Supplementary Information

New insight on 2-naphthylmethyl (NAP) ether as protecting group in carbohydrate synthesis: divergent approach towards high-mannose-type oligosaccharide library

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General Information. All chemicals used were reagent grade and used as supplied except where noted. All reactions were performed in oven-dried glassware under an inert atmosphere (nitrogen) unless noted otherwise. Reagent grade dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O) and toluene (PhMe) were passed through activated neutral alumina column prior to use.[1] Pyridine, triethylamine and acetonitrile were distilled over CaH_2 prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates (0.25mm). Compounds were visualized by UV irradiation or dipping the plate in a cerium sulfate-ammonium molybdate solution. Flash column chromatography (FC) was carried out using forced flow of the indicated solvent on Silicycle P60 (230-400 mesh). HF/Pyridine used in this study was obtained from Acros Organics (Cat# AC18007).

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX400 (400 MHz), Bruker DRX500 (500 MHz), or a Bruker AV600 (600 MHz) spectrometer in $CDCl_3$ with chemical shifts referenced to $CDCl_3$ (7.26 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet for ^1H NMR data. High-resolution mass spectral (HRMS) analyses were performed by the MS-service at the Department of Chemistry at University of Pittsburgh. HRMS-ESI were run on a Water® Q-TOF instrument. Optical rotations were measured using a Perkin-Elmer 241 polarimeter.

General Procedure 1 – cleavage of 2-naphthylmethyl (NAP) ether using HF-Pyr in toluene: To a solution of NAP ether containing substrate (0.5 mmol) in toluene (1 mL) in a plastic centrifuge tube was added HF-Pyr (10 mmol, 0.25mL) at room temperature with vigorous stirring. The reaction solution was stirred for ca. 2-4 hours. After complete consumption of starting material as assessed by TLC, the reaction was diluted with dichloromethane, quenched by the addition of cold aqueous $NaHCO_3$ solution. The mixture was then poured into water (10 mL) and the aqueous layer was extracted with dichloromethane. The combined organic layers were then washed with additional water, brine and dried over Na_2SO_4. Rotary evaporation gave a crude residue, which was subsequently purified by flash silica column chromatography to furnish the desired compound.

General Procedure 2 – tandem cleavage of PMB and silyl ethers in presence of NAP ether

using HF-Pyr in Et_3N-supplemented toluene: To a solution of a substrate (0.5 mmol) that contains PMB and/or silyl ethers with NAP ether groups in toluene (1 mL) in a plastic centrifuge tube was added Et_3N (1.5 mmol, 0.21 mL), HF-Pyr (10 mmol, 0.25mL) at room temperature with vigorous stirring. The reaction solution was stirred for ca. 12-16 hours. After complete consumption of starting material as assessed by TLC, the reaction was diluted with dichloromethane, quenched by the addition of cold aqueous $NaHCO_3$ solution. The mixture was then poured into water (10 mL) and the aqueous layer was extracted with dichloromethane. The combined organic layers were then washed with additional water, brine and dried over Na_2SO_4. Rotary evaporation gave a crude residue, which was subsequently purified by flash silica column chromatography to furnish the desired compound.

General Procedure 3 – cleavage of silyl ether in presence of PMB and/or NAP ether using HF-Pyr in pyridine: To a solution of a substrate (0.5 mmol) that contains silyl ethers with PMB and/or NAP ether groups in pyridine (1 mL) in a plastic centrifuge tube was added HF-Pyr (0.5 mL) at room temperature with vigorous stirring. The reaction solution was stirred for ca. 24 hours. After complete consumption of starting material as assessed by TLC, the reaction was diluted with dichloromethane, quenched by the addition of cold aqueous $NaHCO_3$ solution. The mixture was then poured into water (10 mL) and the aqueous layer was extracted with dichloromethane. The combined organic layers were then washed with additional water, brine and dried over Na_2SO_4. Rotary evaporation gave a crude residue, which was subsequently purified by flash silica column chromatography to furnish the desired compound.

2,3,6-Tri-*O*-acetyl-α-D-glucopyranosyl fluoride (2): General procedure 1 using 3-*O*-naphthylmethyl-1,2,4,6-tetra-*O*-acetyl-D-glucose **1**[1] (3.9 g, 8.0 mmol), toluene (6 mL) and HF-pyr (4 mL) gave **2** (2.06 g, 84%) as a colorless syrup. $[\alpha]_D^{21}$ = +74.1 (*c* = 1.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.70 (dd, 1 H, *J* = 53.1, 2.7 Hz), 5.01 (t, 1 H, *J* = 9.9 Hz), 4.86 (ddd, 1 H, *J* = 24.6, 9.9, 2.7 Hz), 4.32 (dd, 1 H, *J* = 12.6, 4.5 Hz), 4.21–3.00 (m, 3 H), 2.49 (brs, 1 H), 2.18 (s, 3 H), 2.14 (s, 3 H), 2.10 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -149.4 (m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6 (2C), 170.5, 104.0 (d, J = 227 Hz), 73.0, 72.7, 69.9 (2C), 69.7, 69.6, 61.4, 20.7 (2C). HRMS-ESI: *m/z* $C_{12}H_{17}O_8F$ $[M+Na]^+$ calcd 331.0782, found 331.0805.

2-(2,5-Dimethylbenzyl)naphthalene (2a) : General procedure 1 using **1** (98 mg, 0.2 mmol), *p*-xylene (0.2 mL) and HF-pyr (0.1 mL) gave **2** (47 mg, 76%) and **2a** (39 mg, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (m, 3 H), 7.51 (s, 1 H), 7.42 (m, 2 H), 7.29 (d, 1 H, *J* = 8.4 Hz), 7.07 (d, 1 H, *J* = 7.6 Hz), 6.97 (m, 2 H), 4.10 (s, 1 H), 2.28 (s, 1 H), 2.22 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.1, 135.4, 133.6, 133.5, 132.0, 130.8, 130.2, 127.9, 127.6, 127.5, 127.2,

126.8, 125.9, 125.2, 39.6, 21.0, 19.2. HRMS-ESI: *m/z* $[C_{19}H_{18}]^+$ calcd 246.1409, found 246.1430.

2-(Benzyloxy)ethanol (4): General procedure 1 using 2-((2-phenoxyethoxy)methyl)naphthalene **3**[2] (140 mg, 0.50 mmol), toluene (0.5 mL) and HF-pyr (0.13 ml) gave **4** (53 mg, 70%) as colorless oil. Analytical data are in accordance with the literature.[3]

1-*O*-Naphthylmethyl glycerol (5c): General procedure 2 using 1-*O*-naphthylmethyl-2,3-di-*O*-(4-methoxybenzyl) glycerol (94 mg, 0.2 mmol), toluene(0.2 ml), Et_3N (84 uL, 0.60 mmol) and HF-pyr (0.1 mL) gave 1-*O*-naphthylmethyl glycerol (36 mg, 78%) as colorless syrup. Analytical data are in accordance with the literature.[4]

1,2-di-*O*-(4-methoxybenzyl) glycerol (5d): General procedure 3 using 1-*O*-*tert*-butyldiphenylsilyl-2,3-di-*O*-(4-methoxybenzyl) glycerol (57 mg, 0.1 mmol), pyridine (1 mL) and HF-pyr (0.5 mL) gave **5d** (32 mg, 95%) as a colorless syrup. Analytical data are in accordance with the literature.[5]

2,4,6-Tri-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl fluoride (7): General procedure 1 using 2,4,6-tri-*O*-benzoyl-3-*O*-naphthylmethyl-β-D-glucopyranosyl-(1→3)-1,2,4, 6-tetra-*O*-acetyl-D-glucopyranoside **6** (1.2 g, 1.25 mmol), toluene (1.5 ml) and HF-pyr (0.65 mL) gave **7** (712 mg, 73%) as a colorless syrup. $[\alpha]_D^{21}$ = +13.9 (*c* = 1.8, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (m, 4 H), 7.93 (m, 2 H), 7.58 (m, 3 H), 7.43 (m, 6 H), 5.70(dd, 1 H, *J* = 53.5, 2.5 Hz), 5.41 (t, 1 H, *J* = 9.5 Hz), 5.08 (m, 2 H), 4.93 (d, 1 H, *J* =8.0 Hz), 4.78 (m, 1 H), 4.62 (dd, 1 H, *J* = 12.0, 2.5 Hz), 4.48 (dd, 1 H, *J* = 12.0, 5.5 Hz), 4.21 (t, 1 H, *J* = 10.0 Hz), 4.10 (m, 4 H), 3.95(m, 1 H), 2.21(s, 6 H), 1.94(s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$): δ -150.4 (m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.6, 169.5, 169.2, 166.4, 166.1, 166.0, 133.6(2C), 133.4, 129.9, 129.7, 129.4(2C), 129.0, 128.,6, 128.5(3C), 104.6, 102.8, 100.8, 75.4, 74.9, 74.1, 73.0, 72.8, 72.3, 71.9, 70.0, 66.7, 63.2, 61.3, 20.7(2C), 20.5. HRMS-ESI: *m/z* $C_{39}H_{39}O_{16}F$ $[M+Na]^+$ calcd 805.2120, found 805.2111.

Allyl 4-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranside (9a): General procedure 1 using allyl 4-*O*-acetyl- 2-*O*-benzyl-3-*O*-naphthylmethyl-6-*O*-triisopropylsilyl-α-D-glucopyranside **8** (130 mg, 0.2 mmol), toluene (0.2 mL) and HF-pyr (0.1 mL) gave **9a** (46 mg, 65%) as colorless foam. $[\alpha]_D^{21}$ = +54.5 (*c* = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 5 H), 5.90 (m, 1 H), 5.34 (m, 1 H), 5.23 (m, 1 H), 4.82 (m, 1 H), 4.68 (m, 2 H), 4.47 (m, 1 H), 4.21 (dd, 1 H, *J* = 12.0, 2.0 Hz), 4.15 (m, 1 H), 3.85 (m, 2 H), 3.78 (m, 1 H), 3.38 (m, 1 H), 3.07 (brs, 1 H), 2.88 (brs, 1 H), 2.10 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 137.8, 133.5, 133.4, 128.6 (2C), 128.1, 118.2, 95.5, 95.3, 79.0, 72.8, 72.6, 69.9, 69.4, 68.5, 63.2, 20.8. HRMS-ESI: *m/z* $C_{18}H_{24}O_7$ $[M+Na]^+$ calcd 375.1420, found

375.1411.

Allyl 4-*O*-acetyl-2-*O*-benzyl-3-*O*-naphthylmethyl-α-D-glucopyranside (9b): General procedure 2 using allyl 4-*O*-acetyl-2-*O*-benzyl-3-*O*-naphthylmethyl-6-*O*-triisopropylsilyl-α-D-glucopyranside **8** (130 mg, 0.2 mmol), toluene (0.2 mL), Et_3N (84 uL, 0.60 mmol) and HF-pyr (0.1 mL) gave **9b** (91 mg, 93%) as a coloress foam. $[\alpha]_D^{21}$ = +29.2 (*c* = 2.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80–7.28 (m, 12 H), 5.94 (m, 1 H), 5.34 (dd, 1 H, *J* = 17.2.0, 1.6 Hz), 5.24 (dd, 1 H, *J* = 10.4, 1.6 Hz), 5.06 (d, 1 H, *J* = 11.6 Hz), 4.93 (t, 1 H, *J* = 9.6 Hz), 4.85 (m, 2 H), 4.72 (ab, 1 H, *J* = 48.0, 12.0 Hz), 4.05 (m, 2 H), 3.65 (m, 3 H), 3.51 (dd, 1 H, *J* = 12.8, 3.6 Hz), 2.50 (brs, 1 H), 1.90 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 137.8, 136.1, 133.4, 133.2, 132.8, 128.4, 128.1, 128.0, 127.9, 127.8, 127.6, 126.2, 126.0, 125.8, 125.7, 118.4, 95.6, 79.5, 78.8, 75.3, 73.3, 70.6, 69.6, 68.4, 61.0, 20.7. HRMS-ESI: *m/z* $C_{29}H_{32}O_7$ $[M+Na]^+$ calcd 515.2046, found 515.2051.

4-Methoxyphenyl (2,4-di-*O*-benzoyl-α-D-mannopyranosyl)-(1→6)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (10a): General procedure 1 using 4-methoxyphenyl 2,4-di-*O*-benzoyl-3-*O*-naphthylmethyl-6-*O*-triisopropylsilyl-α-D-mannopyranosyl-(1→6)-2,4-di-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-α-D-mannopyranoside **10** (515 mg, 0.40 mmol), toluene (0.8 mL) and HF-pyr (0.4 mL) gave **10a** (309 mg, 89%) as a colorless foam. $[\alpha]_D^{21}$ = - 27.9 (*c* = 1.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.20–7.97 (m, 8 H), 7.65–7.35 (m, 12 H), 7.10 (m, 2 H), 6.86 (m, 2 H), 5.75 (t, 1 H, *J* = 10.0 Hz), 5.68–5.56 (m, 2 H), 5.46 (t, 1 H, *J* = 10.0 Hz), 5.40 (m, 1 H), 5.05 (s, 1 H), 4.60 (m, 1 H), 4.46 (m, 1 H), 4.33 (dd, 1 H, *J* = 10.0, 2.8 Hz), 3.96 (dd, 1 H, *J* = 10.8, 4.4 Hz), 3.82–3.63 (m, 5 H), 3.43 (m, 2 H), 2.69 (brs, 1 H), 2.52 (brs, 1 H), 2.32 (brs, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 166.8, 165.9(2C), 155.3, 149.9, 133.8, 133.7, 133.5, 130.0, 129.9, 129.8, 129.2, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 117.8, 114.7, 97.5, 96.5, 72.7, 70.5, 70.0, 69.9, 69.6, 69.0, 68.5, 66.2, 60.9, 55.5. HRMS-ESI: *m/z* $C_{47}H_{44}O_{16}$ $[M+Na]^+$ calcd 887.2527, found 887.2549.

