SUPPORTING INFORMATION

Efficient Total Syntheses of Resin Glycosides and Analogues by Ring Closing Olefin Metathesis

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General. All reactions were carried out under Ar using Schlenk techniques. All commercially available reagents (Aldrich, Fluka) were used as received. The solvents were dried by distillation over the following drying agents and were transferred under Ar: Et_2O (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), THF (Mg-anthracene), acetonitrile (CaH_2), toluene (Na/K), DMF (Desmodur®/dibutyltin dilaurate), pyridine (first KOH, then CaH_2), triethylamine (first KOH, then CaH_2), MeOH (Mg), EtOH (Mg). Flash chromatography: Merck silica gel 60 (230 - 400 mesh) using hexane/ethyl acetate in various proportions as the eluent. Elemental analyses: Dornis & Kolbe, Mülheim. 6-Heptenoic acid is prepared on large scale according to the procedure reported in the Supporting Information of ref.[35]. NMR: Spectra were recorded on a Bruker AC 200, AMX 300, AMX 400 or DMX 600 spectrometer in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz.

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[35] Fürstner, A.; Seidel, G. *J. Org. Chem.* **1997**, *62*, 2332.

The multiplicity in the ^{13}C NMR spectra refers to the geminal protons (DEPT). In cases where assignments of the signals are given, they are unambiguous and deduced from 2D NMR experiments. IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Varian CH-5 (70 eV); HR-MS: Finnigan MAT SSQ 7000 (70 eV). Specific optical rotations: Perkin Elmer 241. Elemental analyses: Dornis & Kolbe, Mülheim.

5-Hexenal (8). A solution of 5-hexenol (5.00g, 49.9 mmol) in CH_2Cl_2 (100 mL) is added over a period of 30 min to a stirred suspension of PCC (16.15 g, 74.9 mmol) in CH_2Cl_2 (150 mL). After stirring for 4 h at ambient temperature, the insoluble residues are filtered off through a pad of silica which is thoroughly rinsed with CH_2Cl_2 (100 mL in several portions). Evaporation of the combined filtrates gives the rather unstable aldehyde which is immediately used without further purification. ^1H-NMR (200 MHz, $CDCl_3$): δ = 9.77 (t, 1 H, J = 1.6 Hz), 5.77 (ddt, 1 H, J = 17.0 Hz 10.2 Hz 6.7 Hz), 5.09-4.97 (m, 2 H), 2.45 (dt, 2 H, J = 7.3 Hz 1.7 Hz), 2.10 (bq, 2 H, 7.2 Hz), 1.76 (quint., 2 H, J = 7.1). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 201.9, 137.1, 115.1, 42.6, 32.5, 20.7. - MS (EI): m/z (rel. intensity): 98 (>1) [M^+], 80 (46), 70 (11), 69 (17), 55 (41), 54 (100), 44 (14), 43 (12), 42 (30), 39 (58), 29 (31), 27 (29).

(6*S*)-Undec-1-en-6-ol (7). A mixture of (1*R*,2*R*)-bis(trifluoromethanesulfonylamino)cyclohexane (**9**) (229 mg, 0.811 mmol) [20a] and freshly distilled $Ti(O\text{-}iPr)_4$ (20 mL, 67.9 mmol) in toluene (25 mL) is heated at 50 °C for 30 min. The clear solution is then cooled to -35 °C and dipentylzinc (10 g, 48.15 mmol) is added dropwise, causing an intense orange color to appear. A solution of aldehyde **8** (3.87 g, 39.42 mmol) in toluene (10 mL) is slowly introduced and the mixture was stirred at -20 °C for 4 h. The reaction is quenched with saturated aq. NH_4Cl (20 ml), the organic layer is separated, the precipitate is dissolved by adding HCl (10%, ca. 50 mL), and the aqueous layer repeatedly extracted with diethyl ether. The combined organic phases are dried (Na_2SO_4), evaporated, and the crude product purified by flash chromatography with hexane/ethyl acetate (4/1) as the eluent affording pure **7** as a colorless oil (5.74 g, 86%). The enantiomeric excess was determined as ee ≥ 99% by comparison with the racemic product by means of GC on a chiral column: G-TA, trifluoroacetylated γ-cyclodextrine G/212, 30 m (ICT, Internationale Chemie Technik); 70 °C isothermal; 0.9 bar

H_2. $[\alpha]_D^n$ = + 1.6 ° (c 19.2, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.81 (ddt, 1 H, J = 17.0 Hz 10.1 Hz 6.6 Hz), 5.06-4.92 (m, 2 H), 3.59 (br m, 1 H), 2.09-2.02 (m, 2 H), 1.81-1.21 (m, 12 H), 0.89 (t, 3 H, J = 6.3). - ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.8, 114.6, 71.9, 37.5, 36.9, 33.8, 31.9, 25.3, 25.0, 22.7, 14.1. - MS (EI): m/z (rel. intensity): 101 (10), 99 (12), 83 (54), 82 (17), 81 (100), 67 (12), 57 (28), 55 (92), 54 (21), 43 (37), 41 (41), 39 (14), 29 (26), 27 (13). - $C_{11}H_{22}O$ (170.29): *calcd.* C 77.58, H 13.02; *found* C 77.71, H 12.98.

[(6*S*)-1-Undecen-6-yl] 2,3,4-tri-O-acetyl-β-D-fucopyranoside (11). To a solution of 1,2,3,4-tetra-O-acetyl-**D**-fucopyranose (3.0 g, 9.03 mmol)[21] in CH_2Cl_2 (7.5 mL) is added Ac_2O (0.75 mL) and HBr (33% in HOAc, 10 mL) at 0 °C. After stirring the mixture overnight at ambient temperature, the solvents are removed *in vacuo* and the crude 2,3,4-tri-O-acetyl-α-**D**-fucopyranosyl bromide **10** is co-evaporated with toluene in several portions (25 mL each).

A suspension of alcohol **7** (1.05 g, 6.17 mmol) and pre-dried MS 3Å (1.5 g) in CH_2Cl_2 (5 mL) is stirred for 15 min prior to the addition of $AgNO_3$ on silica/alumina (van Boeckel catalyst, 3 g, ca. 9 mmol $AgNO_3$).[22] A solution of crude **10** described above in CH_2Cl_2 (16 mL) is slowly added to this mixture at -10 °C. Stirring is continued for 4 h at that temperature before the mixture is allowed to warm to room temperature overnight. The insoluble residues are filtered off over a pad of silica, rinsed with CH_2Cl_2 in 3 portions (30 mL each), the combined filtrates are evaporated and the residue purified by flash chromatography with hexane/ethyl acetate (4/1) as the eluent affording glycoside **11** as a colorless syrup (1.35 g, 69%). $[\alpha]_D^n$ = - 14.1° (c 10.3, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.78 (ddt, 1 H, J = 17.1 Hz,10.2 Hz, 6.6 Hz), 5.21 (dd, 1 H, J = 1 Hz, 3.5 Hz), 5.15 (dd, 1 H, J = 10.5 Hz, 7.8 Hz), 5.03- 4.94 (m, 3 H), 4.45 (d, 1 H, J = 7.8 Hz), 3.76 (dq, 1 H, J = 1 Hz, 6.3 Hz), 3.55 (q, 1 Hz, J = 5.9 Hz), 2.16 (s, 3 H), 2.04-2.02 (m, 4 H), 1,97 (s, 3 H), 1.50-1.23 (m, 13 H), 1.19 (d, 3 H, J = 6.4 Hz), 0.88 (t, 3 H, J = 6.9 Hz). - ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.3, 169.4, 138.6, 114.7, 100.9, 81.1, 71.6, 70.5, 69.5, 68.9, 34.8, 33.9, 33.5, 31.9, 24.8, 24.3, 22.6, 20.8, 20.7, 20.7, 16.2, 14.1. - MS (EI): m/z (rel. intensity): 273 (25), 184 (53), 171 (10), 157 (74), 153 (30), 142 (35), 115 (32), 111 (20), 97 (11), 83 (25), 69 (11), 55 (20), 43 (100), 41 (11). - $C_{37}H_{55}O_{12}$ (672.65): *calcd.* C 62.42, H 8.65; *found* C 62.49, H 8.62.

[(6*S*)-1-Undecen-6-yl] 3,4-O-isopropylidene-β-D-fucopyranoside (13). Compound **11** (1.90 g, 4.29 mmol) is dissolved in MeOH (10 mL) and treated with KOMe (15 mg, 0.21 mmol) for 6 h. The mixture is neutralized with 2N HCl and the solvent removed *in vacuo.* A solution of crude **12** thus obtained in acetone (5 mL) and 2,2-dimethoxypropane (4 mL) is stirred overnight in the presence of p-TsOH·H_2O (ca. 20 mg). Neutralization with triethylamine, evaporation of the volatiles followed by flash chromatography with hexane/ethyl acetate (4/1) as the eluent affords compound **13** as a colorless syrup (1.20 g, 78%). $[\alpha]_D^n$ = - 0.8 ° (c 11, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.79 (ddt, 1 H, J = 16.9 Hz, 10.2 Hz, 6.6 Hz), 5.04-4.92 (m, 2 H), 4.15 (d, 1 H, J = 8.3 Hz), 4.05-3.97 (m, 2 H), 3.82 (dq, 1 H, J = 6.6 Hz, 2.2 Hz), 3.69-3.56 (m, 2 H), 3.49 (dd, 1 H, J = 8.2 Hz, 7.2 Hz), 2.09-2.02 (m, 2 H), 1.60-1.25 (m, 20 H), 0.89 (t, 3 H, J = 6.8 Hz). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 138.6, 114.7, 109.7, 101.5, 79.5, 79.0, 76.4, 73.7, 68.1, 34.7, 33.8, 33.4, 32.0, 31.9, 28.2, 26.3, 24.5, 22.6, 16.6, 14.1. - MS (EI): m/z (rel. intensity): 187 (30), 131 (27), 129 (16), 128 (11), 111 (10), 101 (53), 100 (74), 99 (100), 97 (17), 85 (13), 83 (41), 73 (59), 71 (56), 69 (21), 59 (76), 57 (29), 55 (45), 43 (50), 41 (29), 29 (14). - $C_{20}H_{36}O_5$ (356.45): *calcd.* C 67.39, H 10.18; *found* C 67.42, H 10.12

O-(2,3-Di-O-acetyl-4,6-O-benzylidene-D-glucopyranosyl) Trichloroacetimidate (17). A suspension of substrate **16** (1.65 g, 5.11 mmol), trichloroacetonitrile (0.94 mL, 9.37 mmol) and Cs_2CO_3 (159 mg, 0.5 mmol) in CH_2Cl_2 (8 mL) is stirred for 12 h at room temperature. The insoluble residues are filtered off and rinsed with the same solvent (75 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography with hexane/ethyl acetate (2/1) as the eluent, thus affording the title compound as a colorless foam (1.82 g, 76%). α : β ≈ 2 : 1 (^{1}H-NMR). - $[\alpha]_D^n$ = + 30.5 ° (c 1.4, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): α-anomer: δ = 8.66 (s, 1 H, NH), 7.47-7.33 (m, 5 H), 6.55 (d, 1 H, J = 3.9 Hz), 5.69 (t, 1 H, J = 9.9 Hz), 5.54 (s, 1 H), 5.15 (dd, 1 H, J = 9.9 Hz, 3.9 Hz), 4.36 (dd, 1 H, J = 10.4 Hz, 4.9 Hz), 4.17-4.09 (m, 1 H), 3.77 (dt, 2 H, J = 10.3 Hz, 6.3 Hz), 2.09 (s, 3 H), 2.03 (s, 3 H); β-anomer (characteristic data): 8.75 (s, NH), 5.99 (d, 1H, J = 7.5 Hz) - ^{13}C-NMR (75 MHz, $CDCl_3$): α-anomer: δ = 170.1, 169.7, 161.2, 141.8, 136.7, 129.2, 128.3, 126.1, 101.6, 93.6, 78.7, 70.4, 68.8, 68.5, 65.1, 20.8, 20.5; β-anomer

(characteristic data): 101.7, 85.9 - MS (EI): m/z (rel. intensity): 495 (5) [M^+], 149 (19), 143 (13), 107 (15), 105 (30), 43 (100). - $C_{19}H_{20}Cl_3NO_8$ (496.73): *calcd.* C 45.94, H 4.06, N 2.82; *found* C 46.10, H 4.14, N 2.85.

Disaccharide 18. $BF_3 \cdot Et_2O$ (0.25M in Et_2O, 1.64 mL) is added to a solution of fucoside **13** (510 mg, 1.43 mmol) and trichloroacetimidate **17** (548 mg, 1.22 mmol) in CH_2Cl_2 (6 mL) and n-hexane (6 mL) at -20 °C. After stirring for 30 min at that temperature, the reaction is quenched with sat. aq. $NaHCO_3$ (20 mL) and the mixture is diluted with CH_2Cl_2 (20 mL). The organic layer is separated, dried over Na_2SO_4, evaporated and the remaining product is purified by flash chromatography with hexane/ethyl acetate (2/1) as the eluent providing compound **18** as a colorless syrup (691 mg, 82%). $[\alpha]_D^n$ = - 20.7 ° (c 19.5, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44-7.34 (m, 5 H), 5.85 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.6 Hz), 5.49 (s, 1 H), 5.33-5.27 (m, 1 H), 5.03-4.94 (m, 3 H), 4.33 (dd, 1 H, J = 10.5 Hz, 5.1 Hz),4.23 (d, 1 H, J = 7.9 Hz), 4.02 (psdt, 1 H, J = 5.7-6.6 Hz), 3.96 (dd, 1 H, J = 5.7 Hz, 2.1 Hz), 3.82-3.44 (m, 6 H), 2.08 (s, 3 H), 2.07-2.05 (m, 1 H), 2.04 (s, 3 H), 1.54-1.26 (m, 23 H), 0.88 (t, 3 H, J = 6.7 Hz). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 170.2, 169.7, 139.1, 136.9, 129.1, 128.2, 126.2, 114.5, 109.7, 101.5, 100.5, 100.3, 79.9, 79.8, 79.4, 78.4, 76.5, 72.9, 72.1, 68.8, 68.5, 66.3, 34.7, 33.9, 33.4, 31.9, 31.6, 27.9, 26.3, 24.8, 24.2, 22.6, 20.8, 16.6, 14.1. - MS (EI): m/z (rel. intensity): 336 (20), 335 (100), 276 (18), 275 (52), 187 (10), 169 (28), 157 (15),149 (76), 127 (13), 109 (15), 107 (14), 105 (16), 100 (83), 99 (93), 97 (18), 91 (10), 83 (21), 81 (10), 69 (21), 59 (12), 57 (17), 55 (23), 43 (86). - $C_{37}H_{54}O_{12}$ (690.82): *calcd.* C 64.23, H 7.87; *found* C 64.25, H 7.95.

Disaccharide 19. A solution of compound **18** (691 mg, 1.0 mmol) in MeOH (10 mL) is treated with KOMe (10 mg) for 4 h at ambient temperature. Neutralization of the mixture with 2N HCl, evaporation of the volatiles *in vacuo* and purification of the residue by flash chromatography with hexane/ethyl acetate (2/1→1/1) affords diol **19** (431 mg, 71%) as a colorless syrup. $[\alpha]_D^n$ = -1.3 ° (c 0.1, CH_2Cl_2).- ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.52-7.35 (m, 5 H), 5.80 (ddt, 1 H, J = 16.9 Hz, 10.3 Hz, 6.7 Hz), 5.51 (s, 1 H), 5.05-4.94 (m, 2 H), 4.64 (d, 1 H, J = 7.7 Hz), 4.30 (dd, 1 H, J = 10.2 Hz, 4.4 Hz), 4.27 (d, 1 H, J = 8.2 Hz), 4.14 (dd, 1 H, J = 5.4 Hz, 2.1 Hz), 3.98 (dd, 1 H, J = 5.4 Hz, 2.1 Hz), 3.86-3.33 (m, 9 H), 2.08-2.03 (m, 2

H), 1.59-1.23 (m, 22 H), 0.89 (t, 3 H, J = 6.9 Hz).- ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 138.7, 137.1, 129.2, 128.3, 126.3, 114.8, 110.3, 104.2, 101.4, 80.9, 80.7, 79.7, 78.7, 76.5, 76.0, 72.7, 68.8, 68.5, 66.9, 34.5, 34.0, 33.2, 31.9, 27.8, 26.2, 24.5, 24.2, 22.6, 16.5, 14.1. - MS (EI): m/z (rel. intensity): 351 (10), 323 (10), 252 (11), 251 (68), 215 (19), 187 (11), 157 (13), 107 (39), 105 (17), 101 (11), 100 (87), 99 (100), 97 (16), 91 (10), 85 (11), 83 (18), 73 (17), 71 (12), 69 (23), 59 (16), 57 (22), 55 (21), 43 (22), 41 (11). - $C_{33}H_{50}O_{10}$ (606.78): *calcd.* C 65.33, H 8.30; *found* C 65.37, H 8.40.

