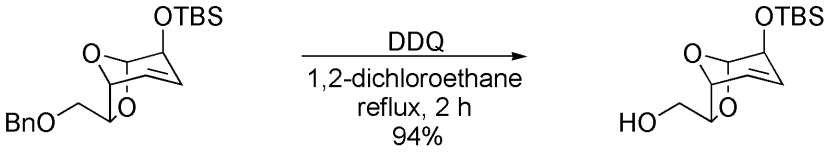
Supporting Information

Experimental Data for Compounds

General Procedures.

^{1}H NMR were measured in $CDCl_3$ solution and referenced to TMS (0.00 ppm) or in C_6D_6 solution and referenced to C_6D_5H (7.16 ppm) using JEOL GSX400 (400 MHz), Bruker AV400N (400 MHz) and Bruker AV500 (500 MHz) spectrometers. ^{13}C NMR were measured in $CDCl_3$ solution and referenced to $CDCl_3$ (77.0 ppm) or in C_6D_6 solution and referenced to C_6D_6 (128.0 ppm) using JEOL GSX400 (100 MHz), Bruker AV400N (100MHz), Bruker AV500 (125 MHz) spectrometers. Chemical shifts are reported in ppm (from TMS). When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broadened. Optical rotations were determined on JAS.CO P-1010-GT. IR spectra were measured on JAS.CO FT/IR-410 spectrometer. Mass spectra were recorded on Waters MICRO MASS LCT-Premier spectrometers. Column chromatography was performed on silica gel 60N (KANTO CHEMICAL, spherical neutral, 63-210 mesh), and flash column chromatography was performed on silica gel (FUJI SILISIA CHEMICAL, spherical neutral, 40-50 μm) using indicated solvent. Thin layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck Kieselgel $60F_{245}$), and compounds were visualized with UV light and *p*-anisaldehyde stain. All melting points were measured with BÜCHI 535 and Yanaco MP-500D melting point apparatus and are uncorrected. All non-aqueous reactions were performed in oven-dried glassware under positive pressure of argon or nitrogen, unless otherwise noted. Reaction mixture was stirred magnetically. Solvents were freshly distilled prior to use or purchased from Kanto Kagaku or Aldrich: tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl or purchased from Kanto Kagaku (Tetrahydrofuran, Dehydrated Stabilizer free): methylene chloride (CH_2Cl_2) was distilled from calcium hydride or purchased from Kanto Kagaku (Methylene chloride, Dehydrated): ether (Et_2O) was purchased from Kanto Kagaku (Diethyl ether, Dehydrated): acetonitrile (CH_3CN) was distilled from calcium hydride and kept over 4Å molecular sieves: pyridine and triethylamine (Et_3N) were distilled from KOH and kept over KOH tablets.

[4-(*tert*-Butyldimethylsilyloxy)-6,8-dioxabicyclo[3.2.1]oct-2-en-7-yl]methanol (7)



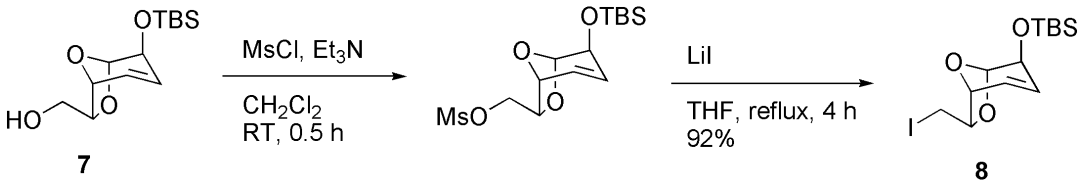
5 **7**

To a stirred solution of **5**[1] (302 mg, 0.834 mmol) in 1,2-dichloroethane (15.0 mL) was added DDQ (410 mg, 1.81 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2 h, the reaction mixture was cooled to room temperature and added saturated aq. $NaHCO_3$. After being stirred for 2 h at room temperature, resultant mixture was extracted with CH_2Cl_2. The combined extracts were washed with saturated aq. $NaHCO_3$, brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane / AcOEt = 70 / 30) to afford **7** (214 mg, 94%) as a colorless oil.

$[\alpha]_D^{28}$ +135.5 (*c* 1.81, $CHCl_3$); IR (neat) 3420, 2955, 2930, 2885, 2857, 1089, 1064 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.25 (ddd, *J* = 10.0, 4.8, 1.2 Hz, 1H), 5.72 (dq, *J* = 10.0, 2.0 Hz, 1H), 5.45 (t, *J* = 1.5 Hz, 1H), 4.51 (d, *J* = 4.8 Hz, 1H), 3.91 (t, *J* = 6.0 Hz, 1H), 3.74 (dt, *J* = 3.6, 1.2 Hz, 1H), 3.63–3.53 (m, 2H), 1.75 (dd, *J* = 6.4, 5.0 Hz, OH, D_2O exchangeable, 1H), 0.91 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 129.6, 127.2, 103.5, 80.4, 71.5, 66.5, 63.9, 25.8, 18.3, –4.6, –4.7; HRMS (ESI) Calcd for $C_{13}H_{25}O_4Si$ ($[M+H]^+$) 273.1522, Found 273.1521.

[1] M. Kanematsu, M. Yoshida and K. Shishido, *Angew. Chem., Int. Ed.*, 2011, **50,** 2618.

***tert*-Butyl-(7-iodomethyl-6,8-dioxabicyclo[3.2.1]oct-2-en-4-yloxy)dimethylsilane (8)**

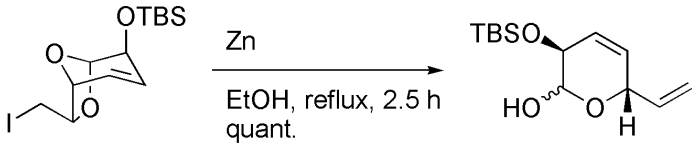


To a stirred solution of **7** (493 mg, 1.81 mmol) in CH_2Cl_2 (15.0 mL) were added Et_3N (0.76 mL, 5.46 mmol) and MsCl (0.28 mL, 3.62 mmol) at 0 °C. After being stirred at room temperature for 0.5 h, the reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give crude as a colorless oil, which was used to the next reaction without further purification.

To a stirred solution of crude in THF (10.0 mL) was added LiI (2.45 g, 18.3 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 4 h, the reaction mixture was diluted with Et_2O and added with saturated aq. $NaHCO_3$ / saturated aq. $Na_2S_2O_3$ (5/1, v/v). The resultant mixture was stirred at room temperature for 0.5 h, and then extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 95 / 5) to afford **8** (633 mg, 92% for 2 steps) as a colorless solid.

Mp: 104.5–105.5 °C; $[\alpha]_D^{28}$ +112.5 (*c* 1.22, $CHCl_3$); IR (neat) 2926, 2879, 2855, 1255, 1088 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.18 (ddd, *J* =10.0, 4.8, 1.0 Hz, 1H), 5.74 (ddd, *J* =9.8, 4.0, 2.0 Hz, 1H), 5.48 (t, *J* = 5.6 Hz, 1H), 4.63 (d, *J* = 4.8 Hz, 1H), 4.06 (dd, *J* = 9.2, 5.6 Hz, 1H), 3.71 (dt, *J* = 3.6, 1.2 Hz, 1H), 3.17 (dd, *J* = 9.6, 5.6, Hz, 1H), 3.10 (dd, *J* = 10.2, 9.8 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 3H) 0.11 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 129.3, 127.4, 104.1, 80.6, 73.3, 65.9, 25.8, 18.3, 6.6, –4.6, –4.7; HRMS (ESI) Calcd for $C_{13}H_{23}O_3NaSiI$ ($[M+Na]^+$) 405.0359, Found 405.0354.

3-(*tert*-Butyldimethylsilyloxy)-6-vinyl-3,6-dihydro-2*H*-pyran-2-ol (3)

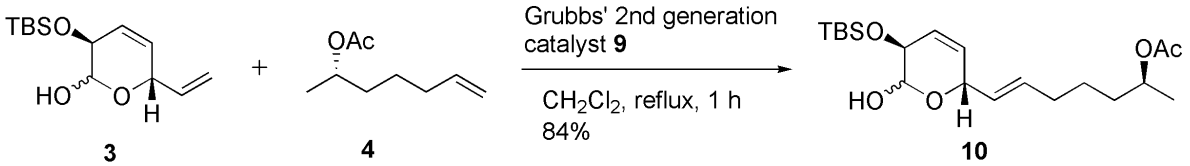


8 **3**

To a stirred solution of **8** (633 mg, 1.66 mmol) in EtOH (19.0 mL) was added Zn powder (1.07 g, 16.6 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2.5 h, the resultant solution was filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 80 / 20) to afford **3** (427 mg, quant., ca. 2.7 : 1 mixture of diastereomers; ^{1}H NMR) as a colorless oil.

