Supporting Information

Dimethylformamide-Modulated Stereoselective Synthesis of α-Kdo Glycosides with Kdo Ynenoate as Donor

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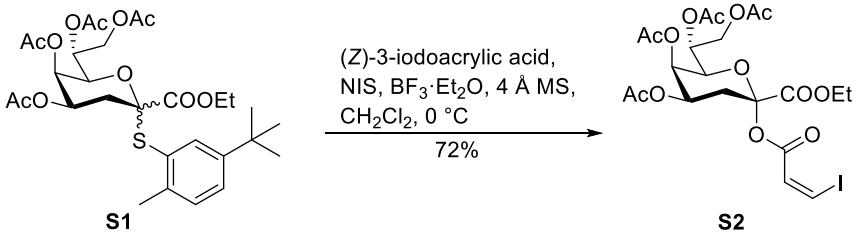
Contents

1. General Information. All reactions were performed with anhydrous solvents in oven-dried glassware with magnetic stirring under argon or nitrogen unless otherwise stated. The chemicals were purchased as reagent grade and used without further purification unless otherwise noted. Dry dichloromethane was distilled over calcium hydride prior to use. Anhydrous DMF (Extra dry) was purchased from Acros Co. The boiling range of petroleum ether (PE) used as fluent in column chromatography was 65-80 ℃. Analytical thin layer chromatography (TLC) was conducted on precoated plates of silica gel (0.25-0.3 mm, Shanghai, China). The TLC plates were visualized by exposure to UV light or by staining with a sulfuric acid-ethanol solution. Silica gel column chromatography was performed on silica gel AR (100-200 mesh, Shanghai, China). Optical rotations (OR) were measured with a Rudolph Research Analytical Autopol I automatic polarimeter. NMR spectra were recorded with a Bruker Avance III 400 spectrometer. The ^{1}H and ^{13}C NMR spectra were calibrated against the residual proton and carbon signals of the solvents as internal references ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.2 ppm). Multiplicities are quoted as singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of doublet of doublets (ddd), doublet of triplets (dt) or multiplet (m). All NMR chemical shifts (δ) were recorded in ppm and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were recorded on ESI-TOF spectrometer.

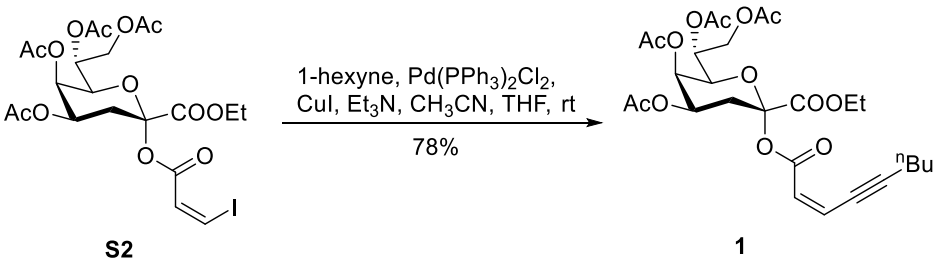
2. Experimental details and characterization data of new compounds

2.1. Synthesis of ethyl ((*Z*)-non-2-en-4-ynoyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy -α-D-*manno*-oct-2-ulopyranoside)onate 1



To a solution of **S1**[1] (2.65 g, 4.4 mmol) in anhydrous CH_2Cl_2 (30 mL) was added (*Z*)-3-iodoacrylic acid (1.8 g, 8.9 mmol) and 4 Å MS (4.5 g). The mixture was stirred

at room temperature for 15 min, and then BF_3 ·Et_2O (1.1 mL, 8.9 mmol) and NIS (2.0 g, 8.9 mmol) were added. After being stirred at room temperature for 1.5 h, the reaction was filtered, diluted with CH_2Cl_2 and washed with saturated aqueous $Na_2S_2O_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 4/1) to give **S2** (1.95 g, 72%) as a pale yellow foam. $[\alpha]_D^{25}$ = +82.0 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1 H, C*H*=CH), 7.00 (d, *J* = 8.8 Hz, 1 H, CH=C*H*), 5.45–5.39 (m, 2 H, H-5/7), 5.23 (ddd, *J* = 2.4, 3.6, 10.0 Hz, 1 H, H-4), 4.49 (dd, *J* = 2.4, 12.4 Hz, 1 H), 4.33–4.26 (m, 2 H), 4.23 (dd, *J* = 1.2, 10.0 Hz, 1 H), 4.13–4.09 (m, 1 H), 2.33–2.22 (m, 2 H, H-3), 2.11 (s, 3 H), 2.00 (s, 6 H), 1.99 (s, 3 H), 1.29 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.2, 169.8, 165.8, 161.6, 128.9, 98.3, 98.1, 70.0, 67.5, 66.2, 64.1, 62.7, 62.2, 31.1, 20.9, 20.8, 14.1; HRMS (ESI) *m/z* calcd for $C_{21}H_{27}O_{13}INa$ [M + Na]$^+$ 637.0394, found 637.0395.

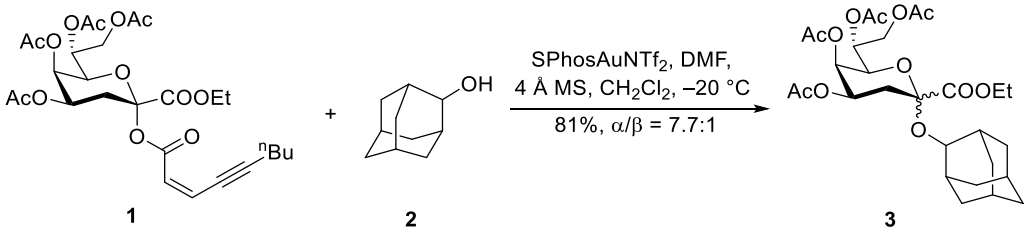


S2 **1**

To a solution of **S2** (2.2 g, 3.6 mmol) in anhydrous CH_3CN (30 mL) was added CuI (68.8 mg, 0.36 mmol) and $Pd(PPh_3)_2Cl_2$ (126.3 mg, 0.18 mmol). After purged with argon for three times, Et_3N (1 mL, 7.2 mmol) and 1-hexyne (618 μL, 5.4 mmol) were added to the solution. After the mixture was stirred at room temperature overnight, the reaction was diluted with CH_2Cl_2 and washed with saturated aqueous NH_4Cl. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 8/1) to afford **1** (1.60 g, 78%) as a yellow syrup. $[\alpha]_D^{25}$ = +85.1 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (dt, *J* = 2.4, 11.6 Hz, 1 H, C*H*=CH), 6.01 (d, *J* = 11.2 Hz, 1 H, CH=C*H*), 5.38–5.35 (m, 2 H, H-5/7), 5.23 (ddd, *J*

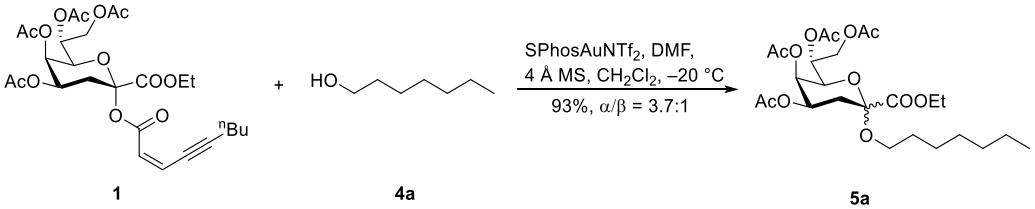
= 2.0, 3.2, 10.0 Hz, 1 H, H-4), 4.44 (dd, *J* = 1.6, 12.4 Hz, 1 H), 4.31–4.24 (m, 3 H), 4.15–4.10 (m, 1 H), 2.46 (td, *J* = 2.0, 7.2 Hz, 2 H), 2.31–2.22 (m, 2 H, H-3), 2.11 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 6 H), 1.58–1.51 (m, 2 H), 1.47–1.39 (m, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H), 0.91 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.6, 170.1, 169.8, 166.2, 161.6, 126.4, 125.4, 106.7, 97.6, 77.9, 69.6, 67.5, 66.3, 64.1, 62.5, 62.3, 31.2, 30.4, 22.2, 20.9, 20.8, 20.7, 19.9, 14.1, 13.7; HRMS (ESI) *m/z* calcd for $C_{27}H_{36}O_{13}Na$ $[M + Na]^+$ 591.2054, found 591.2056.

2.2. Synthesis of ethyl (adamantan-2-yl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-D-*manno*-oct-2-ulopyranoside)onate 3



To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), 2-adamantanol **2** (15.2 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.25 mL) under argon. After being stirred at –20 ℃ for 2 h, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **3**[2] (23.0 mg, 81%, α/β = 7.7:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38–5.33 (m, 2 H, H-4α/5α/7α), 5.26–5.25 (m, 0.13 H, H-5β/7β), 5.19 (dt, *J* = 2.8, 9.6 Hz, 1 H, H-4α/5α/7α), 5.13 (ddd, *J* = 2.4, 4.8, 9.6 Hz, 0.13 H, H-5β/7β), 4.87 (ddd, *J* = 3.2, 4.4, 13.2 Hz, 0.13 H, H-4β), 4.68 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.37 (dd, *J* = 2.4, 12.4 Hz, 0.13 H), 4.31–4.09 (m, 4.52 H), 3.92 (m, 0.14 H), 3.89 (m, 1 H), 2.40 (dd, *J* = 4.4, 12.4 Hz, 0.13 H, H-3β), 2.35–2.31 (m, 1 H, H-3α), 2.10–1.92 (m, 17.86 H), 1.83–1.44 (m, 13.78 H), 1.30 (t, *J* = 7.2 Hz, 3.39 H).

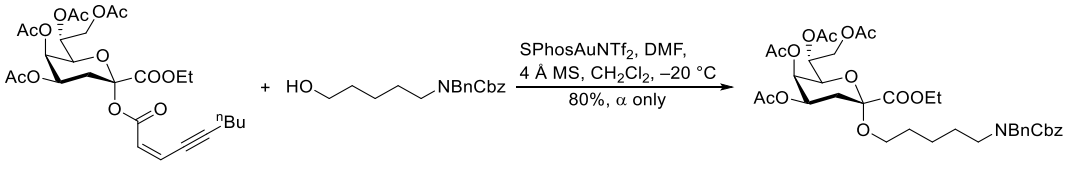
2.3. Synthesis of ethyl (*n*-heptanyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-D-*manno*-oct-2-ulopyranoside)onate 5a



1 4a 5a

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), *n*-heptanol **4a** (14 μL, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.2 mL) under argon. After being stirred at –20 ℃ for 2 h, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5a**[2] (24.8 mg, 93%, α/β = 3.7:1) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36–5.31 (m, 2 H, H-4α/5α/7α), 5.27 (br s, 0.27 H, H-5β/7β), 5.22 (dt, *J* = 2.8, 10.0 Hz, 1 H, H-4α/5α/7α), 5.17 (dt, *J* = 3.2, 9.6 Hz, 0.27 H, H-5β/7β), 4.87 (ddd, *J* = 3.2, 4.4, 13.2 Hz, 0.27 H, H-4β), 4.60 (dd, *J* = 2.4, 12.4 Hz, 1 H), 4.36–4.35 (m, 0.54 H), 4.28–4.22 (m, 2.54 H), 4.20–4.17 (m, 0.27 H), 4.14 (dd, *J* = 3.6, 12.4 Hz, 1 H), 4.08 (d, *J* = 10.0 Hz, 1 H), 3.73 (dt, *J* = 6.4, 9.2 Hz, 0.27 H), 3.46 (dt, *J* = 6.4, 9.2 Hz, 1 H), 3.31–3.25 (m, 1.27 H), 2.36 (dd, *J* = 4.4, 12.4 Hz, 0.27 H, H-3β), 2.20–2.15 (m, 1 H, H-3α), 2.10–1.97 (m, 16.51 H), 1.60–1.53 (m, 2.54 H), 1.34–1.24 (m, 13.97 H), 0.89–0.86 (m, 3.81 H).

2.4. Synthesis of ethyl (*N*-benzyl–benzyloxycarbonyl-5-aminopentyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-$_D$-*manno*-oct-2-ulopyranoside)onate 5b

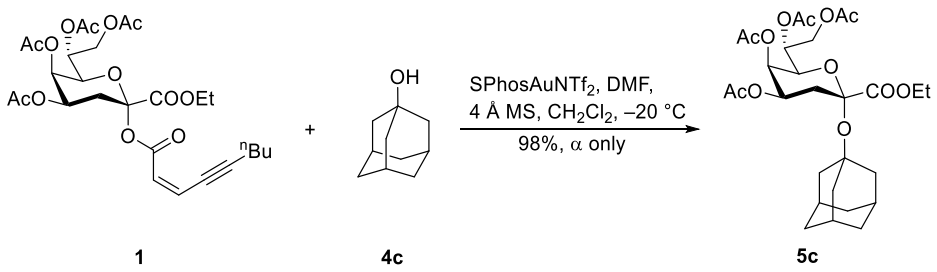


1 4b 5b

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), linker **4b**[3] (32.7 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.2 mL) under argon. After being stirred at –20 ℃ for 2 h, TLC indicated the

disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5b**[2] (29.8 mg, 80%, α only) as a yellow syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.17 (m, 10 H), 5.35–5.31 (m, 2 H, H-4/5/7/Cbz), 5.24–5.16 (m, 3 H, H-4/5/7/Cbz), 4.60 (dd, *J* = 0.8, 12.0 Hz, 1 H), 4.50 (br s, 2 H), 4.24 (q, *J* = 6.8 Hz, 2 H), 4.13 (dd, *J* = 3.2, 12.0 Hz, 1 H), 4.07–4.03 (m, 1 H), 3.44 (br s, 1 H), 3.26–3.20 (m, 3 H), 2.16 (dd, *J* = 4.0, 12.4 Hz, 1 H, H-3), 2.08–1.97 (m, 13 H), 1.54 (br s, 4 H), 1.33–1.25 (m, 5 H).

2.5. Synthesis of ethyl (adamantan-1-yl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate 5c

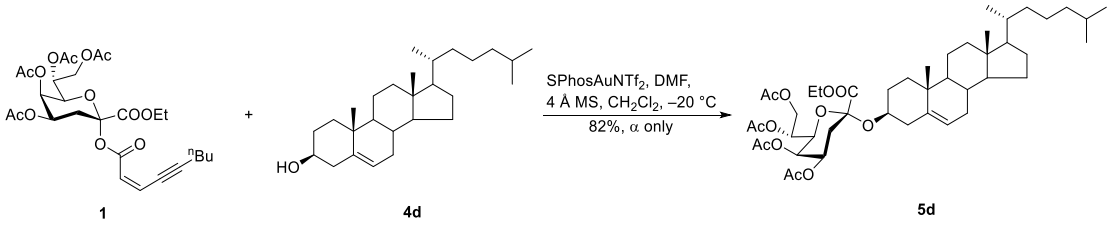


1 **4c** **5c**

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), 1-adamantanol **4c** (15.3 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.25 mL) under argon. After being stirred at –20 ℃ for 2 h, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5c**[2] (27.9 mg, 98%, α only) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37–5.32 (m, 2 H, H-4/5/7), 5.22 (dt, *J* = 3.2, 9.6 Hz, 1 H, H-4/5/7), 4.66 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.35–4.12 (m, 4 H), 2.18 (dd, *J* = 4.4, 12.0 Hz, 1 H, H-3), 2.10 (br s, 3 H), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.98 (s, 3 H), 1.96 (s, 3 H), 1.89 (t, *J* = 12.4 Hz, 1 H, H-3), 1.86 (br s, 6 H), 1.63–1.53 (m, 6 H), 1.34 (t, *J* = 7.2 Hz, 3 H).

2.6. Synthesis of ethyl (cholesteryl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-

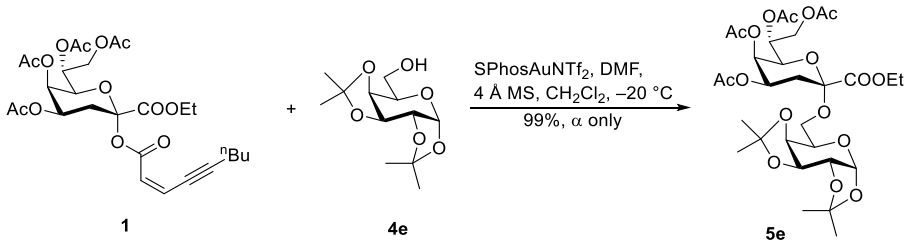
oct-2-ulopyranoside)onate 5d



1 4d 5d

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), cholesterol **4d** (38.7 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.25 mL) under argon. After being stirred at –20 ℃ for 2 h, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5d**[2] (32.9 mg, 82%, α only) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37–5.33 (m, 2 H, H-5/7), 5.24 (ddd, *J* = 2.8, 4.4, 9.6 Hz, 1 H, H-4), 4.69 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.29 – 4.17 (m, 3 H), 4.11 (dd, *J* = 4.4, 12.4 Hz, 1 H), 3.51 (dt, *J* = 4.8, 10.8 Hz, 1 H), 2.39–2.26 (m, 2 H), 2.22 (dd, *J* = 4.0, 12.0 Hz, 1 H, H-3), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.98 (s, 3 H), 1.97 (s, 3 H).

2.7. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside 5e

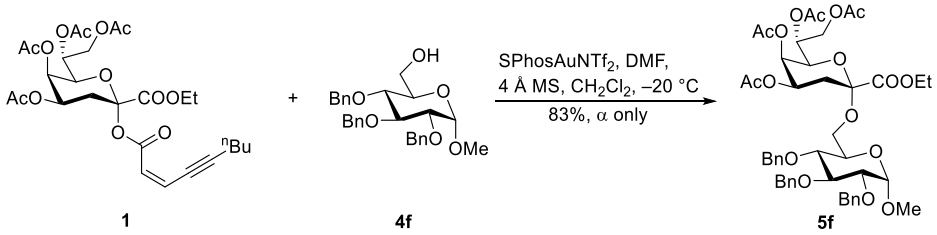


1 4e 5e

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the galactosyl acceptor **4e**[4] (26.0 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.25 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column

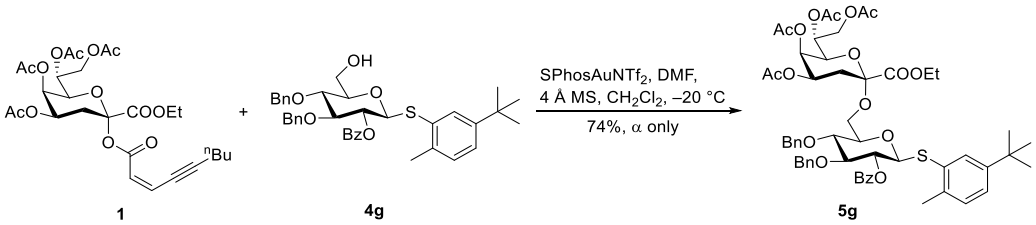
chromatography (petroleum ether/EtOAc: 6/1) to provide **5e**[2] (33.5 mg, 99%, α only) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (d, *J* = 4.8 Hz, 1 H, H-1′), 5.36–5.32 (m, 2 H, H-5/7), 5.27 (ddd, *J* = 2.0, 5.2, 9.6 Hz, 1 H, H-4), 4.60–4.55 (m, 2 H), 4.34 (d, *J* = 9.6 Hz, 1 H), 4.30–4.22 (m, 3 H), 4.19 (dd, *J* = 1.6, 8.0 Hz, 1 H), 4.14 (dd, *J* = 5.6, 12.4 Hz, 1 H), 3.99–3.96 (m, 1 H), 3.67–3.60 (m, 2 H), 2.20–2.16 (m, 1 H, H-3), 2.09–2.05 (m, 7 H), 2.00 (s, 3 H), 1.96 (s, 3 H), 1.56 (s, 3 H), 1.41 (s, 3 H), 1.33–1.30 (m, 9 H).

2.8. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→6)-methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 5f



To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the glucosyl acceptor **4f**[5] (46.4 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise SPhosAuNTf$_2$ in CH_2Cl_2 (0.1 M, 0.25 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 4/1) to provide **5f**[2] (36.6 mg, 83%, α only) as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 15 H), 5.34–5.29 (m, 2 H, H-5/7), 5.18 (ddd, *J* = 2.4, 4.4, 9.6 Hz, 1 H, H-4), 4.99 (d, *J* = 10.8 Hz, 1 H), 4.92 (d, *J* = 10.8 Hz, 1 H), 4.82–4.78 (m, 2 H), 4.67 (d, *J* = 12.0 Hz, 1 H), 4.57 (d, *J* = 3.6 Hz, 1 H, H-1′), 4.55–4.50 (m, 2 H), 4.20–4.11 (m, 3 H), 4.08 (dd, *J* = 4.4, 12.4 Hz, 1 H), 3.99 (t, *J* = 9.2 Hz, 1 H), 3.82 (t, *J* = 8.4 Hz, 1 H), 3.66 (dd, *J* = 1.2, 10.0 Hz, 1 H), 3.48–3.44 (m, 2 H), 3.42 (s, 3 H), 3.24 (dd, *J* = 5.2, 6.0 Hz, 1 H), 2.16 (dd, *J* = 5.2, 12.4 Hz, 1 H, H-3), 2.07–2.04 (m, 4 H), 1.98 (s, 3 H), 1.96 (s, 3 H), 1.88 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H).

2.9. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→6)-5-*tert*-butyl-2-methylphenyl 3,4-di-*O*-benzyl-2-*O*-benzoyl-1-thio-β-D-glucopyranose 5g

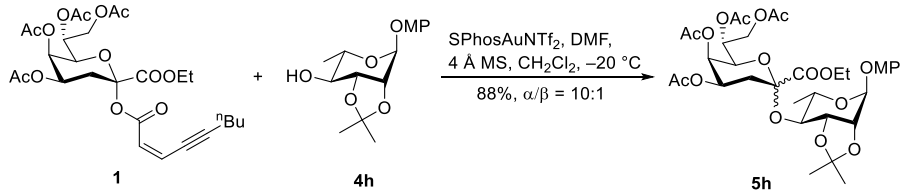


1 4g 5g

To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the glucosyl acceptor **4g**[6] (62.7 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.3 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5g** (38.6 mg, 74%, α only) as a white foam. $[\alpha]_D^{25}$ = +56.4 (*c* 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2 H), 7.61–7.56 (m, 1 H), 7.47–7.43 (m, 3 H), 7.36–7.27 (m, 5 H), 7.19 (dd, *J* = 2.0, 8.0 Hz, 1 H), 7.15–7.10 (m, 6 H), 5.34–5.26 (m, 3 H, H-5/7/1′), 5.22 (ddd, *J* = 2.4, 3.2, 9.6 Hz, 1 H, H-4), 4.94 (d, *J* = 11.2 Hz, 1 H), 4.72 (d, *J* = 11.2 Hz, 1 H), 4.69–4.65 (m, 2 H), 4.63–4.56 (m, 2 H), 4.23–4.16 (m, 2 H), 4.15–4.07 (m, 2 H), 3.87–3.83 (m, 1 H), 3.78 (d, *J* = 10.4 Hz, 1 H), 3.65–3.57 (m, 3 H), 2.30–2.25 (m, 4 H, H-3/ArCH_3), 2.08 (s, 3 H), 2.05 (m, 1 H, H-3), 2.01 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 3 H), 1.27 (t, *J* = 6.4 Hz, 3 H), 1.22 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.6, 169.9, 169.8, 166.9, 165.5, 149.8, 138.0, 137.7, 133.4, 133.2, 130.3, 130.1, 130.0, 128.7, 128.5, 128.2, 128.1, 127.9, 125.5, 99.1, 88.6, 84.5, 78.6, 78.1, 75.5, 75.3, 73.0, 68.5, 67.8, 66.6, 64.4, 64.0, 62.2, 62.1, 34.5, 31.9, 31.4, 21.1, 20.9, 20.8, 20.6, 14.2; HRMS (ESI) *m/z* calcd for $C_{56}H_{66}O_{17}SNa$ $[M + Na]^+$ 1065.3918, found 1065.3917.