Disaccharide 20. A solution of diol **19** (200 mg, 0.33 mmol), DMAP (20 mg, 0.16 mmol) and DCC (80 mg, 0.39 mmol) in CH_2Cl_2 (10 mL) is stirred for 5 min prior to the addition of 6-heptenoic acid (44 μL, 0.33 mmol). The mixture is stirred overnight, the precipitate formed is filtered off over a short pad of silica, the insoluble residues are thoroughly washed with CH_2Cl_2 (70 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography with hexane/ethyl acetate (2/1) as the eluent providing diene **20** as a colorless solid (168 mg, 71%). $[\alpha]_D^{rt}$ = - 58.8 ° (c 1.6, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44-7.26 (m, 5 H), 5.80 (ddt, 1 H, J = 17 Hz, 10.1 Hz, 6.7 Hz), 5.71 (ddt, 1 H, J = 17.0 Hz, 10.1 Hz, 6.7 Hz), 5.47 (s, 1 H), 5.26 (t, 1 H, J = 9.3 Hz), 5.05-4.87 (m, 4 H), 4.74 (d, 1 H, J = 7.7 Hz), 4.33 (dd, 1 H, J = 10.5 Hz, 4.6 Hz), 4.28 (d, 1 H, J = 8.2 Hz), 4.13 (dd, 1 H, J = 7.4 Hz, 5.5 Hz), 4.00 (dd, 1 H, J = 5.5 Hz, 2.1 Hz), 3.82-3.45 (m, 8 H), 2.38 (t, 2 H, J = 7.3 Hz), 2.04 (m, 4 H), 1.70-1.25 (m, 23 H), 0.89 (t, 3 H, J = 6.8 Hz). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 173.1, 138.7, 138.4, 137.0, 129.0, 128.2, 126.1, 114.7, 114.6, 110.2, 104.3, 101.4, 100.2, 80.8, 79.4, 78.9, 78.7, 76.6, 74.2, 72.7, 68.8, 68.6, 66.9, 34.5, 34.2, 33.9, 33.3, 33.1, 31.9, 28.1, 27.9, 26.2, 24.6, 24.5, 24.2, 22.6, 16.5, 14.1. - MS (EI): m/z (rel. intensity): 363 (13), 361 (48), 233 (28), 187 (23), 157 (12), 149 (18), 127 (18), 111 (33), 107 (40), 105 (14), 100 (75), 99 (100), 97 (25), 91 (11), 85 (12), 83 (41), 71 (13), 69 (31), 59 (14), 57 (17), 55 (50), 43 (22), 41 (14). - $C_{40}H_{60}O_{11}$ (716.86): *calcd.* C 67.02, H 8.44, *found* C 67.52, H 8.19.

Macrocycle 21. Solutions of diene **20** (161 mg, 0.224 mmol) and of the ruthenium carbene **22** (11 mg, 5 mol%) in CH_2Cl_2 each (50 mL) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (50 mL) over a period of 8 h. Reflux is continued for 72 h until

TLC shows complete conversion of the substrate. The solvent is removed *in vacuo*, the residue is dissolved in CH_2Cl_2 (5 mL) and filtered through a short pad of silica in order to remove the ruthenium catalyst. The solvent is removed and the residue co-evaporated with EtOH (3 x 5 mL). The crude cycloalkene thus obtained (*E,Z*-mixture) is dissolved in EtOH (15 mL) and hydrogenated (1 atm H_2) over Pd/C (5 % w/w, 20 mg) for 8 h at ambient temperature. Filtration of the catalyst, removal of the solvent and flash chromatography with hexane/ethyl acetate (2/1) affords macrocycle **21** as a colorless solid (119 mg, 77%). $[\alpha]_D^n$ = - 33.6 ° (c 6, CH_2Cl_2). - ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.47-7.32 (m, 5H), 5.51 (s, 1H), 5.24 (t, 1H, J = 9 Hz), 5.06 (d, 1H, J = 7.5 Hz), 4.27 (dd, 1H, J = 10.6 Hz, 5.0 Hz), 4.24 (d, 1H, J = 8.3 Hz), 4.17 (dd, 1H, J = 7.3 Hz, 5.4 Hz), 3.95-3.73 (m, 5H), 3.60-3.39 (m, 3H), 2.47-2.31 (m, 2H), 1.70-1.27 (m, 33H), 0.88 (t, 3H, J = 6.8 Hz). - ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 174.7, 137.1, 129.1, 128.2, 126.2, 109.7, 102.3, 101.6, 98.8, 83.1, 79.4, 78.3, 76.8, 75.1, 74.7, 74.6, 68.8, 66.2, 35.9, 35.6, 34.9, 31.9, 30.5, 29.3, 28.4, 28.3, 27.9, 26.9, 26.5, 25.8, 25.3, 22.6, 16.7, 14.1. - MS (EI): m/z (rel. intensity): 488 (12), 487 (29), 237 (22), 233 (19), 187 (17), 149 (19), 127 (21), 111 (10), 107 (49), 105 (21), 100 (69), 99 (100), 97 (17), 95 (11), 91 (23), 85 (17), 83 (19), 81 (12), 71 (11), 69 (30), 59 (24), 57 (26), 55 (37), 43 (32), 41 (16). The data are in agreement with those reported in ref.[13].

Disaccharide 25a. A solution of diol **19** (100 mg, 0.165 mmol), DMAP (10 mg, 0.08 mmol) and DCC (40 mg, 0.194 mmol) in CH_2Cl_2 (5 mL) is stirred for 10 min prior to the addition of 4-pentenoic acid (17 µL, 0.165 mmol). The mixture is stirred overnight, the precipitate formed is filtered off over a short pad of silica, the insoluble residues are thoroughly washed with CH_2Cl_2 (50 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography (hexane/ethyl acetate 4:1). This affords diene **25a** as a colorless syrup (91 mg, 80 %). $[\alpha]_D^n$ = - 46.0 ° (c 0.7, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.44-7.26 (m, 5 H), 5.85-5.75 (m, 2 H), 5.47 (s, 1 H), 5.27 (t, 1 H, J = 9.4 Hz), 5.11-4.89 (m, 4 H), 4.75 (d, 1 H, J = 7.7 Hz), 4.33 (dd, 1 H, J = 10.5 Hz, 4.8 Hz), 4.25 (d, 1 H, J = 7.7 Hz), 4.14 (dd, 1 H, J = 7.3 Hz, 5.5 Hz), 3.99 (dd, 1 H, J = 5.4 Hz, 2.1 Hz), 3.80-3.49 (m, 7 H), 2.47-2.39 (m, 5 H), 2.10-2.03 (m, 2 H), 1.53-1.28 (m, 20 H), 0.89 (t, 3 H, J = 6.6 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.5, 138.7, 136.9, 136.6, 128.2, 126.1, 115.4,

114.7, 110.2, 104.2, 101.4, 100.2, 80.7, 79.4, 78.8, 78.7, 76.6, 74.2, 72.9, 68.6, 66.9, 34.5, 33.9, 33.6, 33.1, 31.9, 28.9, 28.6, 27.9, 26.2, 24.6, 24.2, 22.6, 16.5, 14.1. – HRMS ($C_{38}H_{56}NaO_{11}$): *calcd.* 711.372023, found 711.368491.

Disaccharide 25b. A solution of diol **19** (100 mg, 0.165 mmol), DMAP (10 mg, 0.08 mmol) and DCC (40 mg, 0.194 mmol) in CH_2Cl_2 (5 mL) is stirred for 10 min prior to the addition of 10-undecenoic acid (34 µL, 0.165 mmol). The mixture is stirred overnight, the precipitate formed is filtered off over a short pad of silica, the insoluble residues are thoroughly washed with CH_2Cl_2 (40 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography (hexane/ethyl acetate 4:1). This affords diene **25b** as a colorless syrup (85 mg, 67 %). $[\alpha]_D^n$ = - 53.5 ° (c 0.55, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.43-7.26 (m, 5 H), 5.87-5.73 (m, 2 H), 5.47 (s, 1 H), 5.26 (t, 1 H, J = 10.0 Hz), 5.05-4.89 (m, 4 H), 4.75 (d, 1 H, J = 7.7 Hz), 4.33 (dd, 1 H, J = 10.4 Hz, 4.7 Hz), 4.28 (d, 1 H, J = 8.2 Hz), 4.14 (dd, 1 H, J = 7.4 Hz, 5.5 Hz), 4.00 (dd, 1 H, J = 5.5 Hz, 2.1 Hz), 3.80-3.49 (m, 7 H), 2.36 (t, 2 H, J = 7.3 Hz), 2.04-1.99 (m, 4 H), 1.53-0.92 (m, 33 H), 0.89 (t, 3 H, J = 6.6 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 173.2, 139.2, 138.7, 137.0, 129.0, 128.2, 126.1, 114.7, 114.1, 110.2, 104.2, 101.4, 100.2, 80.8, 79.4, 78.9, 78.7, 76.6, 74.2, 72.7, 68.6, 66.9, 34.5, 34.4, 33.9, 33.8, 33.1, 31.9, 29.2, 29.1, 29.0, 28.9, 28.8, 27.9, 26.2, 25.1, 24.2, 22.6, 16.5, 14.1.

Macrocycle 26. Solutions of diene **25a** (81 mg, 0.117 mmol) and the ruthenium carbene **22** (22 mg, 10 mol%) in CH_2Cl_2 (50 mL) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (50 mL) over a period of 12 h. Reflux is continued for 12 h until TLC shows complete conversion of the substrate. The solvent is removed in vacuo, the residue is dissolved in CH_2Cl_2 (5 mL) and filtered through a short pad of silica in order to remove the ruthenium catalyst. The isoluble residues are thoroughly washed with CH_2Cl_2 (40 mL in several portions), the combined filtrates are evaporated and the residue co-evaporated with EtOH (3 x 5 mL). The crude mixture of cycloalkenes thus obtained is dissolved in EtOH (10 mL) and hydrogenated (1 atm H_2) over Pd/C (5 % w/w, 20 mg) overnight. Filtration of the catalyst, removal of the solvent and flash chromatography (hexane/ethyl acetate 2:1) affords compound **26** as a colorless syrup (61 mg, 76 %). $[\alpha]_D^n$ = - 52.4 ° (c 0.95, CH_2Cl_2). – ^{1}H-

NMR (300 MHz, $CDCl_3$) δ = 7.47-7.33 (m, 5 H), 5.58 (s, 1 H), 5.14 (d, 1 H, J = 4.8 Hz), 4.95 (dd, 1 H, J = 9.5 Hz, 5.0 Hz), 4.37-4.32 (m, 3 H), 4.15-4.13 (m, 2 H), 3.99 (dd, 1 H, J = 5.4 Hz, 2.1 Hz), 3.93-3.77 (m, 7 H), 2.50-2.36 (m, 2 H), 1.77-1.23 (m, 28 H), 0.88 (t, 3 H, J = 6.5 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 174.6, 137.2, 129.1, 128.3, 126.1, 109.8, 101.4, 100.1, 99.0, 79.7, 79.5, 77.5, 76.7, 76.5, 76.4, 73.5, 73.1, 69.1, 68.8, 66.3, 34.7, 34.3, 33.8, 31.9, 28.4, 27.9, 27.7, 26.6, 25.3, 24.6, 22.9, 22.6, 16.5, 14.1.- HRMS ($C_{36}H_{54}NaO_{11}$): *calcd.* 685.356382, *found* 685.356140.

Macrocycle 27. Prepared using the same protocole as described above for compound **26**, using diene **25b** (84 mg, 0.108 mmol) and the ruthenium carbene **22** (10 mg, 10 mol%). Flash chromatography (hexane/ethyl acetate 2:1) affords compound **27** as a colorless syrup (61 mg, 76 %). $[\alpha]_D^n$ = - 53.3 ° (c 0.75, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.54-7.33 (m, 5 H), 5.49 (s, 1 H), 5.27 (t, 1 H, J = 9.3 Hz), 4.97 (d, 1 H, J = 7.8 Hz), 4.34 (dd, 1 H, J = 10.6 Hz, 5.0 Hz), 4.16 (dd, 1 H, J = 7.1 Hz, 5.5 Hz), 3.97 (dd, 1 H, J = 5.4 Hz, 2.1 Hz), 3.84-3.48 (m, 7 H), 2.43-2.34 (m, 4 H), 1.72-1.19 (m, 37 H), 0.89 (t, 3 H, J = 6.5). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ: 173.9, 137.0, 128.9, 128.2, 128.1, 126.3, 126.1, 126.0, 109.9, 101.4, 101.2, 101.0, 81.4, 79.8, 78.9, 77.3, 76.7, 73.6, 68.7, 66.5, 35.2, 34.3, 33.8, 32.0, 29.9, 29.2, 28.8, 28.2, 27.9, 27.8, 27.6, 27.3, 27.1, 26.4, 25.0, 24.7, 24.6, 22.6, 16.7, 14.1.– HRMS ($C_{42}H_{66}NaO_{11}$): *calcd.* 769.450273, *found* 769.4514474.

3,4-Di-*O*-acetyl-1,2-*O*-[1-(exo-ethoxy)ethyliden]-β-L-rhamnopyranose (29). To a solution of 1,2,3,4-tetra-O-acetyl-**L**-rhamnopyranose (6.6 g, 19.86 mmol) in CH_2Cl_2 (20 mL) is added Ac_2O (2.5 mL, 26.5 mmol) and HBr (33% in HOAc, 23 mL) at 0 °C. After stirring the mixture overnight at ambient temperature, the solvents are removed in vacuo and the crude 2,3,4-tri-O-acetyl-α-**L**-rhamnopyranosyl bromide **28** is co-evaporated with toluene (3 x 25 mL). A solution of **28** and tetrabutylammonium bromide (2.83 g, 8.8 mmol) in *sym*-collidine (10 mL) and EtOH (2 mL) is heated at 80 °C for 8 h. The precipitate formed is dissolved by adding ethyl acetate (100 mL) and water (50 mL), the organic layer is separated, dried over Na_2SO_4, evaporated and the crude product purified by flash chromatography (Alox N, hexane/ethyl acetate 4:1) affording pure **29** as a colorless solid (4.17 g, 66 %). $[\alpha]_D^n$ = + 30.6 ° (c 2.15, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.40 (d, 1 H, J = 2.3 Hz), 5.12-5.02

(m, 2 H), 4.58 (dd, 1 H, J = 3.8 Hz, 2.4 Hz), 3.63-3.49 (m, 3 H), 2.11 (s, 3 H), 2.06 (s, 3 H), 1.74 (s, 3 H), 1.23 (d, 3 H, J = 6.2 Hz), 1.18 (t, 3 H, J = 7.1 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.5, 169.8, 124.2, 97.2, 76.7, 70.8, 70.8, 70.4, 69.2, 58.1, 24.9, 20.8, 20.7, 17.5, 15.1. –MS (EI): m/z (rel intensity): 273 (12), 231 (10), 153 (10), 111 (13), 99 (12), 83 (15), 43 (100). – $C_{14}H_{22}O_8$ (318.32): *calcd.* C 52.83, H 6.97; *found* C 52.68, H 6.91.

3,4-Di-*O*-benzyl-1,2-*O*-[1-(exo-ethoxy)ethyliden]-β-L-rhamnopyranose (30). A solution of ortho ester **29** (2.3 g, 7.22 mmol), finely ground KOH (4 g, 71.3 mmol) and benzyl bromide (3.5 mL, 29.4 mmol) in THF (40 mL) is refluxed for 8 h. The suspension is diluted with CH_2Cl_2 (100 mL), washed with water (3 x 100 mL), saturated aqueous $NaHCO_3$ and water (2 x 50 mL), dried over Na_2SO_4 and evaporated. Flash chromatography (hexane/ethyl acetate 4:1) of the residue delivers compound **30** as a colorless solid (2.34 g, 78 %). $[\alpha]_D^{rt}$ = + 65.1 ° (c 1.6, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.41-7.25 (m, 10 H), 5.26 (d, 1 H, J = 2.3 Hz), 4.96 (d, 1 H, A part of AB, J = 10.9 Hz), 4.77 (s, 2 H), 4.67 (d, 1 H, B part of AB, J = 10.9 Hz), 4.37 (dd, 1 H, J = 2.4 Hz, 4.0 Hz), 3.68 (dd, 1 H, J = 4.1 Hz, 9.1 Hz), 3.60-3.45 (m, 3 H), 3.34-3.29 (m, 1 H), 1.74 (s, 3 H), 1.31 (d, 3 H, J = 6.1 Hz), 1.20 (t, 3 H, J = 3.8 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.3, 137.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 123.6, 97.3, 79.6, 79.1, 75.5, 72.3, 70.3, 58.0, 24.8, 17.9, 15.3. – MS (EI): m/z (rel intensity): 91 (100). – $C_{24}H_{30}O_6$ (414.50): *calcd.* C 69.55, H 7.29; *found* C 69.32, H 7.26.