4-Methoxyphenyl (2,4-di-*O*-benzoyl-3-*O*-naphthylmethyl-α-D-mannopyranosyl)-(1→6)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (10b): General procedure 2 using **10** (255 mg, 0.20 mmol), toluene (0.5 mL), HF-pyr (0.15 mL) and Et_3N (0.6 mmol, 85 μL) gave **10b** (153 mg, 77.2%) as white foam. *Rf* 0.15 (Hexanes/EtOAc = 2:1); $[\alpha]_D^{21}$ = – 11.9 (*c* = 0.9, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 - 7.97 (m, 8H), 7.61 – 7.37 (m, 22H), 7.16 (d, 2H, *J* = 9.2 Hz), 6.90 (d, 2H, *J* = 9.4 Hz), 5.85 (t, 2H, *J* = 10 Hz), 5.75 (m, 2H). 5.57 (t, 1H, *J* = 10 Hz), 4.85 (d, 1H, *J* = 12 Hz), 4.66 (m, 1H), 4.63 (d, 1H, *J* = 12 Hz), 4.40 (dd, 1H, *J* = 4.36, 10 Hz), 4.36 (dd, 1H, *J* = 3.2, 9.6 Hz), 4.04 (dd, 1H, *J* = 4.4, 11.2 Hz), 3.73 (m, 5H), 3.69 (m, 1H), 3.38 (m, 1H), 2.70 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 55.5, 68.2, 68.7, 69.0, 69.5, 69.8, 71.0, 71.8, 72.7, 75.2, 96.5, 97.9, 117.6, 125.6 (2), 125.8, 126.3, 127.4, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.9, 129.1, 129.2,

129.8 (3), 129.9, 132.8, 133.3, 133.4, 133.7, 135.0, 155.3, 165.5, 165.9, 166.6, 166.7 (4 × O*C*OPh). HRMS-ESI (*m/z*): $[M + Na]^+$ Calcd for $C_{58}H_{52}O_{16}Na$, 1027.3153; Found, 1027.3192.

4-Methoxyphenyl 2,4-di-*O*-benzoyl-3-*O*-naphthylmethyl-6-*O*-triisopropylsilyl α-D-mannopyranosyl- (1→6)-2,4-di-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (10c): General procedure 3 using **10** (71 mg, 0.055 mmol), pyridine (0.2 mL) and HF-Pyr (0.1 mL) gave **10c** (61mg, 99%) as a colorless foam. $[\alpha]_D^{21}$ = – 40.1 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21–7.93 (m, 8 H), 7.56–7.10 (m, 23 H), 6.85 (m, 2 H), 6.63 (m, 2 H), 5.90 (t, 1 H, *J* = 10.0 Hz), 5.85 (m, 1 H), 5.75 (m, 1 H), 5.66 (d, 1 H, *J* = 1.0 Hz), 5.55 (t, 1 H, *J* = 9.5 Hz), 5.08 (d, 1 H, *J* = 1.5 Hz), 4.79 (d, 1 H, *J* = 12.0 Hz), 4.69 (d, 1 H, *J* = 12.5 Hz), 4.54 (m, 2 H), 4.38 (dd, 1 H, *J* = 10.0, 3.5 Hz), 4.31(dd, 1 H, *J* = 10.0, 3.5 Hz), 4.27 (m, 1 H), 3.92 (dd, 1 H, *J* = 11.0, 4.5 Hz), 3.74 (m, 1 H), 3.72 (s, 3 H), 3.66 (s, 3 H), 3.65 (m, 1 H), 3.46 (m, 2 H), 2.61 (brs, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 165.8, 165.6, 165.4, 159.2, 135.1, 133.5, 133.4, 133.3(2C), 133.1, 132.8, 130.0, 129.8, 129.6, 129.5(3C), 129.4, 128.6, 128.4(2C), 127.9, 127.8, 127.4, 126.3, 125.7, 125.6, 117.8, 114.7, 113.7, 97.9, 97.2, 75.4, 73.8, 71.9, 71.1, 70.8, 69.9, 68.9, 68.7, 68.5, 67.8, 66.3, 61.1, 61.1, 55.5, 55.1. HRMS-ESI: *m/z* $C_{66}H_{60}O_{17}$ $[M+Na]^+$ calcd 1147.3728, found 1147.3724.

4-Methoxyphenyl 2,4-di-*O*-benzoyl-6-*O*-triisopropylsilyl α-D-mannopyranosyl-(1→6)-2,4-di-*O*- benzoyl-α-D-mannopyranoside (10d): To a solution of **10a** (132 mg, 0.15 mmol) in dry CH_2Cl_2 (2 mL) was added imidazole (31 mg, 0.45 mmol) and TIPSCl (48 uL, 0.23 mmol) at room temperature. The mixture was stirred overnight, then diluted with CH_2Cl_2, washed with aqueous $NaHCO_3$ and brine, separated, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel to give **10d** (120 mg, 80%) as a colorless foam. $[\alpha]_D^{21}$ = +28.6 (*c* = 1.6, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19–8.02 (m, 8 H), 7.64–7.35 (m, 12 H), 7.11 (m, 2 H), 6.85 (m, 2 H), 5.72 (t, 1 H, *J* = 10.0 Hz), 5.69–5.60 (m, 3 H), 5.37 (m, 2 H), 5.01 (d, 1 H, *J* = 1.5 Hz), 4.60 (m, 1 H), 4.37 (m, 2 H), 4.00 (dd, 1 H, *J* = 10.5, 5.0 Hz), 3.90 (m, 1 H), 3.70–3.53 (m, 6 H), 2.65 (m, 2 H), 0.88 (m, 21 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.1, 166.9, 165.9, 165.8, 155.4, 150.0, 133.7, 133.4, 130.0, 129.9(2C), 129.8(2C), 129.6, 129.4, 129.2, 129.1, 128.7, 128.6, 128.5, 128.4(2C), 117.9, 114.8, 114.7, 97.2, 96.6, 72.9, 72.8, 71.1, 70.1(2C), 69.8, 69.4, 69.2, 65.9, 62.1, 55.5, 17.8(2C), 11.8. HRMS-ESI: *m/z* $C_{56}H_{64}O_{16}Si$ $[M+Na]^+$ calcd 1043.3861, found 1043.3826.

4-Methoxyphenyl (2,4-di-*O*-benzoyl-3-*O*-naphthylmethyl-6-*O*-triisopropylsilyl α-D-mannopyranosyl)- (1→6)-2,4-di-*O*-benzoyl-α-D-mannopyranoside (10e): To a solution of **10b** (30 mg, 29.4 μmol) in dry CH_2Cl_2 (1 mL) was added imidazole (6 mg, 88 μmol) and TIPSCl (9 uL, 44 μmol) at room temperature. The mixture was stirred overnight, then diluted with CH_2Cl_2,

washed with aqueous $NaHCO_3$ and brine, separated, dried with Na_2SO_4, and filtered. The solvent was removed under vacuum. The residue was purified by flash chromatography on silica gel to give **10e** (28 mg, 82%) as a colorless foam. *Rf* 0.75 (Hexanes/EtOAc = 2:1); $[\alpha]_D^{21}$ = -5.0 (*c* = 0.15, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21-7.97 (m, 8H), 7.59-7.33 (m, 21H), 7.16 (d, 2H, *J* = 9 Hz), 6.89 (d, 2H, *J* = 9 Hz), 5.72 (m, 4H), 5.65 (dd, 1H, *J* = 1.5, 3.5 Hz), 5.07 (bs, 1H), 4.79 (d, 1H, *J* = 12 Hz), 4.63 (m, 1H), 4.50 (d, 1H, *J* = 12 Hz), 4.39 (m, 1H) 4.22 (dd, 1H, *J* = 3.5, 10 Hz), 4.04 (dd, 1H, *J* = 5, 11 Hz), 3.85 (m, 1H), 3.72 – 3.60 (m, 5H), 2.55 (d, 1H, *J* = 8 Hz), 1.28 (s, 3H), 0.92 (m, 18H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 11.8, 17.8, 29.7, 55.4, 62.7, 65.8, 68.1, 68.9, 69.2, 69.8, 70.0, 71.6, 72.0, 72.9, 76.0, 96.6, 97.6, 114.7, 117.7, 125.5 (2), 125.6, 126.1, 127.5, 127.8 (2), 128.3 (2), 128.6, 128.7, 129.1, 129.2, 129.7, 129.9 (2), 130.0 (2), 132.7, 133.0, 133.1, 133.2, 133.6, 133.7, 135.2, 150.1, 155.3, 165.3, 165.7, 166.0, 166.8 (4 × O*C*OPh). HRMS-ESI (*m/z*): $[M + Na]^+$ Calcd for $C_{67}H_{76}NO_{16}Si$, 1178.4933; Found, 1178.7112.

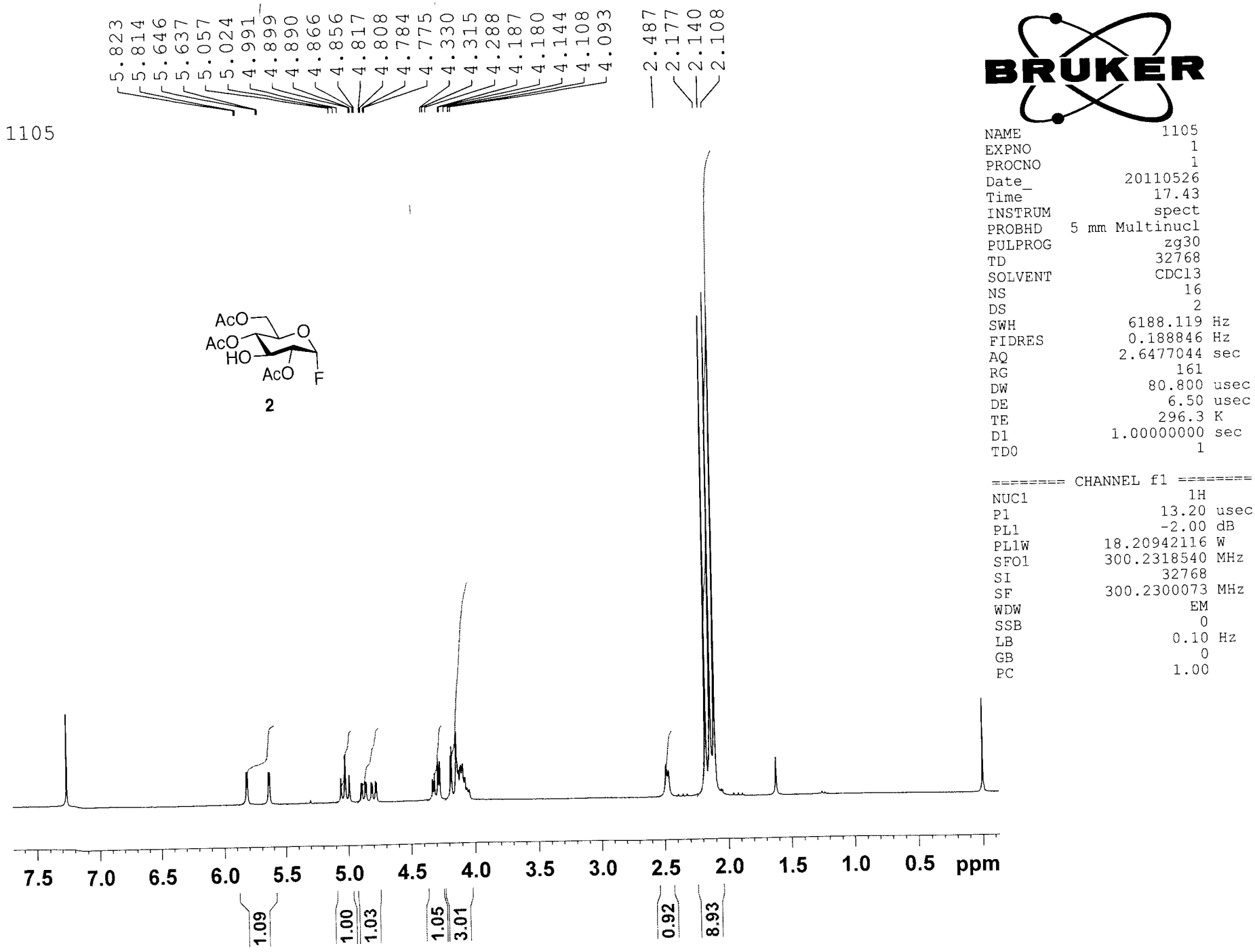
4-Methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzoyl-3-*O*-naphthylmethyl-α-D-mannopyranosyl)-(1→6)-2,4-di-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-α-D-mannopyranoside (13): To a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl trichloroacetimidate **11** (21 mg, 0.032 mmol), dimannoside **10c** (28 mg, 0.025 mmol) and 4Å MS (50 mg) in dry CH_2Cl_2 at 0 ºC was added TBSOTf (0.6 uL, 0.01 mmol) in DCM (0.2 mL) slowly. The mixture was then stirred at 0 ºC for 20 min, quenched with the addtion of Et_3N, diluted with CH_2Cl_2, washed with brine, dried with Na_2SO_4 and concentrated *in vacuo*. Purification by flash column chromatography provided **13** (36 mg, 91%) as a colorless syrup. $[\alpha]_D^{21}$ = + 18.9 (*c* = 2.7, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 8.21–7.90 (m, 8 H), 7.47–7.05 (m, 38 H), 6.86 (m, 2 H), 6.63 (m, 2 H), 5.94 (t, 1 H, *J* = 10.0 Hz), 5.85 (t, 1 H, *J* = 2.8 Hz), 5.77–5.64 (m, 3 H), 5.21(m, 1 H), 5.03 (s, 1 H), 4.80–4.18 (m, 14 H), 3.90–3.76 (m, 4 H), 3.74–3.55 (m, 10 H), 3.43(m, 1 H), 3.32 (dd, 1 H, *J* = 10.8, 2.4 Hz), 2.07 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 170.2, 165.3, 159.2, 150.0 138.7, 138.2, 138.1, 135.1, 133.5, 133.4, 133.3, 133.1(2C), 132.8, 130.0(2C), 129.9, 129.7(2C), 129.6(2C), 128.6, 128.5, 128.4, 128.3(2C), 128.2(2C), 128.0(2C), 127.8(2C), 127.7, 127.6, 127.5(2C), 127.4, 126.4, 125.7, 125.6, 125.5, 117.8, 114.7, 113.7, 97.8, 78.3, 77.2, 74.9, 74.0, 73.2, 71.9, 71.7, 71.3, 70.8, 68.7, 68.5, 55.5, 55.2, 21.1. HRMS-ESI: *m/z* $C_{95}H_{90}O_{23}$ $[M+Na]^+$ calcd 1621.5771, found 1621.5800.