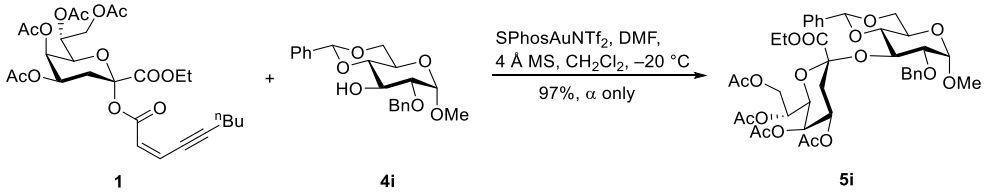
2.10. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-D-*manno*-oct-2-ulopyranoside)onate-(2→4)-4-methoxyphenyl 2,3-*O*-isopropylidene-α-L-

rhamnopyranoside 5h



To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the L-rhamnosyl acceptor **4h**[7] (31.0 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (1 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.5 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 7/1) to provide **5h**[2] (21.6 mg, 88%, α/β = 10:1) as a white foam. **5h**α: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99–6.97 (m, 2 H), 6.84–6.82 (m, 2 H), 5.56 (s, 1 H, H-1′), 5.38–5.30 (m, 3 H, H-4/5/7), 4.65 (dd, *J* = 2.4, 12.4 Hz, 1 H), 4.31–4.20 (m, 6 H), 3.81–3.77 (m, 4 H), 3.63 (dd, *J* = 6.0, 9.6 Hz, 1 H), 2.20 (dd, *J* = 4.8, 12.8 Hz, 1 H, H-3), 2.11–2.08 (m, 7 H), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.53 (s, 3 H), 1.38 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H), 1.16 (d, *J* = 6.4 Hz, 3 H).

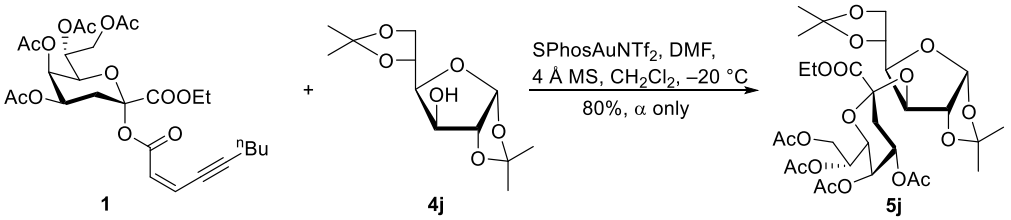
2.11. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→3)-methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-gluco pyranoside 5i



To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the glucosyl acceptor **4i**[8] (78.9 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.2 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column

chromatography (petroleum ether/EtOAc: 6/1) to provide **5i** (38.3 mg, 97%, α only) as a white foam. $[\alpha]_D^{25}$ = +52.5 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.30 (m, 10 H), 5.36–5.31 (m, 2 H, H-4/5/7/PhC*H*), 5.19–5.13 (m, 2 H, H-4/5/7/PhC*H*), 4.79 (d, *J* = 11.6 Hz, 1 H), 4.65–4.57 (m, 4 H, H-1′), 4.29 (t, *J* = 9.2 Hz, 1 H), 4.20–4.11 (m, 2 H), 3.76 (td, *J* = 4.8, 10.0 Hz, 1 H), 3.66 (t, *J* = 10.0 Hz, 1 H), 3.60–3.56 (m, 2 H), 3.43–3.37 (m, 1 H), 3.34 (s, 3 H), 3.16–3.08 (m, 1 H), 2.20 (dd, *J* = 4.4, 12.8 Hz, 1 H, H-3), 2.09 (s, 3 H), 2.04–2.03 (m, 4 H), 1.95 (s, 6 H), 0.89 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.6, 170.1, 170.0, 167.7, 137.8, 137.2, 129.4, 128.8, 128.7, 128.4, 126.9, 102.1, 98.6, 81.7, 79.3, 73.8, 71.3, 69.3, 69.2, 68.4, 66.6, 64.8, 62.8, 62.4, 61.2, 55.4, 32.9, 21.0, 20.9, 20.8, 13.9; HRMS (ESI) *m/z* calcd for $C_{39}H_{48}O_{17}Na$ $[M + Na]^+$ 811.2789, found 811.2791.

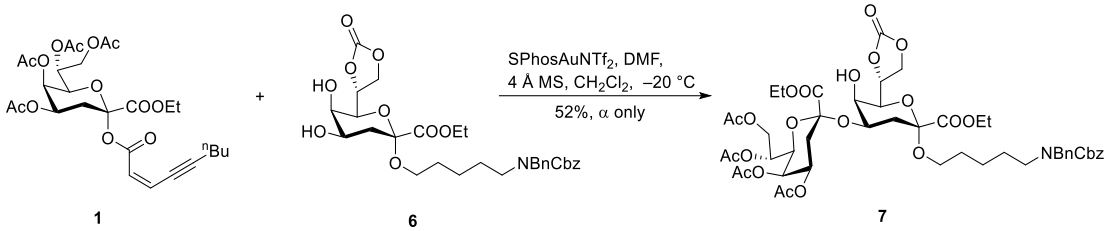
2.12. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→3)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranoside 5j



To a stirred mixture of the Kdo donor **1** (28.4 mg, 0.05 mmol), the glucofunanosyl acceptor **4j**[9] (26.0 mg, 0.1 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 0.4 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to provide **5j** (27.1 mg, 80%, α only) as a white foam. $[\alpha]_D^{25}$ = +16.7 (*c* 0.51, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (d, *J* = 3.6 Hz, 1 H, H-1′), 5.39 (br s, 1 H, H-5/7), 5.27 (ddd, *J* = 3.2, 4.8, 12.4 Hz, 1 H, H-5/7), 5.18 (ddd, *J* = 2.8, 4.0, 9.2 Hz, 1 H, H-4), 4.78 (dd, *J* = 2.8, 12.4 Hz, 1 H), 4.64 (d, *J* = 3.6 Hz, 1 H), 4.35–4.17 (m, 6 H), 4.10–3.99 (m, 3 H), 2.30 (dd, *J* = 4.4, 12.8 Hz, 1 H, H-3), 2.17–2.10 (m, 4 H), 2.08 (s, 3 H), 1.99 (s, 3 H), 1.97 (s, 3 H), 1.49

(s, 3 H), 1.41 (s, 3 H), 1.37–1.34 (m, 6 H), 1.31 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 170.5, 170.1, 169.8, 166.4, 112.4, 109.3, 105.1, 100.0, 83.1, 80.9, 79.1, 72.6, 69.5, 68.1, 67.0, 66.3, 64.5, 62.6, 61.7, 31.9, 27.0, 26.9, 26.7, 26.6, 21.0, 20.9, 20.8, 20.7, 14.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{44}O_{17}Na$ $[M + Na]^+$ 699.2476, found 699.2475.

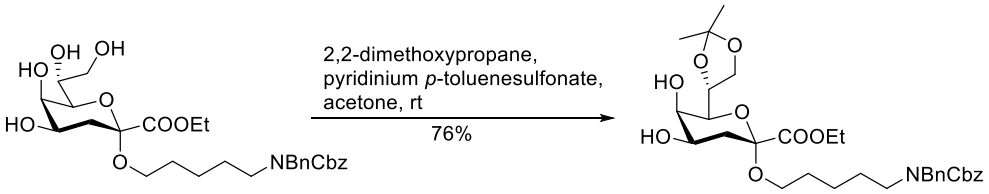
2.13. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→4)-ethyl (*N*-benzyl–benzyloxycarbonyl-5-aminopentyl 7,8-*O*-carbonyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate 7



1 6 7

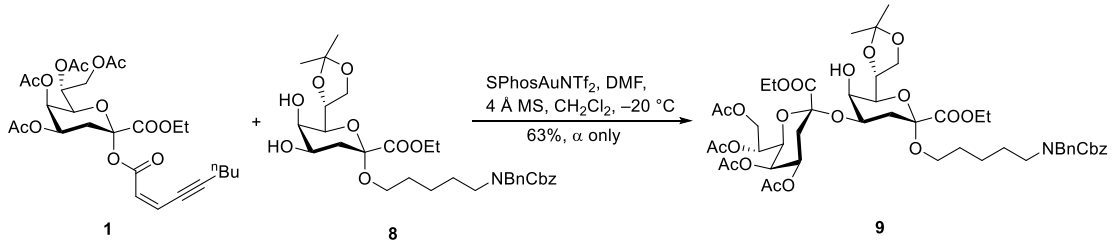
To a stirred mixture of the Kdo donor **1** (56.9 mg, 0.1 mmol), the Kdo acceptor **6**[2] (30.1 mg, 0.05 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 1.0 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1) to provide **7**[2] (26.5 mg, 52%, α only) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.17 (m, 10 H), 5.38 (br s, 1 H, H-4/5/7/Cbz), 5.27–5.15 (m, 4 H, H-4/5/7/Cbz), 4.89–4.84 (m, 1 H), 4.78–4.71 (m, 2 H), 4.53–4.50 (m, 3 H), 4.29–4.21 (m, 5 H), 4.09 (d, *J* = 9.6 Hz, 1 H), 3.97–3.83 (m, 2 H), 3.72–3.69 (m, 1 H), 3.41–3.15 (m, 4 H), 2.22 (dd, *J* = 4.8, 13.2 Hz, 1 H, H-3), 2.09–1.98 (m, 15 H), 1.52–1.50 (m, 4 H), 1.35–1.28 (m, 8 H).

2.14. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→4)-ethyl (*N*-benzyl–benzyloxycarbonyl-5-aminopentyl 7,8-*O*-isopropylidene-5-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate 10



S3 **8**

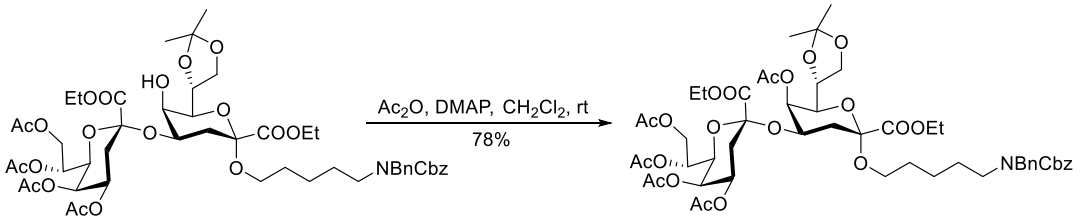
Tetraol **S3** was prepared from compound **5b** in 89% yield upon exposure to K_2CO_3 in ethanol according to our previously reported procedure.[2] To a solution of tetraol **S3** (208 mg, 0.36 mmol) in acetone (2.8 mL) at room temperature was added pyridinium *p*-toluenesulfonate (38 mg, 0.15 mmol) and 2,2-dimethoxypropane (79.7 μL, 0.65 mmol). After the mixture was stirred at room temperature for 2 h, the reaction was quenched with saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1) to afford **8** (170 mg, 76%) as a pale yellow syrup. $[\alpha]_D^{25}$ = +36.2 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16 (m, 10 H), 5.17 (d, *J* = 14.0 Hz, 2 H, Cbz), 4.49 (d, *J* = 6.8 Hz, 2 H), 4.39 (dt, *J* = 6.0, 7.6 Hz, 1 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 4.15 (dd, *J* = 6.4, 8.8 Hz, 1 H), 4.05–3.94 (m, 3 H), 3.53–3.46 (m, 1 H), 3.40–3.36 (m, 1 H), 3.25–3.18 (m, 3 H), 2.62 (br s, 1 H), 2.44 (br s, 1 H), 2.14 (dd, *J* = 4.4, 12.4 Hz, 1 H, H-3), 1.83 (t, *J* = 12.4 Hz, 1 H, H-3), 1.57–1.51 (m, 4 H), 1.39 (s, 3 H), 1.36 (s, 3 H), 1.27 (t, *J* = 7.2 Hz, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 138.0, 128.7, 128.6, 128.1, 128.0, 127.4, 127.3, 109.6, 99.0, 73.8, 72.9, 67.4, 67.2, 66.9, 65.9, 63.8, 61.9, 50.6, 50.3, 47.2, 46.2, 35.2, 29.4, 28.1, 27.7, 27.1, 25.5, 23.7, 14.3; HRMS (ESI) *m/z* calcd for $C_{33}H_{45}O_{10}NNa$ [M + Na]$^+$ 638.2941, found 638.2942.



1 **8** **9**

To a stirred mixture of the Kdo donor **1** (56.9 mg, 0.1 mmol), the Kdo acceptor **8** (30.8 mg, 0.05 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in

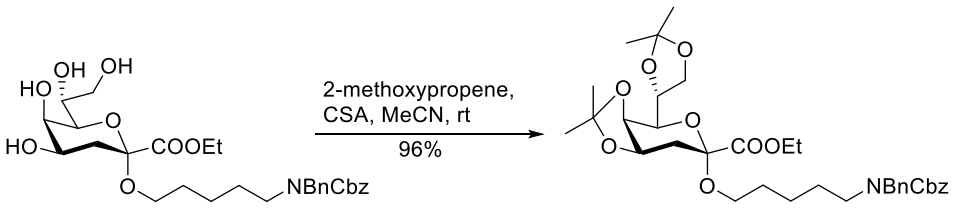
CH_2Cl_2 (0.1 M, 0.8 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1) to provide **9** (32.5 mg, 63%, α only) as a colorless syrup: $[\alpha]_D^{25}$ = +65.3 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16 (m, 10 H), 5.38 (br s, 1 H, H-4/5/7/Cbz), 5.31–5.26 (m, 1 H, H-4/5/7/Cbz), 5.20–5.14 (m, 3 H, H-4/5/7/Cbz), 4.75 (t, *J* = 9.6 Hz, 1 H), 4.48 (br s, 2 H), 4.40–4.35 (m, 1 H), 4.27–4.09 (m, 8 H), 4.00–3.92 (m, 2 H), 3.75 (br s, 1 H), 3.40–3.16 (m, 5 H), 2.28 (dd, *J* = 4.4, 12.8 Hz, 1 H, H-3), 2.11–2.05 (m, 9 H), 1.98 (s, 3 H), 1.97 (s, 3 H), 1.50 (m, 4 H), 1.35–1.28 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.5, 170.2, 169.8, 167.9, 167.7, 156.8, 156.3, 138.1, 137.1, 136.9, 128.7, 128.6, 128.5, 128.0, 127.9, 127.4, 127.3, 109.3, 98.7, 97.8, 73.7, 72.3, 69.3, 68.9, 68.0, 67.3, 67.1, 66.3, 64.5, 64.4, 63.6, 62.6, 61.9, 61.6, 50.6, 50.3, 47.2, 46.3, 33.2, 32.4, 29.3, 28.1, 27.6, 27.0, 25.5, 23.5, 20.9, 20.8, 20.7, 14.3, 14.0; HRMS (ESI) *m/z* calcd for $C_{51}H_{69}O_{21}NNa$ [M + Na]$^+$ 1054.4260, found 1054.4261.



To a solution of compound **9** (26.8 mg, 0.026 mmol) in anhydrous CH_2Cl_2 (0.5 mL) were added DMAP (3.5 mg, 0.03 mmol) and acetic anhydride (11 μL, 0.12 mmol) at room temperature. After the mixture was stirred for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was then extracted with CH_2Cl_2 and dried over Na_2SO_4. After filtration, the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 1/1) to provide **10** (21.8 mg, 78%) as a colorless syrup. $[\alpha]_D^{25}$ = +147.8 (*c* 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.19 (m, 10 H), 5.34 (br s, 1 H, H-4/5/7/5′/Cbz), 5.27 (br s, 1 H, H-4/5/7/5′/Cbz), 5.23–5.13 (m, 4 H, H-4/5/7/5′/Cbz), 4.75–4.72 (m, 1 H), 4.64–4.59 (m, 1 H), 4.50 (br s, 2 H), 4.34–4.22 (m, 4 H), 4.13 (d,

J = 9.6 Hz, 1 H), 4.11–4.06 (m, 1 H), 4.01–3.98 (m, 3 H), 3.60 (m, 1 H), 3.38 (m, 1 H), 3.27–3.19 (m, 3 H), 2.19–1.98 (m, 19 H, H-3), 1.53 (m, 4 H), 1.37 (s, 3 H), 1.36–1.32 (m, 5 H), 1.30 (s, 3 H), 1.26 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.4, 170.0, 169.8, 167.8, 166.7, 156.9, 156.3, 139.5, 138.1, 136.9, 128.7, 128.6, 128.5, 128.1, 128.0, 127.5, 127.4, 109.5, 98.7, 97.9, 73.7, 71.7, 69.3, 68.1, 67.3, 67.2, 66.7, 66.6, 66.4, 64.5, 63.8, 63.7, 62.5, 62.0, 61.7, 50.7, 50.3, 47.2, 46.3, 34.3, 31.8, 31.6, 29.9, 29.8, 29.4, 27.0, 25.6, 23.5, 22.9, 21.1, 21.0, 20.9, 20.8, 20.7, 14.4, 14.0; HRMS (ESI) *m/z* calcd for $C_{53}H_{71}O_{22}NNa$ $[M + Na]^+$ 1096.4365, found 1096.4366.

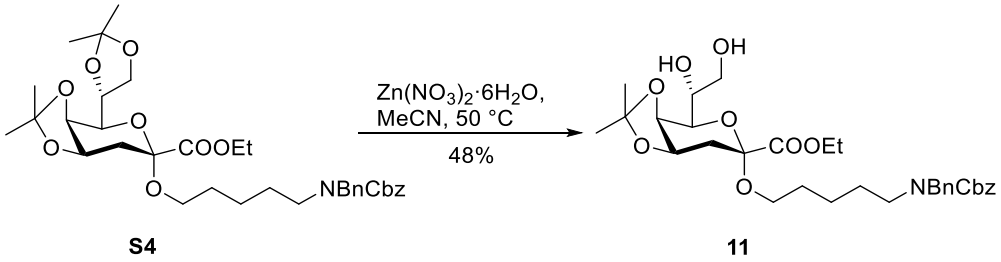
2.15. Synthesis of ethyl (4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate-(2→8)-ethyl (*N*-benzyl–benzyloxycarbonyl-5-aminopentyl 4,5-*O*-isopropylidene-7-*O*-acetyl-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate 13



S3 **S4**

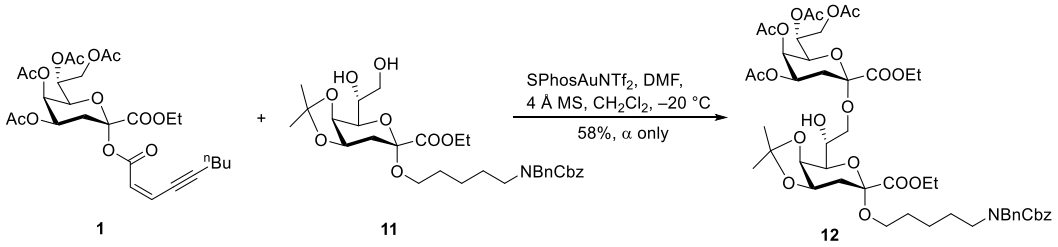
To a solution of tetraol **S3**[2] (100 mg, 0.17 mmol) in anhydrous acetonitrile (3 mL) at room temperature were added 2-methoxypropene (36 μL, 0.38 mmol) and camphorsulfonic acid (8.06 mg, 0.03 mmol). After the mixture was stirred at room temperature for 2 h, the reaction was quenched with Et_3N and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1) to afford **S4** (110 mg, 96%) as a pale yellow syrup. $[\alpha]_D^{25}$ = +12.6 (*c* 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16 (m, 10 H), 5.17 (d, *J* = 13.2 Hz, 2 H, Cbz), 4.50–4.48 (m, 3 H), 4.40–4.36 (m, 1 H), 4.27–4.18 (m, 3 H), 4.15–4.12 (m, 1 H), 3.97 (dd, *J* = 4.4, 8.4 Hz, 1 H), 3.59–3.55 (m, 2 H), 3.25–3.14 (m, 3 H), 2.75 (dd, *J* = 4.0, 15.6 Hz, 1 H, H-3), 1.83 (d, *J* = 15.2 Hz, 1 H, H-3), 1.52–1.48 (m, 4 H), 1.41 (br s, 5 H), 1.37 (s, 3 H), 1.31–1.25 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 156.9, 156.3, 138.1, 137.1, 136.9, 128.7, 128.6, 128.5, 128.1, 127.9, 127.5,

127.4, 127.3, 109.7, 109.3, 97.5, 74.0, 72.2, 71.7, 70.3, 67.3, 67.2, 63.0, 61.6, 50.6, 50.3, 47.3, 46.3, 33.1, 29.5, 27.1, 25.8, 25.5, 25.2, 23.6, 14.3; HRMS (ESI) *m/z* calcd for $C_{36}H_{49}O_{10}NNa$ $[M + Na]^+$ 678.3254, found 678.3256.



S4 **11**

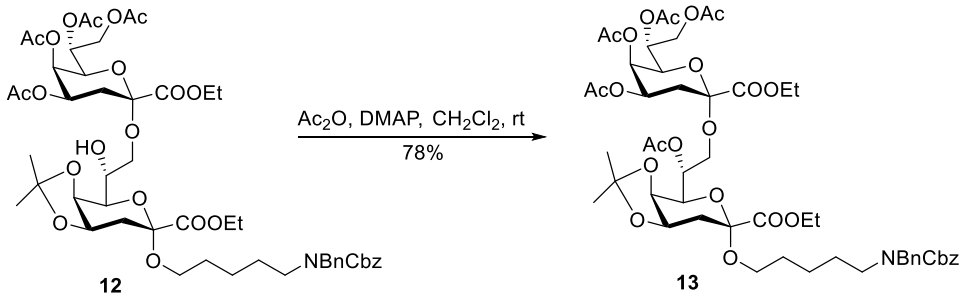
To a solution of **S4** (110 mg, 0.17 mmol) in CH_3CN (0.8 mL) was added $Zn(NO_3)_2$ $6H_2O$[10] (160 mg, 0.54 mmol). After being stirred at 50 ˚C for 2 h, the reaction mixture was diluted with water and the product was extracted with EtOAc. The combined EtOAc phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 1/1) to afford **11** (50 mg, 48%) as a pale yellow syrup and **S3** (47 mg, 48%) as a pale yellow syrup. $[\alpha]_D^{25}$ = +18.9 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.15 (m, 10 H), 5.17 (d, *J* = 15.6 Hz, 2 H, Cbz), 4.54–4.29 (m, 4 H), 4.27–4.18 (m, 2 H), 4.01 (br s, 1 H), 3.85–3.69 (m, 3 H), 3.63–3.50 (m, 1 H), 3.39–3.14 (m, 3 H), 2.62 (dd, *J* = 4.8, 15.2 Hz, 1 H, H-3), 1.91–1.87 (m, 1 H, H-3), 1.60–1.47 (m, 4 H), 1.43 (s, 3 H), 1.33–1.25 (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 156.6, 137.9, 136.7, 128.7, 128.6, 128.1, 128.0, 127.9, 127.5, 127.4, 109.6, 97.6, 72.3, 71.0, 70.4, 67.5, 63.8, 63.2, 62.9, 61.8, 50.6, 50.3, 47.3, 46.2, 33.3, 31.6, 31.1, 30.4, 29.9, 29.3, 27.5, 26.2, 25.4, 23.5, 14.3; HRMS (ESI) *m/z* calcd for $C_{33}H_{45}O_{10}NNa$ $[M + Na]^+$ 638.2941, found 638.2942.



