Supporting Information

Total synthesis of rhynchosporosides via orthogonal one-pot glycosylation and stereoselective α-glycosylation strategies

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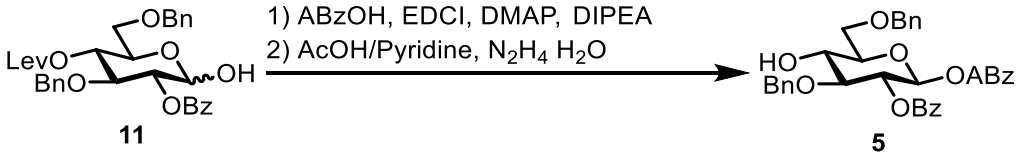
General Methods.

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Crushed 3Å molecular sieves were activated by thorough flame-drying immediately prior to use. Tetrahydrofuran (THF) was distilled immediately before use from sodium-benzophenoneketyl. Methylene chloride (DCM), was distilled from calcium hydride and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on TLC Silica gel 60 F254 (EMD Millipore Corporation) using UV light as visualizing agent and 10% H_2SO_4/EtOH solution as developing agent.

The ^{1}H-NMR, ^{13}C-NMR, H-H COSY and C-H HSQC spectra were measured by a Bruker AVANCE III 400MHz spectrometer or Bruker AV 600MHz spectrometer by using $CDCl_3$ as internal references: chloroform (δH = 7.26 ppm) and CDCl3 (δC = 77.16 ppm). The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Electron spray ionization (ESI) and high-resolution electron spray ionization (HRESI) were obtained on an Agilent 1290 spectrometer. The specific rotation were obtained on a Jasco P-1020, using $CHCl_3$ as solvent.

Experimental Procedures and Characterization of New compounds

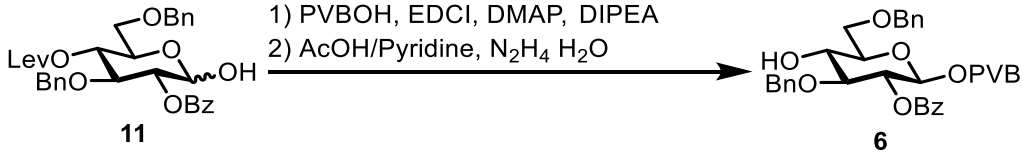
2-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-glucopyranosyl-*ortho*-cyclopropylethynylbenzoate (5)



A suspension of known compound **11**[1] (1.1 g, 1.94 mmol), EDCI (669.0 mg, 3.49 mmol), DMAP (237.0 mg, 1.94 mmol) and ABzOH (541.0 mg, 2.91 mmol) were dissolved in DCM (10.0 mL), and DIPEA (1.0 mL, 5.87 mmol) was added. The mixture was stirred at room temperature overnight and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=5/1-2/1) to afford a colorless syrup (1.4 g, 99%). The above syrup (1.4 g, 1.91 mmol) was dissolved in pyridine (6.0 mL), then AcOH (4.0 mL) and N_2H_4 H_2O (0.2 mL, 3.91 mmol) were added successively at room temperature. The mixture was stirred at room temperature overnight and quenched with acetone, diluted with DCM and washed by 4M HCl, saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA=4/1) to afford **5** as a white foam (721.0 mg, 60%), and 30% α anomer (366.0 mg) was obtained. β anomer $[\alpha]_D^{21}$= +39.40 (*c* 0.10 $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.32 - 7.16 (m, 9H), 7.14 - 7.06 (m, 6H), 5.94 (d, ***J* = 8.2 Hz**, 1H, **1-H**, **β-H**), 5.45 (t, *J* = 8.8 Hz, 1H, **2-H**), 4.67 (s, 2H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 3.88 (t, *J* = 9.2 Hz, 1H), 3.76 - 3.63 (m, 4H), 2.89 (s, 1H, **H-OH**), 1.39 (p, *J* = 6.7 Hz, 1H, **H-CH**), 0.76 (d, *J* = 6.7 Hz, 4H, **H-CH$_2$**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.51, 162.89, 137.16, 136.89, 133.55, 132.52, 131.54, 130.19, 129.05, 128.86, 128.74, 127.75, 127.68, 127.66, 127.29, 127.12, 127.07, 126.33, 124.93, 99.57, 91.96, 81.34, 76.58, 74.29, 73.91, 73.66, 73.06, 71.64, 71.26, 69.06, 8.23, 8.20. HRMS (ESI) calcd for $C_{39}H_{40}O_8N$ $[M+NH_4]^+$650.2748, found 650.2757. α anomer $[\alpha]_D^{21}$= +126.32 (*c* 0.19 $CHCl_3$); ^{1}H

NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.47 - 7.41 (m, 2H), 7.40 - 7.35 (m, 1H), 7.32 - 7.19 (m, 8H), 7.19 - 7.08 (m, 5H), 6.64 (d, ***J* = 3.7 Hz**, 1H, **1-H**, **α-H**), 5.34 (dd, *J* = 9.9, 3.7 Hz, 1H, **2-H**), 4.79 - 4.69 (m, 2H), 4.59 - 4.46 (m, 2H), 4.18 - 4.08 (m, 2H), 3.97 - 3.89 (m, 1H), 3.77 (dd, *J* = 10.5, 4.1 Hz, 1H), 3.68 (dd, *J* = 10.5, 4.1 Hz, 1H), 2.80 (d, *J* = 2.6 Hz, 1H, **H-OH**), 1.45 - 1.32 (m, 1H, **H-CH**), 0.75 - 0.67 (m, 4H, **H-CH$_2$**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.71, 163.36, 137.40, 136.97, 133.99, 132.47, 131.37, 129.93, 129.04, 128.69, 127.74, 127.68, 127.66, 127.10, 127.06, 127.04, 126.31, 124.44, 99.49, 90.13, 78.54 , 74.24, 73.13, 72.12, 71.39, 70.81, 69.01, 8.35, 8.31. HRMS (ESI) calcd for $C_{39}H_{40}O_8N$ $[M+NH_4]^+$650.2748, found 650.2757.

2-*O*-benzoyl-4,6-di-*O*-benzyl-β-D-glucopyranosyl-2-(1-phenylvinyl) benzoate(6)

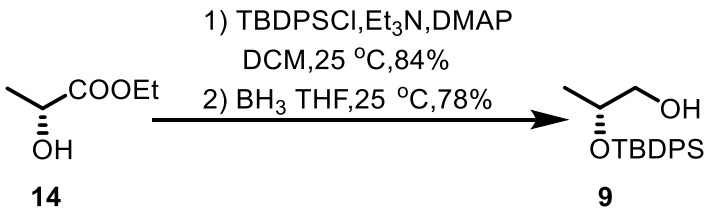


11 **6**

A suspension of known compound **11** (1.1 g, 1.96 mmol), EDCI (675.0 mg, 3.52 mmol), DMAP (239.0 mg, 1.96 mmol) and ABzOH (658.0 mg, 2.93 mmol) were dissolved in DCM (10.0 mL), and DIPEA (1.0 mL, 5.87 mmol) was added. The mixture was stirred at room temperature overnight and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=5/1-3/1) to afford a colorless syrup (1.5 g, 100%). The above syrup (1.5 g, 1.96 mmol) was dissolved in pyridine (6.0 mL), then AcOH (4.0 mL) and $N_2H_4 \cdot H_2O$ (0.2 mL, 3.91 mmol) were added successively at room temperature. The mixture was stirred at room temperature overnight and quenched with acetone, diluted with DCM and washed by 4M HCl, saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA=6/1-4/1) to afford **6** as a white foam (946.5.0 mg, 71%), and 24% α anomer (307.5 mg) was obtained. β anomer $[\alpha]_D^{21}$= +14.31 (*c* 0.13 $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.0 Hz, 2H),

7.86 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.38 - 7.28 (m, 6H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.19 - 7.08 (m, 10H), 5.76 (d, ***J* = 8.3 Hz**, 1H, **1-H**, **β-H**), 5.57 (s, 1H, **H-PVB**), 5.41 (t, *J* = 8.8 Hz, 1H, **2-H**), 5.01 (s, 1H, **H-PVB**), 4.70 (s, 2H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 3.89 (t, *J* = 9.2 Hz, 1H), 3.75 - 3.63 (m, 3H), 3.58 (dd, *J* = 9.3, 4.7 Hz, 1H), 2.83 (s, 1H，**H-OH**). ^{13}C NMR (101 MHz, Chloroform-*d*) *δ* 165.04, 164.64, 148.95, 143.84, 140.32, 137.85, 137.58, 133.19, 132.33, 131.36, 130.60, 129.82, 129.52, 128.80, 128.48, 128.37, 128.36, 128.04, 127.99, 127.89, 127.84, 127.77, 127.63, 127.35, 126.46, 114.01, 92.52, 82.00, 74.65, 74.58, 73.81, 72.16, 72.13, 69.86. HRMS (ESI) calcd for $C_{42}H_{42}O_8N$ $[M+NH_4]^+$688.2905, found 688.2912. α anomer $[\alpha]_D^{21}$= +131.07 (*c* 0.15 $CHCl_3$);^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.90 (d, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.58 - 7.49 (m, 2H), 7.43 - 7.37 (m, 3H), 7.36 - 7.26 (m, 7H), 7.25 - 7.14 (m, 9H), 6.49 (d, ***J* = 3.7 Hz**, 1H, **1-H**, **α-H**), 5.67 (s, 1H, **H-PVB**), 5.20 (dd, *J* = 9.8, 3.7 Hz, 1H, **2-H**), 5.11 (s, 1H, **H-PVB**), 4.63 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 2.8 Hz, 1H), 4.56 (d, *J* = 3.2 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 3.82 - 3.75 (m, 1H), 3.70 (t, *J* = 9.4 Hz, 1H), 3.63 - 3.56 (m, 2H), 3.55 - 3.50 (m, 1H), 2.44 (d, *J* = 3.3 Hz, 1H, **H-OH**). ^{13}C NMR (101 MHz, Chloroform-*d*) *δ* 166.05, 165.40, 148.28, 142.75, 139.91, 138.24, 133.26, 131.90, 131.04, 130.46, 129.74, 129.47, 128.46, 128.39, 127.90, 127.81, 127.75, 127.70, 127.59, 127.01, 114.41, 90.83, 79.21, 74.91, 73.77, 72.75, 72.23, 71.31, 69.52. HRMS (ESI) calcd for $C_{42}H_{42}O_8N$ $[M+NH_4]^+$688.2905, found 688.2912.

(*R*)-2-*O*-(*tert*-butyldiphenylsilyl)-1-propanol (9)

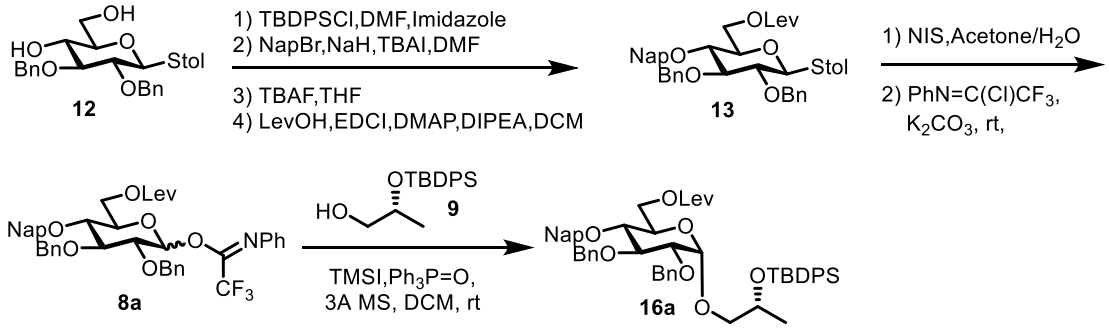


14 **9**

The commercial compound **14** (500 mg, 4.23 mmol) was dissolved in DCM (8.5 mL), then the TBDPSCl (1.32 mL, 5.08 mmol), Et_3N (1.8 mL, 12.7 mmol) and DMAP (52 mg, 0.42 mmol) were added at 0 °C under Ar. The result mixture was

stirred at room temperature overnight and concentrated in vacuo, the result residue was purified by silica gel column chromatography (PE/EA=15/1) to afford a colorless oil **15** (1.262 g, 84%). The above oil (1.262 g, 3.54 mmol) was dissolved in borane-tetrahydrofuran complex (1 mol/L ,7.2 mL, 7.2 mmol) and stirred at room temperature overnight. The result mixture was quenched with H_2O and extracte with DCM, the organic phase was dried by Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=6/1) to afford compound **9** (865 mg, 78%) as a colorless oil. $[\alpha]_D^{21}$= - 13.20 (*c* 0.15, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 - 7.65 (m, 4H), 7.45 - 7.35 (m, 6H), 4.00 - 3.91 (m, 1H, 2-H), 3.54 - 3.47 (m, 1H, 1-H), 3.43 (m, 1H, 1-H), 1.93 (t, *J* = 6.3 Hz, 1H, H-OH), 1.07 (s, 9H, H-TBDPS), 1.05 (d, *J* = 6.3 Hz, 3H, H-CH_3). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.84, 135.72, 129.80, 129.73, 127.75, 127.61, 70.25, 68.26, 27.04, 19.69, 19.27. HRMS (ESI) calcd for $C_{19}H_{26}O_2SiNa$ $[M+Na]^+$337.1594, found 337.1594.

Rhynchosporosides monosaccharide(16a)



The known compound **12**[2] (4.2 g, 9.04 mmol) was dissolved in DMF (11.0 mL) and imidazole (1.9 g, 27.12 mmol) was added, the mixture was cooled to 0 ℃ and TBDPSCl (2.8 mL, 10.85 mmol) was slowly added. The mixture was stirred at 0 ^{o}C for 15 min and reacted at room temperature overnight, then it was quenched with water and diluted with DCM. After being washed with water and brine, the organic phase was dried by Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=20/1-10/1) to afford a yellow syrup. The above syrup was dissolved in DMF (36.0 mL) and NaH (60%, 651.0 mg,

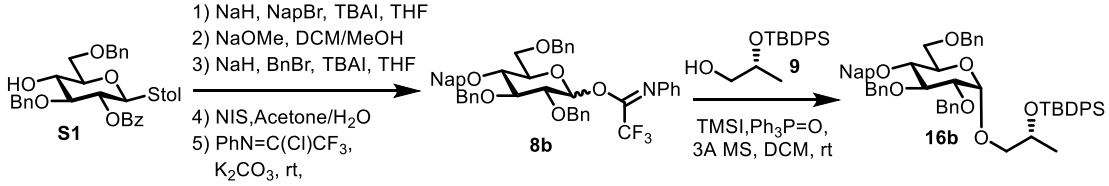
16.23 mmol) was added at 0 ℃ under Ar. After stirring for 15 min, NapBr (2.6 g, 11.75 mmol) and TBAI (668.0 mg, 1.81 mmol) was added successively. The mixture was stirred at at 0 ^{o}C for 15 min and reacted at room temperature overnight, then it was quenched with water and diluted with DCM. After being washed with water and brine, the organic phase was dried by Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=20/1-10/1) to afford a yellow syrup (6 g, 79% for 2 steps). The above syrup was dissolved in a solution of 1M TBAF in THF (23.0 mL, 23.00 mmol) and stirred overnight, then it was quenched with saturated aqueous $NaHCO_3$ and diluted with EA, washed with H_2O and brine successively, the organic phase was dried by Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=30/1-DCM/EA=1/1) to afford a light yellow syrup (3.5 g, 82%). The above syrup was dissolved in DCM (66 mL), EDCI (2.3 g, 11.84 mmol), DMAP (804.0 mg, 6.58 mmol), LevOH (1.1 mL, 9.87 mmol) and DIPEA (3.3 mL, 19.74 mmol) was added successively. The mixture was stirred at room temperature overnight and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (DCM/EA=6/1) to afford **13** as a white solid (4.1 g, 98%).

White solid **13** (1.5 g, 2.09 mmol) was dissolved with acetone/H_2O (20 mL/ 2mL) and NIS (938.0 mg, 4.17 mmol) was added under room temperature. The mixture was stirred at room temperature for another 1.5h, and quenched with saturated aqueous $Na_2S_2O_3$, diluted with EA, washed with saturated aqueous $Na_2S_2O_3$, water and brine successively, the organic phase was dried by Na_2SO_4 and concerntrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=3/1-DCM/EA=1/1) and Sephandex LH-20 (DCM/MeOH=1/1) to afford a light yellow syrup (1.17 g, 94%). The above syrup and (*N*-phenyl) trifluoroacetimidoyl chloride (610.0 mg, 2.94 mmol) were dissolved in acetone and K_2CO_3 (406.0 mg, 2.94 mmol)was added. The mixture was stirred overnight at room temperature and concentrated in vacuo to give a crude. Then it was purified by silica gel column chromatography (PE/EA=12/1-3/1, Et_3N 1%) to afford PTFAI donor **8a** as

a light yellow syrup (1.5 g, 99%), which was directly utilized for the further glycosylation.

A suspension of PTFAI donor **8a** (340.9 mg, 0.44 mmol), alcohol **9** (209.0 mg, 0.66 mmol), $Ph_3P=O$ (739.4 mg, 2.66 mmol) and active 3Å MS (600.0 mg) in 4.4 mL dry DCM was stirred at room temperature for 15 min under Ar, then TMSI (63.3 μL, 0.44 mmol) was added slowly. The mixture was stirred at room temperature for another 40h, then quenched with saturated aqueous $Na_2S_2O_3$ and extracted with EA for 3 times, the organic phase was combined and dried by Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography (PE/EA=5/1-3/1) to afford **16a** as a light yellow syrup (352 mg, 89%, α/β > 20/1). α anomer: $[\alpha]_D^{21}$= +55.43 (*c* 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 - 7.66 (m, 3H), 7.65 - 7.57(m, 5H), 7.39 - 7.13 (m, 19H), 4.92 (m, 2H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.69 - 4.63 (d, *J* =10.8 Hz, 1H), 4.59 (d, *J* = 12.0, 1H), 4.53 (d, ***J* = 3.1 Hz**, 1H, **1-H**, **α-H**), 4.47 (d, *J* = 12.0, 1H), 4.15 - 4.22 (m, 1H), 4.11 (d, J = 11.8 Hz, 1H), 3.98 (q, *J* = 6.2 Hz, 1H, **H-CH**), 3.91 (t, *J* = 9.4, 1H), 3.75 - 3.65 (m, 1H), 3.47 - 3.32 (m, 3H), 3.30 - 3.21 (m, 1H), 2.50 (t, *J* = 6.6 Hz, 2H, **CH_2-Lev**), 2.42 - 2.24 (m, 2H, **CH_2-Lev**), 2.03 (s, 3H, **CH_3-Lev**), 1.05 (d, *J* = 6.4Hz, 3H, **H-CH_3**), 0.98 (s, 9H, **H-TBDPS**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.20, 172.42, 138.78, 138.26, 135.89, 135.56, 134.37, 134.11, 133.26, 133.03, 129.65, 128.44, 128.41, 128.21, 128.00, 127.91, 127.82, 127.69, 127.65, 127.60, 126.88, 126.12, 126.08, 125.92, 96.93, 82.01, 80.12, 77.28, 75.71, 74.97, 73.32, 72.89, 68.71, 67.94, 63.16, 37.79, 29.82, 27.73, 27.03, 21.17, 19.24. HRMS (ESI) calcd for $C_{55}H_{62}O_9SiNa$ $[M+Na]^+$917.4055, found 917.4060.

Rhynchosporosides monosaccharide(16b)

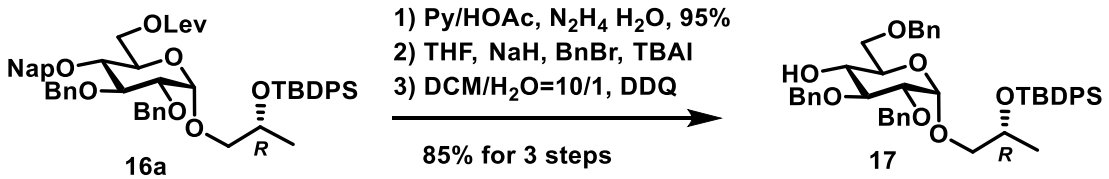


The known compound **S1**[1] (300 mg, 0.523 mmol) was dissolved in THF (2.6 mL) and NaH (60%, 31.5 mg, 0.789 mmol) was added at 0 ℃ under Ar. After 15 min, NapBr (139.5 mg, 0.631 mmol) and TBAI (58 mg, 0.158 mmol) were added successively. The mixture was stirred at 0 ^{o}C for 15 min and reacted at room temperature overnight, then THF was removed in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=10/1-3/1) to afford a white foam. The above foam was dissolved in DCM (1 mL), MeOH (1 mL) and MeONa (57 mg, 1.05 mmol) were added successively, the mixture was reacted at room temperature overnight and neutralized with 1M HCl, then it was filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (PE/EA=10/1-2/1) to afford a colorless syrup (248.4 mg, 78% for 2 steps). The above syrup (248.4 mg, 0.41 mmol) was dissolved in THF (4 mL) and NaH (60%, 25 mg, 0.789 mmol) was added at 0 ℃ under Ar. After 15 min, BnBr (0.07 mg, 0.61 mmol) and TBAI (45 mg, 0.123 mmol) were added successively. The mixture was stirred at 0 ^{o}C for 15 min and reacted at room temperature overnight, then THF was removed in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=10/1-3/1) to afford a colorless syrup (271.7 mg, 95%). The above syrup (271.7 mg, 0.39 mmol) was dissolved with acetone/H_2O (3.6 mL/ 0.4mL) and NIS (175.4 mg, 0.78 mmol) was added under room temperature. The mixture was stirred at room temperature for another 2h, and quenched with saturated aqueous $Na_2S_2O_3$, diluted with EA, washed with saturated aqueous $Na_2S_2O_3$, water and brine successively, the organic phase was dried by Na_2SO_4 and concerntrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=3/1-DCM/EA=1/1) and Sephandex LH-20 (DCM/MeOH=1/1) to afford a white solid (211.5 mg, 92%). The above solid (110 mg, 0.186 mmol) and (*N*-phenyl) trifluoroacetimidoyl chloride (46 mg, 0.223 mmol) were dissolved in 1 mL acetone and K_2CO_3 (39 mg, 0.279 mmol) was added. The mixture was stirred overnight at room temperature and concentrated in vacuo to give a crude. Then it was purified by silica gel column chromatography (PE/EA=15/1, Et_3N 1%) to afford PTFAI donor **8b**

as a light yellow syrup (128.6 mg, 91%), which was directly utilized for the further glycosylation.

A suspension of PTFAI donor **8b** (128.6 mg, 0.169 mmol), alcohol **9** (80 mg, 0.253 mmol), $Ph_3P=O$ (282 mg, 1.013 mmol) and active 3Å MS (220 mg) in 1.7 mL dry DCM was stirred at room temperature for 15 min under Ar, then TMSI (24 μL, 0.169 mmol) was added slowly. The mixture was stirred at room temperature for another 40h, then quenched with saturated aqueous $Na_2S_2O_3$ and extracted with EA for 3 times, the organic phase was combined and dried by Na_2SO_4, concentrated in vacuo and purified by silica gel column chromatography (PE/EA=15/1) to afford **16b** as a light yellow syrup (134.1 mg, 89%, α/β = 15/1). α anomer: ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.83 – 7.78 (m, 1H), 7.76 – 7.66 (m, 6H), 7.55 (s, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.21 (m, 22H), 4.96 (d, *J* = 11.0 Hz, 2H), 4.78 (d, *J* = 10.9 Hz, 1H), 4.70 – 4.53 (m, 5H), 4.41 (d, *J* = 12.1 Hz, 1H), 4.09 – 4.02 (m, 1H), 3.96 (t, *J* = 9.1 Hz, 1H), 3.76 – 3.64 (m, 3H), 3.58 (d, *J* = 10.2 Hz, 1H), 3.53 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.50 – 3.44 (m, 1H), 3.39 – 3.33 (m, 1H), 1.11 (d, *J* = 6.1 Hz, 3H), 1.06 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.00, 138.40, 138.01, 135.94, 135.91, 135.88, 135.76, 134.45, 134.18, 133.32, 132.97, 129.85, 129.79, 129.64, 128.42, 128.39, 128.04, 127.97, 127.95, 127.80, 127.71, 127.68, 127.65, 127.60, 126.48, 126.04, 125.96, 125.86, 97.17, 82.11, 80.16, 77.70, 77.44, 77.13, 76.81, 75.70, 75.06, 73.53, 73.29, 72.92, 70.28, 68.52, 68.30, 68.04, 27.09, 27.06, 21.24.

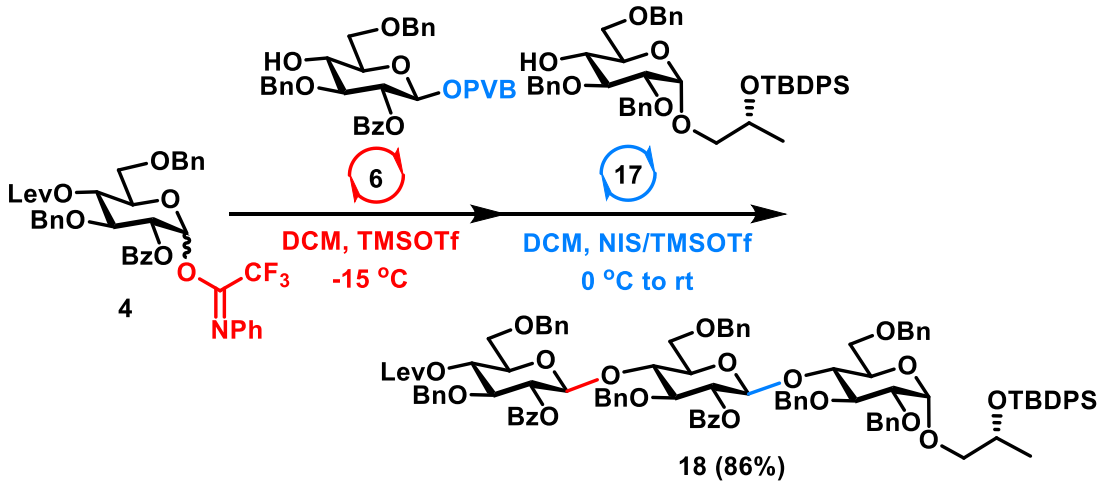
Rhynchosporosides monosaccharide acceptor (17)



The above syrup **16** (617.0 mg, 0.69 mmol) was dissolved in DCM (17.0 mL), Pyridine (2.1 mL), AcOH (1.4 mL)and $N_2H_4 \cdot H_2O$ (0.7 mL, 1.38 mmol) was added successively. The mixture was stirred overnight and quenched with acetone, then

concentrated in vacuo and purified by silica gel column chromatography (PE/EA=3/1) to afford a colorless syrup (521.0 mg, 95%). The above syrup was dissolved in THF (2.1 mL), and NaH (60%, 31.0 mg, 0.78 mmol) was added at 0 ℃ under Ar. The mixture was stirred for 15 min and BnBr (0.1 mL, 0.98 mmol) and TBAI (120.0 mg, 0.33 mmol) was added successively. The mixture was stirred for another 10h and quenched with water, extracted with DCM for 3 times and combined organic phase, dried by Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=6/1) to afford a light yellow syrup. The above syrup was dissolved in DCM/H_2O (6 mL/0.6 mL), and DDQ (149.0 mg, 0.65 mmol) was added at room temperature. The mixture was stirred overnight and quenched with saturated aqueous $Na_2S_2O_3$, then it was extracted with DCM for 3 times, the organic phase was combined, dried by Na_2SO_4, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography (PE/EA=10/1-4/1) to afford 17 as a colorless syrup (435.0 mg, 89% for two steps)。 $[\alpha]_D^{21}$= +22.67 (*c* 0.15 $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 - 7.59 (m, 4H), 7.35 – 7.13 (m, 21H), 4.88 (d, *J* = 11.4 Hz, 1H), 4.64 – 4.53 (m, 3H, **1-H**), 4.51 – 4.40 (m, 3H), 3.98 (q, *J* = 6.1 Hz, 1H, **H-CH**), 3.67 (t, *J* = 9.1 Hz, 1H), 3.62 – 3.49 (m, 4H), 3.41 (td, *J* = 6.2, 3.1 Hz, 2H), 3.27 (dd, *J* = 9.4, 5.3 Hz, 1H), 2.28 (s, 1H, **H-OH**), 1.05 (d, *J* = 6.1 Hz, 3H, **H-CH_3**), 0.99 (s, 9H, **H-TBDPS**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.93, 138.27, 138.09, 135.93, 135.91, 134.44, 134.19, 129.63, 128.55, 128.39, 128.38, 127.97, 127.92, 127.80, 127.78, 127.64, 127.59, 97.07, 81.35, 79.80, 77.29, 75.31, 73.59, 73.19, 72.67, 70.79, 70.07, 69.51, 68.02, 27.05, 21.16, 19.25. HRMS (ESI) calcd for $C_{46}H_{58}O_7SiN$ $[M+NH_4]^+$764.3977, found 764.3987.

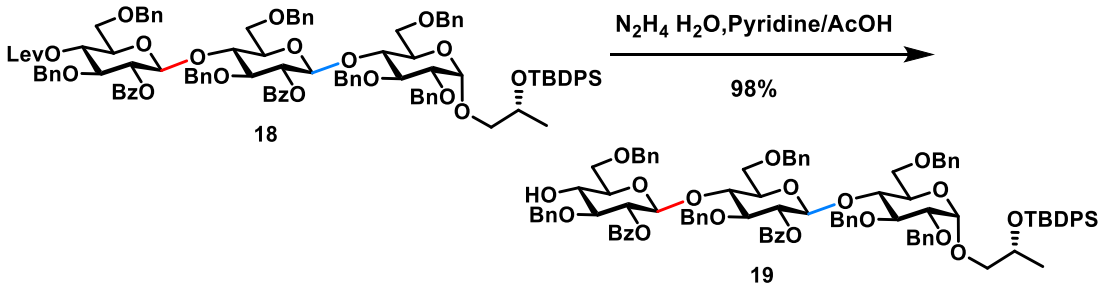
Rhynchosporosides trisaccharide(18)



A suspension of glucosyl trifluoroacetimidate **4**[1] (263.0 mg, 0.359 mmol), glucosyl PVB acceptor **6** (201.0 mg, 0.299 mmol), and activated 3Å MS (700 mg) in dry DCM (2.5 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. A solution of TMSOTf in DCM (0.5 mL, 0.12 M) was slowly added to the mixture. After being stirred at -15 ℃ for another 1h, the reaction mixture was warmed up to 0 ℃, to which a solution of glucosyl acceptor **17** (201.0 mg, 0.269mmol) in DCM (4.7 mL), NIS (91.0 mg, 0.404 mmol) and a solution of TMSOTf (0.5 mL, 0.054 M) were added successively. The resulting mixture was stirred at 0 ℃ to room temperature for another 2h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (PE/EA=2.5/1) to afford **18** (401.3 mg, 86%) as a white foam. $[\alpha]_D^{21}$= +25.05 (*c* 0.17, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.58 - 7.52 (m, 5H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.33 - 7.19 (m, 17H), 7.18 - 7.14 (m, 5H), 7.13 - 7.02 (m, 18H), 6.99 - 6.94 (m, 3H), 5.23 (t, *J* = 8.8 Hz, 1H，**2”-H**), 5.08 - 4.98 (m, 2H，**4”-H** ，**2’-H**), 4.94 (d, *J* = 11.7 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.60 - 4.28 (m, 12H), 4.19 - 4.13 (m, 2H，**1’-H**), 4.06 - 3.94 (m, 3H), 3.86 (q, *J* = 6.1 Hz, 1H，**H-CH**), 3.67 - 3.54 (m, 3H，**3’-H**), 3.50 - 3.35 (m, 4H), 3.30 - 3.13 (m, 8H), 2.79 (d, *J* = 9.8 Hz, 1H，**5’-H**), 2.49 (q, *J* = 6.5 Hz, 2H，**CH_2-Lev**), 2.31 (t, *J* = 7.1 Hz, 2H，**CH_2-Lev**), 2.02 (s, 3H，**CH_3-Lev**), 0.91 (s, 9H，**H-TBDPS**), 0.86 (d, *J* = 6.0 Hz, 3H，**H-CH_3**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.15, 171.53, 164.73, 139.87, 138.70, 138.52, 138.38, 138.30,

137.88, 137.71, 135.87, 134.48, 134.06, 133.44, 132.99, 129.99, 129.76, 129.67, 129.61, 128.73, 128.64, 128.55, 128.48, 128.32, 128.24, 128.17, 127.99, 127.94, 127.88, 127.79, 127.74, 127.61, 127.56, 127.49, 127.33, 127.15, 126.83, 100.47, 99.98, 97.10, 80.35, 80.22, 80.04, 79.02, 76.26, 75.14, 74.76, 74.66, 73.98, 73.74, 73.66, 73.57, 73.43, 73.08, 72.97, 71.91, 69.92, 69.73, 67.75, 67.54, 37.75, 29.78, 27.98, 26.98, 21.08, 19.15. HRMS (ESI) calcd for $C_{105}H_{116}O_{21}SiN$ $[M+NH_4]^+$1754.7804, found 1754.7812.