4-Methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-(2,4-di-*O*-benzoyl-3-*O*-(2-methylnapthyl)-α-D-mannopyranosyl)-(1→6)-2,4-di-*O*-benzoyl-3-*O*-(*4*-methoxybenzyl)-α-D-mannopyranoside (14): A mixture of **10c** (28 mg, 0.024 mmol), dimmanoside **12** [7] (38 mg, 0.037 mmol) and activated MS 4Å (15 mg) in dry CH_2Cl_2 (5 ml) was stirred under nitrogen atmosphere for 15 min. After cooling in ice-water

bath, NIS (12 mg, 0.055 mmol) was added followed by TMSOTf (1.8 μL, 0.001 mmol) and the mixture was stirred for 45 min when TLC (n-hexane–EtOAc, 2:1) showed complete conversion of the acceptor spot. The mixture was filtered through Celite® and washed with CH_2Cl_2 (2 × 5 ml) the filtrate was diluted with CH_2Cl_2 (10 ml) and washed successively with aq. $Na_2S_2O_3$ (2 × 15 ml), aq. $NaHCO_3$ (2 × 15 ml) and brine (15 ml). Organic layer was separated, dried (Na_2SO_4) and evaporated to syrup. The crude product was purified by flash chromatography to afford pure tetrasaccharide **14** (31 mg, 61.3%) as colorless liquid. R_f 0.72 (Hexanes/EtOAc = 2:1); $[\alpha]_D^{21}$ = +24.6 (*c* = 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 - 7.94 (m, 8H), 7.66 - 7.10 (m, 66H), 6.88 (d, 2H, *J* = 9.5 Hz), 6.67 (d, 2H, *J* = 9.5 Hz), 5.95 (t, 1H, *J* = 10 Hz), 5.87 (dd, 1H, *J* = 2, 3.5 Hz), 5.77 (d, 1H, *J* = 11 Hz), 5.73 (dd, 1H, *J* = 3, 5 Hz), 5.68 (bs, 1H), 5.50 (dd, 1H, *J* = 2, 3 Hz), 5.04 (d, 1H, *J* = 1.5 Hz), 4.60 (bs, 1H), 4.55 – 4.47 (m, 5H), 4.44 - 4.37 (m, 4H), 4.35 - 4.27 (m, 6H), 3.93 - 3.8 (m, 5H), 3.76 (s, 3H), 3.74 - 3.67 (m, 4H), 3.65 (s, 3H), 3.64 - 3.54 (m, 4H), 2.11 (s, 3H, COC*H*$_3$); ^{13}C NMR (600 MHz, $CDCl_3$) δ 21.1, 55.1, 55.5, 66.1, 66.2, 67.7, 68.2, 68.6, 68.8, 69.0, 69.4, 70.1, 70.7, 71.7, 71.7, 73.0, 73.2, 73.7, 74.1, 74.3, 74.8, 74.9, 74.9, 75.7, 78.1, 79.7, 97.3, 98.0, 98.7, 99.4, 113.7, 114.7, 117.8, 125.4, 125.6, 125.6, 126.3, 127.0, 127.2, 127.2, 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9 (2), 128.1, 128.2 (4), 128.3, 128.4, 128.5, 128.6, 129.5, 129.7 (2), 129.8, 129.9 (2), 132.7, 133.0, 133.1, 133.2, 133.3, 133.5, 135.1, 138.0, 138.2, 138.4, 138.6, 138.7, 150.0, 155.3, 159.2, 165.2, 165.3, 165.6, 165.8 (4 × O*C*OPh), 170.0 (O*C*OAc). HRMS-ESI (*m*/*z*): $[M + Na]^+$ Calcd for $C_{122}H_{118}O_{28}$, 2053.7707; Found 2053.7642.

References:

1. Xia, J.; Abbas, S. A.; Locke, R. D.; Piskorz, C. F.; Alderfer, J. L.; Matta, K. L.*Tetrahedron Lett*. **1999**, *41*, 169.
2. Gaunt, M. J.; Yu, J.; Spencer, J. B. *J. Org. Chem*. **1998**, *63*, 4172.
3. Wright, J. A.; Yu, J.; Spencer, J. B. *Tetrahedron Lett*. **2001**, *42*, 4033.
4. Miyashita, K.; Miyabe, H.; Tai, K.; Kurozumi, C.; Iwaki, H.; Imanishi, T. *Tetrahedron*, **1999**, *55*, 12109.
5. Kaluza, Z.; Furman, B.; Krajewski, P.; Chmielewski, M. *Tetrahedron*, **2000**, *56*, 5553.
6. Blattner, R.; Furneaux, R. H.; Ludewig, M. *Carbohydr Res*. **2006**, *341*, 299.
7. Teumelsan, N; Huang, X., *J. Org. Chem*. **2007**, *72*, 8976-8979.



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TD	32768
SOLVENT	CDCl3
NS	16
DS	2
SWH	6188.119 Hz
FIDRES	0.188846 Hz
AQ	2.6477044 sec
RG	161
DW	80.800 usec
DE	6.50 usec
TE	296.3 K
D1	1.00000000 sec
TD0	1

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P1	13.20 usec
PL1	-2.00 dB
PL1W	18.20942116 W
SFO1	300.2318540 MHz
SI	32768
SF	300.2300073 MHz
WDW	EM
SSB	0
LB	0.10 Hz
GB	0
PC	1.00

1105C

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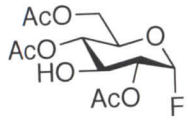
69.86
69.50
69.25
61.48
20.56



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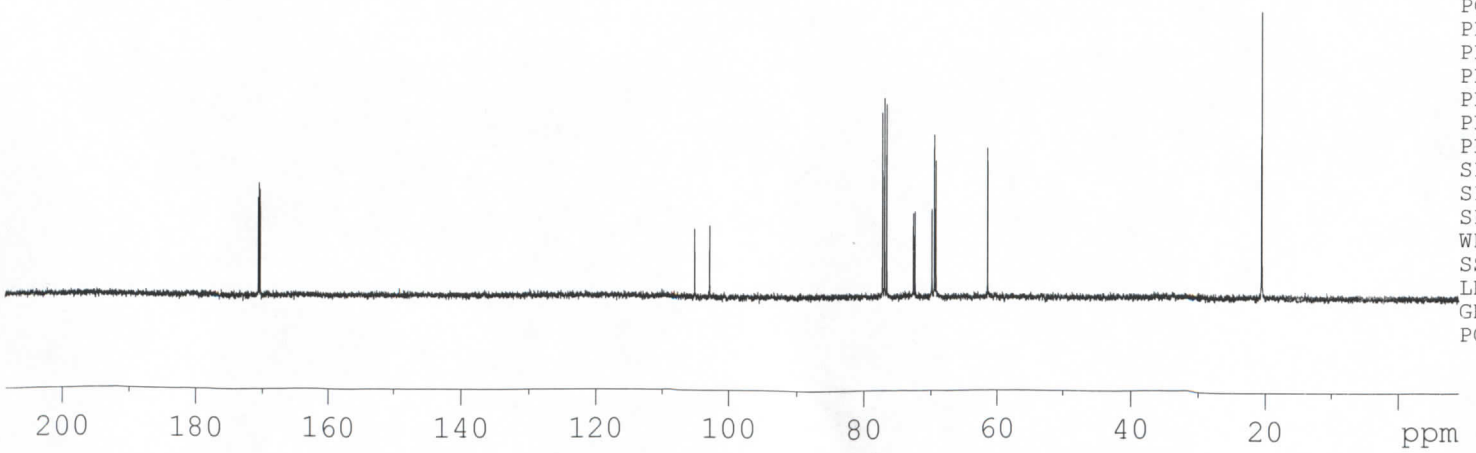

BRUKER

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SOLVENT	CDCl3
NS	37
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FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	40.3
DW	20.800 usec
DE	6.50 usec
TE	296.5 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
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NUC1	13C
P1	10.00 usec
PL1	-0.44 dB
PL1W	39.19395828 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-3.90 dB
PL12	14.22 dB
PL13	22.00 dB
PL2W	23.43061066 W
PL12W	0.36122981 W
PL13W	0.06022594 W
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SI	32768
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WDW	EM
SSB	0
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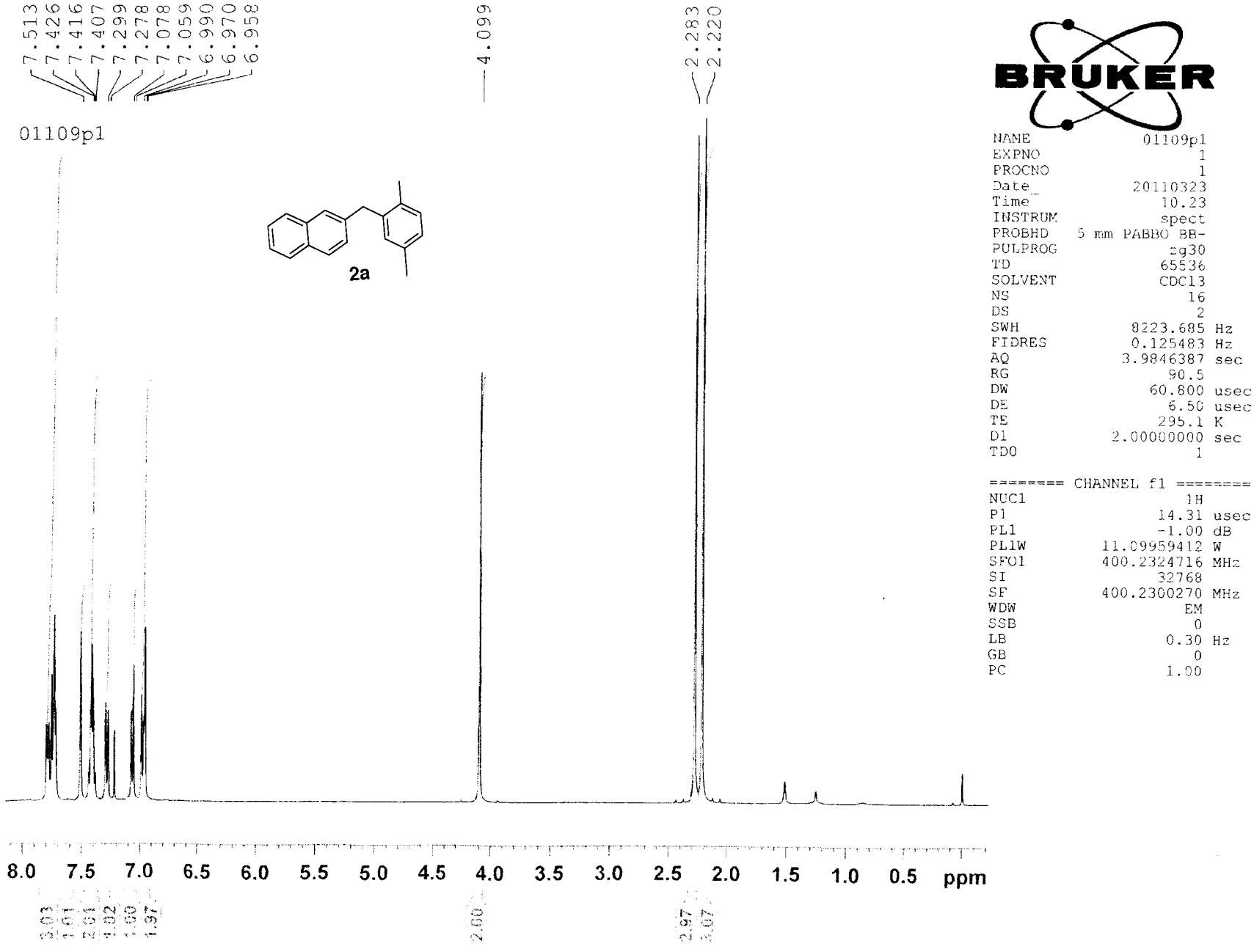
GB	0
PC	1.40



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PROCNO	1
Date_	20110323
Time	10.23
INSTRUM	spect
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PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	90.5
DW	60.800 usec
DE	6.50 usec
TE	295.1 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.31 usec
PL1	-1.00 dB
PL1W	11.09959412 W
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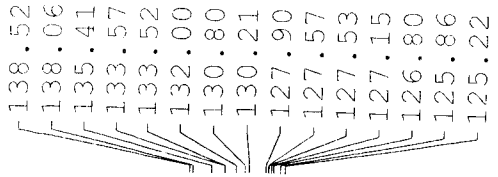
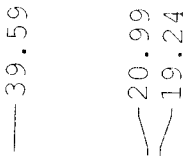
SSB	0
LB	0.30 Hz
GB	0
PC	1.00





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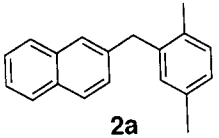