1 **11** **12**

To a stirred mixture of the Kdo donor **1** (56.9 mg, 0.1 mmol), the Kdo acceptor

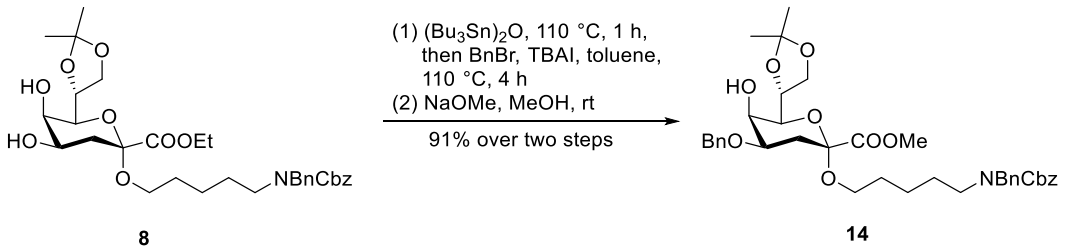
11 (30.8 mg, 0.05 mmol), DMF (23 μL, 0.3 mmol) and freshly activated 4 Å MS (100 mg) in anhydrous CH_2Cl_2 (2 mL) at –20 ℃, was added dropwise $SPhosAuNTf_2$ in CH_2Cl_2 (0.1 M, 1 mL) under argon. After being stirred overnight at –20 ℃, TLC indicated the disappearance of compound **1**. The mixture was filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1) to provide **12** (29.9 mg, 58%, α only) as a colorless syrup. $[\alpha]_D^{25}$ = +39.5 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.16 (m, 10 H), 5.34 (br s, 1 H, H-5/7), 5.32–5.27 (m, 1 H, H-5/7), 5.23 (ddd, *J* = 2.0, 3.6, 9.6 Hz, 1 H, H-4), 5.15 (d, *J* = 16.4 Hz, 2 H, Cbz), 4.54–4.46 (m, 4 H), 4.35 (dd, *J* = 1.6, 7.2 Hz, 1 H), 4.27–4.09 (m, 7 H), 3.65 (br s, 2 H), 3.59 (br s, 1 H), 3.51 (br s, 1 H), 3.26–3.17 (m, 3 H), 3.02 (br s, 1 H), 2.60 (m, 1 H, H-3′), 2.16 (dd, *J* = 5.2, 12.8 Hz, 1 H, H-3), 2.08 (s, 3 H), 2.06 (s, 3 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.89–1.82 (m, 2 H, H-3/3′), 1.51 (m, 4 H), 1.32–1.23 (m, 14 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 170.6, 170.0, 169.9, 168.6, 167.5, 156.9, 156.3, 138.1, 137.1, 136.9, 132.3, 132.2, 132.1, 128.7, 128.6, 128.5, 128.0, 127.9, 127.4, 127.3, 109.7, 99.0, 97.8, 72.0, 70.3, 70.0, 69.5, 68.6, 67.9, 67.3, 66.5, 65.9, 64.5, 63.3, 62.4, 61.6, 60.6, 50.5, 50.3, 47.3, 46.3, 33.2, 32.0, 29.4, 28.1, 27.6, 26.2, 25.4, 23.7, 21.0, 20.9, 20.8, 14.3, 14.2; HRMS (ESI) *m/z* calcd for $C_{51}H_{69}O_{21}NNa$ $[M + Na]^+$ 1054.4260, found 1054.4261.



To a solution of compound **12** (29.9 mg, 0.029 mmol) in anhydrous CH_2Cl_2 (0.5 mL) were added DMAP (3.5 mg, 0.03 mmol) and acetic anhydride (11 μL, 0.12 mmol) at room temperature. After the mixture was stirred for 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The mixture was then extracted with CH_2Cl_2 and dried over Na_2SO_4. After filtration, the mixture was concentrated *in vacuo*. The

residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 1/1) to provide **13** (24.3 mg, 78%) as a colorless syrup. $[\alpha]_D^{25}$ = +125.1 (*c* 0.36, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.18 (m, 10 H), 5.34 (br s, 1 H, H-4/5/7/5′), 5.32–5.15 (m, 5 H, H-4/5/7/5′/Cbz), 4.63 (d, *J* = 11.6 Hz, 1 H), 4.49 (br s, 2 H), 4.44 (dd, *J* = 4.8, 10.4 Hz, 1 H), 4.28–4.09 (m, 7 H), 4.00 (d, *J* = 10.8 Hz, 1 H), 3.87–3.85 (m, 1 H), 3.79 (dd, *J* = 7.6, 10.8 Hz, 1 H), 3.53 (m, 1 H), 3.25–3.19 (m, 3 H), 2.50 (d, *J* = 14.8 Hz, 1 H, H-3′), 2.20 (dd, *J* = 4.8, 12.4 Hz, 1 H, H-3), 2.12–2.03 (m, 10 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.88 (d, *J* = 14.4 Hz, 1 H), 1.51 (m, 4 H), 1.38 (s, 3 H), 1.34–1.25 (m, 11 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.5, 170.1, 170.0, 169.9, 168.3, 167.1, 156.9, 156.3, 138.1, 137.1, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.5, 127.4, 127.3, 109.7, 99.0, 97.9, 71.9, 70.3, 69.9, 68.7, 68.0, 67.3, 66.6, 64.4, 63.4, 63.1, 62.4, 62.1, 61.6, 50.6, 50.3, 47.3, 46.3, 33.4, 31.9, 29.9, 29.5, 28.2, 27.7, 26.3, 25.5, 23.7, 21.2, 20.9, 20.8, 14.3, 14.2; HRMS (ESI) *m/z* calcd for $C_{53}H_{71}O_{22}NNa$ $[M + Na]^+$ 1096.4365, found 1096.4366.

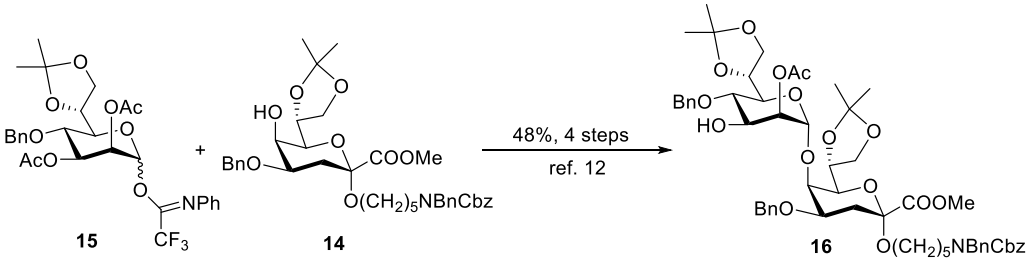
2.16. Synthesis of 2-*O*-acetyl-3-*O*-levulinoyl-4,6-di-*O*-benzyl-7-*O*-*tert*-butyl diphenylsilyl-D-*glycero*-α-D-*manno*-heptopyranosyl-(1→3)-2-*O*-acetyl-4-*O*-benzyl-6,7-*O*-isopropylidene-D-*glycero*-α-D-*manno*-heptopyranosyl-(1→5)-methyl (*N*-benzyl-benzyloxycarbonyl-5-aminopentyl 4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-α-D-*manno*-oct-2-ulopyranoside)onate 18

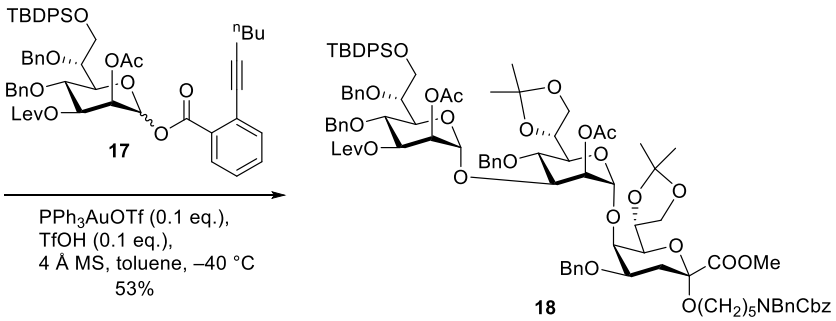


8 **14**

A mixture of compound **8** (61.5 mg, 0.1 mmol), bis(tributyltin) oxide (76.4 μL, 0.15 mmol) in toluene (2 mL) was heated at 110 ℃ for 1 h. After cooling to room temperature, benzyl bromide (21.4 μL, 0.18 mmol) and tetrabutylammonium iodide (22 mg, 0.06 mmol) were added, and the mixture was heated at 110 ℃ for 4 h. The cooling mixture was then filtered and the filtrate was evaporated. The residue was

dissolved in MeOH (5 mL) and sodium methoxide (54 mg, 1 mmol) was added. After being stirred for 2 h, the mixture was neutralized with Amberlite IR120 H^+ resin, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc: 3/1) to give **14**[11] (63 mg, 91%) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.16 (m, 15 H), 5.17 (d, *J* = 14.8 Hz, 2 H, Cbz), 4.64–4.57 (m, 2 H), 4.51–4.44 (m, 3 H), 4.18–4.14 (m, 2 H), 3.97 (dd, *J* = 4.8, 8.4 Hz, 1 H), 3.90 (m, 1 H), 3.76 (s, 3 H), 3.47 (m, 1 H), 3.39 (m, 1 H), 3.26–3.17 (m, 3 H), 2.27 (br s, 1 H), 2.22 (dd, *J* = 4.4, 12.4 Hz, 1 H, H-3), 1.97 (t, *J* = 12.4 Hz, 1 H, H-3), 1.53 (m, 4 H), 1.41 (s, 3 H), 1.38 (s, 3 H), 1.28–1.25 (m, 2 H).





Disaccharide **16** was prepared from *N*-phenyl trifluoroacetimidate **15** and Kdo acceptor **14** according to our previously reported procedure.[12] To a stirred mixture of disaccharide acceptor **16** (21.1 mg, 0.02 mmol), donor **17**[13] (45.8 mg, 0.048 mmol), and freshly activated 4 Å MS (100 mg) in anhydrous toluene (4 mL) at –40 ℃ were added dropwise a solution of PPh_3AuOTf in CH_2Cl_2 (0.1 M, 0.02 mL) and TfOH (0.177 μL, 0.002 mmol) under argon. After being stirred at –40 ℃ for 12 h, the mixture was quenched by triethylamine, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc:

4/1) to afford **18** (19.2 mg, 53%) as a colorless syrup. $[\alpha]_D^{25}$ = +30.7 (*c* 0.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2 H), 7.57 (dd, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 6.4 Hz, 2 H), 7.38–7.05 (m, 32 H), 6.78 (dd, *J* = 7.2, 16.4 Hz, 2 H), 5.35–5.30 (m, 3 H, H-2/3/2′), 5.22 (br s, 1 H, H-1/1′), 5.18–5.14 (m, 2 H, Cbz), 5.05 (m, 1 H, H-1/1′), 4.98 (t, *J* = 11.6 Hz, 1 H), 4.89 (t, *J* = 12.0 Hz, 1 H), 4.80 (dd, *J* = 4.4, 10.0 Hz, 1 H), 4.69–4.65 (m, 2 H), 4.54–4.45 (m, 4 H), 4.34–4.28 (m, 2 H), 4.22–4.17 (m, 3 H), 4.14–4.00 (m, 4 H), 3.87–3.79 (m, 6 H), 3.68 (d, *J* = 8.0 Hz, 4 H), 3.33–3.16 (m, 5 H), 3.07 (t, *J* = 7.6 Hz, 1 H), 2.65–2.40 (m, 4 H), 2.21 (d, *J* = 13.6 Hz, 1 H, H-3″), 2.10 (s, 3 H), 2.04 (dd, *J* = 3.2, 12.0 Hz, 1 H, H-3″), 2.01–1.90 (m, 6 H), 1.48–1.21 (m, 18 H), 1.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 206.1, 171.9, 171.7, 170.1, 170.0, 169.9, 168.6, 168.5, 139.7, 139.6, 138.4, 138.2, 138.1, 138.0, 137.8, 136.0, 135.9, 133.7, 133.6, 129.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 109.7, 109.2, 99.3 ($^1J_{C1,H1}$ = 172.1 Hz), 99.0, 97.6 ($^1J_{C1,H1}$ = 172.1 Hz), 76.5, 76.4, 75.0, 74.9, 74.7, 74.5, 74.4, 73.9, 73.8, 73.6, 73.5, 73.1, 72.6, 72.5, 72.2, 71.8, 71.3, 70.5, 70.3, 70.2, 67.9, 67.3, 66.0, 65.8, 64.8, 64.7, 63.7, 62.1, 52.6, 52.5, 50.6, 50.3, 47.2, 46.3, 37.9, 37.8, 33.0, 29.9, 29.4, 28.1, 28.0, 27.0, 26.9, 26.3, 24.9, 24.2, 23.6, 21.1, 21.0, 20.9, 19.5, 19.2; HRMS (ESI) *m/z* calcd for $C_{102}H_{123}O_{26}NSiNa$ $[M + Na]^+$ 1828.8000, found 1828.7976.

3. References

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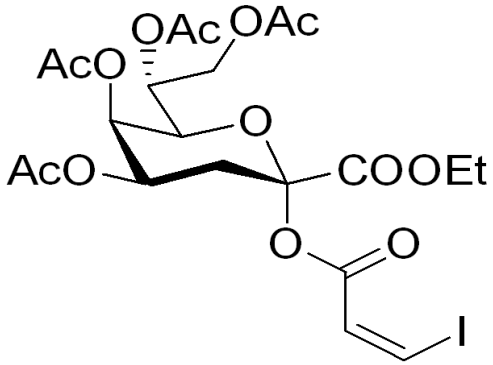

S2

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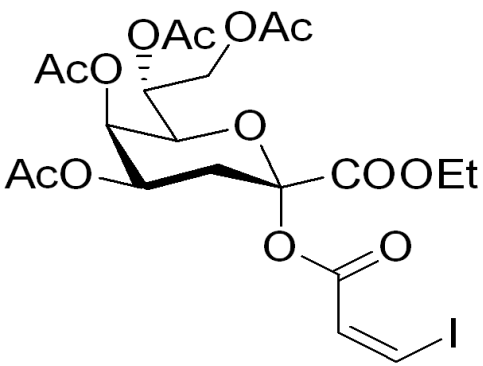

S2

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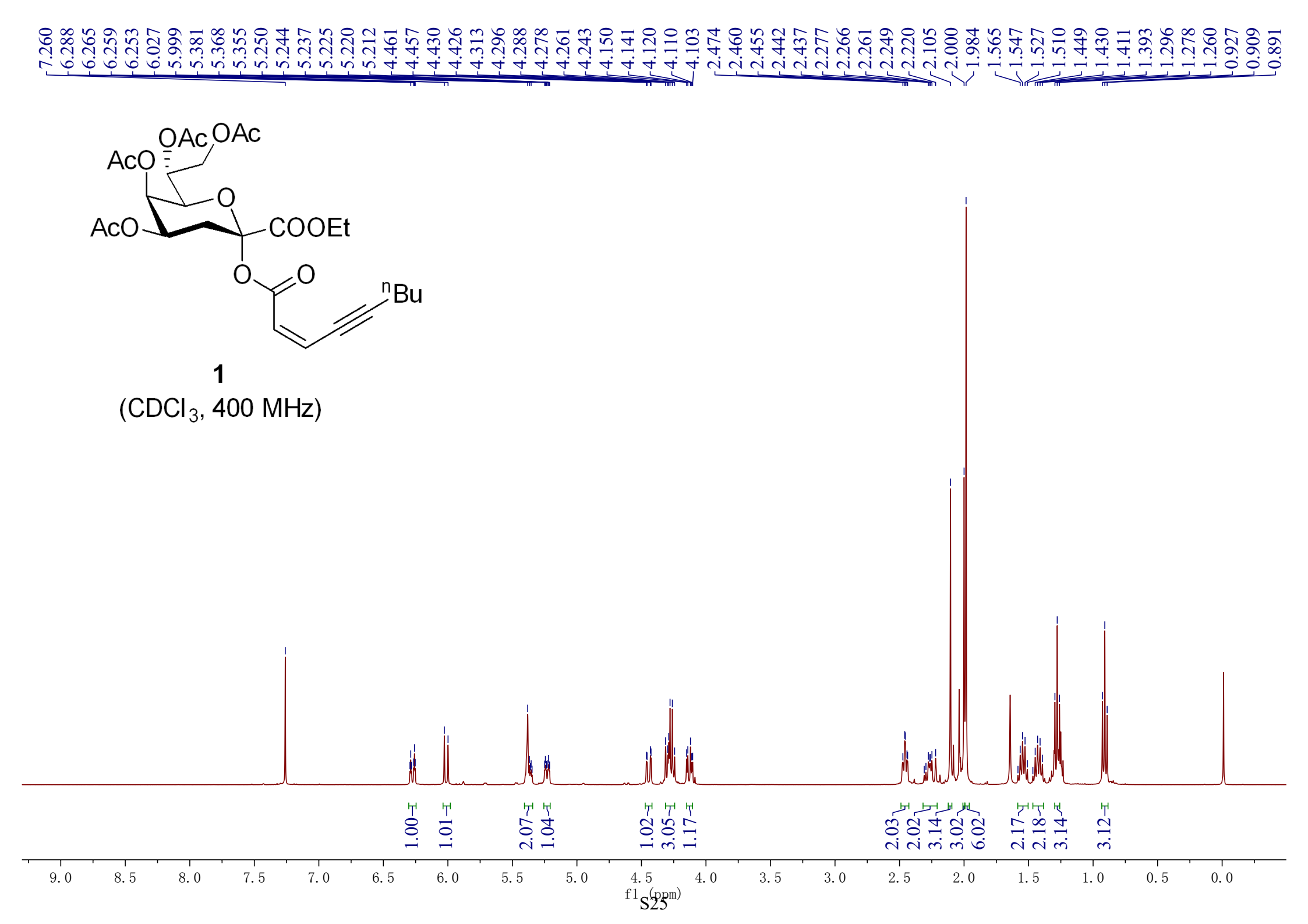

1

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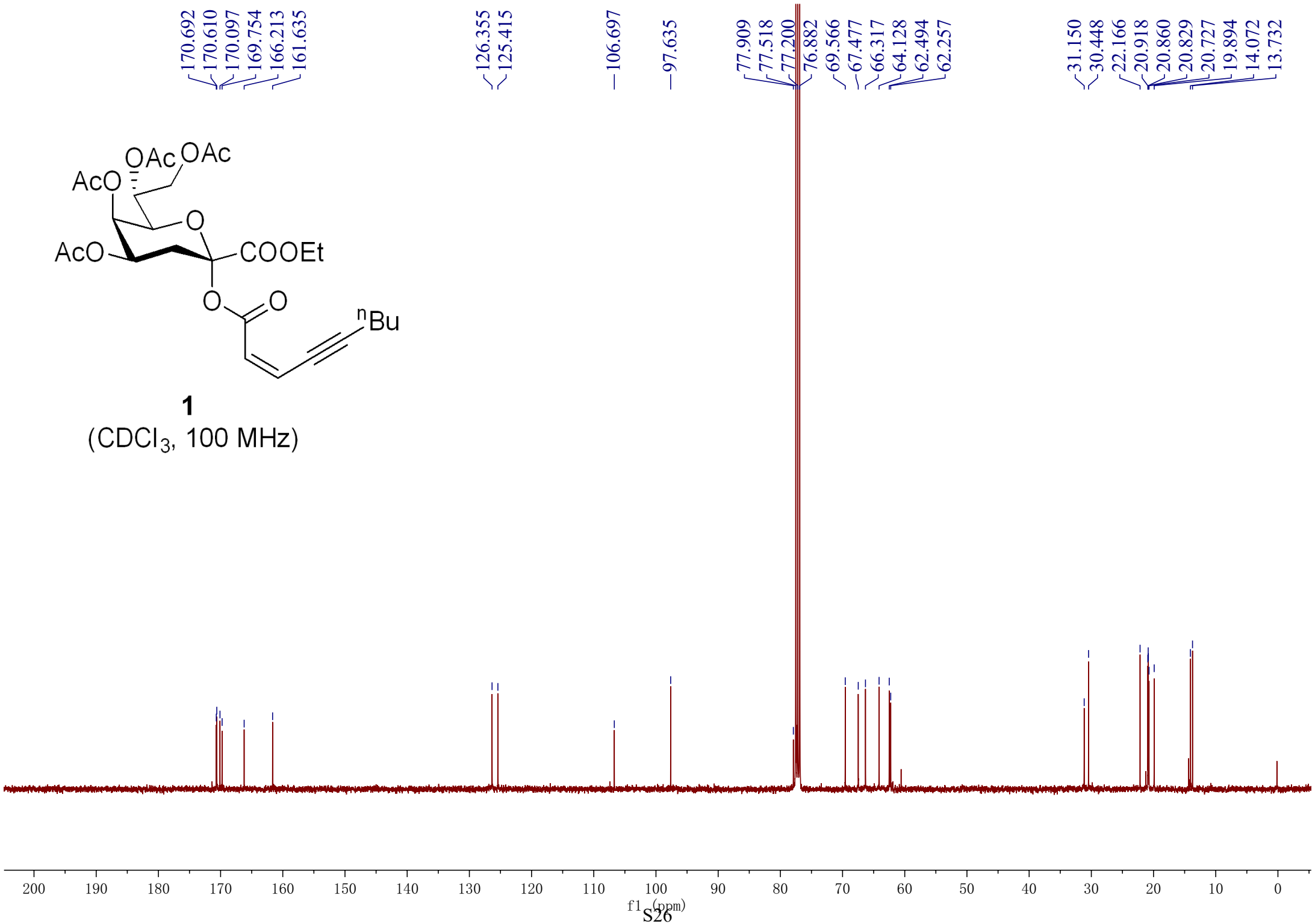

