Supporting information for the article entitled

Chemical and chemoenzymatic syntheses of sialyl Lewis[a] tetrasaccharide antigen

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1. General methods

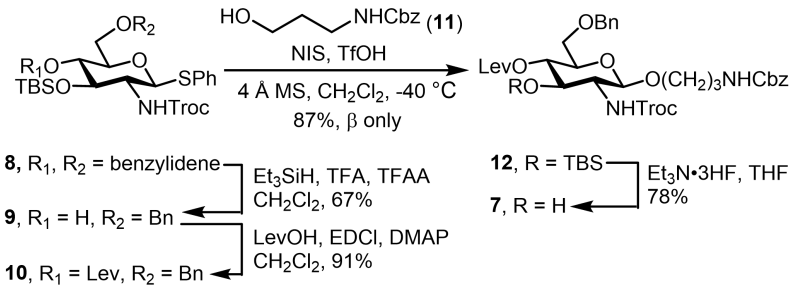
All non-aqueous reactions were performed under a nitrogen atmosphere and monitored by thin layer chromatography (TLC) using Silica Gel GF254 plates with detection by charring with 10% (v/v) H_2SO_4 in EtOH or by UV detection. Solvents used in the reactions were distilled from appropriate drying agents prior to use. All glycosylations were carried out in the presence of 4Å molecular sievess (powder < 50 micron), which were freshly activated before used. Silica gel (200-300 mesh) was used for column chromatography. Size-exclusion chromatography was performed on Bio-Gel P2 and Bio-Gel P4 column. Optical rotations were measured at 25 ± 0.3 ℃ for solutions in a 1.0 dm cell. High resolution mass spectra (HRMS) were recorded on ESI-TOF spectrometer. NMR spectra were recorded with a Varian Unit INOVA-400, Bruker Avance III-400 or Bruker Avance II-600 spectrometer. The ^1H and ^{13}C NMR spectra were calibrated against the residual proton and carbon signals of the solvents as internal references ($CDCl_3$: H = 7.26 ppm and C = 77.2 ppm; D_2O: H = 4.79 ppm). Chemical shifts (were expressed in ppm and coupling constants (J) were given in Hz. Standard splitting patterns are abbreviated: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Structural assignments were made with additional information from gCOSY, gHMQC, non-decoupling HSQC, and gHMBC experiment

2. Materials for chemoenzymatic experiments

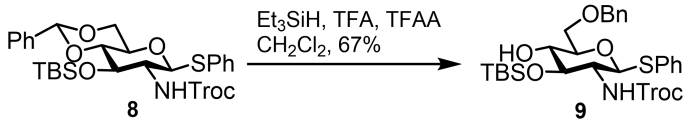
DEAE ion exchange resin was purchased from GE Healthcare Life Science. Bio-Gel P2 or P-4 (45-90 μm) was purchased from Bio-Rad. Calf intestine alkaline phosphatase (CIAP) was purchased from BioLabs® Inc. Cytidine-5'-monophospho-*N*-acetylneuraminic acid (CMP-Neu5Ac) and guanosine 5'-diphospho-β-L-fucose (GDP-Fuc) were purchased from BioChemSyn. *Campylobacter jejuni* α2,3-sialyltransferase I (Cst-I)[1] and α1,3/4-fucosyltransferase (FUT3)[2,3] were expressed and purified as described previously.

3. Experimental procedures and characterizations of new compounds

3.1 Synthesis of acceptor 7



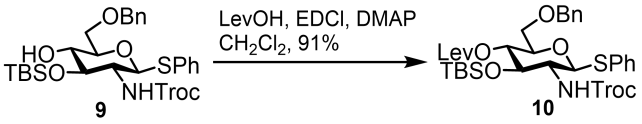
Phenyl 3-*O*-*tert*-butyldimethylsilyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-1-thio-β-D-glucopyranoside (9)



To a solution of compound **8** (7.34 g, 11.3 mmol) in CH_2Cl_2 (56 mL) at 0 ℃ were added Et_3SiH

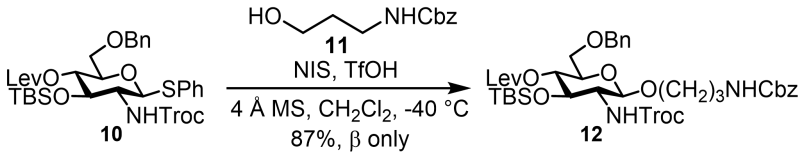
(9.0 mL, 56.5 mmol), trifluoroacetic acid (4.2 mL, 56.5 mmol), and trifluoroacetic anhydride (4.8 mL, 33.9 mmol). The reaction mixture was stirred at 0 ℃ for 3 h, at the end of which time TLC indicated it was finished. The reaction was quenched with saturated aqueous $NaHCO_3$, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10:1) to afford **9** (4.93 g, 7.57 mmol, 67%) as a colorless syrup. R_f = 0.2 (petroleum ether/EtOAc = 8:1); $[\alpha]_D^{25}$ = -14.294 (*c* 0.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H, H-Ar), 7.38-7.28 (m, 5H, H-Ar), 7.26-7.21 (m, 3H, H-Ar), 5.06 (d, *J* = 8.8 Hz, 1H), 4.92 (d, *J* = 10.4 Hz, 1H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 3.80-3.71 (m, 3H), 3.58-3.48 (m, 2H), 3.41 (q, *J* = 9.6 Hz, 1H), 2.56 (s, 1H), 0.88 (s, 9H, $Si(CH_3)_2C(C\mathbf{H_3})_3$), 0.11 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$), 0.08 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9 ($Cl_3CCH_2O\mathbf{C}$=O), 137.9 (C-Ar), 133.5 (C-Ar), 132.2 (C-Ar), 129.1 (C-Ar), 128.6 (C-Ar), 128.0 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 95.3, 86.7, 78.0, 76.6, 74.9, 73.9, 73.4, 70.6, 57.6, 26.0, 18.3, -4.0, -4.6. HRMS (ESI): *m*/*z* calcd for $C_{28}H_{39}Cl_3NO_6SSi$ [M+H$^+$]: 650.1328, found: 650.1328.

Phenyl 3-*O*-*tert*-butyldimethylsilyl-4-*O*-levulinoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-1-thio-β-D-glucopyranoside (10)



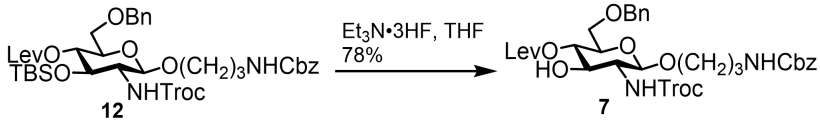
To a solution of compound **9** (5.21 g, 8.00 mmol) in CH_2Cl_2 (80 mL) at 0 ℃ were added levulinic acid (1.5 mL, 16.0 mmol), EDCI (3.00 g, 16.0 mmol), and 4-dimethylaminopyridine (0.20 g, 1.60 mmol). The reaction mixture was stirred at room temperature for 3 h, at the end of which time TLC indicated it was finished. The reaction was diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to afford **10** (5.45 g, 7.27 mmol, 91%) as a white solid. R_f = 0.4 (petroleum ether/EtOAc = 5:1); $[\alpha]_D^{25}$ = -10.250 (*c* 0.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.0 Hz, 2H, H-Ar), 7.39-7.28 (m, 6H, H-Ar), 7.26-7.21 (m, 2H, H-Ar), 5.27 (d, *J* = 8.6 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.92 (t, *J* = 9.0 Hz, 1H), 4.77-4.72 (m, 2H), 4.59-4.50 (m, 2H), 4.08 (t, *J* = 8.7 Hz, 1H), 3.72-3.61 (m, 3H), 3.50-3.40 (m, 1H), 2.78-2.68 (m, 1H), 2.67-2.62 (m, 1H), 2.61-2.48 (m, 2H), 2.17 (s, 3H), 0.86 (s, 9H, $Si(CH_3)_2C(C\mathbf{H_3})_3$), 0.09 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$), 0.05 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 ($CH_3\mathbf{C}$=O), 171.9 ($CH_2\mathbf{C}$=O), 153.8 ($Cl_3CCH_2O\mathbf{C}$=O), 138.3 (C-Ar), 133.5 (C-Ar), 131.9 (C-Ar), 129.1 (C-Ar), 128.4 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 95.3, 86.1, 77.6, 74.9, 73.6, 73.4, 73.1, 70.1, 58.2, 37.9, 29.9, 28.3, 25.7, 18.0, -4.3, -4.3. HRMS (ESI): *m*/*z* calcd for $C_{33}H_{45}Cl_3NO_8SSi$ [M+H$^+$]: 748.1696, found: 748.1696.

***N*-Benzyloxycarbonyl-3-aminopropyl 3-*O*-*tert*-butyldimethylsilyl-4-*O*-levulinoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (12)**



To a solution of acceptor **11** (1.12 g, 5.34 mmol) and donor **10** (2.00 g, 2.67 mmol) in anhydrous CH_2Cl_2 (53 mL) was added freshly activated 4 Å molecular sieves (530 mg). The mixture was stirred at room temperature for 15 min and then cooled down to -78 °C. NIS (901 mg, 4.00 mmol) and TfOH (43 μL, 0.53 mmol) were added. The reaction mixture was gradually warmed to -40 °C and stirred for 30 min at the same temperature. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to afford **12** (1.97 g, 2.32 mmol, 87%, based on donor consumption) as a brown syrup. R_f = 0.2 (petroleum ether/EtOAc = 3:1); $[\alpha]_D^{25}$ = -12.622 (*c* 2.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 10H, H-Ar), 5.56 (d, *J* = 8.5 Hz, 1H), 5.30 (t, *J* = 6.2 Hz, 1H), 5.12-5.04 (m, 2H), 4.87-4.80 (m, 1H), 4.74-4.63 (m, 3H), 4.57 (d, *J* = 8.5 Hz, 1H), 4.48 (q, *J* = 12.0 Hz, 2H), 3.96-3.86 (m, 2H), 3.61-3.48 (m, 4H), 3.48-3.38 (m, 1H), 3.38-3.29 (m, 1H), 3.22-3.12 (m, 1H), 2.73-2.63 (m,1H), 2.62-2.52 (m, 1H), 2.52-2.41 (m, 2H), 2.14 (s, 3H), 1.84-1.64 (m, 2H), 0.82 (s, 9H, $Si(CH_3)_2C(C\mathbf{H_3})_3$), 0.05 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$), 0.01 (s, 3H, $Si(C\mathbf{H_3})_2C(CH_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3 ($CH_3\mathbf{C}$=O), 171.9 ($CH_2\mathbf{C}$=O), 156.8 ($PhCH_2O\mathbf{C}$=O), 154.3 ($Cl_3CCH_2O\mathbf{C}$=O), 138.1 (C-Ar), 136.9 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.2 (C-Ar), 128.0 (C-Ar), 127.7 (C-Ar), 100.5, 95.5, 77.4, 74.8, 73.5, 73.3, 72.4, 69.9, 67.3, 66.7, 59.2, 37.9, 37.7, 29.9, 29.7, 28.3, 25.7, 18.0, -4.3, -4.3. HRMS (ESI): *m*/*z* calcd for $C_{38}H_{54}Cl_3N_2O_{11}Si$ [M+H$^+$]: 847.2557, found: 847.2557.

_N_-Benzyloxycarbonyl-3-aminopropyl 4-_O_-levulinoyl-6-_O_-benzyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-β-D-glucopyranoside (7)

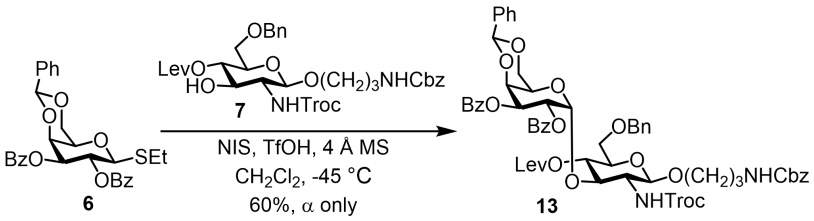


To a solution of compound **12** (1.97 g, 2.32 mmol) in THF at room temperature was added $Et_3N{\cdot}3HF$ (3.8 mL, 23.2 mmol). The reaction mixture was heated to 70 ℃ with an oil bath and refluxed under nitrogen. Upon completion as judged by TLC, the mixture was cooled to room temperature. Then the mixture was diluted with EtOAc, and washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:1) to afford **7** (1.33 g, 1.81 mmol, 78%) as a colorless syrup. R_f = 0.25 (petroleum ether/EtOAc = 1:2); $[\alpha]_D^{25}$ = -6.887 (*c* 4.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 10H, H-Ar), 6.23 (s, 1H), 5.20 (t, *J* = 6.4 Hz, 1H), 5.09 (s, 2H), 4.89 (t, *J* = 9.3 Hz, 1H), 4.72 (d, *J* = 4.5 Hz, 2H), 4.51 (s, 2H), 4.43 (d, *J* = 8.3 Hz, 1H), 3.99-3.89 (m, 1H), 3.83 (t, *J* = 9.5 Hz, 1H), 3.70-3.37 (m, 7H), 3.20-3.08 (m, 1H), 2.74 (t, *J* = 6.4 Hz, 2H), 2.58-2.38 (m, 2H), 2.16 (s, 3H), 1.86-1.76 (m, 1H), 1.69-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4 ($CH_3\mathbf{C}$=O), 172.6 ($CH_2\mathbf{C}$=O), 157.0 ($PhCH_2O\mathbf{C}$=O), 155.8 ($Cl_3CCH_2O\mathbf{C}$=O), 138.1 (C-Ar), 136.9 (C-Ar), 128.7 (C-Ar), 128.5 (C-Ar), 128.3 (C-Ar), 128.1 (C-Ar), 127.9 (C-Ar), 100.9, 95.7, 74.8, 73.7, 73.5, 73.4, 72.7, 69.3,

67.2, 66.9, 58.6, 38.3, 37.5, 30.0, 30.0, 28.2. HRMS (ESI): *m*/*z* calcd for $C_{32}H_{40}Cl_3N_2O_{11}$ [M+H$^+$]: 732.1619, found: 732.1619.

3.2 Synthesis of disaccharide 13

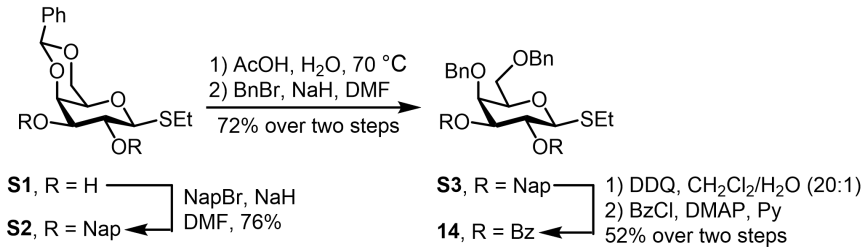
***N*-Benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranosyl-(1→3)-4-*O*-levulinoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (13)**



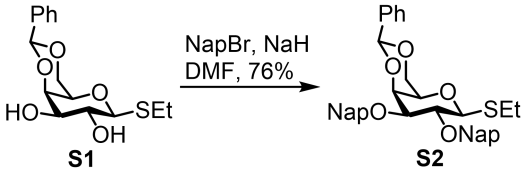
To a solution of acceptor **7** (1.60 g, 2.20 mmol) and donor **6** (1.70 g, 3.30 mmol) in anhydrous CH_2Cl_2 (33 mL) was added freshly activated 4 Å molecular sieves (3.30 g). The mixture was stirred at room temperature for 15 min and then cooled down to -78 °C. NIS (1.10 g, 4.95 mmol) and TfOH (30 μL, 0.33 mmol) were added. The reaction mixture was gradually warmed to -45 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to afford **13** (2.36 g, 1.98 mmol, 60%, based on donor consumption) as a colorless syrup. R_f = 0.45 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = 89 (*c* 0.20, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98-7.87 (m, 4H, H-Ar), 7.55-7.20 (m, 21H, H-Ar), 6.82-6.71 (m, 1H), 5.93 (d, *J* = 7.7 Hz, 1H), 5.81 (d, *J* = 10.3 Hz, 1H, H-2'), 5.66-5.56 (m, 2H, H-1', H-3'), 5.54 (s, 1H), 5.30 (s, 1H), 5.14-5.06 (m, 2H), 5.00-4.94 (m, 1H), 4.94-4.89 (m, 1H, H-4), 4.67-4.63 (m, 1H, H-4'), 4.63-4.59 (m, 1H), 4.48-4.45 (m, 1H, H-1), 4.48-4.38 (m, 2H), 4.33 (d, *J* = 12.8 Hz, 1H, H-6'), 4.19-4.06 (m, 3H, H-3, H-5', H-6'), 3.95-3.87 (m, 1H), 3.72-3.66 (m, 1H, H-2), 3.56-3.53 (m, 1H), 3.53-3.50 (m, 1H, H-5), 3.50-3.48 (m, 1H), 3.48-3.40 (m, 2H, H-6), 3.21-3.11 (m, 1H), 2.46-2.38 (m, 1H), 2.38-2.20 (m, 3H), 1.99 (s, 3H), 1.81-1.76 (m, 1H), 1.72-1.66 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.3 (CH_3**C**=O), 171.3 (CH_2**C**=O), 166.4 (Ph**C**=O), 166.1 (Ph**C**=O), 156.9 ($PhCH_2O$**C**=O), 154.5 (Cl_3CCH_2O**C**=O), 138.1 (C-Ar), 137.6 (C-Ar), 136.9 (C-Ar), 133.5 (C-Ar), 133.5 (C-Ar), 133.5 (C-Ar), 133.3 (C-Ar), 130.1 (C-Ar), 129.9 (C-Ar), 129.9 (C-Ar), 129.5 (C-Ar), 129.3 (C-Ar), 129.2 (C-Ar), 129.0 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 127.9 (C-Ar), 127.6 (C-Ar), 127.1 (C-Ar), 126.2 (C-Ar), 101.9, 101.2 (C-1), 100.8, 97.6 (C-1'), 95.7, 78.8, 76.1 (C-3), 74.7, 74.2 (C-4'), 73.6 (C-5), 73.4, 73.4, 72.7 (C-4), 69.4 (C-6), 69.3 (C-6'), 69.1 (C-3'), 68.7, 68.6, 68.3 (C-2'), 67.3, 66.7, 66.0, 63.0 (C-5'), 56.8 (C-2), 37.6, 37.5, 29.8, 29.7, 27.9. HRMS (ESI): *m*/*z* calcd for $C_{59}H_{62}Cl_3N_2O_{18}$ [M+H$^+$]: 1190.2985, found: 1190.2988.

3.3 Synthesis of donor 14

Scheme S1. Synthesis of the building block 14.

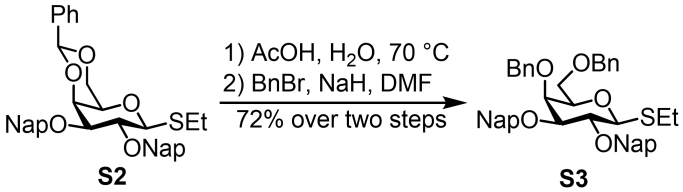


Ethyl 2,3-di-*O*-(2-naphthylmethyl)-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (S2)



To a solution of compound **S1**[4] (1.30 g, 4.16 mmol) in anhydrous DMF (42 mL) at 0 ℃ was added sodium hydride (499 mg, 12.5 mmol). The reaction mixture was stirred at 0 ℃ for 15 min and then 2-(bromomethyl)naphthalene (2.76 g, 12.5 mmol) was added at the same temperature. The reaction mixture was stirred at room temperature for 3 h, at the end of which time TLC indicated it was finished. The reaction was quenched with water, diluted with EtOAc, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 4:1) to afford **S2** (1.90 g, 3.16 mmol, 76%) as a white solid. R_f = 0.45 (petroleum ether/EtOAc = 2.5:1); $[\alpha]_D^{25}$ = 23.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.74 (m, 7H, H-Ar), 7.66 (d, *J* = 7.8 Hz, 1H, H-Ar), 7.60-7.54 (m, 3H, H-Ar), 7.51 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.49-7.35 (m, 7H, H-Ar), 5.48 (s, 1H), 5.10 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.93 (s, 2H), 4.47 (d, *J* = 9.6 Hz, 1H), 4.30 (d, *J* = 12.3 Hz, 1H), 4.18 (d, *J* = 3.5 Hz, 1H), 4.02-3.90 (m, 2H), 3.67 (dd, *J* = 9.2, 3.5 Hz, 1H), 3.34 (s, 1H), 2.94-2.70 (m, 2H), 1.34 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1 (C-Ar), 136.1 (C-Ar), 135.9 (C-Ar), 133.5 (C-Ar), 133.3 (C-Ar), 133.2 (C-Ar), 133.2 (C-Ar), 129.2 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.1 (C-Ar), 126.7 (C-Ar), 126.7 (C-Ar), 126.6 (C-Ar), 126.3 (C-Ar), 126.1 (C-Ar), 126.1 (C-Ar), 125.9 (C-Ar), 101.7, 84.7, 81.1, 77.4, 75.9, 74.2, 72.0, 69.9, 69.5, 24.0 (S**C**$H_2$$CH_3$), 15.2 ($SCH_2$**C**$H_3$). HRMS (ESI): *m*/*z* calcd for $C_{37}H_{37}O_5S$ [M+H$^+$]: 592.2283, found: 592.2283.

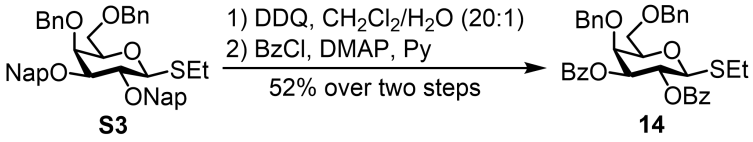
Ethyl 2,3-di-*O*-(2-naphthylmethyl)-4,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside (S3)



Compound **S2** (1.60 g, 2.70 mmol) was dissolved in AcOH/H_2O (27 mL, 4:1, v/v) at room temperature. The reaction mixture was heated to 70 ℃ with an oil bath. Upon completion as judged by TLC, the mixture was cooled to room temperature. Then the mixture was diluted with EtOAc, and washed with water, saturated aqueous $NaHCO_3$ and brine. The organic layer was

separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. To a solution of the obtained residue in anhydrous DMF (24 mL) at 0 ℃ was added sodium hydride (1.18 g, 7.32 mmol). The reaction mixture was stirred at 0 ℃ for 15 min and then benzyl bromide (6.5 mL, 7.32 mmol) was added at the same temperature. The reaction mixture was stirred at room temperature for 4 h, at the end of which time TLC indicated it was finished. The reaction was quenched with water, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1) to afford **S3** (1.34 g, 1.94 mmol, 72%) as a colorless syrup. R_f = 0.5 (petroleum ether/EtOAc = 6:1); $[\alpha]_D^{25}$ = 32.189 (*c* 3.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.68 (m, 7H, H-Ar), 7.65 (d, *J* = 7.9 Hz, 1H, H-Ar), 7.53 (d, *J* = 8.4 Hz, 1H, H-Ar), 7.48-4.39 (m, 5H, H-Ar), 7.36-7.24 (m, 10H, H-Ar), 5.06 (d, *J* = 10.4 Hz, 1H), 5.02-4.94 (m, 2H), 4.92-4.84 (m, 2H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.51-4.38 (m, 3H), 4.01 (s, 1H), 3.92 (t, *J* = 9.4 Hz, 1H), 3.69-3.52 (m, 4H), 2.85-2.67 (m, 2H), 1.31 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9 (C-Ar), 138.0 (C-Ar), 136.0 (C-Ar), 136.0 (C-Ar), 133.4 (C-Ar), 133.4 (C-Ar), 133.2 (C-Ar), 133.1 (C-Ar), 128.6 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.6 (C-Ar), 127.1 (C-Ar), 126.6 (C-Ar), 126.3 (C-Ar), 126.2 (C-Ar), 126.0 (C-Ar), 126.0 (C-Ar), 125.9 (C-Ar), 125.7 (C-Ar), 85.5, 84.1, 78.7, 77.4, 76.0, 74.6, 73.8, 73.7, 72.8, 72.8, 68.9, 25.0 (S**C**$H_2$$CH_3$), 15.2 ($SCH_2$**C**$H_3$). HRMS (ESI): *m*/*z* calcd for $C_{44}H_{45}O_5S$ [M+H^+]: 684.2909, found: 684.2909.

Ethyl 2,3-di-*O*-benzoyl-4,6-di-*O*-benzyl-1-thio-β-D-galactopyranoside (14)

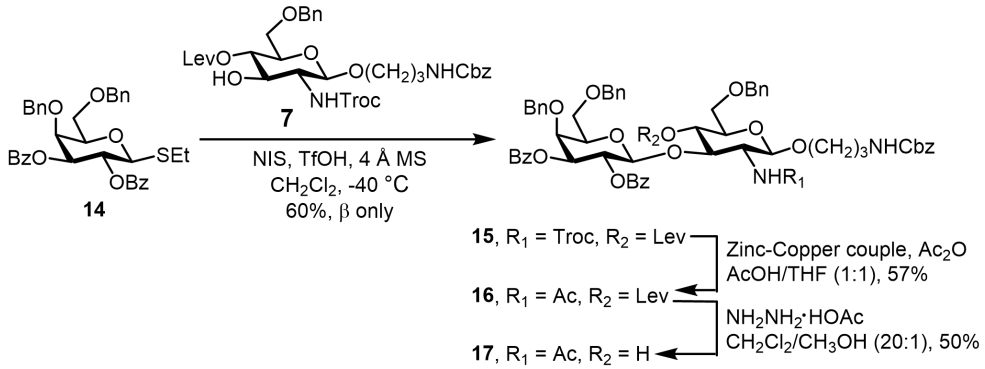


S3 **14**

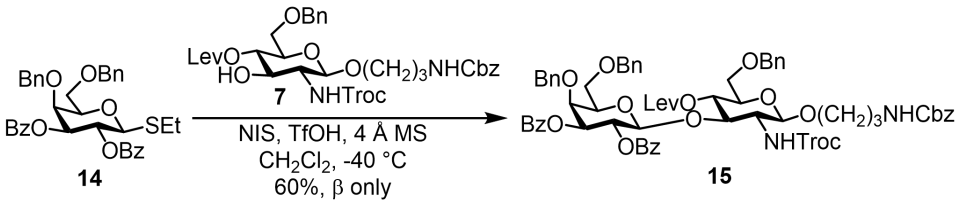
To a solution of compound **S3** (567 mg, 0.83 mmol) in CH_2Cl_2/H_2O (8.4 mL, 20:1, v/v) at 0 ℃ was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (488 mg, 2.15 mmol). The reaction mixture was stirred at room temperature for 3 h, at the end of which time TLC indicated it was finished. The reaction was quenched with saturated aqueous $NaHCO_3$, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. To a solution of the obtained residue in anhydrous pyridine (5.0 mL) at 0 ℃ were added benzoyl chloride (0.23 mL, 1.98 mmol) and 4-dimethylaminopyridine (12.0 mg, 0.10 mmol). The reaction mixture was stirred at room temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with MeOH, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to afford **14** (260 mg, 0.65 mmol, 78%) as a white solid. R_f = 0.7 (petroleum ether/EtOAc = 4:1); $[\alpha]_D^{25}$ = -24.462 (*c* 0.87, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.90 (m, 4H, H-Ar), 7.52-7.44 (m, 2H, H-Ar), 7.40-7.27 (m, 9H, H-Ar), 7.26-7.15 (m, 5H, H-Ar), 5.88 (t, *J* = 10.0 Hz, 1H), 5.38 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.70 (dd, *J* = 15.9, 10.7 Hz, 2H), 4.54-4.41 (m, 3H), 4.25 (d, *J* = 3.1 Hz, 1H), 3.91 (t, *J* = 6.6 Hz, 1H), 3.72-3.62 (m, 2H), 2.85-2.66 (m, 2H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (Ph**C**=O), 165.6 (Ph**C**=O), 138.0 (C-Ar), 137.9 (C-Ar), 133.5 (C-Ar), 133.2 (C-Ar), 130.0 (C-Ar), 129.9 (C-Ar), 129.7 (C-Ar), 129.2 (C-Ar), 128.6 (C-Ar),

128.4 (C-Ar), 128.4 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 127.8 (C-Ar), 83.9, 75.8, 75.1, 74.4, 73.7, 68.7, 68.3, 24.0 (S**C**H_2CH_3), 15.0 (SCH_2**C**H_3). HRMS (ESI): *m/z* calcd for $C_{36}H_{37}O_7S$ [M+H^+]: 612.2182, found: 612.2182.

3.4 Synthesis of disaccharide acceptor 17



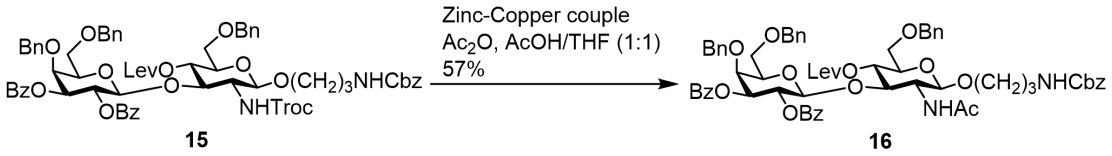
***N*-Benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-galacto-pyranosyl-(1→3)-4-*O*-levulinoyl-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl-amino)-β-D-glucopyranoside (15)**



To a solution of acceptor **7** (420 mg, 0.57 mmol) and donor **14** (525 mg, 0.86 mmol) in anhydrous CH_2Cl_2 (8.6 mL) was added freshly activated 4 Å molecular sieves (800 mg). The mixture was stirred at room temperature for 15 min and then cooled down to -78 °C. NIS (288 mg, 1.29 mmol) and TfOH (7.6 μL, 0.085 mmol) were added. The reaction mixture was gradually warmed to -40 °C and stirred at the same temperature for 1 h. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to afford **15** (441 mg, 0.34 mmol, 60%, based on acceptor consumption) as a colorless syrup. R_f = 0.45 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = 31.457 (*c* 1.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.91 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.52-7.44 (m, 2H, H-Ar), 7.41-7.18 (m, 24H, H-Ar), 5.67 (dd, *J* = 10.4, 7.8 Hz, 1H, H-2'), 5.32-5.24 (m, 2H), 5.20 (dd, *J* = 10.6, 3.1 Hz, 1H, H-3'), 5.07-5.00 (m, 2H), 4.85 (d, *J* = 9.3 Hz, 1H, H-4), 4.80 (d, *J* = 12.3 Hz, 1H), 4.76 (d, *J* = 8.1 Hz, 1H, H-1), 4.70 (d, *J* = 7.4 Hz, 1H, H-1'), 4.67 (d, *J* = 11.4 Hz, 1H), 4.59-4.37 (m, 6H), 4.30 (t, *J* = 9.7 Hz, 1H, H-3), 4.16 (d, *J* = 3.1 Hz, 1H, H-4'), 3.84-3.78 (m, 1H), 3.78-3.73 (m, 1H, H-5'), 3.65-3.59 (m, 3H, H-6', H-5), 3.59-3.53 (m, 1H), 3.59-3.43 (m, 2H, H-6), 3.33-3.23 (m, 1H), 3.19-3.06 (m, 1H), 3.03-2.92 (m, 1H, H-2), 2.67-2.56 (m, 1H), 2.48-2.27 (m, 3H), 1.97 (s, 3H), 1.83-1.69 (m, 1H), 1.67-1.57 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 206.9 (CH_3**C**=O), 171.6 (CH_2**C**=O), 165.9 (Ph**C**=O), 165.0 (Ph**C**=O), 156.7 ($PhCH_2O$**C**=O), 154.0 (Cl_3CCH_2O**C**=O), 138.0 (C-Ar), 138.0 (C-Ar), 137.8 (C-Ar), 136.8 (C-Ar), 133.5 (C-Ar), 133.3 (C-Ar), 130.0 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.1 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar),

128.0 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 101.2 (C-1'), 99.4 (C-1), 95.7, 76.7 (C-3), 75.2, 74.7 (C-3'), 74.5, 74.2 (C-4'), 73.6, 73.5, 73.4 (C-5), 73.4 (C-5'), 70.6 (C-2'), 69.8 (C-4), 69.3 (C-6), 67.9 (C-6'), 67.3, 66.6, 58.4 (C-2), 37.9, 37.6, 29.8, 29.6, 28.0. HRMS (ESI): *m*/*z* calcd for $C_{66}H_{70}Cl_3N_2O_{18}$ [M+H$^+$]: 1282.3611, found: 1282.3610.

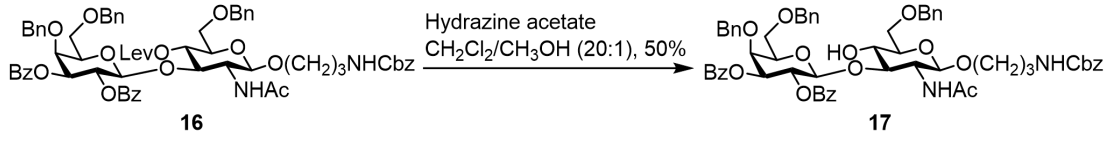
***N*-Benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-galacto-pyranosyl-(1→3)-4-*O*-levulinoyl-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (16)**



15 **16**

To a solution of compound **15** (40.0 mg, 0.031 mmol) in AcOH/THF (3.0 mL, 1:1, v/v) were added Zinc-Copper couple (300 mg, 2.33 mmol) and Ac_2O (0.44 mL, 4.66 mmol). The reaction mixture was stirred at room temperature for 3 h, at the end of which time TLC indicated it was finished. The mixture was filtered to remove Zinc-Copper couple. The reaction was quenched with saturated aqueous $NaHCO_3$, diluted with EtOAc, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1) to afford **16** (20.0 mg, 0.018 mmol, 57%) as a colorless syrup. R_f = 0.3 (petroleum ether/EtOAc = 1:2); $[\alpha]_D^{25}$ = 22.688 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.87 (m, 4H, H-Ar), 7.52-7.44 (m, 2H, H-Ar), 7.38-7.17 (m, 24H, H-Ar), 5.70-5.60 (m, 2H), 5.38-5.30 (m, 2H), 5.10-4.99 (m, 2H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.84 (t, *J* = 9.1 Hz, 1H), 4.73-4.64 (m, 2H), 4.55-4.40 (m, 6H), 4.18 (d, *J* = 3.2 Hz, 1H), 3.86-3.73 (m, 2H), 3.67-3.57 (m, 3H), 3.56-3.44 (m, 3H), 3.28-3.18 (m, 1H), 3.18-3.07 (m, 1H), 3.07-2.97 (m 1H), 2.66-2.53 (m, 1H), 2.48-2.28 (m, 3H), 1.98 (s, 3H), 1.84 (s, 3H), 1.71-1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9 (CH_3**C**=O), 171.6, 171.1, 166.0 (Ph**C**=O), 165.2 (Ph**C**=O), 156.7 ($PhCH_2O$**C**=O), 138.1 (C-Ar), 138.0 (C-Ar), 137.8 (C-Ar), 136.8 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 129.9 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.7 (C-Ar), 129.1 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 100.6, 99.2, 76.3, 75.2, 74.6, 74.2, 73.6, 73.5, 73.3, 71.0, 70.0, 69.5, 67.7, 67.1, 66.6, 58.1, 37.9, 37.7, 29.8, 29.5, 28.1, 23.6; HRMS (ESI): *m*/*z* calcd for $C_{65}H_{71}N_2O_{17}$ [M+H$^+$]: 1150.4674, found: 1150.4671.

***N*-Benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-galacto-pyranosyl-(1→3)-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (17)**

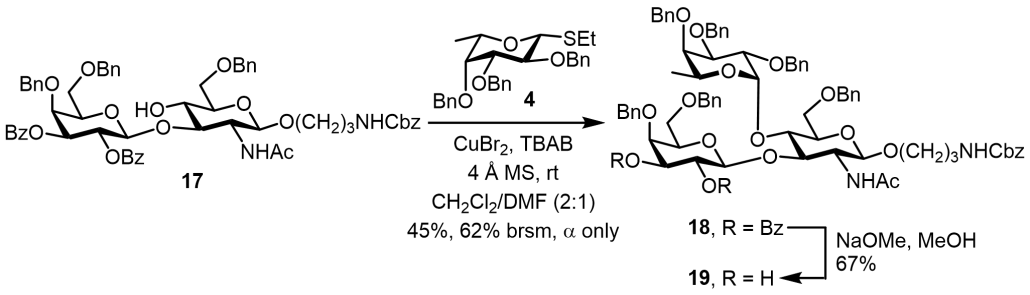


16 **17**

To a solution of compound **16** (20.0 mg, 0.018 mmol) in CH_2Cl_2/MeOH (0.42 mL, 20:1, v/v) at 0 °C was added NH_2NH_2·AcOH (3.00 mg, 0.034 mmol). The reaction mixture was stirred for 5 h at room temperature, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue

was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1) to afford **17** (9.00 mg, 8.50 μmol, 50%) as a colorless syrup. R_f = 0.4 (petroleum ether/EtOAc = 1:3); $[\alpha]_D^{25}$ = 14 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 17.0, 7.6 Hz, 4H, H-Ar), 7.48 (t, *J* = 7.4 Hz, 2H, H-Ar), 7.39-7.19 (m, 24H, H-Ar), 5.82 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.42 (t, *J* = 5.8 Hz, 1H), 5.38 (dd, *J* = 10.6, 3.1 Hz, 1H), 5.07-4.99 (m, 2H), 4.95 (d, *J* = 8.3 Hz, 1H), 4.74-4.66 (m, 2H), 4.56-4.29 (m, 7H), 4.12 (d, *J* = 3.1 Hz, 1H), 3.95 (t, *J* = 6.4 Hz, 1H), 3.85-3.76 (m, 2H), 3.71-3.43 (m, 6H), 3.30-3.20 (m, 1H), 3.19-3.11 (m, 1H) 2.87-3.90 (m, 1H), 1.79-1.60 (m, 2H), 1.29 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1 (CH_3**C**=O), 166.0 (Ph**C**=O), 165.2 (Ph**C**=O), 156.6 ($PhCH_2O$**C**=O), 138.5 (C-Ar), 137.4 (C-Ar), 137.4 (C-Ar), 136.8 (C-Ar), 133.6 (C-Ar), 133.6 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.5 (C-Ar), 128.9 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 127.7 (C-Ar), 127.5 (C-Ar), 101.9, 98.9, 83.9, 75.2, 75.0, 74.3, 73.9, 73.8, 73.4, 70.4, 70.3, 70.0, 69.9, 68.3, 67.2, 66.5, 58.0, 37.8, 29.8, 29.6, 23.0. HRMS (ESI): *m*/*z* calcd for $C_{60}H_{65}N_2O_{15}$ [M+H$^+$]: 1052.4307, found: 1052.4309.

3.5 Synthesis of trisaccharide acceptor 19

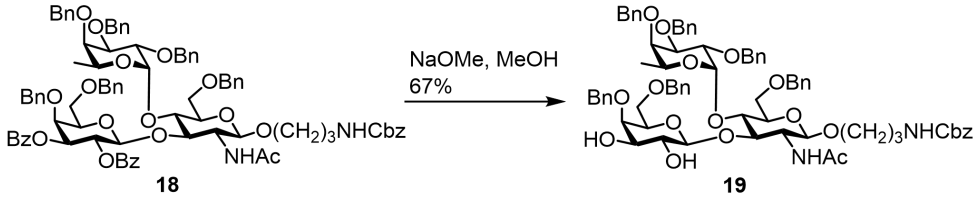


***N*-Benzyloxycarbonyl-3-aminopropyl 2,3-di-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-galacto-pyranosyl-(1→3)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (18)**

To a solution of acceptor **17** (30.0 mg, 0.028 mmol) in anhydrous CH_2Cl_2/DMF (0.60 mL, 2:1, v/v) were added $CuBr_2$ (94.0 mg, 0.042 mmol), tetrabutylammonium bromide (226 mg, 0.084 mmol), and freshly activated 4 Å molecular sieves (200 mg). The mixture was stirred at room temperature for 15 min and then cooled down to 0 °C. Then, donor **4** (134 mg, 0.28 mmol) was added. The reaction mixture was gradually warmed to 15 °C and stirred at the same temperature overnight. Then, the mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$, water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to afford **18** (19.1 mg, 0.013 mmol, 45%, 62% brsm, based on acceptor consumption) as a colorless syrup. R_f = 0.5 (petroleum ether/EtOAc = 1:2.5); $[\alpha]_D^{25}$ = -31.2 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* =

7.8, 5.1 Hz, 4H, H-Ar), 7.53-5.45 (m, 3H, H-Ar), 7.40 -7.21 (m, 38H, H-Ar), 7.19-7.11 (m, 4H, H-Ar), 5.92 (d, *J* = 4.5 Hz, 1H), 5.78 (dd, *J* = 10.5, 8.0 Hz, 1H, H-2'), 5.33 (dd, *J* = 10.5, 3.1 Hz, 1H, H-3'), 5.25 (t, *J* = 6.2 Hz, 1H), 5.05-5.00 (m, 2H), 4.97 (d, *J* = 3.2 Hz, 1H, H-1''), 4.94 (d, *J* = 8.0 Hz, 1H, H-1'), 4.73-4.71 (m, 1H, H-1), 4.71-4.62 (m, 4H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.57-4.50 (m, 2H, H-2, H-5''), 4.45 (d, *J* = 11.9 Hz, 1H), 4.42-4.36 (m, 2H), 4.43-4.26 (m, 3H, H-3, H-5, H-4'), 4.22 (d, *J* = 11.4 Hz, 1H), 3.99 (dd, *J* = 10.1, 3.8 Hz, 1H, H-2''), 3.93-3.85 (m, 2H, H-4, H-5'), 3.83 (dd, *J* = 10.1, 2.6 Hz, 1H, H-3''), 3.77-3.66 (m, 4H, H-6, H-6'', C**H**HO-Linker), 3.66-3.62 (m, 1H), 3.58-3.53 (m, 1H, H-6), 3.39 (d, *J* = 2.7 Hz, 1H, H-4''), 3.37-3.32 (m, 1H), 3.32-3.28 (m, 1H, CH**H**O-Linker), 3.18-3.08 (m, 1H, C**H**HN-Linker), 3.06-2.96 (m, 1H, CH**H**N-Linker), 1.87 (s, 3H, Ac), 1.60-1.51 (m, 1H, C**H**H-Linker), 1.44-1.37 (m, 1H, CH**H**-Linker), 1.26 (d, *J* = 6.4 Hz, 3H, H-6''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5 (CH_3**C**=O), 166.1 (Ph**C**=O), 165.3 (Ph**C**=O), 156.6 ($PhCH_2O$**C**=O), 139.2 (C-Ar), 138.9 (C-Ar), 138.4 (C-Ar), 138.2 (C-Ar), 138.0 (C-Ar), 137.8 (C-Ar), 136.9 (C-Ar), 133.6 (C-Ar), 133.4 (C-Ar), 130.0 (C-Ar), 130.0 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.7 (C-Ar), 129.1 (C-Ar), 129.0 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.5 (C-Ar), 127.5 (C-Ar), 127.4 (C-Ar), 127.4 (C-Ar), 100.1 (C-1'), 98.9 (C-1), 96.1 (C-1''), 80.3 (C-3''), 78.3 (C-4''), 77.5, 77.2, 76.8, 75.8 (C-2''), 75.8 (C-3), 75.2 (C-4'), 75.0 (C-3'), 74.8, 74.4 (C-5), 74.3 (C-2), 73.6, 73.5, 73.1, 72.9 (C-5'), 72.4, 71.3 (C-4), 70.5, 70.4 (C-2'), 68.4 (C-6), 67.5 (C-6''), 66.8 (C-5''), 66.6, 65.9 (**C**H_2O-Linker), 37.7 (**C**H_2N-Linker), 29.3 (**C**H_2-Linker), 23.5 (**C**H_3C=O), 16.7 (C-6''); HRMS (ESI): *m*/*z* calcd for $C_{87}H_{93}N_2O_{19}$ [M+H$^+$]: 1468.6294, found: 1468.6296.

_N_-Benzyloxycarbonyl-3-aminopropyl 4,6-di-_O_-benzyl-β-D-galactopyranosyl-(1→3)-2,3,4-tri-_O_-benzyl-α-L-fucopyranosyl-(1→4)-6-_O_-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (19)

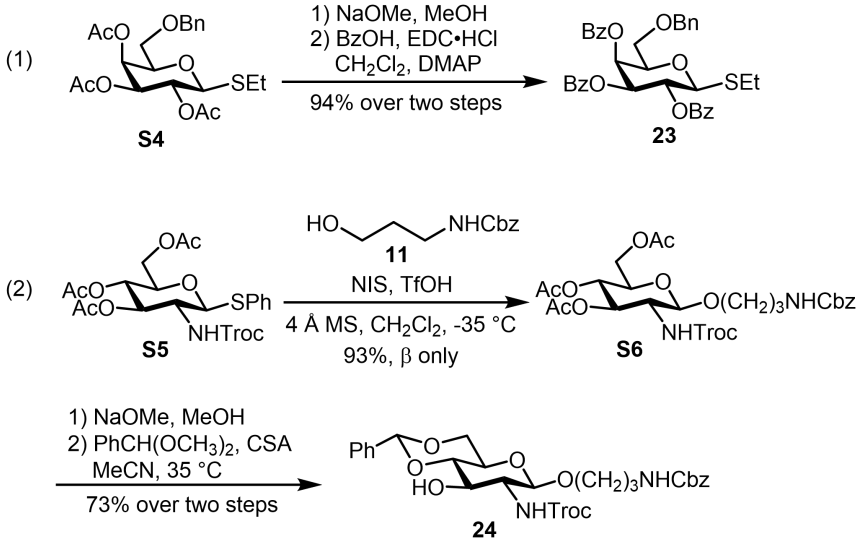


To a solution of compound **18** (27.0 mg, 0.018 mmol) in MeOH (0.20 mL) at 0 °C was added NaOMe (10.0 mg, 0.18 mmol). The reaction mixture was stirred for 2 h at room temperature, at the end of which time TLC indicated it was finished. Then, the reaction mixture was neutralized with Amberlite IR120 H$^+$ resin, filtered and concentrated. The obtained residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 20:1) to afford **19** (14.0 mg, 0.012 mmol, 67%) as a colorless syrup. R_f = 0.35 (CH_2Cl_2/MeOH = 20:1); $[\alpha]_D^{25}$ = -48 (*c* 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.23 (m, 35H, H-Ar), 7.02 (d, *J* = 7.7 Hz, 1H), 5.27 (t, *J* = 6.3 Hz, 1H), 5.10-5.04 (m, 2H), 5.00 (d, *J* = 3.7 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.82-4.74 (m, 2H), 4.74-4.63 (m, 3H), 4.61-4.55 (m, 2H), 4.45-4.30 (m, 7H), 4.20 (q, *J* = 6.6 Hz, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 4.00 (dd, *J* = 10.1, 3.7 Hz, 1H), 3.92-3.82 (m, 3H), 3.82-3.76 (m, 2H), 3.73-3.56 (m, 8H), 3.51-3.42 (m, 3H), 3.35-3.26 (m, 1H), 3.19-3.09 (m, 1H), 1.74 (s, 3H, Ac), 1.71-1.59 (m, 2H),

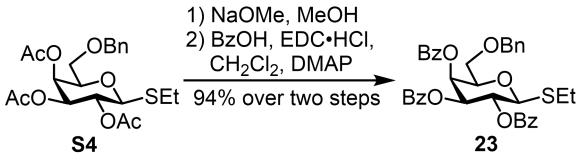
1.10 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (CH_3**C**=O), 156.7 ($PhCH_2O$**C**=O), 138.8 (C-Ar), 138.7 (C-Ar), 138.4 (C-Ar), 138.2 (C-Ar), 138.2 (C-Ar), 137.6 (C-Ar), 136.7 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.5 (C-Ar), 127.5 (C-Ar), 127.5 (C-Ar), 127.3 (C-Ar), 127.3 (C-Ar), 100.9, 100.2, 97.1, 79.8, 77.9, 75.9, 75.3, 75.1, 75.0, 74.1, 74.1, 73.7, 73.4, 73.4, 73.0, 73.0, 72.6, 71.3, 69.0, 68.6, 67.2, 67.2, 66.7, 66.7, 54.1, 37.4, 29.5, 23.3, 16.6; HRMS (ESI): m/z calcd for $C_{73}H_{85}N_2O_{17}$ [M+H$^+$]: 1261.5843, found: 1261.5842.

3.6 Synthesis of donor 23 and acceptor 24

Scheme S2. Preparation of monosaccharide building blocks 23 and 24.



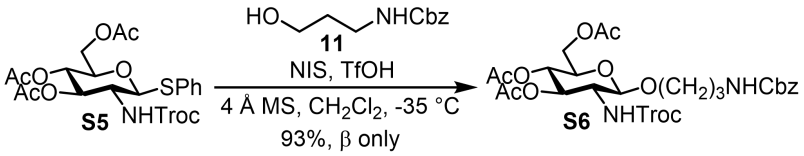
Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-1-thio-β-D-galactopyranoside (23)



To a solution of compound **S4**[5] (5.60 g, 12.7 mmol) in MeOH (127 mL) at 0 °C was added NaOMe (343 mg, 6.4 mmol). The reaction mixture was stirred for 30 min at room temperature, at the end of which time TLC indicated it was finished. Then, the reaction mixture was neutralized with Amberlite IR120 H$^+$ resin, filtered and concentrated. To a solution of the obtained residue in CH_2Cl_2 (64 mL) at 0 °C were added benzoic acid (6.20 g, 50.8 mmol), EDCI (9.80 g, 51.1 mmol), and 4-dimethylaminopyridine (1.50 g, 12.3 mmol). The reaction mixture was stirred for 1.5 h at room temperature, at the end of which time TLC indicated it was finished. The reaction was diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 5:1) to afford **23** (7.50 g, 12.0 mmol, 94%) as a white solid. R_f = 0.5 (petroleum ether/EtOAc = 4:1); $[\alpha]_D^{25}$ = 132.57

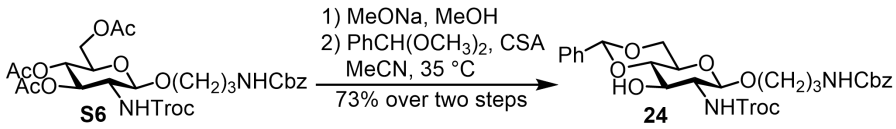
(*c* 1.77, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.97 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.80 (d, *J* = 7.4 Hz, 2H, H-Ar), 7.62 (t, *J* = 7.4 Hz, 1H, H-Ar), 7.53-7.35 (m, 7H, H-Ar), 7.29-7.17 (m, 6H, H-Ar), 6.03 (d, *J* = 3.3 Hz, 1H), 5.83 (t, *J* = 9.9 Hz, 1H), 5.64 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.84 (d, *J* = 9.9 Hz, 1H), 4.55 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.20 (t, *J* = 6.4 Hz, 1H), 3.73 (dd, *J* = 9.7, 6.0 Hz, 1H), 3.65 (dd, *J* = 9.7, 6.7 Hz, 1H), 2.93-2.77 (m, 2H), 1.33 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (Ph**C**=O), 165.5 (Ph**C**=O), 165.5 (Ph**C**=O), 137.5 (C-Ar), 133.5 (C-Ar), 133.3 (C-Ar), 133.3 (C-Ar), 130.0 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.4 (C-Ar), 129.4 (C-Ar), 129.0 (C-Ar), 128.6 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 84.2, 76.6, 73.7, 73.0, 68.7, 68.4, 68.0, 24.4 (S**C**H_2CH_3), 15.0 (SCH_2**C**H_3); HRMS (ESI): *m*/*z* calcd for $C_{36}H_{35}O_8S$ [M+H^+]: 627.2047, found: 627.2047.

