SUPPORTING INFORMATION

Total Syntheses of Ipomoeassin B and E

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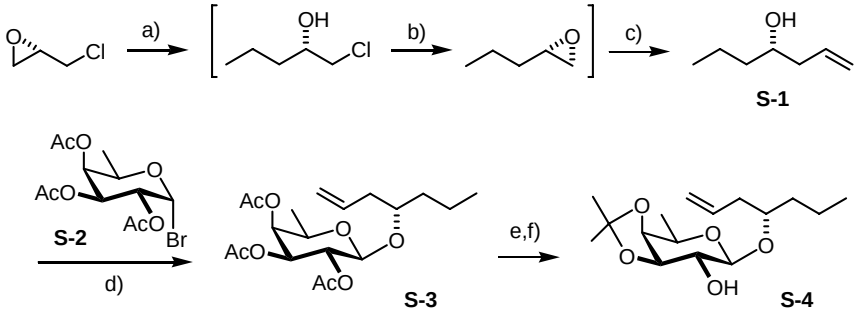
General. All reactions were carried out under Ar atmosphere. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF (Mg-anthracene), CH_2Cl_2 (P_4O_{10}), MeCN, Et_3N, DMSO (CaH_2), MeOH (Mg), toluene (Na/K). Flash chromatography: Merck silica gel 60 (230-400 mesh). NMR: Spectra were recorded on a DPX 300, AV 400 or DMX 600 spectrometer (Bruker) in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (calibration: $CDCl_3$, δ_C = 77.0, δ_H = 7.26; CD_2Cl_2, δ_C = 53.8, δ_H = 5.32). IR: Nicolet FT-7199 spectrometer, wavenumbers in cm^{-1}. MS (EI): Finnigan MAT 8200 (70 eV), HRMS: Finngan MAT 95. Melting points: Büchi melting point apparatus (uncorrected). All commercially available compounds were used as received.

Preparation of the Building Blocks



Scheme S1. Conditions: a) EtMgCl, CuCN (10 mol%), THF, −78 → −20°C; b) NaOH, Et_2O; c) CH_2=CHMgBr, CuCN (10 mol%), THF, −78 → 0°C, 77% (overall), 99% *ee*; d) AgOTf, 2,6-di-*tert*-butylpyridine, MS 4Å, CH_2Cl_2, 0°C → RT, 84%; e) KOMe cat., MeOH; f) 2,2-dimethoxypropane, *p*-TsOH·H_2O cat., acetone, 98% (over both steps).

(*S*)-1-Hepten-4-ol (S-1). A solution of EtMgCl (2 M in THF, 16.2 mL, 32.4 mmol) was added dropwise to a solution of (*S*)-epichlorohydrin (2.00 g, 21.6 mmol) and CuCN (193 mg, 2.16 mmol) in THF (30 mL) at –78 ˚C. The mixture was warmed to –20 ˚C over 3 h before it was poured into sat. aq. NH_4Cl. The organic layer was separated, the aqueous layer was extracted with Et_2O, the combined organic layers were dried over $MgSO_4$, filtered and evaporated to afford crude (*S*)-1-chloro-pentan-2-ol, which was used without further purification.

Powdered NaOH (4.80 g, 121 mmol) was added to a solution of the crude (*S*)-1-chloro-pentene-2-ol in Et_2O (30 mL) and the resulting mixture was stirred at room temperature for 22 h before it was poured into water (10 mL). The organic layer was separated, the aqueous layer was repeatedly extracted with Et_2O, the combined organic phases were dried over $MgSO_4$, filtered and evaporated to give (*S*)-2-propyloxirane, which was used without further purification.

To a stirred solution of the crude oxirane thus formed and CuCN (193 mg, 2.16 mmol) in THF (15 mL) was added a solution of vinylmagnesium bromide (1 M in THF, 28.1 mL, 28.1 mmol) at –78 ˚C over a period of 45 min. The resulting mixture was allowed to warm to 0 ˚C before the reaction was quenched with sat. aq. NH_4Cl. The aqueous layer was repeatedly extracted with Et_2O, the combined ethereal extracts were washed with brine, dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography on silica gel (hexanes/*tert*-butyl methyl ether, 4/1) to give (*S*)-1-hepten-4-ol (**S-1**) as a pale yellow oil (1.91 g, 77%). The NMR data are in full agreement with those previously reported in the literature. $[\alpha]_D^{20}$ = –12.8 (c 0.52, $CHCl_3$); lit.[1] $[\alpha]_D^{20}$ = +12.7 (c 0.54, $CHCl_3$) for (*R*)-enantiomer (99% *ee*).

Compound S-3. A solution of HBr in HOAc (30% *w/w*, 7.1 mL) was added dropwise to a cold (0°C) solution of 1,2,3,4-tetra-O-acetyl-D-fucopyranose[2] (2.08 g, 6.26 mmol) in CH_2Cl_2 (10 mL) and Ac_2O (0.96 mL) and the resulting mixture was stirred for 0.5 h at room temperature once the addition was complete. The mixture was then concentrated in vacuo and the resulting oil was azeotroped with toluene (3 times) to give crude glycosyl bromide **S-2** which was used in the following step without further purification.

To a suspension of activated MS 4Å in CH_2Cl_2 (50 mL) was added a solution of the

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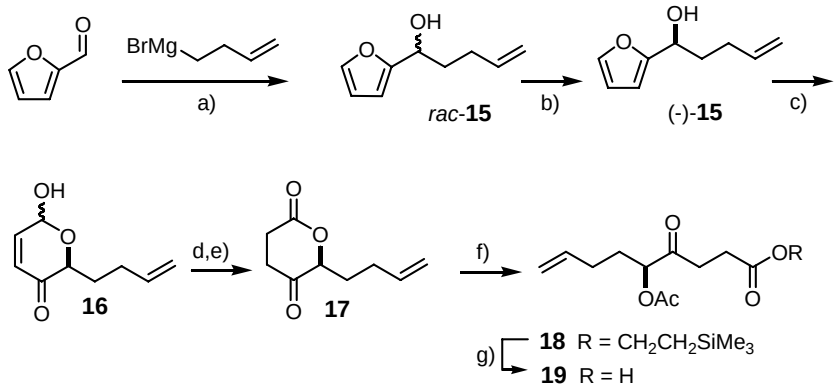
1 Kang, S.-K.; Park, D.-C.; Rho, H.-S.; Yu, C.-M.; Hong, J.-H. *Synth. Comm.* **1995**, *25*, 203-214.

2 Nicolaou, K. C.; Hummel, C. W.; Nakada, M.; Shibayama, K.; Pitsinos, E. N.; Saimoto, H.; Mizuno, Y.; Baldenius, K.-U.; Smith, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 7625-7635.

crude bromide **S-2** prepared above in CH_2Cl_2 (120 mL) and the resulting mixture was stirred at room temperature for 10 minutes before (*S*)-1-hepten-4-ol (**S-1**) (476 mg, 4.17 mmol), 2,6-di-*tert*-butylpyridine (2.40 g, 12.5 mmol), and AgOTf (1.90 g, 7.32 mmol) were successively added. Stirring was continued for 14 h before the suspension was filtered through a pad of Celite and the filtrate was evaporated. The residue was purified by flash chromatography on silica (hexanes/*tert*-butyl methyl ether, 6/1) to give compound **S-3** as a colorless syrup (1.36 g, 84%). $[\alpha]_D^{20}$ = –20.1 (c 0.73, $CHCl_3$). IR (KAP): $\tilde{\nu}$ = 3076, 2961, 2937, 2873, 1752, 1641, 1368, 1250, 1223, 1074, 915. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.77 (ddt, *J* = 7.0, 10.2, 17.2 Hz, 1 H), 5.21 (dd, *J* = 1.1, 3.5 Hz, 1H), 5.17-4.99 (m, 4H), 4.48 (d, *J* = 7.9 Hz, 1H), 3.76 (dq, *J* = 1.0, 6.5 Hz, 1H), 3.64 (m, 1H), 2.25-2.22 (m, 2H), 2.17 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.63-1.34 (m, 4H), 1.20 (d, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 170.8, 170.3, 169.4, 134.4, 117.1, 100.4, 79.7, 71.5, 70.4, 69.3, 68.9, 38.4, 36.6, 20.9, 20.7, 20.6, 18.3, 16.1, 14.0. MS (EI): *m/z* (%): 273 (27), 157 (17), 153 (25), 115 (13), 111 (24), 83 (12), 55 (23), 43 (100). HRMS: calcd. for $C_{19}H_{30}O_8$ $[Na]^+$ 409.183143, found 409.183288.

Compound S-4. Compound **S-3** (1.92 g, 4.97 mmol) was dissolved in MeOH (20 mL) and treated with KOMe (18 mg, 0.25 mmol) for 3 h. The mixture was neutralized with HCl (1 M) and the solvent was evaporated. The residue was suspended in EtOAc, the mixture passed through a short-pad of silica to remove the inorganic salts, and the filtrate was evaporated. A solution containing the resulting crude product, 2,2'-dimethoxypropane (4.4 mL) and TsOH•H_2O (ca. 20 mg) in acetone (15 mL) was stirred at room temperature for 15 h. For work-up, the solvent was evaporated and the residue purified by flash chromatography on silica (hexanes/EtOAc, 6/1 $\rightarrow$ 4/1) to give glycoside **S-4** as a colorless syrup (1.46 g, 98%). $[\alpha]_D^{20}$ = +3.4 (c 1.18, $CHCl_3$). IR (KAP): $\tilde{\nu}$ = 3483, 3076, 2983, 2959, 2935, 2872, 1641, 1380, 1073, 1036, 990, 918. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 5.83 (ddt, *J* = 7.2, 10.1, 17.1 Hz, 1H), 5.13-5.08 (m, 2H), 4.17 (d, *J* = 8.2 Hz, 1H), 4.04-3.98 (m, 2H), 3.83 (dq, *J* = 2.2, 6.6 Hz, 1H), 3.72-3.66 (m, 1H), 3.50 (dd, *J* = 7.3, 8.2 Hz, 1H), 2.35-2.23 (m, 3H), 1.65-1.33 (m, 13H), 0.91 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 134.9, 117.6, 109.8, 101.6, 78.8, 78.7, 76.3, 73.8, 69.1, 38.7, 37.0, 28.2, 26.3, 18.4, 16.6, 14.0. MS (EI): *m/z* (%): 187 (84), 129 (16), 113 (12), 101 (43), 100 (37), 97 (19), 85 (20), 83 (26), 73 (22), 71 (45), 59 (100), 57 (34), 55 (79), 43 (72), 41 (36), 29 (20). HRMS: calcd. for $C_{16}H_{28}O_5$ $[Na]^+$ 323.182872, found 323.182895.



Scheme S2. Conditions: a) 1-bromo-3-pentene, Mg, THF, then 2-furylcarbaldehyde, 82%; b) Ti(O*i*Pr)$_4$, D-(–)-diisopropyltartrate (DIPT), *t*-BuOOH, CH_2Cl_2, –20°C, 47% (= 94% theoretical yield), > 99 *ee*; c) *t*-BuOOH, $VO(acac)_2$ (2 mol%), CH_2Cl_2, 71%; d) CrO_3, H_2SO_4, acetone, 0°C; e) Zn, HOAc, CH_2Cl_2, 78% (over both steps); f) (i) $HO(CH_2)_2SiMe_3$, *p*-TsOH·H_2O cat., CH_2Cl_2; (ii) Ac_2O, DMAP cat., CH_2Cl_2, 93%, 97% *ee* (over both steps); g) TASF, DMF, 68%.

***dl*-5-Hydroxy-5-(2-furyl)-1-pentene (*rac*-15).** Magnesium turnings (335 mg, 13.8 mmol) in THF (1 mL) were activated with 1,2-dibromoethane (25 μL) before additional THF (7.0 mL) was added. A solution of 1-bromo-3-pentene (1.70 g, 12.5 mmol) in THF (2.0 mL) was added over 30 min and the mixture was stirred at ambient temperature for 1 h. The solution of the resulting Grignard reagent was cooled to 0 ˚C before 2-furylcarbaldehyde (1.0 g, 10.4 mmol) was introduced at that temperature. After 2 h, the mixture was quenched with aq. HCl (1 M), the aqueous layer was repeatedly extracted with Et_2O, and the combined ethereal phases were washed with brine, dried over $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 9/1) to give product *rac*-**15** as a pale yellow oil (1.30 g, 82%). IR (KAP): $\tilde{\nu}$ = 3366, 2943, 2863, 1641, 1505, 1149, 1066, 1009, 913, 738, 599. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (dd, *J* = 0.8, 1.8 Hz, 1H), 6.33 (dd, *J* = 1.8, 3.2 Hz, 1H), 6.24 (d, *J* = 3.2 Hz, 1H), 5.84 (ddt, *J* = 6.6, 10.3, 17.0 Hz, 1H), 5.08-4.97 (m, 2H), 4.70 (t, *J* = 6.7 Hz, 1H), 2.20-2.12 (m, 2H), 1.98-1.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 142.0, 137.8, 115.2, 110.1, 105.9, 67.2, 34.6, 29.7. MS (EI): *m/z* (%): 152 (3), 134 (5), 123 (3), 110 (23), 97 (100), 69 (12), 41 (35), 39 (28), 29 (12), 27 (13). HRMS: calcd. for $C_9H_{12}O_2$ 152.083577, found 152.083730.

Kinetic resolution: Preparation of (–)-15. D-(–)-DIPT (2.50 g, 11.8 mmol) was added to a solution of Ti(O*i*Pr)$_4$ (2.90 mL, 9.86 mmol) in CH_2Cl_2 (45 mL) at –20 ˚C. After

stirring for 10 min, the mixture was cooled to –30 ˚C and a solution of *rac*-**15** (1.50 g, 9.86 mmol) in CH_2Cl_2 (2 mL) was slowly introduced. After stirring for 30 min, a solution of *tert*-butylhydroperoxide (5 M in decane, 1.18 mL, 5.92 mmol) was added, and the mixture was stirred for 24 h at –20 ˚C. For work-up, the mixture was filtered through a short pad of silica and the filtrate was evaporated. The residue was purified by flash chromatography on silica (hexanes/EtOAc, 9/1) to give (–)-**15** as a pale yellow oil (701 mg, 47%, >99% *ee*). The *ee* was determined by chiral HPLC (Chiralcel OB-H, Hexane/*i*PrOH = 95/5). The NMR data are identical with those of the racemic sample described above. $[\alpha]_D^{20}$ = –6.6 (c 1.12, $CHCl_3$).

Compound 16. To a solution of alcohol (–)-**15** (333 mg, 2.19 mmol) and $VO(acac)_2$ (6.00 mg, 0.023 mmol) in CH_2Cl_2 (2.0 mL) was added *tert*-butylhydroperoxide (TBHP, 5 M in decane, 0.44 mL, 2.19 mmol). After stirring for 1 h at room temperature, additional $VO(acac)_2$ (6.00 mg, 0.023 mmol) and TBHP (0.44 mL, 2.19 mmol) were added and stirring was continued for 2 h. The mixture was then passed through a short pad of silica, the filtrate was evaporated, and the residue purified by flash chromatography on silica (hexanes/EtOAc, 4/1) to give compound **16** as a mixture of diastereomers (262 mg, 71 %, major/minor = 69/31). IR (KAP): $\tilde{\nu}$ = 3411, 3077, 2926, 1690, 1641, 1089, 1033, 916. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.94 (dd, *J* = 1.5, 10.3 Hz, 1H of minor isomer), 6.90 (dd, *J* = 3.5, 10.3 Hz, 1H of major isomer), 6.16 (dd, *J* = 1.6, 10.3 Hz, 1H of minor isomer), 6.11 (d, *J* = 10.3 Hz, 1H of major isomer), 5.87-5.76 (m, 1H), 5.66-5.65 (m, 1H), 5.18-4.98 (m, 2H), 4.59 (dd, *J* = 3.8, 8.3 Hz, 1H of major isomer), 4.11 (ddd, *J* = 1.2, 3.8, 8.6 Hz, 1H of minor isomer), 3.34 (br, 1H of minor isomer), 3.06 (br, 1H of major isomer), 2.24-2.18 (m, 2H), 2.07-2.03 (m, 1H), 1.18-1.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5 (major), 196.1 (minor), 147.6 (minor), 144.2 (major), 137.7 (major), 137.5 (minor), 128.8 (minor), 127.7 (major), 115.5 (minor), 115.4 (major), 90.9 (minor), 87.7 (major), 78.0 (minor), 73.3 (major), 29.7 (minor), 29.1 (minor), 29.0 (major), 28.8 (major). MS (EI): m/z (rel. intensity): 168 (4), 114 (20), 84 (100), 56 (28), 55 (39), 39 (10), 29 (12), 28 (12), 27 (14). HRMS: calcd. for $C_9H_{12}O_3$ 168.078643, found 168.078521.

Compound 17. Jones' reagent (1.7 mL)[3] was added dropwise to an ice-cold solution of hemiacetal **16** (413 mg, 2.46 mmol) in acetone (13 mL). The resulting mixture was stirred for 3 h at room temperature. The mixture was diluted with *tert*-butyl methyl ether

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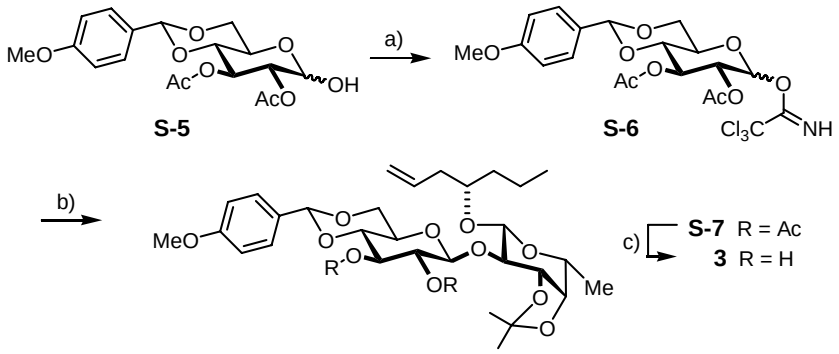
[3] Georgiadis, M. P.; Tsekouras, A.; Kotretsou, S. I.; Haroutounian, S. A.; Polissiou, M. G. *Synthesis* **1991**, 929.

(50 mL) and washed with water, the organic phase was dried over Na_2SO_4, filtered, and evaporated to give the crude oxidation product. To a solution of this material in $CHCl_3$ (26 mL) and AcOH (17 mL) was added zinc powder (1.2 g). The suspension was stirred for 3 h at room temperature before it was filtered through Celite. The filtrate was evaporated aceotropically with benzene to remove residual HOAc and the crude product was purified by flash chromatography (hexanes/*tert*-butyl methyl ether, 2/1 → 1/1) to give compound **17** as a colorless oil (324 mg, 78%). $[\alpha]_D^{20}$ = –246.3 (c 1.08, $CHCl_3$). IR (KAP): $\tilde{\nu}$ = 3079, 2929, 1759, 1735, 1641, 1267, 1171, 999, 919. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.77 (ddt, *J* = 6.7, 10.3, 16.9 Hz, 1H), 5.11-5.02 (m, 2H), 4.68 (dd, *J* = 4.0, 8.2 Hz, 1H), 2.93-2.89 (m, 2H), 2.79-2.64 (m, 2H), 2.34-2.19 (m, 2H), 2.13-2.04 (m, 1H), 1.96-1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.4, 170.0, 136.5, 116.4, 82.2, 33.8, 29.6, 28.6, 28.2. MS (EI): *m/z* (%): 168 (5), 114 (72), 98 (3), 86 (5), 56 (100), 55 (27), 42 (10), 41 (12), 39 (13), 29 (18), 28 (53), 27 (22). HRMS: calcd. for $C_9H_{12}O_3$ 168.078649, found 168.078862.

Compound 18. To a solution of ketolactone **17** (100 mg, 0.59 mmol) and 2-trimethylsilylethanol (0.17 mL, 1.18 mmol) in CH_2Cl_2 (1.0 mL) was added *p*-TsOH•H_2O (2 mg). After stirring for 15 h, the mixture was neutralized with triethylamine and passed through a pad of silica which was carefully rinsed with EtOAc. The filtrate was evaporated, the residue dissolved in CH_2Cl_2 (10 mL) and treated with triethylamine (0.50 mL, 3.54 mmol), Ac_2O (0.22 mL, 2.36 mmol) and DMAP (10 mg, 0.08 mmol). After 3 h, the suspension was filtered through a pad of silica which was carefully rinsed with EtOAc. Evaporation of the solvent followed by flash chromatography of the residue (hexanes/EtOAc, 10/1) gave compound **18** as a colorless oil (156 mg, 93%, 97% *ee*). The *ee* was determined by chiral HPLC column (Chiralcel AD, Heptane/*i*PrOH = 98/2). $[\alpha]_D^{20}$ = –4.3 (c 0.62, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3079, 2954, 1732, 1642, 1249, 1235, 1063, 996, 919, 860, 839, 695. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.81 (ddt, *J* = 6.6, 10.3, 17.0 Hz, 1H), 5.09-4.98 (m, 3H), 4.14 (m, 2H), 2.78-2.72 (m, 2H), 2.56-2.51 (m, 2H), 2.21-2.11 (m, 5H), 1.92-1.80 (m, 2H), 0.97 (m, 2H), 0.04 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 206.2, 172.7, 170.8, 137.4, 115.9, 78.0, 63.2, 33.7, 30.1, 29.6, 27.9, 20.8, 17.6, –1.5 (3C). MS (EI): *m/z* (%): 43 (47), 73 (100), 117 (33), 133 (10), 173 (82). HRMS: calcd. for $C_{16}H_{28}O_5Si_1$ [M^++Na] 351.159826, found 351.159979.

Acid 19. A solution of compound **18** (50 mg, 0.176 mmol) in DMF (1.0 mL) was added to a solution of TASF (73 mg, 0.264 mmol) in DMF (1.0 mL). After stirring for 3 h, the mixture was filtered through a pad of silica which was rinsed with EtOAc several times,

and the combined filtrates were evaporated. Flash chromatography (hexanes/EtOAc/HOAc, 2/1/0.01) of the residue gave carboxylic acid **19** as a colorless oil (28 mg, 68%). $[\alpha]_D^{20}$ = –2.1 (c 0.60, CH_2Cl_2). IR (KAP): ν (cm^{-1}) = 3079, 2928, 1741, 1731, 1713, 1642, 1237, 999, 918. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 5.81 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 5.09-4.99 (m, 3H), 2.80-2.60 (m, 4H), 2.20-2.12 (m, 5H), 1.92-1.80 (m, 2H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 206.1, 177.9, 170.9, 137.4, 115.9, 78.0, 33.5, 30.0, 29.6, 27.5, 20.8. MS (EI): *m/z* (%): 43 (100), 85 (12), 101 (40), 114 (7), 132 (5), 174 (6). HRMS: calcd. for $C_{11}H_{16}O_5$ [M^++Na] 251.088993, found 251.089031.



Scheme S3. Conditions: a) Cl_3CCN, Cs_2CO_3 cat., CH_2Cl_2, 86%; b) compound **S-4**, $BF_3{\cdot}Et_2O$ cat., CH_2Cl_2/pentane (1:1), –20°C, 77%; c) KOMe cat., MeOH, 84%.

Trichloroacetimidate S-6. To a solution of substrate **S-5**[4] (1.00 g, 2.62 mmol) in CH_2Cl_2 (4 mL) were added trichloroacetonitrile (0.48 mL, 4.79 mmol) and Cs_2CO_3 (85 mg, 0.26 mmol). The resulting mixture was stirred for 15 h at ambient temperature before it was filtered through a pad of silica and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 2/1) to give trichloroacetimidate **S-6** as a mixture of anomers (1.19 g, 86%, α:β = 2:1). $[\alpha]_D^{20}$ = +25.9 (c 0.83, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3348, 2940, 1754, 1676, 1616, 1589, 1519, 1236, 1071, 1033, 834. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.81 (s, 1H of β-anomer), 8.71 (s, 1H of α-anomer), 7.37-7.35 (m, 2H), 6.89-6.86 (m, 2H), 6.53 (d, *J* = 3.9 Hz, 1H of α-anomer), 6.00 (d, *J* = 7.7 Hz, 1H of β-anomer), 5.61 (t, *J* = 9.9 Hz, 1H of α-anomer), 5.49 (s, 1H of α-anomer), 5.48 (s, 1H of β-anomer), 5.35 (t, *J* = 8.8 Hz, 1H of β-anomer), 5.26 (dd, *J*

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[4] Fürstner, A.; Radkowski, K.; Grabowski, J.; Wirtz, C.; Mynott, R. *J. Org. Chem.* **2000**, *65*, 8758-8762.

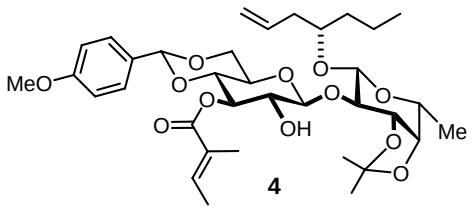
= 7.8, 8.6 Hz, 1H of β-anomer), 5.12 (dd, *J* = 3.9, 9.9 Hz, 1H of α-anomer), 4.37 (dd, *J* = 4.3, 9.8 Hz, 1H of β-anomer), 4.31 (dd, *J* = 5.0, 10.4 Hz, 1H of α-anomer), 4.13-4.05 (m, 1H), 4.88-3.72 (m, 5H), 2.06 (s, 3H of α-anomer), 2.04 (s, 3H of β-anomer), 2.02 (s, 3H of β-anomer), 2.01 (s, 3H of α-anomer). ^{13}C NMR (100 MHz, CD_2Cl_2): α-anomer: $\delta =$ 170.4, 170.0, 161.3, 160.6, 129.7, 127.8 (2C), 113.9 (2C), 102.0, 93.9, 78.9, 70.7, 69.0, 68.7, 67.4, 65.5, 55.6, 21.0, 20.6; β-anomer: $\delta =$ 170.4, 169.4, 161.0, 160.6, 129.7, 127.9 (2C), 113.9 (2C), 102.0, 96.2, 78.3, 71.8, 71.4, 68.7, 67.4, 65.5, 55.6, 20.9, 20.7. MS (EI): *m/z* (%): 527 (22), 365 (9), 179 (16), 137 (51), 136 (100), 135 (71), 43 (85). HRMS: calcd. for $C_{20}H_{22}Cl_3N_1O_9$ [M^++H] 526.043294, found 526.043271.

Disaccharide S-7. BF_3•Et_2O (0.25 M in Et_2O, 1.90 mL) was added to a solution of trichloroacetimidate **S-6** (746 mg, 1.41 mmol) and alcohol **S-4** (500 mg, 1.66 mmol) in CH_2Cl_2/pentane (2.0 mL each) at –20 ˚C. After stirring at that temperature for 30 min, the reaction was quenched with sat. aq. $NaHCO_3$ and the mixture diluted with CH_2Cl_2. The organic layer was separated, dried over Na_2SO_4, and evaporated, and the residue purified by flash chromatography (hexanes/EtOAc, 4/1) to give disaccharide **S-7** as a white solid (696 mg, 77%). mp = 129-130 ˚C. $[\alpha]_D^{20}$ = –35.1 (c 0.70, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3073, 2936, 2873, 1755, 1640, 1616, 1518, 1371, 1244, 1219, 1175, 1099, 1073, 1037, 920, 831. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta =$ 7.35 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.90 (ddt, *J* = 7.2, 10.1, 17.2 Hz, 1H), 5.46 (s, 1H), 5.28-5.23 (m, 1H), 5.10-5.03 (m, 2H), 5.01 (d, *J* = 7.6 Hz, 1H), 4.95-4.91 (m, 1H), 4.33 (dd, *J* = 5.0, 10.4 Hz, 1H), 4.27 (d, *J* = 8.0 Hz, 1H), 4.03-4.00 (m, 1H), 3.96 (dd, *J* = 2.1, 5.6 Hz, 1H), 3.82-3.49 (m, 9H), 2.28-2.24 (m, 2H), 2.05 (s, 3H), 2.02 (s, 3H), 1.52-1.31 (13 H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 170.3, 169.8, 160.6, 135.7, 130.0 (2C), 127.8, 116.8, 113.8 (2C), 110.0, 101.8, 100.6, 100.1, 80.2, 79.7, 78.7, 78.5, 76.9, 73.0, 72.3, 69.0, 68.8, 66.7, 55.6, 38.9, 37.1, 28.1, 26.4, 21.0, 20.9, 18.7, 16.7, 14.2. MS (EI): *m/z* (%): 43 (100), 55 (54), 57 (13), 59 (16), 97 (16), 99 (78), 100 (45), 109 (14), 121 (14), 127 (14), 135 (28), 136 (26), 137 (38), 169 (26), 179 (53), 305 (30), 365 (63), 366 (13), 551 (13). HRMS: calcd. for $C_{34}H_{48}O_{13}$ [M^++H] 665.317321, found 665.316665.

Disaccharide 3. A solution of disaccaride **S-7** (686 mg, 1.06 mmol) and KOMe (10 mg) in MeOH (10 mL) was stirred for 4 h before it was filtered through a pad of silica and evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 2/1 → 0/1) to give disaccharide **3** as a white solid (518 mg, 84%). mp = 68-69 ˚C. $[\alpha]_D^{20}$ = –9.9 (c 1.21, C_2HCl_2). IR (KAP): $\tilde{\nu}$ = 3459, 3072, 2935, 2872, 1640, 1615, 1589, 1518, 1382, 1250, 1075, 1034, 923, 831. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta =$ 7.43 (d, *J* =

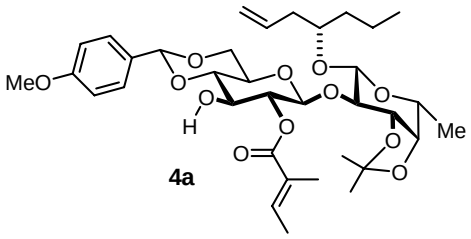
8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 5.95 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.52 (s, 1H), 5.14-5.07 (m, 2H), 4.69 (d, *J* = 7.7 Hz, 1H), 4.35 (d, *J* = 8.2 Hz, 1H), 4.31 (dd, *J* = 4.9, 10.5 Hz, 1H), 4.17 (dd, *J* = 5.5, 7.4 Hz, 1H), 4.04 (dd, *J* = 2.1, 5.4 Hz, 1H), 3.86-3.44 (m, 12H), 2.80 (br, 1H), 2.32 (m, 1H), 1.66 (br, 1H), 1.56-1.30 (m, 13H), 0.94 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 160.6, 135.4, 130.2 (2C), 127.9, 116.9, 113.8 (2C), 110.4, 104.3, 102.1, 100.2, 96.0, 81.0, 79.2, 78.6, 77.0, 76.3, 73.2, 69.0, 68.8, 67.3, 55.6, 38.6, 36.9, 28.0, 26.3, 18.5, 16.6, 14.2. MS (EI): *m/z* (%): 41 (18), 43 (20), 55 (63), 57 (25), 59 (25), 69 (14), 73 (14), 85 (14), 97 (14), 99 (100), 100 (58), 101 (11), 135 (29), 136 (37), 137 (70), 281 (78), 282 (13), 467 (35). HRMS: calcd. for $C_{30}H_{45}O_{11}$ [M^++H] 581.296842, found 581.296186.

