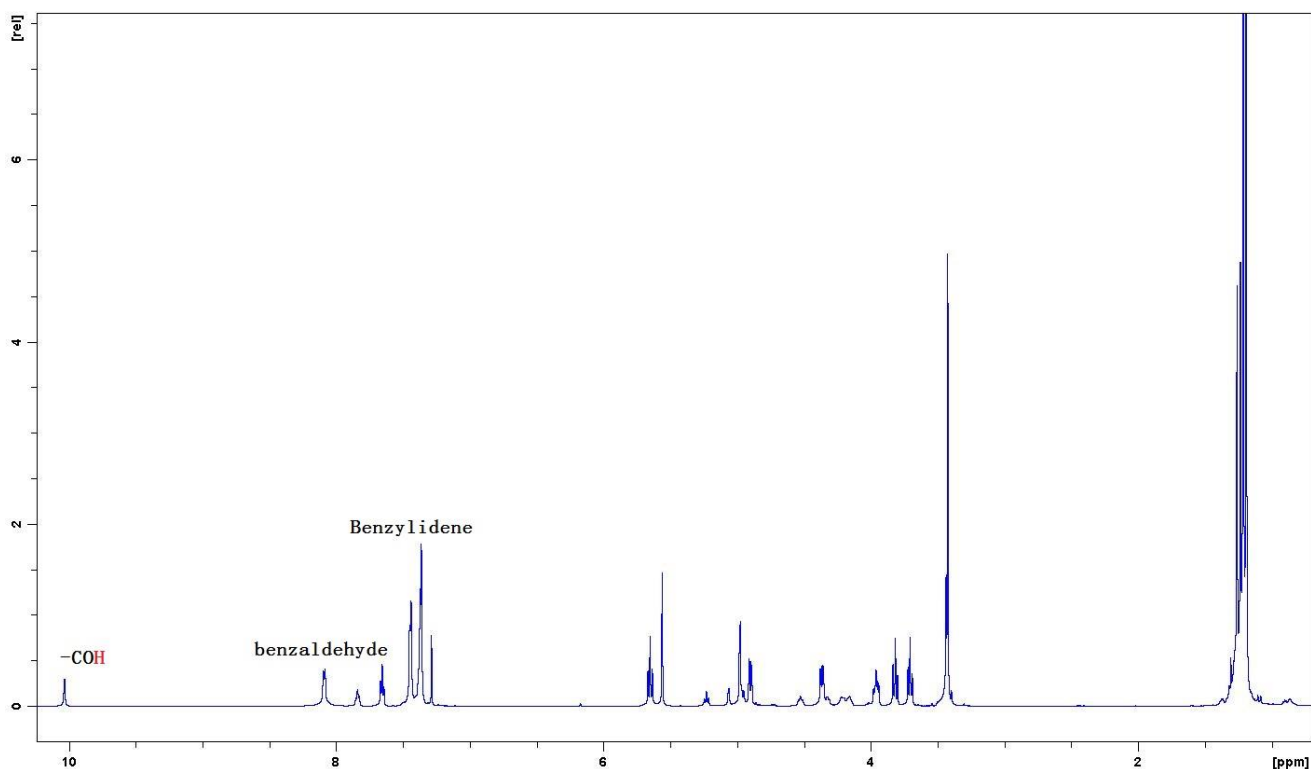


Supporting Information

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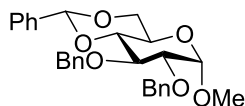
1. Figure S1. Treatment of methyl 2,3-di-O-pivaloyl- α -D-glucopyranoside **8** with 1 equiv of SnCl₄ in dry *d*-CH₃Cl.



Benzaldehyde instead of dichlorotoluene was observed in the NMR spectrum. The reaction was terminated when the trace amounts of water in the *d*-chloroform is consumed.

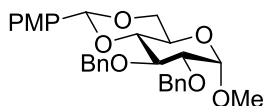
2. Synthesis of substrates

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside **1a**



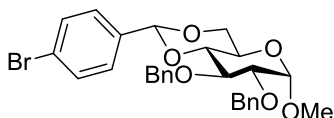
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside **1a** was synthesized as previously reported.¹ ¹H NMR (600 MHz, CDCl₃) δ 7.56 – 7.43 (m, 2H), 7.43 – 7.22 (m, 13H), 5.55 (s, 1H), 4.91 (d, *J* = 11.3 Hz, 1H), 4.84 (dd, *J* = 11.7, 8.4 Hz, 2H), 4.70 (d, *J* = 12.1 Hz, 1H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.26 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.05 (t, *J* = 9.3 Hz, 1H), 3.83 (td, *J* = 10.0, 4.8 Hz, 1H), 3.71 (t, *J* = 10.3 Hz, 1H), 3.60 (t, *J* = 9.4 Hz, 1H), 3.56 (dd, *J* = 9.3, 3.7 Hz, 1H), 3.40 (s, 3H).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)- α -D-glucopyranoside **1b**



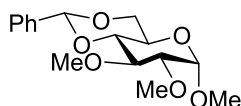
Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)- α -D-glucopyranoside **1b** was synthesized as previously reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.15 (m, 12H), 6.94 – 6.81 (m, 2H), 5.51 (s, 1H), 4.97 – 4.78 (m, 3H), 4.69 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 3.7 Hz, 1H), 4.24 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.04 (t, *J* = 9.3 Hz, 1H), 3.82 (s, 4H), 3.69 (t, *J* = 10.2 Hz, 1H), 3.64 – 3.49 (m, 2H), 3.40 (s, 3H).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-bromobenzylidene)- α -D-glucopyranoside **1c**



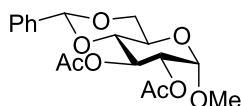
Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-bromobenzylidene)- α -D-glucopyranoside **1c** was synthesized as previously reported.² ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.48 (m, 2H), 7.40 – 7.27 (m, 12H), 5.48 (s, 1H), 4.91 – 4.81 (m, 3H), 4.70 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 3.7 Hz, 1H), 4.25 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.02 (t, *J* = 9.3 Hz, 1H), 3.80 (td, *J* = 9.9, 4.7 Hz, 1H), 3.68 (t, *J* = 10.3 Hz, 1H), 3.61 – 3.53 (m, 2H), 3.40 (s, 3H).

Methyl 2,3-di-*O*-methyl-4,6-*O*-benzylidene- α -D-glucopyranoside **3**



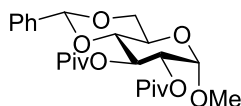
Methyl 2,3-di-*O*-methyl-4,6-*O*-benzylidene- α -D-glucopyranoside **3** was synthesized as previously reported.³ Spectral data of **3**: ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.44 (m, 2H), 7.44 – 7.31 (m, 3H), 5.55 (s, 1H), 4.86 (d, J = 3.7 Hz, 1H), 4.29 (dd, J = 9.9, 4.5 Hz, 1H), 3.82 (td, J = 9.7, 4.5 Hz, 1H), 3.71 (dt, J = 15.3, 9.6 Hz, 2H), 3.64 (s, 3H), 3.56 (s, 3H), 3.45 (s, 3H), 3.30 (dd, J = 9.2, 3.7 Hz, 1H).

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene- α -D-glucopyranoside **5**



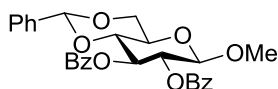
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene- α -D-glucopyranoside **5** was synthesized as previously reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.40 (m, 2H), 7.40 – 7.28 (m, 3H), 5.58 (t, J = 9.7 Hz, 1H), 5.50 (s, 1H), 5.01 – 4.86 (m, 2H), 4.30 (dd, J = 10.3, 4.8 Hz, 1H), 4.16 – 4.05 (m, 1H), 3.92 (td, J = 9.8, 4.6 Hz, 1H), 3.77 (t, J = 10.3 Hz, 1H), 3.65 (t, J = 9.6 Hz, 1H), 3.41 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H).

Methyl 2,3-di-*O*-pivaloyl-4,6-*O*-benzylidene- α -D-glucopyranoside **7**



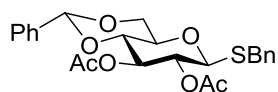
Methyl 2,3-di-*O*-pivaloyl-4,6-*O*-benzylidene- α -D-glucopyranoside **7** was synthesized as previously reported.^{3,4} ¹H NMR (400 MHz, CDCl₃) δ 7.41 (dd, J = 6.8, 2.9 Hz, 2H), 7.37 – 7.30 (m, 3H), 5.61 (d, J = 9.8 Hz, 1H), 5.53 (s, 1H), 4.95 (d, J = 3.8 Hz, 1H), 4.86 (dd, J = 9.9, 3.7 Hz, 1H), 4.32 (dd, J = 10.2, 4.8 Hz, 1H), 3.93 (td, J = 9.9, 4.7 Hz, 1H), 3.78 (t, J = 10.3 Hz, 1H), 3.67 (t, J = 9.6 Hz, 1H), 3.40 (s, 3H), 1.19 (s, 9H), 1.16 (s, 9H).

Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside **9**



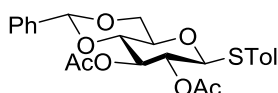
Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside **9** was synthesized as previously reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.96 (t, J = 7.6 Hz, 4H), 7.61 – 7.28 (m, 11H), 5.79 (t, J = 9.6 Hz, 1H), 5.56 (s, 1H), 5.47 (t, J = 8.7 Hz, 1H), 4.72 (d, J = 7.9 Hz, 1H), 4.46 (dd, J = 10.5, 4.9 Hz, 1H), 3.92 (dt, J = 14.3, 9.9 Hz, 2H), 3.71 (td, J = 9.7, 4.9 Hz, 1H), 3.54 (s, 3H).

Benzyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside **11**



Benzyl 4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside (100 mg, 0.27 mmol), pyridine (1.0 mL), and acetic anhydride (0.1 mL, 1.07 mmol) were combined in a round-bottom flask and stirred at room temperature for 2 h. After completion of reaction, the reaction mixture was concentrated under reduced pressure to give the crude compound. Purification on a silica gel column afforded **11** as a white solid (elution with ethyl acetate/petroleum ether = 1:4 (v/v); 110 mg, 90% yield). m.p. 214.8–217.4, $[\alpha]_D^{25}$ = -119.5 (c 0.4, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.27 (m, 11H), 5.50 (s, 1H), 5.27 (t, J = 9.4 Hz, 1H), 5.08 (t, J = 9.5 Hz, 1H), 4.42 (d, J = 10.0 Hz, 1H), 4.35 (dd, J = 10.6, 4.9 Hz, 1H), 3.89 (q, J = 12.9 Hz, 2H), 3.77 (t, J = 10.2 Hz, 1H), 3.68 (t, J = 9.6 Hz, 1H), 3.47 (td, J = 9.7, 4.9 Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.04, 169.67, 136.86, 136.73, 129.16, 129.03, 128.65, 128.26, 127.45, 126.12, 101.49, 83.07, 78.36, 72.71, 70.64, 70.52, 68.45, 34.25, 20.79, 20.72. HRMS (ESI-TOF) m/z $[M + Na]^+$ calcd for [C₂₄H₂₆O₇SN]⁺: 481.1297; found: 481.1295.

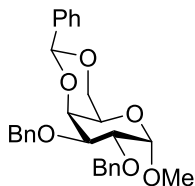
4-Methylphenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside **13**



4-Methylphenyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside **13** was synthesized as previously reported.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.31 (m, 7H), 7.15 (d, J = 7.8 Hz, 2H), 5.49 (s, 1H), 5.33 (t, J = 9.4 Hz, 1H), 4.97 (t, J = 9.5 Hz, 1H), 4.74 (d, J = 10.1 Hz, 1H),

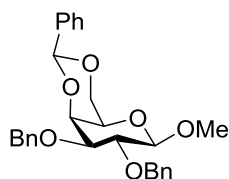
4.38 (dd, $J = 10.7, 4.8$ Hz, 1H), 3.79 (t, $J = 10.2$ Hz, 1H), 3.71 – 3.49 (m, 1H), 2.36 (s, 3H), 2.10 (d, $J = 5.8$ Hz, 3H), 2.03 (s, 3H).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranoside **15**



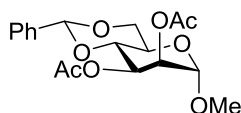
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-galactopyranoside **15** was synthesized as previously reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.47 (m, 2H), 7.35 (tdd, $J = 27.0, 13.9, 7.4$ Hz, 13H), 5.48 (s, 1H), 4.86 (dd, $J = 19.5, 12.2$ Hz, 2H), 4.79 – 4.62 (m, 3H), 4.25 – 4.14 (m, 2H), 4.07 (dd, $J = 10.1, 3.4$ Hz, 1H), 3.99 (td, $J = 10.1, 2.6$ Hz, 2H), 3.58 (s, 1H), 3.38 (s, 3H).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-galactopyranoside **17**



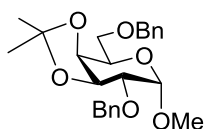
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-galactopyranoside **17** was synthesized as previously reported.⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.52 (m, 2H), 7.34 (dd, $J = 22.1, 16.2$ Hz, 13H), 5.50 (s, 1H), 4.91 (d, $J = 10.9$ Hz, 1H), 4.84 – 4.70 (m, 3H), 4.37 – 4.26 (m, 2H), 4.11 (dd, $J = 3.7, 1.0$ Hz, 1H), 4.02 (dd, $J = 12.3, 1.8$ Hz, 1H), 3.84 (dd, $J = 9.7, 7.7$ Hz, 1H), 3.59 (s, 3H), 3.56 (dd, $J = 9.7, 3.6$ Hz, 1H).

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene- α -D-mannopyranoside **19**



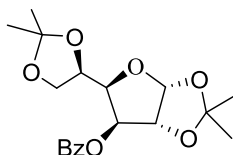
Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene- α -D-mannopyranoside **19** was synthesized according to the procedure for the synthesis of **5**.⁷ ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, $J = 6.8, 2.8$ Hz, 2H), 7.36 (dd, $J = 5.2, 2.1$ Hz, 3H), 5.58 (s, 1H), 5.45 – 5.32 (m, 2H), 4.67 (d, $J = 1.6$ Hz, 1H), 4.29 (dd, $J = 10.0, 4.4$ Hz, 1H), 4.05 (t, $J = 9.7$ Hz, 1H), 3.95 (td, $J = 9.6, 4.4$ Hz, 1H), 3.86 (t, $J = 10.1$ Hz, 1H), 3.40 (s, 3H), 2.17 (s, 3H), 2.01 (s, 3H).

Methyl 2,6-di-*O*-benzyl 3,4-*O*-isopropylidene- α -D-galactopyranoside **21**



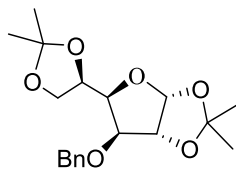
Methyl 2,6-di-*O*-benzyl 3,4-*O*-isopropylidene- α -D-galactopyranoside **21** was synthesized as previously reported.⁸ ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.23 (m, 10H), 4.82 (d, $J = 12.6$ Hz, 1H), 4.76 – 4.61 (m, 3H), 4.53 (d, $J = 12.1$ Hz, 1H), 4.34 (dd, $J = 7.9, 5.4$ Hz, 1H), 4.25 – 4.07 (m, 2H), 3.82 – 3.64 (m, 2H), 3.51 (dd, $J = 7.9, 3.5$ Hz, 1H), 3.40 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzoyl- α -D-glucofuranose **23**



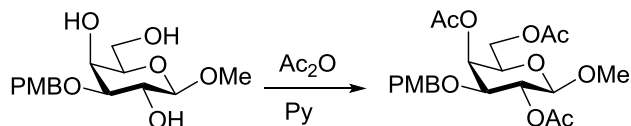
1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzoyl- α -D-glucofuranose **23** was prepared using literature procedure.⁹ ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.95 (m, 2H), 7.67 – 7.54 (m, 1H), 7.46 (t, $J = 7.6$ Hz, 2H), 5.95 (d, $J = 3.7$ Hz, 1H), 5.51 (d, $J = 2.7$ Hz, 1H), 4.64 (d, $J = 3.7$ Hz, 1H), 4.35 (tt, $J = 7.9, 4.0$ Hz, 2H), 4.19 – 4.03 (m, 2H), 1.56 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H).

1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzyl- α -D-glucofuranose **25**



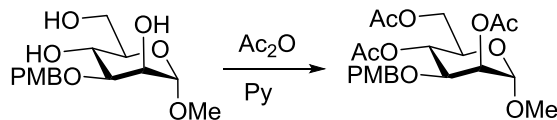
1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzyl- α -D-glucofuranose **25** was synthesized as previously reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.22 (m, 5H), 5.89 (d, J = 3.7 Hz, 1H), 4.73 – 4.60 (m, 2H), 4.58 (d, J = 3.7 Hz, 1H), 4.37 (dt, J = 7.7, 6.0 Hz, 1H), 4.15 (dd, J = 7.7, 3.1 Hz, 1H), 4.10 (dd, J = 8.6, 6.2 Hz, 1H), 4.07 – 3.96 (m, 2H), 1.48 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H).

Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- β -D-galactopyranoside **27**



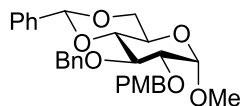
Acetic anhydride (450 μ L, 4.8 mmol) was added to a solution of methyl 3-*O*-(4-methoxybenzyl)- β -D-galactopyranoside (300 mg, 0.95 mmol) in pyridine (2 mL) at 0 °C. The mixture was stirred at room temperature for 2 h, and then poured onto cold saturated NaHCO₃ solution. The aqueous phase was extracted with dichloromethane (3 \times 10 mL). The combined organic phase was washed with saturated NaHCO₃ solution (1 \times 15 mL), dried with anhydrous MgSO₄, and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford **27** as colorless oil (elution with ethyl acetate/petroleum ether = 1:4 (v/v); 387 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.19 (d, J = 8.6 Hz, 2H, Ar-H), 6.86 (d, J = 8.6 Hz, 2H, Ar-H), 5.49 (dd, J = 3.5, 1.2 Hz, 1H, H-4), 5.09 (dd, J = 10.0, 8.0 Hz, 1H, H-2), 4.62 (d, J = 11.9 Hz, 1H, PhCH₂), 4.33 (d, J = 11.9 Hz, 1H, PhCH₂), 4.29 (d, J = 8.1 Hz, 1H, H-1), 4.18 (d, J = 6.6 Hz, 2H, H-6), 3.81 (s, 4H, OMe, H-5), 3.52 (dd, J = 10.0, 3.4 Hz, 1H, H-2), 3.48 (s, 3H, OMe), 2.16 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.04 (s, 3H, OAc). ¹³C NMR (100 MHz, CDCl₃) δ 170.58, 170.46, 169.48, 159.34, 129.48, 129.46, 113.75, 102.03, 76.11, 70.92, 70.86, 70.37, 65.88, 61.99, 56.73, 55.28, 20.97, 20.87, 20.78. HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for [C₁₂H₂₈O₁₀Na]⁺: 463.1580; found: 463.1598.

Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- α -D-mannopyranoside **29**



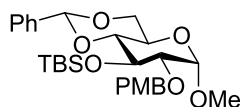
Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- α -D-mannopyranoside **29** was synthesized according to the same procedure as the synthesis of **27**. [α]_D²⁵ = +13.8 (c 0.79, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, J = 8.6 Hz, 2H, Ar-H), 6.90 – 6.82 (m, 2H, Ar-H), 5.35 – 5.30 (m, 1H, H-2), 5.19 (t, J = 9.9 Hz, 1H, H-4), 4.73 (d, J = 1.8 Hz, 1H, H-1), 4.57 (d, J = 11.8 Hz, 1H, PhCH₂), 4.34 (d, J = 11.8 Hz, 1H, PhCH₂), 4.24 (dd, J = 12.2, 5.7 Hz, 1H, H-6a), 4.10 (dd, J = 12.2, 2.4 Hz, 1H, H-6b), 3.89–3.81 (m, 2H, H-3, H-5), 3.80 (s, 3H, OMe), 3.37 (s, 3H, OMe), 2.15 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.01 (s, 3H, OAc). ¹³C NMR (100 MHz, CDCl₃) δ 170.74, 170.34, 169.71, 159.27, 129.73, 129.38, 113.73, 98.85, 73.91, 70.95, 68.51, 68.11, 67.41, 62.79, 55.22, 21.00, 20.81, 20.73. HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for [C₁₂H₂₈O₁₀Na]⁺: 463.1580; found: 463.1593.

Methyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside **31**



Methyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside **31** was synthesized as previously reported.¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 7.49 (dd, J = 7.2, 2.3 Hz, 2H), 7.42 – 7.22 (m, 10H), 6.86 (d, J = 8.2 Hz, 2H), 5.54 (s, 1H), 4.90 (d, J = 11.3 Hz, 1H), 4.87 – 4.75 (m, 2H), 4.63 (d, J = 11.9 Hz, 1H), 4.53 (d, J = 3.6 Hz, 1H), 4.26 (dd, J = 10.0, 4.7 Hz, 1H), 4.02 (t, J = 9.3 Hz, 1H), 3.80 (s, 4H), 3.70 (t, J = 10.2 Hz, 1H), 3.59 (t, J = 9.4 Hz, 1H), 3.53 (dd, J = 9.3, 3.7 Hz, 1H), 3.39 (s, 3H).

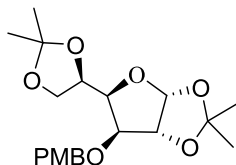
Methyl 2-*O*-(*p*-methoxybenzyl)-3-*O*-(*tert*-butyl-dimethylsilyl)-4,6-*O*-benzylidene- α -D-glucopyranoside **33**



Methyl 3-*O*-(*tert*-butyl-dimethylsilyl)-4,6-*O*-benzylidene- α -D-glucopyranoside (200 mg, 0.5 mmol) was dissolved in DMF (2 mL) and the solution

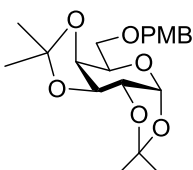
was cooled to 0 °C. NaH (40 mg, 1.0 mmol) and *p*-methoxybenzyl chloride (102 μ L, 0.75 mmol) was added to the mixture slowly. The mixture was then warmed to room temperature and stirred for 3 h. MeOH (1.0 mL) was added to quench the reaction, and the mixture was stirred for a further 10 min. The reaction mixture was diluted with water and extracted with CH₂Cl₂. The organic layers were combined and washed with water and brine sequentially, dried over anhydrous MgSO₄, concentrated in vacuo. The residue was purified by silica gel chromatography to give **33** (216 mg, 83%) as a colourless oil. $[\alpha]_D^{12} = 75.3$ (c 0.15, CH₂Cl₂) ¹H NMR (600 MHz, CDCl₃) δ 7.45 (dq, $J = 5.0, 2.8$ Hz, 2H, Ar-H), 7.38 – 7.22 (m, 5H, Ar-H), 6.89 – 6.82 (m, 2H, Ar-H), 5.44 (s, 1H, PhCH), 4.75 (d, $J = 12.0$ Hz, 1H, PhCH₂), 4.53 – 4.40 (m, 1H, PhCH₂), 4.34 (d, $J = 3.7$ Hz, 1H, H-1), 4.19 (dd, $J = 9.9, 4.6$ Hz, 1H, H-6a), 4.05 (t, $J = 9.0$ Hz, 1H, H-4), 3.78 (s, 3H), 3.73 (dt, $J = 9.7, 5.0$ Hz, 1H, H-6b), 3.63 (t, $J = 10.2$ Hz, 1H, H-5), 3.44 – 3.30 (m, 2H, H-2, H-3), 3.31 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), -0.00 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.44, 137.37, 130.38, 129.92, 128.91, 128.08, 126.26, 113.84, 101.85, 99.40, 82.51, 79.86, 73.70, 71.48, 69.09, 62.13, 55.31, 55.27, 25.88, 18.31, -4.39, -4.49. HRMS (ESI-TOF) m/z [M + Na]⁺ calcd for [C₂₈H₄₀O₇SiNa]⁺: 539.2441; found: 539.2420.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(*p*-methoxybenzyl)- α -D-glucofuranose **35**



1,2:5,6-Di-*O*-isopropylidene-3-*O*-(*p*-methoxybenzyl)- α -D-glucofuranose **35** was prepared using literature procedure.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.19 (m, 3H), 6.87 (d, $J = 8.5$ Hz, 2H), 5.88 (d, $J = 3.7$ Hz, 1H), 4.70 – 4.47 (m, 3H), 4.34 (dt, $J = 7.7, 6.1$ Hz, 1H), 4.23 – 4.03 (m, 2H), 4.00 (d, $J = 2.8$ Hz, 1H), 3.80 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.31 (s, 3H).