_N_-Benzyloxycarbonyl-3-aminopropyl 3,4,6-tri-_O_-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranoside (S7)



To a solution of acceptor **11** (3.50 g, 16.7 mmol) and donor **S5**[6] (8.10 g, 14.1 mmol) in anhydrous CH_2Cl_2 (141 mL) was added freshly activated 4 Å molecular sieves (14.1 g). The mixture was stirred at room temperature for 15 min and then cooled down to -78 °C. NIS (3.80 g, 16.9 mmol) and TfOH (253 μL, 2.86 mmol) were added. The reaction mixture was gradually warmed to -38 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2, and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1.5:1) to afford **S6** (8.80 g, 13.1 mmol, 93%, based on donor consumption) as a white solid. R_f = 0.3 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = -2.18 (*c* 1.83, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.28 (m, 5H, H-Ar), 5.88 (d, *J* = 8.8 Hz, 1H, N**H**Troc), 5.21-5.00 (m, 5H), 4.75-4.65 (m, 2H), 4.42 (d, *J* = 8.4 Hz, 1H), 4.23 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.11 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.94 (m, 1H), 3.70 (q, *J* = 9.2 Hz, 1H), 3.62-3.55 (m, 1H), 3.53-3.41 (m, 2H), 3.13 (m, 1H), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.02 (2, 3H, OAc), 1.84-1.72 (m, 2H, C**H₂**-Linker); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8 (CH_3**C**=O), 170.7 (CH_3**C**=O), 169.5 (CH_3**C**=O), 156.8 ($PhCH_2O$**C**=O), 154.7 (Cl_3CCH_2O**C**=O), 136.8 (C-Ar), 128.6 (C-Ar), 128.2 (C-Ar), 101.3, 95.7, 74.4, 72.5, 71.8, 68.7, 67.4, 66.7, 62.1, 56.1, 37.6 (**C**H_2N-Linker), 29.7 (**C**H_2-Linker), 20.8 (**C**H_3C=O), 20.7 (**C**H_3C=O), 20.7 (**C**H_3C=O); HRMS (ESI): *m*/*z* calcd for $C_{26}H_{34}Cl_3N_2O_{12}$ [M+H^+]: 671.1172, found: 671.1172.

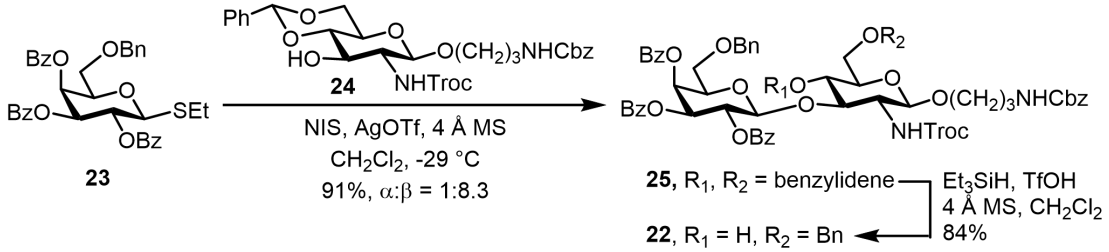
_N_-Benzyloxycarbonyl-3-aminopropyl 4,6-_O_-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-β-D-glucopyranoside (24)



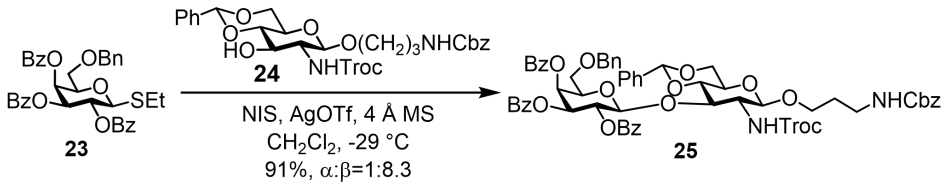
To a solution of compound **S7** (9.60 g, 14.3 mmol) in MeOH (143 mL) at 0 °C was added NaOMe (385 mg, 7.13 mmol). The reaction mixture was stirred for 30 min at room temperature, at the end of which time TLC indicated it was finished. Then, the reaction mixture was neutralized

with Amberlite IR120 H^+ resin, filtered and concentrated. To a solution of the obtained residue in MeCN (72 mL) at 0 °C were added benzaldehyde dimethyl acetal (6.5 mL, 43.3 mmol) and CSA (330 mg, 1.42 mmol). The reaction mixture was stirred for 2 h at room temperature, at the end of which time TLC indicated it was finished. The reaction was diluted with CH_2Cl_2, and then the mixture was washed with water and saturated aqueous $NaHCO_3$. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1.5:1) to afford **24** (6.60 g, 10.4 mmol, 73%) as a white solid. R_f = 0.2 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = -30.58 (*c* 1.37, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H, H-Ar), 7.40-7.30 (m, 8H, H-Ar), 6.35 (d, 1H), 5.51 (s, 1H, PhC**H**), 5.14-5.05 (m, 3H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.37 (d, *J* = 8.3 Hz, 1H), 4.29 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.95-3.82 (m, 2H), 3.74 (t, *J* = 10.3 Hz, 1H), 3.57-3.40 (m, 4H), 3.38-3.30 (m, 1H), 3.16-3.06 (m, 1H), 1.82-1.70 (m, 1H), 1.70-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9 ($PhCH_2O$**C**=O), 155.7 (Cl_3CCH_2O**C**=O), 137.2 (C-Ar), 136.7 (C-Ar), 134.6 (C-Ar), 129.9 (C-Ar), 129.4 (C-Ar), 129.1 (C-Ar), 128.7 (C-Ar), 128.5 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 126.5 (C-Ar), 101.9, 101.7, 95.7, 81.45, 74.7, 72.0, 68.6, 67.3, 66.9, 66.2, 58.8, 37.6 (**C**H_2N-Linker), 30.0 (**C**H_2-Linker); HRMS (ESI): *m/z* calcd for $C_{27}H_{32}Cl_3N_2O_9$ [M+H^+]: 633.1168, found: 633.1168.

3.7 Synthesis of disaccharide acceptor 22



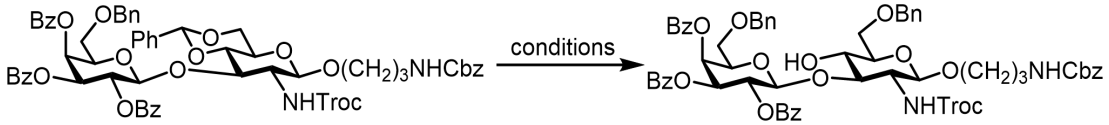
***N*-Benzyloxycarbonyl-3-aminopropyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranosyl-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (25)**



To a solution of acceptor **24** (210 mg, 0.33 mmol) and donor **23** (370 mg, 0.59 mmol) in anhydrous CH_2Cl_2 (6.6 mL) was added freshly activated 4 Å molecular sieves (660 mg). The mixture was stirred at room temperature for 15 min and then cooled down to -73 °C. NIS (200 mg, 0.89 mmol) and AgOTf (46.0 mg, 0.18 mmol) were added. The reaction mixture was gradually warmed to -29 °C and stirred at the same temperature for 1 h. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1) to afford **25** (320 mg, 0.27 mmol, 81%, based on acceptor consumption) as a white solid. R_f = 0.3 (petroleum ether/EtOAc = 1.5:1) ; $[\alpha]_D^{25}$ = 9.115 (*c* 20.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.98 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.75 (d, *J* = 7.7 Hz, 2H, H-Ar),

7.58 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.51-7.46 (m, 3H, H-Ar), 7.45-7.12 (m, 20H, H-Ar), 5.86 (d, *J* = 3.4 Hz, 1H, H-4'), 5.71 (t, *J* = 9.2 Hz, 1H, H-2'), 5.52 (s, 1H, PhC**H**), 5.46 (d, *J* = 10.5 Hz, 1H, H-3'), 5.41 (s, 1H), 5.09-5.02 (m, 2H), 4.98 (d, *J* = 7.9 Hz, 1H, H-1'), 4.75 (d, *J* = 6.4 Hz, 1H, H-1), 4.43-4.33 (m, 3H, H-3), 4.29 (dd, *J* = 11.0, 4.9 Hz, 1H, H-6), 4.21 (d, *J* = 11.9 Hz, 1H), 4.11 (d, *J* = 12.3 Hz, 1H), 3.92-3.88 (m, 1H, H-5'), 3.87-3.82 (m, 1H, C**H**HO-Linker), 3.76-3.70 (m, 2H, H-4, H-6), 3.55 (t, *J* = 8.4 Hz, 1H, H-6'), 3.50-3.39 (m, 3H, H-5, H-6', CH**H**O-Linker), 3.34-3.27 (m, 1H, C**H**HN-Linker), 3.27-3.21 (m, 1H, H-2), 3.17-3.10 (m, 1H, CH**H**N-Linker), 1.73-1.69 (m, 1H, C**H**H-Linker), 1.66-1.63 (m, 1H, CH**H**-Linker); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6 (Ph**C**=O), 165.6 (Ph**C**=O), 165.2 (Ph**C**=O), 156.6 ($PhCH_2O$**C**=O), 154.0 (Cl_3CCH_2O**C**=O), 137.6 (C-Ar), 137.4 (C-Ar), 136.8 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 130.1 (C-Ar), 129.9 (C-Ar), 129.9 (C-Ar), 129.5 (C-Ar), 129.5 (C-Ar), 129.2 (C-Ar), 129.1 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 126.1 (C-Ar), 101.2 (Ph**C**H), 101.2 (C-1'), 100.5 (C-1), 95.7, 80.4 (C-4), 77.6 (C-3), 74.0, 73.7, 72.5 (C-5'), 72.1 (C-3'), 70.6 (C-2'), 68.7 (C-6), 68.3 (C-4'), 67.9 (**C**H_2O-Linker), 67.7 (C-6'), 66.8, 66.3 (C-5), 58.2 (C-2), 38.1 (**C**H_2N-Linker), 29.8 (**C**H_2-Linker); HRMS (ESI): *m/z* calcd for $C_{61}H_{60}Cl_3N_2O_{17}$ [M+H$^+$]: 1197.2952, found: 1197.2952.

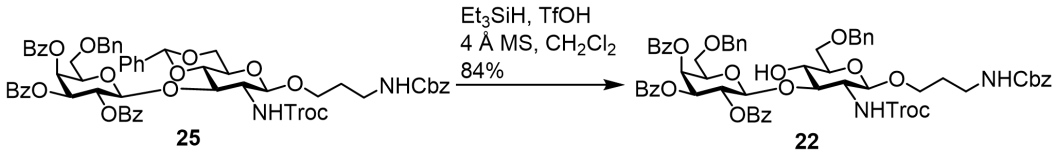
Table S1. Exploration for the conditions of selective benzylidene ring opening.



Entry	Conditions	Result[a]
1	$NaCNBH_3$, HCl/Et_2O, THF, 4 Å MS	no reaction
2	Et_3SiH, BF_3•Et_2O, CH_3CN, 4 Å MS	no reaction
3	BH_3•NMe_3, TMSOTf, THF, 4 Å MS	no reaction
4	Et_3SiH, TfOH, CH_2Cl_2, 4 Å MS	**32**, 84%

[a]Isolated yield.

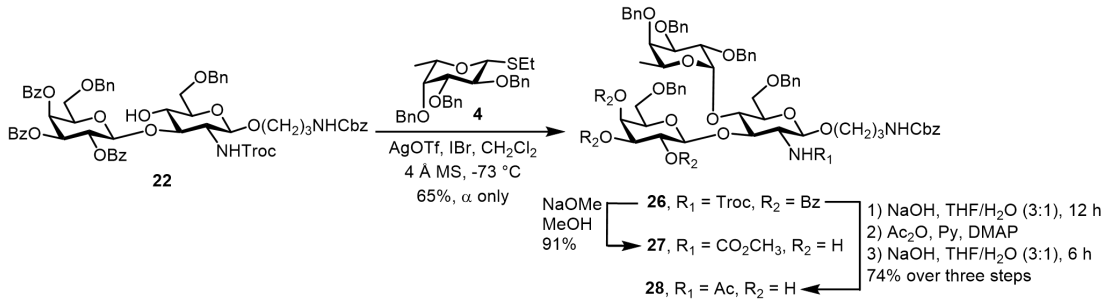
***N*-Benzyloxycarbonyl-3-aminopropyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranosyl-(1→3)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (22)**



To a solution of compound **25** (607 mg, 0.51 mmol) in anhydrous CH_2Cl_2 (17 mL) was added freshly activated 4 Å molecular sieves (3.4 g). The mixture was stirred at room temperature for 20 min and then Et_3SiH (0.45 mL, 2.82 mmol) was added. After being stirred for 15 min at room temperature, the reaction mixture was cooled to -78 °C. TfOH (135 μL, 1.54 mmol) was added. The reaction mixture was stirred at the same temperature for 1 h, at the end of which time TLC indicated it was finished. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1.5:1) to afford **22** (516 mg, 0.43 mmol,

84%) as a white solid. R_f = 0.25 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = 12.945 (*c* 13.43, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 6.7 Hz, 2H, H-Ar), 7.98 (d, *J* = 7.3 Hz, 2H, H-Ar), 7.73 (d, *J* = 7.0 Hz, 2H, H-Ar), 7.60 (m, 1H, H-Ar), 7.47 (m, 3H, H-Ar), 7.41-7.35 (m, 4H, H-Ar), 7.32-7.18 (m, 16H, H-Ar), 5.86 (d, *J* = 3.5 Hz, 1H, H-4'), 5.79 (dd, *J* = 10.5, 8.0 Hz, 1H, H-2'), 5.54 (dd, *J* = 10.5, 3.5 Hz, 1H, H-3'), 5.37 (t, *J* = 6.1 Hz, 1H), 5.33 (s, 1H), 5.05 (m, 2H), 4.87 (d, *J* = 8.0 Hz, 1H, H-1'), 4.66 (d, *J*=7.2 Hz, 1H, H-1), 4.57 (d, *J* = 12.3 Hz, 1H), 4.54 (m, 1H), 4.51 (d, *J* = 11.7 Hz, 1H), 4.41 (d, *J* = 11.7 Hz, 1H), 4.29 (s, 1H), 4.23-4.20 (m, 1H, H-5'), 4.20-4.17 (m, 1H), 4.13-4.06 (m, 1H, H-3), 3.85-3.80 (m, 2H, H-6, C**H**HO-Linker), 3.69-3.62 (m, 3H, H-6, H-6'), 3.60-3.56 (m, 1H, H-4), 3.55-3.48 (m, 2H, H-5, CH**H**O-Linker), 3.38-3.32 (m, 1H, C**H**HN-Linker), 3.18-3.09 (m, 2H, H-2, CH**H**N-Linker), 1.75-1.68 (m, 1H, C**H**H-Linker), 1.64-1.60 (m, 1H, CH**H**-Linker); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6 (Ph**C**=O), 165.5 (Ph**C**=O), 165.2 (Ph**C**=O), 156.7 ($PhCH_2O$**C**=O), 154.0 (Cl_3CCH_2O**C**=O), 138.3 (C-Ar), 137.1 (C-Ar), 136.8 (C-Ar), 133.7 (C-Ar), 133.5 (C-Ar), 133.4 (C-Ar), 130.0 (C-Ar), 129.9 (C-Ar), 129.8 (C-Ar), 129.0 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 128.0 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 102.0 (C-1'), 99.8 (C-1), 95.7, 84.5 (C-3), 75.1 (C-5), 73.8, 73.7, 73.4, 73.1 (C-5'), 71.7 (C-3'), 70.0 (C-4), 69.9 (C-2'), 69.7 (C-6), 68.3 (C-4'), 68.1 (C-6'), 67.3 (**C**H_2O-Linker), 66.6, 57.3 (C-2), 37.6 (**C**H_2N-Linker), 29.7 (**C**H_2-Linker); HRMS (ESI): *m/z* calcd for $C_{61}H_{62}Cl_3N_2O_{17}$ [M+H^+]: 1199.3109, found: 1199.3110.

3.8 Synthesis of trisaccharide acceptors 27 and 28

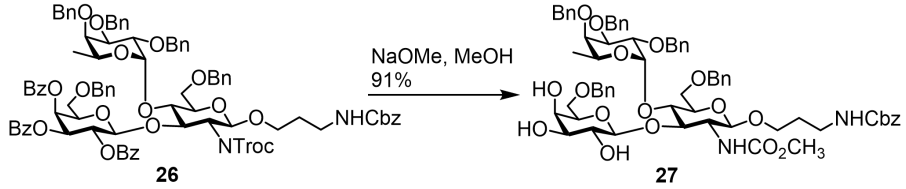


***N*-Benzyloxycarbonyl-3-aminopropyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-β-D-glucopyranoside (26)**

To a solution of acceptor **22** (200 mg, 0.17 mmol) in anhydrous CH_2Cl_2 (11 mL) was added freshly activated 4 Å molecular sieves (3.30 g). The mixture was stirred at room temperature for 15 min, after which time it was cooled to -73 °C and AgOTf (428 mg, 1.67 mmol) was added. The mixture was stirred at the same temperature for 30 min. Then, a solution of IBr (1 mol/L in CH_2Cl_2, 0.80 mL, 0.80 mmol) and a solution of donor **4** (dissolving in 1 mL CH_2Cl_2, 319 mg, 0.67 mmol) was added dropwise. The reaction mixture was stirred at the same temperature for 1 h, at the end of which time TLC indicated it was finished. Then, the mixture was quenched with Et_3N,

diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2:1) to afford **26** (181 mg, 0.11 mmol, 65%, based on acceptor consumption) as a white solid. R_f = 0.3 (petroleum ether/EtOAc = 1.5:1); $[\alpha]_D^{25}$ = -4.448 (*c* 0.97, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 4H, H-Ar), 7.78 (d, *J* = 7.8 Hz, 2H, H-Ar), 7.53 (t, *J* = 7.5 Hz, 1H, H-Ar), 7.46 (d, *J* = 7.4 Hz, 1H, H-Ar), 7.41-7.37 (m, 4H, H-Ar), 7.36-7.31 (m, 8H, H-Ar), 7.30-7.18 (m, 25H, H-Ar), 7.16-7.10 (m, 3H, H-Ar), 5.93 (d, *J* = 3.7 Hz, 1H, H-4'), 5.76 (dd, *J* = 10.4, 8.1 Hz, 1H, H-2'), 5.60 (d, *J* = 8.2 Hz, 1H), 5.53 (dd, *J* = 10.3, 3.6 Hz, 1H, H-3'), 5.24 (t, *J* = 6.2 Hz, 1H), 5.13 (d, *J* = 8.3 Hz, 1H, H-1'), 5.06-5.04 (m, 2H), 5.03 (d, *J* = 3.7 Hz, 1H, H-1''), 4.87 (d, *J* = 11.4 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H, H-1), 4.58-4.54 (m, 2H), 4.49-4.48 (m, 1H, H-5''), 4.47-4.43 (m, 2H), 4.39-4.33 (m, 3H), 4.24 (t, *J* = 6.8 Hz, 1H, H-3), 4.11 (m, 1H, H-5'), 4.03 (m, 1H, H-2''), 4.00 (m, 1H, H-4), 3.91 (dd, *J* = 10.2, 2.7 Hz, 1H, H-3''), 3.73-3.71 (m, 1H), 3.71-3.57 (m, 7H, H-5, H-6, H-6', H-4'', C**H**HO-Linker), 3.40-3.35 (m, 1H, H-2), 3.32-3.27 (m, 1H, CH**H**O-Linker), 3.17-3.10 (m, 1H, C**H**HN-Linker), 3.00-2.93 (m, 1H, CH**H**N-Linker), 1.58-1.52 (m, 1H, C**H**H-Linker), 1.45-1.39 (m, 1H, CH**H**-Linker), 1.34 (d, *J* = 6.5 Hz, 3H, H-6''); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8 (Ph**C**=O), 165.4 (Ph**C**=O), 165.1 (Ph**C**=O), 156.6 ($PhCH_2O$**C**=O), 154.0 (Cl_3CCH_2O**C**=O), 138.9 (C-Ar), 138.7 (C-Ar), 138.3 (C-Ar), 138.0 (C-Ar), 137.5 (C-Ar), 136.8 (C-Ar), 133.6 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 129.8 (C-Ar), 129.8 (C-Ar), 129.7 (C-Ar), 129.7 (C-Ar), 129.3 (C-Ar), 128.9 (C-Ar), 128.7 (C-Ar), 128.6 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.3 (C-Ar), 100.5 (C-1'), 99.2 (C-1), 96.1 (C-1''), 95.6, 80.2 (C-3''), 78.5 (C-4''), 77.4 (C-3), 75.9 (C-2''), 75.1, 74.6, 74.2 (C-5), 74.1 (C-4), 73.6, 73.1, 72.9 (C-5'), 72.8, 72.0 (C-3'), 71.4, 69.7 (C-2'), 68.7 (C-4'), 68.6 (C-6), 67.7 (C-6'), 66.9 (C-5''), 66.5, 66.1 (**C**H_2O-Linker), 56.5 (C-2), 37.5 (**C**H_2N-Linker), 29.3 (**C**H_2-Linker), 16.9 (C-6''); HRMS (ESI): *m*/*z* calcd for $C_{88}H_{90}Cl_3N_2O_{21}$ [M+H$^+$]: 1615.5096, found: 1615.5098.

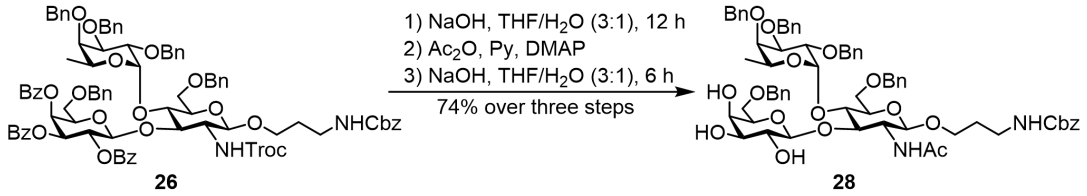
_N_-Benzyloxycarbonyl-3-aminopropyl 6-_O_-benzyl-β-D-galactopyranosyl-(1→3)-2,3,4-tri-_O_-benzyl-α-L-fucopyranosyl-(1→4)-6-_O_-benzyl-2-deoxy-2-methoxycarbonylamino-β-D-gluco-pyranoside (27)



To a solution of compound **26** (180 mg, 0.11 mmol) in MeOH (2.50 mL) at 0 °C was added NaOMe (18 mg, 0.33 mmol). The reaction mixture was stirred at room temperature for 1 d, at the end of which time TLC indicated it was finished. Then, the reaction mixture was neutralized with Amberlite IR120 H$^+$ resin, filtered and concentrated. The obtained residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 25:1) to afford **27** (121 mg, 0.10 mmol, 91%) as a white solid. R_f = 0.4 (CH_2Cl_2/MeOH = 18:1); $[\alpha]_D^{25}$ = -3.853 (*c* 0.97, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.16 (m, 30H, H-Ar), 6.30-6.24 (m, 1H), 5.38 (m, 1H), 5.08-5.01 (m, 2H), 4.96 (d, *J* = 3.2 Hz, 1H, H-1''), 4.92 (d, *J* = 11.4 Hz, 1H), 4.82 (d, *J* = 8.9 Hz, 1H, H-1'), 4.76 (dd, *J* = 11.4,

7.8 Hz, 2H), 4.70 (d, *J* = 11.8 Hz, 1H), 4.58 (dd, *J* = 11.6, 3.3 Hz, 2H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.38 (d, *J* = 7.3 Hz, 1H, H-1), 4.36-4.28 (m, 2H), 4.26-4.18 (m, 2H, H-5', H-5''), 4.02-3.98 (m, 1H, H-2''), 3.94-3.90 (m, 1H, H-3''), 3.88-3.81 (m, 3H, H-3, H-6', C**H**HO-Linker), 3.79-3.73 (m, 2H, H-4, H-6), 3.69-3.64 (m, 2H, H-6', H-4''), 3.63-3.57 (m, 3H, H-2, H-6, H-3'), 3.56 (s, 3H, NHCOC**H**$_3$), 3.55-3.50 (m, 2H, H-5, H-2'), 3.50-3.46 (m, 1H, CH**H**O-Linker), 3.35-3.28 (m, 1H, H-4'), 3.28-3.21 (m, 1H, C**H**HN-Linker), 3.19-3.12 (m, 1H, CH**H**N-Linker), 2.92-2.80 (m, 1H), 1.75-1.68 (m, 1H, C**H**H-Linker), 1.68-1.62 (m, 1H, CH**H**-Linker), 1.13 (d, *J* = 6.4 Hz, 3H, H-6''); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.9 (NH**C**OCH$_3$), 156.6 (PhCH$_2$O**C**=O), 138.7 (C-Ar), 138.7 (C-Ar), 138.4 (C-Ar), 138.2 (C-Ar), 137.7 (C-Ar), 136.7 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.5 (C-Ar), 127.3 (C-Ar), 100.2 (C-1'), 100.0 (C-1), 98.3 (C-1''), 79.6 (C-3''), 78.3 (C-5'), 77.9 (C-4''), 76.1 (C-2''), 75.3 (C-4), 75.1 (C-3'), 74.3 (C-2'), 74.0, 73.5 (C-5), 73.5, 73.2, 73.0, 72.8, 70.9 (C-2), 69.3 (C-6), 68.5 (C-6'), 68.2 (C-3), 67.4 (C-5''), 66.9 (**C**H$_2$O-Linker), 66.5, 55.4 (C-4'), 52.0 (NHCO**C**H$_3$), 37.5 (**C**H$_2$N-Linker), 29.4 (**C**H$_2$-Linker), 16.6 (C-6''); HRMS (ESI): *m*/*z* calcd for $C_{66}H_{79}Cl_3N_2O_{18}$ [M+H$^+$]: 1187.5322, found: 1187.5322

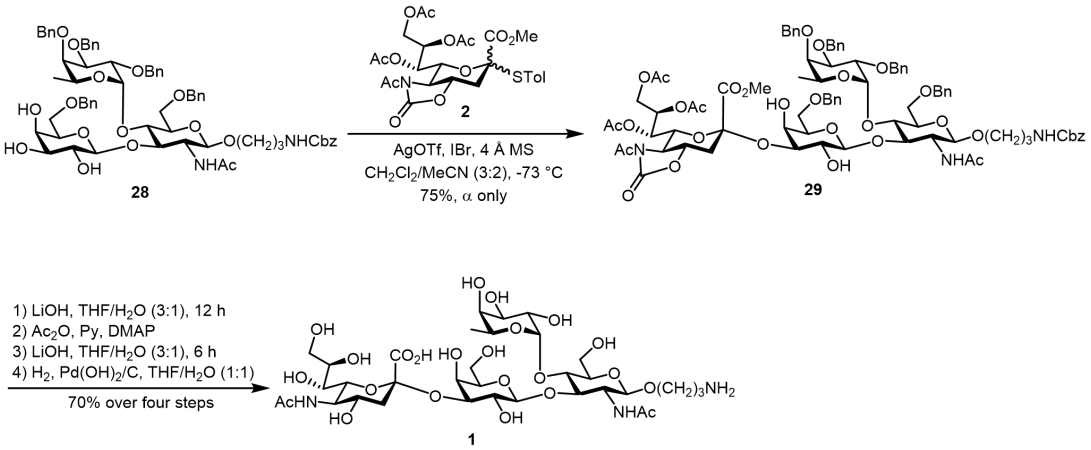
***N*-Benzyloxycarbonyl-3-aminopropyl 6-*O*-benzyl-β-D-galactopyranosyl-(1→3)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (28)**



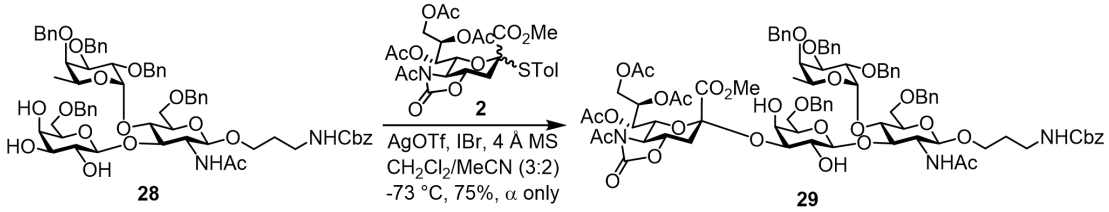
To a solution of compound **26** (600 mg, 0.37 mmol) in THF/H_2O (15 mL, 3:1, v/v) at 0 °C was added NaOH (600 mg, 15 mmol). The reaction mixture was stirred at room temperature for 12 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF and neutralized with Amberlite IR120 H$^+$ resin. After filteration, the filtrate was concentrated to afford a residue for the next step. To a solution of the obtained syrup in pyridine/Ac_2O (20 mL, 3:1, v/v) at 0 °C was added 4-dimethylaminopyridine (10.0 mg, 0.082 mmol). The reaction mixture was stirred at room temperature for 5 h, at the end of which time TLC indicated it was finished. The reaction was diluted with CH_2Cl_2, quenched with saturated aqueous $NaHCO_3$, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. To a solution of the obtained syrup in THF/H_2O (15 mL, 3:1, v/v) at 0 °C was added NaOH (600 mg, 15 mmol). The reaction mixture was stirred at room temperature for 6 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF, neutralized with Amberlite IR120 H$^+$ resin, filtered and concentrated. The obtained residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 20:1) to afford **28** (316 mg, 0.27 mmol, 74%) as a white solid. R_f = 0.2 (CH_2Cl_2/MeOH = 20:1) ; $[\alpha]_D^{25}$ = -50.625 (*c* 0.27, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.19 (m, 30H, H-Ar), 7.14 (d, *J* = 7.7 Hz, 1H), 5.44 (t, *J* = 6.1 Hz, 1H), 5.11-5.01 (m, 3H), 4.93 (d, *J* = 11.4 Hz, 1H), 4.86 (d, *J* = 6.0 Hz, 1H), 4.76-4.68 (m, 3H), 4.61-4.55 (m, 2H), 4.53-4.46 (m, 2H), 4.39-4.32 (m, 3H), 4.19 (t, *J* = 7.4 Hz, 1H), 4.17-4.13 (m, 1H), 4.02 (dd, *J* = 10.1, 3.6 Hz, 1H), 3.91-3.78 (m, 6H), 3.72 (s, 1H), 3.69-3.53 (m, 7H), 3.52-3.46 (m, 1H), 3.29-3.21 (m, 1H),

3.19-3.12 (m, 1H), 1.78-1.64 (m, 2H), 1.68 (s, 3H, Ac), 1.12 (d, J = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3 (CH_3**C**=O), 156.7 ($PhCH_2O$**C**=O), 138.7 (C-Ar), 138.6 (C-Ar), 138.2 (C-Ar), 138.2 (C-Ar), 137.7 (C-Ar), 136.7 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 127.8 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.6 (C-Ar), 127.3 (C-Ar), 100.5, 100.0, 96.9, 79.7, 77.8, 76.1, 75.1, 74.0, 73.6, 73.5, 73.3, 73.0, 72.9, 71.0, 69.5, 68.9, 68.3, 67.3, 66.8, 66.6, 37.6, 29.5, 23.2, 23.0, 16.6; HRMS (ESI): m/z calcd for $C_{66}H_{79}N_2O_{17}$ [M+H$^+$]: 1171.5374, found: 1171.5374.

3.9 Synthesis of tetrasaccharide 29 and target compound 1



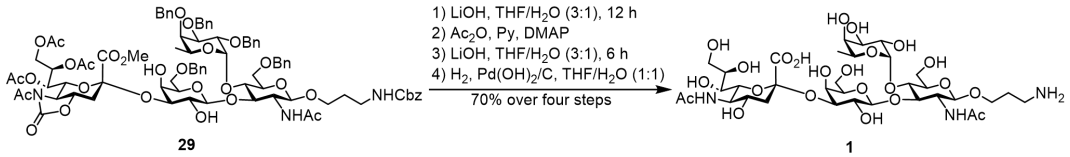
***N*-Benzyloxycarbonyl-3-aminopropyl (methyl 7,8,9-tri-*O*-acetyl-3,5-dideoxy-(*N*-acetyl-5-*N*,4-*O*-carbonyl)-D-glycero-α-D-galacto-2-nonulopyranosonate-(2→3))-6-*O*-benzyl-β-D-galacto-pyranosyl-(1→3)-[2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→4)]-6-*O*-benzyl-2-deoxy-2-acetamido-β-D-glucopyranoside (29)**



To a solution of acceptor **28** (64.0 mg, 0.055 mmol) and donor **2** (96.0 mg, 0.17 mmol) in anhydrous CH_2Cl_2/MeCN (3.3 mL, 3:2, v/v) was added freshly activated 4 Å molecular sieves (700 mg). The mixture was stirred at room temperature for 15 min, after which time it was cooled to -73 °C and AgOTf (106 mg, 0.41 mmol) was added. The mixture was stirred at the same temperature for 30 min. A solution of IBr (1 mol/L in CH_2Cl_2, 0.2 mL, 0.20 mmol) was added dropwise and the reaction mixture was stirred at the same temperature for 1 h, at the end of which time TLC indicated it was finished. Then, the mixture was quenched with Et_3N, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated in vacuo. The obtained residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 1:2.5) to afford **29** (67.0 mg, 0.041 mmol, 75%, based on acceptor consumption) as a white solid. R_f = 0.2 (petroleum ether/EtOAc = 1:2.5); $[\alpha]_D^{25}$ = -31.761 (*c* 1.53, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.21 (m, 30H, H-Ar), 7.06 (d, J = 7.9 Hz, 1H), 5.56 (d, J = 7.5 Hz, 1H, H-7'''), 5.39-5.34 (m, 2H, H-8'''), 5.12-5.04 (m, 3H, H-1''), 4.97-4.92 (m, 2H, H-1), 4.75 (d, J = 9.1 Hz, 1H), 4.73 (d, J = 8.6 Hz, 1H), 4.69 (d, J = 11.7 Hz, 1H), 4.63-4.58 (m, 2H), 4.54-4.50 (m, 2H), 4.48 (d, J = 9.4 Hz, 1H, H-6'''), 4.45 (d, J =

7.6 Hz, 1H, H-1'), 4.41 (dd, *J* = 9.8, 2.4 Hz, 1H, H-9'''), 4.38 (d, *J* = 7.5 Hz, 1H), 4.36-4.33 (m, 1H), 4.20 (t, *J* = 6.7 Hz, 1H, H-3), 4.10-4.08 (m, 1H, H-4'''), 4.08-4.05 (m, 1H, H-5''), 4.05-4.03 (m, 1H, H-2''), 3.95-3.62 (m, 16H, H-2, H-4, H-5, H-6, H-2', H-3', H-4', H-5', H-6', H-3'', H-4'', H-5''', H-9''', 3.95-3.62 (m, 5H), COOC**H**$_3$, C**H**HO-Linker), 3.59-3.54 (m, 1H, CH**H**O-Linker), 3.30-3.24 (m, 1H, C**H**HN-Linker), 3.22-3.16 (m, 1H, CH**H**N-Linker), 2.86 (dd, *J* = 12.7, 3.6 Hz, 1H, H-3eq'''), 2.49 (s, 3H, Ac), 2.44 (t, *J* = 12.7 Hz, 1H, H-3ax'''), 2.10 (s, 3H, Ac), 2.03 (s, 3H, Ac), 2.00 (s, 3H, Ac), 1.77-1.72 (m, 2H, C**H**$_2$-Linker), 1.64 (s, 3H, Ac), 1.12 (d, *J* = 6.4 Hz, 3H, H-6''); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3 (CH_3**C**=O), 170.9 (CH_3**C**=O), 170.8 (CH_3**C**=O), 170.3 (CH_3**C**=O), 169.9 (CH_3**C**=O), 168.4 (C-1'''), 156.6 ($PhCH_2O$**C**=O), 153.7 (AcN**C**=OO), 138.7 (C-Ar), 138.6 (C-Ar), 138.2 (C-Ar), 138.1 (C-Ar), 137.9 (C-Ar), 136.8 (C-Ar), 128.6 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.5 (C-Ar), 128.4 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 127.9 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.7 (C-Ar), 127.4 (C-Ar), 100.8 (C-1'), 99.9 (C-1), 99.2 (C-2'''), 96.1 (C-1''), 79.7 (C-3''), 77.7 (C-4''), 76.6 (C-3), 76.5 (C-3'), 76.1 (C-2''), 75.9 (C-6'''), 75.1, 75.1 (C-4'''), 73.9, 73.5, 73.2 (C-5'), 73.0, 72.6 (C-2), 71.8 (C-7'''), 69.4 (C-8'''), 69.4 (C-6), 69.2 (C-6'), 68.9 (C-2'), 68.5 (C-4'), 68.5 (C-5), 68.2 (C-4), 67.3 (C-5''), 66.6 (**C**H_2O-Linker), 63.3 (C-9'''), 58.8 (C-5'''), 53.4 (COO**C**H_3**)**, 37.6 (**C**H_2N-Linker), 34.8 (C-3'''), 29.3 (**C**H_2-Linker), 24.8 (**C**H_3C=O), 23.2 (**C**H_3C=O), 21.2 (**C**H_3C=O), 21.0 (**C**H_3C=O), 20.9 (**C**H_3C=O), 16.7 (C-6''); HRMS (ESI): *m*/*z* calcd for $C_{85}H_{102}N_3O_{29}$ [M+H$^+$]: 1628.6594, found: 1628.6593.

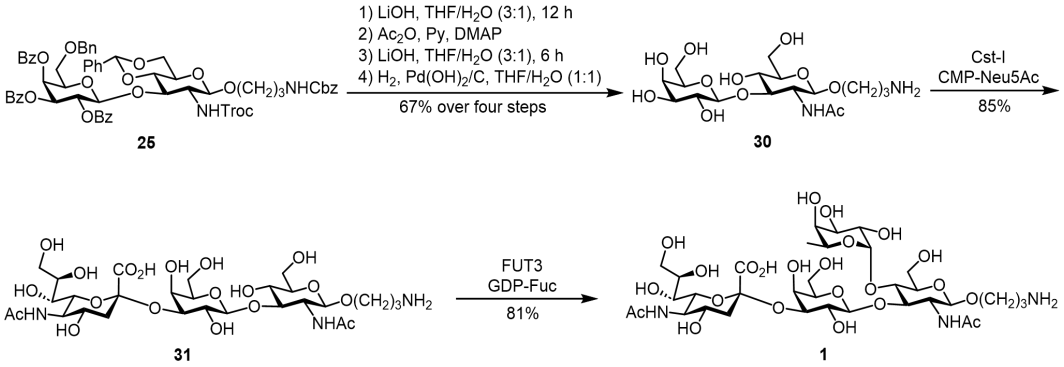
3-Aminopropyl (methyl 3,5-dideoxy-5-acetamido-D-glycero-α-D-galacto-2-nonulo-pyranosonate-(2→3))-β-D-galactopyranosyl-(1→3)-[α-L-fucopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranoside (1)



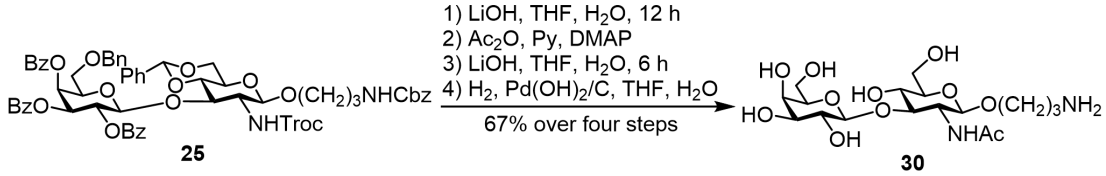
To a solution of compound **29** (44 mg, 0.027 mmol) in THF/H_2O (2.7 mL, 3:1, v/v) at 0 °C was added LiOH (45 mg, 1.89 mmol). The reaction mixture was stirred at room temperature for 12 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated to afford a residue for the next step. To a solution of the obtained syrup in pyridine/Ac_2O (4.0 mL, 3:1, v/v) at 0 °C was added 4-dimethylaminopyridine (3.00 mg, 0.025 mmol). The reaction mixture was stirred at room temperature for 6 h, at the end of which time TLC indicated it was finished. The reaction was diluted with CH_2Cl_2, quenched with saturated aqueous $NaHCO_3$, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. To a solution of the obtained syrup in THF/H_2O (2.7 mL, 3:1, v/v) at 0 °C was added LiOH (45 mg, 1.89 mmol). The reaction mixture was stirred at room temperature for 6 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated to afford a residue for next step. A solution of the resulting residue in THF/H_2O (2.7 mL, 3:1, v/v) was added $Pd(OH)_2$/C (150 mg), and stirred at room temperature for 24 h under an atmosphere of H_2, at the end of which time TLC indicated it was finished. Then, the

reaction mixture was filtered, and the filtrate was lyophilized to give a crude product, which was purified by size-exclusion chromatography (Bio-Gel P2, eluent: H_2O). The obtained product was lyophilized to afford **1**[7] (17 mg, 19 μmol, 70%) as a white amorphous solid. R_f = 0.3 ($MeOH/NH_3·H_2O$ = 7:1); $[\alpha]_D^{25}$ = -43.235 (*c* 0.57, MeOH:H_2O = 1:1); ^1H NMR (600 MHz, D_2O) δ 5.01 (d, *J* = 3.9 Hz, 1H, H-1''), 4.87 (q, *J* = 6.6 Hz, 1H, H-5''), 4.55 (d, *J* = 7.7 Hz, 1H, H-1'), 4.52 (d, *J* = 8.5 Hz, 1H, H-1), 4.09-4.03 (m, 2H, H-3, H-3'), 4.02 (m, 1H, C**H**HO-Linker), 3.99 (dd, *J* = 12.4, 2.3 Hz, 1H, H-6), 3.95-3.91 (m, 1H, H-2), 3.91-3.89 (m, 1H, H-6'''), 3.89-3.83 (m, 4H, H-6, H-3'', H-4'', H-5'''), 3.83-3.81 (m, 1H, H-6'), 3.81-3.77 (m, 2H, H-5, H-2''), 3.75-3.71 (m, 2H, H-4, CH**H**O-Linker), 3.71-3.69 (m, 2H, H-9'''), 3.69-3.63 (m, 2H, H-6', H-4'''), 3.63-3.60 (m, 2H, H-5', H-7'''), 3.58-3.55 (m, 1H, H-4'), 3.55-3.52 (m, 1H, H-8'''), 3.52-3.49 (m, 1H, H-2'), 3.08 (t, *J* = 6.9 Hz, 2H, C**H**$_2$N-Linker), 2.78 (dd, *J* = 12.2, 4.6 Hz, 1H, H-3eq'''), 2.06 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.98-1.92 (m, 2H, C**H**$_2$-Linker), 1.77 (t, *J* = 12.2 Hz, 1H, H-3ax'''), 1.18 (d, *J* = 6.6 Hz, 3H, H-6''); ^{13}C NMR (150 MHz, D_2O) δ 175.0 (CH_3**C**=O), 174.3 (CH_3**C**=O), 173.9 (C-1'''), 102.7 (C-1'), 101.0 (C-1), 99.4 (C-2'''), 98.1 (C-1''), 76.0 (C-3), 75.7 (C-3'), 75.4 (C-4'), 74.8 (C-8'''), 72.7 (C-5'), 72.3 (C-4), 71.9 (C-4''), 71.8 (C-3''), 69.1 (C-2''), 68.8 (C-2'), 68.4 (C-4'''), 68.0 (C-5), 68.0 (C-7'''), 67.7 (**C**H_2O-Linker), 66.9 (C-5''), 66.9 (C-6'''), 62.3 (C-6'), 61.7 (C-9'''), 59.6 (C-6), 55.6 (C-2), 51.7 (C-5'''), 40.0 (C-3'''), 37.7 (**C**H_2N-Linker), 26.7 (**C**H_2-Linker), 22.4 (**C**H_3C=O), 22.0 (**C**H_3C=O), 15.3 (C-6''); HRMS (ESI): *m/z* calcd for $C_{34}H_{60}N_3O_{23}$ [M+H$^+$]: 878.3626, found: 878.3623.

3.10 Chemoenzymatic synthesis of target compound 1



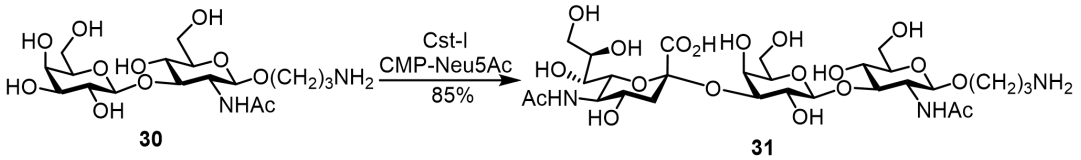
3-Aminopropyl β-D-galactopyranosyl-(1→3)-2-deoxy-2-acetamido-β-D-glucopyranoside (30)



To a solution of compound **25** (100 mg, 83 μmol) in THF/H_2O (4.0 mL, 3:1, v/v) at 0 °C was added LiOH (140 mg, 5.85 mmol). The reaction mixture was stirred at room temperature for 12 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF and neutralized with Amberlite IR120 H$^+$ resin. After filteration, the filtrate was concentrated to afford a residue for the next step. To a solution of the obtained syrup in pyridine/Ac_2O (5.0 mL, 4:1, v/v) at 0 °C was added 4-dimethylaminopyridine (3.00 mg, 0.025 mmol). The reaction mixture was stirred at room temperature for 6 h, at the end of which time TLC indicated it was

finished. The reaction was diluted with CH_2Cl_2, quenched with saturated aqueous $NaHCO_3$, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. To a solution of the obtained syrup in THF/H_2O (4.0 mL, 3:1, v/v) at 0 °C was added LiOH (80 mg, 3.32 mmol). The reaction mixture was stirred at room temperature for 6 h, at the end of which time TLC indicated it was finished. Then, the mixture was diluted with THF and neutralized with Amberlite IR120 H^+ resin. After filteration, the filtrate was concentrated to afford a residue for next step. A solution of the resulting residue in THF/H_2O (4.0 mL, 3:1, v/v) was added $Pd(OH)_2$/C (200 mg), and stirred at room temperature for 48 h under an atmosphere of H_2, at the end of which time TLC indicated it was finished. Then, the reaction mixture was filtered, and the filtrate was lyophilized to give a crude product, which was purified by size-exclusion chromatography (Bio-Gel P2, eluent: H_2O). The obtained product was lyophilized to afford **30** (23 mg, 52 μmol, 62%) as a white amorphous solid. R_f = 0.5 (MeOH/NH_3·H_2O = 3:1); ^{1}H NMR (400 MHz, D_2O) δ 4.45 (d, J = 8.2 Hz, 1H), 4.36 (d, J = 7.8 Hz, 1H), 3.97-3.89 (m, 1H), 3.87-3.81 (m, 2H), 3.80-3.76 (m, 1H), 3.76-3.72 (m, 1H), 3.72-3.70 (m, 1H), 3.70-3.68 (m, 1H), 3.68-3.65 (m, 2H), 3.65-3.60 (m, 2H), 3.56 (dd, J = 10.0, 3.4 Hz, 1H), 3.48-3.38 (m, 3H), 2.99 (t, J = 7.0 Hz, 2H), 1.95 (s, 3H), 1.90-1.82 (m, 2H); ^{13}C NMR (100 MHz, D_2O) δ 174.8, 103.5, 101.0, 82.3, 75.4, 75.3, 72.5, 70.7, 68.7, 68.6, 67.9, 61.1, 60.7, 54.5, 37.6, 26.7, 22.3; HRMS (ESI): m/z calcd for $C_{17}H_{33}N_2O_{11}$ [M+H^+]: 441.2079, found: 441.2079.

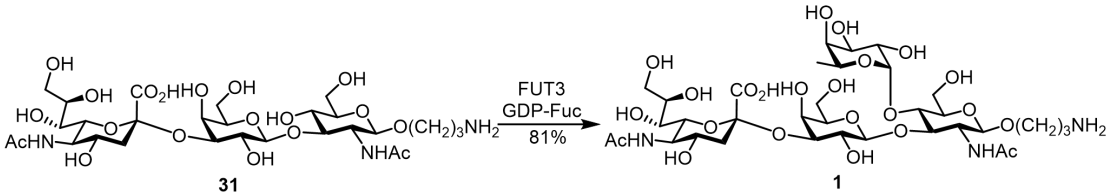
3-Aminopropyl (methyl 3,5-dideoxy-5-acetamido-D-glycero-α-D-galacto-2-nonulo-pyranosonate-(2→3))-β-D-galactopyranosyl-(1→3)-2-deoxy-2-acetamido-β-D-gluco-pyranoside (31)



To a solution of disaccharide **35** (56 mg, 0.127 mmol), CMP-Neu5Ac (125 mg 0.191mmol) and $MnCl_2$ (10 mM) in Tris buffer solution (1.25 mL,100 mM, pH 7.5) was added CSt-I (400 μg), and the reaction mixture was incubated at 37 °C for 2 h. ESI-MS analysis showed that the enzymatic reaction was completed. The reaction mixture was centrifuged, and the resulting supernatant was purified by Bio-Gel P2 column (eluent: 0.1 M NH_4HCO_3). Product containing fractions were combined and lyophilized to afford the α2,3-sialylated glycan **36** as a white amorphous solid (79 mg, 0.11 mmol, 85%); $[\alpha]_D^{25}$ = -25.552 (c 0.11, MeOH:H_2O = 1:1); ^{1}H NMR (600 MHz, D_2O) δ 4.55 (d, J = 8.5 Hz, 1H, H-1), 4.51 (d, J = 7.8 Hz, 1H, H-1'), 4.09 (dd, J = 9.8, 3.2 Hz, 1H, H-3'), 4.05-4.01 (m, 1H, C**H**HO-Linker), 3.96-3.92 (m, 2H, H-6', H-8''), 3.89-3.87 (m, 1H, H-2), 3.87-3.86 (m, 1H, H-5), 3.86-3.84 (m, 1H, H-6), 3.83 (d, J = 3.1 Hz, 1H, H-5''), 3.80-3.78 (m, 1H, H-5'), 3.77-3.75 (m, 1H, H-9''), 3.75-3.71 (m, 3H, H-6', H-9'', CH**H**O-Linker), 3.71-3.67 (m, 2H, H-4, H-4''), 3.67-3.62 (m, 2H, H-6, H-6''), 3.60 (dd, J = 9.0, 2.0 Hz, 1H, H-3), 3.57-3.54 (m, 1H, H-2'), 3.53 (d, J = 7.4 Hz, 1H, H-4'), 3.52-3.48 (m, 1H, H-7''), 3.09 (t, J = 7.0 Hz, 2H, C**H$_2$**N-Linker), 2.76 (dd, J = 12.1, 4.6 Hz, 1H, H-3eq''), 2.04 (s, 3H, Ac), 2.03 (s, 3H, Ac), 1.98-1.93 (m, 2H, C**H$_2$**-Linker), 1.78 (t, J = 12.1 Hz, 1H, H-3ax''); ^{13}C NMR (150 MHz, D_2O) δ 175.0 (CH_3**C**=O), 174.7 (CH_3**C**=O), 173.8 (C-1''), 103.4 (C-1'), 100.9 (C-1), 99.6 (C-2''), 82.3 (C-5'), 75.6 (C-3'), 75.3 (C-7''), 75.1 (C-4), 72.8 (C-6''), 71.8 (C-2), 69.0 (C-2'), 68.6 (C-4'), 68.3 (C-4''), 68.0 (C-3), 67.9 (**C**H_2O-Linker), 67.2 (C-8''), 62.4 (C-6), 61.0 (C-6'), 60.6 (C-9''), 54.4 (C-

5), 51.6 (C-5''), 39.7 (C-3''), 37.6 (**C**H_2N-Linker), 26.6 (**C**H_2-Linker), 22.2 (**C**H_3C=O), 22.0 (**C**H_3C=O); HRMS (ESI): *m*/*z* calcd for $C_{28}H_{50}N_3O_{19}$ [M+H^+]: 732.3046, found: 732.3044.