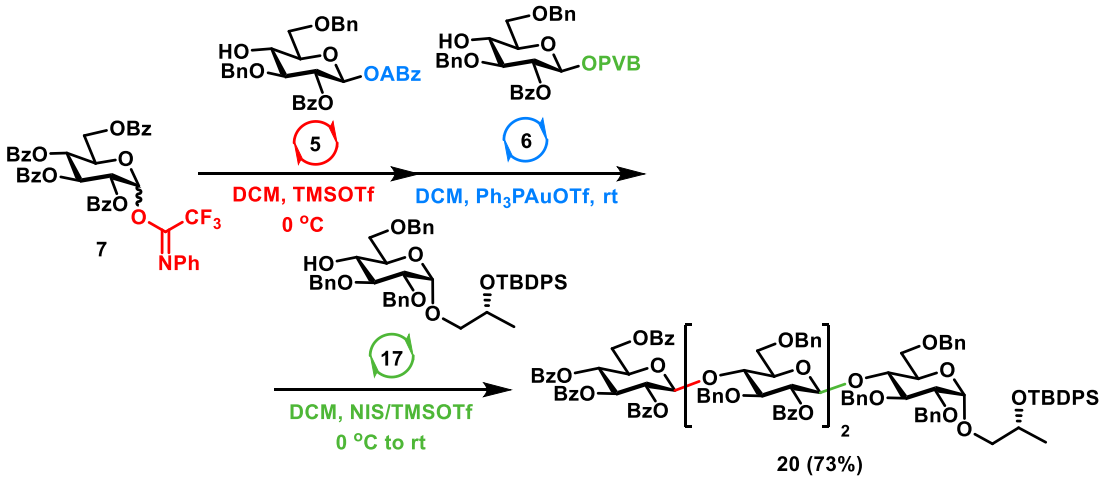
Rhynchosporosides trisaccharide acceptor(19)



The Rhynchosporosides trisaccharide **18** (138.7 mg, 0.080 mmol) was dissolved in DCM (2.0 mL), and a solution of hydrazine hydrate in pyridine/AcOH (1M, 0.2 mL, 0.2 mmol, $V_{hydrazine\ hydrate}/V_{pyridine}/V_{AcOH}$ = 1/11.2/8) was added at room temperature under Ar.The mixture was stirred at room temperature overnight and quenched with acetong, concentrated in vacuo and purified by silica gel column chromatography (PE/EA=2.5/1) to afford **19** (128.8 mg, 98%) as a white foam. $[\alpha]_D^{21}$= +24.00 (*c* 0.12, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.59 - 7.51 (m, 5H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.33 - 6.92 (m, 42H), 5.15 (t, *J* = 8.8 Hz, 1H, **2”-H**), 5.00 (t, *J* = 8.9 Hz, 1H, **2’-H**), 4.94 (d, *J* = 11.7 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.62 - 4.55 (m, 2H), 4.53 - 4.47 (m, 3H), 4.46 - 4.31 (m, 6H), 4.15 (d, *J* = 8.1 Hz, 1H, **1’-H**, **β-H**), 4.04 (d, *J* = 12.2 Hz, 1H), 4.01 - 3.92 (m, 2H), 3.86 (q, *J* = 6.1 Hz, 1H, **H-CH**), 3.71 (t, *J* = 9.1 Hz, 1H, **4”-H**), 3.67 - 3.59 (m, 2H), 3.53 - 3.44 (m, 2H), 3.43 -3.36 (m, 3H), 3.30 - 3.22 (m, 4H), 3.21 - 3.12 (m, 4H), 3.01 (s, 1H, **H-OH**), 2.79 (d, *J* = 9.7 Hz, 1H, **5’-H**), 0.91 (s, 9H, **H-TBDPS**), 0.86 (d, *J* = 6.1 Hz, 3H, **H-CH$_3$**). ^{13}C NMR (101

MHz, Chloroform-*d*) δ 165.00, 164.74, 139.84, 138.74, 138.50, 138.27, 138.23, 137.71, 137.57, 135.85, 134.46, 134.05, 133.35, 132.98, 129.96, 129.78, 129.72, 129.65, 129.59, 128.69, 128.60, 128.52, 128.45, 128.41, 128.31, 128.21, 128.10, 127.93, 127.87, 127.82, 127.70, 127.63, 127.58, 127.54, 127.32, 127.08, 126.83, 100.42, 99.95, 97.08, 81.85, 80.21, 78.99, 77.30, 76.87, 76.04, 75.12, 74.72, 74.46, 74.42, 74.08, 73.79, 73.67, 73.55, 73.39, 73.15, 73.04, 72.95, 71.13, 69.69, 67.72, 67.52, 26.95, 21.07, 19.13. HRMS (ESI) calcd for $C_{100}H_{110}O_{19}SiN$ $[M+NH_4]^+$1656.7436, found 1656.7444

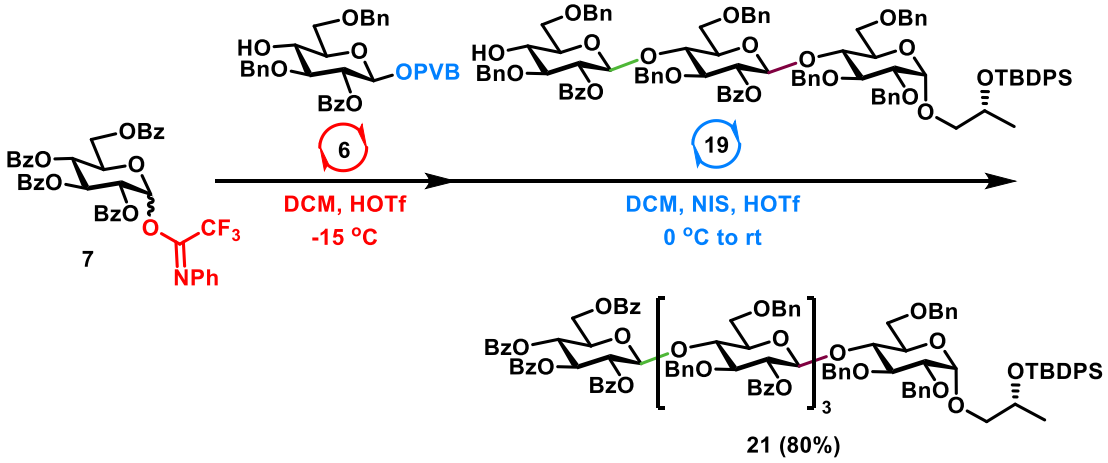
Rhynchosporosides tetrasaccharide(20)



A suspension of glucosyl trifluoroacetimidate **7**[3] (136.5 mg, 0.178 mmol), glucosyl ABz acceptor **5** (95.2mg, 0.150 mmol), and activated 3Å MS (450 mg) in dry DCM (0.5 mL) was stirred at room temperature for 15 min and was then cooled to 0 ℃. A solution of TMSOTf in DCM (0.4 mL, 0.075 M) was slowly added to the mixture. After being stirred at 0 ℃ for another 2h, the reaction mixture was warmed up to room tempurature, to which glucosyl PVB acceptor **6** (91.7 mg, 0.137 mmol) and freshly prepared solution of $Ph_3PAuOTf$ (1.0 mL, 0.027M) were added successively. After being stirred for another 2h, the reaction mixture was cooled to 0 ℃，then the solution of acceptor **17** (92 mg,0.123 mmol) in DCM (1.2 mL), NIS (41.5mg,0.185mmol) and solution of TMSOTf (0.3mL,0.047M) were successively added. The resulting mixture was stirred at 0 ℃ to room temperature for another 2h, then was quenched with Et_3N

(0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (PE/EA=5/1-3/1) to afford **20** (199.8 mg, 73%) as a white foam. $[\alpha]_D^{26}$= +34.47 (*c* 0.14, $CHCl_3$);^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 - 7.86 (m, 8H), 7.84 - 7.77 (m, 4H), 7.65 - 7.56 (m, 6H), 7.55 - 7.49 (m, 2H), 7.48 - 7.42 (m, 7H), 7.41 - 7.31 (m, 15H), 7.30 - 7.25 (m, 6H), 7.18 - 7.04 (m, 21H), 7.02 - 6.91 (m, 6H), 5.69 (t, *J* = 9.5 Hz, 1H, **3'''-H**), 5.61 - 5.53 (m, 2H, **2'''-H**, **4'''-H**), 5.18 (t, *J* = 8.9 Hz, 1H), 5.06 - 4.97 (m, 2H), 4.96 - 4.87 (m, 3H, **1'''-H**), 4.62 (dd, *J* = 11.7, 3.5 Hz, 2H), 4.58 - 4.50 (m, 4H), 4.49 - 4.38 (m, 4H), 4.34 (d, **J = 8.2 Hz**, 1H, **β-H**), 4.26 - 4.15 (m, 4H), 4.09 (d, *J* = 12.2 Hz, 1H), 3.99 - 3.89 (m, 3H), 3.75 - 3.64 (m, 3H), 3.57 (dd, *J* = 11.4, 2.9 Hz, 1H), 3.52 - 3.38 (m, 4H), 3.34 - 3.26 (m, 3H), 3.25 - 3.17 (m, 4H), 2.90 (d, *J* = 9.8 Hz, 1H), 2.78 (d, *J* = 9.8 Hz, 1H), 0.98 (s, 9H, **H-TBDPS**), 0.92 (d, *J* = 6.1 Hz, 3H, **H-CH_3**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.12, 165.76, 165.24, 165.05, 164.86, 164.82, 139.89, 138.85, 138.52, 138.14, 137.96, 137.69, 135.90, 134.47, 134.06, 133.74, 133.50, 133.30, 133.09, 133.01, 129.98, 129.85, 129.78, 129.72, 129.66, 128.98, 128.93, 128.85, 128.74, 128.61, 128.56, 128.48, 128.40, 128.32, 128.26, 128.19, 128.01, 127.98, 127.96, 127.92, 127.90, 127.87, 127.64, 127.61, 127.38, 127.28, 127.05, 126.88, 100.49, 100.35, 99.85, 97.10, 80.28, 80.16, 80.03, 78.97, 77.42, 75.96, 75.17, 74.76, 74.58, 74.50, 74.41, 73.57, 73.49, 73.37, 73.11, 73.06, 73.01, 72.25, 72.01, 69.97, 69.71, 67.75, 67.53, 67.35, 62.97, 27.00, 21.12, 19.17. HRMS (ESI) calcd for $C_{134}H_{132}O_{28}SiNa$ $[M+Na]^+$2239.8567 found 2239.8561.

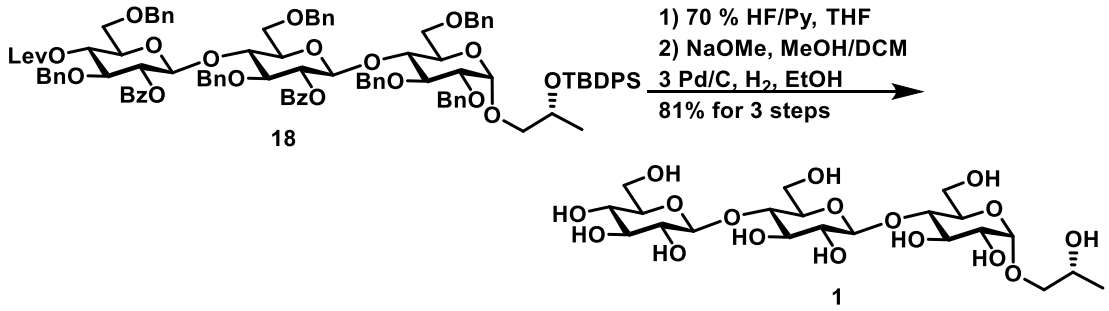
Rhynchosporosides Pentasaccharide(21)



A suspension of glucosyl trifluoroacetimidate **7** (63.1 mg, 0.082 mmol), glucosyl PVB acceptor **6** (52.5 mg, 0.078mmol), and activated 3Å MS (250.0 mg) in dry DCM (0.8 mL) was stirred at room temperature for 15 min and was then cooled to -15 ℃. A solution of HOTf in DCM (0.2 mL, 0.08 M) was slowly added to the mixture. After being stirred at -15 ℃ for another 1h, the reaction mixture was warmed up to 0 ℃, to which DCM (0.4 mL), trisaccharide acceptor **19** (115.5 mg, 0.070mmol), NIS (23.0 mg, 0.106 mmol) and a solution of HOTf (0.7 mL, 0.01 M) were added successively. The resulting mixture was stirred at 0 ℃ to room temperature for another 4h, then was quenched with Et_3N (0.5mL) and filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (PE/EA=5/1-2.5/1) to afford **21** (149.8 mg, 80%) as a white foam. $[\alpha]_D^{22}$= +14.60 (*c* 0.10, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.93 – 7.85 (m, 8H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.7 Hz, 2H), 7.64 – 7.53 (m, 7H), 7.51 – 7.42 (m, 9H), 7.41 – 7.31 (m, 17H), 7.30 – 7.22 (m, 8H), 7.17 – 7.09 (m, 20H), 7.06 (t, *J* = 6.6 Hz, 6H), 7.02 – 6.89 (m, 9H), 5.71 (t, *J* = 9.6 Hz, 1H, **3””-H**), 5.63 - 5.52 (m, 2H, **2””-H**, **4””-H**), 5.21 (t, *J* = 8.8 Hz, 1H), 5.13 (t, *J* = 8.9 Hz, 1H), 5.03 - 4.86 (m, 6H), 4.64 - 4.60 (m, 2H), 4.58 - 4.52 (m, 4H), 4.51 - 4.44 (m, 3H), 4.42 - 4.37 (m, 3H), 4.29 - 4.14 (m, 5H), 4.08 (d, *J* = 12.1 Hz, 1H), 4.05 - 3.97 (m, 2H), 3.97 - 3.89 (m, 3H), 3.74 (dt, *J* = 10.3, 4.8 Hz, 1H), 3.68 (t, *J* = 7.9 Hz, 2H), 3.60 (dd, *J* = 11.3, 2.9 Hz, 1H), 3.55 – 3.40 (m, 5H), 3.39 – 3.35 (m, 1H), 3.30 (td, *J* = 10.7, 10.2, 5.9 Hz, 5H), 3.20 (dd, *J* = 10.5, 7.5 Hz, 4H), 2.95 (d, *J* = 9.8 Hz, 1H), 2.80 – 2.72 (m,

2H), 0.98 (s, 9H, **H-TBDPS**), 0.92 (d, *J* = 6.1 Hz, 3H, **H-CH$_3$**). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.06, 165.72, 165.18, 164.97, 164.89, 164.80, 164.73, 139.85, 138.92, 138.85, 138.51, 138.48, 138.13, 137.87, 137.69, 135.84, 134.48, 134.06, 133.59, 133.41, 133.27, 133.21, 133.14, 133.01, 132.86, 130.01, 129.87, 129.81, 129.74, 129.66, 129.64, 129.58, 129.01, 128.94, 128.78, 128.64, 128.57, 128.51, 128.43, 128.36, 128.32, 128.29, 128.21, 128.19, 128.13, 128.10, 127.95, 127.93, 127.90, 127.84, 127.81, 127.58, 127.53, 127.33, 127.22, 127.01, 126.89, 126.80, 100.42, 100.35, 99.92, 99.80, 97.06, 80.21, 80.14, 79.99, 78.99, 76.91, 76.05, 75.96, 75.09, 74.75, 74.59, 74.56, 74.44, 74.25, 73.56, 73.49, 73.47, 73.39, 73.29, 73.10, 73.04, 72.94, 72.25, 72.00, 69.97, 69.70, 67.72, 67.56, 67.42, 67.32, 67.21, 62.94, 26.95, 21.06, 19.12. HRMS (ESI) calcd for $C_{161}H_{164}O_{34}SiN_2$ $[M+2NH_4]^{2+}$1349.5540 found 1349.5542.

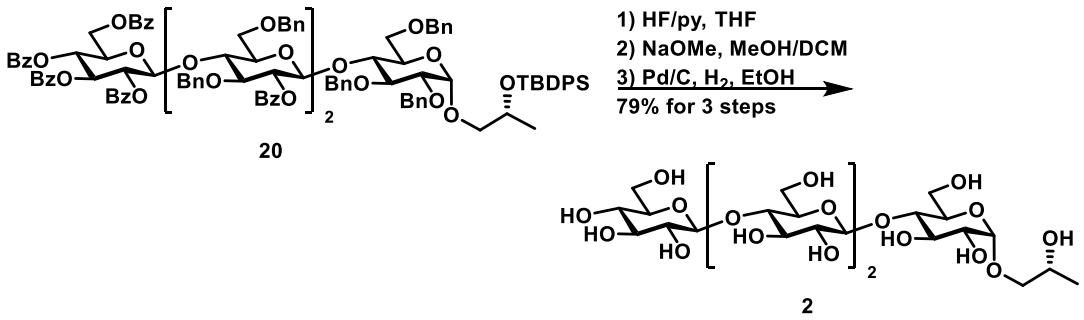
[3R]-rhynchosporosides (1)



The compound **18** (140 mg, 0.081 mmol) was dissolved in THF (6 mL) and excessive HF/Py (70%, 0.2 mL) was added. The mixture was stirred at room temperature for 40h and quenched with Et_3N, then it was diluted with DCM and washed by saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA=4/1-1/1) to afford a white foam (98.1 mg, 81%). The above syrup was dissolved in 0.5 mL DCM, MeOH (3.0 mL) and MeONa (100 mg) were added successively. The mixture was stirred at room temperature for 4 days and neutralized with 1M HCl, then it was filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography

(DCM/MeOH=50/1-20/1) to afford a light yellow syrup (80.6 mg, 100%). The above syrup was dissolved in EtOH (30 mL), and 10% palladium on activated charcoal (542 mg) was added. The flask was degassed using low vacuum and flushed with hydrogen (3 times). The mixture was stirred under a hydrogen balloon overnight at room temperature, then it was filtered celite and concentrated in vacuo. The resulting residue was purified by Sephadex LH-20 (H_2O) to give **1** (40 mg, 100%) as a white amorphous solid. $[\alpha]_D^{24}$= +33.77 (*c* 0.17, H_2O); ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.92 (d, *J* = 3.8 Hz, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.05 (td, *J* = 7.1, 3.1 Hz, 1H), 3.98 (d, *J* = 11.2 Hz, 1H), 3.93 – 3.78 (m, 6H), 3.76 – 3.69 (m, 2H), 3.68 – 3.57 (m, 5H), 3.53 – 3.45 (m, 2H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.39 – 3.28 (m, 3H), 1.17 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 99.94, 99.63, 95.70, 75.89, 75.78, 73.40, 72.86, 72.24, 71.45, 70.56, 70.38, 68.94, 68.65, 67.88, 66.84, 63.94, 57.97, 57.32, 57.18, 15.51. HRMS (ESI) calcd for $C_{21}H_{38}O_{17}Na$ $[M+Na]^+$585.2001 found 585.2001.

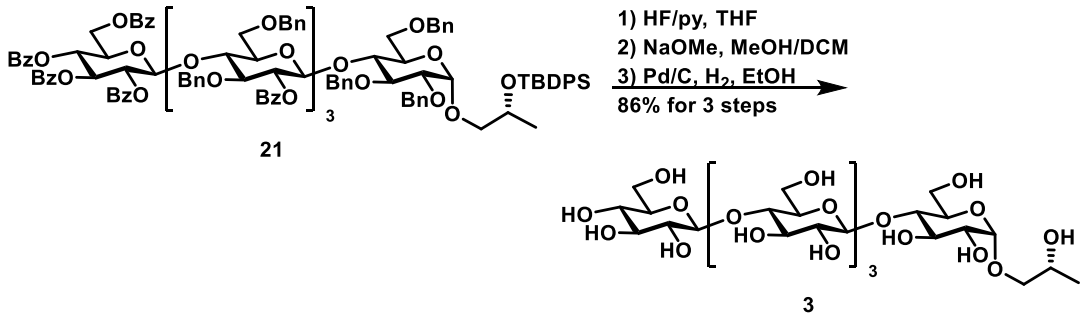
[4R]-rhynchosporosides (2)



The compound **20** (138.5 mg, 0.062 mmol) was dissolved in THF (8 mL) and excessive HF/Py (70%, 0.3 mL) was added. The mixture was stirred at room temperature for 2.5 days and quenched with Et_3N, then it was diluted with DCM and washed by saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA=3/1-1/1) to afford a white foam (112.6 mg, 92%). The above syrup was dissolved in 0.5 mL DCM, MeOH (3.0 mL) and MeONa (100 mg) were added successively. The mixture was stirred at room temperature for 7

days and neutralized with 1M HCl, then it was filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (DCM/MeOH=30/1-10/1) to afford a light yellow syrup (66.4 mg, 86%). The above syrup (59 mg,0.044 mmol) was dissolved in EtOH (20 mL), and 10% palladium on activated charcoal (361 mg) was added. The flask was degassed using low vacuum and flushed with hydrogen (3 times). The mixture was stirred under a hydrogen balloon overnight at room temperature, then it was filtered celite and concentrated in vacuo. The resulting residue was purified by Sephadex LH-20 (H_2O) to give **2** (32 mg, 100%) as a white amorphous solid. $[\alpha]_D^{24}$= +28.13 (*c* 0.15, H_2O); ^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.92 (d, *J* = 3.8 Hz, 1H), 4.52 (d, *J* = 7.7 Hz, 2H), 4.50 (d, *J* = 8.1 Hz, 1H), 4.05 (td, *J* = 7.1, 3.2 Hz, 1H), 3.97 (d, *J* = 12.1 Hz, 2H), 3.92 – 3.79 (m, 7H), 3.75 – 3.58 (m, 10H), 3.52 – 3.46 (m, 2H), 3.41 (d, *J* = 9.2 Hz, 1H), 3.38 – 3.28 (m, 4H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 102.52, 102.30, 102.23, 98.29, 78.47, 78.34, 78.24, 75.98, 75.44, 74.82, 73.99, 73.14, 72.97, 71.53, 71.24, 70.46, 69.42, 66.53, 60.55, 59.87, 59.75, 18.08. HRMS (ESI) calcd for $C_{27}H_{48}O_{22}Na$ $[M+Na]^+$747.2529 found 747.2531.

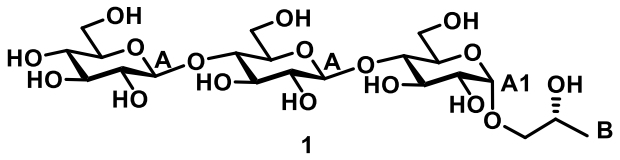
[5R]-rhynchosporosides (3)



The compound **21** (321 mg, 0.120 mmol) was dissolved in THF (5 mL) and excessive HF/Py (70%, 0.3 mL) was added. The mixture was stirred at room temperature for 2 days and quenched with Et_3N, then it was diluted with DCM and washed by saturated aqueous $NaHCO_3$ and brine successively. The organic phase was dried by Na_2SO_4 and concentrated in vacuo, the resulting residue was purified by silica gel column chromatography (PE/EA=5/1-1/1) to afford a white foam (263 mg,

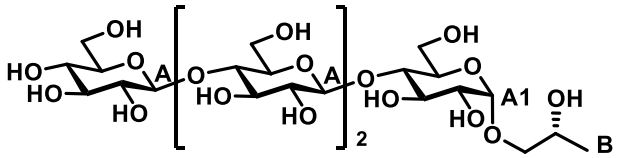
90%). The above syrup (130 mg, 0.053 mmol) was dissolved in 0.5 mL DCM, MeOH (3.0 mL) and MeONa (100 mg) were added successively. The mixture was stirred at room temperature for 7 days and neutralized with 1M HCl, then it was filtered. The filtrates were concentrated under vacuum to give a residue, which was purified by flash column chromatography (DCM/MeOH=30/1-10/1) to afford a light yellow syrup (85.7 mg, 95%). The above syrupn (85.7 mg, 0.050 mmol) was dissolved in EtOH (30 mL), and 10% palladium on activated charcoal (538 mg) was added. The flask was degassed using low vacuum and flushed with hydrogen (3 times). The mixture was stirred under a hydrogen balloon overnight at room temperature, then it was filtered celite and concentrated in vacuo. The resulting residue was purified by Sephadex LH-20 (H_2O) and washed with MeOH to give **3** (44.6 mg, 100%) as a white amorphous solid. $[\alpha]_D^{24}$= +40.80 (*c* 0.10, H_2O);^{1}H NMR (400 MHz, Deuterium Oxide) δ 4.92 (d, *J* = 3.7 Hz, 1H), 4.56 – 4.48 (m, 4H), 4.05 (td, *J* = 7.3, 3.2 Hz, 1H), 3.97 (d, *J* = 12.1 Hz, 3H), 3.93 – 3.78 (m, 8H), 3.76 – 3.59 (m, 13H), 3.54 – 3.46 (m, 2H), 3.42 (d, *J* = 9.2 Hz, 1H), 3.39 – 3.28 (m, 5H), 1.16 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 100.34, 100.12, 100.04, 96.10, 76.29, 76.17, 76.06, 73.80, 72.64, 71.81, 70.96, 70.79, 70.75, 69.34, 69.05, 68.28, 67.25, 64.35, 58.37, 57.69, 57.58, 15.93. HRMS (ESI) calcd for $C_{33}H_{58}O_{27}Na$ $[M+Na]^+$909.3058 found 909.3059.

Comparison of the analytic data between K. C. Nicolaou's synthetic rhynchosporosides[4] and synthetic 1, 2 and 3



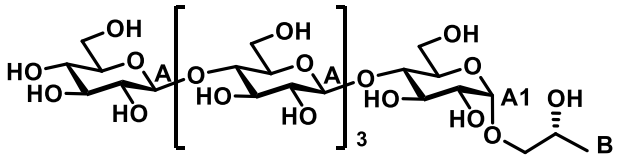
1

Position	K. C. Nicolaou's work	Compound 1
A1	δ 4.92 (d, J=3.7 Hz, 1H)	δ 4.92 (d, J = 3.8 Hz, 1H)
A	δ 4.53 (d, J=7.6 Hz, 2H)	δ 4.53 (d, J = 8.0 Hz, 1H)
	δ 4.50 (d, J=7.4 Hz, 1H)	δ 4.50 (d, J = 7.9 Hz, 1H)
B	δ 1.16 (d, J=6.5 Hz, 3H)	δ 1.17 (d, J = 6.5 Hz, 3H)
		δ 4.05 (td, J = 7.1, 3.1 Hz, 1H), 3.98 (d, J = 11.2 Hz, 1H), 3.93 – 3.78 (m, 6H), 3.76 – 3.69 (m, 2H), 3.68 – 3.57 (m, 5H), 3.53 – 3.45 (m, 2H), 3.42 (d, J = 9.2 Hz, 1H), 3.39 – 3.28 (m, 3H)



2

Position	K. C. Nicolaou's work	Compound 2
A1	δ 4.92 (d, J=3.7 Hz, 1H)	δ 4.92 (d, J = 3.8 Hz, 1H)
A	δ 4.53 (d, J=7.4 Hz, 2H)	δ 4.53 (d, J = 7.7 Hz, 2H)
	δ 4.50 (d, J=7.5 Hz, 1H)	δ 4.50 (d, J = 8.1 Hz, 1H)
B	δ 1.16 (d, J=6.5 Hz, 3H)	δ 1.16 (d, J = 6.5 Hz, 3H)
		δ 4.05 (td, J = 7.1, 3.2 Hz, 1H), 3.97 (d, J = 12.1 Hz, 2H), 3.92 – 3.79 (m, 7H), 3.75 – 3.58 (m, 10H), 3.52 – 3.46 (m, 2H), 3.41 (d, J = 9.2 Hz, 1H), 3.38 – 3.28 (m, 4H)



3

Position	K. C. Nicolaou's work	Compound 3
A1	δ 4.92 (d, J=3.7 Hz, 1H)	δ 4.92 (d, J = 3.8 Hz, 1H)
A	δ 4.53 (d, J=7.3 Hz, 3H) δ 4.50 (d, J=7.5 Hz, 1H)	4.56 – 4.48 (m, 4H)
B	δ 1.16 (d, J=6.5 Hz, 3H)	δ 1.16 (d, J = 6.5 Hz, 3H) δ 4.05 (td, J = 7.3, 3.2 Hz, 1H), 3.97 (d, J = 12.1 Hz, 3H), 3.93 – 3.78 (m, 8H), 3.76 – 3.59 (m, 13H), 3.54 – 3.46 (m, 2H), 3.42 (d, J = 9.2 Hz, 1H), 3.39 – 3.28 (m, 5H)

Reference

(1) A.-R. Jone, B. Hagen, V. Ark, H. S. Overkleeft, J. D. C. Codee and G. A. V. Marel, *J. Org. Chem.* 2012, **77**, 108-125.

(2) L.-D. Lu, C.-R. Shie, S. S. Kulkarni, G.-R. Pan, X.-A. and S.-C. Hung, *Org. Lett.* 2006, **8**, 5995-5998

(3) B. Yu and H. Tao, *J. Org. Chem.* 2002, **67**, 9099-9102

(4) K. C. Nicolaou, J. L. Randall and G. T. Furst, *J. Am. Chem. Soc.* 1985, **107**, 5556-5558.

