Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Sub-Stoichiometric Reductive Etherification of Carbohydrate Substrates and One-Pot Protecting Group Manipulation

Chiao Wen Chen, Ching Chi Wang, Xin Ru Li, Henryk Witek, and Kwok-Kong Tony Mong*[a]

Supporting Information

1. General Experimental

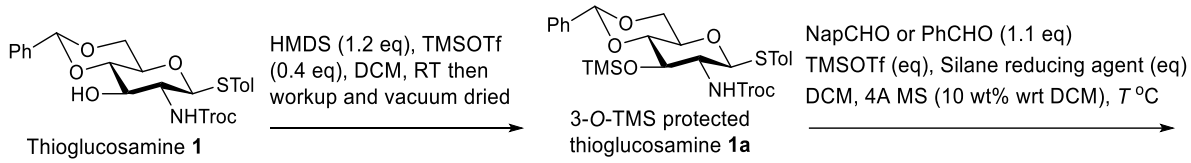
Reagent-grade chemicals were purchased from commercial vendors and used without further purification. Dichloromethane (DCM) and tetrahydrofuran (THF) were dried by Asianwong solvent purification system (AWS-1000). Aluminum plates (60 F-254) coated with silica gel were used for thin layer chromatography (TLC). Et_3SiH, Me_2PhSiH, and PMHS (average Mn 1900) were purchased from Alfa Aesar and were used as received without further purification. Compounds were visualized under ultraviolet (UV) light and by staining with cerium molybdate, *p*-anisaldehyde or ninhydrin solution. Silica gel (Ged6, uran Si-60, 0.063-0.200 mm) for column chromatography was obtained from Merck. ^1H and ^{13}C NMR spectra were recorded on Varian UI (400, 100 MHz) or Varian UI (600, 150 MHz) spectrometers in $CDCl_3$ or at ambient temperature. The proton chemical shifts (in ppm) of reported were calibrated against the proton signal of TMS standard and the carbon chemical shift was calibrated against the ^{13}C signals of deuterated chloroform ($CDCl_3$, 77.16 ppm).

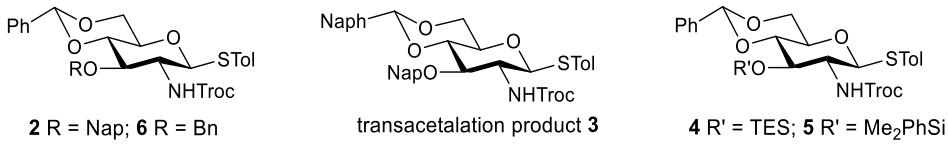
p-Tolyl 4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-*β*-D-glucopyranoside **1**, [1] (2*R*)-1-en-2-hydroxyl-3-*O*-tosyl-*sn*-glycerol **10c**,[2] *p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside **10d**,[3] *p*-Tolyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside **10f**,[4] *p*-Tolyl 4-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside **10g**,[5] *p*-Tolyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside **10h**,[3] *p*-Tolyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside **12h₂**,[6] *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galacto-pyranside **10i**,[7] *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galacto-pyranside **12i**,[7] *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranside **10j**,[12] *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside **12j**,[9] *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranside **10k**,[12] *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside **12k₁**,[11] *p*-tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-

galactopyranside **12k3**,[10] and *p*-tolyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside **24**[13] are known compounds and relevant spectroscopic data have been reported.

2. Experimental Section

2.1 Experimental procedure for Table 1





To a solution of thioglucosamine **1** (203 mg, 0.369 mmol) in dried DCM (12 mL, 0.03 M), hexamethyldisilazane (HMDS) (0.1 mL, 0.44 mmol) and TMSOTf (27 μL, 0.15 mmol) were added. The reaction was stirred at RT under N_2 for 0.5 h. After complete consumption of the starting material, the mixture was diluted with DCM, washed with $NH_4Cl_{(aq)}$ twice and brine. The organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to obtain crude residue 3-*O*-TMS protected thioglucosamine **1a**, which was dried under high *vacuum* for 1 h then taken to etherification.

To a solution of **1a** in DCM (4 mL, 0.1 M), PhCHO or NapCHO (refer Table S1), silane reducing agent (refer Table S1), and activated 4 Å molecular sieves (100 mg/ 1 mL DCM) were added and stirred at RT for 1 h. After then, the mixture was cooled at a specific temperature for 0.5 h (refer Table S1), which was followed by addition of TMSOTf (refer Table S1). When the 3-*O*-TMS protected thioglucosamine (and its corresponding desilylation product i.e. **1**) has been consumed completely as monitored by TLC, the reaction was diluted with DCM and quenched with Et_3N. Then, the mixture was wash with 1 N $HCl_{(aq)}$ and brine. The organic phase was dried

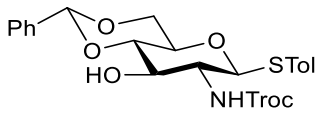
over $MgSO_4$, filtered, and concentrated for column chromatography (Gradient elution: EtOAc/DCM/hexanes = 1/1/20 to 1/1/3) to obtain alkylation product **2** or **6**. Of noted, transacetalation product **3** arising from the use of NapCHO was inseparable from **2**, but was detected by mass spectrometry.

Table S1: Detailed experimental conditions for reductive etherification of TMS protected *N*-Troc-thioglucosamine **1a**

Entry	Aldehyde (mg/μL, mmol)	Silane reagent (mL/μL, mmol)	TMSOTf (μL, mmol)	*T* (°C), Time (h)	Etherification product **2** or **6** (amount, %)[a]	Transilylation product **4** or **5** (amount, %)
1	NapCHO (63 mg, 0.41 mmol)	Et_3SiH (71 μL, 0.44 mmol)	0.1	−30, 2	**2** (141 mg, 56%)	**4** (51 mg, 21%)
2	NapCHO (63 mg, 0.41 mmol)	Et_3SiH (71 μL, 0.44 mmol)	0.1	−78, 2	**2** (155 mg, 61%)	**4** (43 mg, 18%)
3	NapCHO (63 mg, 0.41 mmol)	Et_3SiH (71 μL, 0.44 mmol)	0.2	−78, 2	**2** (183 mg, 80%)	**4** (12 mg, 5%)
4	NapCHO (63 mg, 0.41 mmol)	PMHS (0.7 mL, 0.346 mmol)	0.2	−78, 2	**2** (208 mg, 82%)	Not detected
5	NapCHO (63 mg, 0.41 mmol)	Me_2PhSiH (68 μL, 0.44 mmol)	0.2	−60, 4	**2** (101 mg, 40%)	**5** (50 mg, 20%)[b]
6	NapCHO (63 mg, 0.41 mmol)	PMHS (0.35 mL, 0.184 mmol)	0.2	−60, 2	**2** (210 mg, 83%)	Not detected
7	NapCHO (63 mg, 0.41 mmol)	PMHS (0.17 mL, 0.092 mmol)	0.4	−60, 4	**2** (205 mg, 81%)	Not detected
8	NapCHO (63 mg, 0.41 mmol)	PMHS (0.17 mL, 0.092 mmol)	0.2	−30, 2	**2** (165 mg, 65%)	Not detected
9	PhCHO (42 μL, 0.41 mmol)	PMHS (0.17 mL, 0.092 mmol)	0.2	−30, 2	**6** (195 mg, 83%)	Not detected
10	PhCHO (42 μL, 0.41 mmol)	PMHS (0.1 mL, 0.055 mmol)	0.2	0, 2	**6** (153 mg, 65%)	Not detected

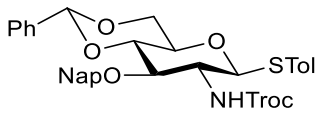
[a] Estimation of the reaction yields of etherification product **2** and transacetalation product **3** was based on isolation adjusted by the percent ratio of **2**:**3** derived from the ^{1}H NMR spectrum**.** [b] Me_2Ph-silyl protected *N*-Troc-thioglucosamine **5** was estimated by isolation of **1a** and **5** adjusted by their percent ration in ^{1}H NMR spectrum.

***p*-Tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-*β*-D-glucopyranoside (1):** [1]



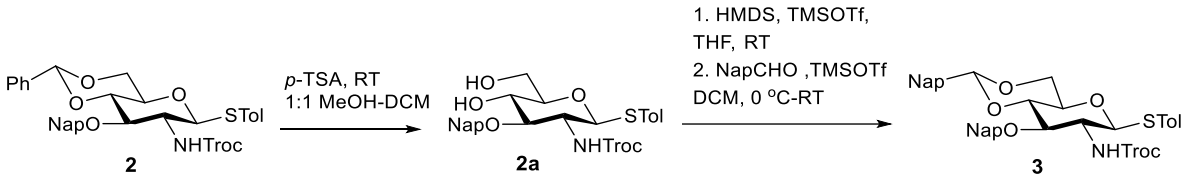
$[\alpha]_D^{22}$ = –13.6 (*c* = 0.146, $CHCl_3$); R*f* = 0.30 (hexanes/EtOAc, 3:1); **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 7.48-7.46 (m, 2H), 7.41-7.35 (m, 5H), 7.15-7.13 (m, 2H), 5.53 (s, 1H), 5.27 (d, *J* = 6.4 Hz, 1H), 4.89 (d, *J* = 10.4 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.39-4.35 (m, 1H), 4.06 (t, *J* = 9.6, 6.4 Hz, 1H), 3.79 (t, *J* = 10.4, 9.6 Hz, 1H), 3.50 (m, 2H), 3.41 (q, *J* = 18.4, 9.6 Hz, 1H), 2.94 (s, 1H), 2.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 154.3, 138.8, 136.8, 133.5, 129.9, 129.4, 128.4, 126.3, 101.9, 86.7, 81.2, 77.2, 74.7, 72.3, 70.3, 68.5, 57.1, 21.2; **HRMS (ESI):** calcd. for $C_{23}H_{25}Cl_3NO_6S$ $[M+H]^+$ 548.0465, found *m/z* 548.0463.

***p*-Tolyl 4,6-*O*-Benzylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-*β*-D-glucopyranoside (2):**



Compound **2** was synthesized from thioglucosamine **1** following the general procedure and the detailed experimental conditions were given in entries 4 or 6 of Table S1. $[\alpha]_D^{19}$ = +8.2 (*c* = 1.22, $CHCl_3$); R*f* = 0.40 (hexanes/EtOAc, 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81-7.71 (m, 4H), 7.51-7.35 (m, 10H), 7.10-7.08 (m, 2H), 5.59 (s, 1H), 5.128 (d, *J* = 6.8 Hz, 1H), 5.03-4.96 (m, 2H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.37 (dd, *J* = 10.4, 5.2 Hz, 1H), 4.04 (t, *J* = 9.2 Hz, 1H), 3.79 (t, *J* = 10.4 Hz, 1H), 3.69 (t, *J* = 9.2 Hz, 1H), 3.50 (m, 1H), 3.36 (d, *J* = 9.2 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.7, 138.6, 137.2, 135.2, 133.5, 133.1, 133.0, 129.8, 129.1, 128.31, 128.25, 128.0, 127.6, 127.4, 126.4, 126.13, 126.05, 126.02, 101.3, 86.6, 82.4, 77.4, 77.2 74.8, 74.3, 70.3, 68.6, 56.6, 21.1; **HRMS (ESI):** calcd. for $C_{34}H_{33}Cl_3NO_6S$ $[M+H]^+$ 688.1031, found *m/z* 688.1089.

2.1.1 Preparation of *p*-tolyl 4,6-*O*-naphthylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (3):

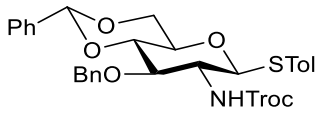


Compound **2** (209 mg, 0.34 mmol) was dissolved in 1:1 MeOH/DCM mixture (30 mL), and to which tosylic acid (p-TSA) (50 mg, 0.26 mmol) was added. The reaction mixture was stirred at RT for 15 h. When compound **2** was completely consumed as monitored by TLC, the reaction was quenched with Et_3N, and the reaction mixture was concentrated for column chromatography (Elution: EtOAc/hexanes = 1/1 gradient to 2/1) to obtain crude product **2a** (116 mg, 0.19 mmol, 57 %).

To a solution of **2a** (116mg, 0.19 mmol) in dried THF (2 mL), HMDS (0.1 mL, 0.475 mmol, 2.5 equiv.) and TMSOTf (31 μL, 0.17 mmol, 0.9 equiv.) was added. The reaction was stirred under N_2 at RT for 0.5 h. After complete consumption of the starting material, the mixture was diluted with EtOAc, then washed with $NH_4Cl_{(aq)}$ (× 2) and brine. The organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to obtain crude di-*O*-TMS protected **2a**, which was dried under high *vacuum* for an hour. To a solution of **2a** in dried DCM (7 mL), NapCHO (33 mg, 0.2 mmol, 1.1 equiv.) and TMSOTf (4 μL, 0.02 mmol, 0.1 equiv.) was added and the mixture was stirred at RT for 1.5 h. After complete consumption of **2a**, the reaction was quenched with Et_3N, and concentrated for column chromatography (Elution: EtOAc/DCM/hexanes = 1/1/20 gradient to 1/1/3) to obtain product **3** (65 mg, 0.09 mmol, 46 %). Analytical data for **3**: $[\alpha]_D^{19}$ = +16.6 (*c* = 0.12, $CHCl_3$); R*f* = 0.4 (hexanes/EtOAc, 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.99 (s, 1H), 7.89-7.85 (m, 3H), 7.80-7.76 (m, 2H), 7.73-7.76 (m, 2H), 7.61 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.52-7.49 (m, 2H), 7.45-7.42 (m, 3H), 7.39 (s, 1H),

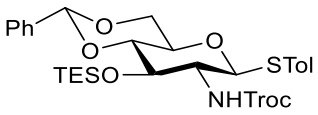
7.37 (s, 1H), 7.12 (s, 1H), 7.10 (s, 1H), 5.75 (s, 1H, 2-naphthylidene-*H*), 5.11 (d, *J* = 9.2 Hz, 1H), 5.05-5.02 (m, 2H), 4.86 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.43 (dd, *J* = 10.4, 5.2 Hz, 1H), 4.09 (t, *J* = 10.0 Hz, 1H), 3.86 (t, *J* = 10.4 Hz, 1H), 3.76 (t, *J* = 9.2 Hz, 1H), 3.57-3.53 (m, 1H), 3.42-3.37 (m, 1H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.7, 138.6, 135.2, 134.6, 133.6, 133.5, 133.1, 133.0, 132.9, 129.8, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.4, 126.5, 126.3, 126.2, 126.1, 126.0, 125.6, 101.5, 86.7, 82.4, 77.5, 77.2, 74.8, 74.3, 70.4, 68.7, 56.6, 21.1; **HRMS (ESI):** calcd for $C_{38}H_{34}Cl_3NNaO_6S$ $[M+Na]^+$ 760.1068, found *m/z* 760.1065.

***p*-Tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6):**



Compound **6** was synthesized from thioglucosamine **1** following the general procedure and the detailed experimental conditions were given in entry 9 of Table S1. $[\alpha]_D^{21}$ = +3.2 (*c* = 0.62, $CHCl_3$); R*f* = 0.40 (hexanes/EtOAc, 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** *δ* 7.49-7.47 (m, 2H), 7.38-7.36 (m, 6H), 7.29-7.24 (m, 4H), 7.11-7.09 (m, 2H), 5.56 (s, 1H, benzylidene-*H*), 4.97 (d, *J* = 10.4 Hz, 1H), 4.87 (d, *J* = 11.6 Hz, 1H), 4.74 (s, 2H), 4.71 (s, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.37 (dd, *J* = 10.8, 5.2 Hz, 1H), 4.39 (t, *J* = 8.8 Hz, 1H), 3.78 (t, *J* = 10 Hz, 1H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.50 (m, 1H), 3.35 (m, 1H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** *δ* 153.8, 138.6, 137.8, 137.2, 133.5, 129.8, 129.1, 128.42, 128.35, 128.30, 128.0, 127.9, 126.0, 101.2, 86.6, 82.3, 77.8, 74.7, 74.5, 70.3, 68.6, 56.5, 21.2; **HRMS (ESI):** calcd for $C_{30}H_{31}Cl_3NO_6S$ $[M+H]^+$ 638.0939, found *m/z* 638.0932.

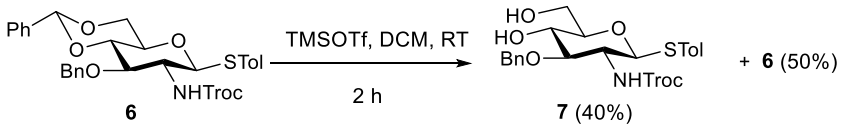
***p*-Tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-3-*O*-triethylsilyl-1-thio-β-D-glucopyranoside (4):**



$[\alpha]_D^{19}$ = –1.0 (*c* = 1.9, $CHCl_3$); R_f = 0.6 (hexanes/EtOAc, 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45-7.35 (m, 7H), 7.12 (d, *J* = 7.6 Hz, 2H), 5.48 (s, 1H, benzylidene-*H*), 5.19 (d, *J* = 8.4 Hz, 1H), 5.02 (d, *J* = 10.4 Hz, 1H), 4.73 (q, *J* = 21.6, 11.6 Hz, 2H), 4.34 (dd, *J* = 10., 4.8 Hz, 1H), 4.06 (t, *J* = 9.2, 8.4 Hz, 1H), 3.78-3.69 (m, 2H), 3.52-3.41 (m, 2H), 3.37-3.30 (m, 1H), 2.34 (s, 3H), 0.83 (t, *J* = 8.0, 7.6 Hz, 9H), 0.60-0.47 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.7, 138.4, 137.1, 133.2, 129.8, 129.1, 128.5, 128.1, 126.2, 101.9, 95.2, 86.8, 81.9, 77.2, 74.8, 72.9, 70.4, 68.6, 58.5, 21.2, 6.7, 4.9; **HRMS (ESI):** calcd for $C_{29}H_{39}Cl_3NO_6SSi$ $[M+H]^+$ 662.1326, found *m/z* 662.1327.

2.2 Products of Scheme 2

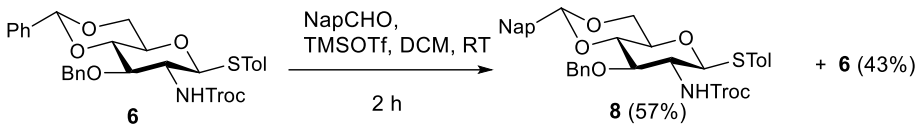
p-Tolyl 3-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (7):



To compound **6** (10 mg, 0.016 mmol) in dried DCM (1 mL), and TMSOTf (0.3 μL, 0.0016 mmol) were added at 0 °C. The reaction was stirred at RT for 2 h under N_2. Then, the mixture was diluted with DCM and quenched with Et_3N. The solution was concentrated under reduced pressure to obtain the crude residue for column chromatography purification (Elution: EtOAc/DCM/hexanes = 1/1/11 gradient to 1/1/6) to obtain deprotection product **7** (3.4 mg, 0.006 mmol, 40%. R*f* = 0.1 (hexanes/EtOAc, 1:1); $[\alpha]_D^{24}$ = –2.85 (*c* 0.7, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38-7.30 (m, 7H), 7.11 (m, 2H), 5.19 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 10.4 Hz, 1H), 4.83-4.67 (m, 4H), 3.88 (d, *J* = 11.2 Hz, 1H), 3.78 (m, 2H), 3.60 (t, *J* = 8.8 Hz, 1H), 3.37 (m, 2H), 2.42 (s, 1H), 2.33 (s, 3H), 2.05 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 153.8, 138.5,

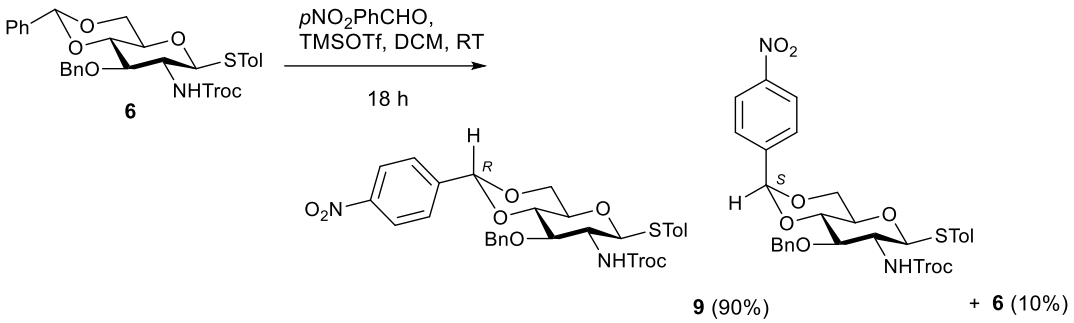
137.8, 133.1, 129.8, 128.7, 128.2, 128.0, 86.0, 82.1, 79.2, 74.8, 74.5, 71.2, 62.6, 56.4, 29.7, 21.1; **HRMS (ESI):** calcd for $C_{23}H_{27}Cl_3NO_6S$ $[M+H]^+$ 550.0619, found *m/z* 550.0615.

***p*-Tolyl 3-*O*-Benzyl-4,6-*O*--naphthylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (8):**



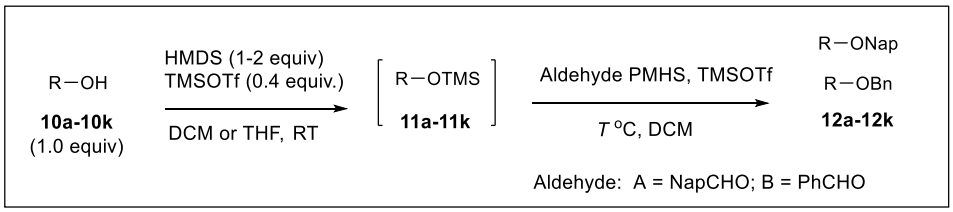
To a solution of compound **6** (36 mg, 0.056 mmol) in dried DCM (2 mL), NapCHO (120 mg, 0.062 mmol) and TMSOTf (1.0 μL, 0.006 mmol) were added at 0 ºC. The reaction was stirred at RT for 2 h under N_2. Then, the mixture was diluted with DCM and quenched with Et_3N. The solution was concentrated under reduced pressure to obtain the crude residue for column chromatography purification (Elution: EtOAc/DCM/hexanes = 1/1/11 gradient to 1/1/6) to obtain the mixture transacetalation product **8** and starting material **6** (28 mg, 0.042 mmol, 75%), which were inseparable by chromatography purification; ratio of **8** to **6** estimated by proton NMR = 1.3:1. Analytical data for compound **8**: R*f* = 0.4 (hexanes/EtOAc, 5:1); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (s, 1H), 7.85 (m, 3H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.48 (m, 2H), 7.38 (m, 4H), 7.29 (m, 3H), 7.11 (m, 2H), 5.73 (s, 1H), 5.15 (m, 1H), 5.01 (m, 1H), 4.89 (m, 1H), 4.75-4.65 (m, 3H), 4.42 (m, 1H), 4.00 (m, 1H), 3.75-3.66 (m, 2H), 3.52 (m, 1H), 3.36 (m, 1H), 2.34 (s, 1H); compound **8 HRMS (ESI):** calcd for $C_{34}H_{33}Cl_3NO_6S$ $[M+H]^+$ 688.1102, found *m/z* 688.1089.

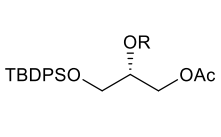
***p*-Tolyl 3-*O*-Benzyl-4,6-*O*-*p*-nitrophenylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (9):**



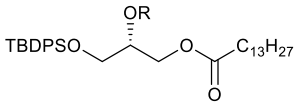
To a solution of compound **6** (49 mg, 0.076 mmol) in dried DCM (1 mL), *p*NO_2PhCHO (12 mg, 0.0836 mmol) and TMSOTf (1.0 μL, 0.008 mmol) were added at 0 ºC. The reaction was stirred at RT for 18 h under N_2. Then, the mixture was diluted with DCM and quenched with Et_3N. The solution was concentrated under reduced pressure to obtain the crude residue for column chromatography purification (Elution: EtOAc /DCM/hexanes = 1/1/11 gradient to 1/1/6) to obtain transacetalation product **9** as a pair of inseparable diasteroemers (50 mg, 0.068 mmol, 90%, ratio of *R*:*S*-diastereomer = 5.7:1). Analytical data for **9**: R*f* = 0.2 (hexanes/EtOAc, 5:1); **^{1}H NMR (600 MHz, $CDCl_3$) of *R*-diastereomer:** δ 8.26-8.23 (m, 2H), 7.63-7.62 (mm, 2H), 7.38-7.27 (m, 7H), 7.12-7.11 (m, 2H), 5.62 (s, 1H), 5.19 (m, 1H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 11.4 Hz, 1H), 4.74-4.73 (m, 2H), 4.67 (d, *J* = 11.4 Hz, 1H), 4.41 (dd, *J* = 10.8, 4.8 Hz, 1H), 4.06 (m, 1H), 3.80 (t, *J* = 10.8 Hz, 1H), 3.67 (t, *J* = 9.6 Hz, 1H), 3.56-3.52 (m, 1H), 3.34-3.32 (m, 1H), 2.34 (s, 3H); **HRMS (ESI):** calcd for $C_{30}H_{30}Cl_3N_2O_8S$ $[M+H]^+$ 683.0778, found *m/z* 683.0783.

2.3 Sequential HMDS silylation and PMHS reductive etherification in Table 2

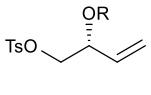




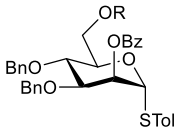
10a R = H;
11a R = TMS
12a R = Nap



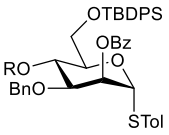
10b R = H;
11b R = TMS
12b R = Nap



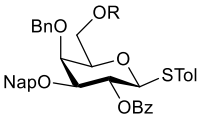
10c R = H;
11c R = TMS
12c$_1$ R = Bn **12c$_2$** R = Nap



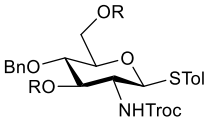
10d R = H;
11d R = TMS
12d R = Nap



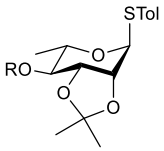
10e R = H;
11e R = TMS
12e R = Nap



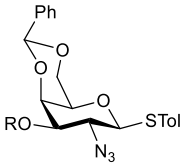
10f R = H;
11f R = TMS
12f R = Bn



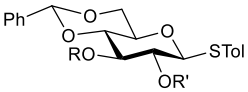
10g R = H
11g R = TMS
12g R = Bn



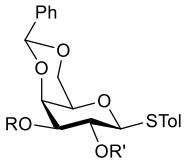
10h R = H
11h R = TMS
12h$_1$ R = Nap; **12h$_2$** R= Bn



10i R = H
11i R = TMS
12i R = Nap



10j R, R' = H
11j R, R' = TMS
12j R = Bn; R' = H



10k R = H
11k R = TMS
12k$_1$R = Bn; R' = H
12k$_2$ R = H; R' = Bn
12k$_3$ R, R' = Bn

Scheme S1: Silylation and reductive etherification procedure for hydroxyl protection.

To a solution of **10a–10f**, **10h**, and **10i** in dried DCM or **10g**, **10j**, and **10k** in dried THF, HMDS (1.2 equiv.) and TMSOTf (0.4 equiv.) was added. The reaction was stirred under N_2 at RT for 0.5 h. After complete consumption of the starting material, the mixture was diluted with DCM, washed with $NH_4Cl_{(aq)}$ (× 2) and brine. The organic layer was dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to obtain crude TMS protected substrate **11a–11k**. The substrate **11a-11k** was dried under high *vacuum* for an hour and then taken to PMHS reductive etherification.

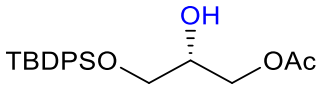
Table S2: Detailed experimental conditions for reductive etherification

Entry	**10a-10k**	Aldehyde	PMHS or Et_3SiH	TMSOTf	*T* (°C)	**12a-12k** (amount, %)
1	**10a** (180 mg, 0.48 mmol)	NapCHO (83 mg, 0.53 mmol)	PMHS (200 µL, 0.12 mmol)	TMSOTf (17 µL, 0.096 mmol)	-30	**12a** (204 mg, 83 %)
2	**10a** (1 g, 2.68 mmol)	NapCHO (452 mg, 2.9 mmol)	Et_3SiH (511 µL, 3.2 mmol)	TMSOTf (50 µL, 0.27 mmol)	-30	**12a** (850 mg, 62 %)
3	**10a** (93 mg, 0.249 mmol)	NapCHO (43 mg, 0.273 mmol)	Et_3SiH (48 µL, 0.298 mmol)	TMSOTf (9 µL, 0.0498 mmol)	-30	**12a** (101 mg, 77 %)
4	**10b** (130 mg, 0.33 mmol)	NapCHO (78 mg, 0.5 mmol)	PMHS (150 µL, 0.08 mmol)	TMSOTf (12 µL, 0.066 mmol)	-30	**12b** (74mg, 42 %)
5	**10c** (194 mg, 0.80 mmol)	PhCHO (90 µL, 0.88 mmol)	PMHS (378 µL, 0.2 mmol)	TMSOTf (14 µL, 0.08 mmol)	-30	**12c$_1$** (229mg, 86 %)
6	**10c** (160 mg, 0.66 mmol)	NapCHO (113 mg, 0.73 mmol)	PMHS (311 µL, 0.165 mmol)	TMSOTf (24 µL, 0.132 mmol)	-30	**12c$_2$** (197 mg, 78 %)
7	**10d** (212 mg, 0.37 mmol)	NapCHO (64 mg, 0.41 mmol)	PMHS (350 µL, 0.185 mmol)	TMSOTf (7 µL, 0.037 mmol)	-30	**12d** (205 mg, 78 %)
8	**10e** (246 mg, 0.34 mmol)	NapCHO (59 mg, 0.37 mmol)	PMHS (350 µL, 0.08 mmol)	TMSOTf (13 µL, 0.07 mmol)	-20	**12e** (213 mg, 73 %)
9	**10f** (2 g, 3.2 mmol)	PhCHO (359 µL, 3.5 mmol)	PMHS (1.5 mL, 0.8 mmol)	TMSOTf (58 µL, 0.32 mmol)	-30	**12f** (1.7 g, 75 %)
10	**10g** (200 mg, 0.36 mmol)	PhCHO (41 µL, 0.4 mmol)	PMHS (0.17 mL, 0.09 mmol)	TMSOTf (13 µL, 0.072 mmol)	-30	**12g** (184 mg, 70 %)
11	**10h** (200 mg, 0.64 mmol)	NapCHO (110 mg, 0.70 mmol)	PMHS (302 µL, 0.16 mmol)	TMSOTf (12 µL, 0.064 mmol)	-30	**12h$_1$** (175 mg, 72 %)
12	**10h** (88 mg, 0.28 mmol)	PhCHO (32 µL, 0.31 mmol)	PMHS (0.13 mL, 0.07 mmol)	TMSOTf (5 µL, 0.028 mmol)	-30	**12h$_2$** (100 mg, 88 %)
13	**10h** (96 mg, 0.309 mmol)	PhCHO (34 µL, 0.34 mmol)	Et_3SiH (59 µL, 0.371 mmol)	TMSOTf (11 µL, 0.062 mmol)	-30	**12h$_2$** (74 mg, 60 %)
14	**10i** (100 mg, 0.25 mmol)	NapCHO (42 mg, 0.275 mmol)	PMHS (240 µL, 0.125 mmol)	TMSOTf (9 µL, 0.05 mmol)	-70	No reaction
15	**10i** (100 mg, 0.25 mmol)	NapCHO (42 mg, 0.275 mmol)	PMHS (240 µL, 0.125 mmol)	TMSOTf (45 µL, 0.25 mmol)	-70	**12i** (115 mg, 85 %)
16	**10j** (198 mg, 0.53 mmol)	PhCHO (59 µL, 0.58 mmol)	PMHS (252 µL, 0.13 mmol)	TMSOTf (10 µL, 0.05 mmol)	-30	**12j** (172 mg, 70 %)
17	**10k** (200 mg, 0.53 mmol)	PhCHO (59 µL, 0.58 mmol)	PMHS (504 µL, 0.26 mmol)	TMSOTf (58 µL, 0.32 mmol)	-70	**12k$_1$-12k$_3$** (180 mg, 73 %)

To a solution of **11a–11k** in dried DCM (0.1 M), PhCHO or NapCHO (refer to Table S2), PMHS or Et_3SiH (refer to Table S2), and activated 4 Å molecular sieves (100 mg/ 1 mL DCM) were added and the mixture was stirred under N_2 at RT for 1 h. Then, the mixture was cooled at temperature specified in Table S2 for 0.5 h. Afterward, TMSOTf (refer to Table S2) was added into the reaction mixture. While the TMS protected substrate was consumed as indicated by TLC,

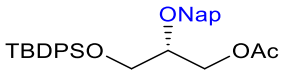
the reaction was diluted with DCM and quenched with Et_3N. The mixture was washed with 1 N $HCl_{(aq)}$ to remove the residual PMHS and its byproducts followed by brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated for column chromatography to obtain alkylation products **12a–12k**.

(2*R*)-1-Acetyl-3-*tert*-butyldiphenylsilyl *sn*-glycerol (10a):



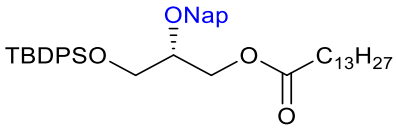
R_f = 0.26 (hexanes/EtOAc, 3:1); $[\alpha]_D^{23}$ = +5.9 (*c* 4.07, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.68–7.65 (m, 4H), 7.43 – 7.35 (m, 6H, A), 4.20 (dd, *J* = 11.4, 4.6 Hz, 1H), 4.14 (dd, *J* = 11.4, 6.0 Hz, 1H), 3.93 (Sextet, *J* = 5.3 Hz, 1H), 3.72 (dd, J = 10.2, 4.9 Hz, 1H), 3.68 (dd, J = 10.2, 5.4 Hz, 1H), 2.83 (d, *J* = 5.4 Hz, 1H), 2.01 (s, 3H), 1.07 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 171.1, 135.5, 132.9, 129.9, 127.8, 69.9 , 65.3, 64.4, 26.8, 20.8, 19.2; HRMS (ESI): calcd for $C_{21}H_{28}NaO_4Si^+$ $[M + Na]^+$ 395.1649, found *m/z* 395.1660.

(2*R*)-1-Acetyl-3-*tert*-butyldiphenylsilyl-2-(2-naphthylmethyl)-*sn*-glycerol (12a):



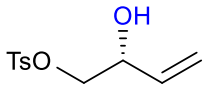
R_f = 0.32 (hexanes/EtOAc, 9:1); $[\alpha]_D^{20}$ = +9.8 (*c* = 4.08, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.83–7.78 (m, 3H), 7.73 (s, 1H), 7.68–7.64 (m, 4H), 7.48–7.45 (m, 2H), 7.44–7.39 (m, 3H), 7.36–7.32 (m, 4H), 4.76 (d, *J* = 12.2 Hz, 1H), 4.72 (d, *J* = 12.2 Hz, 1H), 4.38 (dd, *J* = 11.5, 3.5 Hz, 1H), 4.22 (dd, *J* = 11.6, 5.1 Hz, 1H), 3.81–3.74 (m, 3H), 2.01 (s, 3H), 1.05 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 171.0, 135.9, 135.7, 135.69, 133.39, 133.36, 133.31, 133.1, 129.9, 128.2, 128.0, 127.9, 127.8, 126.6, 126.2, 126.0, 125.9, 77.3, 72.28, 63.9, 63.2, 26.9, 21.0, 19.3; **HRMS (ESI):** calcd for $C_{32}H_{36}NaO_4Si^+$ $[M + Na]^+$ 535.2275, found *m/z* 535.2258.

(2*R*)-3-*tert*-Butyldiphenylsilyl-1-myristoyl-2-(2-naphthylmethyl)-*sn*-glycerol (12b):



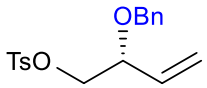
R_f = 0.38 (hexanes/EtOAc, 15:1); $[\alpha]_D^{20}$ = +6.1 (c = 1.3, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.83-7.77 (m, 3H), 7.72 (s, 1H), 7.67-7.63 (m, 4H), 7.49-7.45 (m, 2H), 7.44-7.39 (m, 3H), 7.36-7.32 (m, 4H), 4.76 (d, J = 12.3 Hz, 1H), 4.72 (d, J = 12.2 Hz, 1H), 4.39 (dd, J = 11.5, 3.4 Hz, 1H), 4.22 (dd, J = 11.5, 5.0 Hz, 1H), 3.80-3.74 (m, 3H), 2.26 (t, J = 7.6 Hz, 2H), 1.59-1.54 (m, 4H overlapped with the residual water signal of $CDCl_3$), 1.24 (bs, 20H), 1.05 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 173.9, 135.9, 135.8, 135.7, 133.4, 133.38, 133.35, 133.1, 129.9, 128.2, 128.0, 127.9, 127.8, 126.6, 126.2, 125.98, 125.9, 72.3, 63.6, 63.3, 34.4, 32.1, 29.84, 29.81, 29.78, 29.6, 29.5, 29.4, 29.3, 27.0, 25.1, 22.9, 19.4, 14.3; **HRMS (ESI):** calcd for $C_{44}H_{60}NaO_4Si^+$ $[M + Na]^+$ 703.4153, found *m/z* 703.4167.

(2*R*)-1-*en*-3-*O*-tosyl-*sn*-glycerol (10c):[2]



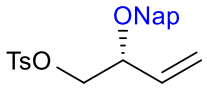
R_f = 0.3 (hexanes/EtOAc, 3:1); $[\alpha]_D^{23}$ = +10.4 (c = 0.93, $CHCl_3$); (Lit. $[\alpha]_D^{25}$ = +11.5); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.79 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 5.75 (m, 1H), 5.38-5.33 (dt, J = 17.2, 1.2 Hz, 1H), 5.23-5.20 (dt, J = 10.8, 1.2 Hz, 1H), 4.38 (m, 1H), 4.06-4.03 (dd, J = 10.4, 3.6 Hz, 1H), 3.94-3.89 (dd, J = 10.4, 7.6 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 145.1, 134.8, 132.5, 129.9, 127.9, 117.9, 73.0, 70.3, 21.6. The [α] value of **10c** is in agreement with the literature data.

(2*R*)-2-*O*-Benzyl-1-*en*-3-*O*-tosyl-*sn*-glycerol (12c$_1$):



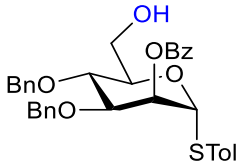
R_f = 0.4 (hexanes/EtOAc, 6:1); $[\alpha]_D^{21}$ = +13.2 (c = 1.36, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.78-7.76 (m, 2H), 7.34-7.25 (m, 7H), 5.66-5.62 (m, 1H), 5.36-5.31 (m, 2H), 4.56 (d, J = 11.6 Hz, 1H), 4.37 (d, J = 12 Hz, 1H), 4.04 (d, J = 2.0 Hz, 3H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.7, 137.8, 133.5, 133.0, 129.7, 128.3, 127.9, 127.6, 120.1, 77.6, 77.2, 71.4, 70.7, 21.6; **HRMS (ESI)**: calcd for $C_{18}H_{24}NO_4S^+$ $[M + NH_4]^+$ 350.1412, found *m/z* 350.1421.

(2*R*)-1-*en*-2-(2-Naphthylmethyl)-3-tosyl-*sn*-glycerol ($12c_2$):



R_f = 0.4 (hexanes/EtOAc, 6:1); $[\alpha]_D^{20}$ = +6.9 (c = 1.72, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.84-7.71 (m, 6H), 7.49-7.46 (m, 2H), 7.39-7.37 (m, 1H), 7.23 (s, 1H), 7.21 (s, 1H), 5.73-5.65 (m, 1H), 5.38-5.33 (m, 2H), 4.74 (d, J = 12.4 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 4.07 (d, J = 2.0 Hz, 3H), 2.37 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 144.7, 135.2, 133.5, 132.99, 132.96, 129.7, 128.1, 127.92, 127.85, 127.7, 126.4, 126.0, 125.9, 125.7, 120.2, 77.5, 77.2, 71.5, 70.7, 21.6; **HRMS (ESI)**: calcd for $C_{22}H_{26}NO_4S^+$ $[M + NH_4]^+$ 400.1579, found *m/z* 400.1577.

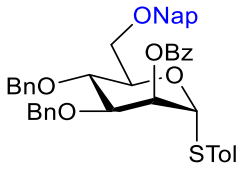
***p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (10d):**[3]



R_f = 0.37 (hexanes/EtOAc, 4:1); $[\alpha]_D^{25}$ = + 45.9 (c = 0.009, $CHCl_3$); (Lit. $[\alpha]_D^{25}$ = + 40.8); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05 (d, J = 7.6 Hz, 2H, Ar*H*), 7.58 (t, J = 7.4 Hz, 1H, Ar*H*), 7.45 (t, J = 7.6 Hz, 2H, Ar*H*), 7.38 – 7.23 (m, 12H, Ar*H*), 7.11 (d, J = 7.8 Hz, 2H, Ar*H*), 5.83 (s, 1H, H-2), 5.51 (s, 1H, H-1), 4.94 (d, J = 10.9 Hz, 1H), 4.79 (d, J = 11.4 Hz, 1H), 4.68 (d, J = 10.9 Hz, 1H), 4.61 (d, J = 11.4 Hz, 1H), 4.25 (d, J = 8.7 Hz, 1H), 4.11 – 3.99 (m, 2H), 3.90 –3.79 (m, 2H), 2.31 (s, 3H, SCH_3), 1.83 (t, J = 6.5 Hz, 1H, OH); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.5, 138.3, 138.1, 137.6, 133.3, 132.8, 129.9, 129.8, 129.7, 129.4, 128.5, 128.40, 128.37,

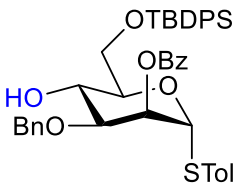
128.12, 128.06, 127.82, 127.77, 86.7, 78.4, 75.3, 74.2, 72.9, 71.7, 70.7, 62.0, 21.1; HRMS (ESI) *m/z* 593.1970 $[M + Na]^+$; calcd for $C_{34}H_{34}NaO_6S$: 593.1968. The [α] value of **10d** is in agreement with the literature data.

***p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-6-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12d):**



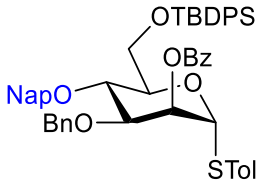
R_f = 0.4 (hexanes/EtOAc, 4:1); $[\alpha]_D^{19}$ = +88 (*c* = 2.75, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05 (d, *J* = 7.6 Hz, 2H), 7.85-7.76 (m, 4H), 7.51-7.46 (m, 4H), 7.40-7.28 (m, 10H), 7.23-7.20 (m, 2H), 7.16-7.14 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 5.86 (t, *J* = 2.4 Hz, 1H), 5.59 (d, *J* = 1.6 Hz, 1H), 4.91-4.80 (m, 3H), 4.67-4.54 (m, 3H), 4.43 (dd, *J* = 9.6, 2.8 Hz, 1H), 4.14 (t, *J* = 9.6 Hz, 1H), 4.07 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.97 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.84 (dd, *J* = 10.8, 1.6 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.6, 138.2, 137.9, 137.6, 135.8, 133.2, 133.1, 132.9, 132.4, 129.9, 129.82, 129.79, 128.4, 128.3, 128.14, 128.06, 127.9, 127.8, 127.7, 127.6, 126.3, 126.0, 125.8, 86.7, 78.6, 77.2, 75.3, 74.6, 73.5, 72.6, 71.7, 70.6, 69.0, 21.1; **HRMS (ESI)**: calcd for $C_{45}H_{42}NaO_6S^+$ $[M + Na]^+$ 733.2607, found *m/z* 733.2594.

***p*-Tolyl 2-*O*-Benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-manno-pyranoside (10e):**



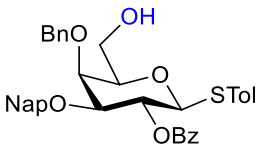
R_f = 0.2 (hexanes/EtOAc, 4:1); $[\alpha]_D^{24}$= +20.7 (c = 1.35, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.17 (d, J = 8 Hz, 2H), 8.05 (d, J = 8 Hz, 2H), 7.72-7.70 (m, 4H), 7.54-7.50 (m, 3H), 7.42-7.24 (m, 11H), 7.04 (d, J = 7.6 Hz, 2H), 5.85 (s, 1H), 5.58 (s, 1H), 4.81 (d, J = 11.2 Hz, 1H), 4.55 (d, J = 11.6 Hz, 1H), 4.32-4.25 (m, 2H), 4.04 (dd, J = 11.2, 3.2 Hz, 1H), 3.94 (d, J = 11.2 Hz, 1H), 3.87 (dd, J = 8.4, 2.4 Hz, 1H), 2.58 (s, 1H), 2.30 (s, 3H), 1.06 (s, 9H) ; **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.7, 137.87, 137.41, 135.78, 135.63, 134.54, 133.42, 133.23, 133.13, 132.35, 130.58, 130.09, 129.94, 129.85, 129.66, 129.61, 128.9, 128.6, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 87.0, 78.2, 73.4, 71.6, 70.1, 67.2, 63.5, 26.8, 21.1, 19.3; **HRMS (ESI):** calcd for $C_{43}H_{46}NaO_6SSi^+$ $[M + Na]^+$ 741.2673, found *m/z* 741.2677.

***p*-Tolyl 2-*O*-Benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12e):**



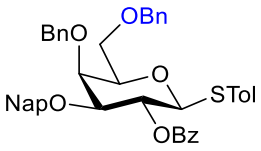
Rf = 0.4 (hexanes/EtOAc, 6:1); $[\alpha]_D^{21}$= +20 (c = 1.5, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.12 (d, J = 8 Hz, 2H), 7.81-7.66 (m, 9H), 7.55-7.21 (m, 18H), 7.05 (d, J = 7.6 Hz, 2H), 5.92 (s, 1H), 5.62 (s, 1H), 5.12 (d, J = 11.2 Hz, 1H), 4.87-4.83 (m, 2H), 4.64 (d, J = 11.6 Hz, 1H), 4.32 (m, 2H), 4.16-4.12 (m, 2H), 3.96 (d, J = 11.2 Hz, 1H), 2.30 (s, 3H), 1.08 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 165.8, 137.8, 137.7, 135.9, 135.6, 133.7, 133.3, 133.2, 133.0, 132.9, 132.0, 130.4, 130.0, 129.87, 129.82, 129.65, 129.55, 128.4, 128.18, 128.09, 127.97, 127.8, 127.74, 127.69, 127.58, 126.6, 126.05, 126.00, 125.8, 86.8, 78.8, 77.4, 77.3, 77.1, 76.7, 75.5, 74.4, 73.7, 71.8, 71.0, 62.8, 26.8, 21.1, 19.3; **HRMS (ESI)**: calcd for $C_{54}H_{58}NO_6SSi^+$ $[M + NH_4]^+$ 876.3746, found *m/z* 876.3749.

***p*-Tolyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (10f):** [4]



R*f* = 0.2 (hexanes/EtOAc, 2:1); $[\alpha]_D^{20}$= +19.4 (*c* = 7.11, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 7.98 (d, *J* = 6.8 Hz, 2H), 7.73 (m, 1H), 7.58-7.51 (m, 4H), 7.44-7.23, (m, 12H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.70 (t, *J* = 10 Hz, 1H), 5.01 (d, *J* = 12 Hz, 1H), 4.80 (d, *J* = 12.4 Hz, 1H), 4.70-4.64 (m, 3H), 3.96 (d, *J* = 2.4 Hz, 1H), 3.88-3.84 (m, 1H), 3.74-3.71 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.62-3.55 (m, 1H), 3.51-3.48 (m, 1H), 3.44-3.39 (m, 1H), 2.26 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 165.3, 138.1, 137.8, 134.9, 133.1, 133.03, 132.9, 132.6, 130.04, 129.9, 129.6, 129.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 126.7, 126.1, 126.0, 125.8, 87.3, 81.1, 79.1, 74.2, 72.2, 72.1, 70.5, 62.2, 21.1. No [*α*] data of **10f** was reported in ref S4.

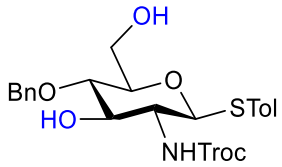
***p*-Tolyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (12f):**



R_f = 0.15 (hexanes/EtOAc, 5:1); $[\alpha]_D^{23}$= +32.2 (*c* = 1.5, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 7.98 (d, *J* = 6.8 Hz, 2H), 7.73-7.70 (m, 1H), 7.58-7.51 (m, 4H), 7.44-7.37 (m, 4H), 7.35-7.22, (m, 13H), 6.97 (d, *J* = 8.0 Hz, 2H), 5.67 (t, *J* = 9.6 Hz, 1H), 5.01 (d, *J* = 12 Hz, 1H), 4.79 (d, *J* = 12.4 Hz, 1H), 4.69-4.60 (m, 3H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.07 (d, *J* = 2.8 Hz, 1H), 3.73-3.63 (m, 4H), 2.26 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 165.4, 138.6, 137.9, 137.7, 135.1, 133.14, 133.11, 133.0, 132.8, 130.2, 130.0, 129.8, 129.6, 128.6,

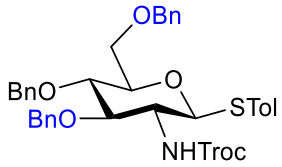
128.4, 128.33, 128.31, 128.18, 128.09, 127.97, 127.95, 127.8, 127.6, 126.7, 126.2, 126.0, 125.9, 87.4, 81.1, 77.8, 74.5, 73.8, 72.6, 71.9, 70.5, 68.9, 21.3; **HRMS (ESI)**: calcd for $C_{45}H_{46}NO_6S^+$ $[M + NH_4]^+$ 728.3040, found *m/z* 728.3040.

***p*-Tolyl 4-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (10g):**[5]



R_f = 0.15 (hexanes/EtOAc, 1:1); $[\alpha]_D^{20}$= +40 (*c* = 0.05, $CHCl_3$); **^{1}H NMR (400 MHz, CD_3OD)**: *δ* 7.42-7.27 (m, 7H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.96-4.87 (m, 2H), 4.77-4.59 (m, 3H), 3.85-3.82 (dd, *J* = 12.0, 2.0 Hz, 1H), 3.70-3.66 (m, 2H), 3.53-3.42 (m, 2H), 3.34-3.32 (m, 3H), 2.32 (s, 3H); **^{13}C NMR (100 MHz, CD_3OD)**: *δ* 155.4, 138.5, 137.3, 131.8, 130.3, 129.1, 127.8, 127.7, 127.6, 95.7, 87.6, 79.8, 78.0, 76.3, 74.5, 74.2, 61.1, 57.2, 19.7. No [*α*] data of **10g** was reported in ref S5.

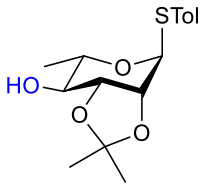
***p*-Tolyl 3,4,6-tri-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (12g):**



R_f = 0.45 (hexanes/EtOAc, 3:1); $[\alpha]_D^{19}$= +8.8 (*c* = 1.125, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: *δ* 7.42 (d, *J* = 8.1 Hz, 2H), 7.35–7.24 (m, 13H), 7.20 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 5.10 (d, *J* = 8.2 Hz, 1H), 4.86 (d, *J* = 10.2 Hz, 1H), 4.79-4.68 (m, 6H), 4.61-4.53 (m, 3H), 3.87 (t, *J* = 9.0 Hz, 1H), 3.80-3.71 (m, 2H), 3.62 (t, *J* = 9.1 Hz, 1H), 3.53 (m, 1H), 3.40 (dd, *J* = 18.8, 9.5 Hz, 1H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: *δ* 153.7, 138.3, 138.1, 137.9, 137.8, 133.3, 129.7, 128.45, 128.43, 128.3, 128.1, 127.85, 127.82, 127.6. 127.5, 85.7, 82.2, 79.3, 78.5,

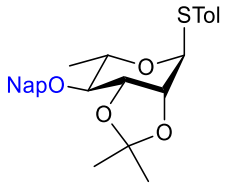
77.2, 75.2, 74.9, 74.5, 73.4, 68.9, 56.6, 21.1; **HRMS (ESI)**: calcd for $C_{30}H_{33}Cl_3NO_6S^+$ $[M + H]^+$ 640.1167, found *m/z* 640.1089.

***p*-Tolyl 2,3-*O*-Isopropylidene-1-thio-α-L-rhamnopyranoside (10h):**[3]



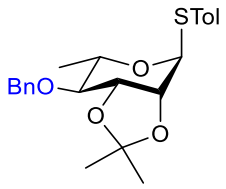
R_f = 0.3 (hexanes/EtOAc, 3:1); $[\alpha]_D^{24}$ = –185 (*c* = 0.475, $CHCl_3$); (Lit. $[\alpha]_D^{35}$ = –170); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 4.33 (d, *J* = 5.6 Hz, 1H), 4.13-4.07 (m, 2H), 3.47-3.43 (m, 1H), 2.82 (d, *J* = 3.2 Hz, 1H), 2.33 (s, 3H), 1.53 (s, 3H), 1.37 (s, 3H), 1.23 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.9, 132.5, 129.8, 129.5, 109.7, 84.0, 78.4, 76.5, 75.1, 66.9, 28.1, 26.4, 21.1, 17.1. The [α] value of **10h** is in agreement with the literature data.

***p*-Tolyl 4-*O*-(2-Naphthylmethyl)-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (12h$_1$):**



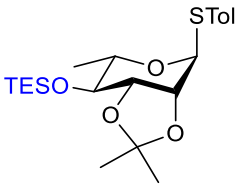
R_f = 0.6 (hexanes/EtOAc, 5:1); $[\alpha]_D^{21}$ = –187 (*c* = 1.26, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.83-7.80 (m, 4H), 7.48-7.33 (m, 5H), 7.11-7.09 (m, 2H), 5.66 (s, 1H), 5.07 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 12.0 Hz, 1H), 4.37-4.33 (m, 2H), 4.20-4.15 (m, 1H), 3.35-3.31 (m, 1H), 2.31 (s, 3H), 1.50 (s, 3H), 1.38 (s, 3H), 1.25 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 137.8, 135.7, 133.2, 133.0, 132.5, 129.8, 129.7, 128.1, 127.9, 127.7, 126.8, 126.07, 126.05, 125.9, 109.4, 84.2, 81.4, 78.5, 76.7, 73.1, 66.1, 28.1, 26.5, 21.3, 17.8; **HRMS (ESI)**: calcd for $C_{27}H_{34}NO_4S^+$ $[M + NH_4]^+$ 468.2199, found *m/z* 468.2103.

p-**Tolyl 4-*O*-Benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (12h$_2$):**[6]



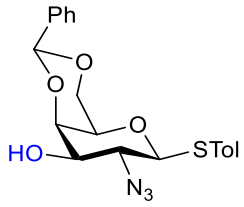
R_f = 0.6 (hexanes/EtOAc, 5:1); $[\alpha]_D^{20}$ = –185 (*c* = 1.74, $CHCl_3$); (Lit. $[\alpha]_D^{25}$ = +25); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.27 (m, 7H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.65 (s, 1H), 4.91 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.35-4.29 (m, 2H), 4.17-4.13 (m, 1H), 3.31-3.27 (dd, *J* = 10.0, 6.0 Hz, 1H), 2.32 (s, 3H), 1.51 (s, 3H), 1.38 (s, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 138.3, 137.8, 132.4, 129.8, 128.3, 128.0, 127.6, 109.4, 84.1, 81.5, 78.4, 77.2, 73.1, 66.1, 28.0, 26.5, 21.1, 17.7. L-Rhamnoside **12h$_2$**, *O*-Nap protected counterpart **12h$_1$**, and their precursor **10h** are –ve [α] data, but the literature data in Ref S6 is a positive value.

p-**Tolyl 4-*O*-Triethylsilanyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (transilylation product of S12h obtained by Et$_3$SiH reductive etherification):**



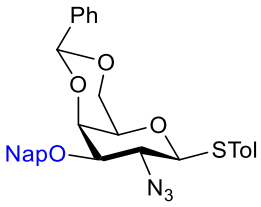
R_f = 0.3 (hexanes/DCM, 3:1); $[\alpha]_D^{24}$ = –140 (*c* = 0.2, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.64 (s, 1H), 4.57 (s, 1H), 4.31 (d, *J* = 5.6 Hz, 1H), 4.06-4.00 (m, 1H), 4.41 (t, *J* = 8.8 Hz, 1H), 2.33 (s, 3H), 1.52 (s, 3H), 1.35 (s, 3H), 1.18 (d, *J* = 6.0 Hz, 3H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.66 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 137.7, 132.4, 129.8, 128.4, 127.8, 127.6, 109.1, 84.2, 78.9, 77.2, 76.2, 72.1, 67.5, 28.1, 26.5, 21.1, 17.4, 6.8, 4.9; **HRMS (ESI)**: calcd for $C_{22}H_{36}NaO_4SSi^+$ $[M + Na]^+$ 447.1996, found *m/z* 447.1993.