***O*-(2-*O*-Acetyl-3,4-di-*O*-benzyl-α-L-rhamnopyranosyl) Trichloroacetimidat (33).** Compound **30** is dissolved in AcOH/water (4:1, 12.5 mL) and the mixture is stirred for 16 h at ambident temperature. The solvents are evaporated and the residue is purified by flash chromatography (hexane/ethyl acetate 4:1 → 2:1). A suspension of the resulting mixture of acetates **31** and **32**, trichloroacetonitrile (5 mL, 49.86 mmol) and Cs_2CO_3 (450 mg, 1.38 mmol) in CH_2Cl_2 (10 mL) is stirred for 14 h at room temperature. The insoluble residues are filtered off and rinsed with the same solvent (40 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography (hexane/ethyl acetate 4:1), thus affording imidate **33** as a colorless syrup (1.38 g, 46 %). $[\alpha]_D^{rt}$ = - 19.6 ° (c 9.5, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.65 (s, 1 H), 7.37-7.23 (m, 10 H), 6.18 (d, 1 H, J = 1.9 Hz), 5.49 (dd, 1 H, J = 2.0 Hz, 3.3 Hz), 4.93 (d, A part of AB, J =

10.8 Hz), 4.73 (d, 1 H, A part of AB, J = 11.2 Hz), 4.63 (d, B part of AB, J = 10.8 Hz), 4.57 (d, 1 H, B part of AB, J = 11.3 Hz), 4.01-3.92 (m, 2 H), 3.53 (t, 1 H, J = 9.6 Hz), 2.18 (s, 1 H), 1.35 (d, 3 H, J = 6.2 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 169.9, 160.1, 138.4, 137.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.5, 95.2, 79.3, 77.5, 77.2, 77.1, 76.6, 75.6, 71.9, 70.7, 67.6, 20.9, 17.9. –MS (EI): m/z (rel intensity): 91 (100), 43 (16). – $C_{24}H_{26}Cl_3NO_6$ (530.83): *calcd.* C 54.30, H 4.98; *found* C 54.15, H 4.84.

Disaccharide 34 and 36. A solution of diol **19** (237 mg, 0.39 mmol) in toluene (150 mL) is refluxed in a Dean Stark apparatus for 6 h in the presence of bis(tributyltin) oxide (200 µL, 0.39 mmol) with azeotropic removal of water. The solution is concentrated to 30 mL, tetrabutylammonium iodide (100 mg, 0.27 mmol) and benzyl bromide (3 mL, 25.2 mmol) are added, and the resulting mixture is refluxed for 5 h. After evaporation of all volatiles, flash chromatography (hexane ethyl acetate 4:1) provides compounds **36** (48 mg, 18 %) and **34** (155 mg, 57 %). Data of **36**: $[\alpha]_D^n$ = - 19.8 ° (c 2.5, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56-7.26 (m, 10 H), 5.81 (ddt, 1 H, J = 17.0 Hz, 10.2 Hz, 6.6 Hz), 5.62 (s, 1 H), 5.02-4.94 (m, 3 H), 4.74 (d, 1 H, J = 11.7 Hz), 4.31-4.25 (m, 2 H), 4.12-4.08 (m, 1 H), 3.95-3.30 (m, 9 H), 2.06 (q, 2 H, J = 6.2 Hz), 1.69-1.28 (m, 22 H), 0.89 (t, 3 H, J = 6.9 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.9, 128.5, 128.3, 127.8, 126.3, 114.6, 109.8, 101.8, 101.1, 100.8, 82.6, 80.7, 80.0, 79.2, 77.6, 76.5, 74.7, 73.3, 68.9, 68.5, 66.1, 34.9, 33.9, 33.6, 31.9, 28.3, 27.7, 26.8, 26.3, 24.9, 24.4, 22.6, 17.3, 16.7, 14.1, 13.6. – MS (EI): m/z (rel. intensity): 341 (12), 215 (39), 163 (17), 149 (10), 100 (18), 99 (32), 91 (100). – HRMS ($C_{40}H_{56}NaO_{10}$): *calcd.* 719.377117, *found* 719.375757.

Data of **34**: $[\alpha]_D^n$ = - 21.1 ° (c 2.4, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56-7.26 (m, 10 H), 5.81 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.7 Hz), 5.05-4.85 (m, 3 H), 4.67 (d, 1 H, J = 7.3 Hz), 4.34-4.27 (m, 2 H), 4.15 (dd, 1 H, J = 5.6 Hz, 7.3 Hz), 4.01 (dd, 1 H, J = 2.1 Hz, 5.5 Hz), 3.80-3.45 (m, 8 H), 2.06-2.03 (m, 2 H), 1.64-1.28 (m, 22 H), 0.89 (t, 3 H, J = 6.9 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 138.8, 128.9, 128.3, 128.2, 127.9, 127.5, 126.1, 114.7, 110.2, 104.3, 101.3, 100.4, 81.4, 80.8, 79.9, 79.6, 78.8, 75.9, 74.5, 68.9, 68.6, 66.9, 34.5, 33.9, 33.1, 31.9, 27.9, 26.8, 26.3, 24.6, 24.3, 22.6, 17.3, 16.6, 14.1, 13.6. –MS (EI): m/z (rel

intensity): 341 (18), 107 (12), 100 (35), 99 (50), 91 (100). – HRMS ($C_{40}H_{56}NaO_{10}$): *calcd.* 719.377136, *found* 719.376788.

Disaccharide 35. Acetic anhydride (10 µL, 0.101 mmol) is added to a solution of **34** (47 mg, 0.067 mmol) and DMAP (20 mg, 0.163 mmol) in CH_2Cl_2 (5 mL) and the mixture is stirred overnight. A standard extractive work-up followed by flash chromatography (hexane/ethyl acetate 2:1) affords acetate **35** (46 mg, 92 %) as a colorless syrup. $[\alpha]_D^n$ = - 20.4 ° (c 1.95, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.50-7.25 (m, 10 H), 5.84 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.6 Hz), 5.57 (s, 1 H), 5.06-4.94 (m, 3 H), 4.88-4.66 (m, 3 H), 4.32 (dd, 1 H, J = 10.5 Hz, 5.0 Hz), 4.23 (d, 1 H, J = 7.8 Hz), 4.03-3.39 (m, 8 H), 2.13-2.03 (m, 5 H), 1.53-1.26 (m, 22 H), 0.88 (t, 3 H, J = 3.5 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.4, 139.2, 138.4, 137.4, 128.9, 128.3, 127.8, 127.6, 126.0, 114.5, 109.6, 101.2, 100.9, 100.5, 81.5, 79.9, 79.5, 78.6, 76.4, 73.9, 73.5, 68.9, 68.4, 66.1, 34.7, 33.9, 33.4, 31.9, 27.9, 26.3, 24.8, 24.2, 22.6, 21.0, 16.6, 14.1. – HRMS ($C_{42}H_{58}NaO_{11}$): *calcd.* 761.387682, *found* 761.389458.

Disaccharide 37. Prepared as described above using acetic anhydride (0.5 mL, 5.3 mmol), disaccharide **36** (40 mg, 0.057 mmol), triethylamine (2 mL, 35.9 mmol) and DMAP (cat.) in CH_2Cl_2 (5 mL). Flash chromatography (hexane/ethyl acetate 2:1) of the crude product affords **37** as a colorless syrup (34 mg, 80 %). $[\alpha]_D^n$ = - 19.6 ° (c 1, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.43-7.25 (m, 10 H), 5.84 (ddt, 1 H, J = 17.2 Hz, 10.3 Hz, 6.7 Hz), 5.45 (s, 1 H), 5.30 (t, 1 H, J = 9.3 Hz), 5.10 (d, 1 H, J = 7.4 Hz), 5.05-4.93 (m, 2 H), 4.88 (d, 1 H, A part of AB, J = 12.0 Hz), 4.66 (d, 1 H, B part of AB, J = 12.0 Hz), 4.32-4.27 (m, 2 H), 4.12 (t, 1 H, J = 6.5 Hz), 3.95 (dd, 1 H, J = 5.7 Hz, 2.1), 3.84-3.38 (m, 6 H), 2.11-2.06 (m, 2 H), 1.94 (s, 3 H), 1.57-1.31 (m, 22 H), 0.89 (t, 3 H, J = 3.5 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 169.9, 138.9, 138.5, 137.1, 131.1, 128.9, 128.3, 128.2, 127.7, 127.6, 126.2, 114.7, 109.8, 101.3, 101.2, 100.6, 80.4, 79.7, 79.2, 78.8, 77.2, 76.5, 74.4, 72.8, 68.9, 68.6, 66.1, 34.9, 33.9, 33.5, 31.9, 27.7, 26.3, 24.9, 24.5, 22.6, 20.9, 16.6, 14.1. – HRMS ($C_{42}H_{58}NaO_{11}$): *calcd.* 761.387512, *found* 761.387379.

Trisaccharide 38. $BF_3{\cdot}OEt_2$ (0.25 M in Et_2O, 0.44 mL) is added to a solution of compound **34** (155 mg, 0.220 mmol) and trichloroacetimidate **33** (150 mg, 0.220 mmol) in CH_2Cl_2 (10 mL) and hexane (10 mL) at – 20 °C. After stirring for 1 h, the reaction is quenched with

saturated aqueous $NaHCO_3$ (10 mL) and the mixture is diluted with CH_2Cl_2 (25 mL). The organic layer is separated, dried over Na_2SO_4, evaporated and the remaining product is purified by flash chromatography (hexane/ethyl acetate 4:1) providing trisaccharide **38** as a colorless syrup (125 mg, 53 %). $[\alpha]_D^n$ = - 23.2 ° (c 5.25, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.46-7.23 (m, 20 H), 5.84 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.5 Hz), 5.54 (s, 1 H), 5.48 (dd, 1H, J =3.3 Hz, 1.9 Hz), 5.33 (d, 1 H, J = 1.8 Hz), 5.07-4.88 (m, 7 H), 4.72 (d, 1 H, B part of AB, J = 11.1 Hz), 4.71 (d, 1 H, A part of AB, J = 11.3 Hz), 4.57 (d, 1 H, B part of AB, J = 10.7 Hz), 4.46 (d, 1 H, B part of AB, J = 11.3 Hz), 4.31 (dd, 1 H, J = 10.5 Hz, 4.9 Hz), 4.21-4.12 (m, 3 H), 3.93 (dd, 1 H, J = 9.2 Hz, 3.4 Hz), 3.81-3.36 (m, 8 H), 2.10-2.04 (m, 4 H), 1.59-1.19 (m, 23 H), 0.89 (t, 3 H, J = 6.6 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 170.0, 139.2, 138.1, 137.4, 128.9, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6, 127.5, 125.9, 114.5, 109.6, 101.1, 82.0, 81.8, 81.1, 80.2, 79.4, 78.2, 77.7, 71.6, 68.3, 68.2, 67.5, 34.9, 33.9, 33.7, 32.0, 27.7, 26.3, 24.8, 24.1, 22.6, 18.3, 16.6, 14.1. – MS (APCI): 1082 ($M + H_2O$).

Trisaccharide 40. A solution of compound **38** (84 mg, 0.079 mmol) in methanol (5 mL) is treated with KOMe (10 mg, 0.14 mmol) for 4 h at ambient temperature. Neutralization of the mixture with 2 N HCl and evaporation of the volatiles in vacuo afforded crude **39** which is used without further purification. 6-Heptenoic acid (10 µl, 0.089 mmol) is added to a solution of this compound, DMAP (cat.) and DCC (16 mg, 0.078 mmol) in CH_2Cl_2 (10 mL) and the mixture is stirred overnight. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate 4:1) affords diene **40** (75 mg, 84 %) as a colorless syrup. $[\alpha]_D^n$ = - 13.5 ° (c 3.75, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.47-7.24 (m, 20 H), 5.84 (ddt, 1 H, J = 17.3 Hz, 10.2 Hz, 6.5 Hz), 5.75 (ddt, 1 H, J = 17.0 Hz, 10.2 Hz, 6.7 Hz), 5.55 (s, 1 H), 5.50 (dd, 1 H, J = 3, 2 Hz), 5.33 (d, 1 H, J = 1.7 Hz), 5.07-4.88 (m, 9 H), 4.73 (d, 1 H, B part of AB, J = 11.1 Hz), 4.71 (d, 1 H, A part of AB, J = 11.2 Hz), 4.56 (d, 1 H, B part of AB, J = 10.7 Hz), 4.46 (d, 1 H, B part of AB, J = 11.2 Hz), 4.33-4.08 (m, 4 H), 3.93 (dd, 1 H, J = 9.2 Hz, 3.3 Hz), 3.85-3.62 (m, 5 H), 3.51-3.34 (m, 4H), 2.37 (dt, 2 H, J = 7.5 Hz, 2.8 Hz), 2.07-1.99 (m, 4 H), 1.67-1.23 (m, 24 H), 1.19 (d, 3 H, J = 6.5 Hz), 0.89 (t, 3 H, J = 6.5 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 172.7, 139.2, 138.5, 128.4, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 125.9, 114.7, 114.5, 109.6, 101.1, 81.2, 77.6, 76.2, 71.5, 68.2,

65.8, 34.9, 34.1, 34.0, 33.7, 33.4, 32.0, 28.2, 27.7, 26.3, 24.8, 24.5, 24.1, 22.6, 18.3, 16.6, 14.1. – HRMS ($C_{67}H_{88}NaO_{15}$): *calcd.* 1155.602091, *found* 1155.603376.

Macrocycle 41. Solutions of diene **40** (65 mg, 0.047 mmol) and the ruthenium carbene **22** (5 mg, 0.005 mmol, 10 mol%) in CH_2Cl_2 each (50 mL) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (50 mL) over a period of 8 h. Reflux is continued for 14 h until TLC shows complete conversion of the substrate. The solvent is removed in vacuo, the residue is dissolved in CH_2Cl_2 (7 mL) and filtered through a short pad of silica in order to remove the ruthenium catalyst. The isoluble residues are thoroughly washed with CH_2Cl_2 (30 mL in several portions), the combined filtrates are evaporated and the residue co-evaporated with EtOH (3 x 10 mL). The crude mixture of cycloalkene thus obtained is dissolved in EtOH (10 mL) and hydrogenated (1 atm H_2) over $Rh(PPh_3)_3Cl$ (16 mg, 0.017 mmol, 37 mol%) overnight. Removal of the solvent and subsequent flash chromatography (hexane/ethyl acetate 4:1) affords compound **41** (59 mg, 93 %) as a colourless syrup. $[\alpha]_D^{rt}$ = - 27.3 ° (c 2.95, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.46-7.21 (m, 20 H), 5.53 (s, 1 H), 5.45 (m, 1 H), 4.97-4.85 (m, 5 H), 4.59 (pst, 2 H, J = 10.7 Hz, 10.5 Hz), 4.41 (d, 1 H, B part of AB, J = 11.2 Hz), 4.31-3.35 (m, 18 H), 2,51-2.32 (m, 2 H), 1.72-1.18 (m, 33 H), 0.88 (t, 3 H, J = 6.2 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 172.9, 138.7, 138.2, 138.1, 128.6, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 126.0, 109.6, 101.1, 81.9, 80.5, 80.5, 79.9, 77.9, 76.8, 75.6, 71.6, 65.6, 35.2, 31.9, 30.2, 29.2, 28.9, 28.5, 27.8, 27.8, 26.6, 25.2, 25.0, 22.6, 18.4, 16.7, 14.1. –HRMS ($C_{65}H_{86}NaO_{15}$): *calcd.* 1129.586440, *found* 1129.584461.

Tricolorin G (2). To a solution of macrocycle **41** (45 mg, 0.041 mmol) in wet CH_2Cl_2 (5 mL) is added trifluoroacetic acid (50 µL, 0.65 mmol) and the solution is stirred for 3 h at ambient temperature. The mixture is treated with triethylamine (2 mL, 14.35 mmol), evaporated in vacuo and the crude residue is dissolved in methanol (10 mL). Pd/C (5 % w/w, 50 mg) and trifluoroacetic acid (100 µL, 1.3 mmol). The reaction flask is filled with H_2 (three freeze/thaw cycles) and the solution is stirred under H_2-atmosphere overnight. For work-up, triethylamine (2 mL, 14.35 mL) is added, the mixture is filtered through a small plug of Celite which is thoroughly washed with methanol (20 mL). The combined filtrates are concentrated and purified by HPLC (125 mm x 20 mm BIAX-column; Nucleosil-7-100-C_{18}/A, 95/25;

mobile phase: acetonitrile/water 60/40) affording compound **2** as a colorless syrup (14.1 mg, 49 %). $[\alpha]_D^n$ = - 41.3 ° (c 0.15, MeOH). – ^{1}H-NMR (600 MHz, d_5-Pyridin) δ = 6.11 (dd, 1 H, J = 3.3 Hz, 1.7 Hz) [Rha H2], 5.74 (d, 1 H, J = 7.7 Hz) [Glu H1], 5.67 (d, 1 H, J = 1.7 Hz) [Rha H1], 4.83 (dq, 1 H, J = 9.5 Hz, 6.2 Hz) [Rha H5], 4.76 (d, 1 H, J = 7.9 Hz) [Fuc H1], 4.75 (dd, 1 H, J = 9.4 Hz, 3.3 Hz) [Rha H3], 4.68 (dd, 1 H, J = 9.4 Hz, 7.9 Hz) [Fuc H2], 4.25 (dd, 1 H, J = 9.5 Hz, 9.5 Hz) [Rha H4], 4.22 (dd, 1 H, J = 9.5 Hz, 3.5 Hz) [Fuc H3], 4.08 [Glu H3], 4.06 [Glu H4], 4.05 [Glu H6], 3.93 (t, 1 H, J = 7.7 Hz) [Glu H2], 3.88 (q, 1 H, J = 5.3 Hz) [Jal H11], 3.83 (dd, 1 H, J = 3.5 Hz, 0.7 Hz) [Fuc H4], 3.73 (dq, 1 H, J = 6.4 Hz, 0.7 Hz) [Fuc H5], 3.52 (dt, 1 H, J = 9 Hz, 3.9 Hz) [Glu H5], 2.44 (ddd, 1 H, J = 14.0 Hz, 8.5 Hz, 3.5 Hz) [Jal H2a], 2.29 (ddd, 1 H, J = 14.0 Hz, 9.0 Hz, 3.5 Hz) [Jal H2b], 1.85-1.12 (m, 30 H), 0.80 (t, 3 H, J = 7 Hz) [Jal H16]. – ^{13}C-NMR (150 MHz, d_5-Pyridin) δ = 173.5 (s) [Jal C1], 102.5 (d) [Fuc C1], 101.3 (d) [Rha C1], 101.2 (d) [Glu C1], 84.9 (d) [Glu C2], 79.4 (d) [Jal C11], 77.8 (d) [Glu C3], 76.9 (d) [Glu C5], 76.5 (d) [Fuc C3], 75.5 (d) [Fuc C2], 74.7 (d) [Rha C4], 74.3 (d) [Rha C2], 73.1 (d) [Fuc C4], 72.4 (d) [Glu C4], 71.2 (d) [Fuc C5], 70.3 (d) [Rha C3], 69.9 (d) [Rha C5], 35.9 (t), 35.1 (t) [Jal C2], 34.9 (t), 32.2 (t), 31.1 (t), 30.0 (t), 29.6 (t), 29.2 (t), 28.4 (t), 25.9 (t), 25.7 (t), 25.4 (t), 22.9 (t) [Jal C15], 19.4 (q) [Rha C6], 17.3 (q) [Fuc C6], 14.3 (q) [Jal C16]. – HRMS ($C_{34}H_{60}NaO_{15}$): *calcd.* 731.382751, *found* 731.381429.

