR (neat) ν_{max} 3419, 2929, 1455, and 1115 cm^{-1}; ^1H NMR ($CDCl_3$) 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); ^{13}C 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, $CHCl_3$); IR (neat) ν_{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 ~ 7.17 (6H, m), and 7.69 ~ 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, $CHCl_3$); 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 μL). The combined organic layer was evaporated in vacuo, and the residue was purified by C_{18} HPLC (Develosil ODS-HG-5, 10 x 250 mm; eluent, CH_3CN/H_2O, 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); ^{1}H NMR (Table S2); ESIMS *m/z* 1849 $(M+Na)^+$; HRESIMS *m/z* 1849.6499 [calcd for $C_{92}H_{101}O_{21}F_{15}Na$ $(M+Na)^+$, 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 μL) by the same procedure as described above to afford the pentakis-(*R*)-MTPA ester (**5b**, 0.08 mg, t_R 13.2 min); ^{1}H 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 CH_2Cl_2 (80 μL) was added TFPA prepared by adding trifluoroacetic anhydride (124 μL) to a 30 % aqueous H_2O_2 (22 μL) in CH_2Cl_2 (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 $LiAlH_4$ (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 CH_2Cl_2 (50 μL), and Et_3N (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 C_{18} HPLC (Wakosil-II 5C18 AR, 10 x 250 mm; eluent, CH_3CN/H_2O, 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:** ^{1}H NMR ($CDCl_3$) δ 1.34 (3H, d, *J* = 6.3 Hz, H_3-39), 1.97 (2H, m, H_2-17), 3.54 (3H, s, OCH_3), 3.56 (3H, s, OCH_3), 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; $[\alpha]_D$ +66° (*c* 1.0, $CHCl_3$); IR (neat) ν_{max} 1749, 1271, and 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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, $CHCl_3$); IR (neat) ν_{max} 1749, 1271, and 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$) 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 $CDCl_3$.

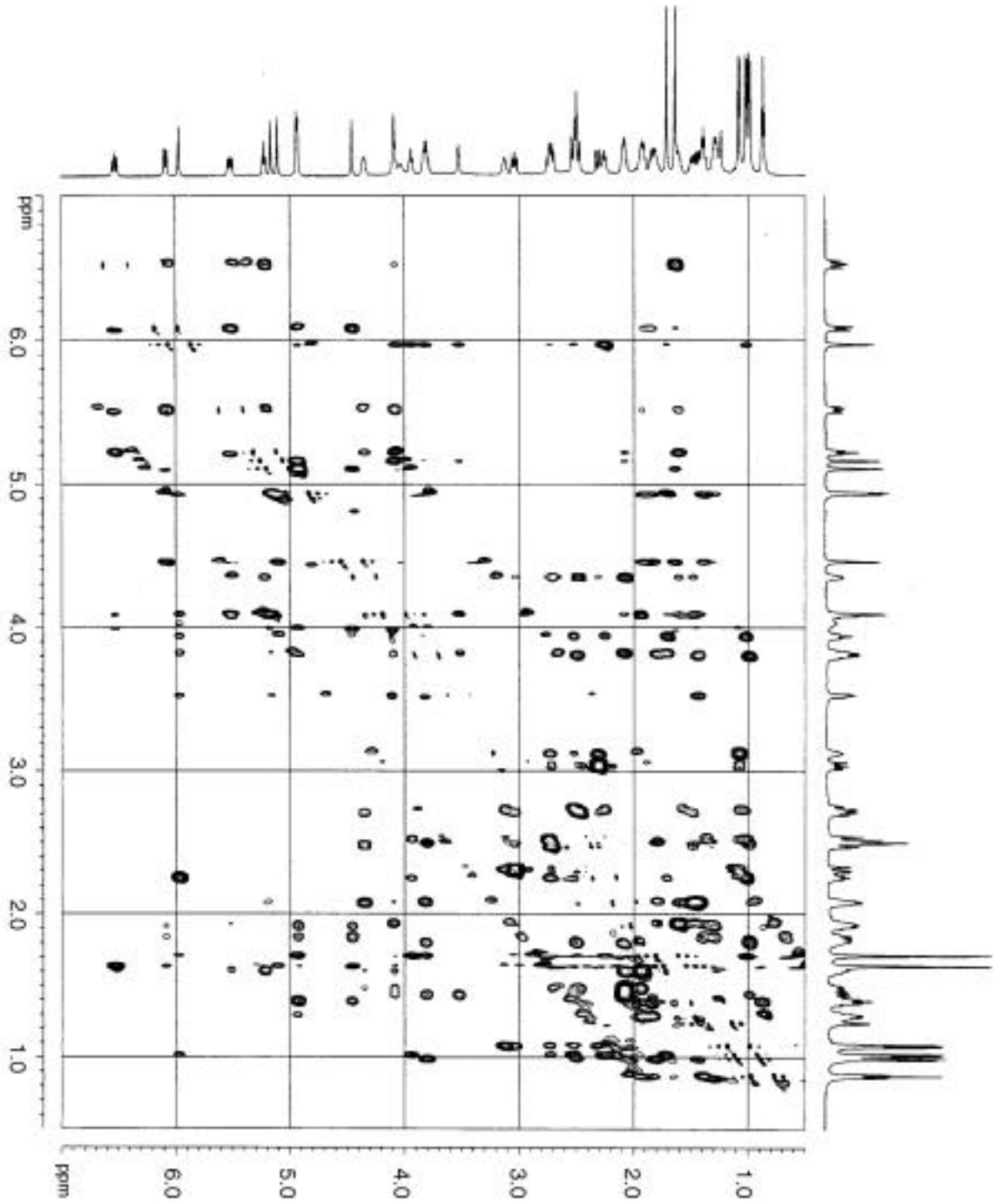
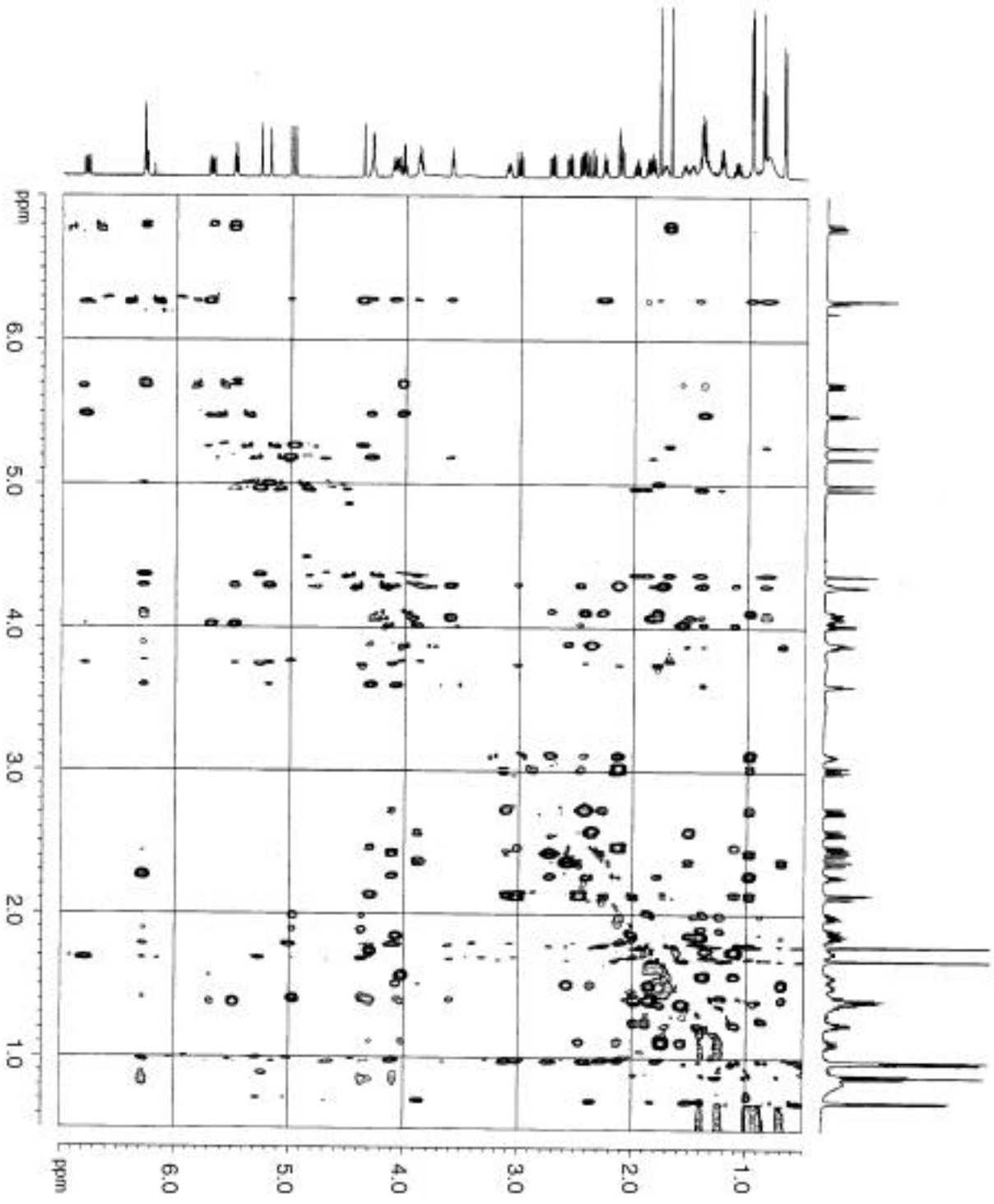