Regioselective Acylation: Preparation of Compound 4. A solution of diol **3** (690 mg, 1.19 mmol), DMAP (73.0 mg, 0.60 mmol) and DCC (293 mg, 1.42 mmol) in CH_2Cl_2 (30 mL) was stirred for 5 min prior to the addition of *(E)*-2-methylbutenoic acid (119 mg, 1.19 mmol). Stirring was continued overnight and the precipitate formed was filtered off through a pad of silica. The insoluble residues were thoroughly washed with EtOAc and the combined filtrates were evaporated. The residue was purified by flash chromatography (hexanes/EtOAc, 4/1 → 0/1) to give disaccharide **4** and its regioisomer **4a** (**4**/**4a** = 9/1). Further purification was performed by preparative HPLC (Nucleodur 100-16-C18/A; MeOH/H_2O = 4/1; flow rate: 35.0 mL/min; pressure: 4.1 MPa) to give pure **4** (432 mg, 55%) and pure **4a** (45 mg, 6%), respectively. Analytical and spectroscopic data of compound **4**: Colorless solid, mp = 72-73˚C. $[\alpha]_D^{20}$ = –24.7 (c 0.42, CH_2Cl_2) IR (KAP): $\tilde{\nu}$ = 3474, 3072, 2935, 2873, 1718, 1651, 1589, 1518, 1381, 1252, 1175, 1075, 1036, 990, 923, 829. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta =$ 7.33 (d, *J* = 8.8 Hz, 2H), 6.91 (m, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.91 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.62 (s, 1H), 5.24 (d, *J* = 9.4 Hz, 1H), 5.11-5.03 (m, 2H), 4.77 (d, *J* = 7.7 Hz, 1H), 4.34-4.29 (m, 2H), 4.15-4.12 (m, 1H), 4.01 (dd, *J* = 2.1, 5.4 Hz, 1H), 3.83-3.50 (m, 9H), 3.36 (d, *J* = 2.7 Hz, 1H), 2.28 (m, 2H), 1.84-1.78 (m, 6H), 1.53-1.33 (m, 14H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 167.7, 160.5, 138.3, 135.4, 130.1, 128.6, 127.8 (2C), 117.0, 113.8 (2C), 110.4, 104.4, 101.9, 100.1, 81.0, 79.3, 79.2, 78.4, 77.0, 74.8, 73.5, 69.0, 68.9, 67.3, 55.6, 38.6, 36.9, 28.1, 26.3, 18.6, 16.6, 14.6, 14.2, 12.3. MS (EI): *m/z* (%): 43 (17), 55 (65), 57 (11), 59 (13), 83 (100), 97 (12), 99 (63), 100 (33), 121 (13), 135 (20), 136 (26), 137 (32), 179 (13), 363 (24), 549 (20). HRMS: calcd. for $C_{35}H_{51}O_{12}$ [M^++H] 663.338772, found 663.338055.

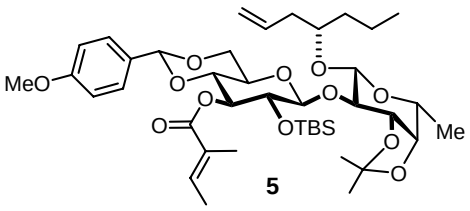


4

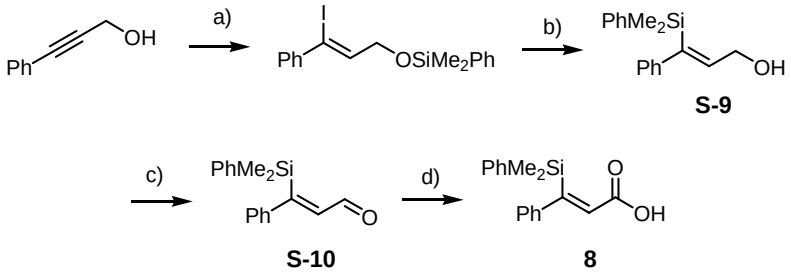
Analytical and spectroscopic data of compound **4a**: mp = 67-68 ˚C. $[\alpha]_D^{20}$ = –7.0 (c 0.83, CH_2Cl_2) IR (KBr): $\tilde{\nu}$ = 3494, 3074, 2935, 2872, 1722, 1651, 1616, 1589, 1519, 1303, 1174, 921, 830. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.39 (d, *J* = 8.8 Hz, 2H), 6.96 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.90 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.51 (s, 1H), 5.09-5.01 (m, 3H), 4.91-4.87 (m, 1H), 4.31 (dd, *J* = 5.0, 10.4 Hz, 1H), 4.25 (d, *J* = 7.9 Hz, 1H), 4.00-3.86 (m, 3H), 3.81-3.71 (m, 4H), 3.65-3.57 (m, 3H), 3.48-3.40 (m, 2H), 2.73 (d, *J* = 3.8 Hz, 1H), 2.27 (m, 2H), 1.86 (m, 3H), 1.81 (m, 3H), 1.51-1.29 (m, 13H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.6, 160.6, 138.6, 135.7, 130.2, 128.6, 127.9 (2C), 116.8, 113.9 (2C), 109.9, 102.1, 100.3, 100.2, 81.3, 79.8, 79.3, 78.8, 76.8, 75.3, 73.1, 69.1, 68.8, 66.5, 55.6, 38.9, 37.1, 28.0, 26.3, 18.7, 16.7, 14.6, 14.2, 12.3. MS (EI): *m/z* (%): 549 (8), 363 (98), 219 (19), 209 (12), 179 (19), 137 (18), 136 (18), 135 (16), 100 (24), 99 (41), 83 (100), 55 (28). HRMS: calcd. for $C_{35}H_{50}O_{12}$ [M^++Na] 685.319445, found 685.319537.



Compound 5. TBSOTf (87.0 mL, 0.30 mmol) was added to a solution of compound **4** (100 mg, 0.15 mmol) and 2,6-lutidine (69.0 mL, 0.75 mmol) in CH_2Cl_2 (2 mL) and the resulting mixture was stirred for 2 h. Evaporation of the solvent followed by purification of the residue by preparative TLC (hexanes/EtOAc, 4/1) gave product **5** as a colorless solid (112 mg, 96%). mp = 54-55 ˚C. $[\alpha]_D^{20}$ = –11.7 (c 0.72, CH_2Cl_2). IR (KBr): $\tilde{\nu}$ = 3073, 2958, 2934, 2859, 1724, 1653, 1616, 1519, 1252, 1181, 1085, 923, 837, 779, 671. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.20 (d, *J* = 8.8 Hz, 2H), 6.78 (m, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.80 (ddt, *J* = 7.0, 10.2, 17.2 Hz, 1H), 5.34 (s, 1H), 5.15 (m, 1H), 5.00-4.93 (m, 3H), 4.21-4.17 (m, 2H), 4.06 (dd, *J* = 5.7, 6.8 Hz, 1H), 3.89 (dd, *J* = 2.0, 5.5 Hz, 1H), 3.73-3.66 (m, 6H), 3.59-3.50 (m, 3H), 3.43-3.39 (m, 1H), 2.18 (m, 2H), 1.71-1.66 (m, 6H), 1.43-1.19 (m, 13H), 0.80 (t, *J* = 5.0 Hz, 3H), 0.73 (s, 9H), –0.02 (s, 3H), –0.11 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 167.2, 160.5, 138.1, 135.6, 130.3, 128.8, 127.7 (2C), 116.8, 113.8 (2C), 110.0, 101.6, 100.6, 100.0, 80.0, 79.6, 78.4, 77.0, 76.2, 74.8, 74.3, 69.1, 68.9, 66.5, 55.6, 38.8, 36.9, 28.0, 26.4, 25.9 (3C), 18.8, 18.3, 16.7, 14.5, 14.2, 12.3, –3.6, –4.8. MS (EI): *m/z* (%): 719 (10), 663 (12), 477 (7), 283 (13), 211 (18), 183 (18), 179 (21), 158 (10), 157 (79), 136 (17), 135 (13), 121 (35), 99 (23), 97 (19), 83 (100), 73 (29), 59 (14), 55 (79), 43 (14). HRMS: calcd. for $C_{41}H_{64}O_{12}Si$ [M^++Na] 799.405930, found 799.405236.



(*Z*)-3-Dimethyl(phenyl)silyl-2-propenoic Acid as Protected Cinnamic Acid Surrogate



Scheme S4. Conditions: a) (i) $NaAlH_2(OCH_2CH_2OMe)_2$, Et_2O, then I_2, (ii) $PhMe_2SiCl$, Et_3N, DMAP cat, CH_2Cl_2, 87%, cf. ref.; b) BuLi, THF, –78°C → RT, 50%, cf. ref.; c) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, –78˚C; d) $NaClO_2$, 2-methyl-2-butene, NaH_2PO_4, *t*BuOH/H_2O, 93% (over both steps).

(*Z*)-3-Dimethyl(phenyl)silyl-2-propenoic acid (8). Oxalyl chloride (0.13 mL, 1.49 mmol) was added dropwise at –78 °C to a solution of DMSO (0.21 mL, 2.99 mmol) in CH_2Cl_2 (5.0 mL) and the mixture as stirred for 15 min at that temperature. A solution of (*Z*)-3-dimethyl(phenyl)silyl-2-propene-1-ol (**S-9**)[5] (267 mg, 1.00 mmol) in CH_2Cl_2 (2.0 mL) was introduced and the resulting suspension was stirred for 45 min, at which point Et_3N (0.56 mL, 3.98 mmol) was added. The reaction mixture was allowed to warm to 0 °C over 1.5 h before it was quenched with sat. aq. NH_4Cl. The aqueous layer was repeatedly extracted with ether, the combined organic phases were washed with brine, dried over Na_2SO_4, and the solvent was evaporated to afford the corresponding aldehyde **S-10** as a pale yellow oil which was used without further purification (239 mg, 90%). Characteristic data: IR (KAP): $\tilde{\nu}$ = 2839, 2739, 1677, 1489, 1428, 1254, 1111, 814, 783, 733, 701, 641, 472. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.83 (d, J = 8.4 Hz, 1H), 7.61-7.58 (m, 2H), 7.42-7.30 (m, 6H), 7.16-7.13 (m, 2H), 6.51 (d, J = 8.4 Hz, 1H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 192.9, 168.4, 144.6, 143.7 (2C), 138.2, 134.1 (2C), 130.0, 128.6 (3C), 127.8, 126.7 (2C), 0.3 (2C). MS (EI): *m/z* (%): 135 (51), 189 (78), 251 (100), 266 (9). HRMS: calcd. for $C_{17}H_{18}O_1Si$ [M^++Na] 289.101916, found 289.101840.

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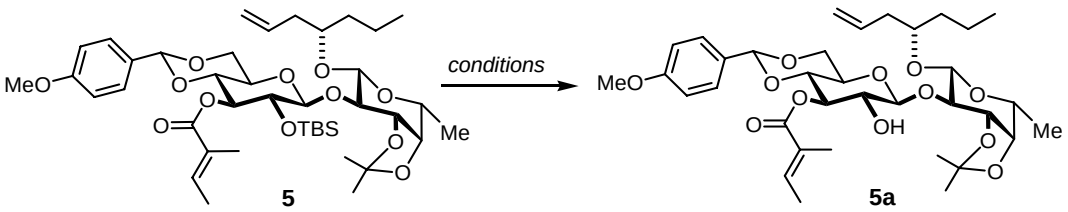
[5] (a) Ukaji, Y.; Sada, K.; Inomata, K. *Chem. Lett.* **1993**, 1227-1230. (b) See also: Amold, L. A.; Naasz, R.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2001**, *123*, 5841-5842.

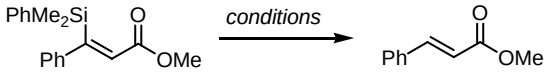
A solution of NaH_2PO_4 (73 mg, 0.61 mmol) in water (0.48 mL), 2-methyl-2-butene (0.21 mL), and $NaClO_2$ (109 mg, 1.2 mmol) were successively added to a solution of the crude aldehyde **S-10** (100 mg, 0.38 mmol) in *t*BuOH (3.0 mL). The mixture was stirred for 2.5 h at ambient temperature, all volatiles were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc/AcOH, 100:10:0.1) to give acid **8** (99.8 mg, 93%) as a white solid. mp = 77-78 ˚C. IR (KAP): $\tilde{\nu}$ = 3022, 2954, 1694, 1589, 1489, 1410, 1313, 1251, 815, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51-7.49 (m, 2H), 7.30-7.24 (m, 6H), 7.08-7.05 (m, 2H), 6.44 (s, 1H), 0.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 144.8, 138.2, 133.7 (2C), 132.9, 128.7, 128.0 (2C), 127.5 (3C), 126.9, 126.4 (2C), 95.7, –0.9 (2C). MS (EI): *m/z* (%): 75 (20), 205 (60), 267 (100), 282 (1). HRMS: calcd. for $C_{17}H_{17}O_2Si$ 281.100333, found 281.100638.

Model Studies Defining the Conditions for the Proto-Desilylation



5 **5a**

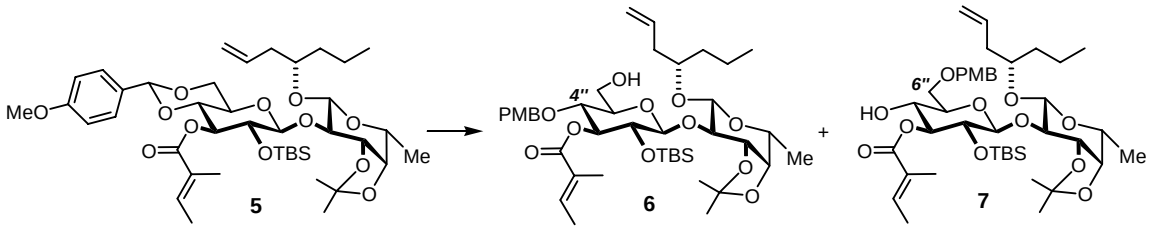
Nr	Reagent	Conditions	Result
1	TBAF	THF, 60°C, 3h	cleavage of tiglate ester
2	TBAF	THF/DMSO, methyl propionate, 80°C, 20 min	cleavage of tiglate ester
3	AgF	THF/MeOH, rt, 20h	no reaction
4	TASF	MeCN, rt, 6h	**5a** (93%)



Nr	Reagent	Conditions	Result
1	$BF_3{\cdot}Et_2O$	$CHCl_3$, rt, 2h	no reaction
2	AgF[6]	THF/MeOH, rt, 5h	methyl cinnamate (32%)
3	TASF	MeCN, rt, 16h	methyl cinnamate (94%)

The model studies summarized above suggested that only TBAF would be appropriate for the final deprotection steps in the projected total syntheses of ipomoeassin B and E.

Reductive Cleavage of the 4,6-O-*p*-Methoxybenzylidene Acetal



Entry	Conditions	Product	Ref.
1	$BH_3{\cdot}THF$, $Cu(OTf)_2$ (15 mol%), THF, RT, 1h	decomposition	7
2	$BH_3{\cdot}THF$, Bu_2BOTf (1 eq.), CH_2Cl_2, RT, 4h	decomposition	8
3	Dibal-H, CH_2Cl_2, 0°C, 5 min	reduction of ester	9
4	PMHS, $AlCl_3$, CH_2Cl_2/Et_2O, RT, 15h	decomposition	10
5	Et_3SiH, $PhBCl_2$, MS 4Å, CH_2Cl_2, –78°C, 1h	decomposition	11
6	$NaBH_3CN$, TMSCl, MS 4Å, MeCN, RT, 15h	81% (**7:6** = 4:1)	12

[6] (a) Fürstner, A.; Radkowski, K. *Chem. Commun.* **2002**, 2182-2183. (b) F. Lacombe, K. Radkowski, A. Fürstner, *Tetrahedron* **2004**, *60*, 7315-7324.

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[9] Crich, D.; Banerjee, A. *Org. Lett*. **2005**, *7*, 1395-1398.

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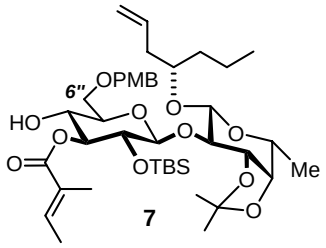
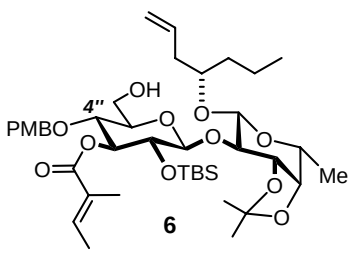
Compounds 6 and 7. Disaccharide **5** (500 mg, 0.643 mmol) was added to a suspension of freshly activated MS 4Å (1.7 g) in CH_3CN (15 mL) and the resulting mixture was stirred for 15 min at that temperature. $NaBH_3CN$ (404 mg, 6.43 mmol) was then introduced before the suspension was cooled to 0 ˚C and TMSCl (0.82 mL, 6.43 mmol) was added. The mixture was allowed to warm to room temperature and stirring was continued for 3 h. The suspension was filtered through Celite, the filtrate was diluted with Et_2O, the organic phase was washed with sat. aq. $NaHCO_3$, dried over sodium sulfate, filtered and evaporated. The residue was purified by flash chromatography to give a mixture of the reduction products (308 mg, 62%, **7**/**6** = 3.5/1). *This mixture does not need to be further purified because compound **9** derived thereof can be isolated in pure form by conventional chromatography at the next step (see below).* For analytical purposes, however, the regioisomers were separated by preparative HPLC (Nucleodur 100-16-C18/A; MeOH/H_2O = 4/1; flow rate: 35.0 mL/min; pressure: 4.1 MPa) to give product **7** (210 mg, 42%) and regioisomer **6** (24 mg, 5%) which showed the following spectroscopic and analytical properties:



7

Compound **7**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.28 (d, *J* = 8.7 Hz, 2H), 6.92 (m, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.90 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.09-4.99 (m, 3H), 4.93 (d, *J* = 7.7 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.30 (d, *J* = 8.1 Hz, 1H), 4.14 (m, 1H), 3.98 (dd, *J* = 2.0, 5.6 Hz, 1H), 3.85-3.40 (m, 11H), 2.75 (br s, 1H), 2.28 (m, 2H), 1.84-1.71 (m, 6H), 1.55-1.31 (m, 13 H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.07 (s, 3H), –0.02 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 168.6, 159.7, 138.7, 135.7, 130.4, 129.9 (2C), 128.7, 116.8, 114.0 (2C), 110.0, 100.1, 99.9, 80.2, 79.3, 78.4, 77.0, 75.9, 74.7, 73.6, 73.3, 71.2, 69.5, 68.9, 55.6, 38.8, 36.9, 28.0, 26.5, 25.9 (3C), 18.8, 18.3, 16.8, 14.5, 14.1, 12.2, –3.5, –4.9. HRMS: calcd. for $C_{41}H_{66}O_{12}Si_1$ [M^++Na] 801.421577, found 801.422035.



6

Compound **6**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.13 (d, *J* = 8.8 Hz, 2H), 6.90 (m, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 5.91 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.22 (t, *J* = 9.2 Hz, 1H), 5.11-5.03 (m, 2H), 4.95 (d, *J* = 7.6 Hz, 1H), 4.45 (m, 2H), 4.29 (d, *J* = 8.1 Hz, 1H), 4.15 (dd, *J* = 5.7, 6.8 H, 1H), 3.98 (dd, *J* = 2.1, 5.6 Hz, 1H), 3.84-3.76 (m, 6H), 3.71-3.65 (m, 2H), 3.61 (t, *J* = 9.5 Hz, 1H), 3.52 (dd, *J* = 7.5, 9.0, 1H), 3.42-3.38 (m, 1H),

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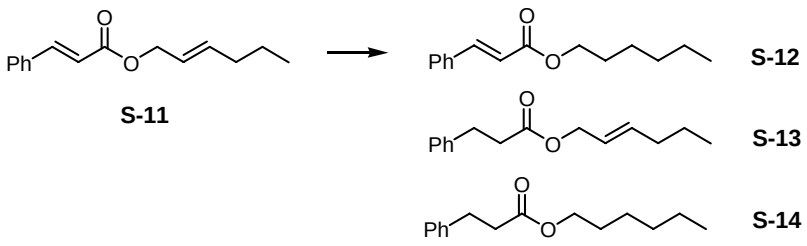
[12] Johansson, R.; Samuelsson, B. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2371-2374.

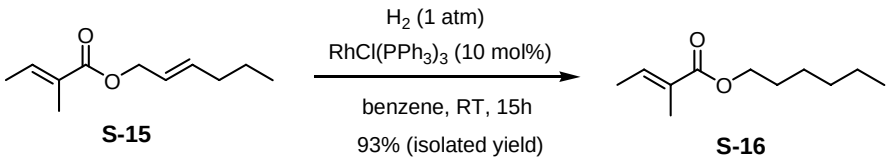
2.28 (m, 2H), 1.84-1.79 (m, 6H), 1.65 (br s, 1H), 1.55-1.32 (m, 13 H), 0.09 (t, J = 7.2 Hz, 3H), 0.82 (s, 9H), 0.07 (s, 3H), –0.03 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta =$ 167.1, 159.7, 138.26, 135.6, 130.5, 130.1 (2C), 129.0, 116.8, 114.0 (2C), 110.0, 100.2, 100.1, 80.0, 78.5, 77.5, 77.0, 76.6, 76.3, 75.5, 74.3, 73.8, 69.0, 62.0, 55.5, 38.8, 36.9, 28.1, 26.3, 25.8 (3C), 18.7, 18.2, 16.7, 14.6, 14.1, 12.3, –3.6, –4.8.

The assigned regiochemistry was further corroborated by acylation of both isomers. The corresponding ring proton H-6,6' (m, 2H) in **6** and H-4 (app. t, 1H) in **7** showed the expected acylation shifts.

Model Studies on Selective Hydrogenation

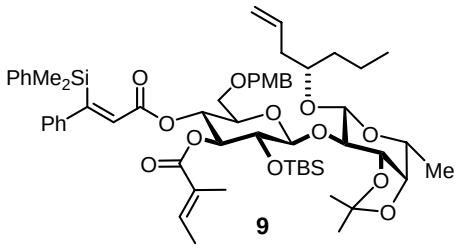


Conditions	**Product Distribution (NMR)**			
	S-11	**S-12**	**S-13**	**S-14**
H_2 (1 atm), $RhCl(PPh_3)_3$ (3 mol%), benzene, RT, 4h	15%	52%	7%	26%
KOOCN=NCOOK (2 eq.), AcOH, MeOH, RT, 15h	44%	14%	33%	9%

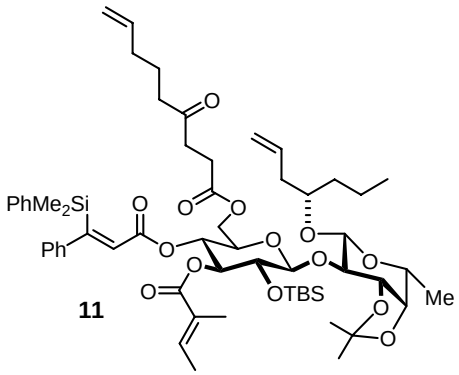


Total Synthesis of Ipomoeassin B

Compound 9. Et_3N (43 μL, 0.305 mmol) and 2,4,6-trichlorobenzoyl chloride (22 mL, 0.139 mmol) were added to a solution of acid **8** (39 mg, 0.139 mmol) in toluene (0.6 mL) and the resulting mixture was stirred for 1.5 h at ambient temperature before a solution of the mixture of alcohols **7** and **6** (54 mg, 0.0693 mmol) and DMAP (8.0 mg, 0.0693 mmol) in CH_2Cl_2 (0.5 mL) was introduced. After stirring for 3 h, the mixture was filtered through a pad of silica, the filtrate was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give product **9** as a colorless oil (56.8 mg, 79%). $[\alpha]_D^{20}$ = –4.4 (c 0.5, $CHCl_3$). IR (KAP): $\tilde{\nu}$ = 3070, 2956, 2932, 2904, 2858, 1730, 1652, 1612, 1587, 1513, 1248, 1160, 1074, 915, 839, 780, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.46 (m, 2H), 7.26-7.18 (m, 10 H), 6.97-6.94 (m, 2H), 6.84-6.80 (m, 3H), 6.31 (s, 1H), 5.94 (ddt, *J* = 7.1, 10.2, 17.2 Hz, 1H), 5.27 (t, *J* = 9.4 Hz, 1H), 5.08-4.99 (m, 3H), 4.90 (d, *J* = 7.6 Hz, 1H), 4.41 (d, *J* = 11.6, 1H), 4.39 (d, *J* = 11.6, 1H), 4.31 (d, *J* = 7.7 Hz, 1H), 4.15 (t, *J* = 6.1 Hz, 1H), 3.97-3.90 (m, 2H), 3.78-3.74 (m, 4H), 3.66-3.53 (m, 3H), 3.36-3.34 (m, 2H), 2.29-2.26 (m, 2H), 1.76-1.75 (m, 6H), 1.56-1.24 (m, 11H), 0.86 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.41 (s, 3H), 0.26 (s, 3H), 0.04 (s, 3H), –0.06 (s, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 165.8, 164.8, 159.0, 144.7, 138.3, 137.9, 135.4, 133.9 (3C), 132.9, 130.3, 129.4 (2C), 128.6, 128.3, 127.8 (2C), 127.4 (2C), 126.8, 126.6 (2C), 116.5, 113.6, 109.7, 100.2, 99.8, 79.6, 78.7, 76.4, 76.0, 75.3, 73.6, 73.3, 73.1, 69.9, 68.5, 68.4, 55.2, 38.5, 36.6, 27.7, 26.3, 25.7 (3C), 18.3, 18.0, 16.7, 14.3, 14.1, 12.0, –0.8, –1.5, –3.9, –5.0. MS (EI): *m/z* (%): 83 (14), 121 (100), 157 (9), 265 (30), 565 (4), 985 (2). HRMS: calcd. for $C_{58}H_{82}O_{13}Si_2$ [M^++Na] 1065.518622, found 1065.517790.



9

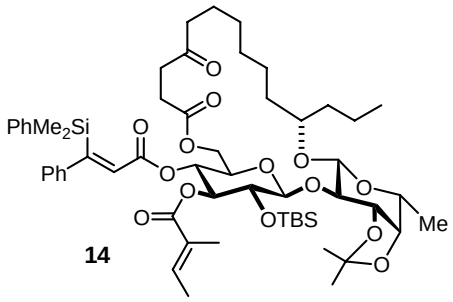


11

Synthesis of 11. DDQ (49.0 mg, 0.216 mmol) was added to a solution of compound **9** (150 mg, 0.144 mmol) in CH_2Cl_2 (6.0 mL) and water (0.3 mL). The mixture was stirred at room temperature for 16 h before it was filtered through a pad of silica which was carefully rinsed with ethyl acetate. The combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give alcohol **10** (150 mg) which contained *p*-methoxybenzaldehyde as an inseparable impurity.

Et_3N (45 μL, 0.318 mmol) and 2,4,6-trichlorobenzoyl chloride (23 μL, 0.148 mmol) were added to a solution of 4-oxo-8-nonenoic acid[13] (25 mg, 0.0862 mmol) in toluene (1.0 mL) and the mixture was stirred for 1.5 h before a solution of the crude alcohol **10** (75 mg, ca. 0.074 mmol) and DMAP (9.0 mg, 0.074 mmol) in toluene (1.5 mL) was introduced. Stirring was continued for 2 h, the mixture was passed through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 8/1) to give disaccharide **11** as a colorless syrup (61.7 mg, 78%). $[\alpha]_D^{20}$ = –4.2 (c 0.43, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3071, 2956, 2933, 1732, 1651, 1588, 1248, 1157, 914, 839, 780, 730, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.44 (m, 2H), 7.28-7.18 (m, 6H), 6.98-6.95 (m, 2H), 6.81 (m, 1H), 6.33 (s, 1H), 5.93 (ddt, *J* = 7.1, 10.1, 17.1 Hz, 1H), 5.77 (ddt, *J* = 6.4, 10.3, 17.0 Hz, 1H), 5.27 (t, *J* = 9.4 Hz, 1H), 5.08-4.96 (m, 5H), 4.94 (d, *J* = 7.6 Hz, 1H), 4.28 (d, *J* = 7.8 Hz, 1H), 4.14 (t, *J* = 5.9 Hz, 1H), 4.01-3.99 (m, 2H), 3.97 (dd, *J* = 2.0, 5.6 Hz, 1H), 3.89-3.85 (m, 1H), 3.77 (m, 1H), 3.68-3.61 (m, 2H), 3.55 (dd, *J* = 7.6, 9.1 Hz, 1H), 2.67-2.42 (m, 6H), 2.27 (m, 2H), 2.09-2.03 (m, 2H), 1.77-1.75 (m, 6H), 1.59-1.34 (m, 15 H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.39 (s, 3H), 0.27 (s, 3H), 0.04 (s, 3H), –0.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 172.4, 166.9, 166.6, 164.7, 144.7, 138.2, 138.0, 135.4, 133.8 (2C), 132.6, 128.7, 128.2, 127.9 (2C), 127.6 (2C), 126.9, 126.6 (2C), 116.5, 115.3, 109.7, 100.3, 99.8, 79.7, 79.1, 77.2, 76.5, 76.0, 75.2, 73.2, 71.5, 69.4, 68.6, 63.0, 41.9, 38.6, 37.1, 36.7, 33.1, 28.0, 27.8, 26.4, 25.7 (3C), 22.8, 18.3, 18.0, 16.7, 14.4, 14.1, 12.1, –0.7, –1.4, –3.8, –4.9. MS (EI): *m/z* (%): 83 (68), 157 (29), 265 (100), 393 (30), 775 (9), 793 (42), 961 (13), 1017 (7). HRMS: calcd. for $C_{59}H_{86}O_{14}Si_2$ [M^++Na] 1097.544832, found 1097.544163.

Compound 14. The ruthenium carbene complex **12** (5.0 mg, 0.00558 mmol) was added to a solution of diene **11** (60 mg, 0.0558 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was refluxed for 4 h before the reaction was quenched with ethyl vinyl ether. Evaporation of all volatile materials followed by flash chromatography of the residue (hexanes/EtOAc, 4/1) gave the corresponding metathesis product **13** as a mixture of (*E*)- and (*Z*)-isomers.



14

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[13] Hodgson, D. M.; Stupple, P. A.; Pierard, F. Y. T. M.; Labande, A. H.; Johnstone, C. *Chem. Eur. J.* **2001**, *7*, 4465.

A solution of cycloalkene **13** thus obtained (42 mg, 0.0398 mmol) and $RhCl(PPh_3)_3$ (7.0 mg, 0.0076 mmol) in EtOH (0.6 mL) was stirred under an atmosphere of H_2 (1 atm) overnight. Evaporation of the solvent and flash chromatography of the crude product (hexanes/EtOAc, 4/1) gave compound **14** as a colorless oil (34 mg, 81%). $[\alpha]_D^{20}$ = +0.6 (c 0.50, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3069, 2932, 2858, 1733, 1652, 1588, 1248, 1155, 1074, 839, 780, 730, 701. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.45 (m, 2H), 7.28-7.17 (m, 6H), 6.97-6.95 (m, 2H), 6.86 (m, 1H), 6.31 (s, 1H), 5.27 (t, *J* = 9.3 Hz, 1H), 5.08 (t, *J* = 9.8 Hz, 1H), 4.93 (d, *J* = 7.7 Hz, 1H), 4.27 (d, *J* = 7.8 Hz, 1H), 4.20-4.13 (m, 2H), 4.00-3.97 (m, 2H), 3.87 (dd, *J* = 6.6, 7.7 Hz, 1H), 3.78 (m, 1H), 3.63 (m, 1H), 3.54 (dd, *J* = 7.8, 9.0 Hz, 1H), 3.51 (m, 1H), 2.81-2.73 (m, 1H), 2.58-2.31 (m, 5H), 1.79-1.24 (m, 29H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.24 (s, 3H), 0.05 (s, 3H), –0.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.6, 171.4, 166.8, 166.3, 164.4, 144.7, 138.4, 138.2, 133.8 (2C), 132.7, 128.6, 128.2, 127.8 (2C), 127.5 (2C), 126.8, 126.6 (2C), 109.7, 101.5, 99.8, 82.0, 79.4, 76.5, 76.4, 75.6, 73.1, 71.7, 68.4, 68.3, 61.7, 42.3, 37.3, 37.0, 33.7, 28.7, 28.3, 28.0, 27.8, 26.3, 25.7 (3C), 24.0, 23.7, 18.4, 18.0, 16.8, 14.4, 14.3, 12.1, –0.5, –1.6, –3.8, –4.9. MS (EI): *m/z* (%): 83 (91), 157 (29), 265 (100), 349 (13), 767 (36), 991 (9). HRMS: calcd. for $C_{57}H_{84}O_{14}Si_2$ [M^++Na] 1071.529187, found 1071.530087.