Trisaccharide 42. $BF_3{\cdot}OEt_2$ (0.25 M in Et_2O, 0.25 mL) is added to a solution of substrate **36** (100 mg, 0.143 mmol) and trichloroacetimidate **33** (76 mg, 0.143 mmol) in CH_2Cl_2 (5 mL) and hexane (5 mL) at – 20 °C. After stirring for 1 h, the reaction is quenched with saturated aqueos $NaHCO_3$ (10 mL) and the mixture is diluted with CH_2Cl_2 (25 mL). The organic layer is separated, dried over Na_2SO_4, evaporated and the remaining product is purified by flash chromatography (hexane/ethyl acetate 4:1) providing trisaccharide **42** as a colorless syrup (90 mg, 59 %). $[\alpha]_D^n$ = - 6.5 ° (c 4, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.47-7.20 (m, 20 H), 5.83 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.6 Hz), 5.49-5.47 (m, 2 H), 5.15 (s, 1 H), 5.01-4.80 (m, 4 H), 4.71 (dd, 2 H, J = 10.9 Hz, 6.5 Hz), 4.50 (dd, 2 H, J = 11.0 Hz, 6.2 Hz), 4.27 (dd, 1 H, J = 10.4 Hz, 4.65 Hz), 4.23 (d, 1 H, J = 7.8 Hz), 4.12-3.72 (m, 8 H), 3.58-3.31 (m, 6 H), 2.14-2.10 (m, 4 H), 1.62-1.29 (m, 22 H), 0.98 (d, 3 H, J = 5.6 Hz), 0.89 (t, 3 H, J = 7.0

Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 170.0, 138.9, 138.8, 138.4, 138.3, 137.2, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 126.2, 114.6, 109.7, 101.5, 101.2, 100.8, 98.2, 83.5, 80.2, 79.4, 79.3, 76.5, 74.9, 71.8, 68.5, 66.4, 34.9, 33.9, 33.6, 31.9, 27.7, 26.3, 24.9, 24.5, 22.6, 21.0, 17.5, 16.7, 14.1. – HRMS ($C_{62}H_{80}NaO_{15}$): *calcd.* 1087.539491, *found* 1087.540453.

Trisaccharide 44. A solution of compound **42** (80 mg, 7.5 x 10^{-5} mol) in methanol (5 mL) is treated with KOMe (10 mg, 0.15 mmol) for 4 h at ambient temperature. Neutralization of the mixture with 2 N HCl and evaporation of the volatiles in vacuo afforded crude **4** which is used without further purification. 6-Heptenoic acid (10 µL, 8.9 x 10^{-5} mol) is added to a solution of this compound, DMAP (cat.) and DCC (16 mg, 7.8 x 10^{-5} mol) in CH_2Cl_2 (10 mL) and the resulting mixture is stirred overnight. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate 4:1) affords diene **44** (70 mg, 82 %) as a colorless syrup. $[\alpha]_D^n$ = - 6.4 ° (c 2.5, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.47-7.20 (m, 20 H), 5.82 (ddt, 1 H, J = 17.0 Hz, 10.2 Hz, 6.6 Hz), 5.73 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.7 Hz), 5.50-5.49 (m, 2 H), 5.14-4.89 (m, 7 H), 4.82 (d, 1 H, J = 11.0 Hz), 4.71 (d, 1 H, J = 10.9 Hz), 4.49 (dd, 2 H, J = 11.0 Hz, 6.2 Hz), 4.29 (dd, 1 H, J = 10.6 Hz, 4.7 Hz), 4.15-3.26 (m, 14 H), 2.37-2.25 (m, 2 H), 2.10-1.96 (m, 2 H), 1.66-1.28 (m, 26 H), 0.94 (d, 3 H, J = 9.2 Hz), 0.89 (t, 3 H, J = 7.0 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 172.7, 138.9, 138.8, 138.5, 138.4, 138.3, 137.2, 128.8, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 126.2, 114.7, 114.6, 109.7, 101.5, 101.3, 100.8, 98.2, 83.5, 80.2, 79.5, 79.3, 78.2, 76.5, 75.0, 74.9, 71.7, 68.9, 68.6, 68.5, 67.4, 66.4, 34.9, 34.1, 33.9, 33.6, 33.4, 31.9, 28.2, 27.7, 26.3, 24.9, 24.5, 22.6, 17.5, 16.7, 14.1. – MS (ESI): 1155 (M + Na).

Macrocycle 45. Solutions of diene **44** (80 mg, 0.071 mmol) and ruthenium carbene **22** (6 mg, 0.007 mmol, 10 mol%) in CH_2Cl_2 each (50 mL) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (50 mL) over a period of 8 h. Reflux is continued for 14 h until TLC shows complete conversion of the substrate. The solvent is removed in vacuo, the residue is dissolved in CH_2Cl_2 (7 mL) and filtered through a short pad of silica which is thoroughly washed with CH_2Cl_2 (30 mL in several portions). The combined filtrates are evaporated and the residue co-evaporated with EtOH (3 x 10 mL). The mixture of the crude

cycloalkenes thus obtained is dissolved in EtOH (10 mL) and hydrogenated (1 atm H_2) over $RhCl(PPh_3)_3$ (16 mg, 0.017 mmol, 24 mol%) overnight. Removal of the solvent followed by flash chromatography (hexane/ethyl acetate 4:1) affords compound **45** (65 mg, 83 %) as a colorless syrup. $[\alpha]_D^n$ = - 28.5 ° (c 1.75, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.87-7.18 (m, 20 H), 5.68 (s, 1 H), 5.33-5.25 (m, 2 H), 5.02 (d, 1 H, J = 7.5 Hz), 4.89-4.73 (m, 3 H), 4.55-4.38 (m, 3 H), 4.30 (dd, 1 H, J = 10.4 Hz, 4.9Hz), 4.13-3.68 (m, 11 H), 3.49-3.36 (m, 5 H), 2.40-2.26 (m, 4 H), 1.75-1.29 (m, 29 H), 1.03 (d, 3 H, J = 6.2 Hz), 0.89 (t, 3 H, J = 6.5). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 173.8, 139.2, 137.5, 128.9, 128.3, 128.2, 128.1, 127.8, 127.7, 127.6, 127.3, 127.2, 126.3, 109.7, 102.0, 101.6, 82.4, 79.6, 76.5, 71.4, 68.6, 68.2, 66.2, 35.6, 34.9, 32.0, 30.7, 29.9, 29.7, 29.1, 28.4, 27.8, 26.4, 25.6, 25.2, 25.1, 22.6, 18.6, 16.7, 14.1. – HRMS ($C_{65}H_{86}NaO_{15}$): *calcd.* 1129.586440, *found* 1129.585372.

Macrocycle 46 and Trisaccharide 47. To a solution of compound **45** (40 mg, 0.036 mmol) in wet CH_2Cl_2 (5 mL) is added trifluoroacetic acid (50 µL, 0.65 mmol) and the solution is stirred for 3 h at ambident temperature. The reaction solution is treated with triethylamine (2 mL, 14.35 mmol), evaporated in vacuo and the crude residue is dissolved in methanol (10 mL). Pd/C (5 % w/w, 50 mg) and trifluoroacetic acid (100 µL, 1.3 mmol). The flask is filled with H_2 (three freeze/thaw cycles) and the mixture is stirred overnight under H_2-atmosphere. For work-up the solution is treated with triethylamine (2 mL, 14.35 mmol), filtered through a small plug of Celite which is thoroughly washed with methanol (20 mL). The combined filtrates are concentrated and the residue is purified by HPLC (125 mm x 20 mm BIAX-column; Nucleosil-7-100-C_{18}/A, 95/25; mobile phase: acetonitrile/water 60/40) affording the tricolorin G analogue **46** (12.8 mg, 56 %) and methyl ester **47** (2.9 mg, 13 %). Data of **46**: $[\alpha]_D^n$ = - 18.0 ° (c 0.2, MeOH). – ^{1}H-NMR (600 MHz, d_5-Pyridin) δ = 6.13 (d, 1 H, J = 1.5 Hz) [Rha H1], 6.06 (dd, 1 H, J = 3.5 Hz, 1.5 Hz) [Rha H2], 5.18 (d, 1 H, J = 8 Hz) [Glu H1], 5.07 (m, 1 H) [Rha H5], 4.94 (d, 1 H, J = 8 Hz), [Fuc H1], 4.68 (dd, 1 H, J = 9 Hz, 3.8 Hz) [Rha H3], 4.54 (dd, 1 H, J = 10 Hz, 8 Hz) [Fuc H2], 4.45 (dd, 1 H, J = 10.5 Hz, 1.5 Hz) [Glu H6a], 4.36 (t, 1 H, J = 9.8 Hz) [Glu H3], 4.27 (dd, 1 H, 9.9 Hz, 3.3 Hz) [Fuc H3], 4.24 (t, 1 H, J = 9.2 Hz) [Rha H4], 4.20 (dd, 1 H, J = 10.8 Hz, 5 Hz) [Glu H6b], 4.02 (m, 1 H) [Fuc H4], 4.01 (m, 1 H) [Glu H4], 4.00 (m, 1 H) [Glu H2], 3.92 (ddd, 1 H, J = 9.5 Hz, 5.7 Hz, 2.4 Hz)

[Glu H5], 3.89 (t, 1 H, J = 5.7 Hz) [Jal H11], 3.75 (dq, 1 H, J = 6.1 Hz) [Fuc H5], 2.48 (ddd, 1 H, J = 14.9 Hz, 9.9 Hz, 3.5 Hz) [Jal 2a], 2.38 (ddd, 1 H, J = 14.9 Hz, 8.3 Hz, 3.5 Hz) [Jal 2b], 1.78-1.20 (m, 30 H), 0.85 (t, 3 H, J = 7.2 Hz) [Jal H16]. – ^{13}C-NMR (150 MHz, d_5-Pyridin) δ = 173.5 (s) [Jal C1], 100.7 (d) [Glu C1], 100.6 (d) [Fuc C1], 98.9 (d) [Rha C1], 81.4 (d) [Glu C3], 80.3 (d) [Jal C11], 78.5 (d) [Glu C5], 77.9 (d) [Fuc C2], 74.5 (d) [Rha C4], 74.2 (d) [Glu C2], 73.9 (d) [Rha C2], 73.2 (d) [Fuc C3], 72.3 (d) [Fuc C4], 71.0 (d) [Fuc C5], 70.6 (d) [Rha C4], 69.7 (d) [Rha C5], 69.3 (d) [Glu C4], 62.5 (t) [Glu C6], 35.5 (t) [Jal C10], 34.6 (t) [Jal C2], 34.2 (t) [Jal C12], 32.3 (t), 30.6 (t), 29.9 (t), 29.6 (t), 28.8 (t), 28.6 (t), 28.2 (t), 25.8 (t), 25.2 (t), 24.8 (t), 22.9 (t) [Jal C15], 18.7 (q) [Rha C6], 17.2 (q) [Fuc C6], 14.3 (q) [Jal C16]. – HRMS ($C_{34}H_{60}NaO_{15}$): *calcd.* 731.382751, *found* 731.380227.

Data of **47**: $[\alpha]_D^n$ = - 18.6 ° (c 0.15, MeOH). – ^{1}H-NMR (600 MHz, d_5-Pyridin) δ = 6.18 (d, 1 H, J = 1.3 Hz) [Rha H1], 5.09 (d, 1 H, J = 8 Hz) [Glu H1], 5.00 (dd, 1 H, J = 9.5 Hz, 6.2 Hz) [Rha H5], 4.78 (d, 1 H, J = 7.7 Hz) [Fuc H1], 4.72 (dd, 1 H, J = 3 Hz, 1.3 Hz) [Rha H2], 4.54 (t, 1 H, J = 3 Hz) [Rha H3], 4.42 (dd, 1 H, J = 9.7 Hz, 7.7 Hz) [Fuc H2], 4.40-4.38 (m, 2 H) [Glu H6a/b], 4.31 (t, 1 H, J = 9 Hz) [Glu H3], 4.30 (dd, 1 H, J = 9.5 Hz, 4 Hz) [Rha H4], 4.22 (dd, 1 H, J = 9.4 Hz, 6 Hz) [Glu H4], 4.13 (m, 1 H) [Fuc H3], 4.05 (ddd, 1 H, J = 9 Hz, 8 Hz, 3.5 Hz) [Glu H2], 4.00 (t, 1 H, J = 4 Hz) [Fuc H4], 3.90 (q, 1 H, J = 5.7 Hz) [Jal H11], 3.77 (ddd, 1 H, J = 9.9 Hz, 4.2 Hz, 3 Hz) [Glu H5], 3.75 (dd, 1 H, J = 7.5 Hz) [Fuc H5], 3.62 (s, 3 H) [Jal OMe], 2.31 (t, 2 H, J = 7.5 Hz) [Jal H2a/b], 1.83-1.17 (m, 30 H), 0.85 (t, 3 H, J = 7 Hz) [Jal H16]. – ^{13}C-NMR (150 MHz, d_5-Pyridin) δ = 173.9 (s) [Jal C1], 105.8 (d) [Glu C1], 102.6 (d) [Rha C1], 101.9 (d) [Fuc C1], 82.7 (d) [Glu C3], 81.7 (d) [Fuc C2], 79.4 (d) [Jal C11], 78.4 (d) [Glu C5], 77.1 (d) [Glu C3], 75.0 (d) [Fuc C3], 74.2 (d) [Rha C4], 72.7 (d) [Rha C3], 72.5 (d) [Rha C2], 72.4 (d) [Fuc C4], 71.0 (d) [Fuc C5], 69.8 (d) [Rha C5], 69.6 (d) [Glu C4], 62.5 (t) [Glu C6], 51.2 (q) [Jal OMe], 34.9 (t), 34.3 (t), 34.1 (t) [Jal C2], 32.3 (t) 30.3 (t), 29.9 (t), 29.8 (t), 29.6 (t), 29.4 (t) [Jal C4], 25.5 (t), 25.3 (t) [Jal C4], 24.9 (t), 22.9 (t) [Jal C15], 18.6 (q) [Rha C6], 17.3 (q) [Fuc C6], 14.3 (q) [Jal C16]. – HRMS ($C_{35}H_{64}NaO_{16}$): *calcd.* 763.409205, *found* 763.412030.

Disaccharide 51. $BF_3{\cdot}OEt_2$ (0.25 M in Et_2O, 0.10 mL) is added to a solution of alcohol **13** (321 mg, 0.9 mmol) and trichloroacetimidate **33** (435 mg, 0.82 mmol) in CH_2Cl_2 (10 mL) and

hexane (10 mL) at – 20 °C. After stirring for 1.5 h, the reaction is quenched with saturated aqueous $NaHCO_3$ (6 mL) and the mixture is diluted with CH_2Cl_2 (20 mL). The organic layer is dried over Na_2SO_4, evaporated and the remaining product purified by flash chromatography (hexane/ethyl acetate 4:1) providing compound **51** as a colorless syrup (411 mg, 69 %). $[\alpha]_D^{rt}$ = - 42.4 ° (c 0.43, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.32-7.25 (m, 10 H), 5.74 (ddt, 1 H, J = 17.0 Hz, 10.2 Hz, 6.5 Hz), 5.49 (dd, 1 H, J = 3.3 Hz, 1.8 Hz), 5.23 (d, 1 H, 1.5 Hz), 4.95-4.89 (m, 3 H), 4.70 (d, 1 H, A of AB, J = 11.0 Hz), 4.61 (d, 1 H, B of AB, J = 11.4 Hz), 4.46 (d, 1 H, J = 11.0 Hz), 4.25 (d, 1 H, J = 8.2 Hz), 4.19 (dd, 1 H, J = 9.7 Hz, 6.3 Hz), 4.13 (dd, 1 H, J = 7.0 Hz, 5.5 Hz), 3.96 (dd, 1 H, J = 5.4 Hz, 2.0 Hz), 3.89 (dd, 1 H, J = 9.3 Hz, 3.4 Hz), 3.79 (dd, 1 H, J = 6.7 Hz, 2.0 Hz), 3.68 (t, 1 H, J = 8.0 Hz), 3.61 (t, 1 H, J = 5.5 Hz), 3.40 (t, 1 H, J = 9.5 Hz), 2.14 (s, 3 H), 1.97 (q, 2 H, J = 6.9 Hz), 1.98-1.26 (m, 24 H), 0.87 (t, 3 H, J = 7.0 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 170.4, 139.1, 138.8, 138.2, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.6, 127.4, 127.3, 114.5, 109.9, 99.8, 96.2, 80.1, 80.0, 78.8, 78.4, 76.6, 74.9, 74.8, 71.8, 68.6, 67.6, 34.6, 33.8, 32.8, 32.0, 28.1, 26.4, 24.6, 24.2, 22.6, 21.2, 17.9, 16.6, 14.1. – HRMS ($C_{62}H_{60}NaO_{10}$): *calcd.* 747.408325, *found* 747.409556.