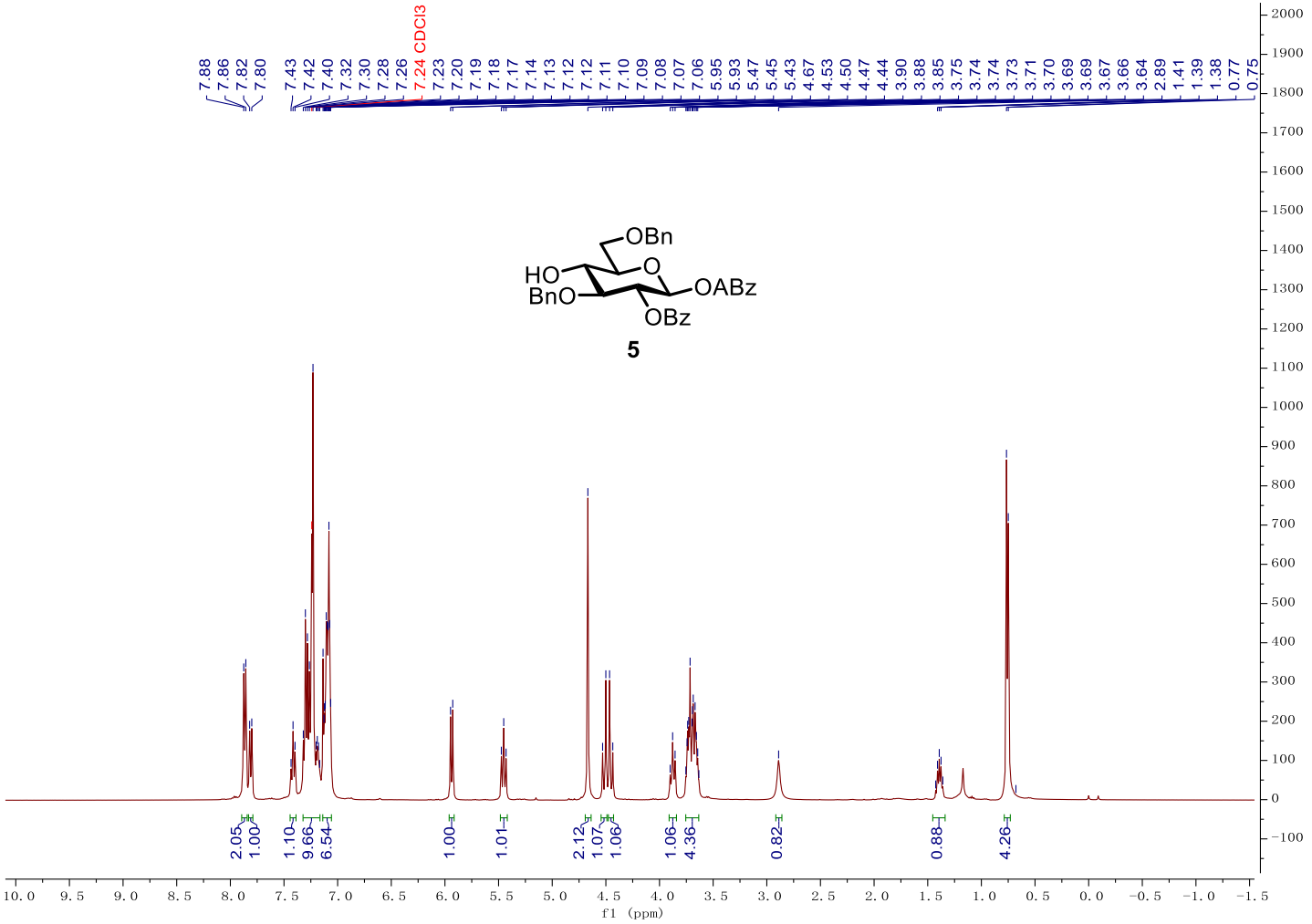


Figure S1. 1H (400 MHz, $CDCl_3$) spectra of compound **5** β anomer

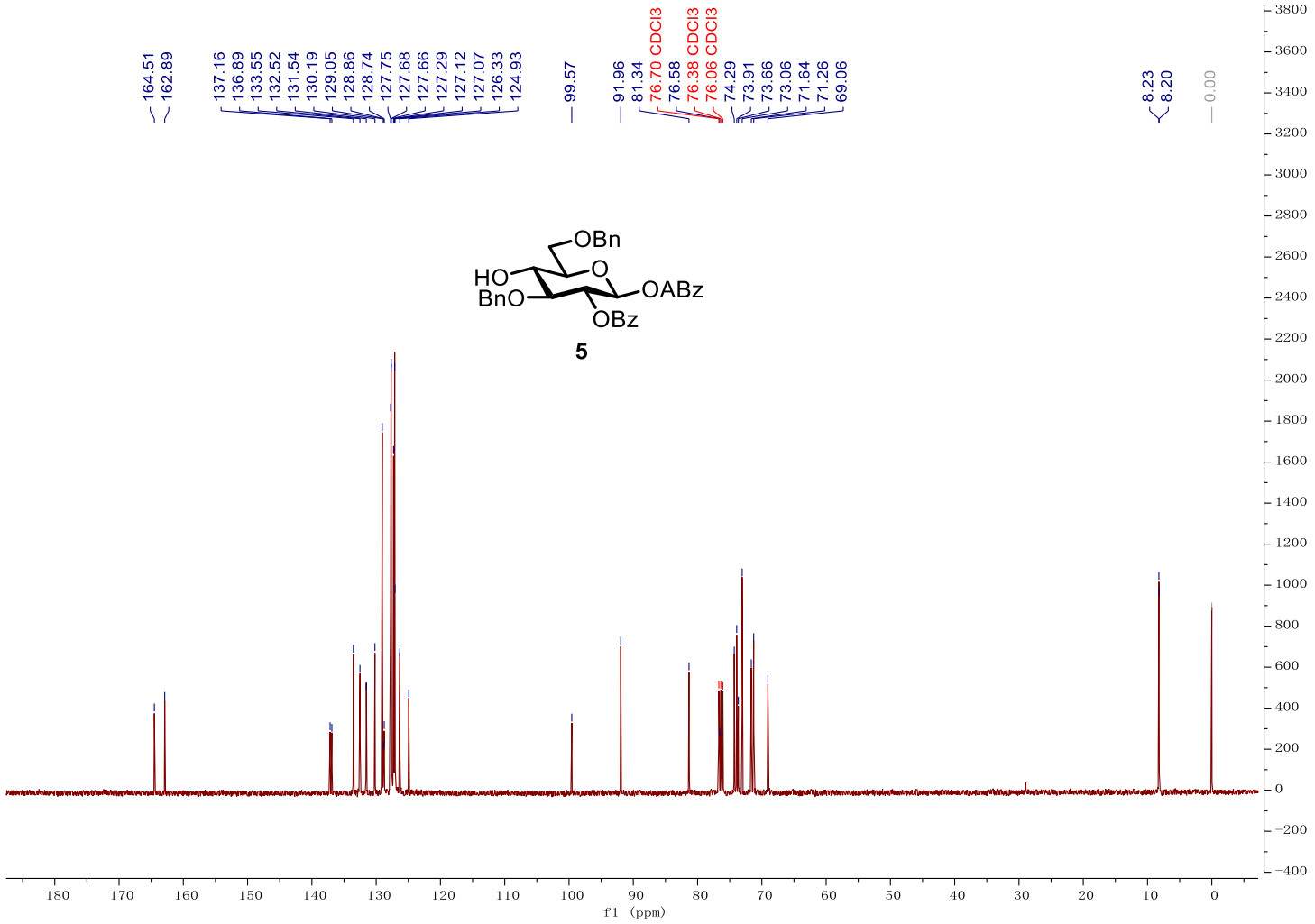


Figure S2. 13C (100 MHz, $CDCl_3$) spectra of compound **5** β anomer

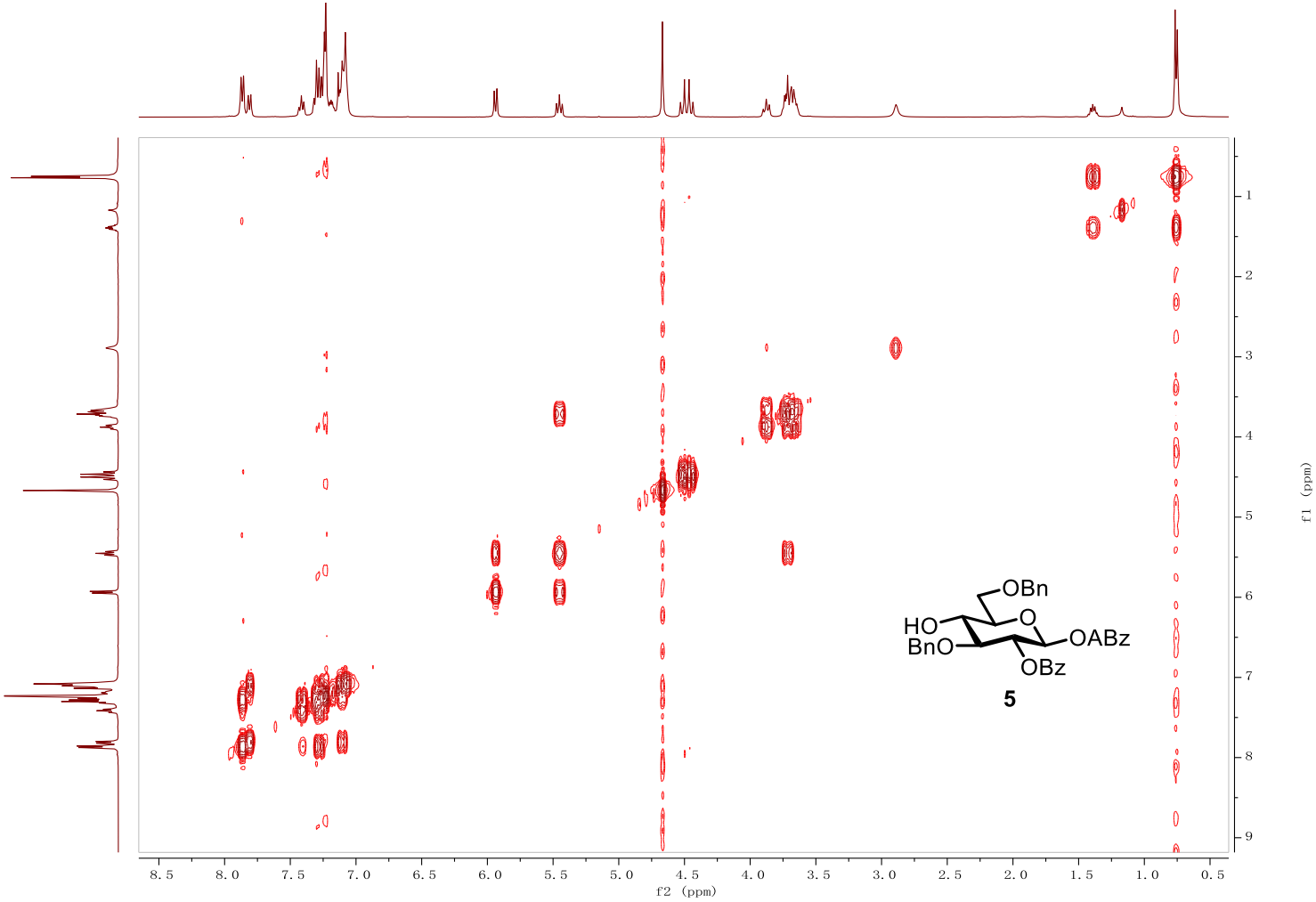


Figure S3. COSY spectra of compound **5** β anomer

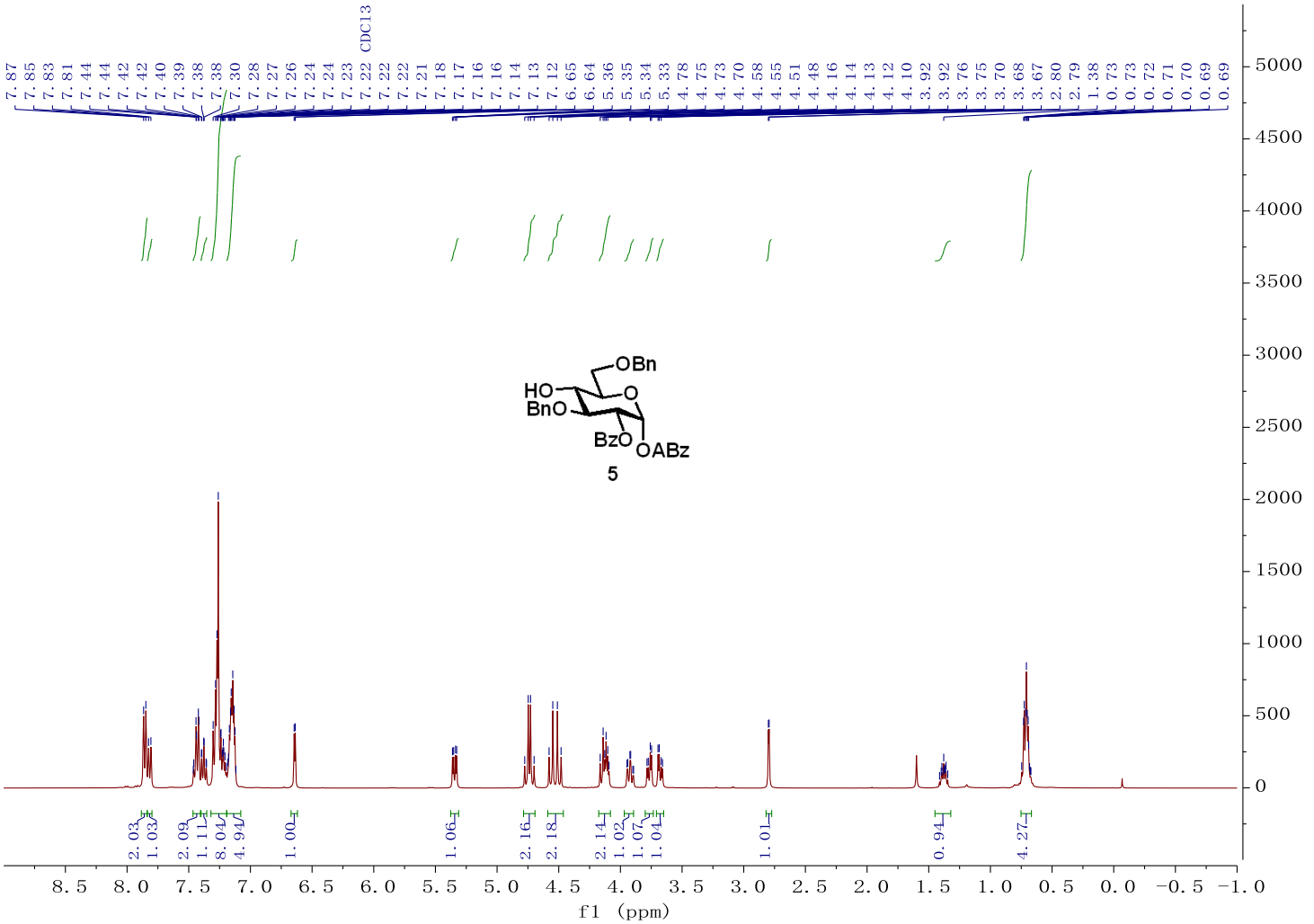


Figure S4. 1H (400 MHz, $CDCl_3$) spectra of compound **5** α anomer

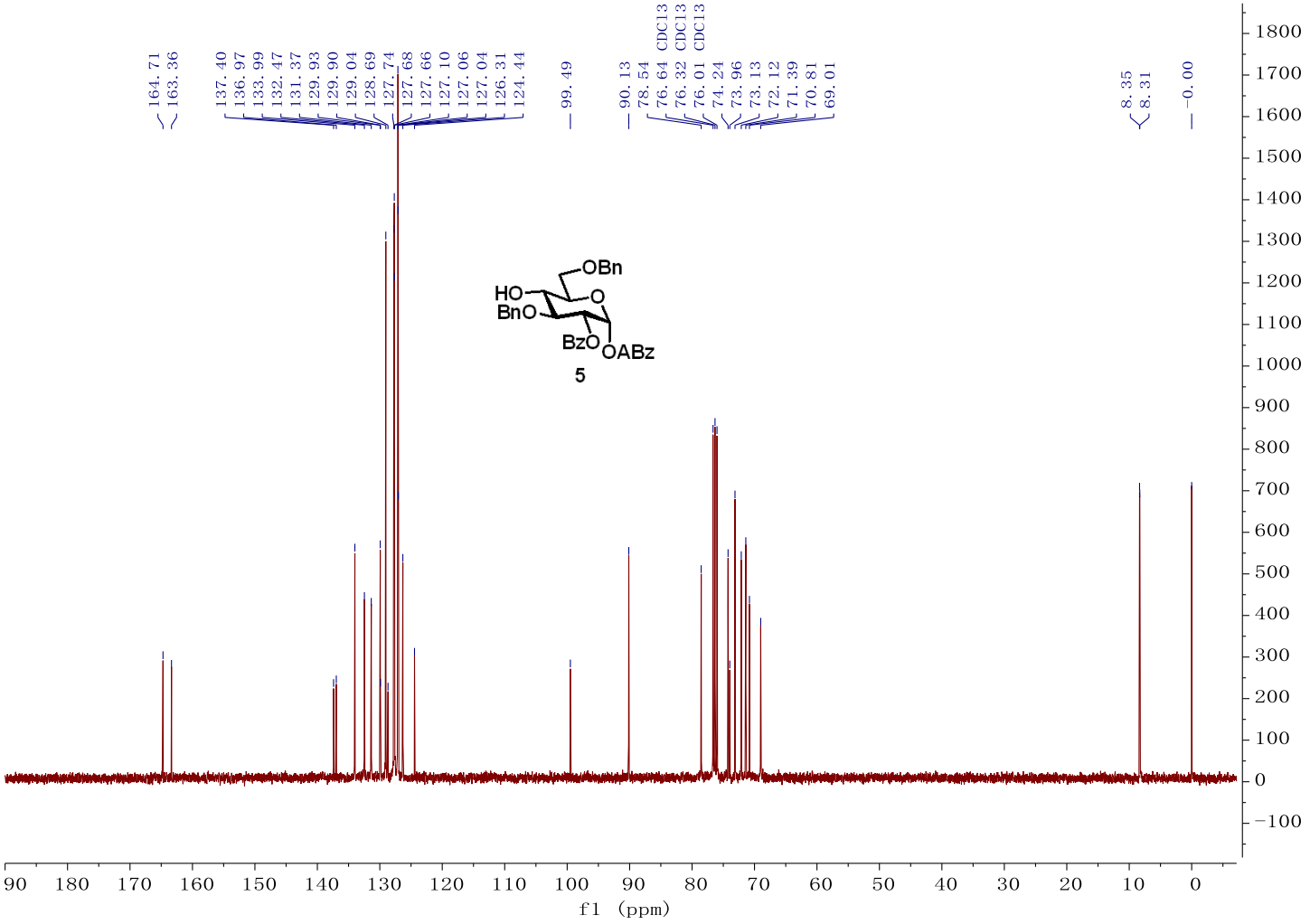


Figure S5. 13C (100 MHz, $CDCl_3$) spectra of compound **5** α anomer

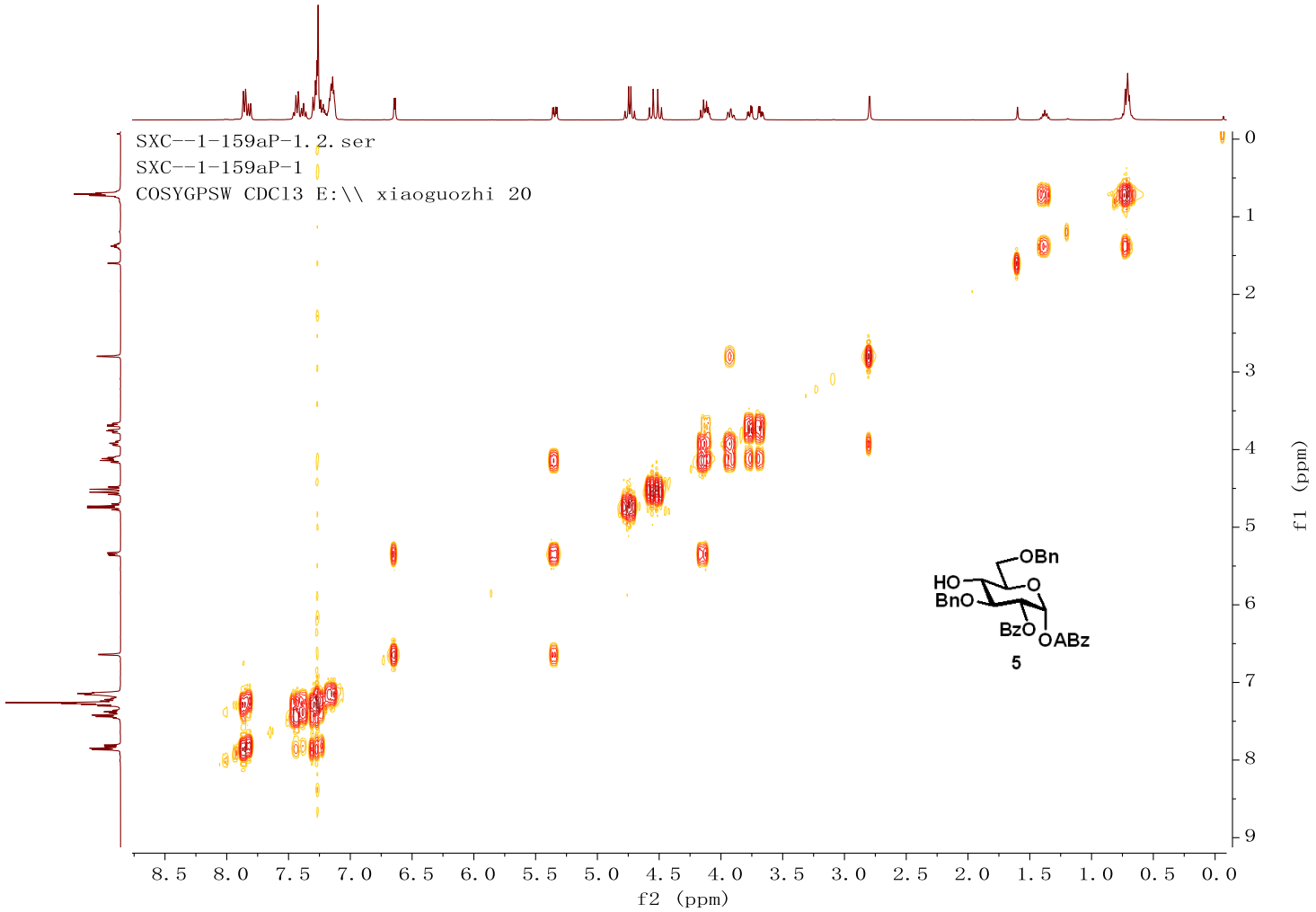


Figure S6. COSY spectra of compound **5** α anomer

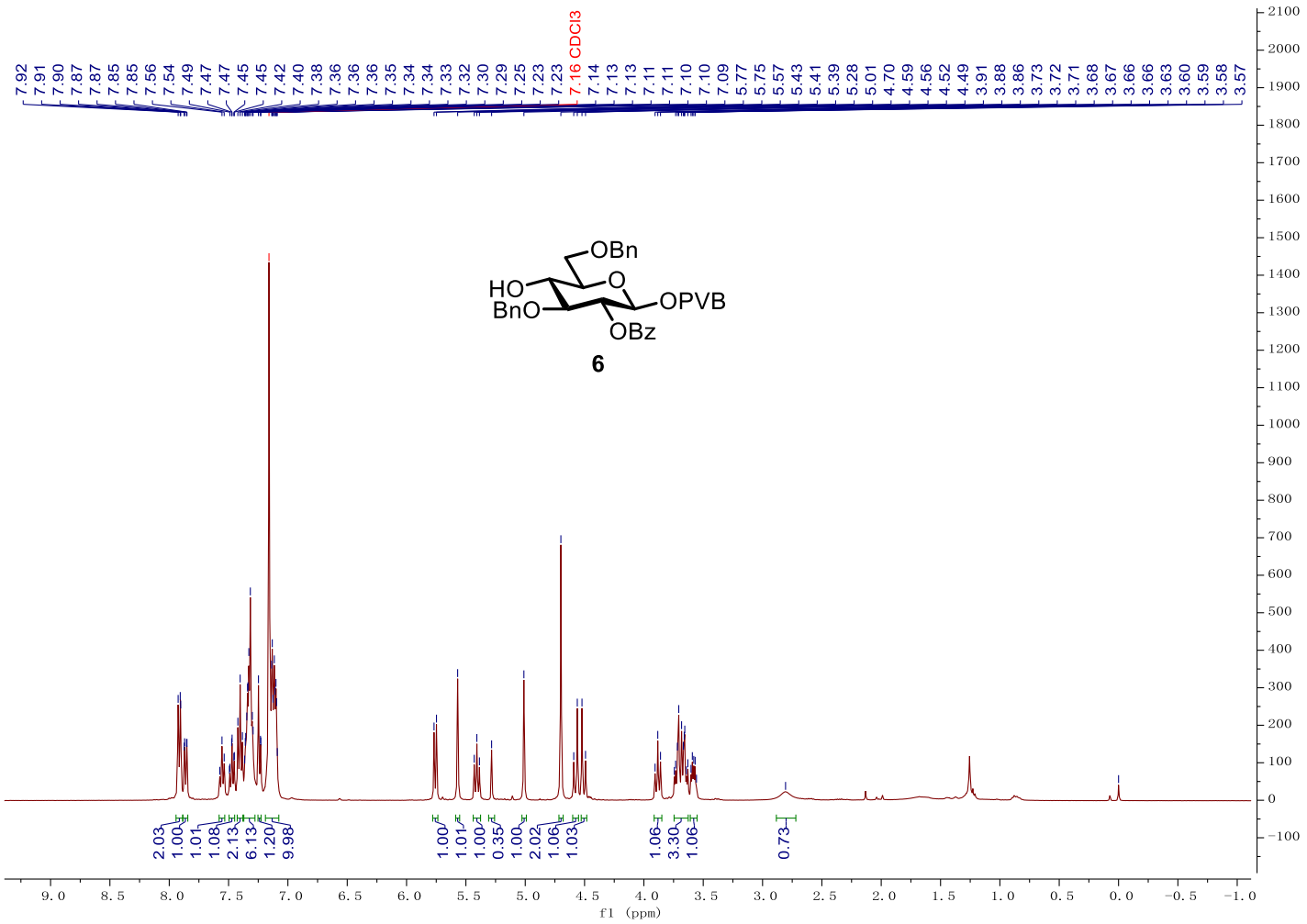


Figure S7. 1H (400 MHz, $CDCl_3$) spectra of compound **6** β anomer

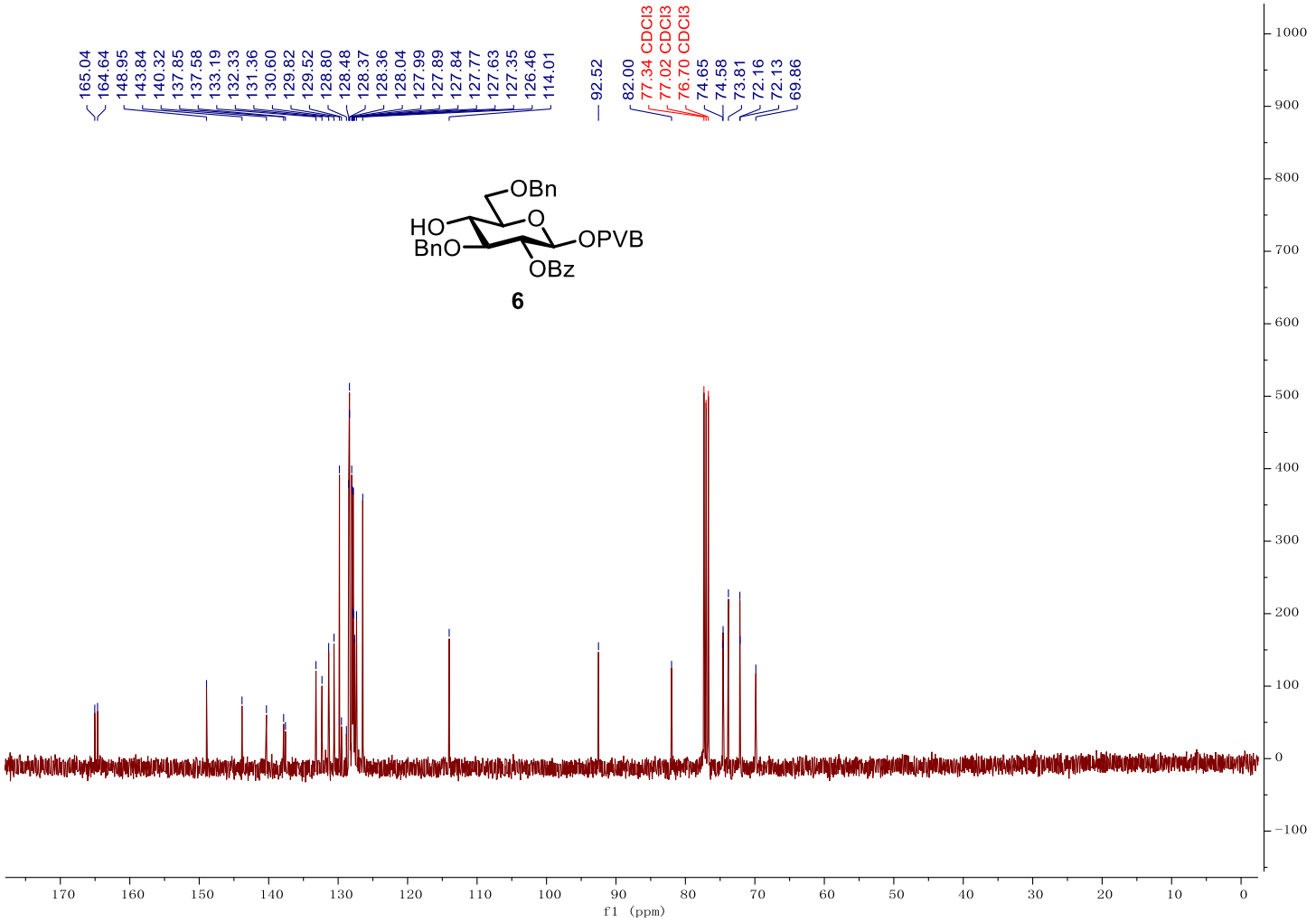


Figure S8. 13C (100 MHz, $CDCl_3$) spectra of compound **6** β anomer

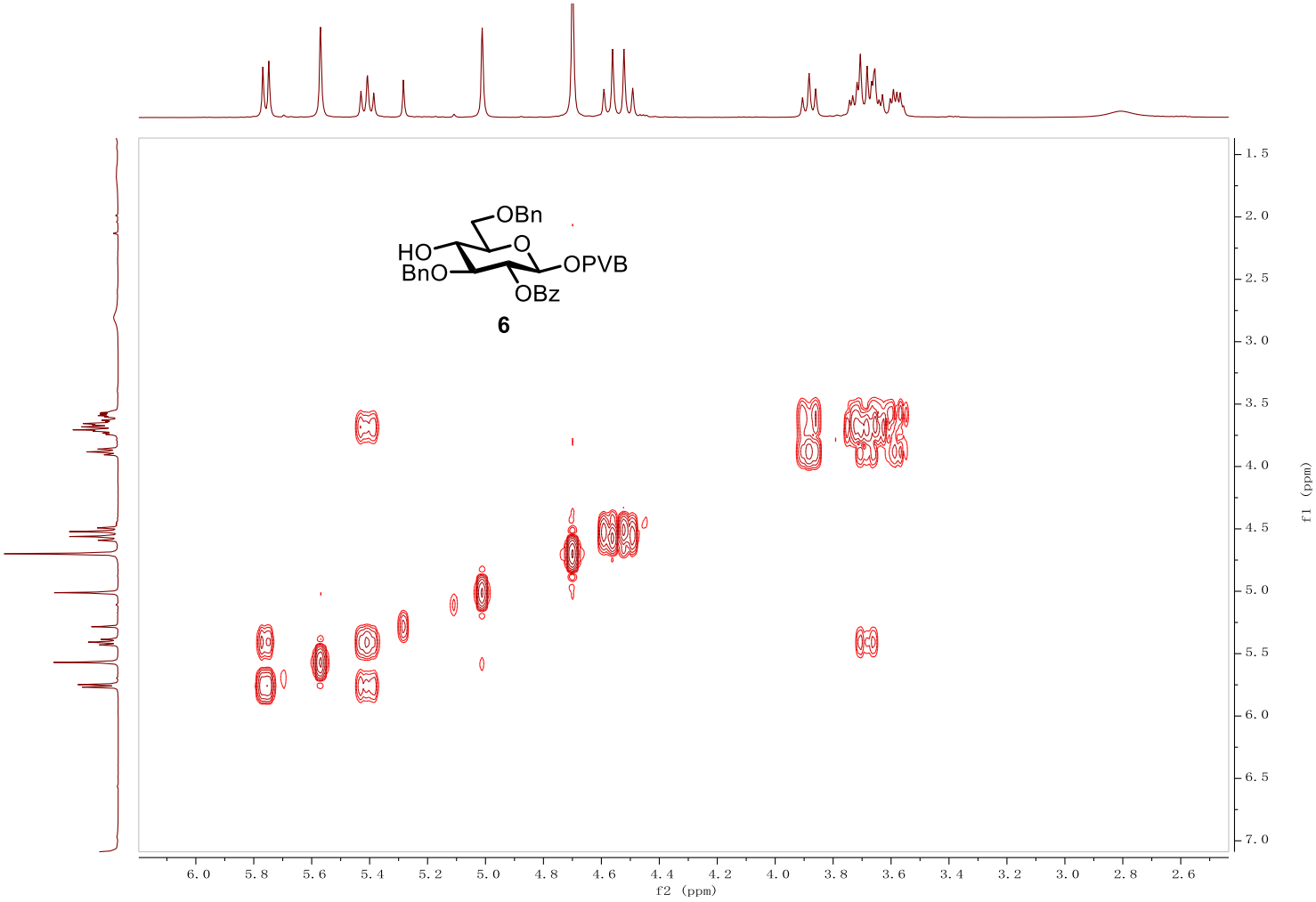


