-Supplementary Material for-

Synthesis and biological evaluation of (–)-dictyostatin and stereoisomers

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Synthesis of 6,16-*bis,epi*-dictyostatin

{3(*R*)-[2-(4-Methoxyphenyl)-5(*S*)-methyl[1(*S*),3]dioxan-4-yl]-2-oxobutyl}phosphonic acid dimethyl ester (7).
BuLi (4.5 mL, 1.6 M solution in hexane) was added dropwise to a stirred solution of dimethyl methanephosphonate (0.77 mL, 7.1 mmol) in THF (7 mL) at –78 ˚C. After 1 h, a solution of 6 (0.46 g, 1.42 mmol) in THF (1 mL) was added. After 30 min, the reaction was then allowed to warm to 0 ˚C, quenched by pouring into brine (10 mL) and extracted with EtOAc (2 x 5 mL) the combined extracts were washed with brine (10 mL), dried and chromatographed (EtOAc/hexane 1:1) gave 7 (0.47 g, 85%) as a colorless oil: IR ($CHCl_3$) 3469, 2957, 2850, 1715, 1615, 1518, 1461, 1393, 1302, 1251, 1173, 1031, 828 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H), 6.89 (m, 2H), 5.50 (s, 1H), 4.14 (dd, *J* = 11.3, 4.7, Hz, 1H), 4.06 (dd, *J* = 10.0, 2.7 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.59 (t, *J* = 11.1 Hz, 1H), 3.38 (dd, *J* = 22.6, 14.5 Hz, 1H), 3.17 (dd, *J* = 21.6, 14.5 Hz, 1H), 3.02 (dq, *J* = 2.8, 7.0 Hz, 1H), 2.06 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 159.5, 130.4, 126.9, 113.1, 100.5, 82.1, 72.4, 54.9, 52.6, 48.6, 39.3, 37.6, 30.6, 11.6, 8.7; LRMS (EI) 386 ($M^{+\bullet}$), 263, 193, 151, 137, 135, 124; HRMS (EI) calcd for $C_{18}H_{27}O_7P$ ($M^{+\bullet}$) 386.1494, found 386.1482; $[\alpha]^{20}_D$ +4.2 (*c* 1.5, $CHCl_3$).

4(*R*)-Benzyl-3-[4-(2,2-dimethyl[1,3(*S*)]dioxolan-4-yl)-3(*S*)-hydroxy-2(*R*)-methylbutyryl]-oxazolidin-2-one (10).
Diisopropylethylamine (13 mL) was added to a solution of propionyloxazolidinone (13.1 g) in anhydrous CH_2Cl_2 (250 mL) at 0 ˚C, followed by dropwise addition of *n*-Bu_2BOTf (1.0M in CH_2Cl_2, 68 mL). The solution was stirred for 1 h at 0 ˚C. A solution of crude aldehyde derived from **9** (8.9 g) in anhydrous CH_2Cl_2 (10 mL) was added slowly at –78 ˚C. After addition, the reaction mixture was warmed to 0 ˚C and stirred for 1 h, then quenched with pH7 phosphate buffer (20 mL). A solution of hydrogen peroxide (30 %, 40 mL) in MeOH (80 mL) was added at 0 ˚C and the mixture was stirred for 1 h. The reaction mixture was extracted with CH_2Cl_2 (50 mL x 2) and dried over $MgSO_4$ followed by flash chromatography (EtOAc/hexane 1:1) to yield 20.7 g of **10** (98%) as a colorless oil: IR ($CHCl_3$) 3434, 2956, 2929, 2858, 1724, 1472, 1463, 1257, 1097, 836, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.33 m, 3H), 7.22 (m 2H), 4.72 (ddd, *J* = 10.5, 6.9, 3.2 Hz, 1H), 4.35 (m, 1H), 4.23 (m, 3H), 4.12 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.82 (ddd, *J* = 10.2, 7.0, 3.2 Hz, 1H), 3.61 (t, *J* = 7.7 Hz, 1H), 3.25 (dd, *J* = 13.4, 3.3 Hz, 1H), 2.82 (dd, *J* = 13.4, 9.4 Hz, 1H), 1.80 (ddd, *J* = 14.2, 9.7, 4.6 Hz, 1H), 1.68 (ddd, *J* = 10.8, 7.8, 3.0 Hz, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 152.9, 134.9, 129.3, 128.8, 127.3, 108.6, 73.4, 69.5, 68.5, 66.0, 54.9, 42.4, 37.6, 37.5, 26.8, 25.6,10.8; $[\alpha]^{20}_D$ –28.1 (*c* 4.1, $CHCl_3$).

6-(2,2-Dimethyl[1,3(*S*)]dioxolan-4-yl)-5(*S*)-hydroxy-4(*R*)-methylhex-2-enoic acid ethyl ester (11).
The aldol product **10** (5.39 g, 14.3 mmol) in 20 mL THF was added slowly to RED-Al (4.6 mL, 15.7 mmol) in 10 mL of THF at –78 ˚C. The solution was stirred for 10-15 min at –78 ˚C, then warmed to –50 ˚C and stirred between –55 and –40 ˚C for 1 h. The reaction was quenched at –50 ˚C with 20 mL of EtOAc and 2 mL of MeOH, then poured into a mixture of a saturated aqueous solution of Rochelle's salt (10 mL) and Et_2O (12 mL) and stirred at –20 ˚C for 10 min. The aqueous layer froze as a gel. The organic layer was separated and the aqueous layer was rinsed quickly with Et_2O (2 x 10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude aldehyde was used without purification. Dry THF (40 mL) was was treated with triethylphosphonoacetate (3.26 mL, 16.4 mmol) and potassium *tert*-

butoxide (1.86 g, 17.4 mmol). The mixture was stirred at room temperature for 10 min before cooling to –78 ˚C. The crude aldehyde was added in THF (10 mL) and stirred overnight while warming to room temperature. The mixture was poured into brine (10 mL), extracted with Et_2O (3 x 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash silica gel chromatography (hexane/EtOAc 3:2) provided **11** (2.02 g, 52 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2984, 2938, 1719, 1651, 1370, 1270, 1183, 1060, 989 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ6.88 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.83 (d, *J* = 15.8 Hz, 1H), 4.28 (m, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 4.03 (dd, *J* = 8.1, 6.0 Hz, 1H), 3.76 (m, 1H), 3.53 (t, *J* = 8.0 Hz, 1H), 2.48 (brs, 1H), 2.41 (m, 1H), 1.72-1.56 (m, 2H), 1.37 (s, 3H), 1.31 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 150.3, 121.6, 108.6, 73.5, 71.3, 69.3, 60.2, 42.8, 37.2, 25.8, 25.5, 14.5, 14.1; LRMS (EI) 257 $(M–CH_3)^+$ 211, 169, 128, 87; HRMS (EI) calcd for $C_{13}H_{21}O_5$ 257.1389 $(M–CH_3)^+$ found 257.1382; $[\alpha]^{20}_D$ –25.7 (*c* 1.6, $CHCl_3$).

(5*S*,7*S*,8)-*tris*(*tert*-Butyldimethylsilanyloxy)-(4*R*)-methyloct-2-enoic acid ethyl ester (12).
Dowex HCR-W2 ion-exchange resin (2.0 g, activated by aqueous 1N HCl for 24 h then filtered, MeOH as eluent) was added to a stirred solution of conjugated ester **11** (1.73 g) in MeOH (20 mL). After stirring for 24 h, the resin was filtered and filtrate was concentrated and dried for 2 h *in vacuo*. The triol was then used in next step without further purification. A stirred solution of triol and 2,6-lutidine (3.3 mL, 28.6 mmol) in CH_2Cl_2 (30 mL) at 0 ˚C was treated with TBSOTf (5.1 mL, 22.2 mmol) and the reaction mixture was stirred for 1 h at 0 ˚C. The reaction mixture was quenched by the addition of H_2O (25 mL). The reaction mixture was extracted by CH_2Cl_2 and dried over $MgSO_4$ followed by the evaporation of the solvent under reduced pressure. The residue was purified by short column chromatography (hexane/EtOAc 9:1) whereupon the **12** (2.96 g, 81 % for 2 steps) was obtained as a colorless oil: IR ($CHCl_3$) 2956, 2930, 2858, 1724, 1652, 1472, 1463, 1362, 1256, 1097, 836, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.04 (dd, *J* = 15.9, 6.7 Hz, 1H), 5.75 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.16 (dq, *J* = 1.3, 7.1 Hz, 2H), 3.84 (quint, *J* = 3.6 Hz, 1H), 3.71 (m, 1H), 3.49 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.36 (dd, *J* = 10.1, 5.8 Hz, 1H), 2.48 (m, 1H), 1.59-1.40 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.85 (m, 27H), 0.056 (s, 3H), 0.049 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H), 0.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 151.7, 120.8, 72.8, 71.4, 68.0, 60.0, 42.2, 39.5, 25.9, 25.7, 18.3, 18.1, 14.2, 13.3, –3.0, –3.6, –4.2, –4.5, –5.4; LRMS (EI) 517 $(M–{}^tBu)^+$ 385, 315, 271, 231, 147; HRMS (EI) calcd for $C_{25}H_{53}O_5Si_3$ 517.3201 $(M–{}^tBu)^+$ found 517.3179; $[\alpha]^{20}_D$ –29.6 (*c* 0.92, $CHCl_3$).

(5*S*),7*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-8-hydroxy-4(*R*)-methyloct-2-enoic acid ethyl ester (13).
A solution of TBS ether **12** (7.4 g, 12.9 mmol) in THF (10 mL) was slowly treated with HF-pyridine in pyridine (40 mL, prepared by slow addition of 12 mL pyridine to 3 mL HF-pyridine complex followed by dilution with 25 mL THF). The mixture was stirred overnight at room temperature and quenched with saturated aqueous $NaHCO_3$ (100 mL). The aqueous layer was separated and extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with saturated aqueous $CuSO_4$ (3 x 50 mL), dried over $MgSO_4$, filtered and concentrated. Flash column chromatography (EtOAc/hexane 1:4) afforded 3.86 g (65%) of the alcohol **13** as a colorless oil: IR ($CHCl_3$) 3492, 2956, 2930, 2857, 1722, 1472, 1367, 1256, 1092, 1039, 836, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.01 dd, *J* = 15.9, 6.7 Hz, 1H), 5.75 (dd, *J* = 15.9, 1.5 Hz, 1H), 4.15 (dq, *J* = 1.2, 7.2 Hz, 2H), 3.75 (m, 1H), 3.56 (m, 1H), 3.40 (m, 1H), 2.44 (m, 1H), 1.85 (t, *J* = 5.9 Hz, 1H), 1.61 (ddd, *J* = 11.5, 6.4, 5.0 Hz, 1H), 1.50 (ddd, *J* = 13.0, 7.2, 5.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.86 (s, 9H), 0.85 (s, 9H), 0.60 (s, 6H), 0.34 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 151.1, 121.1, 72.8, 71.0, 66.9, 60.1, 41.8,

38.7, 25.8, 18.0, 14.2, 13.3, –4.2, –4.3; LRMS (ESI) 461 $[M+H]^+$; HRMS (ESI) calcd for $C_{23}H_{49}O_5Si_2$ 461.3119 $[M+H]^+$, found 461.3091; $[\alpha]^{20}_D$ –24.3 (*c* 5.9, $CHCl_3$).

(5*S*,7*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-(4*R*)-methyl-8-oxooct-2-enoic acid ethyl ester (14). Alcohol **13** (3.86 g, 8.34 mmol) in CH_2Cl_2 (20 mL) was treated with the Dess-Martin periodinane (5.3 g, 12.5 mmol). After 1 h, the mixture was quenched with saturated aqueous $NaHCO_3$ (50 mL). The aqueous layer was extracted with Et_2O (2 x 20 mL) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography (hexane/EtOAc 4:1) to remove the residue from the Dess-Martin reagent provided the aldehyde **14** as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ9.53 (d, *J* = 1.5 Hz, 1H), 7.02 dd, *J* = 15.9, 6.6 Hz, 1H), 5.77 (dd, *J* = 15.9, 1.4 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.07 (ddd, *J* = 7.7, 4.8, 1.4 Hz, 1H), 3.84 (ddd, *J* = 8.6, 6.8, 4.4 Hz, 1H), 2.52 (m, 1H), 1.75-1.56 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 9H), 0.86 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H), 0.03 (s, 6H).

5(*S*),7(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-10(*S*)-[2-(4-methoxybenzyl)-5(*S*)-methyl-[1,3(*R*)]dioxan-4-yl]-4(*R*)-methylundeca-2,8-dienoic acid ethyl ester (15).
NaHMDS (1.0 M in THF, 12.3 mL, 12.3 mmol) was slowly added to a solution of the salt **8** (8.72 g, 13.7 mmol) in dry THF (13.7 mL) at 0 ˚C. The resulting red solution was stirred at room temperature for 20 min. The mixture was cooled to –78 ˚C and a solution of the aldehyde **14** (5.03 g, 10.9 mmol) in THF (2.0 mL) was added dropwise. The mixture was stirred for 20 min at –78 ˚C and then warmed to room temperature. After 4 h at room temperature, the mixture was quenched with saturated NH_4Cl (20 mL) and extracted with diethyl ether (3 x 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, evaporated and the residue was purified by column chromatography (hexane/EtOAc 9:1) to yield **15** (5.65 g, 75 %) as a colorless oil: IR ($CHCl_3$) 2957, 2929, 2856, 1720, 1650, 1617, 1518, 1463, 1370, 1250, 1158, 1073, 1032, 836, 774 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.34 m, 2H), 6.99 (dd, *J* = 15.8, 6.9 Hz, 1H), 6.82 (m, 2H), 5.72 (dd, *J* = 15.8, 1.5 Hz, 1H), 5.36 (s, 1H), 5.32 (dd, *J* = 11.1, 8.6 Hz, 1H), 5.18 (t, *J* = 10.8 Hz, 1H), 4.55 (ddd, *J* = 12.6, 8.6, 4.1 Hz, 1H), 4.12 (m, 2H), 3.99 (d, *J* = 7.2, 2.1 Hz, 1H), 3.91 (m, 1H), 3.77 (s, 3H), 3.52 (dd, *J* = 9.3, 2.1 Hz, 1H), 2.64 (m, 1H), 2.37 (m, 1H), 1.64 (m, 1H), 1.46 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 6H), 0.86 (s, 18H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 159.7, 151.9, 133.8, 132.7, 131.3, 120.8, 113.4, 101.7, 83.6, 73.8, 71.9, 66.4, 60.0, 55.1, 43.6, 42.9, 34.2, 29.8, 26.0, 25.9, 18.1, 15.6, 14.2, 13.5, 11.2, –3.0, –3.8, –4.1, –4.5; LRMS (API-ES) 729.4 $[M+K]^+$; HRMS (ESI) calcd for $C_{36}H_{66}O_7Si_2K$ 729.3984 $[M+K]^+$, found 729.4013; $[\alpha]^{20}_D$ –8.7 (*c* 6.8, $CHCl_3$).

5(*S*),7(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-10(*S*)-[2-(4-methoxybenzyl)-5(*S*)-methyl-[1,3(*R*)]dioxan-4-yl]-4(*R*)-methylundeca-2,8-dien-1-ol (16).
Aqueous KOH (1N, 45 mL) was added to a stirred solution of ester **15** (3.13 g, 4.53 mmol) in EtOH (20 mL), THF (2 mL) and the mixture was refluxed gently until the ester disappeared (about 6 h) as determined by TLC. The ethanolic solution was concentrated and then diluted with EtOAc (50 mL). After the solution was acidified to pH3 with 1N HCl solution, the organic phase was separated and the aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic phases were dried with $MgSO_4$, concentrated and used next step without further purification. The carboxylic acid was treated with NEt_3 (1.5 mL) and ethyl chloroformate (0.67 mL) in dry THF (50 mL) at –10 ˚C. After 15 min, the mixture was warmed to 0 ˚C and a solution of $NaBH_4$ (1.2 g) in H_2O (10 mL) was added. After 4 h, the reaction was quenched by addition of sat'd Rochelle's salt solution and Et_2O. The layers were separated and the organic layer was

washed with H_2O, sat'd $NaHCO_3$ solution and brine, dried with $MgSO_4$. Rotary evaporation and silica column chromatography (hexane/EtOAc 4:1) gave product **16** (1.79 g, 61 %) as a colorless oil: IR ($CHCl_3$) 3433, 2957, 2929, 2856, 1617, 1518, 1462, 1388, 1250, 1074, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (m, 2H), 6.84 (m, 2H), 5.63 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.48 (dt, *J* = 16.0, 5.6 Hz, 1H), 5.37 (t, *J* = 10.6 Hz, 1H), 4.59 (m, 1H), 3.99 (m, 2H), 3.93 (m, 1H), 3.87 (m, 2H), 3.77 (s, 3H), 3.49 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.68 (m, 1H), 2.31 (m, 1H), 1.79 (brs, 1H), 1.64 (m, 1H), 1.44 (m, 2H), 1.15 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.88 (m, 21H), 0.09 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 134.4, 134.3, 132.4, 131.5, 129.1, 127.4, 113.4, 101.5, 83.5, 73.8, 72.8, 66.5, 63.7, 55.2, 42.2, 34.1, 29.8, 26.1, 25.9, 18.14, 18.10, 15.5, 15.2, 11.3, –2.9, –4.1, –4.2; LRMS (API-ESI) 671.3 $[M+Na]^+$; HRMS (ESI) calcd for $C_{36}H_{64}O_6Si_2Na$ 671.4139 $[M+Na]^+$, found 671.4141; $[\alpha]^{20}_D$ –14.0 (*c* 1.5, $CHCl_3$).

4-[4(*S*),6(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-1(*S*),7(*R*)-dimethyl-10-trityloxydeca-2,8-dienyl]-2-(4-methoxybenzyl)-5(*S*)-methyl[1,3(*R*)]dioxane (17).
Trityl chloride (0.094 g) and DMAP (0.041 g) were added to a solution of alcohol **16** (0.11 g) in pyridine (1.6 mL). The mixture was then refluxed for 18 h, cooled to ambient temperature and added to a solution of sat'd $CuSO_4$ (20 mL). The mixture was extracted with Et_2O (2 x 20 mL), washed sat'd $CuSO_4$ (2 x 20 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (EtOAc/hexane 1:9) provided product **17** (0.14 g, 99 %) as a pale yellow oil: IR ($CHCl_3$) 2956, 2926, 2855, 1616, 1517, 1462, 1378, 1249, 1073, 835, 773, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (m, 6H), 7.51 (m, 2H), 7.40 (m, 9H), 6.93 (m, 2H), 5.91 (dd, *J* = 15.7, 6.5 Hz, 1H), 5.66 (dt, *J* = 15.5, 5.2 Hz, 1H), 5.55 (m, 1H), 5.53 (s, 1H), 5.39 (t, *J* = 10.2 Hz, 1H), 4.78 (dt, *J* = 3.1, 8.9 Hz, 1H), 4.10 (m, 3H), 3.80 (s, 3H), 3.70 (m, 3H), 2.85 (m, 1H), 2.45 (m, 1H), 1.78 (m, 1H), 1.65 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.08 (m, 24H), 0.28 (s, 3H), 0.27 (s, 3H), 0.25 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 146.8, 144.3, 135.0, 134.1, 132.4, 131.3, 128.6, 127.8, 127.6, 127.3, 127.1, 126.7, 126.3, 113.3, 101.5, 86.6, 83.4, 73.8, 72.7, 66.6, 65.0, 55.0, 43.5, 42.8, 34.2, 29.9, 26.1, 25.9, 18.1, 15.7, 14.5, 11.3, –2.9, –3.8, –4.1, –4.3; LRMS (API-ESI) 929.5 $[M+K]^+$; HRMS (ESI) calcd for $C_{55}H_{78}O_6Si_2K$ 929.4969 $[M+K]^+$, found 929.5008; $[\alpha]^{20}_D$ –7.3 (*c* 1.1, $CHCl_3$).

7(*S*),9(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-3-(4-methoxybenzyloxy)-2(*S*)(*S*),10(*R*)-trimethyl-13-trityloxytrideca-5,11-dien-1-ol (18). DIBALH (21 mL, 21 mmol, 1.0 M solution in hexane) was added to the PMB acetal **17** (3.75 g, 4.21 mmol) in CH_2Cl_2 (20 mL) at –78 ˚C dropwise and then reaction mixture was warmed up to 0 ˚C and stirred for 1 h. The reaction mixture was quenched by EtOAc (10 mL) and sat'd sodium potassium tartrate solution (50 mL) followed by vigorously stirring for 4 h. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL) and the combined organic layers were washed with brine (30 mL). After drying over $MgSO_4$ and evaporation under vacuum, flash column chromatography (hexane/EtOAc 4:1) provided **18** (2.78 g, 74 %) as a colorless oil: IR ($CHCl_3$) 3434, 2956, 2928, 2856, 1612, 1514, 1471, 1249, 1073, 836, 774, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 6H), 7.29 (m, 11H), 6.84 (m, 2H), 5.84 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.57 (dt, *J* = 15,7, 5.4 Hz, 1H), 5.44 (t, *J* = 8.7 Hz, 2H), 4.63 (m, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 4.46 (d, *J* = 10.9 Hz, 1H), 3.94 (m, 1H), 3.80 (s, 3H), 3.57 (d, *J* = 4.8 Hz, 2H), 3.48 (m, 1H), 3.31 (m, 2H), 2.80 (m, 1H), 2.42 (m, 1H), 1.84 (m, 2H), 1.55 (ddd, *J* = 14.2, 10.1, 1.9 Hz, 1H), 1.40 (ddd, *J* = 13.9, 8.6, 2.0 Hz, 1H), 1.07 (d, *J* = 6.8 Hz, 3H), 0.97 (m, 12H), 0.93 (s, 9H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.16 (s, 3H), 0.15 (s, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 144.3, 134.0, 133.7, 131.5, 130.9, 129.3, 128.6, 127.9, 127.7, 127.2,126.8, 126.5, 113.6, 86.7, 84.0, 73.9, 73.0, 66.2, 65.8, 65.1, 55.2, 42.3, 42.2, 38.0, 35.1, 26.0, 25.9, 18.5, 18.2, 18.1, 14.8, 12.0, –2.9, –4.0, –4.19, –

4.23; LRMS (API-ESI) 931 $[M+K]^+$; HRMS (ESI) calcd for $C_{55}H_{80}O_6Si_2K$ 931.5125 $[M+K]^+$, found 931.5152; $[\alpha]^{20}_D$ –21.4 (*c* 0.52, $CHCl_3$).

9(*S*),11(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-5(*R*)-(4-methoxybenzyloxy)-4(*S*),6(*S*),12(*R*)-trimethyl-15-trityloxypentadeca-2,7,13-trienoic acid ethyl ester (19).
The alcohol **18** (2.01 g, 2.25 mmol) in CH_2Cl_2 (20 mL) was treated with Dess-Martin periodinane (1.43 g, 3.4 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (20 mL). The aqueous layer was extracted with ethyl ether (25 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography (hexane/EtOAc 3:1) to remove the residue from the Dess-Martin reagent provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. To a stirred solution of triethyl phosphonoacetate (0.51 mL, 2.6 mmol) in THF (20 mL) cooled to –78 ˚C was added dropwise potassium *tert*-butoxide (0.29 g, 2.5 mmol) and stirred for 30 min. Thereafter the above aldehyde in THF (5 mL) was added and the solution was stirred for 1 h at –78 ˚C, then 2 h at 0 ˚C. The reaction mixture was quenched by addition of a sat'd NH_4Cl solution (5 mL) and diluted with diethyl ether (20 mL). The layer was separated and organic phase was washed with brine (20 mL) and dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (EtOAc/hexane 1:9), yielding 2.01 g of unsaturated ester **19** (93 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2856, 1718, 1650, 1612, 1514, 1448, 1250, 1180, 1074, 836, 774, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 6H), 7.34 (m, 11H), 7.09 (dd, *J* = 15.8, 7.1 Hz, 1H), 6.89 (m, 2H), 5.89 (dd, *J* = 15.7, 5.8 Hz, 1H), 5.78 (d, *J* = 15.8 Hz, 1H), 5.66 (dt, *J* = 6.0, 15.7 Hz, 1H), 5.45 (m, 2H), 4.66 (m, 1H), 4.51 (m, 2H), 4.23 (m, 2H), 3.99 (m, 1H), 3.83 (s, 3H), 3.66 (d, *J* = 5.3 Hz, 2H), 3.29 (t, *J* = 4.7 Hz, 1H), 2.79 (m, 1H), 2.65 (m, 1H), 2.49 (m, 1H), 1.60 (m, 1H), 1.48 (m, 1H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.11 (d, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.01 (s, 9H), 1.00 (s, 9H), 0.20 (s, 3H), 0.19 (s, 3H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 158.9, 152.2, 144.3, 134.3, 133.9, 131.0, 130.5, 129.3, 128.6, 127.6, 126.7, 126.4, 120.2, 113.5, 107.0, 86.6, 85.5, 73.4, 72.8, 66.3, 65.1, 59.9, 55.1, 42.2, 38.9, 35.2, 26.0, 25.9, 18.2, 18.1, 14.6, 14.2, 13.7, –3.0, –4.1, –4.2, –4.3; LRMS (API-ESI) 999.5 $[M+K]^+$; HRMS (ESI) calcd for $C_{59}H_{84}O_7Si_2K$ 999.5393 $[M+K]^+$, found 999.5387; $[\alpha]^{20}_D$ + 4.6 (*c* 3.1, $CHCl_3$).

9(*S*),11(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-5(*R*)-(4-methoxybenzyloxy)-4(*S*),6(*S*),12(*R*)-trimethyl-15-trityloxypentadeca-7,13-dienoic acid ethyl ester (20).
$NiCl_2$•$6H_2O$ (0.25 g) then portionwise $NaBH_4$ (0.16 g) were added to a stirred solution of unsaturated ester **19** (2.02 g, 2.10 mmol) in MeOH (10 mL), THF (1 mL) at 0 ˚C. After 1 h, the reaction mixture was evaporated and filtered through celite eluting with Et_2O (5 mL). The organic phase was concentrated and the residue was purified by flash chromatography (EtOAc/hexane 1:9) to yield 1.96 g (2.04 mmol) of product **20** (97 %) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2856, 1735, 1613, 1514, 1479, 1448, 1374, 1249, 1174, 1072, 836, 773, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (m, 6H), 7.33 (m, 11H), 6.84 (m, 2H), 5.81 (dd, *J* = 15.7, 6.1 Hz, 1H), 5.65 (m, 1H), 5.45 (m, 2H), 4.65 (m, 1H), 4.56 (d, *J* = 10.9 Hz, 1H), 4.45 (d, *J* = 10.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.96 (m, 1H), 3.80 (s, 3H), 3.62 (m, 2H), 3.14 (m, 1H), 2.79 (m, 1H), 2.43 (m, 1H), 2.23 (m, 1H), 1.72 (m, 2H), 1.54 (m, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.97 (s, 18H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.17 (s, 3H), 0.154 (s, 3H), 0.151 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 158.8, 144.4, 134.6, 133.6, 132.1, 131.2, 129.1, 128.7, 127.7, 126.8, 126.4, 103.4, 86.6, 86.1, 73.8, 72.8, 66.5, 65.2, 60.0, 55.1, 42.8, 42.3, 35.4, 35.1, 32.3, 29.4, 26.0, 25.9, 18.4, 18.1, 14.6, 14.2, 13.9, –2.9, –4.0, –4.1; LRMS (API-ESI) 1001.5 $[M+K]^+$; HRMS (ESI) calcd for $C_{59}H_{86}O_7Si_2K$ 1001.5549 $[M+K]^+$, found 1001.5586; $[\alpha]^{20}_D$ – 9.8 (*c* 0.95, $CHCl_3$).

4(*R*)-Benzyl-3-[9(*S*),11(*S*)-*bis*(*tert*-butyldimethylsilanyloxy)-5(*R*)-(4-methoxybenzyloxy)-4(*R*),6(*S*),12(*S*)-trimethyl-15-trityloxypentadeca-7,13-dienoyl]oxazolidin-2-one (21).
1N aqueous KOH solution (17 mL) was added to a stirred solution of ester **20** (1.61 g, 1.67 mmol) in EtOH (20 mL) and THF (2 mL). The mixture was refluxed gently until the ester disappeared (about 6 h) as determined by TLC analysis. The ethanolic solution was concentrated and then diluted with EtOAc (20 mL). After the solution was acidified to pH3 with 1N HCl solution, organic phase was separated and aqueous phase was extracted with EtOAc (2 x 10 mL). The combined organic phases were dried with $MgSO_4$, concentrated and used as crude without further purification. A solution of the above acid and Et_3N (0.47 mL) in dry THF (17 mL) was cooled to –78 ˚C, treated dropwise with pivaloyl chloride (0.25 mL), stirred in the cold for 1 h, and warmed to 0 ˚C prior to the addition of the Evans (*S*)-oxazolidinone (0.30 g) and LiCl (0.21 g). This reaction mixture was stirred overnight at room temperature and diluted with water (10 mL). The separated aqueous phase was extracted with ether (2 x 10 mL) and the combined organic phase were dried and evaporated and flash column chromatography (EtOAc/hexane 1:4) gave the product **21** (1.52 g, 83 %) as a colorless oil: IR ($CHCl_3$) 2956, 2856, 1785, 1701, 1612, 1513, 1449, 1385, 1249, 1074, 910, 836, 774, 734, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 6H), 7.30 (m, 10H), 7.24 (m, 6H), 6.78 (m, 2H), 5.75 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.54 (dt, *J* = 15.5, 5.5 Hz, 1H), 5.41 (m, 2H), 4.62 (m, 2H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.42 (d, *J* = 11.1 Hz, 1H), 4.16 (m, 2H), 3.91 (m, 1H), 3.75 (s, 3H), 3.56 (m 2H), 3.30 (dd, *J* = 13.4, 3.2 Hz, 1H), 3.15 (dd, *J* = 6.7, 2.2 Hz, 1H), 2.85 (m, 2H), 2.77 (m, 2H), 2.37 (m, 1H), 1.78 (m, 2H), 1.61 (m, 3H), 1.44 (m, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.92 (m, 21H), 0.12 (s, 3H), 0.10 (s, 3H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 158.7, 153.2, 144.3, 135.3, 134.7, 133.6, 132.5, 131.2, 129.3, 129.1, 128.8, 128.6, 127.6, 127.2, 126.7, 126.2, 113.4, 86.5, 85.8, 73.7, 72.7, 66.4, 65.9, 65.1, 55.0, 42.8, 42.4, 37.8, 35.5, 34.9, 33.5, 28.7, 26.0, 25.9, 18.2, 18.1, 14.5, 13.9, –2.9, –4.0, –4.2; LRMS (API-ESI) 1132.4 $[M+K]^+$; HRMS (ESI) calcd for $C_{67}H_{91}NO_8Si_2K$ 1132.5920 $[M+K]^+$, found 1132.5874; $[\alpha]^{20}_D$ +14.8 (*c* 0.61, $CHCl_3$).

4(*R*)-Benzyl-3-[9(*S*),11(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-5(*R*)-(4-methoxybenzyloxy)-2(*S*),4(*S*),6(*S*),12(*R*)-tetramethyl-15-trityloxy-pentadeca-7,13-dienoyl]oxazolidin-2-one (22).
NaHMDS (1.0 M in THF, 1.68 mL) was added at –78 ˚C to a solution of **21** (1.67 g) in THF (4 mL). After 30 min, the reaction mixture was treated with MeI (0.29 mL) at –78 ˚C, stirred for an additional 4 h, quenched with sat'd aqueous NH_4Cl, and extracted with ether (2 x 10 mL). The combined organic layers were dried ($MgSO_4$), concentrated and purified by flash column chromatography (EtOAc/hexane 1:9) to give **22** (1.05 g, 62 %) as a colorless oil: IR ($CHCl_3$) 2957, 2929, 2856, 1783, 1697, 1513, 1449, 1385, 1249, 1074, 836, 774, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (m, 6H), 7.29 (m, 16H), 6.80 (m, 2H), 5.79 (dd, *J* = 15.6, 6.2 Hz, 1H), 5.56 (dt, *J* = 15.6, 5.7 Hz, 1H), 5.42 (m, 2H), 4.62 (m, 2H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 4.17 (m, 1H), 4.05 (m, 1H), 3.92 (m, 1H), 3.77 (s, 3H), 3.58 (d, *J* = 5.2 Hz, 1H), 3.27 (m, 1H), 3.08 (dd, *J* = 6.3, 2.5 Hz, 1H), 2.77 (m, 2H), 2.38 (m,1H), 1.76 (m, 1H), 1.64 (m, 2H), 1.46 (m, 4H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 6.3 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.93 (m, 21H), 0.14 (s, 3H), 0.11 (s, 6H), 0.10(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 158.7, 152.8, 144.4, 135.3, 134.9, 133.6, 132.3, 131.3, 129.4, 128.9, 128.8, 128.6, 127.6, 127.2, 126.7, 126.3, 113.5, 86.6, 86.5, 74.0, 72.8, 66.5, 65.8, 65.2, 43.0, 42.5, 37.8, 35.4, 35.3, 33.0, 26.3, 26.0, 25.9, 18.3, 18.1, 17.4, 14.5, 14.2, –2.9, –4.0, –4.1, –4.2; LRMS (API-ESI) 1146.4 $[M+K]^+$; HRMS (ESI) calcd for $C_{68}H_{93}NO_8Si_2K$ 1146.6077 $[M+K]^+$, found 1146.6079; $[\alpha]^{20}_D$ +16.7 (*c* 1.1, $CHCl_3$).

9(*S*),11(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-5(*R*)-(4-methoxybenzyloxy)-2(*S*),4(*S*),6(*S*),12(*R*)-tetramethyl-15-trityloxypentadeca-7,13-dien-1-ol (23).
MeOH (0.015 mL) and $LiBH_4$ (0.81 mL, 2.0 M soln in THF) were added to a stirred solution of **22** (0.41 g, 0.37 mmol) in THF (1.5 mL) at 0 ˚C dropwise. After stirring 2 h at 0 ˚C, saturated sodium potassium tartrate (10 mL) was added dropwise. The reaction mixture was warmed to room temperature and extracted with CH_2Cl_2 (10 mL x 2). The combined organic layers were washed with brine (10 mL), dried over anhydrous $MgSO_4$, and evaporated. The residue was chromatographed (hexane/EtOAc 4:1) to yield **23** (0.30 g, 87 %) as a colorless oil: IR ($CHCl_3$) 3400, 2956, 2928, 2856, 1613, 1514, 1449, 1377, 1249, 1074, 836, 774, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 6H), 7.29 (m, 11H), 6.84 (m, 2H), 5.78 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.58 (dt, *J* = 15.7, 5.2 Hz, 1H), 5.46 (m, 1H), 5.35 (m, 1H), 4.59 (t, *J* = 9.5, Hz, 1H), 4.48 (q, *J* = 10.9 Hz, 2H), 3.92 (m, 1H), 3.79 (s, 3H), 3.57 (d, *J* = 5.5 Hz, 2H), 3.25 (m, 2H), 3.03 (t, *J* = 4.5 Hz, 1H), 2.75 (m, 1H), 2.41 (m, 1H), 1.75 (m, 1H), 1.55 (m, 2H), 1.32 (m, 2H), 1.17 (m, 2H), 1.07 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.94 (s, 9H), 0.91 (m, 12H), 0.72 (d, *J* = 6.6 Hz, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 144.4, 134.4, 133.4, 131.5, 131.4, 129.1, 128.7, 127.7, 126.8, 126.5, 113.6, 87.6, 86.8, 74.1, 73.0, 68.9, 66.5, 65.4, 55.2, 42.7, 42.4, 37.1, 35.0, 33.1, 26.0, 25.9, 18.9, 18.1, 15.8, 14.9, 14.7, –2.8, –4.0, –4.06, –4.10; LRMS (API-ESI) 973.5 $[M+K]^+$; HRMS (ESI) calcd for $C_{58}H_{86}O_6Si_2K$ 973.6301 $[M+K]^+$, found 973.6264; $[\alpha]^{20}_D$ –31.7 (*c* 1.3, $CHCl_3$).

