Total Synthesis of Neolaulimalide and Isolaulimalide

Supporting Information

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Experimental part

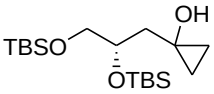
General

All reactions were carried out in oven-dried glassware under an argon atmosphere, unless otherwise stated. Anhydrous toluene was distilled from sodium/benzophenone under argon. Anhydrous CH_2Cl_2 and DMF (*N,N*-dimethylformamide) were distilled from CaH_2 under argon or reduced pressure, respectively. Anhydrous THF (tetrahydrofurane) was purchased from Acros (99.85%, water < 50 ppm). All other solvents were HPLC grade. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with E. Merck silica gel 60-F254 plates. Flash column chromatography was performed with Merck silica gel (0.04-0.063mm, 240-400 mesh) under pressure. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. NMR spectra were recorded on either Bruker Avance DRX 400 or DRX 600 MHz spectrometer. Unless otherwise stated, all NMR spectra were measured in $CDCl_3$ solutions and referenced to the residual $CHCl_3$ signal (^{1}H, δ = 7.26 ppm; ^{13}C, δ =77.16 ppm). All ^{1}H and ^{13}C shifts are given in ppm (s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet; b = broad signal). Assignments of proton resonances were confirmed, when possible, by correlated spectroscopy. Optical rotations were measured on a P 341 Perkin- Elmer polarimeter. Mass spectra were measured on a Micro mass, trio 200 Fisions Instruments. High resolution mass spectra (HRMS) were performed with a Finnigan MAT 8230 with a resolution of 10000.

Procedures:

Synthesis of Fragment **5:**

(S)-1-(2,3-bis(tert-butyldimethylsilyloxy)propyl)cyclopropanol (**8**):



8

To a stirred solution of TBS protected diol **7** (21.20 g, 56.3 mmol) in THF (170 mL) at 10 °C was added Ti(O*i*-Pr)$_4$ (4.80 g, 61.7 mmol). A solution of EtMgBr (56.3 mL, 3 M in Et_2O, 168.9 mmol) was added dropwise over the period of 4 h. After the addition the black solution was stirred for another 1 h at the same temperature. The solvent was removed under vacuum and the oily, black residue was diluted with CH_2Cl_2 (250 mL) and cooled to 0 °C. The solution was quenched with aq. sat. NH_4Cl solution (35 mL). The resulting mixture was filtered and the precipitate was washed with CH_2Cl_2 (5 x 60 mL). The filtrate was washed with aq. sat. $NaHCO_3$ solution, the organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. Crude cyclopropanol **8** (18.9 g) was obtained as a yellow, viscous oil and was used in the next step without further purification. An analytical sample was obtained by column chromatography (silica gel, hexane:EtOAc = 20:1) as a clear, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ=4.02-3.95 (m, 1H), 3.70-3.61 (m, 2 H), 2.00 (ddd, J = 14.7 Hz, J = 5.6 Hz, J = 1.0 Hz, 2H), 1.68 (dd, J = 14.6 Hz, J = 5.3 Hz, 1H), 0.90 (s, 9H), 0.89 (s, 9H), 0.79-0.68 (m, 2H), 0.52-0.46 (m, 1H), 0.43-0.37 (m, 1H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ=73.6 (CH), 67.1 (CH_2), 54.0 (C_q), 42.2 (CH_2), 26.0 (3 x CH_3), 25.9 (3 x CH_3), 18.4 (C_q), 18.1 (C_q), 13.6 (CH_2), 12.6 (CH_2), -4.3 (CH_3), -4.7 (CH_3), -5.2 (CH_3), -5.3 (CH_3).

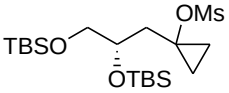
IR [cm^{-1}]: 3443, 2956, 2930, 2886, 2858, 1463, 1257, 1119, 837, 778.

HRMS(EI) calcd. for $C_{18}H_{40}O_3Si_2$: 360.2516, found: 360.2523.

R_f = 0.66 (silica gel, hexane/EtOAc 10:1)

$[\alpha]_D^{20}$ = +13.7 (*c* = 1.15, CH_2Cl_2)

(S)-2-(tert-butyldimethylsilyloxy)-3-(1-(methylsulfonyloxy)cyclopropyl)propyl methanesulfonate (**29**):



29

To a stirred solution of crude **8** (18.8 g) in absolute Et_2O (80 mL) at 0 °C was added Et_3N (1.99 g, 197.1 mol). Methanesulfonyl chloride (11.28 g, 98.5 mmol) was added dropwise over a period of 30 min and the reaction was stirred for another 45 min at the same temperature. The reaction was quenched by adding water (80 mL) and the aqueous layer was extracted 3 times with Et_2O. The organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. Crude mesylate **29** (21.4 g) was obtained

as a yellow, viscous oil and was used in the next step without further purification. An analytical sample was obtained by column chromatography (silica gel, hexane: EtOAc = 15:1) as a clear, colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ=4.07-4.00 (m, 1H), 3.63 (dd, J = 10.1 Hz, J = 4.3 Hz, 1H), 3.50 (dd, J = 10.1 Hz, J = 6.0 Hz, 1H), 2.99 (s, 3H), 2.42 (dd, J = 15.2 Hz, J = 4.0 Hz, 1H), 1.67-1.60 (m, 1H), 1.34-1.25 (m, 1H), 1.24-1.15 (m, 1H), 0.93 – 0.79 (m, 19H), 0.78-0.71 (m, 1H), 0.09 (s, 6H), 0.05 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=70.7 (CH), 67.2 (CH_2), 64.4 (C_q), 40.5 (CH_2), 40.1 CH_3), 26.1 (3 x CH_3), 26.0 (3x CH_3), 18.5 (C_q), 18.1 (C_q), 12.7 (CH_2), 11.4 (CH_2), -4.3 (CH_3), -4.5 (CH_3), -5.2 (2 x CH_3).

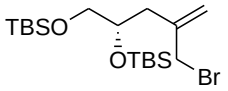
IR [cm^{-1}]: 2930, 2857, 1472, 1361, 1256, 1165, 836, 776, 668.

HRMS(EI) calcd. for $C_{19}H_{42}O_5SSi_2$: 438.2291, found: 438.2281.

R_f = 0.26 (silica gel, hexane/EtOAc 9:1)

$[\alpha]_D^{20}$ = -5.0 (*c* = 1.10, CH_2Cl_2)

(S)-5-(2-(bromomethyl)allyl)-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane (**9**):



9

To a stirred solution of crude Mesylate **29** (21.4 g) in CH_2Cl_2 (200 mL) was $MgBr_2 \cdot Et_2O$ (40.7 g, 157.6 mmol) in one portion. The reaction mixture was refluxed for 3 h, then cooled to 0 °C and quenched with H_2O (150 mL). The aqueous layer was extracted 3 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained yellow oil was purified by column chromatography (silica gel, hexane: EtOAc = 15:1). Yielding **9** as clear, colorless oil (17.5 g, 41.3 mmol, 73% over three steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.25 (br s, 1H), 5.02 (br s, 1H), 4.07 (d, J = 9.9 Hz, 1H), 4.01 (d, J = 9.7 Hz, 1H), 3.86 – 3.78 (m, 1H), 3.52 (dd, J = 10.0 Hz, J = 5.1 Hz, 1H), 3.41 (dd, J = 10.0 Hz, J = 6.7 Hz, 1H), 1H), 2.57 (dd, J = 14.1 Hz, J = 4.7 Hz, 1H), 2.28 (dd, J = 14.1 Hz, J = 6.7 Hz, 1H), 0.90 – 0.87 (m, 18 H), 0.07 – 0.04 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=142.8 (C_q), 118.2 (CH_2), 72.3 (CH), 66.8 (CH_2), 38.2 (CH_2), 37.8 (CH_2), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 18.5 (C_q), 18.2 (C_q), -4.3 (CH_3), -4.5 (CH_3), -5.2 (2 x CH_3).

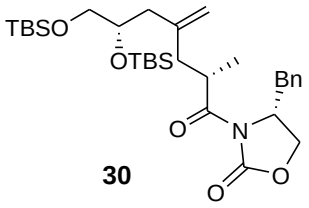
IR [cm^{-1}]: 2956, 2930, 2858, 1472, 1256, 1117, 1083, 836, 811, 776.

HRMS(EI) calcd. for $C_{18}H_{39}O_2BrSi_2$: 422.1672, found: 422.1656.

R_f = 0.9 (silica gel, hexane/EtOAc 20:1)

$[\alpha]_D^{20}$ = +0.9 (*c* = 1.50, CH_2Cl_2)

(R)-4-benzyl-3-((2S,6S)-6,7-bis(tert-butyldimethylsilyloxy)-2-methyl-4-methyleneheptanoyl)oxazolidin-2-one (**30**):



30

To a stirred solution of Evans' N-propionyl-oxazolidinone **10** (9.07 g, 38.9 mmol) in 150 ml THF was added NaHMDS (44.74 mL, 44.74 mmol,1 M soulution in THF) at -78 °C in

30 min. The solution was stirred for 15 min at the same temperature before allylbromide **9** (8.21 g, 19.45 mmol) was added. The reaction was allowed to reach -30 °C and stirred for 8 h at this temperature. The reaction was warmed to 0 °C and quenched by adding 150 ml of aq. sat. NH_4Cl. The aqueous layer was extracted 3 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 20:1 to 6:1). Yielding **28** as clear, colorless oil (6.82 g, 11.85 mmol, 61%) and unconsumed **9** (1.73 g, 4.085 mmol, 21%)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.25-7.26 (m, 3H), 7.23-7.19 (m, 2H), 4.88 (br s, 1H), 4.86 (br s, 1H), 4.71-4.64 (m, 1H), 4.20-4.12 (m, 2H), 4.03 (dt, J = 14.1 Hz, J = 7.0 Hz, 1H), 3.86-3.79 (m, 1H), 3.52 (dd, J = 10.1 Hz, J = 5.3 Hz, 1H), 3.46 (dd, J = 10.0 Hz, J = 5.7 Hz, 1H), 3.29 (dd, J = 13.3 Hz, J = 3.4 Hz, 1H), 2.67 (dd, J = 13.4 Hz, J = 9.9 Hz, 1H), 2.58 (dd, J = 14.4 Hz, J = 7.6 Hz, 1H), 2.34 (dd, J = 13.9 Hz, J = 4.8 Hz, 1H), 2.20 – 2.11 (m, 2 H), 1.18 (d, J = 6.8 Hz, 3H), 0.89 (br s, 9H), 0.88 (br s, 9H), 0.06 (br s, 3H), 0.05 (br s, 3H), 0.04 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=177.1 (C_q), 153.2 (C_q), 143.9 (C_q), 135.6 (C_q), 129.6 (2 x CH), 129.0 (2 x CH), 127.4 (CH), 114.3 (CH_2), 72.3 (CH), 67.3 (CH_2), 66.1 (CH_2), 55.6 (CH), 41.1 (CH_2), 40.4 (CH_2), 38.2 (CH_2), 35.9 (CH), 26.2 (3 x CH_3), 26.1 (3 x CH_3), 18.5 (C_q), 18.3 (C_q), 17.4 (CH_3), -4.1 (CH_3), -4.5 (CH_3), -5.2 (CH_3).

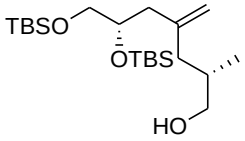
IR [cm^{-1}]: 2955, 2929, 2857, 1784, 1386, 1251, 1103, 835, 776.

HRMS(EI) calcd. for $C_{31}H_{53}NO_5Si_2$: 575.3462, found: 575.3457.

R_f = 0.61 (silica gel, hexane/EtOAc 4:1)

$[\alpha]_D^{20}$ = 25.1 (*c* = 1.15, CH_2Cl_2)

(2S,6S)-6,7-bis(tert-butyldimethylsilyloxy)-2-methyl-4-methyleneheptan-1-ol (**11**):



11

Compound **30** (6.80 g, 11.81 mmol) was dissolved in 150 ml Et_2O, H_2O (1eq) was added and the mixture was cooled to 0 °C. $LiBH_4$ (334 mg, 15.35 mmol, 1.3 eq.) was added portionwise in 30 min and the reaction was stirred for another 5 h at the same temperature. The reaction was quenched by adding 150 mL 0.1 N aq. NaOH. The aqueous layer was extracted 3 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 7:1). Yielding **11** as viscous, colorless oil (4.62 g, 11.47 mmol, 97%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=4.84 (br s, 1H), 4.82 (br s, 1H), 3.81 – 3.74 (m, 1H), 3.55 – 3.49 (m, 2H), 2.48 – 3.40 (m, 2H), 2.32 (dd, J = 13.8 Hz, J = 4.9 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.07 (dd, J = 13.9 Hz, J = 7.1 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.33 (t, J = 5.7 Hz, 1H, OH), 0.92 – 0.86 (m, 21H), 0.06 – 0.03 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=145.0 (C_q), 114.0 (CH_2), 72.4 (CH), 68.5 (CH_2), 67.3 (CH_2), 40.9 (CH_2), 40.8 (CH_2), 34.0 (CH), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 18.5 (C_q), 18.3 (C_q), 16.8 (CH_3), -4.2 (CH_3), -4.5 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

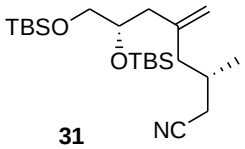
IR [cm^{-1}]: 2930, 2859, 1739, 1683, 1652, 1538, 1471, 1464, 1257, 1121, 834, 671.

HRMS(EI) calcd. for $C_{21}H_{46}O_3Si_2$: 402.2985, found: 402.2974.

R_f = 0.60 (silica gel, hexane/EtOAc = 4:1)

$[\alpha]_D^{20}$ = -1.2 (*c* = 1.05, CH_2Cl_2)

(3S,7S)-7,8-bis(tert-butyldimethylsilyloxy)-3-methyl-5-methyleneoctanenitrile (**31**):



31

Alcohol **11** (300 mg, 0.746 mmol) was dissolved in Et_2O (10 mL) and cooled to 0 °C. PPh_3 (401 mg, 1.490 mmol) and DIAD (301 mg, 1.490 mmol) were added followed by acetone cyanohydrin (137 µL, 128 mg, 1.490 mmol). The yellow reaction mixture was stirred at 0 °C for 1 h and allowed to warm to rt over night. The reaction mixture was flashed threw a short pad of silica gel and the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, hexane:ethylacetate = 20:1). Yielding **31** as slightly yellow oil 288 mg (0.699mmol, 94%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=4.90 (br s, 1H), 4.85 (br s, 1H), 3.79 – 3.72 (m, 1H), 3.52 (dd, J = 10.0 Hz, J = 5.2 Hz, 1H), 3.41 (dd, J = 10.0 Hz, J = 6.4 Hz, 1H), 2.38 – 2.27 (m, 2 H), 2.21 (dd, J = 16.8 Hz, J = 6.7 Hz, 1H), 2.14 – 1.99 (m, 4H), 1.08 (d, J = 6.3 Hz, 3H), 0.89 (br s, 9H), 0.87 (br s, 9H), 0.06 – 0.04 (m, 9H), 0.04 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=143.6 (C_q), 118.8 (C_q), 115.1 (CH_2), 72.5 (CH), 67.0 (CH_2), 43.5 (CH_2), 40.4 (CH_2), 28.7 (CH), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 24.2 (CH_2), 19.6 (CH_3), 18.5 (C_q), 18.3 (C_q), -4.2 (CH_3), -4.6 (CH_3), -5.2 (2 x CH_3).

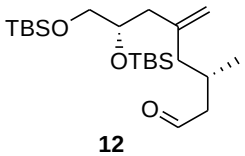
IR [cm^{-1}]: 2956, 2930, 2858, 1733, 1557, 1505, 1472, 1464, 1257, 1115, 835, 777.

HRMS(EI) calcd. for $C_{22}H_{45}NO_2Si_2$: 411.2989, found: 411.2986.

R_f = 0.51 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = +3.2 (*c* = 1.45, CH_2Cl_2)

(3S,7S)-7,8-bis(tert-butyldimethylsilyloxy)-3-methyl-5-methyleneoctanal (**12**):



12

Cyanide **31** (2.63 g, 6.387 mmol) was dissolved in DCM (65 mL) and cooled to -78 °C. DIBAL (6.39 mL, 9.581 mmol, 1.5 M in toluene) was added drop wise over 15 min and the reaction was stirred for 45 min at the same temperature before it was allowed to warm to rt. The reaction was stirred for 5 h at rt and then cooled again to -78 °C. EtOAc (2 mL) was added and the reaction was allowed to warm to 0 °C before it was pored into a 1 L flask containing of sat. aq. KNa-tartrate (200 mL) and EtOAc (200 mL). The cloudy mixture was stirred vigorous for 6 h. The aqueous layer was extracted 3 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane: EtOAc = 10:1). Yielding **12** as colorless oil 2.43 g (5.856 mmol, 92%)

^{1}H NMR (400 MHz, $CDCl_3$) δ=9.75 (t, J = 2.0 Hz, 1H), 4.87 (br s, 1H), 4.80 (br s, 1H), 3.80 – 3.73 (m, 1H), 3.52 (dd, J = 10.0 Hz, J = 5.4 Hz, 1H), 3.42 (dd, J = 10.0 Hz, J = 6.2 Hz, 1H), 2.47 – 2.40 (m, 1H), 2.31 (ddd, J = 14.0 Hz, J = 4.9 Hz, J = 0.8 Hz, 1H), 2.27 – 2.16 (m, 2H), 2.09 – 2.01 (m, 2 H), 1.98 (dd, J = 13.9 Hz, J = 7.1 Hz, 1H), 0.95 (d, J = 6.3 Hz, 3H), 0.89 (br s, 9H), 0.87 (br s, 9H), 0.05 – 0.04 (m, 9H), 0.03 (br s, 3H) .

^{13}C NMR (100 MHz, $CDCl_3$) δ=202.7 (C_q), 144.4 (C_q), 114.7 (CH_2), 72.5 (CH), 67.2 (CH_2), 50.9 (CH_2), 44.4 (CH_2), 40.6 (CH_2), 26.5 (CH), 26.1 (3 x CH_3), 26.0 (3 x CH_3), 20.1 (CH_3), 18.5 (C_q), 18.3 (C_q), -4.2 (CH_3), -4.5 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

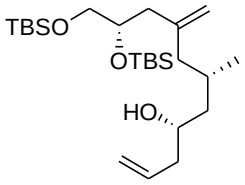
IR [cm^{-1}]: 2956, 2930, 2858, 1729, 1472, 1361, 1256, 1119, 1006, 836, 776.

HRMS(EI) calcd. for $C_{22}H_{46}O_3Si_2$: 414.2985, found:. 414.2988

R_f = 0.72 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = -6.8 (*c* = 1.05, CH_2Cl_2)

(4S,6S,10S)-10,11-bis(tert-butyldimethylsilyloxy)-6-methyl-8-methyleneundec-1-en-4-ol (**13**):



13

Aldehyd **12** (2.40 g, 5.786 mmol) was dissolved in Et_2O (70 mL) and cooled to -100 °C. A solution of (-)-Ipc-allylborane (10.49 mL, 8.390 mmol, 0.8 M solution in pentane) was added precooled (-78 °C) via a canula in 20 min. The reaction was stirred at -100 °C for 2 h and quenched by adding MeOH (4 mL). The reaction was warmed to rt and the solvent was removed under vacuum. The residue was taken up in a 1/1 mixture of H_2O/THF (120 mL), $NaBO_3 \cdot 4H_2O$ (2.23 g, 14.465 mmol) was added and the mixture was stirred over night. The solution was diluted with brine (100 mL) and extracted 3 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane: EtOAc = 40:1). Yielding **13** as colorless oil (2.43 g, 5.509 mmol, 95%, dr = 16:1 detained by HPLC).

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.89 – 5.77 (m, 1H), 5.17 – 5.13 (m, 1H), 5.13 – 5.10 (m, 1H), 4.82 (br s, 1H), 4.78 (br s, 1H), 3.81 – 3.71 (m, 2H), 3.51 (dd, J = 10.0 Hz, J = 5.6 Hz, 1H), 3.43 (dd, J = 9.9 Hz, J = 5.8 Hz, 1H), 2.32 – 2.23 (m, 2H), 2.20 – 2.11 (m, 1H), 2.08 – 1. 99 (m, 2H), 1.92 – 1.84 (m, 2H), 1.54 – 1.46 (m, 1H), 1.44 (d, J = 4.2 Hz, 1H, OH), 1.27 – 1.11 (m, 1H), 0.90 – 0.88 (m, 12H), 0.87 (br s, 9H), 0.05 – 0.04 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=144.9 (C_q), 135.0 (CH), 118.2 (CH_2), 113.9 (CH_2), 72.3 (CH), 68.6 (CH), 67.4 (CH_2), 45.1 (CH_2), 44.4 (CH_2), 43.0 (CH_2), 40.9 (CH_2), 27.5 (CH), 26.2 (3 x CH_3), 26.1 (3 x CH_3), 19.4 (CH_3), 18.5 (C_q), 18.3 (C_q), -4.1 (CH_3), -4.5 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

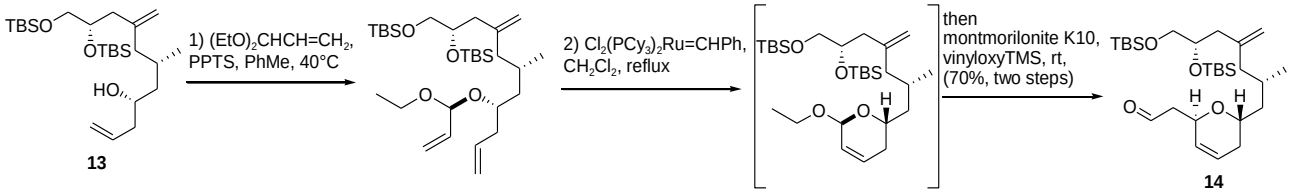
IR [cm^{-1}]: 3368, 2929, 2858, 1643, 1472, 1361, 1256, 1117, 991, 836, 776.

HRMS(EI) calcd. for $C_{25}H_{52}O_3Si_2$: 456.3455, found: 456.3451.

R_f = 0.4 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = +9.5 (*c* = 1.05, CH_2Cl_2)

2-((2R,6R)-6-((2S,6S)-6,7-bis(tert-butyldimethylsilyloxy)-2-methyl-4-methyleneheptyl)-5,6-dihydro-2H-pyran-2-yl)acetaldehyde (**14**):



Acrolein diethyl acetal (6 mL) and a catalytic amount of PPTS were added to homoallylalcohol **13** (2.41 g, 5.275 mmol) in toluene (75 mL). The mixture was rotated on a rotary evaporator at 80 mbar and 40 °C to remove the liberated EtOH. The volume of the reaction was kept constant by adding toluene occasionally. After 90 min the reaction was concentrated to about 5 mL and purified by column chromatography (silica gel, hexane:EtOAc = 50:1 + 1% Et_3N). The obtained mixed acetal was used immediately for the next step.

Grubbs' catalyst I (224 mg, 0.264 mmol) was added in one portion to the mixed acetal dissolved in degased CH_2Cl_2 (300 mL) at 40 °C and the reaction was refluxed over night. The reaction was cooled to rt and air was bubbled threw the reaction for 10 min. The solvent was reduced to 30 mL and vinyloxytrimethylsilane (3.07 g, 26.375 mmol) and montmorillonite K10 (2.5 g) were added. After sirring for 10 min the reaction was filtered threw a short pad of silica gel and concentrated in vacuum. The obtained brown oil was purified by column chromatography (silica gel, hexane:EtOAc = 20:1). Yielding **14** as colorless oil (1.89 g, 3.699 mmol, 70%, over two steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ=9.82 – 9.79 (m, 1H), 5.90 – 5.85 (m, 1H), 5.72 – 5.76 (m, 1H), 4.82 (br s, 1H), 4.80 – 4.71 (m, 2H), 3.80 – 3.71 (m, 2H), 3.49 (dd, J = 10.0 Hz, J = 5.6 Hz, 1H), 3.44 (dd, J = 10.0 Hz, J = 5.6 Hz, 1H), 2.73 (ddd, J = 16.2 Hz, J = 8.9 Hz, J = 3.0 Hz, 1H), 2.53 (ddd, J = 16.2 Hz, J = 4.8 Hz, J = 1.8 Hz, 1H), 2.25 (dd, J = 13.8 Hz, J = 5.6 Hz, 1H), 3.09 – 1.81 (m, 6H), 1.69 – 1.60 (m, 1H), 1.15 – 1.06 (m, 1H), 0.90 – 0.83 (m, 21H), 0.05 (br s, 3H), 0.04 – 0.03 (m, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=201.1 (CH), 144.9 (C_q), 128.0 (CH), 125.8 (CH), 113.8 (CH_2), 72.4 (CH), 68.0 (CH), 67.5 (CH_2), 65.7 (CH_2), 48.1 (CH_2), 45.1 (CH_2), 42.4, (CH_2), 41.0 (CH_2), 31.1 (CH_2), 26.9 (CH), 26.2 (3 x CH_3), 26.1 (3 x CH_3), 19.4 (CH_3), 18.5 (C_q), 18.3 (C_q), -4.2 (CH_3), -4.5 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

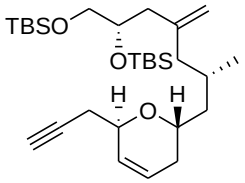
IR [cm^{-1}]: 2928, 1730, 1472, 1361, 1256, 1097, 835, 775.

HRMS(EI) calcd. for $C_{28}H_{54}O_4Si_2$: 510.3561, found:. 510.3556.

R_f= 0.40 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = -32.0 (*c* = 1.12, CH_2Cl_2)

(S)-2,2,3,3,8,8,9,9-octamethyl-5-((S)-4-methyl-2-methylene-5-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)pentyl)-4,7-dioxa-3,8-disiladecane (**16**):



16

To a solution of aldehyde **13** (1.87 g, 3.660 mmol) in MeOH (10 mL) was added K_2CO_3 (1.01 g, 7.320 mmol) and Bestman-Ohira reagent (879 mg, 4.575 mmol). After stirring for 4 h at rt the reaction was quenched with sat. aq. $NaHCO_3$ solution (10 mL), diluted with H_2O (10 mL) and extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 30:1). Yielding **16** as colorless oil (1.39 g, 2.737 mmol, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ= 5.93 – 5.82 (m , 2H), 4.81 (br s, 1H), 4.78 (br s, 1H), 4.36 – 4.28 (m, 1H), 3.85 – 3.73 (m, 2H), 3.54 – 3.40 (m, 2H), 2.55 – 2.39 (m, 2H), 2.32 – 2.23 (m, 1H), 2.10 – 1.83 (m, 7H), 1.68 – 1.57 (m, 1H), 1.16 – 1.07 (m, 1H), 0.90 – 0.80 (m, 21 H), 0.06 – 0.03 (m, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=145.0 (C_q), 128.1 (CH), 125.7 (CH), 113.8 (CH_2), 81.2 (C_q), 72.4 (CH), 70.9 (CH), 70.2 (CH), 67.5 (CH_2), 66.1 (CH), 45.1 (CH_2), 42.6 (CH_2), 41.0 (CH_2), 31.3 (CH_2), 27.0 (CH), 26.2 (3 x CH_3), 26.1 (3x CH_3), 24.7 (CH_2), 19.4 (CH_3), 18.5 (C_q), 18.3 (C_q), -4.1 (CH_3), -4.5 (CH_3), -5.1 (CH_3), -5.2 (CH_3).

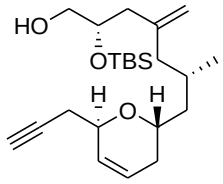
IR [cm^{-1}]: 3314, 2954, 2928, 2122, 1642, 1472, 1255, 1093, 835, 776, 622.

HRMS(EI) calcd. for $C_{29}H_{54}O_3Si_2$: 506.3611, found: 506.3604.

R_f= 0.59 (silica gel, hexane/EtOAc = 20:1)

$[\alpha]_D^{20}$ = - 49.5 (*c* = 1.00, CH_2Cl_2)

(2S,6S)-2-(tert-butyldimethylsilyloxy)-6-methyl-4-methylene-7-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)heptan-1-ol (**32**):



32

To a stirred solution of compound **16** (1.38 g, 2.72 mmol) in MeOH (10 mL) was added NH_4F (4 g) and stirred at rt for 32 h. The reaction was added H_2O (50 mL) and extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 20:1 to 10:1). Yielding **32** as colorless oil (699 mg, 1.78 mmol, 65%, 95% based on recovered starting material) along with recovered **16** (408 mg, 0.80 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ=5.92 – 5.88 (m, 1H), 5.86 – 5.83 (m, 1H), 4.82 (br s, 1H), 4.80 (br s, 1H), 4.35 – 4.30 (m, 1H), 3.90 – 3.84 (m, 1H), 3.83 – 3.78 (m, 1H), 3.60 – 3.55 (m, 1H), 3.47 – 3.42 (m, 1H), 2.51 (ddd, J = 16.4 Hz, J = 6.9 Hz, J = 2.7 Hz, 1H), 2.43 (ddd, J = 16.6 Hz, J = 7.1 Hz, J = 2.6 Hz, 1H), 2.25 – 2.18 (m, 2H), 2.01 (t, J = 2.8 Hz, 1H), 2.00 – 1.95 (m, 3H), 1.95 – 1.87 (m, 3H), 1.65 – 1.59 (m, 1H), 1.08 (ddd, J = 14.0 Hz, J = 9.4 Hz, J = 3.0 Hz, 1H), 0.91 – 0.89 (m, 12H), 0.10 (br s, 3H), 0.09 (br s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ=144.4 (C_q), 128.1 (CH), 125.8 (CH), 114.1 (CH_2), 81.2 (C_q), 71.6 (CH), 71.0 (CH), 70.2 (CH), 66.2 (CH_2), 65.9 (CH), 45.1 (CH_2), 42.3 (CH_2), 40.6 (CH_2), 31.3 (CH_2), 27.0 (CH), 26.0 (3 x CH_3), 24.6 (CH_2), 19.6 (CH_3), 18.3 (C_q), -4.1 (CH_3), -4.5 (CH_3).

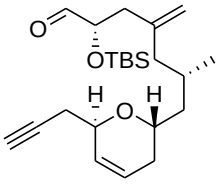
IR [cm^{-1}]: 3452, 3312, 2928, 1256, 1092, 837, 777, 641.

HRMS(EI) calcd. for $C_{23}H_{40}O_3Si_2$: 392.2747, found: 392.2751.

R_f= 0.31 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = -57.0 (*c* = 1.00, CH_2Cl_2)

(2S,6S)-2-(tert-butyldimethylsilyloxy)-6-methyl-4-methylene-7-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)heptanal (**5**):



5

To a refluxing solution of **32** (550 mg, 1.40 mmol) in MeCN was added IBX (784 mg, 2.80 mmol) in one portion. The reaction was refluxed for 20 min, cooled to room temperature and filtrated over celite. The solvent was removed under vacuum and the obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 10:1). Yielding **5** as colorless oil (535 mg, 1.37 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=9.59 (d, J = 1.8 Hz, 1H), 5.93 – 5.89 (m, 1H), 5.86 – 5.81 (m, 1H), 4.87 (br s, 1H), 4.86 (br s, 1H), 4.36 – 4.30 (m, 1H), 4.09 (ddd, J = 7.6 Hz, J = 5.3 Hz, J = 1.8 Hz, 1H), 3.84 – 3.76 (m, 1H), 2.51 (ddd, J = 16.5 Hz, J = 7.0 Hz, J = 2.7 Hz, 1H), 2.42 (ddd, J = 16.4 Hz, J = 7.0 Hz, J = 2.7 Hz, 1H), 2.38 (dd, J = 14.1 Hz, J = 4.9 Hz, 1H), 2.29 (dd, J = 14.2 Hz, J = 7.5 Hz, 1H), 2.06 – 2.00 (m, 1H), 2.02 (t, J = 2.7 Hz, 1H), 2.00 – 1.85 (m, 4H), 1.61 (ddd, J = 13.8 Hz, J = 9.9 Hz, J = 3.4 Hz, 1H), 1.11 (ddd, J = 13.9 Hz, J = 9.1 Hz, J = 3.1 Hz, 1H), 0.90 (br s, 9 H), 0.89 (d, J = 6.2 Hz, 3H), 0.07 (br s, 3H), 0.05 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 203.5 (CH), 142.7 (C_q), 128.1 (CH), 125.8 (CH), 115.2 (CH_2), 81.2 (C_q), 76.7 (CH), 71.2 (CH), 70.2 (CH), 66.2 (CH), 44.9 (CH_2), 42.6 (CH_2), 39.0 (CH_2), 31.3 (CH_2), 26.9 (CH), 25.9 (3 x CH_3), 24.6 (CH_2), 19.3 (CH_3), 18.3 (C_q), -4.5 (CH_3), -4.7 (CH_3).

IR [cm^{-1}]: 3314, 2929, 1737, 1092, 839, 778, 611.

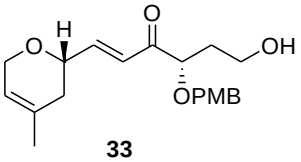
HRMS(EI) calcd. for $C_{23}H_{38}O_3Si$: 390.2590, found: 390.2586.

R_f= 0.58 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = -72.4 (*c* = 1.00, CH_2Cl_2)

Synthesis of sulfones **6a, 6b**:

(S,E)-6-hydroxy-4-(4-methoxybenzyloxy)-1-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)hex-1-en-3-one (**33**):



33

To a solution of compound **17** (3.77 g, 8.184 mmol) in THF (35 mL) was added 7% HF·pyridine (13 mL) over a period of 5 min. The reaction was stirred 30 min and quenched with sat. aq. $NaHCO_3$ solution (90 mL) and extracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed

under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 1:1 + 1% Et_3N). Yielding alcohol **33** as colorless, viscous oil (2.76 g, 7.98 mmol, 98%) which was immediately used for the next step .

^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.26 (d, J = 8.6 Hz, 2 H), 7.04 (dd, J = 15.9 Hz, J = 4.0 Hz, 1H), 6.88 (d, J = 8.6 Hz, 2H), 6.75 (dd, J = 15.9 Hz, J = 1.8 Hz, 1H), 5.46 (br s, 1H), 4.49 (d, J= 11.4 Hz, 1H), 4.33 (d, J = 11.3 Hz, 1H), 4.26 – 4.14 (m, 4H), 3.80 (s, 3H), 3.76 – 3.71 (m, 2H), 2.11 – 1.92 (m, 2H), 1.97 – 1.89 (m, 2H), 1.72 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ= 201.0 (C_q), 159.7 (C_q), 147.4 (CH), 131.2 (C_q), 130.0 (2 x CH), 129.4 (C_q), 122.9 (CH), 120.0 (CH), 114.1 (2 x CH), 82.6 (CH), 72.7 (CH), 72.4 (CH_2), 66.0 (CH_2), 60.1 (CH_2), 55.4 (CH_3), 35.1 (CH_2), 34.8 (CH_2), 23.1 (CH_3).

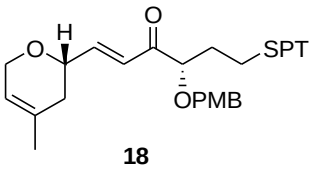
IR [cm^{-1}]: 3436, 3034, 2933, 1692, 1630, 1613, 1132, 1033, 987, 783, 518.

HRMS(ESI) calcd. for $C_{20}H_{26}O_5Na$: 369.1678, found: 369.1669.

R_f= 0.29 (silica gel, hexane/EtOAc = 1:1)

$[\alpha]_D^{20}$ = -153.2 (*c* = 1.30, $CDCl_3$)

(S,E)-4-(4-methoxybenzyloxy)-1-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-6-(1-phenyl-1H-tetrazol-5-ylthio)hex-1-en-3-one (**18**):



18

A solution of alcohol **33** (2.71 g, 7.823 mmol) in THF (35 mL) was cooled to 0 °C and added PPh_3 (3.08 g, 11.734 mmol), 1-phenyl-1*H*-tetrazol-5-thiol (2.09 g, 11.734 mmol) and DEAD (2.45 g, 14.081 mmol). The reaction was stirred at 0 °C for 1 h and 4 h at rt. The reaction was quenched by adding sat. aq. $NaHCO_3$ solution (60 mL) and extracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 3:1). Yielding sulfide **18** as colorless oil (3.66 g, 7.224 mmol, 92%)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.58 – 7.51 (m, 5H), 7.28 – 7.22 (m, 2H), 7.03 (dd, J = 15.7 Hz, J = 4.0 Hz, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.74 (dd, J = 15.8 Hz, J = 1.8 Hz, 1H), 5.45 (br s, 1H), 4.56 (d, J = 11.4 Hz, 1H), 4.32 (d, J = 11.3 Hz, 1H), 4.28 – 4.15 (m, 3H), 4.10 (dd, J = 8.7 Hz, J = 4.4 Hz, 1H), 3.79 (s, 3H), 3.54 – 3.40 (m, 2H), 2.30 – 2.12 (m, 2H), 2.11 – 1.93 (m, 2H), 1.72 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=200.5 (C_q), 159.7 (C_q), 154.1 (C_q), 147.7 (CH), 133.8 (C_q), 131.2 (C_q), 130.2 (CH), 130.1 (2 x CH), 129.9 (2 x CH), 129.3 (C_q), 123.9 (2 x CH), 122.8 (CH), 119.9 (CH), 114.1 (2 x CH), 81.6 (CH), 72.7 (CH), 72.7 (CH_2), 65.9 (CH_2), 55.5 (CH), 35.1 (CH_2), 31.7 (CH_2), 29.5 (CH_2), 23.0 (CH_3).

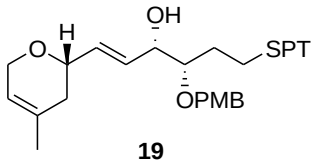
IR [cm^{-1}]: 3469, 2930, 2150, 1692, 1612, 1384, 1302, 1247, 1090, 761, 516.

HRMS(EI) calcd. for $C_{27}H_{30}O_4N_4SNa$: 529.1885, found: 529.1878.

R_f= 0.55 (silica gel, hexane/EtOAc = 2:1)

$[\alpha]_D^{20}$ = -97.5 (*c* = 1.10, CH_2Cl_2)

(3S,4S,E)-4-(4-methoxybenzyloxy)-1-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-6-(1-phenyl-1H-tetrazol-5-ylthio)hex-1-en-3-ol (**19**):



19

Compound **18** (3.61 g, 7.097 mmol) was dissolved in MeOH (35 mL) and cooled to -100 °C. $CeCl_3 \cdot 7H_2O$ (4.49 g, 12.066 mmol) was added and stirred for 10 min. Following $NaBH_4$ (398 mg, 10.646 mmol) was added in 3 portions and stirred for 90 min at the same temperature. The reaction was quenched by adding EtOAc (2 mL), warmed to rt, H_2O (60 mL) was added and extracted 4 times with EtOAc. The combined organic phase was washed with brine, dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 1:1). Yielding alcohol **19** as colorless oil (3.53 g, 6.940 mmol, 98%)

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.58 – 7.54 (m, 5H), 7.27 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 5.89 (dd, J = 15.7 Hz, J = 4.9 Hz, 1H), 5.80 (ddd, J = 15.7 Hz, J = 5.8 Hz, J = 1.0 Hz, 1H), 5.41 (br s, 1H), 4.62 – 4.55 (m, 2H), 4.21 – 4.15 (m, 3H), 4.07 – 4.01 (m, 1H), 3.79 (s, 3H), 3.58 – 3.52 (m, 1H), 3.49 – 3.40 (m, 2H), 2.39 (d, J = 4.8 Hz, 1H, OH), 2.21 – 2.11 (m, 1H), 2.10 – 2.00 (m, 2H), 1.95 – 1.87 (m, 1H), 1.70 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.6 (C_q), 154.4 (C_q), 133.8 (C_q), 133.5 (CH), 131.5 (C_q), 130.2 (CH), 130.1 (C_q), 130.0 (4 x CH), 129.8 (CH), 124.0 (2 x CH), 119.8 (CH), 114.1 (2 x CH), 80.2 (CH), 73.7 (CH), 73.4 (CH), 72.9 (CH_2), 65.8 (CH_2), 55.4 (CH_3), 35.8 (CH_2), 30.5 (CH_2), 29.6 (CH_2), 23.1 (CH_3).

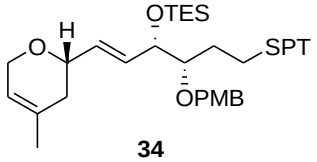
IR [cm^{-1}]: 3430, 2359, 1612, 1513, 1384, 1247, 1174, 1032, 762

HRMS(EI) calcd. for $C_{27}H_{32}O_4N_4S$: 508.2144, found: 508.2158.