Figure S9. COSY spectra of compound **6** β anomer

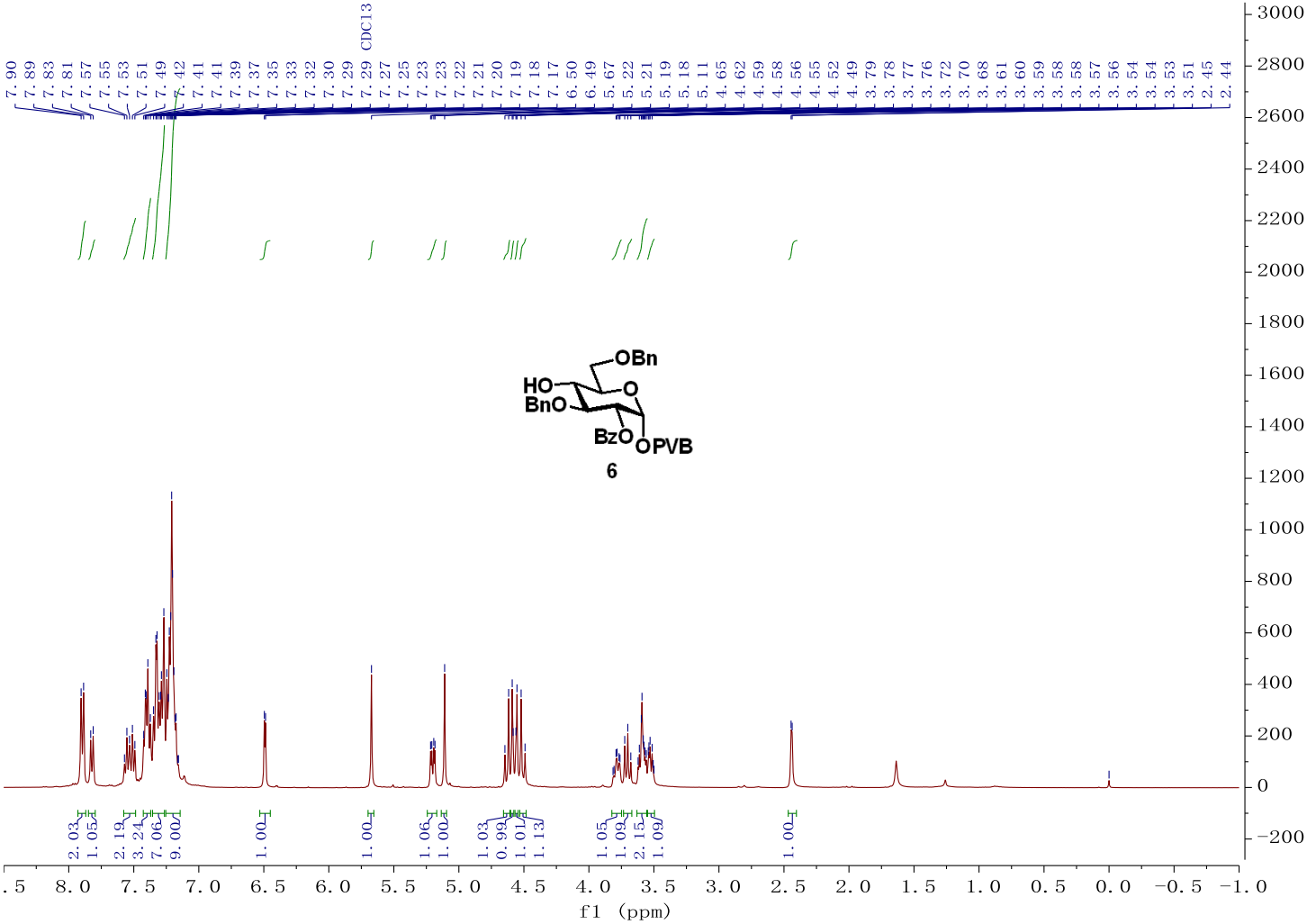


Figure S10. 1H (400 MHz, $CDCl_3$) spectra of compound **6** α anomer

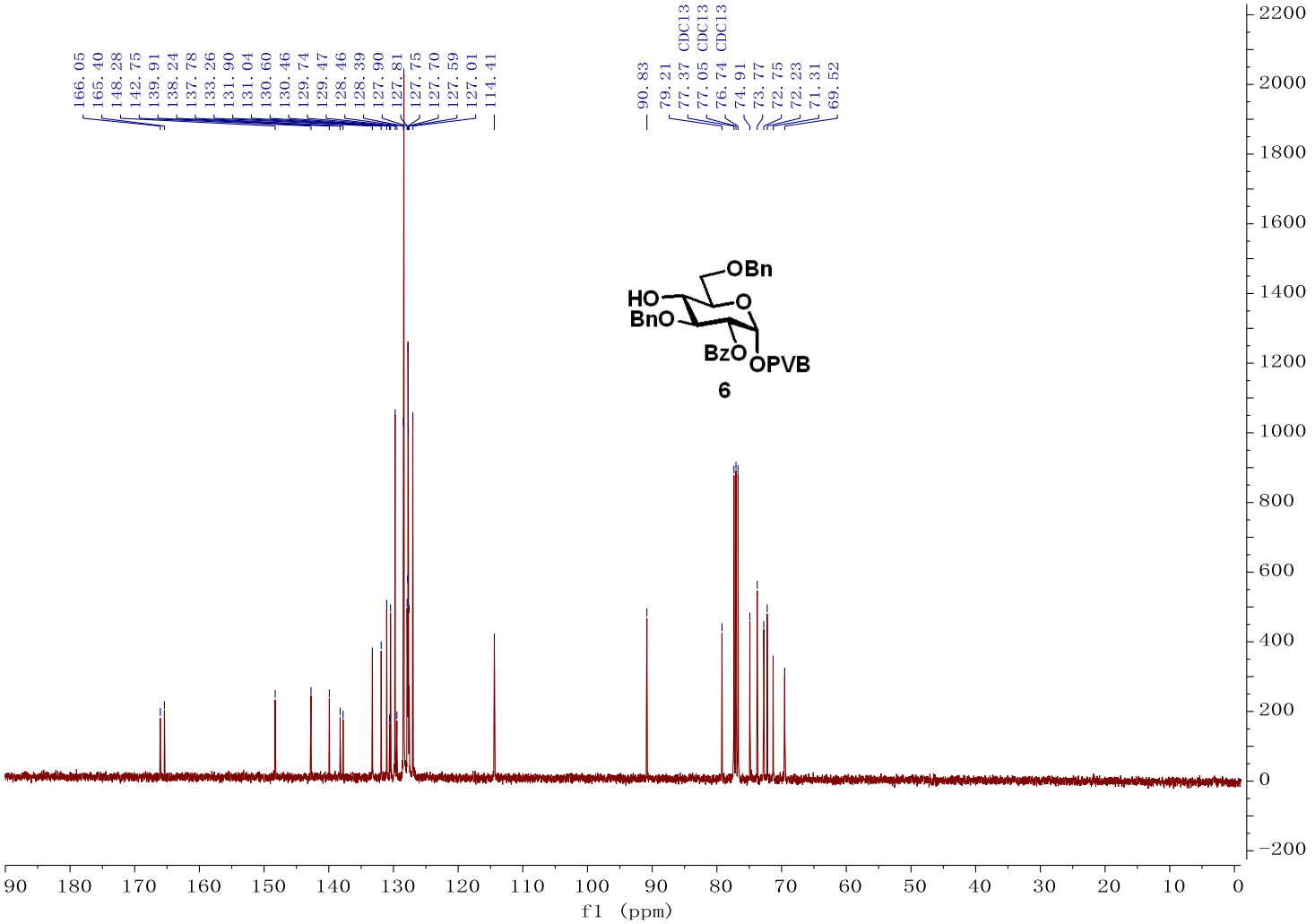


Figure S11. 13C (100 MHz, $CDCl_3$) spectra of compound **6** α anomer

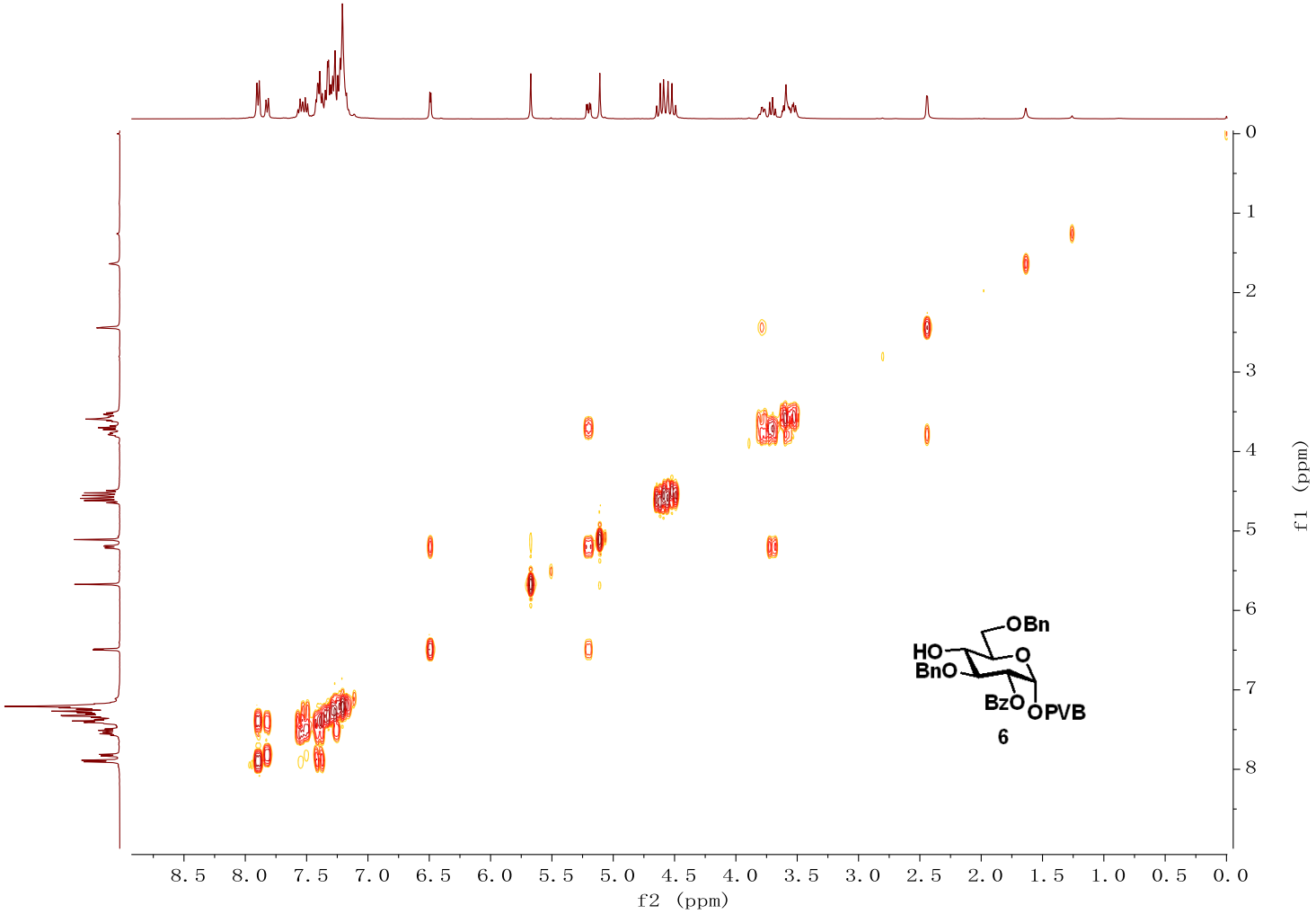


Figure S12. COSY spectra of compound **6** α anomer

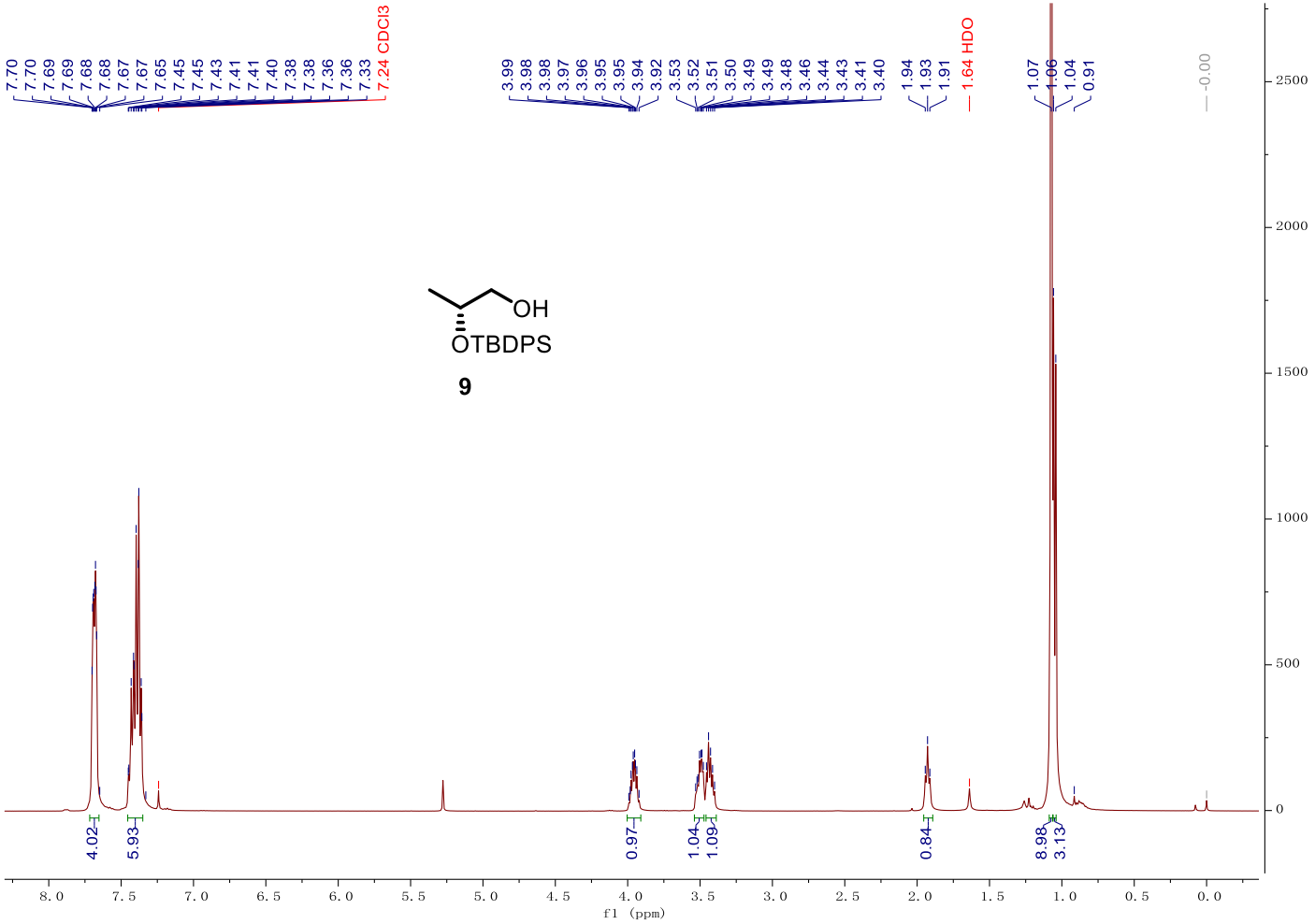


Figure S13. 1H (400 MHz, $CDCl_3$) spectra of compound **9**

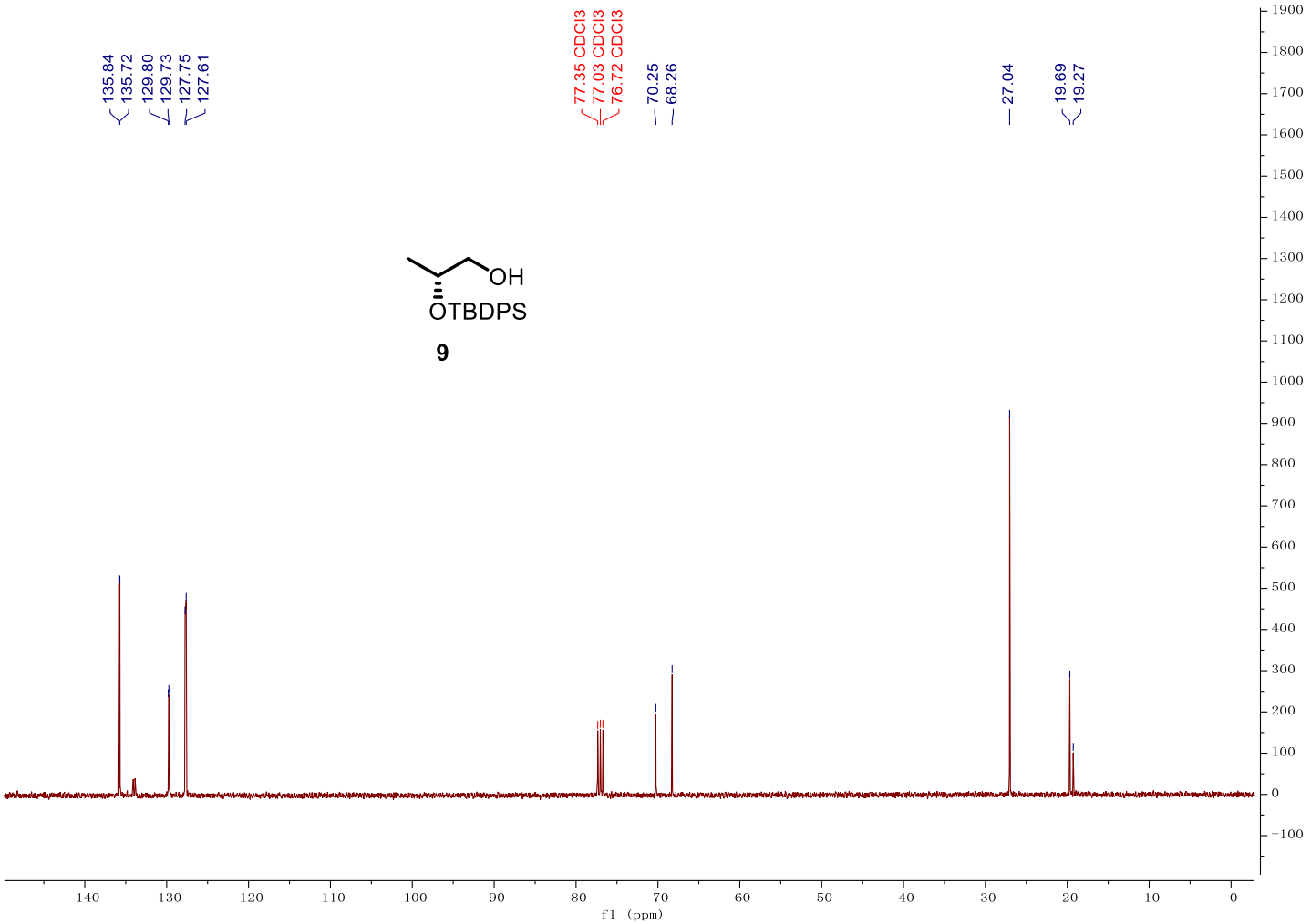


Figure S14. 13C (100 MHz, $CDCl_3$) spectra of compound **9**

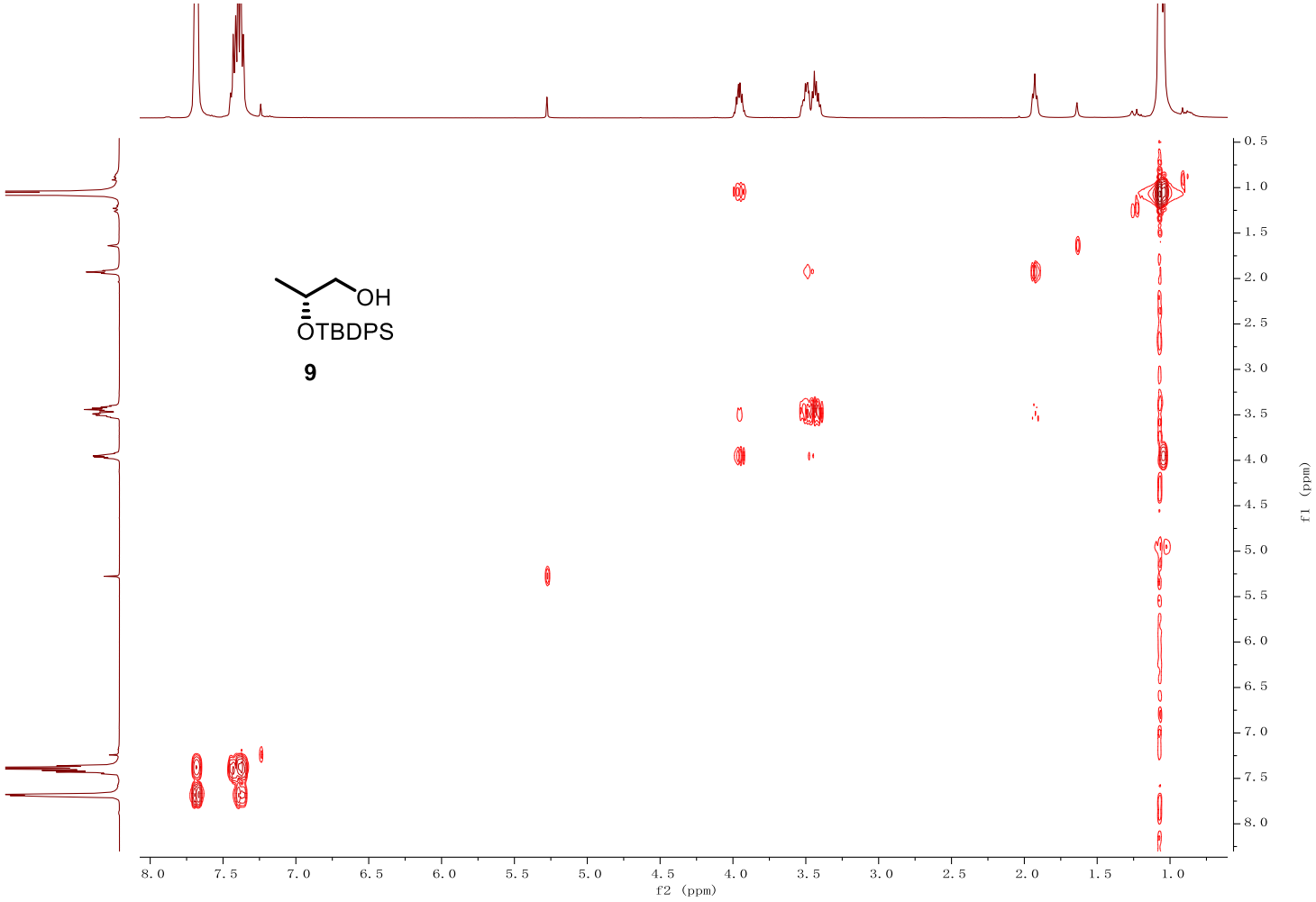


Figure S15. COSY spectra of compound **9**

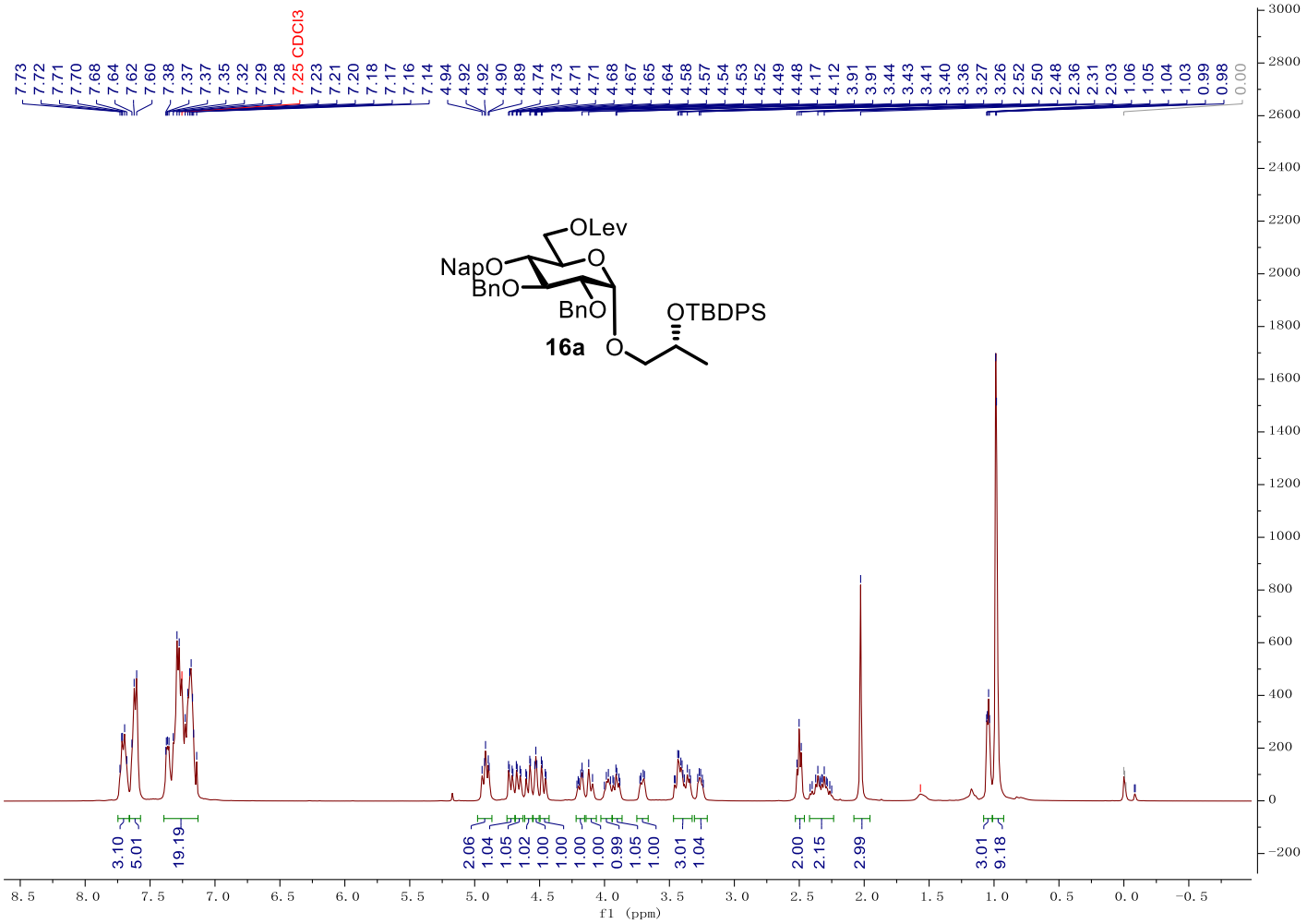


Figure S16. 1H (400 MHz, $CDCl_3$) spectra of compound **16a**

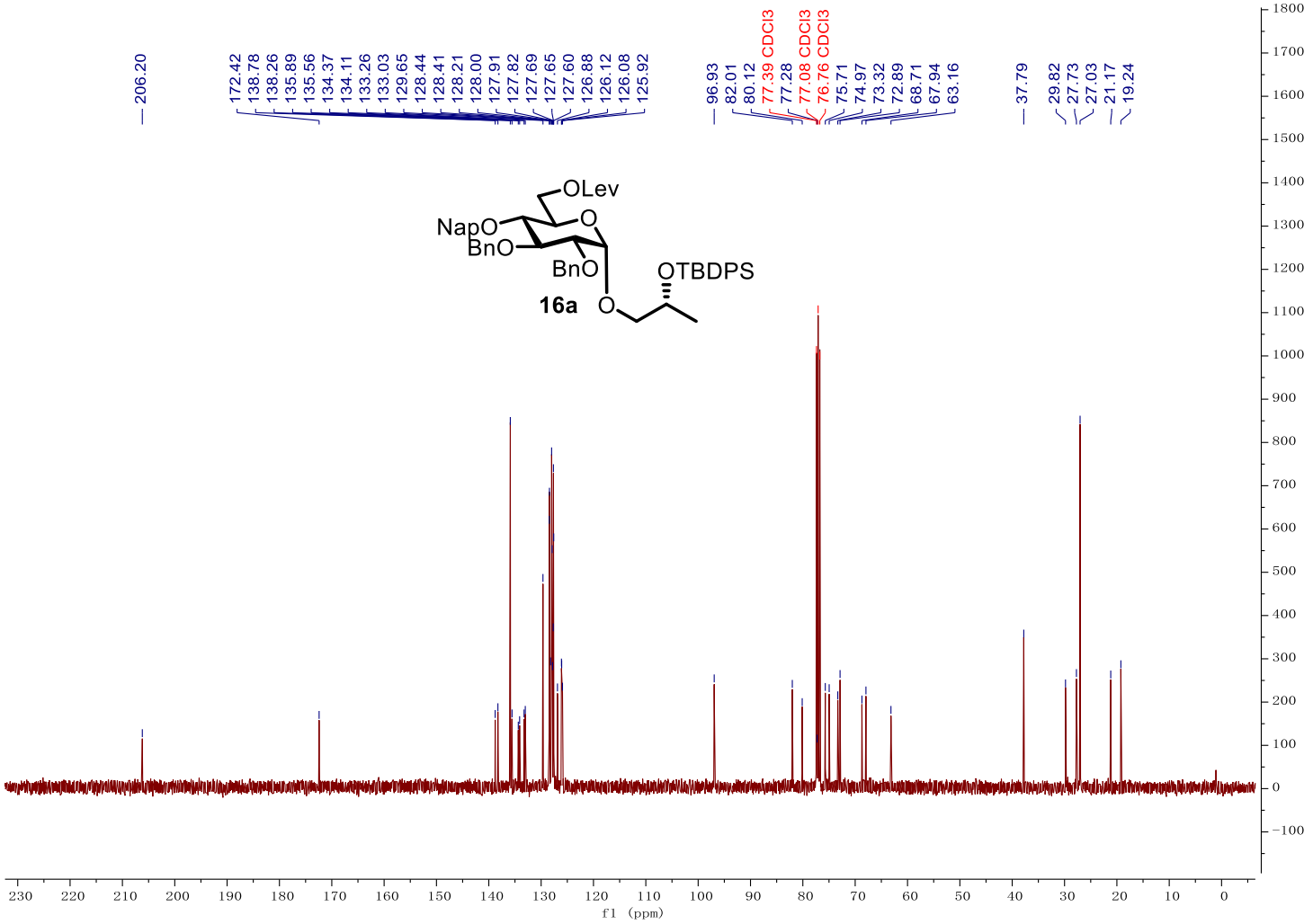


Figure S17. 13C (100 MHz, $CDCl_3$) spectra of compound **16a**