13(*S*),15(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-2-[2-(4-methoxybenzyl)-5(*S*)-methyl-[1,3(*S*)]dioxan-4-yl]-9(*R*)-(4-methoxybenzyloxy)-6(*S*),8(*S*),10(*S*),16(*R*)-tetramethyl-19-trityloxynonadeca-4,11,17-trien-3-one (24).
The alcohol **23** (0.30 g, 0.32 mmol) in CH_2Cl_2 (10 mL) was treated with Dess-Martin periodinane (0.20 g, 0.47 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (10 mL). The aqueous layer was extracted with ethyl ether (10 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography filtration (hexane/EtOAc 4:1) to remove the residue from the Dess-Martin reagent provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. A mixture of ketophosphonate **7** (0.14 g) and $Ba(OH)_2$ (0.043 g, activated by heating to 100 ˚C for 1-2 h before use) in THF (2 mL) was stirred at room temperature for 30 min. A solution of the above aldehyde in wet THF (2 mL + 2 x 1 mL washings, 40:1 THF/H_2O) was then added. After stirring for 12 h, the reaction mixture was diluted with Et_2O (10 mL) and washed with sat'd $NaHCO_3$ (10 mL) and brine (10 mL). The organic solution was dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The residue was chromatographed (hexane/EtOAc 9:2) to yield **24** (0.34 g, 90 %) as a colorless oil: IR ($CHCl_3$) 2957, 2929, 2855, 1615, 1515, 1461, 1249, 1076, 1036, 835, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 6H), 7.38 (m, 2H), 7.28 (m, 12H), 6.89 (m, 2H), 6.78 (m, 2H), 6.22 (d, *J* = 15.6 Hz, 1H), 5.74 (dd, *J* = 15.7, 6.2 Hz, 1H), 5.57 (m, 1H), 5.45 (s, 1H), 5.38 (m, 2H), 4.60 (m, 1H), 4.52 (d, *J* = 11.0 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.12 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.90 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.55 (m, 3H), 3.04 (m, 1H), 2.92 (m, 1H), 2.75 (m, 1H), 2.36 (m, 1H), 2.25 (quint, *J* = 7.2 Hz, 1H), 2.02 (m, 1H), 1.71 (m, 1H), 1.56-1.33 (m, 4H), 1.25 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 7.8 Hz, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.92 (m, 21H), 0.85 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 159.7, 158.8, 153.1, 144.3, 134.6, 133.6, 132.4, 131.2, 131.0, 129.1, 128.6, 127.7, 127.2, 126.8, 126.3, 126.0, 113.5, 113.4, 100.7, 86.6, 85.7, 82.8, 73.8, 72.8, 66.4, 65.2, 55.2, 47.0, 42.8, 42.4, 40.4, 35.5, 34.2, 32.8, 32.2, 26.0, 25.9, 19.2, 18.4, 18.3, 18.1, 14.5, 14.4, 12.4, 10.7, –2.9, –4.0, –4.1; LRMS (API-ESI) 1231.6 $[M+K]^+$; HRMS (ESI) calcd for $C_{74}H_{104}O_9Si_2K$ 1231.6856 $[M+K]^+$, found 1231.6850; $[\alpha]^{20}_D$ +22.8 (*c* 0.88, $CHCl_3$).

13(*S*),15(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-2-[2-(4-methoxybenzyl)-5(*S*)-methyl-[1,3(*S*)]dioxan-4-yl]-9(*R*)-(4-methoxybenzyloxy)-6(*S*),8(*S*),10(*S*),16(*R*)-tetramethyl-19-trityloxynonadeca-11,17-dien-3-one (25).

$NiCl_2$•$6H_2O$ (0.034 g, 0.14 mmol) then portionwise $NaBH_4$ (0.022 g, 0.58 mmol) were added to a stirred solution of unsaturated ketone **24** (0.34 g, 0.29 mmol) in MeOH (4 mL), THF (0.5 mL) at 0 ˚C. After 1 h, the reaction mixture was evaporated and filtered with celite eluting with Et_2O (5 mL). The organic phase was concentrated and the residue was purified by flash chromatography (EtOAc/hexane 1:4) to yield 0.31 g of product **25** (89 %) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2855, 1713, 1614, 1515, 1461, 1249, 1075, 1036, 835, 774, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 6H), 7.29 (m, 13H), 6.87(m, 2H), 6.80 (m, 2H), 5.75 (dd, *J* = 15.7, 6.1 Hz, 1H), 5.55 (m, 1H), 5.45 (s, 1H), 5.38 (m, 2H), 4.60 (m, 1H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.36 (d, *J* = 10.9 Hz, 1H), 4.13 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.93 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.55 (m, 2H), 2.99 (m, 2H), 2.70 (m, 2H), 2.45 (t, *J* = 7.0 Hz, 1H), 2.36 (m, 1H), 2.02 (m, 1H), 1.75 (m, 1H), 1.63 (m, 1H), 1.49 (m, 2H), 1.37 (m, 3H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.91 (m, 21H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.12 (s, 3H), 0.09 (s, 6H), 0.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.9, 159.8, 158.8, 144.6, 144.4, 134.9, 133.4, 132.3, 131.8, 131.5, 131.0, 129.0, 128.9, 128.7, 127.7, 127.6, 127.2, 126.8, 126.7, 126.3, 113.5, 100.8, 87.4, 86.7, 83.1, 74.0, 72.9, 66.6, 65.2, 55.22, 55.18, 48.3, 43.1, 42.5, 41.6, 38.3, 35.5, 32.7, 31.5, 31.3, 29.6, 26.1, 26.0, 19.0, 18.5, 18.1, 14.5, 14.1, 12.1, 9.7, –2.9, –4.0, –4.1, –4.2; LRMS (API-ESI) 1233.6 $[M+K]^+$; HRMS (ESI) calcd for $C_{74}H_{108}O_9Si_2K$ 1233.7013 $[M+K]^+$, found 1233.7036; $[\alpha]^{20}_D$ +3.0 (*c* 1.7, $CHCl_3$).

13(*S*),15(*S*)-*bis*(*tert*-Butyldimethylsilanyloxy)-2-[2-(4-methoxybenzyl)-5(*S*)-methyl-[1,3(*S*)]dioxan-4-yl]-9(*R*)-(4-methoxybenzyloxy)-6(*S*),8(*S*),10(*S*),16(*R*)-tetramethyl-19-trityloxynonadeca-11,17-dien-3-ol (26).

$NaBH_4$ (0.013 g, 0.34 mmol) was added to a solution of **25** (0.27 g, 0.23 mmol) in MeOH (4 mL) at 0 ˚C. After stirring for 2 h at 0 ˚C, the reaction mixture was evaporated and water (5 mL) was added. The reaction mixture was extracted with ether (2 x 20 mL) and washed with brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/hexane 2:9) to yield 0.19 g of major product **26β** (71 %, less polar) and 0.069 g (25 %, more polar) of minor product **26α** as a colorless oil: (**26β**) IR ($CHCl_3$) 3533, 2956, 2929, 2855, 1614, 1515, 1462, 1250, 1072, 1036, 835, 774, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 6H), 7.43 (m, 2H), 7.30 (m, 11H), 6.92 (m, 2H), 6.84 (m, 2H), 5.78 (dd, *J* = 15.6, 6.1 Hz, 1H), 5.61 (m, 1H), 5.57 (s, 1H), 5.43 (m, 2H), 4.65 (m, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.18 (dd, *J* = 11.2, 4.5 Hz, 1H), 3.95 (m, 1H), 3.84 (s, 3H), 3.82 (m, 1H), 3.79 (s, 3H), 3.74 (m, 1H), 3.59 (m, 2H), 3.06 (m, 2H), 2.78 (m, 1H), 2.41 (m, 1H), 2.19 (m, 1H), 1.81 (m, 2H), 1.56 (dd, *J* = 13.8, 8.1 Hz, 3H), 1.44 (m, 3H), 1.34 (m, 3H), 1.08 (d, *J* = 7.0 Hz, 6H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.96 (m, 18H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 6H), 0.16 (s, 3H), 0.14 (s, 6H), 0.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 158.8, 144.6, 144.4, 134.9, 133.4, 132.3, 131.5, 130.7, 129.0, 128.9, 128.7, 127.7, 127.6, 127.2, 126.8, 126.7, 126.3, 113.7, 113.5, 89.0, 87.5, 86.7, 76.7, 74.0, 73.1, 72.8, 66.6, 65.2, 55.2, 55.1, 43.1, 42.5, 41.8, 37.4, 35.5, 34.4, 32.9, 32.4, 30.4, 30.1, 26.0, 25.9, 19.2, 18.5, 18.1, 14.5, 14.1, 11.9, 5.7, –2.9, –4.0, –4.1, –4.2; LRMS (API-ESI) 1235.6 $[M+K]^+$; HRMS (ESI) calcd for $C_{74}H_{108}O_9Si_2K$ 1235.7169 $[M+K]^+$, found 1235.7149; $[\alpha]^{20}_D$ +3.5 (*c* 0.6, $CHCl_3$).

5,15(*S*),17(*S*)-*tris*(*tert*-Butyldimethylsilanyloxy)-11(*R*)-(4-methoxybenzyloxy)-3(*S*)-[2-(4-methoxyphenyl)ethoxy]-2(*S*),4(*R*),8(*S*),10(*S*),12(*S*),18(*R*)-hexamethyl-21-trityloxy-heneicosa-13,19-dien-1-ol (27).

A stirred solution of **26β** (0.19 g, 0.16 mmol) and 2,6-lutidine (0.037 mL, 0.32 mmol) in CH_2Cl_2 (16 mL) at 0 ˚C was treated with TBSOTf (0.055 mL, 0.24 mmol). After stirring 2 h at ambient temperature, the reaction mixture was quenched by the addition of water (5 mL) and extracted by CH_2Cl_2 and dried over $MgSO_4$, followed by the evaporation of the solution under reduced pressure. The residue was purified by short column chromatography (hexane/EtOAc 9:1). To a stirred solution of TBS protected acetal (0.20 g, 0.15 mmol) in anhydrous CH_2Cl_2 (3 mL) under an atmosphere of N_2 at 0 ˚C was added diisobutylaluminum hydride (1.0 M in THF, 1.5 mL, 1.5 mmol) dropwise. After stirring for additional 1 h at 0 ˚C, the reaction mixture was quenched by the careful addition of aqueous sat'd potassium sodium tartrate solution (10 mL), and stirred for 3 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$ followed by the evaporation of the organic solution under reduced pressure. The residue was purified by column chromatography (EtOAc/hexane 1:4) to get **27** (0.19 g, 91 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 3466, 2955, 2928, 2856, 1613, 1514, 1462, 1249, 1072, 1037, 835, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (m, 6H), 7.30 (m, 13H), 6.94 (m, 2H), 6.85 (m, 2H), 5.79 (dd, *J* = 15.7, 6.3 Hz, 1H), 5.59 (dt, *J* = 15.7, 5.9 Hz, 1H), 5.44 (m, 2H), 4.67 (m, 1H), 4.60 (s, 2H), 4.57 (d, *J* = 11.1 Hz, 1H), 4.44 (d, *J* = 10.9 Hz, 1H), 3.97 (m, 1H), 3.91 (m, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.68 (m, 2H), 3.60 (d, *J* = 5.6 Hz, 1H), 3.52 (dd, *J* = 6.6, 4.3 Hz, 1H), 3.07 (m, 2H), 2.97 (brs, 1H), 2.80 (dd, *J* = 14.5, 6.7 Hz, 1H), 2.40 (m, 1H), 2.02 (m, 1H), 1.95 (ddd, *J* = 9.6, 6.9, 4.0 Hz, 1H), 1.81 (m, 1H), 1.71 (m, 1H), 1.56 (m, 3H), 1.47 (m, 3H), 1.33 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 6H), 1.00 (s, 9H), 0.97 (m, 21H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.17 (s, 3H), 0.15 (s, 3H), 0.14 (s, 3H), 0.137 (s, 3H), 0.133 (s, 3H), 0.127 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 158.8, 144.6, 144.4, 135.0, 133.6, 132.5, 131.4, 130.6, 129.2, 129.0, 128.9, 128.7, 127.7, 127.6, 126.8, 126.7, 126.3, 113.9, 113.5, 87.4, 86.7, 85.9, 75.3, 74.0, 73.6, 72.8, 66.6, 65.2, 65.1, 55.2, 55.1, 43.2, 42.5, 42.0, 41.5, 37.0, 35.6, 33.4, 32.9, 31.9, 30.1, 26.08, 26.05, 25.98, 19.4, 18.4, 18.1, 15.8, 14.4, 13.9, 10.0, –2.9, –3.7, –3.9, –4.1, –4.2, –4.4; LRMS (API-ESI) 1351.8 $[M+K]^+$; HRMS (ESI) calcd for $C_{80}H_{124}O_9Si_3K$ 1351.8190 $[M+K]^+$, found 1351.8134; $[\alpha]^{20}_D$ –6.1 (*c* 0.48, $CHCl_3$).

7,17(*S*),19(*S*)-*tris*(*tert*-Butyldimethylsilanyloxy)-5(*S*),13(*R*)-*bis*-(4-methoxybenzyloxy)-4(*S*),6(*S*),10(*R*),12(*S*),14(*S*),20(*S*)-hexamethyl-23-trityloxytetracosa-1,3,15,21-tetraene (30). The alcohol **28** (0.17 g, 0.13 mmol) in CH_2Cl_2 (5 mL) was treated with Dess-Martin periodinane (0.081 g, 0.2 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (5 mL). The aqueous layer was extracted with ethyl ether (5 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography filtration (hexane/EtOAc 9:2) to remove the residue from Dess-Martin reagent provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. To a stirred solution of the above crude aldehyde and 1-bromoallyl trimethylsilane **29** (0.16 g, 0.65 mmol) in anhydrous THF (3 mL) under an atmosphere of N_2 at room temperature was added $CrCl_2$ (0.13 g, 1.1 mmol) and the mixture was stirred for additional 14 h at ambient temperature. The reaction mixture was diluted with hexane followed by filtration through celite. After the evaporation of the solvent under reduced pressure, the residue was purified by short silica gel column chromatography (EtOAc/hexane 1:9). The foregoing product in THF (3 ml) was cooled to 0 ˚C and NaH (95 % w/w, 64 mg, 2.56 mmol) was added in one portion. The ice bath was removed after 15 min and the mixture was stirred for 2 h at ambient temperature. The reaction mixture was cooled to 0 ˚C, quenched with H_2O (5 mL), and extracted with diethyl ether (5 mL x 2). The combined organic layer was washed with brine and dried over $MgSO_4$ followed by the evaporation of the organic solution under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc 9:1) to get **30** (122 mg, 72 % for 3

steps) as a colorless oil: IR ($CHCl_3$) 2955, 2928, 2856, 1613, 1514, 1462, 1249, 1072, 1039, 835, 773, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.47 (m, 6H), 7.28 (m, 13H), 6.89 (m, 2H), 6.79 (m, 2H), 6.61 (ddd, *J* = 16.8, 10.7, 10.6 Hz, 1H), 6.04 (t, *J* = 10.8 Hz, 1H), 5.73 (dd, *J* = 15.6, 6.3 Hz, 1H), 5.61 (t, *J* = 10.4 Hz, 1H), 5.58 (m, 1H), 5.37 (m, 2H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.11 (d, *J* = 10.1 Hz, 1H), 4.54 (m, 3H), 4.50 (d, *J* = 11.0 Hz, 1H), 4.37 (d, *J* = 10.8 Hz, 1H), 3.90 (m, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.62 (m, 1H), 3.54 (d, *J* = 5.3 Hz, 1H), 3.35 (dd, *J* = 7.7, 3.1 Hz, 1H), 3.00 (m, 2H), 2.73 (m, 1H), 2.31 (m, 1H), 1.69 (m, 4H), 1.43 (m, 8H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.96 (s, 9H), 0.92 (s, 3H), 0.91 (s, 3H), 0.89 (m, 6H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.72 (d, *J* = 6.4 Hz, 3H), 0.11 (s, 3H), 0.10 (s, 3H), 0.08 (s, 3H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 158.8, 144.6, 144.4, 135.0, 134.6, 133.7, 133.4, 132.6, 132.4, 131.5, 131.4, 129.1, 129.0, 128.98, 128.94, 128.7, 127.7, 126.8, 126.3, 117.2, 113.7, 113.5, 87.3, 86.7, 84.3, 75.0, 74.0, 72.9, 72.8, 66.6, 65.2, 55.2, 55.1, 43.2, 42.6, 42.0, 40.6, 35.7, 35.3, 33.2, 32.8, 32.3, 30.1, 26.1, 26.0, 19.4, 18.8, 18.3, 18.2, 18.1, 14.4, 14.0, 13.9, –2.9, –3.6, –3.9, –4.1, –4.2, –4.4; $[\alpha]^{20}_D$ +2.5 (*c* 1.2, $CHCl_3$).

7(*S*),9(*S*),19-tris-(*tert*-Butyldimethylsilanyloxy)-13(*R*),21(*S*)-*bis*-(4-methoxybenzyloxy)-6(*R*),12(*S*),14(*S*),16(*S*),20(*R*),22(*S*)-hexamethylhexacosa-2,4,10,23,25-pentaenoic acid methyl ester (32).

A solution of **30** (18.6 mg) in CH_2Cl_2 (0.2 mL) was cooled to ⁻78 ˚C and *B*-chlorocatecholborane (0.25 M in CH_2Cl_2, 0.17 mL) was added. The solution was stirred at –78 ˚C for 1 h followed by treatment with sat'd aqueous $NaHCO_3$ (1 mL). The resulting reaction mixture was then diluted with CH_2Cl_2 (10 mL) and H_2O (3 mL). The layers were separated and the aqueous layer was further extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography (hexane/EtOAc 4:1) on silica gel to yield **31** (9.4 mg) as a colorless oil. The alcohol **31** (20 mg, 0.018 mmol) in CH_2Cl_2 (0.5 mL) was treated with Dess-Martin periodinane (12 mg, 0.028 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (1 mL). The aqueous layer was extracted with ethyl ether (3 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography filtration (hexane/EtOAc 9:2) to remove the residue from the Dess-Martin reagent provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. To a stirred solution of *bis*(2,2,2-trifluoroethyl)-(methoxycarbonylmethyl) phosphate (5.0 mL, 0.024 mmol), 18-crown-6 (0.024 g, 0.09 mmol) in THF (0.5 mL) cooled to –78 ˚C was added dropwise potassium *bis*(trimethylsilyl)amide (0.044 mL, 0.022 mmol, 0.5M solution in toluene). Thereafter the above aldehyde in THF (0.5 mL) was added and the solution was stirred for 6 h at –78 ˚C. The reaction mixture was quenched by addition of a sat'd NH_4Cl solution (1 mL) and diluted with diethyl ether (5 mL). The layers were separated and organic phase was washed with brine (5 mL) and dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (EtOAc/hexane 1:9) to obtain (*E,Z*)-doubly unsaturated ester **32** (17 mg, 82 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2856, 1720, 1613, 1514, 1462, 1249, 1173, 1075, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.22 (m, 5H), 6.82 (m, 4H), 6.55 (ddd, *J* = 16.8, 10.8, 10.8 Hz, 1H), 6.38 (t, *J* = 11.4 Hz, 1H), 6.05 (dd, *J* = 15.4, 6.2 Hz, 1H), 5.98 (t, *J* = 11.0 Hz, 1H), 5.55 (t, *J* = 10.5 Hz, 1H), 5.48 (d, *J* = 11.5 Hz, 1H), 5.31 (m, 2H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.05 (d, *J* = 10.1 Hz, 1H), 4.54 (m, 1H), 4.49 (m, 3H), 4.31 (d, *J* = 10.9 Hz, 1H), 3.87 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.68 (s, 3H), 3.57 (m, 1H), 3.29 (dd, *J* = 7.7, 3.1 Hz, 1H), 2.94 (m, 2H), 2.68 (m, 1H), 2.48 (m, 1H), 1.65 (m, 3H), 1.43-1.28 (m, 6H), 1.20 (m, 2H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.1 Hz, 3H), 0.90 (s, 9H), 0.86 (m, 21H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.71 (d, *J* = 6.4 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H), 0.02 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 159.0,

158.8, 147.7, 146.9, 145.8, 134.6, 133.5, 132.7, 132.5, 131.6, 131.4, 129.1, 128.9, 128.8, 128.7, 128.4, 127.9, 127.7, 127.3, 126.4, 117.2, 114.9, 113.7, 113.6, 87.6, 84.3, 77.2, 74.9, 74.2, 72.9, 72.7, 66.4, 55.3, 55.2, 50.9, 43.1, 42.5, 42.1, 40.6, 35.8, 35.3, 33.6, 33.2, 32.9, 18.14, 18.11, 14.6, 13.9, 9.3, –2.9, –3.6, –3.9, –4.1, –4.4; LRMS (API-ESI) 1185.7 $[M+K]^+$; HRMS (ESI) calcd for $C_{67}H_{114}O_9Si_3K$ 1185.7408 $[M+K]^+$, found 1185.7464; $[\alpha]^{20}_D$ –12.6 (*c* 0.75, $CHCl_3$).

8(*S*),10(*S*),14(*R*),20(*R*)-Tetrahydroxy-7(*S*),13(*S*),15(*S*),17(*R*),21(*S*)-pentamethyl-22(*S*)-(1(*S*)-methylpenta-2,4-dienyl)oxacyclodocosa-3,5,11-trien-2-one (5).

The ester **32** (8.5 mg, 7.4 μmol) was added to CH_2Cl_2 (1 mL) and H_2O (0.05 mL) and DDQ (5.0 mg, 22 μmol) was added at 0 ˚C. After 1 h of stirring at 0 ˚C, the reaction mixture was quenched by adding sat'd $NaHCO_3$ (5 mL). The organic phase was washed by sat'd $NaHCO_3$ solution (3 x 10 mL) and brine, dried over $MgSO_4$ and concentrated. Purification by flash column chromatography (EtOAc/hexane 2:9) furnished diol **33** (6.4 mg, 95%) as a colorless oil. To the stirred solution of the above diol (6.4 mg, 7.06 μmol) in EtOH (0.7 mL) was added 1N aqueous KOH solution (0.07 mL) and the mixture was refluxed gently until the ester disappeared (about 7 h) as determined by TLC analysis. The ethanolic solution was concentrated and then diluted with ether (4 mL). After the solution was acidified to pH3 with 1N HCl solution, the organic phase was separated and aqueous phase was extracted with EtOAc (2 x 2 mL). The combined organic phases were dried with $MgSO_4$, concentrated and **34** was used without further purification. A solution of above dihydroxy acid in THF (0.5 mL) was treated at 0 ˚C with Et_3N (0.006 mL, 43 μmol) and 2,4,6-trichlorobenzoyl chloride (0.0055 mL, 35 μmol). The reaction mixture was stirred at 0 ˚C for 30 min and then added to a 4-DMAP (3.5 mL, 0.02 M solution in toluene) at 25 ˚C. After stirring for 12 h, the reaction mixture was concentrated, EtOAc (5 mL) was added and the organic phase was washed with 1N HCl (2 x 5 mL), and dried over $MgSO_4$. Purification by flash column chromatography (EtOAc/hexane 1:9) furnished macrolactone **5** (3.0 mg, 49 % for 2 steps) as a colorless oil. To a stirred solution of the above macrolactone (2.7 mg, 3.1 μmol) in MeOH (0.5 mL) at 0 ˚C was added 1.0 mL of 3 N HCl (prepared by adding 0.25 mL of conc. HCl to 0.75 mL MeOH). After 2 h at room temperature, the reaction mixture was diluted with EtOAc (2 mL) and H_2O (2 mL) and the organic phase was separated and aqueous phase was extracted with EtOAc (2 x 2 mL). The combined organic phase was washed with sat'd $NaHCO_3$ (5 mL), dried with $MgSO_4$, concentrated and the residue was purified by flash chromatography (EtOAc/hexane 1:1) to yield **5** (1.2 mg, 73 %) as a colorless oil: IR ($CHCl_3$) 3400, 2960, 2926, 2854, 1693, 1635, 1599, 1461, 1378, 1277, 1183, 1075, 964 cm^{-1}; ^1H NMR (500 MHz, CD_3OD) δ 7.34 (dd, *J* = 15.3, 11.3 Hz, 1H), 6.64 (ddd, *J* = 16.9, 10.5, 10.3 Hz, 1H), 6.57 (t, *J* = 11.4 Hz, 1H), 5.96 (t, *J* = 10.9 Hz, 1H), *5.95 (dd, *J* = 15.3, 8.3 Hz, 1H), *5.48 (t, *J* = 10.0 Hz, 1H), *5.47 (d, *J* = 11.6 Hz, 1H), 5.38 (dd, *J* = 11.1, 8.9 Hz, 1H), 5.27 (t, *J* = 10.5 Hz, 1H), 5.16 (d, *J* = 16.9 Hz, 1H), 5.08 (d, *J* = 10.2 Hz, 1H), 5.02 (dd, *J* = 8.0, 3.5 Hz, 1H), 4.65 (dt, *J* = 3.1, 8.4 Hz, 1H), *3.72 (ddd, *J* = 9.0, 6.3, 2.8 Hz, 1H), *3.25 (ddd, *J* = 10.2, 7.4, 2.8 Hz, 1H), *3.16 (dd, *J* = 6.7, 4.5 Hz, 1H), 3.06 (dd, *J* = 16.3, 8.3 Hz, 1H), *2.72 (ddd, *J* = 10.2, 6.7, 6.6 Hz, 1H), 2.36 (dd, *J* = 14.7, 7.2 Hz, 1H), 1.86 (m, 1H), 1.81 (dt, *J* = 6.8, 3.7 Hz, 1H), 1.69 (m, 2H), 1.58 (m, 1H), 1.47 (ddd, *J* = 13.8, 9.5, 3.5 Hz, 1H), 1.37 (m, 1H), 1.25 (m, 1H), 1.17 (m, 1H), 1.13 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 6H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 6.4 Hz, 3H) (*coupling constants were measured in $CDCl_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 147.2, 145.3, 134.39, 134.37, 132.5, 132.3, 130.0, 127.6, 117.8, 116.5, 80.0, 75.4, 74.9, 72.0, 66.2, 43.2, 41.5, 40.7, 40.6, 35.6, 35.4, 35.0, 33.0, 31.2, 30.4, 20.4, 18.1, 17.3, 16.2, 12.4, 10.2; LRMS (API-ESI) 571.3 $[M+K]^+$; HRMS (ESI) calcd for $C_{32}H_{52}O_6K$ 571.3401 $[M+K]^+$, found 571.3397; $[\alpha]^{20}_D$ +32.6 (*c* 0.10, MeOH).

Synthesis of 6,14-*bis*,*epi*-dictyostatin

(*S*)-4-Benzyl-3-[(2*R*,3*S*)-3-hydroxy-2,4-dimethylpent-4-enoyl]oxazolidin-2-one 41.
A solution of **40** in ethyl acetate (185 mL) was treated with $MgCl_2$ (0.35 g, 3.67 mmol), $NaSbF_6$ (2.85 g, 11.01 mmol), triethylamine (10.2 mL, 73.4 mmol), methacrolein (4.6 mL, 44.04 mmol), and TMSCl (7.0 mL, 55.05 mmol). The mixture was stirred at room temperature for three days, and filtered through a pad of silica gel. The filtrate was evaporated under vacuum. The residue was dissolved in a solution of MeOH (200 mL) and TFA (1 mL). The mixture was stirred at room temperature for 1 h. The solvent was removed under vacuum to provide the brown oil. The flash chromatography (CH_2Cl_2:EtOAc, 49:1) afforded the title compound (9.62 g, 86% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.18 (m, 5H), 5.11 (d, *J* = 16.2 Hz, 2H), 4.79 (m, 1H), 4.31-4.09 (m, 4H), 3.41 (dd, *J* = 3.3, 13.5 Hz, 1H), 2.99-2.82 (m, 2H), 1.89 (s, 3H), 1.24 (d, *J* = 6.9 Hz, 3H).

(2*S*,4*S*,5*S*)-2-(4-Methoxyphenyl)-5-methyl-4-(prop-1-en-2-yl)-1,3-dioxane (42).
A solution of **41** (11.62 g, 38.3 mmol) in THF (150 mL) and MeOH (1.7 mL) was treated with a solution of $LiBH_4$ (2.0 M in THF, 23.0 mL, 46.0 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h, then let to warm to room temperature over 1 h. The mixture was quenched with sat. aq. sodium potassium tartrate, then diluted with ethyl ether and water. The aqueous layer was extracted with ethyl ether (2 × 75 mL). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the oil. The flash chromatography (CH_2Cl_2:EtOAc, 19:1 to 3:2) afforded the diol (3.63 g, 73% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (d, *J* = 14.7 Hz, 2H), 4.08 (dd, *J* = 2.7, 8.4 Hz, 1H), 3.82-3.68 (m, 2H), 2.94 (dd, *J* = 3.9, 6.9 Hz, 1H), 2.58 (d, *J* = 2.7 Hz, 1H), 1.99 (m, 1H), 1.82 (s, 3H), 0.89 (d, *J* = 6.9 Hz, 3H).

A solution of the diol (3.61 g 27.7 mmol) and PMB dimethyl acetal (4.95 mL, 29.0 mmol) in toluene (35 mL) was treated with PPTS (0.69 g, 2.77 mmol) at room temperature. The mixture was stirred at room temperature overnight. The mixture was quenched with sat. aq. $NaHCO_3$, then diluted with ethyl ether. The organic layer was washed with water and brine, then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to provide the crude mixture **42**, which was used without purification for the next reaction: ^{1}H NMR (300 MHz, $CDCl_3$) δ7.52 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 5.59 (s, 1H), 5.07 (dd, *J* = 0.9, 4.2 Hz, 2H), 4.28 (dd, *J* = 4.8, 11.4 Hz, 1H), 3.98-3.88 (m, 4H), 3.62 (t, *J* = 11.4 Hz, 1H), 2.15 (m, 1H), 1.90 (d, *J* = 0.9 Hz, 3H), 0.81 (d, *J* = 5.7 Hz, 3H).

(*R*)-2-[(2*S*,4*R*,5*S*)-2-(4-Methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]propan-1-ol (43).
A solution of cyclohexene (8.7 mL, 85.8 mmol) in THF (100 mL) was treated with BH_3•DMS (10.0 M in THF, 4.3 mL, 42.9 mmol) dropwise at 0 °C. The solution was stirred at 0 °C for 1 h. The white precipitates formed. A solution of the crude **42** in THF (2 mL) was added dropwise. The mixture was warmed to room temperature over 3 h, and cooled to 0 °C, then treated with water (3 mL), 3N NaOH (1 mL), and H_2O_2 (1 mL). The mixture was stirred at 0 °C for 20 min, at room temperature for 20 min, and at 50 °C for 20 min. The mixture was cooled to room temperature, and diluted with ethyl ether. The aqueous layer was extracted with ethyl ether (3 × 50 mL). The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to provide the oil. The flash chromatography (CH_2Cl_2:EtOAc, 17:3) afforded the title compound (5.61 g, 76% yield, two steps): IR (NaCl) 3426, 2961, 2932, 1517, 1249, 1032 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.41 (s, 1H), 4.19 (dd, *J* = 4.8, 11.4 Hz, 1H), 3.99 (dd, *J* = 3.6, 11.1 Hz, 1H), 3.83 (s, 3H), 3.67 (dd, *J* = 4.5, 8.4 Hz, 1H), 3.59-3.45 (m, 2H), 2.42 (brs, 1H), 2.18

(m, 1H), 2.01 (m, 1H), 1.24 (d, J = 7.2 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H) ; LRMS (EI) 266 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{15}H_{22}O_4$ 266.1518 ($M^{+\bullet}$), found 266.1512.

(2*S*,4*S*,5*S*)-4-[(*S*)-1-Iodopropan-2-yl]-2-(4-methoxyphenyl)-5-methyl-1,3-dioxane (44).
To a solution of PPh_3 (2.44 g, 9.05 mmol) in CH_2Cl_2 (25 mL) was added imidazole (0.77 g, 11.31 mmol) and iodine (2.58 g, 10.18 mmol) at room temperature. The mixture was vigorously stirred until dissolution of iodine. A solution of **43** (2.00 g, 7.54 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The mixture was stirred at room temperature for 20 h, then concentrated under vacuum. The residue was dissolved in a minimum amount of CH_2Cl_2 and purified by flash chromatography (hexane/EtOAc, 4:1) afforded the title compound (2.79 g, 98% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 8.4 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 4.14 (dd, J = 4.8, 11.4 Hz, 1H), 3.81 (s, 3H), 3.58-3.37 (m, 3H), 3.12 (t, J = 9.9 Hz, 1H), 2.16 (m, 2H), 1.28 (d, J = 6.3 Hz, 3H), 0.83 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 131.2, 127.3, 113.6, 101.1, 86.1, 73.0, 55.4, 38.0, 31.3, 19.0, 12.5, 9.6; LRMS (EI) 376 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{15}H_{21}O_3I$ 376.0533 ($M^{+\bullet}$), found 376.0535.

(2*R*,4*R*)-*N*-[(1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl]-4-[(2*S*,4*R*,5*S*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-*N*,2-dimethylpentanamide (46).
A suspension of LiCl (3.99 g, 94.2 mmol) and diisopropylamine (4.50 mL, 31.8 mmol) in THF (15 mL) was treated with BuLi (1.6 M in hexane, 11.8 mL, 29.5 mmol) at –78 °C dropwise. The mixture was stirred at –78 °C for 10 min and at 0 °C for 5 min, then cooled to –78 °C. A solution of **45** (3.44 g, 15.6 mmol) in THF (30 mL) was added dropwise. The mixture was stirred at –78 °C for 1h, 0 °C for 15 min, and at room temperature for 5 min, then cooled to 0 °C. A solution of **44** (2.79 g, 7.4 mmol) in THF (10 mL) was added. The mixture was allowed to warm to room temperature and stirred for 36 h. The reaction mixture was quenched with half sat. aq. NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to provide the oil. The flash chromatography (hexane:EtOAc, 2:3) afforded the title compound (3.07 g, 88% yield): IR (NaCl) 3380, 2962, 2932, 2874, 2836, 1614, 1249, 1033 cm^{-1}; LRMS (EI) 468 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{28}H_{38}NO_5$ 468.2759 ($M^{+\bullet}$), found 468.2750.

(2*R*,4*R*)-4-[(2*S*,4*R*,5*S*)-2-(4-Methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-2-methylpentan-1-ol (47).
A solution of diisopropylamine (2.70 mL, 26.5 mmol) in THF (20 mL) was treated with BuLi (1.6 M in hexane, 15.4 mL, 24.6 mmol) at –78 °C dropwise. The mixture was stirred at –78 °C for 10 min and at 0 °C for 10 min. BH_3•NH_3 (0.87 g, 25.3 mmol) was added. The mixture was stirred at 0 °C for 15 min and at room temperature for 15 min, then cooled to 0 °C. A solution of **46** (2.97 g, 6.32 mmol) in THF (10 mL) was added. The mixture was warmed to room temperature and stirred for 2 h. The reaction mixture was quenched with half sat. aq. NH_4Cl and extracted with ethyl ether. The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to provide the oil. Flash chromatography (hexane:EtOAc, 7:3) afforded the title compound (1.54 g, 79% yield): IR (NaCl) 3415, 2958, 2929, 2873, 2836, 1517, 1249, 1033 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.42 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 5.43 (s, 1H), 4.12 (dd, J = 4.5, 11.1 Hz, 1H), 3.80 (s, 3H), 3.57-3.33 (m, 4H), 2.06 (m, 1H), 1.91 (m, 1H), 1.70 (m, 1H), 1.43 (m, 1H), 1.24 (m, 1H), 1.06 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.77 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 131.6, 127.3, 113.5, 101.2, 88.0, 73.2, 69.4, 55.3, 33.3, 32.8, 30.9, 30.5, 17.1, 15.8, 12.2; LRMS (EI) 308 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{18}H_{28}O_4$ 308.1991 ($M^{+\bullet}$), found 308.1987.

tert-Butyl{(2*R*,4*R*)-4-[(2*S*,4*R*,5*S*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-2-methylpentyloxy}dimethylsilane (48).
A solution of **47** (1.52 g, 4.92 mmol), imidazole (0.67 g, 9.84 mmol) and DMAP (0.03 g, 0.25 mmol) in CH_2Cl_2 (20 mL) was treated with TBDMSCl (1.11 g, 7.38 mmol) at 0 °C. The white suspension was stirred at room temperature for 3 h, then diluted with CH_2Cl_2 and brine The aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the crude oil (1.95 g, 94% yield): IR (NaCl) 2955, 2928, 2855, 1249, 1093, 834 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 5.53 (s, 1H), 4.21 (dd, *J* = 4.8, 15.9 Hz, 1H), 3.83 (s, 3H), 3.70-3.42 (m, 4H), 2.15 (m, 1H), 2.00 (m, 1H), 1.78 (m, 1H), 1.56 (m, 1H), 1.27 (m, 1H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.02 (s, 9H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.16 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 131.8, 127.4, 113.5, 101.2, 88.1, 73.2, 69.4, 55.3, 33.4, 32.9, 31.0, 30.5, 26.1, 18.4, 17.1, 15.9, 12.2, -5.1; LRMS (EI) 422 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{24}H_{42}O_4Si$ 422.2841 ($M^{+\bullet}$), found 422.2852.