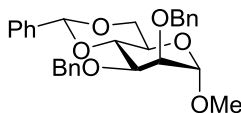
1,2:3,4-Di-*O*-isopropylidene-6-*O*-(*p*-methoxybenzyl)- α -D-galactopyranose **37**



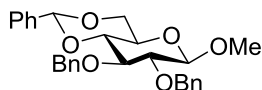
1,2:3,4-Di-*O*-isopropylidene-6-*O*-(*p*-methoxybenzyl)- α -D-galactopyranose **37** was synthesized according to the same procedure as the synthesis of **31**.¹² ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, $J = 8.5$ Hz, 2H), 6.87 (d, $J = 8.4$ Hz, 2H), 5.54 (d, $J = 5.0$ Hz, 1H), 4.66 – 4.44 (m, 3H), 4.29 (ddd, $J = 18.2, 6.5, 2.1$ Hz, 2H), 3.98 (td, $J = 6.4, 1.9$ Hz, 1H), 3.80 (s, 3H), 3.76 – 3.54 (m, 2H), 1.53 (s, 3H), 1.44 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H).

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside **39**

Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-mannopyranoside **39** was synthesized according to the same procedure as the synthesis of **1a**.¹³ ¹H NMR (600 MHz, CDCl₃) δ 7.55 – 7.26 (m, 15H), 5.64 (s, 1H), 4.81 (dd, $J = 12.2, 7.0$ Hz, 2H), 4.73 (d, $J = 12.2$ Hz, 1H), 4.69 (d, $J = 1.6$ Hz, 1H), 4.65 (d, $J = 12.3$ Hz, 1H), 4.29 – 4.21 (m, 2H), 3.94 (dd, $J = 10.0, 3.3$ Hz, 1H), 3.88 (t, $J = 10.3$ Hz, 1H), 3.83 (dd, $J = 3.3, 1.6$ Hz, 1H), 3.77 (dt, $J = 9.9, 5.1$ Hz, 1H), 3.31 (s, 3H).



Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-glucopyranoside **40**



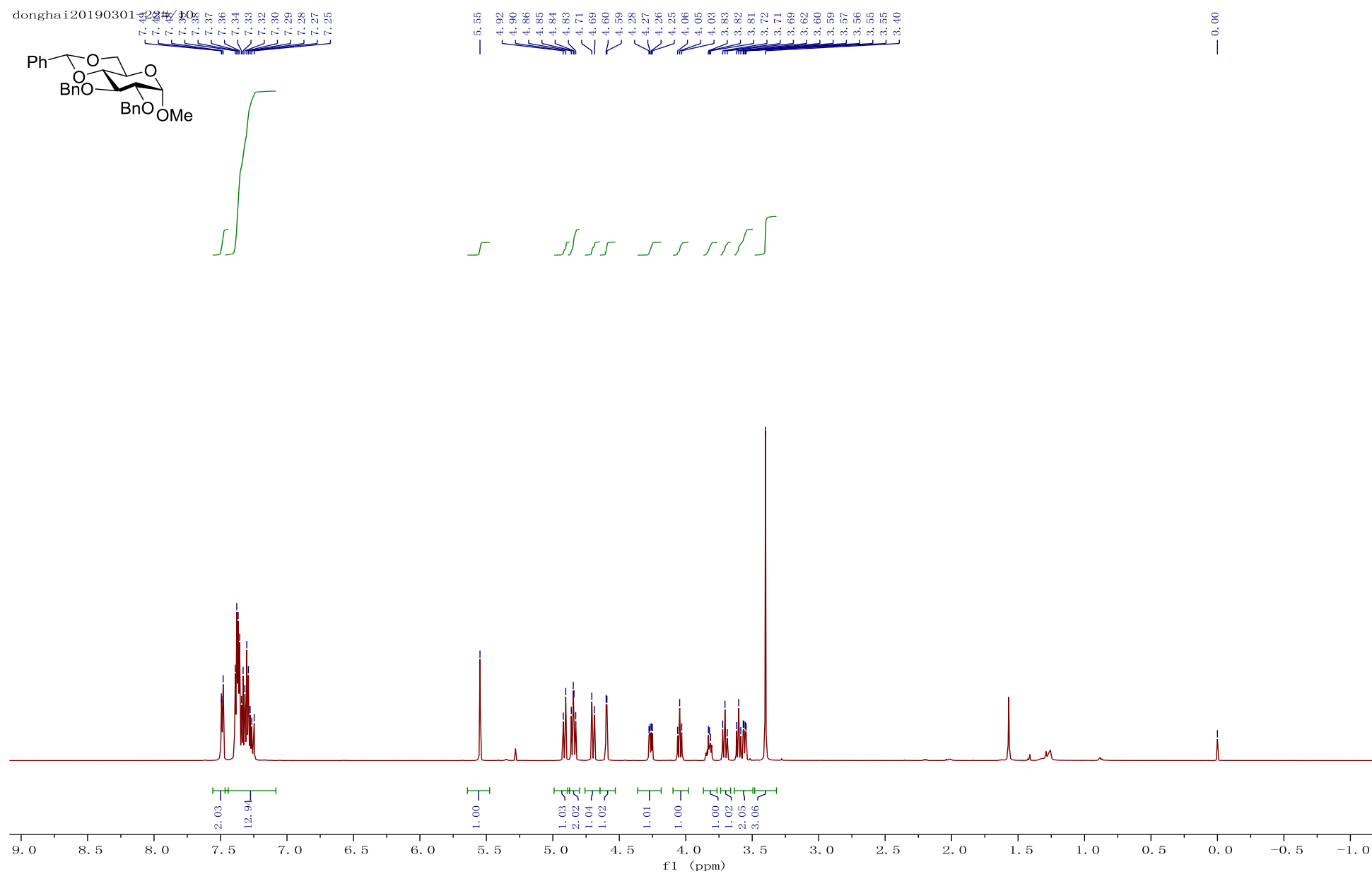
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-glucopyranoside **40** was synthesized according to the same procedure as the synthesis of **1a**.¹⁴ ¹H NMR (600 MHz, CDCl₃) δ 7.57 – 7.23 (m, 15H), 5.57 (s, 1H), 4.89 (dd, $J = 22.4, 10.9$ Hz, 2H), 4.78 (dd, $J = 23.8, 11.1$ Hz, 2H), 4.42 (d, $J = 7.7$ Hz, 1H), 4.39 – 4.33 (m, 1H), 3.77 (dt, $J = 19.5, 9.4$ Hz, 2H), 3.68 (t, $J = 9.3$ Hz, 1H), 3.58 (s, 3H), 3.43 (m, 2H).

3. References

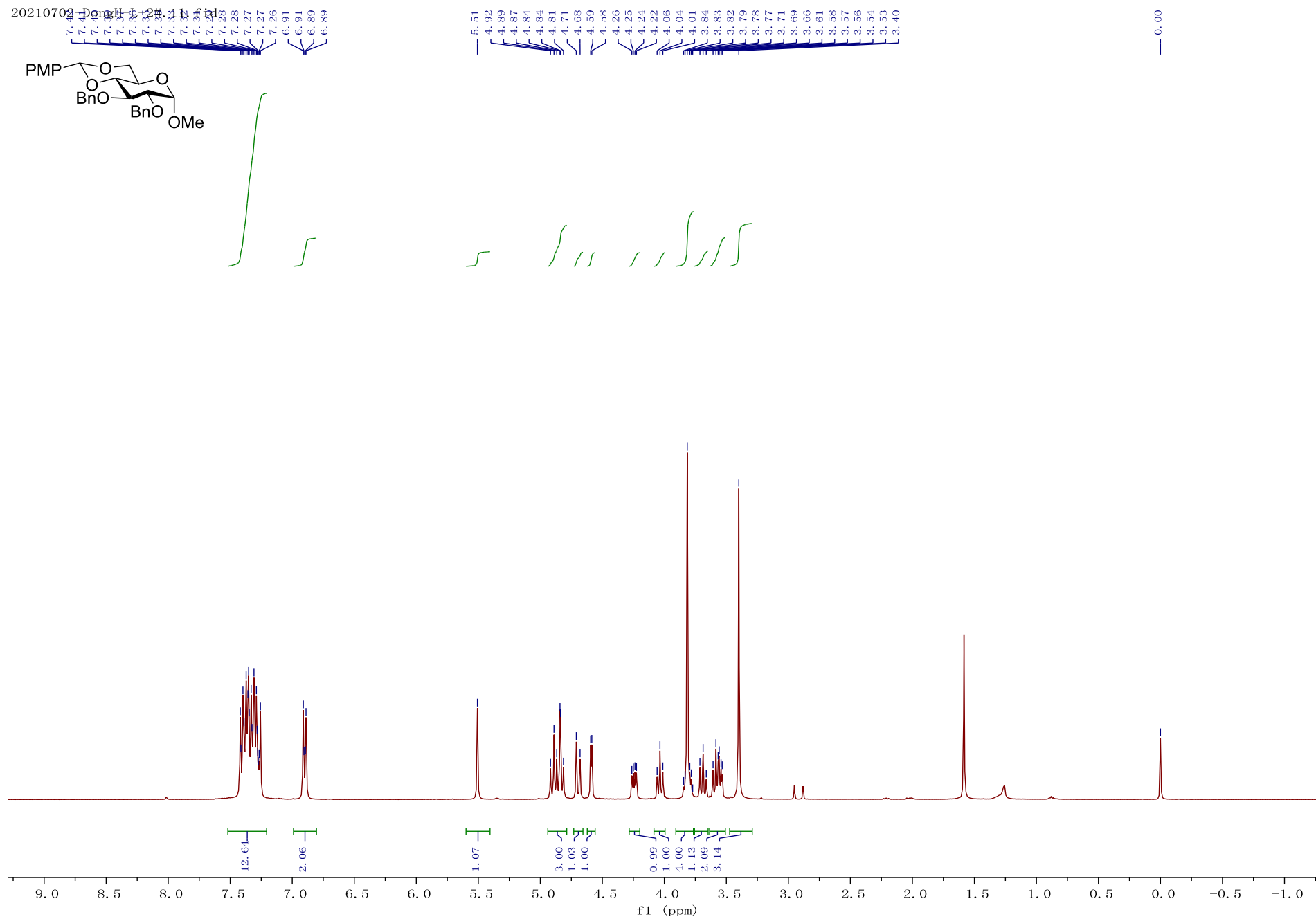
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4. Copies of NMR spectra

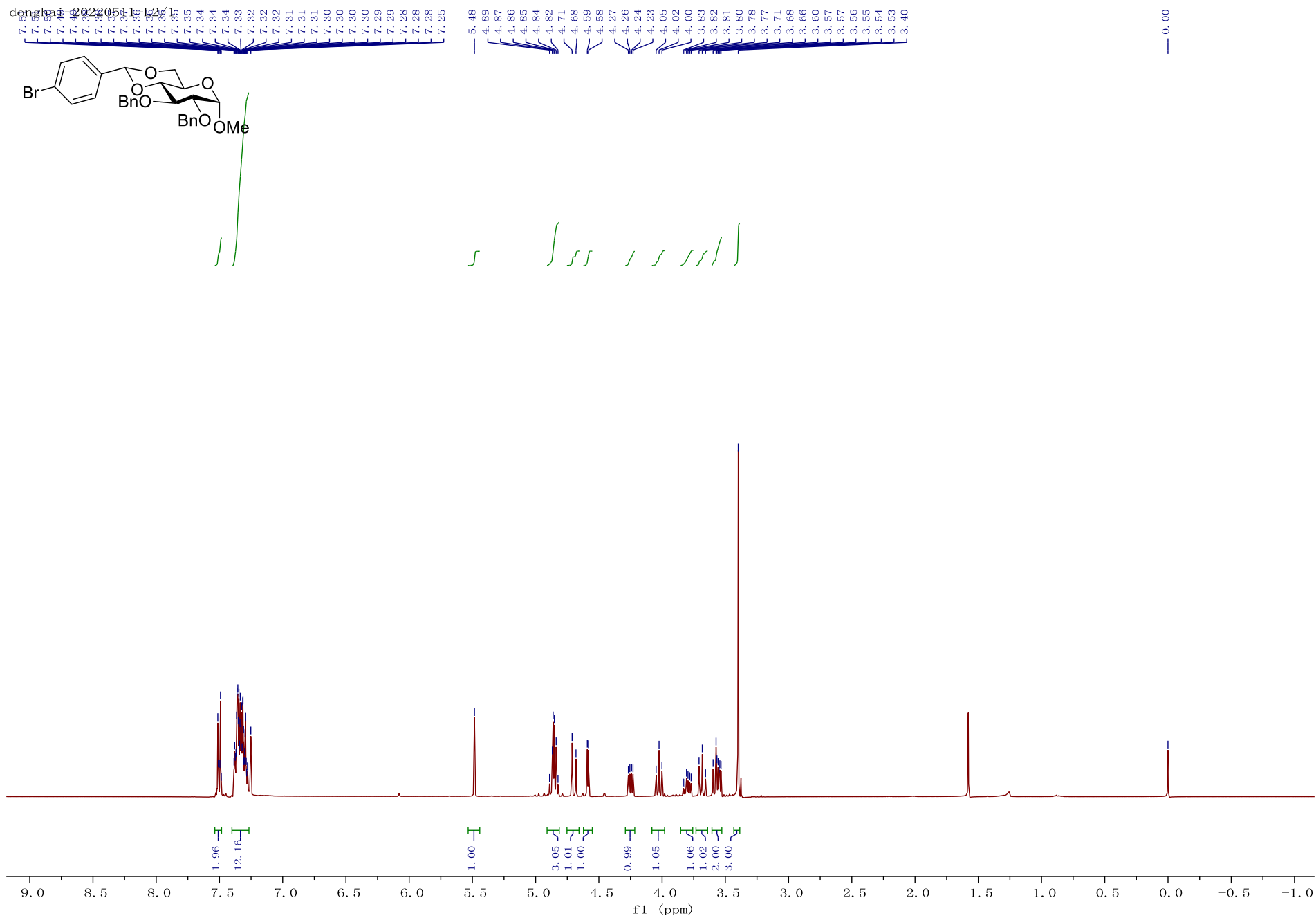
Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside **1a**



Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-methoxybenzylidene)- α -D-glucopyranoside 1b

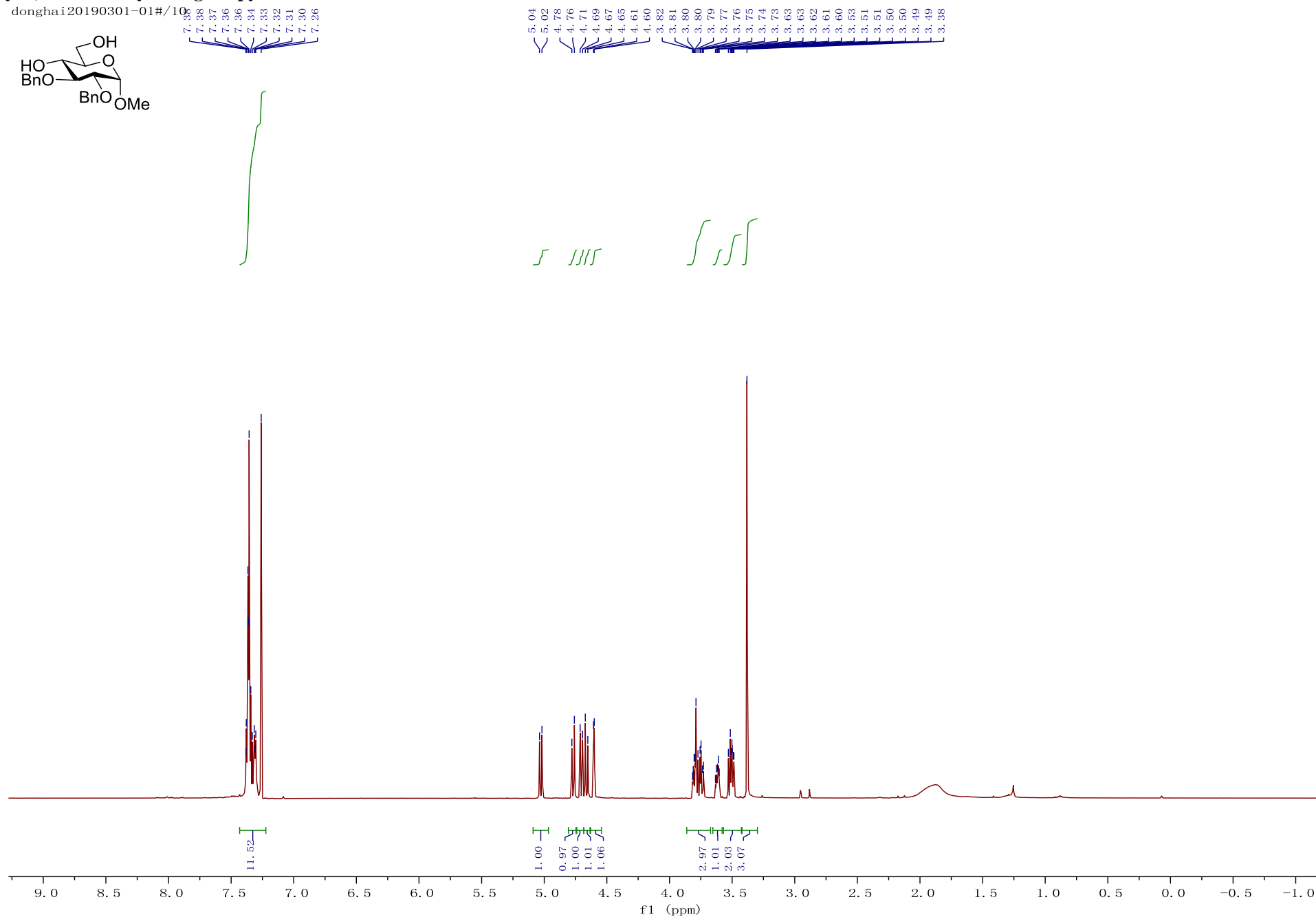
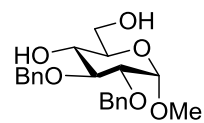


Methyl 2,3-di-*O*-benzyl-4,6-*O*-(*p*-bromobenzylidene)- α -D-glucopyranoside 1c



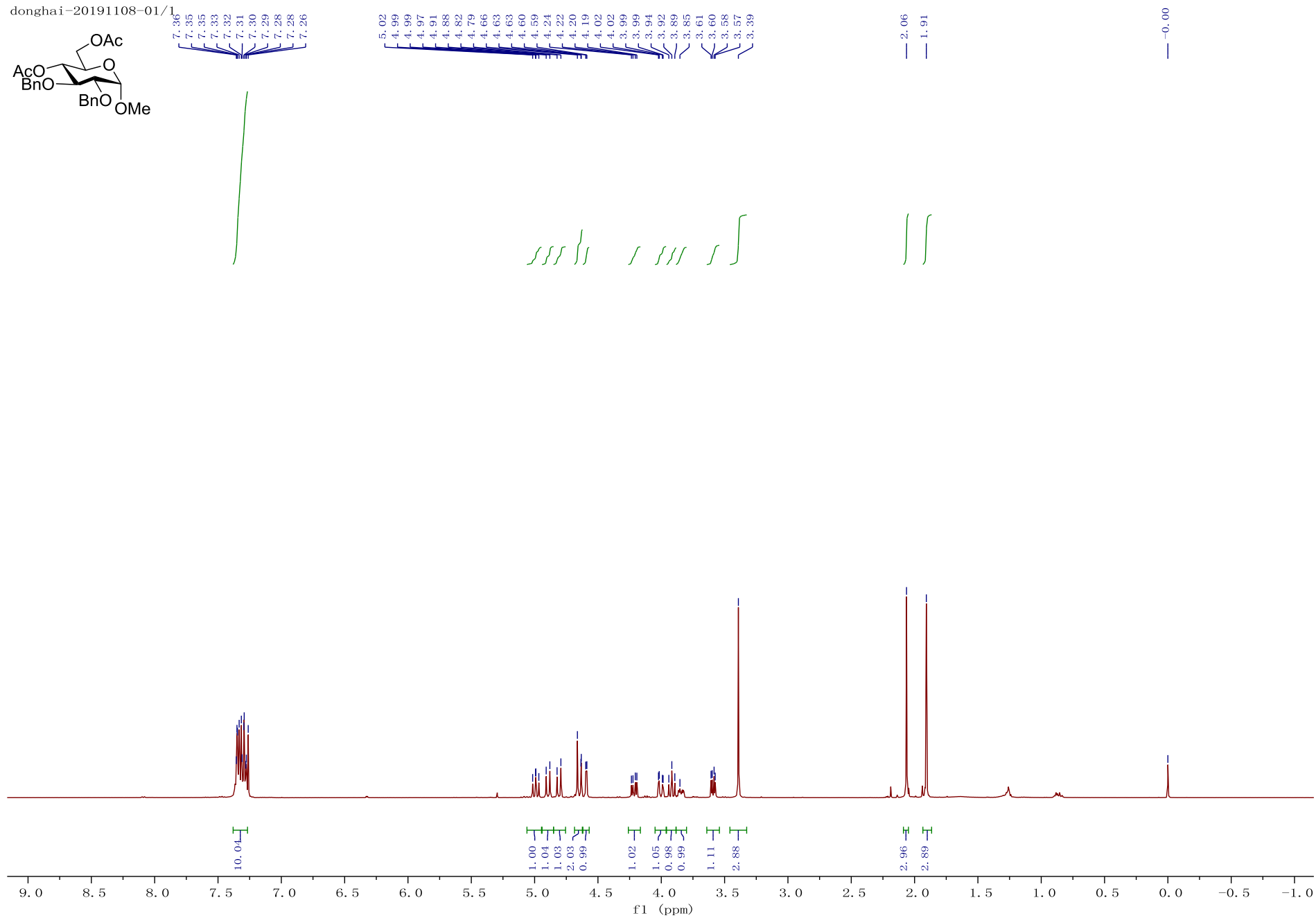
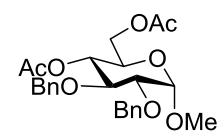
Methyl 2,3-di-*O*-benzyl- α -D-glucopyranoside 2