IR (neat) 3421, 2954, 2929, 2886, 2857, 1472, 1361, 1113, 877, 838, 780 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.90–5.77 (m, 1.27H), 5.71–5.59 (m, 1.73H), 5.33 (dt, *J* = 17.2, 1.6 Hz, 0.73H), 5.31 (dt, *J* = 17.2, 1.6 Hz, 0.27H), 5.22 (dt, *J* = 12.8, 1.2 Hz, 0.27H), 5.19 (dt, *J* = 10.4, 1.2 Hz, 0.73H), 5.15 (dd, *J* = 5.6, 3.6 Hz, 0.27H), 4.82–4.80 (m, 0.27H), 4.76 (dd, *J* = 5.6, 4.0 Hz, 0.73H) 4.77–4.74 (m, 0.73H), 4.22–4.20 (m, 0.27H), 4.09–4.08 (m, 0.73H), 3.41 (d, *J* = 6.0 Hz, OH, D_2O exchangeable, 0.27H), 2.79 (dd, *J* = 5.6, 2.0 Hz, OH, D_2O exchangeable, 0.73H), 0.93 (s, 2.4H), 0.92 (s, 6.6H), 0.13 (s, 1.6H), 0.11 (s, 4.4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 136.5, 136.0, 130.3, 128.8, 128.6, 125.3, 116.7, 97.0, 90.6, 75.8, 70.3, 69.4, 64.8, 25.8, 18.2, –4.5, –4.7, –4.8; HRMS (ESI) Calcd for $C_{13}H_{24}O_3NaSi$ ($[M+Na]^+$) 279.1392, Found 279.1394.

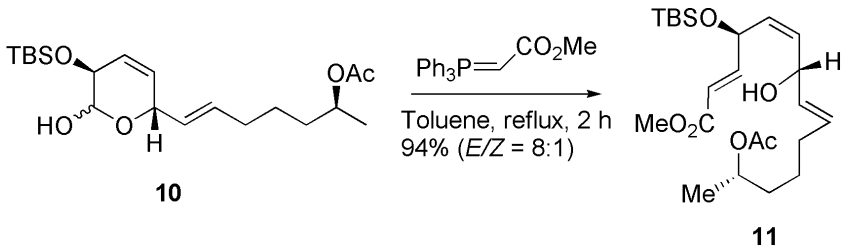
6-[5-(*tert*-Butyldimethylsilyloxy)-6-hydroxy-5,6-dihydro-2*H*-pyran-2-yl]-1-methylhex-5-enyl acetate (10)



To a stirred solution of **3** (10.8 mg, 42.1 μmol) and **4** (32.9 mg, 0.211 mmol) in CH_2Cl_2 (0.5 mL) was added Grubbs' 2nd generation catalyst **9** (1.7 mg, 2.00 μmol) at room temperature, and then the reaction mixture was heated to reflux. After being stirred for 1 h, the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography (hexane / AcOEt = 90 / 10) to afford **10** (13.6 mg, 84%, ca. 4 : 1 mixture of diastereomers; ^{1}H NMR) as a yellow oil.

IR (neat) 3520, 2931, 2860, 1733, 1383, 1249, 839, 781 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.80 (dt, *J* = 10.4, 1.6 Hz, 0.2H), 5.74 (dt, *J* = 15.2, 6.4 Hz, 0.8H), 5.66–5.54 (m, 2H), 5.49–5.39 (m, 1H), 5.13 (dd, *J* = 5.2, 4.0 Hz, 0.2H), 4.94–4.83 (m, 1H), 4.78–4.64 (m, 1.8H), 4.22–4.18 (m, 0.2H), 4.09–4.03 (m, 0.8H), 3.38 (d, *J* = 5.6 Hz, OH, D_2O exchangeable, 0.2H), 2.76 (d, *J* = 5.6 Hz, OH, D_2O exchangeable, 0.8H), 2.08–2.03 (m, 2H), 2.02 (s, 3H), 1.63–1.33 (m, 4H), 1.20 (d, *J* = 6.4 Hz, 3H), 0.92 (d, *J* = 2.4 Hz, 9H), 0.13 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 133.8, 133.5, 130.9, 129.4, 128.8, 128.4, 128.2, 125.0, 97.0, 90.6, 75.6, 70.8, 70.0, 69.4, 64.8, 35.4, 32.0, 31.9, 25.8, 25.7, 24.7, 24.6, 21.3, 19.9, 18.2, 18.1, –4.5, –4.7, –4.8; HRMS (ESI) Calcd for $C_{20}H_{36}NaO_5Si$ ($[M+Na]^+$) 407.2230, Found 407.2227.

13-Acetoxy-4-(*tert*-butyldimethylsilyloxy)-7-hydroxytetradeca-2,5,8-trienoic acid methyl ester (11)



10 **11**

To a stirred solution of **10** (9.7 mg, 25.2 μmol) in toluene (0.3 mL) was added methyl (triphenylphosphoranylidene) acetate (42.2 mg, 0.126 mmol) at room temperature, and then the mixture was heated to reflux. After being stirred for 2 h, the resultant mixture was concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 90 / 10) to afford the ***Z*-isomer** (1.2 mg, 10%) as a colorless oil and **11** (9.2 mg, 84%) as a colorless oil;

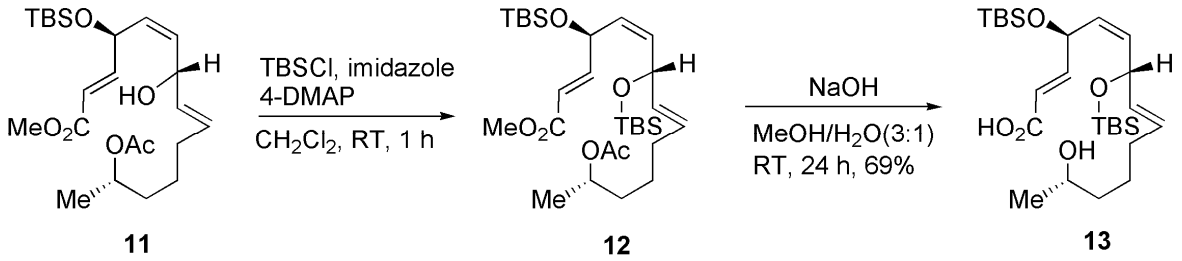
***Z*-isomer**

$[\alpha]_D^{31}$ –91.4 (*c* 1.03, $CHCl_3$); IR (neat) 3476, 2931, 2857, 1722, 1257, 1059, 826 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.28 (dd, *J* = 9.2, 7.2 Hz, 1H), 6.14 (dd, *J* = 11.2, 8.8 Hz, 1H), 5.69 (dd, *J* = 11.2, 1.2 Hz, 1H), 5.60 (dt, *J* = 15.2, 7.6 Hz, 1H), 5.52–5.41 (m, 3H), 5.10 (t, *J* = 5.6 Hz, 1H), 4.94–4.83 (m, 1H), 3.72 (s, 3H), 2.23 (d, *J* = 3.2 Hz, OH, D_2O exchangeable, 1H), 2.03–1.98 (m, 5H), 1.56–1.30 (m, 4H), 1.19 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 166.2, 149.7, 132.8, 131.3, 131.2, 130.7, 116.9, 70.8, 68.7, 65.0, 51.4, 35.4, 32.0, 25.8, 25.0, 21.3, 19.9, 18.1, –4.7; HRMS (ESI) Calcd for $C_{23}H_{41}O_6Si$ ($[M+H]^+$) 441.2672, Found 441.2677.

