Supporting information

Reverse orthogonal strategy for oligosaccharide synthesis

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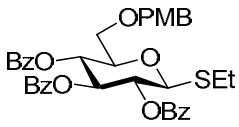
Contents

General experimental procedures

Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40°C. CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, were distilled from CaH_2 directly prior to application. Molecular sieves (3 Å or 4 Å), used for reactions, were crushed and activated *in vacuo* at 390°C during 8 h in the first instance and then for 2-3 h at 390°C directly prior to application. AgOTf was co-evaporated with toluene and was dried *in vacuo* during 2-3 h prior to application. ^{1}H-NMR spectra were recorded in $CDCl_3$ at 300MHz or 500MHz. ^{13}C-NMR spectra were recorded in $CDCl_3$ at 75MHz or 125MHz.

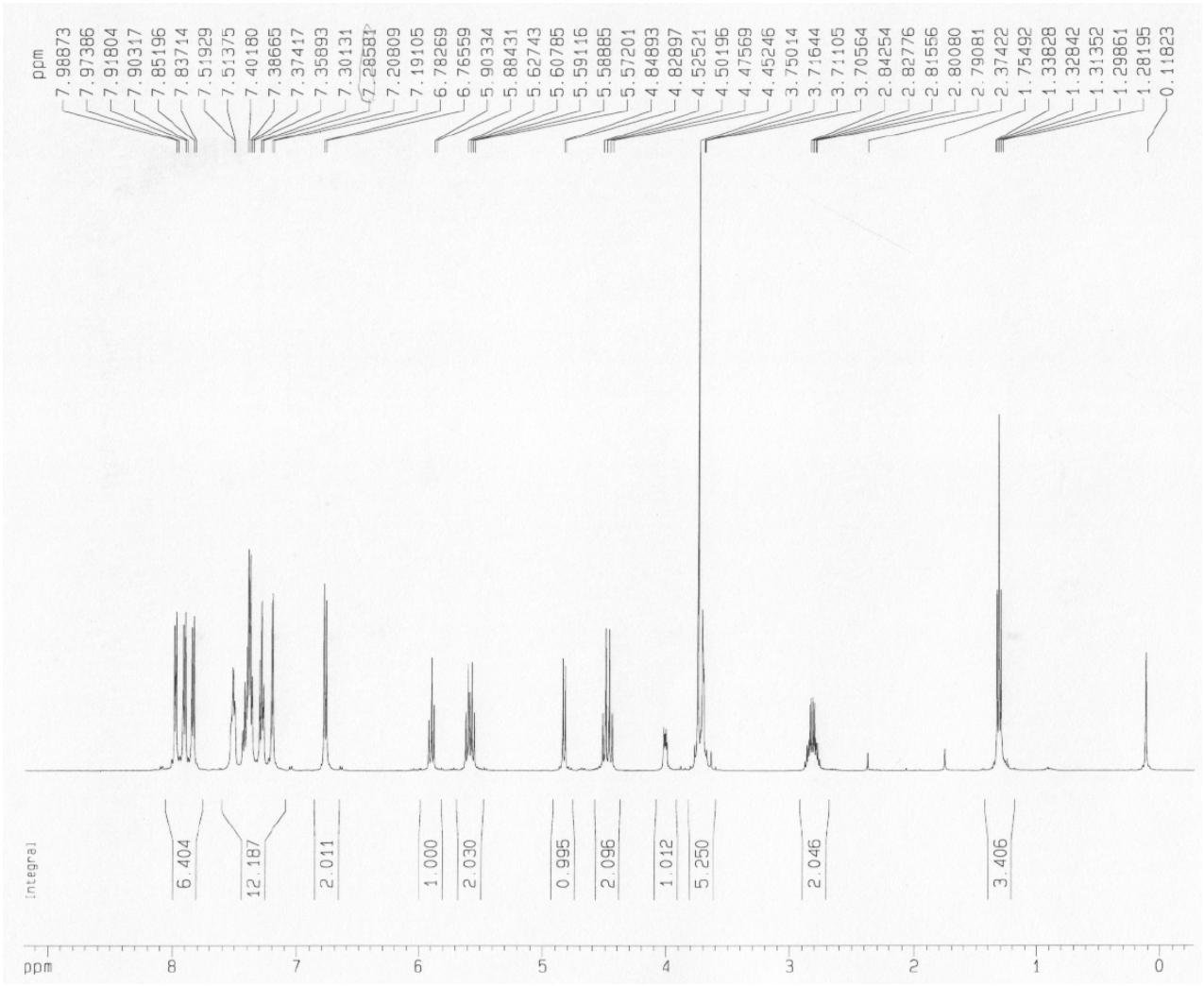
Synthesis of glycosyl donors

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-p-methoxybenzyl-1-thio-β-D-glucopyranoside (1b)

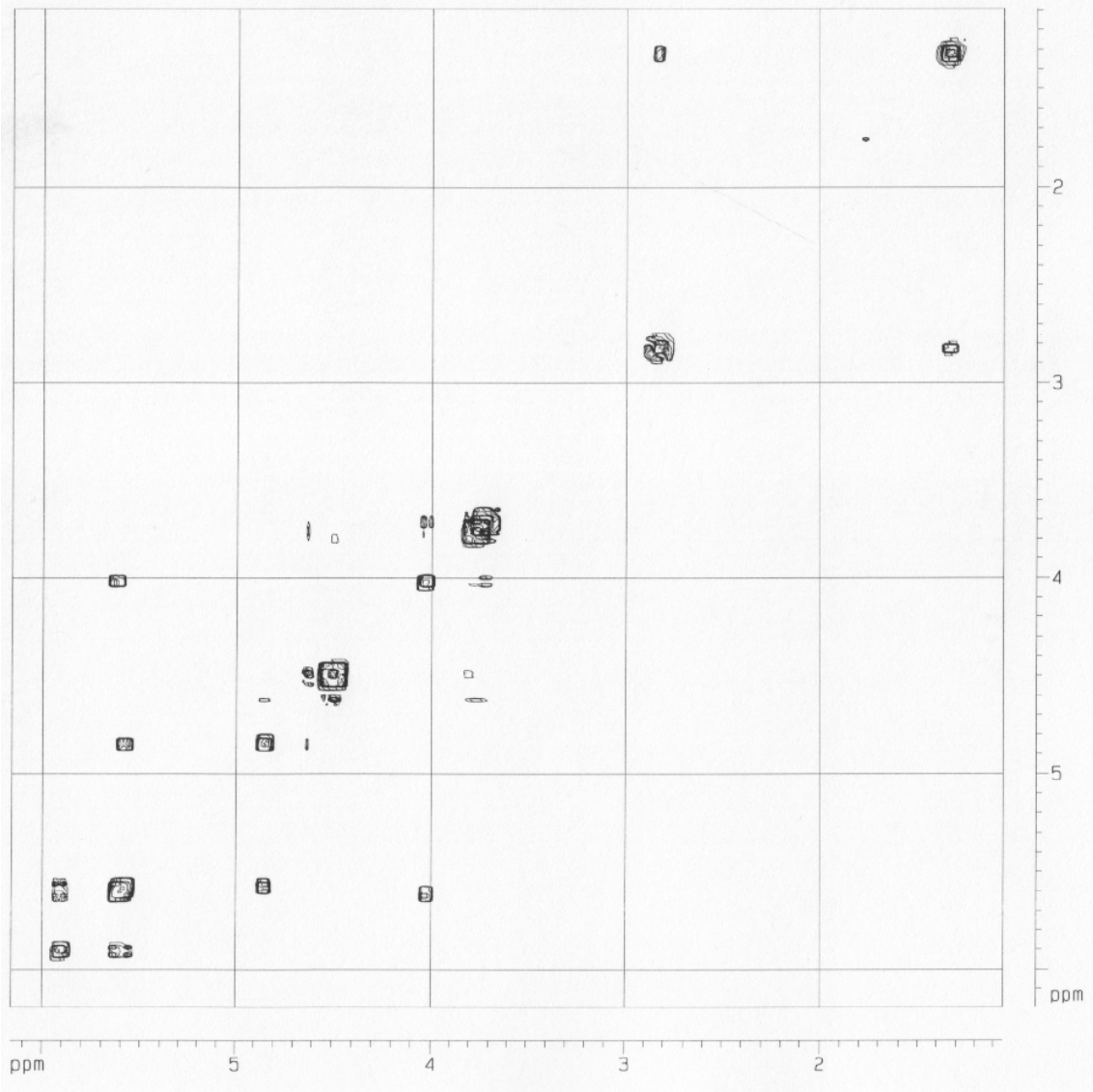


To a solution of ethyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside[1] (720 mg, 1.34 mmol) in DMF (12 mL) was added NaH (60 mg, 1.47 mmol) at 0 °C. The mixture was stirred at

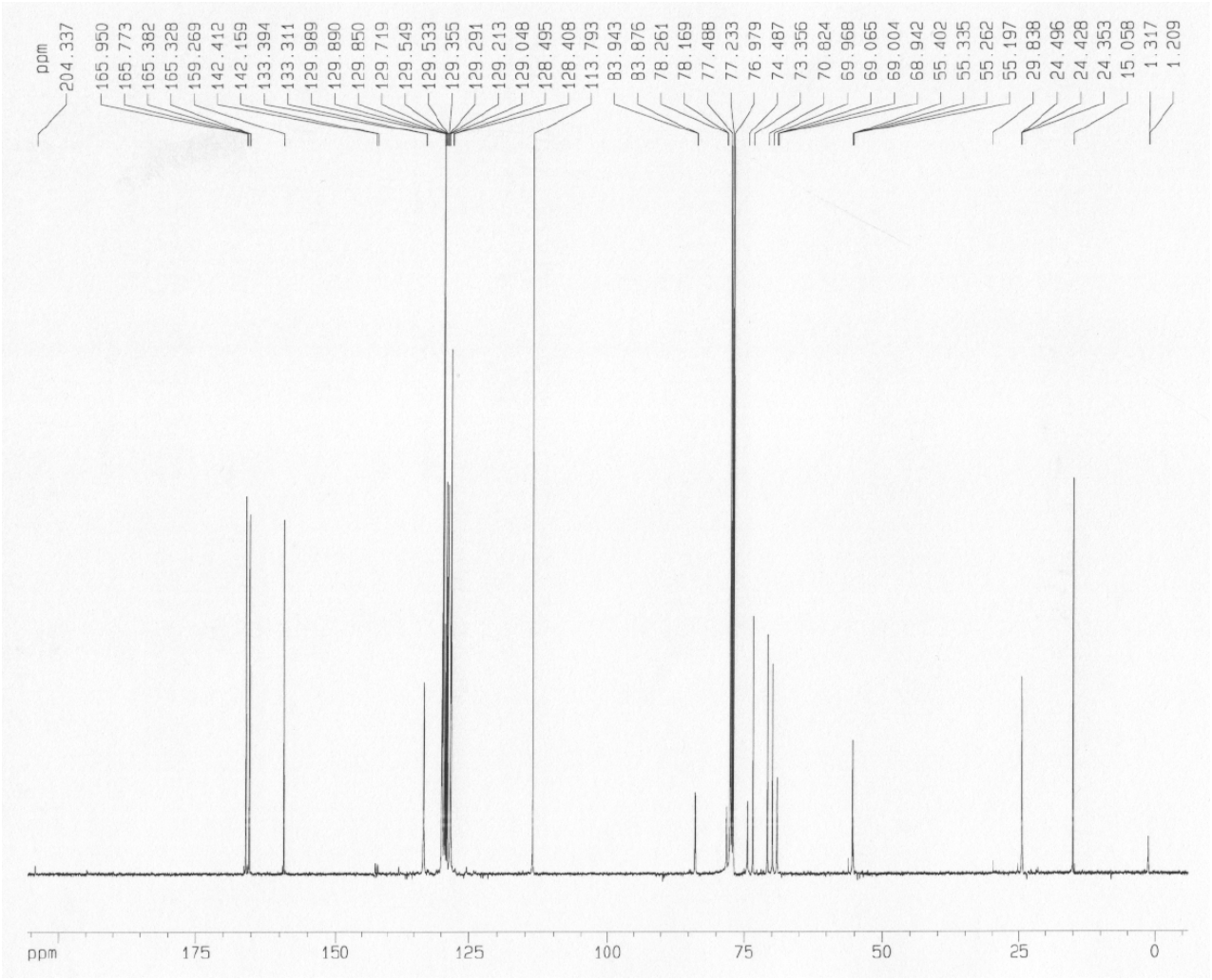
0 °C for 30 min, then pMBCl (0.36 mL, 2.69 mmol) was added at 0 °C. After stirring for 3 h at 0 °C, the reaction mixture was extracted with AcOEt (50 mL) and washed with H_2O (20 mL), and sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by silica gel column chromatography (ethyl acetate / hexane = 1 / 6 elution) to give the title compound **1b** as a colorless foam (281 mg, 32%). Analytical data for **1b**: R_f = 0.48 (ethyl acetate / hexane, 1/3, v/v); $[\alpha]_D^{24}$ = +12.4° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 1.31 (t, 3 H, -SCH_2CH_3), 2.76-2.88 (m, 2 H, -SCH_2-), 3.68-3.73 (m, 2 H, H-6, H-6'), 3.75 (s, 3 H, PhO*Me*), 4.01 (m, 1 H, H-5), 4.46 (dd, 2 H, J_{gem} = 8.7 Hz, CH_2Ph), 4.86 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 5.48-5.61 (m, 2 H, H-2, H-4), 5.90 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 6.77 (d, 1 H, PMP), 7.20 (d, 1 H, PMP), 7.29-7.99 (m, 15 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$) δ 14.8, 15.1, 24.4, 55.3 (× 2), 68.9, 69.0, 69.9, 70.8, 73.4, 78.1, 78.3, 83.9 (× 2), 113.8, 128.4, 128.5, 128.9, 129.0, 129.2, 129.3 (× 2), 129.5 (× 2), 129.7, 129.9 (× 3), 130.8, 133.3, 133.4, 159.3, 165.4, 165.6, 165.9; HR-FAB MS $[M + Na]^+$ calcd for $C_{37}H_{36}O_9Na^+$ 679.1978, found 679.1989.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

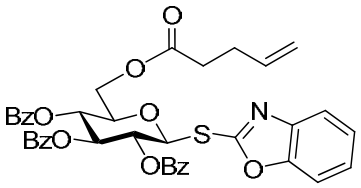


COSY spectrum (500 MHz, $CDCl_3$)

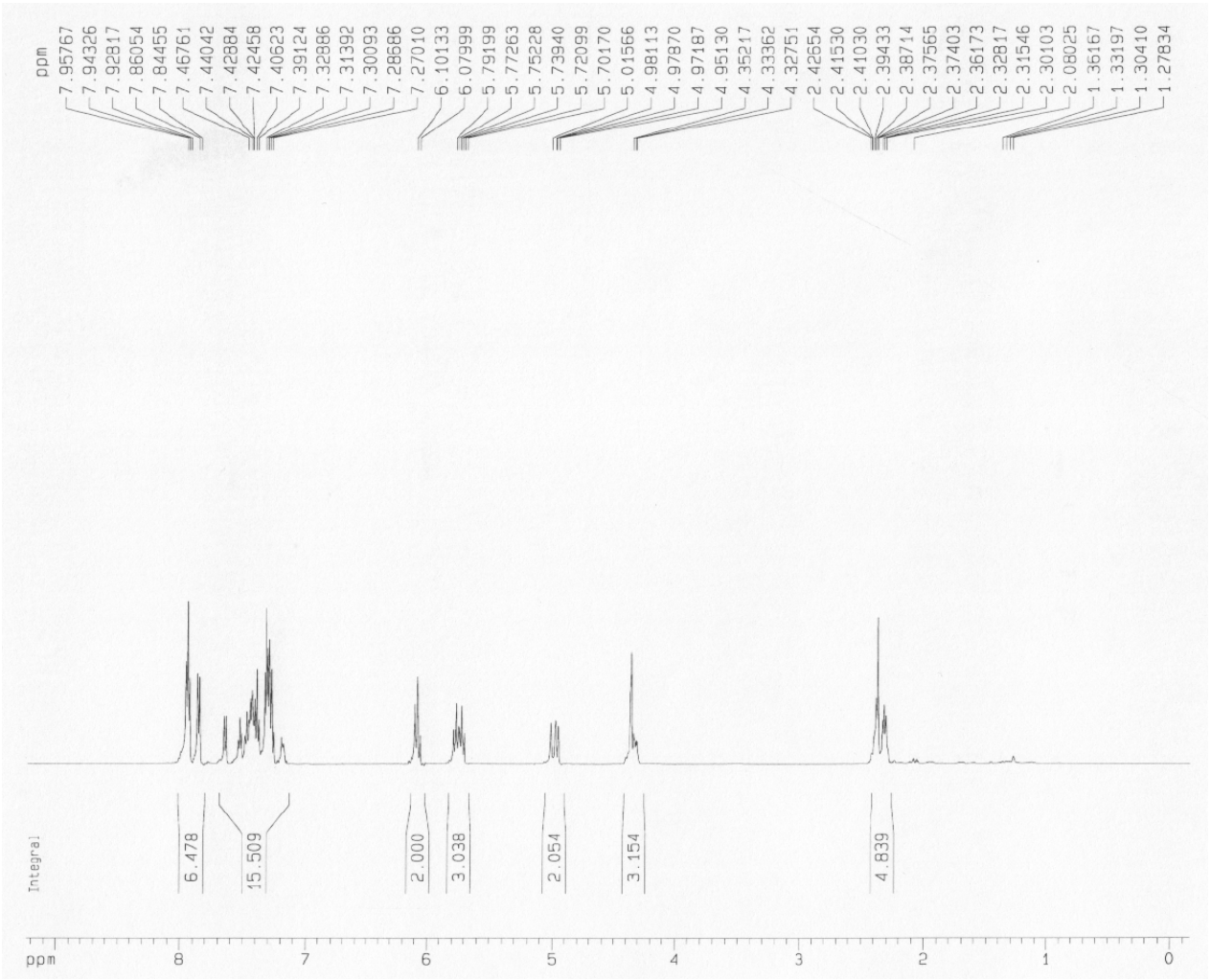


^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

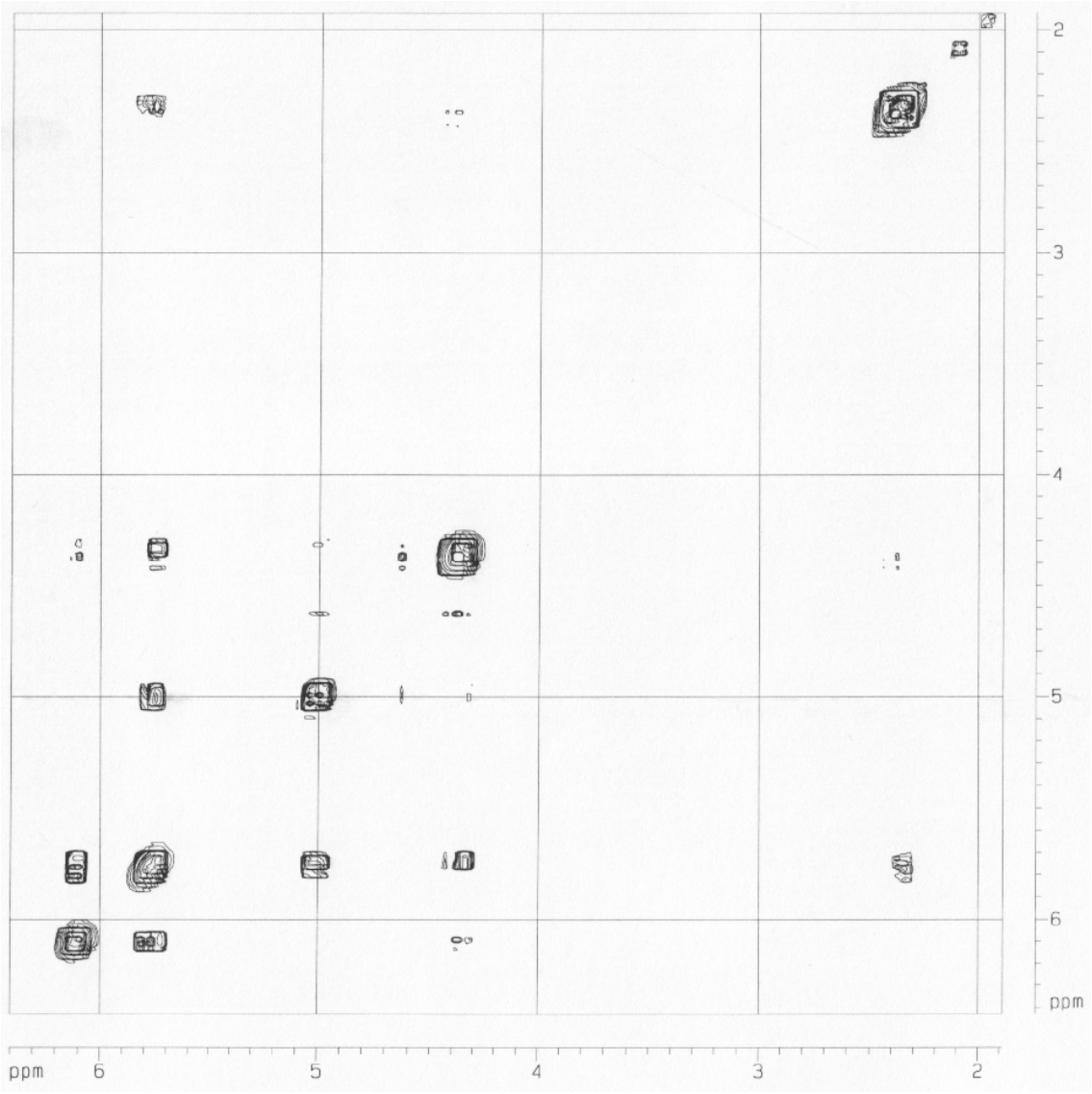
Benzoxazolyl 2,3,4-tri-*O*-benzoyl-6-*O*-pentenoyl-1-thio-β-D-glucopyranoside (1d)



