Supporting Information

Total Synthesis of Pseudodehydrothyrsiferol

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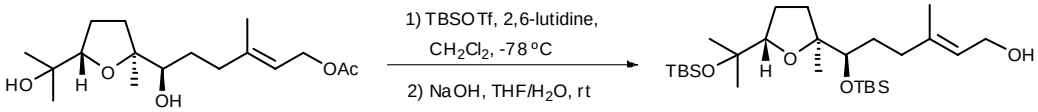
Contents

Experimental details and full characterization of compounds.

General

All reactions involving air- and moisture-sensitive reagents were carried out using oven dried glassware and standard syringe-septum cap techniques. Routine monitorings of reaction were carried out using glass-supported Merck silica gel 60 F254 TLC plates. Column chromatography was performed on Kanto Chemical Silica Gel 60N (spherical, neutral 40–50 μm) with the solvents indicated. All solvents and reagents were used as supplied with following exceptions. Tetrahydrofuran (THF), toluene and benzene were freshly distilled from Na metal/benzophenone under argon. Measurements of optical rotations were performed with a JASCO DIP-370 automatic digital polarimeter. Melting points were taken on a Yanaco MP-3 micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a Varian Gemini-200 (200 MHz), Mercury-300 (300 MHz), GX-400 (400 MHz), Unity-600 (600 MHz), JEOL AL-400 (400 MHz) spectrometer. Chemical shifts were expressed in ppm using Me_4Si ($\delta = 0$) as an internal standard. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), broad (br). Infrared (IR) spectral measurements were carried out with a JASCO FT/IR-4100 spectrometer (ATR method). Low- and High-resolution mass (HRMS) spectra were measured on a JEOL JMS-DX 303/JMA-DA 5000 SYSTEM high resolution mass spectrometer.

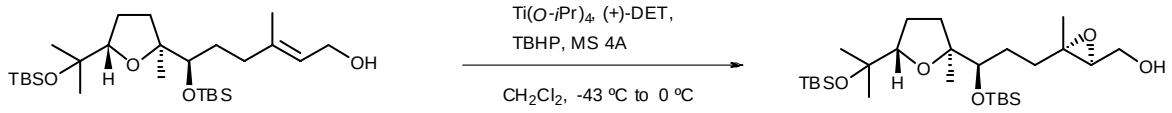
Synthesis of Segment A



2 3

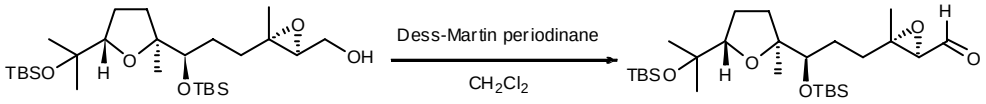
To a stirred solution of **2** (4.24 g, 13.5 mmol) and 2,6-lutidine (9.43 mL, 81 mmol) in CH_2Cl_2 (50 mL) was added TBSOTf (9.3 mL, 40 mmol) at –78 °C. After stirring for 9 h, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (8.0 g), which was used for the next reaction without further purification. The crude compound described above was dissolved in 20 mL of THF/H_2O (3:2). To the solution was added 8 mL NaOH aqueous solution (2 mol·L^{-1}) at rt. After stirring for 4 h, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 9:1) to give **3** (5.94 g, 11.9 mmol, 88% yield, 2 steps) as a colorless oil.

$[\alpha]_D^{18}$= –3.34 (*c* 0.99, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (12H, s), 0.86 (9H, s), 0.89 (9H, s), 1.09 (3H, s), 1.16 (3H, s), 1.17 (3H, s), 1.39–1.59 (3H, m), 1.67 (3H, s), 1.70–2.20 (5H, m), 3.48 (2H, dd, *J* = 6.9, 3.8 Hz), 3.62 (1H, dd, *J* = 8.8, 6.3 Hz), 4.15 (2H, br d, *J* = 6.3 Hz), 5.41 (1H, t, *J* = 6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –4.09 (q), –3.73 (q), –2.06 (q), –2.05 (q), 16.33 (q), 18.14 (s), 18.18 (s), 22.43 (q), 24.85 (q), 25.88 (q), 26.04 (q), 26.49 (t), 28.11 (q), 32.24 (t), 35.09 (t), 36.62 (t), 59.39 (t), 74.34 (s), 77.40 (d), 85.84 (s), 86.93 (d), 122.94 (d), 140.49 (s). CIMS *m*/*z* 501 $[M+H]^+$, 351 (90), 257 (100), 173 (40). HRCIMS calcd 501.3795 for $C_{27}H_{57}O_4Si_2$, found 501.3772 $[M+H]^+$. IR (neat, cm^{-1}) 3327, 2954, 2931, 2857, 1467, 1363, 1252, 1172, 1097, 1067, 1038, 1005, 910, 834, 772.



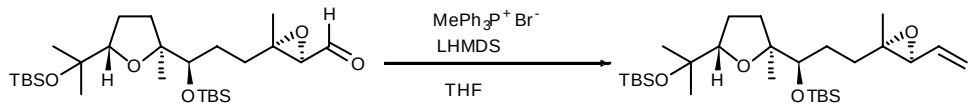
3 **4**

To a stirred suspension of molecular sieves 4A (152 mg) in CH_2Cl_2 was added titanium(IV) isopropoxide (90 μL, 0.30 mmol) and (+)-diethyl L-tartarate (78 μL, 0.76 mmol). After cooling at -30 °C, CH_2Cl_2 solution of **3** (762 mg, 1.520 mmol) and *tert*-butyl hydroperoxide (5.0 – 6.0 mol·L^{-1} in decane, 360 μL, 1.8 – 2.1 mmol) was add to the mixture. The reaction mixture was allowed to warm to 0 °C. After stirring for 2 days, the reaction was quenched by addition of saturated aqueous $NaHSO_3$ and the mixture was filtered through Celite. The filtrate was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 5:1) to give **4** (694 mg, 1.34 mmol, 88 %) as a colorless oil. The compound **4** are obtained in 77% diastereomeric excess which was determined by ^{1}H NMR analysis.
$[\alpha]_D^{18} = -7.49$ (*c* 1.51, $CHCl_3$). ^{1}H NMR (600MHz, $CDCl_3$): δ 0.05 (3H, s), 0.06 (3H, s), 0.07 (6H, s), 0.85 (9H, s), 0.88 (9H, s), 1.08 (3H, s), 1.16 (3H, s), 1.17 (3H, s), 1.28 (3H, s), 1.40 (1H, m), 1.55 (1H, m), 1.62 (2H, m), 1.72–1.88 (4H, m), 1.93 (1H, m), 2.95 (1H, dd, *J* = 6.3, 4.4 Hz), 3.47 (1H, dd, *J* = 6.7, 4.4 Hz), 3.62 (1H, dd, *J* = 9.1, 6.0 Hz), 3.69 (1H, m), 3.84 (1H, m). Selected minor signals. 2.96 (1H), 3.62 (1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –4.16 (q), –3.76 (q), –2.06 (q), 16.77 (q), 18.13 (s), 22.36 (q), 24.89 (q), 25.88 (q), 26.00 (q), 26.46 (t), 28.05 (q), 29.09 (t), 35.19 (t), 35.47 (t), 61.44 (t), 61.53 (s), 62.68 (d), 74.30 (s), 77.33 (d), 85.77 (s), 86.97 (d). CIMS *m*/*z* 517 $[M+H]^+$, 385 (30), 257 (100), 173 (35). HRCIMS calcd 517.3745 for $C_{27}H_{57}O_5Si_2$, found 517.3716 $[M+H]^+$. IR (neat, cm^{-1}) 3389, 2955, 2931, 2857, 1467, 1383, 1253, 1172, 1097, 1067, 1038, 910, 834, 773.



4 **4a**

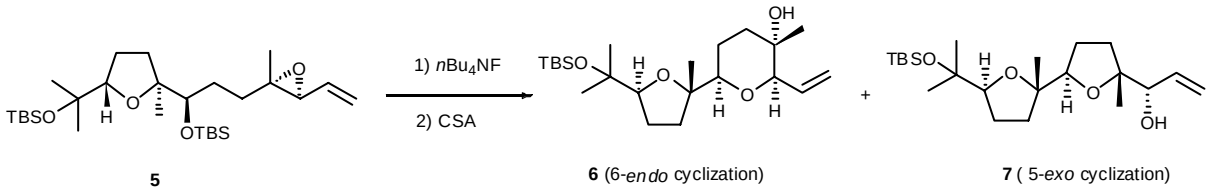
To a stirred solution of **4** (1.01 g, 1.95 mmol) in CH_2Cl_2 (50 mL) was added Dess-Martin periodinane (900 mg, 2.12 mmol) at rt. After stirring for 5 h, the reaction was quenched by addition of 10% aqueous sodium thiosulfate. The mixture was diluted with aqueous sodium hydrogen carbonate and diethyl ether. The phases were separated and the aqueous phase was extracted with diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 15:1) to give a corresponding aldehyde **4a** (999 mg, 1.94 mmol, 99 %) as a colorless oil.
$[\alpha]_D^{18} = +20.0$ (*c* 1.56, $CDCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.04 (3H, s), 0.07 (3H, s), 0.08 (6H, s), 0.85 (9H, s), 0.85 (9H, s), 1.08 (3H, s), 1.16 (6H, s), 1.43 (3H, s), 1.54–1.64 (3H, m), 1.66–1.96 (5H, m), 3.16 (1H, d, *J* = 4.9 Hz), 3.47 (1H, m), 3.62 (1H, m), 9.46 (1H, d, *J* = 4.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): –4.17 (q), –3.77 (q), –2.07 (q), –2.05 (q), 17.23 (q), 18.12 (s), 22.11 (q), 24.93 (q), 25.88 (q), 25.97 (q), 26.42 (t), 27.98 (q), 28.83 (t), 35.23 (t), 35.62 (t), 63.39 (d), 64.52 (s), 74.27 (s), 77.10 (d), 85.67 (s), 87.06 (d), 199.76 (d). CIMS *m*/*z* 515 $[M+H]^+$, 383 (100), 257 (65), 251 (30), 57 (64). HRCIMS calcd 515.3588 for $C_{27}H_{55}O_5Si_2$, found 515.3580 $[M+H]^+$. IR (neat, cm^{-1}) 2956, 2930, 2857, 1725, 1471, 1383, 1253, 1172, 1098, 1066, 1040.



4a **5**

To a stirred suspension of methyltriphenylphosphonium bromide (953 mg, 2.67 mmol) in THF (15 mL) was added lithium bis(trimethylsilyl)amide (2.57 mL, 2.57 mmol, 1.0 mol·L^{-1} hexane solution) at 0 °C. After stirring for further 15 min, a solution of the aldehyde **4a** (980 mg, 1.90 mmol) in THF (5 mL) was added via cannula. After stirring for 1 h, acetone (100 μL, 1.4 mmol) was added to the mixture. The mixture was concentrated and the residue was purified by column chromatography (hexane to toluene) to give **5** (815 mg, 1.59 mmol, 84 %) as

a colorless oil.
$[\alpha]_D^{18}$ = –25.15 (*c* 0.88, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.06 (3H, s), 0.06 (3H, s), 0.07 (6H, s), 0.85 (9H, s), 0.89 (9H, s), 1.09 (3H, s), 1.16 (6H, s), 1.26 (3H, s), 1.35–1.70 (4H, m), 1.70–2.00 (4H, m), 3.18 (1H, d, *J* = 7.0 Hz), 3.48 (1H, dd, *J* = 6.7, 3.4 Hz), 3.63 (1H, dd, *J* = 8.5, 6.3 Hz), 5.32 (1H, dd, *J* = 1.1, 10.4 Hz), 5.43 (1H, d, *J* = 1.1, 17.2 Hz), 5.74 (1H, ddd, *J* = 7.0, 10.4, 17.2 Hz). ^{13}C NMR (75MHz, $CDCl_3$): δ –4.14 (q), –3.74 (q), –2.04 (q), 16.60 (q), 18.15 (s), 22.43 (q), 24.89 (q), 25.89 (q), 26.03 (q), 26.48 (t), 28.09 (q), 29.14 (t), 35.16 (t), 35.41 (t), 62.93 (s), 63.33 (d), 74.32 (s), 77.41 (d), 85.80 (s), 86.98 (d), 119.78 (t), 133.67 (d). CIMS 511 $[M–H]^+$ (10), 381 (43), 257 (100), 173 (90). HRCIMS calcd 511.3639 for $C_{28}H_{55}O_4Si_2$, found 511.3635 $[M–H]^+$. IR (neat, cm^{-1}) 2938, 2862, 1465, 1379, 1251, 1173, 1096, 835, 775.

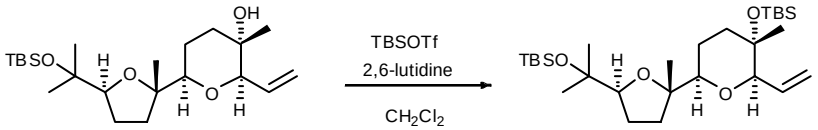


5 **6** (6-*endo* cyclization) **7** (5-*exo* cyclization)

To a stirred solution of **5** (650 mg, 1.27 mmol) in THF (6 mL) was added tetrabutylammonium fluoride (7.6 mL, 7.6 mmol, 1.0 mol·L^{-1} THF solution) at rt. After stirring for 14 h, the reaction was quenched by addition of aqueous sodium hydrogen carbonate. The mixture was diluted with additional aqueous sodium hydrogen carbonate and diethyl ether. The phases were separated and the aqueous phase was extracted with diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (612 mg), which was used for the next reaction without further purification. The crude compound described above was dissolved in CH_2Cl_2 (150 mL). To the solution was added (1*S*)-(+)-10-camphorsulfonic acid (72 mg of 0.31 mmol) at –78 °C. After stirring for 90 min, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ and the mixture was diluted with diethyl ether. The phases were separated and the aqueous phase was extracted with diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (566 mg). The residue was purified by column chromatography (hexane/EtOAc, 9:1) to give **6** (289 mg, 0.724 mmol, 57% yield, 2 steps) along with **7** (67.2 mg, 0.167 mmol, 13% yield, 2 steps).

Compound **6**: colorless oil
$[\alpha]_D^{20}$ = +14.81 (*c* 1.83, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.06 (3H, s), 0.07 (3H, s), 0.84 (9H, s), 1.13 (3H, m), 1.14 (3H, s), 1.15 (3H, s), 1.17 (3H, s), 1.39–1.92 (7H, m), 2.04 (1H, ddd, *J* = 7.4, 8.0, 11.8 Hz), 3.28 (1H, dd, *J* = 2.2, 11.3 Hz), 3.64 (1H, td, *J* = 1.4, 5.5 Hz), 3.70 (1H, t, *J* = 8.0 Hz), 5.22 (1H, ddd, *J* = 1.4, 2.2, 10.7 Hz), 5.30 (1H, ddd, *J* = 1.4, 2.2, 17.6 Hz), 5.89 (1H, ddd, *J* = 5.5, 10.7, 17.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –1.90 (q), 18.36 (s), 21.13 (q), 22.70 (q), 24.87 (t), 25.29 (q), 26.10 (q), 27.04 (t), 27.76 (q), 35.22 (t), 38.86 (t), 69.95 (s), 74.74 (s), 83.19 (d), 84.34 (s), 84.97 (d), 87.45 (d), 116.86 (t), 134.95 (d). CIMS *m*/*z* 399 $[M+H]^+$ (2), 397 (15), 381 (80), 341 (51), 267 (100), 248 (85), 173 (34), 89 (57). HRCIMS calcd 399.2931 for $C_{22}H_{43}O_4Si$, found 399.2912 $[M+H]^+$. IR (neat, cm^{-1}): 3394, 1407, 919.

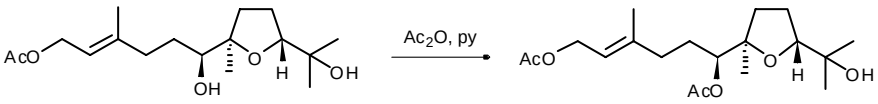
Compound **7**: colorless oil
$[\alpha]_D^{20}$ = +8.06 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.08 (3H, s), 0.08 (3H, s), 0. 85 (9H, s), 1.14 (3H, m), 1.16 (6H, s), 1.17 (3H, s), 1.39–2.13 (8H, m), 3.72 (1H, t, *J* = 8.0 Hz), 3.94 (1H, dd, *J* = 5.4, 10.2 Hz), 4.05 (1H, brd, *J* = 6.3 Hz), 5.21 (1H, brd, *J* = 10.6 Hz), 5.36 (1H, ddd, *J* = 1.4, 2.2, 16.9 Hz), 5.81 (1H, ddd, *J* = 6.3, 10.6, 16.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –2.14 (q), 18.14 (s), 23.79 (q), 24.29 (q), 25.18 (q), 25.87 (q), 26.93 (t), 27.47 (q), 27.69 (t), 31.00 (t), 33.45 (t), 74.46 (s), 78.07 (d), 84.33 (s), 85.41 (s), 87.36 (d), 87.61 (d), 117.17 (t), 136.30 (d). CIMS *m*/*z* 397 $[M–H]^+$ (5), 383 (40), 341 (100), 257 (95), 173 (80). HRCIMS calcd 397.2774 for $C_{22}H_{41}O_4Si$, found 397.2760 $[M–H]^+$. IR (neat, cm^{-1}): 3547, 1041, 918.



6 (6-*endo* cyclization) **8** (segment **A**)

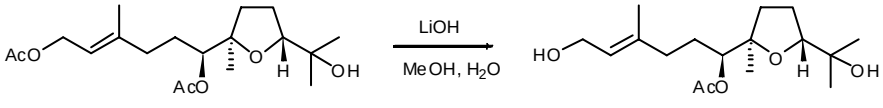
To a stirred solution of **6** (289 mg, 0.725 mmol) and 2,6-lutidine (0.85 mL, 7.3 mmol) in CH_2Cl_2 (5 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (0.67 mL, 2.9 mmol) at –78 °C. The reaction mixture was allowed to warm to –50 °C. After stirring for 2days, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with diethyl ether. The phases were separated and the aqueous phase was extracted with diethyl ether. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (378 mg). The residue was purified by column chromatography (hexane/EtOAc, 30:1) to give **8** (345 mg, 0.673 mmol, 93% yield) as a colorless oil.
$[\alpha]_D^{20}$ = +20.76 (*c* 1.27, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (3H, s), 0.08 (6H, s), 0.09 (3H, s), 0.85 (9H, s), 0.86 (9H, s), 1.10 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.17 (3H, s), 1.43 (1H, m), 1.55–1.73 (4H, m), 1.78–1.93 (3H, m), 2.06 (1H, td, *J* = 7.7, 12.4 Hz), 3.28 (1H, dd, *J* = 2.2, 11.5 Hz), 3.65 (1H, td, *J* = 1.6, 3.8 Hz), 3.72 (1H, dd, *J* = 6.9, 7.7 Hz), 5.12 (1H, ddd, *J* = 1.6, 2.5, 11.0 Hz), 5.30 (1H, ddd, *J* = 1.6, 2.5, 17.6 Hz), 6.00 (1H, ddd, *J* = 3.8, 11.0, 17.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –2.09 (q), –1.95 (q), –1.75 (q), 18.07 (s), 18.17 (s), 21.00 (q), 22.54 (q), 24.67 (t), 25.08 (q), 25.80 (q), 25.90 (q), 26.86 (t), 27.56 (q), 34.96 (t), 39.98 (t), 72.60 (s), 74.58 (s), 82.84 (d), 83.85 (d), 84.25 (s), 87.22 (d), 114.49 (t), 135.28 (d). CIMS *m*/*z* 513 $[M]^+$, 455 (27), 257 (100), 173 (100), 73 (51). HRCIMS calcd 512.3717 for $C_{28}H_{56}O_4Si_2$, found 512.3718 $[M]^+$. IR (neat, cm^{-1}): 919.

Synthesis of Segment B



9 **9a**

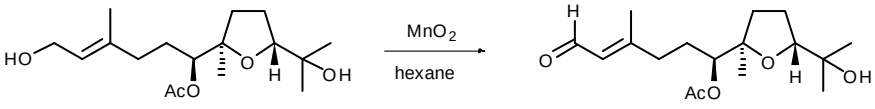
To a stirred solution of **9** (1.37 g, 4.36 mmol) in pyridine (10 mL) was added acetic anhydride (2.1 mL, 22.2 mmol) at rt. After stirring for 6 h, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give **9a** (1.51 g, 4.24 mmol, 97% yield) as a colorless oil.
$[\alpha]_D^{20}$ = –0.31 (*c* 1.09, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.11 (3H, s), 1.19 (6H, s), 1.55 – 2.20 (8H, m), 1.70 (3H, s), 2.06 (3H, s), 2.07 (3H, s), 3.71 (1H, t, *J* = 7.3 Hz), 4.59 (2H, d, *J* = 7.0 Hz), 4.91 (1H, dd, *J* = 2.6, 9.9 Hz), 5.35 (1H, t, , *J* = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.37 (q), 20.89 (q), 20.99 (q), 22.74 (q), 23.97 (q), 25.95 (t), 27.32 (q), 27.73 (t), 34.69 (t), 35.74 (t), 61.19 (t), 70.32 (s), 77.36 (d), 83.89 (s), 86.94 (d), 118.63 (d), 141.38 (s), 170.72 (s), 171.14 (s). CIMS *m*/*z* 357 $[M+H]^+$, 279 (100). HRCIMS calcd 357.2277 for $C_{19}H_{33}O_6$, found 357.2294 $[M+H1]^+$. IR (neat, cm^{-1}): 3513, 1734.



9a **9b**

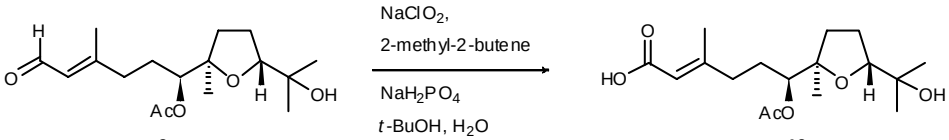
To a stirred solution of **9a** (1.158 g, 3.25 mmol) in 7.5 mL of MeOH and 2.5 mL of H_2O was added lithium hydroxide monohydrate (150 mg, 3.57 mmol) at rt. After stirring for 20 min, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and

concentrated under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc, 1:1) to give **9b** (906 mg, 2.88 mmol, 89% yield) as a colorless oil.
$[\alpha]_D^{18}$ = +2.08 (*c* 1.16, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.11 (3H, s), 1.19 (6H, s), 1.56–2.04 (8H, m), 1.67 (3H, s), 2.07 (3H, s), 3.71 (1H, t, *J* = 7.2 Hz), 4.14 (2H, d, *J* = 7.0 Hz), 4.91 (1H, dd, *J* = 2.6, 10.2 Hz), 5.40 (1H, t, *J* = 7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.10 (q), 21.20 (q), 22.95 (q), 24.02 (q), 26.10 (t), 27.46 (q), 27.72 (t), 34.69 (t), 35.80 (t), 59.29 (t), 70.44 (s), 77.25 (d), 84.00 (s), 87.05 (d), 124.21 (d), 138.54 (s), 170.91 (s): CIMS *m/z* 315 $[M+H]^+$, 279 (100), HRCIMS calcd 315.2172 for $C_{17}H_{31}O_5$, found 315.2154 $[M+H]^+$. IR (neat, cm^{-1}): 3415, 1735.



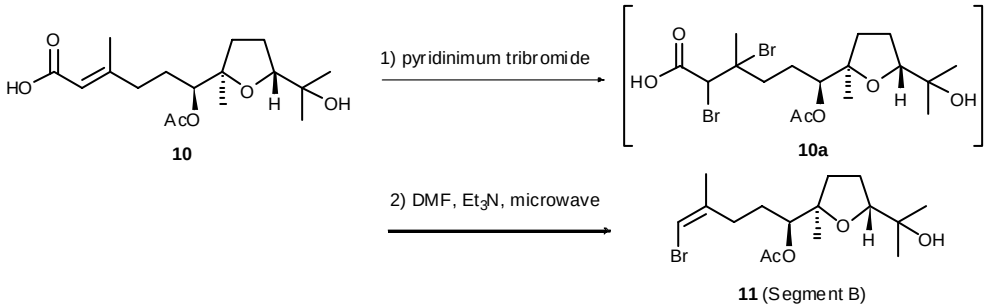
9b **9c**

To a stirred solution of **9b** (1.158 g, 3.37 mmol) in hexane (20 mL) was added manganese dioxide (6 g, 69 mmol) at rt. After stirring for 17 h, the reaction mixture was directly subjected to column chromatography (hexane to hexane/EtOAc, 1:1) to give **9c** (840 mg, 2.69 mmol, 80% yield) as a colorless oil along with starting material **9b** (83.3 mg, 0.265 mmol, 7% yield).
$[\alpha]_D^{21}$ = +2.11 (*c* 1.04, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12, (3H, s), 1.20 (6H, s), 1.64–2.28 (8H, m), 2.08 (3H, s), 2.18 (3H, d, *J* = 1.2 Hz), 3.73 (1H, t, *J* = 7.6 Hz), 4.92 (1H, dd, *J* = 3.0, 10.0 Hz), 5.89 (1H, brd, *J* = 7.7 Hz), 10.00 (1H, d, *J* = 7.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 17.61 (q), 20.91 (q), 22.47 (q), 23.96 (q), 25.89 (t), 27.21 (q), 27.25 (t), 34.29 (t), 36.72 (t), 70.29 (s), 77.09 (d), 83.69 (s), 86.97 (d), 127.12 (d), 162.93 (s), 170.72 (s), 191.19 (d). CIMS *m/z* 313 $[M+H]^+$, 295 (100), HRCIMS calcd 313.2015 for $C_{17}H_{29}O_5$, found 313.2010 $[M+H]^+$. IR (neat, cm^{-1}): 3480, 1735, 1671, 1375, 1236.