***E*-enoate (11)**

$[\alpha]_D^{32}$ +64.7 (*c* 0.34, $CHCl_3$); IR (neat) 3496, 2931 2858, 1730, 1252 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.77 (dd, *J* = 15.6, 4.0 Hz, 1H), 6.02 (dd, *J* = 15.2, 1.2 Hz, 1H), 5.68 (dt, *J* = 15.2, 3.2 Hz, 1H), 5.54–5.49 (m, 1H), 5.49 (ddd, *J* = 10.8, 8.0, 0.8 Hz, 1H), 5.35 (ddd, *J* = 10.8, 8.0, 0.8 Hz, 1H), 5.19–5.16 (m, 1H), 4.92–4.87 (m, 2H), 3.73 (s, 3H), 2.06 (q, *J* = 6.8 Hz, 2H), 2.03 (s, 3H), 1.72 (s, OH, D_2O exchangeable, 1H), 1.53–1.39 (m, 4H), 1.21 (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 167.0, 148.8, 132.2, 131.7, 131.4, 131.2, 119.3, 70.7, 69.3, 68.4, 51.5, 35.4, 31.9, 25.7, 24.7, 21.3, 19.9, 18.2, –4.6, –4.9; HRMS (ESI) Calcd for $C_{23}H_{41}O_6Si$ ($[M+H]^+$) 441.2672, Found 441.2677.

4,7-Bis-(*tert*-butyldimethylsilyloxy)-13-hydroxytetradeca-2,5,8-trienoic acid (13)



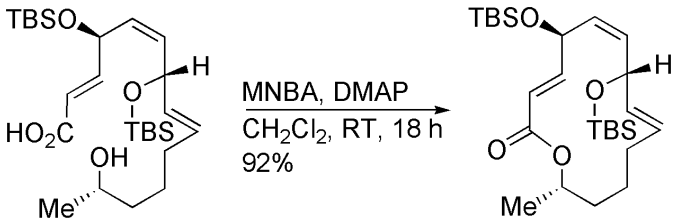
11 **12** **13**

To a stirred solution of **11** (5.4 mg, 12.2 μmol) in CH_2Cl_2 (0.3 mL) were added imidazole (2.5 mg, 36.8 μmol), TBSCl (3.7 mg, 24.5 μmol) and 4-DMAP (0.14 mg, 1.22 μmol) at 0 °C. After being stirred at room temperature for 1 h, the reaction mixture was quenched with H_2O and extracted with $CHCl_3$. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo to give **12** as a colorless oil, which was used to the next reaction without further purification.

To a stirred solution of crude **12** in MeOH/H_2O (0.04 mL, 3/1, v/v) was added NaOH (2.5 mg, 61.3 μmol) at room temperature. After being stirred at room temperature for 24 h, the reaction mixture was quenched with H_2O and extracted with AcOEt. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel column chromatography ($CHCl_3$ / MeOH = 99 / 1) to afford **13** (4.2 mg, 69%) as a colorless oil.

$[\alpha]_D^{26}$ +73.4 (*c* 2.08, $CHCl_3$); IR (neat) 3379, 2953, 2927, 2856, 1699, 1654, 1255, 1075, 837, 776 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.86 (dd, *J* = 15.2, 4.0 Hz, 1H), 6.01 (d, *J* = 15.2 Hz, 1H), 5.57 (dt, *J* = 15.2, 6.8 Hz, 1H), 5.52–5.40 (m, 2H), 5.25 (ddd, *J* = 11.2, 7.6, 1.2 Hz, 1H), 5.20–5.12 (m, 1H), 4.85 (t, *J* = 7.2 Hz, 1H), 3.83–3.82 (m, 1H), 2.06–2.05 (m, 2H), 1.51–1.42 (m, 4H), 1.17 (d, *J* = 4.4 Hz, 3H), 0.91 (s, 9H), 0.88 (s, 9H), 0.09 (d, *J* = 1.6 Hz, 6H), 0.09 (s, 3H), 0.07 (s, 3H), OH protons were not detected; ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.4, 150.6, 133.3, 132.2, 131.3, 129.3, 118.9, 70.9, 68.7, 68.2, 38.7, 32.1, 25.8, 25.4, 22.9, 18.2, –4.2, –4.5, –4.6, –4.8; HRMS (ESI) Calcd for $C_{26}H_{51}O_5Si_2$ ($[M+H]^+$) 499.3275, Found 499.3278.

5,8-Bis-(*tert*-butyldimethylsilyloxy)-14-methyloxacyclotetradeca-3,6,9-trien-2-one (14)

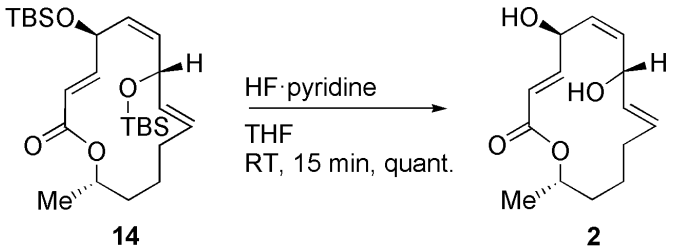


13 **14**

To a stirred solution of **13** (37.0 mg, 74.2 μmol) in CH_2Cl_2 (5.0 mL) were taken up and added dropwise to a solution of 2-methyl-6-nitro benzoic acid anhydride (30.6 mg, 89.0 μmol) and 4-DMAP (21.7 mg, 0.178 mmol) in CH_2Cl_2 (45.0 mL) over a period of 18 h at room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated aq. $NaHCO_3$, and then extracted with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 95 / 5) to afford **14** (32.8 mg, 92%) as a colorless oil.

$[\alpha]_D^{31}$ +92.8 (*c* 1.50, $CHCl_3$); IR (neat) 2930, 2857, 1720, 1254, 1127, 1060, 837, 778 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 15.2, 3.6 Hz, 1H), 5.87 (dd, *J* = 15.2, 1.6 Hz, 1H), 5.68 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.45 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.41–5.33 (m, 2H), 5.15 (s, 1H), 4.77 (t, *J* = 6.8 Hz, 1H), 4.72–4.64 (m, 1H), 2.15–1.88 (m, 2H), 1.87–1.66 (m, 2H), 1.53–1.42 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.90 (s, 9H), 0.09 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.4, 149.5, 132.2, 131.9, 131.8, 131.5, 117.5, 72.0, 71.0, 69.0, 34.6, 32.9, 25.9, 25.8, 24.5, 20.3, 18.3, 18.2, –4.4, –5.0; HRMS (ESI) Calcd for $C_{26}H_{48}NaO_4Si_2$ ($[M+Na]^+$) 503.2989, Found 503.2993.

5,8-Dihydroxy-14-methyloxacyclotetradeca-3,6,9-trien-2-one (2)

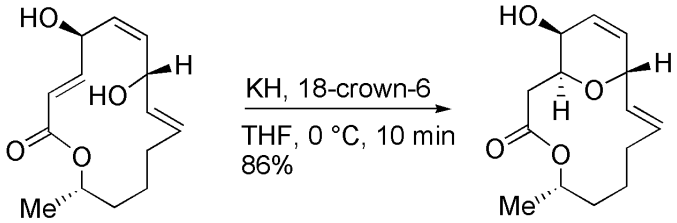


14 **2**

To a stirred solution of **14** (6.5 mg, 13.5 μmol) in THF (0.5 mL) at 0 °C was added HF·pyridine (70.0 μL). After being stirred for 15 min at room temperature, the reaction mixture was quenched with saturated aq. $NaHCO_3$ at 0 °C, and then extracted with AcOEt. The combined extracts were washed with saturated aq. $CuSO_4$, brine, and dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 50 / 50) to afford **2** (3.4 mg, quant.) as a colorless oil.

$[\alpha]_D^{28}$ +188.2 (*c* 0.68, $CHCl_3$); IR (neat) 3362, 2974, 2931, 1698, 1261, 1008, 976 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 15.6, 4.4 Hz, 1H), 5.90 (dd, *J* = 15.6, 2.0 Hz, 1H), 5.86 (ddd, *J* = 15.6, 9.2, 5.6 Hz, 1H), 5.54 (dd, *J* = 11.2, 4.4 Hz, 1H), 5.49 (dd, *J* = 15.2, 7.6 Hz, 1H), 5.46 (ddd, *J* = 10.8, 9.6, 2.4 Hz, 1H), 5.26–5.25 (m, 1H), 4.82 (t, *J* = 8.4 Hz, 1H), 4.75 (dtd, *J* = 16.0, 6.0, 2.0 Hz, 1H), 2.32 (brs, OH, D_2O exchangeable, 1H), 2.13–1.95 (m, 2H), 1.80 (brs, OH, D_2O exchangeable, 1H), 1.87–1.73 (m, 2H), 1.54–1.48 (m, 1H), 1.26 (d, *J* = 6.0, 3H), 1.15–1.08 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.1, 148.3, 134.4, 132.1, 131.2, 130.3, 118.3, 72.0, 70.6, 68.4, 34.5, 32.8, 24.4, 20.2; HRMS (ESI) Calcd for $C_{14}H_{20}O_4Na$ ($[M+Na]^+$) 275.1259, Found 275.1262.