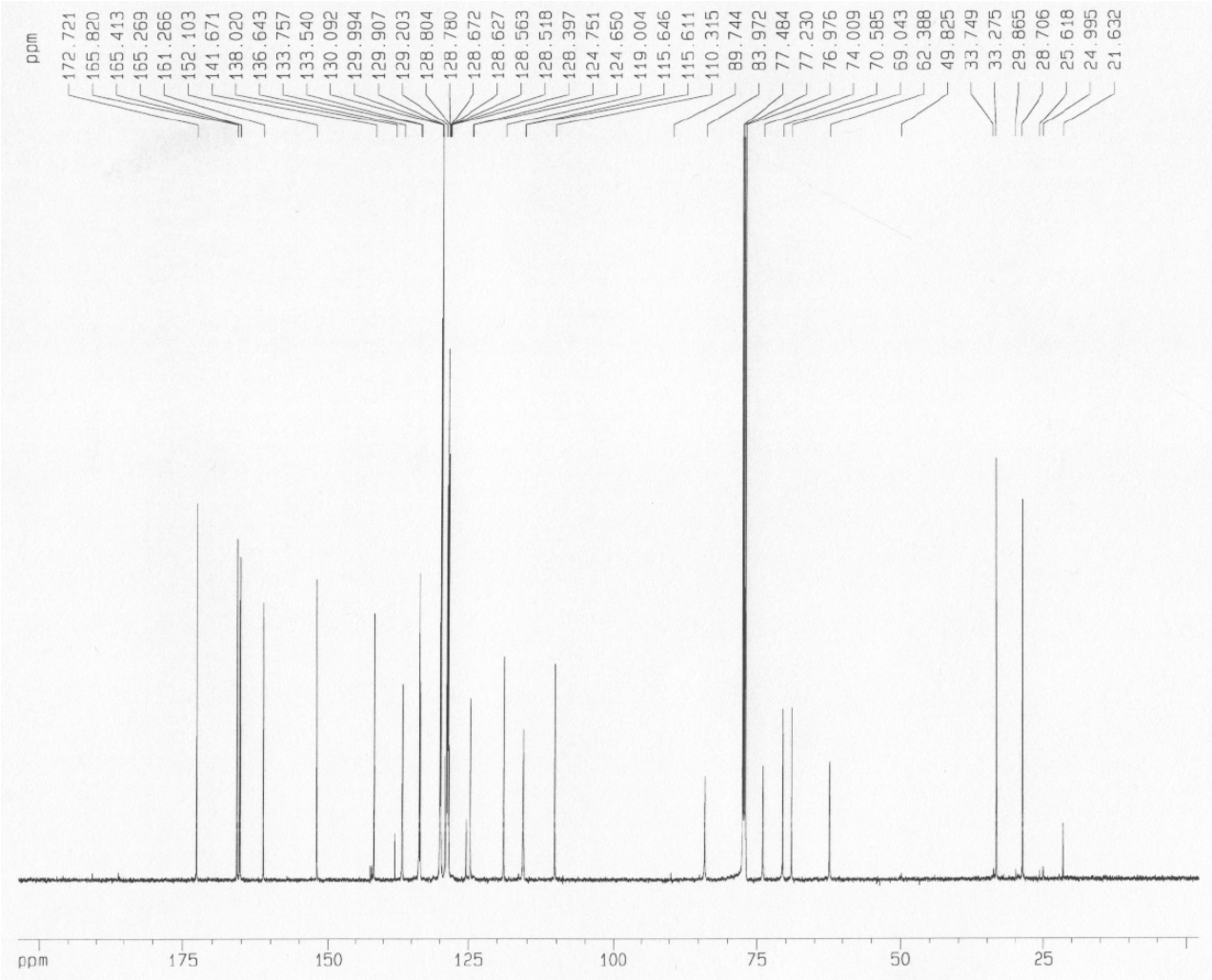
To a solution of benzoxazolyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside[2] (910 mg, 1.46 mmol) in 1,2-dichloroethane (15 mL) was added 4-pentenoic acid (0.18 mL, 1.75 mmol), N,N'-dicyclohexylcarbodiimide (DCC, 361 mg, 1.75 mmol) and 4-dimethylaminopyridine (DMAP, 18 mg, 0.15 mmol) at 0 °C. The mixture was stirred at 40 °C for 17 h, then diluted with dichloromethane (30 mL) and washed with H_2O (20 mL), sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1/6 elution) to give the title compound **1d** as a colorless foam (925 mg, 93%). Analytical data for **1d**: R_f = 0.61 (ethylacetate / hexane, 1 / 2, v / v); $[\alpha]_D^{24}$ = +91.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 2.32-2.43 (m, 4 H, -CH_2CH_2-), 4.31-4.43 (m, 3 H, H-5, H-6, H-6'), 4.91-5.07 (m, 2 H, -CH=CH_2, H-1), 5.64-5.82 (m, 3 H, -CH=CH_2, H-2, H-4), 5.99-6.16 (m, 2 H, -C*H*=CH_2, H-3), 7.27-7.96 (m, 19 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ, 21.6, 28.7, 33.3, 62.4, 69.0, 70.6, 74.0, 83.9, 110.3, 115.6, 119.0, 124.7, 124.8, 125.5, 128.4, 128.5, 128.6 (× 3), 128.7, 128.8, 129.2, 129.7, 129.9, 130.0, 130.1, 133.5, 133.8, 136.6, 138.0, 141.7, 152.1, 161.3, 165.3, 165.4, 165.8, 172.7 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{39}H_{33}NO_{10}SNa^+$ 730.1723, found 730.1713.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)



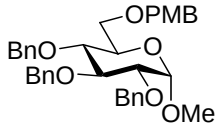
COSY spectrum (500 MHz, $CDCl_3$)



^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

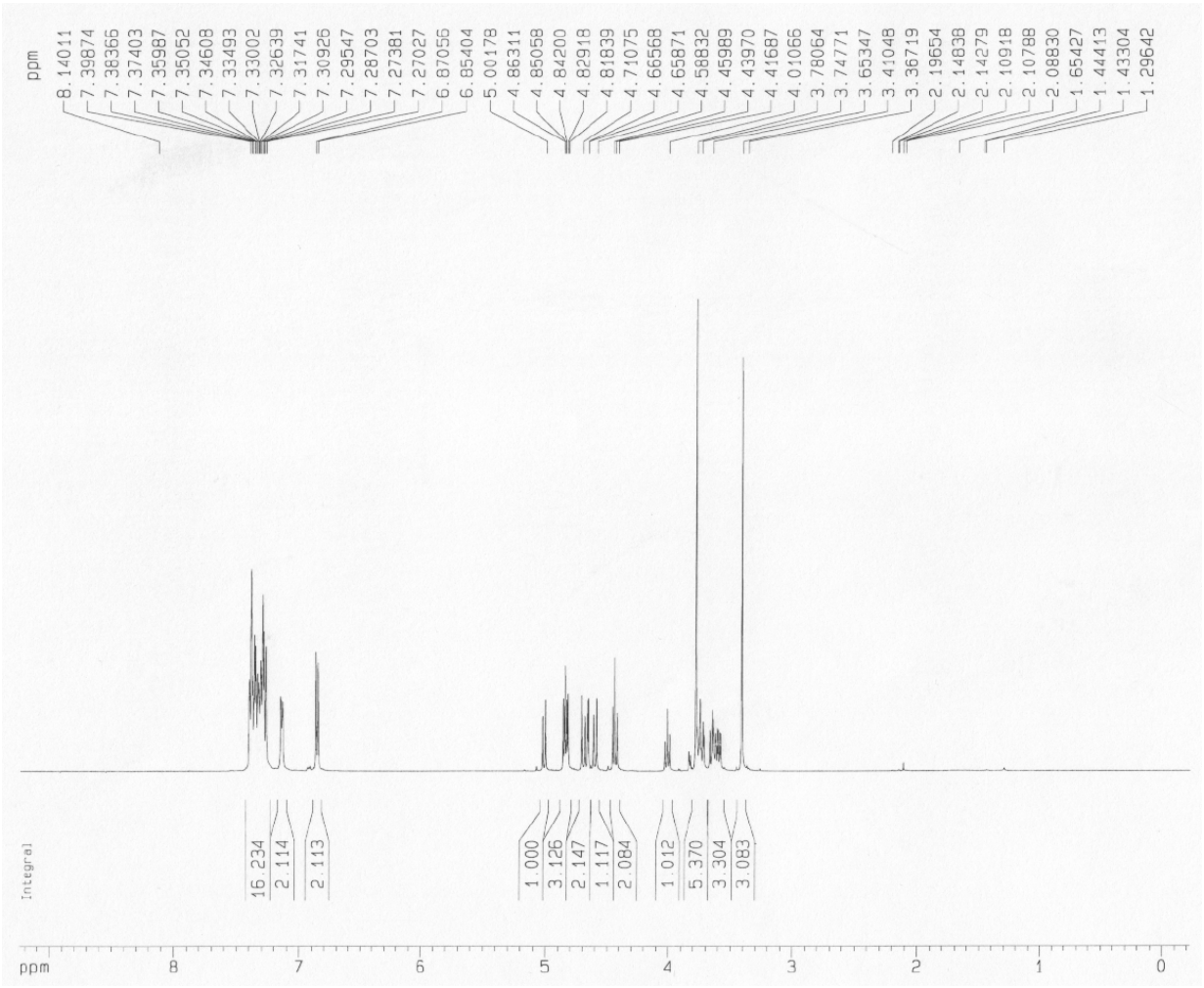
Synthesis of glycosyl acceptors

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-p-methoxybenzyl-α-D-glucopyranoside (2c).

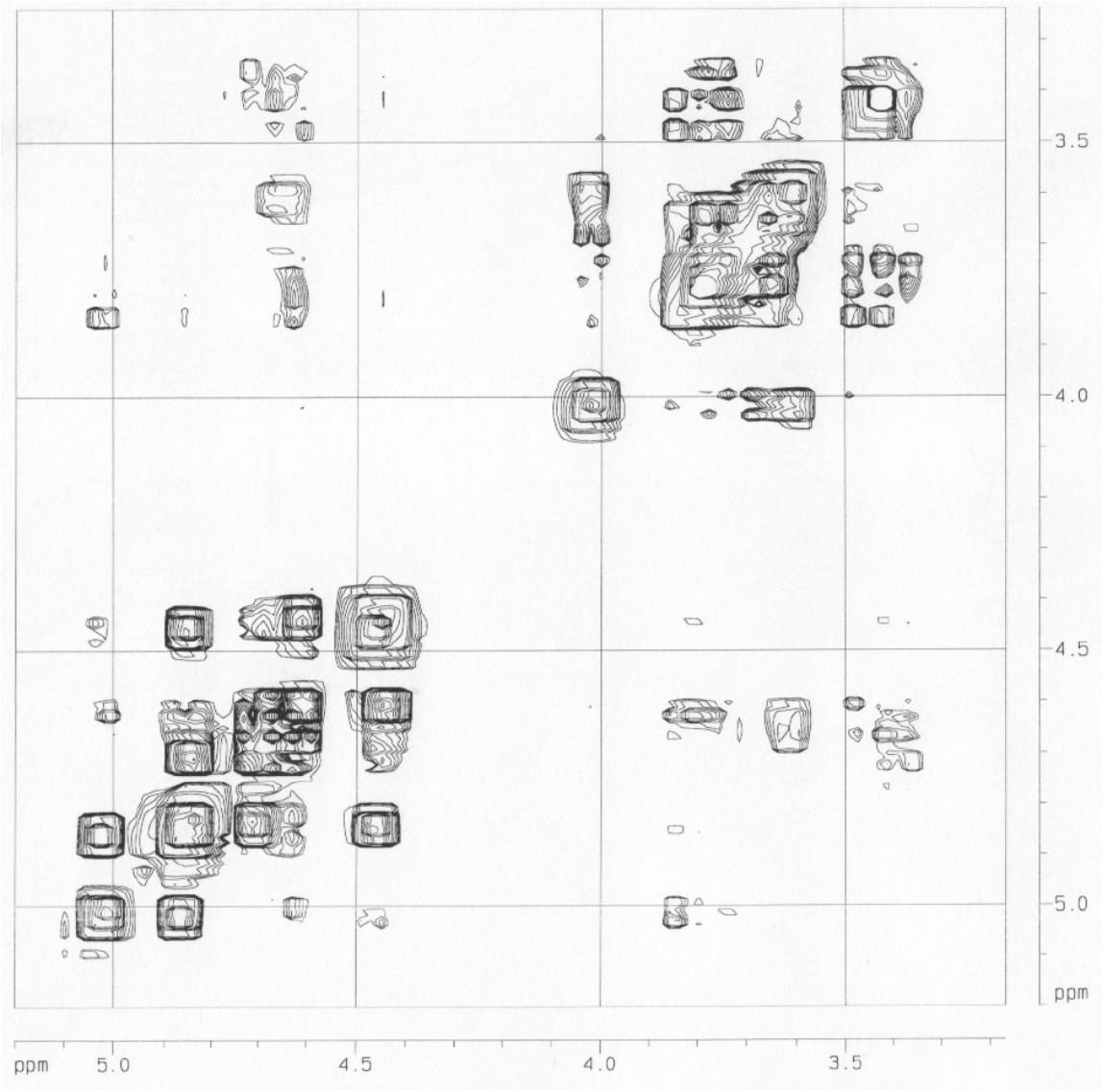


To a solution of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[3, 4] (2.15 g, 4.63 mmol) in DMF (23 mL) was added NaH (370 mg, 9.26 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h then pMBCl (1.26 mL, 9.26 mmol) was added at 0°C. After stirring for 18 h at room temperature, the reaction mixture was extracted with AcOEt (50 mL) and washed with H_2O (20 mL), and sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1 / 5 elution) to give the title compound **2c** as a colorless syrup (2.2 g, 82 %). Analytical data for **2c**: R_f = 0.65 (ethyl acetate / hexane, 1 / 3, v / v); $[\alpha]_D^{23}$ = +19.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 3.41 (s, 3 H, OMe), 3.58-3.67 (m, 3 H, $J_{2,3}$ = 9.2 Hz, H-2, H-4, H-6a), 3.72-3.76 (m, 2 H, H-5, H-6b), 3.78 (s, 3 H, PhO*Me*), 4.01 (t, 1 H, $J_{3,4}$ = 9.2 Hz, H-3), 4.40-4.44 (m, 2 H, CH_2Ph), 4.60 (d, 1 H, J^2 = 11.8 Hz, CH_2Ph), 4.66 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.70 (d, 1 H, CH_2Ph), 4.82-4.86 (m, 3 H, CH_2Ph), 5.01 (d, 1 H, J^2 = 10.9 Hz, CH_2Ph), 6.86-7.40 (m, 19 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ, 55.3, 55.4, 68.0, 70.2, 71.6, 73.2, 73.5, 75.2, 75.9 (× 3), 76.8, 76.9, 77. 8, 79.9, 82.3 (× 2),

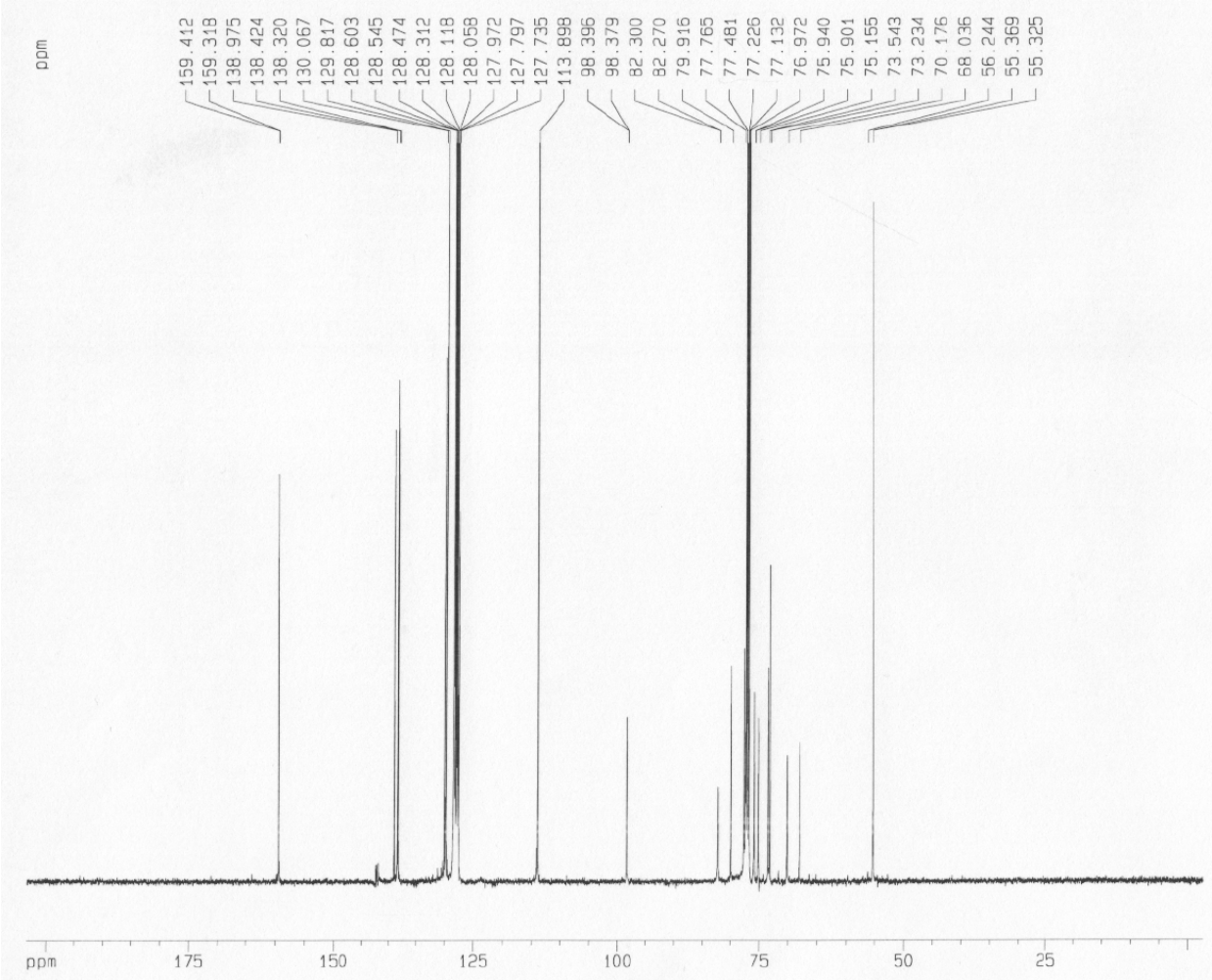
98.4, 113.9, 127.7, 127.8, 128.0, 128.1 (× 2), 128.3, 128.4, 128.5, 128.6, 129.6, 129.8, 130.1, 130.3, 138.3, 138.4, 139.0, 159.4 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{36}H_{40}O_7Na^+$ 607.2672, found 607.2673.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

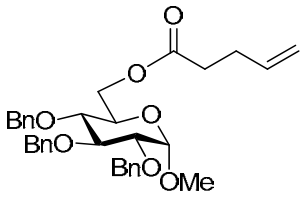


COSY spectrum (500 MHz, $CDCl_3$)



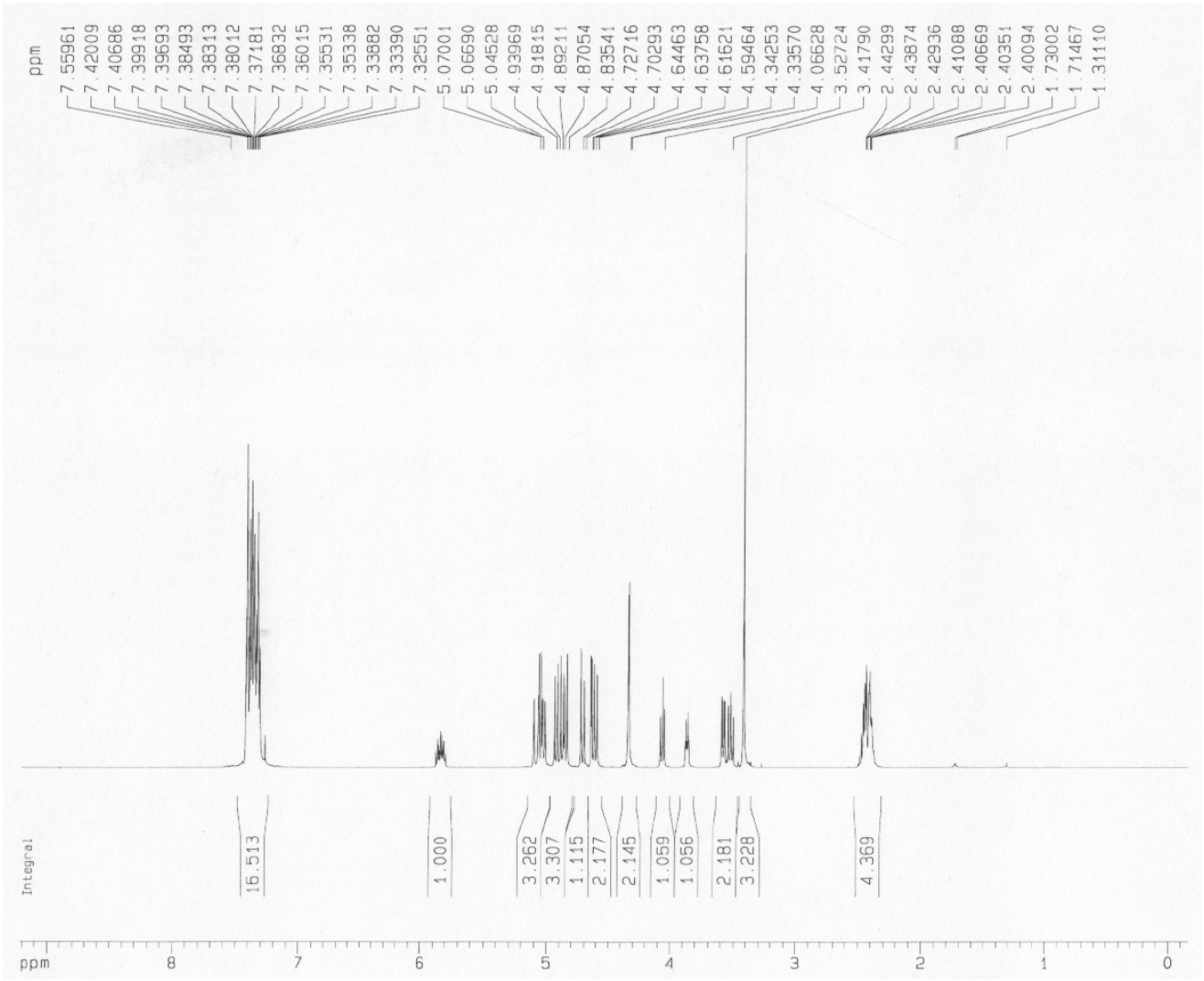
^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-pentenoyl-α-D-glucopyranoside (2d)