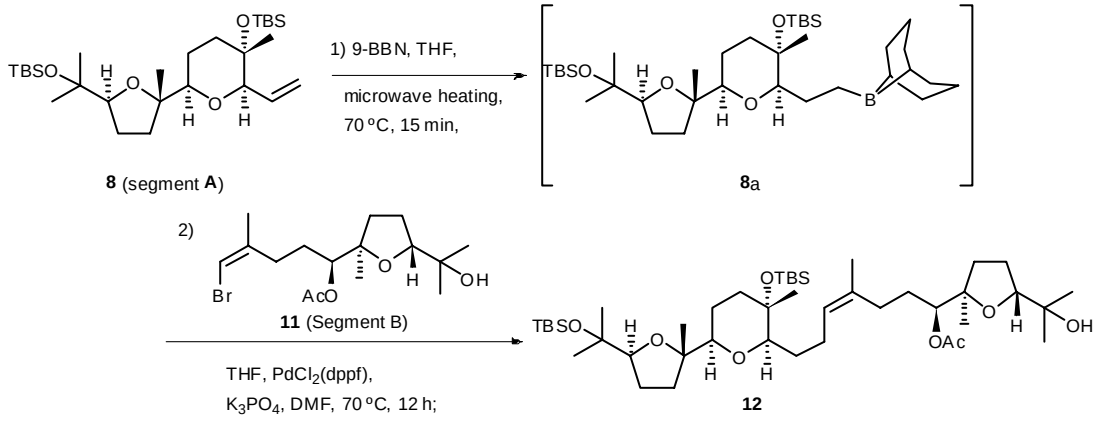
9c **10**

To a stirred mixture of **9c** (354 mg, 1.13 mmol), 2-methyl-2-butene (0.6 mL, 5.66 mmol) and sodium dihydrogenphosphate dihydrate (870 mg, 5.58 mmol) in 10 mL of *t*-BuOH and 4 mL of H_2O was added sodium chlorite (purity 80%, 520 mg, 4.6 mmol) at rt. After stirring for 1 h, the reaction was quenched by addition of aqueous sodium hydrogensulfite. The mixture was diluted with additional aqueous sodium hydrogensulfite and ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 1:2) to give **10** (371 mg, 1.129 mmol, 100% yield) as a colorless oil.
$[\alpha]_D^{18}$ = +3.19 (*c* 0.966, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.12 (3H, s), 1.20 (3H, s), 1.20 (3H, s), 1.62–2.21 (8H, m), 2.08 (3H, s), 2.17 (4H, d, *J* = 1.2 Hz), 3.73 (1H, t, *J* = 7.2 Hz), 4.92 (1H, dd, *J* = 2.6, 10.0 Hz), 5.70 (1H, d, *J* = 1.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 19.07 (q), 21.00 (q), 22.64 (q), 23.97 (q), 25.99 (t), 27.36 (q), 27.59 (t), 34.90 (t), 37.51 (t), 70.52 (s), 77.28 (d), 83.88 (s), 87.03 (d), 115.37 (d), 161.82 (s), 170.90 (s), 171.49 (s). CIMS *m/z* 329 $[M+H]^+$, 311 (100). HRCIMS calcd 329.1964 for $C_{17}H_{29}O_6$, found 329.1960 $[M+H]^+$. IR (neat, cm^{-1}): 3468, 1724, 1645, 1238.



To a stirred solution of **10** (640 mg, 1.95 mmol) in $CHCl_3$ (20 mL) and MeOH (0.5 mL) added pyridinium tribromide (purity 90%, 1.39 g, 3.91 mmol) at rt. After stirring for 2 h, the reaction was quenched by addition of aqueous sodium hydrogensulfite. The mixture was diluted with additional aqueous sodium hydrogensulfite and ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was roughly purified by flash column chromatography (hexane/EtOAc, 1:2) to give crude **10a** (802 mg) as a pale yellow colorless oil, which was used for the next reaction without further purification. To a stirred solution of the crude **10a** in DMF (10 mL) was added Et_3N (0.34 mL, 2.44 mmol). The mixture was divided into two test tubes suitable for microwave reactor (Discover® CEM corporation). Each test tube was sealed and exposed to the microwave irradiation (200 watt, 100 °C, 8 min.). Each solution was combined and diluted with aqueous NH_4Cl and ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give **11** (511 mg, 1.41 mmol, 72% yield) as a colorless oil, which consists of 20:1 mixture of *E* and *Z* geometric isomer. Stereochemistry of **11** was determined by NOE experiment.
$[\alpha]_D^{23}$ = +6.60 (*c* 0.89, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ1.11, (3H, s), 1.20 (6H, s), 1.60 (1H, dtd, *J* = 5.2, 10.7, 14.0 Hz), 1.66 (1H, td, *J* = 4.9, 11.8 Hz), 1.79 (3H, d, *J* = 1.3 Hz), 1.80 – 1.86 (3H, m), 1.95 (1H, ddd, 8.2, 8.8, 10.7 Hz), 2.10 (3H, s), 2.17 – 2.27 (2H, m), 3.72 (1H, t, *J* = 8.2 Hz), 4.92 (1H, dd, *J* = 2.7, 10.7 Hz) 5.87 (1H, d, *J* = 1.3 Hz). selected minor signals for a *Z* isomer, 3.71 (1H, t), 4.89 (1H, dd), 5.93 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.13 (q), 22.04 (q), 22.88 (q), 24.02 (q), 26.03 (t), 27.08 (t), 27.45 (q), 31.02 (t), 34.82 (t), 70.37 (s), 77.50 (d), 83.93 (s), 87.03 (d), 101.21 (d), 140.85 (s), 170.75 (s). CIMS *m/z* 365 $[M+3H]^+$, 363 $[M+H]^+$, 347 (100), 345 (98). HRCIMS calcd 363.1171 for $C_{16}H_{28}O_4Br$, found 363.1185 $[M+H]^+$. IR (neat, cm^{-1}): 3509, 1738.

Synthesis of Pseudodehydrothyrsiferol



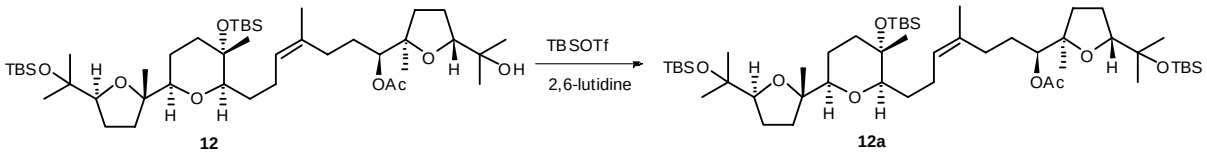
Hydrobration:
9-BBN (7.28 mL, 3.64 mmol, 0.5 mol·L^{-1} THF solution), **8** (595 mg, 1.159 mmol) and THF (10 mL) was placed in a flask equipped with reflux condenser. The flask was put into the Microwave reactor (Discover® CEM

corporation) and exposed to the microwave irradiation for 15 min. (200 watt, 70 °C, open system in Ar atmosphere) to give **8a**.

Suzuki-Miyaura coupling:

[1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (190 mg, 0.23 mmol, dichloromethane adduct) and *tri*-potassium phosphate trihydrate (1.55g, 2.82 mmol) was placed in a flask equipped with reflux condenser. The solution of borane **8a** described above and **11** in DMF (5 mL) was added to the flask via cannula. The mixture was refluxed for 12 h. After the reaction mixture is passed through Celite to remove solid material, the filtrate was evaporated. The residue was purified by column chromatography (hexane/EtOAc, 7:1) to give **12** (762 mg, 0.956 mmol, 82% yield) as a colorless oil.

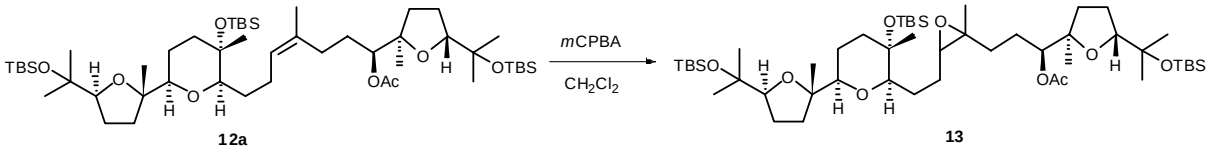
$[\alpha]_D^{20}$ = +15.25 (*c* 1.02, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (6H, s), 0.07 (6H, s), 0.84 (9H, s), 0.85 (9H, s), 1.11 (6H, s), 1.12 (3H, s), 1.15 (3H, s), 1.17 (3H, s), 1.18 (3H, s), 1.19 (3H, s), 1.35–2.05 (20H, m), 2.07 (3H, s), 2.99 (1H, d, *J* = 8.8 Hz), 3.14 (1H, dd, *J* = 1.2, 9.1 Hz), 3.66 (1H, t, *J* = 6.7 Hz), 3.70 (1H, t, *J* = 7.4 Hz), 4.93 (1H, dd, *J* = 2.2, 9.9 Hz), 5.16 (1H, t, *J* = 7.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –2.10 (q), –1.94(q), –1.79(q), 18.03 (s), 18.13 (q), 20.64 (q), 21.16 (q), 22.13 (q), 23.22 (q), 23.41 (q), 24.08 (q), 24.64 (t), 24.75 (t), 24.87 (q), 25.77 (q), 25.86 (q), 26.07 (t), 26.67 (t), 27.57 (q), 27.77 (q), 28.33 (t), 28.38 (t), 29.15 (t), 34.49 (t), 35.49 (t), 40.27 (t), 70.28 (s), 72.44 (s), 74.46 (s), 78.04 (d), 82.98 (d), 84.06 (s), 84.10 (s), 84.41 (d), 87.04 (d), 87.09 (d), 126.19 (d), 134.11 (s), 170.58 (s). FABMS *m*/*z* 820 $[M+Na]^+$ (15), 257 (12), 173 (30), 73 (100). HRFABMS calcd 819.5602 for $C_{44}H_{84}O_8Si_2Na$, found 819.5593 $[M+Na]^+$. IR (neat, cm^{-1}) 3580, 1742.



12 **12a**

To a stirred solution of **12** (162 mg, 0.203 mmol) and 2,6-lutidine (120 μL, 1.03 mmol) in CH_2Cl_2 (3 mL) was added *tert*-butyldimethylsilyl trifluoromethanesulfonate (120 μL, 0.52 mmol) at –78 °C. The reaction mixture was allowed to warm to −10 °C. After stirring for 2 days, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (275 mg), The residue was purified by column chromatography (hexane/EtOAc, 20:1) to give **12a** (184 mg, 0.202 mmol, 100% yield) as a colorless oil.

$[\alpha]_D^{21}$ = +9.85 (*c* 1.02, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05 (6H, s), 0.06 (12H, s), 0.83 (9H, s), 0.83 (18H, s), 1.09 (3H, s), 1.10 (3H, s), 1.13 (6H, s), 1.14 (3H,s), 1.15 (3H, s), 1.15 (3H,s), 1.35–2.20 (20H, m), 2.05 (3H, s), 2.97 (1H, d, *J* = 9.1 Hz), 3.13 (1H, dd, *J* = 1.6, 11.3 Hz), 3.62 (1H, t, *J* = 6.3 Hz), 3.65 (1H, t, *J* = 7.7 Hz), 4.88 (1H, dd, *J* = 2.7, 10.2 Hz), 5.14 (1H, t, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ –2.05 (q), –1.91 (q), –1.75 (q), 18.06 (s), 18.16 (s), 20.67 (q), 21.25 (q), 22.13 (q), 22.85 (q), 23.45 (q), 24.67 (t), 24.76 (t), 24.94 (q), 25.81 (q), 25.90 (q), 26.40 (t), 26.7 (t), 27.74 (q), 27.74 (q), 28.38 (t), 28.49 (t), 29.20 (t), 34.58 (t), 35.57 (t), 40.32 (t), 72.48 (s), 74.27 (s), 74.50 (s), 78.06 (s), 82.99 (d), 83.98 (s), 84.12 (s), 84.46 (d), 87.09 (d), 87.57 (d), 126.00 (d), 134.37 (s), 170.66 (s). FABMS *m*/*z* 934 $[M+Na]^+$ 455 (10), 257 (15), 173 (30), 73 (100). HRFABMS calcd 933.6467 for $C_{50}H_{98}O_8Si_3Na$, found 933.6466 $[M+Na]^+$. IR (neat, cm^{-1}) 1742.

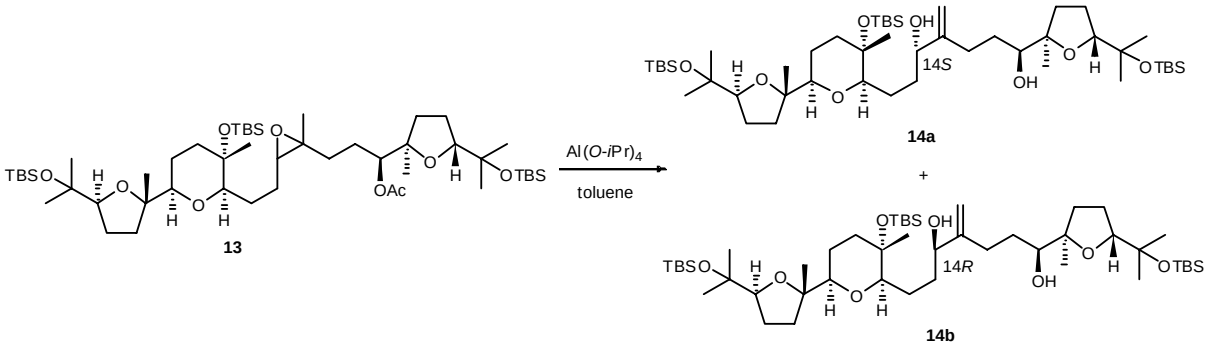


12a **13**

To a stirred solution of **12a** (169 mg, 0.185 mmol) in CH_2Cl_2 (5 mL) was added *m*-chloroperbenzoic acid (purity 75%, 52 mg, 0.226 mmol) at 0 °C. After stirring for 30 min at rt. the reaction was quenched by addition of aqueous sodium sulfite and the mixture was diluted with hexane. The phases were separated and the aqueous phase was extracted with hexane. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 15:1) to give **13** (166 mg, 0.179 mmol, 97%

yield) as a colorless oil. **13** was a 2:1 mixture of inseparable diastreomers. The ratio was determined by the ^{1}H NMR spectrum.

^{1}H NMR (300MHz, $CDCl_3$): Selected signals. δ 1.089 (minor isomer's peak), 1.097 (major isomer's peak) (3H, s), 1.271 (major isomer's peak), 1.280 (minor isomer's peak), (3H, s), 2.040 (minor isomer's peak), 2.047 (major isomer's peak), (3H, s). FABMS *m*/*z* 950 $[M+Na]^+$, 796 (1), 678 (1), 603 (5), 471 (7), 323 (7), 275 (12), 173 (30), 73 (100). HRFABMS calcd 949.6417 for $C_{50}H_{98}O_9Si_3Na$, found 949.6393 $[M+Na]^+$. IR (neat, cm^{-1}) 1742.



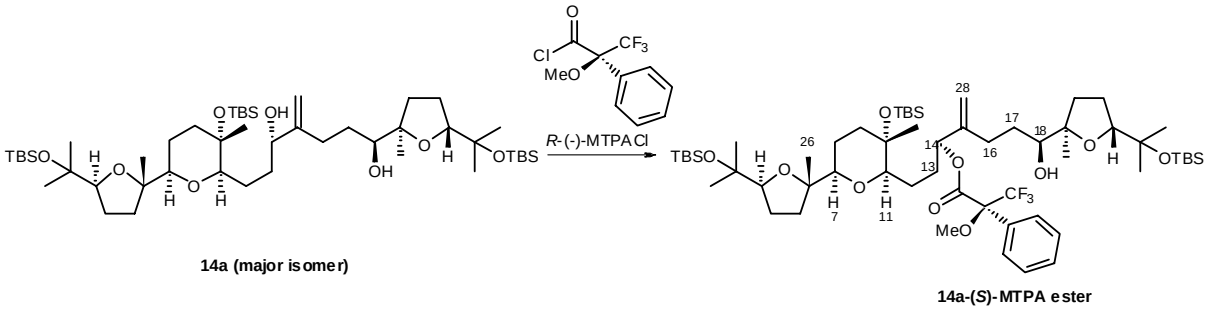
To a stirred solution of **13** (164 mg, 0.177 mmol) in toluene (30 mL) was added aluminum isopropoxide (360 mg, 1.77 mmol). After refluxing for 18 h, the reaction mixture was allowed to rt and was diluted with saturated aqueous potassium sodium tartrate and ethyl acetate. After the mixture was vigorously stirring for 2 h, the phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 9:1) to give **14a** (64.6 mg, 0.073 mmol, 41% yield) and **14b** (35.8 mg, 0.040 mmol, 23% yield) and as a colorless oil. Stereochemistry at C14 was determined by Kusumi method after converting **15a** to (*R*)– and (*S*)– MTPA esters as described as follows.

14a

$[\alpha]_D^{20}$ = +8.48 (*c* 0.59, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.07 (6H, s), 0.07 (6H, s), 0.08 (6H, s), 0.84 (9H, s), 0.85 (9H, s) 0.85 (9H, s), 1.10 (3H, s), 1.12 (3H, s), 1.14 (3H, s), 1.14 (3H, s), 1.16 (3H, s), 1.19 (6H, s), 1.36–1.48 (4H, m), 1.58–1.78 (6H, m), 1.79–1.88 (6H, m), 1.90–2.30 (4H, m), 3.07 (1H, d, *J* = 9.5 Hz), 3.23 (1H, dd, *J* = 2.2, 11.0 Hz), 3.53 (1H, dd, *J* = 1.8, 10.4 Hz), 3.66 (1H, t, *J* = 7.3 Hz), 3.68 (1H, t, *J* = 7.1 Hz), 4.13 (1H, m), 4.87 (1H, brs), 5.06 (1H, brs). ^{13}C NMR (75 MHz, $CDCl_3$): δ –2.05 (q), –1.95 (q), –1.78 (q), 18.05 (s), 18.17 (s), 20.61 (q), 22.33 (q), 24.00 (q), 24.83 (t), 25.05 (q), 25.27 (q), 25.79 (q), 25.90 (q), 26.66 (t), 26.81 (t), 27.60 (q), 27.78 (q), 28.72 (t), 29.97 (t), 31.21 (t), 33.13 (t), 35.28 (t), 40.19 (t), 72.49 (s), 74.21 (s), 74.24 (d), 74.40 (s), 76.17 (d), 83.37 (d), 83.92 (s), 85.40 (d), 85.93 (s), 87.20 (d), 88.61 (d), 109.66 (t), 151.43 (s). FABMS *m*/*z* 908 $[M+Na]^+$, 754 (10), 604 (10), 173 (70), 73 (100). HRFABMS calcd 907.6311 for $C_{48}H_{96}O_8Si_3Na$, found 907.6323. IR (neat, cm^{-1}) 3420, 833.

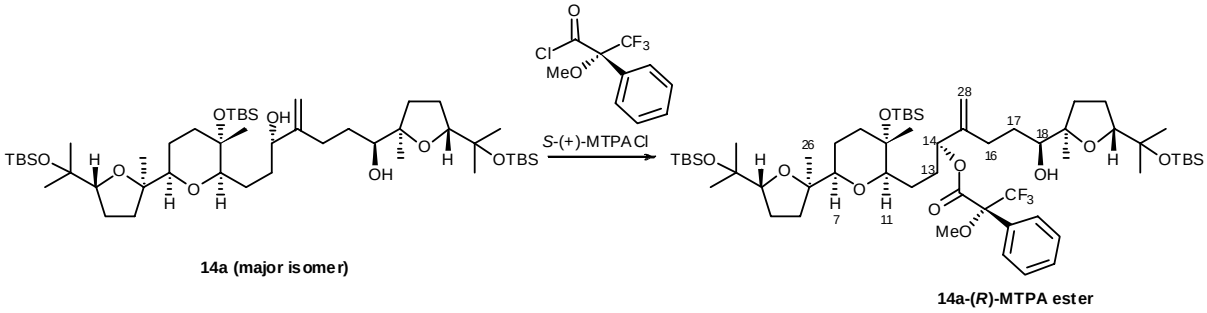
14b

$[\alpha]_D^{20}$ = +16.22 (*c* 0.32, $CHCl_3$), ^{1}H NMR (300MHz, $CDCl_3$): δ 0.07 (6H, s), 0.07 (6H, s), 0.08 (6H, s), 0.84 (9H, s), 0.85 (9H, s) 0.85 (9H, s), 1.10 (3H, s), 1.11 (3H, s), 1.14 (3H, s), 1.16 (6H, s), 1.19 (6H, s), 1.24–1.52 (4H, m), 1.58–1.70 (6H, m), 1.79–1.90 (6H, m), 1.92–2.11 (3H, m), 2.40 (1H, m), 3.10 (1H, d, *J* = 9.2 Hz), 3.25 (1H, dd, *J* = 2.2, 12.0 Hz), 3.51 (1H, dd, *J* = 1.7, 10.4 Hz), 3.67 (1H, t, *J* = 7.7 Hz), 3.68 (1H, t, *J* = 8.4 Hz), 4.04 (1H, dd, 4.0, 8.0 Hz), 4.83 (1H, brs), 5.07 (1H, brs). ^{13}C NMR (75MHz, $CDCl_3$): δ –2.04 (q), –1.95 (q), –1.79 (q), 18.04 (s), 18.18 (s), 20.61 (q), 22.65 (q), 23.97 (q), 25.00 (t), 25.00 (q), 25.29 (q), 25.78 (q), 25.91 (q), 26.64 (t), 26.81 (t), 27.59 (q), 27.95 (q), 28.83 (t), 30.25 (t), 31.26 (t), 33.85 (t), 34.69 (t), 40.20 (t), 72.52 (s), 74.20 (s), 74.37 (s), 75.86 (d), 76.69 (d), 83.19 (d), 84.23 (s), 85.36 (d), 85.94 (s), 87.35 (d), 88.59 (d), 109.21 (t), 152.13 (s). FABMS *m*/*z* 908 $[M+Na]^+$, 754 (10), 604 (10), 173 (30), 73 (100). HRFABMS calcd 907.6311 for $C_{48}H_{96}O_8Si_3Na$, found 949.6337. IR (neat, cm^{-1}) 3380, 834.



To a stirred solution of **14a** (2.1 mg, 2.37 μmol) in pyridine (0.5 mL) was added (*R*)-(–)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*R*)-(–)-MTPACl, 1 μL, 5.3 μmol). After stirring for 24 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 10:1) to give **14a-(*S*)-MTPA ester** (0.9 mg, 0.9 μmol, 38% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.03 (3H, s), 0.05 (3H, s), 0.06 (3H, s), 0.07 (3H, s), 0.08 (3H, s), 0.08 (3H, s), 0.80 (9H, s). 0.85 (9H, s), 0.86 (9H, s), 1.07 (3H, s), 1.08 (3H, s), 1.09 (3H, s), 1.10 (1H, m), 1.15 (3H, s), 1.15 (3H, s), 1.19 (3H, s), 1.19 (3H, s), 1.24–1.32 (2H, m), 1.36–1.44 (2H, m), 1.48 (1H, m), 1.56–1.64 (2H, m), 1.69 (1H, m), 1.72 (1H, m), 1.78–1.88 (6H, m), 1.94 (1H, m), 2.02 (1H, m), 2.09 (1H, m), 2.33 (1H, m), 2.96 (1H, d, *J* = 9.1 Hz), 3.16 (1H, dd, *J* =1.9, 11.3 Hz), 3.46 (1H, brd, *J* = 9.3 Hz), 3.51 (3H, s), 3.63 (1H, t, *J* = 6.9Hz), 3.67 (1H, t, *J* = 6.3Hz), 4.98 (1H, brs), 5.11 (1H, s), 5.51 (1H, t, *J* = 5.8 Hz), 7.38 (3H, m), 7.49 (2H, m).



To a stirred solution of **14a** (1.8 mg, 2.0 μmol) in pyridine (0.5 mL) was added (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride ((*S*)-(+)-MTPACl, 5 μL, 26.5 μmol). After stirring for 18 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (hexane/EtOAc, 10:1) to give **14a-(*R*)-MTPA ester** (1.6 mg, 1.4 μmol, 73% yield) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 0.04 (3H, s), 0.06 (3H, s), 0.06 (3H, s), 0.07 (3H, s), 0.08 (6H, s), 0.81 (9H, s). 0.84 (9H, s), 0.86 (9H, s), 1.08 (3H, s), 1.09 (3H, s), 1.11 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.19 (3H, s), 1.19 (3H, s), 1.21 (1H, m), 1.28–1.42 (4H, m), 1.48 (1H, m), 1.56–1.68 (4H, m), 1.75 (1H, m), 1.78–1.88 (6H, m), 1.94 (1H, m), 1.99 (1H, m), 2.27 (1H, m), 3.00 (1H, d, *J* = 9.1 Hz), 3.17 (1H, dd, *J* =1.9, 11.5 Hz), 3.39 (1H, brd, *J* = 10.1 Hz), 3.56 (3H, s), 3.63 (1H, t, *J* = 6.9 Hz), 3.66 (1H, t, *J* = 6.3 Hz), 4.90 (1H, s), 4.98 (1H, s), 5.46 (1H, t, *J* = 5.5 Hz), 7.38 (3H, m), 7.50 (2H, m).