Aspergillide C (1)



2 **1**

To a stirred suspension of KH (1.7 mg, 30% in oil, 12.5 μmol) in THF (0.1 mL) were added 18-Crown-6 (7.9 mg, 29.7 μmol) and **2** (1.5 mg, 5.95 μmol) in THF (0.2 mL) at 0 °C. After being stirred at the same temperature for 10 min, the reaction mixture was quenched with saturated aq. NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 70 / 30) to afford **1** (1.3 mg, 86%) as a colorless solid.

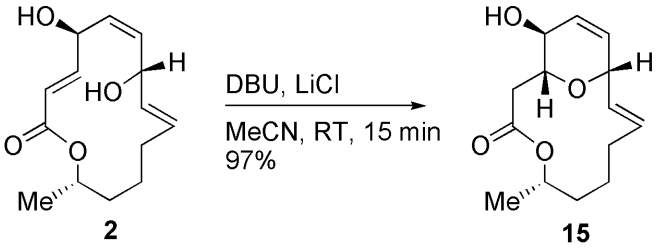
Mp: 104.5–105.5 °C; (lit.[2] mp: 115.5–116 °C); $[\alpha]_D^{29}$ +83.8 (*c* 0.33, MeOH) {lit.[3] $[\alpha]_D^{25}$ +66.2 (*c* 0.19, MeOH), lit.[2] $[\alpha]_D^{25}$ +83.0 (*c* 0.14, MeOH), lit.[4] $[\alpha]_D^{28}$ +77.5 (*c* 0.11, MeOH)}; IR (neat) 3411, 2924, 2852, 1732, 1456, 1375, 1193 cm^{-1}; ^{1}H-NMR (500 MHz, C_6D_6) δ 5.94 (dddd, *J* = 15.5, 9.5, 6.0, 2.0 Hz, 1H), 5.74 (ddd, *J* = 10.5, 6.0, 2.0 Hz, 1H), 5.41 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.18 (dd, *J* = 15.5, 4.0 Hz, 1H), 5.15–5.13 (m, 1H), 4.46–4.45 (m, 1H), 4.03 (dt, *J* = 11.5, 1.5 Hz, 1H), 3.22 (dd, *J* = 10.5, 5.0 Hz, 1H), 2.87 (dd, *J* = 13.5, 11.5 Hz, 1H), 2.25 (dd, *J* = 13.5, 2.0 Hz, 1H), 1.96 (dddd, *J* = 13.0, 9.5, 6.0, 2.0 Hz, 1H), 1.63–1.54 (m, 2H), 1.45–1.36 (m, 1H), 1.32–1.25 (m, 1H), 1.24 (brs, OH, D_2O exchangeable, 1H), 1.20–1.12 (m, 1H), 0.99 (d, *J* = 6.5 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.0, 135.0, 131.8, 128.5, 126.2, 72.0, 69.8, 69.5, 64.5, 38.8, 32.0, 31.0, 23.7, 18.7; HRMS (ESI) Calcd for $C_{14}H_{21}O_4$ ($[M+H]^+$) 253.1440, Found 253.1444.

[2] T. Nagasawa and S. Kuwahara, *Org. Lett.,* 2009, **11**, 761.

[3] K. Kito, R. Ookura, S. Yoshida, M. Namikoshi, T. Ooi and T. Kusumi, *Org. Lett.,* 2008, **10**, 225.

[4] M. Kanematsu, M. Yoshida and K. Shishido, *Tetrahedron Lett.,* 2011, **52,** 1372.

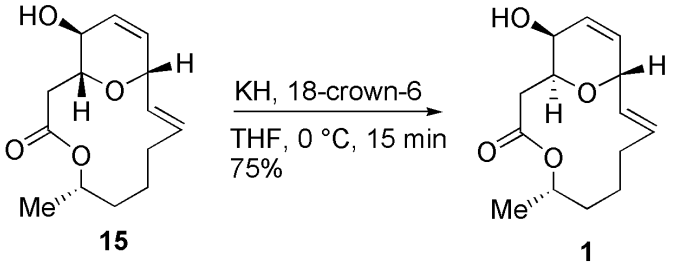
3-*epi*-Aspergillide C (15)



To a stirred solution of **4** (3.0 mg, 1.20 μmol) in MeCN (0.2 mL) were added LiCl (5.0 mg, 11.9 μmol) and DBU (16.7 μL, 11.9 μmol) at room temperature. After being stirred at the same temperature for 15 min, the reaction mixture was quenched with saturated aq. NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 60 / 40) to afford **15** (2.9 mg, 97%) as a colorless oil.

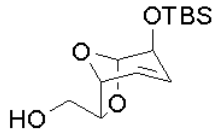
$[\alpha]_D^{31}$ +80.2 (*c* 0.49, $CHCl_3$); IR (neat) 3366, 2926, 2853, 1732, 1263, 1066, 1028 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.07 (dddd, *J* = 10.0, 6.0, 2.5, 1.0 Hz, 1H), 5.99 (dd, *J* = 10.0, 3.0 Hz, 1H), 5.82 (dddd, *J* =15.5, 7.0, 6.0, 1.5 Hz, 1H), 5.58 (ddt, *J* = 16.0, 6.5, 1.5 Hz, 1H), 5.08–5.04 (m, 1H), 4.67 (d, *J* = 4.5 Hz, 1H), 4.59 (dd, *J* = 12.5, 3.0 Hz, 1H), 3.67 (dd, *J* = 10.0, 9.5 Hz, 1H), 2.53 (dd, *J* = 16.0, 11.5 Hz, 1H), 2.37 (dd, *J* = 16.5, 3.5 Hz, 1H), 2.23-2.03 (m, 2H), 2.00 (d, *J* = 9.6 Hz, OH, D_2O exchangeable, 1H), 1.86–1.78 (m, 1H), 1.75–1.56 (m, 3H), 1.20 (d, *J* = 6.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.0, 134.8, 131.8, 130.1, 124.2, 73.6, 70.9, 69.7, 64.2, 38.7, 32.7, 30.8, 21.6, 18.8; HRMS (ESI) Calcd for $C_{14}H_{21}O_4$ ($[M+H]^+$) 253.1440, Found 253.1435.

Interconversion of 3-*epi*-aspergillide C (15) to aspergillide C (1)



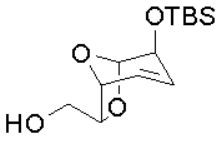
15 **1**

To a stirred suspension of KH (0.9 mg, 30% in oil, 6.66 μmol) in THF (0.1 mL) were added 18-Crown-6 (4.2 mg, 15.9 μmol) and 3-*epi*-aspergillide C (**15**) (0.8 mg, 3.17 μmol) in THF (0.2 mL) at 0 °C. After being stirred for 15 min, the reaction mixture was quenched with saturated aq. NH_4Cl and extracted with AcOEt. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography (hexane / AcOEt = 60 / 40) to afford aspergillide C (**1**) (0.6 mg, 75%) as a colorless solid.