3-Aminopropyl (methyl 3,5-dideoxy-5-acetamido-D-glycero-α-D-galacto-2-nonulo-pyranosonate-(2→3))-β-D-galactopyranosyl-(1→3)-[α-L-fucopyranosyl-(1→4)]-2-deoxy-2-acetamido-β-D-glucopyranoside (1)



To a solution of trisaccharide **31** (73 mg, 0.1 mmol) and GDP-Fuc (76 mg, 0.12 mmol) in Tris buffer solution (1.0 mL, 100 mM, pH 7.5) containing $MnCl_2$ (5 mM) and BSA (1% total volume, stock solution = 10 mg/mL) was added calf intestinal alkaline phosphatase (CIAP, 1% total volume, 1000 U/mL) and FUT3 (50 μg). The reaction mixture was incubated at 37 °C. Reaction progress was monitored by ESI-MS, if starting material remained after 18 h, another portion of FUT3 (30 μg) and GDP-Fuc (23 mg, 0.036 mmol) were added until no starting material could be detected. The reaction mixture was centrifuged, and the resulting supernatant was loaded on a DEAE (GE Healthcare Life Science, #17070910) anion exchange column (eluent: H_2O). Product containing fractions were combined and lyophilized to afford a crude product, which was further purified by size-exclusion chromatography using a Bio-Gel P4 column (eluent: 0.1 M NH_4HCO_3) to provide sLe^a tetrasaccharide **1** as a white amorphous solid (71 mg, 81 μmol, 81%).

4. References

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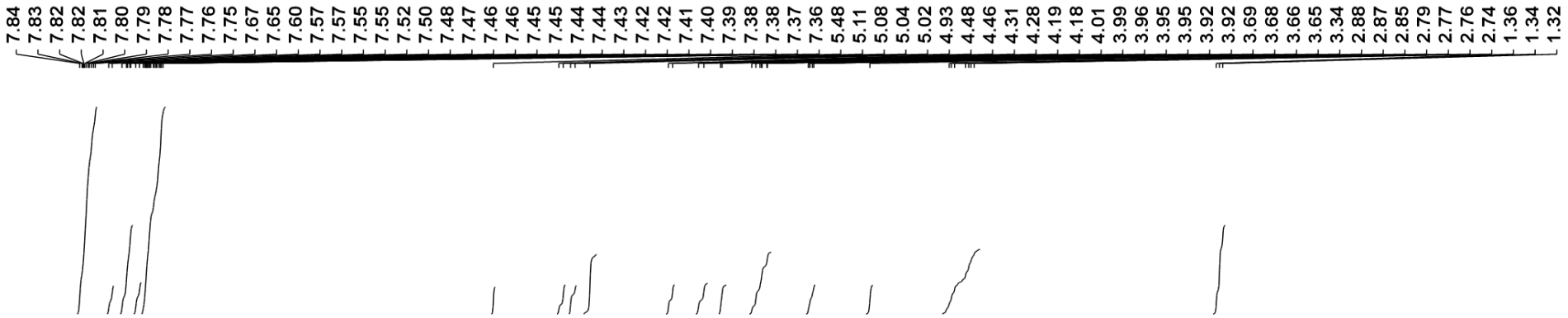
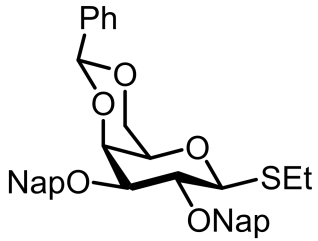
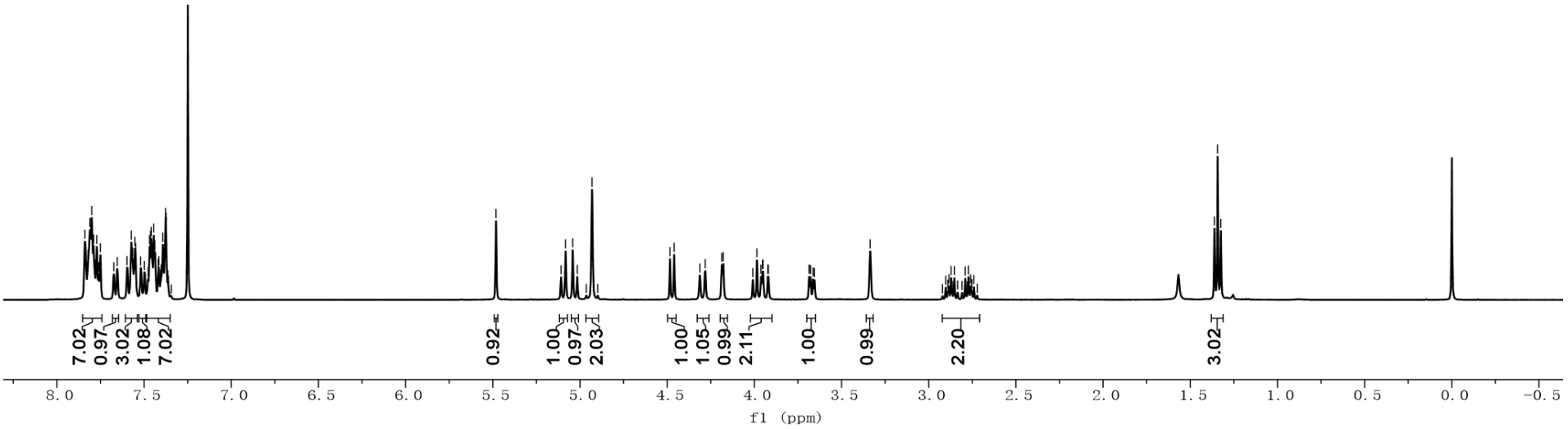
5. NMR Spectra of Products

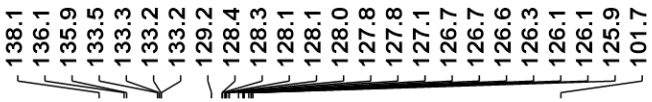


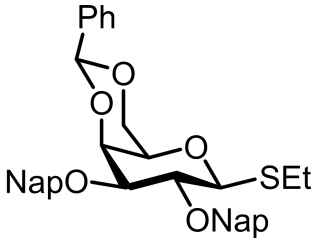


S2

400 MHz, ^{1}H-NMR, $CDCl_3$

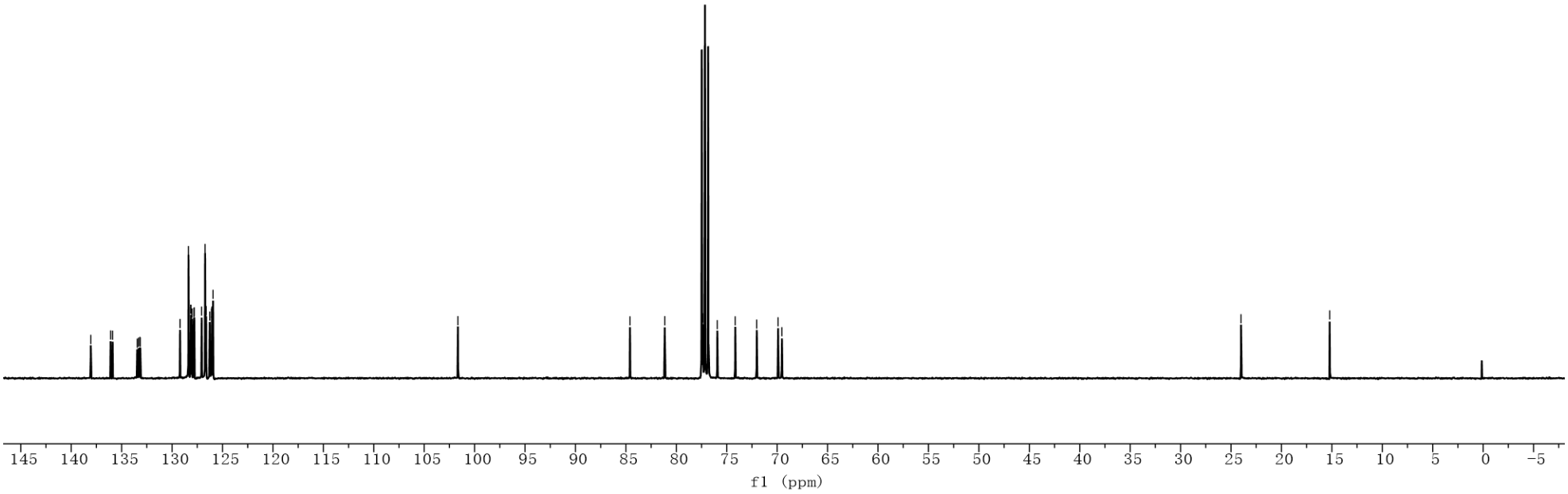


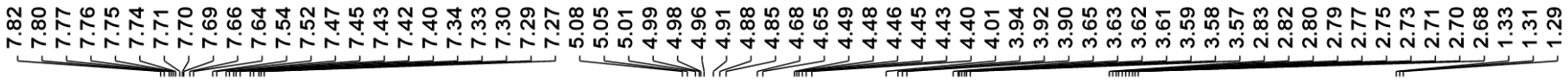


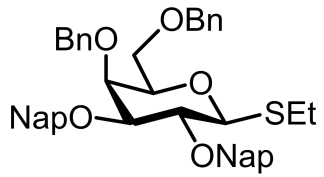


S2

100 MHz, ^{13}C-NMR, $CDCl_3$

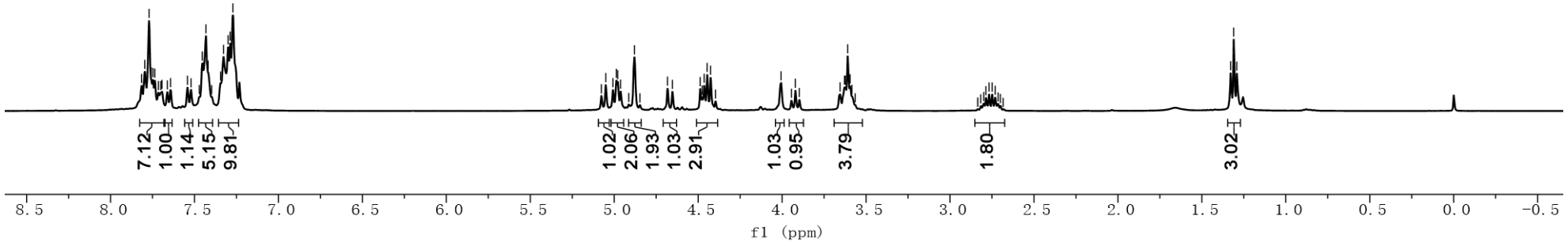


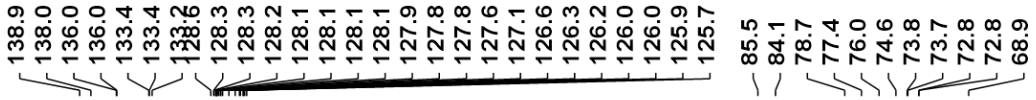


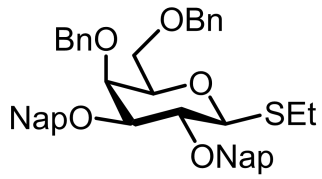


S3

400 MHz, ^{1}H-NMR, $CDCl_3$

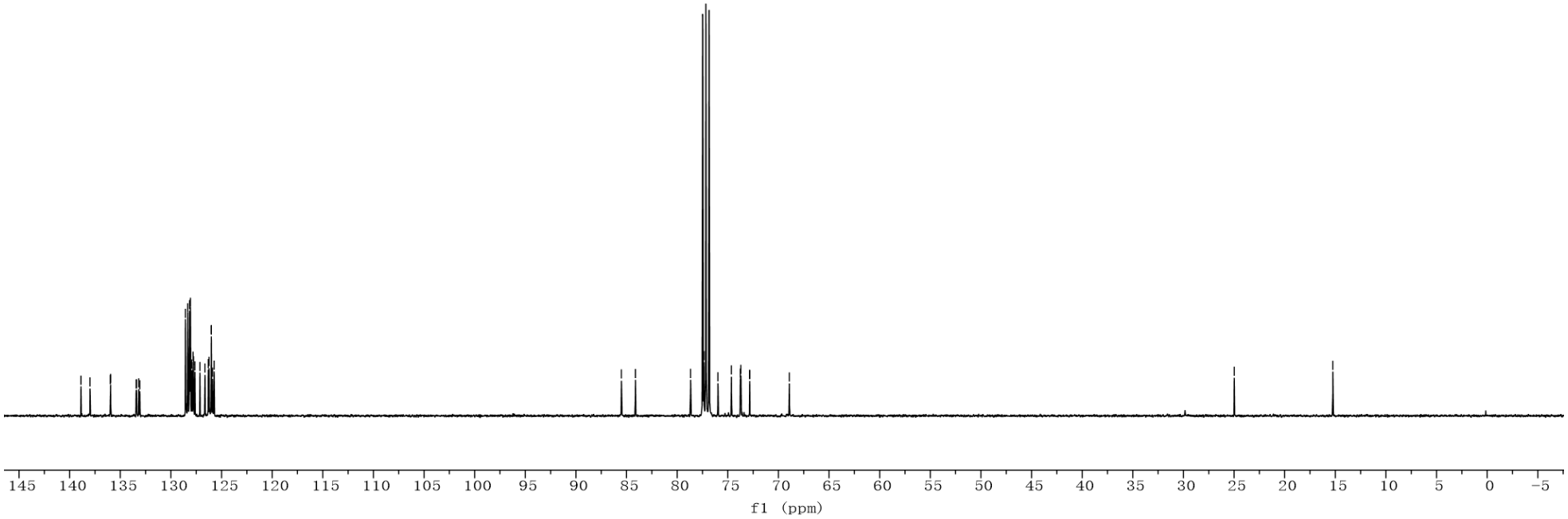


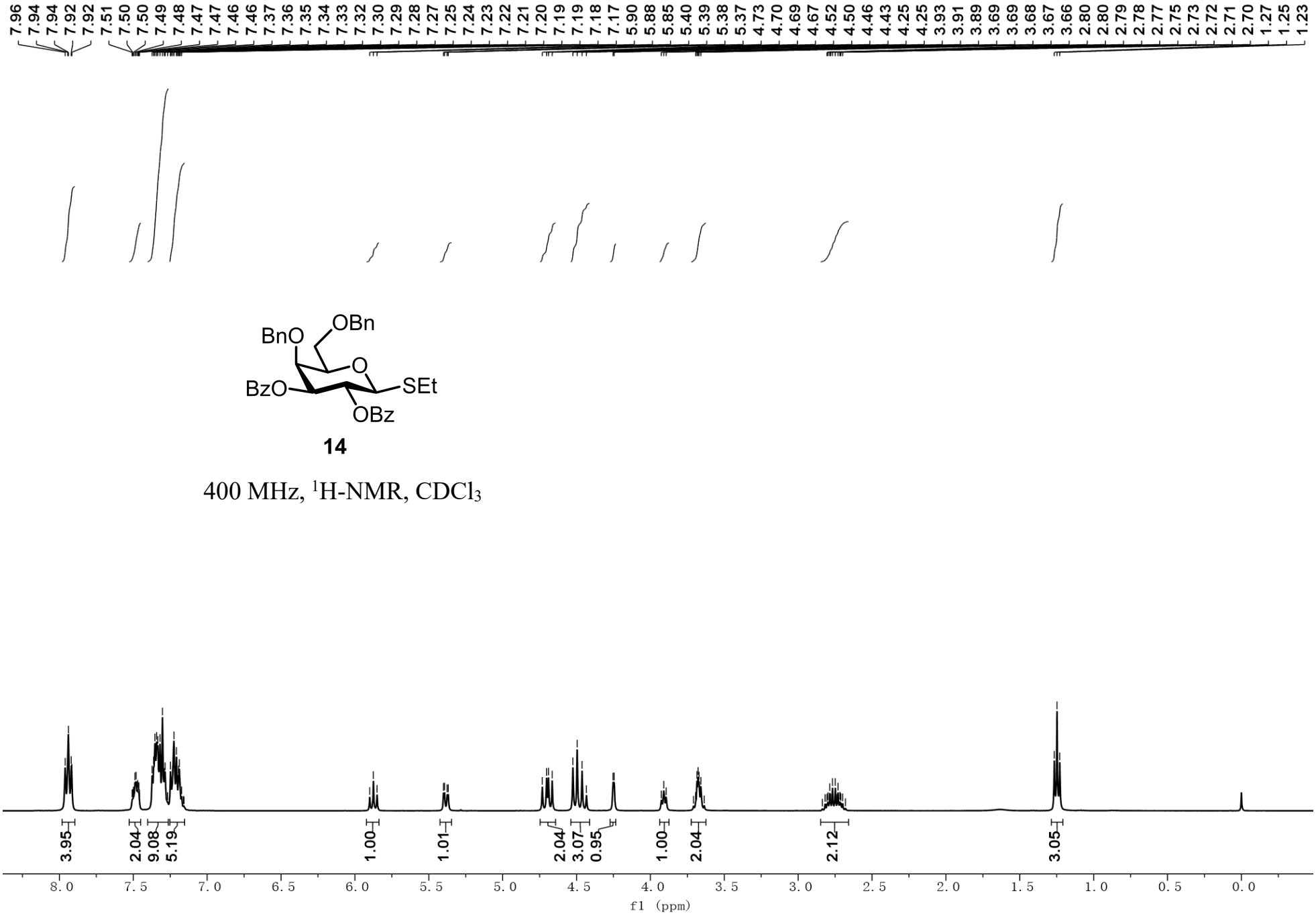


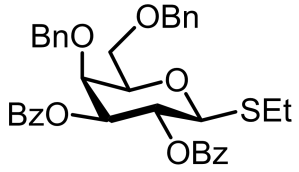


S3

100 MHz, ^{13}C-NMR, $CDCl_3$

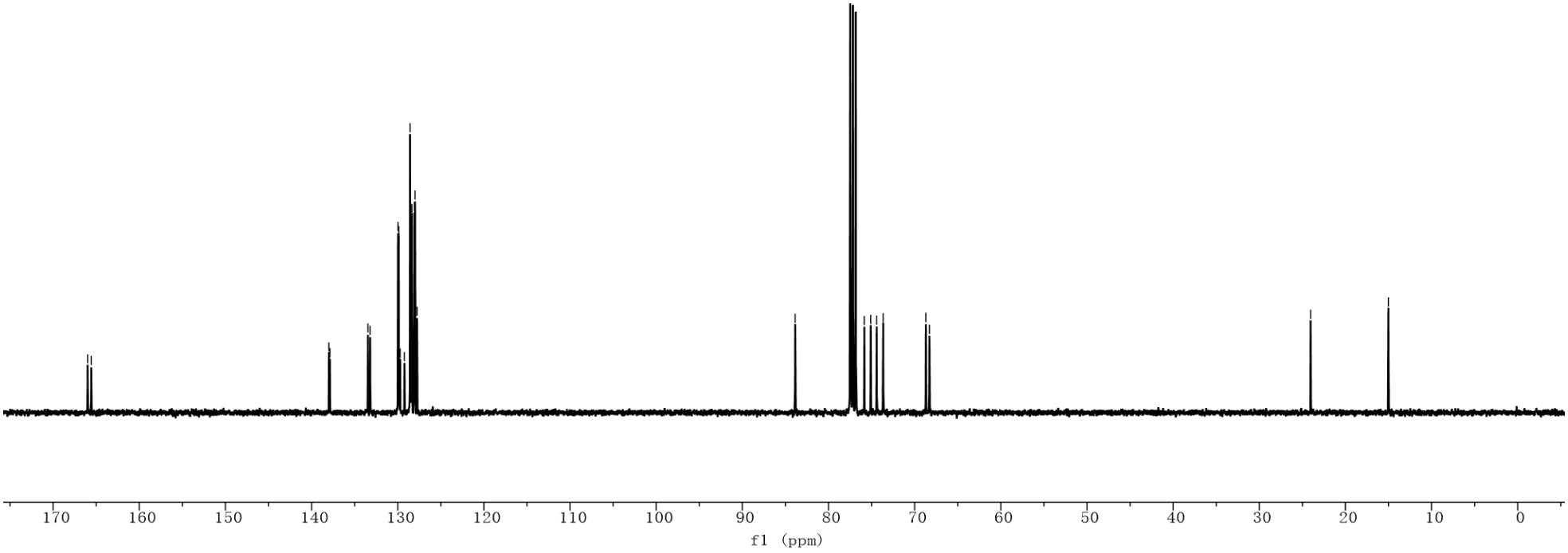


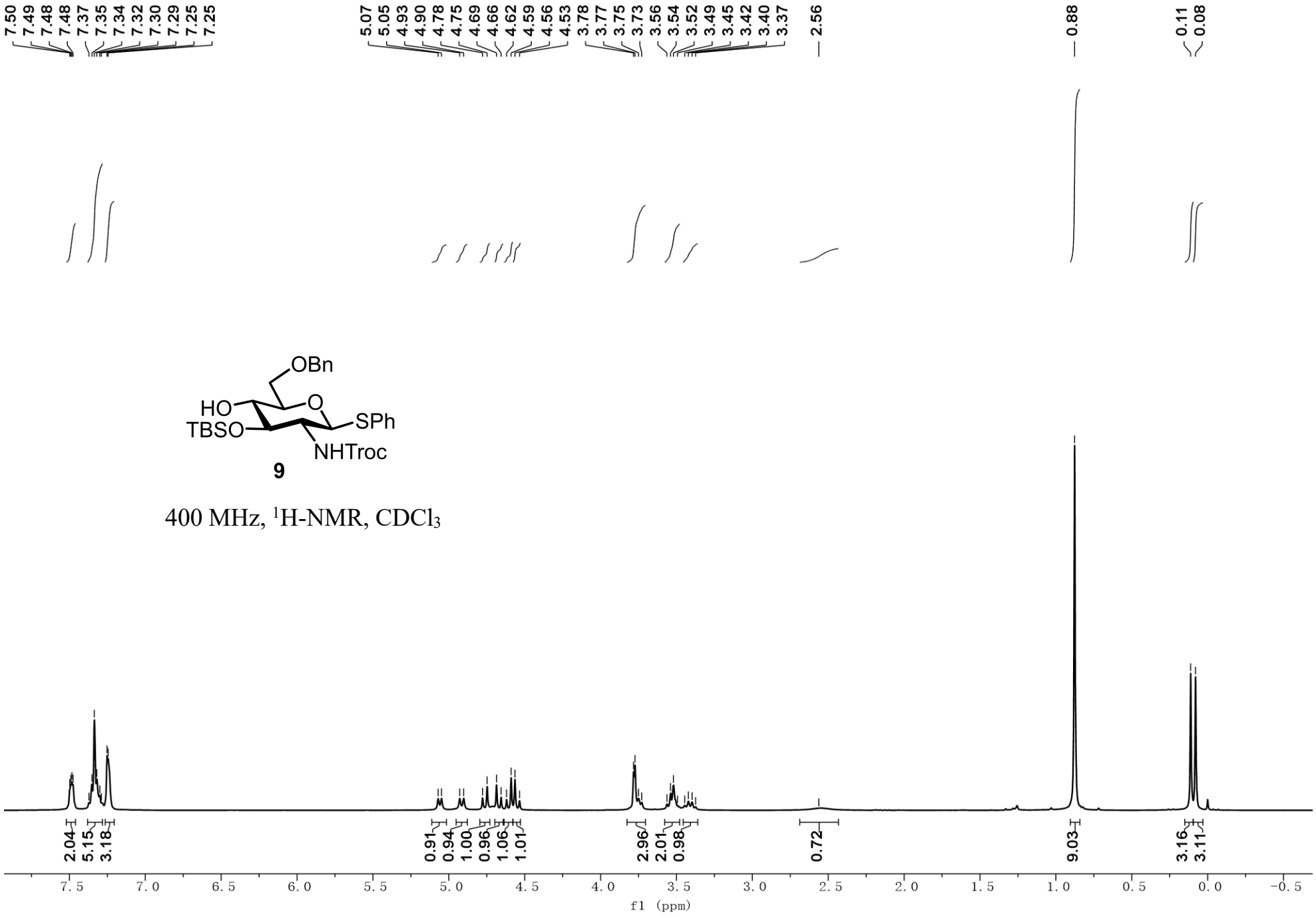

7.96 7.94 7.94 7.92 7.92 7.51 7.50 7.50 7.49 7.48 7.47 7.47 7.46 7.46 7.37 7.36 7.35 7.34 7.33 7.32 7.30 7.29 7.28 7.27 7.25 7.24 7.23 7.22 7.21 7.20 7.19 7.19 7.18 7.17 5.90 5.88 5.85 5.40 5.39 5.38 5.37 4.73 4.70 4.69 4.67 4.52 4.50 4.46 4.43 4.25 4.25 3.93 3.91 3.89 3.69 3.69 3.68 3.67 3.66 2.80 2.80 2.79 2.78 2.77 2.75 2.73 2.72 2.71 2.70 1.27 1.25 1.23
BnO
OBn
O
BzO
SEt
OBz
14
400 MHz, ^{1}H-NMR, $CDCl_3$
3.95 2.04 9.08 5.19 1.00 1.01 2.04 3.07 0.95 1.00 2.04 2.12 3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

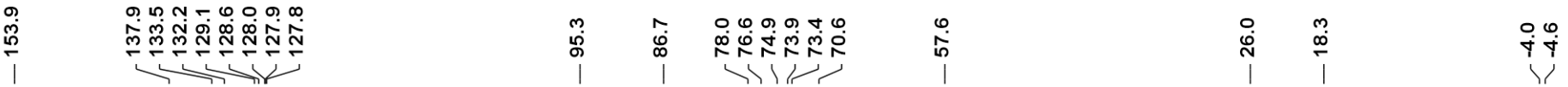


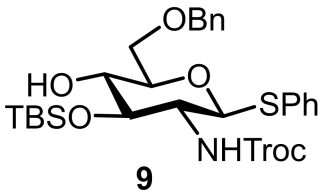
14

100 MHz, ^{13}C-NMR, $CDCl_3$



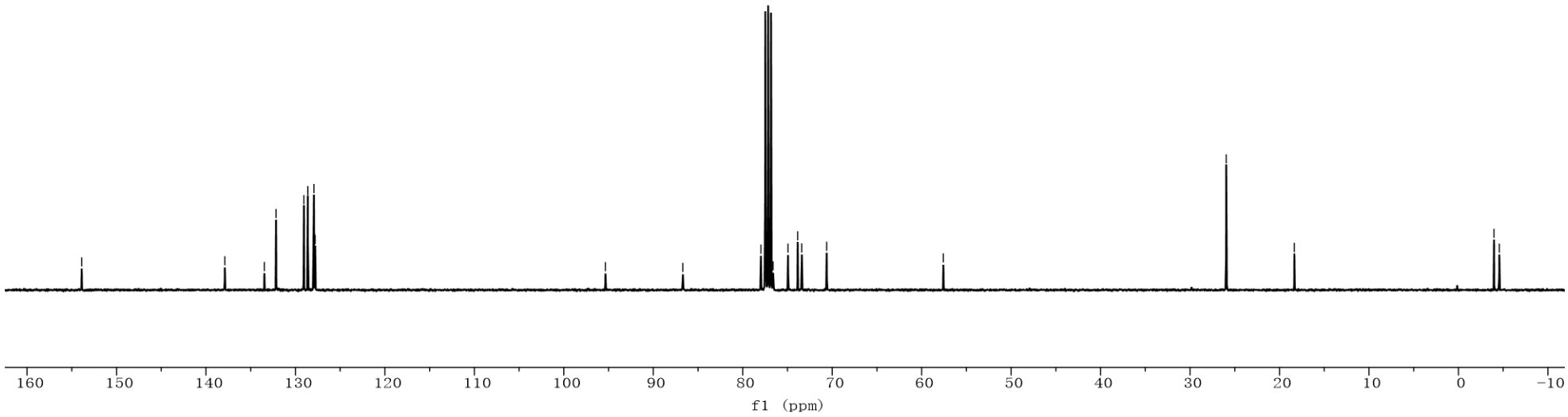

7.50
7.49
7.48
7.48
7.37
7.35
7.34
7.32
7.30
7.29
7.25
7.25
5.07
5.05
4.93
4.90
4.78
4.75
4.69
4.66
4.62
4.59
4.56
4.53
3.78
3.77
3.75
3.73
3.56
3.54
3.52
3.49
3.45
3.42
3.40
3.37
2.56
0.88
0.11
0.08
OBn
HO
O
SPh
TBSO
NHTroc
9
400 MHz, 1H-NMR, CDCl3
2.04
5.15
3.18
0.91
0.94
1.00
0.96
1.06
1.01
2.96
2.01
0.98
0.72
9.03
3.16
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

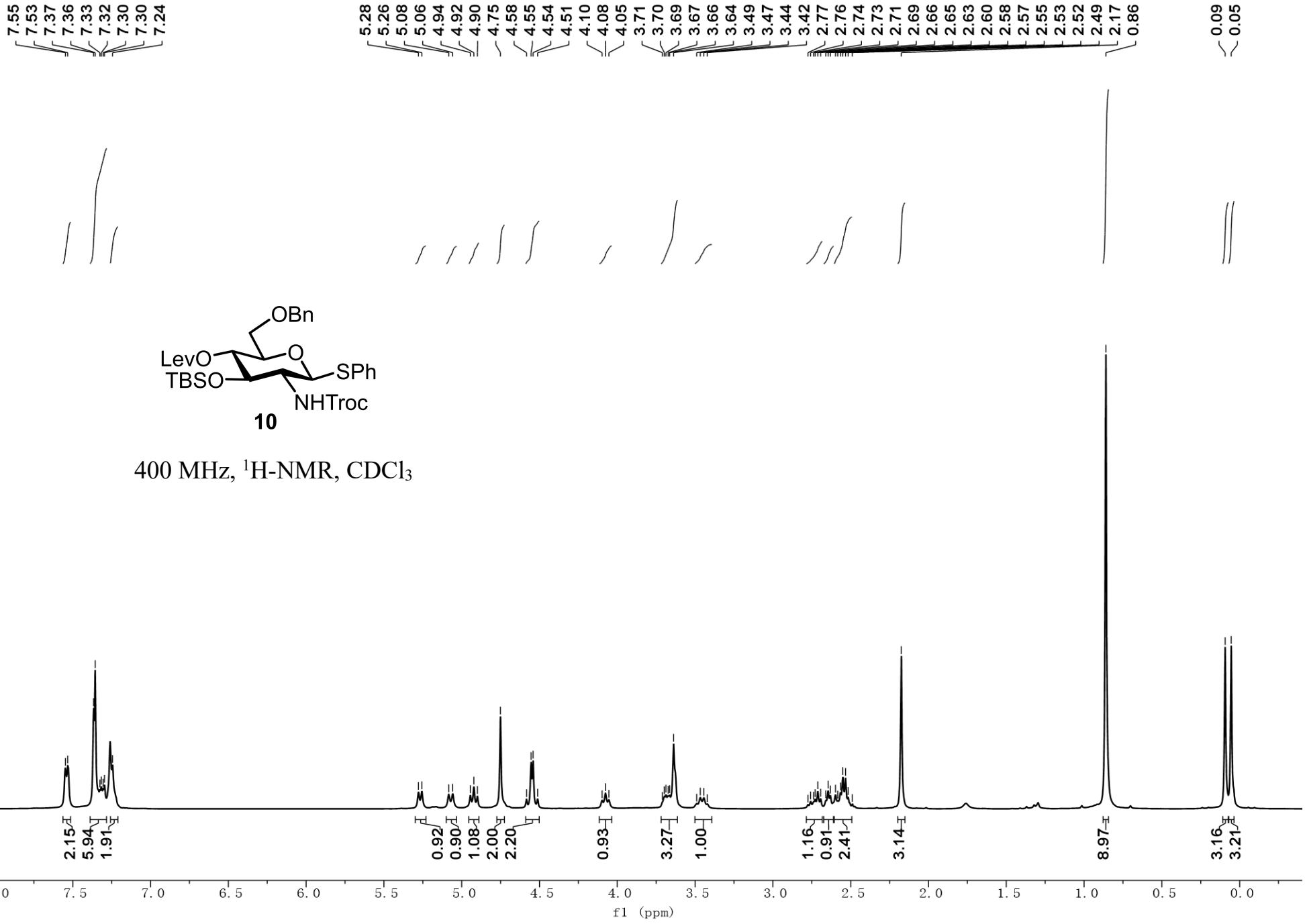




9

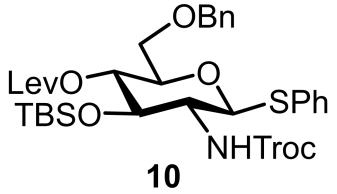
100 MHz, ^{13}C-NMR, $CDCl_3$





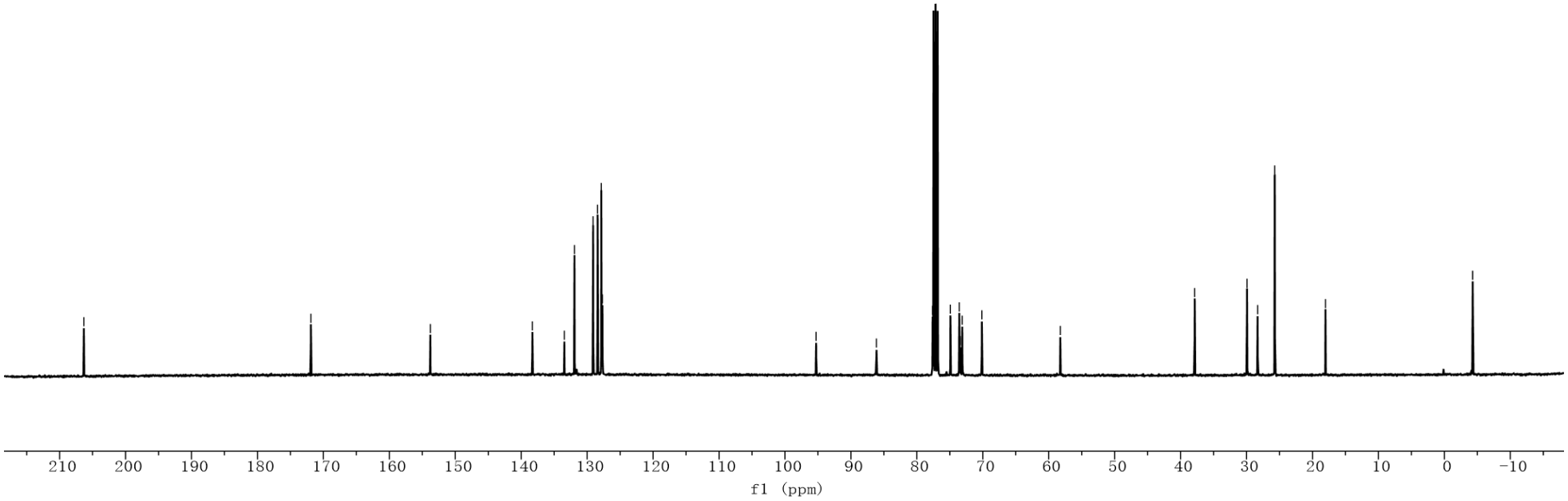
400 MHz, ^{1}H-NMR, $CDCl_3$

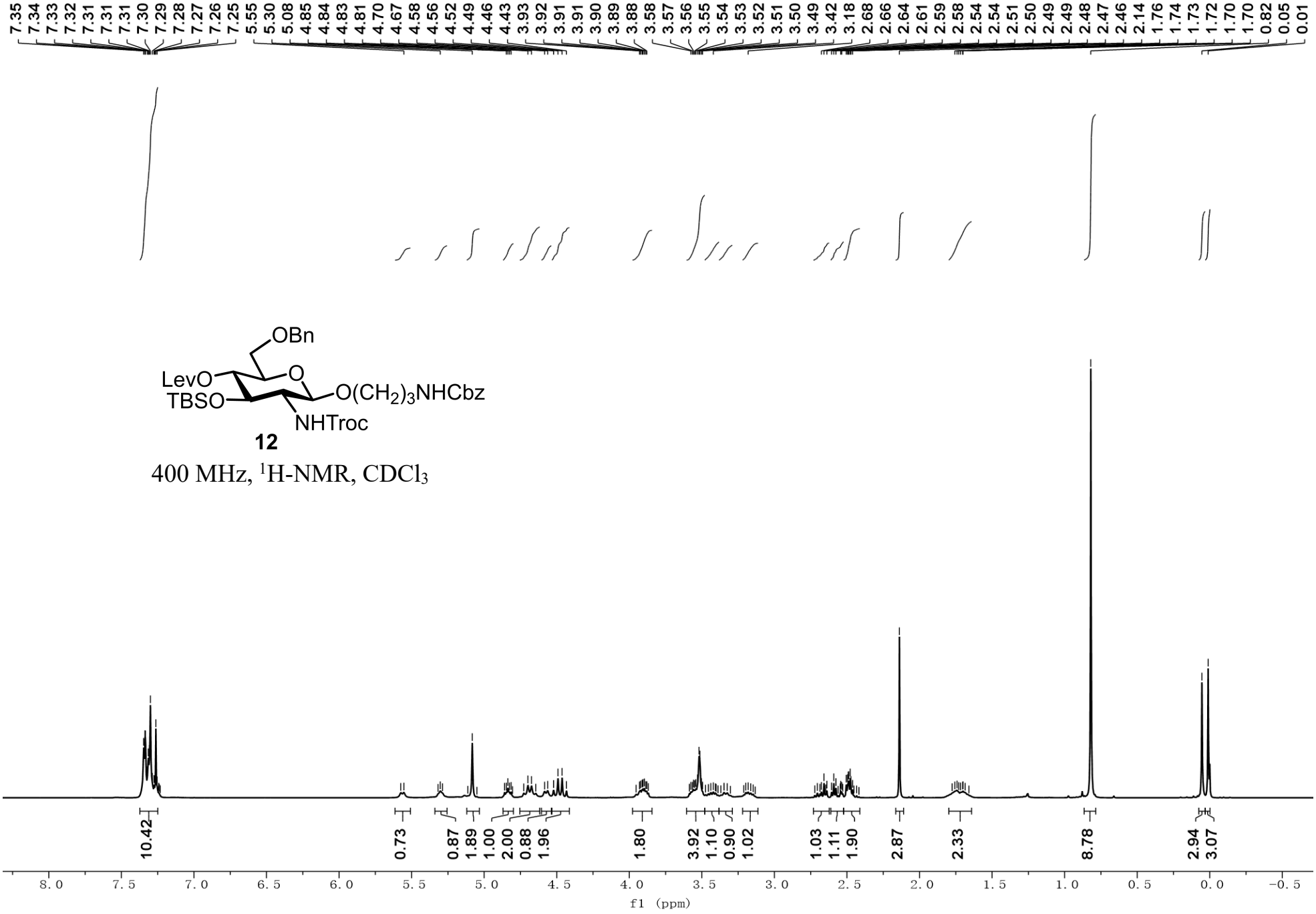
206.3
171.9
153.8
138.3
133.5
131.9
129.1
128.4
127.9
127.8
127.7
95.3
86.1
77.6
74.9
73.6
73.4
73.1
70.1
58.2
37.9
29.9
28.3
25.7
18.0
-4.3
-4.3



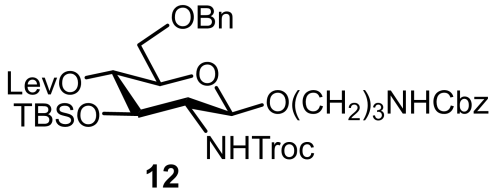
10

100 MHz, ^{13}C-NMR, $CDCl_3$



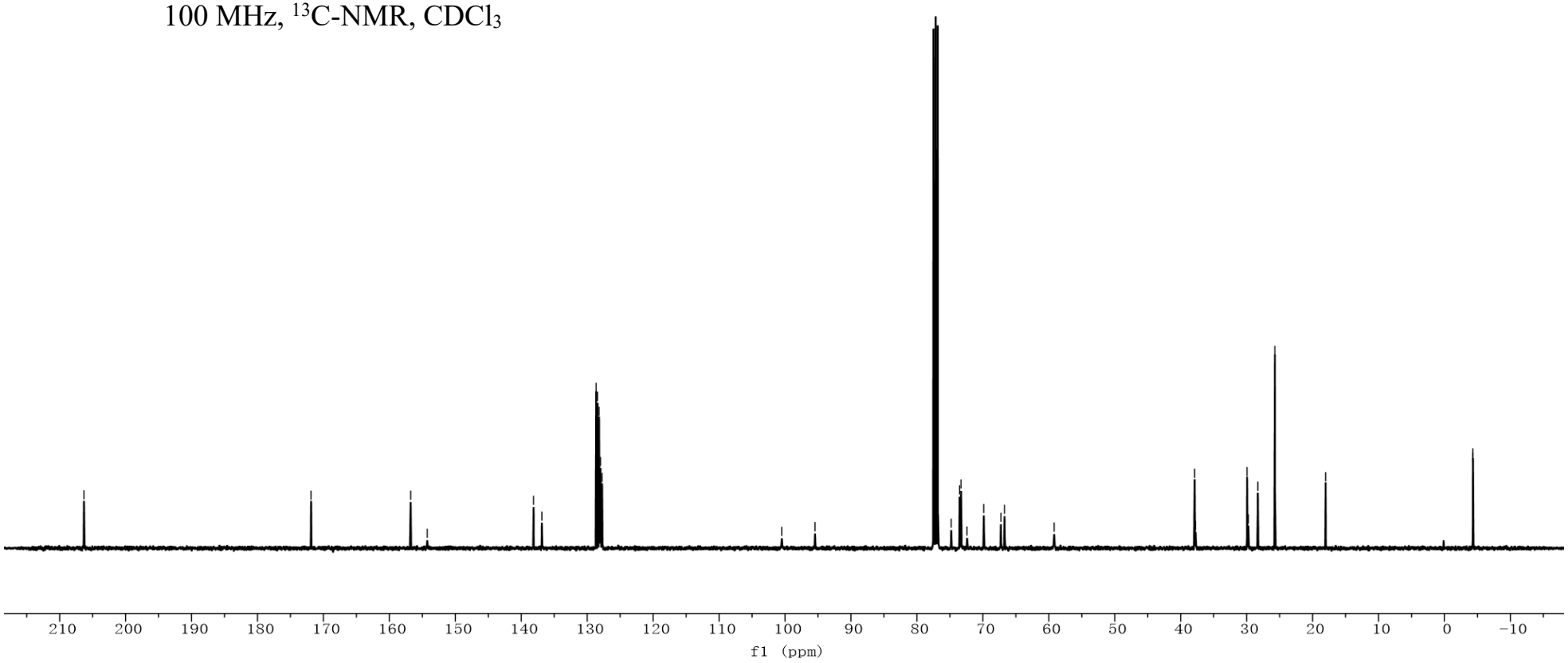

7.35 7.34 7.33 7.32 7.31 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.25
5.55 5.30 5.08 4.85 4.84 4.83 4.81 4.70 4.67 4.58 4.56 4.52 4.49 4.46 4.43 3.93 3.92 3.91 3.91 3.90 3.89 3.88 3.58
3.57 3.56 3.55 3.54 3.53 3.52 3.51 3.50 3.49 3.42 3.18 2.68 2.66 2.64 2.61 2.59 2.58 2.54 2.54 2.51 2.50 2.49 2.49 2.48 2.47 2.46 2.14 1.76 1.74 1.73 1.72 1.70 1.70 0.82 0.05 0.01
OBn
LevO
O
TBSO
O(CH2)3NHCbz
NHTroc
12
400 MHz, 1H-NMR, CDCl3
10.42
0.73
0.87
1.89
1.00
2.00
0.88
1.96
1.80
3.92
1.10
0.90
1.02
1.03
1.11
1.90
2.87
2.33
8.78
2.94
3.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

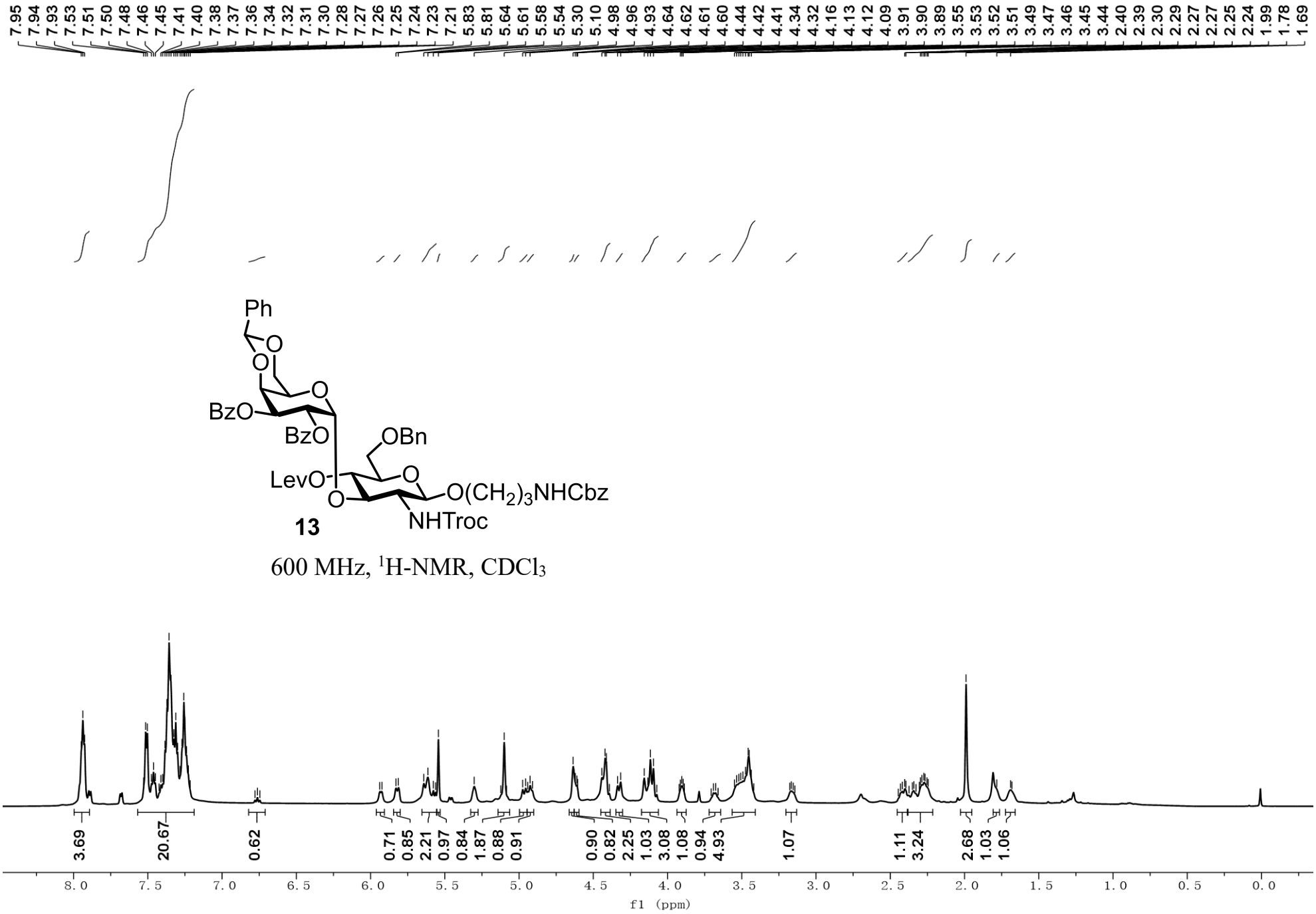
206.3
171.9
156.8
154.3
138.1
136.9
128.6
128.4
128.2
128.0
127.7
100.5
95.5
77.4
74.8
73.5
73.3
72.4
69.9
67.3
66.7
59.2
37.9
37.7
29.9
29.7
28.3
25.7
18.0
-4.3
-4.3