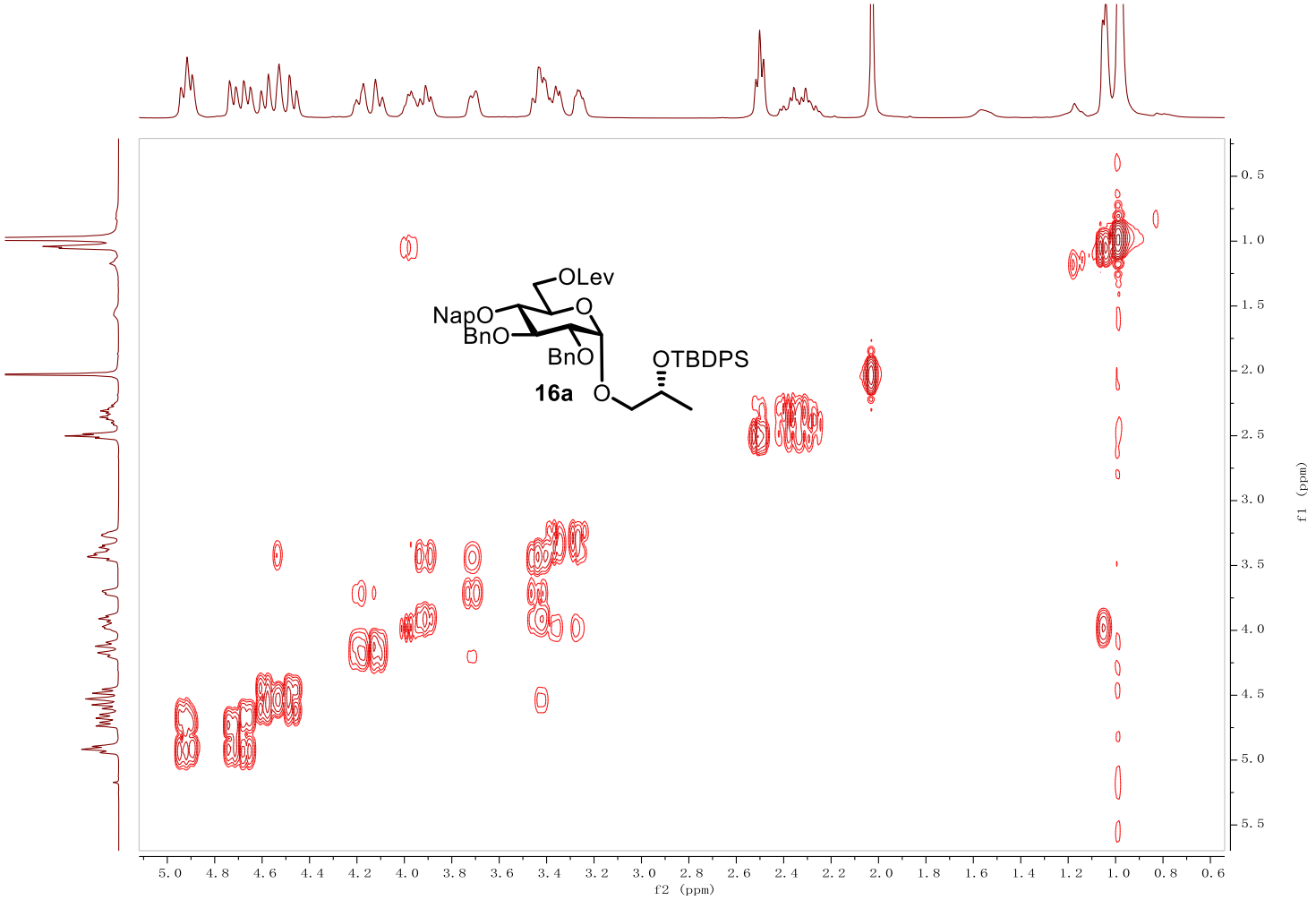


Figure S18. COSY spectra of compound **16a**

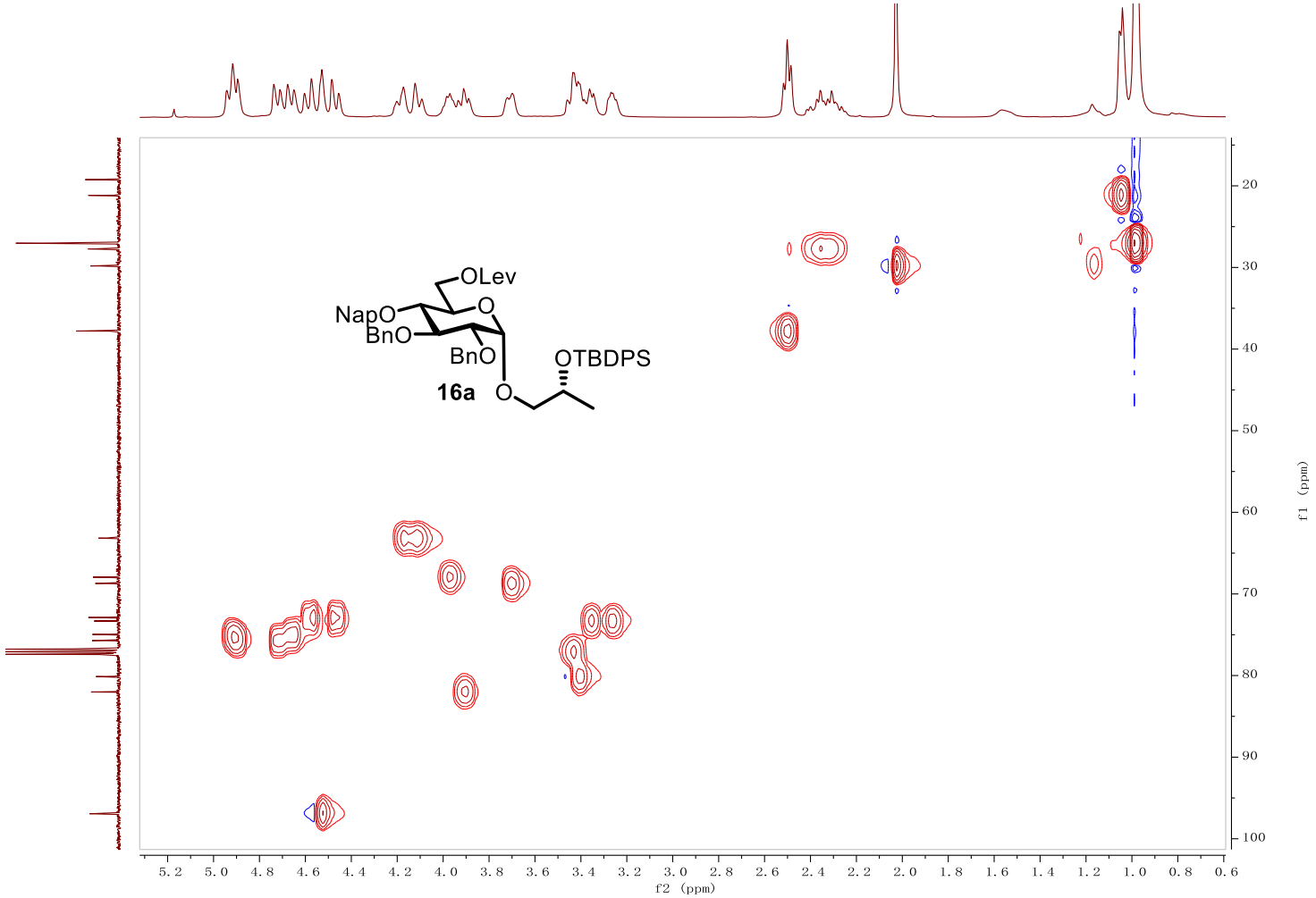


Figure S19. HSQC spectra of compound **16a**

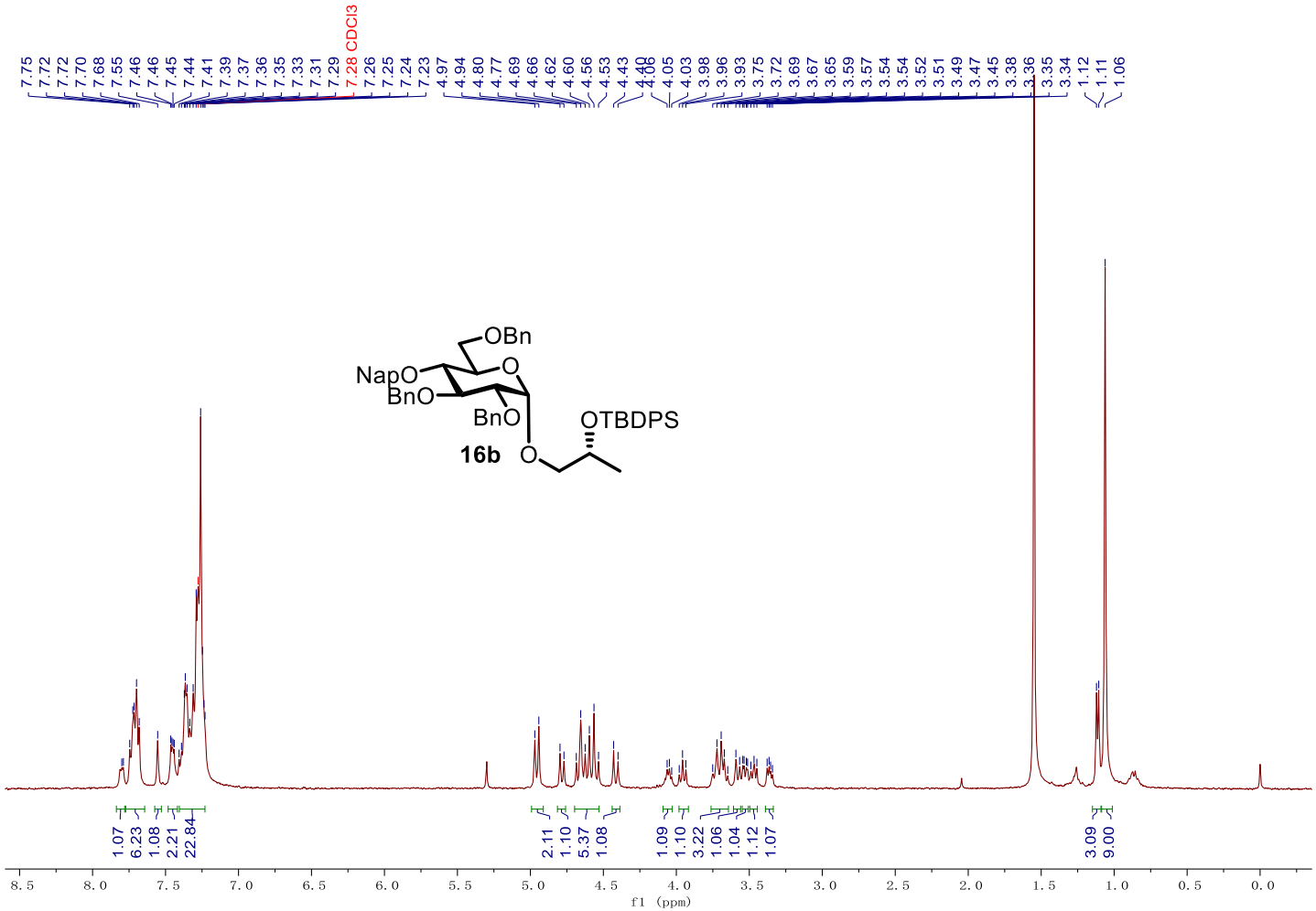


Figure S20. 1H (400 MHz, $CDCl_3$) spectra of compound **16b**

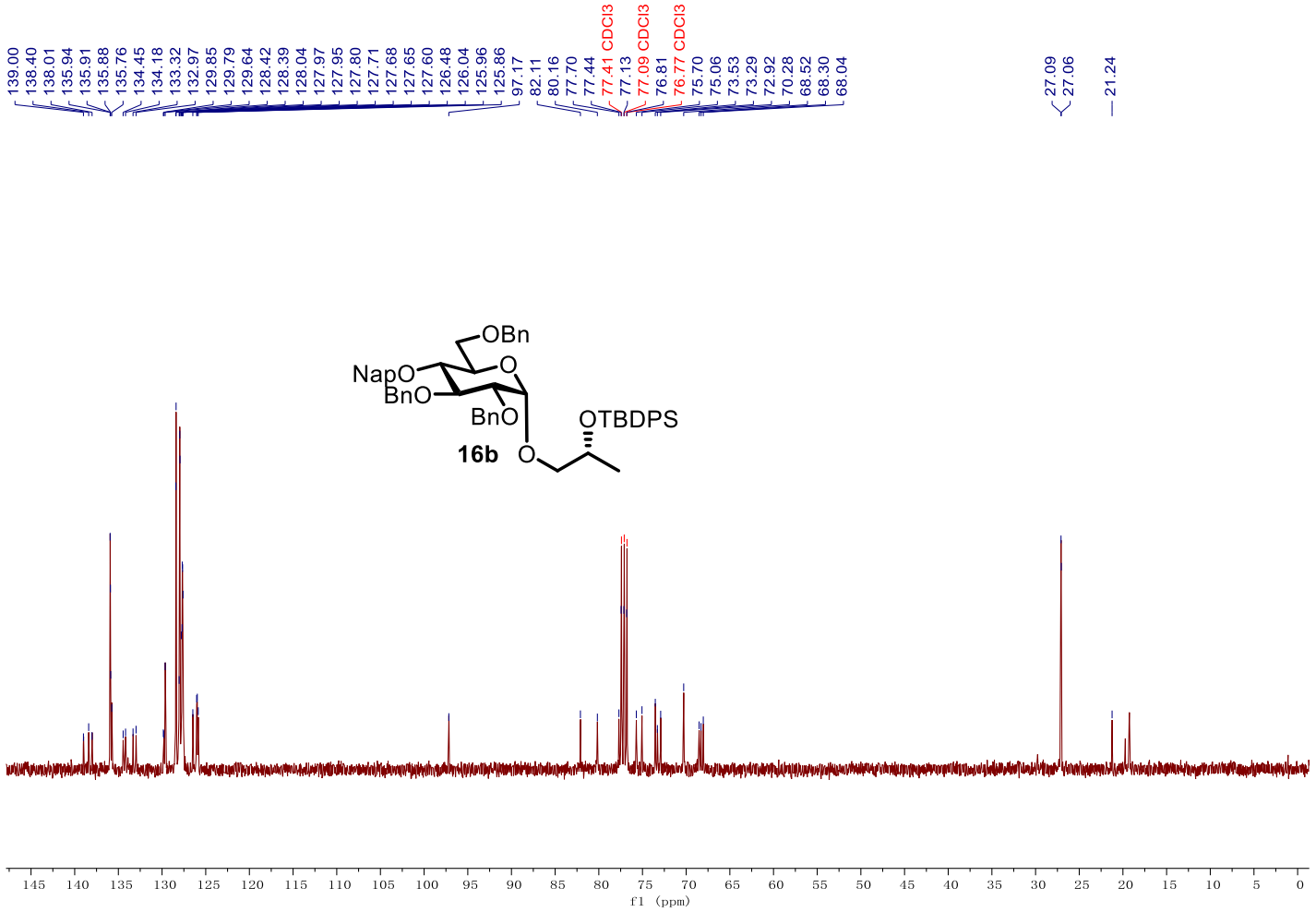


Figure S21. 13C (100 MHz, $CDCl_3$) spectra of compound **16b**

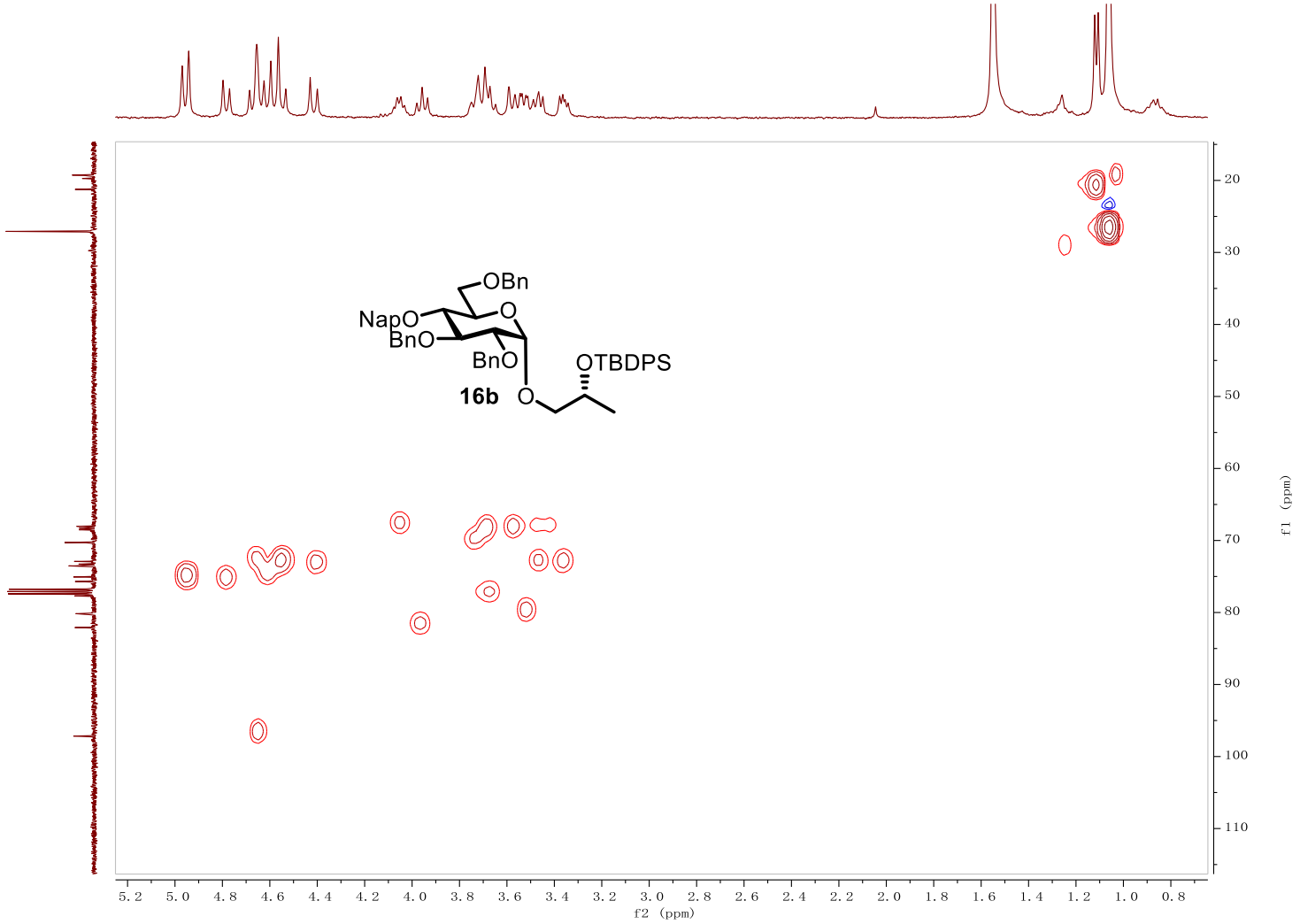


Figure S22. HSQC spectra of compound **16b**

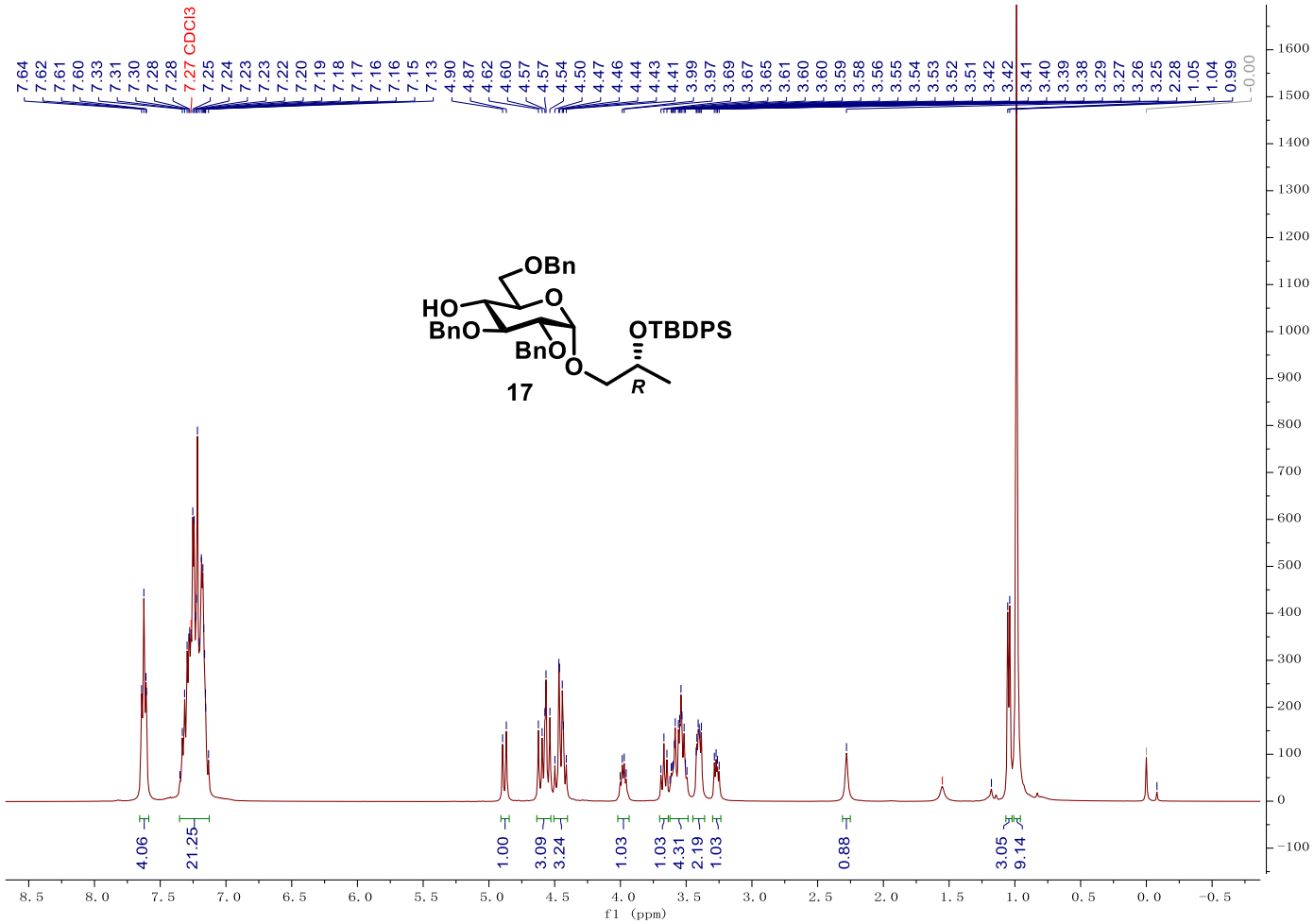


Figure S23. 1H (400 MHz, $CDCl_3$) spectra of compound **17**

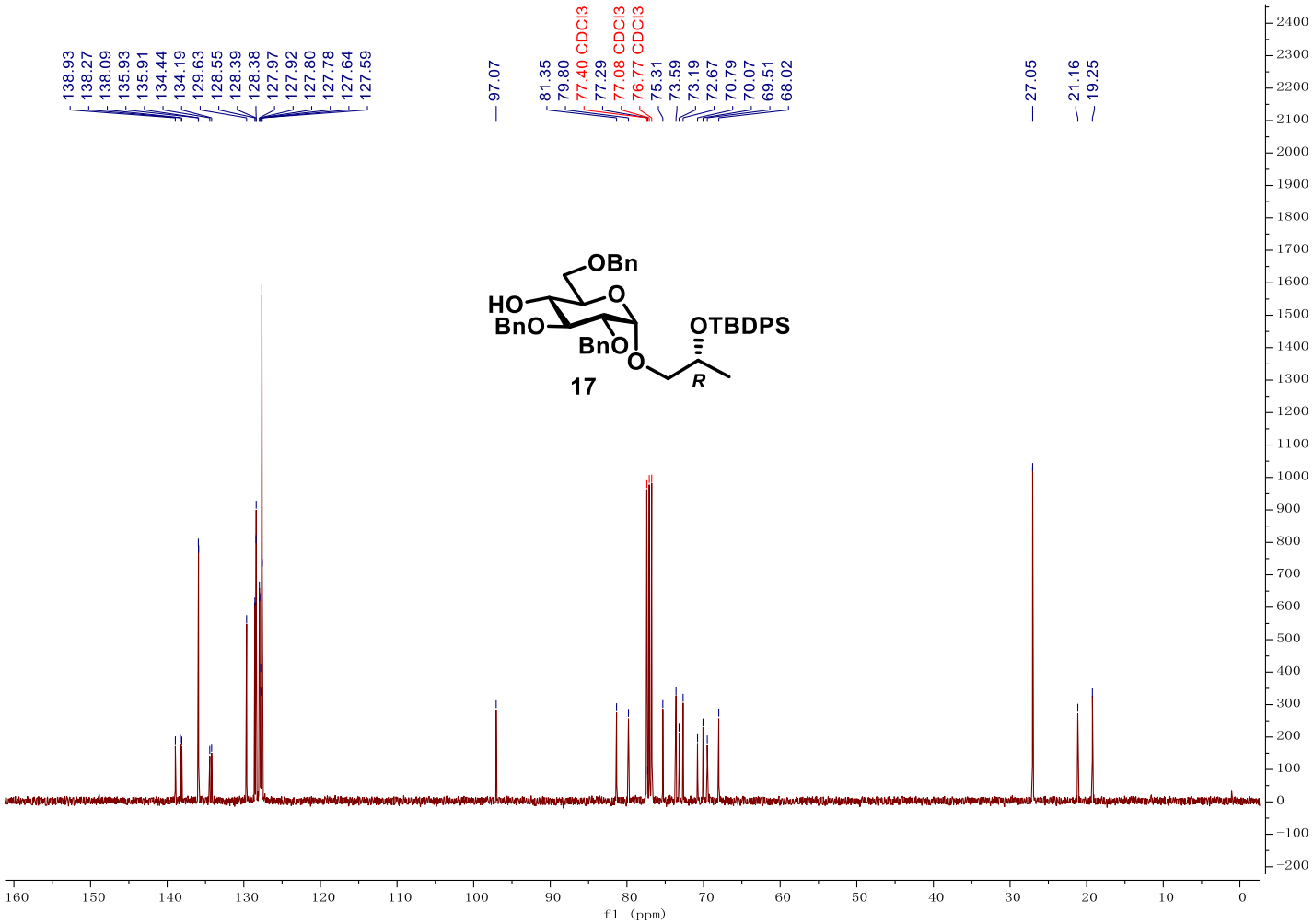


Figure S24. 13C (100 MHz, $CDCl_3$) spectra of compound **17**

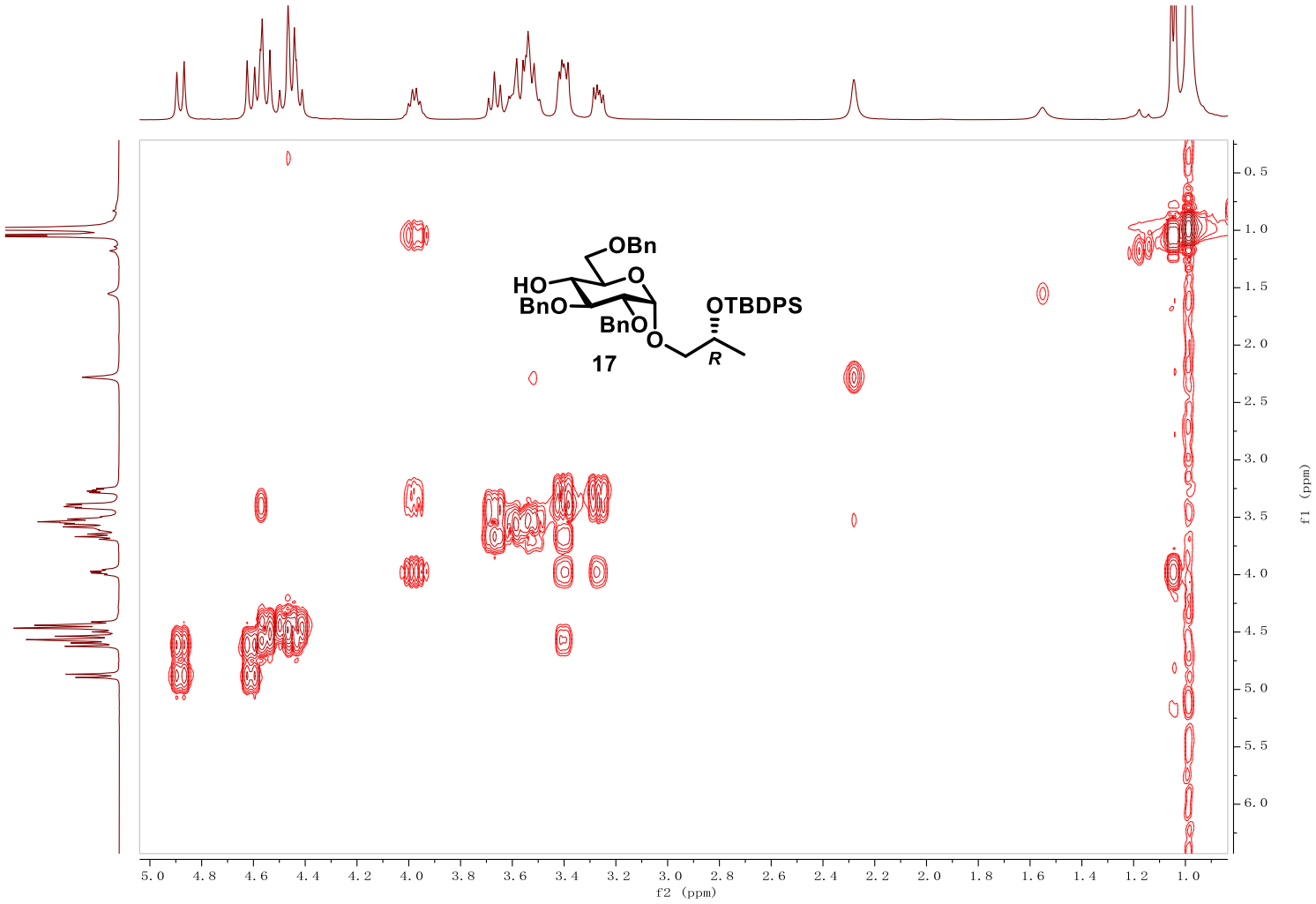


Figure S25. COSY spectra of compound **17**

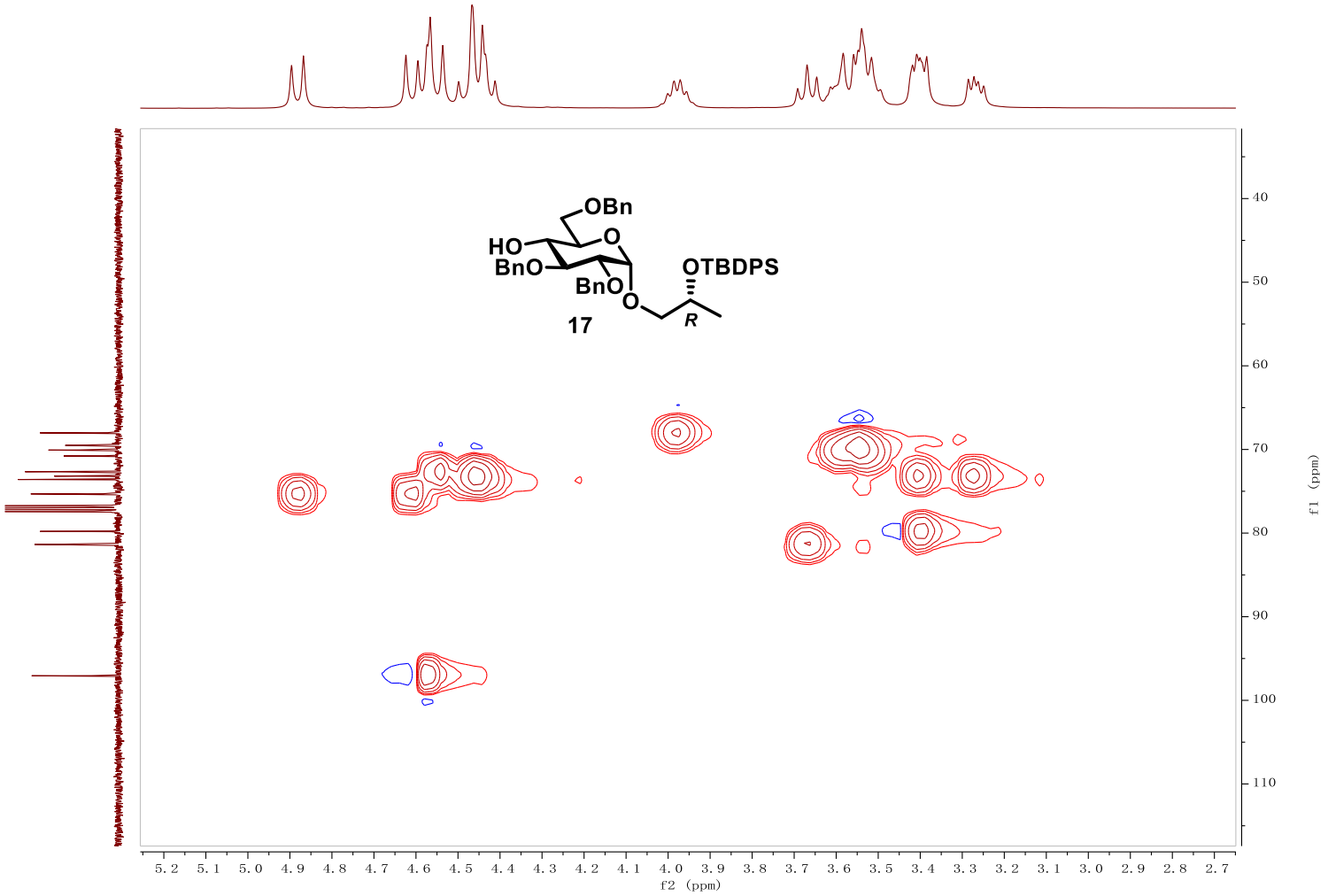


Figure S26. HSQC spectra of compound **17**