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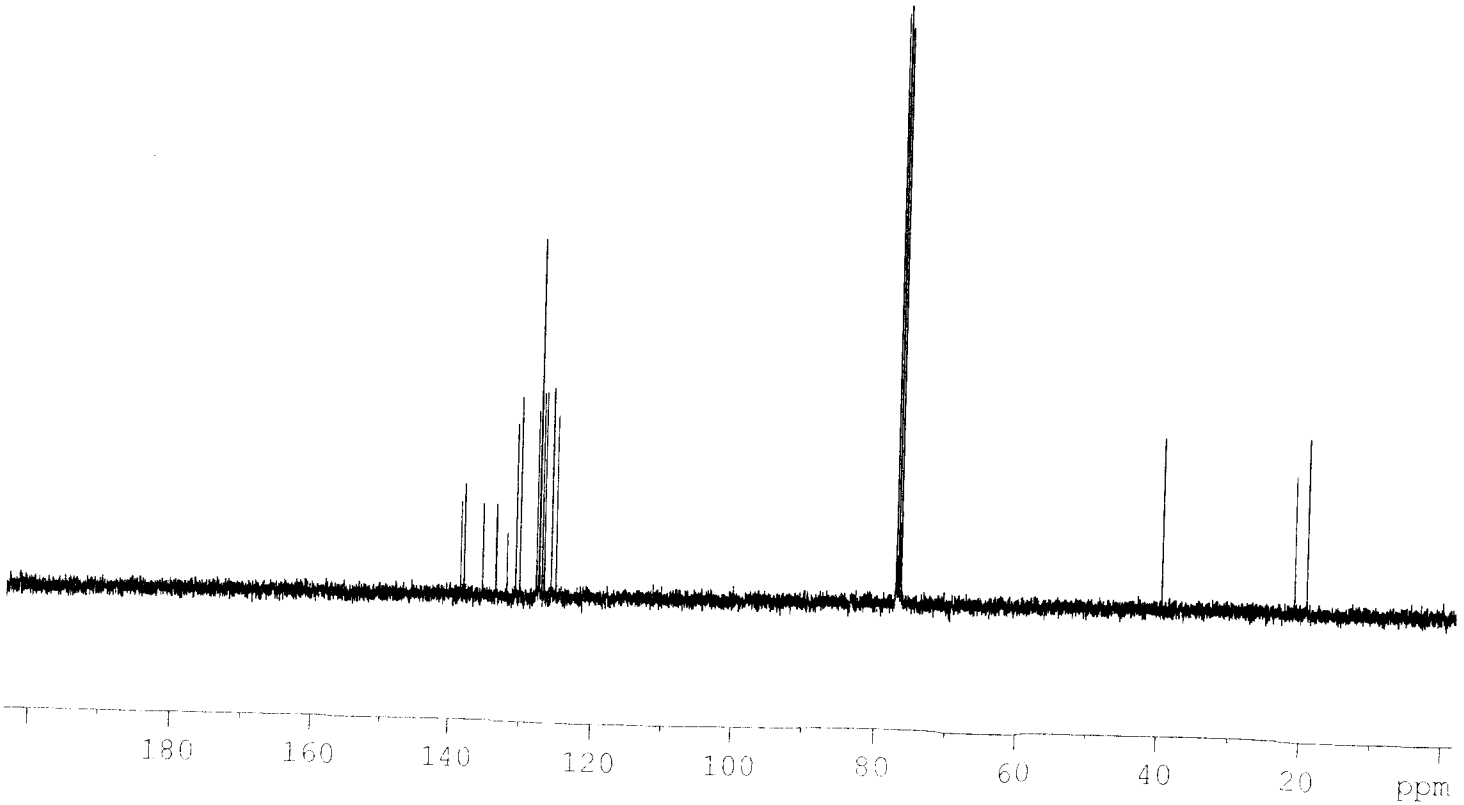

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PROCNO	1
Date_	20110323
Time	10.38
INSTRUM	spect
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PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	56
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.3 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1

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

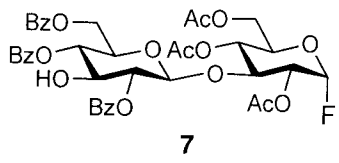
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz

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

CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379207 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

0164p

8.043 7.930 7.614 7.580 7.467 7.419 5.766 5.761 5.659 5.654 5.423 5.405 5.385 5.112 5.093 5.067 5.048 4.943 4.928 4.803 4.798 4.775 4.755 4.637 4.631 4.613 4.607 4.507 4.496 4.483 4.472 4.229 4.210 4.190 4.145 4.137 4.112 4.087 4.069 4.067 3.963 3.943 2.071 1.942



7

Current Data Parameters
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EXPNO 1
PROCNO 1

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PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 161
DW 48.400 usec
DE 6.50 usec
TE 294.1 K
D1 1.00000000 sec

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F2 - Processing parameters
SI 65536
SF 500.1600123 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

0164pc

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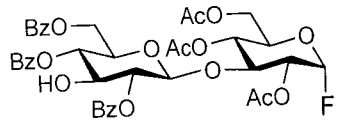

7

BRUKER

Current Data Parameters
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EXPNO 1
PROCNO 1

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Time 11.50
INSTRUM spect
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PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1980
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 203
DW 16.800 usec
DE 6.50 usec
TE 295.1 K
D1 2.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 8.80 usec
PLW1 112.58000183 W
SFO1 125.7779080 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 18.74300003 W
PLW12 0.36736000 W
PLW13 0.18408000 W
SFO2 500.1620006 MHz

F2 - Processing parameters
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SSB 0
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GB 0
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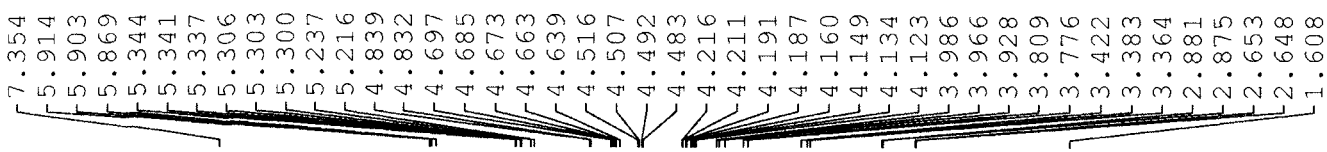
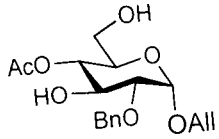
01101p





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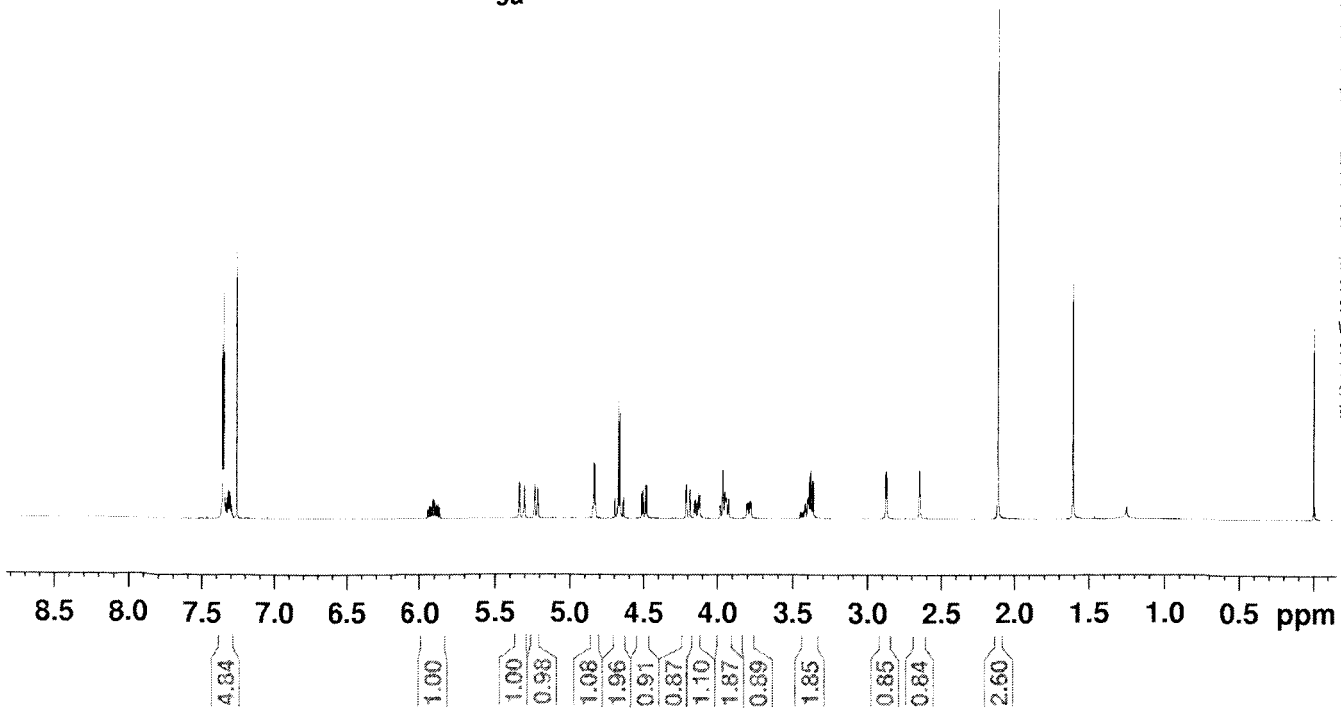


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EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
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INSTRUM               spect
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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                 3.1719923 sec
RG                      161
DW                 48.400 usec
DE                  6.50 usec
TE                 294.2 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.20 usec
PLW1          18.74300003 W
SFO1          500.1630887 MHz

F2 - Processing parameters
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SF            500.1600121 MHz
WDW                      EM
SSB       0
LB                     0.30 Hz
GB        0
PC                     1.00
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01101p

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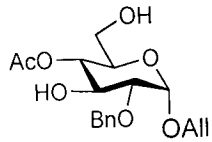
68.49
63.19
20.83



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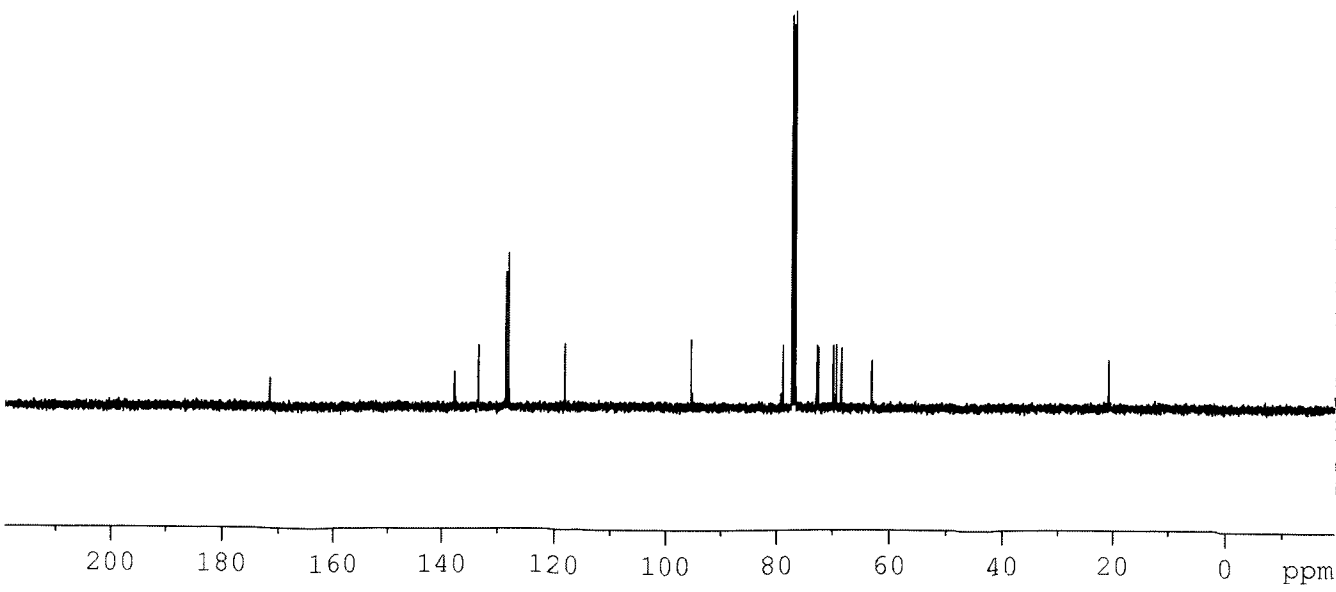