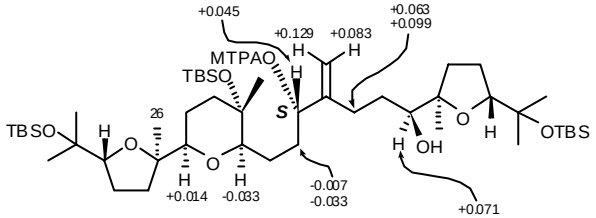
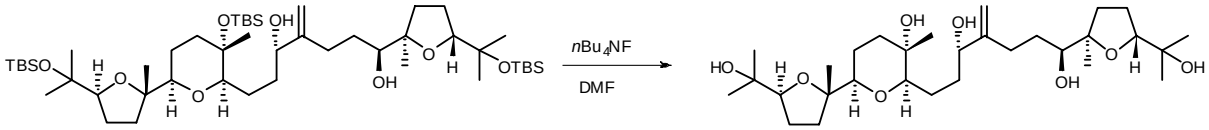


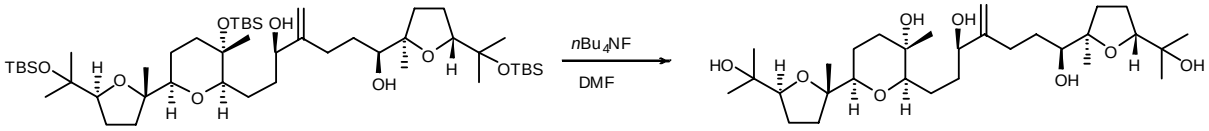
Figure 1 Absolute stereochemistry was determined to be *S* configuration by Kusumi method. Values in the figure refers to Δδ {δ(–MTPA) – δ (+MTPA)}.



14a **15a**

A THF solution of tetra-*n*-butylammonium fluoride (0.6 mL of 1 mol·L^{-1} solution, 0.6 mmol) was evaporated under argon atmosphere and then 5 mL of DMF was added to the residue. To the stirred nBu$_4$NF–DMF solution added **14a (**49.3 mg, 0.0557 mmol) in DMF (5 mL) via cannula. After stirring for 18 h at 60 °C, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (78.1 mg). The residue was purified by column chromatography (EtOAc) to give **15a** (31.3 mg, 0.0577 mmol, 100% yield) as a colorless oil.

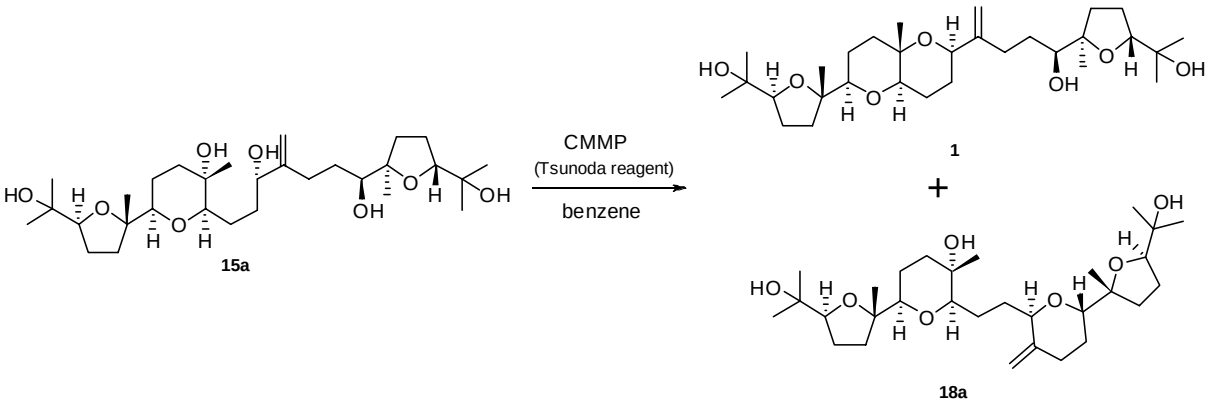
$[\alpha]_D^{20}$ = +3.38 (*c* 0.61, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.12 (3H, s), 1.13 (6H, s), 1.15 (3H, s), 1.16 (3H, s), 1.18 (3H, s), 1.21 (3H, s), 1.30–1.49 (4H, m), 1.58–1.78 (6H, m), 1.79–1.90 (6H, m), 2.00–2.32 (4H, m), 3.14 (1H, d, *J* = 9.6 Hz), 3.28 (1H, dd, *J* = 1.9, 11.3 Hz), 3.56 (1H, dd, *J* = 1.6, 10.4 Hz), 3.77 (1H, t, *J* = 8.2 Hz), 3.80 (1H, t, *J* = 6.0 Hz), 4.85 (1H, brs), 5.06 (1H, brs). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.76 (q), 23.02 (q), 23.37 (q), 23.42 (q), 23.59 (q), 24.85 (t), 24.93 (t), 26.45 (t), 26.53 (t), 26.96 (q), 27.10 (q), 27.78 (t), 29.50 (t), 31.59 (t), 32.76 (t), 34.01 (t), 39.30 (t) , 69.32 (s), 70.52 (s), 70.56 (s), 74.90 (d), 75.56 (d), 83.30 (d), 83.89 (s), 84.37 (d), 85.64 (s), 86.65 (d), 87.12 (d), 109.16 (t), 151.38 (s). CIMS *m/z* 543 $[M+H]^+$ (10), 525 (20), 507 (65), 143 (100). HRCIMS calcd 543.3897 for $C_{30}H_{55}O_8$, found 543.3915 $[M+H]^+$. IR (neat, cm^{-1}): 3388.



14b **15b**

A THF solution of tetra-*n*-butylammonium fluoride (0.35 mL of 1 mol·L^{-1} solution, 0.35 mmol) was evaporated under argon atmosphere and then 3 mL of DMF was added to the residue. To the stirred nBu$_4$NF–DMF solution added **14b (**34.3 mg, 0.0387 mmol) in DMF (7 mL) via cannula. After stirring for 18 h at 60 °C, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil (42.8 mg). The residue was purified by column chromatography (EtOAc) to give **15b** (21.0 mg, 0.0387 mmol, 100% yield) as a colorless oil.

$[\alpha]_D^{20}$ = +18.83 (*c* 0.49, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.13 (3H, s), 1.13 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.17 (6H, s), 1.21 (3H, s), 1.28–1.52 (4H, m), 1.55–1.74 (6H, m), 1.76–1.90 (5H, m), 2.02–2.32 (4H, m), 2.38, (1H, m), 2.84 (1H, brs), 3.18 (1H, d, *J* = 9.1 Hz), 3.36 (1H, dd, *J* = 1.9, 11.0 Hz), 3.54 (1H, dd, *J* = 1.9, 10.4 Hz), 3.58 (2H, m), 4.07 (1H, dd, *J* = 3.3, 8.5 Hz) , 4.84 (1H, brs), 5.09 (1H, brs). ^{13}C NMR (75 MHz, $CDCl_3$): 19.97 (q), 23.55 (q), 23.63 (q), 23.71 (q), 25.35 (t), 25.66 (t), 26.73 (t), 26.90 (t), 27.35 (q), 27.50 (q), 28.51 (t), 30.04 (t), 31.93 (t), 33.56 (t), 33.81 (t), 39.71 (t) , 69.68 (s), 70.75 (s), 70.84 (s), 75.31 (d), 76.22 (d), 83.35 (d), 84.28 (s), 84.48 (d), 85.96 (s), 87.15 (d), 87.42 (d), 109.33 (t), 151.67 (s). FABMS *m/z* 565 $[M+Na]^+$ (40), 73 (100). HRFABMS calcd 565.3716 for $C_{30}H_{54}O_8Na$, found 565.3747 $[M+Na]^+$. IR (neat, cm^{-1}), 3386.



To a stirred solution of **15a** (31.1 mg, 57.3 μmol) in benzene (2 mL) was added CMMP (570 μL, 86 μmol, 0.15 mol・L^{-1} benzene solution) in a sealed tube. After stirring for 24 h at 80 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 1:2) to give **1** (13.6 mg, 25.9 μmol, 45% yield) along with its isomer **18a** (5.9 mg, 11.3 μmol, 20% yield).

1: colorless oil. $[\alpha]_D^{20}$ –2.65 (*c* 1.0, $CHCl_3$, lit., –13.1, (*c* 0.13, $CHCl_3$)). As shown in Table 1, ^{1}H NMR and ^{13}C NMR were identical with those of the natural pseudodehydrothyrsiferol. EIMS *m/z* 524 $[M]^+$ (5), 506 (10), 381 (25), 363 (50), 143 (100). HREIMS calcd 524.3713 for $C_{30}H_{52}O_7$, found 524.3734 $[M]^+$. IR (neat, cm^{-1}): 3427, 1460, 1375, 1097.

18a: colorless oil. $[\alpha]_D^{20}$ +32.5 (*c* 0.59, $CHCl_3$). ^{1}H NMR (600MHz, $CDCl_3$): 1.11 (3H, s), 1.14 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.16 (3H, s), 1.18 (3H, s), 1.20 (3H, s), 1.38–1.48 (3H, m), 1.56–1.70 (7H, m), 1.73 (1H, m), 1.80 (4H, m), 1.86 (1H, td, *J* = 3.8, 8.5 Hz), 2.04–2.12, (2H, m), 2.30 (1H, m), 2.40 (1H, m), 3.13 (1H, dd, *J* = 1.9, 10.5 Hz), 3.24 (1H, dd, *J* = 2.2, 11.5 Hz), 3.55 (1H, dd, *J* = 2.2, 11.8 Hz), 3.77 (1H, dd, *J* = 6.7, 8.5 Hz), 3.80 (1H, dd, *J* = 5.5, 9.9 Hz), 4.23, (1H, dd, *J* = 4.1, 10.4 Hz) , 4.76 (2H, brs). ^{13}C NMR (100 MHz, CDCl3): 20.33 (q), 23.11 (q), 23.21 (q), 23.41 (q), 24.09 (t), 24.18 (t), 25.15 (t), 26.59 (t), 26.85 (t), 27.22 (q), 27.63 (q), 28.04 (t), 28.54 (t), 34.38 (t), 34.81 (t), 39.69 (t) , 69.75 (s), 70.53 (s), 71.17 (s), 74.34 (d), 77.83 (d), 83.30 (d), 83.67 (d), 84.23 (s), 84.26 (s), 86.80 (d), 86.91 (d), 108.51 (t), 146.83 (s). CIMS *m/z* 525 $[M+H]^+$ (5), 507 (85), 489 (100). HRCIMS calcd 525.3791 for $C_{30}H_{53}O_7$, found 525.3786 $[M+H]^+$. IR (neat, cm^{-1}): 3352, 1456, 1065.

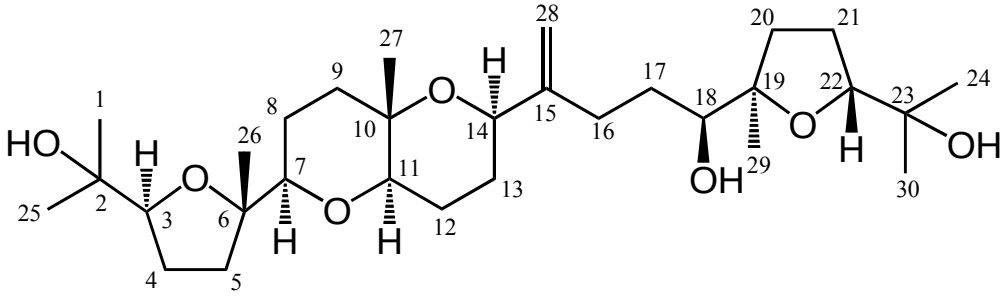
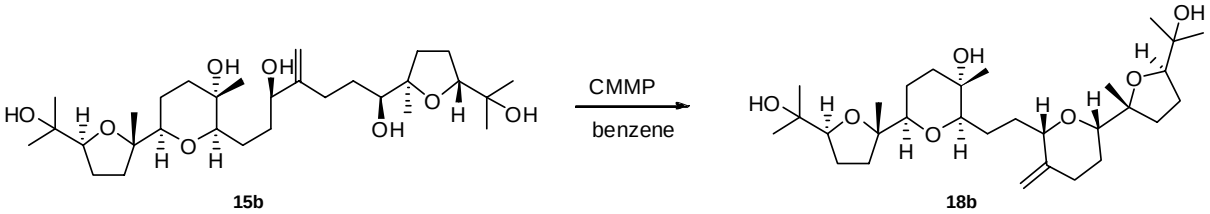


Figure 2 Numbering of carbons in pseudodehydrothyrsiferol (see Table 1).

Table 1 ^{1}H–NMR data for natural and synthetic **1**

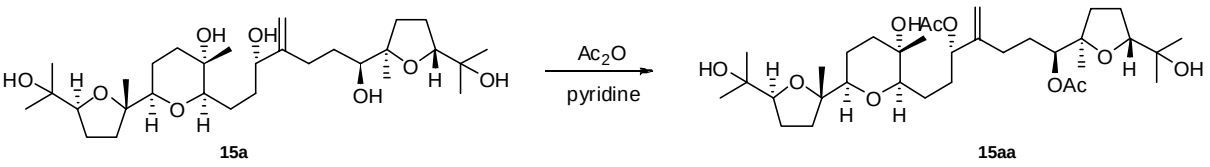
	Natural		Synthetic	
position	^{1}H NMR(500 MHz)	^{13}C NMR (125 MHz)	^{1}H NMR (600 MHz)	^{13}C NMR (150 MHz)
1	1.11 (s)	24.0	1.11 (s)	24.0
2		70.6		70.6
3	3.76 (dd, *J* = 5.8, 9.1 Hz)	86.7	3.76 (dd, *J* = 5.4, 9.8 Hz)	86.7
4	1.84	26.3	1.80	26.3
5	1.66 / 2.04	35.2	1.67 / 2.04	35.2
6		84.0		84.0
7	3.32 (dd, *J* = 2.6, 11.4 Hz)	84.0	3.33 (dd, *J* = 2.7, 11.5 Hz)	84.0
8	1.51 / 1.66	24.5	1.50 / 1.66	24.5
9	1.57 / 1.81	38.7	1.53 / 1.83	38.8
10		72.8		72.8
11	3.46 (dd, *J* = 5.6, 11.7 Hz)	78.9	3.46 (dd, *J* = 5.8, 11.5 Hz)	79.0
12	1.65 / 1.84	21.8	1.65 / 1.85	21.9
13	1.85 / 2.08	26.4	1.85 / 2.08	26.4
14	4.29 (dd, *J* = 4.2, 7.1 Hz)	72.5	4.29 (dd, *J* = 4.4, 7.1 Hz)	72.5
15		151.3		151.3
16	2.20 / 2.46	29.7	2.20 / 2.47	29.5
17	1.48 / 1.64	29.9	1.47 / 1.65	29.9
18	3.53 (dd, *J* = 1.5, 10.8 Hz)	76.2	3.53 (dd, *J* = 1.2, 10.4 Hz)	76.2
19		86.1		86.1
20	1.58 / 2.10	31.6	1.58 / 2.10	31.6
21	1.83 (2H)	26.5	1.84 (2H)	26.6
22	3.76 (dd, *J* = 6.5, 9.8 Hz)	87.6	3.76 (dd, *J* = 6.3, 8.8 Hz)	87.6
23		70.4		70.4
24	1.13 (s)	23.9	1.13 (s)	23.9
25	1.19 (s)	27.5	1.20 (s)	27.5
26	1.14 (s)	22.7	1.14 (s)	22.8
27	1.25 (s)	19.4	1.26 (s)	19.4
28	4.89 / 5.05 (brs/brs)	109.9	4.89 / 5.06 (brs/brs)	109.9
29	1.14 (s)	23.7	1.14 (s)	23.8
30	1.21 (s)	27.7	1.22 (s)	27.7
OH–18	2.38 (s)		2.40 (s)	



15b **18b**

To a stirred solution of **15b** (29.8 mg, 54.9 μmol) in benzene (2 mL) was added CMMP (550 μL, 83 μmol, 0.15 mol・L^{-1} benzene solution) in a sealed tube. After stirring for 24 h at 80 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 2:1) to give **18b** (17.8 mg, 33.9 μmol, 62% yield) as colorless solid.

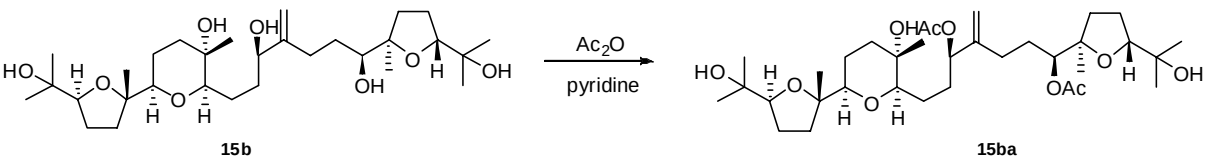
mp 137–141 °C, $[\alpha]_D^{20}$ +9.73 (*c* 1.43, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): 1.11 (3H, s), 1.14 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.16 (3H, s), 1.17 (3H, s), 1.20 (3H, s), 1.26 (1H, m), 1.36–1.52 (4H, m), 1.53–1.70 (5H, m), 1.71–1.86 (5H, m), 1.98–2.16 (3H, m), 2.26, (1H, m), 2.36 (1H, brs), 2.44 (1H, ddd, *J* = 2.2, 4.7, 13.7 Hz), 3.09 (1H, dd, *J* =1.1, 10.4 Hz), 3.25 (1H, dd, *J* = 2.1, 11.5 Hz), 3.44 (1H, dd, *J* = 1.9, 11.5 Hz), 3.67 (1H, brd, *J* = 8.0 Hz), 3.76 (1H, t, *J* = 8.2 Hz), 3.91, (1H, dd, *J* = 5.2, 10.4 Hz) , 4.75 (1H, brs), 4.76 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$): 20.43 (q), 22.92 (q), 23.15 (q), 24.01 (q), 24.15 (q), 25.08 (t), 25.60 (t), 26.50 (t), 26.89 (q), 27.49 (t), 27.71 (q), 28.97 (t), 29.00 (t), 33.16 (t), 33.19 (t), 34.75 (t) , 39.29 (t), 69.64 (s), 70.42 (s), 71.81 (s), 78.87 (d), 83.62 (d), 83.95 (d), 84.14 (s), 84.22 (s), 85.26 (d), 86.81 (d), 87.31 (d), 106.31 (t), 147.33 (s). CIMS *m/z* 524 $[M+H]^+$ (5), 507 (25), 489 (20), 143 (100). HRCIMS calcd 524.3713 for $C_{30}H_{52}O_7$, found 524.3698 $[M]^+$. IR (neat, cm^{-1}): 3441, 1373, 1091.



15a **15aa**

To a stirred solution of **15a** (31.9 mg, 58.8 μmol) in pyridine (3 mL) was added acetic anhydride (0.1 mL, 0.90 mmol). After stirring for 36 h at 50 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 1:2) to give **15aa** (31.9 mg, 50.9 μmol, 87% yield) as a colorless oil.

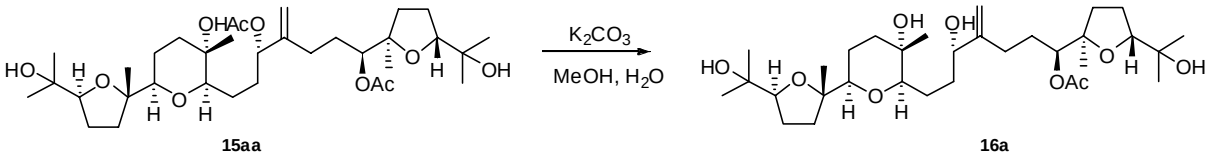
$[\alpha]_D^{20}$ +1.00 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.11 (6H, s), 1.12 (3H, s), 1.14 (3H, s), 1.15 (3H, s), 1.19 (3H, s), 1.19 (3H, s) 1.25 (1H, m), 1.36–1.74 (7H, m), 1.76–1.96 (8H, m), 1.96–2.10 (3H, m), , 2.06 (3H, s), 2.08 (3H, s), 2.18, (1H, brs), 2.25 (1H, brs), 3.03 (1H, dd, *J* =1.8, 8.9 Hz), 3.22 (1H, dd, *J* = 2.3, 11.3 Hz), 3.72 (1H, t, *J* = 6.9 Hz), 3.74 (1H, t, *J* = 8.0 Hz), 4.90 (1H, brs), 4.95, (1H, dd, *J* = 2.3, 10.2 Hz), 5.04 (1H, brs), 5.17, (1H, t, *J* = 7.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 20.17 (q), 21.18 (q), 21.28 (q), 22.86 (q), 23.00 (q), 23.99 (q), 24.17 (q), 24.67 (t), 25.03 (t), 26.12 (t), 26.50 (t), 27.46 (q), 27.46 (q), 27.82 (t), 28.21 (t), 30.23 (t), 34.85 (t), 34.95 (t) , 39.92 (t), 69.76 (s), 70.44 (s), 70.49 (s), 76.73 (d), 77.45 (d), 83.78 (d), 83.95 (s), 84.08 (s), 84.31 (d), 86.87 (d), 87.02 (d), 111.01 (t), 146.88 (s), 170.42 (s), 170.88 (s). CIMS *m/z* 627 $[M+H]^+$ (10), 609 (60), 549 (100). HRCIMS calcd 627.4108 for $C_{34}H_{59}O_{10}$, found 627.4112 $[M+H]^+$. IR (neat, cm^{-1}): 3437, 1738.



15b **15ba**

To a stirred solution of **15b** (24.0 mg, 44.2 μmol) in pyridine (3 mL) was added acetic anhydride (0.1 mL, 0.90 mmol). After stirring for 36 h at 50 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 1:2) to give **15ba** (27.1 mg, 43.3 μmol, 98% yield) as a colorless oil.

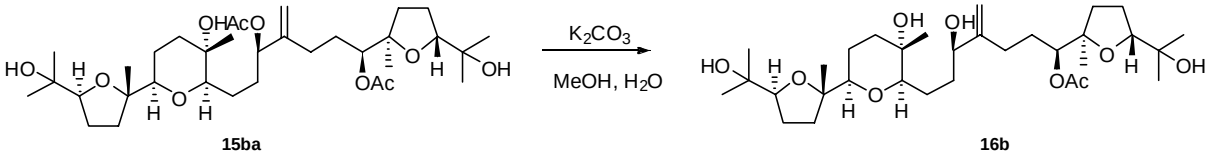
$[\alpha]_D^{20}$ +10.0 (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): 1.11 (3H, s), 1.12 (3H, s), 1.14 (6H, s), 1.19 (3H, s), 1.20 (3H, s), 1.20 (3H, s), 1.22 (1H, m), 1.32–1.72 (6H, m), 1.80–1.99 (8H, m), 2.00–2.07, (5H, m), 2.04 (3H, s), 2.08 (3H, s), 3.05 (1H, d, *J* =9.3 Hz), 3.23 (1H, dd, *J* = 2.2, 11.3 Hz), 3.71 (1H, t, *J* = 6.9 Hz), 3.77 (1H, dd, *J* = 6.2, 8.8 Hz), 4.94 (1H, brs), 4.95, (1H, dd, *J* = 2.2, 10.0 Hz) , 5.06 (1H, brs), 5.22 (1H, t, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 20.08 (q), 21.17 (q), 21.29 (q), 22.77 (q), 23.16 (q), 24.01 (q), 24.41 (t), 25.15 (t), 26.13 (t), 26.62 (t), 27.29 (t), 27.44 (q), 27.64 (t), 29.730 (t), 34.65 (t), 34.93 (t), 39.83 (t), 69.61 (s), 70.46 (s), 70.55 (s), 76.61 (d), 77.15 (d), 83.81 (d), 83.94 (s), 83.99 (d), 84.12 (s), 86.93 (d), 87.05 (d), 112.16 (t), 146.29 (s), 170.48 (s), 171.05 (s). CIMS *m/z* 627 $[M+H]^+$ (3), 609 (40), 549 (100). HRCIMS calcd 627.4108 for $C_{34}H_{59}O_{10}$, found 627.4096 $[M+H]^+$. IR (neat, cm^{-1}): 3453, 1734.



15aa **16a**

To a stirred solution of **15aa** (24.1 mg, 38.4 μmol) in MeOH (2 mL) was added potassium carbonate (1 mL, 1 mmol, 1 mol·L^{-1} aqueous solution). After stirring for 1 h at rt, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil. The residue was purified by column chromatography (hexane/EtOAc, 1:9) to give **16a** (13.4 mg, 22.9 μmol, 60% yield) as a colorless oil along with starting material **15aa** (9.0 mg, 14.4 μmol, 37% yield). The recovered **15aa** was subjected to hydrolysis again as same manner above. Combined yield of **16a** was 92 % (20.7 mg, 35.4 μmol, 92% yield).

$[\alpha]_D^{20}$ –1.43 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): 1.11 (6H, s), 1.14 (3H, s), 1.16 (3H, s), 1.19 (3H, s), 1.19 (3H, s), 1.20 (3H, s) 1.35 (1H, m), 1.46 (1H, m), 1.52–1.73 (6H, m), 1.75–1.87 (8H, m), 1.91–2.12 (4H, m), 2.07 (3H, s), 3.11 (1H, d, *J* =9.9 Hz), 3.28 (1H, dd, *J* = 2.2, 11.4 Hz), 3.72 (1H, t, *J* = 7.3 Hz), 3.78 (1H, t, *J* = 8.4 Hz), 4.12 (1H, dd, *J* = 4.0, 7.3 Hz), 4.87 (1H, brs), 4.97, (1H, dd, *J* = 2.2, 10.3 Hz), 5.09 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$): 20.18 (q), 21.23 (q), 22.83 (q), 23.10 (q), 23.93 (q), 24.04 (q), 24.41 (t), 25.18 (t), 26.14 (t), 26.57 (t), 27.16 (t), 27.47 (q), 27.60 (q), 27.80 (t), 30.62 (t), 34.80 (t), 34.91 (t) , 39.81 (t), 69.83 (s), 70.48 (s), 70.59 (s), 74.65 (d), 77.35 (d), 83.69 (d), 83.95 (s), 84.02 (s), 84.73 (d), 86.86 (d), 86.99 (d), 109.70 (t), 150.69 (s), 171.13 (s). CIMS *m/z* 585 $[M+H]^+$ (3), 567 (40), 549 (100). HRCIMS calcd 585.4003 for $C_{32}H_{57}O_9$, found 585.4021 $[M+H]^+$. IR (neat, cm^{-1}): 3447, 1730.