R_f= 0.63 (silica gel, hexane/EtOAc = 1:1)

$[\alpha]_D^{20}$ = -59.4 (*c* = 1.20, CH_2Cl_2)

5-((3S,4S,E)-3-(4-methoxybenzyloxy)-6-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-4-(triethylsilyloxy)hex-5-enylthio)-1-phenyl-1H-tetrazole (**34**):



34

To a stirred solution of **19** (1.21 g, 2.379 mmol) in CH_2Cl_2 (20 mL) at -30 °C was added 2,6-lutidine (446 mg, 4.163 mmol) and dropwise TESOTf (943 mg, 3.569 mmol). The reaction was stirred at the same temperature for 20 min and then allowed to warm to rt and stirred for another 2 h. The reaction was cooled to -30 °C again, 1 mL Et_3N was added. The reaction was quenched with aq. sat. $NaHCO_3$ (20 mL), warmed to rt and extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained viscous oil was purified by column chromatography (silica gel, hexane:EtOAc = 10:1 + 1 % Et_3N). Yielding sulfide **34** as colorless, viscous oil (1.38 g, 2.215 mmol, 93%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.57 – 7.52 (m, 5H), 7.25 (d, J = 8.9 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 5.81 – 5.78 (m, 2H), 5.21 (br s, 1H), 4.64 (d, J = 11.4 Hz, 1H), 4.47 (d, J = 11.4 Hz, 1H), 4.38 – 4.35 (m, 1H), 4.19 – 4.14 (m, 2H), 4.06

– 4.00 (m ,1H), 3.78 (s, 3H), 3.54 – 3.46 (m, 2H), 3.40 – 3.31 (m, 1H), 2.13 – 1.98 (m, 2H), 1.89 (br d, J = 17.0 Hz, 1H), 1.85 – 1.73 (m, 1H), 1.70 (br s, 3H), 0.91 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.5 (C_q), 154.6 (C_q), 134.0 (C_q), 132.3 (CH), 131.6 (C_q), 130.6 (C_q), 130.1 (CH), 129.9 (2 x CH), 129.8 (2 x CH), 129.5 (CH), 123.9 (2 x CH), 119.9 (CH), 114.0 (2 x CH), 80.1 (CH), 73.6 (CH), 72.5 (CH), 72.5 (CH_2), 65.7 (CH_2), 55.4 (CH_3), 35.9 (CH_2), 30.5 (CH_2), 29.2 (CH_2), 23.1 (CH_3), 7.0 (3 x CH_3), 5.0 (3 x CH_2).

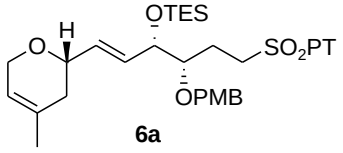
IR [cm^{-1}]: 2954, 1611, 1512, 1500, 1456, 1382, 1246, 1173, 1014, 974, 744.

HRMS(ESI) calcd. for $C_{33}H_{46}O_4N_4SSiNa$: 645.2907, found: 645.2916.

R_f= 0.43 (silica gel, hexane/EtOAc = 4:1)

$[\alpha]_D^{20}$ = -69.4 (*c* = 1.00, CH_2Cl_2)

5-((3S,4S,E)-3-(4-methoxybenzyloxy)-6-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-4-(triethylsilyloxy)hex-5-enylsulfonyl)-1-phenyl-1H-tetrazole (**6b**):



6a

Ammonium molybdate (1.1 g, 0.98 mmol) was added to H_2O_2 (30% aqueous solution, 2.4 mL) and phosphate buffer (0.5 M, 1.2 mL) at 0 °C and stirred for 15 min. The yellow solution was added dropwise to a solution of **34** (950 mg, 1.525 mmol) in EtOH (20 mL) at 0 °C and stirred for 30 min before it was allowed to reach RT. After stirring for another 4 h the reaction was diluted with aq. sat. $NaHCO_3$ (35 mL) and extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 4:1). Yielding sulfone **6a** as viscous oil (612 mg, 0.935 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.61 – 7.55 (m, 5 H), 7.25 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 5.84 – 5.76 (m, 2 H), 5.41 (br s, 1H), 4.62 (d, J = 11.4 Hz, 1H), 4.48 (d, J = 11.4 Hz, 1H), 4.39 – 4.35 (m, 1H), 4.19 – 4.14 (m, 2H), 4.08 – 4.02 (m, 1H), 3.81 (s, 3H), 3.54 – 3.49 (m, 1H), 2.24 – 2.13 (m, 1H), 2.08 – 1.98 (m, 2H), 1.98 – 1.86 (m, 2H), 1.70 (br s, 3H), 0.91 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.7 (C_q), 153.6 (C_q), 133.2 (C_q), 132.8 (CH), 131.6 (CH), 130.1 (2 x C_q), 129.9 (2 x CH), 129.8 (2 x CH), 128.8 (CH), 125.3 (2 x CH), 119.9 (CH), 114.1 (2 x CH), 79.4 (CH), 73.4 (CH), 72.6 (CH), 72.5 (CH_2), 65.7 (CH_2), 55.5 (CH_3), 53.3 (CH_2), 35.8 (CH_2), 23.1 (CH_3), 22.6 (CH_2), 7.0 (3 x CH_3), 5.0 (3 x CH_3).

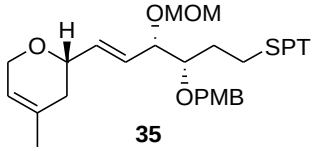
IR [cm^{-1}]: 2954, 2875, 1611, 1513, 1498, 1342, 1248, 1150, 1100, 821, 743.

HRMS(ESI) calcd. for $C_{33}H_{46}O_6N_4SSiNa$: 677.2805, found: 677.2814.

R_f= 0.68 (silica gel, hexane/CH_2Cl_2/EtOAc = 4:3:1)

$[\alpha]_D^{20}$ = -27.5 (*c* = 1.10, CH_2Cl_2)

5-((3S,4S,E)-3-(4-methoxybenzyloxy)-4-(methoxymethoxy)-6-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)hex-5-enylthio)-1-phenyl-1H-tetrazole (**35**):



35

To a solution of **19** (2.12 g, 4.168 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added EtN*i*Pr_2 (5.39 g, 41.680 mmol) and subsequent dropwise MOMCl (1.68 g, 20.840 mmol). The reaction was allowed to reach rt overnight and was stirred 24 h. The reaction was quenched by adding sat. aq. NH_4Cl solution (20 mL) and extracted 4 times with Et_2O. The combined organic phase was washed with brine, dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained colorless oil was purified by column chromatography (silica gel, hexane:EtOAc = 3:1). Yielding sulfide **35** as colorless oil (2.26 g, 4.089 mmol, 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.57 – 7.52 (m, 5H), 7.25 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.83 (ddd, J = 15.7 Hz, J = 5.4 Hz, J = 0.8 Hz, 1H), 5.67 (ddd, J = 15.7 Hz, J = 6.8 Hz, J = 1.3 Hz, 1H), 5.41 (br s, 1H), 4.71 – 4.67 (m, 2H), 4.57 (d, J = 6.8 Hz, 1H), 4.50 (d, J = 11.2 Hz, 1 H), 4.26 – 4.21 (m, 1H), 4.19 – 4.14 (m, 2H), 4.07 – 4.00 (m, 1H), 3.77 (s, 3H), 3.65 – 3.59 (m, 1H), 3.51 – 3.43 (m, 1H), 3.34 (s, 3H), 2.13 – 2.05 (m, 1H), 2.04 – 1.99 (m, 1H), 1.97 – 1.85 (m, 2H), 1.69 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.5 (C_q), 154.5 (C_q), 133.9 (C_q), 131.5 (C_q), 130.4 (CH), 130.0 (2 x CH), 129.9 (2 x CH), 126.9 (CH), 123.9 (2 x CH), 119.8 (CH), 114.0 (2 x CH), 94.6 (CH_2), 78.8 (CH), 77.4 (CH), 73.4 (CH), 72.8 (CH_2), 65.8 (CH_2), 55.8 (CH_3), 55.4 (CH_3), 35.9 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 23.0 (CH_3).

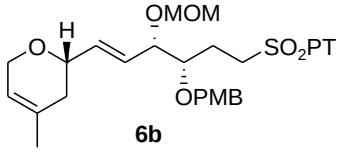
IR [cm^{-1}]: 2931, 1612, 1513, 1500, 1384, 1247, 1032, 821, 762, 694.

HRMS(ESI) calcd. for $C_{29}H_{36}O_5N_4SNa$: 575.2304, found: 575.2321.

R_f= 0.41 (silica gel, hexane/EtOAc = 2:1)

$[\alpha]_D^{20}$ = -62.1 (*c* = 1.00, CH_2Cl_2)

5-((3S,4S,E)-3-(4-methoxybenzyloxy)-4-(methoxymethoxy)-6-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)hex-5-enylsulfonyl)-1-phenyl-1H-tetrazole (**6b**):



6b

Ammonium molybdate (1.1 g, 0.87 mmol) was added to H_2O_2 (30% aqueous solution, 4.4 mL) at 0 °C and stirred for 15 min. The yellow solution was added dropwise to a solution of **35** (2.21 g, 4.000 mmol) in EtOH (40 mL) at 0 °C and stirred for 45 min before it was allowed to reach rt. After stirring for another 3.5 h the reaction was diluted with H_2O (50 mL) and extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 4:1). Yielding sulfone **6b** as white crystals (1.77 g, 3.027 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.68 – 7.55 (m, 5H), 7.26 (d, J = 8.2 Hz, 2H), 6.88 (d, J = 6.8 Hz, 2H), 5.85 (dd, J = 15.8 Hz, J = 5.3 Hz, 1H), 5.68 (dd, J = 15.8 Hz, J = 6.7 Hz, 1H), 5.41 (br s, 1 H), 4.68 (d, J = 6.8 Hz, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.57 (d, J = 6.8 Hz, 1H), 4.50 (d, J = 11.4 Hz, 1H), 4.25 (t, J = 5.9 Hz, 1H), 4.19 – 4.15 (m, 2H), 4.08 – 4.01

(m, 1H), 3.84 – 3.75 (m, 1H), 3.81 (s, 3H), 3.67 – 3.59 (m, 2H), 3.36 (s, 3H), 2.26 – 2.16 (m, 1H), 2.09 – 1.98 (m, 2H), 1.90 (br d, J = 16.7 Hz, 1H), 1.70 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.6 (C_q), 153.6 (C_q), 135.6 (CH), 133.2 (C_q), 131.6 (CH), 131.5 (C_q), 130.0 (2 x CH), 129.9 (C_q), 129.8 (2 x CH), 126.1 (CH), 125.3 (2 x CH), 119.8 (CH), 114.1 (2 x CH), 94.6 (CH_2), 77.8 (CH), 77.0 (CH), 73.3 (CH), 72.7 (CH_2), 65.7 (CH_2), 55.9 (CH_3), 55.4 (CH_3), 53.0 (CH_2), 35.8 (CH_2), 23.5 (CH_2), 23.0 (CH_3).

IR [cm^{-1}]: 2913, 2358, 1613, 1513, 1341, 1248, 1151, 1101, 1033, 764, 689.

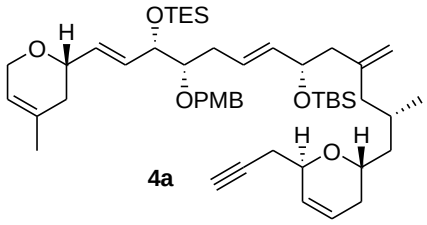
HRMS(ESI) calcd. for $C_{29}H_{36}O_7N_4SNa$: 607.2202, found: 607.2217.

R_f= 0.53 (silica gel, CH_2Cl_2/hexane/EtOAc = 4:3:1)

$[\alpha]_D^{20}$ = -34.1 (*c* = 1.10, CH_2Cl_2)

Synthesis of neolaulimalide (**2**):

(5S,9S,10S,E)-12,12-diethyl-9-(4-methoxybenzyloxy)-2,2,3,3-tetramethyl-5-((S)-4-methyl-2-methylene-5-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)pentyl)-10-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-4,11-dioxa-3,12-disilatetradec-6-ene (**4a**):



To a stirred solution of **6a** (202 mg, 0.313 mmol) in THF (4 mL) at -78 °C was added KHMDS (0.688 mL, 0.344 mmol, 0.5 M in toluene) dropwise over 4 min. The yellow solution was allowed to stir for 3 min before **5** (122 mg, 0.313 mmol, in 0.7 mL THF) was added dropwise over 5 min. After stirring for another 90 min at the same temperature the reaction was quenched by adding H_2O (4 mL) and warmed to rt. The phases were separated and the aqueous phase was extracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 15:1 + 1% Et_3N). Yielding compound **4a** as viscous oil (195 mg, 0.238 mmol, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ=7.26 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.91 – 5.85 (dt, J = 2.5 Hz, J = 1.1 Hz, 1H), 5.84 – 5.82 (m, 1H), 5.81 (ddd, J = 15.4 Hz, J = 4.6 Hz, J = 1.1 Hz, 1H), 5.76 (ddd, J = 15.5 Hz, J = 5.3 Hz, J = 1.1 Hz, 1H), 5.65 – 5.58 (m, 1H), 5.47 (dd, J = 15.5 Hz, J = 6.4 Hz, 1H), 5.41 (br s, 1H), 4.79 (br s, 1H), 4.77 (br s, 1H), 4.53 (br s, 2H), 4.34 – 4.30 (m, 1H), 4.26 (t, J = 4.9 Hz, 1H), 4.19 – 4.15 (m, 3H), 4.03 (ddd, J = 10.0 Hz, J = 4.7 Hz, J = 4.3 Hz, 1H), 3.82 – 3.72 (m, 1H), 3.80 (s, 3H), 3.31 (ddd, J = 8.6 Hz, J = 5.2 Hz, J = 3.3 Hz, 1H), 2.50 (ddd, J = 16.5 Hz, J = 6.7 Hz, J = 2.7 Hz, 1H), 2.43 (ddd, J = 16.5 Hz, J = 7.2 Hz, J = 2.7 Hz, 1H), 2.29 (ddd, J = 14.7 Hz, J = 7.2 Hz, J = 3.0 Hz, 1H), 2.23 (dd, J =13.8 Hz, J = 6.6 Hz, 1H), 2.11 (dd, J = 13.8 Hz, J = 6.6 Hz, 1H), 2.06 – 1.85 (m, 8H), 1.70 (s, 3H), 1.63 (ddd, J = 13.9 Hz, J = 9.9 Hz, J = 3.4 Hz, 1H), 1.09 (ddd, J = 14.0 Hz, J = 9.5 Hz, J = 3.4 Hz, 1H), 0.92 (t, J = 7.9 Hz, 9H), 0.89 (d, J = 6.4 Hz, 3H), 0.87 (s, 9H), 0.58 – 0.53 (m, 6H), 0.03 (br s, 3H), 0.01 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ=159.3 (C_q), 144.7 (C_q), 135.2 (CH), 131.6 (C_q), 131.6 (CH), 131.1 (C_q), 130.4 (CH), 129.5 (2 x CH), 128.1 (CH), 127.4 (CH), 125.7 (CH), 119.9 (CH), 113.9 (CH_2), 113.8 (2 x CH), 82.9 (CH), 82.0 (C_q), 73.7 (CH), 73.0 (CH), 72.6 (CH_2), 71.5 (CH), 70.9 (CH), 70.2 (CH), 66.0 (CH), 65.7 (CH_2), 55.4 (CH_3), 45.3 (CH_2), 45.1 (CH_2), 42.5 (CH_2), 35.8 (CH_2), 32.9 (CH_2), 31.3 (CH_2), 26.9 (CH), 26.1 (3 x CH_3), 24.6 (CH_2), 23.1 (CH_3), 19.4 (CH_3), 18.4 (C_q), 7.1 (3 x CH_3), 5.0 (3 x CH_2), -4.0 (CH_3), -4.6 (CH_3).

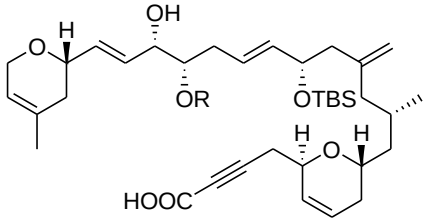
IR [cm^{-1}]: 3312, 2929, 2612, 1513, 1302, 1248, 1091, 1039, 1006, 836,776.

HRMS(ESI) calcd. for $C_{49}H_{78}O_6Si_2Na$: 841.5235, found: 841.5241.

R_f = 0.44 (silica gel, hexane/EtOAc = 10:1)

$[\alpha]_D^{20}$ = -79.3 (*c* = 1.2, CH_2Cl_2)

4-((2R,6R)-6-((2S,6S,7E,10S,11S,12E)-6-(tert-butyldimethylsilyloxy)-11-hydroxy-10-(4-methoxybenzyloxy)-2-methyl-13-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-4-methylenetrideca-7,12-dienyl)-5,6-dihydro-2H-pyran-2-yl)but-2-ynoic acid (**20**):



20

To a stirred solution of compound **4a** (165 mg, 0.2013 mmol) in THF (3 mL) at -78 °C was added nBuLi (0.214 mL, 0.342 mmol, 1.6 M in hexane) dropwise over a period of 5 min. The bright yellow solution was stirred for 5 min and then CO_2(g) was bubbled threw the reaction for 10 min. Now HF·pyridine (7%, 2.8 mL) was added dropwise over 5 min to the colourless reaction mixture and it was allowed to warm to rt and stirred for another 90 min. The reaction was quenched by slow addition of aq. sat. $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (15 mL). The pH of the aqueous phase was set to pH = 3 by addition of HCl (1 N), the phases were separated and the aqueous phase was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, CH_2Cl_2:MeOH = 6:1). Yielding compound **20** as viscous oil (136 mg, 0.182 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.26 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.1 Hz, 2H), 5.95 – 5.87 (m, 1H), 5.72 (dd, J = 15.3 Hz, J = 6.3 Hz, 1H), 5.84 (dd, J = 15.3 Hz, J = 5.4 Hz, 1H), 5.72 – 5.65 (m ,1H), 5.60 – 5.52 (m, 2H), 5.41 (br s, 1H), 4.80 (br s, 1H), 4.78 (br s, 1H), 5.63 (d, J = 11.3 Hz, 1H), 4.46 (d, J = 11.3 Hz, 1H), 4.39 (br s, 1H), 4.23 – 4.16 (m, 3H), 4.11 (t, J = 6.2 Hz, 1H), 4.05 (ddd, J = 9.6 Hz, J = 4.8 Hz, J = 4.6 Hz, 1H), 3.80 (s, 3H), 3.80 – 3.74 (m, 1H), 3.40 (dd, J = 11.1 Hz, J = 5.6 Hz, 1H), 2.64 (dd, J = 17.2 Hz, J = 9.0 Hz, 1H), 2.47 (dd, J = 17.3 Hz, J = 4.3 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.33 – 2.24 (m, 1H), 2.17 (d, J = 6.3 Hz, 2H), 2.12 – 1.79 (m, 7H), 1.70 (br s, 3H), 1.62 (ddd, J = 12.9 Hz, J = 10.0 Hz, J = 3.0 Hz, 1H), 1.05 (t, J = 12.2 Hz, 1H), 0.88 – 0.85 (m, 12H), 0.02 (s, 3H), 0.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.6 (C_q), 154.9 (C_q), 144.6 (2 x C_q), 137.7 (CH), 133.1 (CH), 131.6 (C_q), 130.6 (CH), 129.9 (2 x CH), 127.6 (CH), 126.7 (CH), 124.0 (CH), 119.5 (CH), 114.4 (CH_2), 114.0 (2 x CH), 86.7 (C_q), 81.3 (CH), 74.5 (C_q), 73.9 (CH), 72.8 (CH), 72.1 (CH_2), 71.8 (CH), 70.7 (CH), 66.0 (CH), 65.6 (CH_2), 55.4 (CH_3), 45.4 (CH_2), 44.3 (CH_2), 43.2 (CH_2), 35.8 (CH_2), 32.8 (CH_2), 31.4 (CH_2), 26.8 (CH), 26.1 (3 x CH_3), 24.5 (CH_2), 23.1 (CH_3), 19.4 (CH_3), 18.4 (C_q), -4.0 (CH_3), -4.6 (CH_3).

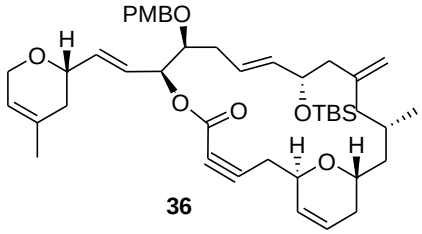
IR [cm^{-1}]: 3450, 2928, 2238, 1708, 1513, 1382, 1249, 1174, 1091, 835, 777, 610.

HRMS(ESI) calcd. for $C_{44}H_{64}O_8SiNa$: 771.4268, found: 771.4284.

R_f= 0.44 (silica gel, CH_2Cl_2:MeOH = 9:1)

$[\alpha]_D^{20}$ = -25.2 (*c* = 1.10, CH_2Cl_2)

(1R,7S,8S,12S,16S,18R,E)-12-(tert-butyldimethylsilyloxy)-8-(4-methoxybenzyloxy)-16-methyl-7-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-14-methylene-6,22-dioxabicyclo[16.3.1]docosa-10,20-dien-3-yn-5-one (**36**):



36

To a stirred solution of *seco* acid **20** (35 mg, 0.0467) in benzene (1 mL) at rt was added Et_3N (13.0 µL, 0.0934 mmol) and dropwise 2,4,6-trichlorobenzoyl chloride (14.4 µL, 0.0794 mmol). The solution was stirred for 4 h before it was diluted with benzene (20 mL) and added over 6 h *via* a syringe pump into a stirred solution of DMAP (57 mg, 0.4673 mmol) in benzene (200 mL). After additional 6 h the mixture was concentrated to about 20 mL, aq. sat. $NaHCO_3$ (30 mL) was added and the mixture was stirred for 20 min. The phases were separated and the aqueous layer was extracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 10:1 to 8:1). Yielding compound **36** as viscous oil (12 mg, 0.0164 mmol, 35%) and the dimer of **20** (3 mg, 0.0021 mmol, 4%).

^{1}H NMR (600 MHz, $CDCl_3$) δ=7.26 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 5.95 – 5.81 (m, 1H), 5.84 – 5.82 (m, 2H), 5.63 – 5.60 (m, 1H), 5.52 – 5.50 (m, 1H), 5.43 – 5.40 (m, 3H), 4.76 (br s, 2H), 4.56 (d, J = 11.7 Hz, 1H), 4.53 (d, J = 11.7 Hz, 1H), 4.46 – 4.42 (m, 1H), 4.22 – 4.16 (m, 3H), 4.04 (ddd, J = 10.5 Hz, J = 3.6 Hz, J = 3.6 Hz, 1H), 3.80 (s, 3H), 3.76 – 3.72 (m, 1H), 3.13 (ddd, J = 7.0 Hz, J = 7.0 Hz, J = 2.8 Hz, 1H), 2.61 (dd, J = 17.4 Hz, J = 10.0 Hz, 1H), 2.48 (dd, J = 17.4 Hz, J = 2.5 Hz, 1H), 2.36 – 2.30 (m, 2H), 2.22 (dd, J = 13.9 Hz, J = 7.9 Hz, 1H), 2.14 (dd, J = 13.9 Hz, J = 5.4 Hz, 1H), 2.10 (dd, J = 13.6 Hz, J = 5.4 Hz, 1H), 2.08 – 2.04 (m, 1H), 1.98 – 1.87 (m, 4H), 1.74 (dd, J = 13.6 Hz, J = 10.0 Hz, 1H), 1.70 (br s, 3H), 1.62 (ddd, J = 13.9 Hz, J = 9.8 Hz, J = 3.9 Hz, 1H), 1.13 (ddd, J = 13.9 Hz, J = 9.7 Hz, J = 2.8 Hz, 1H), 0.86 (m, 9H), 0.83 (d, J = 6.6 Hz, 3H), 0.01 (br s, 3H), 0.00 (br s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ=159.4 (C_q), 153.1 (C_q), 144.5 (C_q), 136.9 (CH), 134.5 (CH), 131.5 (C_q), 130.3 (C_q), 129.7 (2 x CH), 127.7 (CH), 127.0 (CH), 124.7 (CH), 124.5 (CH) 119.9 (CH), 113.9 (2 x CH_2), 88.1 (C_q), 77.9 (CH), 77.5 (CH), 73.5 (C_q), 73.4 (CH), 71.8 (CH), 71.4 (CH), 71.2 (CH), 66.0 (CH), 65.8 (CH_2), 55.4 (CH_3), 45.0 (CH_2), 44.0 (CH_2), 43.4 (CH_2), 35.8 (CH_2), 34.4 (CH_2), 31.3 (CH_2), 27.1 (CH), 26.0 (3 x CH_3), 24.4 (CH_2), 23.1 (CH_3), 19.0 (CH_3), 18.4 (C_q), -4.0 (CH_3), -4.6 (CH_3).

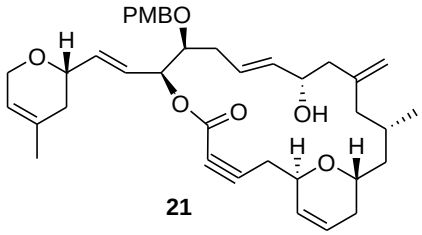
IR [cm^{-1}]: 2926, 2854, 2234, 1709, 1513, 1460, 1247, 1070, 969, 835, 776.

HRMS(ESI) calcd. for $C_{44}H_{62}O_7SiNa$: 753.4162, found: 753.4149.

R_f = 0.42 (silica gel, hexane/EtOAc = 4:1)

$[\alpha]_D^{20}$ = -22.4 (*c* = 0.78, CH_2Cl_2)

(1R,7S,8S,12S,16S,18R,E)-12-(tert-butyldimethylsilyloxy)-8-(4-methoxybenzyloxy)-16-methyl-7-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-14-methylene-6,22-dioxabicyclo[16.3.1]docosa-10,20-dien-3-yn-5-one (**21**):



21

To a stirred solution (**PVC flask**) of compound **36** (10 mg, 0.0137 mmol) in THF (0.75 mL) at 0 °C was added HF·pyridine (35%, 500 µL) dropwise in 5 min. After stirring at 0 °C for another 10 min the reaction was allowed to reach rt and stirred for 5 h. The mixture was diluted with CH_2Cl_2 (4 mL), cooled to 0 °C and quenched by slow addition of aq. sat. $NaHCO_3$ (7 mL). The phases were separated and the aqueous layer was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1). Yielding compound **21** as colorless oil (7.3 mg, 0.0119 mmol, 87%).

^{1}H NMR (600 MHz, $CDCl_3$) δ=7.26 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.94 – 5.90 (m, 1H), 5.87 – 5.80 (m, 2H), 5.62 – 5.55 (m, 3H), 5.51 (dd, J = 15.5 Hz, J = 6.5 Hz, 1H), 5.43 (br s, 1H) 4.88 (br s, 2H), 4.57 (d, J = 11.7 Hz, 1H), 4.54 (d, J = 11.7 Hz, 1H), 4.45 (br d, J = 9.9 Hz, 1H), 4.25 (ddd, J = 9.8 Hz, J = 6.4 Hz, J = 3.4 Hz, 1H) 4.20 – 4.17 (m, 2H), 4.06 – 4.01 (m, 1H), 3.80 (s, 3H), 3.69 – 3.64 (m, 1H), 3.58 (ddd, J = 6.8 Hz, J = 5.3 Hz, J = 2.8 Hz, 1H), 2.58 (dd, J = 17.3 Hz, J = 10.1 Hz, 1H), 2.47 (dd, J = 17.3 Hz, J = 2.3 Hz, 1H), 2.43 – 2.36 (m, 2H), 2.34 (dd, J = 13.9 Hz, J = 3.7 Hz, 1H), 2.22 – 2.16 (m, 2H), 2.11 – 2.04 (m, 1H), 2.02 – 1.89 (m, 4H), 1.88 – 1.83 (m, 2H), 1.70 (br s, 3H), 1.66 (ddd, J = 14.0 Hz, J = 10.5 Hz, J = 2.6 Hz, 1H), 1.10 (ddd, J = 14.0 Hz, J = 10.3 Hz, J = 1.6 Hz, 1H), 0.86 (d, J = 6.5 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ= 159.5 (C_q), 153.2 (C_q), 144.5 (C_q), 135.5 (CH), 134.2 (CH), 131.5 (C_q), 130.2 (C_q), 129.7 (2 x CH), 127.7 (CH), 127.0 (CH), 125.9 (CH), 124.5 (CH) 119.9 (CH), 114.0 (2 x CH_2), 88.5 (C_q), 77.2 (CH), 77.8 (CH), 73.4 (CH), 73.2 (C_q), 71.6 (CH), 71.3 (CH), 69.3 (CH), 66.0 (CH), 65.8 (CH_2), 55.4 (CH_3), 45.7 (CH_2), 43.6 (CH_2), 43.0 (CH_2), 35.8 (CH_2), 34.8 (CH_2), 31.4 (CH_2), 26.8 (CH), 24.3 (CH_2), 23.1 (CH_3), 19.1 (CH_3).

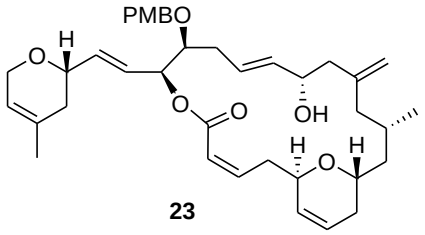
IR [cm^{-1}]: 2925, 2234, 1707, 1513, 1248, 1070.

HRMS(ESI) calcd. for $C_{38}H_{48}O_7Na$: 639.3298, found: 639.3315

R_f = 0.55 (silica gel, hexane/EtOAc = 1:1)

$[\alpha]_D^{20}$ = -38.0 (*c* = 0.38, CH_2Cl_2)

(1R,7S,8S,12S,16S,18R,E)-12-hydroxy-8-(4-methoxybenzyloxy)-16-methyl-7-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-14-methylene-6,22-dioxabicyclo[16.3.1]docosa-10,20-dien-3-yn-5-one (**23**):



To a stirred solution of compound **21** (8.1 mg, 0.01314 mmol) in a 1:1 mixture of EtOAc and cyclohexene (3 mL) at rt was added quinoline (18 µL). H_2 (balloon) was bubbled threw the reaction and Lindlar catalyst (15 mg) was added. After 1 h the reaction was filtered threw a short pad of celite, to remove the catalyst and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 5:1 to 1:1). Yielding **23** as colorless oil (8.0 mg, 0.01293 mmol, 89%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.26 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.43 (ddd, J = 11.5 Hz, J = 9.4 Hz, J = 7.2 Hz, 1H), 5.95 (d, J = 11.5 Hz, 1H), 5.88 (dd, J = 15.9 Hz, J = 5.3 Hz, 1H), 5.85 – 5.77 (m, 2H), 5.69 (dd, J = 10.4 Hz, J = 2.0 Hz, 1H), 5.61 – 5.51 (m, 1H), 5.46 (dd, J = 15.5 Hz, , J = 5.7 Hz, 1H), 5.44 – 5.38 (m, 2H), 4.87 (br s, 1H), 4.85 (br s, 1H), 4.57 (d, J = 11.6 Hz, 1H), 4.52 (d, J = 11.6 Hz, 1H), 4.25 – 4.12 (m, 4H), 4.06 – 4.01 (m, 1H), 3.99 – 3.92 (m, 1H), 3.80 (s, 3H), 3.64 (ddd, J = 8.6 Hz, J = 5.4 Hz, J = 3.2 Hz, 1H), 3.22 (ddd, J = 13.5 Hz, J = 9.1 Hz, J = 4.1 Hz, 1H), 2.47 – 2.26 (m, 5H), 2.34 – 2.26 (m, 2H), 2.12 – 2.00 (m, 2H), 1.89 (br d, J = 16.6 Hz, 1H), 1.81 – 1.71 (m, 4H), 1.70 (br s, 3H), 0.99 (ddd, J = 13.8 Hz, J = 8.4 Hz, J = 3.6 Hz, 1H), 0.86 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=165.4 (C_q), 159.4 (C_q), 147.3 (C_q), 145.0 (C_q), 135.8 (CH), 133.2 (CH), 131.5 (C_q), 130.2 (C_q), 129.7 (2 x CH), 129.3 (CH), 126.4 (CH), 125.9 (CH), 124.1 (CH), 121.4 (CH), 119.9 (CH), 114.7 (CH_2), 113.9 (2 x CH), 78.4 (CH), 73.9 (CH), 73.5 (CH), 71.9 (CH_2), 70.2 (CH), 70.1 (CH), 67.8 (CH), 65.8 (CH_2), 55.4 (CH_3), 45.2 (CH_2), 43.0 (CH_2), 40.7 (CH_2), 35.8 (CH_2), 35.2 (CH_2), 34.2 (CH_2), 30.3 (CH_2), 27.0 (CH), 23.1 (CH_3), 19.4 (CH_3).

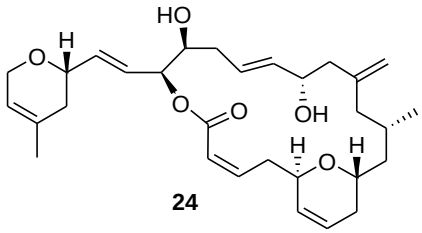
IR [cm^{-1}]: 3469, 2917, 1714, 1513, 1247, 1168, 1033, 819, 447, 419.

HRMS(ESI) calcd. for $C_{38}H_{50}O_7Na$: 641.3454, found: 641.3450.

R_f = 0.49 (silica gel, hexane/EtOAc = 1:1)

$[\alpha]_D^{20}$ = +38.6 (*c* = 0.70, CH_2Cl_2)

Desoxyneolaulimalide (**24**):



To a solution of **23** (6.5 mg, 0.0105 mmol) in a biphasic 1/1 mixture of CH_2Cl_2/aq. (pH = 7) buffer (6 mL) was added DDQ (4 mg) in one portion. The flask was closed with a septum and placed into an ultrasound bath at 35°C. After 1 h additional DDQ (4 mg) was added and the same after 2.5 h. The reaction was diluted with H_2O (10 mL) and CH_2Cl_2 (5 mL) after a total reaction time of 3.5 h. The phases were separated and the aqueous layer was extracted 4 times with CH_2Cl_2. The combined organic layer was washed 4 times with H_2O and dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1 to 1:1). Yielding **24** as white solid (5.0 mg, 0.01003 mmol, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=6.45 (ddd, J = 11.4 Hz, J = 9.2 Hz, J = 7.5 Hz, 1H), 5.95 (d, J = 11.4 Hz, 1H), 5.88 (dd, J = 15.8 Hz, J = 4.4 Hz, 1H), 5.85 – 5.77 (m, 2H), 5.74 – 5.60 (m, 2H), 5.52 (dd, J = 15.5 Hz, J = 5.6 Hz, 1H), 5.42 (br s, 1H), 5.25 (dd, J = 5.2 Hz, J = 3.5 Hz, 1H), 4.89 (br s, 1H), 4.86 (br s, 1H), 4.26 – 4.15 (m, 4H), 4.06 (ddd, J = 10.2 Hz, J = 4.0 Hz, J = 4.0 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.89 – 3.81 (m, 1H), 3.15 – 3.07 (m, 1H), 2.53 (ddd, J = 12.6 Hz, J = 8.5 Hz, J = 8.4 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.28 – 2.11 (m, 4H), 2.11 – 1.99 (m, 1H), 1.92 (br d, J = 16.9 Hz, 1H), 1.86 – 1.67 (m, 5H), 1.69 (br s, 3H), 1.04 – 0.95 (m, 1H), 0.88 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=165.3 (C_q), 144.8 (C_q), 136.6 (CH), 135.0 (CH), 131.5 (C_q), 129.1 (CH), 126.0 (CH), 125.0 (CH), 124.2 (CH), 121.6 (CH), 119.8 (CH), 114.6 (CH_2), 75.4 (CH), 73.2 (CH), 72.1 (CH), 70.8 (CH), 70.3 (CH), 67.9 (CH), 65.8 (CH_2), 45.0 (CH_2), 43.5 (CH_2), 41.3 (CH_2), 37.1 (CH_2), 35.8 (CH_2), 35.5 (CH_2), 30.4 (CH_2), 27.1 (CH), 23.1 (CH_3), 19.5 (CH_3).

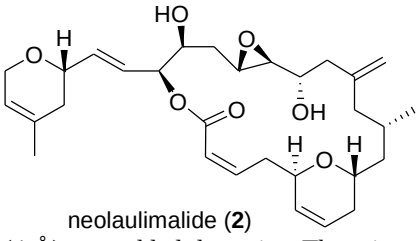
IR [cm^{-1}]: 3401, 2920, 2851, 1716, 1260, 1079, 799, 473, 446, 405.

HRMS(ESI) calcd. for $C_{30}H_{42}O_6Na$: 521.2879, found: 521.2882.

R_f = 0.40 (silica gel, hexane/EtOAc = 1:2)

$[\alpha]_D^{20}$ = 12.9 (*c* = 0.21, CH_2Cl_2)

Neolaulimalide (**2**):



neolaulimalide (**2**)

To a stirred suspension of powdered molecular sieves 4 Å (160 mg) in CH_2Cl_2 (1.7 mL) at -20 °C, was added (+)-diisopropyl tartrate (25.6 µL, 0.0128 mmol, 0.5 M in CH_2Cl_2) and Ti(O*i*Pr)$_4$ (21.4 µL 0.0107 mmol, 0.5 M in CH_2Cl_2). The mixture was stirred at the same temperature for 10 min before t-butyl hydroperoxide (27.3 µL, 0.0150, 0.55 M in CH_2Cl_2, dried over molecular sieves (4 Å) was added dropwise. The mixture was stirred for another 30 min before a solution of **23** (4.4 mg, 0.00882 mmol, in 0.3 mL CH_2Cl_2) was added dropwise. The reaction was stirred for 2.5 h at -20 °C before it was quenched by addition of aq. sat. NH_4Cl (2 mL) and warmed to rt. After stirring for 4 min the mixture was diluted with Et_2O and sat. aq. KNa-tartrate and stirred for 45 min, the phases were separated and the aqueous layer was extracted 4 times with Et_2O. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1 to 1:2). Yielding neolaulimalide (**1**) as white solid (3.3 mg, 0.00641 mmol, 73%), that was identical in every aspect with the reported data of the natural compound.

^{1}H NMR (600 MHz, $CDCl_3$) δ=6.35 (ddd, J = 11.7 Hz, J = 8.1 Hz, J = 8.1 Hz, 1H), 5.91 (ddd, J = 15.7 Hz, J = 4.9 Hz, J = 0.9 Hz, 1H), 5.90 (d, J = 11.7 Hz, 1H), 5.86 – 5.83 (m, 1H), 5.83 (ddd, J = 15.9 Hz, J = 6.8 Hz, J = 1.5 Hz, 1H), 5.73 – 5.70 (m, 1H), 5.42 (br s, 1H), 5.32 (dd, J = 6.8 Hz, J = 4.9 Hz, 1H), 4.95 (br s, 1H), 4.90 (br s, 1H), 4.29 – 4.25 (m, 1H), 4.18 (br s, 2H), 4.10 – 4.07 (m, 1H), 4.07 – 4.03 (m, 1H), 3.96 – 3.91 (m, 1H), 3.83 – 3.80 (m, 1H), 3.19 (dt, J = 6.4 Hz, J = 2.5 Hz, 1H), 3.02 (t, J = 2.5 Hz, 1H), 2.95 – 2.89 (m, 1H), 2.89 – 2.83 (m, 1H), 2.76 (d, J = 6.4 Hz, 1H, OH), 2.37 (dd, J = 14.5 Hz, J = 6.4 Hz, 1H), 2.18 (dd, J = 14.5 Hz, J = 6.8 Hz, 1H), 2.11 – 2.08 (m, 1H), 2.06 – 2.00 (m, 3H, 1 x OH), 1.99 – 1.97 (m, 1H), 196 – 1.93 (m, 1H), 1.92 – 1.89 (m, 1H), 1.89 – 1.85 (m, 1H), 1.80 – 1.74 (m, 1H), 1.69 (br s, 3H), 1.68 – 1.64 (m, 1H), 1.63 – 1.60 (m, 1H), 1.10 (ddd, J = 13.9 Hz, J = 8.6 Hz, J = 4.8 Hz, 1H), 0.90 (d, J = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ=165.6 (C_q), 144.8 (CH), 143.8 (C_q), 136.0 (CH), 131.5 (C_q), 128.6 (CH), 125.2 (CH), 124.8 (CH), 122.5 (CH), 119.7 (CH), 114.1 (CH_2), 77.1 (CH), 73.0 (CH), 72.3 (CH), 70.6 (CH), 67.4 (CH), 66.5 (CH), 65.8 (CH_2), 60.8 (CH), 52.4 (CH), 46.4 (CH_2), 41.9 (CH_2), 38.6 (CH_2), 35.7 (CH_2), 35.4 (CH_2), 35.3 (CH_2), 31.0 (CH_2), 27.0 (CH), 23.0 (CH_3), 20.1 (CH_3).

IR [cm^{-1}]: 3437, 2919, 2850, 1715, 1640, 1607, 1168, 855, 407.