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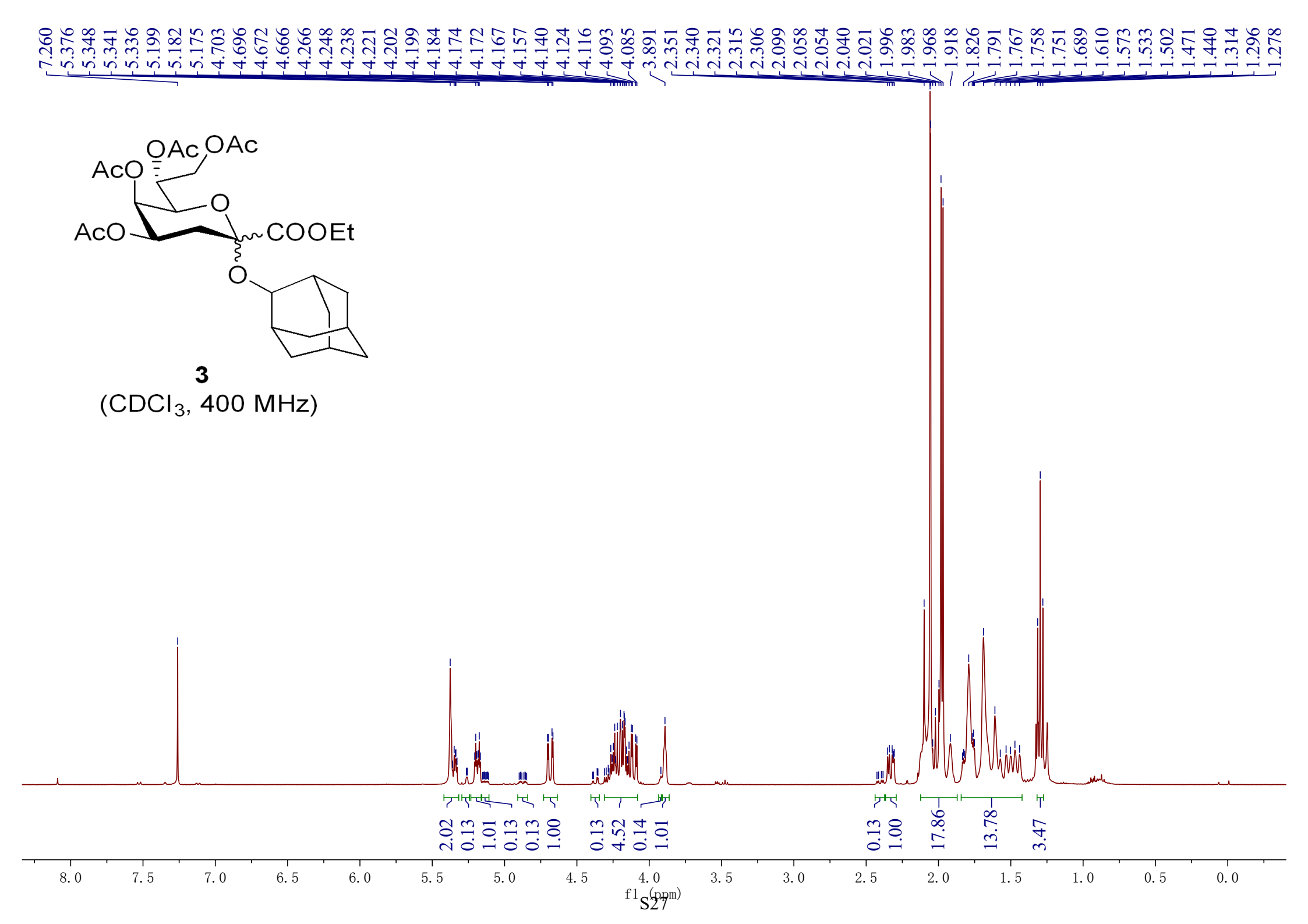
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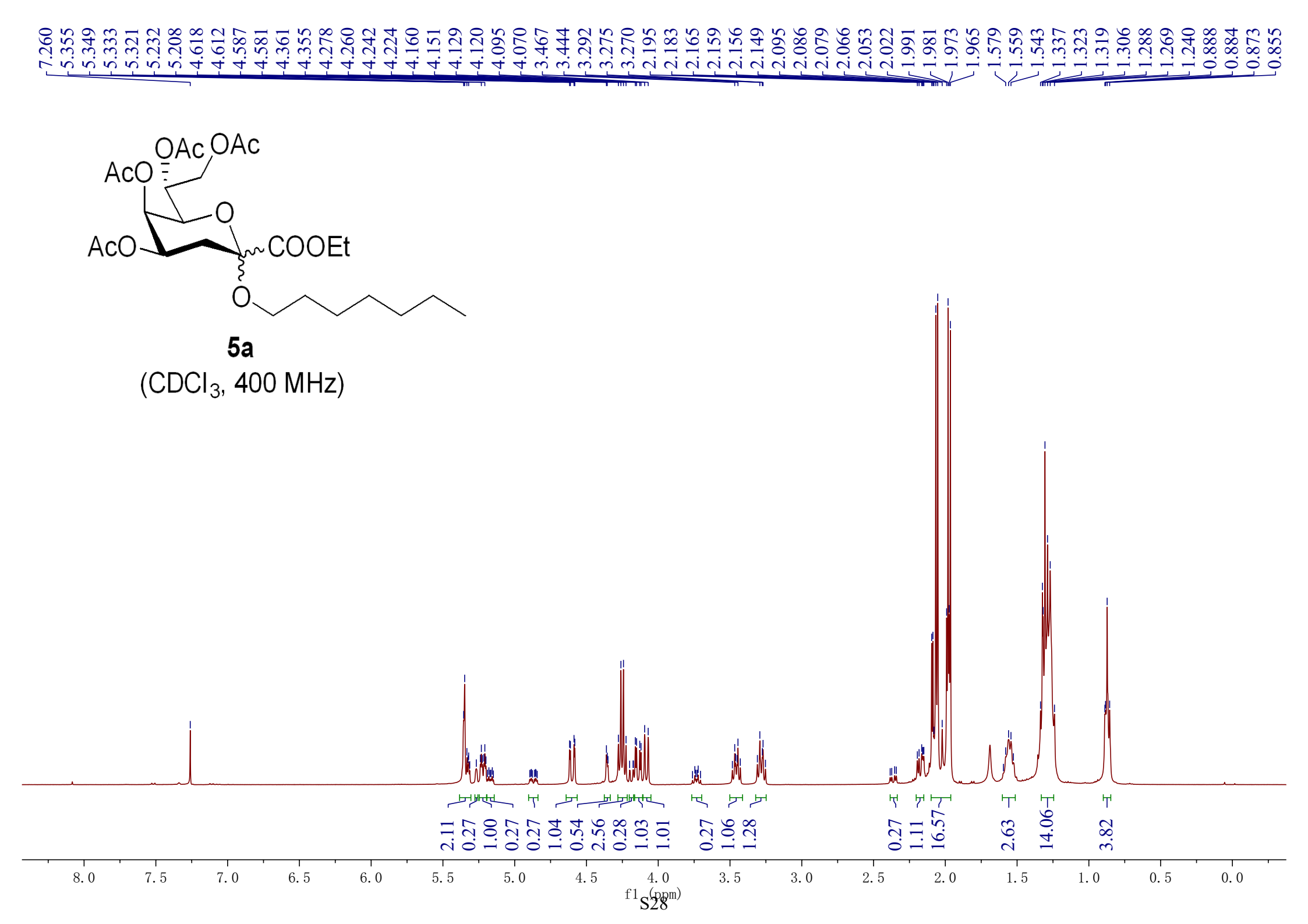
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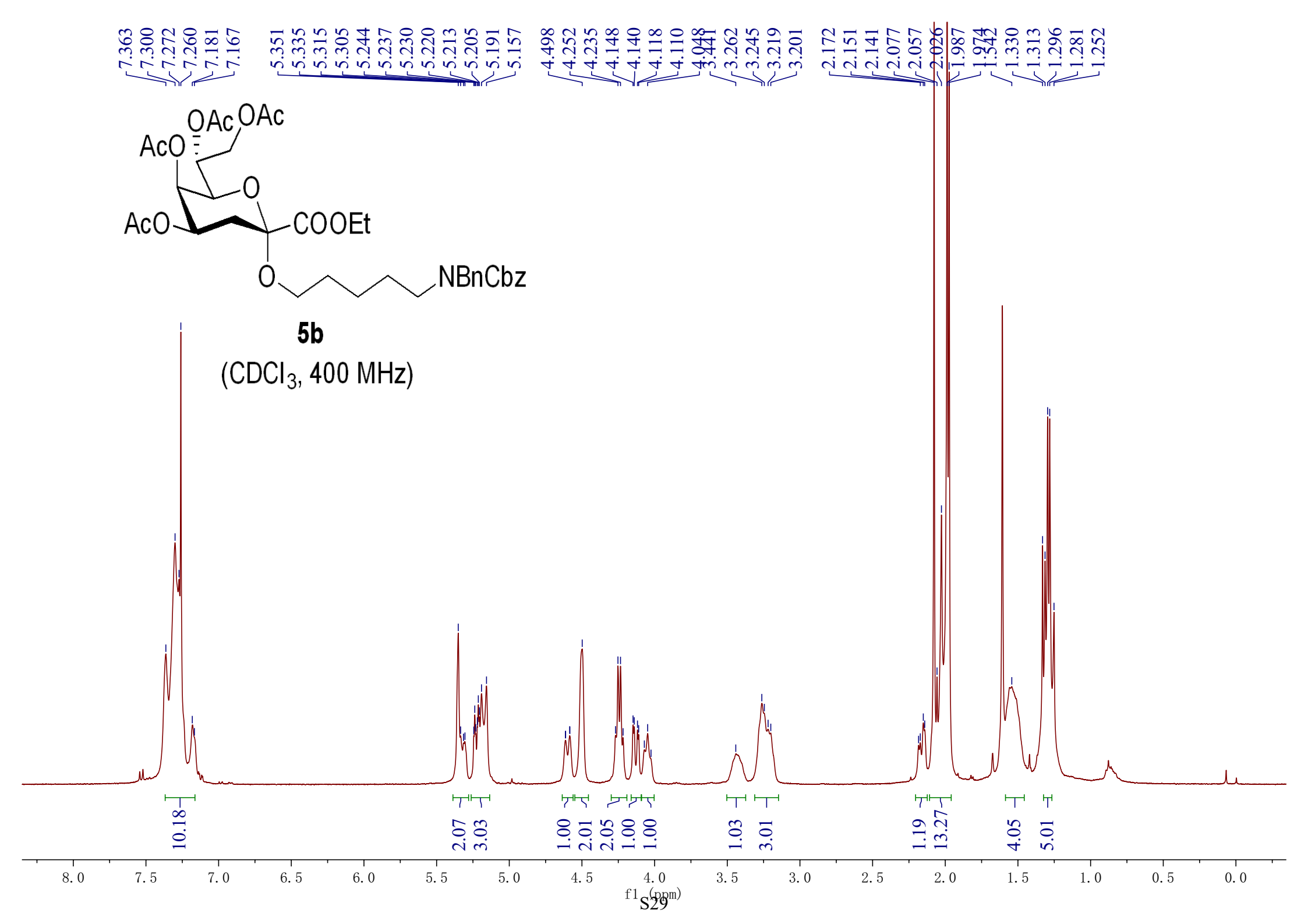
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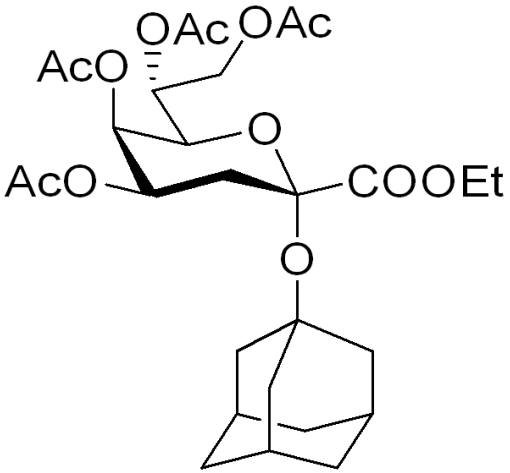
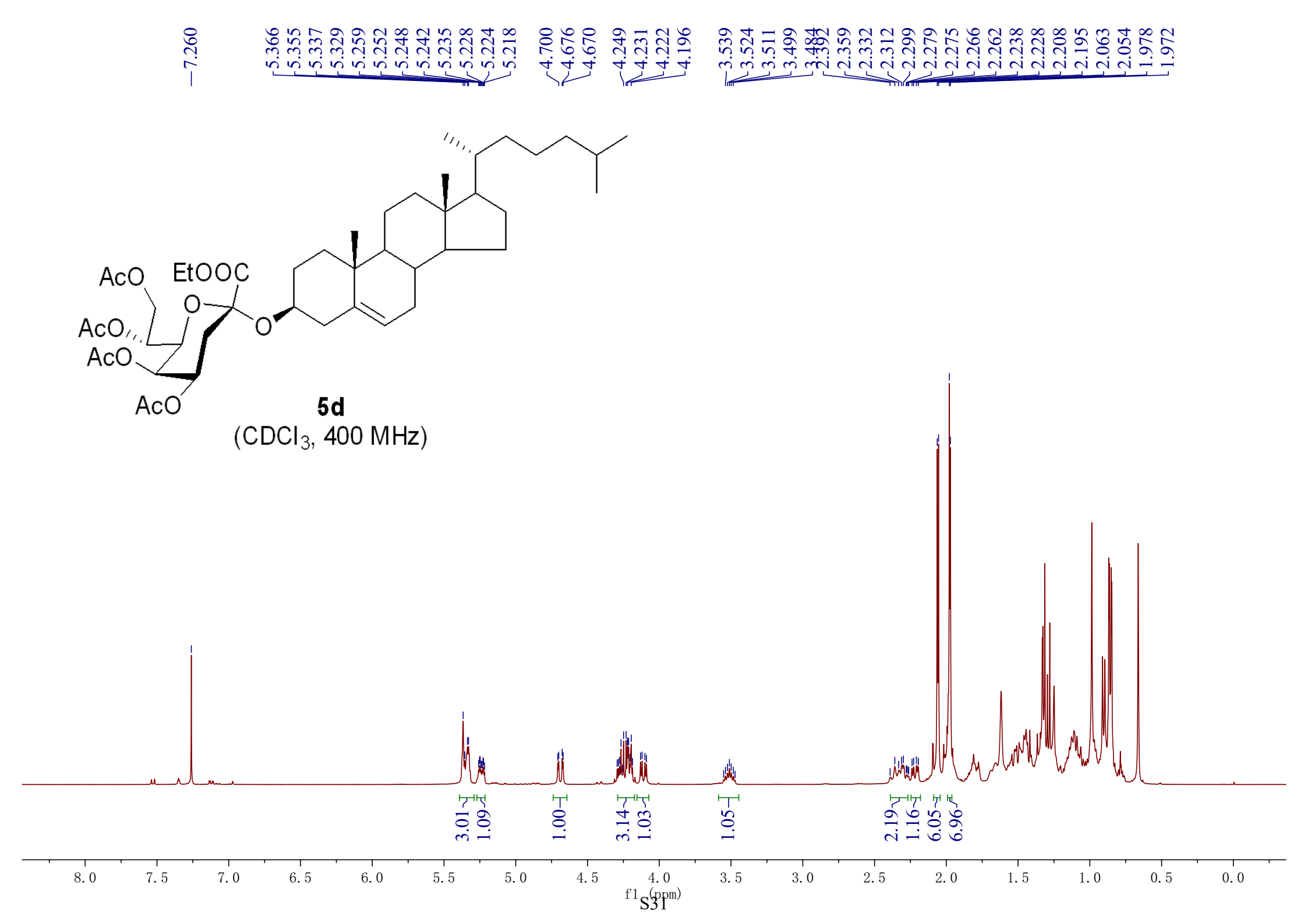
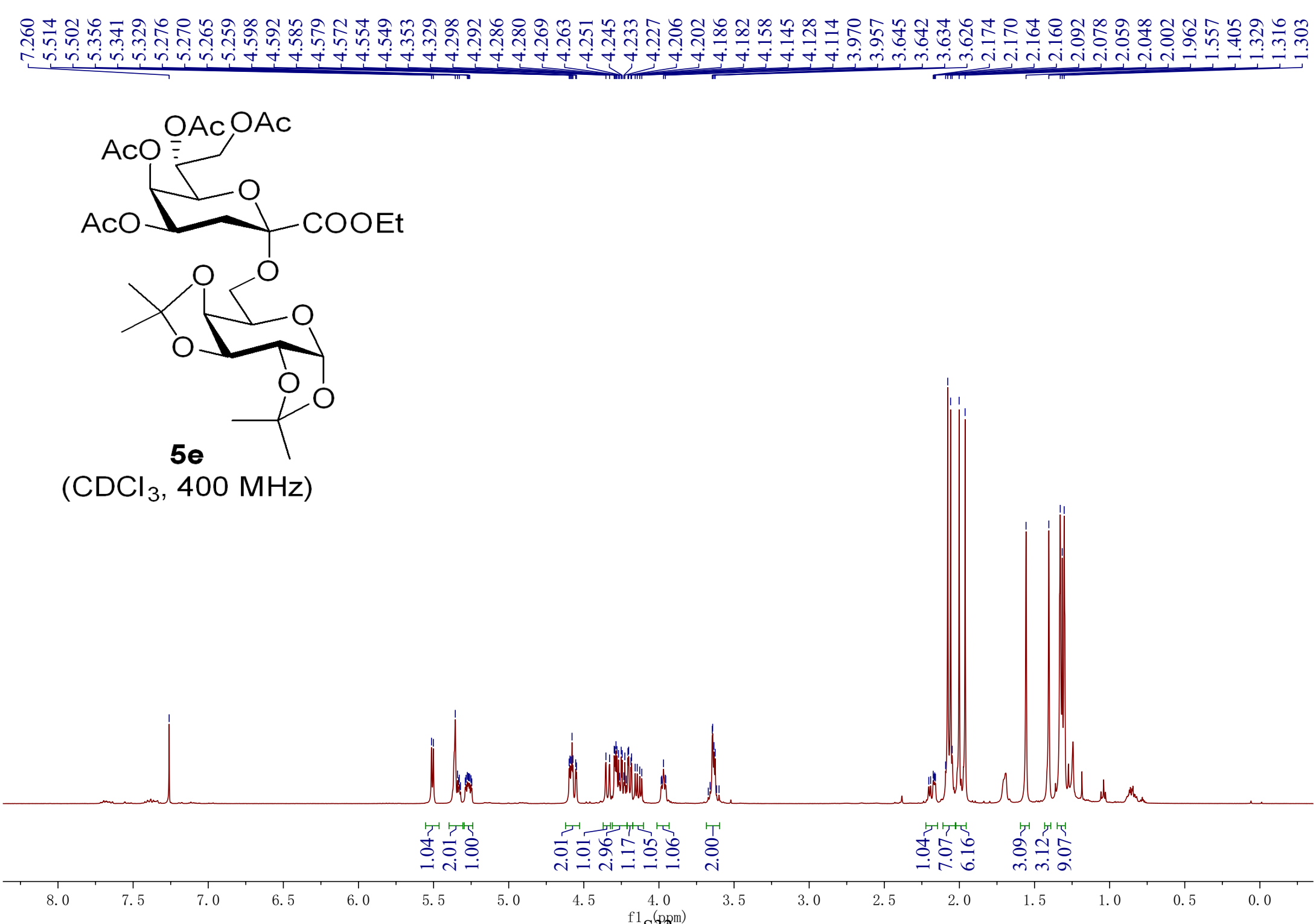


5c

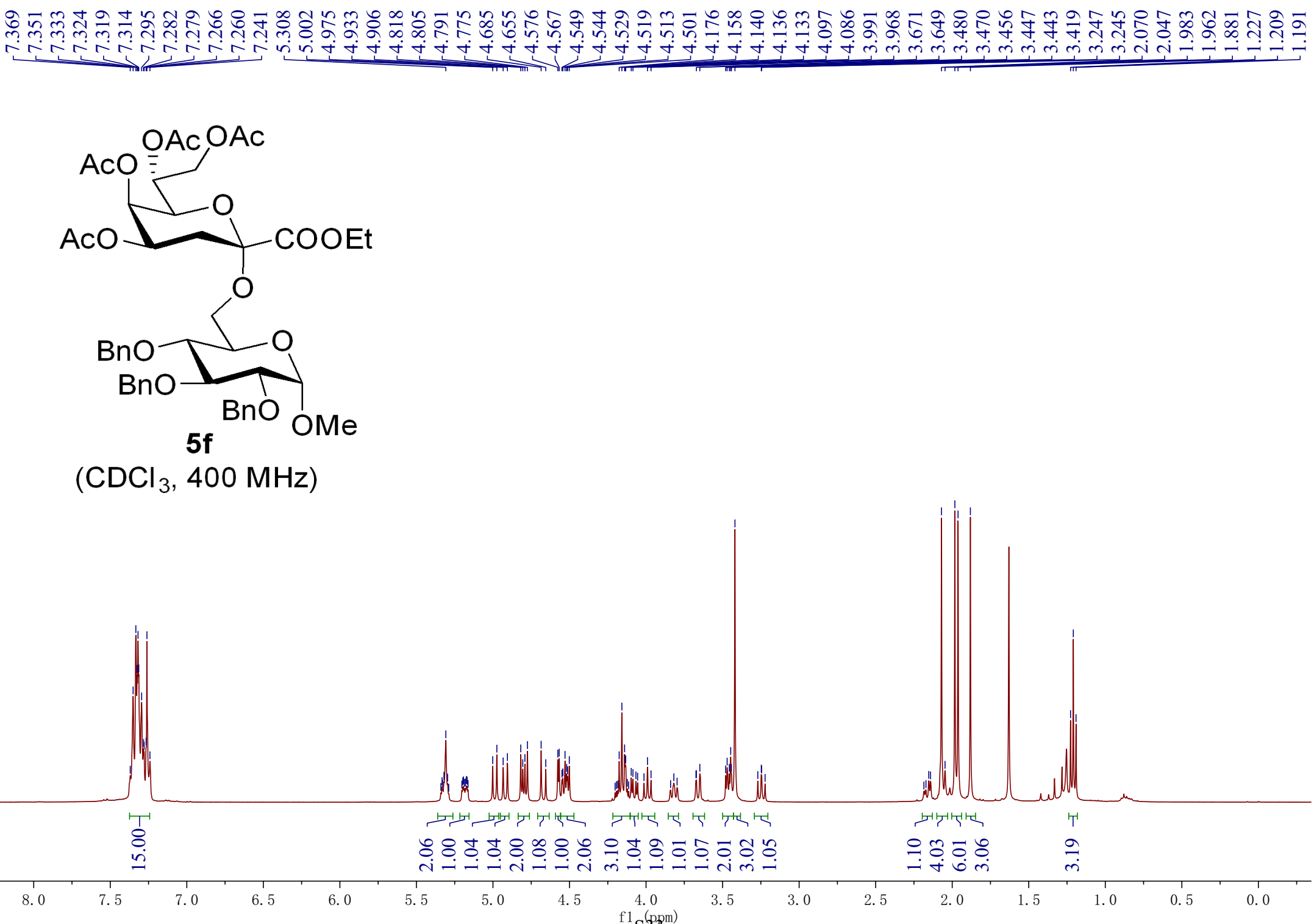
($CDCl_3$, 400 MHz)

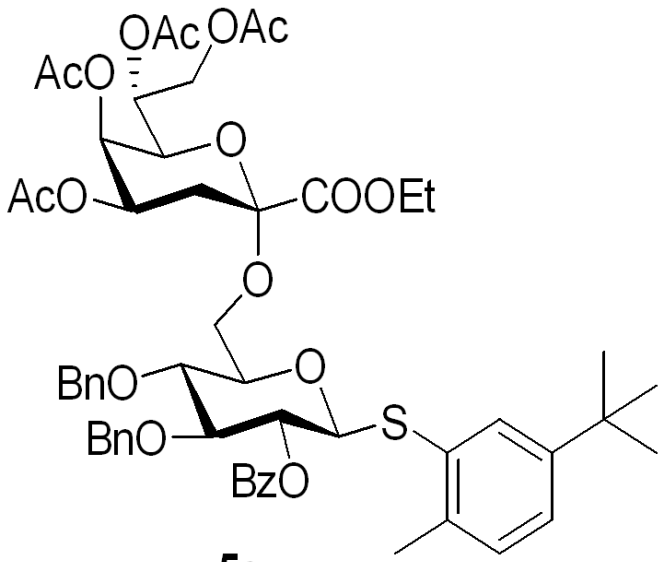

7.260
5.366
5.355
5.337
5.329
5.259
5.252
5.248
5.242
5.235
5.228
5.224
5.218
4.700
4.676
4.670
4.249
4.231
4.222
4.196
3.539
3.524
3.511
3.499
3.484
3.392
2.359
2.332
2.312
2.299
2.279
2.275
2.266
2.262
2.238
2.228
2.208
2.195
2.063
2.054
1.978
1.972
AcO
EtOOC
O
AcO
O
AcO
AcO
5d
(CDCl3, 400 MHz)
3.01
1.09
1.00
3.14
1.03
1.05
2.19
1.16
6.05
6.96
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)



5e

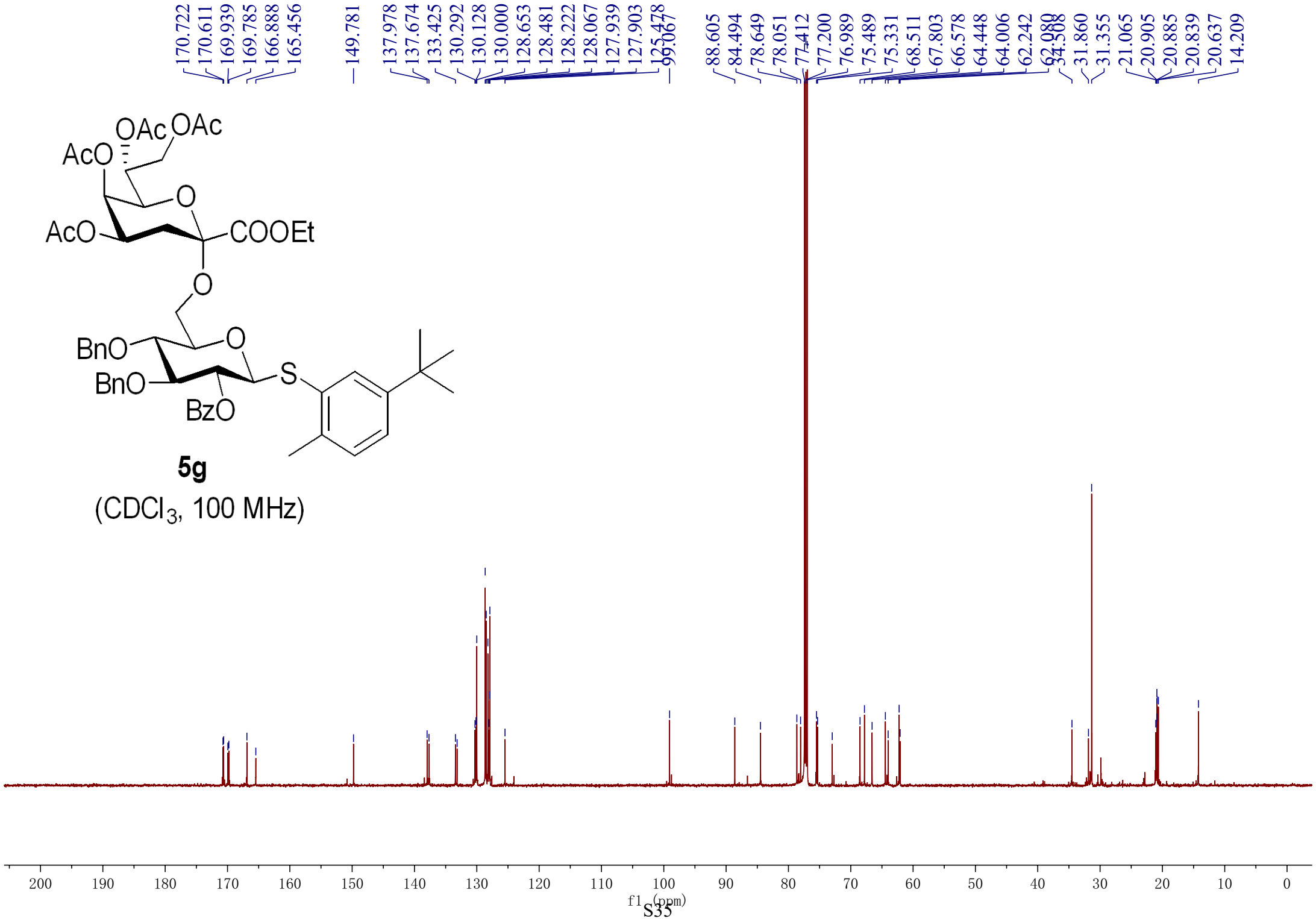
($CDCl_3$, 400 MHz)