donghai20190301-01#/108



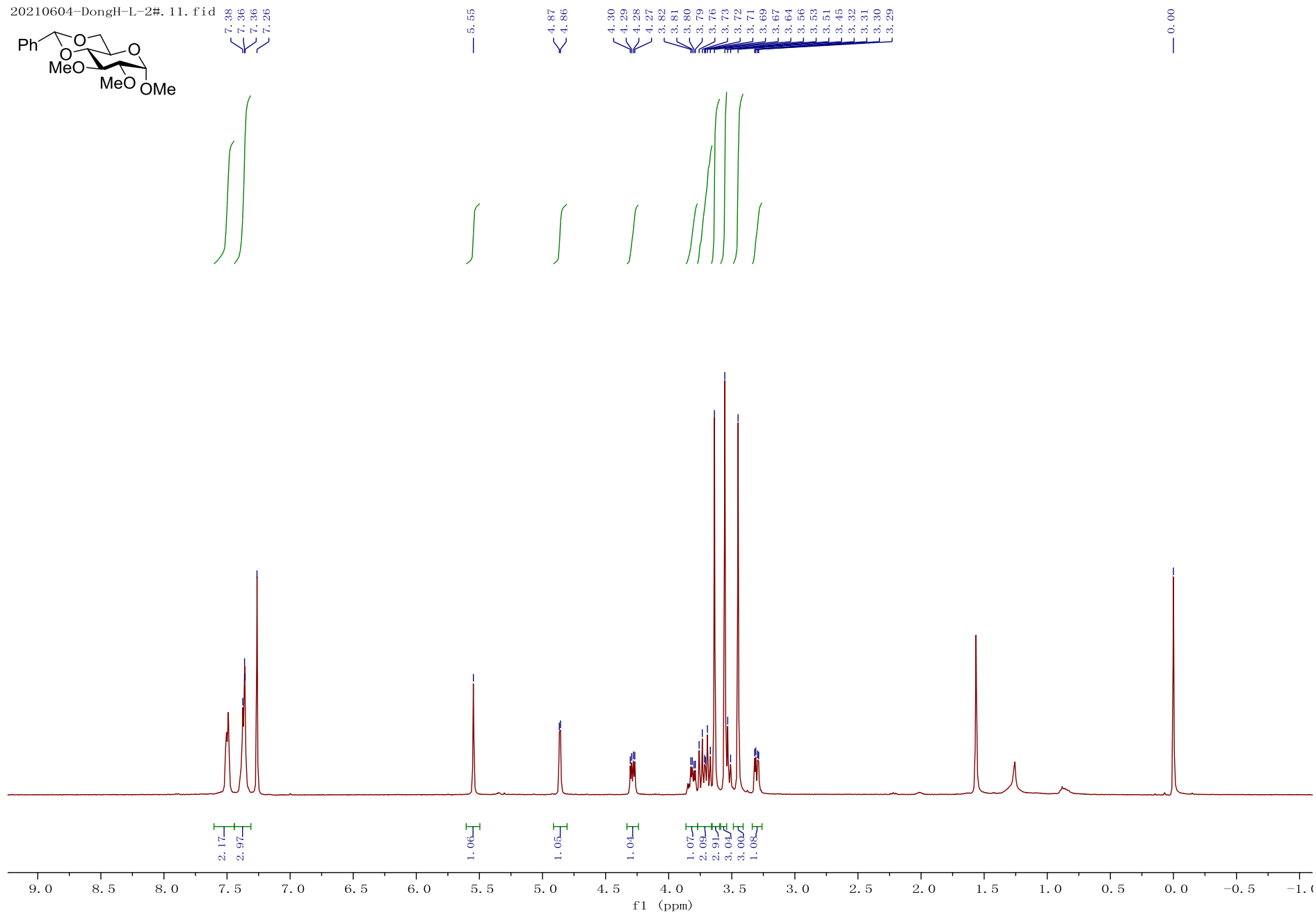
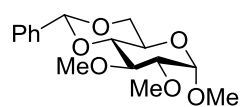
Methyl 2,3-di-*O*-benzyl-4,6-*O*-acetyl- α -D-glucopyranoside 2a

donghai-20191108-01/1



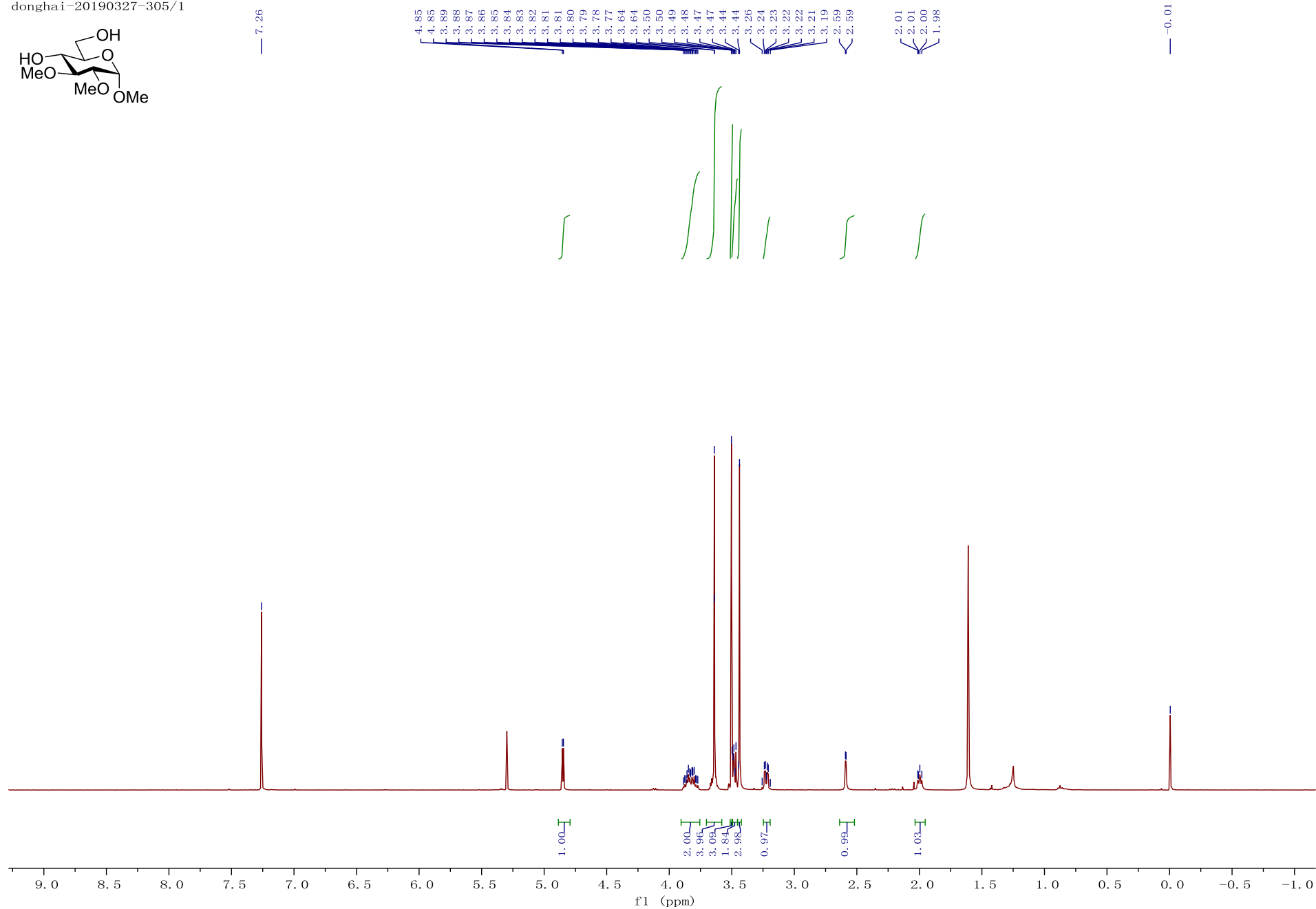
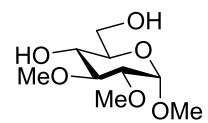
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20210604-DongH-L-2#. 11. fid



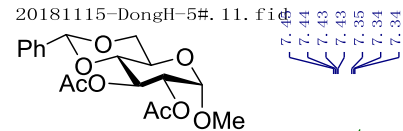
Methyl-2,3-di-*O*-methyl- α -D-glucopyranoside 4

donghai-20190327-305/1



Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene- α -D-glucopyranoside 5

20181115-DongH-5#, 11. f1



7.44
7.43
7.43
7.35
7.34
7.34

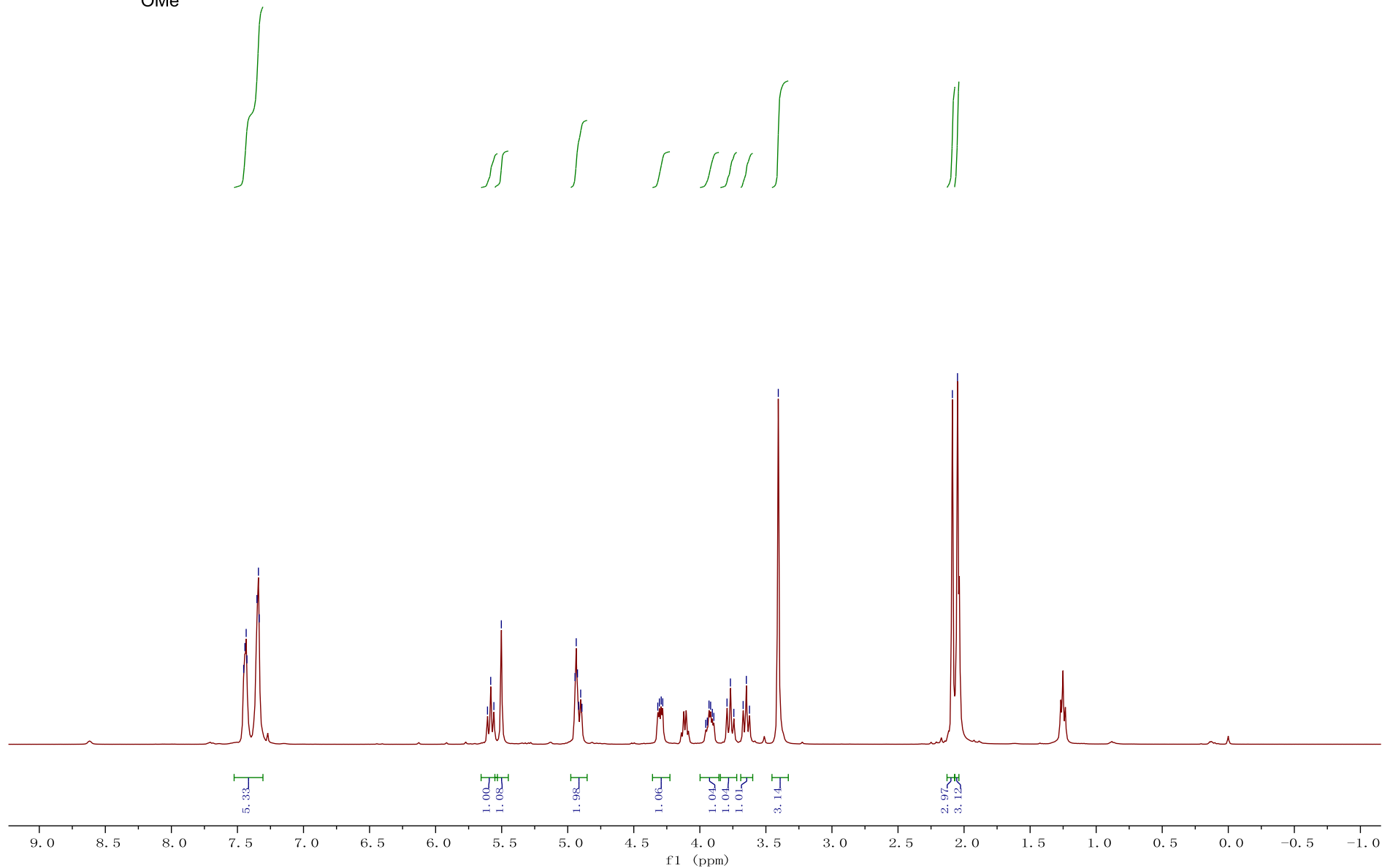
5.61
5.58
5.56
5.50

4.94
4.94
4.93
4.92
4.90
4.89

4.32
4.31
4.29
4.28

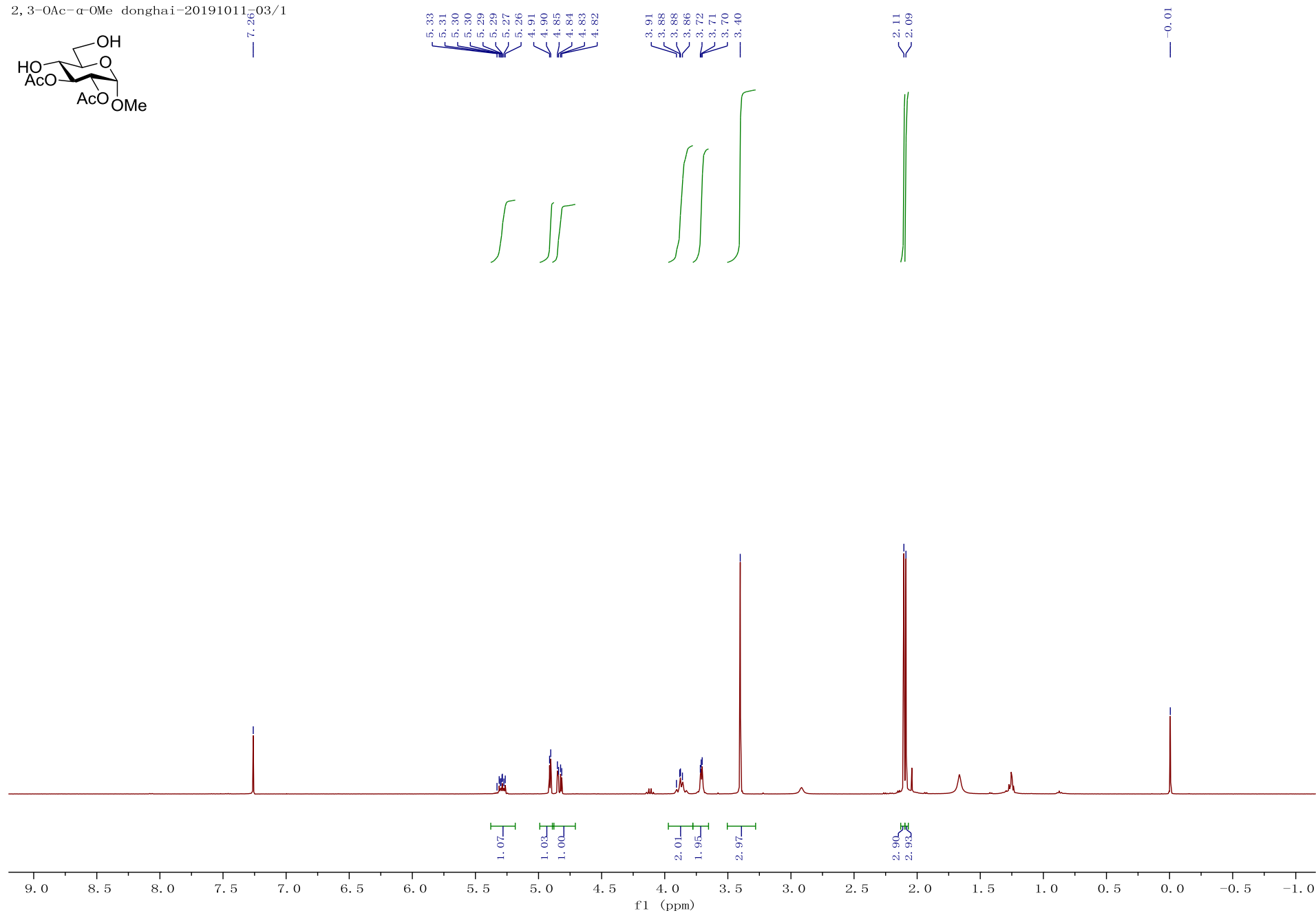
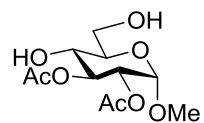
3.96
3.94
3.93
3.92
3.91
3.89
3.79
3.77
3.74
3.67
3.65
3.62
3.41

2.09
2.05



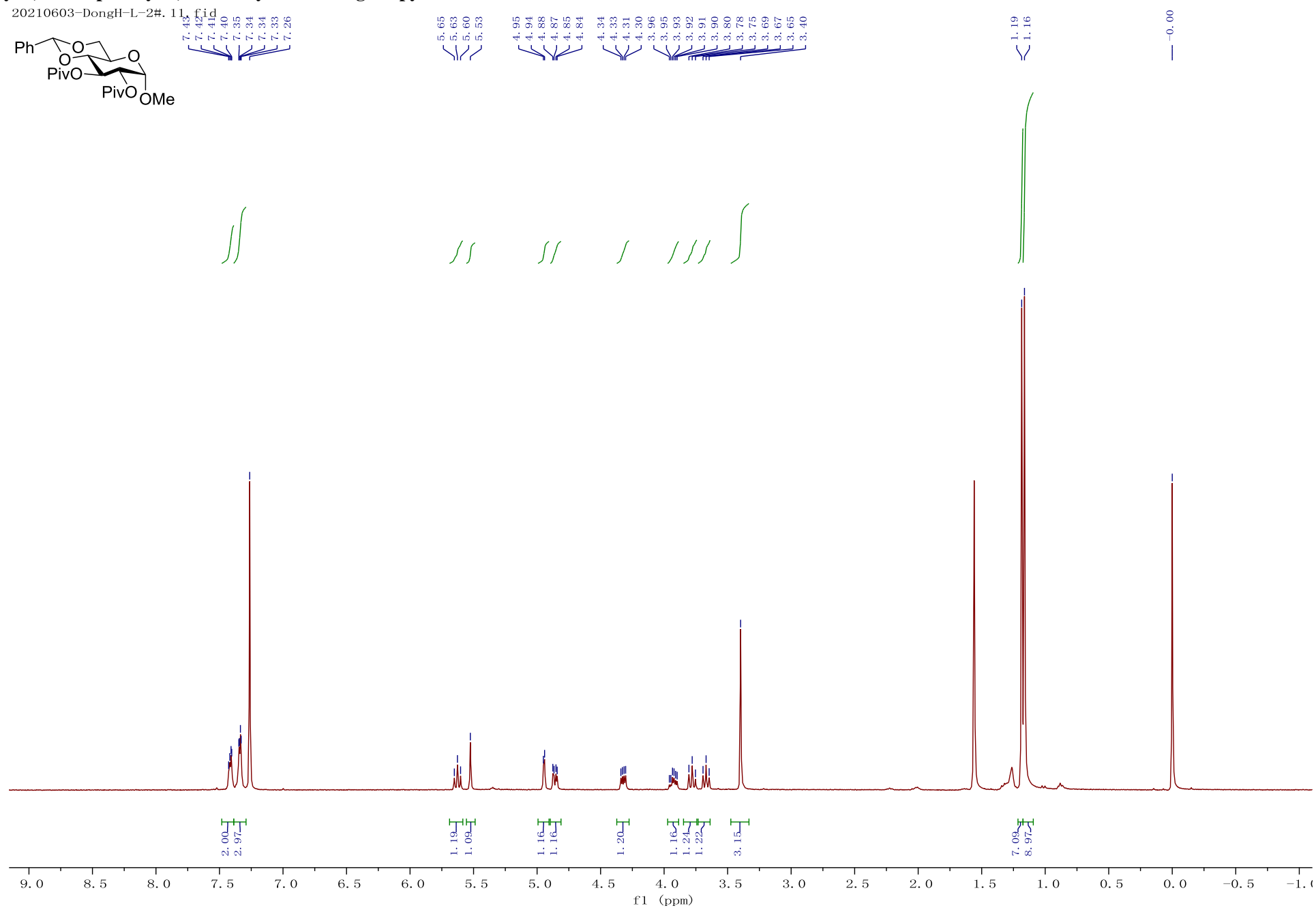
Methyl 2,3-di-*O*-acetyl- α -D-glucopyranoside 6

2,3-OAc- α -OMe donghai-20191011 03/1



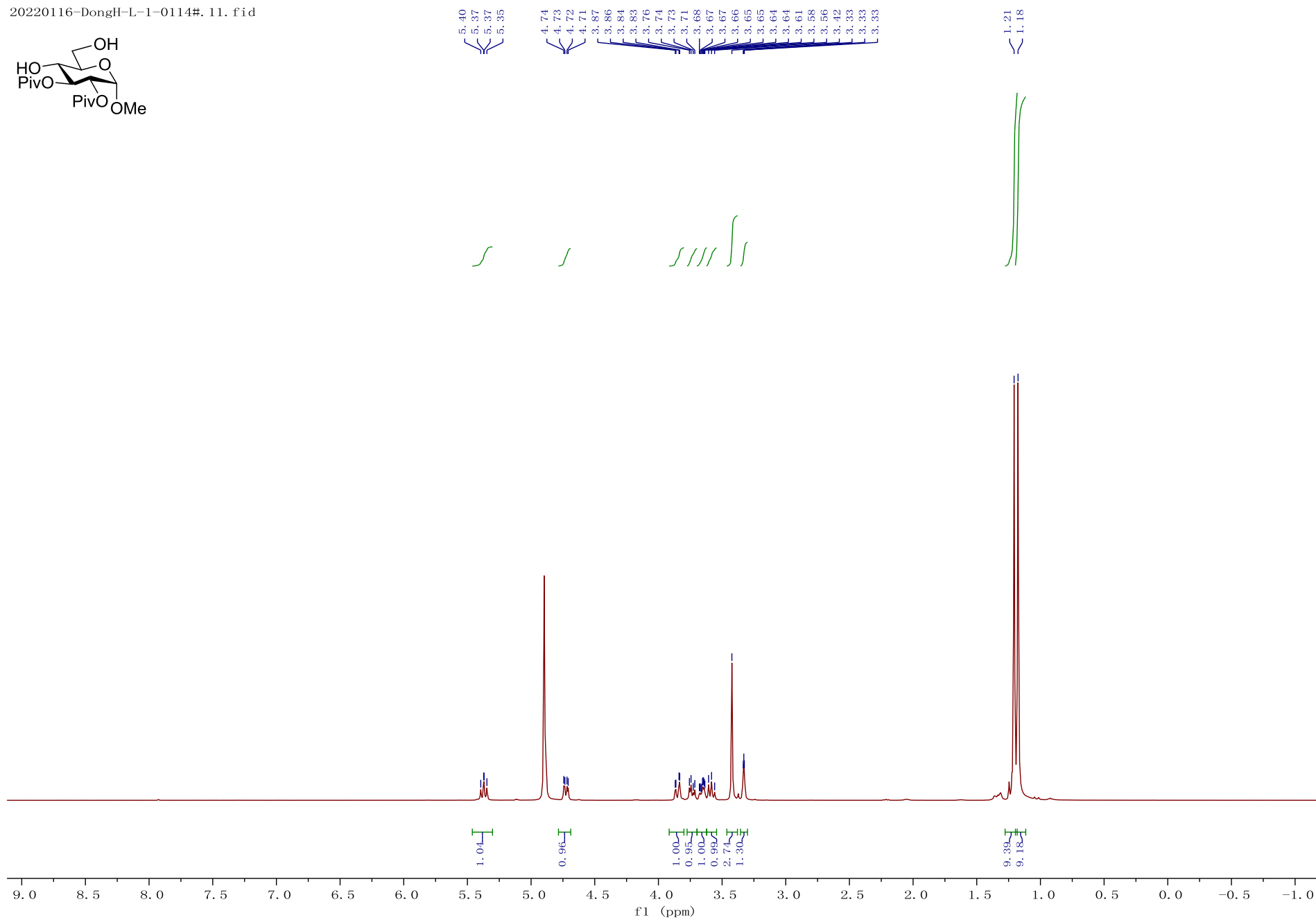
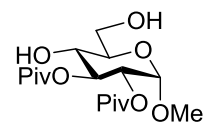
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20210603-DongH-L-2#. 11



