Electronic Supplementary Material (ESI) for Chemical Communications


# *In situ* Formation of β-Glycosyl Imidinium Triflate from Participating Thioglycosyl Donors: Elaboration to Disarmed-Armed Iterative Glycosylation

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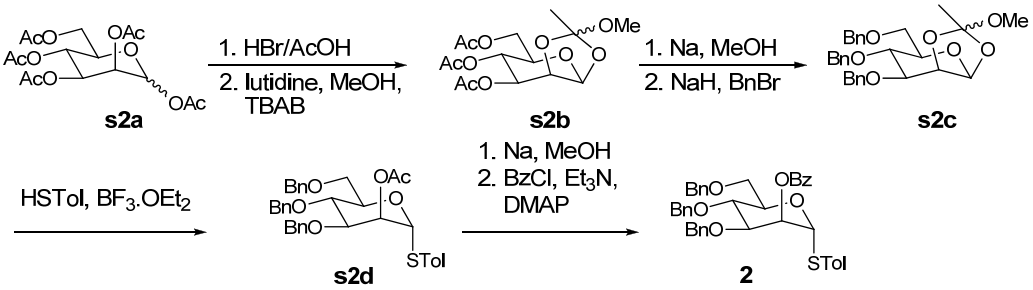
## Section A: Experimental section

Reagent-grade chemicals were purchased from commercial vendors and used without purification. Dichloromethane ($CH_2Cl_2$) was dried by Asianwong solvent system (AWS-1000). *N*,*N*-Dimethylformamide (DMF) was stocked with flame-dried molecular sieves (MS) under $N_2$. Progress of reactions was monitored by thinlayer chromatography on silica gel 60 F-254 plate and visualized under UV illumination and/or by staining with acidic ceric ammonium molybdate or *p*-anisaldehyde. Silica gel (Geduran Si-60, 0.063-0.200 mm) for chromatography was obtained from Merck. NMR spectra were recorded at 300 MHz and 75 MHz spectrometers in Brüker console or 400/500/600 MHz and 100/125/150 MHz in Varian console as specified. Coupling constants in Hz was calculated from chemical shifts of $^1$H NMR spectra. Preparations of glycosyl substrates **1**,[s1] **7**,[s2] **8**,[s2] **9**,[s3] **10**,[s4] **11a**,[s5] **11b**,[s6] **12**,[s7] **s13**,[s8] **s13ba**,[s9] **s14a**,[s9] **16**,[s6] **32**,[s10] **s33a**,[s3] and **34**[s3] were referred to literature methods. Diacetonide galactose **3** was purchased from common venders. Naming of the saccharide molecules follows the nomenclature rules of carbohydrate from IUPAC.[s11]

### *p*-Tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-thiomannopyranoside 2:

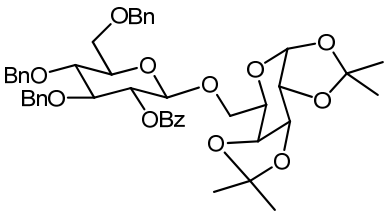



A solution of per-*O*-acetyl mannosyl acetate **s2a** (33.6 g, 86.0 mmol) in $CH_2Cl_2$ (35 mL) was cooled to 0 ˚C and treated with 33% HBr in AcOH (34 mL) under $N_2$. After stirring at 0 ˚C for 30 min, the reaction mixture was brought to RT. Upon the completion of the reaction as checked by TLC (*ca.* 2 h), the reaction mixture was diluted with EtOAc (20 mL × 2) and poured into a separatory funnel. The organic phase was then washed with satd. $NaHCO_3$ (15 mL × 2), brine (50 mL), dried (over

$MgSO_4$), filtered, concentrated, and dried under *vacuo* for 5h. The crude was taken up in dried $CH_3CN$ (98 mL), treated with *tetra*butyl ammonium bromide (TBAB) (5 g, 15.7 mmol), 2,6-lutidine (18.2 mL, 157 mmol), and MeOH (9.5 mL). The reaction was stirred overnight at RT under $N_2$. Upon completion of the reaction, the solvent was reduced by rotary evaporator. The residue was taken up by EtOAc (100 mL × 2), which was washed with satd. $NaHCO_3$ (150 mL × 2), $H_2O$ (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated to give crude per-*O*-acetylated orthoester **s2b** (28.3 g, 78.4 mmol). The per-*O*-acetylated orthoester **s2b** was dissolved in MeOH/$CH_2Cl_2$ solution mixture, then treated with Na(s) at RT. Upon completion of deacetylation, the reaction mixture was concentrated and dried under *vacuo* for 4h. The crude mixture was dissolved in DMF and cooled at 0 ˚C bath under $N_2$. The reaction mixture was treated with sodium hydride (NaH, 13.2 g, 331 mmol) (60% in mineral oil) and benzyl bromide (BnBr, 40 mL, 331 mmol). Upon completion of the reaction, ice was added to quench excessive NaH. The reaction crude was subsequently diluted with EtOAc and $H_2O$ in the separation funnel, then washed with satd. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: $CH_2Cl_2$/EtOAc/Hexane 1/0/3 stepwise to 1/1/3) to give per-*O*-benzyl mannosyl orthoester **s2c** (35.1g). The per-*O*-benzylated mannosyl orthoester **s2c** (10.12 g, 20 mmol) in $CH_2Cl_2$ was treated with *p*-thiocresol (6.21 g, 50 mmol) was cooled to 0 ˚C, then $BF_3.OEt_2$ (6.3 mL, 50 mmol) was added to the mixture. Upon completion of the reaction, the reaction crude was diluted with EtOAc, washed with satd. $NaHCO_3$ and brine in chill, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/19 stepwise to 3/17) to give 2-*O*-acetyl thiomannoside **s2d** (5.2 g, 8.7 mmol) as yellow syrup. The 2-*O*-acetyl thiomannoside **s2d** (7.8 g, 13 mmol) in $CH_2Cl_2$/MeOH mixed solution was treated with $Na_{(s)}$. Upon completed deacetylation, the reaction was neutralized with IR-120 ($H^+$), filtered, and concentrated for column chromatography purification (Elution: recycled EtOAc/Hexane 0~25% stepwise to 25~50%) to give

the 2-hydroxyl unprotected thiomannoside (6.08g, 10.9mmol). The 2-hydroxyl unprotected thiomannoside (6.08g, 10.9mmol) in $CH_2Cl_2$ was subsequently treated with benzoyl chloride (BzCl) (2.56 mL, 21.8 mmol), $Et_3N$ (4.5 mL, 32.7 mmol) and DMAP (133 mg, 1.09 mmol) under $N_2$. Upon completion of the benzoylation, the reaction mixture was diluted with satd. $NaHCO_3$, then washed with EtOAc, $H_2O$ and brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: recycled EtOAc/Hexane 0~25%) to yield target thiomannoside donor **2** (6.11 g, 9.27 mmol). For thiomannoside **2**: $[\alpha]_D^{35}$ +77.11 (*c* 0.42, $CHCl_3$) ; $R_f$ 0.35 (EtOAc/Hexane 1:3); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.05 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.39-7.25 (m, 17 H), 7.23-7.20 (m, 2 H), 7.05 (d, *J* = 8.1 Hz, 2 H), 5.87 (dd, *J* = 2.7, 1.8 Hz, 1 H, H-2), 5.58 (d, *J* = 1.5 Hz, 1 H, H-1), 4.90 (d, *J* = 10.8 Hz, 1 H), 4.81 (d, *J* = 11.4 Hz, 1 H), 4.70 (d, *J* = 11.7 Hz, 1 H), 4.58 (t, *J* = 11.4 Hz, 2 H), 4.49 (d, *J* = 11.7 Hz, 1 H), 4.40 (dd, *J* = 9.3, 2.1 Hz, 1 H), 4.16 (t, *J* = 9.6 Hz, 1 H), 4.06 (dd, *J* = 9, 2.7 Hz, 1 H), 3.95 (dd, *J* = 10.8, 4.2 Hz, 1 H), 3.79 (dd, *J* = 10.5, 1.5 Hz, 1 H), 2.29 (s, 3 H, $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 166.0 (C=O), 138.8, 138.7, 138.4, 138.1, 133.7, 132.8, 130.4, 130.3, 130.2, 128.9, 128.81, 128.77, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 87.1 (C-1'), 79.0, 75.8, 75.0, 73.8, 73.0, 72.1, 71.0, 69.5, 21.6; HRMS (*m/z*): $[M + Na]^+$ calcd. for $C_{41}H_{40}NaO_6S^+$, 683.2438; found, 683.2450.

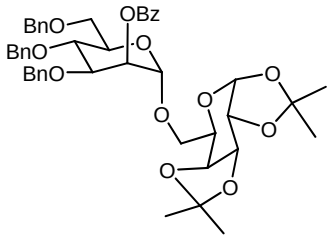
**6-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 4**




Disaccharide **4** was prepared from thioglucoside **1** and diacetonide galactose acceptor **3** by general modulated glycosylation procedure. Purification of **4** was

performed by column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:2:10 stepwise to 1:2:7). For **4**: $[\alpha]_D^{35}$ –30.00 (*c* 0.36, $CHCl_3$); $R_f$ 0.275 (EtOAc/$CH_2Cl_2$/Hexane 1:2:5); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.03 (d, *J* = 7.5 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.42-7.27 (m, 10 H), 7.20-7.17 (m, 2 H), 7.12 (s, 5 H), 5.38 (d, *J* = 4.8 Hz, 1 H, H-1), 5.30 (t, *J* = 8.1 Hz, 1 H, H-2'), 4.82 (d, *J* = 10.8 Hz, 1 H), 4.46 (d, *J* = 11.1 Hz, 1 H), 4.68-4.63 (m, 3 H), 4.59-4.55 (m, 2 H), 4.39 (dd, *J* = 7.8, 1.8 Hz, 1 H), 4.19-4.17 (m, 1 H), 4.10 (d, *J* = 8.1 Hz, 1 H), 4.02 (dd, *J* = 10.8, 5.1 Hz, 1 H), 3.82-3.71 (m, 6 H), 3.56 (d, *J* = 1.8 Hz, 1 H), 1.38 (s, 3 H, C*H*$_3$), 1.21 (s, 3 H, C*H*$_3$), 1.17 (s, 6 H, C*H*$_3$ × 2); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 165.6 (*C*=O), 138.5, 138.3, 138.2, 133.2, 130.4, 130.3, 128.8, 128.7, 128.6, 128.34, 128.31, 128.19, 128.15, 128.1, 109.5 (quaternary-C), 108.8 (quaternary-C), 101.8, 96.6, 83.3, 78.4, 75.7, 75.5, 74.1, 74.0, 69.1, 68.4, 67.7, 26.4, 26.1, 25.3, 24.6; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{46}H_{51}NaO_{12}$, 819.3351; found, 819.3343.

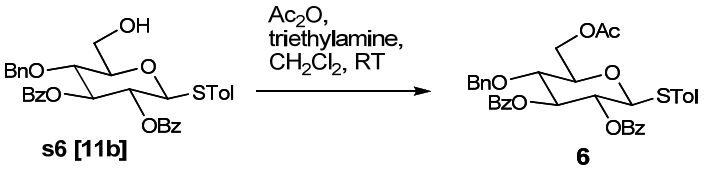
**2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-D-mannopyranosyl-α(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 5**




Disaccharide **5** was prepared from thiomannoside **2** and galactose acceptor **3** by general modulated glycosylation procedure. Purification of **5** was performed by column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:2:15 stepwise to 1:2:10). For disaccharide **5**: $[\alpha]_D^{35}$ –18.34 (*c* 0.52, $CHCl_3$); $R_f$ 0.375 (EtOAc/$CH_2Cl_2$/Hexane 1:2:5); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.07 (d, *J* = 8.1 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.40-7.18 (m, 17 H), 5.67 (s, 1 H), 5.52 (d, *J* = 4.8 Hz, 1 H, H-1), 5.04 (s, 1 H), 4.86 (d, *J* = 10.8 Hz, 1 H), 4.78 (t, *J* = 11.1 Hz, 2 H), 4.63-4.51 (m, 4 H), 4.31 (dd, *J* =

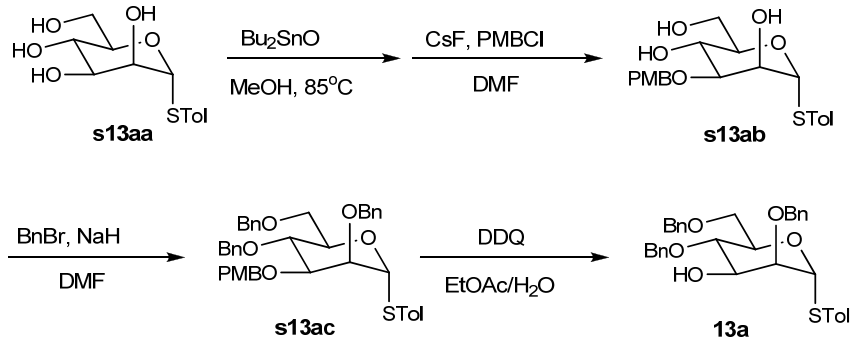
4.8, 1.8 Hz, 1 H), 4.24 (d, *J* = 8.1 Hz, 1 H), 4.12 (s, 2 H), 3.99-3.91 (m, 3 H), 3.87-3.71 (m, 3 H), 1.53 (s, 3H, $CH_3$), 1.43 (s, 3 H, $CH_3$), 1.34 (d, *J* = 6.6 Hz, 6 H, $CH_3 \times 2$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$166.0 (*C*=O), 138.9, 138.8, 138.5, 130.4, 130.3, 128.8, 128.73, 128.71, 128.68, 128.4, 128.03, 127.97, 127.93, 127.86, 109.8 (quaternary-C), 109.0 (quaternary-C), 98.4, 96.7, 78.6, 75.7, 74.7, 73.8, 72.2, 72.0, 71.2, 71.02, 70.97, 69.4, 69.3, 66.6, 66.4, 26.6, 26.4, 25.3, 24.9; HRMS-ESI (*m/z*): [M + Na]$^+$ calcd. for $C_{46}H_{51}NaO_{12}$, 819.3351; found, 819.3339.

***p*-Tolyl 6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-thio-β-D-glucopyranoside 6**:




Known thioglucoside **s6** (1.0 g, 1.71 mmol) in EtOAc (4 mL) was treated with $Ac_2O$ (0.2 mL, 2.05 mmol), $Et_3N$ (0.35 mL, 2.56 mmol), and DMAP (20 mg, 0.171 mmol). Upon completion of acetylation, the reaction mixture was diluted with EtOAc and washed with satd. $NaHCO_3$, $H_2O$, brine, dried (over $MgSO_4$), filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:4) to furnish **6** (quantitative). For compound **6**: $[\alpha]_D^{35}$ +63.1 (*c* 0.30, $CHCl_3$); $R_f$ 0.4 (EtOAc/Hexane 3/7); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$7.96–7.91 (m, 4 H), 7.53–7.48 (m, 2 H), 7.39–7.34 (m, 6 H), 7.20-7.17 (m, 3 H), 7.13–7.08 (m, 4 H), 5.73 (t, *J* = 9.6 Hz, 1 H), 5.32 (t, *J* = 10.0 Hz, 1 H), 4.84 (d, *J* = 10.0 Hz, 1 H, H-1), 4.56 (d, *J* = 11.2 Hz, 1 H), 4.50–4.46 (m, 2H), 4.25 (dd, *J* = 12.0, 4.8 Hz, 1 H), 3.83–3.74 (m, 2 H), 2.33 (s, 3 H, C*H*$_3$), 2.09 (s, 3 H, C*H*$_3$C=O); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$171.1 (*C*=O), 166.1 (*C*=O), 165.8 (*C*=O), 139.0, 137.3, 134.1, 133.73, 133.70, 130.3, 130.2, 130.1, 129.8, 128.90, 128.88, 128.8, 128.7, 128.6, 86.7 (C-1), 77.6, 76.9, 76.1, 75.3, 71.2, 63.3, 21.7, 21.4; HRMS-ESI (*m/z*): [M + Na]$^+$ calcd. for $C_{36}H_{34}NaO_8S$, 649.1867; found, 649.1900.

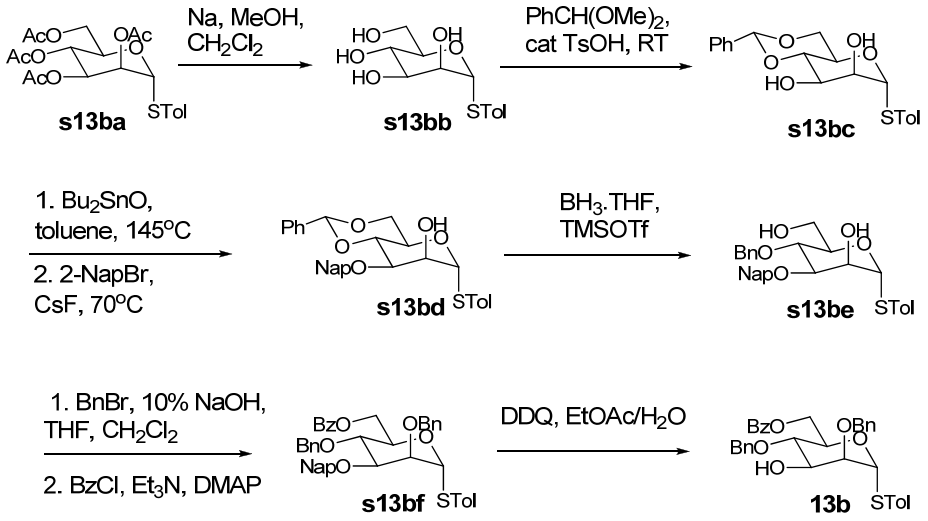
***p*-Tolyl 2,4,6-Tri-*O*-benzyl-thio-α-D-mannopyranoside 13a:**




Unprotected thiomannoside **s13aa**[s8] (2 g, 7 mmol) was treated with $Bu_2SnO$ (2.3 g, 9.3 mmol) in MeOH (23.3 mL) and heated to 85 ˚C. Upon Until a clear the reaction reaction mixture solution clearlywas observed, the reaction mixture was cooled to RT, concentrated, and dried high vacuum *ca* 2h. The reaction residue was treated with cesium fluoride (1.3 g, 8.4 mmol), *p*-methoxybenzyl chloride (1.4 mL, 10.2 mmol) in DMF. Upon completion of the alkylation, the reaction mixture was filtered and the filtrate was concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/2 stepwise to 1/0) to furnish crude 3-OH protected thiomannoside **s13ab** (1.78 g). The thiomannoside **s13ab** (1.78 g, 4.38 mmol) in dried in DMF was treated with benzyl bromide (BnBr) (2.4 mL, 19.7 mmol) and sodium hydride (NaH) (800 mg in 60% mineral oil, 19.7 mmol). Upon completion of the benzylation, the DMF was removed by high *vacuo* rotary evaporator and the residue was taken up with EtOAc. The organic phase was washed with water and, brine, dried over $MgSO_4$, concentrated, and dried under *vacuo* for *ca* 4 h to furnish fully protected thiomannoside **s13ac**. *p*-Methoxybenzyl ether (PMB) protection in **s13ac** was removed by treatment with 2,3-dichloro-5,6-dicyano quinone (DDQ) (835 mg, 3.68 mmol) in 10:1 EtOAc/$H_2O$ (10/1) mixture. Upon completion of the PMB deprotection, the crude reaction mixture was diluted with EtOAc, and the organic phase was washed with $Na_2S_2O_{3(aq)}$, $NaOH_{(aq)}$, water and brine. After drying (over $MgSO_4$) and filtration, the EtOAc solution was concentrated for column chromatography

purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/2/15 stepwise to 1/2/13) to furnish target thiomannoside acceptor **13a** (473 mg, 12%, three steps unoptimized). For thiomannoside **13a**: $[\alpha]_D^{35}$ +115.1 (*c* 0.40, $CHCl_3$); $R_f$ 0.27 (EtOAc/$CH_2Cl_2$/Hexane 1:2:6); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.38-7.21 (m, 17H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.61 (s, 1H, H-1), 4.87 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 12 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.48 (dd, *J* = 11.7, 4.8 Hz, 2H), 4.33-4.28 (m, 1H), 4.03-3.96 (m, 2H), 3.86-3.72 (m, 3H), 2.44 (d, *J* = 9 Hz, 1H), 2.30 (s, 3H); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 138.8, 138.7, 132.8, 130.7, 130.2, 129.0, 128.8, 128.7, 128.5, 128.43, 128.37, 128.2, 127.9, 85.7 (C-1), 80.0, 77.3, 75.3, 73.8, 72.7, 72.5, 72.4, 69.6, 21.6 ($CH_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{34}H_{36}NaO_5S$, 579.2176; found, 579.2192.

***p*-Tolyl 6-*O*-Benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside 13b**:

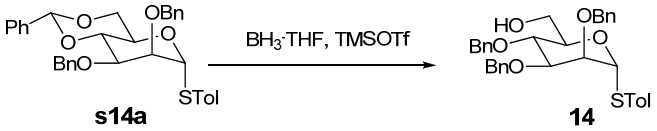



Per-*O*-acetyl thiomannoside **s13ba**[s9] (15.2 g, 39 mmol) in MeOH/$CH_2Cl_2$ mixture (150 mL) was treated with $Na_{(s)}$ (120 mg) for deacetylation. Upon completion of deacetylation, the reaction solution was neutralized with IR-120 ($H^+$), and the mixture was filtered to remove resin, followed by concentration (by rotary evaporator) and dried (under *vacuo*) to give crude unprotected thiomannoside **s13bb**. The thiomannoside **s13bb** (11.1 g, 39 mmol) in anhydrous $CH_3CN$ (300 mL) was treated

with benzaldehyde dimethyl acetal (11.7 mL, 78.0 mmol) and *p*-toluenylsulfonic acid (TsOH, 740 mg, 3.9 mmol) to form the 4,6-*O*-benzylidene protected thiomannoside. Upon completion of the acetalation, the reaction was quenched by neutralization with $Et_3N$. The 4,6-*O*-benzylidene protected thiomannoside was precipitated in the reaction solution, and it was obtained by filtration and washing the precipitate with minimal amount of hexane/$Et_2O$ mixture. The washed precipitate was dried under *vacuo* to give benzylidene acetal derivative **s13bc** (11.9 g). The acetal derivative **s13bc** (11.9 g, 32.0 mmol) suspended in toluene (160 mL) was treated with dibutyl tin oxide ($Bu_2SnO$, 11.9 g, 48.0 mmol) and refluxed at 145 ˚C for 8–10 h under Dean-Stark trap. The volume of toluene was then reduced approximately by half and the reaction mixture was cooled to RT. After then, 2-(bromomethyl)-naphthalene (2-NAP-Br, 10.54 g, 48.0 mmol), cesium fluoride (CsF, 7.2 g, 48.0 mmol), and $CH_3CN$ (80 mL) were added and resulting mixture was stirred at 70 ˚C for *ca.* 11 h. Upon the completion of alkylation, the reaction mixture was filtered (over celite), and concentrated for column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 0.1:1:3 stepwise to 0.3:2:2) to furnish amorphous white solid of the 2-naphthylmethyl derivative **s13bd** (12.3 g). The derivative **s13bd** (10.24 g, 19.9 mmol) in $BH_3$.THF solution (1 M, 59.7 mL, 59.7 mmol) was treated with trimethylsilyl triflate (TMSOTf) (180 μL) at 0 ˚C. Upon completion of the reductive ring opening, the mixture was neutralized with $Et_3N$, followed by addition of MeOH. The resulting mixture was then concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/5 stepwise to 1/1) to yield 2,6-dihydroxyl thiomannoside **s13be** (8.8 g). The 2,6-dihydroxyl thiomannoside **s13be** (9.44 g, 18.3 mmol) in 10% NaOH (13.3 mL) THF solution was treated with BnBr (2.2 mL, 18.3 mmol) and TBAB (5.9 g, 18.3 mmol) and the mixture was stirred vigorously. Upon the completion of benzylation, THF was removed by rotary evaporator. The residual aqueous mixture was extracted with EtOAc, which was washed with $H_2O$, brine, dried over $MgSO_4$, and concentrated for column chromatography purification (Elution:

EtOAc/$CH_2Cl_2$/Hexane 1/1/5) to give surprisingly 2-*O*-benzyl thiomannoside. The C2 position of benzyl function was confirmed by $^1$H, $^{13}$C, HSQC, and HMBC spectroscopy (HSQC and HMBC spectra were unpublished data). To the 2-*O*-benzyl thiomannoside in $CH_2Cl_2$ was added BzCl (2.6 mL, 22.0 mmol), $Et_3N$ (4 mL, 29.4 mmol), and DMAP (180 mg, 1.47 mmol). Upon completion of the benzoylation, satd. $NaHCO_3$ was added to the mixture and the product was extracted with EtOAc. The EtOAc solution was washed with $H_2O$, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification to give fully protected thiomannoside **s13bf**. The thiomannoside **s13bf** (10.45 g, 14.7 mmol) was treated with DDQ (10 g, 44.1 mmol) in 10/1 v/v EtOAc/$H_2O$ mixture. Upon completion of the deprotection, the reaction mixture was diluted with EtOAc, which was washed with satd. $Na_2S_2O_3$, water, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:10) to furnish thiomannoside **13b** (6.2 g, 68% from **s13be**). For thiomannoside **13b**: $[\alpha]_D^{35}$ +126.4 (*c* 0.44, $CHCl_3$); $R_f$ 0.3 (EtOAc/Hexane 1:4); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.99 (d, *J* = 7.8 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.39-7.19 (m, 14H), 6.98 (d, *J* = 7.8 Hz, 2H), 5.62 (s, 1H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.73 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 8.1 Hz, 1H), 4.58-4.47 (m, 4H), 1.11-4.04 (m, 2H), 3.80 (t, *J* = 9 Hz, 1H), 2.58 (d, *J* = 9.3 Hz, 1H, OH), 2.26 (s, 3H, $CH_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 166.7 (C=O), 138.4, 138.2, 137.8, 133.3, 132.6, 130.3, 130.2, 129.0, 128.9, 128.7, 128.53, 128.48, 128.3, 128.2, 85.4 (C-1), 70.1, 77.0, 75.4, 72.8, 72.5, 70.7, 64.4, 21.5 (*C*$H_3$); HRMS-EI (*m/z*): [M + Na]$^+$ calcd. for $C_{34}H_{34}NaO_6S$, 593.1968; found, 593.1979.

***p*-Tolyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-thio-α-D-mannopyranoside 14**:

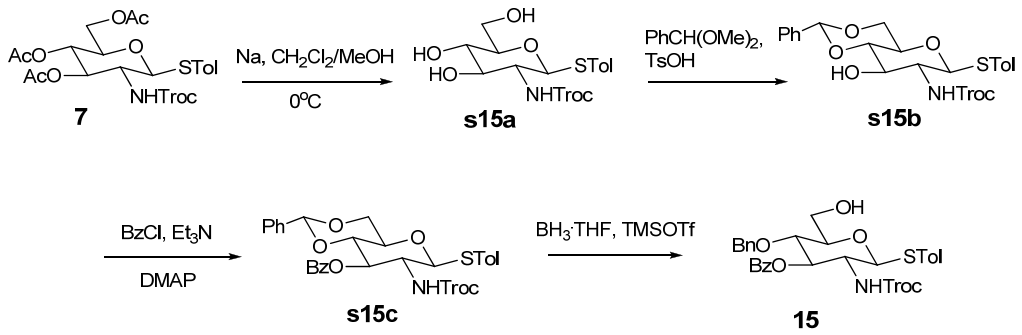



**s14a** **14**

Fully protected thiomannoside **s14a**[s9] in $BH_3$·THF solution (10.8 mL, 10.8

mmol) was treated with TMSOTf (78.0 μL, 0.43 mmol) at 0 ˚C. Upon completion of the reductive cleavage of acetal function, the reaction was quenched with $Et_3N$, followed by addition of MeOH to react with excess borane reagent. The resulting mixture was concentrated for column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:2.5:10 stepwise to 1:2.5:7) to produce thiomannoside **14**. For thiomannoside **14**: $[\alpha]_D^{35}$ +81.4 (*c* 0.52, $CHCl_3$); $R_f$ 0.19 (EtOAc/Hexane 1/3); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.34-7.23 (m, 17 H), 7.09 (d, *J* = 8.1 Hz, 2 H), 5.43 (s, 1 H, H-1), 4.95 (d, *J* = 11.1 Hz, 1 H), 4.73-4.58 (m, 5 H), 4.13 (d, *J* = 9.3 Hz, 1 H), 4.06-3.98 (m, 2 H), 3.89 (dd, *J* = 9, 2.7 Hz, 2 H), 3.80 (s, 2 H), 2.32 (s, 3 H), 1.99 (s, 1 H, OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 138.8, 138.5, 138.4, 138.2, 132.9, 130.5, 130.3, 128.9, 128.5, 128.4, 128.3, 128.21, 128.19, 86.8 (C-1), 80.5, 76.8, 75.7, 75.2, 73.6, 72.7, 72.6, 62.6, 21.6 (*C*$H_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{34}H_{36}NaO_5S$, 579.2176; found, 579.2179.

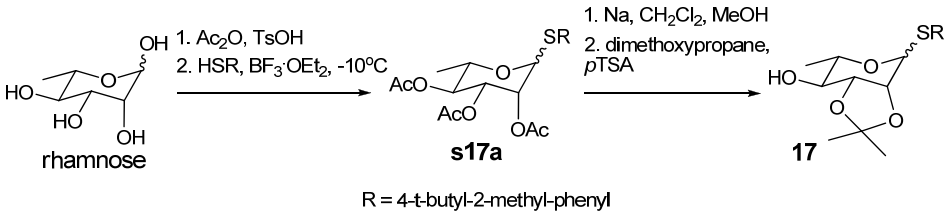
**_p_-Tolyl 2-_O_-Benzoyl-2-_O_-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-β-D-glucopyranoside 15:**




Per-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-thioglucopyranoside **7** (9.44 g, 16.1 mmol)[s2] was treated with Na(s) in $CH_2Cl_2$/MeOH mixture at 0 ˚C. Upon the completion of the reaction, the reaction was neutralized with IR-120 ($H^+$), filtered, concentrated, and dried under *vacuo* to obtain the thioglucoside **s15a** (7.24 g, 98%). **s15a** (5.24 g, 11.4 mmol) was treated with benzaldehyde dimethyl acetal (2.2 mL, 14.8 mmol) and TsOH (230 mg, 1.2 mmol) in dried $CH_3CN$ (48 mL).

Upon completion of the acetal formation, the reaction was neutralized by $Et_3N$, filtered, concentrated to produce 4,6-*O*-benzylidene-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-β-D-thioglucopyranoside **s15b** (4.67 g, 75%). **s15b** (2.5 g, 4.55 mmol) in dried $CH_2Cl_2$ (23 mL) was treated with BzCl (0.8 mL, 6.83 mmol), $Et_3N$ (1.3 mL, 9.1 mmol), and DMAP (56 mg, 0.46 mmol). Upon completion of benzoylation, the reaction mixture was diluted with EtOAc. The EtOAc solution was washed with satd. $NaHCO_3$, $H_2O$, brine, dried (over $MgSO_4$), filtered, and concentrated. The fully protected 2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-thioglucopyranoside **s15c** (2 g, 68%) was obtained by precipitation of the concentrated solution in Hexane/EtOAc mixture. The 2-amino-2-deoxy-β-D-thioglucopyranoside **s15c** (2 g, 3.1 mmol) in $BH_3$·THF (15.5 mL, 15.5 mmol) was treated with TMSOTf (112 μL, 0.62 mmol) at 0 ˚C. Upon completion of the reductive clealvage of acetal function, excessive borane reagent was quenched with $Et_3N$ and MeOH. The resulting mixture was concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/4) to furnish C6 hydroxyl unprotected thioglucosaminyl acceptor **15** (1.41 g, 70%). For **15**: $[\alpha]_D^{35}$ –6.2 (*c* 0.42, $CHCl_3$); $R_f$ 0.25 (EtOAc/Hexane 1/2); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.99 (d, *J* = 7.8 Hz, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.44-7.38 (m, 4 H), 7.12-7.00 (m, 7 H), 5.98 (d, *J* = 9.9 Hz, 1 H, N*H*), 5.60 (t, *J* = 9.9 Hz, 1 H, H-2), 4.74 (d, *J* = 10.5 Hz, 1 H), 4.63 (q, *J* = 11.7 Hz, 2 H), 4.50 (s, 2 H), 3.98 (q, *J* = 10.2 Hz, 1 H), 3.85-3.66 (m, 3 H), 3.48 (d, *J* = 9.3 Hz, 1 H), 2.28 (s, 3 H, $CH_3$), 2.08 (s, 1 H, OH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 167.2 (*C*=O), 154.9 (*C*=O), 138.8, 137.5, 134.0, 130.4, 130.2, 129.5, 129.3, 129.0, 128.8, 128.7, 128.4, 95.8 (*C*$Cl_3$), 88.2 (C-1), 79.6, 75.8, 75.3, 74.8, 62.0, 55.8, 21.6 (*C*$H_3$); HRMS-EI (*m/z*): $[M + Na]^+$ calcd. for $C_{30}H_{30}Cl_3NNaO_7S$, 676.0701; found, 676.0719.

**(4-*t*-Butyl-2-methylphenyl) 2,3-*O*-Isopropylidene-thio-α-L-rhamnopyranoside 17**




L-Rhamnose (5 g, 30.5 mmol) in acetic anhydride ($Ac_2O$, 17.3 mL, 183 mmol) was treated with dried TsOH (580 mg, 3.05 mmol) in ice bath. Upon completion of acetylation, the anhydride reagent was quenched with MeOH under ice bath *ca* 1 h and concentrated. After then, the concentrated residue was diluted with EtOAc, washed with *ca.* 10% NaOH, brine, ice, and dried over $MgSO_4$. The solution was filtered, concentrated, and dried under *vacuo* to give crude per-*O*-acetyl rhamnosyl acetate. The crude acetate in dried $CH_2Cl_2$ was cooled to –10 ˚C and treated with (4-*t*-butyl-2-methyl)-thiophenol (3.2 mL, 17.6 mmol) and $BF_3{\cdot}OEt_2$ (3 mL, 23.4 mmol). Upon completion of thioglycosidation, the reaction was quenched with 10% $NaOH_{(aq)}$ at 0 ˚C and the mixture was washed with 10% $NaOH_{(aq)}$, chilled $H_2O$, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: EtOAc/Hexane 1/8) to furnish per-*O*-acetyl thiorhamnoside **s17a** (4.34 g, 74%). **s17a** (4.34 g, 8.6 mmol) in MeOH/$CH_2Cl_2$ mixture (35 mL, MeOH/$CH_2Cl_2$ 1/2) was treated with Na(s). Upon completion of the deacetylation, the reaction mixture was neutralized with IR-120 ($H^+$), and filtered to remove resin. The filtrate was concentrated and dried under *vacuo* to give crude deacetylated thiorhamnoside intermediate. The crude thiorhamnoside intermediate in dried acetone (29 mL) was then treated with 2,2-dimethoxypropane (2.1 mL, 17.2 mmol) and TsOH (170 mg, 0.86 mmol). Upon completion of the acetalation, the reaction was neutralized with $Et_3N$, and followed by concentration for column chromatograph purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:1:6 stepwise to 1:1:5) to furnish thiorhamnoside acceptor **17** (2.17 g, 69%, α/β 10:1). For thiorhamnoside **17**: $[\alpha]_D^{35}$ –170.0 (*c* 0.50, $CHCl_3$); $R_f$ 0.423 (EtOAc/$CH_2Cl_2$/Hexane 1:1:2); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.59 (d, $J$ = 2.1 Hz, 1 H, Ar*H*), 7.21 (dd, $J$ = 7.8, 1.8 Hz, 1 H, Ar*H*), 7.14 (d, $J$ = 8.1 Hz, 1 H, Ar*H*),

5.74 (s, 1 H, H-1), 4.40 (d, $J$ = 5.4 Hz, 1 H), 4.18-4.06 (m, 2 H), 3.50-3.43 (m, 1 H), 2.88 (d, $J$ = 3.6 Hz, 1 H), 1.55 (s, 3 H, C$H_3$), 1.39 (s, 3 H, C$H_3$), 1.30 (s, 9 H, *t*Bu-*H*), 1.24 (d, $J$ = 6 Hz, 3 H, C$H_3$ × 2); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 150.1, 136.9, 132.5, 130.4, 130.1, 125.3, 110.2 (quaternary-C), 83.3 (C-1), 79.0, 77.4, 75.7, 67.4, 34.9, 31.8, 28.6, 26.9, 20.6, 17.6; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{20}H_{30}NaO_4S$, 389.1757; found, 389.1761.

**Table S1:** Temperature optimization for DMF-modulated glycosylation of diacetonide galactose acceptor **3** with thioglucoside **1**.

| Entry | Donor (equiv) | DMF (equiv) | $T$ (˚C)[a] | Time (h) | Product, **4** | |
|---|---|---|---|---|---|---|
| | | | | | Yield% | α/β ratio |
| 1 | **1** (1.2) | 1.2 | 0 | 4 | 50 | β only |
| 2 | **1** (1.2) | 1.2 | –10 | 4 | 75 | β only |
| 3 | **1** (1.2) | 1.2 | –20 | 5 | 75 | β only |
| 4 | **1** (1.2) | 1.2 | –40 | 5 | 71 | β only |
| 5 | **1** (1.2) | 1.2 | –60 | 6 | 60 | β only |

[a] $T$ = temperature at pre-activation and coupling reaction

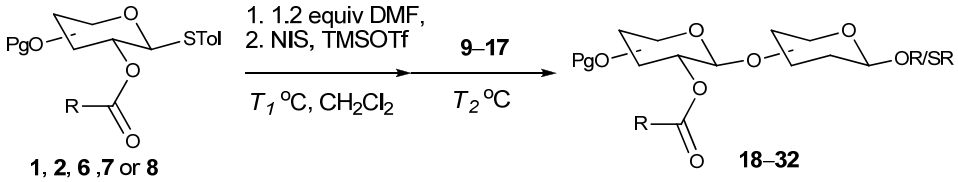
**Table S2:** Characteristic NMR data for reaction intermediates **40α**, **40β**, and **41**

| Entry | Selected NMR data | Observed reaction intermediates | | |
|---|---|---|---|---|
| | | **40α** | **40β** | **41** |
| 1 | $^1$H signal at C-1/ppm ($^3J_{HH}$/Hz) | 6.19 (s) | 5.79 (7.8) | 5.22 (9.0) |
| 2 | $^1$H signal at C-2/ppm | 5.22 | 5.30 | 5.87 |
| 3 | $^1$H signal at C-1/ppm ($^1J_{CH}$/Hz) | 103.0 (183 ) | 102.0 (174) | 78.6 (ND) |
| 4 | $^1$H signal of imidate /ppm | 8.75 | 9.17 | - |

**General DMF-modulated glycosylation procedure for participating thioglycosyl donors** (refer to Table 2 in main text): 1.2 Equiv of thioglycoside donor (**1**, **2**, **6**, **7**, or **8**), DMF (1.2 equiv), and activated molecular sieve (4 Å) were suspended in dried $CH_2Cl_2$. The mixture was stirred at RT for 5 min and cooled to –30, –20 or –10 ˚C at

least 15 min in cooling reactor (Eyela model: PCL 1810 or PCL 1800). Subsequently, 1.2 equiv of NIS and 1.2 (or 1.8 for thiomannoside donors) equiv of TMSOTf (for most of thioglycoside acceptors used) or TfOH (for glycosylation of **13b**) were added. Upon completion of pre-activation at –30, –20 or –10 ˚C, acceptors (**9**–**17**, 1 equiv) was added to reaction solution. The temperature for each coupling reaction needed optimization. Upon completion of glycosylation, the reaction was quenched with satd. $NaHCO_3$ and solid $Na_2S_2O_3$, then stirred vigorously at RT until the dark red coloration of the solution turning to pale yellow. The mixture was dried by $MgSO_4$ powder, followed by filtration and concentration to give crude concentrate for column chromatography purification giving the glycosylation products **18**–**32**. Exact amount of substrates and reagents used were given in Table S3

**Table S3:** Amounts of glycosyl substrates and promoting reagents used in DMF-modulated glycosylations

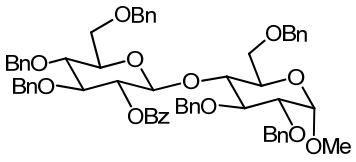



| Entry | Donor, (mg, mmol) | Acceptor, (mg, mmol) | NIS (mg, mmol) | TMSOTf (μL, mmol) | $T_1$, $T_2$ (˚C)[a] | Product, mg, yield (%) |
|---|---|---|---|---|---|---|
| 1 | **1**, 150, 0.23 | **9**, 88, 0.19 | 55.8, 0.25 | 41, 0.23 | -10, -10 | **18**, 125, 65 |
| 2 | **1**, 250, 0.38 | **10**, 176, 0.32 | 93, 0.41 | 68, 0.38 | -10, -10 | **19**, 216, 67 |
| 3 | **1**, 172, 0.26 | **11a**, 120, 0.22 | 64, 0.28 | 47, 0.260 | -10, -10 | **20**, 164, 70 |
| 5 | **1**, 143, 0.22 | **16**, 100, 0.18 | 53, 0.23 | 39, 0.22 | -10, -10 | **21**, 137, 70 |
| 6 | **1**, 150, 0.227 | **17**, 69, 0.19 | 55.8, 0.25 | 41, 0.23 | -10, -10 | **22 ,** 84, 55 |
| 7 | **6** , 200, 0.3 | **11a**, 141, 0.25 | 72, 0.3 | 86, 0.48 | -20, -10 | **23**, 178, 66 |
| 8 | **6** , 200, 0.3 | **11b** , 149, 0.25 | 72, 0.3 | 86, 0.48 | 0, 10 | **24**, 172, 63 |
| 9 | **2**, 500, 0.758 | **12**, 384, 0.69 | 188, 0.828 | 206, 1.14 | -20, 0 | **25**,339, 61 |
| 10 | **2**, 200, 0.303 | **13a**, 141, 0.253 | 74.7, 0.329 | 82.1, 0.46 | -20, -20 | **26**, 166, 60 |
| 11 | **2**, 2000, 3.03 | **13b**, 1440, 2.53 | 717, 3.16 | 767, 4.56[b] | -20, 0 | **27**, 2050, 73 |
| 12 | **2**, 150, 0.23 | **14**, 105, 0.19 | 55.8, 0.25 | 61, 0.34 | -10, -10 | **28**, 128, 62 |
| 13 | **7**, 182, 0.31 | **11a**, 144, 0.26 | 76.5, 0.34 | 56.1, 0.31 | -10, -10 | **29**, 183, 64 |
| 14 | **7**, 100, 0.17 | **15**, 94, 0.14 | 42, 0.19 | 31, 0.17 | -10, -10 | **30**, 64, 40 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15 | **8**, 200, 0.30 | **16**, 134, 0.24 | 68, 0.30 | 65, 0.36 | -30, -30 | **31**, 186, 57 |

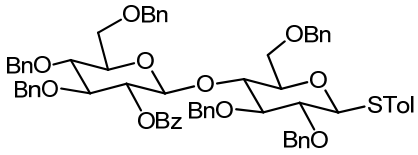
[a]$T_1$ = pre-activation temperature; $T_2$ = coupling temperature. [b]2.5 M stock solution of triflic acid (TfOH in $Et_2O$) was used as acid promoter.

**Methyl 4-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside 18:**



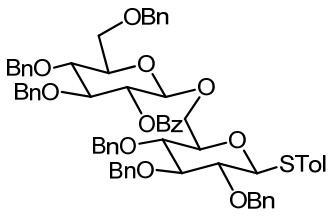

Disaccharide **18** was prepared from thioglucoside **1** and methyl glucoside **9** (Table S3, entry 1). Purification of **18** was achieved by standard column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 0.5:4:7 stepwise to 1:4:5). For disaccharide **18**: $[\alpha]_D^{35}$ +30.6 (*c* 0.36, $CHCl_3$); $R_f$ 0.35 (EtOAc/$CH_2Cl_2$/Hexane 1/4/5); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.88 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.56 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.43–7.35 (m, 6H, Ar*H*), 7.32–7.18 (m, 20H, Ar*H*), 7.14–7.05 (m, 6H, Ar*H*), 5.23 (dd, *J* = 9.3, 8.1 Hz, 1H), 5.08 (d, *J* = 11.4 Hz, 1H), 4.81 (s, 1H), 4.77 (s, 1H), 4.75–4.68 (m, 2H), 4.66–4.63 (m, 1H), 4.60–4.54 (m, 3H), 4.50 (dd, *J* = 9.9, 6.3 Hz, 2H), 4.45 (d, *J* = 12.3 Hz, 1H), 4.36 (d, *J* = 12.3 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 3.91–3.82 (m, 2H), 3.76–3.68 (m, 2H), 3.63–3.59 (m, 2H), 3.56–3.49 (m, 2H), 3.45–3.35 (m, 3H), 3.25 (s, 3H, OC*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.3, 140.1, 138.9, 138.8, 138.5, 138.4, 138.2, 133.6, 130.2, 129.0, 128.90, 128.87, 128.79, 128.76, 128.70, 128.61, 128.57, 128.5, 128.44, 128.37, 128.3, 128.24, 128.20, 128.12, 128.08, 128.07, 127.9, 127.5, 100.8 (C-1'), 98.8 (C-1), 83.3, 80.7, 79.3, 78.6, 77.2, 75.9, 75.8, 75.6, 75.3, 74.7, 74.0, 73.9, 70.0, 69.2, 68.2, 55.7; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{62}H_{64}NaO_{12}$, 1023.4290; found, 1023.4347.