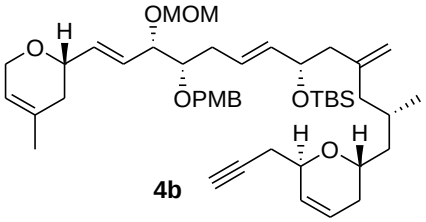
HRMS(ESI) calcd. for $C_{30}H_{42}O_6Na$: 537.2828, found: 537.2831

R_f= 0.41 (silica gel, hexane/EtOAc = 1:2)

$[\alpha]_D^{20}$ = -53.3 (*c* = 0.30, CH_2Cl_2)

Synthesis of isolaulimalide (**3**)

(5S,6S,10S,E)-6-(4-methoxybenzyloxy)-12,12,13,13-tetramethyl-10-((S)-4-methyl-2-methylene-5-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)pentyl)-5-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-2,4,11-trioxa-12-silatetradec-8-ene (**4b**):



To a stirred solution of **6b** (253 mg, 0.4327 mmol) in THF (8 mL) at -78 °C was added KHMDS (0.952 mL, 0.4760 mmol, 0.5 M in toluene) dropwise over 5 min. The yellow solution was allowed to stir for 3 min before **5** (144 mg, 0.369 mmol, in 1.0 mL THF) was added dropwise over 5 min. After stirring for another 90 min at the same temperature the reaction was quenched by adding H_2O (7 mL) and warmed to rt. The phases were separated and the aqueous phase was extracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 4:1). Yielding compound **4b** as viscous oil (273 mg, 0.3164 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.26 (d, J = 8.5 Hz, 2H), 6,84 (d, J = 8.5 Hz, 2H), 5.92 – 5.81 (m, 2H), 5.79 (dd, J = 15.7 Hz, J = 5.3 Hz, 1H), 5.68 (dd, J = 15.7 Hz, J = 6.7 Hz, 1H), 5.64 – 55.6 (m, 1H), 5.51 (dd, J = 15.4 Hz, J = 6.0 Hz, 1H), 5.42 (br s, 1H), 4.79 (br s, 1H), 4.77 (br s, 1H), 4.68 (d, J = 6.6 Hz, 1H), 4.58 (d, J = 6.6 Hz, 1H), 4.55 (s, 2H), 4.35 – 4.28 (m, 1H), 4.22 – 4.11 (m, 4H), 4.06 – 3.99 (m, 1H), 3.85 – 3.77 (m, 1H), 3.79 (s, 3H), 3.46 – 3.40 (m, 1H), 3.35 (s, 3H), 2.50 (ddd, J = 16.4 Hz, J = 6.8 Hz, J = 2.5 Hz, 1H), 2.42 (ddd, J = 16.4 Hz, J = 7.0 Hz, J = 2.6 Hz, 1H), 2.38 – 2.29 (m, 1H), 2.27 – 2.16 (m, 2H), 2.27 – 2.16 (m, 9H), 1.70 (br s, 3H), 1.62 (ddd, J = 13.5 Hz, J = 10.1 Hz, J = 3.2 Hz, 1H), 1.09 (ddd, J = 13.6 Hz, J = 9.5 Hz, J = 3.2 Hz, 1H), 0.92 – 0.84 (m, 12H), 0.03 (br s, 3H), 0.01 (br s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.4 (C_q), 144.7 (C_q), 135.9 (CH), 134.5 (CH), 131.5 (C_q), 131.0 (C_q), 129.6 (2 x CH), 128.1 (CH), 127.8 (CH), 126.4 (CH), 125.7 (CH), 119.9 (CH), 113.9 (CH_2), 113.8 (2 x CH), 94.6 (CH_2), 81.5 (C_q), 81.4 (CH), 77.4 (CH), 73.5 (CH), 72.7 (CH), 72.5 (CH), 70.9 (CH), 70.3 (CH), 66.5 (CH), 65.7 (CH_2), 55.8 (CH_3), 55.4 (CH_3), 45.3 (CH_2), 45.0 (CH_2), 42.5 (CH_2), 35.9 (CH_2), 33.7 (CH_2), 31.3 (CH_2), 27.0 (CH), 26.1 (3 x CH_3), 24.6 (CH_2), 23.1 (CH_3), 19.5 (CH_3), 18.4 (C_q), -4.0 (CH_3), -4.6 (CH_3).

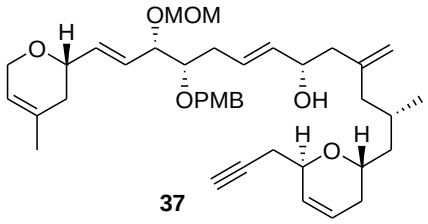
IR [cm^{-1}]: 3855, 2927, 1700, 1653, 1513, 1249, 1038, 835, 668.

HRMS(ESI) calcd. for $C_{45}H_{68}O_7Na$: 771.4632, found: 771.4626.

R_f = 0.52 (silica gel, hexane/EtOAc = 3:1)

$[\alpha]_D^{20}$ = -49.6 (*c* = 0.72, CH_2Cl_2)

(2S,6S,7E,10S,11S,12E)-10-(4-methoxybenzyloxy)-11-(methoxymethoxy)-2-methyl-13-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)-4-methylene-1-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)trideca-7,12-dien-6-ol (**37**):



To a stirred solution of compound **4b** (235 mg, 0.3137 mmol) in THF (3.5 mL) at 0 °C was added HF·pyridine (70%, 1.0 mL) dropwise in 10 min. After stirring at 0 °C for another 10 min the reaction was allowed to reach RT and stirred for 2 h. The mixture was diluted with CH_2Cl_2 (50 mL), cooled to 0 °C and quenched by slow addition of aq. sat. $NaHCO_3$ (100 mL). The phases were separated and the aqueous layer was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1). Yielding compound **37** as viscous oil (189 mg, 0.2977 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.27 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.92 – 5.87 (m, 1H), 5.86 – 5.76 (m, 3H), 5.74 – 5.64 (m, 2H), 5.59 – 5.48 (m, 1H), 5.42 (br s, 1H), 4.89 (br s, 1H), 4.88 (br s, 1H), 4.69 (dd, J = 13.2 Hz, J = 6.2 Hz, 1H), 4.61 – 4.52 (m, 3H), 4.35 – 4.29 (m, 1H), 4.22 – 4.13 (m, 4H), 4.03 (ddd, J = 9.7 Hz, J = 4.7 Hz, J = 4.7 Hz, 1H), 3.85 – 3.76 (m, 1H), 3.79 (s, 3H), 3.47 (ddd, J = 7.5 Hz, J = 5.0 Hz, J = 5.0 Hz, 1H), 3.37 (s, 3H), 2.51 (ddd, J = 16.5 Hz, J = 7.0 Hz, J = 2.6 Hz, 1H), 2.42 (ddd, J = 16.5 Hz, J = 6.8 Hz, J = 2.6 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.29 – 2.12 (m, 3H), 2.12 – 2.02 (m, 2H), 2.02 (t, J = 2.7 Hz, 1H), 2.01 – 1.79 (m, 5H), 1.70 (br s, 3H), 1.63 (ddd, J = 14.0 Hz, J = 9.9 Hz, J = 3.4 Hz, 1H), 1.14 (ddd, J = 14.0 Hz, J = 9.6 Hz, J = 3.2 Hz, 1H), 0.89 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.3 (C_q), 144.8 (C_q), 135.0 (CH), 134.7 (CH), 131.5 (C_q), 131.0 (C_q), 129.8 (2 x CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 125.8 (CH), 119.9 (CH), 114.5 (CH_2), 113.8 (2 x CH), 94.5 (CH_2), 81.2 (C_q), 80.9 (CH), 77.7 (CH), 73.5 (CH), 72.8 (CH_2), 71.1 (CH), 70.2 (CH), 70.0 (CH), 66.1 (CH), 65.7 (CH_2), 55.8 (CH_3), 55.4 (CH_3), 44.6 (CH_2), 44.3 (CH_2), 42.7 (CH_2), 35.9 (CH_2), 33.9 (CH_2), 31.3 (CH_2), 27.0 (CH), 24.6 (CH_2), 23.1 (CH_3), 19.5 (CH_3).

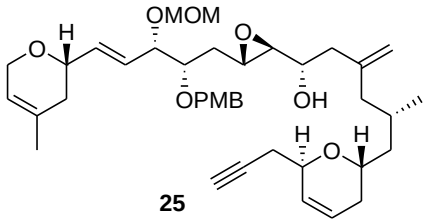
IR [cm^{-1}]: 3468, 2912, 1612, 1513, 1247, 1091, 1034, 707.

HRMS(ESI) calcd. for $C_{39}H_{54}O_7Na$: 657.3767, found: 657.3777.

R_f = 0.31 (silica gel, hexane/EtOAc = 2:1)

$[\alpha]_D^{20}$ = -69.0 (*c* = 1.40, CH_2Cl_2)

(1S,5S)-1-((2S,3S)-3-((2S,3S,E)-2-(4-methoxybenzyloxy)-3-(methoxymethoxy)-5-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)pent-4-enyl)oxiran-2-yl)-5-methyl-3-methylene-6-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)hexan-1-ol (**25**):



To a stirred suspension of powdered molecular sieves 4 Å (1.4 g) in CH_2Cl_2 (4.5 mL) at -20 °C, was added (+)-diisopropyl tartrate (708 µL, 0.354 mmol, 0.5 M in CH_2Cl_2) and Ti(O*i*Pr)$_4$ (590 µL 0.295 mmol, 0.5 M in CH_2Cl_2). The mixture was stirred for 30 min at the same temperature before t-butyl hydroperoxide (749 µL, 0.412, 0.55 M in CH_2Cl_2, dried over molecular sieves 4 Å) was added dropwise. The mixture was stirred for another 30 min before a solution of **37** (155 mg, 0.244 mmol, in 1.2 mL CH_2Cl_2) was added dropwise. The reaction was stirred for 3.5 h at -20 °C before it was quenched by addition of aq NaOH (4 mL, 1 M in brine). After stirring for 10 min the mixture was diluted with CH_2Cl_2 and brine, the phases were separated and the aqueous layer was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:ethylacetate = 3:1). Yielding epoxide **25** as colorless oil (115 mg, 0.177 mmol, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.29 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.92 – 5.86 (m, 1H), 5.85 – 5.77 (m, 2H), 5.67 (dd, J = 15.9 Hz, J = 6.8 Hz, 1H), 5.41 (br s, 1H), 4.90 (br s, 1H), 4.88 (br s, 1H), 4.71 – 4.66 (m, 2H), 4.62 – 4.56 (m, 2H), 4.35 – 4.29 (m, 1H), 4.24 – 4.19 (m, 1H), 4.17 (br s, 2H), 4.03 (ddd, J = 9.8 Hz, J = 4.7 Hz, J = 4.5 Hz, 1H), 3.82 – 3.76 (m, 1H), 3.79 (s, 3H), 3.71 (ddd, J = 9.3 Hz, J = 5.1 Hz, J = 3.7 Hz, 1H), 3.36 (s, 3H), 3.17 – 3.12 (m, 1H), 2.79 (dd, J = 4.0 Hz, J = 2.3 Hz, 1H), 2.51 (ddd, J = 16.5 Hz, J = 7.1 Hz, J = 2.7 Hz, 1H), 2.42 (ddd, J = 16.5 Hz, J = 6.8 Hz, J = 2.7 Hz, 1H), 2.30 (dd, J = 14.3 Hz, J = 3.9 Hz, 1H), 2.17 (dd, J = 14.4 Hz, J = 9.1 Hz, 1H), 2.11 – 2.00 (m, 3H), 1.99 – 1.83 (m, 6H), 1.83 – 1.77 (m, 1H), 1.70 (br s, 3H), 1.65 – 1.59 (m, 3H), 1.13 (ddd, J = 13.8 Hz, J = 9.5 Hz, J = 3.2 Hz, 1H), 0.89 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.5 (C_q), 144.2 (C_q), 134.9 (CH), 131.5 (C_q), 130.7 (C_q), 129.8 (2 x CH), 128.1 (CH), 127.1 (CH), 125.8 (CH), 119.9 (CH), 114.5 (CH_2), 113.8 (2 x CH), 94.6 (CH_2), 81.3 (C_q), 78.5 (CH), 77.4 (CH), 73.5 (CH), 73.2 (CH_2), 71.1 (CH), 70.3 (CH), 67.5 (CH), 66.1 (CH), 65.7 (CH_2), 61.5 (CH), 55.8 (CH_3), 55.4 (CH_3), 53.4 (CH), 44.6 (CH_2), 42.7 (CH_2), 40.5 (CH_2), 35.9 (CH_2), 33.7 (CH_2), 31.3 (CH_2), 27.1 (CH), 24.6 (CH_2), 23.1 (CH_3), 19.4 (CH_3).

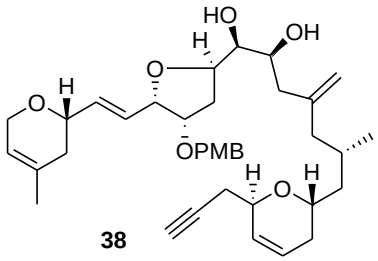
IR [cm^{-1}]: 2927, 1653, 1617, 1513, 1248, 1093, 1035, 668.

HRMS(ESI) calcd. for $C_{39}H_{54}O_8Na$: 673.3716, found: 673.3728.

R_f = 0.31 (silica gel, hexane/EtOAc = 2:1)

$[\alpha]_D^{20}$ = -82.5 (*c* = 1.18, CH_2Cl_2)

(1S,2S,6S)-1-((2R,4S,5S)-4-(4-methoxybenzyloxy)-5-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)tetrahydrofuran-2-yl)-6-methyl-4-methylene-7-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)heptane-1,2-diol (**38**):



To a stirred solution of epoxide **25** (83 mg, 0.1275 mmol) in THF (2 mL) at -20 °C was added thiophenol (114 µL, 1.02 mmol) and dropwise $BF_3 \cdot Et_2O$ (61.4 µL, 0.4845 mmol). The mixture was stirred at the same temperature for 6 h and then allowed to warm to rt and stirred for another 3 h. Et_3N (1.4 mL) was added, the reaction quenched with aq. sat. $NaHCO_3$ (10 mL) and diluted with CH_2Cl_2 (12 mL). The phases were separated and the aqueous layer was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 4:1 to 1:1). Yielding diol **38** as colorless oil (54 mg, 0.0890 mmol, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.25 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.96 (ddd, J = 15.7 Hz, J = 7.3 Hz, J = 1.0 Hz, 1H), 5.92 – 5.86 (m, 1H), 5.85 – 5.78 (m, 2H), 5.42 (br s, 1H), 4.92 (br s, 1H), 4.91 (br s, 1H), 4.52 (d, J = 11.7 Hz, 1H), 4.44 (d, J = 11.7 Hz, 1H), 4.43 – 4.39 (m, 2H), 4.36 – 4.29 (m, 1H), 4.19 (br s, 2H), 4.10 – 4.03 (m, 2H), 3.82 – 3.73 (m, 3H), 3.80 (s, 3H), 2.56 – 2.46 (m, 2H), 2.42 (ddd, J = 16.5 Hz, J = 6.9 Hz, J = 2.6 Hz, 1H), 2.31 – 2.25 (m, 2H), 2.22 (ddd, J = 13.1 Hz, J = 6.3 Hz, J = 1.8 Hz, 1H), 2.17 – 2.02 (m, 4H), 1.98 – 1.84 (m, 5H), 1.70 (br s, 3H), 1.67 – 1.59 (m, 2H), 1.16 (ddd, J = 13.8 Hz, J = 9.0 Hz, J = 3.2 Hz, 1H), 0.89 (d, J = 6.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.3 (C_q), 145.0 (C_q), 134.1 (CH), 131.6 (C_q), 130.6 (C_q), 129.2 (2 x CH), 128.0 (CH), 127.9 (CH), 125.8 (CH), 119.9 (CH), 114.8 (CH_2), 113.9 (2 x CH), 83.1 (CH), 81.3 (C_q), 80.8 (CH), 78.7 (CH), 75.1 (CH), 73.8 (CH), 71.4 (CH_2), 71.1 (CH), 70.3 (CH), 69.8 (CH), 66.2 (CH), 65.7 (CH_2), 55.4 (CH_3), 44.3 (CH_2), 42.6 (CH_2), 39.9 (CH_2), 35.9 (CH_2), 33.4 (CH_2), 31.3 (CH_2), 27.2 (CH), 24.6 (CH_2), 23.1 (CH_3), 19.4 (CH_3).

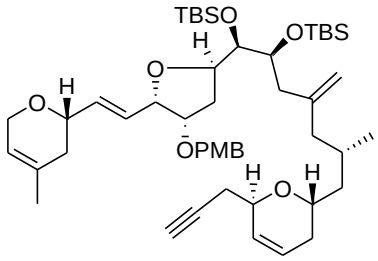
IR [cm^{-1}]: 3436, 2913, 1613, 1513, 1248, 1174, 1037, 706.

HRMS(ESI) calcd. for $C_{37}H_{50}O_7Na$: 629.3454, found: 629.3446.

R_f = 0.37 (silica gel, hexane/EtOAc = 1:1)

$[\alpha]_D^{20}$ = -51.4 (*c* = 1.05, CH_2Cl_2)

(5R,6S)-5-((2R,4S,5S)-4-(4-methoxybenzyloxy)-5-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)tetrahydrofuran-2-yl)-2,2,3,3,8,8,9,9-octamethyl-6-((S)-4-methyl-2-methylene-5-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)pentyl)-4,7-dioxa-3,8-disiladecane (**26**):



26

To a stirred solution of diol **38** (52 mg, 0.0857 mmol) in CH_2Cl_2 (2 mL) at -20 °C was added 2,6-lutidine (55 mg, 0.510 mmol) and dropwise TBSOTf (114 mg, 0.431 mmol). The reaction was allowed to reach rt after addition and was stirred for 8 h. The mixture was cooled to 0 °C, diluted with CH_2Cl_2 (70 mL) and quenched with sat. aq. $NaHCO_3$ (10 mL). The phases were separated and the aqueous phase extracted 3 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, hexane:EtOAc = 10:1 to 5:1). Yielding compound **26** as colorless, viscous oil (62 mg, 0.0742 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=7.26 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.94 (ddd, J = 15.6 Hz, J = 7.3 Hz, J = 0.9 Hz, 1H), 5.91 – 5.86 (m, 1H), 5.85 – 5.81 (m, 1H), 5.78 (dd, J = 15.6 Hz, J = 6.0 Hz, 1H), 5.42 (br s, 1H), 4.84 (br s, 1H), 4.80 (br s, 1H), 4.50 (d, J = 11.6 Hz, 1H), 4.43 (d, J = 11.6 Hz, 1H), 4.34 – 4.27 (m, 3H), 4.19 (br s, 2H), 4.09 – 4.03 (m, 1H), 4.03 – 3.98 (m, 1H), 3.90 – 3.86 (m, 1H), 3.85 – 3.82 (m, 1H), 3.82 – 3.77 (m, 2H), 3.80 (s, 3H), 2.49 (ddd, J = 16.4 Hz, J = 6.7 Hz, J = 2.7 Hz, 1H), 2.42 (ddd, J = 16.4 Hz, J = 7.2 Hz, J = 2.7 Hz, 1H), 2.20 (dd, J = 14.3 Hz, J = 6.9 Hz, 1H), 2.16 – 2.05 (m, 4 H), 2.00 (t, J = 2.7 Hz, 1H), 1.98 – 1.85 (m, 6 H), 1.70 (br s, 3H), 1.68 – 1.59 (m, 1H), 1.13 – 1.02 (m, 1H), 0.94 – 0.82 (m, 21H), 0.08 (s, 3H), 0.06 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=159.2 (C_q), 144.7 (C_q), 133.4 (CH), 131.8 (C_q), 130.9 (C_q), 129.2 (2 x CH), 128.8 (CH), 128.1 (CH), 125.7 (CH), 119.9 (CH), 114.4 (CH_2), 113.9 (2 x CH), 83.9 (CH), 81.4 (CH), 81.2 (C_q), 78.0 (CH), 77.3 (CH), 74.3 (CH), 74.0 (CH_2), 71.3 (CH), 70.8 (CH), 70.2 (CH), 65.9 (CH), 65.8 (CH_2), 55.4 (CH_3), 44.9 (CH_2), 42.3 (CH_2), 40.6 (CH_2), 35.9 (CH_2), 33.8 (CH_2), 31.2 (CH_2), 27.1 (CH), 26.2 (6 x CH_3), 24.6 (CH_2), 23.1 (CH_3), 19.6 (CH_3), 18.4 (C_q), 18.3 (C_q), -3.8 (CH_3), -3.9 (CH_3), -4.5 (2 x CH_3).

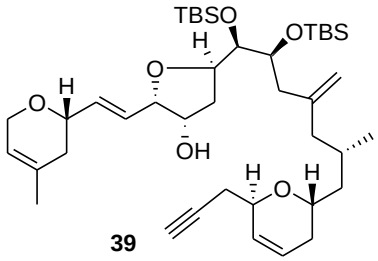
IR [cm^{-1}]: 2928, 1514, 1249, 1091, 835, 776.

HRMS(ESI) calcd. for $C_{49}H_{78}O_7Si_2Na$: 857.5184, found: 857.5195.

R_f= 0.66 (silica gel, hexane/EtOAc = 3:1)

$[\alpha]_D^{20}$ = - 82.3 (*c* = 0.65, CH_2Cl_2)

(2S,3S,5R)-2-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)-5-((5R,6S)-2,2,3,3,8,8,9,9-octamethyl-6-((S)-4-methyl-2-methylene-5-((2R,6R)-6-(prop-2-ynyl)-3,6-dihydro-2H-pyran-2-yl)pentyl)-4,7-dioxa-3,8-disiladecan-5-yl)tetrahydrofuran-3-ol (**39**):



To a stirred solution of compound **26** (52 mg, 0.06225 mmol) in a biphasic 1/1 mixture of CH_2Cl_2/aq. (pH = 7) buffer (4 mL) was added DDQ (55 mg, 0.2573 mmol) portionwise at rt. The reaction was stirred over night and diluted with aq. sat. $NaHCO_3$ (15 mL) and CH_2Cl_2 (10 mL). The phases were separated and the aqueous layer was extracted with 4 times with CH_2Cl_2. The combined organic layer was washed 2 times with aq. sat. $NaHCO_3$, dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 10:1 to 4:1). Yielding **39** as viscous oil (41 mg, 0.05733 mmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.93 – 5.86 (m, 2H), 5.85 – 5.79 (m, 2H), 5.42 (br s, 1H), 4.84 (br s, 1H), 4.80 (br s, 1H), 4.37 – 4.29 (m, 3H), 4.27 – 4.23 (m, 1H), 4.18 (br s, 2H), 4.09 – 4.03 (m, 1H), 3.95 – 3.91 (m, 1H), 3.84 (br d, J = 4.1 Hz, 1H), 3.82 – 3.77 (m, 1H), 2.50 (ddd, J = 16.4 Hz, J = 6.8 Hz, J = 2.8 Hz, 1H), 2.42 (ddd, J = 16.4 Hz, J = 7.2 Hz, J = 2.8 Hz, 1H), 2.24 (dd, J = 14.4 Hz, J = 6.6 Hz, 1H), 2.21 – 2.02 (m, 4 H), 2.01 (t, J = 2.6 Hz, 1H), 2.00 – 1.83 (m, 6H), 1.70 (br s, 3H), 1.68 – 1.59 (m, 1H), 1.10 (ddd, J = 13.7 Hz, J = 9.6 Hz, J = 3.1 Hz, 1H), 0.93 – 0.85 (m, 21H), 0.10 (s, 3H), 0.05 (s, 6H), 0.03 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=144.8 (C_q), 134.5 (CH), 131.6 (C_q), 128.1 (CH), 127.3 (CH), 125.8 (CH), 119.8 (CH), 114.4 (CH_2), 82.6 (CH), 81.2 (C_q), 78.0 (CH), 77.8 (CH), 74.7 (CH), 74.1 (CH), 73.7 (CH), 70.9 (CH), 70.2 (CH), 66.0 (CH), 65.8 (CH_2), 44.9 (CH_2), 42.5 (CH_2), 40.1 (CH_2), 37.5 (CH_2), 35.9 (CH_2), 31.3 (CH_2), 27.0 (CH), 26.2 (6 x CH_3), 24.6 (CH_2), 23.1 (CH_3), 19.4 (CH_3), 18.4 (C_q), 18.3 (C_q), -3.7 (CH_3), -4.0 (CH_3), -4.5 (CH_3), -4.6 (CH_3).

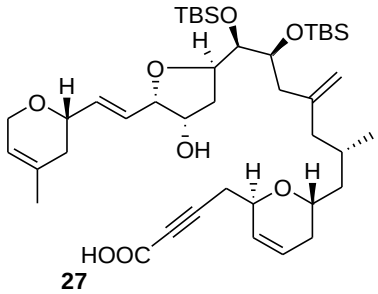
IR [cm^{-1}]: 3313, 2929, 2856, 1407, 1254, 1123, 836, 777, 636.

HRMS(ESI) calcd. for $C_{41}H_{70}O_6Si_2Na$: 737.4609, found: 737.4625.

R_f = 0.44 (silica gel, hexane/EtOAc = 3:1)

$[\alpha]_D^{20}$ = -43.7 (*c* = 1.23, CH_2Cl_2)

4-((2R,6R)-6-((2S,6S,7R)-6,7-bis(tert-butyldimethylsilyloxy)-7-((2R,4S,5S)-4-hydroxy-5-((E)-2-((S)-4-methyl-3,6-dihydro-2H-pyran-2-yl)vinyl)tetrahydrofuran-2-yl)-2-methyl-4-methyleneheptyl)-5,6-dihydro-2H-pyran-2-yl)but-2-ynoic acid (**27**):



To a stirred solution of compound **39** (35 mg, 0.0489 mmol) in THF (1.5 mL) at -78 °C was added *n*BuLi (0.122 mL, 0.195 mmol, 1.6 M in hexane) dropwise over a period of 5 min. The bright yellow solution was stirred for 5 min and then CO_2(g) was bubbled threw the reaction for 15 min. The reaction was warmed to rt, quenched by addition of aq. sat. NH_4Cl (7 mL) and diluted with CH_2Cl_2 (10 mL), the phases were separated and the aqueous phase was extracted 4 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The obtained oil was purified by column chromatography (silica gel, CH_2Cl_2:MeOH = 6:1). Yielding compound **27** as viscous oil (32 mg, 0.0421 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$) δ=5.93 – 5.82 (m, 4H), 5.40 (br s, 1H), 4.84 (br s, 1H), 4.80 (br s, 1H), 4.37 – 4.27 (m, 4H), 4.20 (br s, 2H), 4.11 – 4.05 (m, 1H), 3.96 – 3.90 (m, 1H), 3.82 (br d, J = 3.9 Hz, 1H), 3.87 – 3.70 (m, 1H), 2.57 (dd, J = 16.3 Hz, J = 5.8 Hz, 1H), 2.48 (dd, J = 16.3 Hz, J = 7.9 Hz, 1H), 2.24 – 1.94 (m, 8H), 1.94 – 1.79 (m, 4 H), 1.69 (br s, 3H), 1.67 – 1.08 (m, 1H), 1.16 – 1.08 (m, 1H), 0.91 – 0.86 (m, 21 H), 0.11 (s, 3H), 0.05 (s, 6H), 0.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ=160.1 (C_q), 144.7 (C_q), 134.1 (CH), 131.5 (C_q), 128.2 (2 x CH), 125.8 (CH), 119.7 (CH), 114.4 (CH_2), 88.6 (C_q), 82.8 (CH), 78.3 (CH), 78.1 (CH), 74.8 (CH), 74.0 (CH), 73.1 (C_q), 73.7(CH), 70.4 (CH), 66.4 (CH), 65.8 (CH_2), 45.2 (CH_2), 42.5 (CH_2), 37.5 (CH_2), 37.5 (CH_2), 31.6 (CH_2), 29.9 (CH_2), 27.2 (CH), 26.3 (6 x CH_3), 24.9 (CH_2), 23.1 (CH_3), 19.6 (CH_3), 18.4 (C_q), 18.3 (C_q), -3.7 (CH_3), -3.9 (CH_3), -4.5 (CH_3), -4.6 (CH_3).

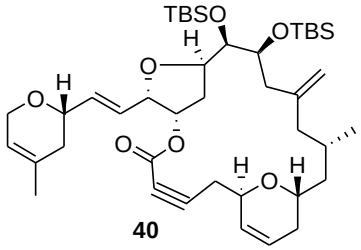
IR [cm^{-1}]:2929, 2857, 1580, 1388, 1254, 1046, 835, 777.

HRMS(ESI) calcd. for $C_{42}H_{70}O_8Si_2Na$: 781.4507, found: 781.4519.

R_f = 0.23 (silica gel, CH_2Cl_2/MeOH = 8:1)

$[\alpha]_D^{20}$ = -37.8 (*c* = 0.88, CH_2Cl_2)

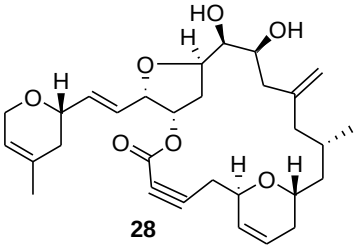
Macrocycle **40**



To a stirred solution of *seco* acid **27** (15.0 mg, 0.0198) in benzene (1 mL) at rt was added Et_3N (8.2 µL, 0.0812 mmol) and dropwise 2,4,6-trichlorobenzoyl chloride (7.6 µL, 0.0312 mmol). The solution was stirred for 4 h before it was diluted with benzene (10 mL) and added over 6 h *via* a syringe pump into a stirred solution of DMAP (24.2 mg, 0.1982 mmol) in benzene (130 mL). After additional 6 h the

mixture was concentrated to about 20 mL, aq. sat. $NaHCO_3$ (15 mL) was added and the mixture was stirred for 20 min. The phases were separated and the aqueous layer was exracted 4 times with EtOAc. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 10:1 to 7:1). Yielding a 4:1 mixture of **40** and the dimer as viscous oil (8.4 mg) that was used without further separation in the next step.

Diol **28**:



To a stirred solution (**PVC flask**) of a 4:1 mixture of compound **40** and the dimer (7 mg) in THF (1 mL) at 0 °C was added HF·pyridine (70 %, 400 µL) dropwise in 5 min. After stirring at 0 °C for another 10 min the reaction was allowed to reach rt and stirred for 5 h. The mixture was diluted with CH_2Cl_2 (5 mL), cooled to 0 °C and quenched by slow addition of aq. sat. $NaHCO_3$ (8 mL). The phases were separated and the aqueous layer was extracted 5 times with CH_2Cl_2. The combined organic phase was dried over magnesium sulfate, filtered and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1 to 1:2). Yielding compound **43** as colorless oil (3.2 mg, 0.00619 mmol, 32 % over two steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ=5.93 – 5.89 (m, 1H), 5.86 – 5.84 (m, 2H), 5.63 – 5.60 (m, 1H), 5.43 – 5.41 (m, 2H), 4.92 (br s, 2H) 4.55 (dd, J = 6.2 Hz, J = 4.9 Hz, 1H), 4.43 (br d, J = 10.6 Hz, 1H), 4.29 (ddd, J = 11.7 Hz, J = 3.8 Hz, J = 1.5 Hz, 1H), 4.20 (br s, 1H), 4.20 – 4.16 (m, 2H), 3.78 – 3.73 (m, 1H), 2.72 (dd, J = 18.0 Hz, J = 11.1 Hz, 1H), 2.41 (dd, J = 18.0 Hz, J = 2.3 Hz, 1H), 2.34 (d, J = 2.6 Hz, 1H), 2.22 (ddd, J = 13.6 Hz, J = 11.7 Hz, J = 3.4 Hz, 1H), 2.17 – 2.08 (m, 3H), 2.05 (dd, J = 13.6 Hz, J = 4.2 Hz, 1H), 2.03 – 1.98 (m, 1H), 1.98 – 1.92 (m, 3H), 1.86 (dd, J = 13.6 Hz, J = 11.0 Hz, 1H), 1.70 (br s, 3H), 1.60 (ddd, J = 14.0 Hz, J = 10.6 Hz, J = 3.0 Hz, 1H), 1.15 (ddd, J = 14.0 Hz, J = 11.1 Hz, J = 2.6 Hz, 1H), 0.80 (d, J = 6.4 Hz, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$) δ=153.1 (C_q), 144.2 (C_q), 135.8 (CH), 131.5 (C_q), 127.6 (CH), 126.6 (CH), 126.0 (CH), 119.8 (CH), 113.9 (CH_2), 87.7 (C_q), 80.9 (CH), 78.7 (CH), 78.3 (CH), 73.8 (C_q), 73.6 (CH), 71.8 (CH), 71.1 (CH), 69.7 (CH), 65.7 (CH_2), 64.4 (CH), 46.2 (CH_2), 44.4 (CH_2), 35.8 (CH_2), 35.4 (CH_2), 34.6 (CH_2), 31.6 (CH_2), 25.8 (CH), 24.2 (CH_2), 23.1 (CH_3), 17.3 (CH_3).

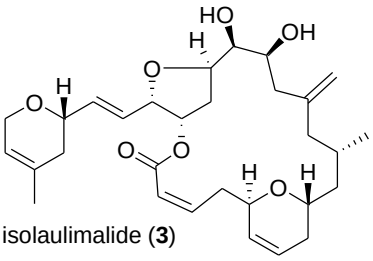
IR [cm^{-1}]: 2924, 2853, 2236, 1713, 1459, 1247, 1071, 672.

HRMS(ESI) calcd. for $C_{30}H_{40}O_7Na$: 535.2672, found: 535.2682.

R_f = 0.32 (silica gel, hexane/EtOAc = 1:2)

$[\alpha]_D^{20}$ = 26.2 (*c* = 0.13, CH_2Cl_2)

Isolaulimalide (**3**):



isolaulimalide (**3**)

To a stirred solution of diol **28** (3.1 mg, 0.00602 mmol) in a 1:1 mixture of EtOAc and cyclohexene (1 mL) at rt was added quinoline (3.6 µL). H_2 (balloon) was bubbled threw the reaction and Lindlar catalyst (3 mg) was added. After 2 h the reaction was filtered threw a short pad of celite, to remove the catalyst and subsequently the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel, hexane:EtOAc = 2:1 to 1:2). Yielding isolaulimalide (**3**) as white solid (3.0 mg, 0.00583 mmol, 97%), that was identical in every aspect with the reported data of the natural compound.

^{1}H NMR (600 MHz, $CDCl_3$) δ=6.19 (ddd, J = 11.7 Hz, J = 10.6 Hz, J = 6.8 Hz, 1H), 5.90 (ddd, J = 15.7 Hz, J = 5.8 Hz, J = 1.4 Hz, 1H), 5.88 – 5.84 (m, 2H), 5.76 – 5.72 (m, 1H), 5.70 (ddd, J = 15.7 Hz, J = 5.9 Hz, J = 1.4 Hz, 1H), 5.56 (t, J = 4.02 Hz, 1H), 5.37 (br s, 1H), 4.89 (br s, 1H), 4.88 (br s, 1H), 4.63 – 4.60 (m, 1H), 4.36 (ddd, J = 10.9 Hz, J = 4.8 Hz, J = 4.8 Hz, 1H), 4.32 – 4.27 (m, 1H), 4.15 – 4.11 (m, 3H), 4.06 (br d, J = 9.4 Hz, 1H), 4.00 – 3.96 (m, 1H), 3.66 – 3.61 (m, 1H), 3.18 (dddd, J = 12.0 Hz, J = 10.5 Hz, J = 5.3 Hz, J = 1.5 Hz, 1H), 2.51 (dddd, J = 12.1 Hz, J = 9.7 Hz, J = 6.9 Hz, J = 0.8 Hz, 1H), 2.36 (ddd, J = 13.7 Hz, J = 10.9 Hz, J = 4.4 Hz, 1H), 2.30 – 2.24 (m, 1H), 2.21 (dd, J = 13.5 Hz, J = 5.2 Hz, 1H), 2.23 – 2.17 (m, 2H), 2.12 – 2.08 (m, 1H), 2.02 – 1.92 (m, 4H), 1.87 – 1.81 (m, 2H), 1.67 (br s, 3H), 1.51 (ddd, J = 14.0 Hz, J = 9.2 Hz, J = 2.2 Hz, 1H), 1.13 (ddd, J = 14.0 Hz, J = 9.4 Hz, J = 2.6 Hz, 1H), 0.86 (d, J = 6.4 Hz, 3H).

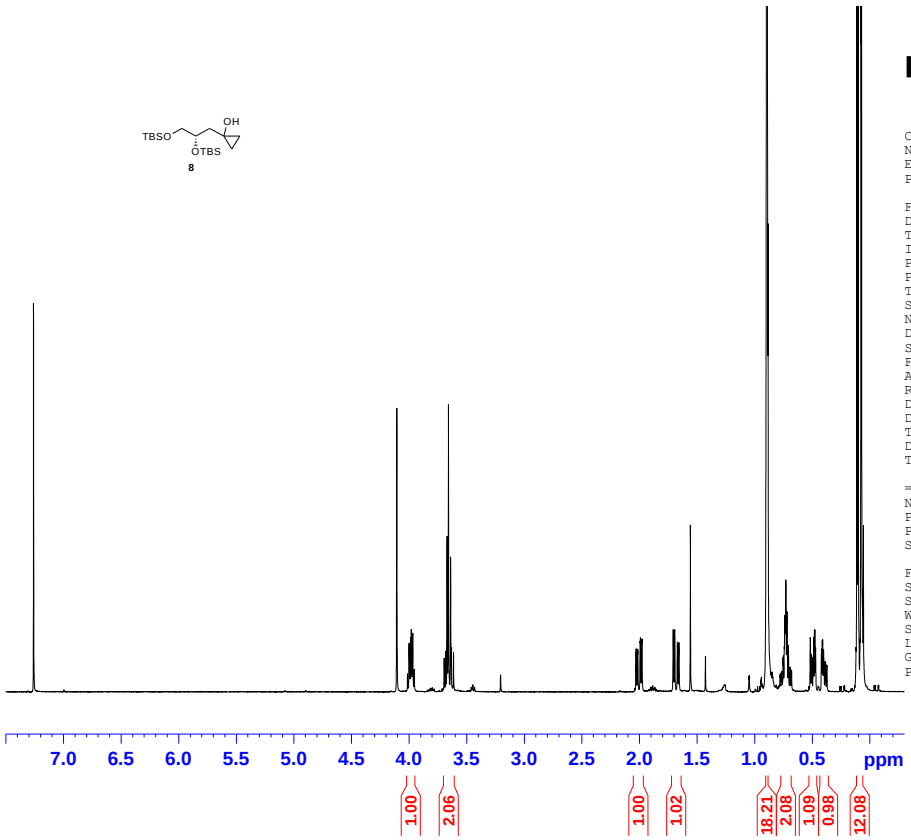
^{13}C NMR (150 MHz, $CDCl_3$) δ=165.5 (C_q), 145.0 (C_q), 143.2 (CH), 134.1 (CH), 131.5 (C_q), 128.3 (CH), 125.9 (CH), 125.7 (CH), 123.1 (CH), 119.9 (CH), 113.8 (CH_2), 81.6 (CH), 78.2 (CH), 76.8 (CH), 74.6 (CH), 73.5 (CH), 73.0 (CH), 70.6 (CH), 66.9 (CH), 65.6 (CH_2), 45.7 (CH_2), 43.0 (CH_2), 36.0 (CH_2), 35.7 (CH_2), 35.5 (CH_2), 34.7 (CH_2), 31.9 (CH_2), 27.5 (CH), 23.1 (CH_3), 19.9 (CH_3).

IR [cm^{-1}]: 3425, 2917, 1713, 1644, 1033.

HRMS(EI) calcd. for $C_{30}H_{42}O_7$ 514.2931, found: 514.2922.