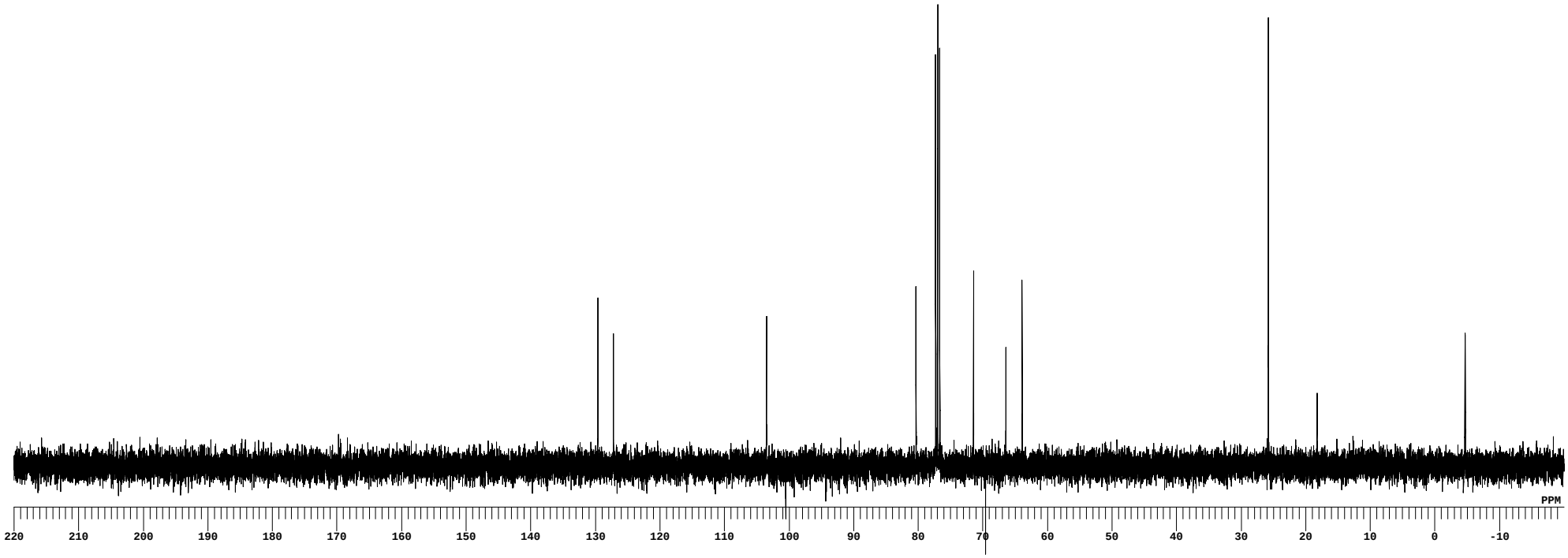
7

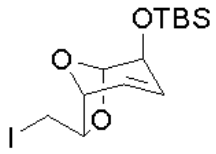
^{1}H NMR (400 MHz) in $CDCl_3$



7

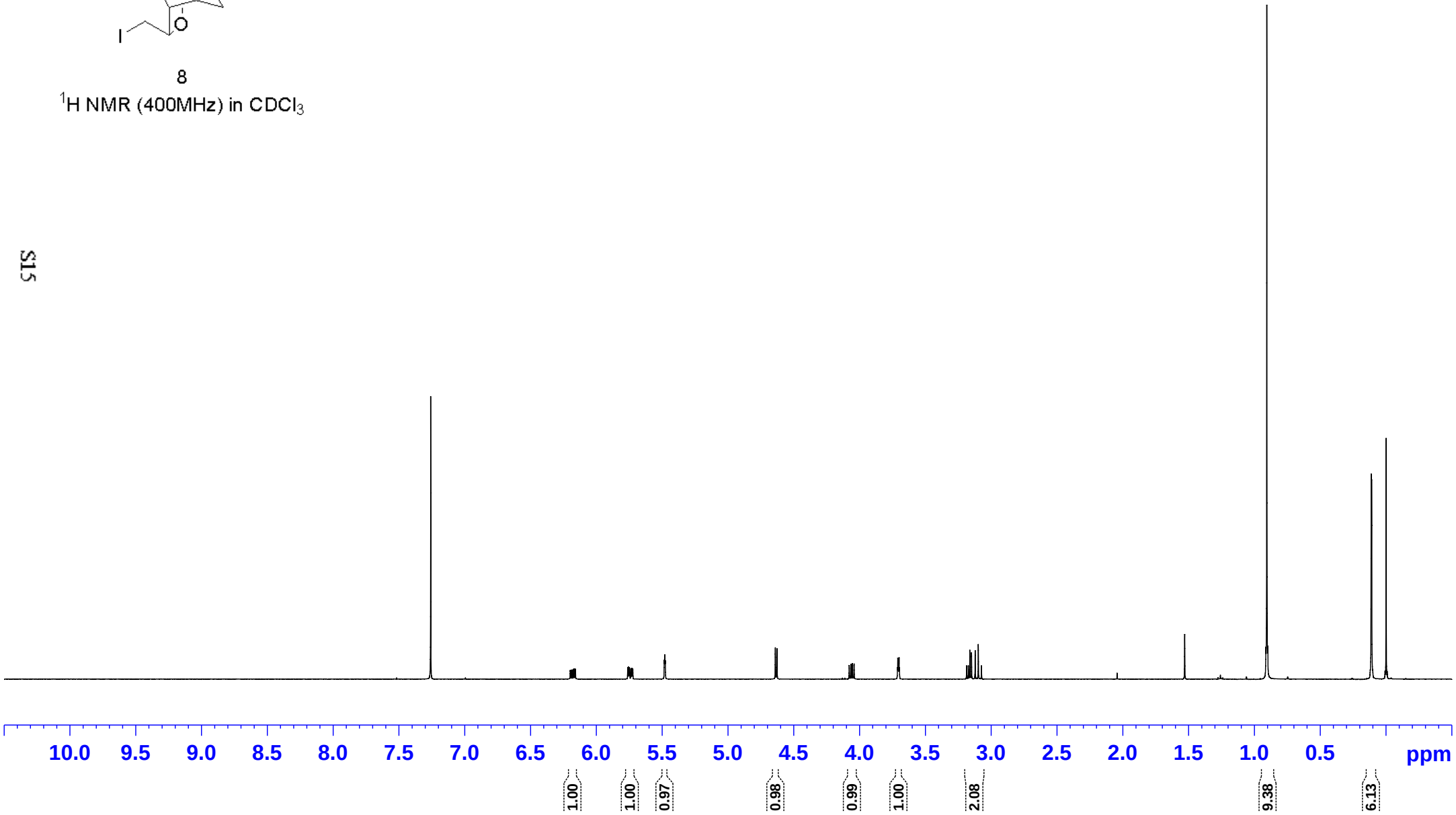
^{13}C NMR (100 MHz) in $CDCl_3$

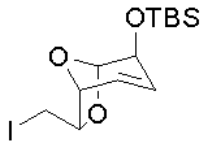




8