Disaccharide 53. A solution of acetate **51** (411 mg, 0.57 mmol) in methanol (10 mL) is treated with KOMe (20 mg, 0.28 mmol) for 4 h at ambient temperature. Neutralization of the mixture with 2 N HCl and evaporation of all volatile components in vacuo affords crude **52** which is used without further purification. 6-Heptenoic acid (77 μL, 0.57 mmol) is added to a solution of this compound, DMAP (cat.) and DCC (117 mg, 0.57 mmol) in CH_2Cl_2 (10 mL) and the mixture is stirred overnight. Evaporation of the solvent followed by flash chromatography (hexane/ethyl acetate 2:1) affords diene **53** (345 mg, 77 %) as a colorless syrup. $[\alpha]_D^{rt}$ = - 47.5 ° (c 0.80, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.31-7.24 (m, 10 H), 5.74 (ddt, 1 H, J = 16.8 Hz, 10.1 Hz, 6.5 Hz), 5.73 (ddt, 1 H, J = 17.1 Hz, 10.2 Hz, 6.7 Hz), 5.50 (dd, 1 H, J = 3.3 Hz, 1.8 Hz), 5.21 (d, 1 H, J = 1.6 Hz), 4.95-4.87 (m, 5 H), 4.69 (d, 1 H, A part of AB, J = 10.9 Hz), 4.60 (d, 1 H, A part of AB, J = 11.3 Hz), 4.44 (d, 1 H, B part of AB, J = 10.9 Hz), 4.25 (d, 1 H, J = 8.2 Hz), 4.18 (dd, 1 H, J = 9.6 Hz, 6.2 Hz), 4.13 (dd, 1 H, J = 7.1 Hz, 5.6 Hz), 3.97 (dd, 1 H, J = 6.6 Hz, 2.0 Hz), 3.68 (t, 1 H, J = 7.9 Hz), 3.61 (t, 1

H, J = 5.5 Hz), 3.36 (t, 1 H, J = 9.5 Hz), 2.40 (dt, 2 H, J = 7.5 Hz, 1.6 Hz), 2.05-1.96 (m, 4 H), 1.64-1.25 (m 27 H), 0.87 (t, 3 H, J = 6.9 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 173.0, 139.1, 138.8, 138.5, 138.3, 128.4, 128.2, 128.1, 128.0, 127.5, 127.3, 114.6, 114.5, 109.9, 99.8, 96.3, 80.0, 78.9, 78.5, 74.9, 71.7, 68.6, 68.4, 67.6, 34.6, 34.2, 33.8, 33.4, 32.8, 32.0, 28.2, 28.1, 27.0, 26.4, 24.6, 24.5, 24.2, 22.6, 17.9, 16.6, 14.1. – HRMS ($C_{47}H_{68}NaO_{10}$): *calcd.* 815.470886, *found* 815.471565.

Macrocycle 54. Solutions of diene **53** (280 mg, 0.35 mmol) and ruthenium carbene **22** (33 mg, 10 mol%) in CH_2Cl_2 each (50 mL) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (50 mL) over a period of 6 h. Reflux is continued for 10 h until TLC shows complete conversion of the substrate. The solvent is removed in vacuo, the residue is dissolved in CH_2Cl_2 (5 mL) and filtered through a short pad of silica which is thoroughly washed with CH_2Cl_2 (40 mL in several portions). The combined filtrates are evaporated and the residue co-evaporated with EtOH (3 x 10 mL). The mixture of the crude cycloalkenes thus obtained is dissolved in EtOH (10 mL) and hydrogenated (1 atm H_2) over $RhCl(PPh_3)_3$ (81 mg, 0.088 mmol, 25 mol%) overnight. Removal of the solvent and flash chromatography (hexane/ethyl acetate 10:1) affords compound **54** (210 mg, 78 %) as a colorless syrup. $[\alpha]_D^n$ = - 28.3 ° (c 10.50, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$) δ = 7.37-7.25 (m, 10 H), 5.58 (t, 1 H, J = 2.6 Hz), 4.95 (d, 1 H, J = 1.7 Hz), 4.91 (d, 1 H, A part of AB, J = 10.8 Hz), 4.72 (d, 1 H, A part of AB, J = 11.3 Hz), 4.59 (d, 1 H, B part of AB, J = 10.7 Hz), 4.56 (d, 1 H, B part of AB, J = 11.2 Hz), 4.35 (d, 1 H, J = 6.9 Hz), 4.15-4.05 (m, 2 H), 3.98 (dd, 1 H, J = 5.8 Hz, 2 Hz), 3.90 (m, 1 H), 3.75 (dq, 1 H, J = 6.6 Hz, 2 Hz), 3.60 (m, 1 H), 3.52 (t, 1 H, J = 6.7 Hz), 3.44 (t, 1 H, J = 9.5 Hz), 2.54 (m, 1 H), 2.31 (m, 1 H), 1.73-1.25 (m, 36 H), 0.89 (t, 3 H, J= 6.5 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 173.0, 138.6, 138.3, 128.3, 128.3, 128.2, 128.0, 127.6, 109.8, 103.0, 98.6, 98.1, 83.1, 80.2, 79.2, 77.8, 77.5, 76.0, 75.4, 71.3, 69.0, 68.2, 67.7, 34.2, 33.2, 33.1, 27.9, 27.7, 27.5, 27.3, 27.2, 26.3, 25.0, 24.9, 23.2, 22.7, 18.4, 16.7, 14.1. – HRMS ($C_{45}H_{66}NaO_{10}$): *calcd.* 789.455368, *found* 789.559630.

Macrocycle 55. To a solution of compound **54** (190 mg, 0.25 mmol) in methanol (25 mL) is added acetic acid (100 µL, 1.75 mmol) and Pd/C (5 % w/w, 30 mg). The reaction flask is filled with H_2 (three freeze/thaw cycles) and the solution is stirred for 2.5 d under H_2 (1 atm).

For work-up, triethylamine (2 mL, 14.35 mmol) is added, the mixture is filtered through a small plug of Celite which is thoroughly washed with ethyl acetate (30 mL). Evaporation of the combined filtrates followed by flash chromatograpy delivers product **55** as a colorless syrup (100 mg, 59 %). $[\alpha]_D^{rt}$ = - 46.8 ° (c 0.50, CH_2Cl_2). – ^{1}H-NMR (600 MHz, $CDCl_3$) δ = 7.36-7.27 (m, 5 H), 5.55 (dd, 1 H, J = 3.1 Hz, 2.2 Hz) [Rha H2], 4.96 (d, 1 H, J = 2.2 Hz) [Rha H1], 4.69 (d , 1 H, A part of AB, J = 11.3 Hz), 4.43 (d, 1 H, J = 11.3 Hz), 4.33 (d, 1 H, J = 7.3 Hz) [Fuc H1], 4.07 (dd, 1 H, J = 6.6 Hz, 5.9 Hz) [Fuc H3], 3.98 (dd, 1 H, J = 5.9 Hz, 2.2 Hz) [Fuc H4], 3.84 (dd, 1 H, J = 9.5 Hz, 2.9 Hz) [Rha H3], 3.81 (dd, 1 H, J = 9.5 Hz, 6.2 Hz) [Rha H5], 3.75 (dq, 1 H, J = 6.6 Hz, 2.2 Hz) [Fuc H5], 3.58 (m, 1 H) [Jal H11], 3.53 (t, 1 H, J = 9.5 Hz) [Rha H5], 3.49 (t, 1 H, J = 7.0 Hz) [Fuc H2], 2.45 (m, 1 H) [Jal H2a], 2.26 (m, 1 H) [Jal H2b], 1.66-1.22 (m, 36 H), 0.86 (t, 3 H, J = 7.0 Hz) [Jal Me 16]. – ^{13}C-NMR (150 MHz, $CDCl_3$) δ = 172.8 (s) [Jal C1], 137.9 (s) [Phe C1], 128.5 (d) [Phe C3], 128.2 (d) [Phe C2], 127.9 (d) [Phe C4], 103.0 (d, JCH = 157 Hz) [Fuc C1], 109.9 (s) [acetonide C1], 98.7 (d, JCH = 170 Hz) [Rha C1], 83.3 (d) [Jal C11], 79.1 (d) [Fuc C2], 77.9 (d) [Fuc C3], 76.9 (d) [Rha C3], 76.1 (d) [Fuc C4], 71.6 (d) [Rha C4], 70.9 (t) [Benz C1], 69.4 (d) [Rha C5], 68.2 (d) [Fuc C5], 66.7 (d) [Rha C2], 34.1 (t) [Jal C2, C12], 33.2 (t) [Jal C10], 32.0 (t) [Jal C14], 27.9 (q) [acetonide C2a], 27.8 (t), 27.7 (t) [Jal C4], 27.4 (t), 27.3 (t), 27.1 (t), 26.4 (q) [acetonide C2b], 24.9 (t) [Jal C13], 24.7 (t) [Jal C3], 23.1 (t) [Jal C9], 22.6 (t) [Jal C15], 18.1 (q) [Rha C6], 16.6 (q) [Fuc C6], 14.0 (q) [Jal C16]. – HRMS ($C_{38}H_{60}NaO_{10}$): cald 699.408418 , *found* 699.409919.

1-Undecene-(6*S*)-yl 6-heptenoate (56). A solution of alcohol **7** (984 mg, 5.77 mmol), DMAP (70 mg, 0.58 mmol) and DCC (1.19 g, 5.77 mmol) in CH_2Cl_2 (20 mL) is stirred for 10 min prior to the addition of 6-heptenoic acid (783 µL, 5.77 mmol). The mixture is stirred overnight, the precipitate formed is filtered off over a short pad of silica, the insoluble residues are thoroughly washed with CH_2Cl_2 (40 mL in several portions), the combined filtrates are evaporated and the crude product is purified by flash chromatography (hexane/ethyl acetate 30:1) affording ester **56** as a colorless oil (1.44 g, 87 %). - $[\alpha]_D^{rt}$ = – 0.7 ° (c 2.4, CH_2Cl_2). – ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.88-5.71 (m, 2 H), 5.04-4.87 (m, 4 H), 2.30 (t, 2 H, J = 7.4 Hz), 2.11-2.01 (m, 4 H), 1.69-1.21 (m, 17 H), 0.88 (t, 3 H, J = 7.0 Hz). –

^{13}C NMR (75 MHz, $CDCl_3$) δ = 173.5, 138.5, 138.4, 114.70, 114.65, 73,9, 34.5, 34.1, 33.6, 33.4, 31.7, 28.4, 25.0, 24.62, 24.59, 22.6, 14.0. – MS (EI): m/z (rel intensity): 280 (1) [M+], 152 (19), 128 (19), 124 (11), 111 (67), 110 (32), 97 (26), 96 (37), 95 (17), 83 (79), 82 (47), 81 (43), 69 (58), 68 (47), 67 (36), 57 (12), 56 (11), 55 (100), 54 (26), 43 (21), 41 (49), 29 (12). – HRMS ($C_{18}H_{32}O_2$): calc 280.240229, *found* 280.239835.

(12*S*)-Pentyl-1-oxacyclododecane-2-on (57). Solutions of diene **56** (100 mg, 0.36 mmol) and ruthenium carbene **22** (9 mg, 2.5 mol%) in CH_2Cl_2 (100 mL each) are simultaneously added via two dropping funnels to refluxing CH_2Cl_2 (100 mL) over a period of 8 h. Reflux is continued for 16 h and an additonal amount of ruthenium carbene **22** (9 mg, 2.5 mol%) is introduced. After a total reaction time of 2.5 d, the solvent is removed in vacuo, the residue is dissolved in CH_2Cl_2 (5 mL) and filtered through a short pad of silica which is then thoroughly washed with CH_2Cl_2 (40 mL in several portions). The combined filtrates are evaporated and the residue co-evaporated with EtOH (3 x 5 mL). The mixture of the crude cycloalkenes thus obtained is dissolved in EtOH (10 mL) and hydrogenated (1 atm H_2) over Pd/C (5 % w/w, 20 mg) for 8 h. Removal of the catalyst by filtration and subsequent flash chromatography (hexane/ethyl acetate 100:1) affords lactone **57** as a colorless syrup (39 mg, 43 %). – $[\alpha]_D^n$ = + 3.5 ° (c 1.90, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.01 (m, 1 H), 2.46 (m, 1 H), 2.22 (m, 1 H), 1.62-1.28 (m, 24 H), 0.88 (t, 3 H, J = 6.8 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 172.9, 72.7, 33.7, 32.1, 30.7, 29.2, 24.5, 24.2, 24.1, 23.9, 22.6, 22.5, 22.3, 21.5, 19.2, 13.0. – MS (EI): m/z (rel intensity): 254 (12) [M^+], 236 (47), 183 (56), 165 (12), 155 (24), 154 (50), 147 (10), 125 (17), 113 (31), 112 (30), 111 (59), 99 (16), 98 (89), 97 (32), 96 (28), 95 (32), 94 (12), 85 (19), 84 (36), 83 (37), 82 (23), 81 (44), 71 (30), 70 (27), 69 (65), 68 (20), 67 (33), 58 (14), 57 (29), 56 (35), 55 (100), 54 (16), 43 (61), 42 (22), 41 (89), 39 (13), 29 (39), 27 (15).

(11*S*)-(+)-Jalapinolic acid (58). Lactone **57** (30 mg, 0.118 mmol) is added to a solution of KOH (0.2 g, 3.56 mmol) in methanol (7 mL) and the mixture is stirred at 65 °C for 1.5 d. After cooling to rt, the solvent is evaporated, the residue is dissolved in ether (30 mL) and treated with 2N aq. HCl (10 mL). The organic layer is dried over Na_2SO_4, the solvent is evaporated and the residue purified by flash chromatography (hexane/ethyl acetate 10:1)

furnishing acid **58** (28 mg, 87 %) as a colorless solid. – $[\alpha]_D^{rt}$ = + 0.7 ° (c 1.4, CH_2Cl_2). – ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 3.59 (m, 1 H), 2.34 (t, 2 H, J = 7.4 Hz), 1.65-1.26 (m, 26 H), 0.89 (t, 3 H, J = 6.6 Hz). – ^{13}C-NMR (75 MHz, $CDCl_3$) δ = 179.3, 72.1, 37.4, 34.0, 31.9, 29.6, 29.5, 29.3, 29.2, 29.0, 25.6, 25.3, 24.7, 22.7, 14.1. – MS (EI): m/z (rel. intensity): 201 (11), 184 (12), 183 (100), 165 (10), 147 (10), 129 (18), 111 (12), 100 (17), 98 (17), 95 (20), 85 (14), 83 (38), 82 (10), 81 (25), 73 (21), 71 (16), 69 (23), 67 (15), 60 (12), 57 (18), 55 (54), 43 (22), 41 (27), 29 (13). – HRMS ($C_{16}H_{33}O_3$) *calcd.* 273.242969, *found* 273.243308.