R_f = 0.31 (silica gel, hexane/EtOAc = 1:2)

$[\alpha]_D^{20}$ = -17.9 (*c* = 0.28, CH_2Cl_2)

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EXPNO                 120
PROCNO                  1

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Time                14.23
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   181
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300094 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
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PC                  1.00
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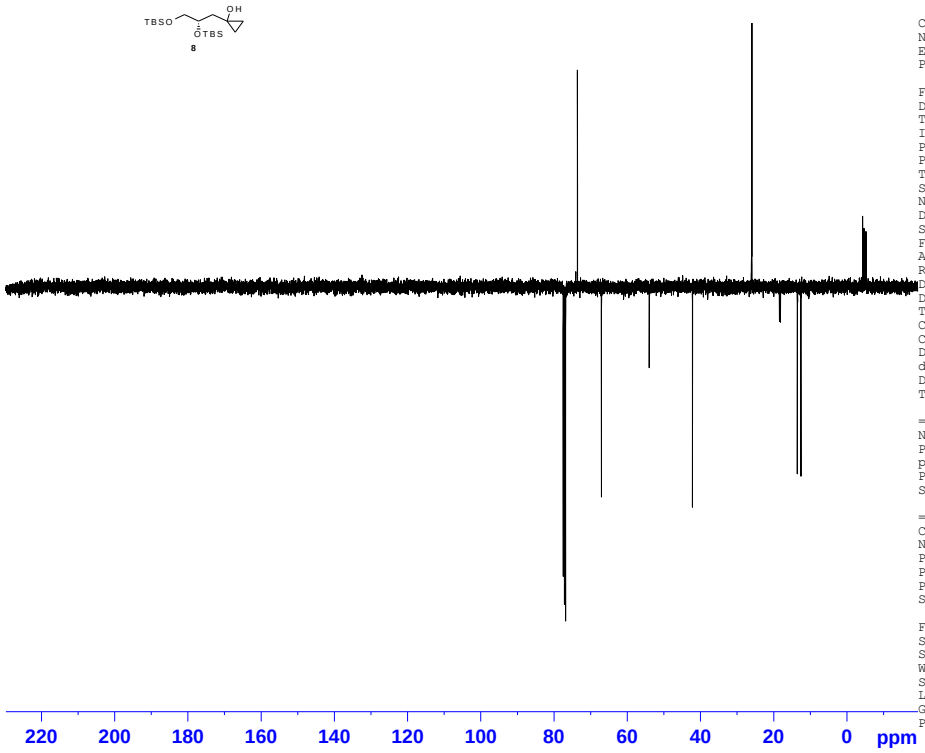


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Current Data Parameters
NAME              ango115
EXPNO                 121
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060725
Time                14.21
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG              jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG               14596.5
DW                19.950 usec
DE                 6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127526 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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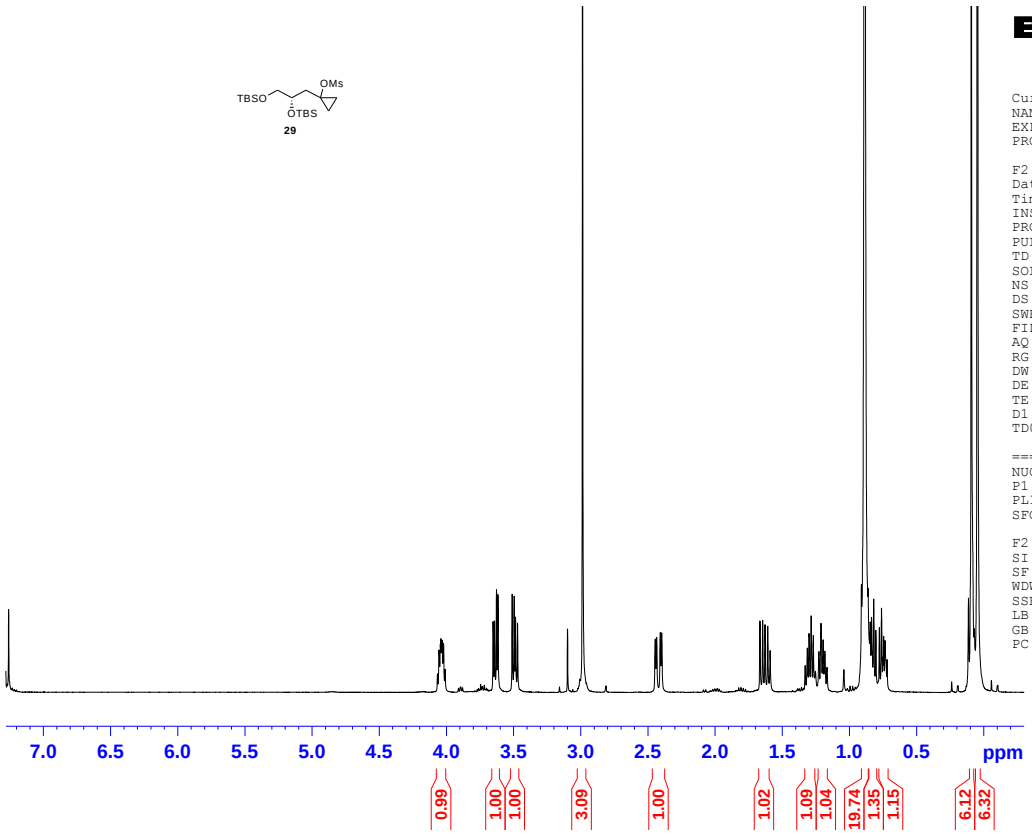


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Current Data Parameters
NAME              ango117
EXPNO                  80
PROCNO                  1

F2 - Acquisition Parameters
Date_             20060921
Time                 14.23
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                   80.6
DW                 60.400 usec
DE                   6.00 usec
TE                  300.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.75 usec
PL1                  -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300096 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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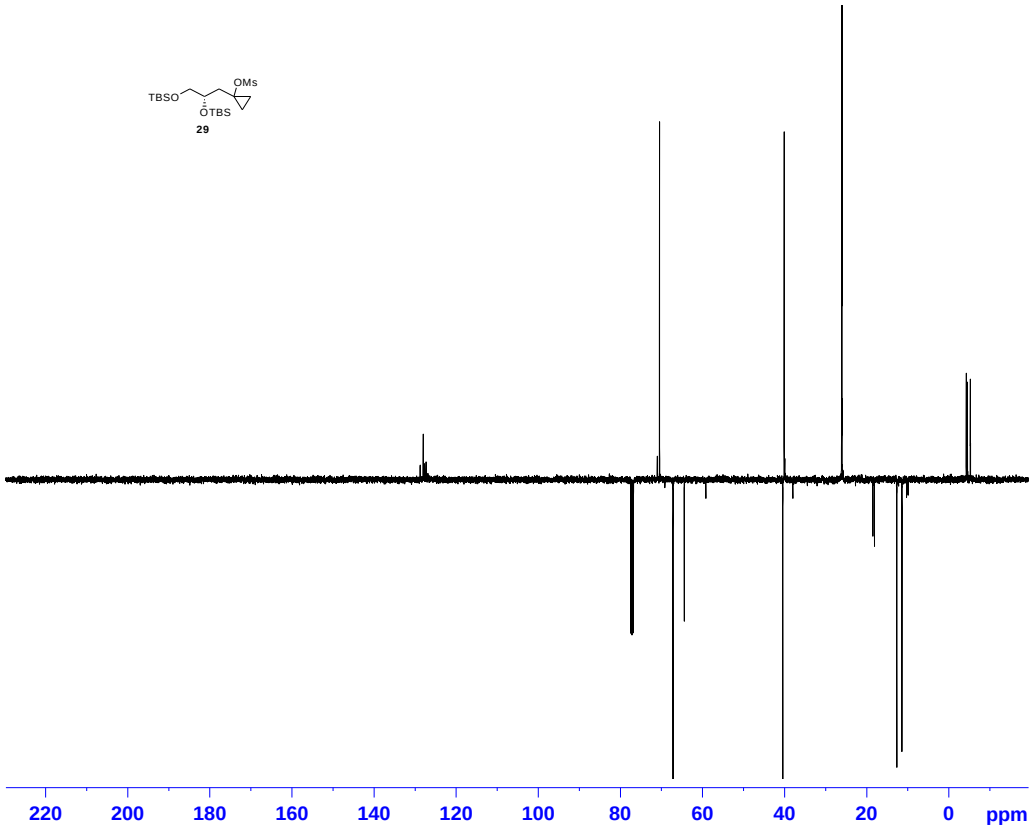


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Current Data Parameters
NAME              ango117
EXPNO                  81
PROCNO                  1

F2 - Acquisition Parameters
Date_             20060921
Time                 15.21
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG                jmod
TD                   65536
SOLVENT              CDCl3
NS                    1000
DS                       2
SWH             25062.656 Hz
FIDRES           0.382426 Hz
AQ              1.3074932 sec
RG                  9195.2
DW                  19.950 usec
DE                   6.00 usec
TE                  300.2 K
CNST2         145.0000000
CNST11          1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.30 usec
p2                   20.60 usec
PL1                  -1.00 dB
SFO1          100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                100.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127541 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
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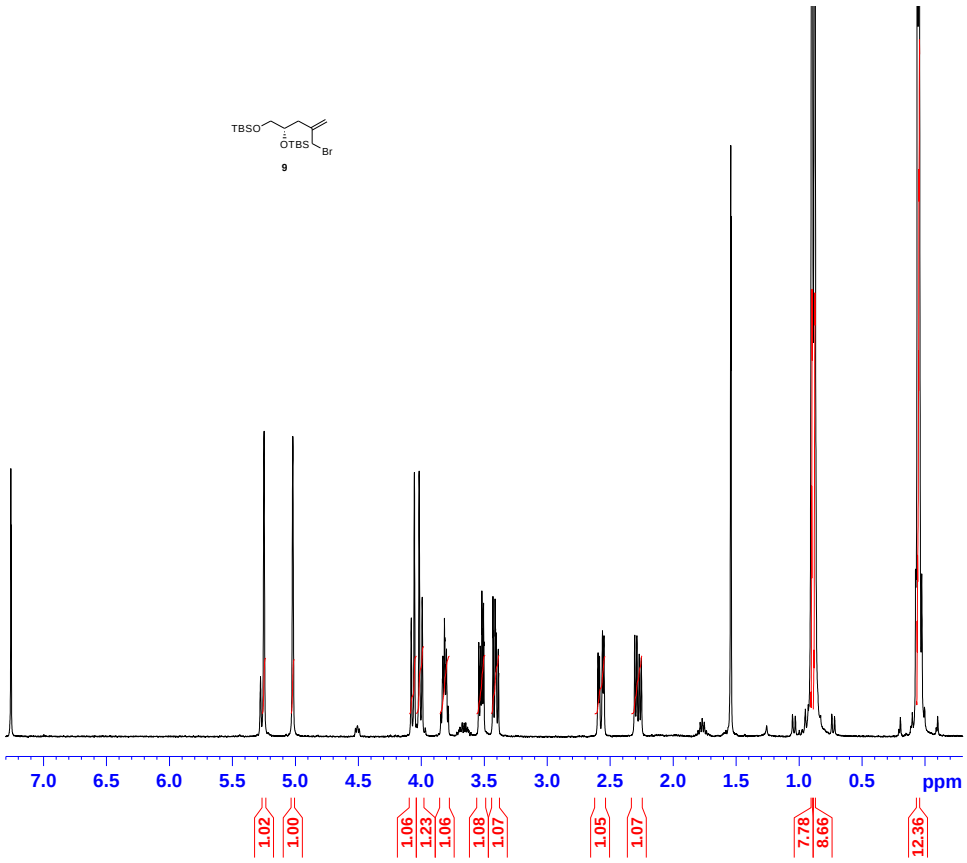


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Current Data Parameters
NAME              ango329
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080803
Time                19.50
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                    256
DW                 60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  8.75 usec
PL1                -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300096 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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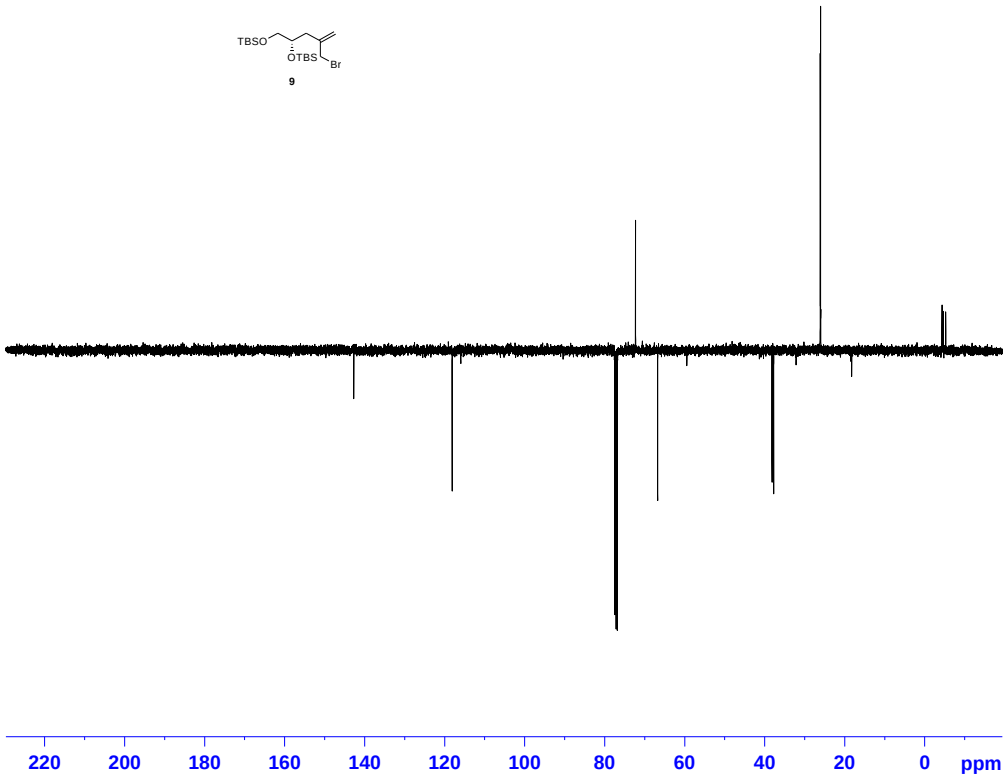


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Current Data Parameters
NAME              ango329
EXPNO                  10
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080803
Time                18.31
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                  65536
SOLVENT             CDCl3
NS                   1500
DS                      2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                 10321.3
DW                  19.950 usec
DE                    6.00 usec
TE                   300.2 K
CNST2        145.0000000
CNST11         1.00000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.30 usec
p2                  20.60 usec
PL1                 -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 -3.00 dB
PL12                16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127530 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
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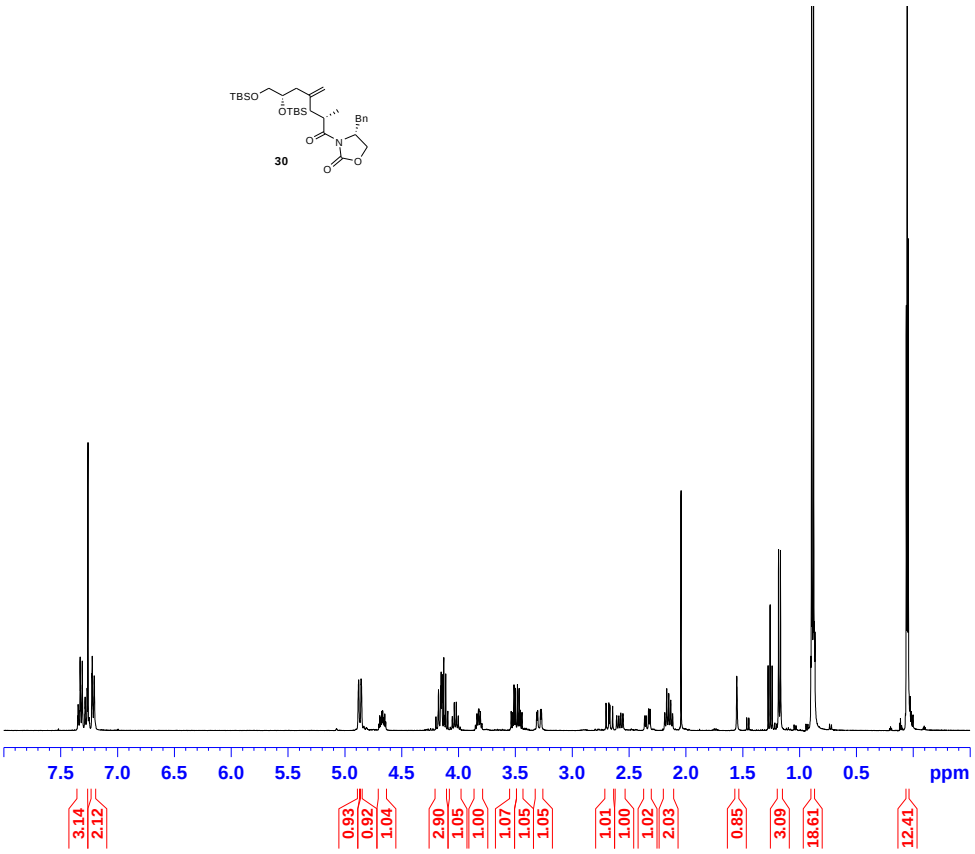


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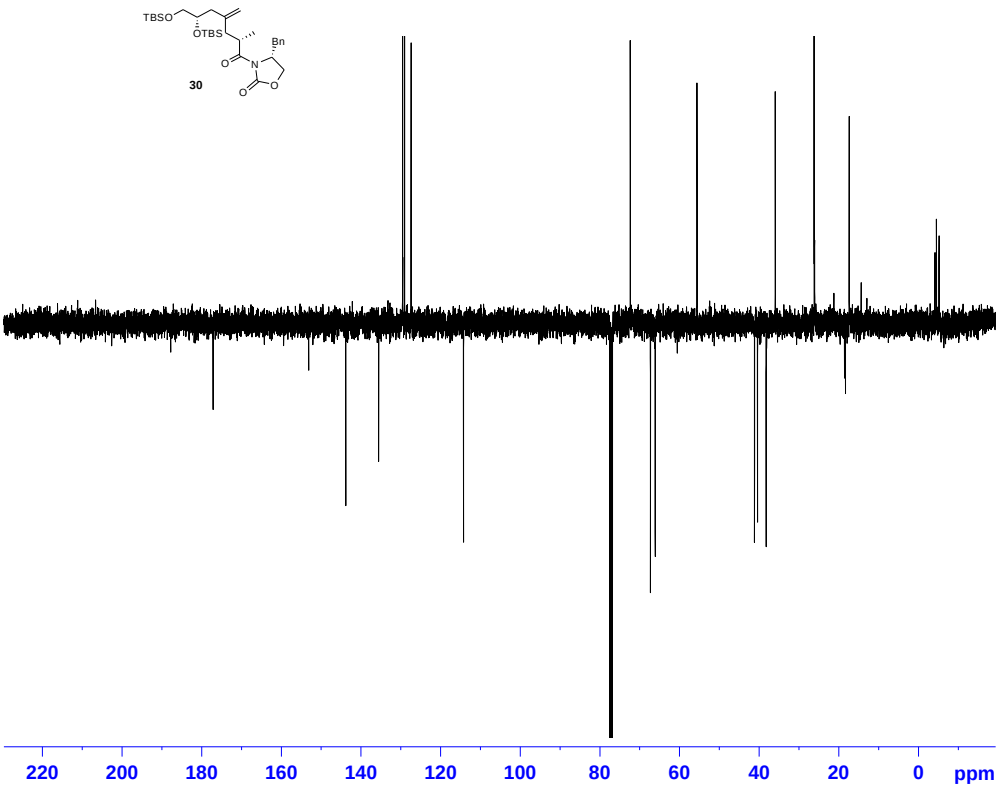
Current Data Parameters
NAME              ango177
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_            20061003
Time               11.02
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 322.5
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.75 usec
PL1                -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

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Current Data Parameters
NAME              ango177
EXPNO                  21
PROCNO                  1

F2 - Acquisition Parameters
Date_            20061003
Time               12.00
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                9195.2
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
p2                 20.60 usec
PL1                -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -3.00 dB
PL12               16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127534 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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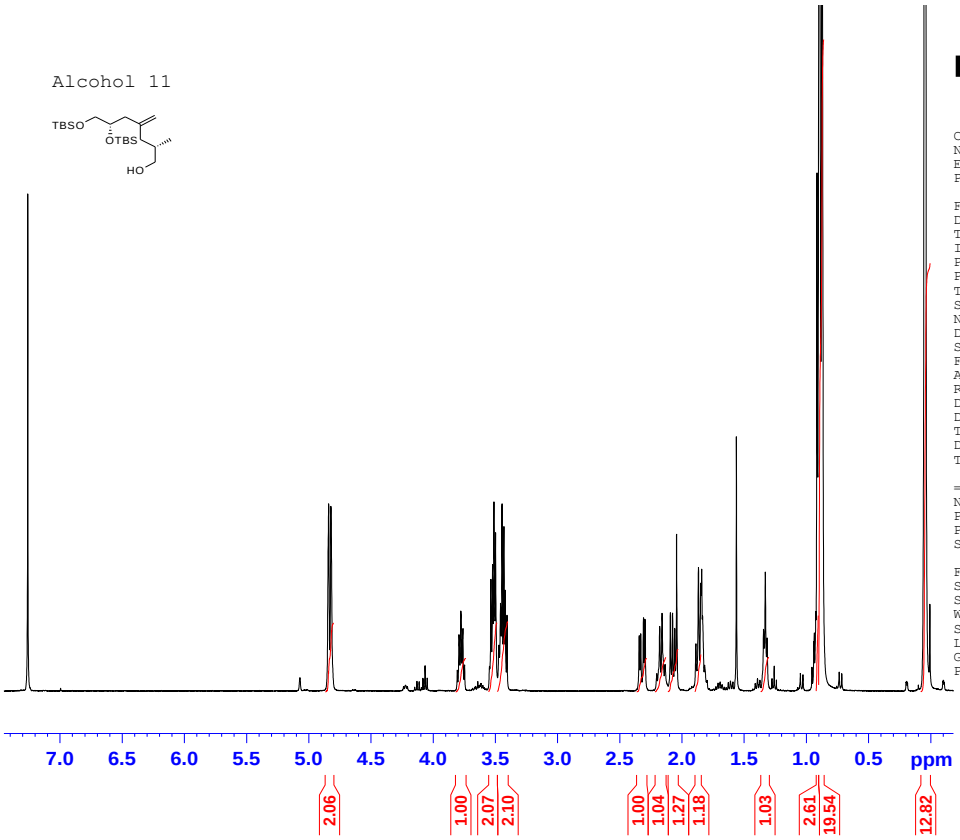
Alcohol 11

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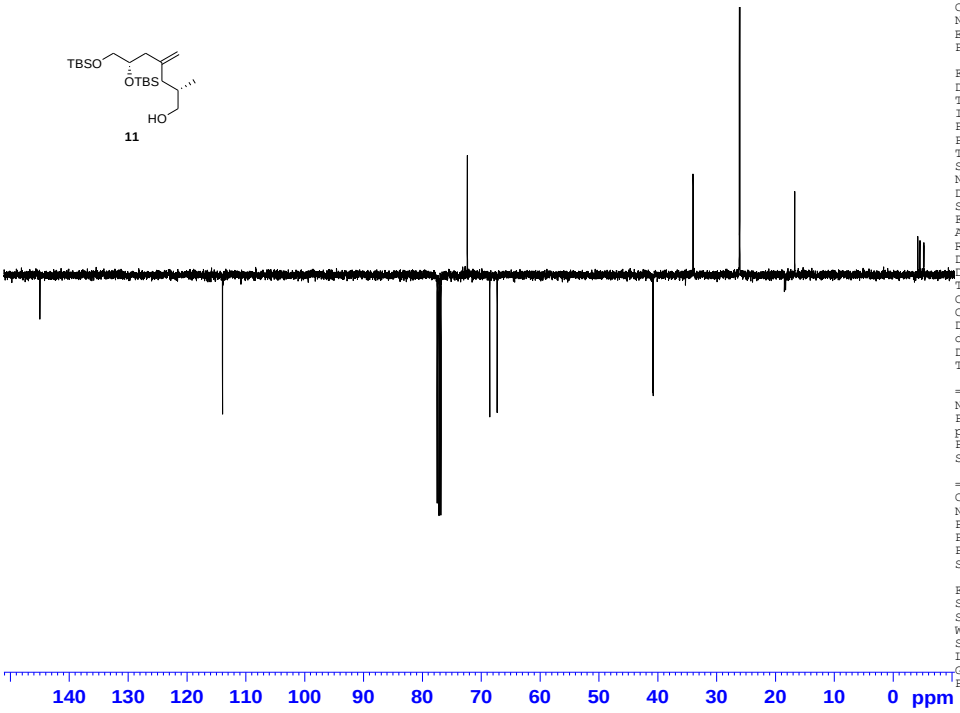
Current Data Parameters
NAME              ango138
EXPNO                 100
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060823
Time               17.12
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   256
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```


11

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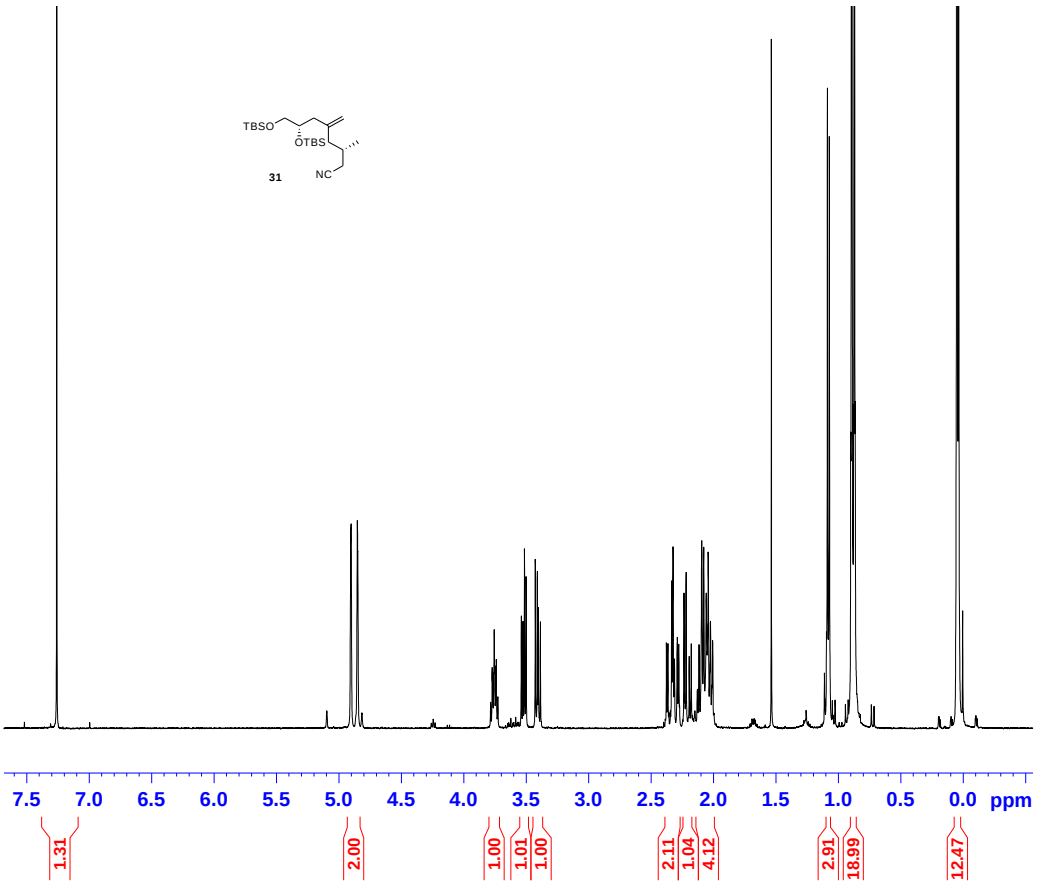
Current Data Parameters
NAME              ango138
EXPNO                 101
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060823
Time               16.56
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                7298.2
DW                19.950 usec
DE                 6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127530 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```




```
Current Data Parameters
NAME              ango140
EXPNO                  40
PROCNO                  1

F2 - Acquisition Parameters
Date_             20060825
Time                 15.50
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDC13
NS                     16
DS                      2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 322.5
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.75 usec
PL1                 -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF           400.1300093 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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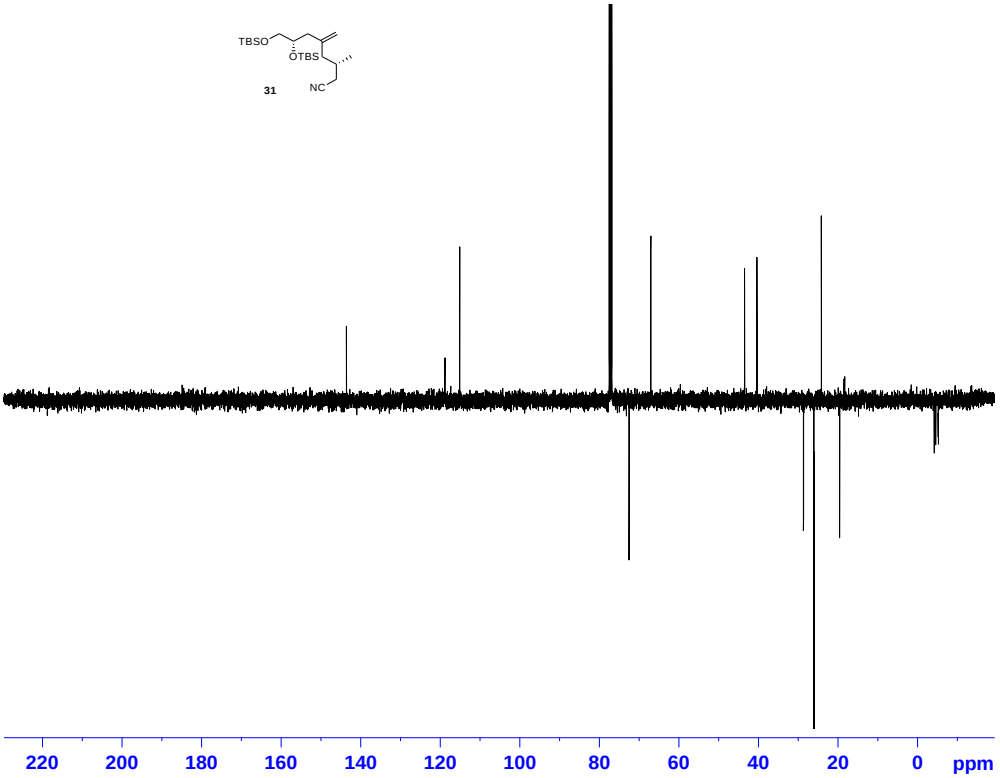


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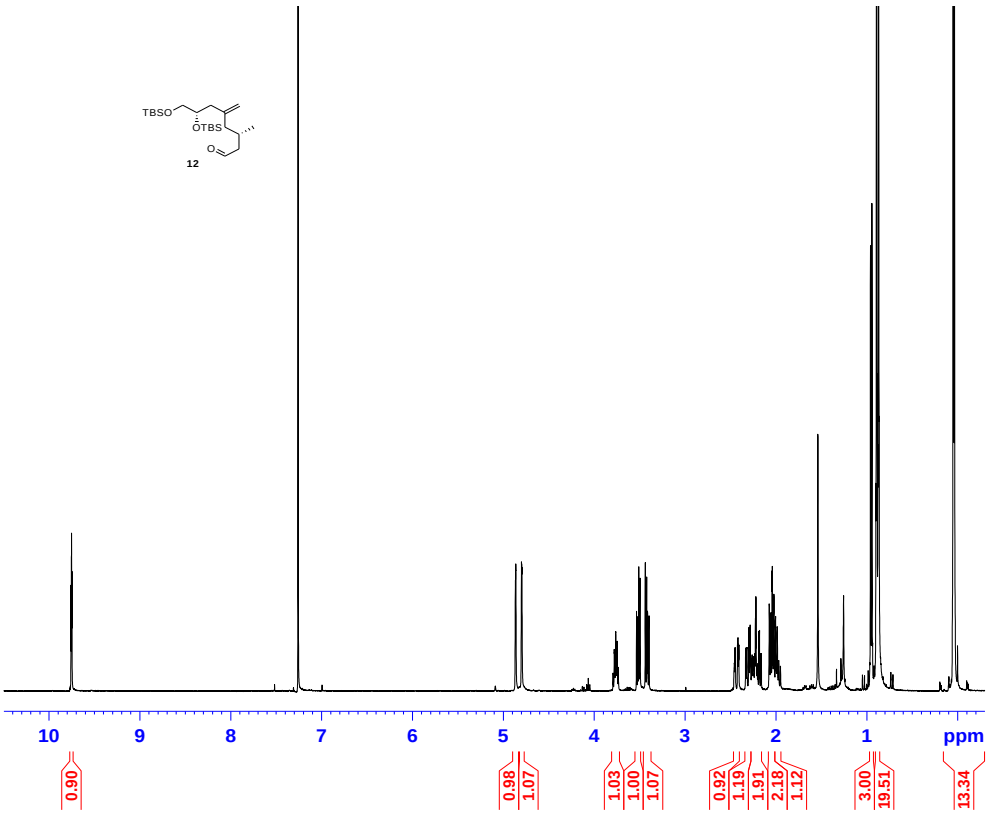
Current Data Parameters
NAME              ango140
EXPNO                  41
PROCNO                  1

F2 - Acquisition Parameters
Date_             20060825
Time                 15.52
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG              jmod
TD                  65536
SOLVENT             CDC13
NS                   1000
DS                      2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                 7298.2
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.30 usec
p2                  20.60 usec
PL1                 -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2             100.00 usec
PL2                 -3.00 dB
PL12                16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF           100.6127529 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

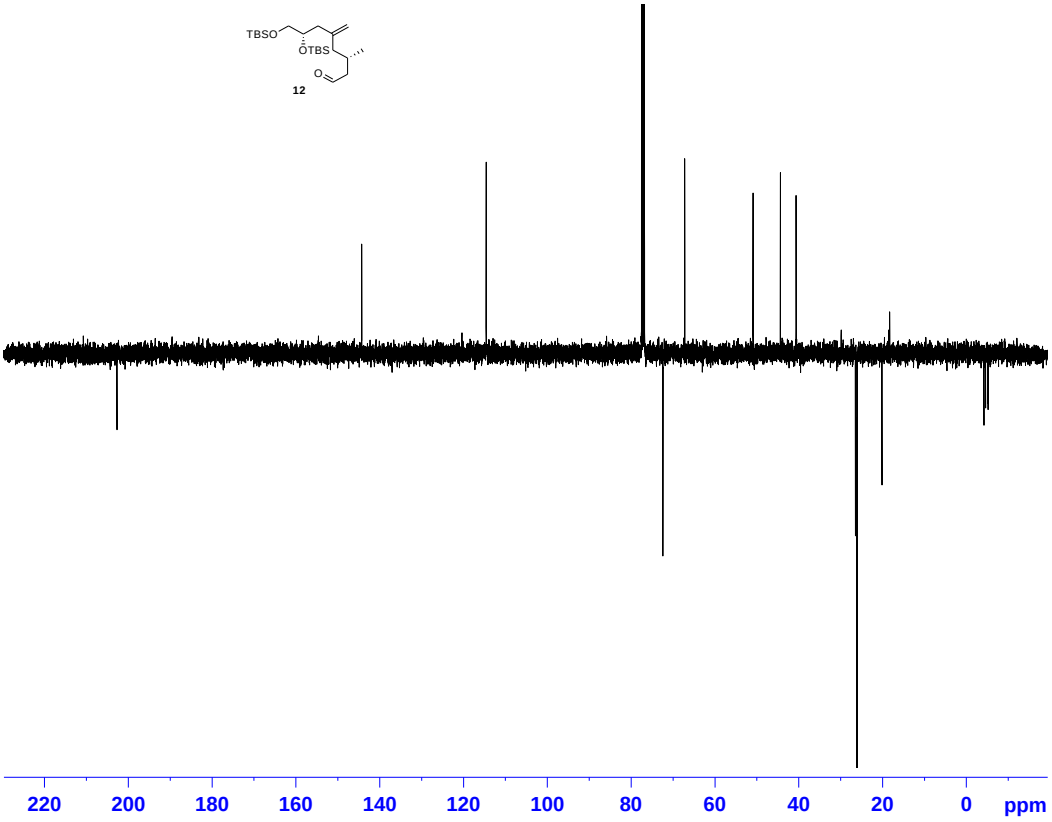



```
Current Data Parameters
NAME              ango134
EXPNO                  20
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060821
Time               12.30
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 406.4
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300094 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



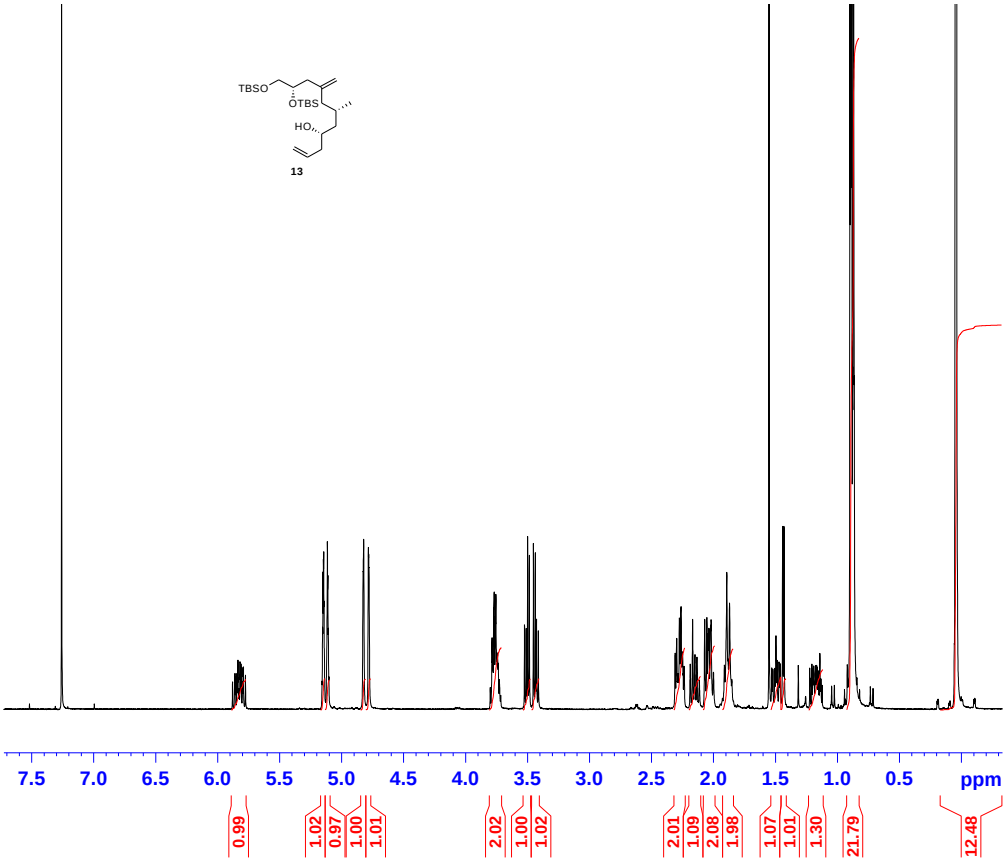

```
Current Data Parameters
NAME              ango134
EXPNO                  21
PROCNO                  1

F2 - Acquisition Parameters
Date_            20060821
Time               14.23
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  2000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                5792.6
DW                19.950 usec
DE                  6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127530 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

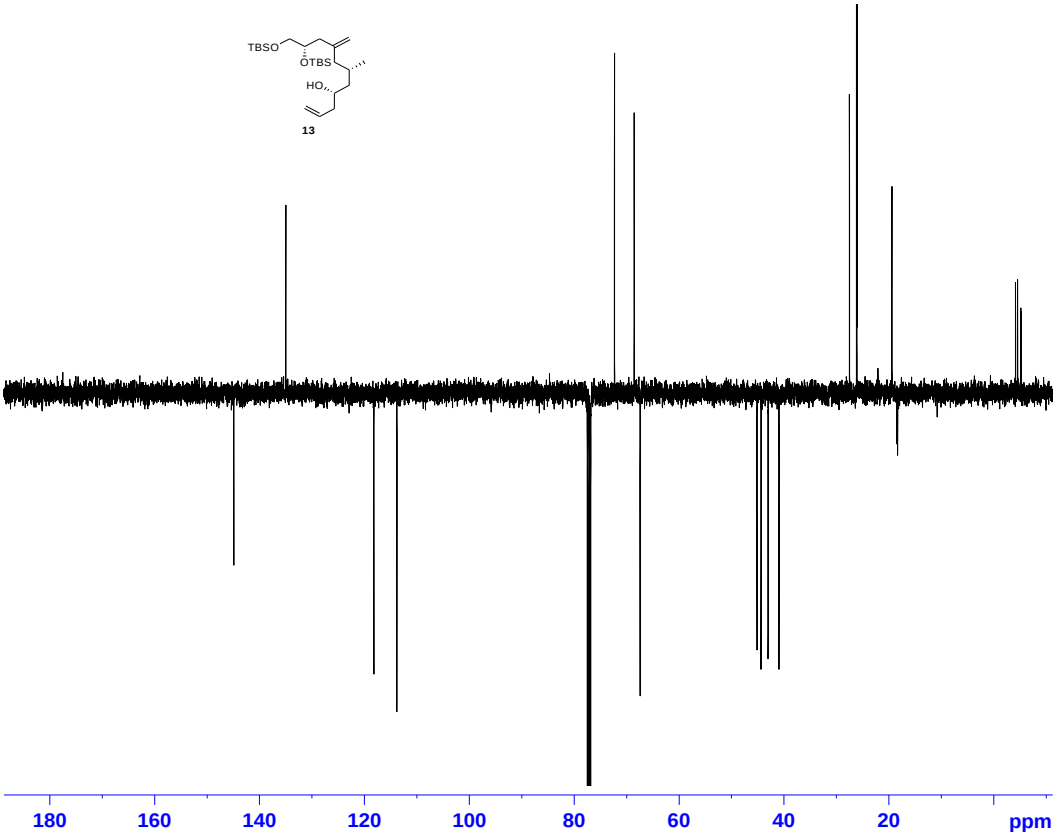



```
Current Data Parameters
NAME          ango145-1
EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20060901
Time               8.57
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG               287.4
DW              60.400 usec
DE                6.00 usec
TE               300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



