Supporting Information

Synthesis of 17-membered azalides from a 16-membered macrolide utilizing amide-selective silane reduction

Atsushi Seki,*[a] Toshihiro Mori,[a] Kouji Sasaki,[a] Yoshiaki Takahashi,[a] Toshiaki Miyake[a] and Yuzuru Akamatsu[b]

[a] *Institute of Microbial Chemistry (BIKAKEN), Hiyoshi, Japan*

[b] *Institute of Microbial Chemistry (BIKAKEN), Tokyo, Japan*

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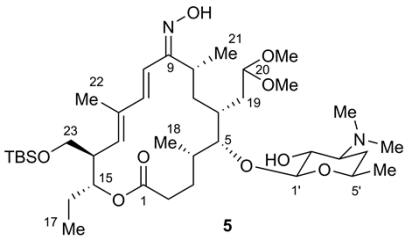
1. General Information

Melting points were recorded on an MP-S3 micro melting apparatus (Yanaco New Science Inc., Japan) and were uncorrected. Optical rotations were determined with a 241 polarimeter (PerkinElmer Inc., Waltham, MA, USA). NMR spectra were recorded with an AVANCE 500 (^{1}H at 500, ^{13}C at 125.8 MHz) and AVANCE 400 (^{1}H at 400, ^{13}C at 100.6 MHz) spectrometer (Bruker BioSpin, Rheinstetten, Germany) at 300 K, unless stated otherwise. Chemical shifts (δ) of ^{1}H and ^{13}C spectra were measured downfield from internal Me_4Si (for ^{1}H and ^{13}C), and were confirmed, when necessary, by shift-correlated two-dimensional spectra. Data are reported as ovlp = overlapping, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Mass spectra were recorded using a LTQ Orbitrap mass spectrometer (Thermo Fisher Scientific, San Jose, CA, USA). Hydorosilylations were carried out in oven-dried glassware sealed with rubber septa under nitrogen, and solutions were transferred by syringe. Unless indicated otherwise, reagents and solvents were purchased and used without purification. Preparative high performance liquid chromatography (HPLC) was carried out on a Waters Delta 600 chromatograph or Senshu SSC-6200 equipped with or without a UV wavelength detector. Column chromatography was carried out on Wakogel C-300 (Wako Pure Chemical Industries, Ltd., Osaka, Japan). TLC was performed on a Kieselgel 60 F_{254} (Merck, Darmstadt, Germany). TLC plates were visualized under UV light and treatment with either acidic *p*-anisaldehyde stain or aqueous ceric ammonium molybdate solution followed by gentle heating.

2. Preparation of (9*E*)-20-deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]-9-hydroxyiminotylonolide (5) and (9*Z*)-20-deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]-9-hydroxyiminotylonolide (6)

To a solution of 20-deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*- hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]tylonolide (**4**, 1.45 g, 2.0 mmol) in methanol (2.8 mL), hydroxylamine hydrochloride (276 mg, 4.0 mmol) and pyridine (0.34 mL) were added and the mixture was heated at 50°C for 6 h. Concentration gave a residue, which was diluted with $CHCl_3$. The organic solution was washed with 5 wt% aqueous $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to give a solid (1.57 g). The solid was purified by preparative HPLC [Senshu Pak Silica-6251S normal phase column (30 mm × 250mm) using $CHCl_3$/MeOH/28% NH_4OH (40:1:0.1) solvent system, flow rate of 13 mL/min] yielded (*E*)-oxime **5** (16 min, 579 mg, 39%) and (*Z*)-oxime **6** (20 min, 326 mg, 22%) as crystalline solids.



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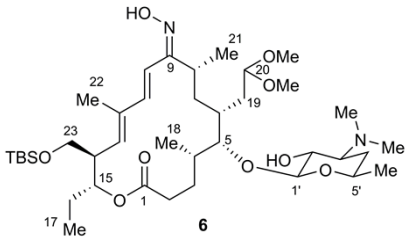


6

(9*E*)-20-Deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]-9-hydroxyiminotylonolide (5):

mp 88-89 °C ($CHCl_3$/hexane); $[\alpha]_D^{20}$ +20° (*c* 1.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.025 and 0.033 (each s, 3H, Me_2Si-), 0.88 (s, 9H, Me_3C-Si), 0.92 (t, *J* = 7.5 Hz, 3H, Me-17), 1.05 (d, *J* = 6.5 Hz, 3H, Me-18), 1.10 (d, *J* = 7.0 Hz, 3H, Me-21), 1.19 (ovlp, 1H, H-3a), 1.24 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.26 (ovlp, 1H, H-4'*ax*), 1.50 (ovlp, 1H, H-3b), 1.53 (ovlp, 2H, H-7a,b), 1.54 (ovlp, 1H, H-6), 1.57 (ovlp, 1H, H-16a), 1.65 (ovlp, 1H, H-4'*eq*), 1.68 (m, 1H, H-4), 1.78 (s, 3H, Me-22), 1.78 (ovlp, 1H, H-19a), 1.86 (ddd, *J* = 3.0, 12.5, and 16.0 Hz, 1H, H-2a), 1.87 (ovlp, 1H, H-16b), 2.27 (s, 6H, Me_2N-3'), 2.38 (ddd, *J* = 6.0, 12.5, and 16.0 Hz, 1H, H-2b), 2.49 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.73 (apparently septet, *J* = 5.0 Hz, 1H, H-14), 3.23 (s, 3H, MeO), 3.25 (dd, *J* = 7.5 and 10.0 Hz, 1H, H-2'), 3.30 (d, *J* = 10.0 Hz, 1H, H-5), 3.32 (s, 3H, MeO), 3.41 (br s, 1H, HO-2'), 3.49 (m, 1H, H-5'), 3.65 (dd, *J* = 4.5 and 10.0 Hz, 1H, H-23a), 3.67 (dd, *J* = 5.0 and 10.0 Hz, 1H, H-23b), 3.71 (m, 1H, H-8), 4.25 (d, *J* = 7.5 Hz, 1H, H-1'), 4.58 (dd, *J* = 5.0 and 7.5 Hz, 1H, H-20), 4.89 (dt, *J* = 2,5, 9.5, and 9.5 Hz, 1H, H-15), 5.50 (d, *J* = 10.5 Hz, 1H, H-13), 5.91 (d, *J* = 15.5 Hz, 1H, H-10), 6.77 (d, *J* = 15.5 Hz, 1H, H-11), and 7.71 (br s, 1H, NOH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.1 (2C, Me_3C-Si$\underline{Me_2}$), 10.2 (C-17), 13.3 (C-22), 16.0 (C-18), 18.6 ($Me_3\underline{C}$-Si), 19.2 (C-21), 21.5 (C-6'),

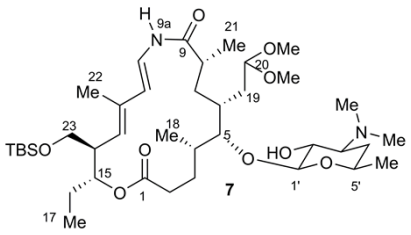
26.1 (C-16), 26.2 ($\underline{Me_3}$C-Si), 26.7 (C-8), 28.8 (C-3), 28.9 (C-4'), 31.2 (C-19), 32.8 (C-2), 33.0 (C-7), 33.4 (C-6), 36.9 (C-4), 40.7 (Me_2N-3'), 46.9 (C-14), 50.3 (MeO), 54.1 (MeO), 63.8 (C-23), 66.1 (C-3'), 69.8 (C-5'), 71.0 (C-2'), 75.6 (C-15), 85.2 (C-5), 103.5 (C-20), 105.0 (C-1'), 117.9 (C-10), 135.5 (C-12), 135.9 (C-13), 138.5 (C-11), 162.8 (C-9), and 174.1 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{73}O_9N_2Si$ $[M + H]^+$ 741.5080, *m/z* obsd 741.5074.

(9*E*)-20-Deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]- 9-hydroxyiminotylonolide (6):

mp 72-73 °C ($CHCl_3$/hexane); $[\alpha]_D^{21}$ −16° (*c* 1.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.032 and 0.037 (each s, 3H, Me_2Si-), 0.88 (s, 9H, Me_3C-Si), 0.92 (t, *J* = 7.5 Hz, 3H, Me-17), 1.03 (d, *J* = 6.5 Hz, 3H, Me-18), 1.16 (d, *J* = 7.0 Hz, 3H, Me-21), 1.24 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.26 (ovlp, 1H, H-4'*ax*), 1.27 (ovlp, 1H, H-3a), 1.50 (ovlp, 1H, H-3b), 1.51 (ovlp, 2H, H-7a,b), 1.59 (ovlp, 1H, H-16a), 1.65 (ovlp, 1H, H-4'*eq*), 1.68 (ovlp, 1H, H-4), 1.70 (ovlp, 1H, H-19a), 1.71 (ovlp, 1H, H-6), 1.80 (s, 3H, Me-22), 1.88 (ddd, *J* = 3.0, 12.0, and 15.5 Hz, 1H, H-2a), 1.88 (ovlp, 1H, H-16b), 1.96 (ddd, 1H, *J* = 5.0, 10.0, and 15.0, H-19b), 2.28 (s, 6H, Me_2N-3'), 2.37 (ddd, *J* = 6.0, 12.5, and 15.5 Hz, 1H, H-2b), 2.50 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.65 (m, 1H, H-8), 2.79 (apparently septet, *J* = 5.0 Hz, 1H, H-14), 3.25 (dd, *J* = 7.2 and 10.0 Hz, 1H, H-2'), 3.27 (s, 3H, MeO), 3.32 (s, 3H, MeO), 3.36 (d, *J* = 9.0 Hz, 1H, H-5), 3.44 (slightly br s, 1H, HO-2'), 3.49 (m, 1H, H-5'), 3.67 (d, *J* = 5.0 Hz, 2H, H-23a,b), 4.28 (d, *J* = 7.2 Hz, 1H, H-1'), 4.62 (dd, *J* = 5.0 and 7.0 Hz, 1H, H-20), 4.90 (dt, *J* = 2.5, 9.5, and 9.5 Hz, 1H, H-15), 5.54 (d, *J* = 10.5Hz, 1H, H-13), 5.92 (d, *J* = 16.0 Hz, 1H, H-10), 7.30 (d, *J* = 16.0 Hz, 1H, H-11), and 8.59 (br s, 1H, NOH); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.5 (2C, Me_3C-Si$\underline{Me_2}$), 9.7 (C-17), 12.5 (C-22), 15.4 (C-18), 18.2 ($Me_3\underline{C}$-Si), 19.7 (C-21), 21.1 (C-6'), 25.9 (4C, $\underline{Me_3}$C-Si and C-16), 28.7 (C-4'), 28.9 (C-3), 30.9 (C-19), 32.5 (C-2), 33.9 (2C, C-6 and 7), 35.5 (C-8), 36.2 (C-4), 40.3 (Me_2N-3'), 46.5 (C-14), 50.4 (MeO), 53.2 (MeO), 63.7 (C-23), 65.6 (C-3'), 69.4 (C-5'), 70.5 (C-2'), 75.4 (C-15), 84.5 (C-5), 102.8 (C-20), 104.8 (C-1'), 113.2 (C-10), 135.8 (C-12), 136.4 (C-13), 144.9 (C-11), 157.9 (C-9), and 173.8 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{73}O_9N_2Si$ $[M + H]^+$ 741.5080, *m/z* obsd 741.5076. Anal calcd for $C_{39}H_{72}O_9N_2Si$: C, 63.21; H, 9.73; N, 3.78. Found: C, 63.57, H, 9.79; N, 3.89.

3. Beckmann rearrangement of 5 and 6

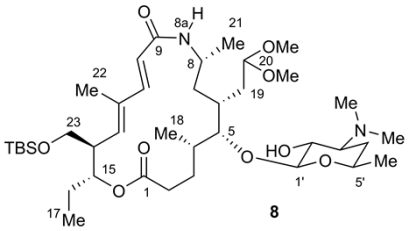
9a-Aza-9a-homo-20-deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]tylonolide (7):



To a stirred solution of **5** (371 mg, 0.5 mmol) in acetone (5 mL), 2,4,6-trimethylbenzenesulfonyl chloride (226 mg, 1.03 mmol) in acetone (20 mL) and $NaHCO_3$ (150 mg, 1.79 mmol) in water (18.5 mL) were added dropwise at 0 °C and the mixture was stirred for 3 days at room temperature. The solution was concentrated to a small volume, diluted with $CHCl_3$, and the organic solution was dried over Na_2SO_4 and concentrated. The resulting residue was purified by preparative HPLC [Senshu Pak Silica-6251S normal phase column (30 mm × 250 mm) using $CHCl_3$/MeOH/28% NH_4OH (40:1:0.1) solvent system] yielded lactam **7** (222 mg, 60%) as a colorless solid, $[\alpha]_D^{23}$ +60° (*c* 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 6H, Me_2Si-), 0.88 (s, 9H, Me_3C-Si), 0.92 (t, *J* = 7.5 Hz, 3H, Me-17), 0.95 (d, *J* = 6.5 Hz, 3H, Me-18), 1.14 (d, *J* = 6.5 Hz, 3H, Me-21), 1.16 (ovlp, 1H, H-3a), 1.24 (ovlp, 1H, H-4), 1.25 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.28 (ovlp, 1H, H-4'*ax*), 1.31 (ovlp, 1H, H-7a), 1.55 (ovlp, 1H, H-3b), 1.55 (ovlp, 1H, H-19a), 1.58 (ovlp, 1H, H-16a), 1.64 (ovlp, 1H, H-6), 1.66 (ovlp, 1H, H-7b), 1.68 (ovlp, 1H, H-4'*eq*), 1.76 (s, 3H, Me-22), 1.77 (ovlp, 1H, H-2a), 1.87 (ddq, *J* = 2.5, 7.5, 7.5, 7.5, and 14.5 Hz, 1H, H-16b), 2.20 (ddd, *J* = 2.5, 9.0, and 14.0 Hz, 1H, H-19b), 2.25 (ovlp, 1H, H-8), 2.30 (s, 6H, Me_2N-3'), 2.33 (ovlp, 1H, H-2b), 2.52 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.69 (apparently septet, *J* = 5.0 Hz, 1H, H-14), 3.07 (d, 1H, *J* = 10.0 Hz, H-5), 3.24 (dd, *J* = 7.0 and 10.0 Hz, 1H, H-2'), 3.41 (s, 3H, MeO), 3.51 (ovlp, 1H, H-5'), 3.53 (s, 3H, MeO), 3.66 (d, *J* = 5.1 Hz, 2H, H-23a,b), 4.13 (d, *J* = 7.0 Hz, 1H, H-1'), 4.41 (dd, *J* = 2.5 and 7.5 Hz, 1H, H-20), 4.82 (dt, *J* = 2.5, 9.5, and 9.5 Hz, 1H, H-15), 5.04 (d, *J* = 10.5 Hz, 1H, H-13), 5.75 (d, *J* = 14.5 Hz, 1H, H-11), 6.96 (dd, *J* = 11.0 and 14.5 Hz, 1H, H-10), and 7.65 [d, *J* = 11.0 Hz, 1H, NH(9a)]; ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.47 (Me_3C-Si<u>Me</u>), −5.42 (Me_3C-Si<u>Me</u>), 10.2 (C-17), 13.3 (C-22), 15.2 (C-18), 18.2 (Me_3<u>C</u>-Si), 17.3 (C-21), 21.2 (C-6'), 25.8 (<u>Me$_3$</u>C-Si), 26.5 (C-16), 28.9 (C-4'), 30.7 (C-3), 31.4 (C-2), 34.5 (C-6), 35.6 (C-19), 37.4 (C-4), 37.5 (C-7), 38.3 (C-8), 40.3 (Me_2N-3'), 46.5 (C-14), 52.7 (MeO), 55.2 (MeO), 64.0 (C-23), 65.5 (C-3'), 69.3 (C-5'), 70.5 (C-2'), 76.0 (C-15), 86.1 (C-5), 104.5 (C-20), 104.6 (C-1'), 117.3 (C-11), 121.7 (C-10), 128.0 (C-13), 134.6 (C-12), 174.1 (C-1), and 175.1 (C-9); HRMS (ESI) *m/z* calcd for $C_{39}H_{73}O_9N_2Si$ $[M + H]^+$ 741.5080, *m/z* obsd 741.5073.