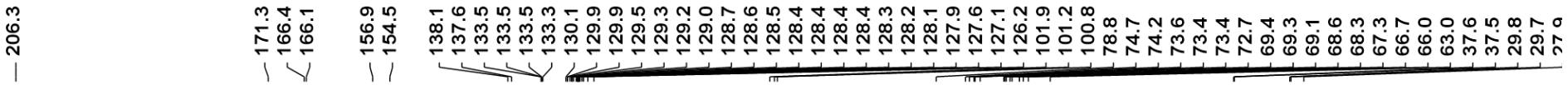
12

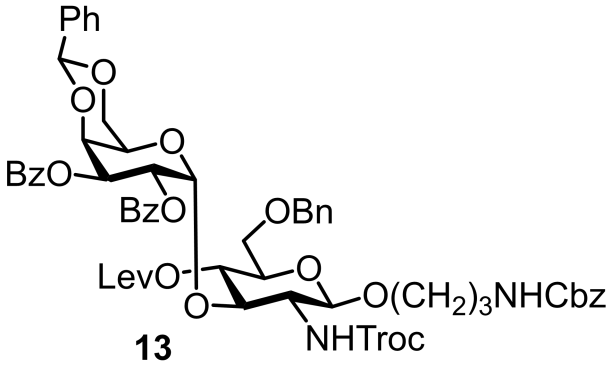
100 MHz, ^{13}C-NMR, $CDCl_3$





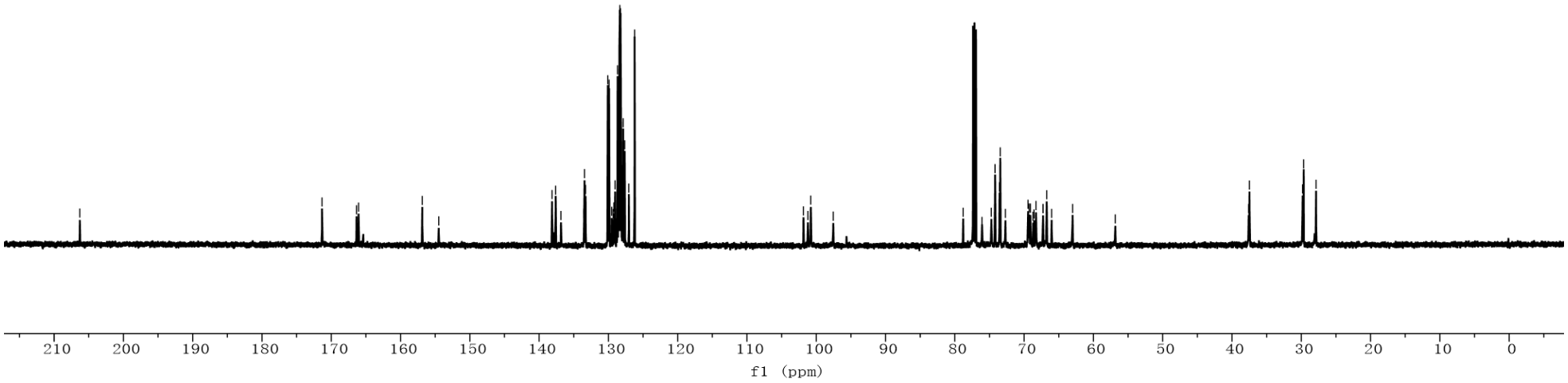
600 MHz, ^{1}H-NMR, $CDCl_3$

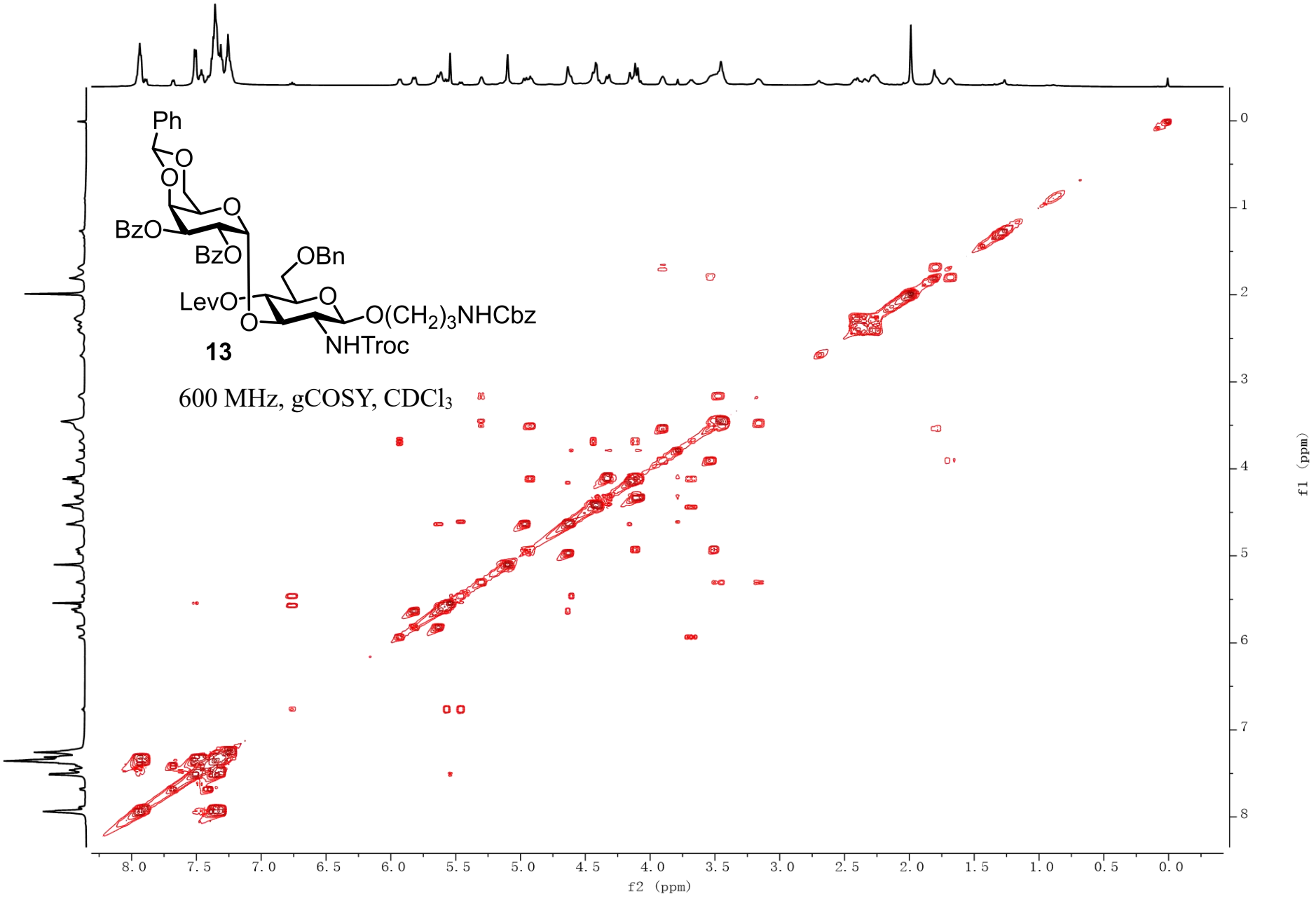


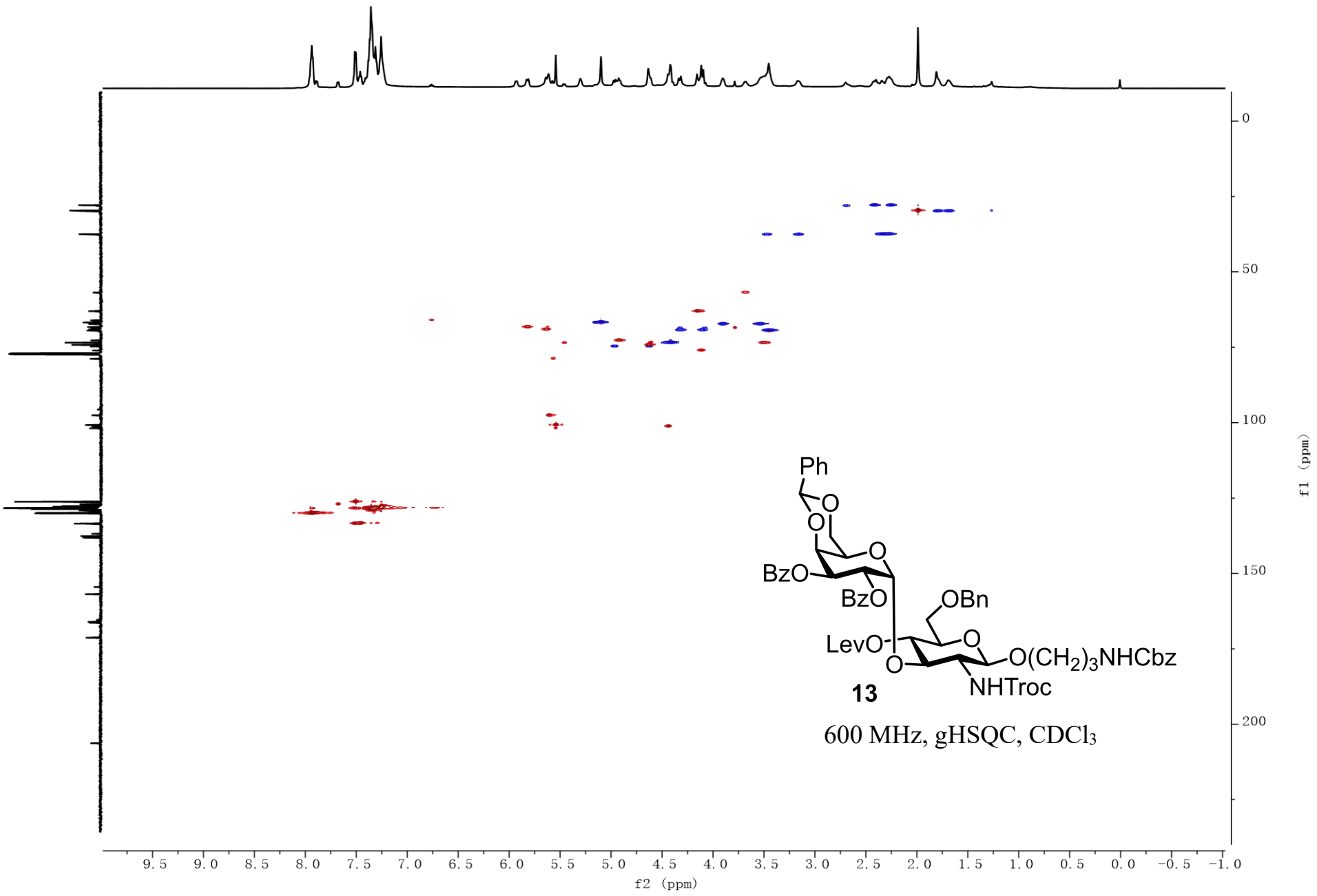


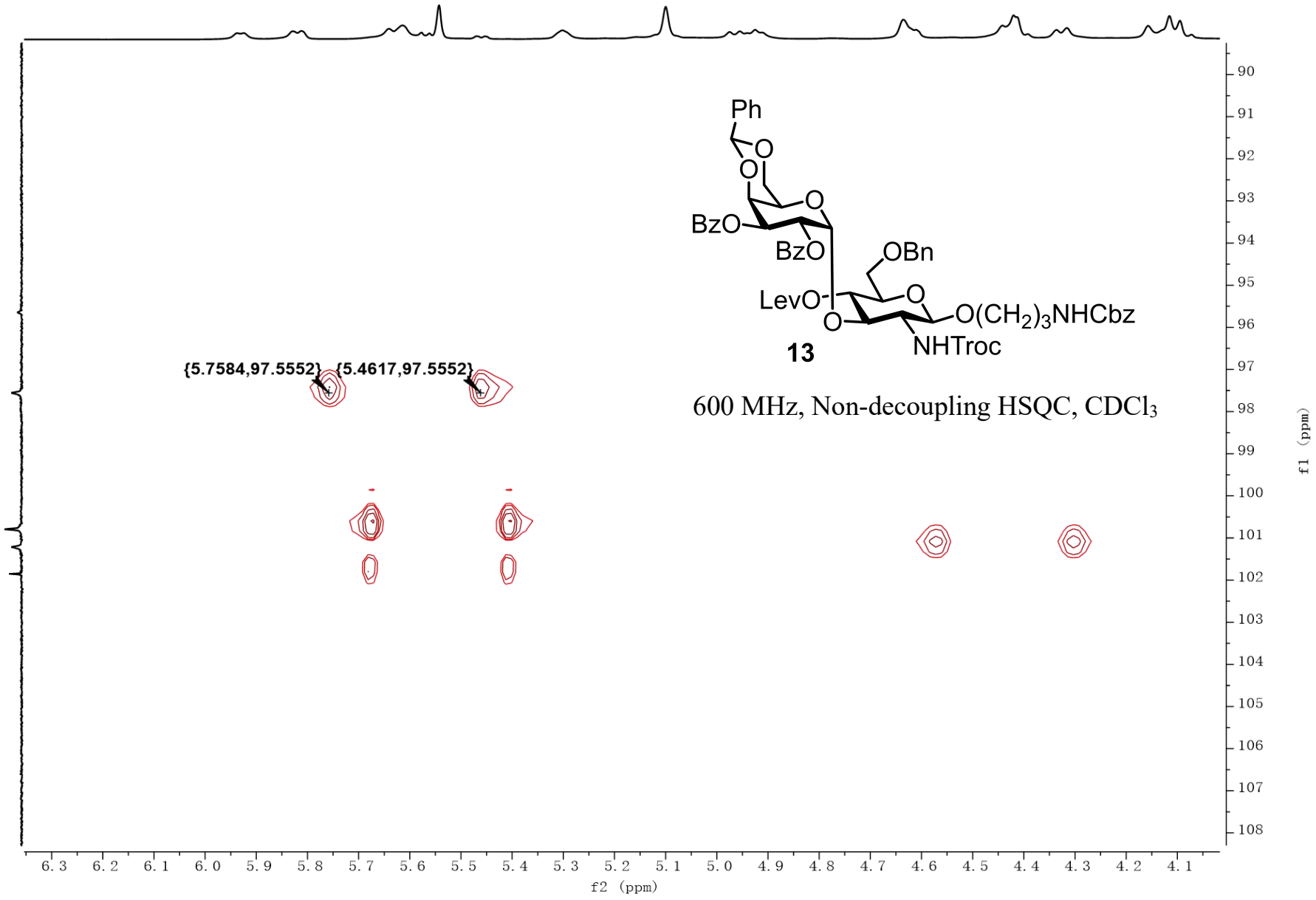
13

150 MHz, ^{13}C-NMR, $CDCl_3$




Ph
O
O
O
BzO
BzO
OBn
LevO
O
O
O(CH2)3NHCbz
NHTroc
13
600 MHz, gCOSY, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


Ph
O
O
O
BzO
BzO
OBn
LevO
O
O
O(CH2)3NHCbz
NHTroc
13
600 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)


{5.7584,97.5552}
{5.4617,97.5552}
Ph
O
O
BzO
O
BzO
OBn
LevO
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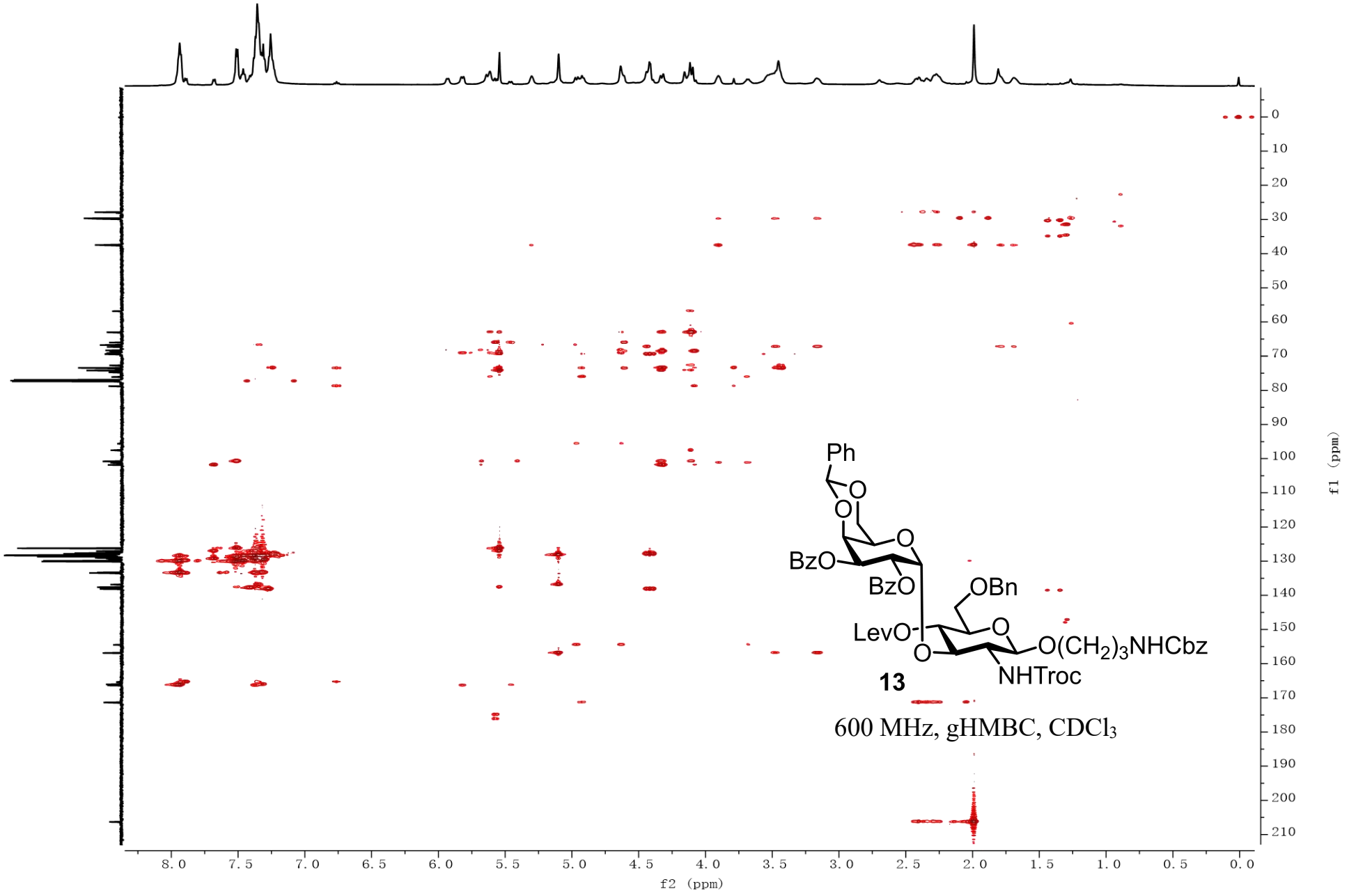
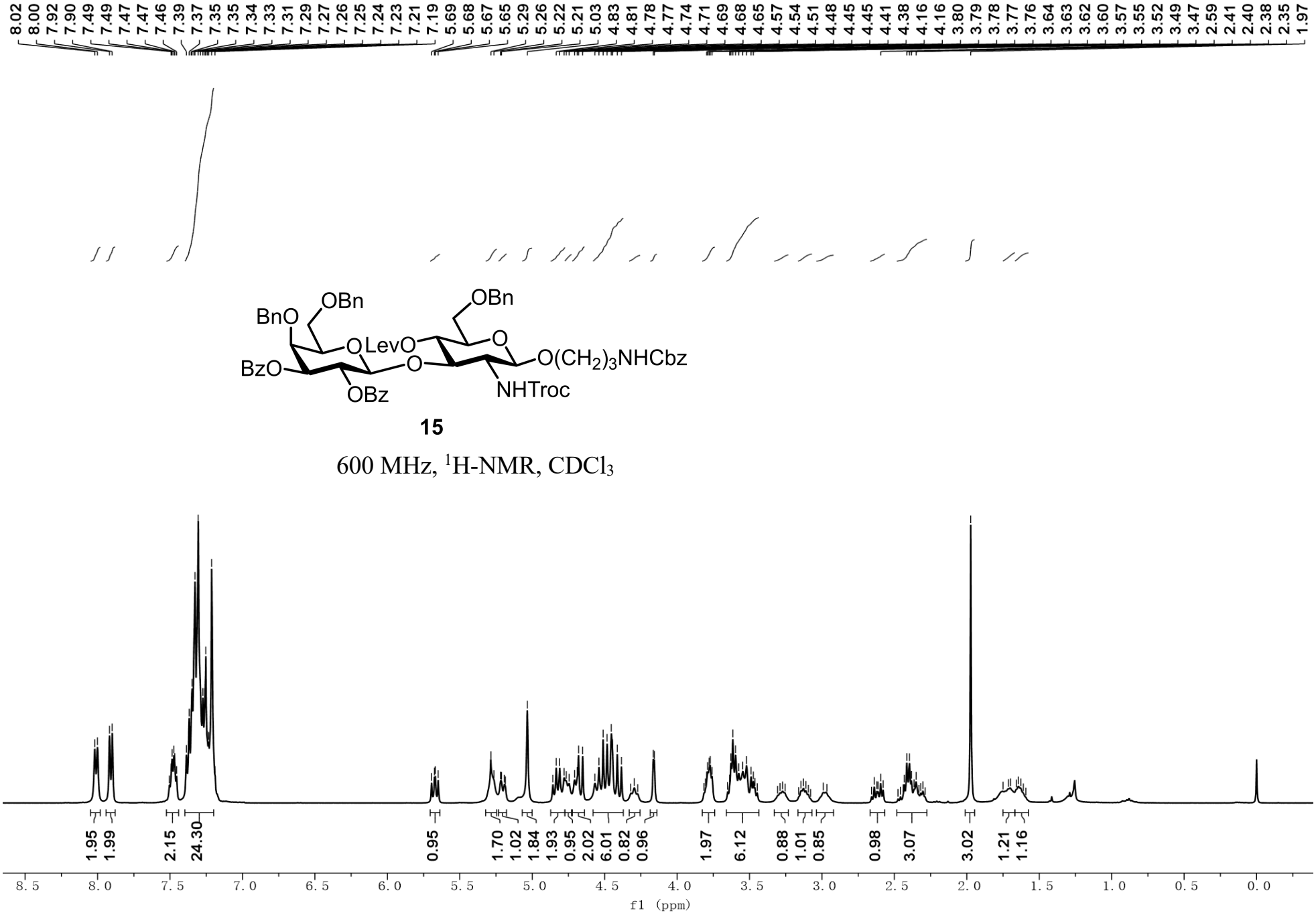
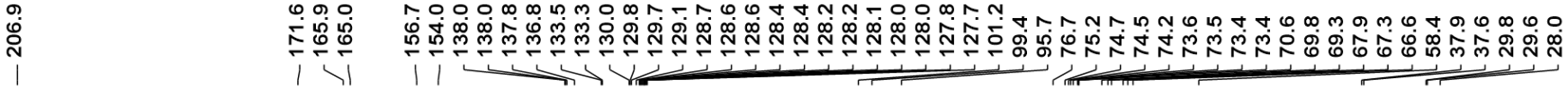
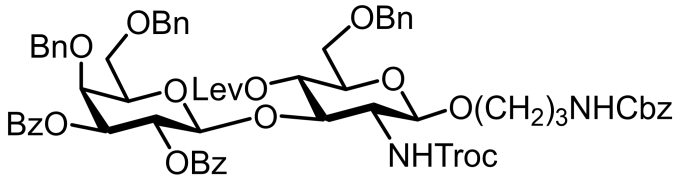
NHTroc
13
600 MHz, Non-decoupling HSQC, CDCl3
f2 (ppm)
f1 (ppm)


Ph
O
O
O
BzO
BzO
OBn
LevO
O
O
O(CH2)3NHCbz
NHTroc
13
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

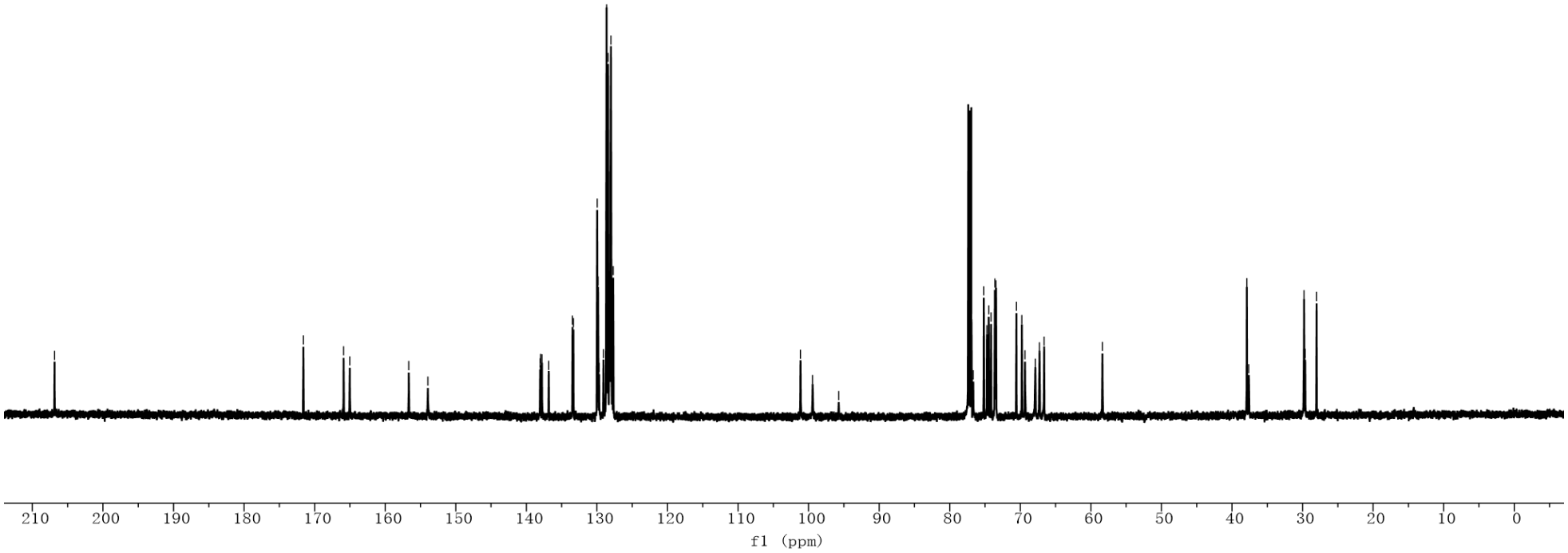

8.02 8.00 7.92 7.90 7.49 7.49 7.47 7.47 7.46 7.39 7.37 7.35 7.35 7.34 7.33 7.31 7.29 7.27 7.26 7.25 7.24 7.23 7.21 7.19 5.69 5.68 5.67 5.65 5.29 5.26 5.22 5.21 5.03 4.83 4.81 4.78 4.77 4.74 4.71 4.69 4.68 4.65 4.57 4.54 4.51 4.48 4.45 4.45 4.41 4.38 4.16 4.16 3.80 3.79 3.78 3.77 3.76 3.64 3.63 3.62 3.60 3.57 3.55 3.52 3.49 3.47 2.59 2.41 2.40 2.38 2.35 1.97
BnO
OBn
OLevO
O
OBn
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
15
600 MHz, 1H-NMR, CDCl3
1.95 1.99 2.15 24.30 0.95 1.70 1.02 1.84 1.93 0.95 2.02 6.01 0.82 0.96 1.97 6.12 0.88 1.01 0.85 0.98 3.07 3.02 1.21 1.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

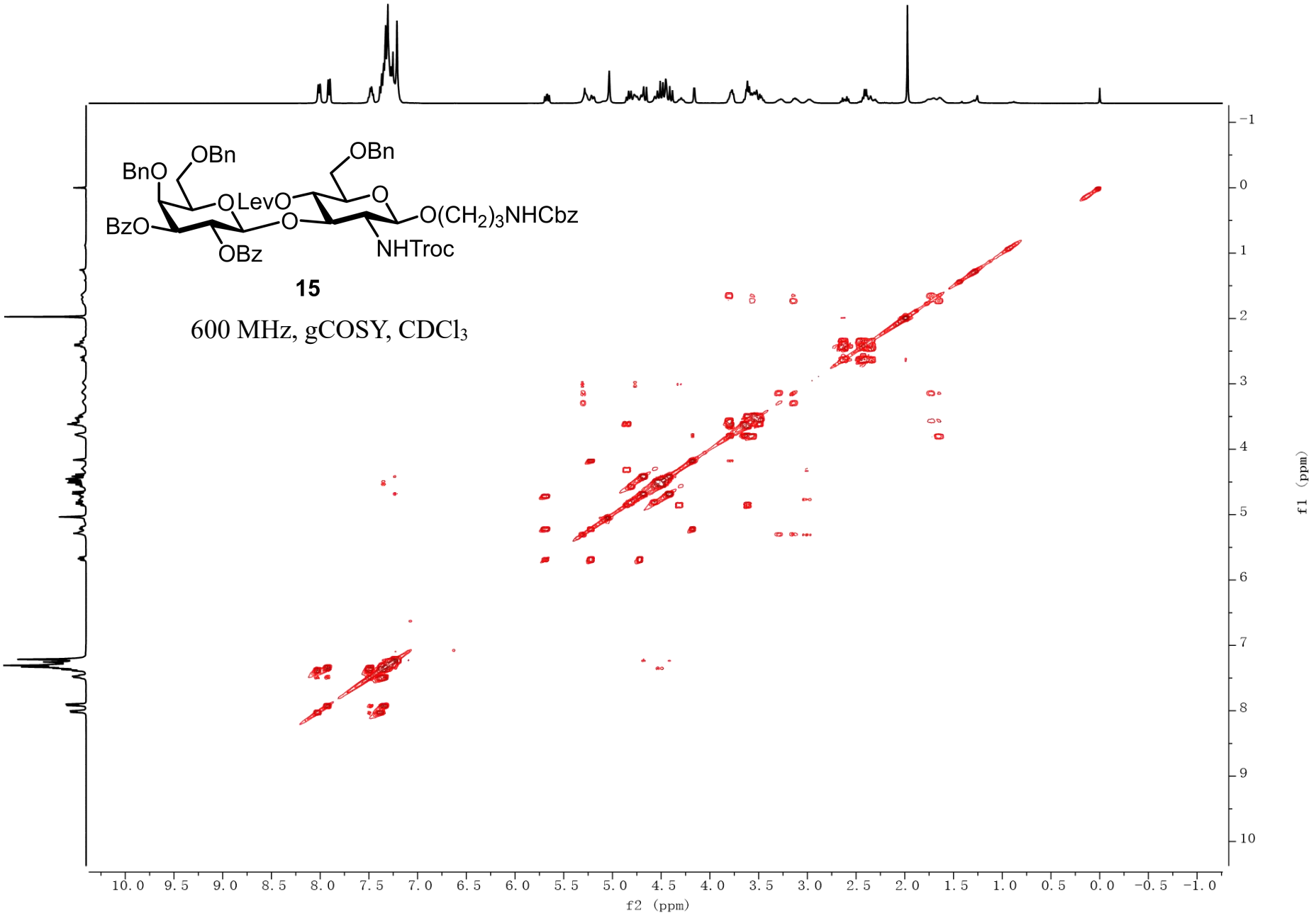


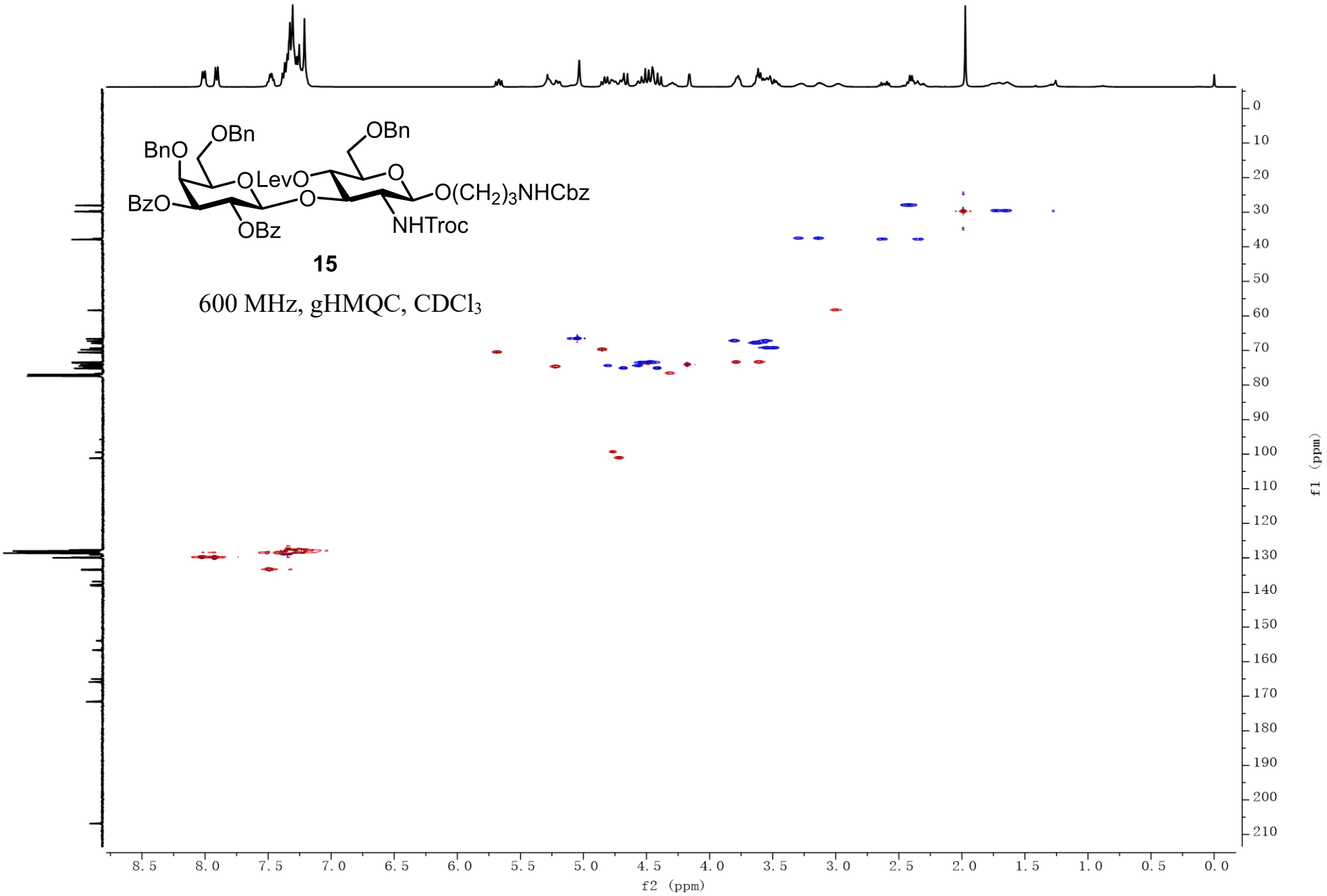


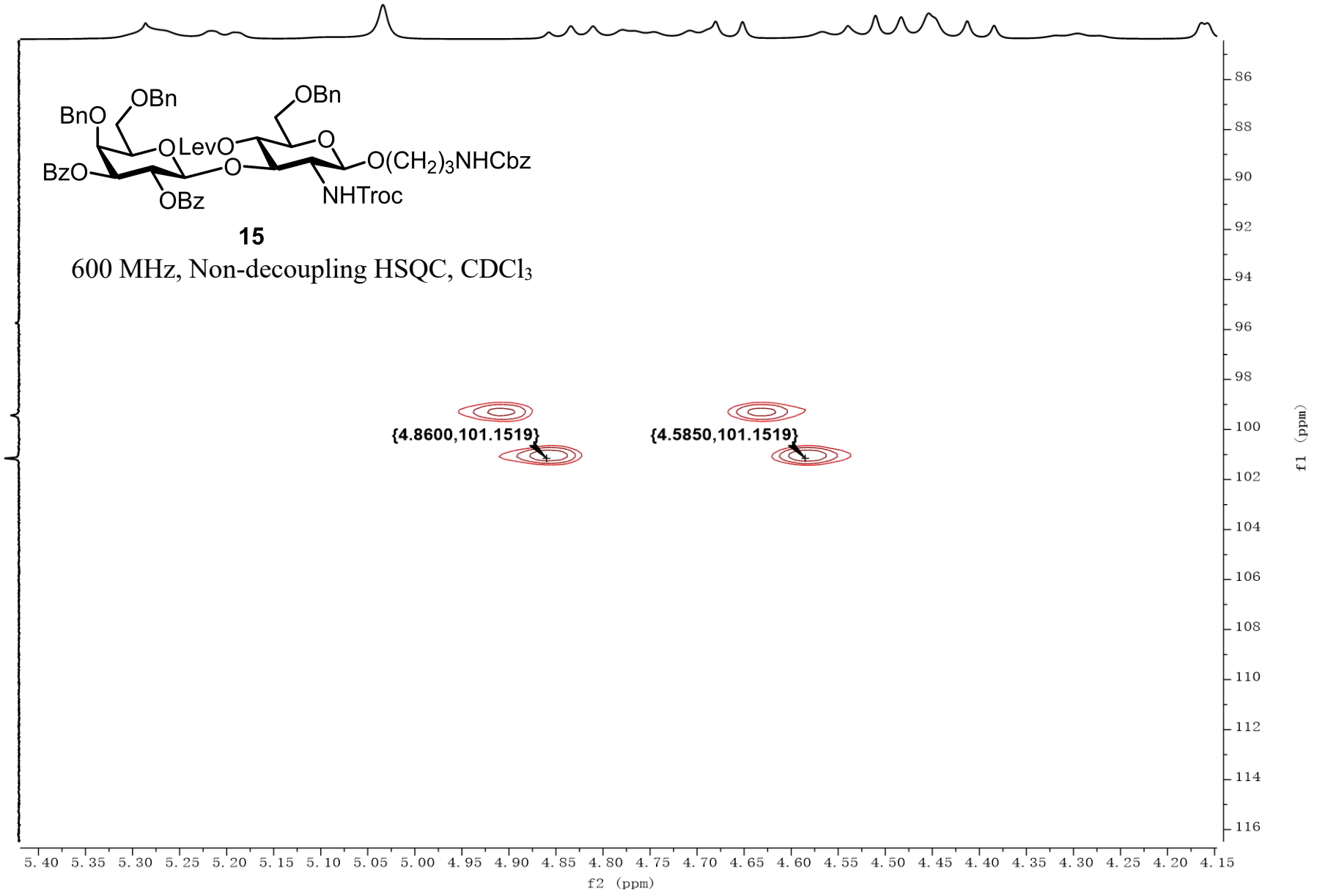
15

150 MHz, ^{13}C-NMR, $CDCl_3$



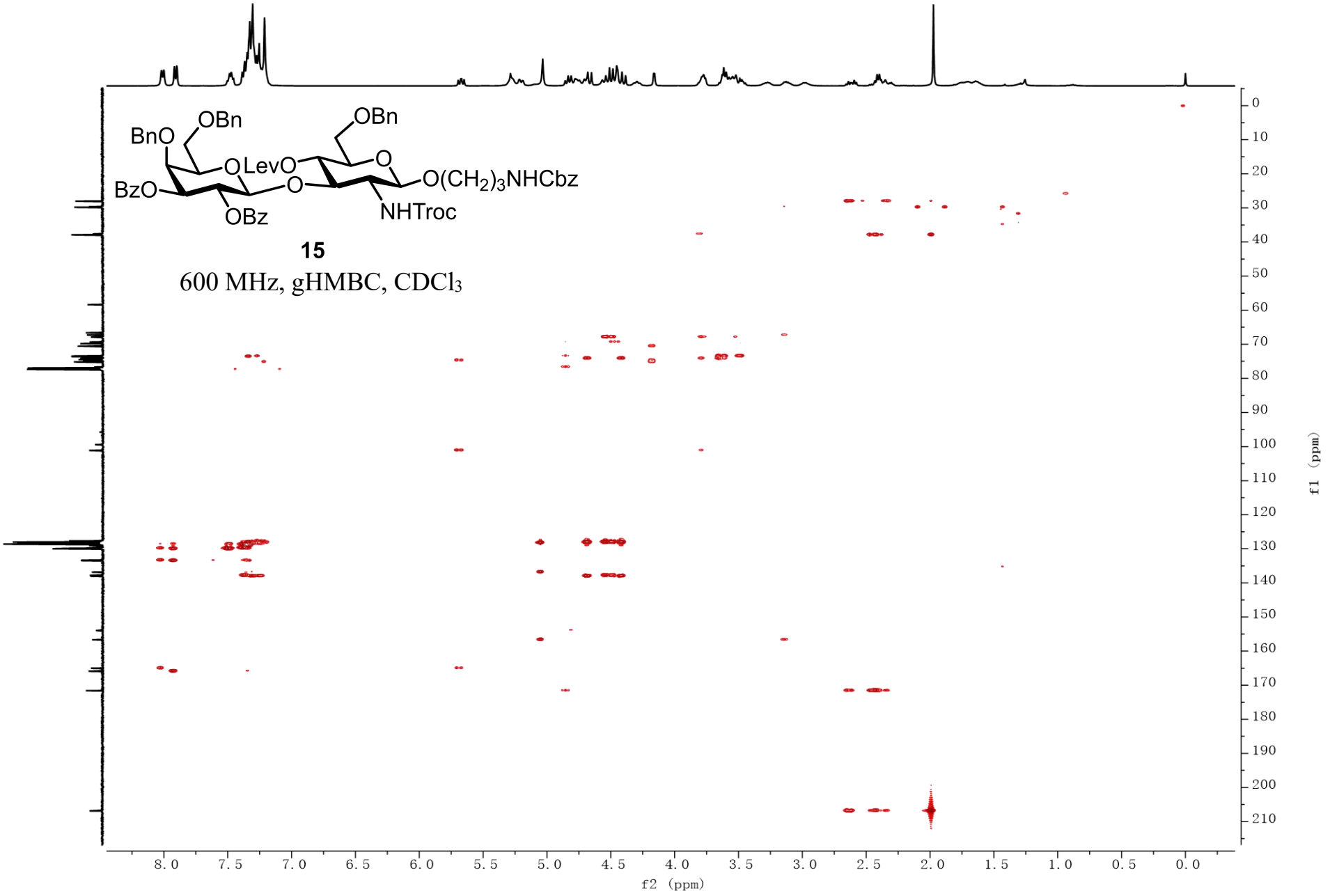

OBn
OBn
BnO
OLevO
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
15
600 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

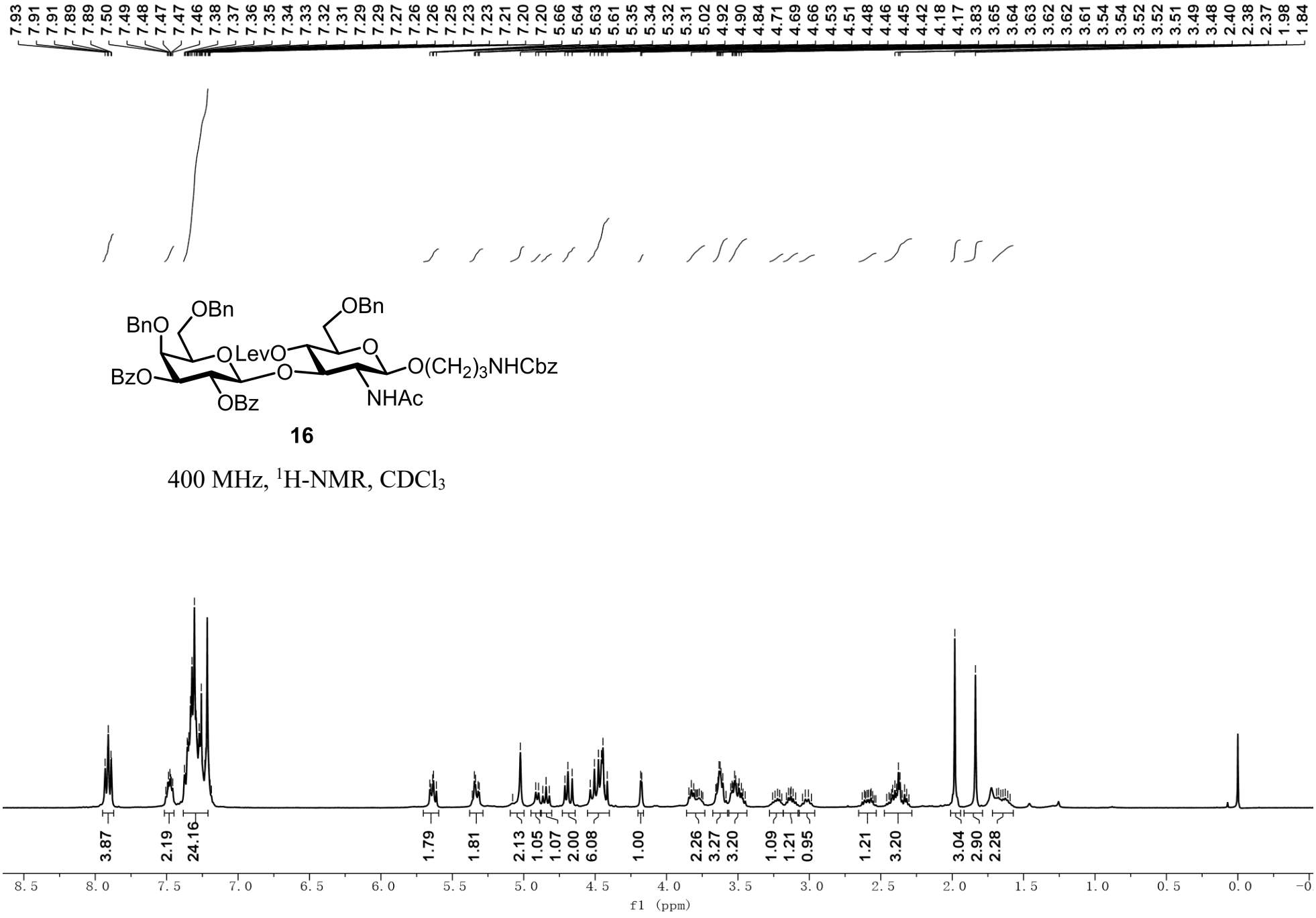

BnO
OBn
OLevO
O
OBn
O
O(CH2)3NHCbz
BzO
OBz
NHTroc
15
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)



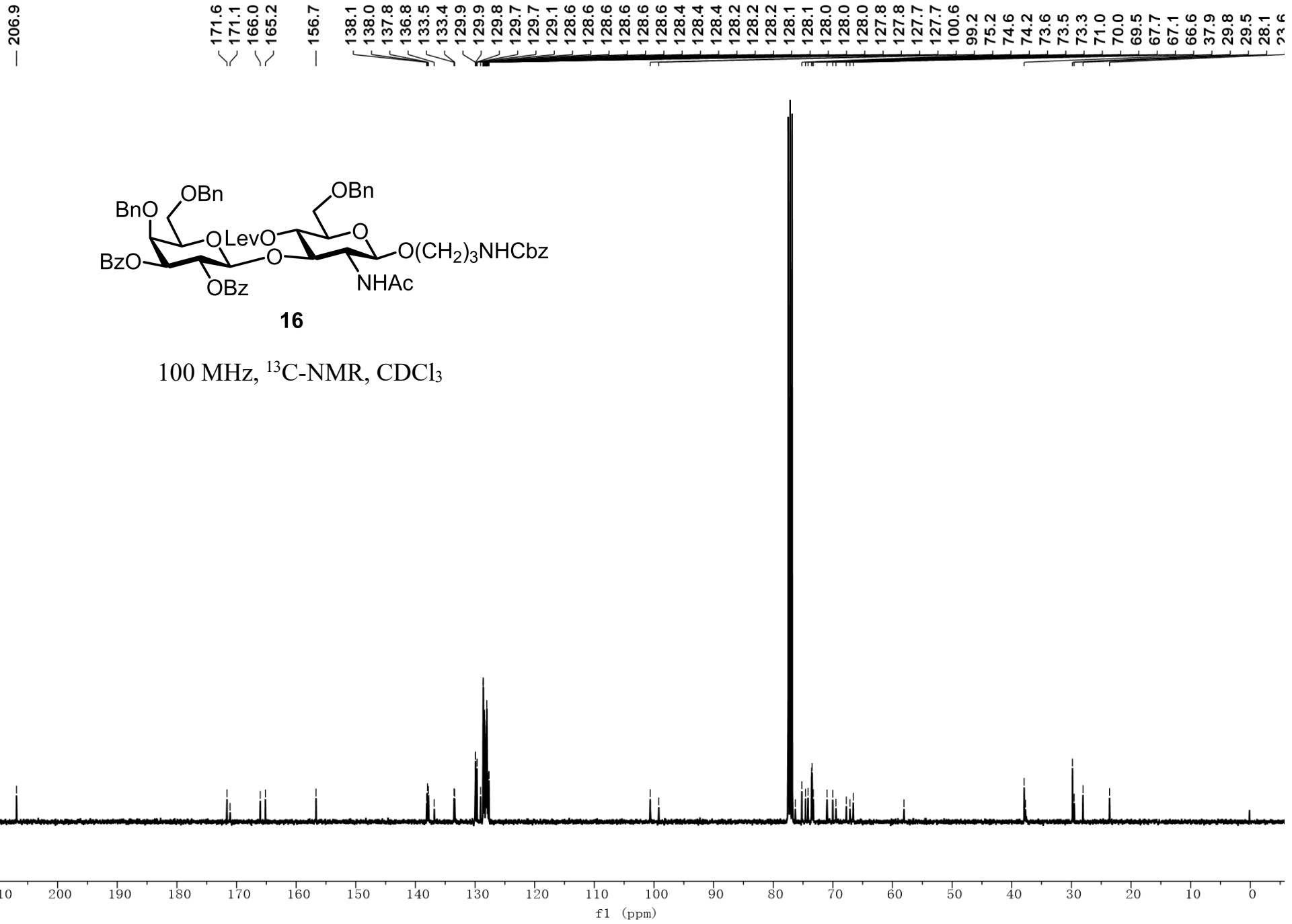
15

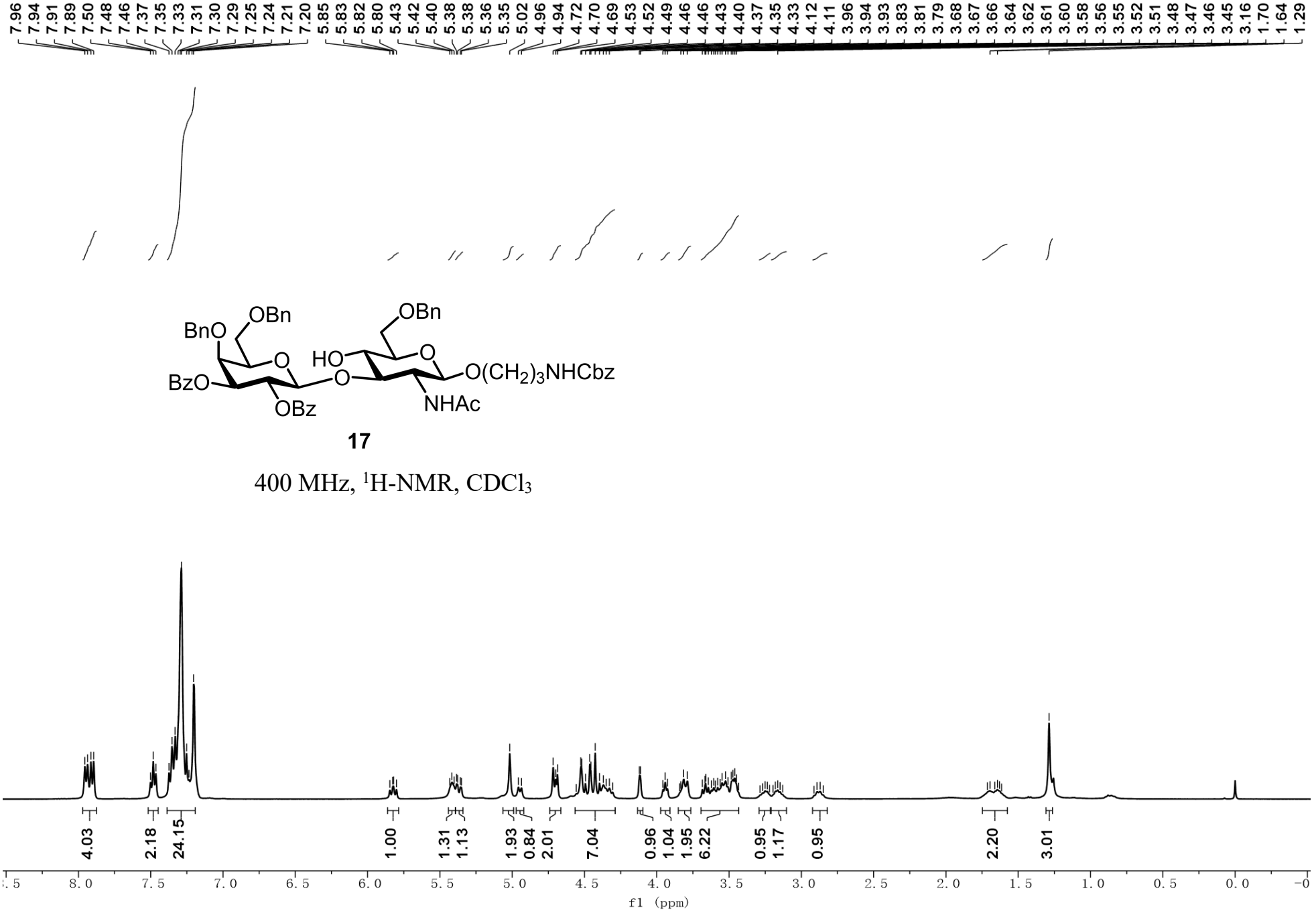
600 MHz, Non-decoupling HSQC, $CDCl_3$


BnO
OBn
OLevO
O
OBn
O
BzO
O(CH2)3NHCbz
OBz
NHTroc
15
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)