Table 1. Characteristic Infrared Absorptions of New Compounds (cm^{-1})

Product	IR
2	3429, 2930, 2857, 1726, 1458,1383, 1260, 1175, 1136, 1069, 902, 808, 763
7	3354, 3078, 2956, 2931, 2859, 1823, 1641, 1459, 1441, 1415, 1378, 1324, 1265, 1233, 1196, 1127, 1056, 994, 966, 910, 827, 725, 634, 557
8	3432, 3079, 2978, 2938, 2866, 2722, 1826, 1726, 1642, 1414, 1391, 1365, 1244, 1173, 1117, 1074, 996, 915, 863, 805, 704, 630, 554, 519
11	3077, 2936, 2861, 2722, 1753, 1641, 1459, 1437, 1368, 1314, 1251, 1224, 1174, 1133, 1075, 1021, 971, 931, 910, 729, 675, 653, 628, 596, 535
13	3485, 3076, 2983, 2934, 2862, 1641, 1458, 1415, 1380, 1346, 1291, 1245, 1219, 1182, 1156, 1130, 1072, 1036, 994, 912, 871, 802, 688, 509
17	3474, 3308, 3071, 3038, 2987, 2940, 2875, 1755, 1677, 1498, 1458, 1431, 1418, 1372, 1292, 1235, 1220, 1183, 1140, 1102, 1070, 1033, 969, 907, 833, 798, 752, 735, 700, 645, 600, 560, 486
18	3487, 3072, 3037, 2983, 2871, 2729, 1756, 1640, 1498, 1457, 1414, 1379, 1371, 1241, 1219, 1181, 1156, 1127, 1099, 1075, 1036, 915, 870, 802, 752, 699, 604, 510
19	3460, 3070, 3037, 2982, 2933, 2870, 1640, 1500, 1456, 1381, 1298, 1242, 1221, 1179, 1073, 1033, 915, 896, 803, 762, 699, 623, 557, 509
20	3544, 3070, 2982, 2935, 1749, 1641, 1627, 1581, 1536, 1459, 1415, 1382, 1349, 1310, 1249, 1218, 1178, 1154, 1099, 1081, 1038, 1010, 987, 916, 867, 812, 748, 696
21	3573, 3069, 3039, 2931, 2857, 1741, 1721, 1640, 1553, 1459, 1411, 1381, 1372, 1302, 1244, 1224, 1184, 1155, 1074, 1038, 1004, 921, 866, 800, 748, 697, 631, 581, 507

Table 1. continued

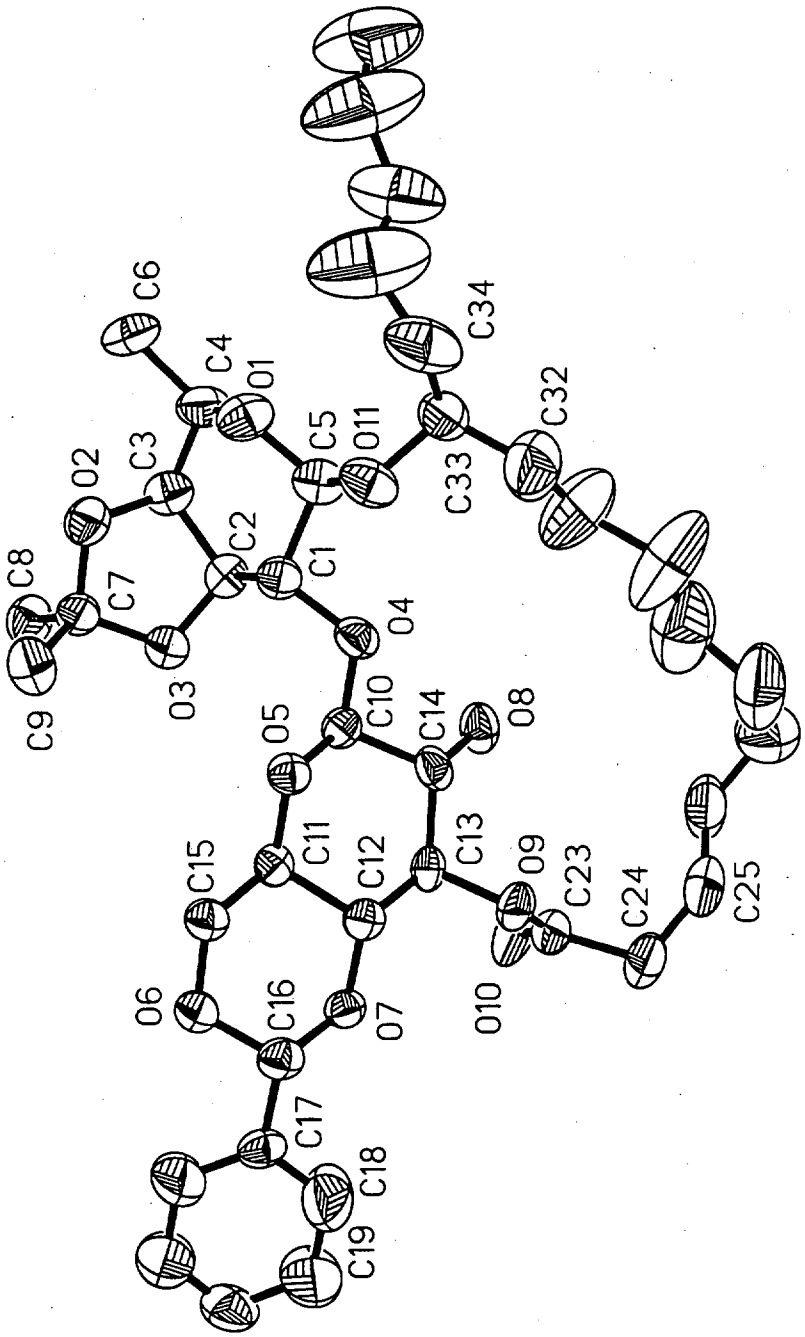
Product	IR
25a	3470, 3075, 2978, 2929, 2857, 1738, 1641, 1498, 1457, 1416, 1372, 1301, 1243, 1222, 1181, 1155, 1075, 1032, 1003, 911, 869, 749, 698
25b	3427, 3079, 2980, 2934, 2873, 1749, 1642, 1454, 1418, 1372, 1298, 1270, 1246, 1221, 1181, 1076, 1034, 1020, 969, 922, 749, 699
26	3473, 2934, 2861, 1734, 1457, 1383, 1245, 1223, 1182, 1117, 1075, 1032, 869, 808, 749, 697, 653
27	3489, 2928, 2856, 1745, 1458, 1371, 1241, 1224, 1181, 1102, 1093, 1075, 1031, 1001, 749, 698
29	2984, 2947, 2916, 1756, 1381, 1373, 1245, 1048, 895, 812
30	3063, 3028, 3028, 2983, 2935, 2904, 2862, 1607, 1499, 1455, 1379, 1252, 1089, 1048, 1008, 893, 762, 732, 702
33	3338, 3064, 3031, 2978, 2935, 2916, 1751, 1675, 1497, 1454, 1370, 1230, 1163, 1106, 1060, 797, 738, 699
34	3440, 3072, 2954, 2922, 2860, 1639, 1455, 1385, 1373, 1180, 1131, 1019, 967, 918, 805, 749, 698
36	3476, 3065, 2955, 2933, 2871, 1640, 1456, 1380, 1180, 1077, 993, 914, 750, 698
35	3066, 3033, 2983, 2934, 2871, 1754, 1640, 1497, 1455, 1381, 1370, 1231, 1180, 1075, 1032, 870, 734, 698
37	3066, 3031, 2955, 2933, 2870, 1748, 1498, 1454, 1414, 1369, 1261, 1226, 1180, 1076, 1039, 1016, 915, 869, 801, 750, 699
38	3064, 3030, 2924, 2855, 1745, 1640, 1593, 1496, 1454, 1368, 1308, 1240, 1175, 1073, 915, 870, 801, 748, 698
40	3065, 3032, 2978, 2933, 2870, 1740, 1640, 1497, 1454, 1381, 1369, 1174, 1142, 1098, 1076, 1030, 998, 913, 750, 698
41	3089, 3067, 3032, 2930, 2856, 1736, 1498, 1455, 1382, 1370, 1301, 1279, 1243, 1222, 1183, 1101, 1073, 997, 915, 749, 734, 697

Table 1. continued

Product	IR
44	3070, 3035, 2978, 2935, 2872, 1740, 1641, 1498, 1455, 1182, 1142, 1077, 1050, 996, 913, 751, 699
45	3064, 3032, 2928, 2857, 1735, 1598, 1497, 1454, 1380, 1368, 1301, 1279, 1242, 1220, 1180, 1077, 1043, 1000, 869, 800, 735, 698, 649
46	3442, 2931, 1741, 1461, 1378, 1243, 1177, 1136, 1067, 1002, 904
47	3421, 2930, 2857, 1742, 1460, 1381, 1300, 1174, 1070, 1044, 904
51	3067, 3022, 2935, 2871, 1746, 1641, 1578, 1498, 1455, 1370, 1237, 1181, 1075, 985, 914, 735, 698
53	3066, 3032, 2978, 2934, 2861, 1740, 1641, 1497, 1455, 1381, 1368, 1241, 1220, 1181, 1157, 1138, 1076, 1037, 992, 913, 748, 736, 698
54	3064, 3031, 2933, 2858, 1736, 1607, 1588, 1498, 1455, 1382, 1368, 1244, 1219, 1179, 1134, 1106, 1074, 1045, 989, 868, 790, 734, 697
55	3461, 2929, 2858, 1734, 1457, 1384, 1261, 1220, 1037, 1041, 866, 792, 699, 615
56	3078, 2934, 2860, 1733, 1641, 1459, 1441, 1418, 1378, 1344, 1259, 1234, 1173, 1129, 1056, 993, 911
57	2931, 2861, 1730, 1467, 1446, 1384, 1248, 1178, 1144, 1099, 1015, 809
58	3438, 2957, 2922, 2850, 1701, 1469, 1262, 1215, 1131, 1070, 1024, 905, 720

Molecular structure of macrocycle **21** in the crystal

Anisotropic displacement parameter are shown at the 50% probability level, all hydrogen atoms are omitted for clarity.



Molecular structure of macrocycle **21** in the crystal:

At 100 K the lattice parameters in monoclinic space group $P2_1$ are: a = 22.502(5), b = 17.339(4), c = 25.011(5) Å, β = 92.49(3) °, V = 9749(3) Å^3, Z = 10. M = 705.67, ρ = 1.202 Mg m^{-3}, μ = 0.087 mm^{-1}, F(000) = 3824. The complete lists of atomic coordinates, bond length and angles have been deposited with the Cambridge Crystallographic Data Center, Cambridge, U.K., under the deposition number **CCDC 127495** and may be obtained free of charge by applying to: „The Director, Cambridge Crystallographic Data Center, 12 Union Road, CB2 1EZ Cabridge, UK.

A full report on the X-ray structure determination of this compound can be found in: Lehmann, C. W.; Fürstner, A.; Müller, Th., *Z. Kristallogr.*, submitted.

Selected Bond Distances in Å:

O(1) - C(4)	1.46(1)	O(1) - C(5)	1.43(1)
O(2) - C(3)	1.42(1)	O(2) - C(7)	1.44(1)
O(3) - C(2)	1.41(1)	O(3) - C(7)	1.43(1)
O(4) - C(1)	1.42(1)	O(4) - C(10)	1.39(1)
O(5) - C(10)	1.42(1)	O(5) - C(11)	1.42(1)
O(6) - C(15)	1.42(1)	O(6) - C(16)	1.41(1)
O(7) - C(12)	1.43(1)	O(7) - C(16)	1.43(1)
O(8) - C(14)	1.44(1)	O(9) - C(13)	1.44(1)
O(9) - C(23)	1.32(1)	O(10) - C(23)	1.22(1)
O(11) - C(5)	1.39(1)	O(11) - C(33)	1.44(1)
C(1) - C(2)	1.54(1)	C(1) - C(5)	1.52(1)
C(2) - C(3)	1.52(1)	C(3) - C(4)	1.50(1)
C(4) - C(6)	1.52(2)	C(7) - C(8)	1.54(1)
C(7) - C(9)	1.53(1)	C(10) - C(14)	1.50(1)
C(11) - C(12)	1.53(1)	C(11) - C(15)	1.51(1)
C(12) - C(13)	1.52(1)	C(13) - C(14)	1.52(1)
C(16) - C(17)	1.48(1)	C(17) - C(18)	1.33(2)
C(17) - C(22)	1.35(2)	C(18) - C(19)	1.42(2)
C(19) - C(20)	1.35(2)	C(20) - C(21)	1.32(2)
C(21) - C(22)	1.39(2)	C(23) - C(24)	1.50(1)
C(24) - C(25)	1.49(2)	C(25) - C(26)	1.44(2)
C(26) - C(27)	1.54(2)	C(27) - C(28)	1.48(3)
C(28) - C(29)	1.47(3)	C(29) - C(30)	1.50(3)
C(30) - C(31)	1.57(3)	C(31) - C(32)	1.44(2)
C(32) - C(33)	1.50(2)	C(33) - C(34)	1.54(2)
C(34) - C(35)	1.38(3)	C(35) - C(36)	1.39(3)
C(36) - C(37)	1.38(3)	C(37) - C(38)	1.37(4)

Selected Bond Angles (°):

C(5) - O(1) - C(4)	110.9(7)	C(7) - O(2) - C(3)	105.3(6)
C(7) - O(3) - C(2)	108.9(6)	C(10) - O(4) - C(1)	118.8(6)
C(11) - O(5) - C(10)	108.6(6)	C(16) - O(6) - C(15)	113.5(6)
C(16) - O(7) - C(12)	110.5(6)	C(23) - O(9) - C(13)	117.5(7)
C(33) - O(11) - C(5)	116.3(7)	C(5) - C(1) - C(2)	109.7(7)
C(5) - C(1) - O(4)	105.3(6)	C(2) - C(1) - O(4)	113.8(7)
C(3) - C(2) - C(1)	112.4(7)	C(3) - C(2) - O(3)	103.4(7)
C(1) - C(2) - O(3)	112.0(7)	C(4) - C(3) - C(2)	117.5(8)
C(4) - C(3) - O(2)	111.8(8)	C(2) - C(3) - O(2)	102.0(7)
C(6) - C(4) - C(3)	115.2(9)	C(6) - C(4) - O(1)	105.5(9)
C(3) - C(4) - O(1)	110.9(8)	C(1) - C(5) - O(11)	108.9(7)
C(1) - C(5) - O(1)	109.7(7)	O(11) - C(5) - O(1)	107.0(7)
C(9) - C(7) - C(8)	112.3(8)	C(9) - C(7) - O(3)	110.9(7)
C(9) - C(7) - O(2)	108.1(7)	C(8) - C(7) - O(3)	108.4(7)
C(8) - C(7) - O(2)	110.9(7)	O(3) - C(7) - O(2)	106.0(7)
C(14) - C(10) - O(5)	110.1(7)	C(14) - C(10) - O(4)	105.1(7)
O(5) - C(10) - O(4)	110.0(6)	C(15) - C(11) - C(12)	108.0(7)
C(15) - C(11) - O(5)	110.5(6)	C(12) - C(11) - O(5)	110.2(6)
C(13) - C(12) - C(11)	109.4(7)	C(13) - C(12) - O(7)	109.6(6)
C(11) - C(12) - O(7)	107.3(6)	C(14) - C(13) - C(12)	109.8(7)
C(14) - C(13) - O(9)	108.5(6)	C(12) - C(13) - O(9)	109.9(6)
C(13) - C(14) - C(10)	111.6(7)	C(13) - C(14) - O(8)	106.8(7)
C(10) - C(14) - O(8)	109.7(7)	C(11) - C(15) - O(6)	107.4(6)
C(17) - C(16) - O(7)	109.2(7)	C(17) - C(16) - O(6)	108.3(7)
O(7) - C(16) - O(6)	111.4(7)	C(22) - C(17) - C(18)	114(1)
C(22) - C(17) - C(16)	124.5(9)	C(18) - C(17) - C(16)	121(1)
C(19) - C(18) - C(17)	124(1)	C(20) - C(19) - C(18)	118(1)
C(21) - C(20) - C(19)	120(1)	C(22) - C(21) - C(20)	119(1)
C(21) - C(22) - C(17)	124(1)	C(24) - C(23) - O(10)	123.3(9)
C(24) - C(23) - O(9)	111.6(8)	O(10) - C(23) - O(9)	125.1(9)
C(25) - C(24) - C(23)	115(1)	C(26) - C(25) - C(24)	116(1)
C(27) - C(26) - C(25)	118(1)	C(28) - C(27) - C(26)	120(1)
C(29) - C(28) - C(27)	112(2)	C(30) - C(29) - C(28)	117(2)
C(31) - C(30) - C(29)	109(2)	C(32) - C(31) - C(30)	117(1)
C(33) - C(32) - C(31)	113(1)	C(34) - C(33) - C(32)	107(1)
C(34) - C(33) - O(11)	106.7(9)	C(32) - C(33) - O(11)	111.3(9)
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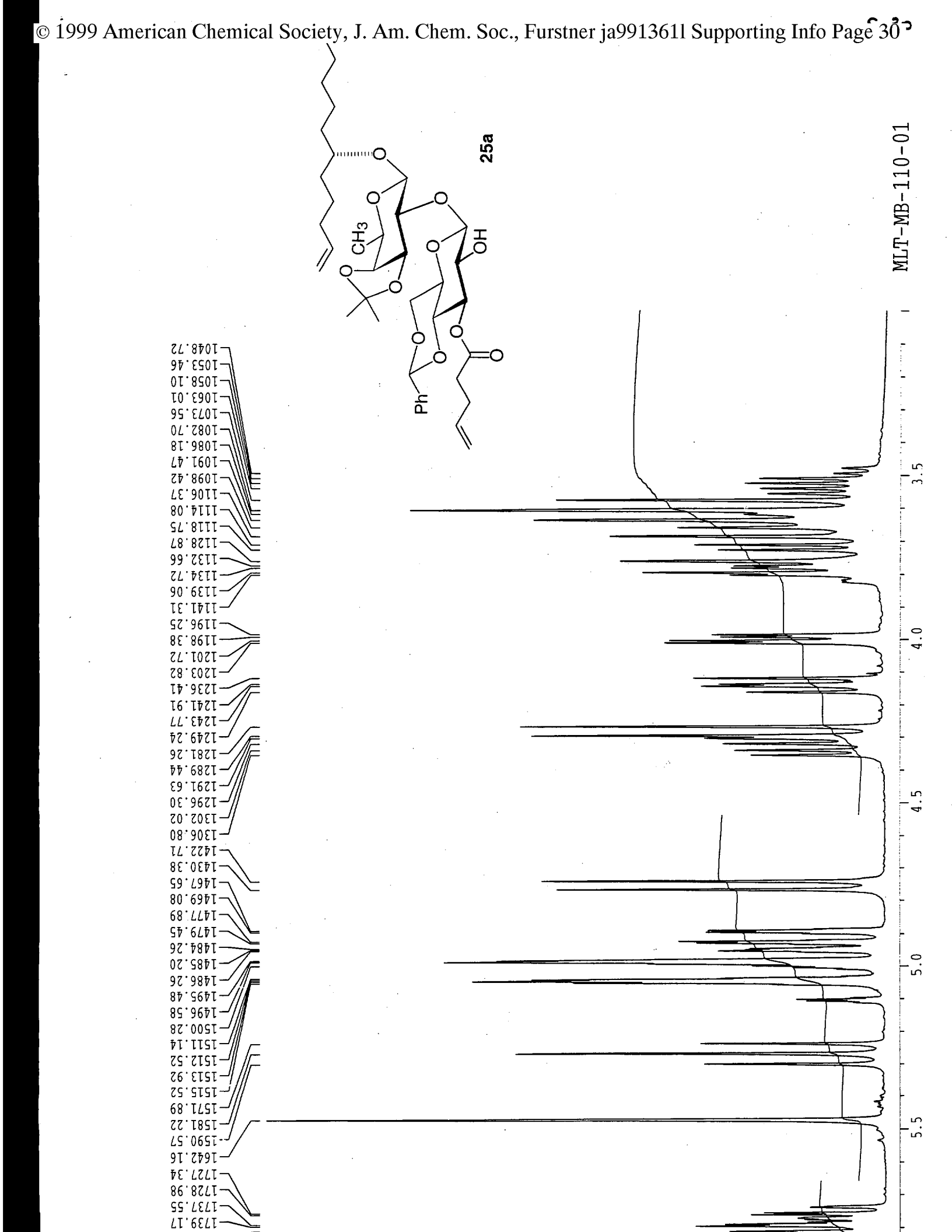