Figure S2. NOESY spectrum of amphidinolide C (**1**) in C_6D_6.



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

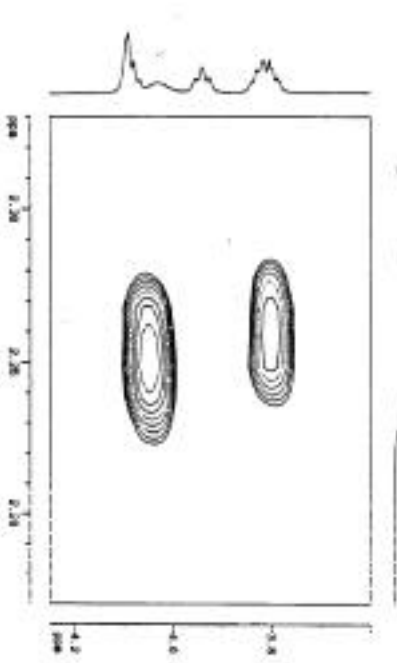


Figure S3. J(C-13,H-12)

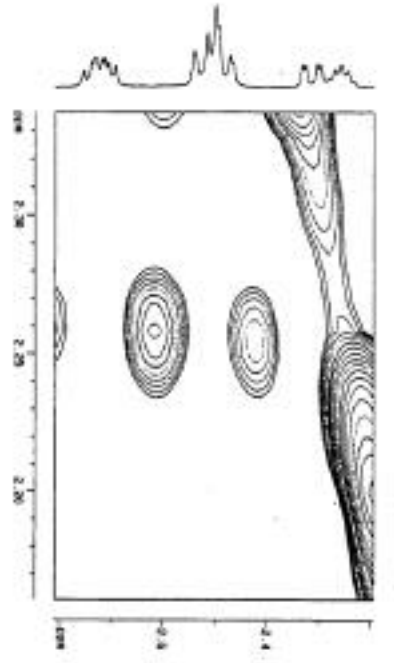


Figure S4. J(C-14,H-12)

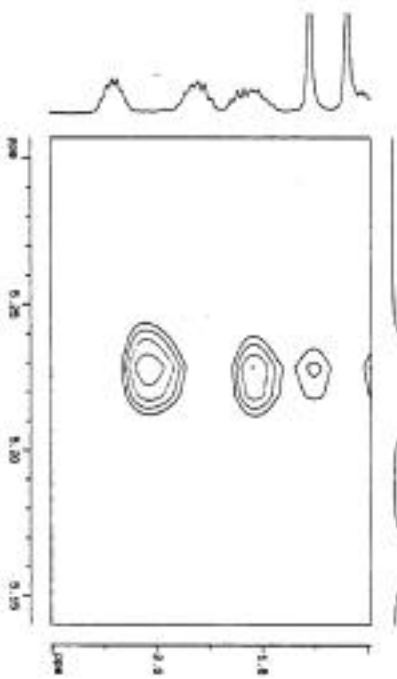


Figure S5. J(C-22,H-24)

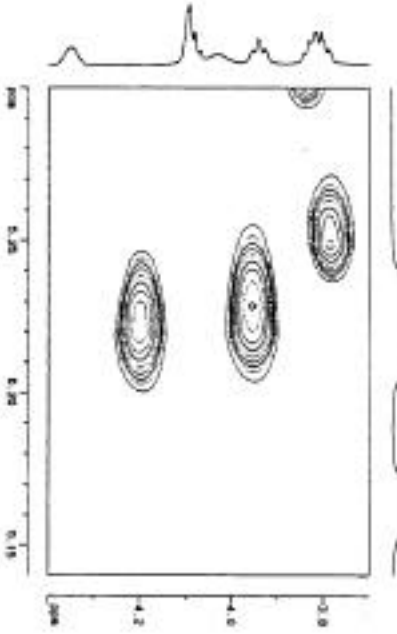


Figure S6. J(C-23,H-24)

Figures S7 and S8. HETLOC spectra (partial) of amphidinolide C (**1**) in $CDCl_3$.

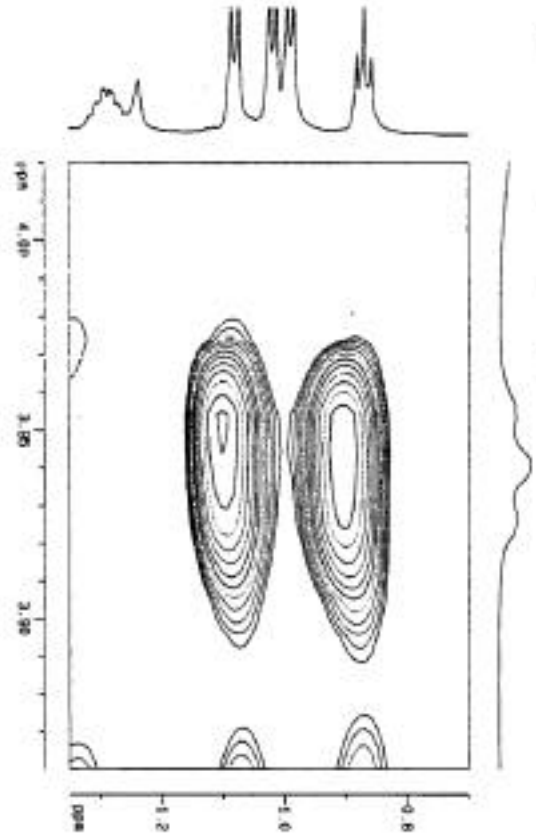


Figure S7. J(C-38,H-13)

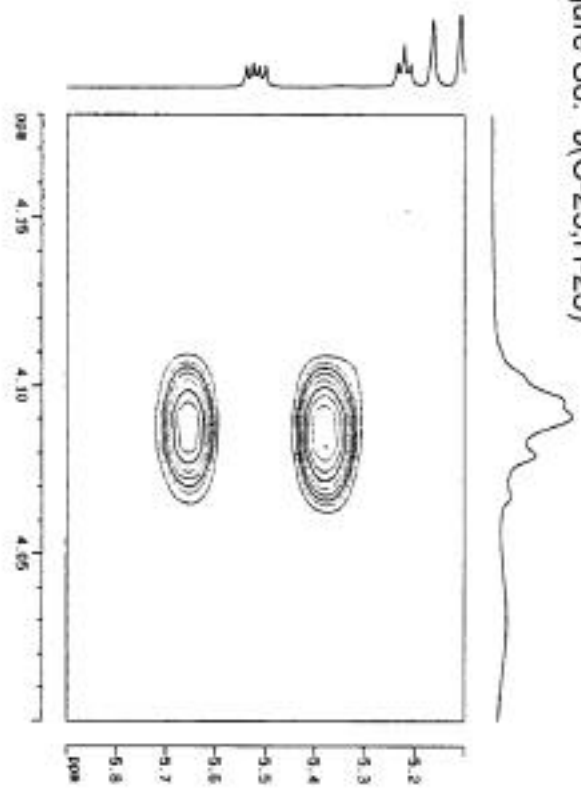


Figure S8. J(C-25,H-23)

Figure S9. ^{1}H NMR spectrum of 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**) in $CDCl_3$.