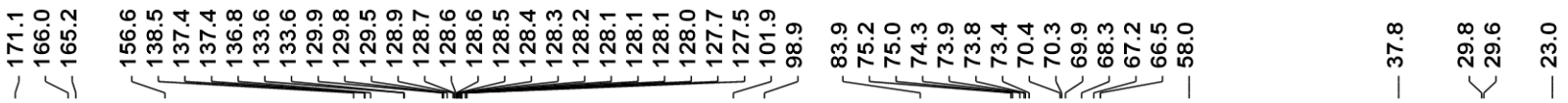
400 MHz, ^{1}H-NMR, $CDCl_3$

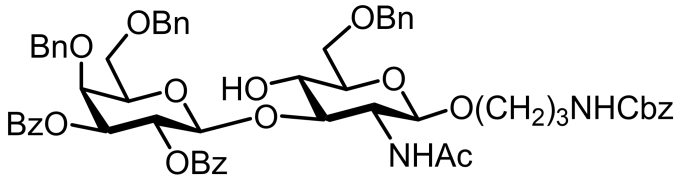

206.9
171.6
171.1
166.0
165.2
156.7
138.1
138.0
137.8
136.8
133.5
133.4
129.9
129.9
129.8
129.7
129.7
129.1
128.6
128.6
128.6
128.6
128.6
128.4
128.4
128.4
128.2
128.2
128.2
128.1
128.1
128.0
128.0
128.0
127.8
127.8
127.7
127.7
100.6
99.2
75.2
74.6
74.2
73.6
73.5
73.3
71.0
70.0
69.5
67.7
67.1
66.6
37.9
29.8
29.5
28.1
BnO
OBn
OLevO
O
OBn
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
16
100 MHz, 13C-NMR, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



17

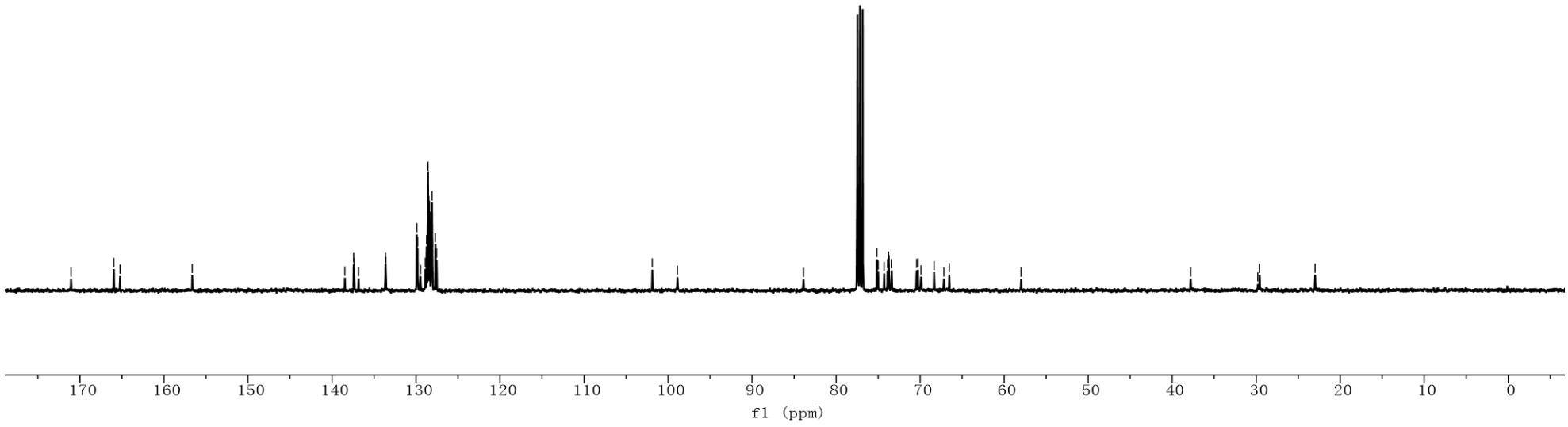
400 MHz, ^{1}H-NMR, $CDCl_3$

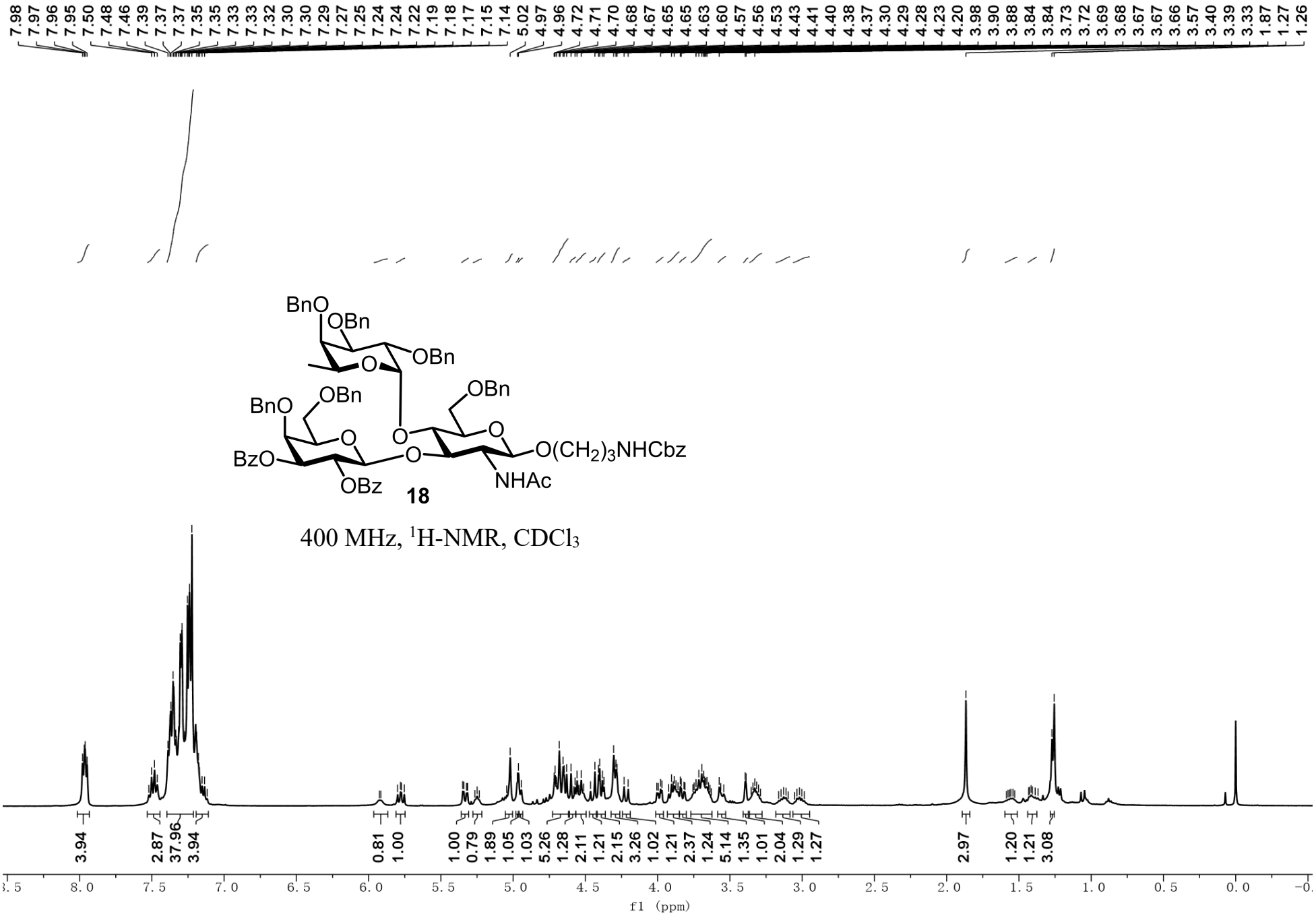


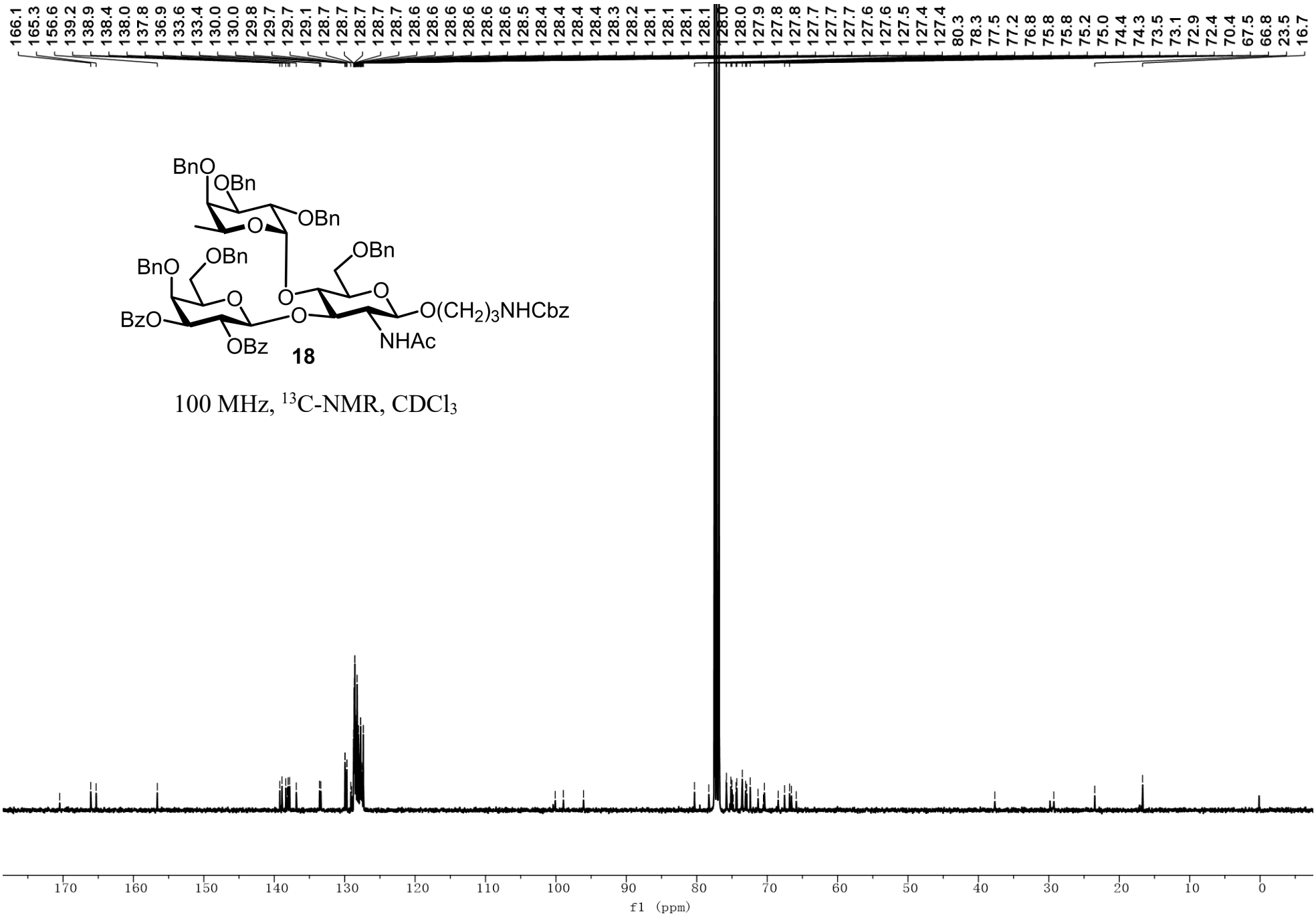


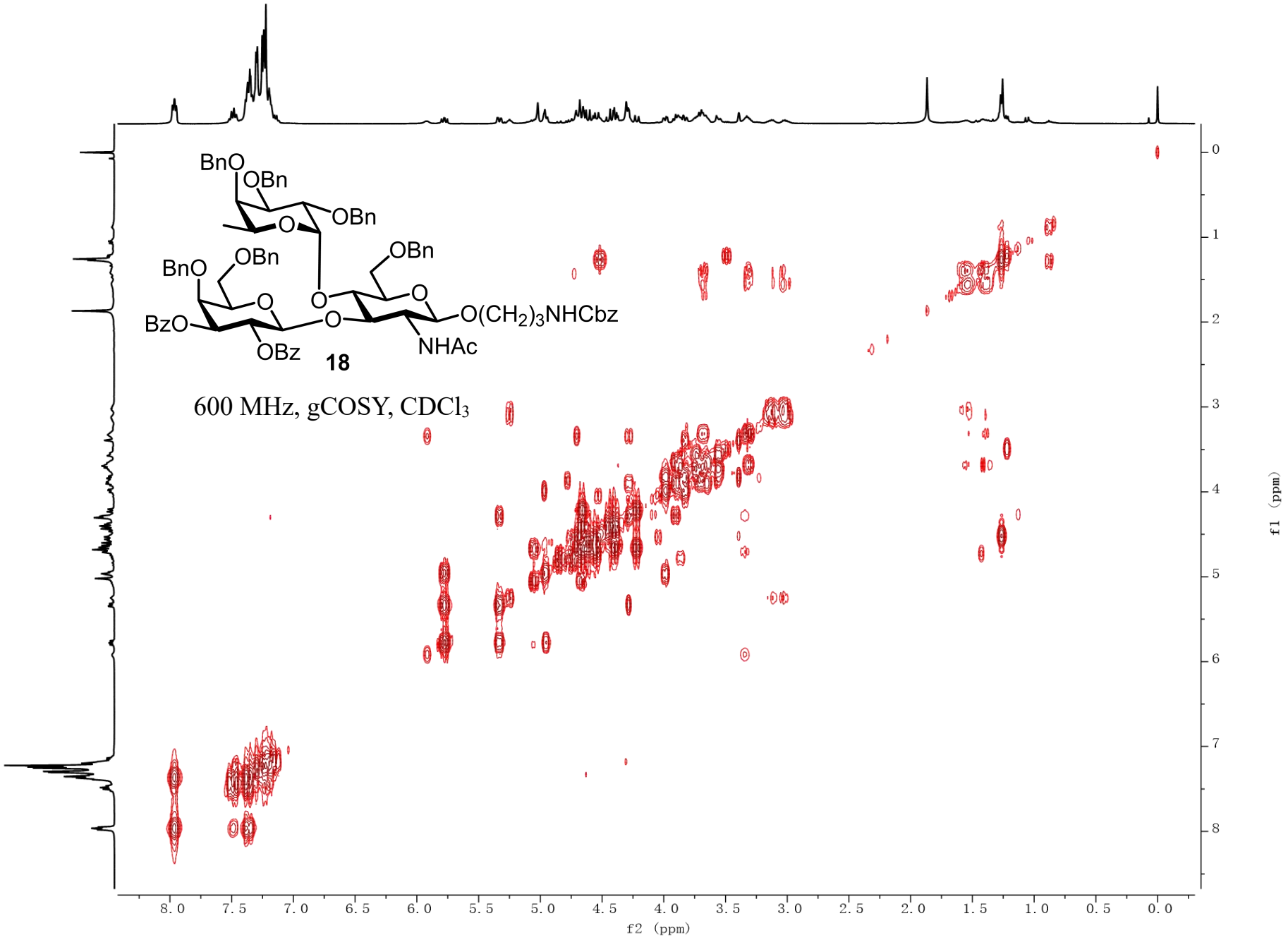
17

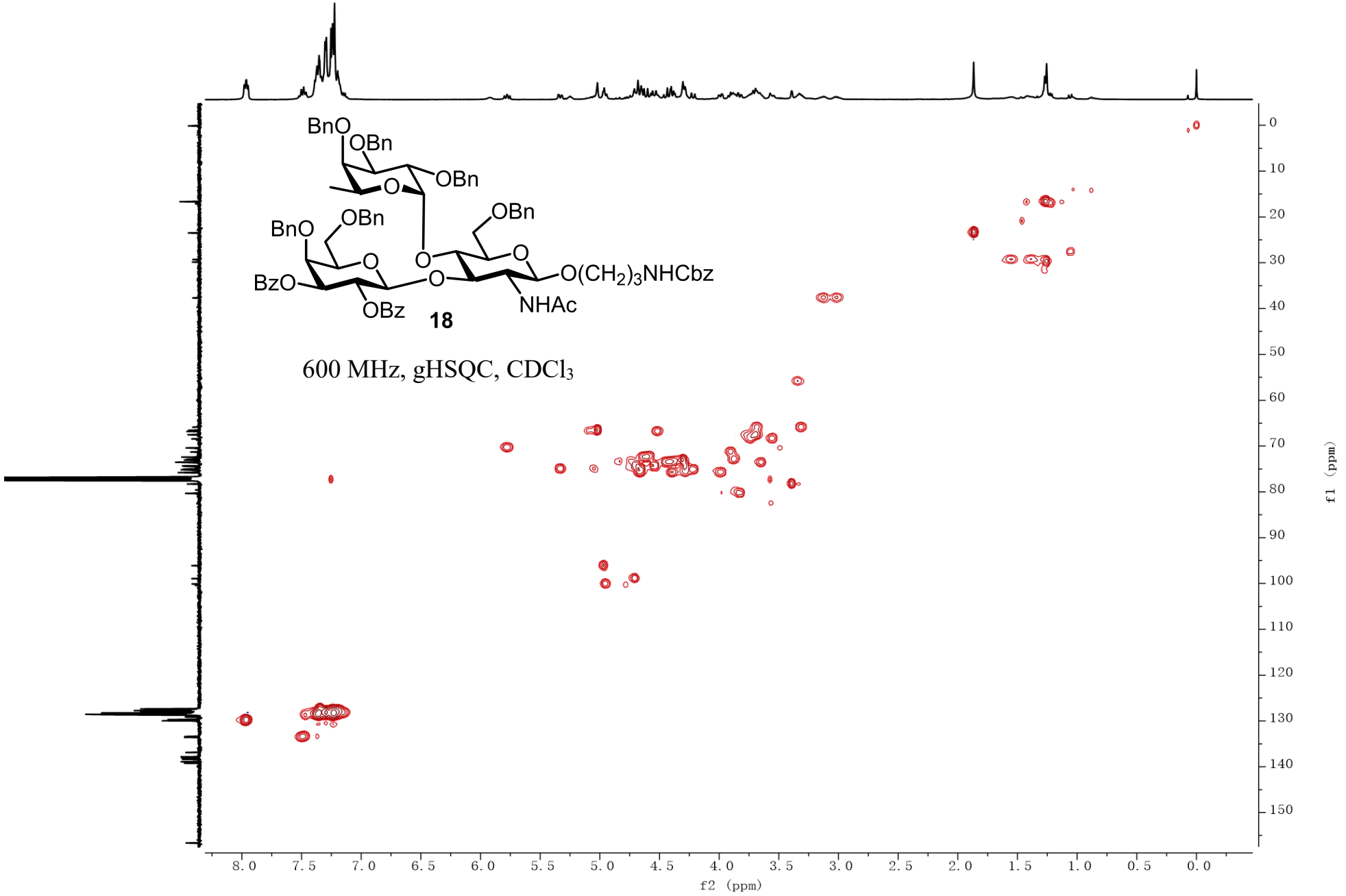
100 MHz, ^{13}C-NMR, $CDCl_3$

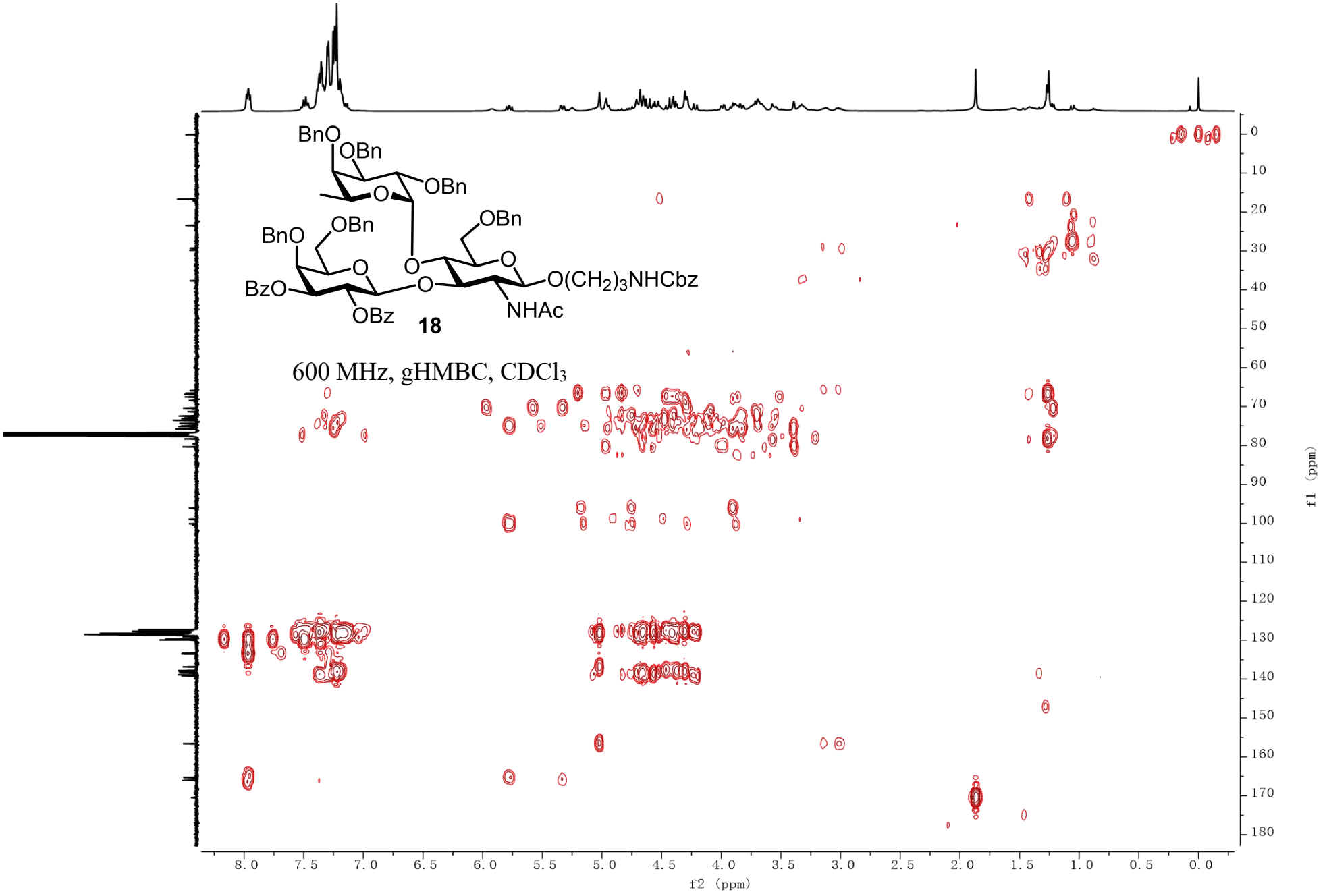


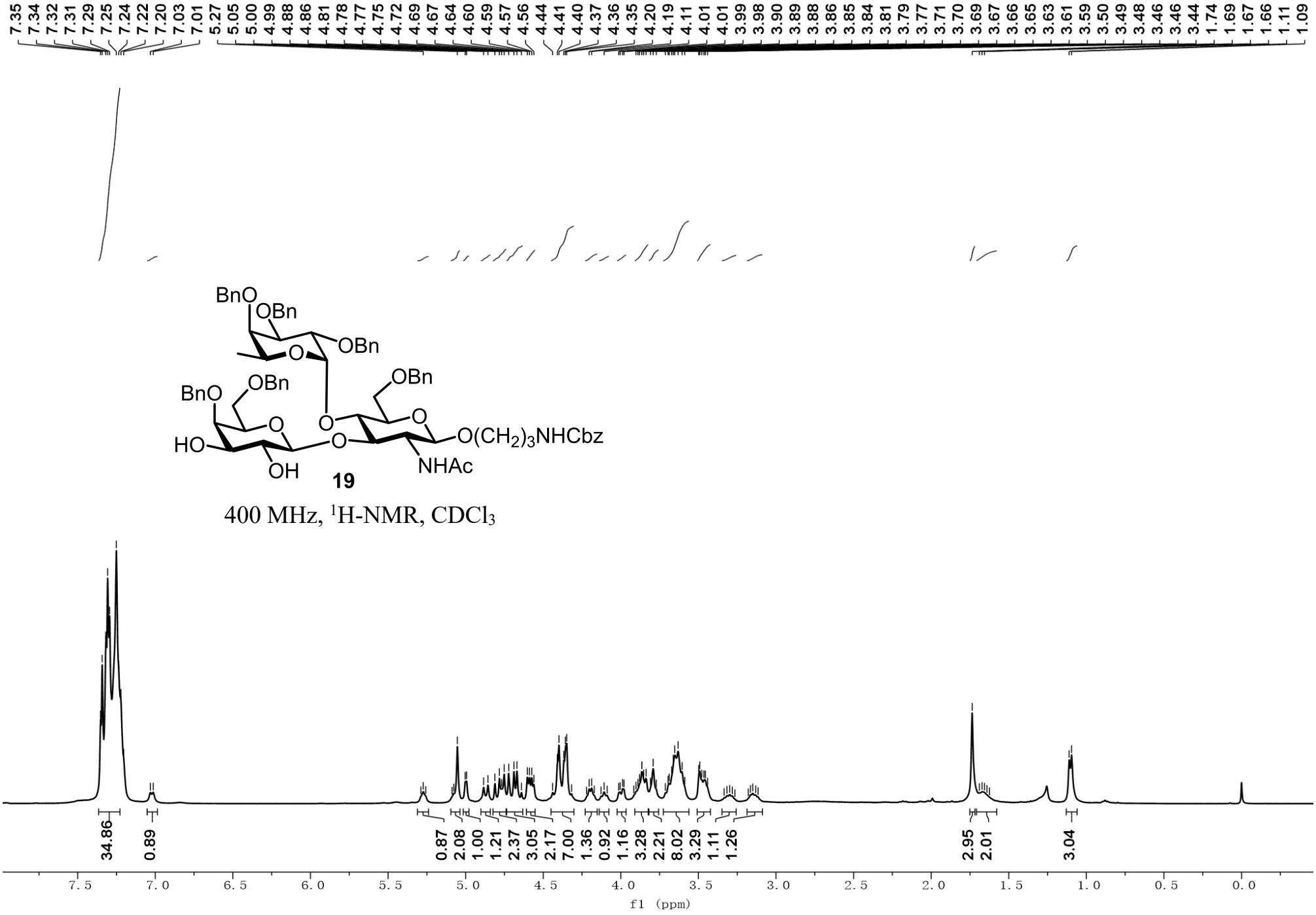

7.98 7.97 7.96 7.95 7.50 7.48 7.46 7.39 7.37 7.37 7.35 7.35 7.33 7.33 7.32 7.30 7.30 7.29 7.27 7.25 7.24 7.24 7.22 7.19 7.18 7.17 7.15 7.14 5.02 4.97 4.96 4.72 4.71 4.70 4.68 4.67 4.65 4.65 4.63 4.60 4.57 4.56 4.53 4.43 4.41 4.40 4.38 4.37 4.30 4.29 4.28 4.23 4.20 3.98 3.90 3.88 3.84 3.84 3.73 3.72 3.69 3.68 3.67 3.67 3.66 3.57 3.40 3.39 3.33 1.87 1.27 1.26
BnO
OBn
OBn
O
BnO
OBn
OBn
O
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
18
400 MHz, 1H-NMR, CDCl3
3.94 2.87 37.96 3.94 0.81 1.00 1.00 0.79 1.89 1.05 1.03 5.26 1.28 2.11 1.21 2.15 3.26 1.02 1.21 2.37 1.24 5.14 1.35 1.01 2.04 1.29 1.27 2.97 1.20 1.21 3.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

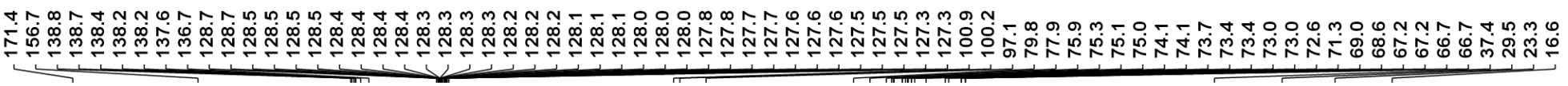

166.1 165.3 156.6 139.2 138.9 138.4 138.0 137.8 136.9 133.6 133.4 130.0 130.0 129.8 129.7 129.7 129.1 128.7 128.7 128.7 128.7 128.7 128.6 128.6 128.6 128.6 128.6 128.5 128.4 128.4 128.4 128.4 128.3 128.2 128.1 128.1 128.1 128.1 128.0 128.0 127.9 127.8 127.8 127.7 127.7 127.7 127.6 127.6 127.5 127.4 127.4 80.3 78.3 77.5 77.2 76.8 75.8 75.8 75.2 75.0 74.4 74.3 73.5 73.1 72.9 72.4 70.4 67.5 66.8 23.5 16.7
BnO
OBn
OBn
O
OBn
BnO
OBn
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
18
100 MHz, 13C-NMR, CDCl3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

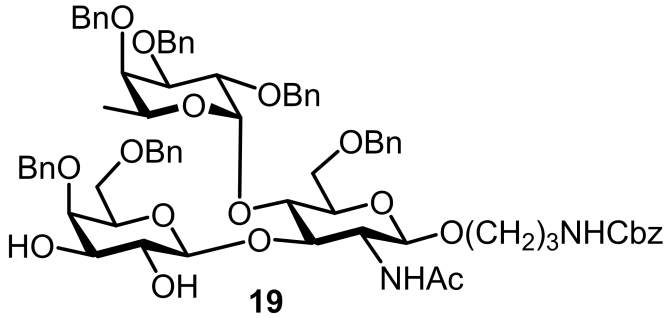

BnO
OBn
OBn
O
BnO
OBn
OBn
O
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
18
600 MHz, gCOSY, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


BnO
OBn
OBn
O
OBn
BnO
OBn
O
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
18
600 MHz, gHSQC, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OBn
OBn
O
OBn
BnO
OBn
O
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHAc
18
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

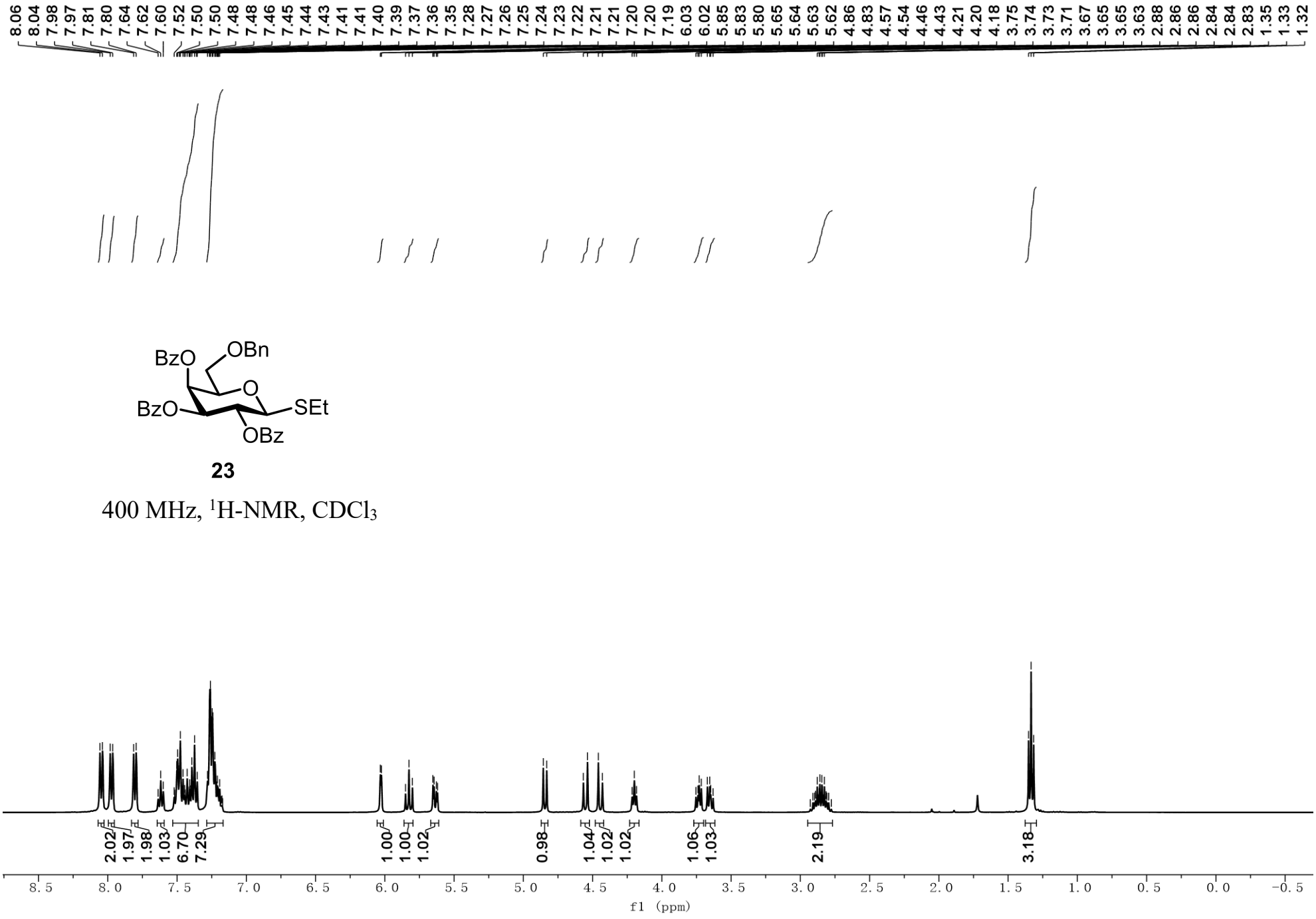

7.35 7.34 7.32 7.31 7.29 7.25 7.24 7.22 7.20 7.03 7.01 5.27 5.05 5.00 4.99 4.88 4.86 4.81 4.78 4.77 4.75 4.72 4.69 4.67 4.64 4.60 4.59 4.57 4.56 4.44 4.41 4.40 4.37 4.36 4.35 4.20 4.19 4.11 4.01 4.01 3.99 3.98 3.90 3.89 3.88 3.86 3.85 3.84 3.81 3.79 3.77 3.71 3.70 3.69 3.67 3.66 3.65 3.63 3.61 3.59 3.50 3.49 3.48 3.46 3.46 3.44 1.74 1.69 1.67 1.66 1.11 1.09
BnO
OBn
OBn
OBn
BnO
OBn
O
O
O
HO
O
O(CH2)3NHCbz
OH
NHAc
19
400 MHz, 1H-NMR, CDCl3
34.86
0.89
0.87
2.08
1.00
1.21
2.37
3.05
2.17
7.00
1.36
0.92
1.16
3.28
2.21
8.02
3.29
1.11
1.26
2.95
2.01
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)





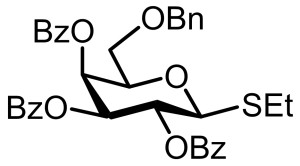
19

100 MHz, ^{13}C-NMR, $CDCl_3$



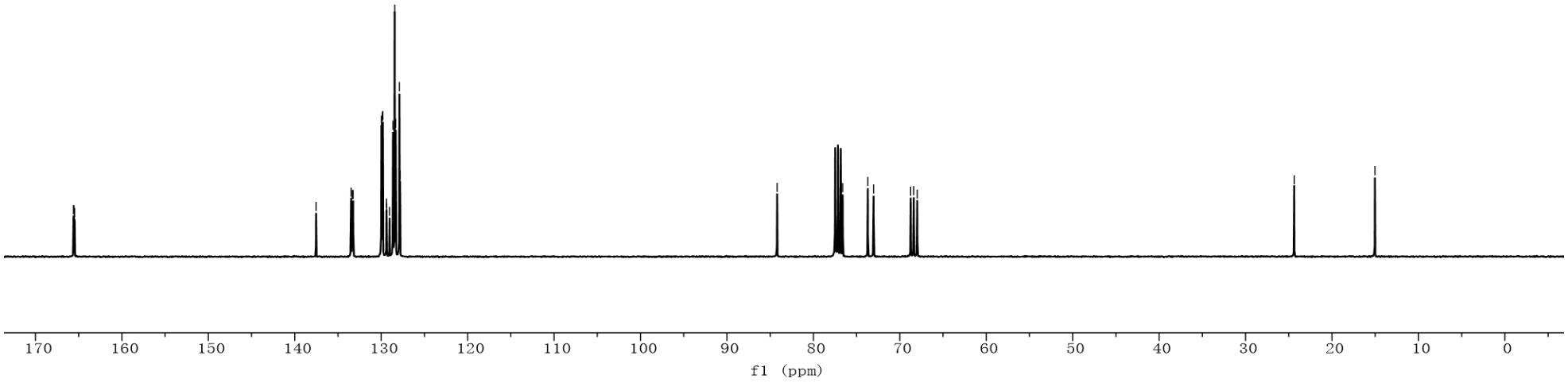
23

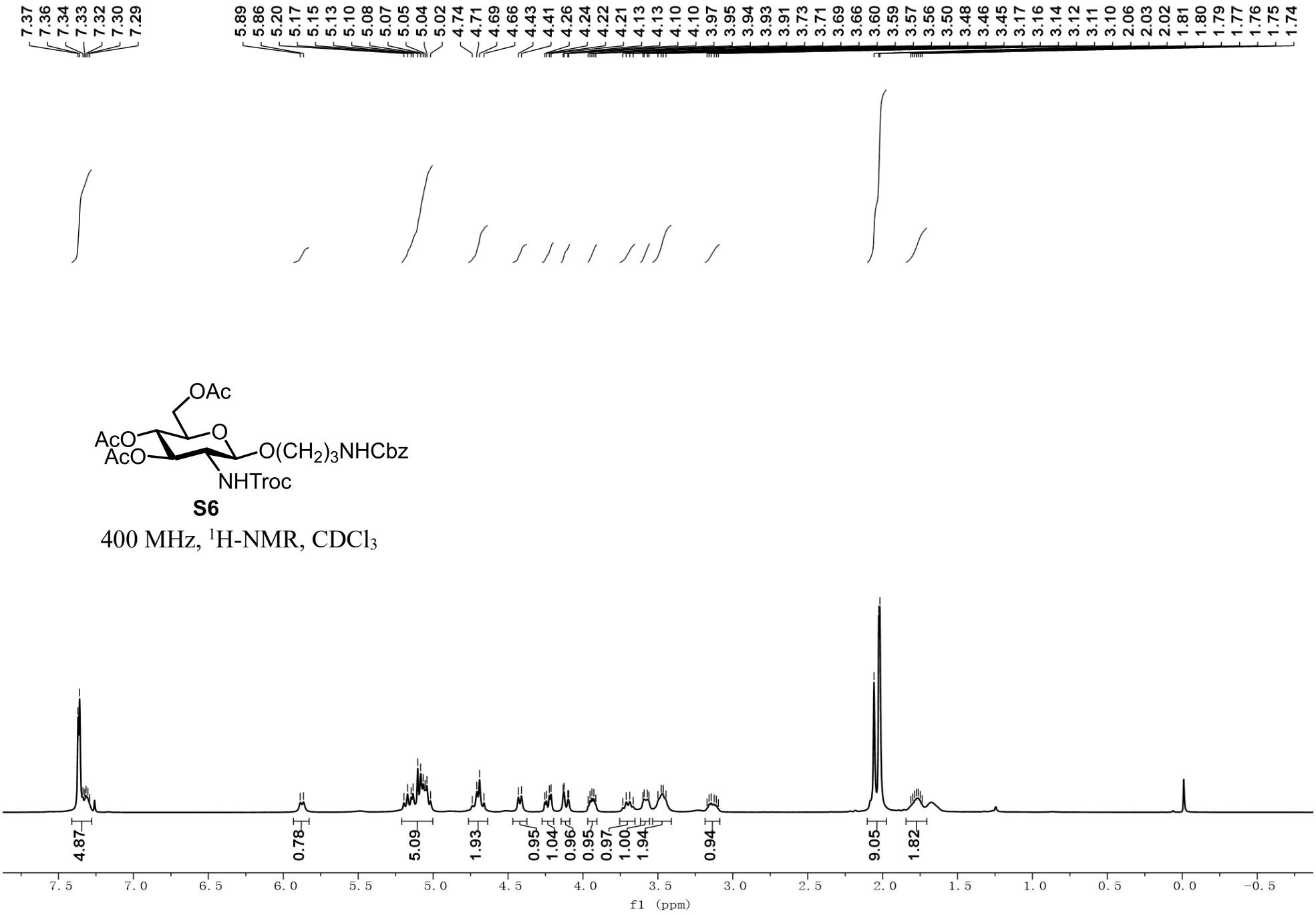
400 MHz, ^{1}H-NMR, $CDCl_3$

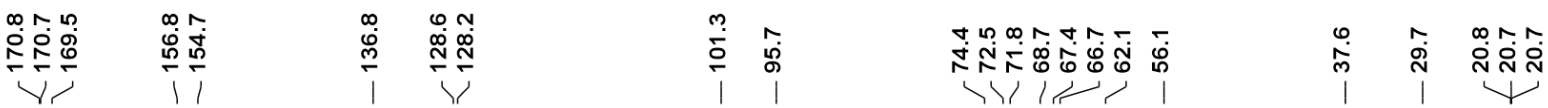


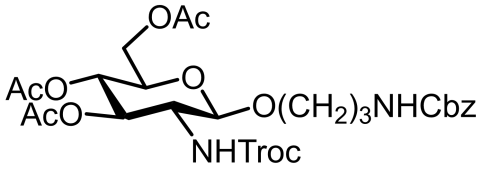
23

100 MHz, ^{13}C-NMR, $CDCl_3$



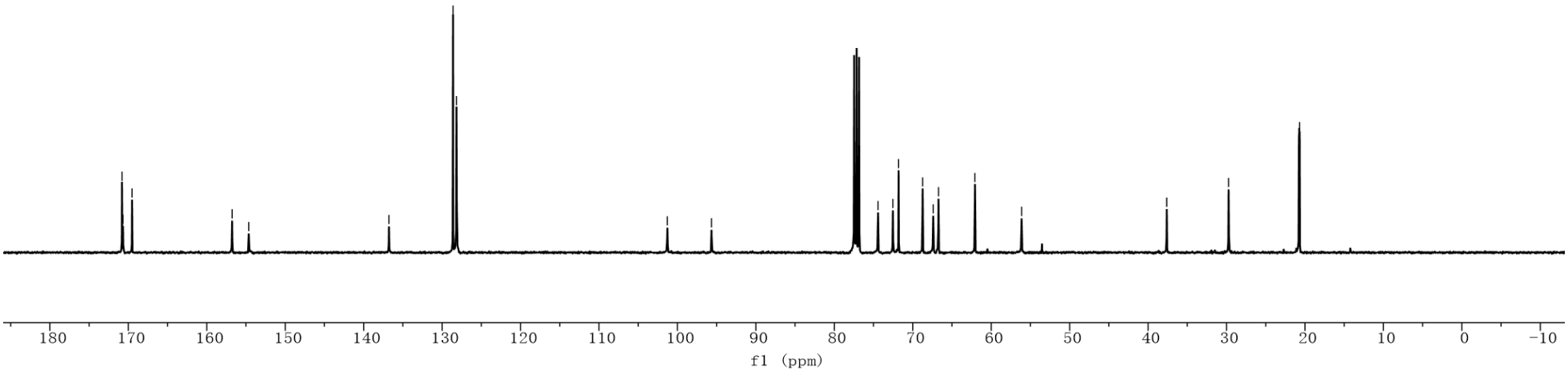

7.37 7.36 7.34 7.33 7.32 7.30 7.29
5.89 5.86 5.20 5.17 5.15 5.13 5.10 5.08 5.07 5.05 5.04 5.02 4.74 4.71 4.69 4.66 4.43 4.41 4.26 4.24 4.22 4.21 4.13 4.13 4.10 4.10 3.97 3.95 3.94 3.93 3.91 3.73 3.71 3.69 3.66 3.60 3.59 3.57 3.56 3.50 3.48 3.46 3.45 3.17 3.16 3.14 3.12 3.11 3.10 2.06 2.03 2.02 1.81 1.80 1.79 1.77 1.76 1.75 1.74
OAc
AcO
AcO
O
O(CH2)3NHCbz
NHTroc
S6
400 MHz, 1H-NMR, CDCl3
4.87 0.78 5.09 1.93 0.95 1.04 0.96 0.95 0.97 1.00 1.94 0.94 9.05 1.82
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