8a-Aza-8a-homo-20-deoxo-3-deoxy-5-*O*-(3,4,6-trideoxy-3-dimethylamino-β-D-*xylo*-

hexopyranosyl)-20,20-dimethoxy-23-*O*-[(1,1-dimethylethyl)dimethylsilyl]tylonolide (8):



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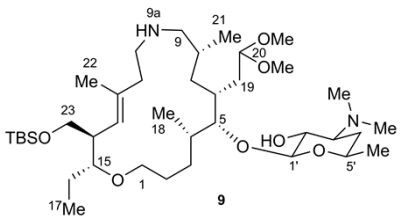
To a stirred solution of (*Z*)-oxime **6** (247 mg, 0.33 mmol) in acetone (3.3 mL), 2,4,6-trimethylbenzenesulfonyl chloride (150 mg, 0.69 mmol) in acetone (13 mL) and sodium hydrogen carbonate (100 mg, 1.19 mmol) in water (12 mL) were added dropwise at 0 °C and the mixture was stirred for 3 days at room temperature. After evaporation of acetone, resulting aqueous solution was extracted with $CHCl_3$. The organic solution was dried over Na_2SO_4 and concentrated *in vacuo* to give a residue, which was purified by preparative HPLC [Senshu Pak Silica-6251S normal phase column (30 mm × 250 mm) using $CHCl_3$/MeOH/28% NH_4OH (40:1:0.1) solvent system] to give lactam **8** (223 mg, 90%). $[\alpha]_D^{23}$ +31° (*c* 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.019 and 0.030 (each s, 3H, Me_2Si-), 0.87 (s, 9H, Me_3C-Si), 0.91 (t, *J* = 7.5 Hz, 3H, Me-17), 0.99 (d, *J* = 7.0 Hz, 3H, Me-18), 1.12 (ovlp, 1H, H-3a), 1.15 (d, *J* = 6.5 Hz, 3H, Me-21), 1.15 (ovlp, 1H, H-7a), 1.23 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.25 (ovlp, 1H, H-4'*ax*), 1.31 (ovlp, 1H, H-4), 1.40 (ovlp, 1H, H-6), 1.40 (ovlp, 1H, H-7b), 1.55 (ovlp, 1H, H-3b), 1.56 (ovlp, 1H, H-16a), 1.62 (ovlp, 1H, H-19a), 1.67 (ovlp, 1H, H-4'*eq*), 1.70 (ovlp, 1H, H-2a), 1.77 (s, 3H, Me-22), 1.85 (m, 1H, H-16b), 2.02 (ddd, *J* = 6.0, 8.0, and 14.0 Hz, 1H, H-19b), 2.29 (s, 6H, Me_2N-3'), 2.35 (ddd, *J* = 4.5, 13.5, and 17.0 Hz, 1H, H-2b), 2.52 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.73 (apparently septet, *J* = 5.0 Hz, 1H, H-14), 3.21 (dd, *J* = 7.0 and 10.0 Hz, 1H, H-2'), 3.30 (d, *J* = 9.0 Hz, 1H, H-5), 3.34 (s, 3H, MeO), 3.36 (s, 3H, MeO), 3.50 (m, 1H, H-5'), 3.67 (d, *J* = 5.0 Hz, 2H, H-23a,b), 4.15 (ovlp, 1H, H-8), 4.16 (d, *J* = 7.0 Hz, 1H, H-1'), 4.55 (t, *J* = 6.0 Hz, 1H, H-20), 4.86 (dt, *J* = 2.5, 9.5, and 9.5 Hz, 1H, H-15), 5.16 [d, *J* = 10.0 Hz, 1H, HN(8a)], 5.58 (d, *J* = 10.5 Hz, 1H, H-13), 5.78 (d, *J* = 15.5 Hz, 1H, H-10), and 7.12 (d, *J* =15.5 Hz, 1H, H-11); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.46 (Me_3C-Si<u>Me</u>), −5.45 (Me_3C-Si<u>Me</u>), 10.0 (C-17), 13.0 (C-22), 15.6 (C-18), 18.2 (Me_3<u>C</u>-Si), 21.2 (C-6'), 22.3 (C-21), 25.9 (<u>Me$_3$</u>C-Si), 26.1 (C-16), 28.7 (C-4'), 29.2 (C-3), 32.0 (C-2), 34.3 (C-6), 35.1 (C-19), 37.5 (C-4), 40.3 (Me_2N-3'), 41.1 (C-7), 43.4 (C-8), 46.9 (C-14), 51.5 (MeO), 54.1 (MeO), 63.3 (C-23), 65.8 (C-3'), 69.3 (C-5'), 70.5 (C-2'), 75.2 (C-15), 85.3 (C-5), 104.3 (C-1'), 104.7 (C-20), 119.6 (C-10), 134.9 (C-12), 137.9 (C-13), 144.8 (C-11), 166.8 (C-9), and 173.3 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{73}O_9N_2Si$ $[M + H]^+$ 741.5080, *m/z* obsd 741.5069.

4. Hydrosilylative Reduction of Lactams 7 and 8

Reaction of lactam 7 with phenylsilane without additive

Lactam **7** (200 mg, 0.27 mmol) in anhydrous THF (10 mL) was treated with phenylsilane (583 mg, 5.4 mmol) in the presence of rhodium (III) chloride trihydrate (17.0 mg, 0.081 mmol) at room temperature for 18 h. Methanol (10 mL) was added dropwise to the reaction mixture. After the generation of gas was ceased, the solution was concentrated. The residue obtained was extracted with $CHCl_3$ and the organic solution was washed with water, dried over Na_2SO_4 and concentrated to give a solid. Purification by short column chromatography [$CHCl_3$-MeOH-28% NH_4OH (1:0:0~5:1:0.1)] and followed by preparative HPLC [Senshu Pak Aquasil SPS normal phase column (20 mm × 250 mm) using $CHCl_3$-MeOH-28% NH_4OH (99.46:0.49:0.049~5:1:0.1) solvent system] gave cyclic ether **9** (34.0 mg, 18%), cyclic ether **10** (26.0 mg, 14%), and azalide **11** (5.6 mg, 3%) as colorless solids.

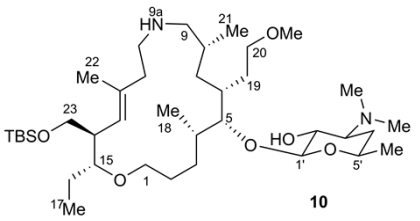
Spectral data of 9-11



9

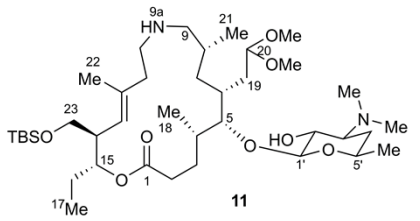
Cyclic ether **9** had $[\alpha]_D^{21}$ −11° (*c* 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 6H, Me_2Si-), 0.87 (t, *J* = 7.5 Hz, 3H, Me-17), 0.89 (s, 9H, Me_3C-Si), 0.97 (d, *J* = 6.5 Hz, 3H, Me-21), 1.02 (d, *J* = 6.5 Hz, 3H, Me-18), 1.06 (ovlp, 1H, H-7a), 1.23 (q, *J* = 12.0 Hz, 1H, H-4'*ax*), 1.23 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.24 (ovlp, 1H, H-3a), 1.30 (ovlp, 1H, H-16b), 1.38 (ovlp, 1H, H-7b), 1.40 (ovlp, 1H, H-2a), 1.42 (ovlp, 1H, H-19a), 1.56 (dq, *J* = 7.5, 7.5, 7.5, and 13.0 Hz, 1H, H-16b), 1.60 (ovlp, 1H, H-8), 1.62 (s, 3H, Me-22), 1.65 (ovlp, 1H, H-2b), 1.65 (ovlp, 1H, H-3b), 1.65 (ovlp, 1H, H-4'*eq*), 1.79 (ovlp, 1H, H-4), 2.07 (ovlp, 1H, H-6), 2.09 (ovlp, 1H, H-19b), 2.20 (ovlp, 2H, H-11a,b), 2.23 (ovlp, 1H, H-9a), 2.28 (s, 6H, Me_2N-3'), 2.50 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.52 (ovlp, 1H, H-14), 2.66 (ovlp, 1H, H-9b), 2.68 (ovlp, 1H, H-10a), 2.72 (ovlp, 1H, H-10b), 3.25 (dd, *J* = 7.2 and 10.0 Hz, 1H, H-2'), 3.31 (ovlp, 1H, H-1a), 3.29 (s, 3H, MeO), 3.32 (s, 3H, MeO), 3.39 (ddd, *J* = 2.0, 5.5, and 7.5 Hz, 1H, H-15), 3.42 (m, 1H, H-5), 3.43 (dd, *J* = 6.0 and 9.5 Hz, 1H, H-23a), 3.49 (m, 1H, H-5'), 3.56 (ovlp, 1H, H-1b), 3.59 (apparently t, *J* = 9.0 Hz, 1H, H-23b), 4.26 (d, *J* = 7.2 Hz, 1H, H-1'), 4.53 (t, *J* = 6.0 Hz, 1H, H-20), and 5.19 (d, *J* = 10.0 Hz, 1H, H-13); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.32 (Me_3C-Si<u>Me</u>), −5.26 (Me_3C-Si<u>Me</u>), 10.5 (C-17), 15.6 (C-18), 16.6 (C-22), 18.2 (Me_3<u>C</u>-Si), 18.8 (C-21), 21.2 (C-6'), 25.3 (C-16), 25.9 (<u>Me</u>$_3$C-Si), 27.5 (C-2), 29.1 (C-4'), 31.0 (C-8), 32.0 (br, C-3), 32.7 (C-19), 34.2 (C-4), 35.4 (br, C-6), 35.9 (C-7), 38.2 (C-11), 40.4 (Me_2N-3'), 44.6

(C-14), 45.8 (C-10), 51.4 (MeO), 52.8 (MeO), 55.6 (C-9), 63.8 (C-23), 65.4 (C-3'), 69.0 (C-1), 69.4 (C-5'), 70.7 (C-2'), 79.2 (C-15), 84.7 (C-5), 103.4 (C-20), 105.5 (C-1'), 123.5 (C-13), and 134.7 (C-12); HRMS (ESI) *m/z* calcd for $C_{39}H_{79}O_7N_2Si$ $[M + H]^+$ 715.5651, *m/z* obsd 715.5655.



10

Cyclic ether **10** had $[\alpha]_D^{22}$ +15° (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 6H, Me_2Si-), 0.87 (t, *J* = 7.5 Hz, 3H, Me-17), 0.89 (s, 9H, Me_3C-Si), 0.96 (d, J = 6.5 Hz, 3H, Me-21), 1.02 (d, *J* = 6.5 Hz, Me-18), 1.03 (ovlp, 1H, H-7a), 1.22 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.24 (ovlp, 1H, H-3a), 1.26 (q, *J* = 12.0 Hz, 1H, H-4'*ax*), 1.29 (ovlp, 1H, H-16a), 1.39 (ovlp, 1H, H-7b), 1.41 (ovlp, 1H, H-2a), 1.44 (ovlp, 1H, H-19a), 1.56 (dq, *J* = 7.5, 7.5, 7.5, and 13.0 Hz, 1H, H-16b), 1.61 (ovlp, 1H, H-8), 1.62 (s, 3H, Me-22), 1.64 (ovlp, 1H, H-2b), 1.65 (ovlp, 1H, H-4'*eq*), ~1.65 (ovlp, 1H, H-3b), 1.82 (m, 1H, H-4), 1.99 (ovlp, 1H, H-6), 2.03 (apparently sextet, *J* = 6.5 Hz, 1H, H-19b), 2.22 (ovlp, 2H, H-11a,b), 2.23 (ovlp, 1H, H-9a), 2.29 (s, 6H, Me_2N-3'), 2.50 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.52 (ovlp, 1H, H-14), 2.63 (ovlp, 1H, H-9b), ~2.71 (ovlp, 1H, H-10a), ~2.76 (ovlp, 1H, H-10b), 3.27 (dd, *J* = 7.2 and 10.0 Hz, 1H, H-2'), 3.30 (ovlp, 1H, H-1a), 3.31 (s, 3H, MeO), 3.39 (ovlp, 1H, H-15), 3.41 (ovlp, 2H, H-20a,b), 3.41 (ovlp, 1H, H-5), 3.43 (ovlp, 1H, H-23a), 3.48 (m, 1H, H-5'), 3.57 (ovlp, 1H, H-1b), 3.59 (apparently t, *J* = 9.0 Hz, 1H, H-23b), 4.24 (d, *J* = 7.2 Hz, 1H, H-1'), and 5.19 (d, *J* = 10.0 Hz, 1H, H-13); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ –5.31 (Me_3C-Si<u>Me</u>), –5.26 (Me_3C-Si<u>Me</u>), 10.5 (C-17), 15.6 (C-18), 16.6 (C-22), 18.3 (Me_3<u>C</u>-Si), 18.9 (C-21), 21.2 (C-6'), 25.4 (C-16), 26.0 (<u>Me$_3$</u>C-Si), 27.5 (C-2), 29.1 (C-4'), 30.0 (C-19), 31.0 (C-8), 31.9 (C-3), 33.9 (C-4), 35.9 (C-7), 38.1 (C-11), 40.4 (Me_2N-3'), 44.6 (C-14), 45.8 (C-10), 55.6 (C-9), 58.4 (MeO), 63.8 (C-23), 65.5 (C-3'), 69.0 (C-1), 69.4 (C-5'), 70.6 (C-2'), 72.0 (C-20), 79.2 (C-15), 84.4 (C-5), 105.4 (C-1'), 123.7 (C-13), and 134.6 (C-12); HRMS (ESI) *m/z* calcd for $C_{38}H_{77}O_6N_2Si$ $[M + H]^+$ 685.5545, *m/z* obsd 685.5539.