(2*S*,3*R*,4*R*,6*R*)-3-(4-Methoxybenzyloxy)-7-(*tert*-butyldimethylsilyloxy)-2,4,6-trimethylheptan-1-ol (49).
A solution of **48** (1.59 g, 3.77 mmol) in CH_2Cl_2 (30 mL) was treated with DIBALH (1.0 M in hexane, 17.0 mL, 17.0 mmol) at –78 °C dropwise. The mixture was stirred at –78 °C for 15 min and at 0 °C for 20 min. The reaction mixture was quenched with sat. aq. sodium potassium tartrate, diluted with ethyl ether and water, then stirred vigorously until the phases were clear. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the oil. The flash chromatography (hexane:EtOAc, 7:3) afforded the title compound (1.23 g, 77% yield): IR (NaCl) 3453, 2956, 2928, 2856, 1514, 1249, 1089, 836 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 4.70 (d, *J* = 10.5 Hz, 1H), 4.56 (d, *J* = 10.5 Hz, 1H), 3.88 (s, 3H), 3.82 (dd, *J* = 3.6, 11.1 Hz, 1H), 3.65 (dd, *J* = 5.7, 10.8 Hz, 1H), 3.51 (dd, *J* = 6.3, 9.9 Hz, 1H), 3.43 (dd, *J* = 6.3, 9.9 Hz, 1H), 3.30 (dd, *J* = 4.5, 6.6 Hz, 1H), 2.88 (brs, 1H), 1.99 (m, 2H), 1.77 (m, 1H), 1.50-1.25 (m, 2H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 7.2 Hz, 3H), 0.99 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.13 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 130.6, 129.4, 113.9, 90.1, 74.9, 69.4, 66.5, 55.3, 37.4, 35.0, 33.4, 33.3, 26.1, 18.4, 17.0, 16.1, 15.9, -5.1; LRMS (ESI) 447.2 $[M+Na]^+$; HRMS (ESI) calcd for $C_{24}H_{45}O_4Si$ 425.3087 $[M+H]^+$, found 425.3060.

[(2*R*,4*R*,5*R*,6*S*)-5-(4-Methoxybenzyloxy)-2,4,6-trimethyloct-7-ynyloxy](*tert*-butyl)dimethylsilane (38).
A solution of **49** (0.54 g, 1.26 mmol) in CH_2Cl_2 (25 mL) was treated with Dess-Martin periodinane (1.07 g, 2.52 mmol) at room temperature. The mixture was stirred for 2 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the oil, which was used for the next reaction without further purification.

A solution of CBr_4 (0.84 g, 2.52 mmol) in CH_2Cl_2 (3 mL) was treated with PPh_3 (1.36 g, 5.05 mmol) at 0 °C. The mixture was stirred until the formation of precipitates. A solution of the crude aldehyde and 2,6-lutidine (0.29 mL, 2.52 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 2 h. The reaction mixture was quenched with water. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the oil. The flash chromatography (hexane:EtOAc, 9:1) afforded the dibromoalkene (0.58 g, 79% yield, two steps): IR (NaCl) 2955,

2928, 1514, 1249, 1092, 836 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.60 (d, *J* = 9.6 Hz, 1H), 4.60 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 3.85 (s, 3H), 3.48 (dd, *J* = 6.3, 9.9 Hz, 1H), 3.39 (dd, *J* = 6.3, 9.9 Hz, 1H), 3.12 (dd, *J* = 3.0, 6.3 Hz, 1H), 2.79 (m, 1H), 1.77 (m, 2H), 1.29 (m, 2H), 1.13 (d, *J* = 6.9 Hz, 3H), 0.94 (s, 9H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H), 0.09 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 141.2, 131.0, 129.3, 113.8, 87.6, 87.3, 74.3, 69.4, 55.4, 41.1, 36.2, 33.7, 33.4, 26.1, 18.5, 17.6, 16.1, 15.7, -5.1; LRMS (EI) 578 ($M^{+\bullet}$); HRMS (EI) calcd for $C_{25}H_{42}Br_2O_3Si$ 576.1279 ($M^{+\bullet}$), found 576.1270.

A solution of the dibromoalkene (0.46 g, 0.80 mmol) in THF (5 mL) was treated with BuLi (1.6 M in hexane, 1.50 mL, 2.40 mmol) at –78 °C dropwise. The mixture was stirred at –78 °C for 40 min. The reaction mixture was quenched with sat. aq. NH_4Cl. The aqueous layer was extracted with ethyl ether. The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the oil. Flash chromatography (hexane:EtOAc, 9:1) afforded the title compound (0.32 g, 96% yield): ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.70 (d, *J* = 10.8 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 3.81 (s, 3H), 3.44 (dd, *J* = 6.3, 9.6 Hz, 1H), 3.32 (dd, *J* = 6.3, 9.0 Hz, 1H), 3.11 (t, *J* = 5.7 Hz, 1H), 2.79 (m, 1H), 2.09 (d, *J* = 2.4 Hz, 1H), 1.93 (m, 1H), 1.69 (m, 1H) 1.24 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.90 (s, 9H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 131.1, 129.4, 113.7, 87.1, 86.6, 74.2, 69.6, 69.4, 55.3, 34.9, 33.3, 33.1, 29.1, 26.0, 18.4, 18.3, 16.5, 15.9, -5.1.

(4*S*,5*S*,*E*)-Ethyl 5,7-*bis*(*tert*-butyldimethylsilyloxy)-4-methylhept-2-enoate (53).
A cooled (0 ˚C) stirred suspension of NaH (0.18 g, 7.07 mmol, 95 % dispersion in mineral oil) in THF (63 mL) was treated dropwise with a solution of triethyl phosphonoacetate (1.12 mL, 7.19 mmol) over 10 min period. The mixture was brought to room temperature with a water bath (30 min) and then cooled back to –78 ˚C and the aldehyde from **52**[i] (2.05 g, 5.66 mmol) in THF (5 mL) was added. The resulting mixture was stirred for 1 h at 0 ˚C then pH 7 phosphate buffer solution (10 mL) and diethyl ether (50 mL) were added. The mixture was allowed to warm to room temperature and the phases were separated. The organic phase was washed with sat'd NH_4Cl solution (30 mL) and brine (30 mL), dried with $MgSO_4$, filtered and concentrated to give crude product. Purification by flash chromatography (EtOAc/hexane 1:9) afforded pure ester **53** (1.68 g, 69 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2928, 2855, 1720, 1652, 1472, 1388, 1366, 1258, 1180, 1038, 832, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.05 (dd, *J* = 15.8, 7.0 Hz, 1H), 5.79 (d, *J* = 15.9 Hz, 1H), 4.18 (q, *J* = 7.1Hz, 2H), 3.82 (m, 1H), 3.64 (m, 2H), 2.48 (m, 1H), 1.72-1.49 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.88 (s, 9H), 0.05-0.03 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 151.6, 120.9, 72.1, 59.95, 59.52, 41.8, 36.8, 25.8, 18.1, 18.0, 14.2, 13.8, –4.56, –4.61, –5.4; LRMS (EI) 415 $(M–CH_3)^+$ 373, 303, 189, 147; HRMS (EI) calcd for $C_{21}H_{43}O_4Si_2$ 415.2700 $(M–CH_3)^+$ found 415.2700; $[\alpha]^{20}_D$ –31.6 (*c* 1.36, $CHCl_3$).

(4*S*,5*S*,*E*)-5,7-*bis*(*tert*-Butyldimethylsilyloxy)-4-methylhept-2-en-1-ol (54).
DIBALH (8.8 mL, 8.8 mmol, 1.0 M solution in hexane) was added to the above ester **53** (1.52 g. 3.53 μmol) in CH_2Cl_2 (35 mL) at –78 ˚C dropwise and stirred for 1 h. The reaction mixture was quenched by EtOAc (5 mL) and sat'd sodium potassium tartrate solution (20 mL) followed by vigorous stirring for 4 h. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were washed with brine (10 mL). After drying over $MgSO_4$ and evaporation under vacuum, flash column chromatography (hexane/EtOAc 4:1) provided 1.33 g of alcohol (97 %) as a colorless oil: IR ($CHCl_3$) 3344, 2853, 1471, 1387, 1255, 1096, 974, 834, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ5.69 (dd, *J* = 15.5, 6.6 Hz, 1H), 5.57 (dt, *J* = 15.6, 5.6

Hz, 1H), 4.04 (m, 2H), 3.70-3.54 (m, 3H), 2.29 (m, 1H), 1.96 (br, 1H), 1.62-1.45 (m, 2H), 0.92 (d, J = 7.0 Hz, 3H), 0.85 (s, 18H), 0.00 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.1, 128.8, 72.8, 63.8, 59.8, 41.6, 36.4, 25.9, 18.2, 18.1, 15.1, –4.4, –4.6, –5.4; LRMS (EI) 331 $(M–^tBu)^+$ 303, 171, 147; HRMS (EI) calcd for $C_{16}H_{35}O_3Si_2$ 331.2125 $(M–^tBu)^+$ found 331.2135; $[\alpha]^{20}_D$ –32.4 (*c* 0.90, $CHCl_3$).

((4*S*,5*S*,*E*)-5,7-*bis*(*tert*-Butyldimethylsilyloxy)-4-methylhept-2-enyloxy)triphenylmethane (55).

Trityl chloride (2.0 g) and DMAP (0.88 g) were added to a solution of alcohol **54** (1.33 g) in pyridine (34 mL). The mixture was then refluxed for 18 h, cooled to ambient temperature and added to a solution of sat'd $CuSO_4$ (200 mL). The mixture was extracted with Et_2O (2 x 20 mL), washed sat'd $CuSO_4$ (2 x 20 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Flash column chromatography (EtOAc/hexane 1:19) provided product (2.16 g, 94 %) as a pale yellow oil: IR ($CHCl_3$) 2955, 2928, 2856, 1490, 1471, 1448, 1255, 1093, 835, 774, 705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.55-7.53 (m, 6H), 7.38-7.27 (m, 9H), 5.91 (dd, J = 15.7, 6.7 Hz, 1H), 5.64 (dt, J = 15.5, 5.4 Hz, 1H), 3.84-3.70 (m, 3H), 3.65 (d, J = 5.2 Hz, 2H), 2.43 (m, 1H), 1.78-1.54 (m, 2H), 1.05 (d, J = 6.9 Hz, 3H), 0.98 (s, 9H), 0.97 (s, 9H), 0.14 (s, 6H), 0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 134.4, 128.7, 127.7, 126.8, 126.4, 86.7, 72.9, 65.1, 60.0, 41.8, 36.5, 26.0, 18.3, 18.1, 15.0, –4.3, –4.5, –5.2; LRMS (EI) 573 $(M–^tBu)^+$ 367, 303, 243; HRMS (EI) calcd for $C_{35}H_{49}O_3Si_2$ 573.3220 $(M–^tBu)^+$ found 573.3218; $[\alpha]^{20}_D$ –18.0 (*c* 1.2, $CHCl_3$).

(3*S*,4*S*,*E*)-3-(*tert*-Butyldimethylsilyloxy)-4-methyl-7-(trityloxy)hept-5-en-1-ol (56).

A solution of TBS ether **55** (1.68 g, 2.67 mmol) in THF (10 mL) was treated slowly with HF-pyridine in pyridine (40 mL, prepared by slow addition of 12 mL pyridine to 3 mL HF-pyridine complex followed by dilution with 25 mL THF). The mixture was stirred overnight at room temperature and quenched with sat'd $NaHCO_3$ (100 mL). The aqueous layer was separated and extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with sat'd $CuSO_4$ (3 x 50 mL), dried over $MgSO_4$, and concentrated. Flash column chromatography (EtOAc/hexane 3:17) afforded 1.13 g (82 %) of the alcohol as a colorless oil: IR ($CHCl_3$) 3390, 2955, 2928, 2855, 1448, 1380, 1255, 1060, 836, 774 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.75-7.72 (m, 6H), 7.55-7.42 (m, 9H), 6.09 (dd, J = 15.6, 6.4 Hz, 1H), 5.86 (dt, J = 15.6, 5.2 Hz, 1H), 4.07-3.94 (m, 3H), 3.86 (d, J = 5.0 Hz, 2H), 2.70 (m, 2H), 1.93 (m, 1H), 1.54 (br, 1H), 1.27 (d, J = 6.7 Hz, 3H), 1.20 (s, 9H), 0.38 (s, 3H), 0.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 133.6, 128.5, 127.6, 126.84, 126.76, 86.7, 74.5, 64.9, 59.9, 41.6, 35.1, 25.8, 17.9, 15.6, –4.4, –4.6; LRMS (API-ESI) 539.2 $[M+Na]^+$; HRMS (ESI) calcd for $C_{33}H_{44}O_3Si_1Na$ 539.2957 $[M+Na]^+$ found 539.2006; $[\alpha]^{20}_D$ –31.8 (*c* 3.1, $CHCl_3$).

(3*S*,4*S*,*E*)-3-(*tert*-Butyldimethylsilyloxy)-*N*-methoxy-*N*,4-dimethyl-7-(trityloxy)hept-5-enamide (39).

The alcohol **56** (0.34 g, 0.66 mmol) in CH_2Cl_2 (10 mL) was treated with Dess-Martin periodinane (0.41 g, 0.99 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (10 mL). The aqueous layer was extracted with ethyl ether (10 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography (hexane/EtOAc 4:1) to remove the Dess-Martin residue provided the aldehyde as a colorless oil, which was used for the next reaction without further purification. A solution of the above aldehyde in THF (10 mL) and H_2O (5 mL) was treated with a 2 M solution of 2-methyl-2-butene (1.9 mL, 0.95 mmol) in THF, NaH_2PO_4•H_2O (0.27 g, 1.96 mmol) and $NaClO_2$ (0.22 g, 1.96 mmol). The reaction mixture was stirred for 2 h, diluted with 1N HCl (20

mL) and extracted with CH_2Cl_2 (2 x 40 mL). The combined organic layers were dried over $MgSO_4$, concentrated *in vacuo* and the crude **57** was used for the next reaction without further purification. To a solution of acid in CH_2Cl_2, *N,O*-dimethylhydroxylamine hydrochloride (0.064 g, 0.65 mmol), Et_3N (0.09 mL, 0.65 mmol), DMAP (8 mg, 0.065 mmol) were successively added. The reaction mixture was cooled to 0 ˚C, DCC (0.14 g, 0.65 mmol) was added. The mixture was stirred at ambient temperature for 15 h and filtered. The filtrate was washed with 0.5 N HCl, saturated aqueous $NaHCO_3$, and brine, dried over anhydrous $MgSO_4$ and concentrated. Purification by column chromatography over silica gel (hexane/EtOAc 4:1) gave the Weinreb amide **39** (0.37 g, 81 % for 3 steps) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2855, 1661, 1448, 1385, 1251, 1089, 1054, 1003, 836, 775, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.64-7.61 m, 6H), 7.45-7.33 (m, 9H), 6.09 (dd, *J* = 15.7, 6.6 Hz, 1H), 5.75 (dt, *J* = 15.7, 5.2 Hz, 1H), 4.42 (m, 1H), 3.76 (s, 3H), 3.70 (m, 2H), 3.29 (s, 3H), 2.88 (m, 1H), 2.55 (m, 2H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.06 (s, 9H), 0.27 (s, 3H), 0.20 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 144.2, 133.5, 128.5, 127.6, 126.8, 86.5, 72.8, 64.6, 61.1, 42.2, 36.0, 31.9, 25.8, 18.0, 14.8, –4.7, –4.8; LRMS (EI) 573 ($M^{+\bullet}$), 558, 516, 246, 165; HRMS (EI) calcd for $C_{35}H_{47}O_4NSi$ 573.3290 ($M^{+\bullet}$), found 573.3290; $[\alpha]^{20}_D$ –40.1 (*c* 1.2, $CHCl_3$).

(4*S*,5*S*,10*S*,11*R*,12*R*,14*R*,*E*)-11-(4-Methoxybenzyloxy)-5,15-*bis*(*tert*-butyldimethylsilyloxy)-4,10,12,14-tetramethyl-1-(trityloxy)pentadec-2-en-8-yn-7-one (58).
Alkyne **38** (7.75 g, 18.5 mmol) was taken up in THF (185 mL) and cooled to –78 ˚C. *n*-BuLi (11.6 mL, 1.6 M solution in hexane) was added slowly. After 5 min, the mixture was warmed to 0 ˚C and stirred for 30 min. The mixture was then cooled to –78 ˚C and amide **39** (5.31 g, 9.26 mmol) in THF (15 mL) was added slowly. After 5 min the solution was warmed to 0 ˚C and stirred for 1 h. The reaction was quenched with aq NH_4Cl and the mixture was partitioned in a separatory funnel. The aqueous phase was extracted with ether (50 mL x 3) and combined organic extracts were washed with brine and dried over $MgSO_4$. Filtration and concentration under reduced pressure, followed by flash chromatography on silica gel (hexane/EtOAc 19:1) afforded ynone **58** (8.45 g, 98 %) as a pale yellow oil: IR ($CHCl_3$) 2955, 2929, 2856, 2208, 1674, 1514, 1470, 1249, 1092, 836, 775, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ7.50-7.47 m, 6H), 7.35-7.22 (m, 11H), 6.88-6.84 (m, 2H), 5.81 (dd, *J* = 15.6, 6.7 Hz, 1H), 5.58 (dt, *J* = 15.6, 5.2 Hz, 1H), 4.64 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.27 (m, 1H), 3.80 (s, 3H), 3.59 (d, *J* = 5.2 Hz, 2H), 3.44-3.34 (m, 2H), 3.18 (t, *J* = 5.4 Hz, 1H), 2.94 (m, 1H), 2.62 (m, 1H), 2.38 (m, 1H), 1.89 (m, 1H), 1.68 (m, 1H), 1.26 (d, *J* = 7.0 Hz, 3H), 1.24 (m, 1H), 0.99 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.92 (s, 9H), 0.91 (m, 1H), 0.89 (s, 9H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.09-0.05 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.4, 159.1, 144.3, 133.5, 130.7, 129.2, 128.7, 127.7, 127.3, 126.9, 113.7, 96.8, 86.8, 86.2, 82.6, 74.0, 72.3, 69.2, 64.9, 55.2, 50.5, 42.3, 34.9, 33.2, 33.0, 29.5, 26.0, 25.9, 18.3, 18.1, 17.2, 16.3, 15.9, 14.8, –4.50, –4.55, –5.3; LRMS (ESI) 953.6 $[M+Na]^+$; HRMS (ESI) calcd for $C_{58}H_{82}O_6Si_2Na$ 953.5548 $[M+Na]^+$, found 953.5552; $[\alpha]^{20}_D$ –9.5 (*c* 2.8, $CHCl_3$).

(4*S*,5*S*,7*S*,10*S*,11*R*,12*R*,14*R*,*E*)-11-(4-Methoxybenzyloxy)-5,15-*bis*(*tert*-butyldimethylsilyloxy)-4,10,12,14-tetramethyl-1-(trityloxy)pentadec-2-en-8-yn-7-ol (59).
Ynone **58** (7.06 g, 7.59 mmol) was taken up in *i*-PrOH (100 mL). Noyori catalyst (1.02 g, 1.52 mmol, 20 mol%) was added in one portion and the solution was stirred for 12 h. The solvent was removed under vacuum, and the crude residue was purified by flash chromatography on silica gel (hexane/EtOAc 9:1), affording propargylic alcohol **59** (6.16 g, 87 %) as a pale yellow oil: IR ($CHCl_3$) 3434, 2955, 2928, 2855, 1613, 1513, 1462, 1250, 1091, 836, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59-7.57 (m, 6H), 7.42-7.30 (m, 11H), 6.96-6.93 (m, 2H), 5.96 (dd, *J* = 15.7, 6.4 Hz, 1H), 5.68 (dt, *J* = 15.2, 5.3 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.67 (m, 1H), 4.63 (d, *J* =

10.9 Hz, 1H), 4.07 (m, 1H), 3.86 (s, 3H), 3.69 (d, *J* = 4.7 Hz, 2H), 3.49 (m, 2H), 3.22 (t, *J* = 5.5 Hz, 1H), 2.91 (m, 1H), 2.67 (d, *J* = 5.3 Hz, 1H), 2.56 (m, 1H), 1.98 (m, 1H), 1.86 (m, 2H), 1.77 (m, 1H), 1.36 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.09 (d, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 7.1 Hz, 3H), 1.03 (s, 9H), 1.02 (s, 9H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.24 (s, 3H), 0.22 (s, 3H), 0.15 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 144.3, 133.2, 131.0, 129.1, 128.6, 127.7, 127.0, 126.8, 113.5, 87.5, 86.79, 86.74, 82.6, 74.0, 73.3, 69.3, 65.0, 59.6, 55.1, 41.4, 40.2, 34.5, 33.1, 32.7, 29.1, 25.9, 18.3, 18.0, 17.9, 16.6, 15.8, 15.3, –4.3, –4.5, –5.4; LRMS (ESI) 955.6 $[M+Na]^+$; HRMS (ESI) calcd for $C_{58}H_{84}O_6Si_2Na$ 955.5704 $[M+Na]^+$, found 955.5734; $[\alpha]^{20}_D$ –8.5 (*c* 1.5, $CHCl_3$).

(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*R*)-11-(4-Methoxybenzyloxy)-5-(*tert*-butyldimethylsilyloxy)-15-(*tert*-butyldimethylsilyloxy))-4,10,12,14-tetramethyl-1-(trityloxy)pentadeca-2,8-dien-7-ol (60).

A catalytic amount of Lindlar catalyst (ca. 200 mg) was added to a solution of alcohol **59** (3.11 g, 3.33 mmol) in toluene (100 mL). The flask was fitted with a H_2 balloon, and stirred under an atmosphere of H_2 until starting material was consumed (usually 1 h), as indicated by TLC analysis. The mixture was filtered through a pad of celite and concentrated under reduced pressure to afford the olefin **60** as a colorless oil (2.81 g, 90 %): IR ($CHCl_3$) 3434, 2956, 2928, 2856, 1613, 1514, 1471, 1249, 1062, 836, 774 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.55 (m, 6H), 7.4-7.29 (m, 1H), 6.93 (m, 2H), 5.90 (dd, *J* = 15.6, 6.6 Hz, 1H), 5.68 (dt, *J* = 15.7, 5.4 Hz, 1H), 5.60 (dd, *J* = 11.1, 8.9 Hz, 1H), 5.51 (dd, *J* = 11.2, 7.3 Hz, 1H), 4.66 (m, 1H), 4.58 (d, *J* = 10.9 Hz, 1H), 4.55 (d, *J* = 10.9 Hz, 1H), 3.95 (m, 1H), 3.86 (s, 3H), 3.66 (dd, *J* = 4.9 Hz, 1H), 3.52-3.38 (m, 2H), 3.01 (m, 2H), 2.89 (br, 1H), 2.55 (m, 1H), 1.79 (m, 1H), 1.70 (m, 1H), 1.62 (m, 2H), 1.33-1.29 (m, 2H), 1.12 (d, *J* = 5.8 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.02 (s, 9H), 1.01 (s, 9H), 0.89 (d, *J* = 6.1 Hz, 3H), 0.87 (d, *J* = 6.3 Hz, 3H), 0.19 (s, 6H), 0.14 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 144.3, 134.1, 133.5, 132.6, 131.0, 129.0, 128.6, 127.7, 126.8, 126.7, 113.5, 88.4, 86.7, 74.9, 73.5, 69.4, 65.2, 65.1, 55.1, 41.8, 40.2, 35.0, 34.6, 33.1, 25.9, 19.1, 18.3, 18.0, 16.6, 15.8, 15.6, –4.4, –4.5, –5.3; LRMS (ESI) 957.6 $[M+Na]^+$; HRMS (ESI) calcd for $C_{58}H_{86}O_6Si_2Na$ 957.5861 $[M+Na]^+$, found 957.5900; $[\alpha]^{20}_D$ +2.0 (*c* 1.2, $CHCl_3$).

[(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*R*)-11-(4-Methoxybenzyloxy)-5,7,15-*tris*(*tert*-butyldimethylsilyloxy)-4,10,12,14-tetramethylpentadeca-2,8-dienyloxy]triphenylmethane (61).

TBSOTf (1.05 mL, 4.57 mmol) was added to a stirred solution of the alcohol **60** (3.89 g, 4.16 mmol) and 2,6-lutidine (0.58 mL, 5.01 mmol) in CH_2Cl_2 (14 mL) at 0 ˚C. After stirring for 1 h at 0 ˚C, the reaction mixture was quenched by the addition of water (25 mL), and extracted by CH_2Cl_2 and dried over $MgSO_4$, followed by the evaporation of the solvent under reduced pressure. The residue was purified by short column chromatography (hexane/EtOAc 9:1) to obtain the product **61** (4.36 g, quantitative) as a colorless oil: IR ($CHCl_3$) 2956, 2928, 2856, 1613, 1514, 1471, 1462, 1250, 1088, 836, 773, 705 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.58 (m, 6H), 7.43-7.31 (m, 11H), 6.97-6.94 (m, 2H), 5.95 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.67 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.62-5.46 (m, 2H), 4.71 (m, 1H), 4.62 (m, 2H), 4.05 (m, 1H), 3.87 (s, 3H), 3.69 (d, *J* = 5.3 Hz, 2H), 3.53-3.40 (m, 2H), 3.08 (m, 1H), 2.91 (m, 1H), 2.51 (m, 1H), 1.76 (m, 1H), 1.66 (m, 2H), 1.50-1.40 (m, 2H), 1.32 (m, 1H), 1.22 (d, *J* = 6.8 Hz, 6H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.06-0.96 (m, 27H), 0.91 (d, *J* = 6.6 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H), 0.25-0.17 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 144.4, 134.3, 133.7, 131.4, 129.4, 129.0, 128.6, 127.7, 126.8, 126.4, 113.5, 88.8, 86.7, 74.8, 72.8, 69.5, 66.3, 65.1, 55.1, 43.0, 42.3, 35.4, 35.1, 33.4, 33.1, 26.1, 26.0, 18.8, 18.3, 18.1, 16.7, 15.7, 14.6, –2.8, –3.9, –4.1, –4.2, –5.3; LRMS (ESI)

1071.9 $[M+Na]^+$; HRMS (ESI) calcd for $C_{64}H_{100}O_6Si_3Na$ 1071.6725 $[M+Na]^+$, found 1071.6779; $[\alpha]^{20}_D$ –9.5 (*c* 3.0, $CHCl_3$).

(2*R*,4*R*,5*R*,6*S*,7*Z*,9*S*,11*S*,12*S*,13*E*)-1,9,11-*tris*(*tert*-Butyldimethylsilyloxy)-2,4,6,12-tetramethyl-15-(trityloxy)pentadeca-7,13-dien-5-ol (62).
The above PMB alcohol **61** (2.90 g, 2.77 mmol) was added to CH_2Cl_2 (25 mL) and H_2O (1 mL), and DDQ (0.94 g, 4.15 mmol) was added. After 1 h of stirring, the reaction mixture was quenched by adding sat'd $NaHCO_3$ (200 mL). The organic phase was washed by sat'd $NaHCO_3$ solution (3 x 100 mL) and brine, dried over $MgSO_4$ and concentrated. Purification by flash column chromatography (EtOAc/hexane 1:19) furnished **62** (2.16 g, 84 %) as a colorless oil: IR ($CHCl_3$) 3477, 2956, 2928, 2856, 1471, 1386, 1254, 1088, 836, 774 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55-7.52 (m, 6H), 7.38-7.25 (m, 9H), 5.92 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.62 (dt, *J* = 15.7, 5.5 Hz, 1H), 5.52 (dd, *J* = 11.1, 9.3 Hz, 1H), 5.35 (t, *J* = 10.5 Hz, 1H), 4.63 (m, 1H), 3.97 (m, 1H), 3.63 (d, *J* = 5.4 Hz, 2H), 3.51-3.36 (m, 2H), 3.18 (m, 1H), 2.68 (m, 1H), 2.47 (m, 1H), 1.71-1.59 (m, 3H), 1.42-1.27 (m, 2H), 1.17 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.99 (s, 9H), 0.97 (s, 9H), 0.96 (s, 9H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.18 (s, 3H), 0.16 (s, 3H), 0.15 (s, 3H), 0.13 (s, 3H), 0.12 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 135.2, 134.1, 131.1, 128.7, 127.7, 126.8, 126.4, 86.7, 79.8, 72.8, 69.6, 66.2, 65.2, 43.0, 42.1, 35.5, 33.7, 32.8, 32.5, 26.1, 26.0, 25.9, 18.4, 18.1, 17.6, 16.8, 16.3, 14.7, –2.9, –4.0, –4.15, –4.22, –5.3; LRMS (ESI) 951.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{56}H_{92}O_5Si_3Na$ 951.6150 $[M+Na]^+$, found 951.6165; $[\alpha]^{20}_D$ 30.0 (*c* 3.6, $CHCl_3$).

[(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*R*)-5,7,11,15-*tetrakis*(*tert*-Butyldimethylsilyloxy)-4,10,12,14-tetramethylpentadeca-2,8-dienyloxy]triphenylmethane (63).
The procedure for **61** was used with above **62** (3.34 g, 3.60 μmol), TBSOTf (1.82 mL, 7.9 mmol) to yield 3.53 g (94 %) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: IR ($CHCl_3$) 2956, 2928, 2856, 1471, 1462, 1361, 1254, 1088, 836, 773, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.50-7.48 (m, 6H), 7.34-7.22 (m, 9H), 5.82 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.57 (dt, *J* = 15.8, 5.9 Hz, 1H), 5.48 (dd, *J* = 11.0, 9.9 Hz, 1H), 5.32 (dd, *J* = 11.0, 8.7 Hz, 1H), 4.56 (m, 1H), 3.93 (m, 1H), 3.59 (d, *J* = 5.5 Hz, 2H), 3.39 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.31-3.27 (m, 2H), 2.62(m, 1H), 2.40 (m, 1H), 1.58-1.50 (m, 3H), 1.35 (m, 1H), 1.20-1.09 (m, 2H), 1.02 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.91 (s, 9H), 0.90 (s, 9H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.6 Hz, 3H), 0.13-0.05 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 134.5, 133.0, 131.8, 128.7, 127.7, 126.8, 126.4, 86.7, 81.2, 72.8, 69.3, 66.6, 65.3, 43.1, 42.3, 35.9, 35.1, 33.3, 29.7, 26.2, 26.1, 26.0, 19.6, 18.4, 18.3, 18.2, 16.3, 16.0, 14.6, –2.8, –3.5, –3.6, –4.0, –4.1, –5.3; LRMS (ESI) 1065.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{62}H_{106}O_5Si_4Na$ 1065.7015 $[M+Na]^+$, found 1065.7068; $[\alpha]^{20}_D$ –22.5 (*c* 2.0, $CHCl_3$).

(2*R*,4*R*,5*R*,6*S*,7*Z*,9*S*,11*S*,12*S*,13*E*)-5,9,11-*tris*(*tert*-Butyldimethylsilyloxy)-2,4,6,12-tetramethyl-15-(trityloxy)pentadeca-7,13-dien-1-ol (64).
HF-pyridine in pyridine (40 mL, prepared by slow addition of 12 mL pyridine to 3 mL HF-pyridine complex followed by dilution with 25 mL THF) was slowly added to a solution of TBS ether **63** (3.54 g, 4.10 mmol) in THF (5 mL) at 0 ˚C. The mixture was stirred for 2 days at 0 ˚C and quenched with sat'd $NaHCO_3$ (100 mL). The aqueous layer was separated and extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with sat'd $CuSO_4$ (3 x 50 mL), dried over $MgSO_4$, and concentrated. Flash column chromatography (EtOAc/hexane 3:17) afforded 2.08 g (66 %) of the alcohol as a colorless oil: IR ($CHCl_3$) 3400, 2956, 2928, 2856, 1471, 1448, 1254, 1075, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 6H), 7.36-7.24 (m, 9H), 5.87 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.59 (dt, *J* = 15.7, 5.7 Hz, 1H), 5.55 (dd, *J* = 10.6,

10.4 Hz, 1H), 5.33 (dd, *J* = 11.0, 8.7 Hz, 1H), 4.58 (m, 1H), 3.94 (m, 1H), 3.60 (d, *J* = 5.5 Hz, 2H), 3.38-3.32 (m, 2H), 3.25 (m, 1H), 2.62 (m, 1H), 2.45 (m, 1H), 1.59 (m, 1H), 1.55 (m, 1H), 1.47 (m, 1H), 1.35 (m, 1H), 1.09 (m, 1H), 1.04 (d, *J* = 7.6 Hz, 3H), 1.01 (d, *J* = 7.2 Hz, 3H), 0.96 (s, 9H), 0.94 (s, 9H), 0.93 (s, 9H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H), 0.15 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 134.0, 132.7, 131.3, 128.7, 127.7, 126.8, 126.5, 86.8, 81.0, 73.0, 69.2, 66.5, 65.3, 42.6, 42.2, 36.2, 35.5, 34.6, 33.3, 26.2, 26.1, 25.9, 20.0, 18.4, 18.2, 18.1, 15.7, 15.6, 14.9, –2.8, –3.7, –3.8, –4.0, –4.1, –4.2; LRMS (ESI) 951.6 $[M+Na]^+$; HRMS (ESI) calcd for $C_{56}H_{92}O_5Si_3Na$ 951.6150 $[M+Na]^+$, found 951.6158; $[\alpha]^{20}_D$ –33.5 (*c* 2.0, $CHCl_3$).

(2*R*,4*E*,6*R*,8*R*,9*R*,10*S*,11*Z*,13*S*,15*S*,16*S*,17*E*)-9,13,15-*tris*(*tert*-Butyldimethylsilyloxy)-2-[(4*S*,5*S*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-6,8,10,16-tetramethyl-19-(trityloxy)nonadeca-4,11,17-trien-3-one (65).

The alcohol **64** (2.04 g, 2.20 mmol) in CH_2Cl_2 (30 mL) was treated with Dess-Martin periodinane (1.40 g, 3.30 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (30 mL) and $Na_2S_2O_3$ (30 mL). The aqueous layer was extracted with ethyl ether (30 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography filtration (hexane/EtOAc 4:1) to remove the residue from the Dess-Martin reagent provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. A mixture of ketophosphonate **7** (0.85 g, 2.20 mmol) and $Ba(OH)_2$ (0.30 g, activated by heating to 100 ˚C for 1-2 h before use) in THF (40 mL) was stirred at room temperature for 30 min. A solution of the above aldehyde in wet THF (4 mL + 4 x 1 mL washings, 40:1 THF/H_2O) was then added. After stirring for 12 h, the reaction mixture was diluted with Et_2O (30 mL) and washed with sat'd $NaHCO_3$ (50 mL) and brine (50 mL). The organic solution was dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The residue was chromatographed (hexane/EtOAc 9:1) to yield **65** (2.04 g, 78 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2957, 2929, 2855, 1618, 1518, 1461, 1388, 1251, 1078, 1036, 836, 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.46 (m, 6H), 7.39 (m, 2H), 7.33-7.21 (m, 9H), 6.89 (m, 2H), 6.79 (dd, *J* = 15.7, 7.4 Hz, 1H), 6.20 (d, *J* = 15.6 Hz, 1H), 5.85 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.58 (dt, *J* = 15.7, 4.6 Hz, 1H), 5.49 (dd, *J* = 11.0, 10.4 Hz, 1H), 5.46 (s, 1H), 5.34 (dd, *J* = 11.1, 8.6 Hz, 1H), 4.56 (m, 1H), 4.12 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.92 (m, 2H), 3.81 (s, 3H), 3.57 (d, *J* = 5.6 Hz, 1H), 3.54 (m, 1H), 3.29 (dd, *J* = 5.6, 2.4 Hz, 1H), 2.93 (m, 1H), 2.61 (m, 1H), 2.43 (m, 1H), 2.18 (m, 1H), 2.01 (m, 1H), 1.59-1.46 (m, 2H), 1.43 (m, 1H), 1.35-1.29 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 0.92 (s, 9H), 0.91 (s, 9H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.13 (s, 3H), 0.12 (s, 3H), 0.09 (s, 3H), 0.08 (s, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 159.8, 153.3, 144.3, 134.0, 133.3, 131.1, 130.8, 128.6, 127.7, 127.2, 126.8, 126.5, 125.7, 113.4, 100.8, 86.7, 82.7, 80.4, 72.8, 66.5, 65.8, 65.2, 55.2, 47.0, 42.8, 42.1, 39.1, 35.6, 34.9, 34.0, 32.3, 26.1, 26.0, 25.9, 19.7, 18.39, 18.36, 18.1, 16.4, 15.2, 14.7, 12.4, 10.7, –2.8, –3.6, –3.7, –4.0, –4.1; LRMS (ESI) 1209.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{72}H_{110}O_8Si_3Na$ 1209.7406 $[M+Na]^+$, found 1209.7466; $[\alpha]^{20}_D$ – 8.6 (*c* 2.5, $CHCl_3$).