Synthesis of Ipomoeassin B (1). A solution of TASF (79 mg, 0.286 mmol) in MeCN (2.0 mL) was added to a solution of compound **14** (30 mg, 0.0286 mmol) in wet MeCN (1.5 mL). After stirring for 4 h, the mixture was filtered through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated, and the residue was treated with trifluoroacetic acid (16 μL, 215 mmol) in CH_2Cl_2 (2.0 mL). After stirring for 3 h, the solution was neutralized with Et_3N, the solvent was evaporated, and the residue purified by flash chromatography (CH_2Cl_2/MeOH, 20/1) to afford Ipomoeassin B (**1**) as a colorless syrup which solidifies when kept in the freezer (10 mg, 45%). $[\alpha]_D^{25}$ = –48.0 (c 0.36, EtOH); lit.[14] $[\alpha]_D^{25}$ = –39 (c 0.3, EtOH). IR (KAP): $\tilde{\nu}$ = 3365, 3062, 2932, 1744, 1719, 1631, 1371, 1316, 1265, 1249, 1157, 1138, 1073. ^{1}H NMR (400 MHz, C_6D_6) and ^{13}C NMR (100 MHz, C_6D_6) data, see Table S1 and S2, respectively. MS (EI): *m/z* (%): 513 (11), 467 (14), 349 (10), 241 (13), 223 (42), 131 (44), 111 (13), 83 (100), 55 (28). HRMS: calcd. for $C_{40}H_{56}O_{14}$ [M^++Na] 783.356230, found 783.356291.

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[14] Cao, S.; Guza, R. C.; Wisse J. H.; Miller, J. S.; Evans, R.; Kingston, D. G. I. *J. Nat. Prod.* **2005**, *68*, 487.

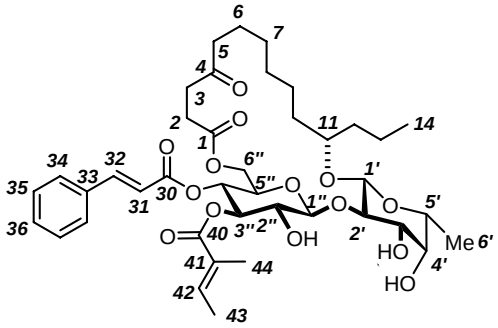


Table S1. Comparison of the published ^{1}H NMR data (C_6D_6) of Ipomoeassin B (**1**) (500 MHz) with those of the synthetic sample (Bruker dpx300, 300 MHz). Numbering scheme as shown in the insert.

Position	Ipomoeassin B (*J* in Hz)	Synthetic Sample (*J* in Hz) [a]
2	2.38 ddd (17.4, 9.4, 3.4)	2.37 ddd (17.1, 9.3, 3.5)
	2.13 ddd (17.4, 7.7, 3.5)	2.15 ddd (17.1, 7.6, 3.3)
3	2.62 ddd (16.1, 7.7, 3.4)	2.63 ddd (16.1, 7.7, 3.3)
	2.50 ddd (16.1, 9.4, 3.5)	2.49 ddd (16.1, 9.2, 3.4)
5	2.07 t (6.2)	2.08 t (6.2)
11	3.71 m	3.73 m
14	0.96 t (7.1)	0.97 t (7.0)
1'	4.38 d (7.6)	4.39 d (7.6)
2'	3.88 dd (9.5, 7.6)	3.88 dd (9.8, 7.5)
3'	3.65 dd (9.5, 3.3)	3.65 dd (9.6, 3.3)
4'	3.53 brs	3.53 br s
5'	3.11 brq (6.4)	3.11 br q (6.3)
6'	1.29 d (6.4)	1.29 d (6.4)
1"	4.59 d (7.8)	4.61 d (7.8)
2"	3.95 dd (9.7, 7.8)	3.95 dd (9.6, 8.0)
3"	5.50 t (9.7)	5.51 t (9.6)
4"	5.72 t (9.7)	5.73 t (9.6)
5"	3.44 brd (9.7)	3.46 brm
6"	4.66 dd (12.6, 2.1)	4.64 m
	4.16 brd (12.6)	4.18 br d (12.4)
31	6.40 d (16.1)	6.41 d (16.0)
32	7.81 d (16.1)	7.82 d (16.0)
34	6.88-7.07	6.88-7.08
35	6.88-7.07	6.88-7.08
36	6.88-7.07	6.88-7.08
42	6.95 m	6.94 m
43	1.27 d (7.1)	1.29 d (7.1)
44	1.72 brs	1.73 brs

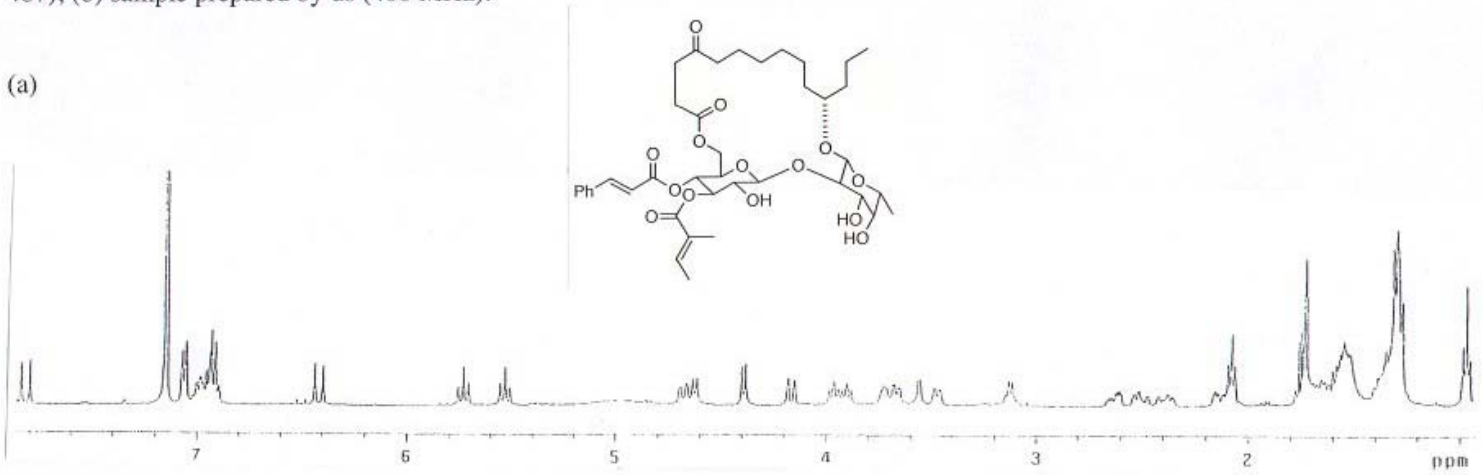
[a] The protons at positions 6-10, 12 and 13 appear between δ 1.73-1.26 as complicated multiplet.

Table S2. Comparison of the published ^{13}C NMR data (C_6D_6) of Ipomoeassin B (**1**) (100 MHz) with those of the synthetic samples (Bruker DMX-600, 150 MHz).

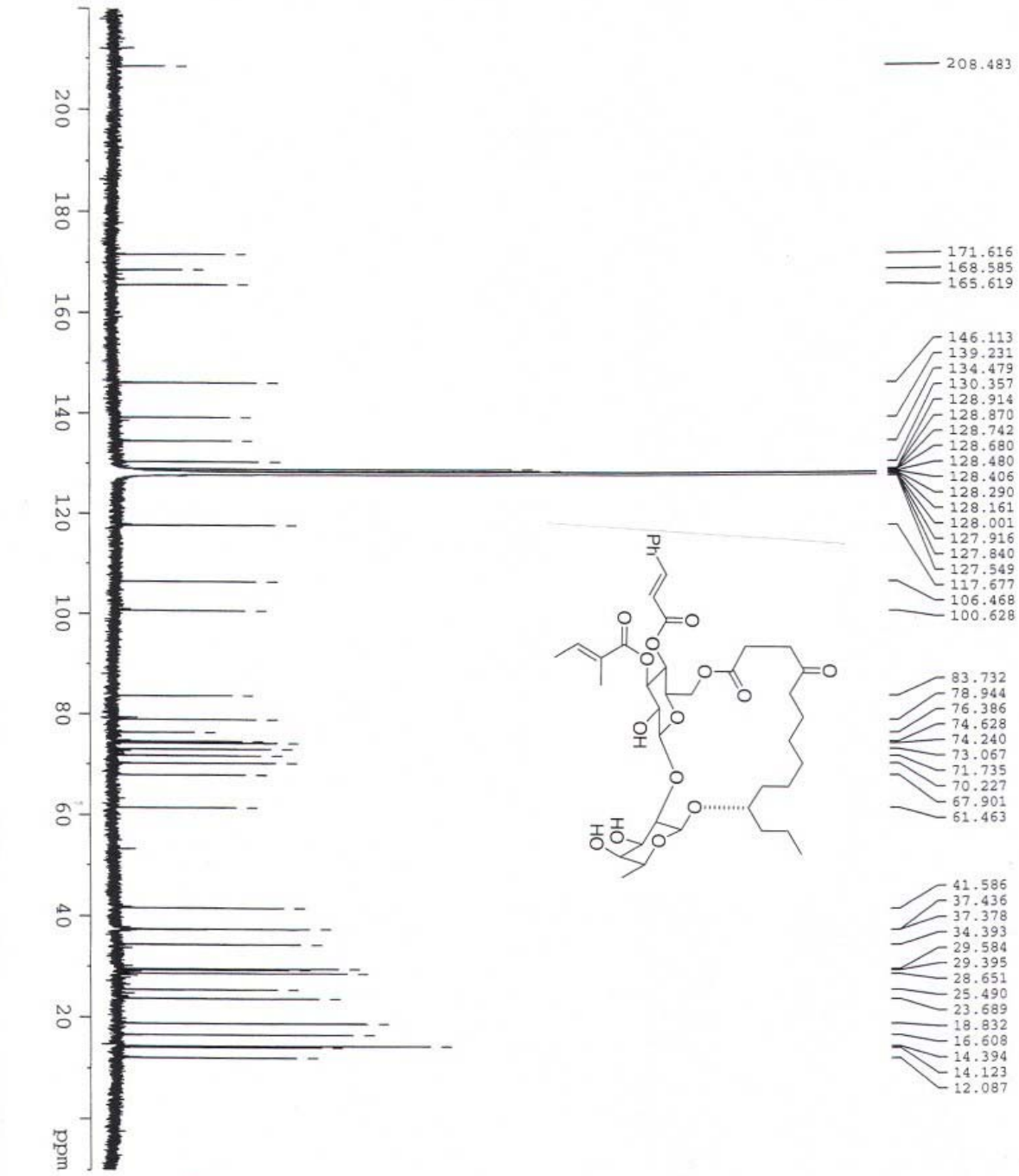
Position	Ipomoeassin B	Synthetic Sample
1	171.5	171.6
2	37.4	37.4
3	29.5	29.6
4	208.3	208.5
5	41.5	41.6
6	23.6	23.7
7	28.6	28.7
8	29.3	29.4
9	25.4	25.5
10	34.3	34.4
11	78.8	78.9
12	37.4	37.4
13	18.8	18.8
14	14.3	14.4
1'	100.6	100.6
2'	83.7	83.7
3'	74.2	74.2
4'	71.6	71.7
5'	70.2	70.2
6'	14.0	14.1
1"	106.4	106.5
2"	74.6	74.6
3"	76.3	76.4
4"	67.8	67.9
5"	73.0	73.1
6"	61.4	61.5
30	165.5	165.6
31	117.6	117.7
32	146.0	146.1
33	134.4	134.5
34	128.4	128.5
35	128.8	128.9
36	130.3	130.4
40	168.5	168.6
41	128.0	127.9
42	139.1	139.2
43	16.6	16.6
44	12.0	12.1

^{1}H NMR spectra of Ipomoeassin B in C_6D_6: (a) natural product reported in literature (500 MHz, Kingston et al. *J. Nat. Prod.* **2005**, *68*, 487); (b) sample prepared by us (400 MHz).

(a)



(b)



C609535

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PROCNO 1

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DE 5.50 usec
TE 303.0 K
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d11 0.03000000 sec
TD0 1

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========== CHANNEL f2 ==========
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PL12 16.31 dB
SFO2 600.2234213 MHz

F2 - Processing parameters
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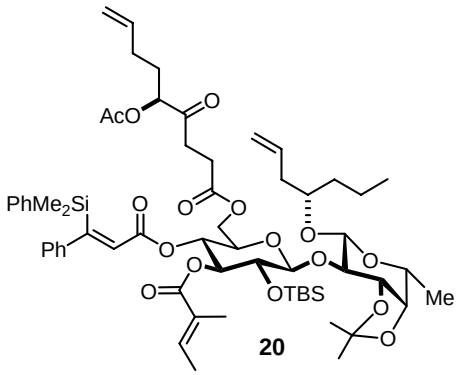
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

NAG-NB-052-02

DMX-600

Total Synthesis of Ipomoeassin E

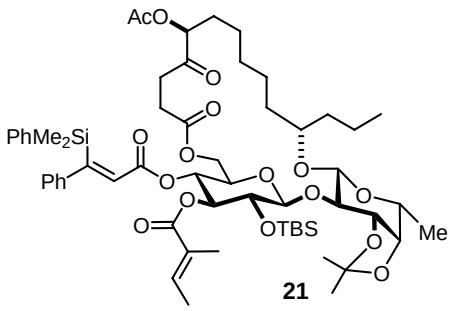
Disaccharide 20. DDQ (19.0 mg, 0.0830 mmol) was added to a solution of compound **9** (57.7 mg, 0.0553 mmol) in CH_2Cl_2 (2.0 mL) and water (0.1 mL), and the resulting mixture was stirred at ambient temperature for 16 h. The suspension was then filtered through a pad of silica which was rinsed with ethyl acetate, the combined filtrates were evaporated, and the residue was purified by flash chromatography (hexanes/EtOAc, 6/1) to give alcohol **10** (45.6 mg) which contained traces of *p*-methoxybenzaldehyde.



20

Et_3N (26 μL, 0.185 mmol) and 2,4,6-trichlorobenzoyl chloride (13 mL, 0.0862 mmol) were added to a solution of carboxylic acid **19** (19.7 mg, 0.0862 mmol) in toluene (0.5 mL). After stirring for 1.5 h at ambient temperature, a solution of the crude alcohol **10** (45.6 mg) and DMAP (5.0 mg, 0.0431 mmol) in toluene (1.0 mL) was introduced and stirring was continued for 2 h. The mixture was then filtered through a pad of silica which was carefully rinsed with EtOAc, the combined filtrates were evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 8/1) to give product **20** as a colorless syrup (54.6 mg, 87% over both steps). $[\alpha]_D^{20}$ = –3.7 (c 0.40, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3072, 2956, 2932, 2858, 1732, 1651, 1642, 1586, 1428, 1248, 1113, 916, 839, 780. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.47-7.45 (m, 2H), 7.29-7.19 (m, 6H), 7.00-6.97 (m, 2H), 6.82 (m, 1H), 6.33 (s, 1H), 5.89 (ddt, *J* = 6.9, 10.2, 17.2 Hz, 1H), 5.81 (ddt, *J* = 6.6, 10.3, 17.0 Hz, 1H), 5.25 (t, *J* = 9.4 Hz, 1H), 5.10-4.99 (m, 7H), 4.30 (d, *J* = 8.1 Hz, 1H), 4.16-4.03 (m, 3H), 3.99 (dd, *J* = 1.9, 5.5 Hz, 1H), 3.82-3.65 (m, 4H), 3.60 (m, 1H), 2.83-2.47 (m, 4H), 2.28 (m, 2H), 2.18-2.11 (m, 5H), 1.96-1.74 (m, 8H), 1.55-1.32 (m, 13 H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.28 (s, 3H), 0.07 (s, 3H), –0.04 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ = 205.8, 172.4, 170. 7, 167.1, 166.9, 165.0, 145.1, 138.7, 137.5, 135.6, 134.2 (2C), 133.0, 129.0, 128.5, 128.2 (2C), 127.9 (2C), 127.2, 126.9 (2C), 116.8, 115.9, 110.0, 100.1, 100.0, 80.2, 78.6, 78.0, 77.1, 76.4, 75.6, 73.5, 72.0, 69.6, 69.0, 63.1, 38.8, 36.9, 33.7, 33.6, 30.1, 29.6, 28.2, 27.5, 26.4, 25.8 (3C), 20.8, 18.8, 18.2, 16.7, 14.6, 14.2, 12.2, –0.7, –1.2, –3.6, –4.8. MS (EI): *m/z* (%): 83 (63), 157 (29), 265 (100), 265 (100), 451 (32), 833 (10), 851 (49), 1019 (17), 1075 (8). HRMS: calcd. for $C_{61}H_{88}O_{16}Si_2$ [M^++Na] 1155.550316, found 1155.548973.

Product 21. The ruthenium carbene complex **12** (6.0 mg, 0.00653 mmol) was added to a solution of compound **20** (74 mg, 0.0653 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was refluxed for 4 h before the reaction was quenched with ethyl vinyl ether. Evaporation of all volatile materials followed by flash chromatography of the residue (hexanes/EtOAc, 4/1) gave the corresponding cycloalkene (*E*,*Z*-mixture). This product was dissolved in EtOH (1.0 mL) and stirred overnight in the presence $RhCl(PPh_3)_3$ (12 mg, 0.0125 mmol) under an atmosphere of H_2 (1 atm). The catalyst was filtered off through a pad of silica, the filtrate was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc, 4/1) to give compound **21** as a colorless syrup (60 mg, 83% over both steps). $[\alpha]_D^{20}$ = +0.4 (c 0.77, CH_2Cl_2). IR (KAP): $\tilde{\nu}$ = 3069, 2931, 2858, 1732, 1652, 1588, 1379, 1371, 1247, 1155, 1074, 839, 780, 731, 702. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 7.46-7.44 (m, 2H), 7.29-7.19 (m, 6H), 6.99-6.97 (m, 2H), 6.81 (m, 1H), 6.31 (s, 1H), 5.28 (t, *J* = 9.2 Hz, 1H), 5.06-5.00 (m, 2H), 4.94 (d, *J* = 7.7 Hz, 1H), 4.25 (d, *J* = 7.8 Hz, 1H), 4.13 (t, *J* = 6.0 Hz, 1H), 4.03-4.02 (m, 1H), 3.98 (dd, *J* = 2.0, 5.8 Hz, 1H), 3.86 (dd, *J* = 6.4, 7.8 Hz, 1H), 3.78 (m, 1H), 3.65 (dt, *J* = 2.7, 10.0 Hz, 1H), 3.54-3.48 (m, 2H), 2.87 (dt, *J* = 6.8, 18.8 Hz, 1H), 2.62 (dt, *J* = 6.8, 18.8 Hz, 1H), 2.49 (m, 2H), 2.14 (s, 3H), 1.77-1.26 (m, 30 H), 0.09 (t, *J* = 7.3 Hz, 3H), 0.81 (s, 9H), 0.37 (s, 3H), 0.23 (s, 3H), 0.05 (s, 3H), –0.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 205.9, 170.9, 170.6, 166.8, 166.6, 164.4, 144.6, 138.3, 138.0, 133.6 (2C), 132.5, 128.7, 128.2, 127.9 (2C), 127.6 (2C), 126.9, 126.6 (2C), 109.7, 101.3, 99.7, 81.9, 79.4, 78.4, 77.2, 76.3, 75.4, 73.1, 71.6, 68.5, 68.3, 61.8, 37.3, 33.9, 33.8, 29.9, 28.5, 28.0, 27.8, 26.3, 25.6 (3C), 24.2 (2C), 20.6, 18.3, 18.0, 16.8, 14.4, 14.3, 12.1, –0.4, –1.6, –3.8, –4.9. MS (EI): *m/z* (%): 83 (66), 157 (26), 265 (100), 567 (11), 825 (41), 1049 (9). HRMS: calcd. for $C_{59}H_{86}O_{16}Si_2$ [M^++Na] 1129.534663, found 1129.535235.



21

Ipomoeassin E (2). A solution of TASF (75 mg, 0.27 mmol) in MeCN (1.0 mL) was added to a solution of compound **21** (30 mg, 0.027 mmol) in wet MeCN (1.0 mL) and the resulting mixture was stirred for 5 h before it was filtered through a pad of silica which was carefully rinsed with EtOAc. The combined filtrates were evaporated and the residue was treated with trifluoroacetic acid (36 μL, 0.49 mmol) in CH_2Cl_2 (3.0 mL) for 3 h at ambinent temperature. The mixture was neutralized with triethylamine and concentrated in vacuo, and the crude product was purified by preparative HPLC (YMC-PACK ODS A, 5 μm 12 nm; MeOH/H_2O = 70/30; flow rate: 10 mL/min;

pressure: 3.6 MPa) to afford Ipomoeassin E (**2**) as a colorless syrup which solidifies when kept in the freezer (14 mg, 63% over both steps). $[\alpha]_D^{25}$ = –32 (c 0.21, EtOH); lit. $[\alpha]_D^{25}$ = –24 (c 0.2, EtOH). IR (KAP): $\tilde{\nu}$ = 3408, 2933, 2869, 1725, 1636, 1450, 1374, 1309, 1248, 1156, 1073, 768. ^{1}H NMR (400 MHz, C_6D_6) and ^{13}C NMR (75 MHz, C_6D_6) data, see Table S3 and S4, respectively. MS (EI): *m/z* (%): 655 (5), 571 (7), 525 (7), 407 (9), 281 (40), 239 (11), 221 (19), 192 (11), 131 (58), 110 (10), 83 (100), 55 (20), 43 (19). HRMS: calcd. for $C_{42}H_{58}O_{16}$ [M^++Na] 841.36172, found 841.362452.

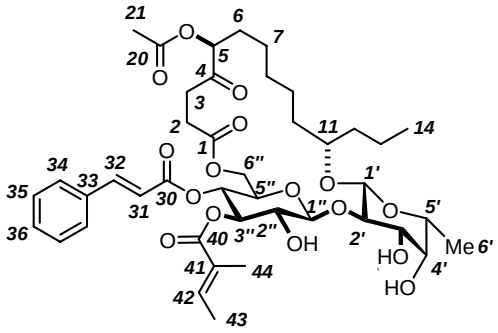


Table S3. Comparison of the ^{1}H NMR data (C_6D_6) reported for Ipomoeassin E (**2**) (500 MHz) with those of the synthetic material recorded on a Bruker av400 spectrometer (400 MHz). Numbering scheme as shown in the insert.

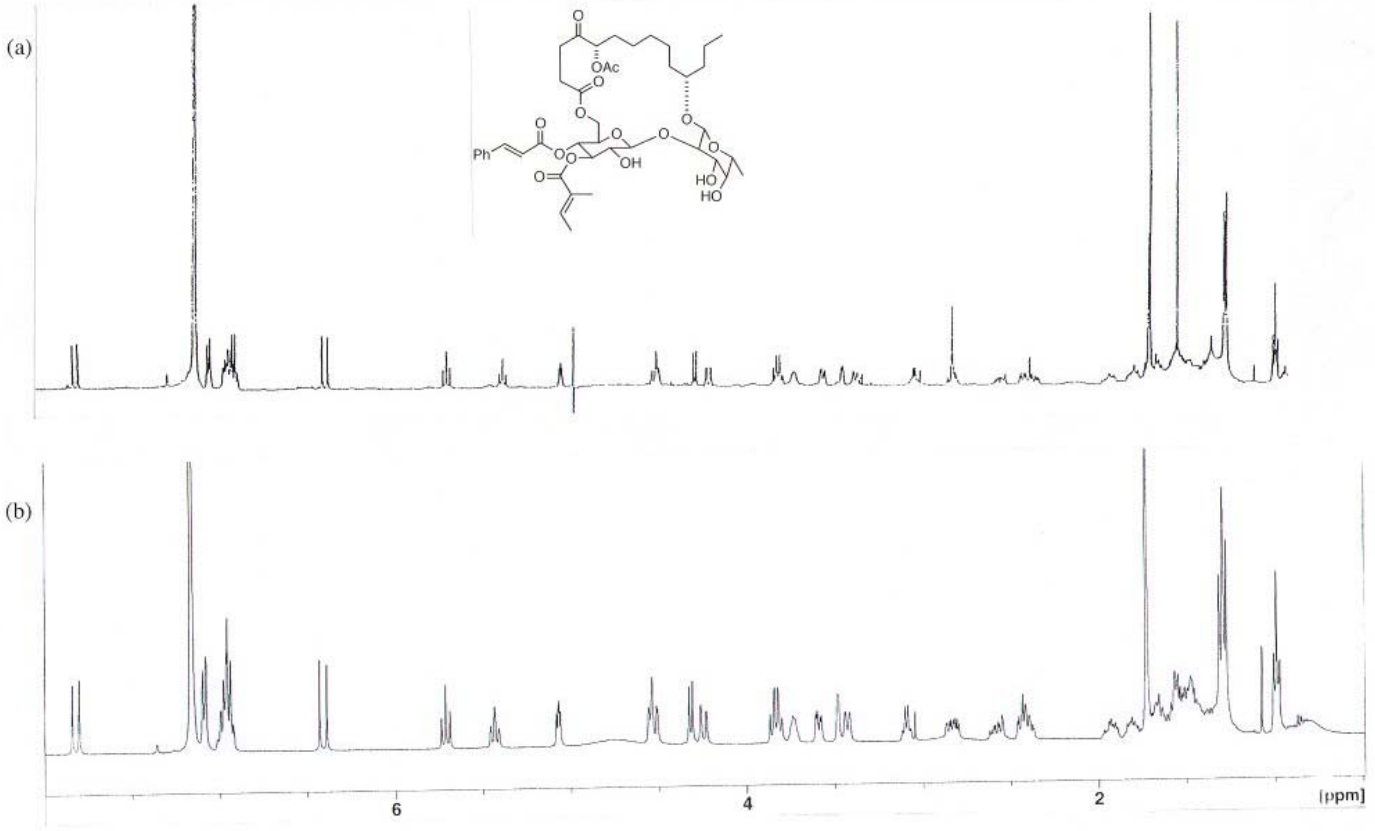
Position	Ipomoeassin E (*J* in Hz)	Synthetic Sample (*J* in Hz)[a,b]
2	2.55 ddd (18.1, 9.2, 2.8)	2.59 ddd (18.0, 9.2, 3.1)
	2.34 ddd (18.1, 7.8, 3.4)	2.46-2.36 m
3	2.81 ddd (16.3, 9.2, 3.4)	2.82 ddd (16.5, 9.2, 3.5)
	2.39 ddd (16.3, 7.8, 2.8)	2.46-2.36 m
5	5.04 dd (6.2, 3.9)	5.07 dd (6.1, 3.9)
11	3.71 m	3.74 brm
14	0.97 t (6.9)	0.99 t (7.0)
1'	4.28 d (7.6)	4.32 d (7.6)
2'	3.80 dd (9.5, 7.6)	3.82 appt (9.4)
3'	3.55 dd (9.5, 3.7)	3.59 dd (9.3, 3.2)
4'	3.44 brs	3.48 brs
5'	3.02 brq (6.4)	3.09 brq (6.4)
6'	1.25 d (6.4)	1.28 d (6.6)
1"	4.50 d (7.8)	4.55 d (8.0)
2"	3.81 dd (9.7, 7.8)	3.84 appt (9.5)
3"	5.38 t (9.7)	5.43 t (9.5)
4"	5.70 t (9.7)	5.71 t (9.7)
5"	3.36 brd (9.7)	3.43 brd (9.8)
6"	4.51 dd (11.0, 2.0)	4.52 dd (11.4, 2.2)
	4.20 brd (11.0)	4.24 brd (11.5)
21	1.67 brs	1.73 brs
31	6.40 d (16.1)	6.41 d (16.0)
32	7.81 d (16.1)	7.82 d (16.0)
34	6.88-7.03	6.91-7.09
35	6.88-7.03	6.91-7.09
36	6.88-7.03	6.91-7.09
42	6.95 m	6.95 m
43	1.25 d (7.1)	1.30 d (7.3)
44	1.67 brs	1.73 brs

[a] The chemical shifts depend on the concentration of the sample and the dryness of the C_6D_6 used; see below; the data compiled in this Table were recorded using 3 mg of compound **2** in 0.6 mL of freshly distilled (CaH_2) C_6D_6. [b] The protons at positions 6-10, 12 and 13 appear between δ 1.96-1.36 as complicated multiplet.

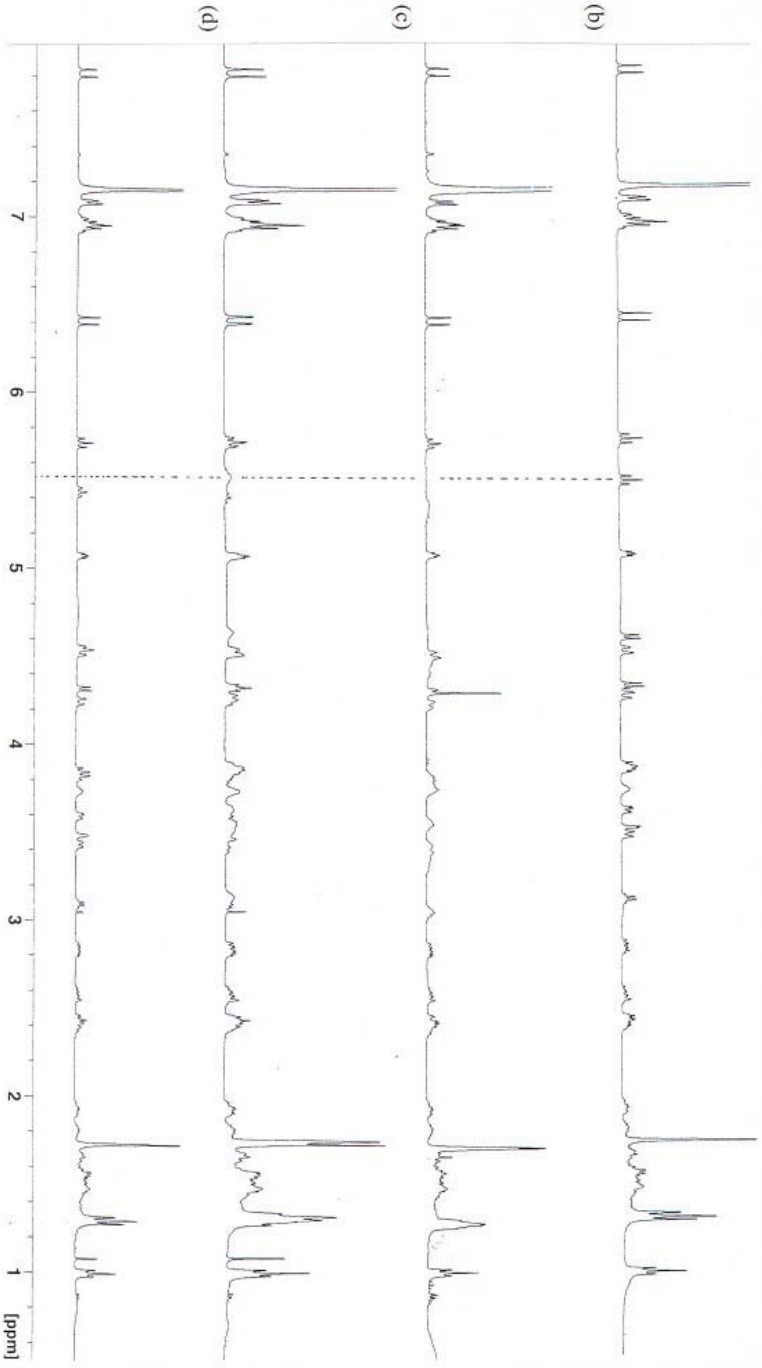
Table S4. Comparison of the ^{13}C NMR data (C_6D_6) reported for Ipomoeassin E (**2**) (125 MHz) with those of the synthetic sample (Bruker AMX-300 spectrometer, 75 MHz).