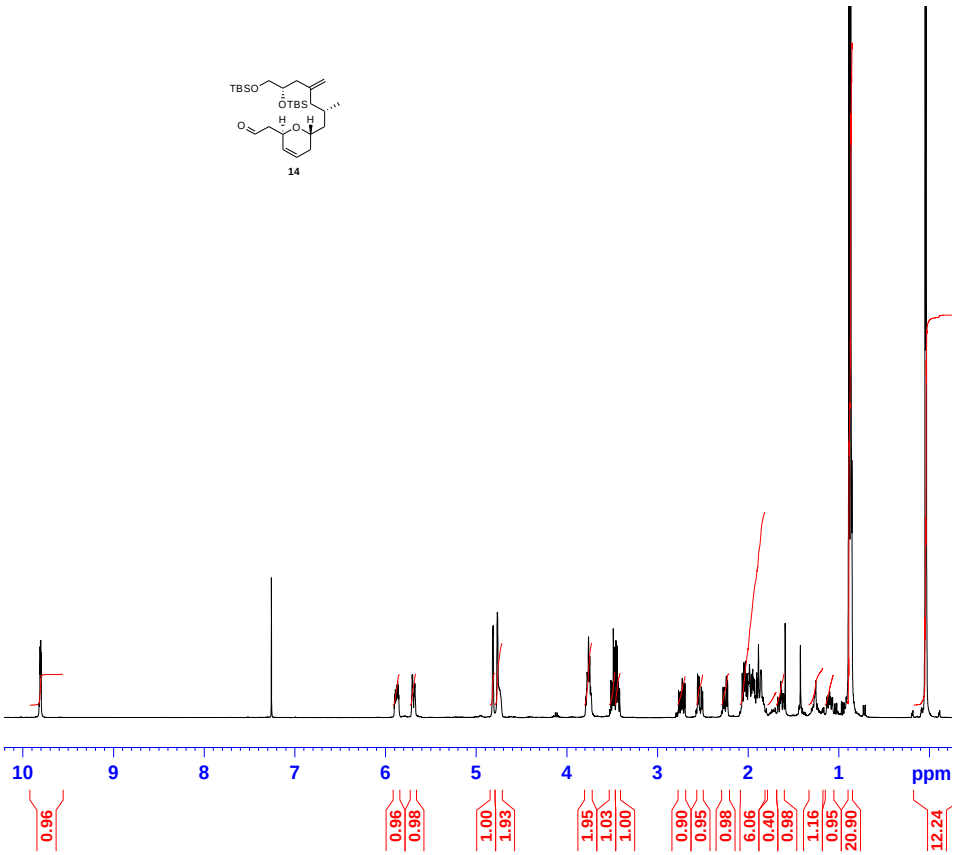

```
Current Data Parameters
NAME          ango145-1
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20060901
Time              10.22
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                65536
SOLVENT           CDCl3
NS                 1500
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG               5792.6
DW              19.950 usec
DE                6.00 usec
TE               300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.30 usec
p2                20.60 usec
PL1              -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127530 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

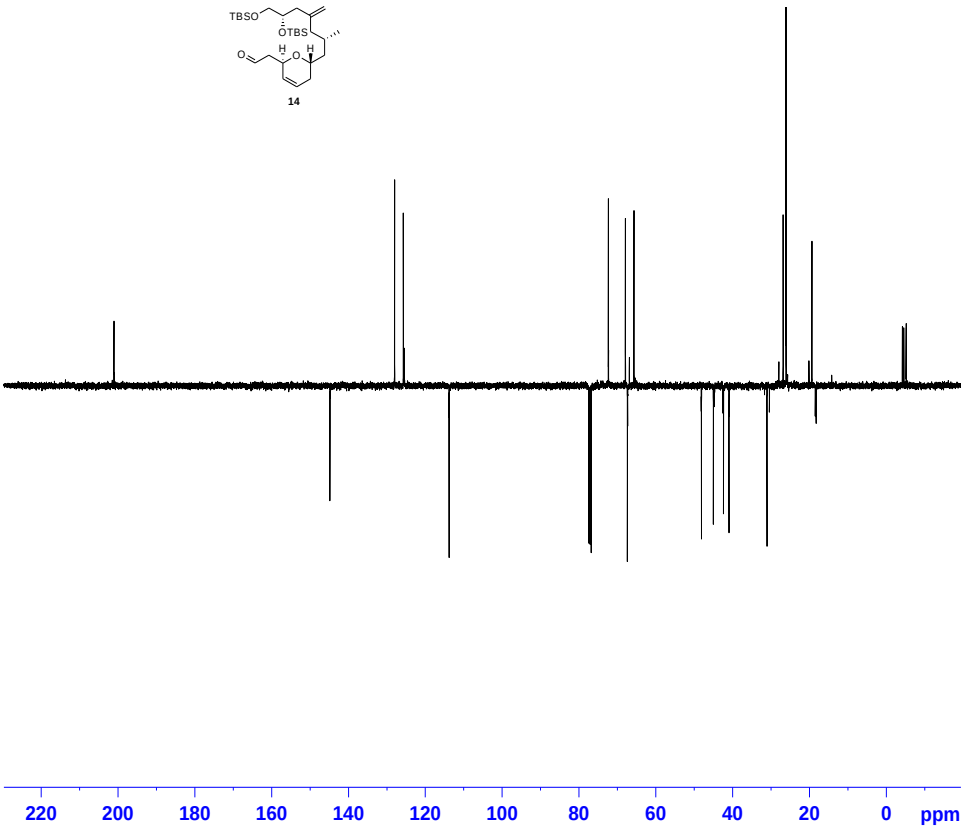


Current Data Parameters
NAME ango244
EXPNO 80
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061206
Time 0.37
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 101.6
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.75 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1298695 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



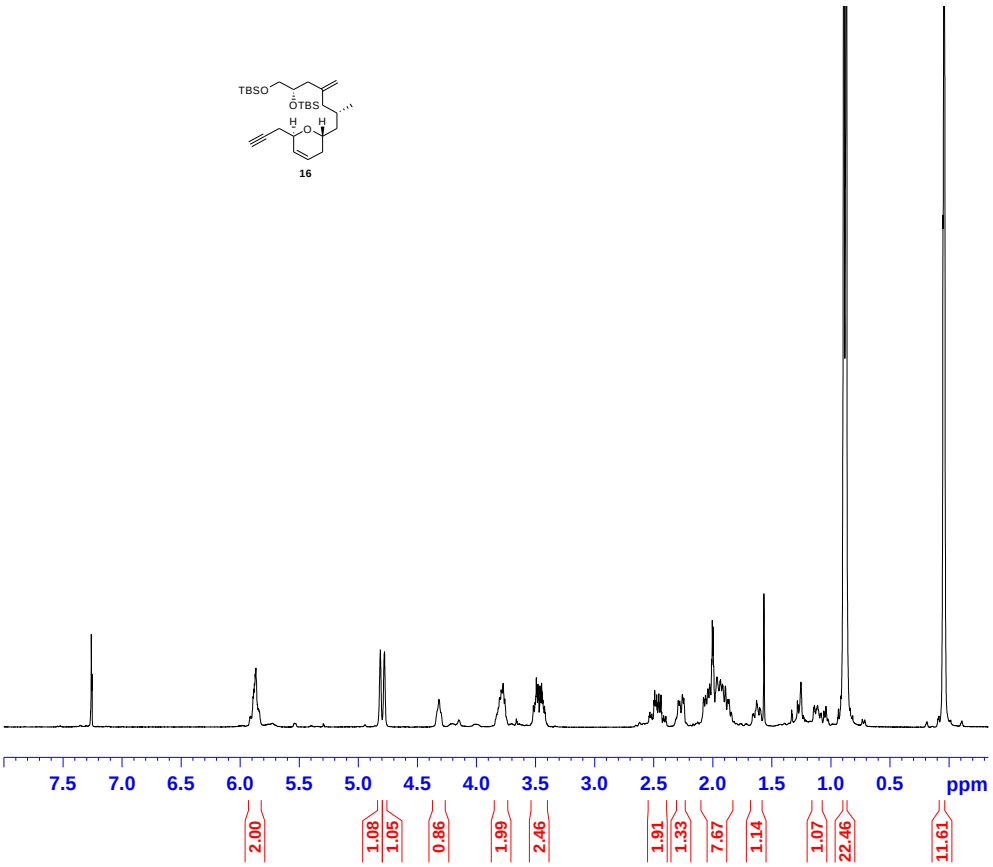
Current Data Parameters
NAME ango244
EXPNO 81
PROCNO 1

F2 - Acquisition Parameters
Date_ 20061206
Time 1.33
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 1000
DS 2
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 7298.2
DW 19.950 usec
DE 6.00 usec
TE 300.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001311 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
p2 20.60 usec
PL1 -1.00 dB
SFO1 100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127536 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

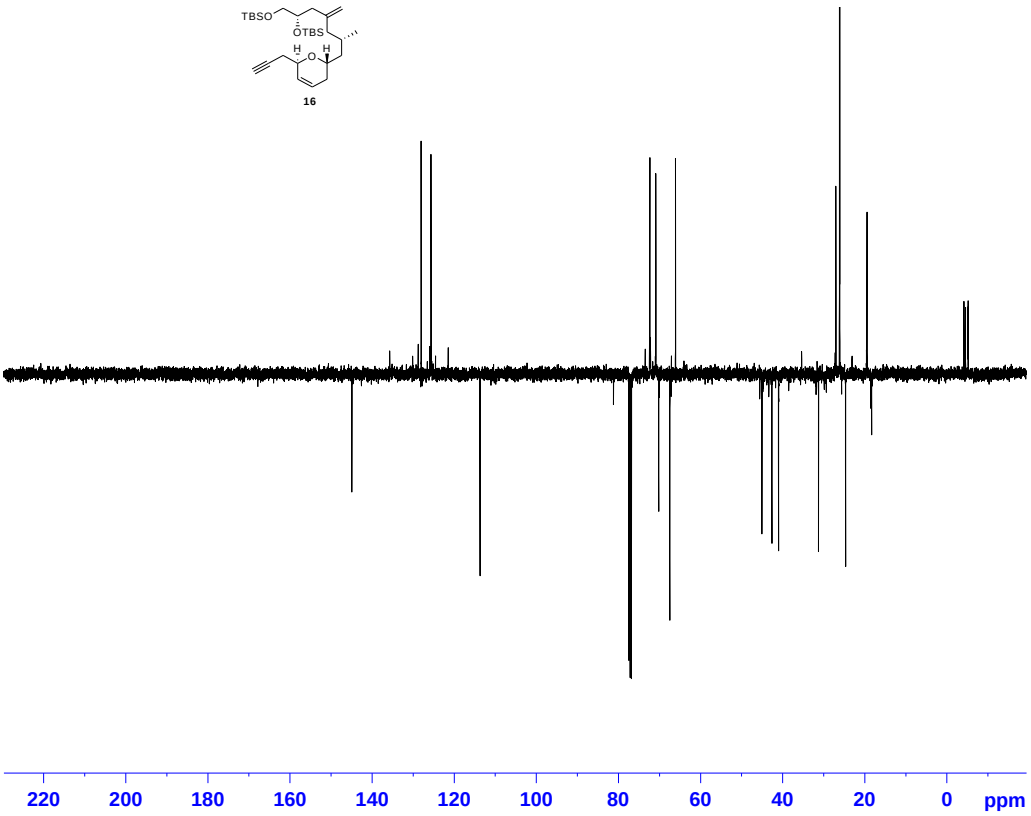



```
Current Data Parameters
NAME            ango157
EXPNO               181
PROCNO                1

F2 - Acquisition Parameters
Date_           20060915
Time                5.17
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   128
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300098 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



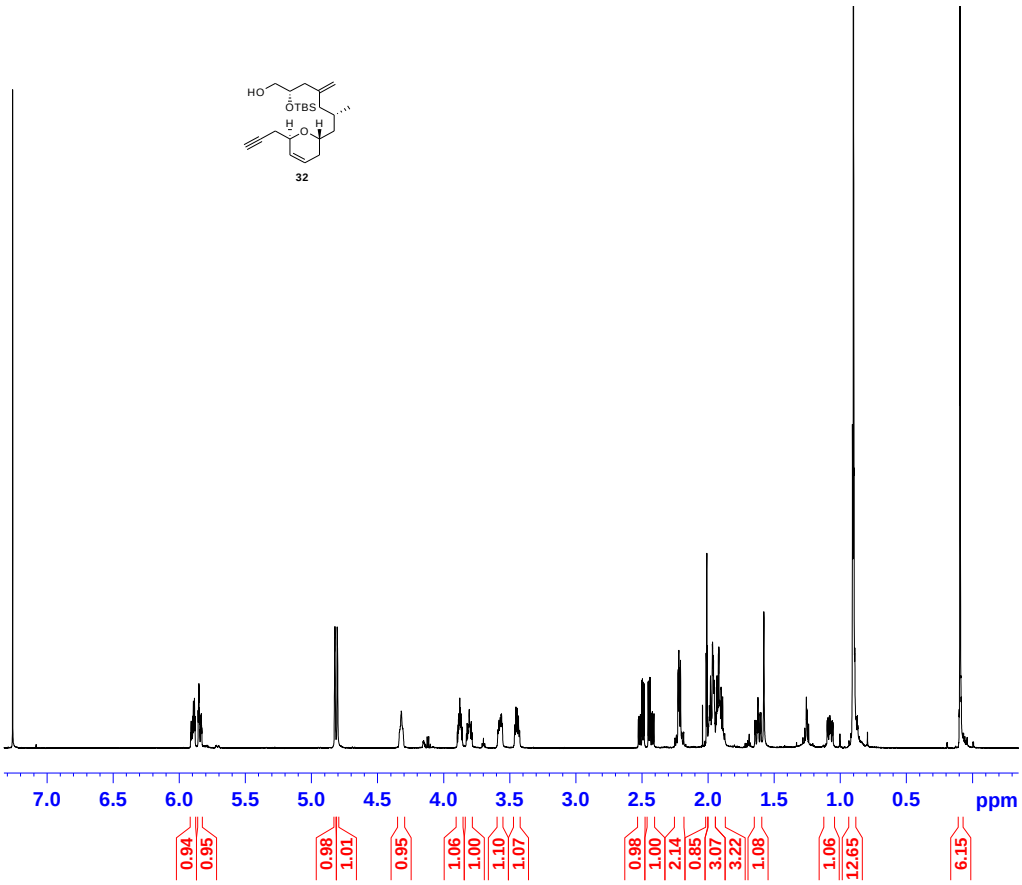

```
Current Data Parameters
NAME            ango157
EXPNO               180
PROCNO                1

F2 - Acquisition Parameters
Date_           20060915
Time                5.15
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                14596.5
DW                19.950 usec
DE                 6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127530 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

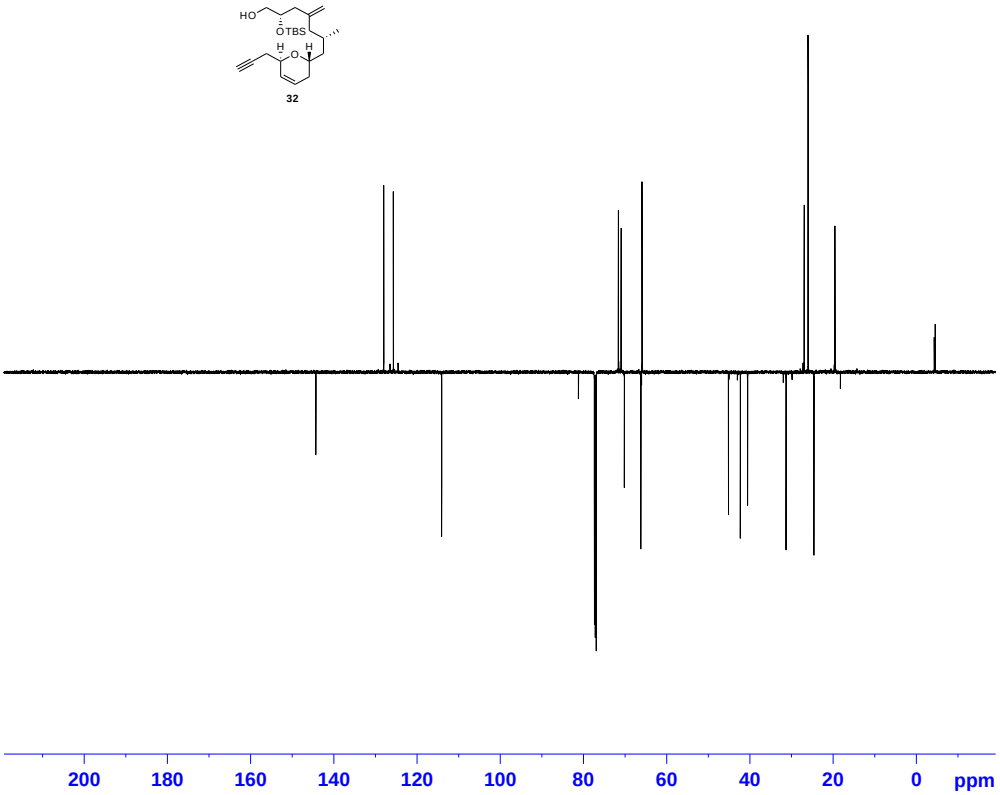



```
Current Data Parameters
NAME            6Sep1806
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_            20060918
Time               18.13
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477449 sec
RG                   256
DW                40.400 usec
DE                 6.00 usec
TE                300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.85 usec
PL1               -6.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 32768
SF           600.1300174 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME            6Sep1806
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_            20060919
Time                4.53
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  7000
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                  3251
DW                13.900 usec
DE                 6.00 usec
TE                300.0 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001019 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.00 usec
p2                16.00 usec
PL1                0.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.20 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF           150.9027876 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

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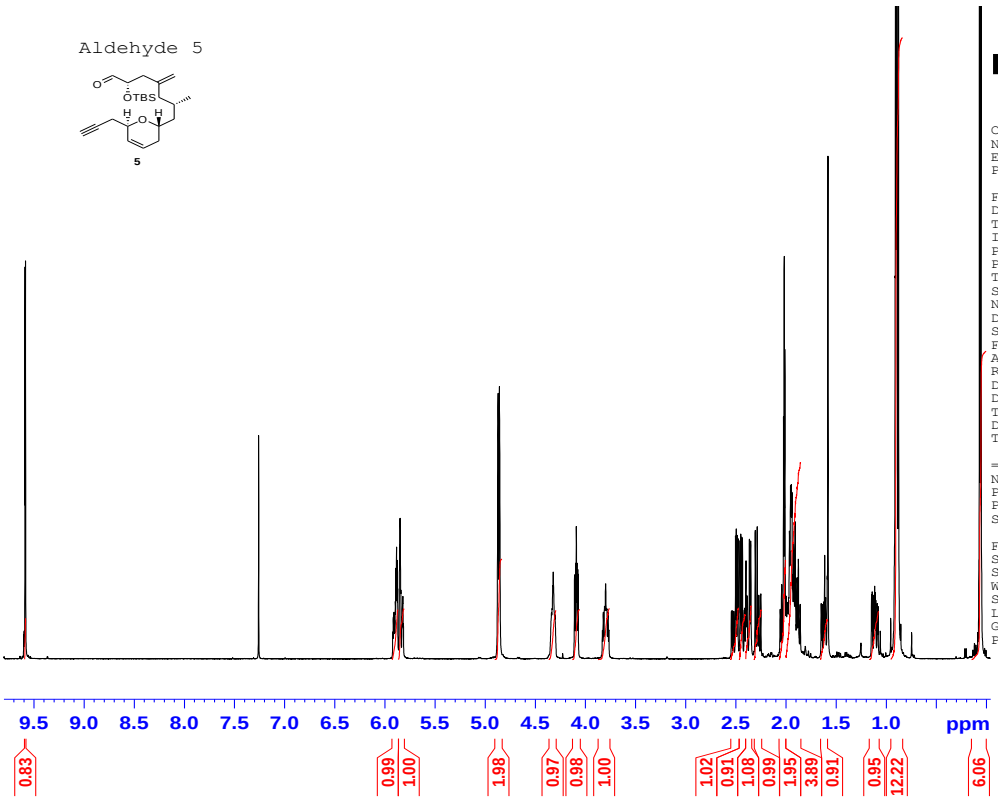
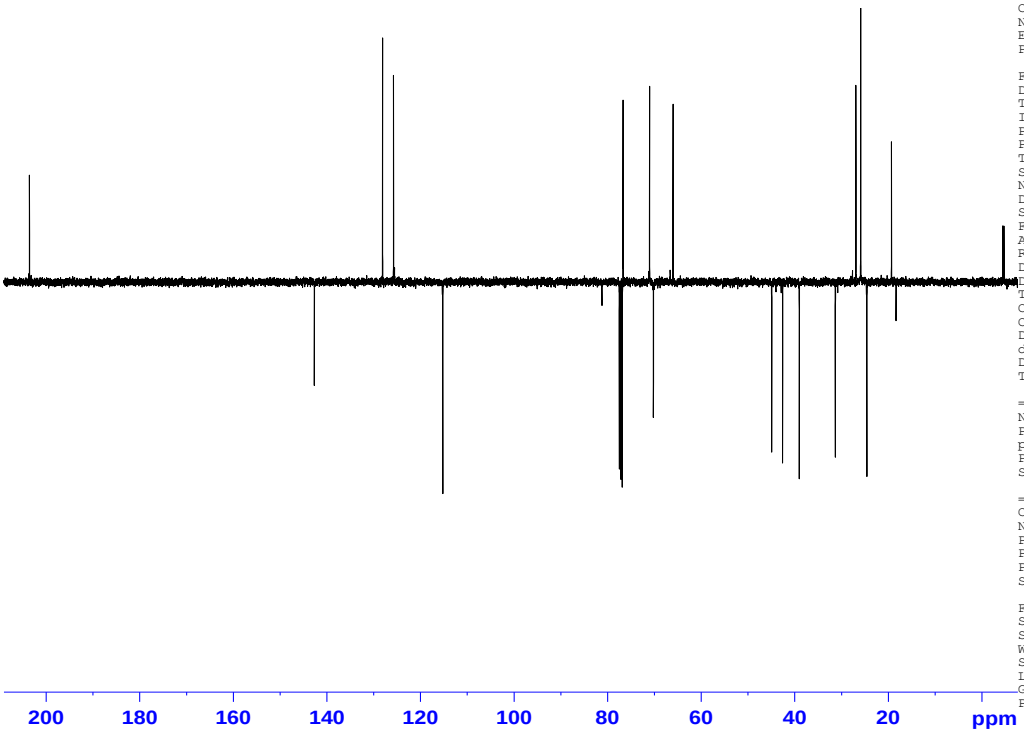



```
Current Data Parameters
NAME              ango481
EXPNO                  51
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080804
Time               18.37
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 161.3
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  8.75 usec
PL1                -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



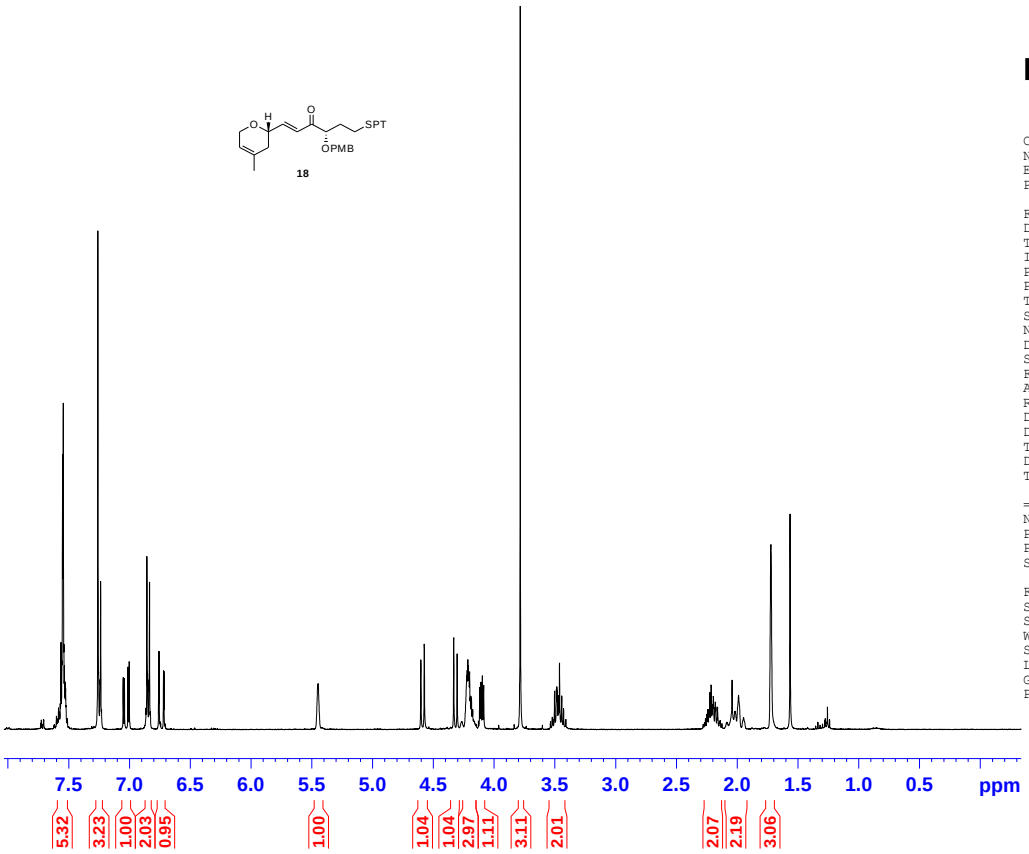

```
Current Data Parameters
NAME              ango481
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080804
Time               18.35
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                5792.6
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.30 usec
p2                 20.60 usec
PL1                -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             100.00 usec
PL2                -3.00 dB
PL12               16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127537 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

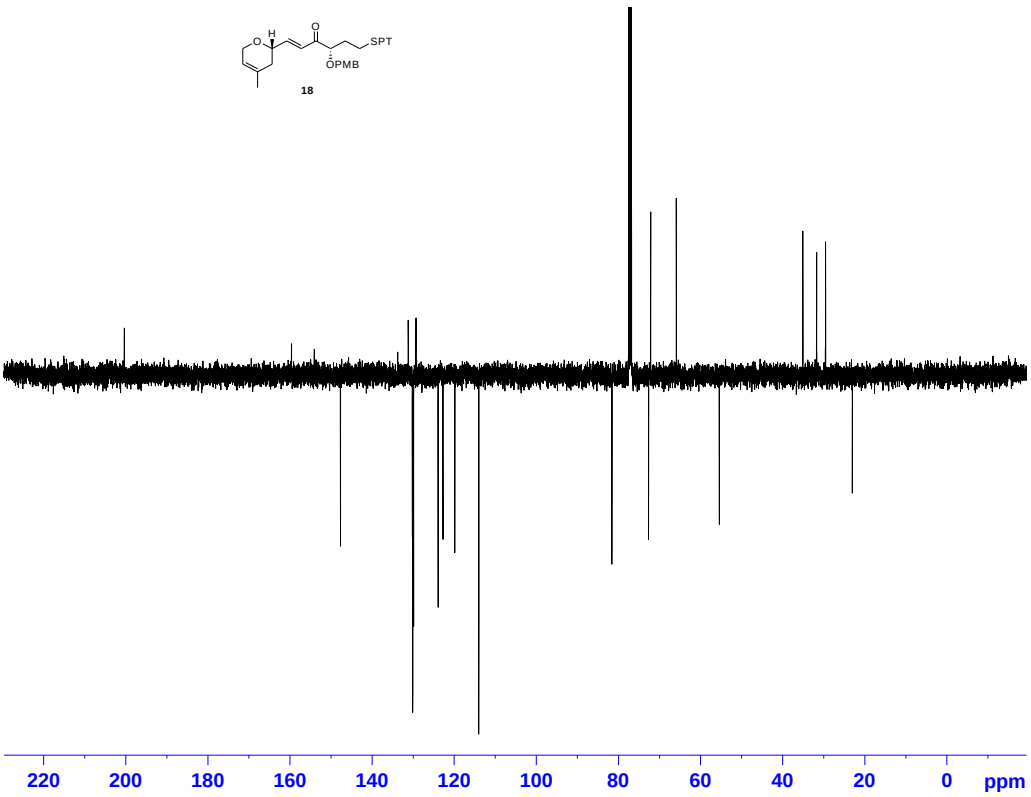



```
Current Data Parameters
NAME              ango472
EXPNO                  30
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070704
Time               18.36
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 287.4
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



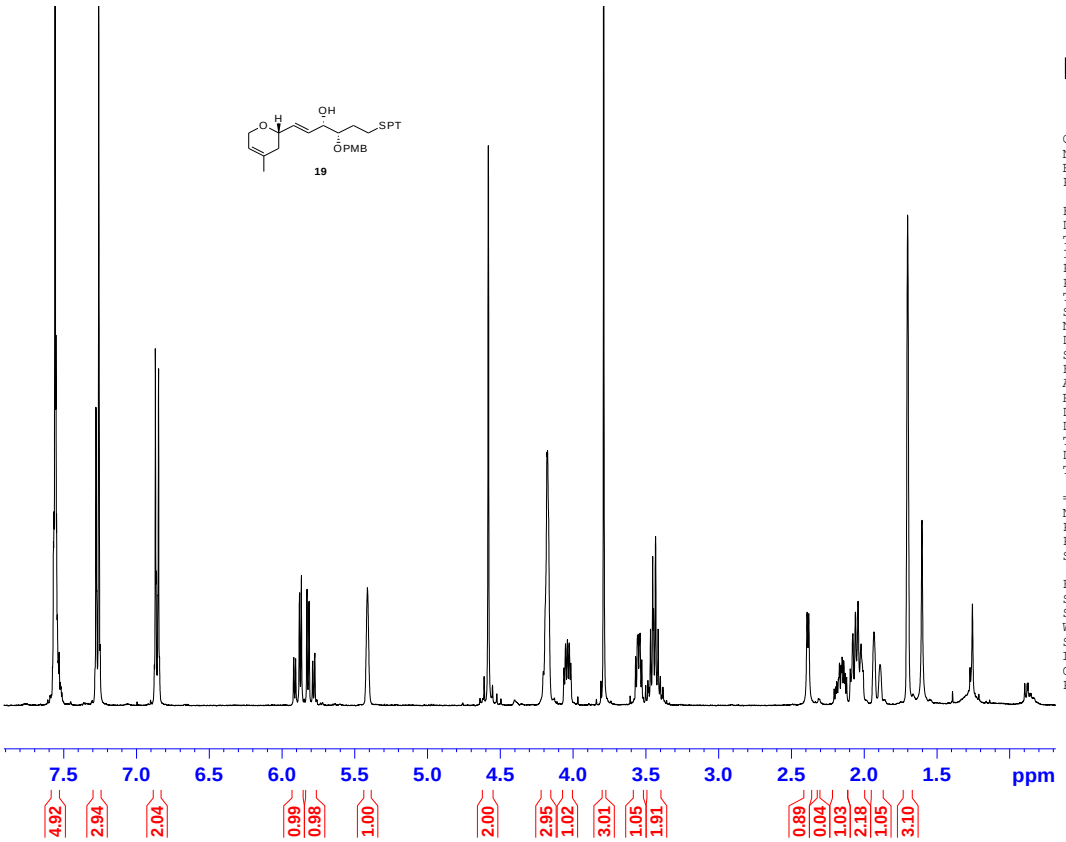

```
Current Data Parameters
NAME              ango246
EXPNO                 101
PROCNO                  1

F2 - Acquisition Parameters
Date_            20061207
Time                8.51
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG               jmod
TD                 65536
SOLVENT            CDCl3
NS                  1780
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG               10321.3
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127534 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

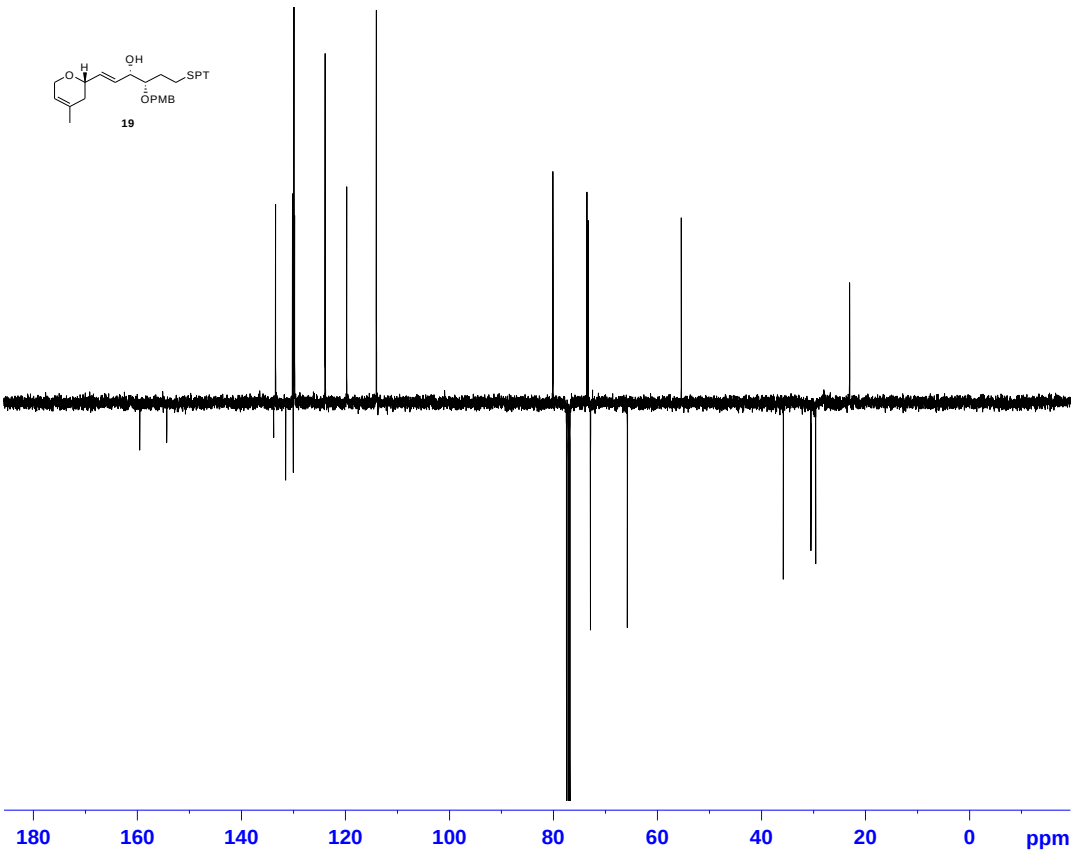



```
Current Data Parameters
NAME            ango328
EXPNO               140
PROCNO                1

F2 - Acquisition Parameters
Date_          20070302
Time              16.56
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                287.4
DW               60.400 usec
DE                 6.00 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300095 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



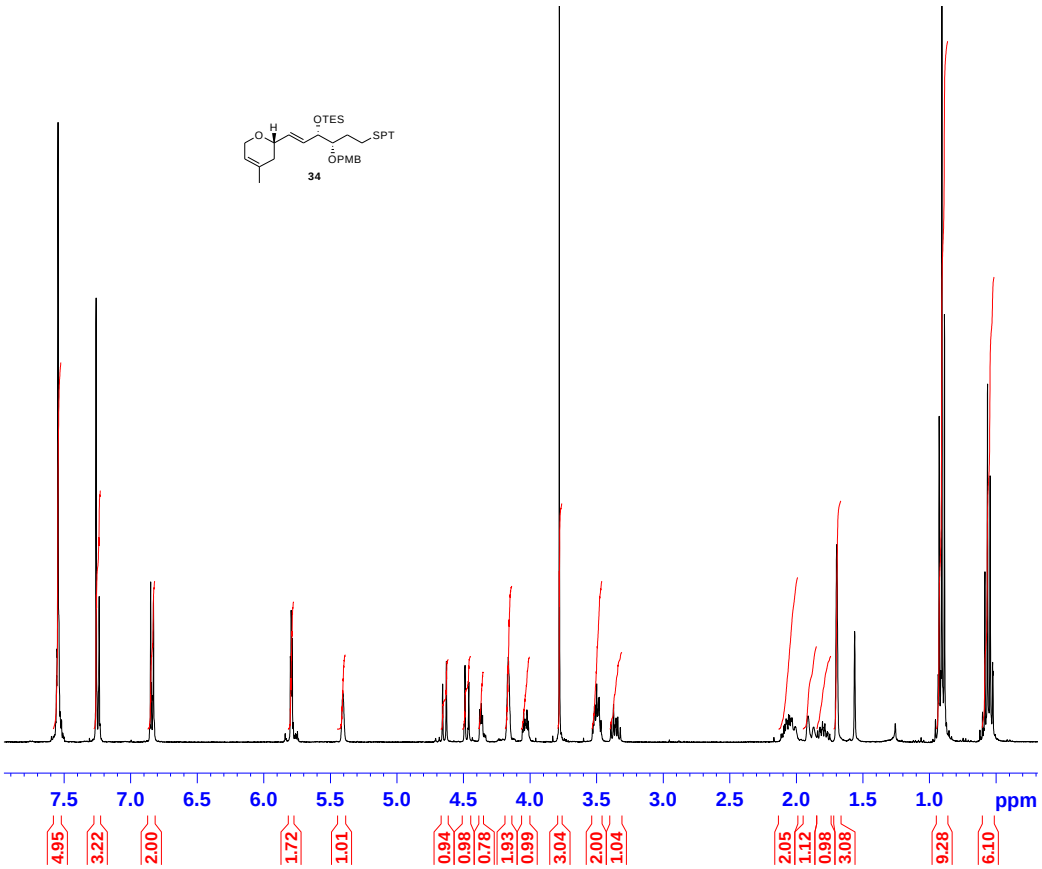

```
Current Data Parameters
NAME            ango328
EXPNO               141
PROCNO                1

F2 - Acquisition Parameters
Date_          20070302
Time              18.04
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                65536
SOLVENT           CDCl3
NS                 1200
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG                 6502
DW               19.950 usec
DE                 6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127545 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

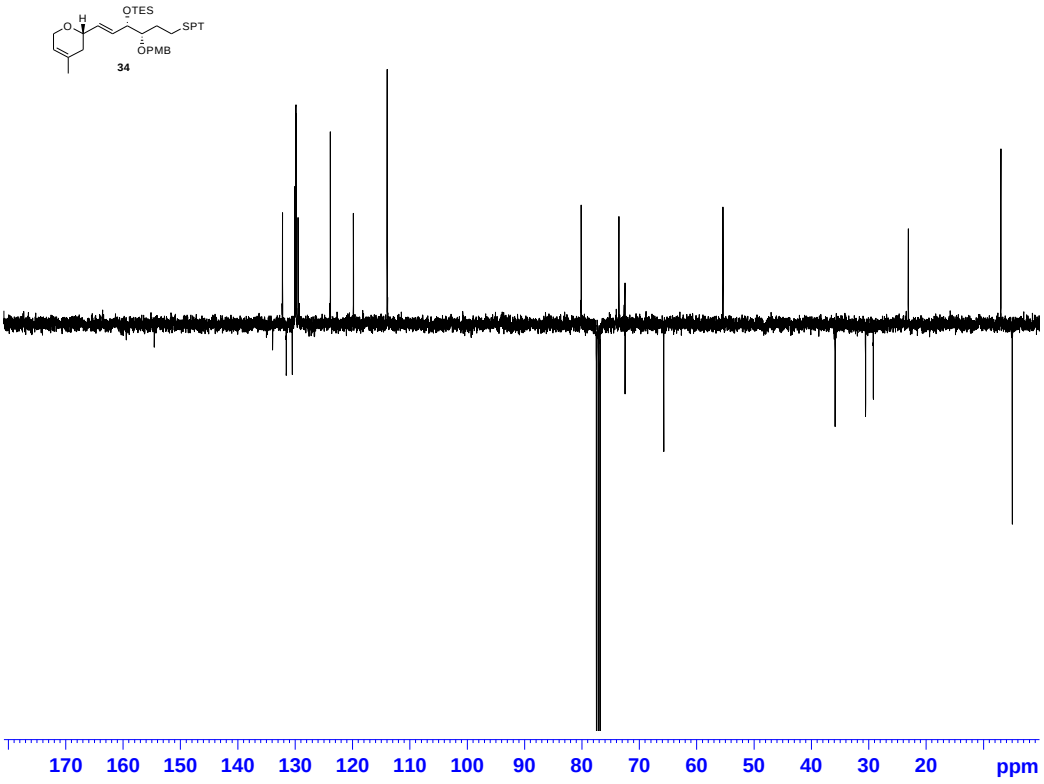



```
Current Data Parameters
NAME              ango485
EXPNO                  30
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070712
Time               13.07
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 287.4
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



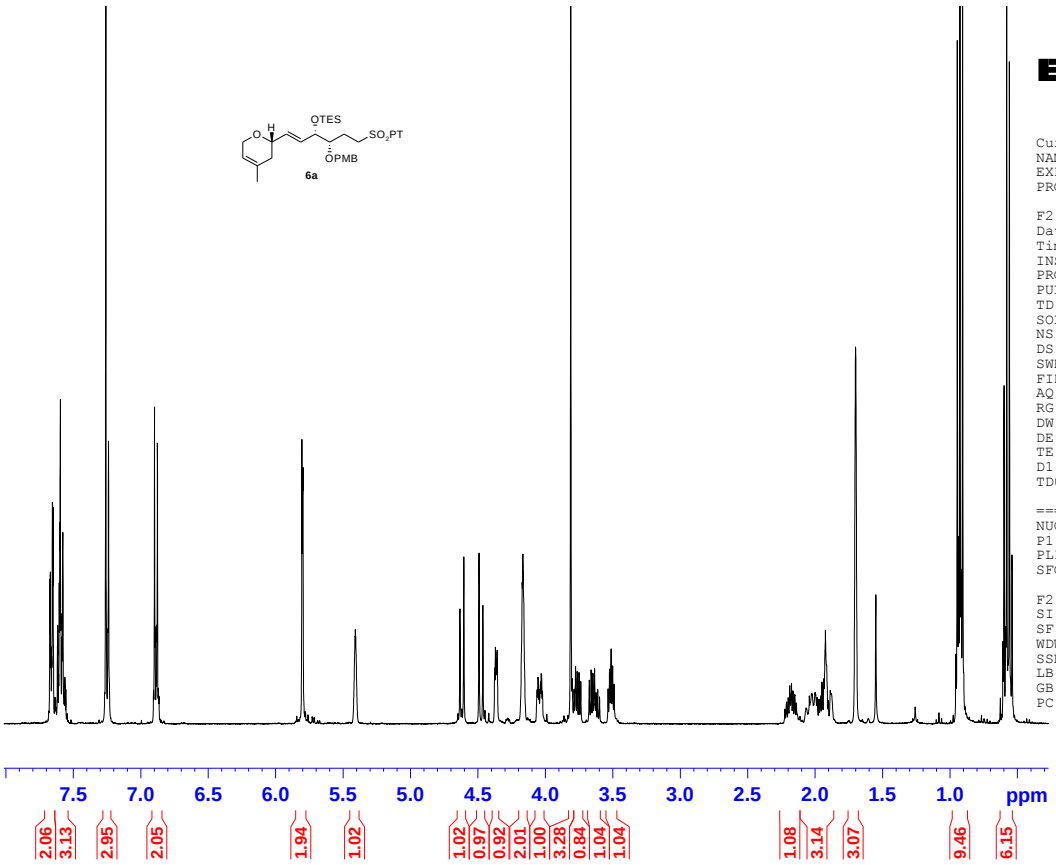