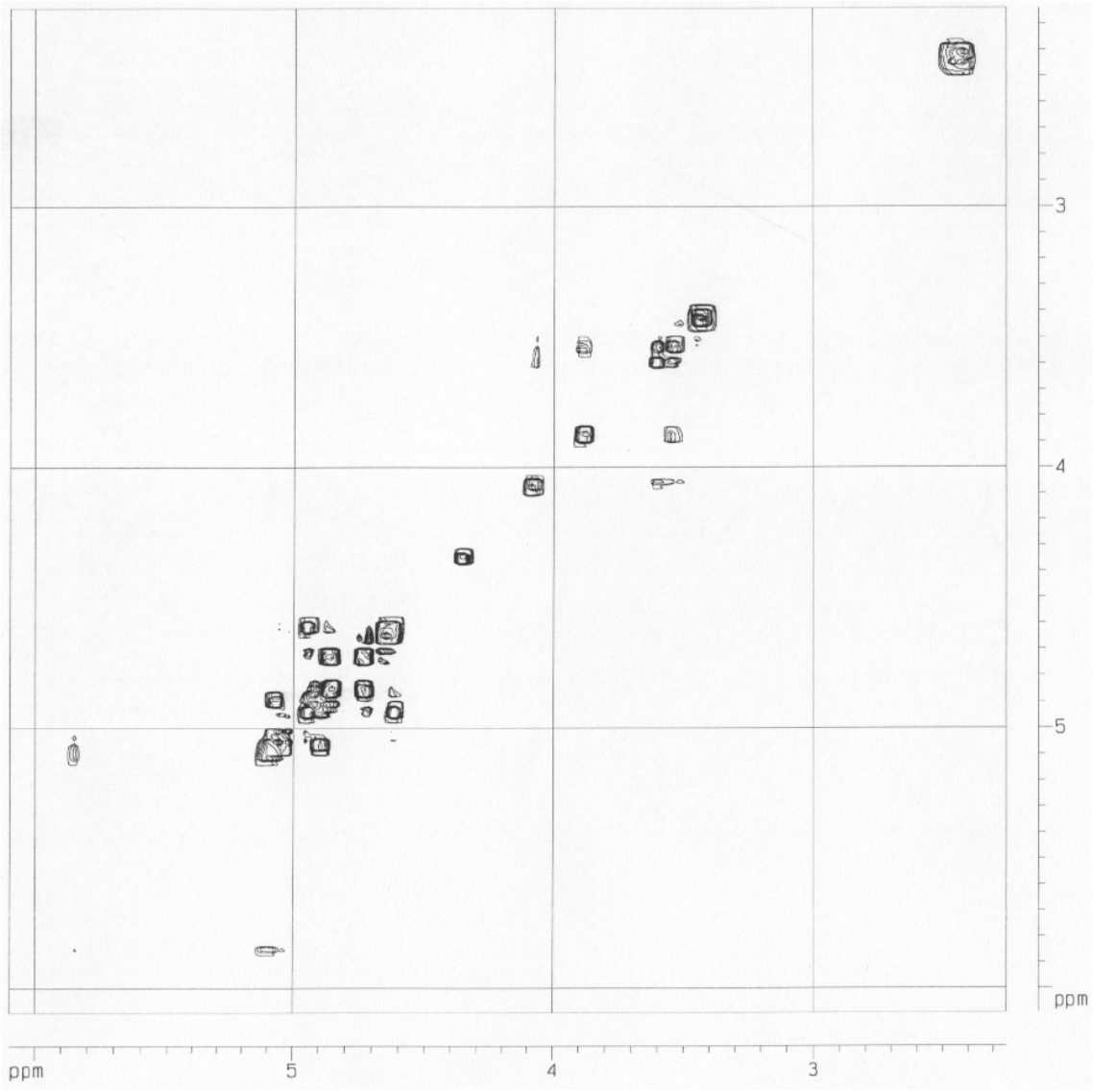


To a solution of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[3, 4] (1.94 g, 4.18 mmol) in dichloromethane (42 mL) was added 4-pentenoic acid (0.52 mL, 5.0 mmol) and DCC (1.0 g, 5.0 mmol) at 0 °C. The mixture was stirred at room temperature for 19 h then it was diluted with dichloromethane (50 mL) and washed with H_2O (20 mL), sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1 / 9 elution) to give the title compound **2d** as a white amorphous solid (1.9 g, 83 %). Analytical data for **2d**: R_f = 0.55 (ethyl acetate / hexane, 1 / 4, v / v); $[\alpha]_D^{23}$ = +40.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.37-2.49 (m, 4 H, -CH_2CH_2-), 3.41 (s, 3 H, OMe), 3.52 (m, 1 H, $J_{4,5}$ = 9.2 Hz, H-4), 3.58 (dd, 1 H, $J_{2,3}$ = 9.2 Hz, H-2), 3.87 (m, 1 H, H-5), 4.07 (t, 1 H, $J_{3,4}$ = 9.2 Hz, H-3), 4.33-4.34 (m, 2 H, H-6a, H-6b), 4.60 (d, 1 H, J^2 = 10.9 Hz, CH_2Ph), 4.64 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1), 4.71 (d, 1 H, J^2 = 12.1 Hz, CH_2Ph), 4.84-4.94 (m, 3 H, CH_2Ph), 5.01-5.11 (m, 3 H, CH=CH_2, CH_2Ph), 5.86 (m, 1 H, CH=CH_2), 7.35-7.40 (m, 15 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 28.8, 33.4, 55.3, 63.0, 68.8, 73.5, 74.3, 75.2, 75.3, 75.9, 76.0, 76. 8, 77.6, 79.9, 82.1, 98.1, 98.2, 115.7, 115.8, 127.8, 128.0, 128.1, 128.2 (× 2), 128.6 (× 2), 136.6,

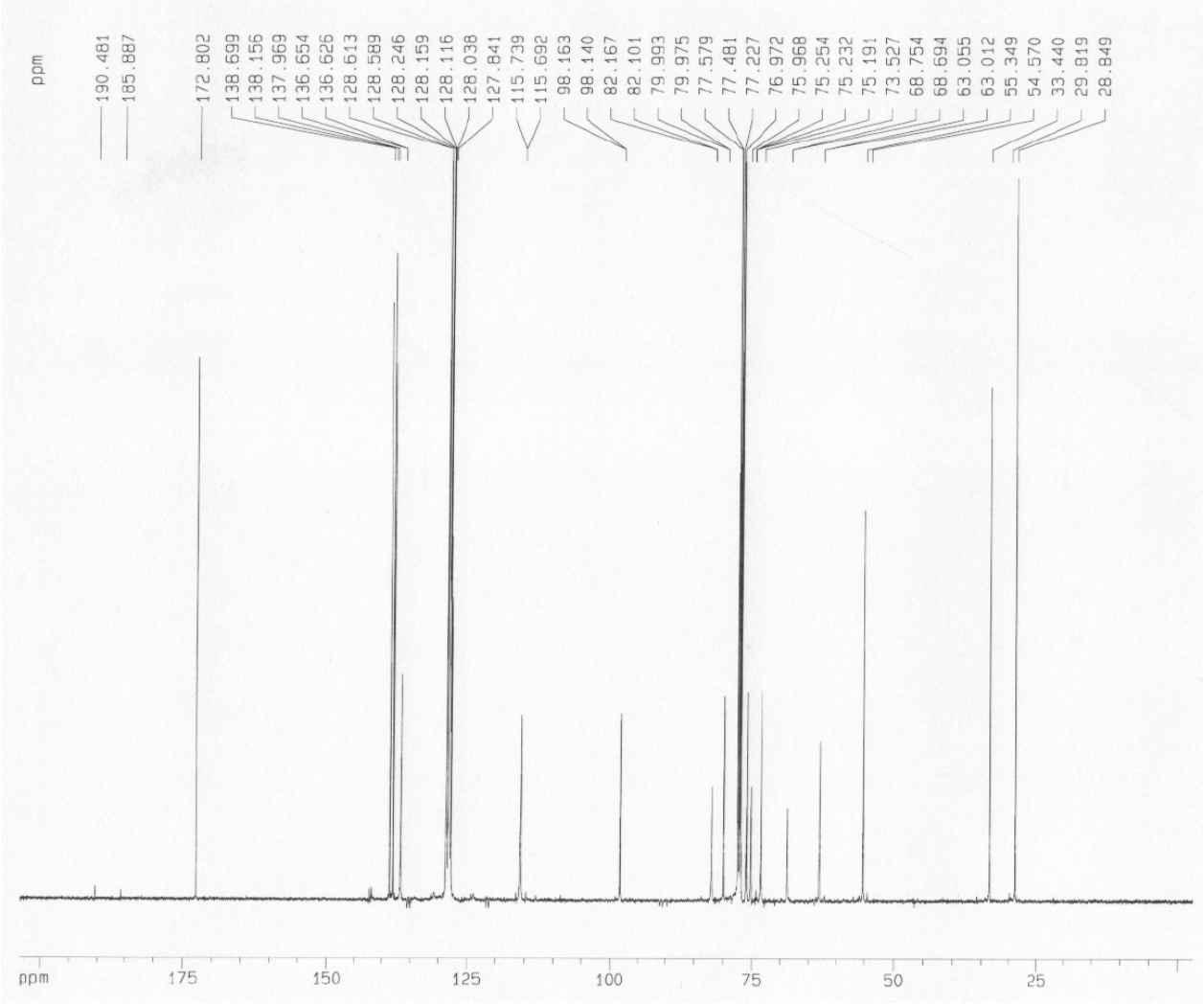
137.7, 137.9, 138.2, 138.5, 138.7, 172.8 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{33}H_{38}O_7Na^+$ 569.2515, found 569.2527.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

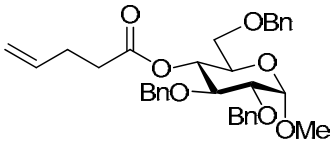


COSY spectrum (500 MHz, $CDCl_3$)

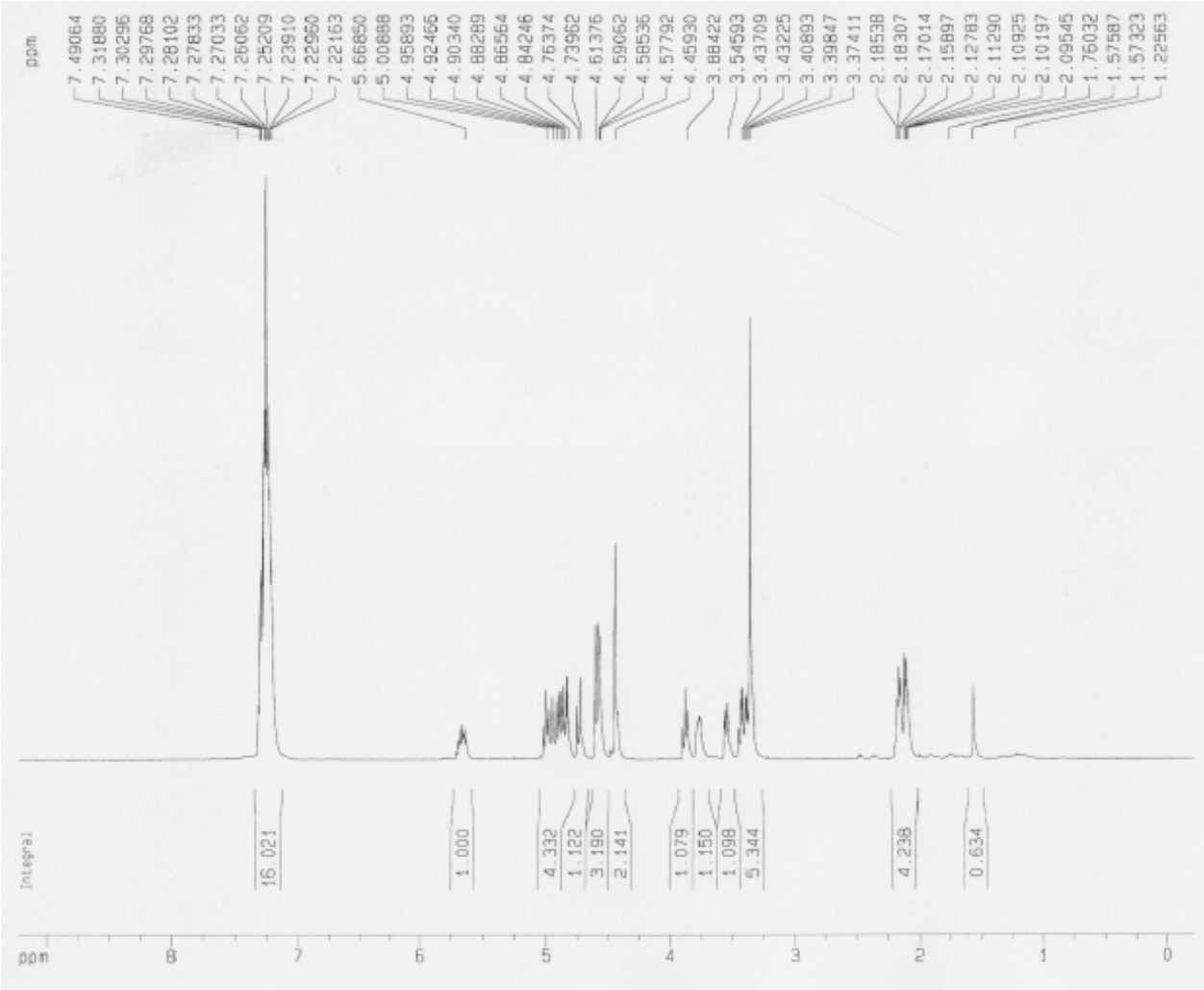


^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

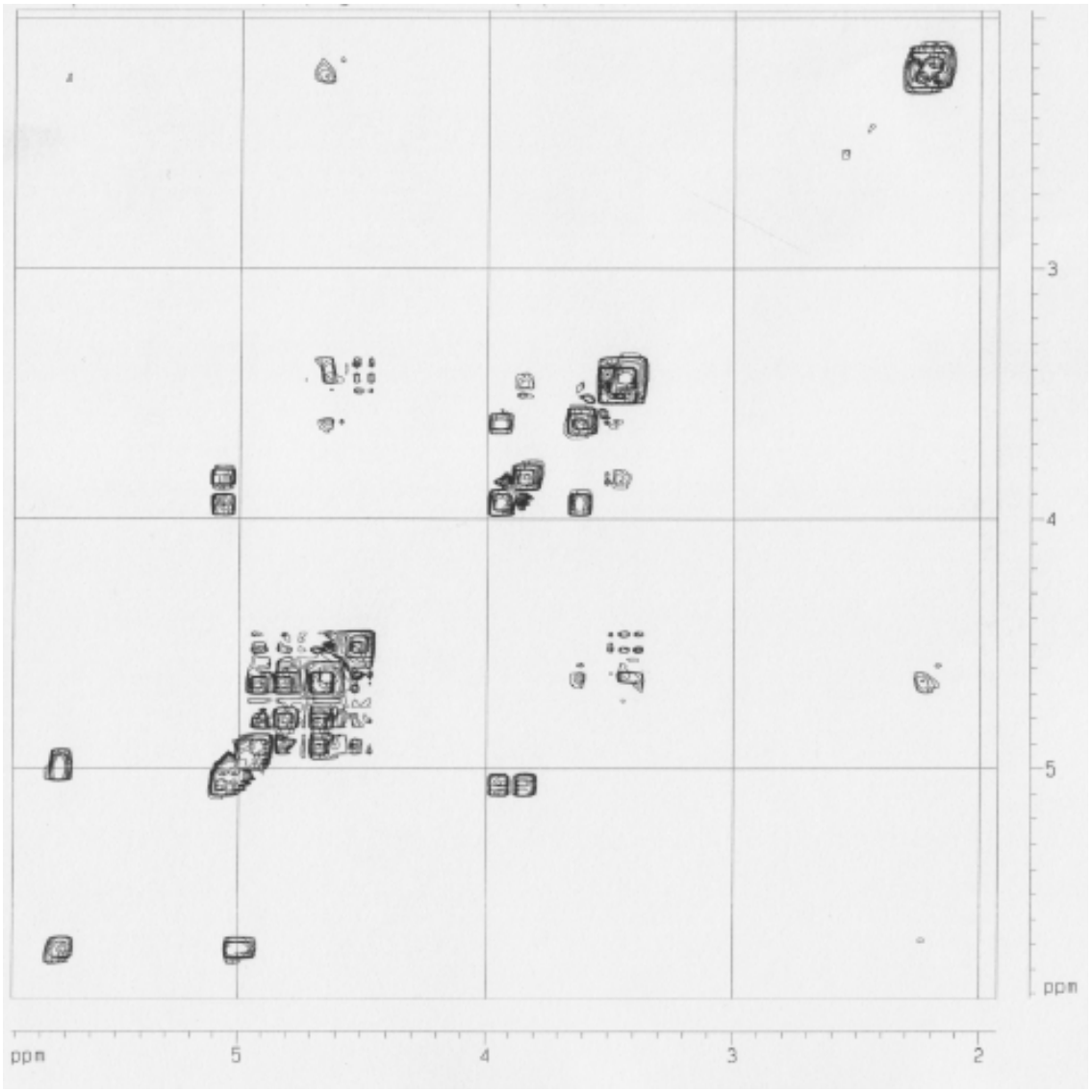
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-pentenoyl-α-D-glucopyranoside (7a)



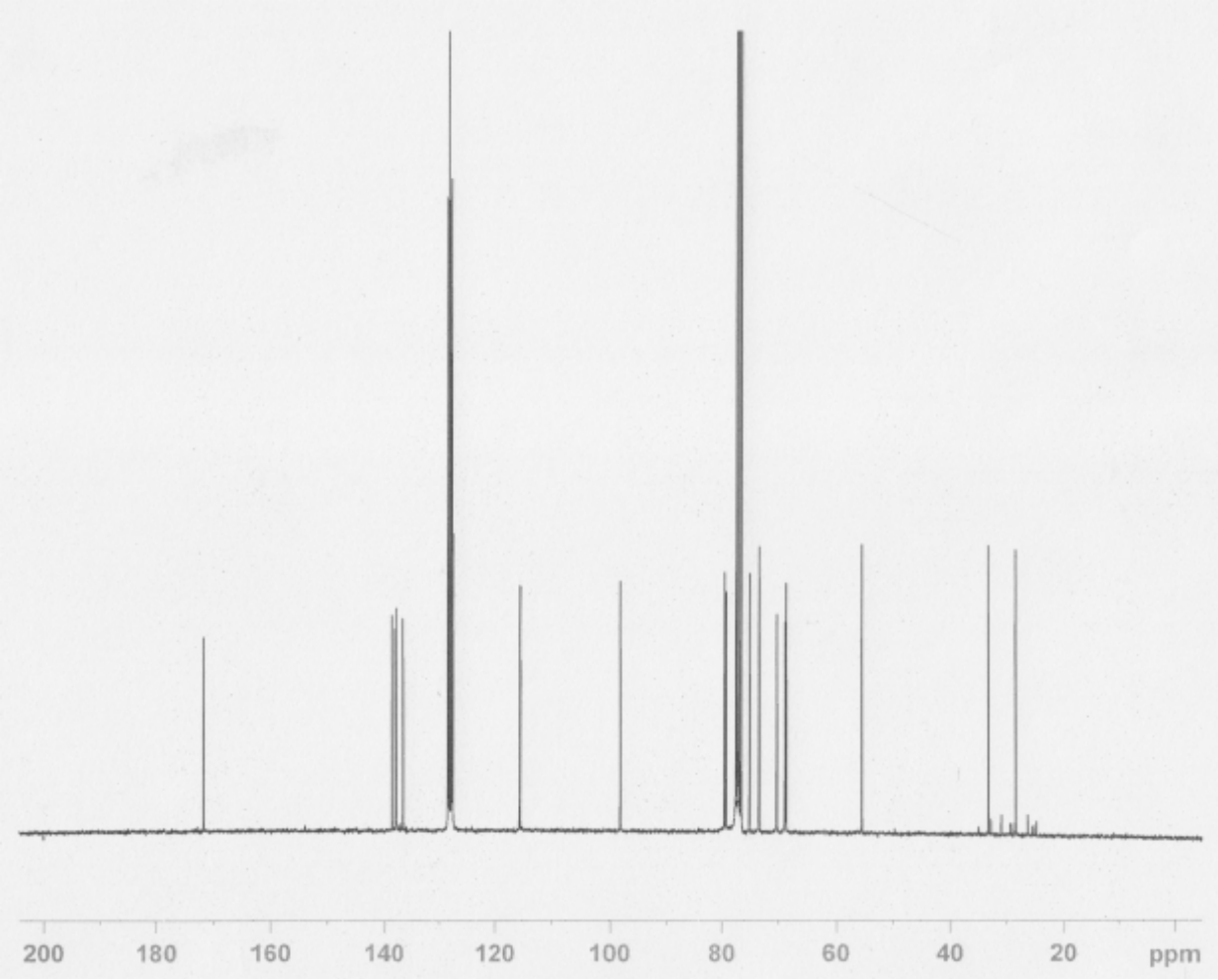
To a solution of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[5] (682 mg, 1.47 mmol) in dichloromethane (15 mL) was added 4-pentenoic acid (0.18 mL, 1.76 mmol) and DCC (363 mg, 1.76 mmol) at rt. The mixture was stirred at rt for 19 h then it was diluted with dichloromethane (50 mL) and washed with H_2O (20 mL), sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1/5 elution) to give the title compound as a white solid (664 g, 83 %). Analytical data for **7a**: R_f = 0.62 (ethyl acetate / hexane, 1/3, v/v); $[\alpha]_D^{24}$ = +2.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.09-2.19 (m, 4 H, -CH_2CH_2-), 3.37 (s, 3 H, OMe), 3.38-3.47 (m, 2 H, H-6, H-6'), 3.56 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, H-2), 3.76 (m, 1 H, H-5), 3.88 (t, 1 H, $J_{2,3}$ = 9.5 Hz, H-3), 4.44 (s, 2 H, CH_2Ph), 4.57-4.61 (m, 3 H, H-1, CH_2Ph, CH=CH_2), 4.75 (d, 1 H, CH_2Ph), 4.84-4.99 (m, 3 H, CH_2Ph, CH=CH_2), 5.01 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.3 Hz, H-4), 5.66 (m, 3 H, CH=CH_2, CH_2Ph), 7.22-7.30 (m, 15 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.4, 28.6, 31.0, 33.3, 55.4, 68.7, 68.9, 70.4, 73.5, 73.6, 75.3, 76.7, 77.1, 77.3, 77.5, 79.3, 79.6, 98.2, 115.6, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.5, 136.6, 137.8, 137.9, 138.6, 171.7 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{33}H_{38}O_7Na^+$ 569.2515, found 569.2523.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

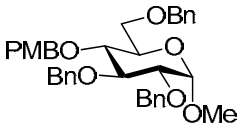


COSY spectrum (500 MHz, $CDCl_3$)