***p*-Tolyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranside (10i):**[8]



R_f = 0.1 (hexanes/EtOAc, 3:1); $[\alpha]_D^{20}$ = –28.5 (*c* = 14.6, $CHCl_3$); (Lit. $[\alpha]_D^{25}$ = –31.9); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.37 (m, 5H), 7.09 (d, *J* = 7.6 Hz, 2H), 5.46 (s, 1H), 4.30 (d, *J* = 10.8 Hz, 2H), 4.06 (s, 1H), 3.93 (d, *J* = 12.4 Hz, 1H), 3.54-3.44 (m, 2H), 3.38 (s, 1H), 2.87 (s, 1H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 137.5, 134.6, 129.8, 129.5, 128.3, 126.6, 126.5, 101.3, 85.1, 74.5, 73.0, 69.8, 69.2, 61.9, 21.3. The [α] value of **10i** is in agreement with the literature data.

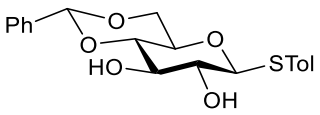
***p*-Tolyl 2-Azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranside (12i):**[7]



R_f = 0.35 (hexanes/EtOAc, 2:1); $[\alpha]_D^{19}$ = –28.5 (*c* = 0.91, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.84-7.76 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.51-7.34 (m, 8H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.41 (s, 1H), 4.87 (d, *J* = 12.8 Hz, 1H), 4.83 (d, *J* = 12.8 Hz, 1H), 4.35-4.31 (m, 2H), 4.07 (d, *J* = 2.8 Hz, 1H), 3.94-3.91 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.49-3.45 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.34 (d, *J* = 0.8 Hz, 1H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 137.6, 135.0, 134.9, 133.1, 129.8, 129.2, 128.3, 128.1, 127.8, 127.7, 126.7, 126.6, 126.3, 126.1, 126.0, 125.7, 101.2, 85.1, 79.5, 77.2, 72.3, 71.8, 69.8, 69.4, 59.7, 21.3; **HRMS (ESI)**:

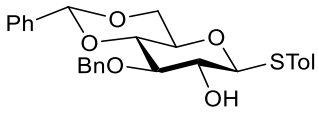
calcd for $C_{31}H_{30}N_3O_4S^+$ $[M + H]^+$ 540.1954, found *m/z* 540.1952. No [α] value of **10j** was provided in the literature.

***p*-Tolyl 4,6-*O*-Benzylidene-1-thio-β-D-glucopyranside (10j):**[12]



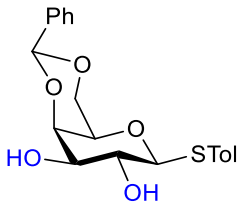
R_f = 0.15 (hexanes/EtOAc, 1:1); $[\alpha]_D^{23}$ = –29.6 (*c* = 1.28, $CHCl_3$) (Lit. $[\alpha]_D^{25}$ = –34.4); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.47-7.33 (m, 7H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.48 (s, 1H), 4.51 (d, *J* = 9.6 Hz, 1H), 4.35-4.31 (m, 1H), 3.79-3.70 (m, 2H), 3.47-3.27 (m, 4H), 3.02 (s, 1H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 139.0, 137.2, 133.8, 130.2, 129.6, 128.6, 127.7, 126.6, 102.2, 88.9, 80.5, 74.8, 72.8, 70.3, 68.8, 53.8, 21.5. The [α] value of **10j** is in agreement with the literature data.

***p*-Tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (12j):**[9]



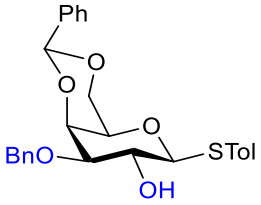
R_f = 0.3 (hexanes/EtOAc, 3:1); $[\alpha]_D^{23}$ = –26.6 (*c* = 0.45, $CHCl_3$); (Lit. $[\alpha]_D^{29}$ = –87.8); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.48-7.27 (m, 12H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.56 (s, 1H), 4.93 (d, *J* = 11.6 Hz, 1H), 4.78 (d, *J* = 11.6 Hz, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.39-4.36 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.78 (t, *J* = 10.0 Hz, 1H), 3.71-3.60 (m, 2H), 3.52-3.45 (m, 2H), 2.52 (d, *J* = 2.0 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 138.2, 137.2, 133.8, 129.8, 128.9, 128.4, 128.2, 128.1, 127.9, 125.9, 101.2, 88.6, 81.6, 81.1, 74.8, 72.1, 70.7, 68.6, 21.2. The [α] value of **12j** was smaller than the literature data.

***p*-Tolyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (10k):**[12]



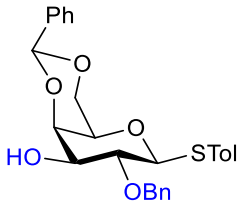
R_f = 0.1 (hexanes/EtOAc, 1:1); $[\alpha]_D^{24}$ = −14.0 (c = 0.42, $CHCl_3$); (Lit.$[\alpha]_D^{25}$ = −72.8); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.56-7.53 (m, 2H), 7.38-7.32 (m, 5H), 7.07 (d, J = 8.0 Hz, 2H), 5.45 (s, 1H), 4.40-4.38 (m, 1H), 4.33-4.29 (dd, J = 12.4, 1.6 Hz, 1H), 4.49 (d, J = 2.0 Hz, 1H), 3.96-3.92 (dd, J = 12.8, 2.0 Hz, 1H), 3.60 (d, J = 7.2 Hz, 2H), 3.41 (d, J = 0.8 Hz, 1H), 2.95 (s, 2H), 2.33 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.6, 137.9, 134.2, 129.9, 129.5, 128.5, 127.2, 126.8, 101.6, 87.3, 75.7, 73.9, 70.2, 69.5, 68.9, 21.5. The [α] value of **10k** was smaller than the literature data.

***p*-Tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_1$):** [11]



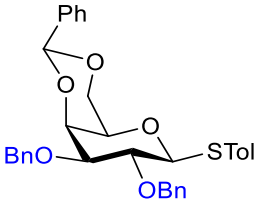
R_f = 0.2 (hexanes/EtOAc, 3:1); $[\alpha]_D^{24}$ = +12 (c = 0.5, $CHCl_3$); (Lit. $[\alpha]_D^{22}$ = +219.4); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.56 (d, J = 8.0 Hz, 2H), 7.40-7.27 (m, 10H), 7.05 (d, J = 8.0 Hz, 2H), 5.41 (s, 1H), 4.75-4.68 (dd, J = 13.2, 12.4 Hz, 2H), 4.46 (d, J = 9.6 Hz, 1H), 4.36-4.33 (dd, J = 12.4, 1.2 Hz, 1H), 4.12 (d, J = 3.2 Hz, 1H), 3.98-3.95 (dd, J = 12.4, 1.6 Hz, 1H), 3.87 (t, J = 9.6 Hz, 1H), 3.52-3.48 (dd, J = 9.2, 3.2 Hz, 1H), 3.43 (d, J = 1.2 Hz, 1H), 2.48 (s, 1H), 2.33 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.7, 138.3, 138.2, 134.7, 130.0, 129.4, 128.8, 128.4, 128.3, 126.9, 126.7, 101.5, 87.5, 80.6, 77.5, 73.7, 72.0, 70.4, 69.8, 67.5, 21.6. The [α] value of **12k$_1$** was smaller than the literature data.

***p*-Tolyl 2-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_2$):**[10]



R_f = 0.1 (hexanes/EtOAc, 3:1); $[\alpha]_D^{19}$ = –39.2 (*c* = 1.58, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.51-7.39 (m, 7H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.55 (s, 1H), 4.79 (d, *J* = 10.4 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.57 (d, *J* = 9.6 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 3.6 Hz, 1H), 4.04 (d, *J* = 11.2 Hz, 1H), 3.81-3.78 (m, 1H), 3.62 (t, *J* = 9.2 Hz, 1H), 3.52 (s, 1H), 2.43 (d, *J* = 8.8 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.3, 137.8, 137.6, 133.3, 129.6, 129.3, 128.8, 128.4, 128.2, 128.1, 127.8, 126.6, 101.4, 86.4, 77.1, 75.8, 75.3, 74.5, 69.8, 69.3, 21.2; **HRMS (ESI)**: calcd for $C_{27}H_{29}O_5S^+$ $[M + H]^+$ 465.1727, found *m/z* 465.1730. No $[\alpha]$ value of **12k$_2$** was provided in ref 10.

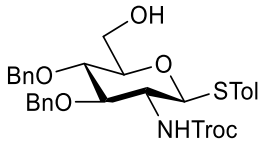
***p*-Tolyl 2,3-di-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_3$):**[10]



R_f = 0.6 (hexanes/EtOAc, 3:1; $[\alpha]_D^{24}$ = –26 (*c* = 5.38, $CHCl_3$) (Lit. $[\alpha]_D^{20}$ = –23); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.61-7.59 (m, 2H), 7.53-7.50 (m, 2H), 7.44-7.26 (m, 13H), 6.99 (d, *J* = 8.0 Hz, 2H), 5.47 (s, 1H), 4.72-4.70 (m, 4H), 4.56 (d, *J* = 9.6 Hz, 1H), 4.38-4.34 (dd, *J* = 12.4, 1.6 Hz, 1H), 4.13 (d, *J* = 2.8 Hz, 1H), 3.98-3.95 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.84 (t, *J* = 9.2 Hz, 1H), 3.63-3.59 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.39 (s, 1H), 2.29 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 138.6, 138.1, 137.9, 137.6, 133.5, 129.6, 129.0, 128.7, 128.4, 128.3, 128.2, 128.1, 127.81,

127.78, 127.67, 126.7, 101.3, 86.2, 81.4, 75.4, 75.3, 73.7, 71.8, 69.5, 69.5, 21.2. The [α] value of **12k3** is in agreement with the literature value.

***p*-Tolyl 3,4-di-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (17):**

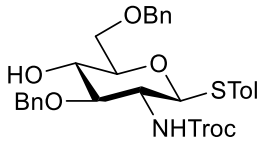


17

To a solution of unprotected *N*-Troc thioglucosamine **13** (298 mg, 0.65 mmol) in dried THF (7 mL), HMDS (0.3 mL, 1.56 mmol, 2.4 equiv.), and TMSOTf (90 µL, 0.52 mmol, 0.8 equiv.) were added. The reaction was stirred under N_2 at RT for 0.5 h. After complete consumption of **11**, the mixture was diluted with EtOAc, then washed with $NH_4Cl_{(aq)}$ (× 2) followed by washing with brine solution. The organic layer was dried over $MgSO_4$, filtered, and concentrated to obtain crude *per*-*O*-TMS protected thioglucosamine **16**, which was dried under *vacuum* for an hour. In etherification, dried TMS-protected **16** was dissolved in DCM (7 mL), which was treated with PhCHO (76 µL, 0.715 mmol, 1.1 equiv.) and activated 4 Å molecular sieves (100 mg/ 1 mL DCM) and the mixture was stirred at RT for 1 h. Then, the solution was cooled at –30 °C for 0.5 h and TMSOTf (11 µL, 0.065 mmol, 0.1 equiv.) was added. When TMS-protected **16** was completely consumed as monitored by TLC, PhCHO (65 µL, 0.65 mmol, 1.0 equiv.), PMHS (0.3 mL, 0.16 mmol, 0.25 equiv.), and TMSOTf (11 µL, 0.065 mmol, 0.1 equiv.) were added in sequence. After the reaction mixture was continuously stirred at –30 °C for 2 h, 3-*O*-benzyl protected **6** was produced. At this point, BH_3-THF (3.2 mL, 0.8 mmol, 5 equiv.) and TMSOTf (23 µL, 0.13 mmol, 0.2 equiv.) were added. The reaction mixture was warmed to RT and stirred at RT for 14 h. When 3-*O*-benzyl protected **6** was completely consumed, the reaction mixture was diluted with DCM and quenched with Et_3N and MeOH. The mixture was wash with 1N

$HCl_{(aq)}$ and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated for column chromatography (Elution: EtOAc/hexanes = 1/4 gradient to 1/2) to obtain 6-hydroxyl acceptor **17** (185 mg, 0.29 mmol, 45% over 4 steps). Analytical data for **17**: R_f = 0.3 (hexanes/EtOAc, 2:1); $[\alpha]_D^{19}$ = +8.5 (c = 2.1, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.38-7.27 (m, 12H), 7.12-7.10 (d, J = 8.0 Hz, 2H), 5.09 (d, J = 8.4 Hz, 1H), 4.91 (d, J = 10.0 Hz, 1H), 4.84-4.64 (m, 6H), 3.90-3.86 (m, 2H), 3.73-3.70 (m, 1H), 3.56 (t, J = 9.6, 8.8 Hz, 1H), 3.43-3.37 (m, 2H), 2.33 (s, 3H), 2.06 (s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.8, 138.4, 137.7, 133.2, 129.8, 128.51, 128.49, 128.06, 127.97, 127.92, 95.4, 85.9, 82.0, 79.5, 78.3, 77.2, 75.2, 75.0, 74.5, 62.0, 56.8, 21.1; **HRMS (ESI):** calcd for $C_{30}H_{32}Cl_3NNaO_6S^+$ $[M + Na]^+$ 662.0911, found *m/z* 662.0908.

***p*-Tolyl 3,6-di-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (18):**

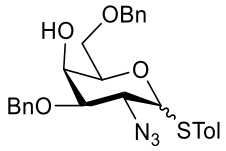


18

3-*O*-Benzyl protected **6** from the synthesis of 6-hydroxyl acceptor **17** was treated with triethylsilane (TES) (1 mL, 6.3 mmol, 10 equiv.) and trifluoroacetic acid (TFA) (0.05 mL, 0.63 mmol, 1 equiv.) at −30 °C. Then, the temperature was raised to −20 °C and the mixture was stirred for 1.5 h when alkylation intermediate **6** was completely cleaved. The reaction was diluted with DCM and quenched with Et_3N. The mixture was wash with satd. $NaHCO_{(aq)}$, H_2O, and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated for column chromatography (Elution: EtOAc/hexanes = 1/5 gradient to 1/3) to obtain product **18** (200 mg, 0.31 mmol, 50% over 4 steps). Analytical data for **18**: R_f = 0.5 (hexanes/EtOAc, 1:1); $[\alpha]_D^{19}$ = −10.5 (c = 1.52, $CHCl_3$); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.74-7.28 (m, 12H), 7.04 (d, J = 8.0 Hz, 2H), 5.13 (d, J = 8.0 Hz, 1H), 4.89 (d, J = 10.4 Hz, 1H), 4.79-4.72 (m, 4H), 4.59 (d, J =12.0 Hz, 1H), 4.53 (d, J = 12.0 Hz, 1H), 3.81-3.64 (m, 4H), 3.53-3.50 (m, 1H), 3.93-3.32 (m, 1H), 2.80 (s, 1H), 2.30 (s,

1H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 153.8, 138.2, 138.0, 137.7, 133.2, 129.7, 128.6, 128.5, 128.1, 128.0, 127.8, 127.7, 95.4, 86.1, 81.8, 77.9, 77.2, 74.7, 74.5, 73.7, 72.9, 70.6, 56.1, 21.1; **HRMS (ESI)**: calcd for $C_{30}H_{32}Cl_3NNaO_6S^+$ $[M + Na]^+$ 662.0906, found *m/z* 662.0908.

***p*-Tolyl 2-Azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-β-D-galactopyranside (21):**

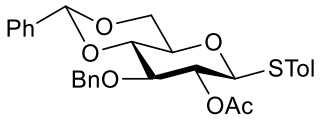


21

To a THF solution of unprotected 2-azido-2-dexoy-thiogalactosamine **14** (150 mg, 0.48 mmol) (5 mL), HMDS (0.25 mL, 1.2 mmol, 2.5 equiv.) and TMSOTf (78 µL, 0.43 mmol, 0.9 equiv.) were added. The reaction was stirred under N_2 at RT for 0.5 h. After complete consumption of **14**, the reaction mixture was diluted with EtOAc, then washed with $NH_4Cl_{(aq)}$ (× 2) and brine. The organic phase was subsequently dried (over $MgSO_4$), filtered, and concentrated to give *per*-*O*-TMS protected thiogalactosamine **19**. *per*-*O*-TMS protected **19** was dried under high *vacuum* for an hour, which was dissolved in DCM (5 mL), then PhCHO (58 µL, 0.58 mmol, 1.2 equiv.) and activated 4 Å molecular sieves (100 mg/ 1 mL DCM) were added. The resulting mixture was stirred at RT for 1 h, then cooled at −30 °C for 0.5 h followed by addition of TMSOTf (13 µL, 0.072 mmol, 0.15 equiv.). As intermediate **19** was completely reacted to give benzylidene **11i**, additional PhCHO (53µL, 0.53 mmol, 1.1 equiv.), PMHS (0.27 mL, 0.14 mmol, 0.3 equiv.), and supplementary dose of TMSOTf (39µL, 0.22 mmol, 0.45 equiv.) were added to initiate the reductive etherification. The reaction mixture was stirred at −40 °C for 4 h to give etherification product **20**, then TES (0.76 mL, 4.8 mmol, 10 equiv.), and TFA (54 µL, 2.2 mmol, 4.5 equiv.) were added to initiate the reductive acetal cleavage reaction. In reductive cleavage reaction, the mixture was stirred at −20 °C for 14 h. Upon the complete consumption of **20**, the reaction mixture was diluted with DCM followed by quenching with few drops of Et_3N.

The resulting mixture was washed with 1N $HCl_{(aq)}$, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography (Elution: EtOAc/hexanes = 1/8 gradient to 1/4) to obtain desired acceptor **21** (141 mg, 0.29 mmol, 60% over 4 steps). Analytical data for **21**: R*f* = 0.2 (hexanes/EtOAc, 4:1); **^{1}H NMR (400 MHz, $CDCl_3$) for *β* anomer**: δ 7.40-7.30 (m, 12H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.67 (d, *J* = 5.6 Hz, 2H), 4.56 (s, 2H), 4.31 (d, *J* = 10.4 Hz, 1H, H-1), 4.05 (s, 1H), 3.81-3.75 (m, 3H), 3.53 (t, *J* = 5.6 Hz, 1H), 3.40-3.37 (m, 1H), 2.46 (s, 1H), 2.31 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$) for *α* and *β*-anomer mixture**: δ 138.5, 137.8, 137.03, 137.00, 133.9, 133.0, 129.8, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.07, 128.05, 127.82, 127.78, 127.72, 127.66, 127.5, 87.8, 86.3, 81.2, 77.8, 77.2, 77.1, 73.7, 73.6, 72.04, 71.95, 69.7, 69.5, 69.4, 66.7, 65.7, 60.9, 59.7, 21.2, 21.1; **HRMS (ESI):** calcd for $C_{27}H_{33}N_4O_4S^+$ [M + NH_4]$^+$ 509.2223, found *m/z* 509.2217.

_p_-Tolyl 2-_O_-Acetyl-3-_O_-benzyl-4,6-_O_-benzylidene-1-thio-β-D-glucopyranside (24):[13]



24

To a THF solution of unprotected thioglucoside **15** (200 mg, 0.7 mmol) was added HMDS (0.75 mL, 3.5 mmol, 5.0 equiv.) and TMSOTf (51 μL, 0.28 mmol, 0.4 equiv.). The reaction mixture was stirred under N_2 at RT for 3.5 h. After complete trimethylsilylation, the reaction mixture was diluted with EtOAc, which was washed with $NH_4Cl_{(aq)}$ (× 2), brine, dried over $MgSO_4$, filtered, and concentrated to give *per-O*-TMS protected **22**. Crude TMS protected **22** was dried under vacuum for about an hour and was dissolved in DCM (7 mL). To the DCM of **22**, PhCHO (72 μL, 0.7 mmol, 1.0 equiv.) and activated 4 Å molecular sieves (100 mg/ 1 mL DCM) were added and resulting mixture was stirred at RT for 1 h. Then the mixture was cooled at −30 °C for 0.5 h followed by addition of TMSOTf (13 μL, 0.07 mmol, 0.1 equiv.) to trigger the benzylidenation reacton. When the formation of acetal-protected intermediate **11j** was

complete (about 0.5 h), supplementary PhCHO (72 μL, 0.7 mmol, 1.0 equiv.), PMHS (0.33 mL, 0.175 mmol, 0.25 equiv.), and TMSOTf (13 μL, 0.07 mmol, 0.1 equiv.) were added to initiate the reductive etherification. The etherification mixture was stirred at −30 °C for 1.5 h, then Ac_2O (66 μL, 0.7 mmol, 1.0 equiv.) was added to start the acetylation. The acetylation mixture was stirred for 1.5 h at −30 °C, then diluted with DCM quenched with Et_3N. The reaction solution was washed with 1 N $HCl_{(aq)}$, brine, dried over $MgSO_4$, filtered, and concentrated for column chromatography (gradient elution: EtOAc/hexanes = 1/15 to 1/4) to obtain desired donor **24** (184 mg, 0.36 mmol, 52% over 4 steps). Analytical data for **24**: R_f= 0.5 (hexanes/EtOAc, 3:1); $[\alpha]_D^{19}$= +18.6 (c = 1.82, $CHCl_3$) [Lit. $[\alpha]_D^{18}$= +65.9]; **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.47-7.25 (m, 12H), 7.11 (d, J = 8.0 Hz, 2H), 5.56 (s, 1H), 4.98 (t, J = 10.0 Hz, 1H), 4.86 (d, J = 8.0 Hz, 1H), 4.64 (t, J = 12.0 Hz, 2H), 4.38 (dd, J = 10.4, 4.8 Hz, 1H), 3.79 (t, J = 10.4 Hz, 1H), 3.72 (m, 2H), 3.52-3.46 (m, 1H), 2.33 (s, 3H), 2.03 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 169.6, 138.8, 138.5, 137.5, 133.7, 133.3, 130.2, 130.0, 129.4, 128.8, 128.7, 128.6, 128.55, 128.46, 128.3, 128.0, 126.5, 126.3, 101.6, 81.7, 80.2, 74.7, 71.7, 70.9, 68.9, 21.5, 21.3; **HRMS (ESI)**: calcd for $C_{29}H_{34}NO_6S^+$ $[M + NH_4]^+$ 524.2098, found m/z 524.2101. The optical rotation of **24** was smaller than that of the literature. Hence, the measurement of optical rotation was repeated.

3. Reference

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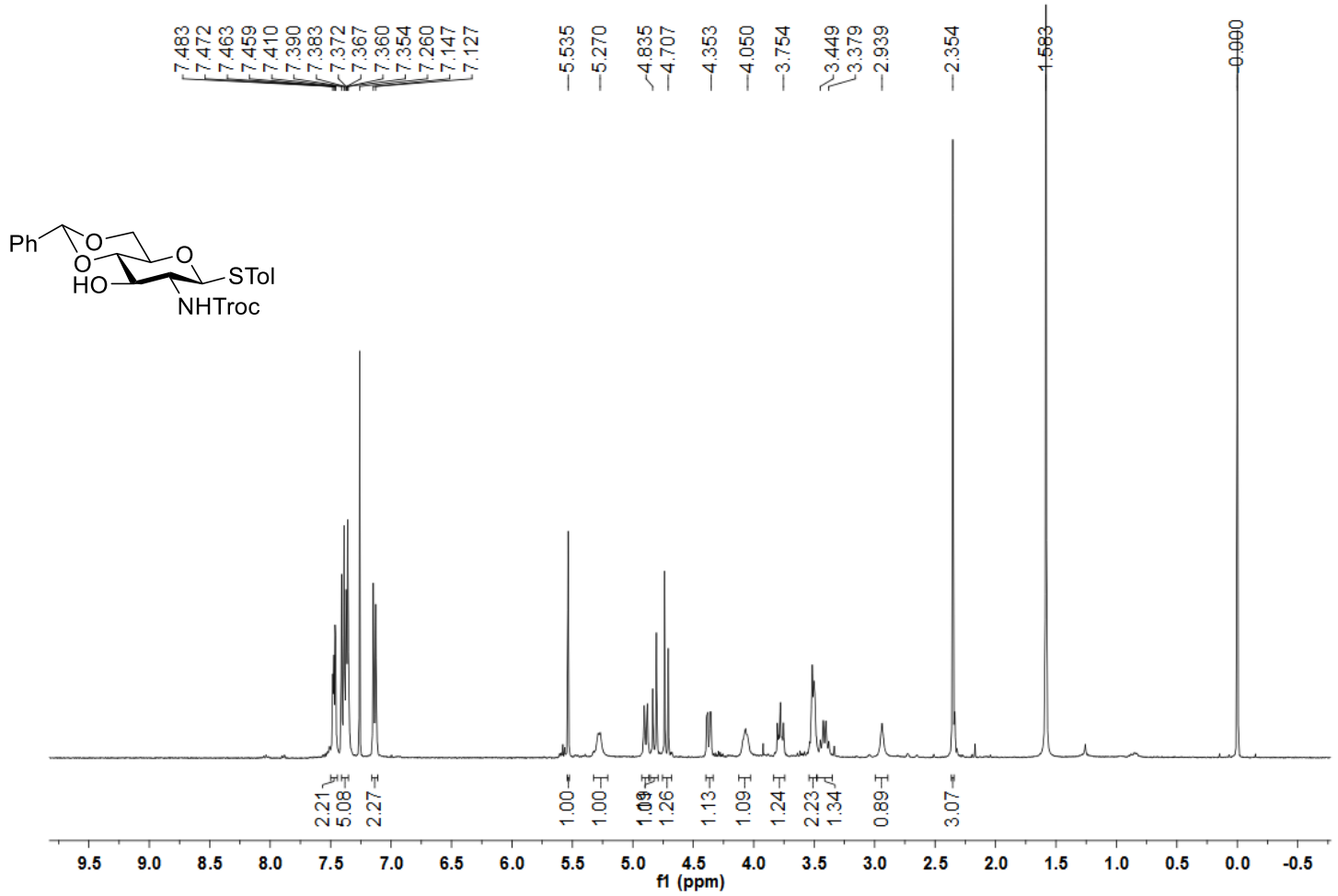
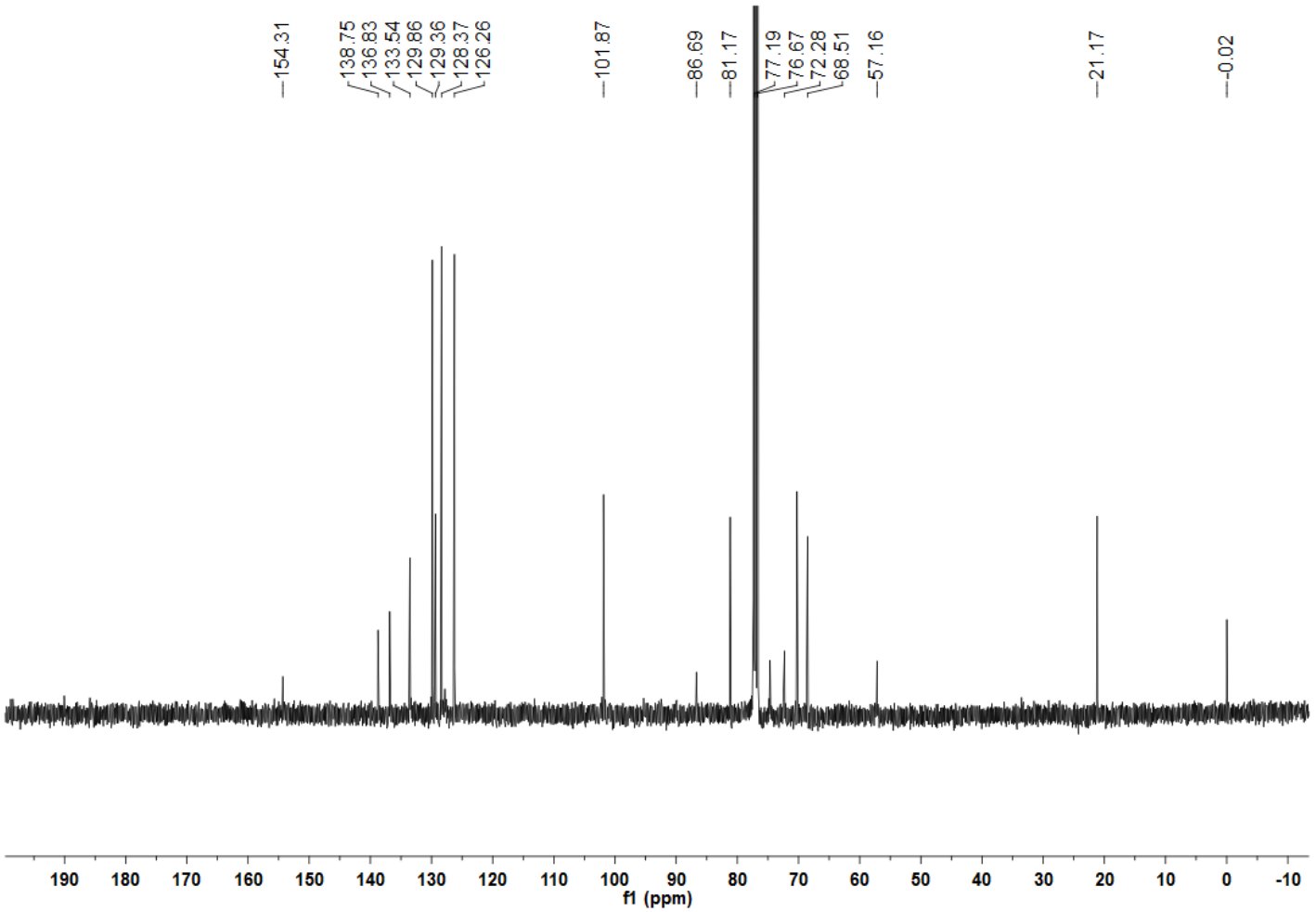
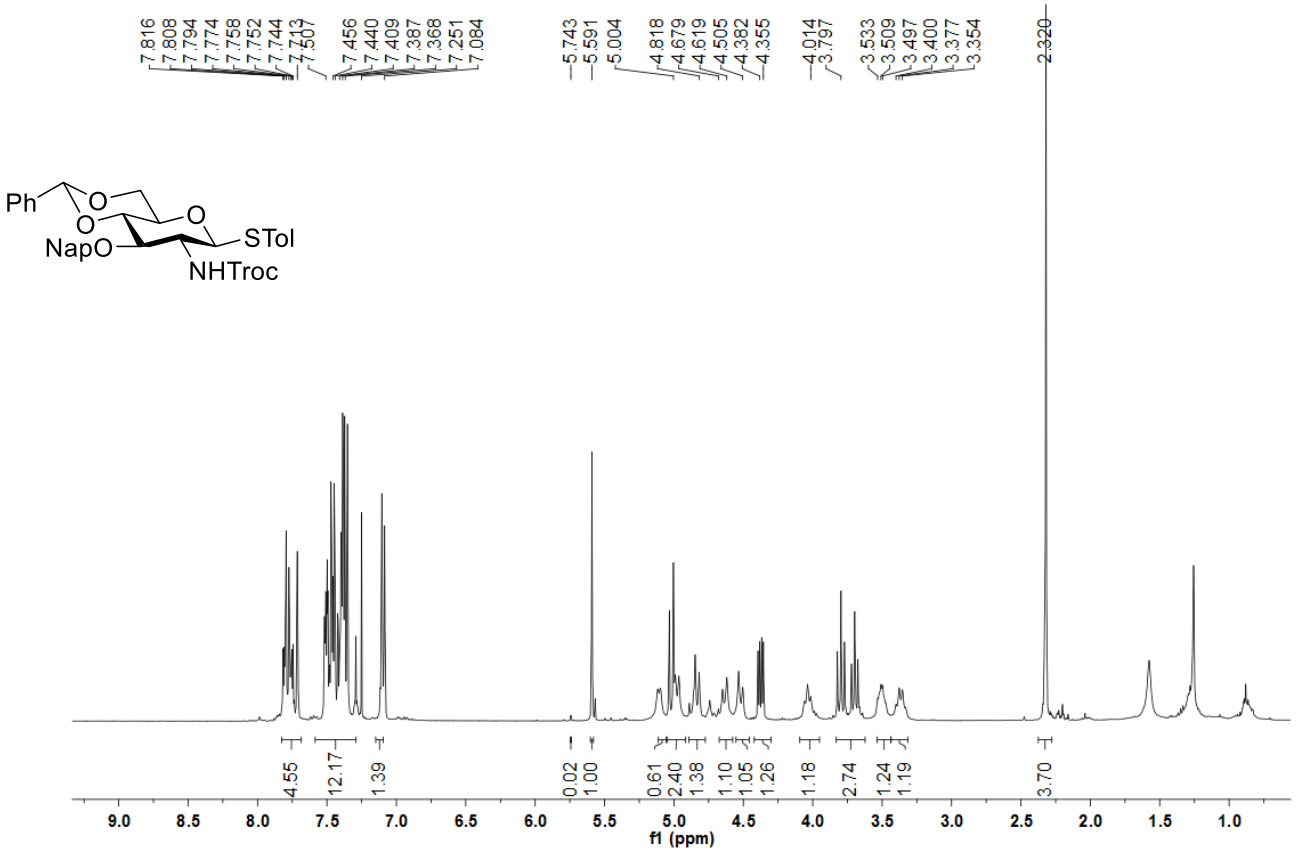
^{1}H 400 MHz NMR spectrum of *p*-Tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-*β*-D-glucopyranoside (1):



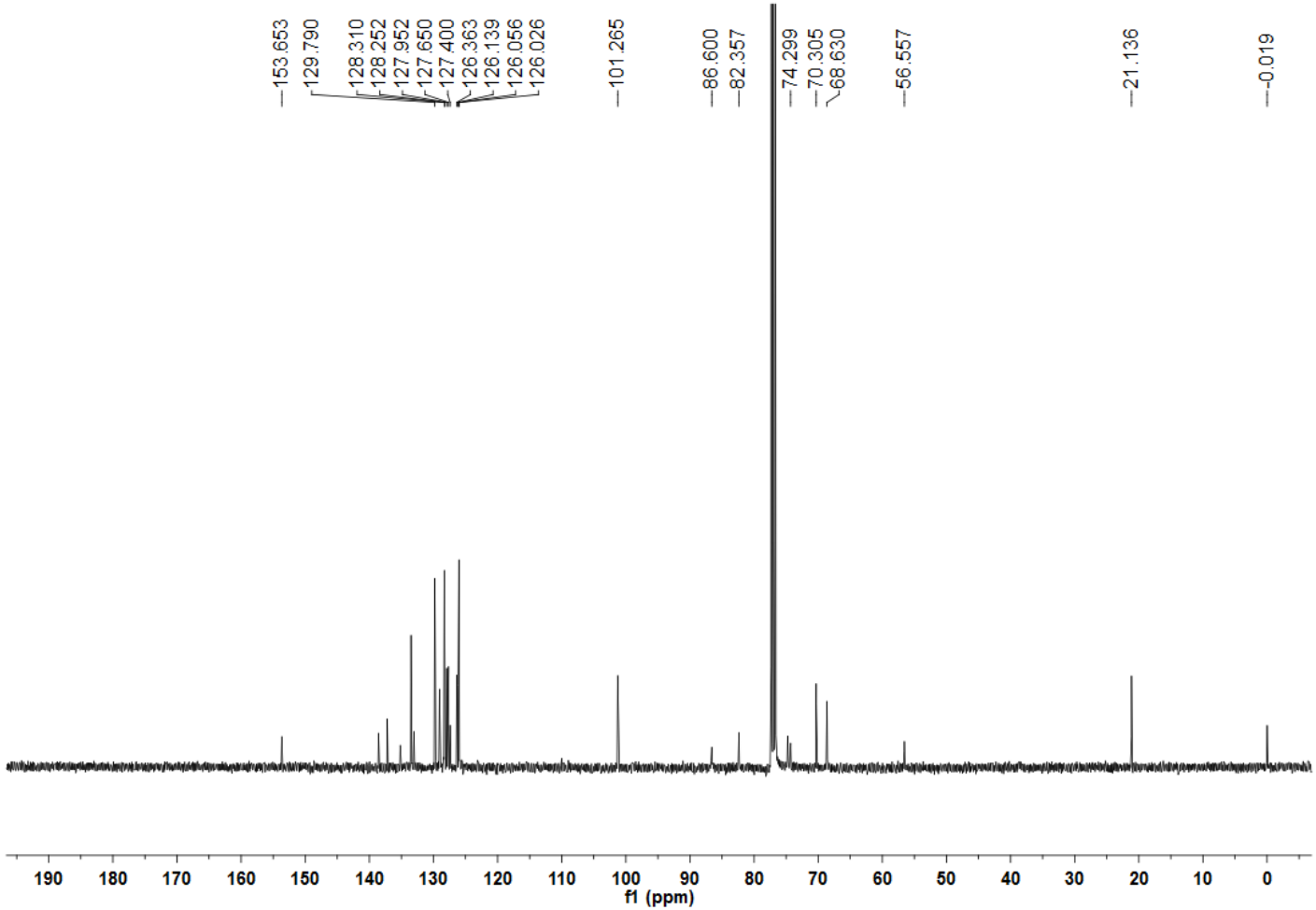
^{13}C 100 MHz NMR spectrum of *p*-Tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-*β*-D-glucopyranoside (1):



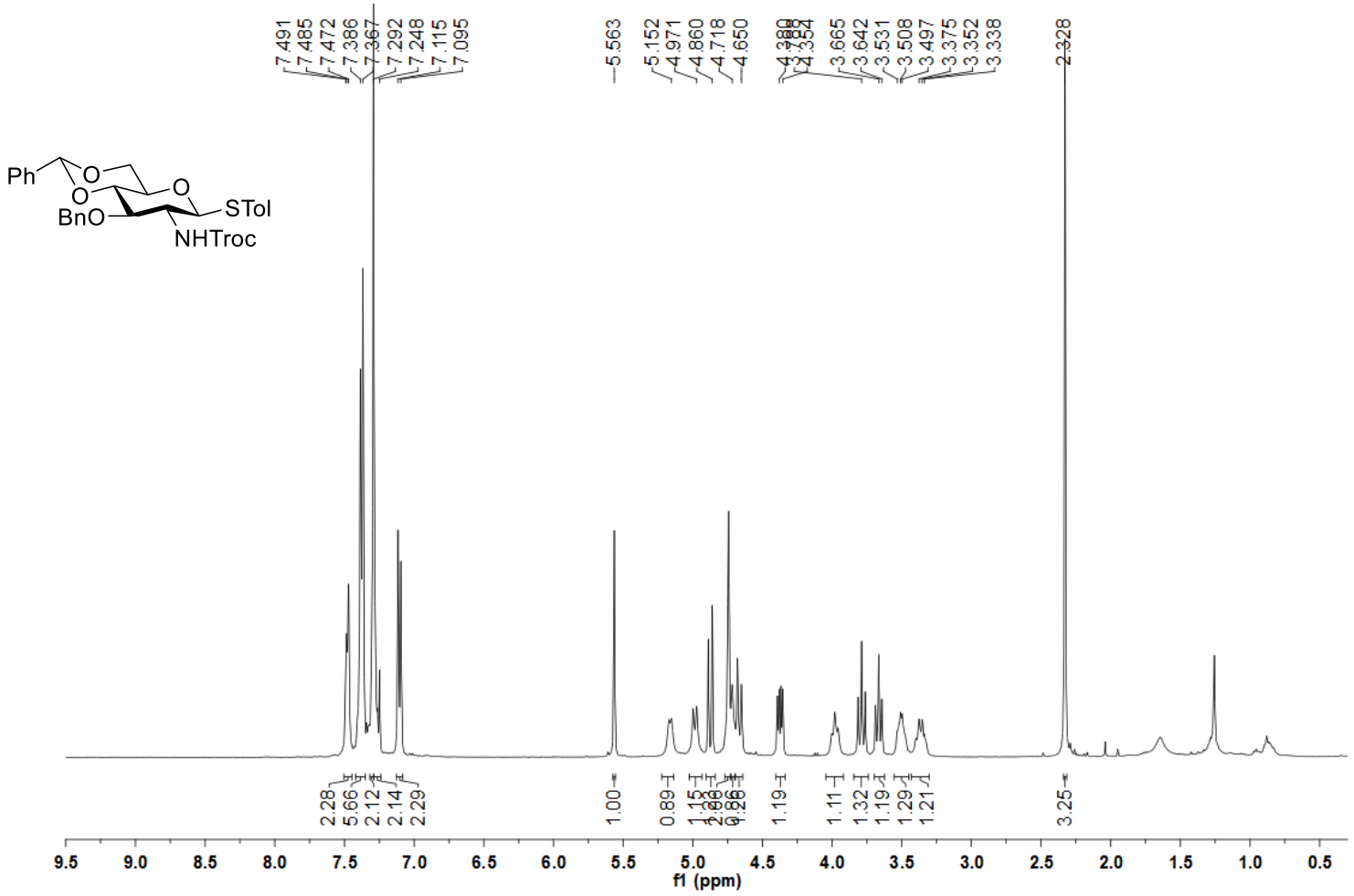
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4,6-*O*-Benzylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (2)



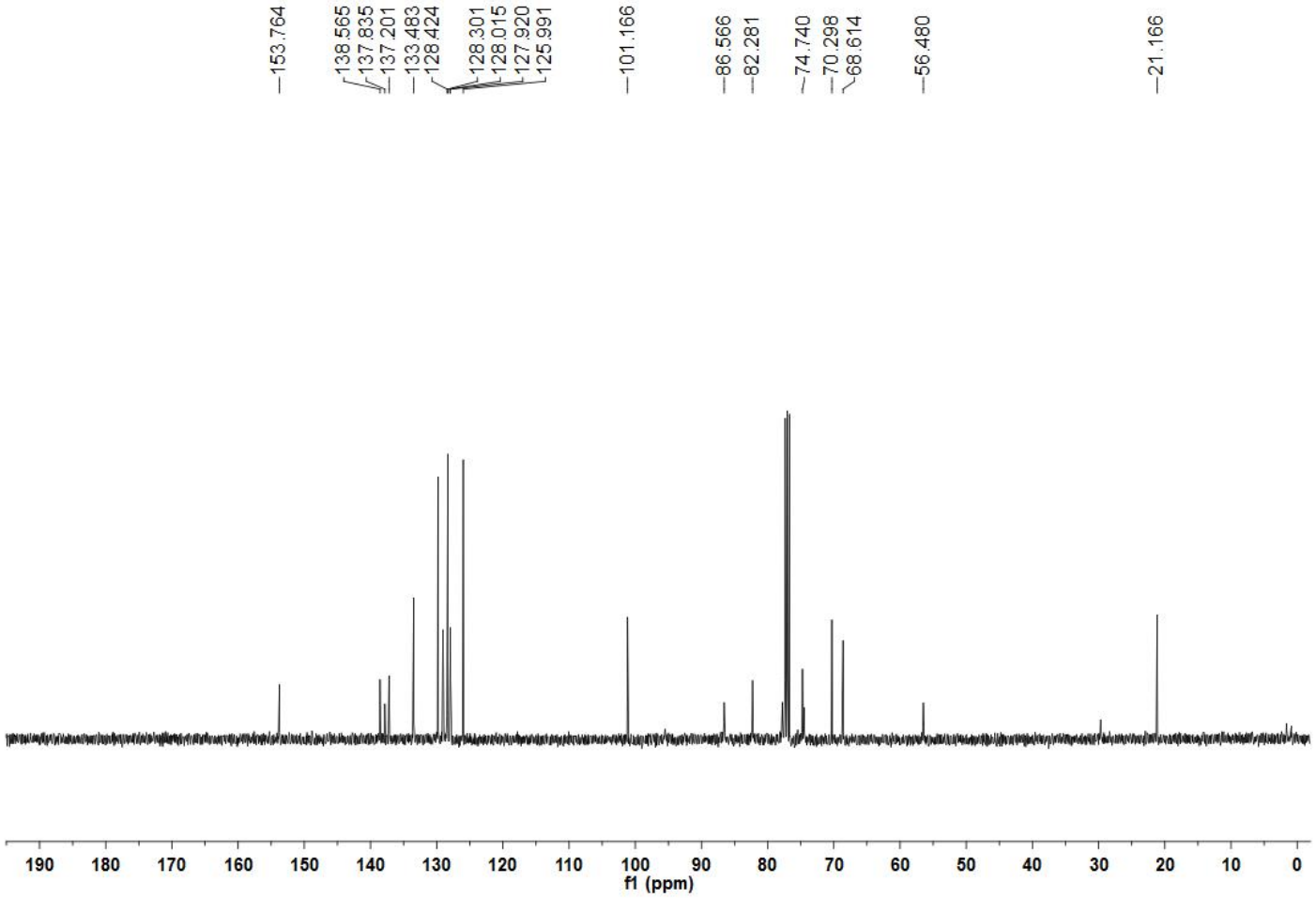
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4,6-*O*-Benzylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (2)



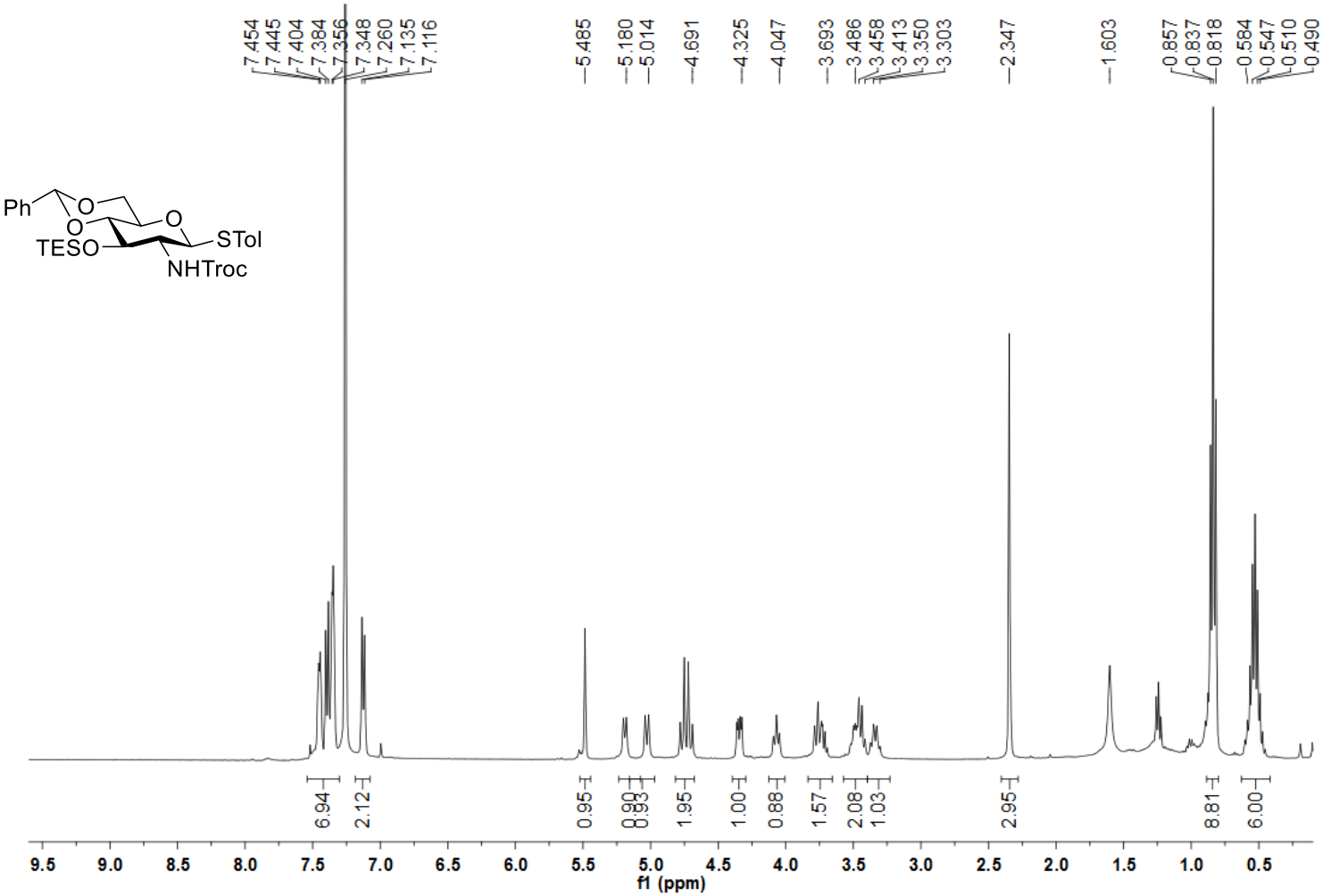
^{1}H 400 MHz NMR spectrum *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6):



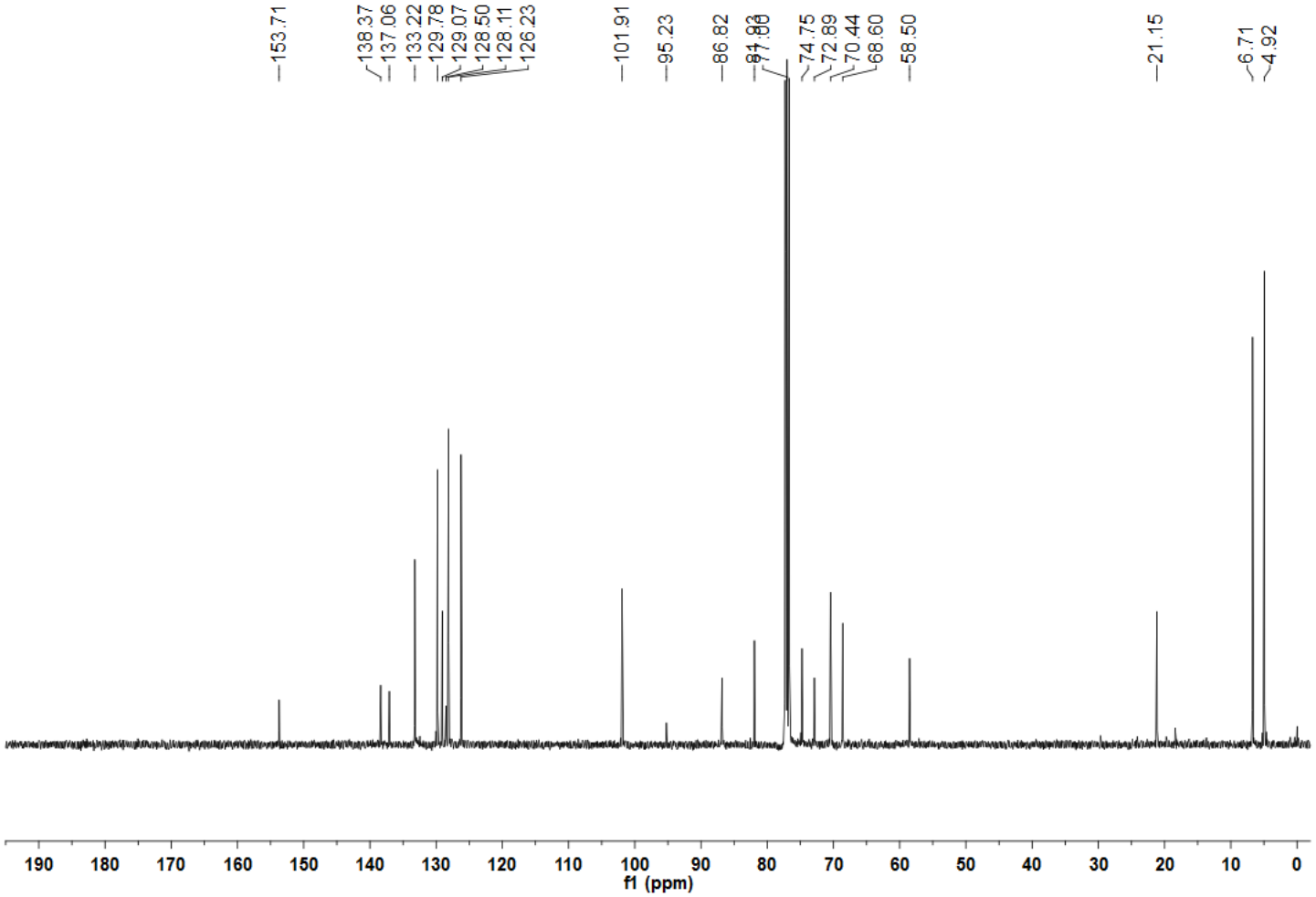
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6):