```
Current Data Parameters
NAME              ango485
EXPNO                  31
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070712
Time               13.14
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG            jmod
TD                 65536
SOLVENT            CDCl3
NS                  1200
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                 5792.6
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127536 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

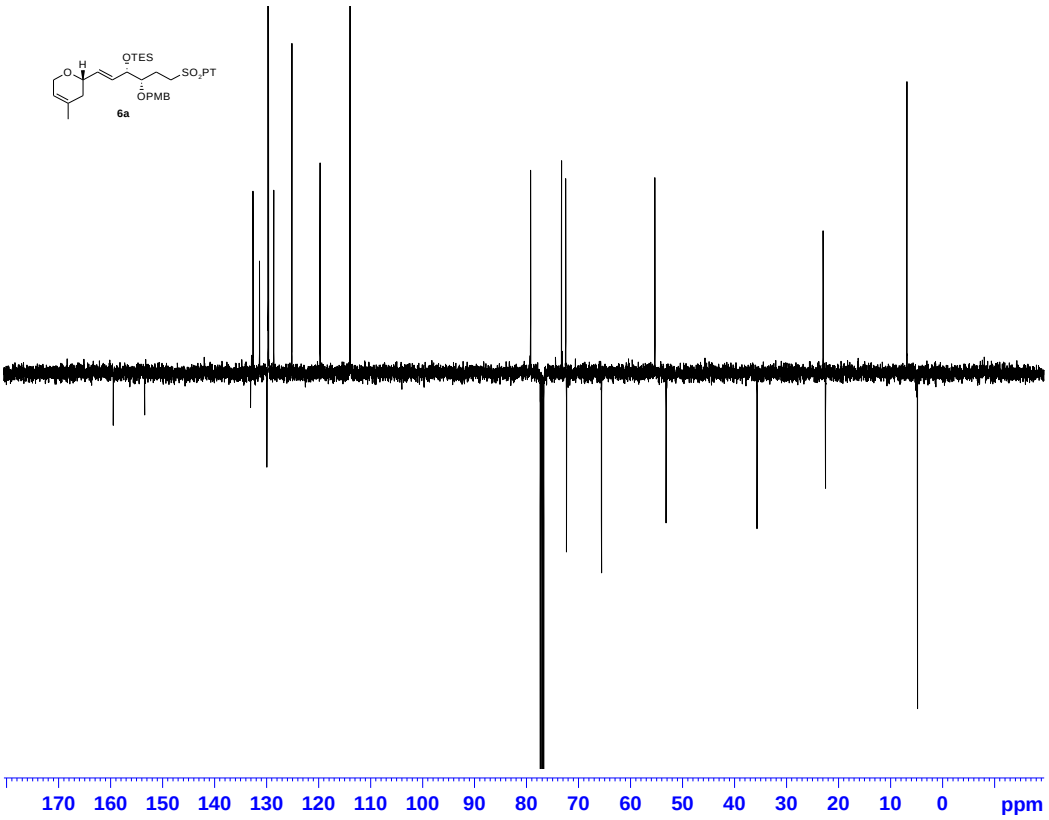



```
Current Data Parameters
NAME            ango712
EXPNO                80
PROCNO                1

F2 - Acquisition Parameters
Date_           20080429
Time              23.16
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  256
DW               60.400 usec
DE                6.00 usec
TE               300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



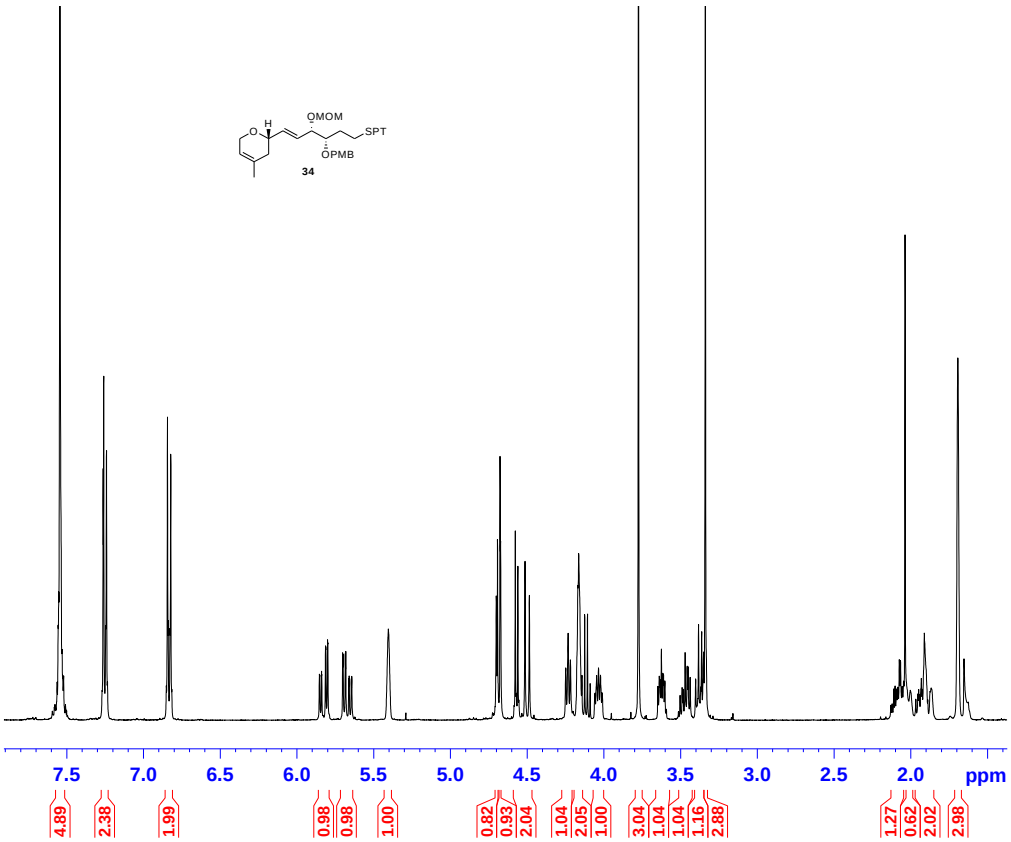

```
Current Data Parameters
NAME            ango712
EXPNO                81
PROCNO                1

F2 - Acquisition Parameters
Date_           20080430
Time               0.41
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                 1500
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG               5792.6
DW               19.950 usec
DE                6.00 usec
TE               300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               10.30 usec
p2               20.60 usec
PL1              -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2              -3.00 dB
PL12             16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127699 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

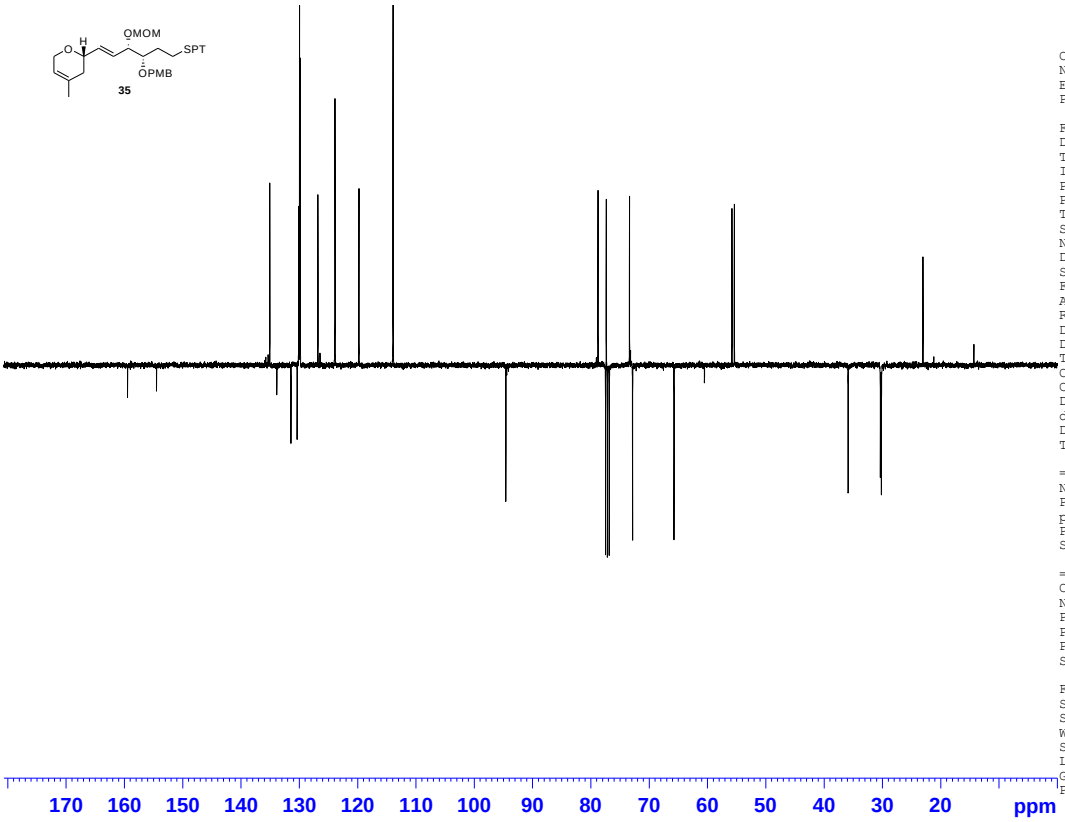



```
Current Data Parameters
NAME            ango478
EXPNO                60
PROCNO                1

F2 - Acquisition Parameters
Date_          20070707
Time               5.40
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                  181
DW               60.400 usec
DE                6.00 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300094 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



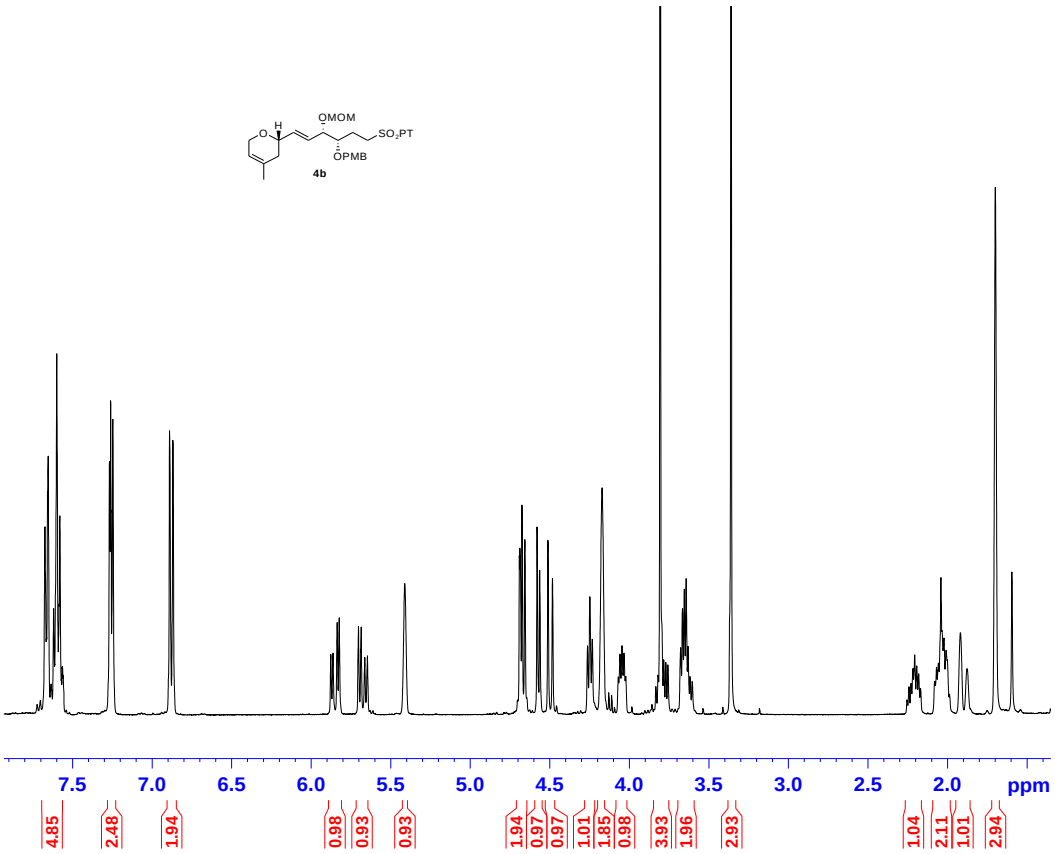

```
Current Data Parameters
NAME            ango478
EXPNO                61
PROCNO                1

F2 - Acquisition Parameters
Date_          20070707
Time               7.33
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                65536
SOLVENT           CDCl3
NS                 2000
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG              11585.2
DW               19.950 usec
DE                6.00 usec
TE                300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127555 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

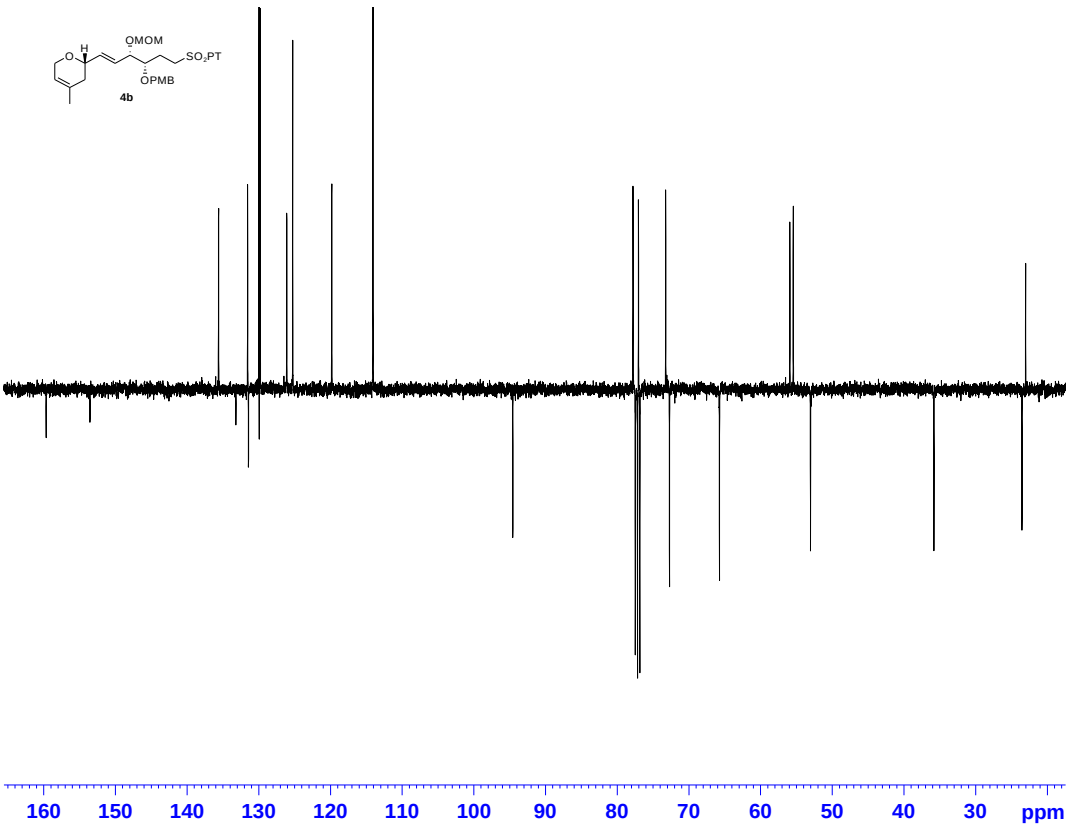



```
Current Data Parameters
NAME            ango278
EXPNO               110
PROCNO                1

F2 - Acquisition Parameters
Date_           20070109
Time               9.14
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ           3.9584243 sec
RG               161.3
DW              60.400 usec
DE               6.00 usec
TE              300.2 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1       400.1324710 MHz

F2 - Processing parameters
SI                32768
SF         400.1300092 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



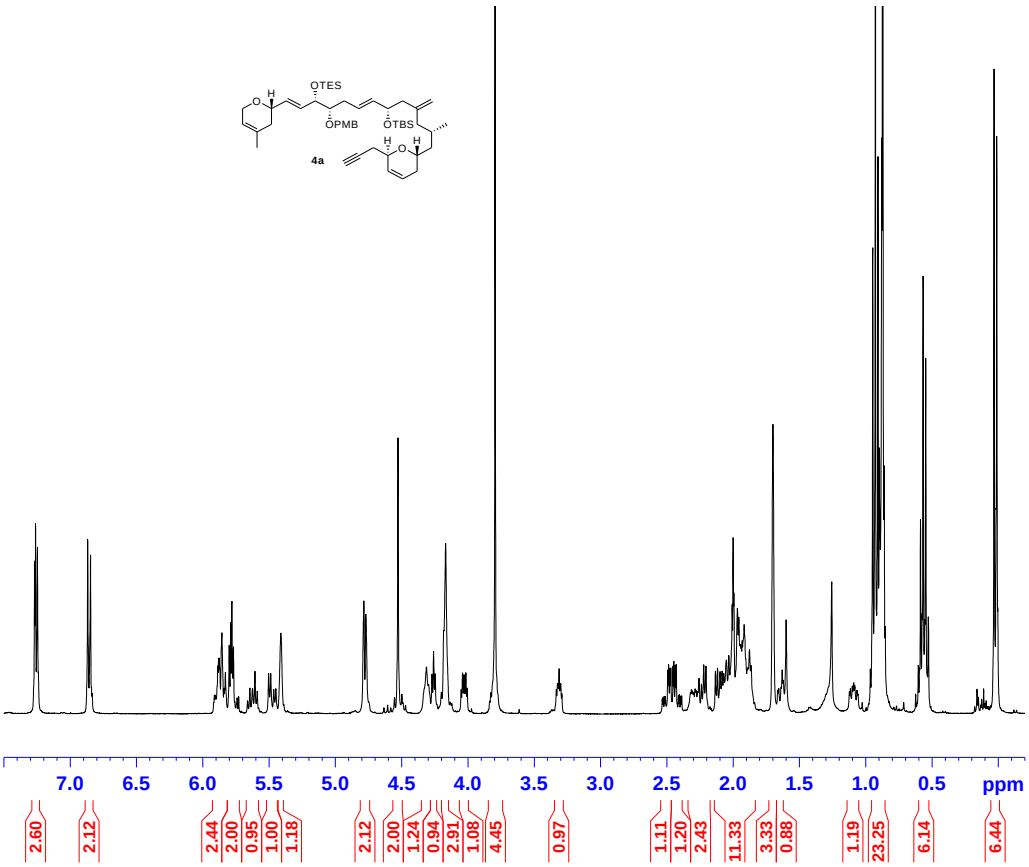

```
Current Data Parameters
NAME            ango278
EXPNO               111
PROCNO                1

F2 - Acquisition Parameters
Date_           20070108
Time              19.53
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                65536
SOLVENT           CDCl3
NS                  800
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG                 6502
DW              19.950 usec
DE               6.00 usec
TE              300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1              10.30 usec
p2              20.60 usec
PL1             -1.00 dB
SFO1       100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2              -3.00 dB
PL12             16.00 dB
SFO2       400.1316005 MHz

F2 - Processing parameters
SI                32768
SF         100.6127095 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

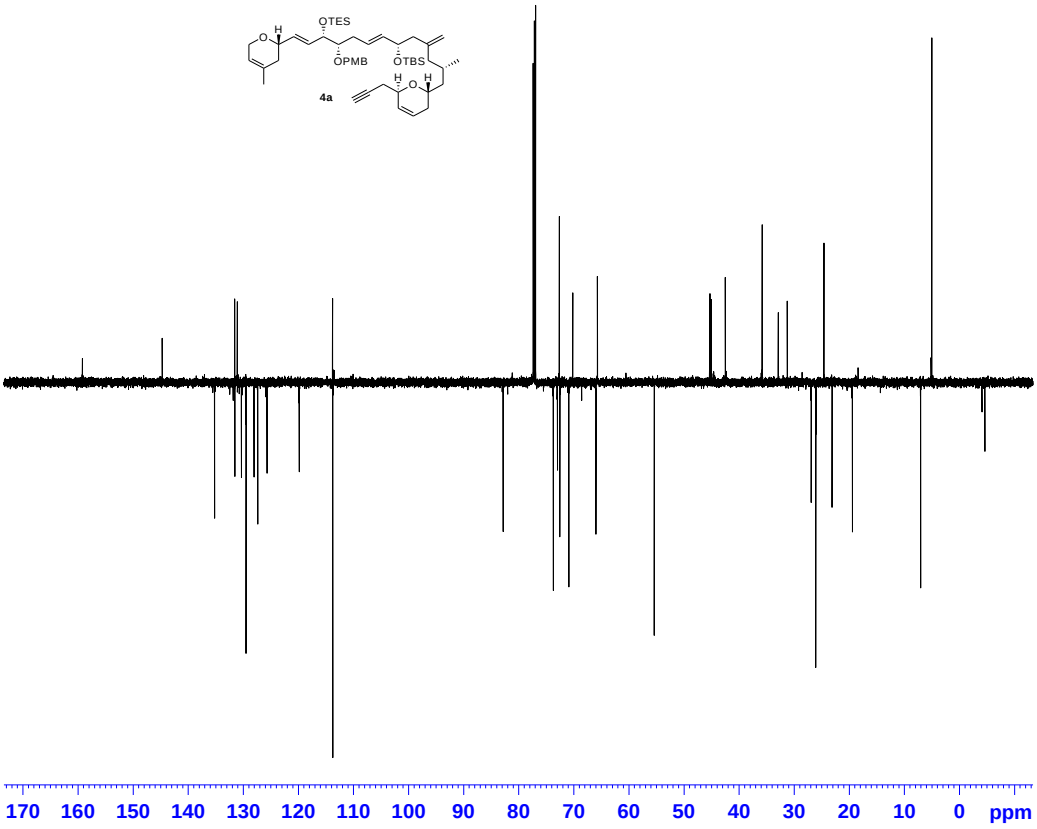



```
Current Data Parameters
NAME            ango500
EXPNO               230
PROCNO                1

F2 - Acquisition Parameters
Date_           20070731
Time               2.33
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                 90.5
DW               60.400 usec
DE                 6.00 usec
TE                300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



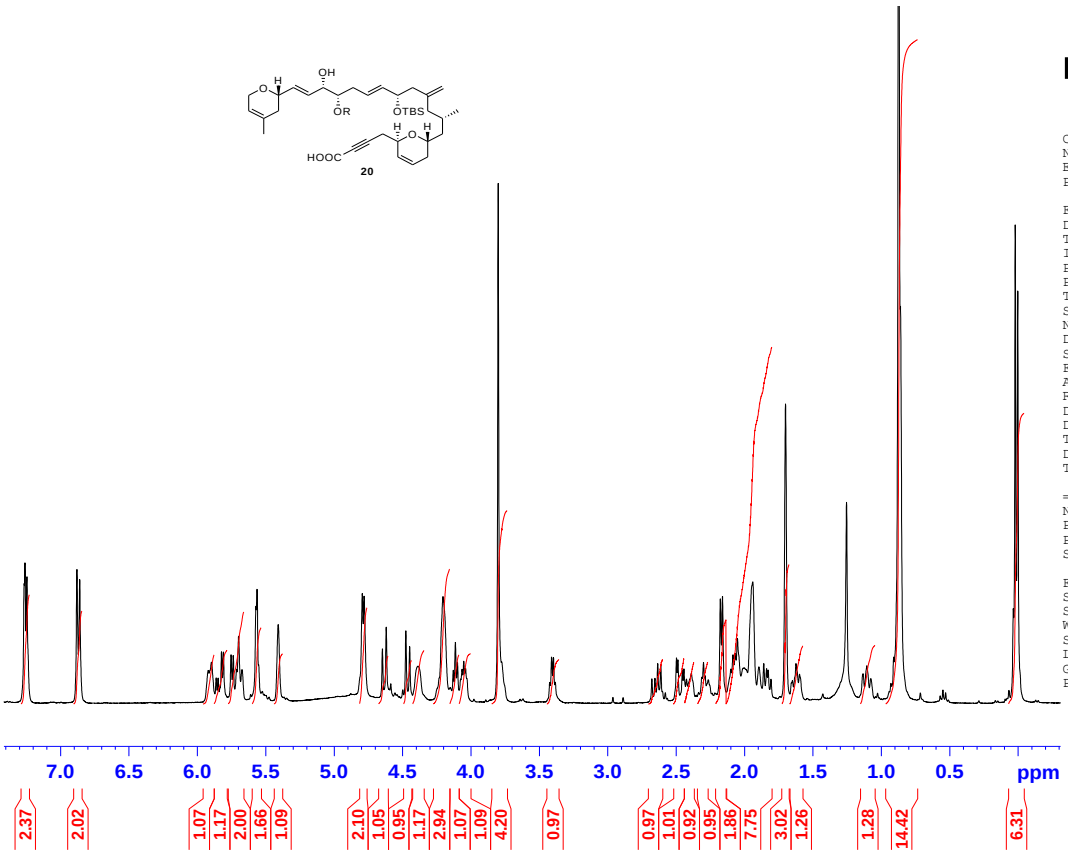

```
Current Data Parameters
NAME             6May0108
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080501
Time              16.46
INSTRUM       avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  3000
DS                     4
SWH           35971.223 Hz
FIDRES         0.548877 Hz
AQ            0.9110143 sec
RG               5160.6
DW               13.900 usec
DE                 6.00 usec
TE                298.1 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00000828 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.50 usec
p2                 13.00 usec
PL1                 0.00 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.20 dB
SFO2        600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF          150.9027889 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

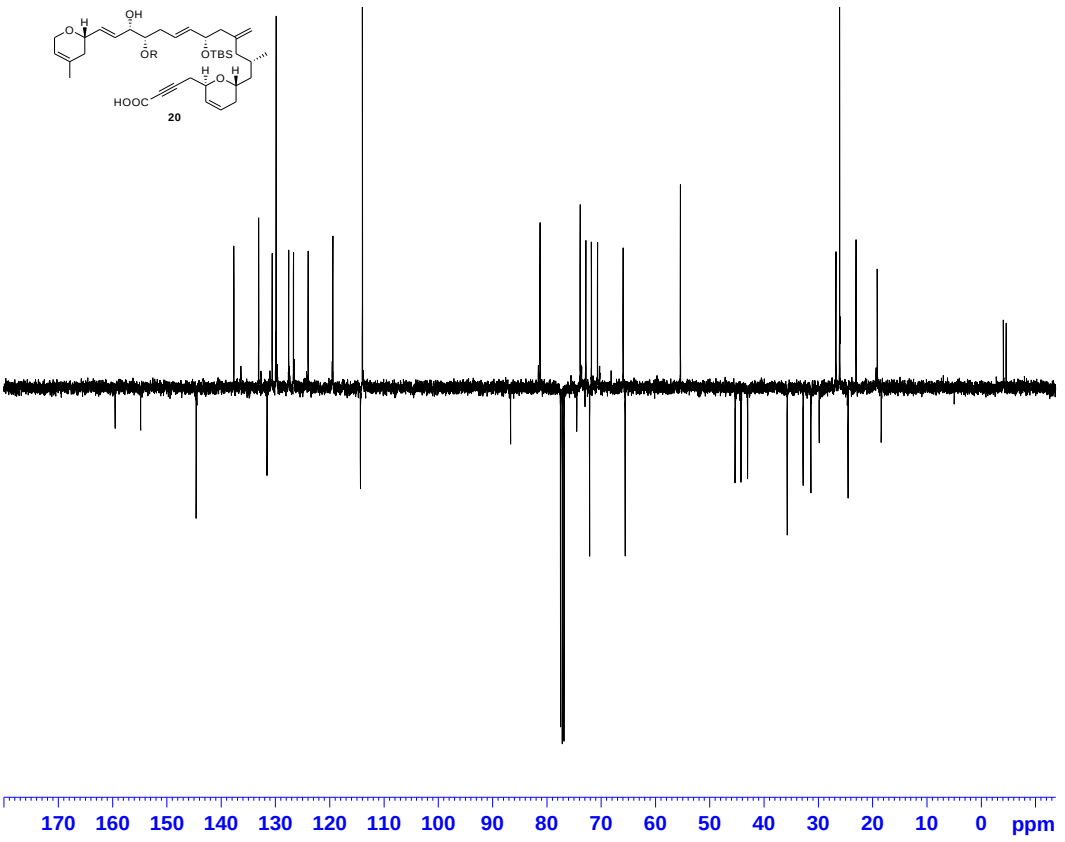



```
Current Data Parameters
NAME              ango701
EXPNO                  50
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080611
Time                19.52
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  143.7
DW                 60.400 usec
DE                  6.00 usec
TE                  300.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   8.75 usec
PL1                 -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300096 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```



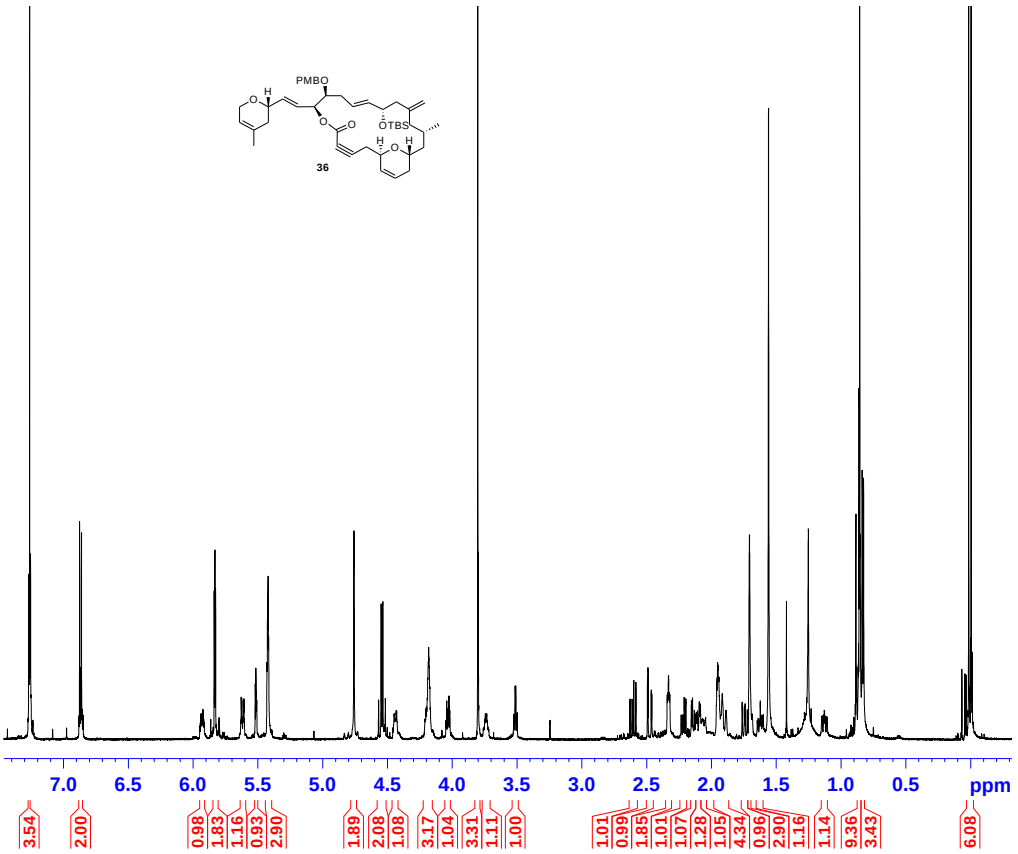

```
Current Data Parameters
NAME              ango701
EXPNO                  51
PROCNO                  1

F2 - Acquisition Parameters
Date_            20080611
Time                21.02
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG             jmod
TD                  65536
SOLVENT             CDCl3
NS                    1200
DS                      2
SWH             25062.656 Hz
FIDRES           0.382426 Hz
AQ              1.3074932 sec
RG                 10321.3
DW                 19.950 usec
DE                  6.00 usec
TE                  300.2 K
CNST2          145.0000000
CNST11           1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.30 usec
p2                  20.60 usec
PL1                 -1.00 dB
SFO1          100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                 -3.00 dB
PL12                16.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            100.6127540 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

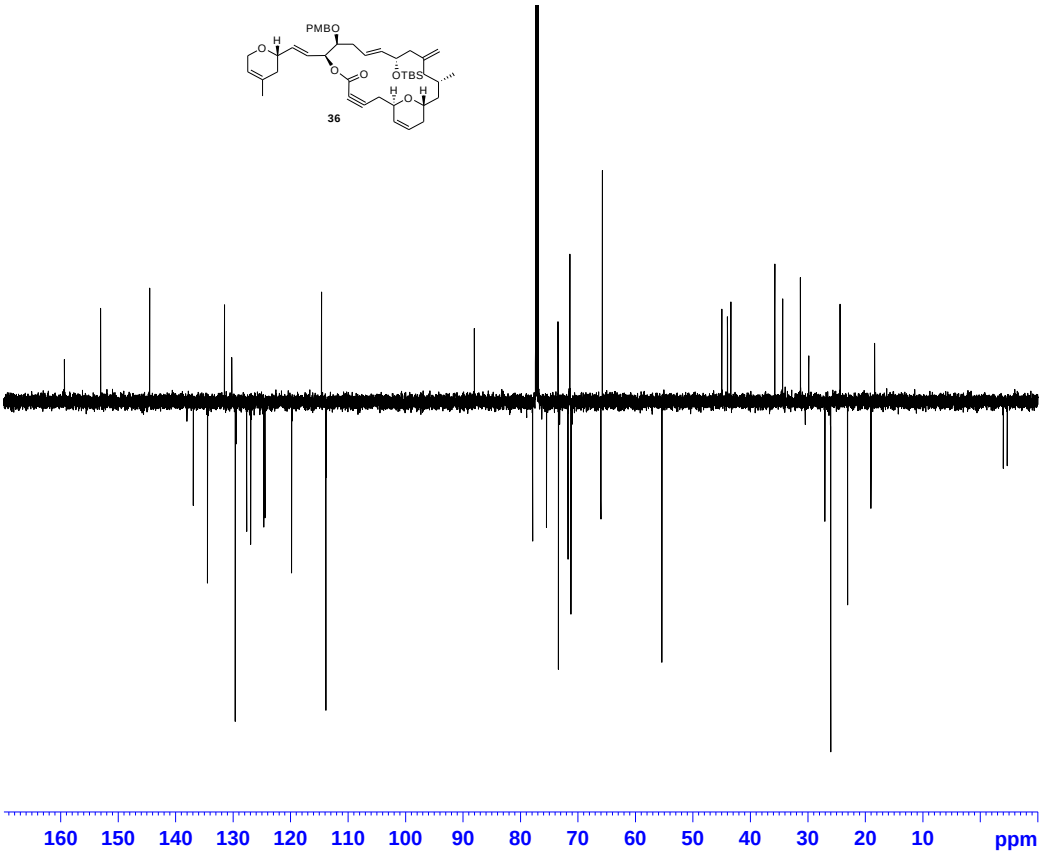


Current Data Parameters
NAME 6May1508
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080515
Time 17.46
INSTRUM avance600
PROBHD 5 mm PAQNP Swi
PULPROG zg30
TD 43100
SOLVENT CDCl3
NS 128
DS 2
SWH 5387.931 Hz
FIDRES 0.125010 Hz
AQ 3.9998229 sec
RG 574.7
DW 92.800 usec
DE 6.00 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.85 usec
PL1 -6.00 dB
SFO1 600.1321005 MHz

F2 - Processing parameters
SI 32768
SF 600.1300175 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00



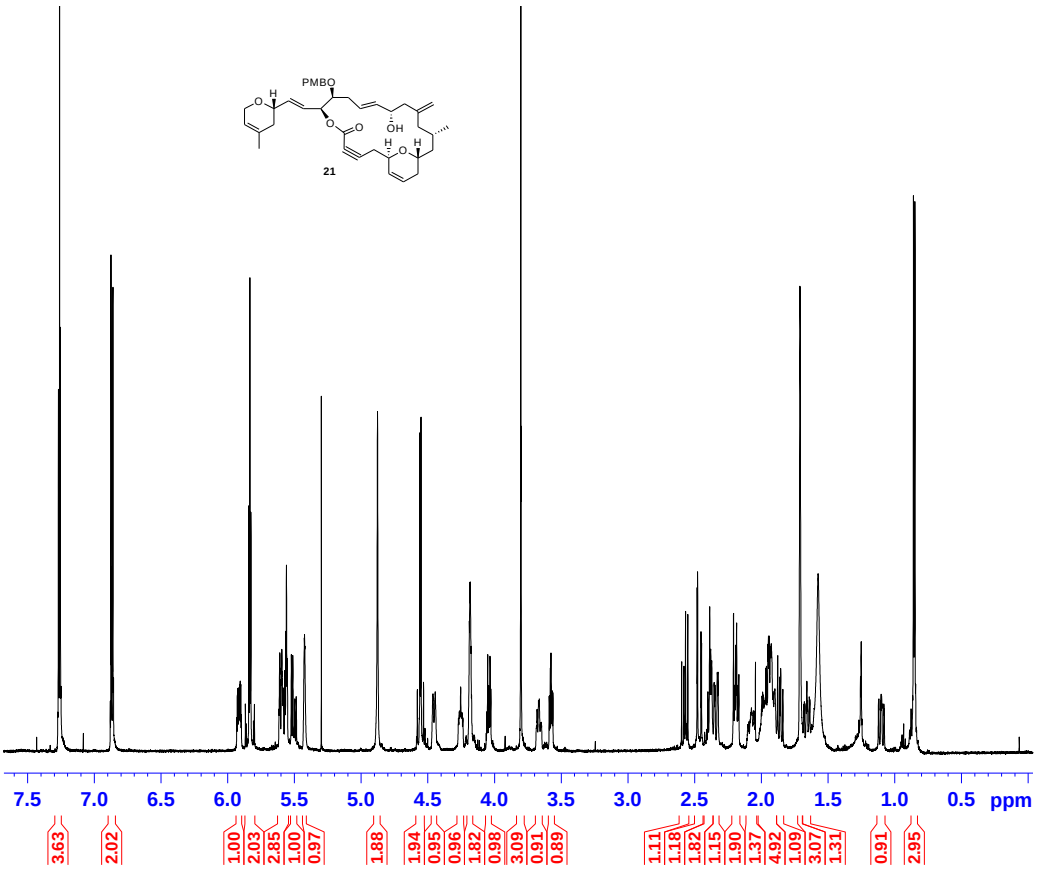
Current Data Parameters
NAME 6May1508
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20080516
Time 8.48
INSTRUM avance600
PROBHD 5 mm PAQNP Swi
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 18914
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 2580.3
DW 13.900 usec
DE 6.00 usec
TE 298.1 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00000828 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 6.50 usec
p2 13.00 usec
PL1 0.00 dB
SFO1 150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 12.20 dB
SFO2 600.1324005 MHz

F2 - Processing parameters
SI 32768
SF 150.9027889 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