***p*-Tolyl 4-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-thio-β-D-glucopyranoside 19:**




Disaccharide **19** was prepared from thioglucosides **1** and **10** (Table S3, entry 2). Purification of **19** was achieved by standard column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:1:15). For disaccharide **19**: $[\alpha]_D^{35}$ +10.1 (*c* 0.34, $CHCl_3$); $R_f$ 0.47 (EtOAc/$CH_2Cl_2$/Hexane 1:1:4); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.92 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 7.55 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.43-7.22 (m, 25H, Ar*H*), 7.20-7.16 (m, 5H, Ar*H*), 7.10-7.09 (m, 5H, Ar*H*), 6.97 (d, *J* = 7.8 Hz, 2H, Ar*H*), 5.25 (t, *J* = 8.4 Hz, 1 H), 5.14 (d, *J* = 11.4 Hz, 1H), 4.80-4.65 (m, 6H), 4.60 (s, 1H), 4.55 (d, *J* = 10.2 Hz, 2H), 4.47 (d, *J* = 9.9 Hz, 1H), 4.38-4.32 (m, 3H), 3.96 (t, *J* = 9.6 Hz, 1H), 3.85-3.48 (m, 8H), 3.42-3.35 (m, 2 H), 3.2 (d, *J* = 9.3 Hz, 1H), 2.26 (s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.3 (*C*=O), 139.7, 138.74, 138.7, 138.6, 138.4, 138.2, 138.0, 133.6, 133.1, 130.1, 130.0, 128.92, 128.88, 128.8, 128.70, 128.69, 128.66, 128.6, 128.5, 128.32, 128.29, 128.21, 128.16, 128.1, 128.03, 128.01, 127.9, 127.5, 100.9 (C-1'), 88.1 (C-1), 85.3, 83.3, 80.7, 79.0, 78.6, 77.0, 75.78, 75.74, 75.5, 75.3, 74.7, 73.9, 73.8, 69.1, 68.6, 21.5 (*C*$H_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4436.

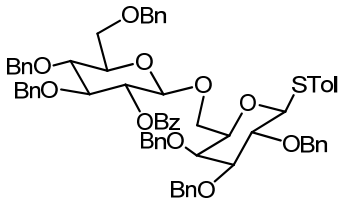
***p*-Tolyl 6-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside 20:**




Disaccharide **20** was prepared from thioglucosides **1** and **11a** (Table S3, entry 3). Purification of **20** was achieved by standard column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:1:6). For disaccharide **20**: $[\alpha]_D^{35}$ +4.9 (*c* 0.32, $CHCl_3$); $R_f$

0.45 (EtOAc/Hexane 1:2); $^{1}$H-NMR (300 MHz, $CDCl_3$): $\delta$7.92 (d, $J$ = 6.9 Hz, 2H, Ar*H*), 7.50–7.43 (m, 3H, Ar*H*), 7.38–7.18 (m, 25H, Ar*H*), 7.13–7.11 (m, 7H, Ar*H*), 7.07–7.03 (m, 2H, Ar*H*), 5.36 (t, $J$ = 7.8 Hz, 1H), 4.84 (d, $J$ = 3.3 Hz, 1H), 4.81 (d, $J$ = 2.4 Hz, 1H), 4.78 (s, 1H), 4.69-4.64 (m, 3H), 4.62 (s, 1H), 4.60 (s, 1H), 4.57 (s, 1 H), 4.54-4.48 (m, 2H), 4.40 (d, $J$ = 10.8 Hz, 1H), 4.13 (d, $J$ = 10.8 Hz, 1H), 3.85–3.71 (m, 5H), 3.57 (t, $J$ = 7.2 Hz, 2H), 3.41 (p, $J$ = 9.6 Hz, 3H), 2.30 (s, 3H, C$H_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$165.5 (*C*=O), 138.8, 138.6, 138.4, 138.3, 138.21, 138.17, 133.4, 133.3, 130.2, 130.1, 130.1, 128.9, 128.80, 128.76, 128.70, 128.6, 128.4, 128.2, 128.1, 128.0, 101.3 (C-1'), 87.9 (C-1), 87.0, 83.3, 80.7, 79.2, 78.5, 77.8, 76.0, 75.8, 75.7, 75.5, 75.4, 75.2, 74.2, 74.0, 69.3, 68.0, 21.6 (*C*H$_3$); HRMS-ESI (*m/z*): [M + Na]$^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4436.

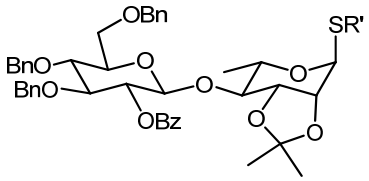
***p*-Tolyl 6-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside 21:**




Disaccharide **21** was prepared from thioglucoside **1** and thiogalactoside **16** (Table S3, entry 5). Purification of **21** was achieved by standard column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:3:11). For disaccharide **21**: $[\alpha]_D^{35}$ +17.5 (*c* 0.42, $CHCl_3$); $R_f$ 0.41 (EtOAc/$CH_2Cl_2$/Hexane 1:2:5); $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$7.95 (d, $J$ = 7.2 Hz, 2H, Ar*H*), 7.50 (t, $J$ = 7.2 Hz, 1H, Ar*H*), 7.42 (t, $J$ = 8.4 Hz, 3H, Ar*H*), 7.37–7.21 (m, 24H, Ar*H*), 7.20–7.15 (m, 2H, Ar*H*), 7.11 (s, 5H, Ar*H*), 6.97 (d, $J$ = 7.8 Hz, 2H, Ar*H*), 5.27 (t, $J$ = 8.7 Hz, 1H), 4.82 (dd, $J$ = 11.4, 9 Hz, 2H), 4.75–4.64 (m, 5 H), 4.61–4.58 (m, 2H), 4.54 (s, 1H), 4.47 (d, $J$ = 5.7 Hz, 1H), 4.43 (d, $J$ = 3.3 Hz, 1 H), 4.39 (d, $J$ = 3.6 Hz, 2H), 4.01 (dd, $J$ = 7.5 Hz, 1H), 3.84–3.71 (m, 7H), 3.52–3.47 (m, 1H), 3.41 (t, $J$ = 6.0 Hz, 1H), 3.33 (dd, $J$ = 9.3,2.7 Hz, 1H), 2.25

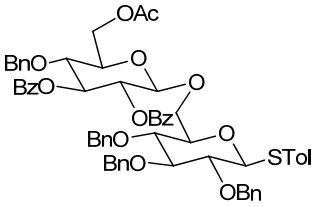
(s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.6 (*C*=O), 139.2, 138.8, 138.6, 138.40, 138.36, 138.2, 137.8, 133.7, 133.0, 130.3, 130.2, 130.1, 130.0, 129.0, 128.84, 128.82, 128.8, 128.73, 128.71, 128.7, 128.5, 128.4, 128.35, 128.30, 128.2, 128.09, 128.07, 128.0, 127.9, 127.7, 101.5 (C-1'), 88.3 (C-1), 84.5, 83.1, 78.2, 77.3, 76.0, 75.55, 75.47, 75.45, 74.8, 74.3, 73.9, 73.4, 72.6, 68.9, 67.8, 21.6 (*C*H$_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4465.

**4-(*t*-Butyl)-2-methylphenyl 4-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-gluco pyranosyl)-2,3-*O*-isopropylidene-thio-α-L-rhamnopyranoside 22:**



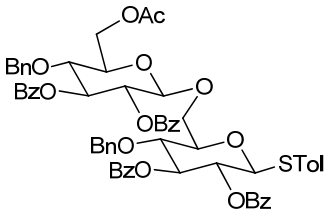

Disaccharide **22** was prepared from thioglucoside **1** and thiorhamnoside **17** (Table S3, entry 6). Purification of **22** was achieved by column chromatography purification (Elution: EtOAc/Hexane 1:15). For disaccharide **22**: $[\alpha]_D^{35}$ –77.9 (*c* 0.83, $CHCl_3$); $R_f$ 0.3 (EtOAc/Hexane 1:4); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.11 (d, *J* = 6.9 Hz, 2H, Ar*H*), 7.61-7.56 (m, 1H, Ar*H*), 7.51 (d, *J* = 2.1 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.33-7.09 (m, 17H, Ar*H*), 5.63 (s, 1H), 5.26 (t, *J* = 8.1 Hz, 1H), 4.99 (d, *J* = 7.8 Hz, 1H), 4.84 (d, *J* = 10.8 Hz, 1H), 4.76–4.68 (m, 2H), 4.65–4.53 (m, 3H), 4.22 (d, *J* = 5.7 Hz, 1H), 4.07–4.00 (m, 2H), 3.89–3.74 (m, 4H), 3.63 (dd, *J* = 9.9, 7.5 Hz, 1H), 3.52 (d, *J* = 9.3 Hz, 1H), 2.34 (s, 3H, C*H*$_3$), 1.48 (s, 3H, C*H*$_3$), 1.28–1.26 (m, 15H); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 166.0 (*C*=O), 150.1, 138.6, 138.5, 138.4, 137.1, 133.5, 132.4, 130.8, 130.4, 128.9, 128.84, 128.76, 128.7, 128.44, 128.41, 128.3, 128.09, 128.06, 125.3, 109.7 (quaternary-C), 101.0 (C-1'), 83.4 (C-1), 80.8, 78.4, 77.4, 75.8, 75.4, 74.5, 74.0, 69.1, 66.3, 34.9, 31.8, 28.4, 26.8, 20.6, 18.0; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{54}H_{62}NaO_{10}S$, 925.3956; found, 925.4029.

**_p_-Tolyl 6-_O_-(6-_O_-Acetyl-2,3-di-_O_-benzoyl-4-_O_-benzyl-β-D-glucopyranosyl)-2,3,4-tri-_O_-benzyl-thio-β-D-glucopyranoside 23:**



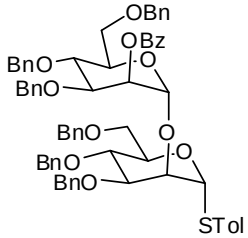

Disaccharide **23** was prepared from thioglucosides **6** and **11a** by the general DMF-modulated glycosylation procedure (Table S3, entry 7). The disaccharide **23** was obtained as white semisolid after column chromatography purification (Elution: EtOAc/Hexane 1:4). For disaccharide **23**: $[\alpha]_D^{35}$ +28.0 (*c* 0.80, $CHCl_3$); $R_f$ 0.3 (EtOAc/Hexane 3:7); $^1$H NMR (400 MHz,$CDCl_3$): $\delta$ 7.97 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.81 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.53–7.47 (m, 4H, Ar*H*), 7.40-7.37 (m, 5H), 7.34–7.13 (m, 19H, Ar*H*), 7.09–7.07 (m, 2H, Ar*H*), 5.70 (t, *J* = 9.2 Hz, 1H), 5.44–5.39 (m, 1H), 4.87–4.71 (m, 5H), 4.66 (d, *J* = 10.4 Hz, 1H), 4.60-4.53 (m, 3H), 4.50 (d, *J* = 1.6 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.27 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.67 (d, *J* = 9.2 Hz, 1H), 3.60-3.56 (m, 1H), 3.43-3.35 (m, 3H), 2.34 (s, 3H, C*H*$_3$), 2.05 (s, 3H, C*H*$_3$CO); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 171.2 (*C*=O), 166.1 (*C*=O), 165.7 (*C*=O), 138.8, 138.53, 138.48, 138.3, 137.3, 133.7, 133.5, 133.3, 130.4, 130.22, 130.18, 130.0, 129.82, 129.76, 128.90, 128.87, 128.85, 128.83, 128.75 128.7, 128.6, 128.3, 128.24, 128.18, 128.13, 128.10, 127.9, 127.8, 101.2 (C-1'), 88.2 (C-1), 81.0, 79.2, 76.2, 76.1, 75.8, 75.7, 75.3, 75.2, 75.1, 73.5, 72.5, 68.2, 63.1, 21.6, 21.4; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{63}H_{61}NaO_{13}S$, 1081.3803; found, 1081.3784.

**_p_-Tolyl 6-_O_-(6-_O_-Acetyl-2,3-di-_O_-benzoyl-4-_O_-benzyl-β-D-glucopyranosyl)-2,3-di-_O_-benzoyl-4-_O_-benzyl-thio-β-D-glucopyranoside 24:**



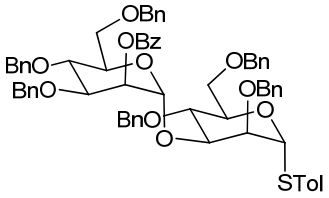

Disaccharide **24** was prepared from thioglucosides **6** and **11b** by the general DMF-modulated glycosylation procedure (Table S3, entry 8). Purification of **24** was achieved by column chromatography purification (Elution: EtOAc/Hexane 1:4). For disaccharide **24**: $[\alpha]_D^{35}$ +41.5 (*c* 0.13, $CHCl_3$); $R_f$ 0.2 (EtOAc/Hexane 1:5 two times); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.98 (d, *J* = 6.8 Hz, 2H, Ar*H*), 7.90 (dd, *J* = 14.4, 7.2 Hz, 4H, Ar*H*), 7.83 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.54–7.46 (m, 4H, Ar*H*), 7.43-7.30 (m, 9H), 7.27 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.21-7.20 (m, 3H, Ar*H*), 7.17-7.10 (m, 6H, Ar*H*), 6.95-6.93 (m, 2H, Ar*H*), 5.74 (t, *J* = 9.2 Hz, 1H), 5.61 (t, *J* = 9.2 Hz, 1H), 5.46 (dd, *J* = 9.6, 1.6 Hz, 1H), 5.27 (t, *J* = 10.0 Hz, 1H), 4.80 (d, *J* = 7.6 Hz, 1H), 4.76 ( d, *J* = 8.0 Hz, 2H), 4.63–4.50 (m, 4H), 4.34–4.27 (m, 3H), 4.16 (d, *J* = 11.2 Hz, 1H), 3.94 (t, *J* = 9.6 Hz, 1H), 3.84 ( dd, *J* = 8.7, 3.3 Hz, 1H), 3.75-3.69 (m, 2H), 3.64 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.33 (s, 3H, C*H*$_3$), 2.08 (s, 3H, C*H*$_3$CO); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 171.1 (*C*=O), 166.1 (*C*=O), 166.0 (*C*=O), 165.7 (*C*=O), 165.6 (*C*=O), 139.0, 137.6, 137.3, 134.1, 133.8, 133.6, 130.3, 130.24, 130.21, 130.18, 130.16, 129.9, 129.8, 128.93, 128.89, 128.8, 128.74, 128.69, 128.6, 128.3, 101.3 (C-1), 86.7 (C-1), 79.4, 76.9, 76.2, 76.1, 75.7, 75.22, 75.15, 73.6, 72.5, 71.2, 68.2, 63.1, 21.7, 21.4; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{63}H_{57}NaO_{15}S$, 1109.3389; found, 1109.3373.

***p*-Tolyl 2-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside 25:**



Disaccharide **25** was prepared from thiomannosides **2** and **12** by the general DMF-modulated glycosylation procedure for participating donor (Table S3, entry 9). **25** was purified by standard column chromatography ($Et_2O/CH_2Cl_2$/Hexane 0.5:2:10 stepwise to 0.1:2:8). For disaccharide **25**: $[\alpha]_D^{35}$ +42.5 (*c* 0.33, $CHCl_3$); $R_f$ 0.4 ($Et_2O/CH_2Cl_2$/Hexane 1:1:4); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.07 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.54 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.39-7.12 (m, 34H, Ar*H*), 7.00 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.76 (s, 1H), 5.58 (s, 1 H), 5.17 (s, 1H), 4.90 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.76-4.61 (m, 5 H), 4.57 (s, 1H), 4.49 (s, 1H), 4.46-4.40 (m, 3H), 4.30 (s, 1H), 4.23 (s, 1H), 4.08-4.06 (m, 1H), 4.02-3.96 (m, 2H), 3.93-3.91 (m, 2H), 3.85-3.71 (m, 3H), 3.63 (d, *J* = 10.5 Hz, 1H), 2.54 (s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.9 (*C*=O), 138.94, 138.85, 138.8, 138.5, 138.1, 133.5, 132.8, 130.7, 130.4, 130.2, 128.9, 128.81, 128.75, 128.70, 128.67, 128.52, 128.46, 128.33, 128.25, 128.2. 128.1, 128.0, 127.9, 127.8, 100.2 (C-1'), 88.0 (C-1), 80.4, 78.5, 75.7, 75.6, 75.3, 74.8, 73.6, 73.3, 72.8, 72.6, 72.1, 69.7, 69.5, 69.3, 21.5 (*C*H$_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4451.

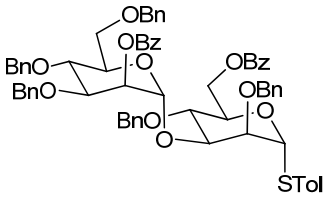
***p*-Tolyl 3-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside 26:**




Disaccharide **26** was prepared from thiomannosides **2** and **13a** by the general DMF-modulated glycosylation procedure (Table S3, entry 10). Purification of **26** was performed with column chromatography (Elution: $Et_2O/CH_2Cl_2$/Hexane 1:1:16 stepwise to 1:1:11). For disaccharide **26**: $[\alpha]_D^{35}$ +46.9 (*c* 0.35, $CHCl_3$); $R_f$ 0.4 ($Et_2O/CH_2Cl_2$/Hexane 1:1:4); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.06 (d, *J* = 7.2 Hz, 2H,

Ar*H*), 7.53 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.38–7.16 (m, 34H, Ar*H*), 7.03 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.78 (t, *J* = 2.1 Hz, 1H), 5.56 (s, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 10.8 Hz, 1H), 4.78 (dd, *J* = 12.3, 10.8 Hz, 2H), 4.72–4.63 (m, 3H), 4.58–4.45 (m, 6H), 4.30 (dd, *J* = 9, 3.6 Hz, 1H), 4.20–4.12 (m, 4H), 4.04 (t, *J* = 9.6 Hz, 1H), 4.97 (d, *J* = 9.6 Hz, 1H), 3.87–3.70 (m, 4H), 2.28 (s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.8 (*C*=O), 139.0, 138.8, 138.7, 138.3, 138.2, 137.9, 133.5, 132.6, 130.9, 130.3, 130.2, 130.1, 128.84, 128.79, 128.76, 128.71, 128.67, 128.6, 128.44, 128.42, 128.2, 128.01, 127.97, 127.89, 127.87, 127.85, 100.2 (C-1'), 85.9 (C-1), 79.2, 78.5, 75.6, 75.4, 74.8, 73.9, 73.7, 73.2, 72.8, 71.8, 69.6, 69.5, 21.5 (*C*H$_3$); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4472.

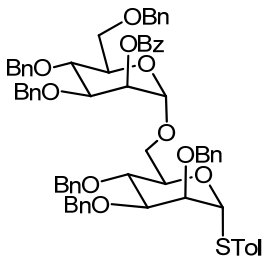
***p*-Tolyl 3-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside 27:**




Disaccharide **27** was prepared from thiomannosides **2** and **13b** by the general DMF-modulated glycosylation procedure (Table S1, entry 11). Purification of **27** was performed with column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 0.2:2:8 stepwise to 0.4:2:8). For disaccharide **27**: $[\alpha]_D^{35}$ +50.2 (*c* 0.33, $CHCl_3$); $R_f$ 0.44 (EtOAc/Hexane 1/2); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.08 (d, *J* = 7.2 Hz, 2H, Ar*H*), 8.00 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.53 (dd, *J* = 13.8, 7.2 Hz, 2H, Ar*H*), 7.39-7.16 (m, 31H, Ar*H*), 7.00 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.79 (s, 1 H), 5.57 (s, 1 H), 5.40 (s, 1H), 4.89 (t, *J* = 10.8 Hz, 2H), 4.76 (d, *J* = 11.4 Hz, 1H), 4.72 (t, *J* = 12.3 Hz, 2H), 4.60-4.52 (m, 7H), 4.50-4.46 (m, 1H), 4.24-4.10 (m, 4H), 4.06 (d, *J* = 5.7 Hz, 2H), 3.83-3.75 (m, 2H), 2.26 (s, 3H); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 166.7 (*C*=O), 165.9 (*C*=O), 138.9, 138.7, 138.24, 138.17, 138.1, 137.8, 133.6, 133.3, 132.4, 130.6, 130.3,

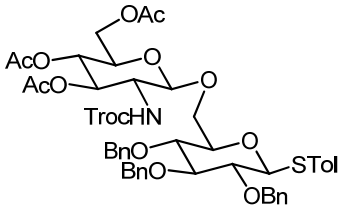
130.22, 130.17, 128.94, 128.87, 128.8, 128.74, 128.71, 128.69, 128.65, 128.4, 128.2, 128.03, 127.95, 127.9, 100.4 (C-1'), 85.6 (C-1), 80.8, 79.4, 78.4, 75.9, 75.4, 75.1, 74.8, 74.0, 72.9, 72.0, 71.7, 71.4, 69.7, 69.5, 64.1, 21.5 (*C*$H_3$); HRMS-ESI (*m/z*): [M + Na]$^+$ calcd. for $C_{68}H_{66}NaO_{12}S$, 1129.4167; found, 1129.4195.

***p*-Tolyl 6-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-thio-α-D-mannopyranoside 28:**




Disaccharide **28** was prepared from thiomannosides **2** and **14** by the general DMF-modulated glycosylation procedure for participating donors (Table S3, entry 12). Purification of **28** was performed with column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1:2:20 stepwise to 1:2:10). For disaccharide **28**: $[\alpha]_D^{35}$ +30.8 (*c* 0.34, $CHCl_3$); $R_f$ 0.325 (EtOAc/$CH_2Cl_2$/Hexane 1:2:10); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$8.08 (dd, *J* = 8.1, 0.9 Hz, 2H, Ar*H*), 7.52 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.39–7.12 (m, 34H, Ar*H*), 7.07 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.74 (s, 1H), 5.53 (d, *J* = 1.5 Hz, 1H), 5.07 (d, *J* = 1.8 Hz, 1H), 4.95 (d, *J* = 1.1 Hz, 1H), 4.89 (d, *J* = 1.1 Hz, 1H), 4.79–4.69 (m, 3H), 4.64–4.59 (m, 3H), 4.54 (s, 1H), 4.50–4.43 (m, 3H), 4.27 (dd, *J* = 9.6, 3.6 Hz, 1H), 4.11 (d, *J* = 6 Hz, 2H), 4.04–3.97 (m, 3H), 3.89–3.79 (m, 3H), 3.70 (t, *J* = 9.9 Hz, 2H), 2.16 (s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$165.9 (*C*=O), 139.1, 138.9, 138.8, 138.5, 138.3, 137.9, 133.4, 131.9, 131.3, 130.4, 130.3, 128.86, 128.84, 128.79, 128.74, 128.71, 128.6, 128.5, 128.32, 128.3, 128.20, 128.16, 128.02, 127.96, 127.90, 127.86, 98.7 (C-1'), 86.3 (C-1), 80.7, 78.2, 76.5, 75.7, 75.6, 75.0, 74.6, 72.6, 72.3, 72.3, 72.0, 71.7, 69.3, 69.1, 67.3, 21.4 (*C*$H_3$); HRMS-ESI (*m/z*): [M + Na]$^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4374; found, 1115.4421.

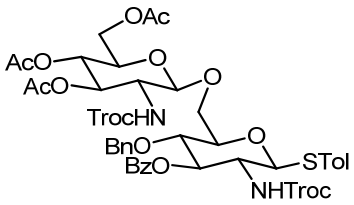
***p*-Tolyl 6-*O*-[3,4,6-Tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside 29**:




Disaccharide **29** was prepared from thioglucosaminyl donor **7** and thioglucoside acceptor **11a** by the general DMF-modulated glycosylation procedure for participating donors (Table S3, entry 13). Purification of **29** was performed by column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 0.2:1:2 stepwise to 0.5:1:2). For disaccharide **29**: $[\alpha]_D^{35}$ –0.6 (*c* 0.33, $CHCl_3$); $R_f$ 0.36 (EtOAc/$CH_2Cl_2$/Hexane 1:1:2); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 7.48 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.39–7.30 (m, 13H, Ar*H*), 7.25–7.21 (m, 4H, Ar*H*), 5.05–4.98 (m, 2H), 4.89 (dd, *J* = 10.8, 6.3 Hz, 2H), 4.84 (s, 1H), 4.81 (s, 1H), 4.74–4.67 (m, 3H), 4.62 (d, *J* = 8.4 Hz, 2H), 4.55 (d, *J* = 10.5 Hz, 2H), 4.26 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.09 (t, *J* = 12.6 Hz, 2H), 3.76–3.66 (m, 3H), 3.63–3.59 (m, 1H), 3.52–3.44 (m, 2H), 3.41–3.32 (m, 1H), 2.34 (s, 3H, C*H*$_3$), 2.07 (s, 3H, C*H*$_3$C=O), 2.03 (s, 3H, C*H*$_3$C=O), 2.01 (s, 3H, C*H*$_3$C=O); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 171.2 (*C*=O), 170.9 (*C*=O), 170.0 (*C*=O), 154.6 (O*C*=O), 138.8, 138.6, 138.3, 138.2, 133.2, 130.7, 129.8, 129.0, 128.95, 128.9, 128.6, 128.5, 128.4, 128.3, 101.4 (C-1'), 95.9 (*C*$Cl_3$), 88.1 (C-1), 87.1, 81.2, 80.1, 78.2, 76.3, 75.8, 75.4, 74.9, 72.7, 72.0, 69.2, 68.3, 62.4, 56.3, 21.5 (*C*$H_3$), 21.2 (C*H*$_3$C=O), 21.12 (C*H*$_3$C=O), 21.10 (C*H*$_3$C=O); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{49}H_{54}Cl_3NaNO_{14}S$, 1040.2223; found, 1040.2437.

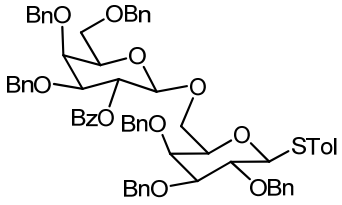
***p*-Tolyl 6-*O*-[3,4,6-Tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-β-D-glucopyranosyl]-3-*O*-benzoyl-4-*O*-benzyl-2-(2,2,2-trichloroethoxycarbonyl**

**amino)-2-deoxy-thio-β-D-glucopyranoside 30:**



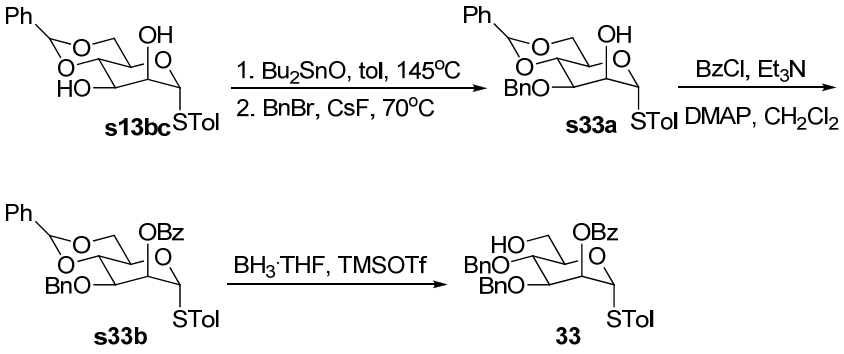

Disaccharide **30** was prepared from thioglucosaminyl donor **7** and thioglucosaminyl acceptor **15** by the general DMF-modulated glycosylation procedure for participating donors (Table S1, entry 14). Purification of **30** was performed by column chromatography (EtOAc/$CH_2Cl_2$/Hexane 1:3:2). For disaccharide **30**: $[\alpha]_D^{35}$ –5.3 (*c* 0.35, $CHCl_3$); $R_f$ 0.36 (EtOAc/$CH_2Cl_2$/Hexane 1:3:2); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.01 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.58 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.46-7.40 (m, 4H, Ar*H*), 7.17-7.00 (m, 7H, Ar*H*), 6.06 (bs, 1H, carbamate-*H*), 5.59 (t, *J* = 8.7 Hz, 1H), 5.40 (s, 1H, carbamate-*H*), 5.28 (t, *J* = 9.6 Hz, 1H), 5.06 (t, *J* = 9.3 Hz, 1H), 4.79-4.65 (m, 4 H), 4.58-4.40 (m, 4H), 4.28 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.15 (d, *J* = 11.4 Hz, 1H), 4.00-3.91 (m, 2H), 3.74-3.66 (m, 5H), 2.32 (s, 3H, C*H*$_3$), 2.06 (s, 3H, C*H*$_3$C=O), 2.03 (s, 3H, C*H*$_3$C=O), 2.1 (s, 3H, C*H*$_3$C=O); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 171.2 (*C*=O), 170.9 (*C*=O), 169.9 (*C*=O), 167.0 (*C*=O), 154.7 (*C*=O), 154.5 (*C*=O), 138.8, 137.4, 134.0, 133.6, 130.3, 129.3, 128.9, 128.76, 128.5, 128.4, 100.5 (C-1'), 95.8 (*C*$Cl_3$), 95.7 (*C*$Cl_3$), 87.6 (C-1), 79.0, 76.3, 75.0, 74.6, 72.5, 72.0, 69.1, 67.3, 62.3, 56.0, 55.4, 30.0, 21.5 (C*H*$_3$), 21.1 (C*H*$_3$C=O), 21.00 (C*H*$_3$C=O), 20.97 (C*H*$_3$C=O); HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{45}H_{48}Cl_6N_2NaO_{16}S$, 1137.0748; found, 1139.0757.

***p*-Tolyl 6-*O*-(2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside 31:**




Disaccharide **31** was prepared from 2-*O*-benzoyl thiogalactoside **8** and thiogalactoside **16** by general DMF-modulated glycosylation procedure (Table S1, entry 15). For disaccharide **31**: $[\alpha]_D^{35}$ +17.6 (*c* 0.75, $CHCl_3$); $R_f$ 0.4 (EtOAc/Hexane 1:4); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 7.97 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.51 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.40 (d, *J* = 8.0 Hz, 4H, Ar*H*), 7.36-7.21 (m, 25H, Ar*H*), 7.14 (bs, 5H, Ar*H*), 6.95 (d, *J* = 7.6 Hz, 2H, Ar*H*), 5.61 (t, *J* = 8.8 Hz, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 4.65-4.60 (m, 5H), 4.53 (d, *J* = 7.6 Hz, 1H), 4.48-4.31 (m, 6H), 4.02-3.98 (m, 2H), 3.85 (s, 1H), 3.77 (t, *J* = 9.6 Hz, 1H), 3.72 (dd, *J* = 10.0, 4.8 Hz, 1H), 3.63-3.57 (m, 3H), 3.54-3.51 (m, 1H), 3.41 (t, *J* = 6.0 Hz, 1H), 3.32 (d, *J* = 9.2 Hz, 1H), 2.25 (s, 3H, C*H*$_3$); $^{13}$C-NMR (100 MHz, $CDCl_3$): $\delta$ 165.7 (*C*=O), 139.4, 138.91, 138.87, 138.67, 138.2, 138.0, 137.7, 133.6, 132.8, 130.5, 130.4, 130.2, 130.0, 129.9, 128.74, 128.71, 128.68, 128.46, 128.40, 128.3, 128.12, 128.09, 128.05, 127.94, 127.90, 127.6, 101.8 (C-1'), 88.3 (C-1), 84.5, 80.3, 77.3, 76.0, 75.0, 74.8, 74.03, 73.99, 73.3, 72.9, 72.6, 72.5, 72.1, 68.7, 67.4, 21.6 (*C*H$_3$). HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{68}H_{68}NaO_{11}S$, 1115.4375; found, 1115.4376.

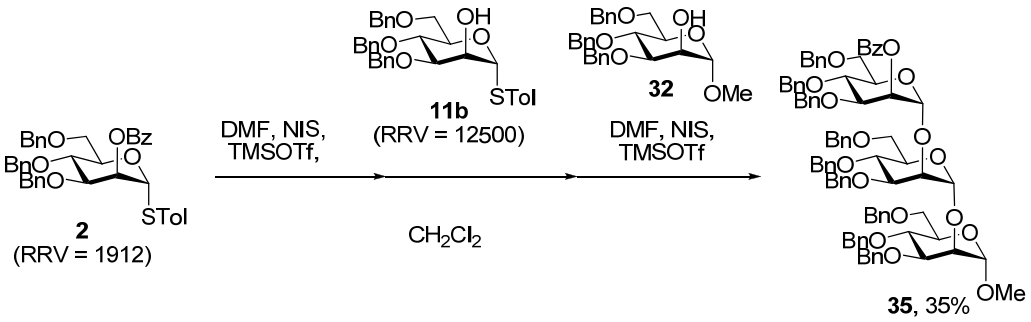
### *p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-thio-α-D-mannopyranoside 33



Acetal derivative **s13bc** (5.0 g, 13.4 mmol) suspended in toluene (67 mL) was treated with di-butyl tin oxide ($Bu_2SnO$, 5.0 g, 20.1 mmol) and the solution was heated to reflux with Dean-Stark trap for 4 h (at 145 ˚C). The volume of toluene was then reduced approximately by half and the reaction mixture was cooled to RT. After then, benzyl bromide (2.4 ml, 20.1 mmol), cesium fluoride (CsF, 3.0 g, 20.1 mmol), and $CH_3CN$ (33 mL) were added and the resulting mixture was stirred at 70 ˚C for *ca.* 16 h. Upon the completion of alkylation, the reaction mixture was filtered (over celite), and concentrated for column chromatography purification (Elution EtOAc/Hexane 1/8 stepwise to 1/3) to afford **s33a** (4.72 g, 10.17 mmol). **s33a** (3.36 g, 7.2 mmol) was treated with BzCl (1.3 mL, 10.8 mmol), $Et_3N$ (2 mL, 14.4 mmol) and DMAP (85 mg, 0.7 mmol) in $CH_2Cl_2$. Upon completion of the reaction, the mixture was diluted with satd. $NaHCO_3$, then the mixture was extracted with EtOAc (× 2). The EtOAc solution was then washed with $H_2O$ and brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: Ether/$CH_2Cl_2$/Hexane 0.08/1/4 stepwise to 0.1/1/4) to furnish fully protected mannoside derivative **s33b** (3.18 g, 5.6 mmol). The derivative **s33b** (0.755 g, 1.33 mmol) in $BH_3$.THF solution (1 M, 5.32 mL, 5.32 mmol) was treated with trimethylsilyl triflate (TMSOTf) (49 μL) at 0 ˚C. Upon completion of the reductive acetal cleavage, the mixture was neutralized with $Et_3N$, excess borane was quenched with addition of MeOH. The resulting mixture was then concentrated for column chromatography purification (Elution: EtOAc/Hexane 1:8 stepwise to 1:6) to afford thiomannoside acceptor **33** (0.71 g, 1.24 mmol). For monosaccharide **33**: $[\alpha]_D^{35}$ +40.8 (*c* 0.34, $CHCl_3$); $R_f$ 0.34 (EtOAc/Hexane 1/2); $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.06 (d, $J$ = 6.9 Hz, 2 H), 7.56 (t, $J$ = 7.5 Hz, 1 H), 7.46-7.41 (m, 2 H), 7.37-7.25 (m, 12 H), 7.09 (d, $J$ = 8.1 Hz, 2 H), 5.85-5.83 (m, 1 H), 5.50 (d, $J$ = 1.5 Hz, 1 H), 4.94 (d, $J$ = 10.8 Hz, 1 H), 4.79 (d, $J$ = 11.4 Hz, 1 H), 4.67 (d, $J$ = 11.1 Hz, 1 H), 4.60 (d, $J$ = 11.4 Hz, 1 H), 4.27-4.24 (m, 1 H), 4.11-4.01 (m, 2 H), 3.85 (s, 2 H), 2.30 (s, 3 H), 1.97 (s, 1 H); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 166.0, 138.7, 138.5, 138.0, 133.8, 133.2, 130.4,

130.3, 130.1, 129.8, 128.93, 128.85, 128.8, 128.6, 128.5, 128.3, 128.2, 87.1, 78.8, 75.7, 74.5, 73.3, 72.1, 71.1, 62.4, 21.6; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{34}H_{34}NaO_6S$, 593.1968; found, 593.1977.

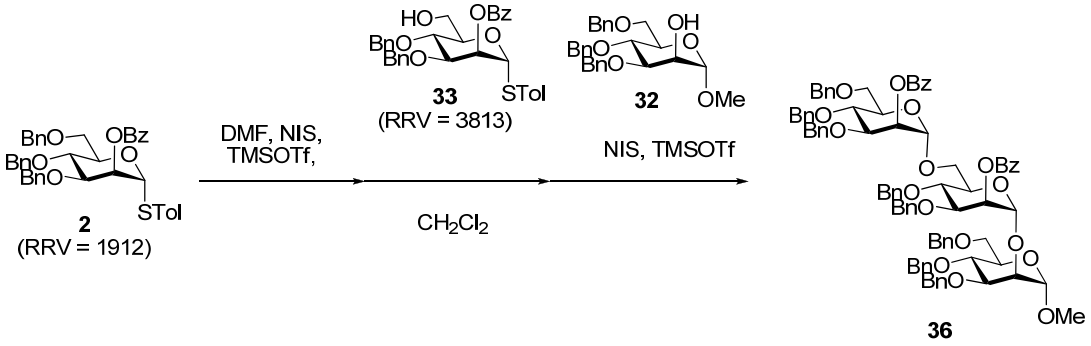
**Methyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside 35**




Trisaccharide **35** was prepared from one pot disarmed-armed glycosylation method. In the first step, thiomannoside donor **2** (200 mg, 0.303 mmol) and DMF (23.5 μL, 0.303 mmol) were treated with NIS (74.7 mg, 0.329 mmol) and TMSOTf (83 μL, 0.455 mmol) in dried $CH_2Cl_2$ at –20 ˚C. Upon the completion of the pre-activation (*ca* 0.5 h), thiomannoside acceptor **12** (141 mg, 0.253 mmol) was added to the mixture, which was stirred at –20 ˚C for *ca.* 7.5 h. Progress of the reaction was monitored by TLC ($R_f$ of disaccharide product = 0.4, developed with 1/1/4 v/v $Et_2O/CH_2Cl_2$/Hexane). Upon the completion of glycosylation (*ca* 7.5 h), methyl mannoside **32** (117 mg, 0.253 mmol), DMF (55 μL, 0.708 mmol), NIS (68.8 mg, 0.303 mmol) and TMSOTf (82 μL, 0.455 mmol) was added to the mixture and the reaction temperature was stirred raised at 10 ˚C for *ca.* 14.5 h. Followed by standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/2/12 stepwise to 1/1/8), target trisaccharide **35** was obtained as white glassy solid (126.7 mg, 35%). For **35**: $[\alpha]_D^{35}$ +10.0 (*c* 0.32, $CHCl_3$); $R_f$ 0.47 (EtOAc/$CH_2Cl_2$/Hexane

1/1/4); $^{1}$H-NMR (300 MHz, $CDCl_3$): $\delta$ 8.09 (d, $J$ = 7.8 Hz, 2 H), 7.55 (t, $J$ = 7.5 Hz, 1 H), 7.39-7.10 (m, 49 H), 7.05 (t, $J$ = 8.1 Hz, 1 H), 5.77 (s, 1 H), 5.25 (s, 1 H), 5.12 (s, 1 H), 4.88-4.82 (m, 4 H), 4.77 (d, $J$ = 11.1 Hz, 1 H), 4.70-4.45 (m, 14 H), 4.37 (d, $J$ = 12.0 Hz, 1 H), 4.12-4.06 (m, 3 H), 4.01-3.93 (m, 4 H), 3.87-3.69 (m, 9 H), 3.60 (d, $J$ = 1 H), 3.23 (s, 3 H); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 165.9, 139.0, 138.9, 138.8, 138.5, 133.5, 130.5, 130.4, 128.84, 128.82, 128.76, 128.7, 128.6, 128.4, 128.3, 128.14, 128.08, 128.0, 127.94, 127.86, 101.1, 100.2, 99.9, 80.1, 79.7, 78.5, 75.7, 75.52, 75.45, 75.3, 75.2, 74.8, 73.8, 73.7, 72.7, 72.6, 72.5, 72.1, 72.0, 70.0, 69.8, 69.5, 55.1; HRMS-ESI ($m/z$): $[M + Na]^+$ calcd. for $C_{89}H_{92}NaO_{17}$, 1455.6227; found, 1455.6222.

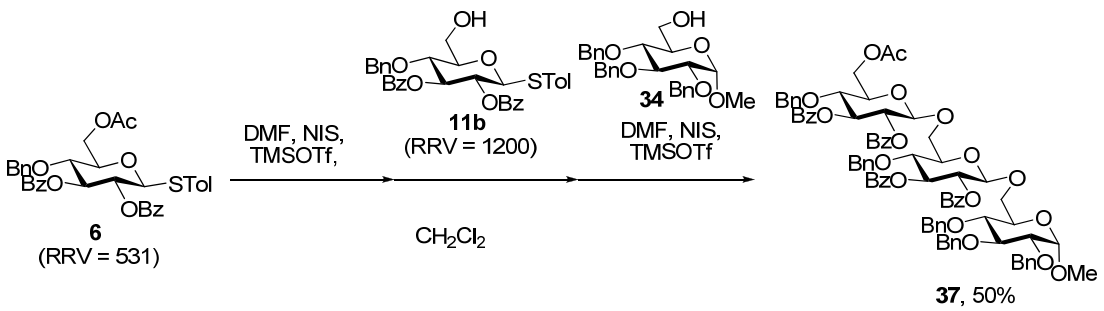
**Methyl 2-*O*-Benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside 36**




Trisaccharide **36** was prepared from one pot disarmed-armed glycosylation method. In the first step, thiomannoside donor **2** (200 mg, 0.303 mmol) and DMF (23.5 μL, 0.303 mmol) were treated with NIS (74.7 mg, 0.329 mmol) and TMSOTf (83 μL, 0.455 mmol) in dried $CH_2Cl_2$ at –20 ˚C. Upon the completion of donor activation (*ca* 0.5 h), thiomannoside acceptor **33** (141 mg, 0.253 mmol) was added to the mixture, which was stirred at 0 ˚C for *ca.* 4.5 h. Progress of the reaction was monitored by TLC examination ($R_f$ of disaccharide product = 0.55, developed with 1/1/3 v/v $Et_2O/CH_2Cl_2$/Hexane). Upon the completion of the glycosylation (*ca* 4.5 h), the reaction temperature was decreased to –20 ˚C, methyl mannoside acceptor **32**

(105.8 mg, 0.228 mmol), NIS (68.8 mg, 0.303 mmol) and TMSOTf (68.6 μL, 0.380 mmol) were added to the mixture and the mixture was stirred at –20 ˚C for *ca.* 2 h. Followed by standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/2/10 stepwise to 1/2/7), trisaccharide **36** was obtained as a white glassy solid (181.2 mg, 55%). For trisaccharide **36**: $[\alpha]_D^{35}$ +21.1 (*c* 1.05, $CHCl_3$); $R_f$ 0.30 (EtOAc/Hexane 1/3); $^1$H-NMR (400 MHz, $CDCl_3$): $\delta$ 8.12 (dd, *J* = 7.2, 1.6 Hz, 2 H), 8.08 (d, *J* = 7.6 Hz, 2 H), 7.55-7.46 (m, 5 H), 7.36-7.17 (m, 36 H), 7.15-7.06 (m, 7 H), 5.79 (s, 2 H), 5.24 (s, 1 H), 5.15 (s, 1 H), 4.88-4.82 (m, 4 H), 4.79-4.75 (m, 3 H), 4.70-4.59 (m, 5 H), 4.52-4.42 (m, 6 H), 4.14-4.09 (m, 4 H), 4.03-3.98 (m, 2 H), 3.93-3.86 (m, 3 H), 3.83-3.69 (m, 7 H), 3.64 (d, *J* = 10.4 Hz, 1 H), 3.33 (s, 3 H); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.97, 165.95, 138.94, 138.88, 138.6, 138.5, 138.2, 133.6, 133.5, 130.6, 130.44, 130.37, 130.3, 129.0, 128.83, 128.79, 128.77, 128.75, 128.70, 128.69, 128.6, 128.5, 128.4, 128.3, 128.1, 128.03, 128.02, 127.97, 127.9, 100.3, 99.7, 98.5, 80.4, 78.9, 78.6, 75.7, 75.6, 75.5, 74.9, 74.61, 74.59, 74.2, 73.82, 73.80, 72.6, 72.3, 72.16, 72.15, 71.8, 69.6, 69.4, 69.3, 69.1, 66.7, 55.2; HRMS MALDI-TOF (*m/z*): $[M + Na]^+$ calcd. for $C_{89}H_{90}NaO_{18}$, 1469.6019; found, 1469.5842.