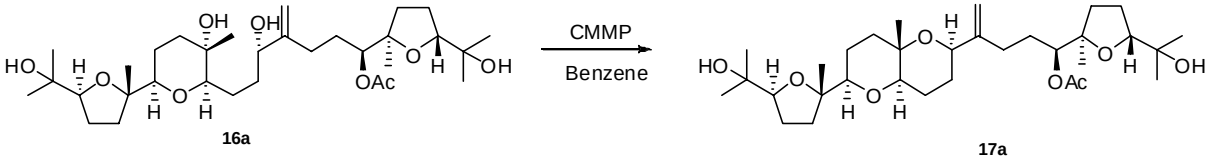


15ba **16b**

To a stirred solution of **15ba** (20.8 mg, 33.2 μmol) in MeOH (2 mL) was added potassium carbonate (1 mL, 1 mmol, 1 mol·L^{-1} aqueous solution). After stirring for 1 h at rt, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil. The residue was purified by column chromatography (hexane/EtOAc, 1:8) to give **16b** (8.9 mg, 15.2 μmol, 46% yield) as a colorless oil along with starting material **15ba** (9.3 mg, 14.8 μmol, 45% yield). The recovered **15ba** was subjected to hydrolysis again as same manner above. Combined yield of **16b** was 92 % (17.0 mg, 29.1 μmol, 88% yield).

$[\alpha]_D^{20}$ +11.1 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): 1.11 (3H, s), 1.12 (3H, s), 1.14 (3H, s), 1.17 (3H, s),

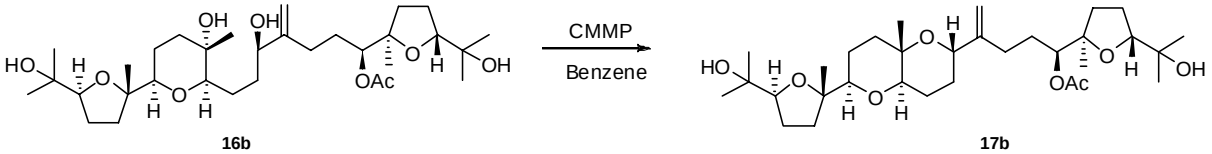
1.18 (3H, s), 1.19 (6H, s) 1.35 (1H, m), 1.42 (1H, m), 1.52–1.75 (6H, m), 1.75–1.96 (9H, m), 2.02–2.18 (3H, m), 2.07 (3H, s), 3.16 (1H, d, *J* = 9.5 Hz), 3.34 (1H, dd, *J* = 2.2, 11.4 Hz), 3.71 (1H, t, *J* = 7.0 Hz), 3.79 (1H, dd, *J* = 5.5, 9.5 Hz), 4.04 (1H, dd, *J* =4.0, 9.5 Hz), 4.83 (1H, brs), 4.94, (1H, dd, *J* = 4.0, 8.1 Hz), 5.08 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$): 20.08 (q), 21.24 (q), 22.89 (q), 23.48 (q), 23.64 (q), 24.04 (q), 25.35 (t), 26.01 (t), 26.15 (t), 26.83 (t), 27.47 (q), 27.60 (t), 27.67 (q), 28.05 (t), 33.92 (t), 34.05 (t), 34.85 (t) , 39.79 (t), 69.79 (s), 70.48 (s), 70.61 (s), 75.91 (d), 77.63 (d), 83.42 (d), 84.03 (s), 84.25 (s), 84.94 (d), 87.02 (d), 87.15 (d), 109.45 (t), 150.90 (s), 171.01 (s). CIMS *m/z* 585 $[M+H]^+$ (5), 567 (30), 549 (100). HRCIMS calcd 585.4003 for $C_{32}H_{57}O_9$, found 585.3998 $[M+H]^+$. IR (neat, cm^{-1}): 3420, 1734.



16a **17a**

To a stirred solution of **16a** (19.8 mg, 33.9 μmol) in benzene (2 mL) was added CMMP (1.11mL, 169 μmol, 153 mol・L^{-1} benzene solution) in a sealed tube. After stirring for 24 h at 80 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 1:1) to give **17a** (12.7 mg, 22.4 μmol, 66% yield) as a colorless oil.

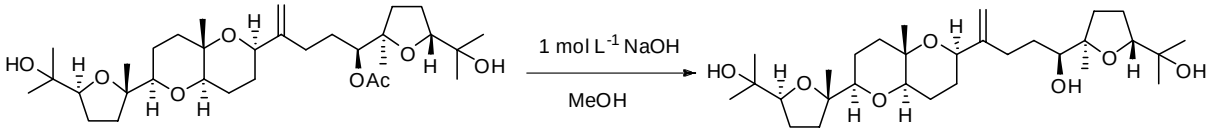
$[\alpha]_D^{20}$ –4.84 (*c* 0.20, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.11 (3H, s), 1.14 (6H, s), 1.19 (6H, s), 1.19 (3H, s), 1.19 (3H, s), 1.40–1.70 (8H, m), 1.72–1.90 (6H, m), 1.90–2.21 (6H, m), 2.08 (3H, s), 3.33 (1H, dd, *J* =2.9, 11.0 Hz), 3.45 (1H, dd, *J* = 5.6, 11.4 Hz), 3.70 (1H, t, *J* = 7.4 Hz), 3.75 (1H, t, *J* = 8.2 Hz), 4.28 (1H, dd, *J* =3.6, 7.6 Hz), 4.87 (1H, brs), 4.94, (1H, dd, *J* = 2.7, 10.0 Hz), 5.05 (1H, brs). ^{13}C NMR (75MHz, $CDCl_3$): 19.48 (q), 21.19 (q), 21.85 (t), 22.77 (q), 23.02 (q), 24.05 (q), 24.05 (q), 24.53 (t), 26.12 (t), 26.27 (t), 26.48 (t), 27.53 (q), 28.77 (t), 29.72 (t), 34.77 (t), 35.24 (t), 38.83 (t), 70.40 (s), 70.68 (s), 72.53 (d), 72.72 (s), 78.93 (d), 84.03 (s), 84.03 (s), 86.73 (d), 87.03 (d), 110.18 (t), 150.81 (s), 170.79 (s). EIMS *m/z* 566 $[M]^+$ (5), 548 (5), 507 (5), 143 (100). HREIMS calcd 566.3819 for $C_{32}H_{54}O_8$, found 566.3823 $[M]^+$. IR (neat, cm^{-1}): 3430, 1734.



16b **17b**

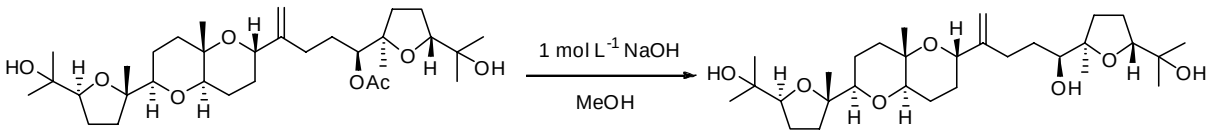
To a stirred solution of **16b** (10.9 mg, 18.7 μmol) in benzene (1.5 mL) was added CMMP (187 μL, 28.0 μmol, 150 mol・L^{-1} benzene solution) in a sealed tube. After stirring for 24 h at 80 °C, the reaction mixture was concentrated. The residue was purified by column chromatography (hexane/EtOAc, 3:2) to give **17b** (1.1 mg, 1.94 μmol, 10% yield) as a colorless oil along with starting material **16b** (6.0 mg, 10.3 μmol, 55% yield).

$[\alpha]_D^{20}$ –4.84 (*c* 0.41, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): 1.11 (6H, s), 1.16 (3H, s), 1.19 (6H, s), 1.20 (3H, s), 1.22 (3H, s), 1.44–1.74 (8H, m), 1.74–1.86 (7H, m), 1.88–2.22 (5H, m), 2.08 (3H, s), 3.11 (1H, dd, *J* = 4.4, 11.3 Hz), 3.35 (1H, dd, *J* = 3.3, 10.7 Hz), 3.72 (1H, t, *J* = 7.4 Hz), 3.75 (1H, t, *J* = 8.2 Hz), 4.09 (1H, brd, *J* = 9.9 Hz), 4.84 (1H, brs), 4.95, (1H, dd, *J* = 2.5, 10.2 Hz), 5.06 (1H, brs). ^{13}C NMR (75 MHz, $CDCl_3$): 21.20 (q), 22.78 (q), 23.04 (q), 24.06 (q), 24.12 (q), 24.50 (t), 24.98 (t), 26.08 (t), 26.45 (t), 27.54 (q), 27.58 (q), 28.55 (t), 29.04 (t), 31.11 (t), 34.79 (t), 35.32 (t), 37.76 (t), 70.36 (s), 70.65 (s), 72.17 (d), 72.61 (s), 77.92 (d), 80.88 (d), 84.03 (s), 84.07 (s), 84.17 (d), 86.72 (d), 87.05 (d), 109.91 (t), 149.60 (s), 170.79 (s). EIMS *m/z* 566 $[M]^+$ (2), 548 (10), 507 (10), 143 (100). HREIMS calcd 566.3819 for $C_{32}H_{54}O_8$, found 566.3823 $[M]^+$. IR (neat, cm^{-1}): 3440, 1734.



17a **1**

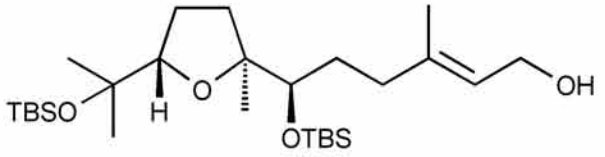
To a stirred solution of **17a** (1.5 mg, 2.6 μmol) in MeOH (1 mL) was sodium hydroxide (0.5 mL, 0.5 mmol, 1 mol·L^{-1} aqueous solution). After stirring for 6 h at rt, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give **1** (1.4 mg, 2.6 μmol, 100% yield) as a colorless oil. Spectral data were identical with those of the synthetic compound form **15a**. See page S-12.



17b **19**

To a stirred solution of **17b** (8.2 mg, 14.5 μmol) in MeOH (4 mL) was sodium hydroxide (2 mL, 2 mmol, 1 mol·L^{-1} aqueous solution). After stirring for 9 h at rt, the reaction was quenched by addition of saturated aqueous NH_4Cl and the mixture was diluted with ethyl acetate. The phases were separated and the aqueous phase was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated to give a colorless oil. The residue was purified by column chromatography (hexane/EtOAc, 6:1) to give **19** (6.5 mg, 12.4 μmol, 86% yield) as a colorless oil.

$[\alpha]_D^{20}$ +7.64 (*c* 0.35, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): 1.11 (3H, s) 1.13 (3H, s), 1.15 (3H, s) 1.16 (3H, s), 1.20 (3H, s) 1.22 (3H, s) 1.24 (3H, s), 1.45 (1H, m), 1.52–1.63 (3H, m), 1.64–1.76 (5H, m),1.78–1.90 (5H, m), 2.02–2.21 (3H, m), 2.16–2.22 (2H, m), 2.33 (1H, m), 2.55 (br s), 3.13 (dd, J = 4.1, 11.5 Hz), 3.35 (1H, m), 3.54 (d, *J* = 10.4 Hz), 3.76 (2H, m), 4.16 (dd, *J* = 2.5, 11.6 Hz), 4.86 (1H, brs), 5.08 (1H, brs). ^{13}C NMR (100 MHz, $CDCl_3$): 14.63 (q), 22.76 (q), 23.64 (q), 23.94 (q), 24.02 (q), 24.47 (t), 24.93 (t), 26.41 (t), 26.54 (t), 27.51 (q), 27.70 (q), 28.94 (t), 30.22 (t) , 31.05 (t), 31.84 (t), 35.27 (t), 37.71 (t), 70.46 (s), 70.62 (s), 72.72 (s), 72.75 (d), 76.13 (d), 80.82 (d), 84.03 (s), 84.15 (d), 85.96 (s), 86.70 (d), 87.52 (d), 110.45 (t), 149.81 (s). EIMS *m/z* 524 $[M]^+$ (5), 506 (20), 465 (20), 447 (20), 143(100). HREIMS calcd 524.3713 for $C_{30}H_{52}O_7$, found 524.3708 $[M]^+$. IR (neat, cm^{-1}): 3696, 2971, 1375.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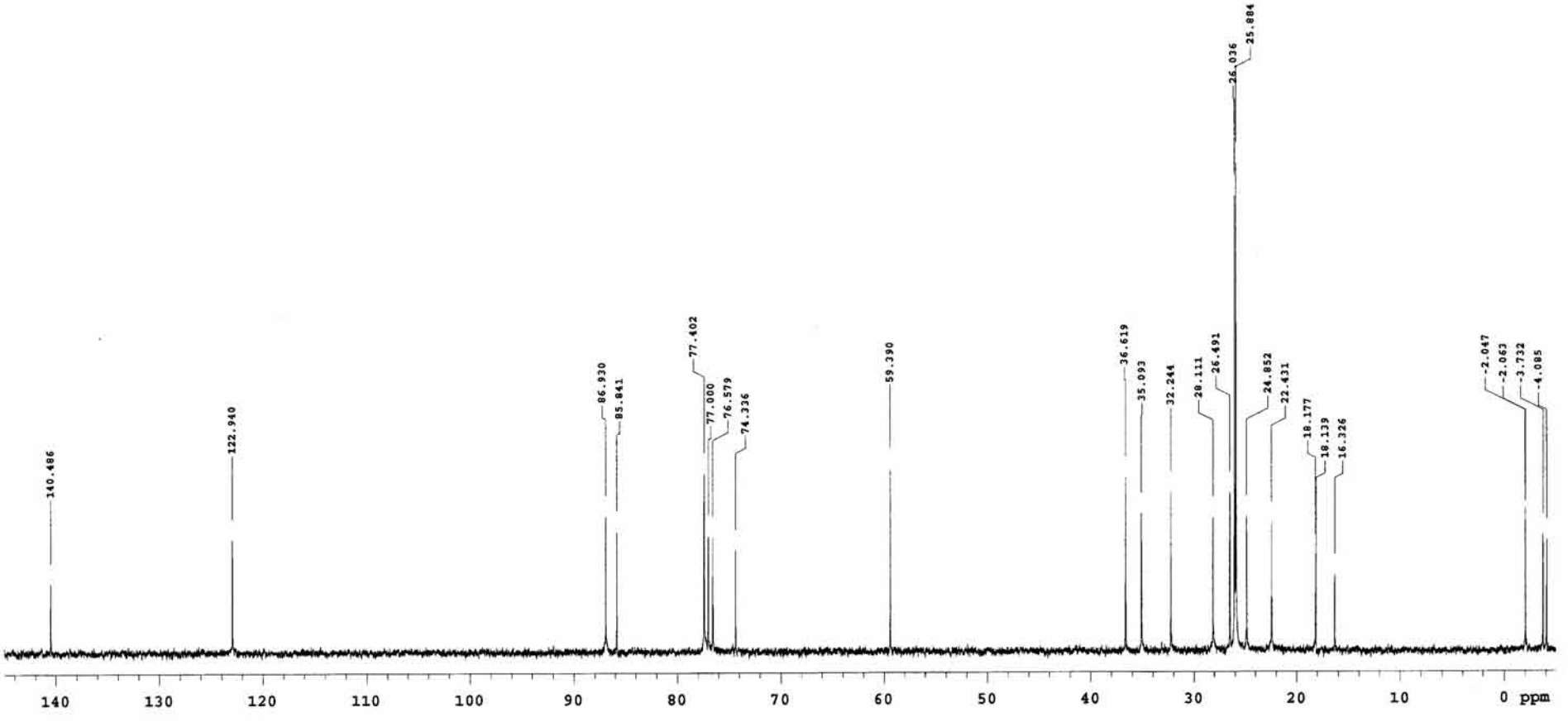
OTBS
OH

3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74.336
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32.244
28.111
26.491
26.036
25.884
24.852
22.431
18.177
18.139
16.326
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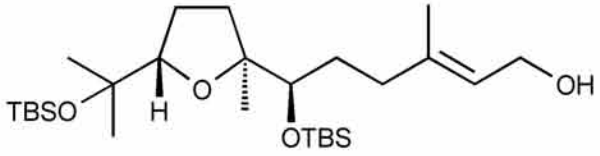
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H
O
OTBS
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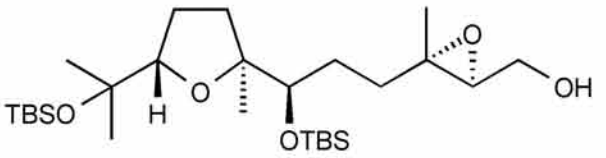
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OTBS
O
OH

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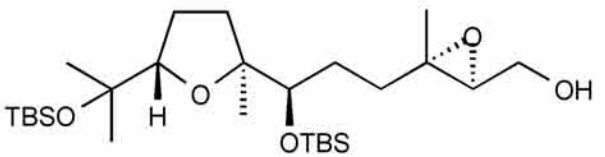
18.97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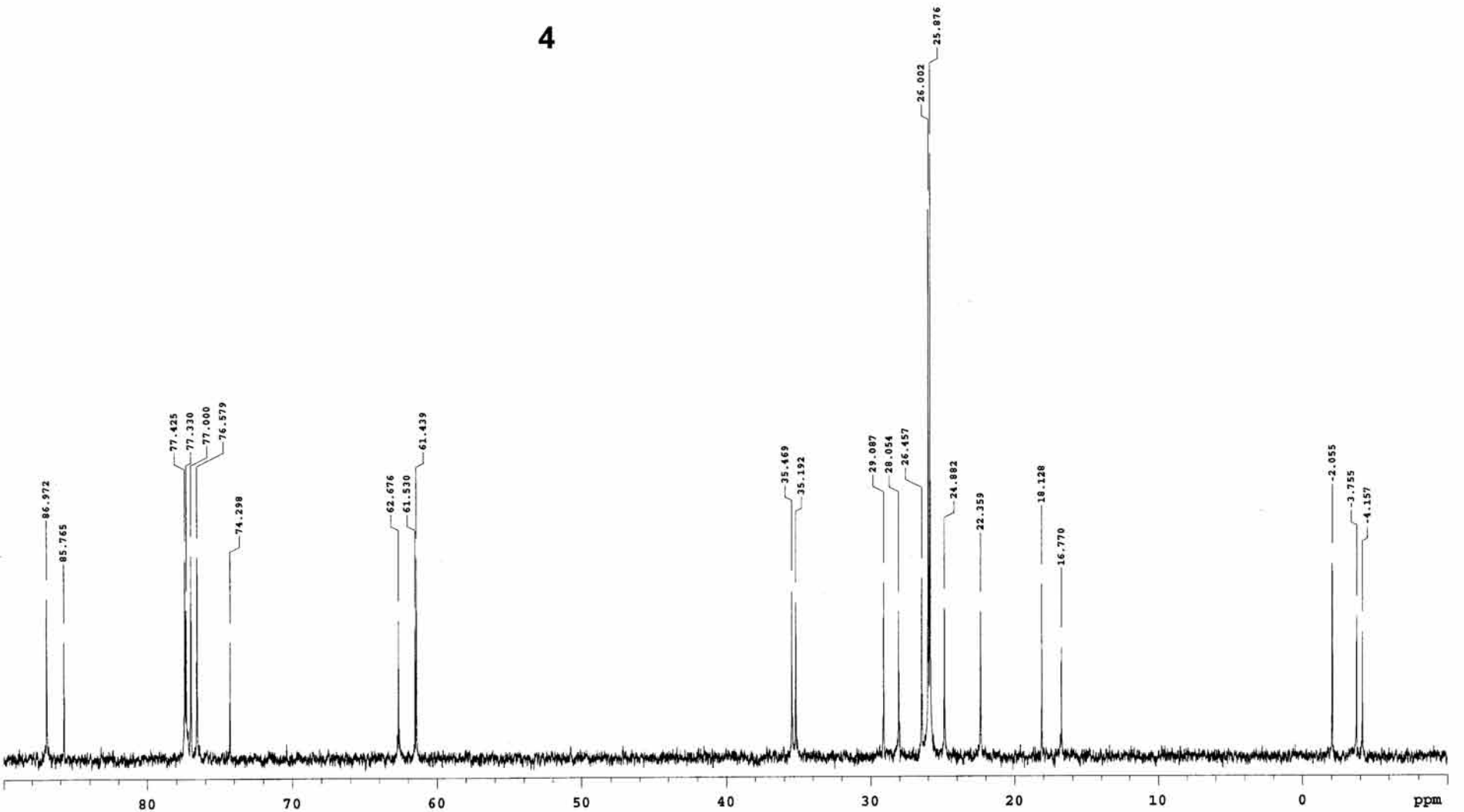
O
OTBS
O
OH

4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29.087
28.054
26.457
26.002
25.876
24.882
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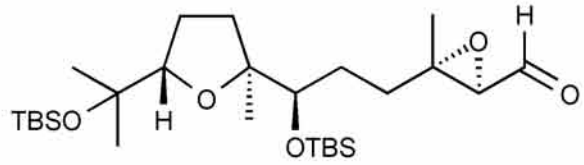
ppm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H
O
O

4a

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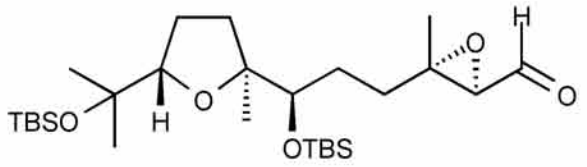
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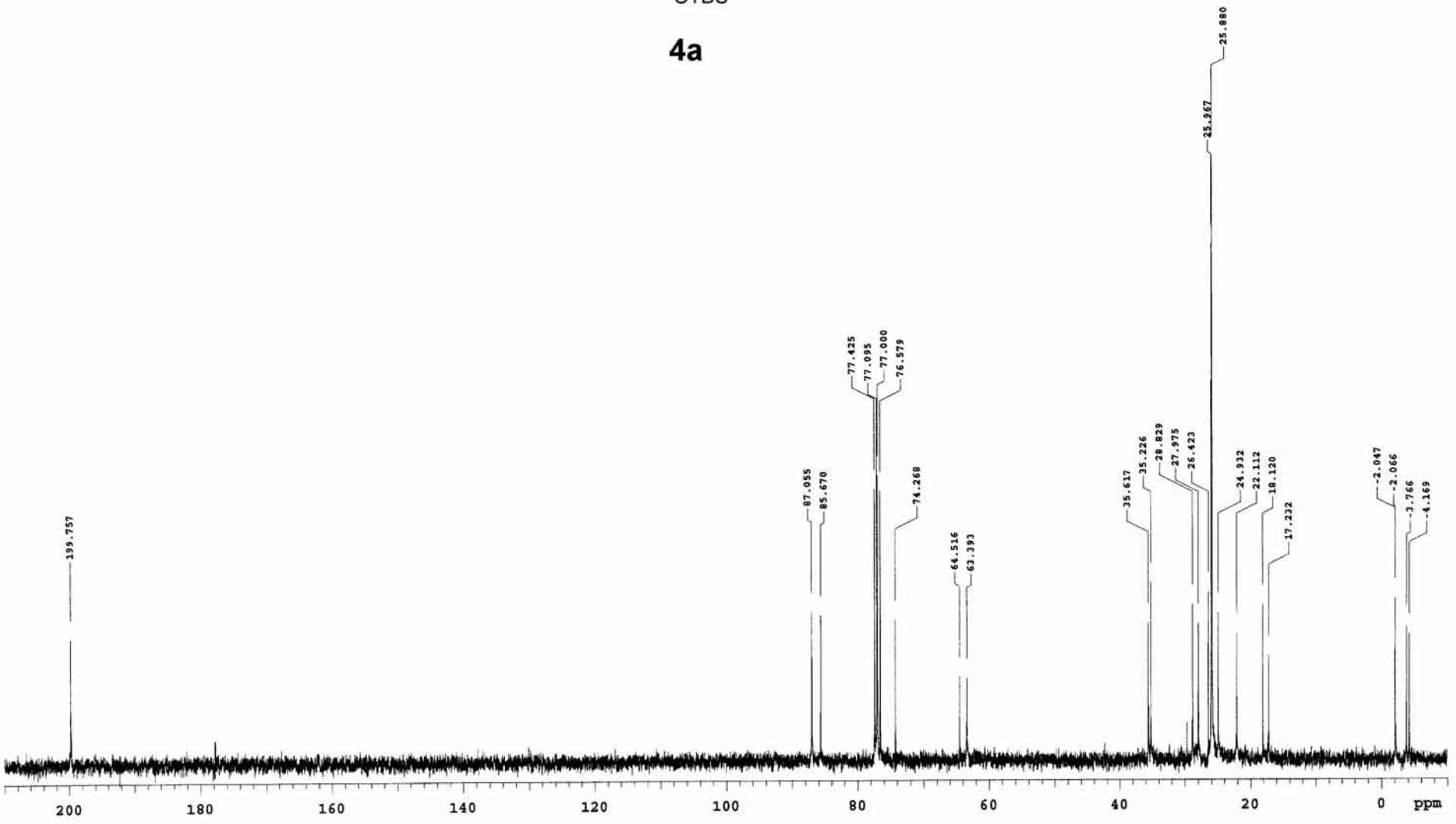
OTBS
O
H
O

4a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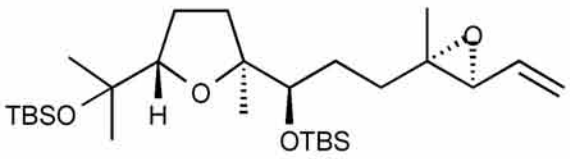
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OTBS

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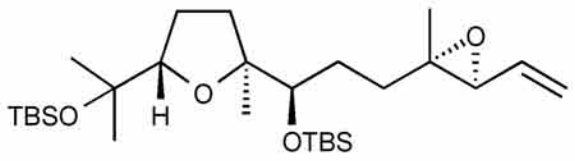
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H
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OTBS
O

5

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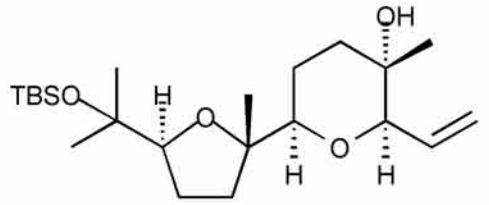