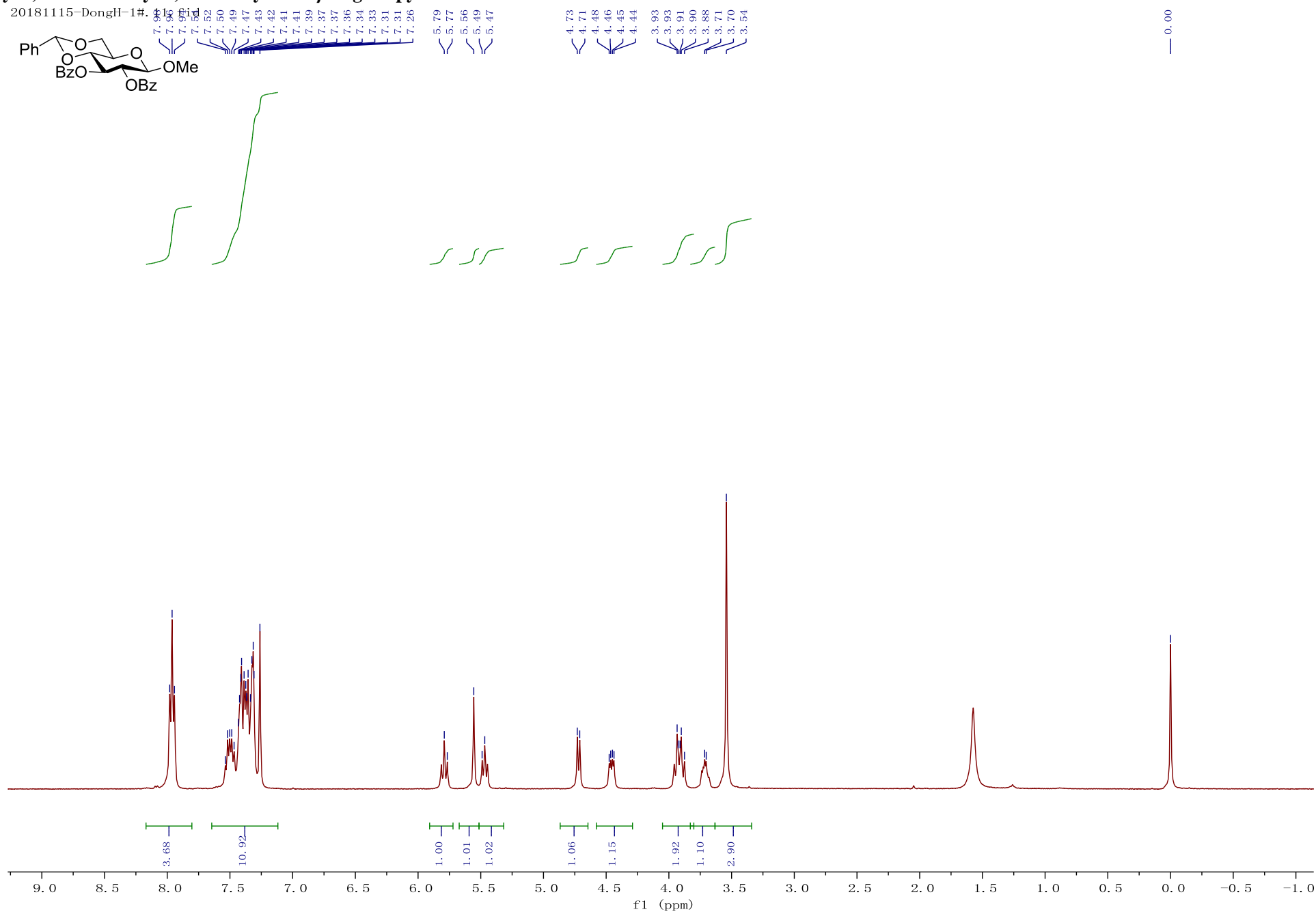
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20220116-DongH-L-1-0114#, 11. fid



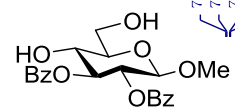
Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene- β -D-glucopyranoside **9**

20181115-DongH-1#



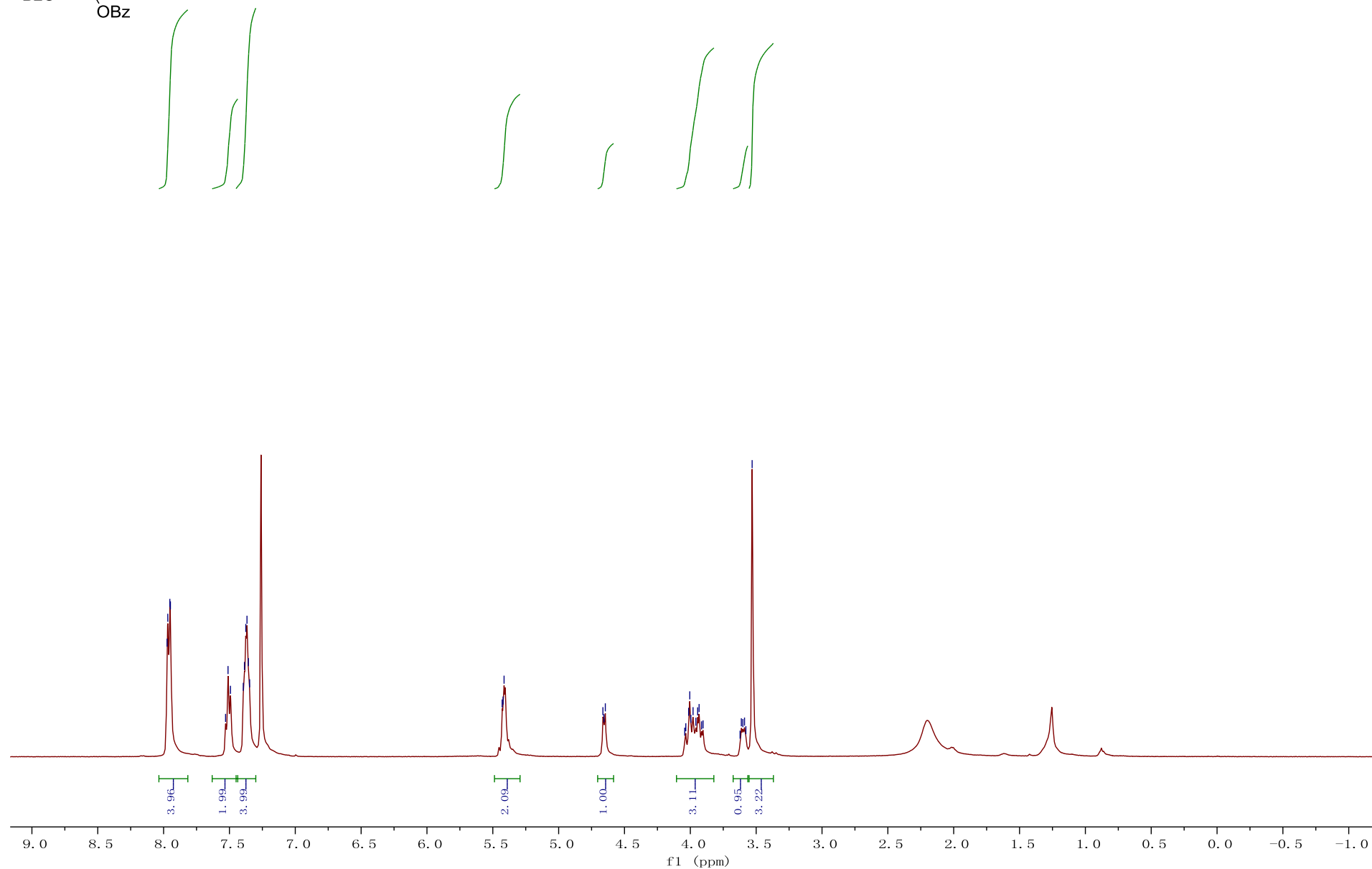
Methyl 2,3-di-*O*-benzoyl- β -D-glucopyranoside 10

20181120-DongH-3#-f1cd

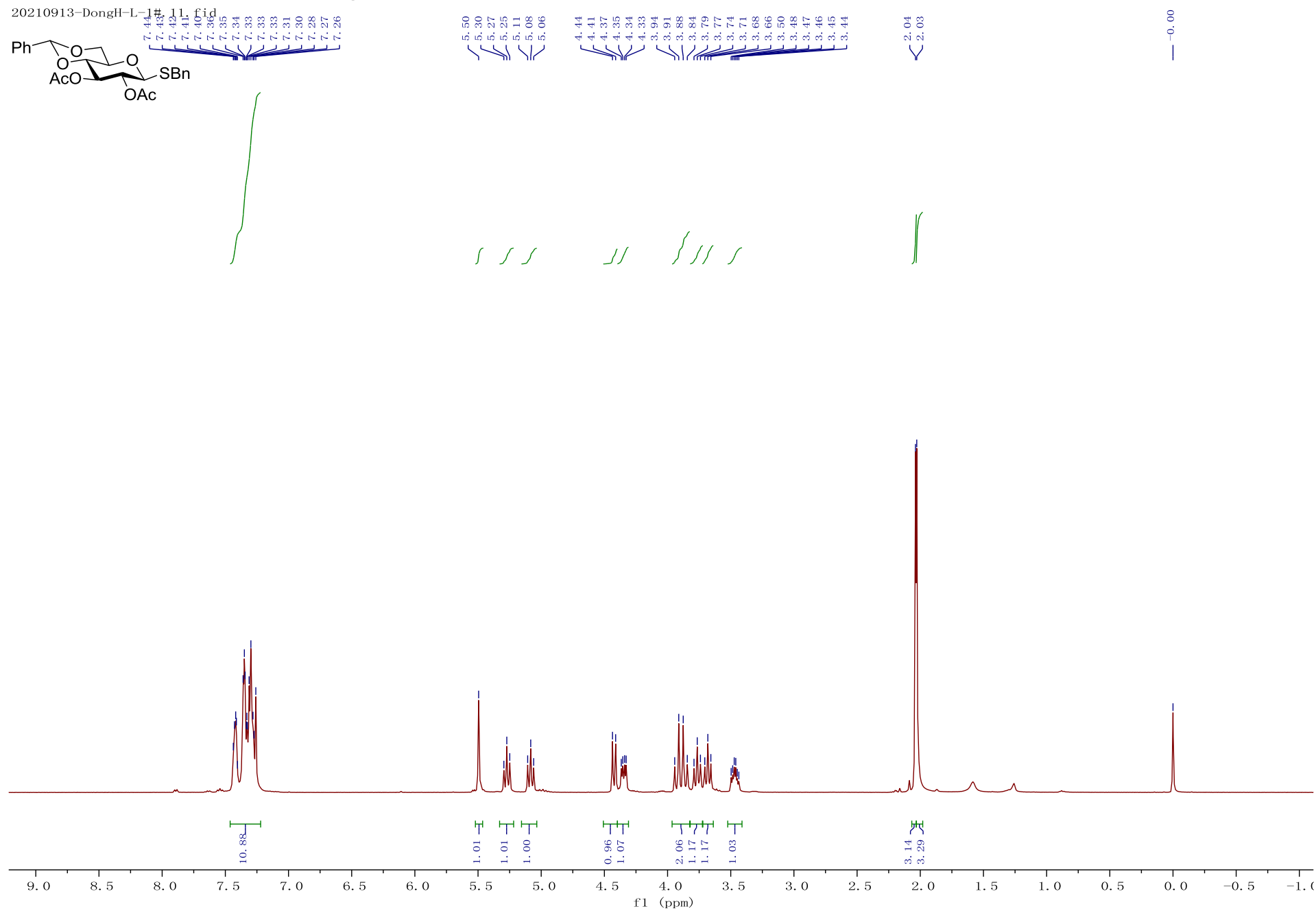


7.97
7.95
7.93
7.51
7.49
7.39
7.38
7.37
7.36
7.35

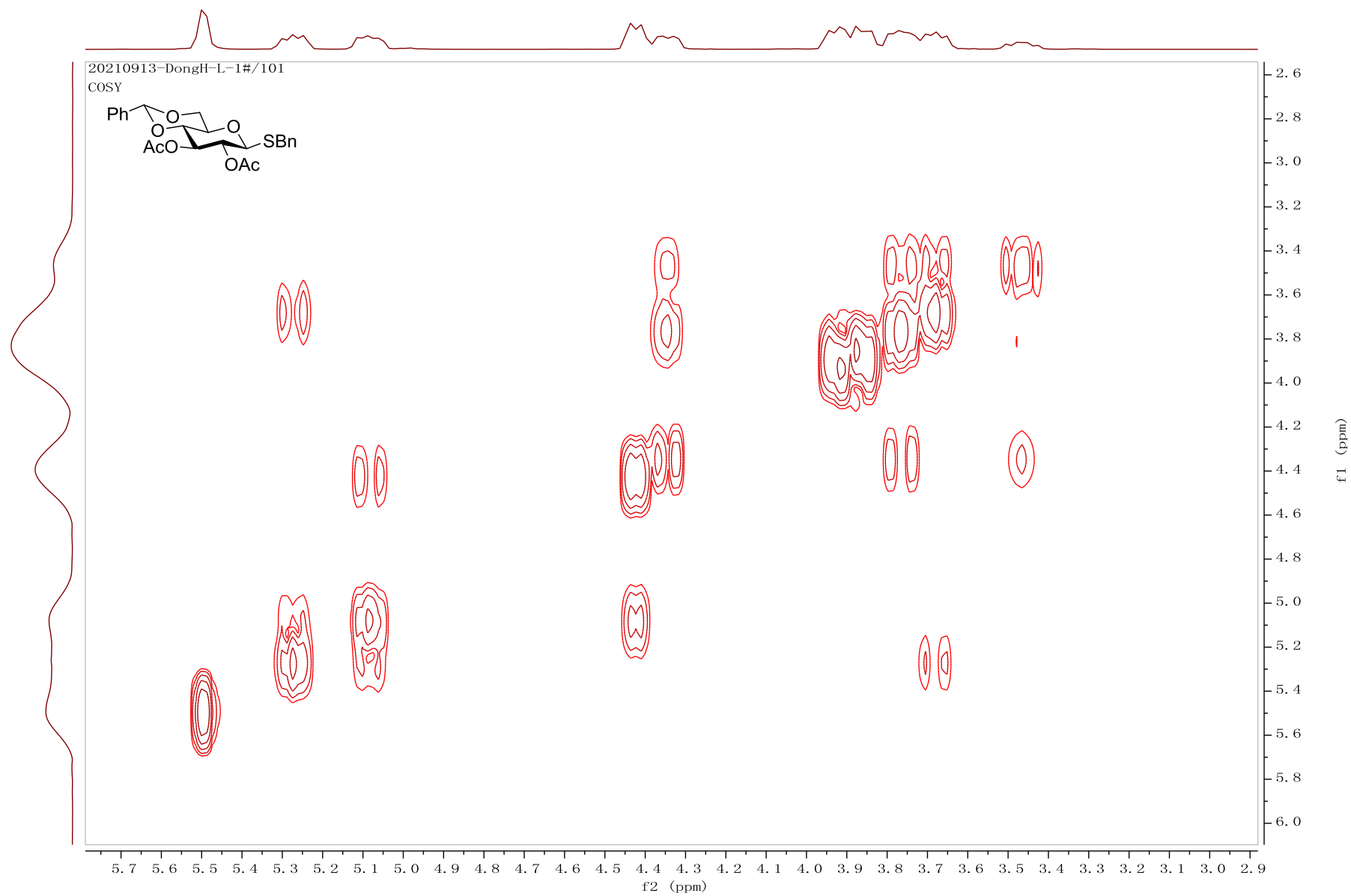
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5.41
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4.65
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4.03
4.01
4.00
3.98
3.96
3.94
3.93
3.91
3.90
3.62
3.61
3.60
3.59
3.58
3.53



Benzyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside **11**

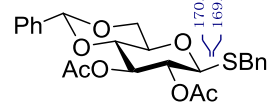


Benzyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside 11



Benzyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-1-thio- β -D-glucopyranoside **11**

20210913-DongH-L-11-21.fid



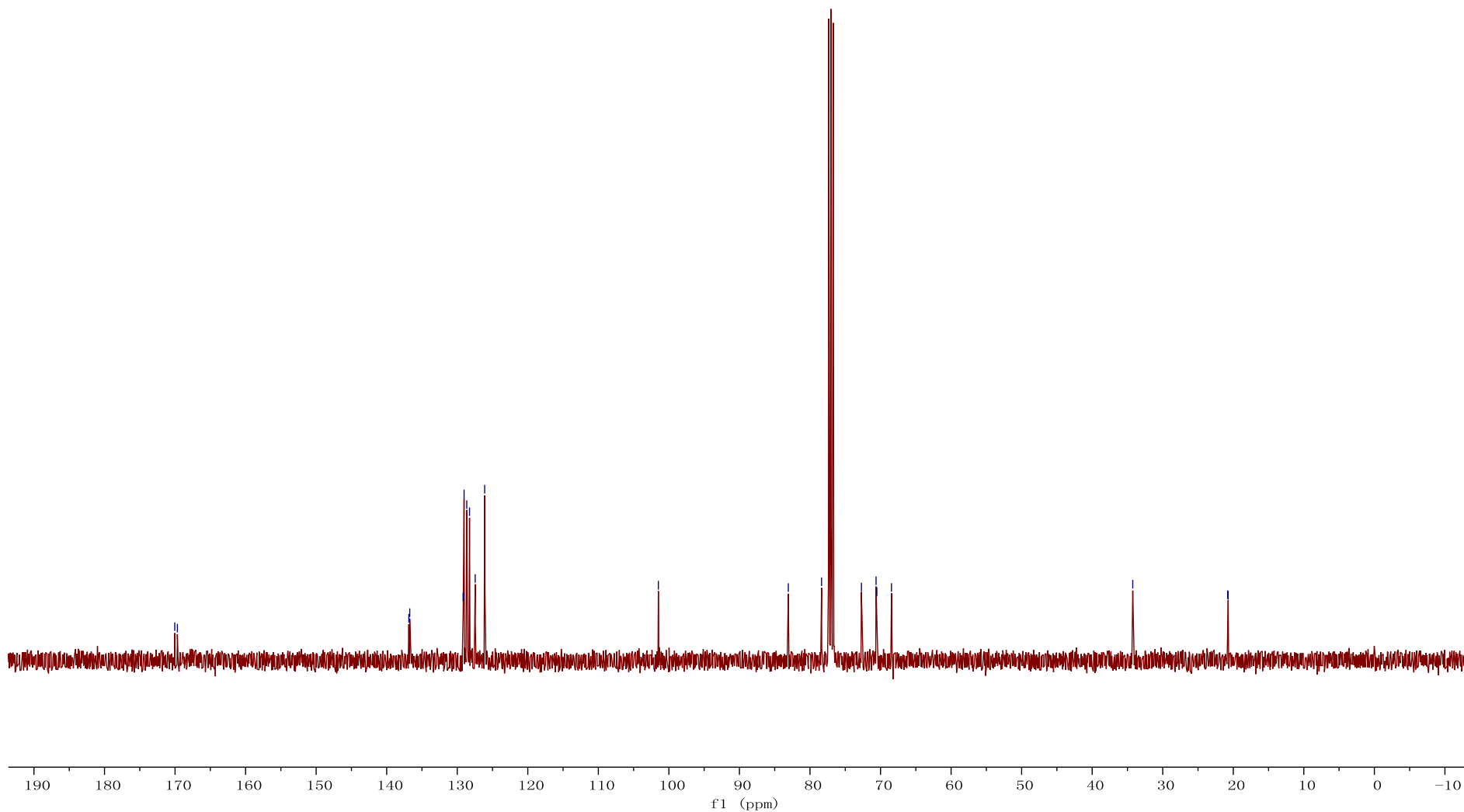
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129.16
129.03
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128.26
127.45
126.12

101.49

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78.36
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70.64
70.52
68.45

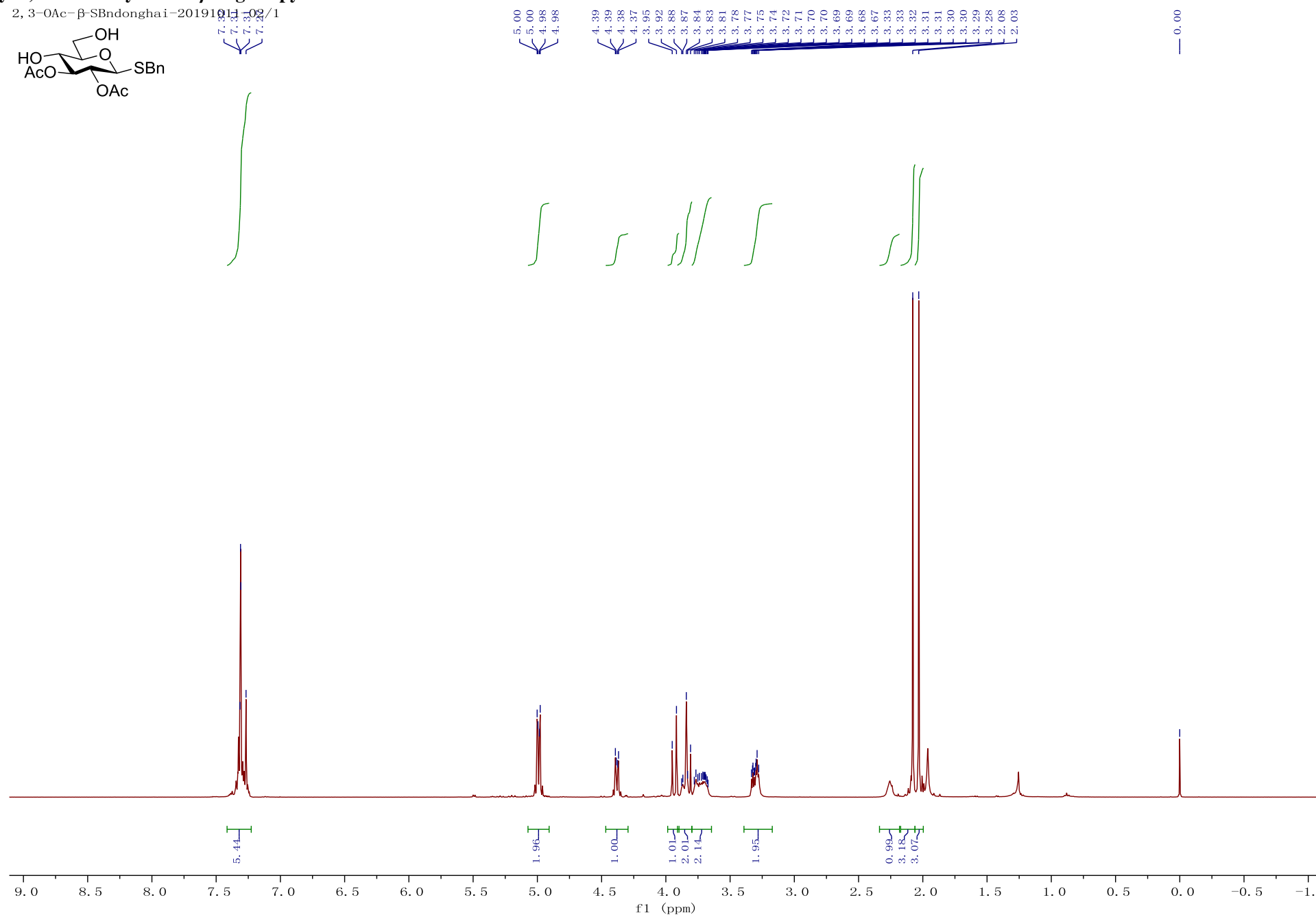
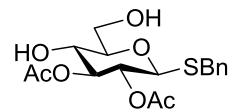
34.25