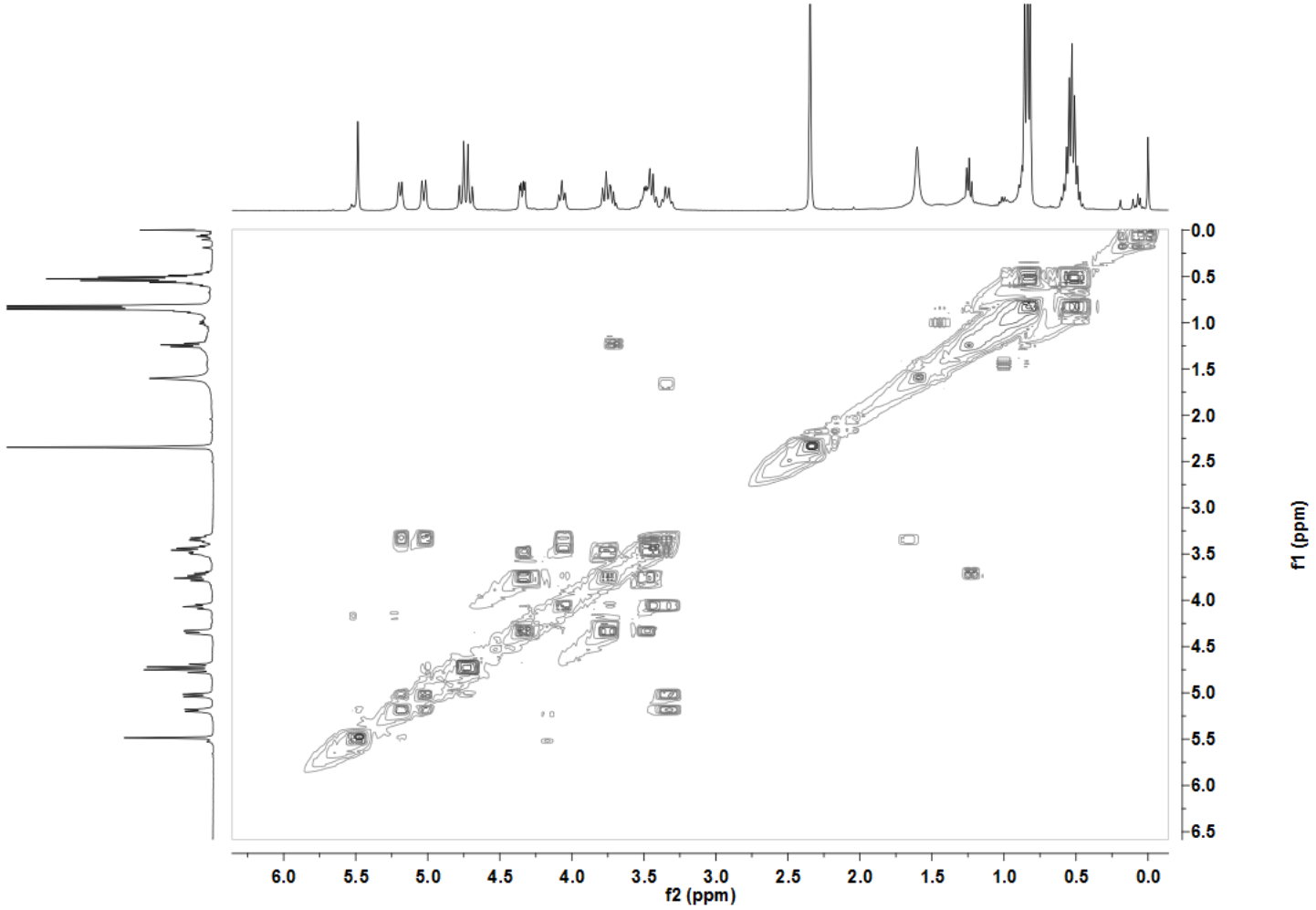
^{1}H 400 MHz NMR spectrum of of *p*-tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-3-*O*-triethylsilyl-1-thio-β-D-glucopyranoside (4):



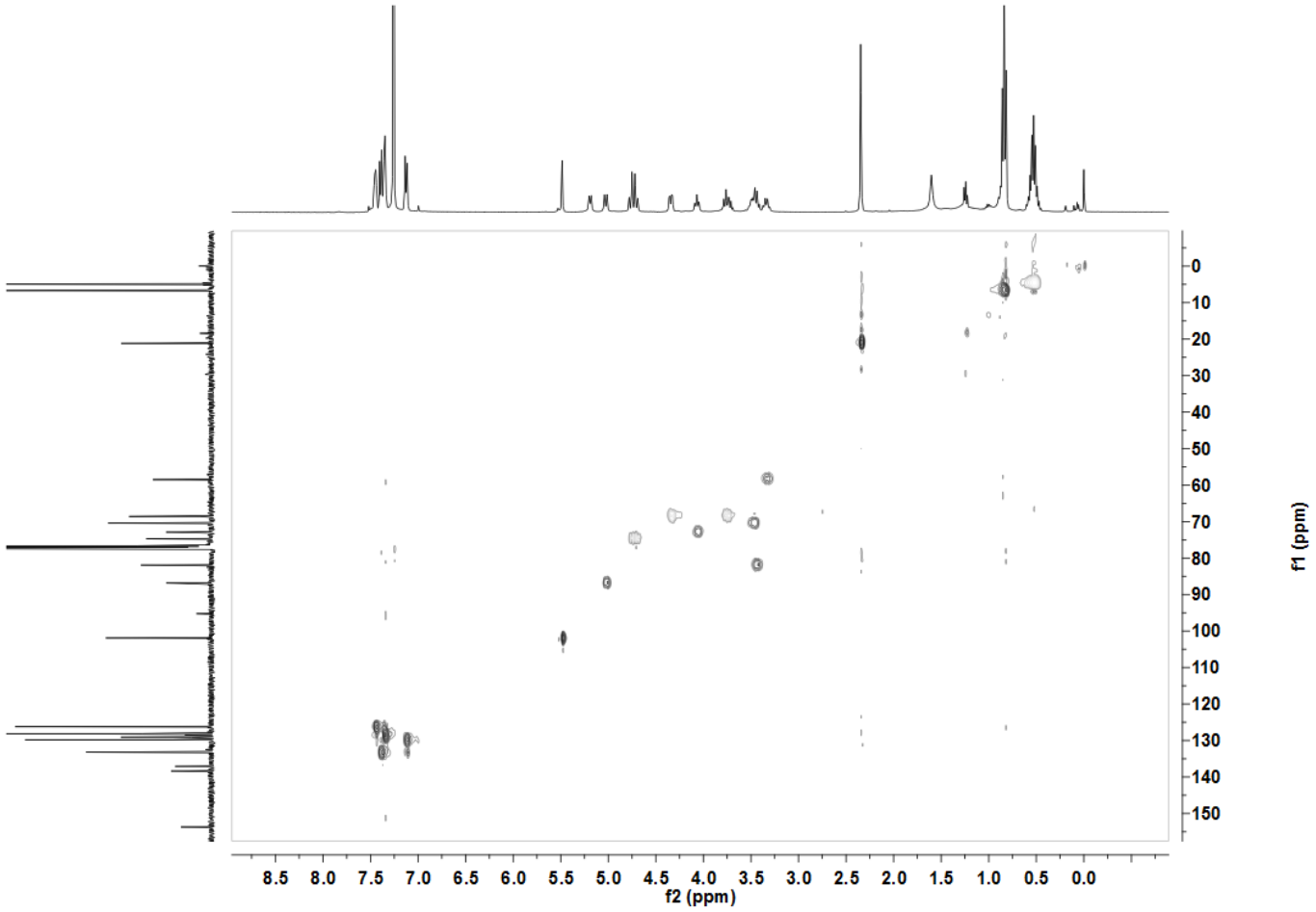
^{13}C 100 MHz NMR spectrum of of *p*-tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-3-*O*-triethylsilyl-1-thio-β-D-glucopyranoside (4):



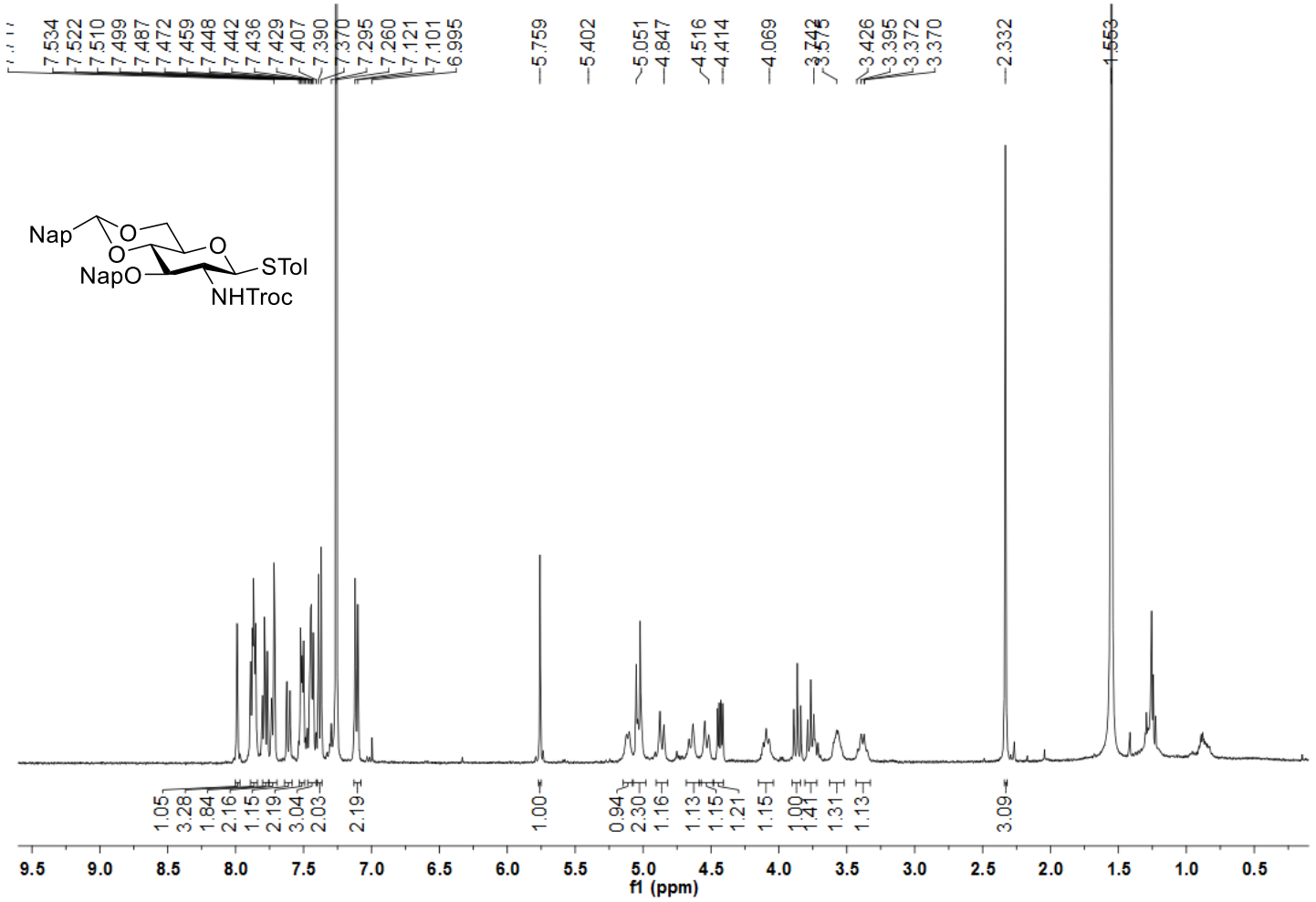
COSY NMR spectrum of *p*-tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-3-*O*-triethylsilyl-1-thio-β-D-glucopyranoside (4):



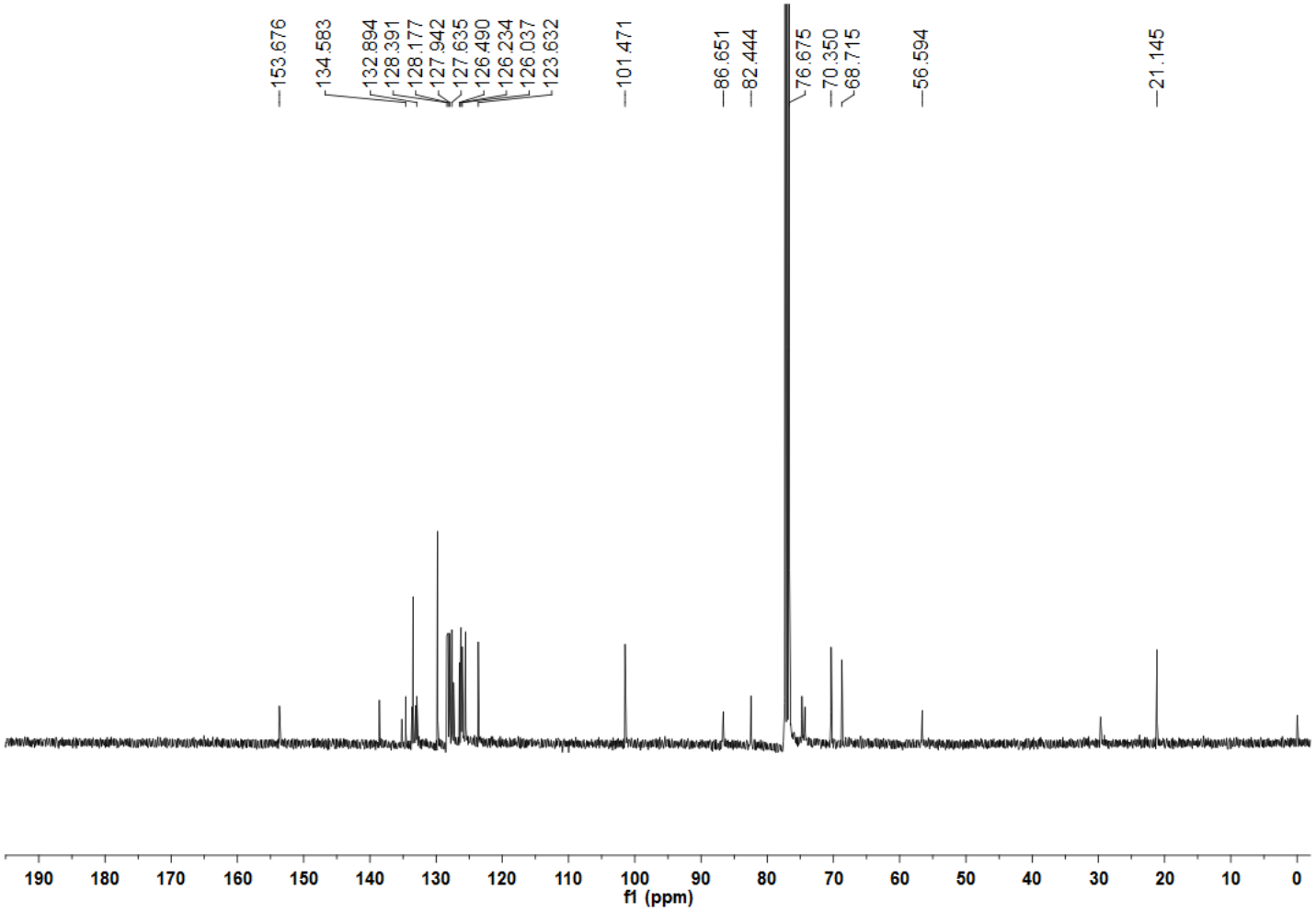
HSQC NMR spectrum of *p*-tolyl 4,6-*O*-Benzylidene-2-*N*-trichloroethoxycarbonyl-3-*O*-triethylsilyl-1-thio-β-D-glucopyranoside (4):



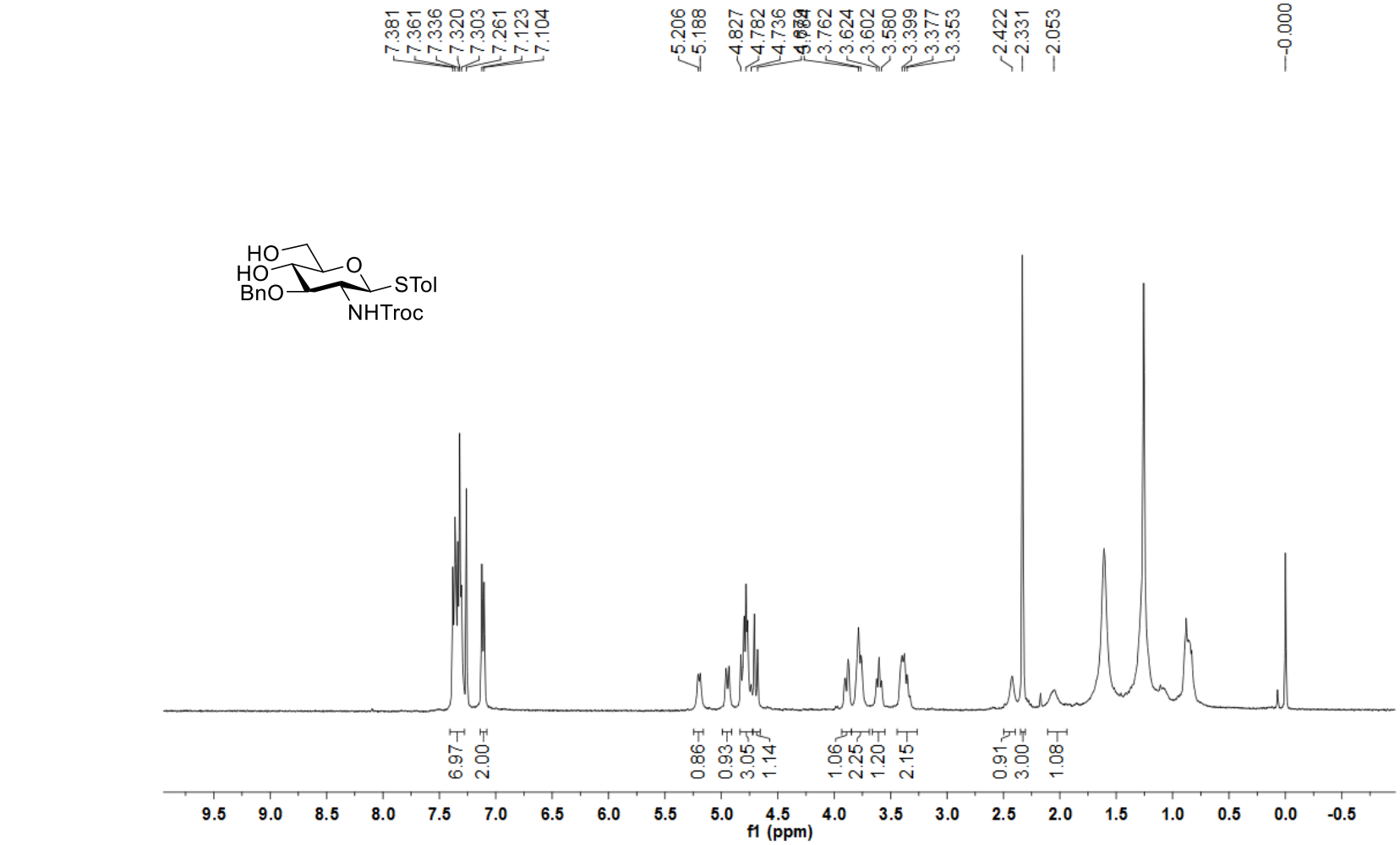
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4,6-*O*-Naphthylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (3):



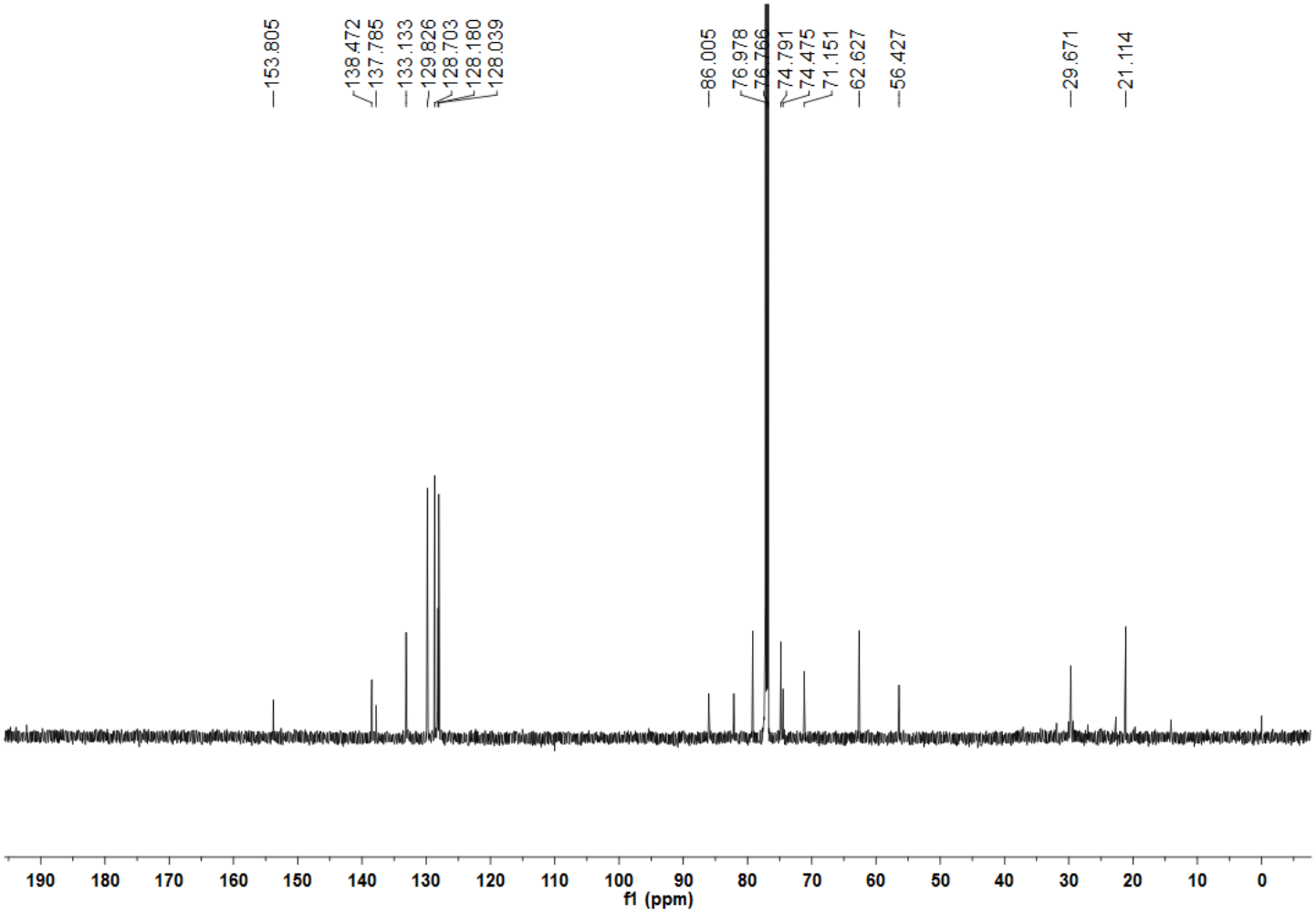
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4,6-*O*-Naphthylidene-3-*O*-(2-naphthylmethyl)-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (3):



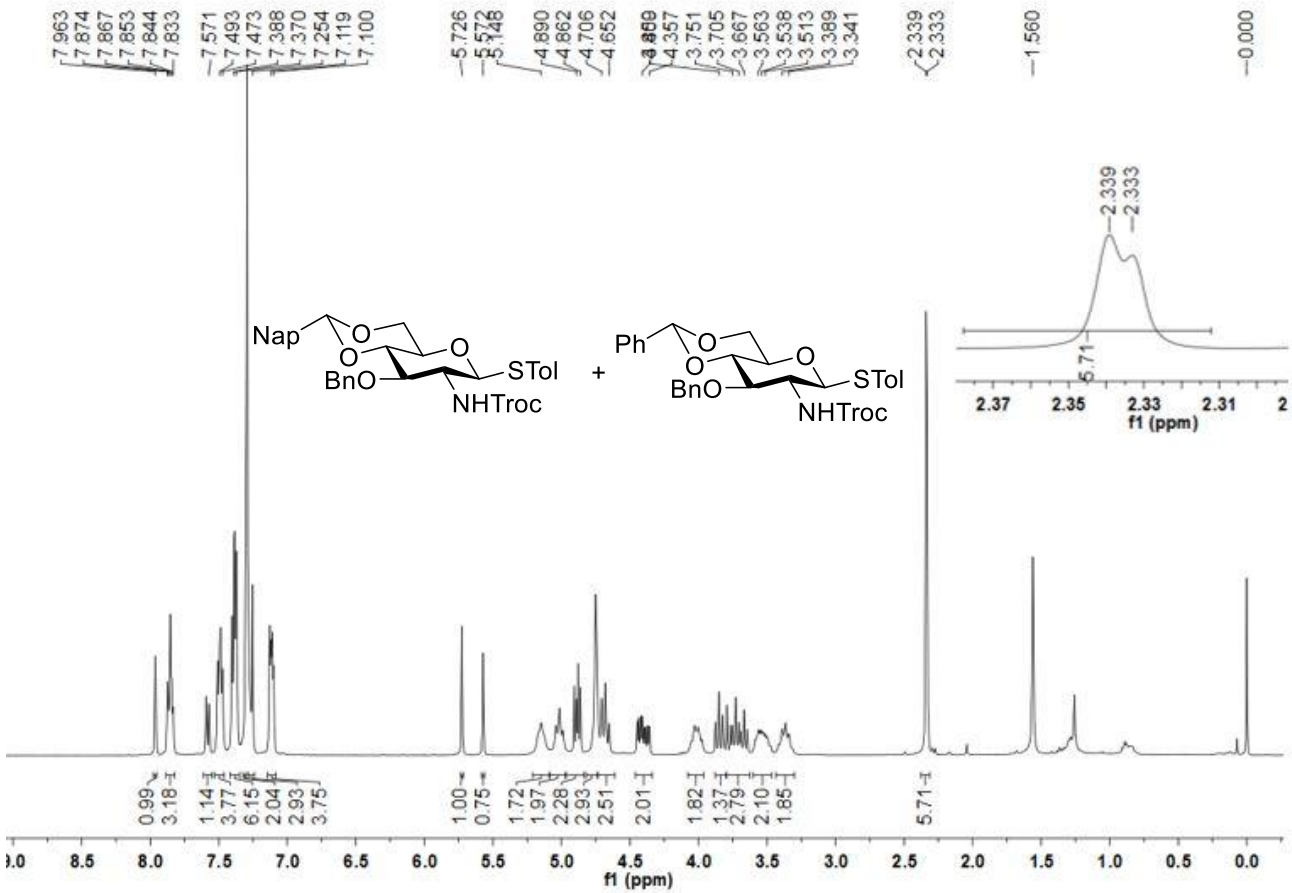
^{1}H 400 MHz NMR spectrum of *p*-Tolyl 3-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (7):



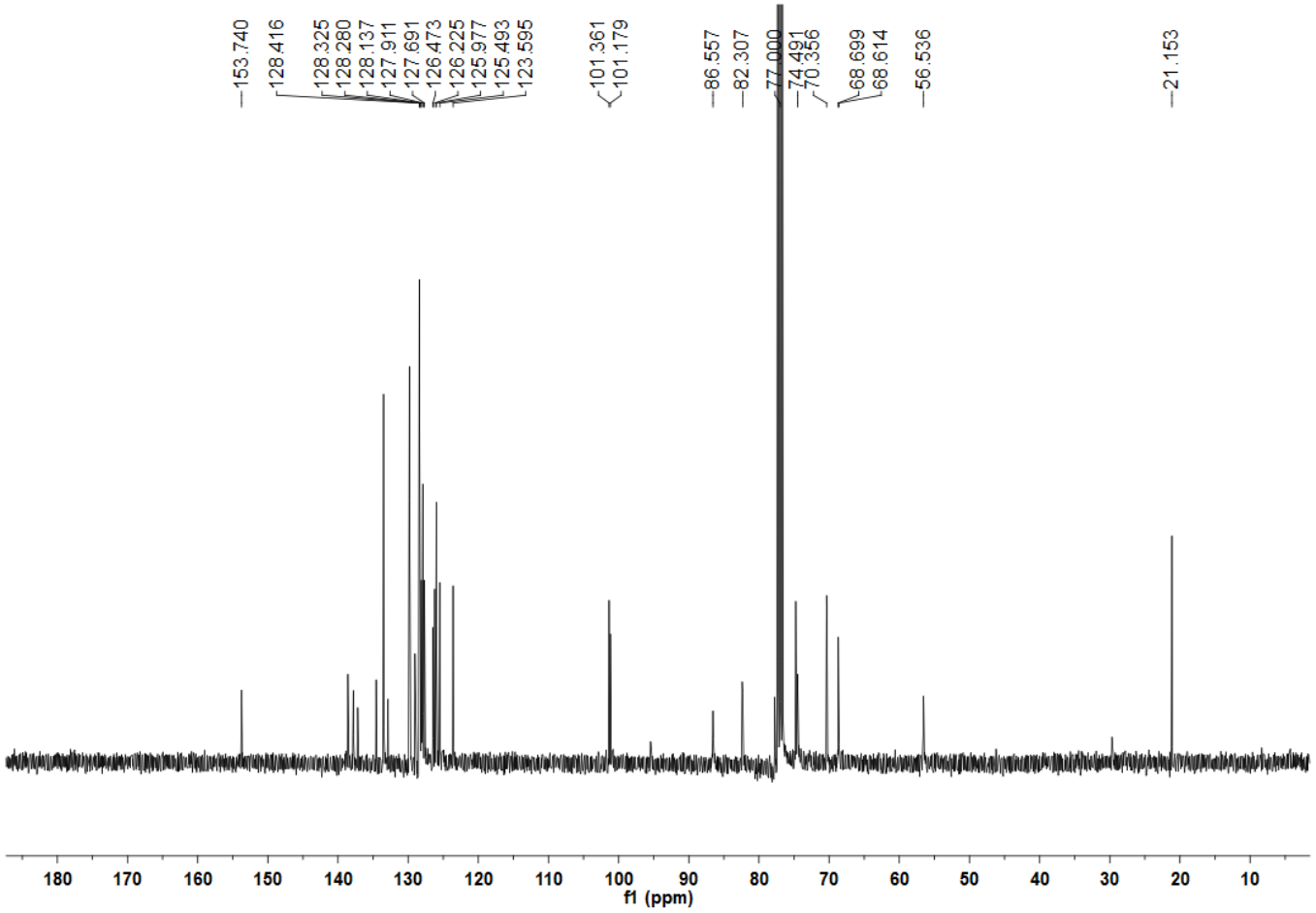
^{13}C 100 MHz NMR spectrum of *p*-Tolyl 3-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (7):



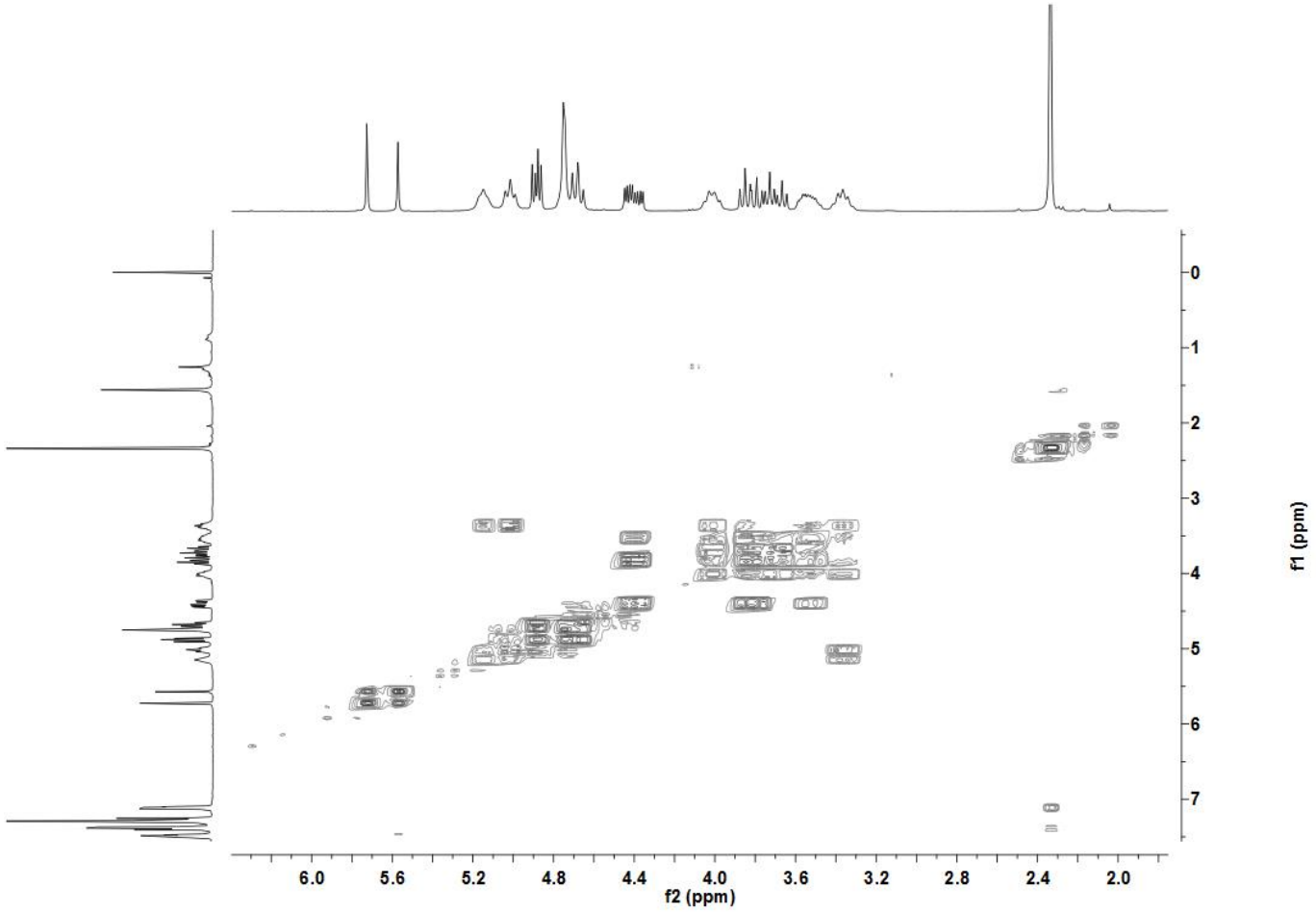
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6) and *p*-Tolyl 3-*O*-Benzyl-4,6-*O*--naphthylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (8):



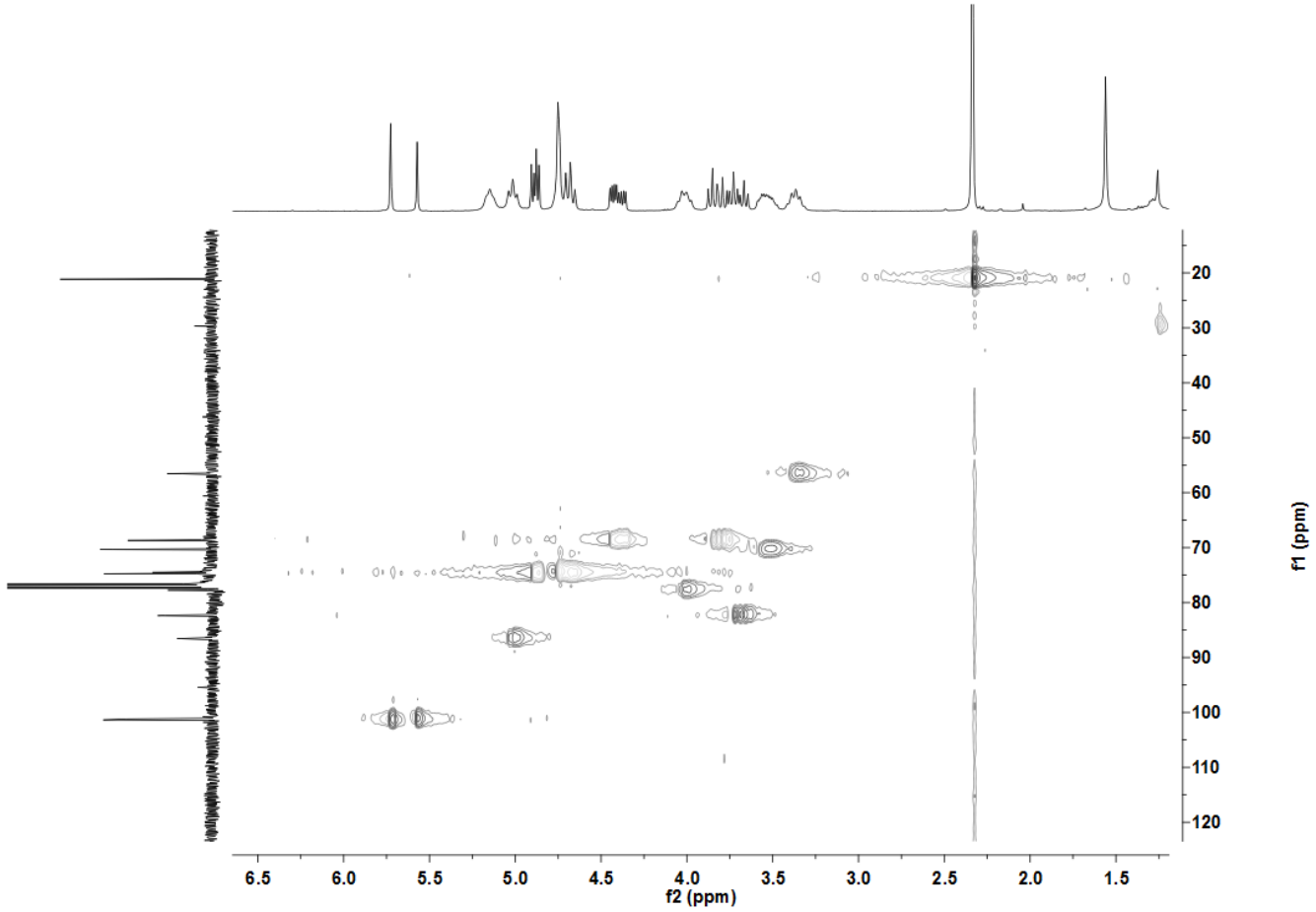
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6) and *p*-Tolyl 3-*O*-Benzyl-4,6-*O*--naphthylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (8):



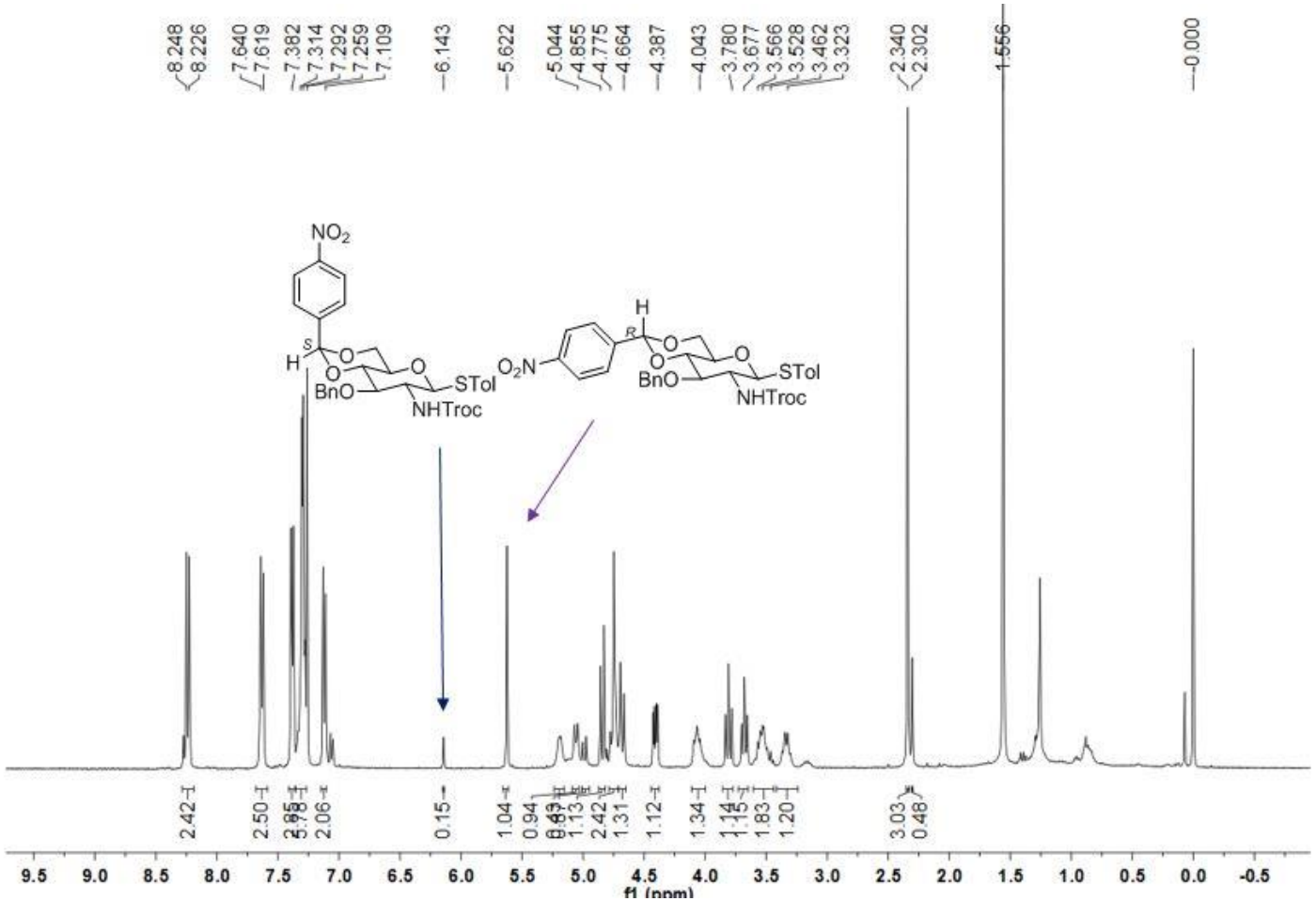
COSY NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6) and *p*-Tolyl 3-*O*-Benzyl-4,6-*O*--naphthylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (8):



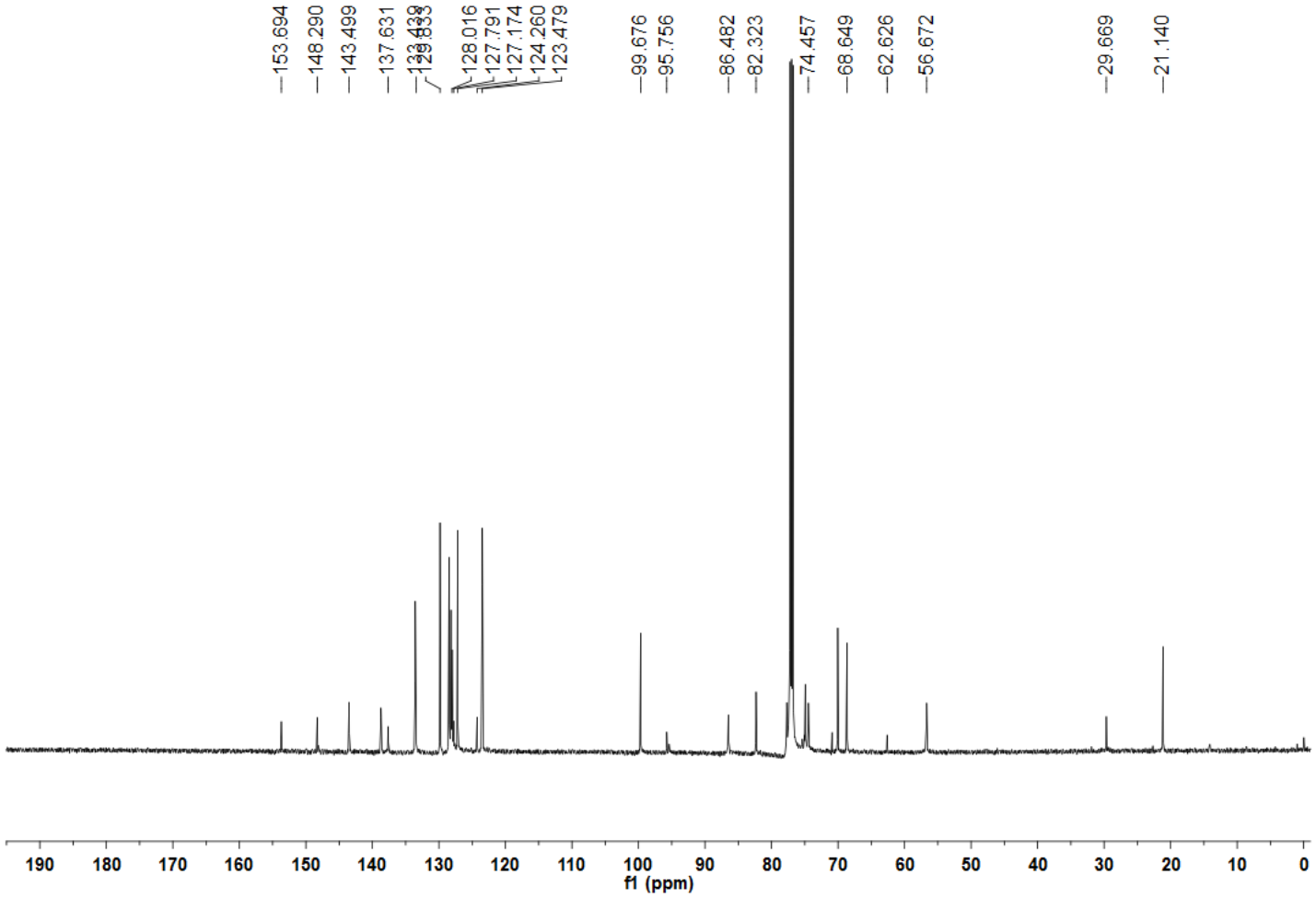
HSQC NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-benzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (6) and *p*-Tolyl 3-*O*-Benzyl-4,6-*O*--naphthylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (8):



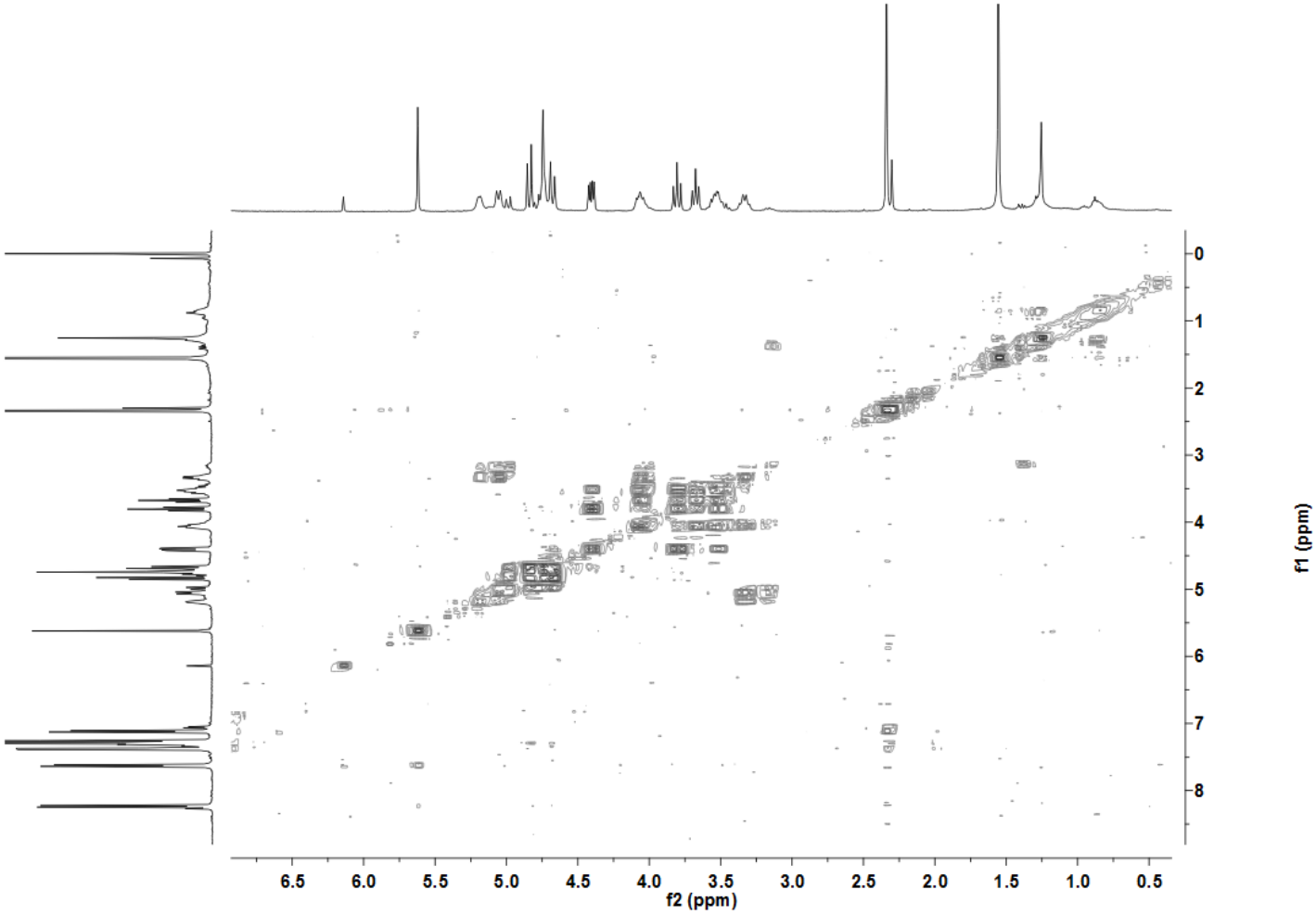
^{1}H 600 MHz NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-*p*-nitrobenzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (9):



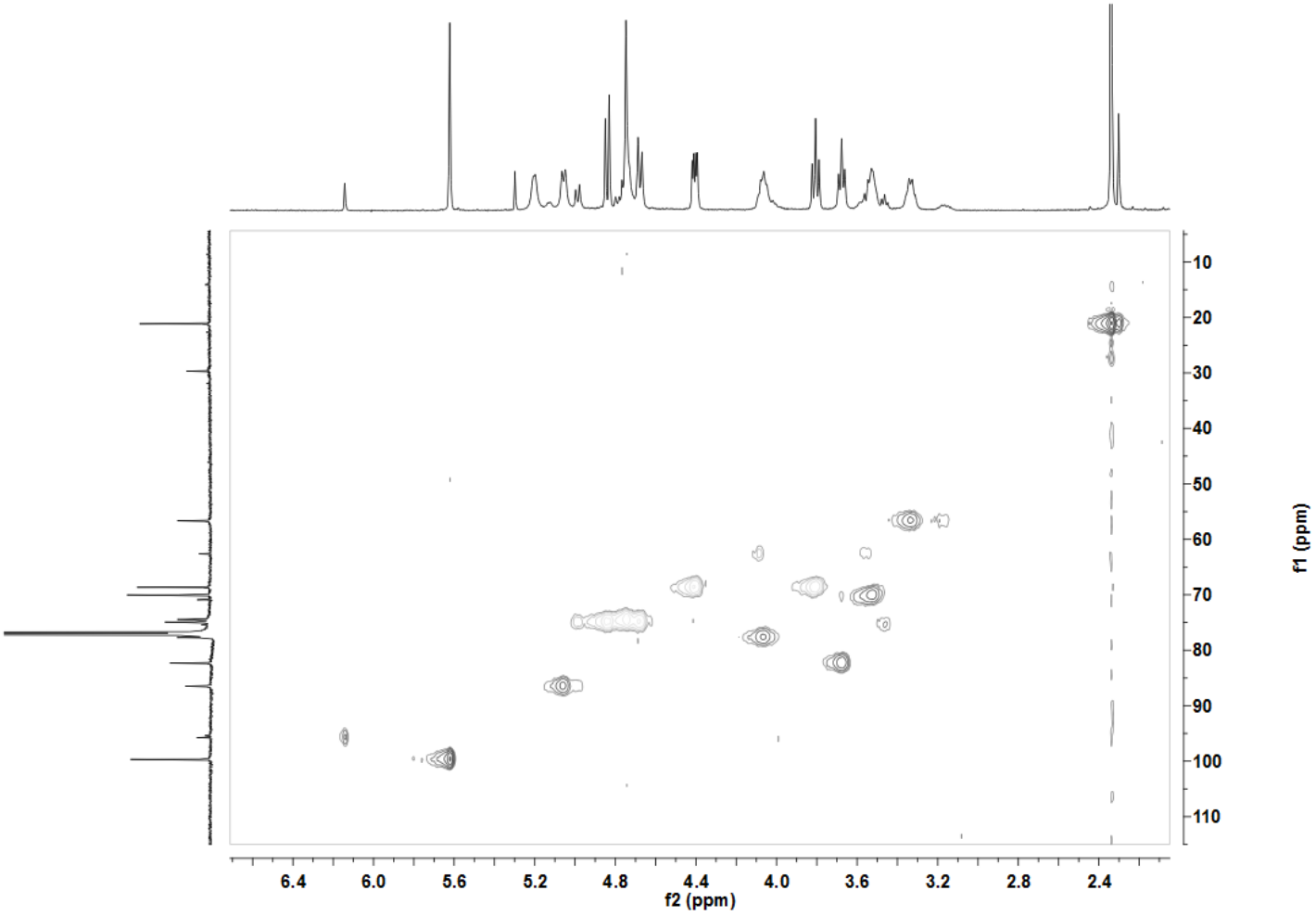
^{13}C 150 MHz NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-*p*-nitrobenzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (9):



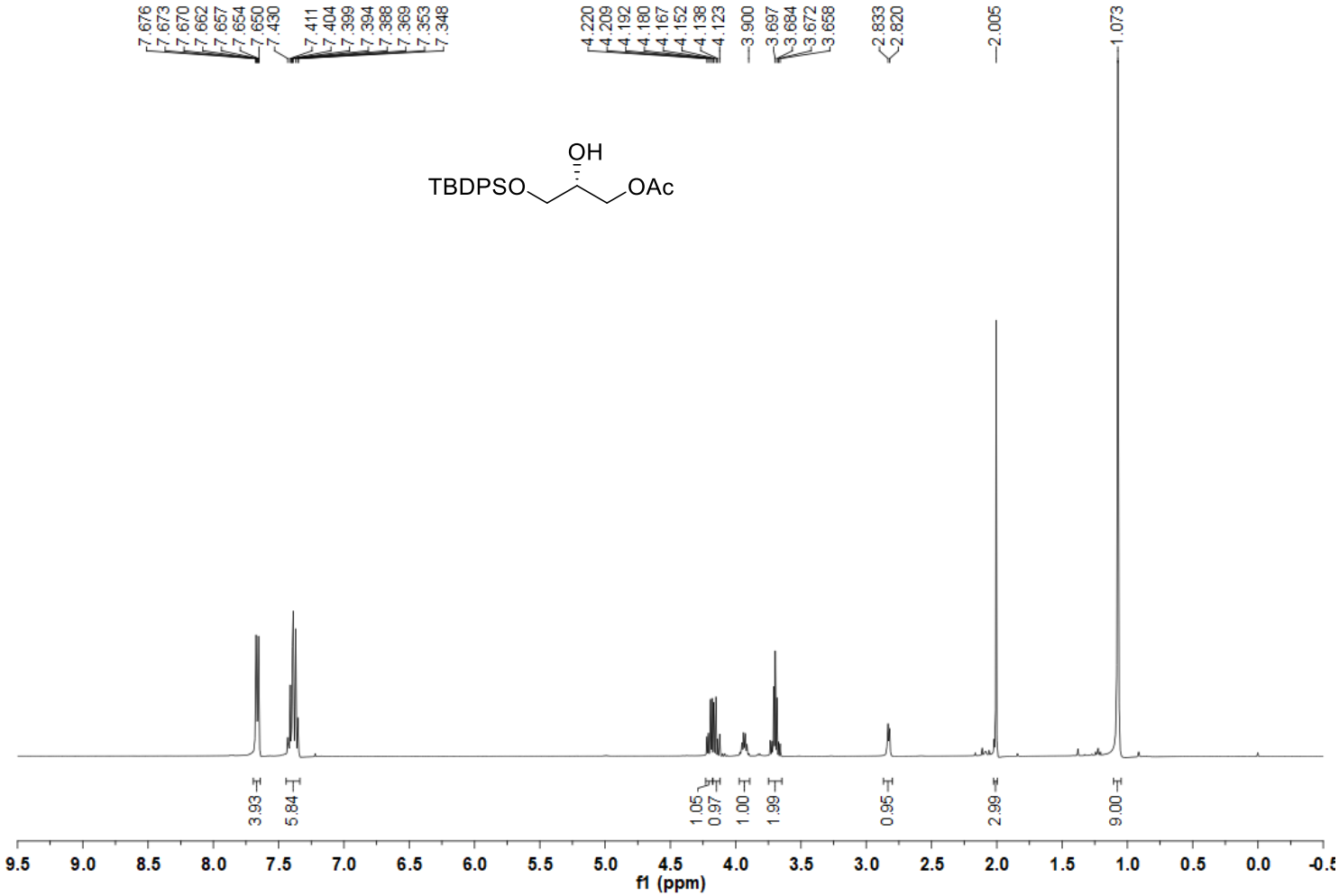
COSY NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-*p*-nitrobenzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (9):