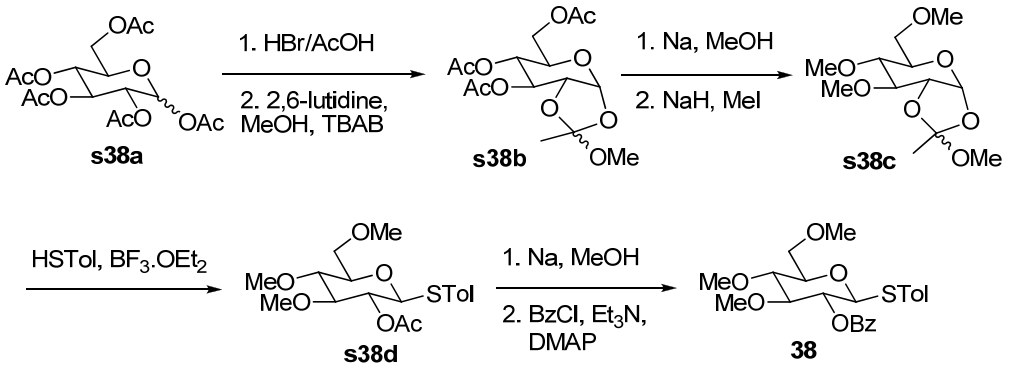
**Methyl 6-*O*-Acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside 37**




Trisaccharide **37** was prepared from one pot disarmed-armed glycosylation

method. In first step, thioglucoside **6** (200 mg, 0.319 mmol) and DMF (30 μL, 0.389 mmol) were treated with NIS (72 mg, 0.319 mmol) and TMSOTf (86 μL, 0.479 mmol) in dried $CH_2Cl_2$ at −10 ˚C. Upon the completion of pre-activation, thioglucoside acceptor **11b** was added to the mixture and the reaction temperature was raised to 0 ˚C. The mixture was stirred at 0 ˚C for *ca* 6 h and the reaction was monitored by TLC examination ($R_f$ of disaccharide = 0.27, developed by 1/4 v/v EtOAc/Hexane × 2). Upon the completion of the first glycosylation, DMF (20 μL, 0.319 mmol), NIS (72 mg, 0.319 mmol) and TNSOTf (85 μL, 0.479 mmol) were added to the reaction mixture to react with the disaccharide for *ca.* 1 h at 0 ˚C. Upon the completion of the disaccharide activation, methyl glycoside acceptor **34** (151 mg, 0.256 mmol) was added to the mixture and the reaction temperature was raised to 10 ˚C. The reaction mixture was stirred at 10 ˚C for *ca.* 8 h. After standard workup (as described in general modulated glycosylation procedure) and column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/22), target trisaccharide **37** was obtained as a light yellow glassy substance (255 mg, 52%). For trisaccharide **37**: $[\alpha]_D^{35}$ +35.7 (*c* 2.1, $CHCl_3$); $R_f$ 0.23 (EtOAc/Hexane: 1/4 × 2); $^1$H NMR (400 MHz,$CDCl_3$): $\delta$ 7.86 (d, *J* = 7.2 Hz, 2 H), 7.82 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.74 (t, *J* = 8.4 Hz, 4 H, Ar*H*), 7.41-7.34 (m, 3 H), 7.31-7.14 (m, 22 H, Ar*H*), 7.09-7.02 (m, 10 H), 6.91-6.86 (m, 4 H, Ar*H*), 5.63 (t, *J* = 9.6 Hz, 1 H), 5.52 (t, *J* = 9.6 Hz, 1 H), 5.35-5.26 (m, 2 H), 4.80-4.78 (m, 2 H), 4.61 (t, *J* = 12.8 Hz, 2 H), 4.51-4.48 (m, 3 H), 4.44-4.38 (m, 3 H), 4.29-4.17 (m, 4 H), 4.09-3.95 (m, 3 H), 3.83-3.69 (m, 3 H), 3.64-3.48 (m, 5 H), 3.35-3.27 (m, 2 H), 3.17 (s, 3 H), 2.00 (s, 3 H, C*H*$_3$); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 171.0, 166.0, 165.6, 165.4, 139.2, 138.62, 138.57, 137.4, 137.2, 133.7, 133.6, 133.3, 130.07, 130.05, 130.0, 129.8, 129.6, 128.84, 128.78, 128.70, 128.67, 128.6, 128.5, 128.3, 128.2, 127.83, 127.77, 101.5, 101.1, 98.4, 82.2, 80.1, 77.6, 76.4, 76.0, 75.9, 75.7, 75.5, 75.4, 75.2, 75.03, 74.96, 73.69, 73.65, 72.5, 72.2, 69.8, 68.3, 68.2, 63.0, 55.6, 21.3; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{84}H_{82}NaO_{21}$, 1449.5241; found, 1449.5242.

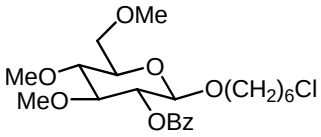
**_p_-Tolyl 2-_O_-Benzoyl 3,4,6-tri-_O_-methyl-thio-β-D-glucopyranoside 38**




Per-*O*-acetyl glucosyl acetate **s38a**[s2] (31.1g, 79.7mmol) in $CH_2Cl_2$ (20 mL) was cooled to 0 ˚C and treated with 33% HBr in AcOH (31.0 mL) under $N_2$. After 30 min, the reaction mixture was brought to RT. Upon completion of the bromination, the reaction mixture was extracted with EtOAc, and the EtOAc solution was washed with $H_2O$, 8% $NaOH_{(aq)}$, NaCl, dried (over $MgSO_4$), filtered, and concentrated, and dried under *vacuo* to give crude bromide derivative. The bromide derivative dissolved in $CH_3CN$ (75 mL) was treated with TBAB (4.9 g, 15.2 mmol), 2,6-lutidine (17.6 mL, 152 mmol), and MeOH (9.2 mL). The reaction mixture was stirred at RT under $N_2$ overnight. Upon completion of the orthoester formation, the solvent was reduced by rotary evaporator. The residue was dissolved by EtOAc, which was washed with satd. $NaHCO_3$, $H_2O$, brine, followed by dried over $MgSO_4$, filtered, and concentrated to give per-*O*-acetyl glucosyl orthoester **s38b** (32.5 g). **s38b** (32.5 g) in MeOH/$CH_2Cl_2$ mixture (120 mL, MeOH/$CH_2Cl_2$ 2/1) was treated with Na(s) (120 mg) at RT. Upon completion of deacetylation, the reaction mixture was concentrated and dried under *vacuo* for 4 h. The crude deacetyl compound (14.3 g, 60.5 mmol) was then dissolved in dried DMF (120 mL) and the solution was cooled to 0 ˚C under $N_2$. The solution was treated with (7.3 g, 181.5 mmol) (60% in mineral oil), followed by iodomethane (MeI) (11.3 mL, 182 mmol). Upon completion of methylation, $H_2O$ was added to quench the reaction. The reaction mixture was diluted with EtOAc, and the resulting solution was washed with $H_2O$, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (EtOAc/Hexane 3/7) to furnish per-*O*-methyl

glucosyl orthoester **s38c** (7.20 g). **s38c** (7.20 g, 25.9 mmol) in dried $CH_2Cl_2$ (52 mL) was treated with *p*-thiocresol (4.8 g, 38.9 mmol) at 0˚C, followed by treatment with $BF_3.OEt_2$ (4.93 mL, 39 mmol). Upon completion of the reaction, the reaction mixture was diluted with 8% $NaOH_{(aq)}$, and the reaction solution was washed with satd. $NaHCO_3$, EtOAc, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography purification (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/4/9 stepwise to 1/3/7) to give 2-*O*-acetyl-3,4,6-tri-*O*-methyl thioglucoside **s33d** (7.1 g, 74%) as yellow syrup. **s33d** (6.8 g, 18.4 mmol) in $CH_2Cl_2$/MeOH (120 mL) was treated with Na(s) (150 mg). Upon completion of deacetylation, the reaction was neutralized with IR-120 ($H^+$), filtered, concentrated, and column chromatography purification (EtOAc/Hexane 1/3 stepwise to 1/2) to furnish (4.6 g, 76%). The preceding derivative in $CH_2Cl_2$ was treated with BzCl (2.4 mL, 20.1 mmol), $Et_3N$ (3.7 mL, 26.8 mmol) and DMAP (170 mg, 1.4 mmol) under $N_2$. Upon completion of benzoylation, the reaction solution was diluted with satd. $NaHCO_3$, followed by extraction with EtOAc. The EtOAc solution was washed with $H_2O$, brine, dried over $MgSO_4$, filtered, and recrystalized to obtain target 2-*O*-benzoyl-3,4,6-tri-*O*-methyl-β-D-thioglucoside **38** (4.02g, 69%). For thioglucoside **38**: $[\alpha]_D^{35}$ +33.8 (*c* 0.5, $CHCl_3$); $R_f$ 0.375 (EtOAc/Hexane 1/2); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.09 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.56 (t, *J* = 7.2 Hz, 1H, Ar*H*), 7.44 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.35 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.05 (d, *J* = 7.8 Hz, 2H, Ar*H*), 5.15 (t, *J* = 9.6 Hz, 1H), 4.70 (d, *J* = 10.2 Hz, 1H), 3.70-3.60 (m, 2H), 3.54-3.41 (m, 11H), 3.35-3.29 (m, 1H), 2.28 (s, 3H, C*H*$_3$); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.4 (*C*=O), 138.1, 133.5, 133.0, 130.2, 130.0, 129.8, 129.7, 128.7, 87.0 (C-1), 86.6, 79.5, 79.3, 72.7, 71.6, 60.8, 60.7, 59.7, 21.3; HRMS-ESI (*m/z*): $[M + Na]^+$ calcd. for $C_{23}H_{28}NaO_6S$, 455.1499; found, 455.1493.

**6-Chlorohexyl 2-*O*-benzoyl-3,4,6-tri-*O*-methyl β-D-glucopyranoside 42:**




6-Chlorohexyl glucoside **42** was prepared from glycosylation of chlorohexanol **39** with thioglucoside **38** under the general DMF-modulated glycosylation procedure. The glucoside **42** was purified by column chromatography (Elution: EtOAc/$CH_2Cl_2$/Hexane 1/2/15). For **42**: $[\alpha]_D^{35}$ +8.2 (*c* 0.41, $CHCl_3$); $R_f$ 0.5 (EtOAc/$CH_2Cl_2$/Hexane 1:2:5); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.08 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.59 (t,*J* = 7.2 Hz, 1H, Ar*H*), 7.46 (t, *J* = 7.8 Hz, 2H. Ar*H*), 5.13 (dd, *J* = 9.3,7.8 Hz, 1H, H-2), 4.46 (d, *J* = 8.1 Hz, 1H, H-1), 3.91–3.86 (m, 1H), 3.71–3.67 (m, 1 H), 3.64 (d, J = 4.5 Hz, 1 H), 3.61-3.56 (m, 4 H), 3.50 (s, 3 H), 3.47–3.38 (m, 6 H), 3.35-3.29 (m, 3 H), 1.50–1.43 (m, 4H), 1.26–1.16 (m, 4H); $^{13}$C-NMR (75 MHz, $CDCl_3$): $\delta$ 165.6 (*C*=O), 133.5, 130.5, 130.1, 128.8, 101.5 (C-1), 85.2, 79.7, 75.4, 74.0, 71.7, 69.9, 60.9, 60.8, 59.8, 45.3, 32.8, 29.6, 26.8, 25.5; HRMS (*m/z*): $[M + Na]^+$ calcd. for $C_{22}H_{33}ClNaO_7$ , 467.1807; found,467.1801.

**Determination of RRV for thioglycosides**:[s2]

The RRV calculation formula: $\frac{K_1}{K_2} = \frac{\ln([A_1,_t]/[A_1,_0])}{\ln([A_2,_t]/[A_2,_0])}$

0.3 g of particle molecular sieve was flame-dried for 5 times. Tested thioglycoside $\boldsymbol{A_2}$ (0.02 mmol) and reference thioglycoside $\boldsymbol{A_1}$ (0.02 mmol) were dissolved in 2 mL $CH_2Cl_2$ and stirred in RT for 10 min, 100 μL of reaction solution was removed for determination of time-zero absorbance [$A_{1,0}$] and [$A_{2,0}$]. The remainder of the reaction solution was treated with 4 μL MeOH (0.1 mmol) and particle molecular sieve stirred in 0 ˚C. 0.5 M NIS solution (40 μL, 0.02 mmol) and 0.1 M TMSOTf solution (20 μL, 0.002 mmol) were added to the reaction solution and stirred for 2 h. Upon the reaction completed, the reaction mixture was treated with few drops of 10% $NaHCO_3$/$Na_2SO_3$

solution. After stirring for 15 min, the reaction temperature was raised to RT. The mixture was dried over $MgSO_4$, filtered and concentrated. The crude residue was dissolved in 2 mL $CH_2Cl_2$ for determination of final absorbance [$A_{1,t}$] and [$A_{2,t}$] at 2 h reaction. As an example, the HPLC traces from thioglucoside **11b** and reference compound **1** before and after the reaction were given (**Figure s1**). The RRV of tested thioglycoside was calculated by substitution of the absorbance values (before and after the reaction) and the RRV value of the reference compound from literature into the equation above (Table S4).

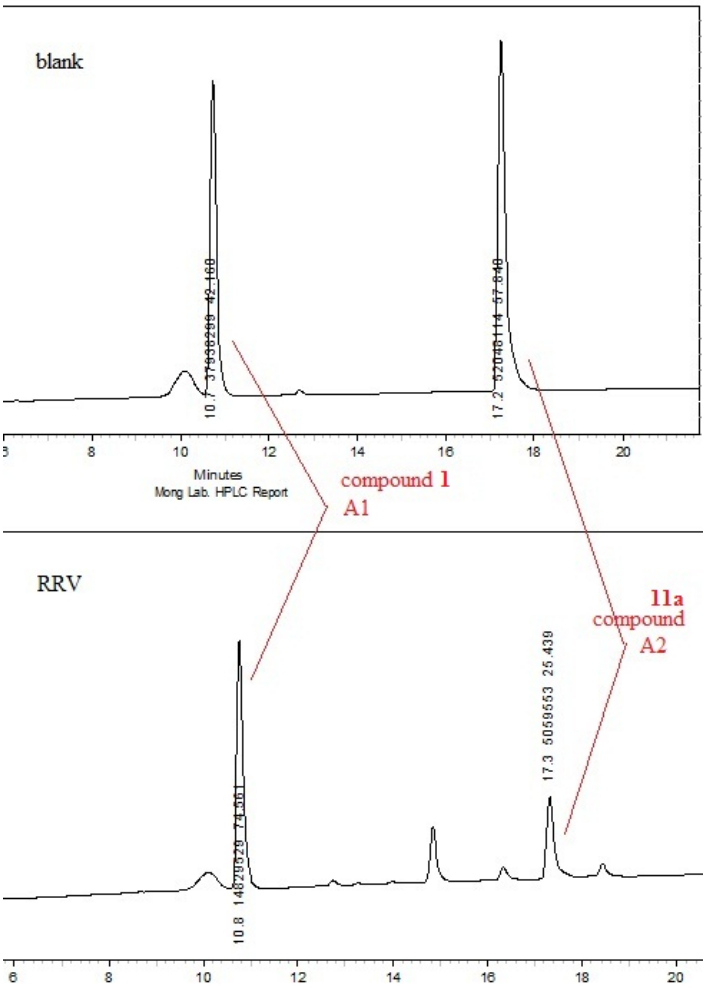
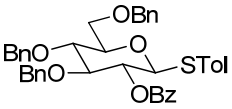
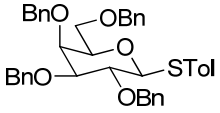
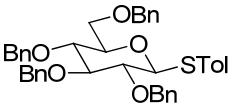
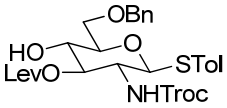
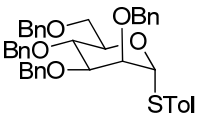


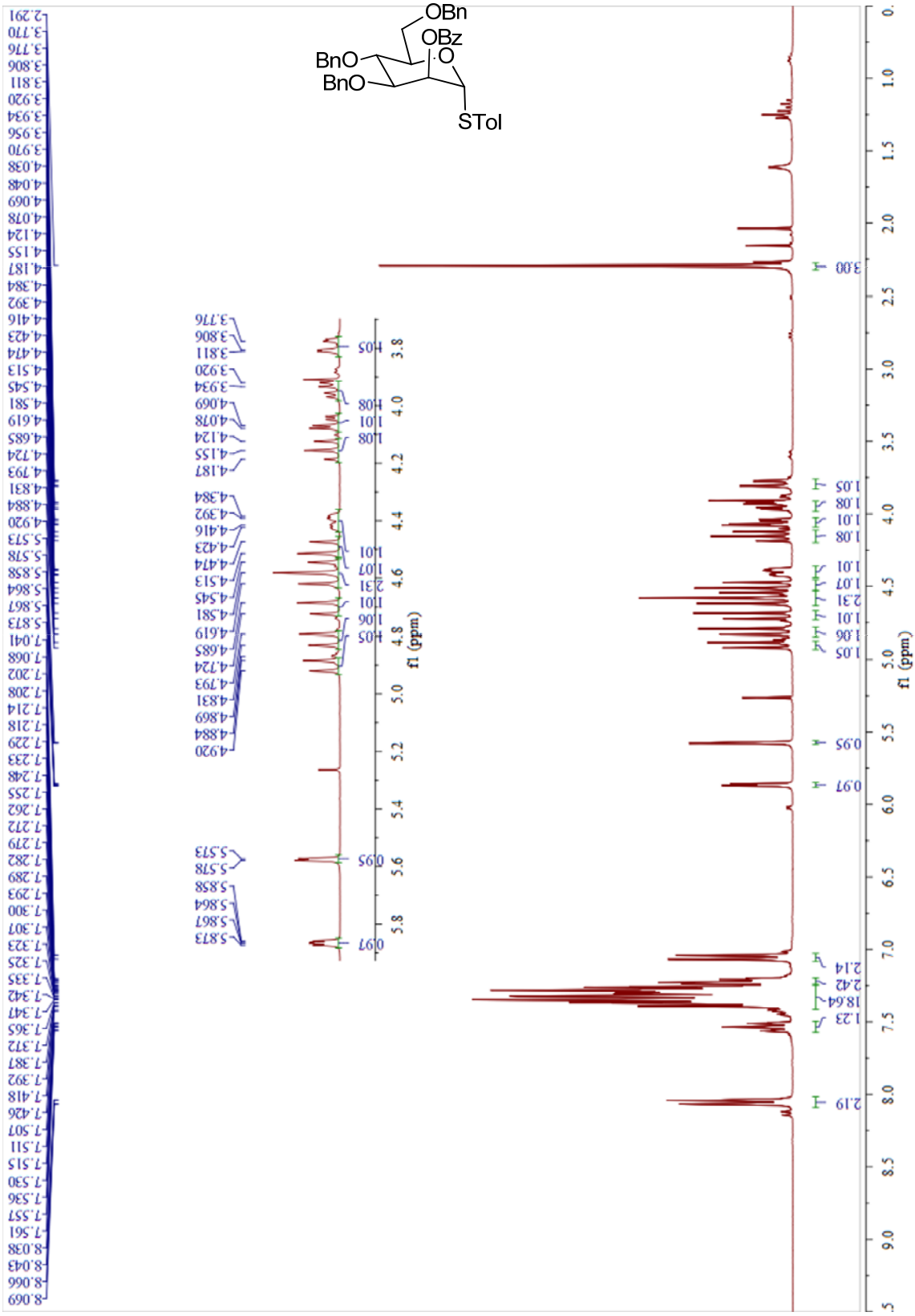

**Figure S1.** HPLC traces of thioglucoside **11b** and **1** before and after the glycosylation in RRV determination

**Table S4**. Reference thioglycosides and thioglycosides for RRV measurement

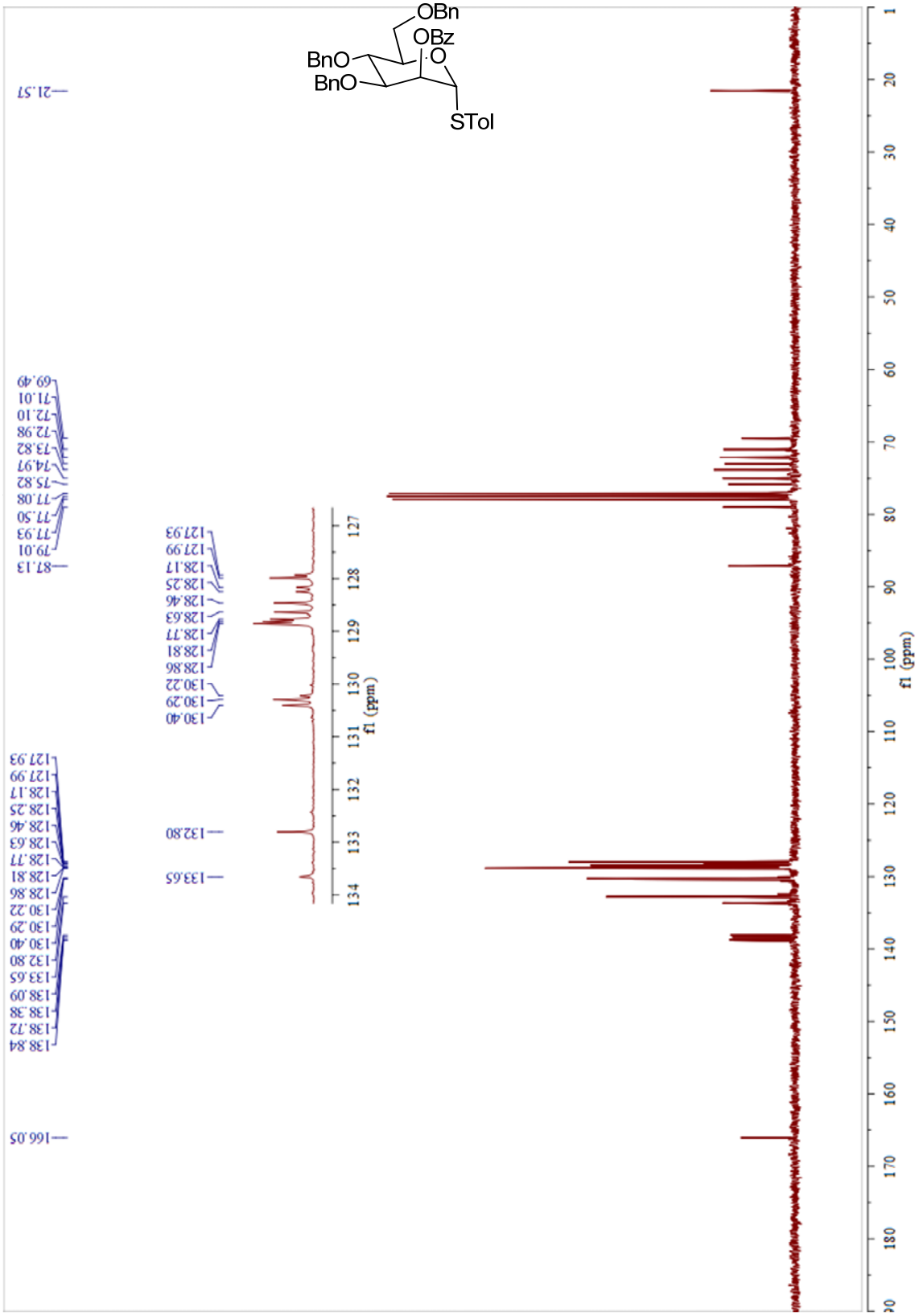
| reference thioglycosides $A_1$ | thioglycosides for RRV measurement $A_2$ | reference thioglycosides $A_1$ | thioglycosides for RRV measurement $A_2$ |
|---|---|---|---|
|  | **6, 10, 11a,17** |  | **16** |
|  | **1, 11b, 12** |  | **15** |
|  | **2, 13a, 13b, 14** | **2** | **33** |

## Section B: NMR spectra:

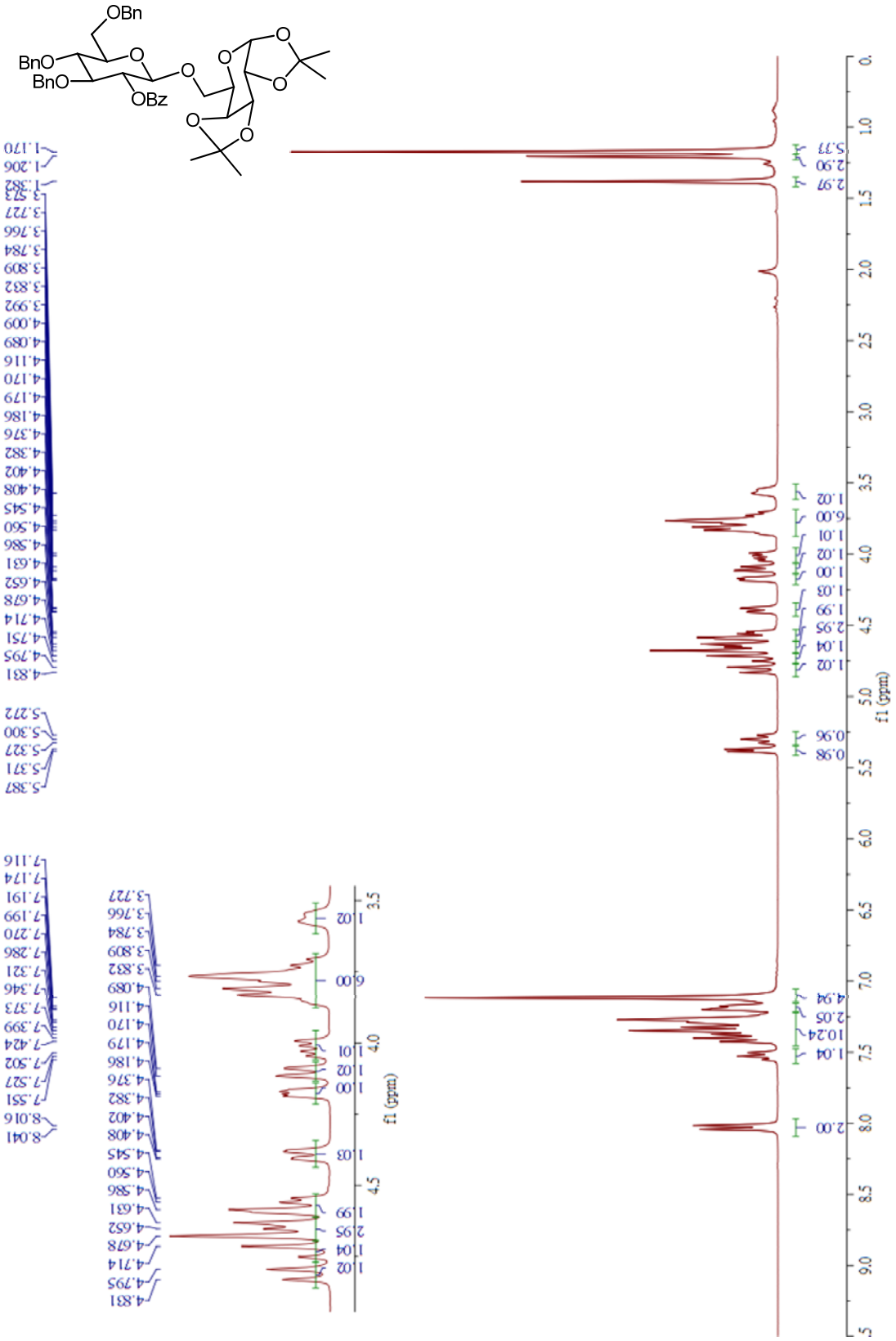
$^{1}$H spectrum of *p*-tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **2**



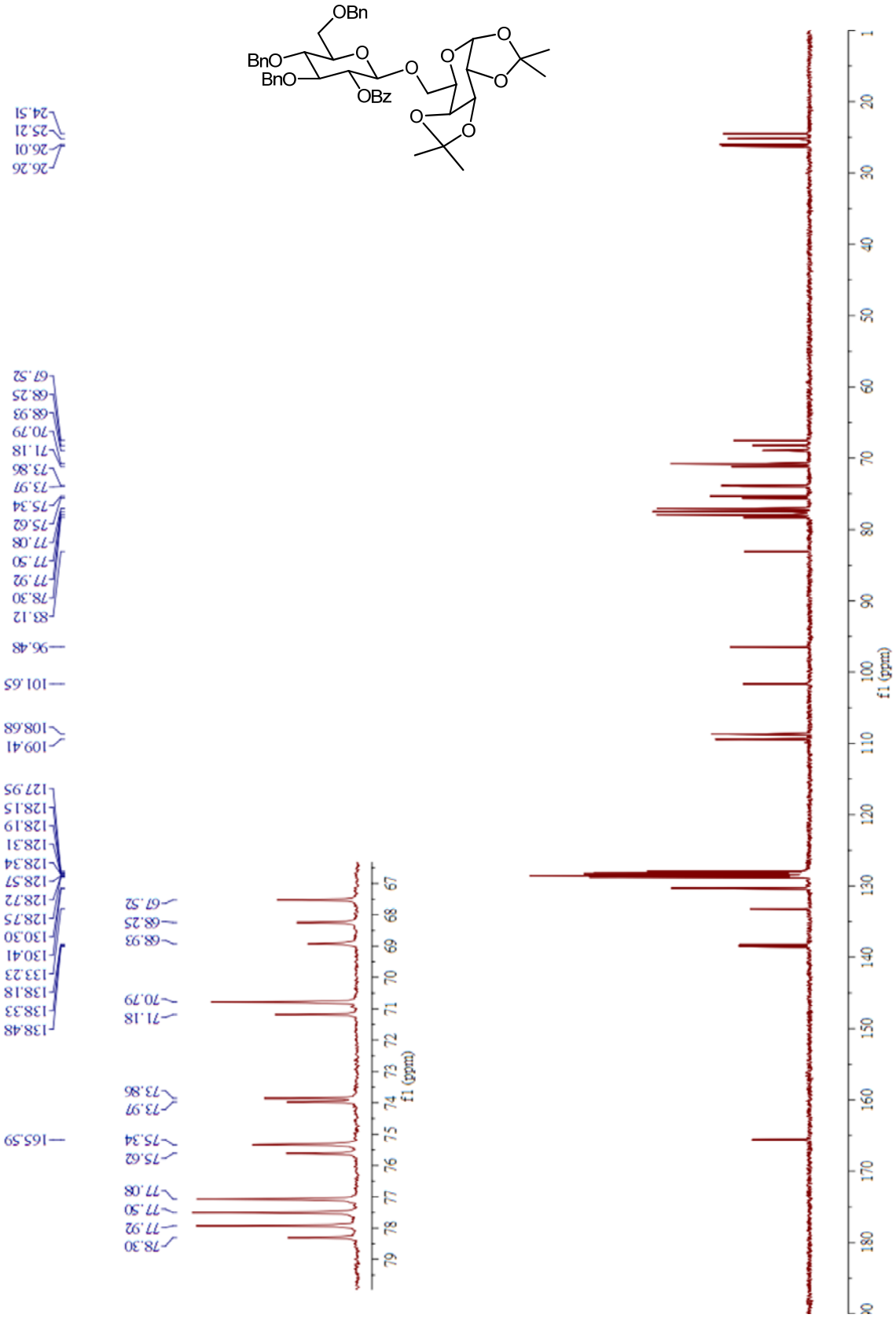
$^{13}$C spectrum of *p*-tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **2**



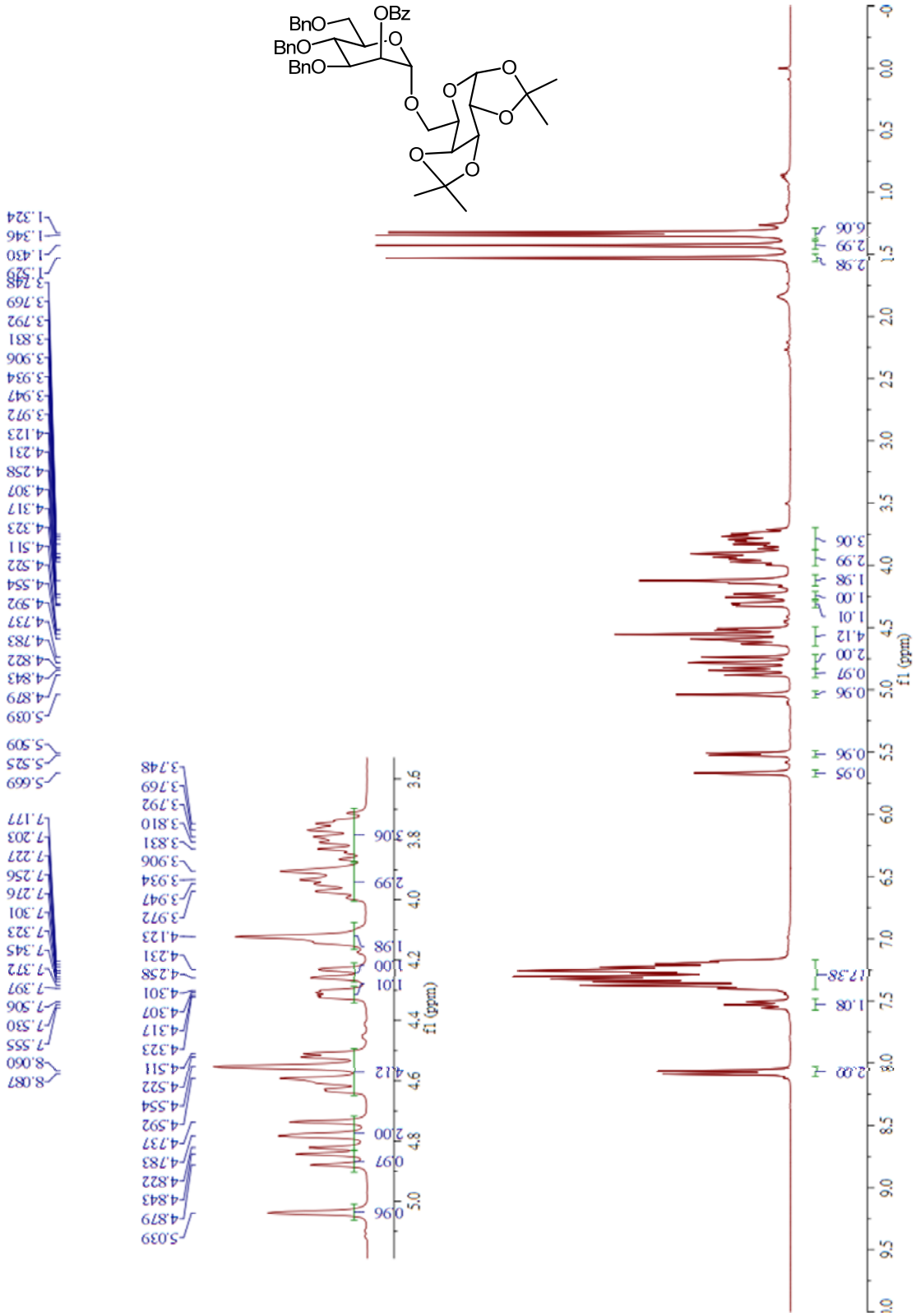
$^{1}$H spectrum of 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **4**



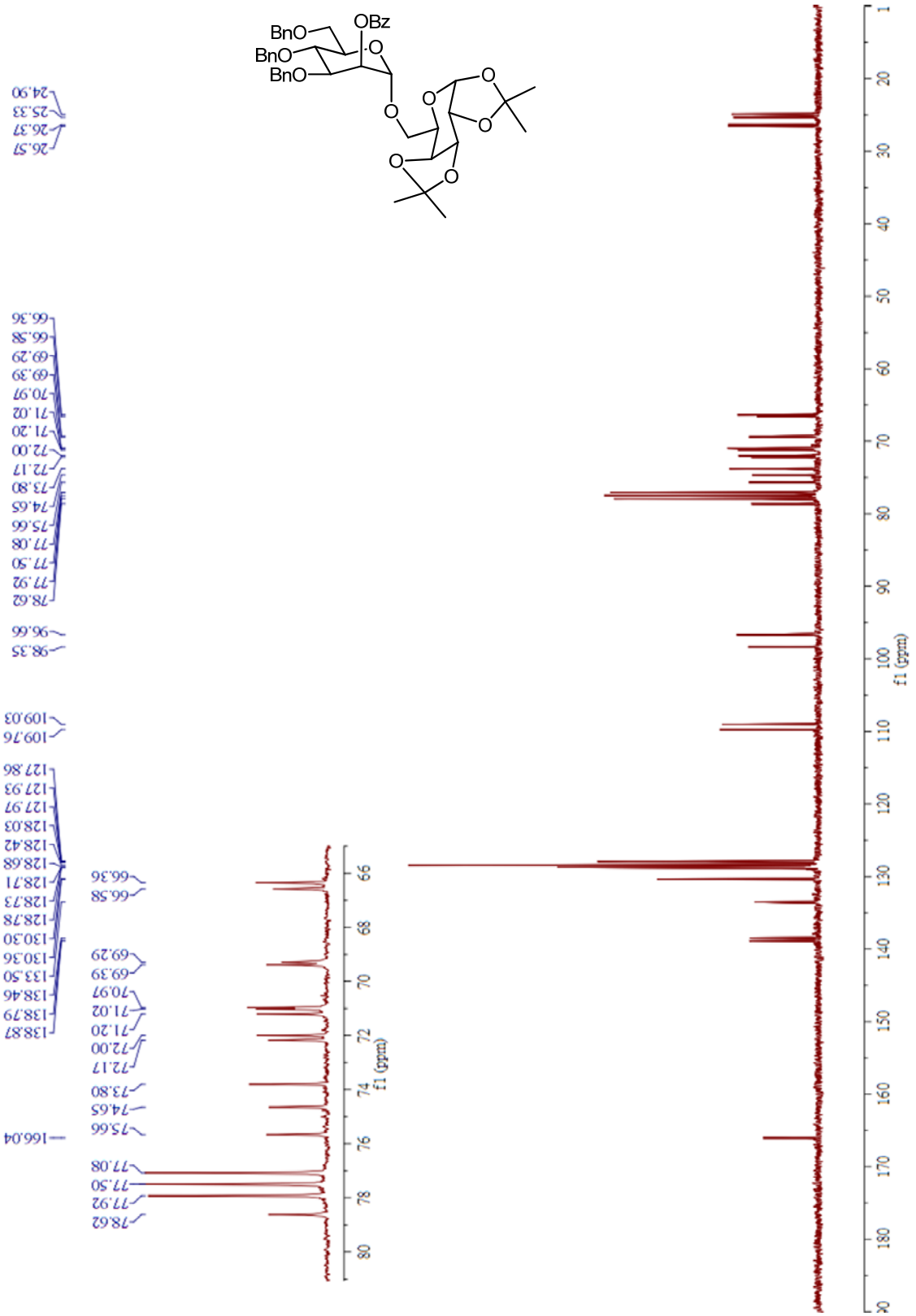
$^{13}$C spectrum of 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **4**



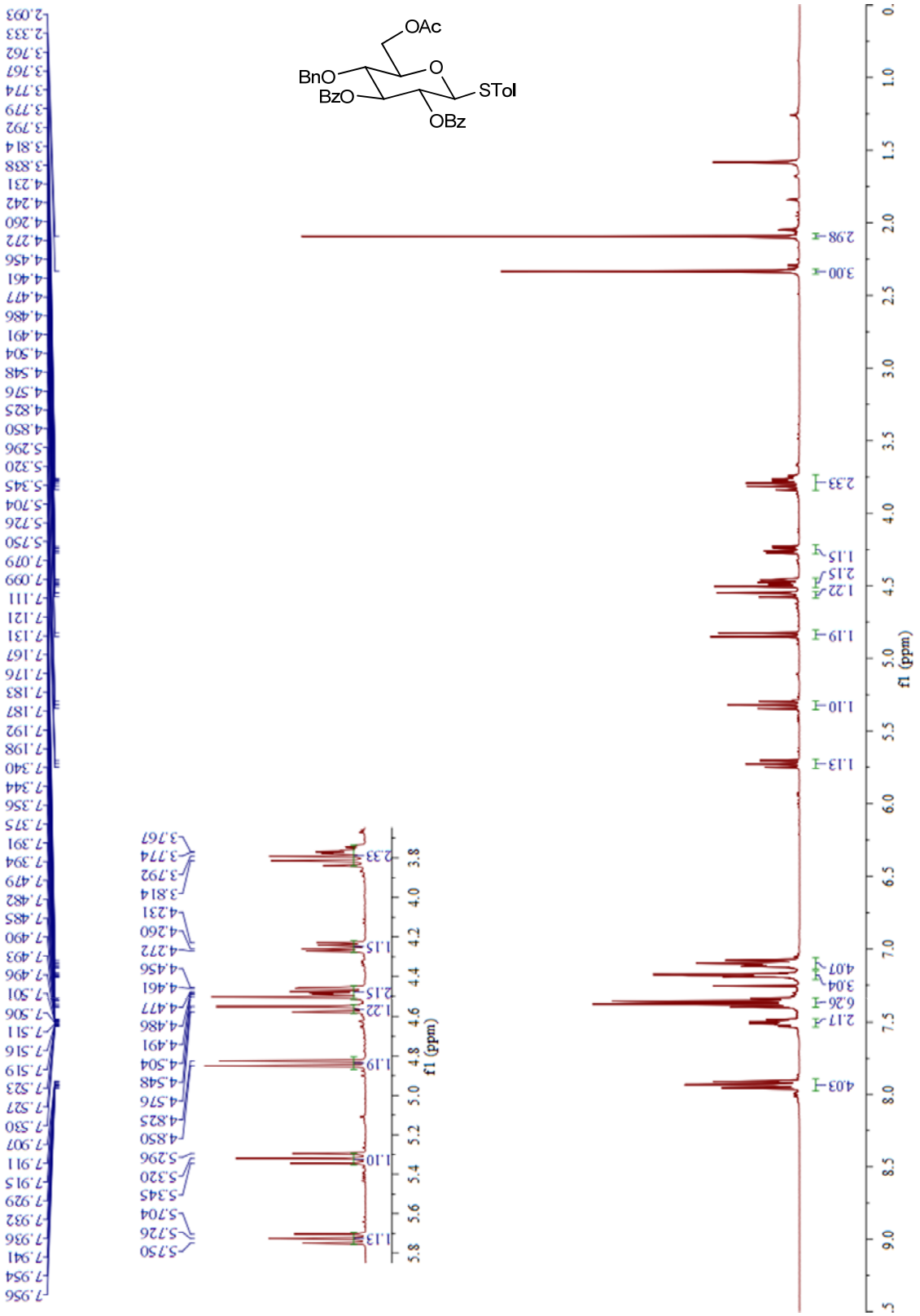
$^{1}$H spectrum of 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **5**