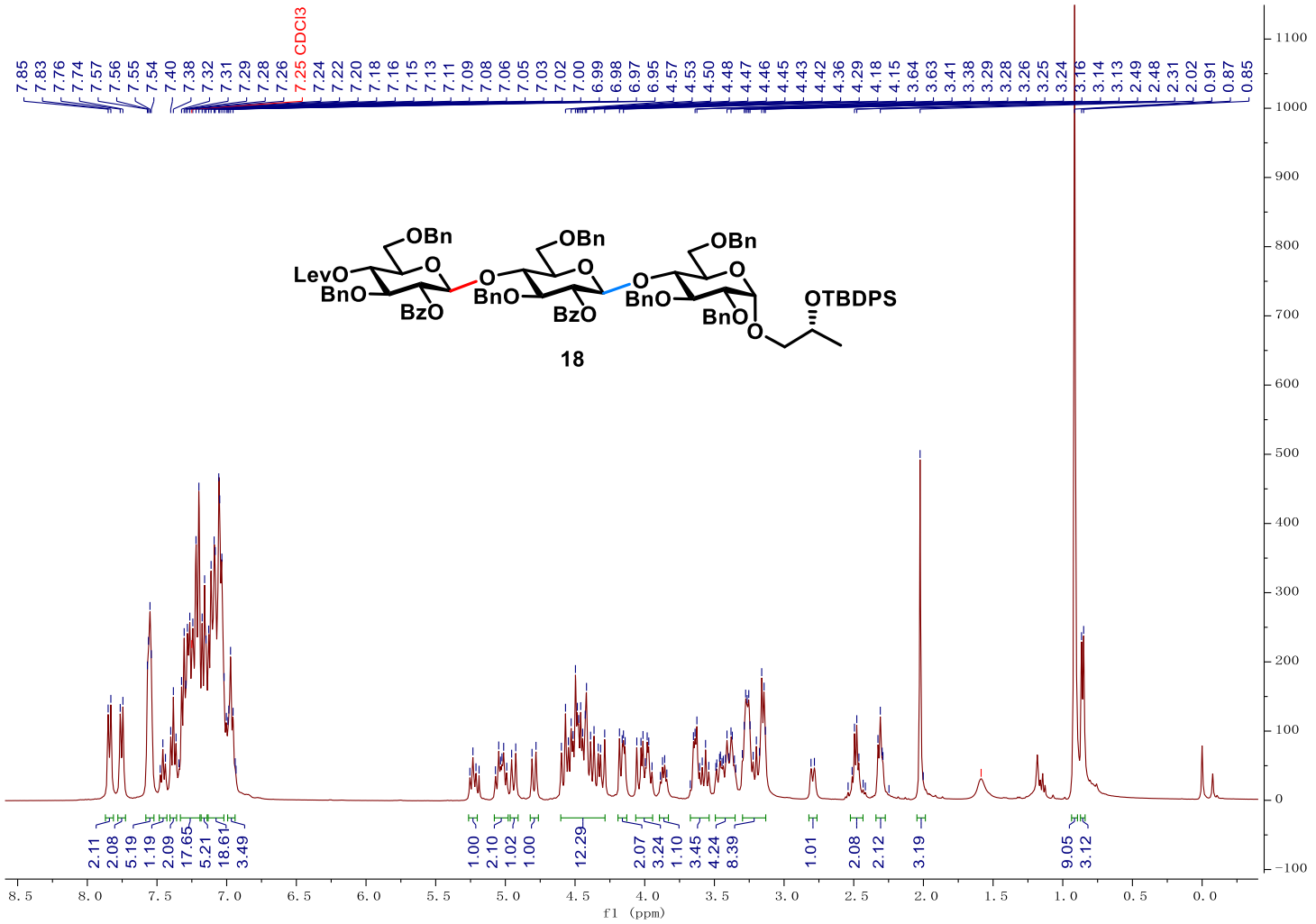


Figure S27. 1H (400 MHz, $CDCl_3$) spectra of compound **18**

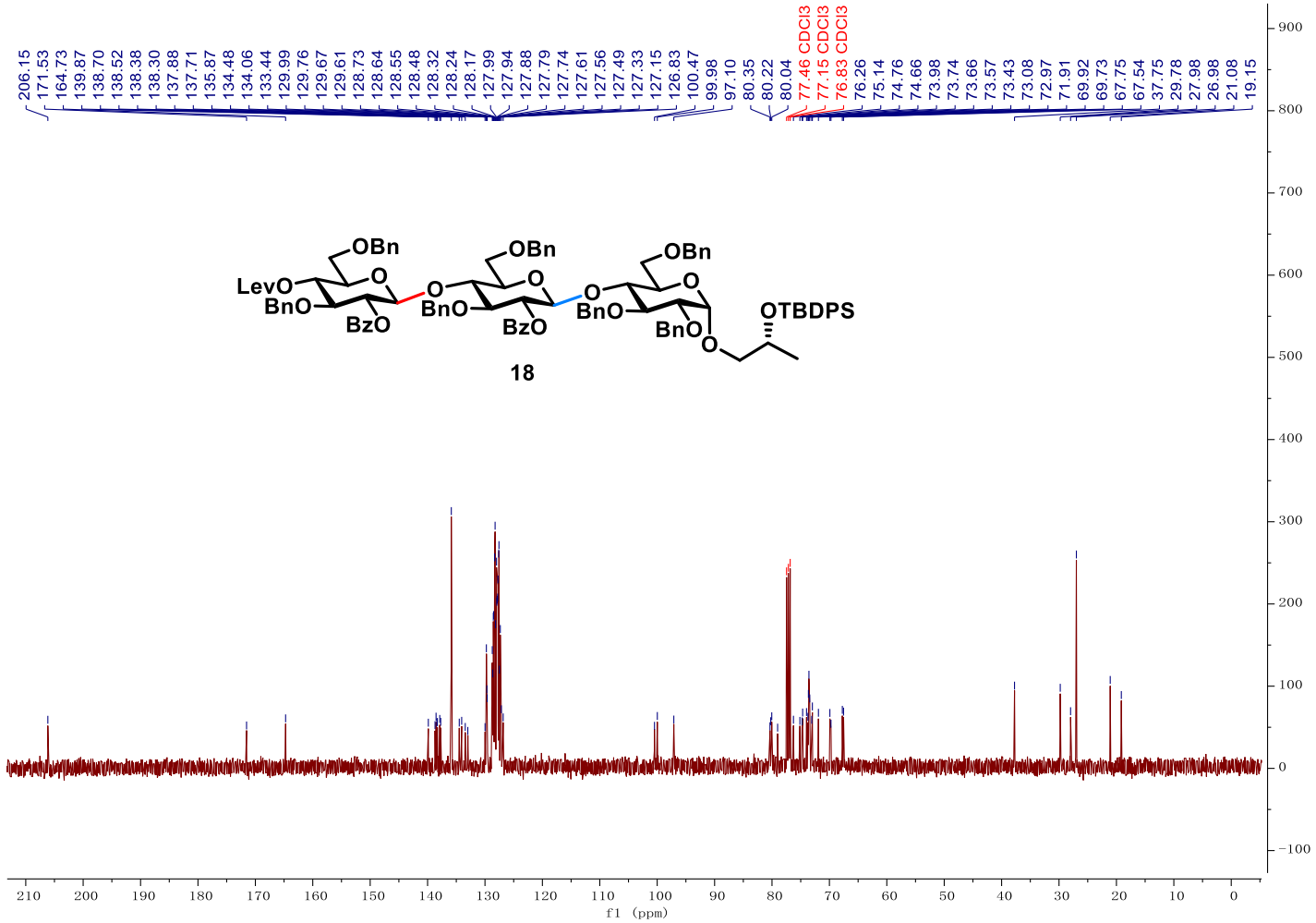


Figure S28. 13C (100 MHz, $CDCl_3$) spectra of compound **18**

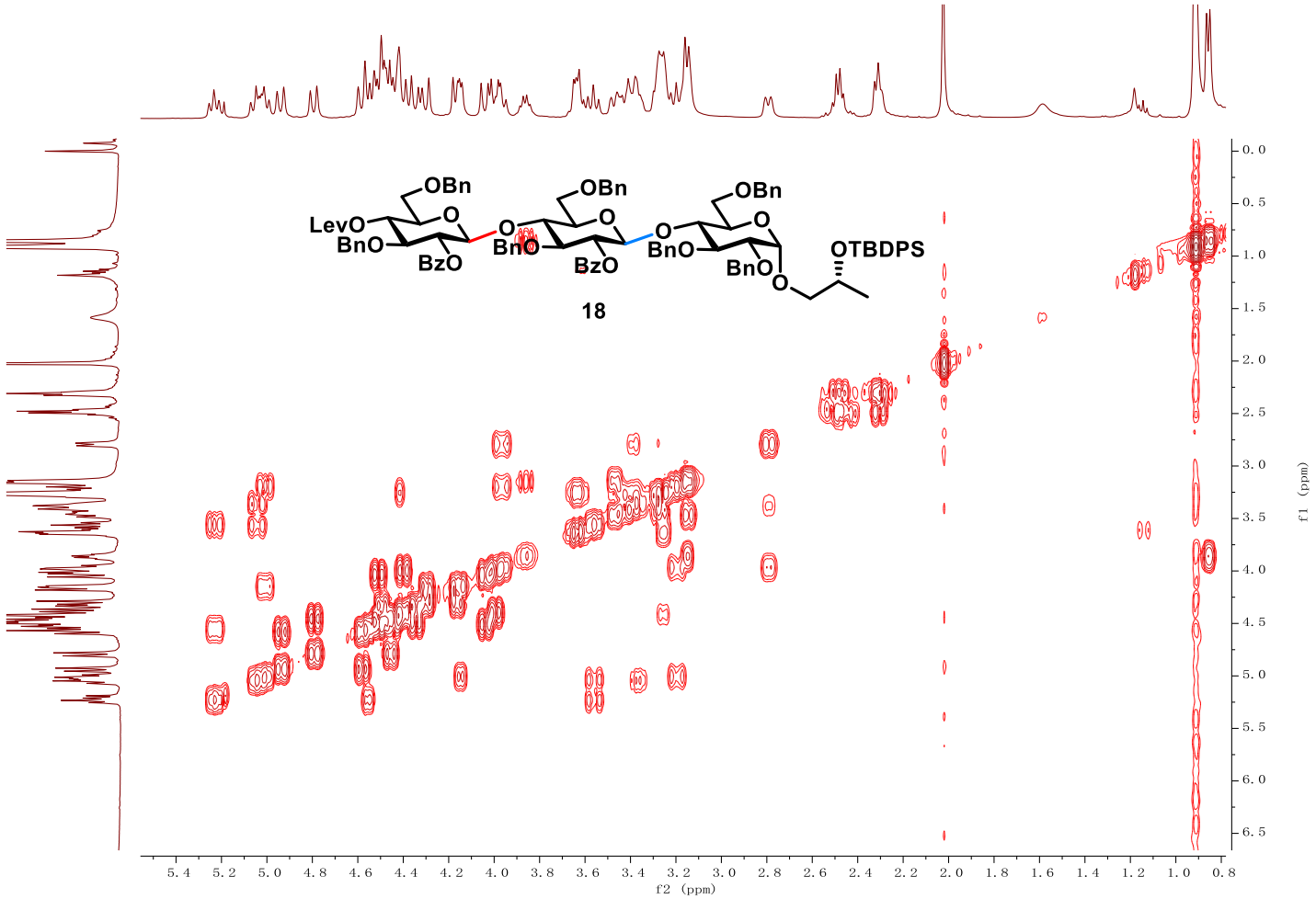


Figure S29. COSY spectra of compound **18**

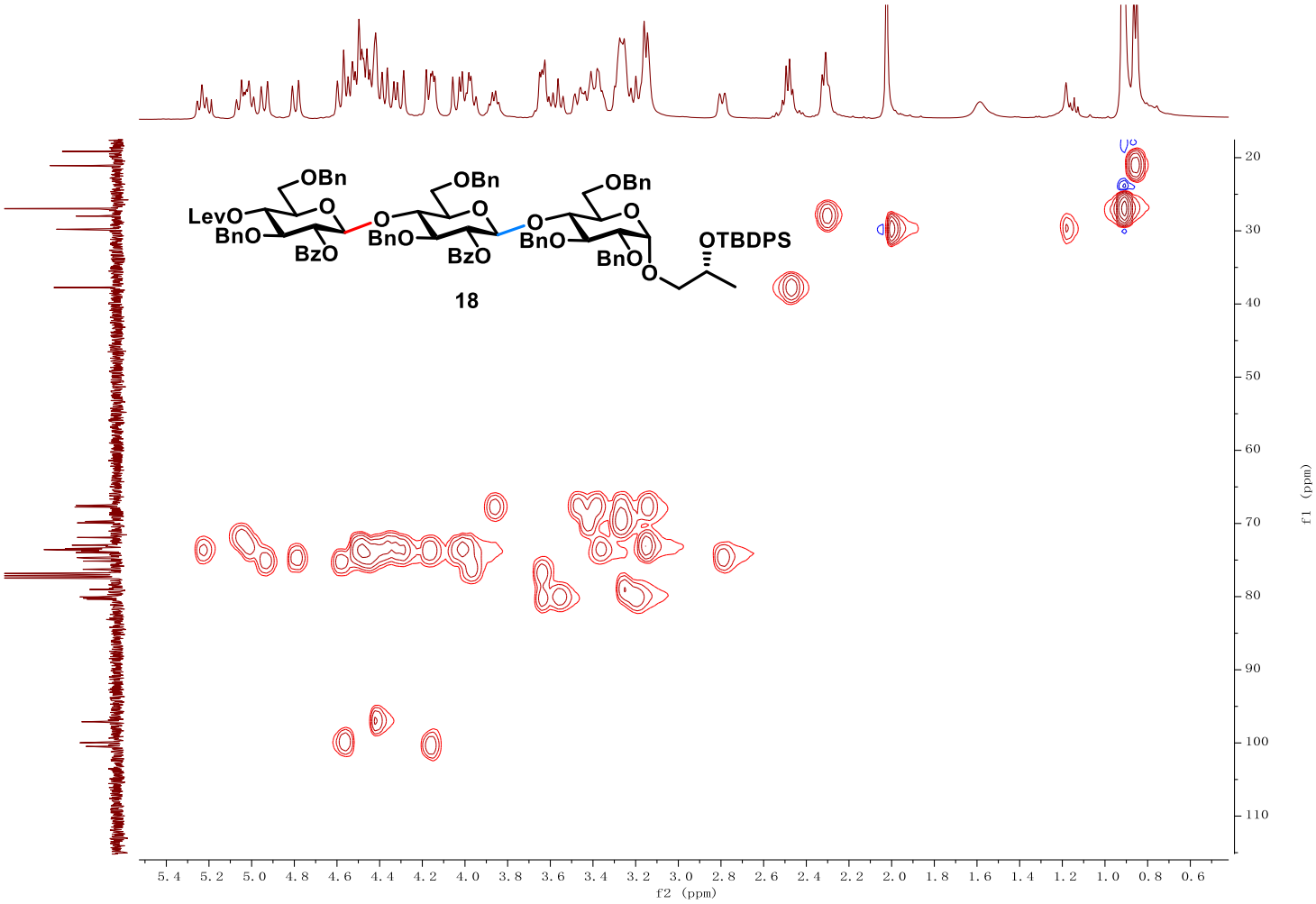


Figure S30. HSQC spectra of compound **18**

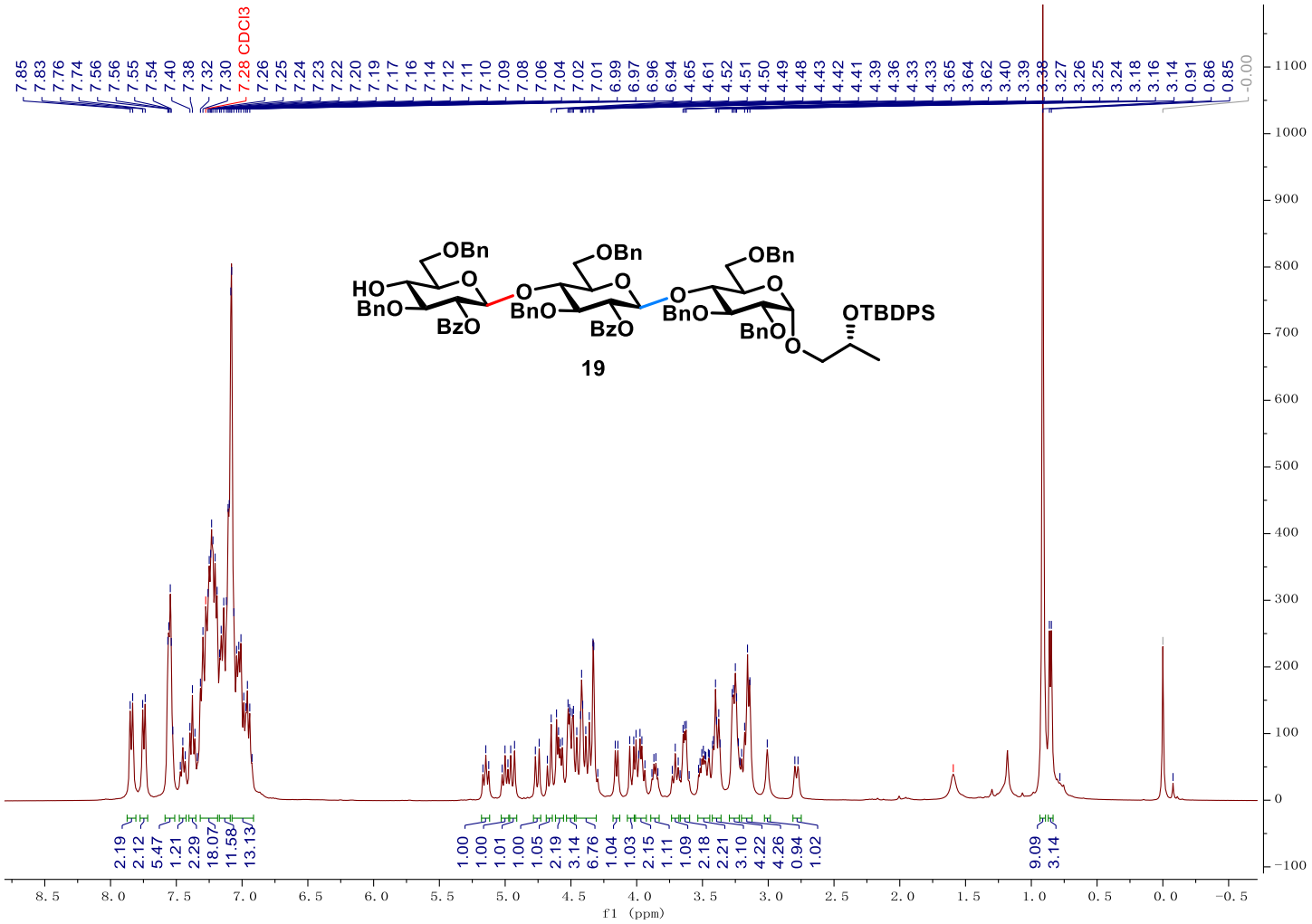


Figure S31. 1H (400 MHz, $CDCl_3$) spectra of compound **19**

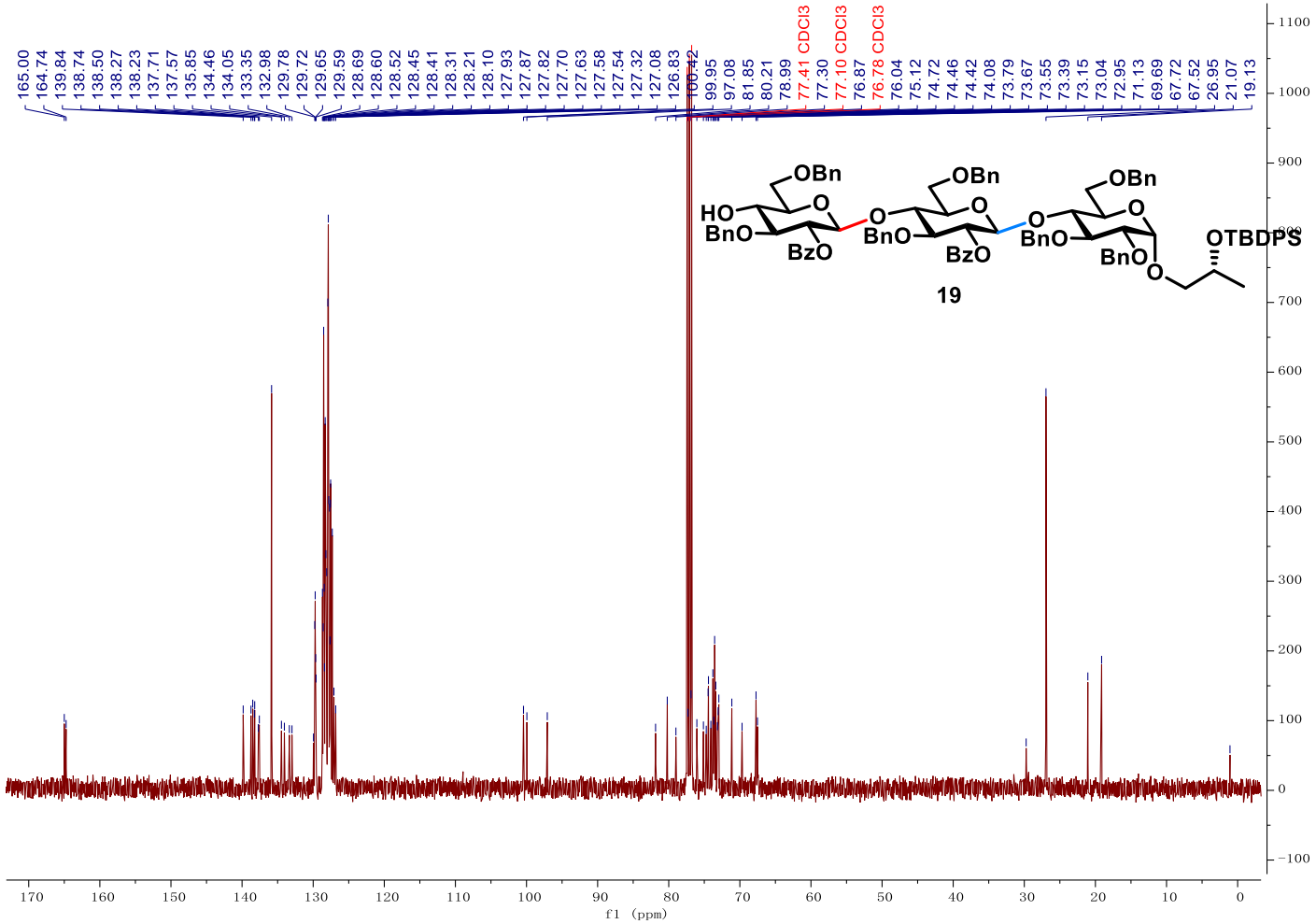


Figure S32. 13C (100 MHz, $CDCl_3$) spectra of compound **19**

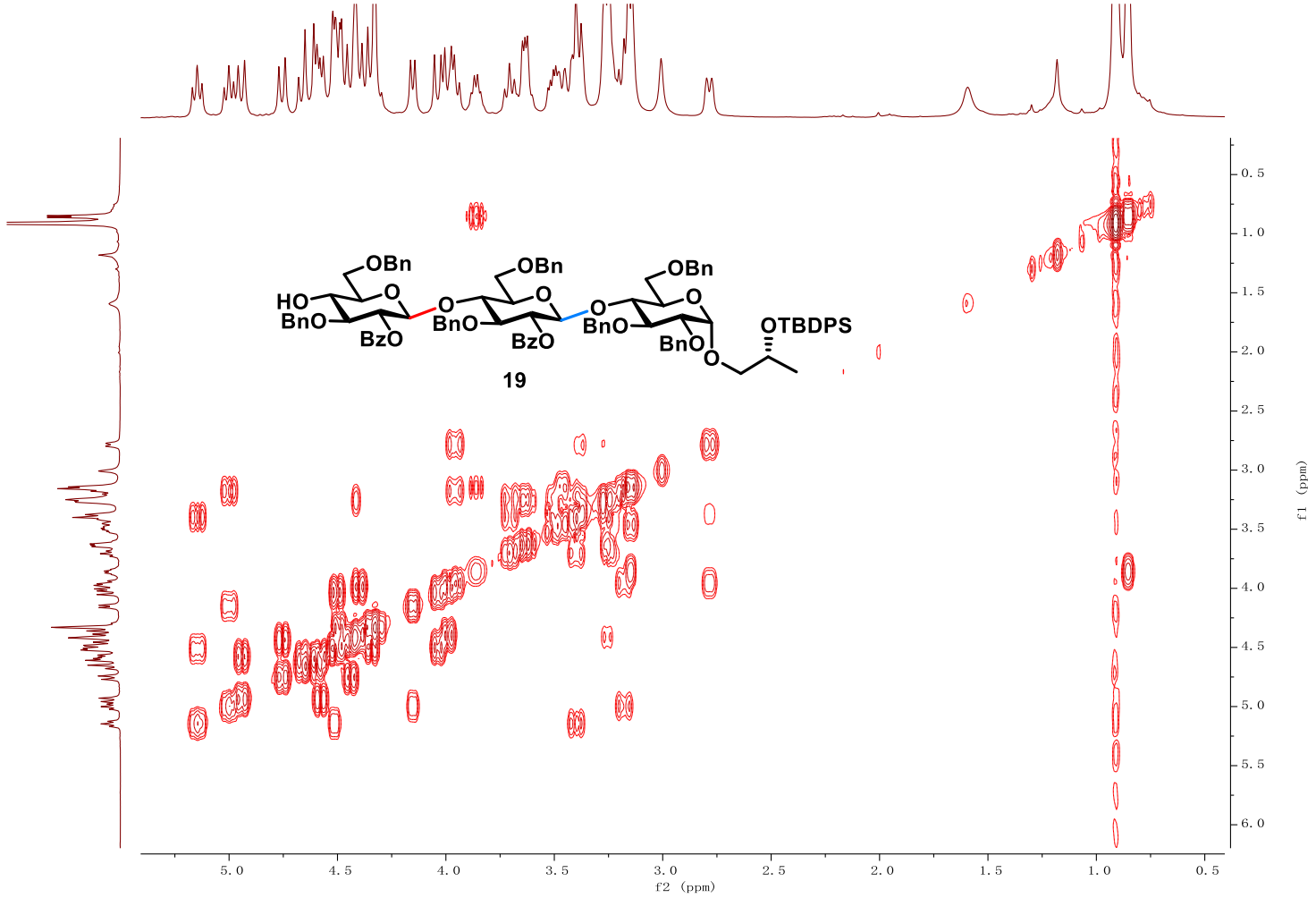


Figure S33. COSY spectra of compound **19**

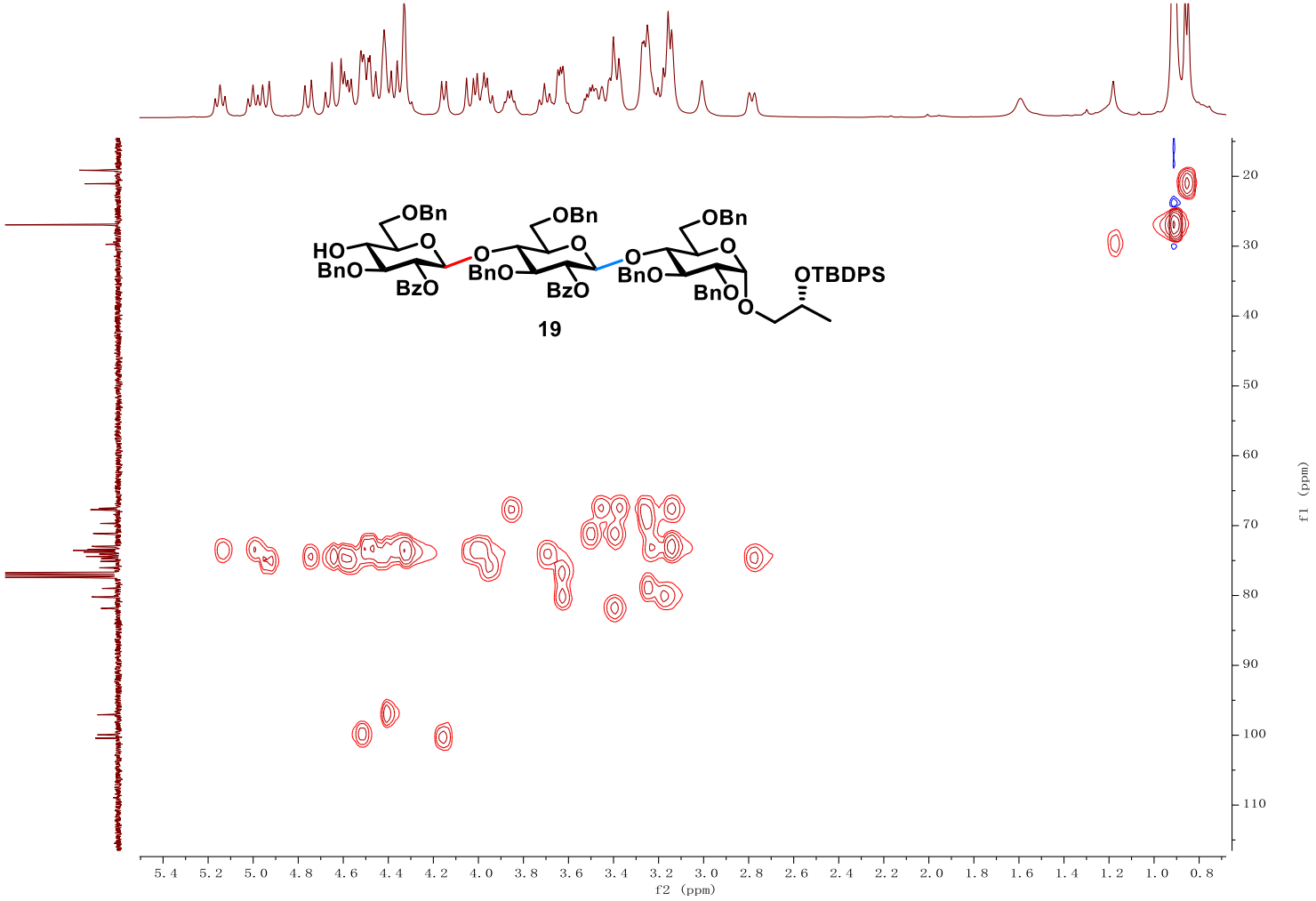


Figure S34. HSQC spectra of compound **19**

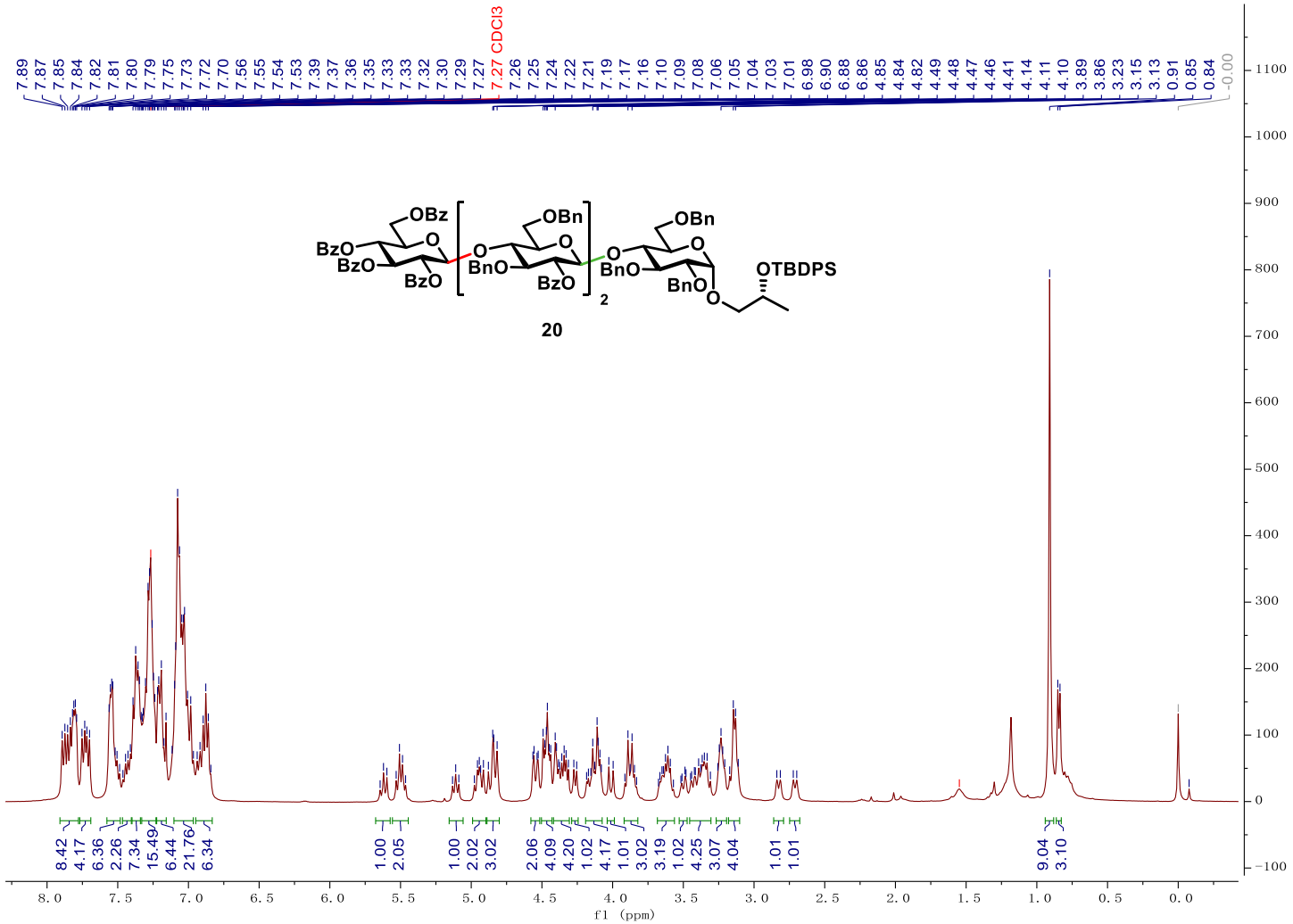


Figure S35. 1H (400 MHz, $CDCl_3$) spectra of compound **20**

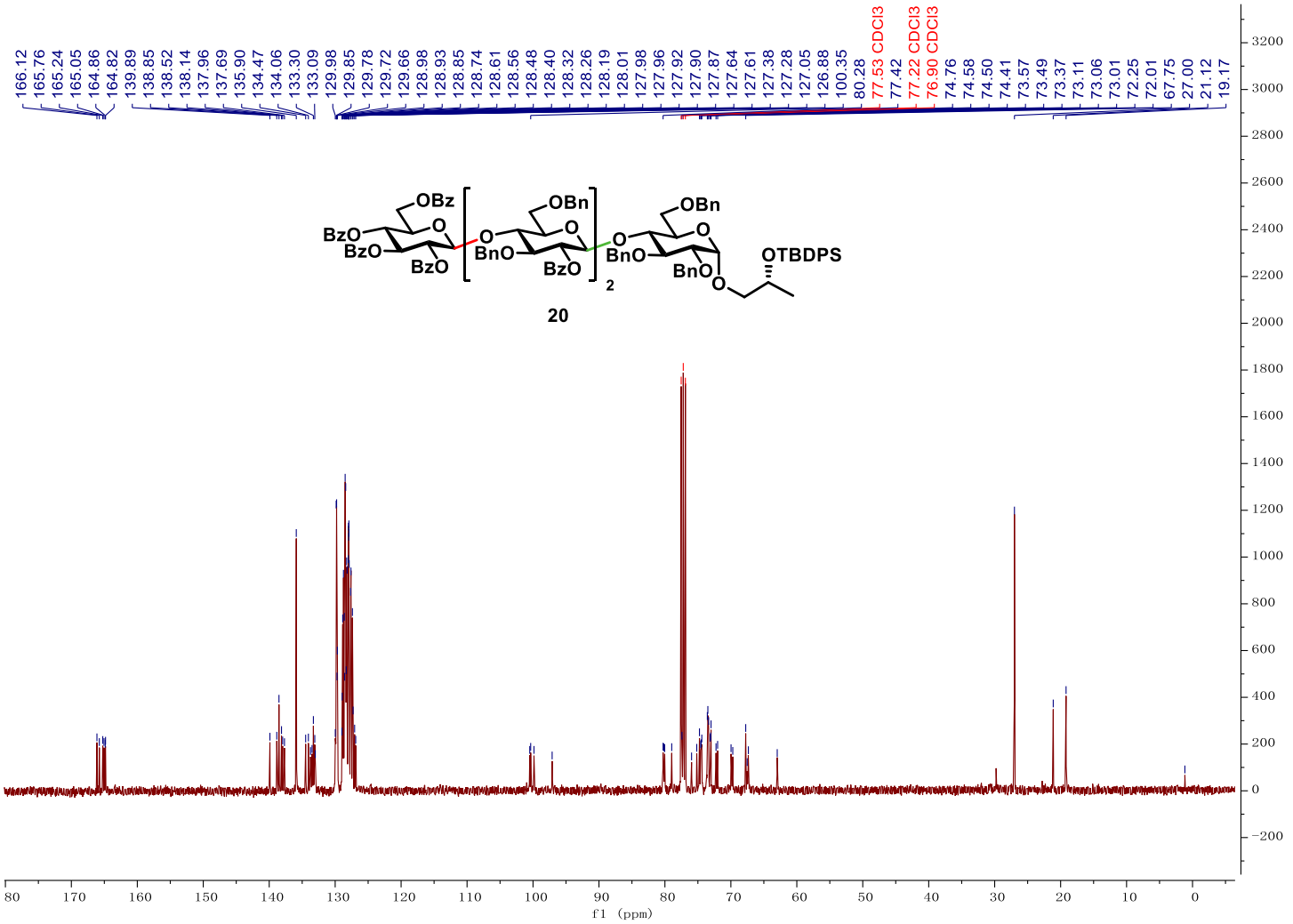