(2*R*,6*S*,8*R*,9*R*,10*S*,11*Z*,13*S*,15*S*,16*S*,17*E*)-9,13,15-*tris*(*tert*-Butyldimethylsilyloxy)-2-[(4*S*,5*S*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-6,8,10,16-tetramethyl-19-(trityloxy)nonadeca-11,17-dien-3-one (66).

$NiCl_2$•$6H_2O$ (0.20 g, 0.84 mmol) then portionwise $NaBH_4$ (0.17 g, 4.49 mmol) were added to a stirred solution of unsaturated ketone **65** (2.60 g, 1.72 mmol) in MeOH (60 mL), THF (20 mL) at 0 ˚C. After 1 h, the reaction mixture was evaporated and filtered with celite using Et_2O as an eluent (30 mL). The organic phase was concentrated and the residue was purified by flash

chromatography (EtOAc/hexane 1:9) to yield **66** (1.55 g, 76 %) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2855, 1713, 1616, 1518, 1462, 1251, 1076, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.50 (m, 6H), 7.42-7.24 (m, 11H), 6.92-6.86 (m, 2H), 5.87 (dd, *J* = 15.7, 6.0 Hz, 2H), 5.60 (dt, *J* = 15.8, 5.9 Hz, 1H), 5.50 (m, 1H), 5.49 (s, 1H), 5.37 (dd, *J* = 10.9, 8.5 Hz, 1H), 4.59 (m, 1H), 4.17 (dd, *J* = 11.3, 4.7 Hz, 1H), 3.98 (m, 2H), 3.82 (s, 3H), 3.62-3.55 (m, 3H), 3.29 (m, 1H), 2.73 (m, 1H), 2.65 (m, 1H), 2.49 (m, 2H), 2.06 (m, 1H), 1.63-1.50 (m, 2H), 1.47-1.32 (m, 2H), 1.27 (d, *J* = 7.1 Hz, 3H), 1.26 (m, 1H), 1.06 (d, *J* = 7.3 Hz, 3H), 1.03 (d, *J* = 7.2 Hz, 3H), 0.97-0.94 (m, 27H), 0.90-0.84 (m, 2H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.76 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 5.7 Hz, 3H), 0.17-0.05 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 159.8, 144.4, 134.3, 133.1, 131.4, 130.9, 128.6, 127.9, 127.6, 127.1, 126.8, 126.4, 113.4, 100.8, 86.7, 82.9, 81.0, 72.8, 66.5, 65.2, 55.2, 48.3, 43.0, 42.2, 39.8, 38.3, 35.2, 35.1, 31.9, 31.3, 29.7, 26.2, 26.0, 25.9, 19.6, 18.6, 18.4, 18.1, 16.3, 14.6, 12.1, 9.7, –2.9, –3.5, –3.6, –4.0, –4.1, –4.2; LRMS (ESI) 1211.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{72}H_{112}O_8Si_3Na$ 1211.7563 $[M+Na]^+$, found 1211.7629; $[\alpha]^{20}_D$ –4.3 (*c* 1.0, $CHCl_3$).

(2*S*,3*R*,6*S*,8*R*,9*R*,10*S*,11*Z*,13*S*,15*S*,16*S*,17*E*)-9,13,15-*tris*(*tert*-Butyldimethylsilyloxy)-2-[(4*S*,5*S*)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxan-4-yl]-6,8,10,16-tetramethyl-19-(trityloxy)nonadeca-11,17-dien-3-ol (67).

$NaBH_4$ (0.074 g, 1.96 mmol) was added to a solution of ketone **66** (1.55 g, 1.30 mmol) in MeOH (21 mL) at 0 ˚C. After stirring for 2 h at 0 ˚C, the reaction mixture was evaporated and water (30 mL) was added. The reaction mixture was extracted with ether (2 x 40 mL) and washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography (EtOAc/hexane 1:9) to yield 1.02 g of major product β (less polar, 62 %) and 0.60 g (more polar, 36 %) of minor product α as colorless oils: (**67β**) IR ($CHCl_3$) 3540, 2956, 2929, 2855, 1615, 1518, 1461, 1385, 1252, 1074, 835, 773, 706 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.50 (m, 6H), 7.42 (m, 2H), 7.37-7.25 (m, 9H), 6.94-6.91 (m, 2H), 5.88 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.61 (dt, *J* = 16.0, 5.7 Hz, 1H), 5.56 (s, 1H), 5.50 (m, 1H), 5.37 (dd, *J* = 10.8, 8.6 Hz, 1H), 4.60 (m, 1H), 4.17 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.96 (m, 1H), 3.87 (m, 1H), 3.84 (s, 3H), 3.74 (m, 1H), 3.64-3.53 (m, 3H), 3.32 (m, 1H), 3.20 (br, 1H), 2.67 (m, 1H), 2.44 (m,1H), 2.18 (m, 1H), 1.83 (m, 1H), 1.67-1.51 (m, 2H), 1.50-1.32 (m, 3H), 1.26 (m, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.07 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 7.4 Hz, 3H), 0.98-0.85 (m, 2H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.0 Hz, 3H), 0.18-0.09 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 144.5, 144.4, 134.4, 132.9, 131.6, 130.7, 128.6, 127.6, 127.2, 126.8, 126.7, 126.4, 113.6, 101.2, 89.1, 86.7, 81.1, 76.8, 73.1, 72.8, 66.5, 55.2, 43.0, 42.3, 39.9, 37.2, 35.3, 35.1, 34.7, 32.3, 30.4, 30.2, 26.2, 26.1, 25.9, 19.6, 18.8, 18.4, 18.13, 18.10, 16.3, 14.6, 11.9, 5.5, –2.8, –3.56, –3.61, –4.0, –4.1, –4.16, –4.25; LRMS (API-ES) 1213.6 [M+Na]+, 557.0, 359.2, 243.1; HRMS (ESI) calcd for $C_{72}H_{114}O_8Si_3Na$ 1213.7719 [M+Na]+, found 1213.7717; $[\alpha]^{20}_D$ –0.68 (*c* 7.1, $CHCl_3$): (**67α**) IR ($CHCl_3$) 3531, 2956, 2929, 2855, 1615, 1518, 1462, 1383, 1252, 1075, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.53-7.49 (m, 6H), 7.44-7.41 (m, 2H), 7.36-7.24 (m, 9H), 6.94-6.91 (m, 2H), 5.86 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.60 (dt, *J* = 15.7, 5.7 Hz, 1H), 5.54 (s, 1H), 5.56-5.47 (m, 1H), 5.36 (dd, *J* = 11.0, 8.6 Hz, 1H), 4.60 (m, 1H), 4.17 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.97-3.91 (m, 2H), 3.84 (s, 3H), 3.62 (d, *J* = 4.9 Hz, 2H), 3.61-3.53 (m, 2H), 3.32 (m, 1H), 2.67 (m, 1H), 2.44 (m,1H), 2.16 (m, 1H), 1.82 (m, 1H), 1.72-1.50 (m, 4H), 1.42-1.33 (m, 2H), 1.32-1.22 (m, 2H), 1.14 (d, *J* = 7.1 Hz, 3H), 1.06 ((d, *J* = 7.0 Hz, 3H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.97-0.92 (m, 27H), 0.90-0.85 (m, 2H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 5.7 Hz, 3H), 0.17-0.09 (m, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 144.6, 144.4, 134.4, 133.0, 131.6, 131.1, 128.7, 127.7, 127.6, 127.3, 126.8, 126.7, 126.4, 113.6, 101.0, 86.7, 82.8, 81.2, 75.1, 73.3, 72.8, 66.6, 65.2, 55.2, 43.0, 42.3, 39.9, 37.9, 35.3, 35.1, 34.6, 33.4, 30.3, 26.3, 26.1, 26.0, 19.7, 19.0, 18.4, 18.1, 16.4, 14.6, 11.9, 11.1, –

2.8, –3.5, –4.0, –4.07, –4.13; LRMS (ESI) 1213.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{72}H_{114}O_8Si_3Na$ 1213.7719 $[M+Na]^+$, found 1213.7766; $[\alpha]^{20}_D$ –1.4 (*c* 4.7, $CHCl_3$).

(4*S*,5*S*)-4-[(2*R*,3*R*,6*S*,8*R*,9*R*,10*S*,11*Z*,13*S*,15*S*,16*S*,17*E*)-3,9,13,15-*tetrakis*(*tert*-Butyldimethylsilyloxy)-6,8,10,16-tetramethyl-19-(trityloxy)nonadeca-11,17-dien-2-yl]-2-(4-methoxyphenyl)-5-methyl-1,3-dioxane (68β).
TBSOTf (0.30 mL, 2.57 mmol) was added to a stirred solution of alcohol **67β** (1.02 g, 0.86 mmol) and 2,6-lutidine (0.20 mL, 1.71 mmol) in CH_2Cl_2 (17 mL) at 0 ˚C and the reaction mixture was stirred for 1 h at ambient temperature. The reaction mixture was quenched by the addition of water (50 mL). The reaction mixture was extracted by CH_2Cl_2 and dried over $MgSO_4$ followed by the evaporation of the solution under reduced pressure. The residue was purified by short column chromatography (hexane/EtOAc 9:1) to yield product (0.97 g, 86 %) as a colorless oil: IR ($CHCl_3$) 2955, 2928, 2856, 1615, 1518, 1471, 1462, 1387, 1251, 1074, 1038, 835, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52-7.46 (m, 6H), 7.45-7.42 (m, 2H), 7.35-7.22 (m, 9H), 6.92-6.89 (m, 2H), 5.86 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.59 (dt, *J* = 15.7, 4.9 Hz, 1H), 5.48 (m, 1H), 5.47 (s, 1H), 5.36 (dd, *J* = 11.1, 8.6 Hz, 1H), 4.58 (m, 1H), 4.15 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.96 (m, 1H), 3.81 (s, 3H), 3.73-3.66 (m, 2H), 3.60 (d, *J* = 5.6 Hz, 2H), 3.55 (m, 1H), 3.19 (m, 1H), 2.65 (m 1H), 2.42 (m, 1H), 2.07 (m, 1H), 1.91 (m, 1H), 1.57 (m, 2H), 1.40-1.21 (m, 3H), 1.14 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 5.9 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.96-0.92 (m, 36H), 0.88-0.84 (m, 3H), 0.80 (m, 1H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.4 Hz, 3H), 0.71 (d, *J* = 5.1 Hz, 3H), 0.16-0.03 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 144.6, 144.4, 134.4, 133.2, 131.7, 131.4, 128.7, 127.7, 127.2, 126.8, 126.4, 113.4, 100.4, 86.7, 81.8, 81.4, 75.0, 73.3, 72.8, 66.5, 65.2, 55.2, 43.1, 42.3, 39.7, 38.9, 35.3, 35.0, 34.0, 31.2, 30.7, 30.6, 26.2, 26.1, 26.00, 25.95, 19.5, 19.1, 18.4, 18.13, 18.10, 16.5, 14.5, 12.4, 10.6, –2.8, –3.4, –3.95, –3.98, –4.2, –4.3; LRMS (ESI) 1327.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{78}H_{128}O_8Si_4Na$ 1327.8584 $[M+Na]^+$, found 1327.8534; $[\alpha]^{20}_D$ +6.7 (*c* 0.65, $CHCl_3$).

(2*S*,3*S*,4*R*,5*R*,8*S*,10*R*,11*R*,12*S*,13*Z*,15*S*,17*S*,18*S*,19*E*)-3-(4-Methoxybenzyloxy)-5,11,15,17-*tetrakis*(*tert*-butyldimethylsilyloxy)-2,4,8,10,12,18-hexamethyl-21-(trityloxy)henicosa-13,19-dien-1-ol (69β).
DIBALH (1.0 M in hexane, 7.4 mL, 7.4 mmol) was added to a stirred solution of TBS protected acetal **68β** (0.97 g, 0.74 mmol) in anhydrous CH_2Cl_2 (3 mL), under an atmosphere of N_2 at 0 ˚C dropwise. After stirring for additional 30 min at 0 ˚C, the reaction mixture was quenched by the careful addition of aqueous sat'd potassium sodium tartrate solution (30 mL) and stirred for 3 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$ followed by the evaporation of the organic solution under reduced pressure. The residue was purified by column chromatography (EtOAc/hexane 1:9) to obtain **69β** (0.94 g, 97 %) as a colorless oil: IR ($CHCl_3$) 3501, 2956, 2929, 2856, 1613, 1514, 1471, 1462, 1251, 1075, 835, 773, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55-7.51 (m, 6H), 7.37-7.25 (m, 11H), 6.94-6.92 (m, 2H), 5.90 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.62 (dt, *J* = 15.6, 5.6 Hz, 1H), 5.56-5.48 (m, 1H), 5.40 (dd, *J* = 11.2, 8.5 Hz, 1H), 4.61 (m, 1H), 4.60 (s, 2H), 3.99 (m, 1H), 3.90 (m, 1H), 3.83 (s, 3H), 3.69 (m, 1H), 3.64 (d, *J* = 5.3 Hz, 1H), 3.53 (m, 1H), 3.31 (m, 1H), 2.99 (m 1H), 2.70 (m, 1H), 2.47 (m, 1H), 2.00 (m, 2H), 1.65-1.52 (m, 3H), 1.45-1.37 (m, 1H), 1.33 (m, 1H), 1.30 (m, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 7.0 Hz, 3H), 1.00-0.96 (m, 36H), 0.92-0.86 (m, 2H), 0.82 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 5.5 Hz, 3H), 0.19-0.11 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 144.5, 144.4, 134.3, 133.1, 131.5, 130.5, 129.2, 128.6, 127.6, 126.8, 126.4, 113.8, 86.7, 86.0, 81.1, 75.3, 73.6, 72.8, 66.5, 65.1, 65.0, 55.1, 43.0, 42.3, 40.5, 40.0, 36.8, 35.2, 35.1, 34.0, 32.1, 30.4, 26.2, 26.1, 26.0, 25.9, 19.6, 18.9, 18.4,

18.1, 16.5, 15.8, 14.6, 9.9, –2.8, –3.4, –3.5, –3.8, –4.0, –4.2, –4.4; LRMS (ESI) 1329.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{78}H_{130}O_8Si_4Na$ 1329.8741 $[M+Na]^+$, found 1329.8778; $[\alpha]^{20}_D$ –9.9 (*c* 0.36, $CHCl_3$).

[(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*S*,17*R*,18*R*,19*S*,20*S*,21*Z*)-19-(4-Methoxybenzyloxy)-7,11,17-*tris*(*tert*-butyldimethylsilyloxy)-5-(*tert*-butyldimethylsilyloxy))-4,10,12,14,18,20-hexamethyltetracosa-2,8,21,23-tetraenyloxy]triphenylmethane (70β).

The alcohol **69β** (0.94 g, 0.72 mmol) in CH_2Cl_2 (20 mL) was treated with Dess-Martin periodinane (0.46 g, 1.08 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (20 mL). The aqueous layer was extracted with ethyl ether (20 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography (hexane/EtOAc 9:1) to remove Dess-Martin residue provided crude aldehyde as a colorless oil, which was used for the next reaction without further purification. To a stirred solution of the above crude aldehyde and 1-bromoallyl trimethylsilane **29** (0.89 g) in anhydrous THF (18 mL) under an atmosphere of N_2 at room temperature was added $CrCl_2$ (0.73 g, 5.94 mmol), and the mixture was stirred for additional 14 h at ambient temperature. The reaction mixture was diluted with hexane followed by filtration through celite. After the evaporation of the solvent under reduced pressure, the residue was purified by short silica gel column chromatography (EtOAc/hexane 1:9) as the eluent. The foregoing product in THF (40 mL) was cooled to 0 ˚C and NaH (95 % w/w, 0.36 g, 14.4 mmol) was added in one portion. The ice bath was removed after 15 min and the mixture was stirred for 2 h at ambient temperature. The reaction mixture was cooled to 0 ˚C, quenched with H_2O (5 mL), extracted with ethyl ether (20 mL x 2). The combined organic layers were washed with brine and dried over $MgSO_4$ followed by the evaporation of the organic solution under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc 49:1) to obtain **70β** (0.81 g, 85 % for 3 steps) as a colorless oil: IR ($CHCl_3$) 2955, 2928, 2856, 1614, 1514, 1471, 1462, 1249, 1076, 835, 772, 705 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60-7.56 (m, 6H), 7.43-7.27 (m, 11H), 6.99-6.96 (m, 1H), 6.71 (ddd, *J* = 16.9, 10.6, 10.5 Hz, 1H), 6.14 (t, *J* = 11.0 Hz, 1H), 5.97 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.82-5.77 (m, 1H), 5.74-5.70 (m, 1H), 5.68-5.62 (m, 1H), 5.61-5.56 (m, 1H), 5.46 (dd, *J* = 11.1, 8.6 Hz, 1H), 5.28 (d, *J* = 16.9 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.66 (m, 3H), 4.05 (m, 1H), 3.86 (s, 3H), 3.76 (m, 1H), 3.69 (d, *J* = 5.2 Hz, 1H), 3.48 (m, 1H), 3.35 (m, 1H), 3.15 (m, 1H), 2.76 (m, 1H), 2.53 (m, 1H), 2.34 (m, 1H), 1.82 (m, 1H), 1.70-1.57 (m, 3H), 1.56-1.32 (m, 3H), 1.25 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 7.1 Hz, 3H), 1.12 (m, 2H), 1.11 (d, *J* = 7.1 Hz, 3H), 1.08-1.03 (m, 36H), 0.98-0.90 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.76 (d, *J* = 5.1 Hz, 3H), 0.25-0.13 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 146.2, 144.6, 144.4, 134.5, 134.3, 133.2, 132.4, 131.4, 130.2, 129.0, 128.7, 127.7, 126.8, 126.5, 117.2, 113.7, 86.7, 84.5, 81.3, 75.1, 72.9, 66.6, 65.2, 55.1, 43.0, 42.3, 40.6, 40.2, 35.6, 35.25, 35.19, 33.9, 32.6, 30.3, 26.3, 26.1, 26.04, 25.99, 19.6, 18.9, 18.4, 18.2, 16.6, 14.7, 9.2, –2.8, –3.36, –3.4, –3.5, –3.9, –4.1, –4.4; LRMS (ESI) 1351.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{81}H_{132}O_7Si_4Na$ 1351.8948 $[M+Na]^+$, found 1351.8973; $[\alpha]^{20}_D$ +0.4 (*c* 0.51, $CHCl_3$).

(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*S*,17*R*,18*R*,19*S*,20*S*,21*Z*)-19-(4-Methoxybenzyloxy)-5,7,11,17-*tetrakis*(*tert*-butyldimethylsilyloxy)-4,10,12,14,18,20-hexamethyltetracosa-2,8,21,23-tetraen-1-ol (71β).

$ZnBr_2$ solution (0.42 g in 5 mL CH_2Cl_2 and 0.8 mL of MeOH) was added to a stirred solution of trityl ether **70β** (0.50 g, 0.38 mmol) in MeOH (3 mL), CH_2Cl_2 (18 mL) at 0 ˚C dropwise for 30 min. After 4 h, the reaction mixture was quenched with saturated $NaHCO_3$ solution (20 mL) and extracted with Et_2O (10 mL x 2). The organic phase was separated, dried with $MgSO_4$ and concentrated. The residue was purified by flash chromatography (EtOAc/hexane 1:9) to yield

0.34 g of product **71β** (83 %) as a colorless oil: IR ($CHCl_3$) 3410, 2956, 2929, 2856, 1613, 1514, 1471, 1251, 1076, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.31-7.29 (m, 2H), 6.90-6.87 (m, 2H), 6.60 (ddd, *J* = 16.8, 10.6, 10.5 Hz, 1H), 6.02 (t, *J* = 11.0 Hz, 1H), 5.79 (dd, *J* = 15.6, 5.8 Hz, 1H), 5.62 (d, *J* = 9.3 Hz, 1H), 5.60 (m, 1H), 5.47 (t, *J* = 10.3 Hz, 1H), 5.32 (dd, *J* = 10.7, 8.9 Hz, 1H), 5.18 (d, *J* = 16.8 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 4.54 (m, 3H), 4.07 (d, *J* = 5.9 Hz, 2H), 3.89 (m, 1H), 3.81 (s, 3H), 3.64 (m, 1H), 3.35 (m, 1H), 3.24 (br, 1H), 3.00 (m, 1H), 2.61 (m, 1H), 2.40 (m, 1H), 1.68 (m, 1H), 1.55-1.42 (m, 3H), 1.38-1.21 (m, 3H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.02-0.99 (m, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.94-0.89 (m, 40H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.76 (d, *J* = 6.3 Hz, 3H), 0.11-0.06 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 134.9, 134.5, 133.1, 132.4, 131.5, 131.4, 129.1, 128.9, 128.7, 117.2, 113.7, 84.5, 81.3, 75.1, 72.7, 66.4, 64.1, 55.3, 42.7, 42.0, 40.5, 40.4, 35.5, 35.23, 35.20, 33.9, 32.6, 30.5, 26.3, 26.03, 26.00, 25.96, 19.7, 18.9, 18.8, 18.5, 18.2, 18.1, 16.6, 14.7, 9.2, –2.8, –3.47, –3.53, –4.03, –4.05, –4.2, –4.5, –4.7; LRMS (ESI) 1109.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{62}H_{118}O_7Si_4Na$ 1109.7852 $[M+Na]^+$, found 1109.7898; $[\alpha]^{20}_D$ –2.0 (*c* 2.6, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*R*,20*R*,21*S*,22*S*,23*Z*)-Methyl-21-(4-methoxybenzyloxy)-7,9,13,19-*tetrakis*(*tert*-butyldimethylsilyloxy)-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoate (72β).

The alcohol **71β** (0.34 g, 0.31 mmol) in CH_2Cl_2 (20 mL) was treated with Dess-Martin periodinane (0.20 g, 0.47 mmol). After 1 h, the mixture was quenched with saturated $NaHCO_3$ (5 mL) and $Na_2S_2O_3$ (5 mL). The aqueous layer was extracted with ethyl ether (10 mL x 2) and the combined extracts were dried over anhydrous $MgSO_4$. Filtration and concentration followed by short flash column chromatography (hexane/EtOAc 9:1) to remove the Dess-Martin residue provided the crude aldehyde as a colorless oil, which was used for the next reaction without further purification. To a stirred solution of *bis*(2,2,2-trifluoroethyl)-(methoxycarbonylmethyl) phosphate (0.080 mL, 0.37 mmol), 18-crown-6 (0.41 g, 1.55 mmol) in THF (6 mL) cooled to –78 ˚C was added dropwise potassium *bis*(trimethylsilyl)amide (0.75 mL, 0.37 mmol, 0.5M solution in toluene). Thereafter the above aldehyde in THF (1 mL) was added and the solution was stirred for 4 h at –78 ˚C. The reaction mixture was quenched by addition of a sat'd NH_4Cl solution (5 mL) and diluted with diethyl ether (20 mL). The layers were separated and organic phase was washed with brine (30 mL) and dried with $MgSO_4$, filtered, and concentrated. The residue was purified by flash chromatography (EtOAc/hexane 1:19) to obtain (*E,Z*)-doubly unsaturated ester **72β** (0.32 g, 90 % for 2 steps) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2885, 1722, 1641, 1514, 1471, 1250, 1174, 1075, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 15.5, 11.2 Hz, 1H), 7.29-7.26 (m, 2H), 6.87-6.84 (m, 2H), 6.56 (ddd, *J* = 17.0, 10.6, 10.5 Hz, 1H), 6.52 (t, *J* = 11.4 Hz, 1H), 6.19 (dd, *J* = 15.5, 6.4 Hz, 1H), 5.99 (t, *J* = 11.0 Hz, 1H), 5.57 (t, *J* = 10.5 Hz, 1H), 5.54 (d, *J* = 11.3 Hz, 1H), 5.42 (m, 1H), 5.30 (m, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.51 (m, 3H), 3.92 (m, 1H), 3.78 (s, 3H), 3.70 (s, 3H), 3.61 (m, 1H), 3.32 (dd, *J* = 7.9, 2.8 Hz, 1H), 3.20 (m, 1H), 2.97 (m, 2H), 2.57 (m, 2H), 1.65 (m, 1H), 1.56-1.39 (m, 3H), 1.29-1.16 (m, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.93-0.83 (m, 39H), 0.77 (m, 1H), 0.91 (s, 9H), 0.87 (s, 9H), 0.83 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.0 Hz, 3H), 0.13 (s, 3H), 0.76 (d, *J* = 6.6 Hz, 3H), 0.71 (d, *J* = 5.9 Hz, 3H), 0.10-0.02 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.0, 147.2, 145.6, 134.5, 133.1, 132.4, 131.5, 131.4, 129.0, 128.9, 126.4, 117.1, 115.1, 113.7, 84.4, 81.3, 75.0, 72.8, 72.7, 66.4, 55.2, 50.9, 42.9, 42.6, 40.5, 40.2, 35.3, 35.2, 33.8, 32.6, 30.5, 26.3, 26.0, 25.9, 19.6, 18.9, 18.8, 18.4, 18.2, 18.1, 16.7, 14.5, 9.2, –2.8, –3.4, –3.5, –3.6, –4.07, –4.14, –4.24, –4.49; LRMS (ESI) 1163.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{65}H_{120}O_8Si_4Na$ 1163.7958 $[M+Na]^+$, found 1163.8004; $[\alpha]^{20}_D$ –27.3 (*c* 5.0, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*R*,20*R*,21*S*,22*S*,23*Z*)-Methyl-7,9,13,19-*tetrakis*(*tert*-butyldimethylsilyloxy)-21-hydroxy-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoate (73β).

The ester **72β** (0.15 g, 0.14 mmol) was added to CH_2Cl_2 (5 mL) and H_2O (0.2 mL) and DDQ (34 mg, 0.15 mmol) was added at 0 ˚C. After 1 h of stirring at 0 ˚C, the reaction mixture was quenched by adding sat'd $NaHCO_3$ (5 mL). The organic phase was washed by sat'd $NaHCO_3$ solution (3 x 10 mL) and brine, dried over $MgSO_4$ and concentrated. Purification by flash column chromatography (EtOAc/hexane 1:9) furnished **73β** (0.12 g, 90 %) as a colorless oil (**Caution!** Do not use excess DDQ. It will react with the C2-C4 diene to form Diels-Alder adducts): IR ($CHCl_3$) 3540, 2956, 2929, 2856, 1641, 1601, 1471, 1462, 1407, 1379, 1361, 1255, 1174, 1089, 1004, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 15.5, 11.2 Hz, 1H), 6.61 (ddd, *J* = 16.9, 10.5, 10.4 Hz, 1H), 6.51 (t, *J* = 11.4 Hz, 1H), 6.17 (dd, *J* = 15.5, 5.9 Hz, 1H), 6.07 (t, *J* = 11.0 Hz, 1H), 5.54 (d, *J* = 11.3 Hz, 1H), 5.45-5.37 (m, 2H), 5.28 (m, 1H), 5.18 (d, *J* = 16.8 Hz, 1H), 5.09 (d, *J* = 10.1 Hz, 1H), 4.51 (m, 1H), 3.91 (m, 1H), 3.74 (m, 1H), 3.69 (s, 3H), 3.45 (m, 1H), 3.23 (m, 1H), 3.76 (m, 1H), 2.56 (m, 2H), 2.29 (br, 1H), 1.68 (m, 1H), 1.56-1.41 (m, 3H), 1.34-1.17 (m, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.90-0.84 (m, 40H), 0.81 (d, *J* = 5.8 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H), 0.76 (d, *J* = 6.2 Hz, 3H), 0.08-0.01 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 147.3, 145.5, 135.3, 133.0, 132.3, 131.5, 129.9, 126.4, 117.6, 115.2, 81.3, 77.5, 76.7, 72.7, 66.4, 50.9, 42.9, 42.6, 40.1, 37.9, 36.1, 35.4, 35.2, 33.8, 32.2, 30.6, 26.2, 26.0, 25.9, 19.6, 19.0, 18.4, 18.10, 18.05, 17.7, 16.6, 14.4, 6.9, –2.8, –3.5, –3.6, –3.7, –4.1, –4.15, –4.21, –4.4; LRMS (ESI) 1043.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{57}H_{112}O_7Si_4Na$ 1043.7383 $[M+Na]^+$, found 1043.7433; $[\alpha]^{20}_D$ –40.3 (*c* 2.1, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*R*,20*R*,21*S*,22*S*,23*Z*)-7,9,13,19-*tetrakis*(*tert*-Butyldimethylsilyloxy)-21-hydroxy-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoic acid (74β).

1N aqueous KOH solution (1.2 mL) was added to a stirred solution of the above **73β** (0.12 g, 0.12 mmol) in EtOH (12 mL), THF (1 mL) and the mixture was refluxed gently until the ester disappeared (about 5 h) as determined by TLC analysis. The ethanolic solution was concentrated and then diluted with ether (4 mL). After the solution was acidified to pH 3 with 1N HCl solution, organic phase was separated and aqueous phase was extracted with Et_2O (2 x 5 mL). The combined organic phases were dried with $MgSO_4$, concentrated and used without further purification: IR ($CHCl_3$) 2957, 2929, 2857, 1692, 1471, 1462, 1254, 1089, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 15.1, 11.4 Hz, 1H), 6.64 (ddd, *J* = 16.0, 10.8, 10.5 Hz, 1H), 6.61 (t, *J* = 11.2 Hz, 1H), 6.22 (dd, *J* = 15.4, 6.0 Hz, 1H), 6.09 (t, *J* = 11.0 Hz, 1H), 5.58 (d, *J* = 11.3 Hz, 1H), 5.49-5.39 (m, 2H), 5.34-5.28 (m, 1H), 5.20 (d, *J* = 16.7 Hz, 1H), 5.11 (d, *J* = 10.2 Hz, 1H), 4.55 (m, 1H), 3.95 (m, 1H), 3.76 (m, 1H), 3.50 (m, 1H), 3.27 (m, 1H), 2.81 (m, 1H), 2.58 (m, 2H), 1.71 (m, 1H), 1.57-1.50 (m, 3H), 1.44-1.31 (m, 3H), 1.25 (d, *J* = 7.3 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.96-0.89 (m, 40H), 0.81 (d, *J* = 6.2 Hz, 3H), 0.79 (d, *J* = 5.9 Hz, 3H), 0.11-0.05 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 148.1, 147.3, 135.2, 132.8, 132.3, 131.6, 129.9, 126.6, 117.6, 115.0, 81.3, 77.6, 72.7, 66.4, 58.3, 43.0, 42.6, 40.1, 37.9, 36.0, 35.4, 35.2, 33.8, 32.2, 30.6, 26.3, 26.0, 25.9, 25.2, 19.6, 19.0, 18.4, 18.09, 18.05, 17.7, 16.6, 14.5, 7.0, –2.8, –3.45, –3.54, –3.7, –4.1, –4.2, –4.4; LRMS (ESI) 1029.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{56}H_{110}O_7Si_4Na$ 1029.7226 $[M+Na]^+$, found 1029.7257; $[\alpha]^{20}_D$ –41.7 (*c* 1.4, $CHCl_3$).

8(*S*),10(*S*),14(*R*),20(*R*)-*tetrakis*(*tert*-Butyldimethylsilyloxy)-7(*S*),13(*S*),15(*R*),17(*S*),21(*S*)-pentamethyl-22(*S*)-(1(*S*)-methylpenta-2,4-dienyl)oxacyclodocosa-3,5,11-trien-2-one (75β).

A solution of above acid **74β** in THF (2 mL) was treated at 0 ˚C with Et_3N (0.10 mL, 0.72 mmol) and 2,4,6-trichlorobenzoyl chloride (0.095 mL, 0.60 mmol). The reaction mixture was stirred at 0 ˚C for 30 min and then added to 4-DMAP (60 mL, 0.02 M solution in toluene) at 25 ˚C and stirred overnight. The reaction mixture was concentrated, Et_2O (10 mL) was added and the crude was washed with 0.5 N HCl (2 x 10 mL), dried over $MgSO_4$. Purification by flash column chromatography (EtOAc/hexane 1:49) furnished macrolactone **75β** (81 mg, 68 % for 2 steps) as a colorless oil along with an impure fraction (31 mg, 21%) containing mostly the 2*Z* isomer of **75β**: **75β**, IR ($CHCl_3$) 2957, 2929, 2856, 1745, 1715, 1581, 1471, 1369, 1270, 1117, 1082, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 15.3, 10.5 Hz, 1H), 6.59 (ddd, *J* = 16.8, 10.7, 10.5 Hz, 1H), 6.22 (dd, *J* = 15.4, 6.0 Hz, 1H), 6.07 (dd, *J* = 15.4, 10.6 Hz, 1H), 5.92 (t, *J* = 10.9 Hz, 1H), 5.70 (d, *J* = 15.4 Hz, 1H), 5.46 (t, *J* = 10.5 Hz, 1H), 5.35-5.27 (m, 2H), 5.20 (d, *J* = 8.4 Hz, 1H), 5.12 (d, *J* = 16.8 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H), 4.53 (m, 1H), 3.91 (m, 1H), 3.41 (m, 1H), 3.19 (m, 1H), 2.94 (m, 1H), 2.55 (m, 2H), 1.94 (m, 1H), 1.40-1.29 (m, 3H), 1.26-1.15 (m, 3H), 1.00-0.85 (m, 52H), 0.74 (d, *J* = 6.7 Hz, 3H), 0.63 (d, *J* = 6.2 Hz, 3H), 0.08-0.00 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 144.93, 144.88, 136.0, 135.0, 133.5, 132.4, 130.7, 129.3, 120.2, 117.2, 80.3, 75.7, 73.9, 72.7, 66.3, 42.4, 41.0, 40.6, 39.3, 36.5, 35.8, 35.1, 34.5, 31.9, 29.7, 26.2, 26.0, 25.9, 21.6, 19.8, 19.7, 18.4, 18.11, 18.07, 17.9, 14.9, 11.3, –2.6, –3.6, –3.8, –4.2, –4.5, –4.6; LRMS (ESI) 1011.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{56}H_{108}O_6Si_4Na$ 1011.7121 $[M+Na]^+$, found 1011.7148; $[\alpha]^{20}_D$ –16.9 (*c* 1.24, $CHCl_3$). 2*Z* isomer of **75β**, ^1H NMR (300 MHz, $CDCl_3$) *δ* 7.35 (dd, *J* = 11.2, 15.5 Hz, 1H), 6.63 (dt, *J* = 10.5, 16.8 Hz, 1H), 6.44 (t, *J* = 11.3 Hz, 1H), 6.01–5.80 (m, 2H), 5.57 (t, *J* = 10.6 Hz, 1H), 5.50 (d, *J* = 11.4 Hz, 1H), 5.38 (t, *J* = 10.3 Hz, 1H), 5.30 (dd, *J* = 8.5, 11.0 Hz, 1H), 5.22–5.01 (m, 3H), 4.47 (m, 1H), 3.77 (m, 1H), 3.48 (m, 1H), 3.30 (m, 1H), 2.97 (m, 1H), 2.56 (m, 1H), 2.44 (m, 1H), 1.91 (m, 1H), 1.65 (m, 1H), 1.52–0.71 (m, 63H), 0.12–0.04 (m, 24H).

8(*S*),10(*S*),14(*R*),20(*R*)-Tetrahydroxy-7(*S*),13(*S*),15(*R*),17(*S*),21(*S*)-pentamethyl-22(*S*)-(1(*S*)-methyl-penta-2,4-dienyl)-oxa-cyclodocosa-3(*E*),5(*E*),11(*Z*)-trien-2-one (76).