20.79
20.72

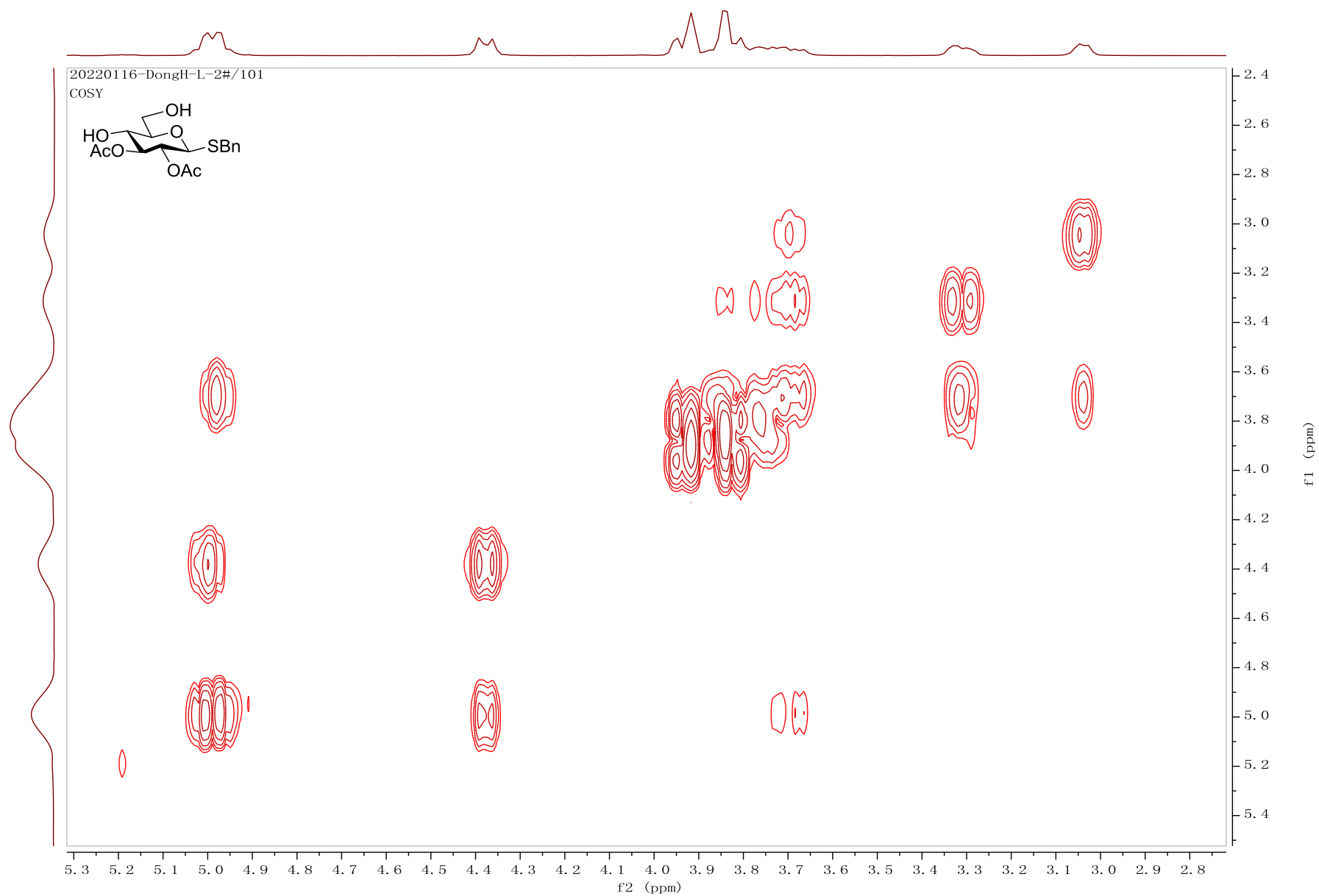


Benzyl 2,3-di-*O*-acetyl-1-thio- β -D-glucopyranoside 12

2, 3-OAc- β -SBndonghai-20191011-08/1

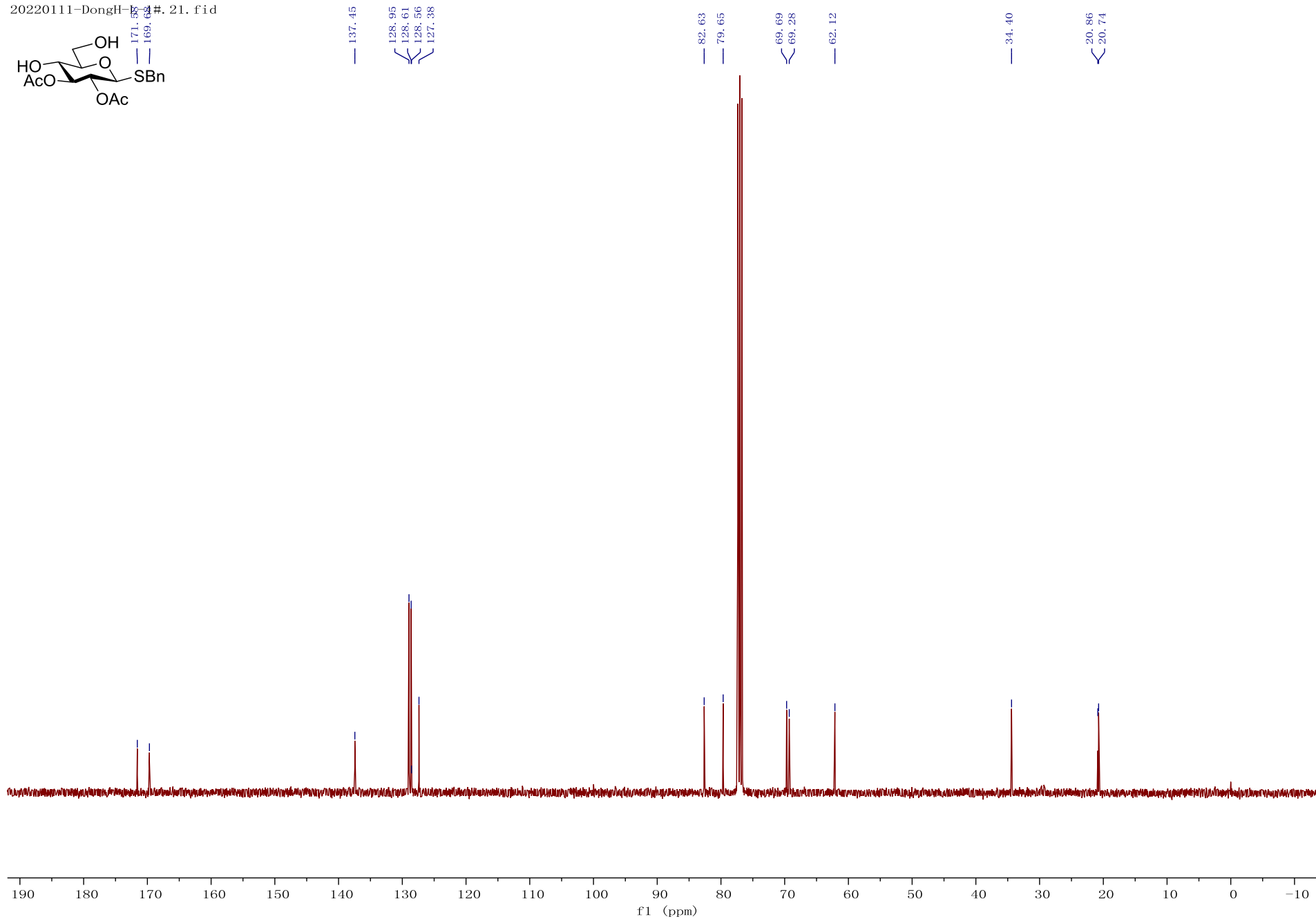
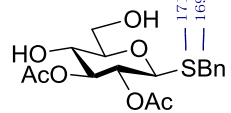


Benzyl 2,3-di-*O*-acetyl-1-thio- β -D-glucopyranoside 12



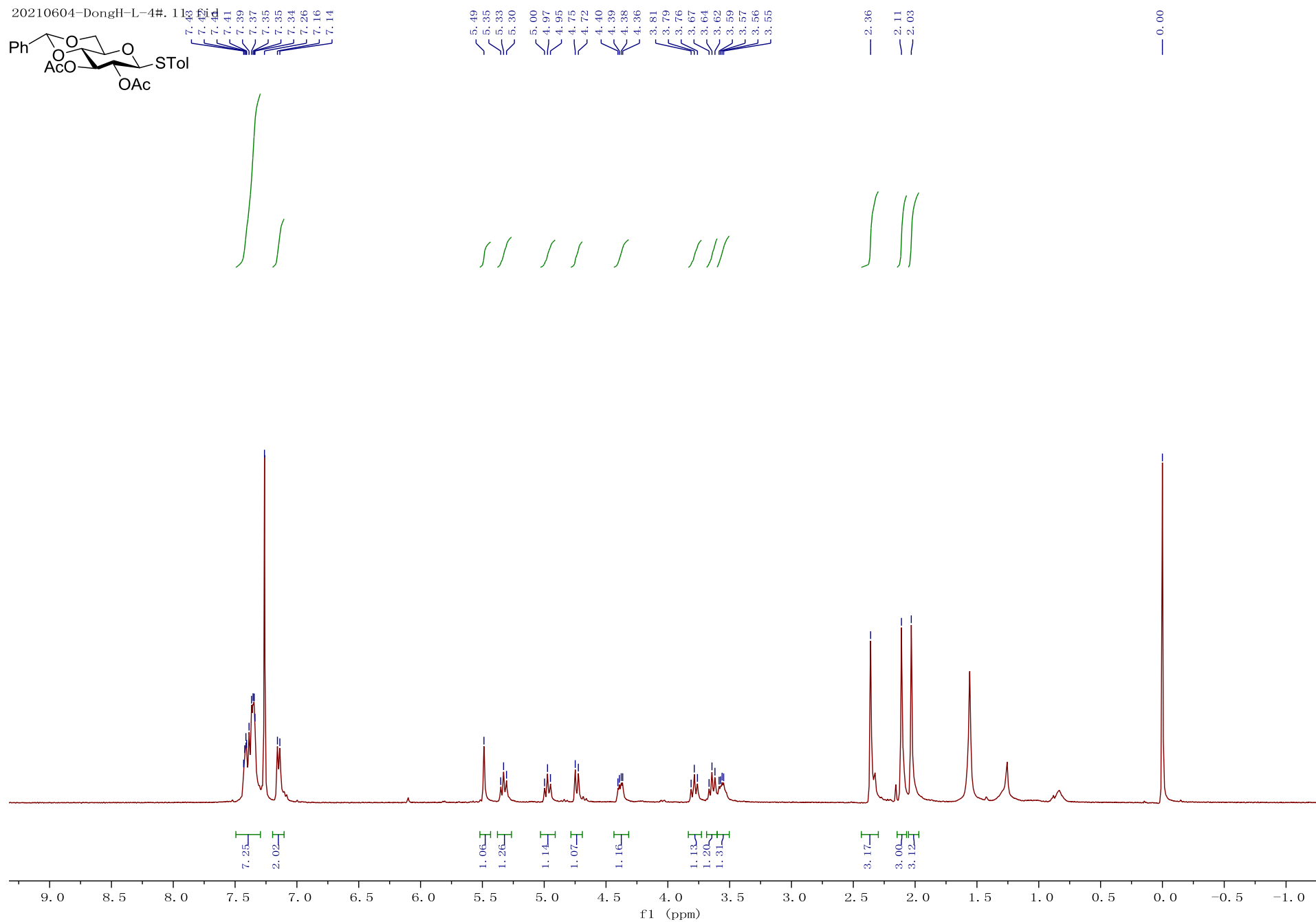
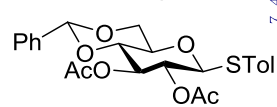
Benzyl 2,3-di-*O*-acetyl-1-thio- β -D-glucopyranoside 12

20220111-DongH-84#. 21. fid



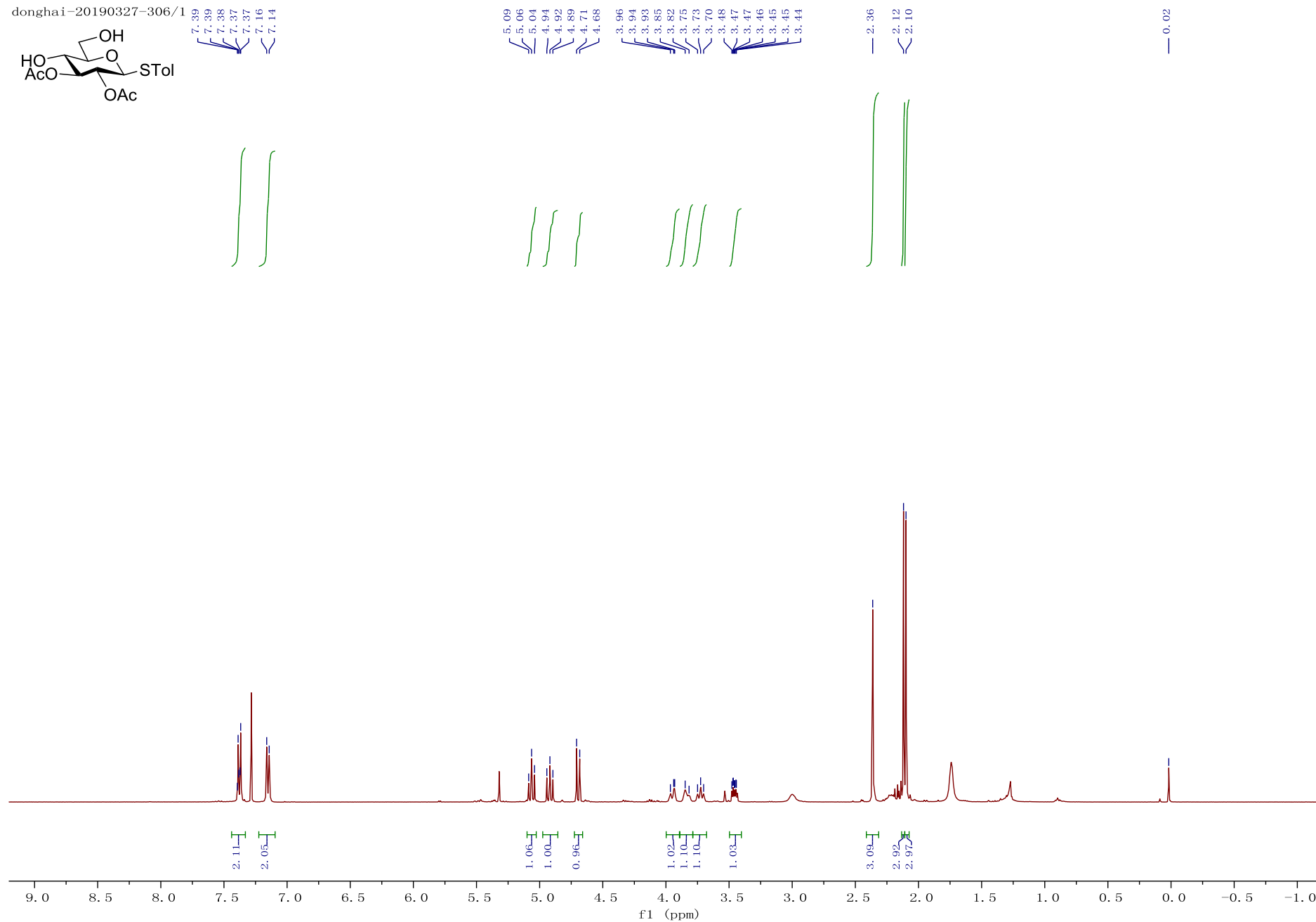
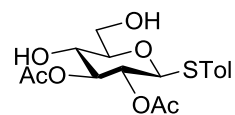
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20210604-DongH-L-4#. 11