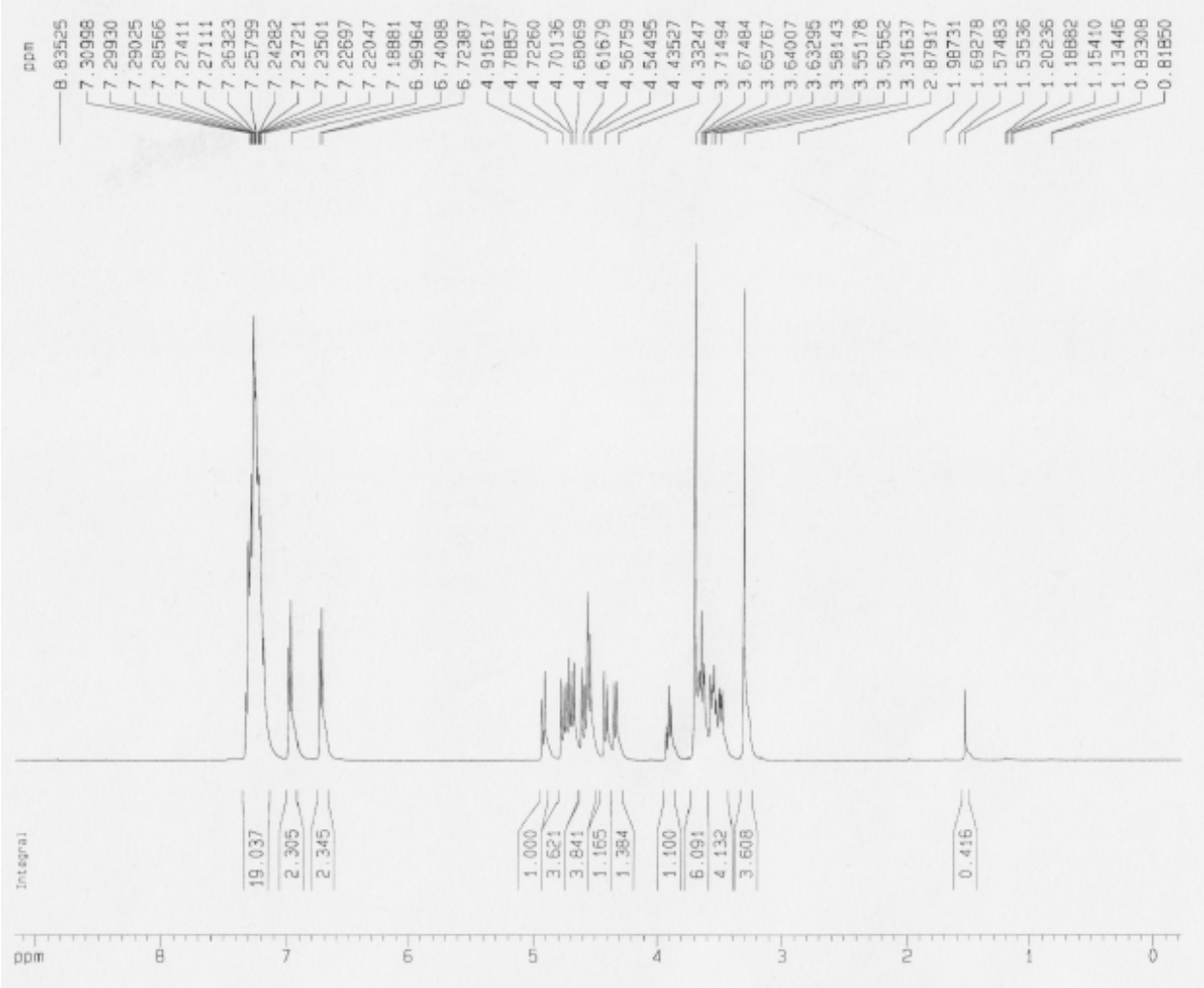


^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

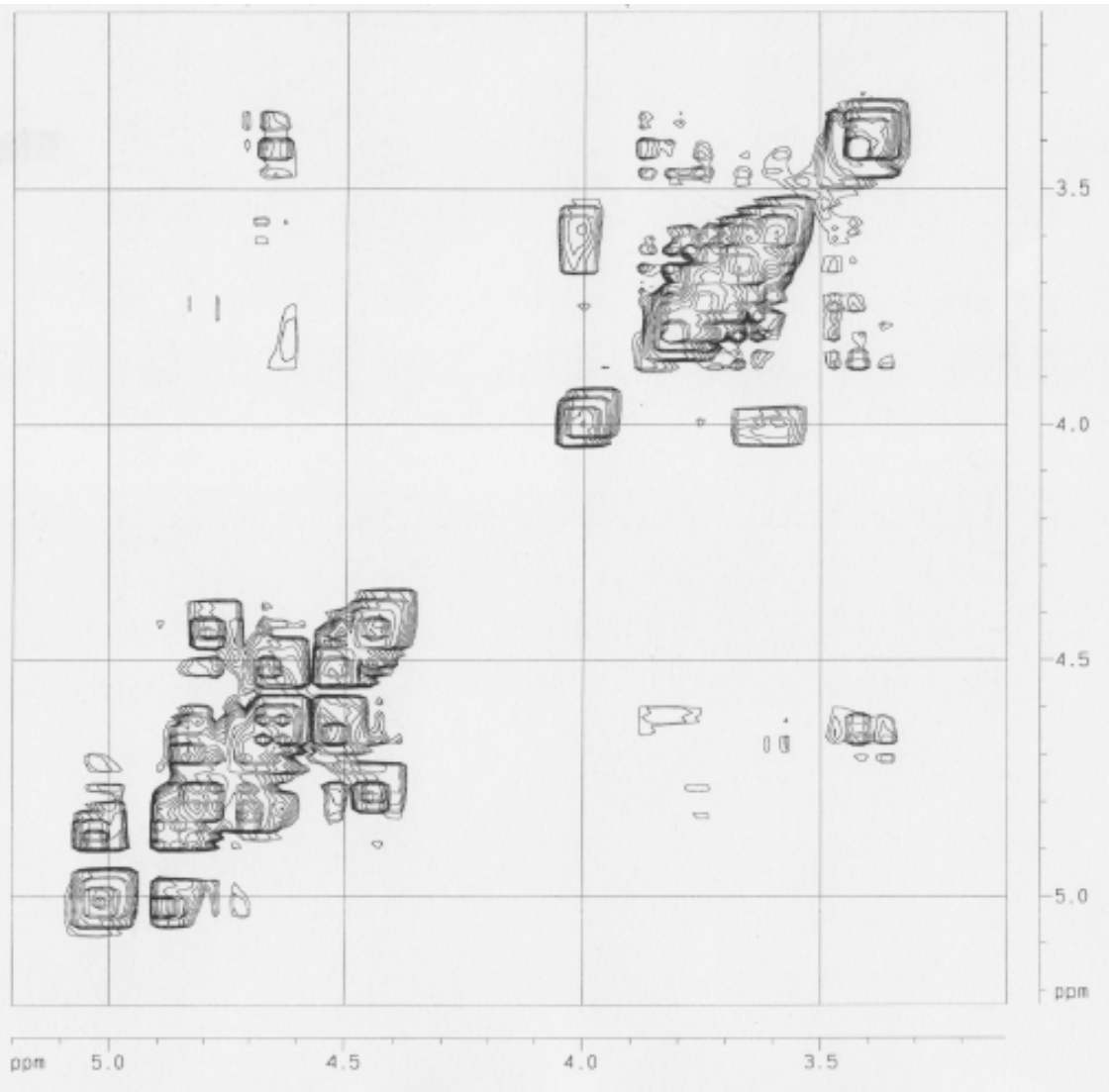
Methyl 2,3,6-tri-*O*-benzyl-4-*O*-p-methoxybenzyl-α-D-glucopyranoside (7b).



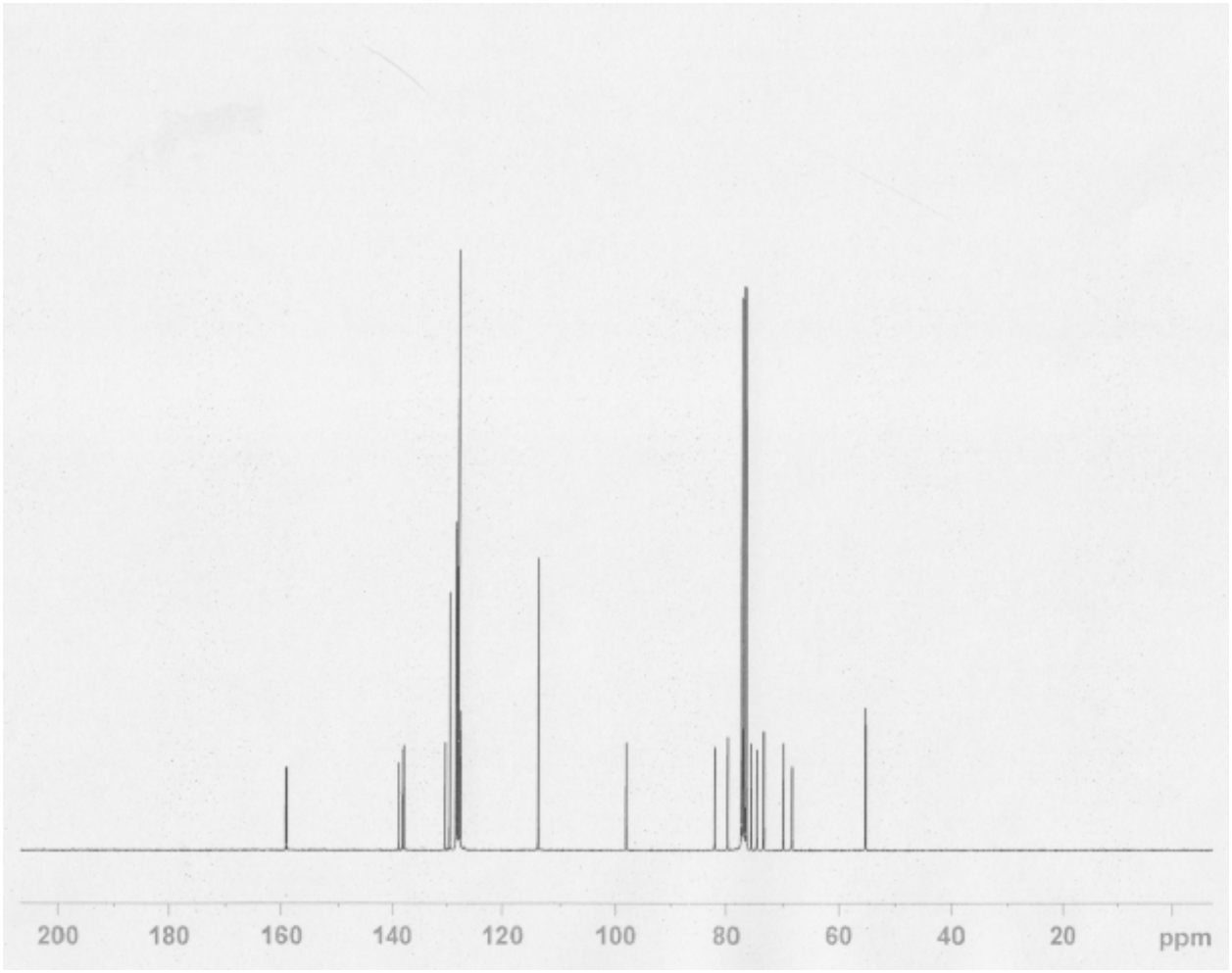
To a solution of methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside[5] (300 mg, 0.646 mmol) in DMF (3.2 mL) was added NaH (52 mg, 1.29 mmol) at 0 °C. The mixture was stirred at room temperature for 1 h then PMBCl (0.18 mL, 1.29 mmol) was added at 0°C. After stirring for 18 h at room temperature, the reaction mixture was extracted with AcOEt (50 mL) and washed with H_2O (20 mL), and sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethylacetate / hexane = 1 / 5 elution) to give the title compound as a colorless syrup (320 mg, 85 %). Analytical data for **7b**: R_f = 0.55 (ethyl acetate / hexane, 1/2, v/v); $[\alpha]_D^{23}$ = +38.5° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 3.31 (s, 3 H, OMe), 3.46 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, H-2), 3.51-3.58 (m, 2 H, H-4, H-5), 3.63-3.66 (m, 2 H, H-6, H-6'), 3.71 (s, 3 H, OMe), 3.91 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 4.34 (d, 1 H, C*H*$_2$Ph), 4.42 (d, 1 H, J^2 = 11.8 Hz, C*H*$_2$Ph), 4.54-4.63 (m, 3 H, H-1, C*H*$_2$Ph × 2), 4.68-4.79 (m, 3 H, C*H*$_2$Ph × 3), 4.92 (d, 1 H, C*H*$_2$Ph), 6.73 (d, 2 H, PM*Ph*), 6.96 (d, 2 H, PM*Ph*), 7.19-7.31 (m, 15 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ, 55.1, 55.2, 68.4, 70.0, 73.3, 73.4, 74.6, 75.7, 76.6, 77.0, 77.2, 77.3, 77.4, 79.8, 82.1, 98.1, 113.7, 126.9, 127.5, 127.6, 127.8, 127.9, 128.1, 128.3, 128.4 (× 2), 129.5, 130.4, 137.9, 138.1, 138.8, 159.2 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{36}H_{40}O_7Na^+$ 607.2672, found 607.2684.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)



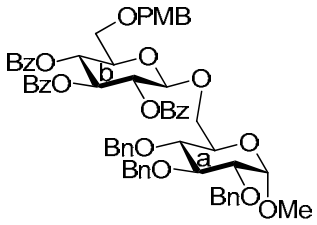
COSY spectrum (500 MHz, $CDCl_3$)



^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

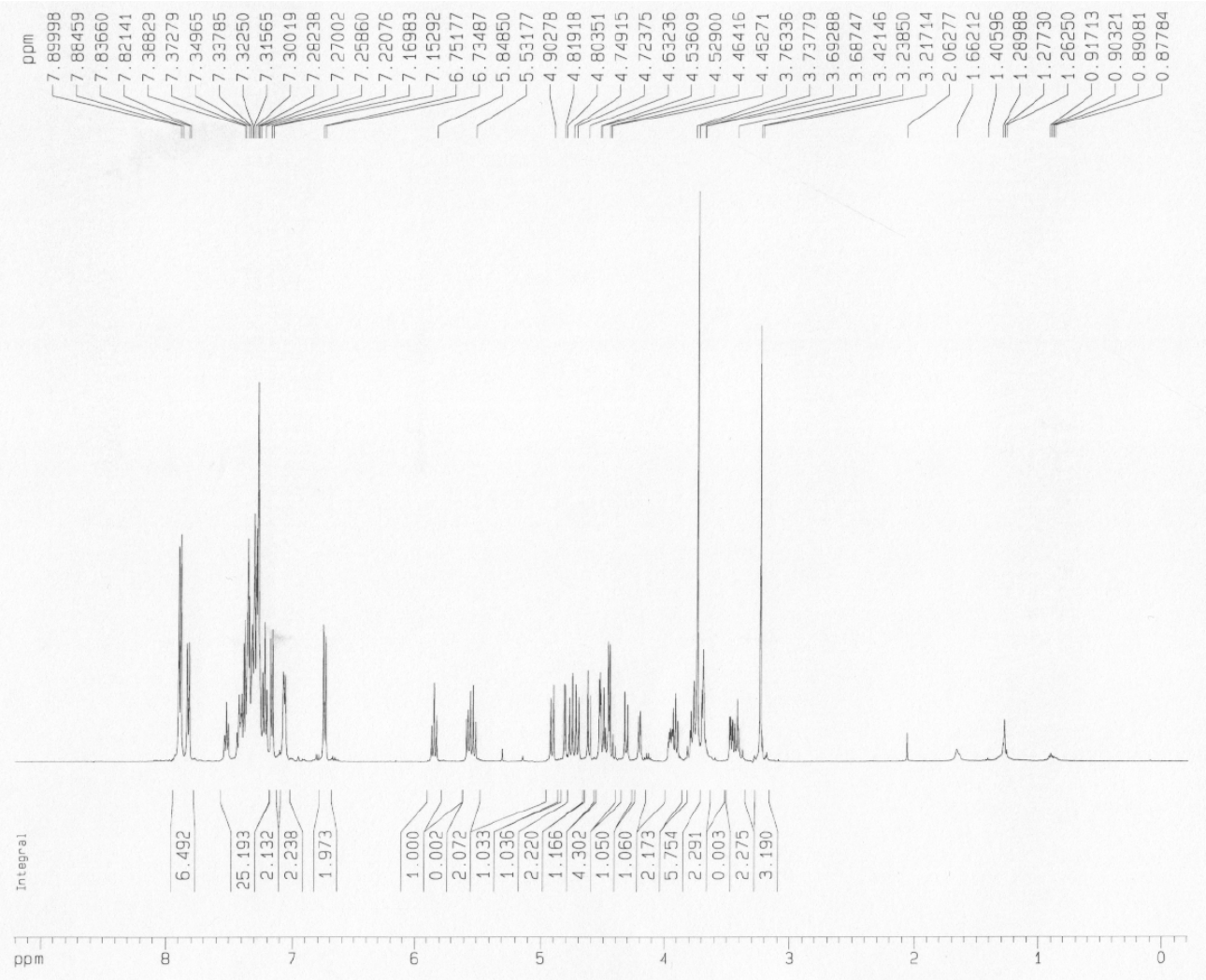
Synthesis of oligosaccharides

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-p-methoxybenzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (3b).

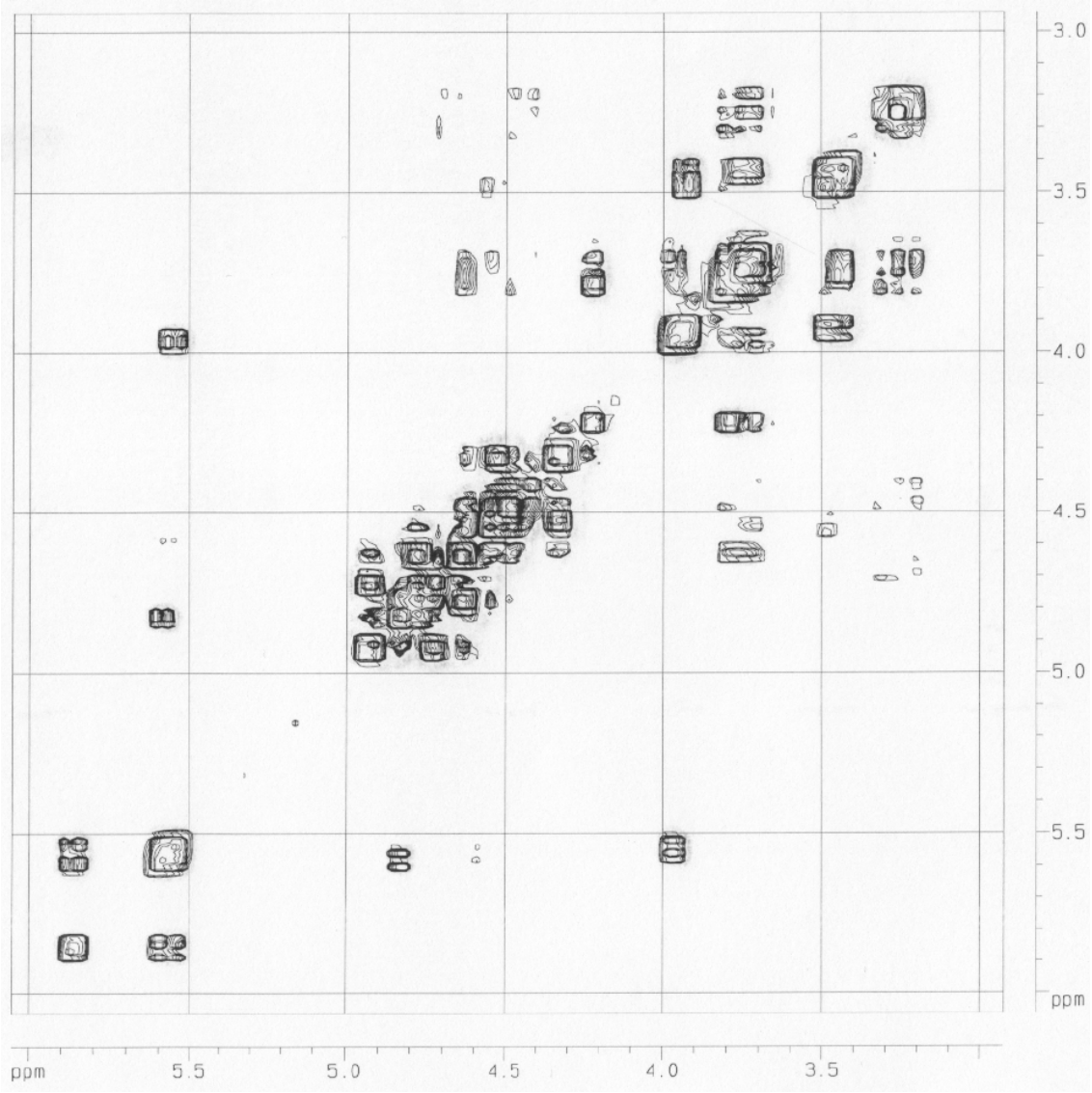


To a solution of **2d** (42 mg, 0.076 mmol) in 1,2-dichloroethane (3.0 mL) was added H_2O (1.4 μL, 0.076 mmol), NIS (52 mg, 0.23 mmol) and TfOH (10 μL, 0.11 mmol) at 0 °C. The mixture was stirred at room temperature for 10 min. After confirming of cleavage of pentenoyl group, molecular sieves 4 Å (500 mg) were added and the resulting mixture was stirred at room temperature for 20 min. Donor **1b** (50 mg, 0.076 mmol) was then added and the resulting mixture was stirred at room temperature for 2 h. After that, the reaction mixture was diluted with dichloromethane (10 mL) and the solids were filtered-off and rinsed with dichloromethane. The combined filtrate (20 mL) was washed with sat. aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1 / 3 elution) to give the title compound **3b** as a colorless syrup (65 mg, 81 %). Analytical data for **3b**: R_f = 0.65 (toluene / ethyl acetate, 4 / 1, v / v); $[\alpha]_D^{24}$ = +10.1° (*c* 1.0, $CHCl_3$); ^{1}H-NMR

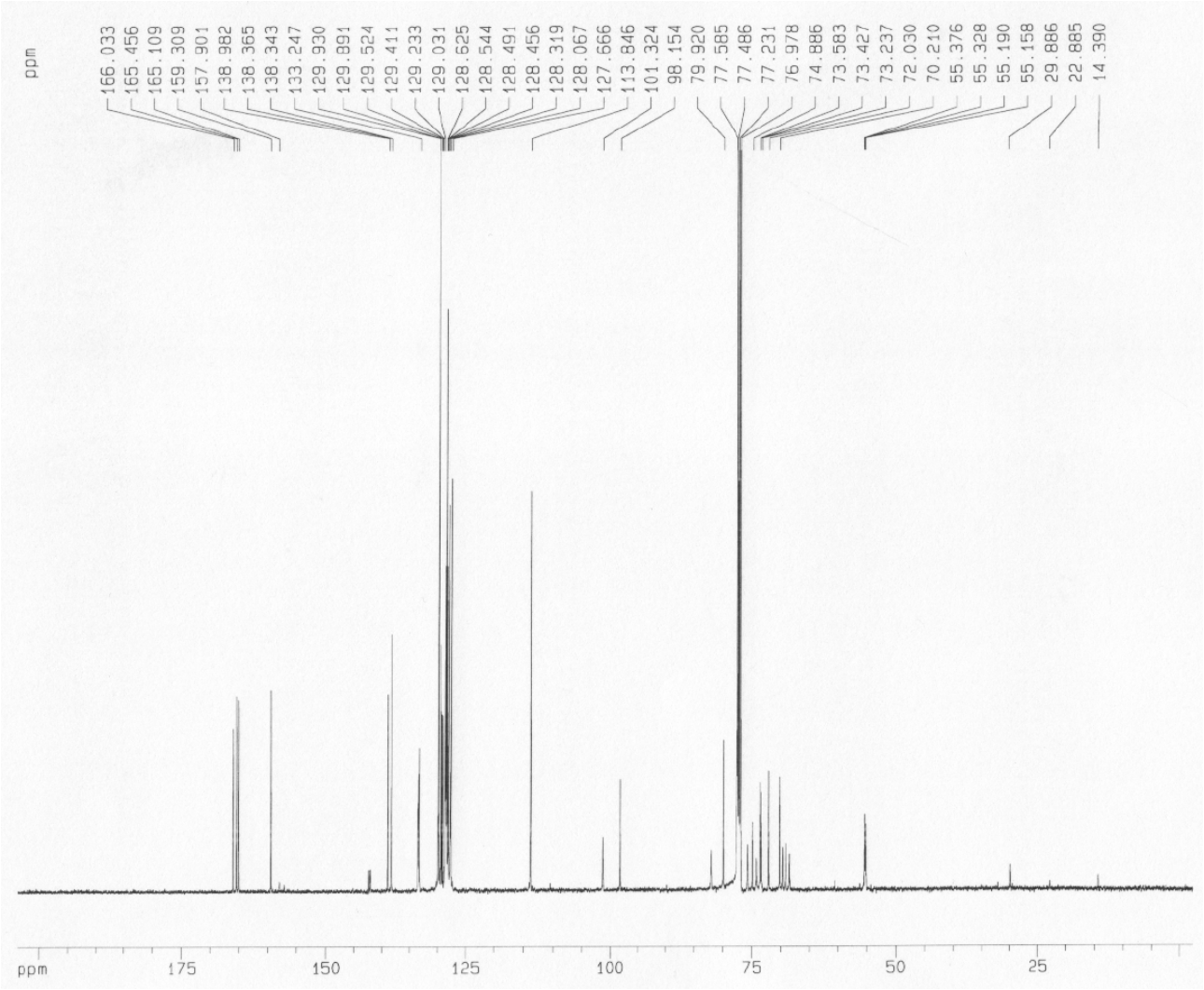
(500 MHz, $CDCl_3$): δ, 3.24 (s, 3 H, OMe), 3.42 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4a) 3.46 (dd, 1 H, $J_{2,3}$ = 9.6 Hz, H-2a), 3.67-3.69 (m, 2 H, H-6'a, H-6'b), 3.74-3.78 (m, 5 H, PhO*Me*, H-3a, H-6a), 3.89-3.94 (m, 2 H, H-5a, H-5b), 4.20 (m, 1 H, H-6b), 4.31 (d, 1 H, C*H*$_2$Ph), 4.45-4.53 (m, 4 H, $J_{1,2}$ = 3.5 Hz, H-1a, C*H*$_2$Ph), 4.62 (d, 1 H, J_{gem} = 12.1 Hz, C*H*$_2$Ph), 4.72-4.79 (m, 2 H, C*H*$_2$Ph), 4.80 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1b), 4.91 (d, 1 H, J_{gem} = 10.9 Hz, C*H*$_2$Ph), 5.51-5.58 (m, 2 H, H-2b, H-4b), 5.84 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.6 Hz, H-3b), 6.74-7.90 (m, 34 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ, 14.4, 22.9, 55.2 (× 2), 55.3, 55.4, 60.6, 68.4, 69.1, 69.7, 70.2, 72.0, 73.2, 73.4, 73.6, 74.2, 74.3, 74.9, 75.7, 77.6, 79.9, 82.1, 98.2, 101.3 (× 2), 113.8, 127.7, 128.1, 128.3, 128.5 (× 3), 128.6, 129.2, 129.4, 129.5, 129.9 (× 2), 133.1, 133.2, 133.4, 133.5, 138.3, 138.4, 138.9, 159.3, 165.1, 165.5, 166.0 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{63}H_{62}O_{15}Na^+$ 1081.3986, found 1081.3967.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