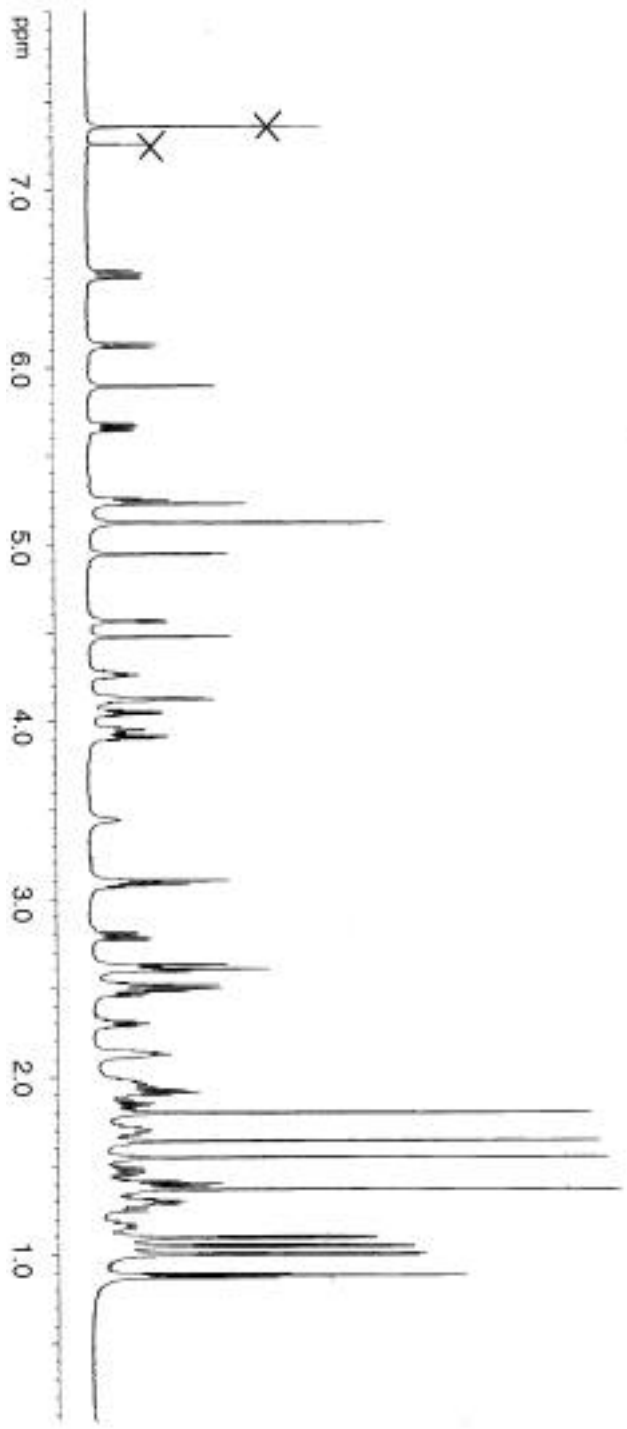


Figure S10. NOESY spectrum of 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**) in $CDCl_3$.

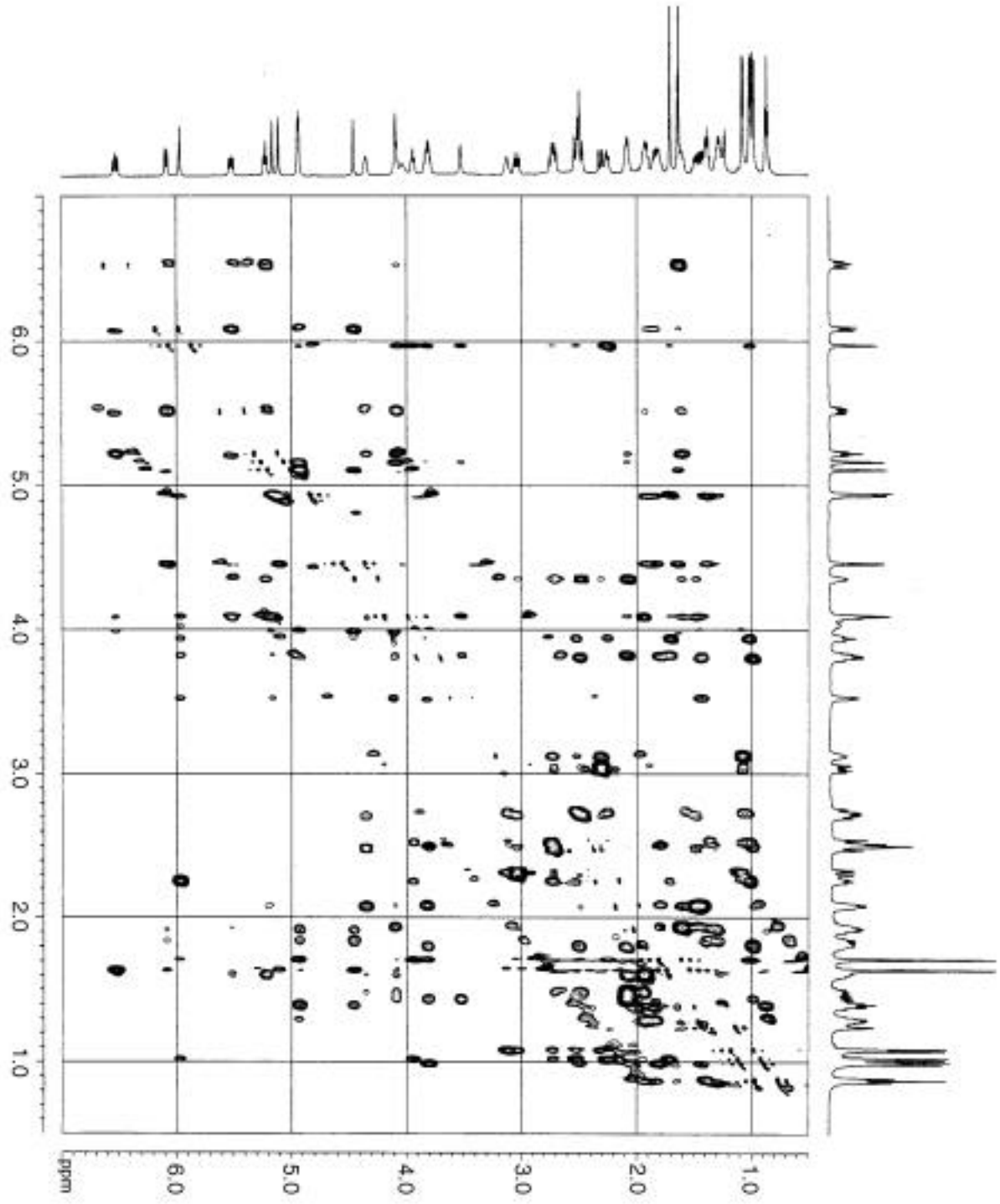


Figure S11. ^{1}H NMR spectrum of (*S*)-MTPA esters (**3a**) of the 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**) in $CDCl_3$.