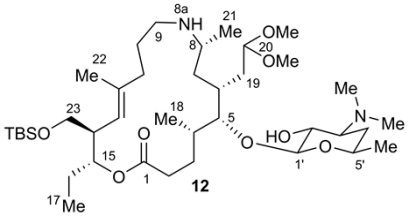
11

Azalide **11** had $[\alpha]_D^{23}$ +9° (c 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.01 and 0.02 (each s, 3H, Me_2Si-), 0.88 (s, 9H, Me_3C-Si), 0.89 (t, *J* = 7.5 Hz, 3H, Me-17), 0.95 (d, *J* = 6.5 Hz, 3H, Me-21), 1.03 (ovlp, 1H, H-7a), 1.04 (d, *J* = 7.0 Hz, 3H, Me-18), 1.23 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.24 (q, *J* = 12.0 Hz, 1H, H-4'*ax*), 1.41 (ovlp, 1H, H-7b), 1.41 (ovlp, 1H, H-19a), 1.52 (ovlp, 1H, H-3a), 1.55 (ovlp, 2H, H-16a,b), 1.64 (s, 3H, Me-22), 1.65 (ovlp, 1H, H-4'*eq*), 1.66 (ovlp, 1H, H-8), 1.76 (m, 1H, H-4), 1.84 (m, 1H, H-3b), 2.08 (ovlp, 1H, H-6), 2.18 (ovlp, 1H, H-11a), 2.23 (ovlp, 1H, H-2a), 2.25 (ovlp, 1H, H-11b), 2.28 (s, 6H, Me_2N-3'), 2.41 (dd, *J* = 5.5 and 12.0 Hz, 1H, H-9a), 2.42 (ovlp, 1H, H-2b), 2.48 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.56 (dd, *J* = 6.5 and 12.0 Hz, 1H, H-9b),

2.65 (ovlp, 1H, H-14), 2.66 (ovlp, 1H, H-10a), 2.73 (dt, *J* = 5.5, 5.5, and 12.0 Hz, 1H, H-10b), 3.24 (dd, *J* = 7.2 and 10.0 Hz, 1H, H-2'), 3.29 (s, 3H, MeO), 3.31 (s, 3H, MeO), 3.44 (dd, *J* = 6.0 and 10.0 Hz, 1H, H-23a), 3.45 (ovlp, 1H, H-5), 3.48 (dd, *J* = 7.5 and 10.0 Hz, 1H, H-23b), 3.49 (ovlp, 1H, H-5'), 4.26 (d, *J* = 7.2 Hz, 1H, H-1'), 4.51 (t, *J* = 6.0 Hz, 1H, H-20), 5.06 (dt, *J* = 3.8, 7.0, and 7.0 Hz, 1H, H-15), and 5.09 (d, *J* = 9.0 Hz, 1H, H-13); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ –5.46 (Me_3C-Si$\underline{Me_2}$), 10.1 (C-17), 15.3 (C-18), 16.8 (C-22), 18.2 ($Me_3\underline{C}$-Si), 18.9 (C-21), 21.2 (C-6'), 25.9 ($\underline{Me_3}$C-Si), 26.2 (C-16), 28.9 (C-4'), 31.0 (2C, C-3 and 8), 32.7 (C-2), 32.9 (C-19), 34.4 (C-4), 35.5 (2C, C-6 and 7), 39.0 (C-11), 40.4 (Me_2N-3'), 44.1 (C-14), 46.3 (C-10), 51.4 (MeO), 52.9 (MeO), 56.1 (C-9), 63.9 (C-23), 65.5 (C-3'), 69.5 (C-5'), 70.5 (C-2'), 74.8 (C-15), 84.3 (C-5), 103.4 (C-20), 105.5 (C-1'), 122.8 (C-13), 136.2 (C-12), and 173.0 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{77}O_8N_2Si$ $[M + H]^+$ 729.5444, *m/z* obsd 729.5441.

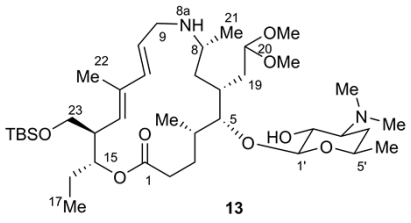
Reaction of lactam 7 with phenylsilane and triethylamine. Lactam **7** (400 mg, 0.54 mmol) in anhydrous THF (20 mL) was reacted with phenylsilane (1.17 g, 10.8 mmol) and rhodium (III) chloride trihydrate (34.0 mg, 0.162 mmol) in the presence of triethylamine (1.51 mL, 10.8 mmol) at room temperature for 18 h under stirring. A similar treatment as described above gave cyclic ethers **9** (13.4 mg, 4%), **10** (3.7 mg, 1%), and azalide **11** (67.3 mg, 17%) as colorless solids, along with recovered **7** (47.8 mg, 12%).

Reaction of lactam 8 with dipheylsilane and triethylamine (Scheme 3): Lactam (**8**, 300 mg, 0.405 mmol) in anhydrous THF (15 mL) was treated with diphenylsilane (1.49 mL, 8.10 mmol) and rhodium (III) chloride trihydrate (25.0 mg, 0.122 mmol) in the presence of triethylamine (1.13 mL, 8.10 mmol) at room temperature for 18 h under stirring. A similar treatment as described above gave azalides **12** (56.7 mg, 19%) and **13** (37.4 mg, 13%) as colorless solids.



Azalide **12** had $[\alpha]_D^{22}$ +24° (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.019 and 0.026 (each s, 3H, Me_2Si-), 0.87 (t, *J* = 7.5 Hz, 3H, Me-17), 0.88 (s, 9H, Me_3C-Si), 1.05 (d, *J* = 6.0 Hz, 3H, Me-21), 1.08 (d, *J* = 6.5 Hz, 3H, Me-18), 1.25 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.26 (ovlp, 1H, H-7a), 1.26 (ovlp, 1H, H-4'*ax*), 1.49 (ovlp, 1H, H-3a), 1.51 (ovlp, 1H, H-7b), 1.52 (ovlp, 1H, H-16a), 1.53 (ovlp, 1H, H-19a), 1.57 (ovlp, 1H, H-16b), 1.63 (s, 3H, Me-22), 1.65 (ovlp, 1H, H-4'*eq*), 1.67 (ovlp, 2H, H-10a,b), 1.85 (ovlp, 1H, H-4), 1.87 (ovlp, 1H, H-3b), 2.01 (ovlp. 1H, H-6), 2.07 (ovlp, 1H, H-11a), 2.11 (ovlp, 1H, H-19b), 2.17 (ovlp, 1H, H-11b), 2.21 (ddd, *J* = 5.0, 11.0, and 14.5 Hz, 1H, H-2b), 2.28 (s, 6H, Me_2N-3'), 2.39 (ddd, *J* = 5.0, 11.0, and 14.5 Hz, 1H, H-2b), 2.49 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.60 (ovlp, 1H, H-9a), 2.62 (ovlp, 1H, H-14), 2.69 (ovlp, 1H, H-9b), 2.73 (ovlp, 1H, H-8),

3.25 (dd, *J* = 7.5 and 10.0 Hz, 1H, H-2'), 3.29 (s, 3H, MeO), 3.31 (s, 3H, MeO), 3.40 (d, *J* = 7.0 Hz, 1H, H-5), 3.44 (dd, *J* = 6.0 and 10.0 Hz, 1H, H-23a), 3.48 (dd, *J* = 8.0 and 10.0 Hz, 1H, H-23b), 3.51 (m, 1H, H-5'), 4.27 (d, *J* = 7.5 Hz, 1H, H-1'), 4.54 (dd, *J* = 5.0 and 7.0 Hz, 1H, H-20), 5.04 (dt, *J* = 3.5, 6.5, and 6.5 Hz, 1H, H-15), and 5.12 (d, *J* = 10.0 Hz, 1H, H-13); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ −5.33 (Me_3C-Si<u>Me</u>), −5.31 (Me_3C-Si<u>Me</u>), 10.2 (C-17), 16.0 (C-18), 16.5 (C-22), 18.4 (Me_3<u>C</u>-Si), 20.9 (C-21), 21.3 (C-6'), 26.0 (<u>Me$_3$</u>C-Si), 26.2 (C-16), 28.9 (C-4'), 30.2 (C-3), 32.6 (C-2), 33.2 (C-19), 33.7 (C-6), 35.4 (C-4), 36.4 (C-11), 37.9 (C-7), 40.5 (Me_2N-3'), 44.2 (2C, C-9 and 14), 48.6 (C-8), 51.8 (MeO), 53.1 (MeO), 64.0 (C-23), 65.8 (C-3'), 69.7 (C-5'), 70.6 (C-2'), 75.0 (C-15), 84.5 (C-5), 103.4 (C-20), 105.2 (C-1'), 122.3 (C-13), 137.7 (C-12), and 173.1 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{77}O_8N_2Si$ $[M + H]^+$ 729.5444, *m/z* obsd 729.5442.

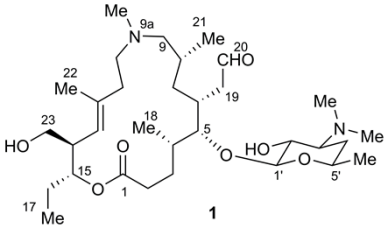


13

Azalide **13** had $[\alpha]_D^{23}$ +30° (*c* 0.42, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.026 and 0.032 (each s, 3H, Me_2Si-), 0.88 (s, 9H, Me_3C-Si), 0.92 (t, *J* = 7.5 Hz, 3H, Me-17), 1.06 (d, *J* = 6.0 Hz, 3H, Me-21), 1.10 (d, *J* = 6.5 Hz, 3H, Me-18), 1.19 (ovlp, 1H, H-7a), 1.23 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.24 (ovlp, 1H, H-4'*ax*), 1.28 (ovlp, 1H, H-3a), 1.51 (ovlp, 1H, H-19a), 1.53 (ovlp, 1H, H-4), 1.55 (ovlp, 1H, H-7b), 1.56 (ovlp, 1H, H-16a), 1.65 (ddd, *J* = 2.0, 4.0, and 12.5 Hz, 1H, H-4'*eq*), 1.68 (ovlp, 1H, H-3b), 1.74 (s, 3H, Me-22), 1.84 (ovlp, 1H, H-2a), 1.85 (ovlp, 1H, H-16b), 1.87 (ovlp, 1H, H-6), 2.08 (dt, *J* = 6.0, 6.0, and 14.0 Hz, 1H, H-19b), 2.28 (s, 6H, Me_2N-3'), 2.42 (ddd, *J* = 5.5, 12.5, and 17.0 Hz, 1H, H-2b), 2.49 (ddd, *J* = 4.0, 10.0, and 12.0 Hz, 1H, H-3'), 2.51 (ovlp, 1H, H-8), 2.69 (apparently septet, *J* = 5.0 Hz, 1H, H-14), 3.06 (dd, *J* = 10.0 and 13.0 Hz, 1H, H-9a), 3.23 (dd, *J* = 7.0 and 10.0 Hz, 1H, H-2'), 3.30 (s, 3H, MeO), 3.33 (s, 3H, MeO), 3.33 (ovlp, 1H, H-5), 3.45 (dd, *J* = 4.5 and 13.0 Hz, 1H, H-9b), 3.50 (ddq, *J* = 2.0, 6.0, 6.0, 6.0, and 11.0 Hz, 1H, H-5'), 3.63 (dd, *J* = 4.5 and 10.0 Hz, 1H, H-23a), 3.66 (dd, *J* = 5.0 and 10.0, 1H, H-23b), 4.26 (d, *J* = 7.0 Hz, 1H, H-1'), 4.48 (t, *J* = 6.0 Hz, 1H, H-20), 4.91 (dt, *J* = 2.5, 9.5, and 9.5 Hz, 1H, H-15), 5.30 (d, *J* = 10.5 Hz, 1H, H-13), 5.55 (ddd, *J* = 4.5, 10.0, and 15.5 Hz, 1H, H-10), and 6.10 (d, *J* = 15.5 Hz, 1H, H-11); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ −5.37 (Me_3C-Si<u>Me</u>), −5.34 (Me_3C-Si<u>Me</u>), 10.0 (C-17), 13.3 (C-22), 15.4 (C-18), 18.4 (Me_3<u>C</u>-Si), 19.4 (C-21), 21.4 (C-6'), 26.0 (4C, <u>Me$_3$</u>C-Si and C-16), 29.0 (C-4'), 29.8 (C-3), 32.3 (C-2), 34.5 (C-6), 35.8 (C-19), 36.2 (C-4), 39.1 (C-7), 40.5 (Me_2N-3'), 46.2 (C-14), 48.6 (C-9), 49.4 (C-8), 52.3 (MeO), 52.8 (MeO), 63.9 (C-23), 65.6 (C-3'), 69.5 (C-5'), 70.7 (C-2'), 75.6 (C-15), 84.4 (C-5), 103.4 (C-20), 105.0 (C-1'), 125.5 (C-10), 131.3 (C-13), 135.2 (C-12), 138.1 (C-11), and 173.7 (C-1); HRMS (ESI) *m/z* calcd for $C_{39}H_{75}O_8N_2Si$ $[M + H]^+$ 727.5287, *m/z* obsd 727.5285.

5. Conversion of azalide 11, 12, and 14 into 1, 2, and 3 (Representative procedure; Table 2)

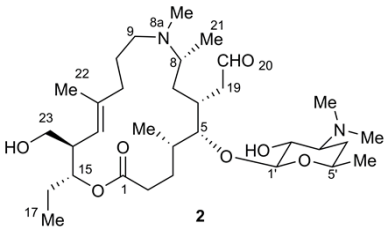
To a solution of azalide **11** (72.9 mg, 0.10 mmol) in acetonitrile (1.0 mL) were added 20 vol% AcOH-MeOH (10 μL), 37wt% aqueous formalin (41 μL, 0.50 mmol), and sodium cyanoborohydride (9.4 mg, 0.15 mmol), and the mixture was stirred overnight at room temperature. The solution was concentrated to a small volume. After extraction with $CHCl_3$, the organic solution was washed with water, dried over Na_2SO_4, and concentrated to give a residue. To a solution of the residue in acetonitrile (3.0 mL), 0.3 M aqueous HCl (0.25 mL) was added and the solution was kept for 2 h at room temperature. After neutralization with saturated aqueous sodium hydrogen carbonate, the mixture was extracted with $CHCl_3$. The organic solution was dried over Na_2SO_4 and concentrated to give a solid (25.1 mg), which was purified by HPLC [Senshu Pak Aquasil SPS normal phase column (20 mm × 250 mm) using $CHCl_3$-MeOH-28% NH_4OH (98.24:1.6:0.16) ~ (90.98:8.2:0.82) solvent system] to afford azalide **1** (19.7 mg, 40%) as a colorless solid.