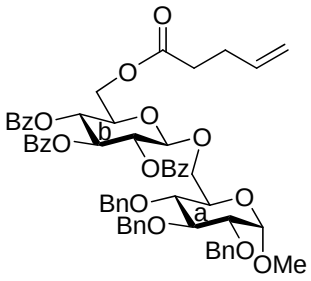


COSY spectrum (500 MHz, $CDCl_3$)



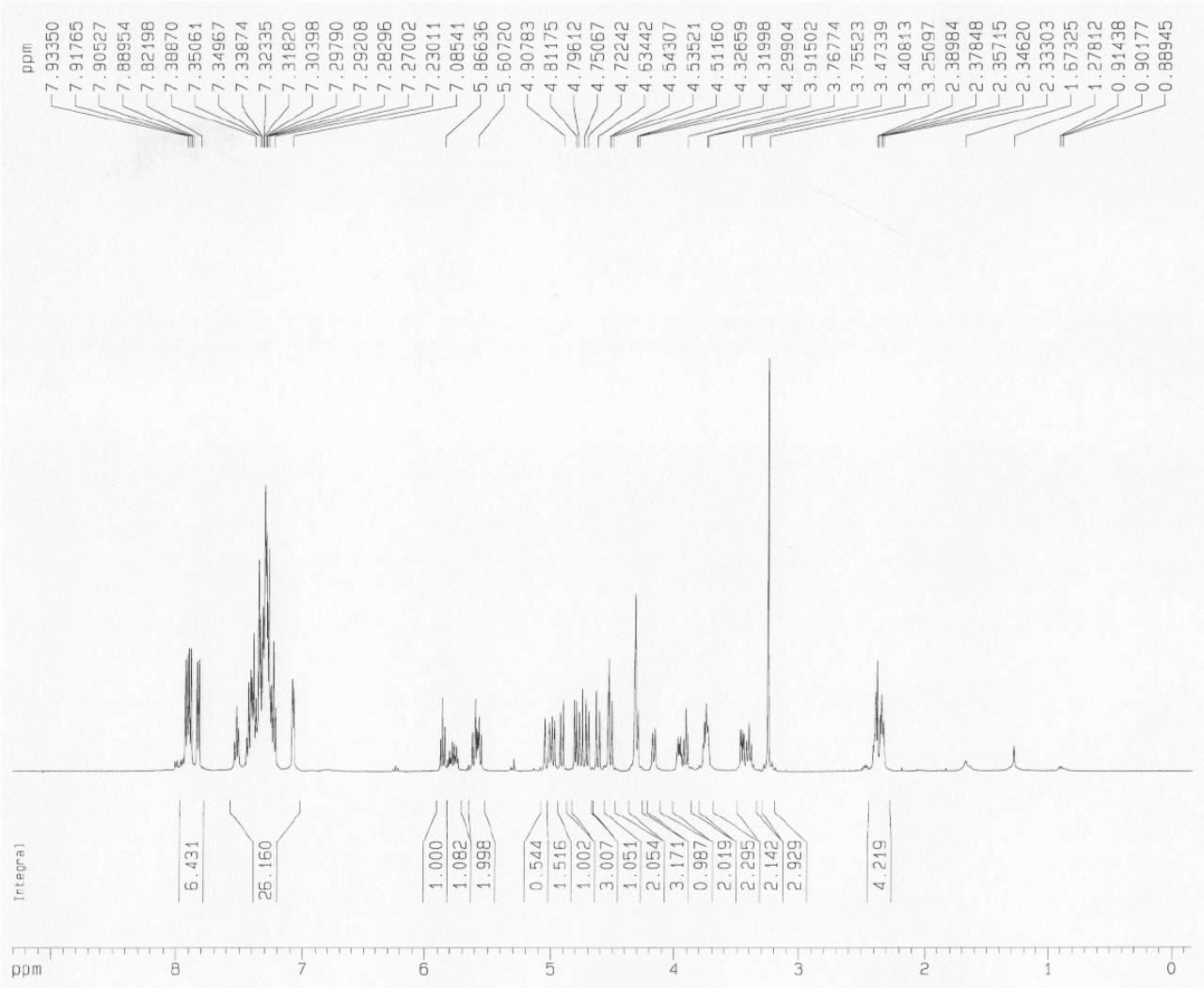
^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-pentenoyl-β-D-glucopyranosyl) -α-D-glucopyranoside (3c).

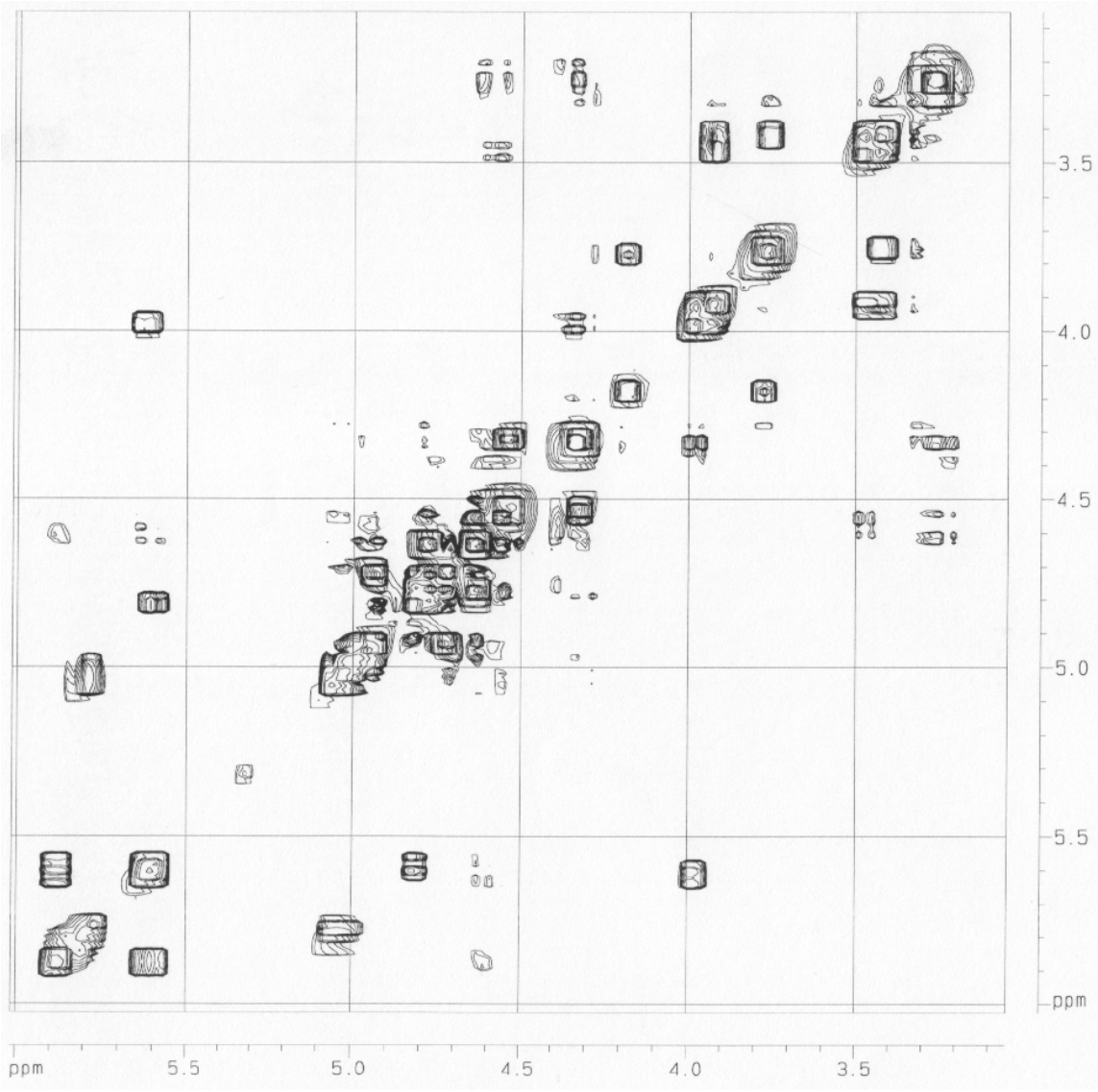


To a solution of donor **1d** (55 mg, 0.078 mmol), acceptor **2c** (45 mg, 0.078 mmol), and molecular sieves 3 Å (500 mg) in 1,2-dichloroethane (2.8 mL) were added TMSI (16 μL, 0.12 mmol) at 0 °C. The mixture was stirred in the dark at room temperature for 30 min, then AgOTf (40 mg, 0.156 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. The mixture was then diluted with dichloromethane (10 mL), the solid was filtered off and rinsed with dichloromethane. The combined filtrate (20 mL), was washed with sat. aq. $NaHCO_3$ (10 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethylacetate / hexane = 1 / 4 elution) to give the title compound **3c** as a colorless syrup (68 mg, 85 %). Analytical data for **3c**: R_f = 0.5 (toluene / ethylacetate, 4 / 1, v / v); $[\alpha]_D^{24}$ = +13.9° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 2.33-2.39 (m, 4 H, -CH_2CH_2-), 3.25 (s, 3 H, OMe), 3.41 (t, 1 H, H-3a), 3.46 (dd, 1 H, $J_{1,2}$ = 3.5 Hz, $J_{2,3}$ = 9.6 Hz, H-2a), 3.74-3.77 (m, 2 H, H-5a, H-6'a), 3.92 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ =9.3 Hz, H-4a), 3.96 (m, 1 H, H-5b), 4.17 (m, 1 H, H-6a), 4.29-4.32 (m, 3 H, C*H*$_2$Ph, H-6b,

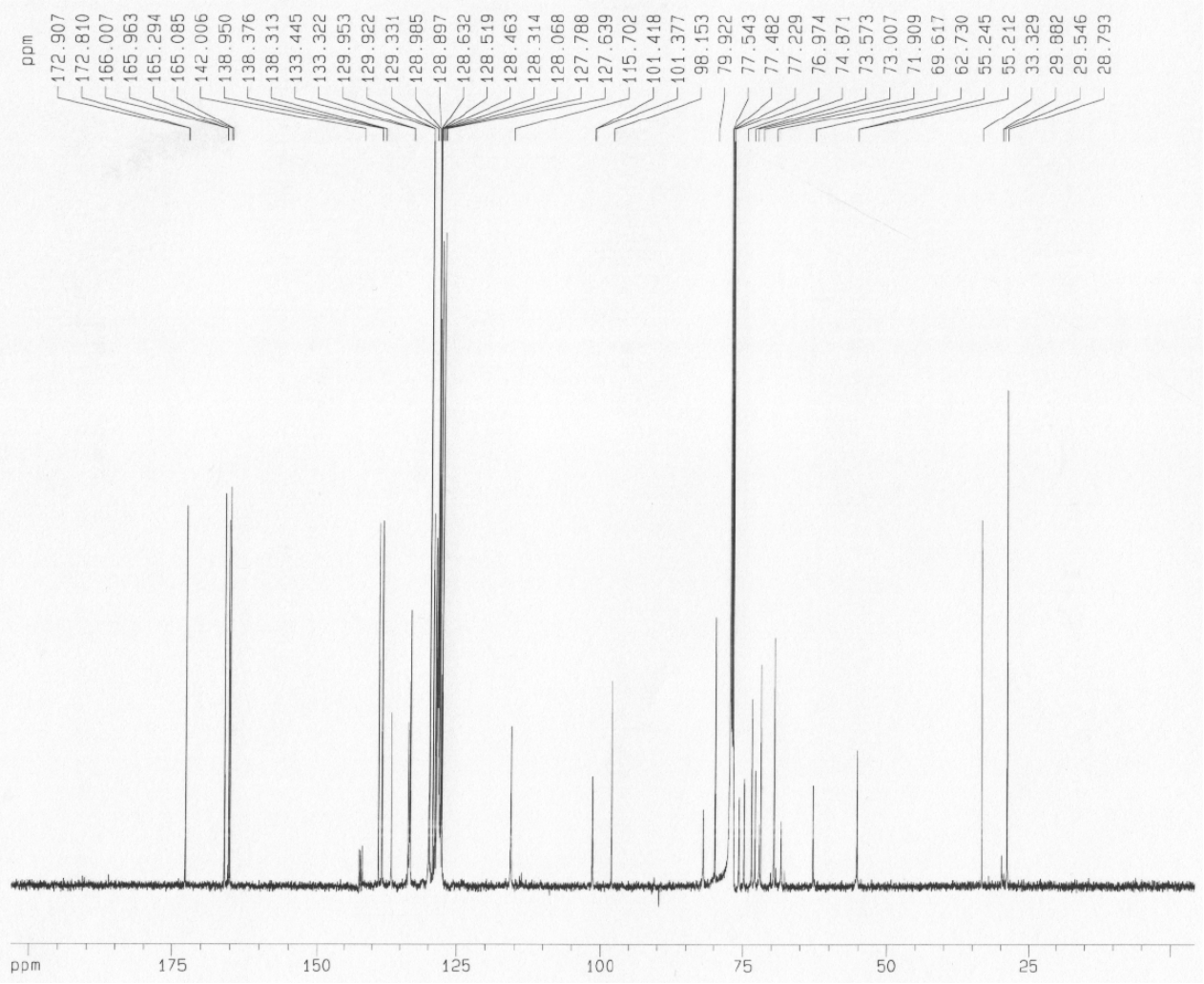
H-6'b), 4.51-4.54 (m, 2 H, H-1a, C*H*$_2$Ph), 4.61-4.77 (m, 3 H, C*H*$_2$Ph), 4.80 (d, 1 H, $J_{1,2}$ =7.8 Hz, H-1b), 4.91 (d, 1 H, J_{gem} =10.9 Hz, C*H*$_2$Ph), 4.97-5.05 (m, 2 H, -CH=C*H*$_2$), 5.56-5.63 (m, 2 H, H-2b, H-4b), 5.79 (m, 1 H, -C*H*=CH$_2$), 5.87 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ =9.6 Hz, H-3b), 7.09-7.93 (m, 30 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ, 28.8, 29.9, 33.3, 55.2 (× 2), 62.7, 67.8, 68.5, 69.3, 69.6, 70.2, 71.9, 72.2, 72.3, 73.0, 73.6, 74.9, 75.7, 75.8, 77.5, 77.6, 79.9, 82.1, 98.2, 101.4 (× 2), 115.7, 127.6, 127.8, 128.1, 128.3, 128.5 (× 2), 128.6, 128.9 (× 2), 129.3, 129.9 (× 2), 130.1, 133.3, 133.4, 136.7 (× 3), 138.3, 138.4, 138.9, 165.1, 165.3, 165.4, 165.9, 172.8 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{60}H_{60}O_{15}Na^+$ 1043.3830, found 1043.3880.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

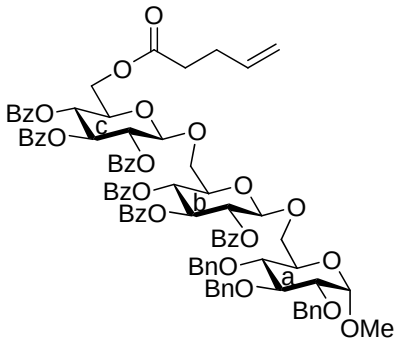


COSY spectrum (500 MHz, $CDCl_3$)



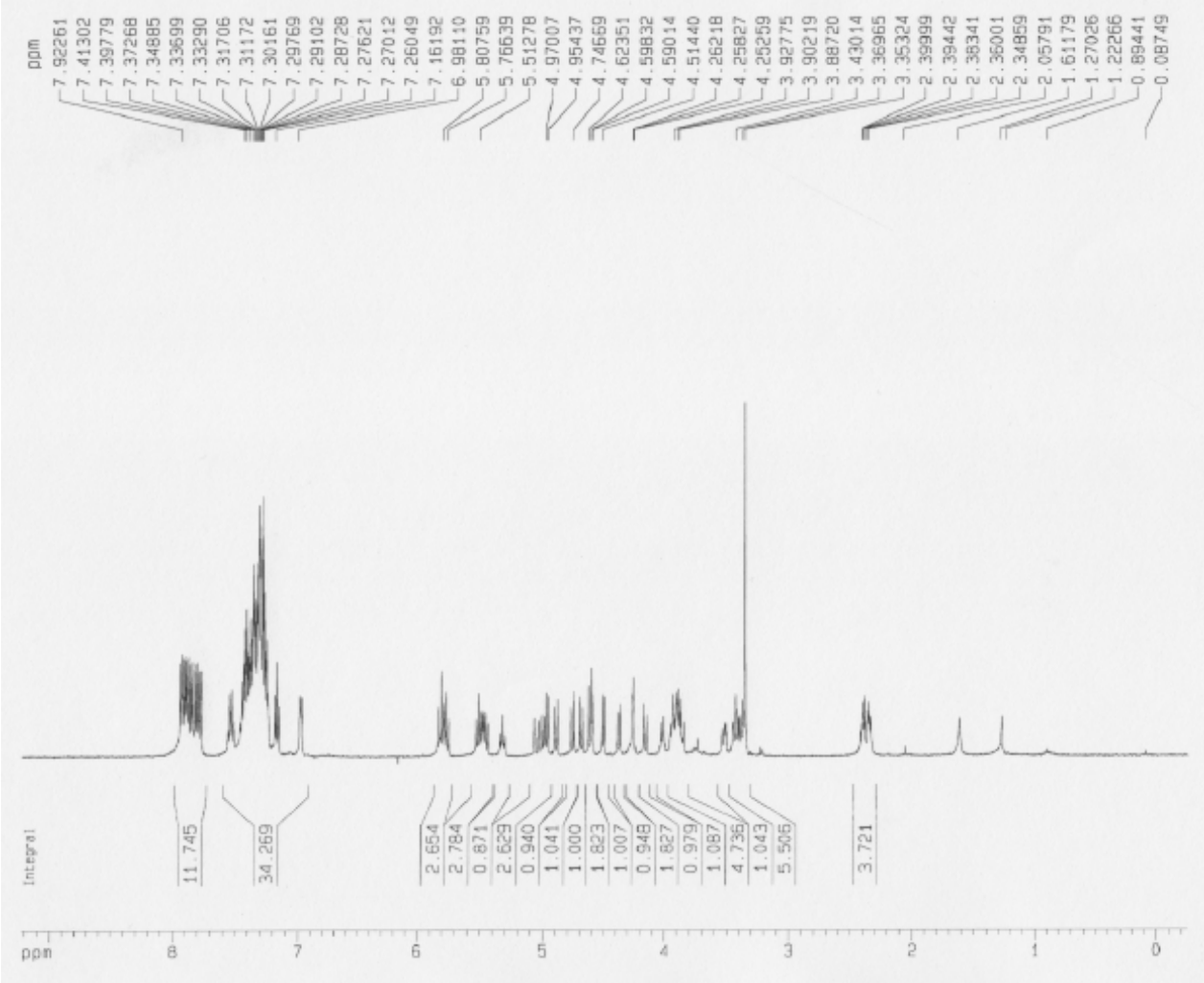
^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-pentenoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-α-D-glucopyranoside (4).