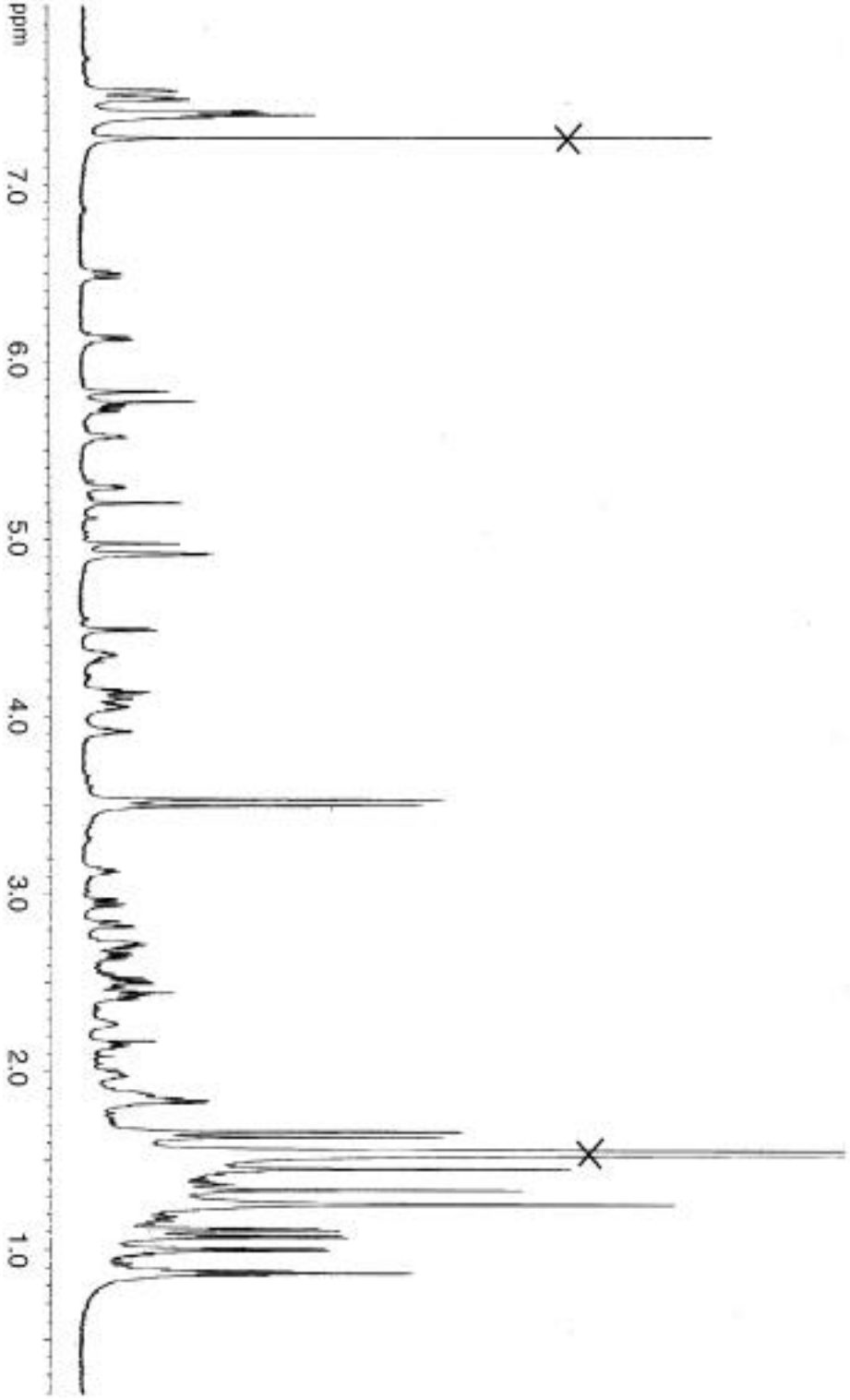


Figure S12. ^{1}H NMR spectrum of (*R*)-MTPA esters (**3b**) of the 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**) in $CDCl_3$.

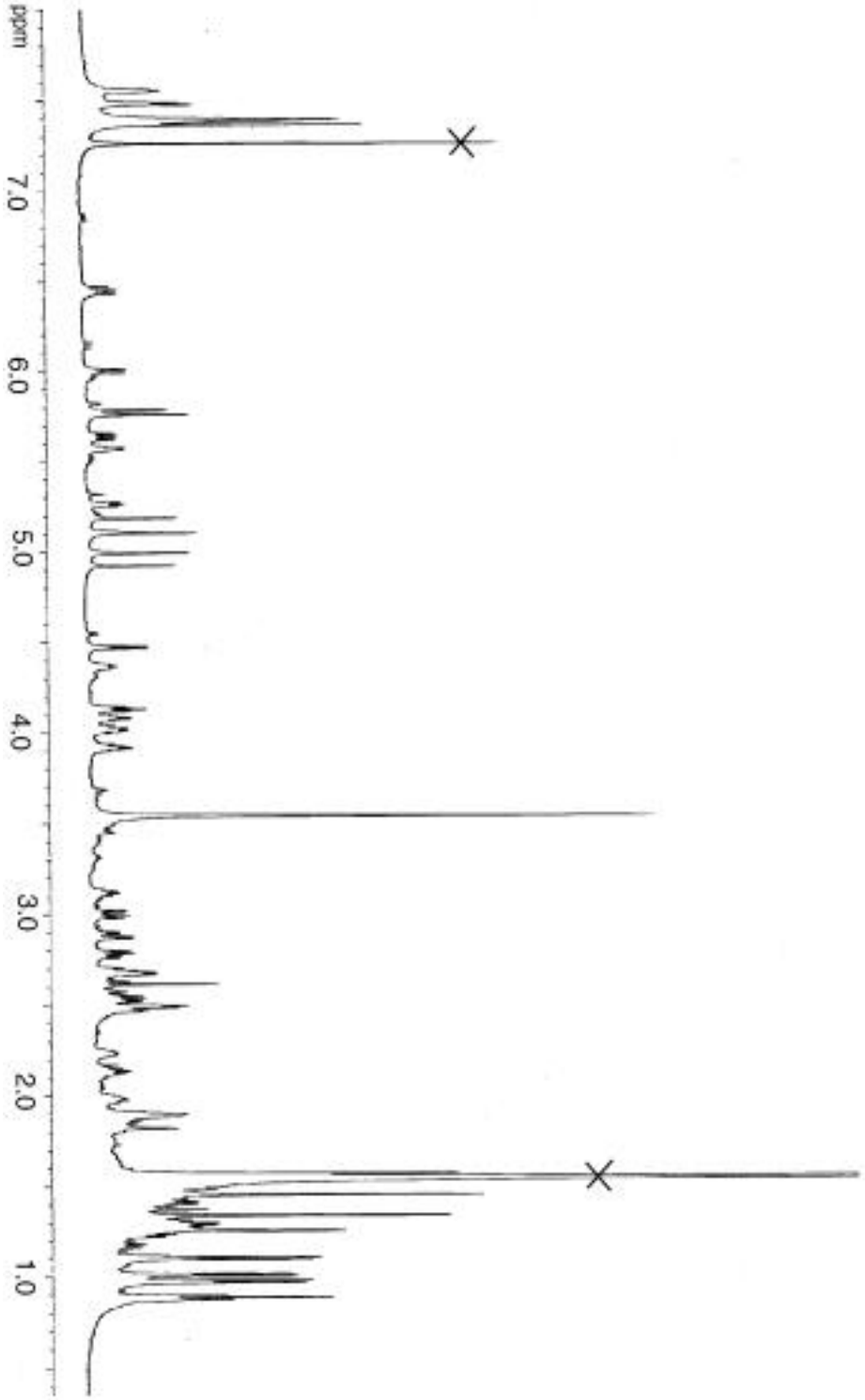


Figure S13. ^{1}H NMR spectrum of bis-(*S*)-MTPA ester (**4a**) of C-1–C-7 segment derived from amphidinolide C (**1**) in C_6D_6.