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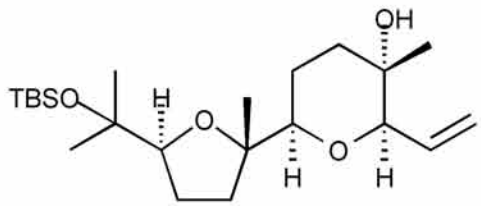
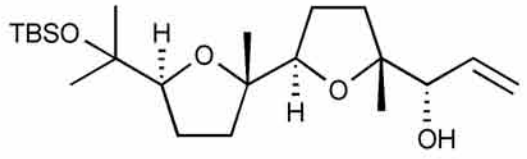
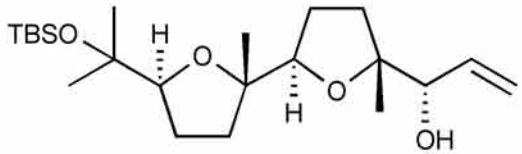


6 (6-endo cyclization)



7 (5-exo cyclization)



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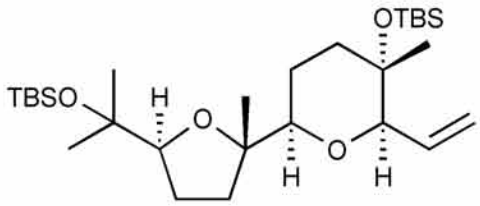
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O
O
H
H

8 (Segment A)

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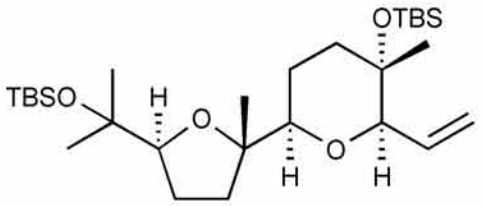
9.60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TBSO
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O
H
H

8 (Segment A)

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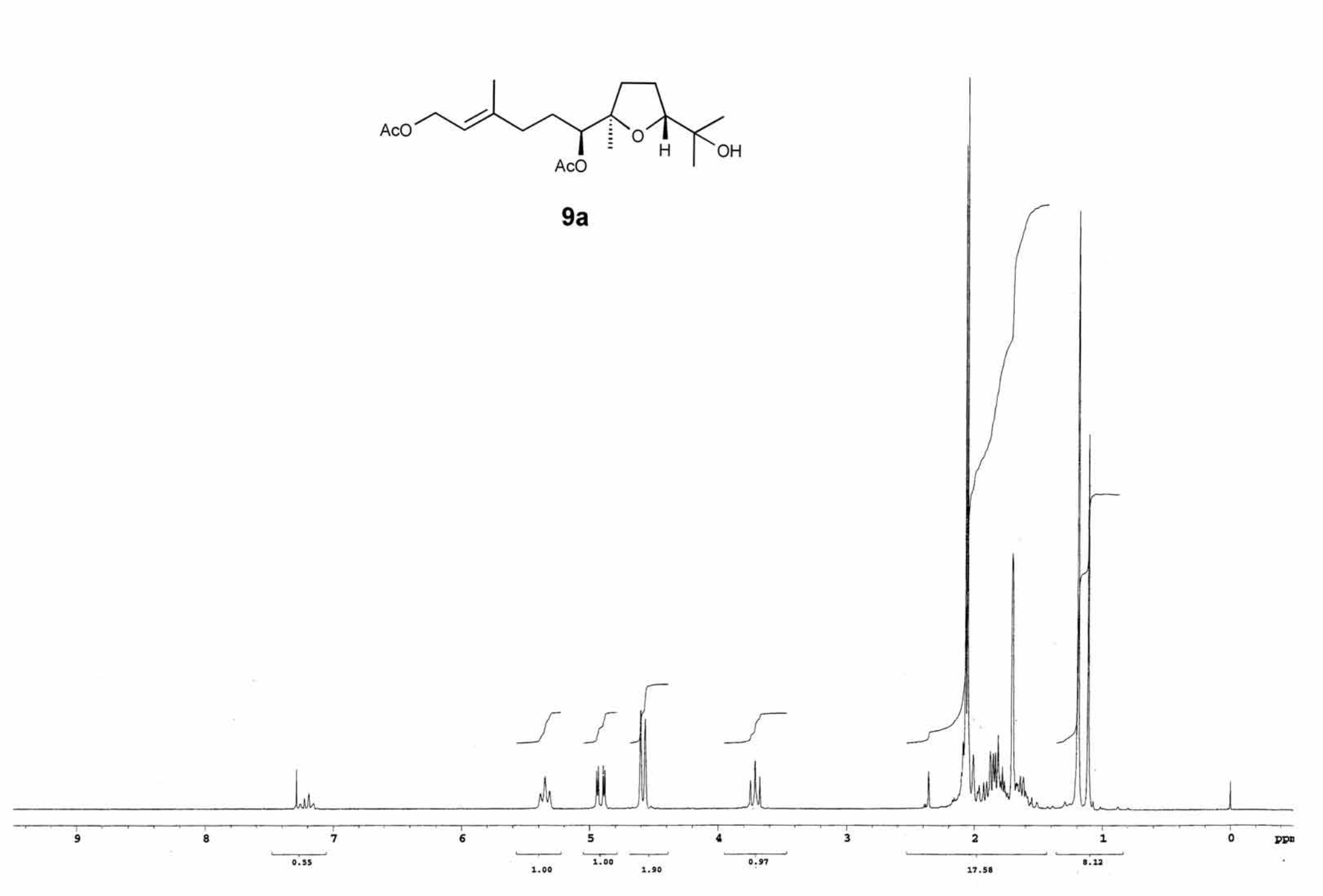
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OH
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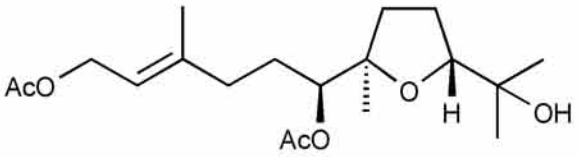
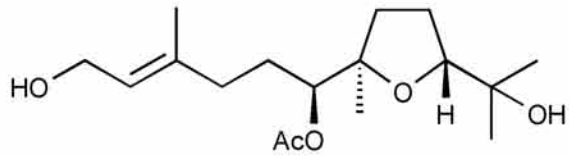


9a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AcO
O
H
OH

9b

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6
5
4
3
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1.00
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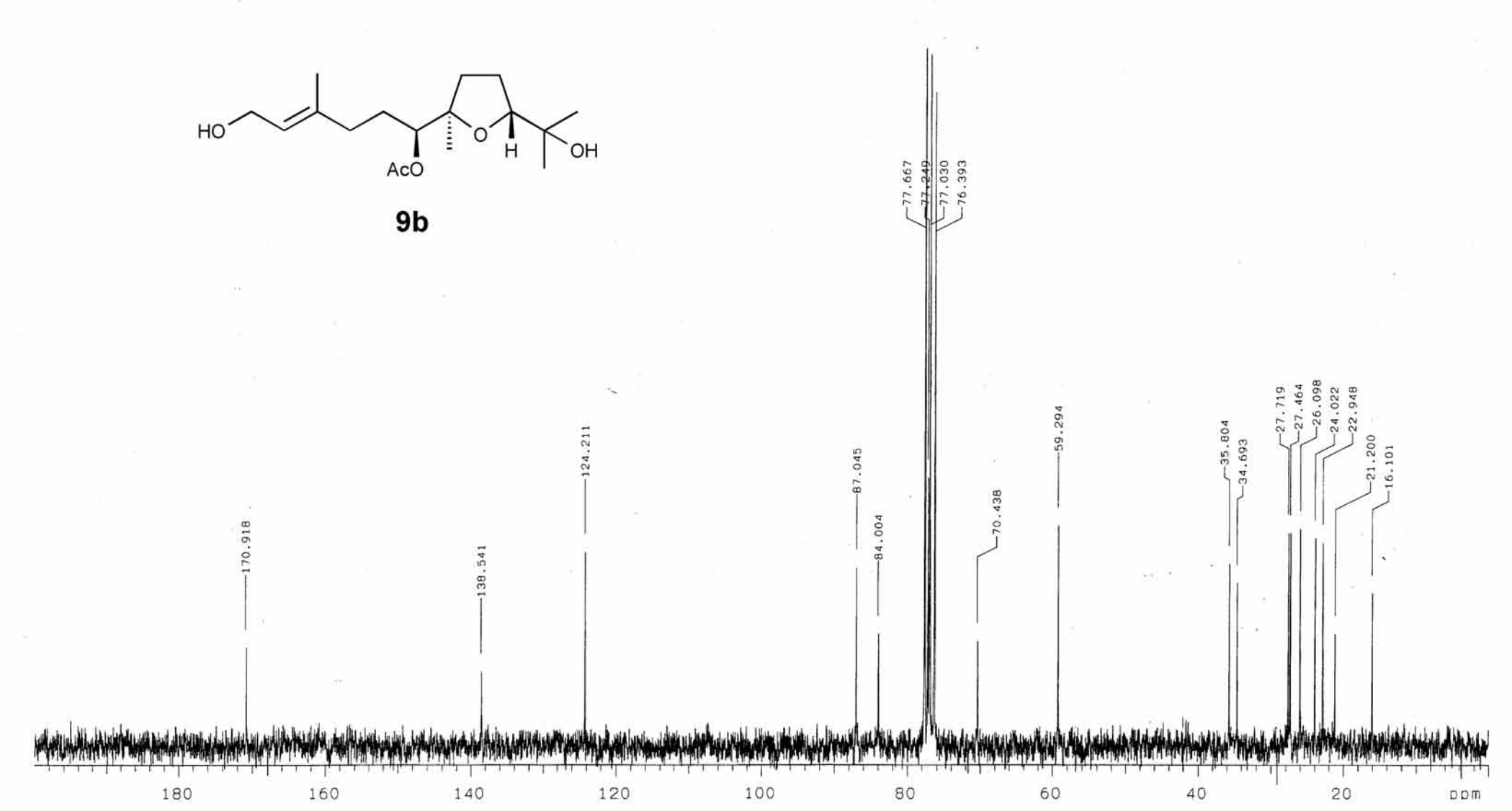
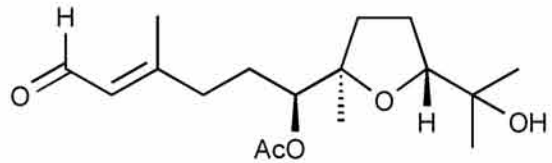
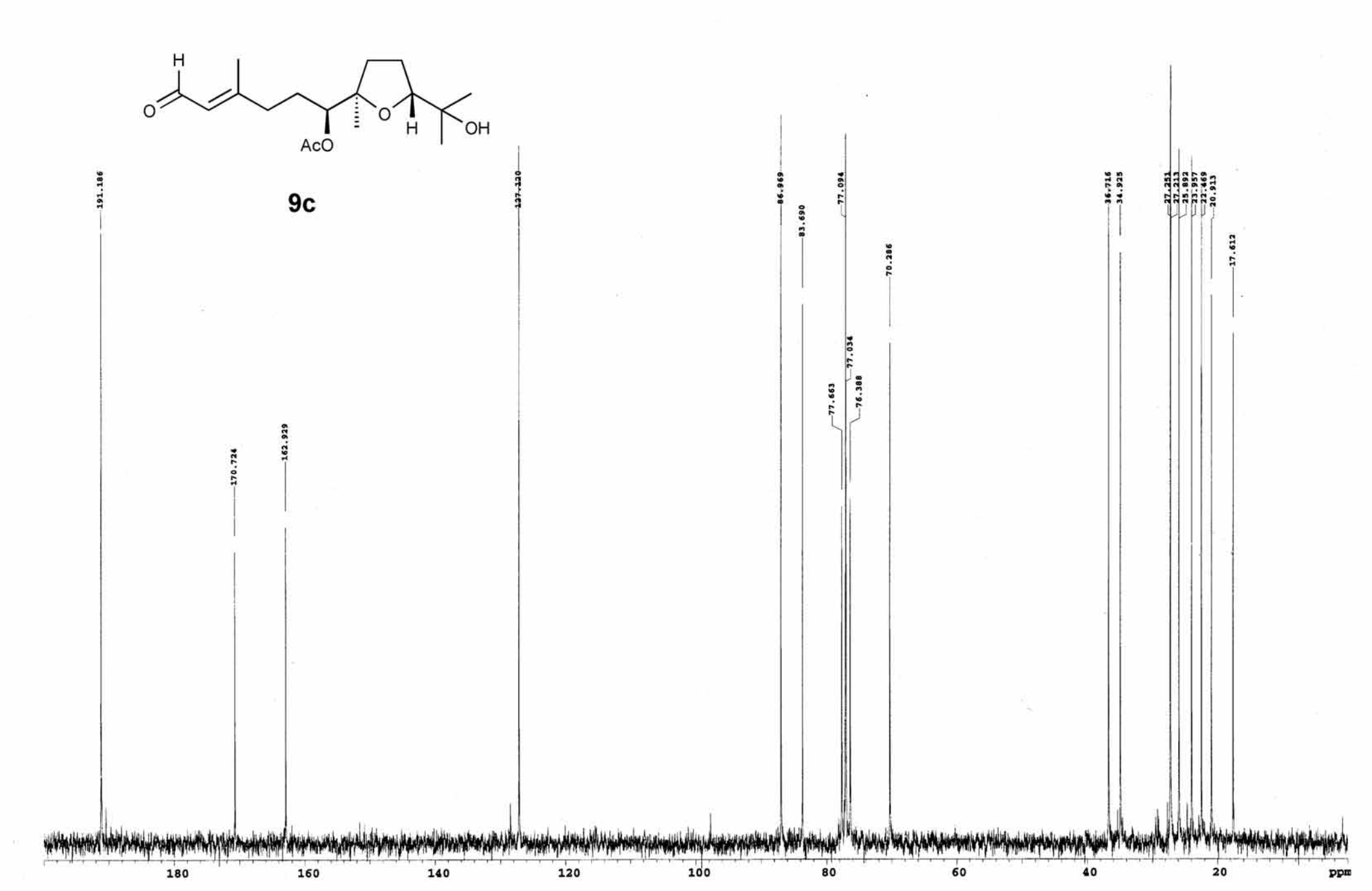
1.03
16.59
9.74
0.38
0.15

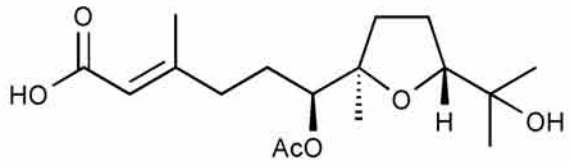

HO
AcO
O
H
OH
9b
170.918
138.541
124.211
87.045
84.004
77.667
77.249
77.030
76.393
70.438
59.294
35.804
34.693
27.719
27.464
26.098
24.022
22.948
21.200
16.101
180
160
140
120
100
80
60
40
20
ppm


H
O
AcO
O
H
OH

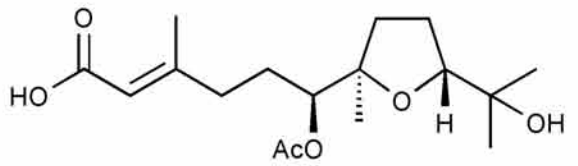
9c

11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.88
0.10
1.00
1.02
0.96
15.71
9.77
0.24


H
O
AcO
O
H
OH
9c
191.186
170.724
162.929
137.330
86.969
83.690
77.663
77.094
77.034
76.388
70.286
36.716
34.925
27.251
27.233
25.892
23.957
22.469
20.913
17.612
180
160
140
120
100
80
60
40
20
ppm

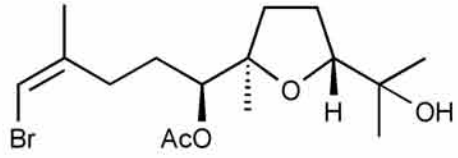


10


O
HO
AcO
O
H
OH

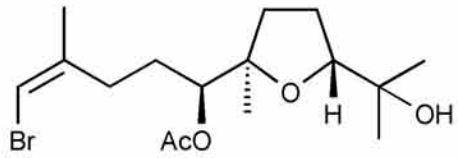
10

171.494
170.902
161.817
115.374
87.034
83.876
77.660
77.340
77.030
76.392
70.525
37.509
34.898
27.589
27.361
25.988
23.969
22.640
21.001
19.066
180
160
140
120
100
80
60
40
20
ppm


Br
AcO
O
H
OH

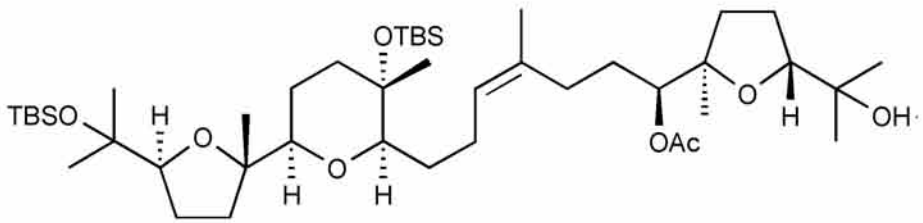
11 (Segment B)

6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
3.15
3.35
3.43
23.42
3.93
22.43
7.78
32.51


Br
AcO
O
H
OH

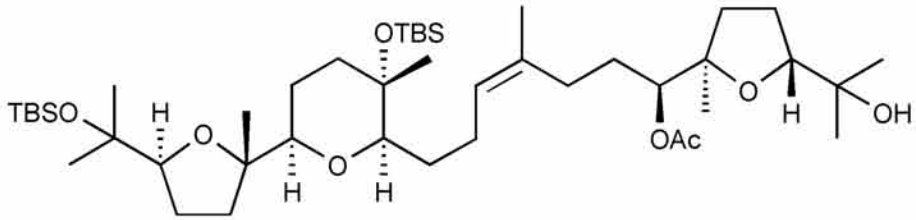
11 (Segment B)

170.754
140.854
101.212
87.027
83.931
77.667
77.503
77.030
76.393
70.365
34.821
31.015
27.446
27.082
26.026
24.022
22.878
22.038
21.127
180
160
140
120
100
80
60
40
20
ppm


OTBS
TBSO
H
O
O
H
H
OAc
O
H
OH

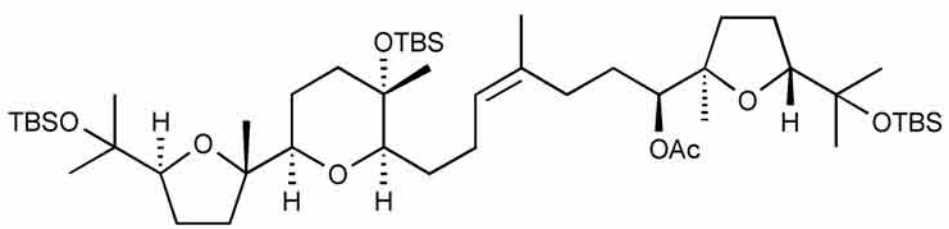
12

9
8
7
6
5
4
3
2
1
0
ppm
1.56
1.00
1.00
1.93
0.66
0.66
-0.27
4.81
7.20
1.55
4.96
15.69
28.01
21.51
12.77


OTBS
TBSO
H
O
O
H
H
O
H
OAc
OH

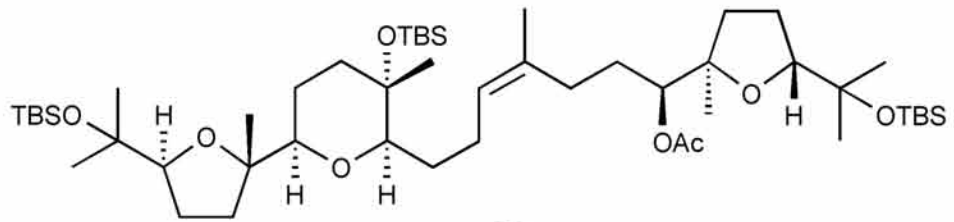
12

170.581
134.112
126.189
87.086
87.040
84.410
84.103
84.061
82.980
78.039
77.455
77.235
77.030
76.605
74.461
72.442
70.283
40.272
35.487
34.489
29.154
28.380
28.331
27.769
27.568
26.665
26.065
25.860
25.769
24.874
24.745
24.642
24.077
23.409
23.219
22.130
21.159
20.635
18.131
18.025
1.794
1.942
2.098
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OTBS
TBSO
H
O
O
H
H
OAc
O
H
OTBS

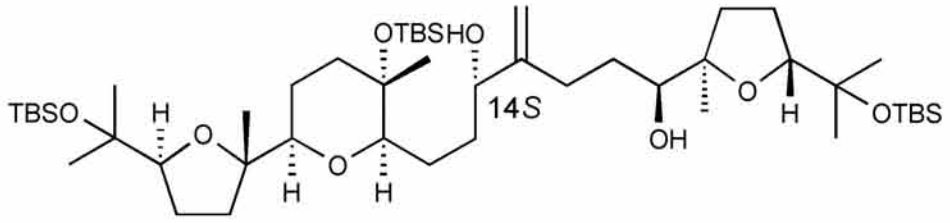
12a

9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.94
0.83
0.81
3.58
5.07
3.63
7.04
6.30
20.93
26.98
16.26


OTBS
TBSO
H
O
O
H
H
O
OAc
H
OTBS

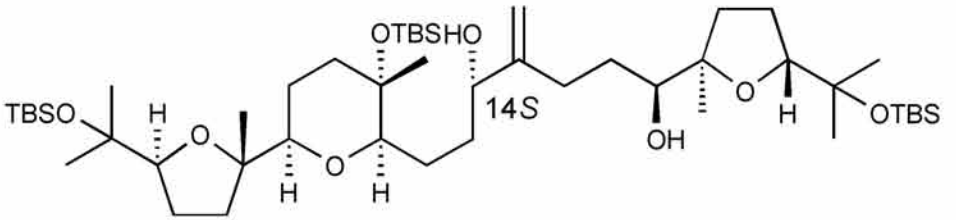
12a

170.660
134.366
126.004
87.566
87.093
84.461
84.118
83.980
82.989
78.060
77.450
77.236
77.030
76.603
74.497
74.268
72.483
40.324
35.571
34.579
29.201
28.491
28.384
27.743
26.706
26.400
25.897
25.805
24.936
24.760
24.669
23.448
22.853
22.128
21.251
20.671
18.161
18.061
-1.752
-1.905
-2.050
180
160
140
120
100
80
60
40
20
ppm


OTBSHO
TBSO
H
O
14S
OH
O
H
OTBS
O
H
H

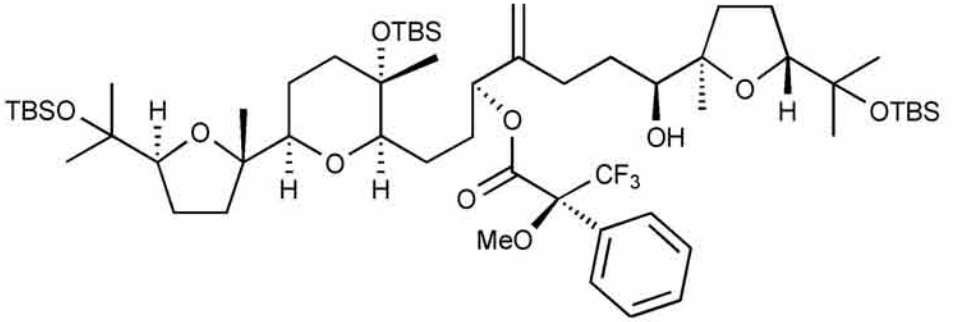
14a

9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.04
0.96
2.07
0.91
0.86
0.86
3.50
13.63
4.84
24.16
31.79
19.26

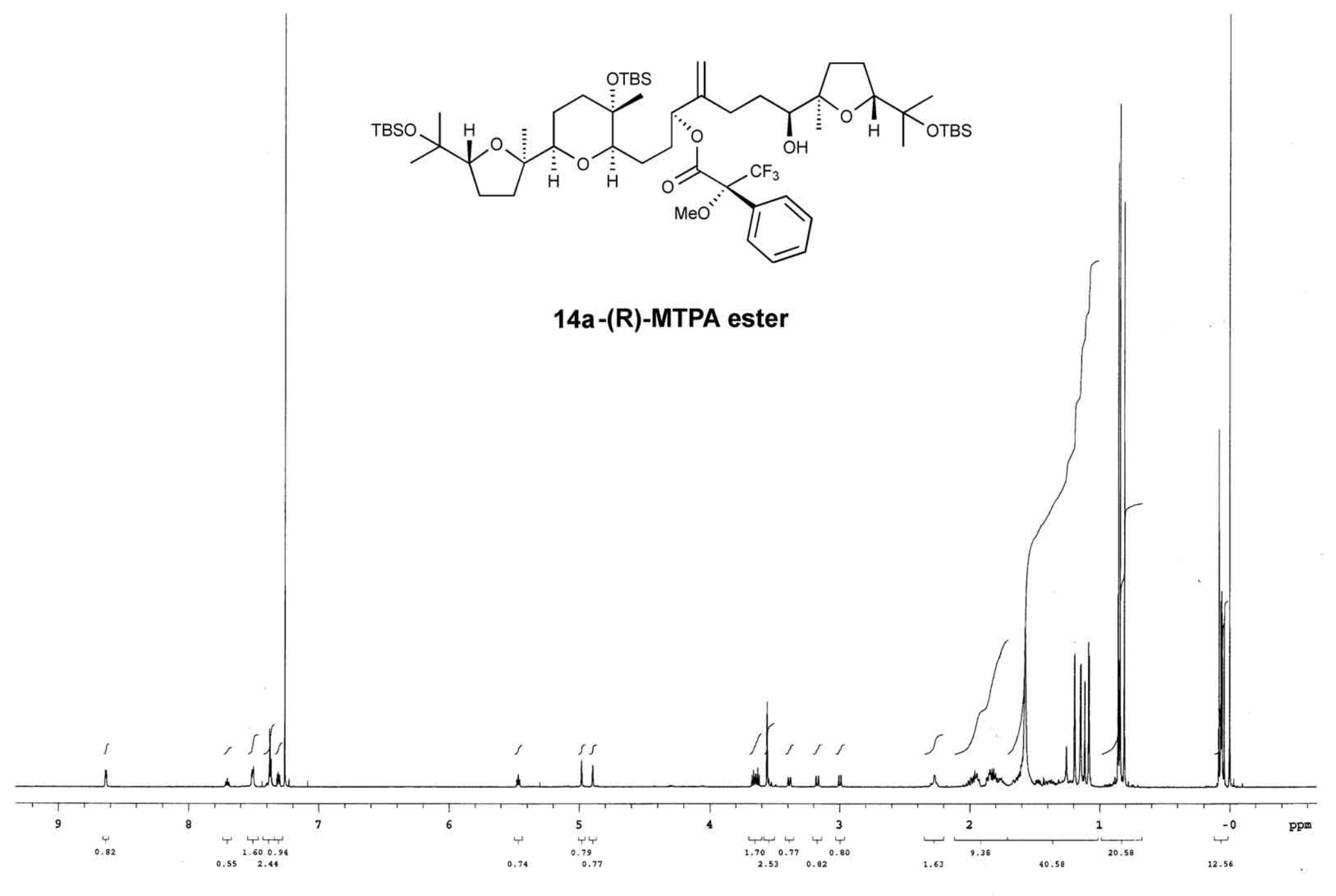

OTBSHO
TBSO
H
O
14S
O
H
OTBS
OH
O
H
H

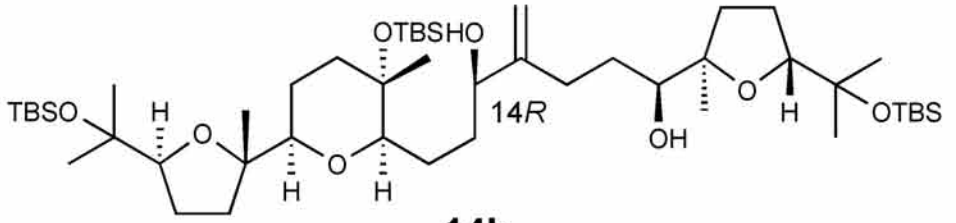
14a

25.904
25.790
25.274
77.453
77.032
76.607
88.605
87.197
85.934
85.402
83.922
83.372
76.170
74.398
74.239
72.493
151.428
109.657
40.194
35.276
33.132
31.205
29.971
28.715
27.778
27.604
26.807
26.663
25.054
24.834
24.003
22.329
20.606
18.174
18.045
-1.778
-1.945
-2.051
180
160
140
120
100
80
60
40
20
0
ppm