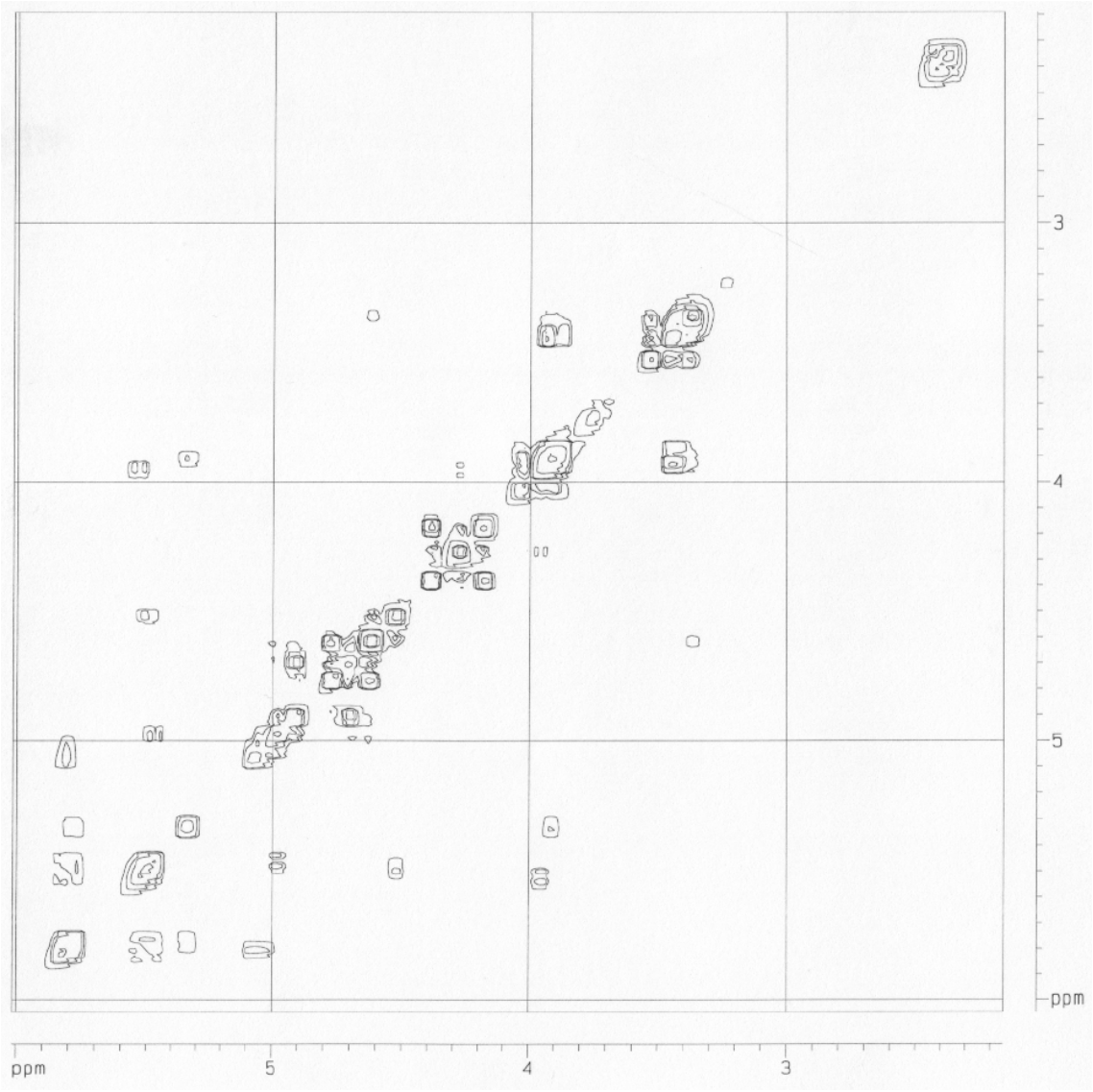


To a solution of donor **1d** (160 mg, 0.23 mmol), acceptor **3b** (200 mg, 0.19 mmol) and molecular sieves 3 Å (1.5 g) in 1,2-dichloroethane (8.3 mL) were added TMSI (52 μL, 0.38 mmol) at 0 °C. The mixture was stirred in the dark at room temperature for 30 min, AgOTf (175 mg, 0.68 mmol) was added and the resulting mixture was stirred at 40 °C for 2 h. After that, the mixture was diluted with dichloromethane (20 mL), the solid was filtered off and rinsed with dichloromethane. The combined filtrate (40 mL), was washed with sat. aq. $NaHCO_3$ (20 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethylacetate / hexane = 1 / 2 elution) to give the title compound **4** as a colorless syrup (231 mg, 82 %). Analytical data for **4**: R_f = 0. 48 (ethylacetate / hexane, 1 / 2, v / v); $[\alpha]_D^{24}$ = -10.4° (*c* 0.7, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 2.34-2.39 (m, 4 H, -CH_2CH_2-), 3.35 (s, 3 H, OMe), 3.37-3.43 (m, 3 H, H-2a, H-4a, H-6b), 3.51 (m, 1 H, H-6'b), 3.86-3.92 (m, 5 H, H-3a, H-5a, H-6'a, H-5b, H-5c), 4.01 (m, 1

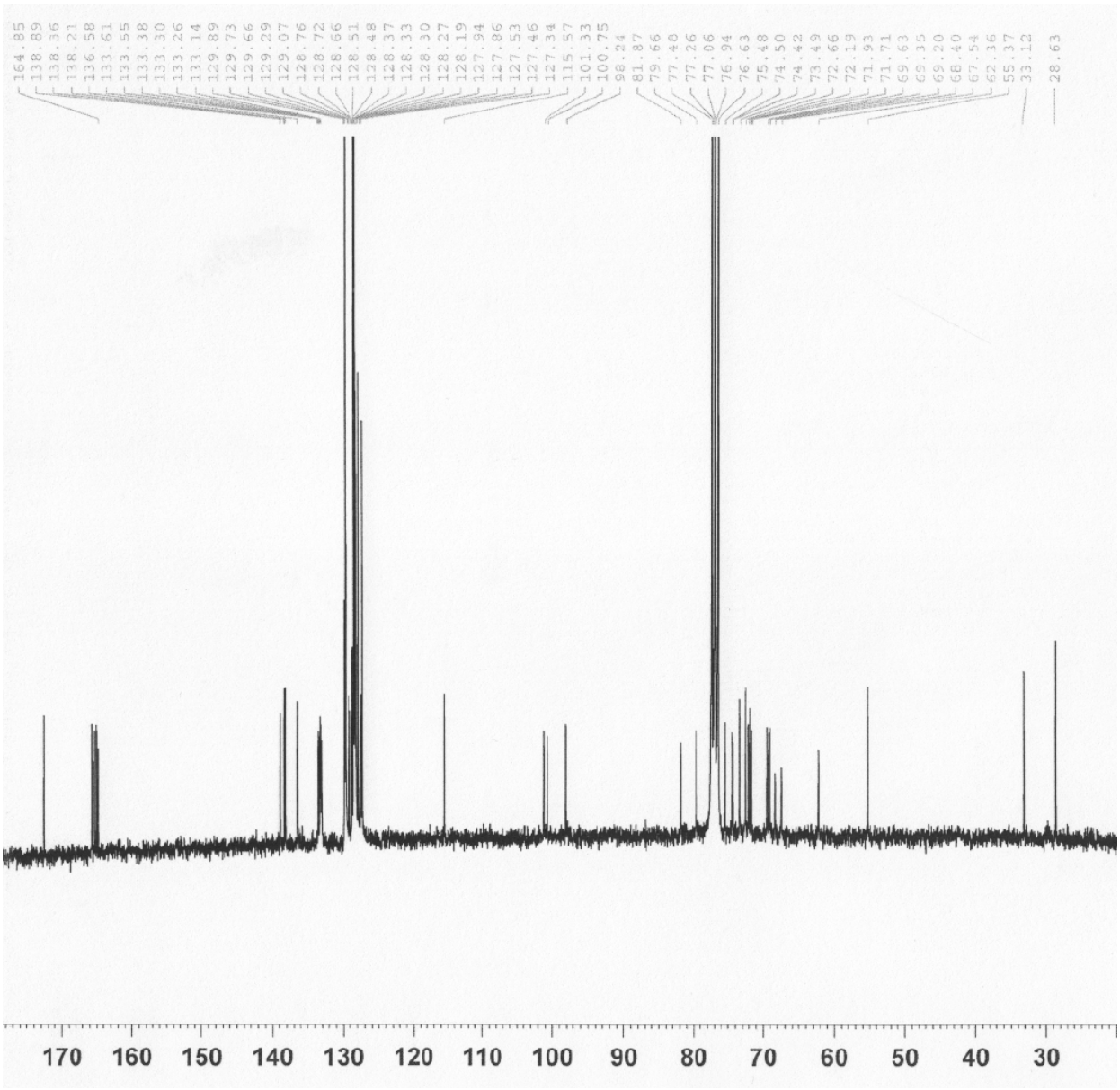
H, H-6a), 4.16 (d, 1 H, J_{gem} =11.3 Hz, CH_2Ph), 4.25-4.26 (m, 2 H, H-6c, H-6'c), 4.37 (d, 1 H, J_{gem} =11.3 Hz, CH_2Ph), 4.50 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1c), 4.59-4.62 (m, 2 H, $J_{1,2}$ = 4.1 Hz, H-1a, CH_2Ph), 4.68 (d, 1 H, J_{gem} =12.5 Hz, CH_2Ph), 4.76 (d, 1 H, J_{gem} =12.1 Hz, CH_2Ph), 4.89 (d, 1 H, J_{gem} =10.9 Hz, CH_2Ph), 4.95-5.09 (m, 3 H, $J_{1,2}$ = 7.9 Hz, -CH=CH_2, H-1b), 5.32 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.8 Hz, H-4b), 5.46-5.51 (m, 3 H, H-2b, H-2c, H-4c), 5.77-5.83 (m, 3 H, -C*H*=CH_2, H-3c, H-3b), 6.98-7.92 (m, 45 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ, 28.6, 33.1, 55.4, 62.4, 67.5, 68.4, 69.2, 69.3, 69.6, 71.7, 71.9, 72.2, 72.7, 73.5, 74.4, 74.5, 75.5, 76.6, 76.9, 79.7, 81.9, 98.2, 100.8, 101.3, 115.6, 127.3, 127.5 (× 2), 127.9 (× 2), 128.2, 128.3 (× 3), 128.4, 128.5 (× 2), 128.7 (× 2), 128.8, 129.1, 129.3, 129.7 (× 2), 129.9, 133.1, 133.3 (× 2), 133.4, 133.6 (× 2), 136.6, 138.2, 138.7, 138.9, 164.9, 165.1 (× 2), 165.4, 165.7, 165.8, 172.6 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{87}H_{82}O_{23}Na^+$ 1517.5145, found 1517.5133.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

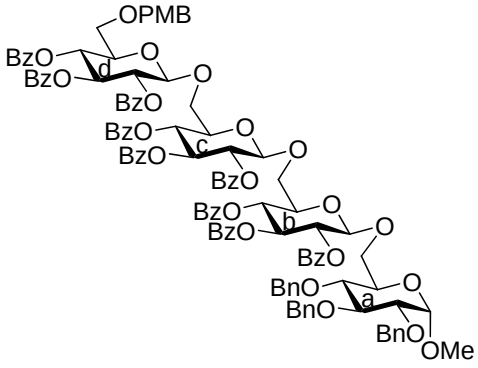


COSY spectrum (500 MHz, $CDCl_3$)



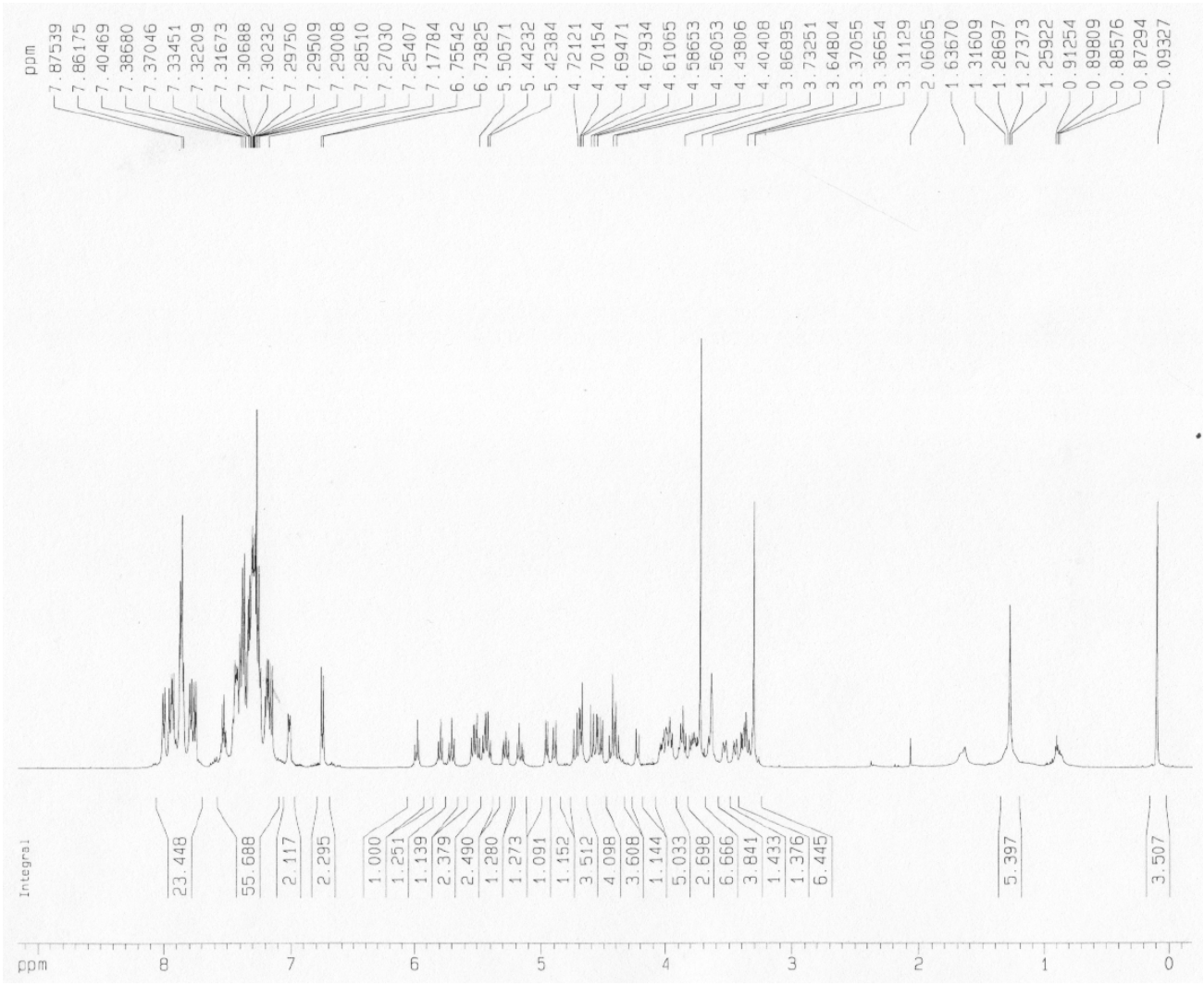
^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-{2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-p-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-α-D-glucopyranoside (5).

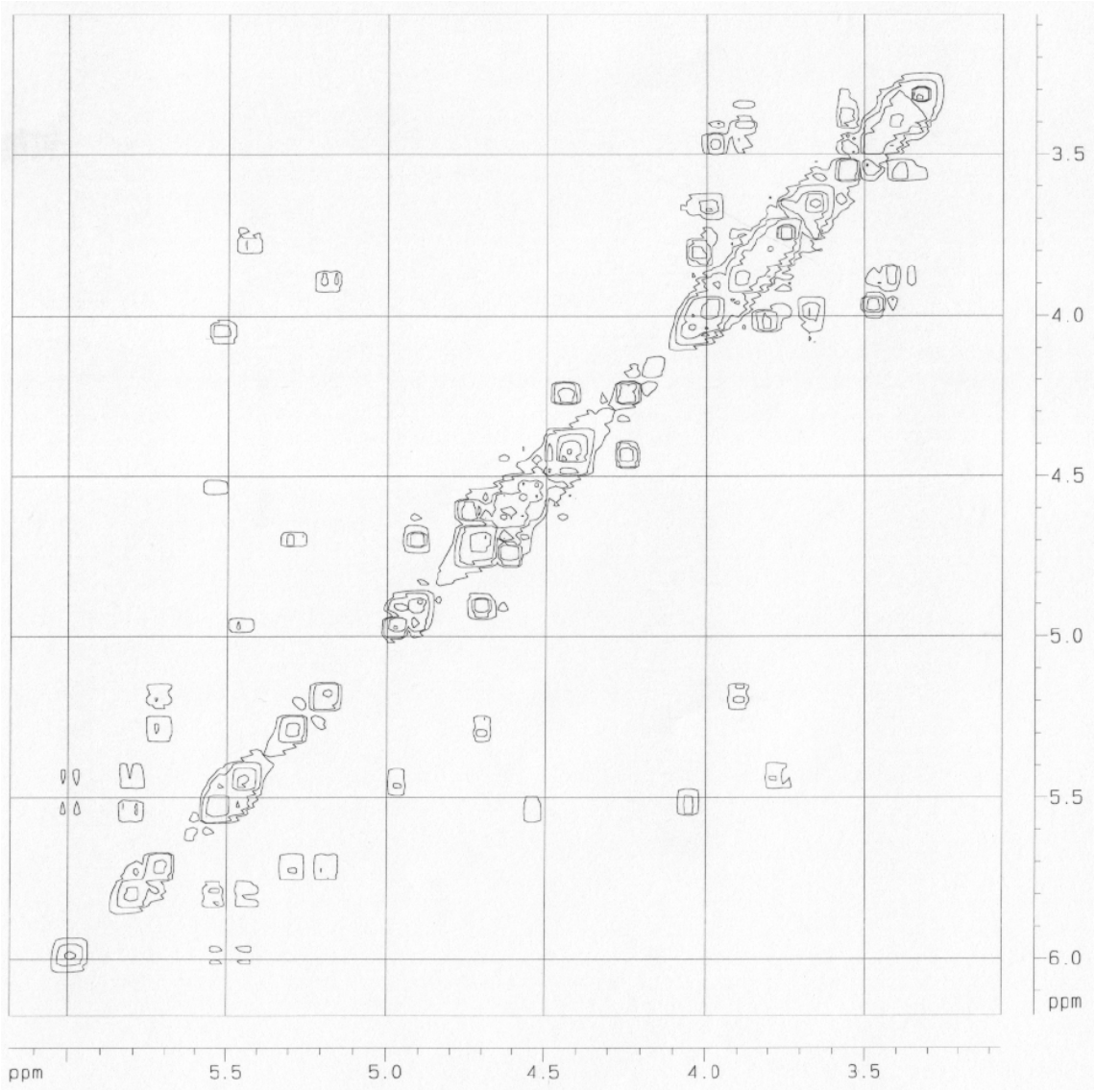


To a solution of acceptor **4** (77 mg, 0.052 mmol) in 1,2-dichloroethane (2.3 mL) was added H_2O (0.9 μL, 0.052 mmol), NIS (35 mg, 0.16 mmol) and TfOH (6.8 μL, 0.077 mmol) at 0 °C. The mixture was stirred at room temperature for 10 min. After confirming of the cleavage of the pentenoyl group by TLC, molecular sieves 4 Å (500 mg) were added and the resulting mixture was stirred at room temperature for 20 min. Donor **1b** (41 mg, 0.062 mmol) was added and the reaction mixture was stirred at room temperature for 1 h, then diluted with dichloromethane (10 mL), the solid was filtered-off and rinsed with dichloromethane. The combined filtrate (20 mL) was washed with sat. aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethylacetate / hexane = 1 / 2 elution) to give the title compound **5** as a colorless syrup (73 mg, 71%). Analytical data for **5**: Rf = 0.38

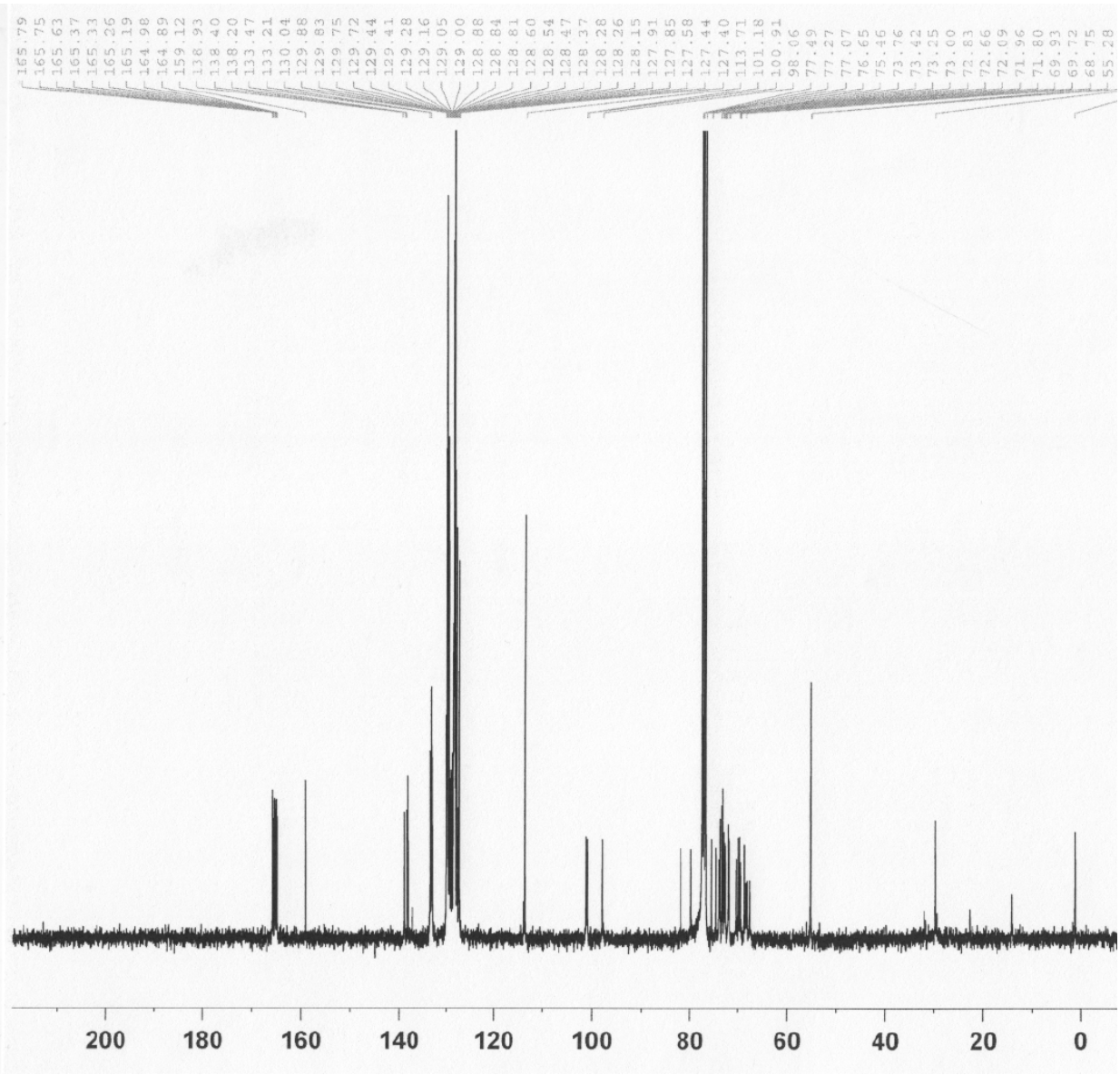
(ethylacetate / hexane, 1 / 2, v / v); $[\alpha]_D^{24}$ = -4.7° (*c* 0.5, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 3.31 (s, 3 H, OMe), 3.31-3.39 (m, 3 H, H-2a, H-4a, H-6'a), 3.40 (m, 1 H, H-6d), 3.55 (m, 1 H, H-6a), 3.64-3.65 (m, 2 H, H-5a, H-6c), 3.73-3.80 (m, 5 H, H-5b, H-6'b, PhO*Me*), 3.84-3.88 (m, 2 H, H-3a, H-5d), 3.94-4.02 (m, 4 H, H-6b, H-5c, H-6'c, H-6'd), 4.24 (d, 1 H, J_{gem} = 12.1 Hz, C*H*$_2$Ph), 4.32-4.43 (m, 3 H, C*H*$_2$Ph), 4.51-4.61 (m, 3 H, $J_{1,2}$ = 3.4 Hz, H-1a, $J_{1,2}$ = 7.9 Hz, H-1c, C*H*$_2$Ph), 4.69-4.74 (m, 3 H, H-1d, C*H*$_2$Ph), 4.89 (d, 1 H, J_{gem} = 11.1 Hz, C*H*$_2$Ph), 4.95 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1b), 5.17 (t, 1 H, $J_{4,5}$ = 9.6 Hz, H-4d), 5.28 (t, 1 H, $J_{1,2}$ = 9.6 Hz, H-2d), 5.41-5.50 (m, 2 H, H-2b, H-4b), 5.50-5.52 (m, 2 H, H-2c, H-4c), 5.70 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3d), 5.79 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3b), 5.98 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.8 Hz, H-3c), 6.74-8.05 (m, 64 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ, 1.1, 14.2, 22.7, 29.4, 29.7, 31.9, 55.2, 55.3, 67.7, 68.2, 68.4, 68.7, 69.5, 69.7, 69.9, 70.3, 71.8, 71.9, 72.1, 72.7, 72.8, 73.0, 73.2, 73.4, 73.8, 73.9, 74.6, 75.5, 76.6, 79.8, 81.9, 98.1, 100.9, 101.0, 101.2, 113.7, 113.9, 127.3, 127.4 (× 2), 127.6, 127.9 (× 2), 128.1, 128.3 (× 2), 128.4, 128.5 (× 2), 128.6, 128.8 (× 2), 128.9, 129.0, 129.1, 129.2, 129.3, 129.4 (× 2), 129.7 (× 2), 129.8, 129.9, 130.0, 133.2, 133.5,137.3, 138.2, 138.4, 138.9, 159.1, 164.8, 164.9, 165.2, 165.3 (× 2), 165.4, 165.6, 165.7, 165.8 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{117}H_{106}O_{31}Na^+$ 2029.6616, found 2029.6638.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