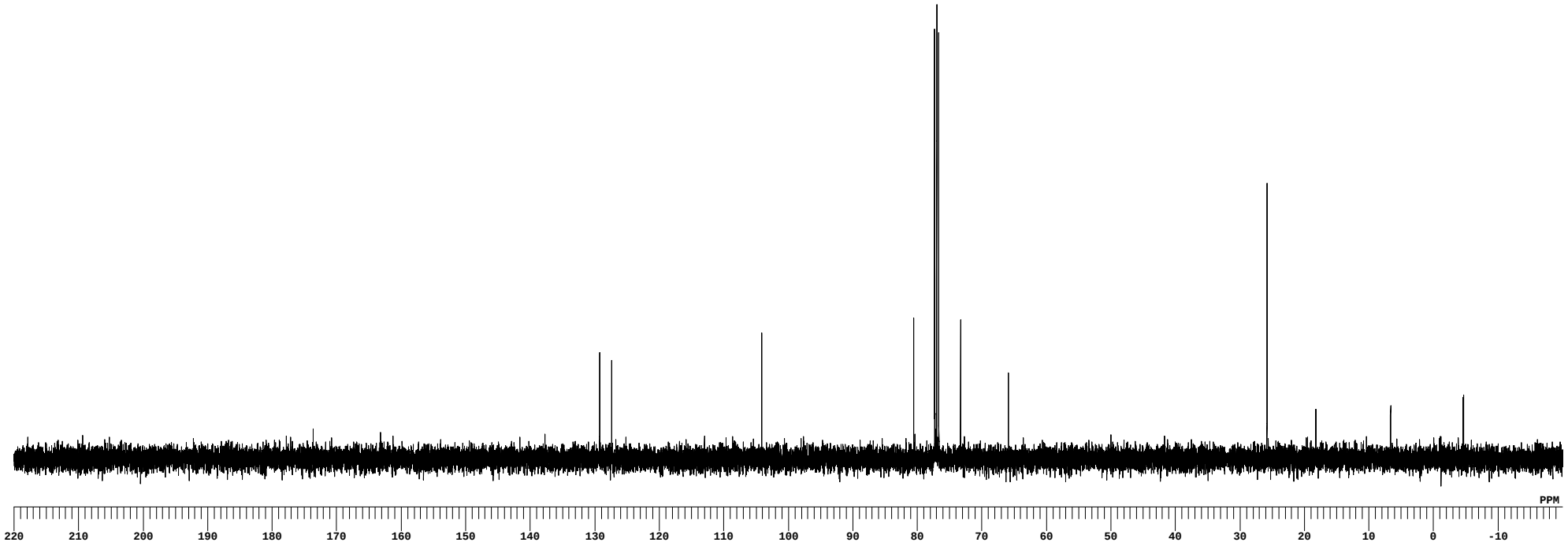
^{1}H NMR (400MHz) in $CDCl_3$

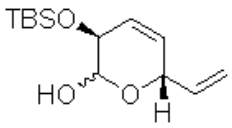




8

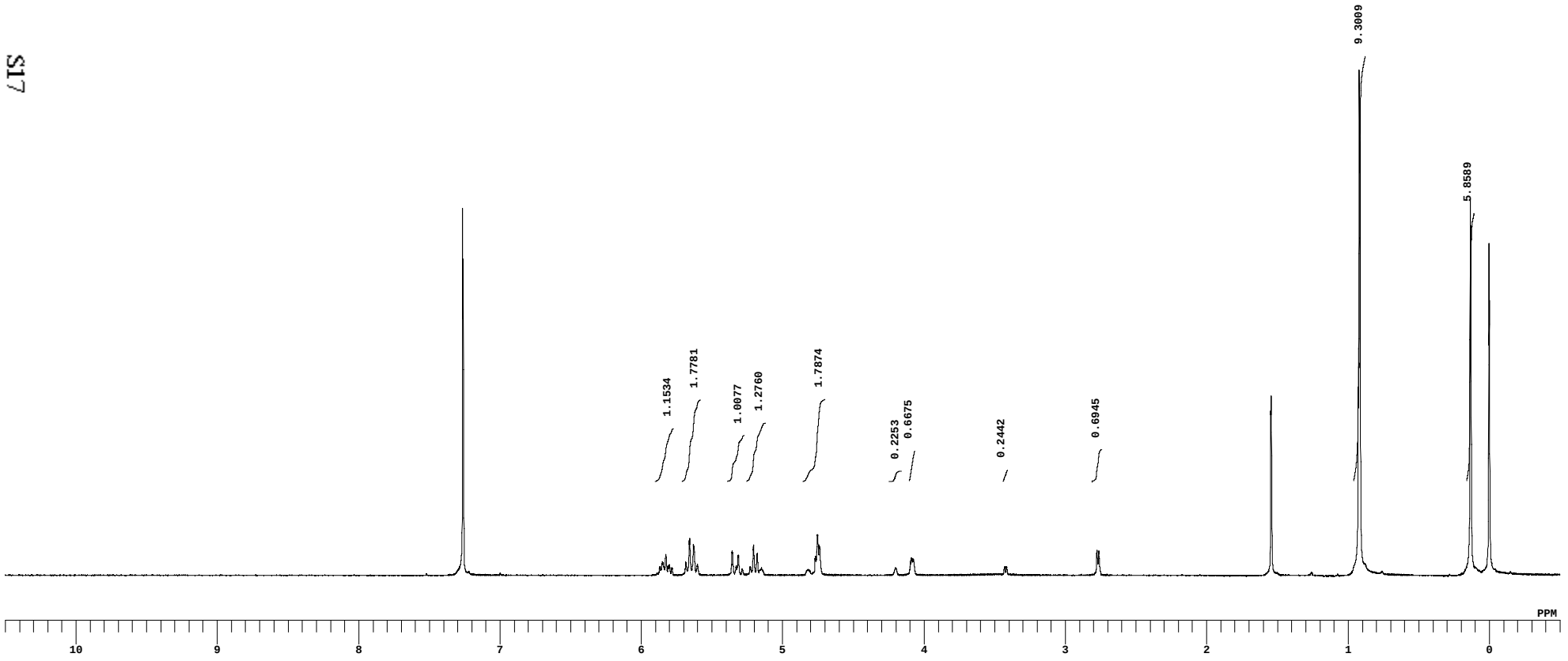
^{13}C NMR (100MHz) in $CDCl_3$

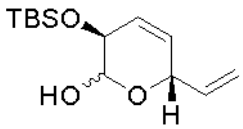




3 (*dr* = 2.7 : 1)