1

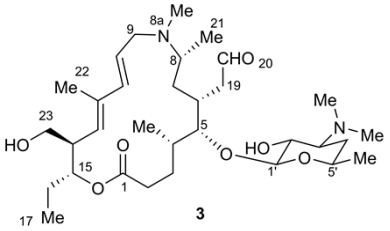
Azalide **1** had $[\alpha]_D^{22}$ +16° (*c* 1.52, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.5 Hz, 3H, Me-17), 0.94 (d, *J* = 6.5 Hz, 3H, Me-21), 0.96 (ovlp, 1H, H-7a), 1.03 (d, *J* = 6.5 Hz, 3H, Me-18), 1.20 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.23 (ovlp, 1H, H-4'*ax*), 1.53 (m, 1H, H-3a), 1.59 (ovlp, 2H, H-16a,b), 1.61 (ovlp, 1H, H-7b), 1.65 (ovlp, 1H, H-4'*eq*), 1.66 (s, 3H, Me-22), 1.66 (ovlp, 1H, H-8), 1.78 (m, 1H, H-4), 1.88 (m, 1H, H-3b), 2.06 (m, 1H, H-11a), 2.12 (dd, *J* = 6.5 and 12.0 Hz, 1H, H-9a), 2.18 (ovlp, 1H, H-2a), 2.19 (ovlp, 1H, H-9b), 2.20 (ovlp, 1H, H-11b), 2.22 [s, 3H, MeN(9a)], 2.26 (ovlp, 1H, H-19a), 2.28 (s, 6H, Me_2N-3'), 2.40 (br m, 1H, H-10a), 2.48 (ovlp, 1H, H-10b), 2.48 (ovlp, 1H, H-3'), 2.51 (ovlp, 1H, H-2b), 2.63 (br t, *J* = 6.5 Hz, 1H, H-6), 2.70 (m, 1H, H-14), 3.09 (dd, *J* = 8.0 and 17.5 Hz, 1H, H-19b), 3.22 (dd, *J* = 7.2 and 10.0 Hz, 1H, H-2'), 3.42 (dd, *J* = 7.5 and 11.0 Hz, 1H, H-23a), 3.47 (dd, *J* = 6.5 and 11.0 Hz, 1H, H-23b), 3.48 (ovlp, 1H, H-5'), 3.53 (dd, *J* = 3.0 and 6.5 Hz, 1H, H-5), 4.25 (d, *J* = 7.2 Hz, 1H, H-1'), 4.94 (q, *J* = 6.0 Hz, 1H, H-15), 4.99 (d, *J* = 10.0 Hz, 1H, H-13), and 9.73 (s, 1H, H-20); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 10.0 (C-17), 15.0 (C-18), 17.7 (C-22), 19.2 (C-21), 21.3 (C-6'), 25.9 (C-16), 28.7 (C-4'), 28.8 (C-8), 29.7 (C-3), 32.1 (C-2), 33.0 (C-6), 35.2 (2C, C-4 and 7), 36.5 (C-11), 40.3 (Me_2N-3'), 43.7 [MeN(9a)], 45.2 (C-14), 46.0 (C-19), 54.9 (C-10), 63.0 (C-23), 64.6 (C-9), 65.6 (C-3'), 69.6 (C-5'), 70.4 (C-2'), 74.7 (C-15), 83.7 (C-5), 105.3 (C-1'), 121.1 (C-13), 139.6 (C-12), 174.0 (C-1), and 203.4 (C-20); HRMS (ESI) *m/z* calcd for $C_{32}H_{59}N_2O_7$ $[M + H]^+$ 583.4317, *m/z* obsd 583.4319.

Conversion of azalide 12 into 2: Azalide **12** (226 mg, 0.31 mmol) was subjected to the reductive methylation and the subsequent hydrolysis as described above to give azalide **2** (106.6 mg, 59%) as a colorless solid. Azalide **2** had $[\alpha]_D^{23}$ +13° (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (d, *J* = 6.5 Hz, 3H, Me-21), 0.89 (t, *J* = 7.5 Hz, 3H, Me-17), 1.06 (ddd, *J* = 3.5, 10.0, and 14.0 Hz, 1H, H-7a), 1.09 (d, *J* = 6.5 Hz, 3H, Me-18), 1.21 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.24 (ovlp, 1H, H-4'*ax*), 1.52 (ovlp, 1H, H-16a), 1.54 (ovlp, 1H, H-3a), 1.55 (ovlp, 2H, H-10a,b), 1.61 (s, 3H, Me-22), 1.64 (ovlp, 1H, H-16b), 1.66 (ovlp, 1H, H-4'*eq*), 1.71 (br t, *J* = 13.0 Hz, 1H, H-7b), 1.86 (m, 1H, H-11a), 1.92 (m, 1H, H-4), 2.07 [s, 3H, MeN(8a)], 2.12 (ovlp, 1H, H-11b), 2.15 (ovlp, 1H, H-3b), 2.21 (slightly br dt, *J* = 4.0, 13.0, and 13.0 Hz, 1H, H-2a), 2.29 (s, 6H, Me_2N-3'), 2.29 (ovlp, 1H, H-19a), 2.36 (ovlp, 2H, H-9a,b), 2.51 (ovlp, 1H, H-3'), 2.53 (ovlp, 1H, H-2b), 2.67 (ovlp, 1H, H-8), 2.69 (ovlp, 1H, H-14), 2.87 (br t, *J* = 10.0 Hz, 1H, H-6), 3.19 (ovlp, 1H, H-19b), 3.22 (dd, *J* = 7.0 and 10.0 Hz, 1H, H-2'), 3.36 (ovlp, 1H, H-23a), 3.38 (d, *J* = 9.0 Hz, 1H, H-5), 3.42 (ovlp, 1H, H-23b), 3.47 (ovlp, 1H, H-5'), 4.21 (d, *J* = 7.0 Hz, 1H, H-1'), 5.05 (ddd, *J* = 2.0, 5.0, and 8.5 Hz, 1H, H-15), 5.09 (d, *J* = 10.5 Hz, 1H, H-13), and 9.75 (s, 1H, H-20); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 10.3 (C-17), 11.7 (C-21), 15.7 (C-18), 17.0 (C-22), 21.3 (C-6'), 24.5 (C-10), 26.2 (C-16), 28.8 (C-4'), 29.8 (C-3), 30.3 (C-6), 33.0 (C-7), 33.2 (C-2) 35.2 [MeN(8a)], 35.8 (C-11), 36.5 (C-4), 40.3 (Me_2N-3'), 45.0 (C-14), 46.0 (C-19), 50.9 (C-8), 52.1 (C-9), 63.1 (C-23), 65.7 (C-3'), 69.5 (C-5'), 70.5 (C-2'), 74.5 (C-15), 84.5 (C-5), 104.6 (C-1'), 120.3 (C-13), 138.5 (C-12), 174.8 (C-1), and 203.4 (C-20); HRMS (ESI) *m/z* calcd for $C_{32}H_{59}N_2O_7$ $[M + H]^+$ 583.4317, *m/z* obsd 583.4312.



2

Conversion of azalide 13 into 3: Azalide **13** (116 mg, 0.16 mmol) was subjected to the reductive methylation and the subsequent hydrolysis as described above to give azalide **3** (62.3 mg, 67%) as a colorless solid. Azalide **3** had $[\alpha]_D^{23}$ +20° (*c* 0.23, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, *J* = 6.5 Hz, 3H, Me-21), 0.94 (t, *J* = 7.5 Hz, 3H, Me-17), 0.98 (d, *J* = 6.5 Hz, 3H, Me-18), 1.19 (ovlp, 1H, H-7a), 1.20 (d, *J* = 6.0 Hz, 3H, Me-6'), 1.23 (ovlp, 1H, H-4'*ax*), 1.42 (m, 1H, H-3b), 1.60 (ovlp, 1H, H-16a), 1.62 (ovlp, 1H, H-7b), 1.63 (ovlp, 1H, H-4), 1.65 (ovlp, 1H, H-4'*eq*), 1.72 (m, 1H, H-3b), 1.78 (s, 3H, Me-22), 1.78 (ovlp, 1H, H-16b), 1.91 (ddd, *J* = 16.5, 12.0, and 4.0 Hz, 1H, H-2a), 2.21 [s, 3H, MeN(8a)], 2.24 (ovlp, 1H, H-19a), 2.28 (s, 6H, Me_2N-3'), 2.42 (ddd, *J* = 5.5, 12.0, and 16.5 Hz, 1H, H-2b), 2.48 (ovlp, 1H, H-3'), 2.51 (ovlp, 1H, H-6), 2.62 (m, 1H, H-8), 2.83 (ovlp, 1H, H-14), 2.84 (dd, *J* = 7.5 and 15.0 Hz, 1H, H-9a), 3.00 (dd, *J* = 8.0 and



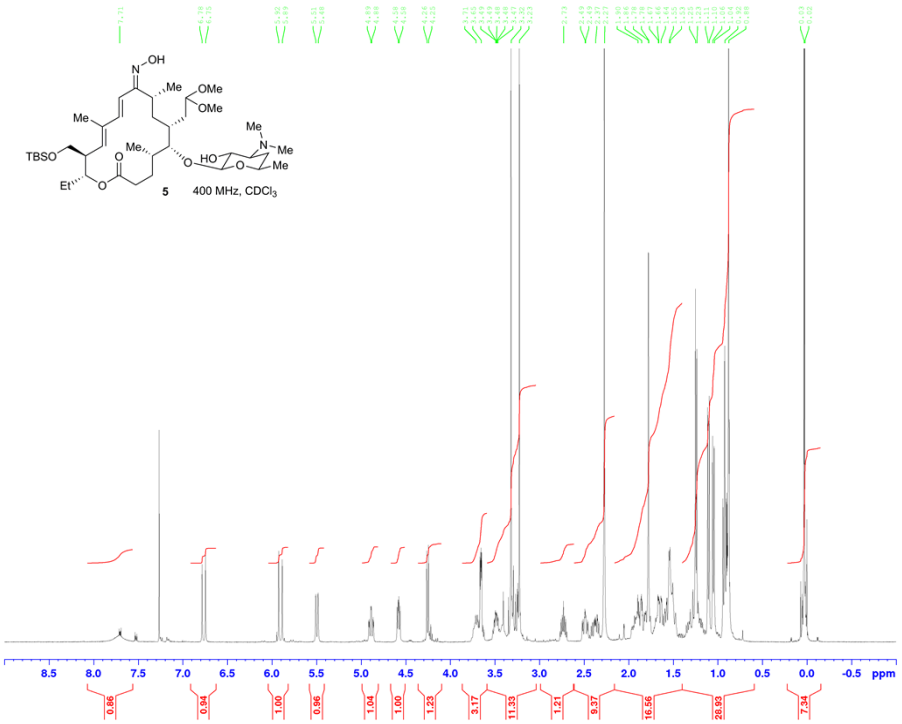
3

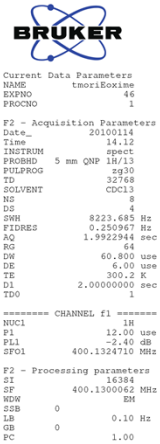
17.5 Hz, 1H, H-19b), 3.15 (br d, *J* = 15.0 Hz, 1H, H-9b), 3.21 (dd, *J* = 7.0 and 10.0 Hz, 1H, H-2'), 3.44 (dd, *J* = 2.0 and 6.0 Hz, 1H, H-5), 3.48 (m, 1H, H-5'), 3.58 (dd, *J* = 7.5 and 10.5 Hz, 1H, H-23a), 3.68 (dd, *J* = 4.5 and 10.5 Hz, 1H, H-23b), 4.22 (d, *J* = 7.0 Hz, 1H, H-1'), 4.82 (dt, *J* = 3.0, 9.5, and 9.5 Hz, 1H, H-15), 5.24 (d, *J* = 10.0 Hz, 1H, H-13), 5.63 (ddd, *J* = 4.0, 7.5, and 15.5 Hz, 1H, H-10), 6.19 (d, *J* = 15.5 Hz, 1H, H-11), and 9.74 (s, 1H, H-20); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 9.8 (C-17), 10.6 (C-21), 13.6 (C-22), 14.7 (C-18), 21.2 (C-6'), 26.2 (C-16), 28.9 (C-4'), 29.7 (C-3), 31.9 (C-2), 33.0 (C-6), 35.5 (C-4), 35.9 (C-7), 38.1 [MeN(8a)], 40.4 (Me_2N-3'), 46.8 (C-14), 47.1 (C-19), 53.2 (C-8), 54.3 (C-9), 63.5 (C-23), 65.4 (C-3'), 69.5 (C-5'), 70.5 (C-2'), 74.7 (C-15), 84.0 (C-5), 104.8 (C-1'), 126.8 (C-10), 129.0 (C-13), 135.4 (C-11), 138.1 (C-12), 174.0 (C-1), and 203.3 (C-20); HRMS (ESI) *m/z* calcd for $C_{32}H_{57}N_2O_7$ $[M + H]^+$ 581.4160, *m/z* obsd 581.4158.