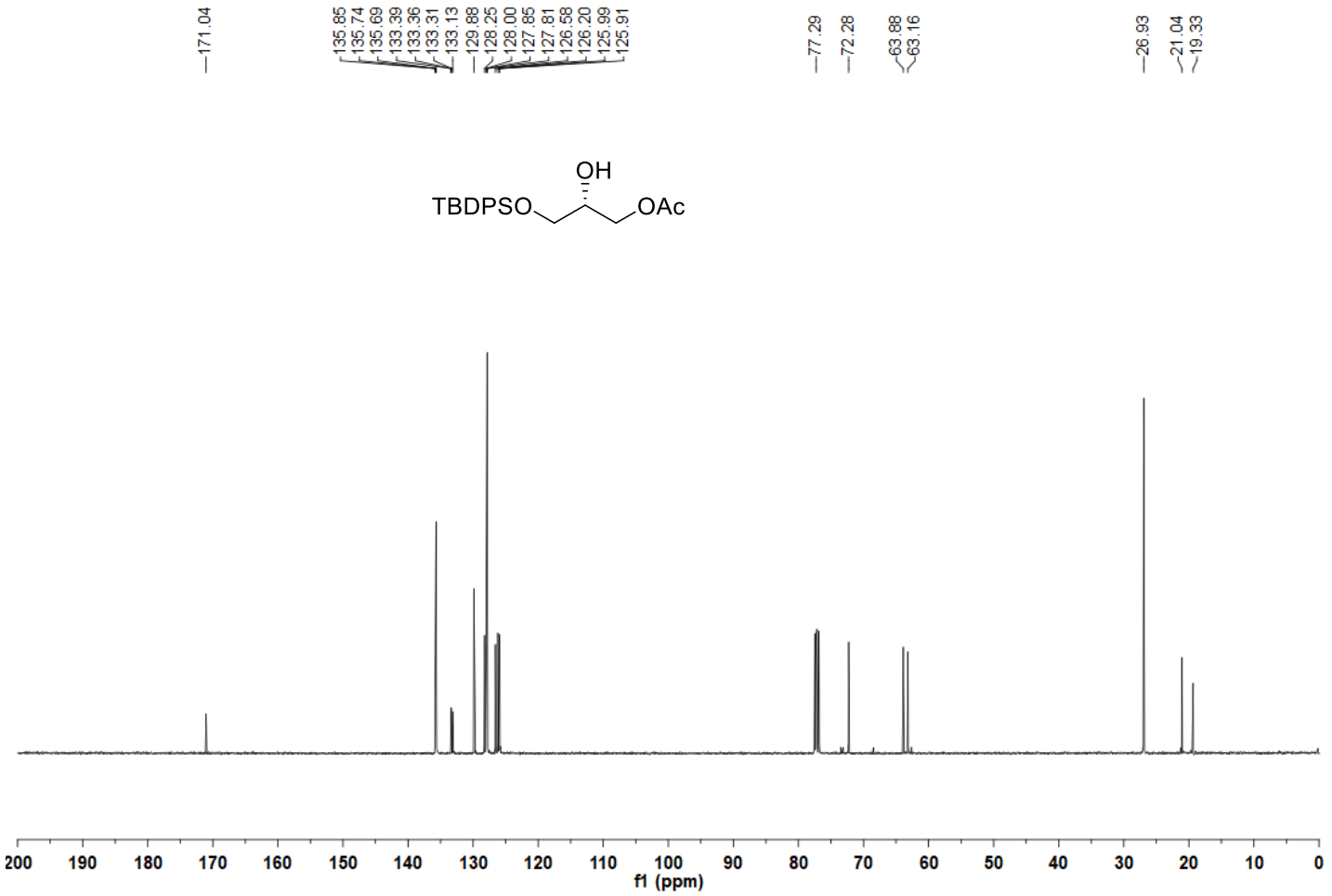
HSQC NMR spectrum of *p*-tolyl 3-*O*-Benzyl-4,6-*O*-*p*-nitrobenzylidene-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (9):



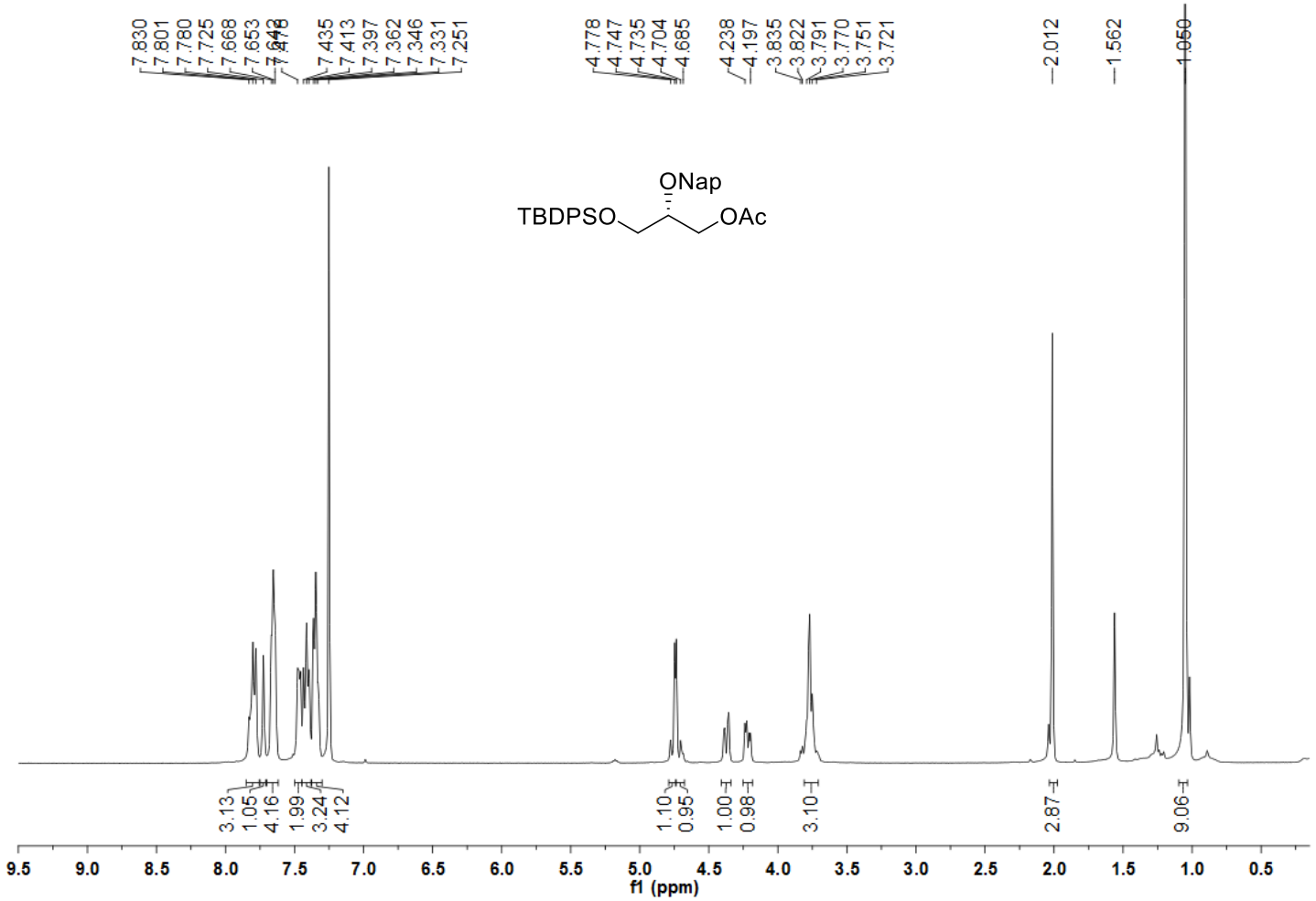
^{1}H 400 MHz NMR spectrum of (2*R*)-1-Acetyl-3-*tert*-butyldiphenylsilyl *sn*-glycerol (10a):



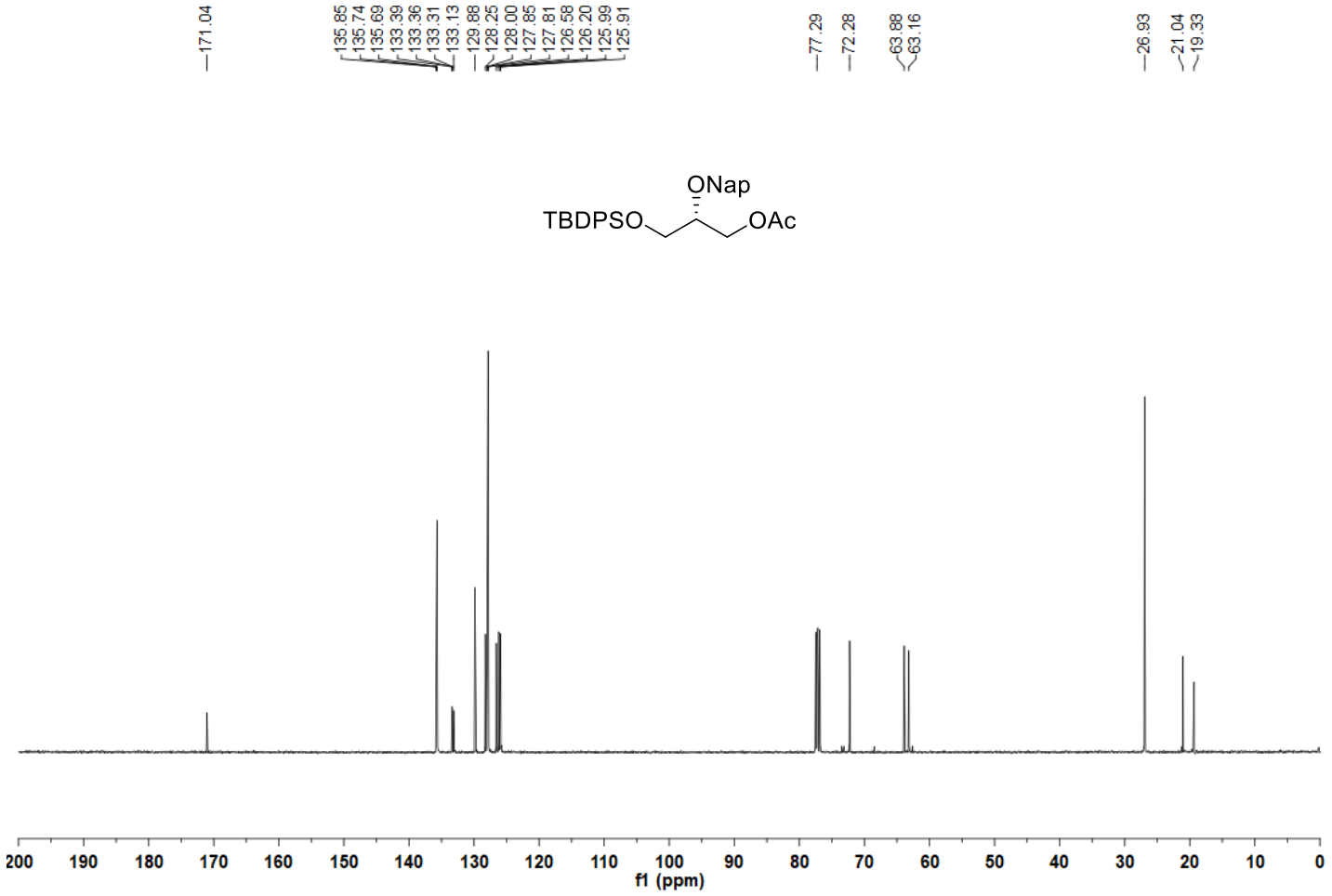
^{13}C 400 MHz NMR spectrum of (2*R*)-1-Acetyl-3-*tert*-butyldiphenylsilyl *sn*-glycerol (10a):



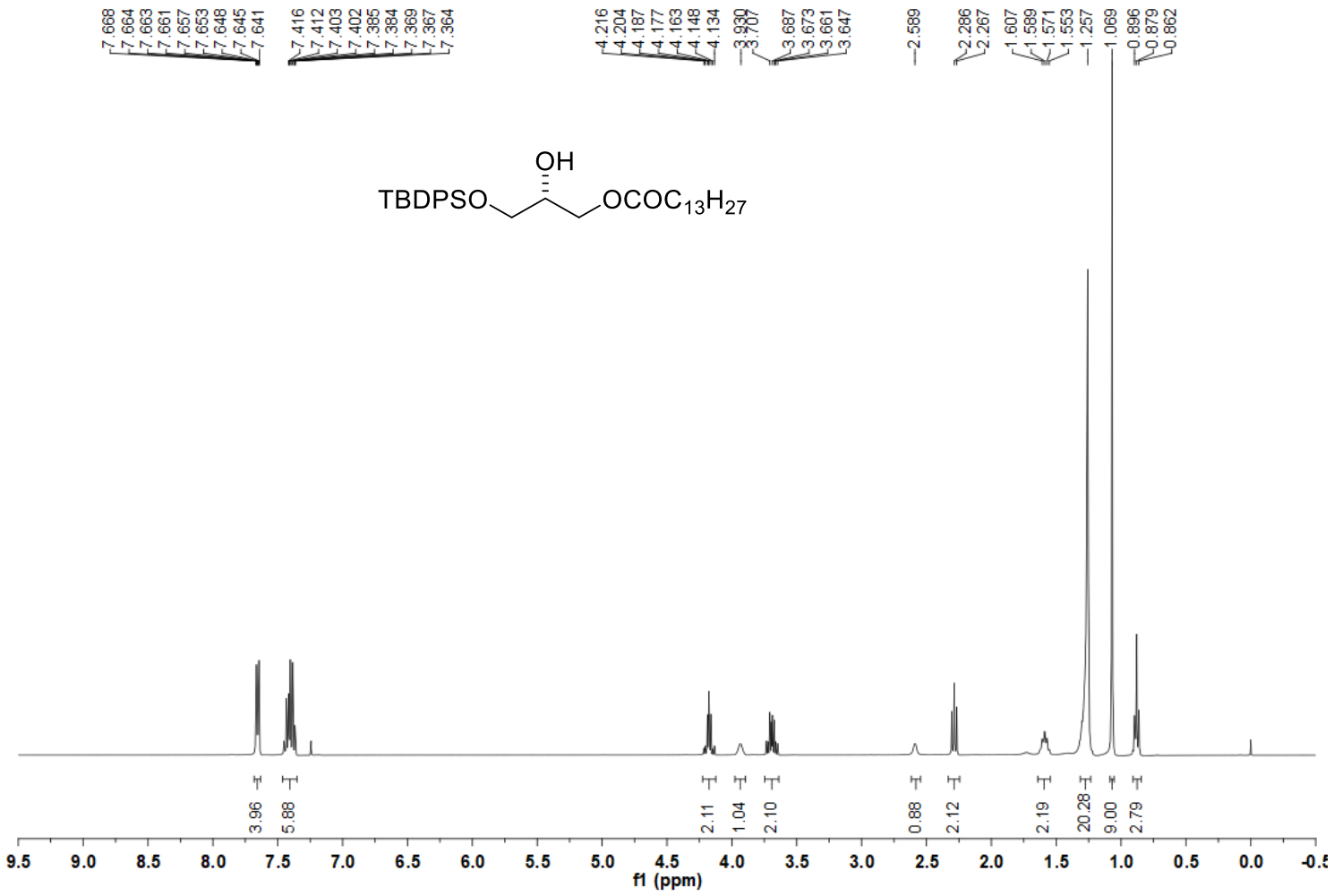
^{1}H 400 MHz NMR spectrum of (2*R*)-1-acetyl-3-*tert*-butyldiphenylsilyl-2-(2-naphthylmethyl)-*sn*-glycerol (12a)



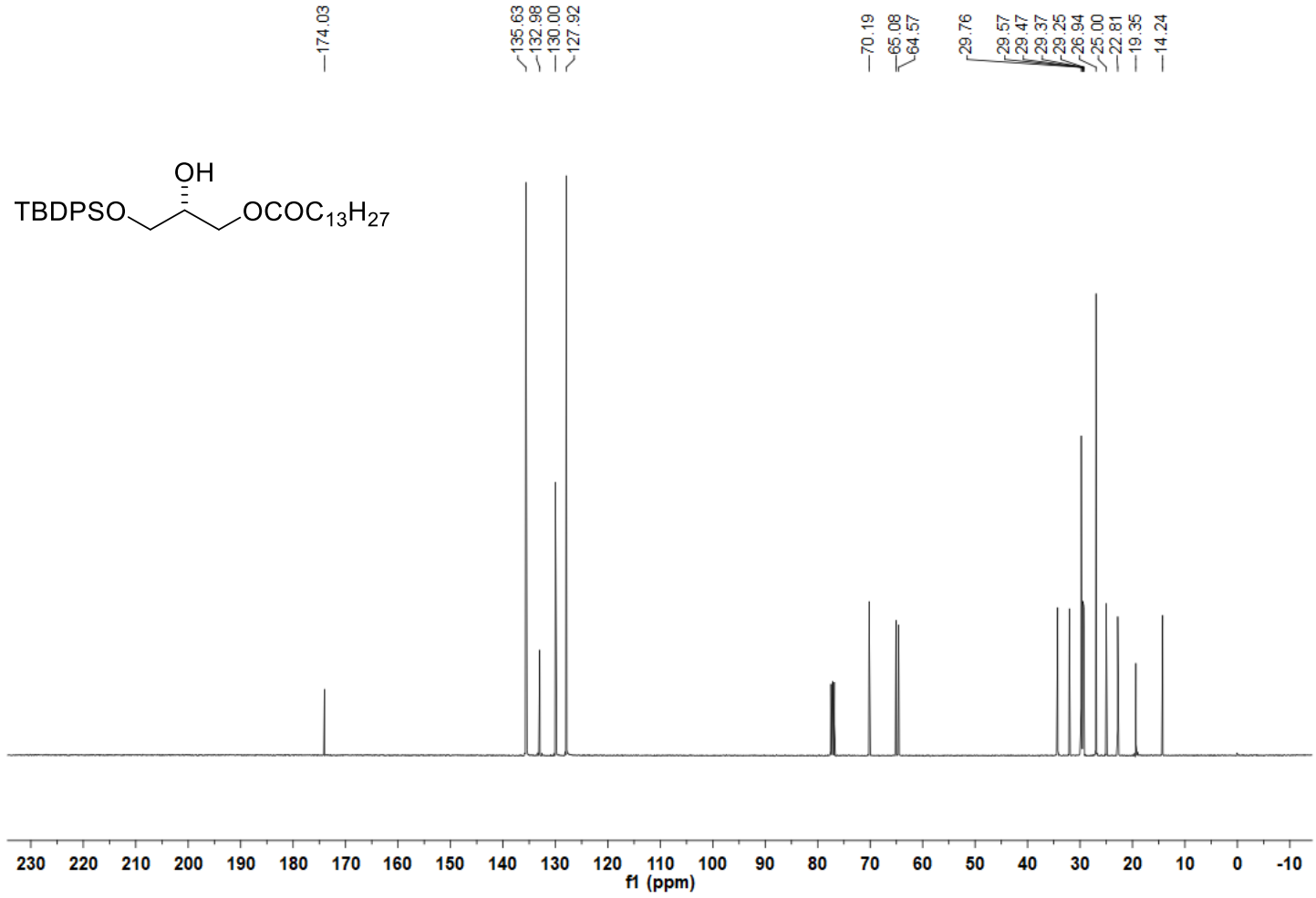
^{13}C 100 MHz NMR spectrum of (2*R*)-1-acetyl-3-*tert*-butyldiphenylsilyl-2-(2-naphthylmethyl)-*sn*-glycerol (12a)



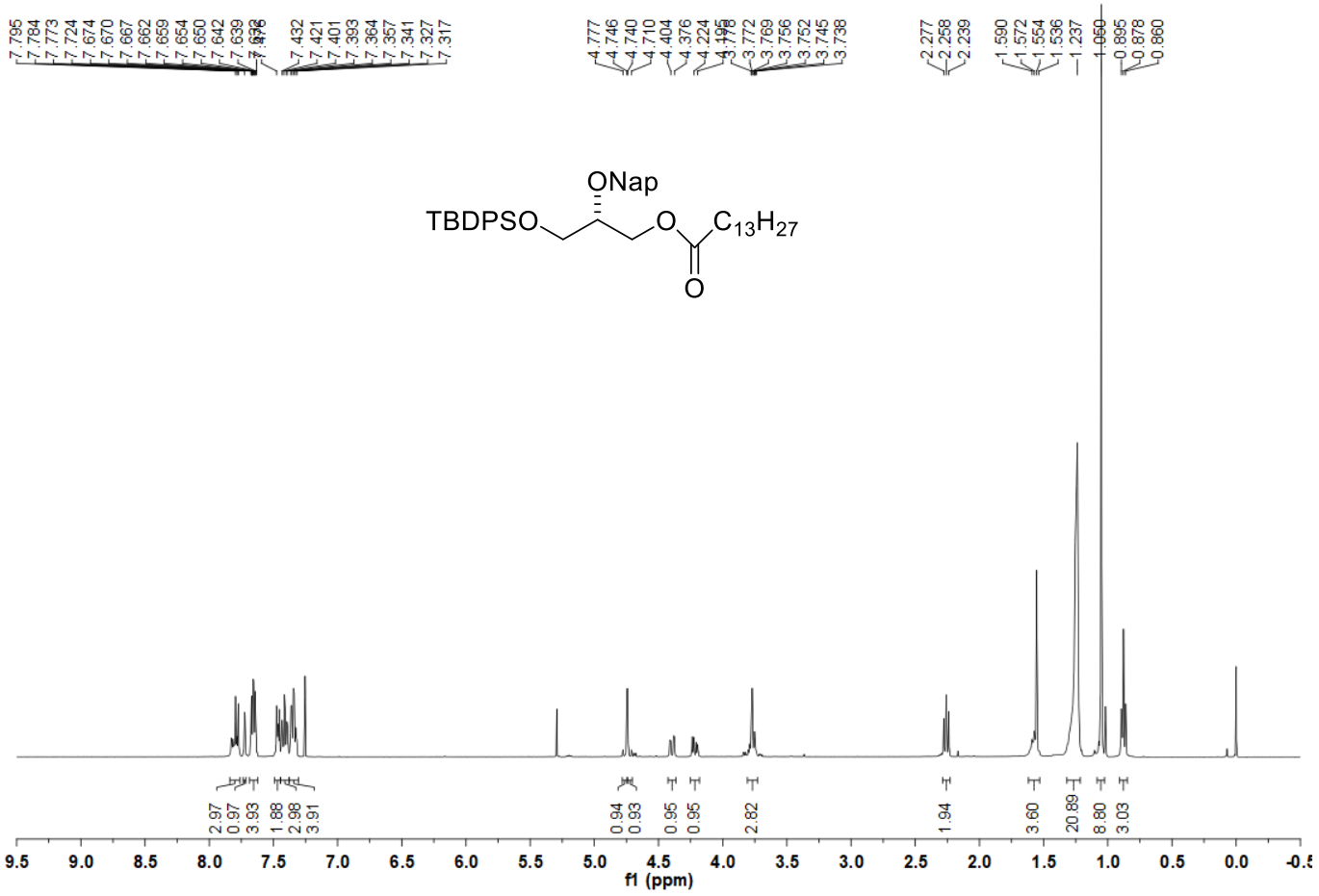
^{1}H 400 MHz NMR spectrum of (2*R*)-3-*tert*-butyldiphenylsilyl-1-myristoyl *sn*-glycerol (10b):



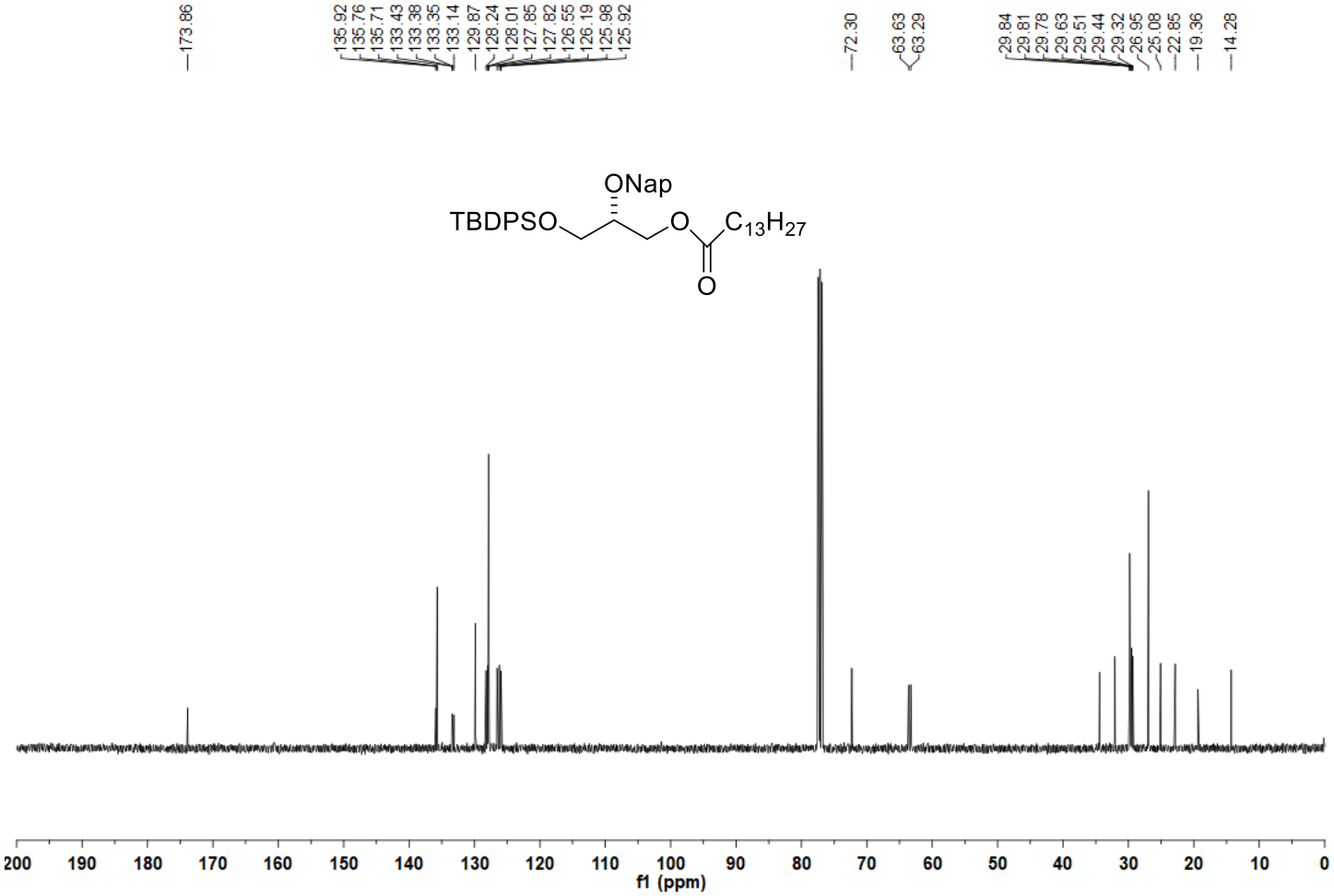
^{13}C 400 MHz NMR spectrum of (2*R*)-3-*tert*-butyldiphenylsilyl-1-myristoyl *sn*-glycerol (10b):



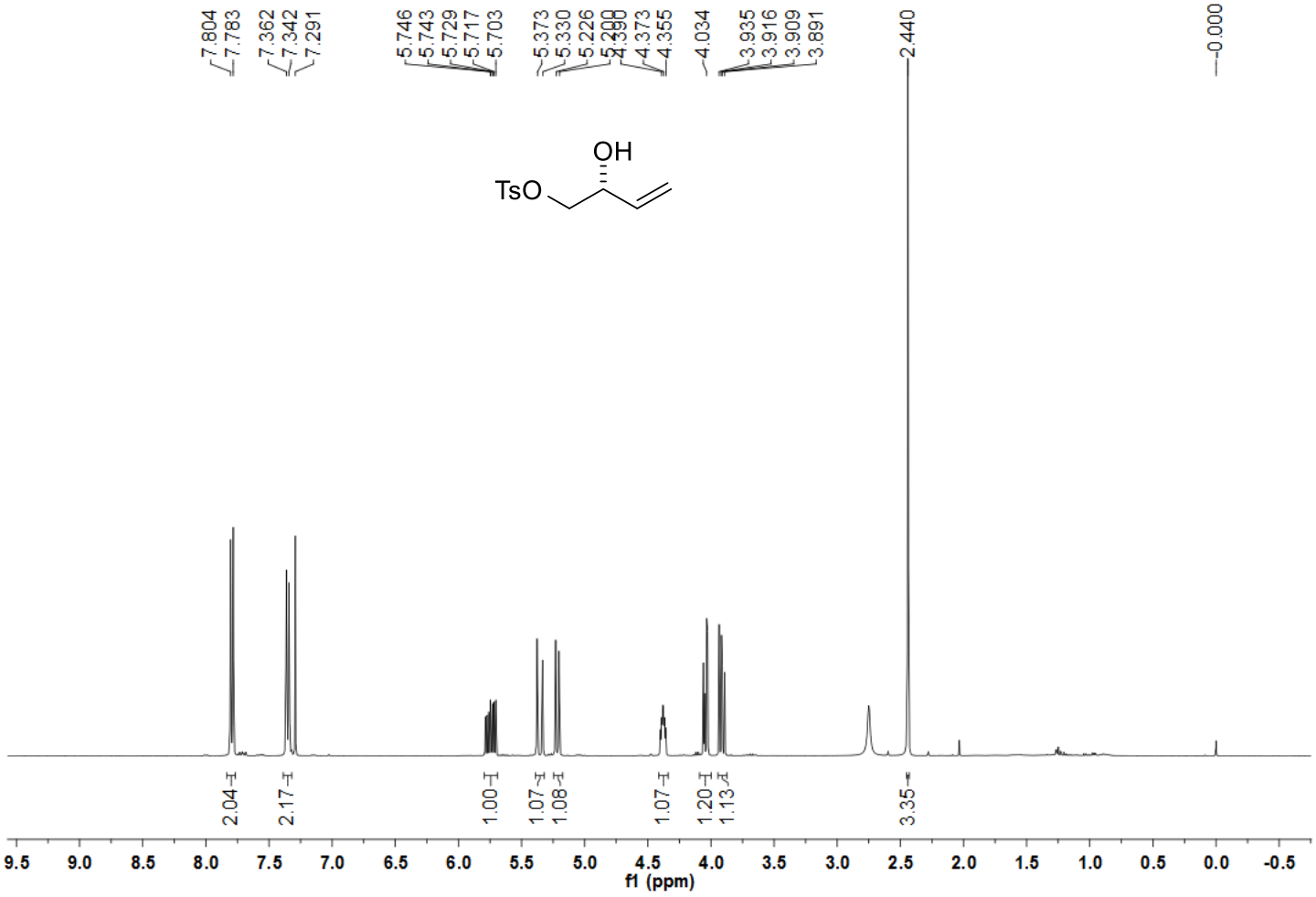
^{1}H 400 MHz NMR spectrum of (2*R*)-3-*tert*-butyldiphenylsilyl-1-myristoyl-2-(2-naphthylmethyl)-*sn*-glycerol (12b):



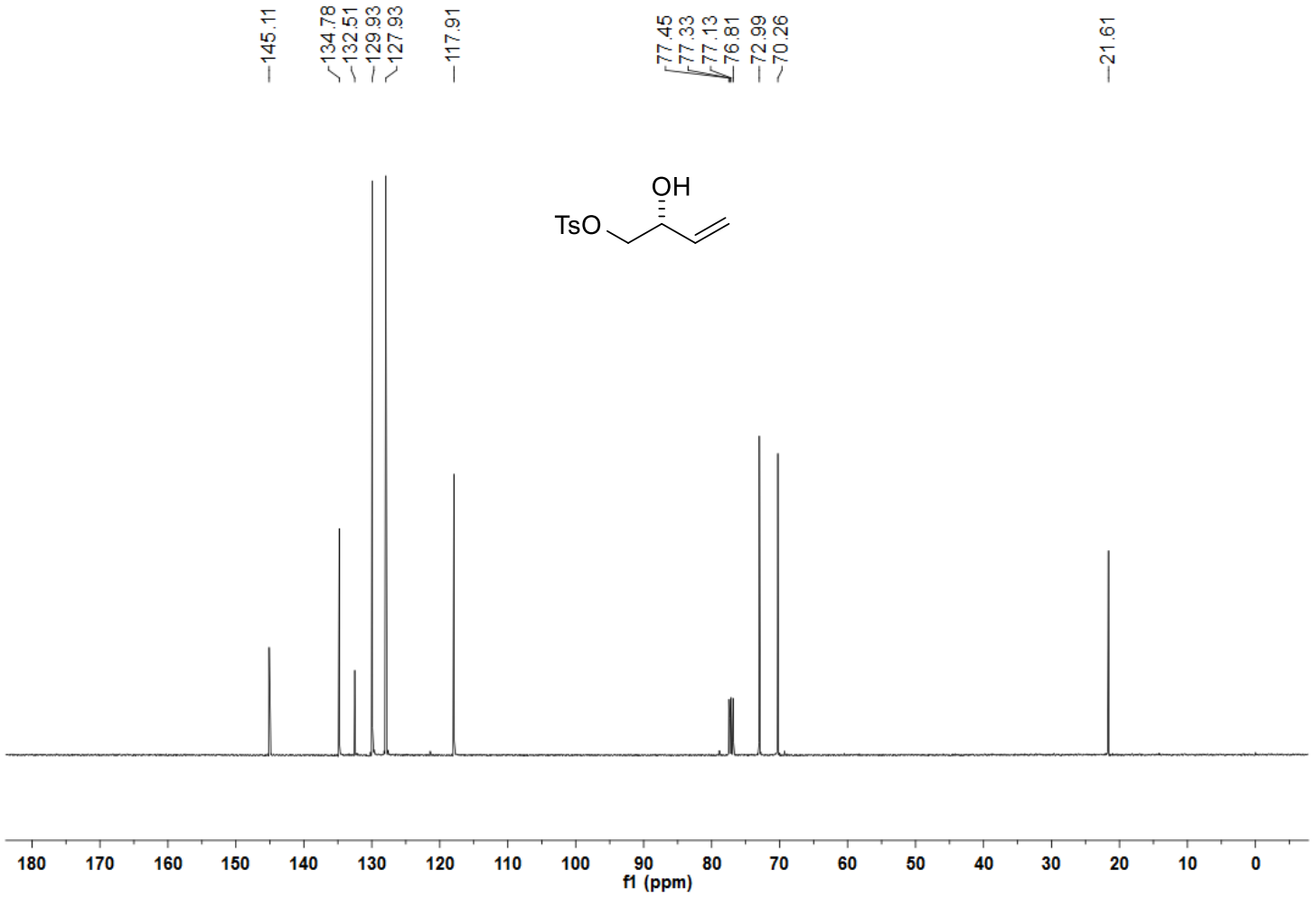
^{13}C 100 MHz NMR spectrum of (2*R*)-3-*tert*-butyldiphenylsilyl-1-myristoyl-2-(2-naphthylmethyl)-*sn*-glycerol (12b):



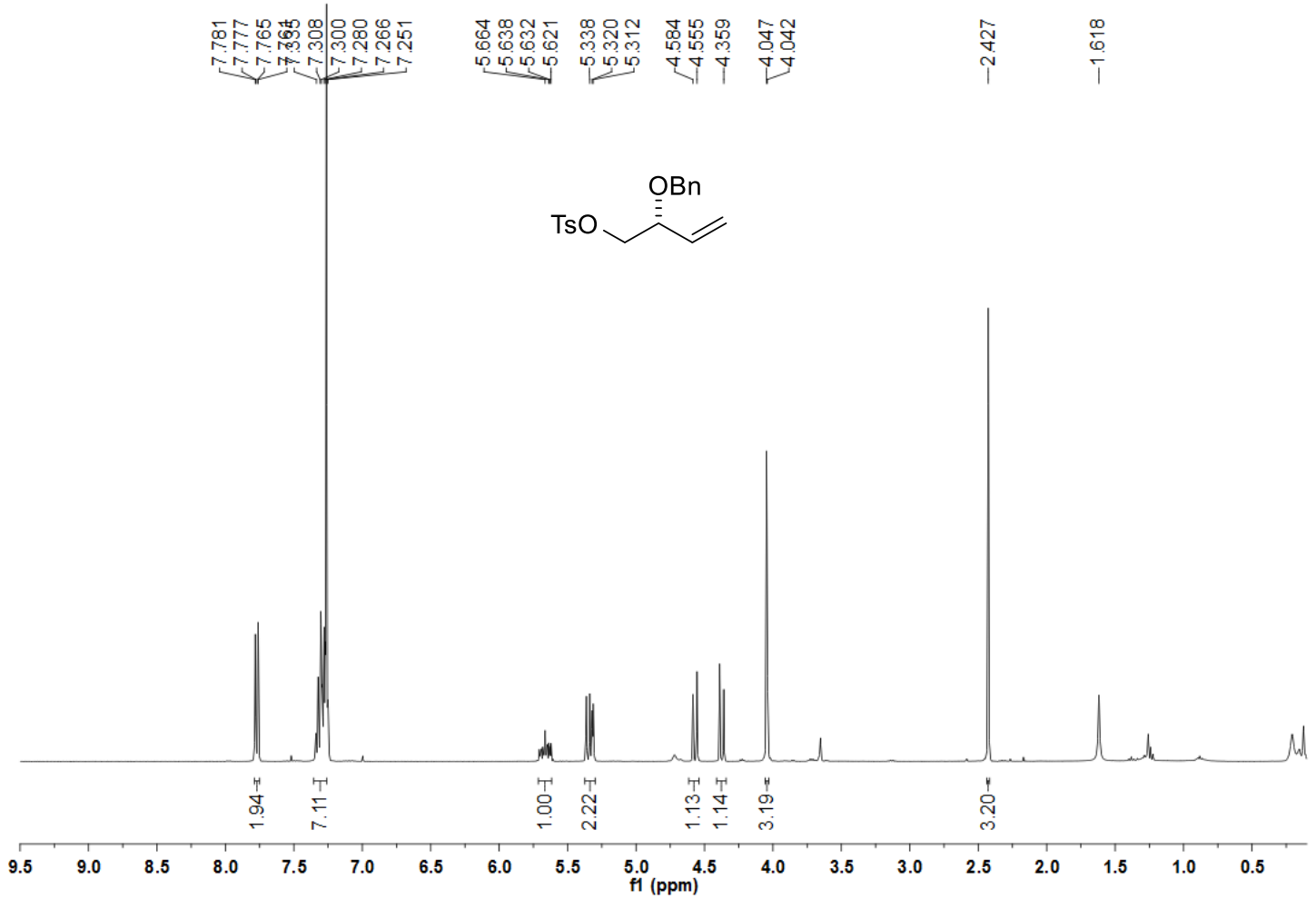
^{1}H 400 MHz NMR spectrum of (2*R*)-1-*en*-3-*O*-tosyl-*sn*-glycerol (10c):



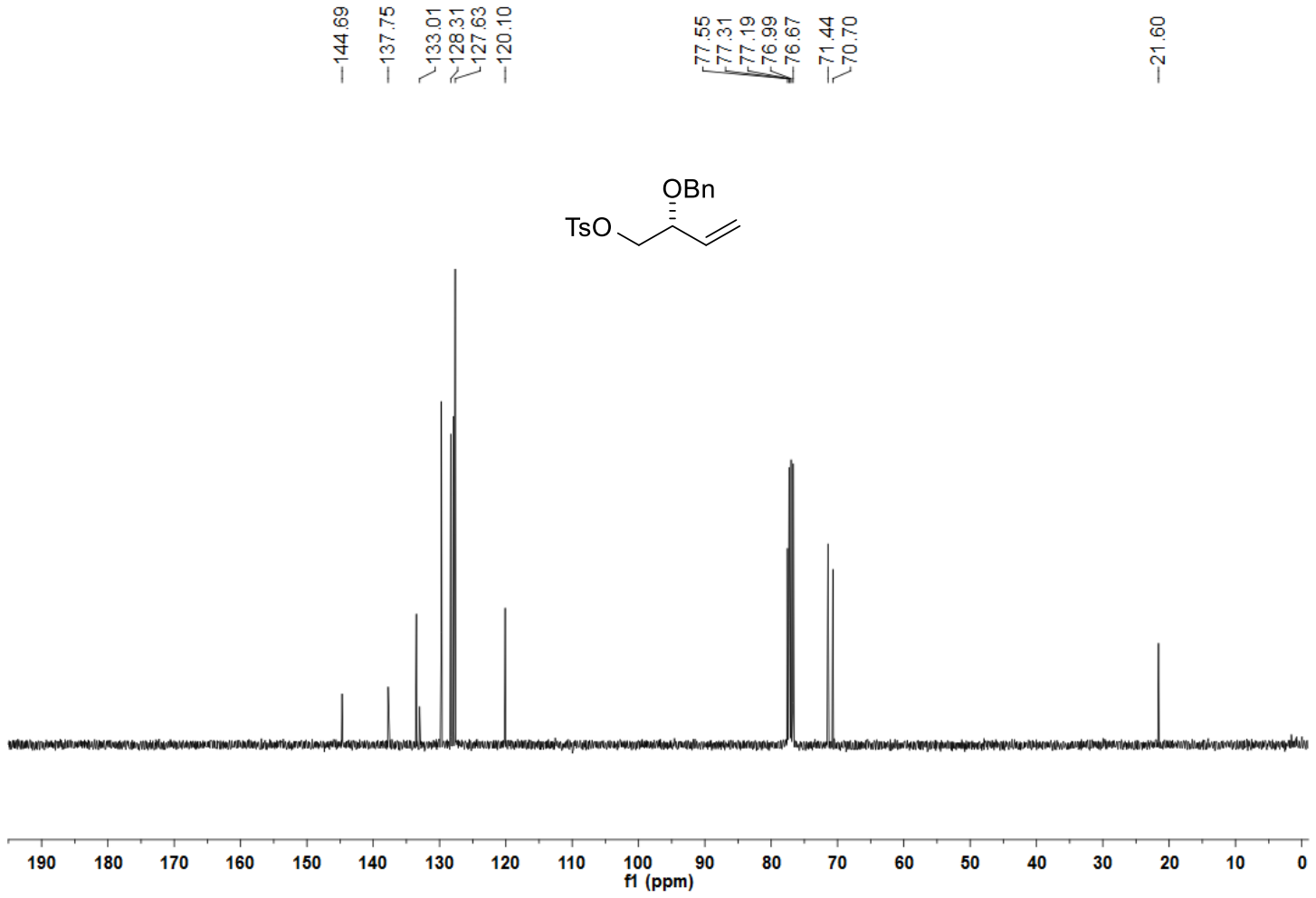
^{13}C 100 100 MHz NMR spectrum of (2*R*)-1-*en*-3-*O*-tosyl-*sn*-glycerol (10c):



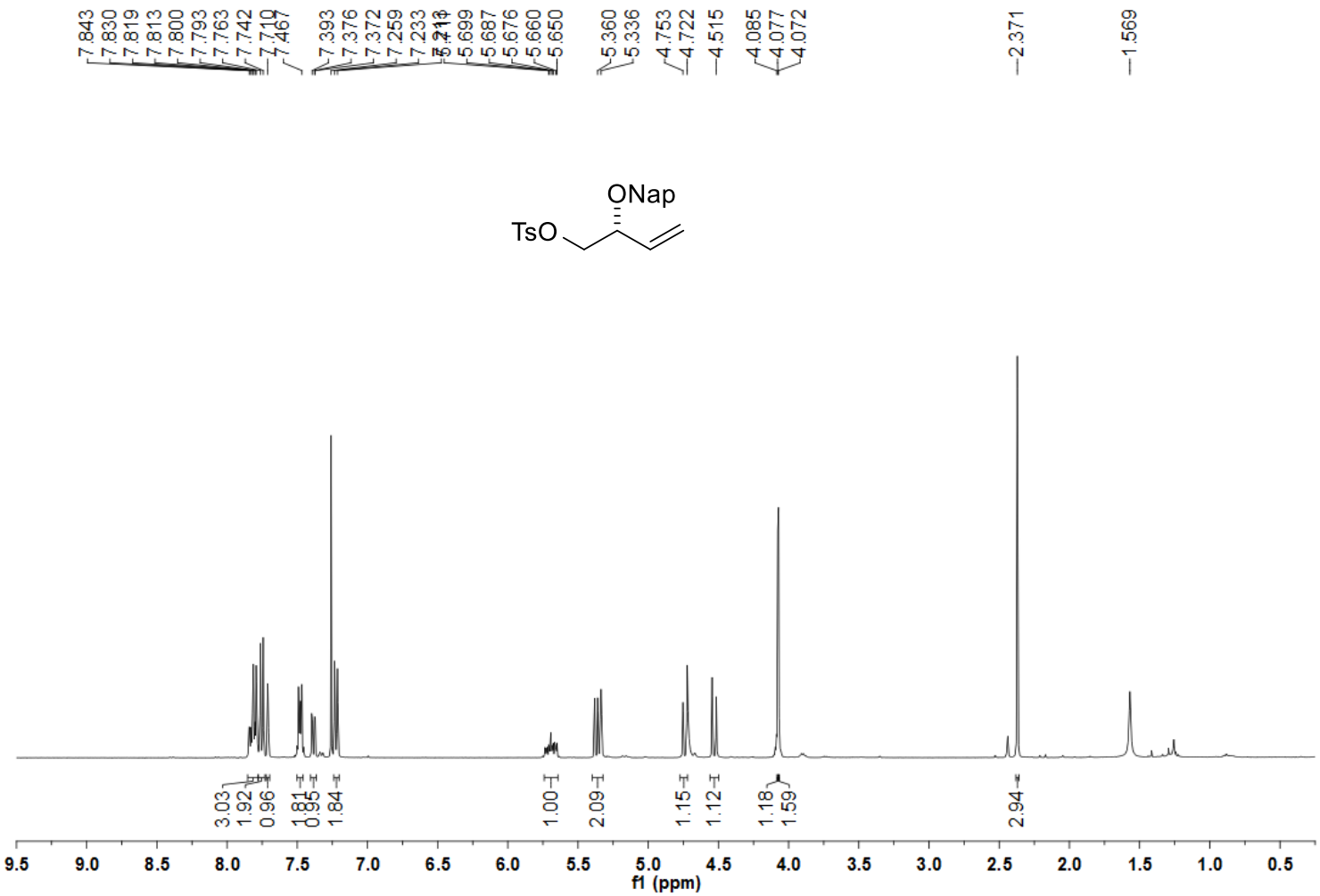
^{1}H 400 MHz NMR spectrum of (2*R*)-2-benzyl-1-*en*-3-tosyl-*sn*-glycerol (12c$_1$):



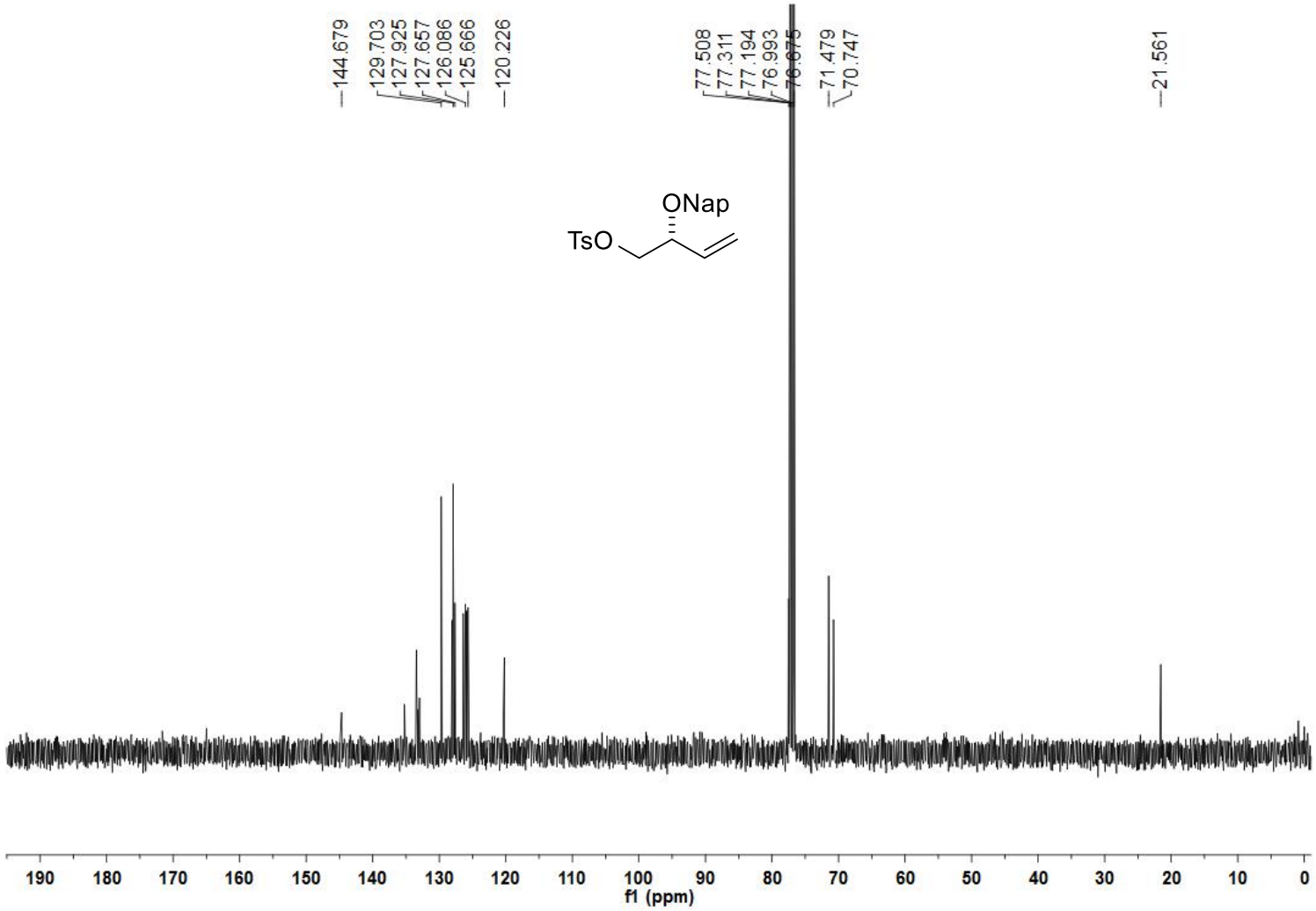
^{13}C 100 MHz NMR spectrum of (2*R*)-2-benzyl-1-*en*-3-tosyl-*sn*-glycerol (12c$_1$):



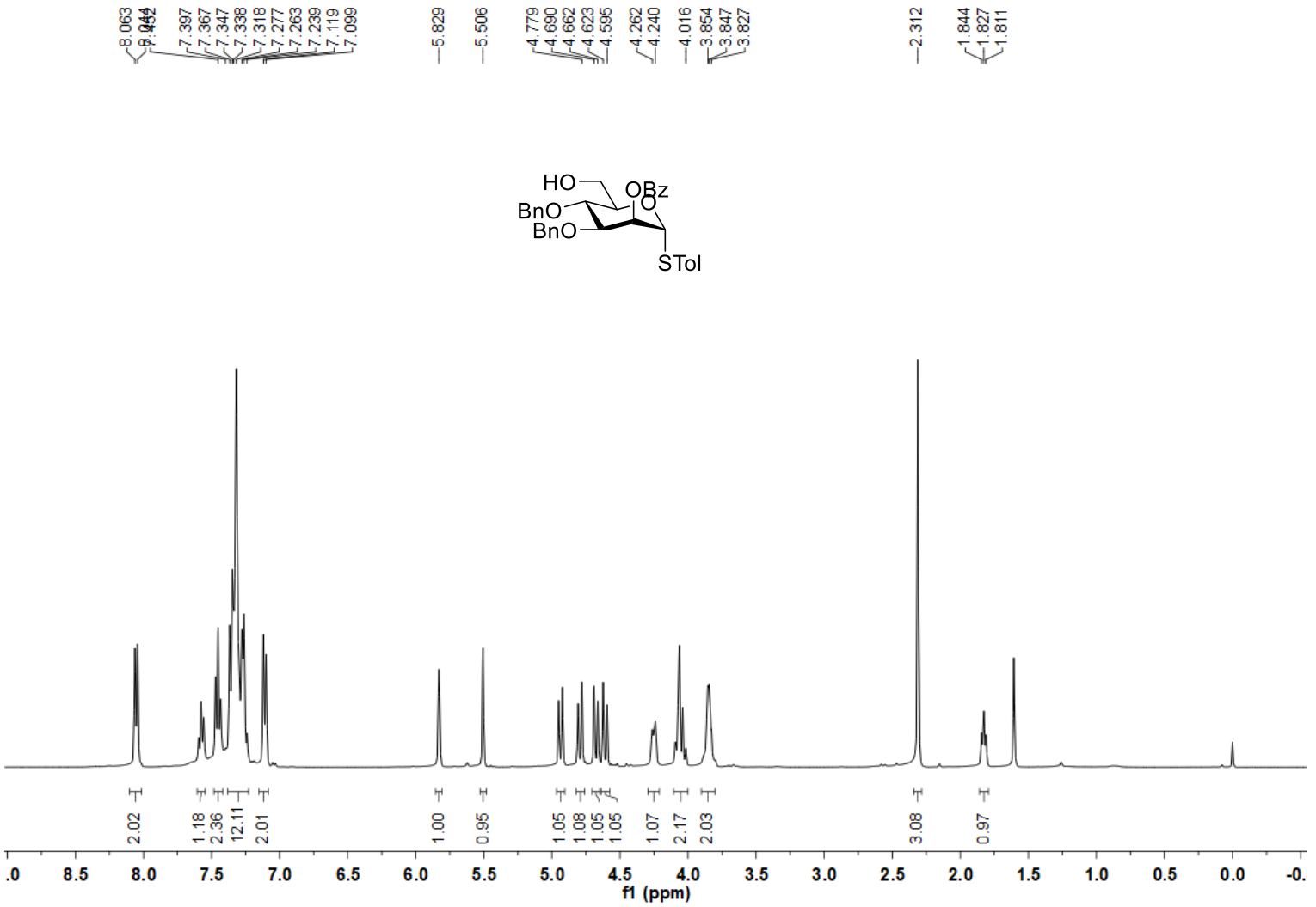
^{1}H 400 MHz NMR spectrum of (2*R*)-1-*en*-2-(2-naphthylmethyl)-3-tosyl-*sn*-glycerol (12c$_2$):