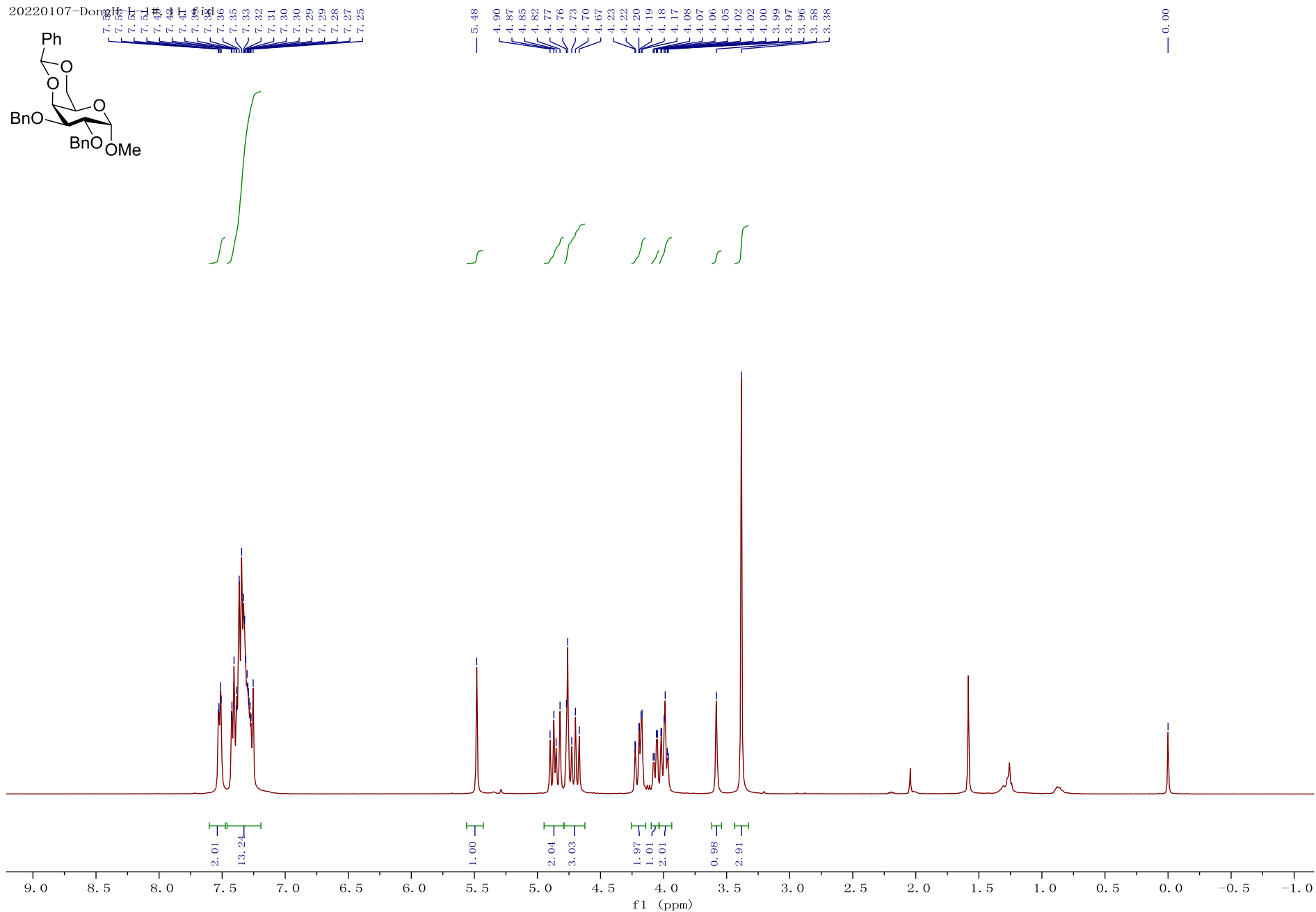


4-Methylphenyl 2,3-di-*O*-acetyl-1-thio- β -D-glucopyranoside 14

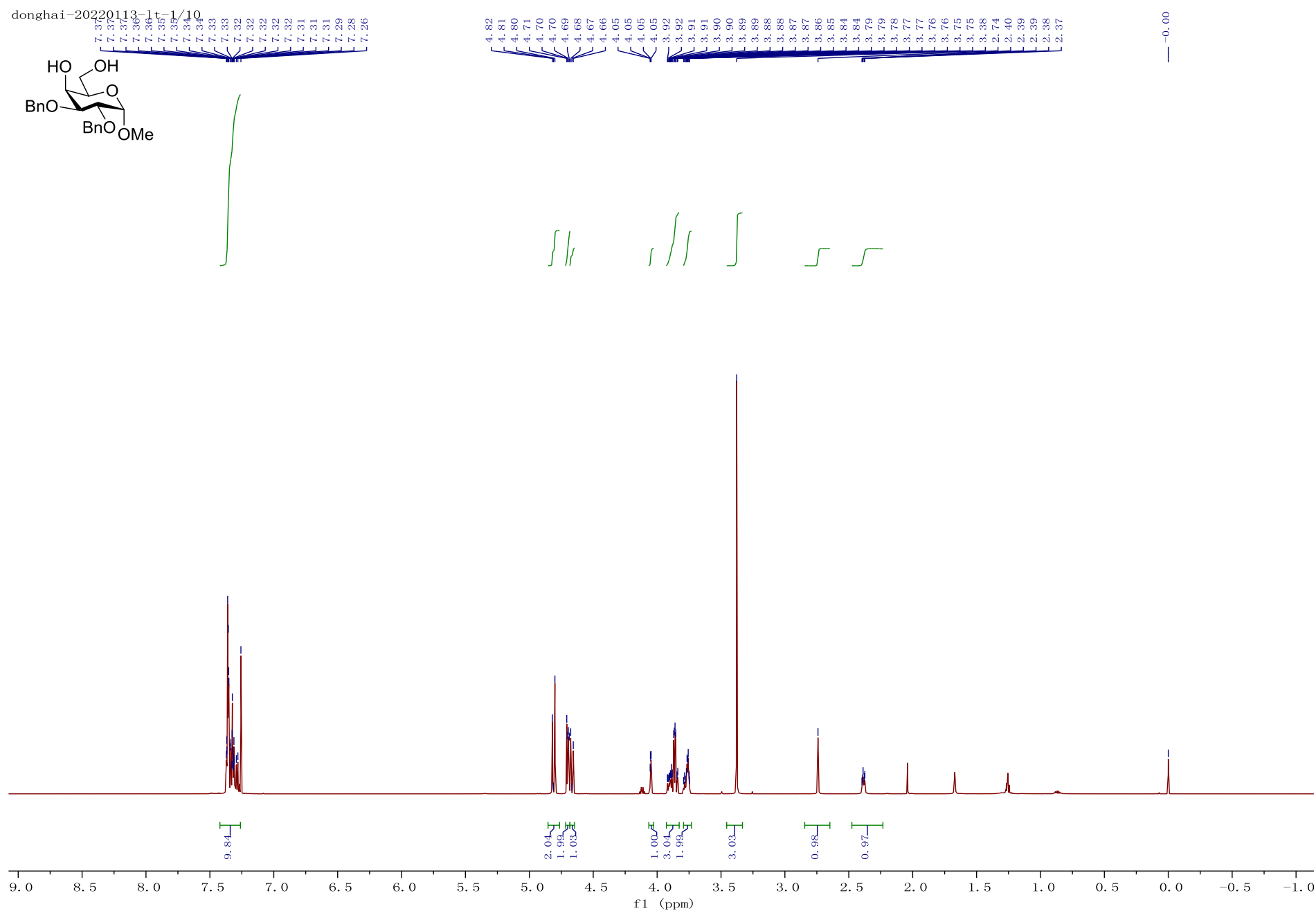
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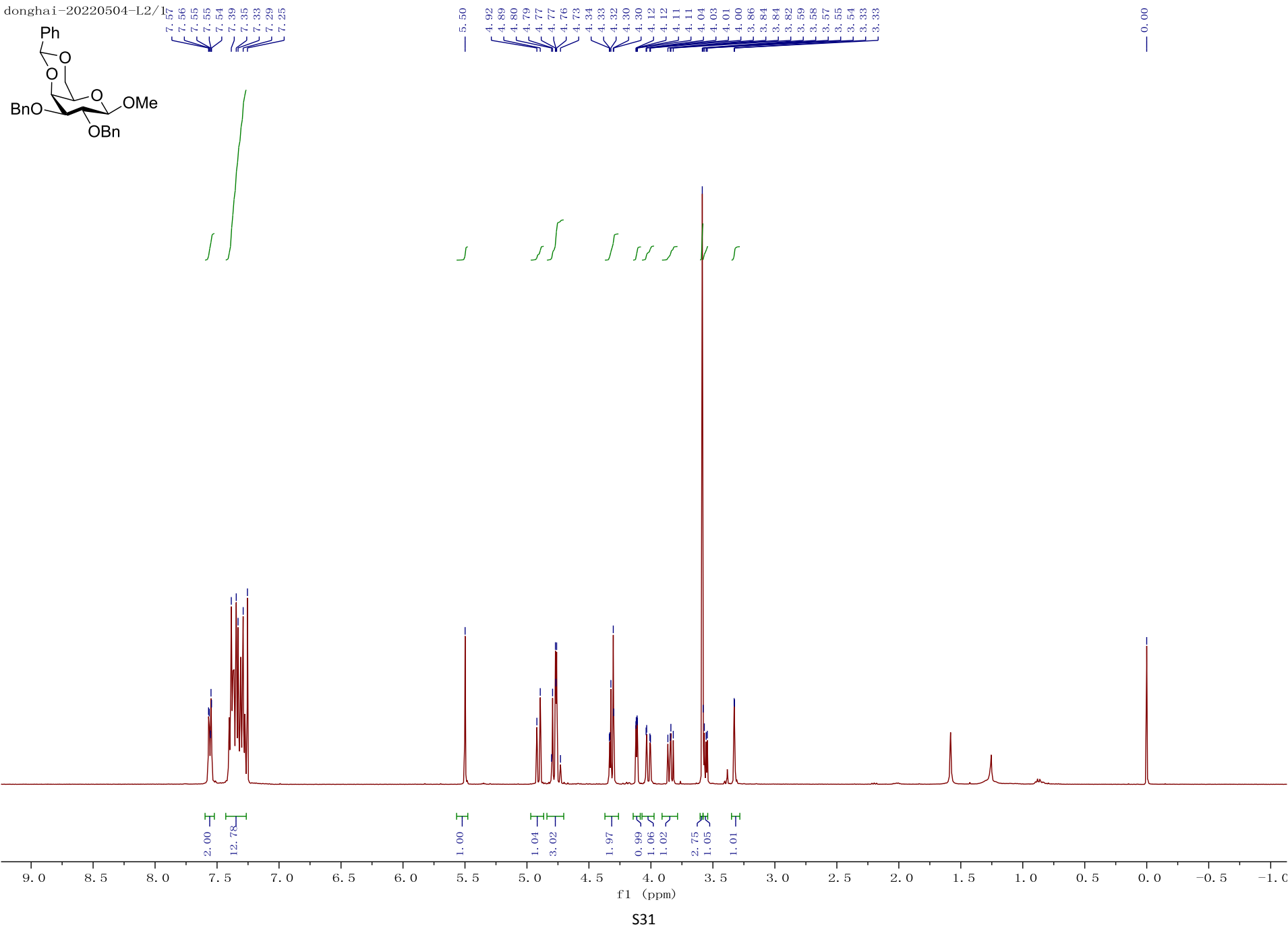
Methyl 2,3-di-O-benzyl-4,6-O-benzylidene- α -D-galactopyranoside 15



Methyl 2,3-di-*O*-benzyl- α -D-galactopyranoside 16

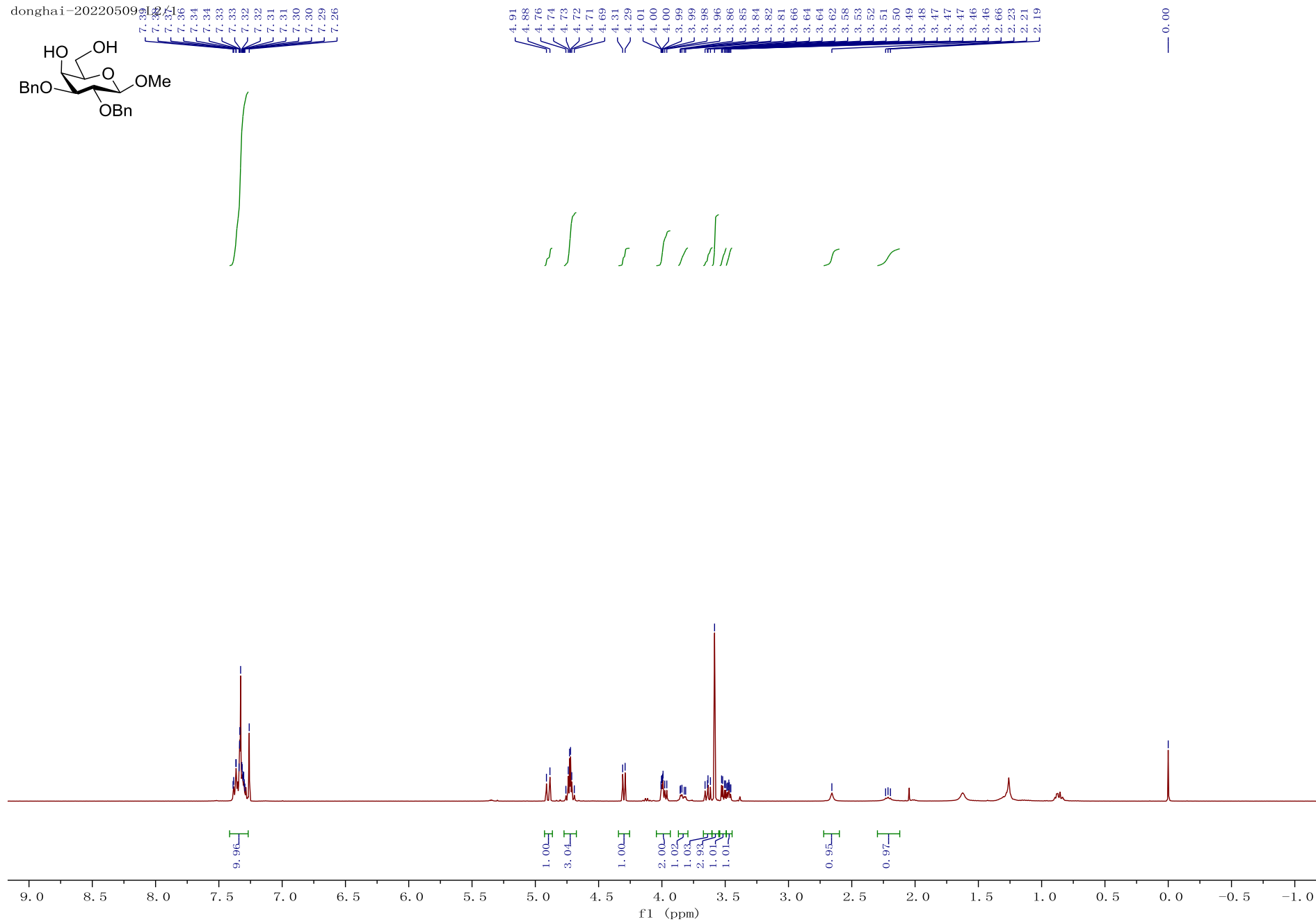
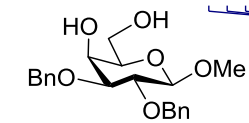


Methyl 2,3-di-O-benzyl-4,6-O-benzylidene-β-D-galactopyranoside 17



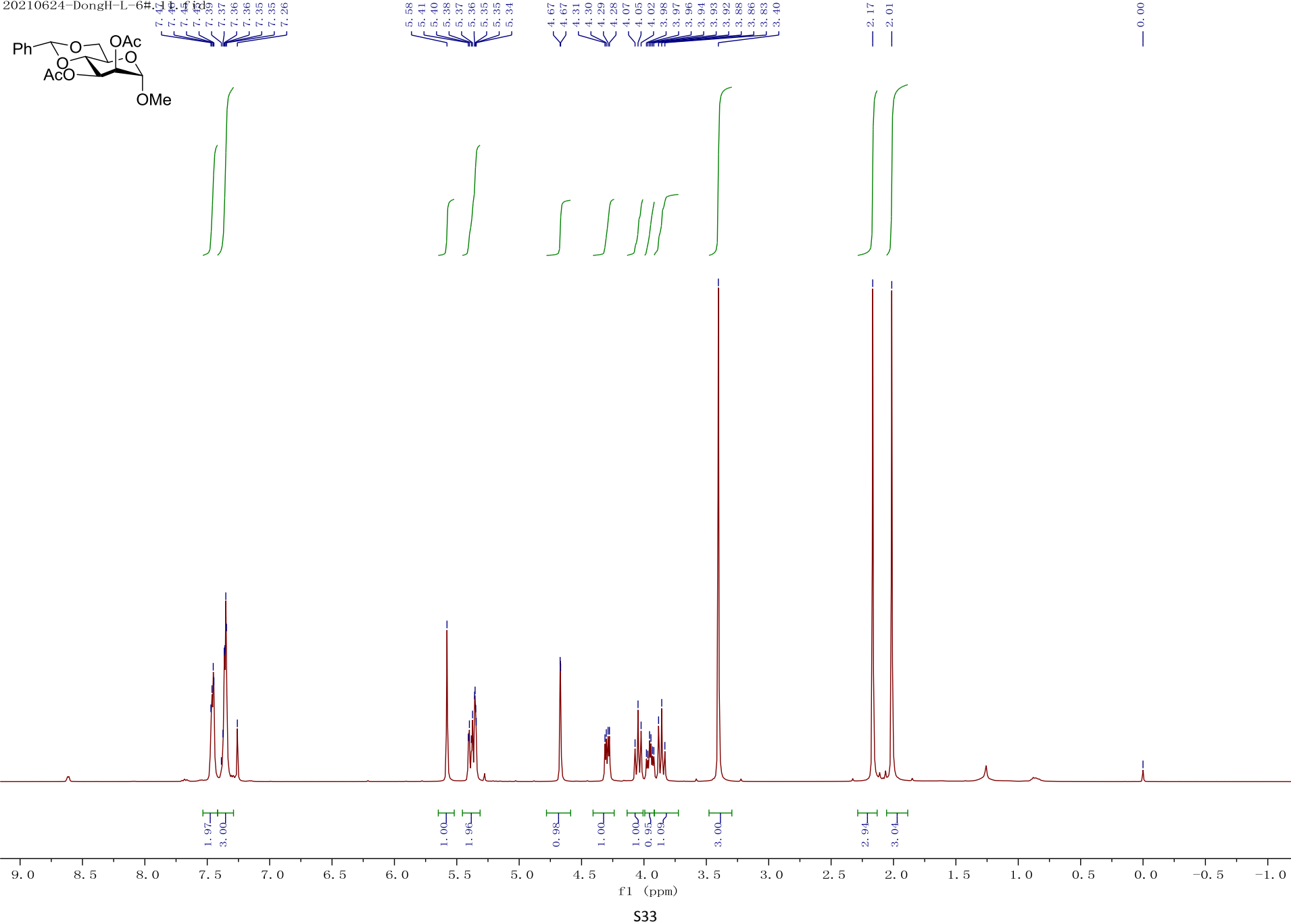
Methyl 2,3-di-*O*-benzyl- β -D-galactopyranoside 18

donghai-20220509-12



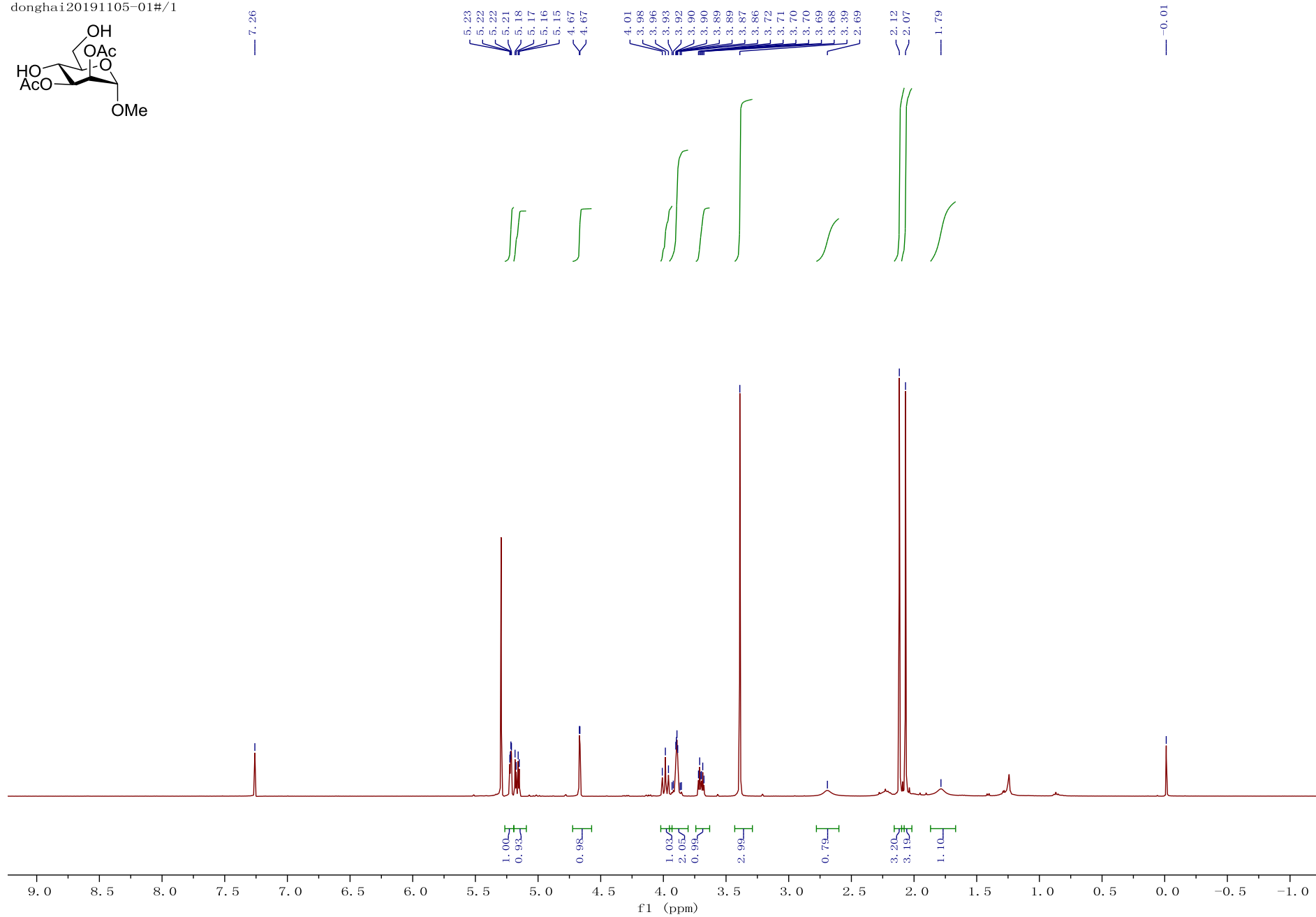
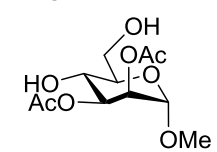
Methyl 2,3-di-O-acetyl-4,6-O-benzylidene- α -D-mannopyranoside 19

20210624-DongH-L-6#14

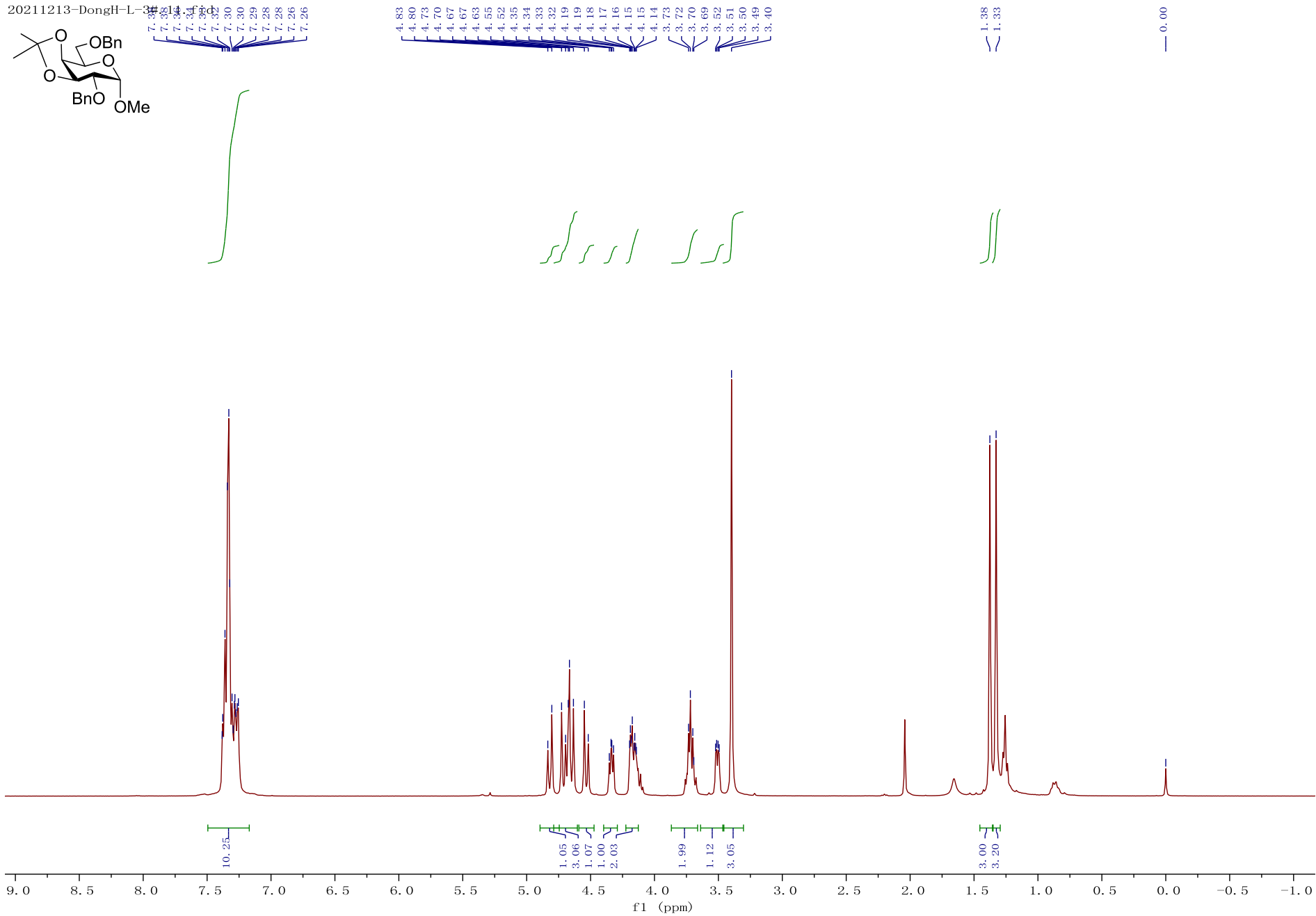


Methyl 2,3-di-*O*-acetyl- α -D-mannopyranoside 20

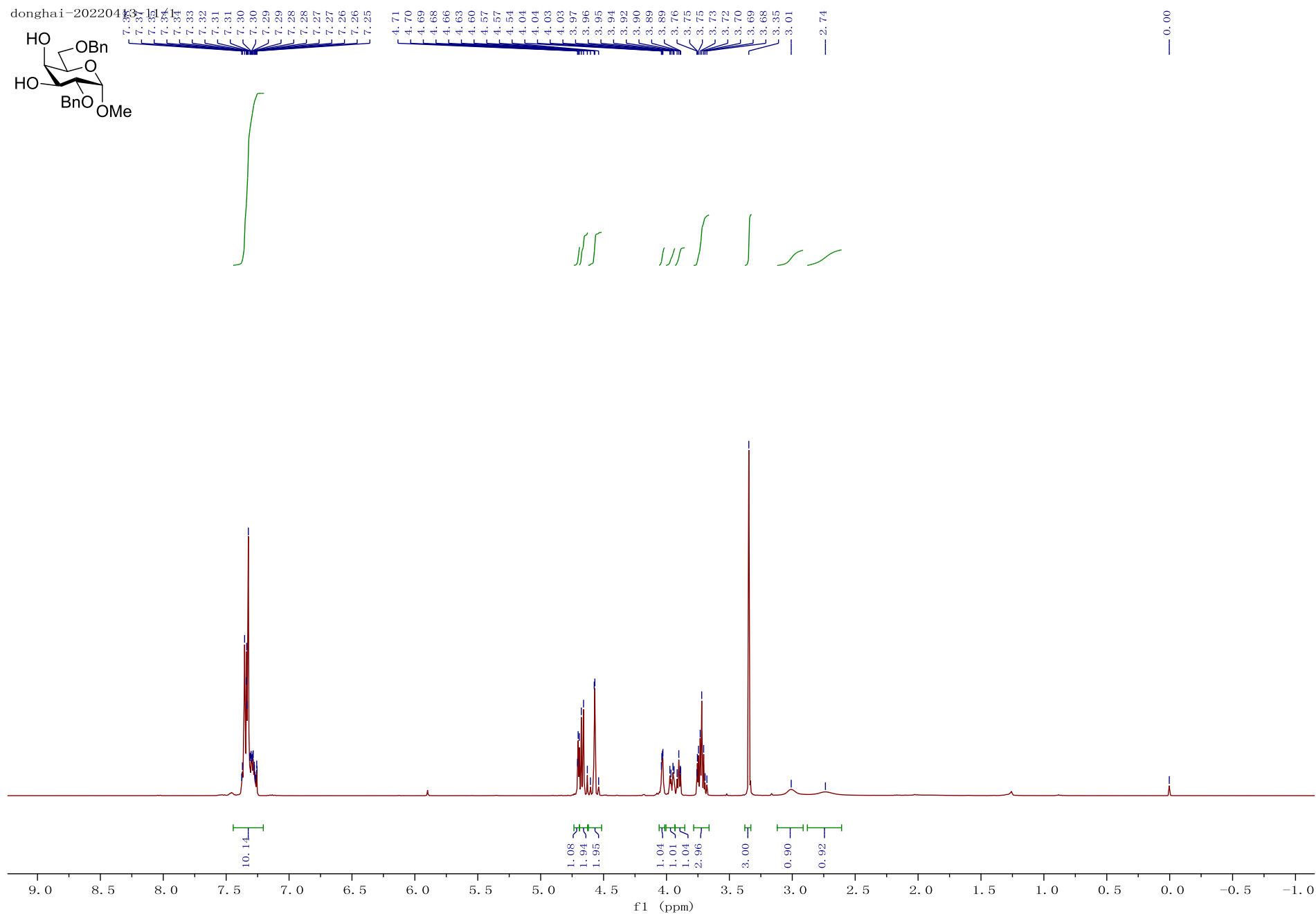
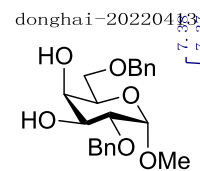
donghai20191105-01#/1