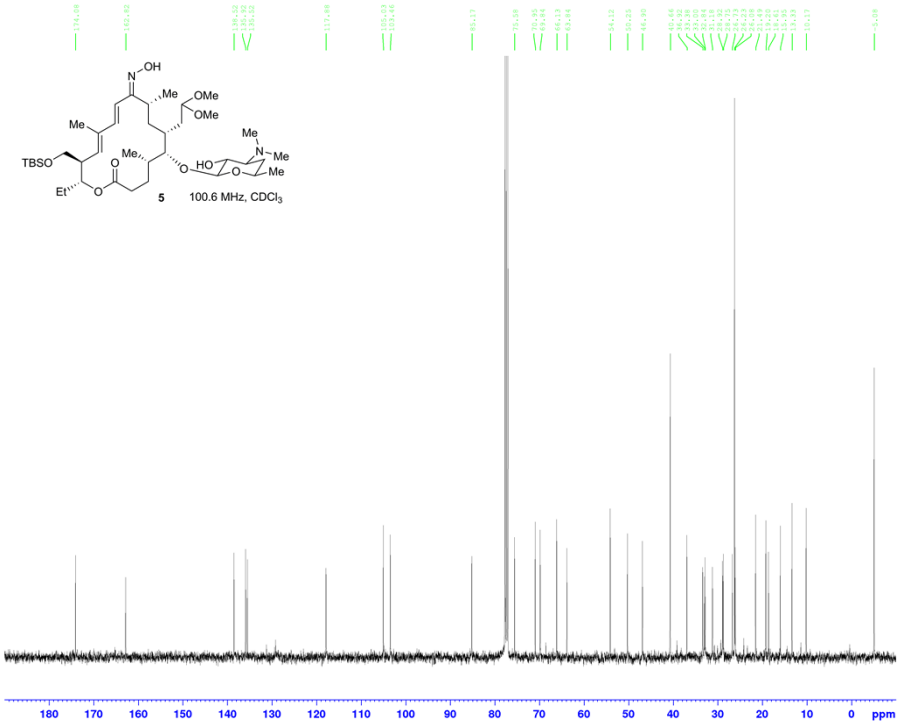
6. Determination of the MICs by the agar dilution method against *Streptococcus pneumoniae* and *Haemophilus influenzae*

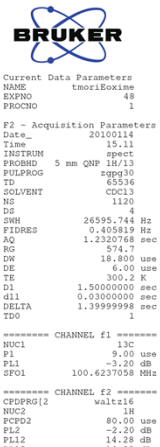
The MICs were examined by a serial agar dilution method using Mueller-Hinton agar supplemented with 5% defibrinated sheep blood (Nippon Biotest Laboratories Inc., Tokyo, Japan) under 5% CO_2 for *Streptococcus pneumoniae* and Mueller-Hinton agar enrichment supplemented with 5% Fildes enrichment peptic digest of sheep blood (Becton, Dickinson and Company) under 5% CO_2 for *Haemophilus influenzae*. The test suspension was prepared at approximately 10^4 CFU per 5 μl using a microplanter MIT-P inoculum replicating apparatus. The MIC was defined as the lowest concentration of antibiotic that inhibited development of visible growth on the agar after 18 h of incubation at 37 °C.

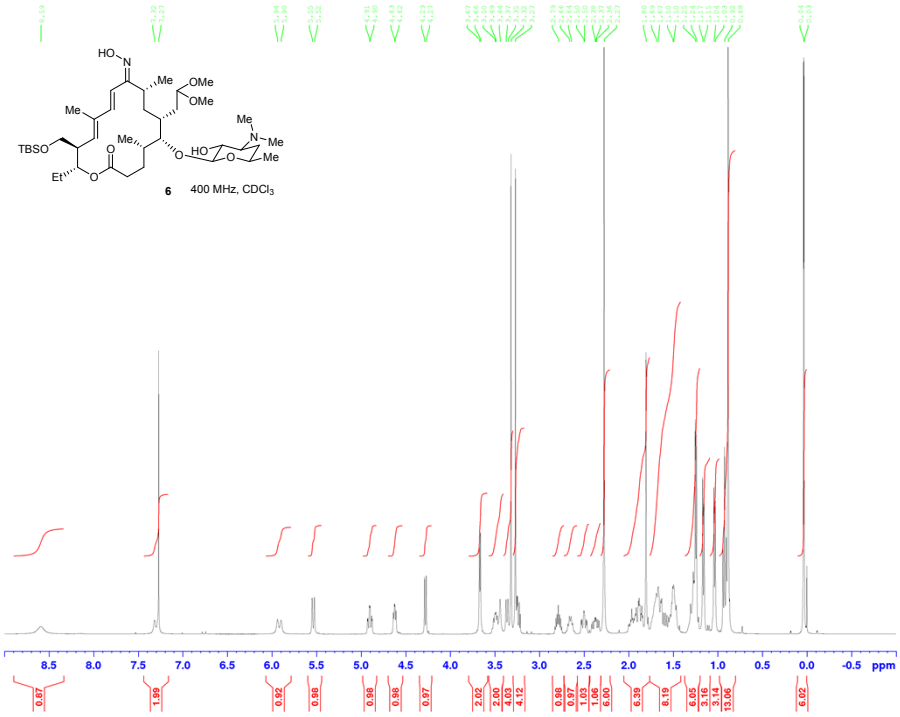
7. ^{1}H and ^{13}C NMR spectra for new compounds (**5–13** and **1–3**)

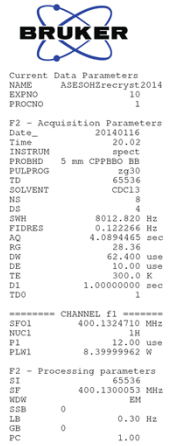










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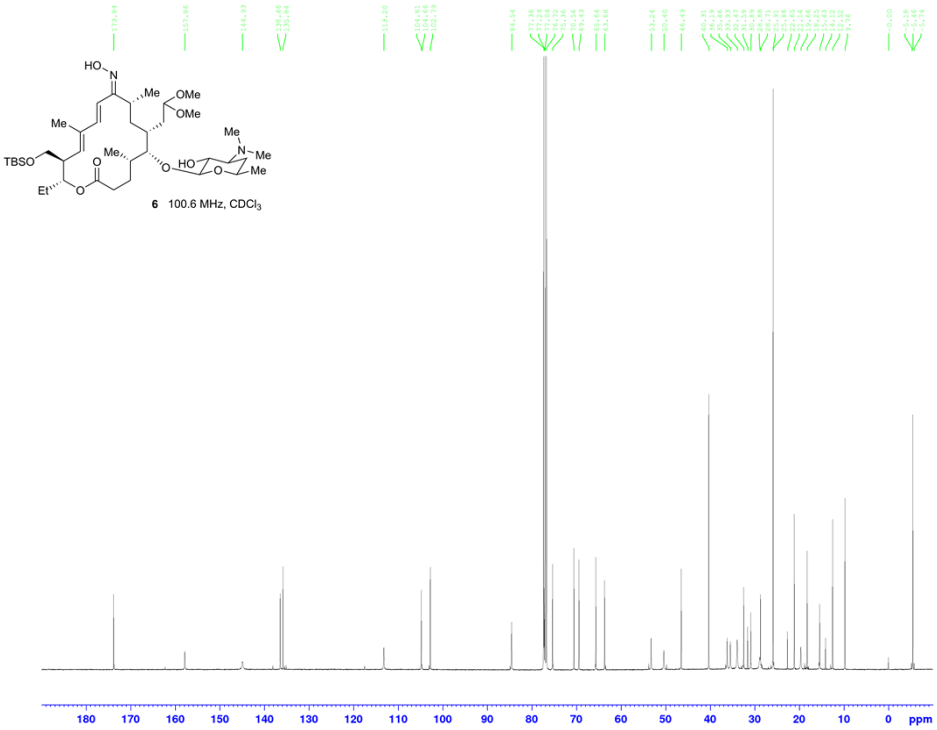


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PLW12               0.18900000 W
PLW13               0.18900000 W

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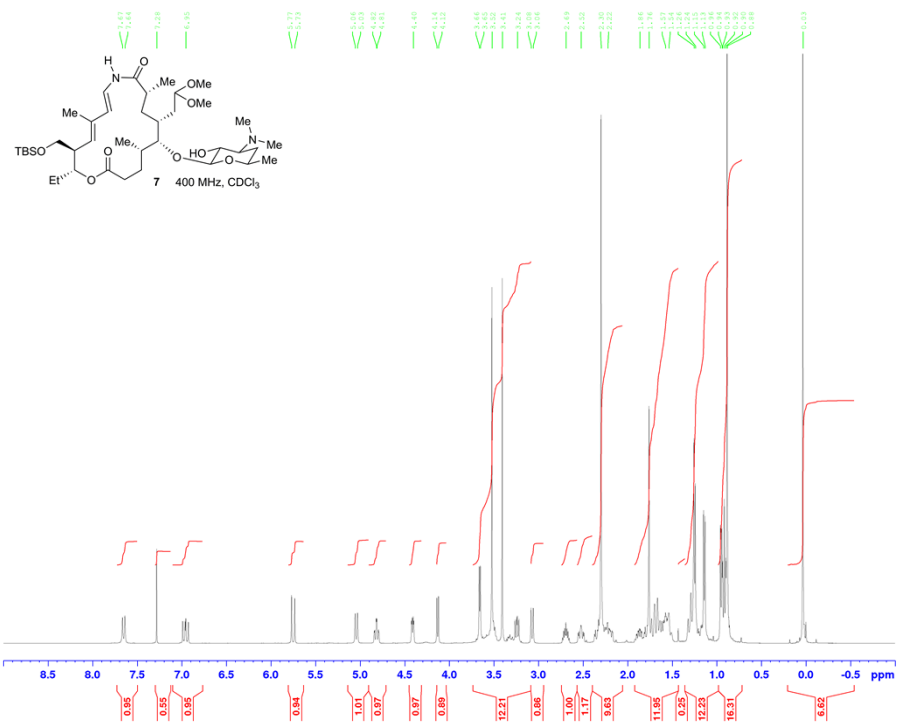
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BRUKER
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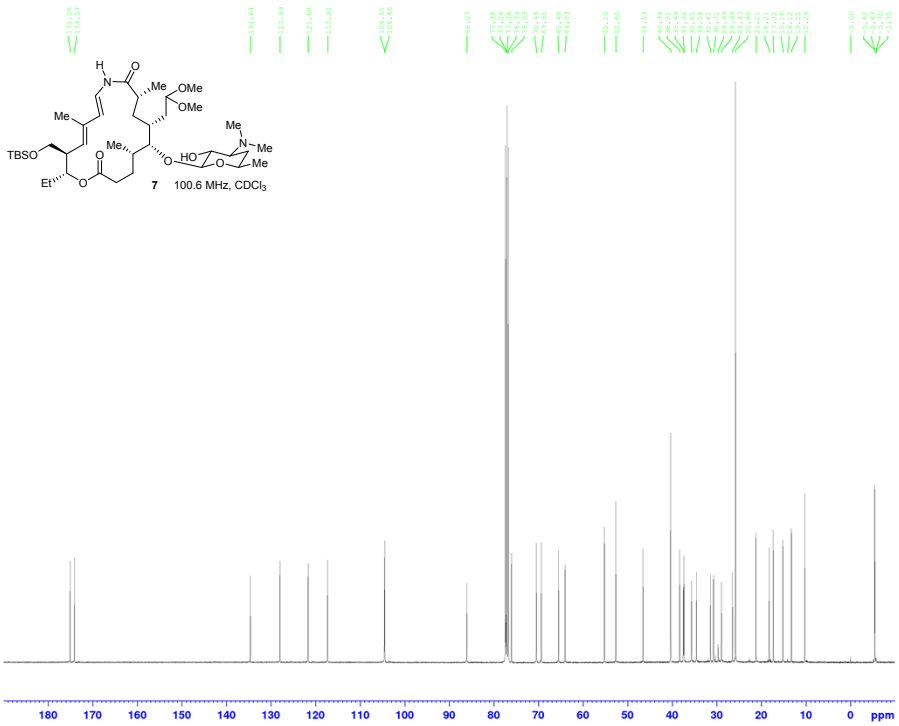
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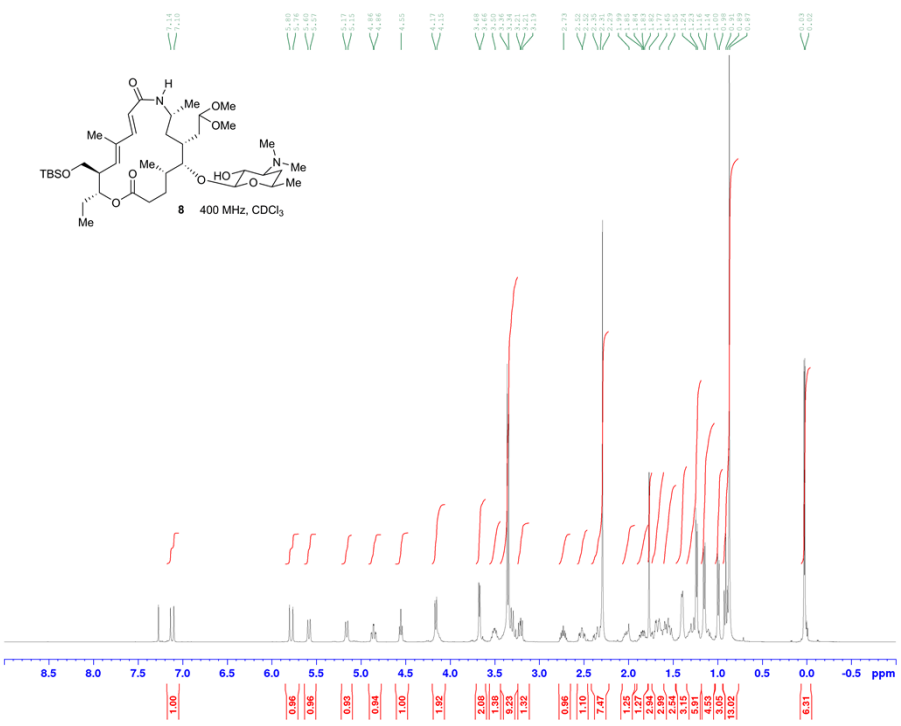
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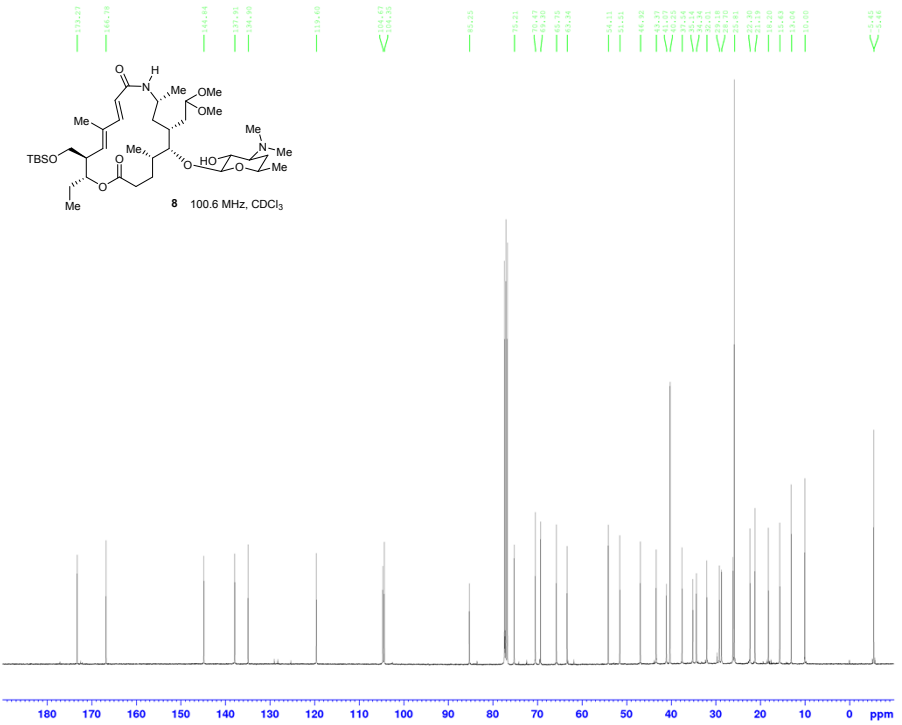
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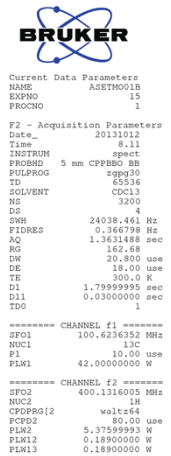
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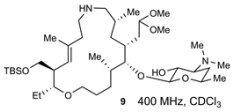