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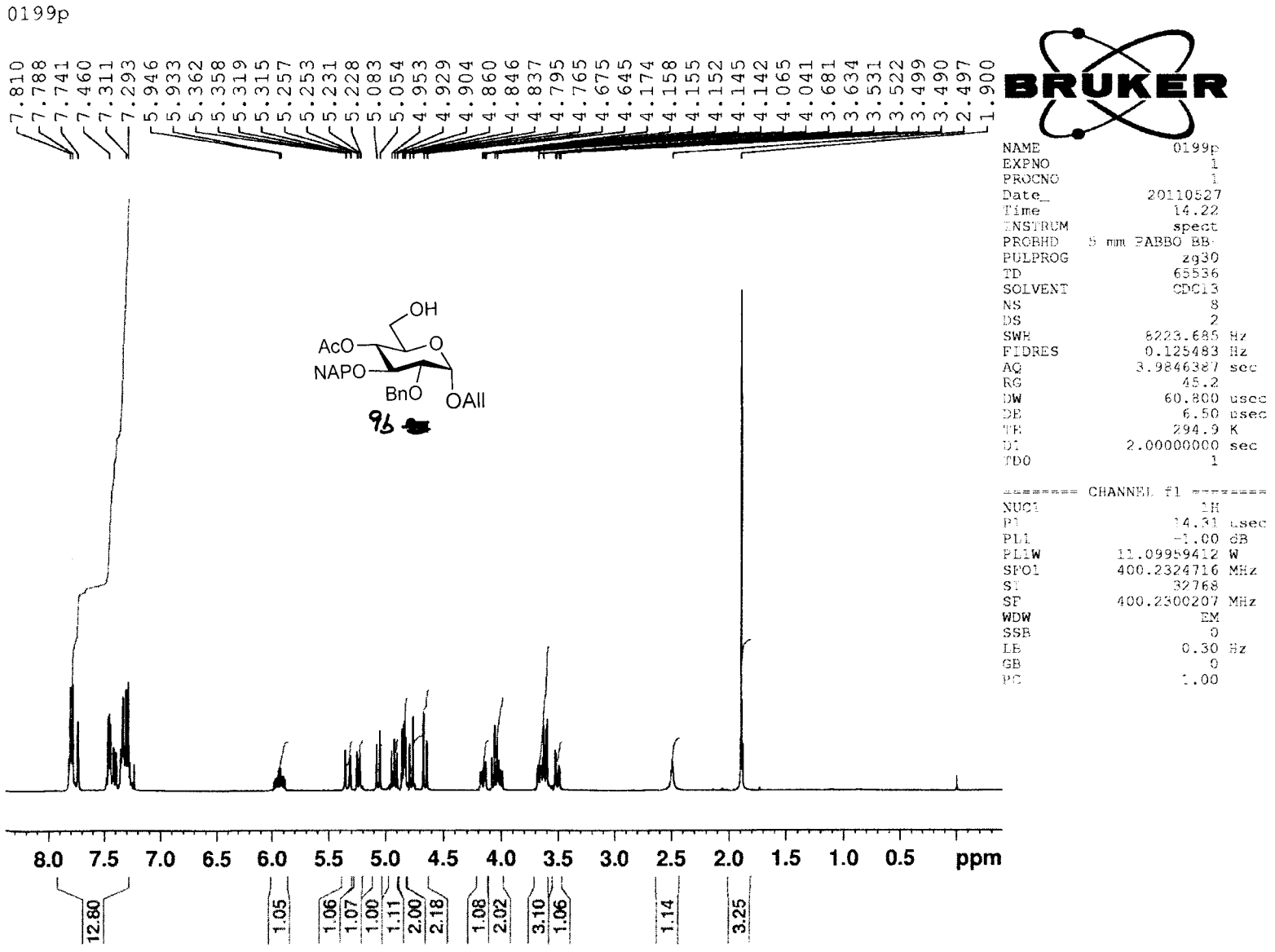
SOLVENT	CDCl3
NS	108
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.4 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08916721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379197 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



BRUKER

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PROCNO	1
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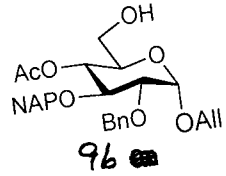
Time	14.22
INSTRUM	spect
PROBHD	5 mm PABBO BB
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	45.2
DW	60.800 usec
DE	6.50 usec
TE	294.9 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.31 usec
PL1	-1.00 dB
PL1W	11.09959412 W
SFO1	400.2324716 MHz
SI	32768
SF	400.2300207 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

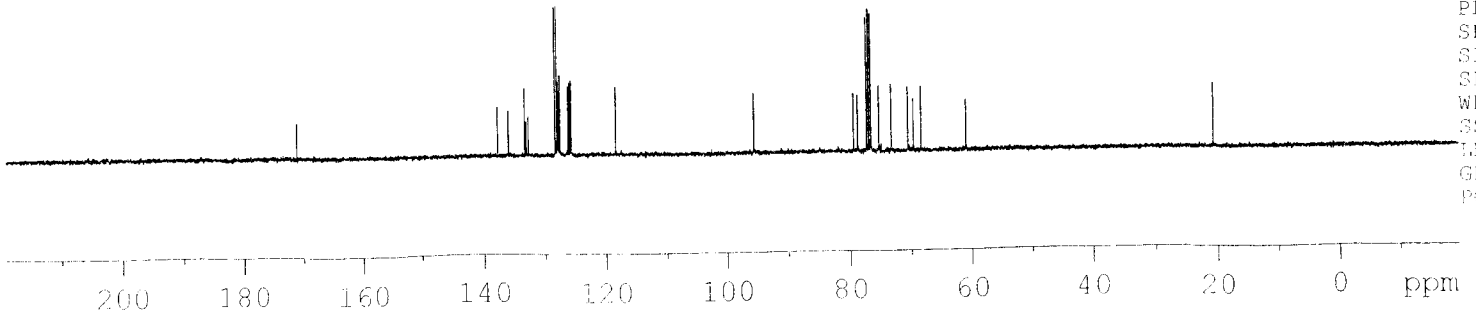
0199p

171.16
137.83
136.07
133.43
133.18
132.81
128.39
128.05
127.95
127.90
127.81
127.56
126.19
126.01
125.77
125.73
118.40
95.61
79.45
78.78
75.30
73.26
70.55
69.64
68.39
61.01

20.73

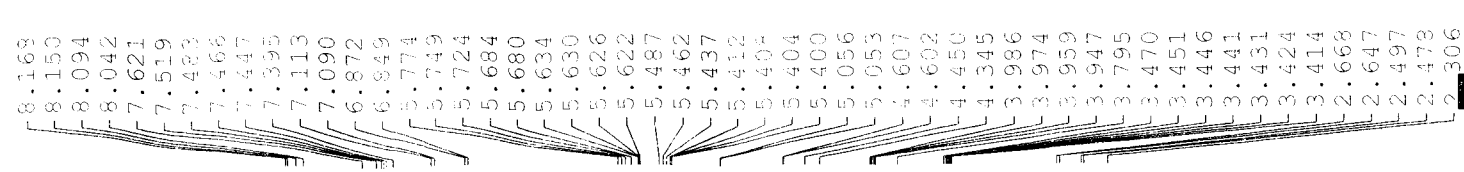


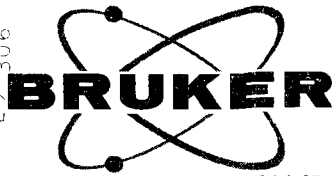
96



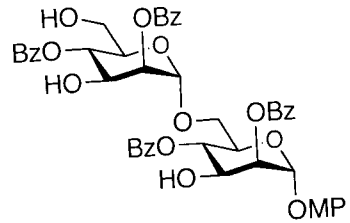
BRUKER

NAME	0199p
EXPNO	2
PROCNO	1
Date_	20110315
Time	14.31
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	40
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.5 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379278 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40





01167

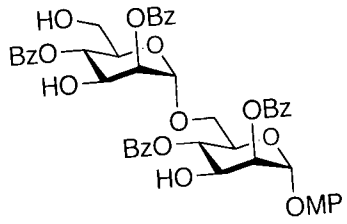


10a

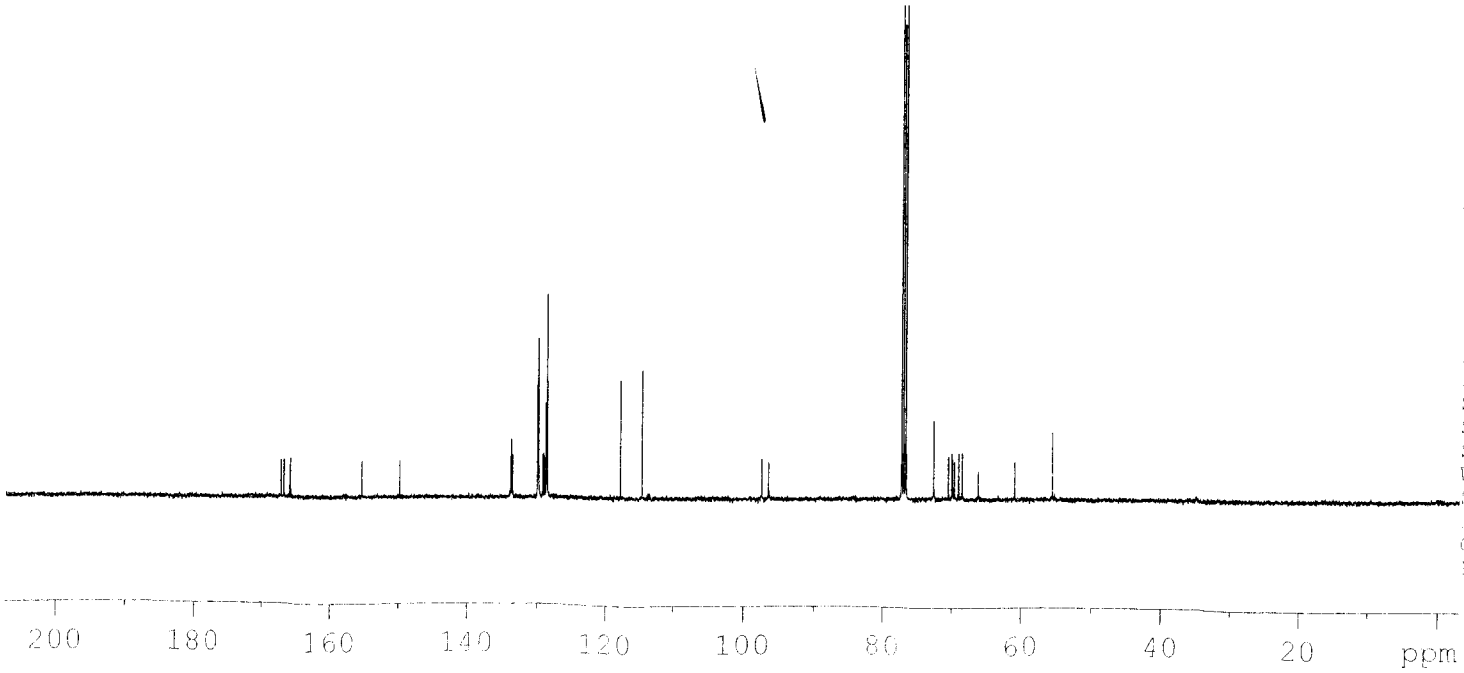
NAME	01167
EXPNO	1
PROCNO	1
Date_	20110518
Time	17.02
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	12
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	90.5
DW	60.800 usec
DE	6.50 usec
TE	295.0 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.31 usec
PL1	-1.00 dB
PL1W	11.09959412 W
SFO1	400.2324716 MHz
SI	32768
SF	400.2300135 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

167.29
166.83
165.92
165.86
155.34
149.85
133.78
133.72
133.54
129.97
129.87
129.82
129.17
129.12
129.02
128.94
128.70
128.58
128.54
117.83
114.67
97.45
96.52
72.67
70.54
70.04
69.90
69.63
69.01
68.52
66.15
60.92
55.54

01166p



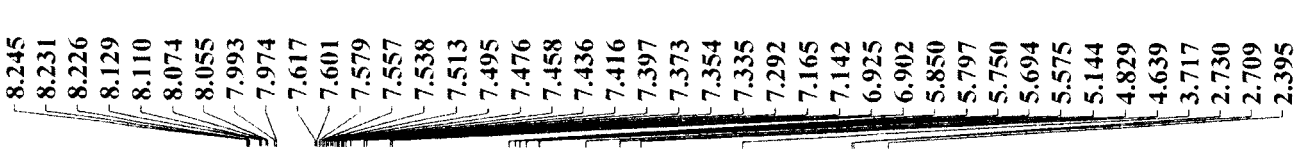
10a

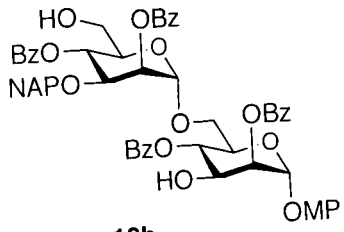


BRUKER

NAME	01166p
EXPNO	2
PROCNO	1
Date_	20110511
Time	14.56
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	452
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.3 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379211 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