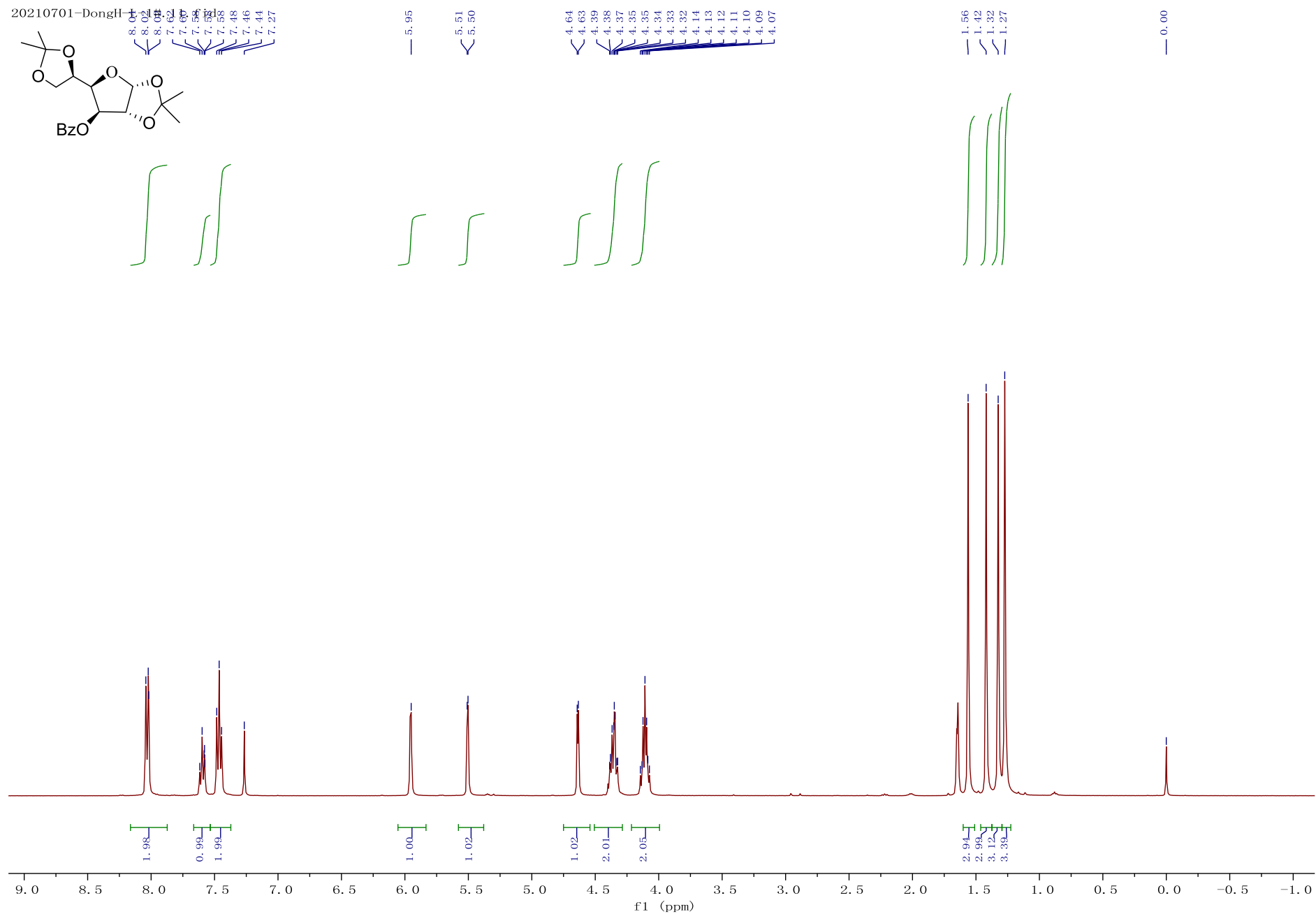
Methyl 2,6-di-O-benzyl 3,4-O-isopropylidene- α -D-galactopyranoside 21



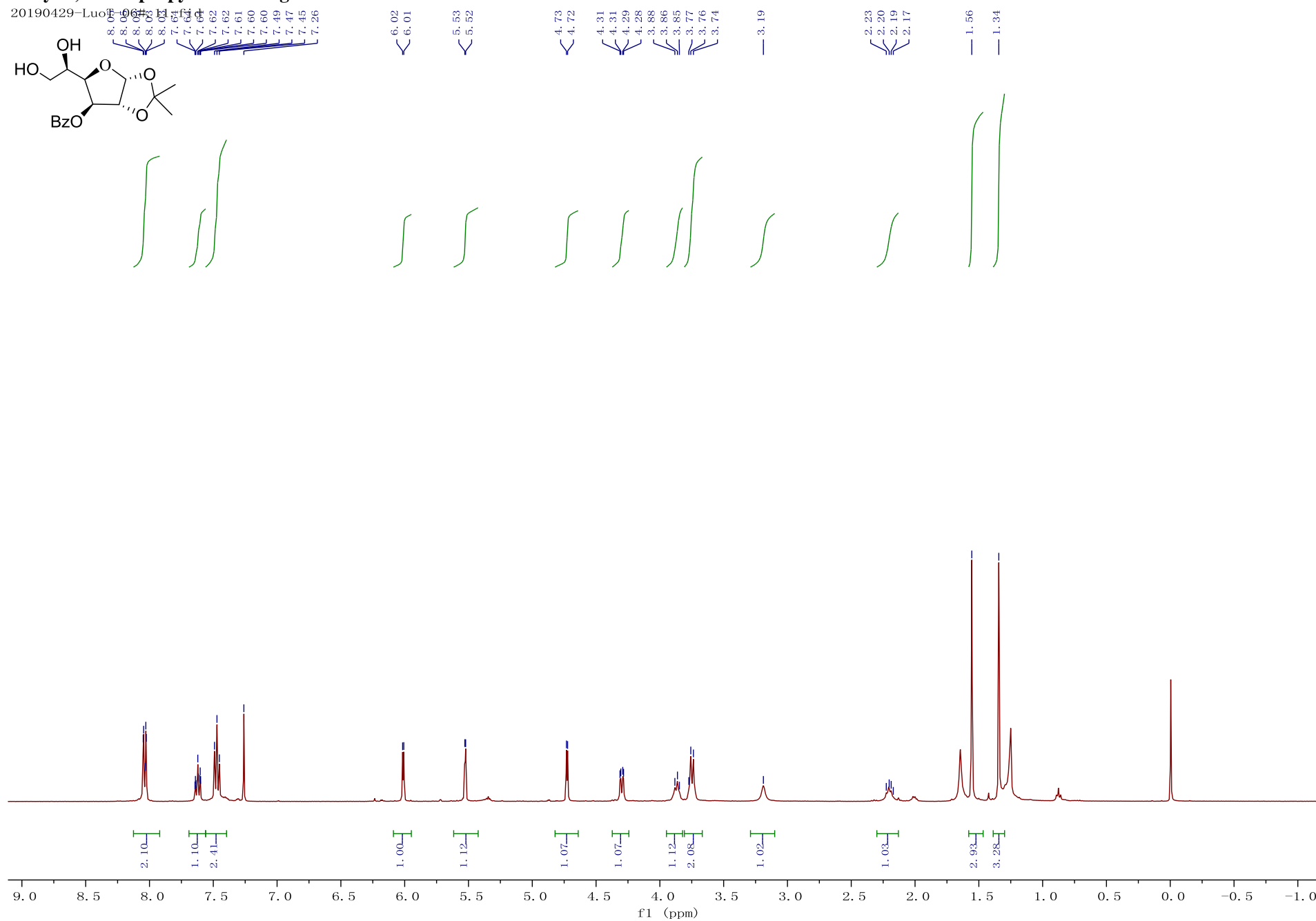
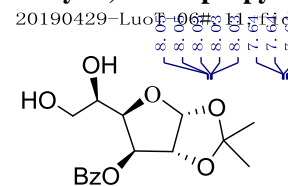
Methyl 2,6-di-*O*-benzyl- α -D-galactopyranoside 22



1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzoyl- α -D-glucufuranose **23**

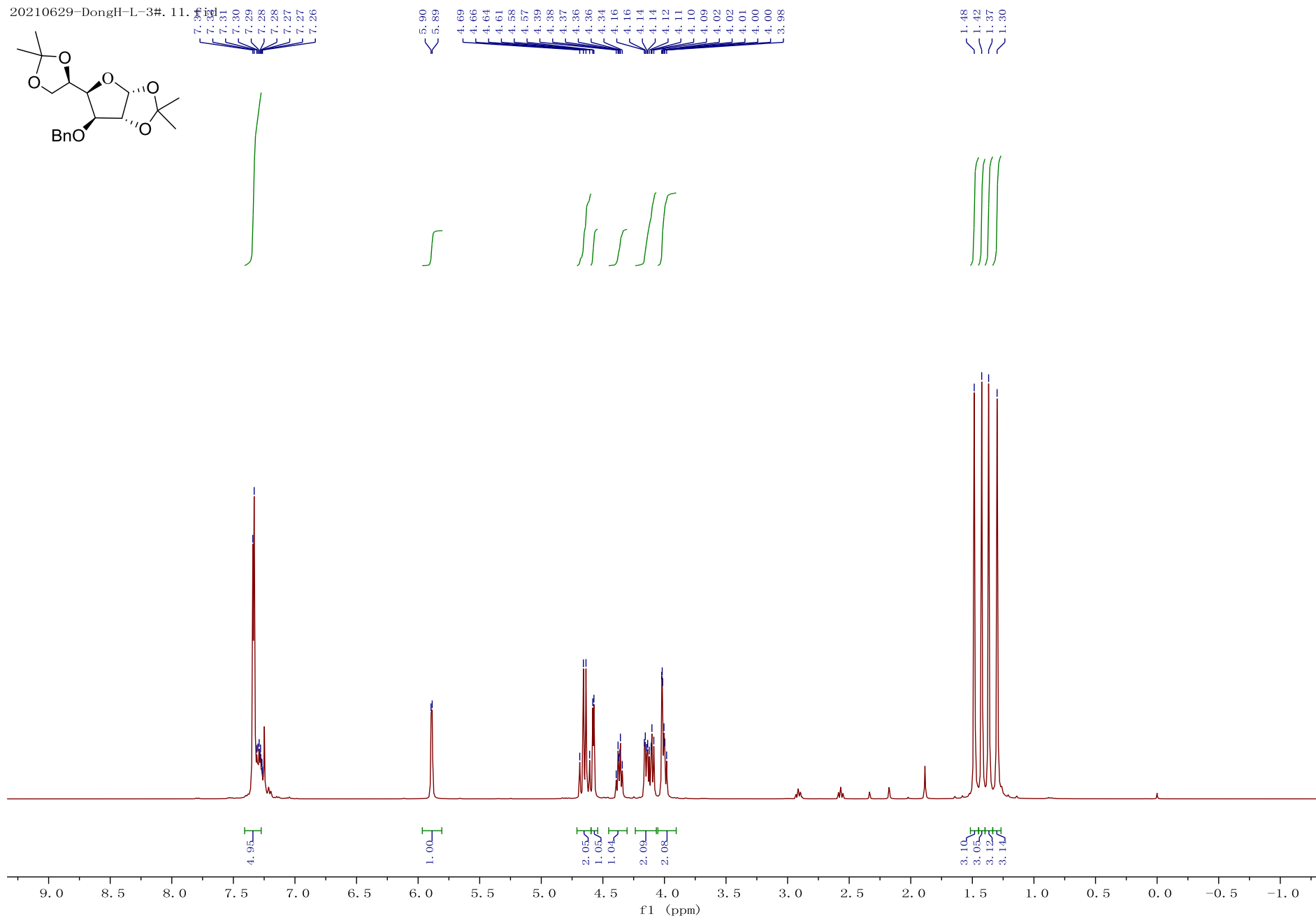
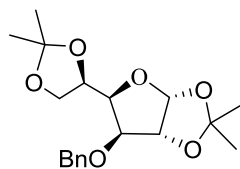


3-*O*-Benzoyl-1,2-*O*-isopropylidene- α -D-glucofuranose 24

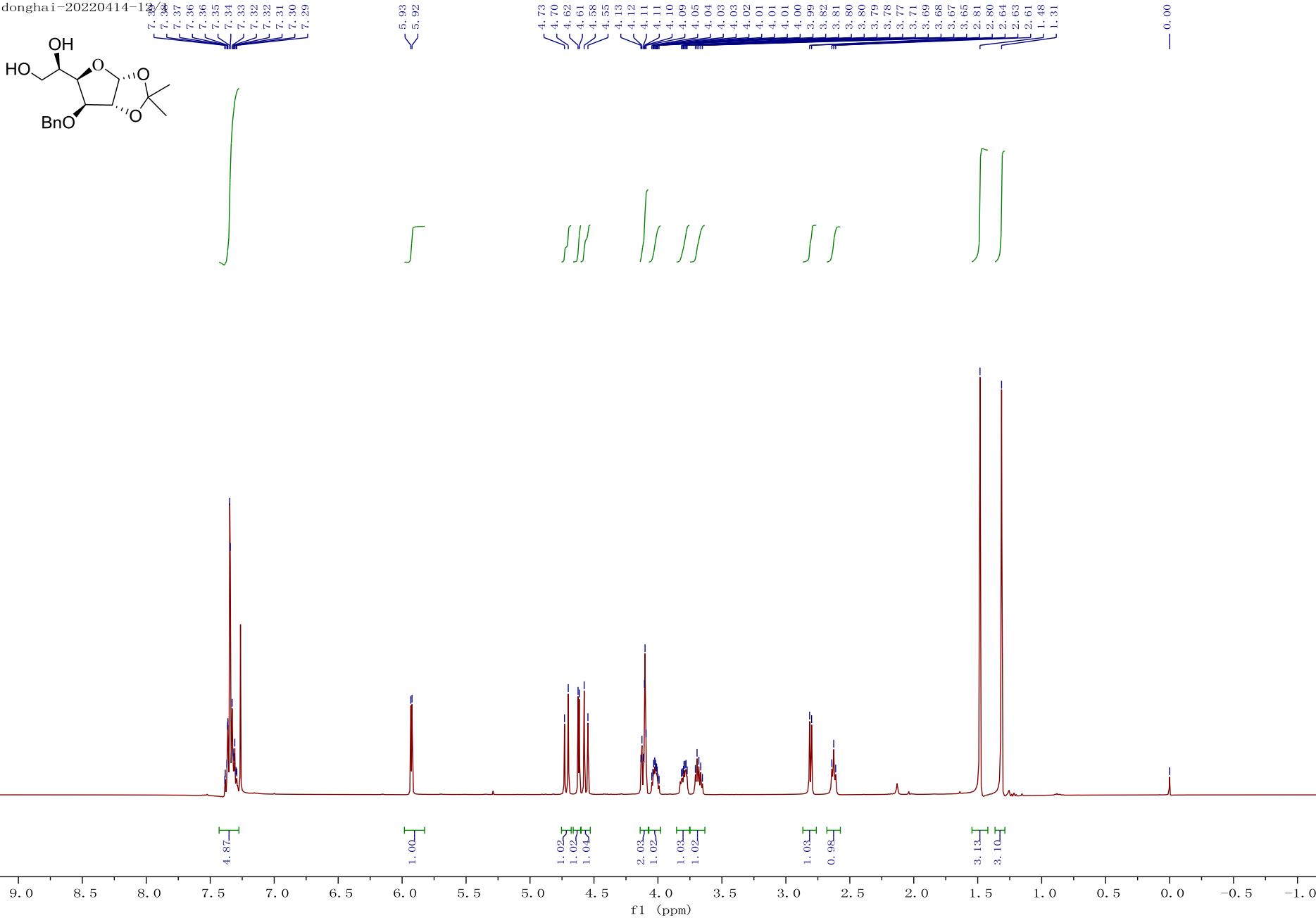


1,2:5,6-Di-*O*-isopropylidene-3-*O*-benzyl- α -D-glucofuranose 25

20210629-DongH-L-3#. 11.