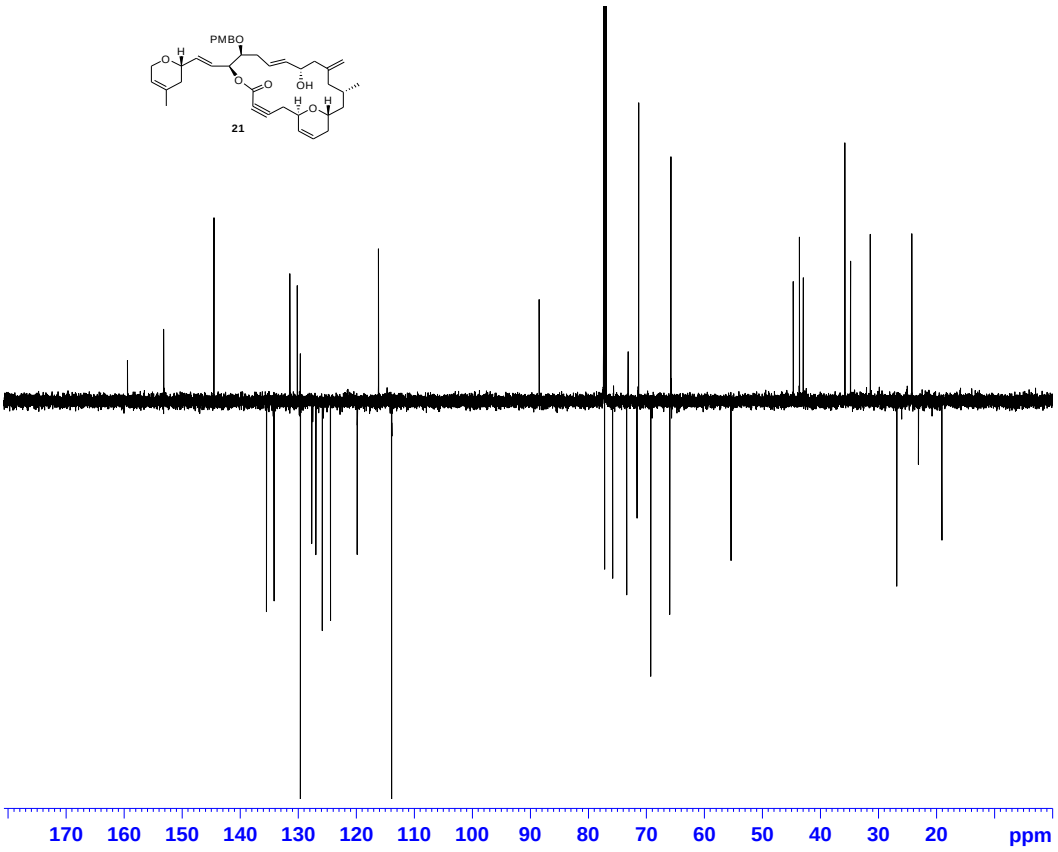



```
Current Data Parameters
NAME            6May2008
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080520
Time              17.13
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             zg30
TD                 48074
SOLVENT            CDCl3
NS                   128
DS                     2
SWH             6009.615 Hz
FIDRES          0.125008 Hz
AQ             3.9998901 sec
RG                 645.1
DW                83.200 usec
DE                  6.00 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.85 usec
PL1                -6.00 dB
SFO1         600.1327006 MHz

F2 - Processing parameters
SI                 32768
SF           600.1300176 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



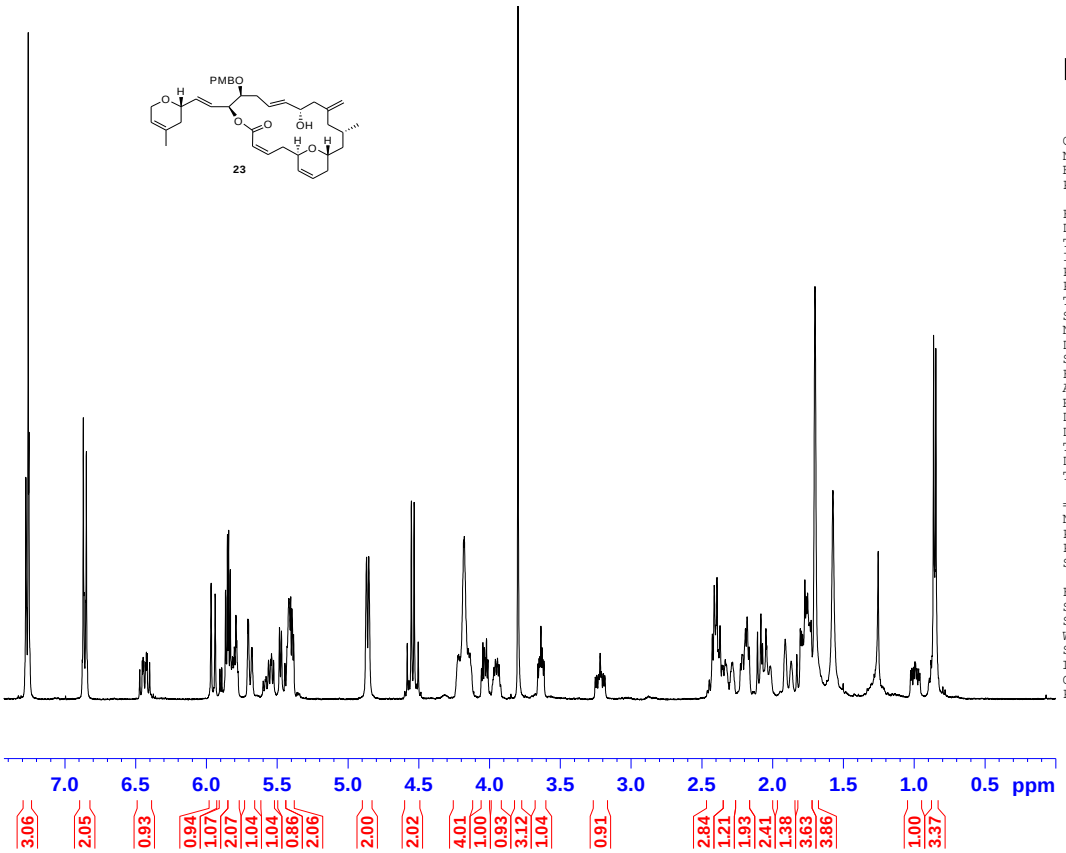

```
Current Data Parameters
NAME            6May2008
EXPNO                 15
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080521
Time                8.55
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                 11104
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                  3251
DW                13.900 usec
DE                  6.00 usec
TE                 298.1 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00000828 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.50 usec
p2                 13.00 usec
PL1                 0.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.20 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF           150.9027891 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

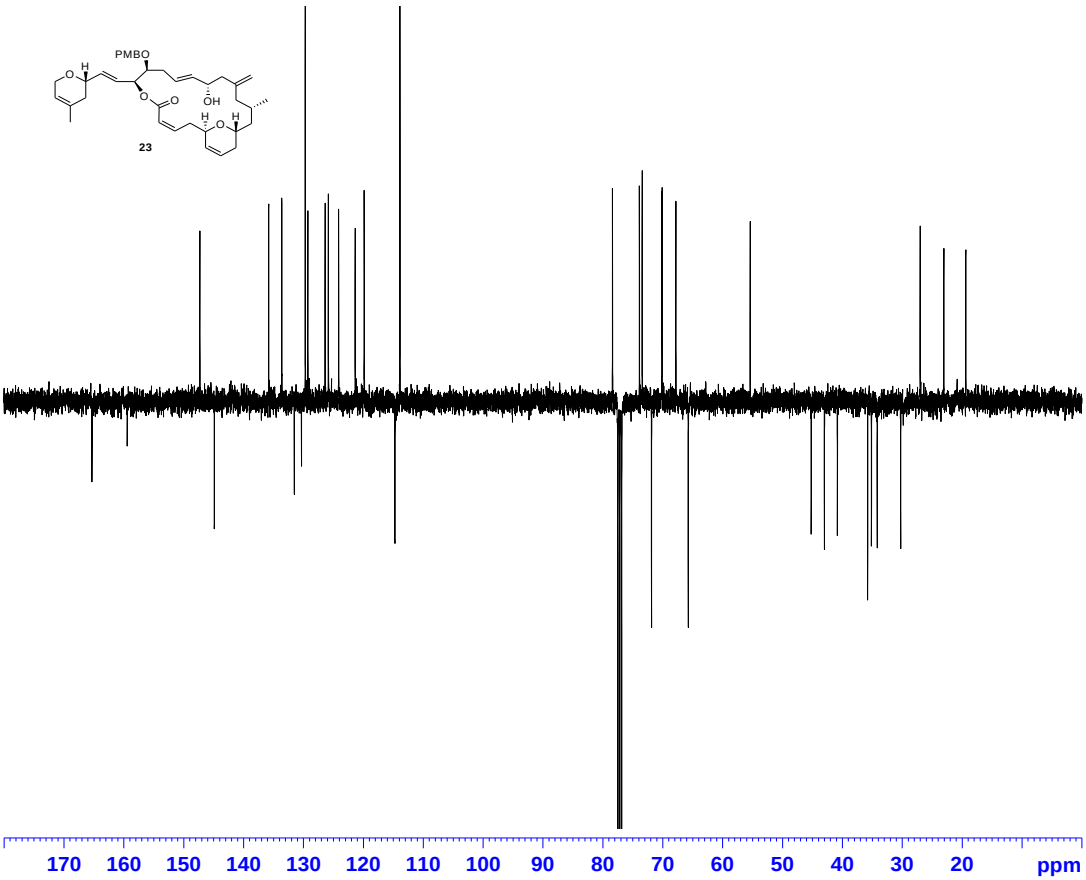



```
Current Data Parameters
NAME            ango785
EXPNO                50
PROCNO                1

F2 - Acquisition Parameters
Date_          20080718
Time              19.49
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ           3.9584243 sec
RG                  256
DW               60.400 usec
DE                6.00 usec
TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



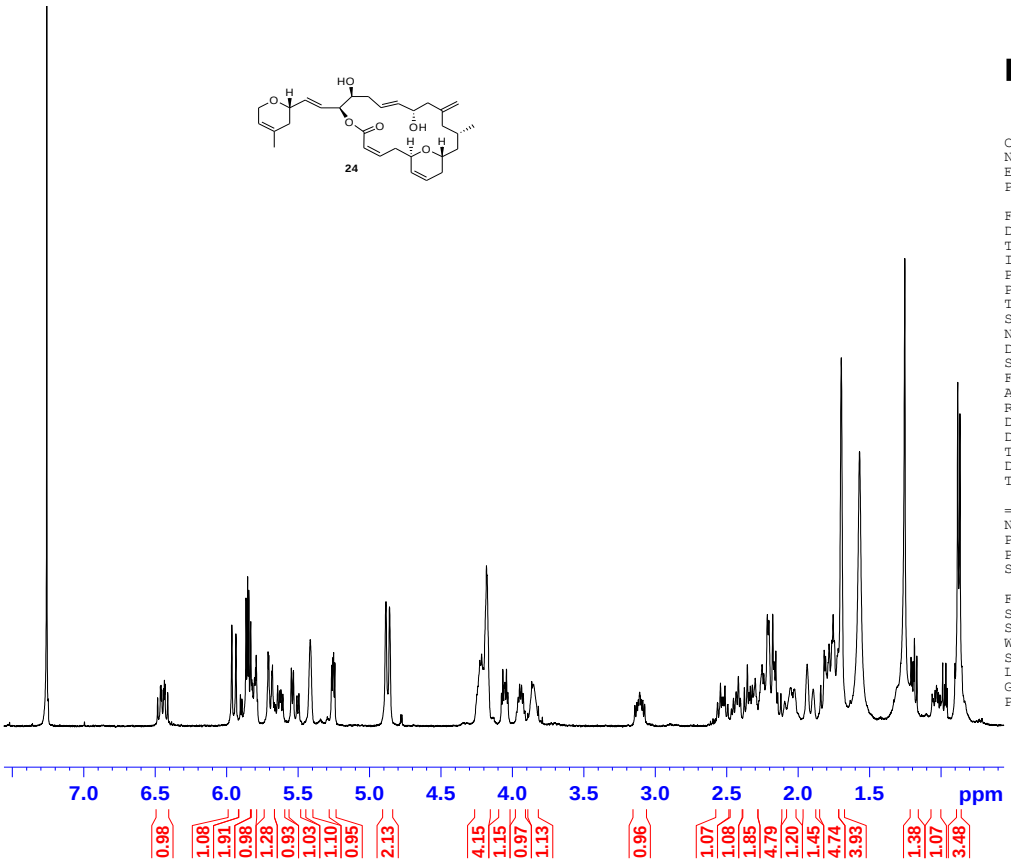

```
Current Data Parameters
NAME            ango785
EXPNO                51
PROCNO                1

F2 - Acquisition Parameters
Date_          20080718
Time              22.09
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                 2500
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG               5792.6
DW               19.950 usec
DE                6.00 usec
TE                300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1               10.30 usec
p2               20.60 usec
PL1              -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2              -3.00 dB
PL12             16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127539 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

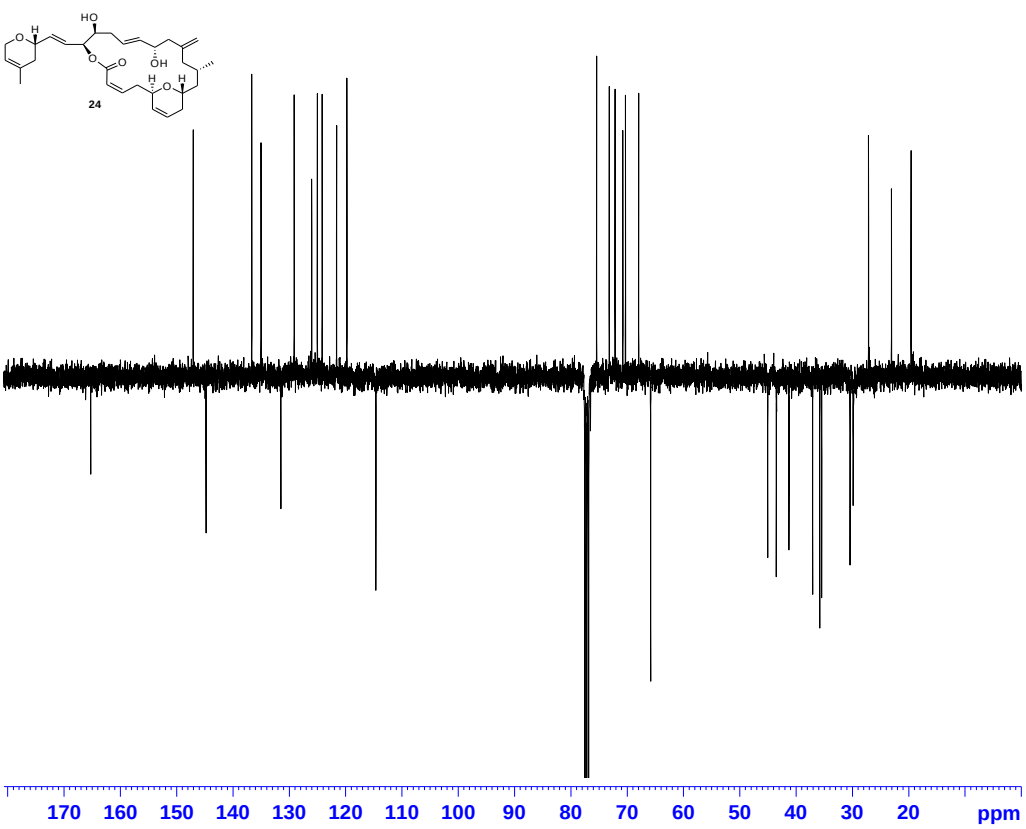



```
Current Data Parameters
NAME              ango788
EXPNO                  60
PROCNO                  1

F2 - Acquisition Parameters
Date_             20080730
Time                 10.07
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       2
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ               3.9584243 sec
RG                   406.4
DW                  60.400 usec
DE                    6.00 usec
TE                   300.2 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.75 usec
PL1                  -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300093 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```




```
Current Data Parameters
NAME              ango788
EXPNO                  61
PROCNO                  1

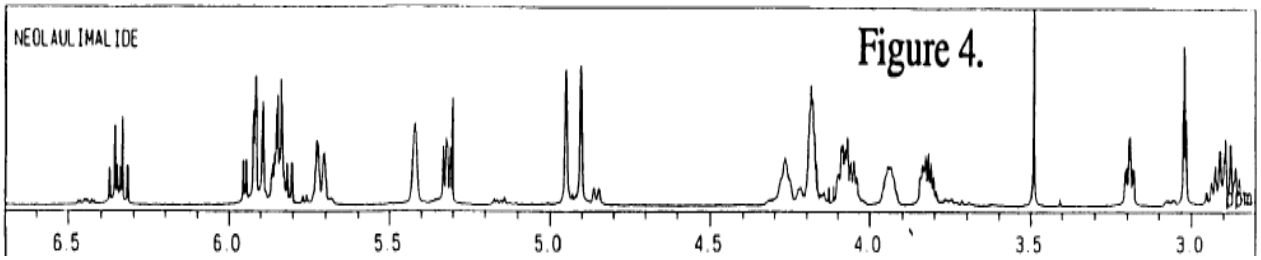
F2 - Acquisition Parameters
Date_             20080730
Time                  8.50
INSTRUM         avance400
PROBHD    5 mm BBO BB-1H
PULPROG                jmod
TD                   65536
SOLVENT              CDCl3
NS                   12472
DS                       2
SWH              25062.656 Hz
FIDRES            0.382426 Hz
AQ               1.3074932 sec
RG                    8192
DW                  19.950 usec
DE                    6.00 usec
TE                   300.2 K
CNST2          145.0000000
CNST11           1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.30 usec
p2                   20.60 usec
PL1                  -1.00 dB
SFO1          100.6233329 MHz

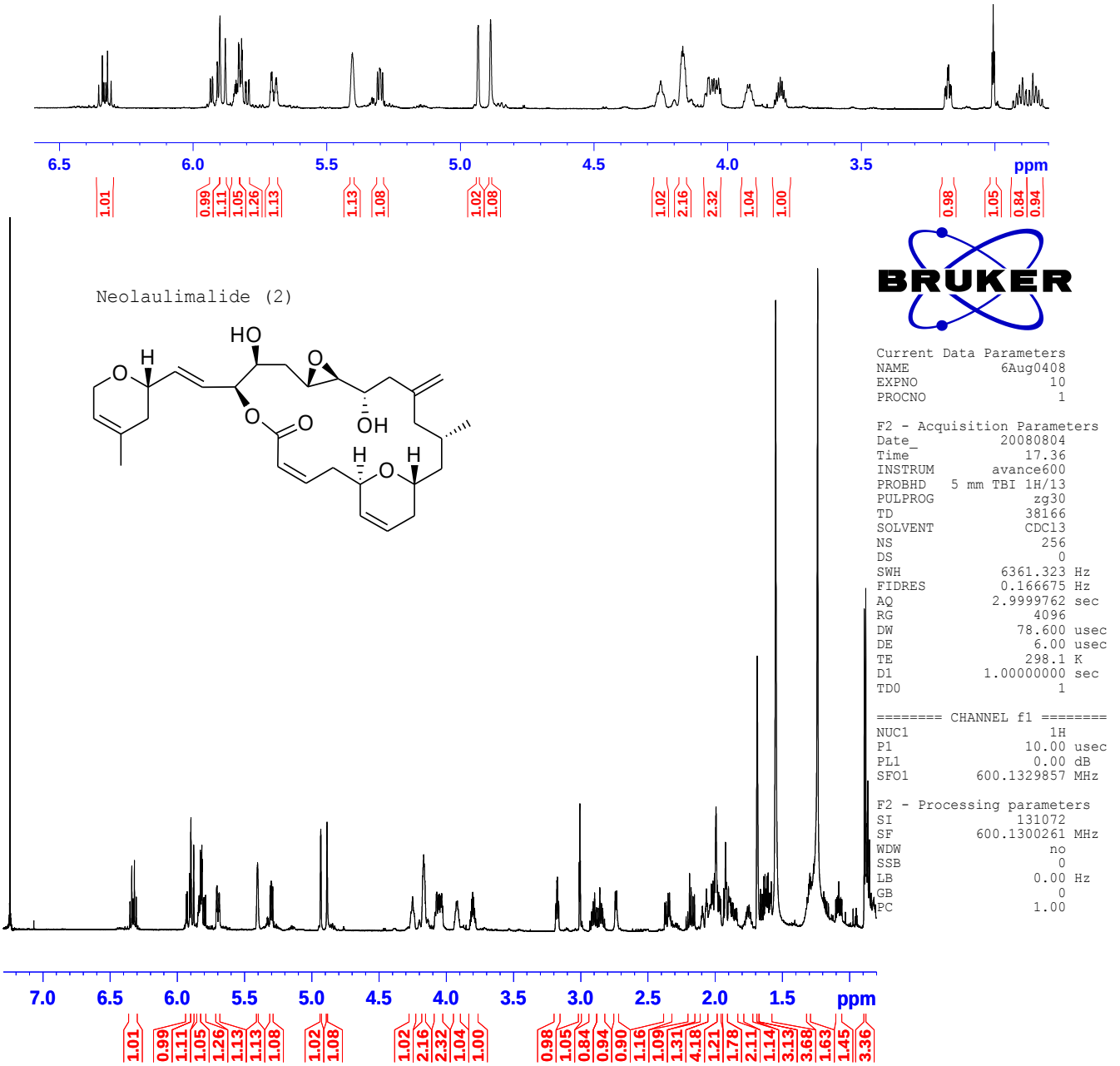
======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2               100.00 usec
PL2                  -3.00 dB
PL12                 16.00 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127537 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

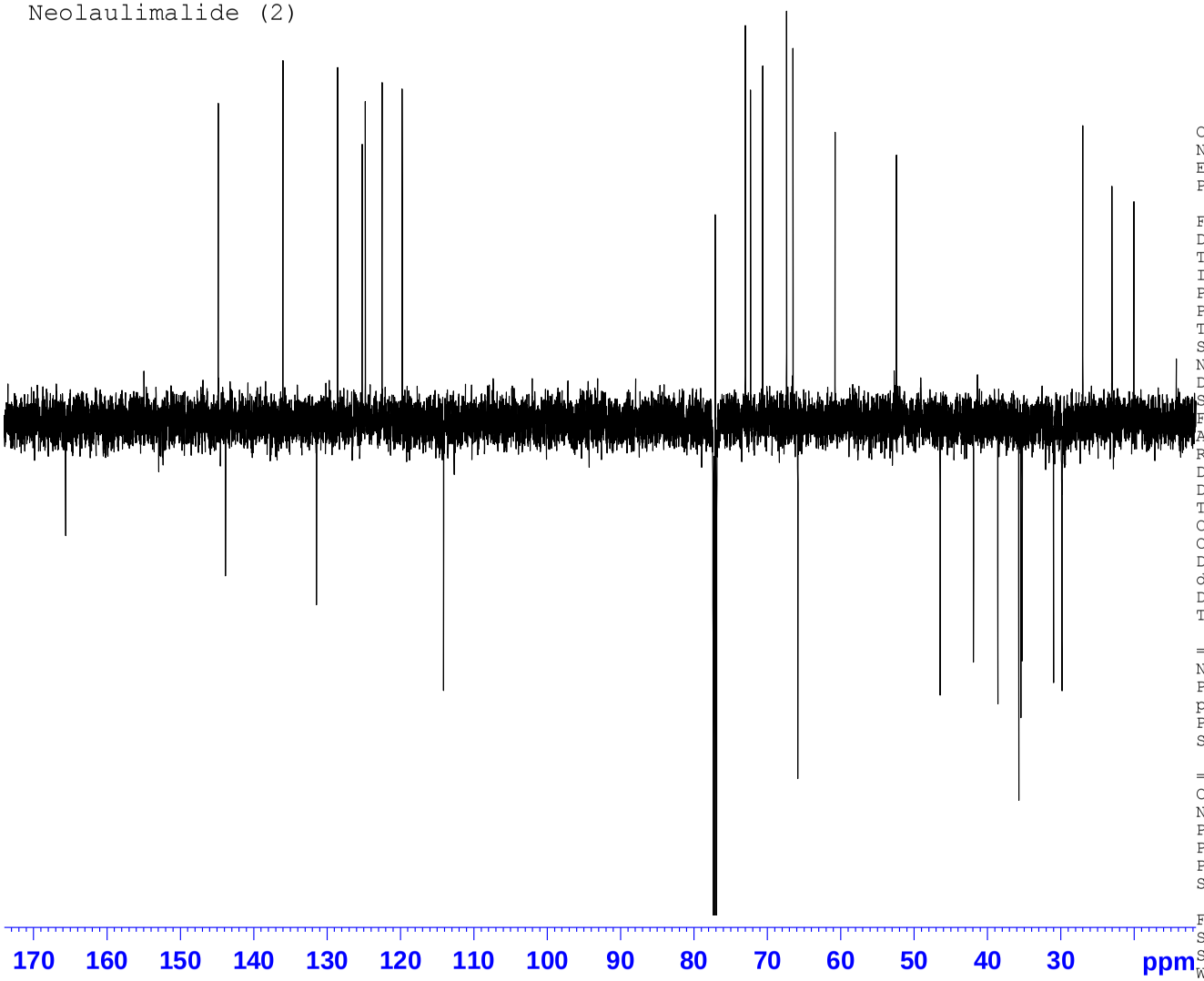
Isolation NMR, taken from PCT/GB96/02240 ; WO 97/10242



Synthetic neolaulimalide



Neolaulimalide (2)



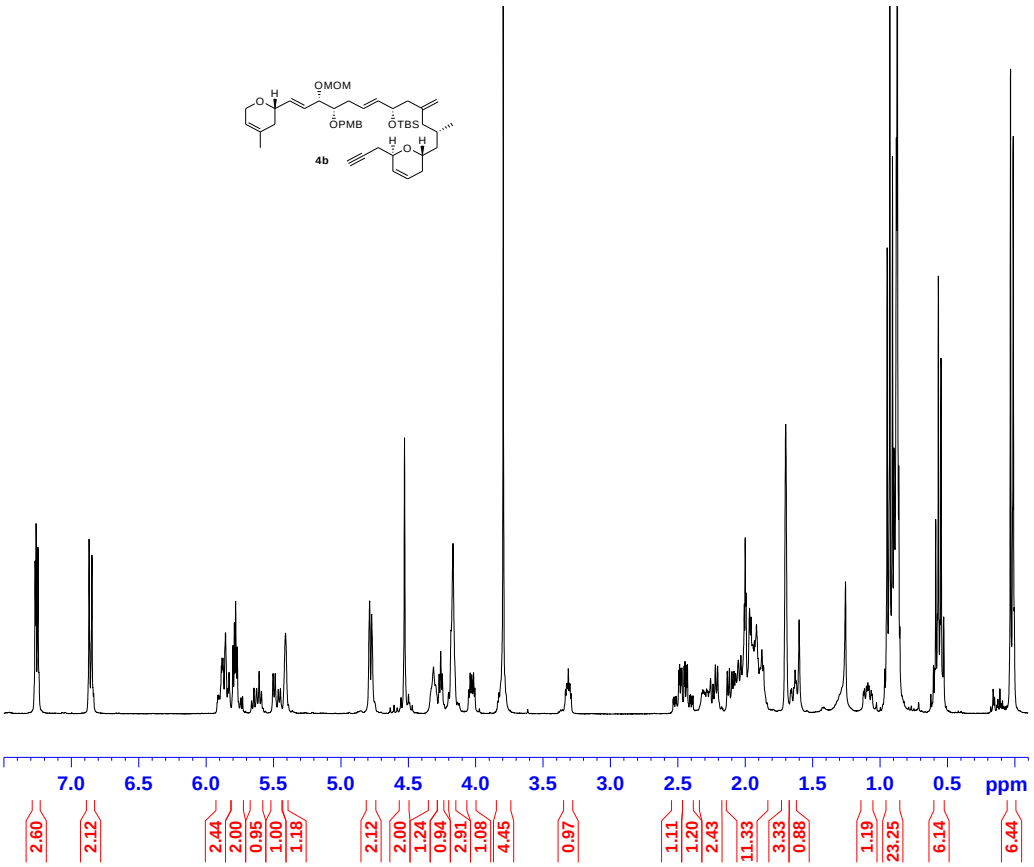

```
Current Data Parameters
NAME            6Aug0308
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080803
Time               18.32
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  3500
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                2896.3
DW                 13.900 usec
DE                  6.00 usec
TE                 298.1 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00000828 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  6.50 usec
p2                 13.00 usec
PL1                 0.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.20 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF          150.9027890 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

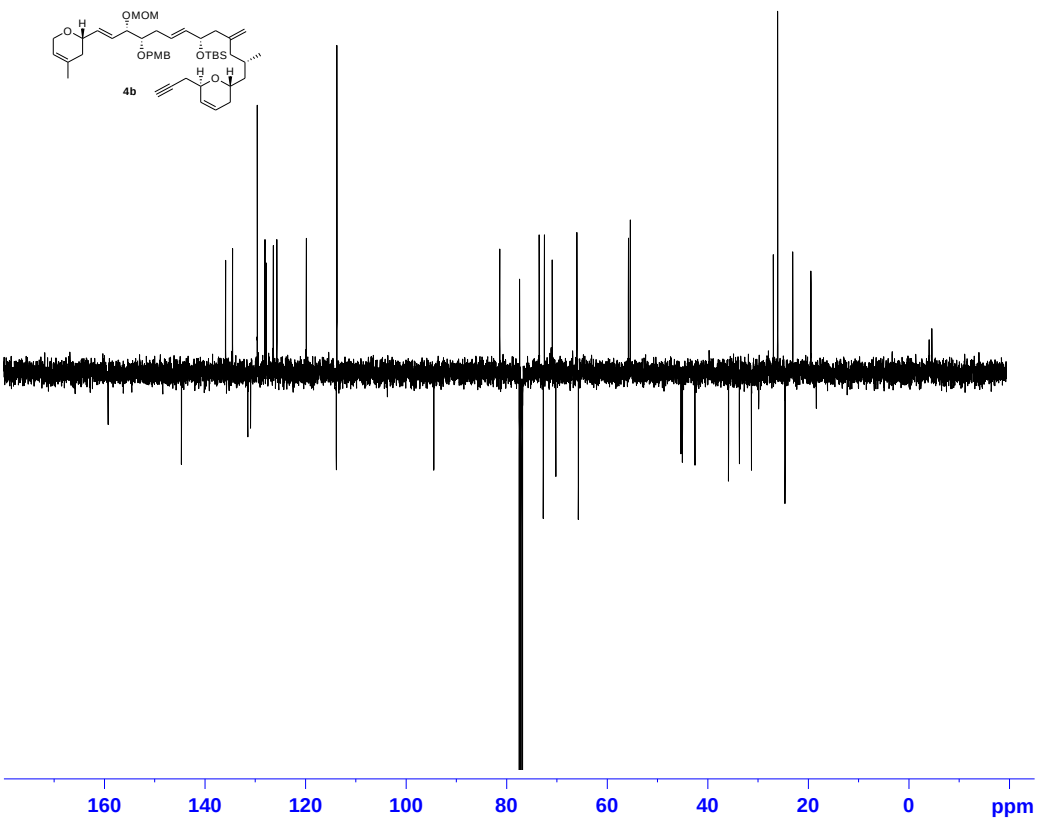



```
Current Data Parameters
NAME              ango500
EXPNO                 230
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070731
Time                 2.33
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                  90.5
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300093 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



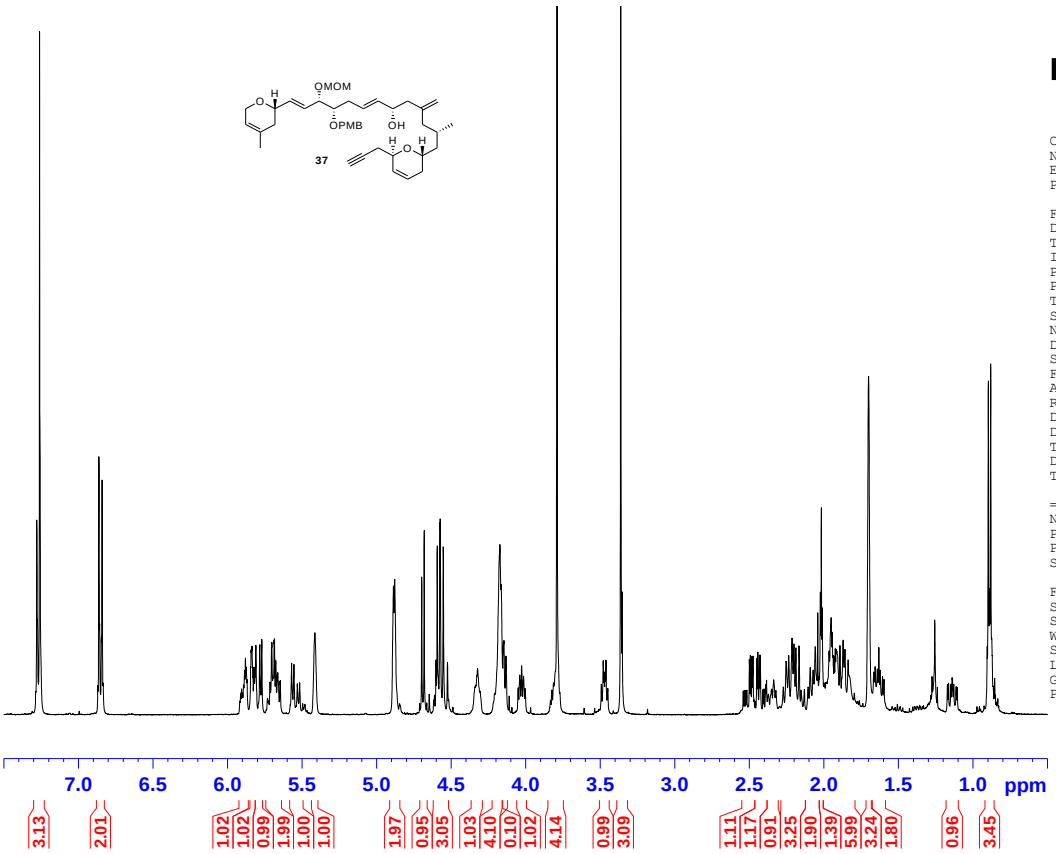

```
Current Data Parameters
NAME              ango283
EXPNO                  41
PROCNO                  1

F2 - Acquisition Parameters
Date_            20070110
Time                13.19
INSTRUM        avance400
PROBHD    5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1200
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                  8192
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1             2.00000000 sec
d20            0.00689655 sec
DELTA          0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1         100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127534 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

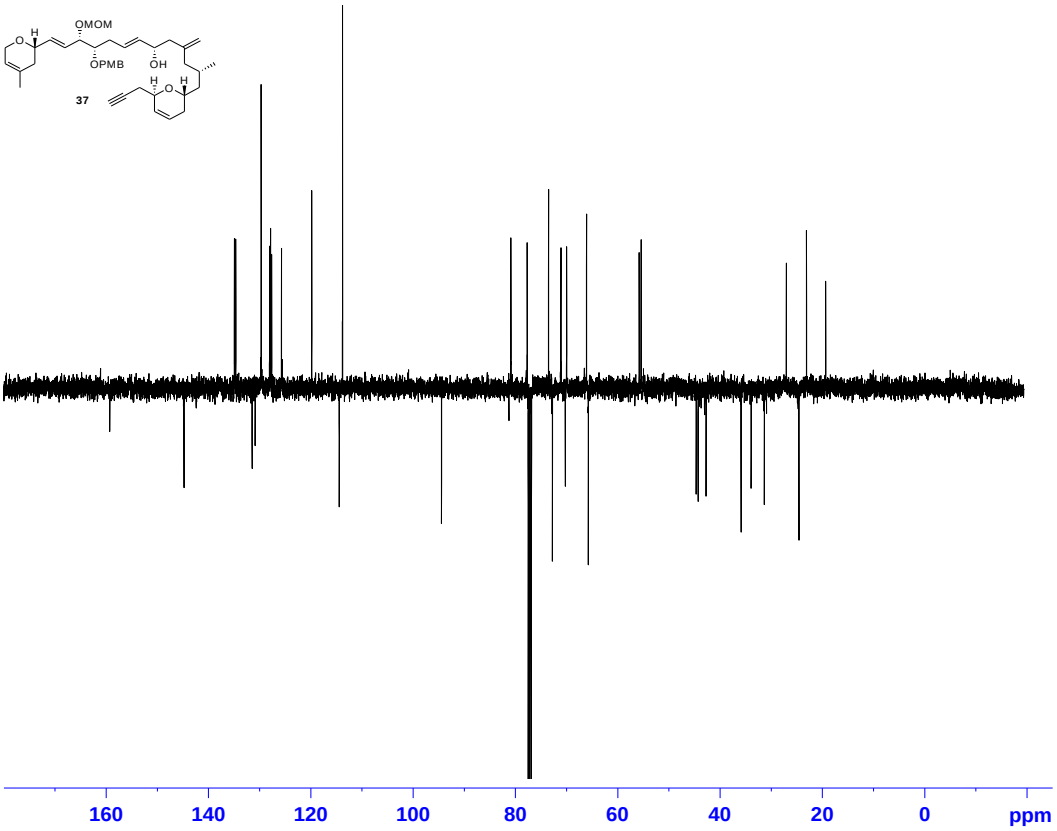


Current Data Parameters
NAME ango295
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070122
Time 9.00
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 203.2
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.75 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300093 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



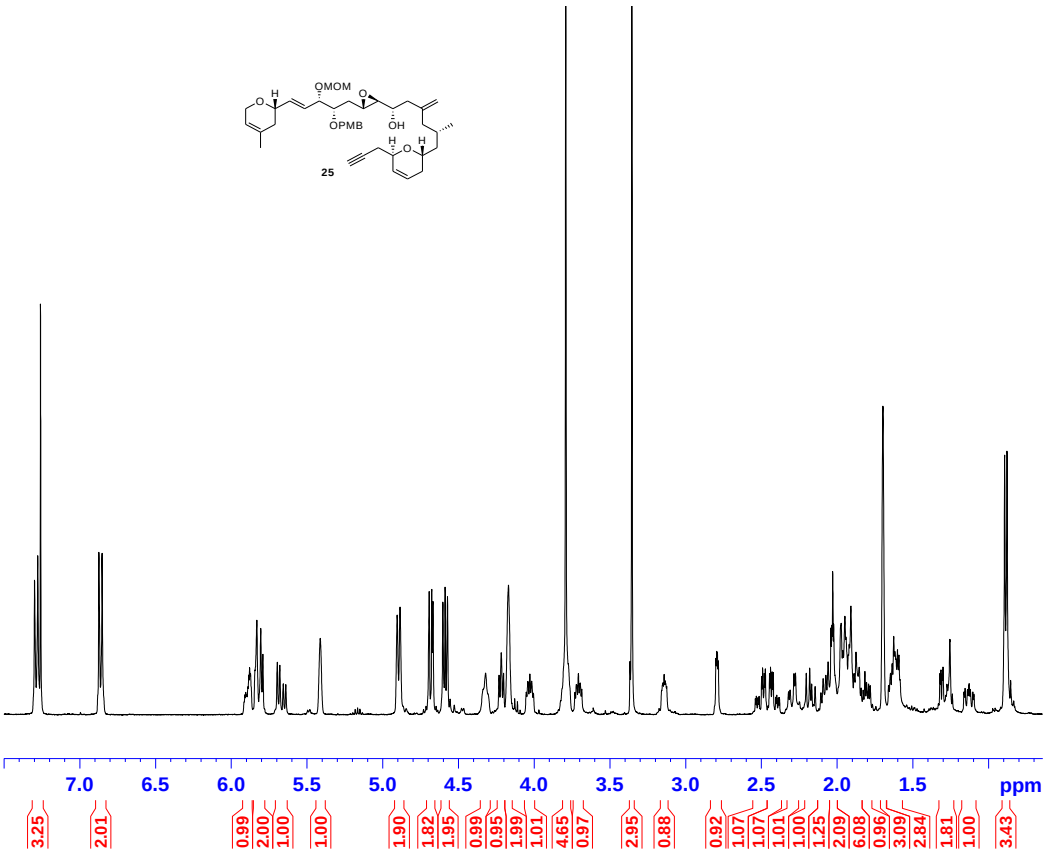
Current Data Parameters
NAME ango295
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20070122
Time 9.36
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 632
DS 2
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 4597.6
DW 19.950 usec
DE 6.00 usec
TE 300.2 K
CNST2 145.0000000
CNST11 1.00000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001311 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
p2 20.60 usec
PL1 -1.00 dB
SFO1 100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127540 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

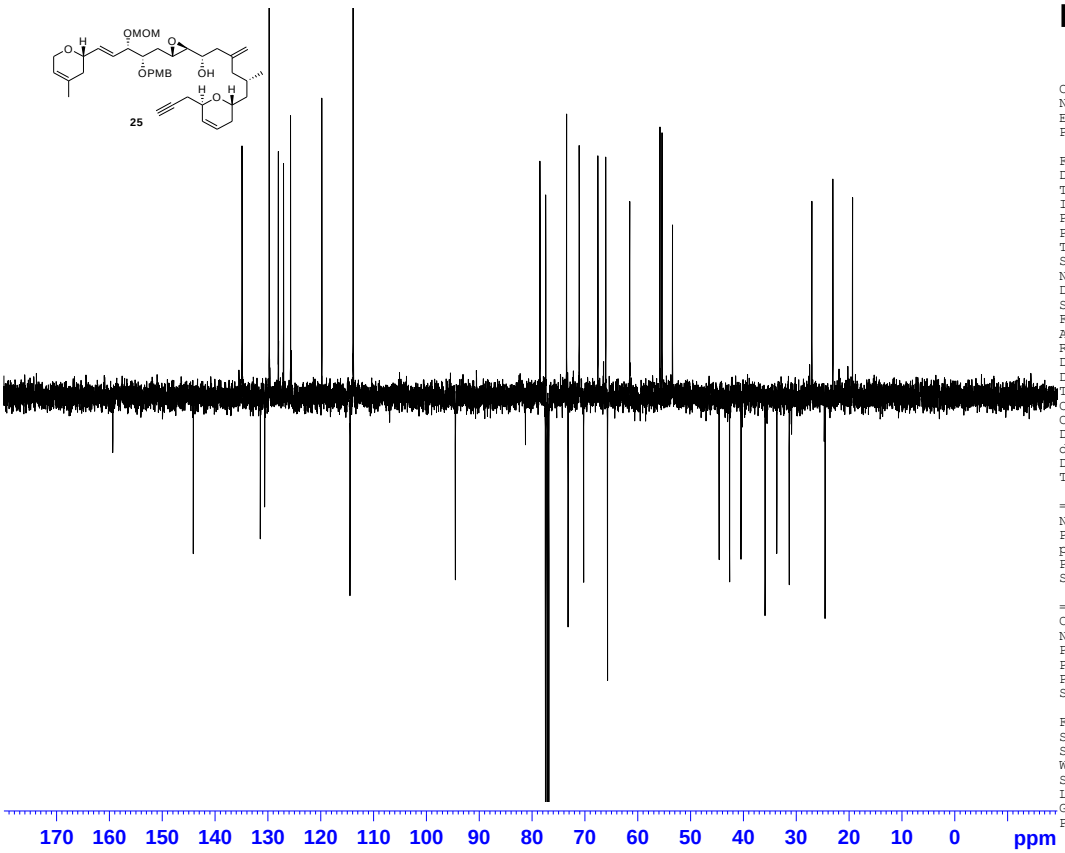



```
Current Data Parameters
NAME            ango303
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_           20070125
Time                8.19
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 228.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300097 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