Position	Natural Product	Synthetic Sample
1	171.4	171.4
2	34.0	34.1
3	28.3	28.3
4	205.8	205.7
5	78.2	78.2
6	30.3	30.3
7	24.0	24.0
8	30.5	30.5
9	25.2	25.2
10	34.0	34.1
11	78.5	78.5
12	37.7	37.7
13	18.9	19.0
14	14.4	14.4
1'	100.5	100.4
2'	84.2	84.3
3'	74.0	74.0
4'	71.6	71.6
5'	70.0	70.0
6'	14.1	14.1
1"	106.7	106.7
2"	74.9	74.9
3"	76.6	76.7
4"	67.7	67.7
5"	72.9	73.0
6"	61.2	61.3
20	169.8	169.8
21	20.3	20.3
30	165.5	165.5
31	117.5	117.6
32	146.2	146.2
33	134.4	134.5
34	128.3	128.2
35	128.5	128.3
36	130.4	130.4
40	168.9	168.9
41	128.0	128.0
42	139.6	139.5
43	16.6	16.5
44	12.0	12.0

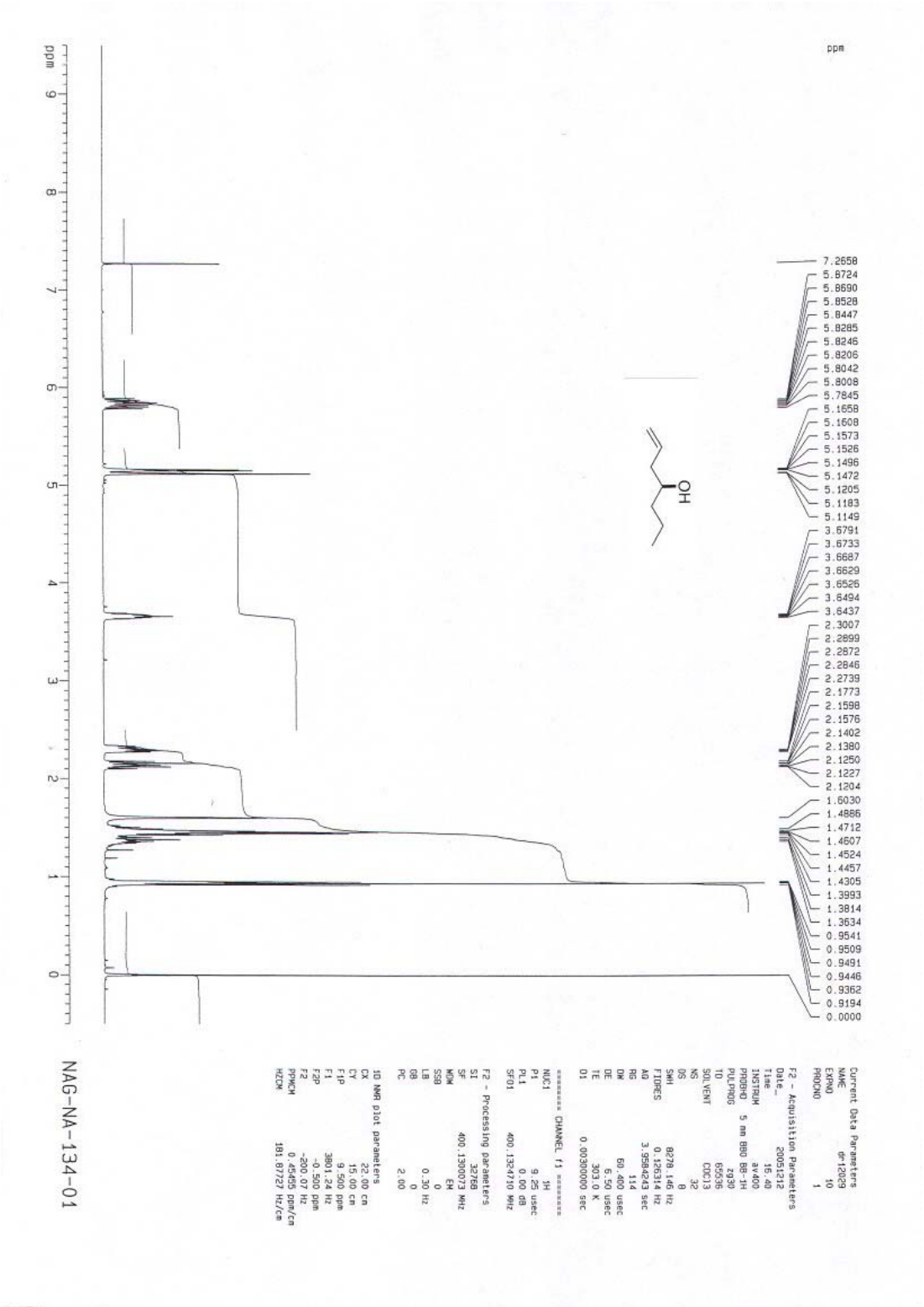
^{1}H NMR spectra of Ipomoeassin E in C_6D_6: (a) natural product reported in literature (500 MHz, Kingston et al. *J. Nat. Prod.* **2005**, *68*, 487); (b) sample prepared by us (400 MHz).



^{1}H NMR spectra of Compound 1 at different concentrations showed remarkable change of chemical shift. (a) 14 mg in 0.6 mL of nondistilled C_6D_6; (b) 4 mg in 0.6 mL of nondistilled C_6D_6; (c) 6 mg in 0.6 mL of distilled C_6D_6; (d) 3 mg in 0.6 mL of distilled C_6D_6



Spectra of New Compounds

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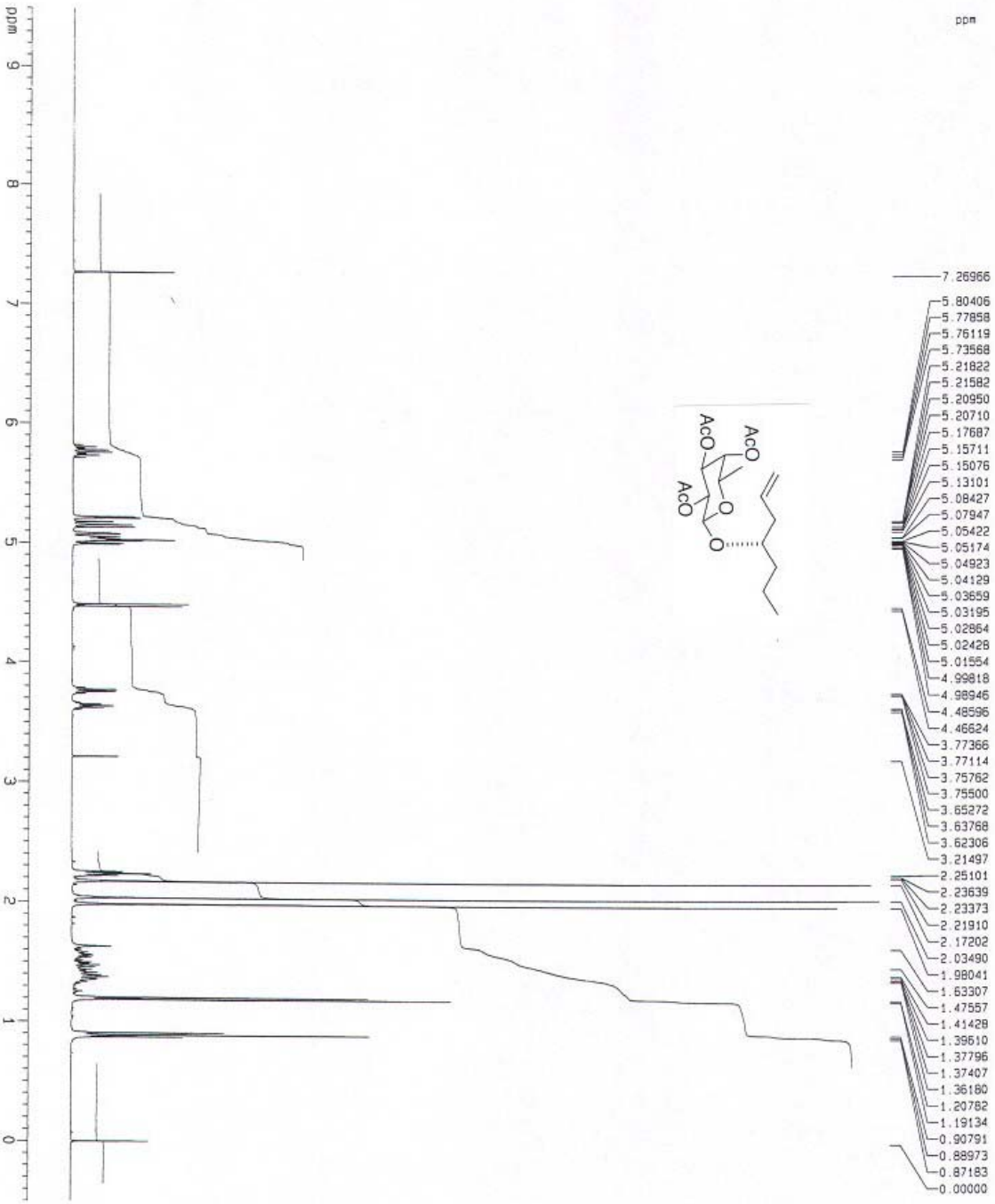


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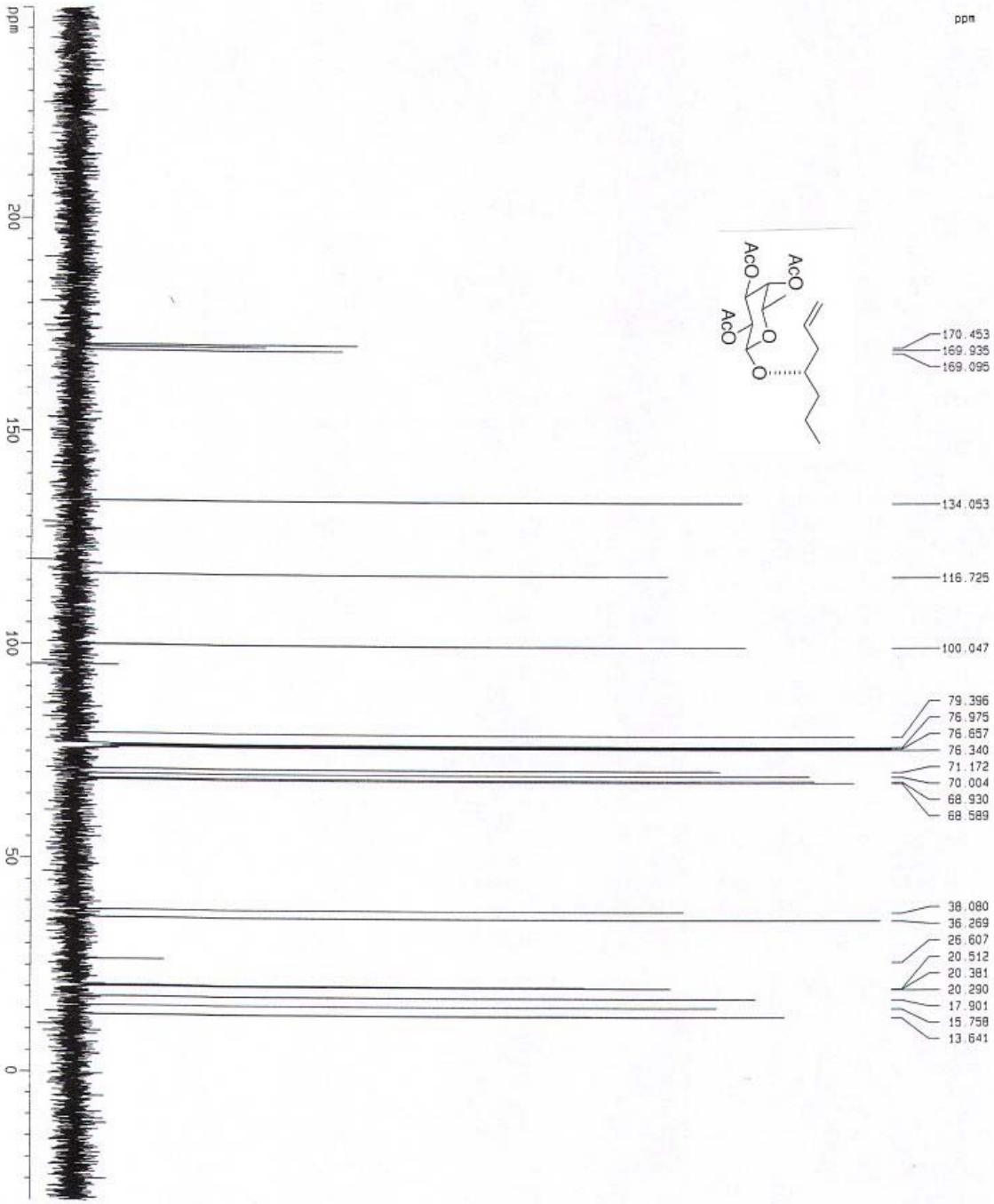

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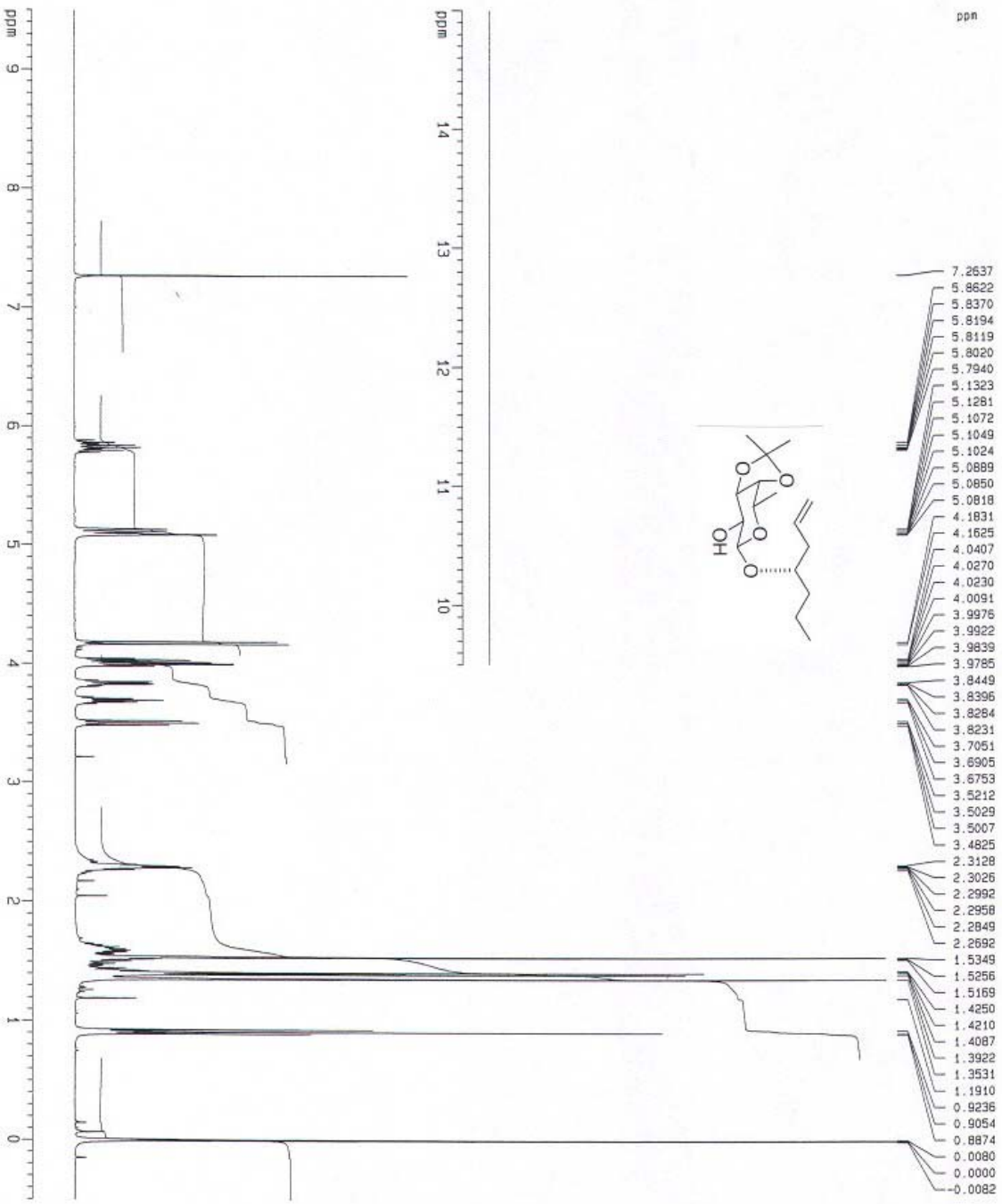


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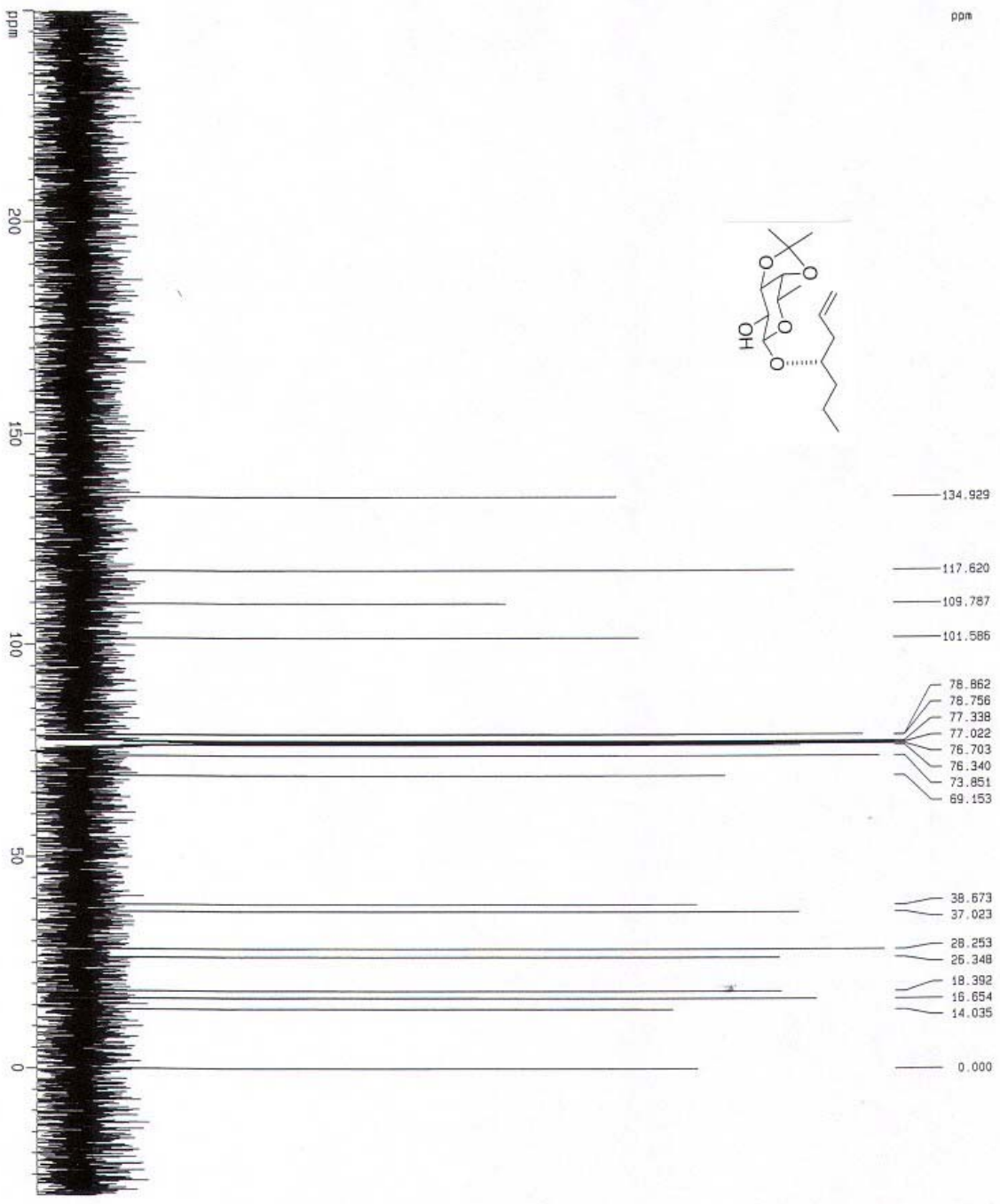

NAG-NA-124-01

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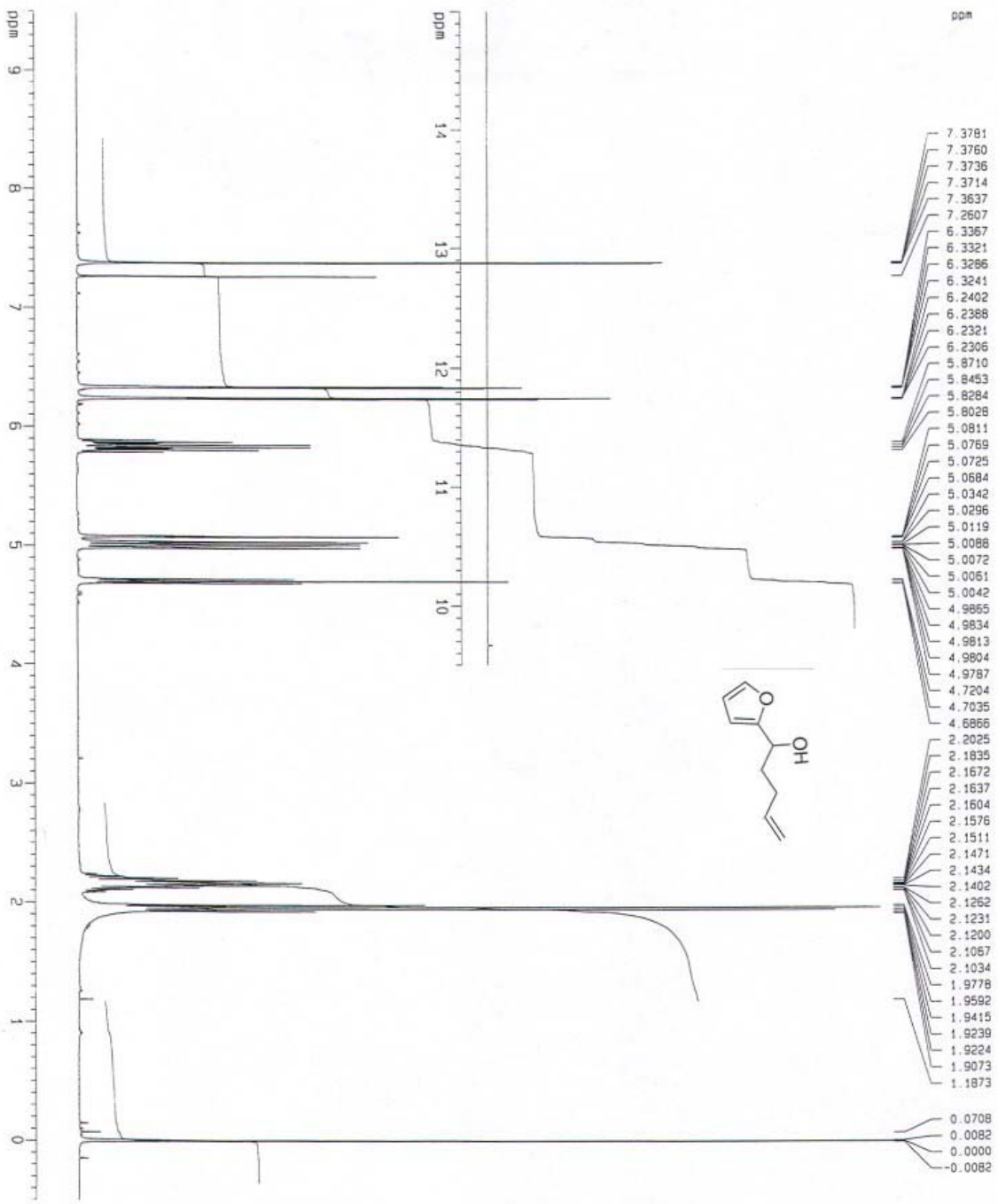


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GB                         0
PC                  2.00

1D NMR plot parameters
CX                  22.00 cm
CY                  15.00 cm
F1P                 9.500 ppm
F1                  3801.24 Hz
F2P                 -0.500 ppm
F2                  -200.07 Hz
PPMCM               0.45455 ppm/cm
HZCM                181.87727 Hz/cm
```

NAG-NA-120-03

NAG-NA-120-03

Current Data Parameters
NAME dr01010
EXPNO 11
PROCNO 1

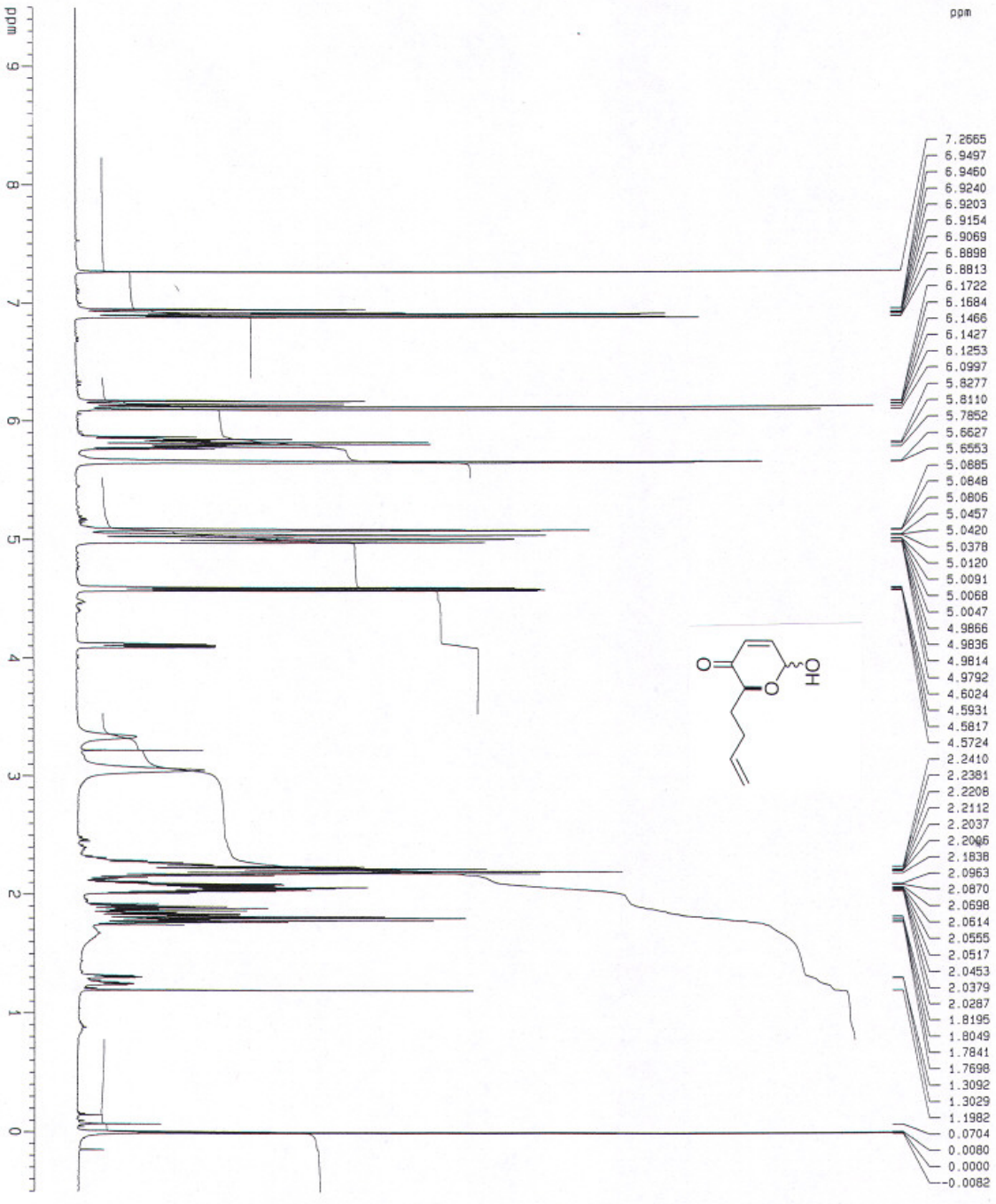
F2 - Acquisition Parameters
Date_ 20051201
Time 12.20
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.989643 sec
RG 18390.4
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

========== CHANNEL f1 ==========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242799 MHz

========== CHANNEL f2 ==========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6127622 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.52632 Hz/cm



NAG-NA-157-01

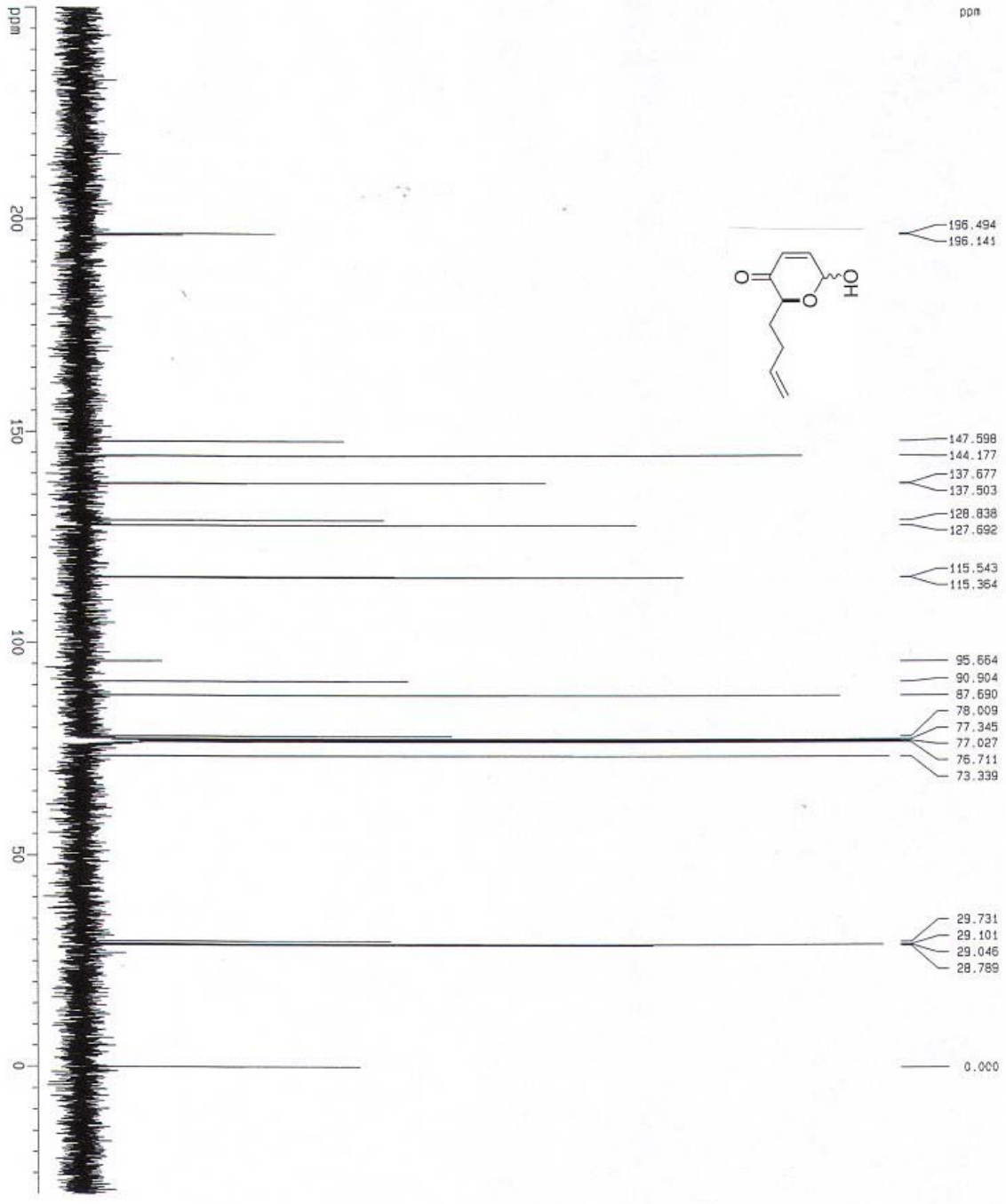
```
Current Data Parameters
NAME                  jr23018
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20060123
Time                   14.25
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      181
DW                 60.400 usec
DE                  6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                      32768
SF            400.1300070 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                    9.500 ppm
F1                  3801.24 Hz
F2P                   -0.500 ppm
F2                  -200.07 Hz
PPMCM                0.45455 ppm/cm
HZCM                181.87727 Hz/cm
```




```
Current Data Parameters
NAME                  jr23018
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_              20060123
Time                   14.54
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES           0.505258 Hz
AQ               0.9895435 sec
RG                    16384
DW                15.100 usec
DE                 6.00 usec
TE                 303.0 K
D1               0.03000000 sec
d11              0.03000000 sec