3 N HCl (3 mL from a solution prepared by adding 2.5 mL of conc. HCl to 7.5 mL MeOH) was added to a stirred solution of the above macrolactone **75β** (81 mg, 0.082 mmol) in THF (1 mL) at 0 ˚C. After 24 h at room temperature, the reaction mixture was diluted with EtOAc (4 mL) and H_2O (4 mL) and the organic phase was separated and aqueous phase was extracted with EtOAc (2 x 4 mL). The combined organic phases were washed with sat'd $NaHCO_3$ (10 mL), dried with $MgSO_4$, concentrated and the residue was purified by flash chromatography (EtOAc/hexane 3:2) to yield the product **76** (6.6 mg, 15%) as a colorless oil: IR ($CHCl_3$) 3404, 2962, 2916, 1692, 1639, 1455, 1244, 1061, 1001 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.15 (dd, *J* = 15.3, 10.5 Hz, 1H), 6.64 (ddd, *J* = 16.8, 10.6, 10.3 Hz, 1H), 6.29 (dd, *J* = 15.4, 6.3 Hz, 1H), 6.22 (dd, *J* = 15.5, 10.5 Hz, 1H), 5.92 (t, *J* = 10.9 Hz, 1H), 5.72 (d, *J* = 15.3 Hz, 1H), 5.44-5.37 (m, 2H), 5.25 (t, *J* = 10.3 Hz, 1H), 5.13 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 5.04 (dd, *J* = 9.1, 1.8 Hz, 1H), 4.68 (ddd, *J* = 9.9, 7.2, 2.4 Hz, 1H), 3.82 (ddd, *J* = 9.2, 6.2, 2.7 Hz, 1H), 3.40 (ddd, *J* = 10.2, 6.2, 2.3 Hz, 1H), 3.06 (m, 1H), 2.99 (dd, *J* = 8.0, 3.3 Hz, 1H), 2.62 (m, 1H), 2.58 (m, 1H), 1.88 (m, 1H), 1.62 (m, 1H), 1.55 (ddd, *J* = 14.0, 10.5, 2.7 Hz, 1H), 1.38 (ddd, *J* = 12.3, 9.6, 2.7 Hz, 1H), 1.34-1.23 (m, 4H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.95-0.88 (m, 2H), 0.87-0.82 (m, 1H), 0.79 (d, *J* = 5.3 Hz, 3H), 0.68 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.5, 147.7, 147.4, 135.7, 134.4, 133.6, 131.7, 130.8, 129.1, 120.7, 118.0, 80.7, 76.9, 74.2, 72.8, 65.9, 44.0, 42.5, 40.9, 39.5, 36.5, 36.3, 36.1, 35.5, 31.7, 31.2, 21.1, 19.0, 17.9, 17.7, 15.7, 11.3; LRMS (ESI) 555.6 $[M+Na]^+$; HRMS (ESI) calcd for $C_{32}H_{52}O_6$ 555.3662 $[M+Na]^+$, found 555.3684; $[\alpha]^{20}_D$ – 6.5 (*c* 0.17, MeOH).

(4*S*,5*S*)-4-((2*R*,3*S*,6*S*,8*R*,9*R*,10*S*,11*Z*,13*S*,15*S*,16*S*,17*E*)-3,9,13,15-*tetrakis*(*tert*-Butyldimethylsilyloxy)-6,8,10,16-tetramethyl-19-(trityloxy)nonadeca-11,17-dien-2-yl)-2-(4-methoxyphenyl)-5-methyl-1,3-dioxane (68α).
The same procedure for **68β** was used with above **67α** (0.60 g, 0.50 mmol), TBSOTf (0.17 mL, 0.75 mmol) and 2,6-lutidine (0.12 mL, 1.0 mmol) to yield 0.61 g (93 %) of the product by flash column chromatography (EtOAc/hexane 1:9) as a colorless oil: IR ($CHCl_3$) 2956, 2928, 2856, 1518, 1471, 1462, 1251, 1075, 835, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56-7.48 (m, 8H), 7.38-7.26 (m, 9H), 6.97-6.94 (m, 1H), 5.91 (dd, *J* = 15.6, 5.9 Hz, 1H), 5.63 (dt, *J* = 15.7, 5.3 Hz, 1H), 5.58-5.50 (m, 1H), 5.52 (s, 1H), 5.41 (dd, *J* = 10.8, 8.6 Hz, 1H), 4.65 (m, 1H), 4.19 (dd, *J* = 11.1, 4.5 Hz, 1H), 4.01 (m, 1H), 3.90 (m, 1H), 3.84 (s, 3H), 3.66 (d, *J* = 5.0 Hz, 2H), 3.56 (t, *J* = 11.1 Hz, 1H), 3.36 (m, 1H), 2.71 (m 1H), 2.48 (m, 1H), 2.12 (m, 1H), 1.88 (m, 1H), 1.76-1.56 (m, 3H), 1.52-1.42 (m, 2H), 1.40-1.31 (m, 2H), 1.09 (d, *J* = 7.7 Hz, 3H), 1.07 (d, *J* = 7.5 Hz, 3H), 1.05-0.94 (m, 42H), 0.93-0.90 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.3 Hz, 3H), 0.21-0.13 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7, 144.6, 144.4, 134.4, 133.0, 131.9, 131.8, 128.7, 127.7, 127.3, 126.8, 126.4, 113.4, 100.8, 86.7, 81.6, 81.3, 73.4, 72.8, 72.0, 66.6, 65.2, 55.1, 43.1, 42.3, 39.7, 38.2, 35.4, 35.3, 31.3, 30.8, 30.7, 30.3, 26.2, 26.1, 26.04, 25.97, 19.5, 18.8, 18.4, 18.1, 16.6, 14.6, 12.2, 9.1, –2.8, –3.4, –3.6, –3.9, –4.0, –4.1, –4.3; LRMS (ESI) 1327.9 $[M+Na]^+$; HRMS (ESI) calcd for $C_{78}H_{128}O_8Si_4Na$ 1327.8584 $[M+Na]^+$, found 1327.8622; $[\alpha]^{20}_D$ +5.9 (*c* 0.3, $CHCl_3$).

(2*S*,3*S*,4*R*,5*S*,8*S*,10*R*,11*R*,12*S*,13*Z*,15*S*,17*S*,18*S*,19*E*)-3-(4-Methoxybenzyloxy)-5,11,15,17-*tetrakis*(*tert*-butyldimethylsilyloxy)-2,4,8,10,12,18-hexamethyl-21-(trityloxy)henicosa-13,19-dien-1-ol (69α).
The procedure for **69β** was used with **68α** (0.61 g, 0.47 mmol), DIBALH (4.6 mL, 4.6 mmol) to yield 0.53 g (87 %) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: IR ($CHCl_3$) 3453, 2956, 2929, 1514, 1471, 1251, 1075, 835, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 6H), 7.38-7.26 (m, 11H), 6.96-6.93 (m, 2H), 5.91 (dd, *J* = 15.7, 6.0 Hz, 1H), 5.64 (dt, *J* = 15.4, 5.5 Hz, 1H), 5.55-5.50 (m, 1H), 5.42 (dd, *J* = 11.1, 8.4 Hz, 1H), 4.70-4.58 (m, 3H), 4.01 (m, 1H), 3.83 (s, 3H), 3.79 (m, 2H), 3.67-3.61 (m, 3H), 3.35 (m, 1H), 3.30 (m 1H), 2.72 (m, 1H), 2.48 (m, 1H), 1.93 (m, 2H), 1.76-1.55 (m, 3H), 1.51-1.26 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.07 (d, *J* = 6.7 Hz, 3H), 1.01-0.98 (m, 39H), 0.93-0.89 (m, 2H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 4.6 Hz, 3H), 0.21-0.13 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 144.5, 144.4, 134.3, 133.1, 131.7, 130.6, 129.1, 128.6, 127.6, 126.8, 126.7, 126.4, 113.8, 86.7, 85.1, 81.3, 74.9, 74.4, 72.8, 66.5, 65.9, 65.1, 55.1, 43.0, 42.3, 41.8, 40.1, 38.4, 35.3, 35.1, 32.8, 30.7, 30.5, 26.2, 26.1, 26.0, 25.9, 19.5, 18.6, 18.4, 18.13, 18.10, 16.5, 15.4, 14.6, 10.5, –2.8, –3.4, –3.6, –3.9, –4.0, –4.2, –4.4; LRMS (ESI) 1329.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{78}H_{130}O_8Si_4Na$ 1329.8741 $[M+Na]^+$, found 1329.8788; $[\alpha]^{20}_D$ –9.8 (*c* 2.6, $CHCl_3$).

[(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*S*,17*S*,18*R*,19*S*,20*S*,21*Z*)-19-(4-Methoxybenzyloxy)-5,7,11,17-*tetrakis*(*tert*-butyldimethylsilyloxy)-4,10,12,14,18,20-hexamethyltetracosa-2,8,21,23-tetraenyloxy]triphenylmethane (70α).
The procedure for **70β** was used with **69α** (0.52 g, 0.40 mmol), Dess-Martin reagent (0.25 g, 0.59 mmol) and 1-bromoallyl trimethylsilane (0.49 g, 2.0 mmol), $CrCl_2$ (0.41 g, 3.32 mmol) and NaH (0.20 g, 8.0 mmol) to yield 0.46 g (88 %) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: IR ($CHCl_3$) 2956, 2856, 1614, 1514, 1471, 1249, 1074, 835, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.59-7.56 (m, 6H), 7.41-7.27 (m, 11H), 6.98-6.95 (m, 2H), 6.71 (ddd, *J* = 16.7, 10.6, 10.5 Hz, 1H), 6.14 (t, *J* = 11.0 Hz, 1H), 5.94 (dd, *J* = 15.6, 5.6 Hz, 1H), 5.80-5.67 (m, 2H), 5.64-5.55 (m, 1H), 5.46 (dd, *J* = 11.0, 8.5 Hz, 1H), 5.31 (d, *J* = 16.8

Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 4.70-4.62 (m, 3H), 4.04 (m, 1H), 3.86 (s, 3H), 3.69 (d, *J* = 4.7 Hz, 1H), 3.34 (m, 2H), 2.96 (m, 1H), 2.77 (m, 1H), 2.51 (m, 1H), 1.93 (m, 1H), 1.78 (m, 1H), 1.75-1.63 (m, 3H), 1.57-1.31 (m, 5H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 6.1 Hz, 3H), 1.12 (d, *J* = 6.7 Hz, 3H), 1.00 (d, J = 7.3 Hz, 3H), 1.05-1.01 (m, 36H), 0.96-0.93 (m, 2H), 0.89 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 5.3 Hz, 3H), 0.25-0.11 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 146.2, 144.6, 144.4, 134.4, 134.3, 132.2, 131.3, 130.2, 129.0, 128.7, 127.7, 126.8, 126.5, 117.5, 113.7, 86.7, 84.9, 81.4, 74.9, 73.1, 72.9, 66.6, 65.2, 55.1, 43.1, 42.9, 42.3, 40.4, 35.9, 35.6, 35.3, 35.1, 34.5, 30.2, 29.4, 26.3, 26.1, 26.0, 19.6, 18.8, 18.6, 18.5, 18.2, 18.14, 18.11, 16.5, 14.7, 10.5, –1.1, –2.8, –3.0, –3.3, –3.5, –3.9, –4.2, –4.3; LRMS (ESI) 1351.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{81}H_{132}O_7Si_4Na$ 1351.8948 $[M+Na]^+$, found 1351.8998; $[\alpha]^{20}_D$ –9.3 (*c* 1.5, $CHCl_3$).

(2*E*,4*S*,5*S*,7*S*,8*Z*,10*S*,11*R*,12*R*,14*S*,17*S*,18*R*,19*S*,20*S*,21*Z*)-19-(4-Methoxybenzyloxy)-5,7,11,17-*tetrakis*(*tert*-butyldimethylsilyloxy)-4,10,12,14,18,20-hexamethyltetracosa-2,8,21,23-tetraen-1-ol (71α).

The procedure for **71β** was used with **70α** (0.33 g, 0.25 mmol) and ZnBr (0.28 g, 1.25 mmol) to yield 0.18 g (65 %) of the product by flash column chromatography (EtOAc/hexane 1:9) as a colorless oil: IR ($CHCl_3$) 3417, 2956, 2856, 1613, 1514, 1471, 1250, 1074, 836, 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 6.90-6.87 (m, 2H), 6.60 (ddd, *J* = 16.9, 10.6, 10.5 Hz, 1H), 6.04 (t, *J* = 11.0 Hz, 1H), 5.81 (dd, *J* = 15.7, 5.9 Hz, 1H), 5.67-5.60 (m, 2H), 5.51-5.44 (m, 1H), 5.34 (dd, *J* = 11.2, 8.7 Hz, 1H), 5.21 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.60-4.52 (m, 3H), 4.10 (d, *J* = 5.7 Hz, 1H), 3.91 (m, 1H), 3.81 (s, 3H), 3.59 (m, 1H), 3.31-3.23 (m, 2H), 2.86 (m, 1H), 2.65 (m, 1H), 2.40 (m, 1H), 1.82 (m, 1H), 1.66-1.42 (m, 5H), 1.36-1.20 (m, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 7.3 Hz, 3H), 1.01 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 5.8 Hz, 3H), 0.94-0.89 (m, 38H), 0.84 (d, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H), 0.13-0.00 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.0, 135.0, 134.5, 133.2, 132.2, 131.5, 131.4, 129.1, 129.0, 128.7, 117.4, 113.7, 84.8, 81.4, 74.8, 73.1, 72.7, 66.5, 64.1, 55.2, 42.8, 42.7, 42.0, 40.4, 35.9, 35.4, 35.2, 34.4, 30.3, 29.4, 26.3, 26.03, 26.97, 25.95, 19.6, 18.7, 18.6, 18.5, 18.1, 16.6, 14.7, 10.5, –2.8, –3.4, –3.5, –4.0, –4.1, –4.2, –4.3, –4.4; LRMS (ESI) 1109.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{62}H_{118}O_7Si_4Na$ 1109.7852 $[M+Na]^+$, found 1109.7874; $[\alpha]^{20}_D$ –15.0 (*c* 0.94, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*S*,20*R*,21*S*,22*S*,23*Z*)-Methyl-21-(4-methoxybenzyloxy)-7,9,13,19-*tetrakis*(*tert*-butyldimethylsilyloxy)-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoate (72α).

The procedure for **72β** was used with **71α** (0.18 g, 0.16 mmol), Dess-Martin reagent (0.10 g, 0.24 mmol) and *bis*(2,2,2-trifluoroethyl)-(methoxycarbonylmethyl) phosphate (0.041 mL, 0.19 mmol), 18-crown-6 (0.21 g, 0.19 mmol) and KHMDS (0.39 mL, 0.19 mmol) to yield 0.16 g (84 %) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: IR ($CHCl_3$) 2956, 2929, 2856, 1721, 1514, 1462, 1250, 1174, 1074, 836, 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 15.4, 11.2 Hz, 1H), 7.32-7.29 (m, 2H), 6.91-6.86 (m, 2H), 6.60 (ddd, *J* = 17.0, 10.6, 10.5 Hz, 1H), 6.56 (t, *J* = 11.3 Hz, 1H), 6.23 (dd, *J* = 15.5, 5.9 Hz, 1H), 6.05 (t, *J* = 11.0 Hz, 1H), 5.68-5.56 (m, 2H), 5.50-5.43 (m, 1H), 5.38-5.31 (m, 1H), 5.23 (d, *J* = 16.8 Hz, 1H), 5.12 (d, *J* = 10.2 Hz, 1H), 4.61-4.52 (m, 3H), 3.98 (m, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 3.59 (m, 1H), 3.29-3.23 (m, 2H), 2.86 (m, 1H), 2.68-2.59 (m, 2H), 1.83 (m, 1H), 1.63-1.51 (m, 2H), 1.49-1.35 (m, 3H), 1.34-1.22 (m, 2H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H), 1.03 (d, *J* = 5.0 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.94-0.89 (m, 38H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.1 Hz, 3H), 0.14-0.00 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.1, 147.2, 145.7, 134.4, 133.2, 132.2, 131.6, 131.4, 129.2, 129.0, 126.4, 117.5, 115.2, 113.7, 84.7, 81.5, 74.9, 73.0, 72.7, 66.4, 55.2, 50.9, 42.9, 42.8, 42.6, 40.3, 35.9, 35.4, 35.2, 34.4, 30.4, 29.5, 26.3,

26.03, 25.98, 19.6, 18.8, 18.7, 18.5, 18.1, 16.7, 14.5, 10.5, –2.8, –3.3, –3.5, –4.0, –4.1, –4.17, –4.22, –4.4; LRMS (ESI) 1163.8 $[M+Na]^+$; HRMS (ESI) calcd for $C_{65}H_{120}O_8Si_4Na$ 1163.7958 $[M+Na]^+$, found 1163.7981; $[\alpha]^{20}_D$ –45.3 (*c* 0.36, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*S*,20*R*,21*S*,22*S*,23*Z*)-Methyl-7,9,13,19-*tetrakis*(*tert*-butyldimethylsilyloxy)-21-hydroxy-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoate (73α).

The procedure for **73β** was used with **72α** (0.16 g, 0.14 mmol) and DDQ (0.034 g, 0.15 mmol) to yield 0.13 g (90 %) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: IR ($CHCl_3$) 3512, 2956, 2929, 2857, 1772, 1639, 1471, 1462, 1255, 1193, 1076, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 15.4, 11.2 Hz, 1H), 6.61 (ddd, *J* = 16.9, 10.6, 10.5 Hz, 1H), 6.53 (t, *J* = 11.3 Hz, 1H), 6.19 (dd, *J* = 15.6, 6.0 Hz, 1H), 6.09 (t, *J* = 11.0 Hz, 1H), 5.56 (d, *J* = 11.3 Hz, 1H), 5.44 (t, *J* = 11.0 Hz, 1H), 5.31 (dd, *J* = 11.0, 8.4 Hz, 1H), 5.19 (d, *J* = 16.8 Hz, 1H), 5.10 (d, *J* = 10.1 Hz, 1H), 4.55 (m, 1H), 3.94 (m, 1H), 3.71 (s, 3H), 3.25 (m, 2H), 2.75 (m, 1H), 2.58 (m, 2H), 1.72 (m, 1H), 1.67-1.60 (m, 1H), 1.59-1.49 (m, 2H), 1.40 (m, 1H), 1.32-1.25 (m, 2H), 1.22-1.13 (m, 2H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.91-0.86 (m, 41H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.0 Hz, 3H), 0.11-0.05 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 147.2, 145.6, 136.4, 133.2, 132.6, 131.5, 129.5, 126.4, 117.3, 115.2, 81.3, 78.6, 74.3, 72.7, 66.4, 50.9, 42.9, 42.6, 39.7, 36.2, 35.8, 35.4, 35.3, 34.1, 32.4, 30.6, 26.3, 26.0, 25.9, 19.6, 19.2, 18.5, 18.1, 18.0, 17.4, 16.7, 14.5, 10.9, –2.8, –3.4, –3.5, –4.06, –4.11, –4.2, –4.3, –4.4; LRMS (ESI) 1043.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{57}H_{112}O_7Si_4Na$ 1043.7383 $[M+Na]^+$, found 1043.7424; $[\alpha]^{20}_D$ –37.8 (*c* 1.4, $CHCl_3$).

(2*Z*,4*E*,6*S*,7*S*,9*S*,10*Z*,12*S*,13*R*,14*R*,16*S*,19*S*,20*R*,21*S*,22*S*,23*Z*)-7,9,13,19-*tetrakis*(*tert*-Butyldimethylsilyloxy)-21-hydroxy-6,12,14,16,20,22-hexamethylhexacosa-2,4,10,23,25-pentaenoic acid (75α).

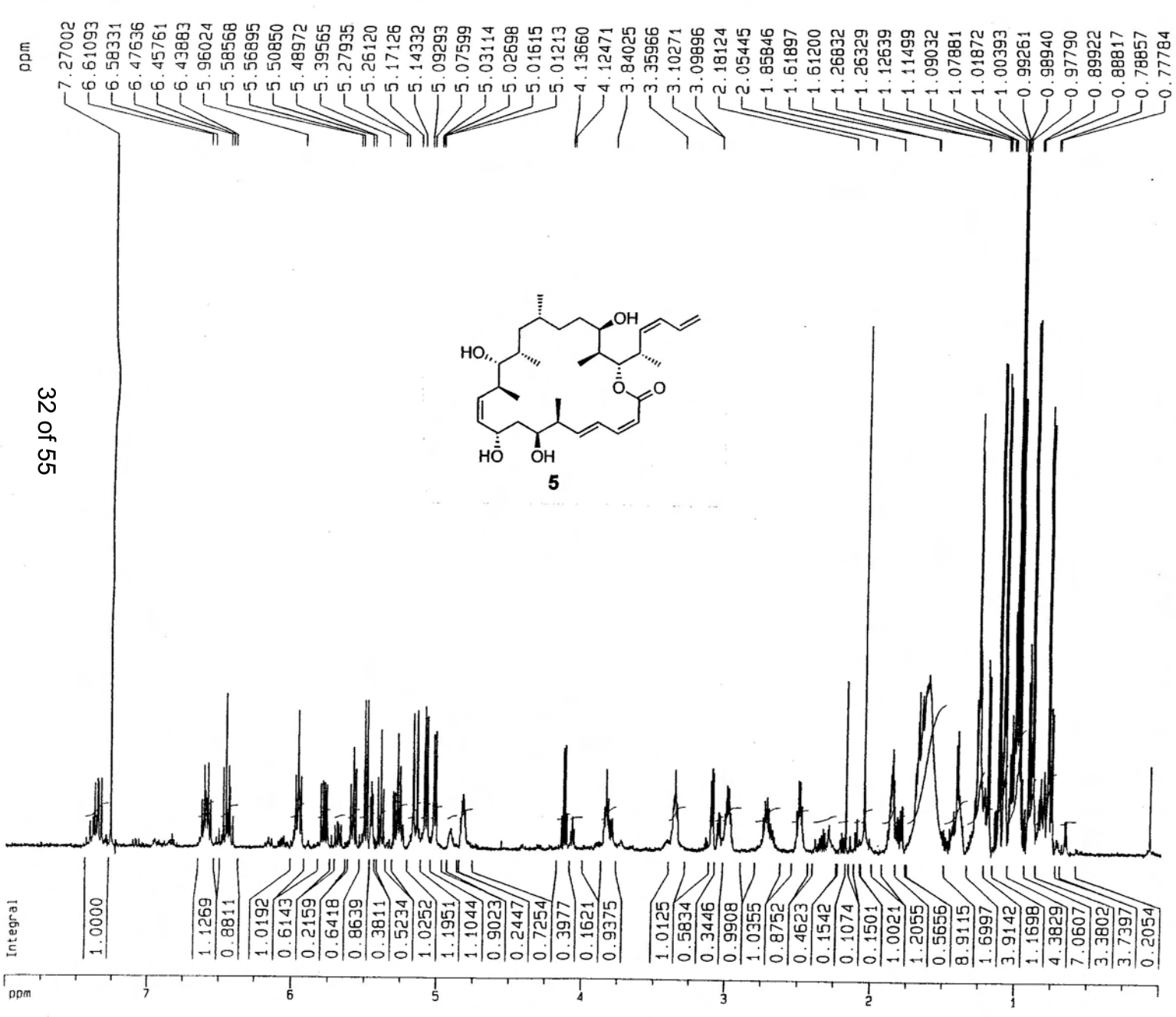
The procedure for **75β** was used with **73α** (0.13 g, 0.13 mmol) and 1N KOH (1.2 mL, 1.3 mmol), 2,4,6-trichlorobenzoyl chloride (0.094 mL, 0.60 mmol) and Et_3N (0.10 mL, 0.78 mmol), 4-DMAP (60 mL, 1.3 mmol) to yield 0.054 g (45 % for 2 steps) of the product by flash column chromatography (EtOAc/hexane 1:19) as a colorless oil: (seco acid) IR ($CHCl_3$) 2956, 2857, 1692, 1634, 1471, 1462, 1254, 1076, 836, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 15.2, 11.3 Hz, 1H), 6.66 (ddd, *J* = 16.8, 10.8, 10.6 Hz, 1H), 6.62 (t, *J* = 11.3 Hz, 1H), 6.23 (dd, *J* = 15.3, 6.0 Hz, 1H), 6.09 (t, *J* = 11.0 Hz, 1H), 5.57 (d, *J* = 11.2 Hz, 1H), 5.48-5.42 (m, 1H), 5.35-5.28 (m, 1H), 5.20 (d, *J* = 16.8 Hz, 1H), 5.10 (d, *J* = 10.2 Hz, 1H), 4.55 (m, 1H), 3.95 (m, 1H), 3.74 (m, 1H), 3.26 (m, 1H), 2.78 (m, 1H), 2.58 (m, 2H), 1.75-1.64 (m, 2H), 1.62-1.49 (m, 3H), 1.44-1.37 (m, 1H), 1.32-1.19 (m, 3H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.01 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.95-0.86 (m, 41H), 0.82 (d, *J* = 7.1 Hz, 3H), 0.81 (d, *J* = 6.4 Hz, 3H), 0.12-0.05 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 148.3, 147.4, 136.4, 133.1, 132.6, 131.5, 129.5, 126.6, 117.3, 115.0, 81.3, 78.6, 74.3, 72.7, 66.4, 43.0, 42.7, 39.7, 36.2, 35.8, 35.5, 35.3, 34.1, 32.4, 30.6, 26.3, 26.0, 25.94, 25.92, 19.6, 19.2, 18.5, 18.1, 18.0, 17.4, 16.7, 14.5, 11.0, –2.8, –3.4, –3.5, –4.1, –4.25, –4.32, –4.7; LRMS (ESI) 1029.7 $[M+Na]^+$; HRMS (ESI) calcd for $C_{56}H_{110}O_7Si_4Na$ 1029.7226 $[M+Na]^+$, found 1029.7252; $[\alpha]^{20}_D$ –32.7 (*c* 0.51, $CHCl_3$).

8(*S*),10(*S*),14(*R*),20(*S*)-Tetrahydroxy-7(*S*),13(*S*),15(*R*),17(*S*),21(*S*)-pentamethyl-22(*S*)-(1(*S*)-methyl-penta-2,4-dienyl)oxacyclodocosa-3(*Z*),5(*E*),11(*Z*)-trien-2-one (37) and 8(*S*),10(*S*),14(*R*),20(*S*)-Tetrahydroxy-7(*S*),13(*S*),15(*R*),17(*S*),21(*S*)-pentamethyl-22(*S*)-(1(*S*)-methyl-penta-2,4-dienyl)oxacyclodocosa-3(*E*),5(*E*),11(*Z*)-trien-2-one (77).

The procedure for **76β** was used with **75α** (0.054 g, 0.054 mmol) in 3N HCl (5 mL) and THF (2 mL) to yield 13 mg (45 %) of **37** and 4.5 mg (15 %) of **77** by flash column chromatography (EtOAc/hexane 7:3) as a colorless oil: (**37**) IR ($CHCl_3$) 3416, 2961, 2927, 2873, 1692, 1635, 1455, 1421, 1379, 1190, 1086, 998 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.26 (dd, *J* = 15.2, 11.3 Hz, 1H), 6.65 (ddd, *J* = 16.8, 10.6, 10.3 Hz, 1H), 6.56 (t, *J* = 11.3 Hz, 1H), 5.97 (t, *J* = 10.9 Hz, 1H), 5.91 (dd, *J* = 15.2, 9.3 Hz, 1H), 5.49 (d, *J* = 10.7 Hz, 1H), 5.42 (t, *J* = 8.6 Hz, 1H), 5.20 (t, *J* = 10.4 Hz, 1H), 5.15 (dd, *J* = 16.9, 1.3 Hz, 1H), 5.08 (d, *J* = 10.1 Hz, 1H), 5.05 (dd, *J* = 9.6, 1.3 Hz, 1H), 4.62 (ddd, *J* = 11.5, 7.7, 4.3 Hz, 1H), 3.65 (ddd, *J* = 10.0, 7.3, 3.1 Hz, 1H), 3.07 (dd, *J* = 6.7, 4.0 Hz, 1H), 3.01 (m, 1H), 2.66 (m, 1H), 2.26 (m, 1H), 1.90 (m, 1H), 1.66 (ddd, *J* = 11.5, 8.4, 3.4 Hz, 1H), 1.49 (ddd, *J* = 14.1, 10.0, 4.0 Hz, 1H), 1.45 (m, 1H), 1.38 (m, 1H), 1.32 (m, 1H), 1.27 (m, 1H), 1.11 (d, *J* = 6.7 Hz, 3H), 1.06 (m, 1H), 1.03 (ddd, *J* = 11.3, 7.2, 4.4 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.93 (m, 1H), 0.89 (m, 1H), 0.85 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 5.9 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 168.1, 148.7, 146.6, 135.7, 134.0, 133.7, 132.9, 131.1, 128.2, 118.0, 117.0, 80.9, 78.4, 74.4, 72.4, 66.3, 46.4, 43.4, 42.5, 40.9, 36.3, 35.90, 35.88, 35.7, 31.8, 31.5, 19.9, 19.3, 18.3, 17.5, 8.5; LRMS (ESI) 555.3 $[M+Na]^+$; HRMS (ESI) calcd for $C_{32}H_{52}O_6$ 555.3662 $[M+Na]^+$, found 555.3680; $[\alpha]^{20}_D$ +76.5 (*c* 0.52, MeOH): (**77**) IR ($CHCl_3$) 3428, 2962, 2928, 1690, 1635, 1380, 1243, 1145, 1064, 1000 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.20 (dd, *J* = 15.2, 10.8 Hz, 1H), 6.65 (ddd, *J* = 17.0, 10.6, 10.5 Hz, 1H), 6.38 (dd, *J* = 15.5, 5.4 Hz, 1H), 6.23 (dd, *J* = 14.4, 10.9 Hz, 1H), 5.95 (t, *J* = 11.0 Hz, 1H), 5.77 (d, *J* = 15.3 Hz, 1H), 5.40-5.39 (m, 2H), 5.23 (t, *J* = 10.5 Hz, 1H), 5.13 (d, *J* = 18.1 Hz, 1H), 5.12 (dd, *J* = 8.2, 1.5 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.66 (m, 1H), 3.90 (ddd, *J* = 7.6, 5.1, 2.5 Hz, 1H), 3.22 (dd, *J* = 9.8, 7.9 Hz, 1H), 3.04 (m, 1H), 2.95 (dd, *J* = 9.7, 2.1 Hz, 1H), 2.72 (m, 1H), 2.65 (m, 1H), 1.83 (m, 1H), 1.58 (m, 1H), 1.46 (m, 1H), 1.35-1.23 (m, 4H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.94 (m, 2H), 0.78 (m, 1H), 0.71 (d, *J* = 6.4 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 169.4, 147.5, 147.4, 135.9, 134.3, 133.7, 131.0, 128.9, 120.0, 118.0, 80.5, 78.5, 72.6, 72.0, 65.2, 43.6, 42.6, 42.1, 39.3, 36.3, 35.8, 35.6, 35.3, 31.4, 29.7, 19.3, 18.5, 17.4, 17.1, 14.8, 9.0; LRMS (ESI) 555.5 $[M+Na]^+$; HRMS (ESI) calcd for $C_{32}H_{52}O_6$ 555.3662 $[M+Na]^+$, found 555.3687; $[\alpha]^{20}_D$ –17.3 (*c* 0.15, MeOH).

[i] Phukan, P.; Sasmal, S.; Maier, M. E. *Eur. J. Org. Chem*. **2003**, 1733.

600.83 MHz 1H NMR spectrum of YSS479 in CDCl3 at 297K,
d1=12 sec.,



Current Data Parameters

NAME	yss479
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	
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PULPROG	zg
TD	65536
SOLVENT	CD2Cl2
NS	32
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	10
DW	55.600 use
DE	6.00 use
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ===

NUC1	1H
P1	9.60 use
PL1	0.00 dB
SFO1	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	600.8300272 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	8.000 ppm
F1	4806.64 Hz
F2P	0.000 ppm
F2	0.00 Hz
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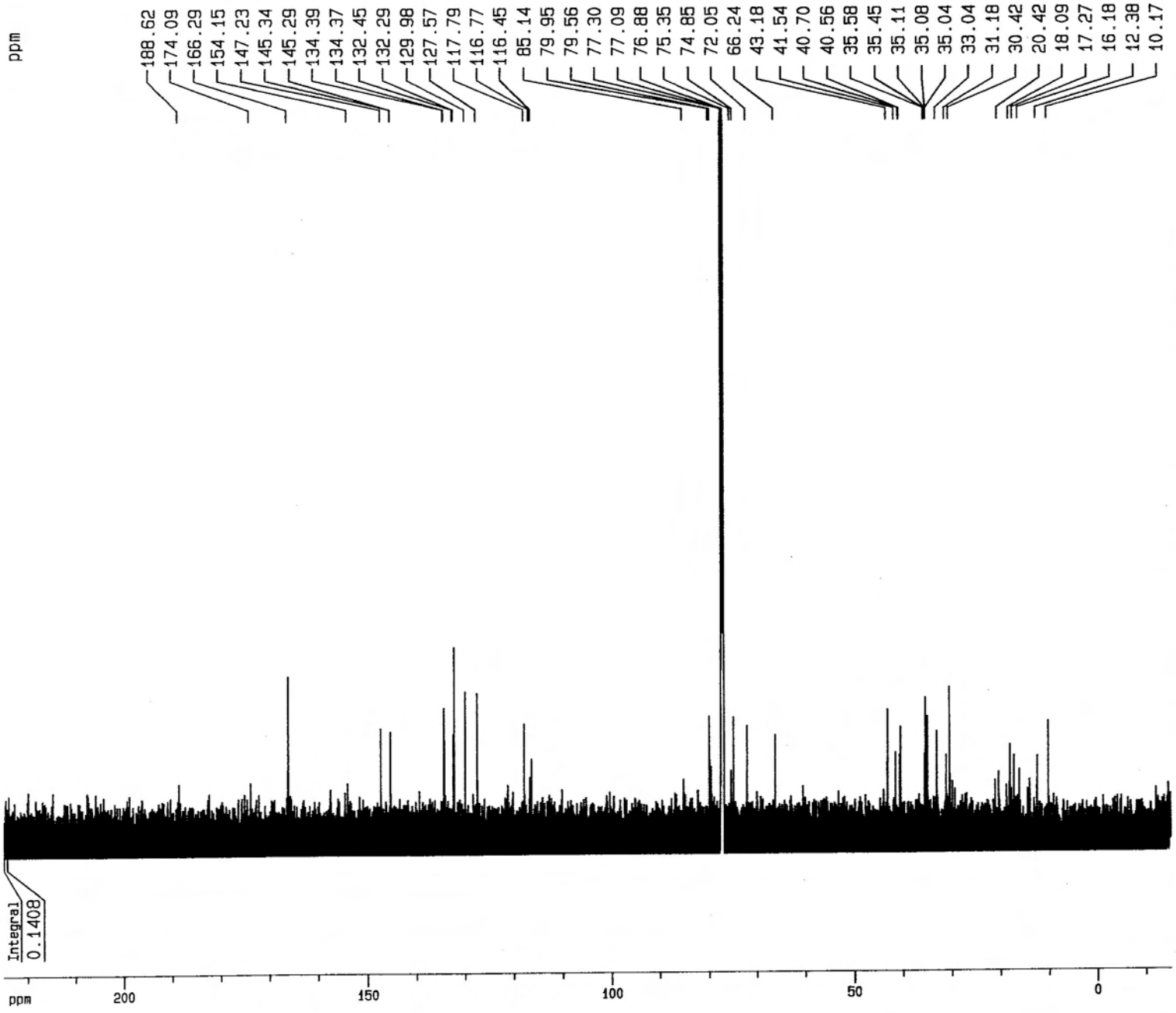
HZCM	240.33200 Hz/

151.1 MHz 1H-decoupled 13C NR spectrum of YSS479
in CDCl3 at 297K, d1=8 sec.



Current Data Parameters

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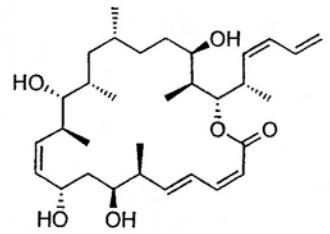
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters



5

RG	32768
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DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	151.0788173 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	225.000 ppm
F1	33992.73 Hz
F2P	-15.000 ppm
F2	-2266.18 Hz
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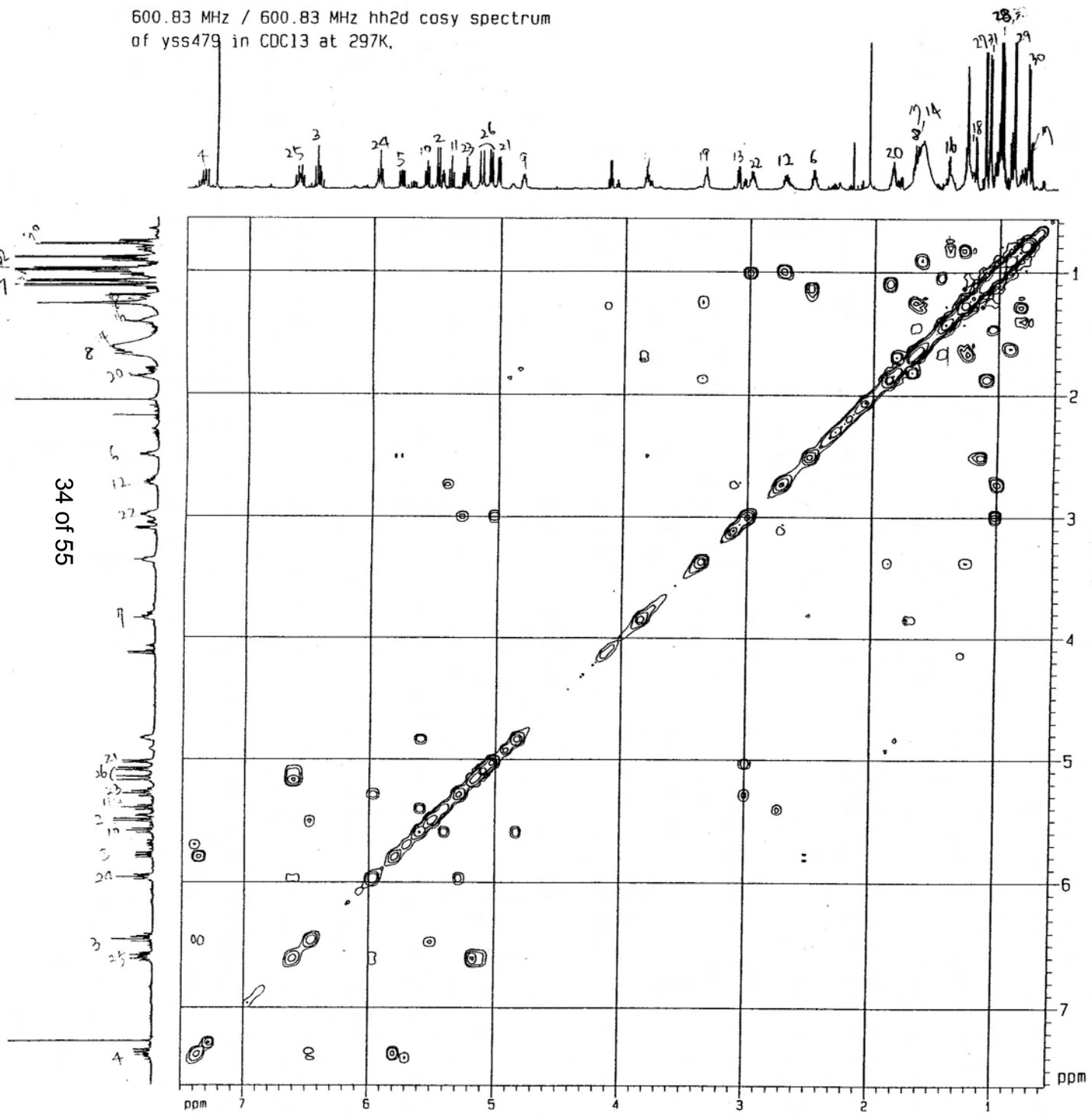
yss

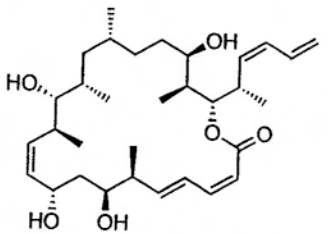
600.83 MHz / 600.83 MHz hh2d cosy spectrum
of yss479 in CDCl3 at 297K.