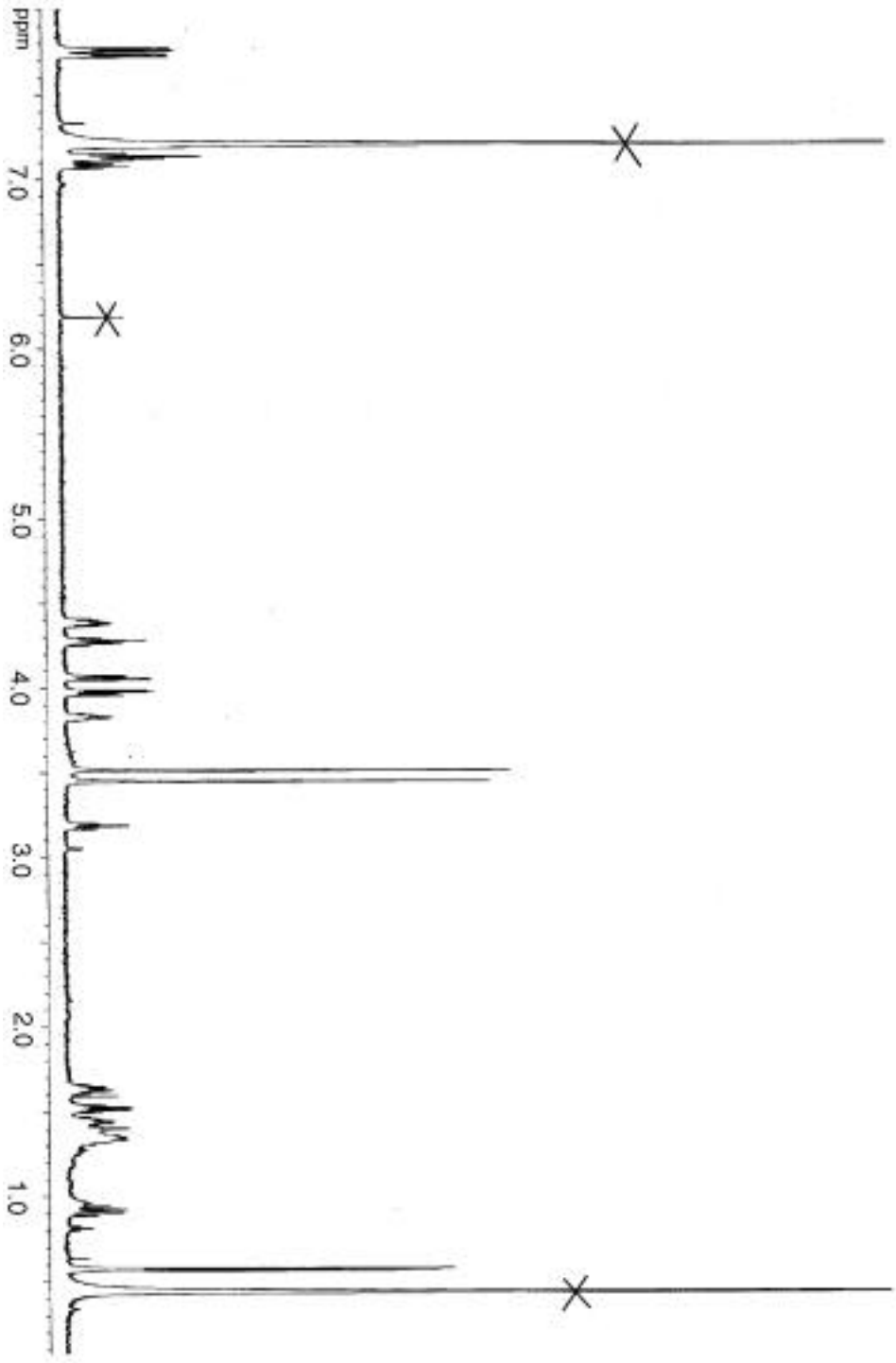


Figure S14. ^{1}H NMR spectrum of synthetic bis-(*S*)-MTPA ester (**4a**) of C-1–C-7 segment in C_6D_6.

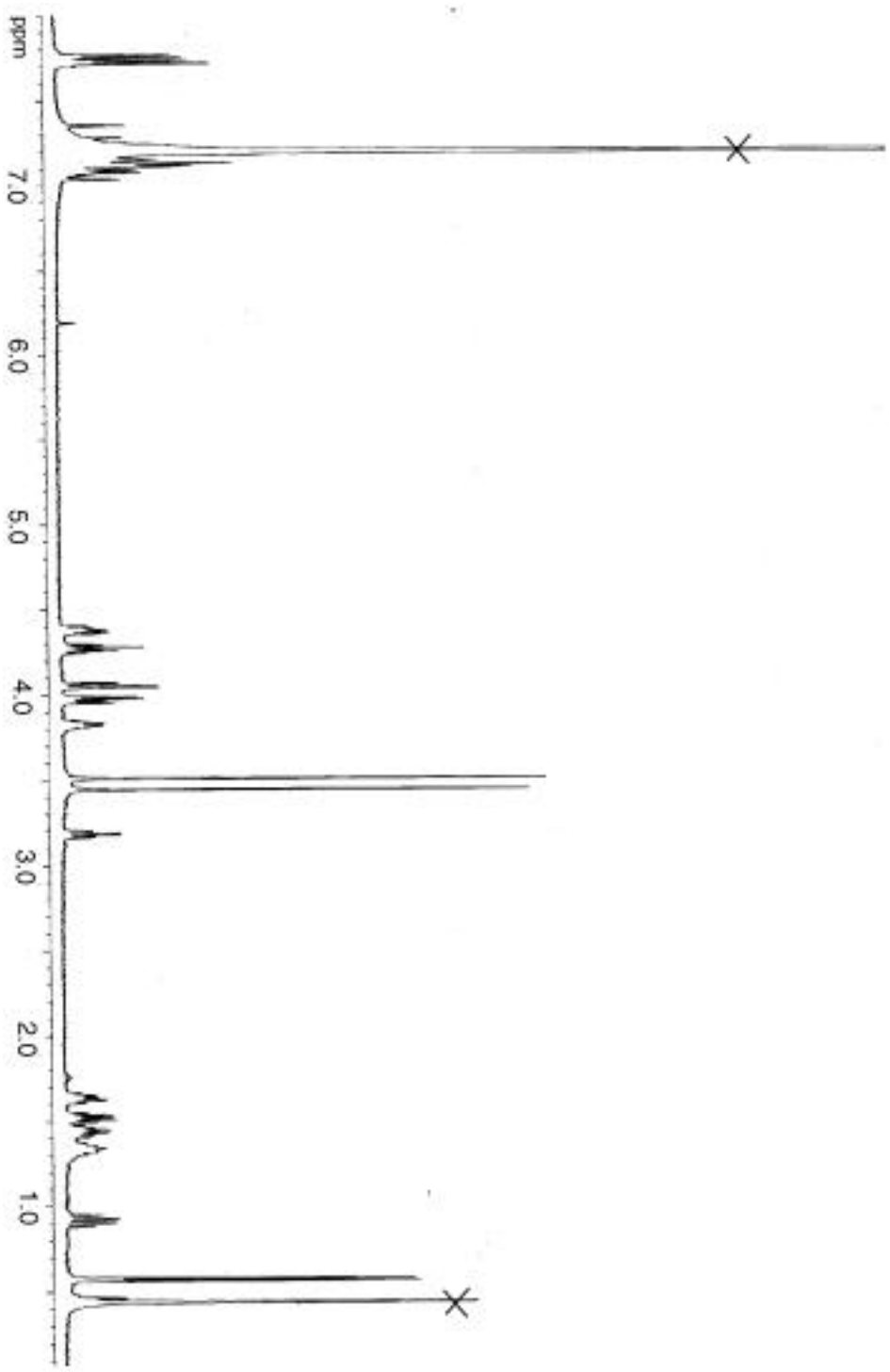


Figure S15. ^{1}H NMR spectrum of synthetic bis-(*R*)-MTPA ester (**4b**) of C-1–C-7 segment in C_6D_6.