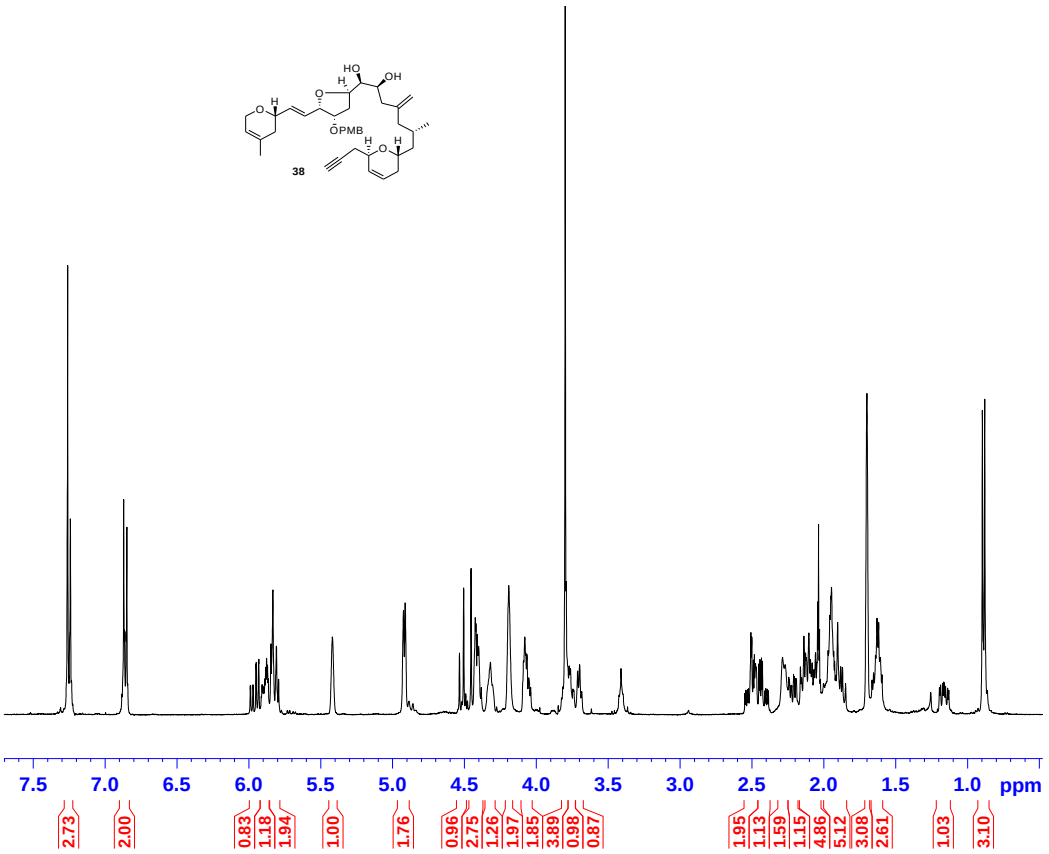

```
Current Data Parameters
NAME            ango303
EXPNO               161
PROCNO                1

F2 - Acquisition Parameters
Date_           20070124
Time               19.50
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1200
DS                     2
SWH            25062.656 Hz
FIDRES          0.382426 Hz
AQ             1.3074932 sec
RG                  3251
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2        145.0000000
CNST11         1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127539 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

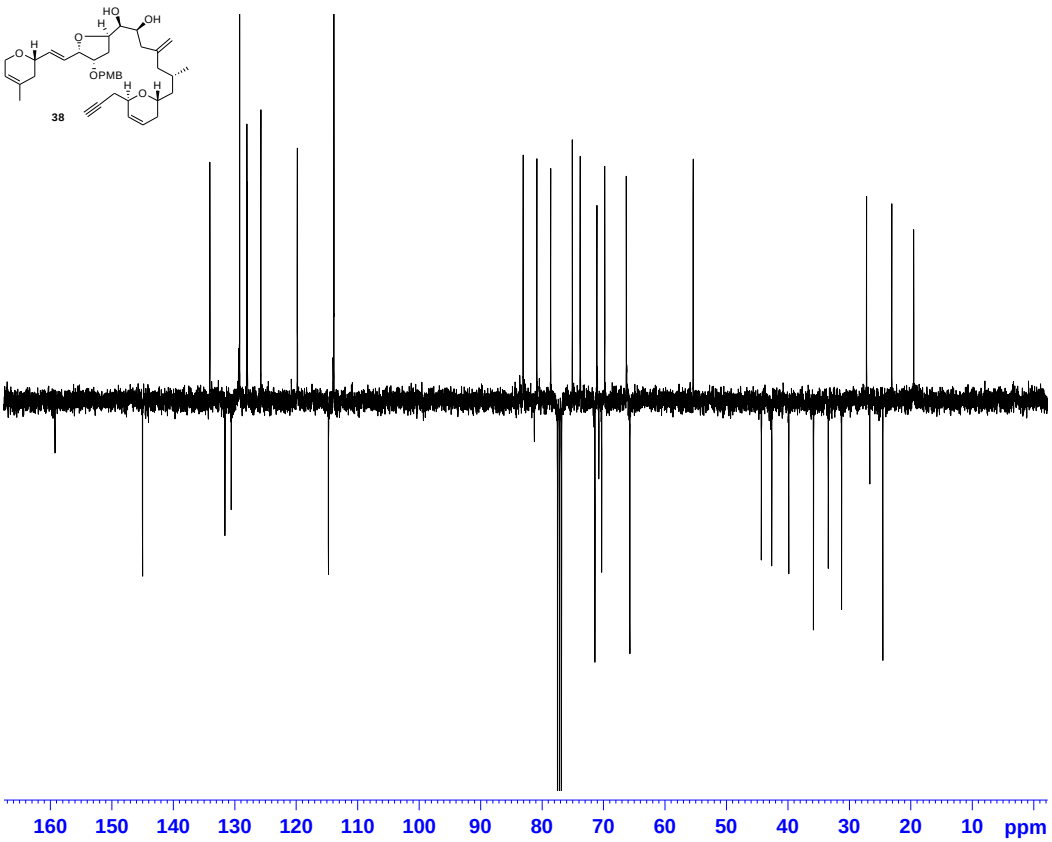



```
Current Data Parameters
NAME          ango573-1
EXPNO                70
PROCNO                1

F2 - Acquisition Parameters
Date_          20071018
Time              22.14
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ           3.9584243 sec
RG               203.2
DW              60.400 usec
DE               6.00 usec
TE              300.2 K
D1          1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300093 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



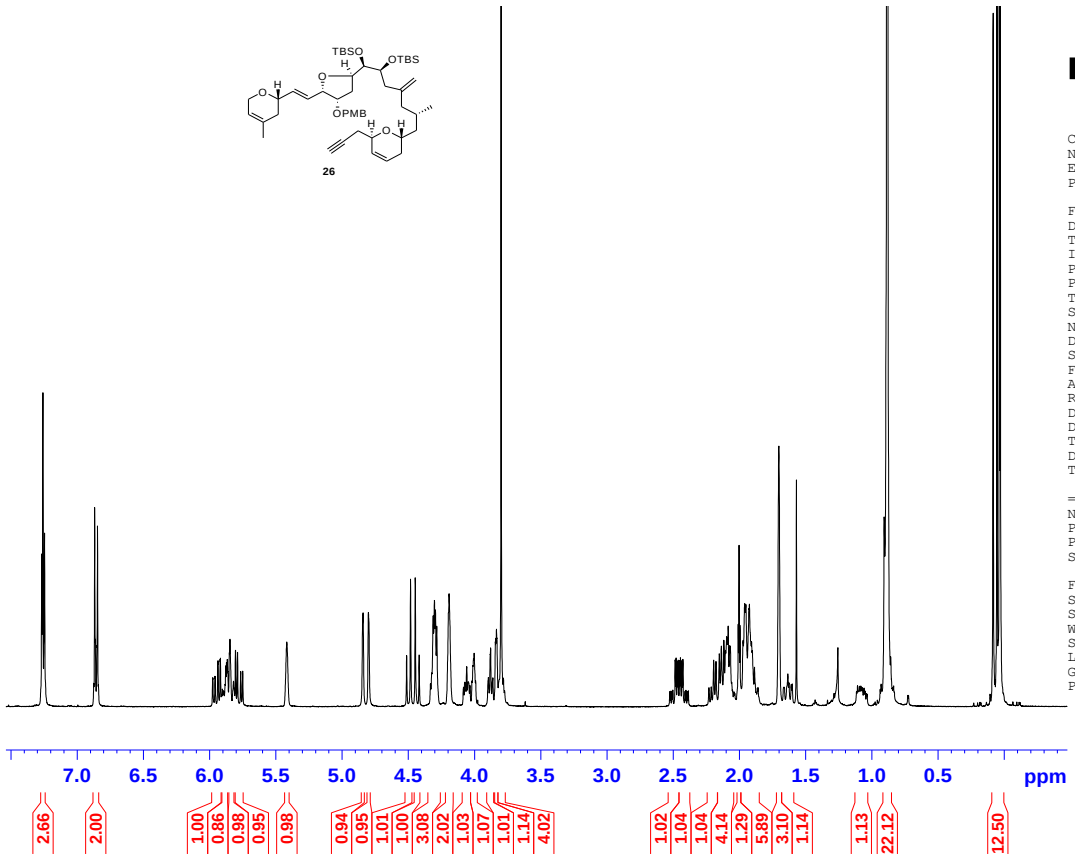

```
Current Data Parameters
NAME          ango573-1
EXPNO                75
PROCNO                1

F2 - Acquisition Parameters
Date_          20071019
Time               1.39
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            jmod
TD                65536
SOLVENT           CDCl3
NS                 1200
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ           1.3074932 sec
RG              7298.2
DW              19.950 usec
DE               6.00 usec
TE              300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1              10.30 usec
p2              20.60 usec
PL1              -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2              -3.00 dB
PL12             16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127543 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

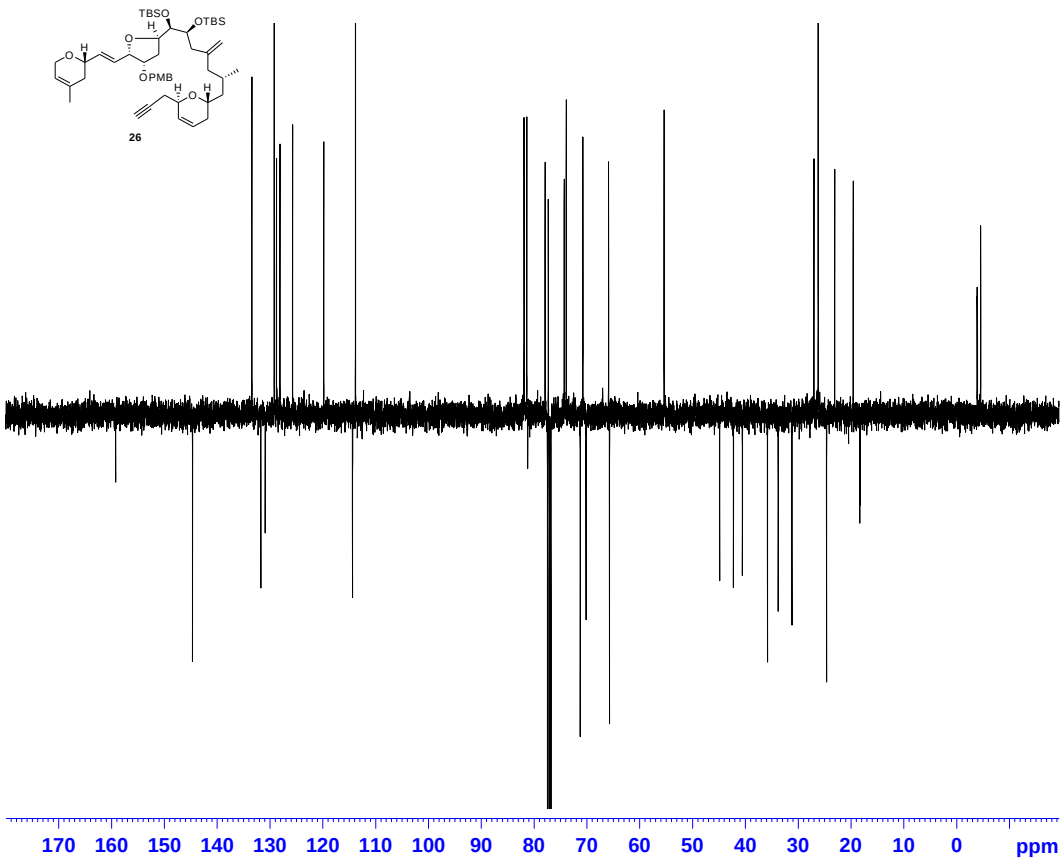



```
Current Data Parameters
NAME            ango575
EXPNO                21
PROCNO                1

F2 - Acquisition Parameters
Date_          20071022
Time              11.03
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG               161.3
DW              60.400 usec
DE                6.00 usec
TE               300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                8.75 usec
PL1              -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300092 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



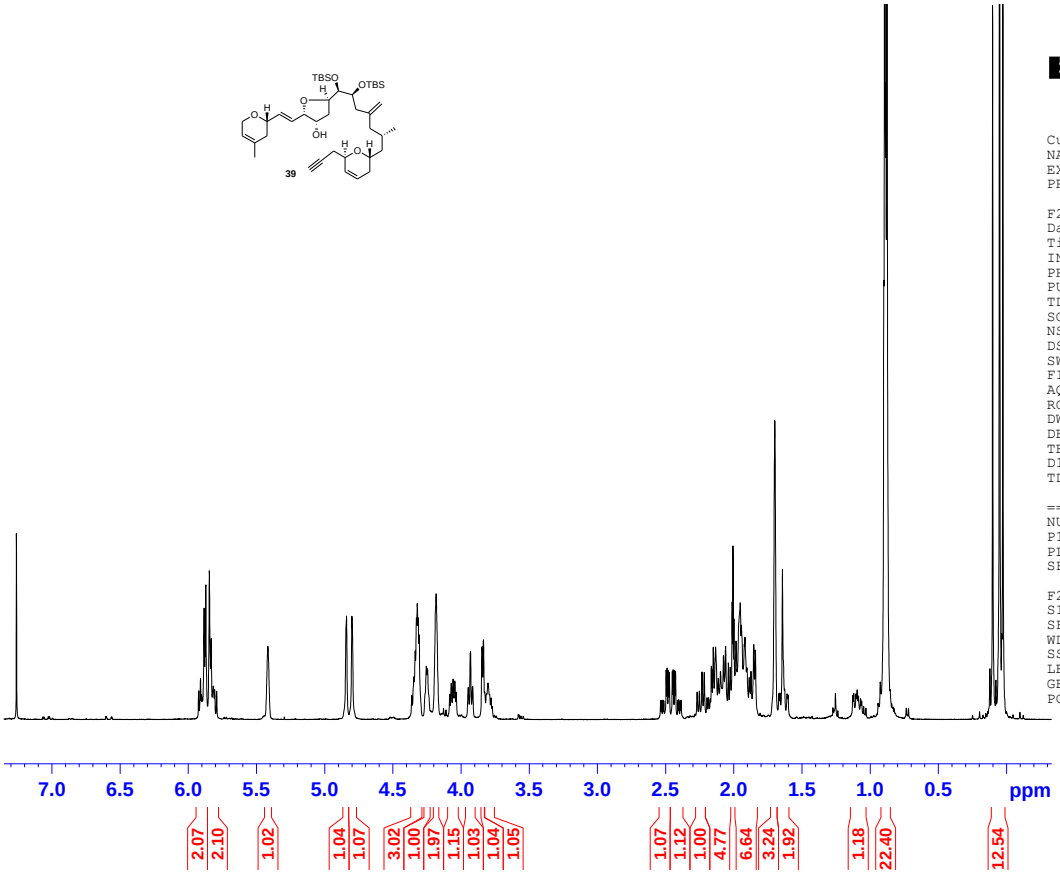

```
Current Data Parameters
NAME            ango575
EXPNO                20
PROCNO                1

F2 - Acquisition Parameters
Date_          20071022
Time              11.00
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                65536
SOLVENT           CDCl3
NS                 1019
DS                    2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ            1.3074932 sec
RG            11585.2
DW              19.950 usec
DE                6.00 usec
TE               300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1          2.00000000 sec
d20         0.00689655 sec
DELTA       0.00001311 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1               10.30 usec
p2               20.60 usec
PL1              -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2              -3.00 dB
PL12             16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

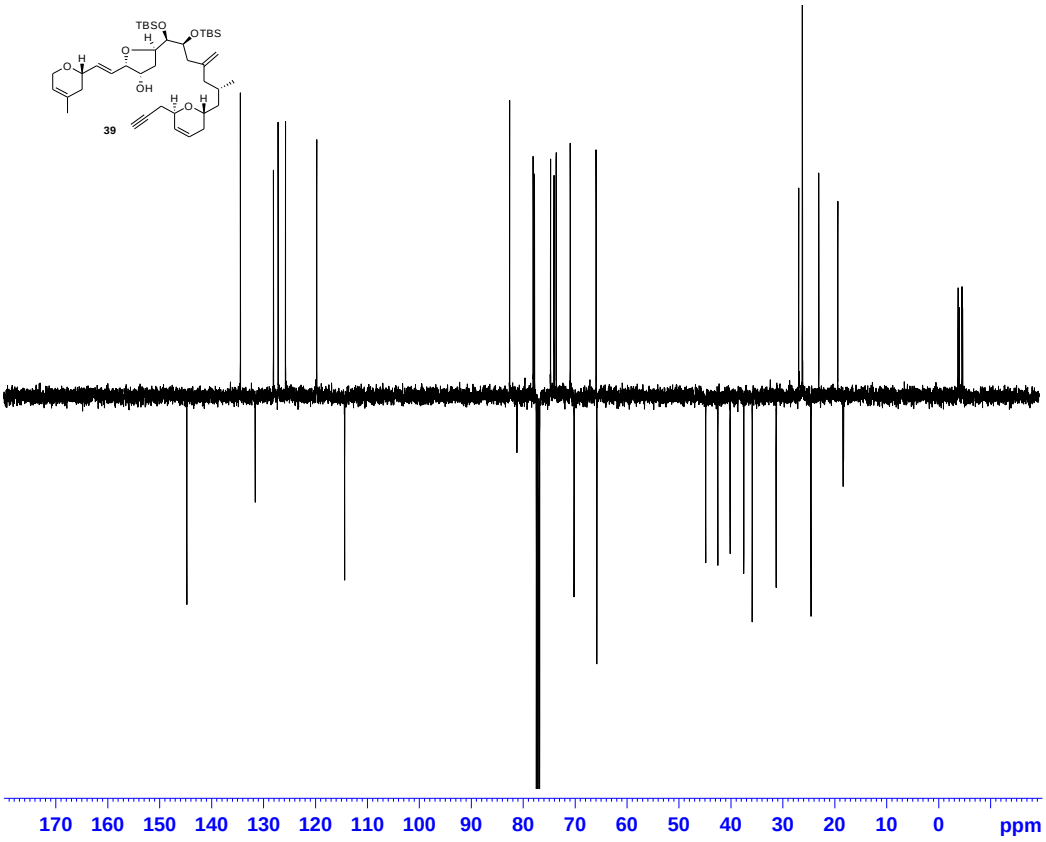



```
Current Data Parameters
NAME            ango581
EXPNO                50
PROCNO                1

F2 - Acquisition Parameters
Date_           20071029
Time               13.14
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ           3.9584243 sec
RG                   114
DW               60.400 usec
DE                 6.00 usec
TE                300.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300094 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



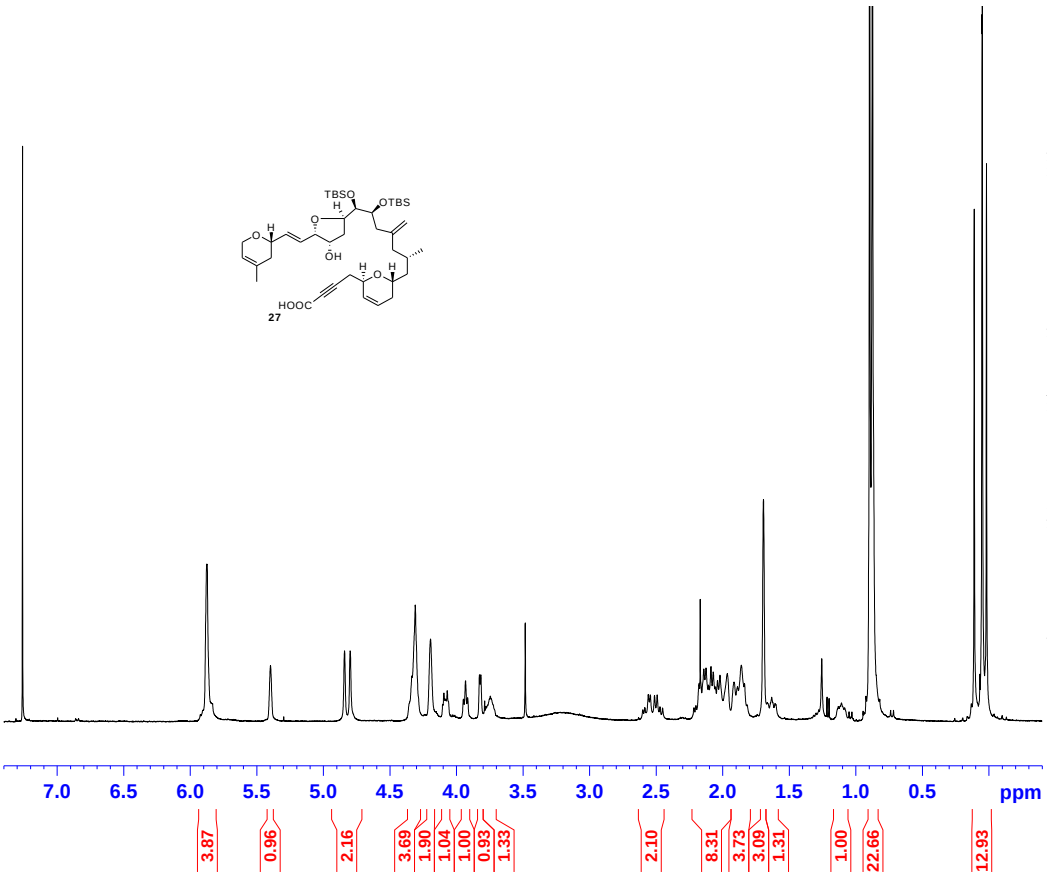

```
Current Data Parameters
NAME            ango581
EXPNO                51
PROCNO                1

F2 - Acquisition Parameters
Date_           20071029
Time               14.11
INSTRUM        avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  1000
DS                     2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ           1.3074932 sec
RG             10321.3
DW               19.950 usec
DE                 6.00 usec
TE                300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF          100.6127538 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
```

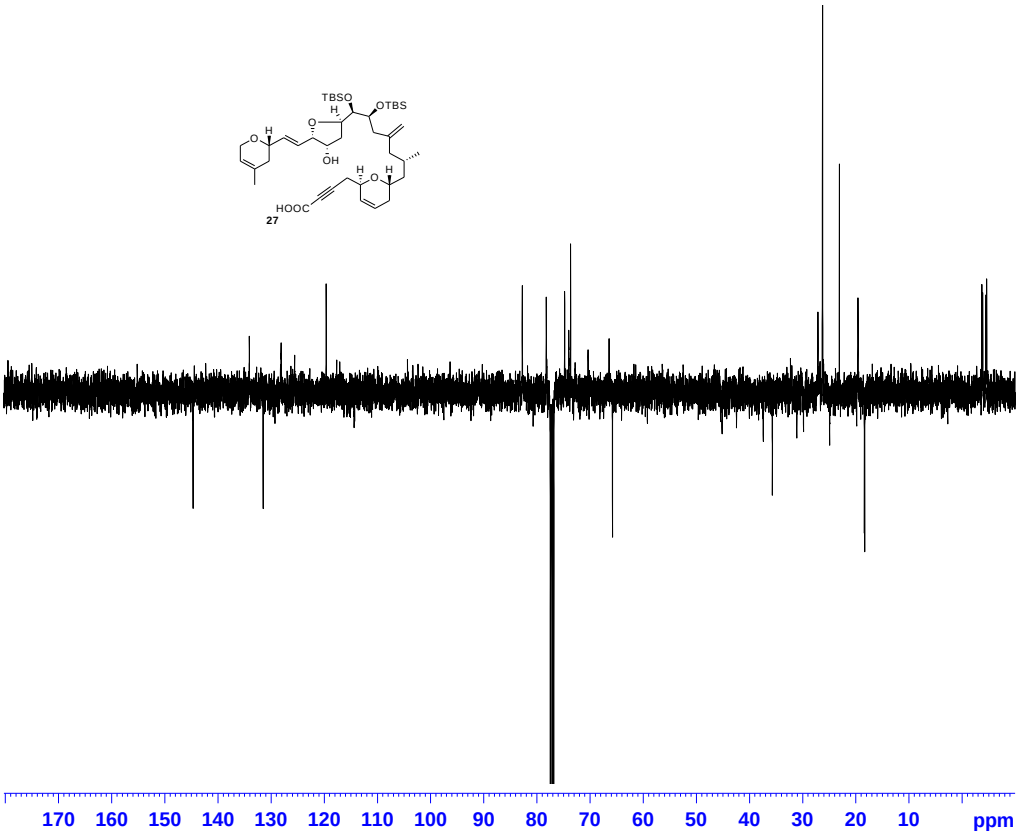



```
Current Data Parameters
NAME            ango584
EXPNO               270
PROCNO                1

F2 - Acquisition Parameters
Date_            20071030
Time               21.27
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ           3.9584243 sec
RG                 228.1
DW                60.400 usec
DE                  6.00 usec
TE                 300.2 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.75 usec
PL1               -3.00 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300092 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



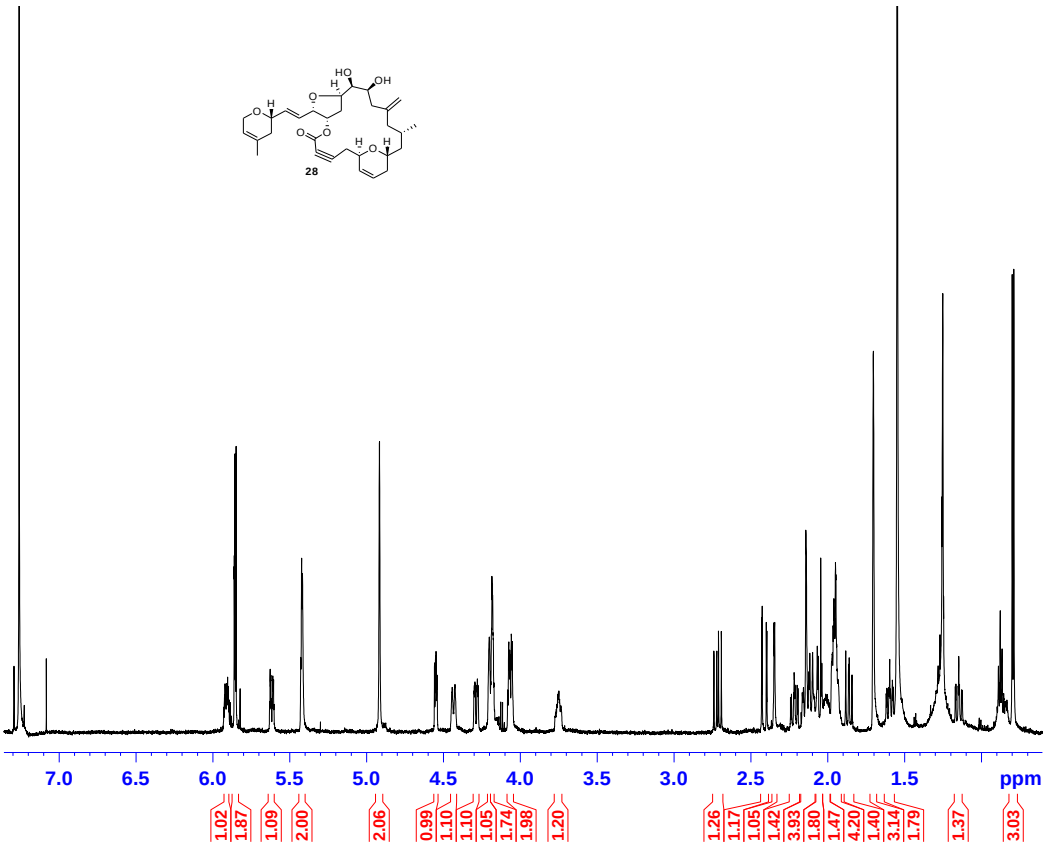

```
Current Data Parameters
NAME            ango584
EXPNO               275
PROCNO                1

F2 - Acquisition Parameters
Date_            20071031
Time                1.43
INSTRUM       avance400
PROBHD   5 mm BBO BB-1H
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  2500
DS                     2
SWH           25062.656 Hz
FIDRES         0.382426 Hz
AQ           1.3074932 sec
RG                7298.2
DW                19.950 usec
DE                  6.00 usec
TE                 300.2 K
CNST2       145.0000000
CNST11        1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00001311 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.30 usec
p2                20.60 usec
PL1               -1.00 dB
SFO1        100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2               -3.00 dB
PL12              16.00 dB
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF          100.6127530 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

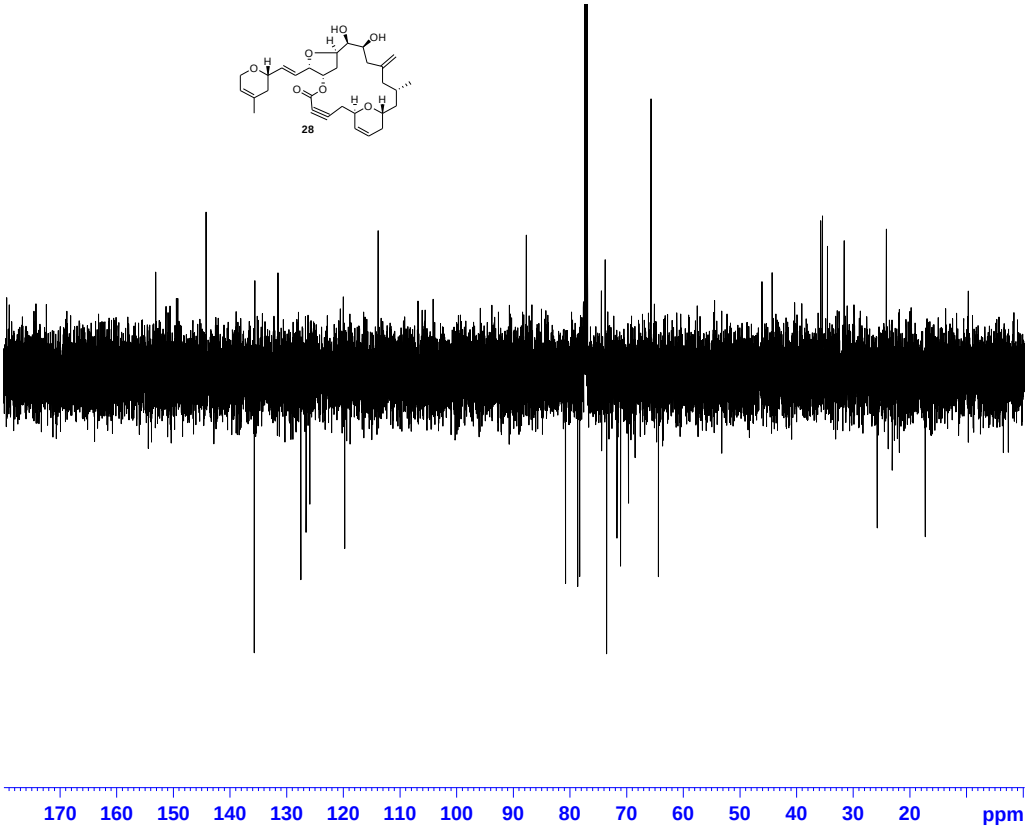



```
Current Data Parameters
NAME            6Mar1008
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080310
Time               19.00
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477449 sec
RG                  1024
DW                40.400 usec
DE                 6.00 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.85 usec
PL1               -6.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 32768
SF          600.1300174 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME            6Mar1008
EXPNO                 15
PROCNO                 1

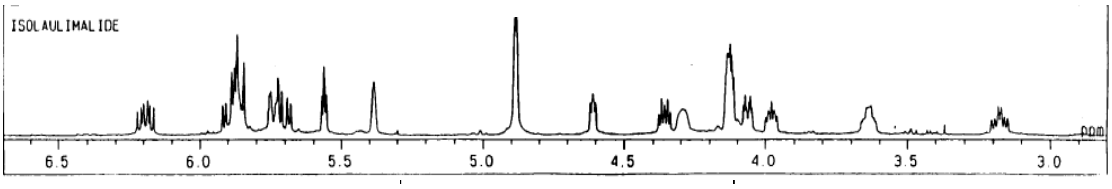
F2 - Acquisition Parameters
Date_           20080311
Time                8.43
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  8913
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                2896.3
DW                13.900 usec
DE                 6.00 usec
TE                298.1 K
CNST2        145.0000000
CNST11         1.0000000
D1            2.00000000 sec
d20           0.00689655 sec
DELTA         0.00001019 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 8.00 usec
p2                16.00 usec
PL1                0.00 dB
SFO1         150.9178988 MHz

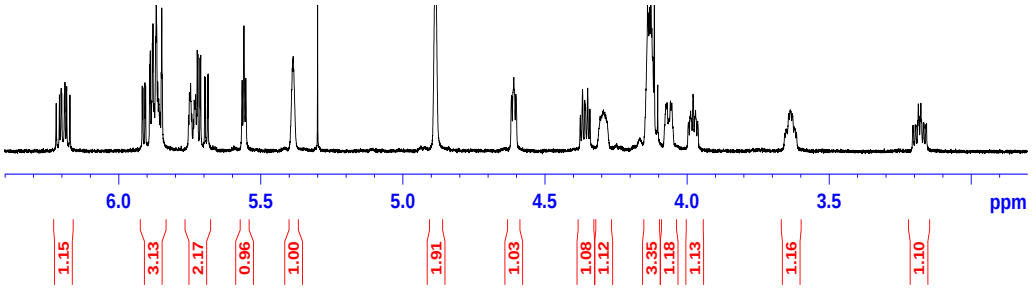
======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             80.00 usec
PL2               -6.00 dB
PL12              12.20 dB
SFO2         600.1324005 MHz

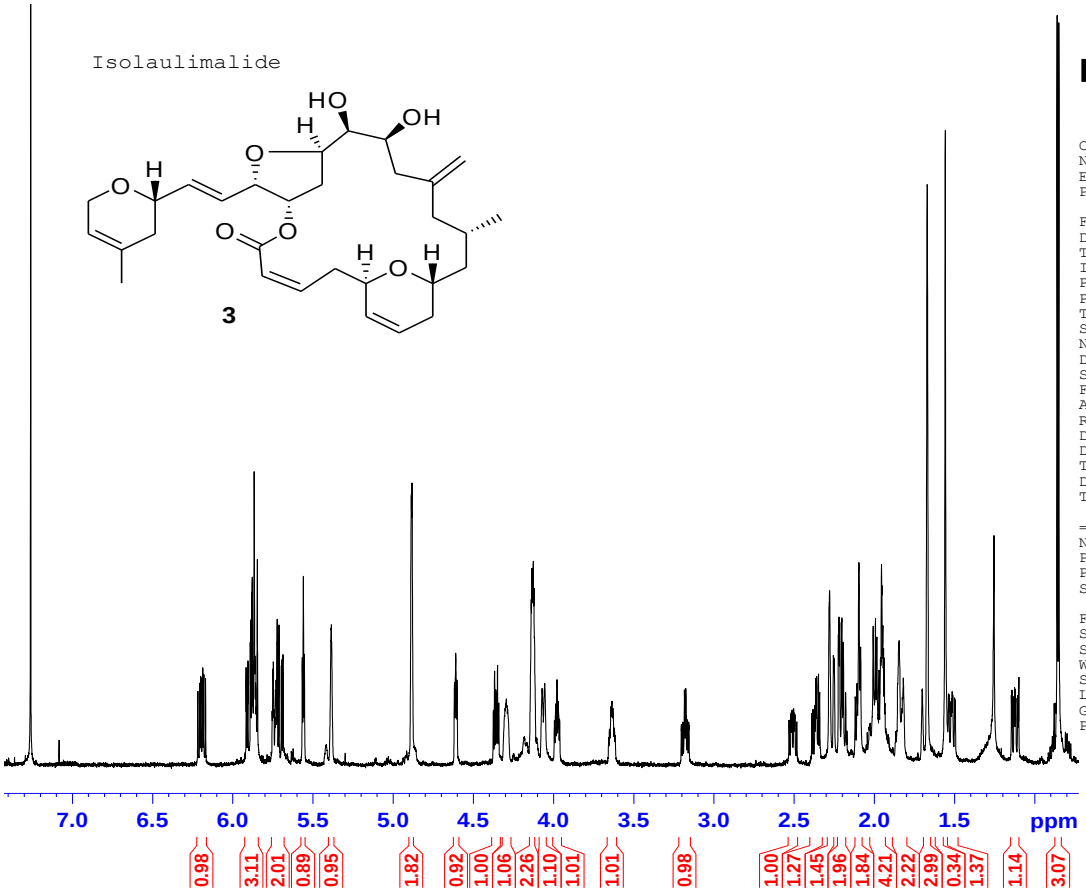
F2 - Processing parameters
SI                 32768
SF          150.9027884 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```

Isolation NMR, taken from PCT/GB96/02240; WO 97/10242



Synthetic isolaulimalide





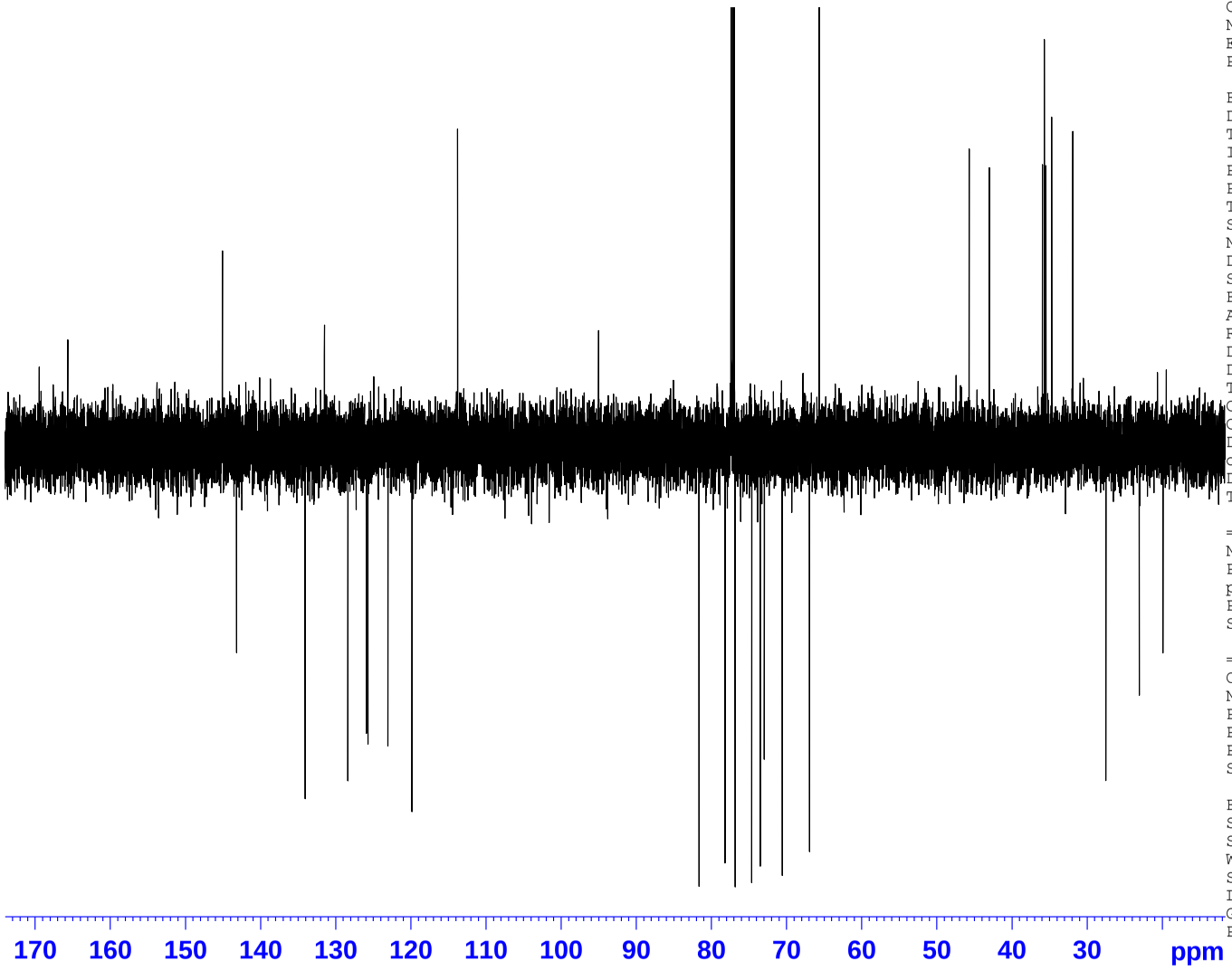

```
Current Data Parameters
NAME            6Mar2608
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080326
Time               15.02
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            12376.237 Hz
FIDRES          0.188846 Hz
AQ             2.6477449 sec
RG                 724.1
DW                40.400 usec
DE                 6.00 usec
TE                300.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                13.85 usec
PL1               -6.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                32768
SF          600.1300174 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                  1.00
```

Isolaulimide




```
Current Data Parameters
NAME            6Mar2608
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080326
Time               13.28
INSTRUM        avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  2151
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                9195.2
DW                13.900 usec
DE                  6.00 usec
TE                300.0 K
CNST2        145.0000000
CNST11         1.0000000
D1           2.00000000 sec
d20          0.00689655 sec
DELTA        0.00000828 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.50 usec
p2                  13.00 usec
PL1                  0.00 dB
SFO1        150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -6.00 dB
PL12                12.20 dB
SFO2        600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF          150.9027876 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```