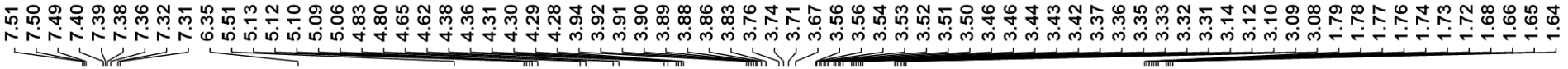


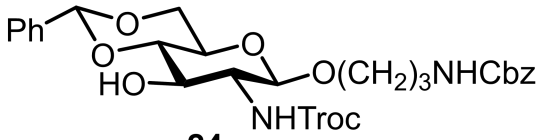


S6

100 MHz, ^{13}C-NMR, $CDCl_3$

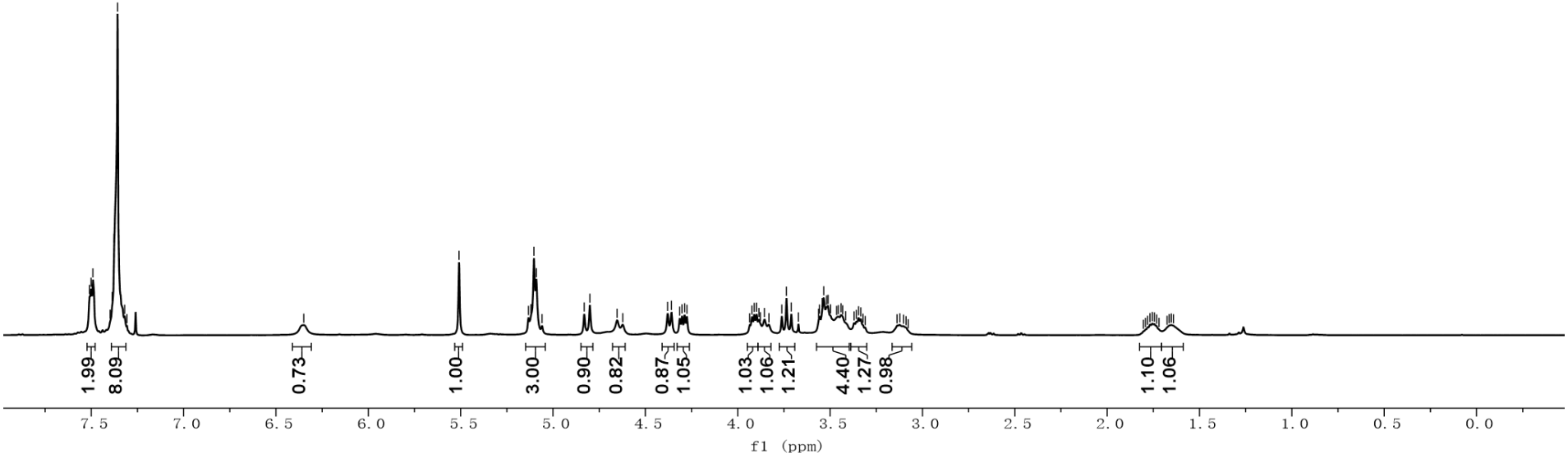


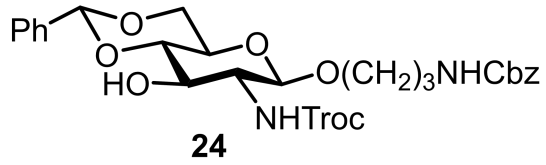




24

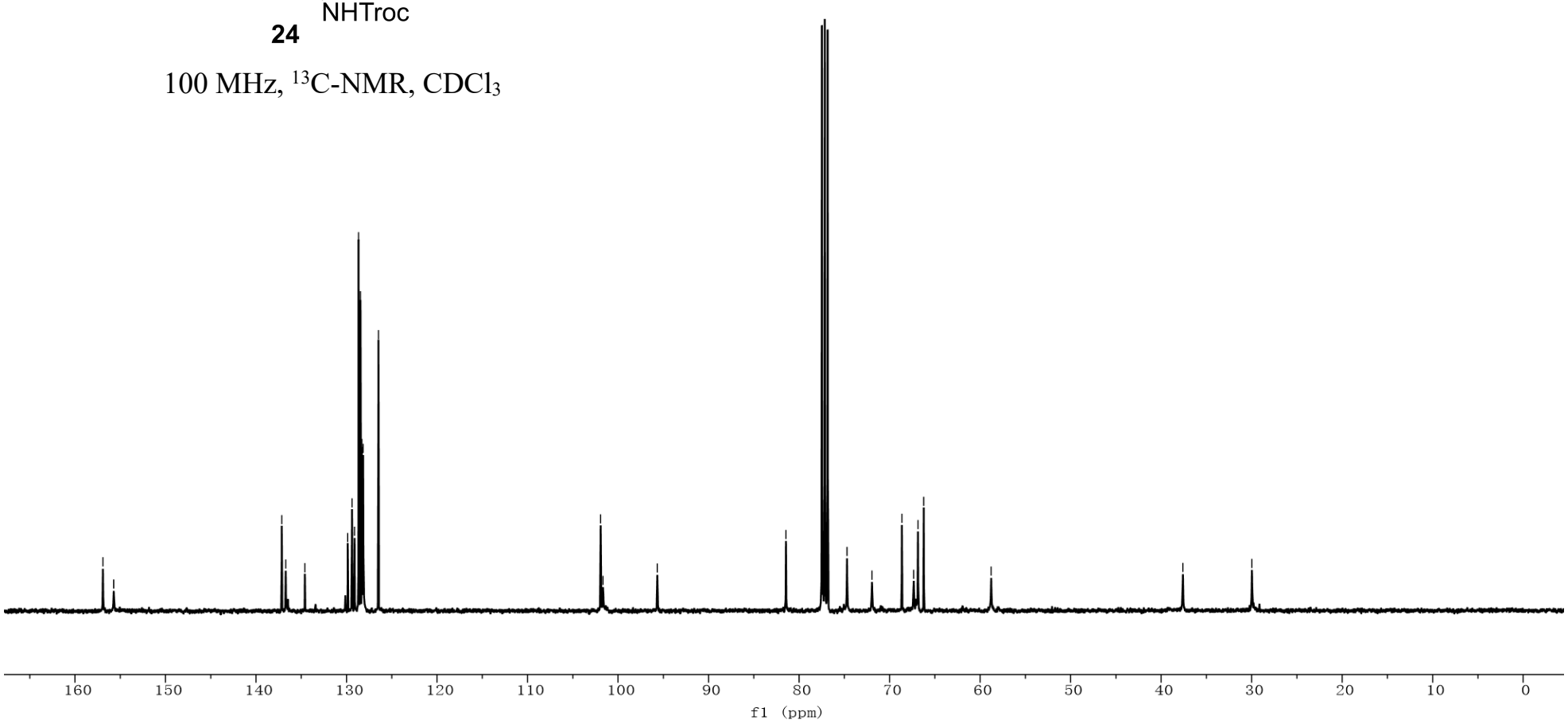
400 MHz, ^{1}H-NMR, $CDCl_3$

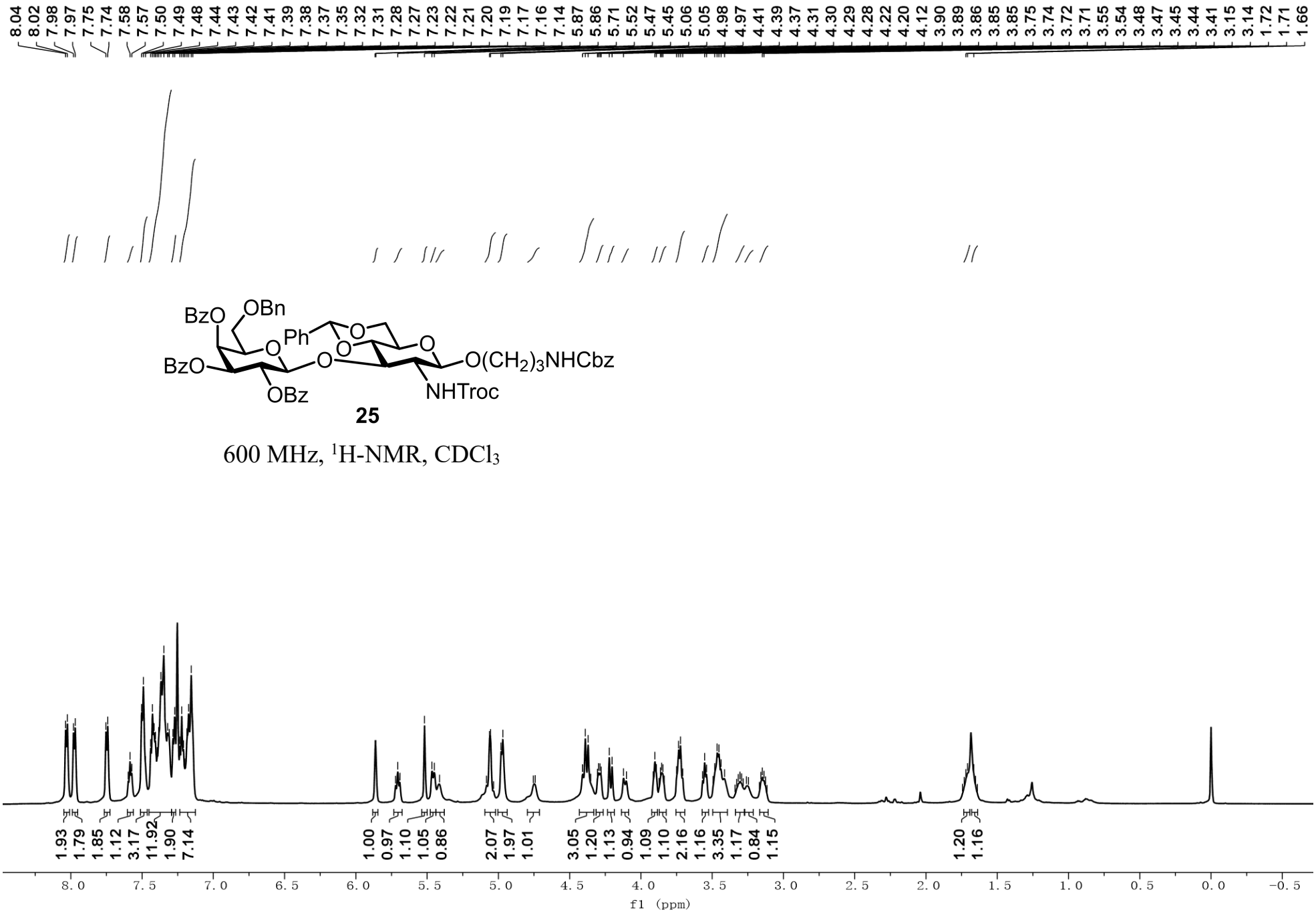




24

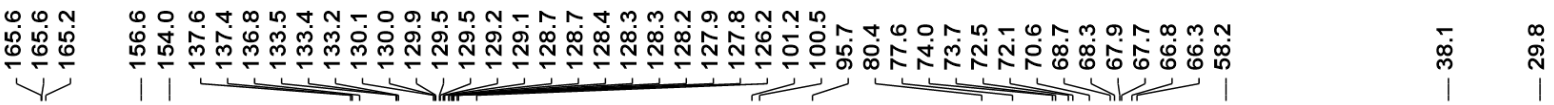
100 MHz, ^{13}C-NMR, $CDCl_3$

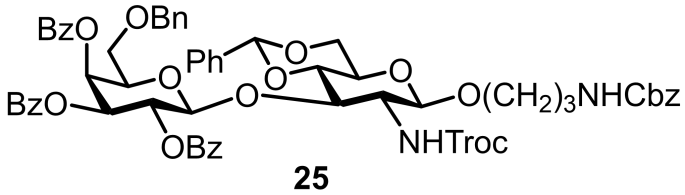




25

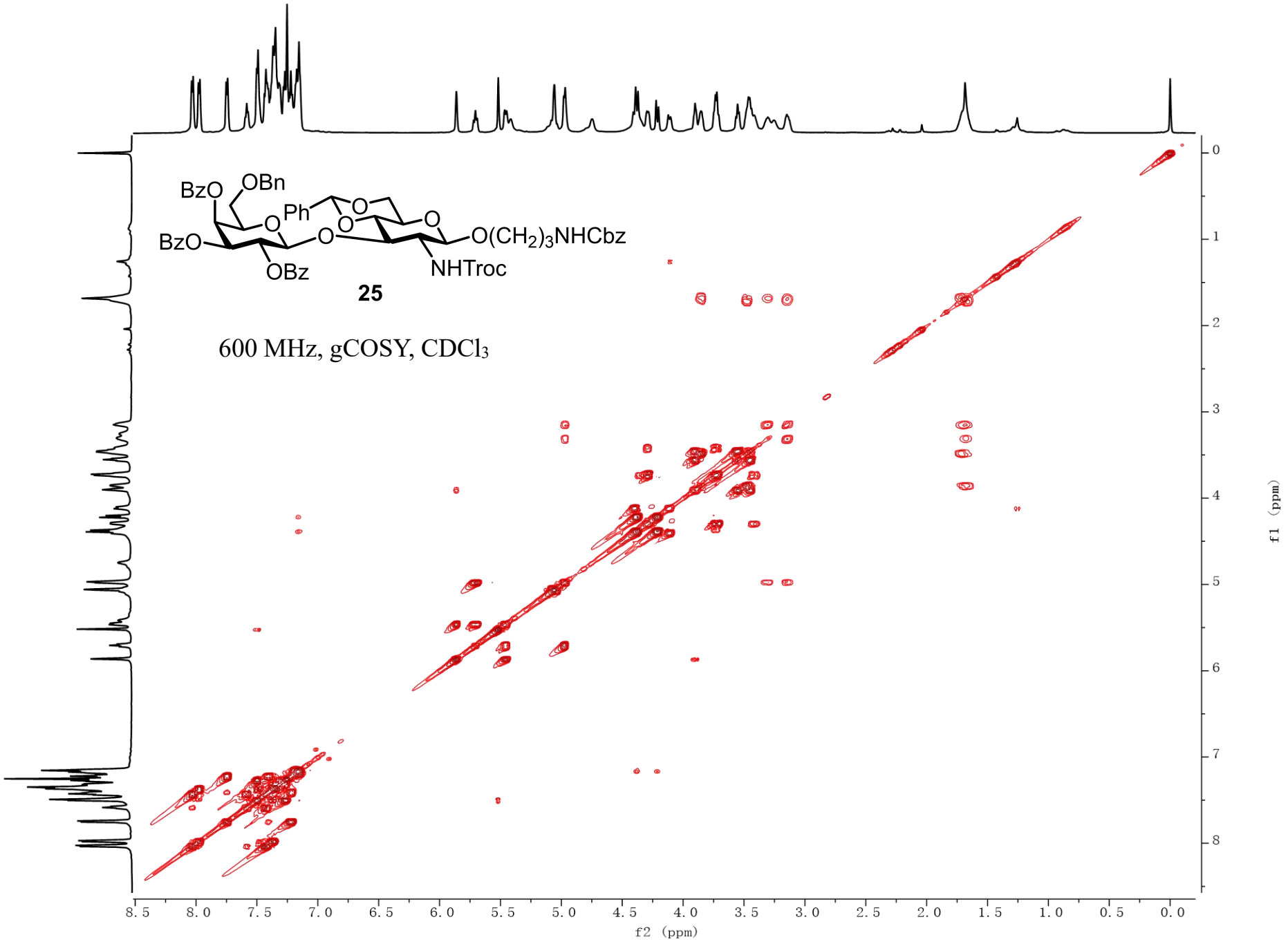
600 MHz, ^{1}H-NMR, $CDCl_3$

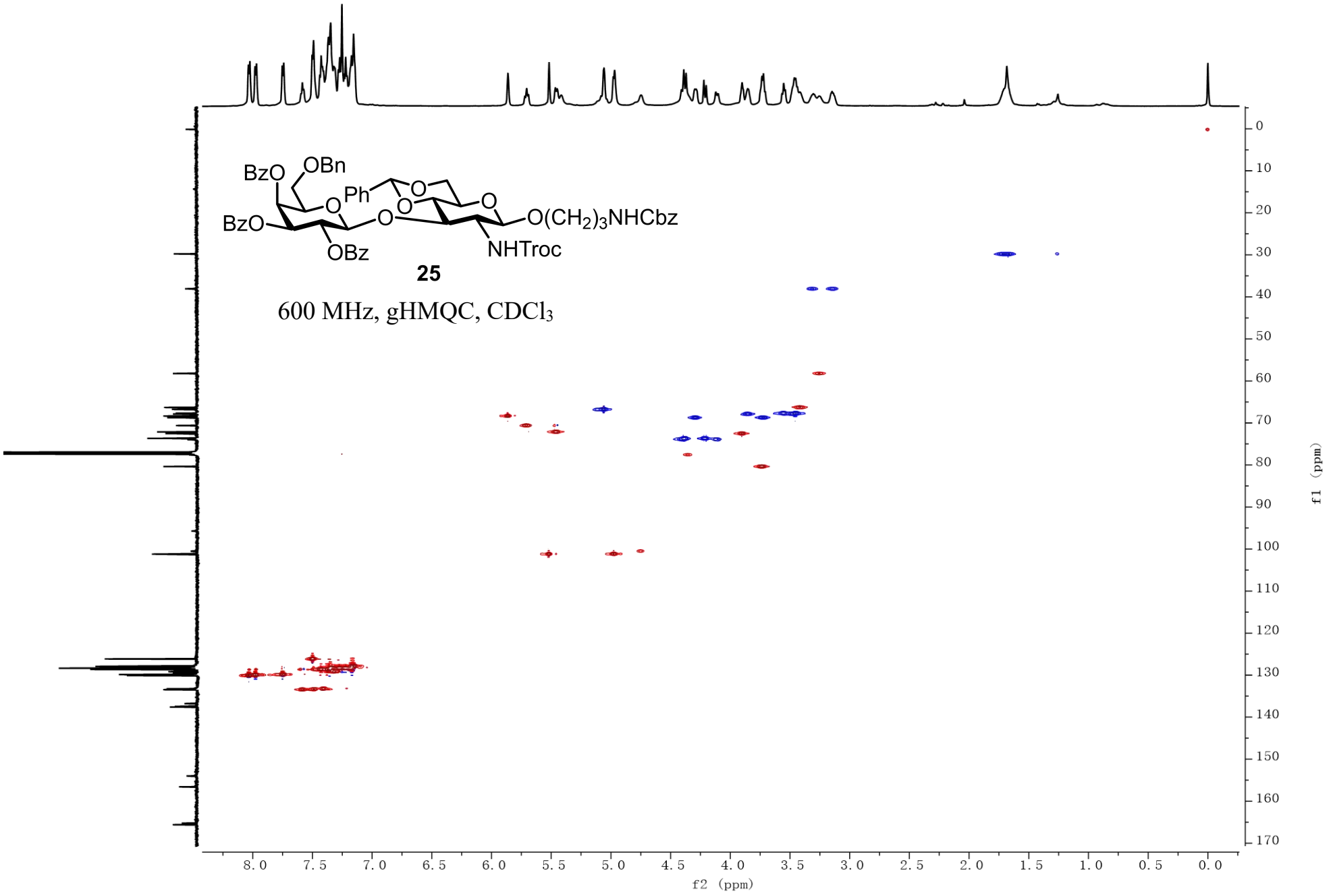


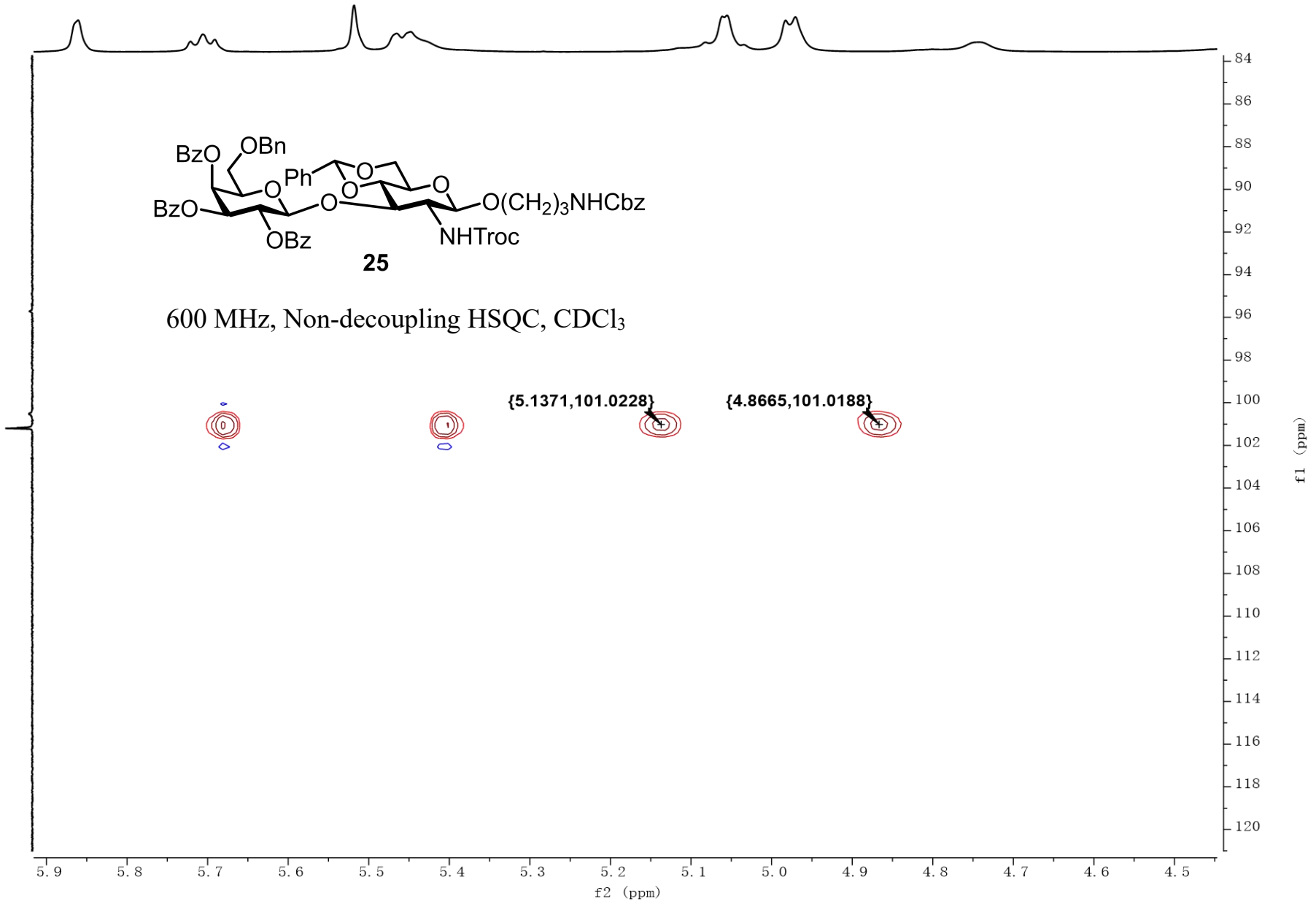


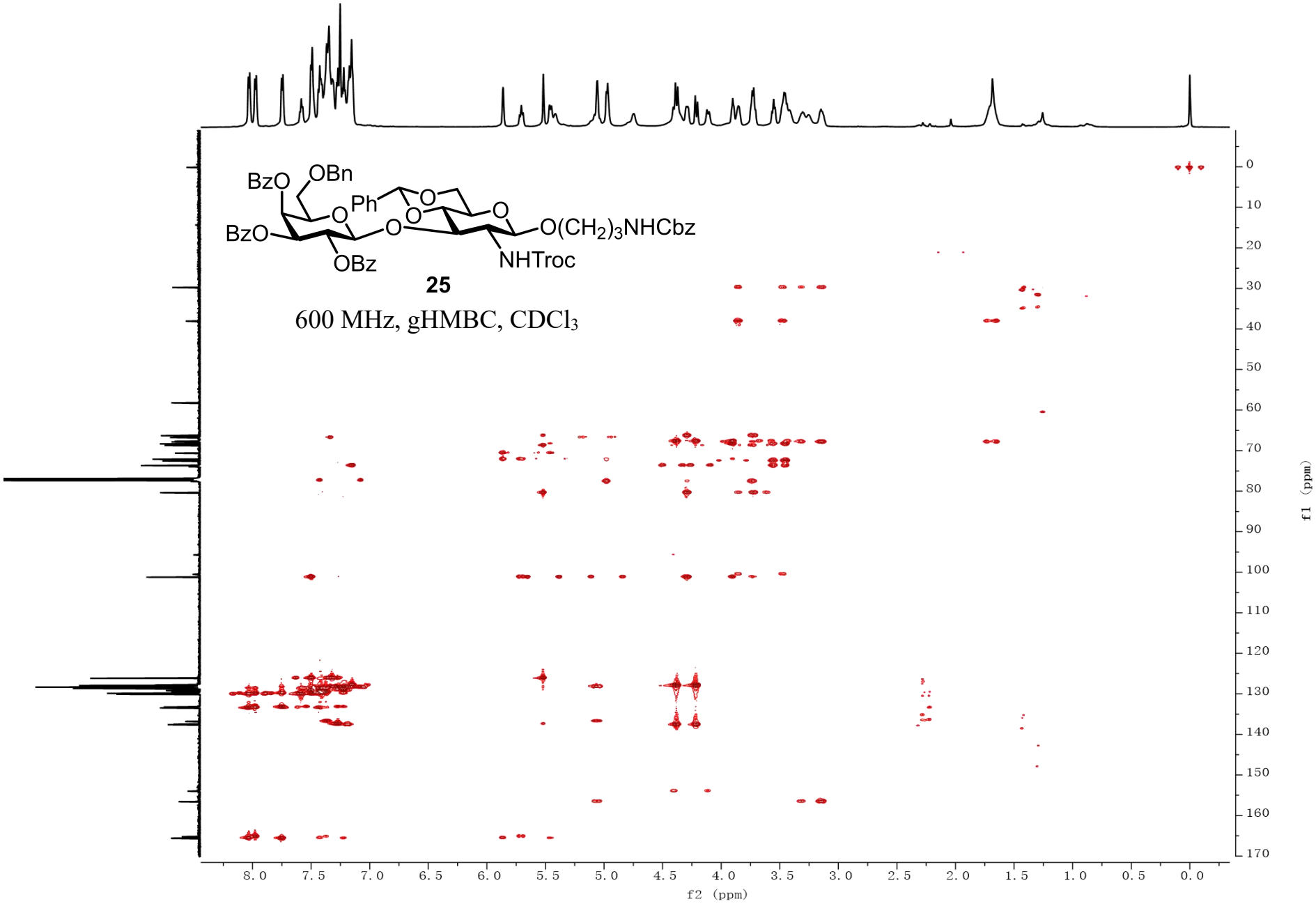
25

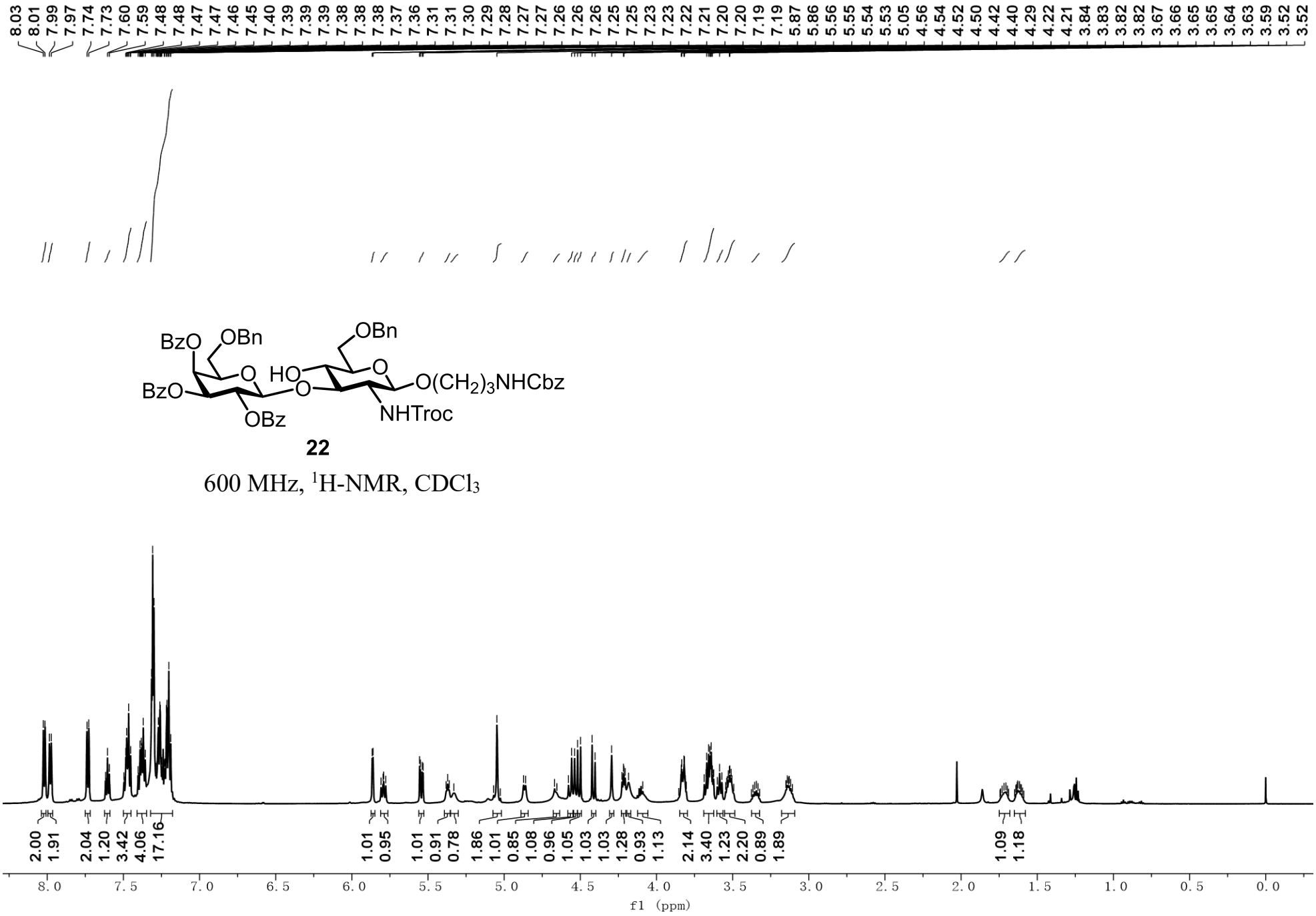
150 MHz, ^{13}C-NMR, $CDCl_3$

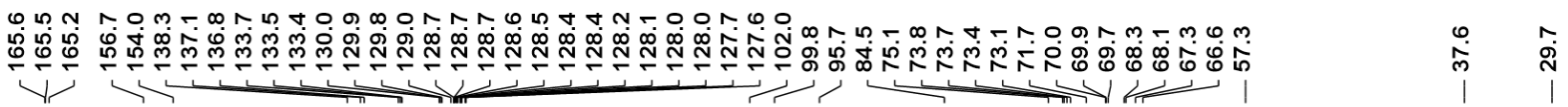

BzO
OBn
Ph
O
BzO
OBz
O(CH2)3NHCbz
NHTroc
25
600 MHz, gCOSY, CDCl3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
0 1 2 3 4 5 6 7 8
f1 (ppm)

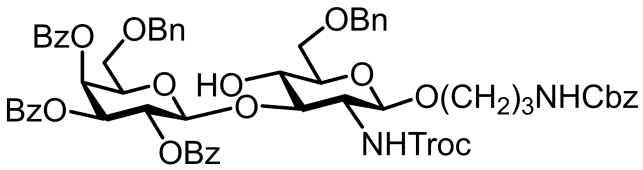

BzO
OBn
Ph
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
25
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)


BzO
OBn
Ph
O
O
O
BzO
O
O
O(CH2)3NHCbz
OBz
NHTroc
25
600 MHz, Non-decoupling HSQC, CDCl3
{5.1371,101.0228}
{4.8665,101.0188}
84
86
88
90
92
94
96
98
100
102
104
106
108
110
112
114
116
118
120
f1 (ppm)
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
f2 (ppm)


BzO
OBn
Ph
O
O
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
25
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

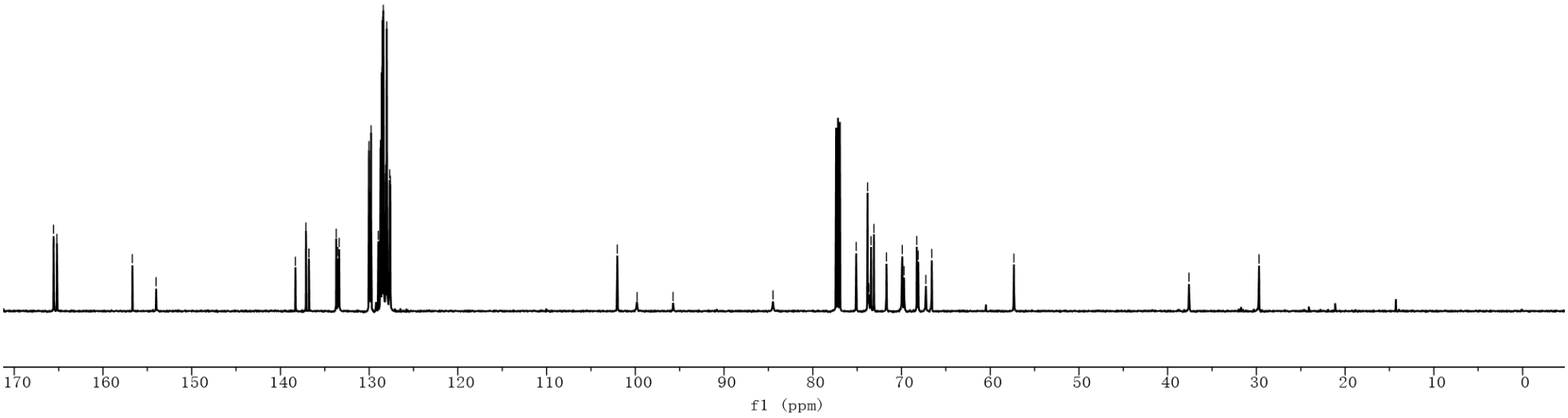

8.03 8.01 7.99 7.97 7.74 7.73 7.60 7.59 7.48 7.48 7.47 7.47 7.46 7.45 7.40 7.39 7.39 7.38 7.38 7.38 7.37 7.36 7.31 7.31 7.30 7.29 7.28 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.23 7.23 7.22 7.21 7.20 7.20 7.19 7.19 5.87 5.86 5.56 5.55 5.54 5.53 5.05 4.56 4.54 4.52 4.50 4.42 4.40 4.29 4.22 4.21 3.84 3.83 3.82 3.82 3.67 3.66 3.65 3.65 3.64 3.63 3.59 3.52 3.52
BzO
OBn
O
HO
OBn
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
22
600 MHz, 1H-NMR, CDCl3
2.00 1.91 2.04 1.20 3.42 4.06 17.16 1.01 0.95 1.01 0.91 0.78 1.86 1.01 0.85 1.08 0.96 1.05 1.03 1.03 1.28 0.93 1.13 2.14 3.40 1.23 2.20 0.89 1.89 1.09 1.18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

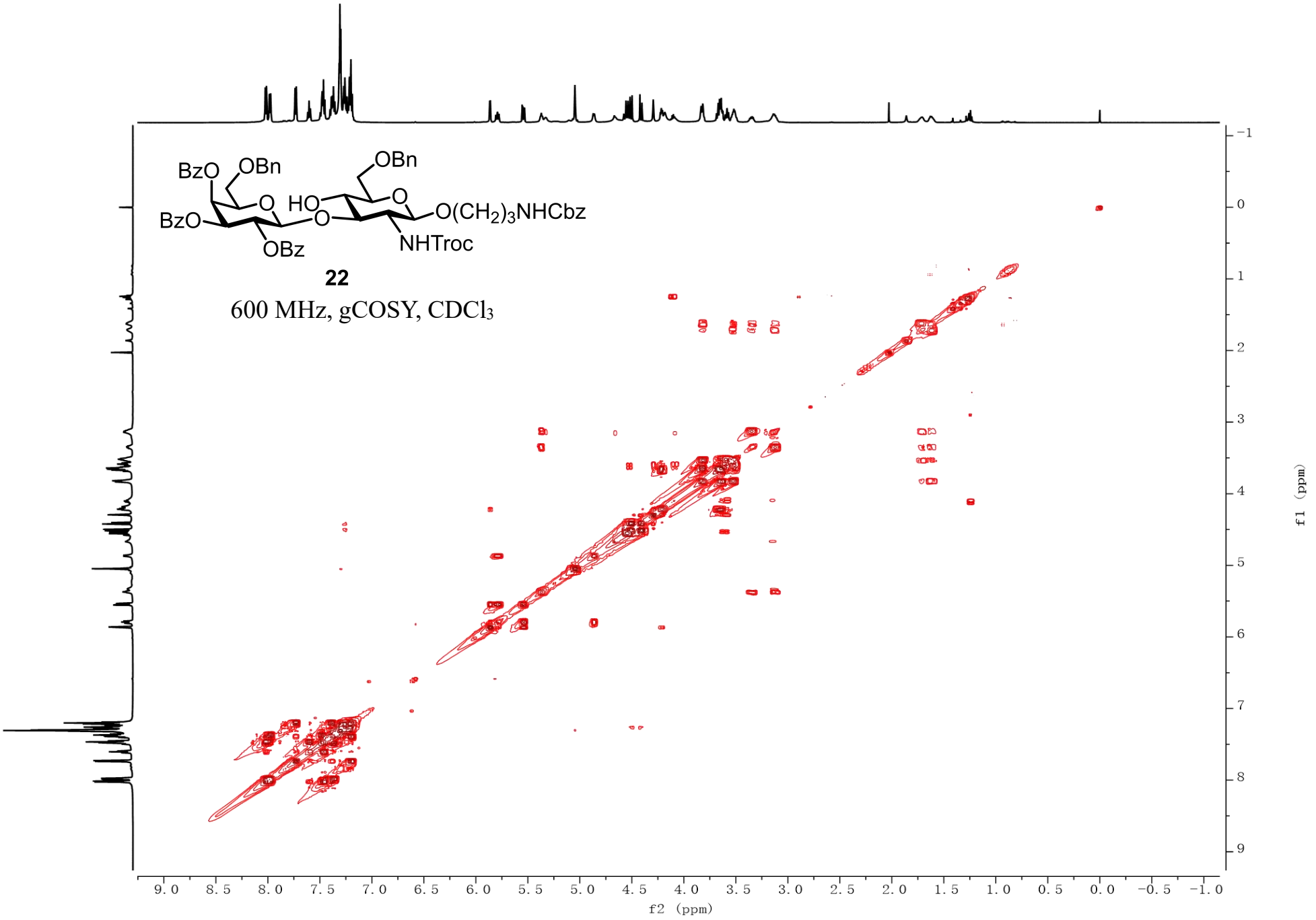


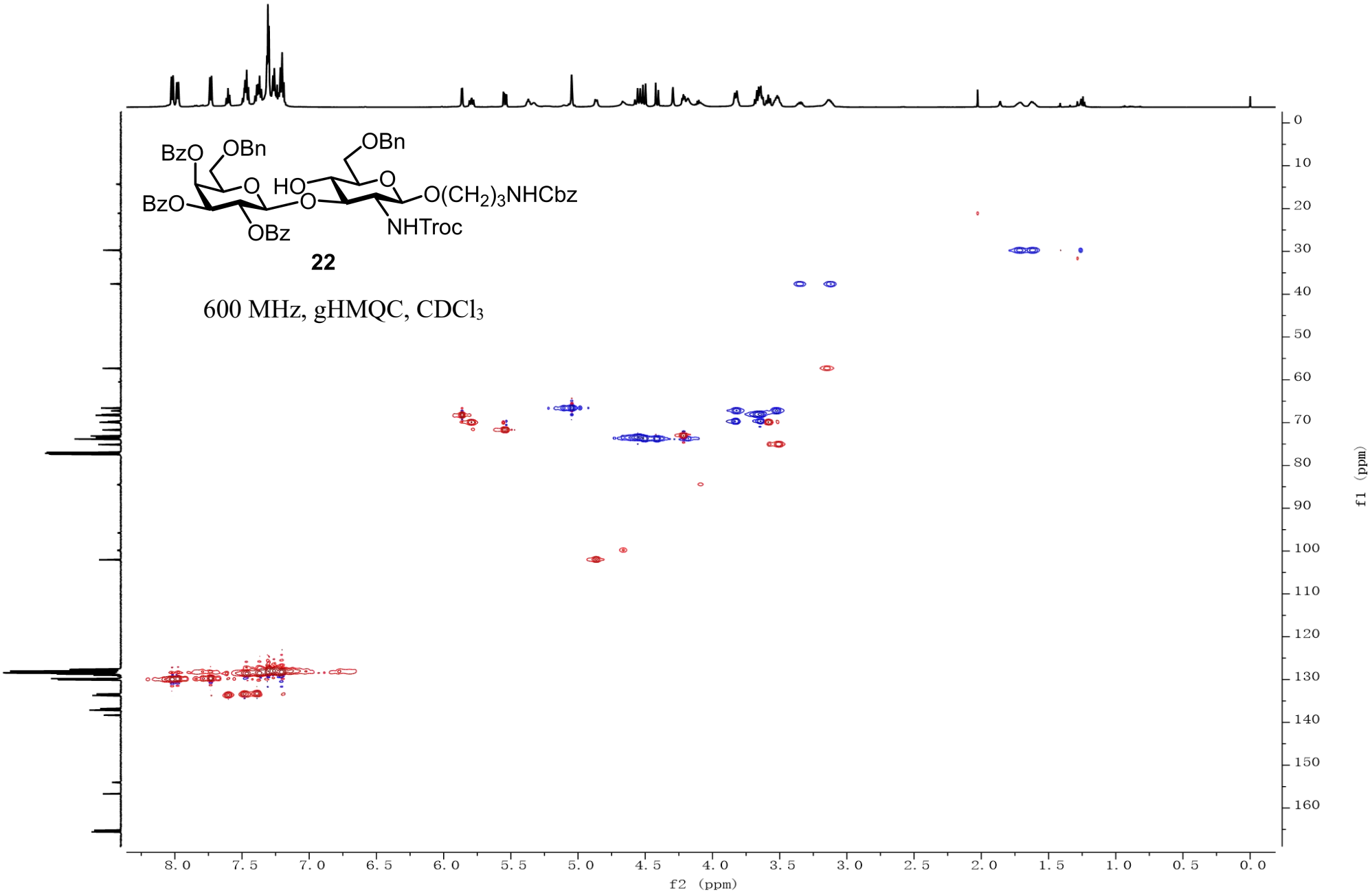


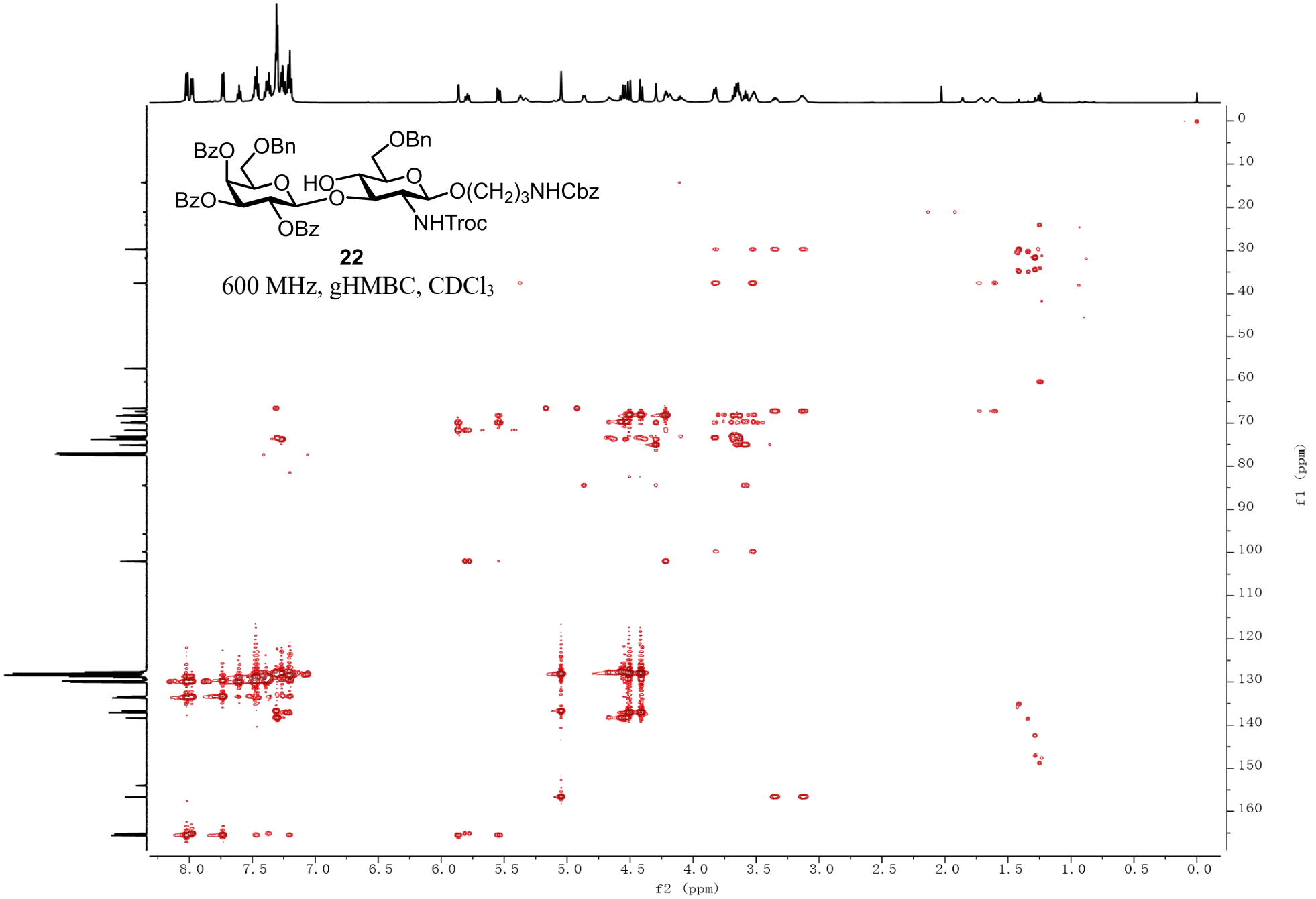
22

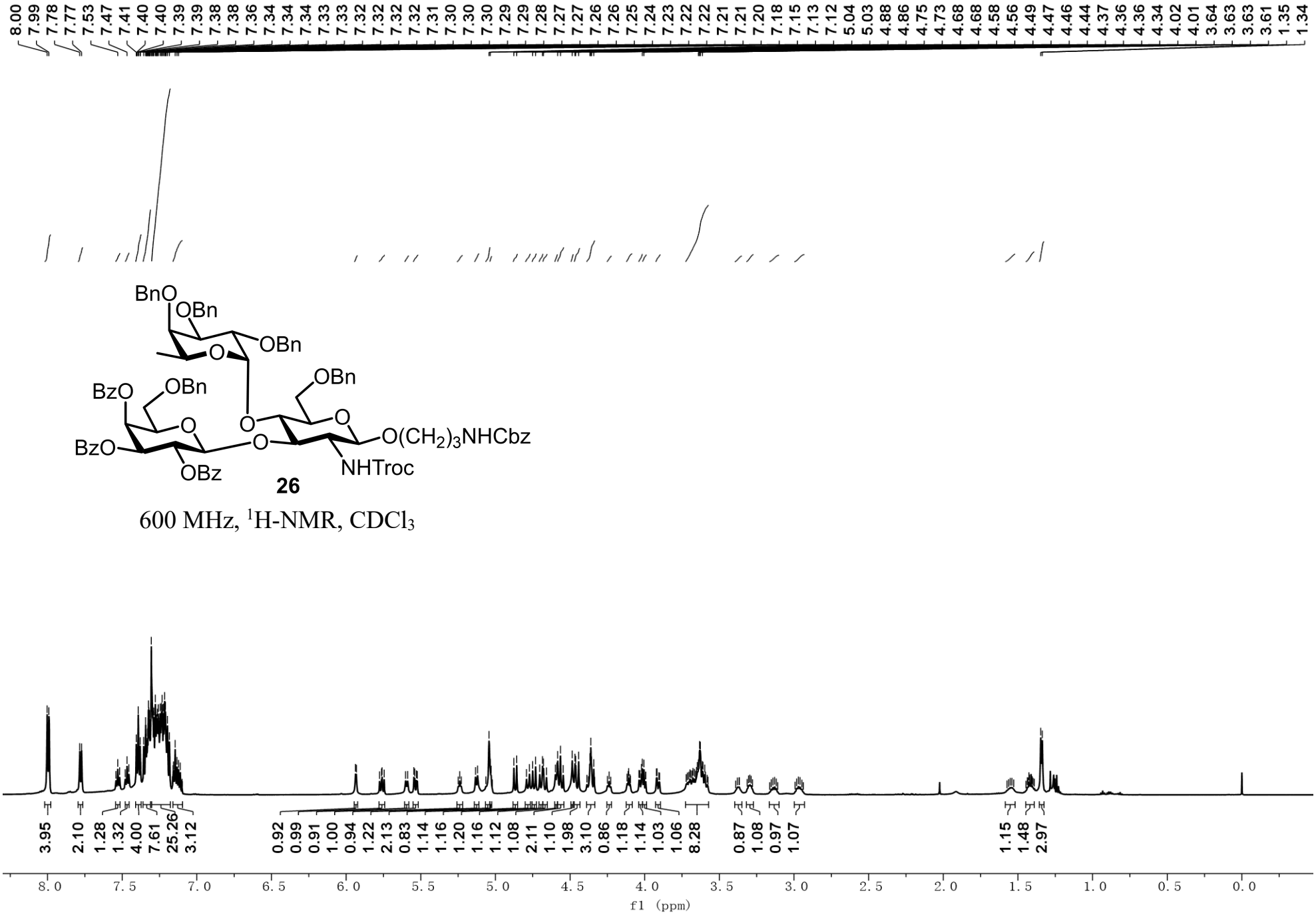
150 MHz, ^{13}C-NMR, $CDCl_3$



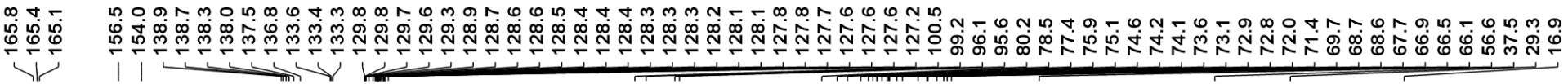

BzO
OBn
O
HO
OBn
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
22
600 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

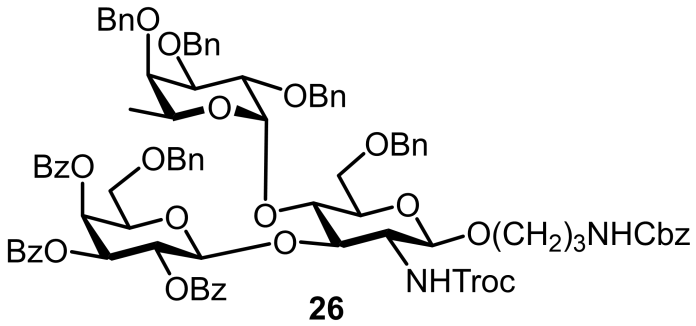

BzO
OBn
O
HO
OBn
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
22
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)


BzO
OBn
O
HO
OBn
O
BzO
O
O(CH2)3NHCbz
OBz
NHTroc
22
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)