Current Data Parameters

NAME	yss479
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters



5

D1	1.00000000 sec
IN0	0.00013320 sec

CHANNEL f1

NUC1	1H
P0	8.20 usec
P1	8.20 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.8336 MHz
FIDRES	29.326200 Hz
SW	12.495 ppm

F2 - Processing parameters

SI	512
SF	600.8300210 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

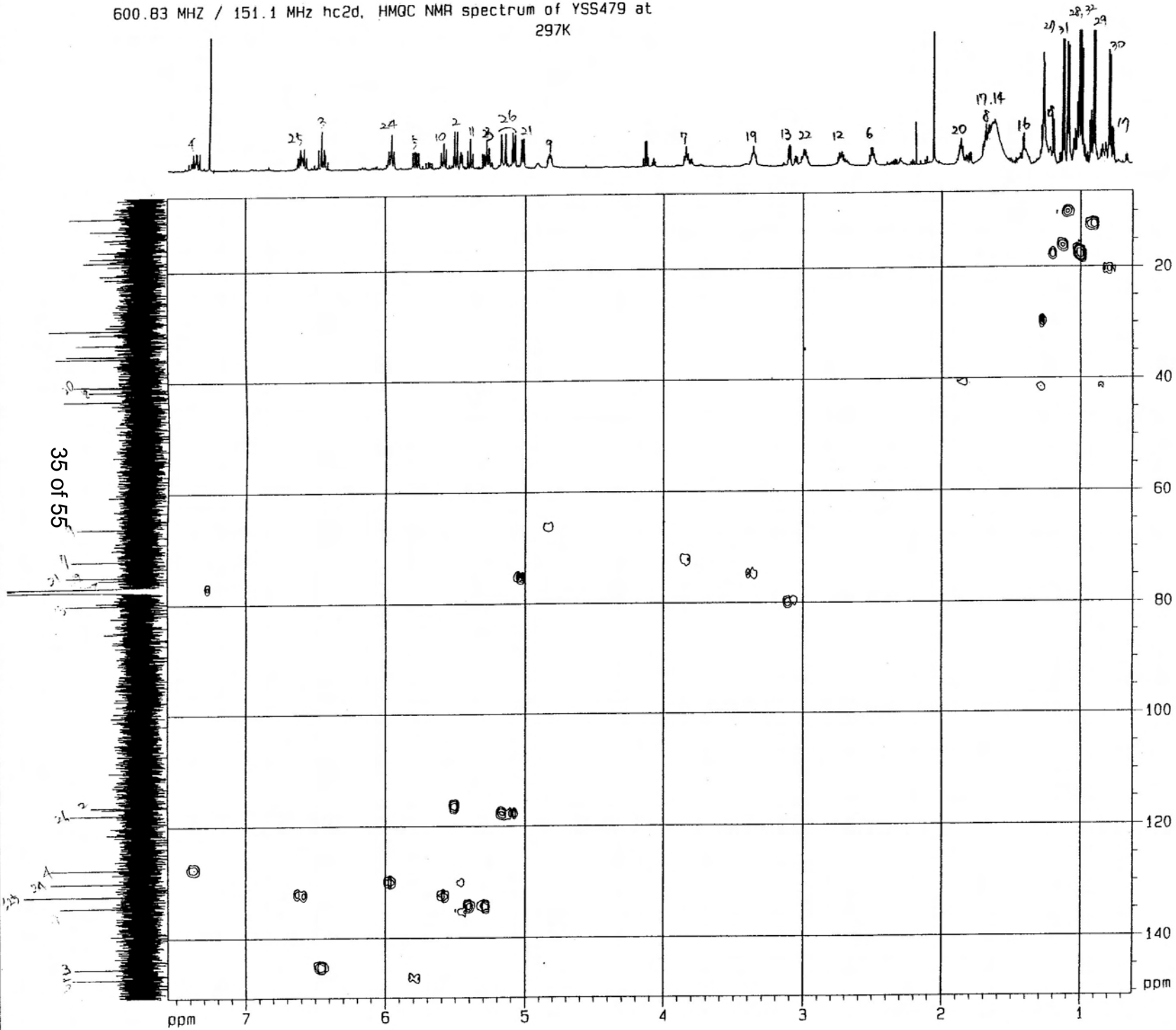
F1 - Processing parameters

SI	512
MC2	QF
SF	600.8300220 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

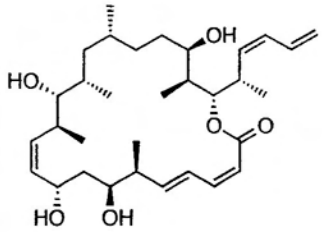
CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.503 ppm
F2LO	4507.75 Hz
F2PHI	0.547 ppm
F2HI	328.77 Hz
F1PLO	7.623 ppm
F1LO	4580.05 Hz
F1PHI	0.570 ppm
F1HI	342.42 Hz
F2PPMCM	0.46369 ppm/cm
F2HZCM	278.59894 Hz/cm
F1PPMCM	0.47020 ppm/cm
F1HZCM	282.50906 Hz/cm

600.83 MHZ / 151.1 MHz hc2d, HMQC NMR spectrum of YSS479 at 297K



Current Data Parame

NAME	yss479
EXPNO	12
PROCNO	1



5

d0	0.00000300 se
D1	1.50000000 se
d2	0.00344828 se
d12	0.00002000 se
d13	0.00000300 se
D16	0.00050000 se
d20	0.00242528 se
IN0	0.00001325 se

CHANNEL f1

NUC1	1H
P1	9.60 us
p2	19.20 us
PL1	0.00 dB
SF01	600.8342058 MH

CHANNEL f2

CPDPRG2	garp
NUC2	13C
P3	13.50 us
PCPD2	100.00 us
PL2	0.00 dB
PL12	12.00 dB
SF02	151.0953827 MH

GRADIENT CHANN

P16	1000.00 us

F1 - Acquisition para

NDO	2
ID	256
SF01	151.0954 MH
F1DRES	147.405655 Hz
SW	249.749 pp

F2 - Processing para

SI	1024
SF	600.8300216 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

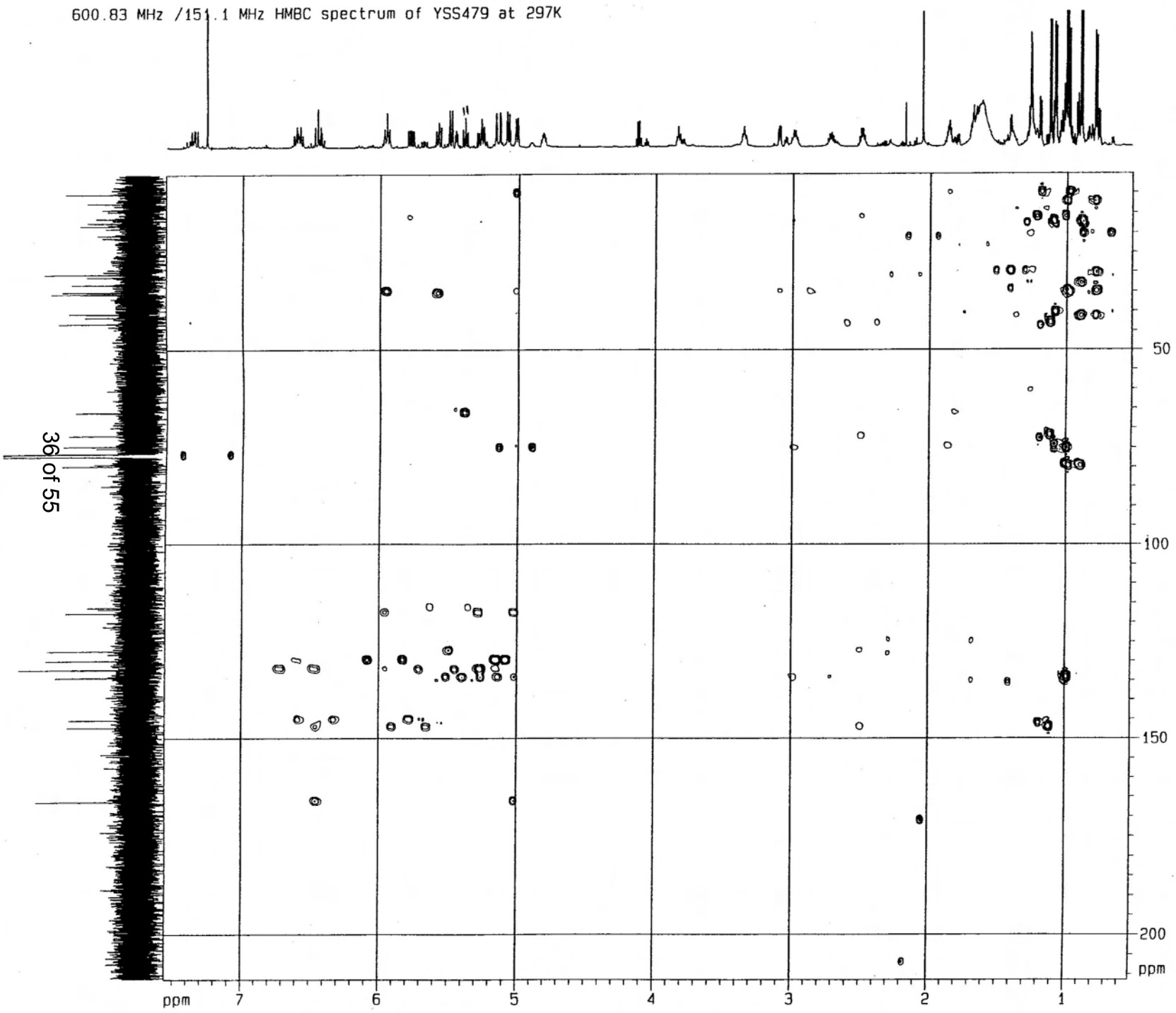
F1 - Processing para

SI	1024
MC2	QF
SF	151.0788222 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parame

CX2	18.00 cm
CX1	15.00 cm
F2PL0	7.563 pp
F2L0	4544.31 Hz
F2PH1	0.621 pp
F2H1	372.84 Hz
F1PL0	150.838 pp
F1L0	22788.37 Hz
F1PH1	6.436 pp
F1H1	972.33 Hz
F2PPMCM	0.38571 pp
F2HZCM	231.74820 Hz
F1PPMCM	9.62678 pp
F1HZCM	1454.40283 Hz

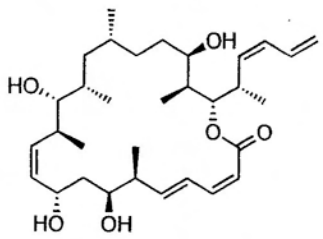
600.83 MHz /151.1 MHz HMBC spectrum of YSS479 at 297K



Current Data Parameters

NAME	yss479
EXPNO	1122
PROCNO	1

F2 - Acquisition Parameter



5

GO	0.00000300 sec
D1	1.00000000 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00050000 sec
IN0	0.00001325 sec
========== CHANNEL f1 ======	
NUC1	1H
P1	9.60 usec
p2	19.20 usec
PL1	0.00 dB
SFO1	600.8336050 MHz
========== CHANNEL f2 ======	
NUC2	13C
P3	13.50 usec
PL2	0.00 dB
SFO2	151.0953827 MHz
========== GRADIENT CHANNEL =	
P16	1000.00 usec

F1 - Acquisition parameter

NDO	2
TD	256
SFO1	151.0954 MHz
FIDRES	147.405655 Hz
SW	249.749 ppm

F2 - Processing parameter

SI	1024
SF	600.8300280 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

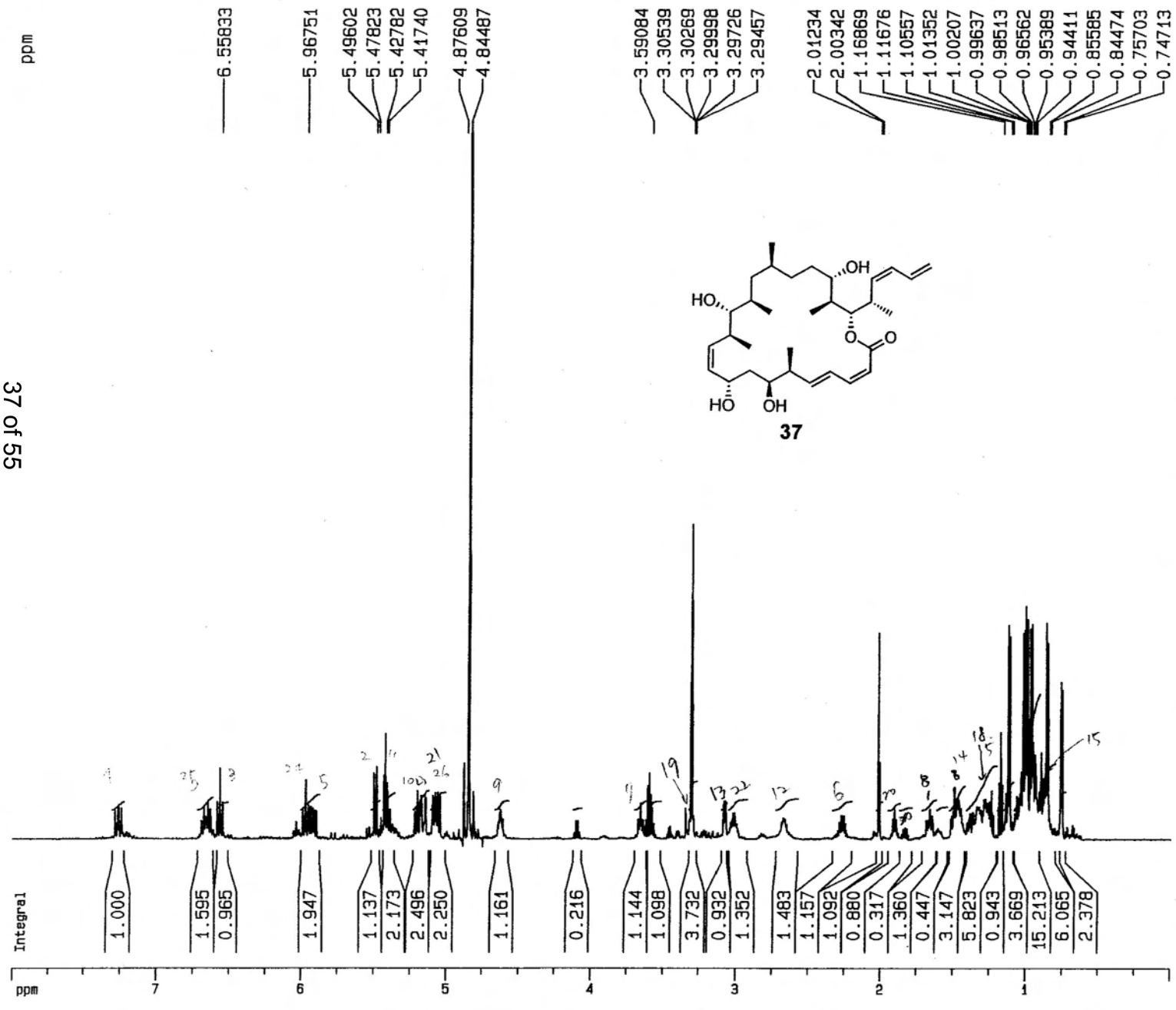
F1 - Processing parameter

SI	2048
MC2	QF
SF	151.0788437 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	7.561 ppm
F2LO	4542.96 Hz
F2PHI	0.516 ppm
F2HI	310.02 Hz
F1PLO	211.431 ppm
F1LO	31942.80 Hz
F1PHI	5.317 ppm
F1HI	803.34 Hz
F2PPMCM	0.39140 ppm/cm
F2HZCM	235.16344 Hz/cm
F1PPMCM	13.74093 ppm/cm
F1HZCM	2075.96411 Hz/cm

yss675-1 cd3od 298K 600MHz 1H delay 12sec 7/16/04 ftl



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Current Data Parameters	
NAME	yss675-1-ftl
EXPNO	1
PROCNO	1

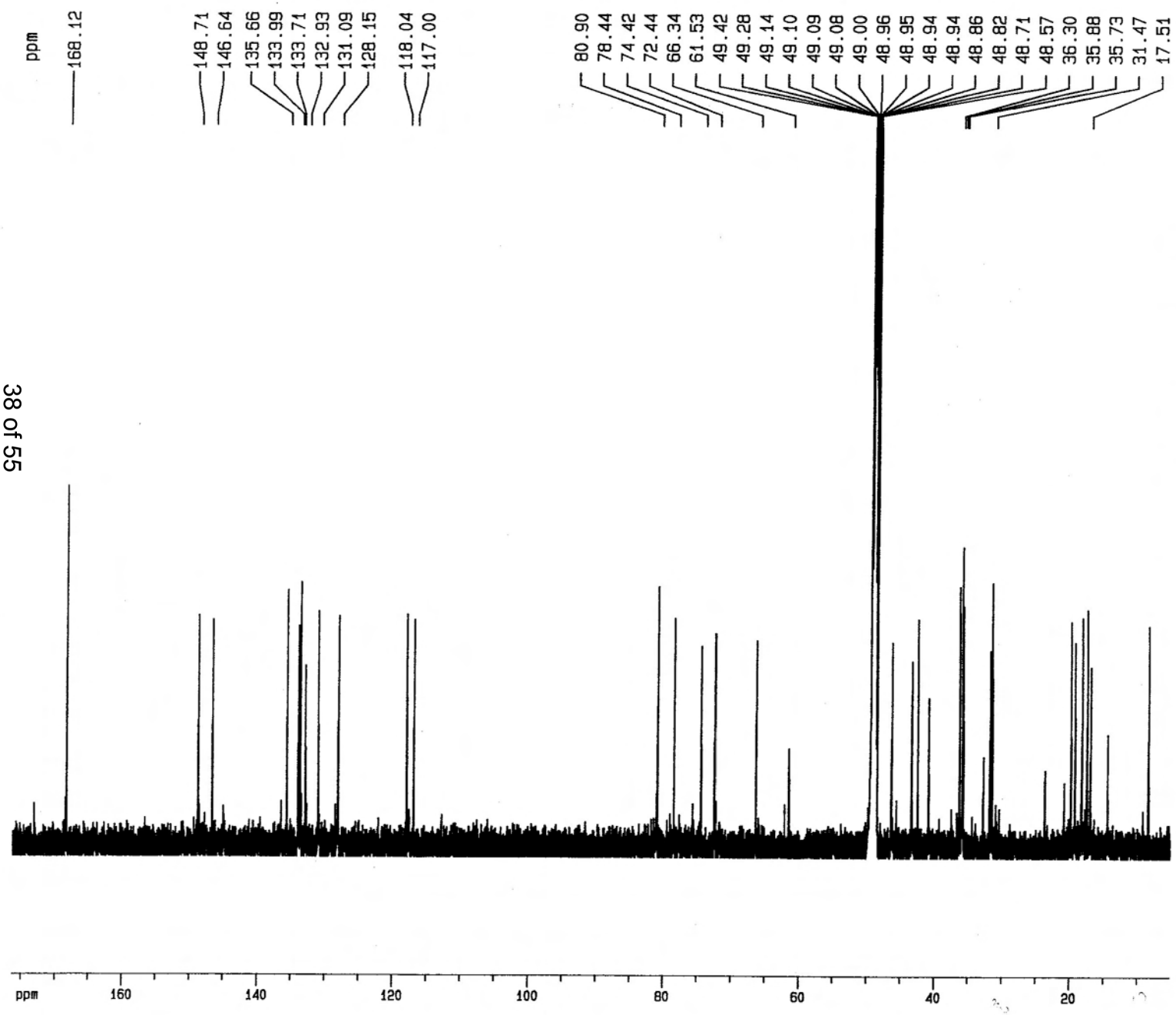
F2 - Acquisition Parameters	
Date_	20040716
Time	10.40
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zg
TD	65536
SOLVENT	CD2Cl2
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	10
DW	55.600 usec
DE	6.00 usec
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

F2 - Processing parameters	
SI	65536
SF	600.8300180 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters	
CX	20.00 cm
F1P	8.000 ppm
F1	4806.64 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.40000 ppm/cm
HZCM	240.33200 Hz/cm

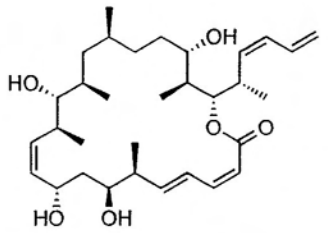
yss675-1 cd3od 298K 151MHz13C 1H decp delay 8sec 7/15/04



Current Data Parameters

NAME	yss675-1-ftl
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters



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AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	12.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

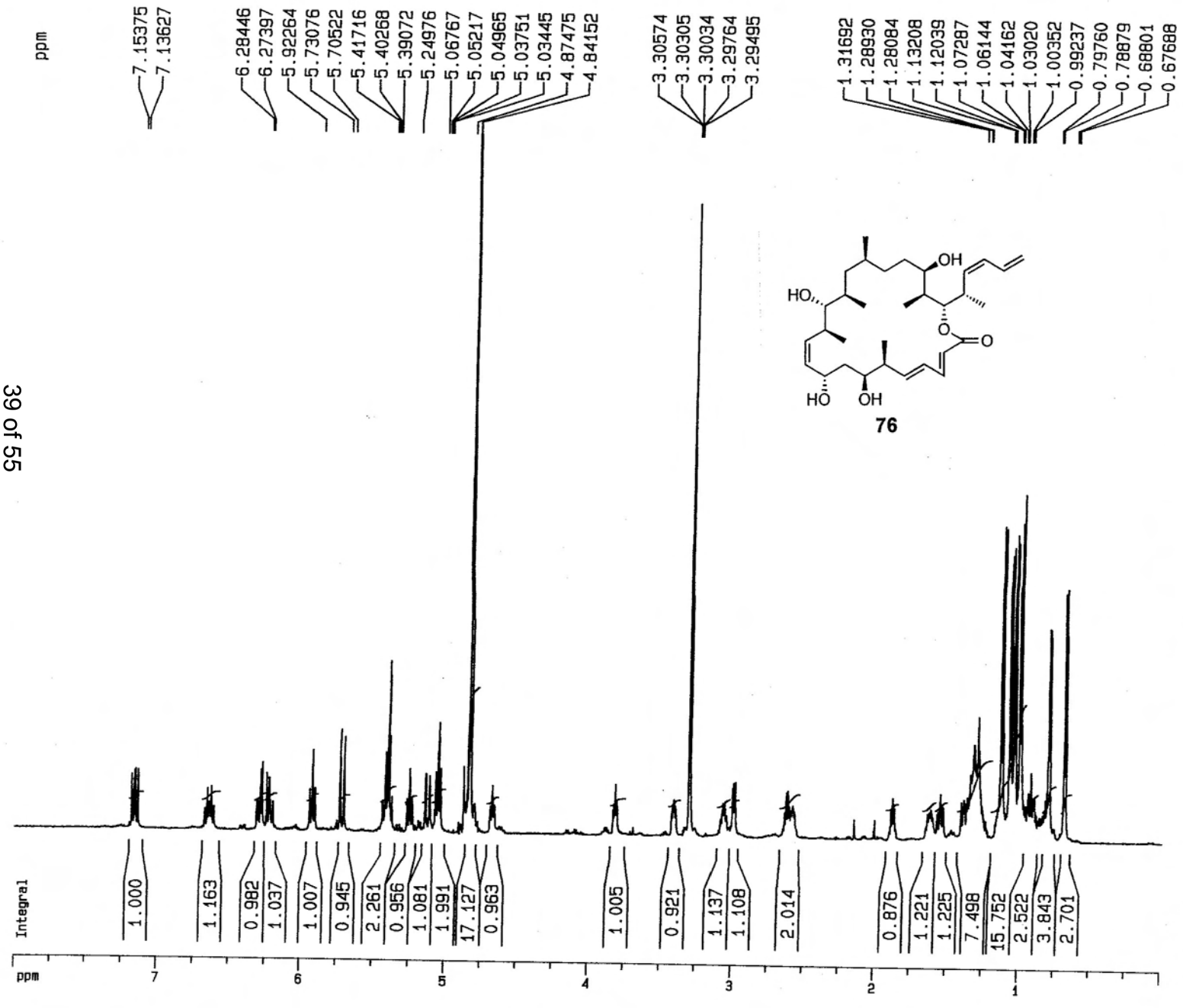
F2 - Processing parameters

SI	65536
SF	151.0786142 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	176.293 ppm
F1	26634.11 Hz
F2P	5.179 ppm
F2	782.37 Hz
PPMCM	8.55572 ppm/cm
HZCM	1292.58691 Hz/cm

yss665-2 cd3od 298K 600MHz 1H delay 12sec 7/11/04 ftl



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Current Data Parameters	
NAME	yss665-2-ftl
EXPNO	1
PROCNO	1

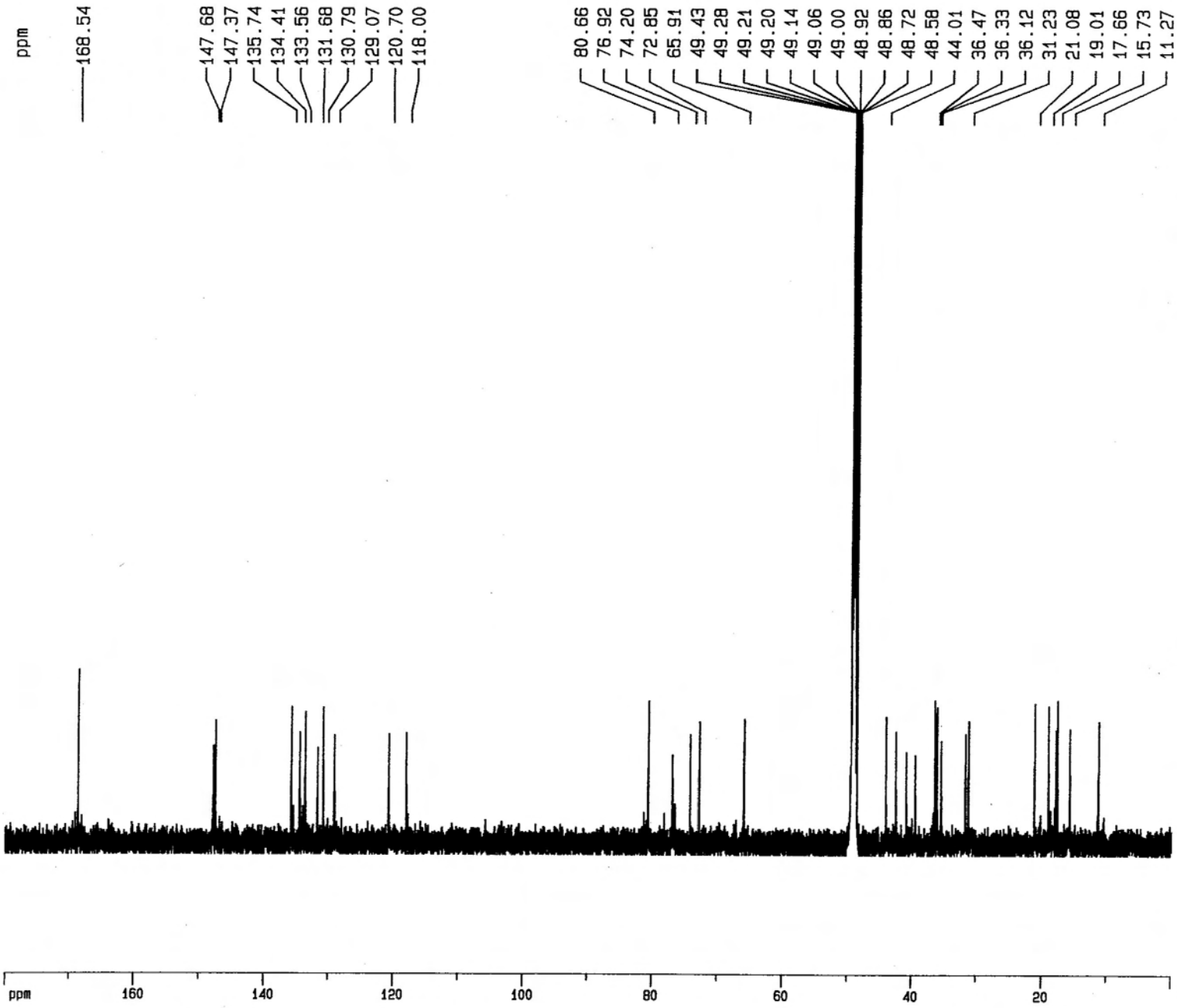
F2 - Acquisition Parameters	
Date_	20040711
Time	10.12
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zg
TD	65536
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	10
DW	55.600 usec
DE	6.00 usec
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ========	
NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

F2 - Processing parameters	
SI	65536
SF	600.8300180 MHz
WDW	EM
SSB	0
LB	0.40 Hz
GB	0
PC	1.00

1D NMR plot parameters	
CX	20.00 cm
F1P	8.000 ppm
F1	4806.64 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.40000 ppm/cm
HZCM	240.33200 Hz/cm

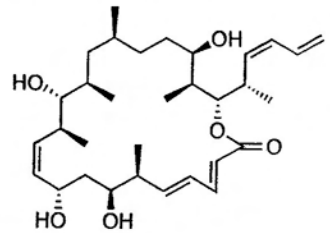
yss665-2 cd3od 298K 151MHz 13C 1H decp delay 8sec 7/13/04 ftl



Current Data Parameters

NAME	yss665-2-ftl
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters



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AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

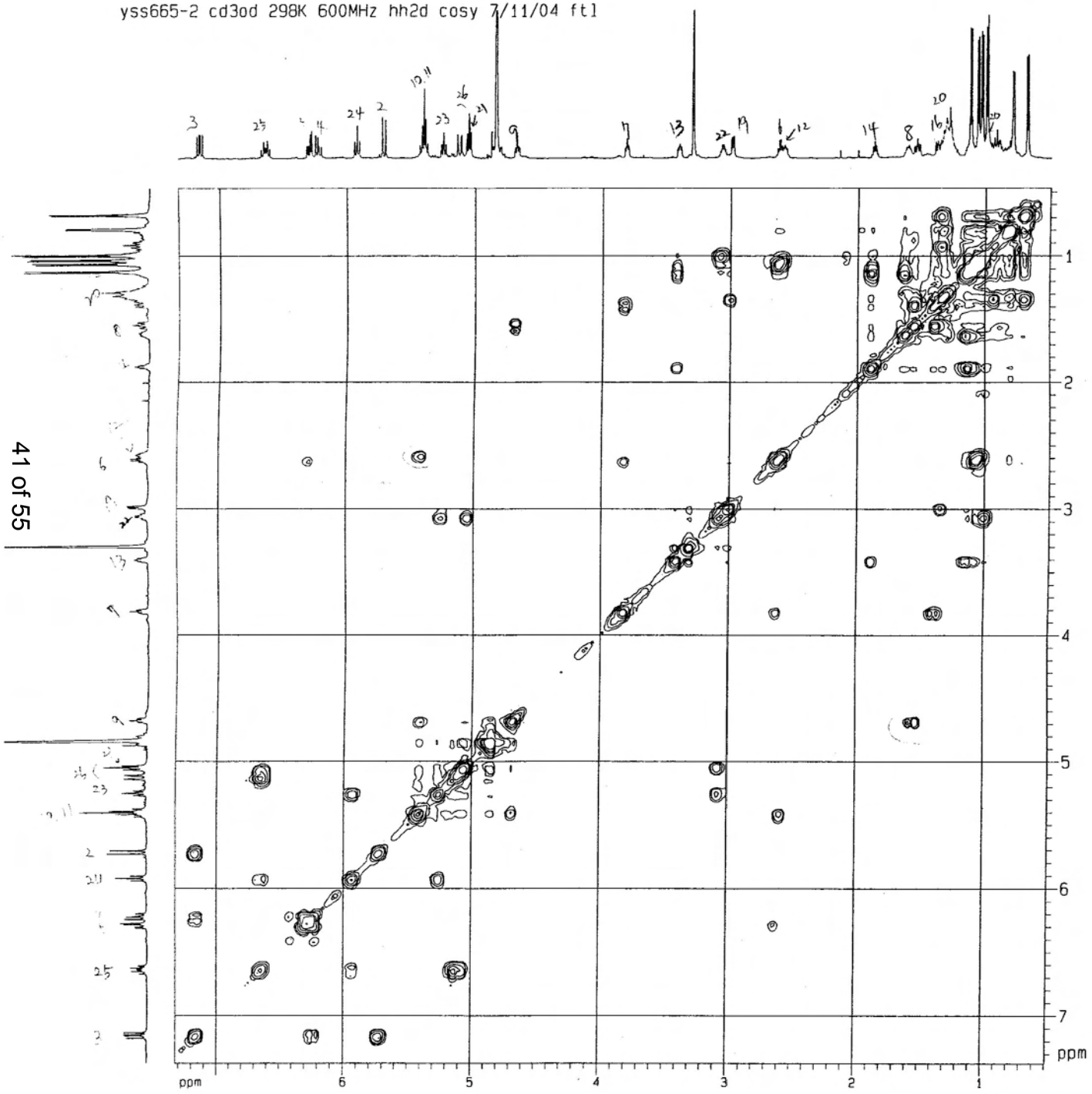
F2 - Processing parameters

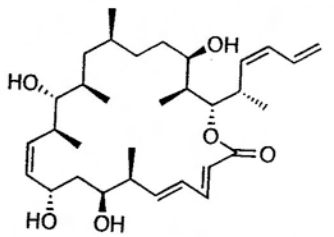
SI	65536
SF	151.0786124 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	180.000 ppm
F1	27194.15 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	9.00000 ppm/cm
HZCM	1359.70752 Hz/cm

yss665-2 cd3od 298K 600MHz hh2d cosy 7/11/04 ftl





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Current Data Parameters

NAME	yss665-2-ftl
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

D1	1.00000000 sec
INO	0.00013320 sec

CHANNEL f1

NUC1	1H
P0	8.20 usec
P1	9.60 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.8336 MHz
FIDRES	29.326200 Hz
SW	12.495 ppm