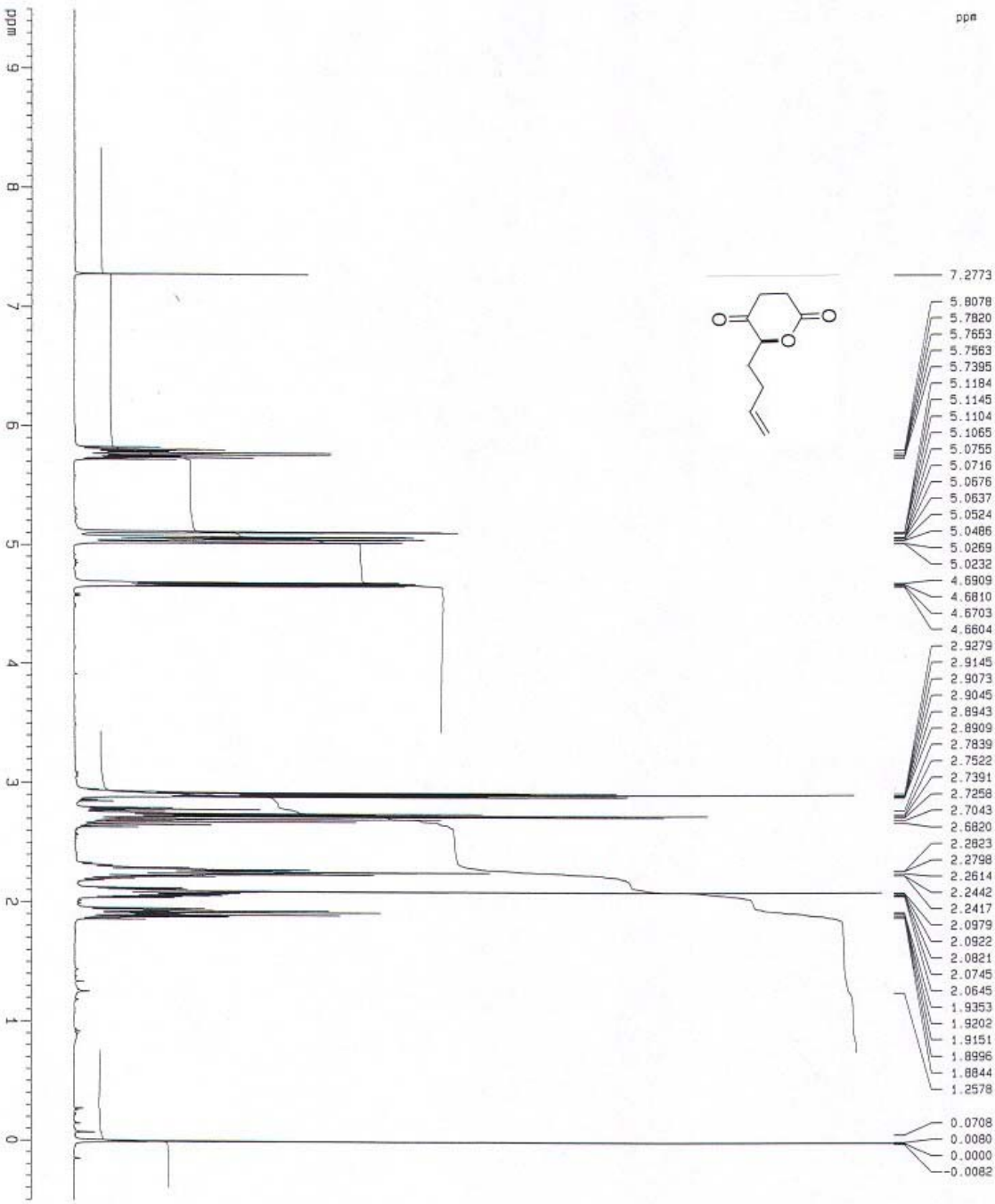
======== CHANNEL f1 ========
NUC1                    13C
P1                    10.94 usec
PL1                    5.00 dB
SFO1          100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              19.76 dB
SFO2          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            100.6127672 MHz
WDW                     EM
SSB                      0
LB                1.00 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                  22.00 cm
CY                  15.00 cm
F1P               250.000 ppm
F1              25193.19 Hz
F2P               -30.000 ppm
F2              -3018.38 Hz
PPMCM             12.72727 ppm/cm
HZCM          1280.52612 Hz/cm
```

NAG-NA-157-01




```
Current Data Parameters
NAME                  jr25046
EXPNO                      10
PROCNO                      1

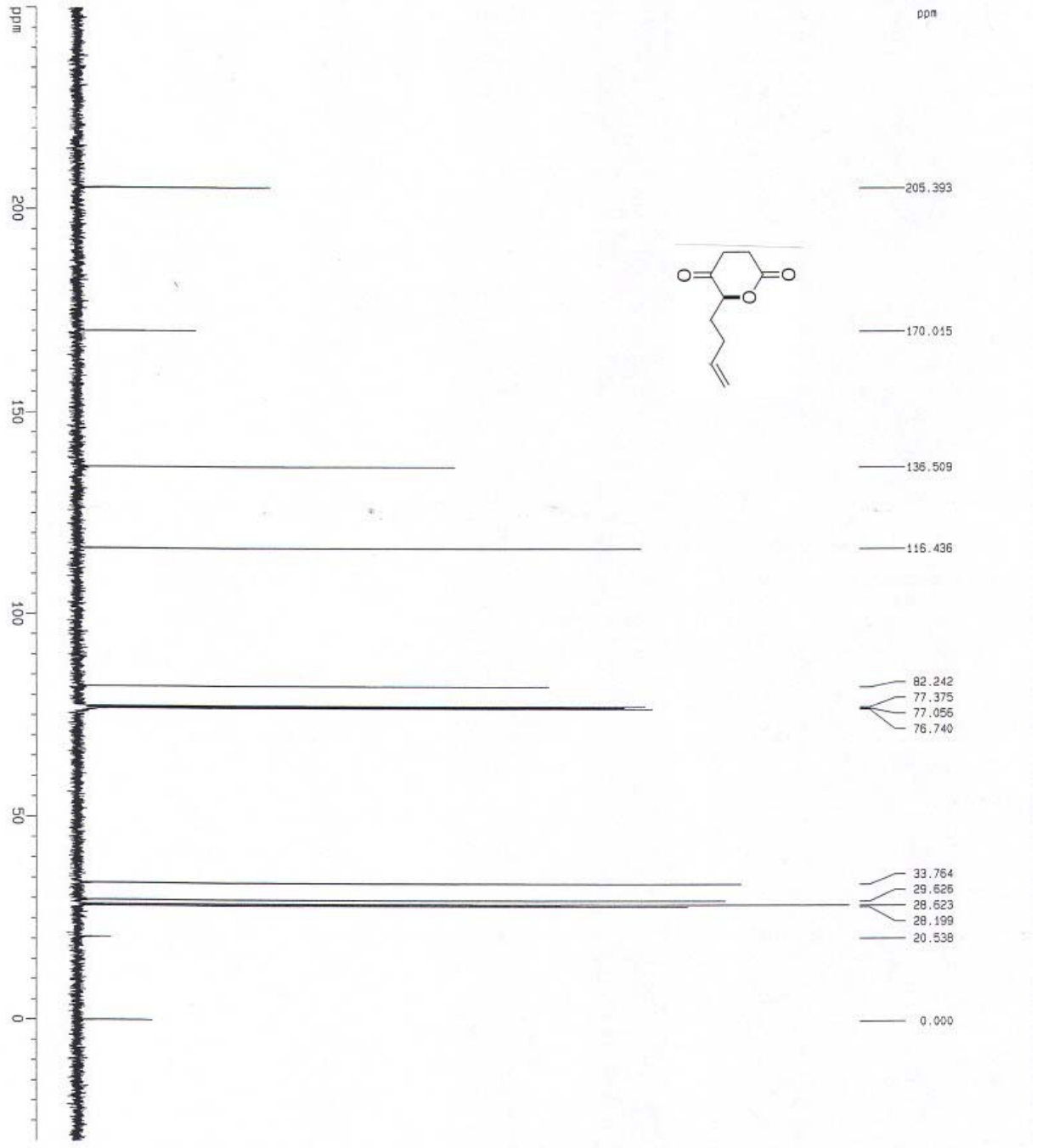
F2 - Acquisition Parameters
Date_              20060126
Time                   14.25
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                r930
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                       114
DW                  60.400 usec
DE                   6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF             400.1300028 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                   9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                  -200.07 Hz
PPMCM              0.49495 ppm/cm
HZCM               181.87727 Hz/cm
```

NAG-NA-160-01




```
Current Data Parameters
NAME                  jr25046
EXPNO                      11
PROCNO                      1

F2 - Acquisition Parameters
Date_              20060126
Time                  14.54
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES           0.505258 Hz
AQ               0.9896436 sec
RG                    16384
DW                15.100 usec
DE                    6.00 usec
TE                303.0 K
D1               0.03000000 sec
d11              0.03000000 sec

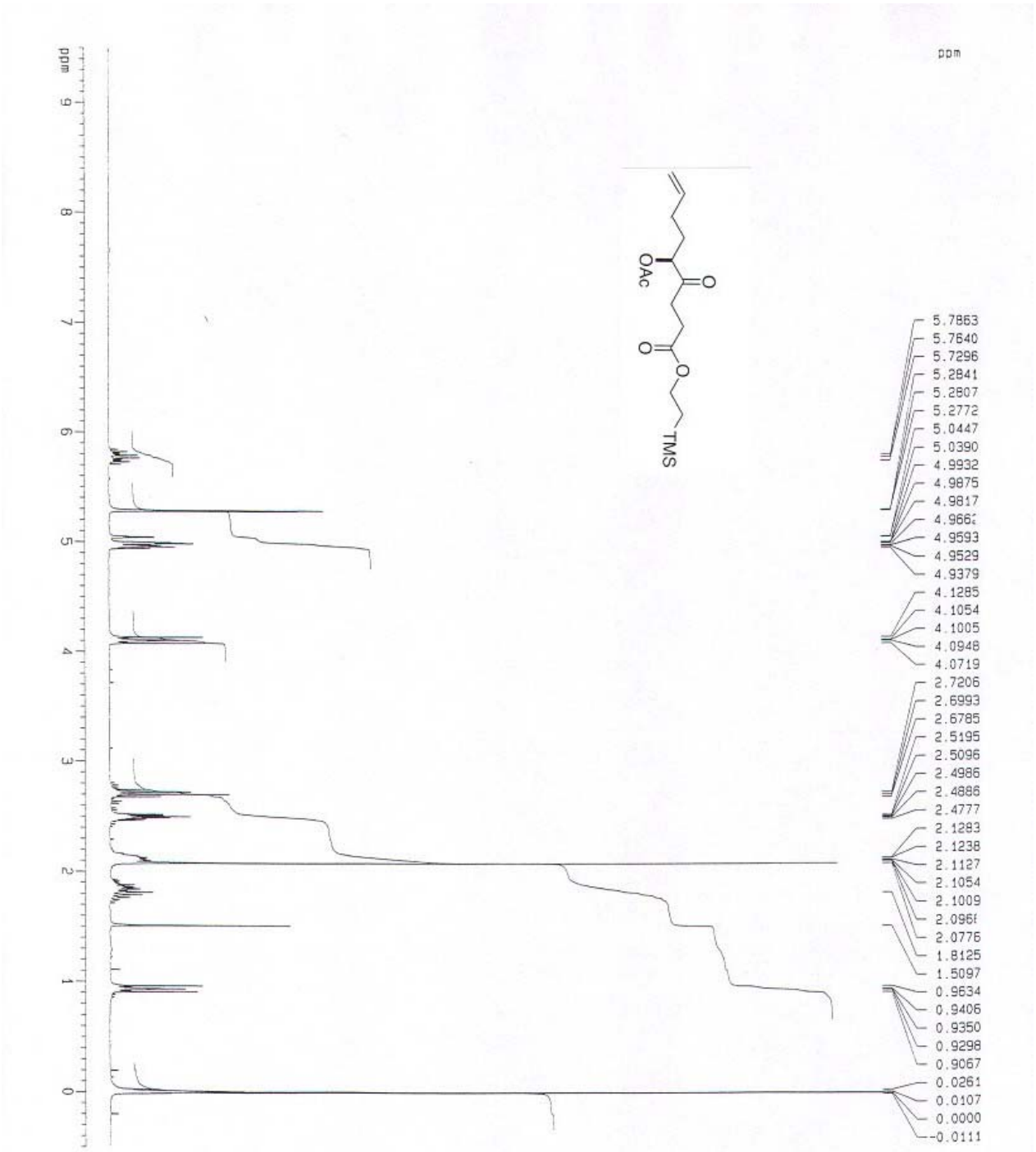
======== CHANNEL f1 ========
NUC1                    13C
P1                   10.94 usec
PL1                   5.00 dB
SFO1          100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2              90.00 usec
PL2                   0.00 dB
PL12                 19.76 dB
SFO2          400.1324710 MHz

F2 - Processing parameters
SI                    32768
SF            100.6127663 MHz
WDW                      EM
SSB                       0
LB                 1.00 Hz
GB                        0
PC                     2.00

1D NMR plot parameters
CX                   22.00 cm
CY                   15.00 cm
F1P                250.000 ppm
F1                25153.19 Hz
F2P                -30.000 ppm
F2                 -3018.38 Hz
PPMCM             12.72727 ppm/cm
HZCM           1280.52512 Hz/cm
```

NAG-NA-160-01




```
Current Data Parameters
NAME                  jun2019
EXPNO                      10
PROCNO                      1

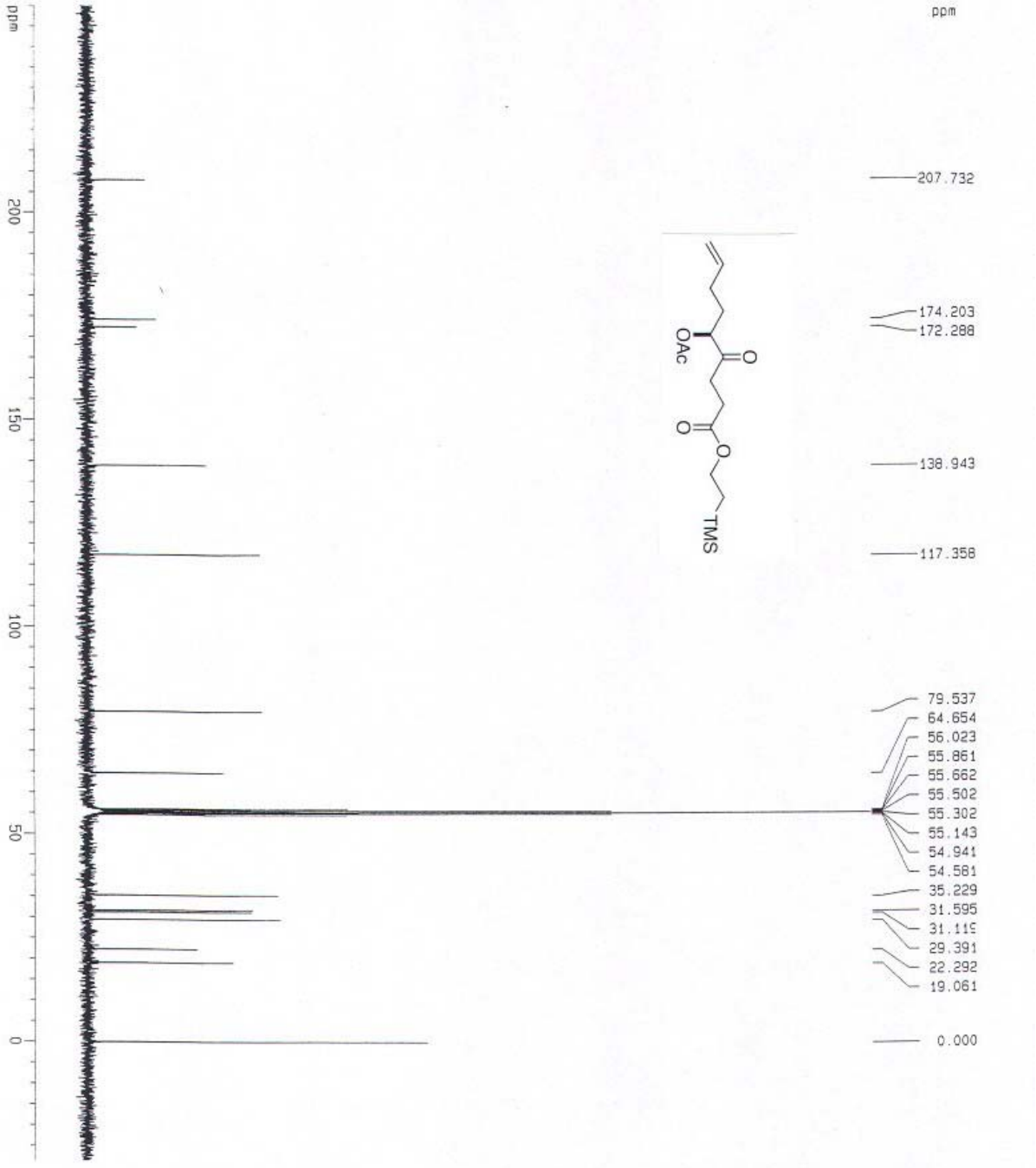
F2 - Acquisition Parameters
Date_              20060602
Time                  14.15
INSTRUM             dpx300
PROBHD     5 mm QNP 1H/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH              6172.839 Hz
FIDRES           0.188380 Hz
AQ               2.6542580 sec
RG                   456.1
DW                81.000 usec
DE                 4.50 usec
TE                 300.0 K
D1               2.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.56 usec
PL1                 -6.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                    16384
SF           300.1300224 MHz
WDW                      EM
SSB                       0
LB                 0.30 Hz
GB                        0
PC                   2.00

1D NMR plot parameters
CX                   22.00 cm
CY                   15.00 cm
F1P                  9.500 ppm
F1                2851.24 Hz
F2P                -0.500 ppm
F2                 -150.07 Hz
PPMCM             0.45455 ppm/cm
HZCM           136.42274 Hz/cm
```

NAG-NA-004-02




```
Current Data Parameters
NAME                  jul02019
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_              20060502
Time                   14.47
INSTRUM                dpx300
PROBHD     5 mm QNP 1H/
PULPROG                zgdc30
TD                     65536
SOLVENT                CDCl2
NS                      1200
DS                         2
SWH                21231.422 Hz
FIDRES             0.323956 Hz
AQ                 1.5434228 sec
RG                     4597.6
DW                    23.550 usec
DE                     4.50 usec
TE                    300.0 K
D1                 0.03000000 sec
D11                0.03000000 sec

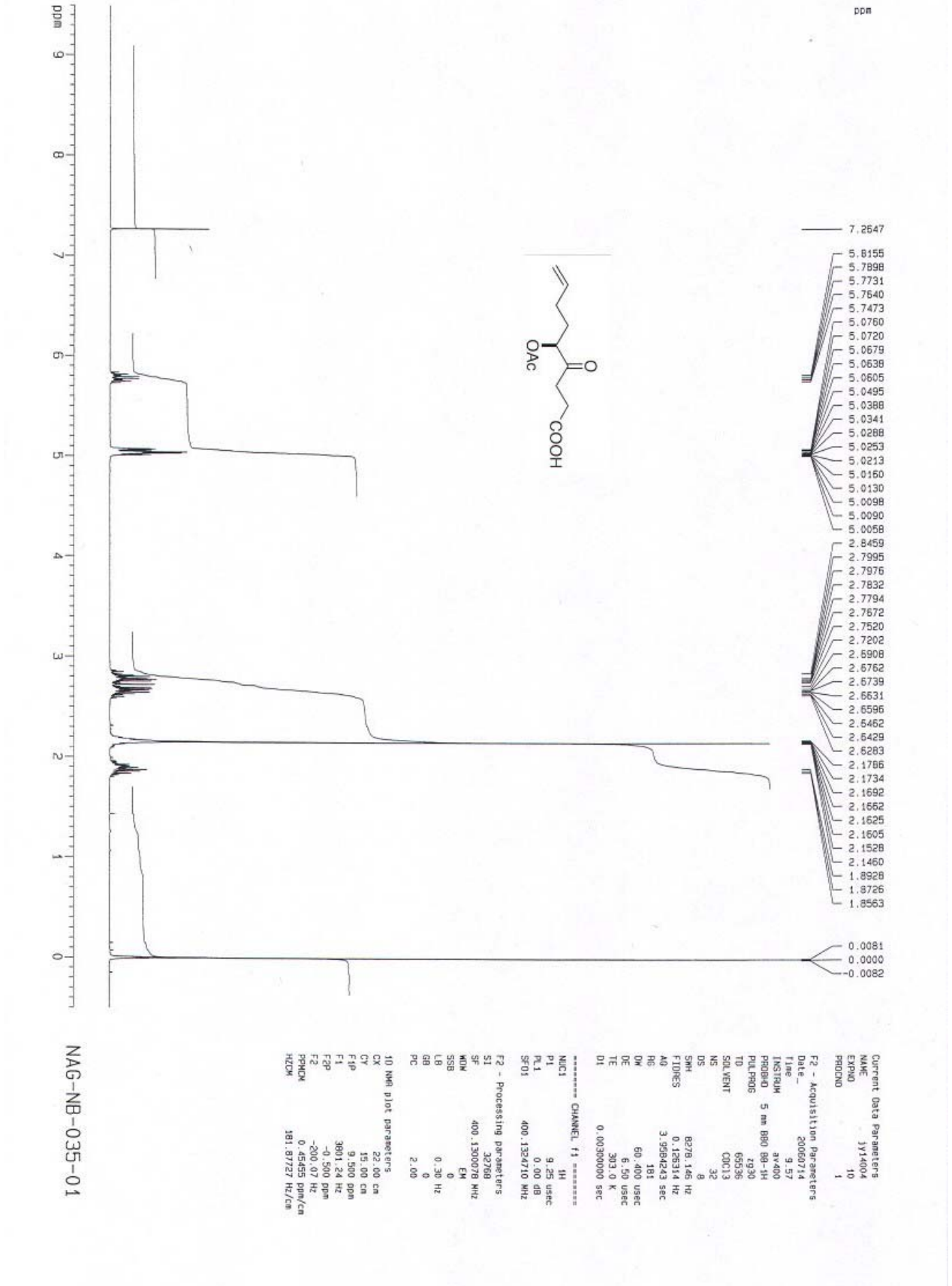
======== CHANNEL f1 ========
NUC1                      13C
P1                       6.91 usec
PL1                    -6.00 dB
SFO1             75.4760670 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  80.00 usec
PL2                    -6.00 dB
PL12                   14.49 dB
SFO2             300.1312005 MHz

F2 - Processing parameters
SI                        32768
SF               75.4676044 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         1.40

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                  250.000 ppm
F1                  18866.90 Hz
F2P                  -30.000 ppm
F2                  -2264.03 Hz
PPMCM                12.72727 ppm/cm
HZCM                960.49583 Hz/cm
```

NAG-NA-004-02


ppm
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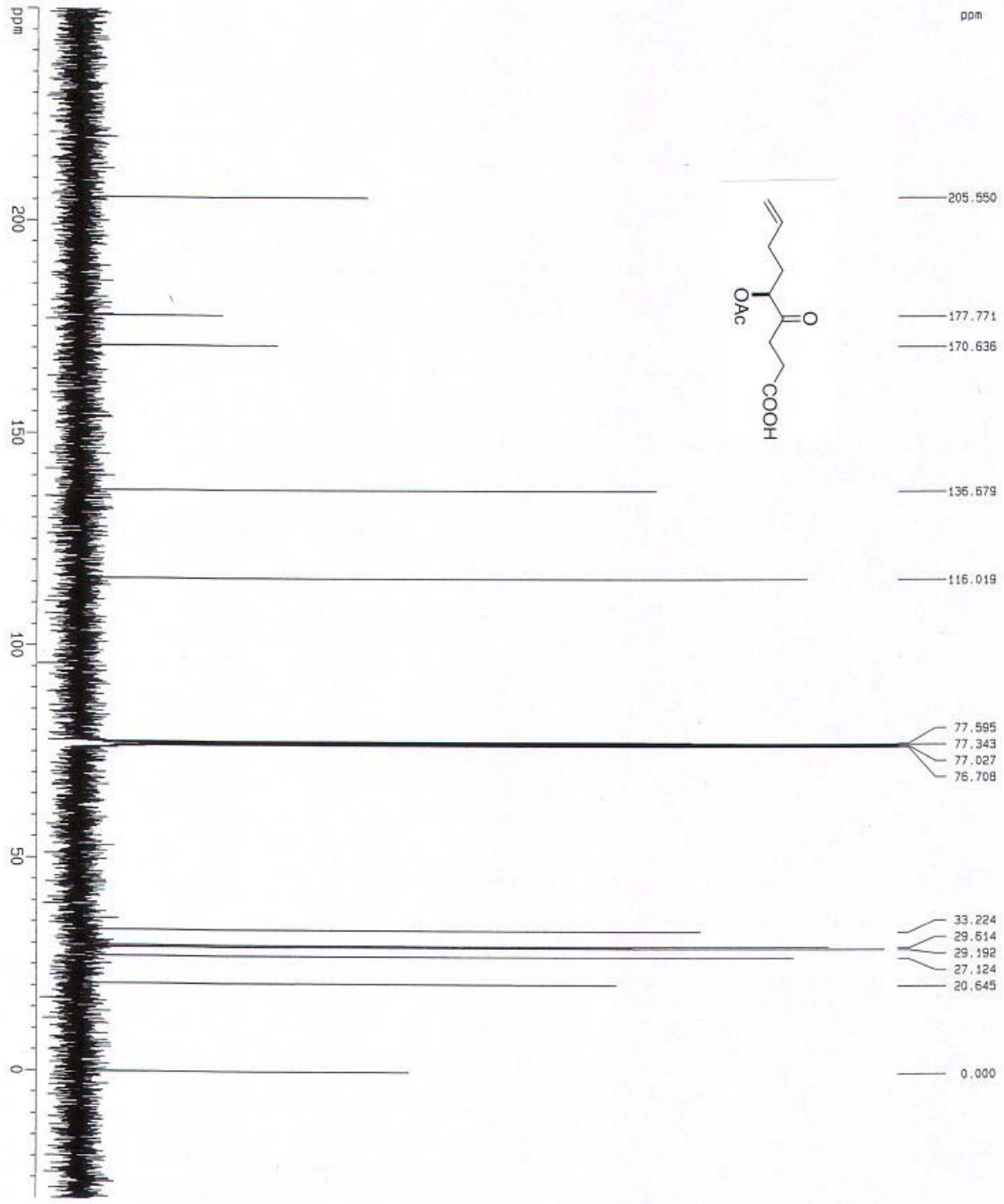
5.8155
5.7898
5.7731
5.7640
5.7473
5.0760
5.0720
5.0679
5.0638
5.0605
5.0495
5.0388
5.0341
5.0288
5.0253
5.0213
5.0160
5.0130
5.0098
5.0090
5.0058
2.8459
2.7995
2.7976
2.7832
2.7794
2.7672
2.7520
2.7202
2.6908
2.6762
2.6739
2.6631
2.6596
2.5462
2.5429
2.6283
2.1786
2.1734
2.1692
2.1562
2.1625
2.1605
2.1528
2.1460
1.8928
1.8726
1.8563
0.0081
0.0000
-0.0082
OAc
O
COOH
ppm 9 8 7 6 5 4 3 2 1 0
NAG-NB-035-01
Current Data Parameters
NAME jy14004
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060714
Time 9.57
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.956243 sec
RG 181
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300078 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87727 Hz/cm



NAG-NB-035-01

```
Current Data Parameters
NAME                  jy14004
EXPNO                       11
PROCNO                       1

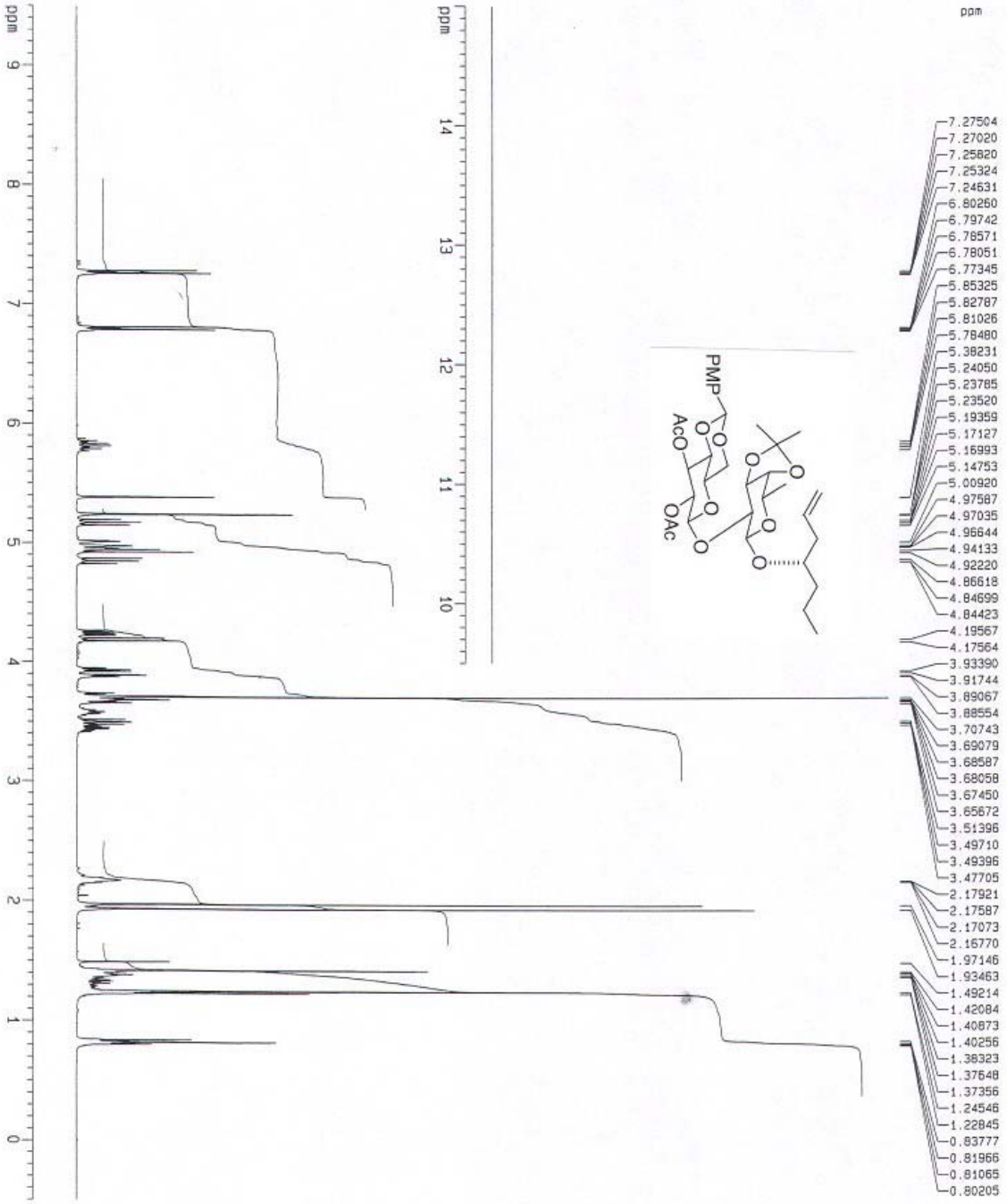
F2 - Acquisition Parameters
Date_              20060714
Time                   10.26
INSTRUM                av400
PROBHD     5 mm BBO BB-1H
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES            0.505258 Hz
AQ                0.9895436 sec
RG                  18390.4
DW                 15.100 usec
DE                  8.00 usec
TE                  303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                   10.94 usec
PL1                   5.00 dB
SFO1             100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2              90.00 usec
PL2                   0.00 dB
PL12                 19.76 dB
SFO2             400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF               100.6127666 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                        2.00