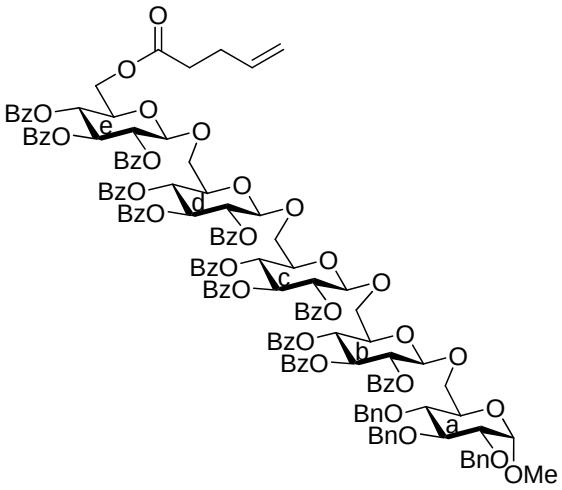


COSY spectrum (500 MHz, $CDCl_3$)



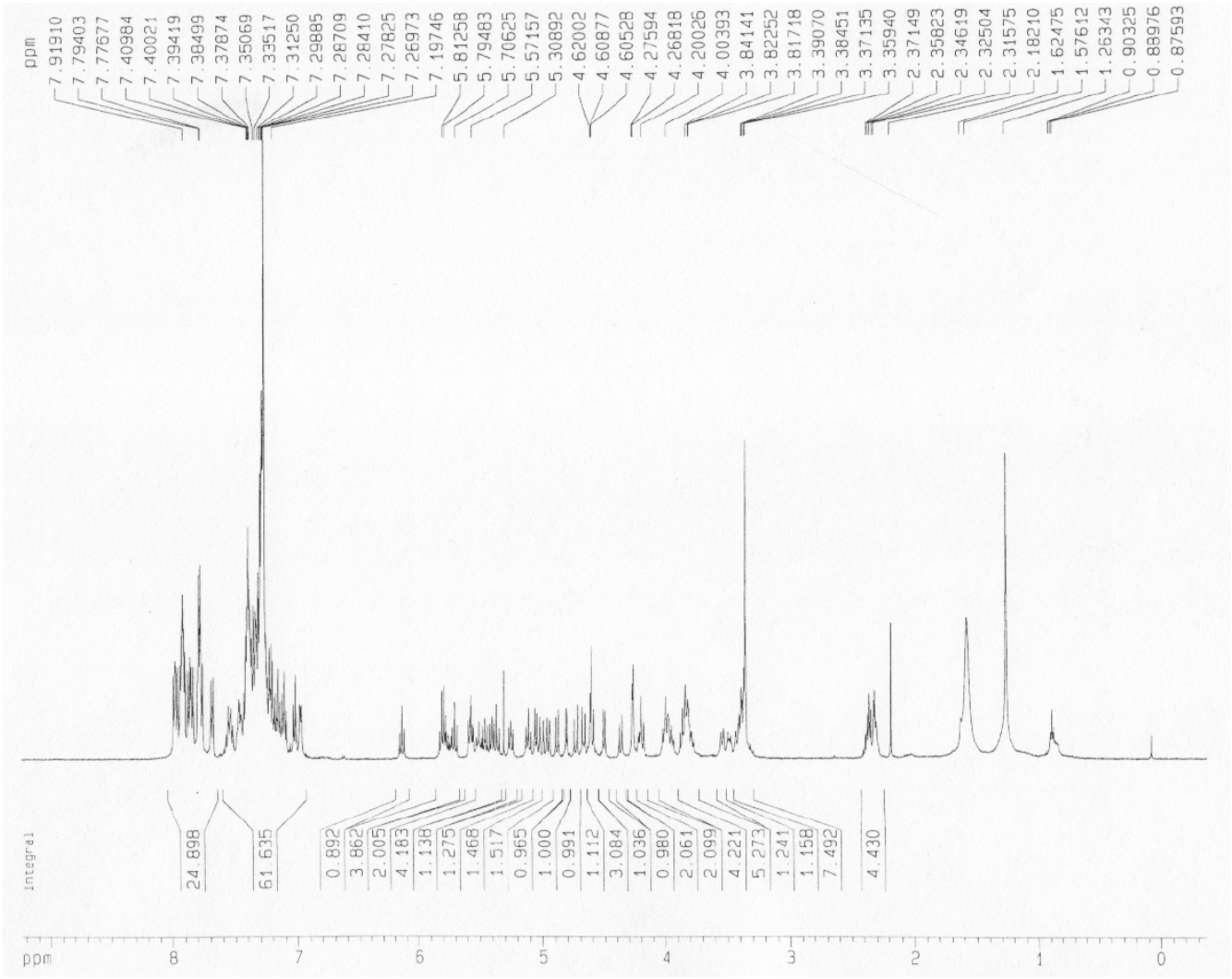
^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-{2,3,4-tri-*O*-benzoyl-6-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-pentenoyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranosyl}-β-D-glucopyranosyl]-α-D-glucopyranoside (6).

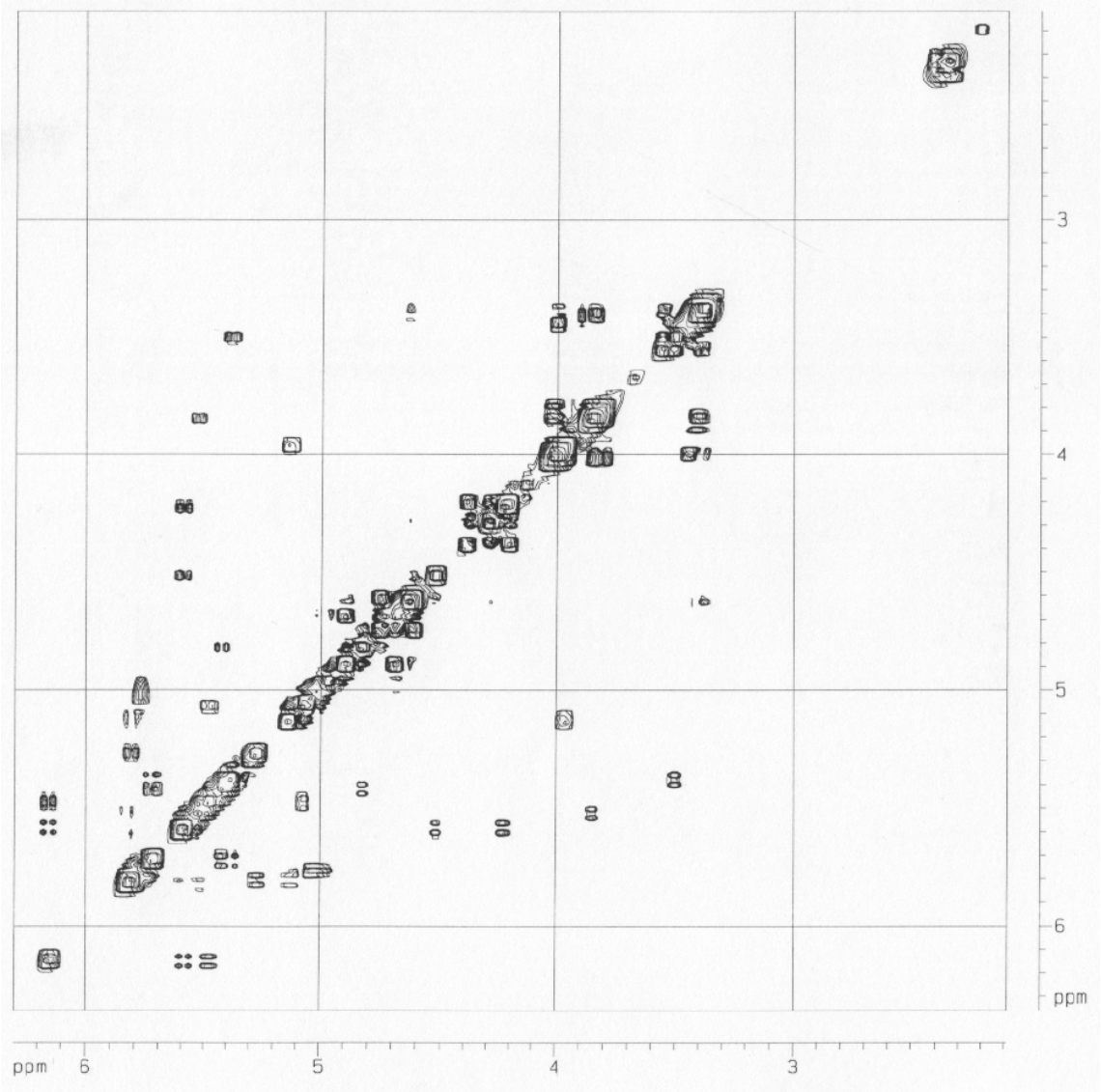


To a solution of donor **1d** (21 mg, 0.030 mmol), acceptor **5** (50 mg, 0.025 mmol) and molecular sieves 3 Å (500 mg) in 1,2-dichloroethane (2.0 mL) TMSI (6.8 μL, 0.050 mmol) was added at 0 °C. The resulting mixture was stirred in the dark at room temperature for 30 min. After that, AgOTf (23 mg, 0.090 mmol) was added and the reaction mixture was stirred at 40 °C for 2 h, then diluted with dichloromethane (20 mL), the solid was filtered-off and rinsed with dichloromethane. The combined filtrate (30 mL), was washed with sat. aq. $NaHCO_3$ (10 mL). The organic layer was concentrated *in vacuo* and the resulting residue was purified by column chromatography on silica gel (ethylacetate / hexane = 1 / 2, toluene / ethylacetate / methanol = 70 / 5 / 1 elution) to give the title compound **6** as a colorless syrup (45 mg, 75 %). Analytical data for **6**: R_f = 0.51 (ethylacetate / hexane, 1 / 2, v / v); $[\alpha]_D^{24}$ =

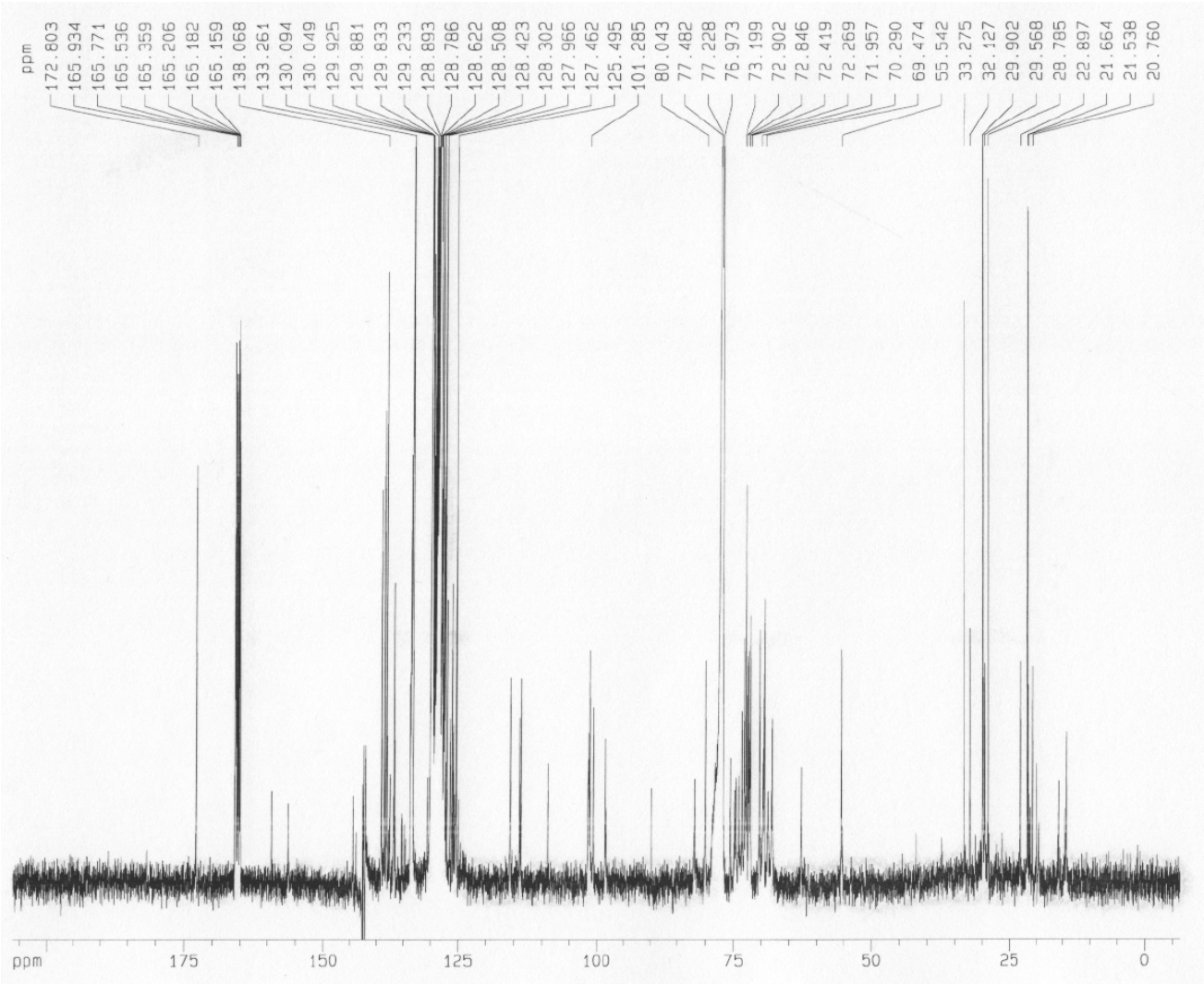
-10.5° (*c* 0.3, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 2.30-2.42 (m, 4 H, -CH_2CH_2-), 3.21-3.55 (m, 10 H, H-2a, H-4a, H-6b, H-6'b, H-5d, H-6d, H-6'd, OMe), 3.78-3.86 (m, 5 H, H-3a, H-5a, H-6'a, H-5c, H-6'c), 3.95-4.02 (m, 3 H, H-5b, H-6a, H-6c), 4.17-4.22 (m, 2 H, H-5e, CH_2Ph), 4.26-4.28 (m, 2 H, H-6e, H-6'e), 4.36 (d, 1 H, J_{gem} =11.3 Hz, CH_2Ph), 4.50 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1c), 4.61-4.62 (m, 3 H, H-1a, H-1b, CH_2Ph), 4.67-4.74 (m, 2 H, CH_2Ph), 4.81 (d, 1 H, $J_{1,2}$ = 7.9 Hz, H-1d), 4.88 (d, 1 H, J_{gem} =11.1 Hz, CH_2Ph), 4.94-5.03 (m, 2 H, -CH=CH_2), 5.05 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1e), 5.11 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4b), 5.25 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 7.7 Hz, H-2b), 5.37-5.53 (m, 4 H, H-4c, H-2d, H-4d, H-2e), 5.55-5.60 (m, 2 H, H-2c, H-4e), 5.69-5.83 (m, 4 H, -C*H*=CH_2, H-3b, H-3c, H-3d), 6.14 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.7 Hz, H-3e), 6.98-7.98 (m, 75 H, aromatic) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ, 14.3, 14.6, 15.9, 19.4, 19.9, 20.8, 21.1, 21.4, 21.5, 21.7, 22.9, 28.8, 29.6, 29.9, 32.1, 33.3, 55.5, 62.7, 68.0, 69.5, 69.6, 69.7, 70.3, 70.4, 71.9, 72.0, 72.2, 72.3, 72.4, 72.7, 72.8, 72.9, 73.2, 73.6, 74.2, 75.6, 80.0, 82.1, 89.8, 98.3, 100.7, 101.3, 101.5, 108.9, 113.9, 114.1, 115.7, 125.5, 127.5, 128.0, 128.3, 128.4, 128.5, 128.6, 128.8, 128.9, 129.2, 129.8, 129.9 (× 2), 130.0, 130.1, 133.3 (× 2), 133.5, 136.8, 138.1, 138.4, 138.6, 139.1, 142.0, 142.3, 144.4, 156.4, 159.3, 165.0, 165.2 (× 3), 165.4 (× 2), 165.5, 165.7, 165.8 (× 2), 165.9 (× 2), 172.8 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{141}H_{126}O_{39}Na^+$ 2465.7774, found 2465.7751.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

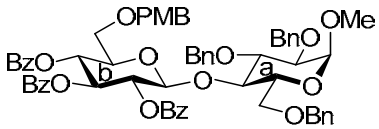


COSY spectrum (500 MHz, $CDCl_3$)



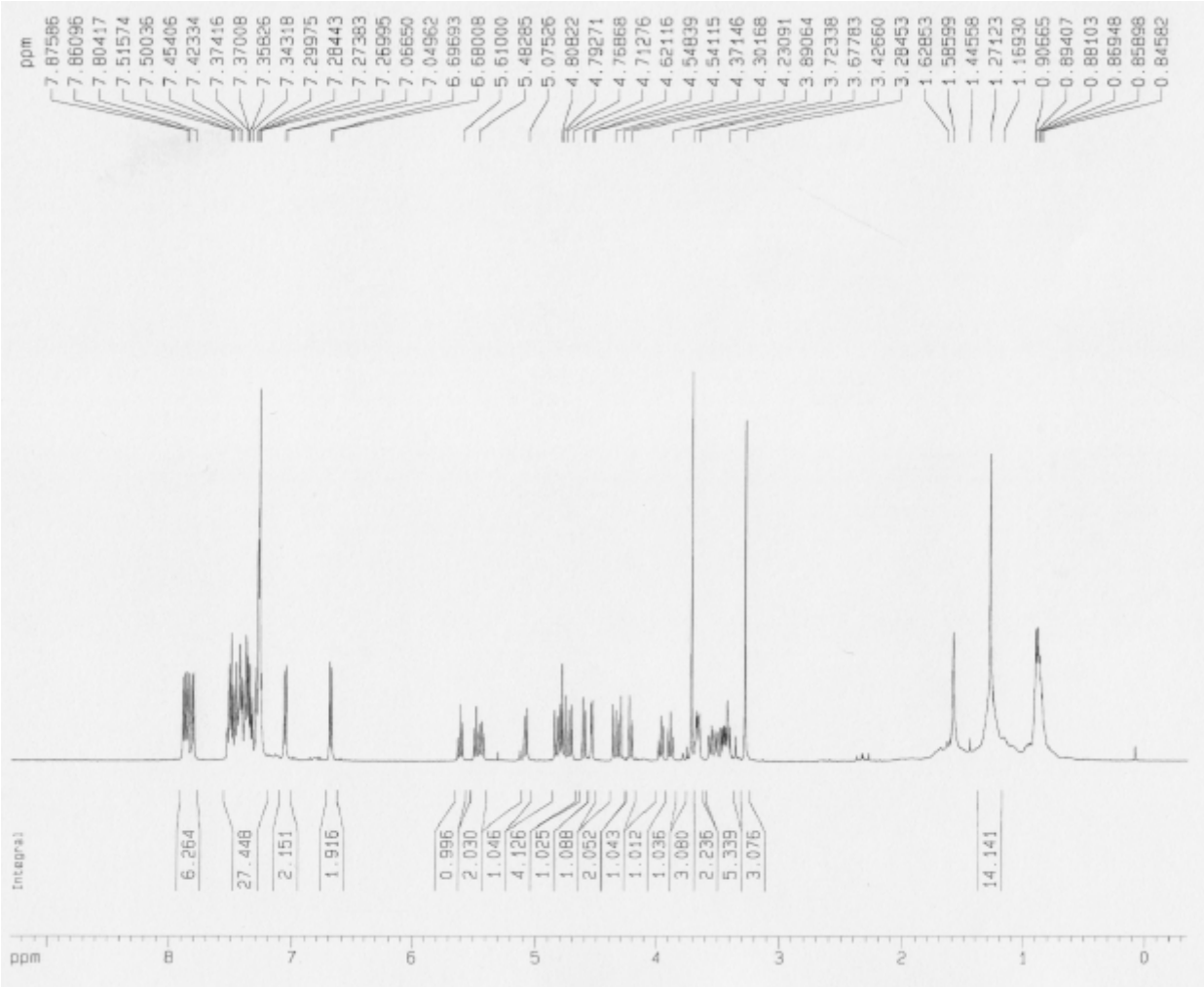
^{13}C-NMR spectrum (125 MHz, $CDCl_3$)

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-p-methoxybenzyl-β-D-glucopyranosyl)-α-D-glucopyranoside (8a).