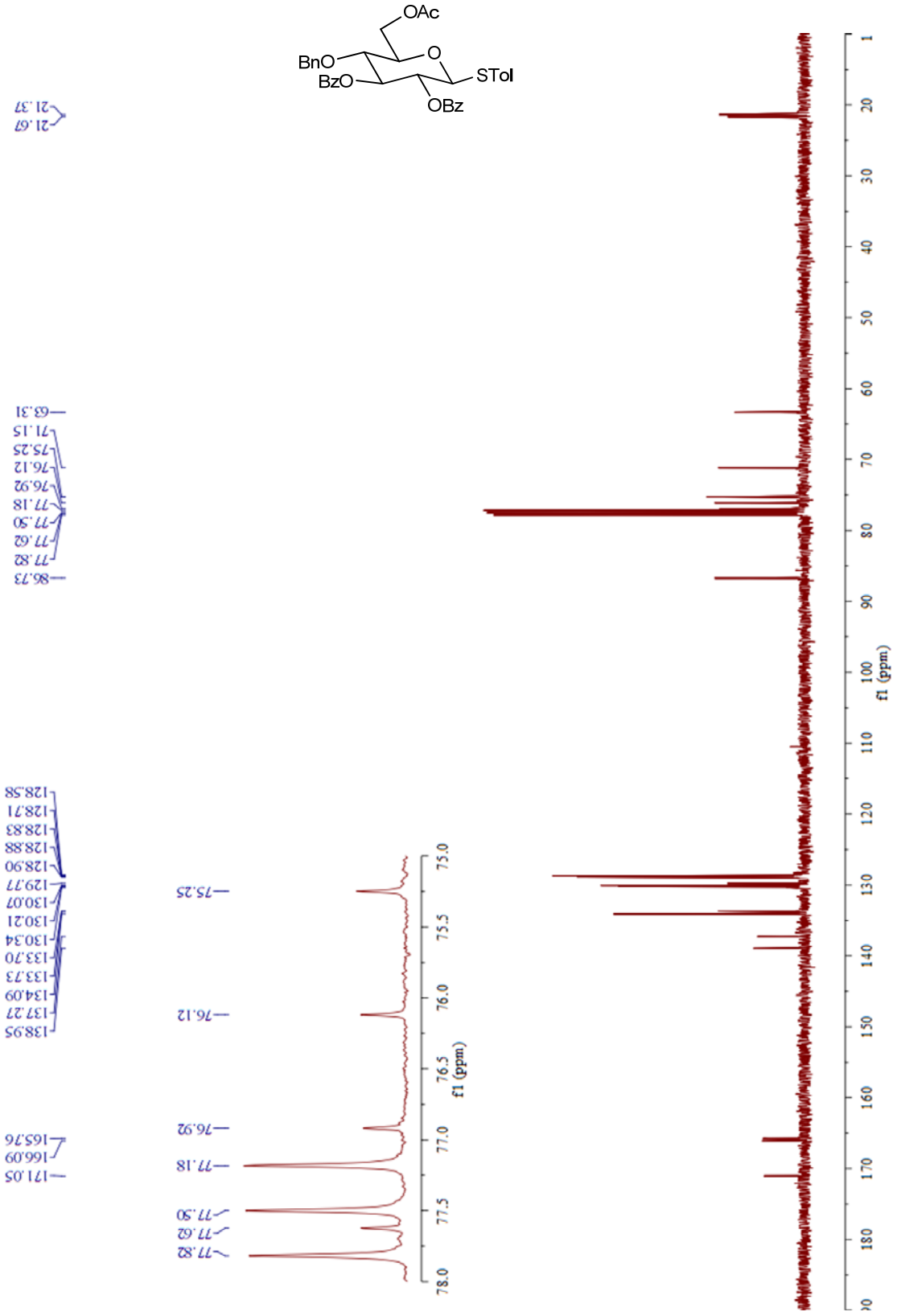
$^{13}$C spectrum of 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose **5**



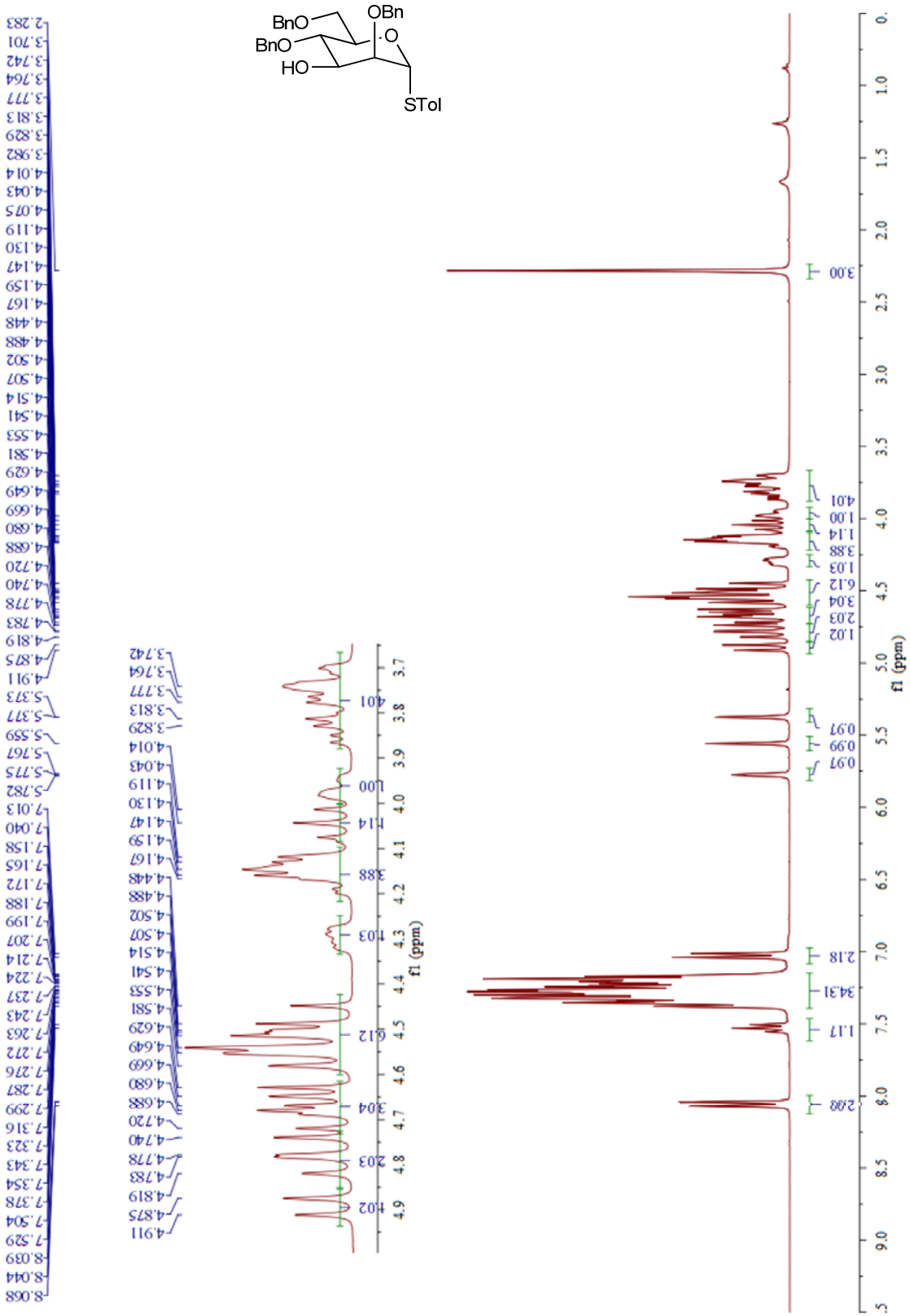
$^{1}$H spectrum of *p*-tolyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-thio-β-D-gluco-pyranoside **6**



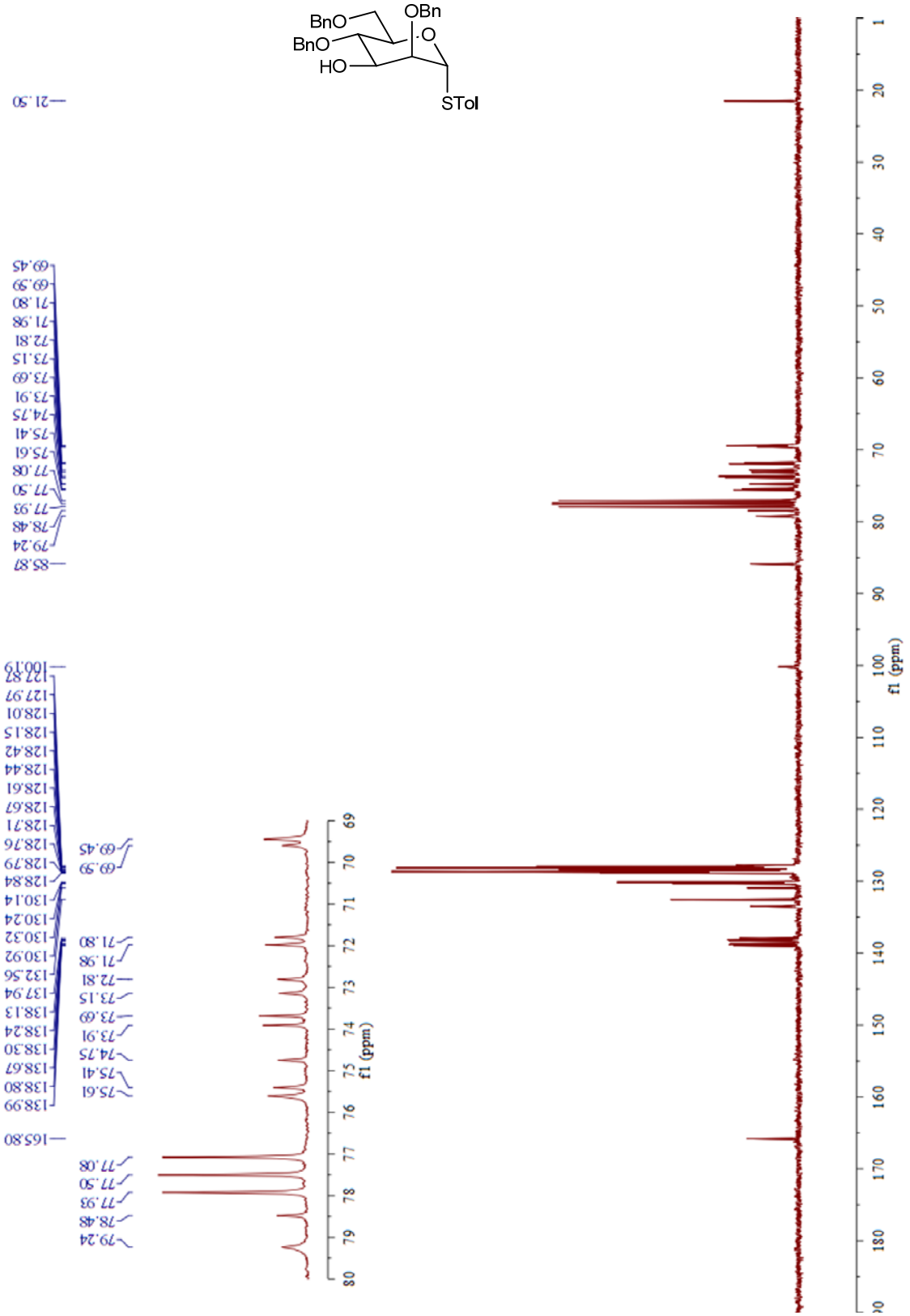
$^{13}$C spectrum of *p*-tolyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl thio-β-D-gluco-pyranoside **6**



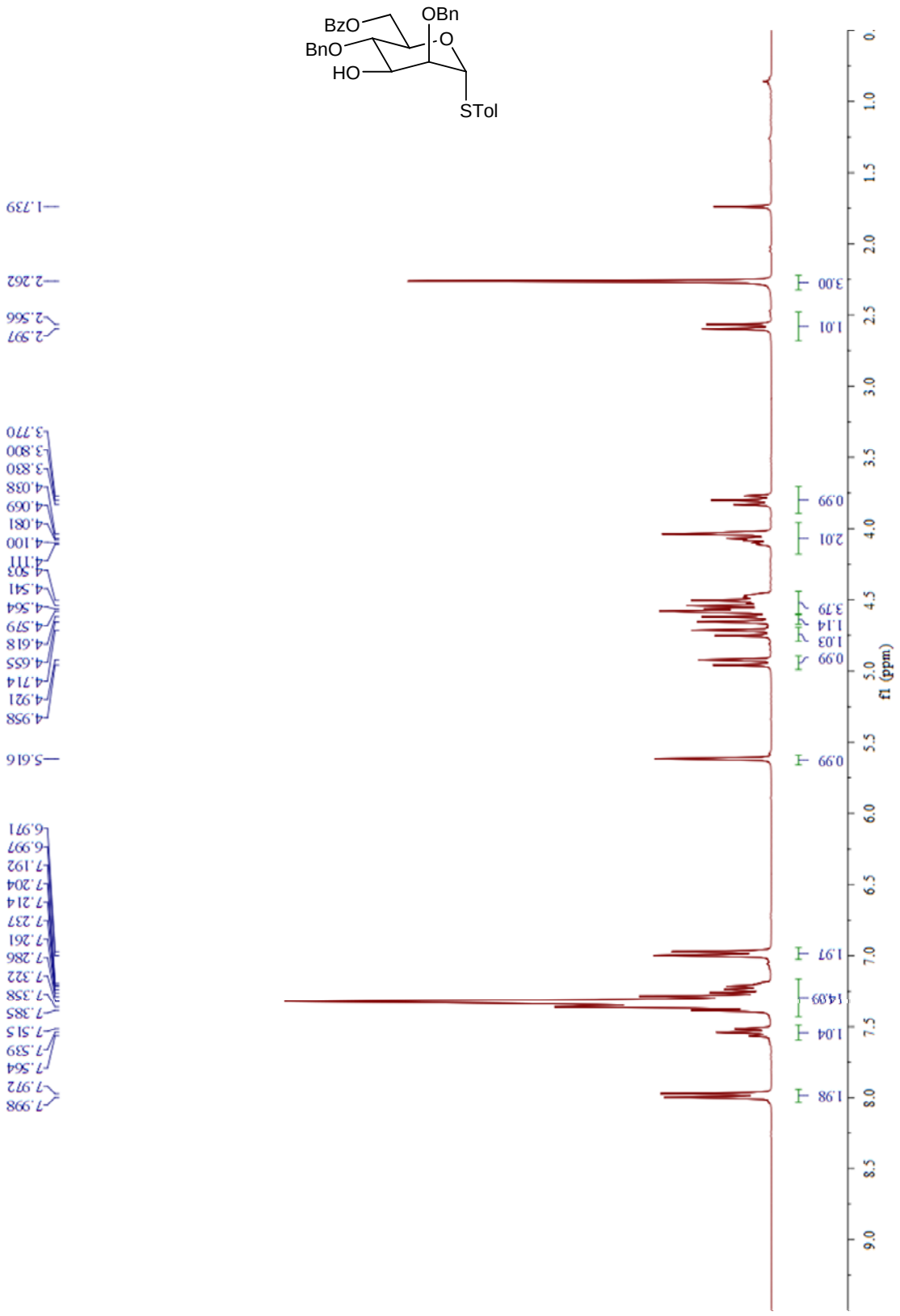
$^{1}$H spectrum of *p*-tolyl 2,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **13a**



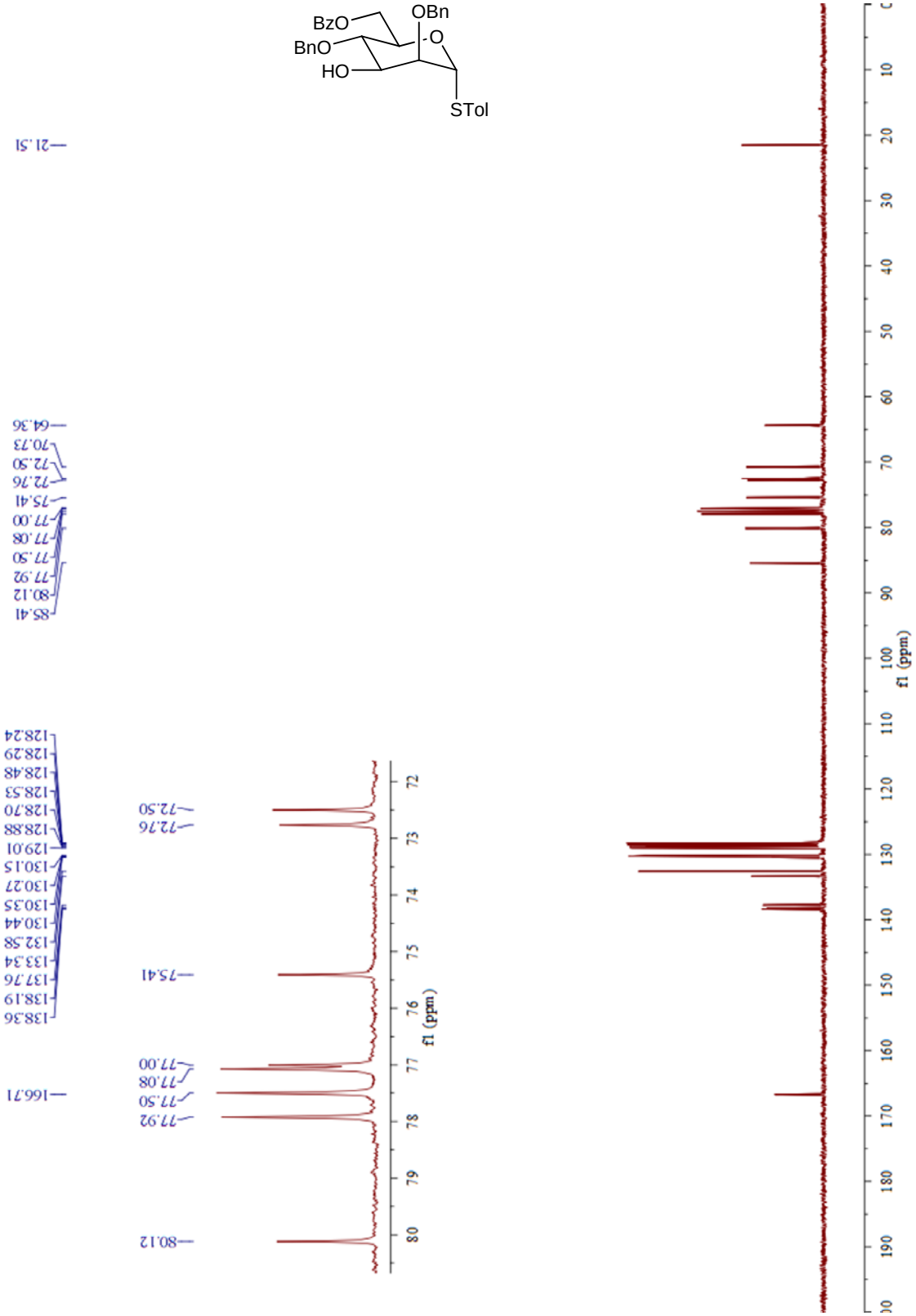
$^{13}$C spectrum of *p*-tolyl 2,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **13a**



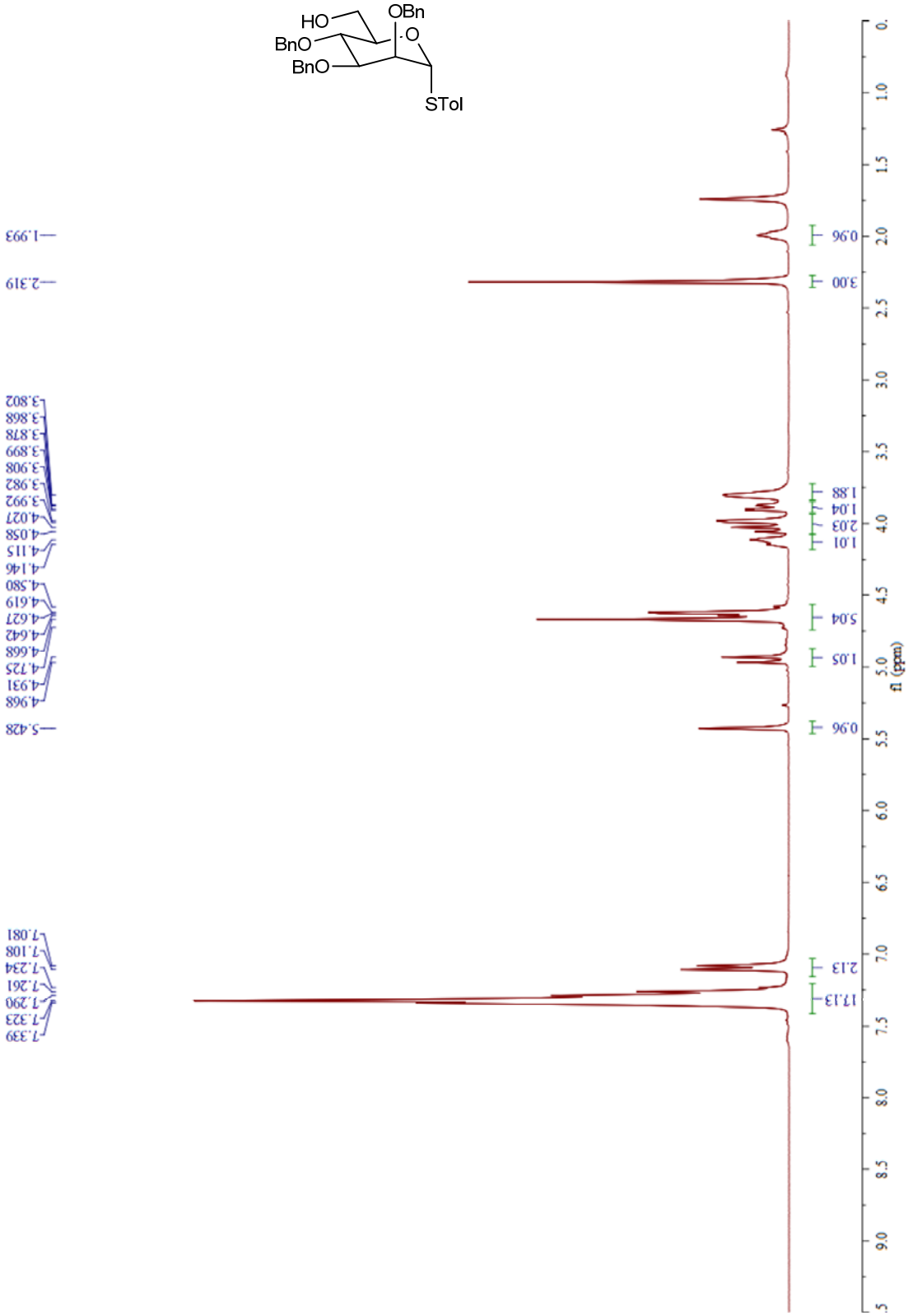
$^{1}$H spectrum of *p*-tolyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside **13b**



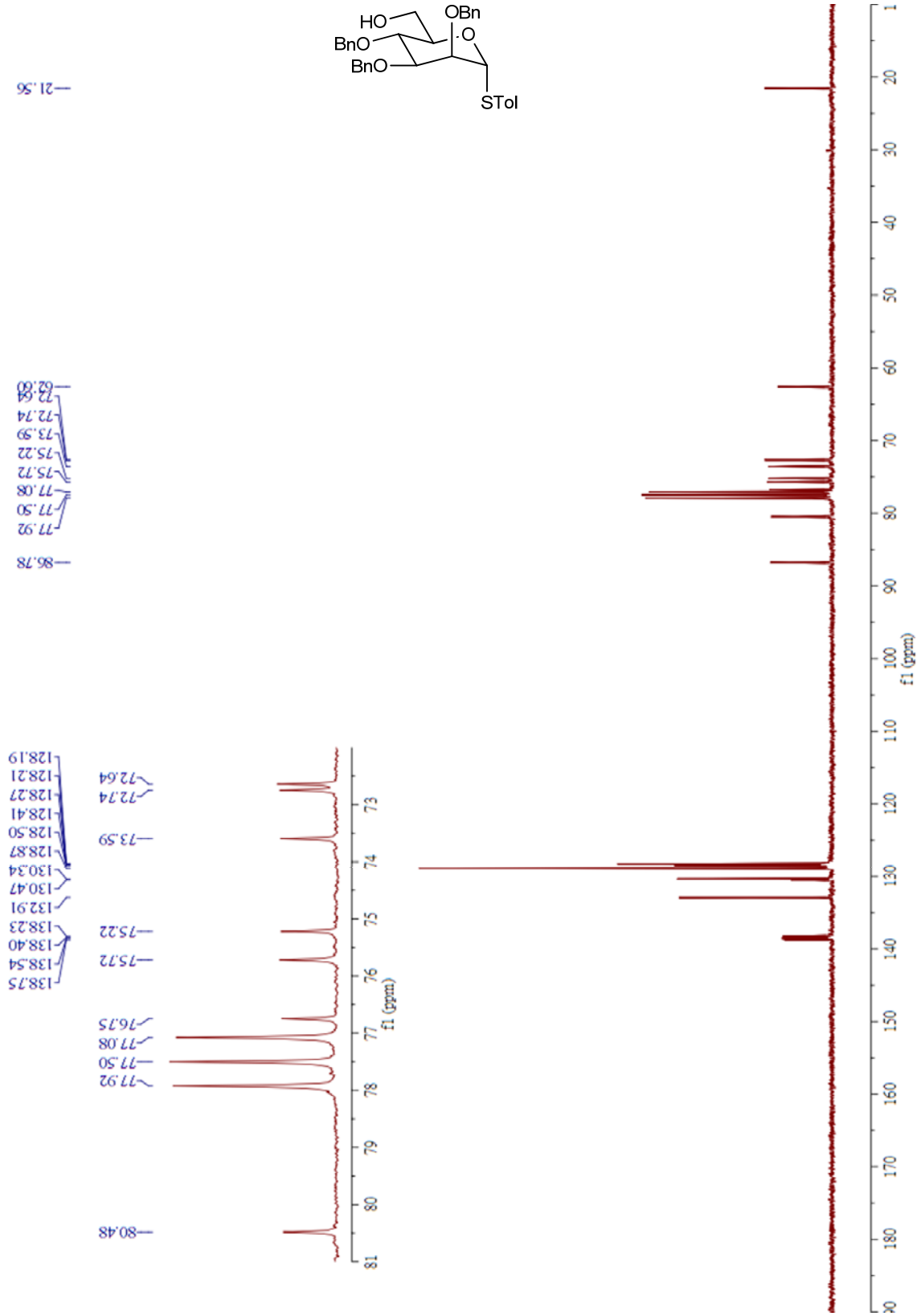
$^{13}$C spectrum of *p*-tolyl 6-*O*-benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside **13b**



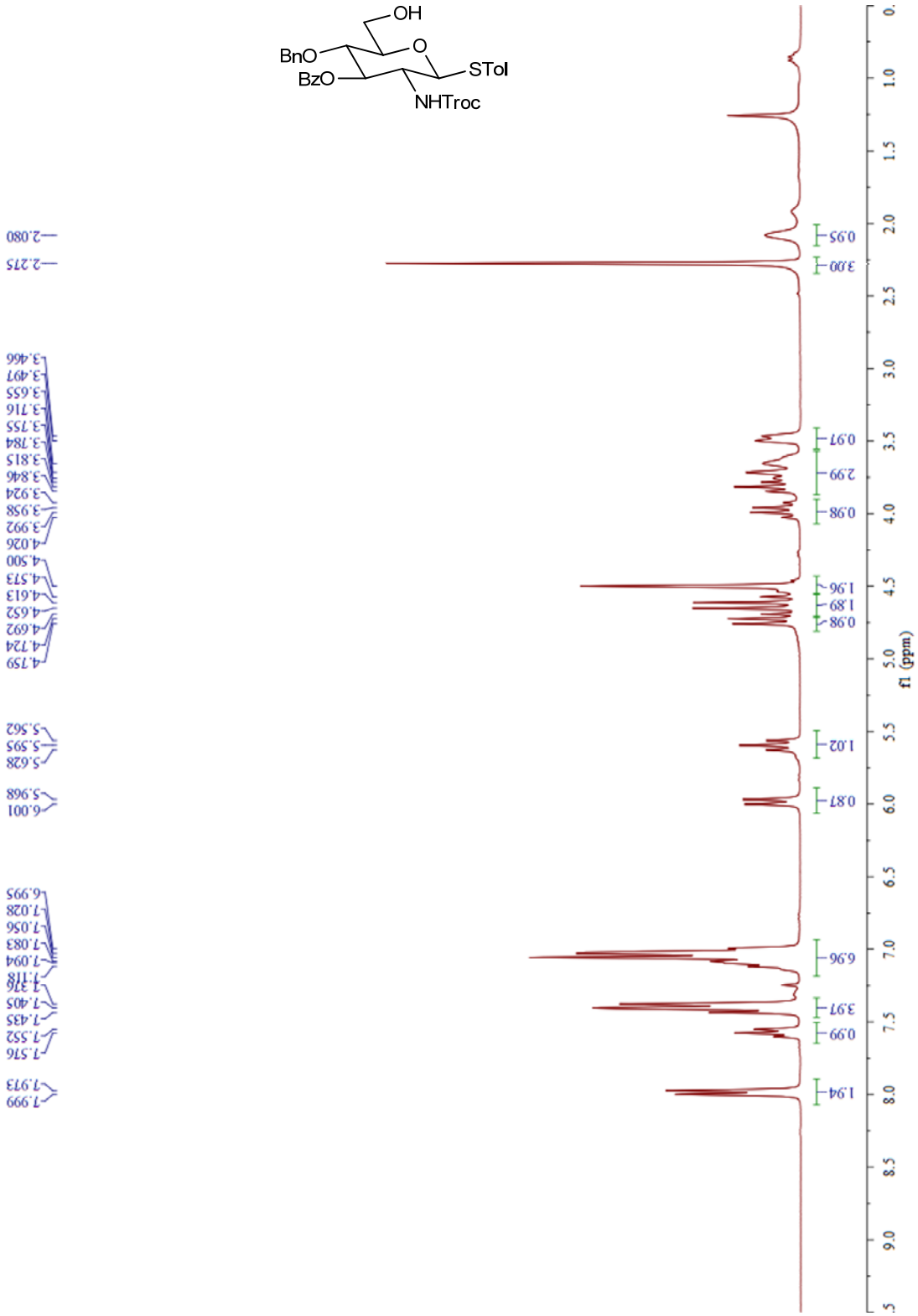
$^{1}$H spectrum of *p*-tolyl 2,3,4-tri-*O*-benzyl-thio-α-D-mannopyranoside **14**



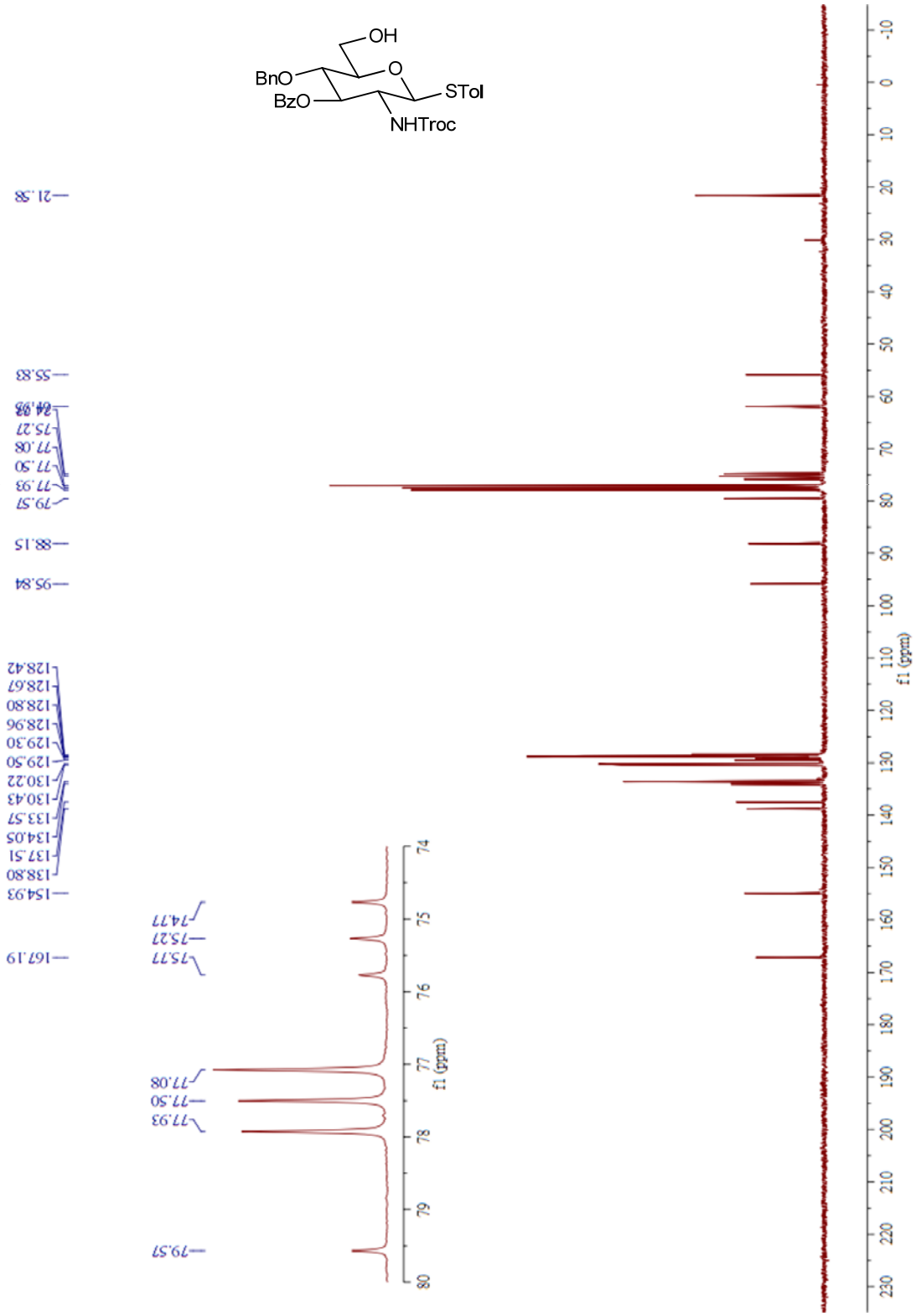
$^{13}$C spectrum of *p*-tolyl 2,3,4-tri-*O*-benzyl-thio-α-D-mannopyranoside **14**



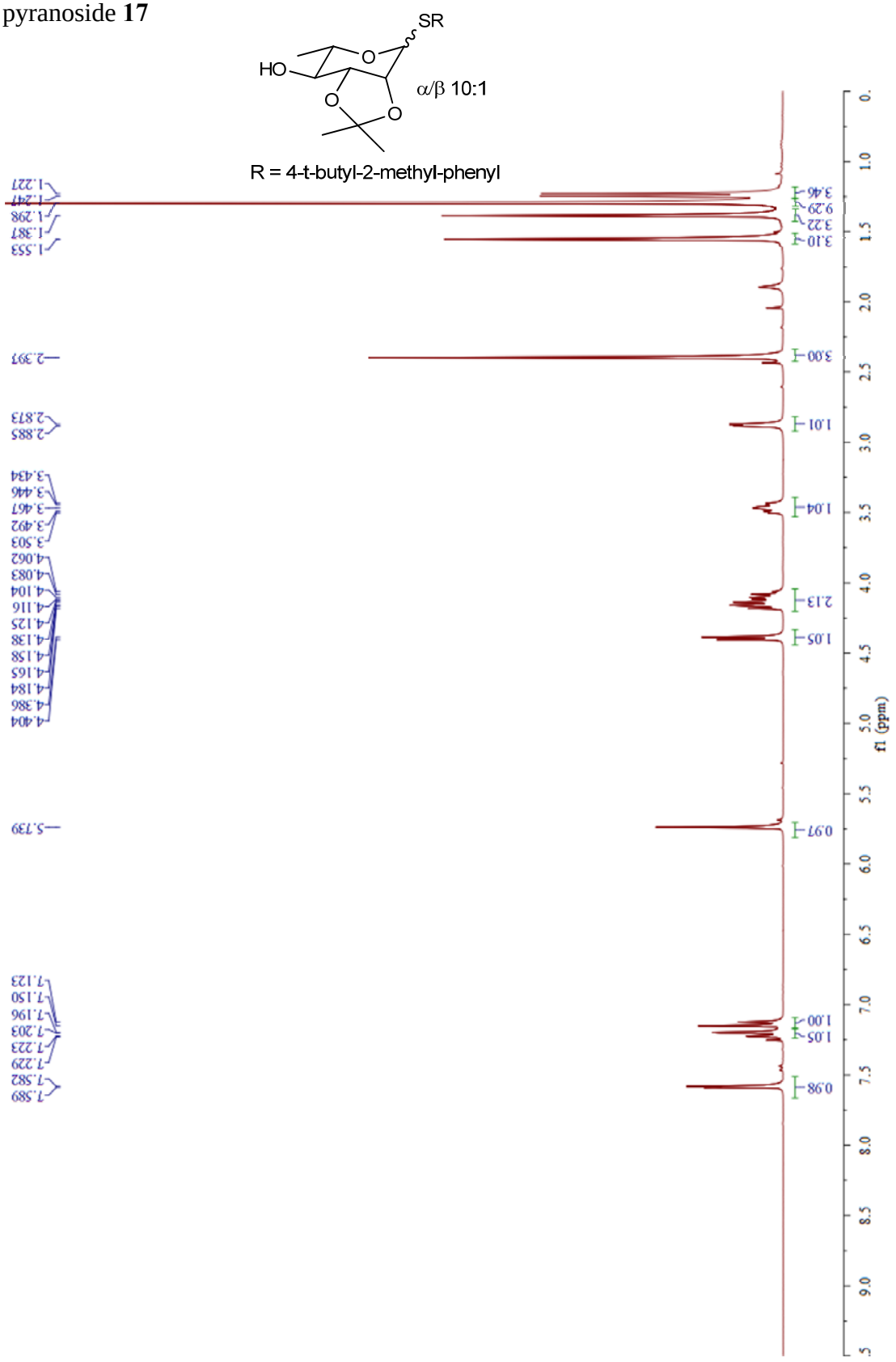
$^{1}$H spectrum of *p*-tolyl 3-*O*-benzoyl-4-*O*-benzyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-thio-β-D-glucopyranoside **15**



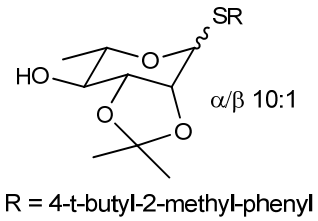
$^{13}$C spectrum of *p*-tolyl 3-*O*-benzoyl-4-*O*-benzyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-thio-β-D-glucopyranoside **15**



$^{1}$H spectrum of 4-(*t*-butyl)-2-methylphenyl 2,3-*O*-isopropylidene-thio-α-L-rhamno pyranoside **17**

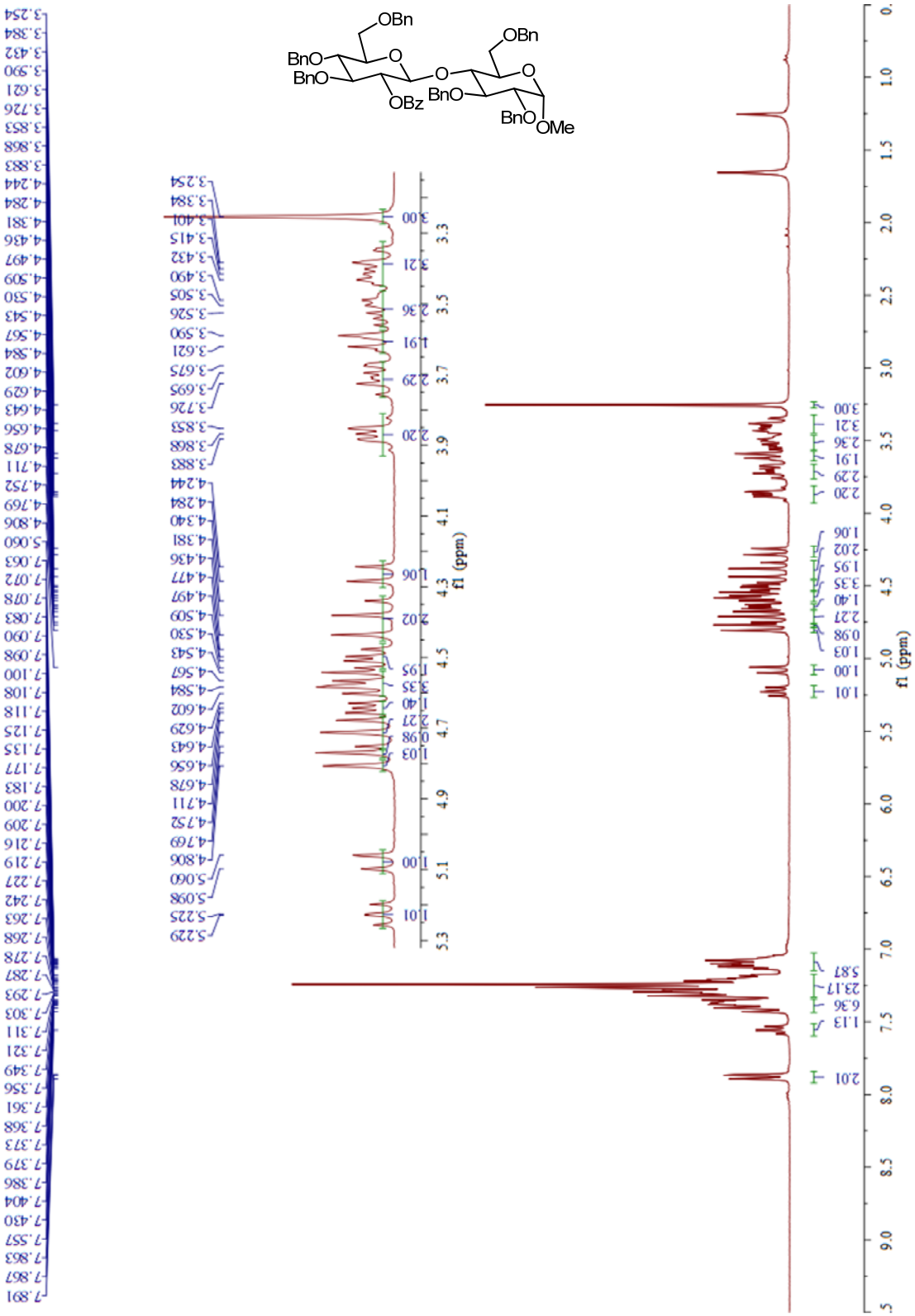


$^{13}$C spectrum of 4-(*t*-butyl)-2-methylphenyl 2,3-*O*-isopropylidene-thio-α-L-rhamno pyranoside **17**