F2 - Processing parameters

SI	512
SF	600.8300091 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

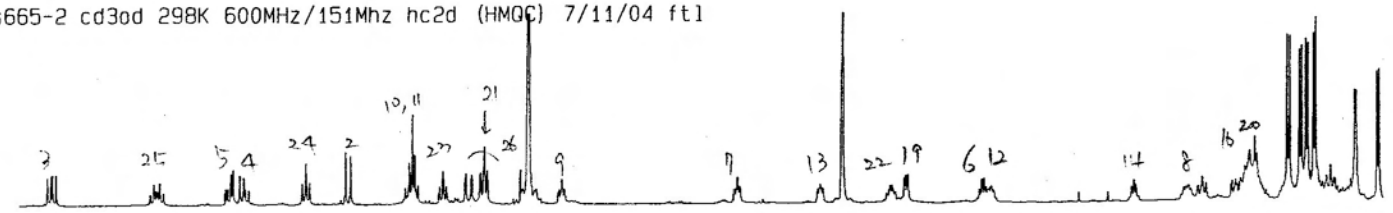
F1 - Processing parameters

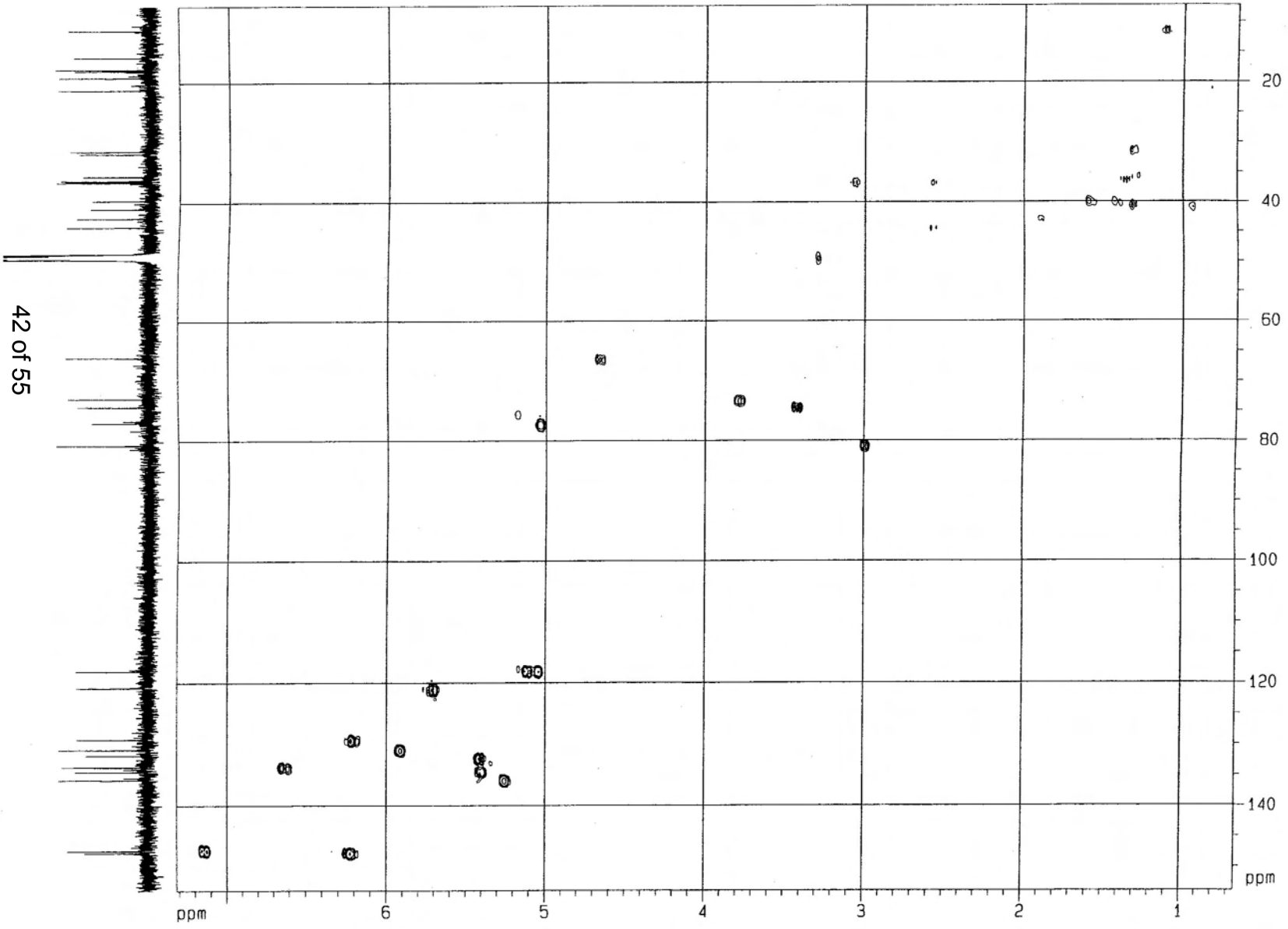
SI	512
MC2	QF
SF	600.8300094 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

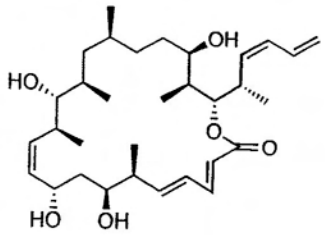
2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.327 ppm
F2LO	4402.33 Hz
F2PHI	0.494 ppm
F2HI	296.66 Hz
F1PLO	7.375 ppm
F1LO	4431.39 Hz
F1PHI	0.469 ppm
F1HI	281.73 Hz
F2PPMCM	0.45556 ppm/cm
F2HZCM	273.71121 Hz/cm
F1PPMCM	0.46044 ppm/cm
F1HZCM	276.64383 Hz/cm

yss665-2 cd3od 298K 600MHz/151Mhz hc2d (HMQC) 7/11/04 ftl







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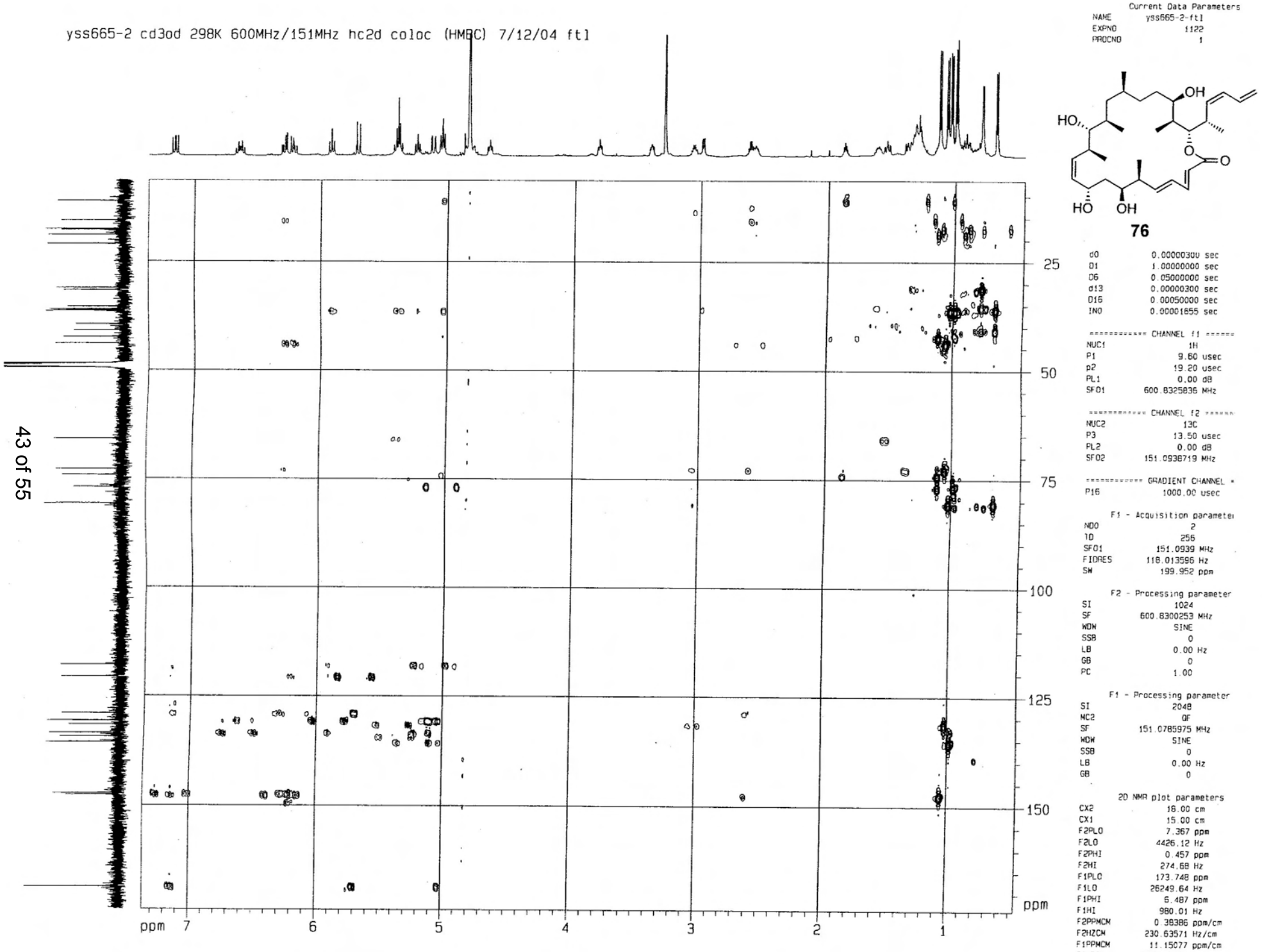
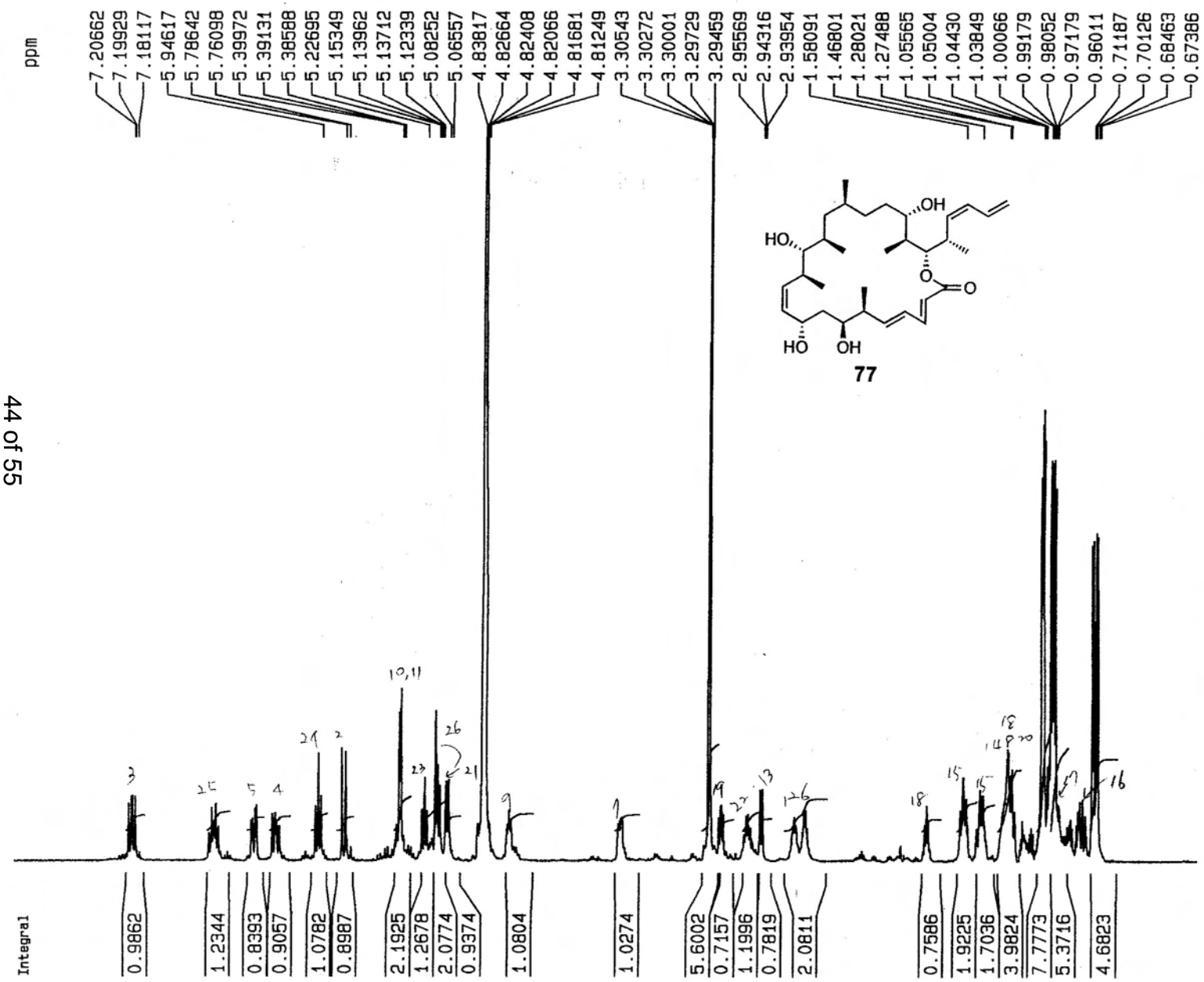
Current Data Parame

NAME	yss665 2-ft1
EXPNO	12
PROCNO	1

d0	0.00000300 se
D1	1.50000000 se
d2	0.00344828 se
d12	0.00002000 se
d13	0.00000300 se
D16	0.00050000 se
d20	0.00242528 se
IN0	0.00001655 se
========== CHANNEL f1 ==	
NUC1	1H
P1	9.60 us
p2	19.20 us
PL1	0.00 dB
SFO1	600.8325836 MH
========== CHANNEL f2 ==	
CPDPRG2	garp
NUC2	13C
P3	13.50 us
PCPD2	100.00 us
PL2	0.00 dB
PL12	12.00 dB
SFO2	151.0935697 MH
========== GRADIENT CHAN	
P16	1000.00 us
F1 - Acquisition para	
NDO	2
TD	256
SFO1	151.0936 MH
FIDRES	118.013596 Hz
SW	199.952 ppi
F2 - Processing para	
SI	1024
SF	600.8300219 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00
F1 - Processing para	
SI	1024
MC2	QF
SF	151.0785695 MH
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
2D NMR plot parame	
CX2	18.00 cm
CX1	15.00 cm
F2PLO	7.320 ppi
F2LO	4397.98 Hz
F2PHI	0.656 ppi
F2HI	393.86 Hz
F1PLO	153.979 ppi
F1LO	23262.93 Hz
F1PHI	7.320 ppi
F1HI	1105.91 Hz
F2PPMCM	0.37024 ppi
F2HZCM	222.45093 Hz
F1PPMCM	9.77726 ppi
F1HZCM	1477.13452 Hz


yss665-2 cd3od 298K 600MHz/151MHz hc2d coloc (HMBC) 7/12/04 ft1
ppm 7
6
5
4
3
2
1
ppm
25
50
75
100
125
150
Current Data Parameters
NAME yss665-2-ft1
EXPNO 1122
PROCNO 1
OH
HO
O
O
HO
OH
76
d0 0.0000030U sec
D1 1.00000000 sec
D6 0.05000000 sec
d13 0.00000300 sec
D16 0.00050000 sec
IN0 0.00001655 sec
CHANNEL f1
NUC1 1H
P1 9.60 usec
p2 19.20 usec
PL1 0.00 dB
SF01 600.8325836 MHz
CHANNEL f2
NUC2 13C
P3 13.50 usec
PL2 0.00 dB
SF02 151.0938719 MHz
GRADIENT CHANNEL
P16 1000.00 usec
F1 - Acquisition parameter
ND0 2
TD 256
SF01 151.0939 MHz
FIDRES 118.013596 Hz
SW 199.952 ppm
F2 - Processing parameter
SI 1024
SF 600.8300253 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing parameter
SI 2048
MC2 QF
SF 151.0785975 MHz
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
2D NMR plot parameters
CX2 18.00 cm
CX1 15.00 cm
F2PL0 7.367 ppm
F2L0 4426.12 Hz
F2PHI 0.457 ppm
F2HI 274.68 Hz
F1PL0 173.748 ppm
F1L0 26249.64 Hz
F1PHI 6.487 ppm
F1HI 980.01 Hz
F2PPMCM 0.38386 ppm/cm
F2HZCM 230.63571 Hz/cm
F1PPMCM 11.15077 ppm/cm
F1HZCM 1684.64209 Hz/cm



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Current Data Parameters

NAME	yss675-2-ftl
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20040717
Time	11.18
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zg
TD	65536
SOLVENT	CDCl3
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	10
DW	55.600 usec
DE	6.00 usec
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ========

NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

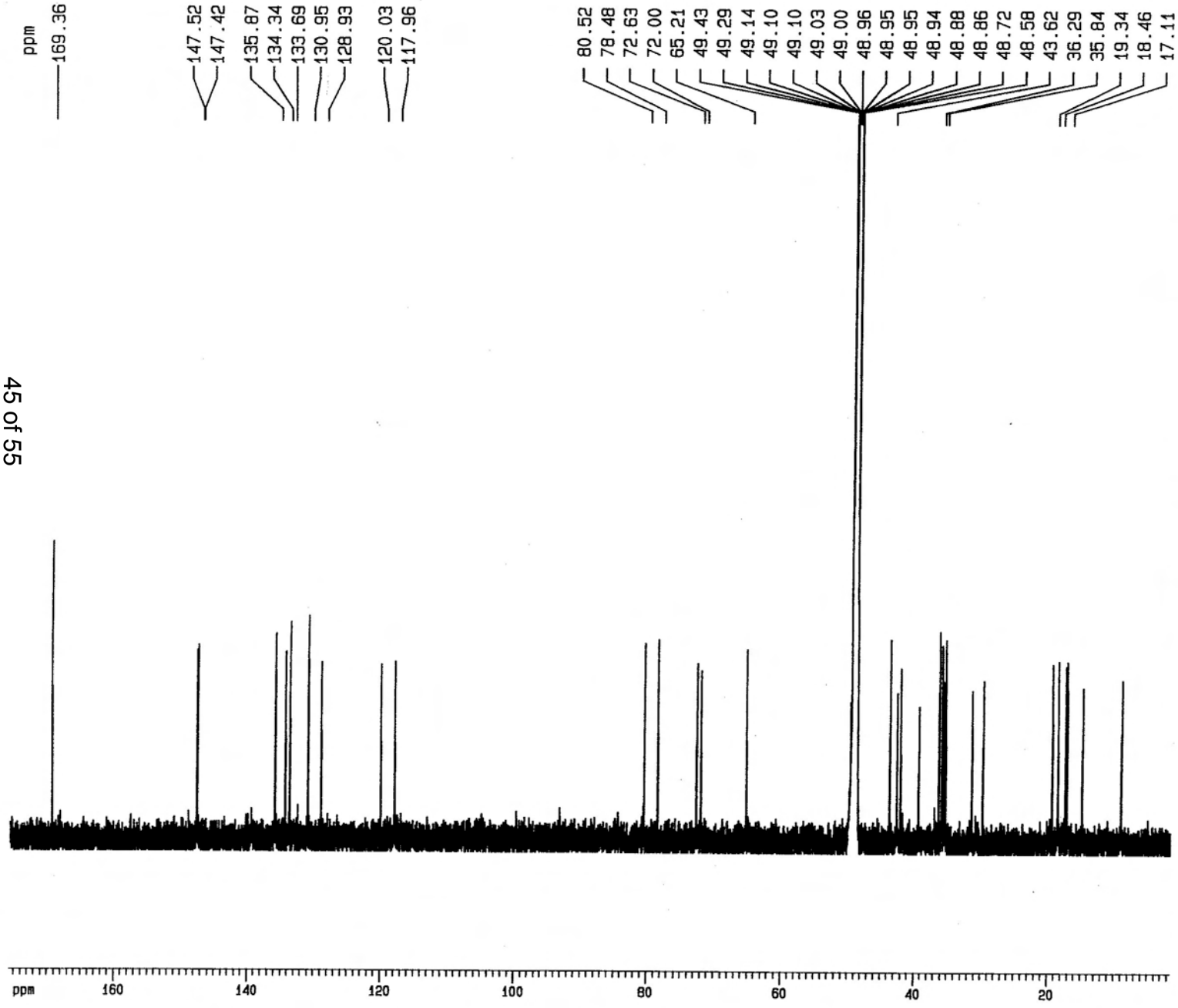
F2 - Processing parameters

SI	65536
SF	600.8300181 MHz
WDW	EM
SSB	0
LB	0.40 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	8.000 ppm
F1	4806.64 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	0.40000 ppm/cm
HZCM	240.33200 Hz/cm

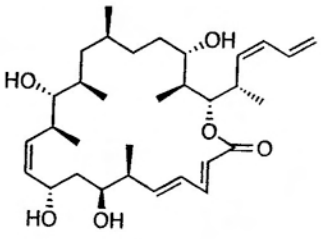
yss675-2 cd3od 298K 151MHz 13C 1H decp delay 8sec 7/19/04 ftl



Current Data Parameters

NAME	yss675-2-ftl
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters



77

AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ==========

CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

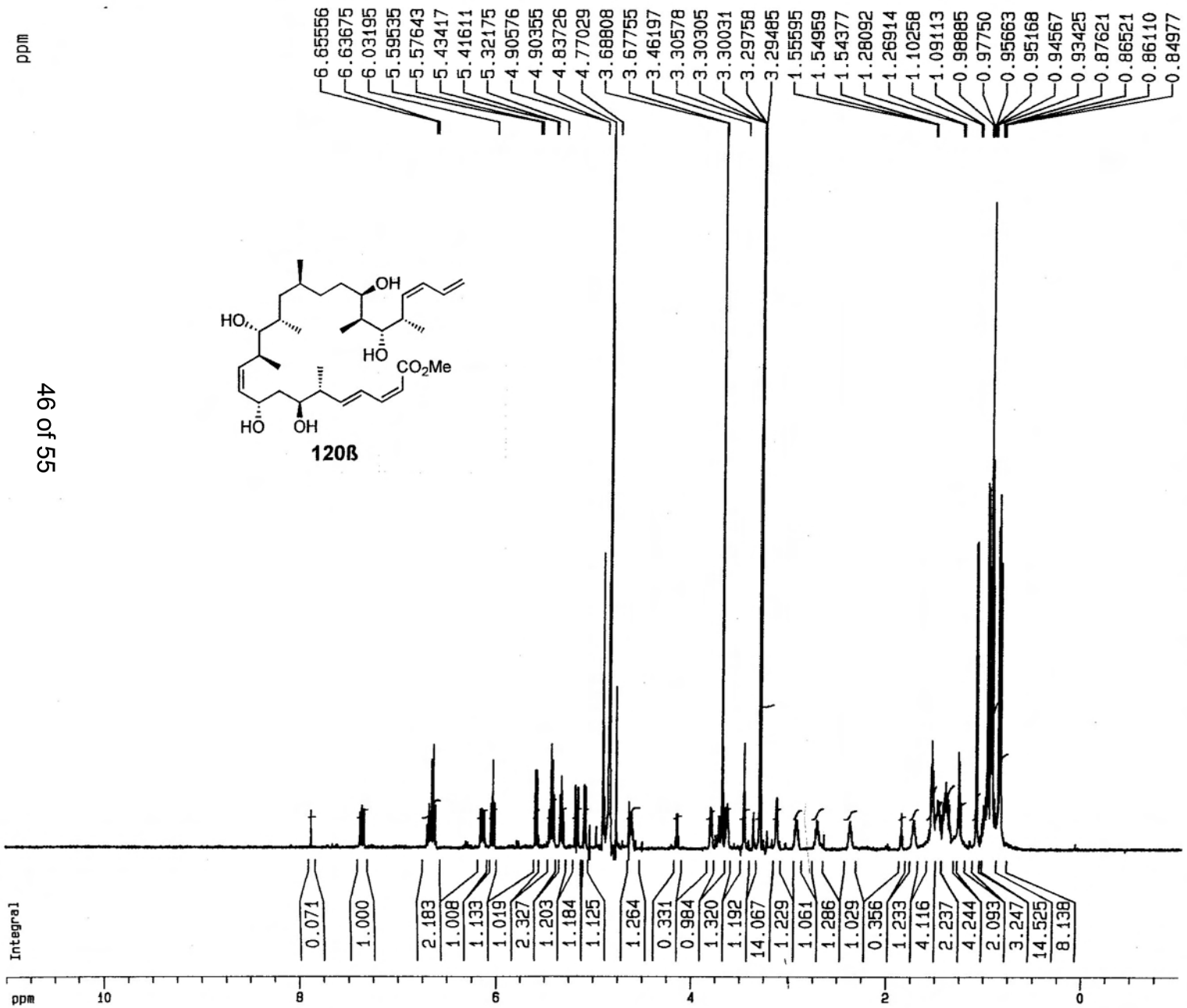
F2 - Processing parameters

SI	65536
SF	151.0786118 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	175.742 ppm
F1	26550.83 Hz
F2P	1.511 ppm
F2	228.29 Hz
PPMCM	8.71154 ppm/cm
HZCM	1316.12720 Hz/cm

yss629 cdcl3 298K 600MHz 1H delay 12sec 5/27/04 ft1



120ß

Current Data Parameters

NAME	yss629-ft1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters

Date_	20040527
Time	19.45
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zg
TD	65536
SOLVENT	MeOH
NS	8
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	40
DW	55.600 usec
DE	6.00 usec
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ========

NUC1	1H
P1	9.00 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

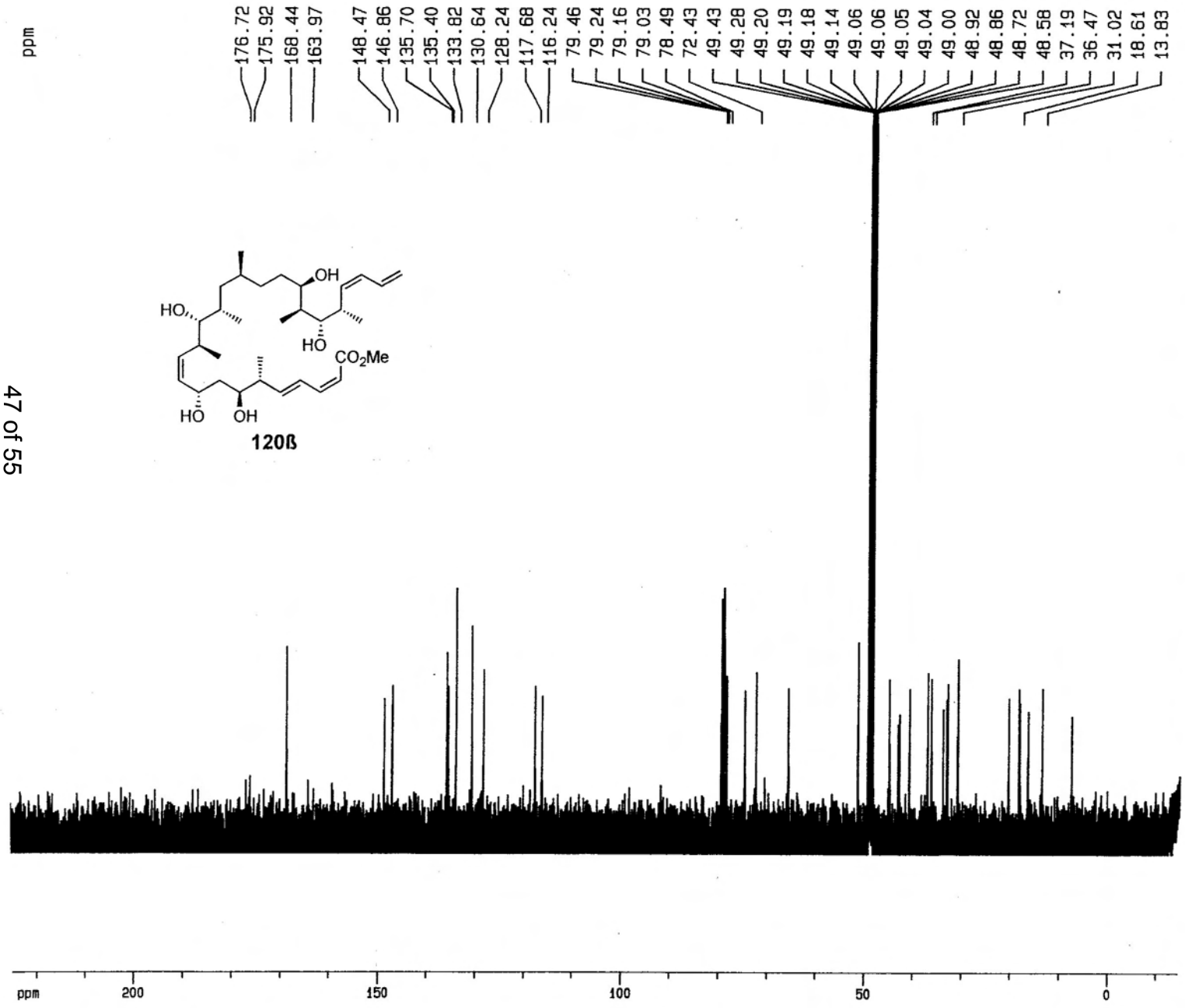
F2 - Processing parameters

SI	65536
SF	600.8300180 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	11.000 ppm
F1	6609.13 Hz
F2P	-1.000 ppm
F2	-600.83 Hz
PPMCM	0.60000 ppm/cm
HZCM	360.49802 Hz/cm

yss629 cd3od 298K 151MHz 13C 1H decp delay 8sec 6/3/04 ft1



120ß

Current Data Parameters

NAME	yss629-ft1
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20040604
Time	11.30
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	c13wonoe
TD	65536
SOLVENT	CDC13
NS	8399
DS	0
SWH	37878.789 Hz
FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ==========

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ==========

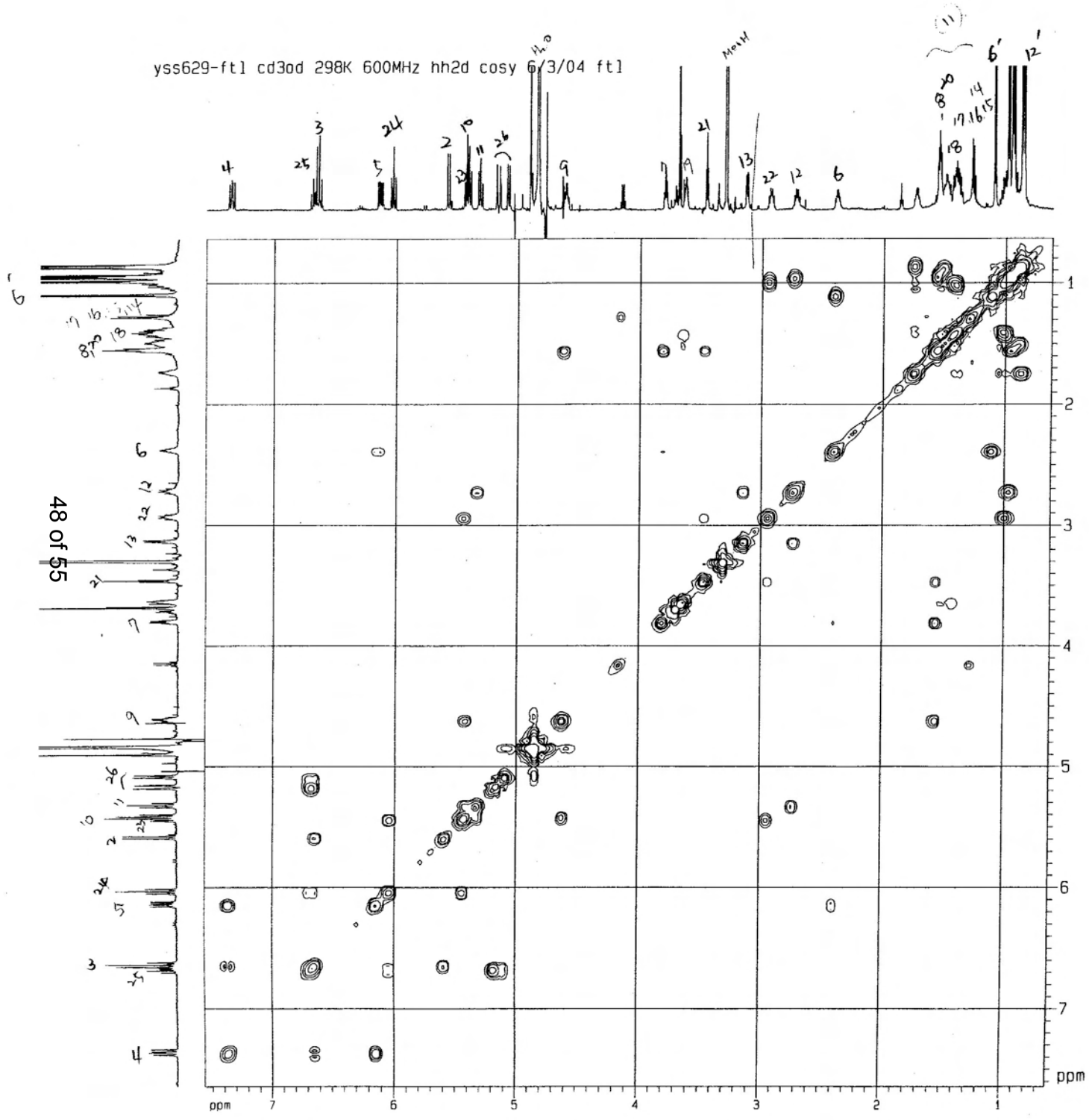
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	151.0786153 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	20.00 cm
F1P	225.000 ppm
F1	33992.69 Hz
F2P	-15.000 ppm
F2	-2266.18 Hz
PPMCM	12.00000 ppm/cm
HZCM	1812.94336 Hz/cm

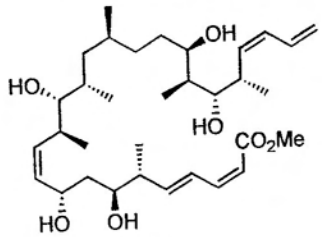


Current Data Parameters

NAME	yss629-ftl
EXPNO	11
PROCNO	1

F2 - Acquisition Parameters

Date_	20040602
Time	13.38



120ß

INU	0.00013320 sec

CHANNEL f1

NUC1	1H
P0	8.20 usec
P1	9.60 usec
PL1	0.00 dB
SFO1	600.8336050 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SFO1	600.8336 MHz
FIDRES	29.326200 Hz
SW	12.495 ppm