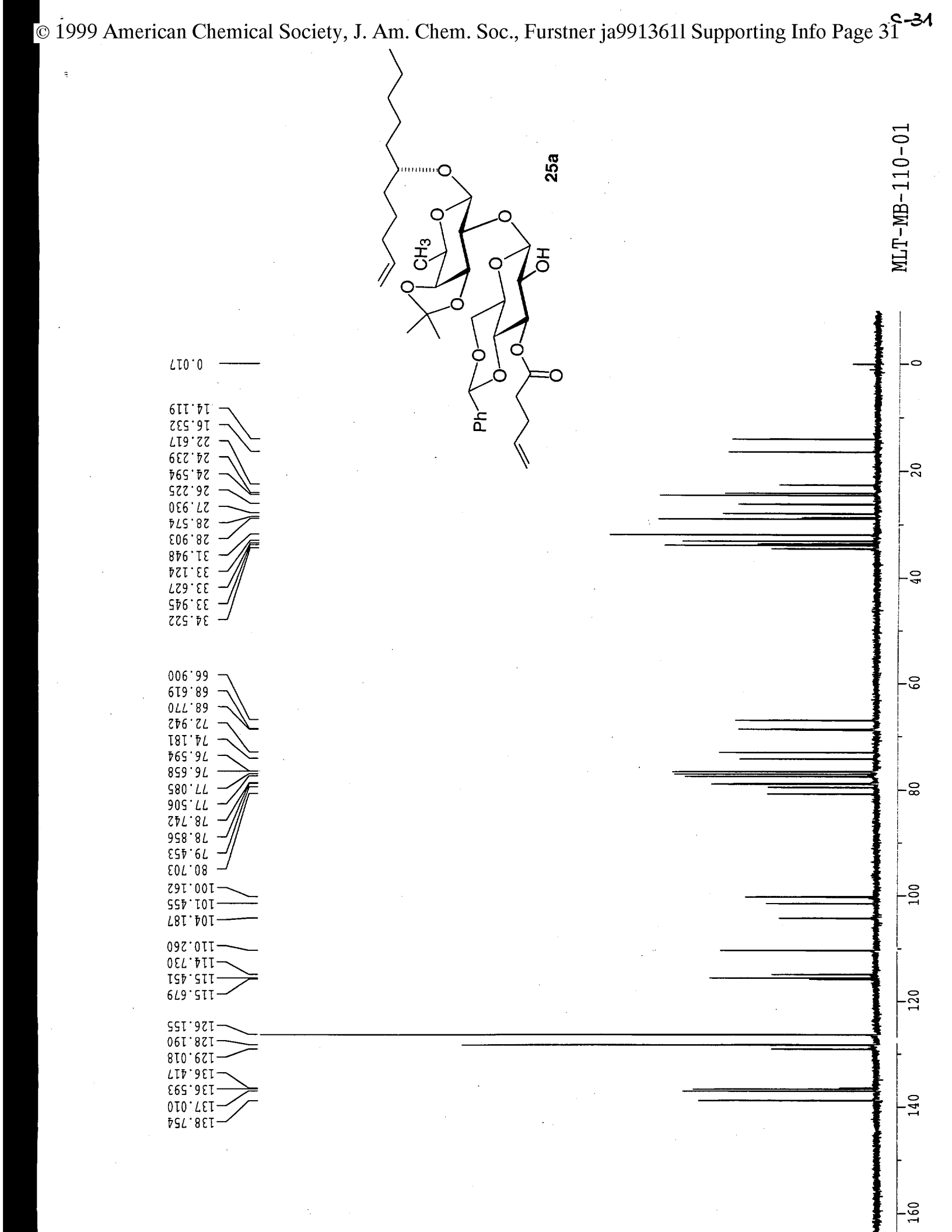
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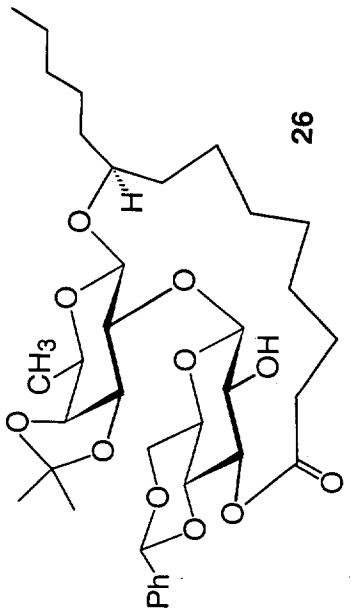
160



MLT-MB 113-01

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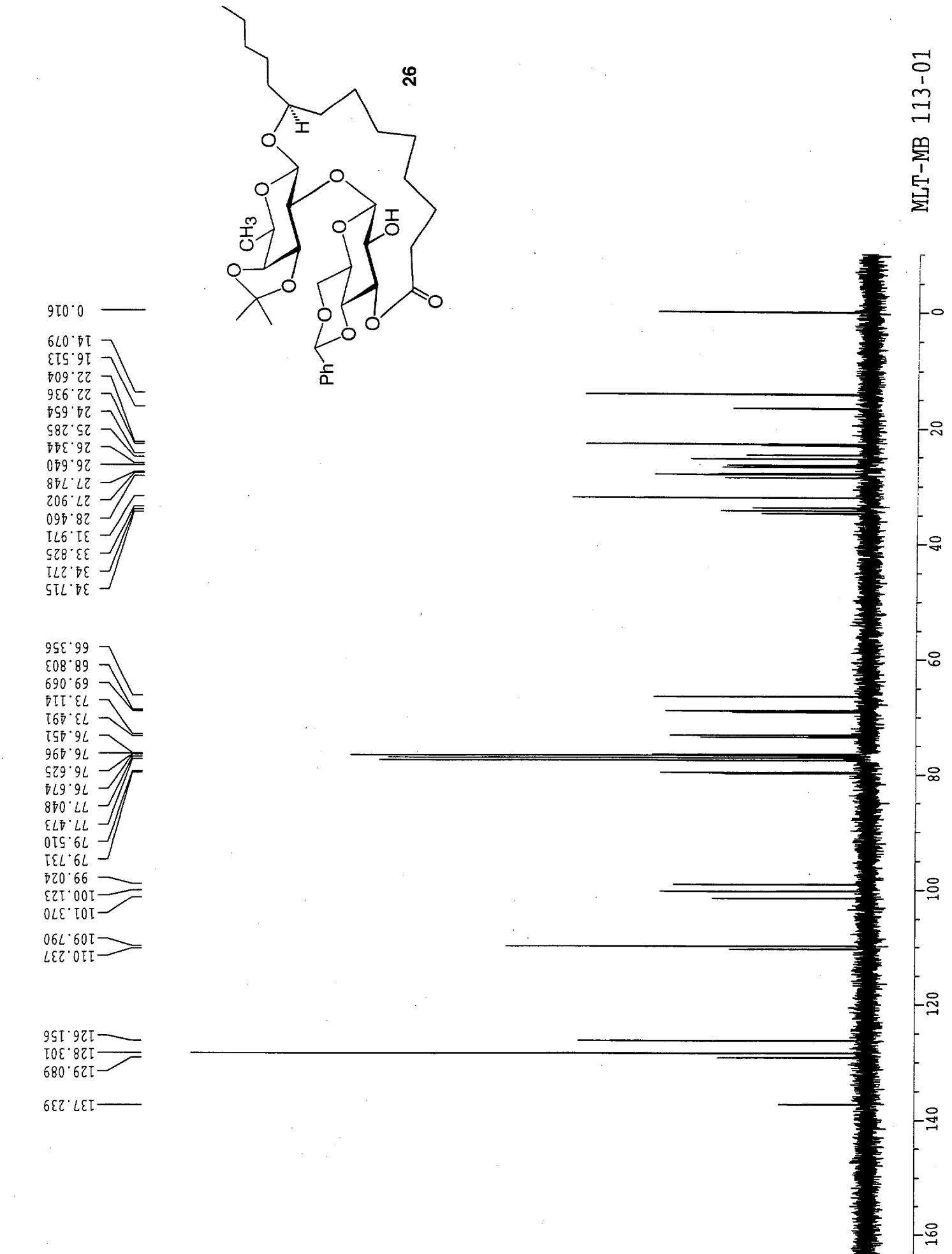

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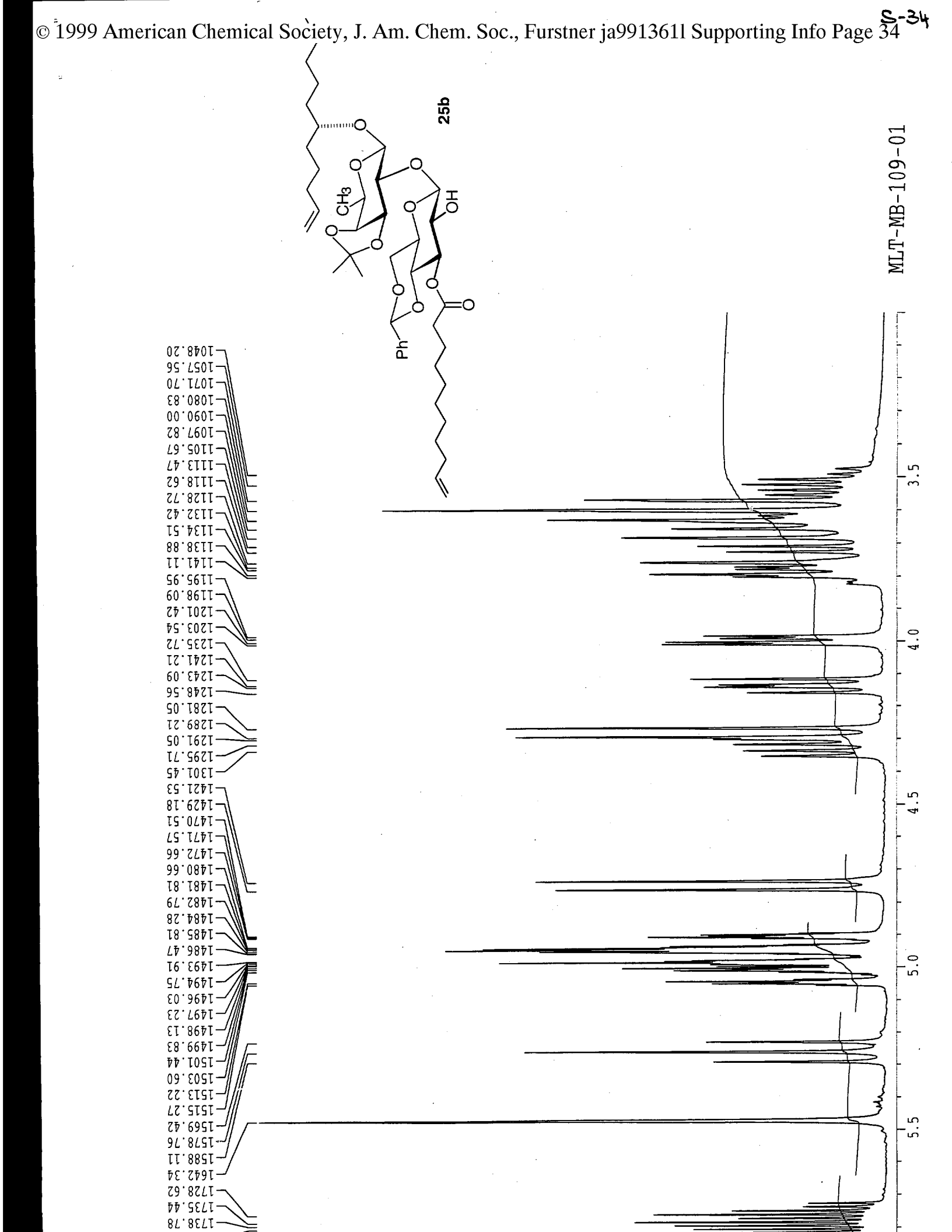
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1195.95
1198.09
1201.42
1203.54
1235.72
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1295.71
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1470.51
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1482.79
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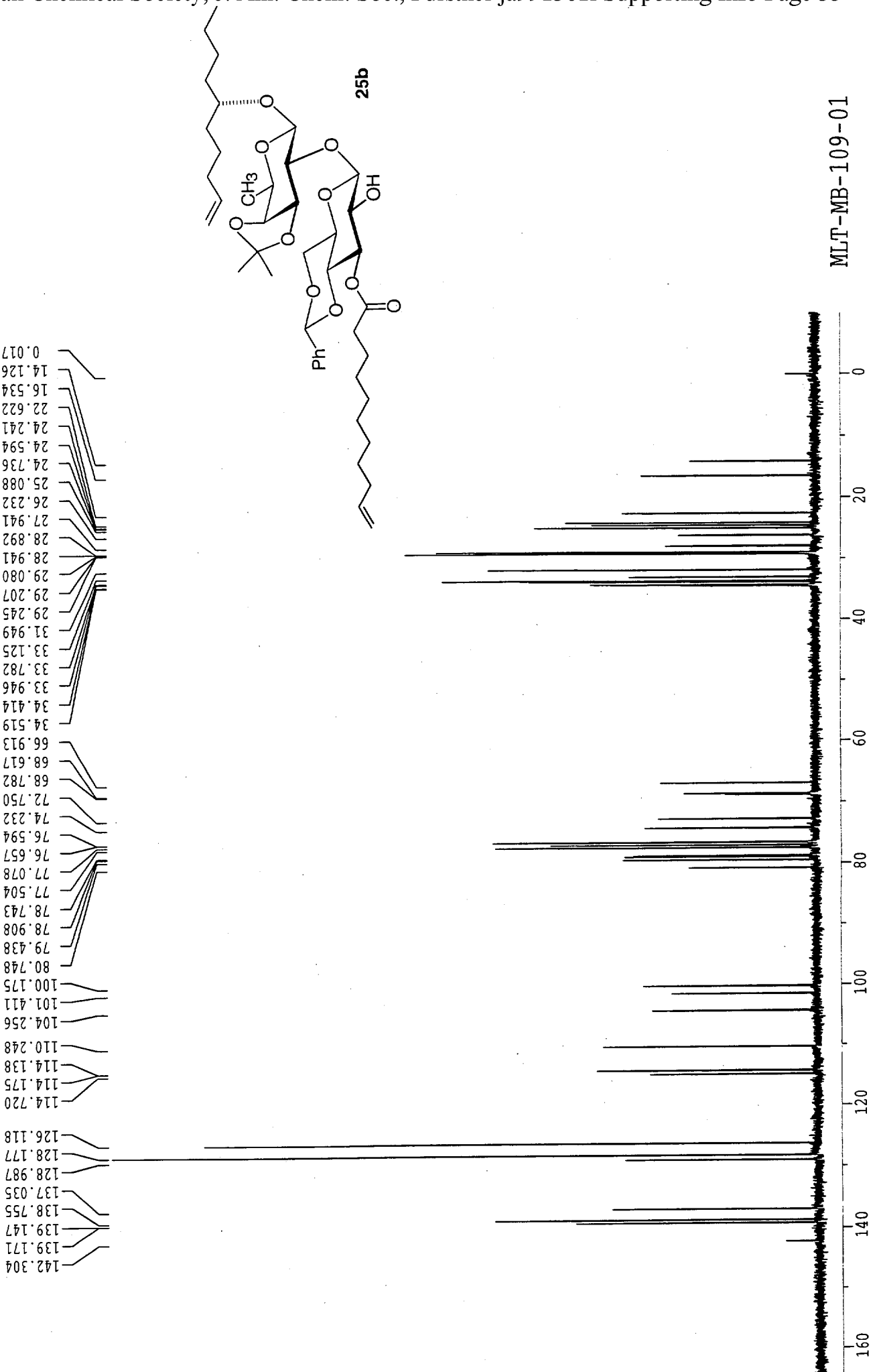
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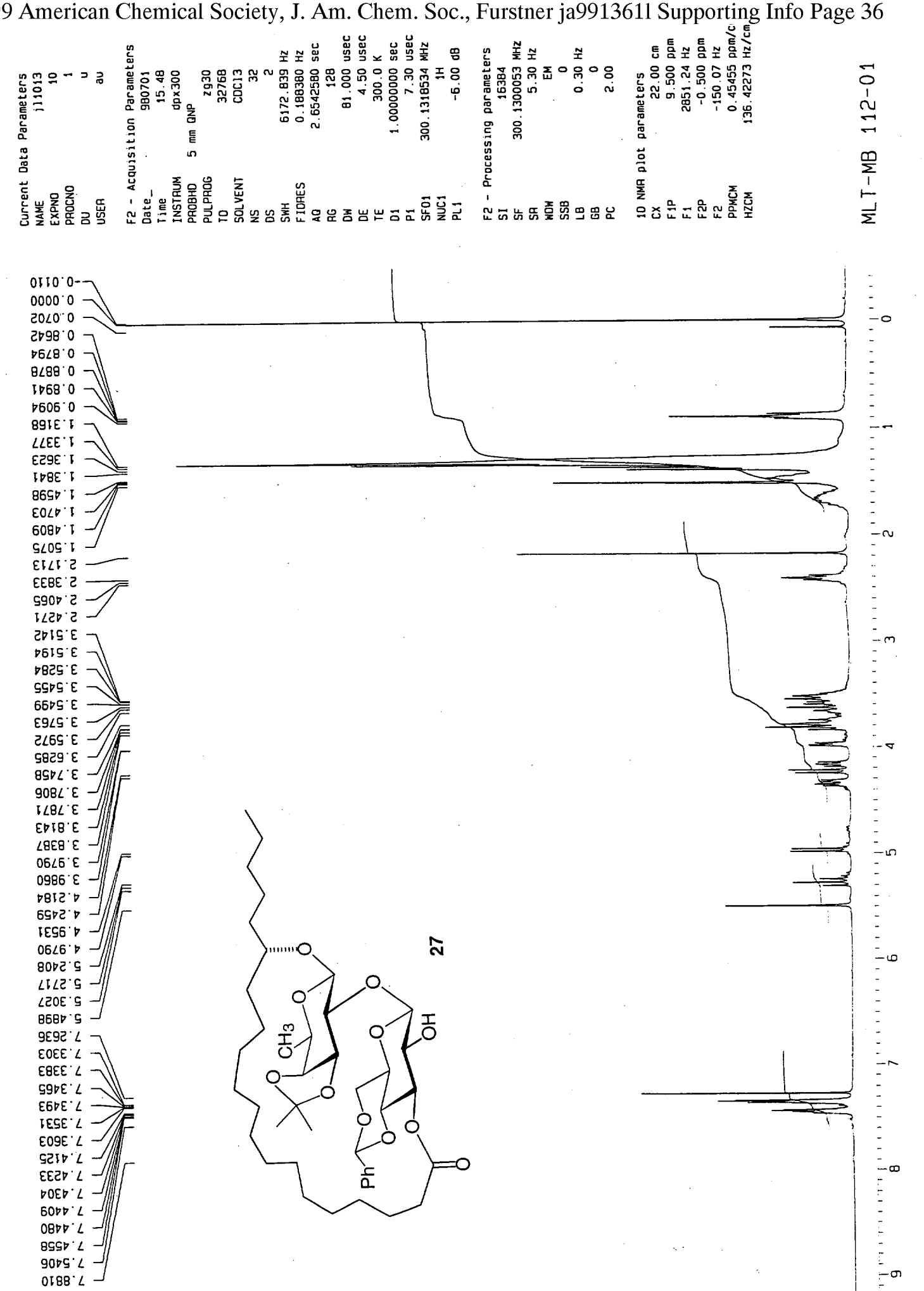