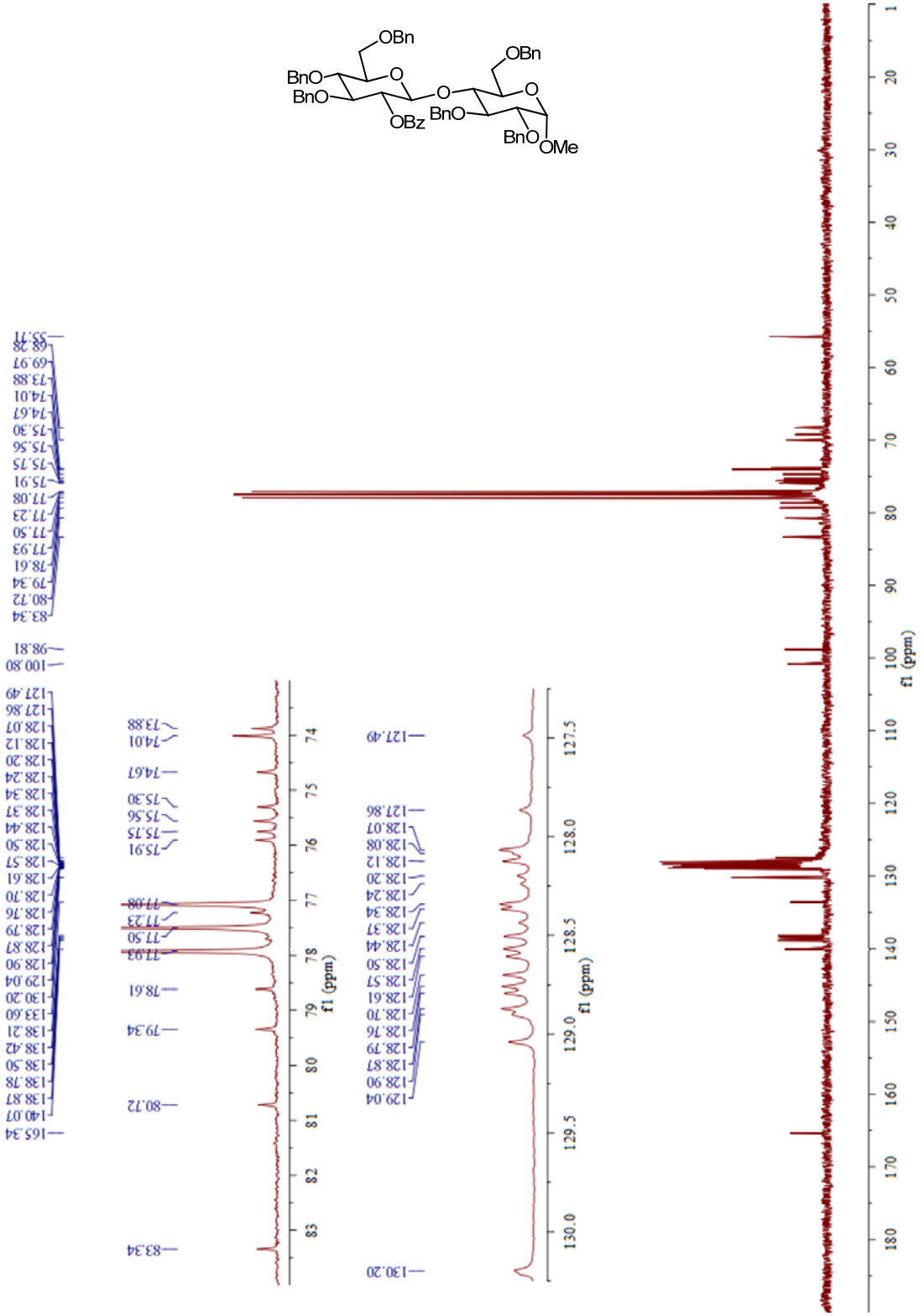



R = 4-t-butyl-2-methyl-phenyl

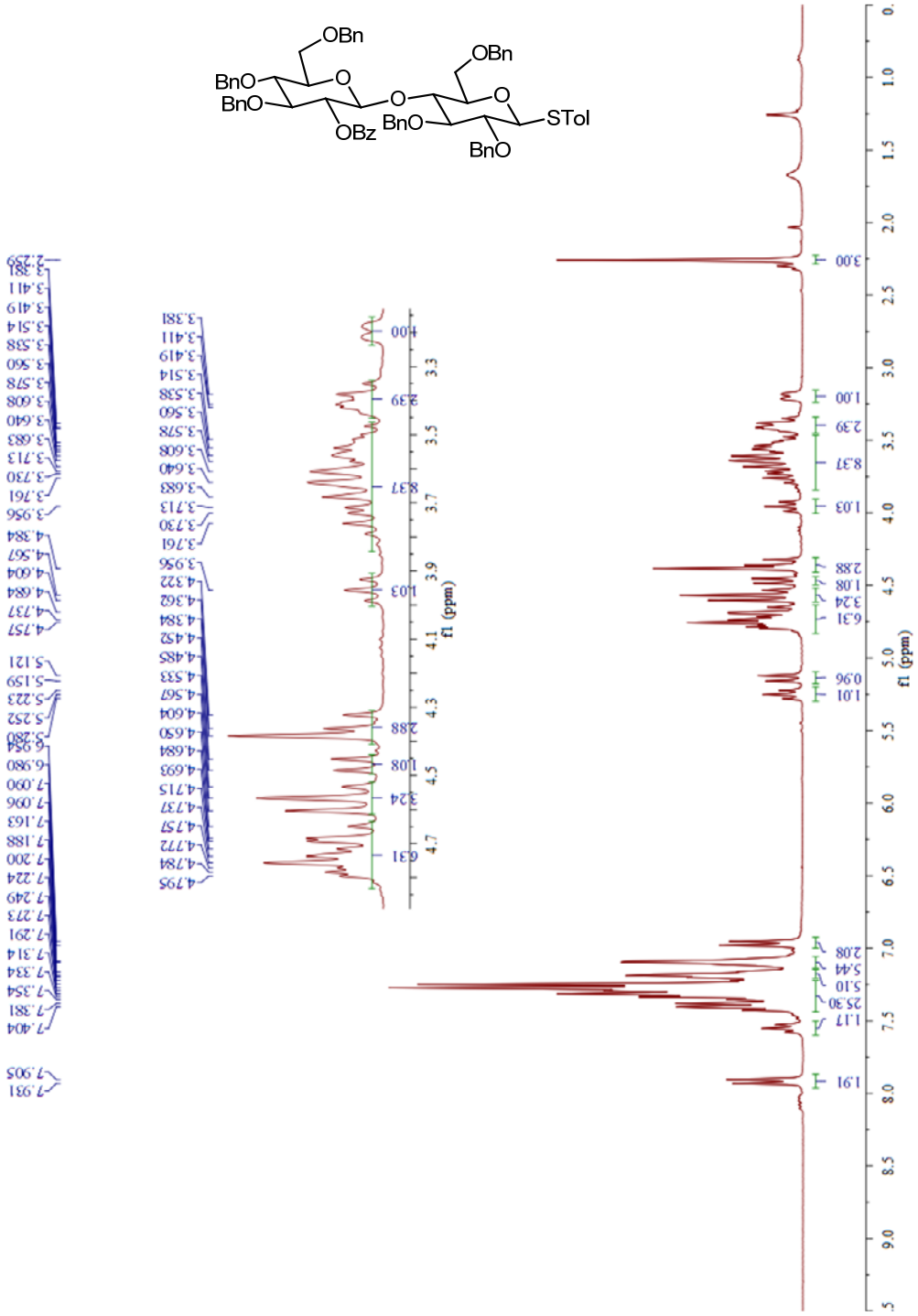
$^{1}$H spectrum of methyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **18**



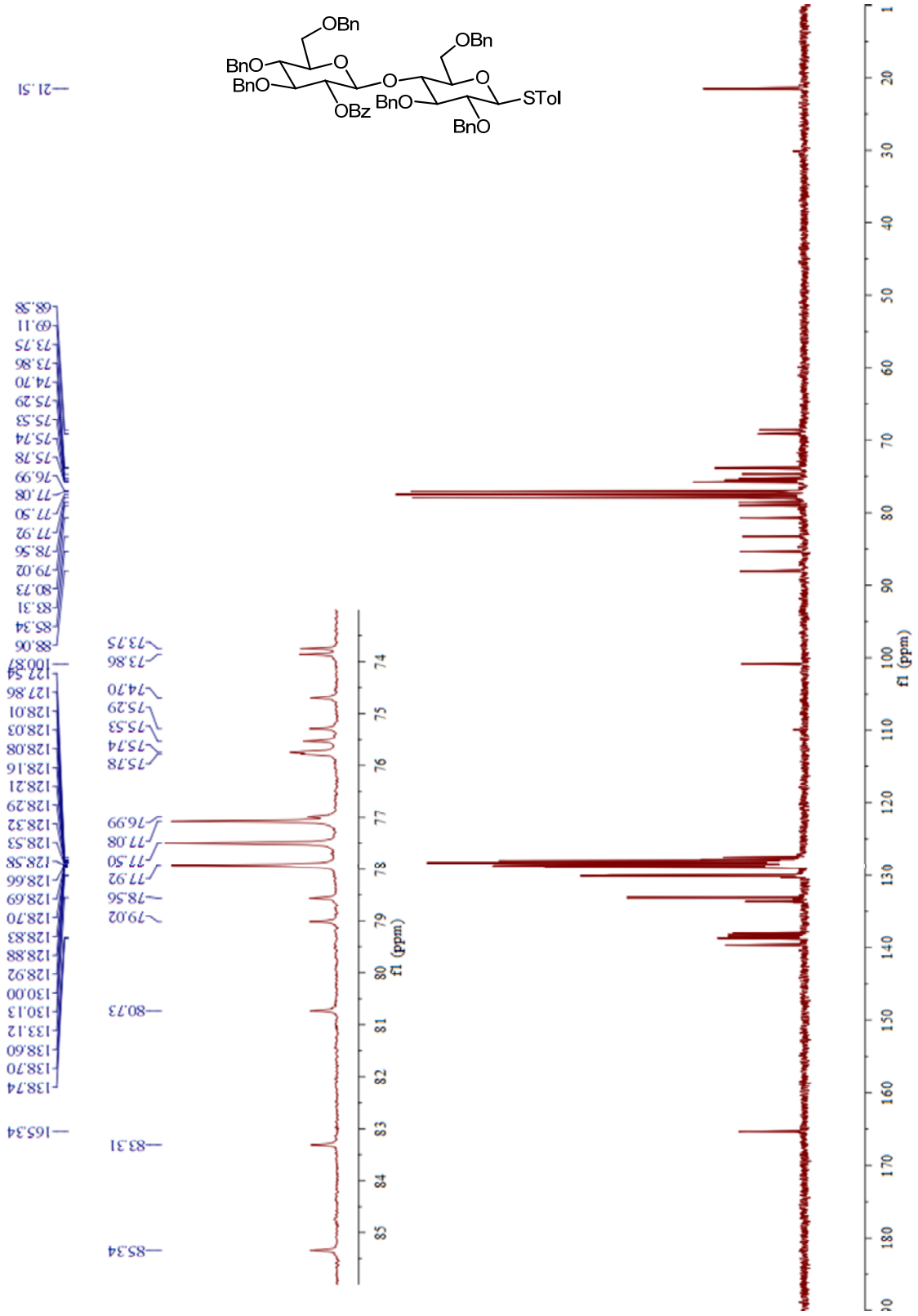
$^{13}$C spectrum of methyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside **18**



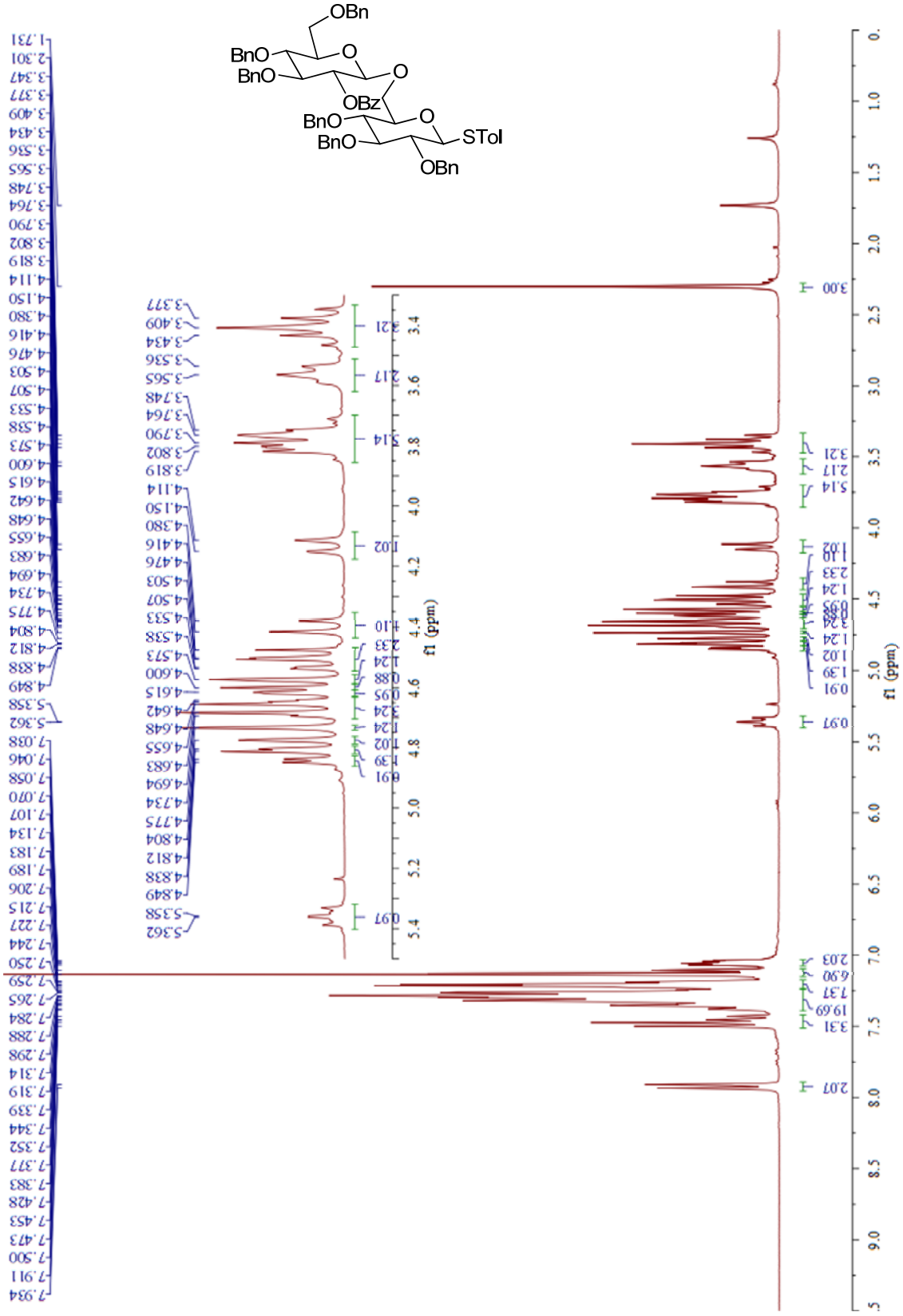
$^{1}$H spectrum of *p*-tolyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-thio-β-D-glucopyranoside **19**



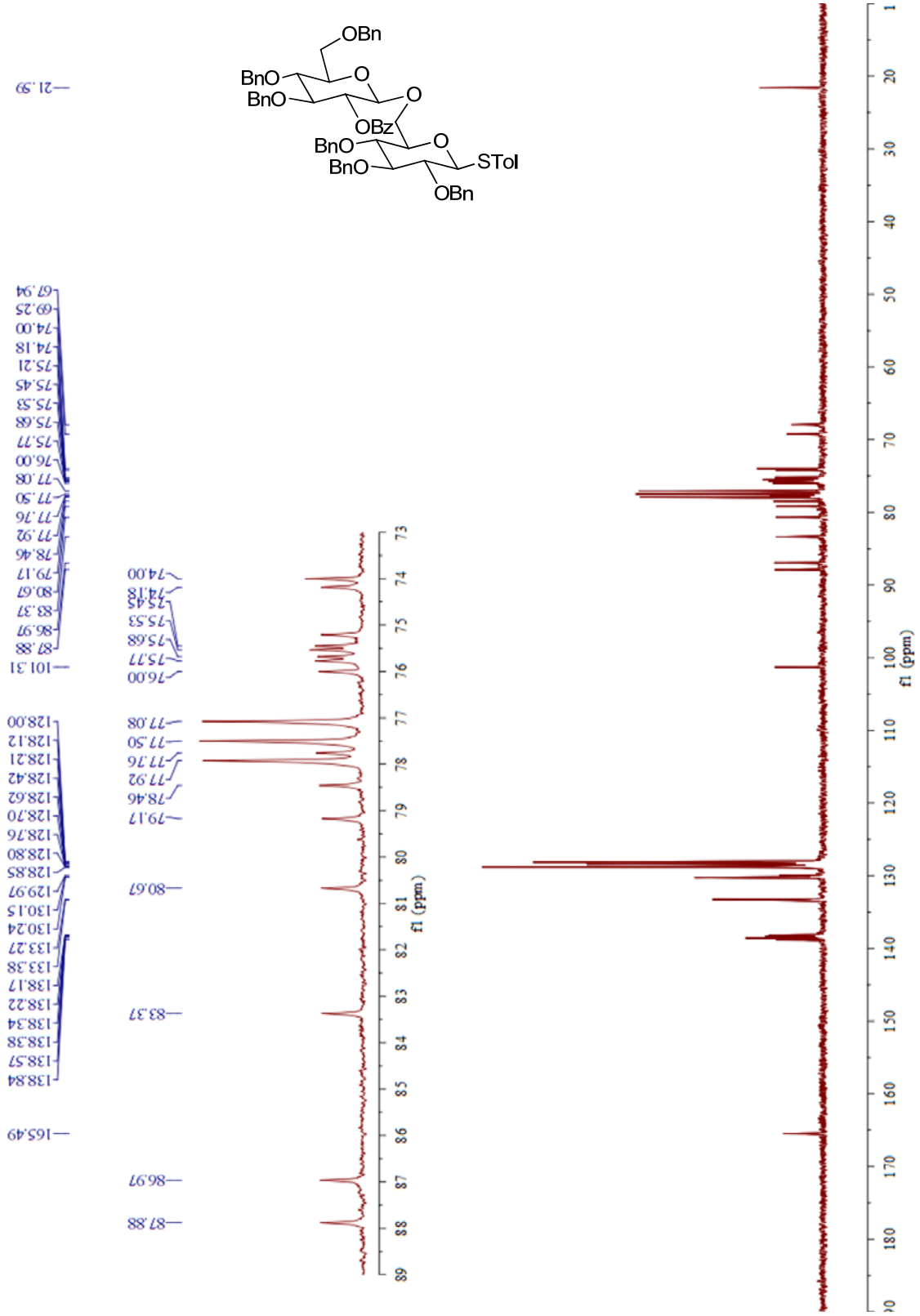
$^{13}$C spectrum of *p*-tolyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-thio-β-D-glucopyranoside **19**



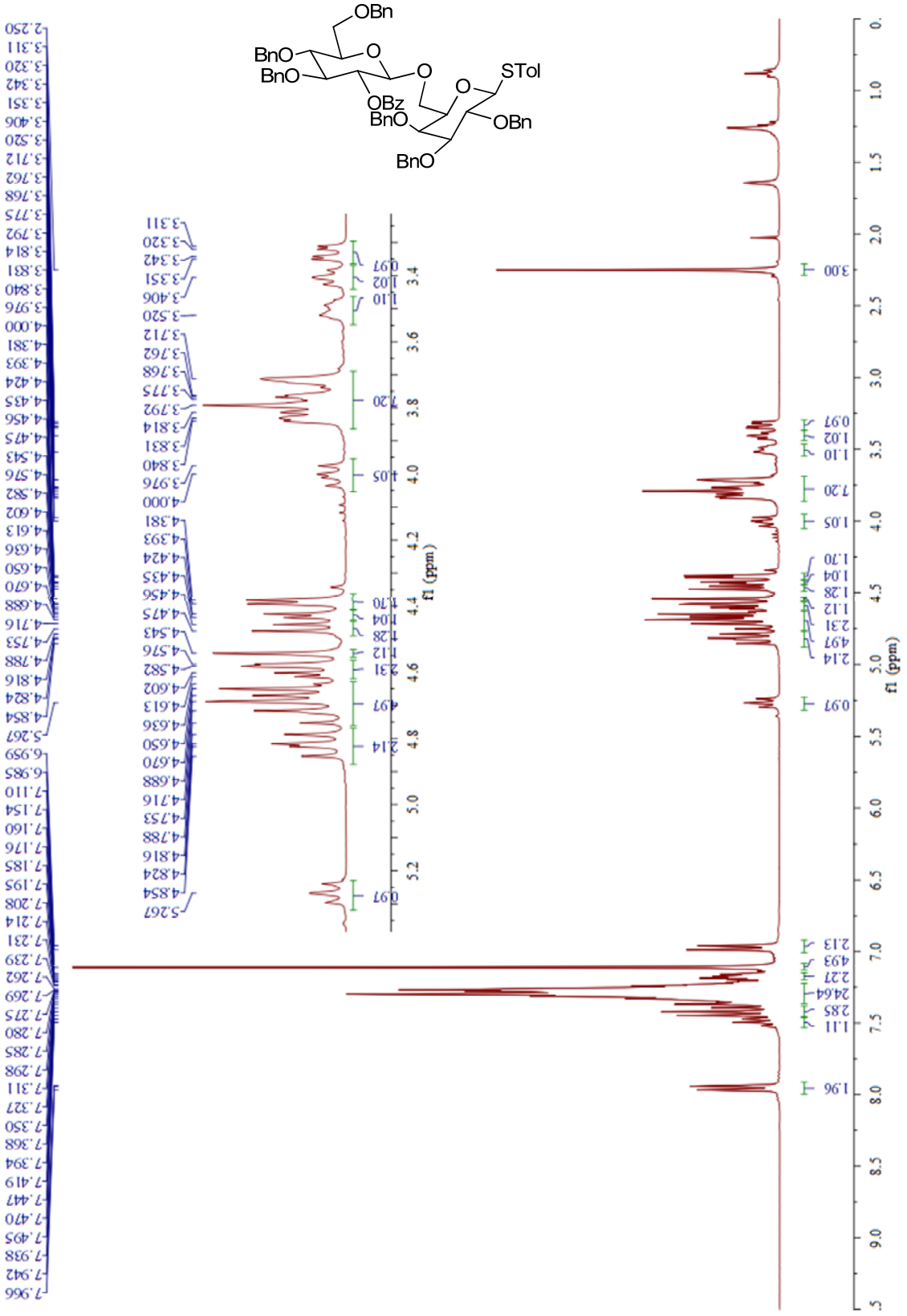
$^{1}$H spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **20**



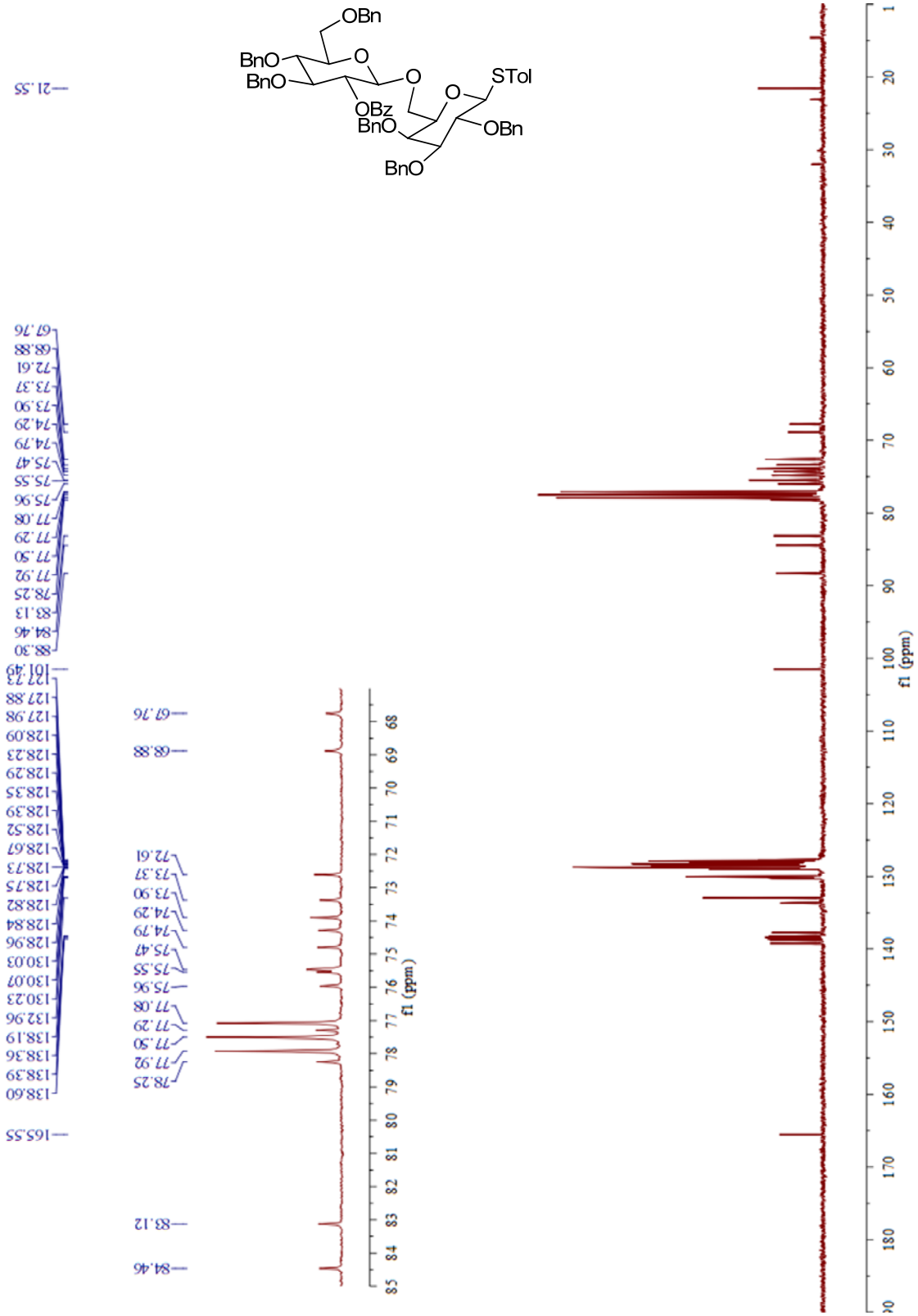
$^{13}$C spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **20**



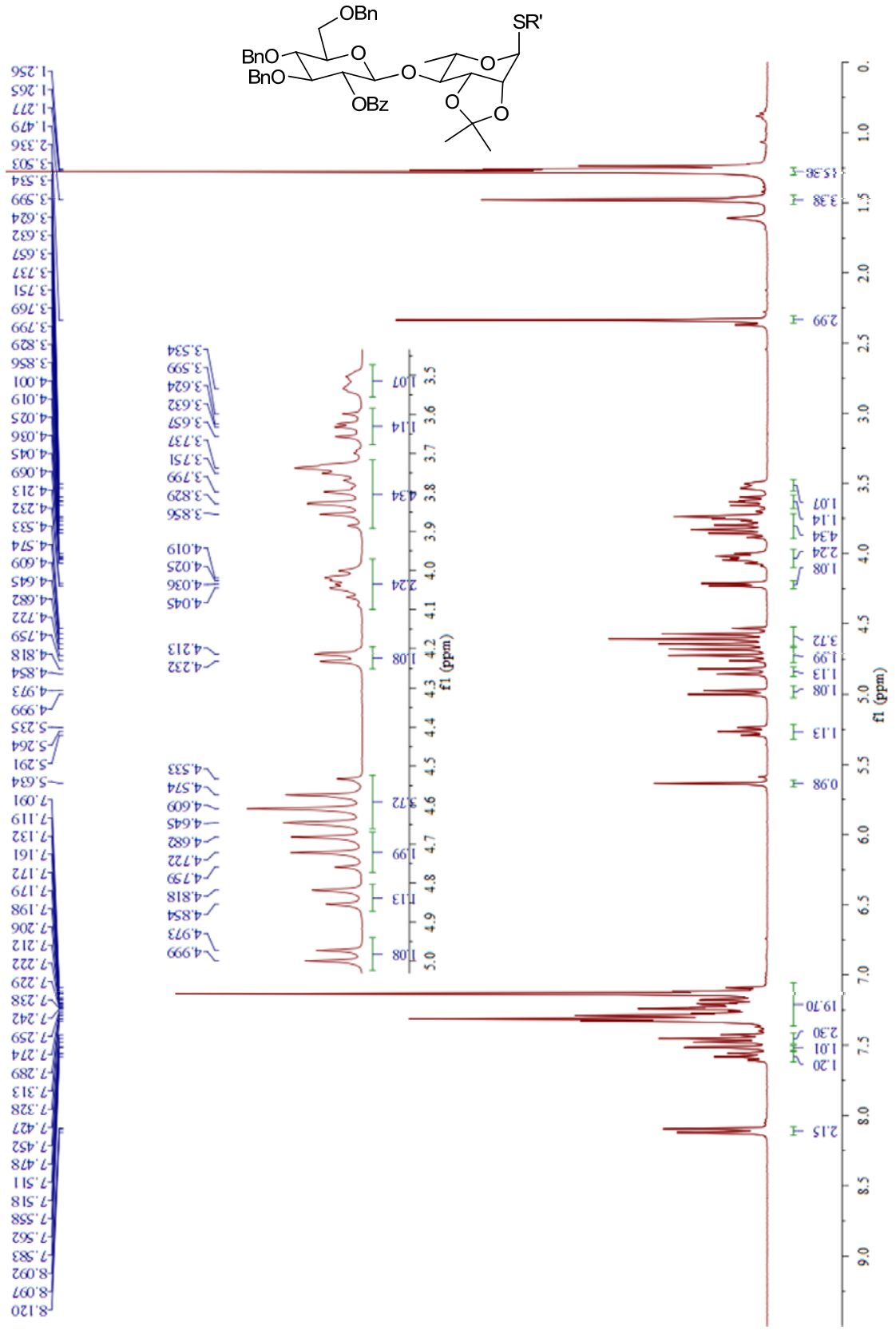
$^{1}$H spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside **21**



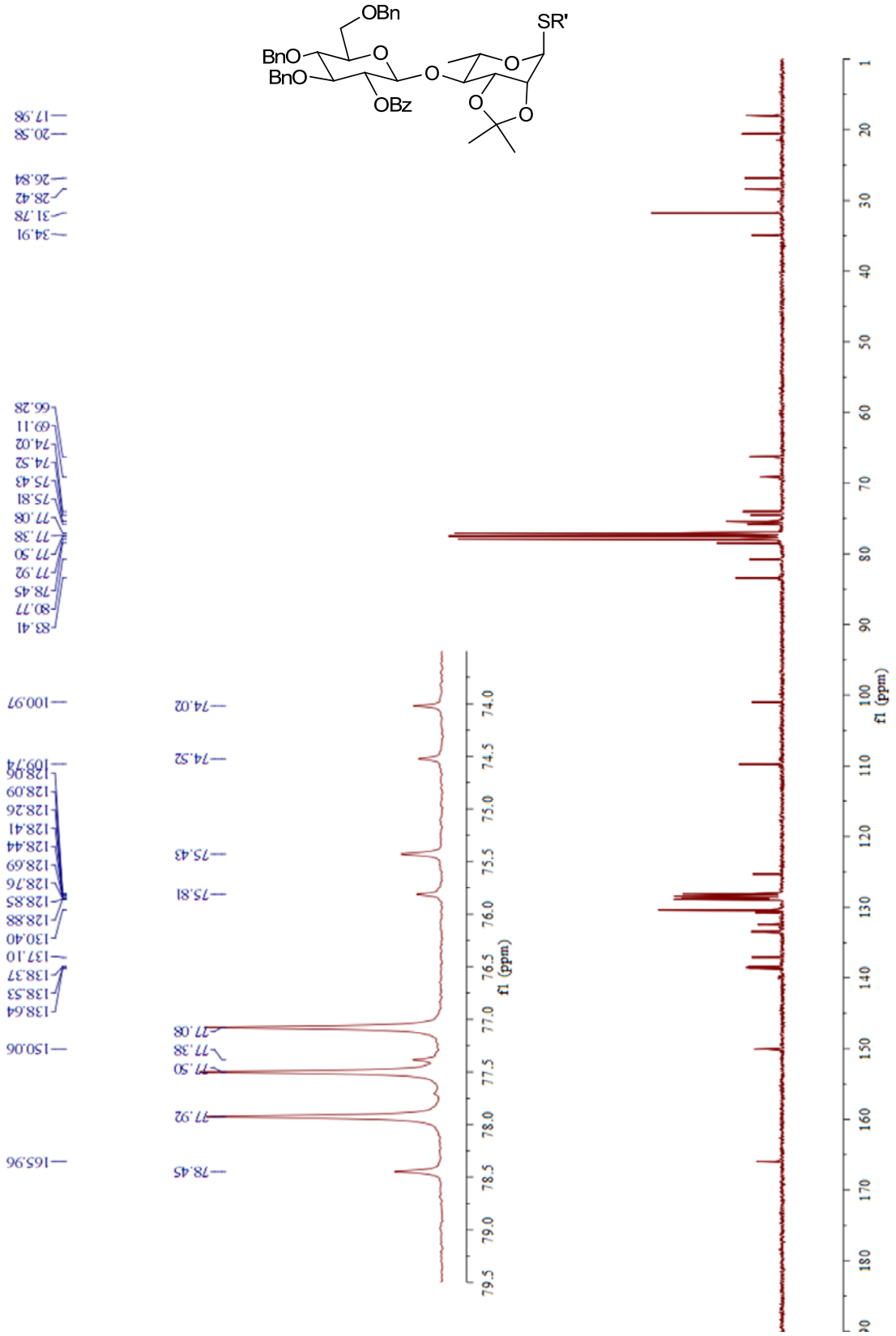
$^{13}$C spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside **21**



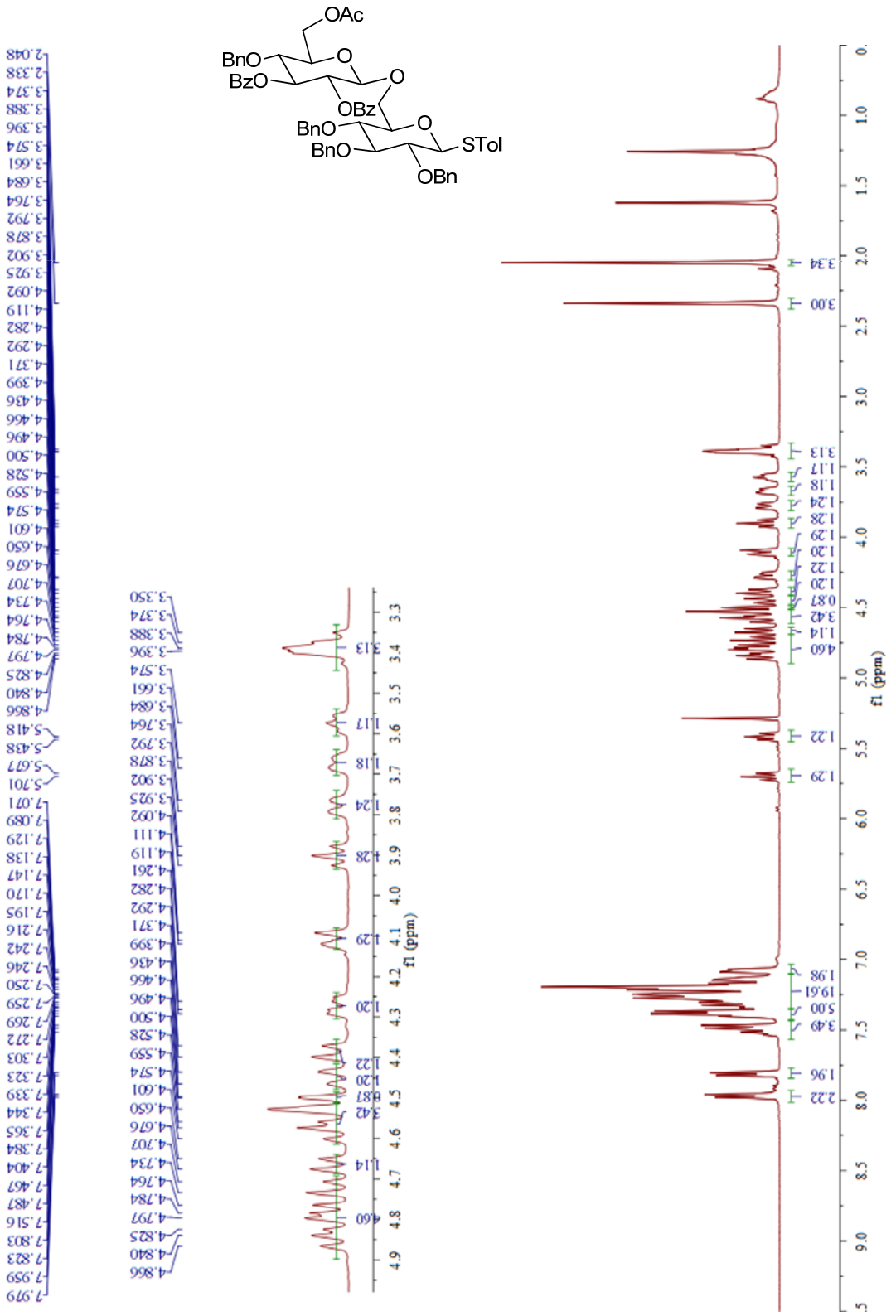
$^{1}$H spectrum of 4-(*t*-butyl)-2-methylphenyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-thio-α-L-rhamnopyranoside **22**



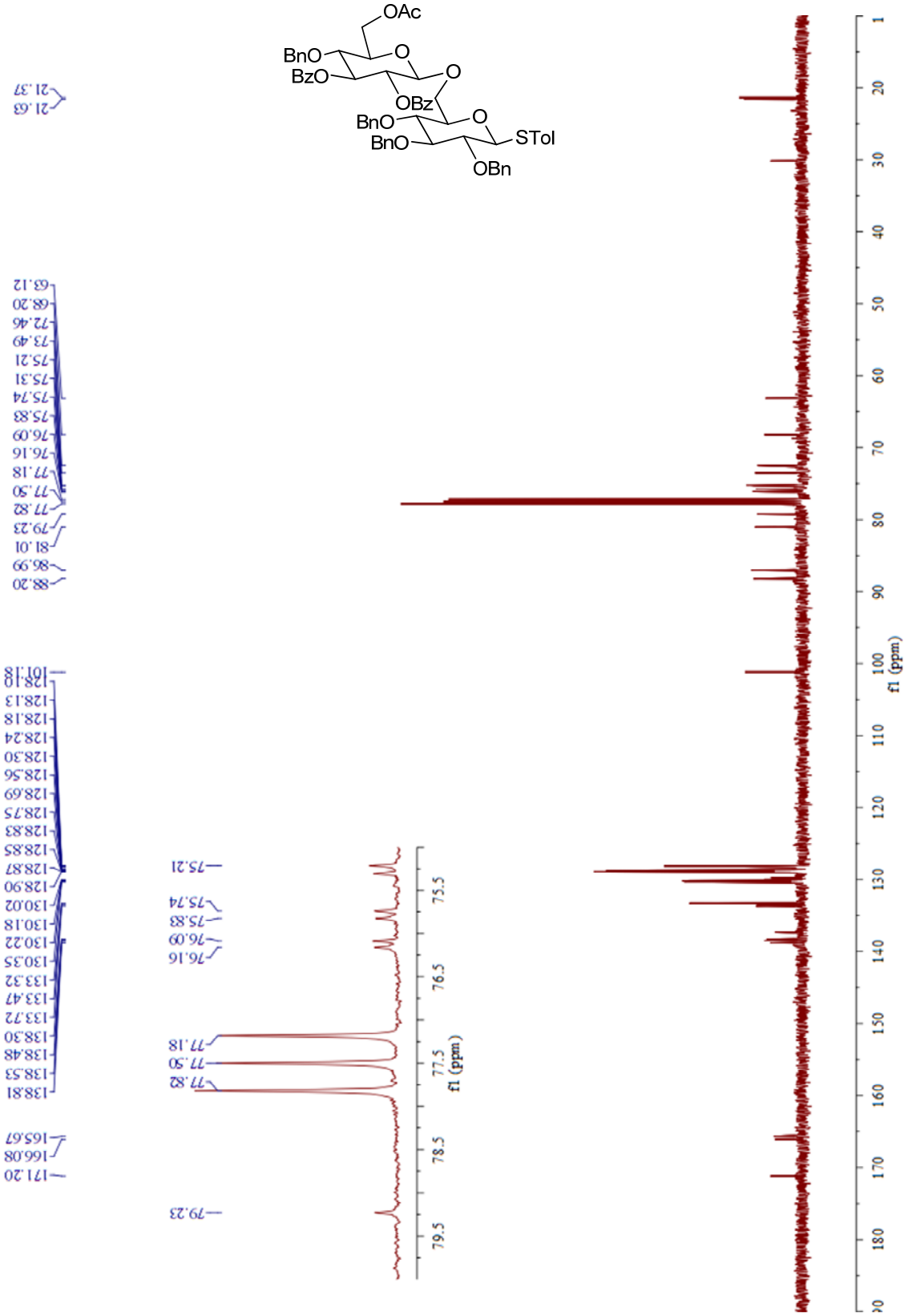
$^{13}$C spectrum of 4-*t*-butyl-2-methylphenyl 4-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-2,3-*O*-isopropylidene-thio-α-L-rhamnopyranoside **22**



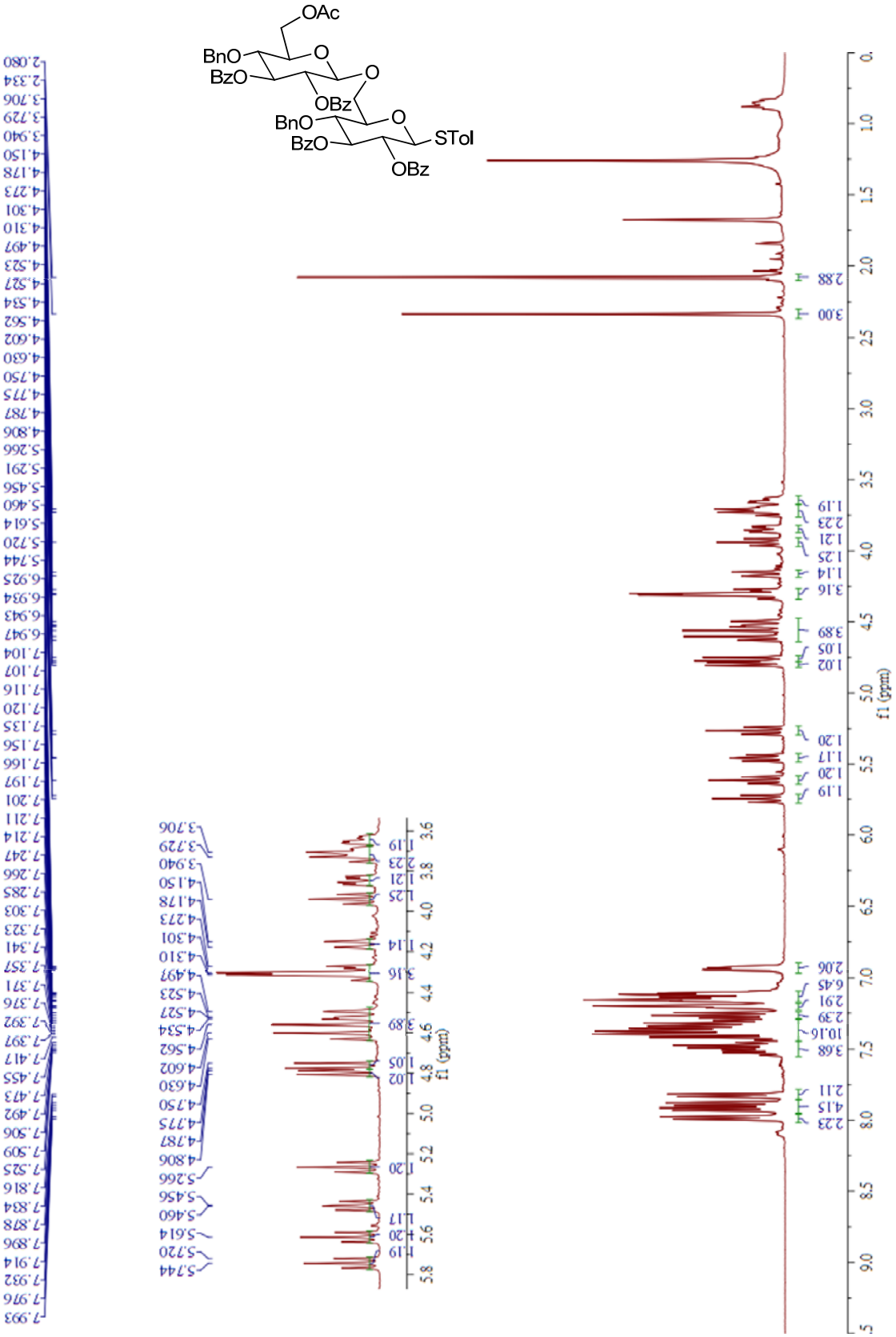
$^{1}$H spectrum of *p*-tolyl 6-*O*-(6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-gluco pyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **23**



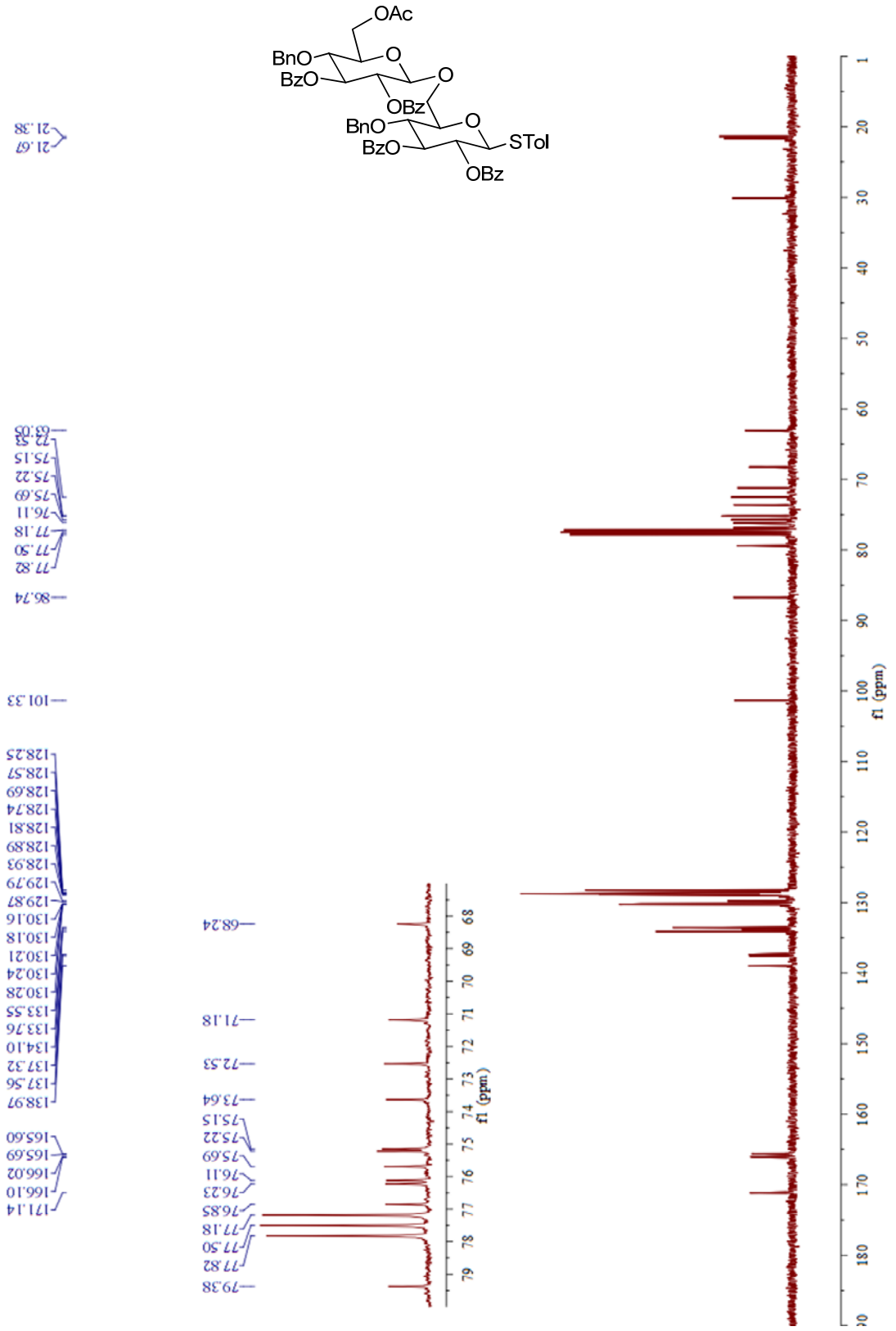
$^{13}$C spectrum of *p*-tolyl 6-*O*-(6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-gluco pyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **23**