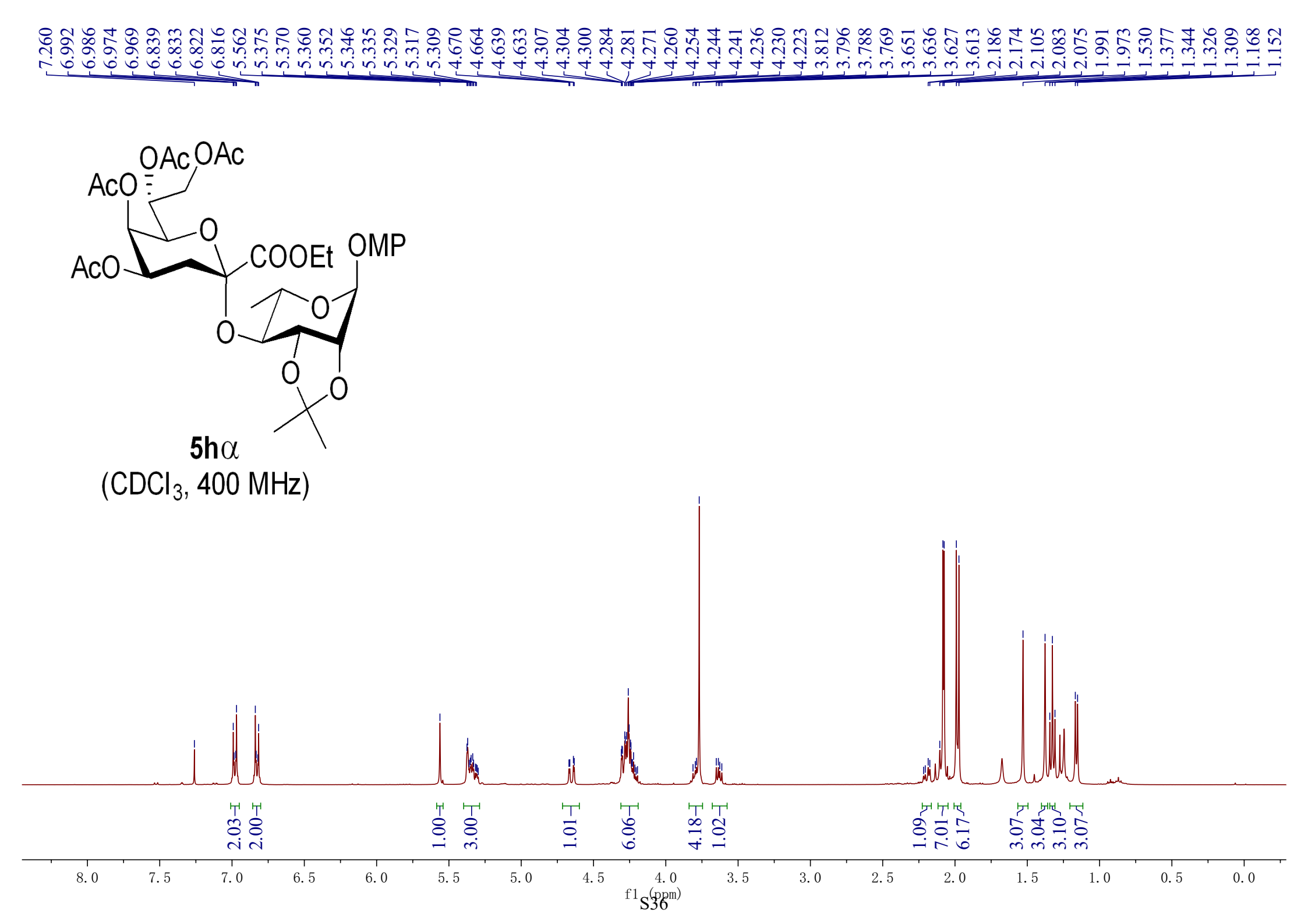

7.369
7.351
7.333
7.324
7.319
7.314
7.295
7.282
7.279
7.266
7.260
7.241
5.308
5.002
4.975
4.933
4.906
4.818
4.805
4.791
4.775
4.685
4.655
4.576
4.567
4.549
4.544
4.529
4.519
4.513
4.501
4.176
4.158
4.140
4.136
4.133
4.097
4.086
3.991
3.968
3.671
3.649
3.480
3.470
3.456
3.447
3.443
3.419
3.247
3.245
2.070
2.047
1.983
1.962
1.881
1.227
1.209
1.191
OAc
OAc
AcO
O
AcO
COOEt
O
BnO
O
BnO
BnO
OMe
5f
(CDCl3, 400 MHz)
15.00
2.06
1.00
1.04
1.04
2.00
1.08
1.00
2.06
3.10
1.04
1.09
1.01
1.07
2.01
3.02
1.05
1.10
4.03
6.01
3.06
3.19
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)

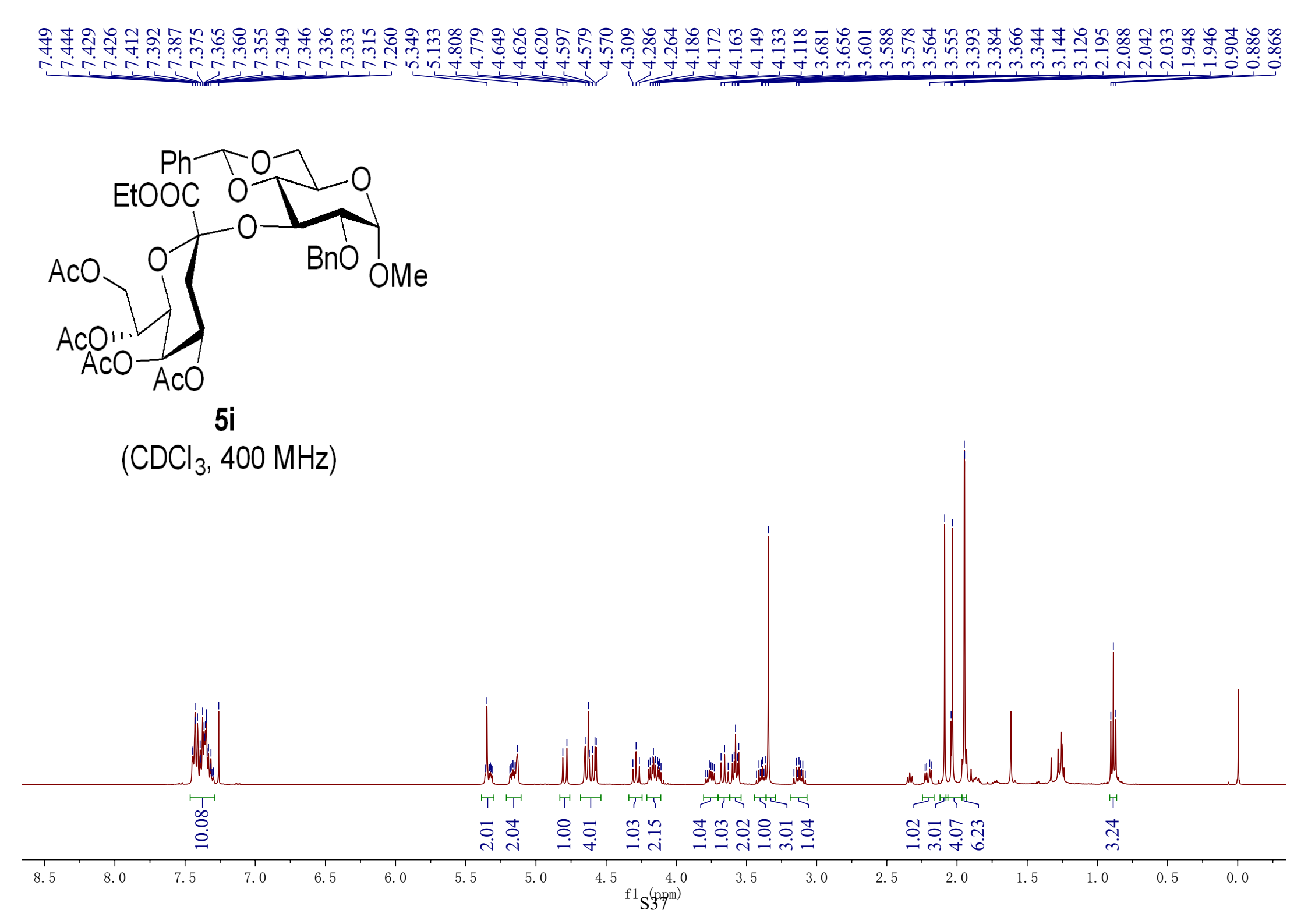


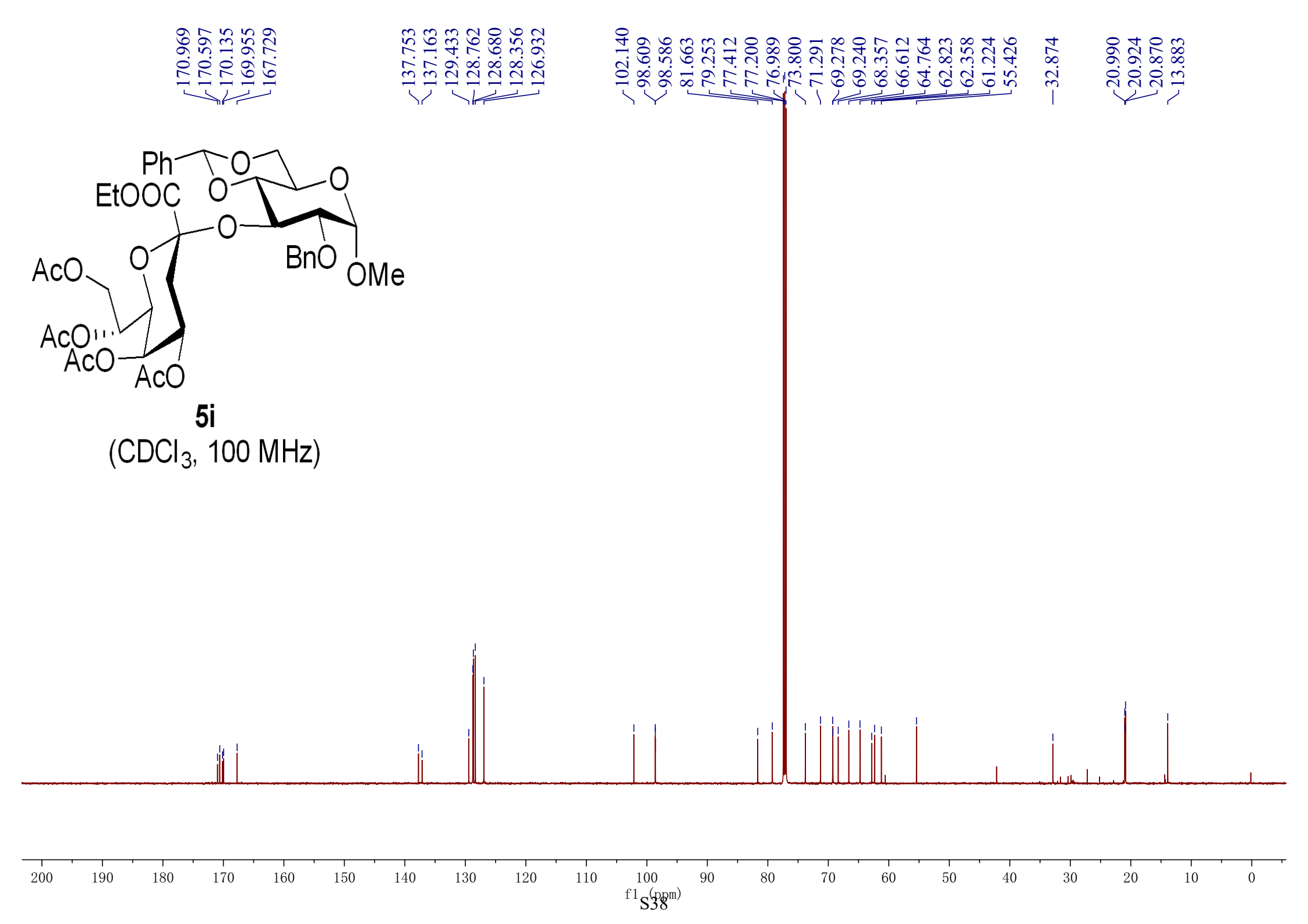
5g

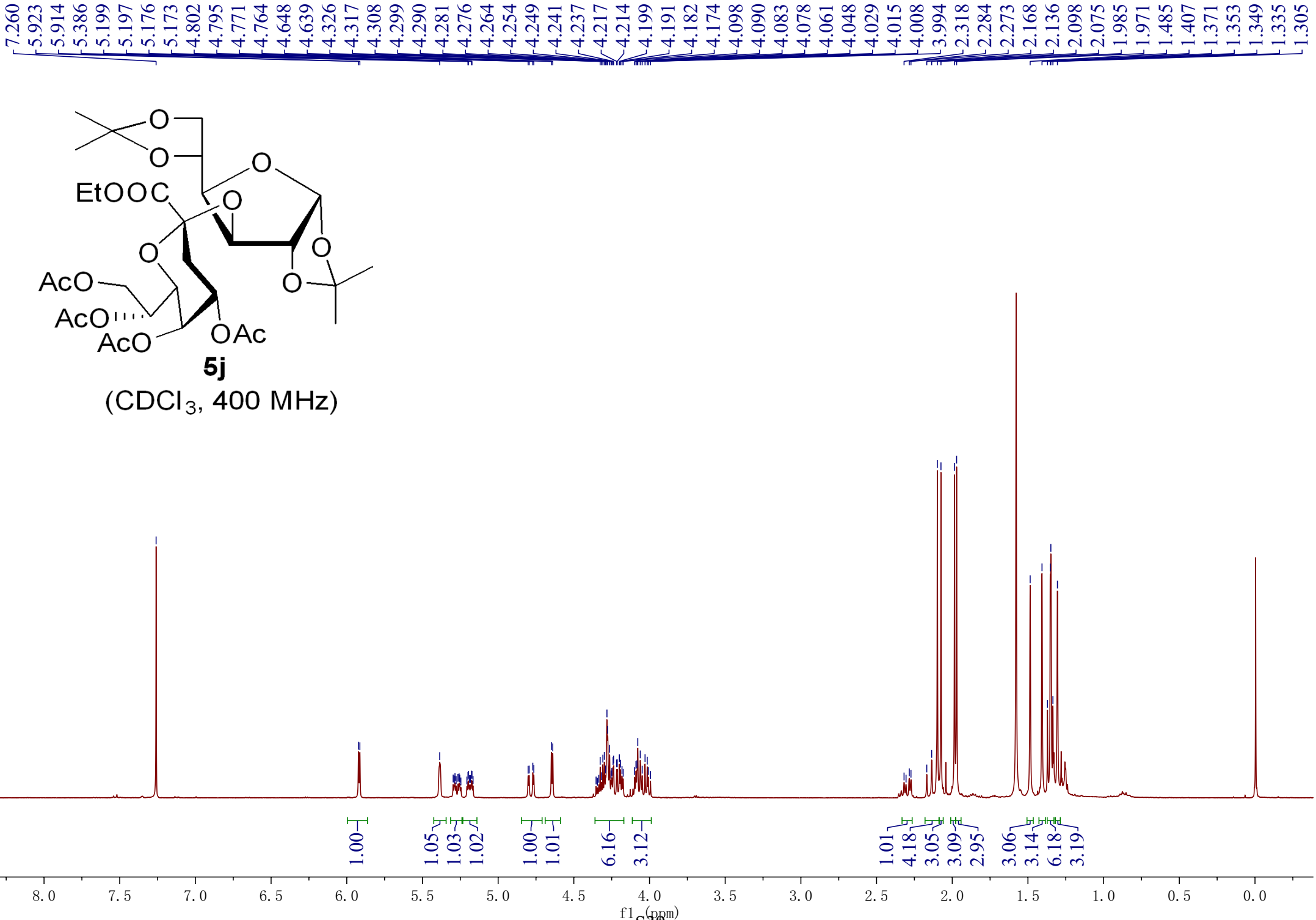
($CDCl_3$, 400 MHz)

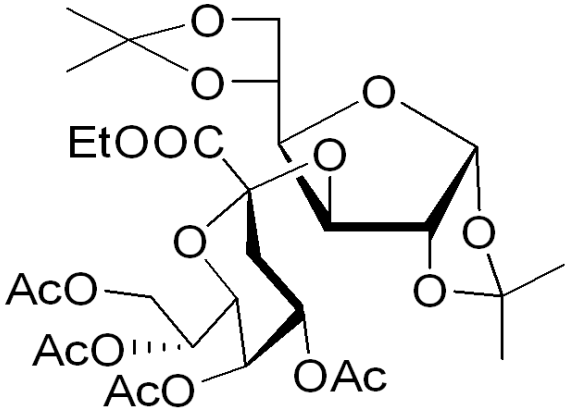

170.722
170.611
169.939
169.785
166.888
165.456
149.781
137.978
137.674
133.425
130.292
130.128
130.000
128.653
128.481
128.222
128.067
127.939
127.903
125.478
99.067
88.605
84.494
78.649
78.051
77.412
77.200
76.989
75.489
75.331
68.511
67.803
66.578
64.448
64.006
62.242
62.080
34.508
31.860
31.355
21.065
20.905
20.885
20.839
20.637
14.209
OAc
OAc
AcO
O
AcO
COOEt
O
BnO
O
BnO
S
BzO
5g
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
6.992
6.986
6.974
6.969
6.839
6.833
6.822
6.816
5.562
5.375
5.370
5.360
5.352
5.346
5.335
5.329
5.317
5.309
4.670
4.664
4.639
4.633
4.307
4.304
4.300
4.284
4.281
4.271
4.260
4.254
4.244
4.241
4.236
4.230
4.223
3.812
3.796
3.788
3.769
3.651
3.636
3.627
3.613
2.186
2.174
2.105
2.083
2.075
1.991
1.973
1.530
1.377
1.344
1.326
1.309
1.168
1.152
OAc
OAc
AcO
O
COOEt
OMP
AcO
O
O
O
O
5hα
(CDCl3, 400 MHz)
2.03
2.00
1.00
3.00
1.01
6.06
4.18
1.02
1.09
7.01
6.17
3.07
3.04
3.10
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
f1 (ppm)


7.449
7.444
7.429
7.426
7.412
7.392
7.387
7.375
7.365
7.360
7.355
7.349
7.346
7.336
7.333
7.315
7.260
5.349
5.133
4.808
4.779
4.649
4.626
4.620
4.597
4.579
4.570
4.309
4.286
4.264
4.186
4.172
4.163
4.149
4.133
4.118
3.681
3.656
3.601
3.588
3.578
3.564
3.555
3.393
3.384
3.366
3.344
3.144
3.126
2.195
2.088
2.042
2.033
1.948
1.946
0.904
0.886
0.868
Ph
O
EtOOC
O
O
O
O
BnO
OMe
AcO
AcO
AcO
AcO
5i
(CDCl3, 400 MHz)
10.08
2.01
2.04
1.00
4.01
1.03
2.15
1.04
1.03
2.02
1.00
3.01
1.04
1.02
3.01
4.07
6.23
3.24
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)

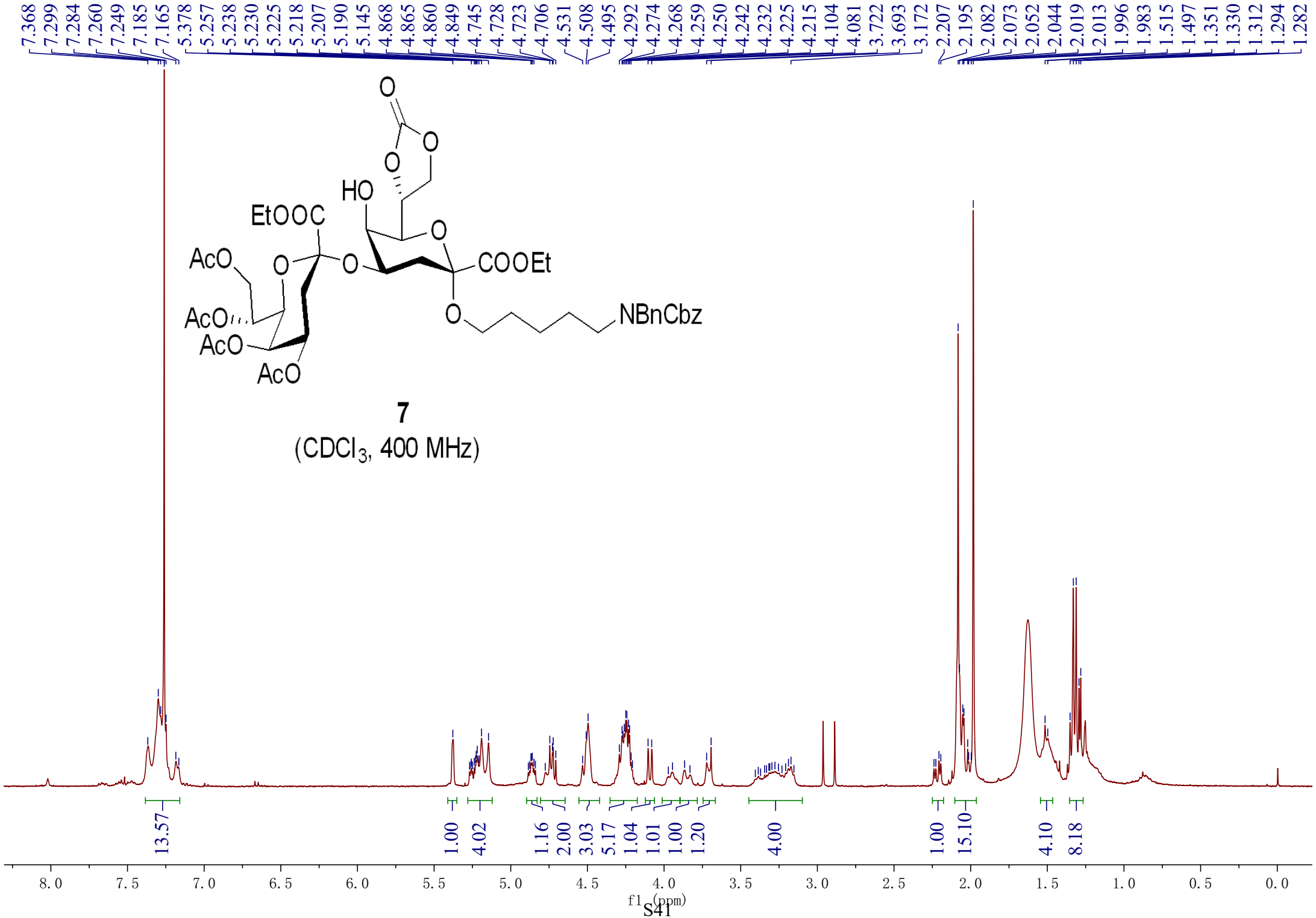

170.969
170.597
170.135
169.955
167.729
137.753
137.163
129.433
128.762
128.680
128.356
126.932
102.140
98.609
98.586
81.663
79.253
77.412
77.200
76.989
73.800
71.291
69.278
69.240
68.357
66.612
64.764
62.823
62.358
61.224
55.426
32.874
20.990
20.924
20.870
13.883
Ph
EtOOC
AcO
AcO
AcO
AcO
BnO
OMe
5i
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