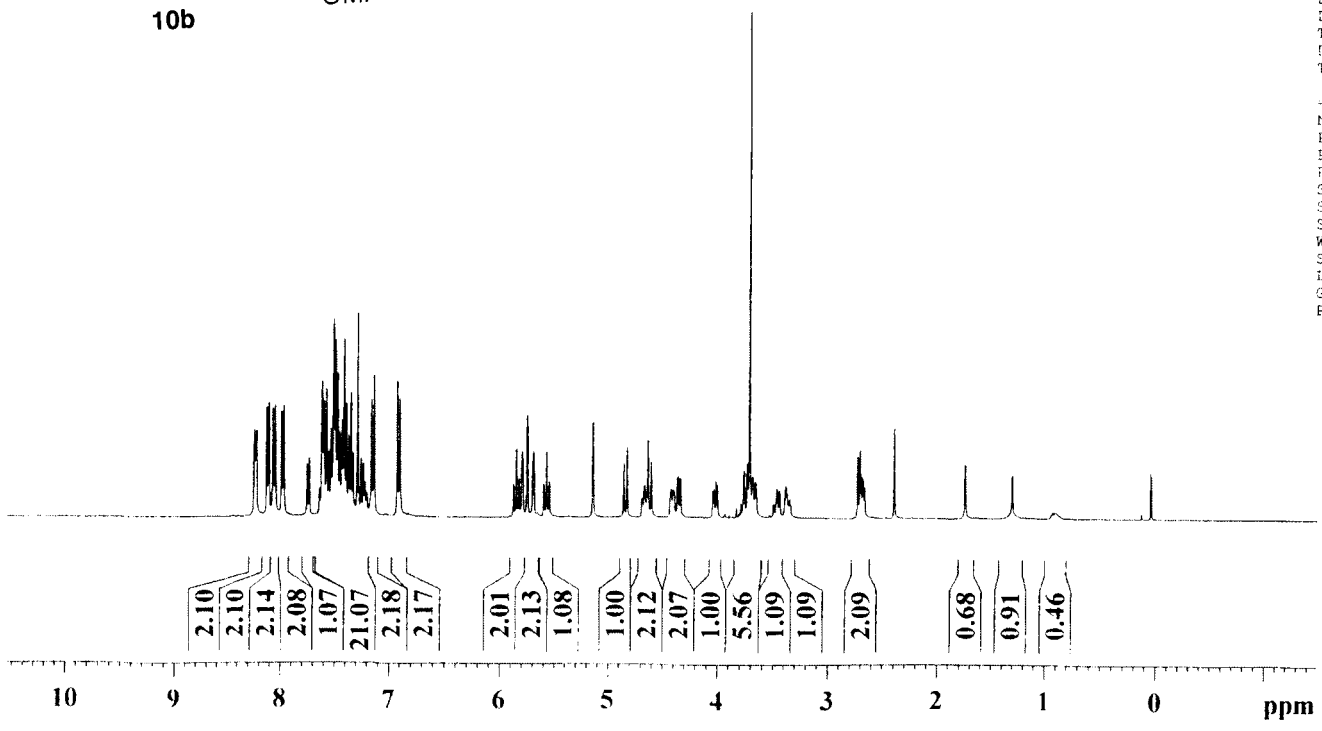
BR-85





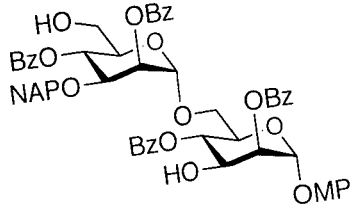
10b

```
NAME                BR-85
EXPNO                   1
PROCNO                  1
Date_            20110510
Time                15.14
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              9223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                     64
DW                60.800 usec
DE                 6.50 usec
TE                295.0 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.31 usec
PL1                -1.00 dB
PL1W        11.09959412 W
SFO1        400.2324716 MHz
SI                  32768
SF          400.2300000 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



BR-85

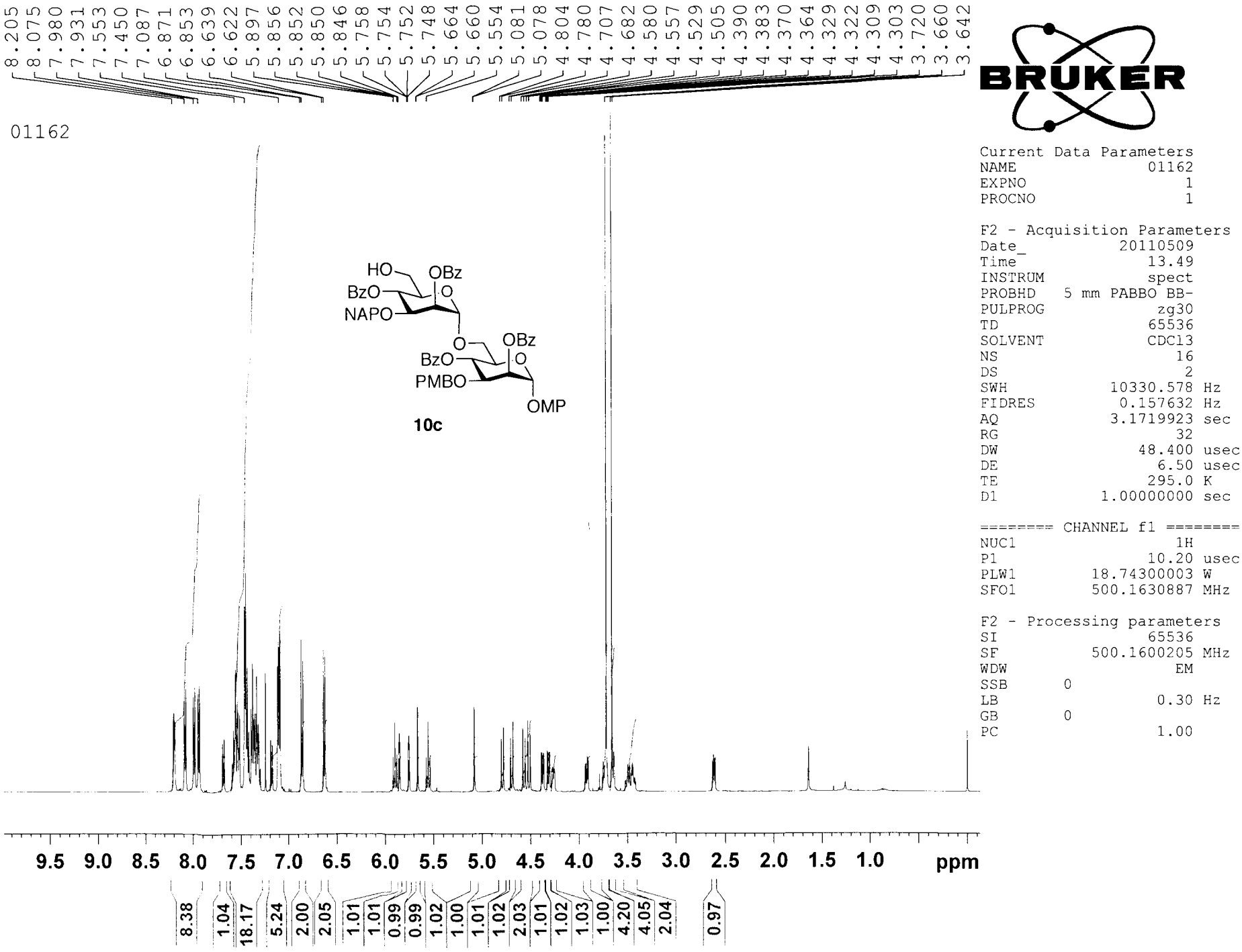
166.76 166.68 155.33 135.03 133.73 133.48 133.30 132.80 129.96 129.89 129.85 129.83 129.24 129.11 128.94 128.66 128.53 128.44 128.39 127.92 127.85 127.48 126.37 125.80 125.67 125.63 117.66 114.69 97.93 96.59 75.28 72.79 71.89 71.07 69.89 69.52 69.09 68.73 68.29 55.50



10b

BRUKER

DATA	BR-85
EXPNO	1
PROCNO	1
SOLVENT	CDCl3
NS	512
SWH	24038.46 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.1 K
D1	3.00000000 sec
D11	0.03000000 sec
TD	1
======== CHANNEL f1 ========	
NUC1	13C
P1	16.00 usec
PL1	-1.00 dB
PL1W	91.07763672 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	95.00 usec
PL2	-1.00 dB
PL12	17.49 dB
PL13	20.00 dB
PL2W	11.09950256 W
PL12W	0.10337070 W
PL13W	0.05616211 W
SFO2	400.1316005 MHz
SI	32768
SF	150.6378021 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.00



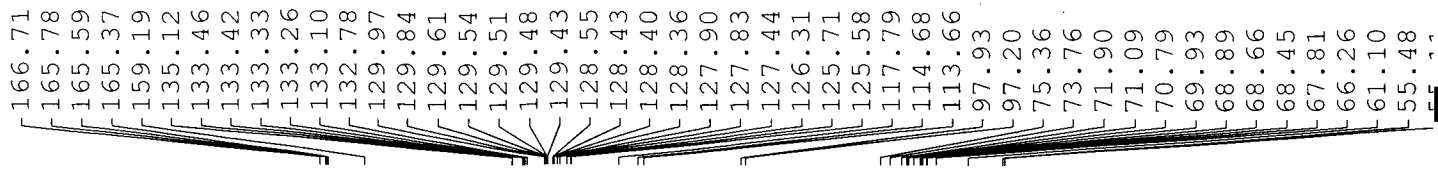
BRUKER

Current Data Parameters
NAME 01162
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20110509
Time 13.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 32
DW 48.400 usec
DE 6.50 usec
TE 295.0 K
D1 1.00000000 sec

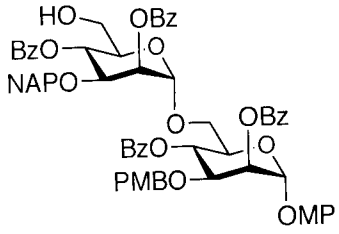
======== CHANNEL f1 ========
NUC1 1H
P1 10.20 usec
PLW1 18.74300003 W
SFO1 500.1630887 MHz

F2 - Processing parameters
SI 65536
SF 500.1600205 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

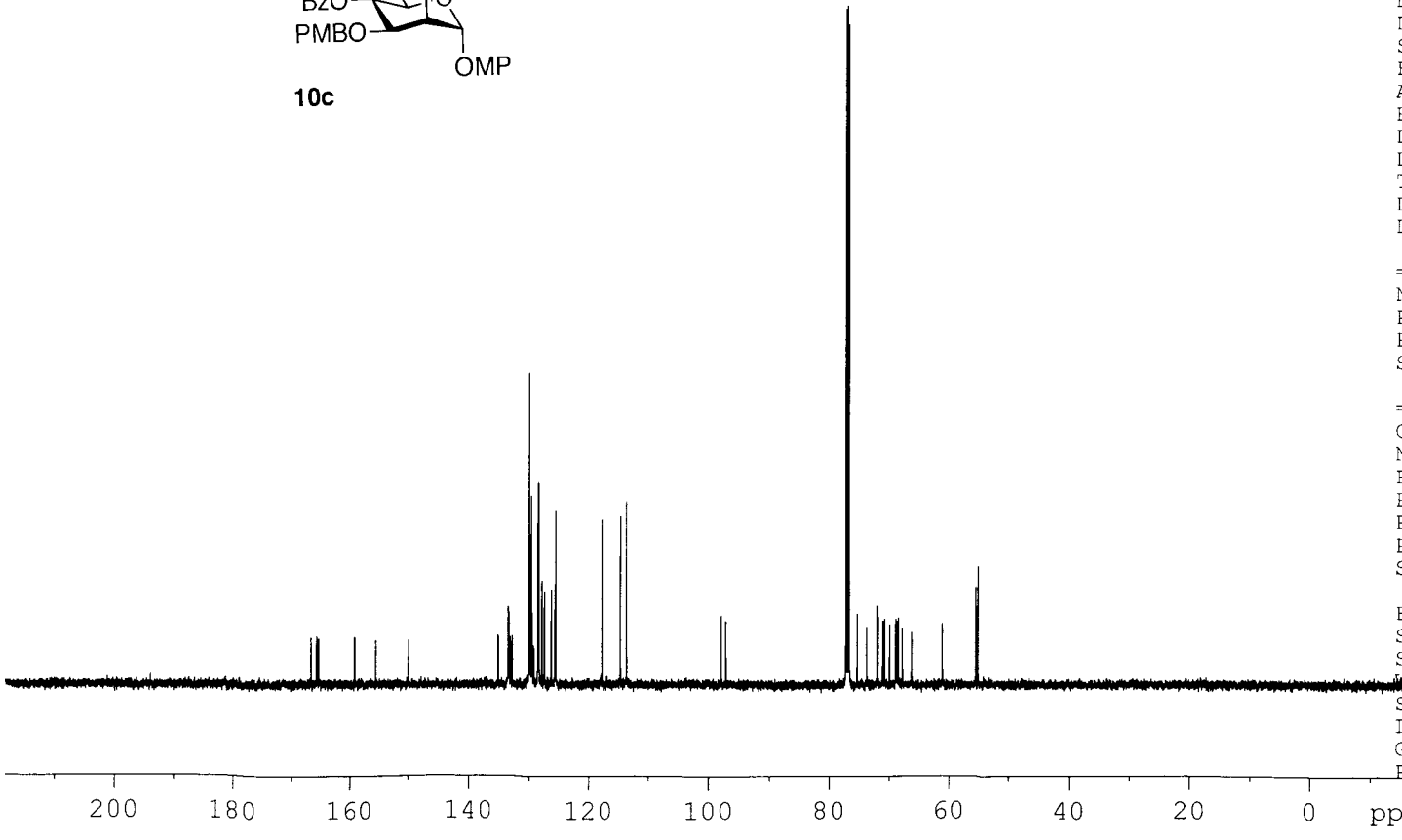


BRUKER

01162

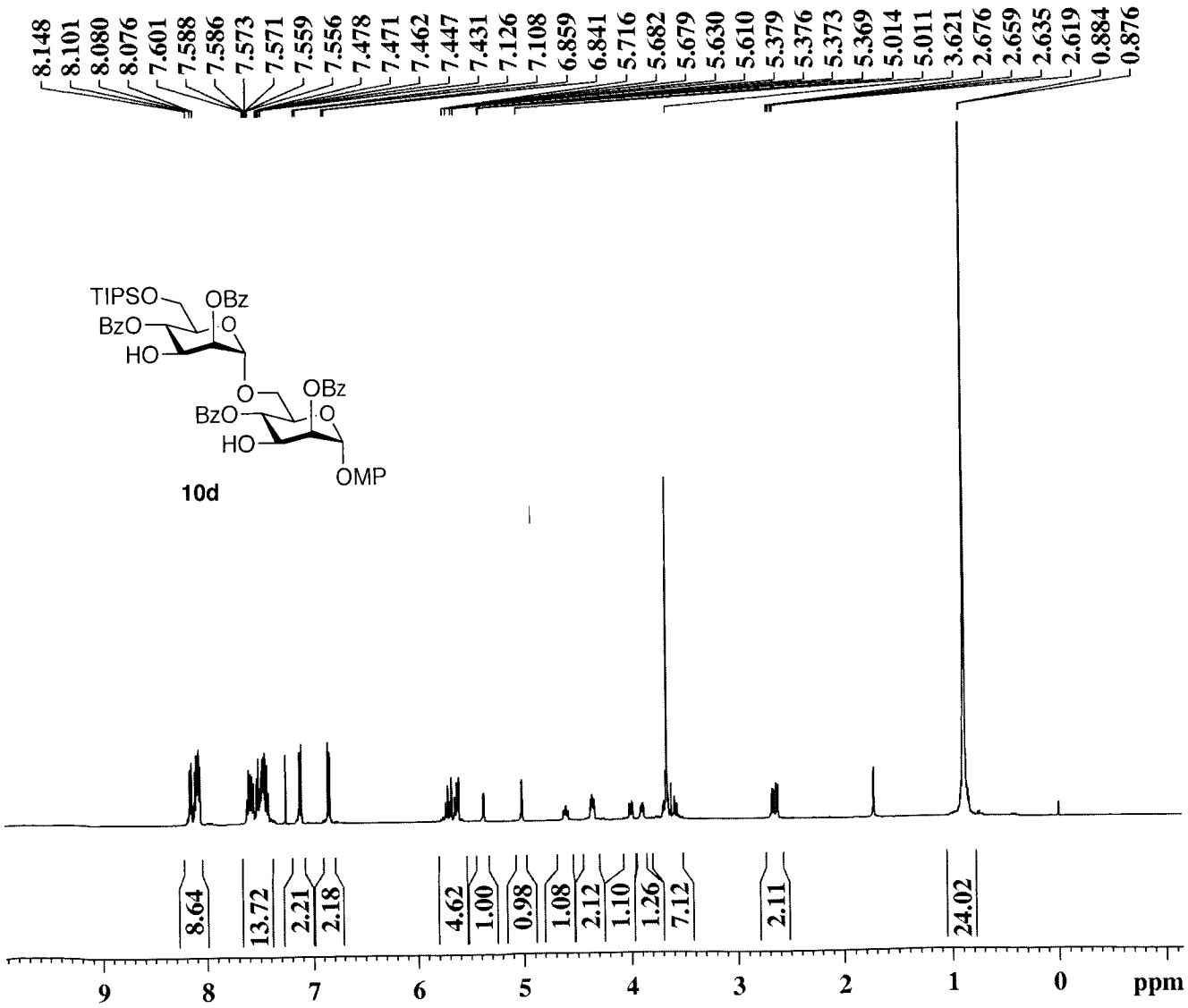


10c



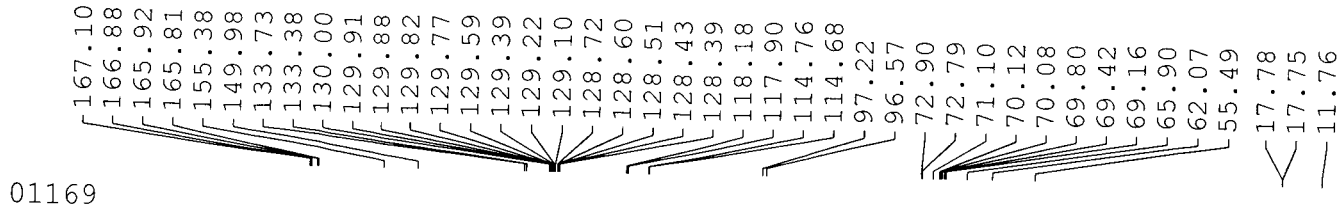