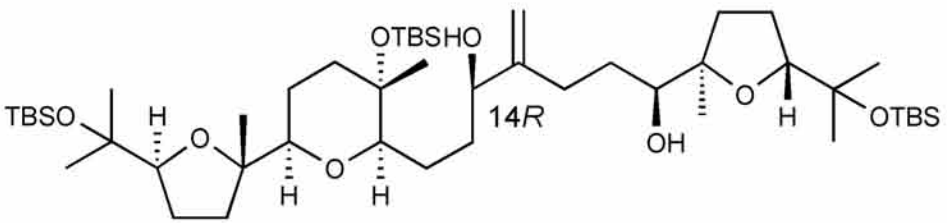
14a-(S)-MTPA ester


OTBS
TBSO
H
O
H
O
H
O
OH
O
H
OTBS
O
CF3
MeO
14a-(R)-MTPA ester
9
8
7
6
5
4
3
2
1
-0
ppm
0.82
0.55
1.60
0.94
2.44
0.74
0.79
0.77
1.70
0.77
0.80
2.53
0.82
1.63
9.38
40.58
20.58
12.56


OTBSHO
TBSO
H
O
14R
OH
O
H
OTBS
O
H
H

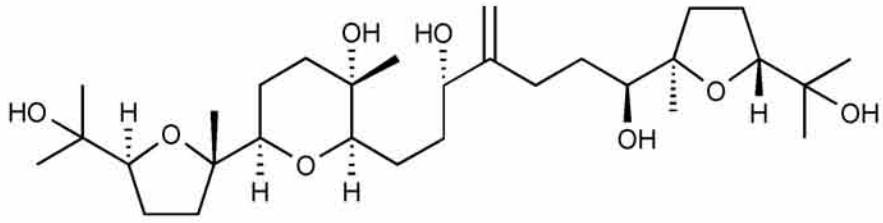
14b

9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
0.93
2.22
1.10
1.06
1.14
1.16
3.36
7.38
7.21
7.96
25.67
33.45
20.20


OTBSHO
TBSO
H
O
14R
OH
O
H
OTBS
H
O
H

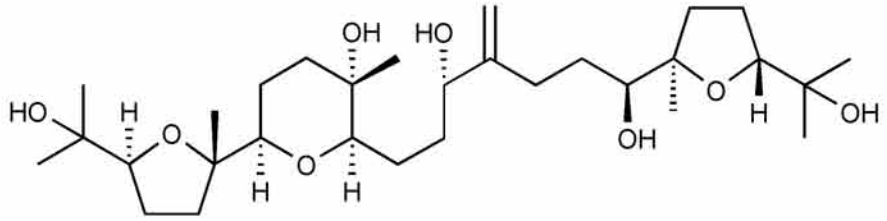
14b

152.126
109.213
88.594
87.353
85.841
85.361
84.226
83.194
77.449
77.028
76.650
76.607
75.863
74.368
74.201
72.520
40.198
34.692
33.853
31.258
30.252
28.833
27.953
27.588
26.607
26.644
25.907
25.775
25.289
25.000
23.965
23.652
20.610
18.178
1.793
1.952
2.043
180
160
140
120
100
80
60
40
20
0
ppm

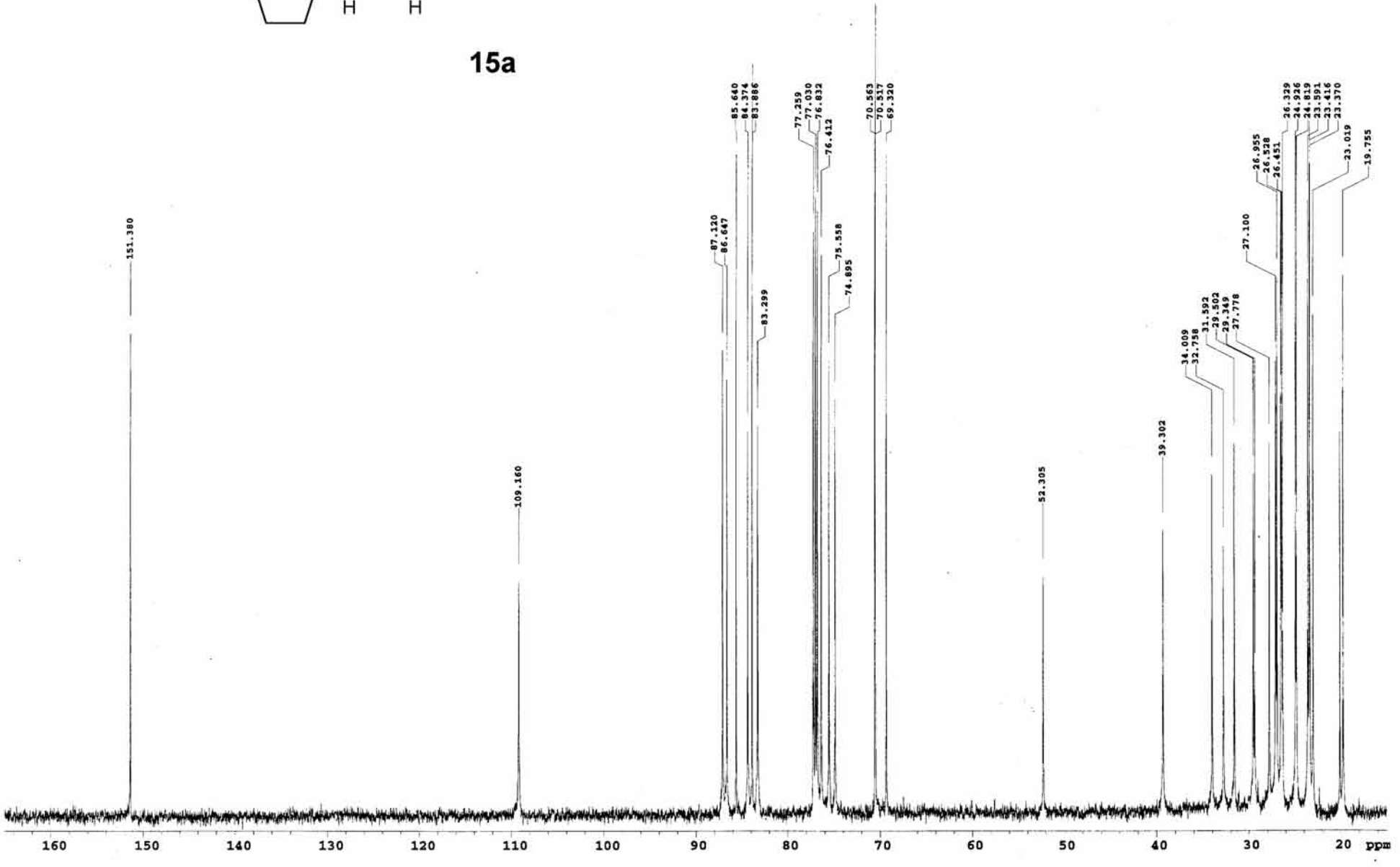

HO
H
O
OH
HO
H
O
H
OH
O
H
OH

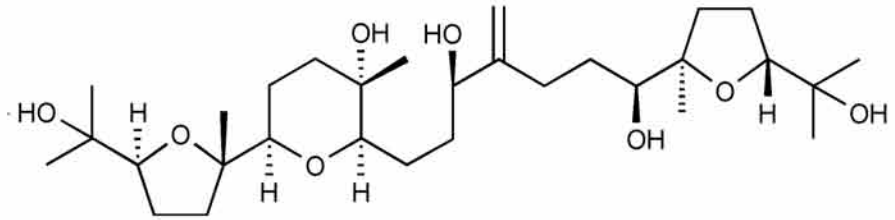
15a

9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.93
1.72
2.07
1.03
1.10
1.23
4.77
5.88
7.00
10.60
21.60
1.13


HO
H
O
OH
HO
H
O
H
OH
O
H
OH

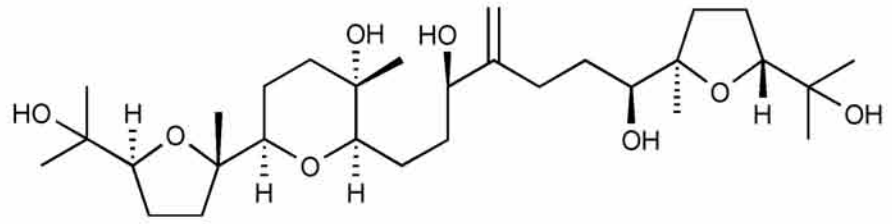
15a


151.380
109.160
87.120
86.647
85.640
84.374
83.886
83.299
77.259
77.030
76.832
76.412
75.558
74.895
70.563
70.517
69.320
52.305
39.302
34.009
32.758
31.592
29.502
29.349
27.778
27.100
26.955
26.528
26.451
26.329
24.926
24.819
23.591
23.416
23.370
23.019
19.755
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

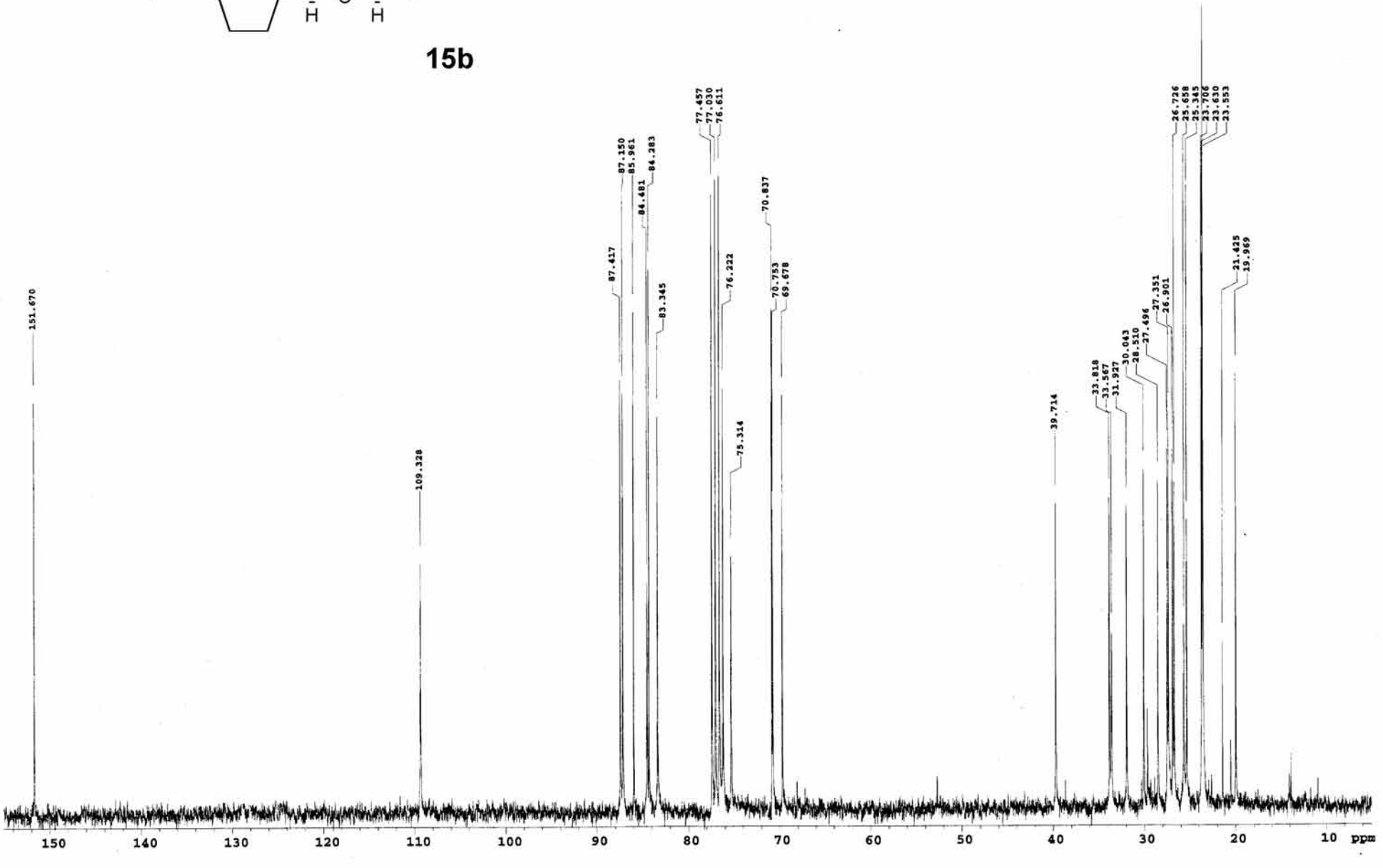

HO
H
O
OH
HO
H
O
H
OH
O
H
OH

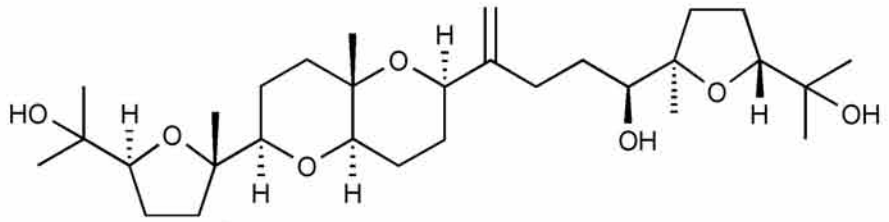
15b

9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.00
2.35
1.31
1.24
1.22
2.26
1.33
4.85
17.86
4.77
23.77
2.08
0.10

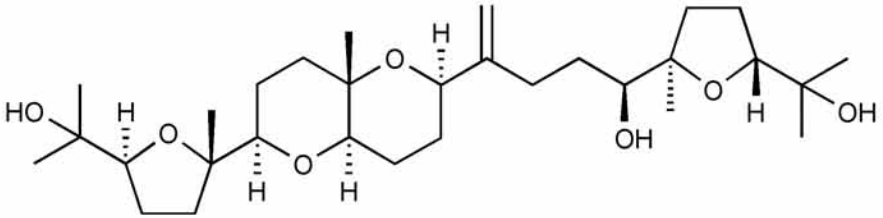

HO
H
O
OH
HO
H
O
H
OH
O
H
OH

15b

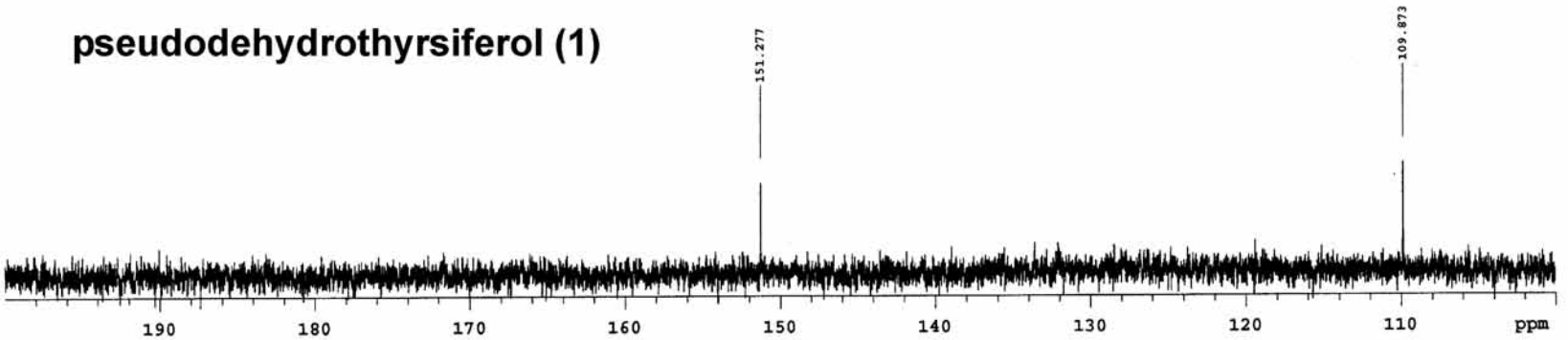

151.670
109.328
87.417
87.150
85.961
84.481
84.283
83.345
77.457
77.030
76.611
76.222
75.314
70.837
70.753
69.678
39.714
33.818
33.567
31.927
30.043
28.510
27.496
27.351
26.901
26.726
25.658
25.345
23.706
23.630
23.553
21.425
19.969
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

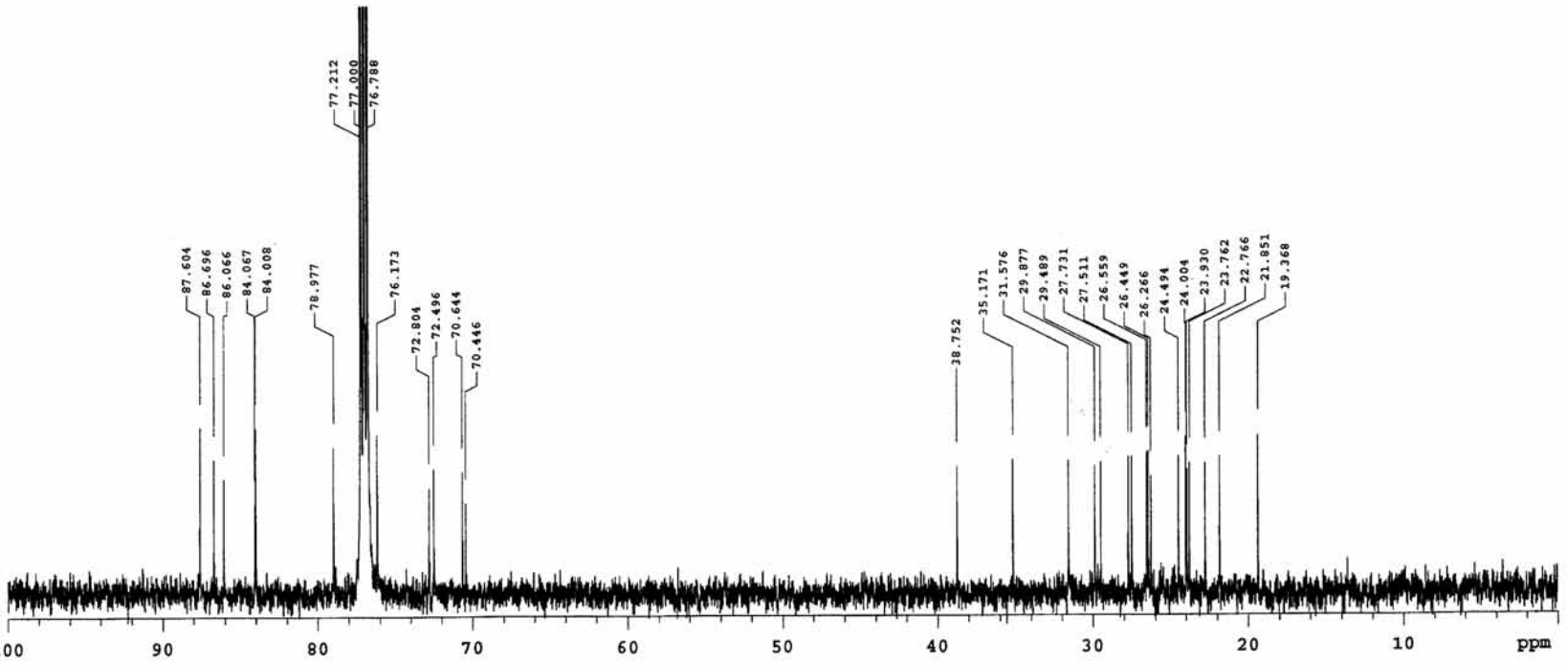


pseudodehydrothyrsiferol (1)



pseudodehydrothyrsiferol (1)

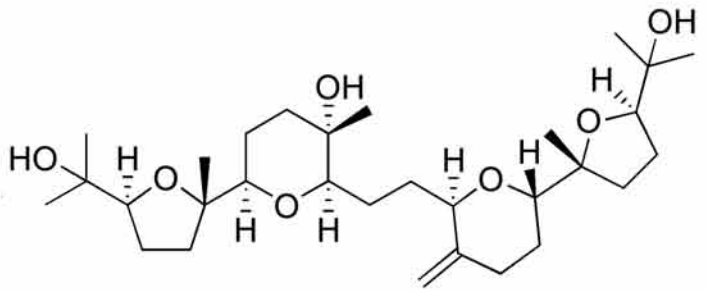




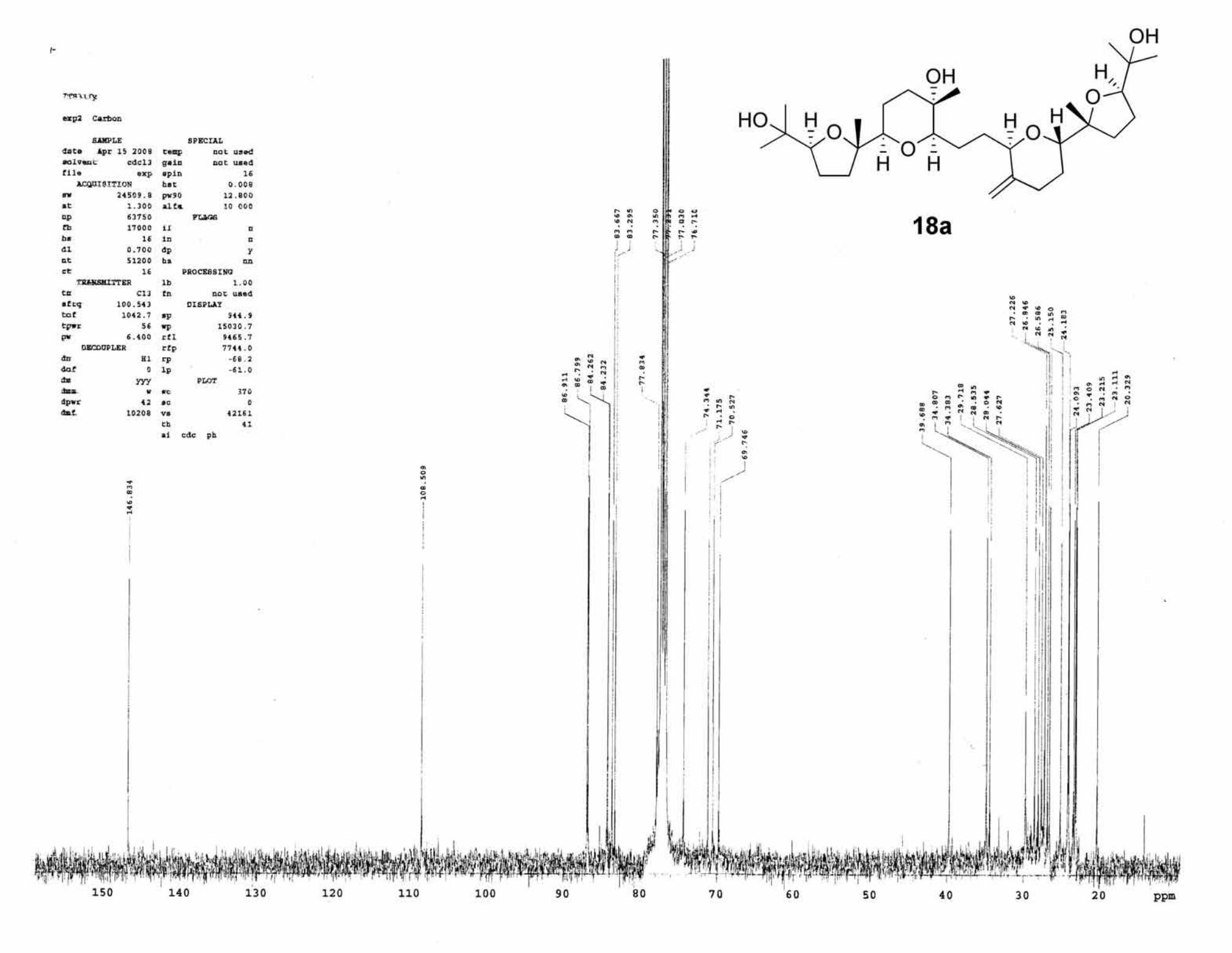
7TS311c

expl s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2008	dfrq	599.963
solvent	CDCl3	dn	H1
file	/export/home/-	dpwr	46
vnmr1/vnmrsys/data-		dof	0
/fuku7/7ts311c_1h.-		dm	nnn
	fid	dmm	c
ACQUISITION		dmf	11600
sfrq	599.963	dseq	
tn	H1	dres	1.0
at	3.641	homo	n
np	65536	temp	25.0
sw	9000.9	PROCESSING	
fb	5000	wtfile	
bs	4	proc	ft
tpwr	57	fn	65536
pw	10.3	math	f
dl	1.359		
tof	-600.0	werr	
nt	128	wexp	
ct	128	wbs	
alock	n	wnt	wft
gain	60		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	354.9		
wp	2800.0		
vs	471		
sc	0		
wc	400		
hzmm	7.00		
is	977.69		
rfl	745.8		
rfp	0		
th	7		
ins	100.000		
nm	ph		