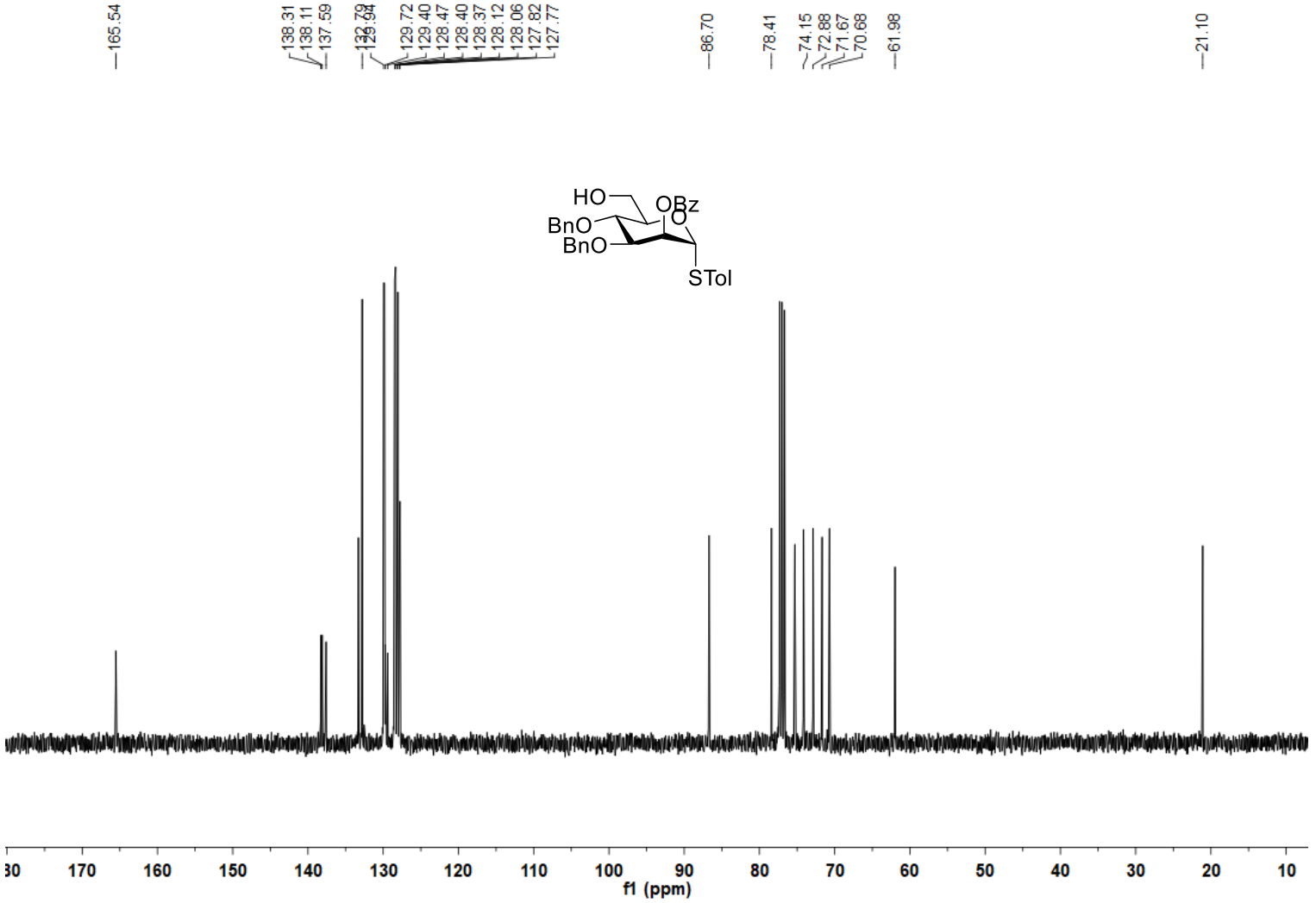
^{13}C 100 MHz NMR spectrum of (2*R*)-1-*en*-2-(2-naphthylmethyl)-3-tosyl-*sn*-glycerol (12c$_2$):



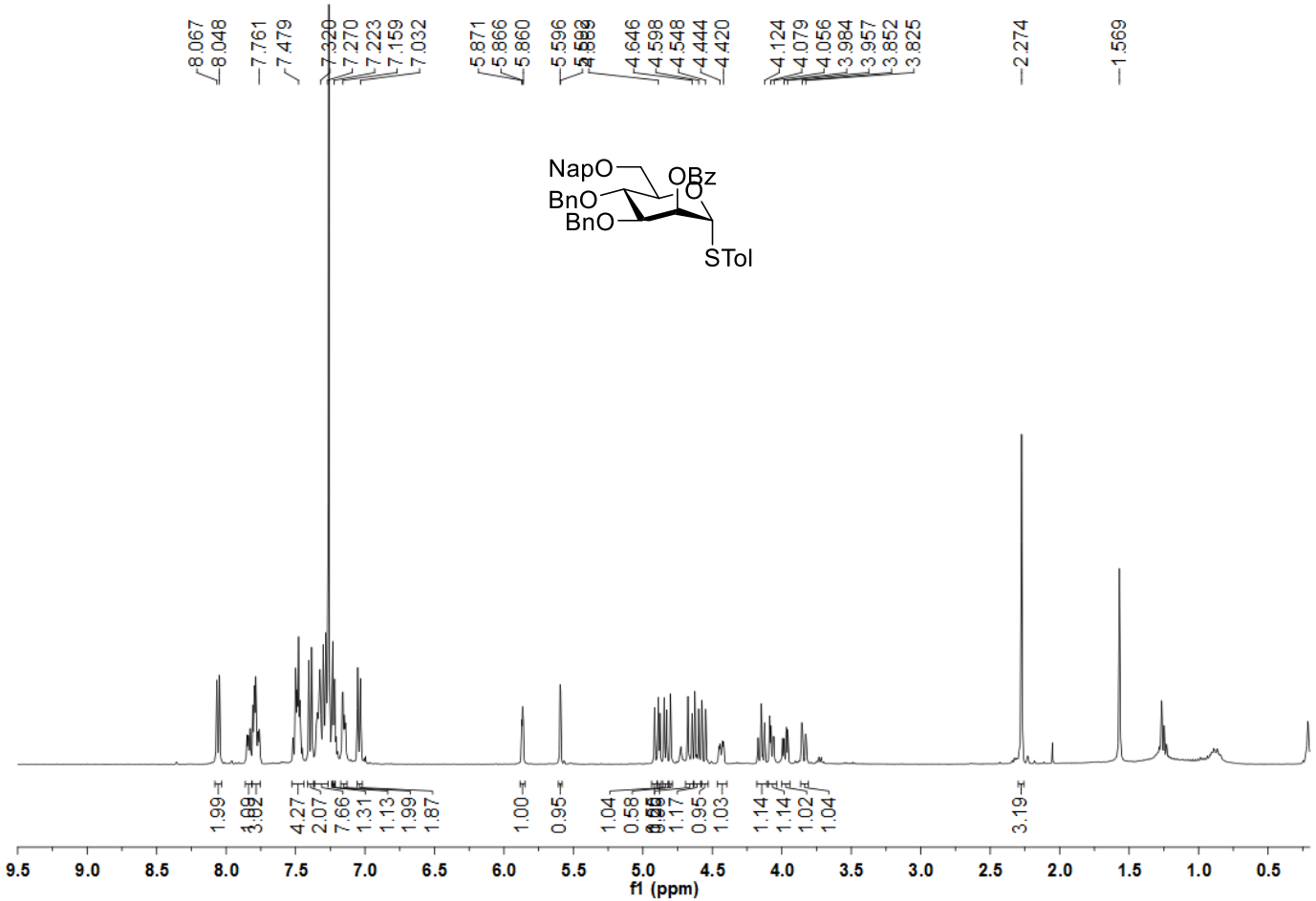
^{1}H 400 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (10d):



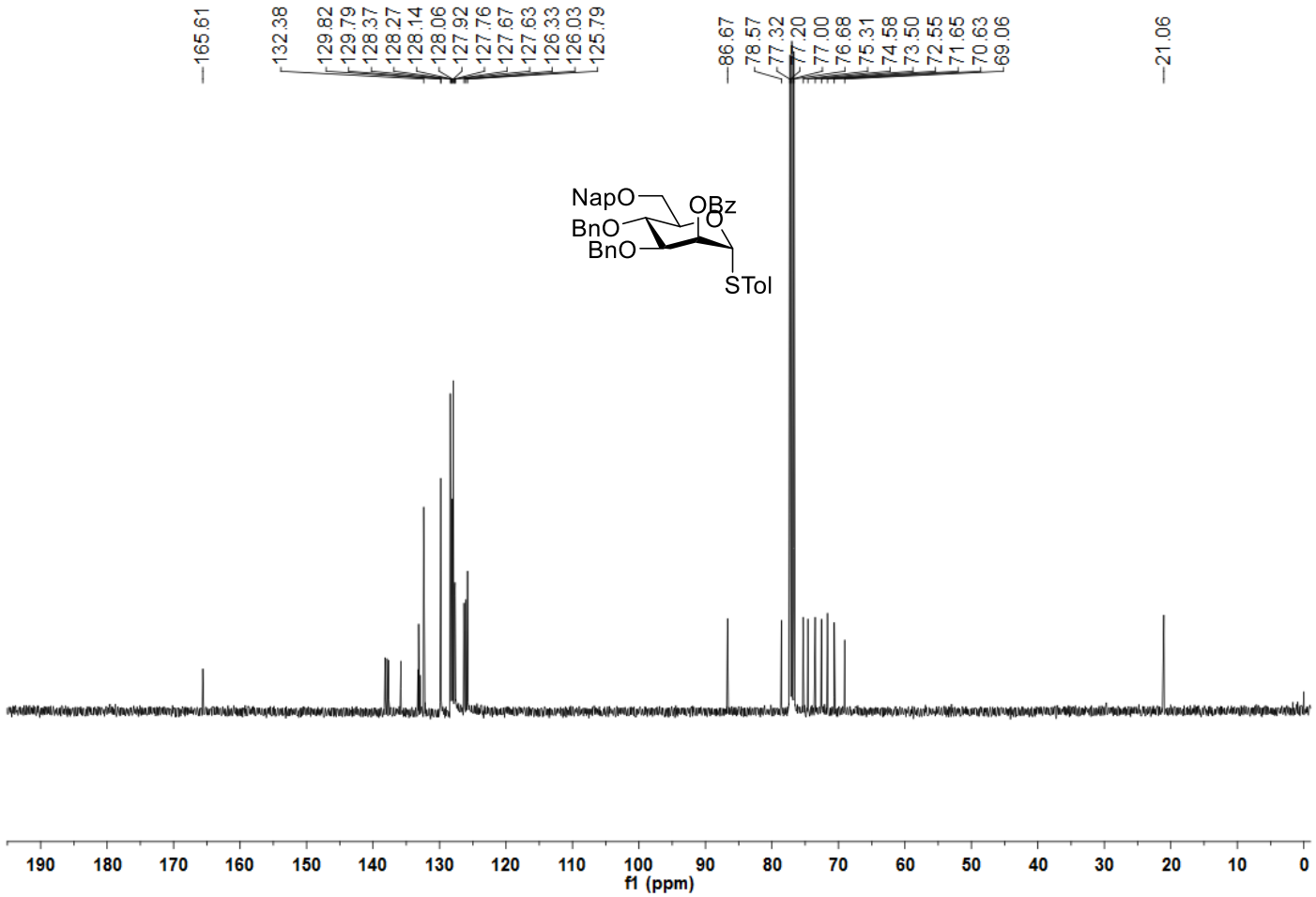
^{13}C 100 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (10d):



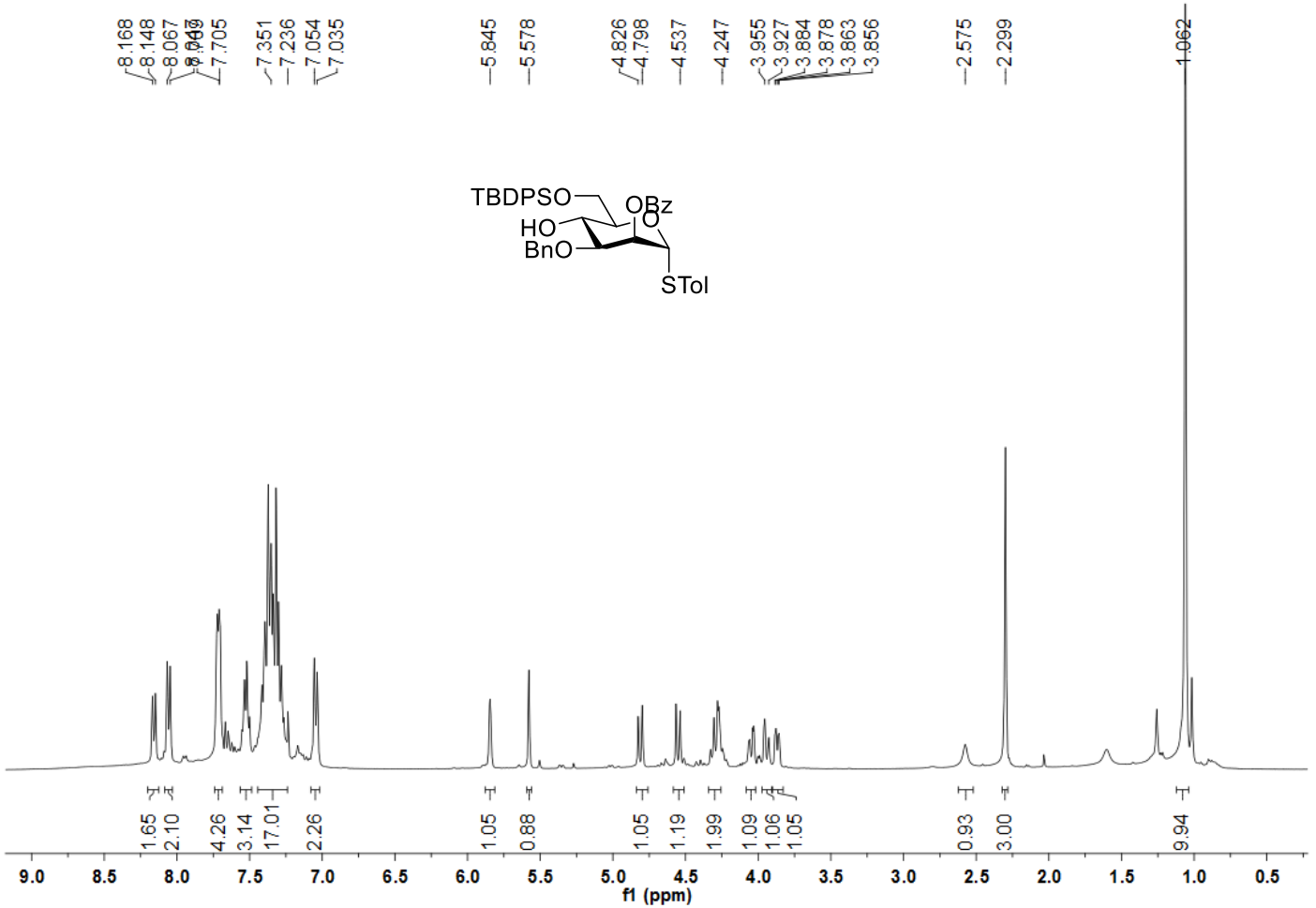
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-*O*-Benzoyl-3,4-di-*O*-benzyl-6-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12d):



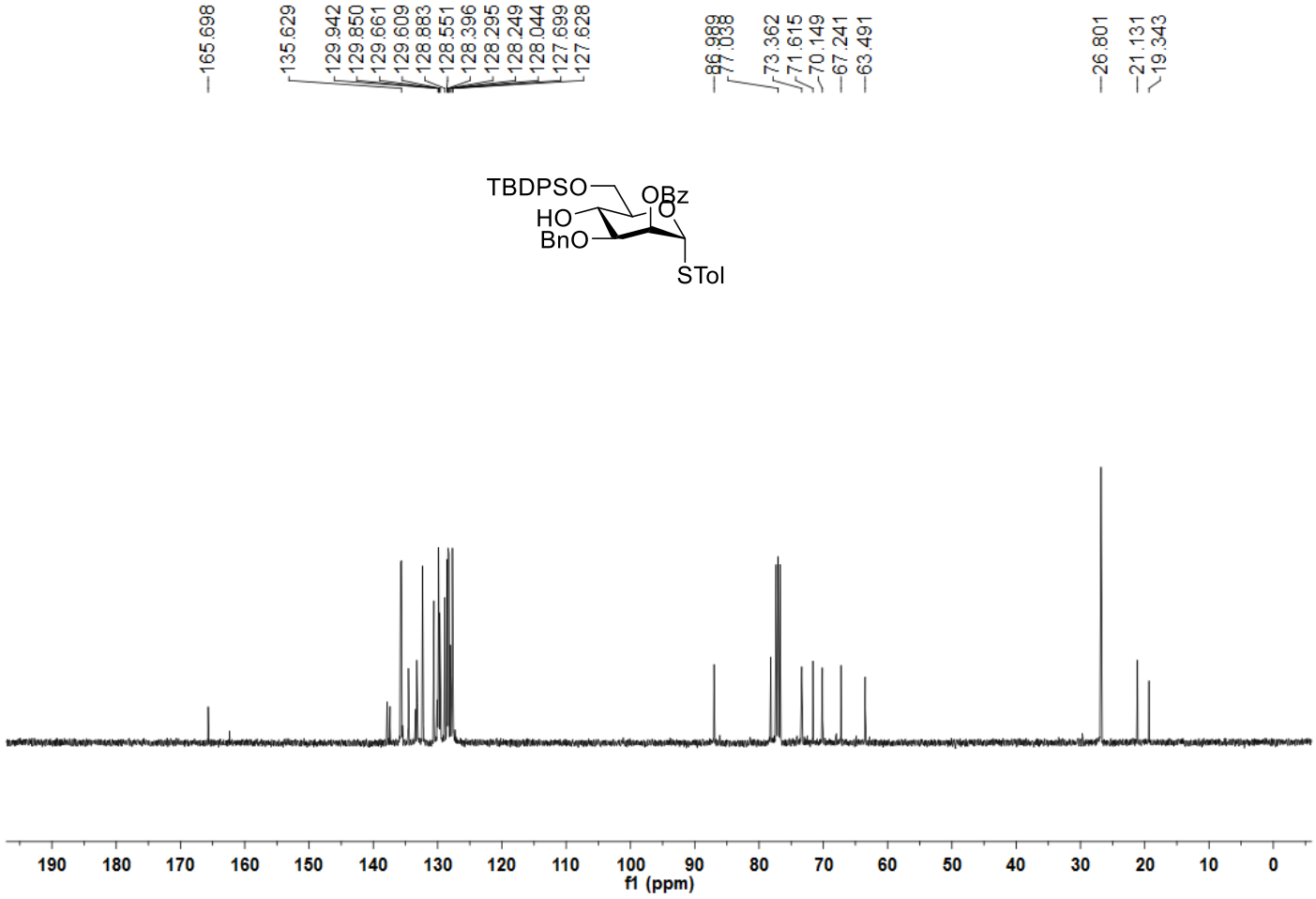
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12d):



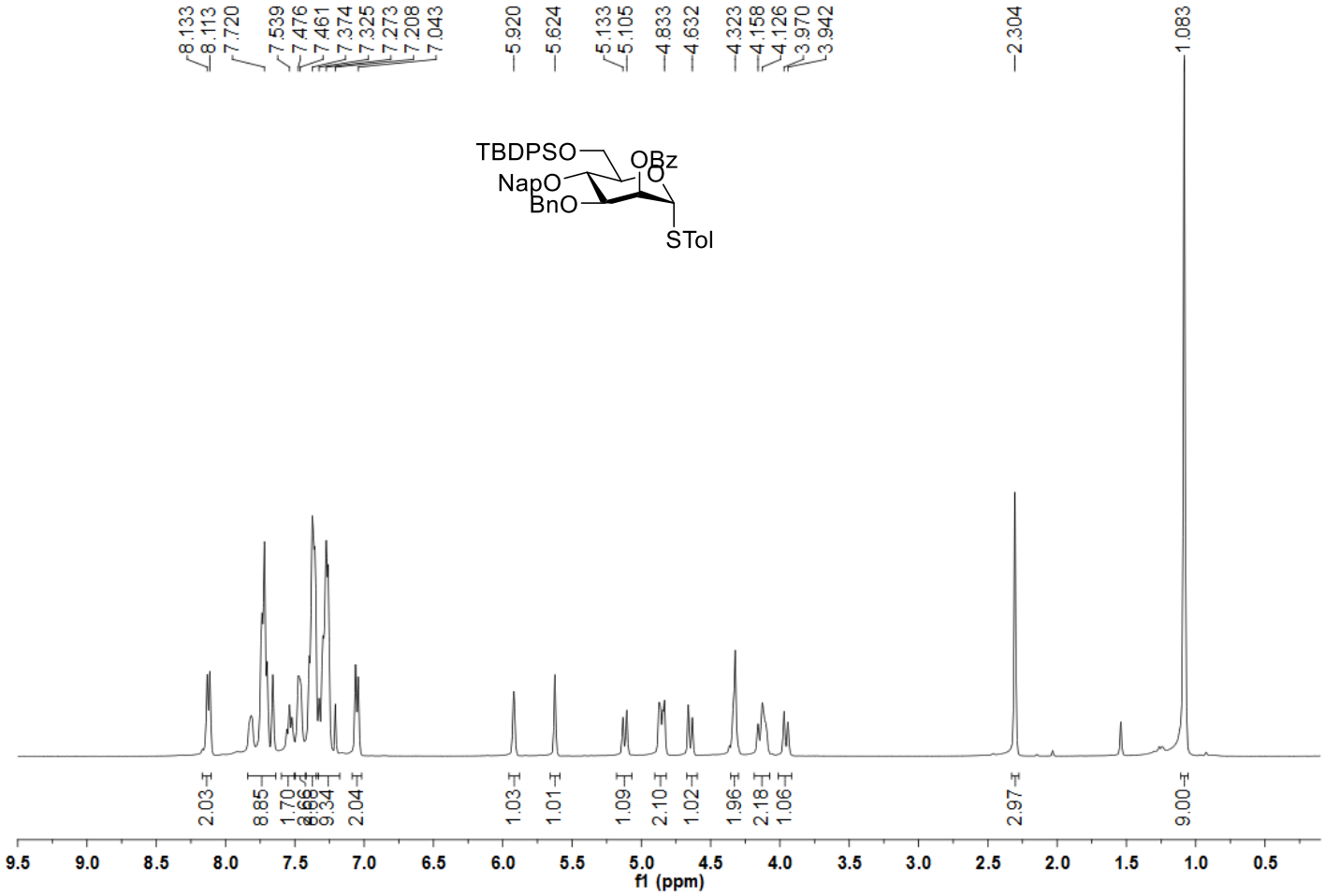
^{1}H 400 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-mannopyranoside (10e):



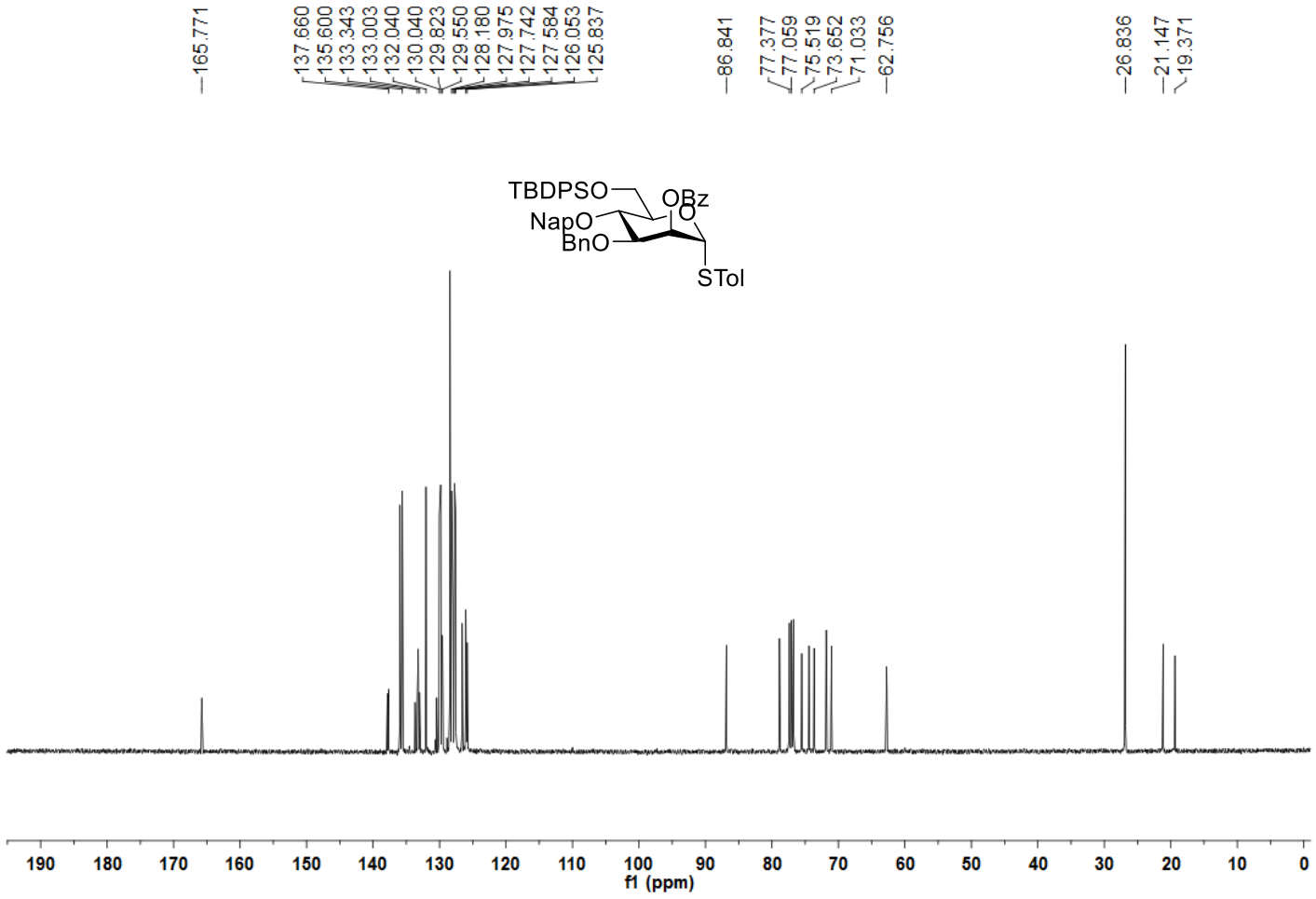
^{13}C 400 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-α-D-mannopyranoside (10e)



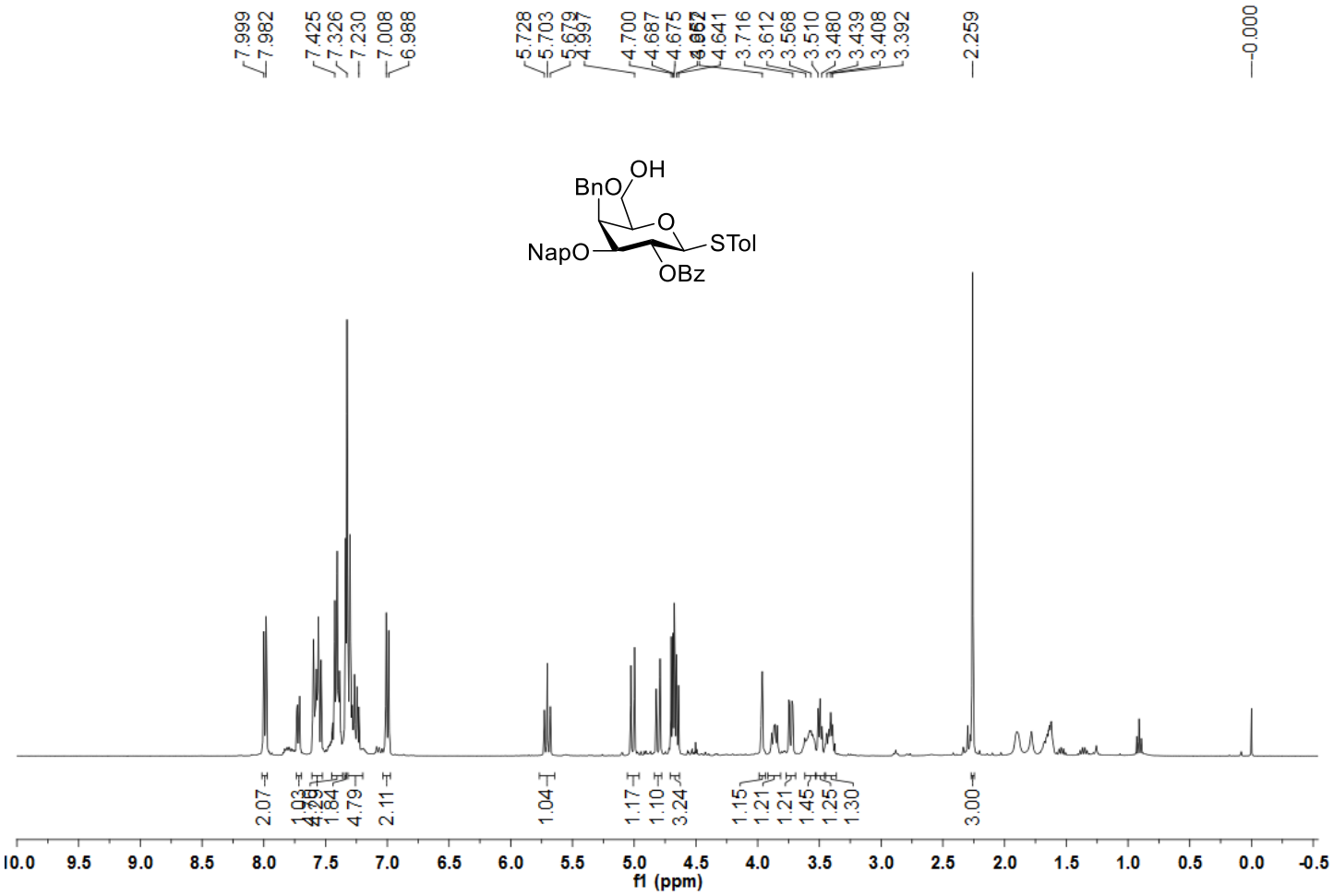
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-*O*-Benzoyl-3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12e):



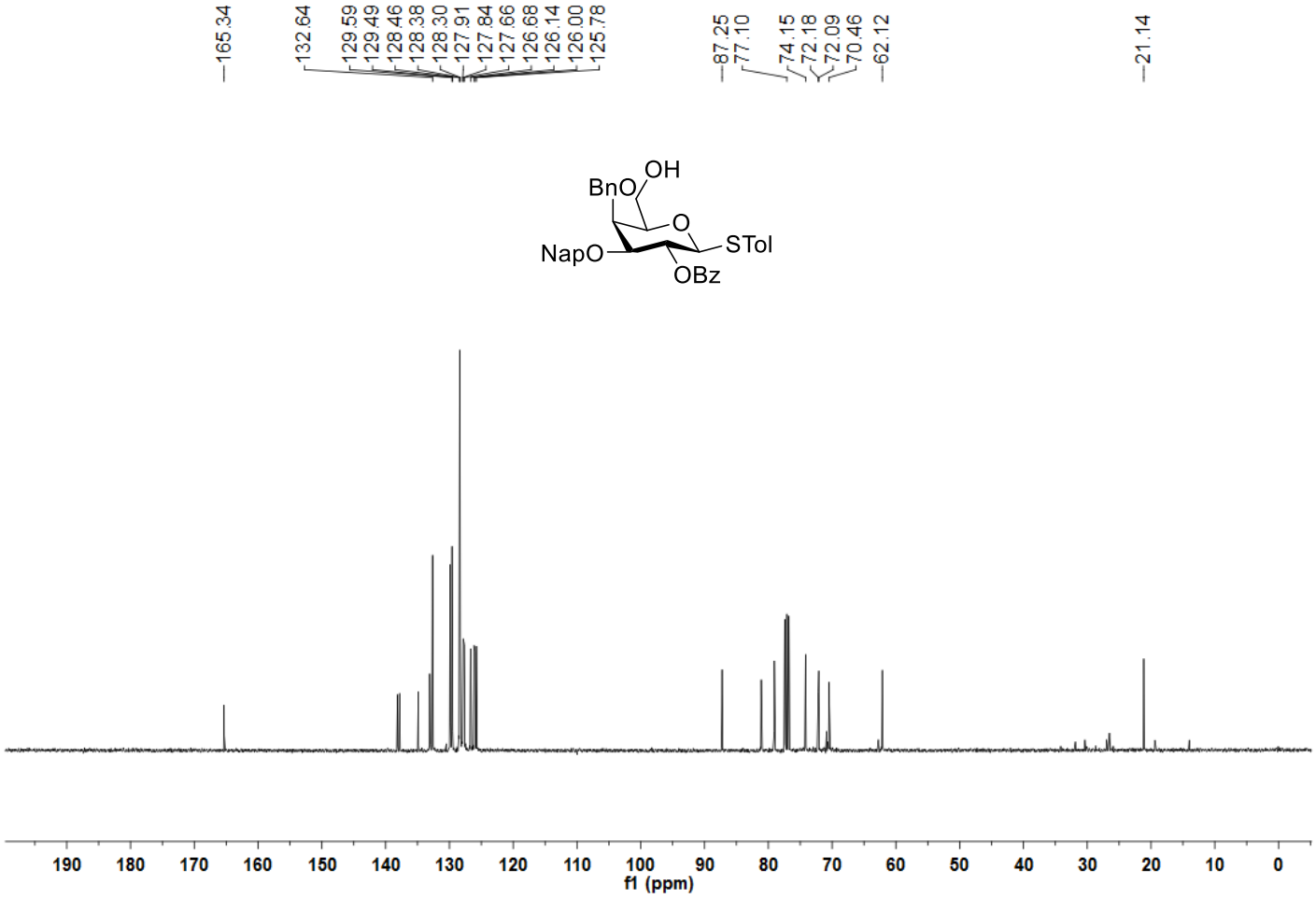
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-*O*-Benzoyl-3-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(2-naphthylmethyl)-1-thio-α-D-mannopyranoside (12e):



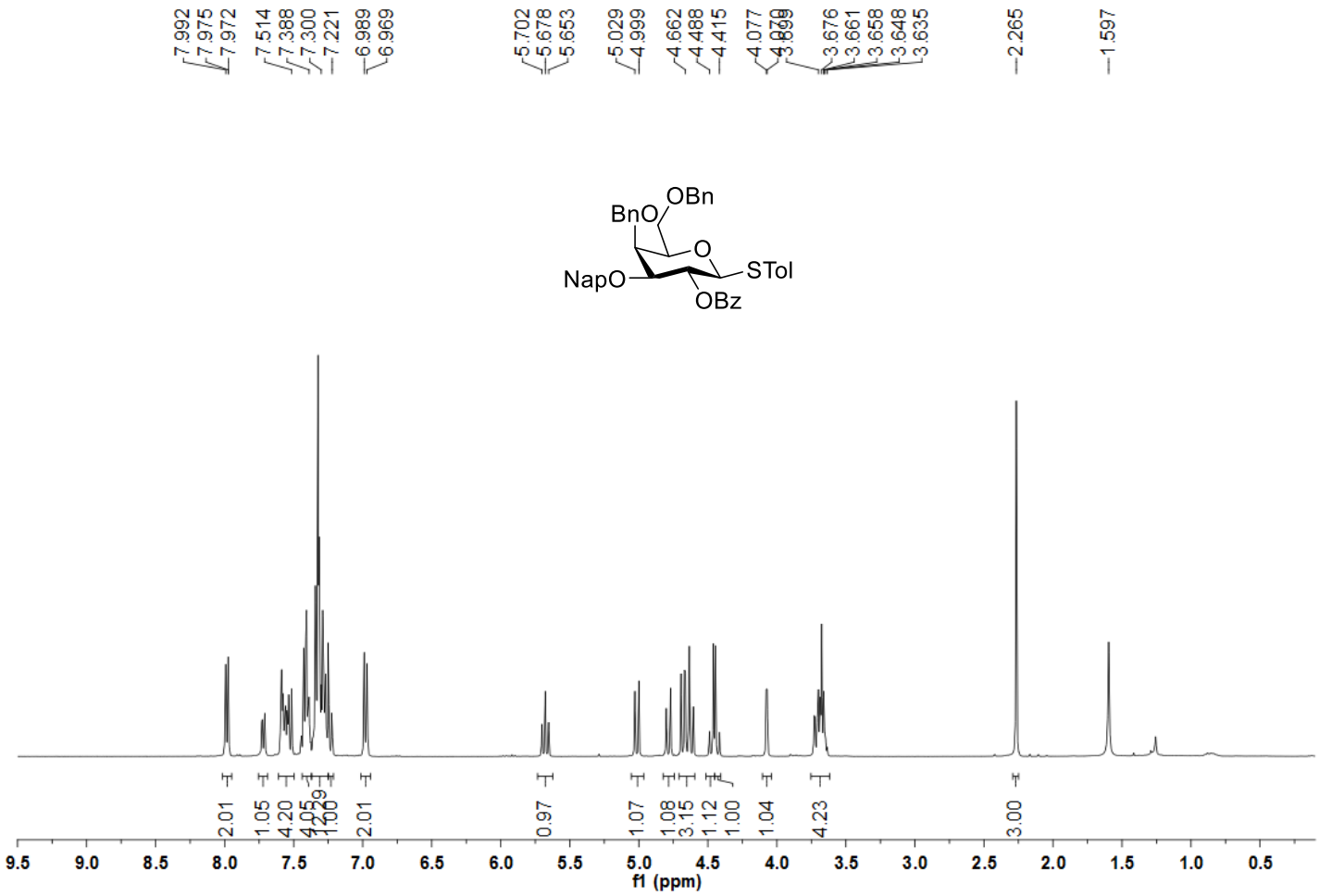
^{1}H 400 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (10f):



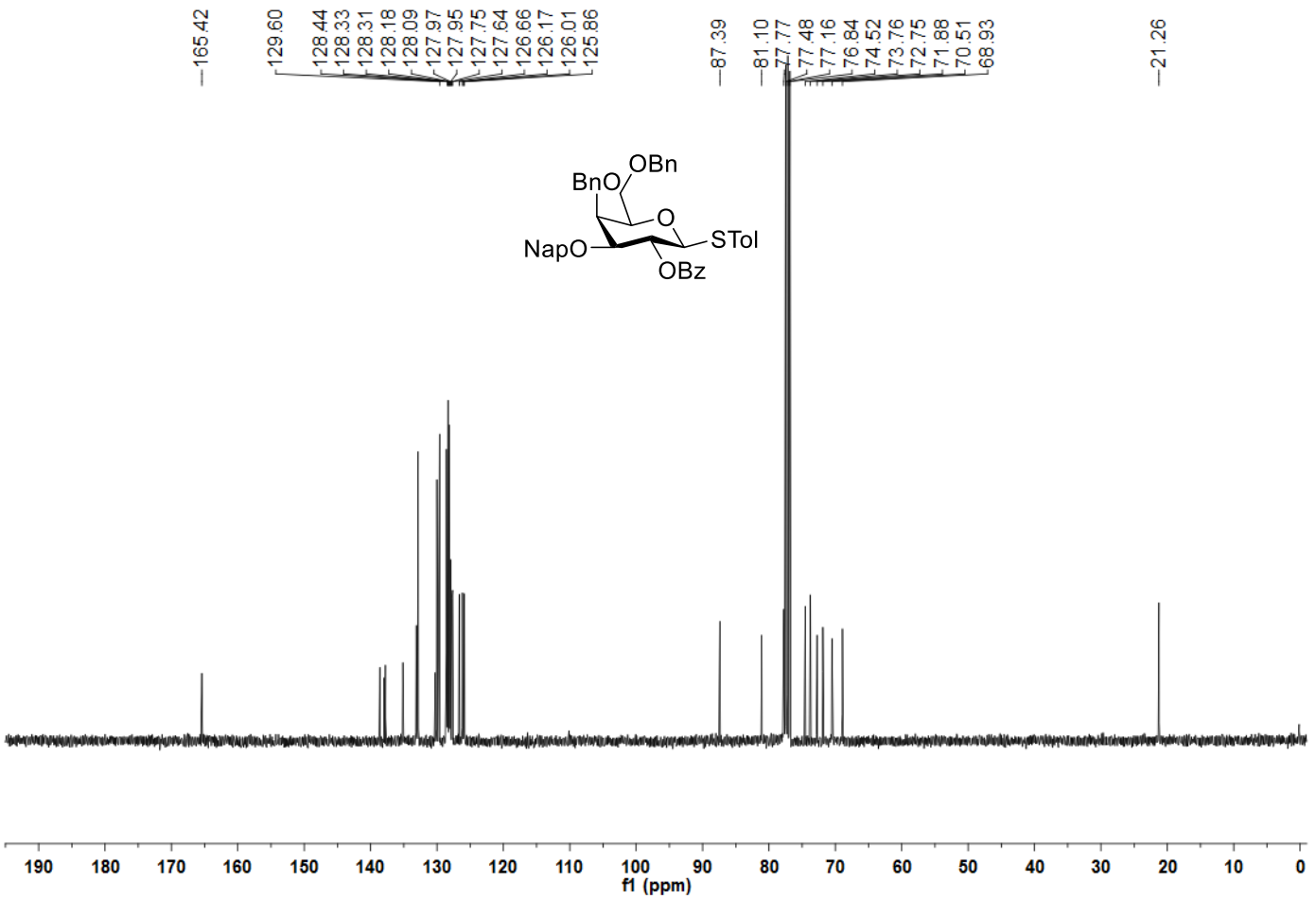
^{13}C 100 MHz NMR spectrum of *p*-Tolyl 2-*O*-Benzoyl-4-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (10f):



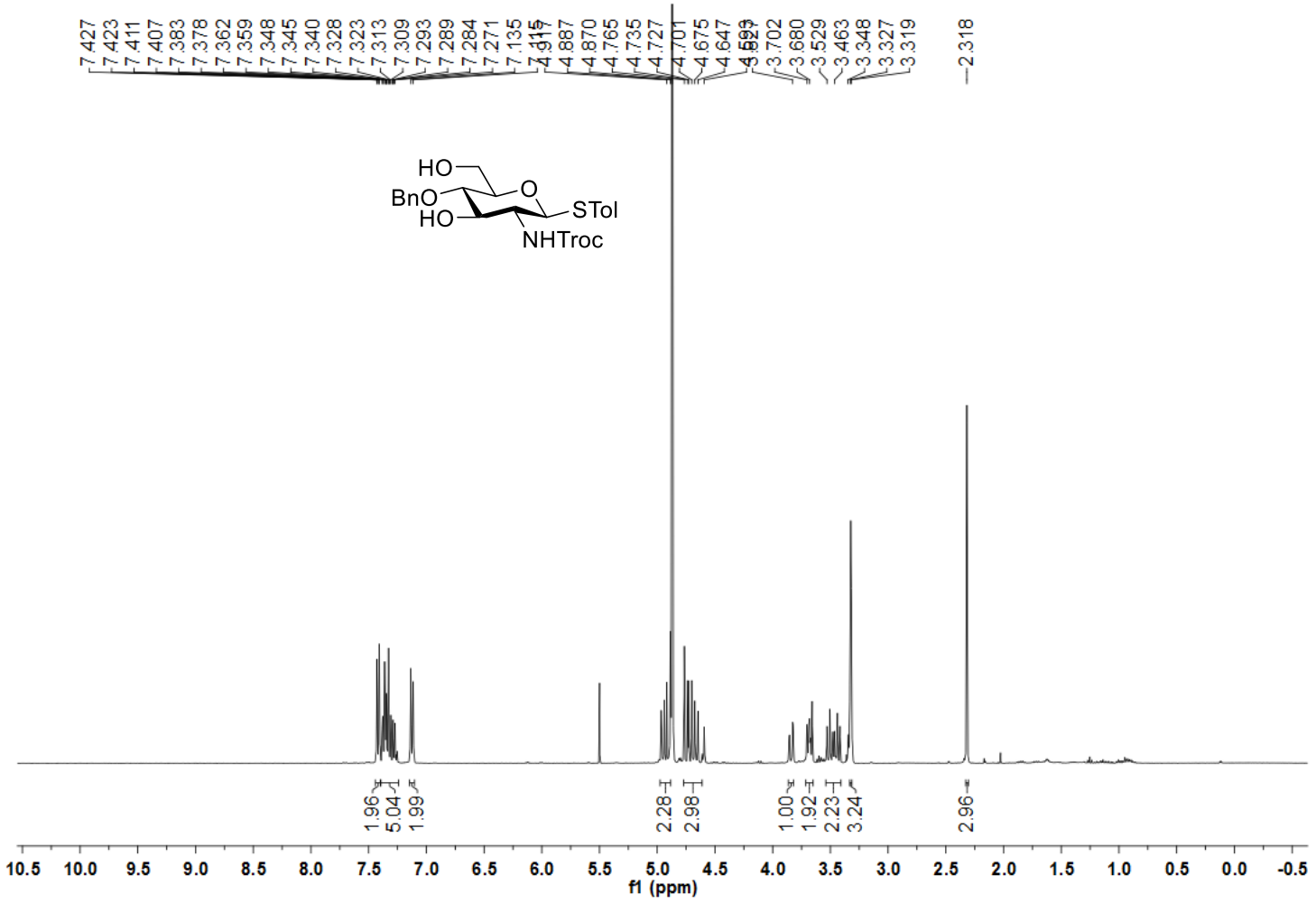
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (12f):



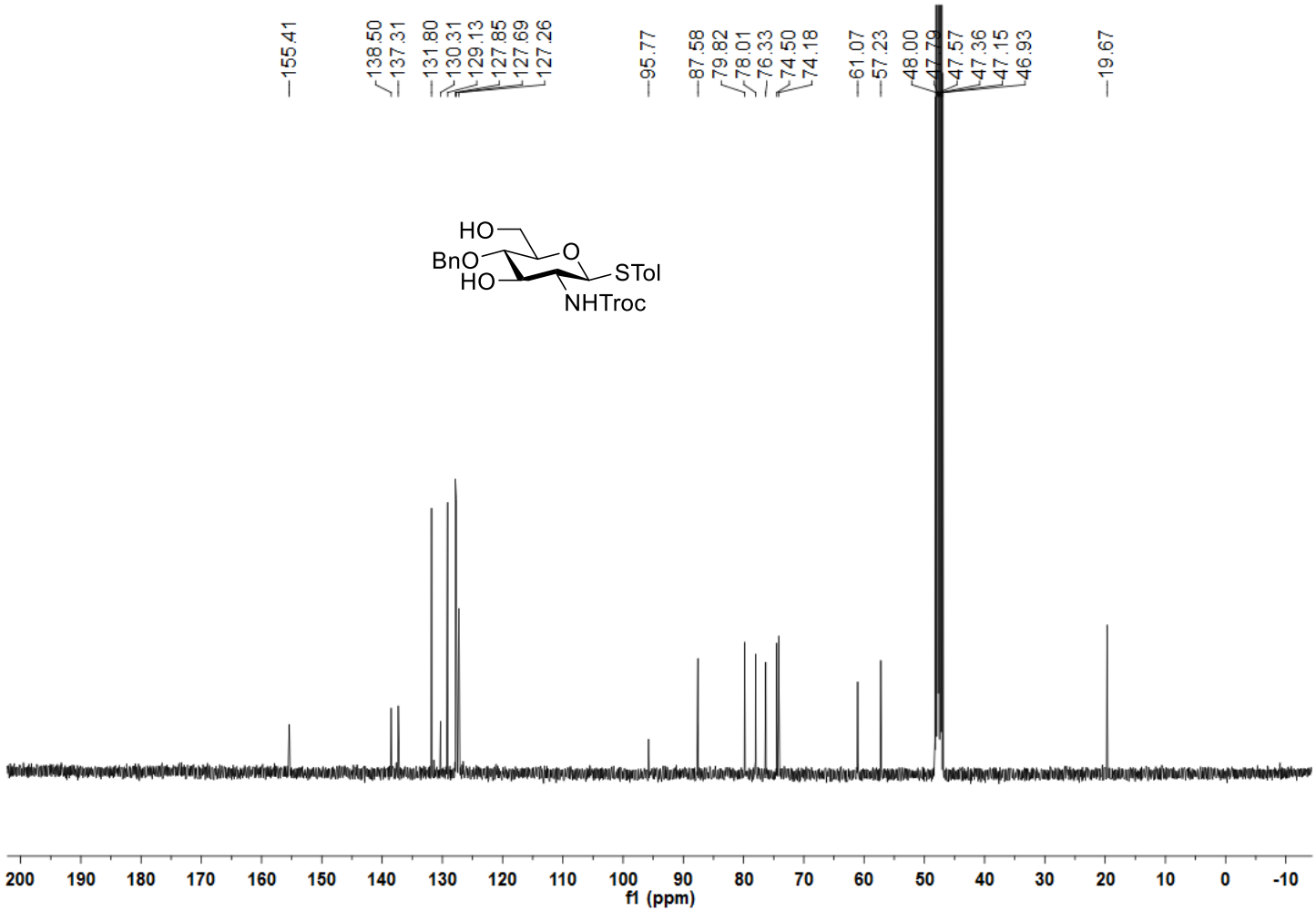
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-*O*-Benzoyl-4,6-di-*O*-benzyl-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranoside (12f):



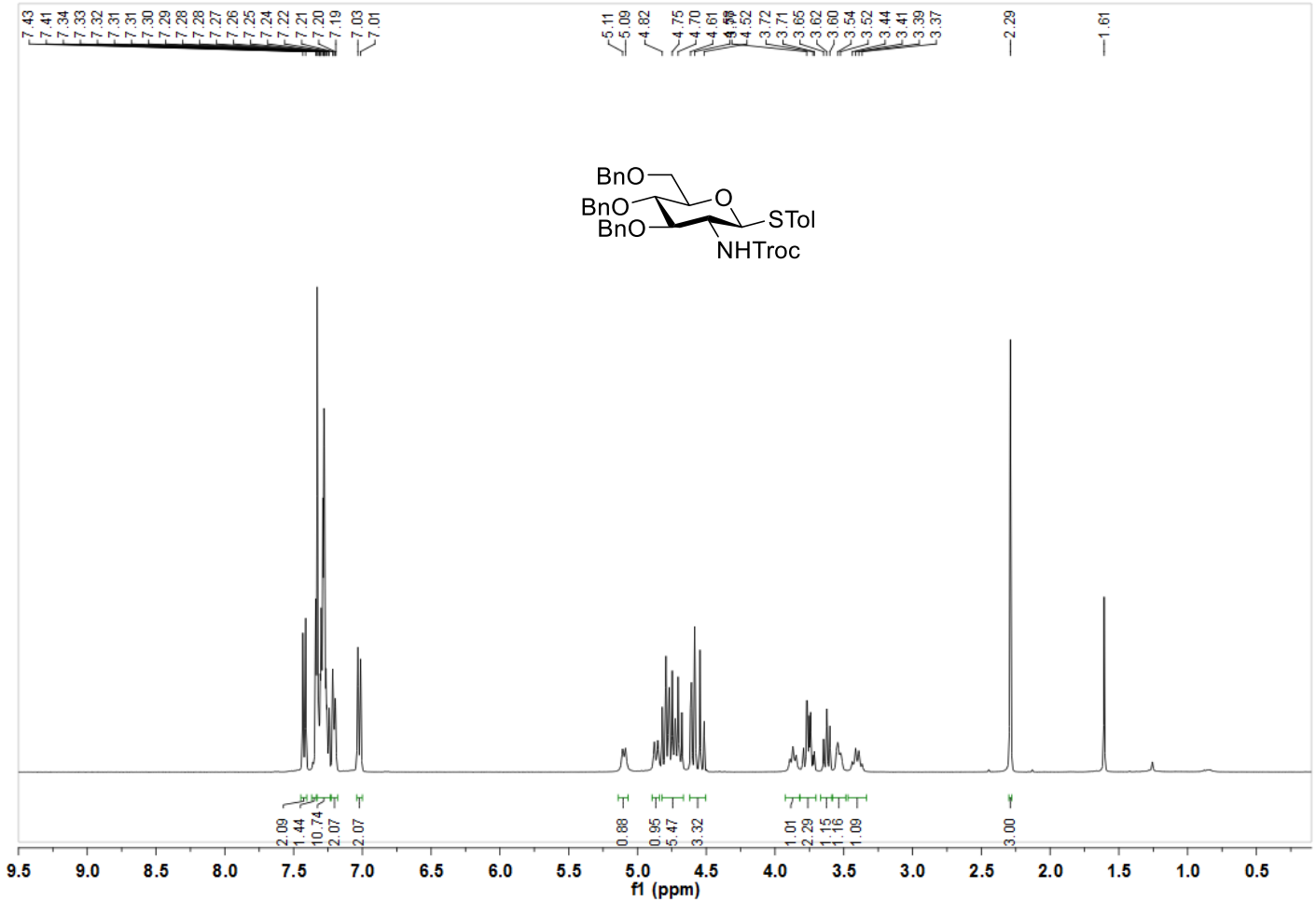
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (10g):



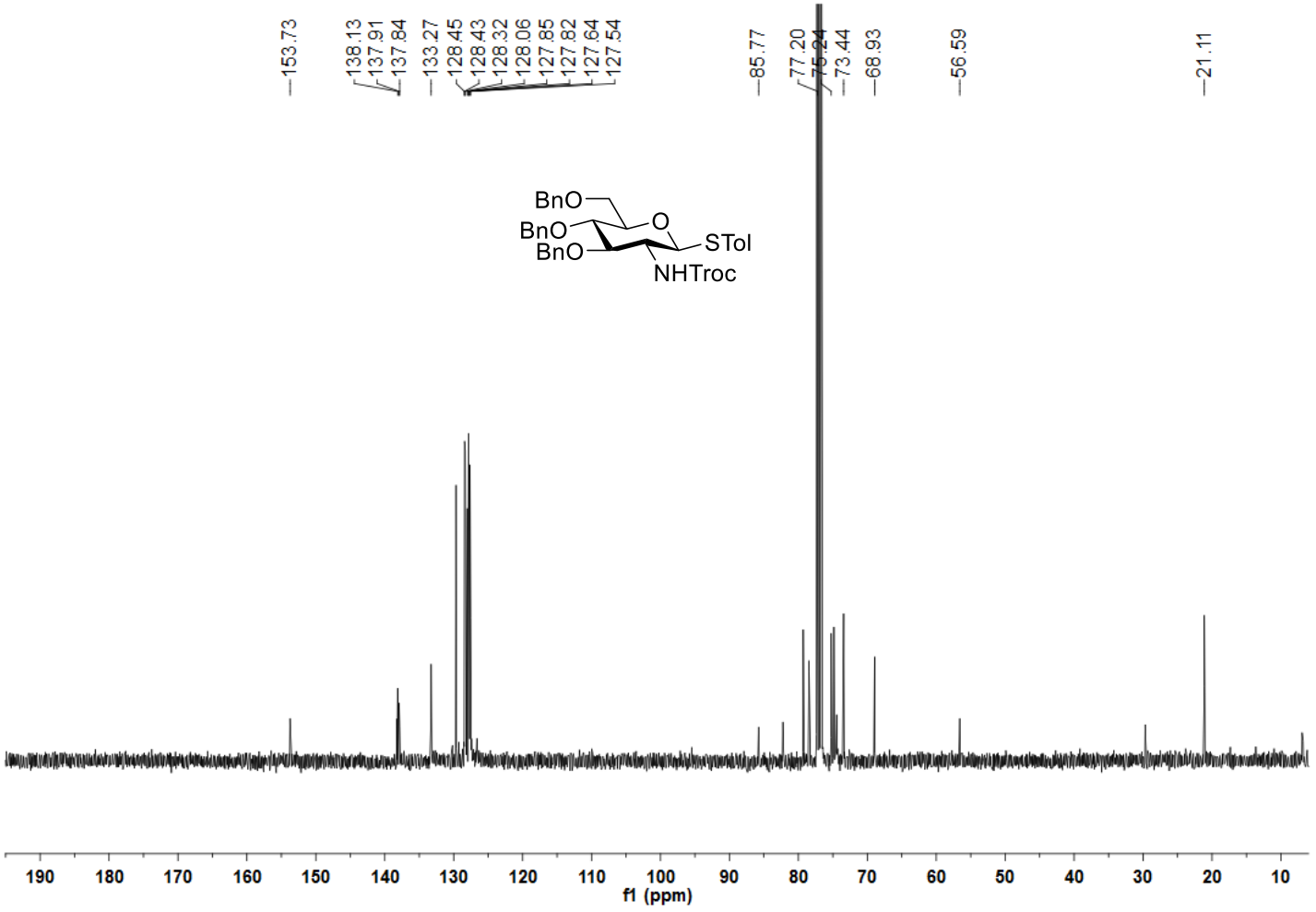
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (10g):