Figure S36. 13C (100 MHz, $CDCl_3$) spectra of compound **20**

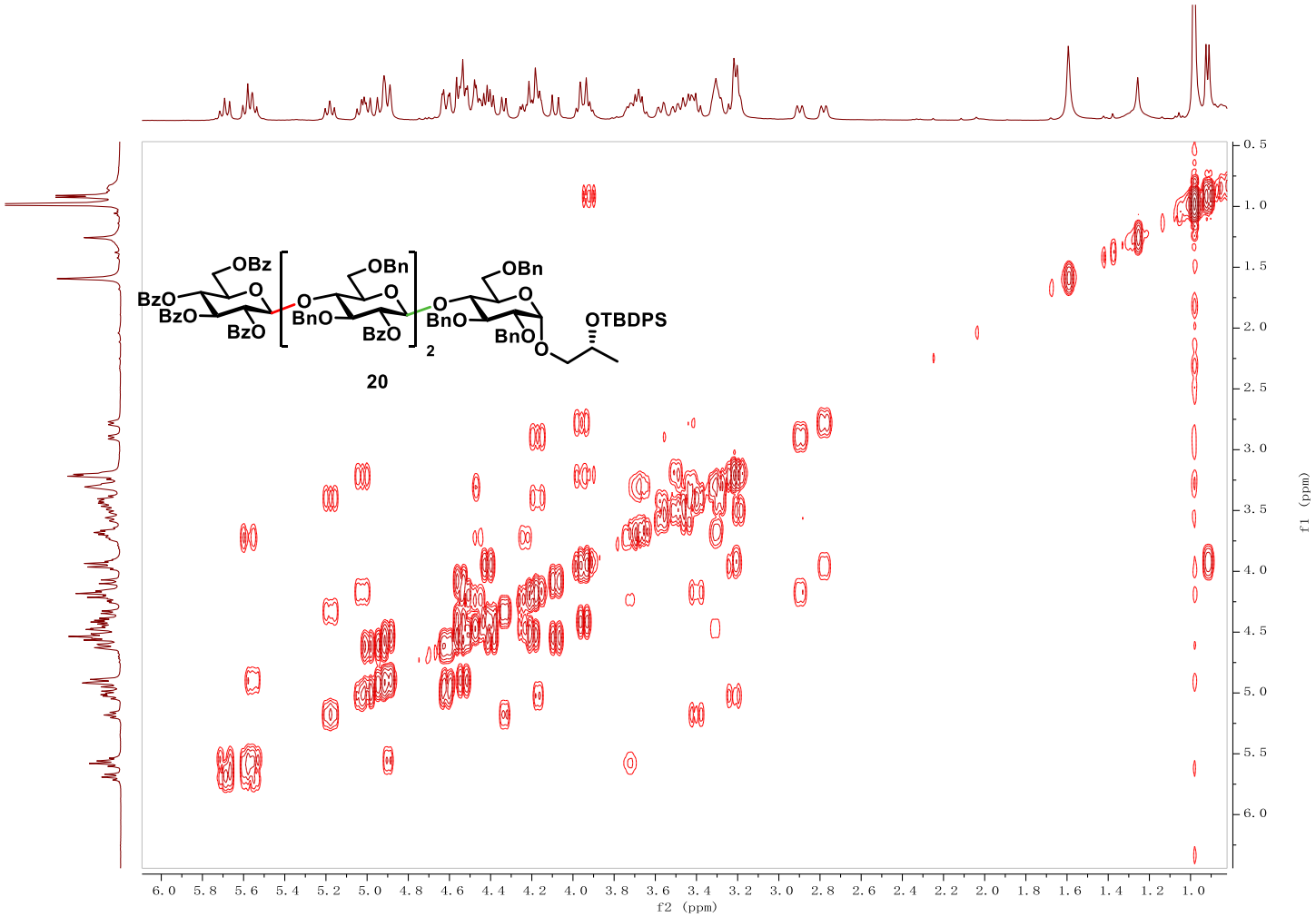


Figure S37. COSY spectra of compound **20**

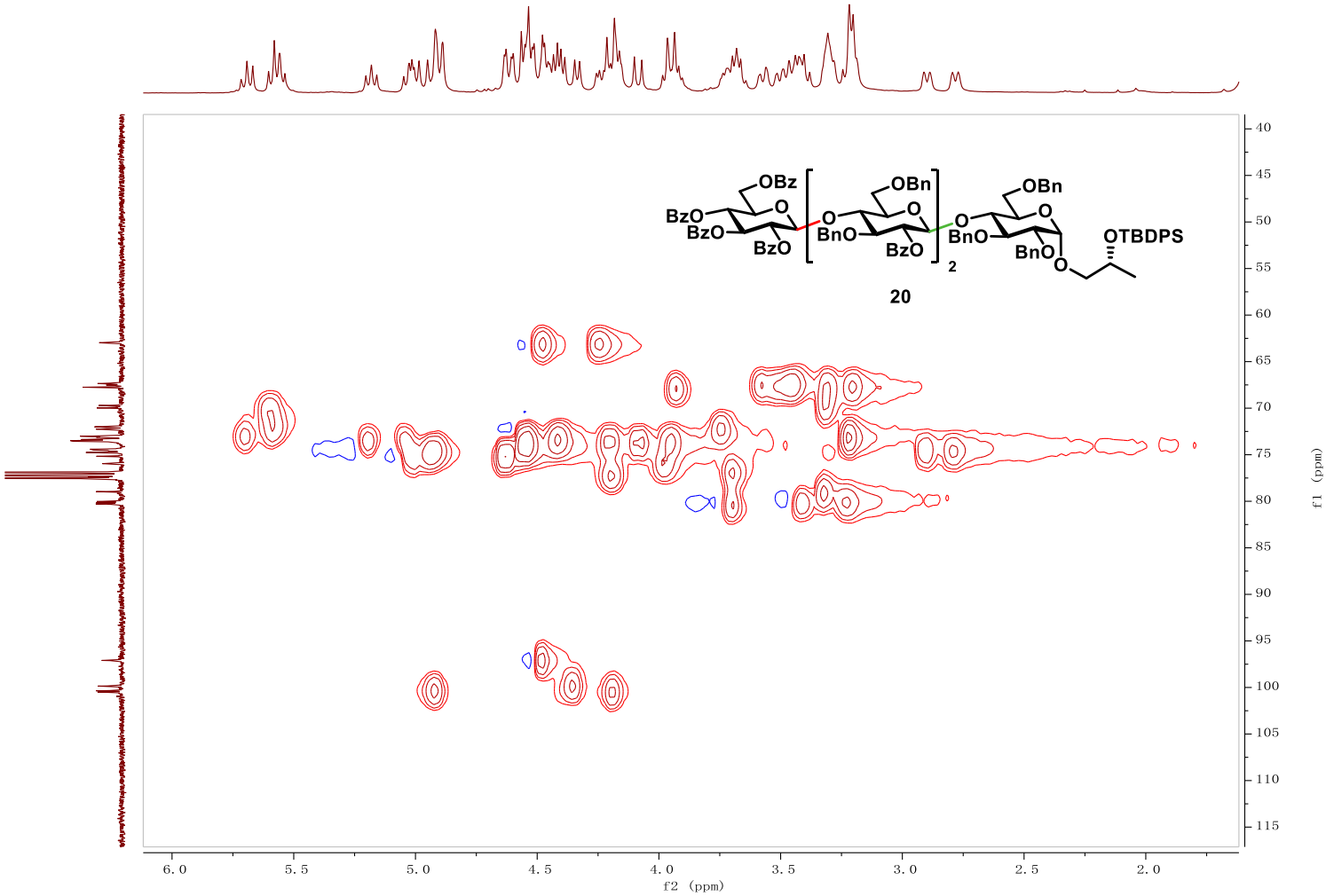


Figure S38. HSQC spectra of compound **20**

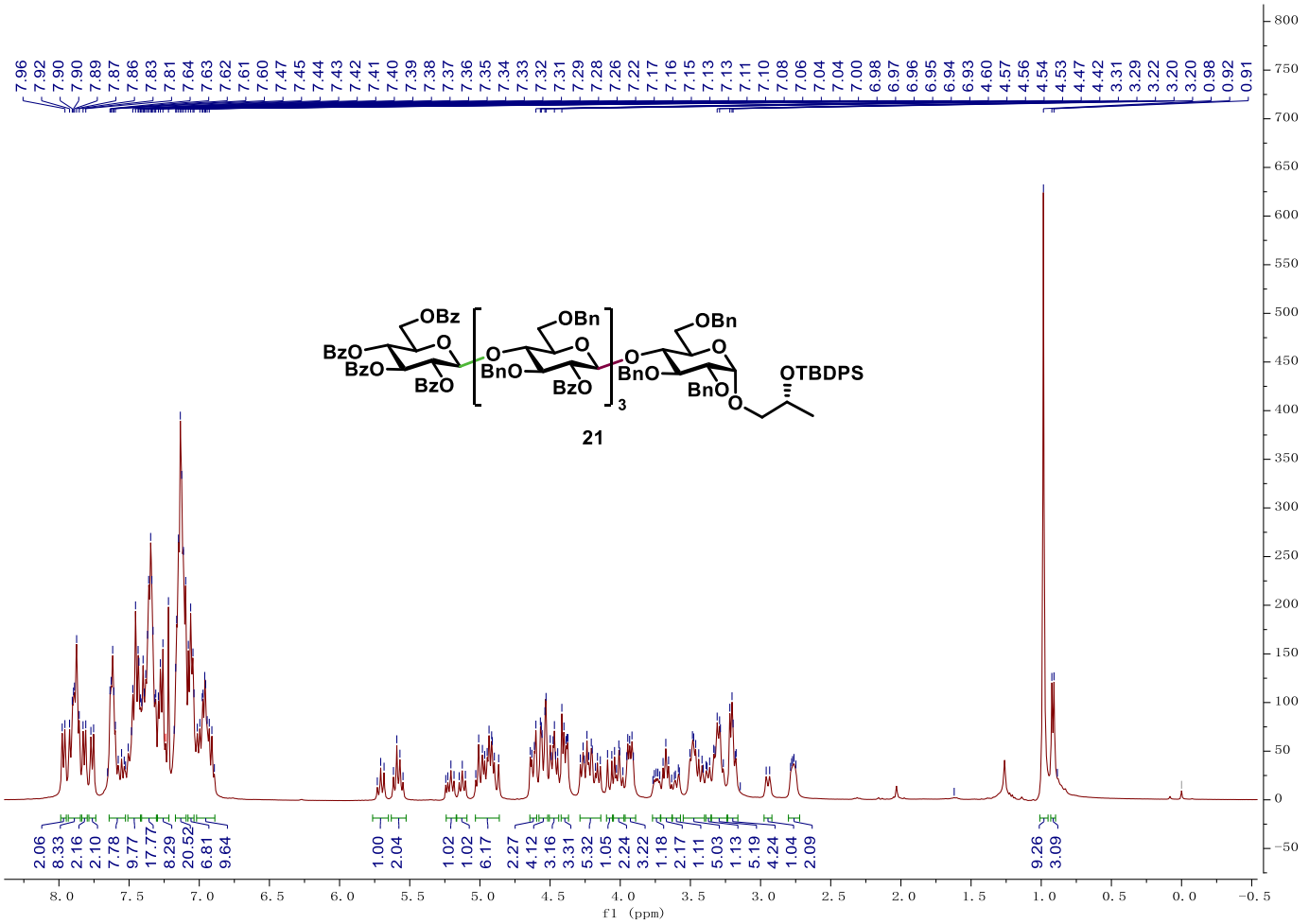


Figure S39. 1H (400 MHz, $CDCl_3$) spectra of compound **21**

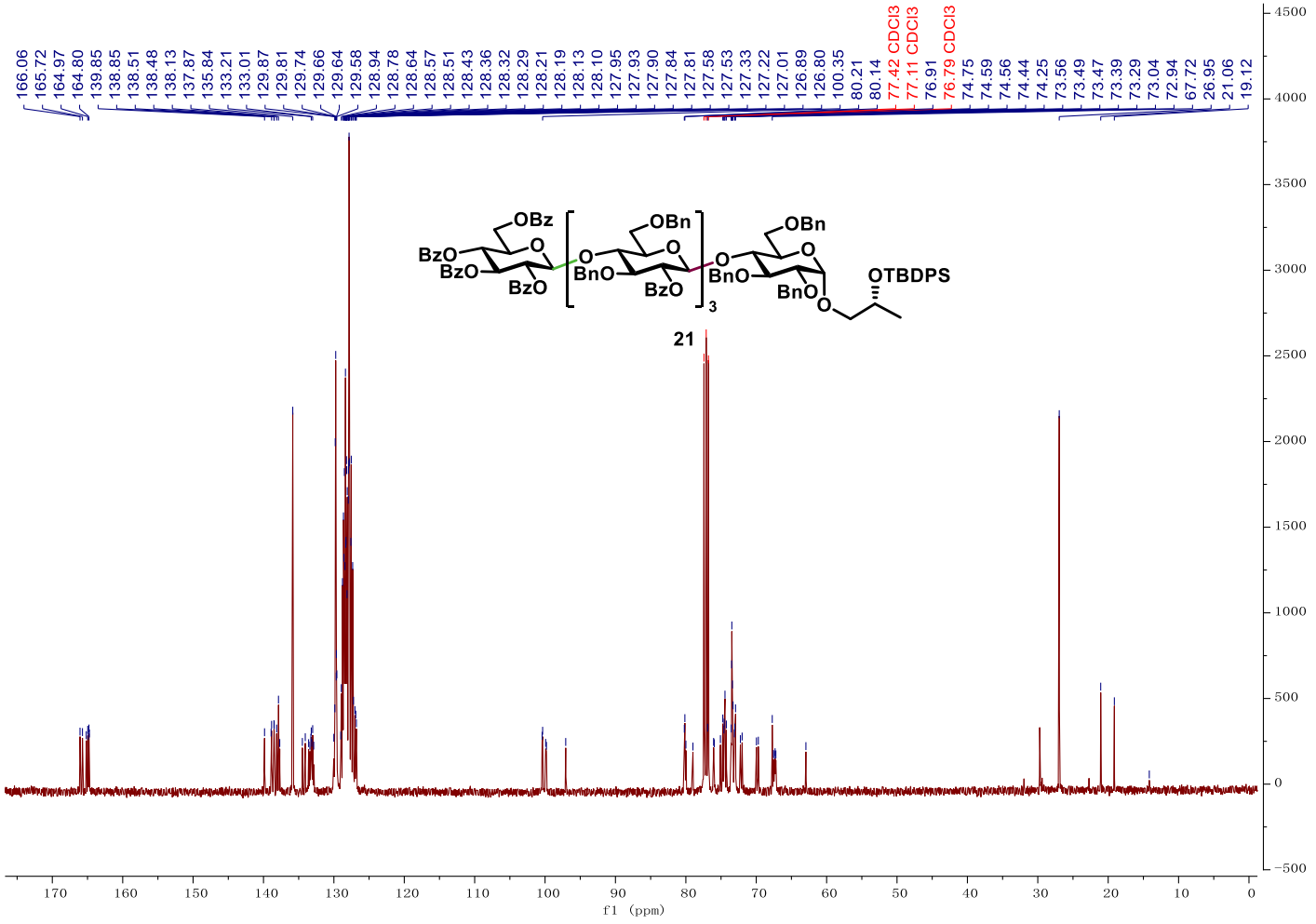


Figure S40. 13C (100 MHz, $CDCl_3$) spectra of compound **21**

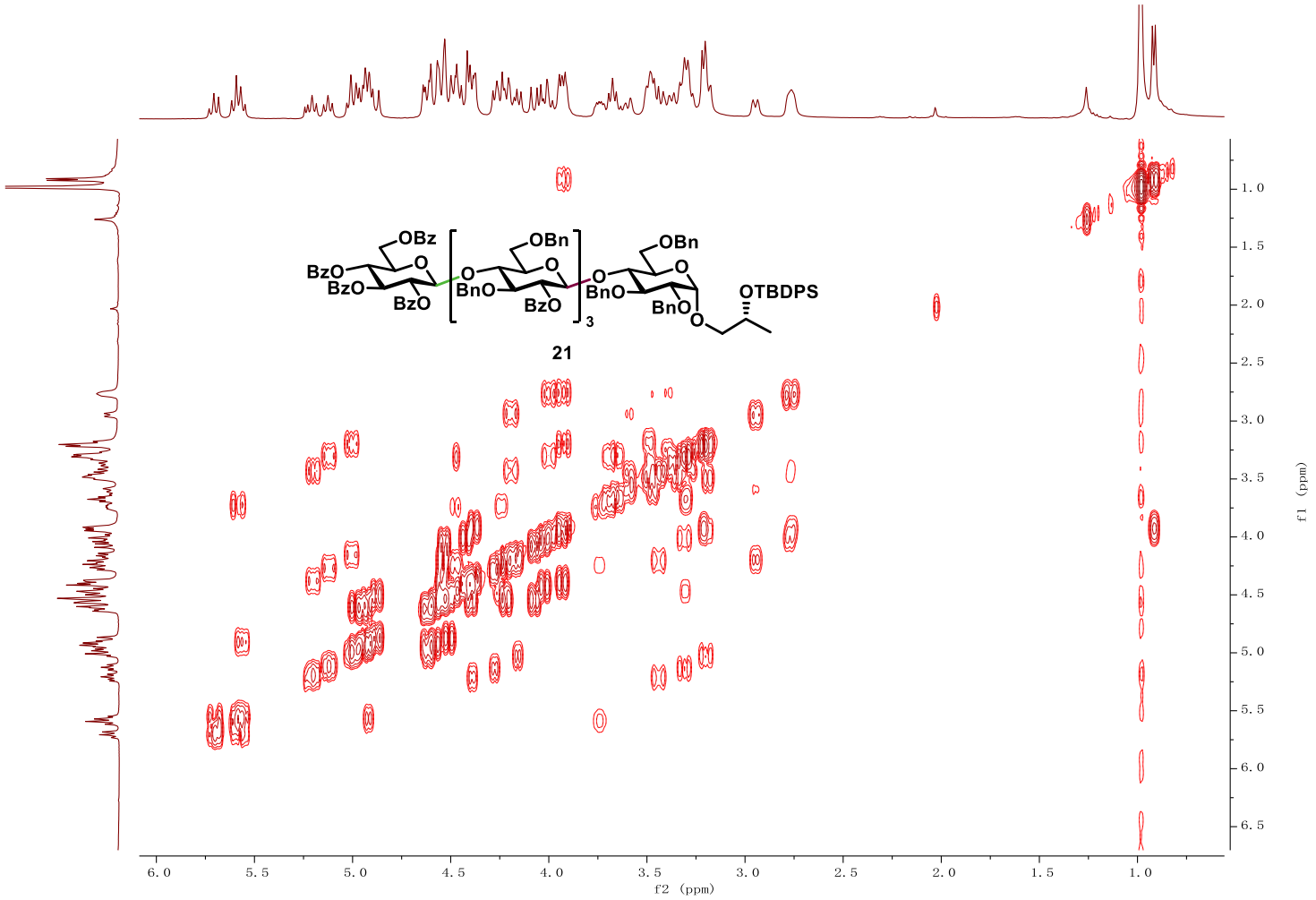


Figure S41. COSY spectra of compound **21**

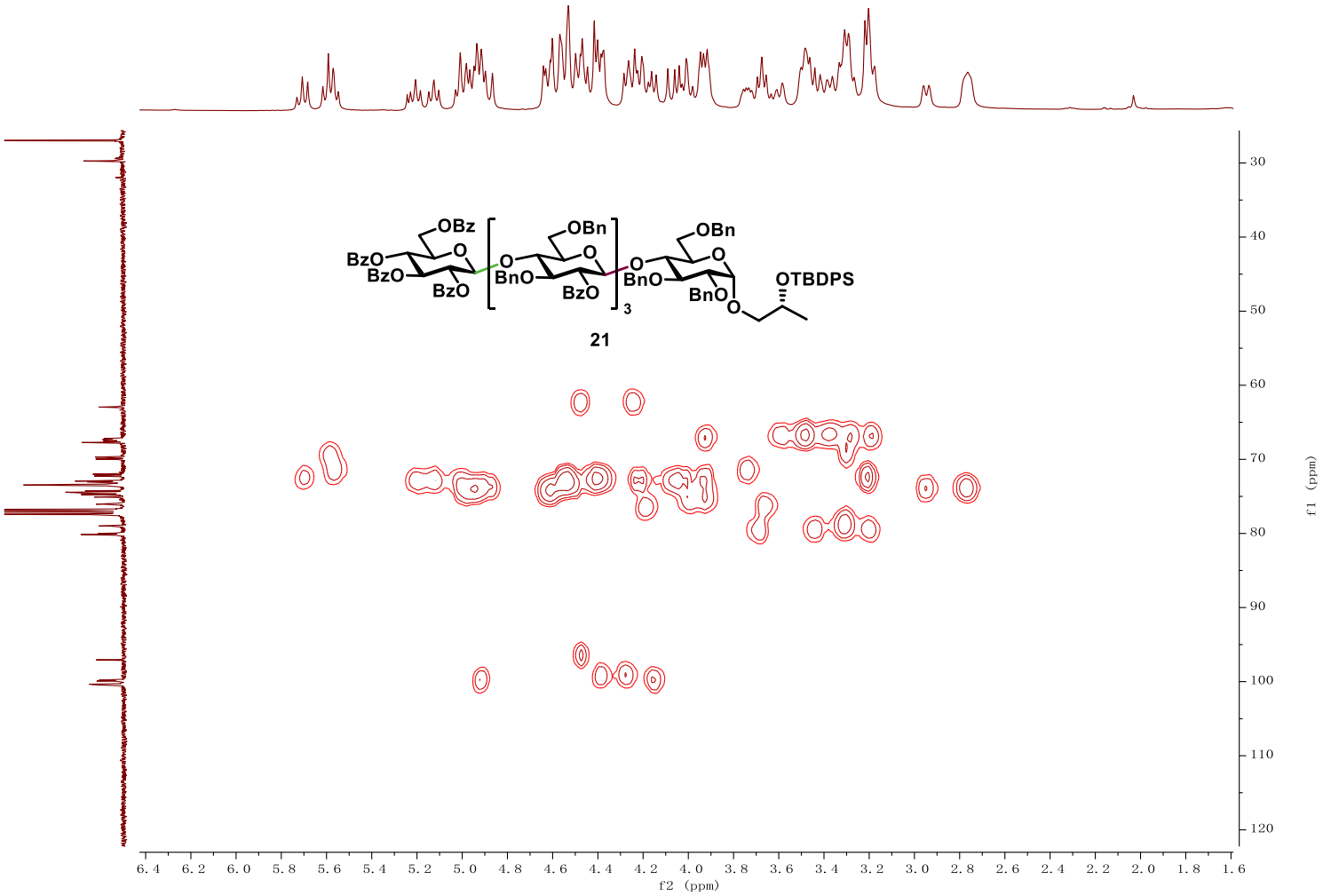


Figure S42. HSQC spectra of compound **21**

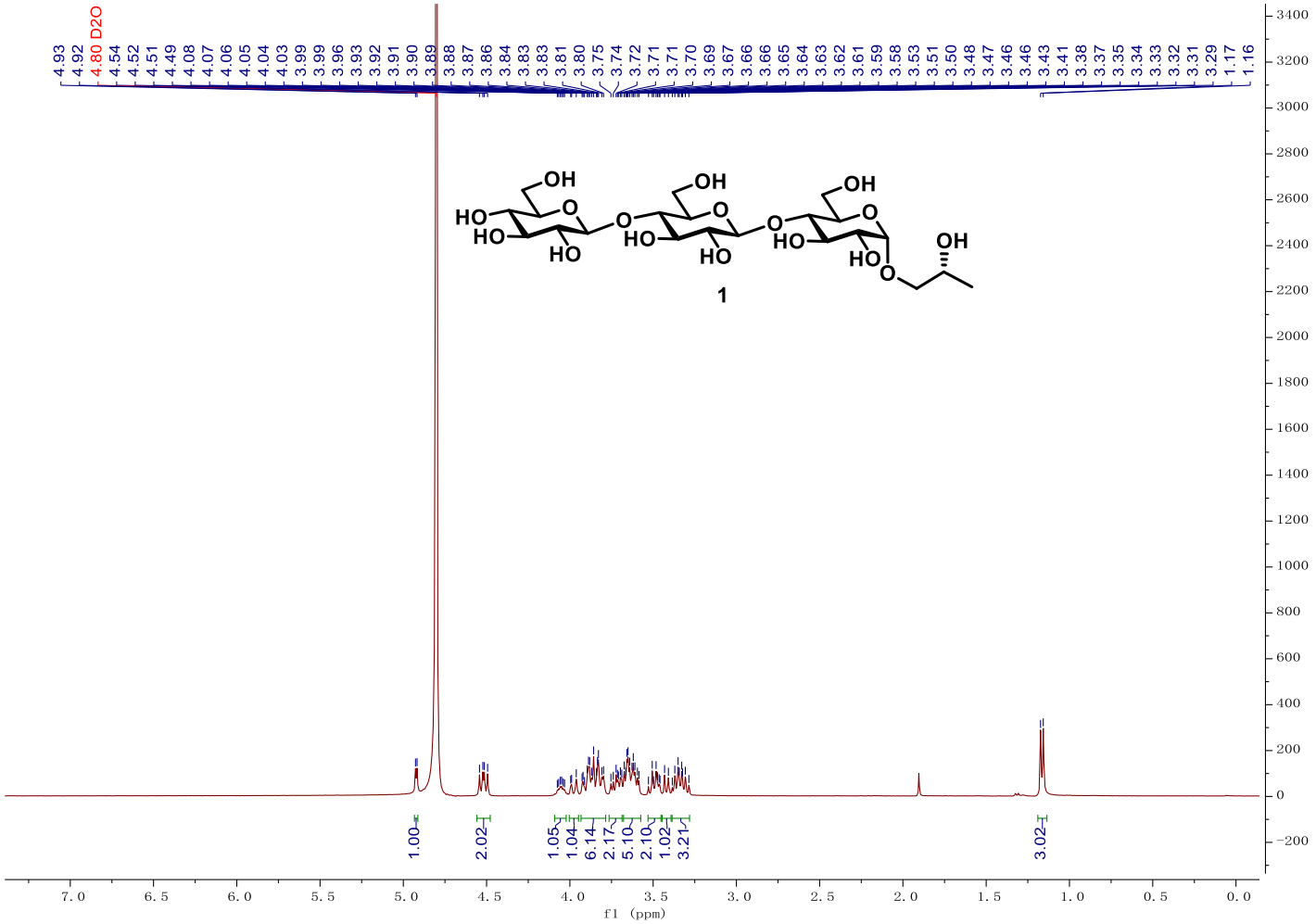


Figure S43. 1H (400 MHz, $CDCl_3$) spectra of compound **1**

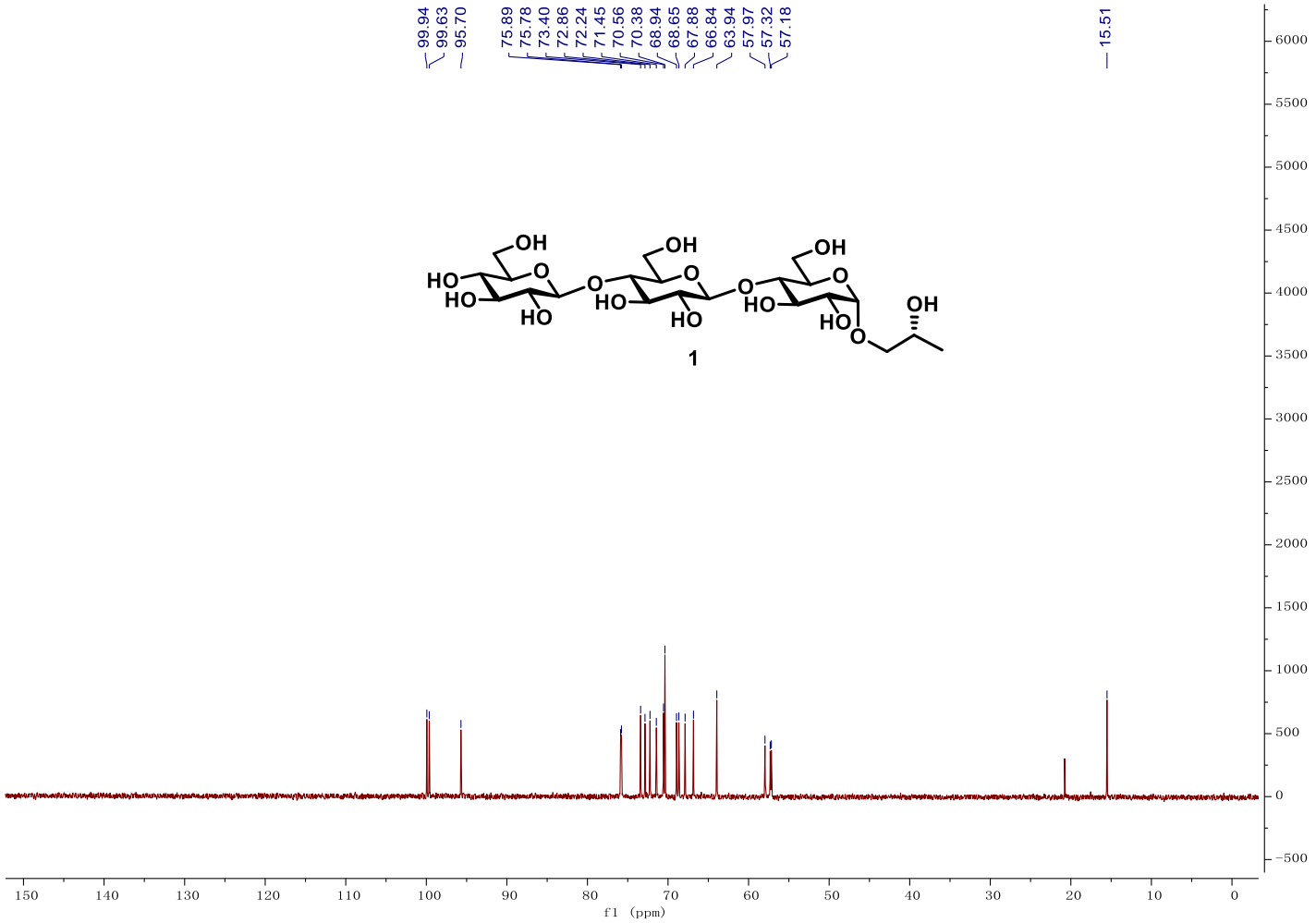


Figure S44. 13C (100 MHz, $CDCl_3$) spectra of compound **1**

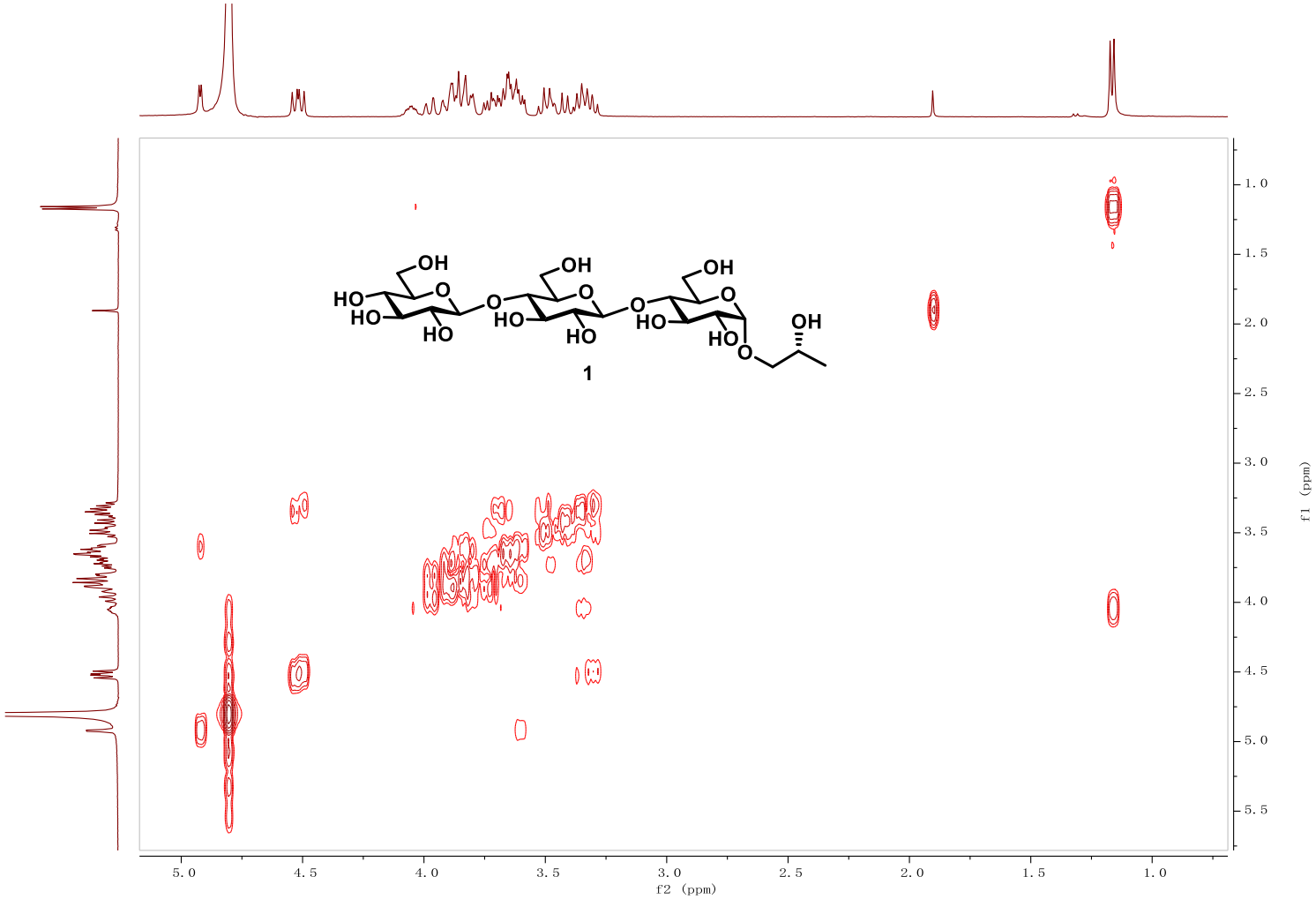