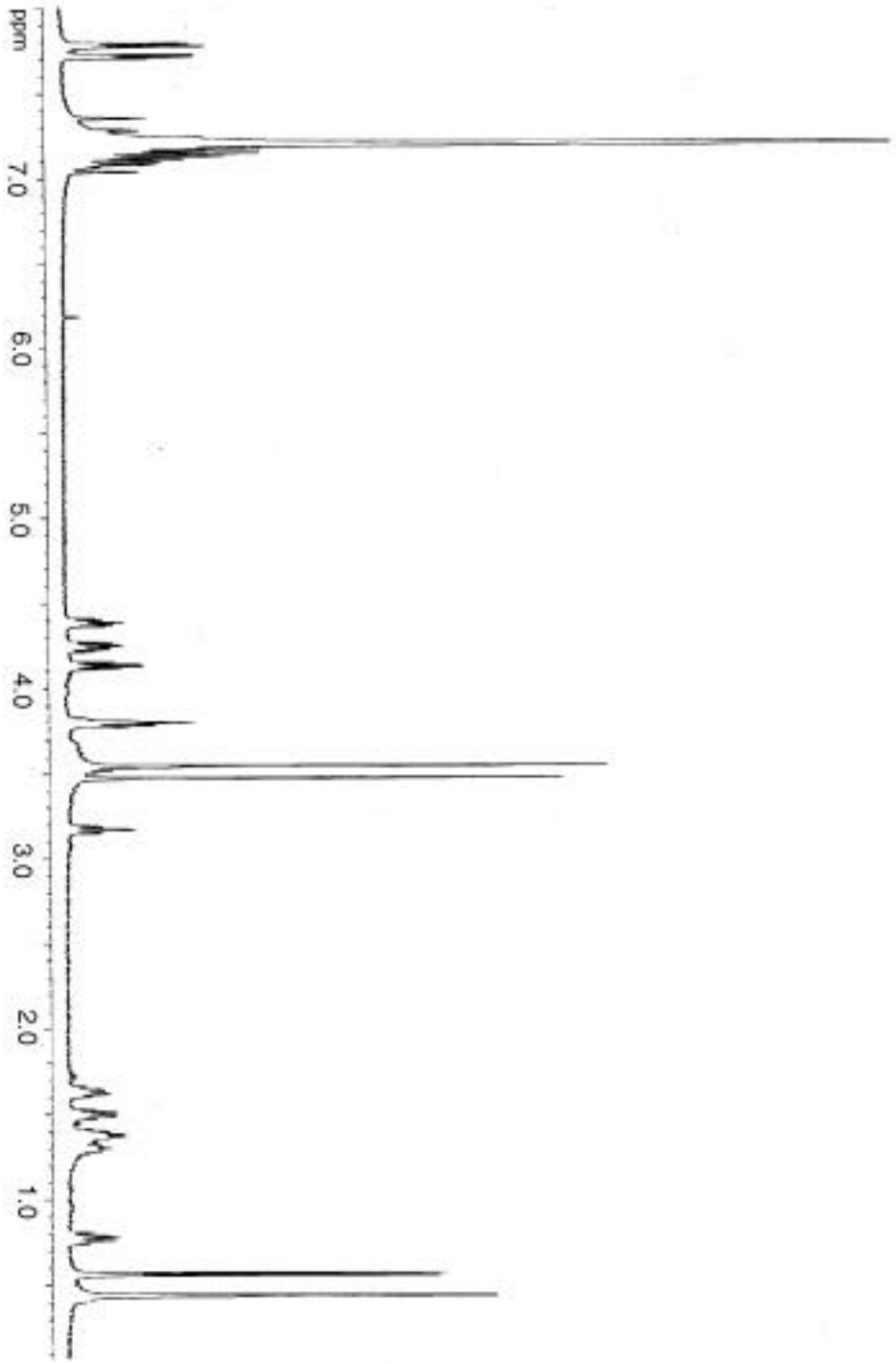


Figure S16. ^{1}H NMR spectrum of the pentakis-(*S*)-MTPA esters (**5a**) of the linear methyl ester of amphidinolide C (**1**) in $CDCl_3$.

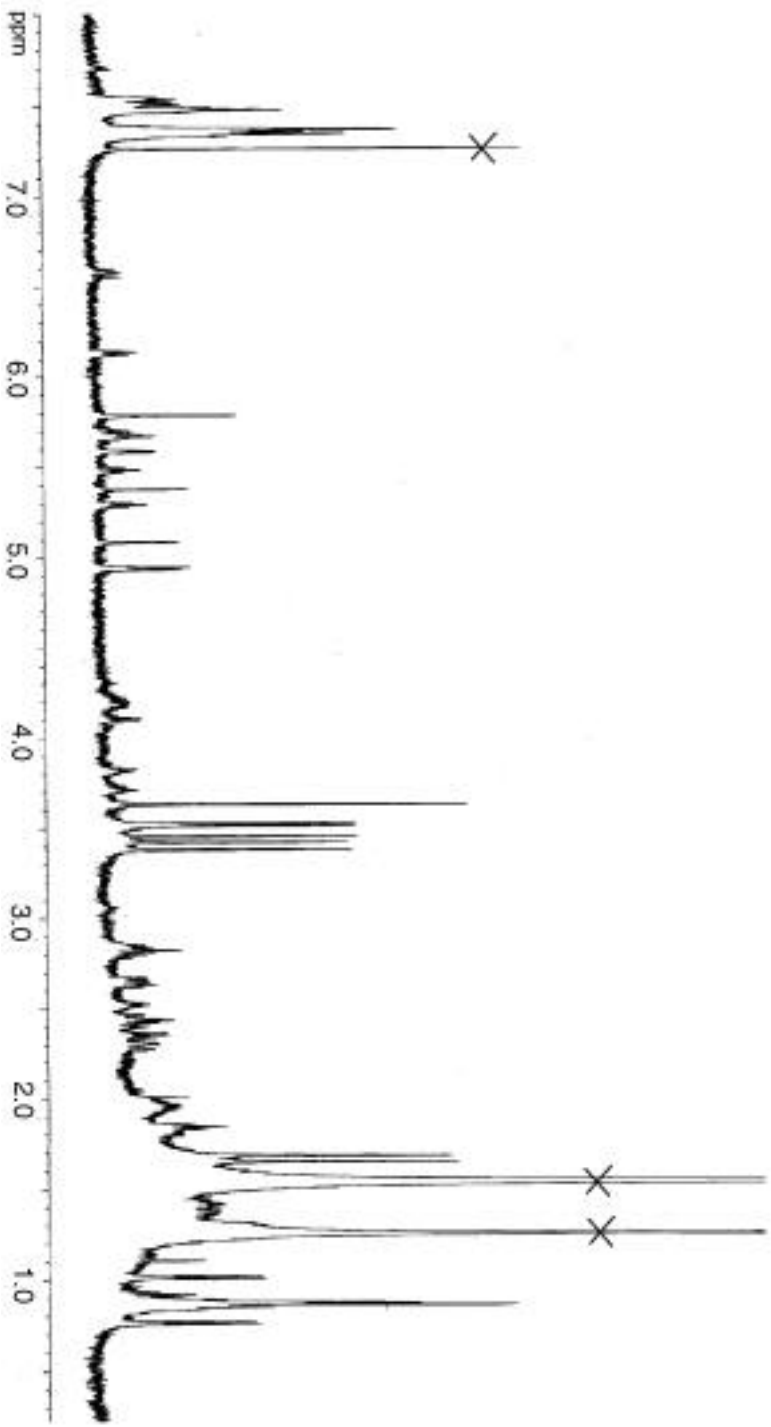


Figure S17. ^{1}H NMR spectrum of the pentakis-(*R*)-MTPA esters (**5b**) of the linear methyl ester of amphidinolide C (**1**) in $CDCl_3$.