18a

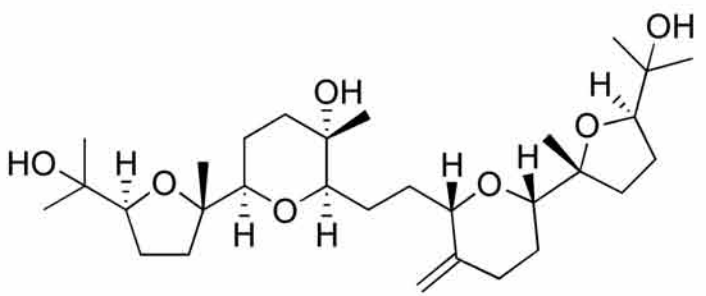

exp2 Carbon
SAMPLE
date Apr 15 2008
solvent cdcl3
file exp
ACQUISITION
sw 24509.8
at 1.300
np 63750
fb 17000
bs 16
d1 0.700
nt 51200
ct 16
TRANSMITTER
tn C13
sfrq 100.543
tof 1042.7
tpwr 56
pw 6.400
DECOUPLER
dn H1
dof 0
dm yyy
dmm w
dpwr 42
dmf 10208
SPECIAL
temp not used
gain not used
spin 16
hst 0.008
pw90 12.800
alfa 10.000
FLAGS
il n
in n
dp y
hs nn
PROCESSING
lb 1.00
fn not used
DISPLAY
sp 944.9
wp 15030.7
rfl 9465.7
rfp 7744.0
rp -68.2
lp -61.0
PLOT
sc 370
wc 0
vs 42161
th 41
ai cdc ph
146.834
108.509
86.911
86.799
84.262
84.232
83.667
83.295
77.834
77.350
77.030
76.710
74.344
71.175
70.527
69.746
39.688
34.807
34.383
29.718
28.535
28.044
27.627
27.226
26.946
26.586
25.150
24.183
24.093
23.409
23.215
23.111
20.329
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

18a

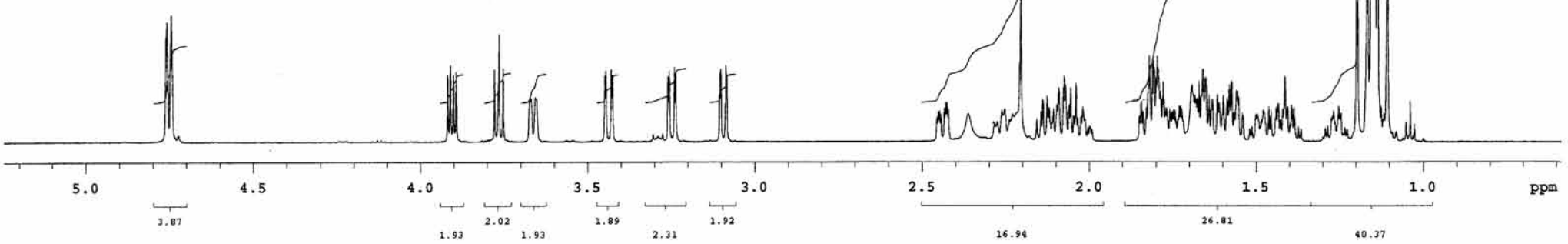
7TS310f

exp1 s2pul

SAMPLE		DEC. & VT	
date	Mar 14 2008	dfrq	599.963
solvent	CDCl3	dn	H1
file	/export/home/-	dpwr	46
vnmr1/vnmrsys/data-		dof	0
/fuku7/7ts310f_1h.-		dm	nnn
	fid	dmm	c
ACQUISITION		dmf	11600
sfrq	599.963	dseq	
tn	H1	dres	1.0
at	3.641	homo	n
np	65536	temp	25.0
sw	9000.9	PROCESSING	
fb	5000	wtfile	
bs	4	proc	ft
tpwr	57	fn	65536
pw	10.3	math	f
dl	1.359		
tof	-600.0	werr	
nt	32	wexp	
ct	32	wbs	
alock	n	wnt	wft
gain	45		
FLAGS			
il	n		
in	n		
dp	y		
hs	nn		
DISPLAY			
sp	347.8		
wp	2800.0		
vs	212		
sc	0		
wc	400		
hzmm	7.00		
is	1258.66		
rfl	743.3		
rfp	0		
th	7		
ins	100.000		
nm	ph		

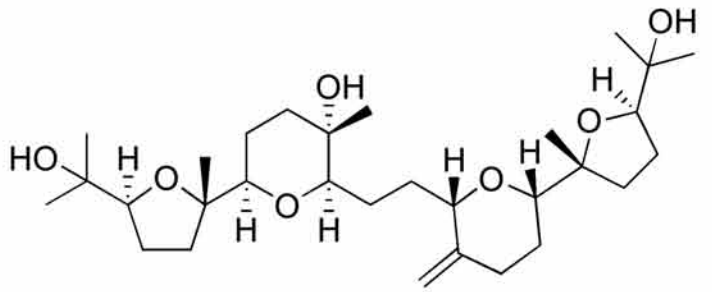


18b



exp2 Carbon

SAMPLE		SPECIAL	
date	Apr 10 2008	temp	not used
solvent	cdcl3	gain	not used
file	exp	spin	16
ACQUISITION		hst	0.008
sw	24509.8	pw90	12.800
at	1.300	alfa	10.000
np	63750	FLAGS	
fb	17000	il	n
bs	16	in	n
d1	0.700	dp	y
nt	100000	hs	nn
ct	19936	PROCESSING	
TRANSMITTER		lb	1.00
tn	C13	fn	not used
sfrq	100.543	DISPLAY	
tof	1042.7	sp	478.9
tpwr	56	wp	15592.4
pw	6.400	rf1	9465.7
DECOUPLER		rfp	7744.0
dn	H1	rp	-33.1
dcrf	0	lp	-9.0
dm	yyy	PLOT	
dmm	w	wc	176
dpwr	42	sc	0
dmf	10208	vs	9743
		th	31
		ai	cdc ph

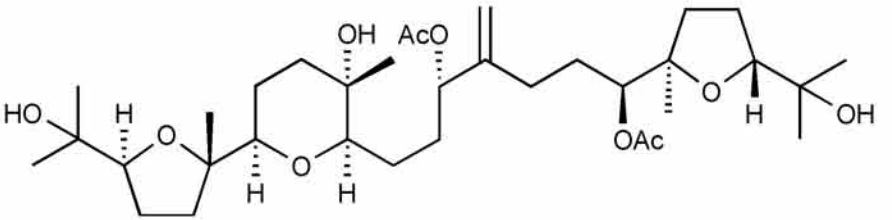


18b

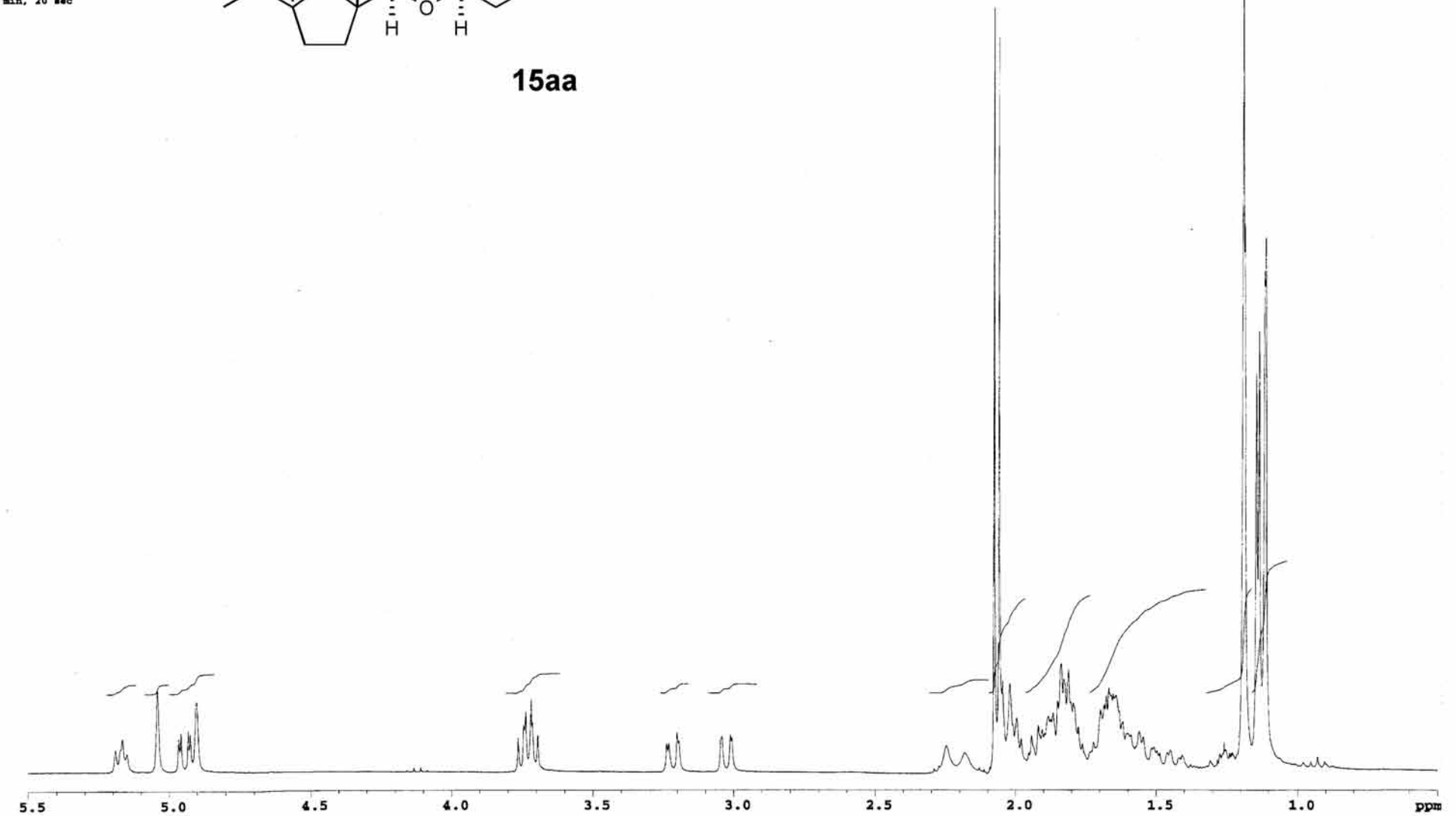
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YN630m-HO62806_11_40
INOVA-600 "NMR"

Relax. delay 1.000 sec
Pulse 38.7 degrees
Acq. time 4.000 sec
Width 4504.5 Hz
16 repetitions
OBSERVE H1, 300.0445617 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 20 sec



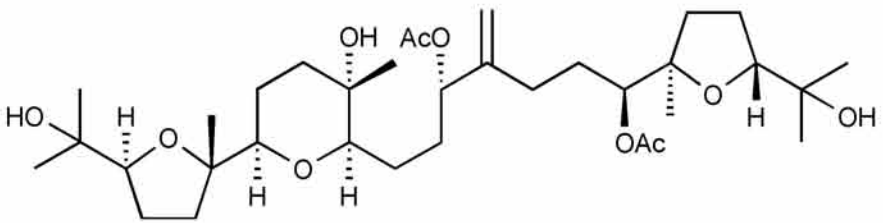
15aa



13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM630m-C062806_12_03
INOVA-600 "NMR"

Pulse 54.2 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
320 repetitions
OBSERVE C13, 75.4462649 MHz
DECOUPLE H1, 300.0461196 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 9 min, 43 sec

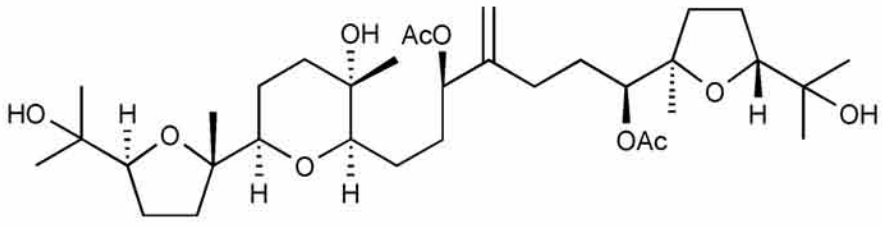


15aa

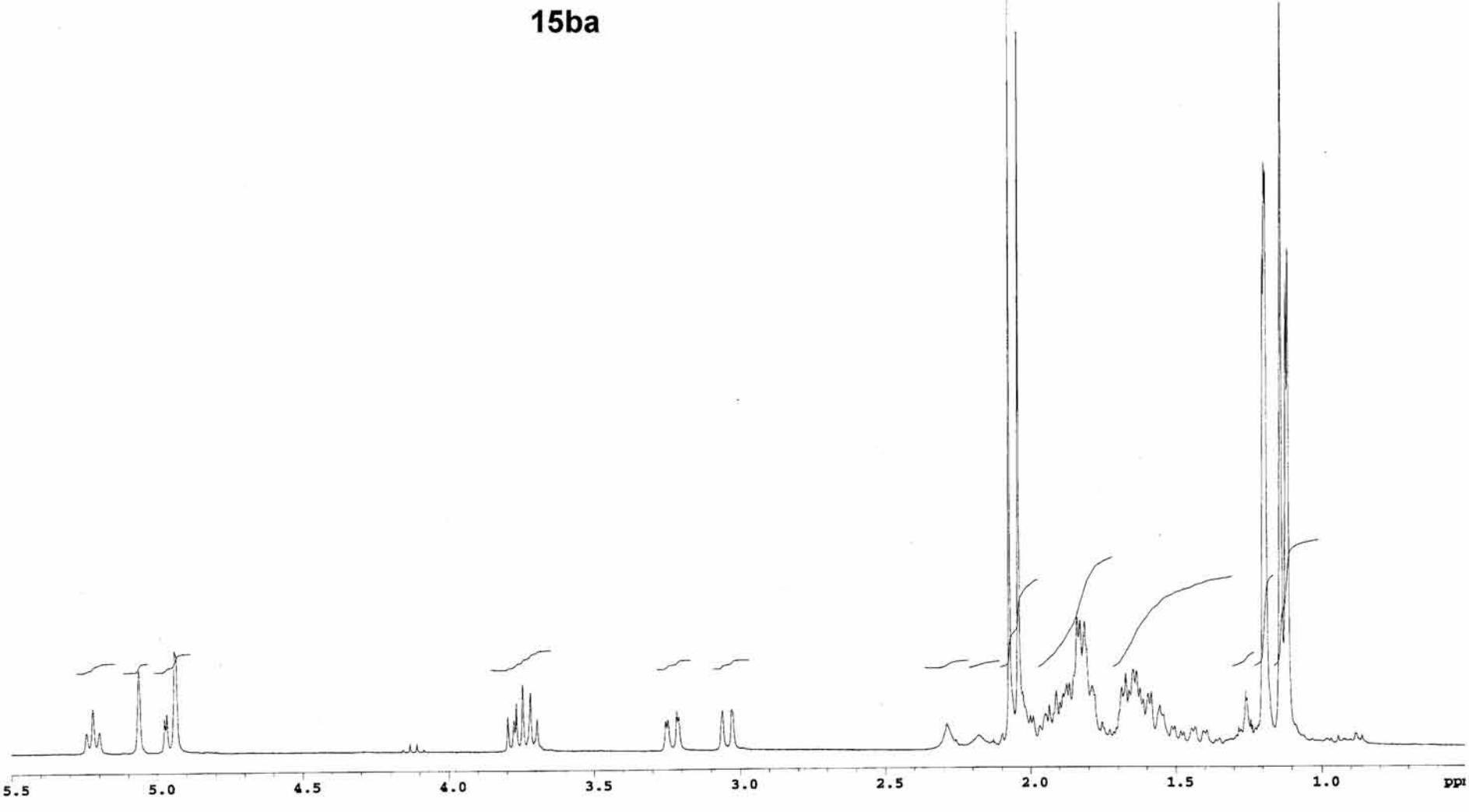
STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM629m-H062806_10_52
INOVA-600 "NMR"

Relax. delay 1.000 sec
Pulse 38.7 degrees
Acq. time 4.000 sec
Width 4504.5 Hz
16 repetitions
OBSERVE H1, 300.0445621 MHz
DATA PROCESSING
FT size 65536
Total time 1 min, 20 sec



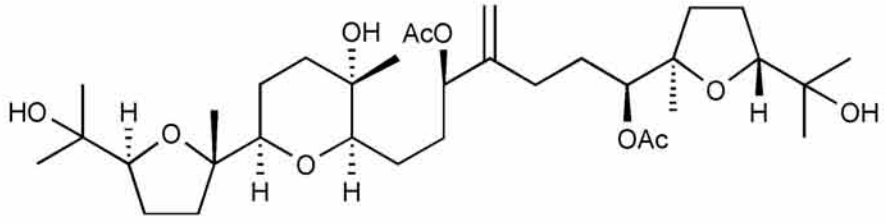
15ba



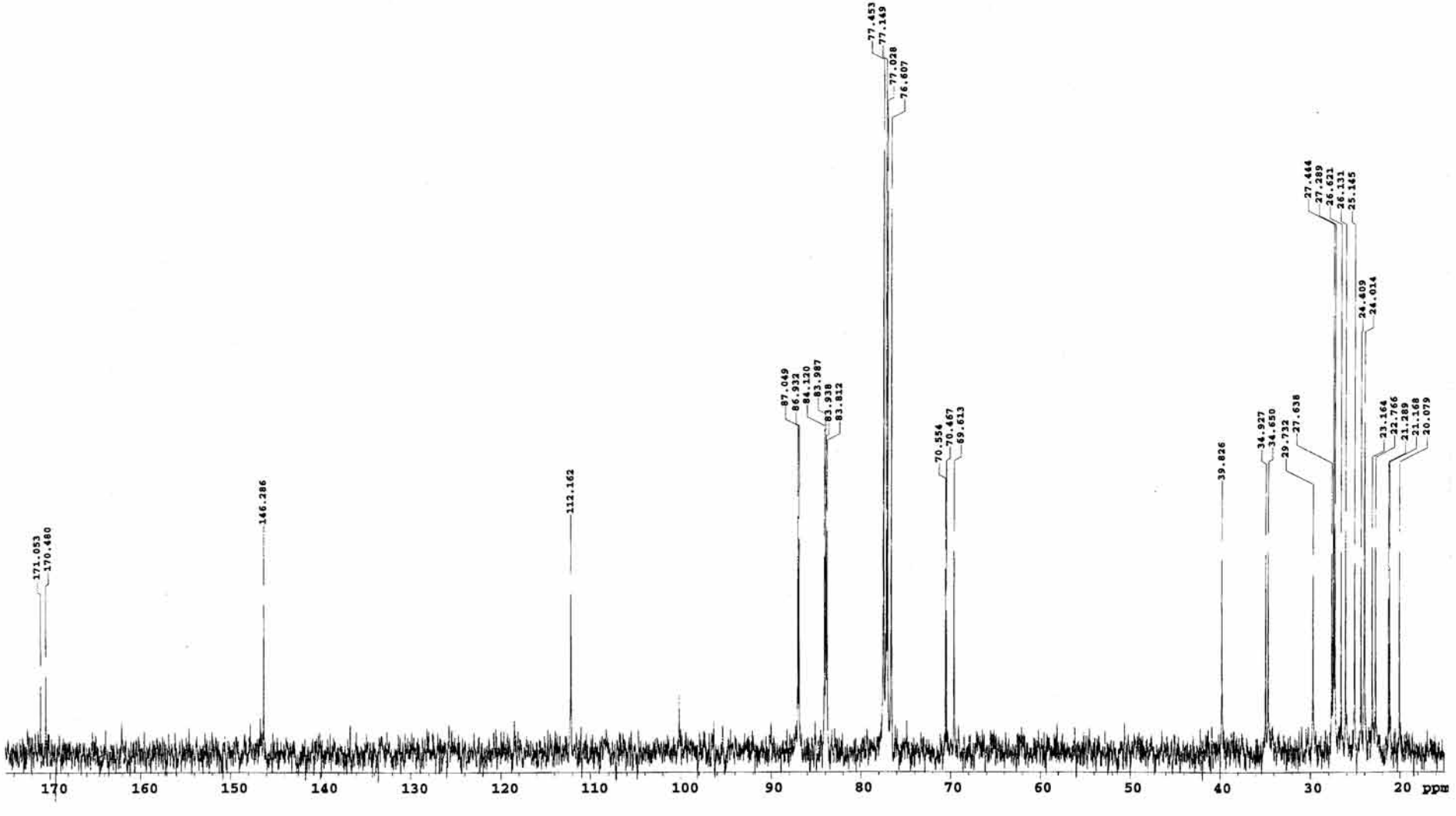
13C OBSERVE

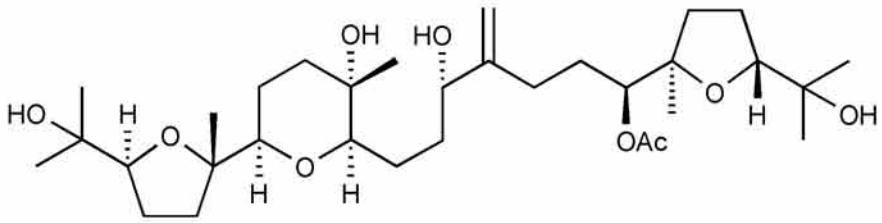
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM629m-C062806_11_13
INOVA-600 "NMR"

Pulse 54.2 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
339 repetitions
OBSERVE C13, 75.4462649 MHz
DECOUPLE H1, 300.0461196 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 30 min, 23 sec