1D NMR plot parameters
CX                      22.00 cm
CY                      15.00 cm
F1P                   250.000 ppm
F1                  25153.19 Hz
F2P                   -30.000 ppm
F2                  -3018.38 Hz
PPMCM                12.72727 ppm/cm
HZCM              1280.52612 Hz/cm
```




```
Current Data Parameters
NAME                  jr25039
EXPNO                      10
PROCNO                      1

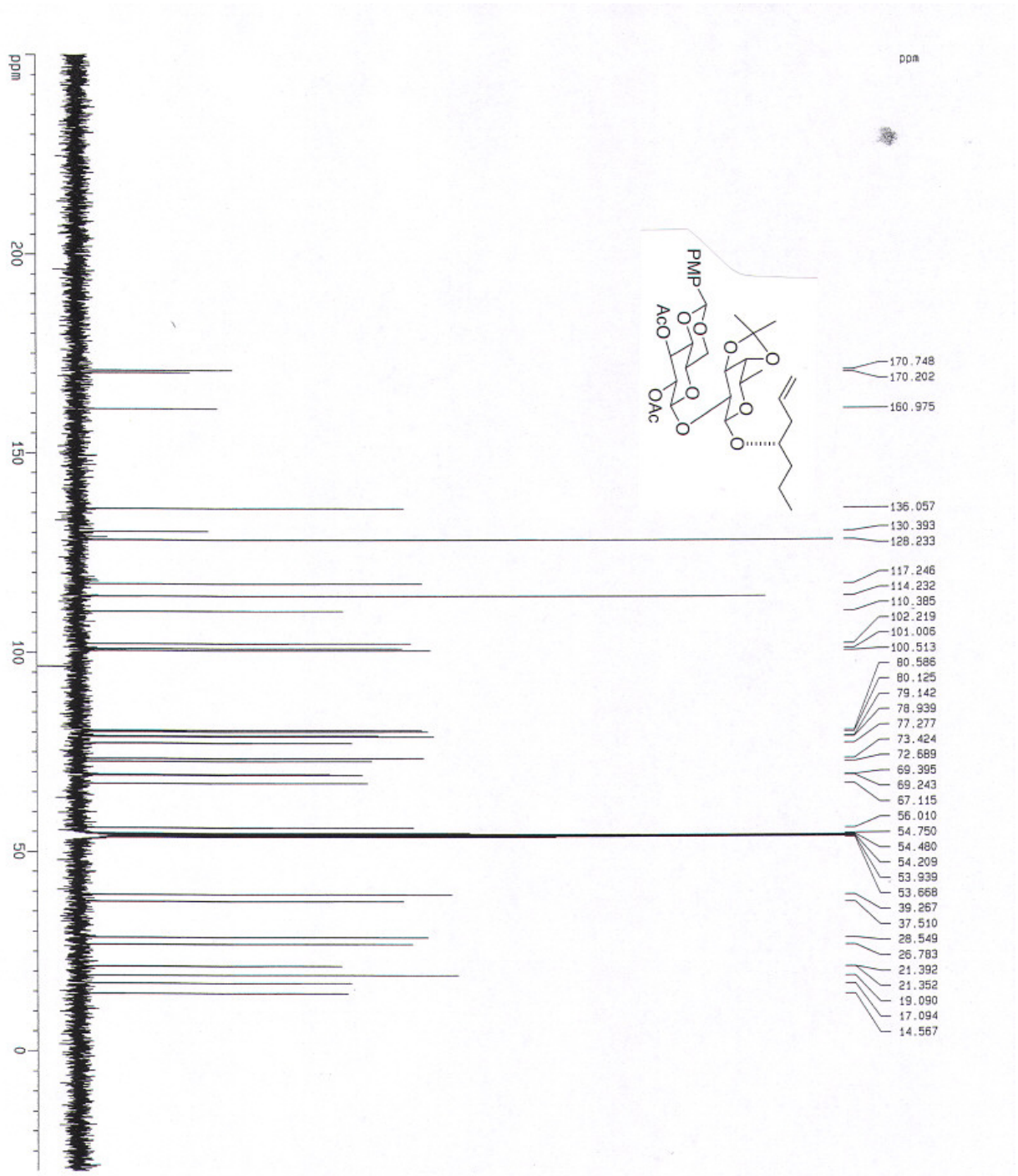
F2 - Acquisition Parameters
Date_              20060126
Time                   12.15
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CD2Cl2
NS                        32
DS                         8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                       114
DW                  60.400 usec
DE                   6.50 usec
TE                     303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      9.25 usec
PL1                     0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF             400.1300482 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                   9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                  -200.07 Hz
PPMCM                0.45455 ppm/cm
HZCM                181.87729 Hz/cm
```


NAG-NA-146-01




```
Current Data Parameters
NAME                  jr25039
EXPNO                       11
PROCNO                       1

F2 - Acquisition Parameters
Date_              20060126
Time                   12.43
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG              zgdc30
TD                    65536
SOLVENT              CD2Cl2
NS                     1500
DS                        2
SWH                33112.582 Hz
FIDRES             0.505258 Hz
AQ                 0.9895436 sec
RG                     16384
DW                  15.100 usec
DE                   8.00 usec
TE                   303.0 K
D1                 0.03000000 sec
d11                0.03000000 sec

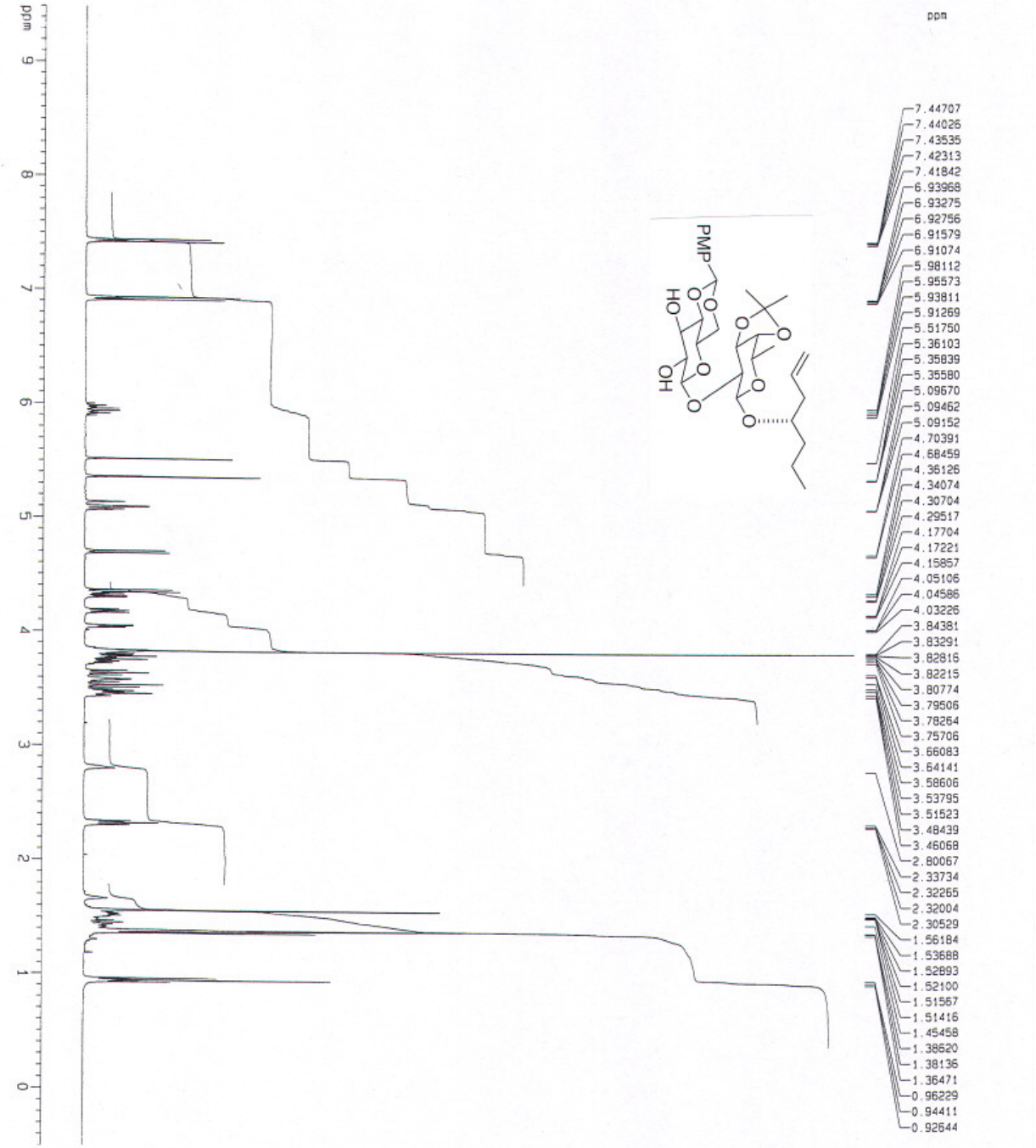
======== CHANNEL f1 ========
NUC1                      13C
P1                    10.94 usec
PL1                    5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF             100.6126888 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                 250.000 ppm
F1                  25153.17 Hz
F2P                 -30.000 ppm
F2                  -3018.38 Hz
PPMCM               12.72727 ppm/cm
HZCM              1280.52515 Hz/cm
```

NAG-NA-146-01



Current Data Parameters
NAME nr10101
EXPNO 20
PROCNO 1

F2 - Acquisition Parameters
Date_ 20051111
Time 22.31
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87727 Hz/cm

NAG-NA-110-01


```
Current Data Parameters
NAME                  nr10101
EXPNO                       21
PROCNO                       1

F2 - Acquisition Parameters
Date_              20051111
Time                   23.00
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG              zgpe30
TD                    65536
SOLVENT              CDCl3
NS                     1500
DS                        2
SWH               33112.582 Hz
FIDRES            0.505358 Hz
AQ                0.9896436 sec
RG                    18390.4
DW                   15.100 usec
DE                    6.00 usec
TE                   303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

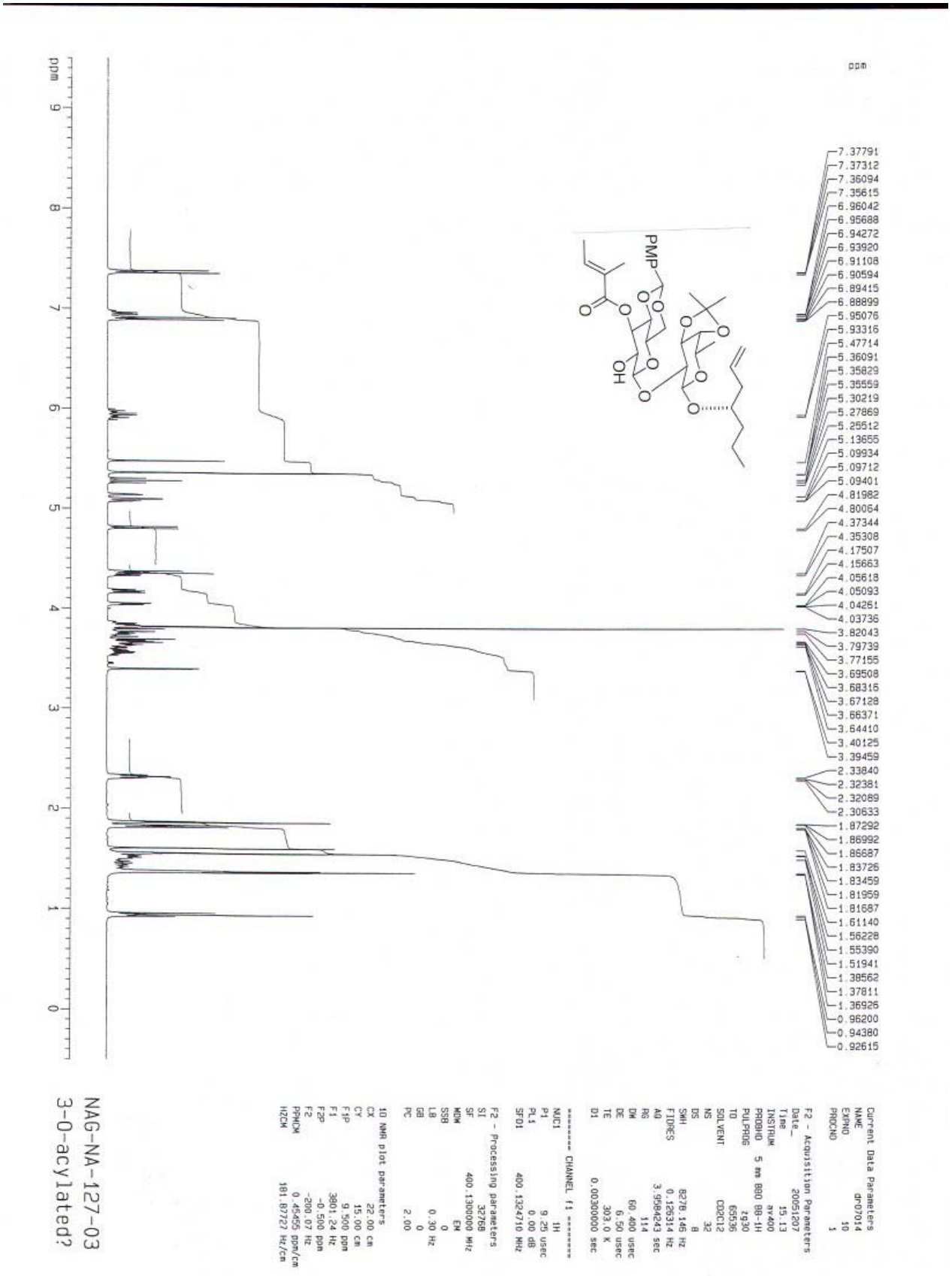
======== CHANNEL f1 ========
NUC1                     13C
P1                     10.94 usec
PL1                    5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SFO2           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF              100.6126888 MHz
WDW                       EM
SSB                        0
LB                  1.00 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                 250.000 ppm
F1                25153.17 Hz
F2P                -30.000 ppm
F2                -3018.38 Hz
PPMCM              12.72727 ppm/cm
HZCM            1280.52515 Hz/cm
```

NAG-NA-110-01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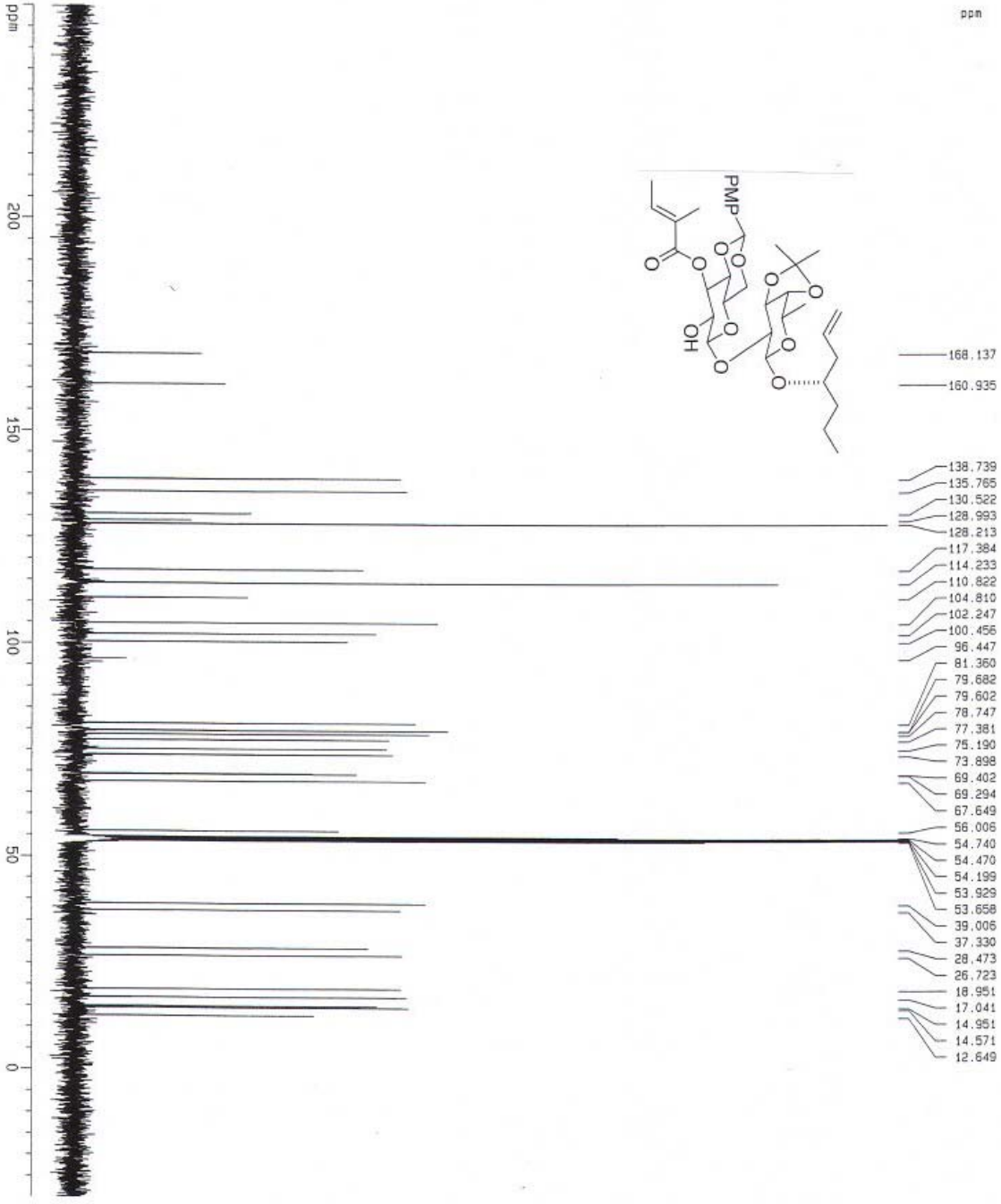
7.35615
6.96042
6.95688
6.94272
6.93920
6.91108
6.90594
6.89415
6.88899
5.95076
5.93316
5.47714
5.36091
5.35829
5.35559
5.30219
5.27869
5.25512
5.13655
5.09934
5.09712
5.09401
4.81982
4.80064
4.37344
4.35308
4.17507
4.15663
4.05618
4.05093
4.04261
4.03736
3.82043
3.79739
3.77155
3.69508
3.68316
3.67128
3.66371
3.64410
3.40125
3.39459
2.33840
2.32381
2.32089
2.30633
1.87292
1.86992
1.86687
1.83726
1.83459
1.81959
1.81687
1.61140
1.56228
1.55390
1.51941
1.38562
1.37811
1.36926
0.96200
0.94380
0.92615
PMP
OH
ppm 9 8 7 6 5 4 3 2 1 0
NAG-NA-127-03
3-O-acylated?
Current Data Parameters
NAME
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051207
Time 15.13
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.8727 Hz/cm




```
Current Data Parameters
NAME                  df07036
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20051207
Time                   20.26
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG              zgdc30
TD                    65536
SOLVENT              CD2Cl2
NS                      1500
DS                         2
SWH                33112.582 Hz
FIDRES             0.505258 Hz
AQ                 0.9896436 sec
RG                     16384
DW                    15.100 usec
DE                     6.00 usec
TE                     303.0 K
D1                 0.03000000 sec
d11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.94 usec
PL1                      5.00 dB
SFO1              100.6242799 MHz

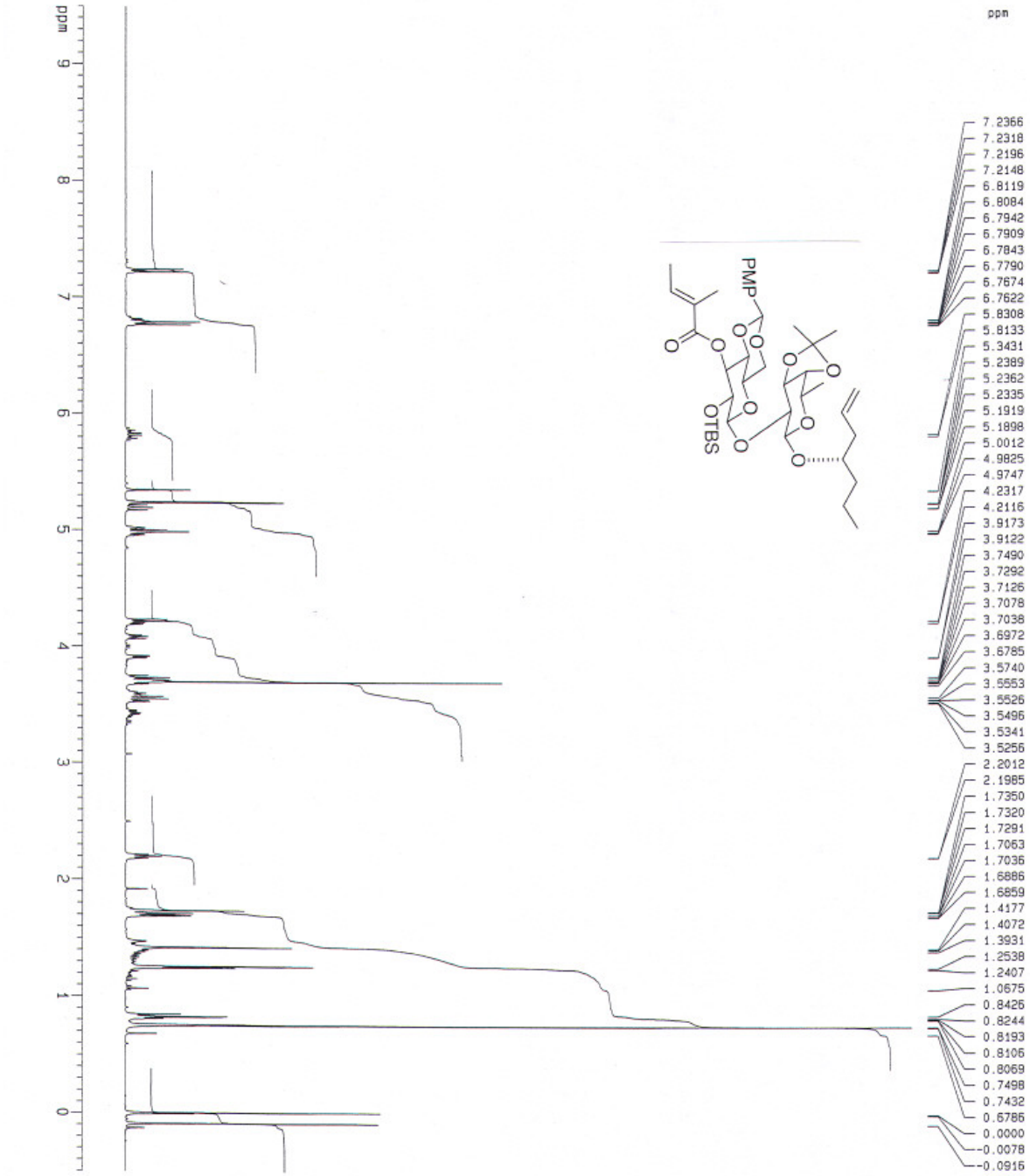
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SFO2              400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                100.6126888 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                  250.000 ppm
F1                 25153.17 Hz
F2P                 -30.000 ppm
F2                 -3018.38 Hz
PPMCM              12.72727 ppm/cm
HZCM               1280.52515 Hz/cm
```

NAG-NA-127-03

3-O-acyl?

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Current Data Parameters
NAME                  dr09010
EXPNO                      10
PROCNO                      1

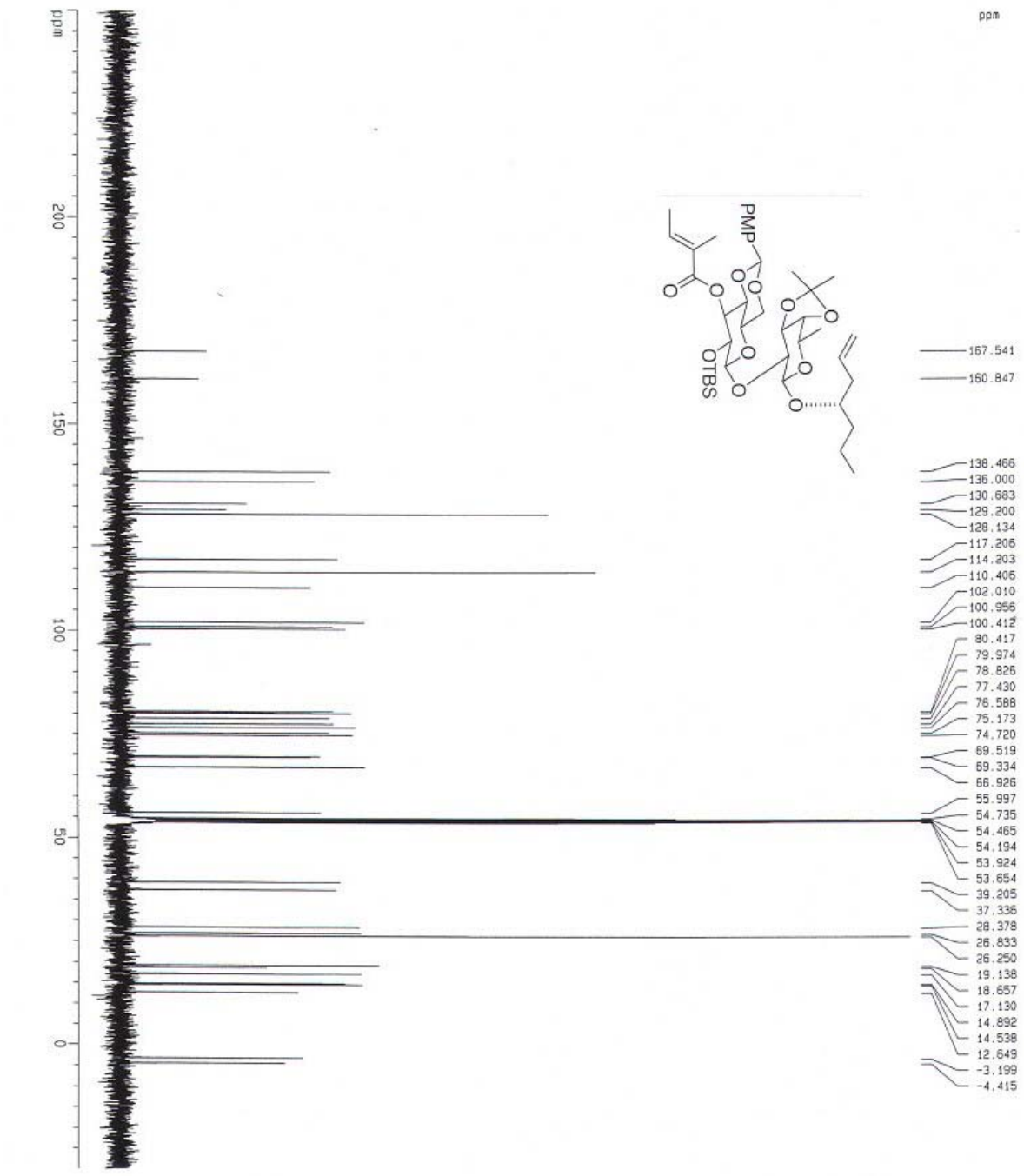
F2 - Acquisition Parameters
Date_              20051209
Time                   12.03
INSTRUM                av400
PROBHD     5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        0
SWH               8278.146 Hz
FIDRES               0.126314 Hz
AQ                3.9584243 sec
RG                       114
DW                  60.400 usec
DE                   6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                    9.25 usec
PL1                   0.00 dB
SF01          400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF            400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                      22.00 cm
CY                      15.00 cm
F1P                    9.500 ppm
F1                  3801.24 Hz
F2P                   -0.500 ppm
F2                   -200.07 Hz
PPMCM                0.45455 ppm/cm
HZCM                 181.87729 Hz/cm
```

NAG-NA-133-01



NAG-NA-133-01

```
Current Data Parameters
NAME                  dr09010
EXPNO                      11
PROCNO                      1

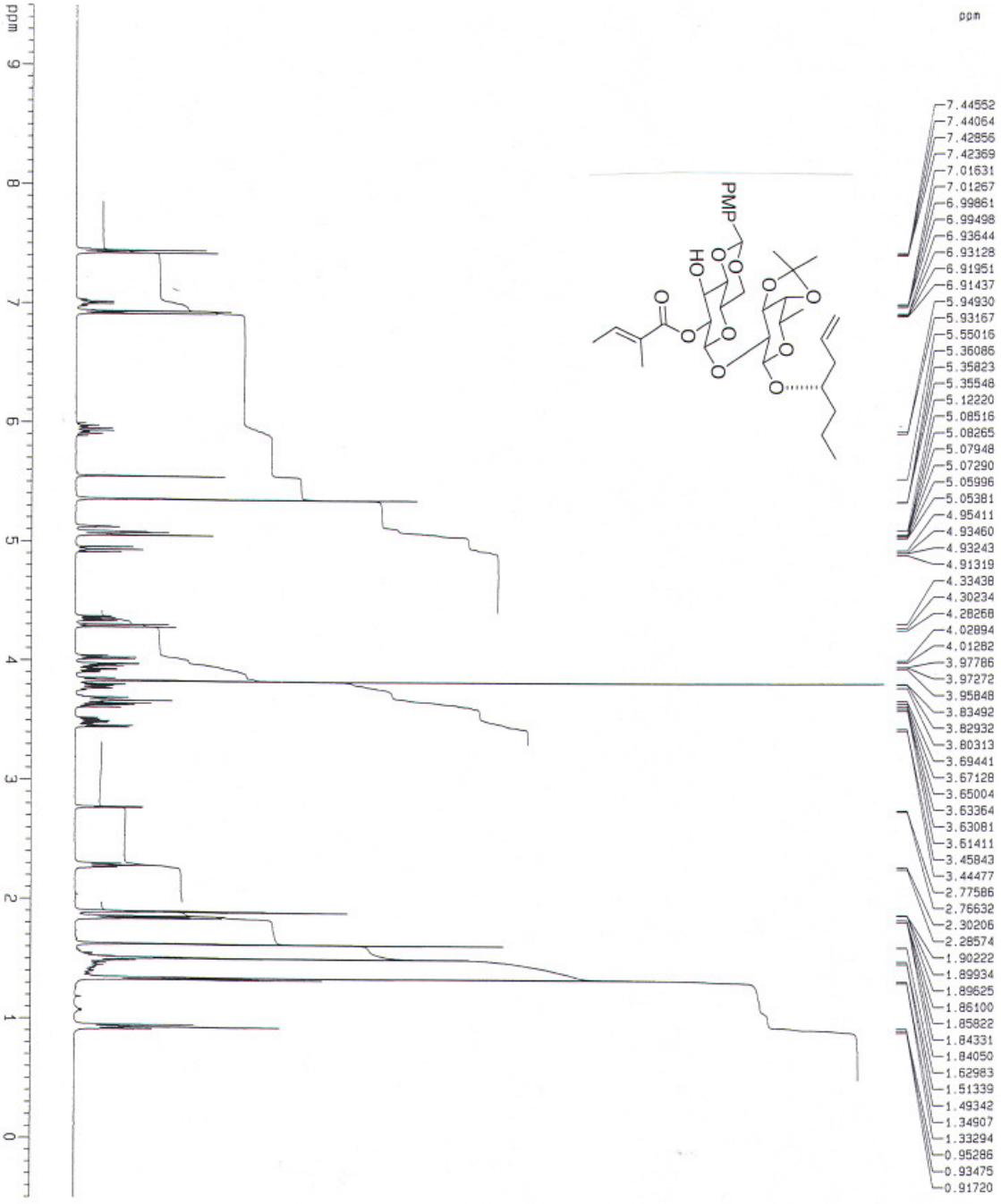
F2 - Acquisition Parameters
Date_              20051209
Time                   12.31
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                zgdc30
TD                     65536
SOLVENT                CDCl3
NS                      1500
DS                         2
SWH                33112.582 Hz
FIDRES                 0.505258 Hz
AQ                 0.9896436 sec
RG                     16384
DW                    15.100 usec
DE                     6.00 usec
TE                    303.0 K
D1                 0.03000000 sec
d11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.94 usec
PL1                      5.00 dB
SFO1              100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                     0.00 dB
PL12                   19.76 dB
SFO2              400.1324710 MHz

F2 - Processing parameters
SI                         32768
SF                400.6126088 MHz
WDW                           EM
SSB                            0
LB                      1.00 Hz
GB                             0
PC                          2.00

1D NMR plot parameters
CX                        22.00 cm
CY                        15.00 cm
F1P                     250.000 ppm
F1                    25153.17 Hz
F2P                    -30.000 ppm
F2                    -3018.38 Hz
PPMCM                 12.72727 ppm/cm
HZCM                  1280.52515 Hz/cm
```