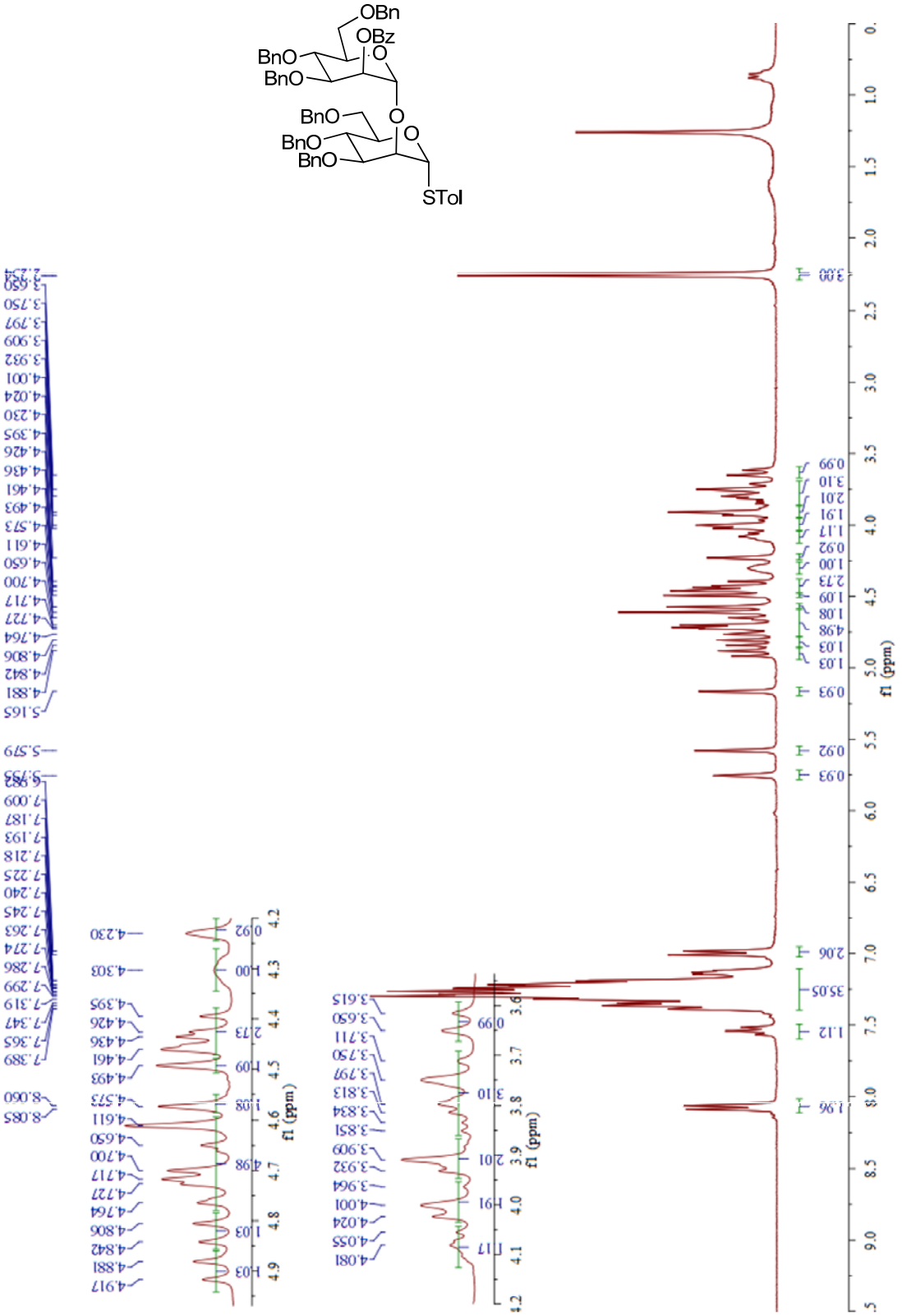
$^{1}$H spectrum of *p*-tolyl 6-*O*-(6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-gluco pyranosyl)-2,3-di-*O*-benzoyl-4-*O*-benzyl-thio-β-D-glucopyranoside **24**



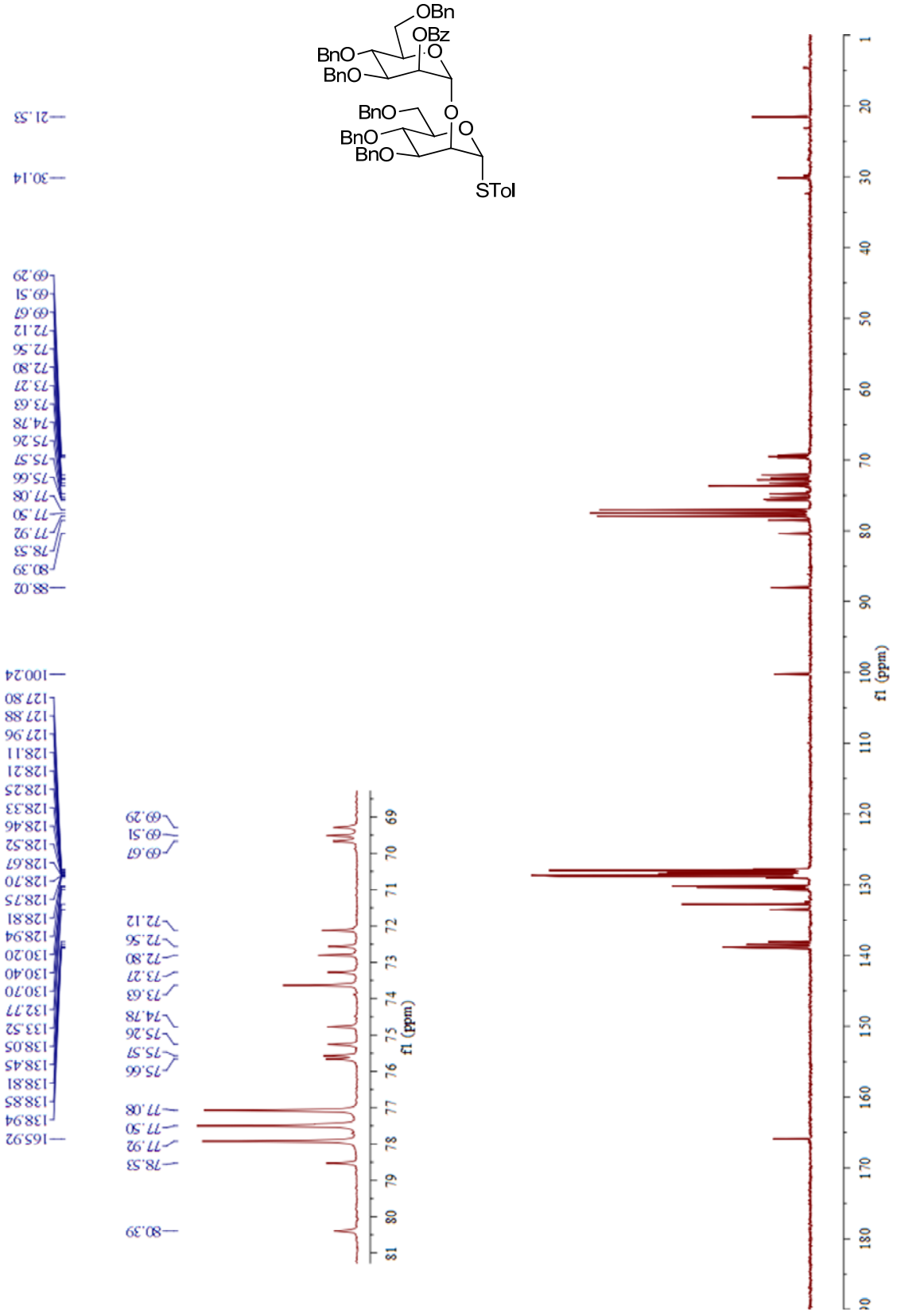
$^{13}$C spectrum of *p*-tolyl 6-*O*-(6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl)-2,3-di-*O*-benzoyl-4-*O*-benzyl-thio-β-D-glucopyranoside **24**



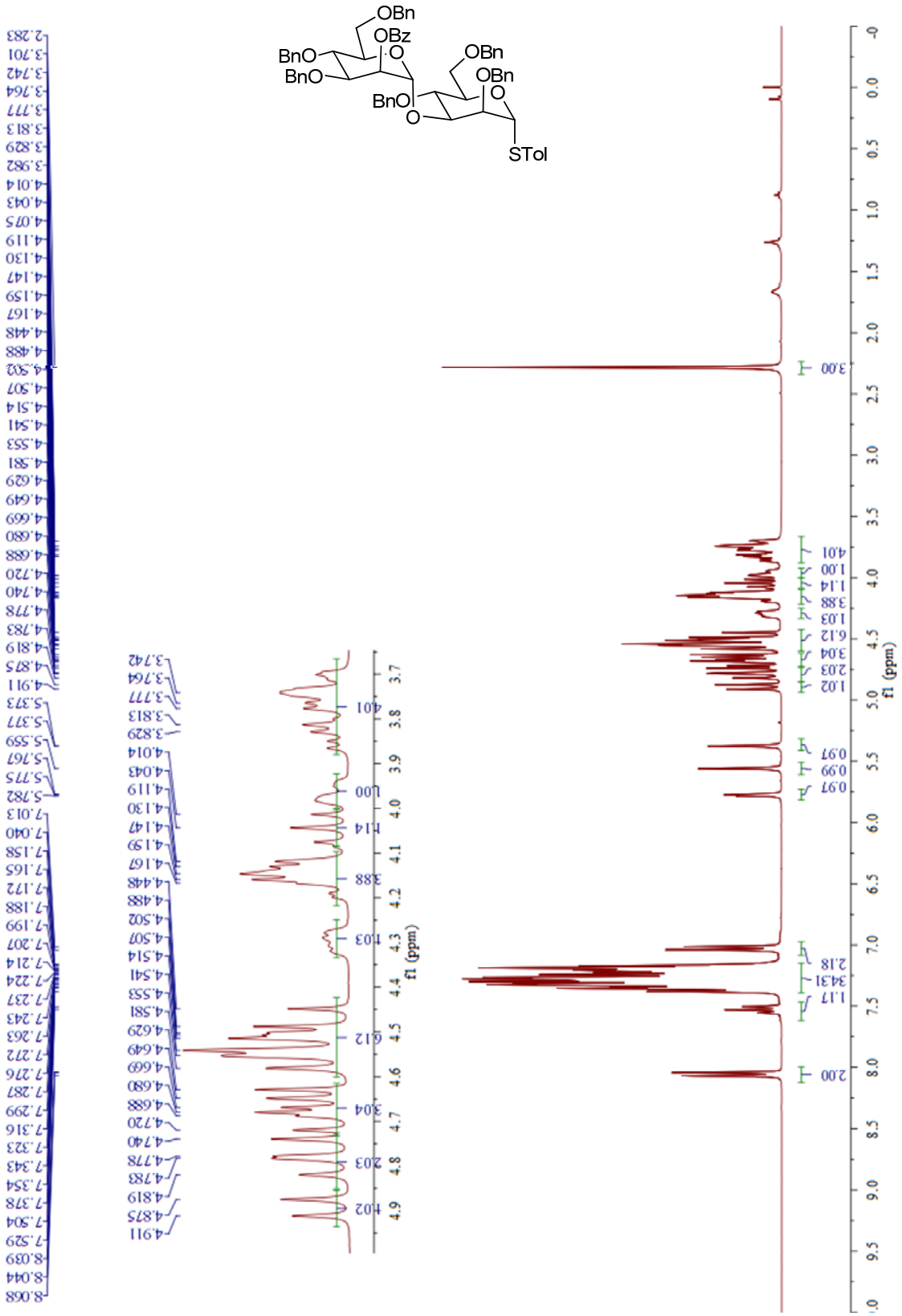
$^{1}$H spectrum of *p*-tolyl 2-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **25**



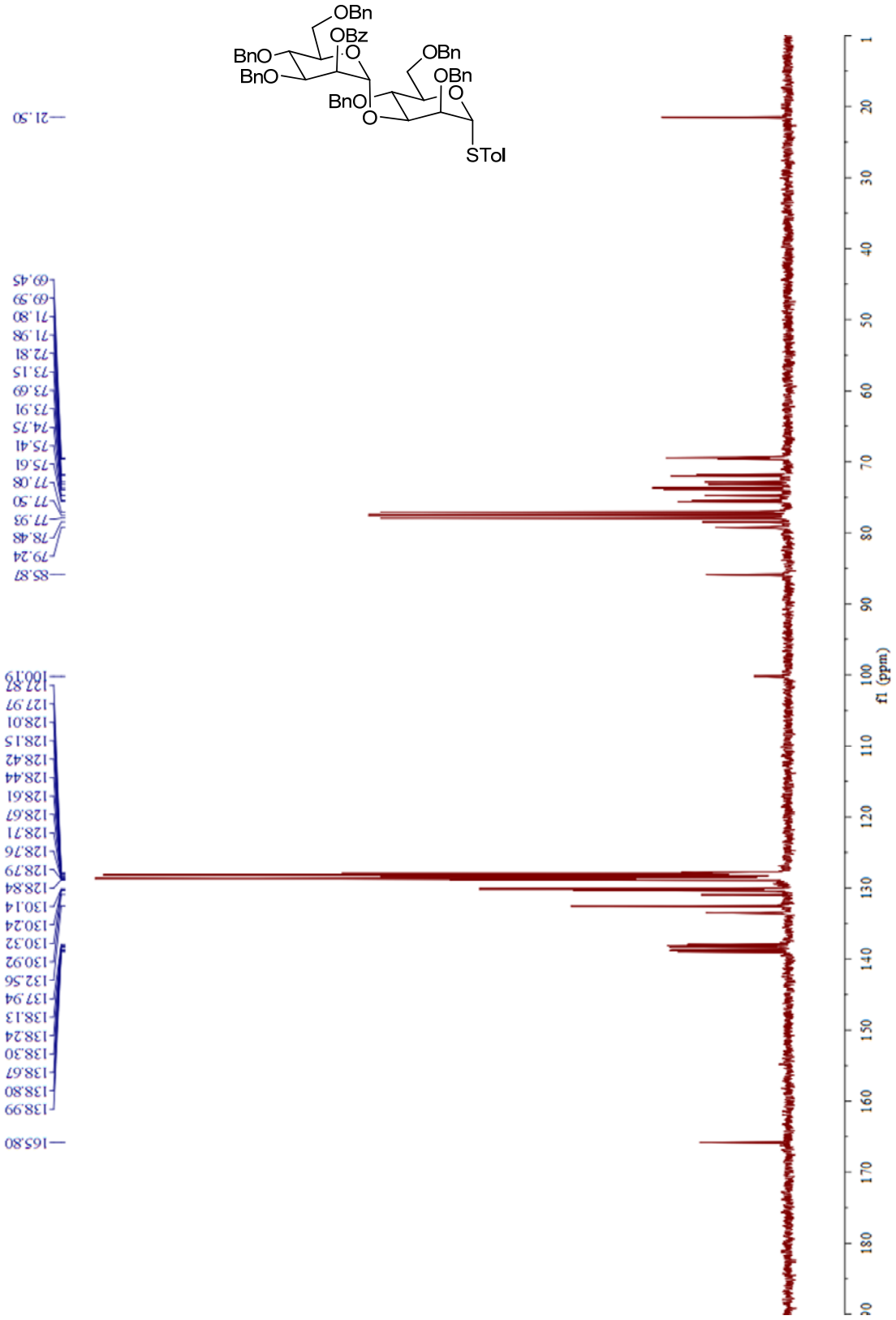
$^{13}$C spectrum of *p*-tolyl 2-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **25**



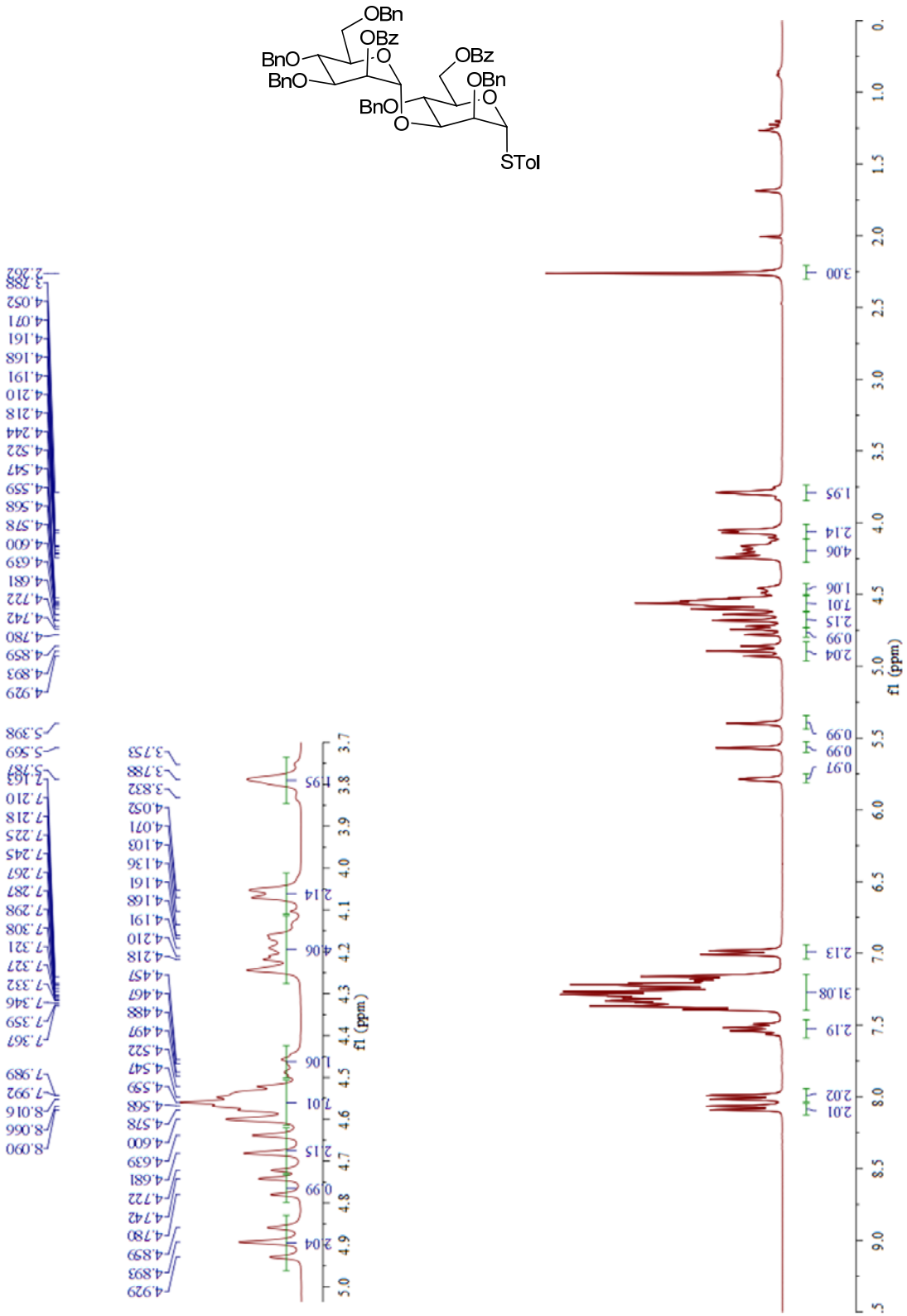
$^{1}$H spectrum of *p*-tolyl 3-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **26**



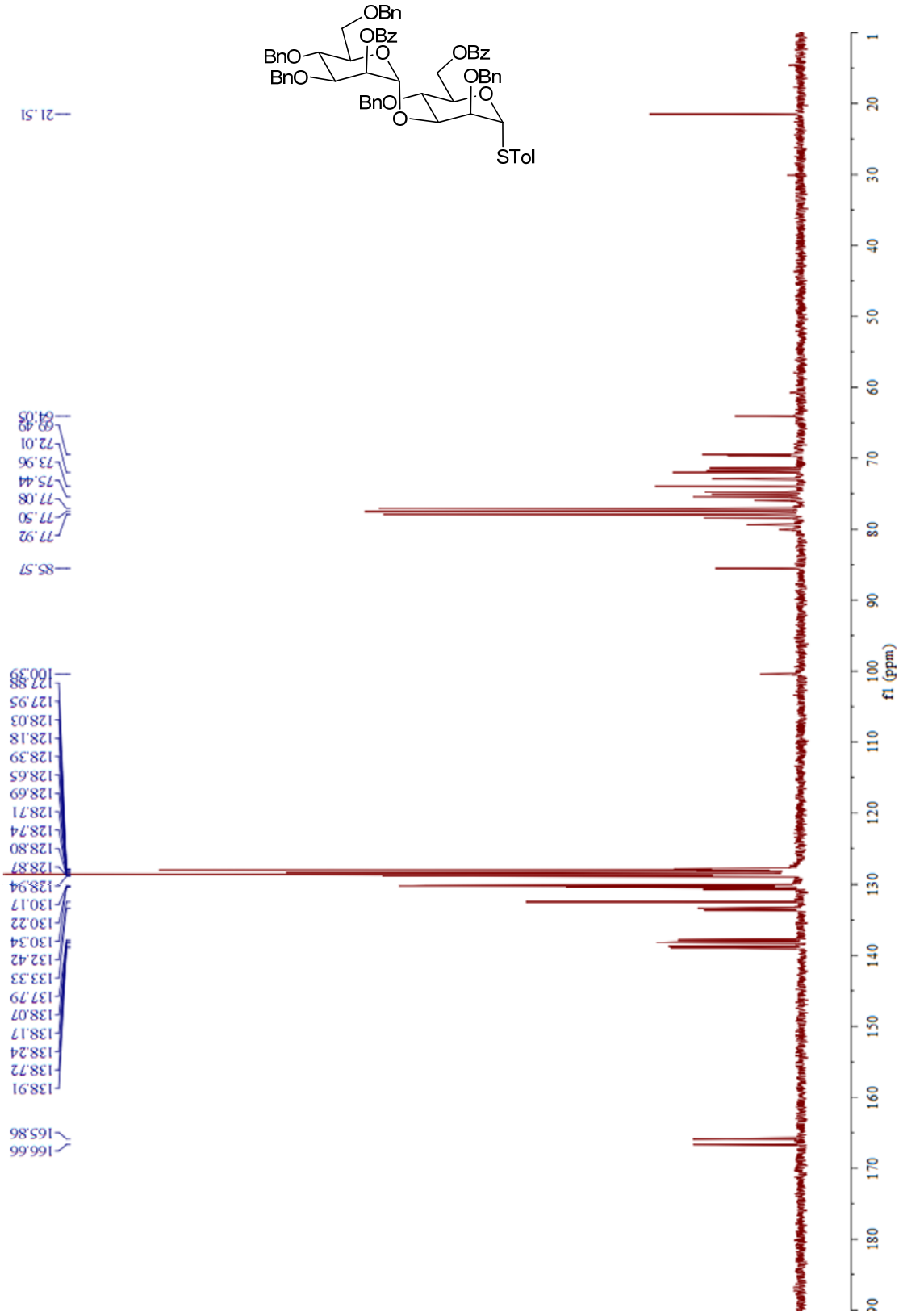
$^{13}$C spectrum of *p*-tolyl 3-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,4,6-tri-*O*-benzyl-thio-α-D-mannopyranoside **26**



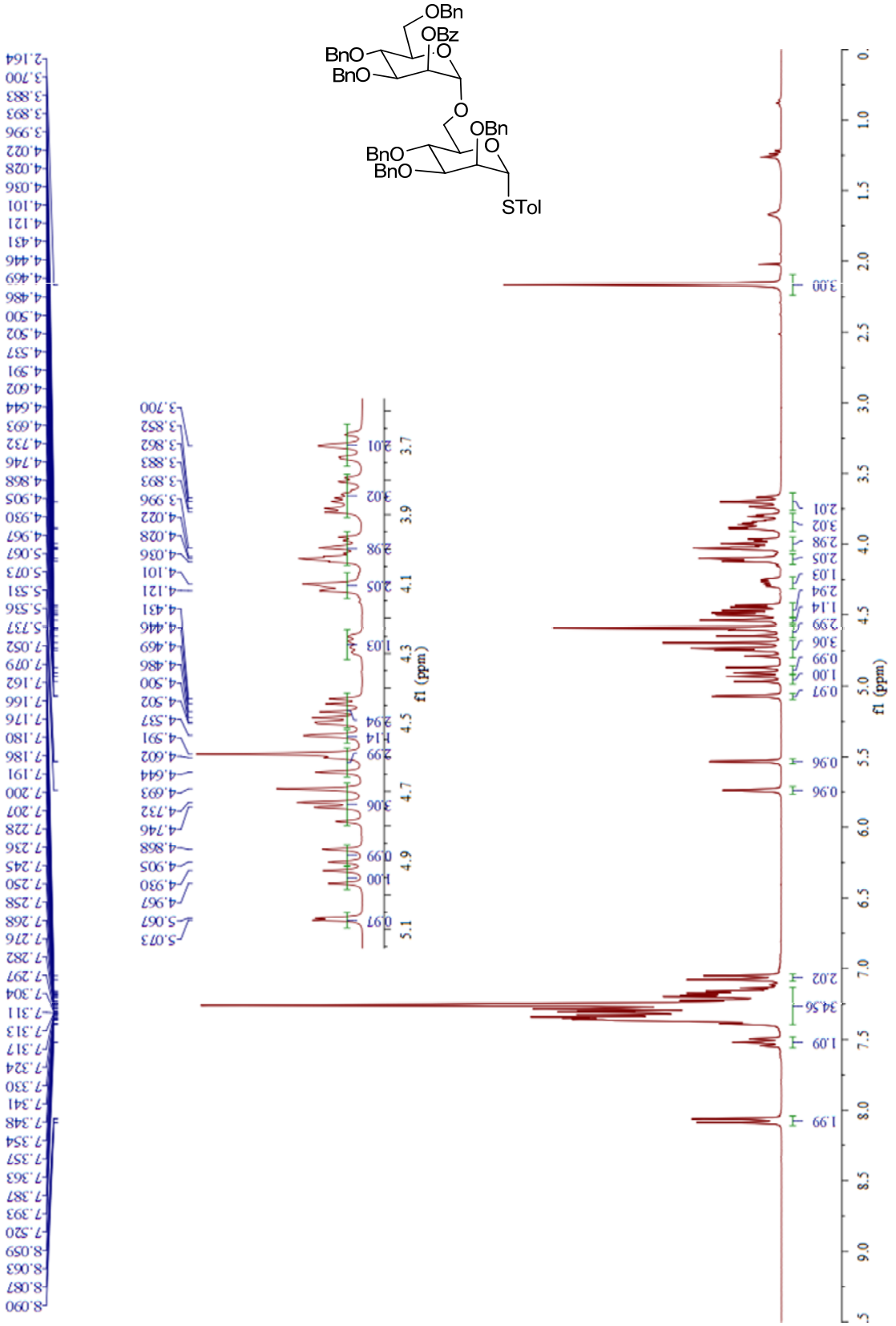
$^{1}$H spectrum of *p*-tolyl 3-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-6-*O*-benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside **27**



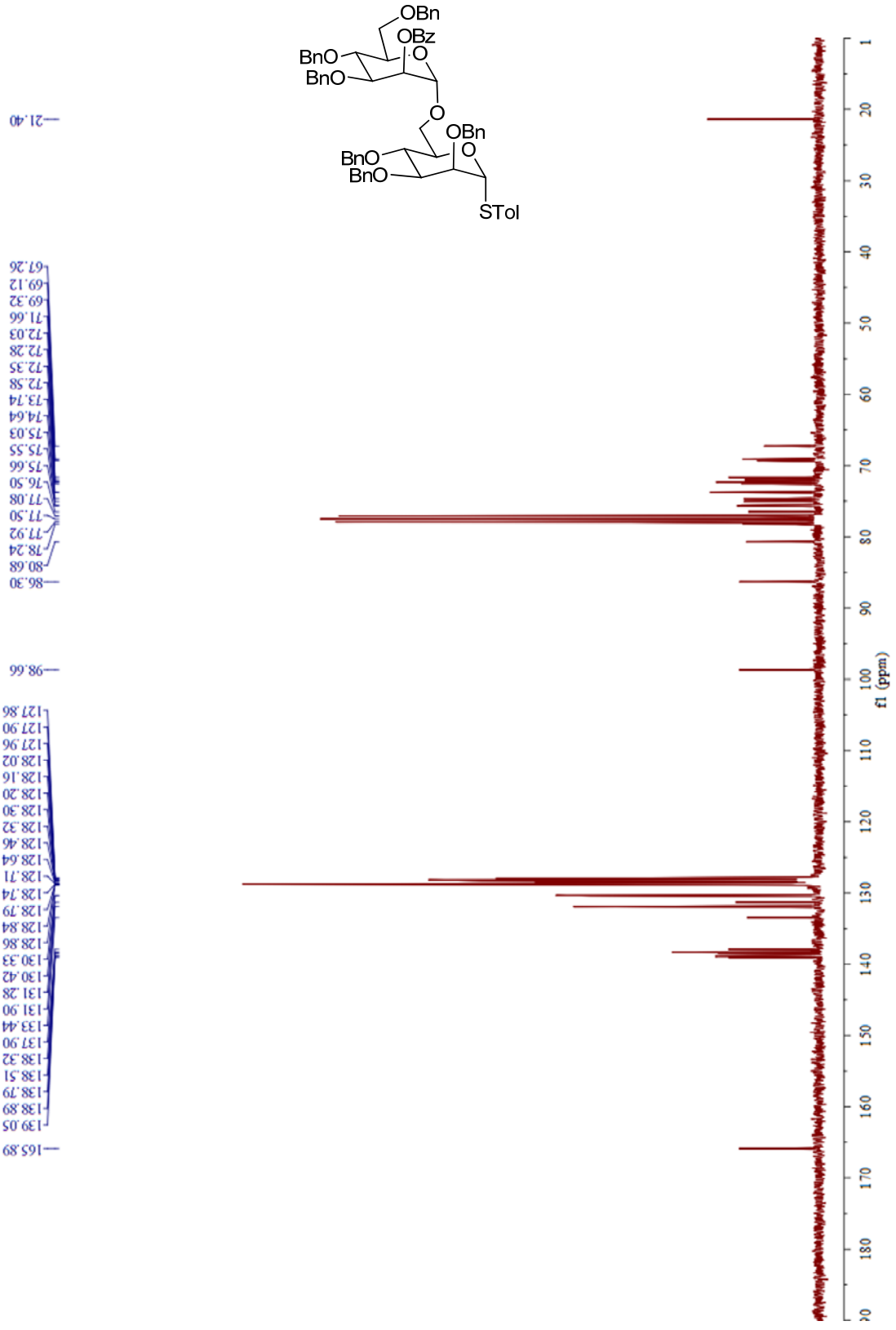
$^{13}$C spectrum of *p*-tolyl 3-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-
-6-*O*-benzoyl-2,4-di-*O*-benzyl-thio-α-D-mannopyranoside **27**



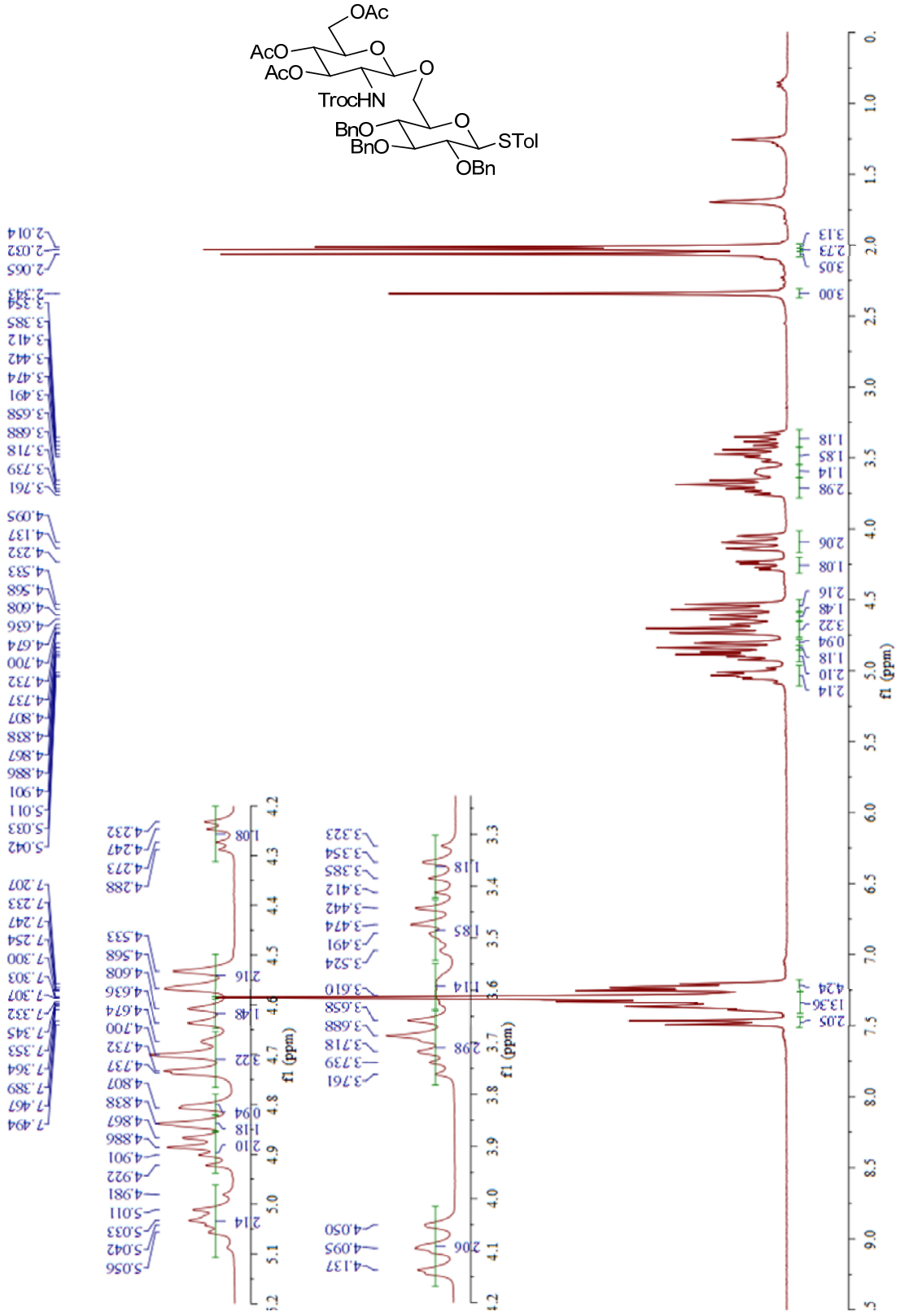
$^{1}$H spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-thio-α-D-mannopyranoside **28**



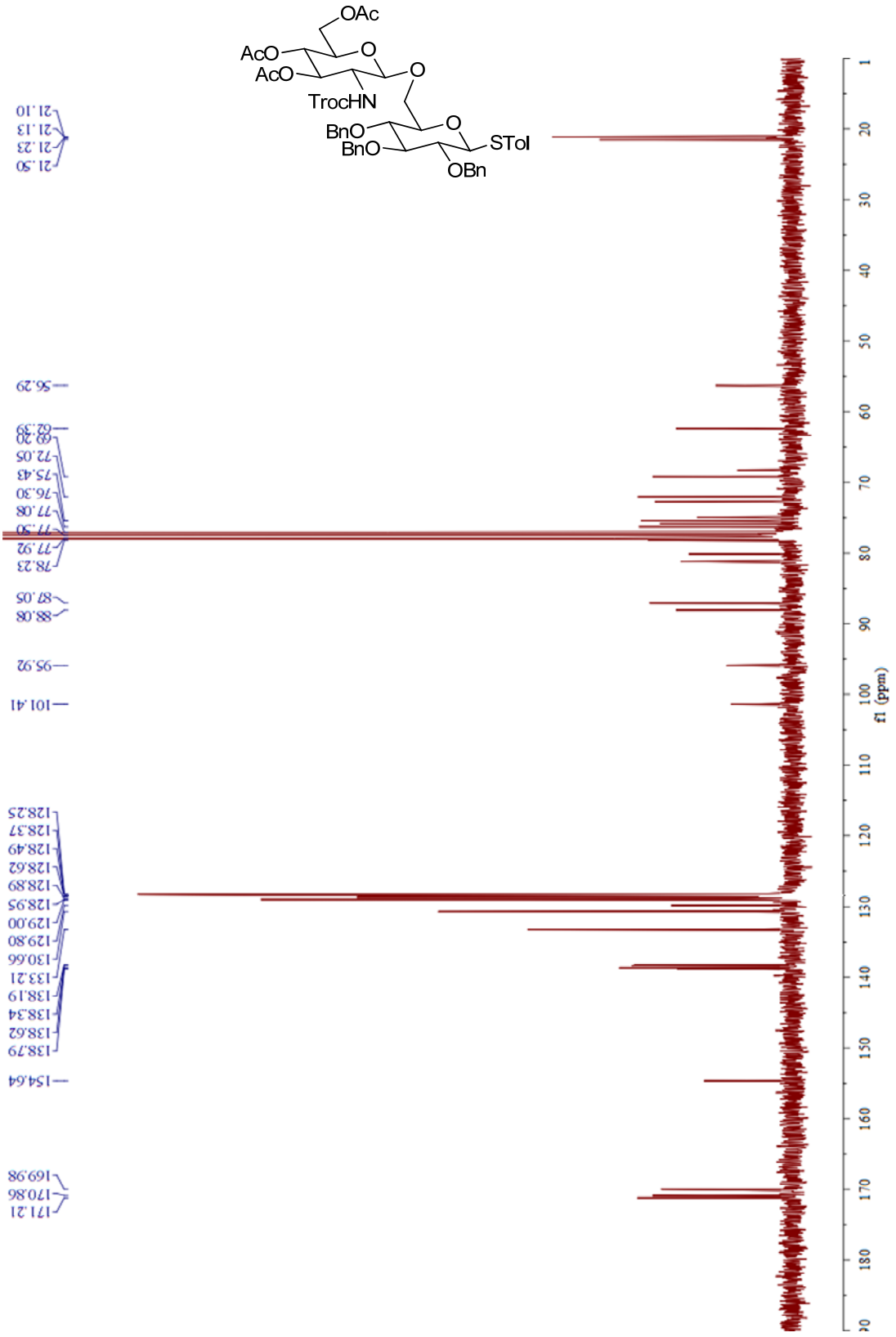
$^{13}$C spectrum of *p*-tolyl 6-*O*-(2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-thio-α-D-mannopyranoside **28**



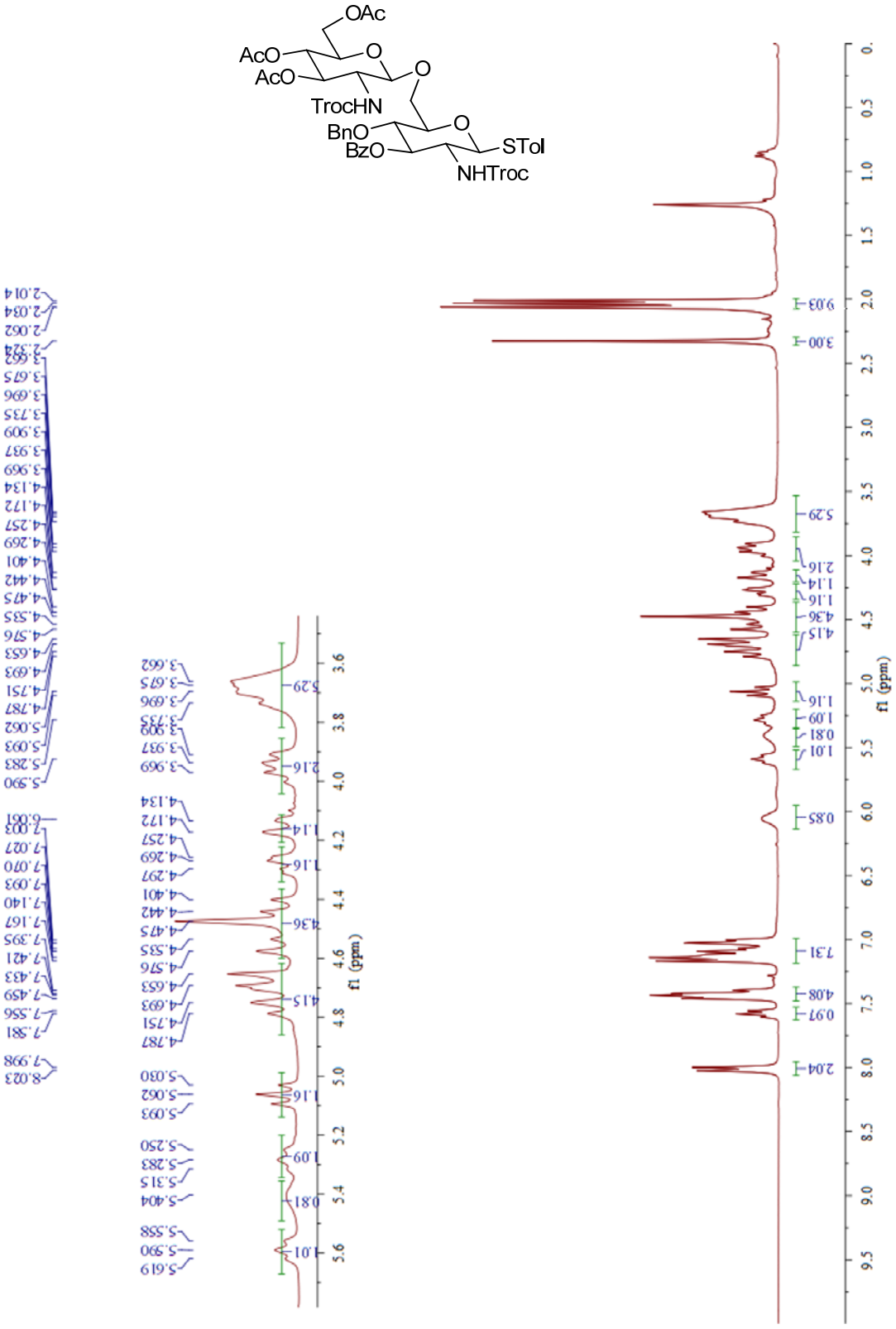
$^{1}$H spectrum of *p*-tolyl 6-*O*-[3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **29**