```
Current Data Parameters
NAME                 01162
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110509
Time                 14.23
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     462
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ                1.1010548 sec
RG                     203
DW                16.800 usec
DE                 6.50 usec
TE                 295.0 K
D1             2.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   13C
P1                  8.80 usec
PLW1         112.58000183 W
SFO1          125.7779080 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              80.00 usec
PLW2          18.74300003 W
PLW12          0.36736000 W
PLW13          0.18408000 W
SFO2          500.1620006 MHz

F2 - Processing parameters
SI                   32768
SF            125.7653407 MHz
WDW                     EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

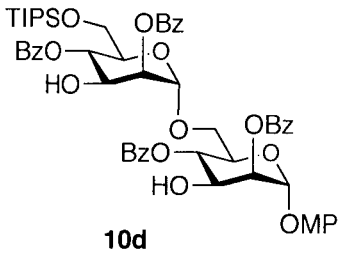
01169



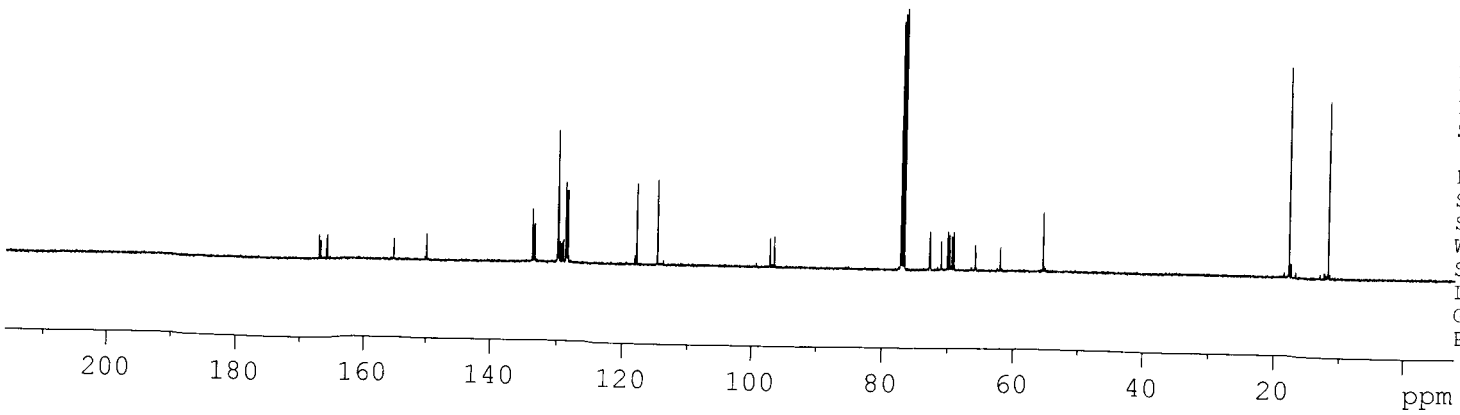
BRUKER

```
Current Data Parameters
NAME                  01169
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20110516
Time                  13.32
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH               10330.578 Hz
FIDRES             0.157632 Hz
AQ                3.1719923 sec
RG                       32
DW                  48.400 usec
DE                   6.50 usec
TE                  295.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.20 usec
PLW1             18.74300003 W
SFO1            500.1630987 MHz

F2 - Processing parameters
SI                        65536
SF              500.1600157 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```





10d



Current Data Parameters

NAME	01169
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	20110516
Time	14.08
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	532
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	295.0 K
D1	2.00000000 sec
D11	0.03000000 sec

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

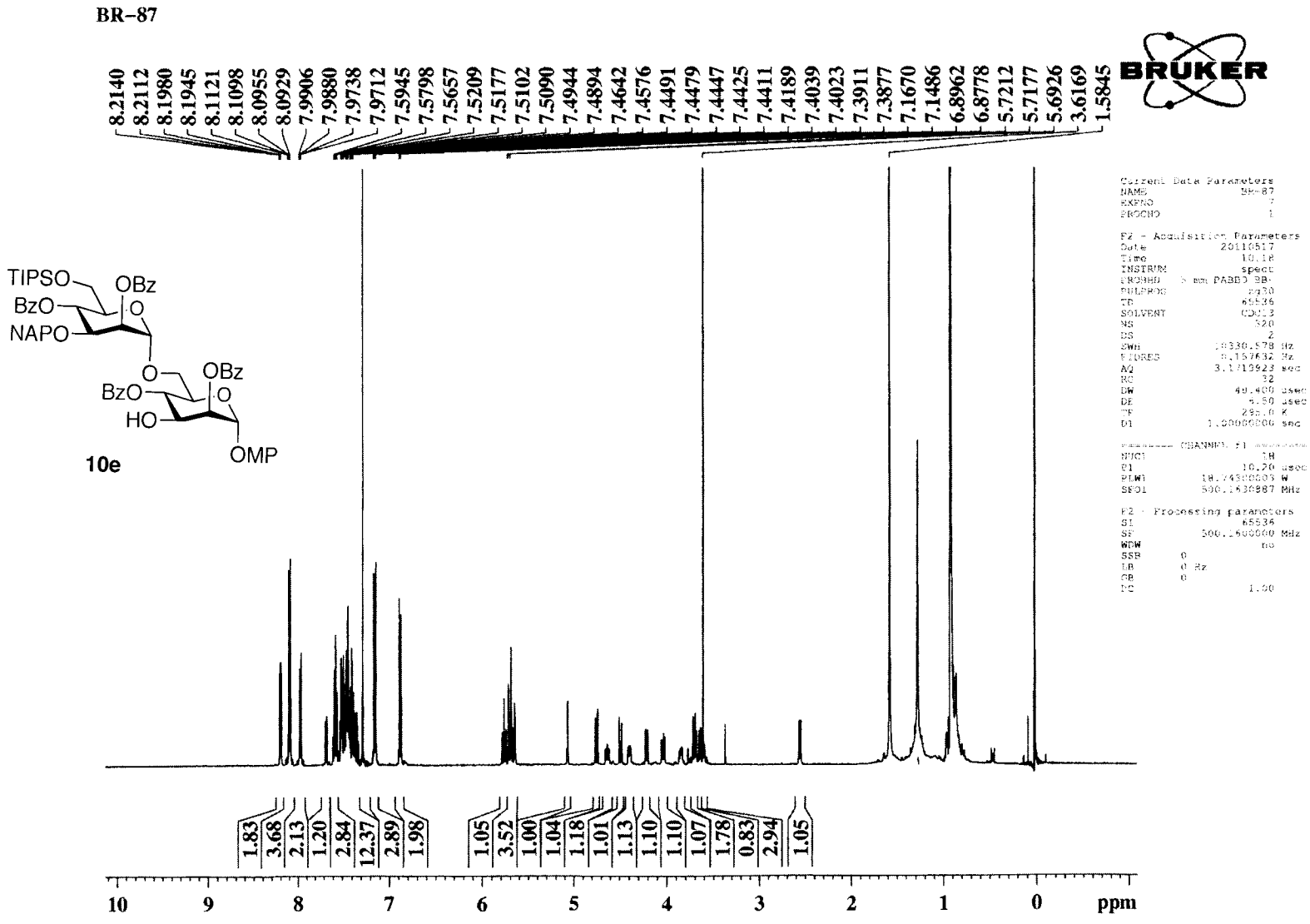
NUC1	13C
P1	8.80 usec
PLW1	112.58000183 W
SFO1	125.7779080 MHz

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

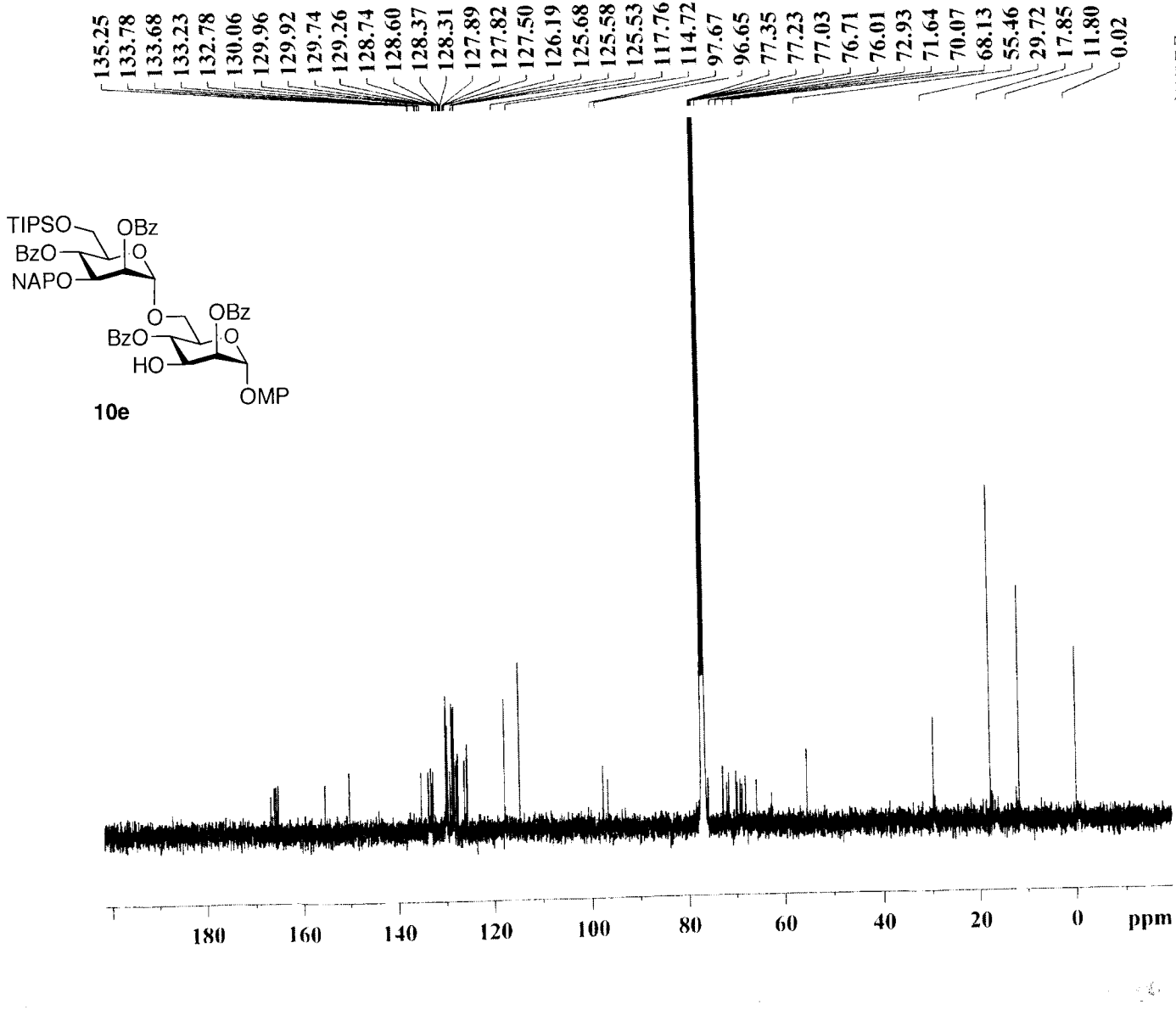
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PLW2	18.74300003 W
PLW12	0.36736000 W
PLW13	0.18408000 W