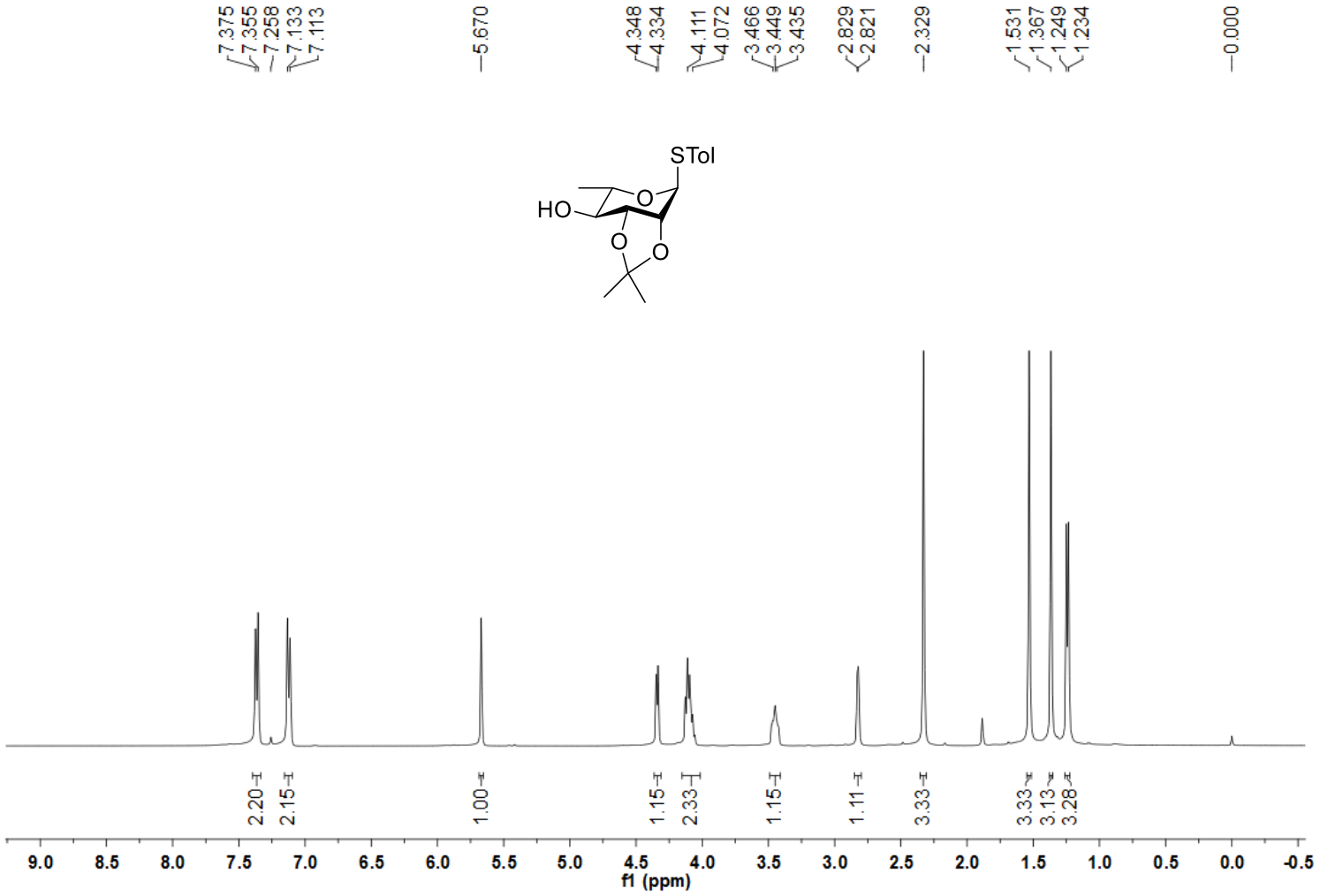
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3,4,6-tri-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (12g):



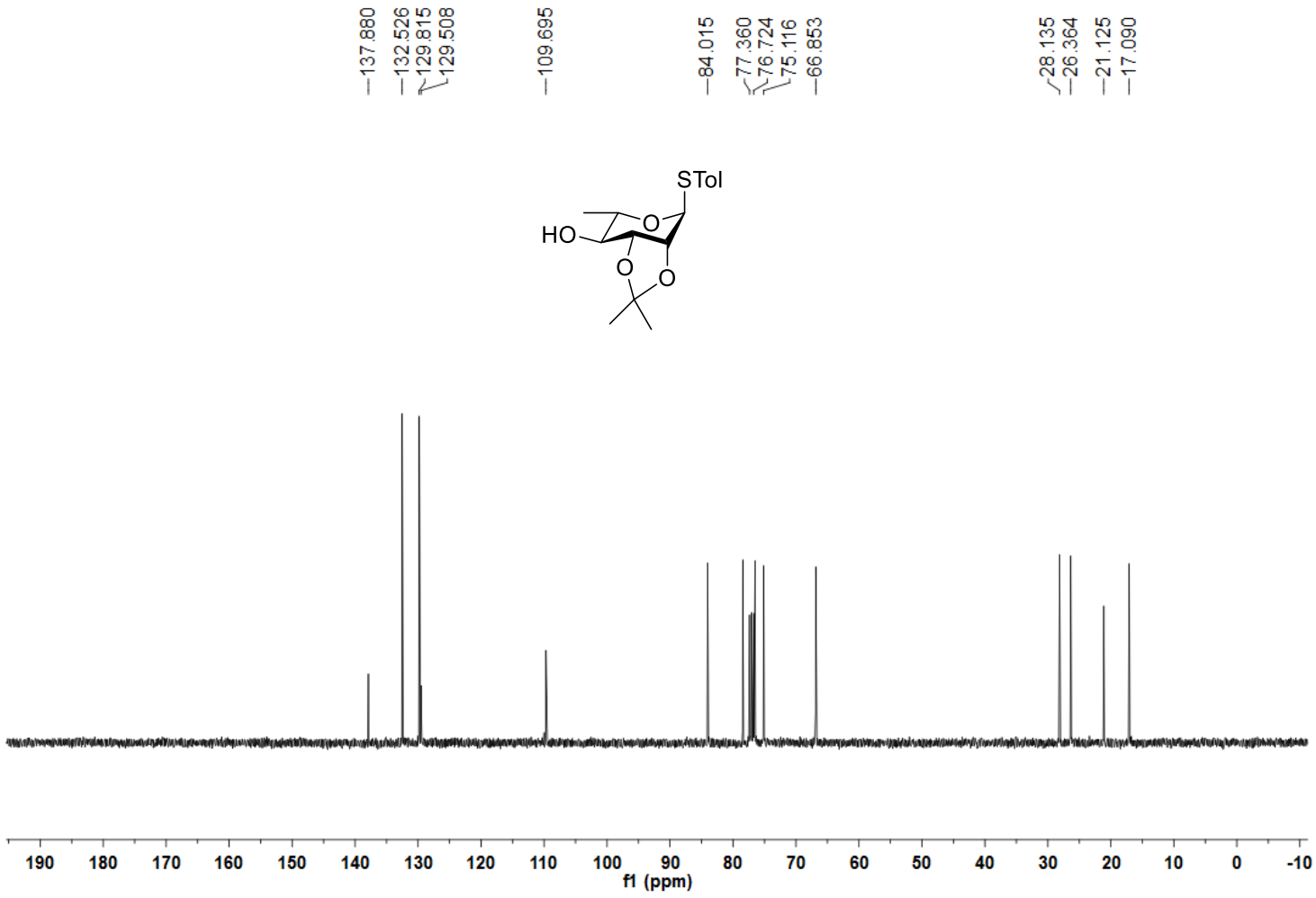
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3,4,6-tri-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (12g):



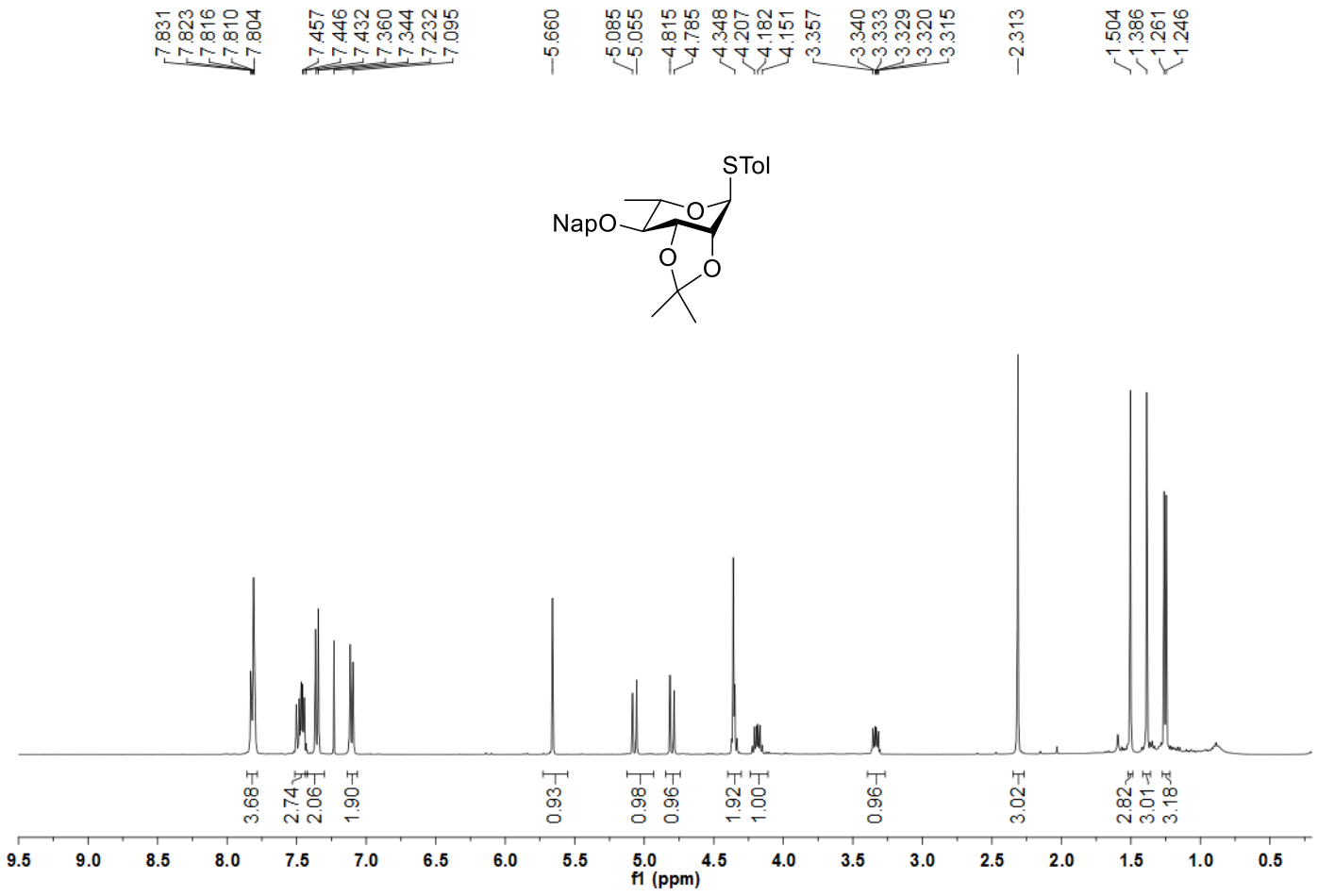
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (10h):



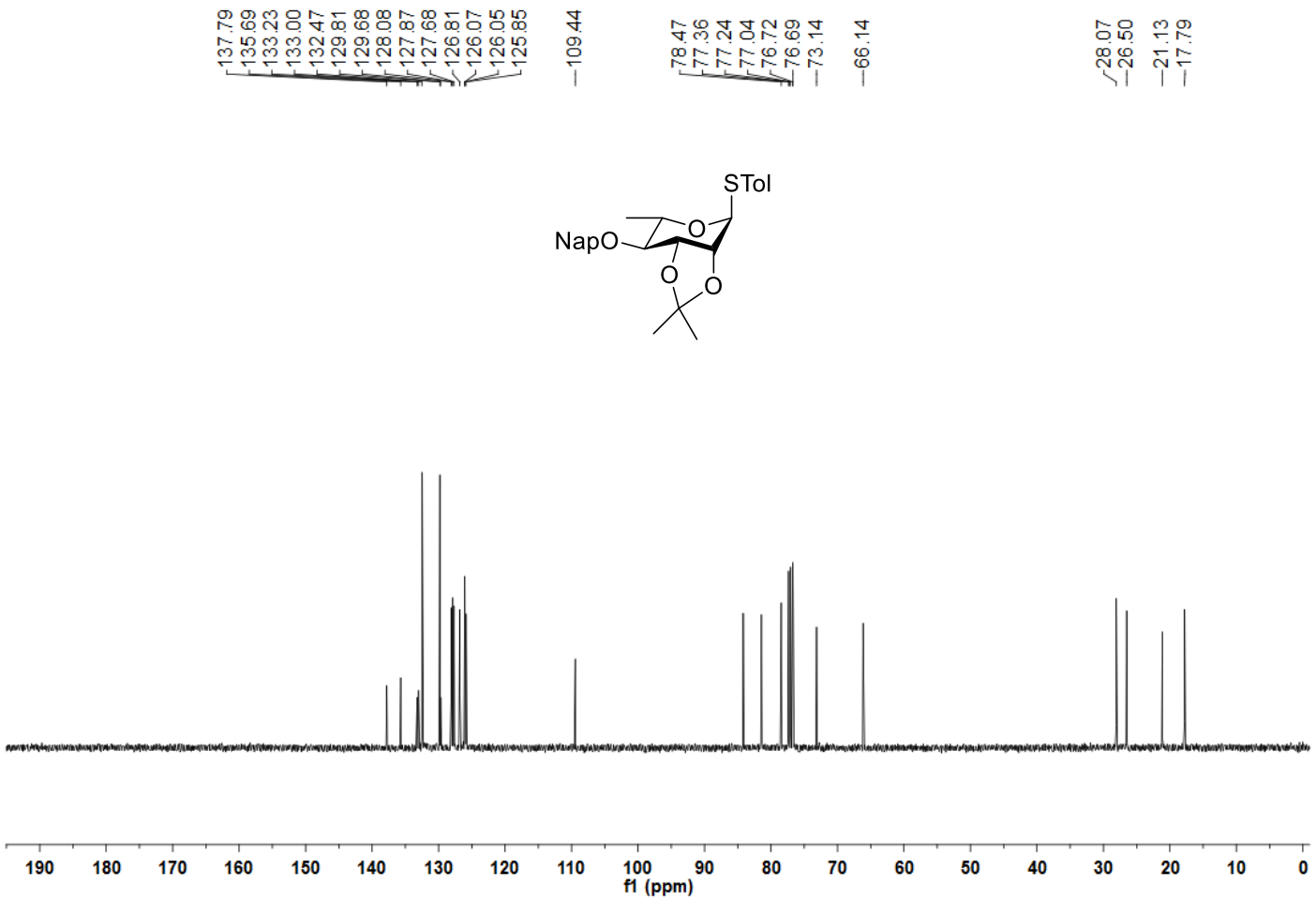
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (10h):



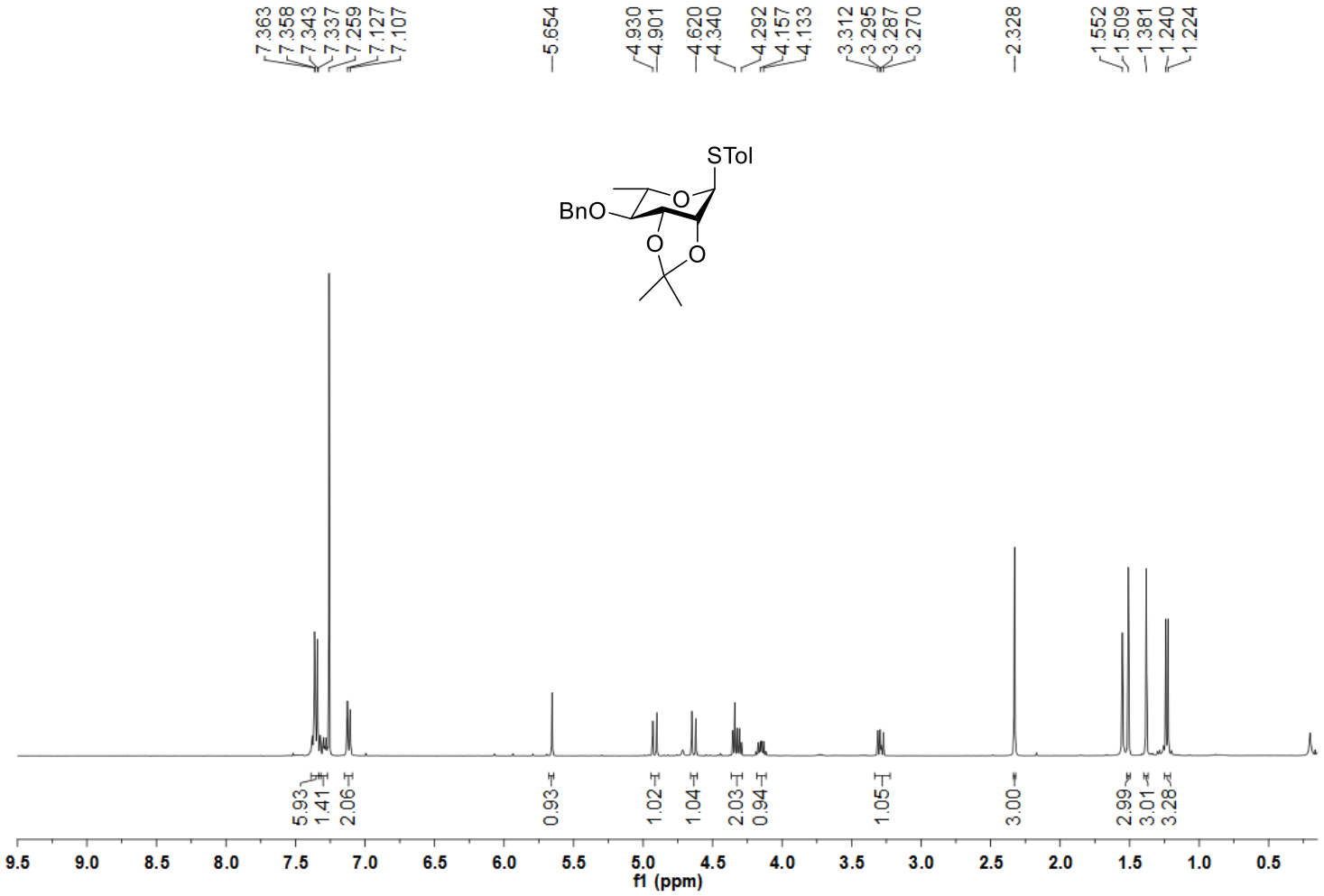
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4-*O*-(2-naphthylmethyl)-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside ($12h_1$):



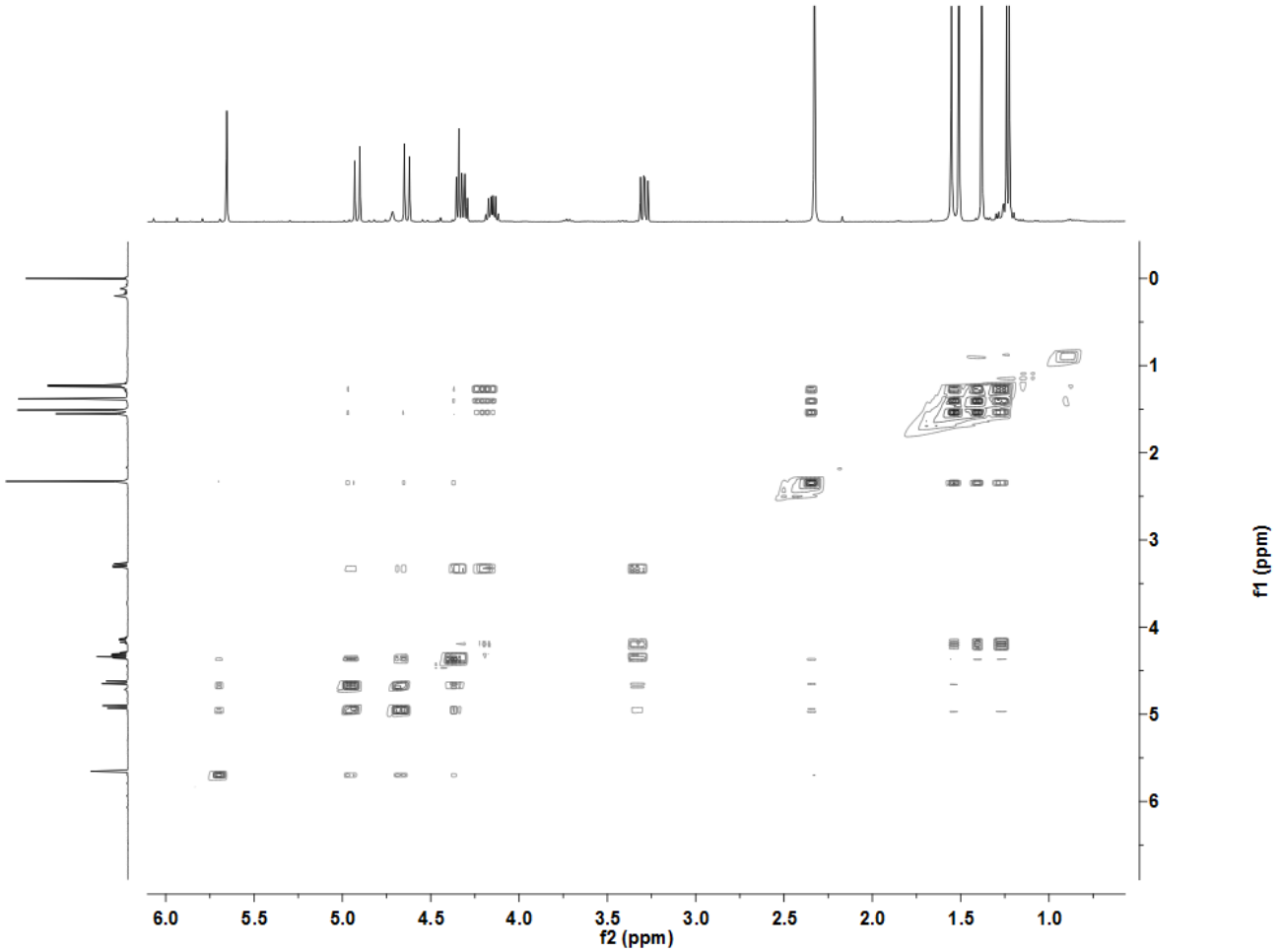
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4-*O*-(2-naphthylmethyl)-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside ($12h_1$):



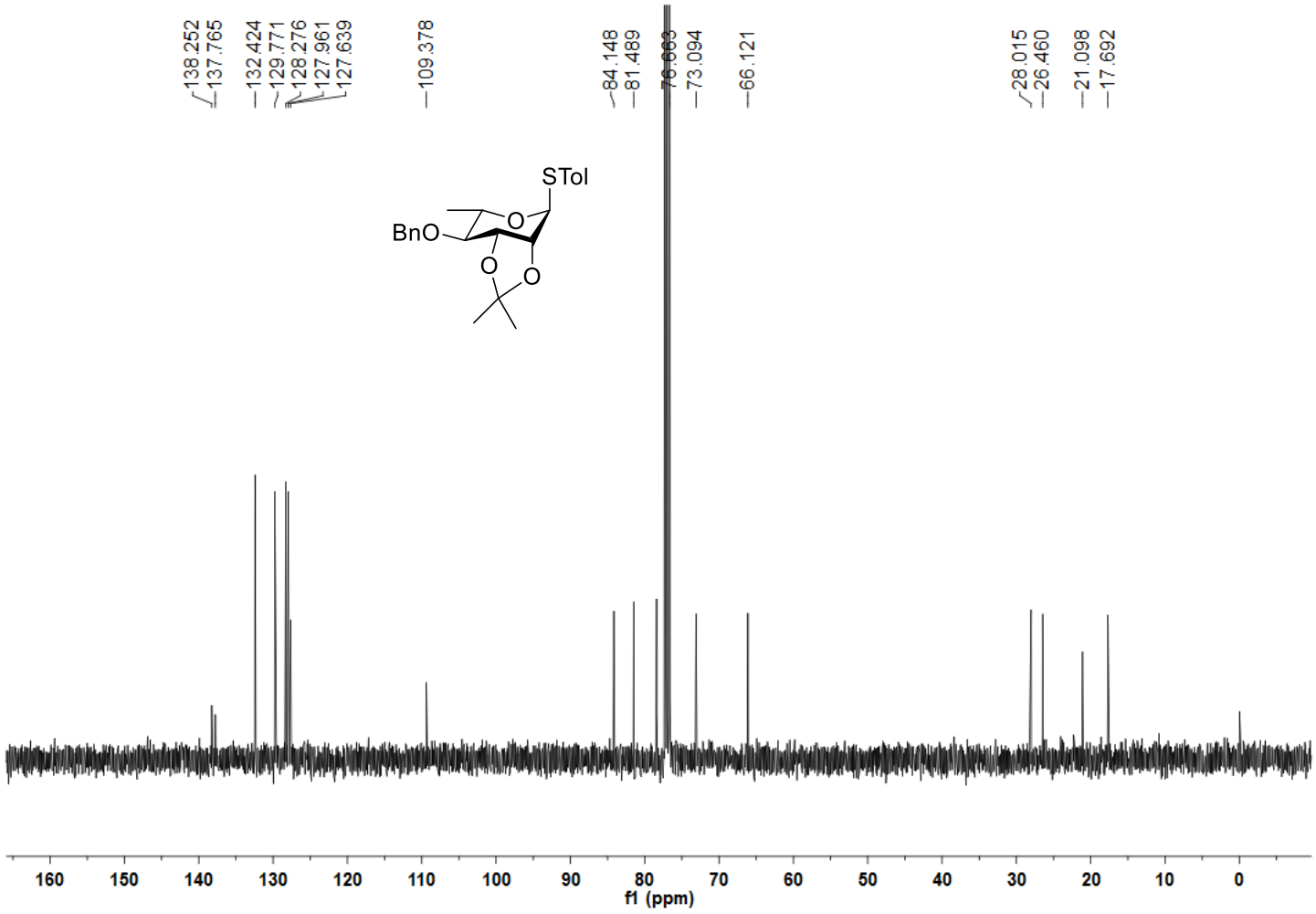
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4-*O*-Benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (12h$_2$):



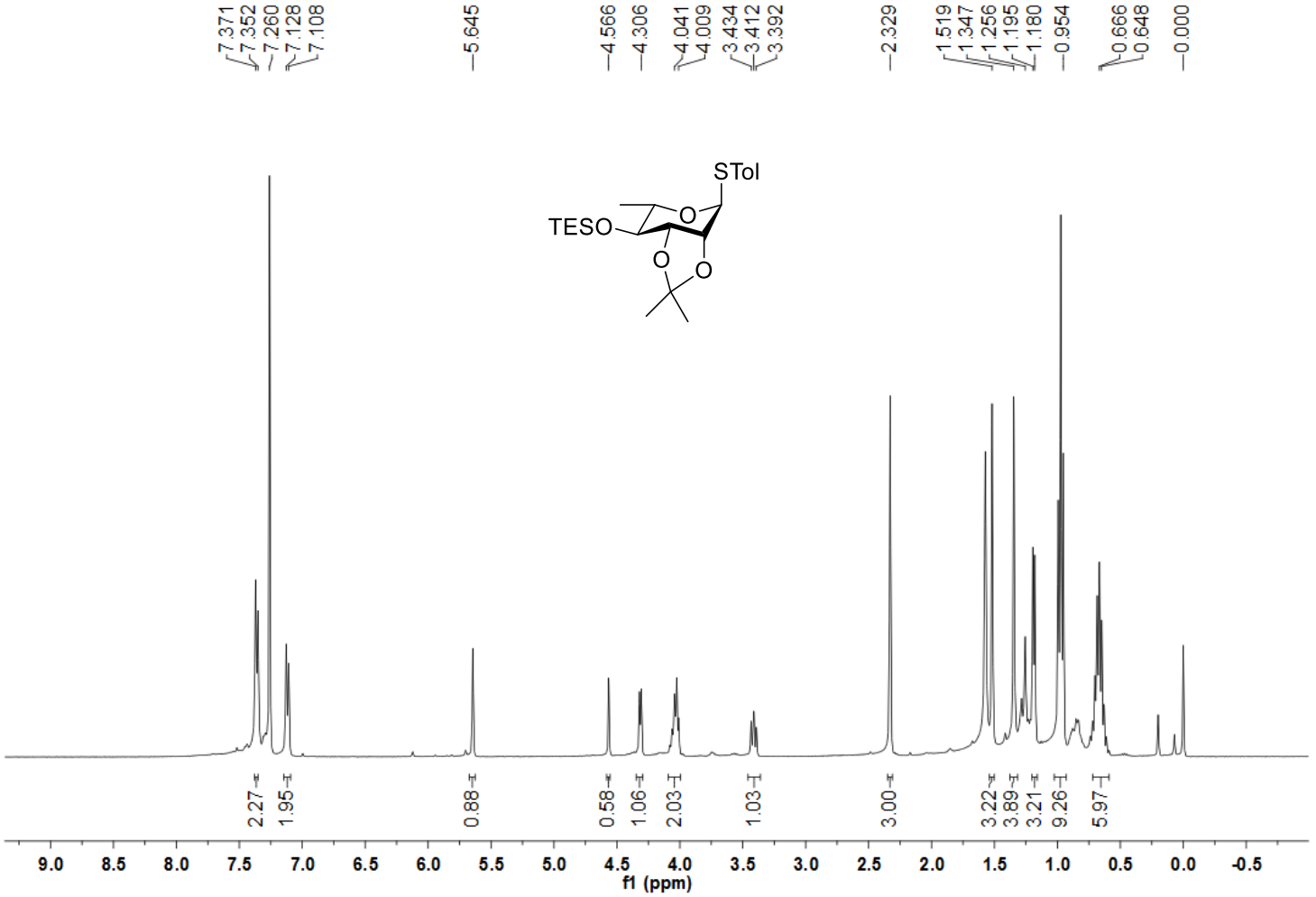
COSY NMR spectrum of *p*-tolyl 4-*O*-Benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (12h$_2$):



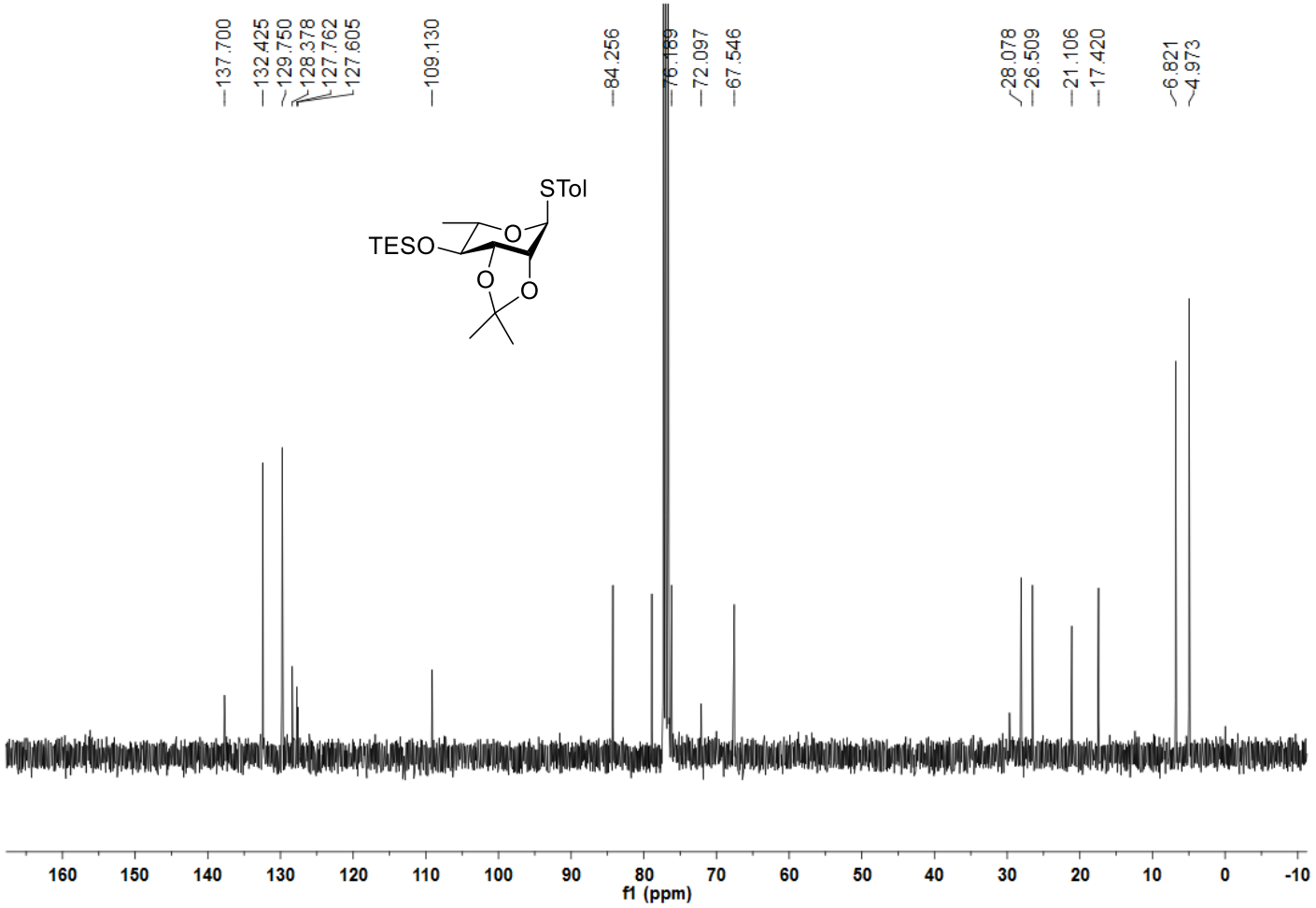
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4-*O*-benzyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (12h$_2$):



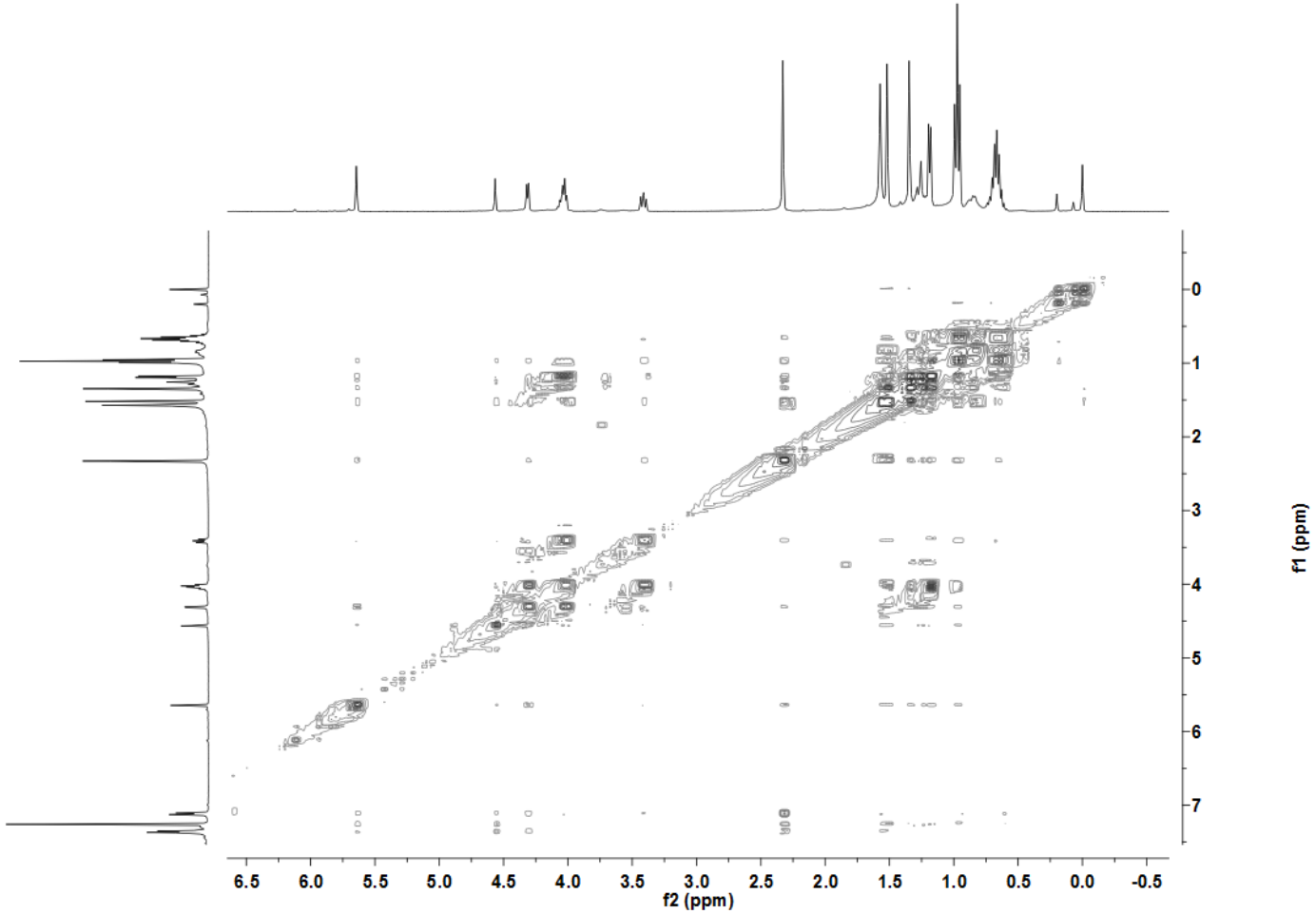
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4-*O*-triethylsilanyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S12h):



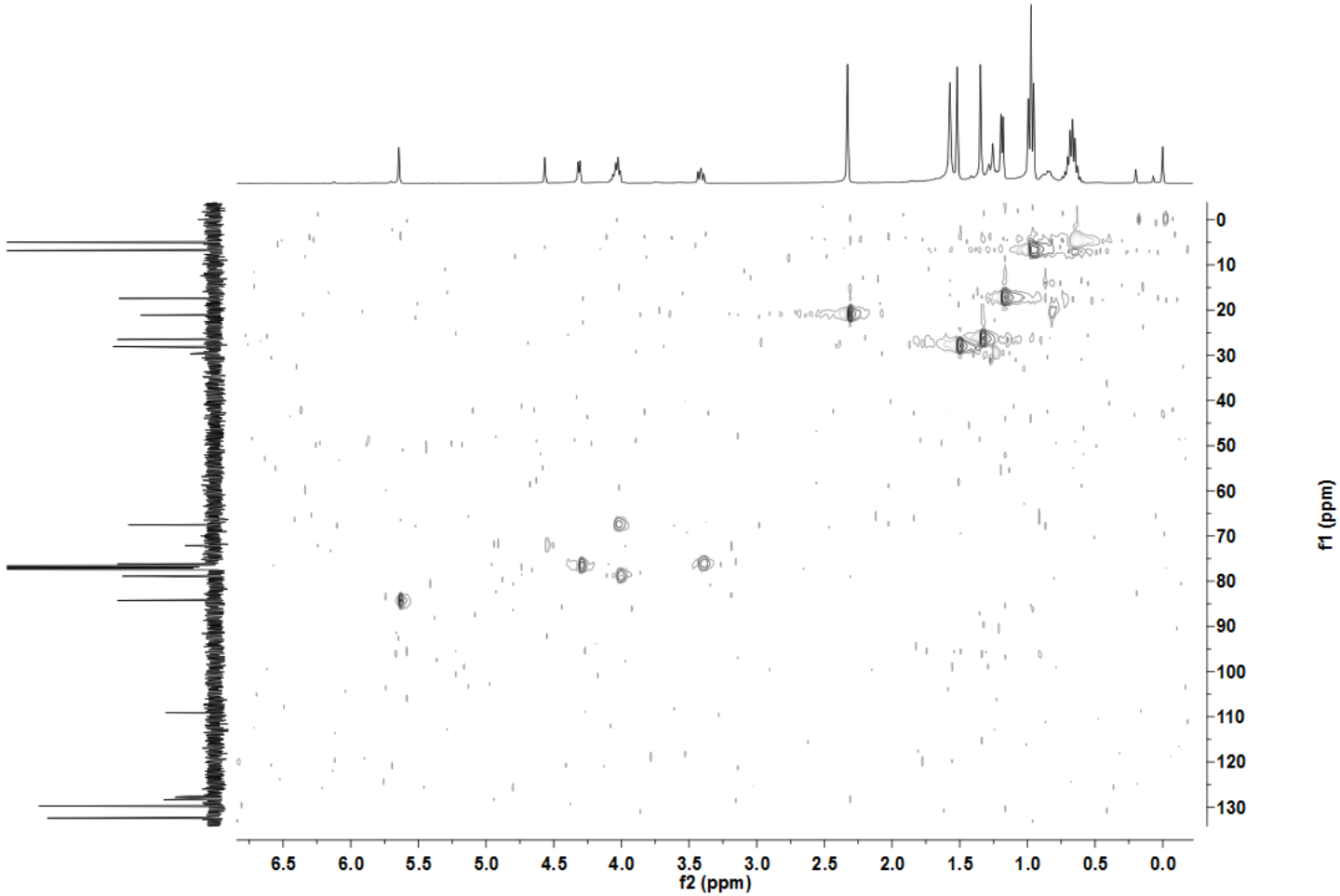
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4-*O*-triethylsilanyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S12h):



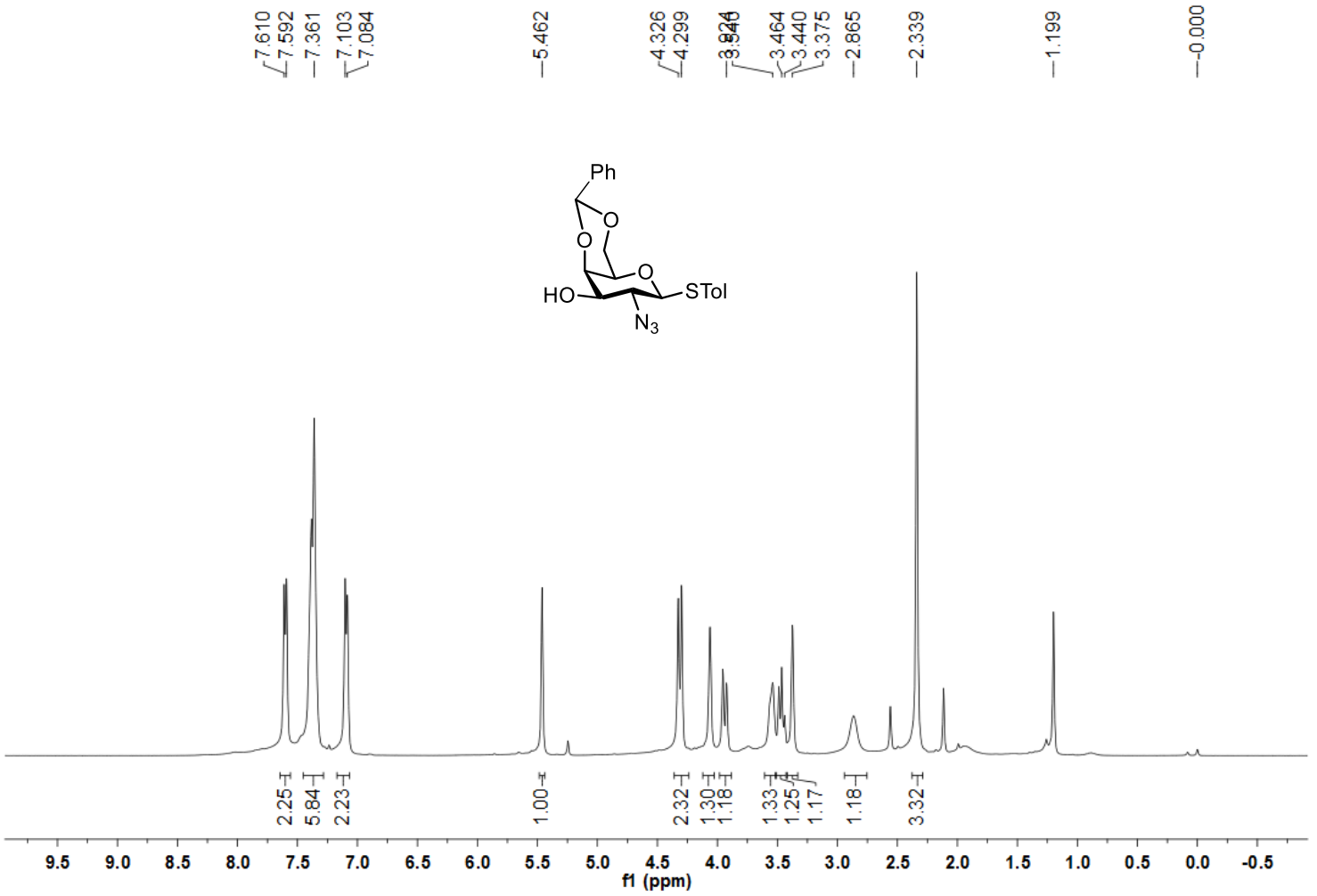
COSY NMR spectrum of *p*-tolyl 4-*O*-triethylsilanyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S12h):



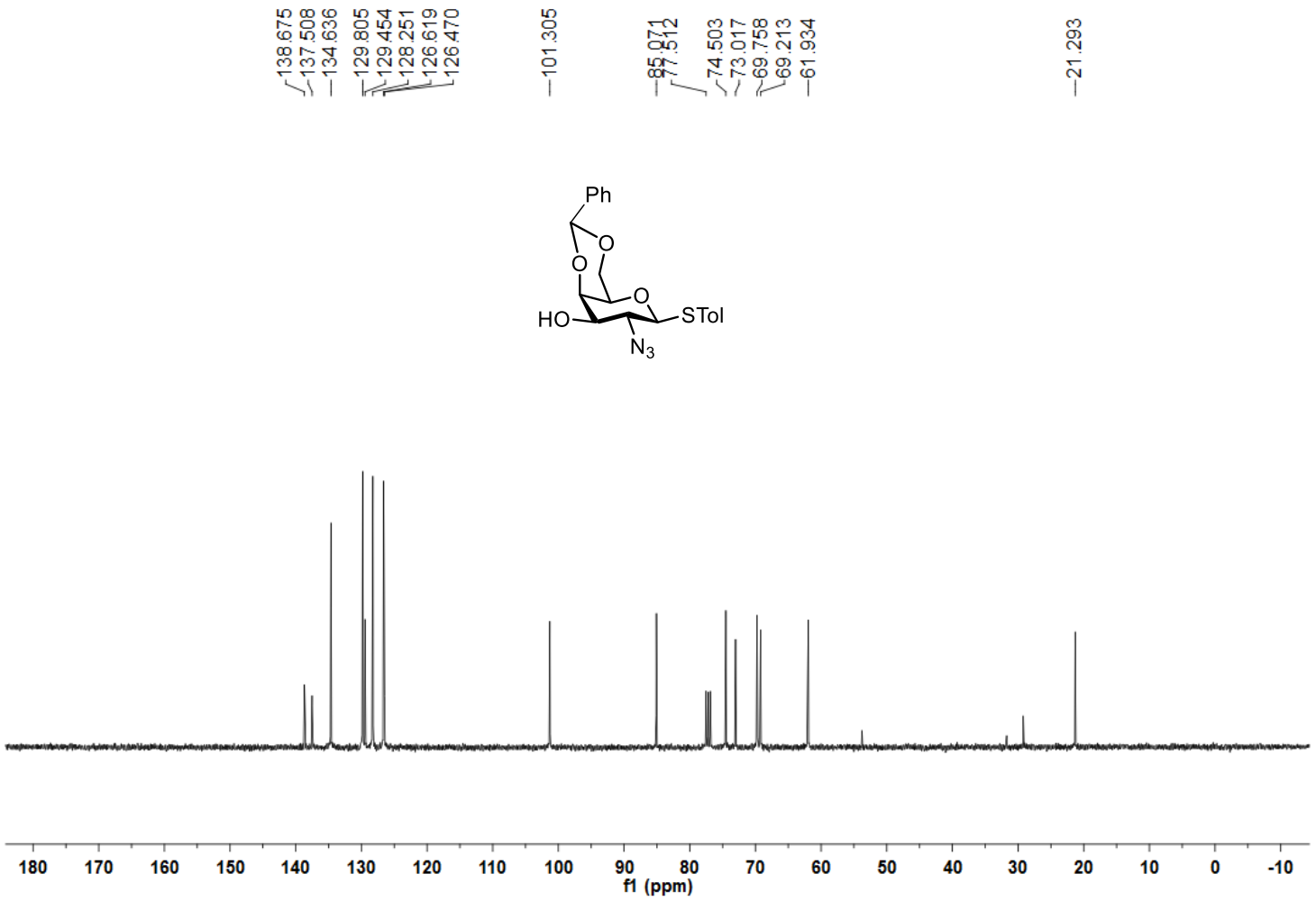
HSQC NMR spectrum of *p*-tolyl 4-*O*-triethylsilanyl-2,3-*O*-isopropylidene-1-thio-α-L-rhamnopyranoside (S12h):



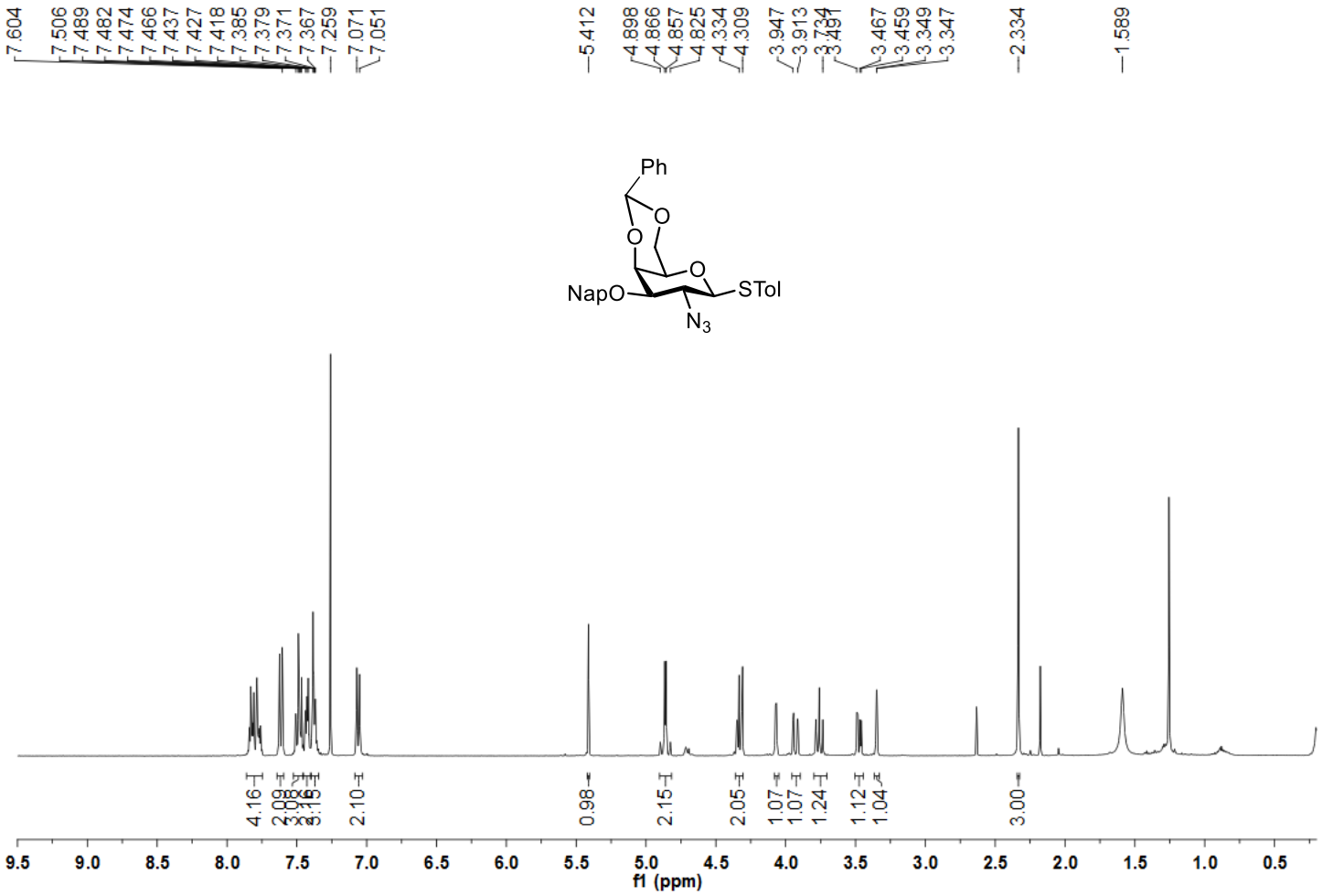
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranside (10i):



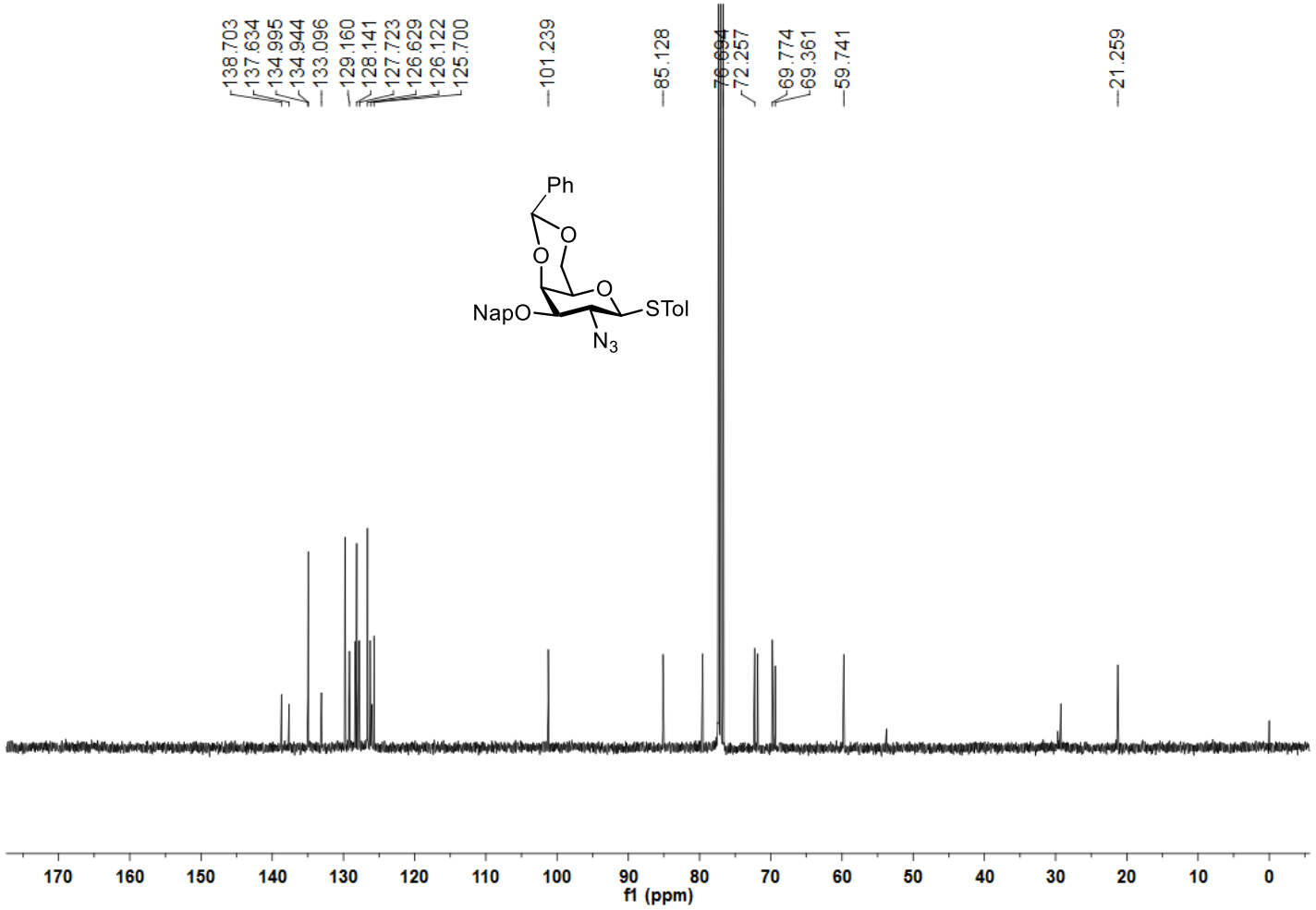
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranside (10i):