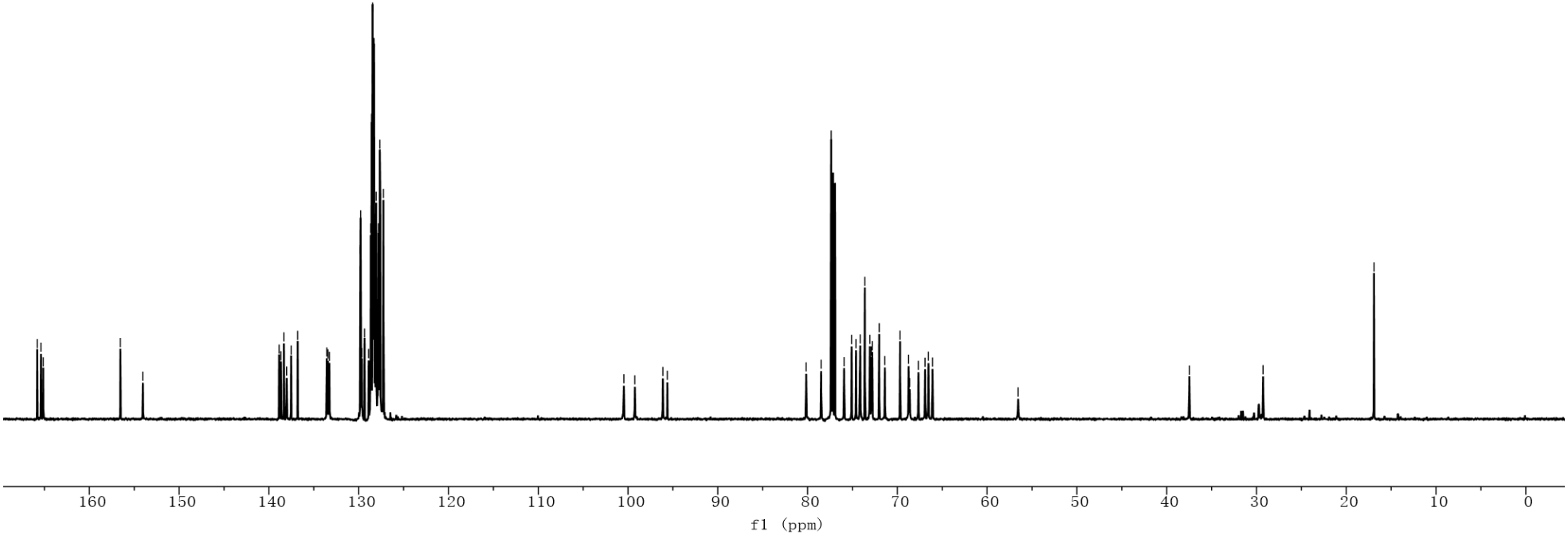
600 MHz, ^{1}H-NMR, $CDCl_3$

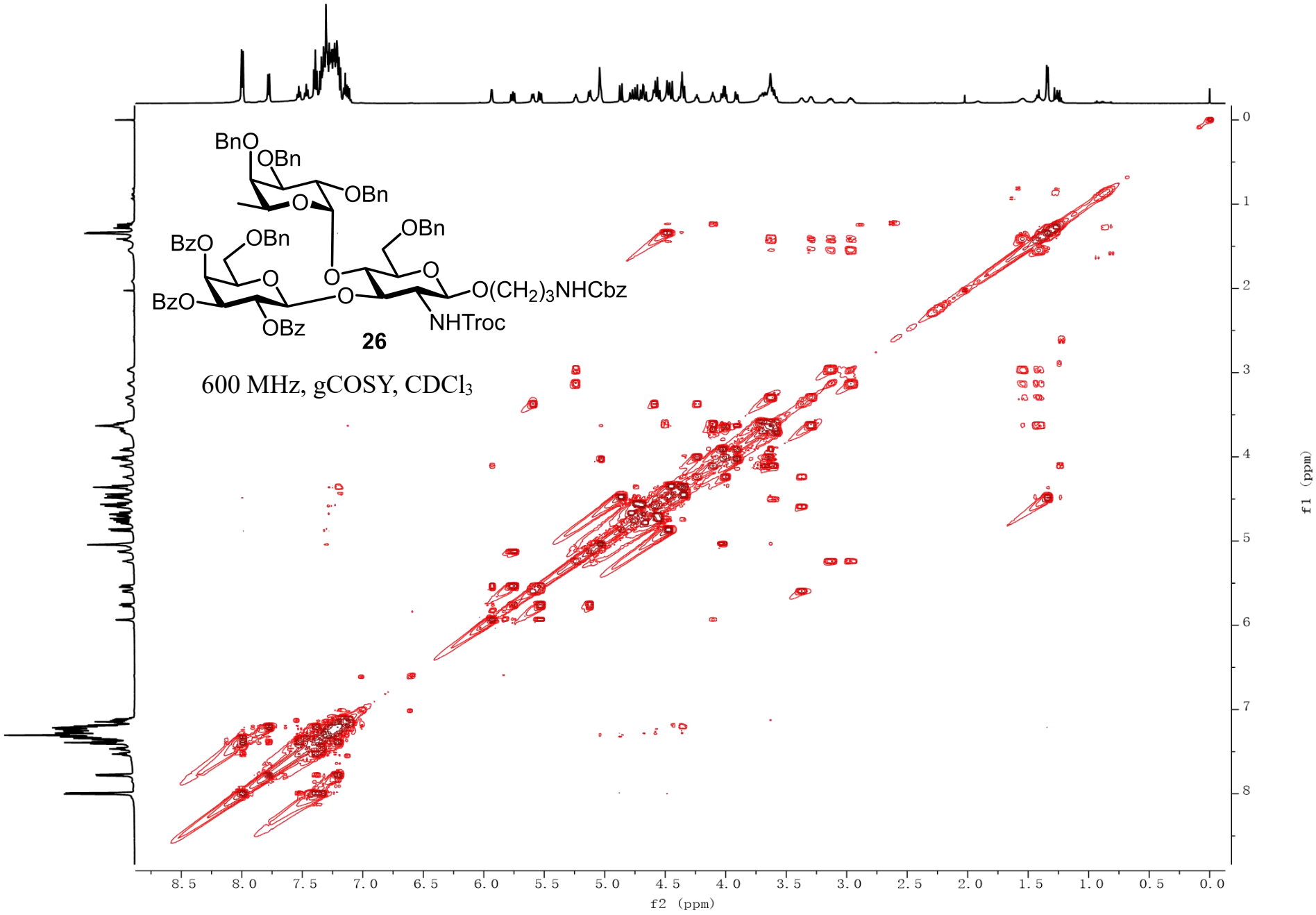


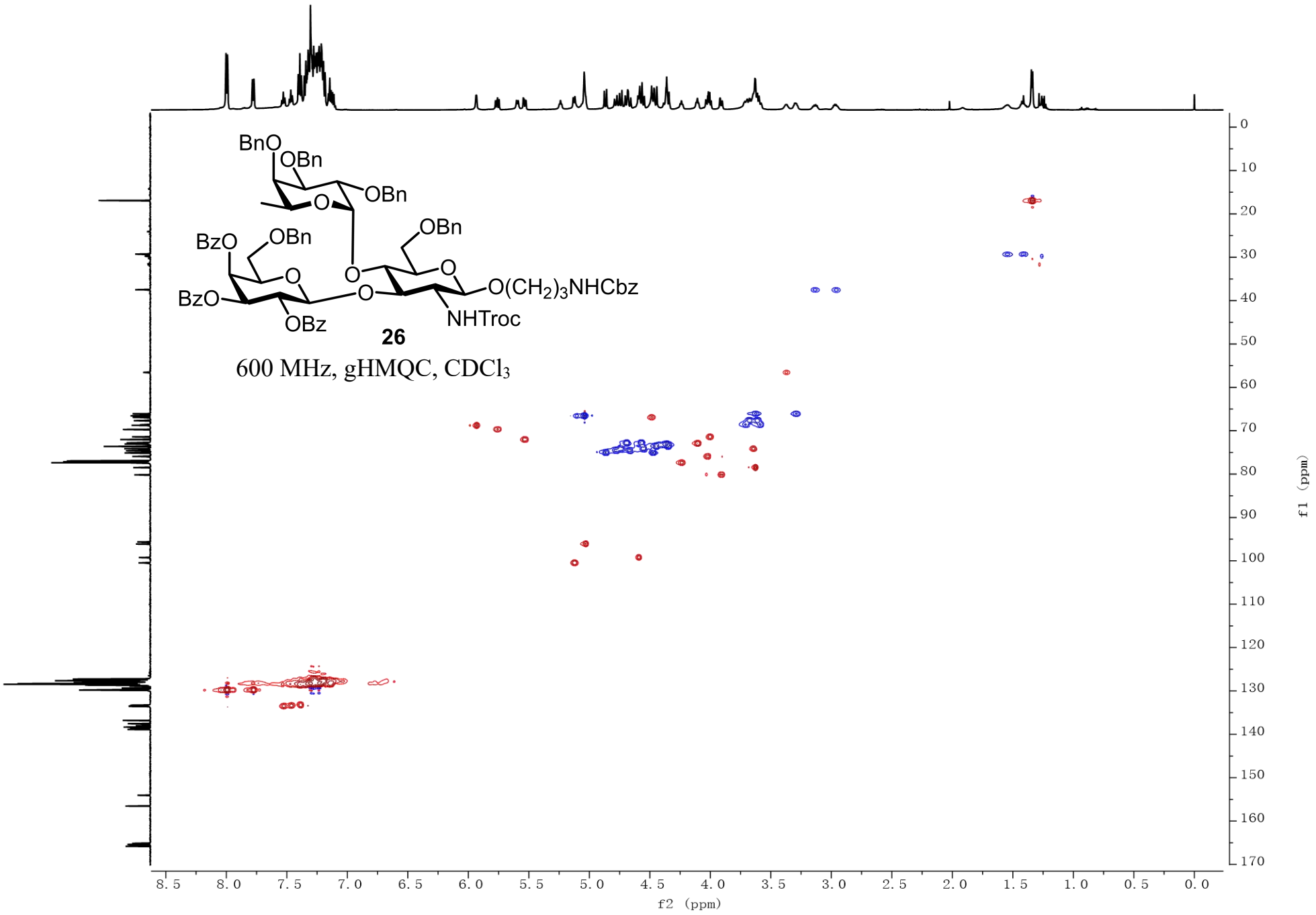


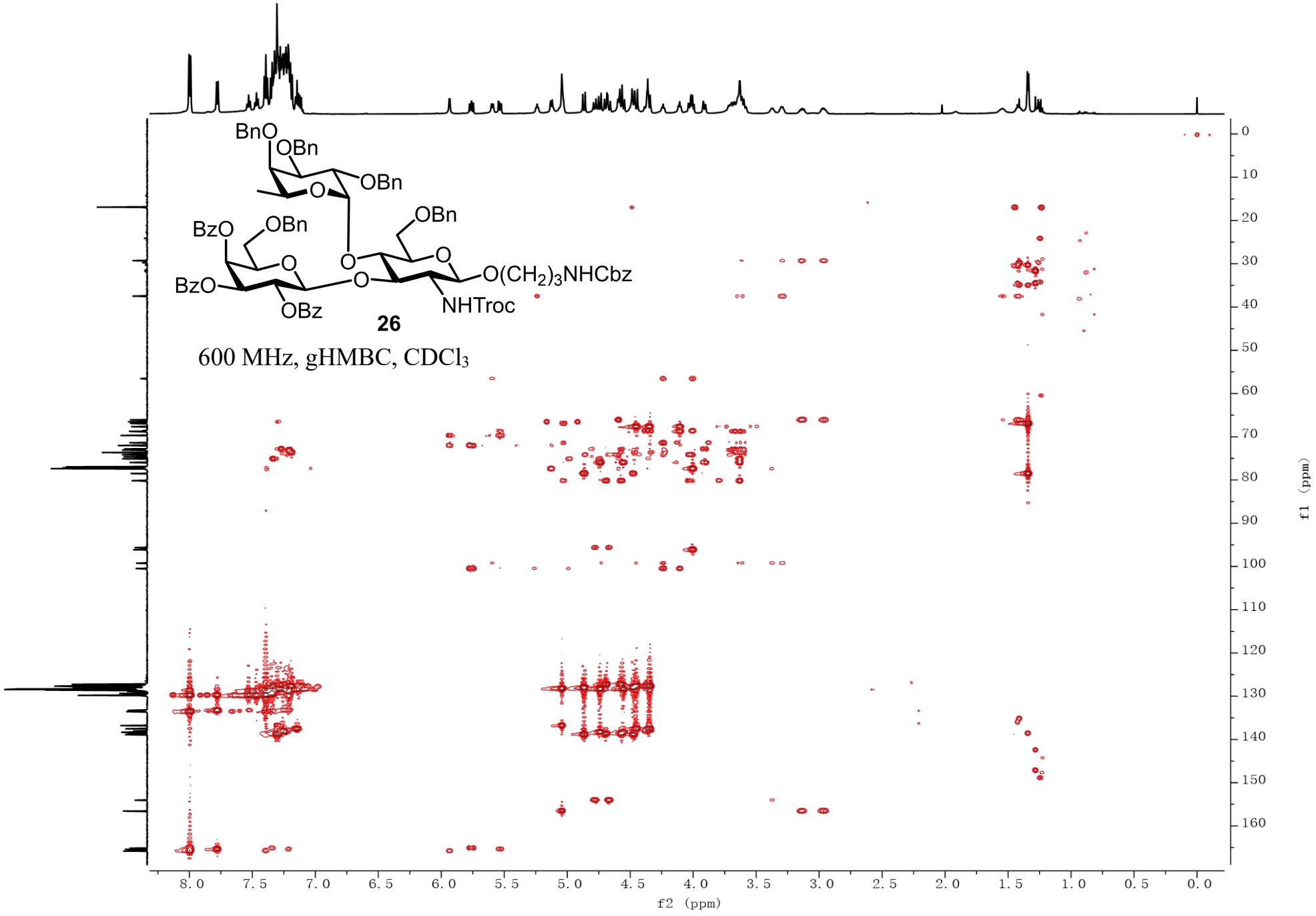
26

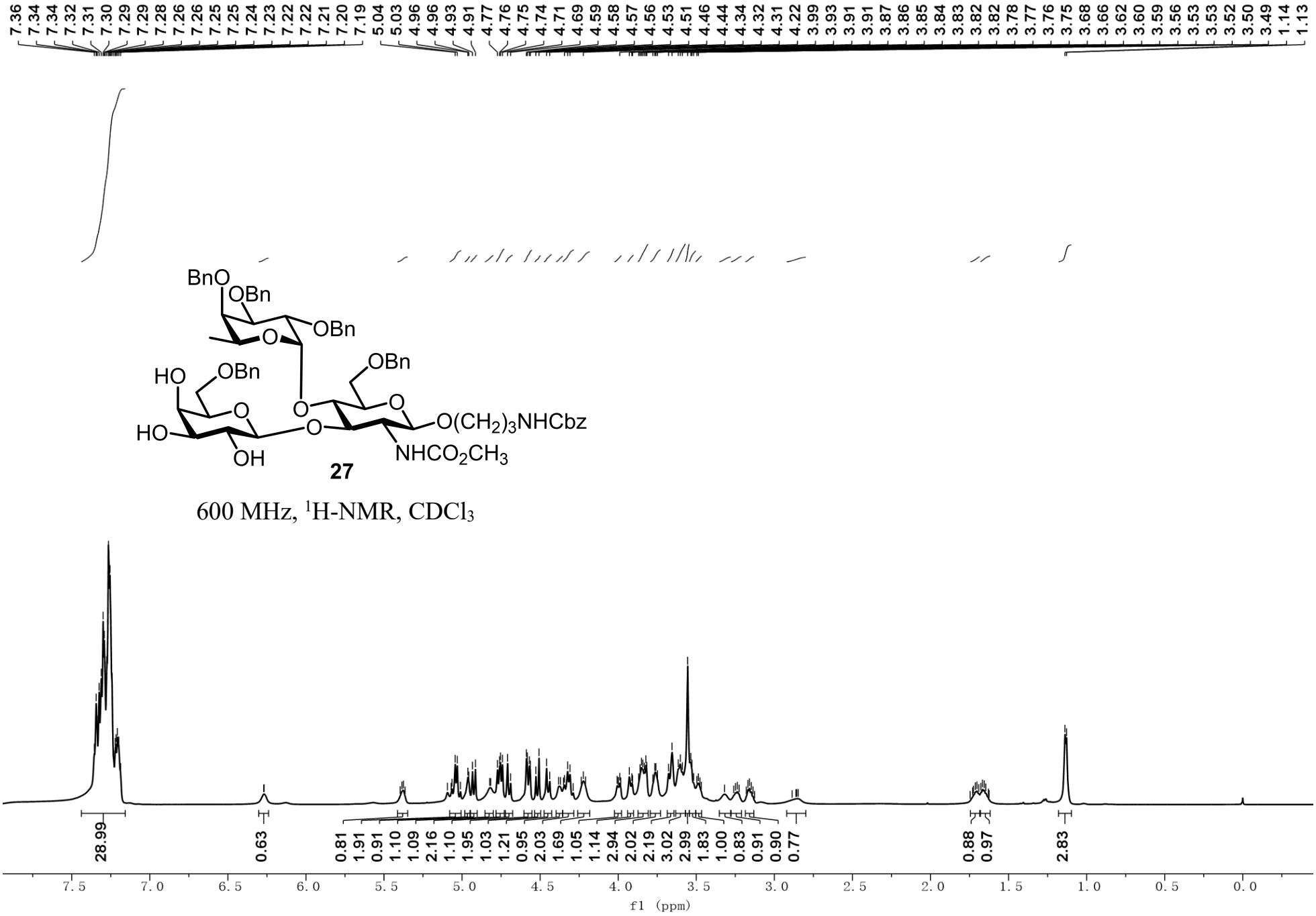
150 MHz, ^{13}C-NMR, $CDCl_3$

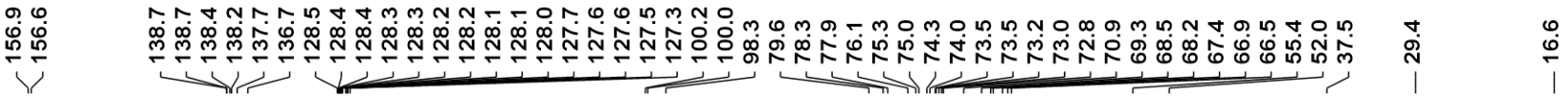


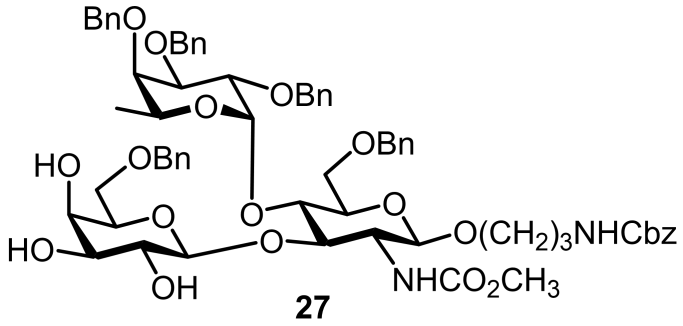

BnO
OBn
OBn
BzO
OBn
OBn
O
O
O
O
O
BzO
OBz
NHTroc
O(CH2)3NHCbz
26
600 MHz, gCOSY, CDCl3
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


BnO
OBn
OBn
BzO
OBn
OBn
O
O
O
O
O
BzO
OBz
O(CH2)3NHCbz
NHTroc
26
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OBn
OBn
BzO
OBn
OBn
BzO
OBz
O(CH2)3NHCbz
NHTroc
26
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

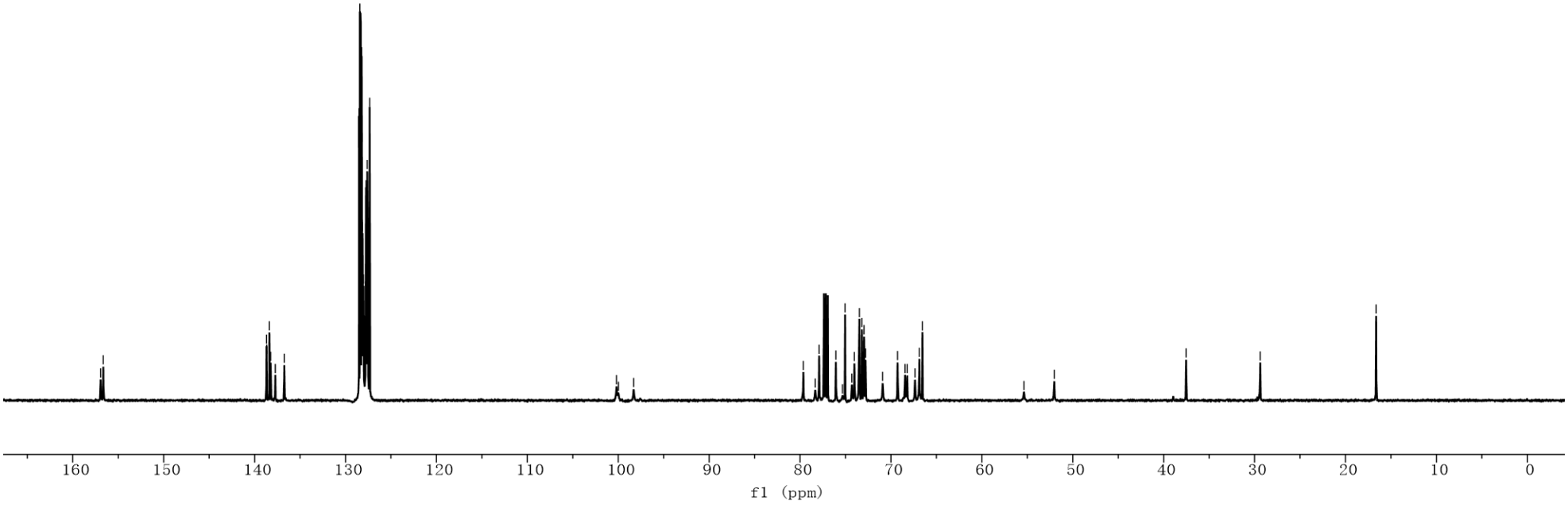

7.36 7.34 7.34 7.32 7.31 7.30 7.29 7.29 7.28 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19
5.04 5.03 4.96 4.96 4.93 4.91 4.77 4.76 4.75 4.74 4.71 4.69 4.59 4.58 4.57 4.56 4.53 4.51 4.46 4.44 4.34 4.32 4.31 4.22 3.99 3.93 3.91 3.91 3.87 3.86 3.85 3.84 3.83 3.82 3.82 3.78 3.77 3.76 3.75 3.68 3.66 3.62 3.60 3.59 3.56 3.53 3.53 3.52 3.50 3.49 1.14 1.13
BnO
OBn
OBn
O
OBn
HO
OBn
O
O
O
HO
O
O(CH2)3NHCbz
OH
NHCO2CH3
27
600 MHz, 1H-NMR, CDCl3
28.99
0.63
0.81 1.91 0.91 1.10 1.09 2.16 1.10 1.95 1.03 1.21 0.95 2.03 1.69 1.05 1.14 2.94 2.02 2.19 3.02 2.99 1.83 1.00 0.83 0.91 0.90 0.77
0.88 0.97
2.83
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

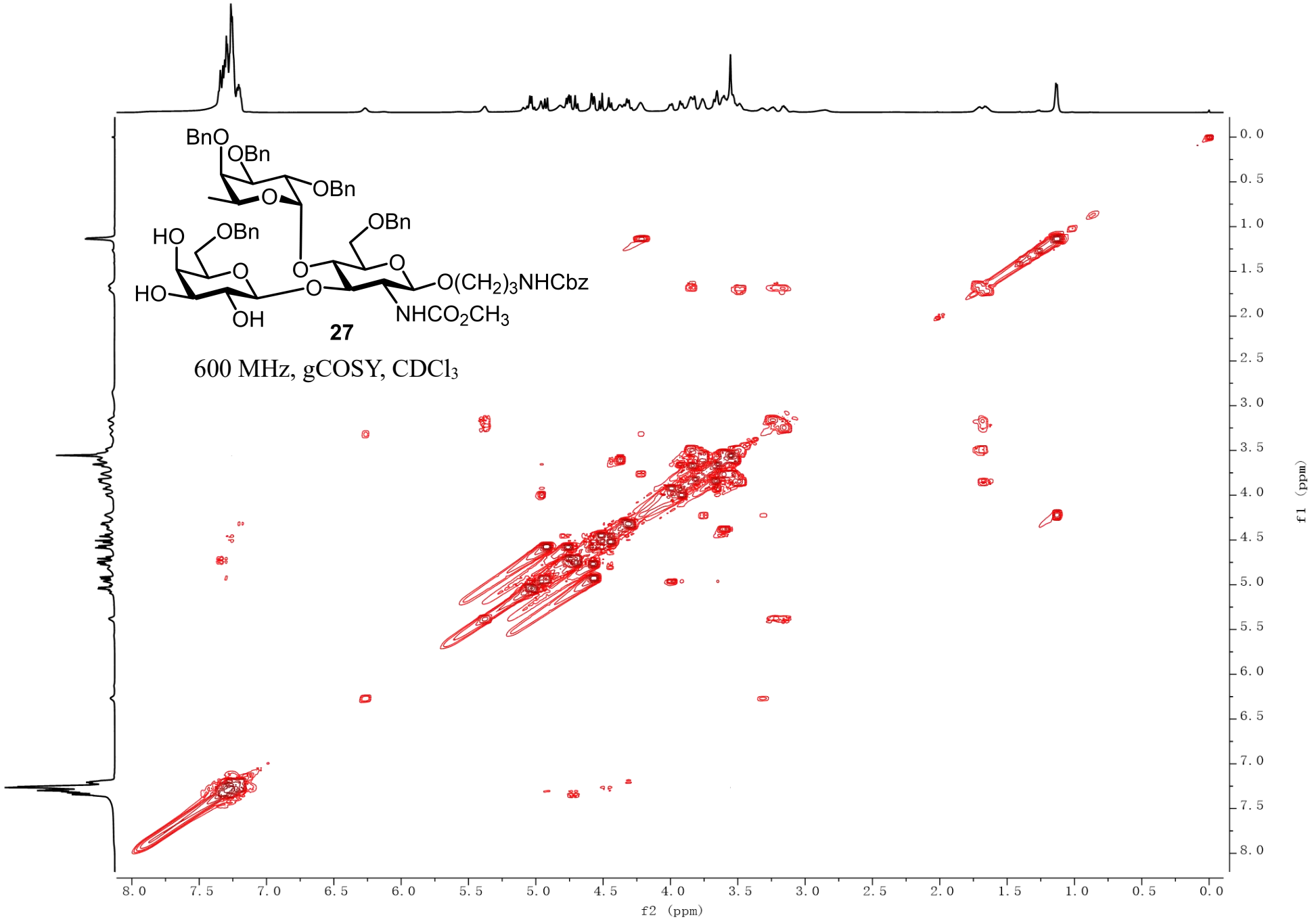


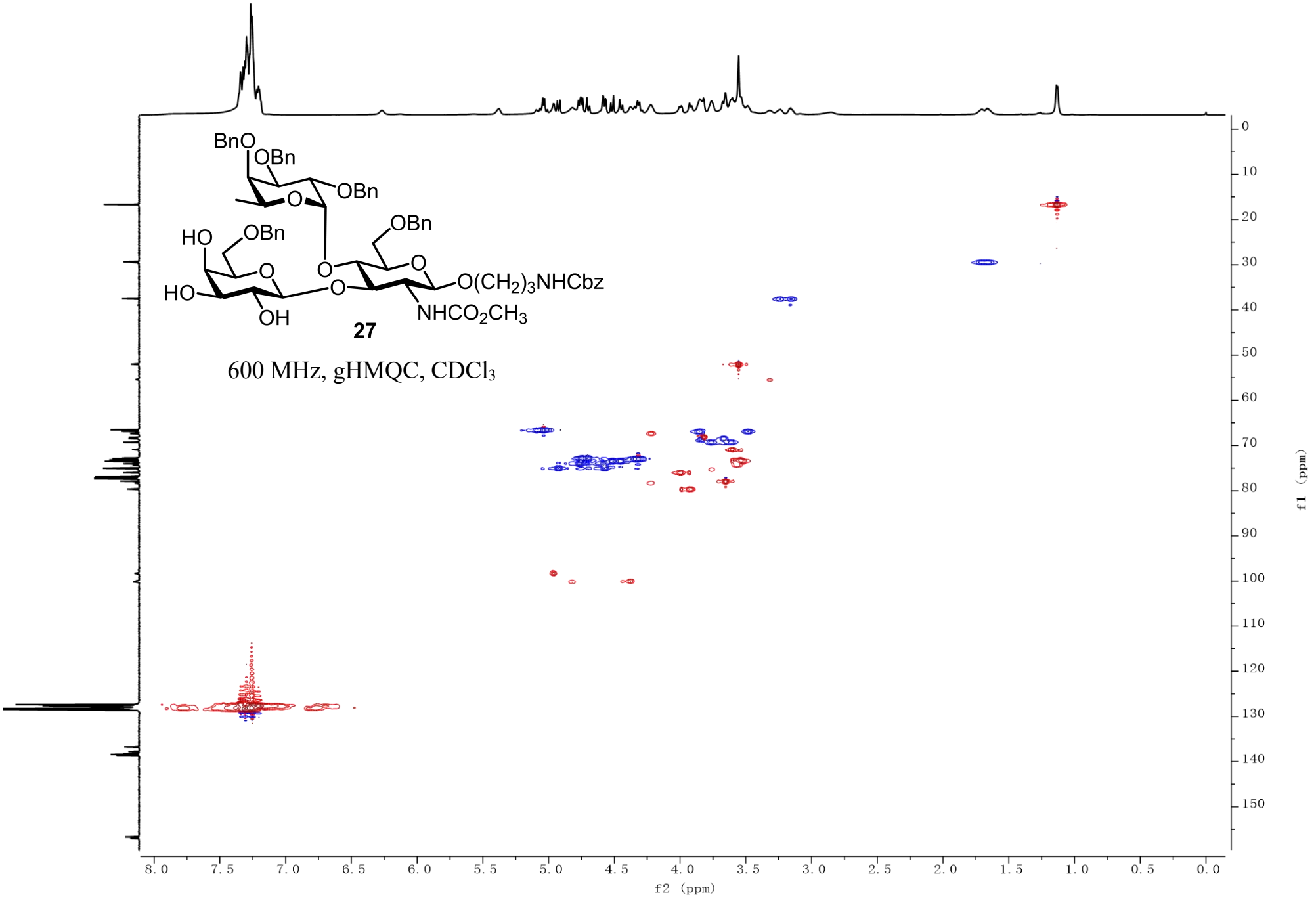


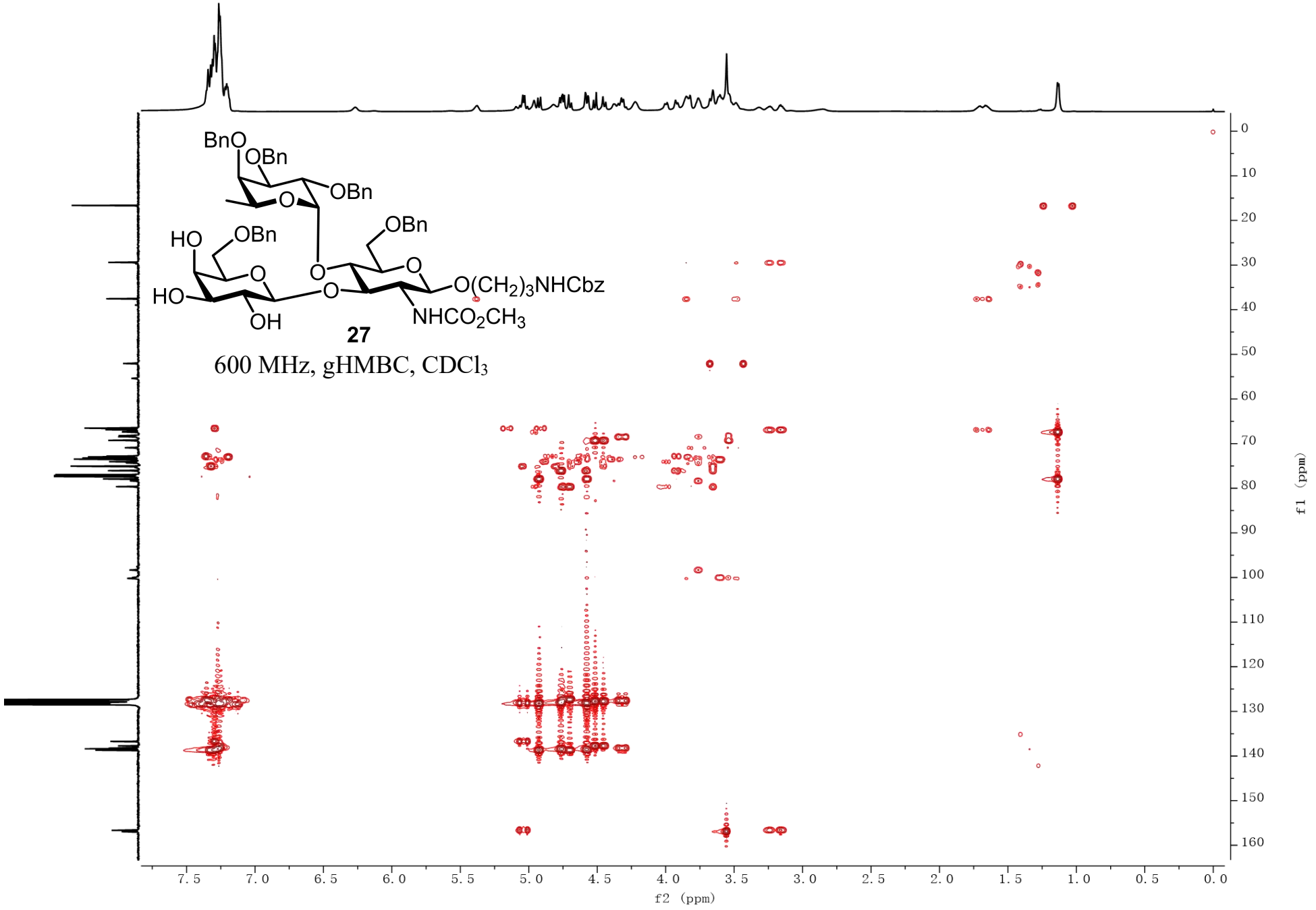
27

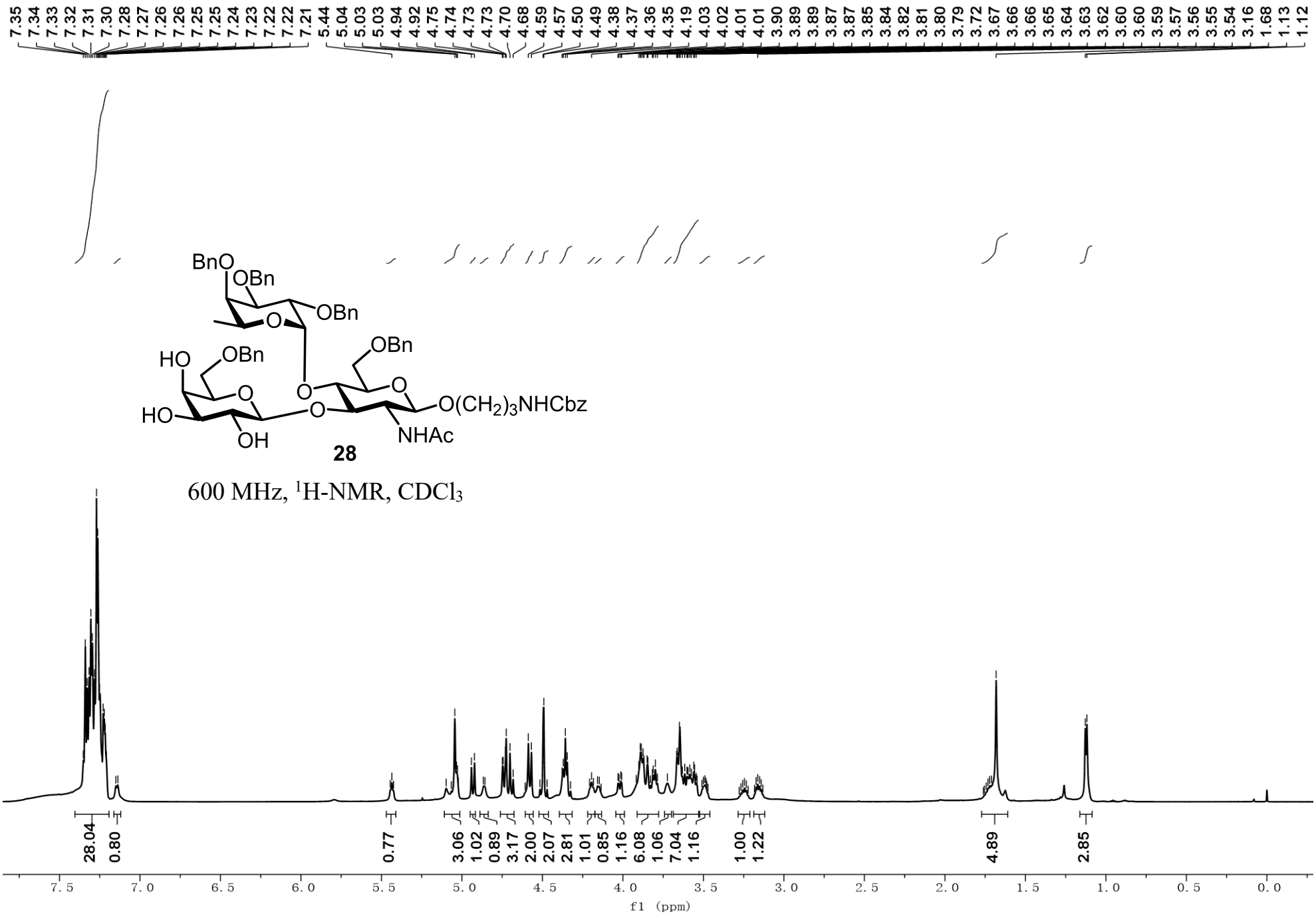
150 MHz, ^{13}C-NMR, $CDCl_3$

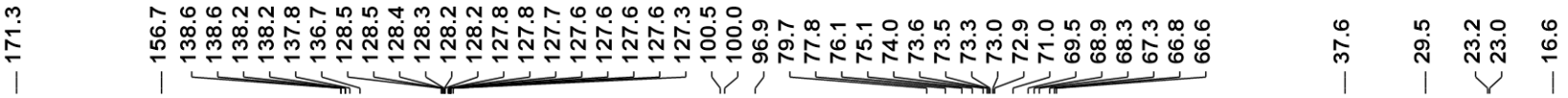


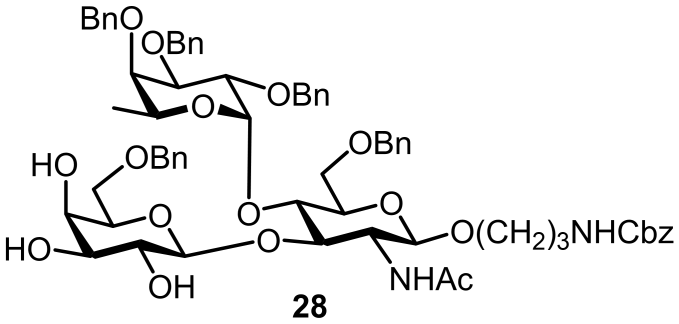

BnO
OBn
OBn
OBn
HO
OBn
HO
OH
O(CH2)3NHCbz
NHCO2CH3
27
600 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OBn
OBn
O
HO
OBn
OBn
O
O
O
O
HO
O
O(CH2)3NHCbz
OH
NHCO2CH3
27
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OBn
OBn
OBn
HO
OBn
HO
OH
O(CH2)3NHCbz
NHCO2CH3
27
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)

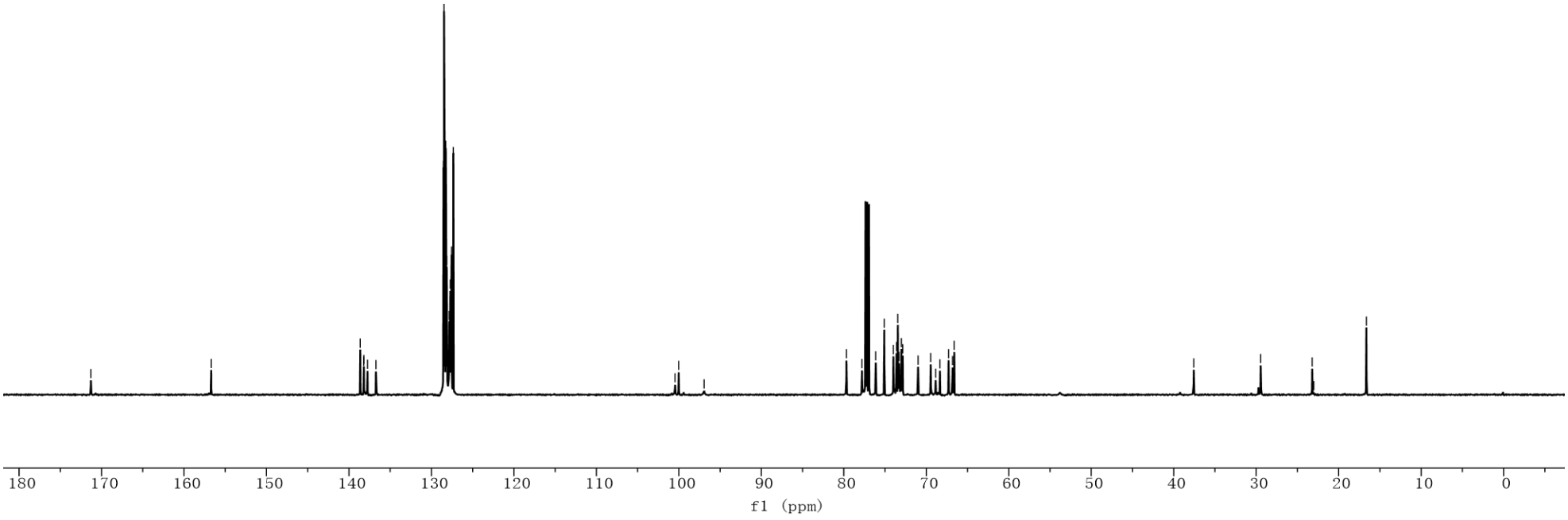

7.35 7.34 7.33 7.32 7.31 7.30 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21
5.44 5.04 5.03 5.03 4.94 4.92 4.75 4.74 4.73 4.73 4.70 4.68 4.59 4.57 4.50 4.49 4.38 4.37 4.36 4.35 4.19 4.03 4.02 4.01 4.01 3.90 3.89 3.89 3.87 3.87 3.85 3.84 3.82 3.81 3.80 3.79 3.72 3.67 3.66 3.66 3.65 3.64 3.63 3.62 3.60 3.60 3.59 3.57 3.56 3.55 3.54 3.16 1.68 1.13 1.12
BnO
OBn
OBn
OBn
HO
OBn
HO
OH
O(CH2)3NHCbz
NHAc
28
600 MHz, 1H-NMR, CDCl3
28.04
0.80
0.77
3.06
1.02
0.89
3.17
2.00
2.07
2.81
1.01
0.85
1.16
6.08
1.06
7.04
1.16
1.00
1.22
4.89
2.85
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

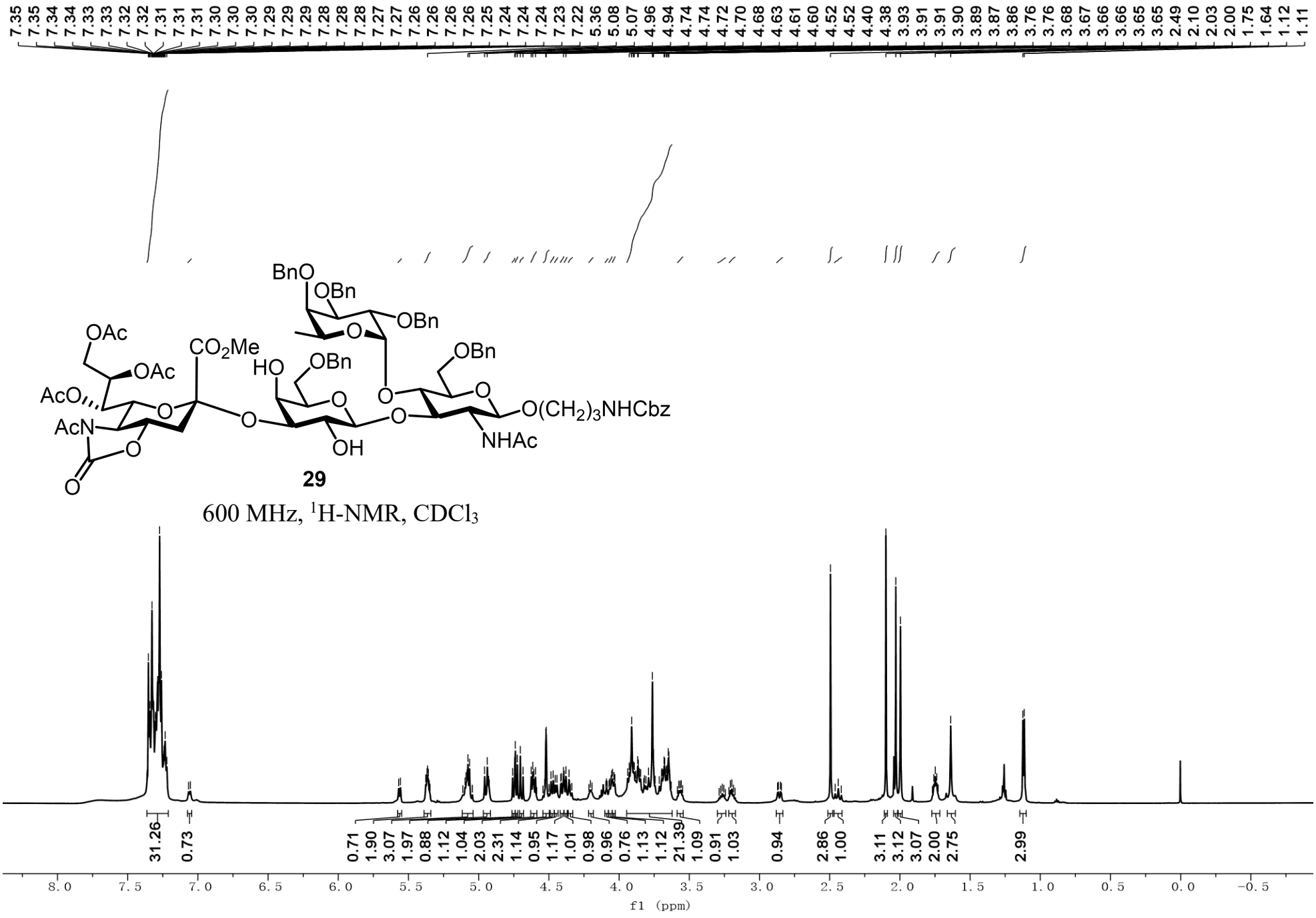


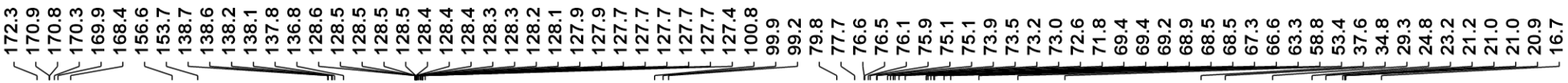


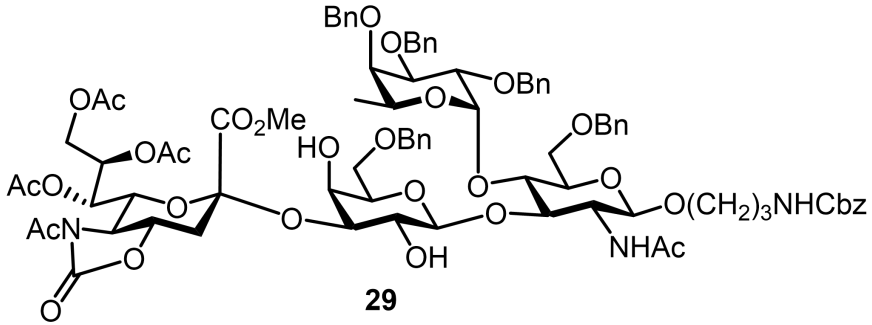
28

150 MHz, ^{13}C-NMR, $CDCl_3$




7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.26 7.26 7.25 7.24 7.24 7.24 7.23 7.22 5.36 5.08 5.07 4.96 4.94 4.74 4.74 4.72 4.70 4.68 4.63 4.61 4.60 4.52 4.52 4.40 4.38 3.93 3.91 3.91 3.90 3.89 3.87 3.86 3.76 3.76 3.68 3.67 3.66 3.66 3.65 3.65 2.49 2.10 2.03 2.00 1.75 1.64 1.12 1.11
BnO
OBn
OBn
OAc
CO2Me
OAc
HO
OBn
OBn
AcO
O
O
O
O
O(CH2)3NHCbz
AcN
O
O
OH
NHAc
O
29
600 MHz, 1H-NMR, CDCl3
31.26
0.73
0.71
1.90
3.07
1.97
0.88
1.12
1.04
2.03
2.31
1.14
0.95
1.17
1.01
0.98
0.96
0.76
1.13
1.12
21.39
1.09
0.91
1.03
0.94
2.86
1.00
3.11
3.12
3.07
2.00
2.75
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