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Current Data Parameters
NAME                  dr07013
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20051207
Time                   15.05
INSTRUM                av400
PROBHD     5 mm BBO BB-1H
PULPROG                 z930
TD                     65536
SOLVENT                CDCl2
NS                        32
DS                         8
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                       114
DW                  60.400 usec
DE                   6.50 usec
TE                     303.0 K
D1                 0.00300000 sec

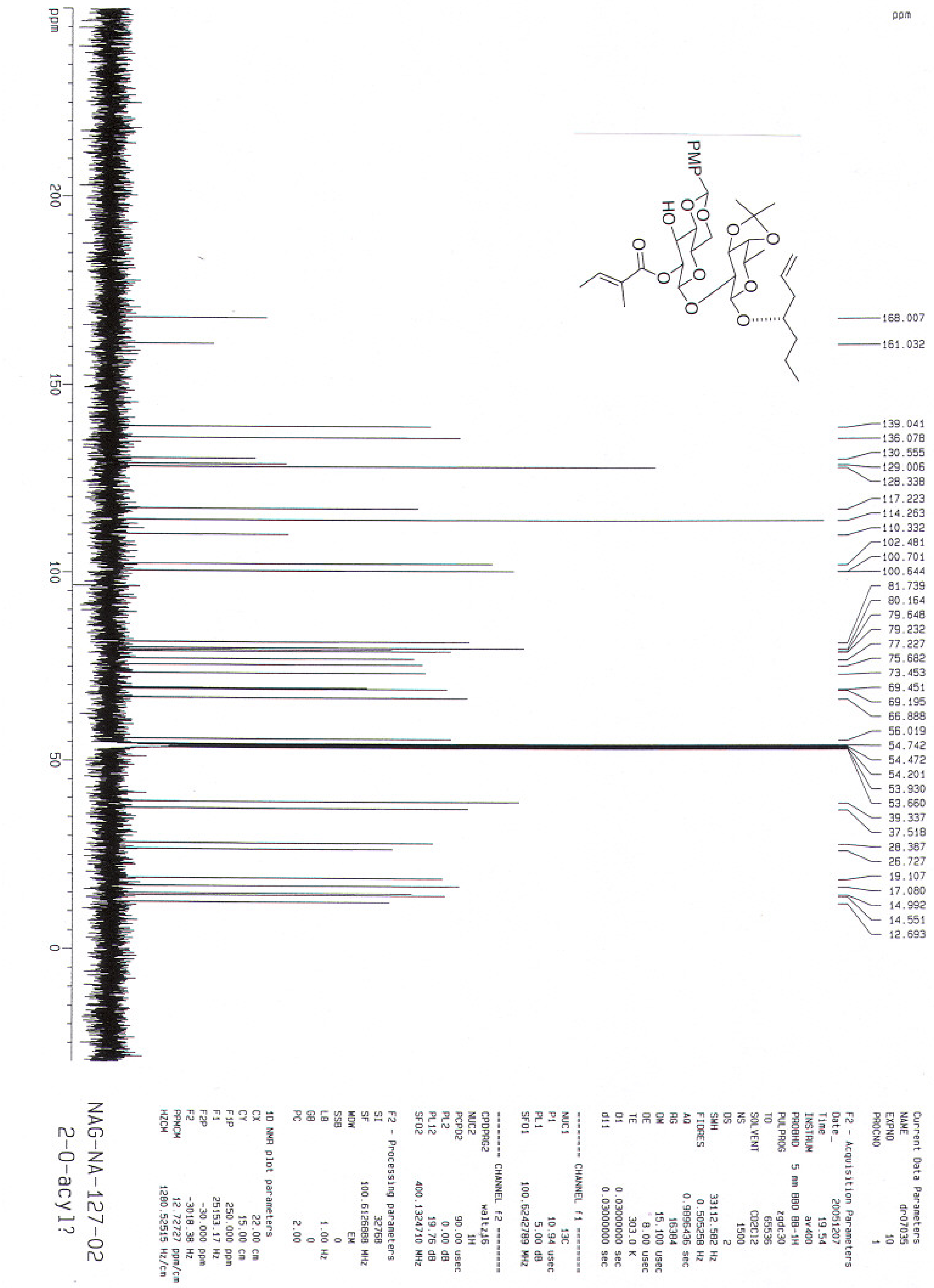
======== CHANNEL f1 ========
NUC1                       1H
P1                       9.25 usec
PL1                      0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF             400.1300000 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       2.00

1D NMR plot parameters
CX                      22.00 cm
CY                      15.00 cm
F1P                     9.500 ppm
F1                   3801.24 Hz
F2P                   -0.500 ppm
F2                   -200.07 Hz
PPMCM                0.45455 ppm/cm
HZCM                 181.87727 Hz/cm
```

NAG-NA-127-02

2-O-acylated?


PMP
HO
O
ppm
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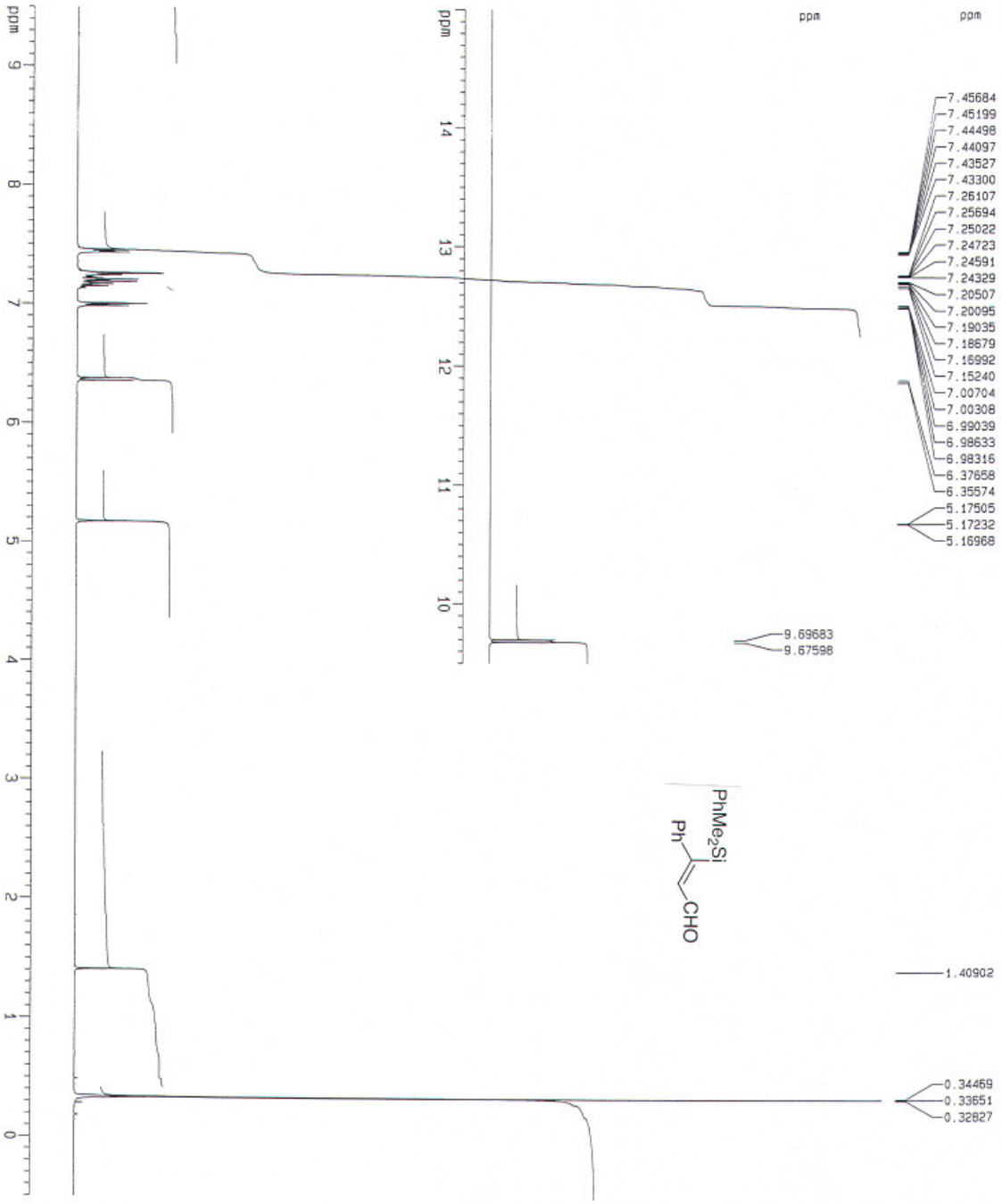
161.032
139.041
136.078
130.555
129.006
128.338
117.223
114.263
110.332
102.481
100.701
100.644
81.739
80.164
79.648
79.232
77.227
75.682
73.453
69.451
69.195
66.888
56.019
54.742
54.472
54.201
53.930
53.660
39.337
37.518
28.387
26.727
19.107
17.080
14.992
14.551
12.693
Current Data Parameters
NAME dr07035
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ 20051207
Time 19.54
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CD2Cl2
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896436 sec
RG 16384
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 100.6126888 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.17 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.52515 Hz/cm
NAG-NA-127-02
2-O-acyl?



NAG-NB-032-01

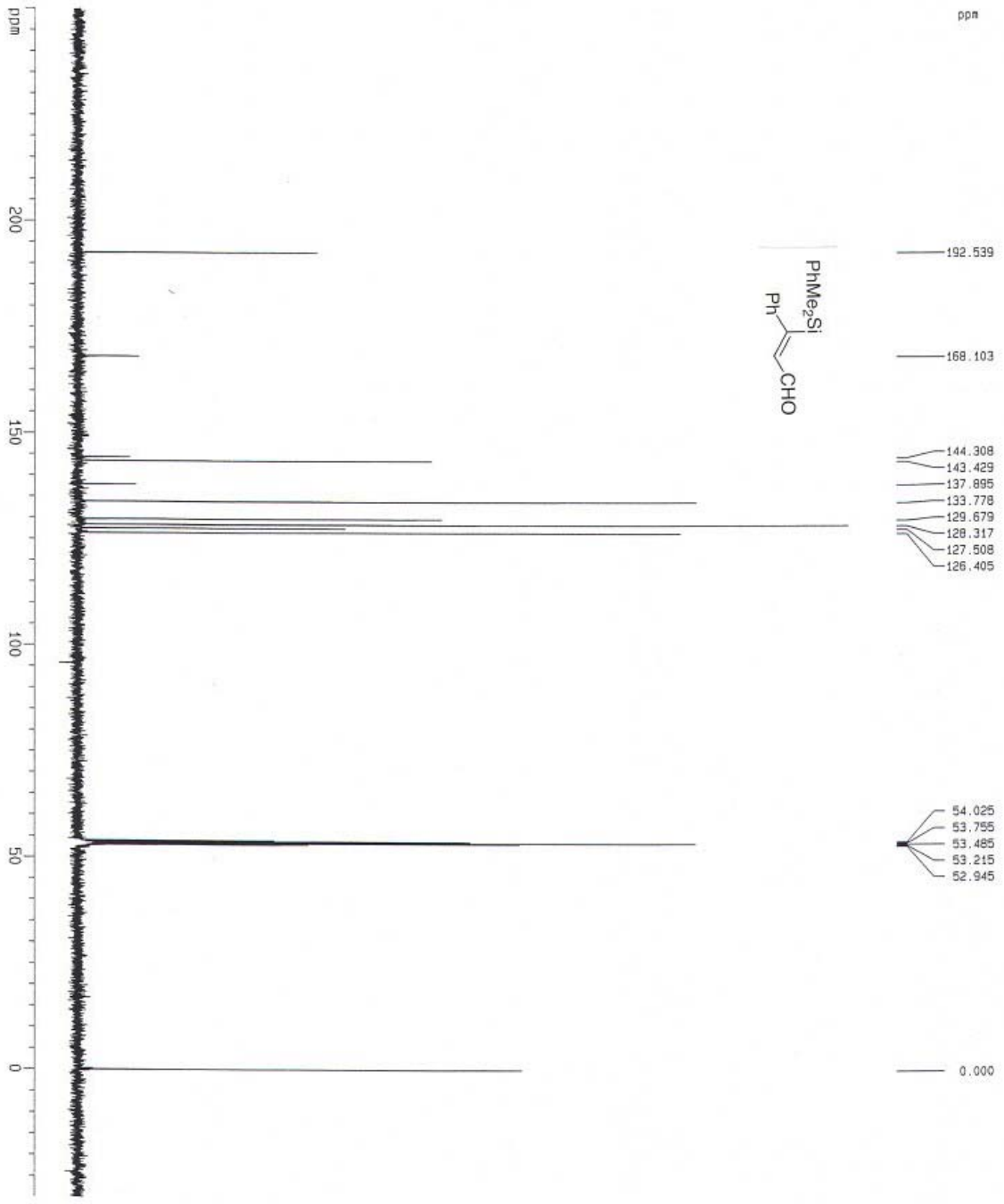
Current Data Parameters
NAME jy11031
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060712
Time 0.54
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300745 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87730 Hz/cm



NAG-NB-032-01

```
Current Data Parameters
NAME                  jyli031
EXPNO                      11
PROCNO                      1

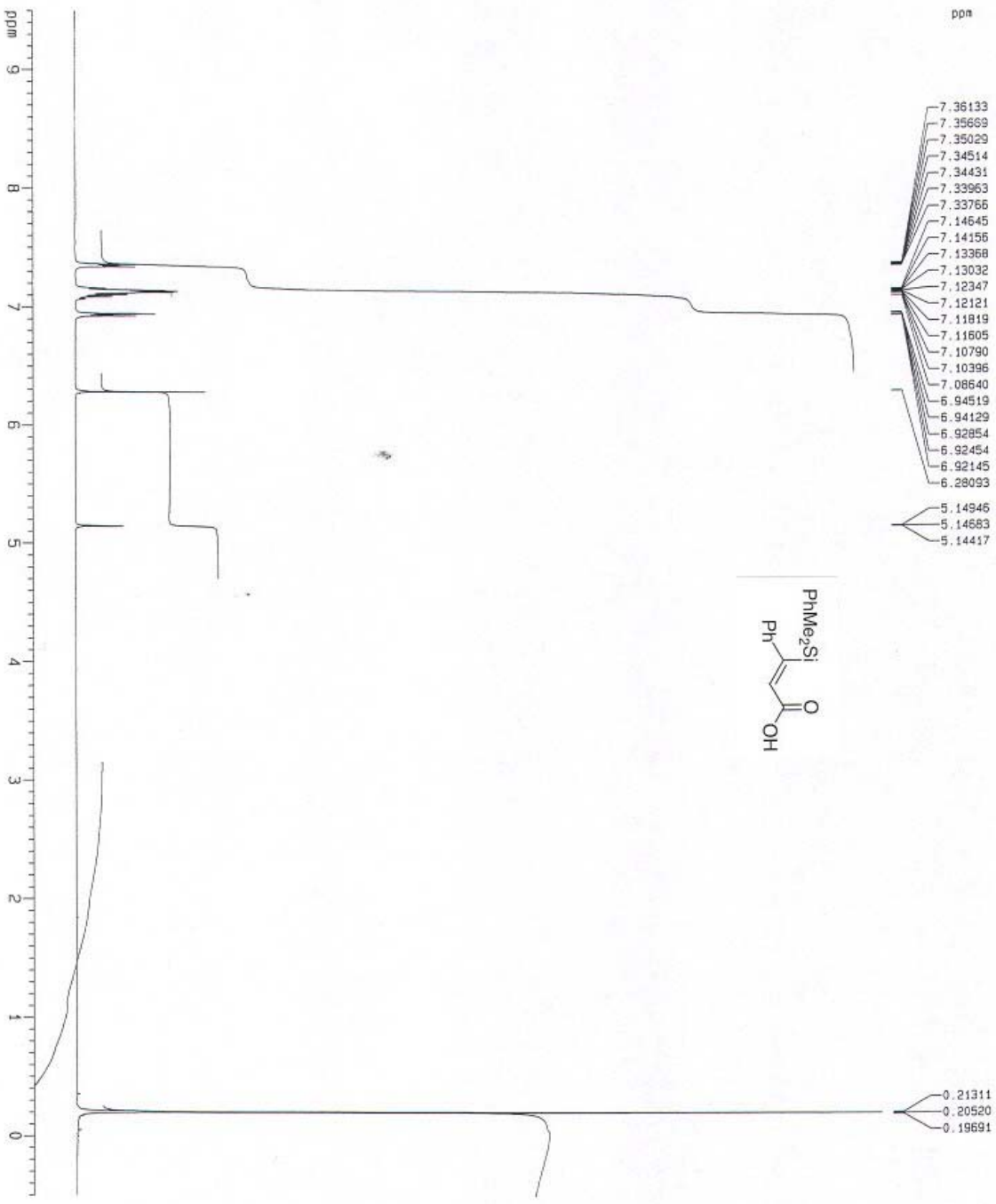
F2 - Acquisition Parameters
Date_              20060712
Time                   1.23
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG              zgdc30
TD                    65536
SOLVENT               CDCl2
NS                     1500
DS                        2
SWH                33112.582 Hz
FIDRES                0.505258 Hz
AQ                 0.9896436 sec
RG                    18390.4
DW                    15.100 usec
DE                     8.00 usec
TE                    303.0 K
D1                 0.03000000 sec
d11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.94 usec
PL1                      5.00 dB
SFO1              100.6242799 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                     0.00 dB
PL12                   19.76 dB
SFO2              400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127604 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         2.00

1D NMR plot parameters
CX                       22.00 cm
CY                       15.00 cm
F1P                    250.000 ppm
F1                   25153.19 Hz
F2P                    -30.000 ppm
F2                   -3018.38 Hz
PPMCM                12.72727 ppm/cm
HZCM              1280.52612 Hz/cm
```



NAG-NB-033-01

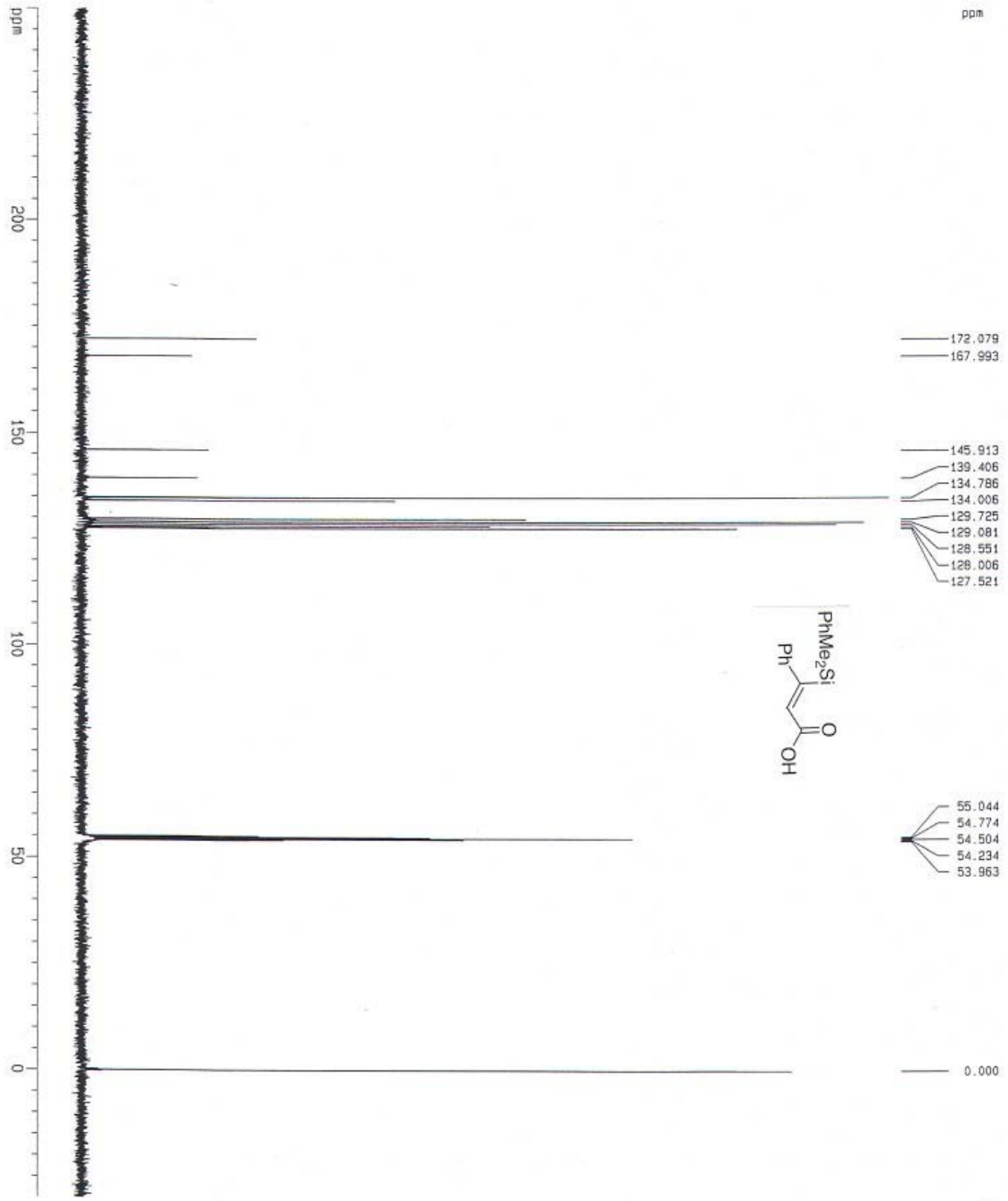
```
Current Data Parameters
NAME                  jy12072
EXPNO                      10
PROCNO                      1

F2 - Acquisition Parameters
Date_              20060713
Time                  10.38
INSTRUM               av400
PROBHD  5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       8
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                     114
DW                  60.400 usec
DE                   6.50 usec
TE                  303.0 K
D1                  0.00300000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   9.25 usec
PL1                  0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                   32768
SF            400.1300049 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    2.00

1D NMR plot parameters
CX                   22.00 cm
CY                   15.00 cm
F1P                  9.500 ppm
F1                3801.24 Hz
F2P                 -0.500 ppm
F2                -200.07 Hz
PPMCM             0.45455 ppm/cm
HZCM              181.87732 Hz/cm
```



NAG-NB-033-01

```
Current Data Parameters
NAME                  iy12072
EXPNO                      11
PROCNO                      1

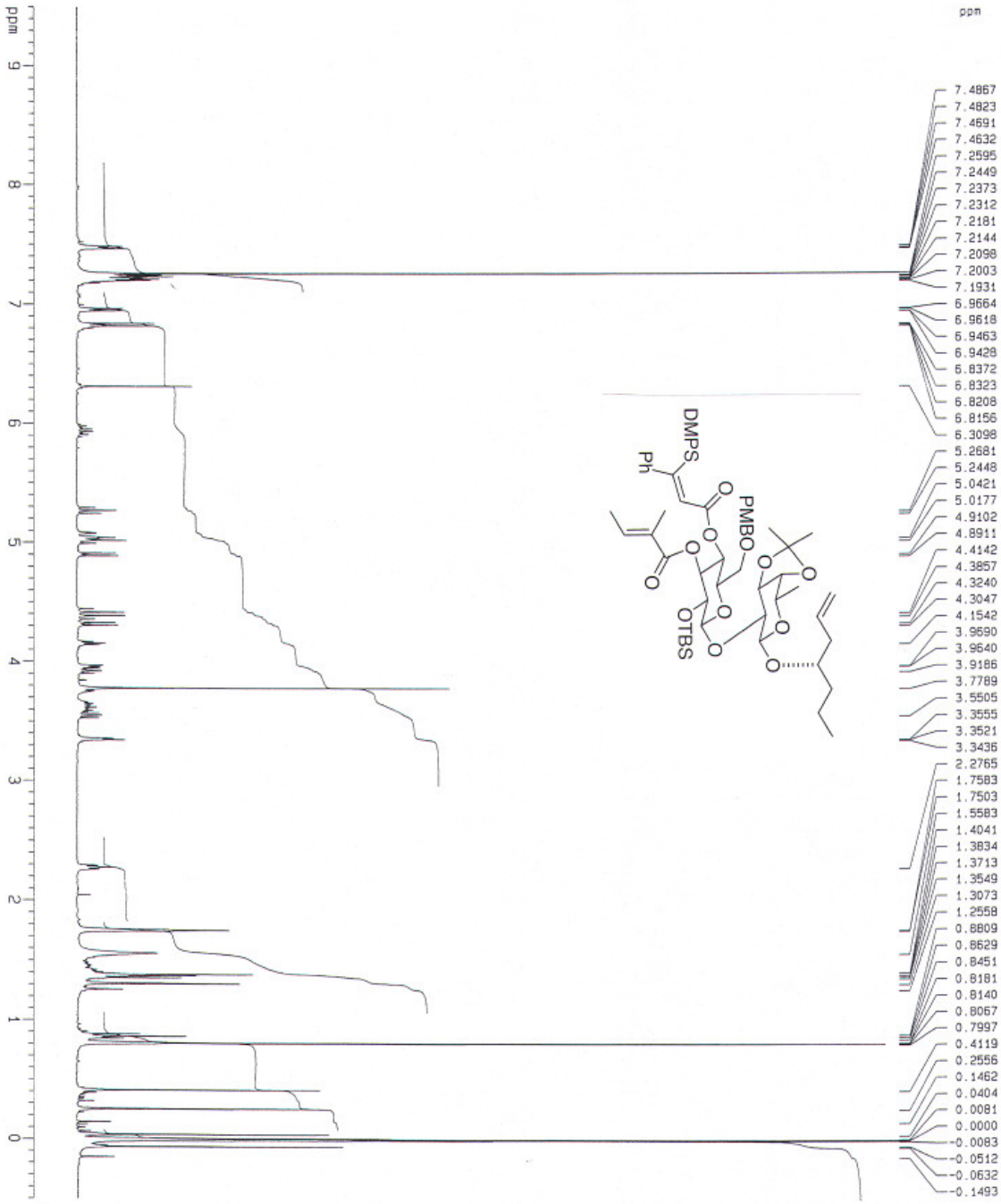
F2 - Acquisition Parameters
Date_              20060713
Time                   11.05
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES           0.505258 Hz
AQ               0.9896435 sec
RG                  18390.4
DW                 15.100 usec
DE                  8.00 usec
TE                  303.0 K
D1               0.03000000 sec
d11              0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.94 usec
PL1                   5.00 dB
SFO1           100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2              90.00 usec
PL2                 0.00 dB
PL12               19.76 dB
SF02           400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF             100.6126580 MHz
WDW                       EM
SSB                        0
LB                  1.00 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                 250.000 ppm
F1                  25153.17 Hz
F2P                 -30.000 ppm
F2                  -3018.38 Hz
PPMCM               12.72727 ppm/cm
HZCM             1280.52466 Hz/cm
```




```
Current Data Parameters
NAME                  mm08025
EXPNO                      10
PROCNO                      1

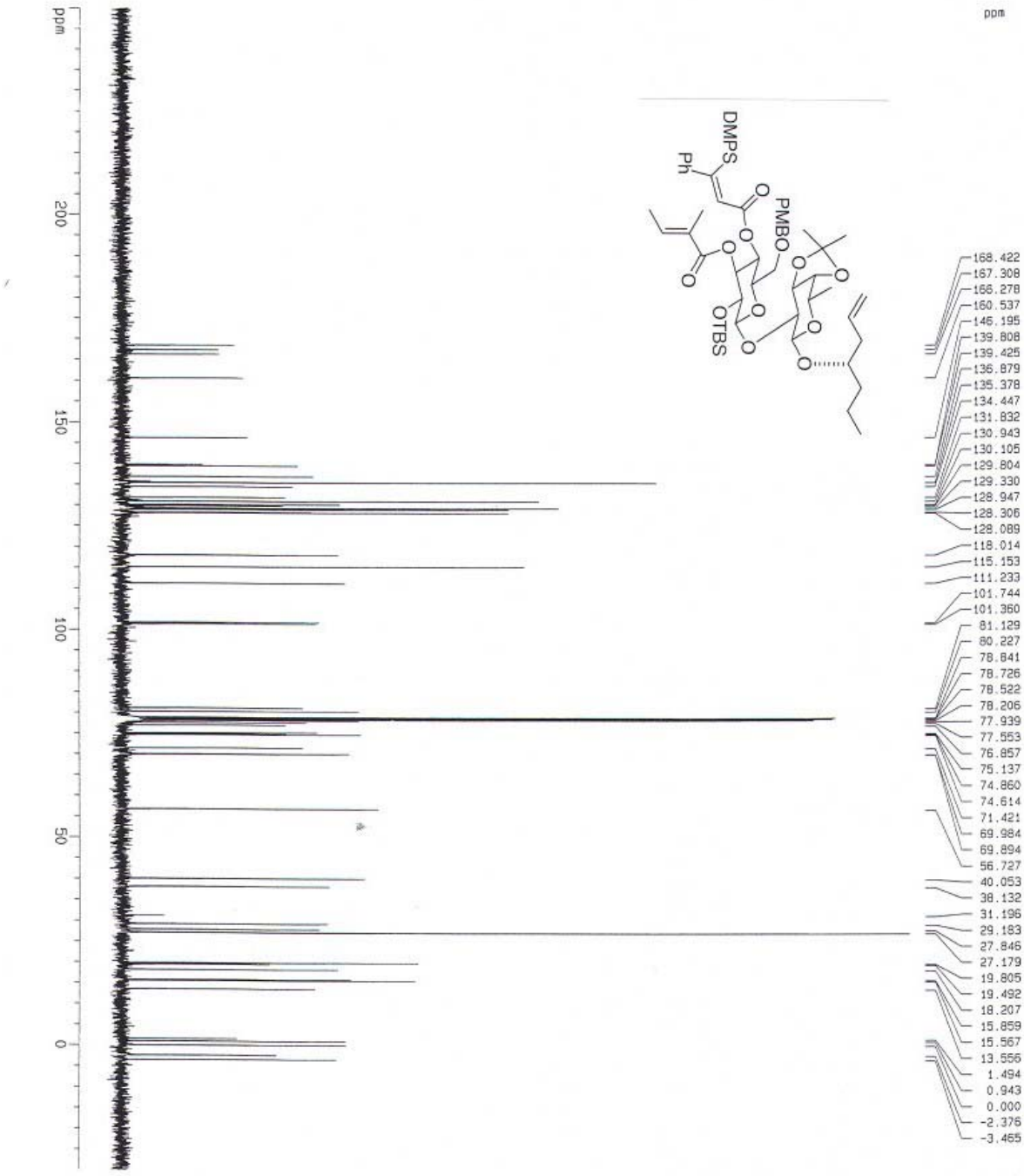
F2 - Acquisition Parameters
Date_              20060508
Time                   14.16
INSTRUM                av400
PROBHD     5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH               8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9568243 sec
RG                     322.5
DW                60.400 usec
DE                 6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF            400.1300099 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                   9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                  -200.07 Hz
PPMCM              0.45455 ppm/cm
HZCM               181.87727 Hz/cm
```

NAG-NA-229-02



NAG-NA-229-02

```
Current Data Parameters
NAME                  nv08031
EXPNO                       10
PROCNO                       1

F2 - Acquisition Parameters
Date_              20060508
Time                   16.21
INSTRUM              av400
PROBHD  5 mm BBO BB-1H
PULPROG              zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH                33112.582 Hz
FIDRES                0.505258 Hz
AQ                 0.9896436 sec
RG                    18390.4
DW                   15.100 usec
DE                    6.00 usec
TE                   303.0 K
D1                 0.03000000 sec
d11                0.03000000 sec

======== CHANNEL f1 ========
NUC1                      13C
P1                      10.94 usec
PL1                      5.00 dB
SFO1              100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  90.00 usec
PL2                     0.00 dB
PL12                   19.76 dB
SFO2              400.1324710 MHz

F2 - Processing parameters
SI                        32768
SF                100.6126177 MHz
WDW                          EM
SSB                           0
LB                     1.00 Hz
GB                            0
PC                         2.00