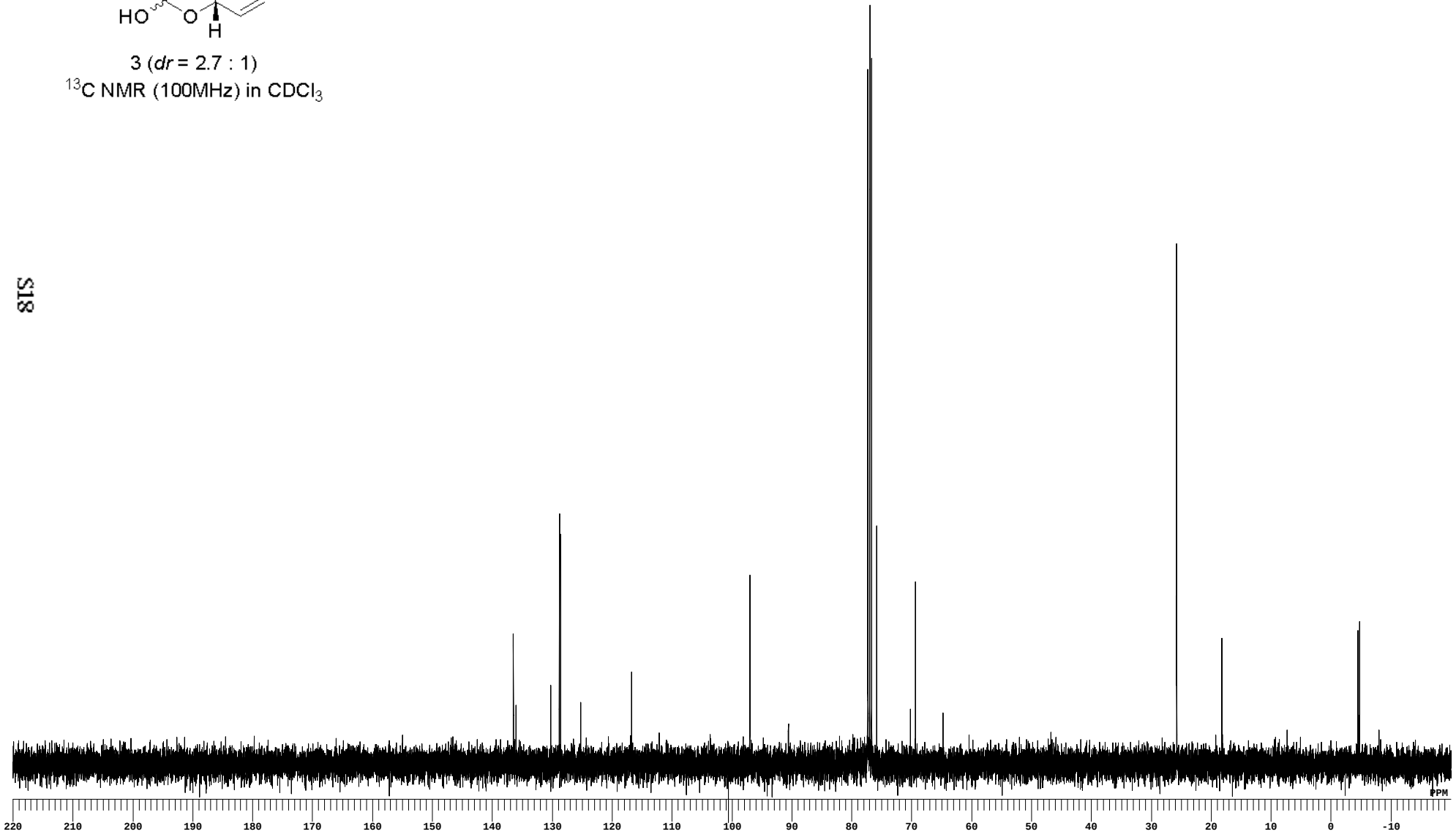
^{1}H NMR (400MHz) in $CDCl_3$

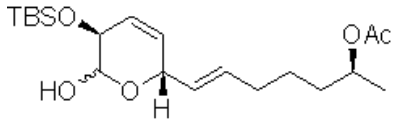




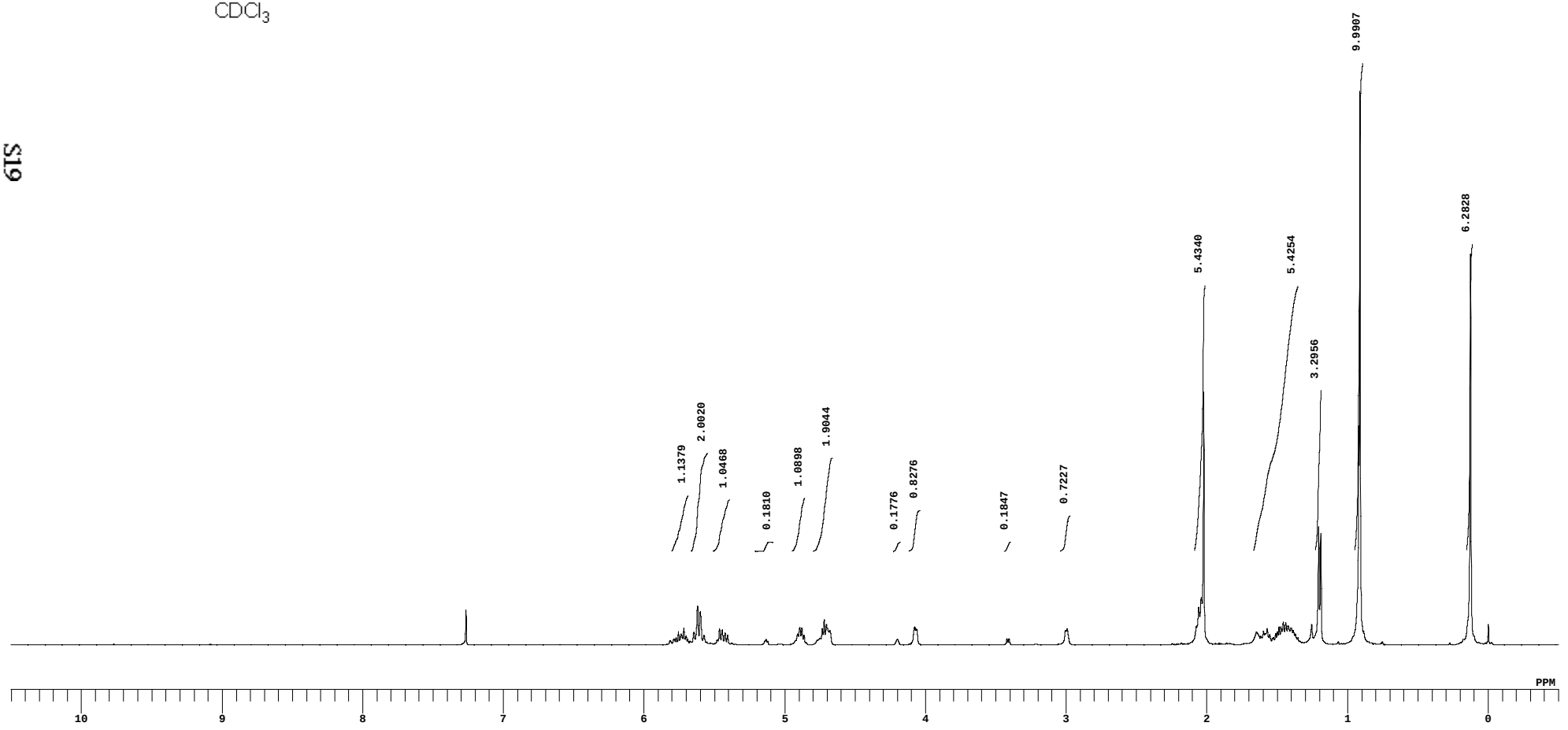
3 (*dr* = 2.7 : 1)

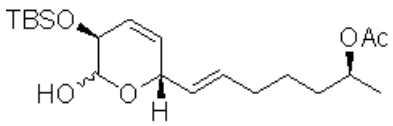
^{13}C NMR (100MHz) in $CDCl_3$





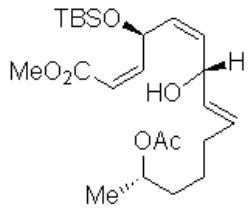
10 (*dr* = 4 : 1)
^{1}H NMR (400MHz) in
$CDCl_3$





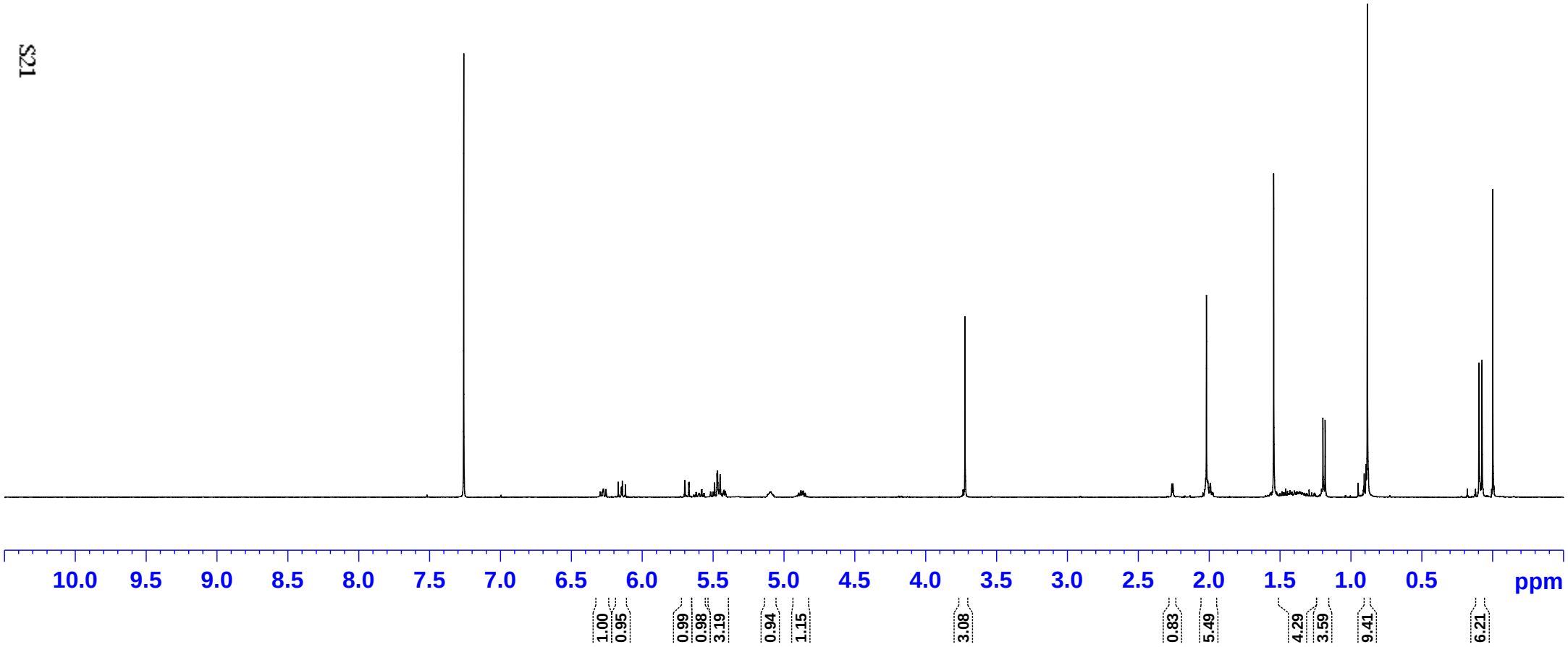
10 (*dr* = 4 : 1)