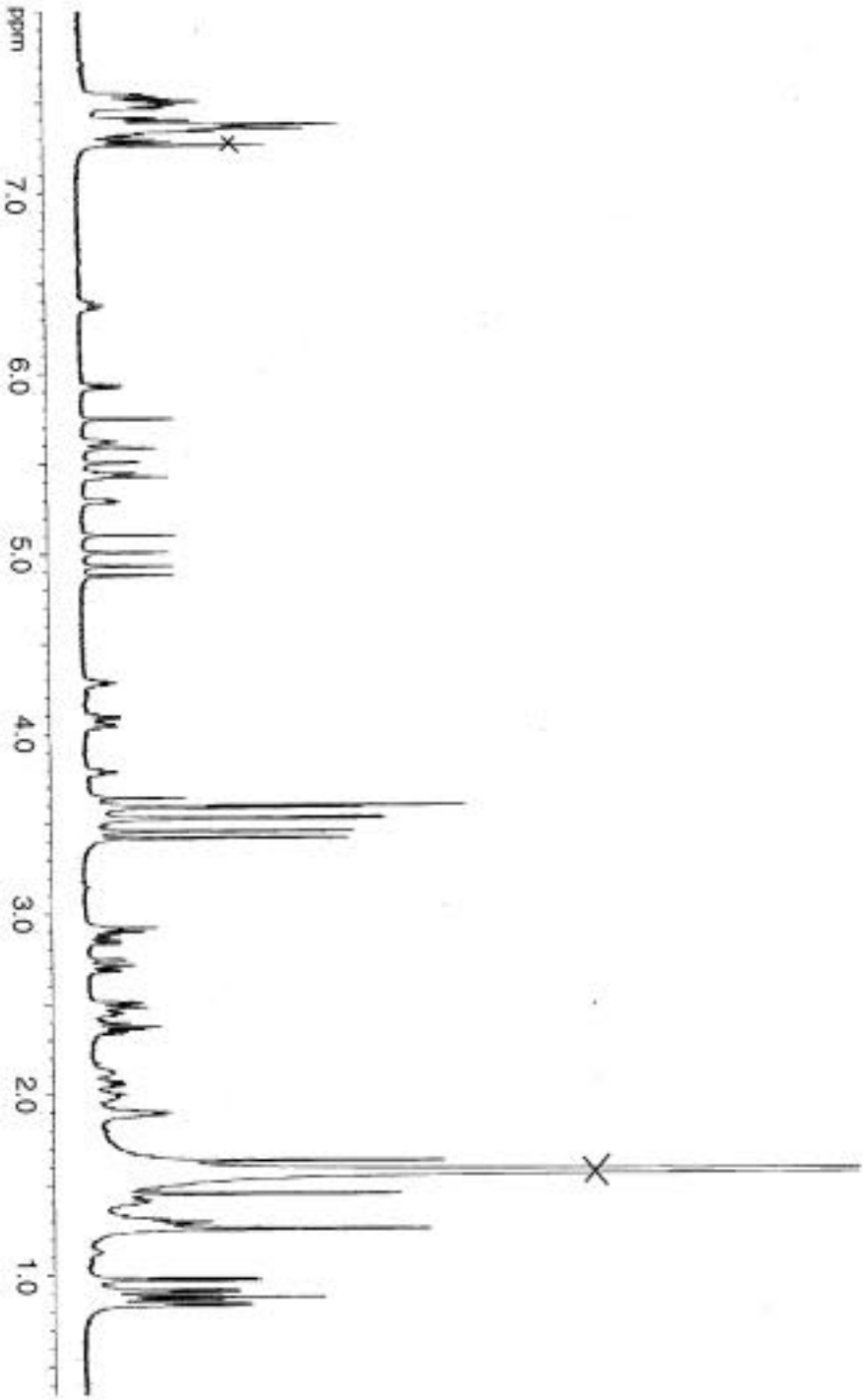


Figure S18. ^{1}H NMR spectrum of bis-(*R*)-MTPA ester (**6a**) of C-16–C-18 segment derived from amphidinolide C (**1**) in $CDCl_3$.

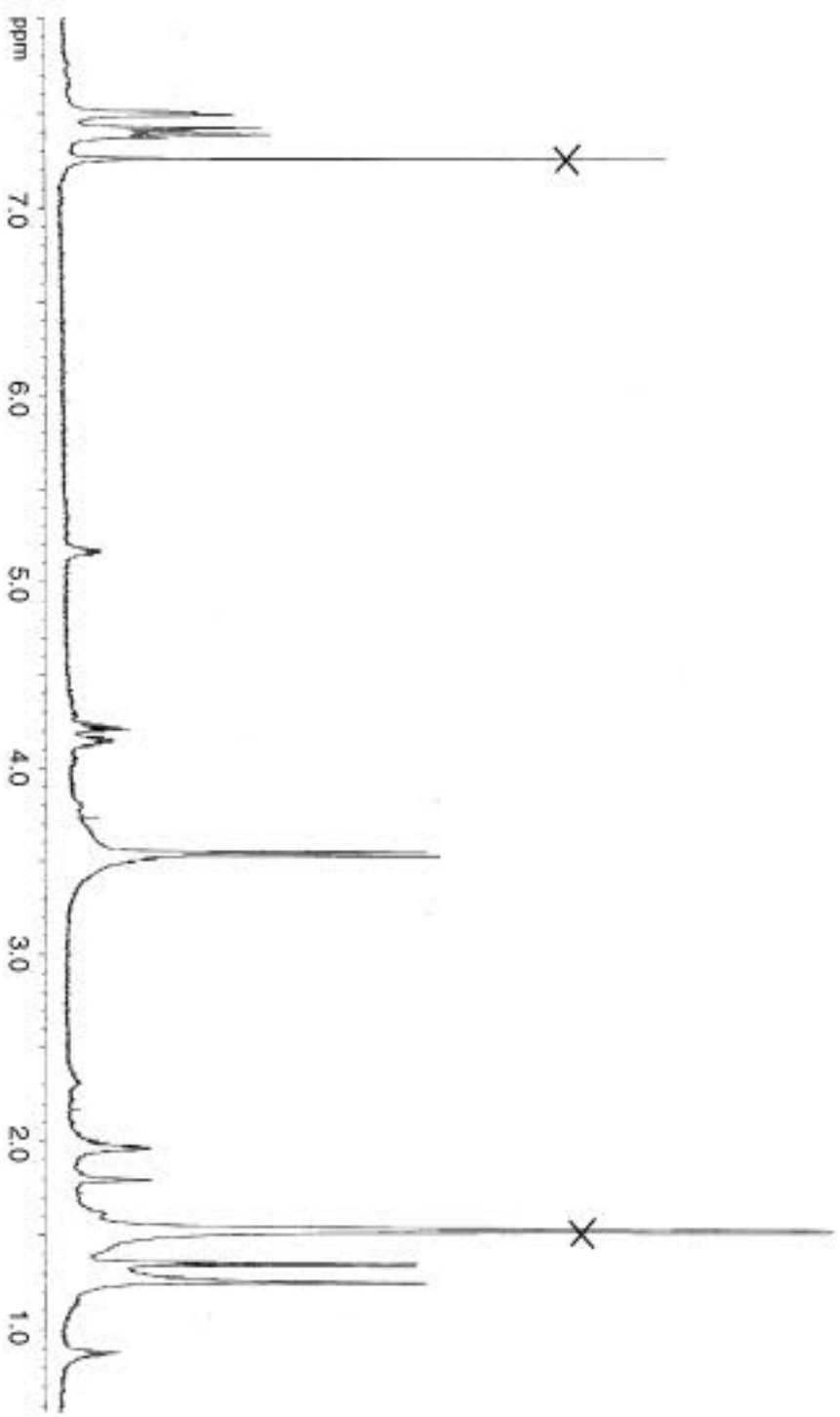


Figure S19. ^{1}H NMR spectrum of bis-(*R*)-MTPA ester (**6a**) of (*S*)-1,3-butanediol in $CDCl_3$.