Figure S45. COSY spectra of compound **1**

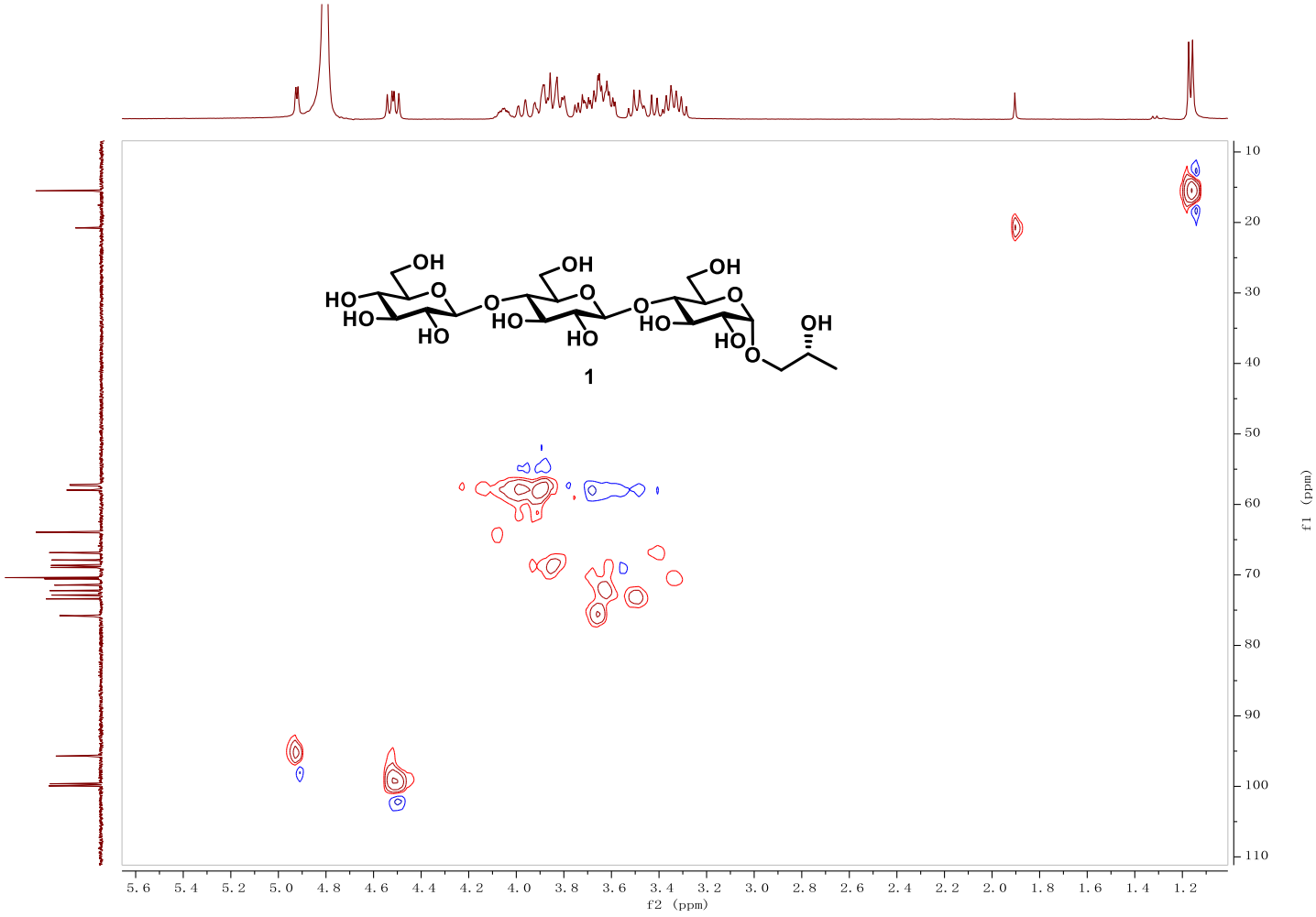


Figure S46. HSQC spectra of compound **1**

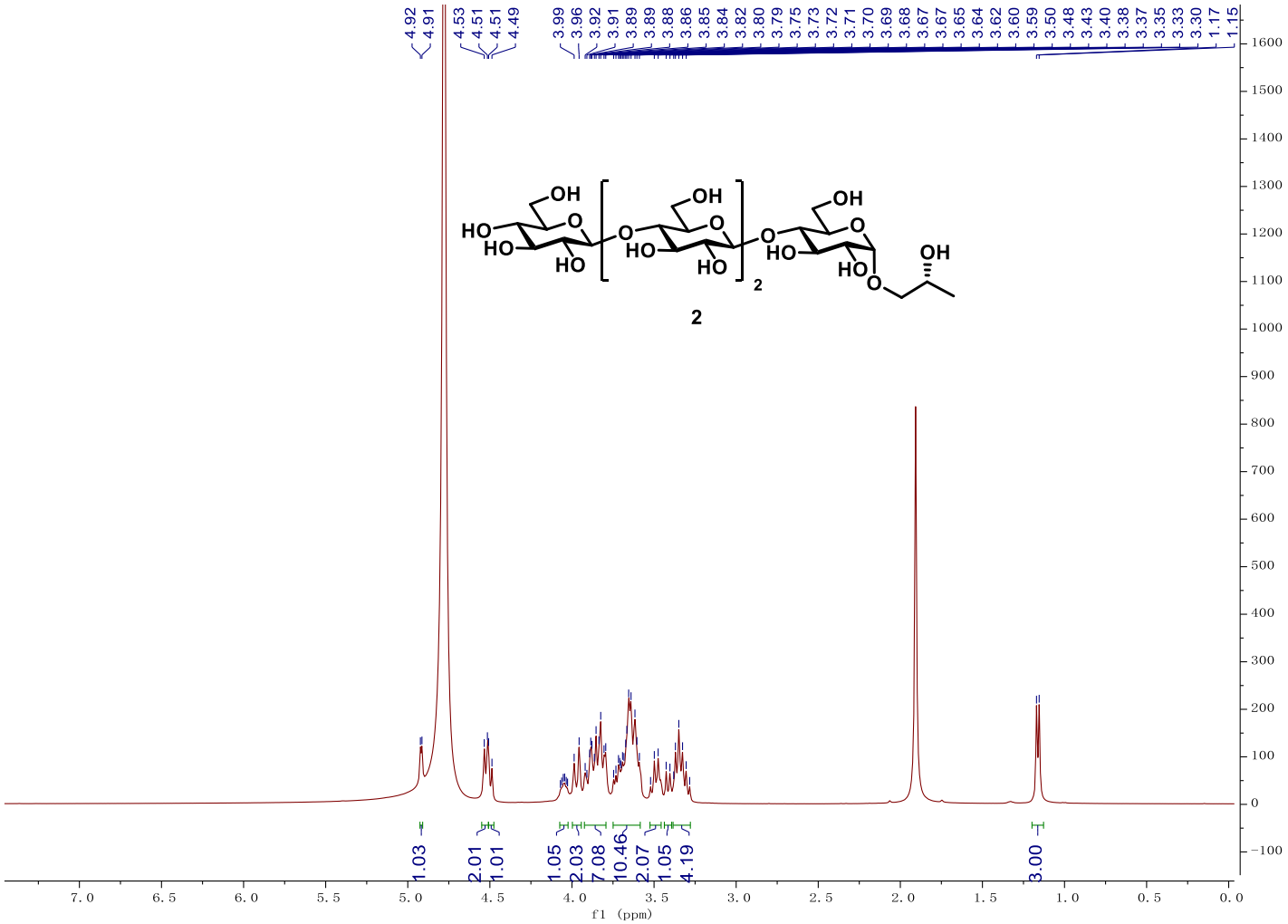


Figure S47. 1H (400 MHz, $CDCl_3$) spectra of compound **2**

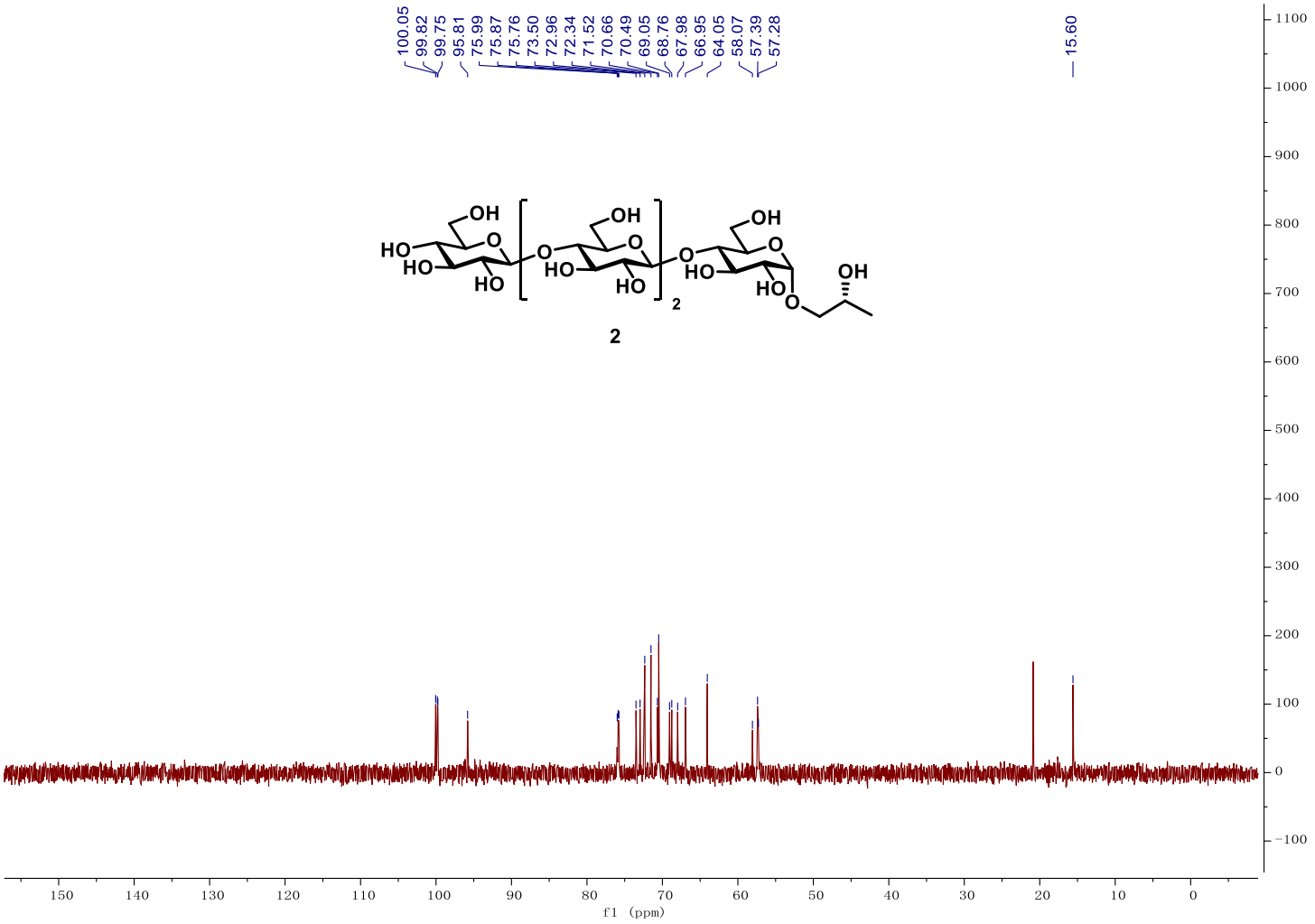


Figure S48. 13C (100 MHz, $CDCl_3$) spectra of compound **2**

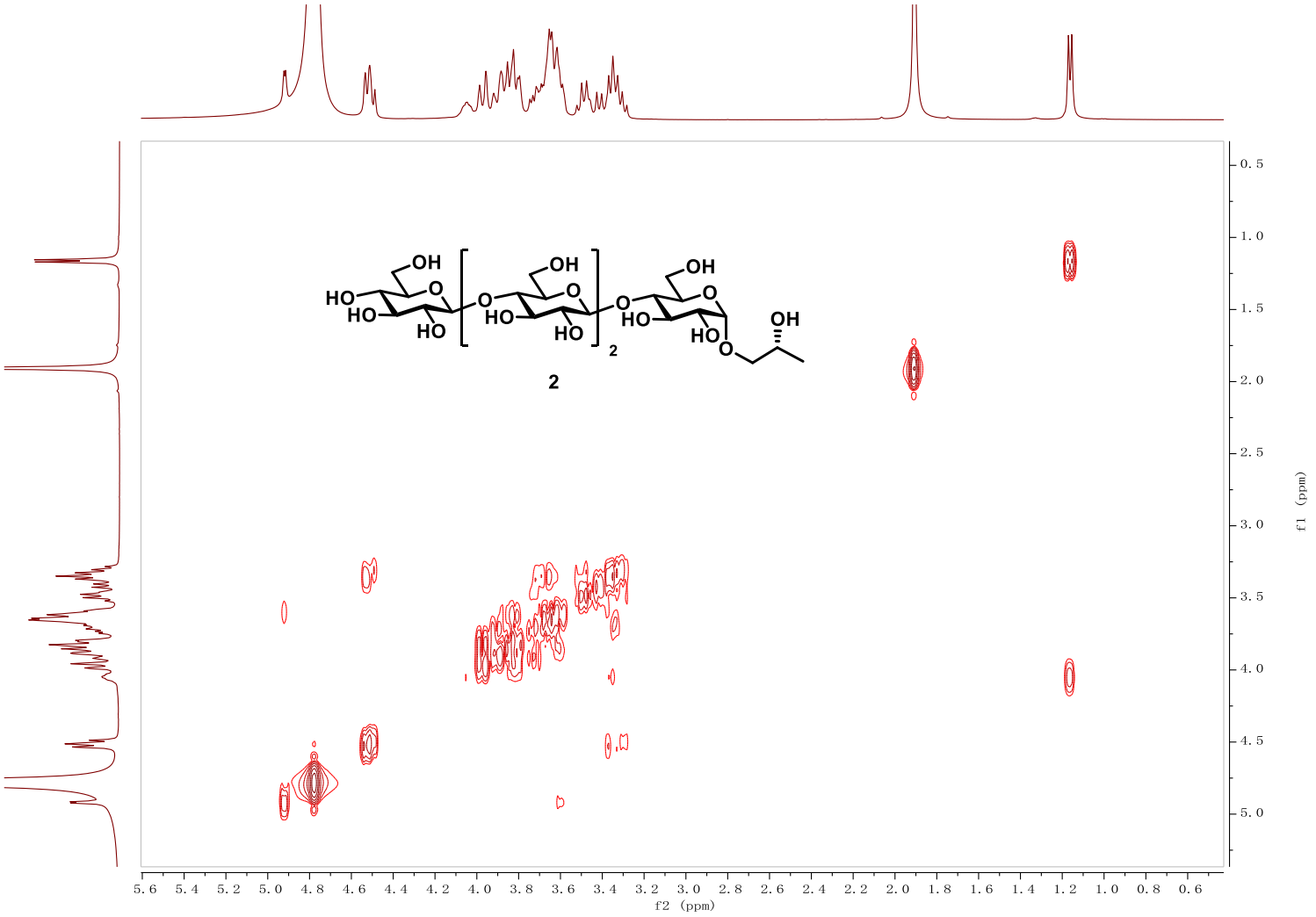


Figure S49. COSY spectra of compound **2**

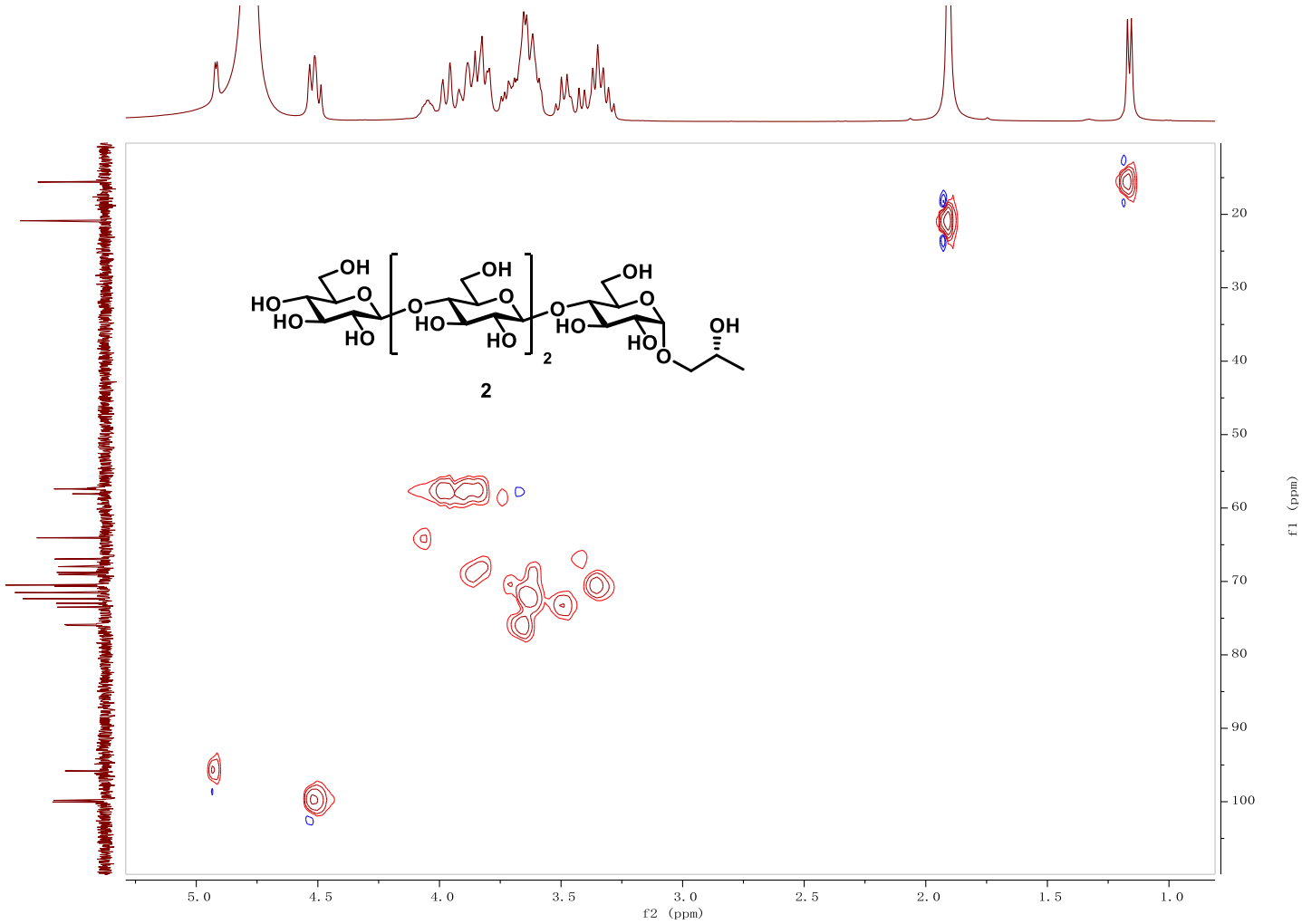


Figure S50. HSQC spectra of compound **2**

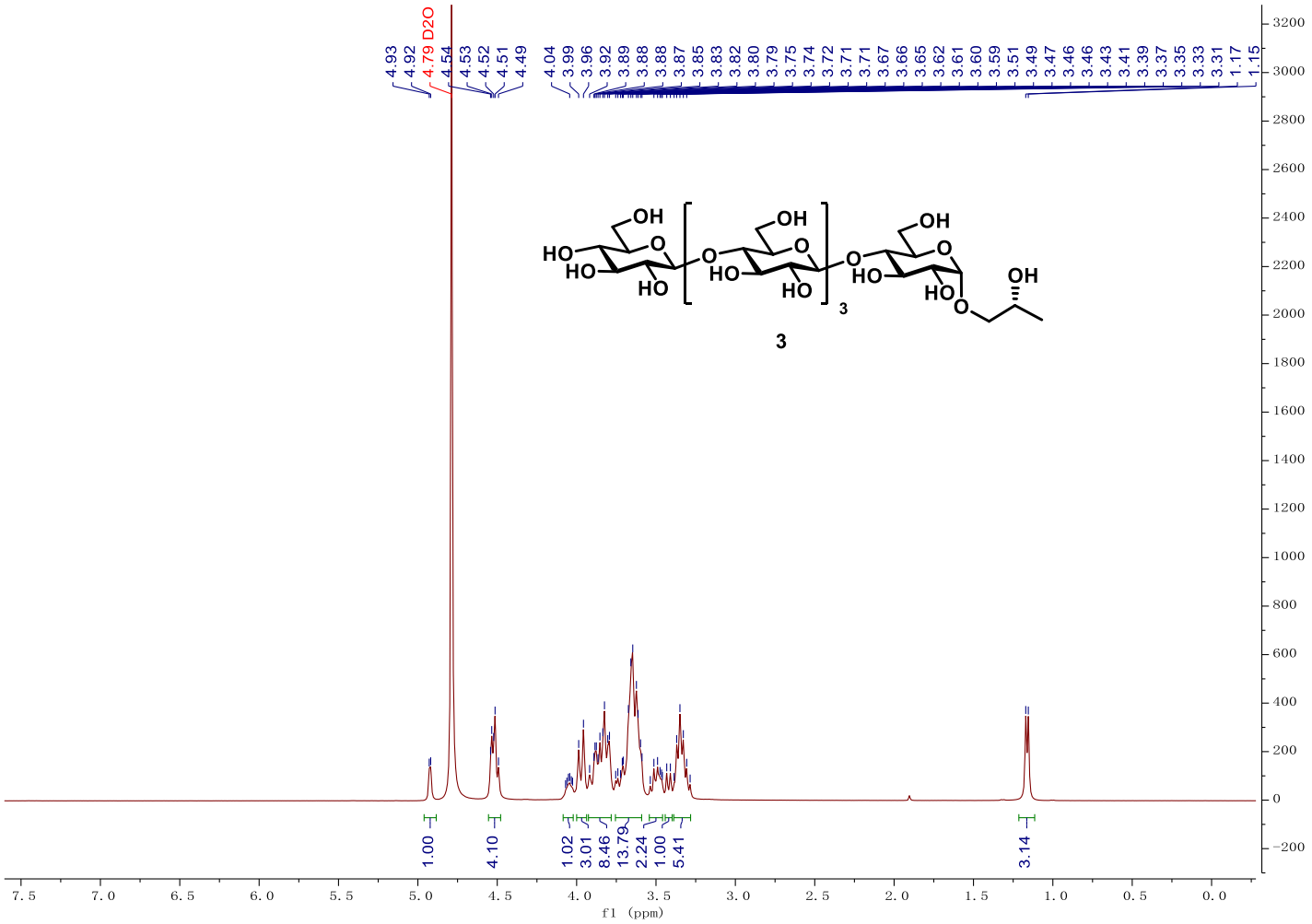


Figure S51. 1H (400 MHz, $CDCl_3$) spectra of compound **3**

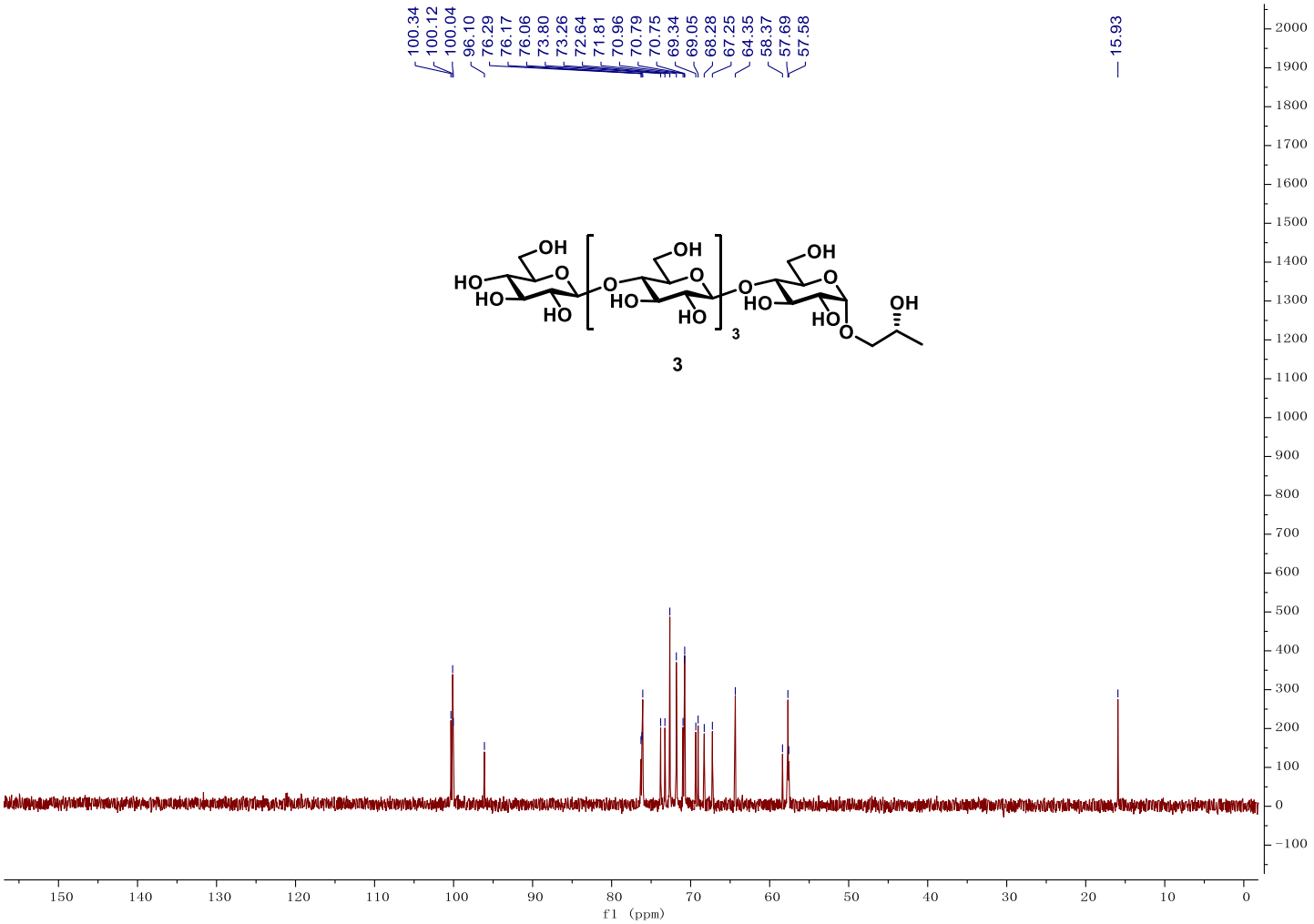


Figure S52. 13C (100 MHz, $CDCl_3$) spectra of compound **20**

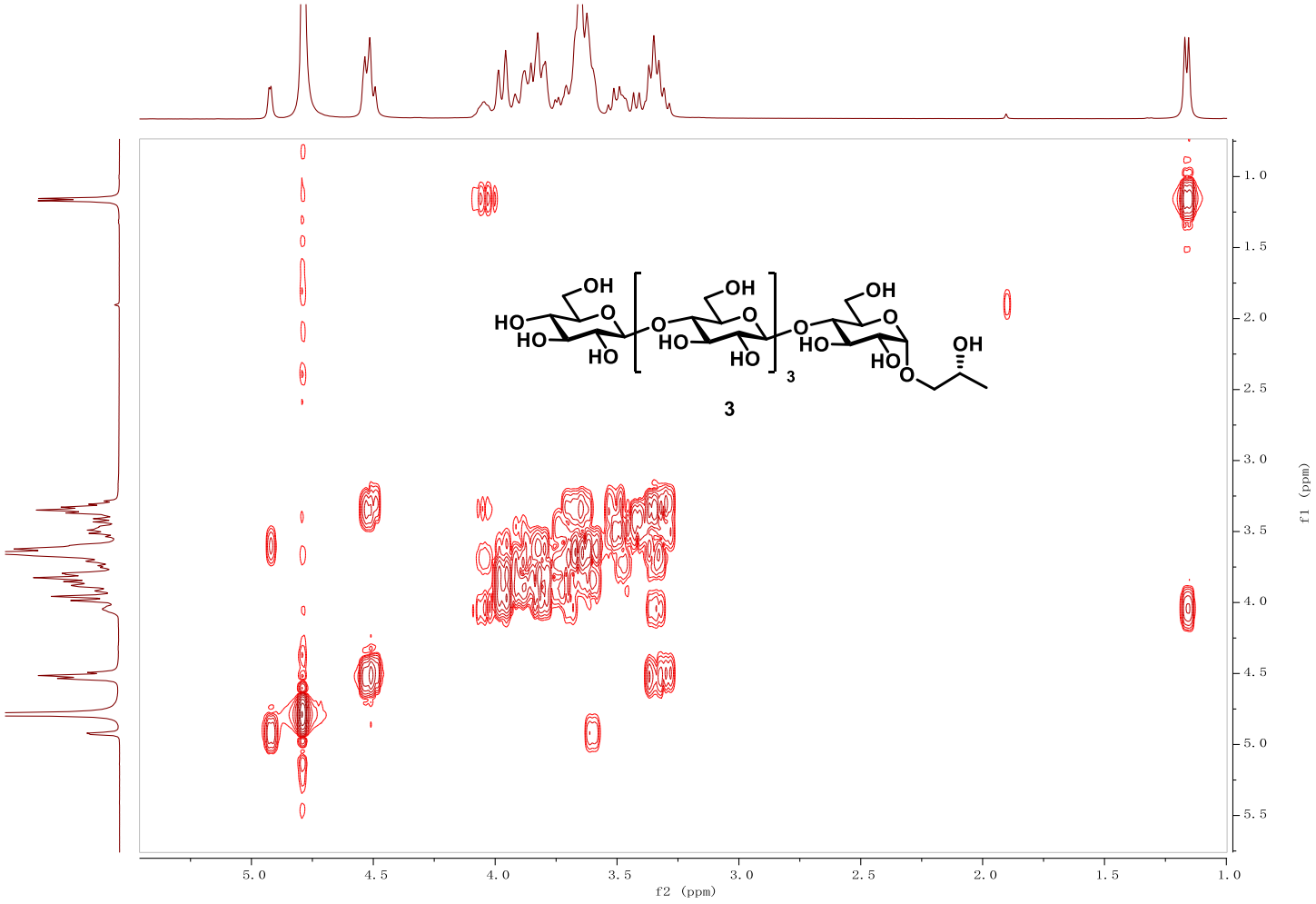


Figure S53. COSY spectra of compound **3**

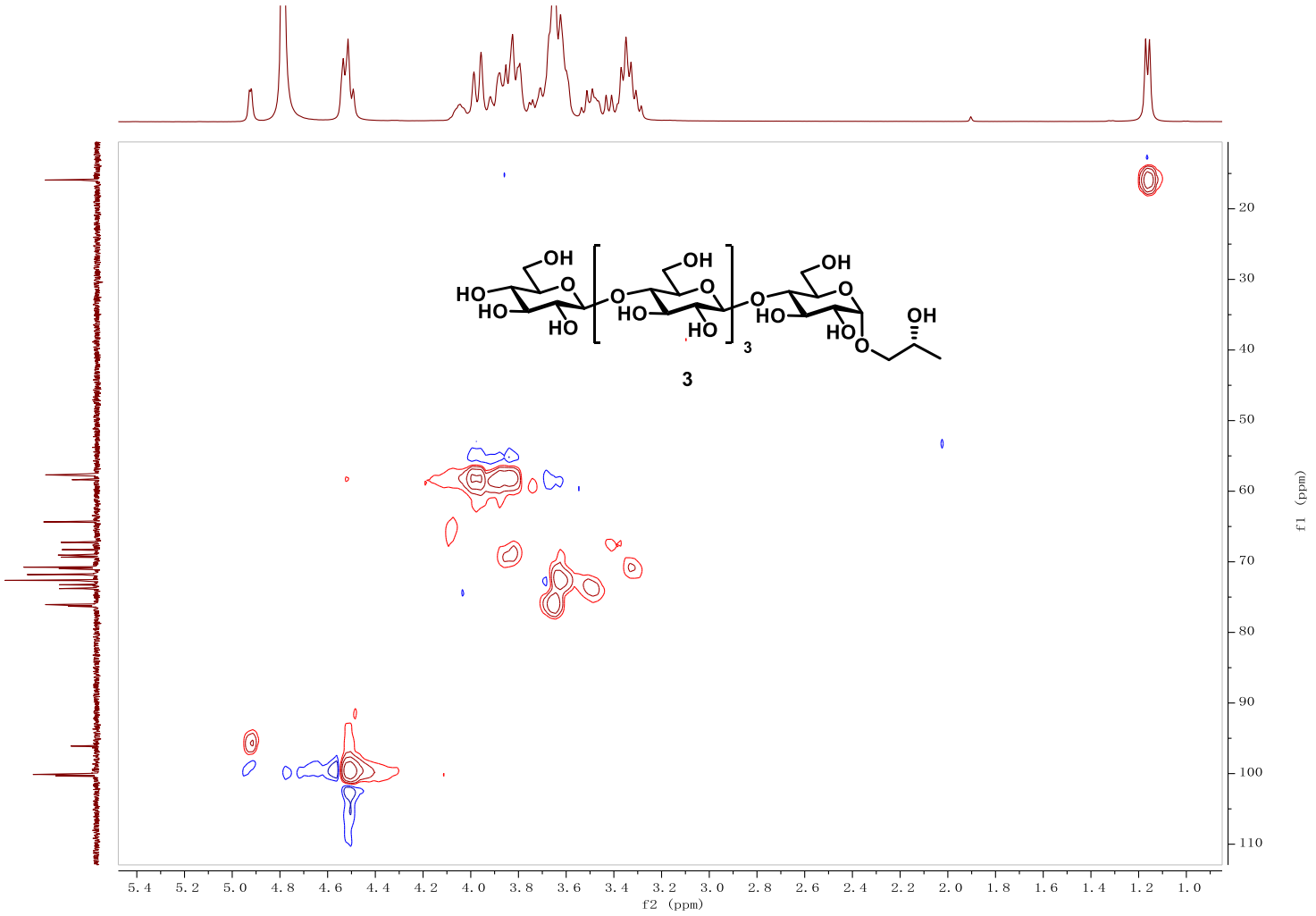


Figure S54. HSQC spectra of compound **3**