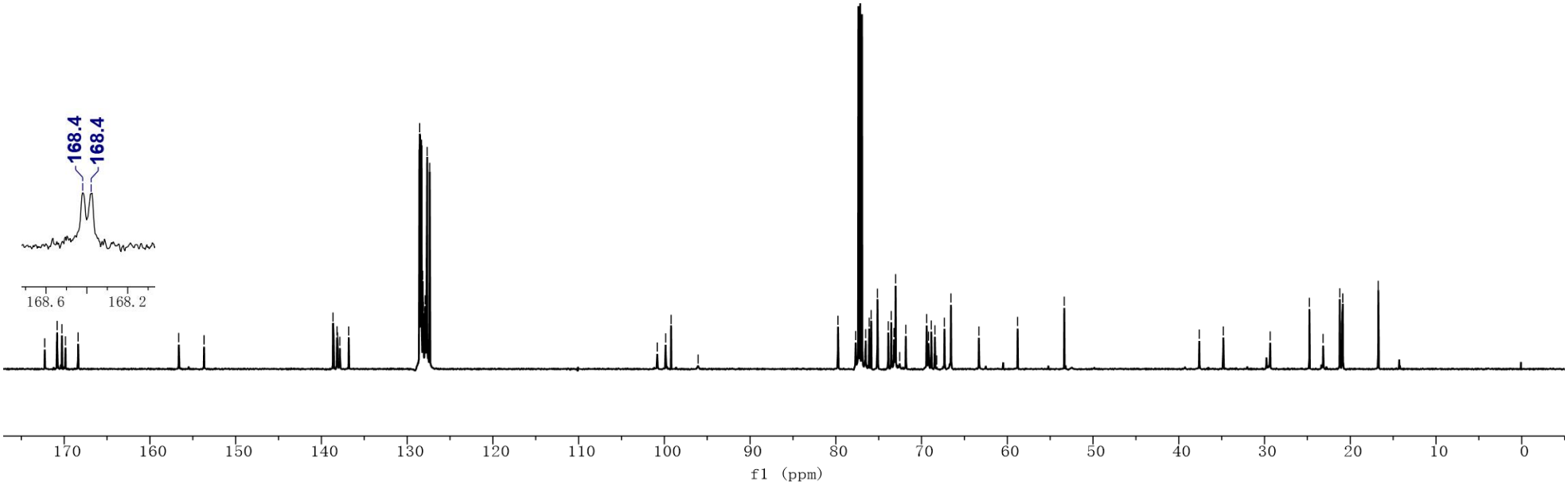


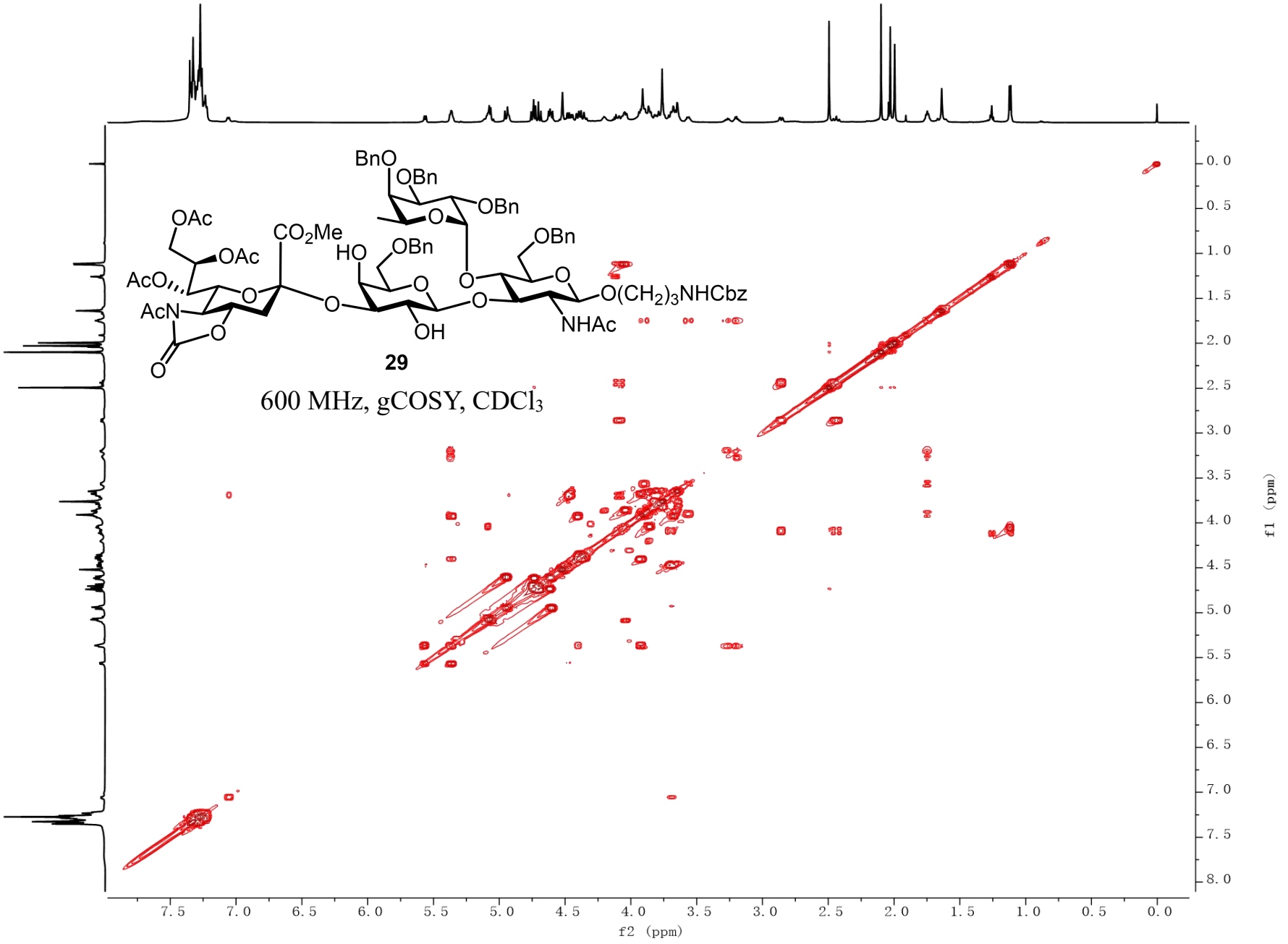


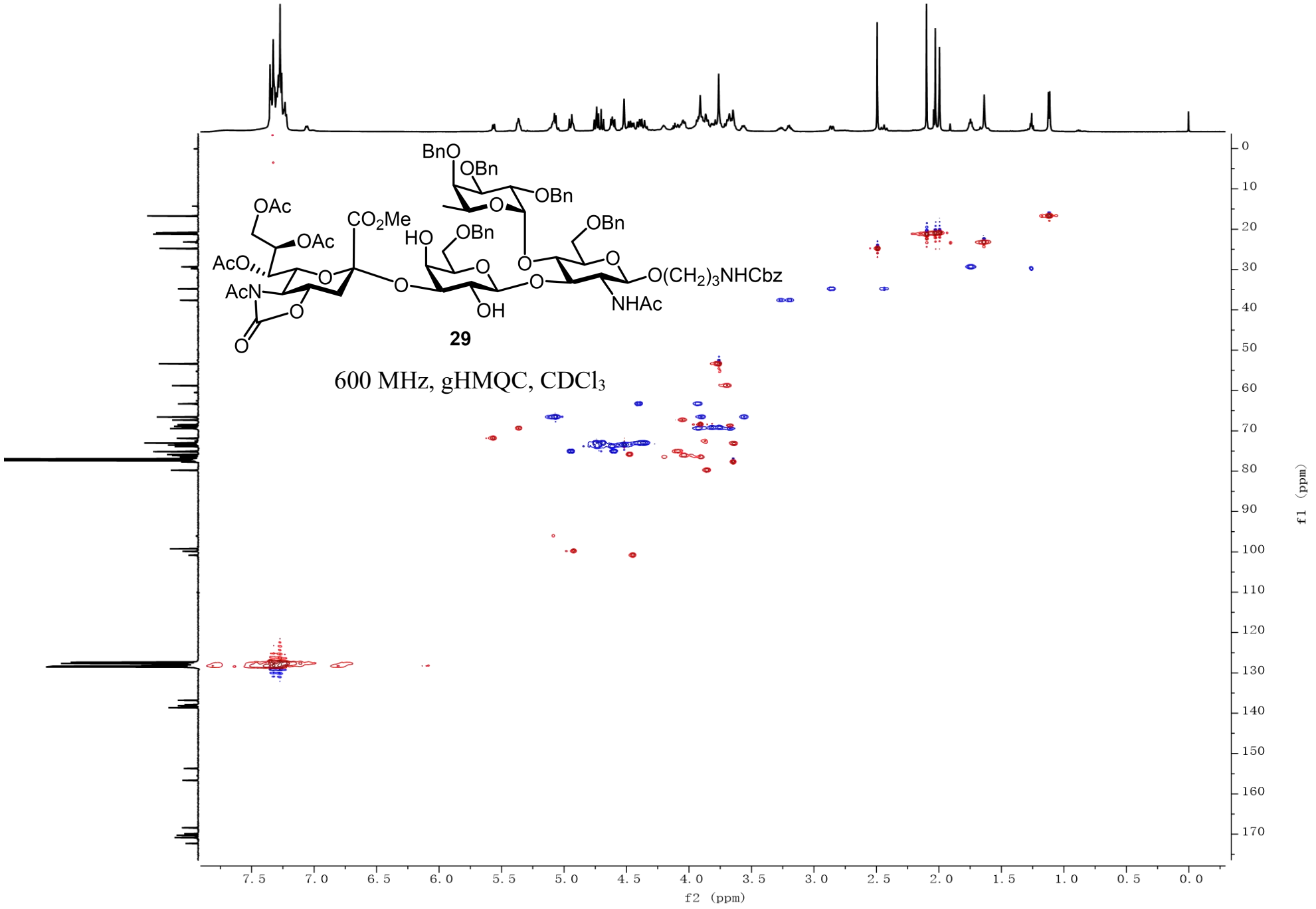
29

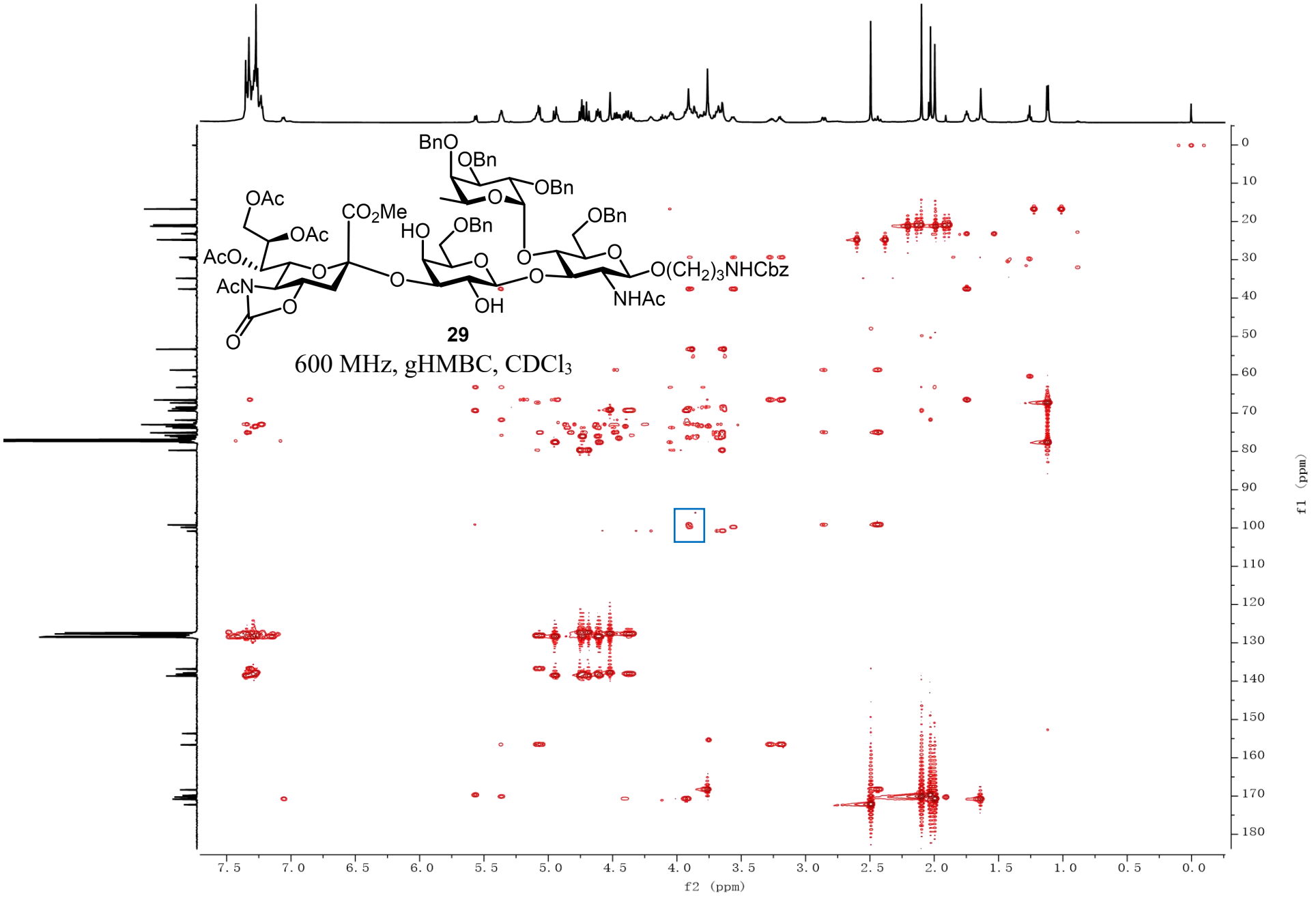
150 MHz, ^{13}C-NMR, $CDCl_3$

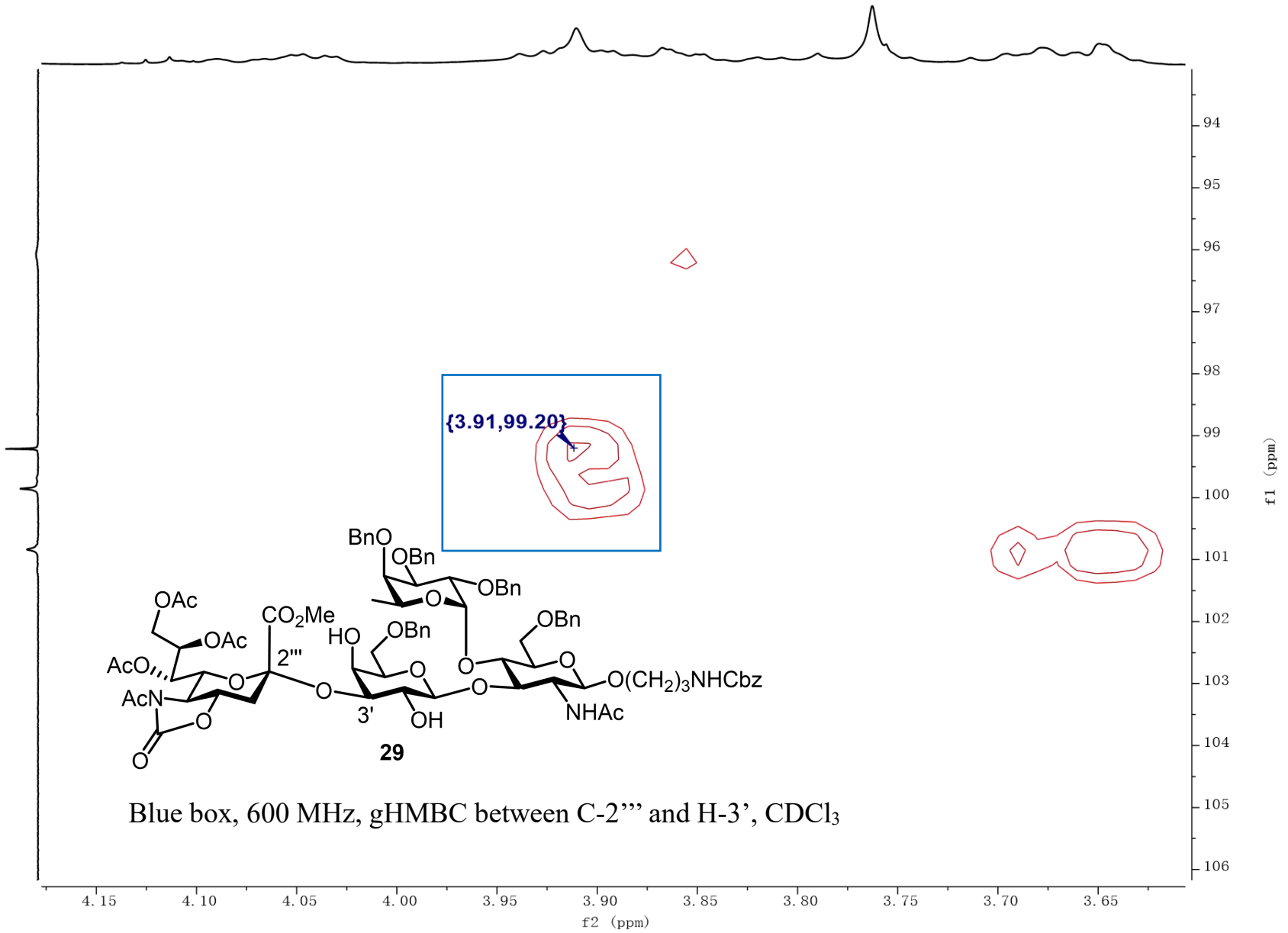
150 MHz, Non-decoupling ^{13}C-NMR, $CDCl_3$



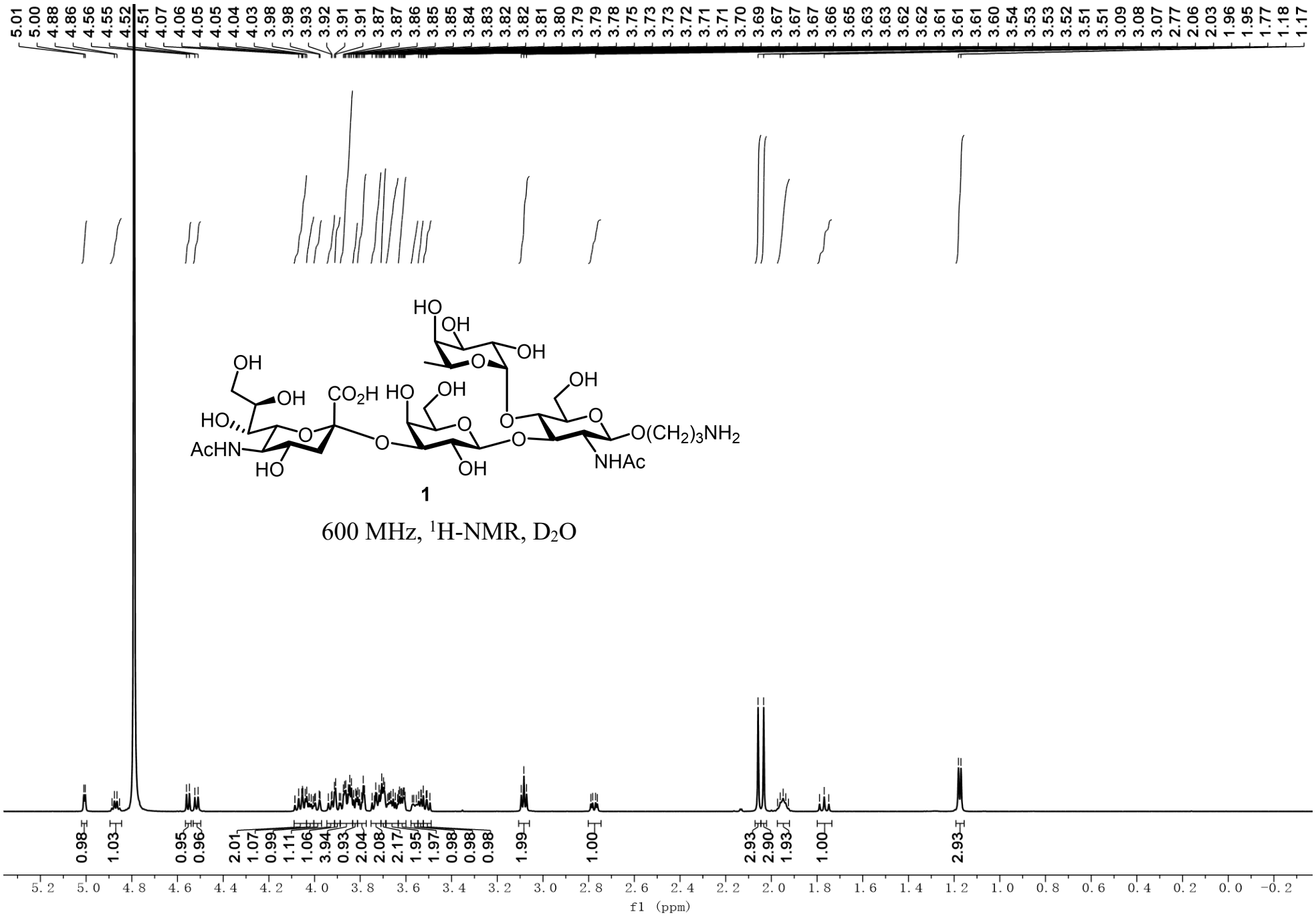

BnO
OBn
OBn
OBn
OAc
OAc
CO2Me
HO
OBn
AcO
AcN
O(CH2)3NHCbz
NHAc
OH
29
600 MHz, gCOSY, CDCl3
f2 (ppm)
f1 (ppm)

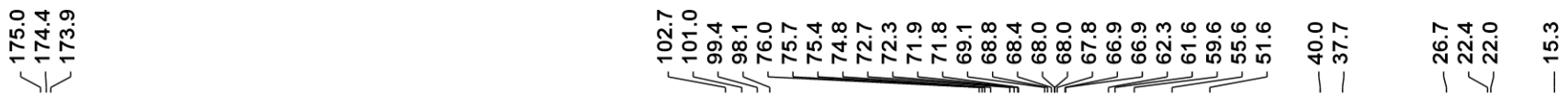

BnO
OBn
OBn
OBn
OAc
OAc
CO2Me
HO
OBn
AcO
AcN
O(CH2)3NHCbz
NHAc
OH
29
600 MHz, gHMQC, CDCl3
f2 (ppm)
f1 (ppm)

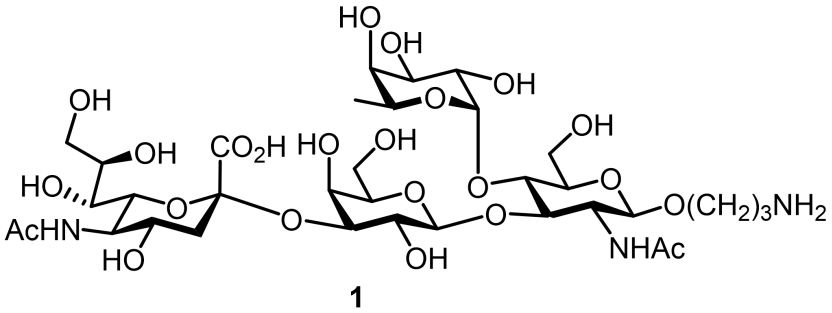

BnO
OBn
OBn
OBn
O
OAc
OAc
CO2Me
HO
OBn
AcO
AcN
O
O
O
O
O
O
O
O(CH2)3NHCbz
NHAc
OH
O
29
600 MHz, gHMBC, CDCl3
f2 (ppm)
f1 (ppm)



Blue box, 600 MHz, gHMBC between C-2’’’ and H-3’, $CDCl_3$


5.01 5.00 4.88 4.86 4.56 4.55 4.52 4.51 4.07 4.06 4.05 4.05 4.04 4.03 3.98 3.98 3.93 3.92 3.91 3.91 3.87 3.87 3.86 3.85 3.85 3.84 3.83 3.82 3.82 3.81 3.80 3.79 3.79 3.78 3.75 3.73 3.73 3.72 3.71 3.71 3.70 3.69 3.67 3.67 3.67 3.66 3.65 3.63 3.63 3.62 3.61 3.61 3.61 3.60 3.54 3.53 3.53 3.52 3.51 3.51 3.09 3.08 3.07 2.77 2.06 2.03 1.96 1.95 1.77 1.18 1.17
HO
OH
OH
O
OH
OH
CO2H
HO
OH
HO
O
O
O
O(CH2)3NH2
AcHN
O
O
NHAc
HO
OH
1
600 MHz, 1H-NMR, D2O
0.98 1.03 0.95 0.96 2.01 1.07 0.99 1.11 1.06 3.94 0.93 2.04 2.08 2.17 1.95 1.97 0.98 0.98 0.98 1.99 1.00 2.93 2.90 1.93 1.00 2.93
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 −0.2
f1 (ppm)

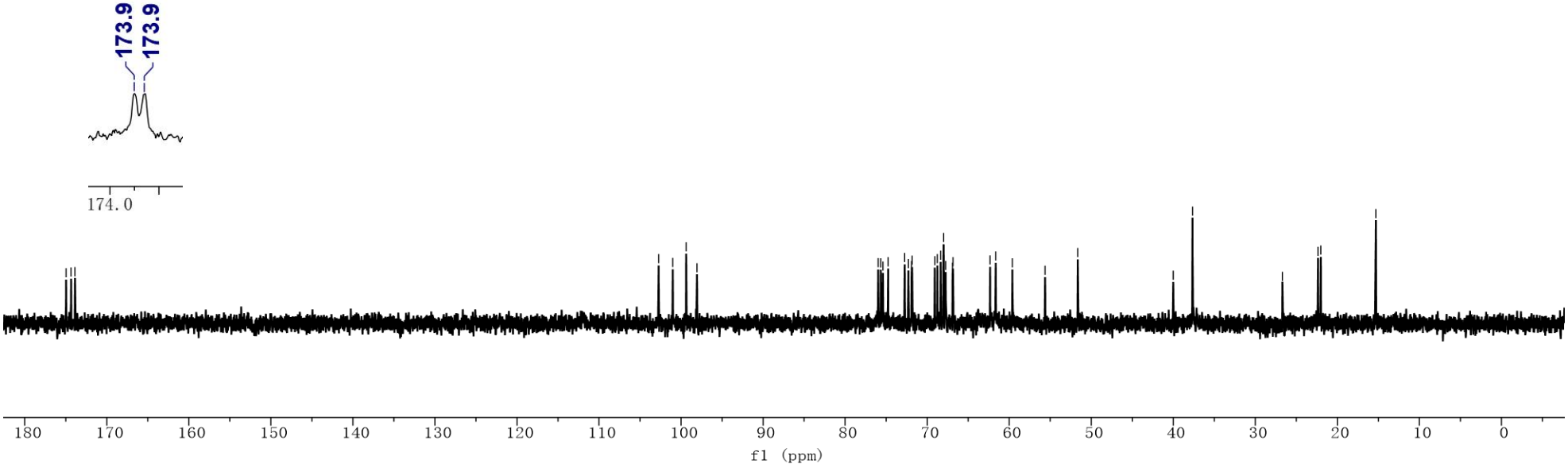


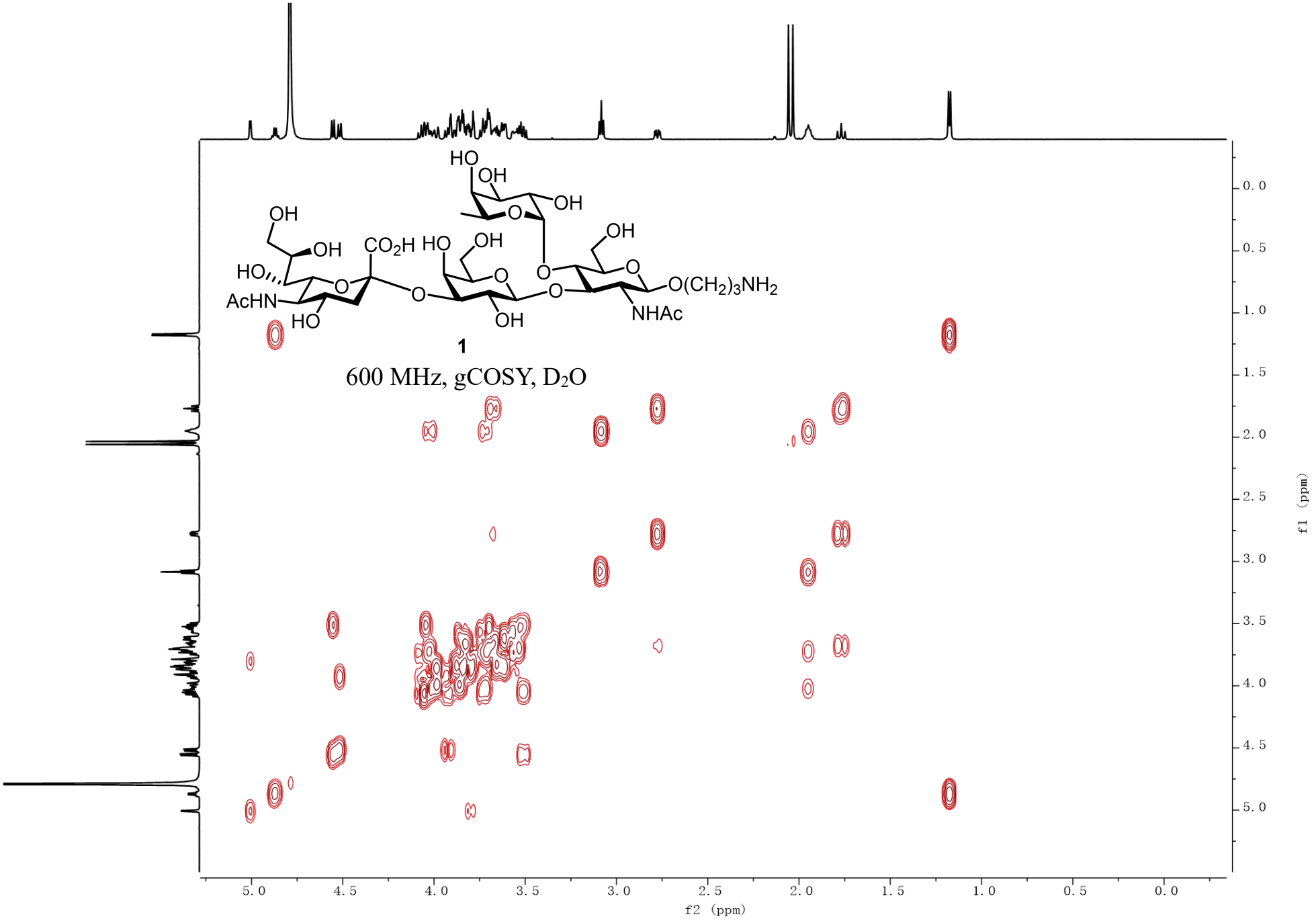


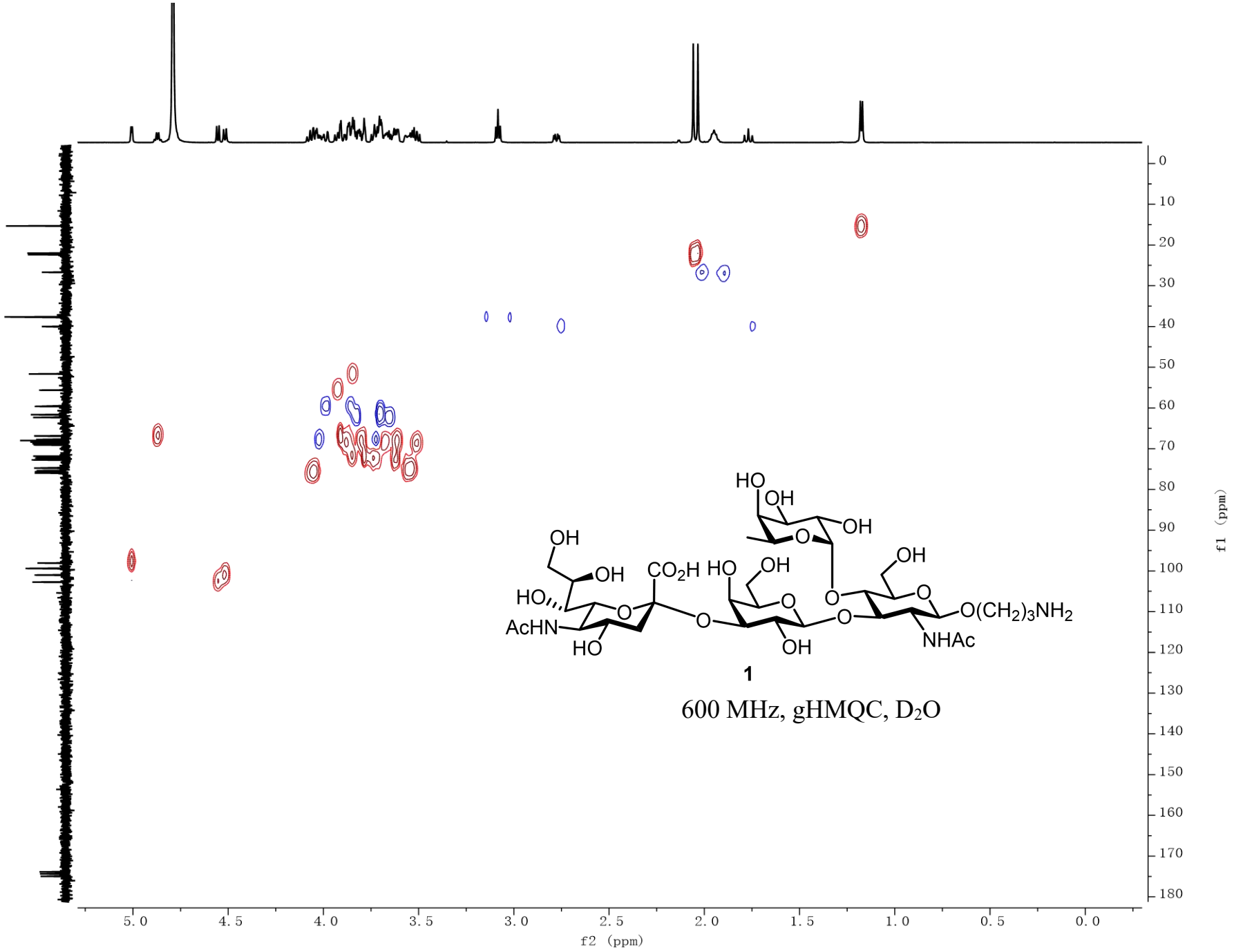
1

150 MHz, ^{13}C-NMR, D_2O

150 MHz, Non-decoupling ^{13}C-NMR, D_2O

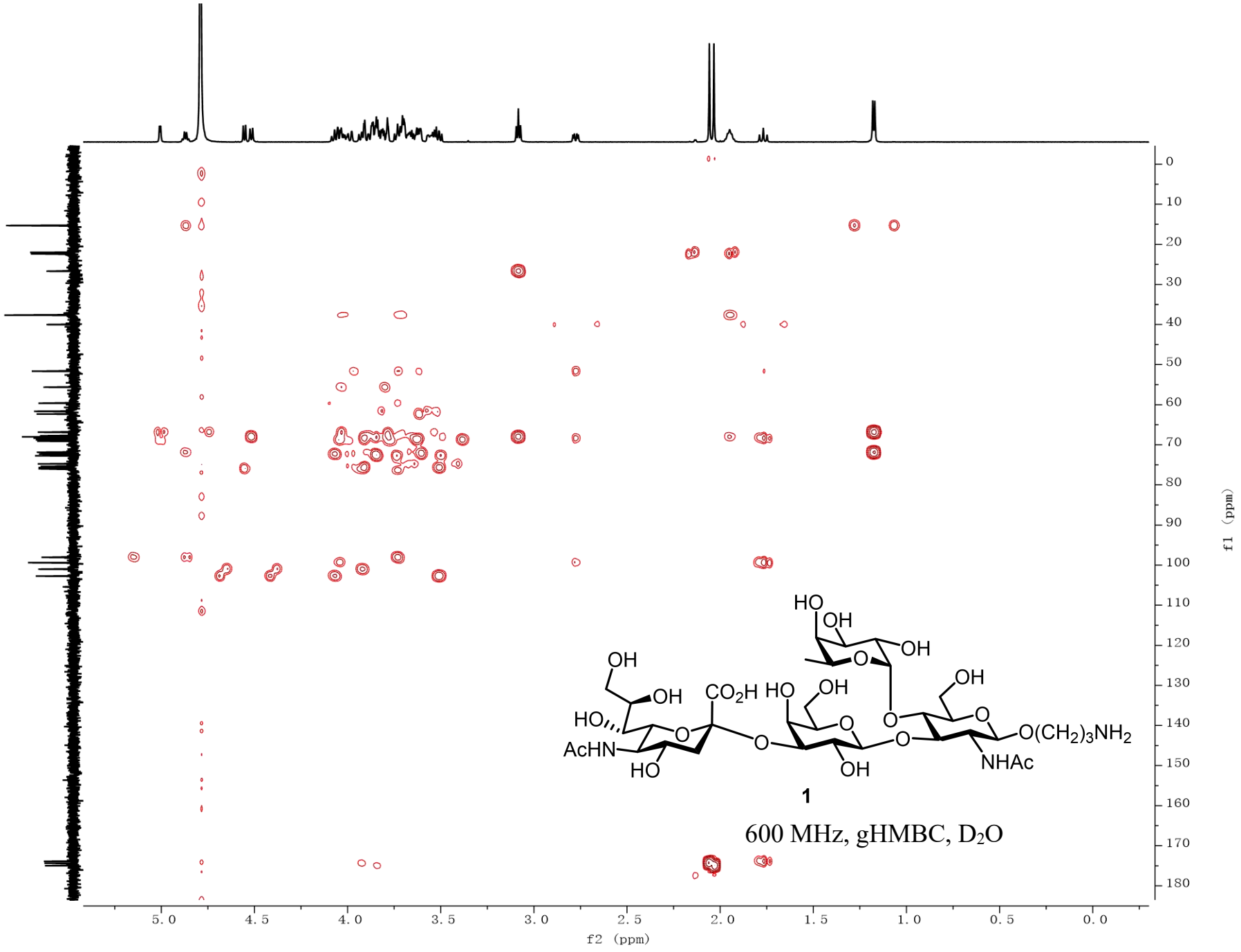


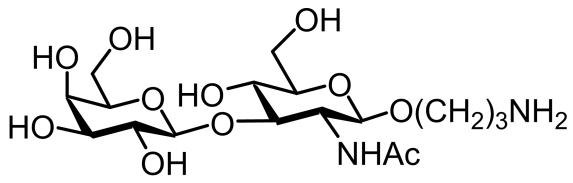

HO
OH
OH
OH
O
OH
OH
CO2H
HO
OH
HO
O
O
O
O
O(CH2)3NH2
AcHN
O
O
NHAc
HO
OH
1
600 MHz, gCOSY, D2O
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
f1 (ppm)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)



1

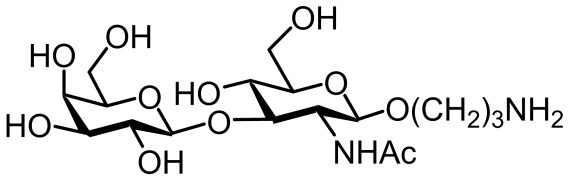
600 MHz, gHMQC, D_2O


f2 (ppm)
f1 (ppm)
1
600 MHz, gHMBC, D2O



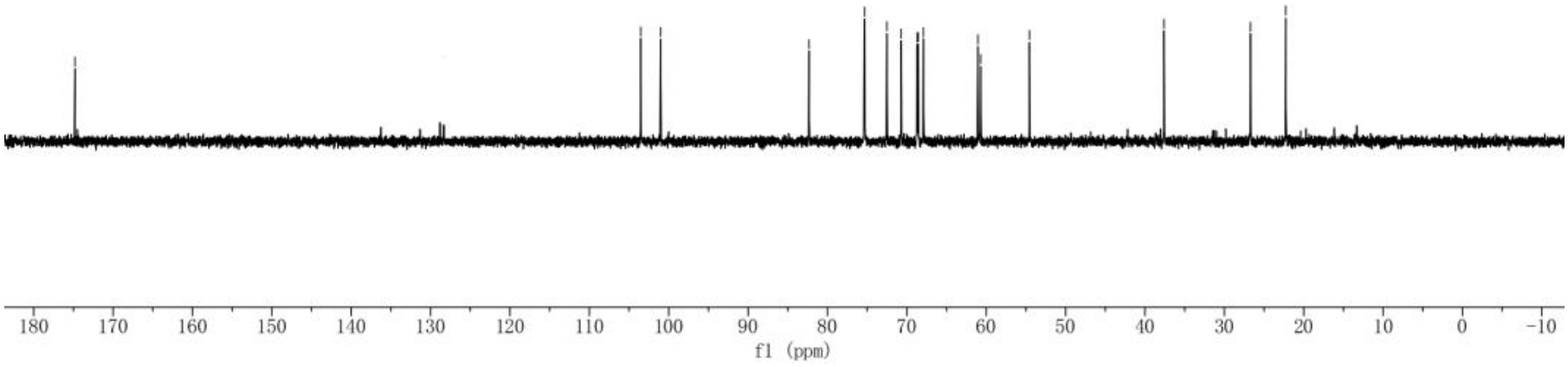
30

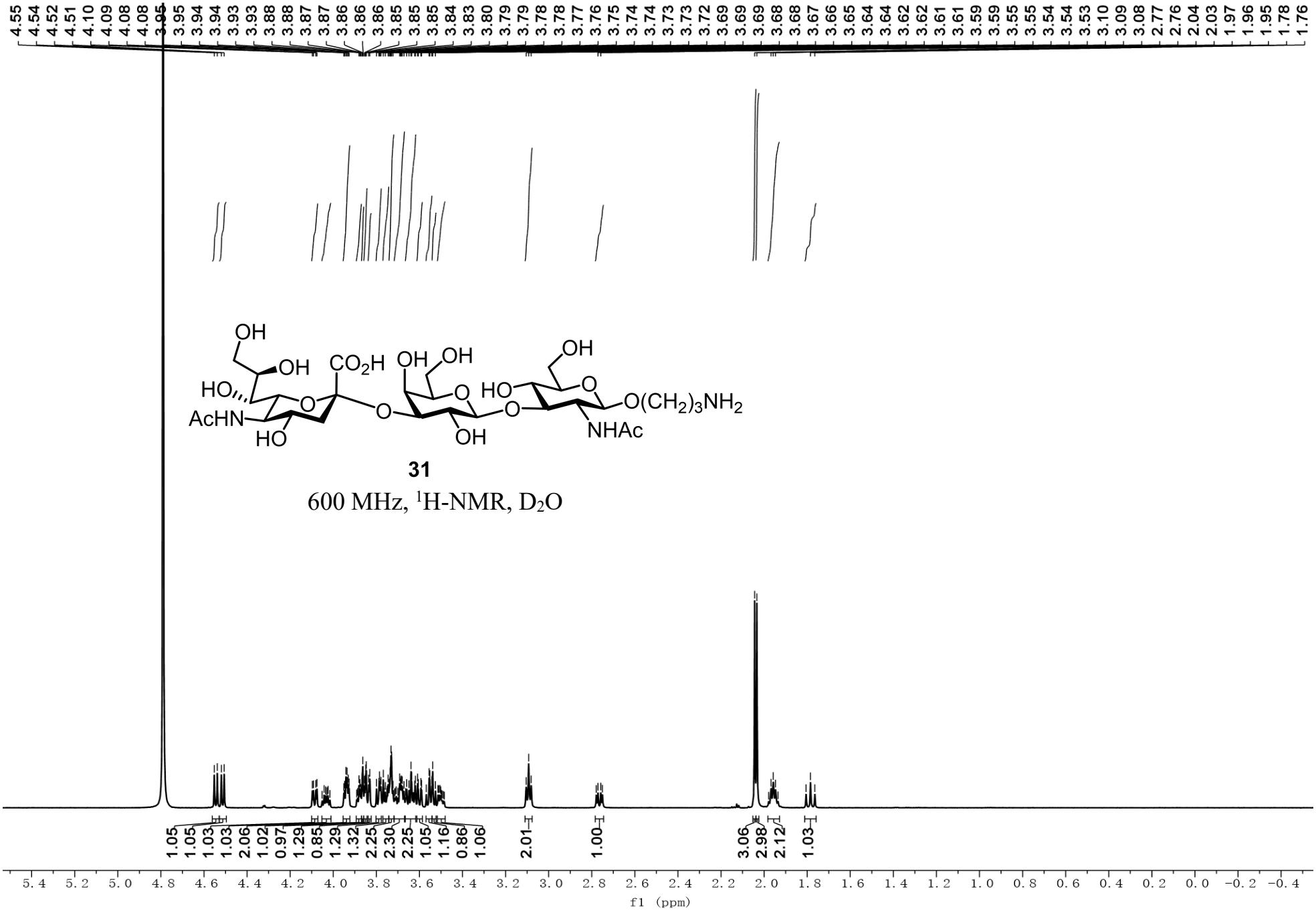
400 MHz, ^{1}H-NMR, D_2O



30

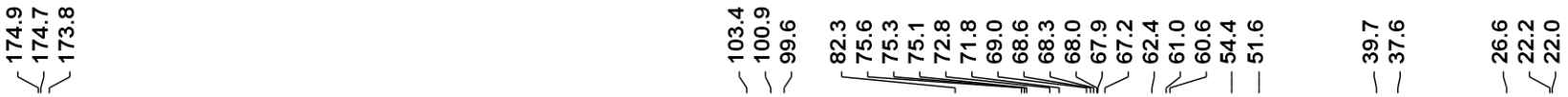
100 MHz, ^{13}C-NMR, D_2O

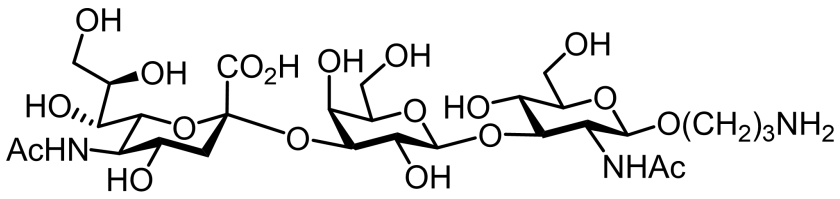




31

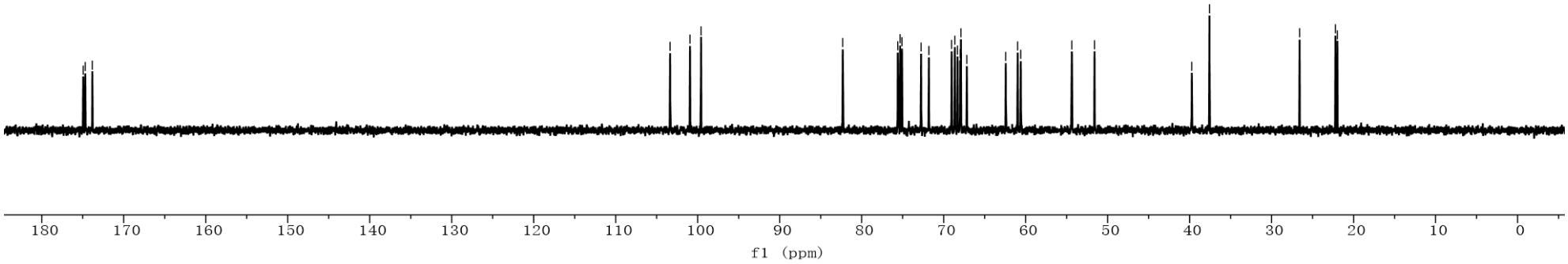
600 MHz, ^{1}H-NMR, D_2O

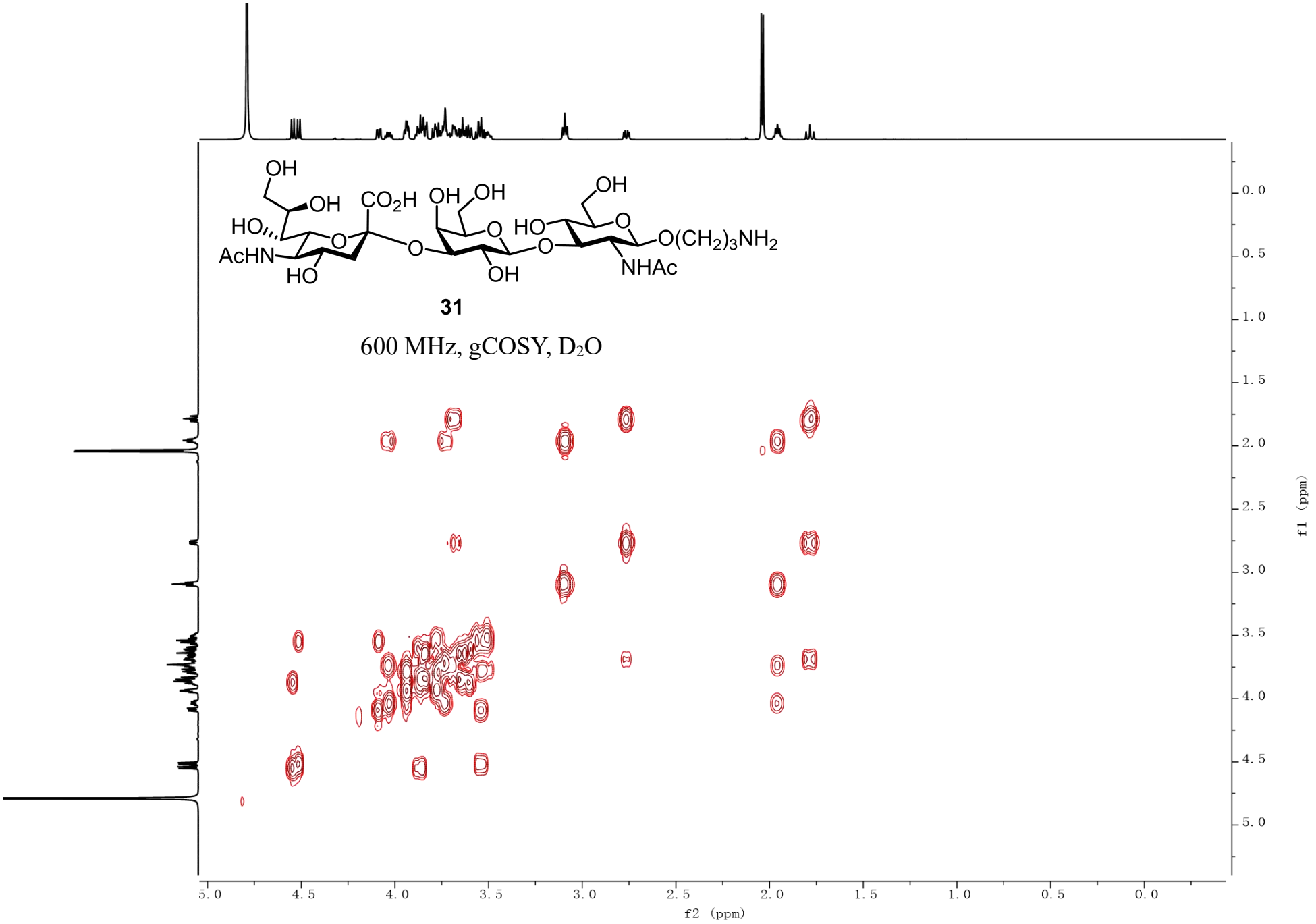


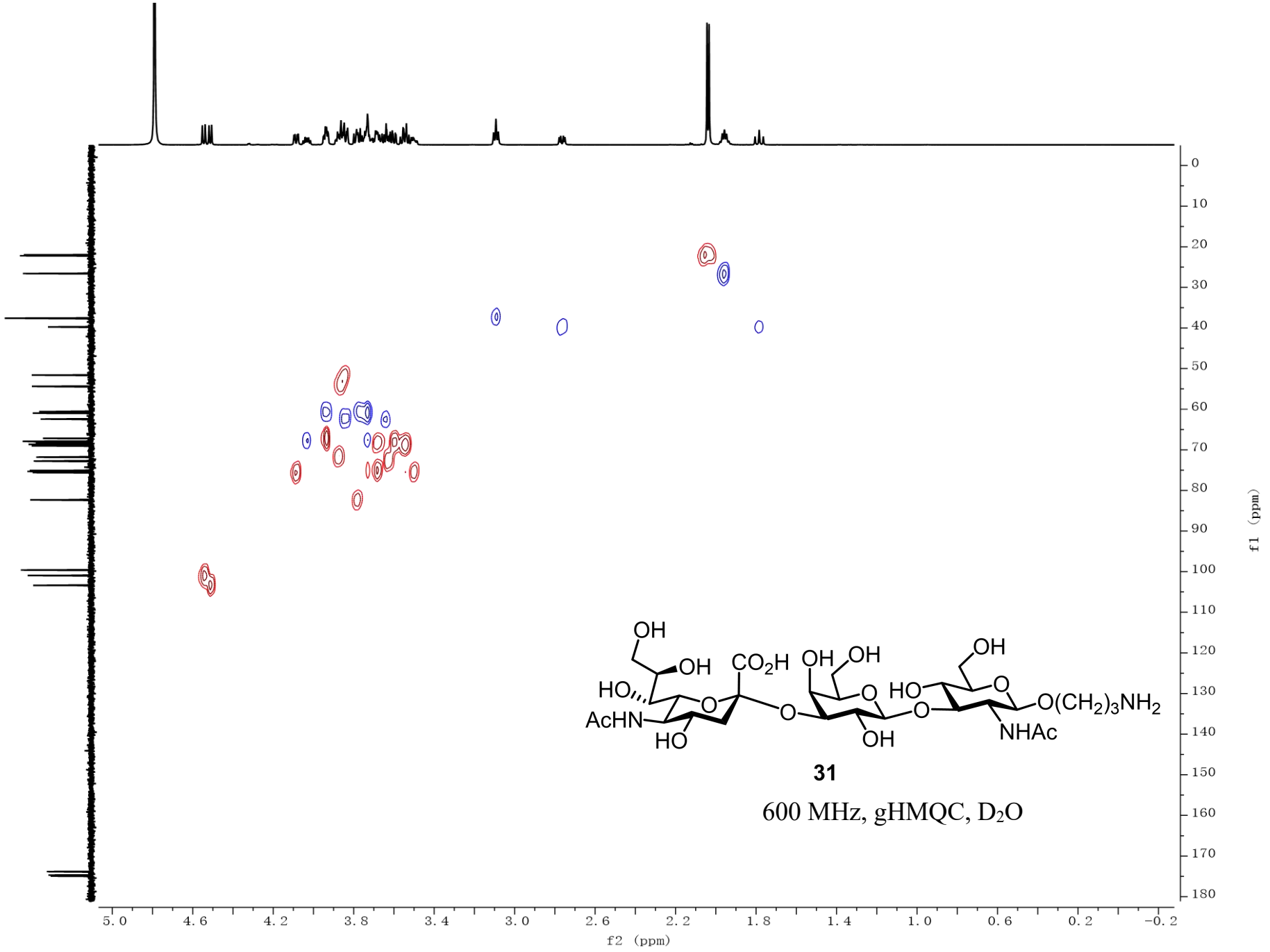


31

150 MHz, ^{13}C-NMR, D_2O

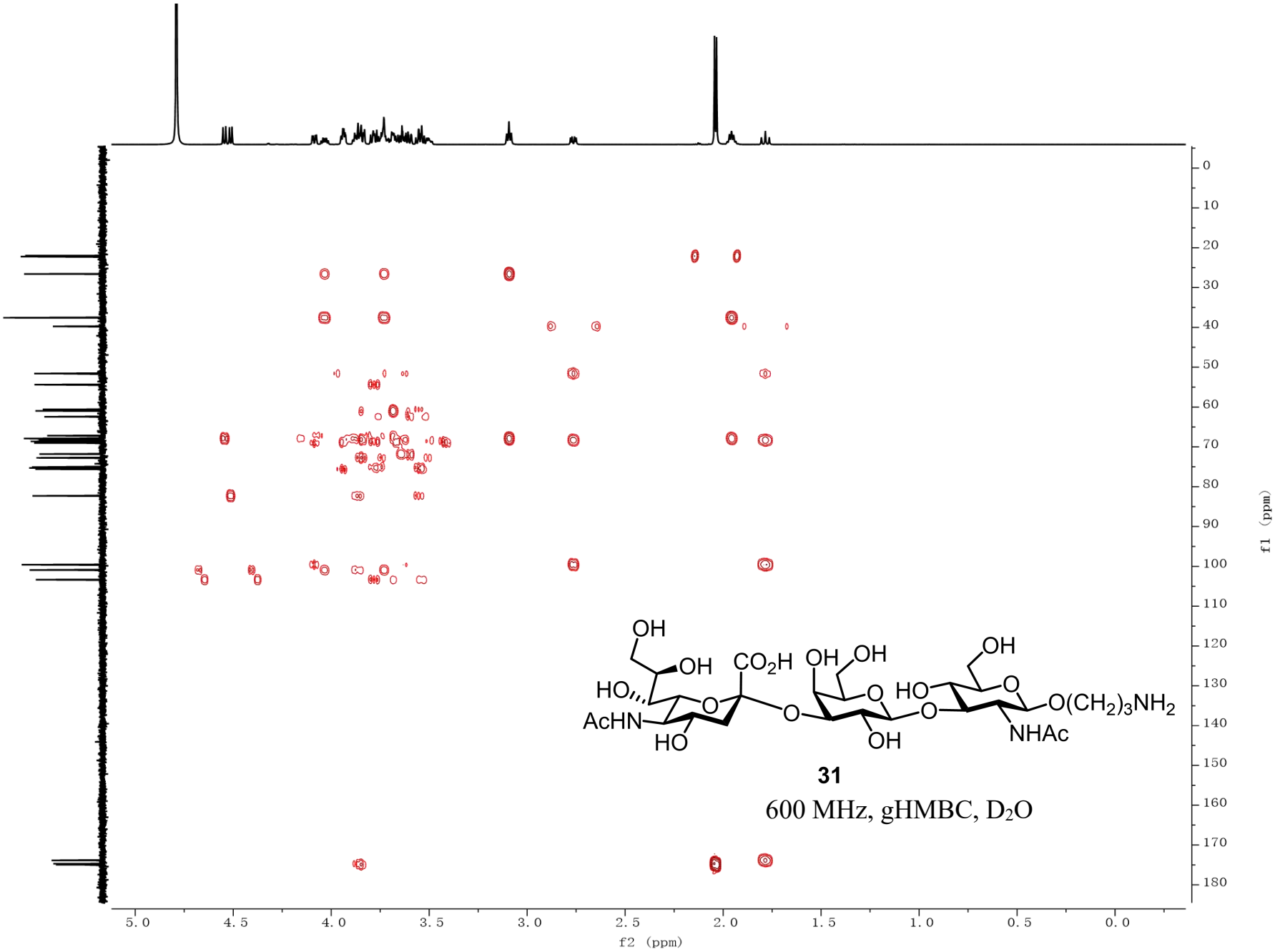



OH
OH
CO2H
OH
OH
HO
O
O
O
HO
O
O(CH2)3NH2
AcHN
HO
OH
NHAc
31
600 MHz, gCOSY, D2O
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)



31

600 MHz, gHMQC, D_2O



31

600 MHz, gHMBC, D_2O