F2 - Processing parameters

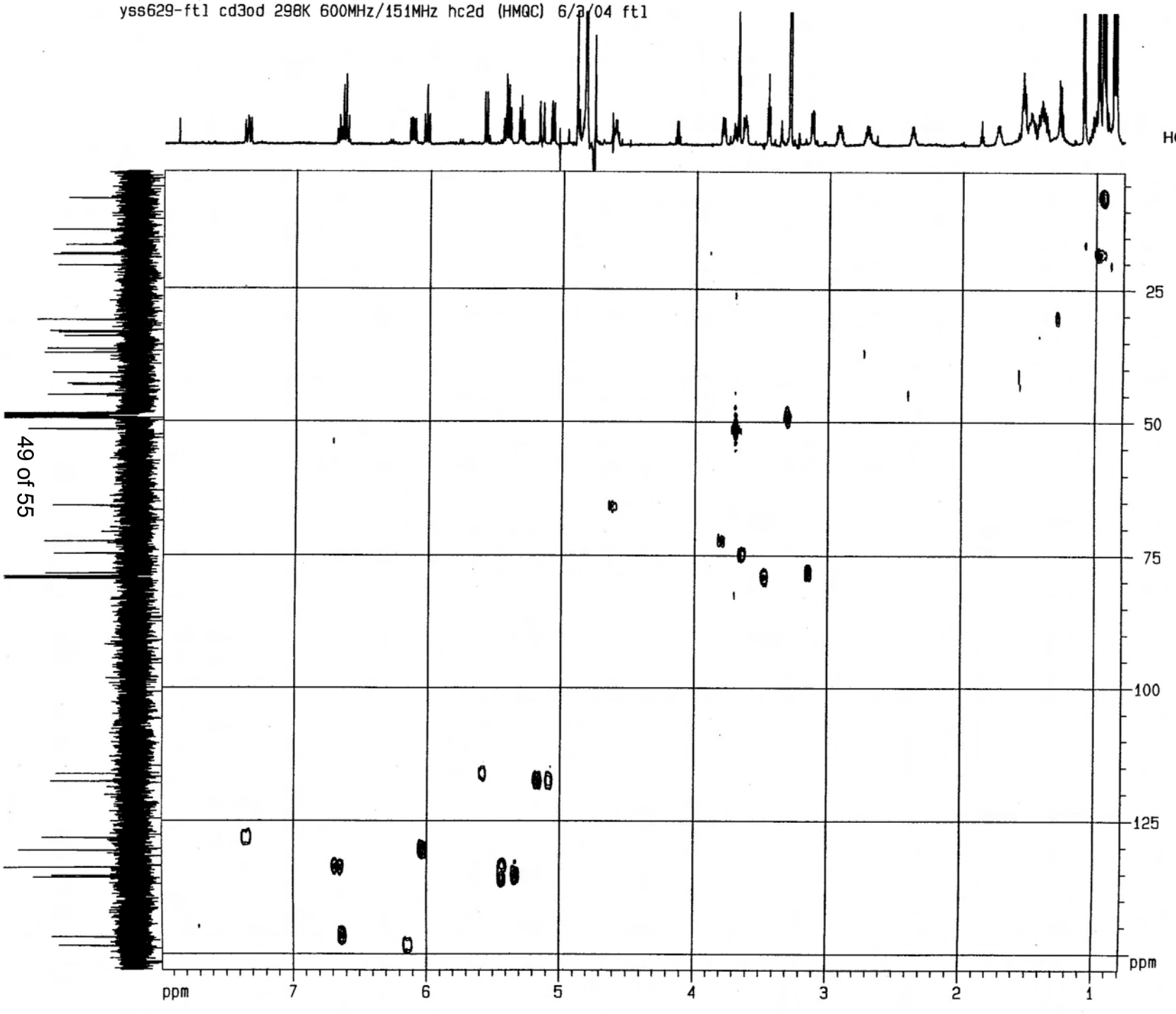
SI	512
SF	600.8300100 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	512
MC2	QF
SF	600.8300099 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.570 ppm
F2LO	4548.05 Hz
F2PHI	0.614 ppm
F2HI	369.07 Hz
F1PLO	7.643 ppm
F1LO	4592.22 Hz
F1PHI	0.639 ppm
F1HI	383.91 Hz
F2PPMCM	0.46369 ppm/cm
F2HZCM	278.59894 Hz/cm
F1PPMCM	0.46694 ppm/cm
F1HZCM	280.55396 Hz/cm

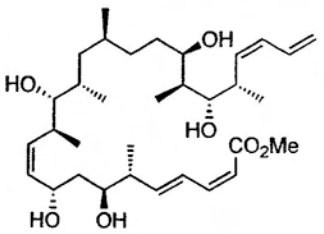


Current Data Parameters

NAME	yss629-ftl
EXPNO	12
PROCNO	1

F2 - Acquisition Parameters

Date_	20040603
Time	5.04



120ß

d13	0.00000300 sec
D16	0.00050000 sec
d20	50000000.00000000 sec
INO	0.00001855 sec

CHANNEL f1

NUC1	1H
P1	9.80 usec
p2	19.20 usec
PL1	0.00 dB
SFO1	600.8325836 MHz

CHANNEL f2

CPDPRG2	garp
NUC2	13C
P3	13.50 usec
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	151.0935697 MHz

GRADIENT CHANNEL

P16	1000.00 usec

F1 - Acquisition parameters

NDO	2
TD	158
SFO1	151.0936 MHz
FIDRES	191.211899 Hz
SW	199.952 ppm

F2 - Processing parameters

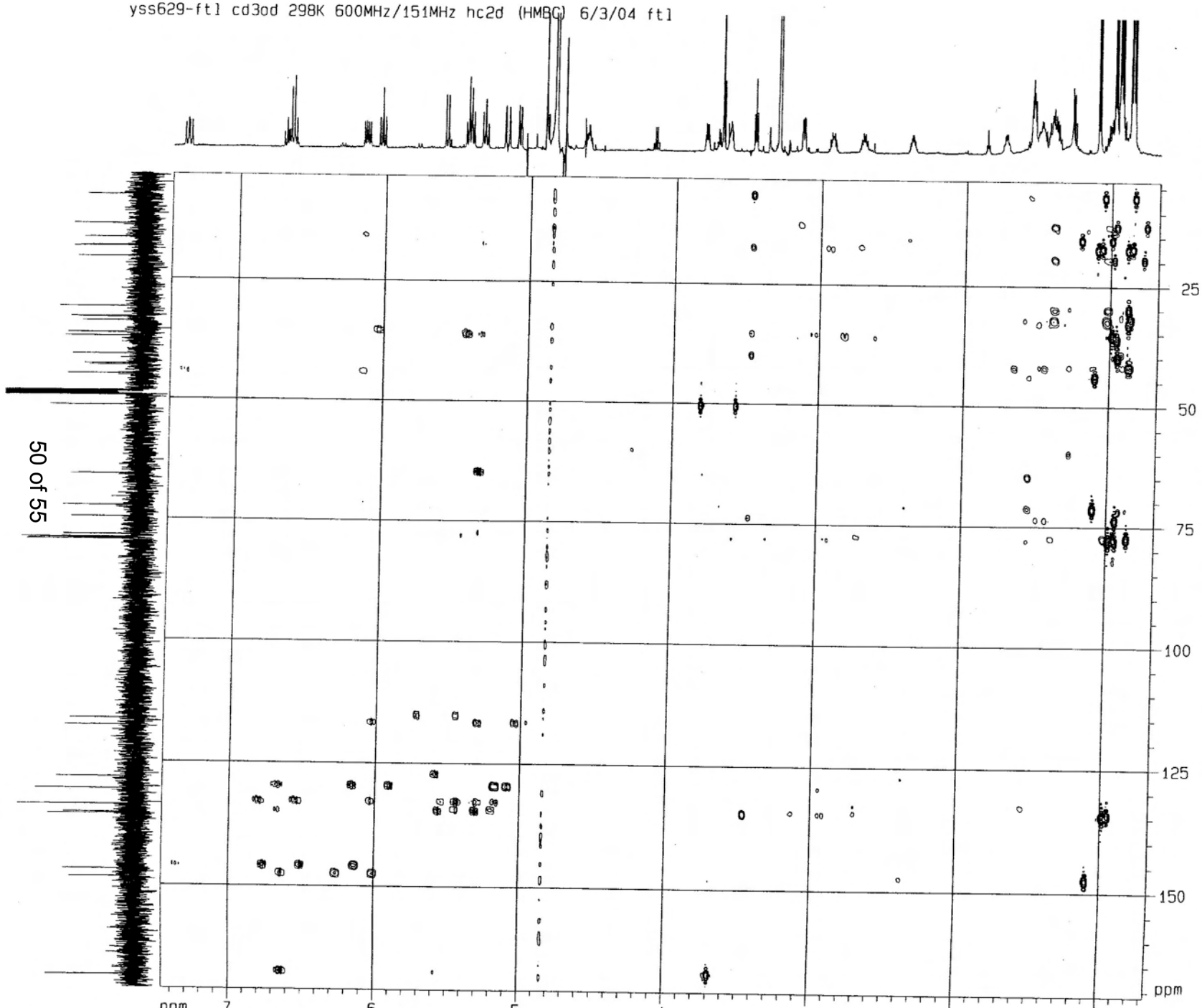
SI	1024
SF	600.8300143 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

SI	1024
MC2	QF
SF	151.0786436 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	7.989 ppm
F2LO	4800.20 Hz
F2PHI	0.791 ppm
F2HI	475.12 Hz
F1PLO	153.067 ppm
F1LO	23128.21 Hz
F1PHI	2.522 ppm
F1HI	381.09 Hz
F2PPMCM	0.39992 ppm/cm
F2HZCM	240.28207 Hz/cm
F1PPMCM	10.03785 ppm/cm
F1HZCM	1516.47481 Hz/cm

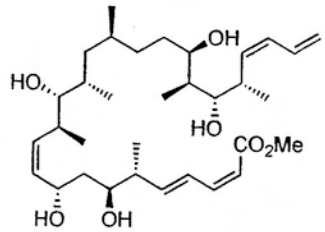


Current Data Parameters

NAME	yss629-ftl
EXPNO	1122
PROCNO	1

F2 - Acquisition Parameter

Date_	20040603



120ß

D1	1.00000000 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00050000 sec
IN0	0.00001655 sec

========== CHANNEL f1 ======

NUC1	1H
P1	9.60 usec
p2	19.20 usec
PL1	0.00 dB
SF01	600.8325836 MHz

========== CHANNEL f2 ======

NUC2	13C
P3	13.50 usec
PL2	0.00 dB
SF02	151.0938719 MHz

========== GRADIENT CHANNEL =

P16	1000.00 usec

F1 - Acquisition parameter

ND0	2
TD	256
SF01	151.0939 MHz
FIDRES	118.013596 Hz
SW	199.952 ppm

F2 - Processing parameter

SI	1024
SF	600.8300154 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

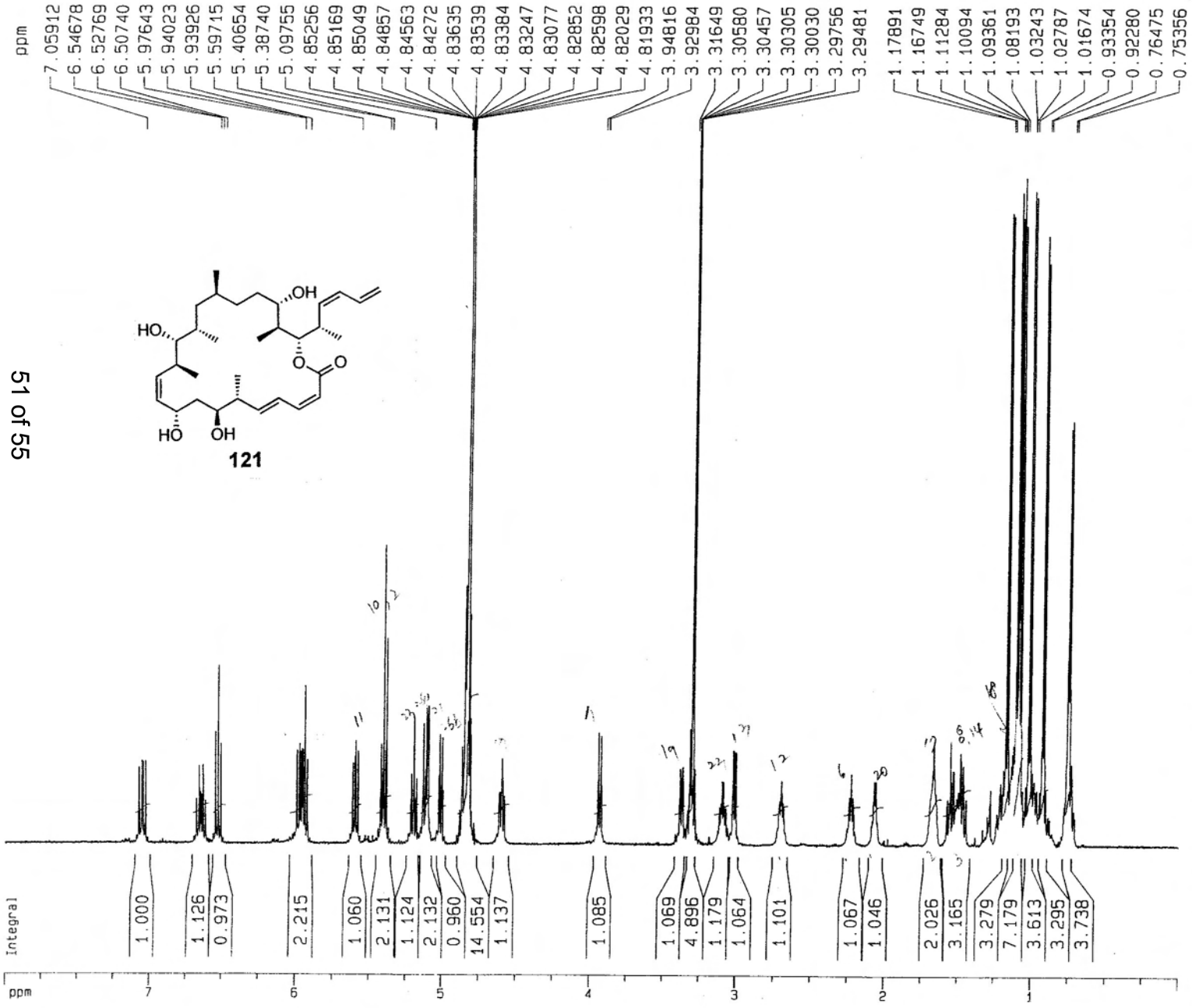
F1 - Processing parameter

SI	2048
MC2	QF
SF	151.0787645 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	7.463 ppm
F2LO	4484.00 Hz
F2PHI	0.667 ppm
F2HI	400.95 Hz
F1PLO	171.080 ppm
F1LO	25846.58 Hz
F1PHI	3.623 ppm
F1HI	547.41 Hz
F2PPMCM	0.37754 ppm/cm
F2HZCM	226.83563 Hz/cm
F1PPMCM	11.16379 ppm/cm
F1HZCM	1686.61096 Hz/cm

yss652-2 cd3od 298K 600MHz 1H delay 12sec 7/2/04 ft1



Current Data Parameters

NAME	yss652-2-ft1
EXPNO	10
PROCNO	1

F2 - Acquisition Parameters

Date_	20040702
Time	11.44
INSTRUM	spect
PROBHD	5 mm TBI 1H/
PULPROG	zg
TD	65536
SOLVENT	CD2C12
NS	8
DS	0
SWH	8992.806 Hz
FIDRES	0.137219 Hz
AQ	3.6438515 sec
RG	10
DW	55.600 use
DE	6.00 use
TE	290.0 K
D1	12.00000000 sec

========== CHANNEL f1 ===

NUC1	1H
P1	9.00 use
PL1	0.00 dB
SFO1	600.8336050 MHz

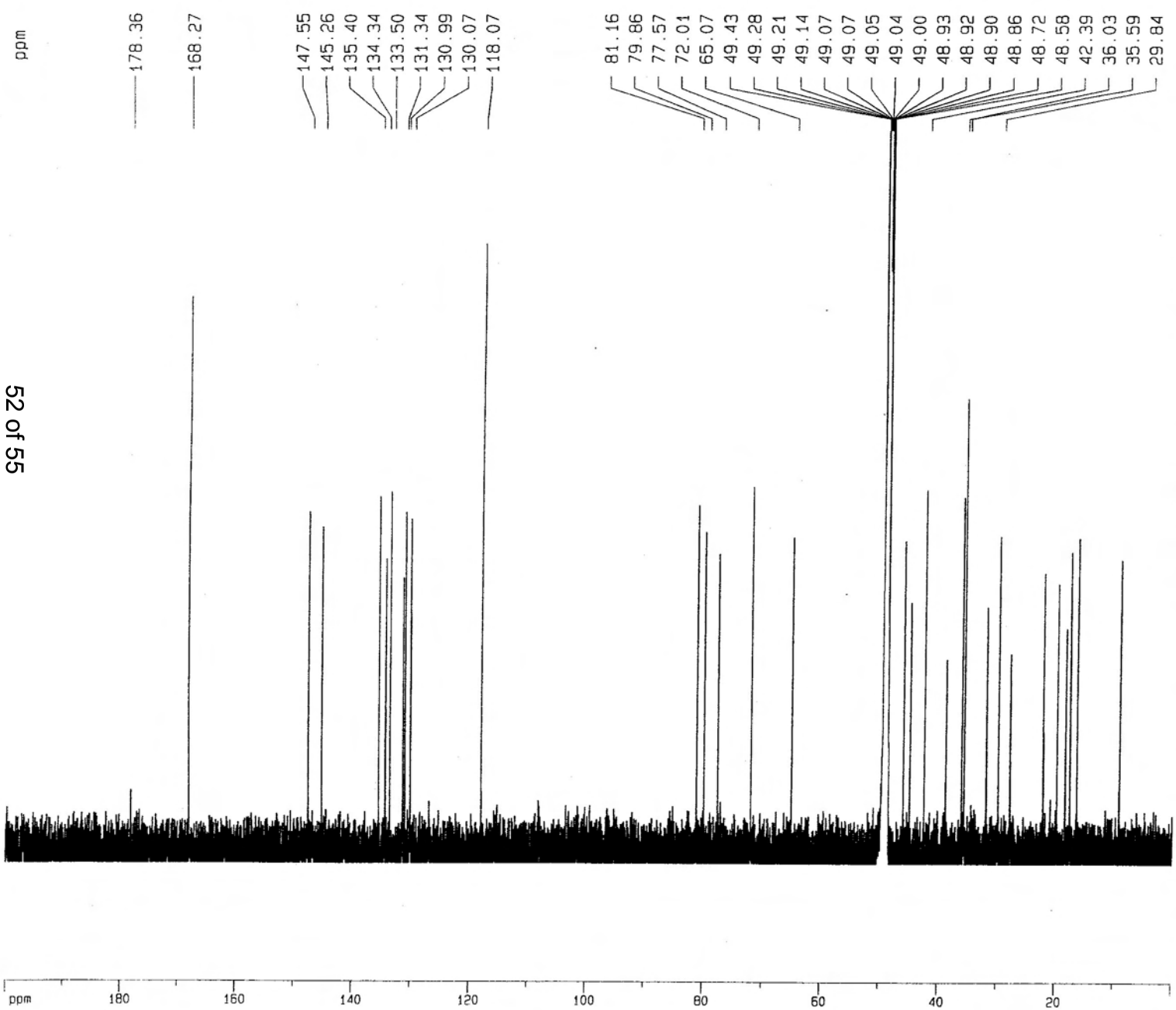
F2 - Processing parameters

SI	65536
SF	600.8300180 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1D NMR plot parameters

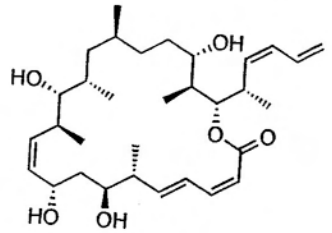
CX	20.00 cm
F1P	8.000 ppr
F1	4806.64 Hz
F2P	0.000 ppr
F2	0.00 Hz
PPMCM	0.40000 ppr
HZCM	240.33200 Hz

yss652-2 cd3od 298K 151MHz 13C 1H decp delay 8sec 7/2/04 ftl



Current Data Parameters

NAME	yss652-2-ftl
EXPNO	2
PROCNO	1



121

FIDRES	0.577984 Hz
AQ	0.8651252 sec
RG	32768
DW	13.200 usec
DE	6.00 usec
TE	290.0 K
D1	8.00000000 sec
D3	0.00100000 sec

========== CHANNEL f1 ======

NUC1	13C
P1	13.50 usec
PL1	0.00 dB
SFO1	151.0953827 MHz

========== CHANNEL f2 ======

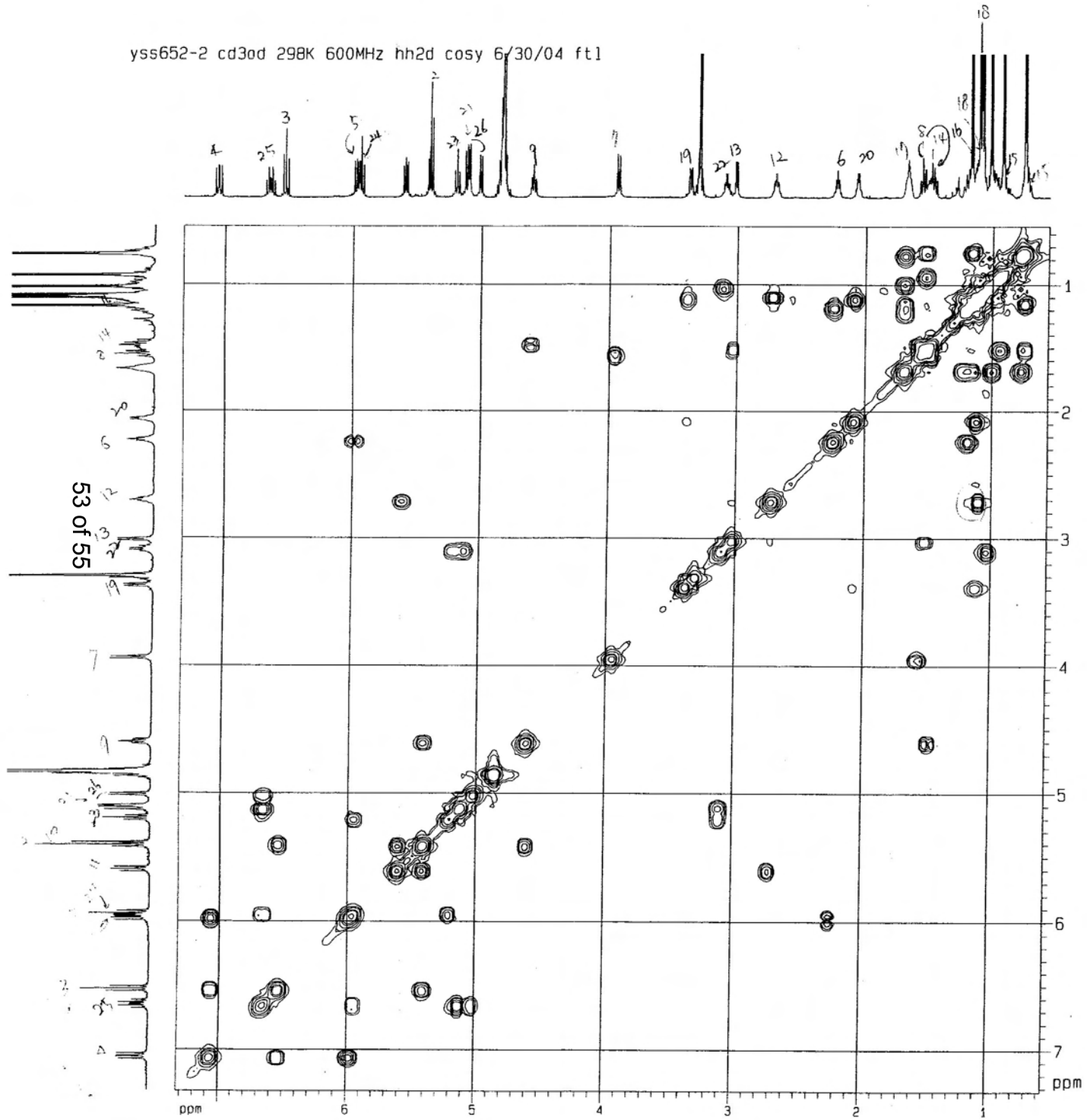
CPDPRG2	waltz16
NUC2	1H
PCPD2	100.00 usec
PL2	0.00 dB
PL12	12.00 dB
SFO2	600.8336050 MHz

F2 - Processing parameters

SI	65536
SF	151.0786118 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00

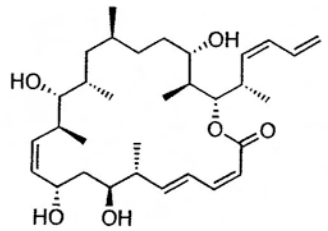
1D NMR plot parameters

CX	20.00 cm
F1P	200.000 ppm
F1	30215.72 Hz
F2P	0.000 ppm
F2	0.00 Hz
PPMCM	10.00000 ppm/cm
HZCM	1510.78613 Hz/cm



Current Data Parameters

NAME	yss652-2-ft1
EXPNO	11
PROCNO	1



121

TE	296.0 K
d0	0.00000300 sec
D1	1.00000000 sec
IN0	0.00013320 sec

========== CHANNEL f1 ==========

NUC1	1H
P0	8.20 usec
P1	9.60 usec
PL1	0.00 dB
SF01	600.8336050 MHz

F1 - Acquisition parameters

NDO	1
TD	256
SF01	600.8336 MHz
FIDRES	29.326200 Hz
SW	12.495 ppm

F2 - Processing parameters

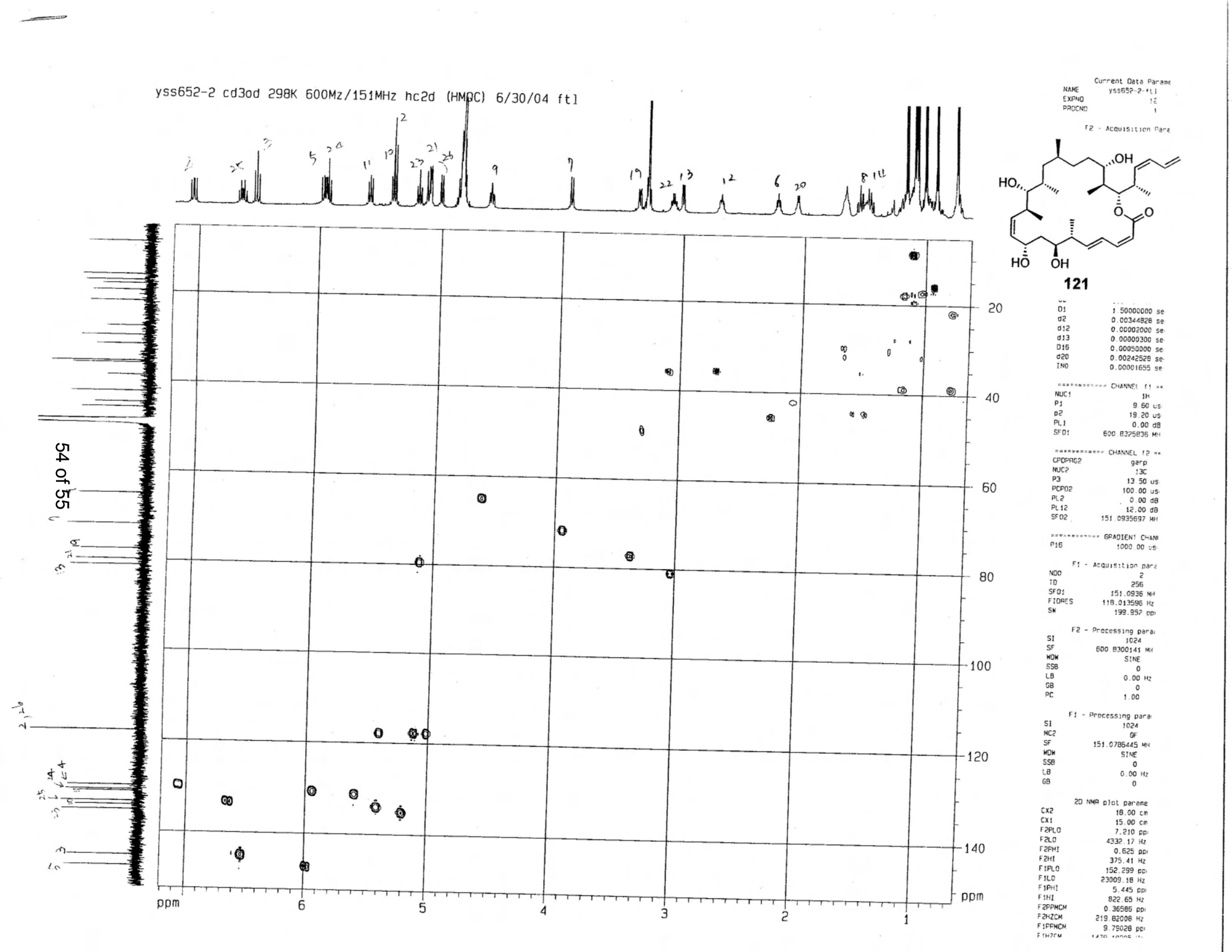
SI	512
SF	600.8300091 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameters

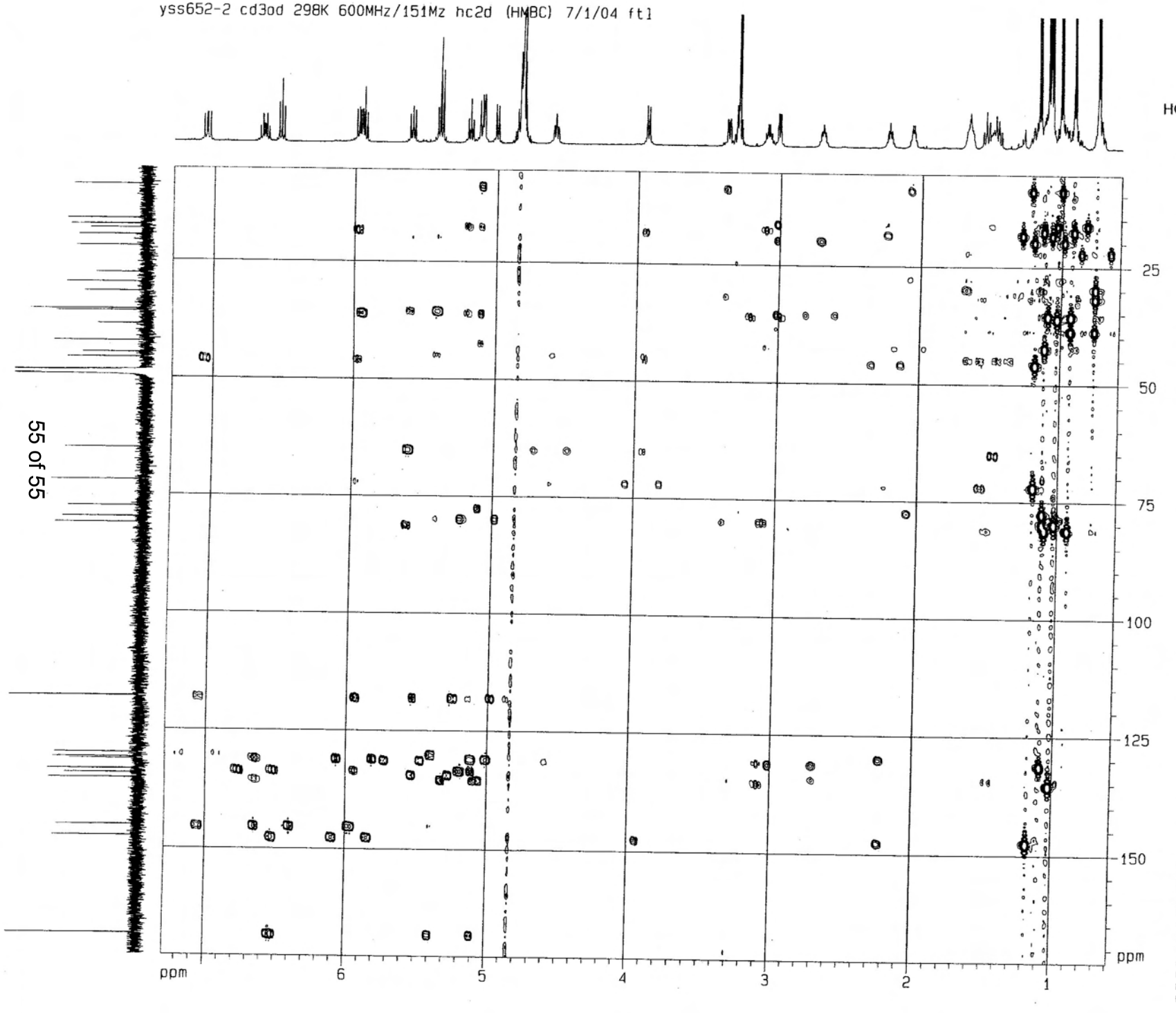
SI	512
MC2	QF
SF	600.8300097 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

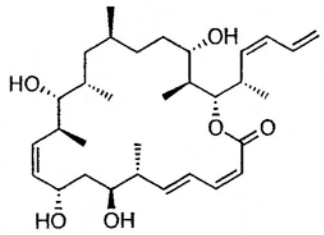
2D NMR plot parameters

CX2	15.00 cm
CX1	15.00 cm
F2PLO	7.327 ppm
F2LO	4402.37 Hz
F2PHI	0.567 ppm
F2HI	340.69 Hz
F1PLO	7.326 ppm
F1LO	4401.75 Hz
F1PHI	0.542 ppm
F1HI	325.41 Hz
F2PPMCM	0.45067 ppm/cm
F2HZCM	270.77859 Hz/cm
F1PPMCM	0.45230 ppm/cm
F1HZCM	271.75613 Hz/cm


yss652-2 cd3od 298K 600Mz/151MHz hc2d (HMQC) 6/30/04 ftl
ppm
ppm
121
Current Data Parame
NAME yss652-2-ftl
EXPNO 12
PROCNO 1
F2 - Acquisition Para
D1 1.50000000 se
d2 0.00344828 se
d12 0.00002000 se
d13 0.00000300 se
D16 0.00050000 se
d20 0.00242528 se
INO 0.00001655 se
CHANNEL f1
NUC1 1H
P1 9.60 us
p2 19.20 us
PL1 0.00 dB
SFO1 600.8325836 MH
CHANNEL f2
CPDPRG2 garp
NUC2 13C
P3 13.50 us
PCPD2 100.00 us
PL2 0.00 dB
PL12 12.00 dB
SFO2 151.0935697 MH
GRADIENT CHAN
P16 1000.00 us
F1 - Acquisition para
NDO 2
TD 256
SFO1 151.0936 MH
FIDRES 118.013596 Hz
SW 199.952 ppm
F2 - Processing para
SI 1024
SF 600.8300141 MH
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
PC 1.00
F1 - Processing para
SI 1024
MC2 QF
SF 151.0786445 MH
WDW SINE
SSB 0
LB 0.00 Hz
GB 0
2D NMR plot parame
CX2 18.00 cm
CX1 15.00 cm
F2PLO 7.210 ppm
F2LO 4332.17 Hz
F2PHI 0.625 ppm
F2HI 375.41 Hz
F1PLO 152.299 ppm
F1LO 23009.18 Hz
F1PHI 5.445 ppm
F1HI 822.65 Hz
F2PPMCM 0.36586 ppm
F2HZCM 219.82008 Hz
F1PPMCM 9.79028 ppm

yss652-2 cd3od 298K 600MHz/151Mz hc2d (HMBC) 7/1/04 ft1





121

Current Data Parameters

NAME	yss652-2-ft1
EXPNO	1122
PROCNO	1

d0	0.00000300 sec
D1	1.00000000 sec
D6	0.05000000 sec
d13	0.00000300 sec
D16	0.00050000 sec
IN0	0.00001655 sec

========== CHANNEL f1 ======

NUC1	1H
P1	9.60 usec
p2	19.20 usec
PL1	0.00 dB
SF01	600.8325836 MHz

========== CHANNEL f2 ======

NUC2	13C
P3	13.50 usec
PL2	0.00 dB
SF02	151.0938719 MHz

========== GRADIENT CHANNEL =

P16	1000.00 usec

F1 - Acquisition parameter

NDO	2
TD	256
SF01	151.0939 MHz
FIDRES	118.013596 Hz
SW	199.952 ppm

F2 - Processing parameter

SI	1024
SF	600.8300155 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

F1 - Processing parameter

SI	2048
MC2	QF
SF	151.0785971 MHz
WDW	SINE
SSB	0
LB	0.00 Hz
GB	0

2D NMR plot parameters

CX2	18.00 cm
CX1	15.00 cm
F2PLO	7.287 ppm
F2LO	4378.05 Hz
F2PHI	0.587 ppm
F2HI	352.89 Hz
F1PLO	172.774 ppm
F1LO	26102.51 Hz
F1PHI	5.610 ppm
F1HI	847.60 Hz
F2PPMCM	0.37219 ppm/cm
F2HZCM	223.62018 Hz/cm
F1PPMCM	11.14427 ppm/cm