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PROCNO                      1
DU                          u
USER                       au

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DE                      4.50 usec
TE                     300.0 K
D11                 0.03000000 sec
PL12                   16.20 dB
CPDPRG2                waltz16
PCPD2                  80.00 usec
SFO2                300.1312005 MHz
NUC2                        1H
PL2                    -6.00 dB
D1                  0.03000000 sec
P1                      6.60 usec
SFO1                75.4760670 MHz
NUC1                        13C
PL1                    -6.00 dB

F2 - Processing parameters
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SR                   -546.87 Hz
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SSB                           0
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GB                            0
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1D NMR plot parameters
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F1P                  250.000 ppm
F1                  18866.79 Hz
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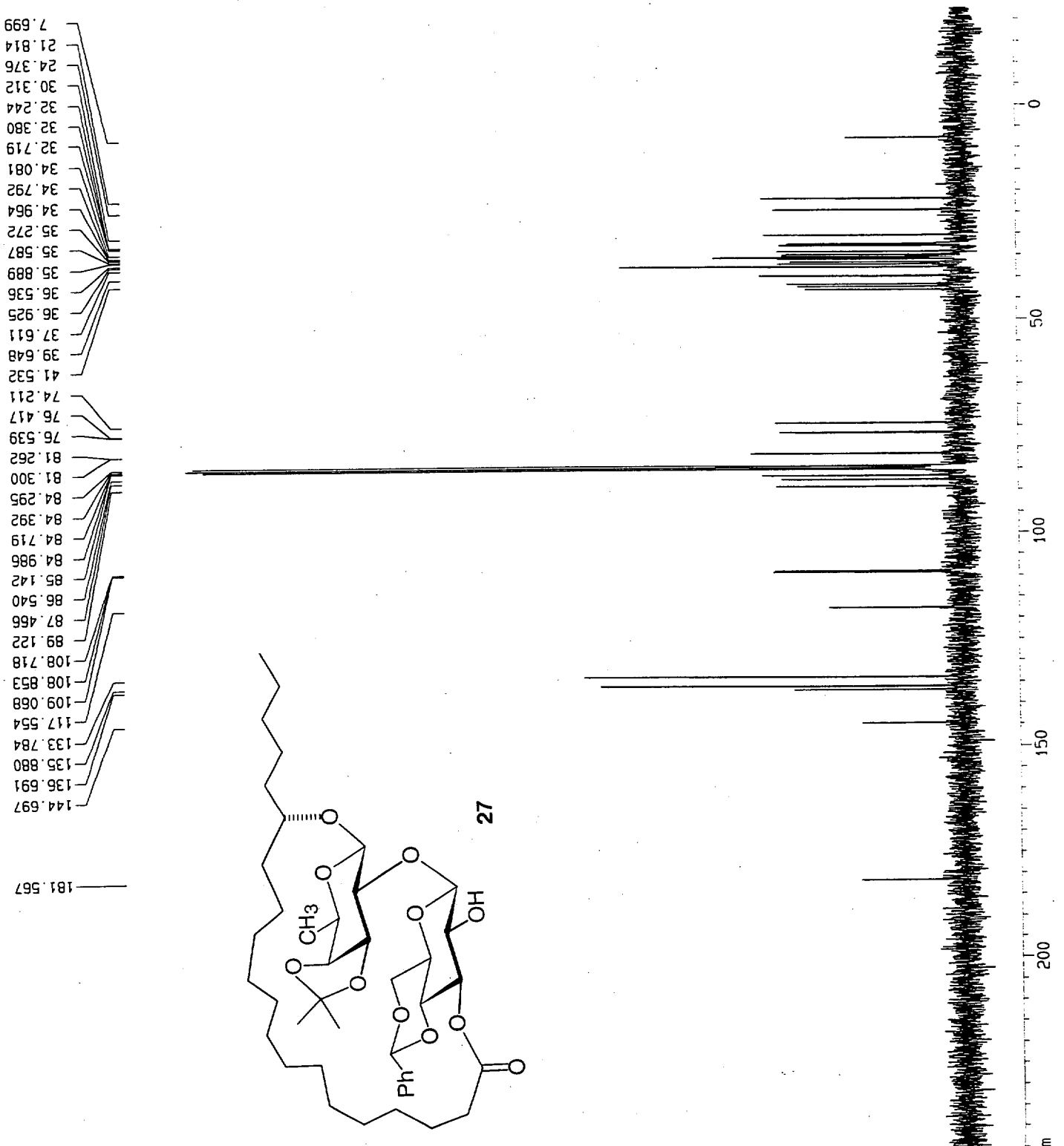
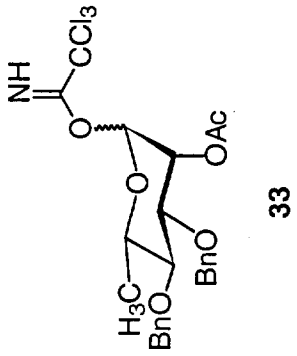
MLT-MB 112-01





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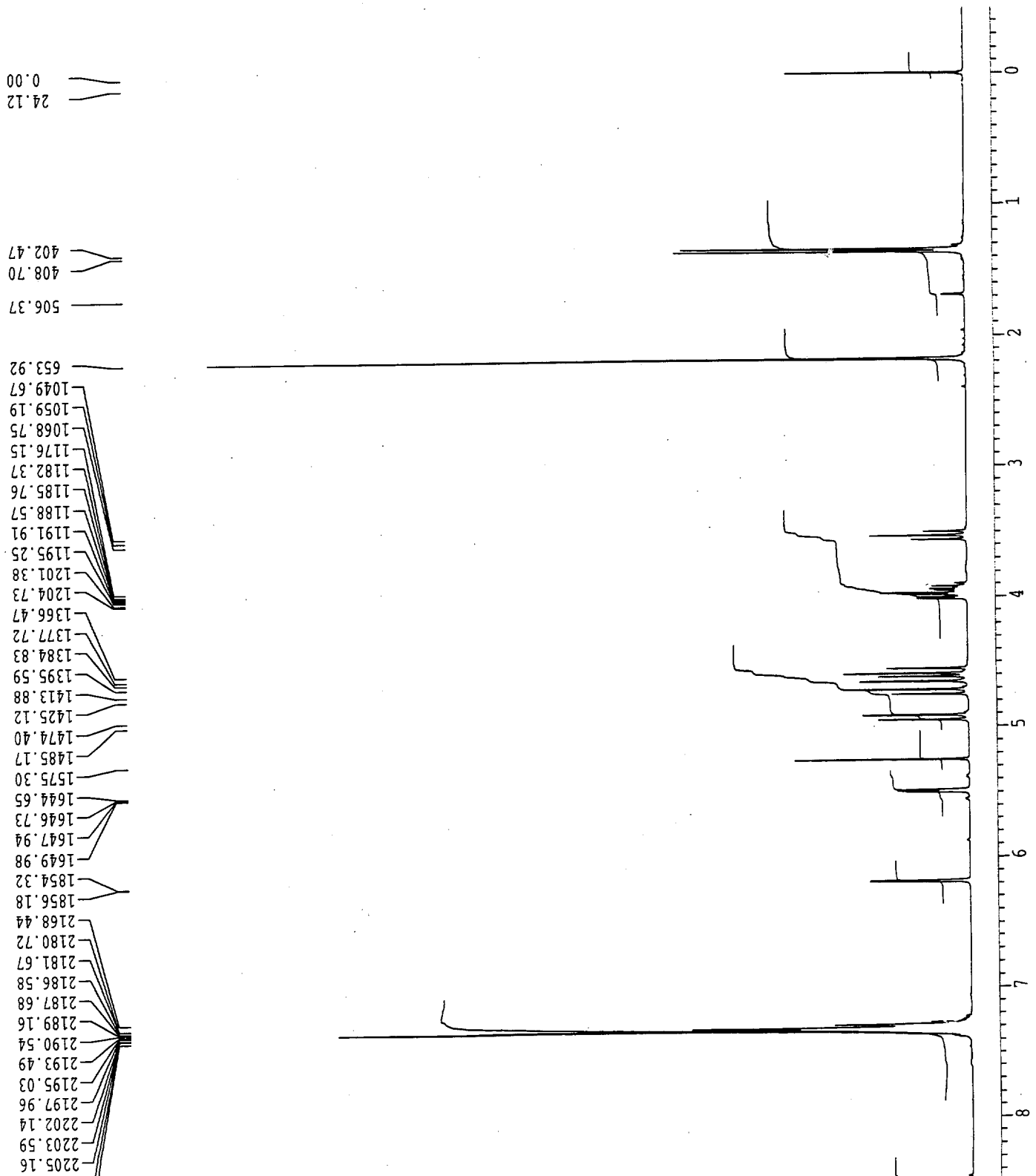

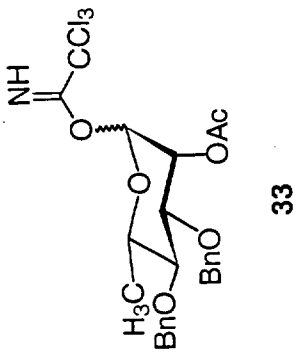

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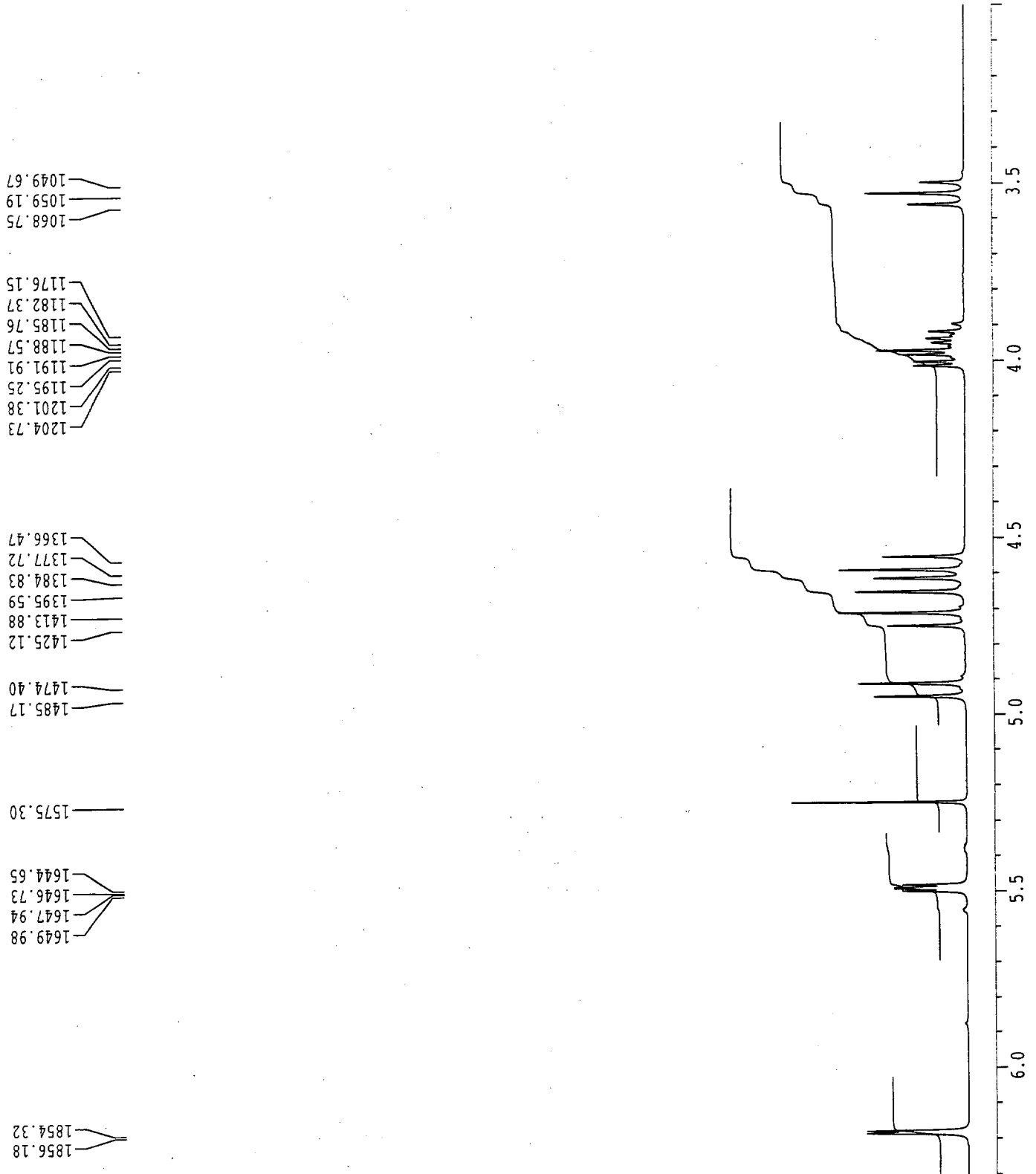

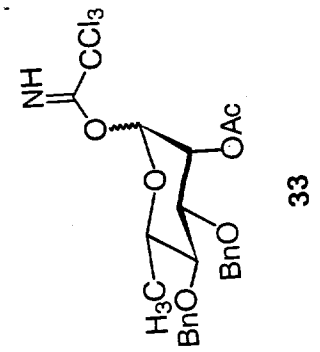

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