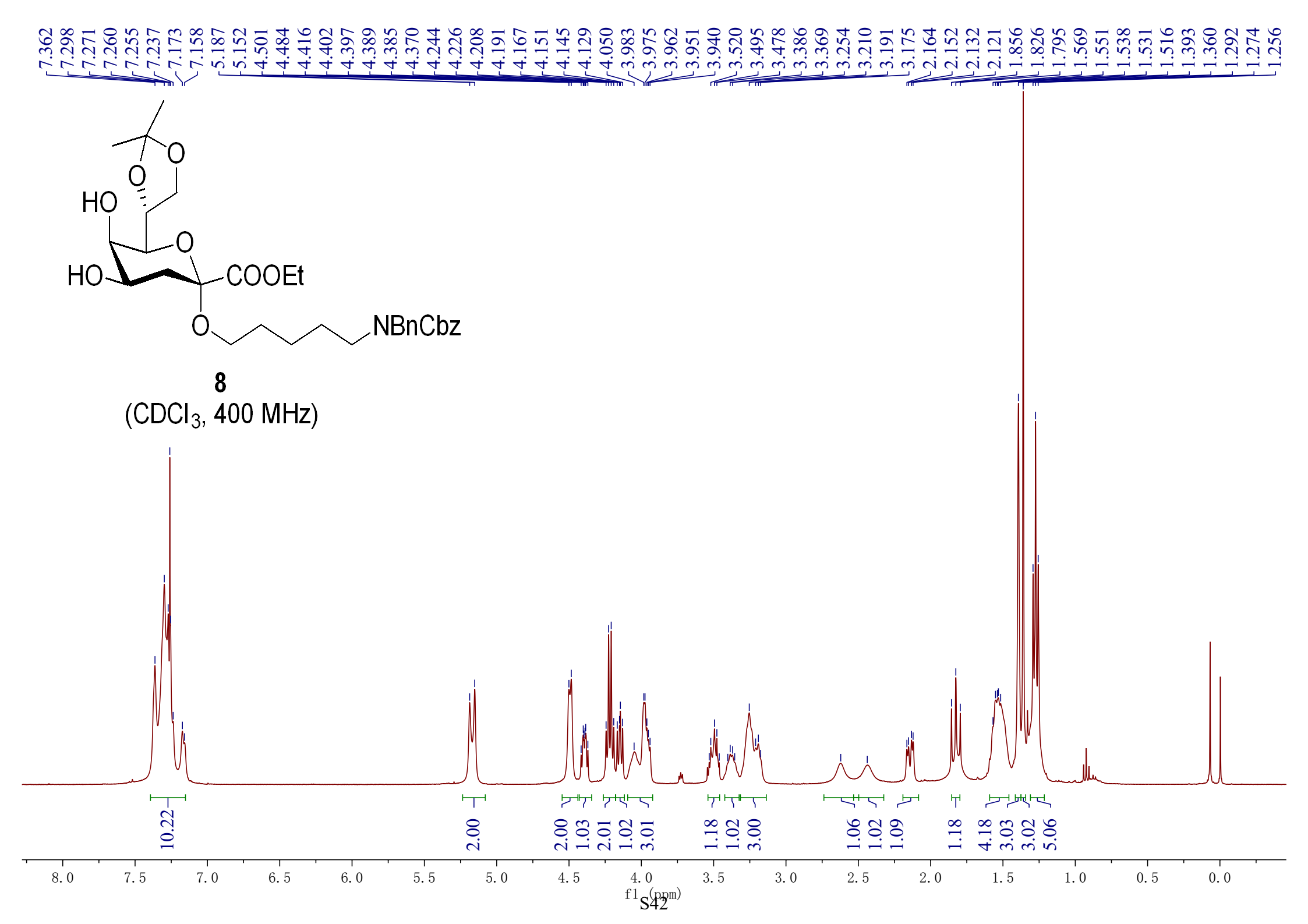

7.260
5.923
5.914
5.386
5.199
5.197
5.176
5.173
4.802
4.795
4.771
4.764
4.648
4.639
4.326
4.317
4.308
4.299
4.290
4.281
4.276
4.264
4.254
4.249
4.241
4.237
4.217
4.214
4.199
4.191
4.182
4.174
4.098
4.090
4.083
4.078
4.061
4.048
4.029
4.015
4.008
3.994
2.318
2.284
2.273
2.168
2.136
2.098
2.075
1.985
1.971
1.485
1.407
1.371
1.353
1.349
1.335
1.305
EtOOC
AcO
AcO
AcO
OAc
5j
(CDCl3, 400 MHz)
1.00
1.05
1.03
1.02
1.00
1.01
6.16
3.12
1.01
4.18
3.05
3.09
2.95
3.06
3.14
6.18
3.19
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)

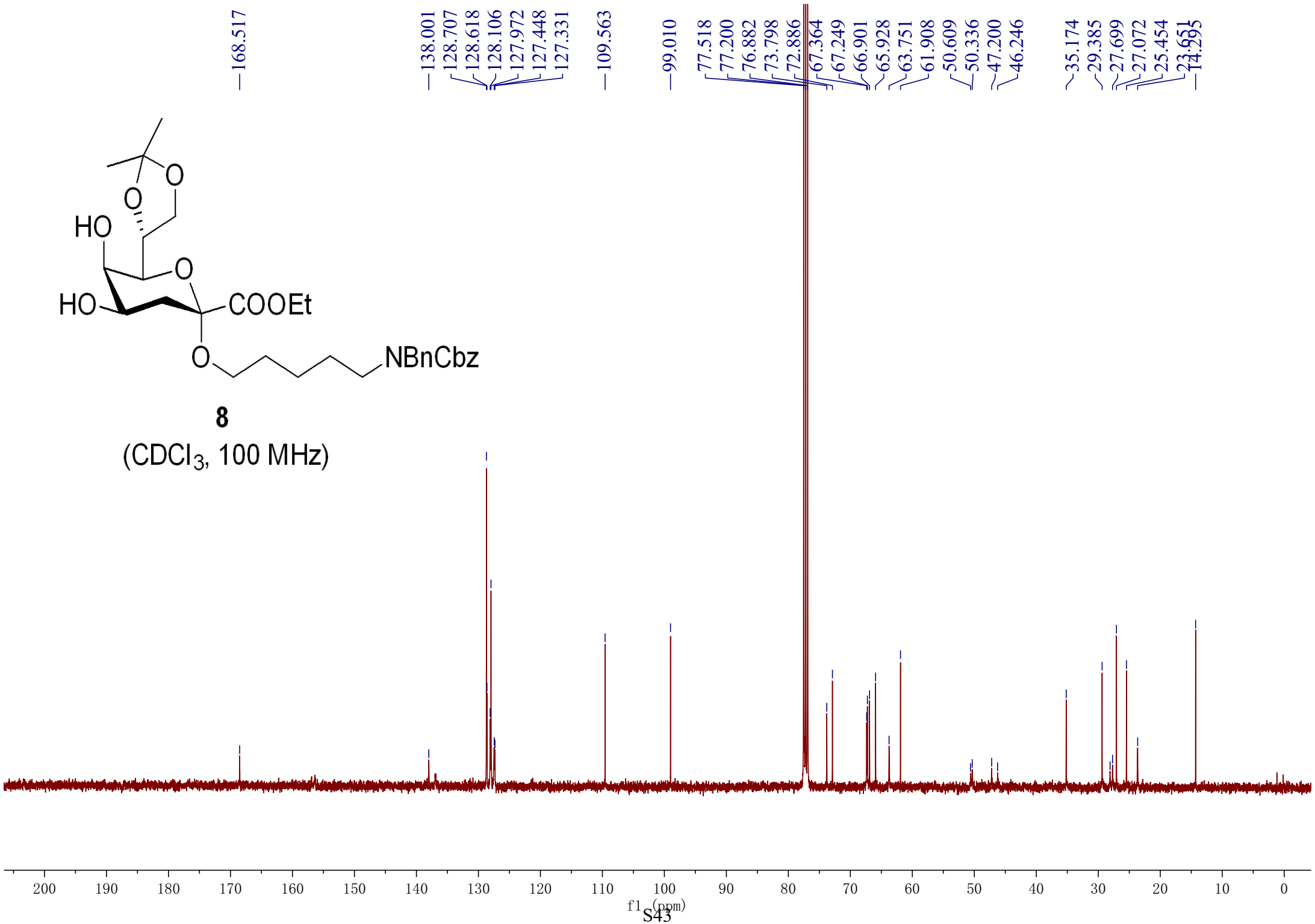


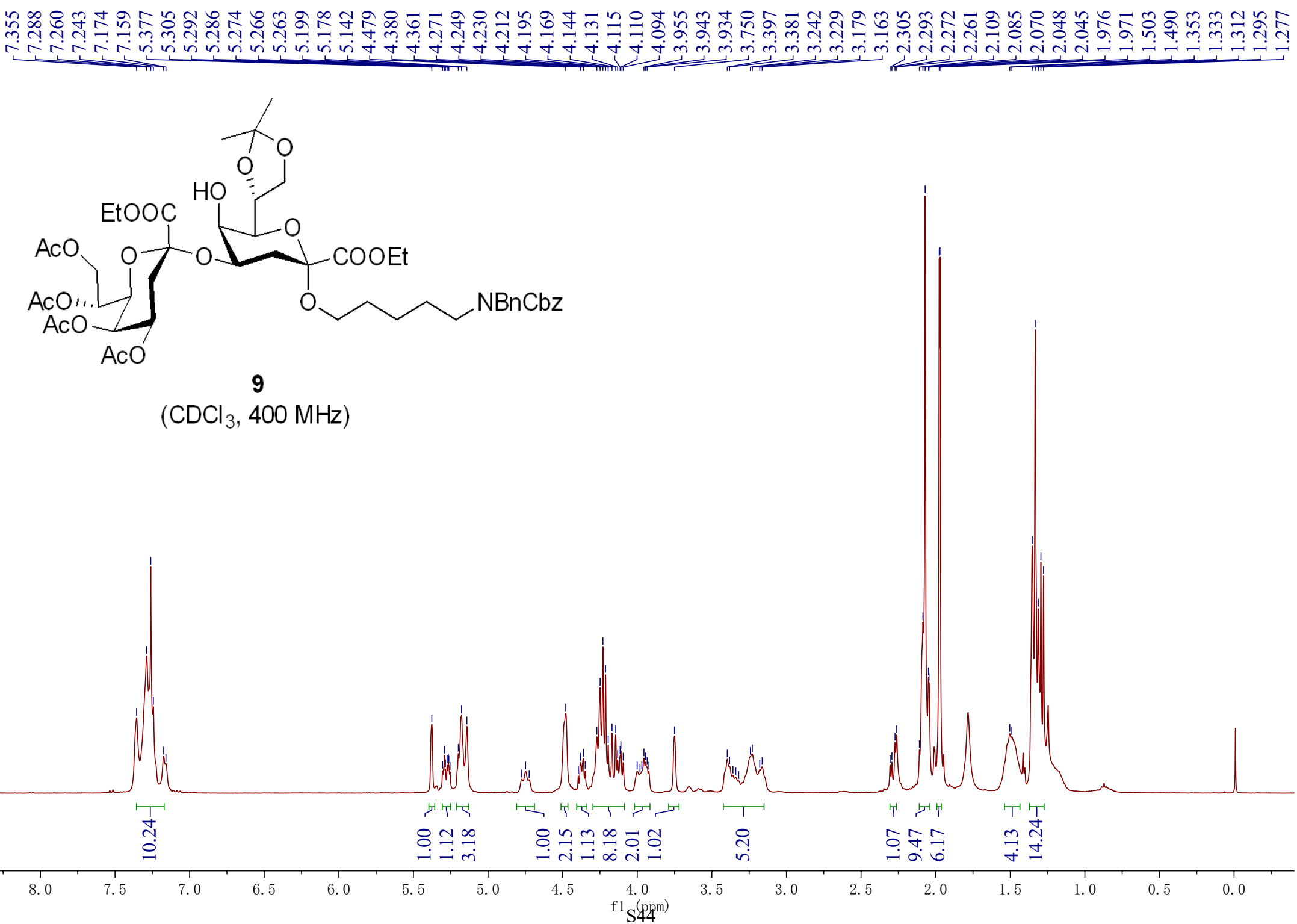
5j

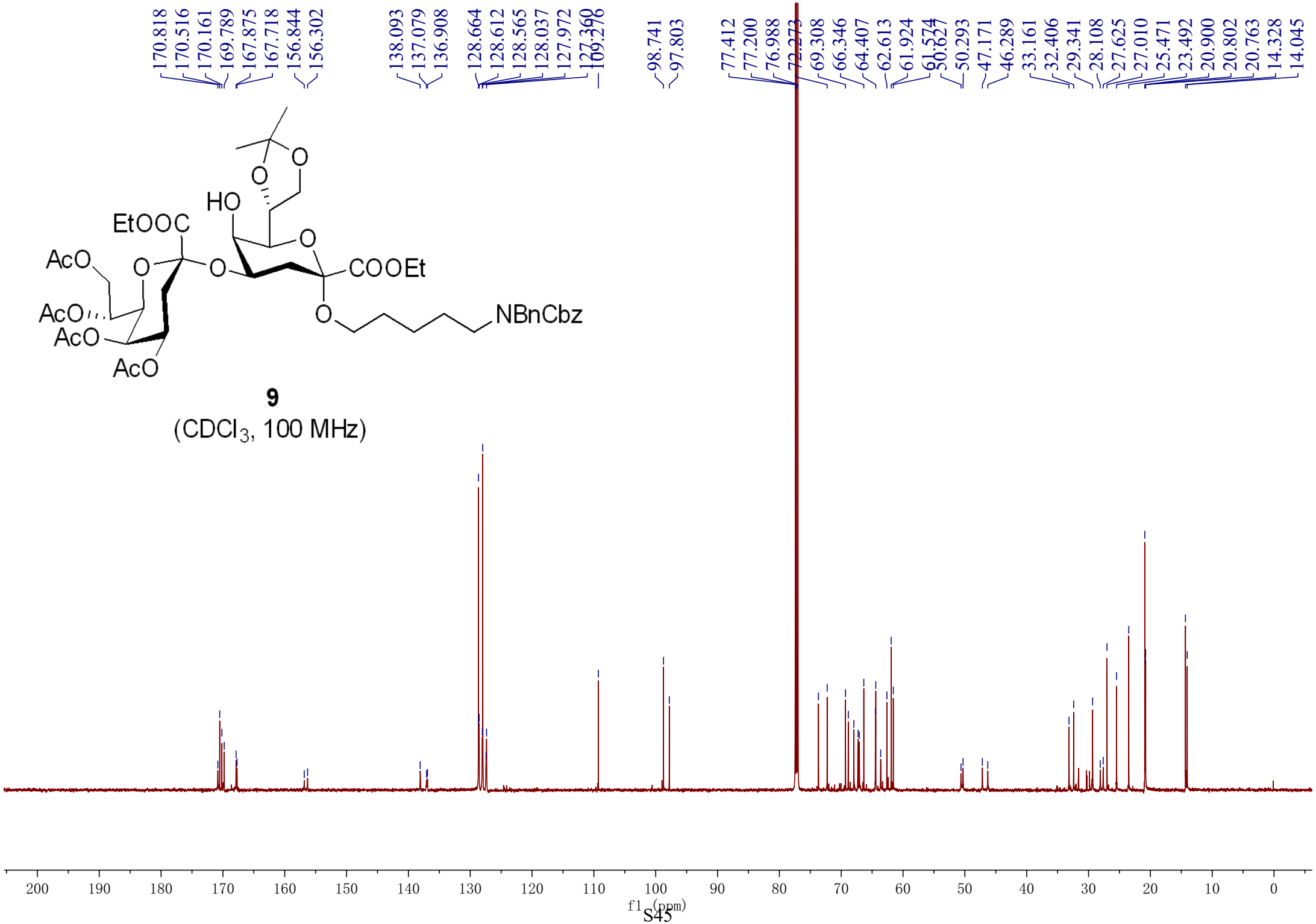
($CDCl_3$, 100 MHz)

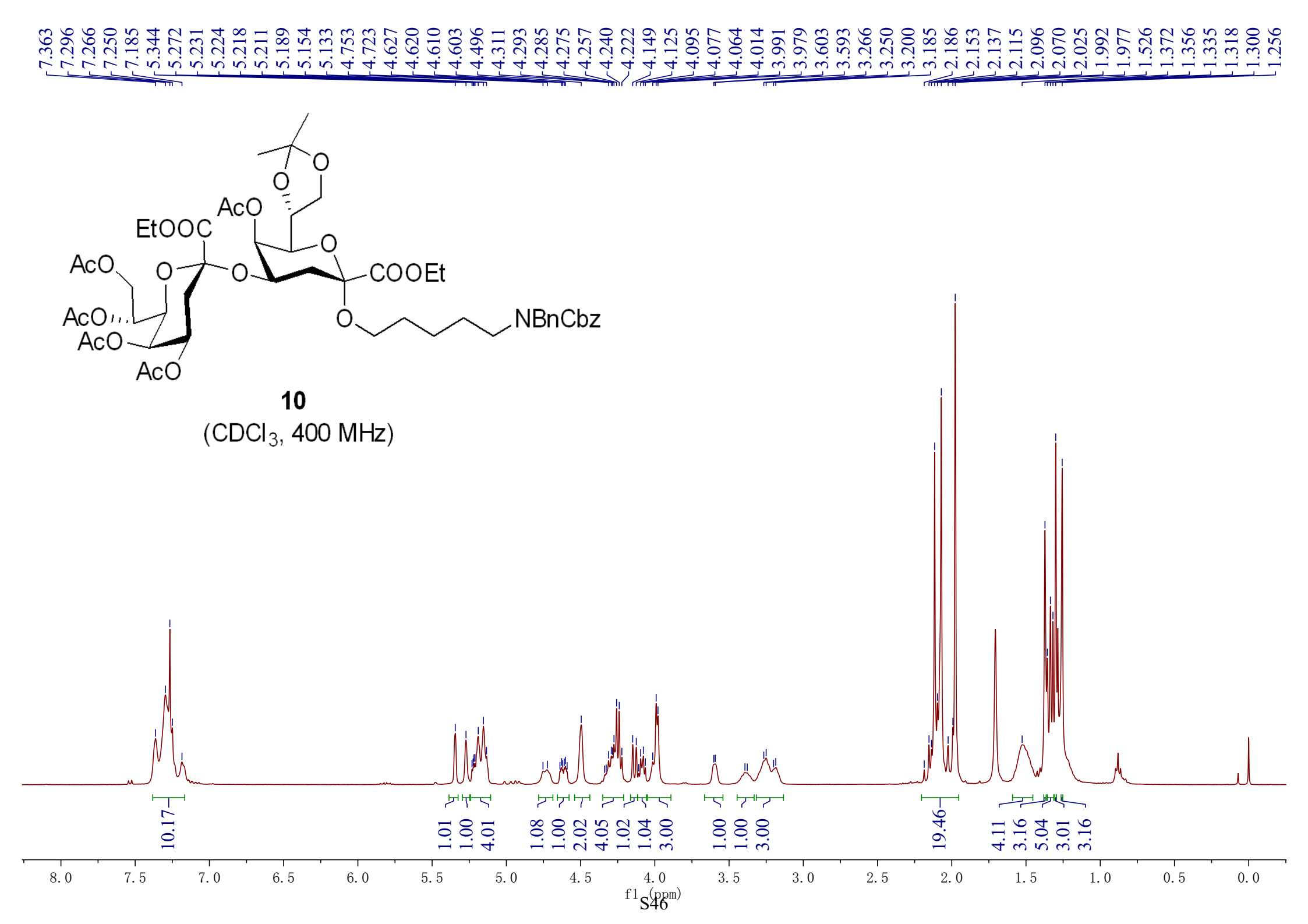

7.368
7.299
7.284
7.260
7.249
7.185
7.165
5.378
5.257
5.238
5.230
5.225
5.218
5.207
5.190
5.145
4.868
4.865
4.860
4.849
4.745
4.728
4.723
4.706
4.531
4.508
4.495
4.292
4.274
4.268
4.259
4.250
4.242
4.232
4.225
4.215
4.104
4.081
3.722
3.693
3.172
2.207
2.195
2.082
2.073
2.052
2.044
2.019
2.013
1.996
1.983
1.515
1.497
1.351
1.330
1.312
1.294
1.282
HO
EtOOC
AcO
AcO
AcO
AcO
COOEt
NBnCbz
7
(CDCl3, 400 MHz)
13.57
1.00
4.02
1.16
2.00
3.03
5.17
1.04
1.01
1.00
1.20
4.00
1.00
15.10
4.10
8.18
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)

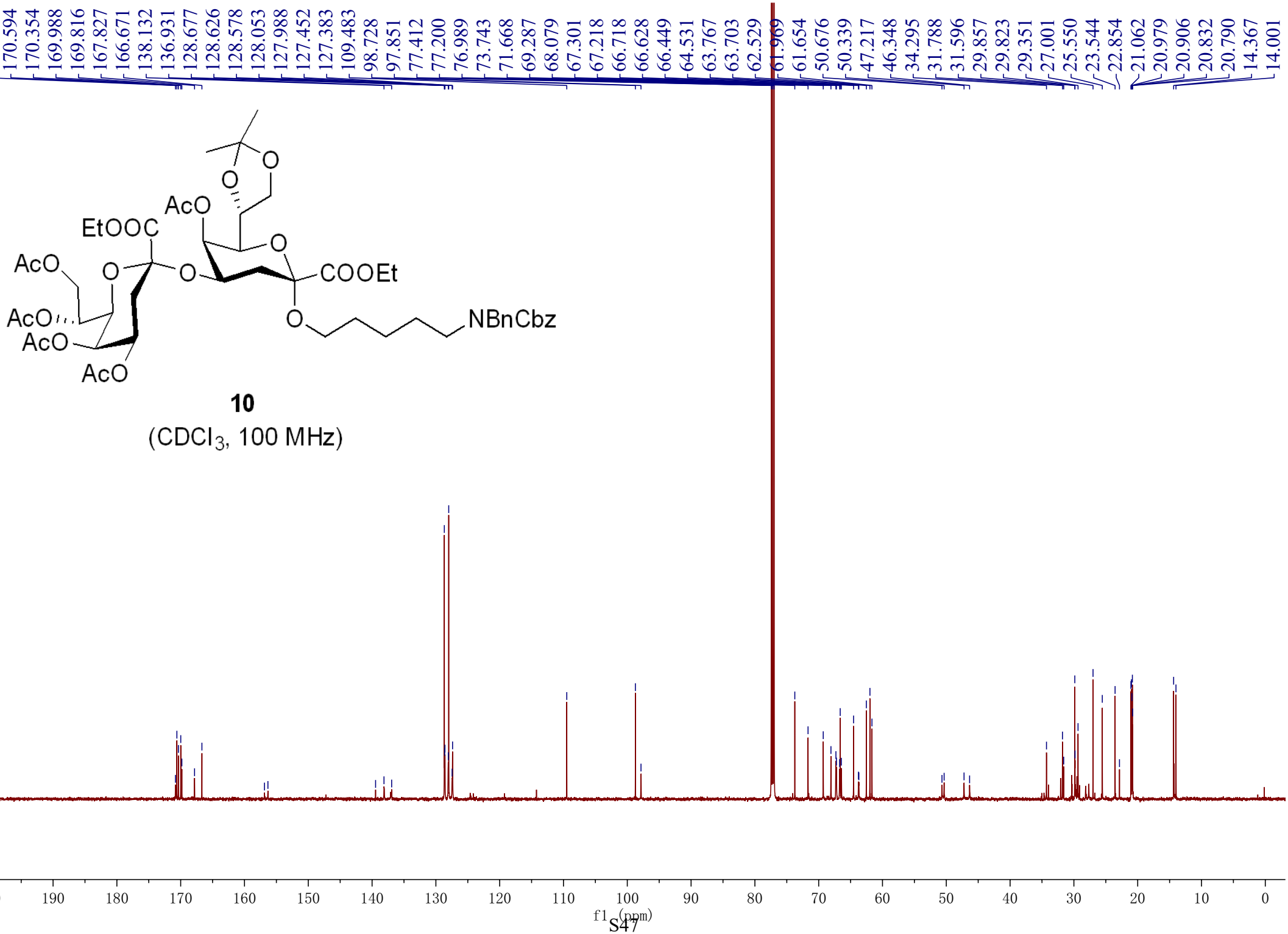

HO
O
O
HO
O
COOEt
O
NBnCbz
8
(CDCl3, 400 MHz)
f1 (ppm)