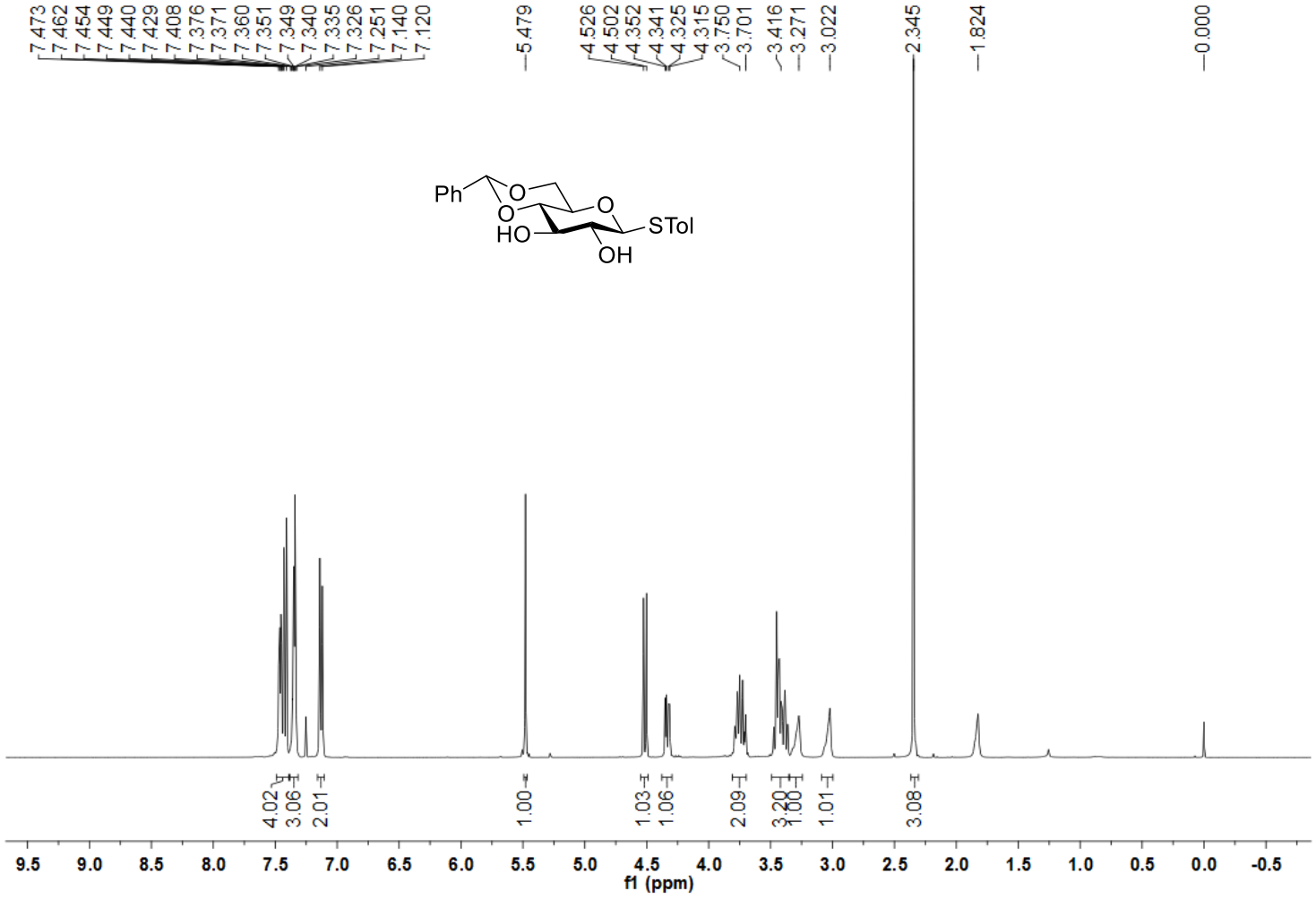
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranside (12i):



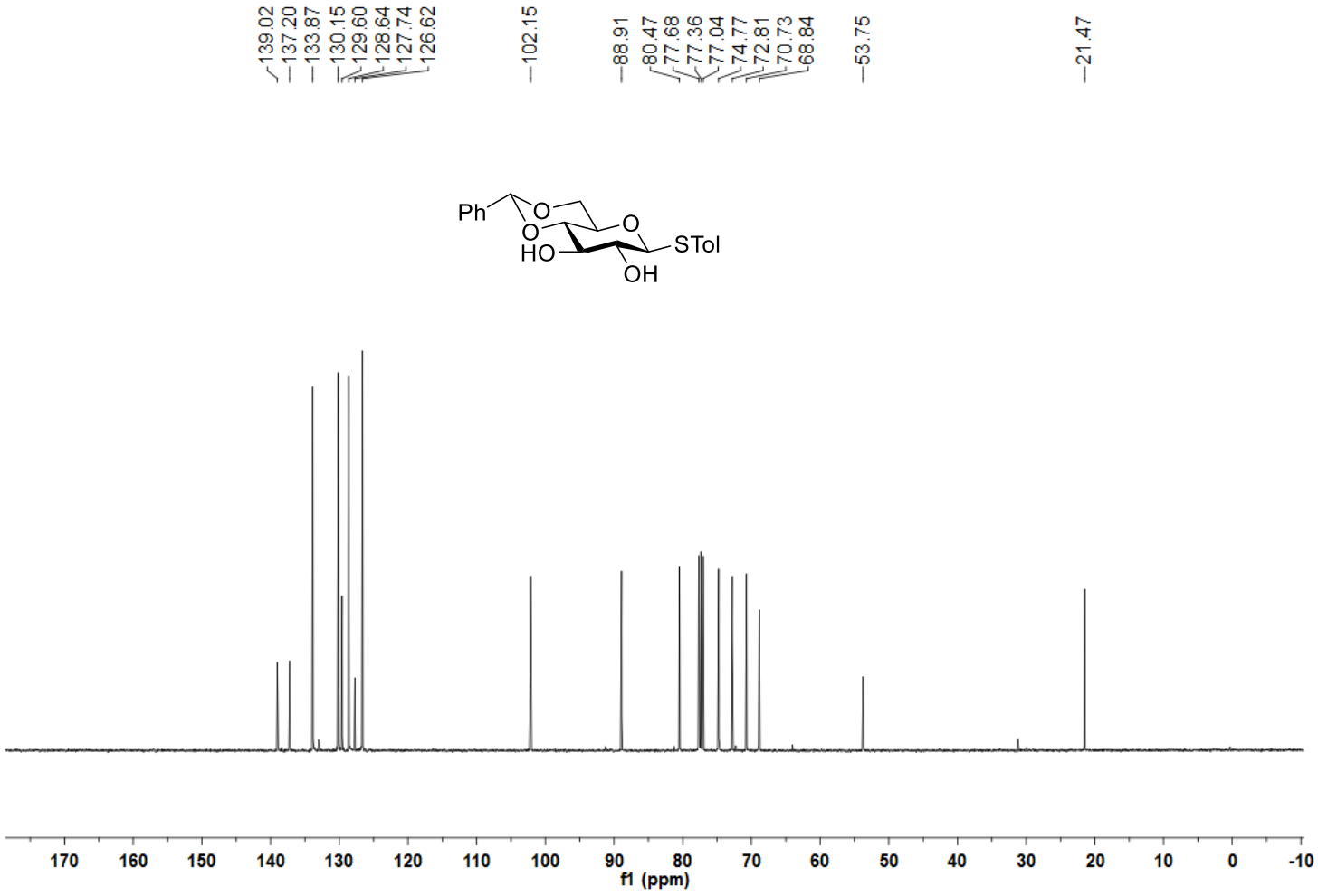
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2-naphthylmethyl)-1-thio-β-D-galactopyranside (12i):



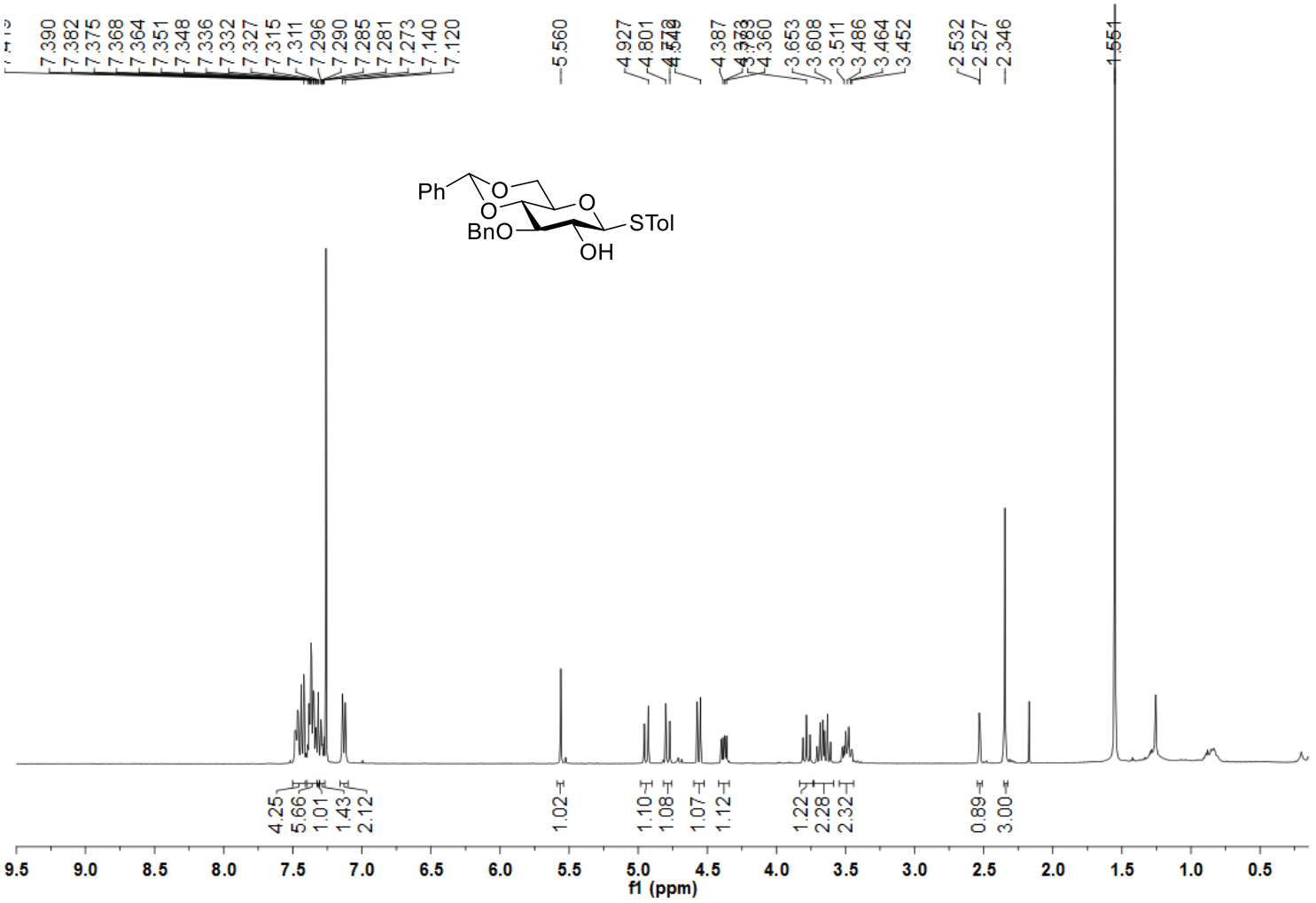
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (10j):



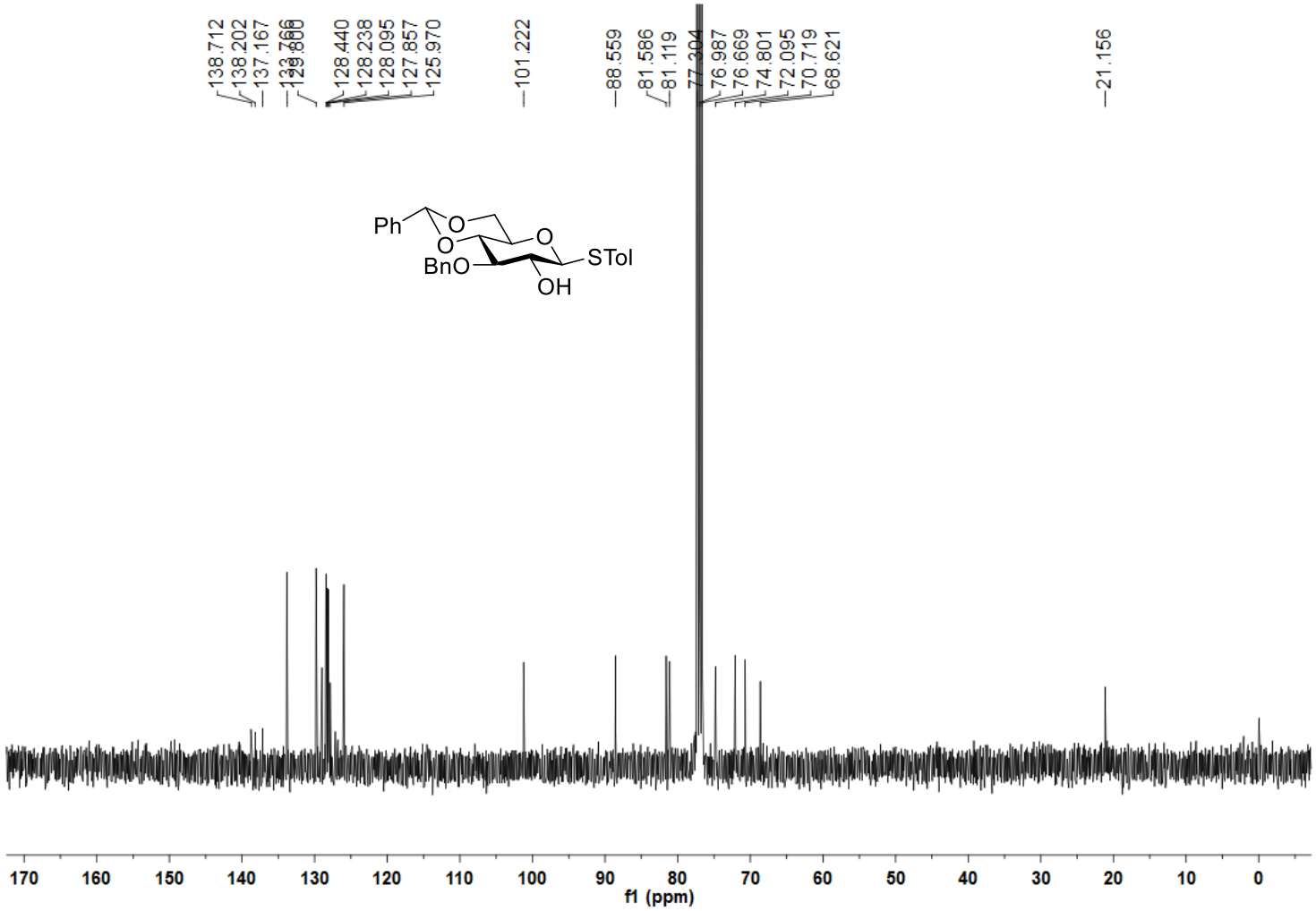
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (10j):



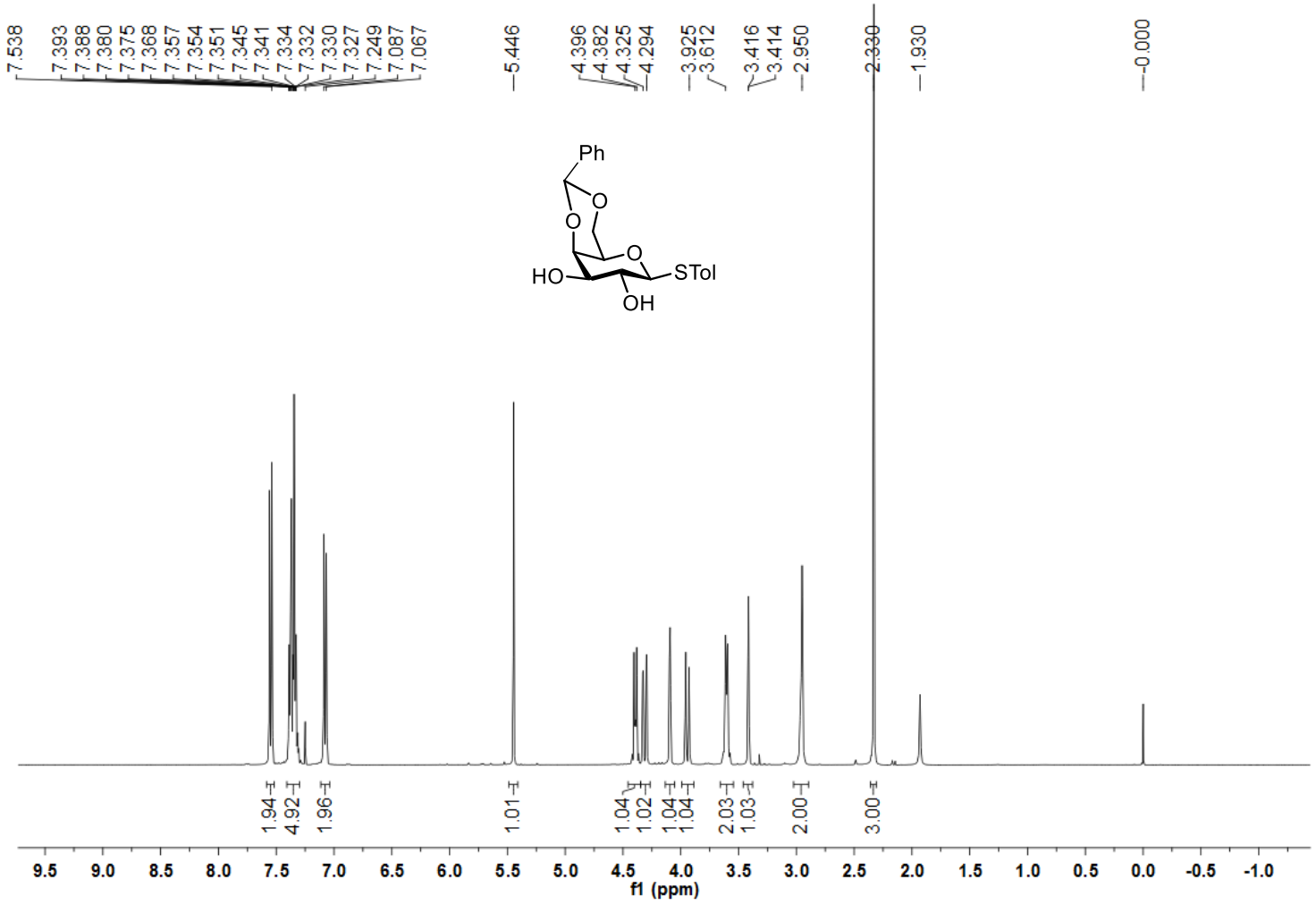
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (12j):



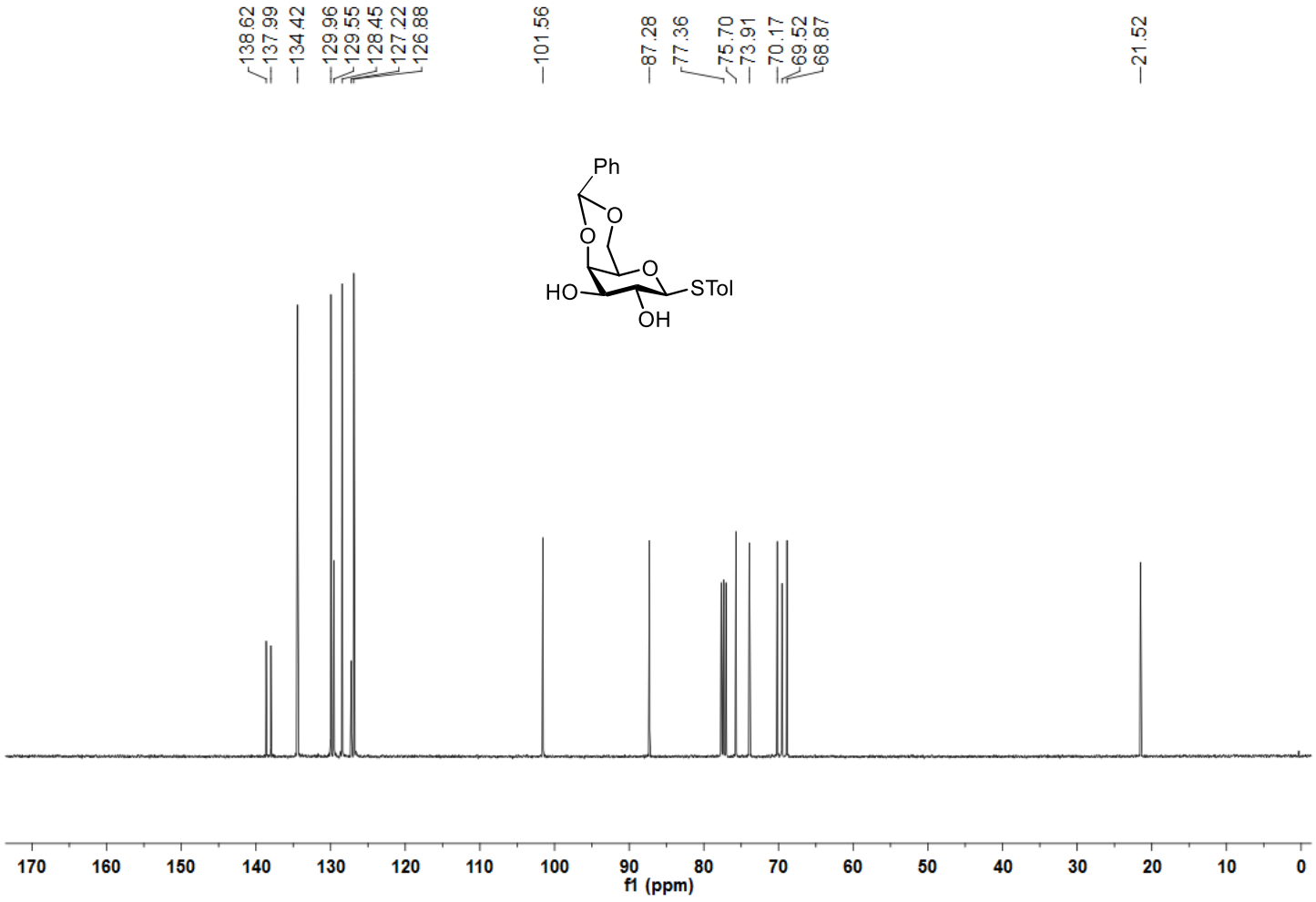
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (12j):



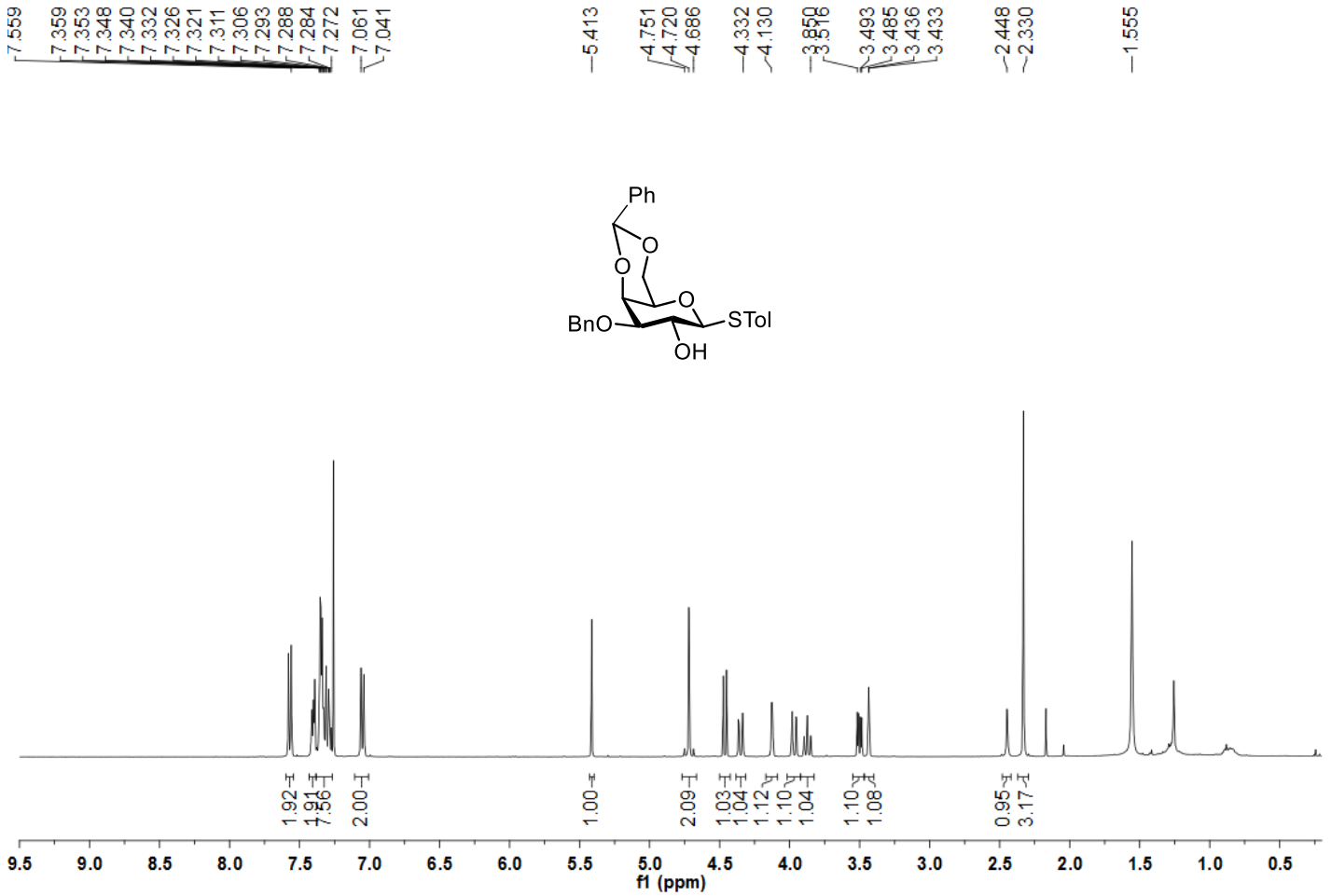
^{1}H 400 MHz NMR spectrum of *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (10k):



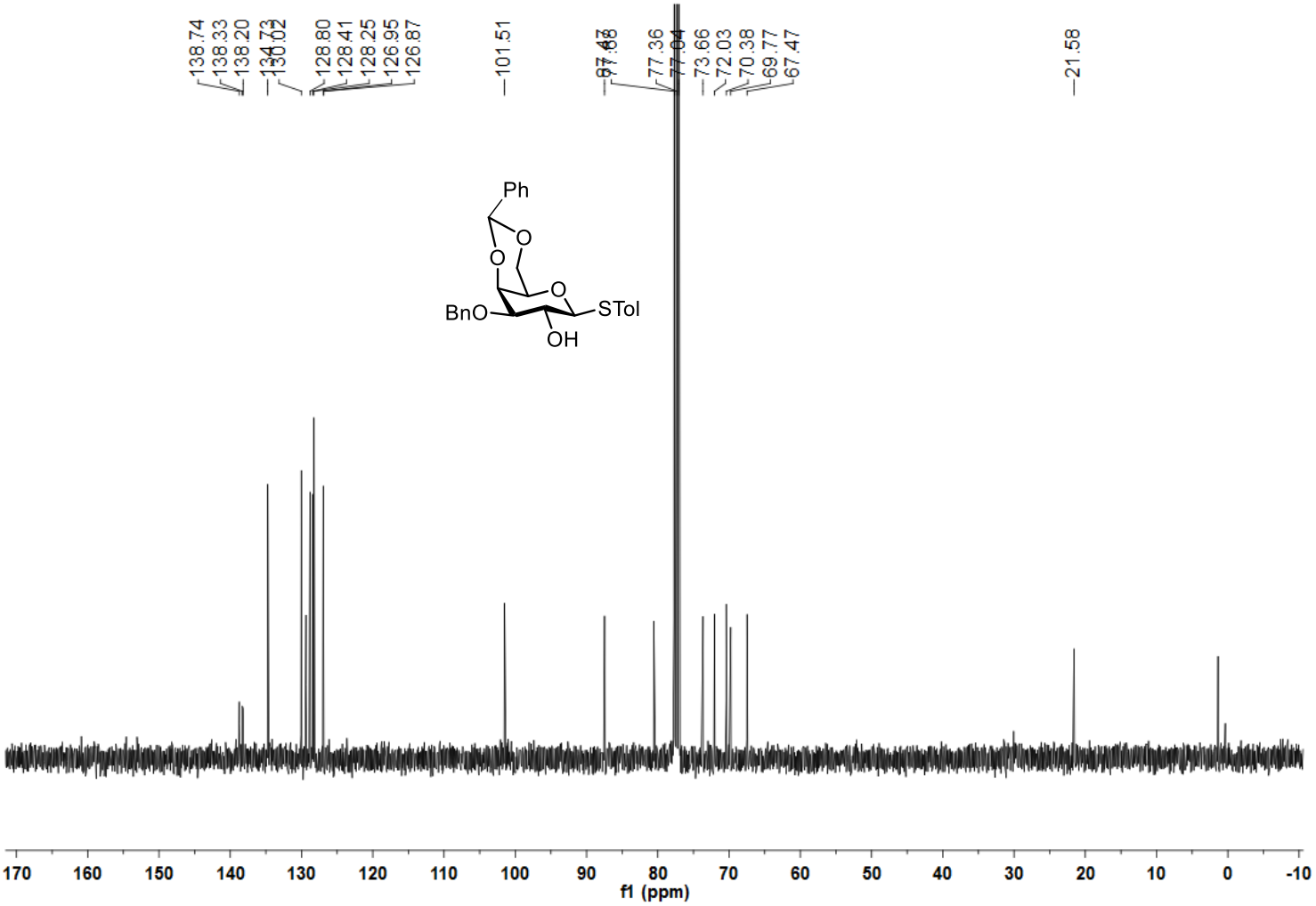
^{13}C 100 MHz NMR spectrum of *p*-tolyl 4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (10k):



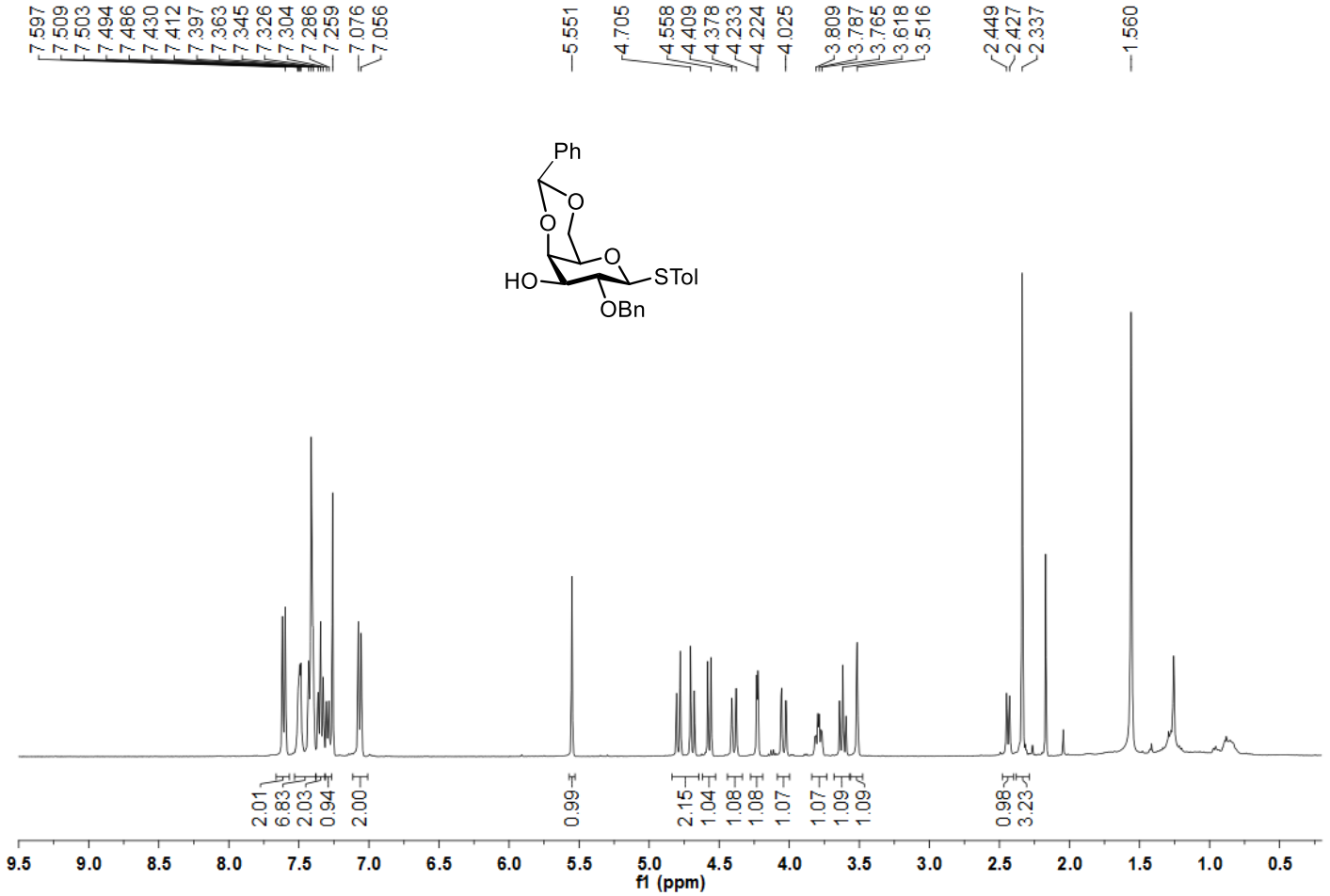
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_1$):



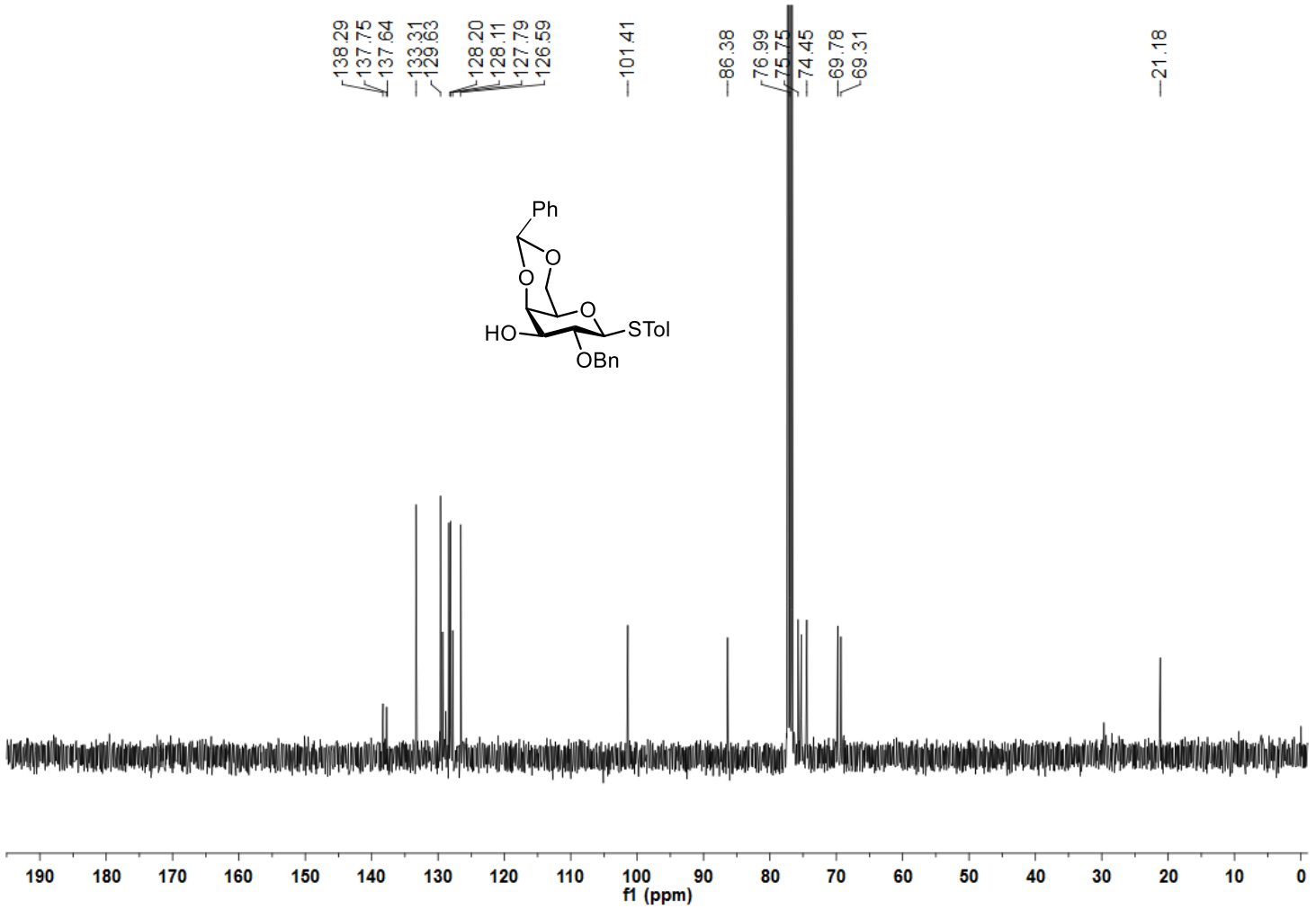
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_I$):



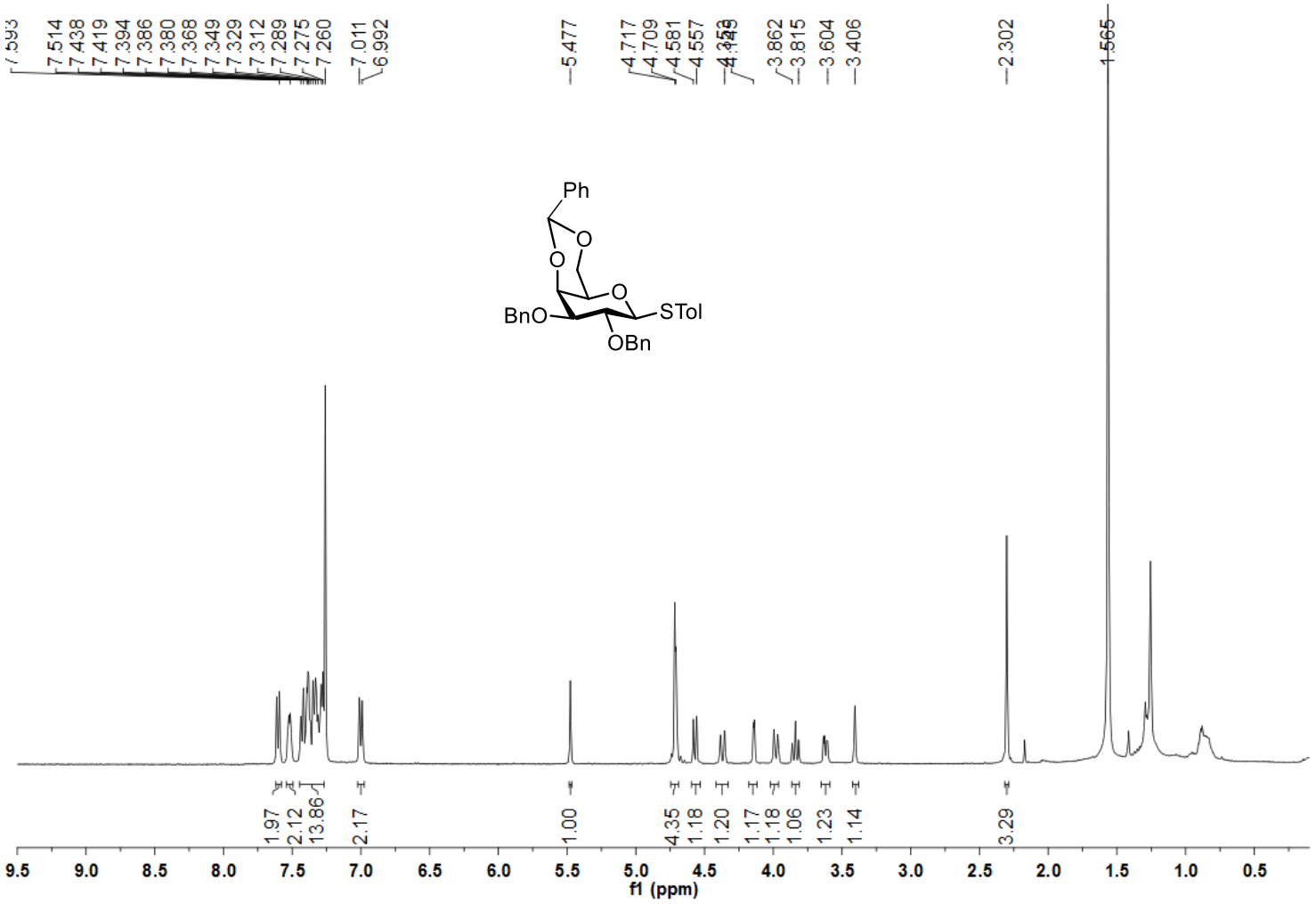
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_2$):



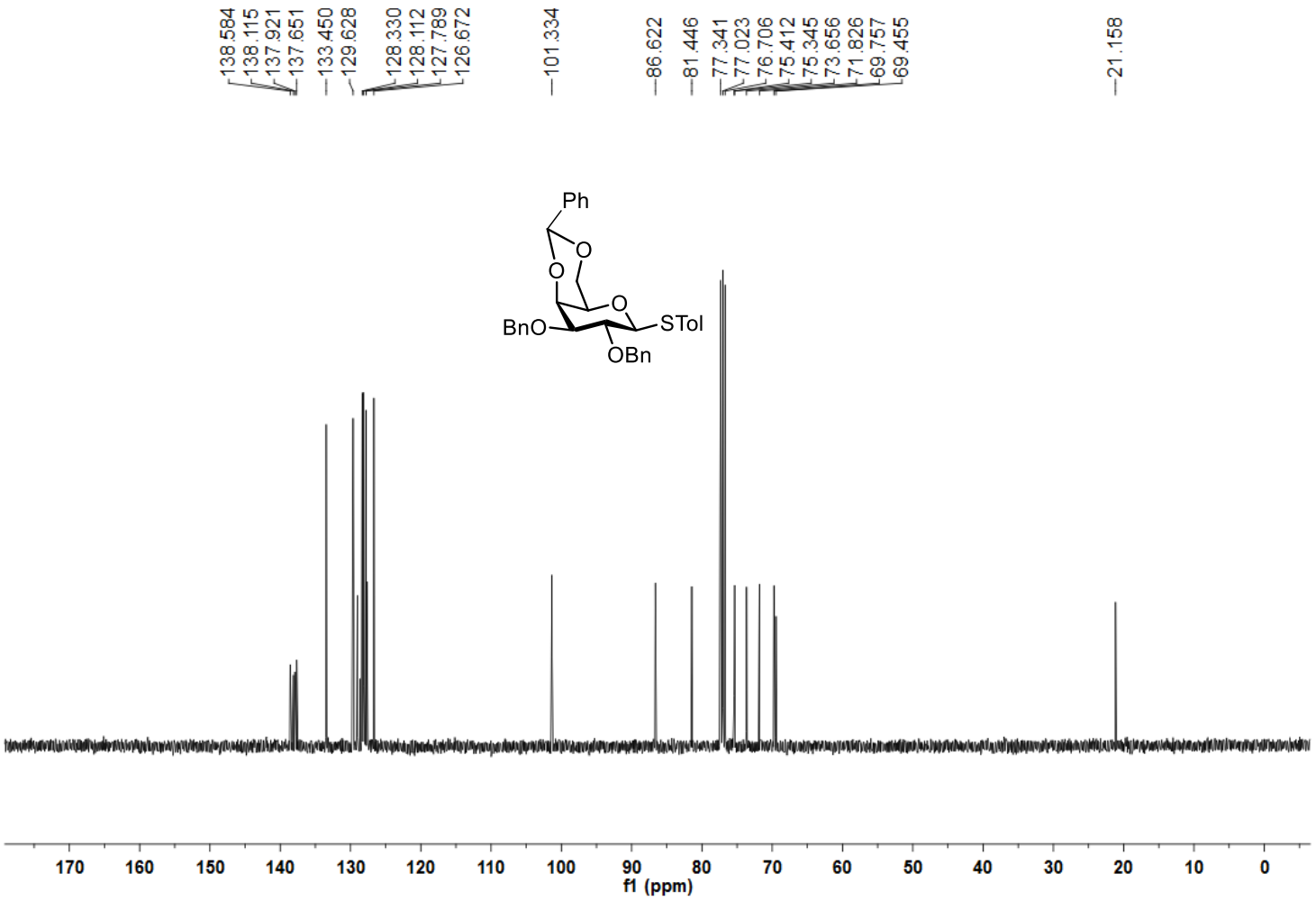
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_2$):



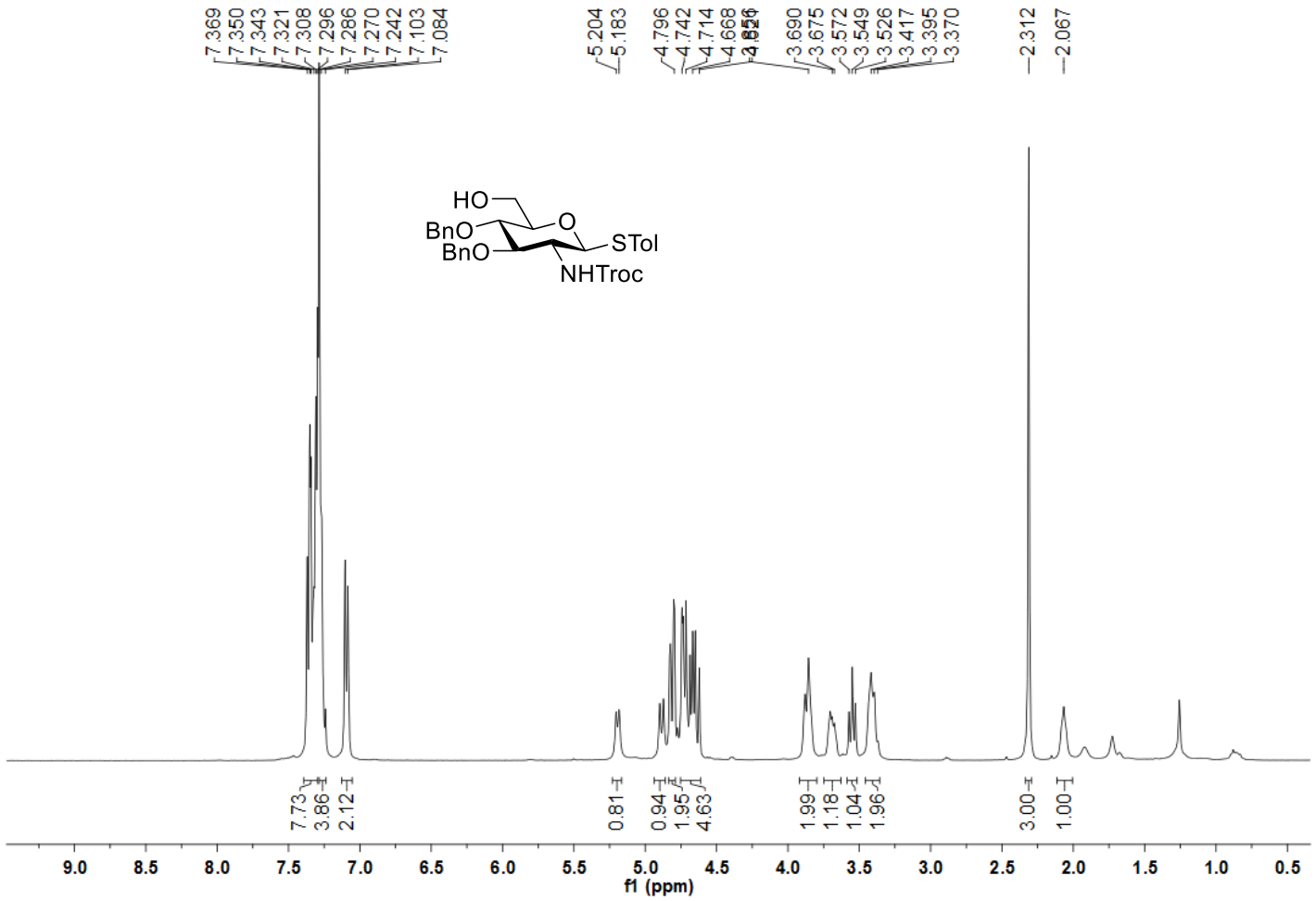
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_3$):



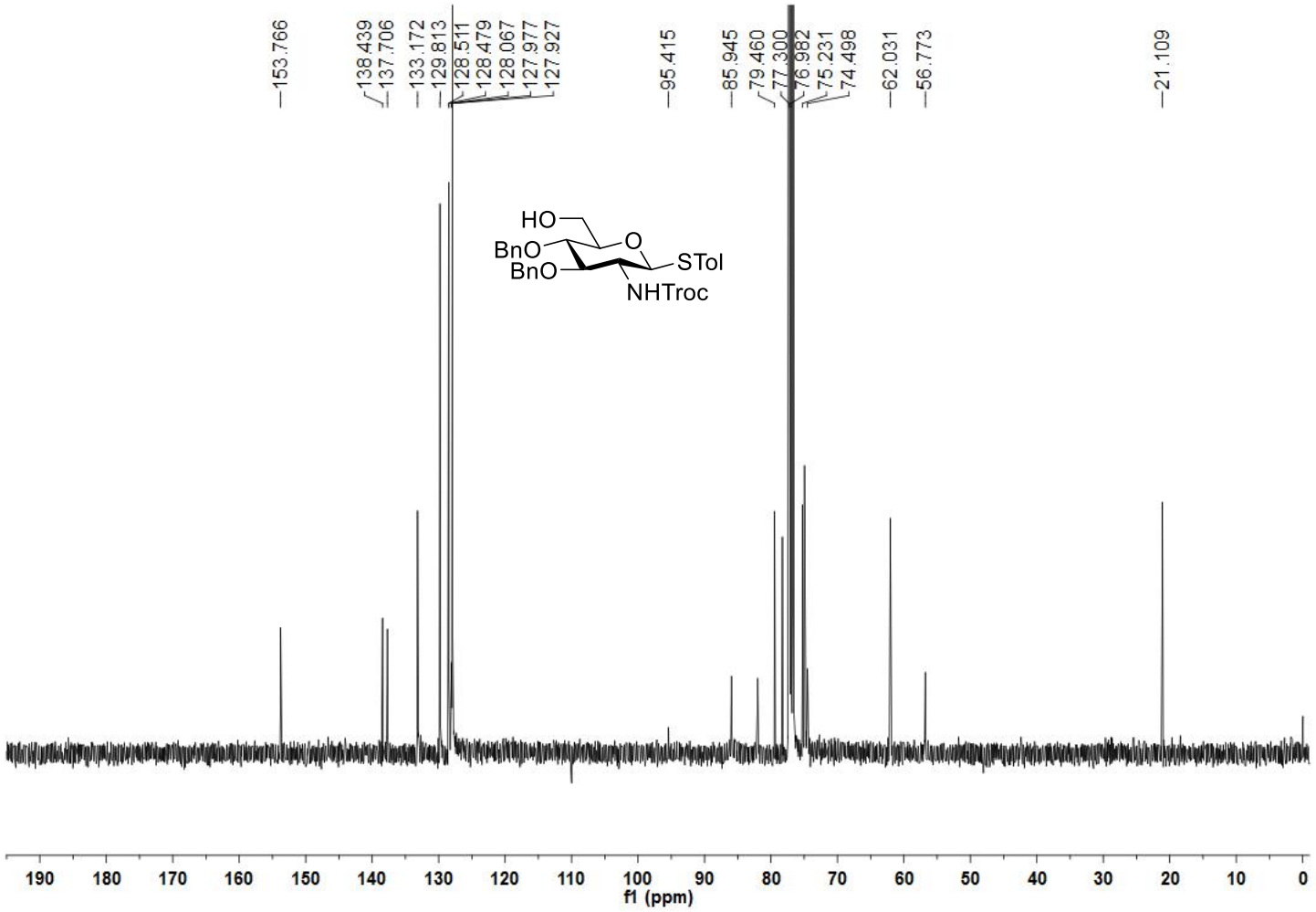
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranside (12k$_3$):