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RG                    25.3
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DE                   10.00 use
TE                  300.0 K
D1                2.00000000 sec
TD0                      1

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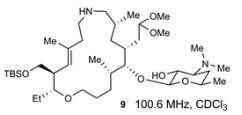
P1                   12.00 use
PLW1           8.39999962 W

F2 - Processing parameters
SI                   65536
SF              400.1300057 MHz
WDW                     EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
```



9 100.6 MHz, $CDCl_3$

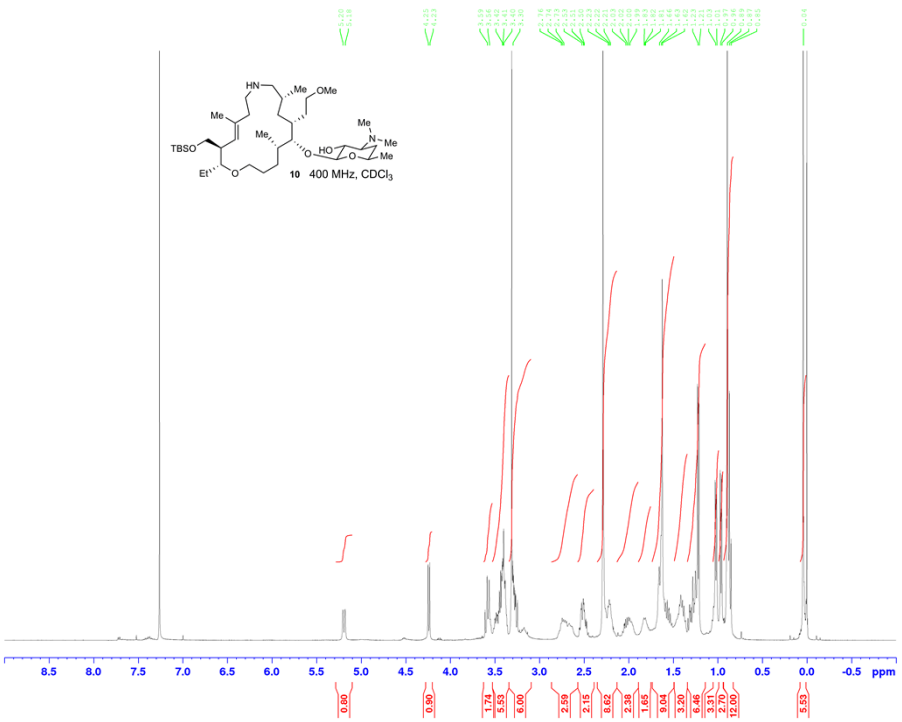

```
Current Data Parameters
NAME       ASE1700,H88,89
EXPNO                1778
PROCNO                  1

F2 - Acquisition Parameters
Date_              20130308
Time                 18.26
INSTRUM              spect
PROBHD   5 mm CPPBBO BB
PULPROG           zgpg30
TD                  65536
SOLVENT              CDCl3
NS                    6400
DS                       4
SWH              24038.461 Hz
FIDRES               0.366798 Hz
AQ                1.3631488 sec
RG                   208.13
DW                   20.800 use
DE                   18.00 use
TE                  300.0 K
D1                1.50000000 sec
D11               0.03000000 sec
TD0                      1

======== CHANNEL f1 =======
SFO1            100.6218241 MHz
NUC1                    13C
P1                   10.00 use
PLW1          42.00000000 W

======== CHANNEL f2 =======
SFO2            400.1316005 MHz
NUC2                    1H
CPDPRG[2             waltz64
PCPD2                80.00 use
PLW2           5.37599993 W
PLW12          0.18900000 W
PLW13          0.18900000 W

F2 - Processing parameters
SI                   32768
SF              100.6127675 MHz
WDW                     EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

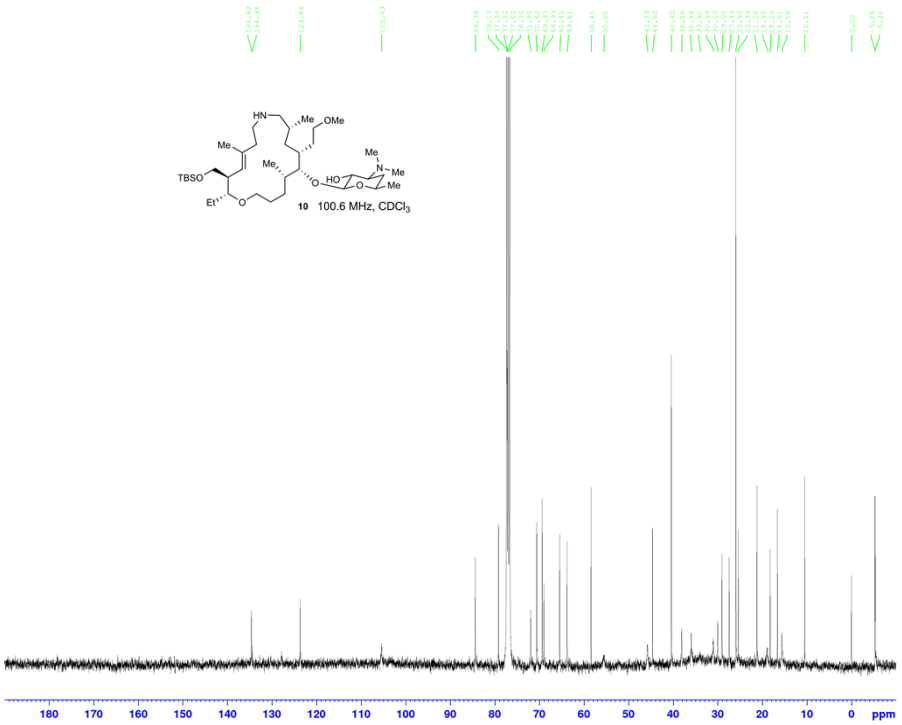



```
Current Data Parameters
NAME                  Azalide10
EXPNO                      1785
PROCNO                        1

F2 - Acquisition Parameters
Date_                 20130311
Time                      18.08
INSTRUM                   spect
PROBHD     5 mm CPPBBO BB
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                          24
DS                           4
SWH                   8012.820 Hz
FIDRES                0.122266 Hz
AQ                    4.0894465 sec
RG                       125.11
DW                       62.400 usec
DE                       10.00 usec
TE                       300.0 K
D1                    2.00000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                400.1332010 MHz
NUC1                        1H
P1                       12.00 usec
PLW1                8.39999962 W

F2 - Processing parameters
SI                       65536
SF                  400.1300094 MHz
WDW                         EM
SSB                  0
LB                       0.30 Hz
GB                   0
PC                       1.00
```



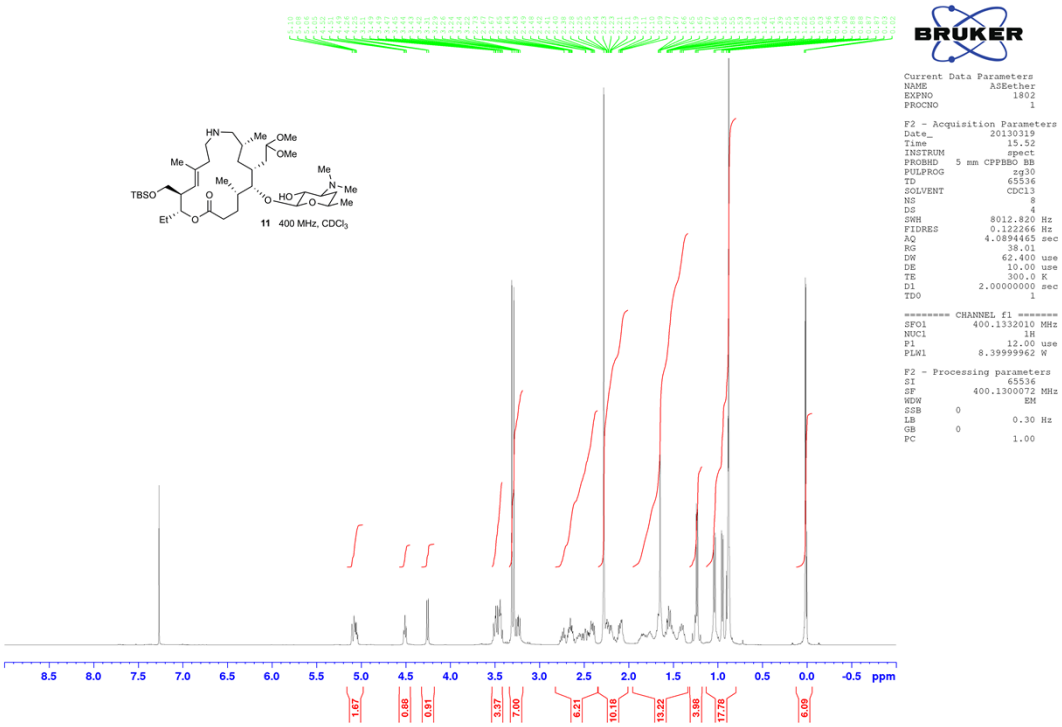

```
Current Data Parameters
NAME                  Azalide10
EXPNO                      1788
PROCNO                        2

F2 - Acquisition Parameters
Date_                 20130313
Time                      10.21
INSTRUM                   spect
PROBHD     5 mm CPPBBO BB
PULPROG                zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        6616
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631488 sec
RG                       208.13
DW                       20.800 usec
DE                       18.00 usec
TE                       300.0 K
D1                    1.50000000 sec
D11                   0.03000000 sec
TD0                           1

======== CHANNEL f1 ========
SFO1                100.6223272 MHz
NUC1                        13C
P1                       10.00 usec
PLW1                42.00000000 W

======== CHANNEL f2 ========
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz64
PCPD2                    80.00 usec
PLW2                 5.37599993 W
PLW12                0.18900000 W
PLW13                0.18900000 W

F2 - Processing parameters
SI                       32768
SF                  100.6127681 MHz
WDW                         EM
SSB                  0
LB                       1.50 Hz
GB                   0
PC                       1.40
```

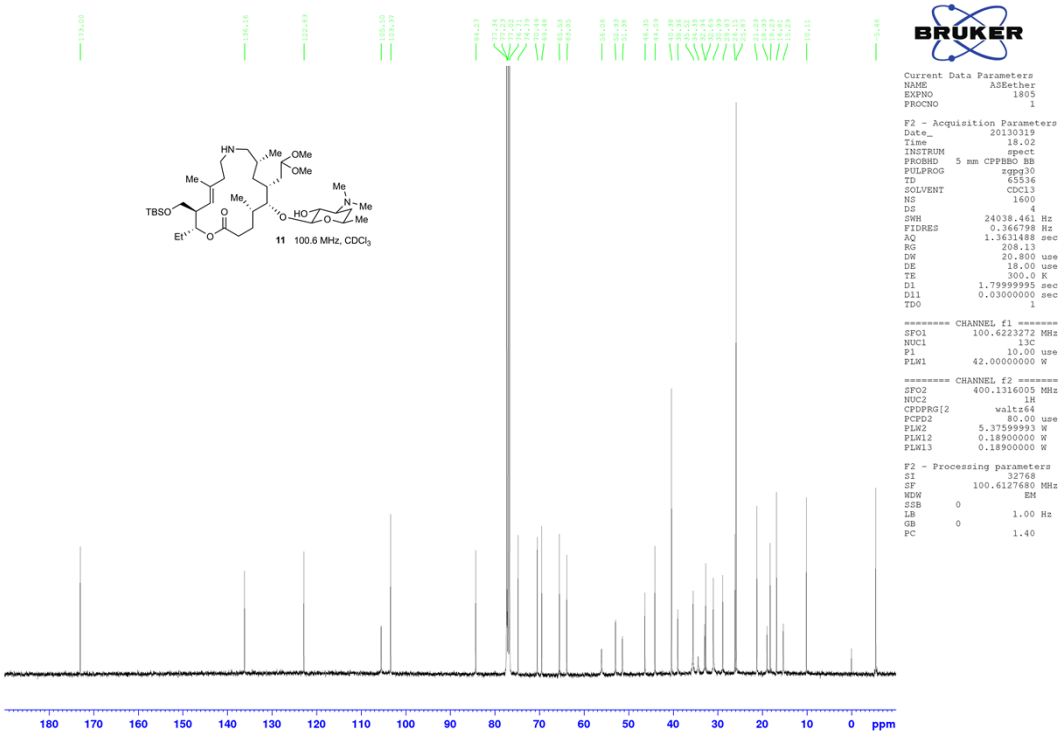



```
Current Data Parameters
NAME                  A3Ether
EXPNO                    1802
PROCNO                      1

F2 - Acquisition Parameters
Date_                20130319
Time                    15.52
INSTRUM                 spect
PROBHD    5 mm CPPBBO BB
PULPROG                 zg30
TD                     65536
SOLVENT                 CDCl3
NS                          8
DS                          4
SWH                  8012.820 Hz
FIDRES               0.122266 Hz
AQ                   4.0894465 sec
RG                       38.01
DW                      62.400 use
DE                      10.00 use
TE                      300.0 K
D1                   2.00000000 sec
TD0                         1

======== CHANNEL f1 =======
SFO1                400.1332010 MHz
NUC1                        1H
P1                      12.00 use
PLW1                 8.39999962 W

F2 - Processing parameters
SI                         65536
SF                  400.1300072 MHz
WDW                           EM
SSB                 0
LB                       0.30 Hz
GB                  0
PC                       1.00
```