15ba

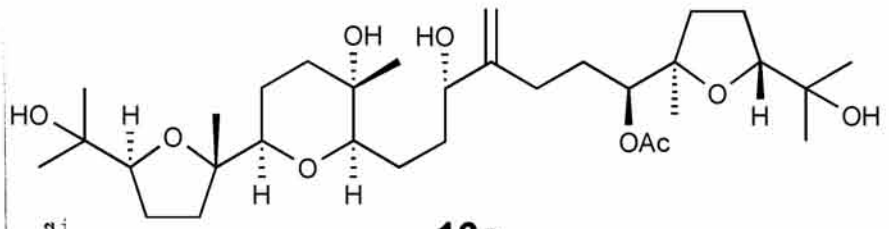




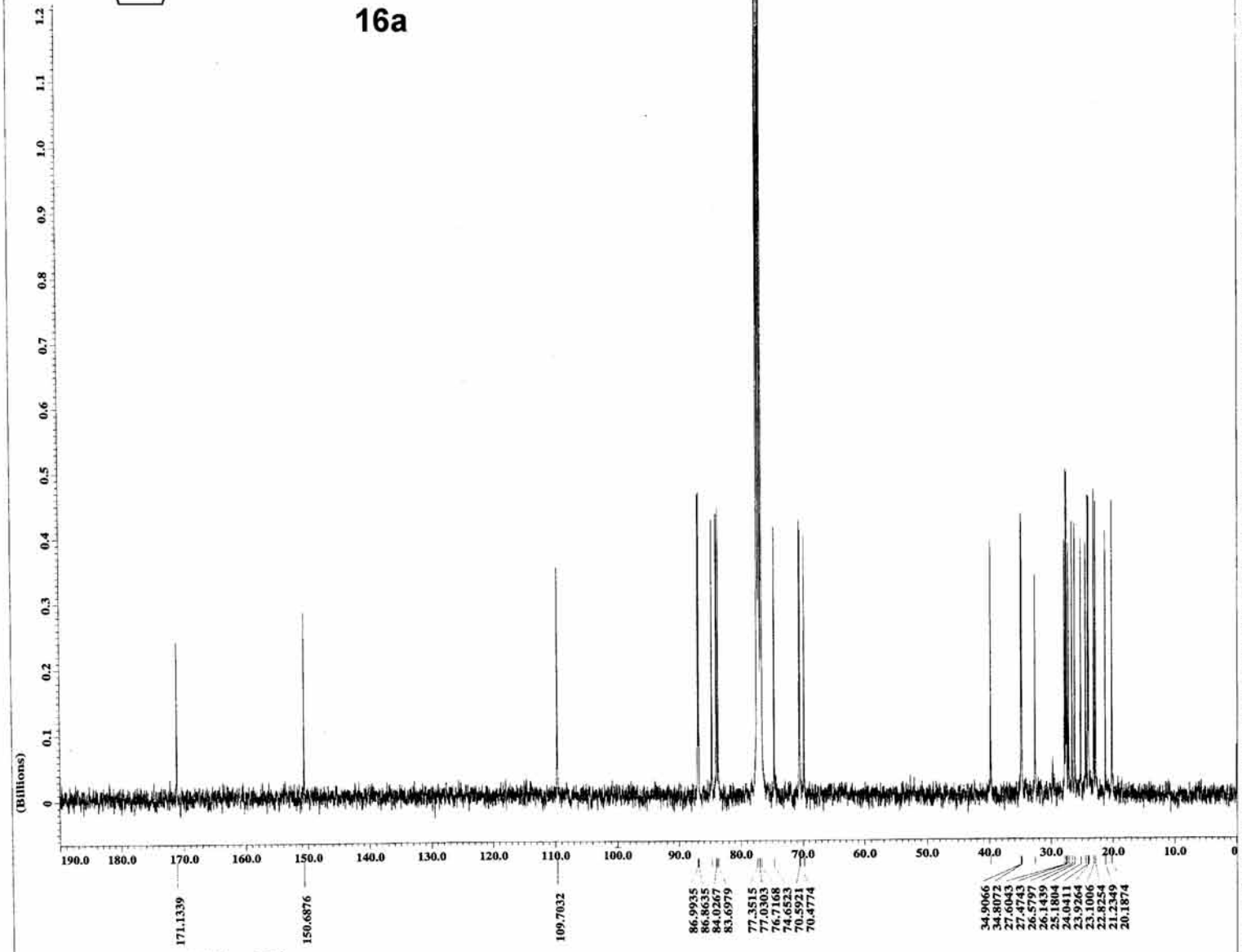
16a

JEOL

```
----- ACQUISITION PARAMETERS -----
File Name            = 1d_spectrum.2303
Author               =
Sample ID            = 7TS318z
Content              = Single Pulse Experimen
Creation Date        =  7-JUN-2008 14:25:02
Revision Date        =  7-JUN-2008 15:11:41

Spec Site            = JNM-ECP400
Spec Type            = DELTA_NMR

Data Format          = 1D COMPLEX
Dimensions           = X
Dim Title            = 1H
Dim Size             = 16384
Dim Units            = [ppm]
Scans                        = 8
Mod_return                   = 1
X_points                     = 16384
X_prescans                   = 0
X_domain                     = 1H
X_offset                     = 5[ppm]
X_freq                       = 399.7841973[MHz]
X_sweep                      = 5.99880024[kHz]
X_resolution                 = 0.36616006[Hz]
X_acq_duration               = 2.7312128[s]
Digital_filter               = FALSE
Filter_factor                = 1
Delay_of_start               = 1[s]
Actual_start_time            =  7-JUN-2008 14:24
Acq_delay                    = 0.1639[ms]
X90                          = 11.2[us]
Irr90                        = 11.2[us]
Tri90                        = 10[us]
Qua90                        = 10[us]
X90_hi                       = 11.2[us]
Irr90_hi                     = 11.2[us]
Tri90_hi                     = 10[us]
Qua90_hi                     = 10[us]
X90_lo                       = 44[us]
Irr90_lo                     = 44[us]
Tri90_lo                     = 10[us]
Qua90_lo                     = 10[us]
Spin_lock_90                 = 38[us]
Spin_lock_attn               = 12[dB]
Deut_grad_shim_90            = 10[us]
Deut_grad_shim_attn          = 63.875[dB]
Adc_card                     = 16/1MHz/20
Field_strength               = 9.389766[T]
Filter_mode                  = BUTTERWORTH
Filter_width                 = 2.99836649[kHz]
Recvr_gain                   = 19
Irr_code                     = 210
Obs_pwidth                   = 1[us]
Obs_noise                    = WADGH
Irr_pwidth                   = 44[us]
Irr_noise                    = WALTZ
Tri_pwidth                   = 1[us]
Tri_noise                    = WALTZ
Qua_pwidth                   = 1[us]
Qua_noise                    = WADGH
Solvent                      = CHLOROFORM-D
Lock_strength                = 825
Lock_level                   = 180
Lock_gain                    = 27
Lock_osc_offset              = 61.6311[kHz]
Lock_phase                   = 336.4[deg]
Lock_osc_state               = 2H OSC ON
Lock_state                   = LOCK ON
Autolock_level               = 180
Sawtooth_range               = 4
Lock_status                  = IDLE
Lock_settle_point            = 4096
Lock_achieve_point           = 0
Spin_action                  = SPIN ON
Spin_state                   = SPIN ON
Spin_status                  = SPIN ON
Spin_get                     = 14[Hz]
Spin_set                     = 15[Hz]
Spin_gas_source              = N2
Temp_action                  = TEMP OFF
Temp_state                   = TEMP OFF
Temp_status                  = TEMP OFF
Temp_get                     = 22.8[dC]
Temp_set                     = 25[dC]
Temp_comp                    = 0
Temp_delay                   = 0[s]
Temp_limit_hi                = 150[dC]
Temp_limit_lo                = -100[dC]
Temp_melting                 = -63[dC]
Temp_boiling                 = 61[dC]
Temp_ramp_step               = 0[dC]
Temp_ramp_wait               = 0[s]
Temp_ambient                 = 25[dC]
Temp_limit_hi_max            = 160[dC]
Temp_limit_hi_min            = 20[dC]
Temp_limit_md_max            = 50[dC]
Temp_limit_md_min            = -40[dC]
Temp_limit_lo_min            = -110[dC]
```

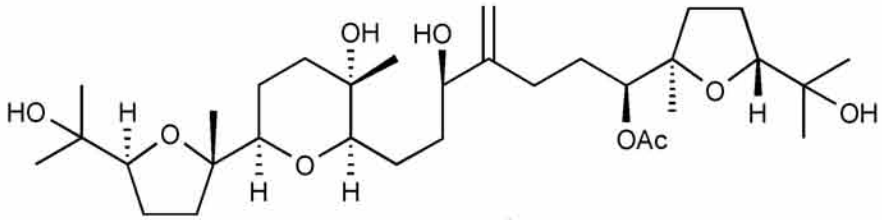


16a



JEOL

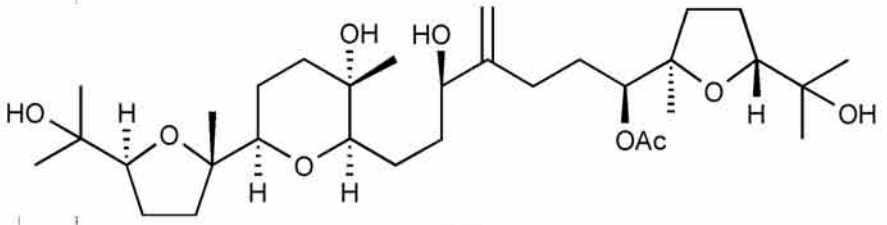
```
----- ACQUISITION PARAMETERS -----
File Name          = 1d_13c_spectrum_copy.2
Author             =
Sample ID          = 7T8318z
Content            = Single Pulse with Broa
Creation Date      =  7-JUN-2008 19:29:54
Revision Date      =  7-JUN-2008 20:17:30

Spec Site          = JNM-ECP400
Spec Type          = DELTA_NMR

Data Format        = 1D COMPLEX
Dimensions         = X
Dim Title          = 13C
Dim Size           = 32768
Dim Units          = [ppm]
Scans                  = 6920
Mod_return             = 1
X_points               = 32768
X_prescans             = 4
X_domain               = 13C
X_offset               = 100[ppm]
X_freq                 = 100.53535686[MHz]
X_sweep                = 25.18891688[kHz]
X_resolution           = 0.7687282[Hz]
Irr_domain             = 1H
Irr_offset             = 5.0[ppm]
Irr_freq               = 399.7841973[MHz]
X_acq_duration         = 1.3008896[s]
Digital_filter         = FALSE
Filter_factor          = 1
Delay_of_start         = 1[s]
Actual_start_time      =  7-JUN-2008 19:29
Acq_delay              = 39.2[us]
X90                    = 10[us]
Irr90                  = 11.2[us]
Tri90                  = 10[us]
Qua90                  = 10[us]
X90_hi                 = 10.4[us]
Irr90_hi               = 11.2[us]
Tri90_hi               = 10[us]
Qua90_hi               = 10[us]
X90_lo                 = 37.5[us]
Irr90_lo               = 44[us]
Tri90_lo               = 10[us]
Qua90_lo               = 10[us]
Spin_lock_90           = 38[us]
Spin_lock_attn         = 12[dB]
Deut_grad_shim_90      = 10[us]
Deut_grad_shim_attn    = 63.875[dB]
Adc_card               = 16/1MHz/20
Field_strength         = 9.389766[T]
Filter_mode            = BUTTERWORTH
Filter_width           = 12.56566292[kHz]
Recvr_gain             = 30
Irr_code               = 210
Obs_pwidth             = 1[us]
Obs_noise              = WALTZ
Irr_pwidth             = 44[us]
Irr_noise              = WALTZ
Tri_pwidth             = 1[us]
Tri_noise              = WALTZ
Qua_pwidth             = 1[us]
Qua_noise              = WALTZ
Solvent                = CHLOROFORM-D
Lock_strength          = 1019.0
Lock_level             = 180
Lock_gain              = 27
Lock_osc_offset        = 61.6311[kHz]
Lock_phase             = 336.4[deg]
Lock_osc_state         = 2H OSC ON
Lock_state             = LOCK ON
Autolock_level         = 180
Sawtooth_range         = 4
Lock_status            = IDLE
Lock_settle_point      = 4096
Lock_achieve_point     = 0
Spin_action            = SPIN ON
Spin_state             = SPIN ON
Spin_status            = SPIN ON
Spin_get               = 17[Hz]
Spin_set               = 15[Hz]
Spin_gas_source        = N2
Temp_action            = TEMP OFF
Temp_state             = TEMP OFF
Temp_status            = TEMP OFF
Temp_get               = 25.9[dC]
Temp_set               = 25[dC]
Temp_comp              = 0
Temp_delay             = 0[s]
Temp_limit_hi          = 150[dC]
Temp_limit_lo          = -100[dC]
Temp_melting           = -63[dC]
Temp_boiling           = 61[dC]
Temp_ramp_step         = 0[dC]
Temp_ramp_wait         = 0[s]
Temp_ambient           = 25[dC]
Temp_limit_hi_max      = 160[dC]
Temp_limit_hi_min      = 20[dC]
```



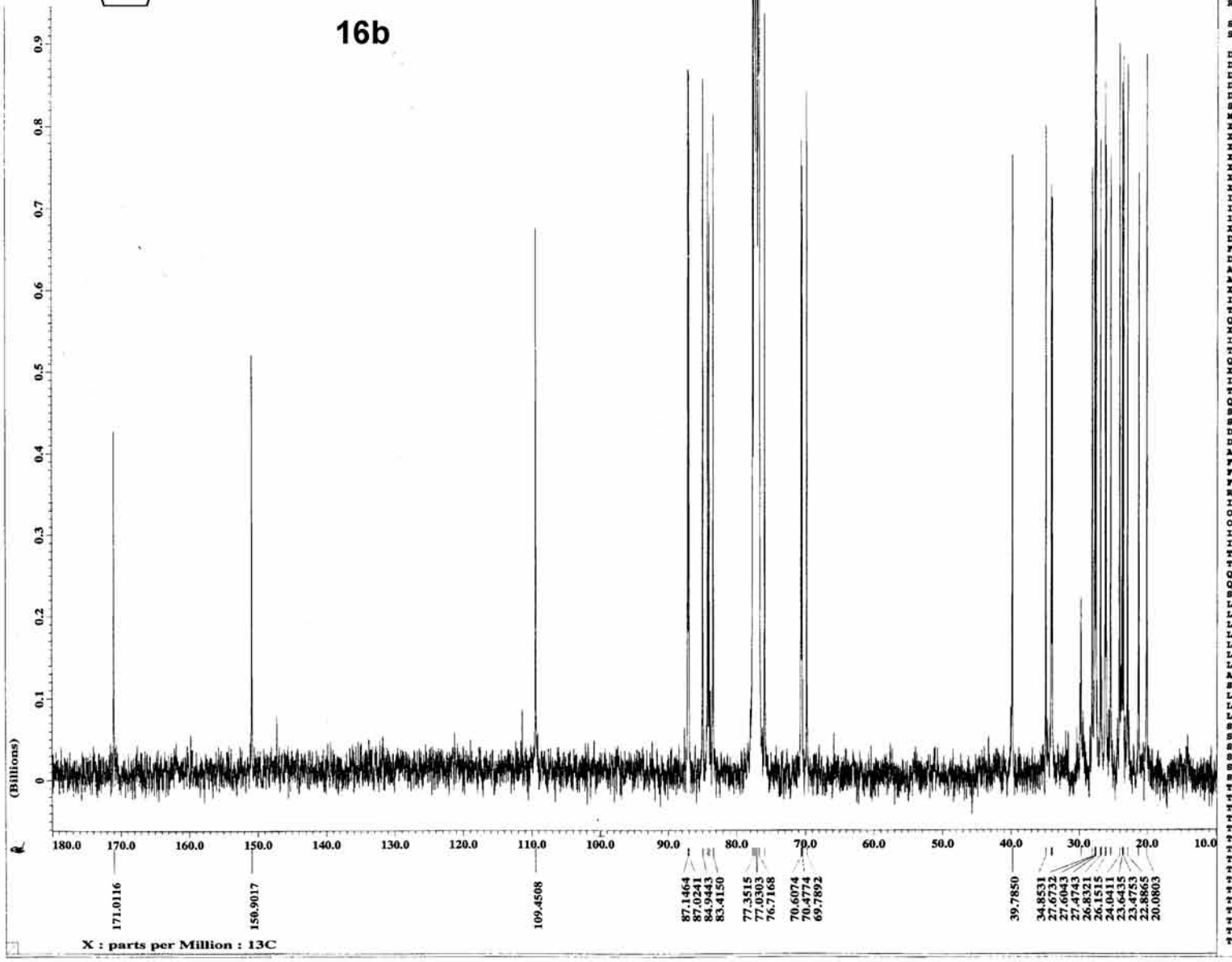
16b

JEOL

```
----- ACQUISITION PARAMETERS -----
File Name           = 1d_spectrum.2299
Author              =
Sample ID           = 7TS316x
Content             = Single Pulse Experimen
Creation Date       =  4-JUN-2008 23:19:24
Revision Date       =  5-JUN-2008 00:06:30

Spec Site           = JNM-ECP400
Spec Type           = DELTA_NMR

Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 1H
Dim Size            = 16384
Dim Units           = [ppm]
Scans                 = 8
Mod_return            = 1
X_points              = 16384
X_prescans            = 0
X_domain              = 1H
X_offset              = 5[ppm]
X_freq                = 399.7841973[MHz]
X_sweep               = 5.99880024[kHz]
X_resolution          = 0.36616006[Hz]
X_acq_duration        = 2.7312128[s]
Digital_filter        = FALSE
Filter_factor         = 1
Delay_of_start        = 1[s]
Actual_start_time     =  4-JUN-2008 23:18
Acq_delay             = 0.1639[ms]
X90                   = 11.2[us]
Irr90                 = 11.2[us]
Tri90                 = 10[us]
Qua90                 = 10[us]
X90_hi                = 11.2[us]
Irr90_hi              = 11.2[us]
Tri90_hi              = 10[us]
Qua90_hi              = 10[us]
X90_lo                = 44[us]
Irr90_lo              = 44[us]
Tri90_lo              = 10[us]
Qua90_lo              = 10[us]
Spin_lock_90          = 38[us]
Spin_lock_attn        = 12[dB]
Deut_grad_shim_90     = 10[us]
Deut_grad_shim_attn   = 63.875[dB]
Adc_card              = 16/1MHz/20
Field_strength        = 9.389766[T]
Filter_mode           = BUTTERWORTH
Filter_width          = 2.99836649[kHz]
Recvr_gain            = 18
Irr_code              = 210
Obs_pwidth            = 1[us]
Obs_noise             = WAUGH
Irr_pwidth            = 44[us]
Irr_noise             = WALTZ
Tri_pwidth            = 1[us]
Tri_noise             = WALTZ
Qua_pwidth            = 1[us]
Qua_noise             = WAUGH
Solvent               = CHLOROFORM-D
Lock_strength         = 1010
Lock_level            = 180
Lock_gain             = 28
Lock_osc_offset       = 61.6311[kHz]
Lock_phase            = 336.4[deg]
Lock_osc_state        = 2H OSC ON
Lock_state            = LOCK ON
Autolock_level        = 180
Sawtooth_range        = 4
Lock_status           = IDLE
Lock_settle_point     = 4096
Lock_achieve_point    = 0
Spin_action           = SPIN ON
Spin_state            = SPIN ON
Spin_status           = SPIN ON
Spin_get              = 14[Hz]
Spin_set              = 15[Hz]
Spin_gas_source       = N2
Temp_action           = TEMP OFF
Temp_state            = TEMP OFF
Temp_status           = TEMP OFF
Temp_get              = 23[dC]
Temp_set              = 25[dC]
Temp_comp             = 0
Temp_delay            = 0[s]
Temp_limit_hi         = 150[dC]
Temp_limit_lo         = -100[dC]
Temp_melting          = 63[dC]
Temp_boiling          = 61[dC]
Temp_ramp_step        = 0[dC]
Temp_ramp_wait        = 0[s]
Temp_ambient          = 25[dC]
Temp_limit_hi_max     = 160[dC]
Temp_limit_hi_min     = 20[dC]
Temp_limit_md_max     = 50[dC]
Temp_limit_md_min     = -40[dC]
Temp_limit_lo_min     = -110[dC]
```



16b



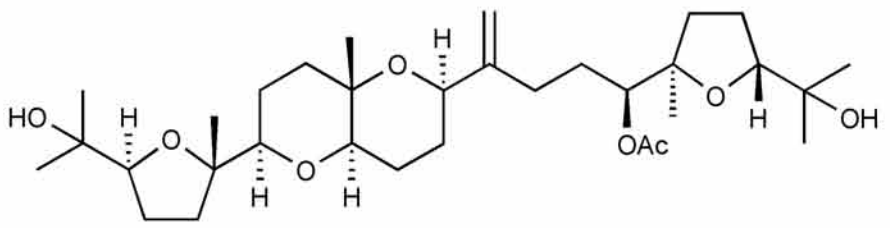
JEOL

```
----- ACQUISITION PARAMETERS -----
File Name           = 1d_13c_spectrum.432
Author              =
Sample ID           = TS316x
Content             = Single Pulse with Broa
Creation Date       =  5-JUN-2008 09:08:16
Revision Date       =  5-JUN-2008 10:56:13

Spec Site           = JNM-ECP400
Spec Type           = DELTA_NMR

Data Format         = 1D COMPLEX
Dimensions          = X
Dim Title           = 13C
Dim Size            = 32768
Dim Units           = [ppm]
Scans                   = 15000
Mod_return              = 1
X_points                = 32768
X_prescans              = 4
X_domain                = 13C
X_offset                = 100[ppm]
X_freq                  = 100.53535686[MHz]
X_sweep                 = 25.18891688[kHz]
X_resolution            = 0.7687282[Hz]
Irr_domain              = 1H
Irr_offset              = 5.0[ppm]
Irr_freq                = 399.7841973[MHz]
X_acq_duration          = 1.3008896[s]
Digital_filter          = FALSE
Filter_factor           = 1
Delay_of_start          = 1[s]
Actual_start_time       =  4-JUN-2008 23:32
Acq_delay               = 39.2[us]
X90                     = 10[us]
Irr90                   = 11.2[us]
Tri90                   = 10[us]
Qua90                   = 10[us]
X90_hi                  = 10.4[us]
Irr90_hi                = 11.2[us]
Tri90_hi                = 10[us]
Qua90_hi                = 10[us]
X90_lo                  = 37.5[us]
Irr90_lo                = 44[us]
Tri90_lo                = 10[us]
Qua90_lo                = 10[us]
Spin_lock_90            = 38[us]
Spin_lock_attn          = 12[dB]
Deut_grad_shim_90       = 10[us]
Deut_grad_shim_attn     = 63.875[dB]
Adc_card                = 16/18Hz/20
Field_strength          = 9.389766[T]
Filter_mode             = BUTTERWORTH
Filter_width            = 12.56566292[kHz]
Recvr_gain              = 30
Irr_code                = 210
Obs_pwidth              = 1[us]
Obs_noise               = WAUGH
Irr_pwidth              = 44[us]
Irr_noise               = WALTZ
Tri_pwidth              = 1[us]
Tri_noise               = WALTZ
Qua_pwidth              = 1[us]
Qua_noise               = WAUGH
Solvent                 = CHLOROFORM-D
Lock_strength           = 1220
Lock_level              = 180
Lock_gain               = 28
Lock_osc_offset         = 61.6311[kHz]
Lock_phase              = 336.4[deg]
Lock_osc_state          = 2H OSC ON
Lock_state              = LOCK ON
Autolock_level          = 180
Sawtooth_range          = 4
Lock_status             = IDLE
Lock_settle_point       = 4096
Lock_achieve_point      = 0
Spin_action             = SPIN ON
Spin_state              = SPIN ON
Spin_status             = SPIN ON
Spin_get                = 15[Hz]
Spin_set                = 15[Hz]
Spin_gas_source         = N2
Temp_action             = TEMP OFF
Temp_state              = TEMP OFF
Temp_status             = TEMP OFF
Temp_get                = 25.9[dC]
Temp_set                = 25[dC]
Temp_comp               = 0
Temp_delay              = 0[s]
Temp_limit_hi           = 150[dC]
Temp_limit_lo           = -100[dC]
Temp_melting            = -63[dC]
Temp_boiling            = 61[dC]
Temp_ramp_step          = 0[dC]
Temp_ramp_wait          = 0[s]
Temp_ambient            = 25[dC]
Temp_limit_hi_max       = 160[dC]
Temp_limit_hi_min       = 20[dC]
```

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM632m-H063006_23_24
INOVA-600 "NMR"

Relax. delay 1.000 sec
Pulse 38.7 degrees
Acq. time 4.000 sec
Width 4504.5 Hz
511 repetitions
OBSERVE H1, 300.0445660 MHz
DATA PROCESSING
FT size 65536
Total time 1 hr, 23 min, 28 sec

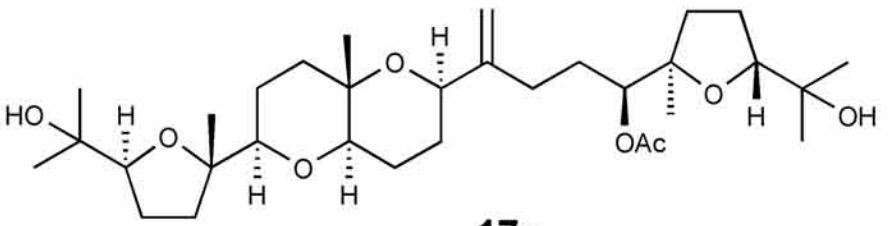


17a

13C OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM640mm-C080206_15_58
INOVA-600 "MMR"

Pulse 54.2 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
8002 repetitions
OBSERVE C13, 75.4462634 MHz
DECOUPLE H1, 300.0461196 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 5 hr, 3 min, 58 sec

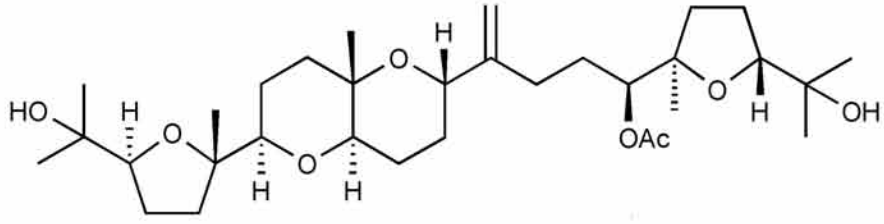


17a

3YM639c

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM639c-H071506_17_13
INOVA-600 "NMR"

Relax. delay 0.500 sec
Pulse 31.3 degrees
Acq. time 3.555 sec
Width 4500.5 Hz
16 repetitions
OBSERVE H1, 300.0738798 MHz
DATA PROCESSING
FT size 32768
Total time 1 min, 5 sec

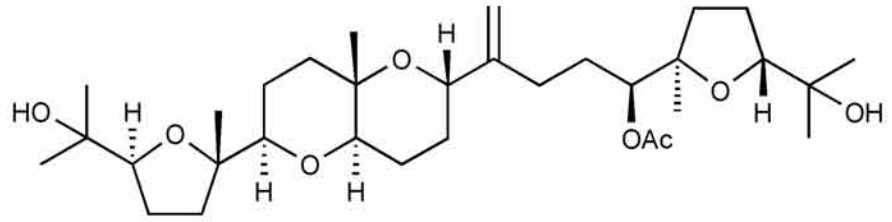


17b

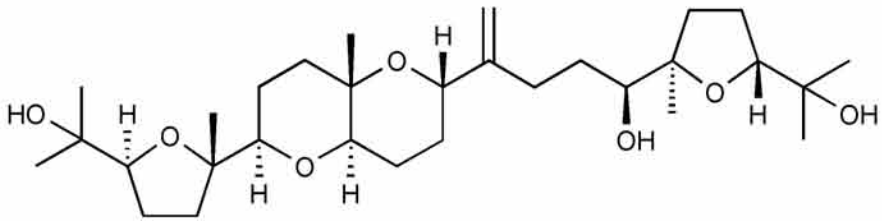
3YM639m

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: 3YM639m-C082206_17_30
INOVA-600 "NMR"

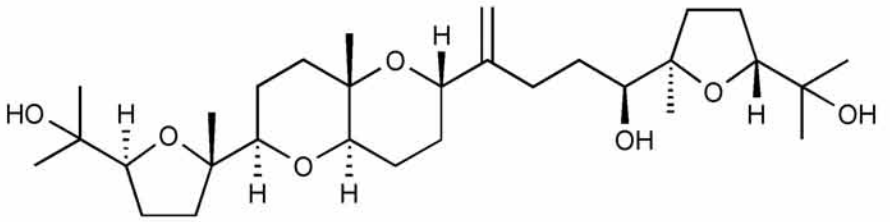
Pulse 54.2 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
2062 repetitions
OBSERVE C13, 75.4462637 MHz
DECOUPLE H1, 300.0461196 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 2 hr, 31 min, 59 sec



17b



14-epi-pseudodehydrothyrsiferol (19)



14-epi-pseudodehydrothyrsiferol (19)