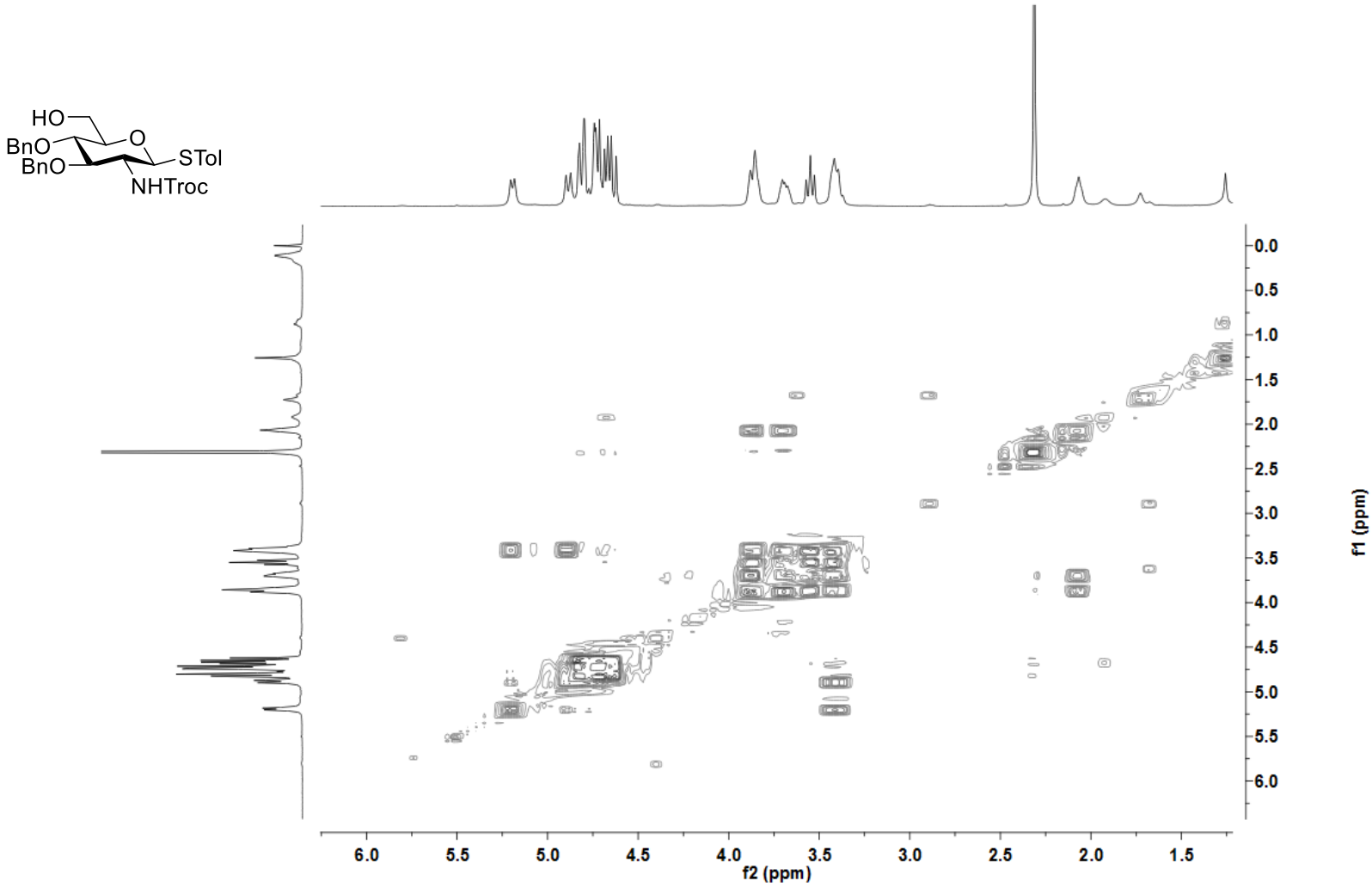
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3,4-di-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (17):



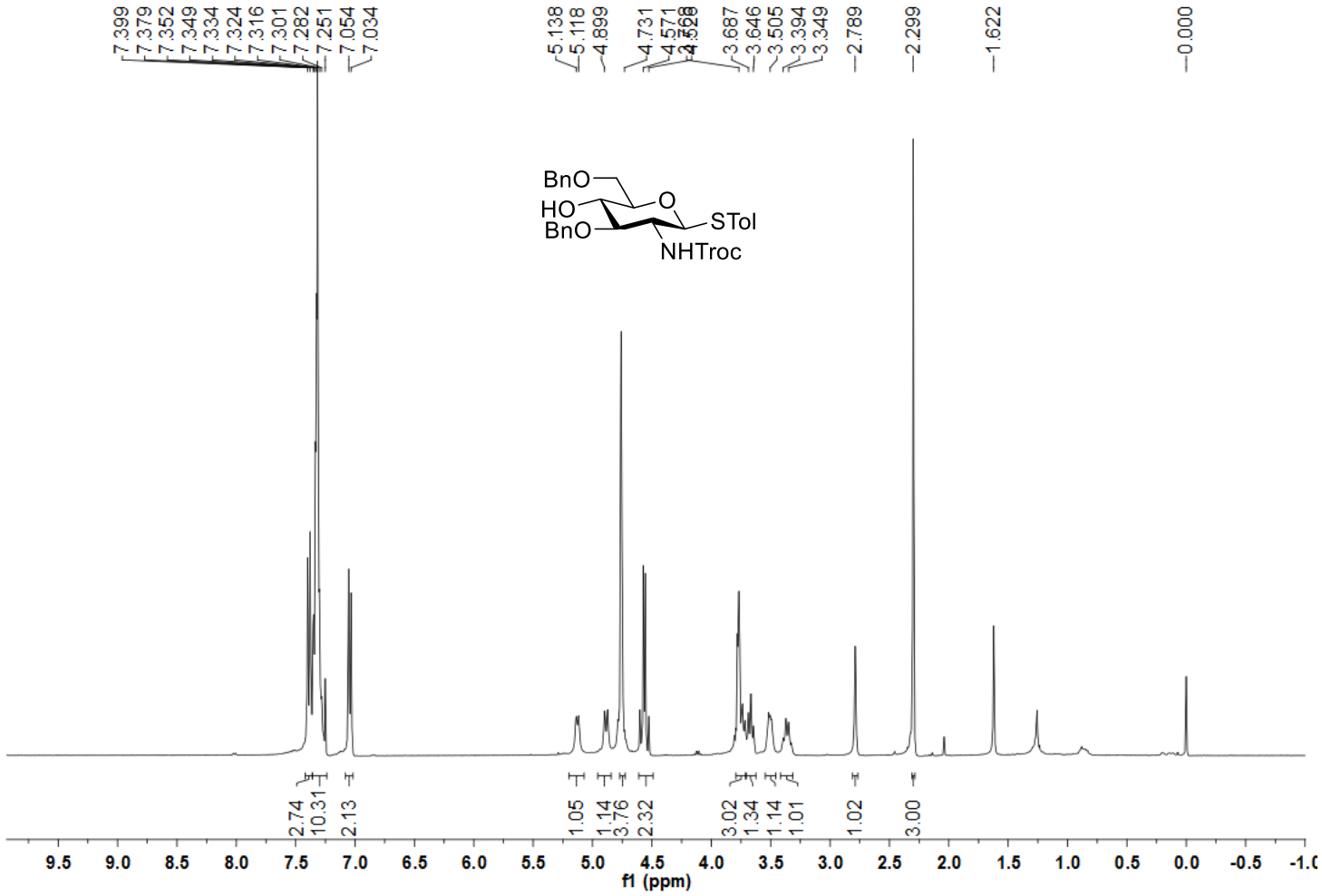
^{13}C 100 MHz NMR spectrum of of *p*-tolyl 3,4-di-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (17):



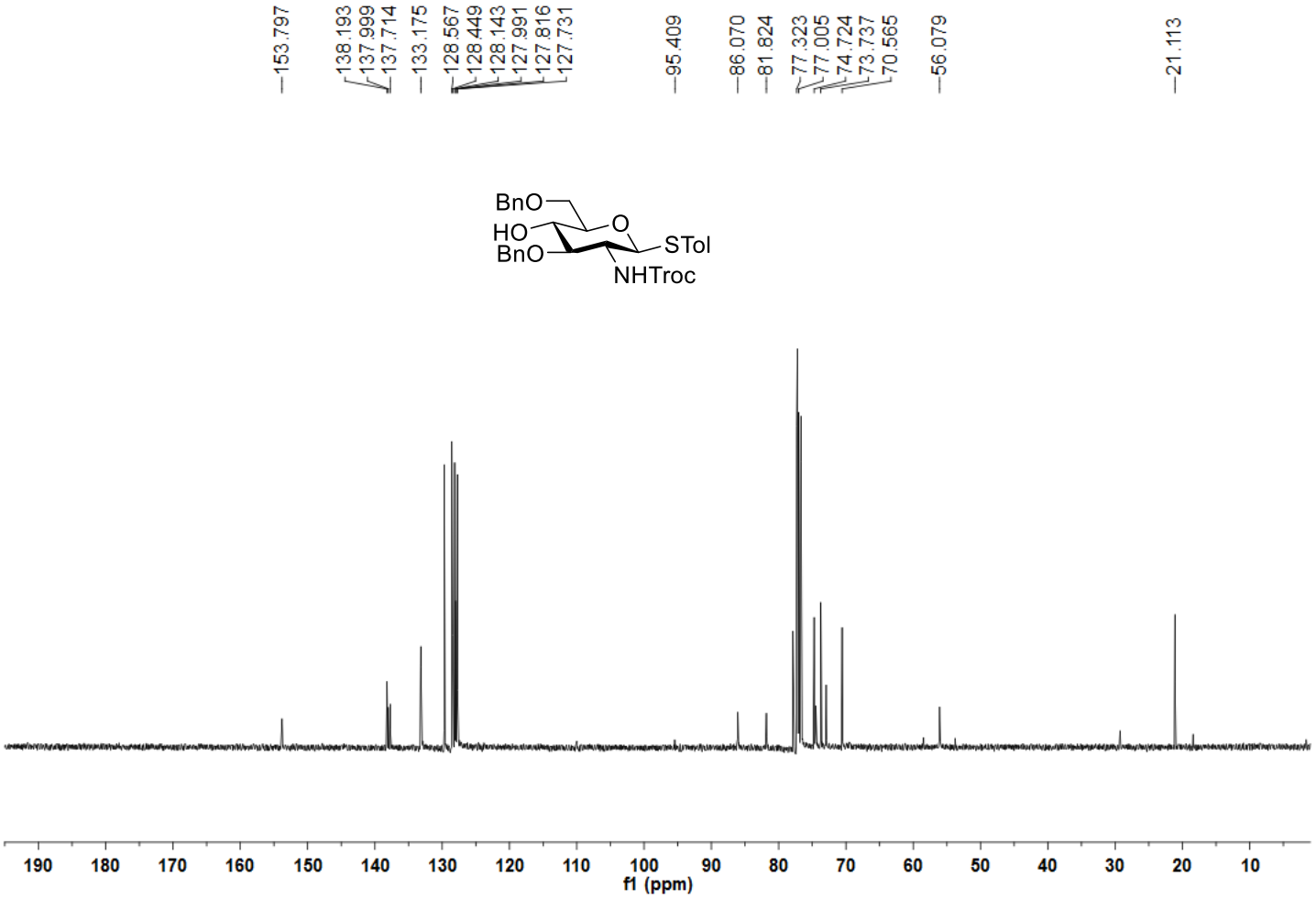
COSY NMR spectrum of of *p*-tolyl 3,4-di-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (17):



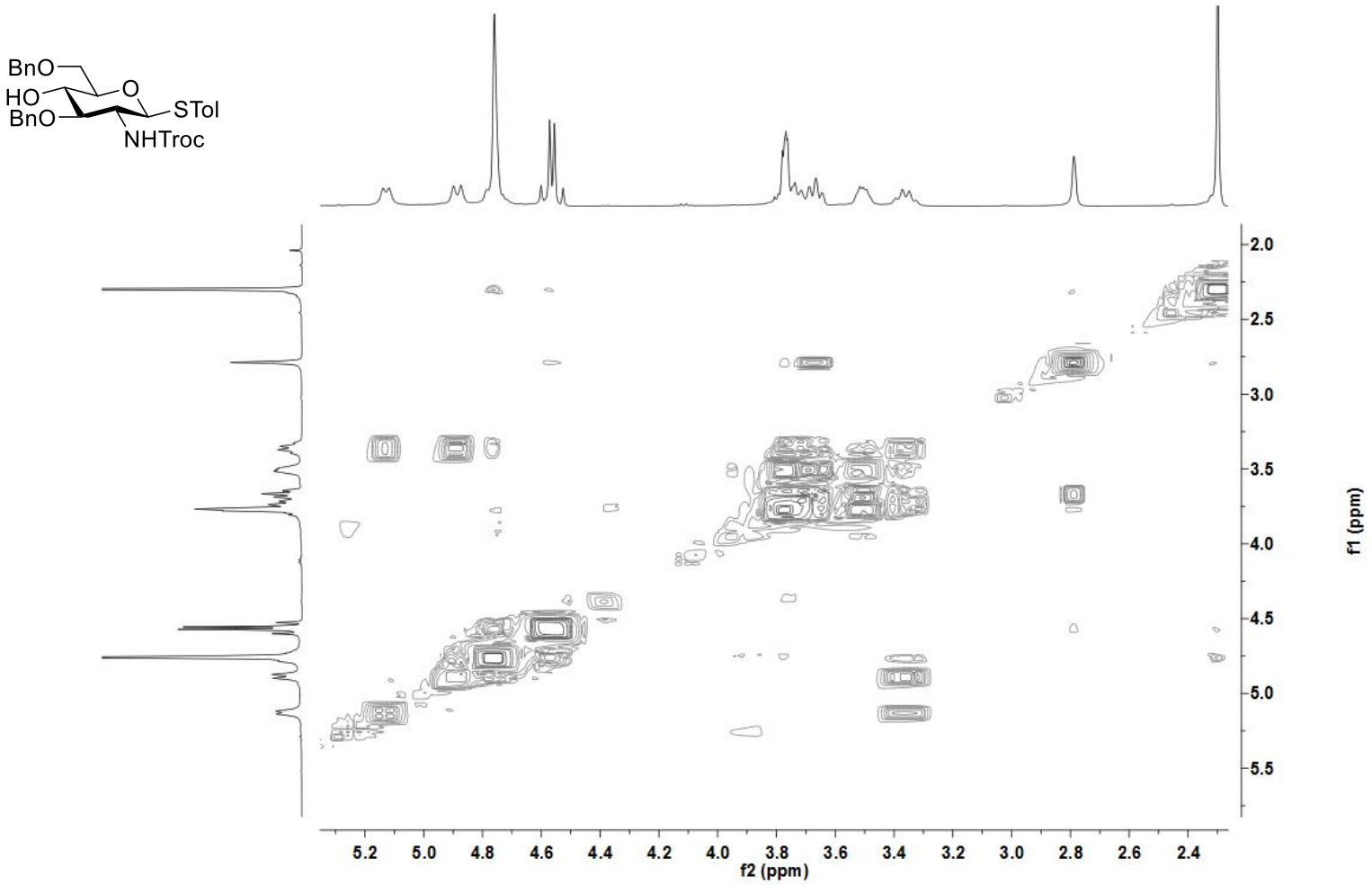
^{1}H 400 MHz NMR spectrum of *p*-tolyl 3,6-di-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (18):



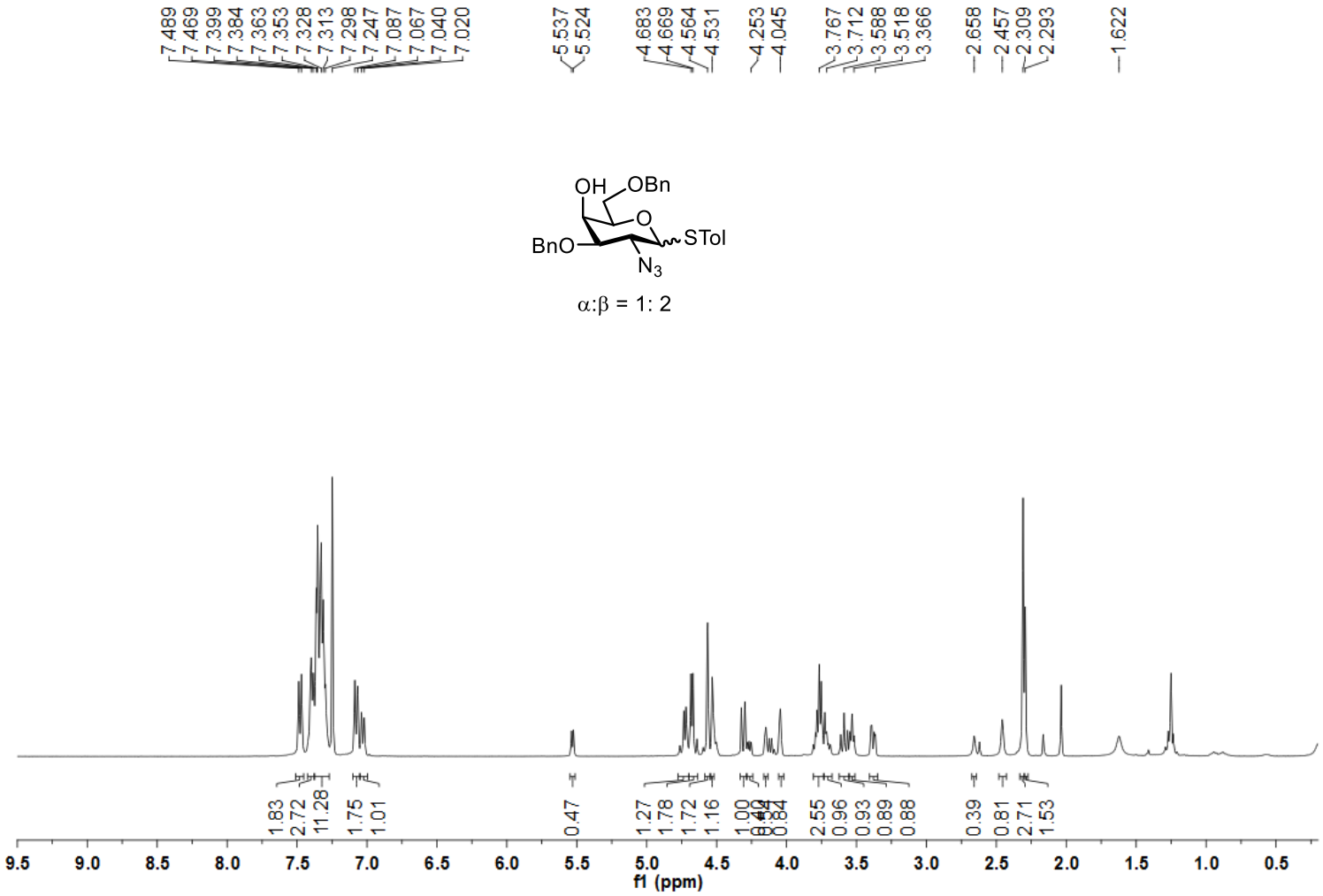
^{13}C 100 MHz NMR spectrum of *p*-tolyl 3,6-di-*O*-Benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (18):



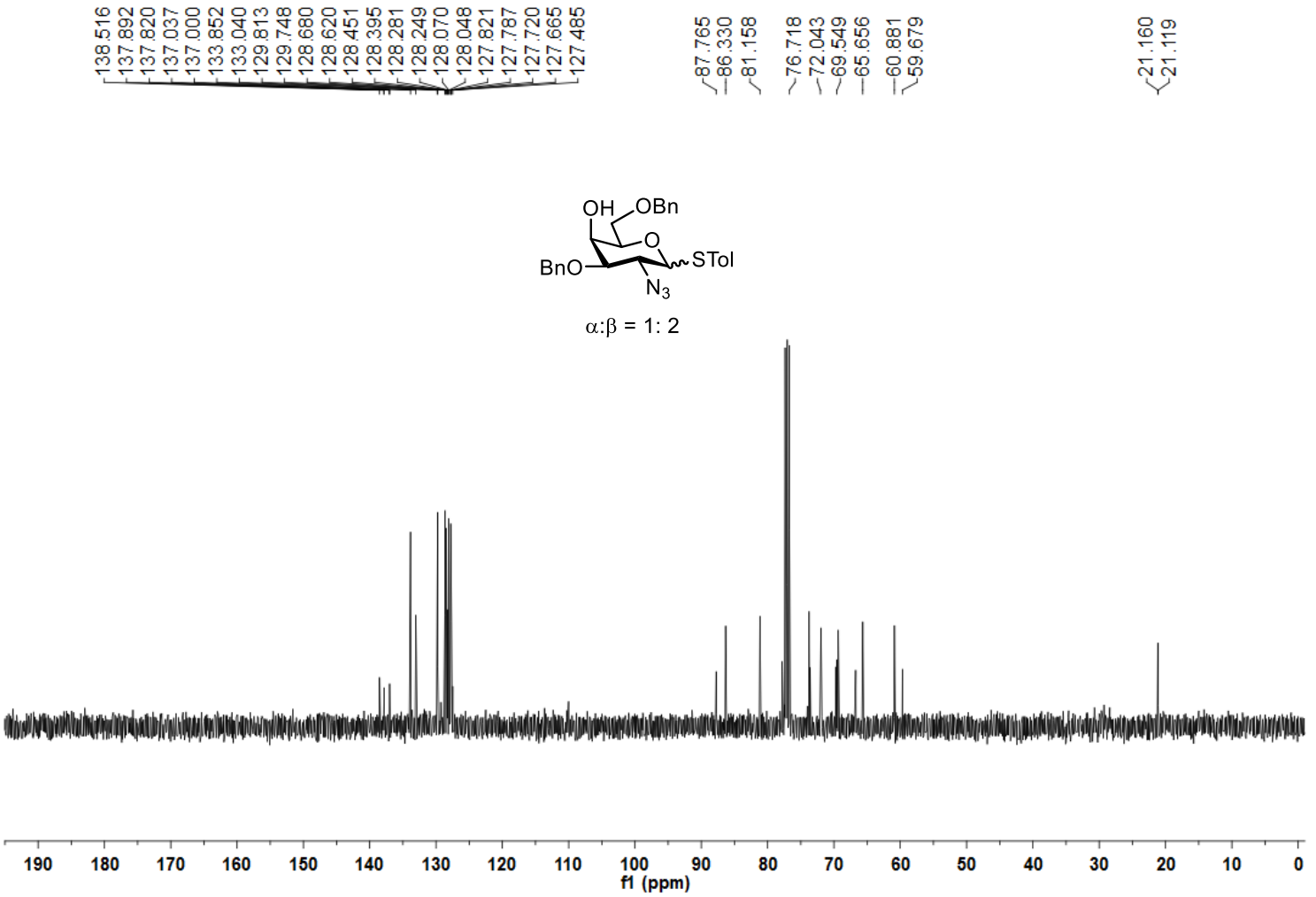
COSY NMR spectrum of *p*-tolyl 3,6-di-*O*-benzyl-2-*N*-trichloroethoxycarbonyl-1-thio-β-D-glucopyranoside (18):



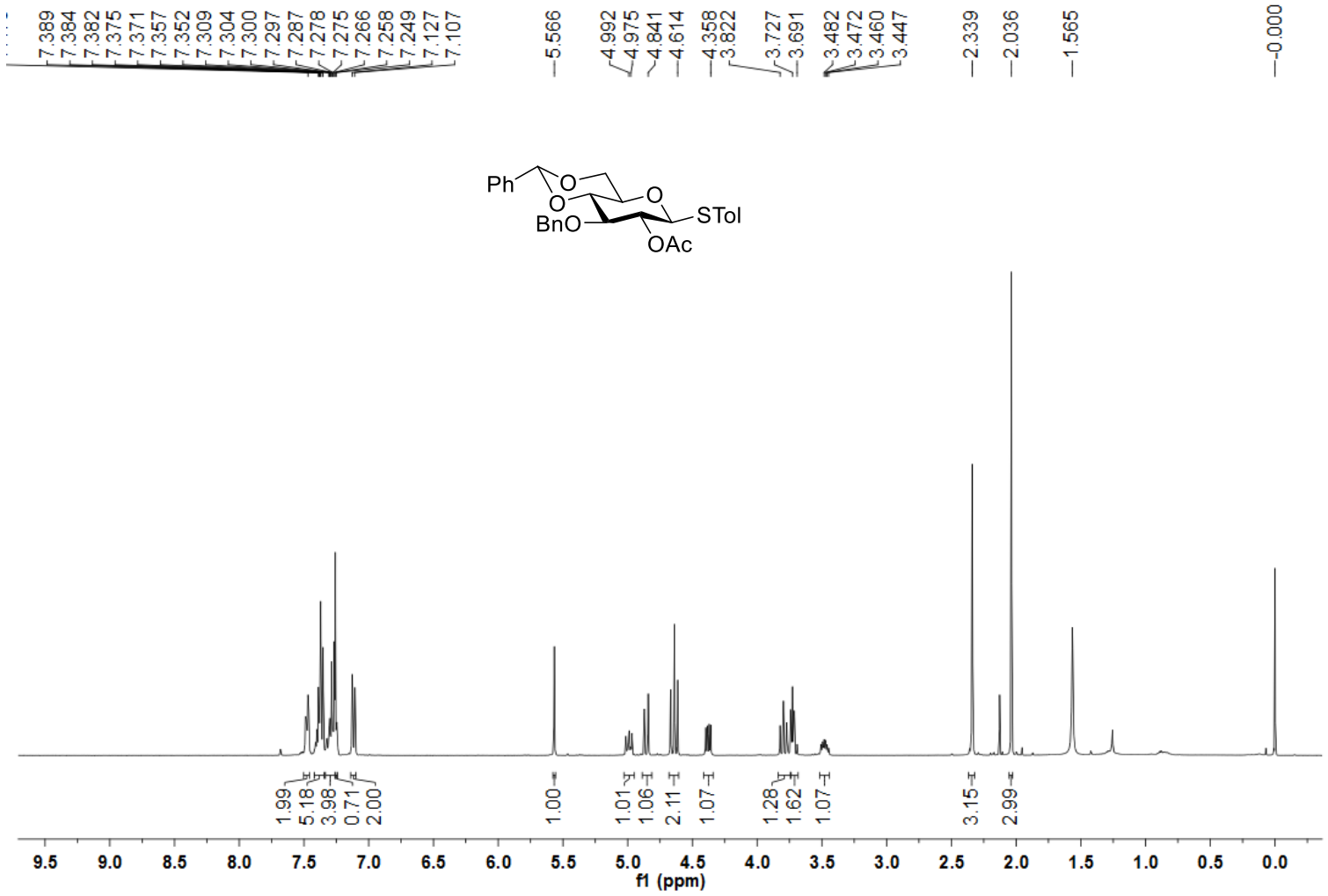
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-D-galactopyranside (21):



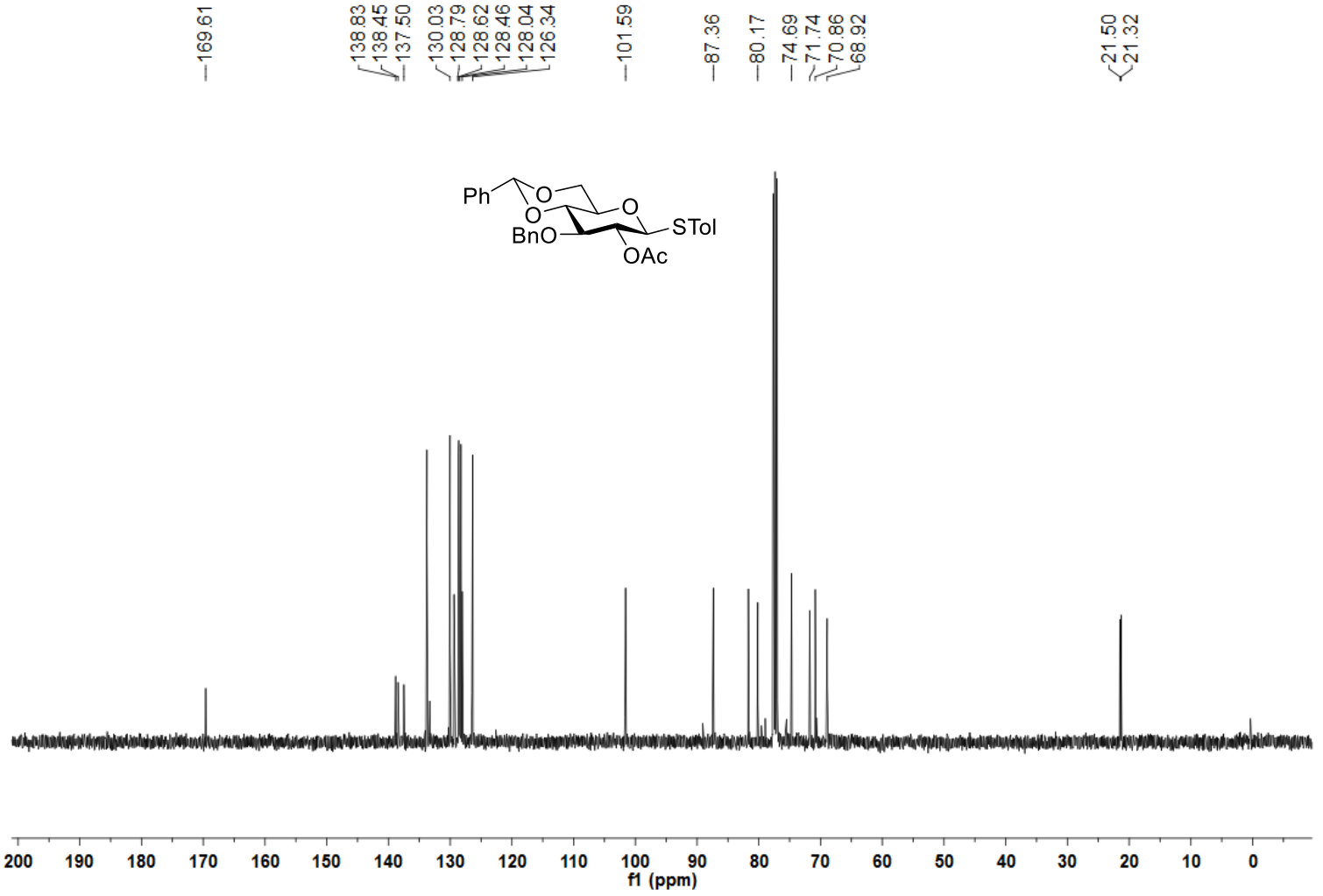
^{13}C 100 MHz NMR spectrum *p*-tolyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-1-thio-D-galactopyranside (21):



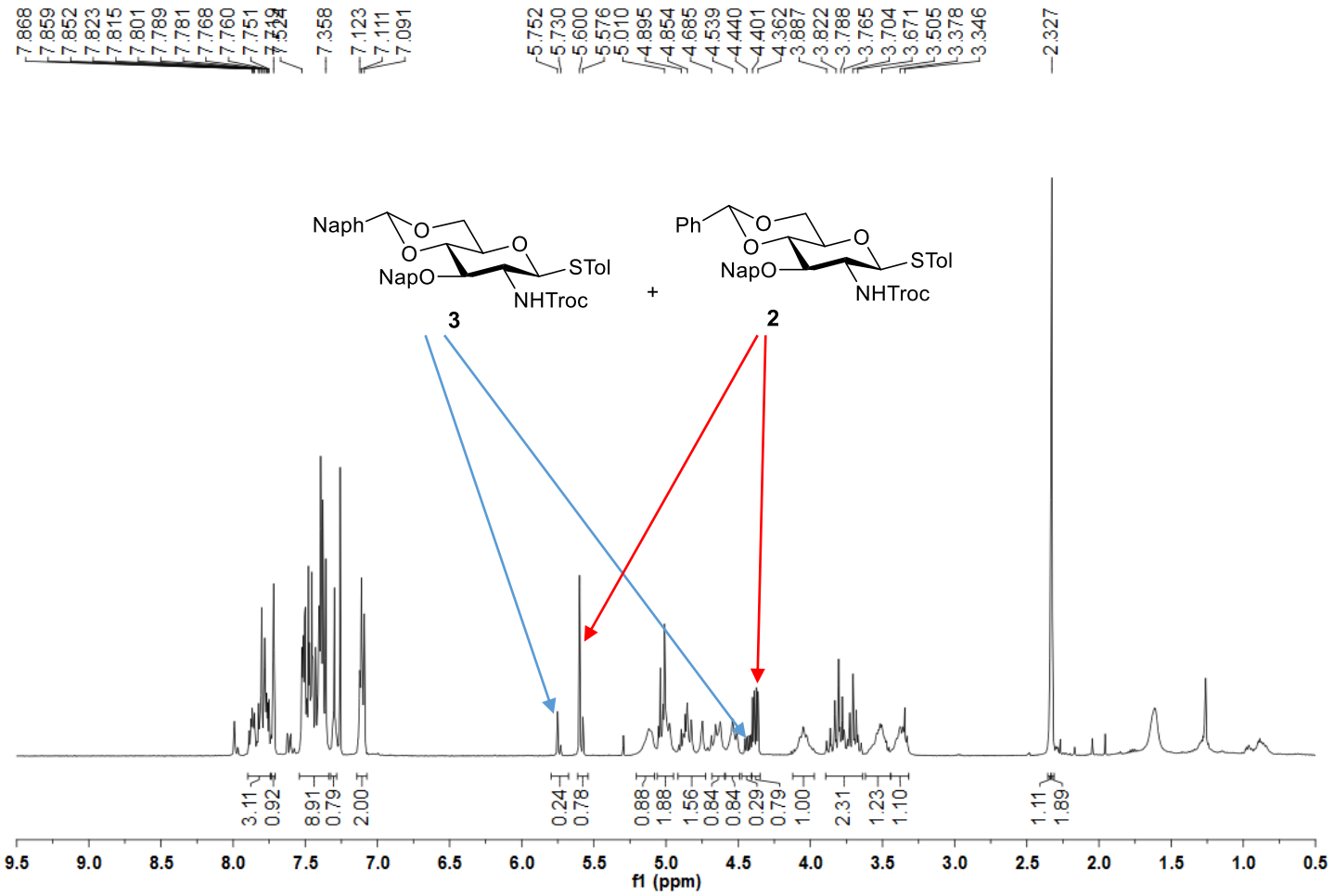
^{1}H 400 MHz NMR spectrum of *p*-tolyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (24):



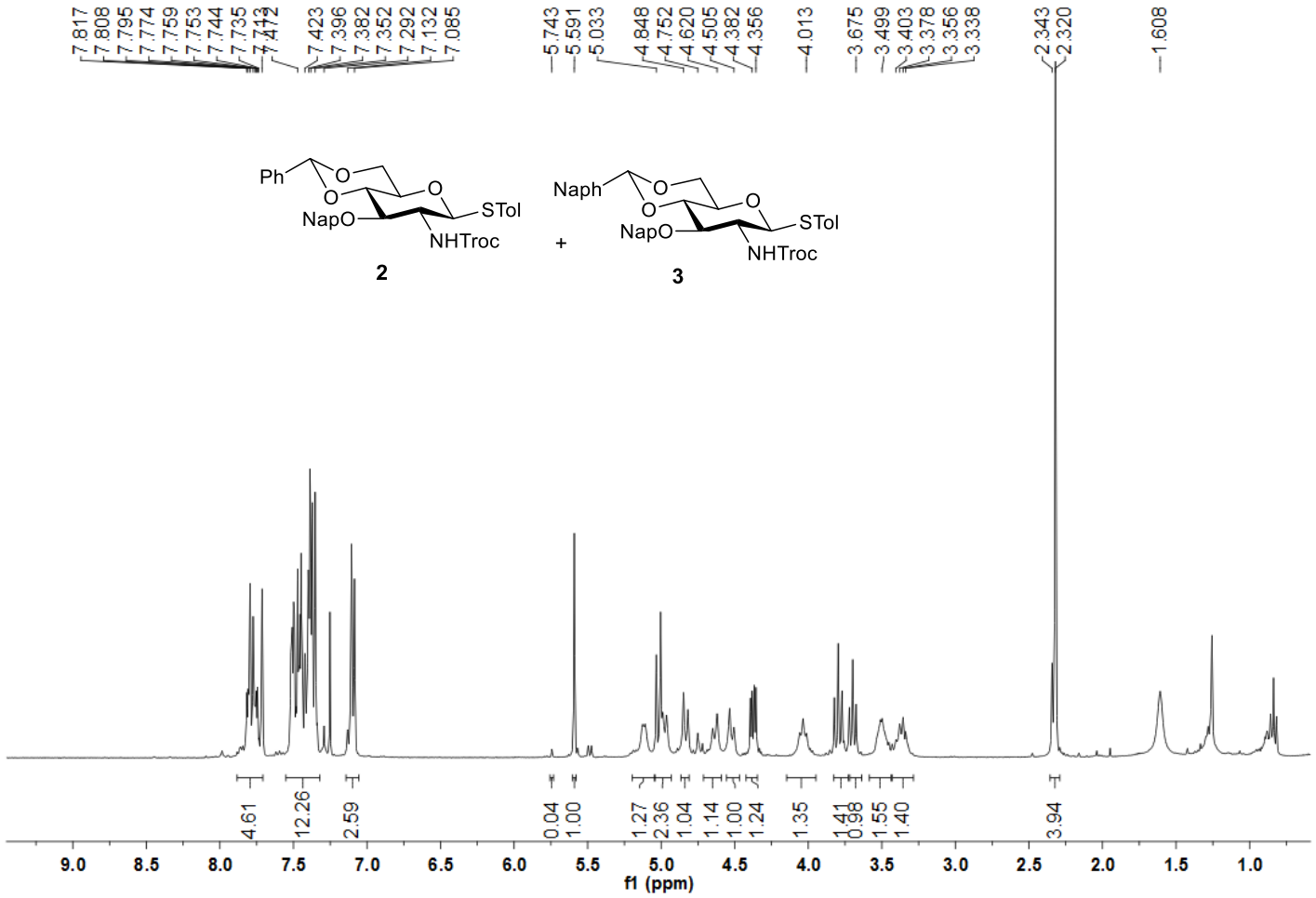
^{13}C 100 MHz NMR spectrum of *p*-tolyl 2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranside (24):



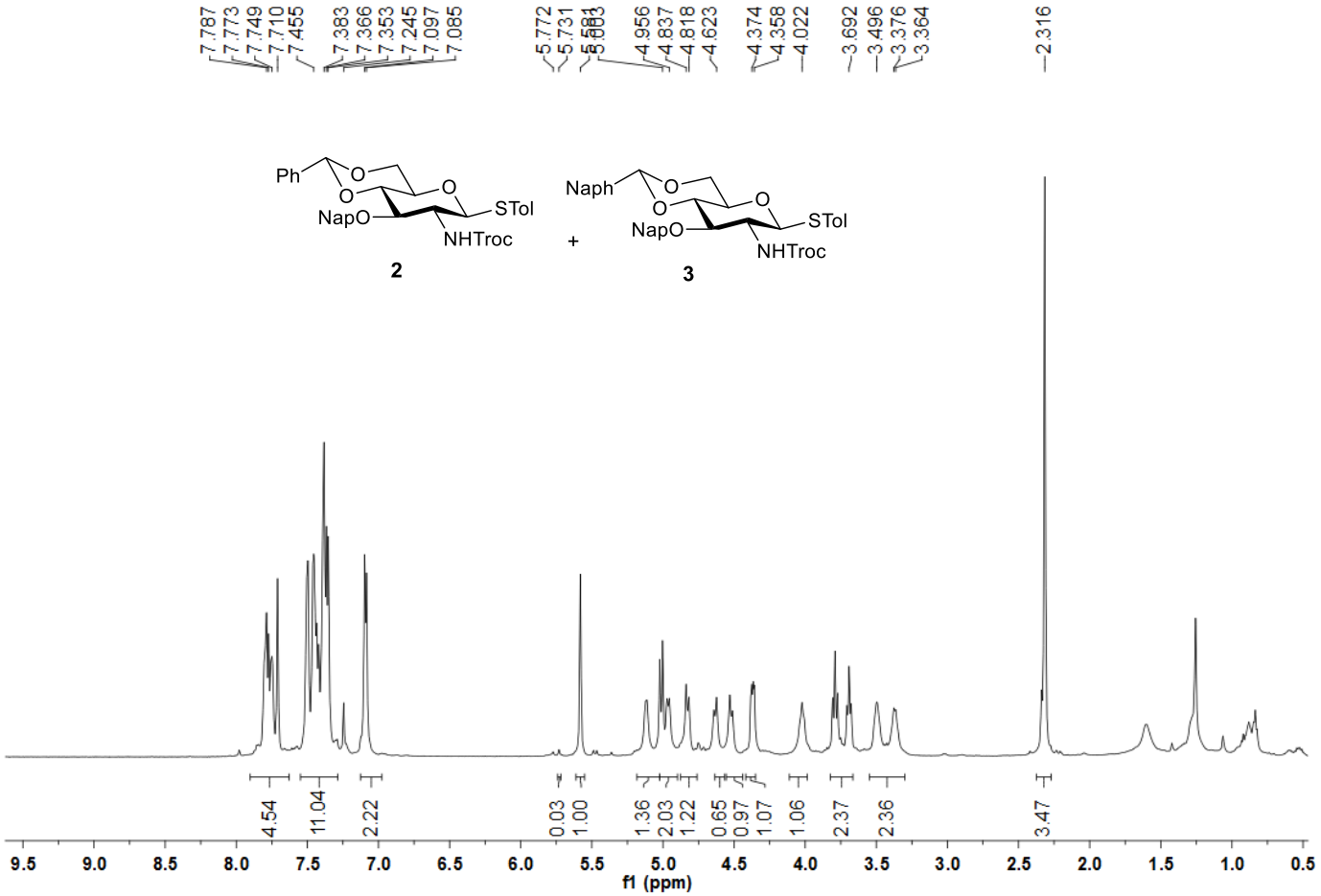
Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum (Figure 1)



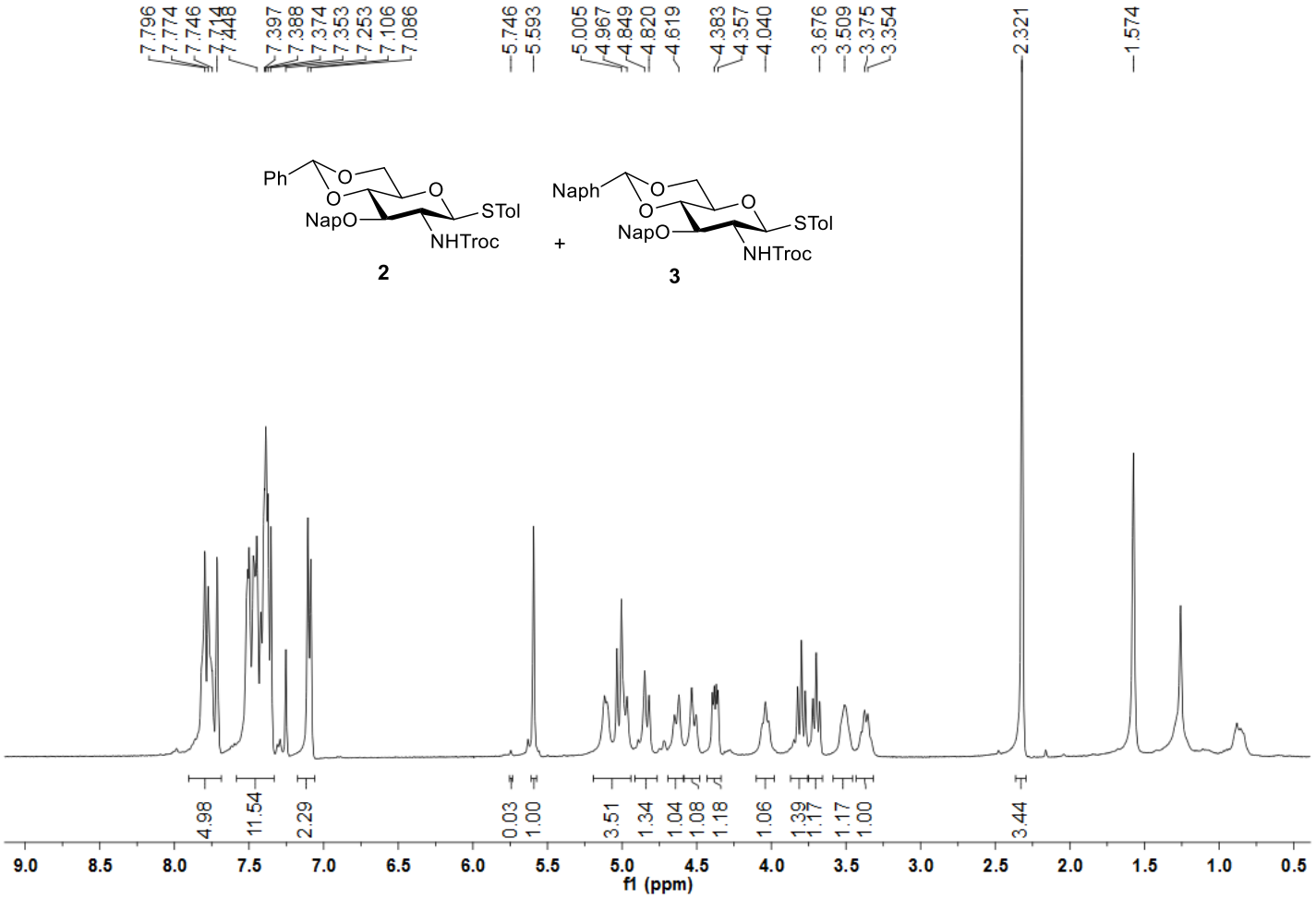
Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 1 of Table 1



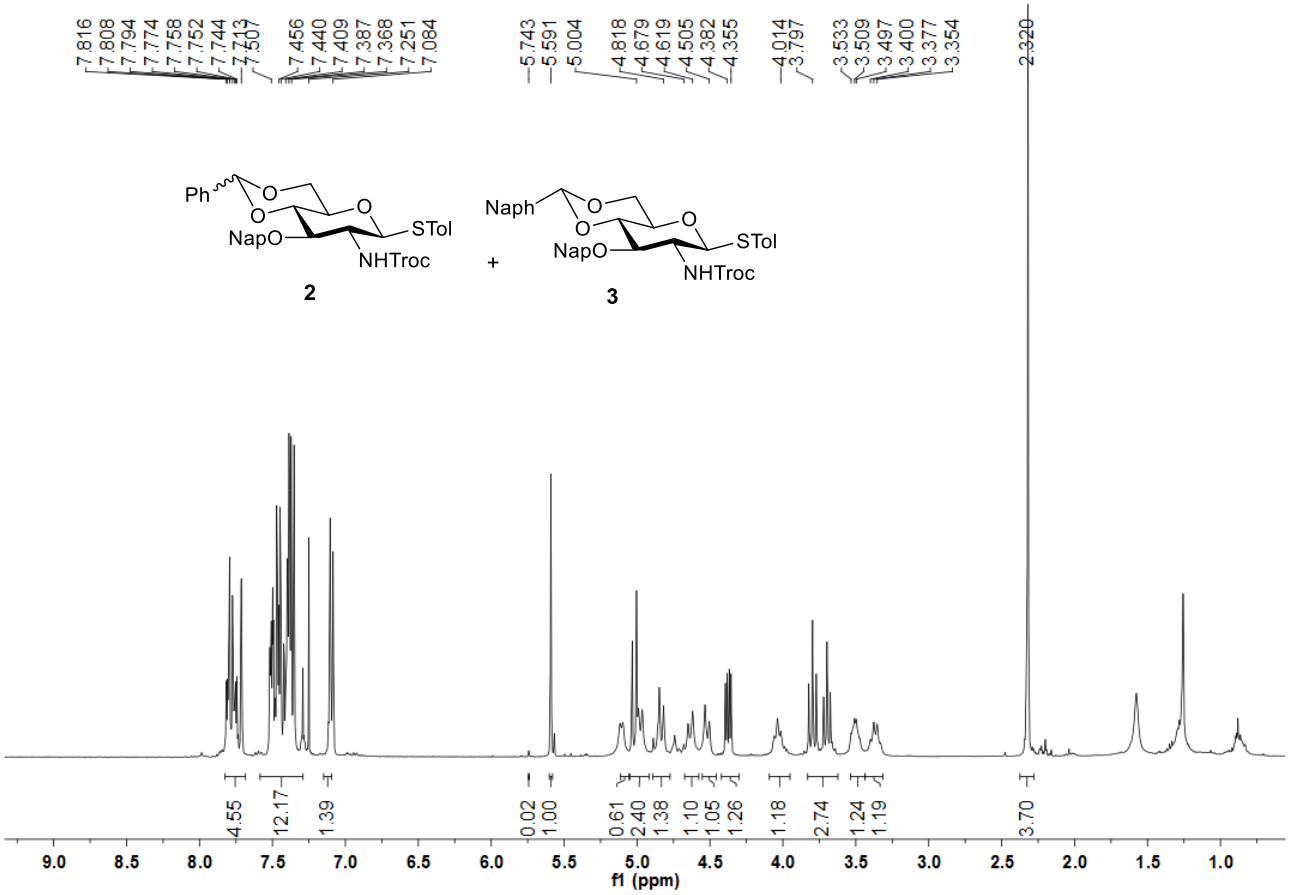
Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 2 of Table 1



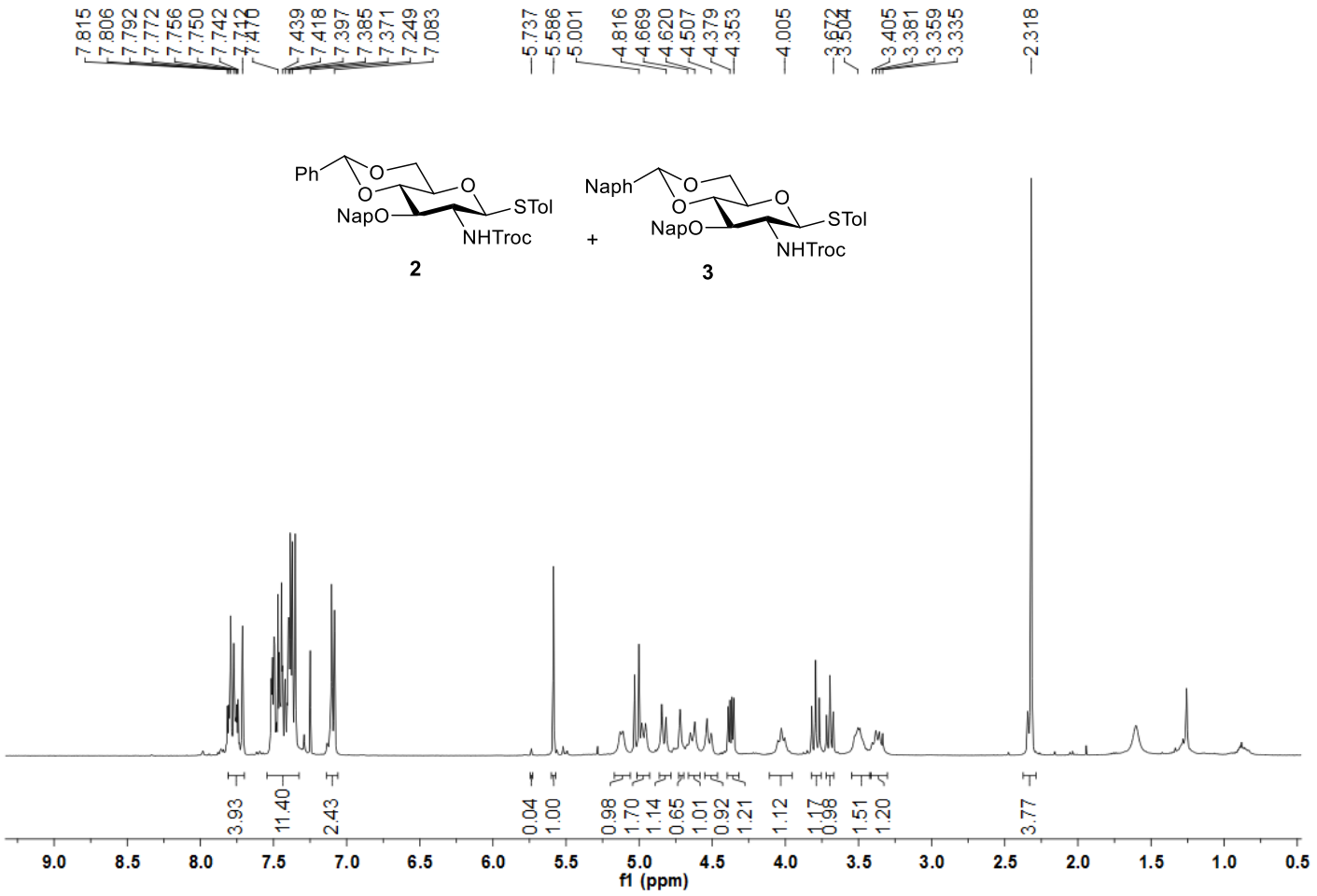
Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 3 of Table 1



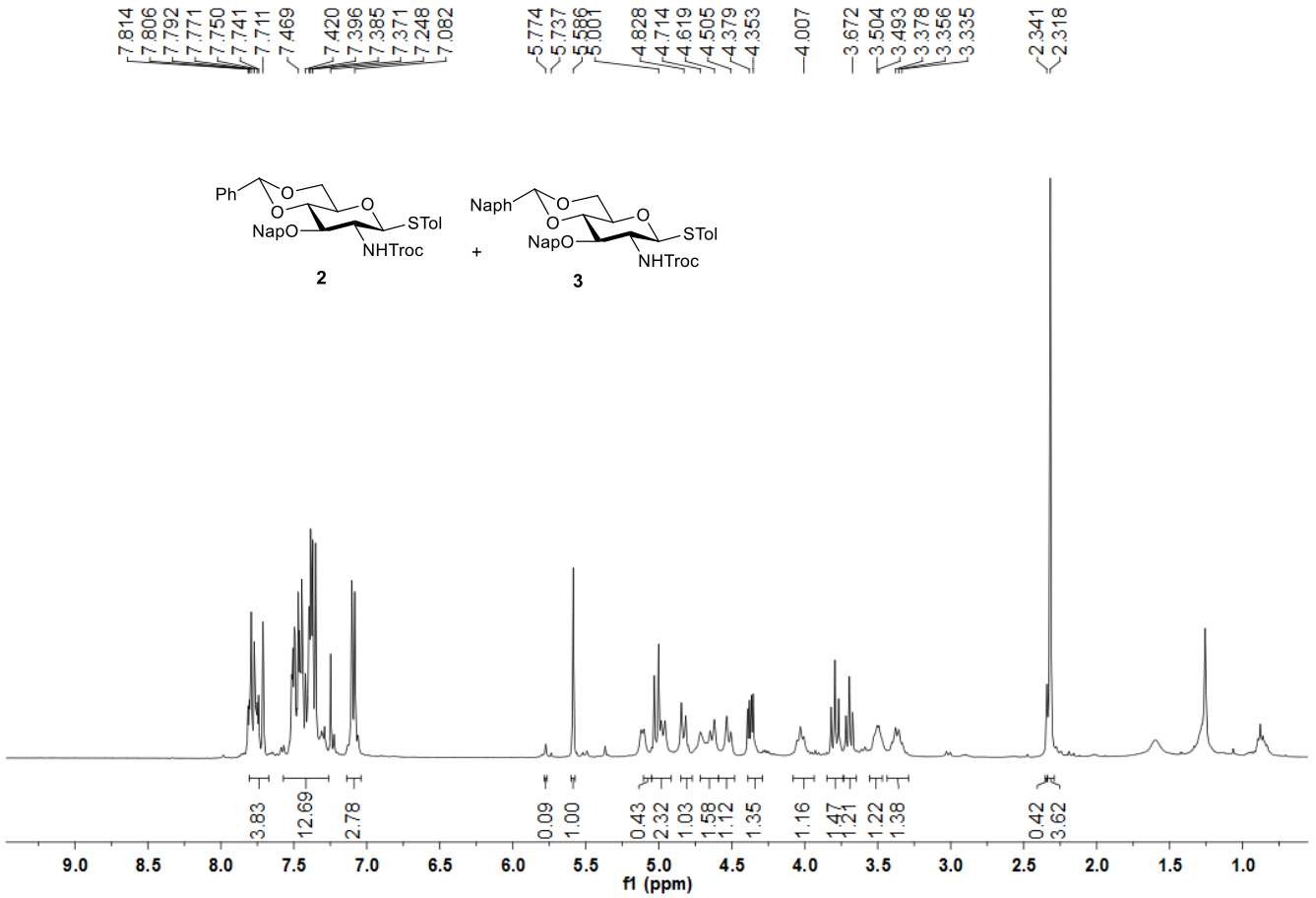
Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 4 of Table 1



Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 5 of Table 1



Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 6 of Table 1



Ratio of alkylation product 2 and tranacetalation product 3 from crude ^{1}H 400 MHz NMR spectrum for entry 8 of Table 1