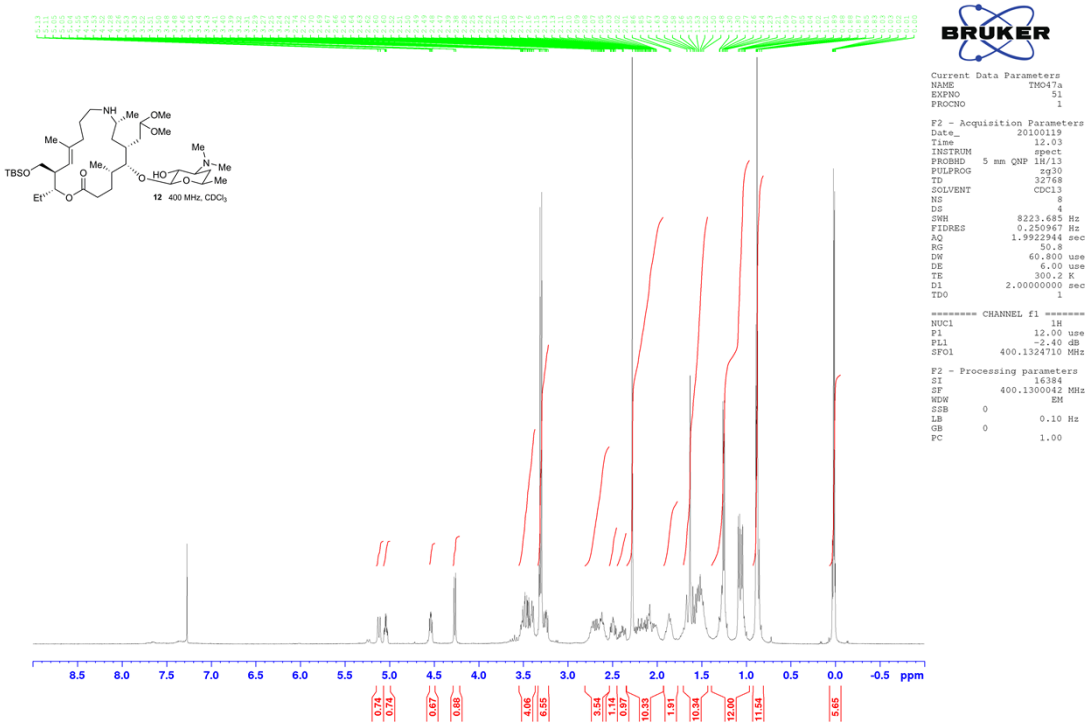

```
Current Data Parameters
NAME                  A3Ether
EXPNO                    1805
PROCNO                      1

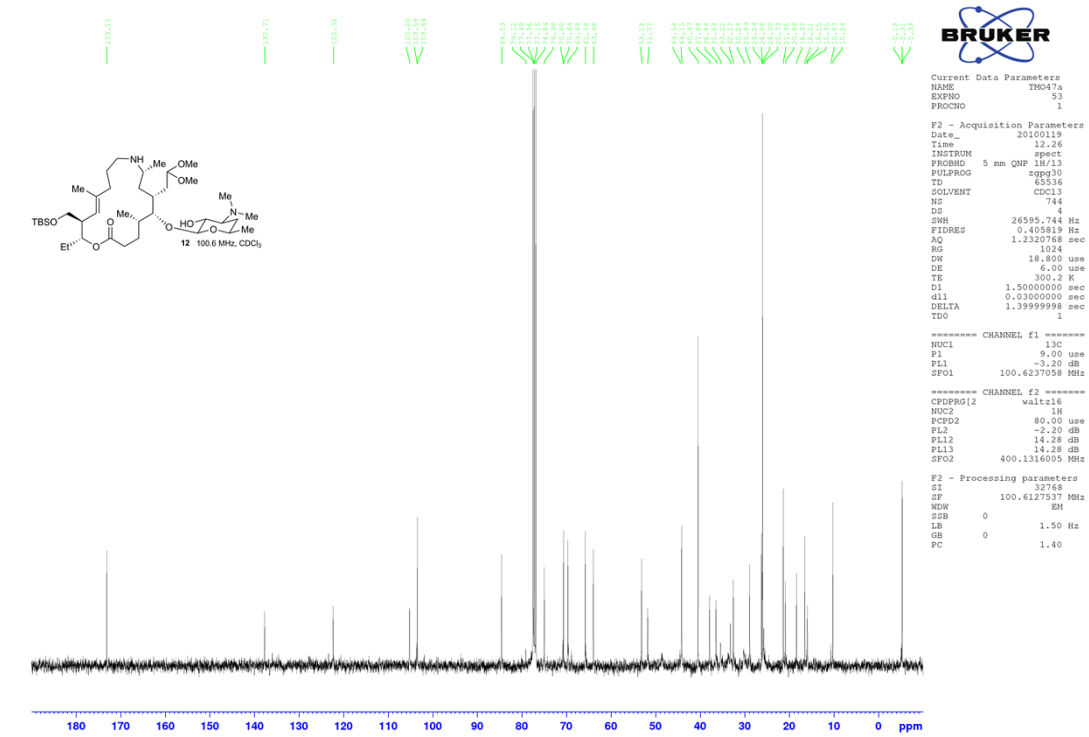
F2 - Acquisition Parameters
Date_                20130319
Time                    18.02
INSTRUM                 spect
PROBHD    5 mm CPPBBO BB
PULPROG              zgpg30
TD                     65536
SOLVENT                 CDCl3
NS                       1600
DS                          4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631488 sec
RG                      208.13
DW                      20.800 use
DE                      18.00 use
TE                      300.0 K
D1                   1.79999995 sec
D11                  0.03000000 sec
TD0                         1

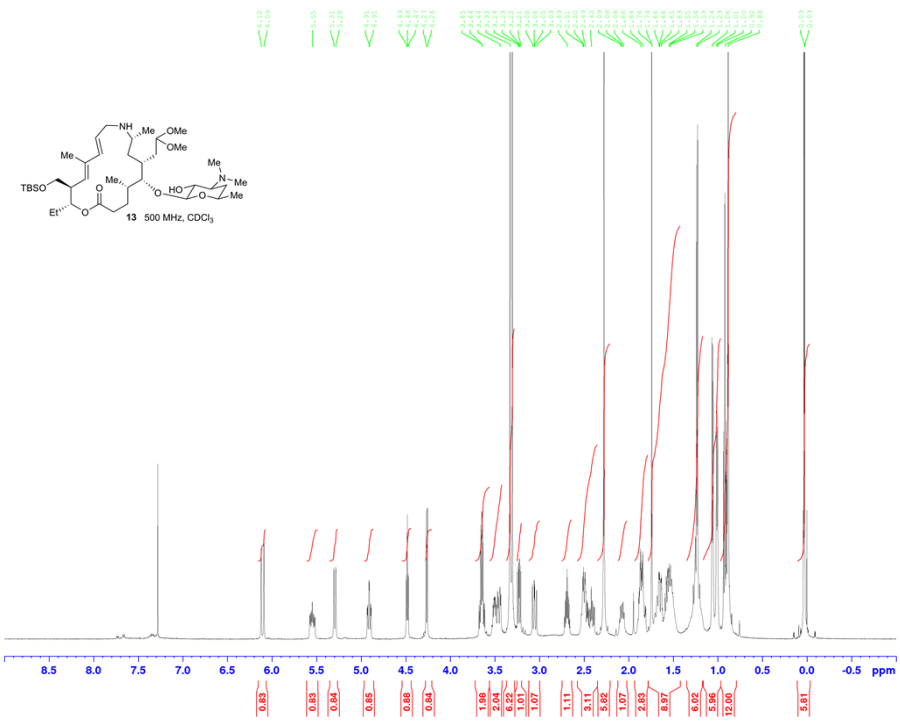
======== CHANNEL f1 =======
SFO1                100.6223272 MHz
NUC1                        13C
P1                      10.00 use
PLW1                42.00000000 W

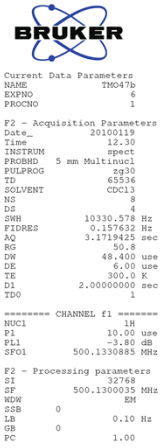
======== CHANNEL f2 =======
SFO2                400.1316005 MHz
NUC2                        1H
CPDPRG[2                waltz64
PCPD2                    80.00 use
PLW2                 5.37599993 W
PLW12                0.18900000 W
PLW13                0.18900000 W

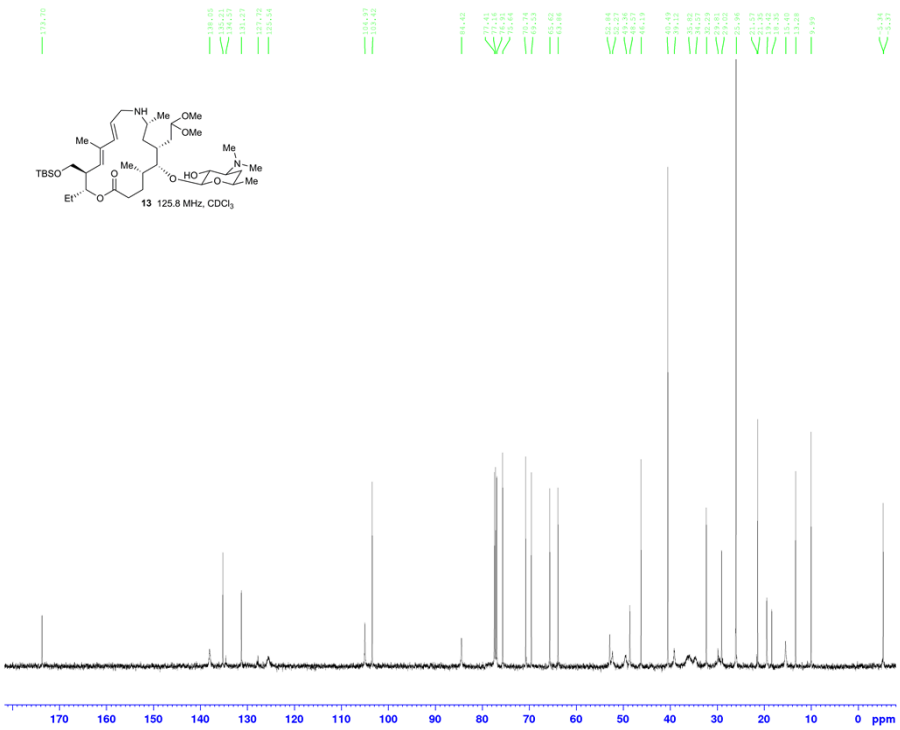
F2 - Processing parameters
SI                         32768
SF                  100.6127680 MHz
WDW                           EM
SSB                 0
LB                       1.00 Hz
GB                  0
PC                       1.40
```


12 400 MHz, CDCl3
Current Data Parameters
NAME TM047a
EXPNO 51
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100119
Time 12.03
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 4
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 50.8
DW 60.800 use
DE 6.00 use
TE 300.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 use
PL1 -2.40 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300042 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.74 0.74 0.67 0.68 4.06 6.55 3.54 1.14 0.97 10.33 1.81 10.34 12.00 11.54 5.65

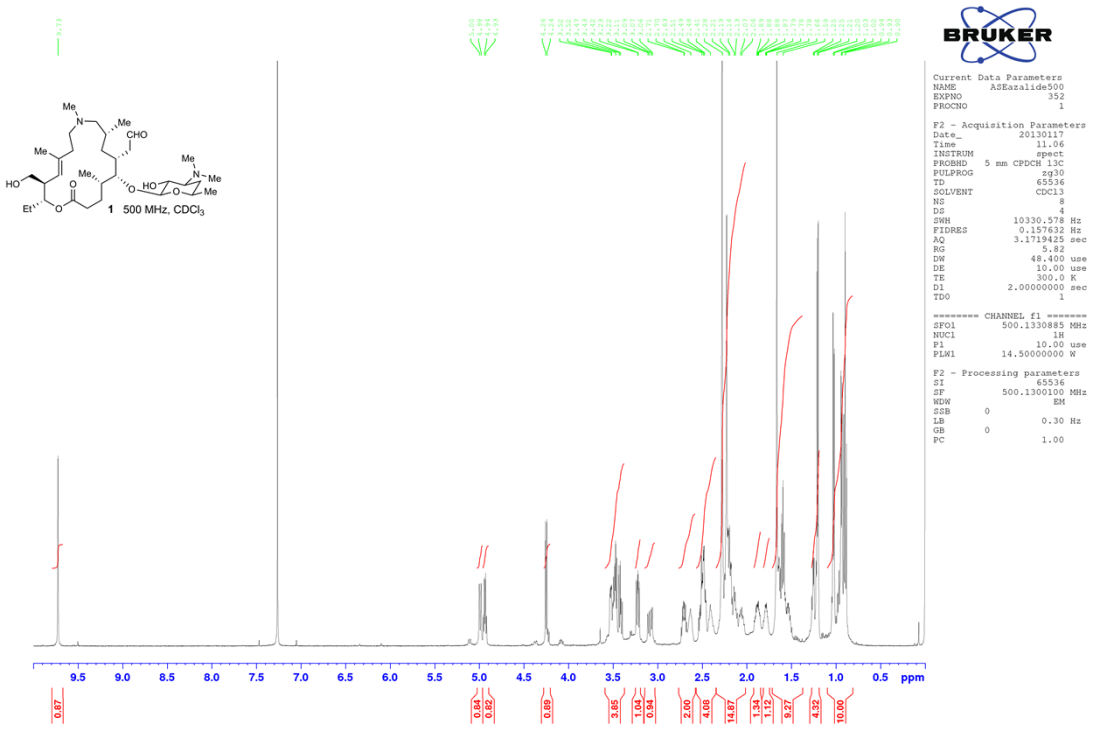

12 100.6 MHz, CDCl3
Current Data Parameters
NAME TM047a
EXPNO 53
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100119
Time 12.26
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 744
DS 4
SWH 26595.744 Hz
FIDRES 0.405819 Hz
AQ 1.2320768 sec
RG 1024
DW 18.800 use
DE 6.00 use
TE 300.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 use
PL1 -3.20 dB
SFO1 100.6237058 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 -2.20 dB
PL12 14.28 dB
PL13 14.28 dB
SFO2 400.1316005 MHz
F2 - Processing parameters
SI 32768
SF 100.6127537 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

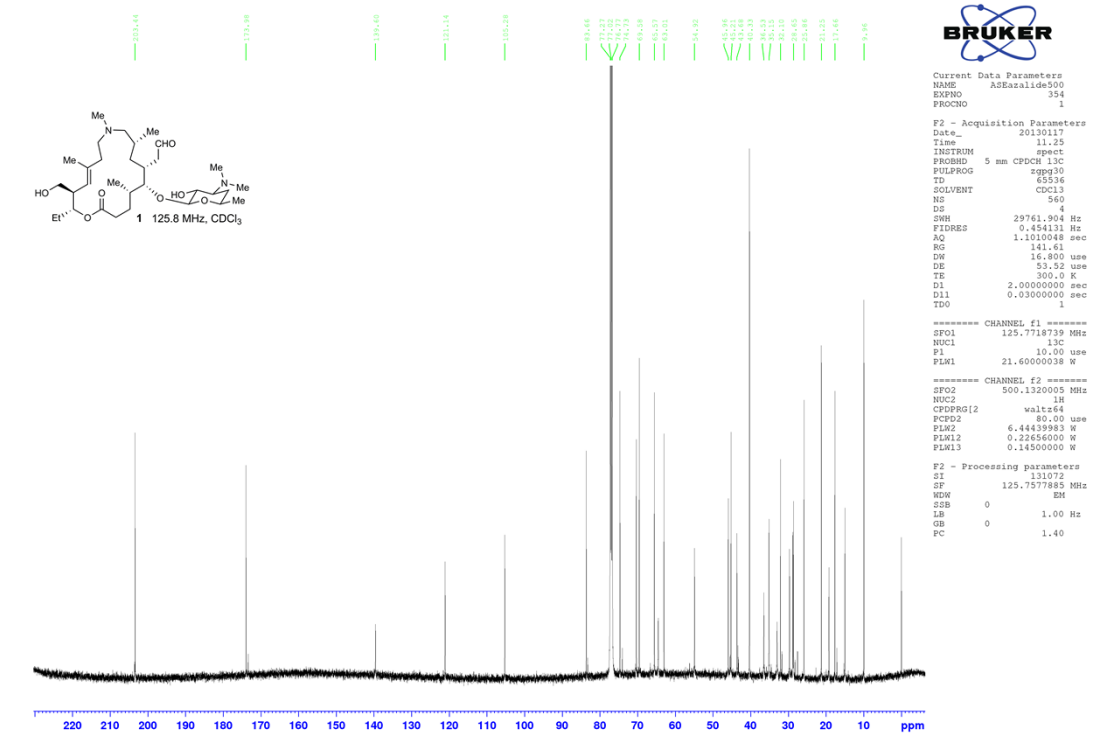

13 500 MHz, CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
0.63 0.83 0.84 0.85 0.88 0.84 1.00 2.04 4.22 1.10 1.07 1.11 3.11 5.82 1.07 2.83 6.97 6.02 5.96 12.00 5.61