168.517
138.001
128.707
128.618
128.106
127.972
127.448
127.331
109.563
99.010
77.518
77.200
76.882
73.798
72.886
67.364
67.249
66.901
65.928
63.751
61.908
50.609
50.336
47.200
46.246
35.174
29.385
27.699
27.072
25.454
23.651
14.295
HO
HO
O
O
O
O
COOEt
NBnCbz
8
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.355
7.288
7.260
7.243
7.174
7.159
5.377
5.305
5.292
5.286
5.274
5.266
5.263
5.199
5.178
5.142
4.479
4.380
4.361
4.271
4.249
4.230
4.212
4.195
4.169
4.144
4.131
4.115
4.110
4.094
3.955
3.943
3.934
3.750
3.397
3.381
3.242
3.229
3.179
3.163
2.305
2.293
2.272
2.261
2.109
2.085
2.070
2.048
2.045
1.976
1.971
1.503
1.490
1.353
1.333
1.312
1.295
1.277
HO
EtOOC
AcO
AcO
AcO
AcO
COOEt
NBnCbz
9
(CDCl3, 400 MHz)
10.24
1.00
1.12
3.18
1.00
2.15
1.13
8.18
2.01
1.02
5.20
1.07
9.47
6.17
4.13
14.24
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)

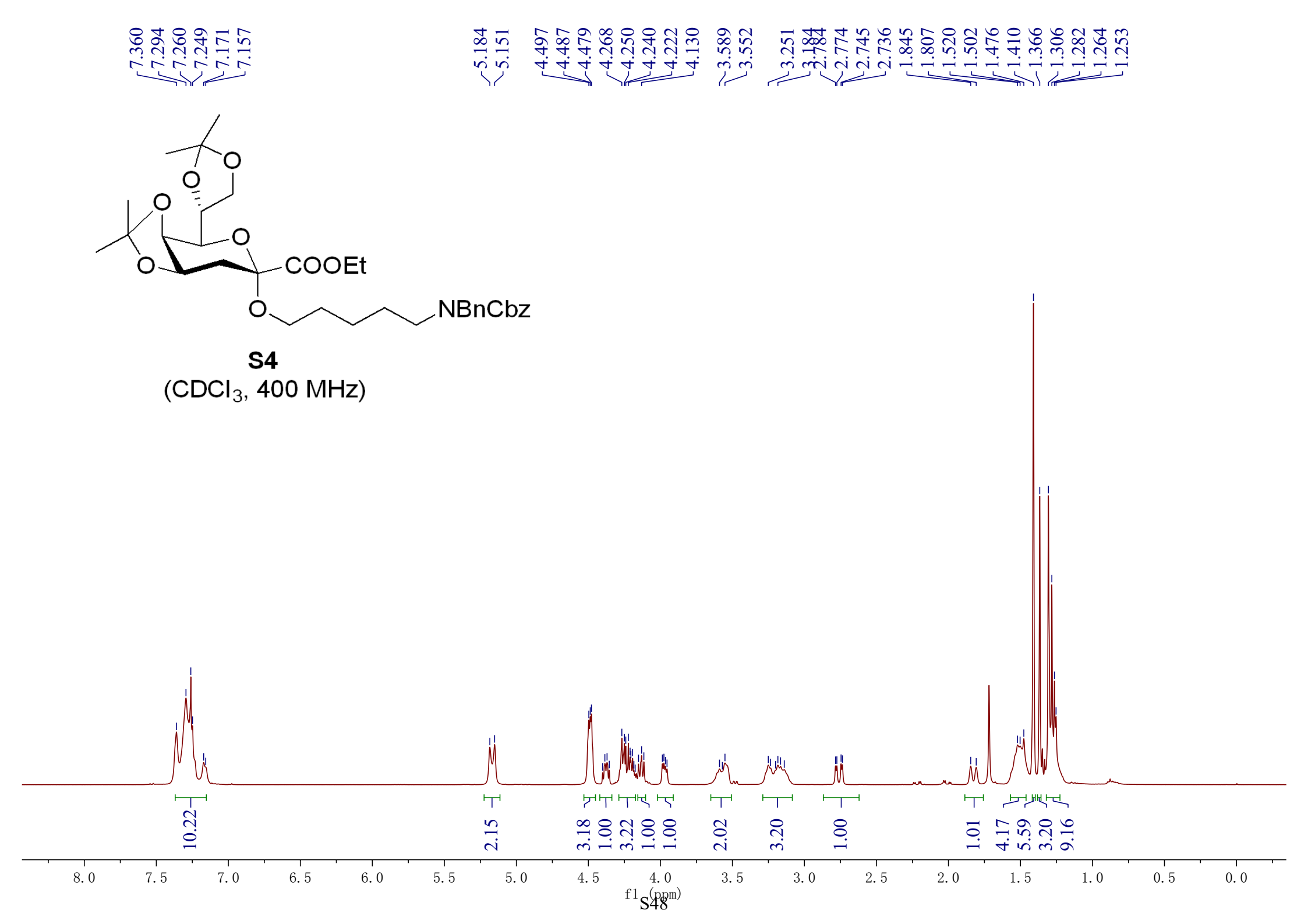

170.818
170.516
170.161
169.789
167.875
167.718
156.844
156.302
138.093
137.079
136.908
128.664
128.612
128.565
128.037
127.972
127.360
109.276
98.741
97.803
77.412
77.200
76.988
72.273
69.308
66.346
64.407
62.613
61.924
61.574
50.627
50.293
47.171
46.289
33.161
32.406
29.341
28.108
27.625
27.010
25.471
23.492
20.900
20.802
20.763
14.328
14.045
HO
EtOOC
AcO
AcO
AcO
AcO
COOEt
NBnCbz
9
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.363
7.296
7.266
7.250
7.185
5.344
5.272
5.231
5.224
5.218
5.211
5.189
5.154
5.133
4.753
4.723
4.627
4.620
4.610
4.603
4.496
4.311
4.293
4.285
4.275
4.257
4.240
4.222
4.149
4.125
4.095
4.077
4.064
4.014
3.991
3.979
3.603
3.593
3.266
3.250
3.200
3.185
2.186
2.153
2.137
2.115
2.096
2.070
2.025
1.992
1.977
1.526
1.372
1.356
1.335
1.318
1.300
1.256
AcO
EtOOC
AcO
O
O
O
COOEt
AcO
O
AcO
AcO
O
NBnCbz
AcO
10
(CDCl3, 400 MHz)
10.17
1.01
1.00
4.01
1.08
1.00
2.02
4.05
1.02
1.04
3.00
1.00
1.00
3.00
19.46
4.11
3.16
5.04
3.01
3.16
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)



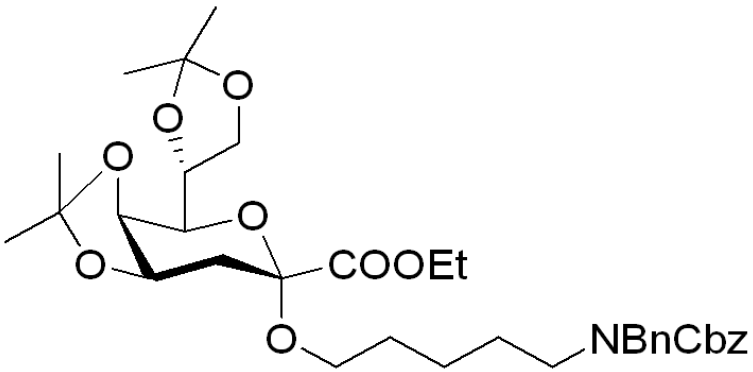
10

($CDCl_3$, 100 MHz)



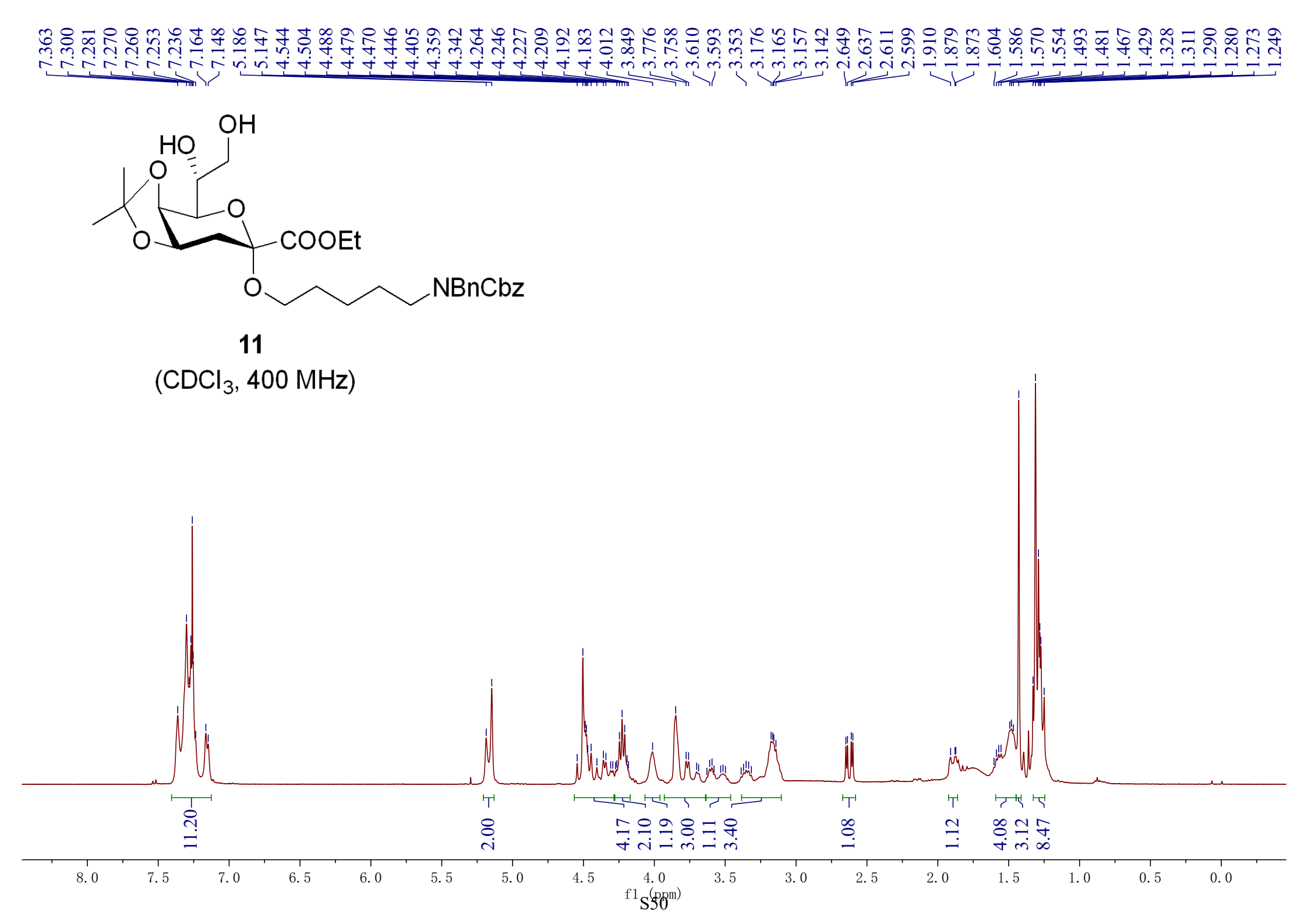
S4

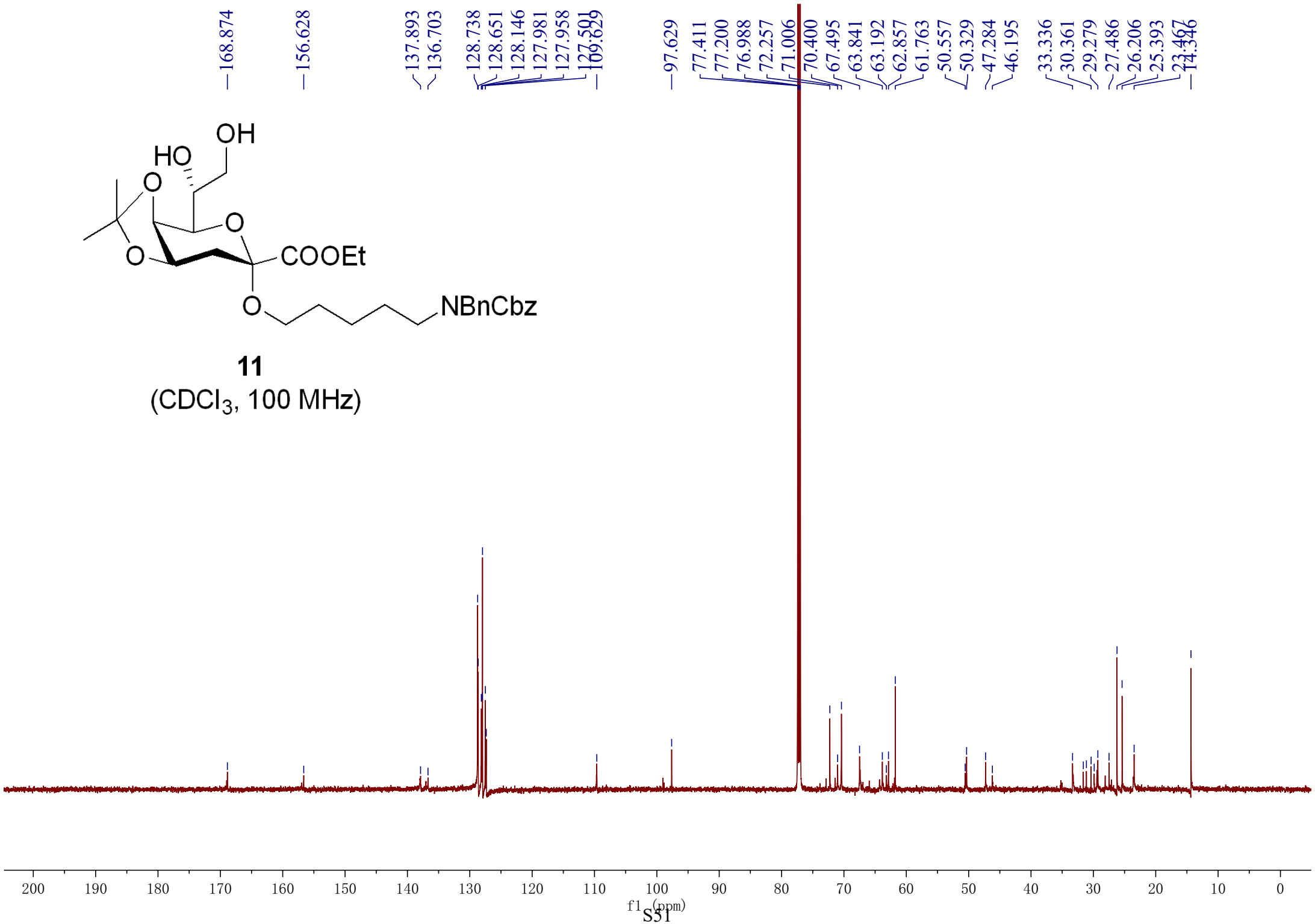
($CDCl_3$, 400 MHz)

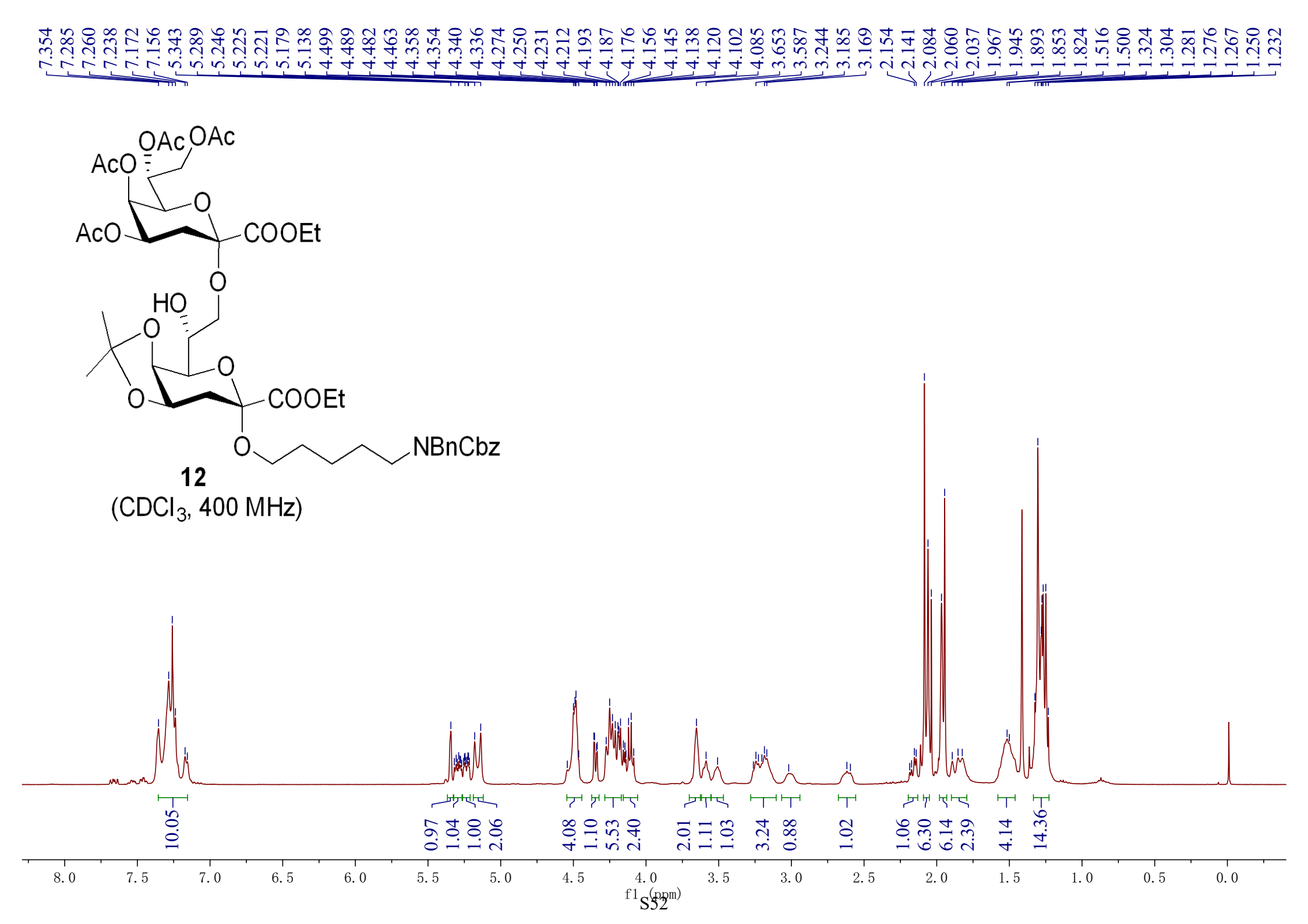


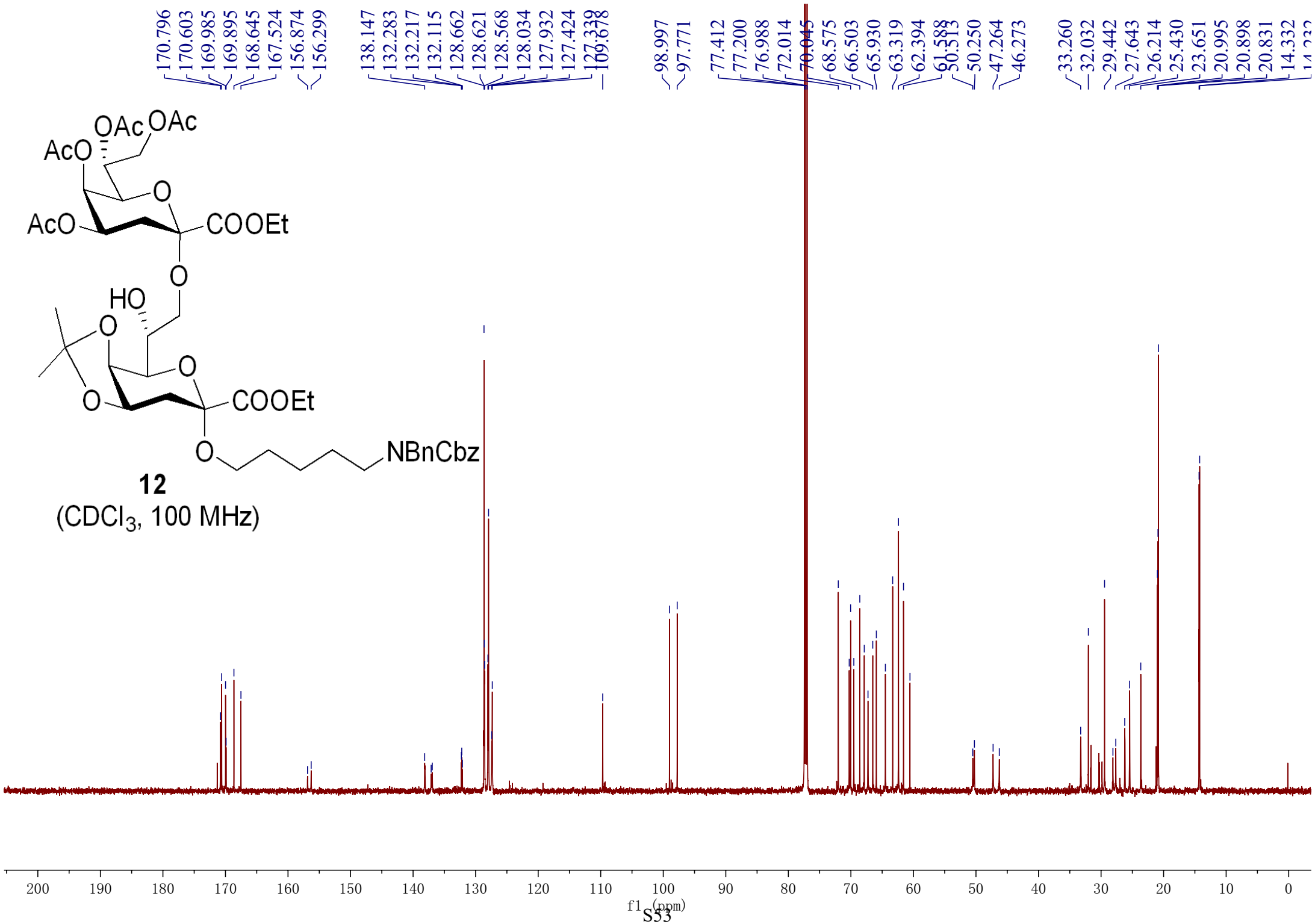
S4

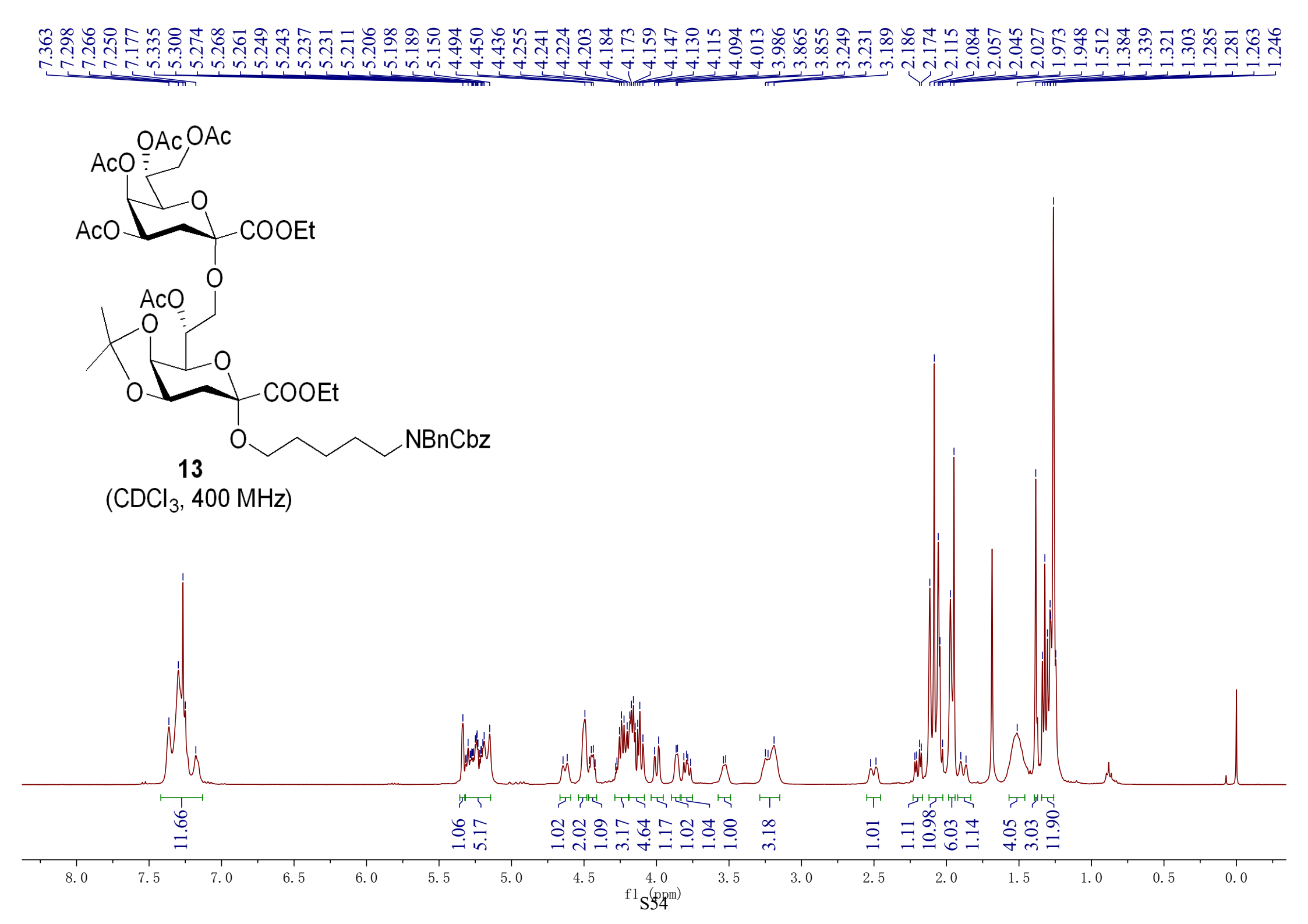
($CDCl_3$, 100 MHz)