SFO2	500.1620006 MHz

F2 - Processing parameters

SI	32768
SF	125.7653382 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

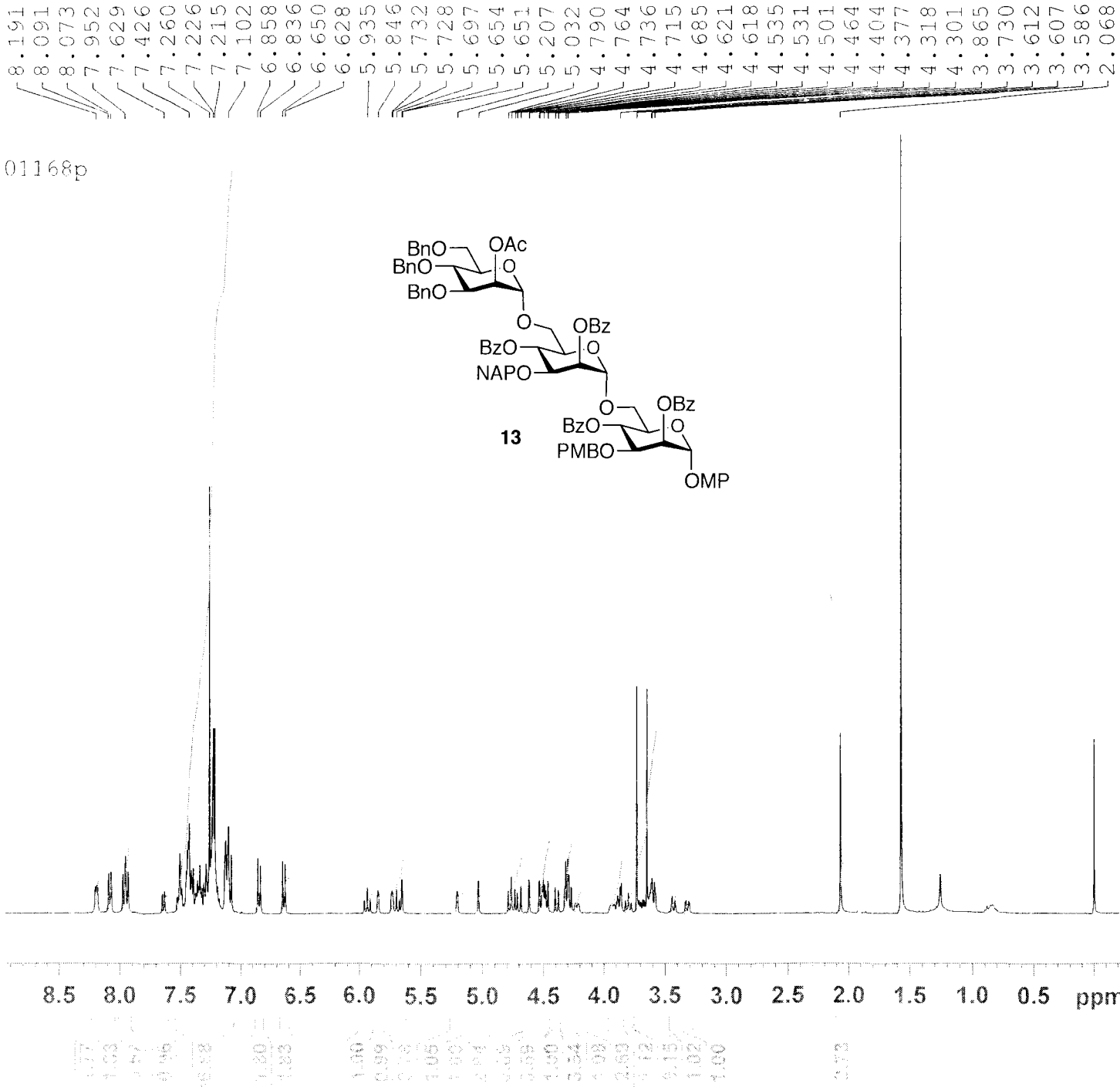


BR-87

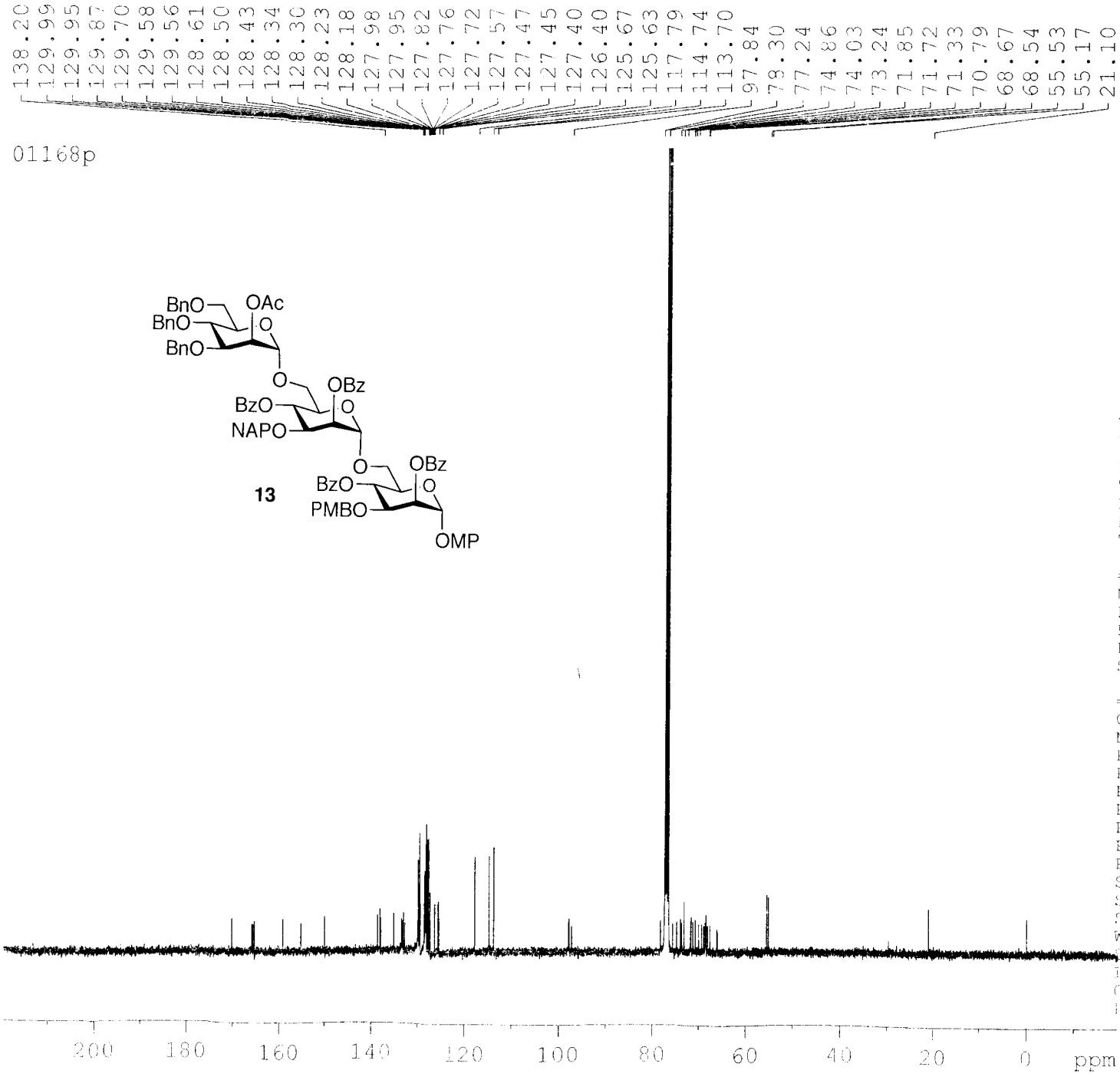


BRUKER

NAME	BR-87
EXPNO	1
PROCNO	1
Date_	20110517
Time	19.38
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10240
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.1 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40



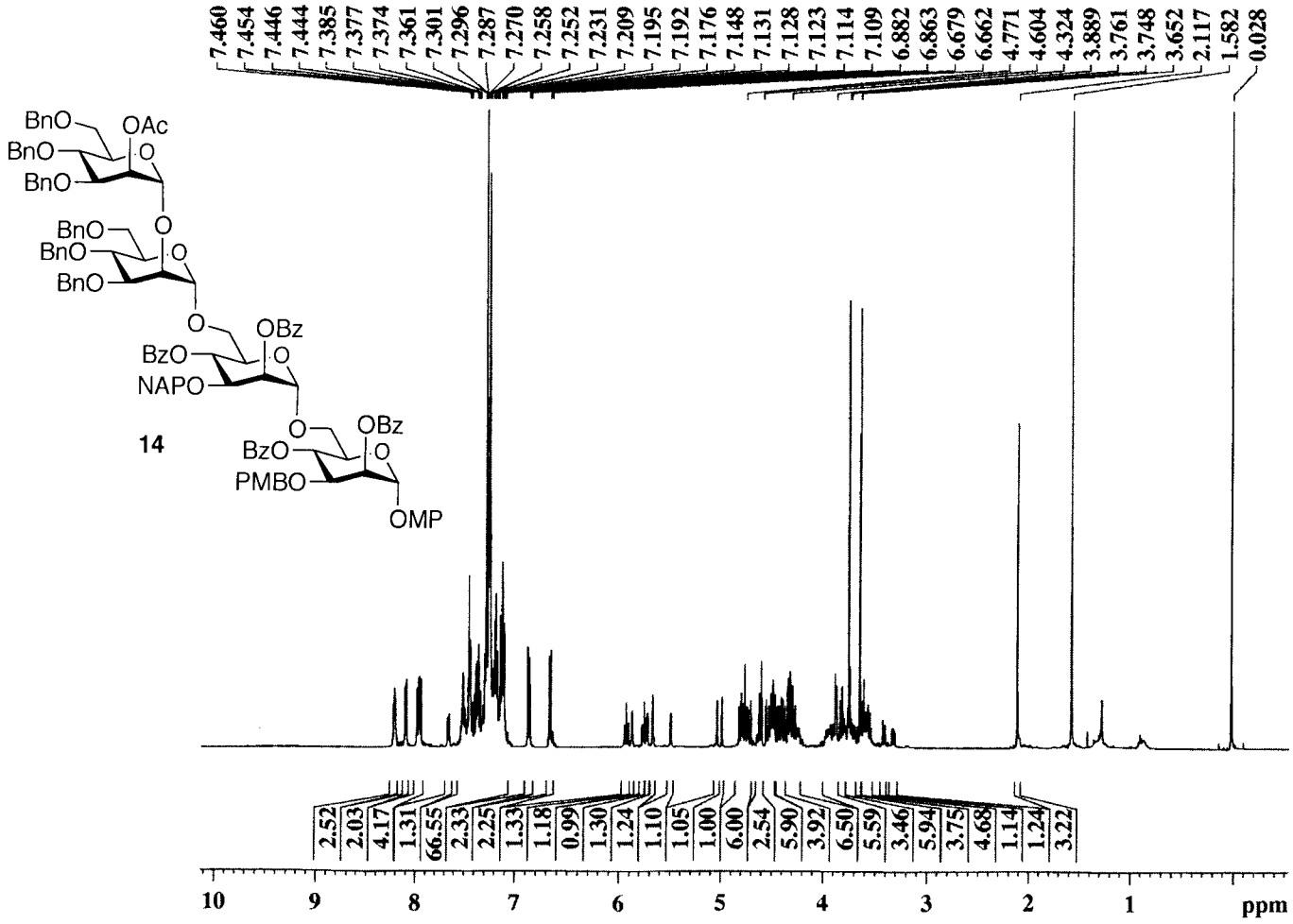
NAME	01168p
EXPNO	1
PROCNO	1
Date_	20110512
Time	19.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	161
DW	60.800 usec
DE	6.50 usec
TE	295.4 K
D1	2.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.31 usec
PL1	-1.00 dB
PL1W	11.09959412 W
SFO1	400.2324716 MHz
SI	32768
SF	400.2300129 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



BRUKER

NAME	01168p
EXPNO	3
PROCNO	1
Date_	20110513
Time_	8.23
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	10240
DS	4
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	203
DW	20.800 usec
DE	6.50 usec
TE	295.3 K
D1	3.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	10.00 usec
PL1	-1.59 dB
PL1W	51.07626343 W
SFO1	100.6479773 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	75.00 usec
PL2	-1.00 dB
PL12	13.39 dB
PL13	20.00 dB
PL2W	11.09959412 W
PL12W	0.40393090 W
PL13W	0.08816721 W
SFO2	400.2316009 MHz
SI	32768
SF	100.6379140 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

BR-89



BRUKER

```
Current Data Parameters
NAME                  BR-89
EXPNO                      4
PROCNO                     1

F2 - Acquisition Parameters
Date              20110517
Time                   17.43
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                      282
DS                        2
SWH              10330.578 Hz
FIDRES            0.157622 Hz
AQ                3.1719923 sec
RG                      114
DW                 48.400 usec
DE                  6.50 usec
TE                 295.0 K
D1               1.00000000 sec

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.20 usec
PLW1           18.74300003 W
SFO1           500.1620087 MHz

F2 - Processing parameters
SI                    65536
SF             500.1600000 MHz
WDW                       EM
SSB          0
LB                     0.30 Hz
GB           0
PC                     1.00
```