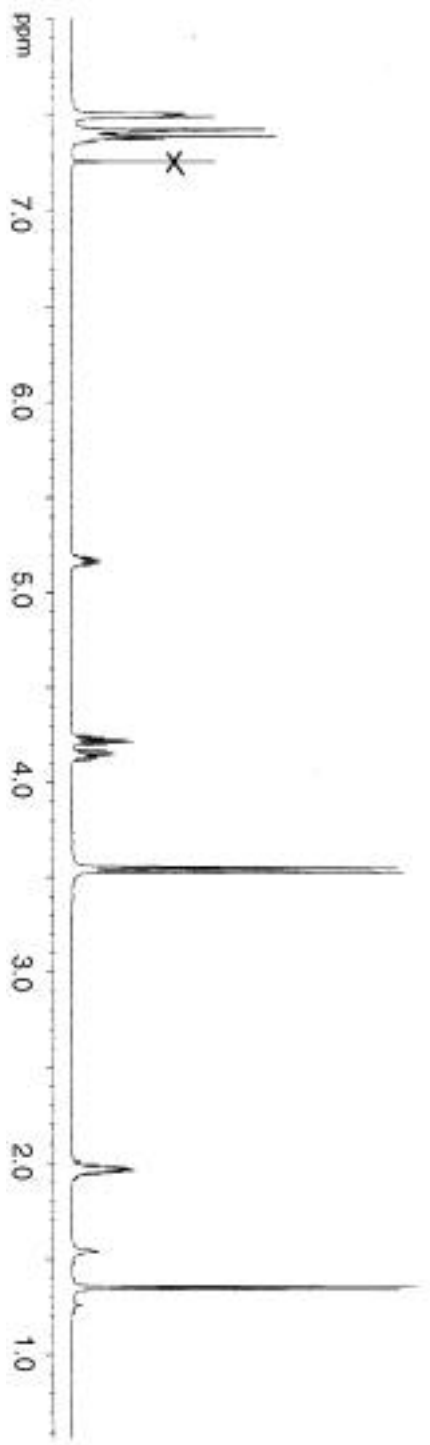


Figure S20. ^{1}H NMR spectrum of bis-(*R*)-MTPA ester (**6b**) of (*R*)-1,3-butanediol in $CDCl_3$.

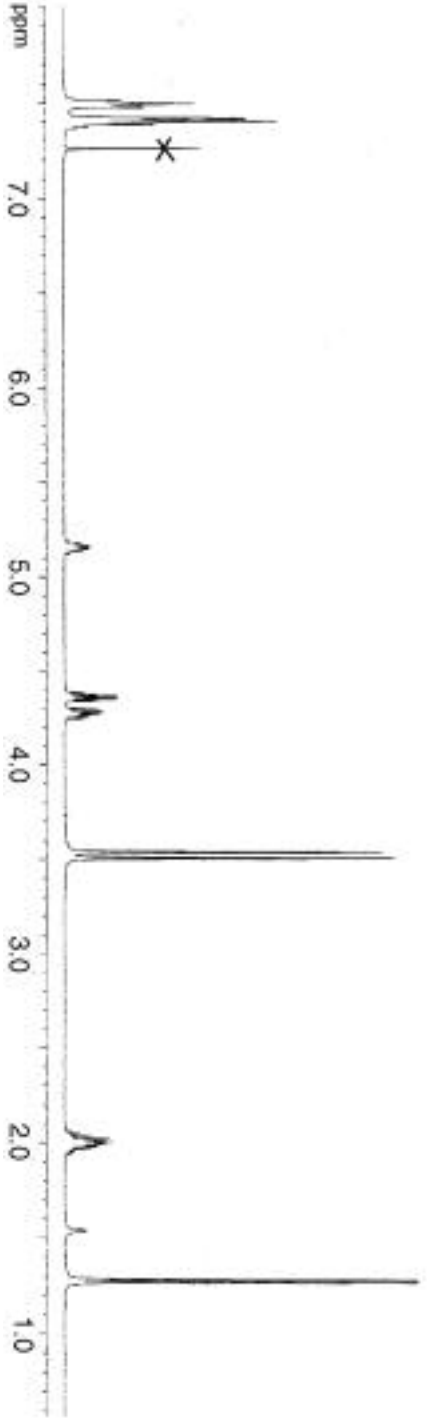


Table S1. ^{1}H NMR data of bis-(*S*)- and bis-(*R*)-MTPA esters (**3a** and **3b**, respectively) of the 7,8-*O*-isopropylidene derivative (**2**) of amphidinolide C (**1**)

		3a			**3b**	
positn.	δ_H	m	Hz	δ_H	m	Hz
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	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
8	4.486	d	6.9	4.472	d	7.1
10	5.829	s		5.787	s	
12	2.722	m		2.683	m	
13	5.576	dt	7.5, 4.8	5.573	dt	6.3, 5.2
14a	2.831	dd	15.9, 4.9	2.885	dd	16.4, 5.6
14b	2.651	dd	15.9, 7.5	2.779	dd	16.4, 7.1
16	3.132	m		3.123	dq	13.0, 7.1
17a	2.950	dd	18.3, 8.1	3.001	dd	18.2, 7.8
17b	2.424	dd	18.3, 5.1	2.508	dd	18.2, 5.6
19a	2.711	dd	14.2, 6.7	2.686	dd	14.1, 7.4
19b	2.437	m		2.481	dd	14.1, 6.0
20	4.347	m		4.366	dt	14.9, 6.0
21a	2.274	m		2.245	m	
21b	1.437	m		1.471	m	
22a	1.981	m		1.990	m	
22b	1.871	m		1.837	m	
23	4.099	dt	4.3, 7.3	4.081	dt	4.5, 7.3
24	5.290	dd	7.5, 3.9	5.266	dd	7.8, 4.5
25	5.736	dd	15.5, 7.5	5.639	dd	15.3, 7.8
26	6.493	dd	15.5, 10.8	6.451	dd	15.3, 10.8
27	6.130	d	10.8	6.003	d	10.8
29	5.772	s		5.762	s	
31	1.835[a]	m		1.902[a]	m	
32	1.373[a]	m		1.410[a]	m	
33	1.263[a]	m		1.293[a]	m	
34	0.870[b]	t	7.3	0.886[b]	t	7.4
35	1.001[b]	d	6.5	1.013[b]	d	6.3
36a	5.201	s		5.188	s	
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
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_3-2	1.335[b]	s		1.338[b]	s	
Ph	7.36 ~ 7.54[c]		m	7.34 ~ 7.58[c]		m
OCH_3-1	3.529[b]	s		3.541[b]	s	
OCH_3-2	3.495[b]	s		3.541[b]	s	

[a]2H. [b]3H. [c]10H.

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

		5a			**5b**	
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	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		2.858	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	1.841[a]	m		1.900[a]	m	
32	1.377[a]	m		1.409[a]	m	
33	1.283[a]	m		1.299[a]	m	
34	0.875[b]	t	7.3	0.879[b]	t	7.4
35	0.867[b]	d	6.5	0.978[b]	d	6.4
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
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 ~ 7.56[c]	m		7.27 ~ 7.56[c]	m	
OCH_3-1	3.381[b]	s		3.420[b]	s	
OCH_3-2	3.422[b]	s		3.457[b]	s	
OCH_3-3	3.454[b]	s		3.527[b]	s	
OCH_3-4	3.513[b]	s		3.534[b]	s	
OCH_3-5	3.526[b]	s		3.588[b]	s	

[a]2H. [b]3H. [c]25H.