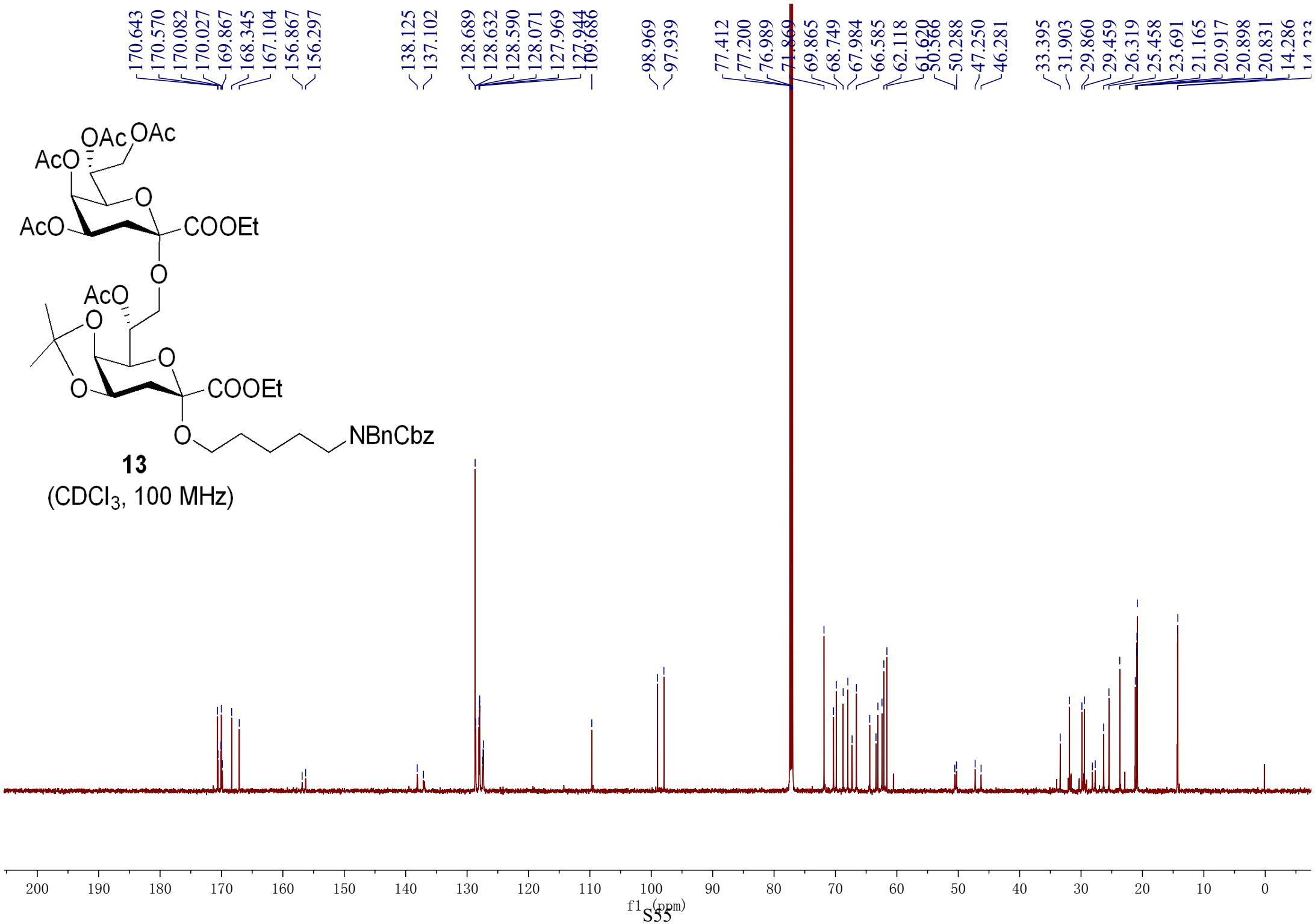

7.363
7.300
7.281
7.270
7.260
7.253
7.236
7.164
7.148
5.186
5.147
4.544
4.504
4.488
4.479
4.470
4.446
4.405
4.359
4.342
4.264
4.246
4.227
4.209
4.192
4.183
4.012
3.849
3.776
3.758
3.610
3.593
3.353
3.176
3.165
3.157
3.142
2.649
2.637
2.611
2.599
1.910
1.879
1.873
1.604
1.586
1.570
1.554
1.493
1.481
1.467
1.429
1.328
1.311
1.290
1.280
1.273
1.249
OH
HO
O
O
O
COOEt
O
NBnCbz
11
(CDCl3, 400 MHz)
11.20
2.00
4.17
2.10
1.19
3.00
1.11
3.40
1.08
1.12
4.08
3.12
8.47
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)

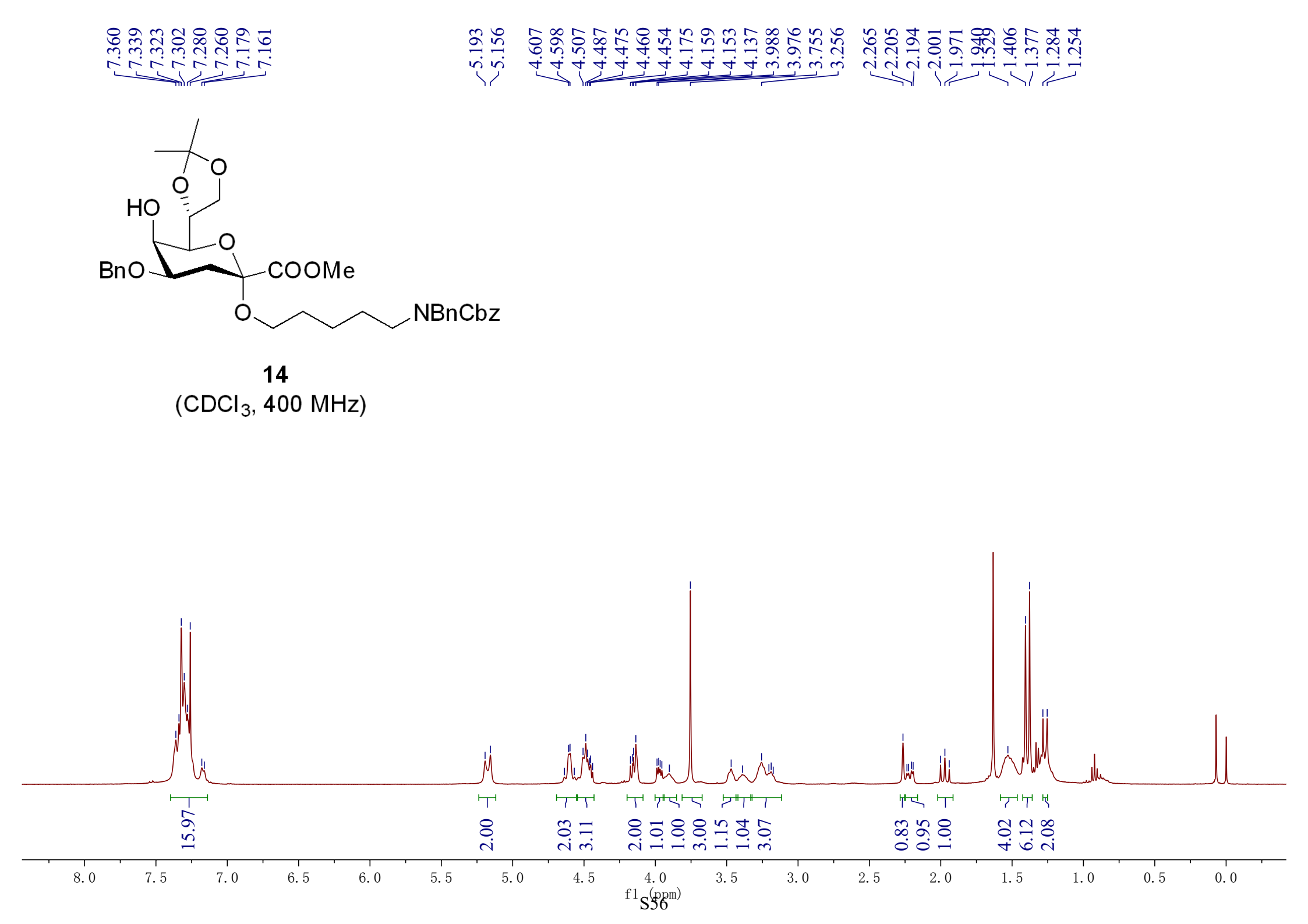

168.874
156.628
137.893
136.703
128.738
128.651
128.146
127.981
127.958
127.501
109.629
97.629
77.411
77.200
76.988
72.257
71.006
70.400
67.495
63.841
63.192
62.857
61.763
50.557
50.329
47.284
46.195
33.336
30.361
29.279
27.486
26.206
25.393
23.467
14.346
OH
HO
O
O
O
O
COOEt
O
NBnCbz
11
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

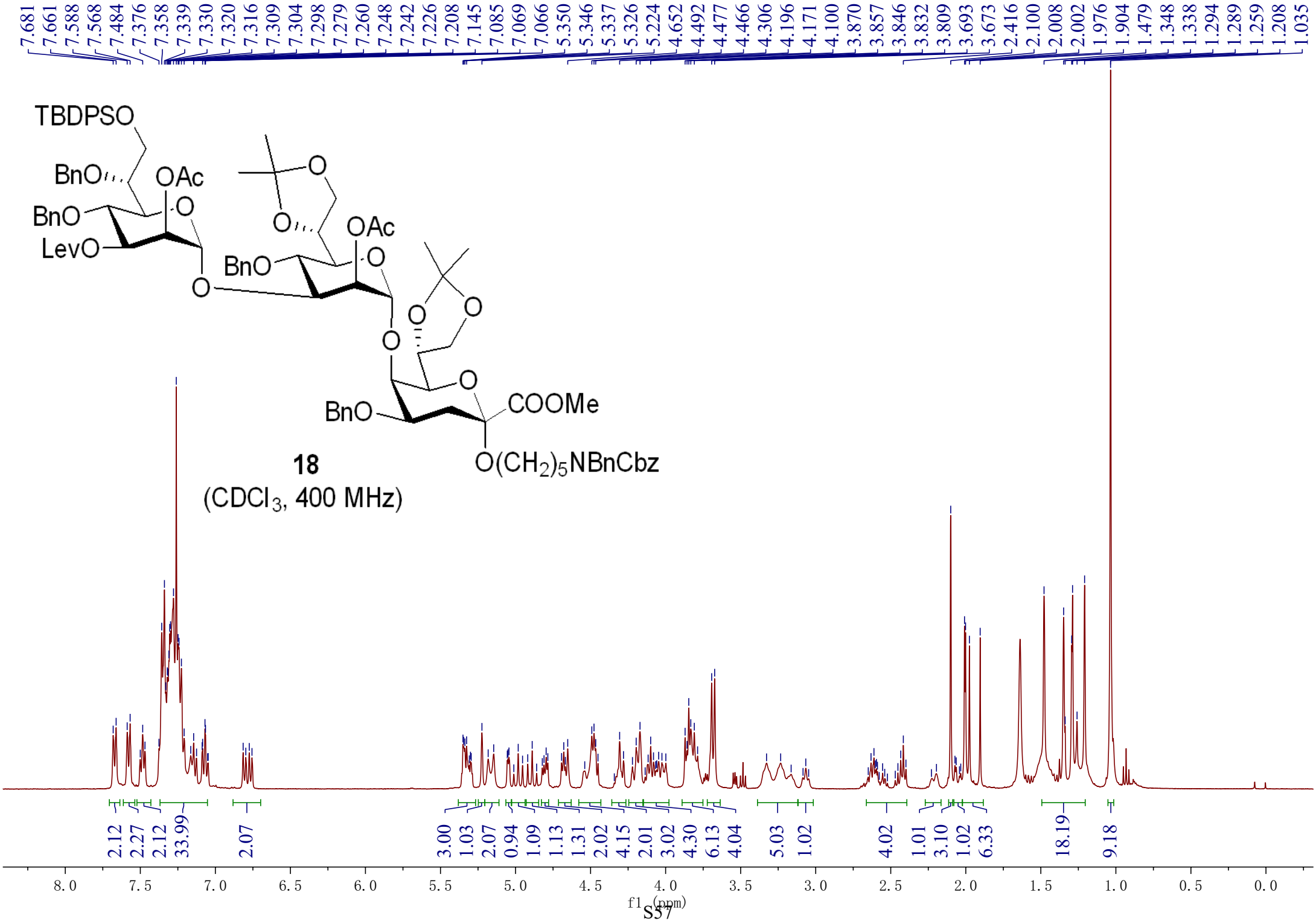

7.354 7.285 7.260 7.238 7.172 7.156 5.343 5.289 5.246 5.225 5.221 5.179 5.138 4.499 4.489 4.482 4.463 4.358 4.354 4.340 4.336 4.274 4.250 4.231 4.212 4.193 4.187 4.176 4.156 4.145 4.138 4.120 4.102 4.085 3.653 3.587 3.244 3.185 3.169 2.154 2.141 2.084 2.060 2.037 1.967 1.945 1.893 1.853 1.824 1.516 1.500 1.324 1.304 1.281 1.276 1.267 1.250 1.232
OAc
OAc
AcO
O
AcO
COOEt
O
HO
O
O
O
COOEt
O
NBnCbz
12
(CDCl3, 400 MHz)
10.05
0.97
1.04
1.00
2.06
4.08
1.10
5.53
2.40
2.01
1.11
1.03
3.24
0.88
1.02
1.06
6.30
6.14
2.39
4.14
14.36
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)

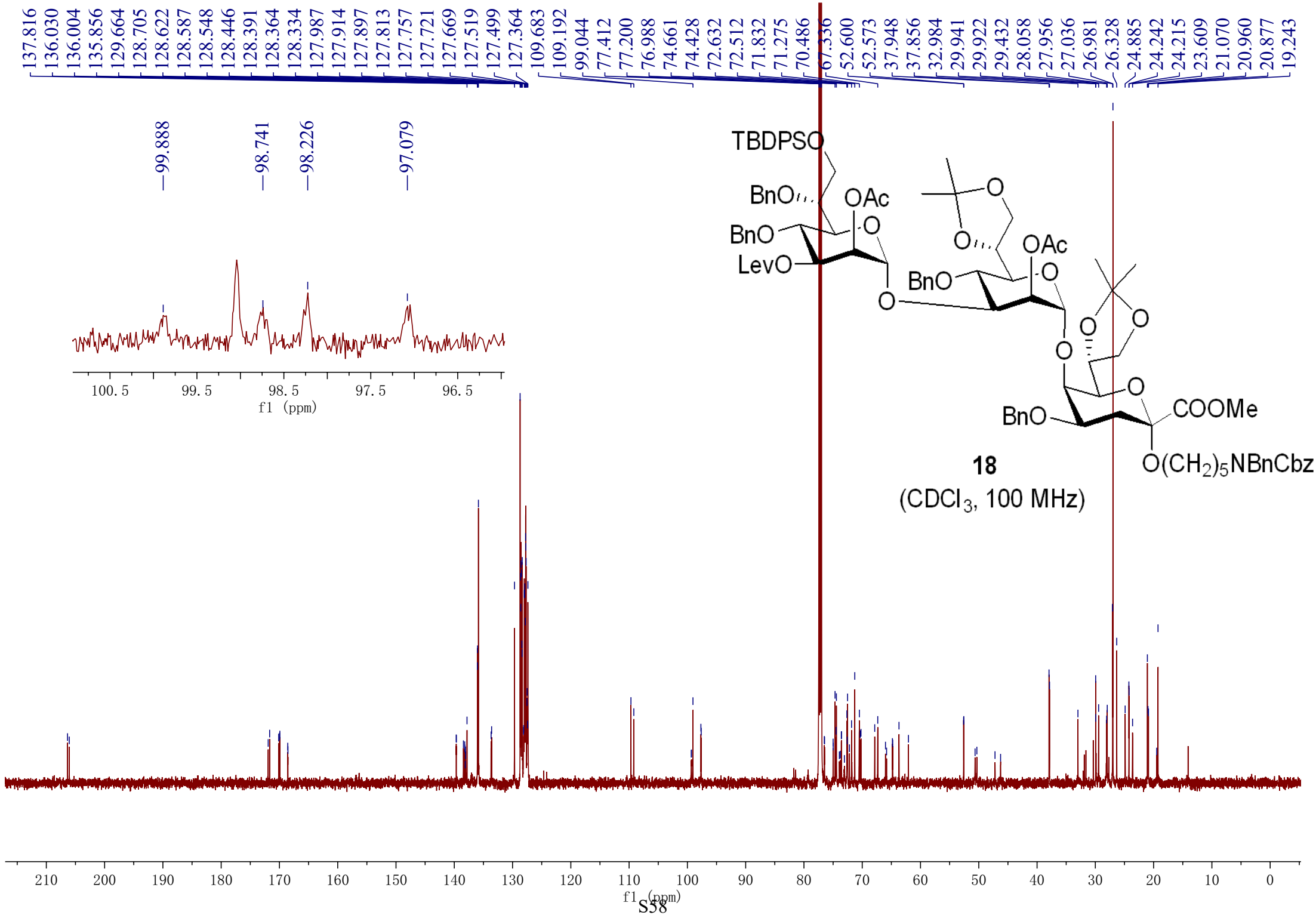

170.796
170.603
169.985
169.895
168.645
167.524
156.874
156.299
138.147
132.283
132.217
132.115
128.662
128.621
128.568
128.034
127.932
127.424
127.339
109.678
98.997
97.771
77.412
77.200
76.988
72.014
70.045
68.575
66.503
65.930
63.319
62.394
61.588
50.513
50.250
47.264
46.273
33.260
32.032
29.442
27.643
26.214
25.430
23.651
20.995
20.898
20.831
14.332
OAc
OAc
AcO
O
AcO
COOEt
O
HO
O
O
O
COOEt
O
NBnCbz
12
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.363 7.298 7.266 7.250 7.177 5.335 5.300 5.274 5.268 5.261 5.249 5.243 5.237 5.231 5.211 5.206 5.198 5.189 5.150 4.494 4.450 4.436 4.255 4.241 4.224 4.203 4.184 4.173 4.159 4.147 4.130 4.115 4.094 4.013 3.986 3.865 3.855 3.249 3.231 3.189 2.186 2.174 2.115 2.084 2.057 2.045 2.027 1.973 1.948 1.512 1.384 1.339 1.321 1.303 1.285 1.281 1.263 1.246
OAc
OAc
AcO
O
AcO
COOEt
O
AcO
O
O
O
COOEt
O
NBnCbz
13
(CDCl3, 400 MHz)
11.66
1.06
5.17
1.02
2.02
1.09
3.17
4.64
1.17
1.02
1.04
1.00
3.18
1.01
1.11
10.98
6.03
1.14
4.05
3.03
11.90
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)


170.643
170.570
170.082
170.027
169.867
168.345
167.104
156.867
156.297
138.125
137.102
128.689
128.632
128.590
128.071
127.969
127.944
109.686
98.969
97.939
77.412
77.200
76.989
71.869
69.865
68.749
67.984
66.585
62.118
61.620
50.566
50.288
47.250
46.281
33.395
31.903
29.860
29.459
26.319
25.458
23.691
21.165
20.917
20.898
20.831
14.286
OAc
OAc
AcO
O
AcO
COOEt
O
AcO
O
O
O
COOEt
O
NBnCbz
13
(CDCl3, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.360
7.339
7.323
7.302
7.280
7.260
7.179
7.161
5.193
5.156
4.607
4.598
4.507
4.487
4.475
4.460
4.454
4.175
4.159
4.153
4.137
3.988
3.976
3.755
3.256
2.265
2.205
2.194
2.001
1.971
1.940
1.529
1.406
1.377
1.284
1.254
HO
O
O
O
BnO
COOMe
O
NBnCbz
14
(CDCl3, 400 MHz)
15.97
2.00
2.03
3.11
2.00
1.01
1.00
3.00
1.15
1.04
3.07
0.83
0.95
1.00
4.02
6.12
2.08
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)


TBDPSO
BnO
OAc
BnO
LevO
O
O
O
OAc
BnO
O
O
O
O
O
BnO
COOMe
O(CH2)5NBnCbz
18
(CDCl3, 400 MHz)
f1 (ppm)


137.816
136.030
136.004
135.856
129.664
128.705
128.622
128.587
128.548
128.446
128.391
128.364
128.334
127.987
127.914
127.897
127.813
127.757
127.721
127.669
127.519
127.499
127.364
109.683
109.192
99.044
77.412
77.200
76.988
74.661
74.428
72.632
72.512
71.832
71.275
70.486
67.336
52.600
52.573
37.948
37.856
32.984
29.941
29.922
29.432
28.058
27.956
27.036
26.981
26.328
24.885
24.242
24.215
23.609
21.070
20.960
20.877
19.243
99.888
98.741
98.226
97.079
100.5
99.5
98.5
97.5
96.5
f1 (ppm)
TBDPSO
BnO
OAc
BnO
LevO
O
O
O
OAc
BnO
O
O
O
O
O
BnO
COOMe
O(CH2)5NBnCbz
18
(CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)