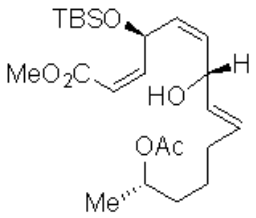
^{13}C NMR (100MHz) in $CDCl_3$



11-*Z*

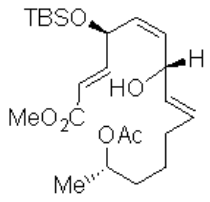
^{13}C NMR (100MHz) in $CDCl_3$





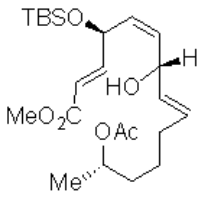
11-*Z*

^{1}H NMR (400MHz) in $CDCl_3$



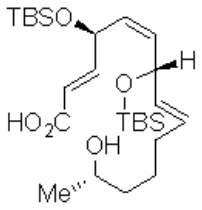
11-*E*

^{1}H NMR (400MHz) in $CDCl_3$



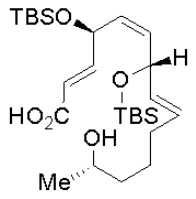
11-*E*

^{13}C NMR (100MHz) in $CDCl_3$



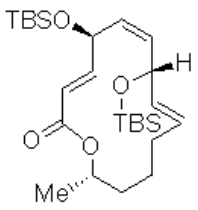
13

^{1}H NMR (400MHz) in $CDCl_3$



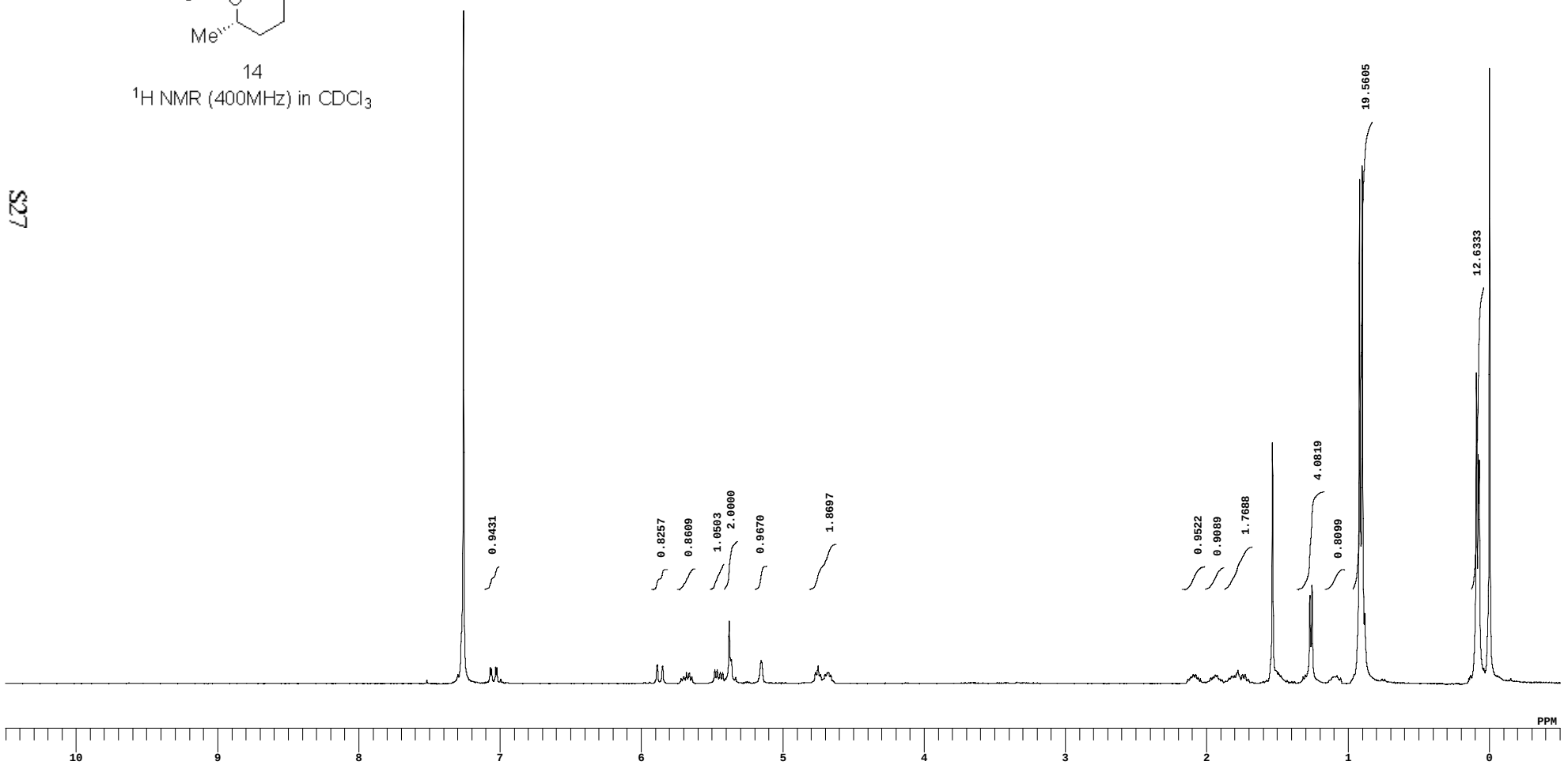
13

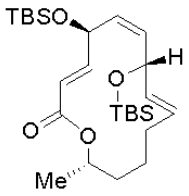
^{13}C NMR (100MHz) in $CDCl_3$



14

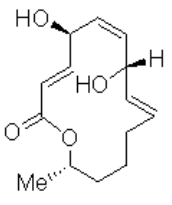
^{1}H NMR (400MHz) in $CDCl_3$





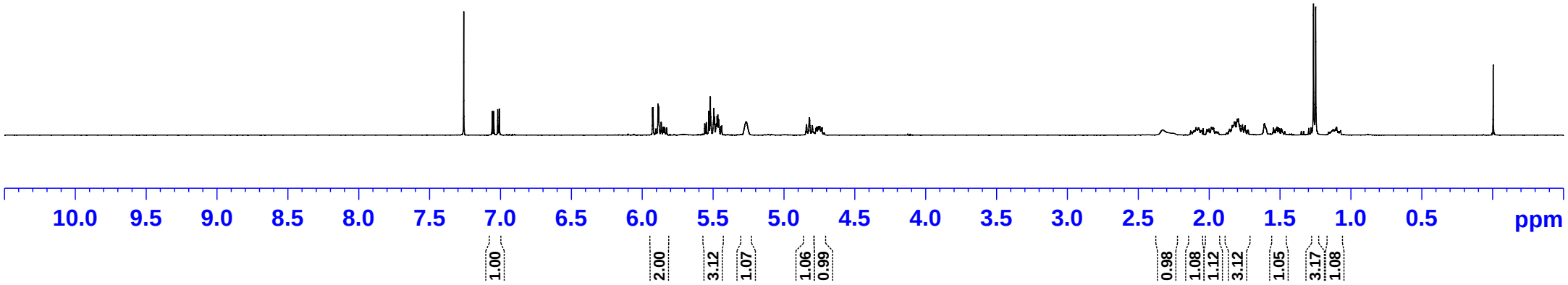
14

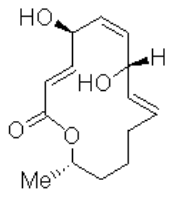
^{13}C NMR (100MHz) in $CDCl_3$



2

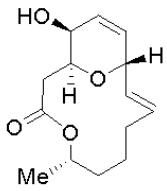
^{1}H NMR (400MHz) in $CDCl_3$





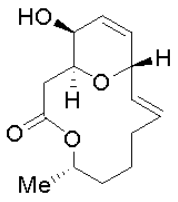
2

^{13}C NMR (100MHz) in $CDCl_3$



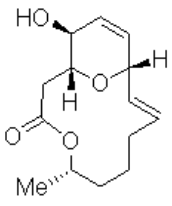
1

^{1}H NMR (500MHz) in C_6D_6



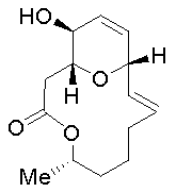
1

^{13}C NMR (125MHz) in C_6D_6



15

^{1}H NMR (500MHz) in $CDCl_3$



15

1H NMR (100MHz) in $CDCl_3$