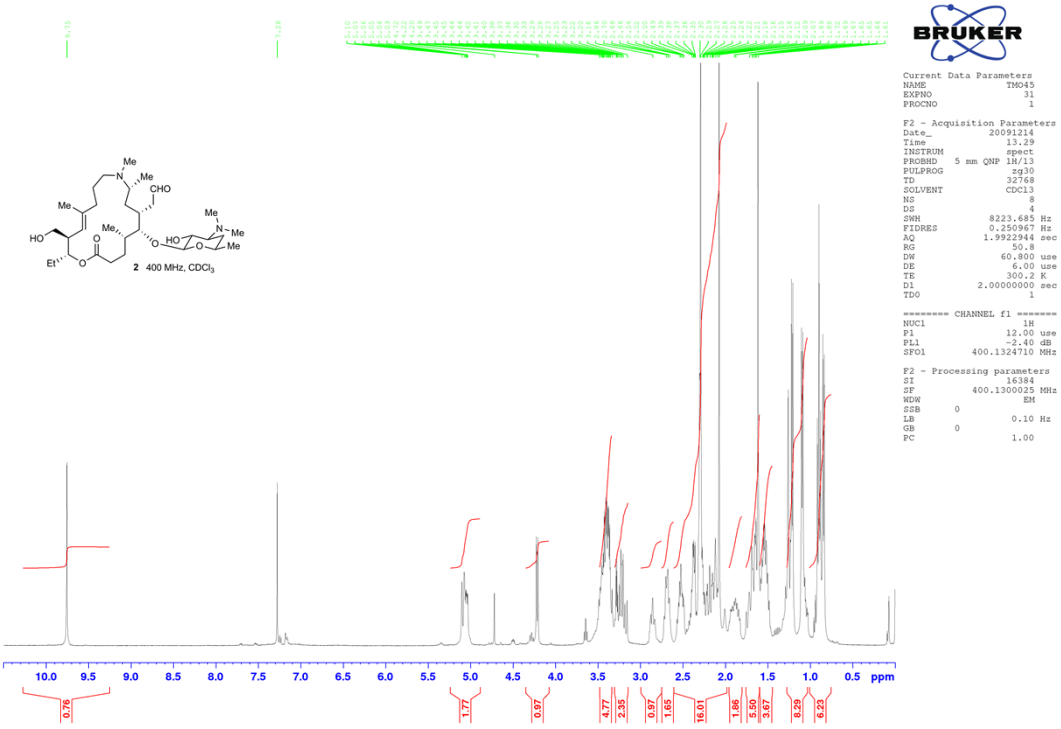

Current Data Parameters
NAME TM047b
EXPNO 6
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100119
Time 12.30
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 4
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 50.8
DW 48.400 use
DE 6.00 use
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 10.00 use
PL1 -3.80 dB
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 32768
SF 500.1300035 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00

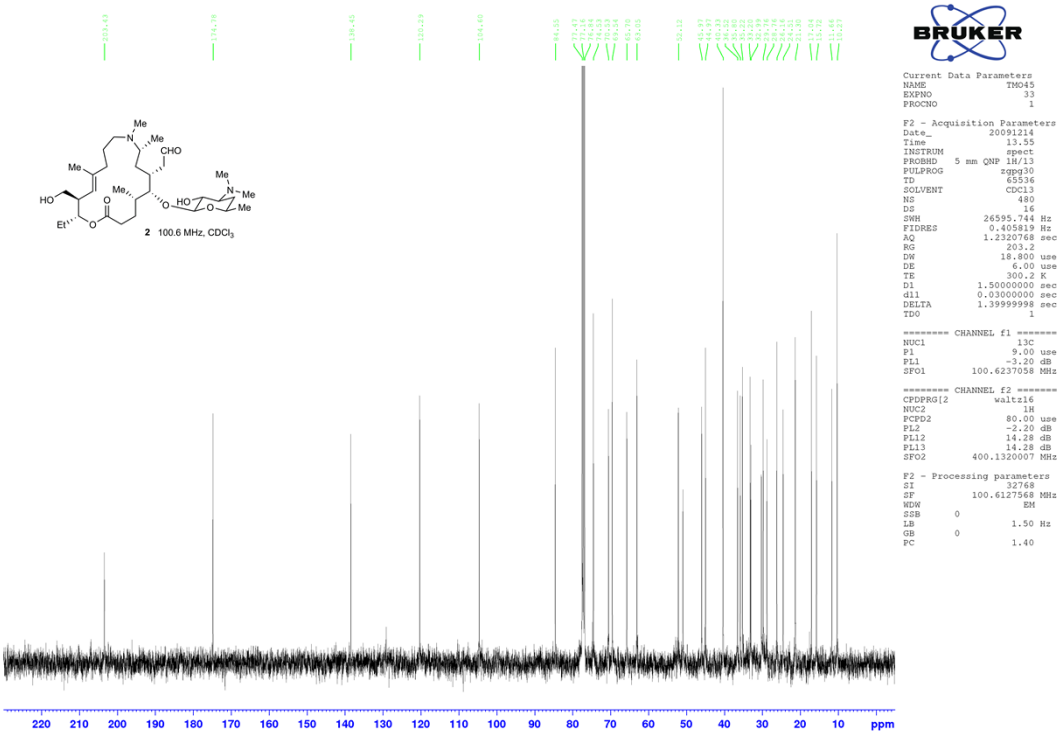

13 125.8 MHz, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

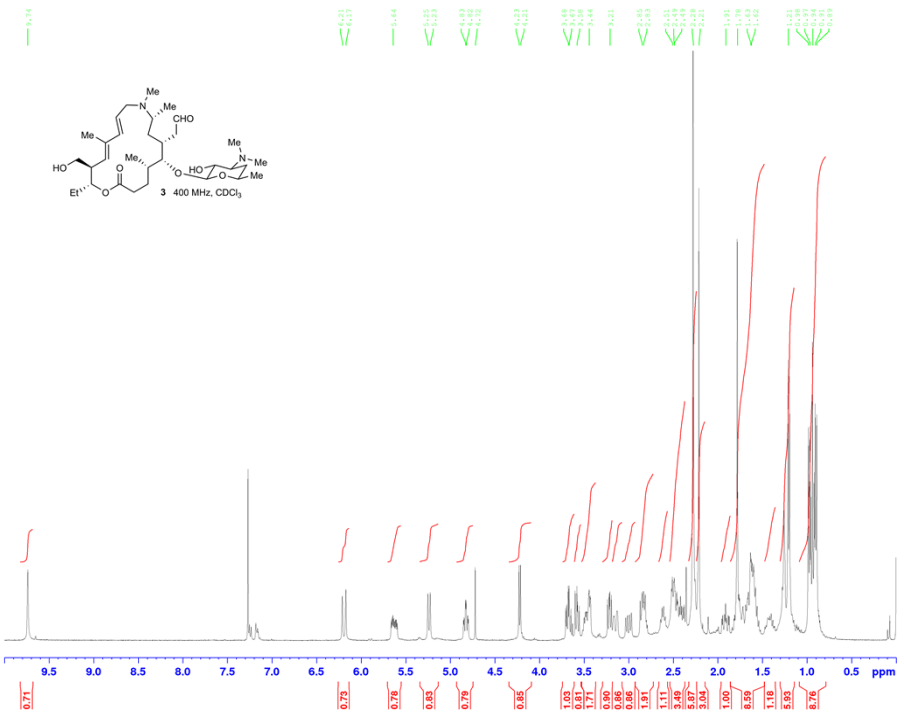

Current Data Parameters
NAME TM047b
EXPNO 8
PROCNO 1
F2 - Acquisition Parameters
Date_ 20100119
Time 12.52
INSTRUM spect
PROBHD 5 mm Multinucl
PULPROG zgpdc
TD 65536
SOLVENT CDCl3
NS 565
DS 4
SWH 30030.029 Hz
FIDRES 0.458222 Hz
AQ 1.0911744 sec
RG 4597.6
DW 16.650 use
DE 6.00 use
TE 300.0 K
D1 1.50000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P0 8.00 use
PL1 1.50 dB
SFO1 125.7703143 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 0 dB
PL12 14.50 dB
SFO2 500.1319597 MHz
F2 - Processing parameters
SI 32768
SF 125.7577724 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40

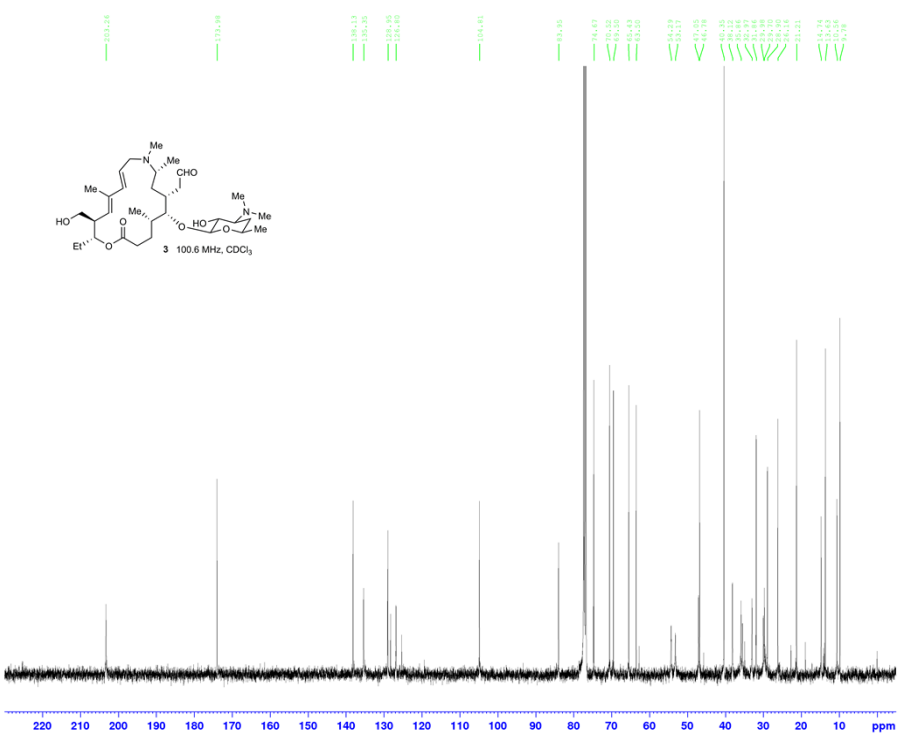

1 500 MHz, CDCl3
Current Data Parameters
NAME ASEazalide500
EXPNO 352
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130117
Time 11.06
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 4
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719425 sec
RG 5.82
DW 48.400 use
DE 10.00 use
TE 300.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 10.00 use
PLW1 14.50000000 W
F2 - Processing parameters
SI 65536
SF 500.1300100 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.87
0.84
0.82
0.89
3.85
1.04
0.94
2.00
4.08
14.87
1.34
1.12
9.27
4.32
10.00


1 125.8 MHz, CDCl3
Current Data Parameters
NAME ASEazalide500
EXPNO 354
PROCNO 1
F2 - Acquisition Parameters
Date_ 20130117
Time 11.25
INSTRUM spect
PROBHD 5 mm CPDCH 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 560
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 141.61
DW 16.800 use
DE 53.92 use
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7718739 MHz
NUC1 13C
P1 10.00 use
PLW1 21.60000038 W
======== CHANNEL f2 ========
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2 waltz64
PCPD2 80.00 use
PLW2 6.44439983 W
PLW12 0.22656000 W
PLW13 0.14500000 W
F2 - Processing parameters
SI 131072
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


2 400 MHz, CDCl3
Current Data Parameters
NAME TM045
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091214
Time 13.29
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 4
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 50.8
DW 60.800 use
DE 6.00 use
TE 300.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 use
PL1 -2.40 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300025 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.76 1.77 0.97 4.77 2.35 0.97 1.65 16.01 1.86 5.50 3.67 8.29 6.23


2 100.6 MHz, CDCl3
Current Data Parameters
NAME TM045
EXPNO 33
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091214
Time 13.55
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 480
DS 16
SWH 26595.744 Hz
FIDRES 0.405819 Hz
AQ 1.2320768 sec
RG 203.2
DW 18.800 use
DE 6.00 use
TE 300.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 use
PL1 -3.20 dB
SFO1 100.6237058 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 -2.20 dB
PL12 14.28 dB
PL13 14.28 dB
SFO2 400.1320007 MHz
F2 - Processing parameters
SI 32768
SF 100.6127568 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


3 400 MHz, CDCl3
Current Data Parameters
NAME TMO44
EXPNO 38
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091214
Time 18.17
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 4
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9922944 sec
RG 101.6
DW 60.800 use
DE 6.00 use
TE 300.2 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 12.00 use
PL1 -2.40 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 16384
SF 400.1300052 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 1.00


3 100.6 MHz, CDCl3
Current Data Parameters
NAME TMO44
EXPNO 40
PROCNO 1
F2 - Acquisition Parameters
Date_ 20091214
Time 22.38
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 4800
DS 16
SWH 26595.744 Hz
FIDRES 0.405819 Hz
AQ 1.2320768 sec
RG 228.1
DW 18.800 use
DE 6.00 use
TE 300.2 K
D1 1.50000000 sec
d11 0.03000000 sec
DELTA 1.39999998 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.00 use
PL1 -3.20 dB
SFO1 100.6237058 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 use
PL2 -2.20 dB
PL12 14.28 dB
PL13 14.28 dB
SFO2 400.1319606 MHz
F2 - Processing parameters
SI 32768
SF 100.6127673 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40