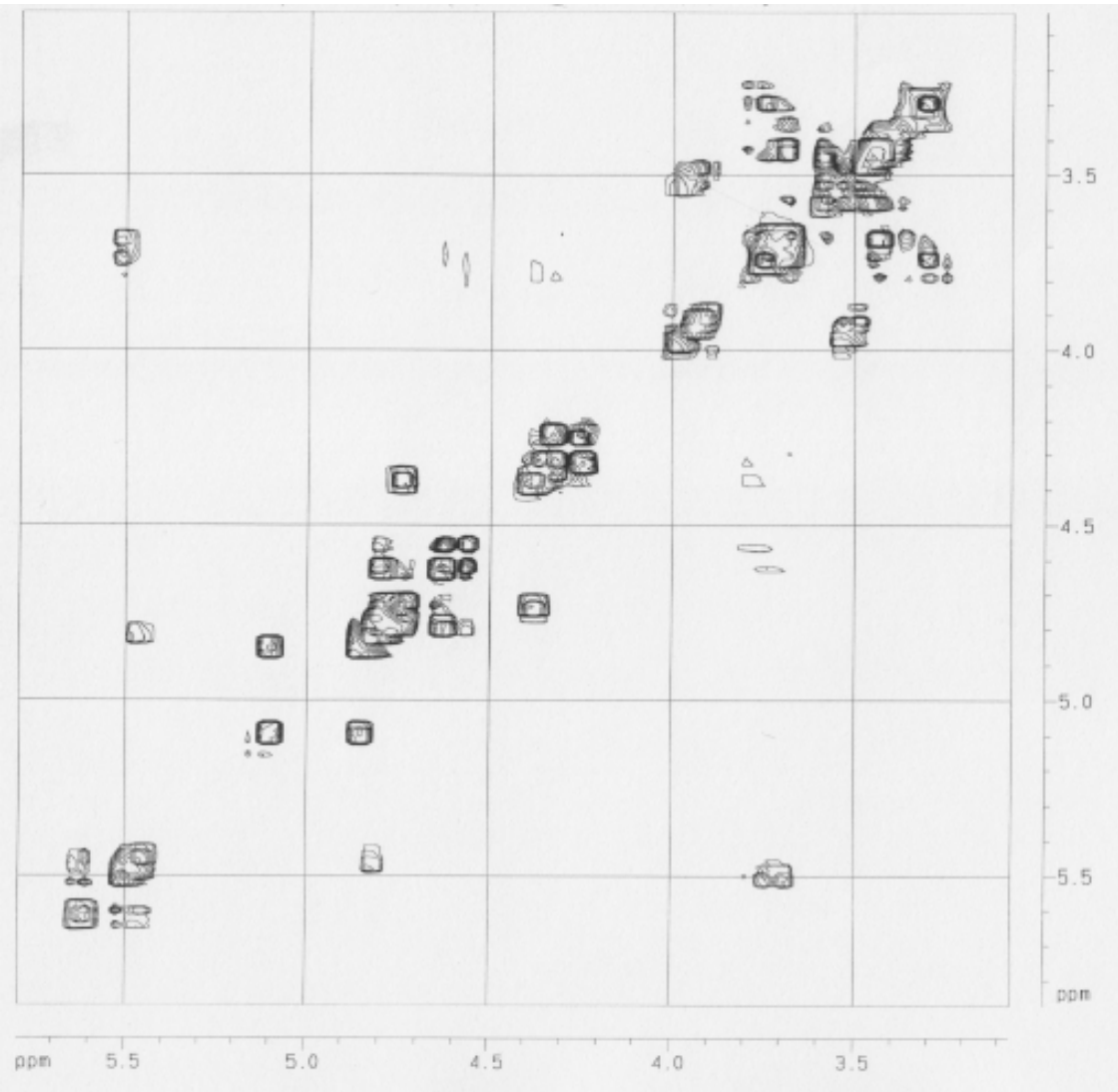


To a solution of **7a** (42 mg, 0.076 mmol) in 1,2-dichloroethane (3.0 mL) was added H_2O (1.4 μL, 0.076 mmol), NIS (52 mg, 0.23 mmol) and TfOH (10 μL, 0.11 mmol) at 0 °C. The mixture was stirred at room temperature for 10 min. After confirming of the cleavage of pentenoyl group, molecular sieves 4 Å (500 mg) were added and the resulting mixture was stirred at room temperature for 20 min. Donor **1b** (50 mg, 0.076 mmol) was then added and the resulting mixture was stirred at room temperature for 2 h. After that, the reaction mixture was diluted with dichloromethane (10 mL) and the solids were filtered-off and rinsed with dichloromethane. The combined filtrate (20 mL) was washed with sat. aq. $NaHCO_3$ (10 mL) and sat. aq. $Na_2S_2O_3$ (10 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1 / 3.5 elution) to give the title compound as a colorless syrup (49 mg, 61 %). Analytical data for **8a**: R_f = 0.48 (ethyl acetate / hexane, 1/2, v/v); $[\alpha]_D^{24}$ = +1.5° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 3.28 (s, 3 H, OMe), 3.32-3.46 (m, 3 H, H-6'b, H-6'a, H-2a) 3.52 (m, 1 H, H-5a), 3.54 (dd, 1 H, $J_{5,6}$ = 3.3 Hz, $J_{6,6'}$ = 15.2 Hz, H-6a), 3.65-3.72 (m, 2 H, H-5b, H-6b), 3.72 (s, 3 H, OMe), 3.91 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3a), 3.97 (t, 1 H, $J_{4,5}$ = 9.5 Hz, H-4a), 4.22 (d, 1

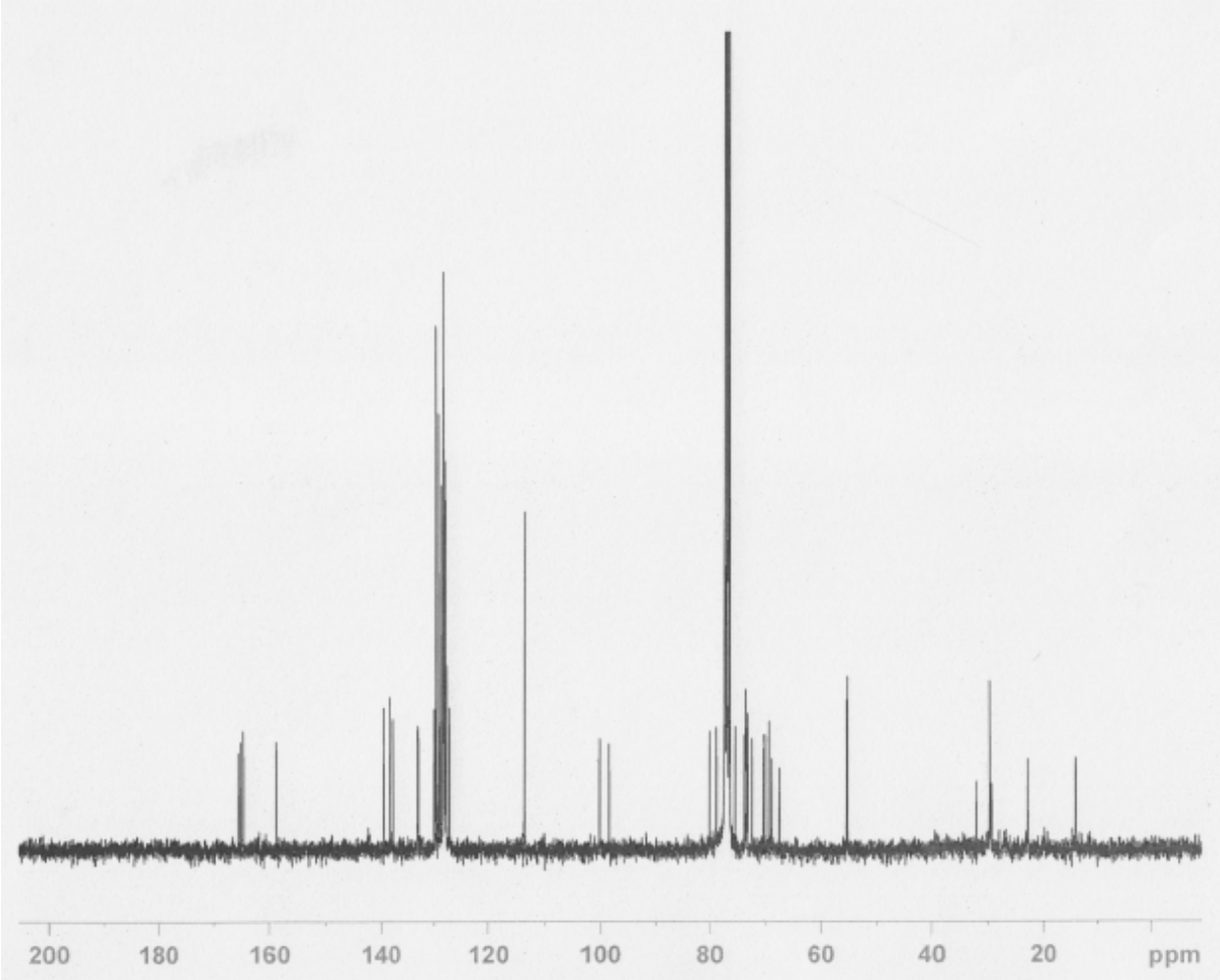
H, C*H*$_2$Ph), 4.30-4.37 (m, 2 H, C*H*$_2$Ph × 2), 4.54 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1a), 4.61 (d, 1 H, J_{gem} = 10.9 Hz, C*H*$_2$Ph), 4.72 (d, 1 H, C*H*$_2$Ph), 4.77-4.85 (m, 3 H, H-1b, C*H*$_2$Ph × 2), 5.08 (d, 1 H, C*H*$_2$Ph), 5.46 (t, 1 H, $J_{2,3}$ = 8.3 Hz, H-2b), 5.48 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4b), 5.61 (t, 1 H, H-3b), 6.69 (d, 2 H, PM*Ph*), 7.05 (d, 2 H, PM*Ph*), 7.27-7.88 (m, 30 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ, 14.2, 22.7, 29.4, 29.7, 32.0, 55.2, 55.4, 67.6, 69.0, 69.5, 70.3, 72.4, 73.3, 73.4, 73.6, 73.7, 73.8, 75.6, 76.6, 77.0, 77.2, 77.5, 78.9, 80.2, 98.5, 100.2, 113.6, 127.2, 127.8, 127.9, 128.1, 128.2, 128.3 (× 2), 128.4 (× 2), 128.8, 129.0, 129.2, 129.3, 129.7, 130.1, 133.1, 133.2, 133.3, 137.8, 138.4, 139.5, 158.9, 164.8, 165.3, 165.8 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{63}H_{62}O_{15}Na^+$ 1081.3986, found 1081.4006.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)

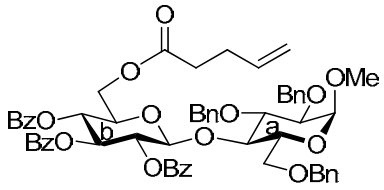


COSY spectrum (500 MHz, $CDCl_3$)



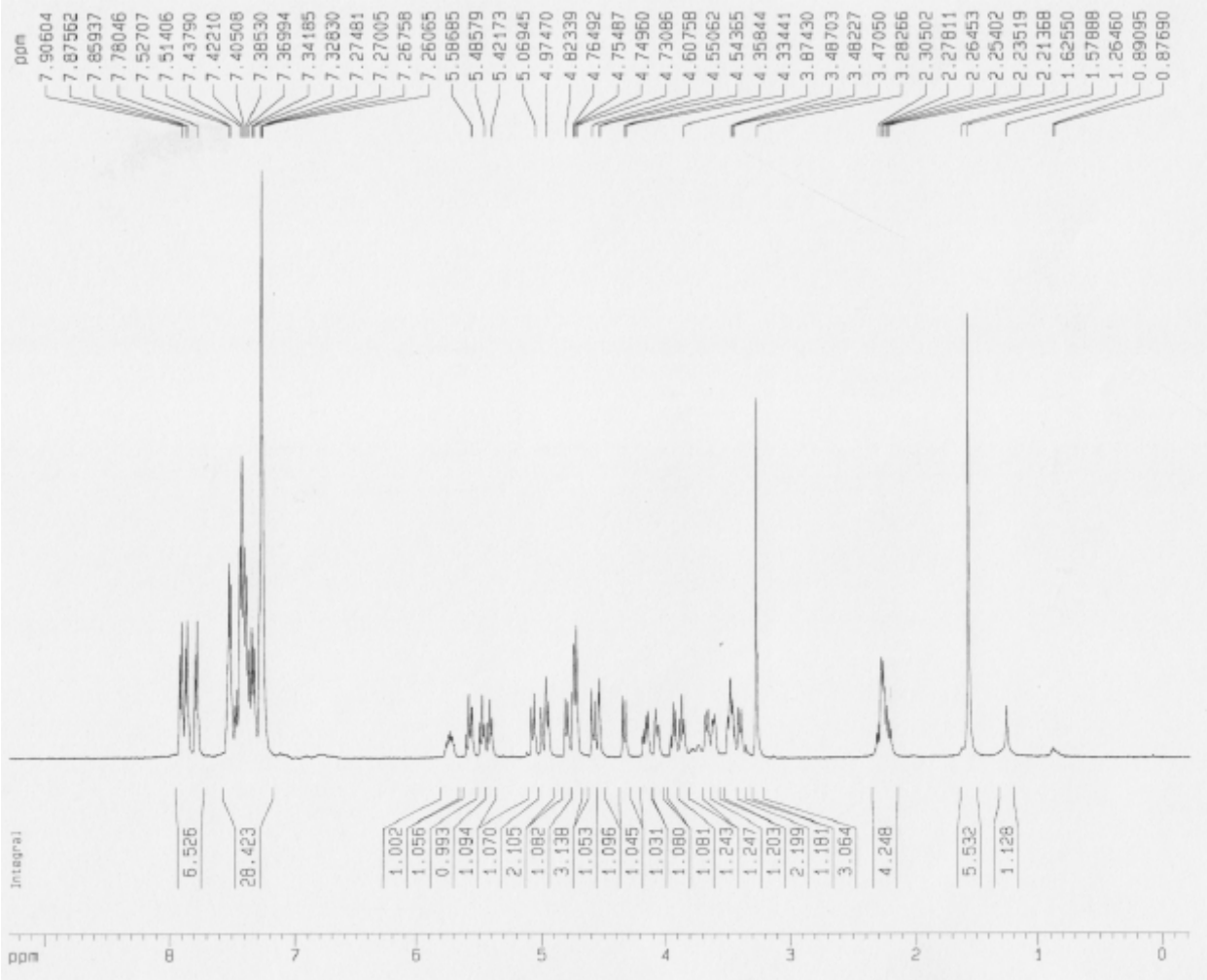
^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4-tri-*O*-benzoyl-6-*O*-pentenoyl-β-D-glucopyranosyl) -α-D-glucopyranoside (8b).

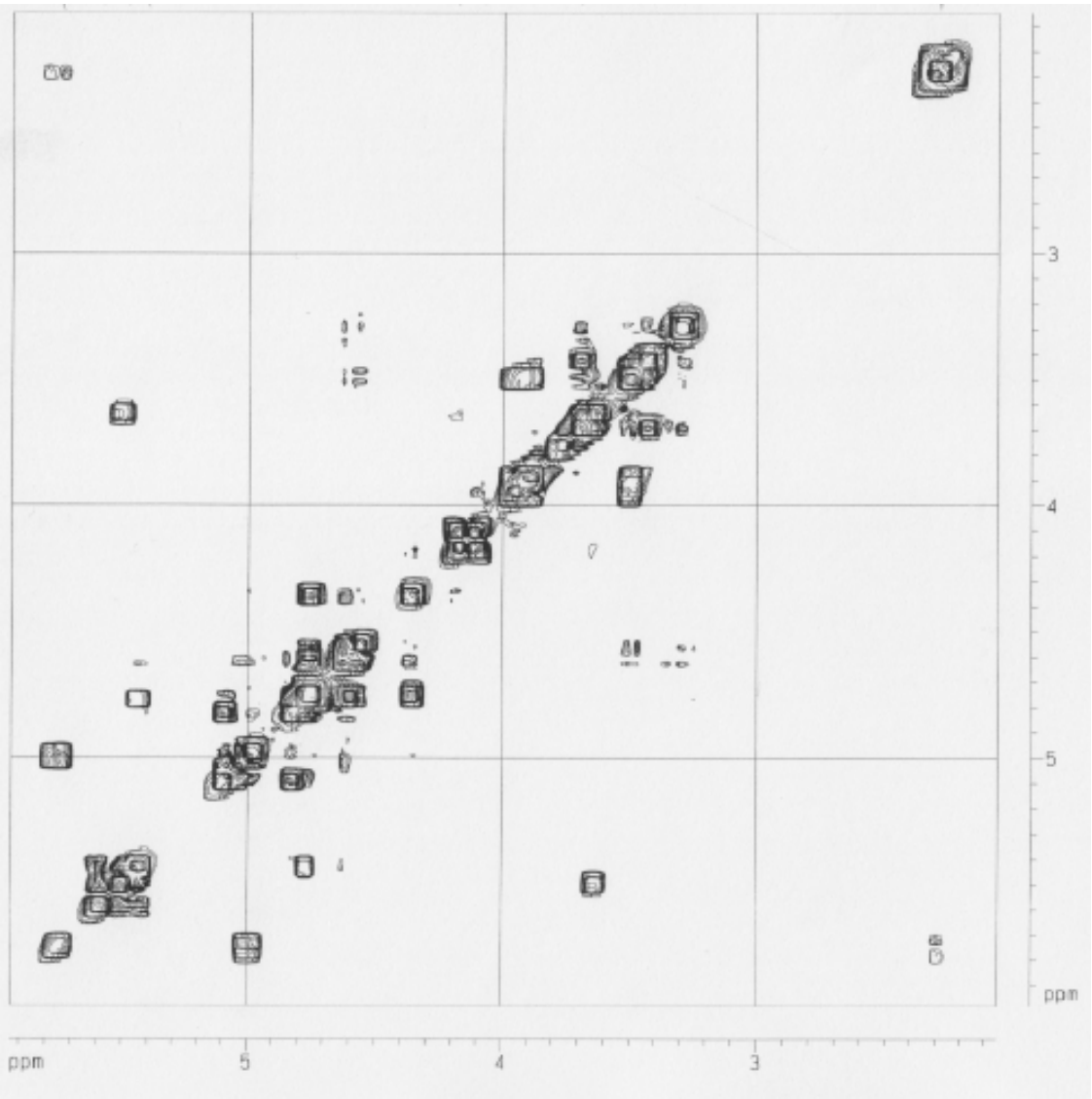


To a solution of **1d** (61 mg, 0.086 mmol), acceptor **7b** (50 mg, 0.086 mmol), and molecular sieves 3 Å (500 mg) in 1,2-dichloroethane (3.0 mL) were added TMSI (18 μL, 0.13 mmol) at 0 °C. The mixture was stirred in the dark at room temperature for 30 min, then MeOTf (30 μL, 0.26 mmol) was added and the resulting mixture was stirred at 40 °C for 4 h. The mixture was then diluted with dichloromethane (10 mL), the solid was filtered off and rinsed with dichloromethane. The combined filtrate (20 mL), was washed with sat. aq. $NaHCO_3$ (10 mL). The organic layer was concentrated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate / hexane = 1/4 elution) to give the title compound as a colorless syrup (55 mg, 64 %). Analytical data for **8b**: R_f = 0.52 (toluene / ethyl acetate, 4/1, v/v); $[\alpha]_D^{24}$ = -21.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR (500 MHz, $CDCl_3$): δ, 2.21-2.31 (m, 4 H, -CH_2CH_2-), 3.28 (s, 3 H, OMe), 3.38 (m, 1 H, H-6'a), 3.46-3.51 (m, 2 H, H-2a, H-5a), 3.62 (m, 1 H, H-5b), 3.67 (m, 1 H, H-6a), 3.87 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3a), 3.95 (t, 1 H, $J_{4,5}$ = 9.0 Hz, H-4a), 4.08 (dd, 1 H, H-6'b), 4.17 (dd, 1 H, $J_{5,6}$ = 4.4 Hz, $J_{6,6'}$ = 12.2 Hz, H-6b), 4.34 (d, 1 H, C*H*$_2$Ph), 4.55 (d, 1 H, $J_{1,2}$ = 3.5 Hz, H-1a), 4.59 (d, 1 H, C*H*$_2$Ph), 4.73-4.76 (m,

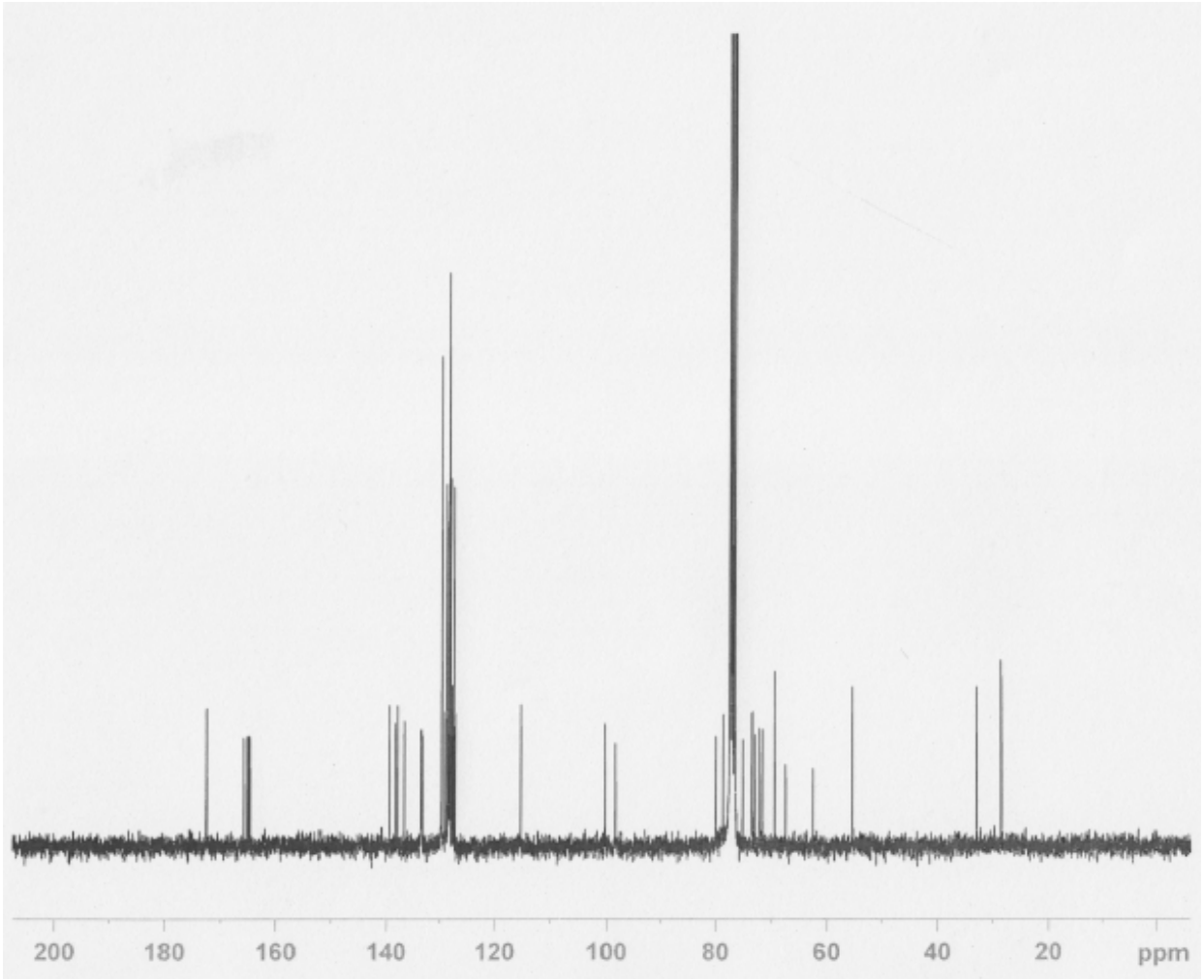
3 H, H-1b, C*H*$_2$Ph × 2), 4.81 (d, 1 H, C*H*$_2$Ph), 4.95-5.01 (m, 2 H, -CH=C*H*$_2$), 5.08 (d, 1 H, C*H*$_2$Ph), 5.42 (t, 1 H, $J_{1,2}$ = $J_{2,3}$ = 8.3 Hz, H-2b), 5.49 (t, 1 H, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H-4b), 5.59 (t, 1 H, H-3b), 5.74 (m, 1 H, -C*H*=CH$_2$), 7.26-7.91 (m, 30 H, aromatic) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ, 28.5, 33.0, 55.3, 62.4, 67.6, 69.4, 71.7, 72.2, 73.1, 73.5, 73.6, 75.3, 76.6, 77.0, 77.2, 77.4, 78.7, 80.0, 98.4, 100.3, 115.4, 127.2, 127.4, 127.7, 128.1 (× 2), 128.3 (× 2), 128.4 (× 3), 128.8, 128.9, 129.1, 129.7 (× 2), 133.1, 133.3, 133.4, 136.6, 137.8, 138.3, 139.4, 164.8, 165.0, 165.7, 172.5 ppm; HR-FAB MS $[M + Na]^+$ calcd for $C_{60}H_{60}O_{15}Na^+$ 1043.3830, found 1043.3828.



^{1}H-NMR spectrum (500 MHz, $CDCl_3$)



COSY spectrum (500 MHz, $CDCl_3$)



^{13}C-NMR spectrum (75 MHz, $CDCl_3$)

References

1. G. H. Veeneman and J. H. van Boom, *Tetrahedron Lett.*, 1990, **31**, 275-278.
2. M. N. Kamat and A. V. Demchenko, *Org. Lett.*, 2005, **7**, 3215-3218.
3. J. M. Kuester and I. Dyong, *Justus Liebigs Ann. Chem.*, 1975, 2179-2189.
4. A. Liptak, I. Jodal and P. Nanasi, *Carbohydr. Res.*, 1975, **44**, 1-11.
5. P. J. Garegg and H. Hultberg, *Carbohydr. Res.*, 1981, **93**, C10-C11.