1D NMR plot parameters
CX                       22.00 cm
CY                       15.00 cm
F1P                     250.000 ppm
F1                     25153.16 Hz
F2P                    -30.000 ppm
F2                     -3018.38 Hz
PPMCM                 12.72727 ppm/cm
HZCM                1280.52417 Hz/cm
```

ppm

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167.308
166.278
160.537
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139.425
136.879
135.378
134.447
131.832
130.943
130.105
129.804
129.330
128.947
128.306
128.089
118.014
115.153
111.233
101.744
101.360
81.129
80.227
78.841
78.726
78.522
78.206
77.939
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76.857
75.137
74.860
74.614
71.421
69.984
69.894
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40.053
38.132
31.196
29.183
27.846
27.179
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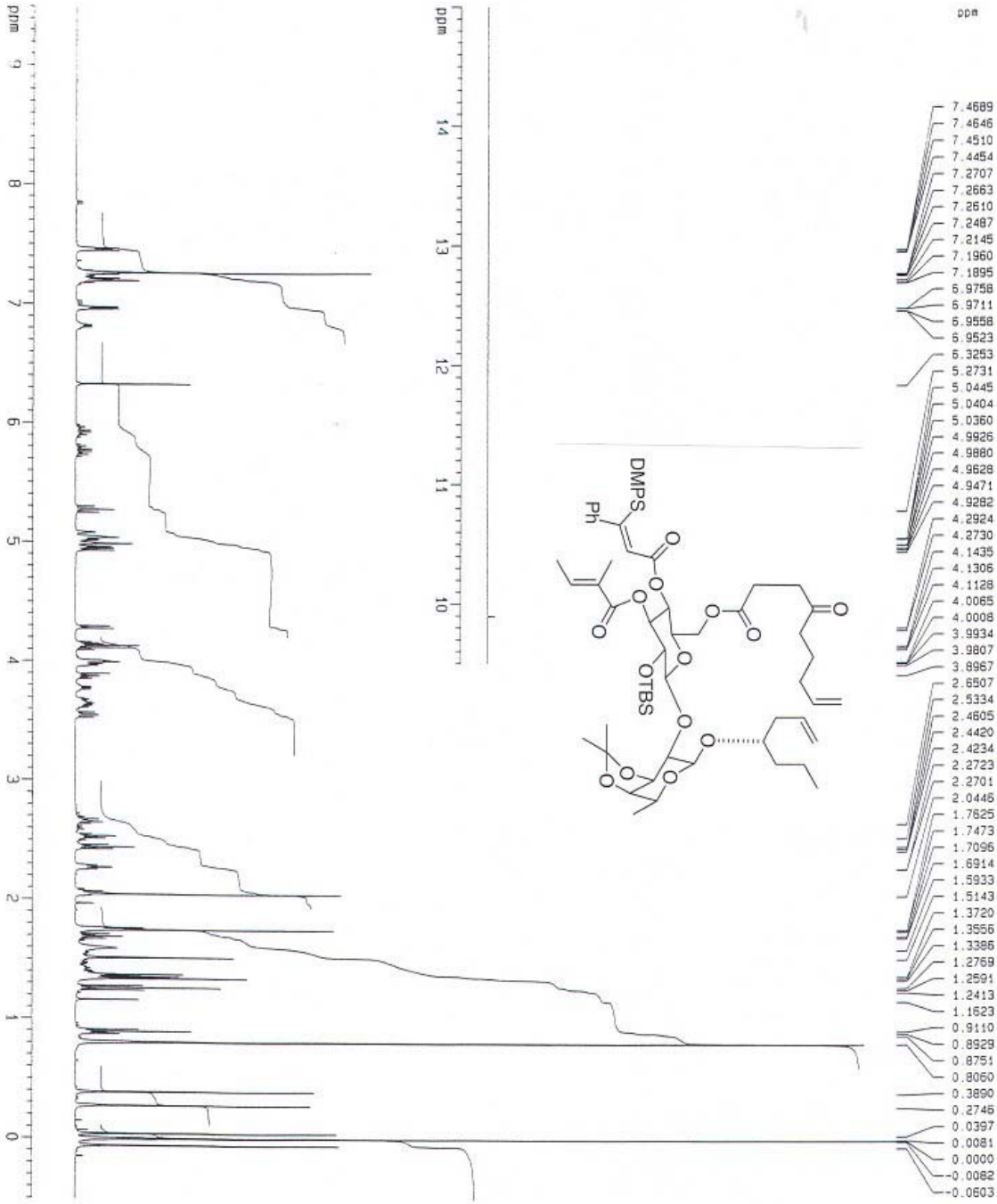
-3.465




```
Current Data Parameters
NAME                  jy19027
EXPNO                      10
PROCNO                      1

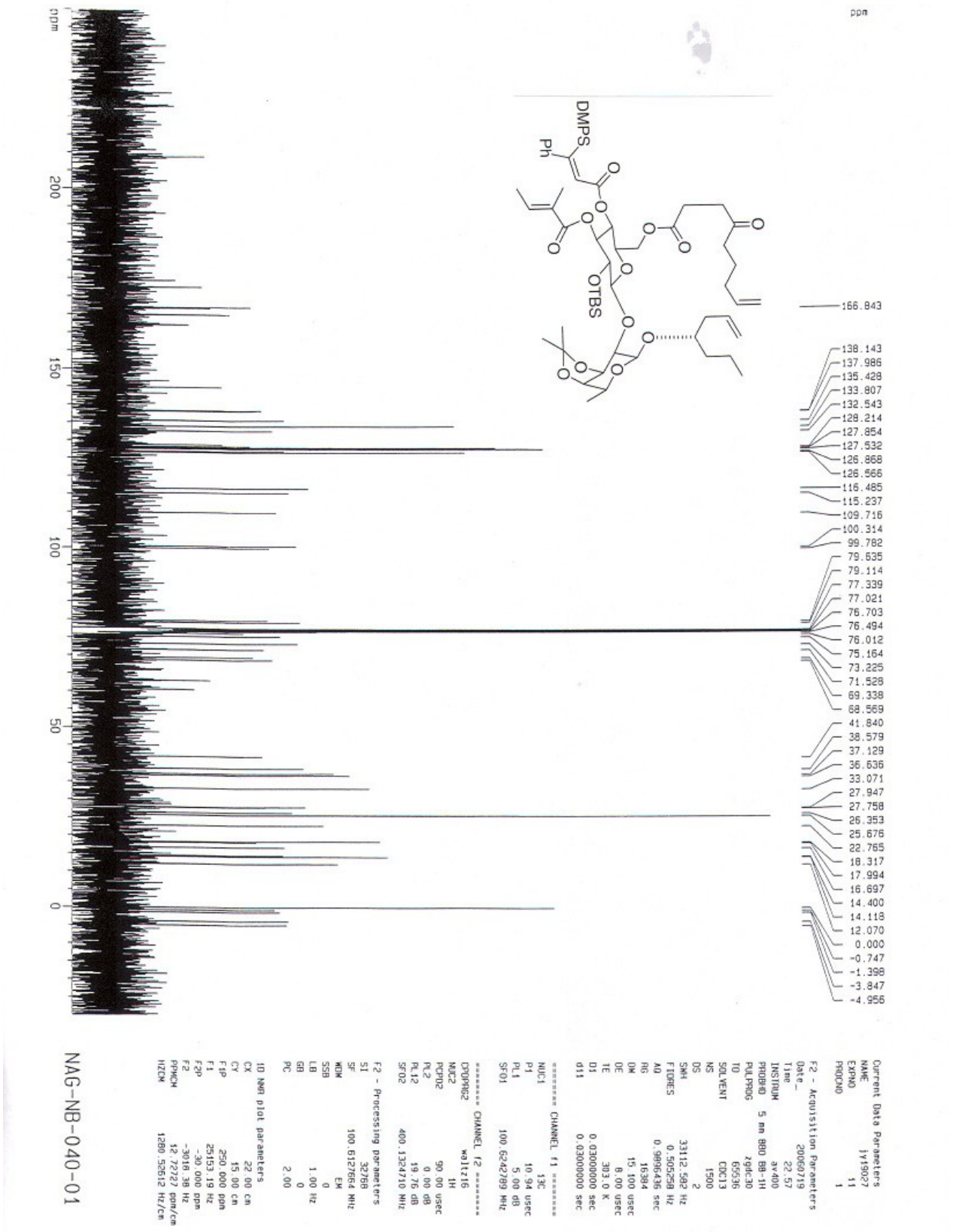
F2 - Acquisition Parameters
Date_              20060719
Time                   22.29
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH                8278.146 Hz
FIDRES             0.126314 Hz
AQ                 3.9584243 sec
RG                       181
DW                  60.400 usec
DE                   6.50 usec
TE                   303.0 K
D1                 0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                      9.25 usec
PL1                     0.00 dB
SFO1           400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF             400.1300093 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                  9.500 ppm
F1                  3801.24 Hz
F2P                 -0.500 ppm
F2                  -200.07 Hz
PPMCM               0.45455 ppm/cm
HZCM               181.87727 Hz/cm
```

NAG-NB-040-01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DMPS
Ph
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126.868
126.566
116.485
115.237
109.716
100.314
99.782
79.635
79.114
77.339
77.021
76.703
76.494
76.012
75.164
73.225
71.528
69.338
68.569
41.840
38.579
37.129
36.636
33.071
27.947
27.758
26.353
25.676
22.765
18.317
17.994
16.697
14.400
14.118
12.070
0.000
-0.747
-1.398
-3.847
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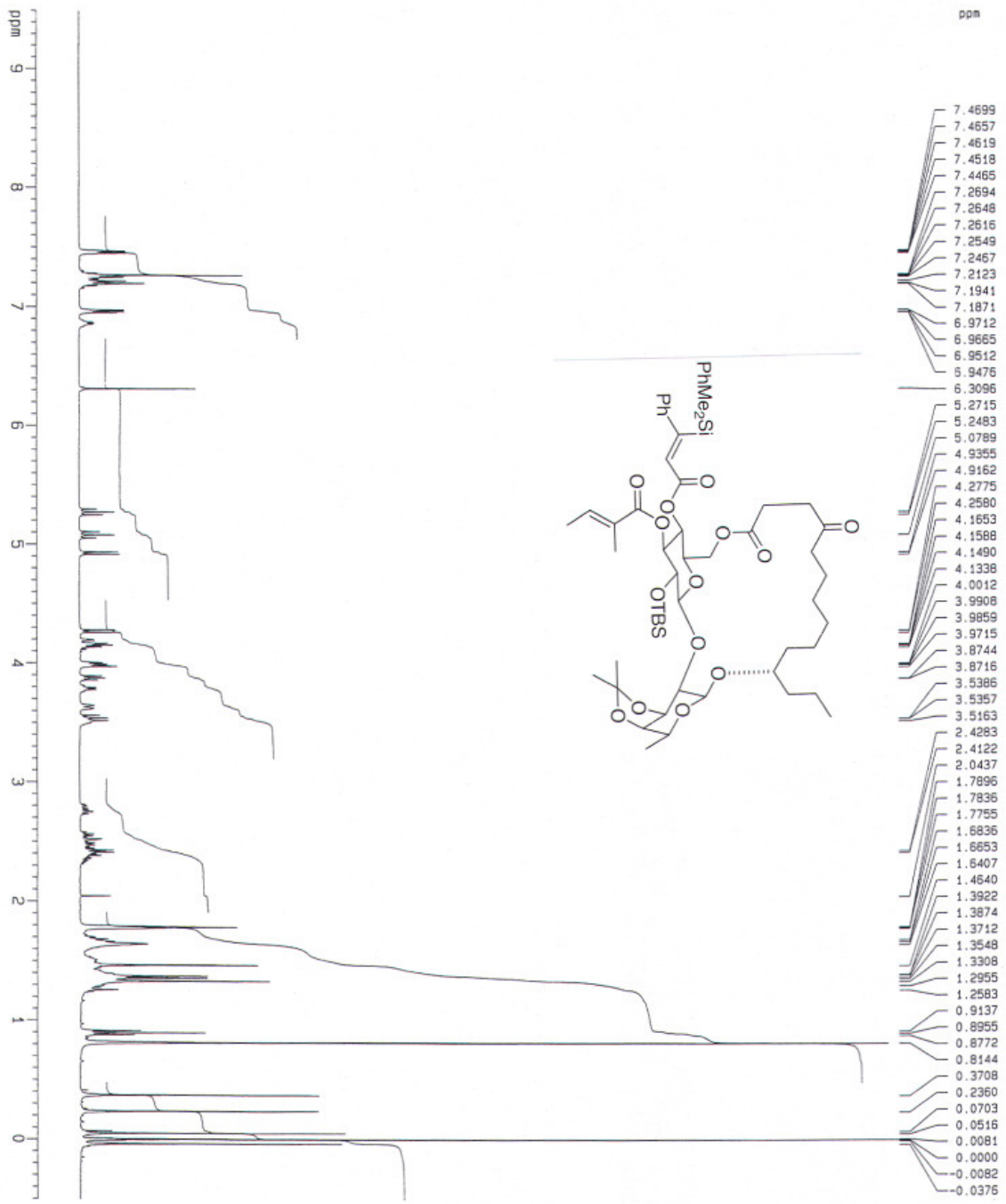
Current Data Parameters
NAME jyl9027
EXPNO 11
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060719
Time 22.57
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896496 sec
RG 16384
DW 15.100 usec
DE 6.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz
F2 - Processing parameters
SI 32768
SF 100.6127664 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00
1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.19 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.52512 Hz/cm
NAG-NB-040-01



Current Data Parameters
NAME NAG-NB-049-01
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060725
Time 15.09
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87727 Hz/cm

NAG-NB-049-01
IpoB H2 colum

NAG-NB-049-01

IpoB H2 colum

```
Current Data Parameters
NAME                  jy2504
EXPNO                      11
PROCNO                      1

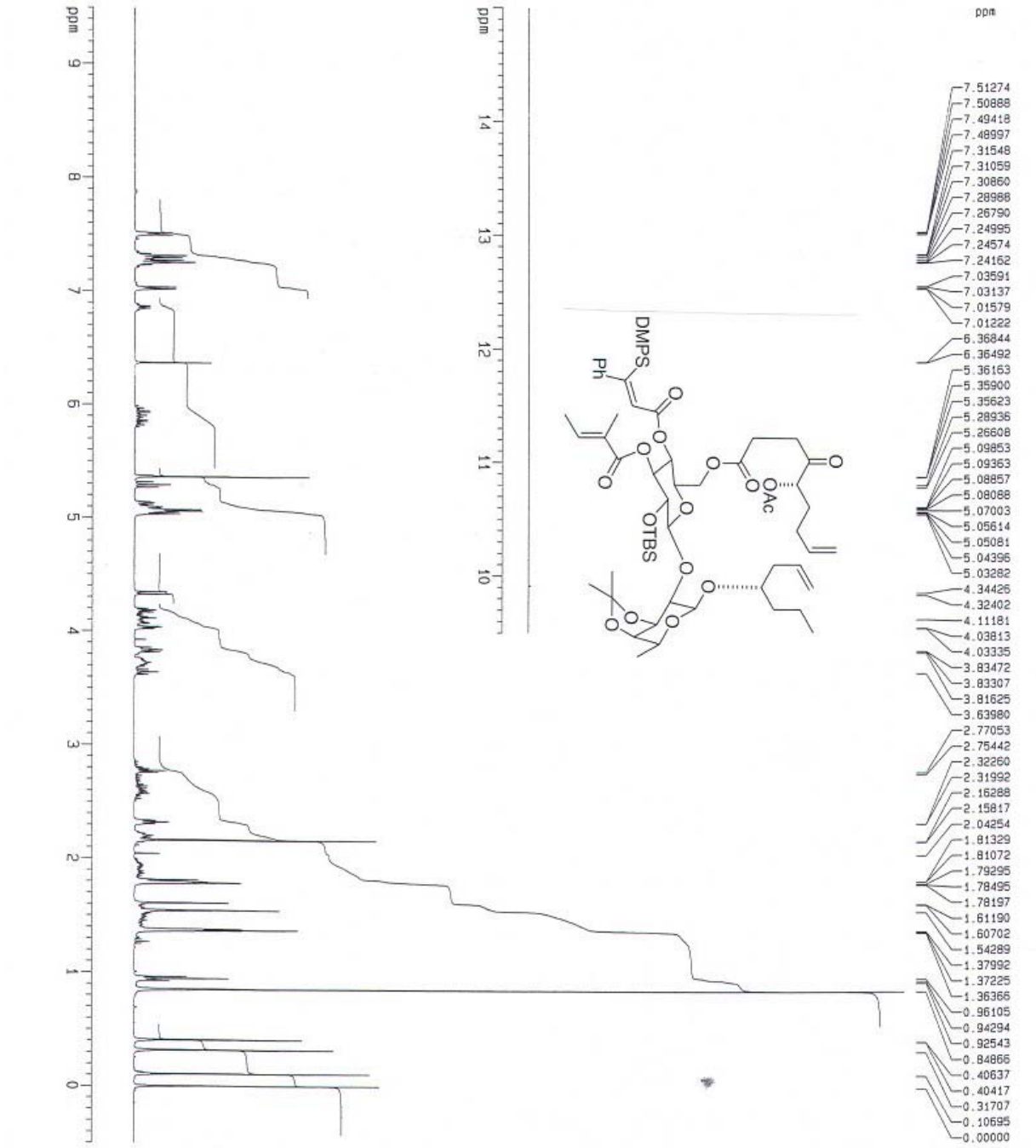
F2 - Acquisition Parameters
Date_              20060725
Time                   15.37
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG             zgdc30
TD                   65536
SOLVENT              CDCl3
NS                    1500
DS                       2
SWH              33112.582 Hz
FIDRES            0.505258 Hz
AQ                0.9896436 sec
RG                   18390.4
DW                  15.100 usec
DE                   6.00 usec
TE                   303.0 K
D1                0.03000000 sec
d11               0.03000000 sec

======== CHANNEL f1 ========
NUC1                     13C
P1                     10.94 usec
PL1                    5.00 dB
SF01           100.6242799 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 90.00 usec
PL2                    0.00 dB
PL12                  19.76 dB
SF02           400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF             100.6127654 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                        2.00

1D NMR plot parameters
CX                    22.00 cm
CY                    15.00 cm
F1P                  250.000 ppm
F1                 25153.19 Hz
F2P                 -30.000 ppm
F2                 -3016.38 Hz
PPMCM                12.72727 ppm/cm
HZCM               1280.52612 Hz/cm
```



Current Data Parameters
NAME jy17020
EXPNO 10
PROCNO 1

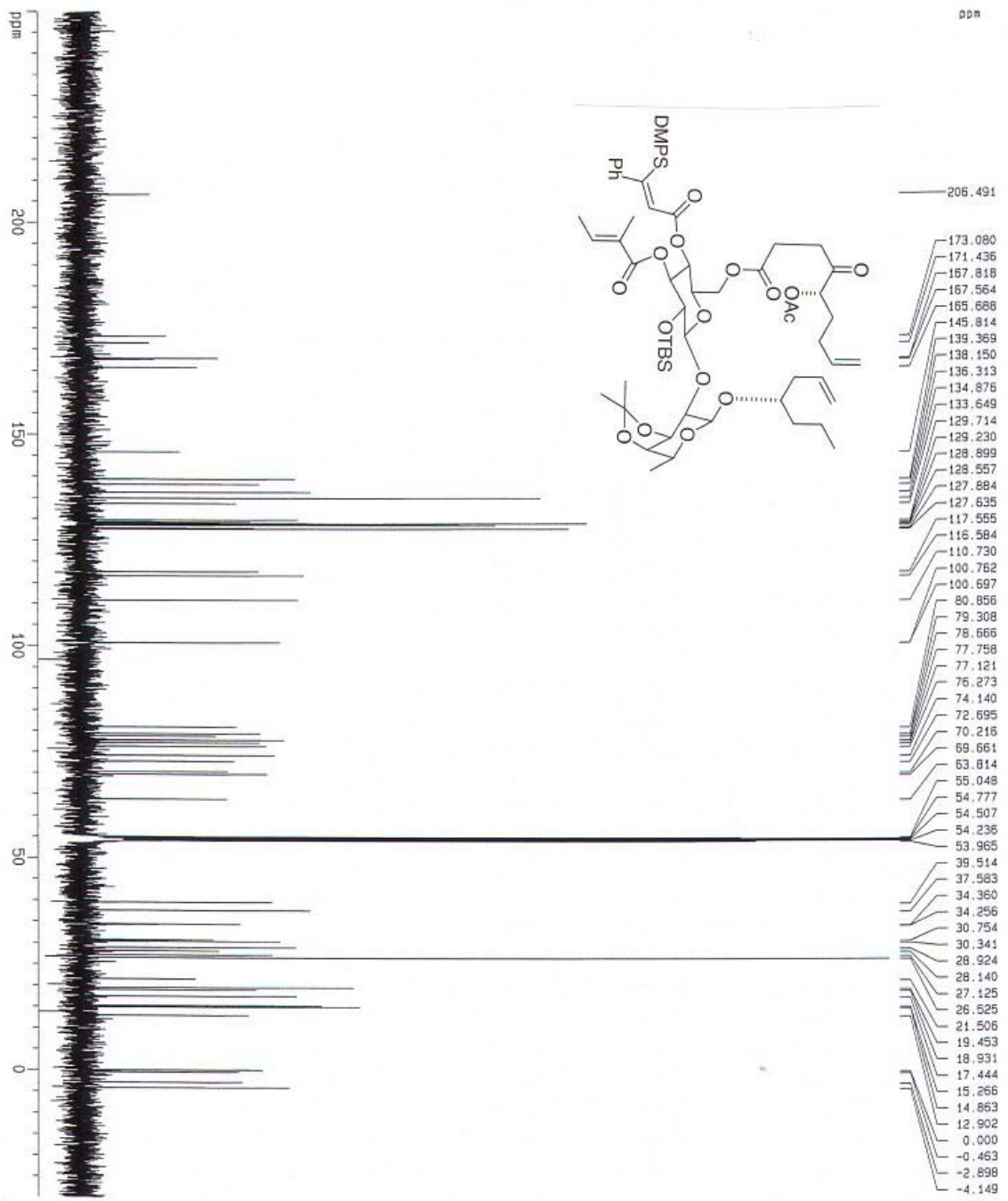
F2 - Acquisition Parameters
Date_ 20060717
Time 16.01
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 32
DS 8
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.50 usec
TE 303.0 K
D1 0.00300000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 9.25 usec
PL1 0.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 9.500 ppm
F1 3801.24 Hz
F2P -0.500 ppm
F2 -200.07 Hz
PPMCM 0.45455 ppm/cm
HZCM 181.87727 Hz/cm

NAG-NB-038-02



Current Data Parameters
NAME jy17020
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060717
Time 16.29
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CD2Cl2
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9895436 sec
RG 16384
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

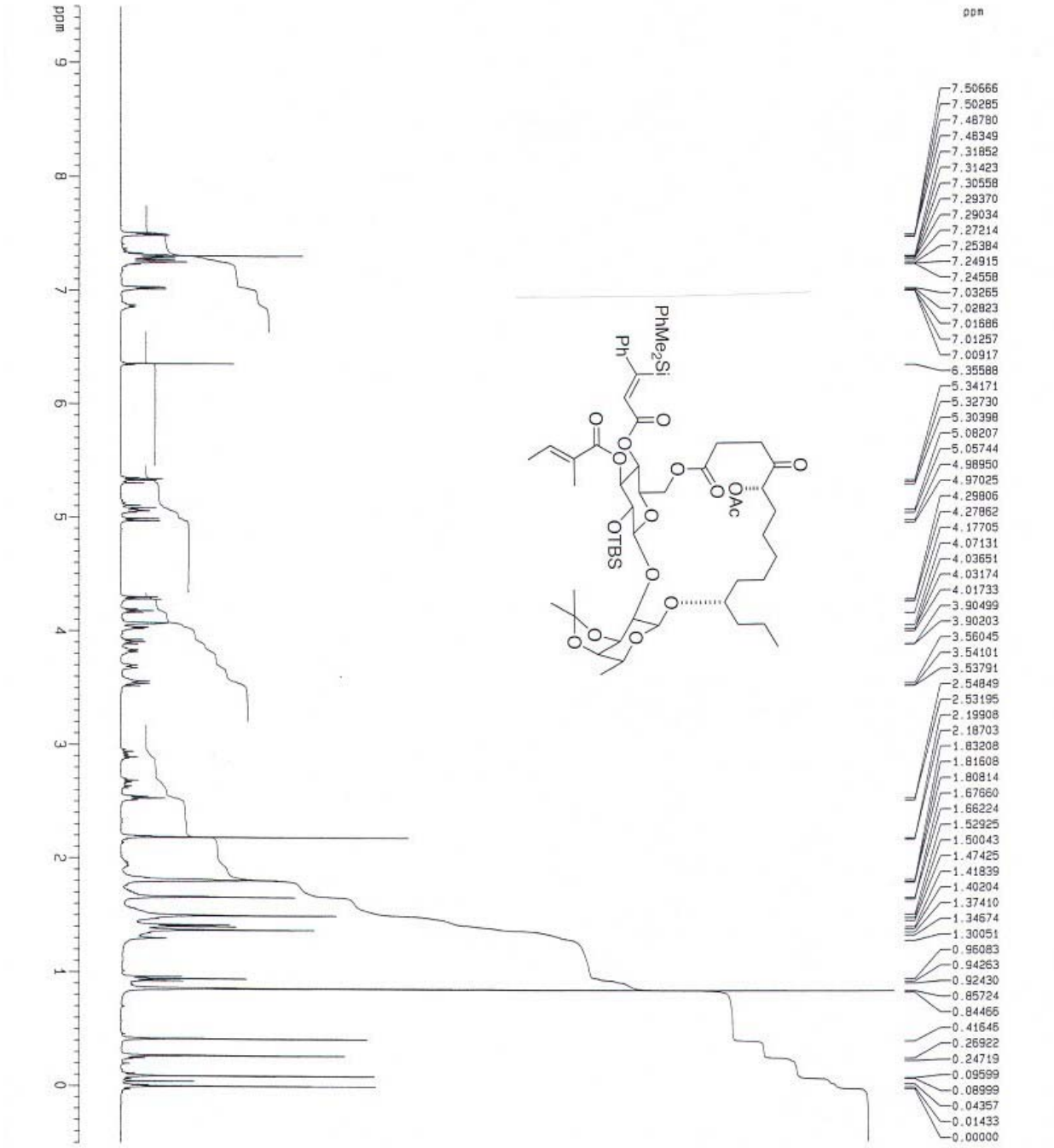
======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SF01 100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SF02 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6126571 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.17 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.52466 Hz/cm

NAG-NB-038-02




```
Current Data Parameters
NAME                  jn26097
EXPNO                      10
PROCNO                      1

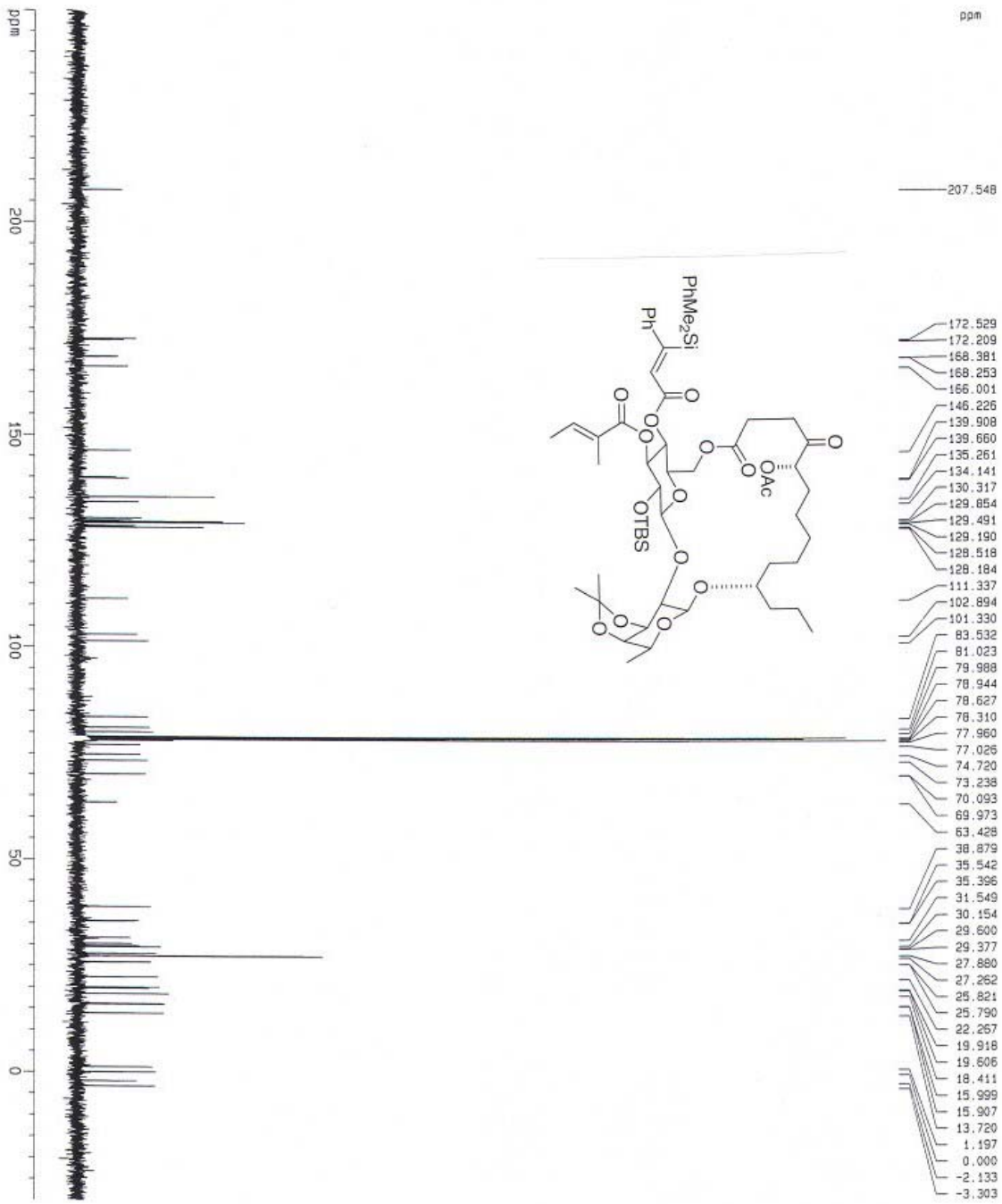
F2 - Acquisition Parameters
Date_              20060628
Time                   0.07
INSTRUM                av400
PROBHD  5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       32
DS                        8
SWH               8278.146 Hz
FIDRES               0.126314 Hz
AQ                3.9584243 sec
RG                      114
DW                   60.400 usec
DE                    6.50 usec
TE                   303.0 K
D1                0.00300000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                    0.00 dB
SF01          400.1324710 MHz

F2 - Processing parameters
SI                       32768
SF            400.1299915 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      2.00

1D NMR plot parameters
CX                     22.00 cm
CY                     15.00 cm
F1P                    9.500 ppm
F1                  3801.24 Hz
F2P                  -0.500 ppm
F2                   -200.07 Hz
PPMCM                0.45455 ppm/cm
HZCM                181.87727 Hz/cm
```

NAG-NB-015-02



NAG-NB-015-02

Current Data Parameters
NAME 1n26097
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060628
Time 0.50
INSTRUM av400
PROBHD 5 mm BBO BB-1H
PULPROG zgdc30
TD 65536
SOLVENT CDCl3
NS 1500
DS 2
SWH 33112.582 Hz
FIDRES 0.505258 Hz
AQ 0.9896435 sec
RG 16384
DW 15.100 usec
DE 8.00 usec
TE 303.0 K
D1 0.03000000 sec
d11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 10.94 usec
PL1 5.00 dB
SFO1 100.6242789 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 19.76 dB
SFO2 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 100.6126055 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 2.00

1D NMR plot parameters
CX 22.00 cm
CY 15.00 cm
F1P 250.000 ppm
F1 25153.15 Hz
F2P -30.000 ppm
F2 -3018.38 Hz
PPMCM 12.72727 ppm/cm
HZCM 1280.52405 Hz/cm