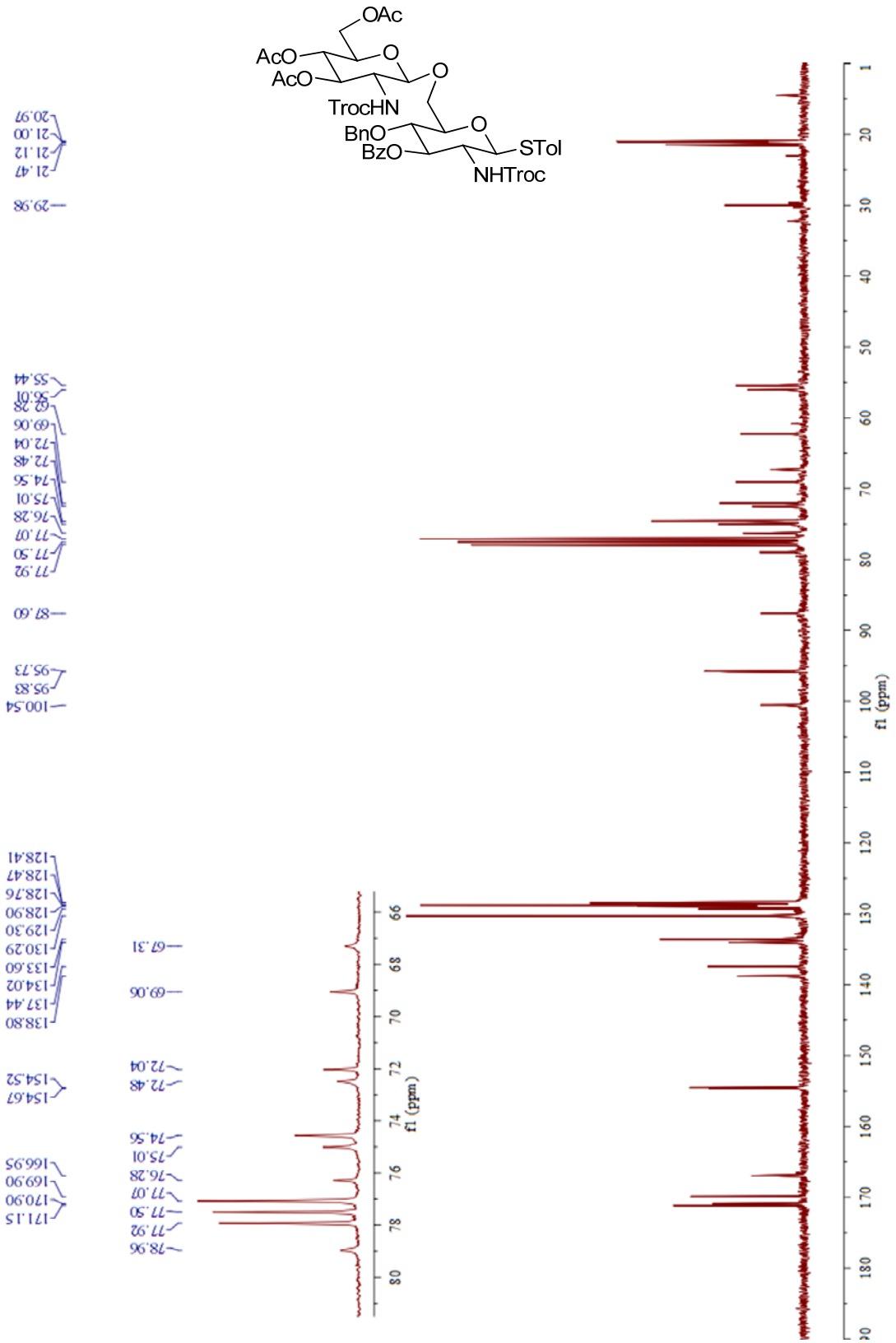
$^{13}$C spectrum of *p*-tolyl 6-*O*-[3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-β-D-glucopyranosyl]-2,3,4-tri-*O*-benzyl-thio-β-D-glucopyranoside **29**



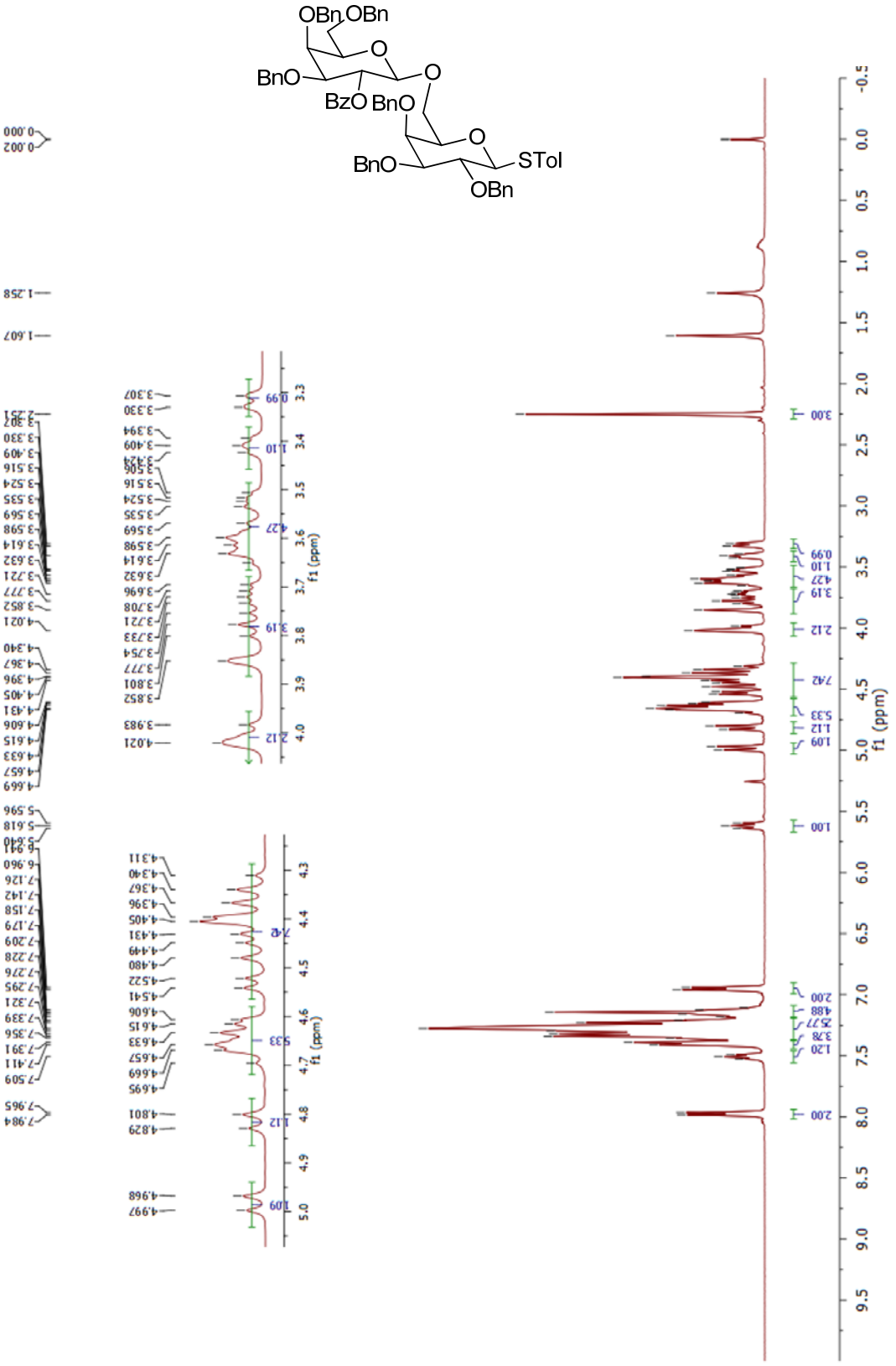
$^{1}$H spectrum of *p*-tolyl 6-*O*-[3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-β-D-glucopyranosyl]-3-*O*-benzoyl-4-*O*-benzyl-2-(2,2,2-trichloroetho xycarbonylamino)-2-deoxy-thio-β-D-glucopyranoside **30**



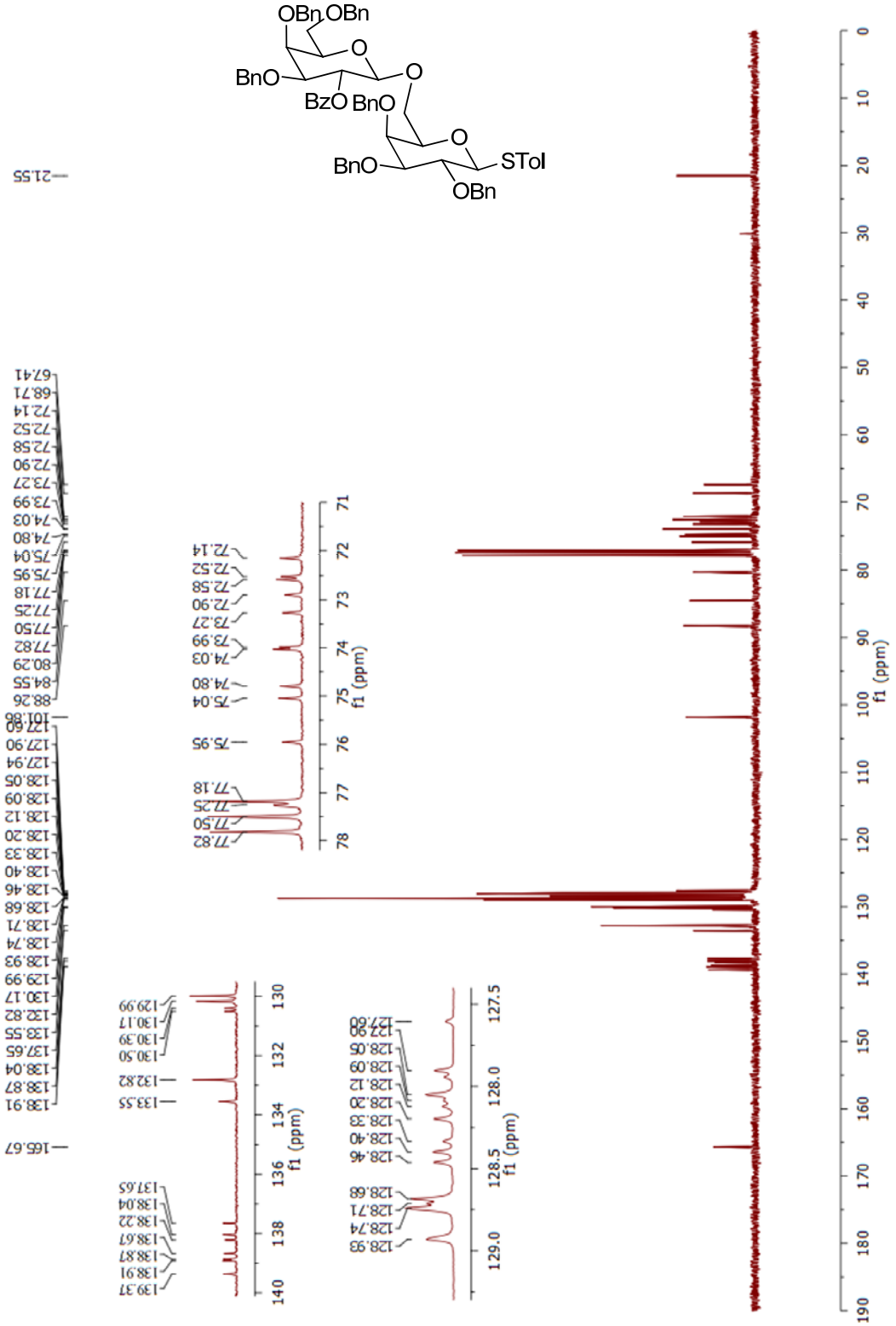
$^{13}$C spectrum of *p*-tolyl 6-*O*-[3,4,6-tri-*O*-acetyl-2-(2,2,2-trichloroethoxycarbonyl amino)-2-deoxy-β-D-glucopyranosyl]-3-*O*-benzoyl-4-*O*-benzyl-2-(2,2,2-trichloroethoxycarbonylamino)-2-deoxy-thio-β-D-glucopyranoside **30**



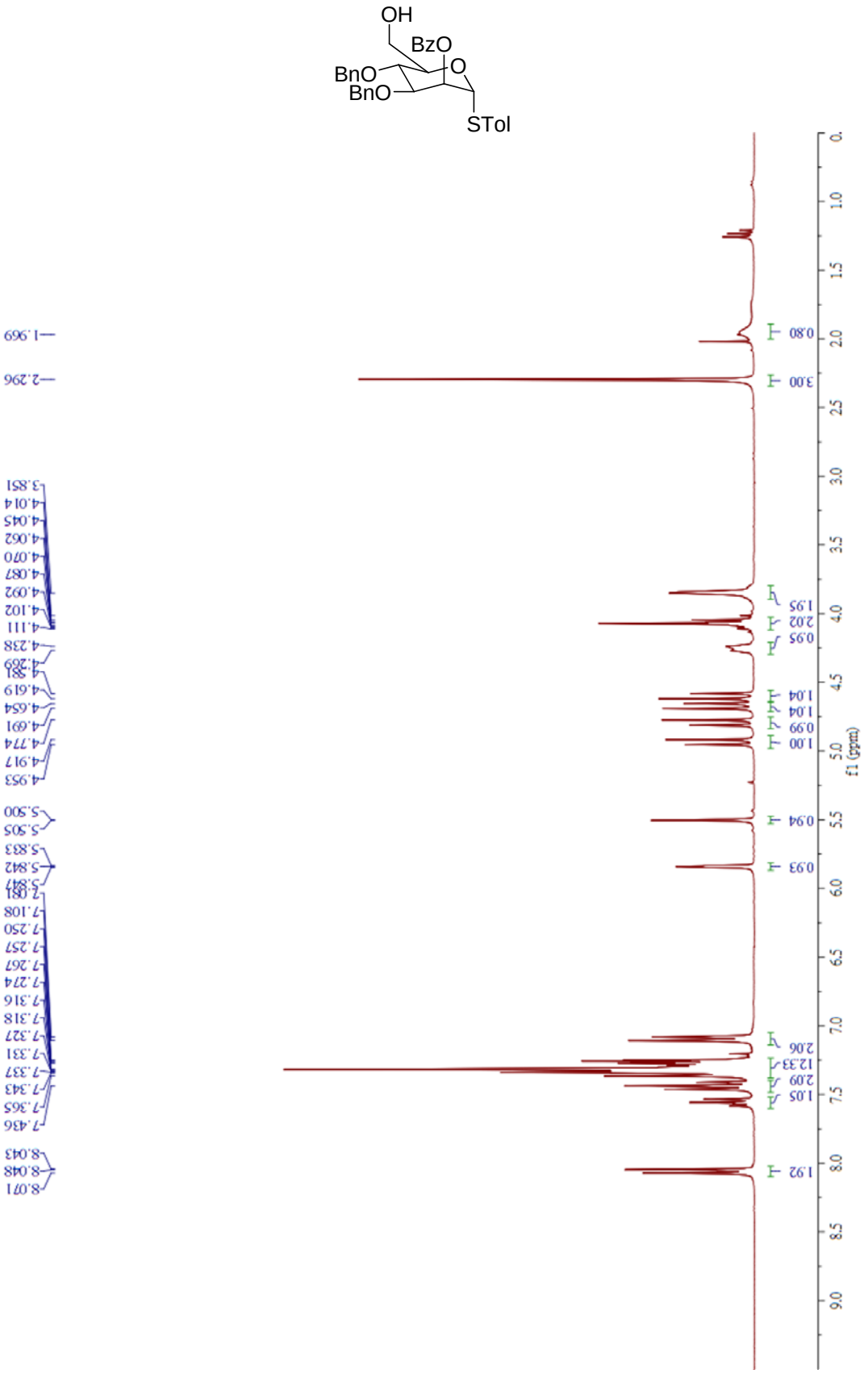
$^{1}$H spectrum of *p*-tolyl 6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside **31**



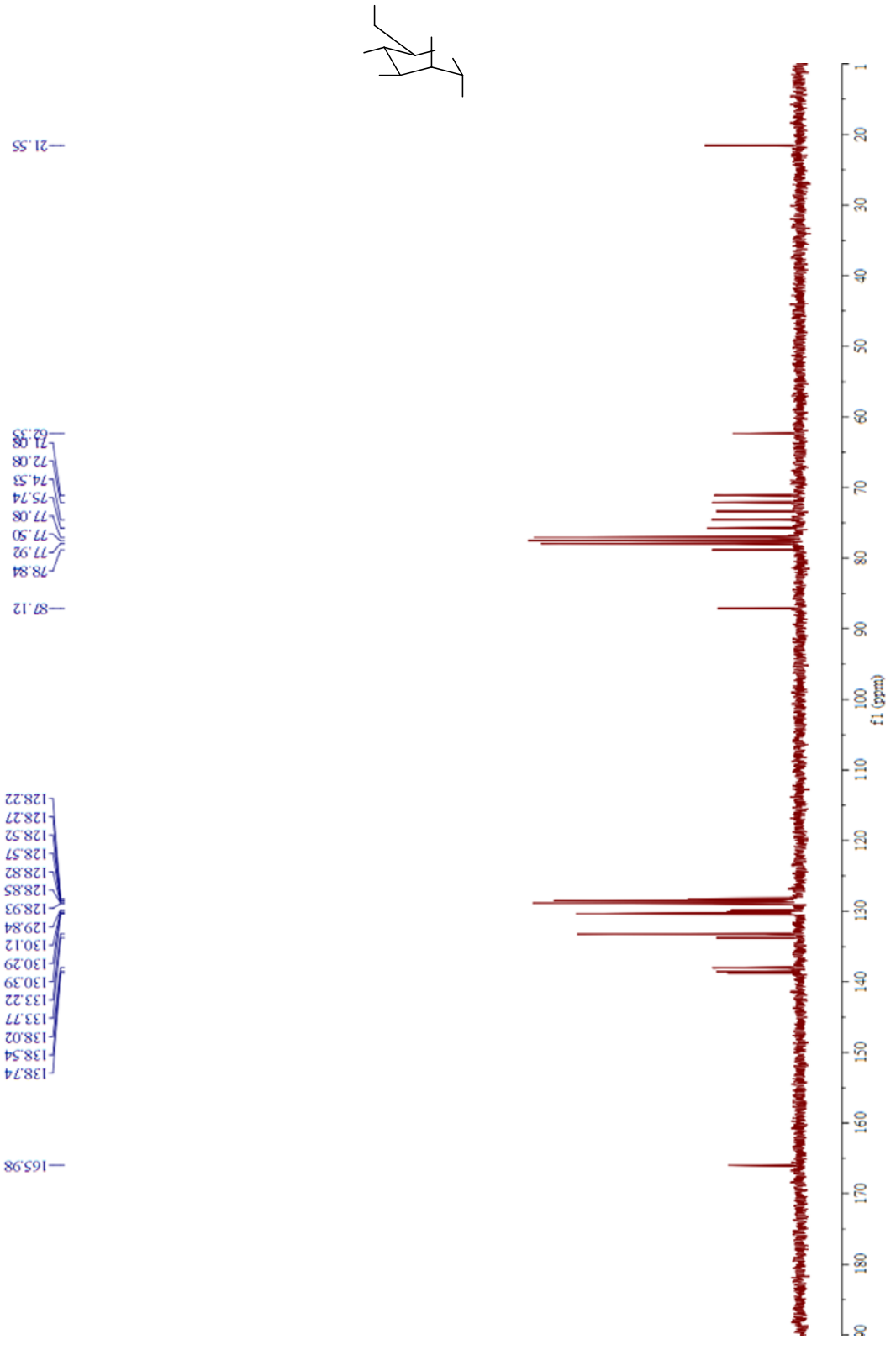
$^{13}$C spectrum of *p*-tolyl 6-*O*-(2-benzoyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-thio-β-D-galactopyranoside **31**



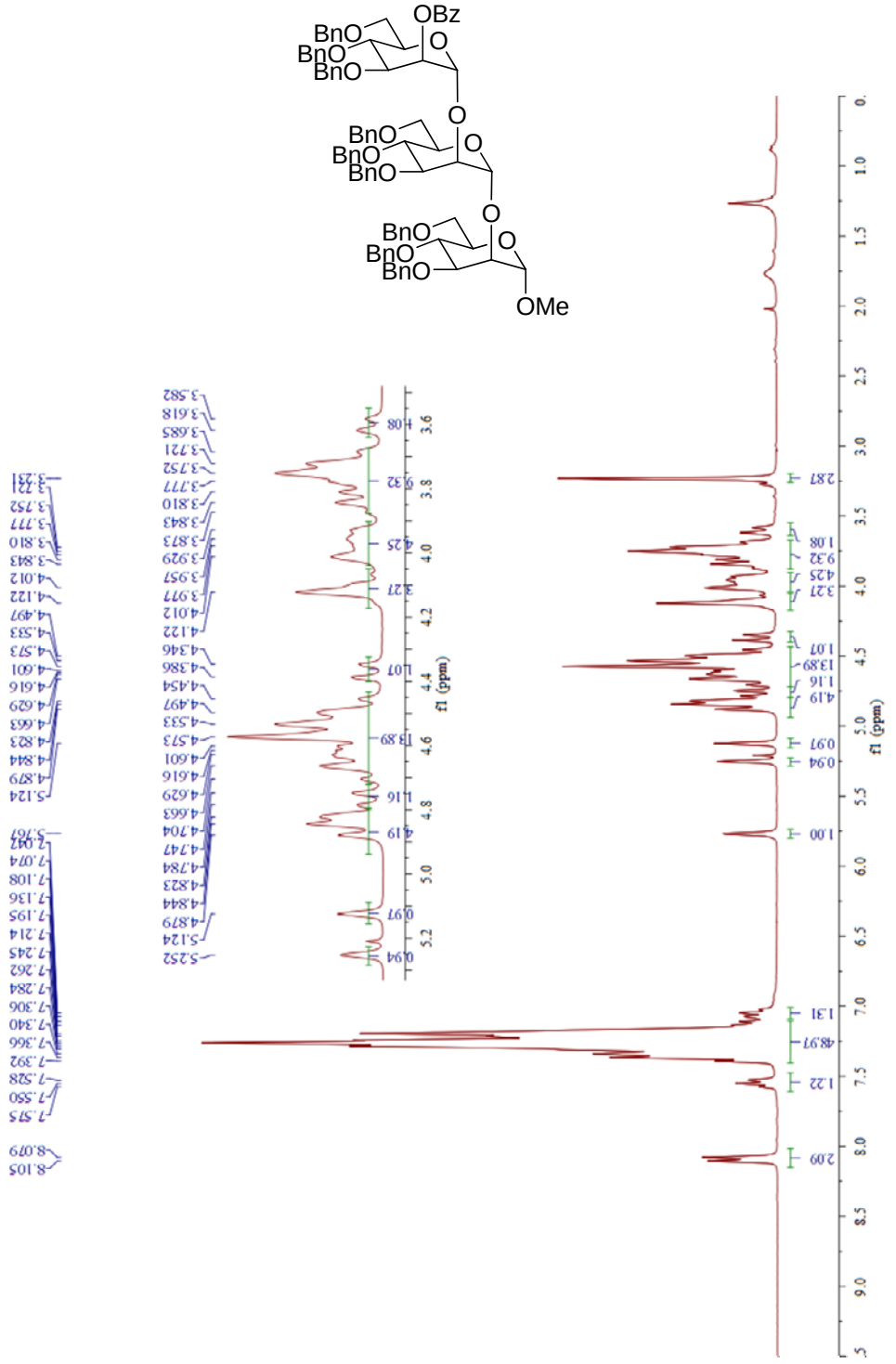
$^{1}$H spectrum of *p*-tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-thio-α-D-mannopyranoside **33**



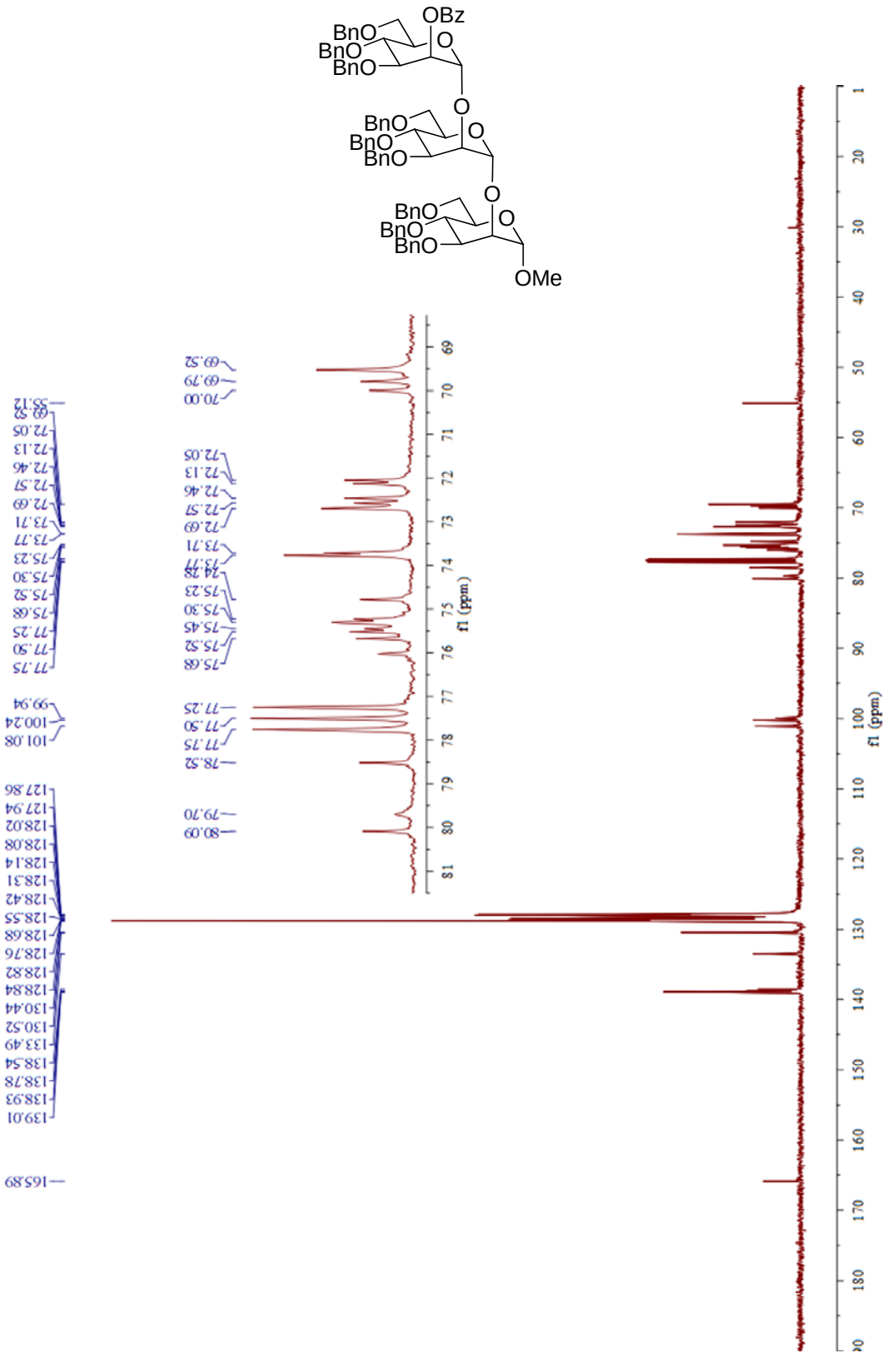
$^{13}$C spectrum of *p*-tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-thio-α-D-mannopyranoside **33**



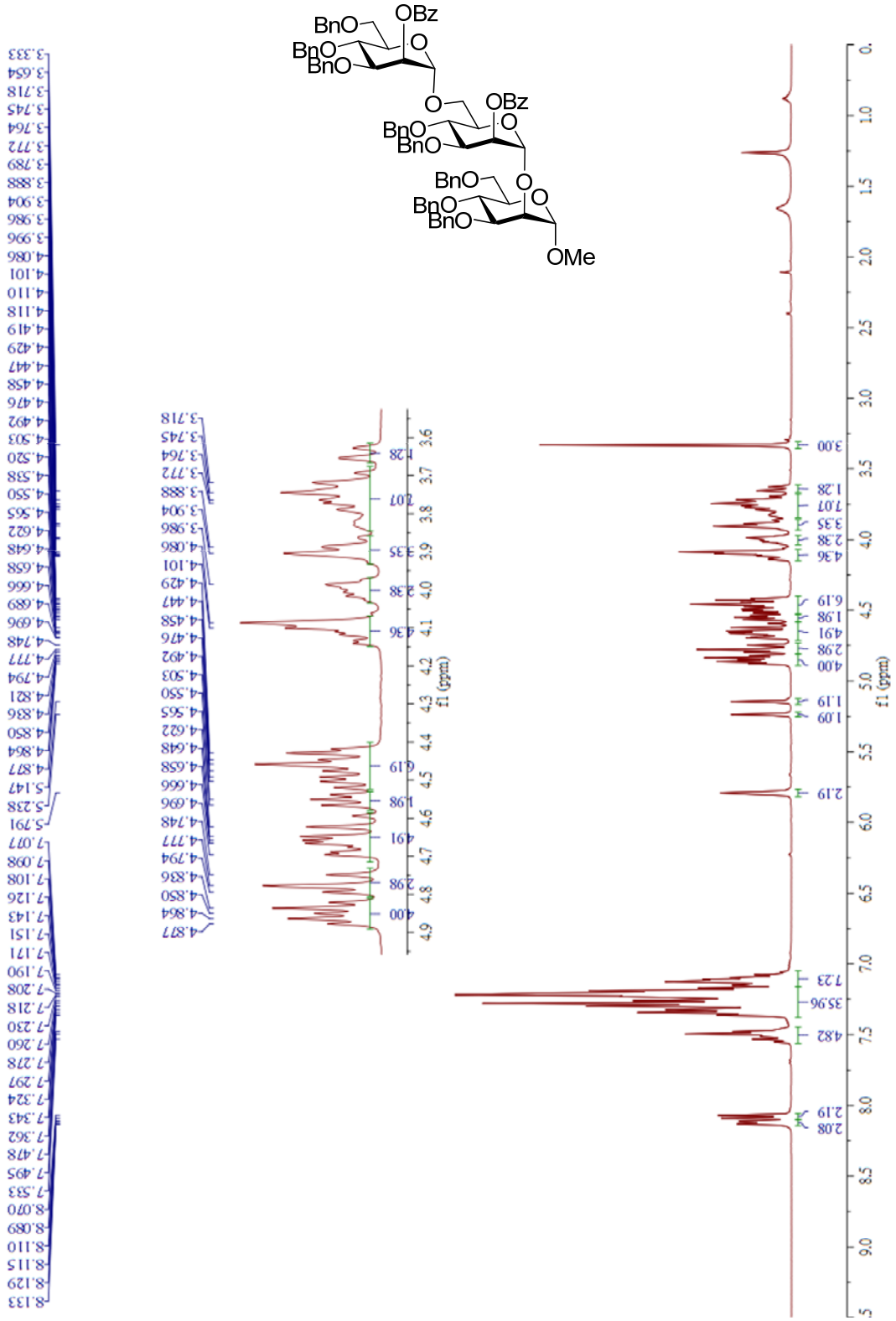
$^{1}$H spectrum of methyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **35**



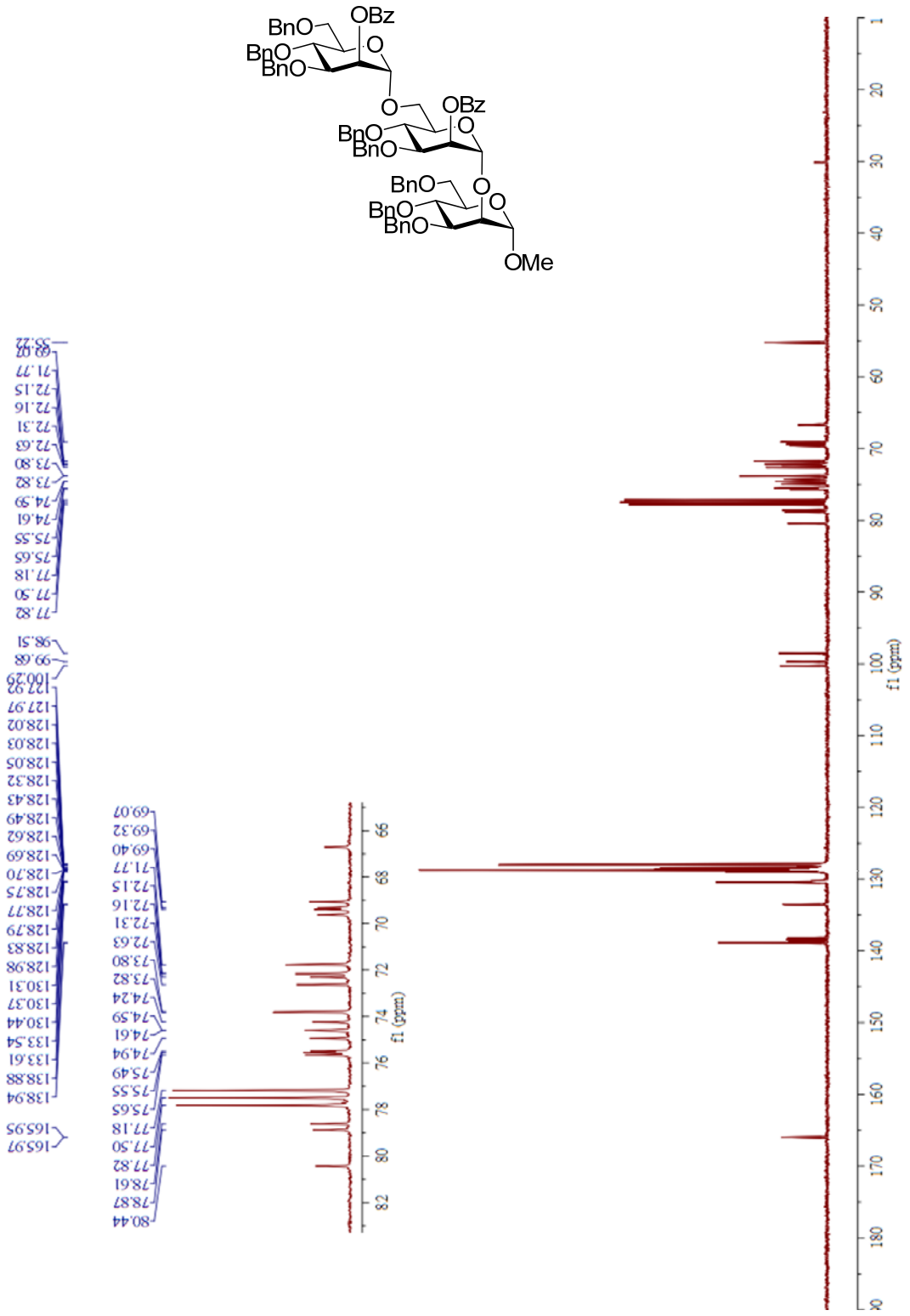
$^{13}$C spectrum of methyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **35**



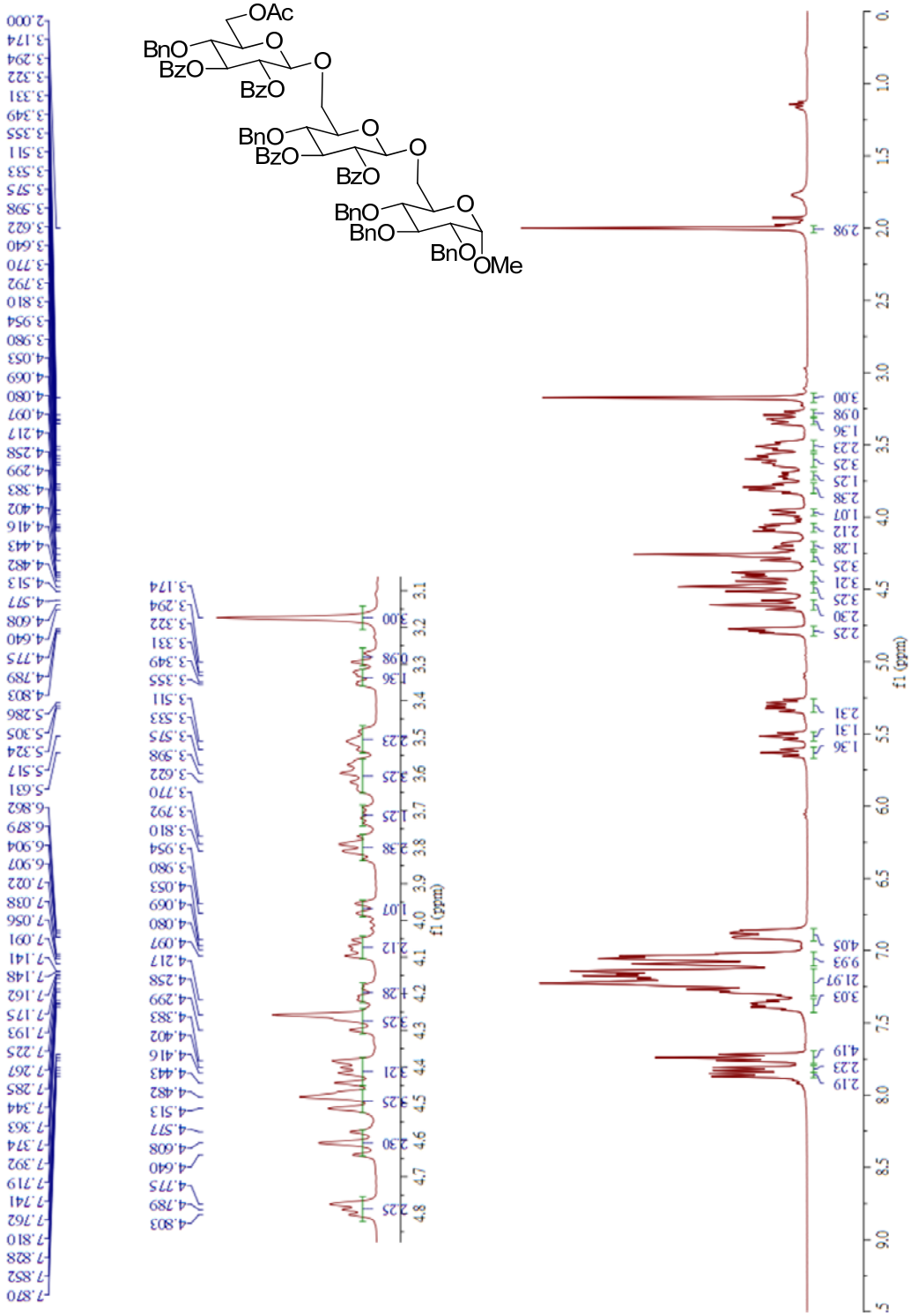
$^{1}$H spectrum of methyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **36**



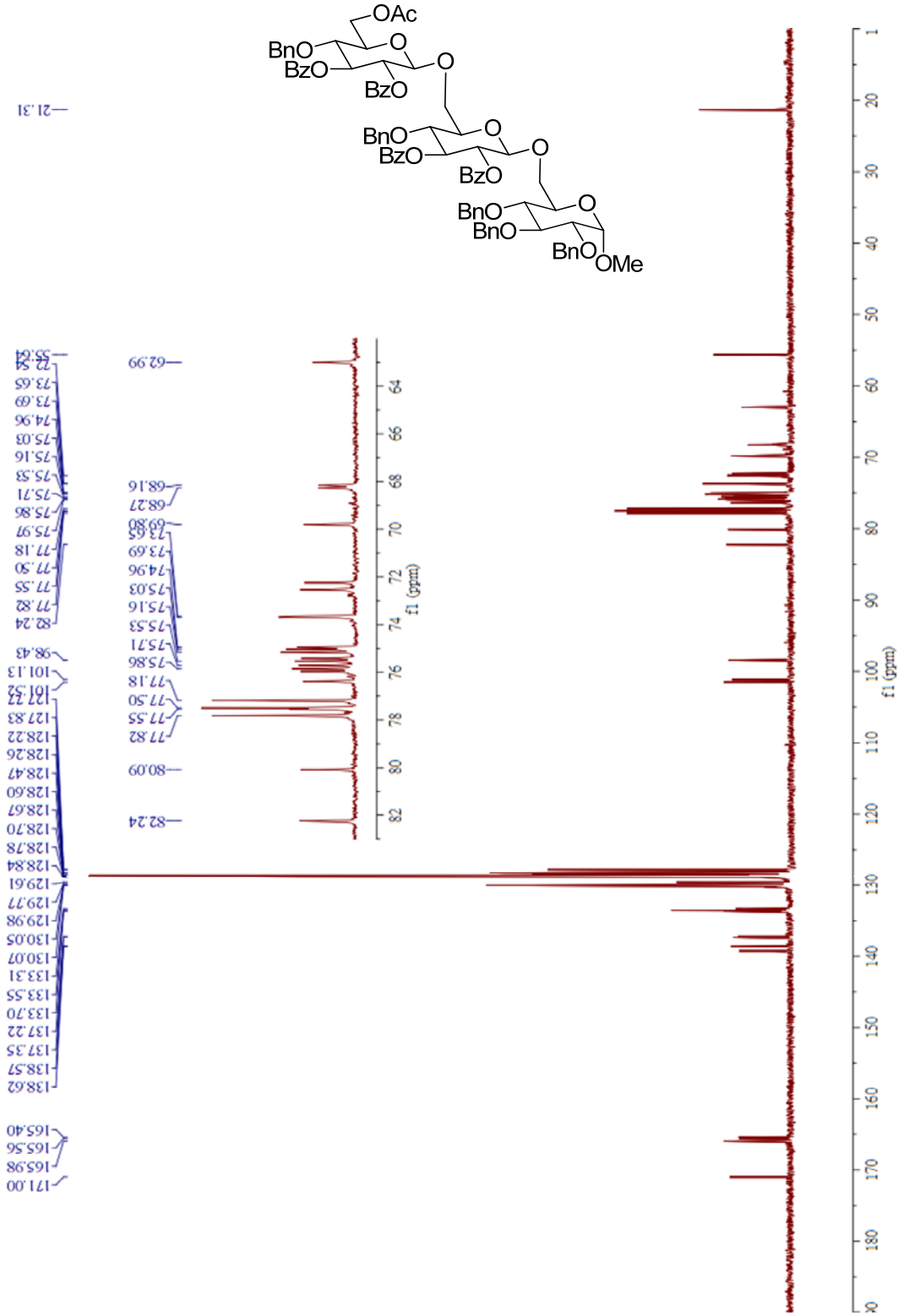
$^{13}$C spectrum of methyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→6)-2-*O*-benzoyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside **36**



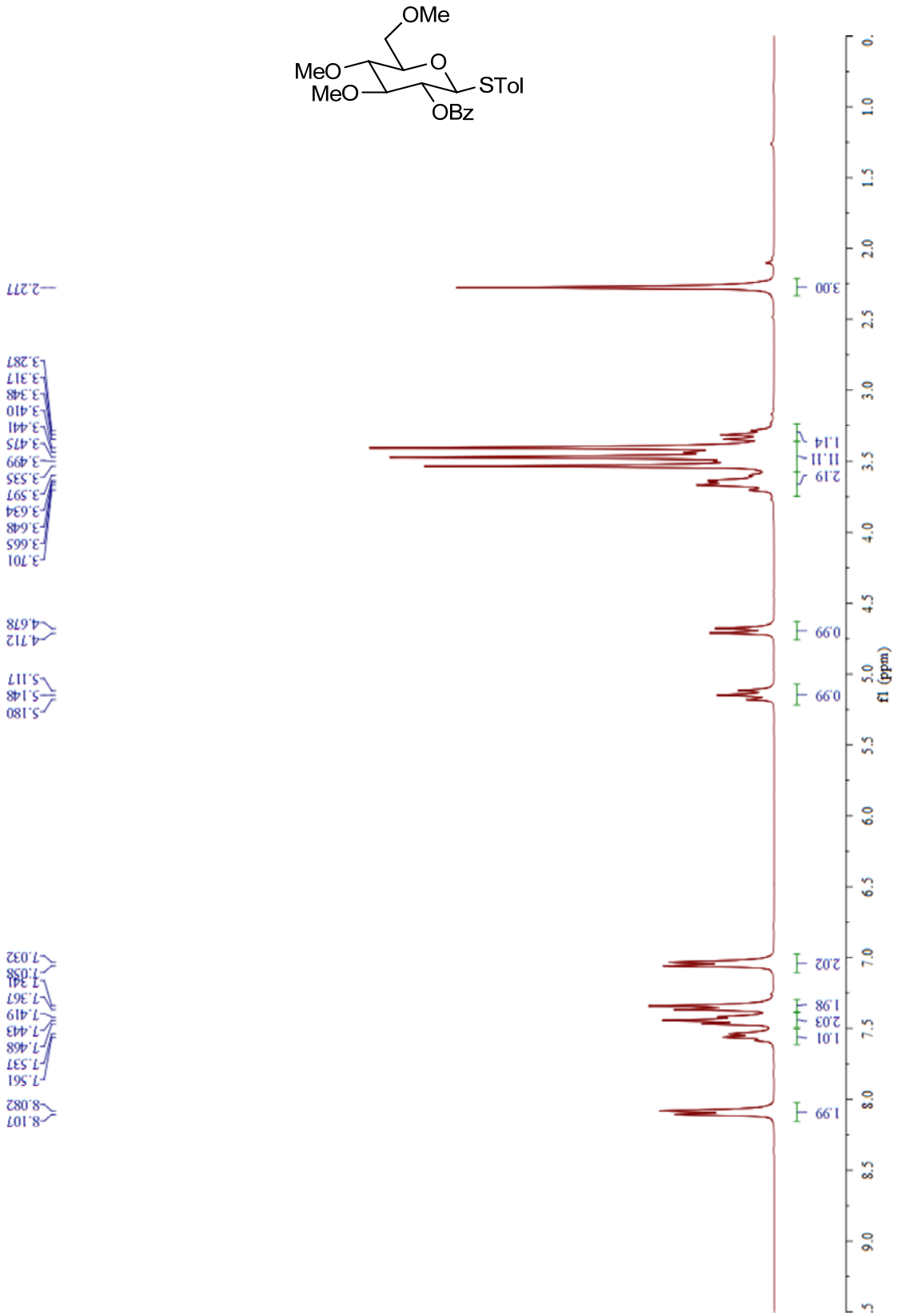
$^{1}$H spectrum of methyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-glucopyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside **37**



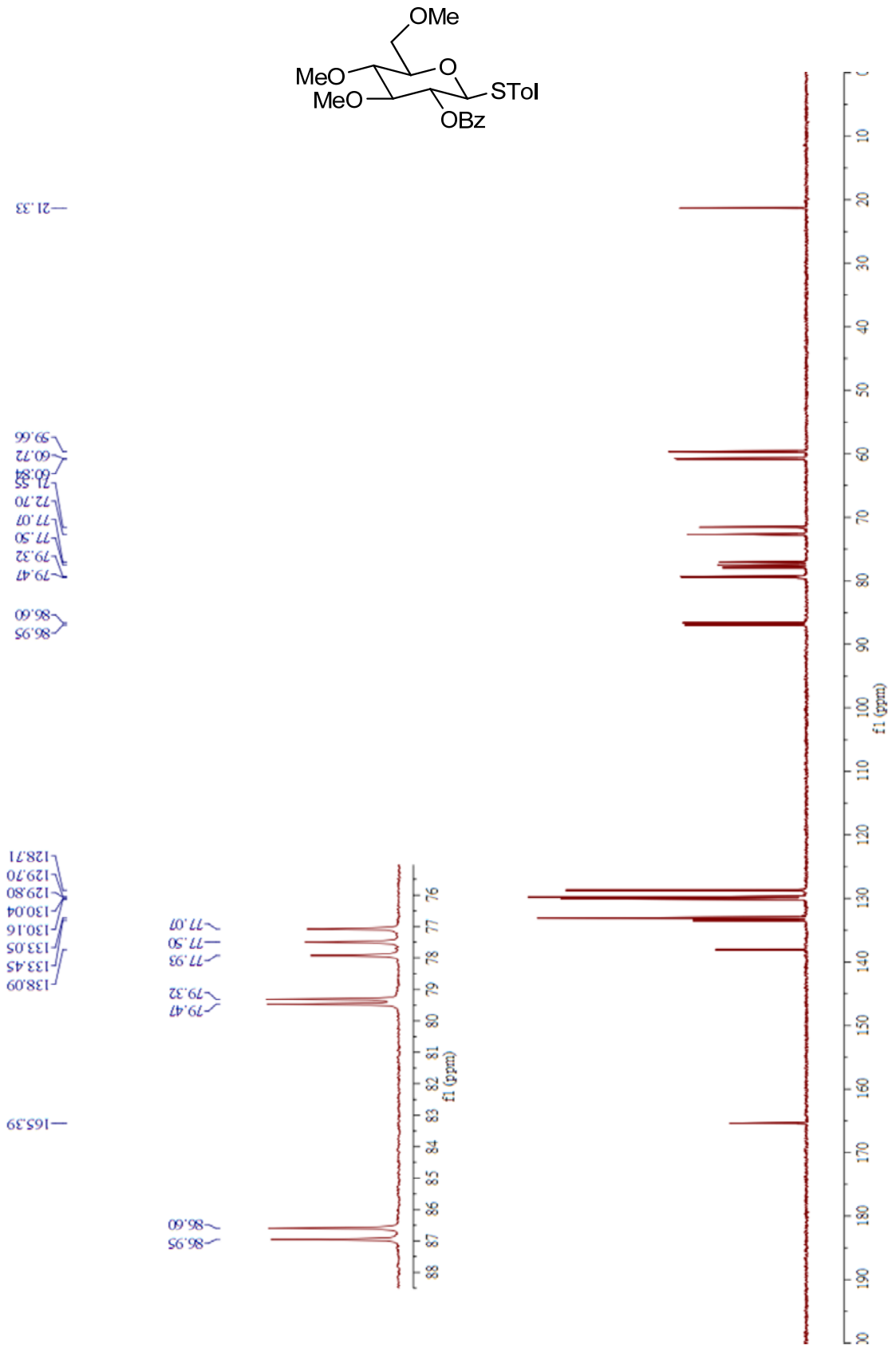
$^{13}$C spectrum of methyl 6-*O*-acetyl-2,3-di-*O*-benzoyl-4-*O*-benzyl-β-D-gluco pyranosyl-(1→6)-2,3-di-*O*-benzoyl-4-benzyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside **37**



$^{1}$H spectrum of *p*-tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-methyl-thio-β-D-glucopyranoside **38**

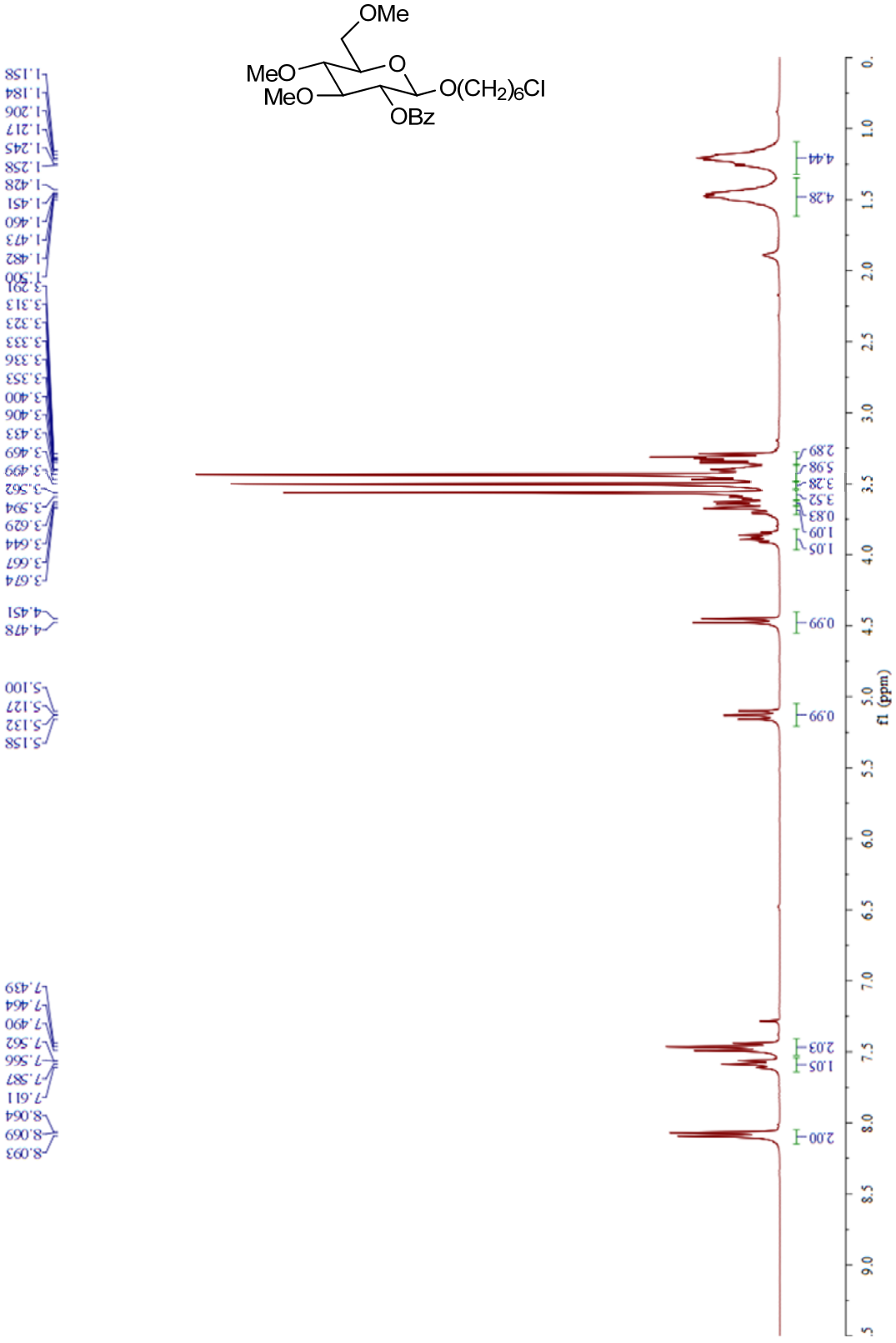


$^{13}$C spectrum of *p*-tolyl 2-*O*-benzoyl-3,4,6-tri-*O*-methyl-thio-β-D-glucopyranoside **38**



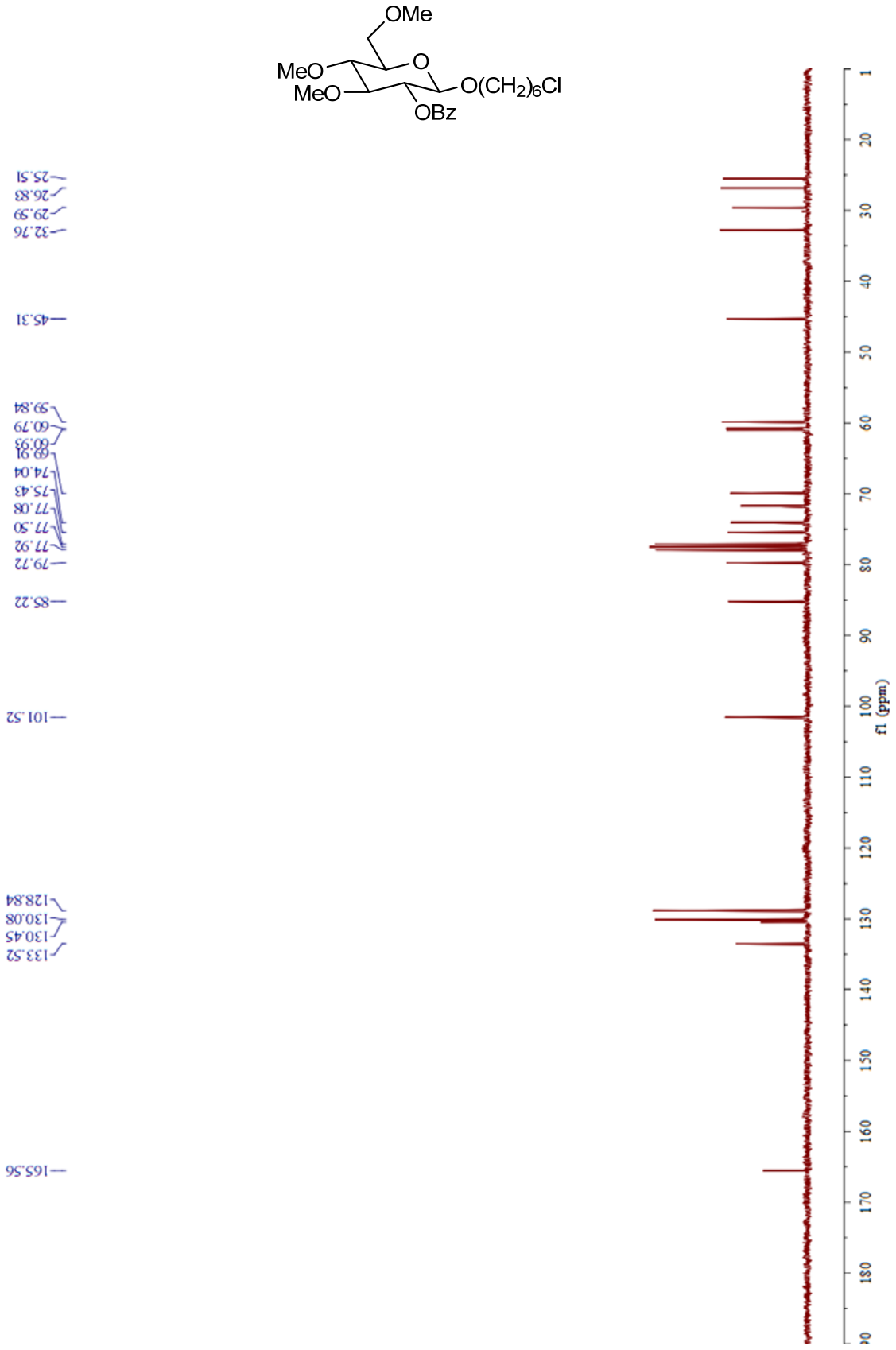
$^{1}$H spectrum of 6-chlorohexyl 2-*O*-benzoyl-3,4,6-tri-*O*-methyl-β-D-glucopyranoside

**42**

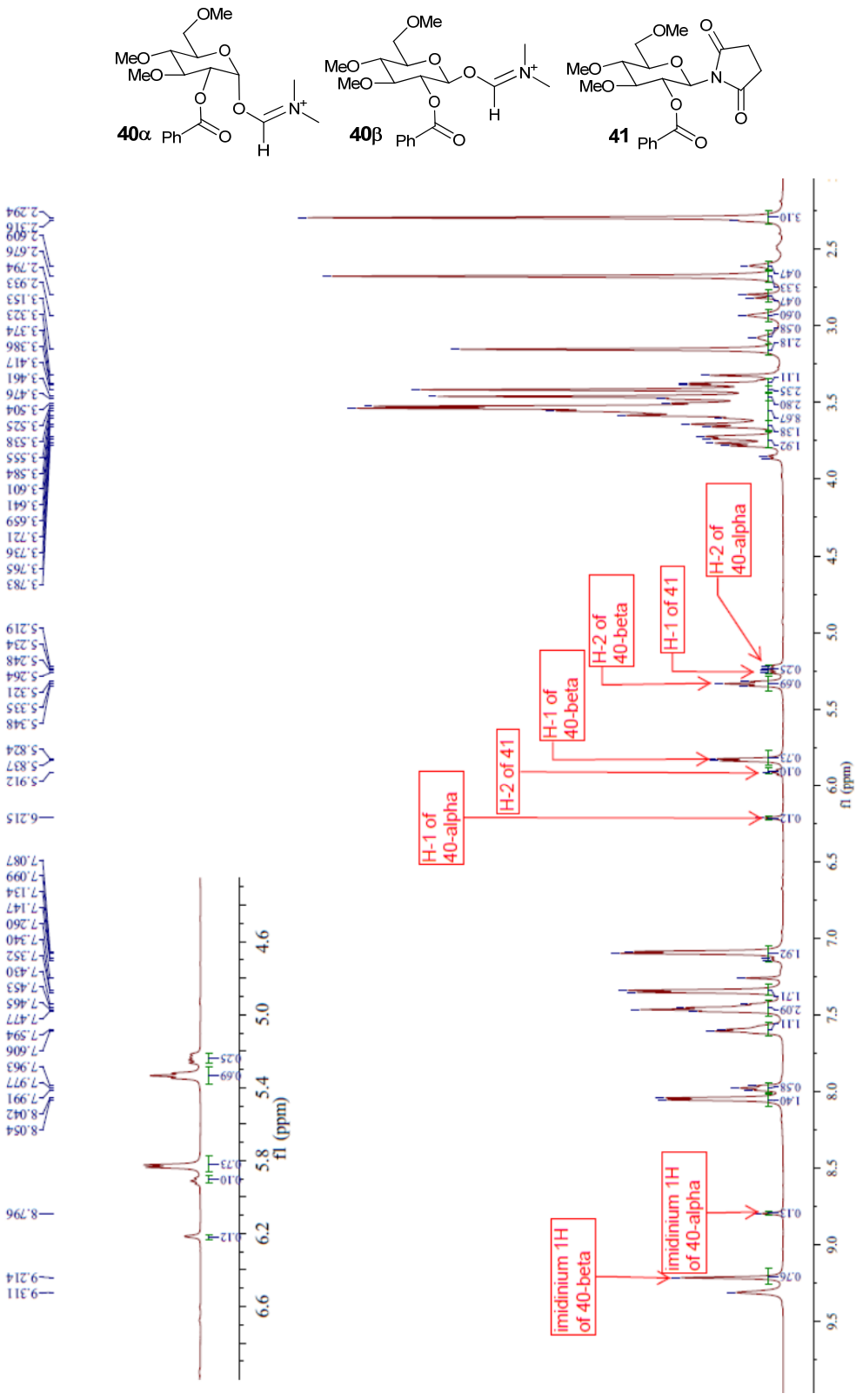


$^{13}$C spectrum of 6-chlorohexyl 2-*O*-benzoyl-3,4,6-tri-*O*-methyl-β-D-glucopyranoside

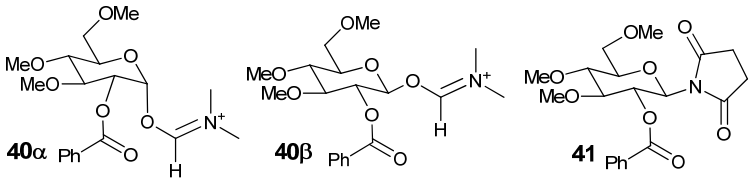
**42**

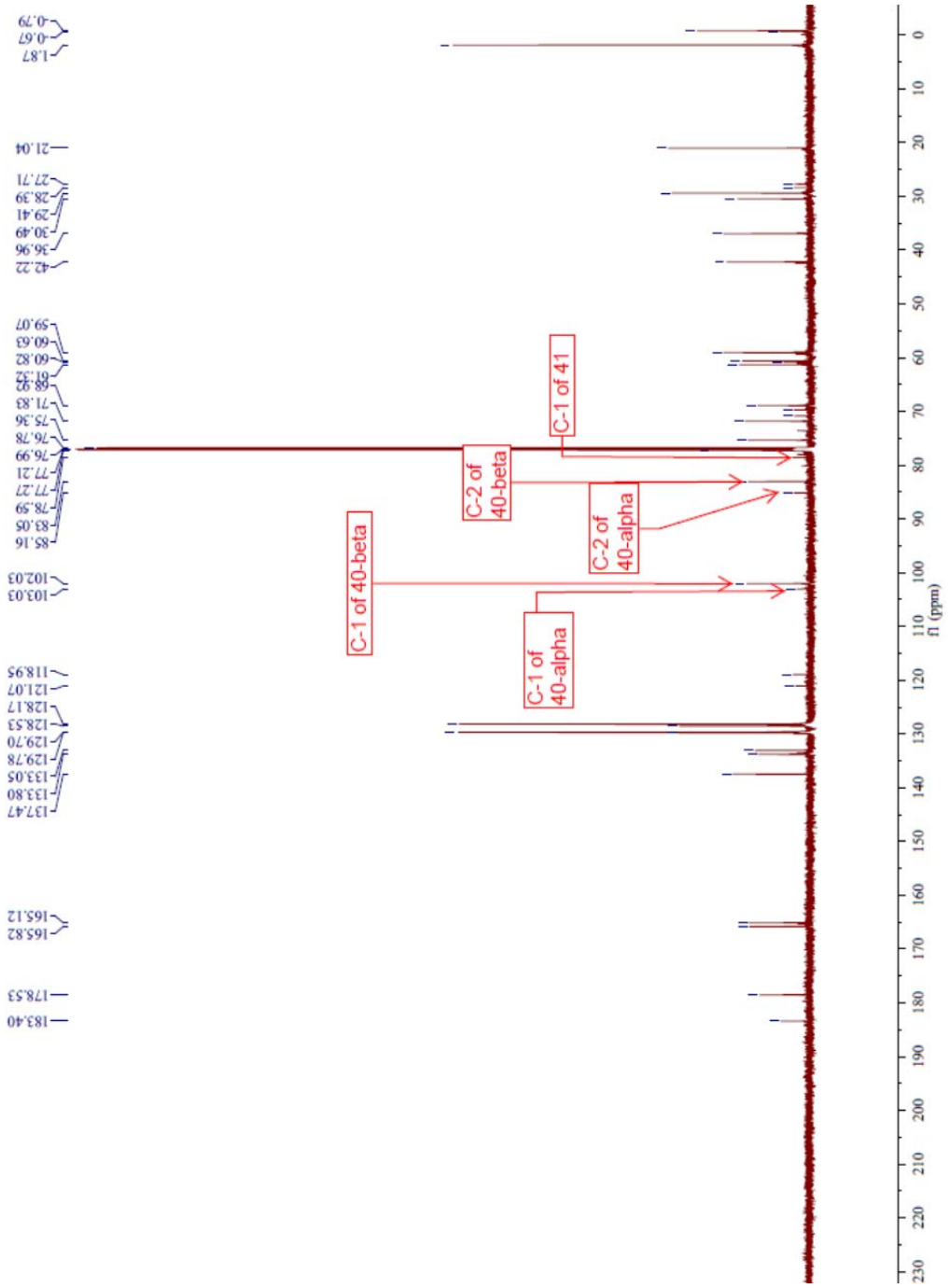


$^{1}$H NMR spectrum of crude pre-activation mixture of **38** (refer to Fig 2 and scheme 3 in main context)

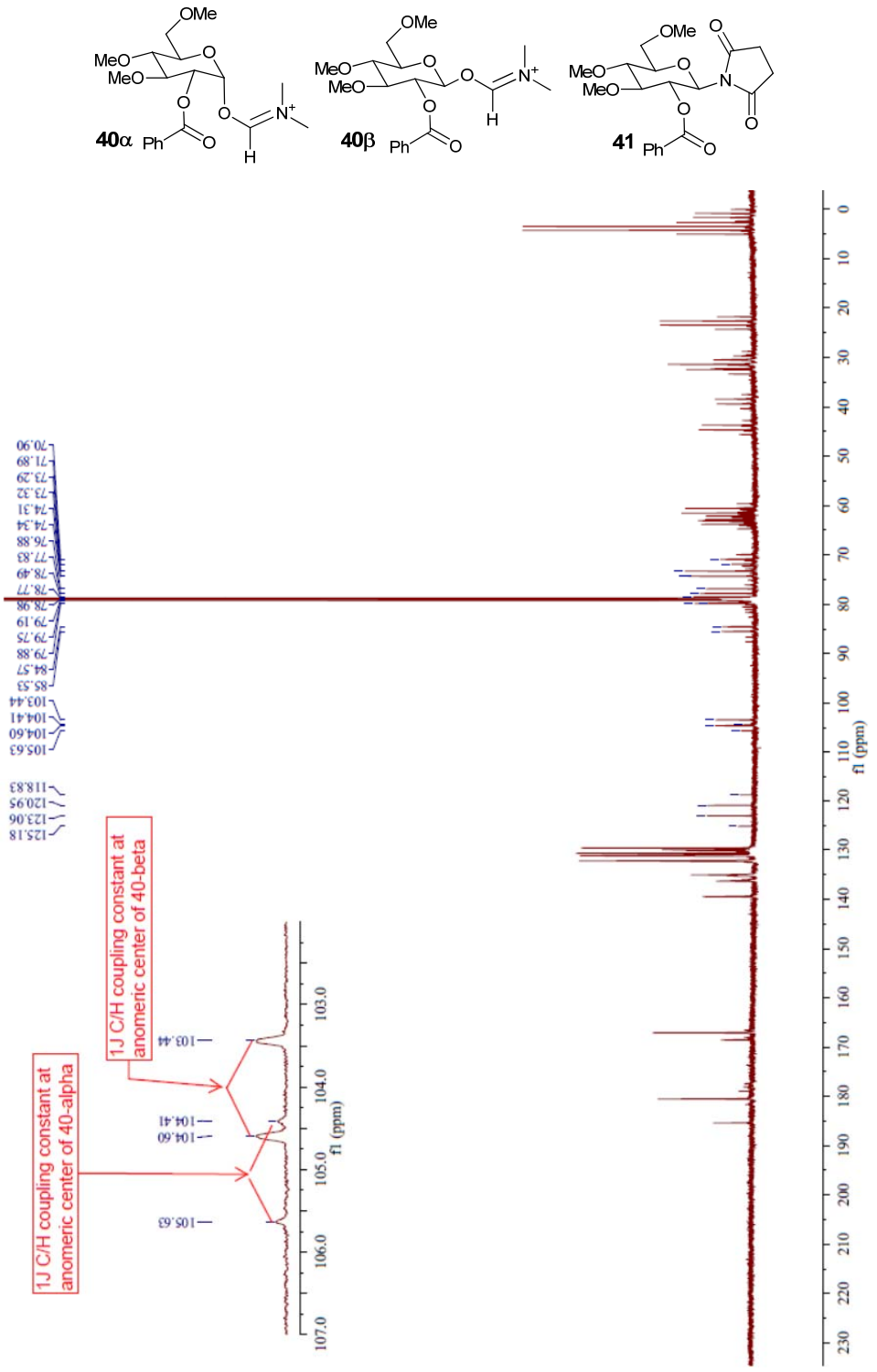


$^{13}$C NMR spectrum of crude pre-activation mixture of **38** (refer to Fig 2 and scheme 3 in main context)

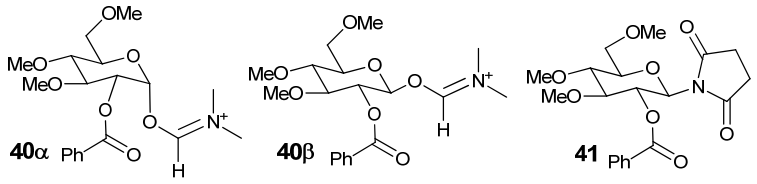


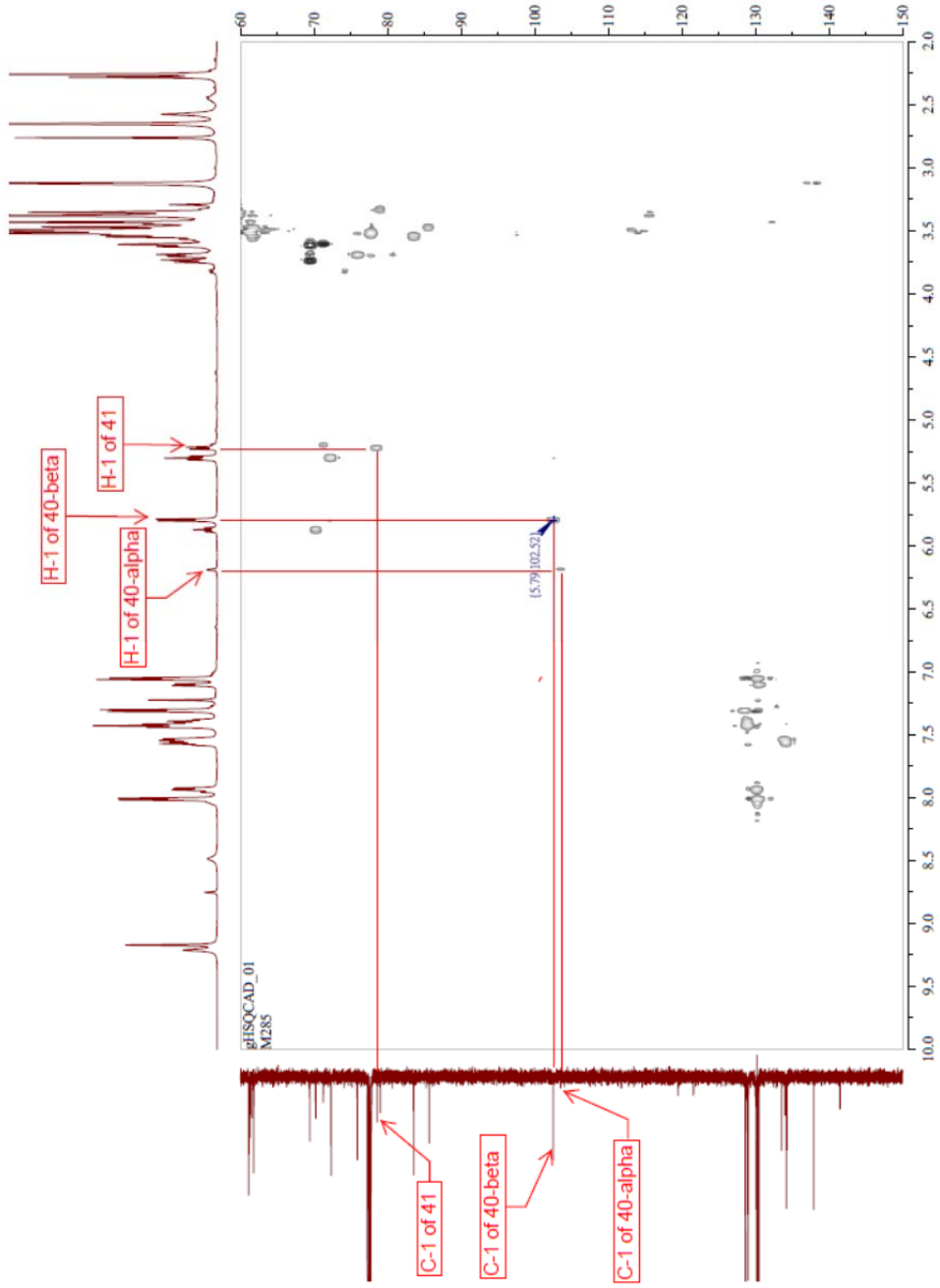



$^{13}$C non-decoupling NMR spectrum of crude pre-activation mixture of **38** (refer to Fig 2 and scheme 3 in main context)

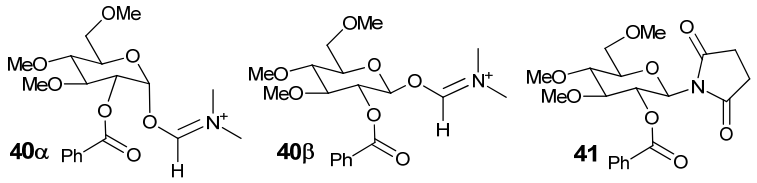


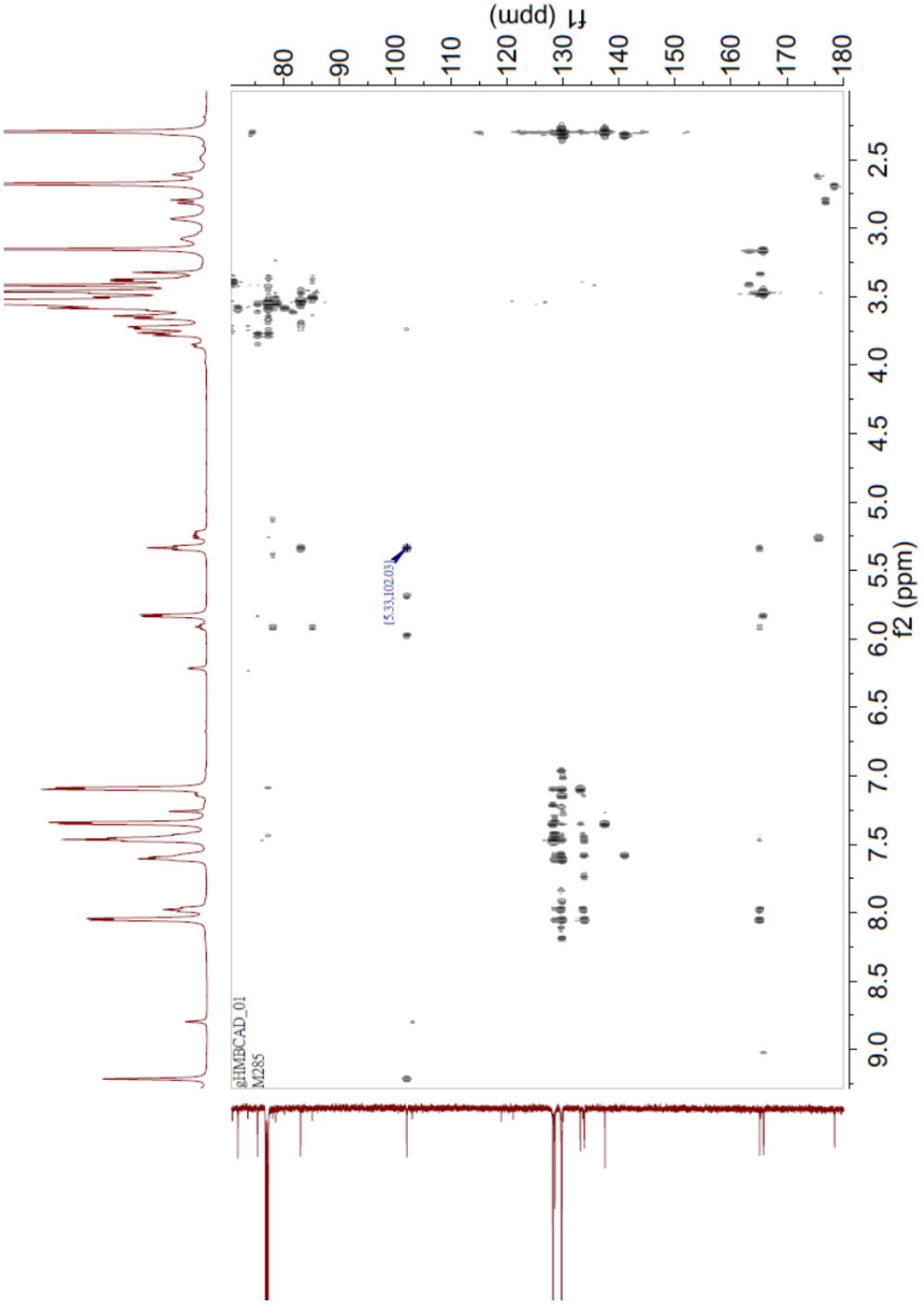
HSQC spectrum of crude pre-activation mixture of **38** (refer to Fig 2 and scheme 3 in main context)



HMBC spectrum of crude pre-activation mixture of **38** (see Fig S1 in following page for selected expansion)



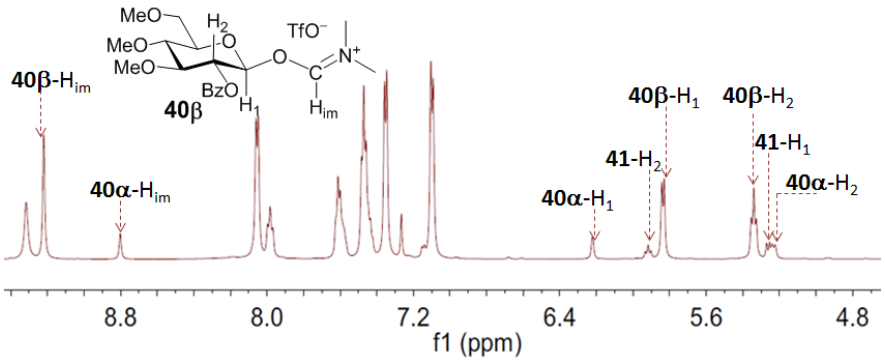



**Figure S2.** Selected 1H NMR spectrum of pre-activation mixture of **38**

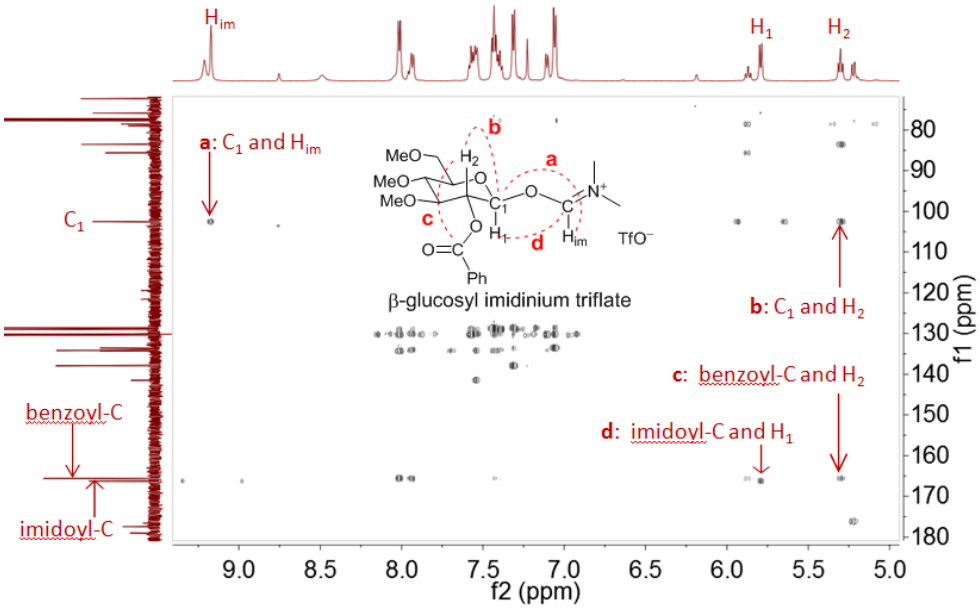



**Figure S3.** HMBC spectrum of β-glucosyl imidinium triflate **40β** in reaction mixture

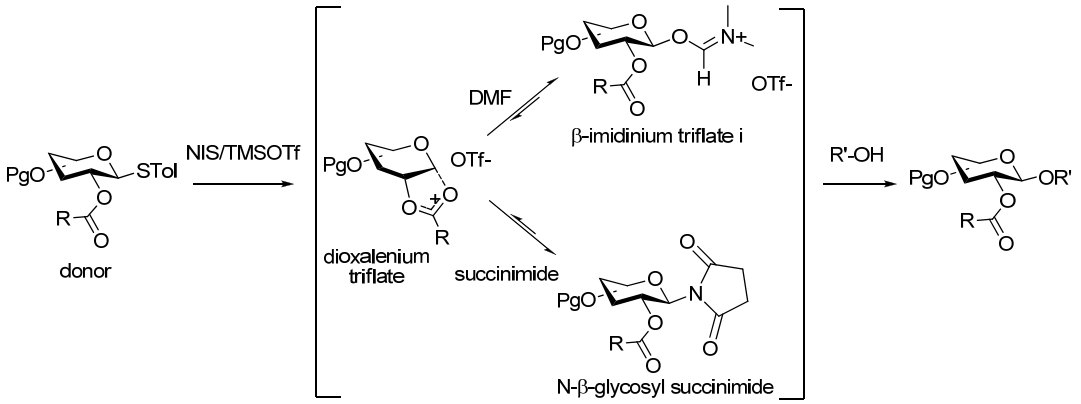



**Figure S4.** Proposed mechanism for modulated glycosylations

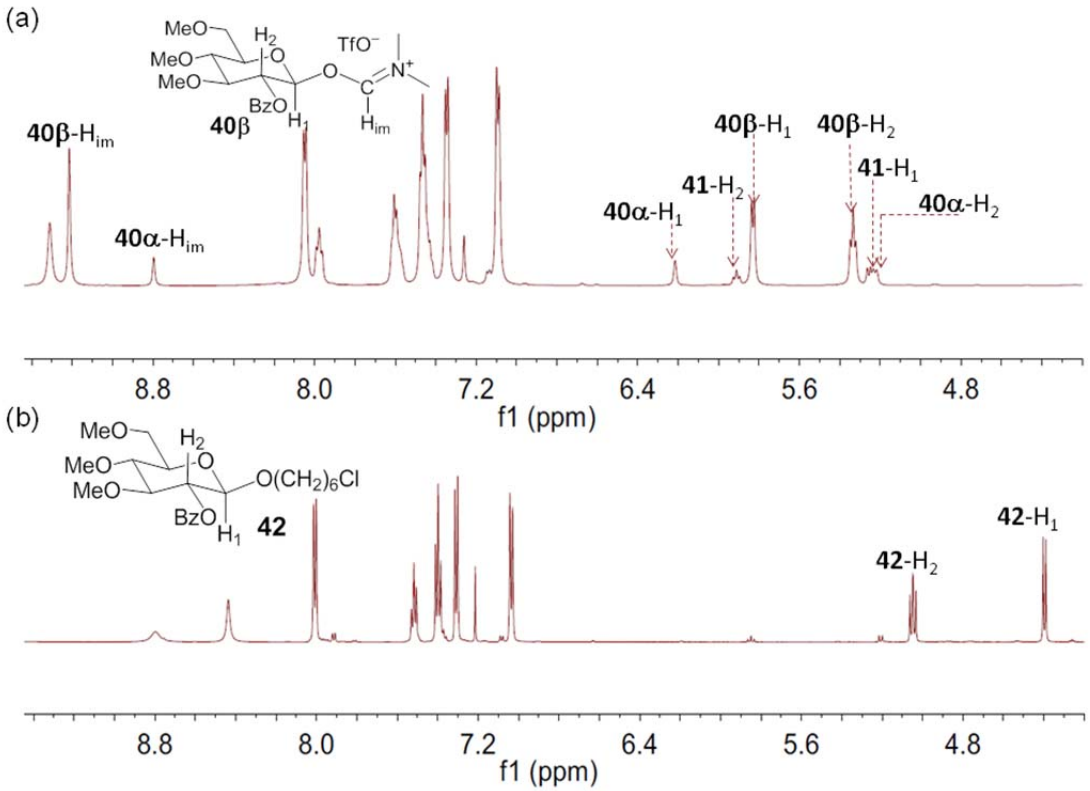
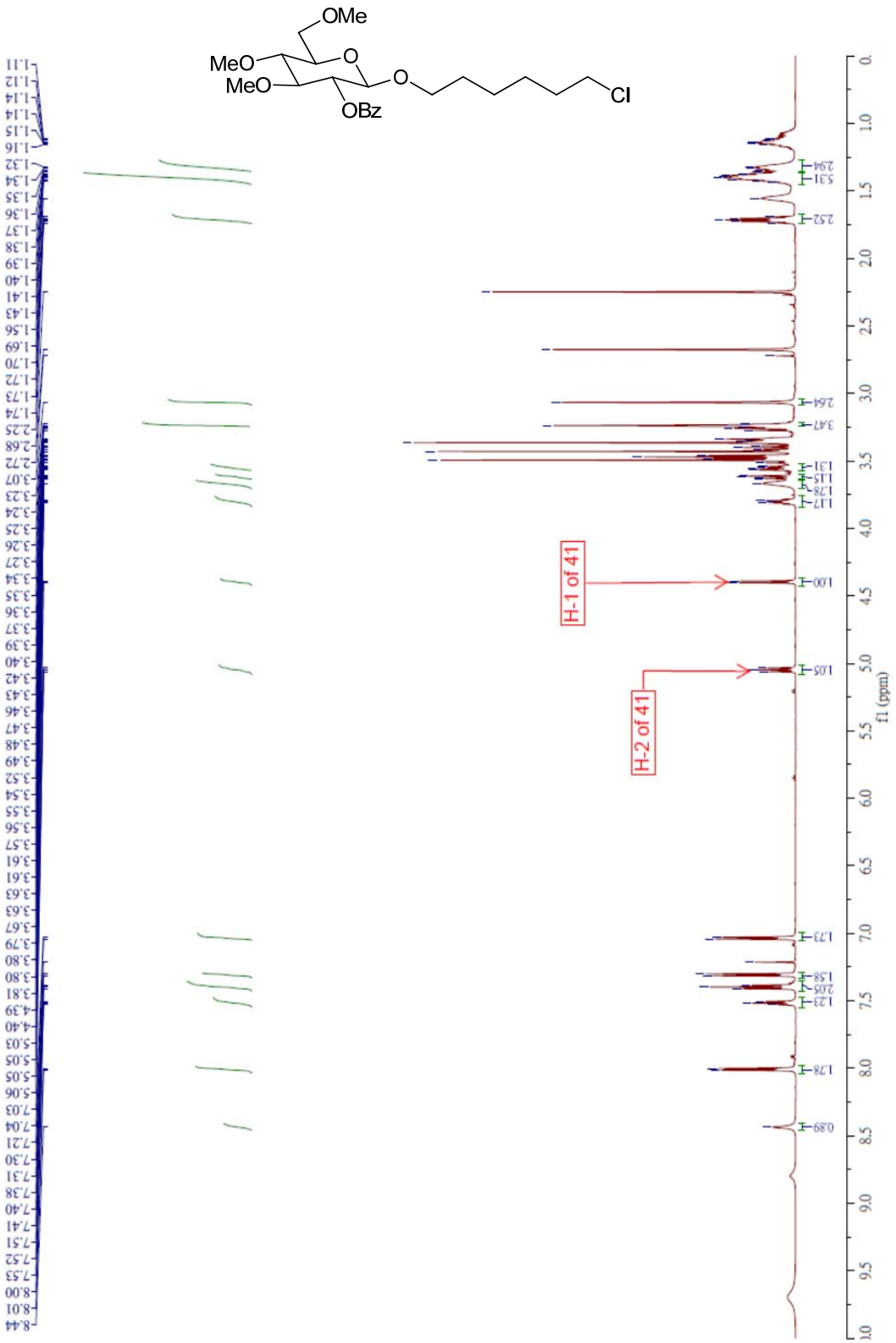



**Figure S5.** (a) Selected $^{1}$H NMR spectrum of pre-activation of **38**. (b) Selected $^{1}$H NMR spectrum of the crude reaction after adding acceptor **39**.

Crude $^{1}H$ spectrum of the reaction mixture after addition of **39** (formation of **42**)



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