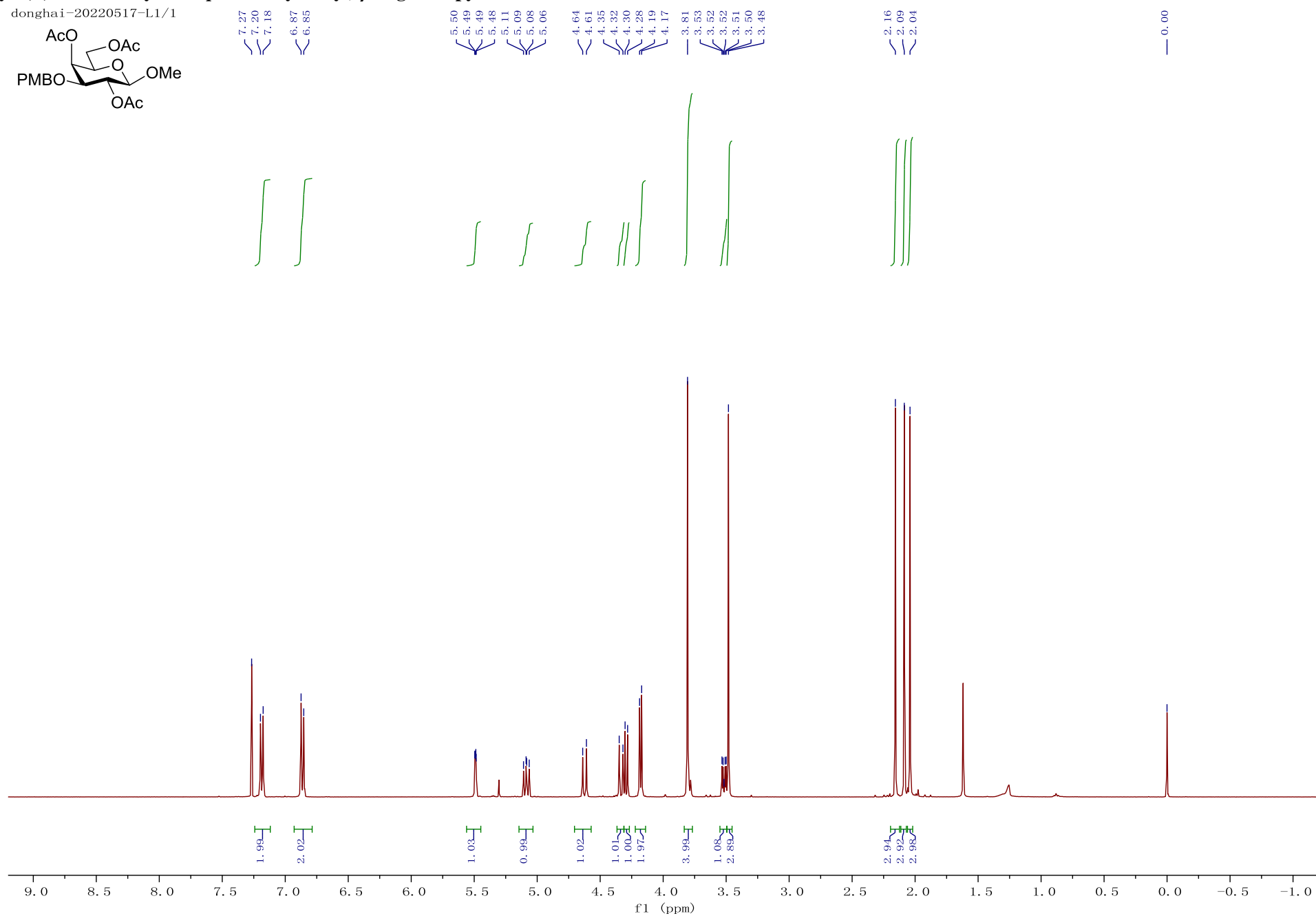


3-O-Benzyl-1,2-O-isopropylidene- α -D-glucofuranose 26

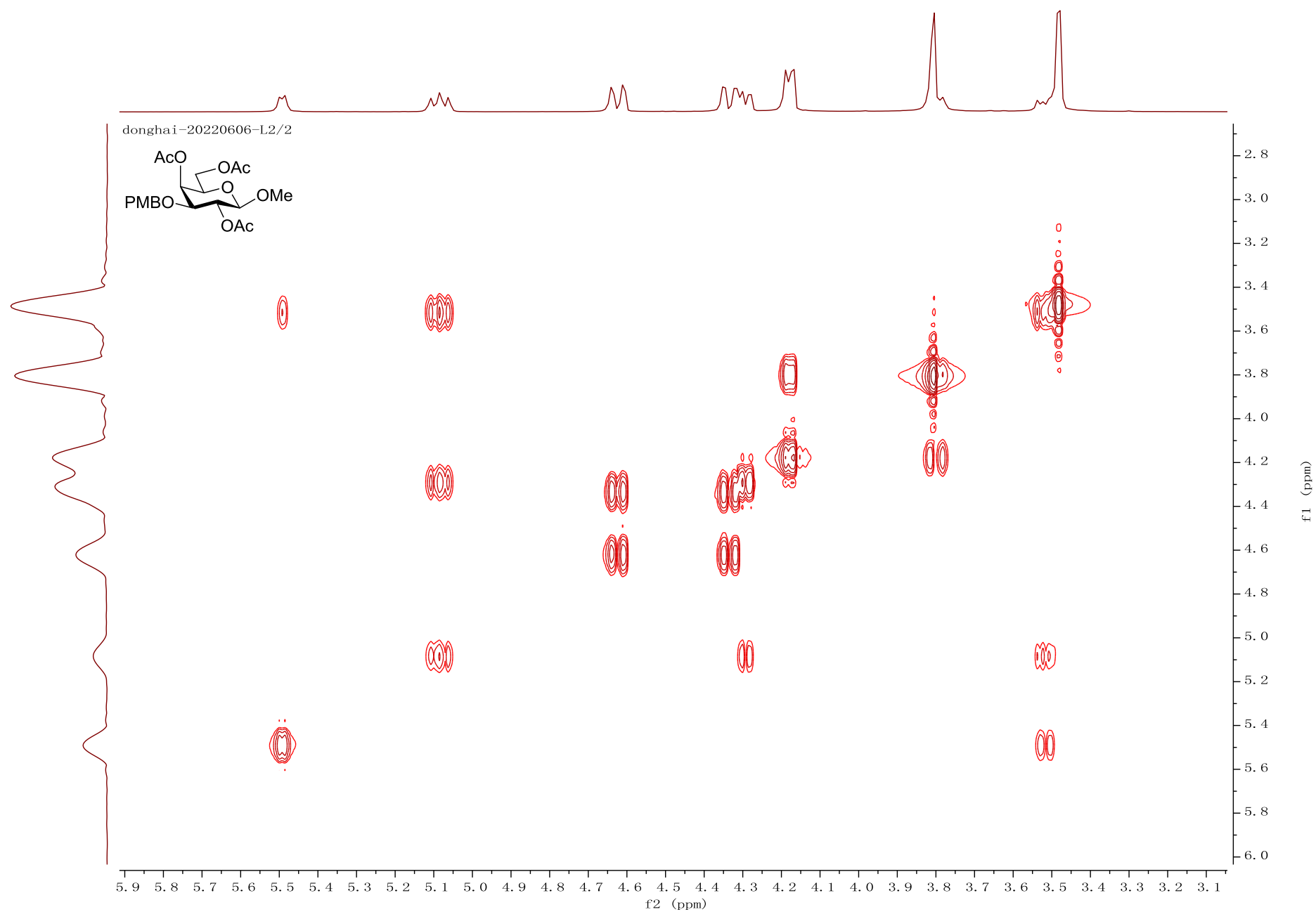


Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- β -D-galactopyranoside 27

donghai-20220517-L1/1

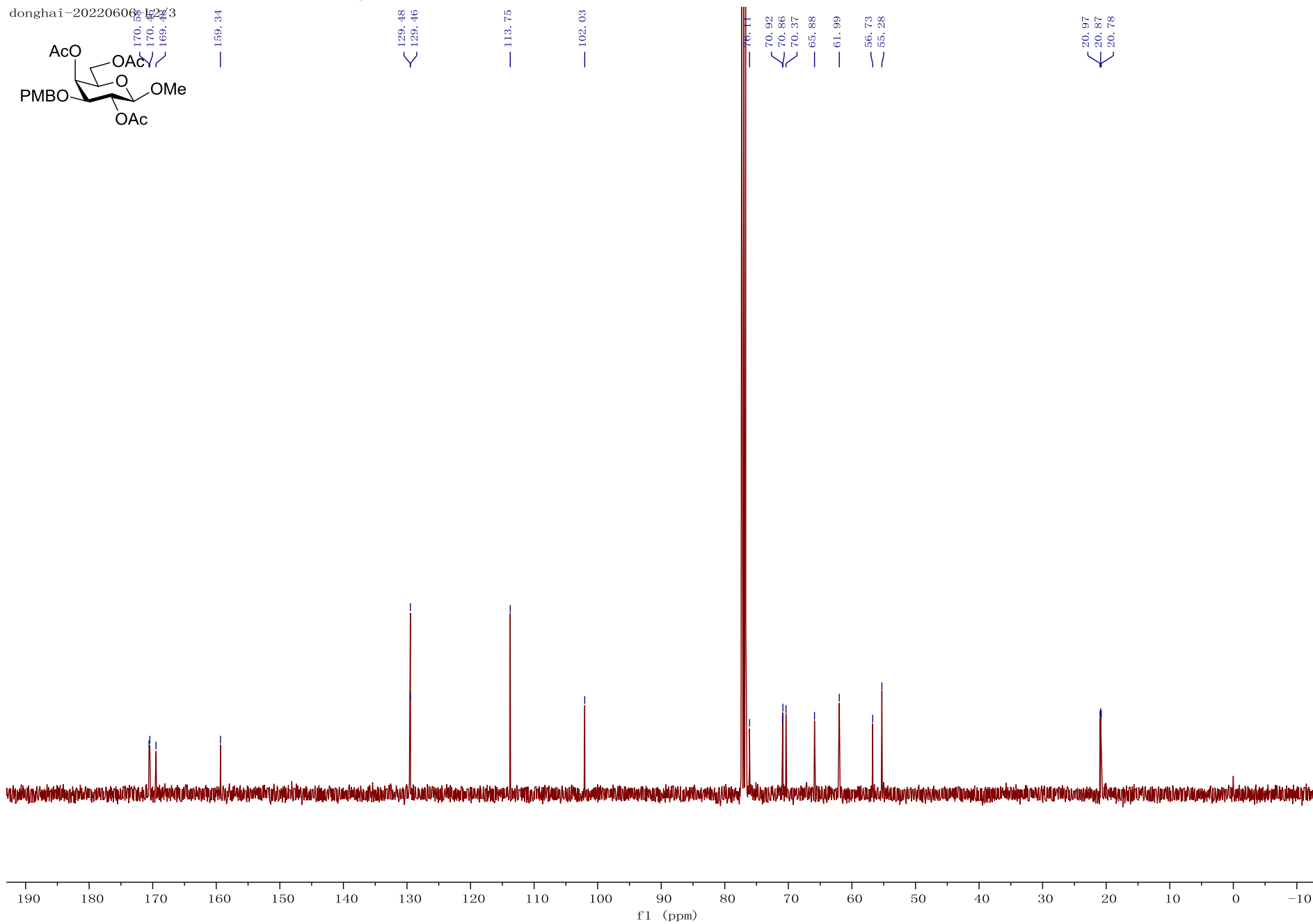
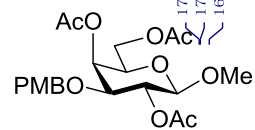


Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- β -D-galactopyranoside **27**



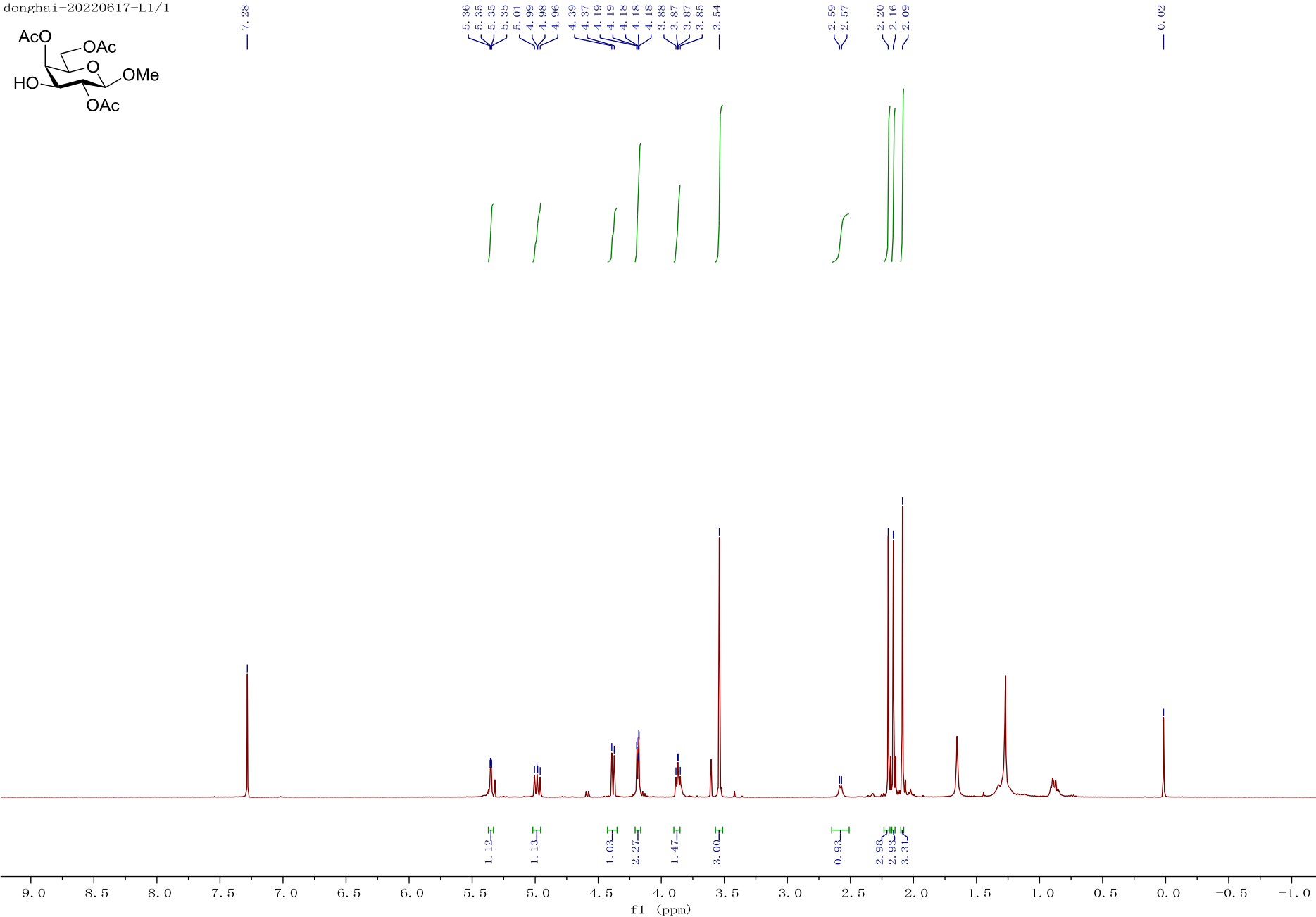
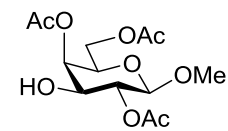
Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- β -D-galactopyranoside 27

donghai-20220606-15223



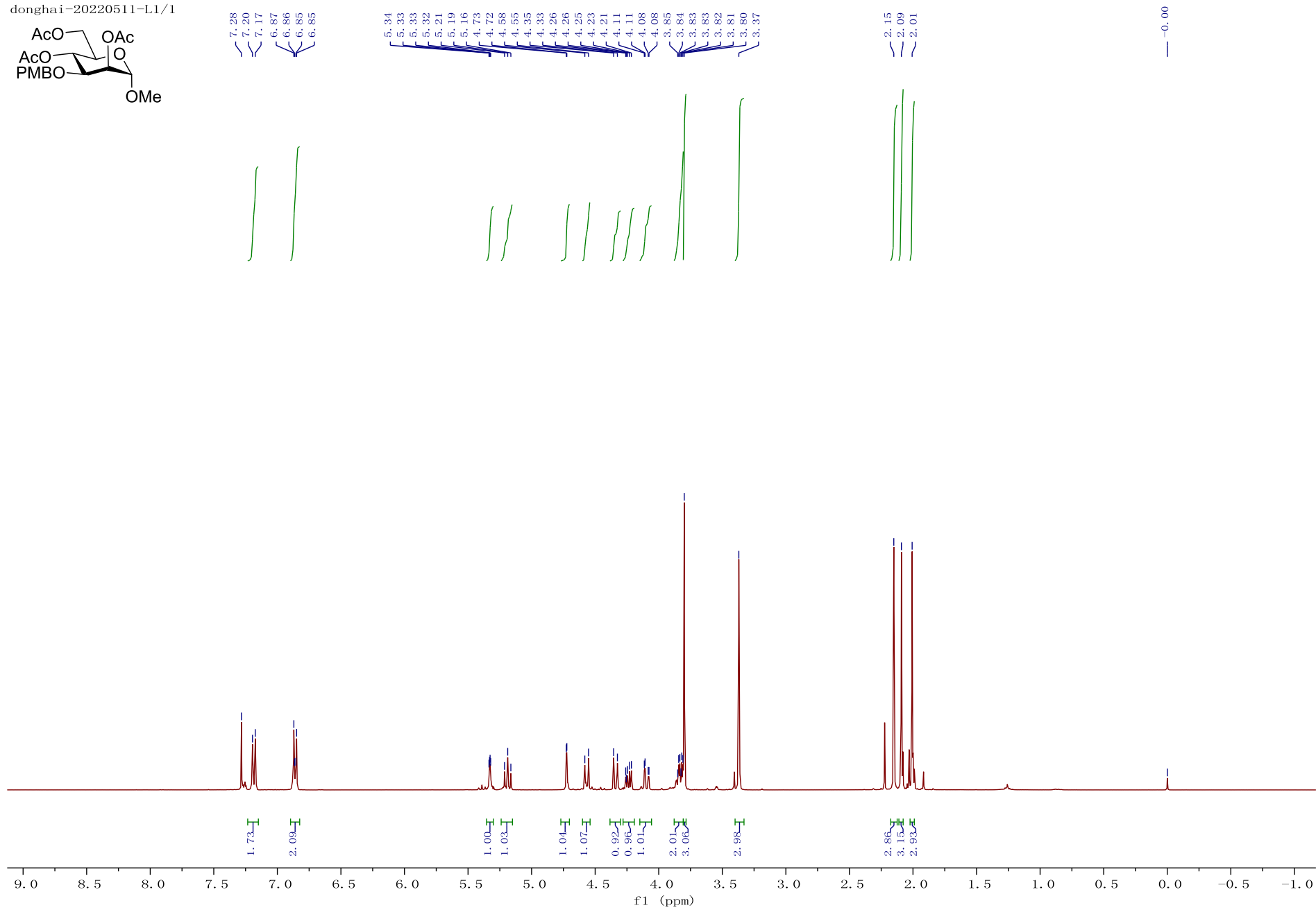
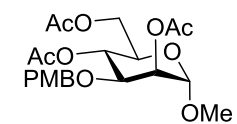
Methyl 2,4,6-tri-*O*-acetyl- β -D-galactopyranoside 28

donghai-20220617-L1/1

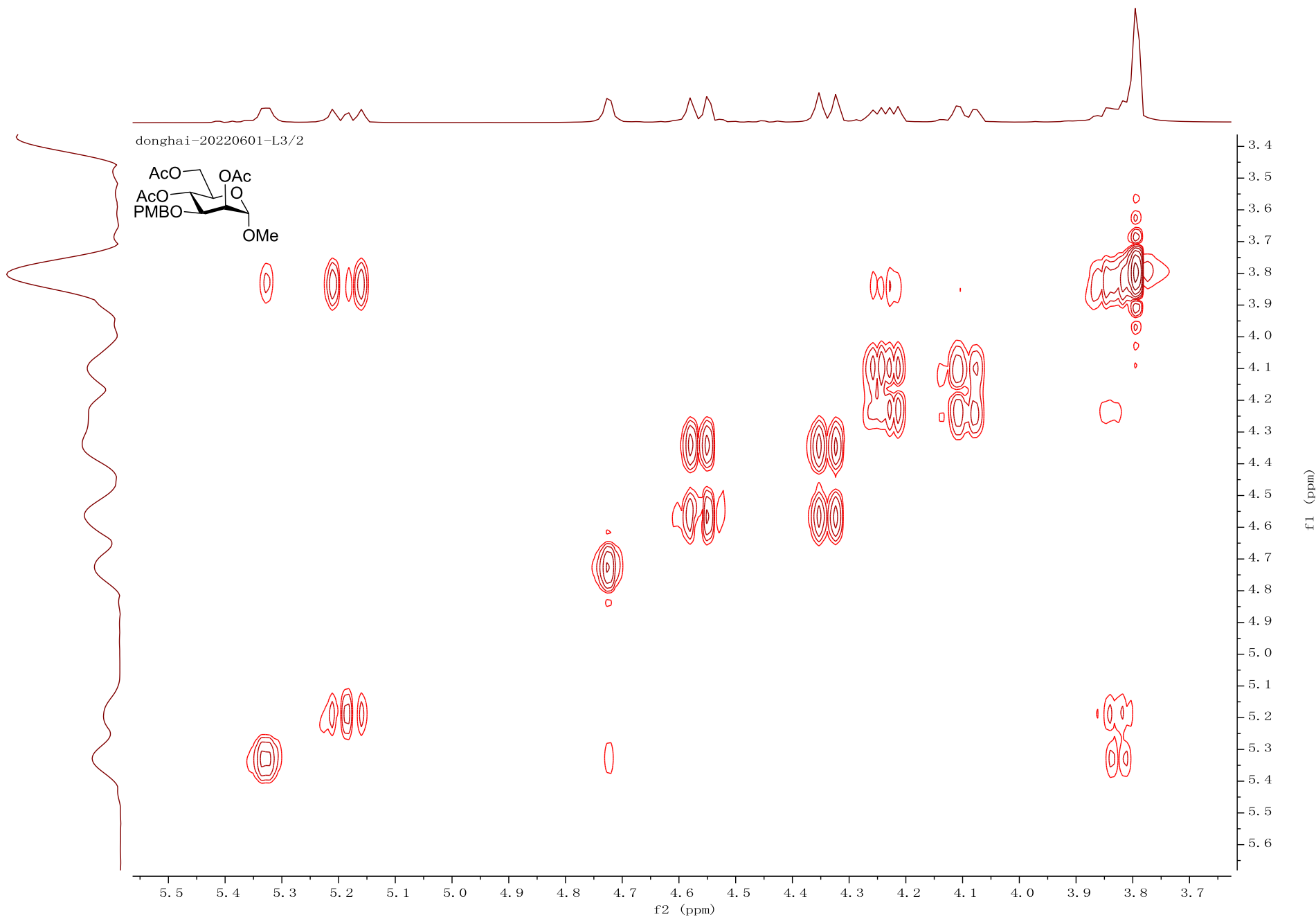


Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- α -D-mannopyranoside 29

donghai-20220511-L1/1

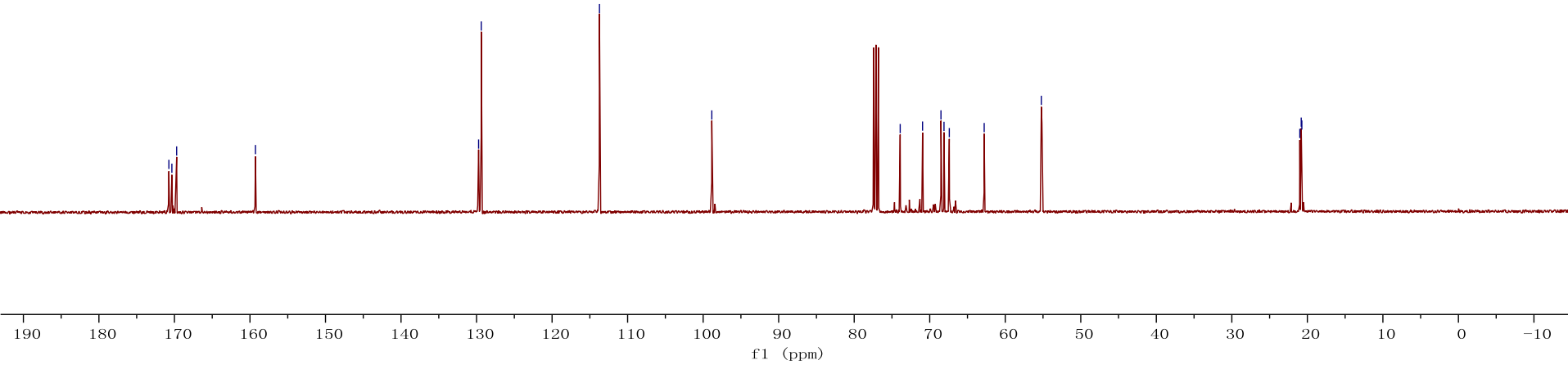
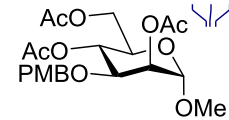


Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- α -D-mannopyranoside 29



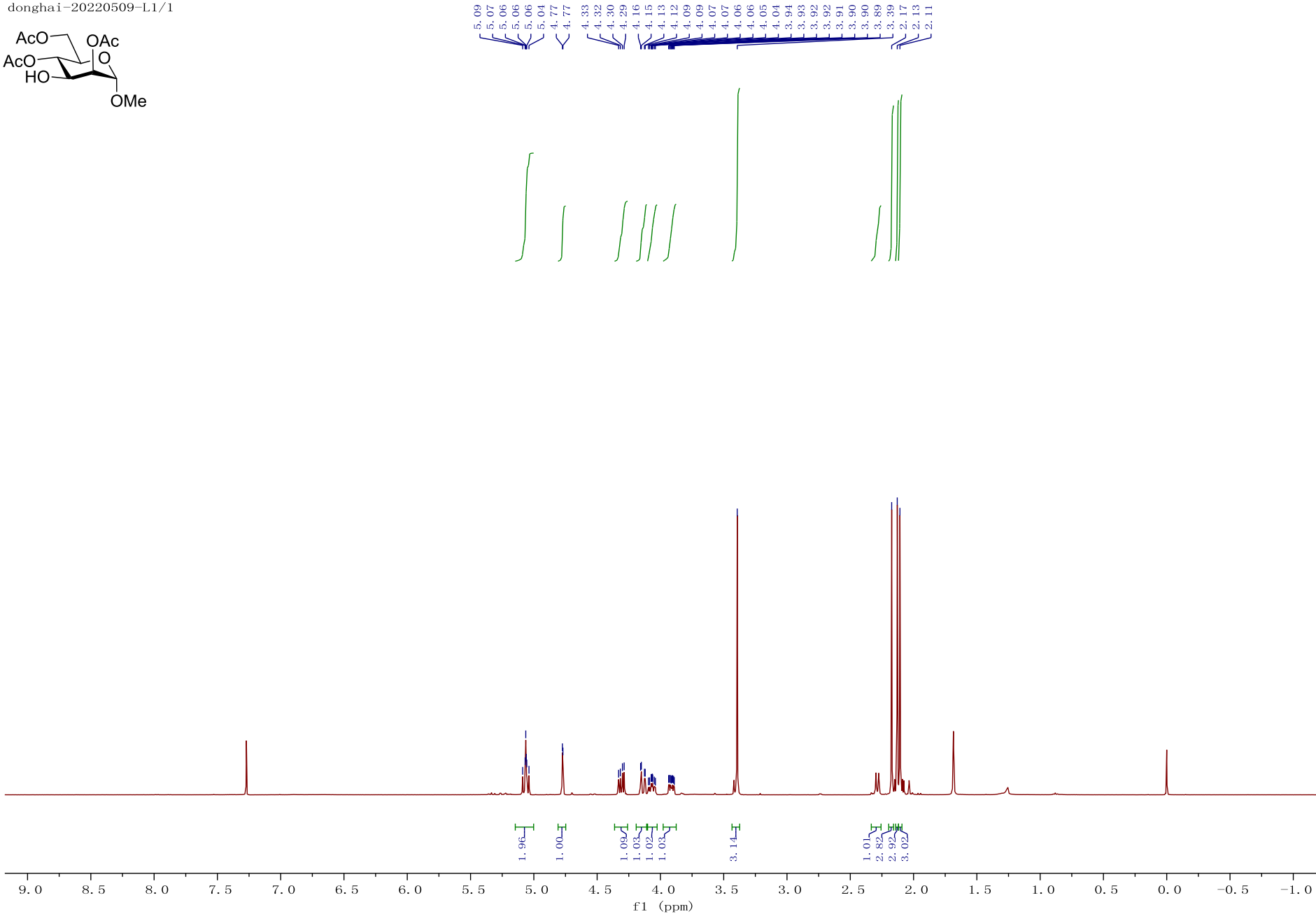
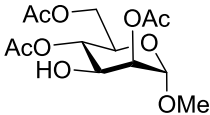
Methyl 2,4,6-tri-*O*-acetyl-3-*O*-(*p*-methoxybenzyl)- α -D-mannopyranoside 29

donghai-20220601-11373

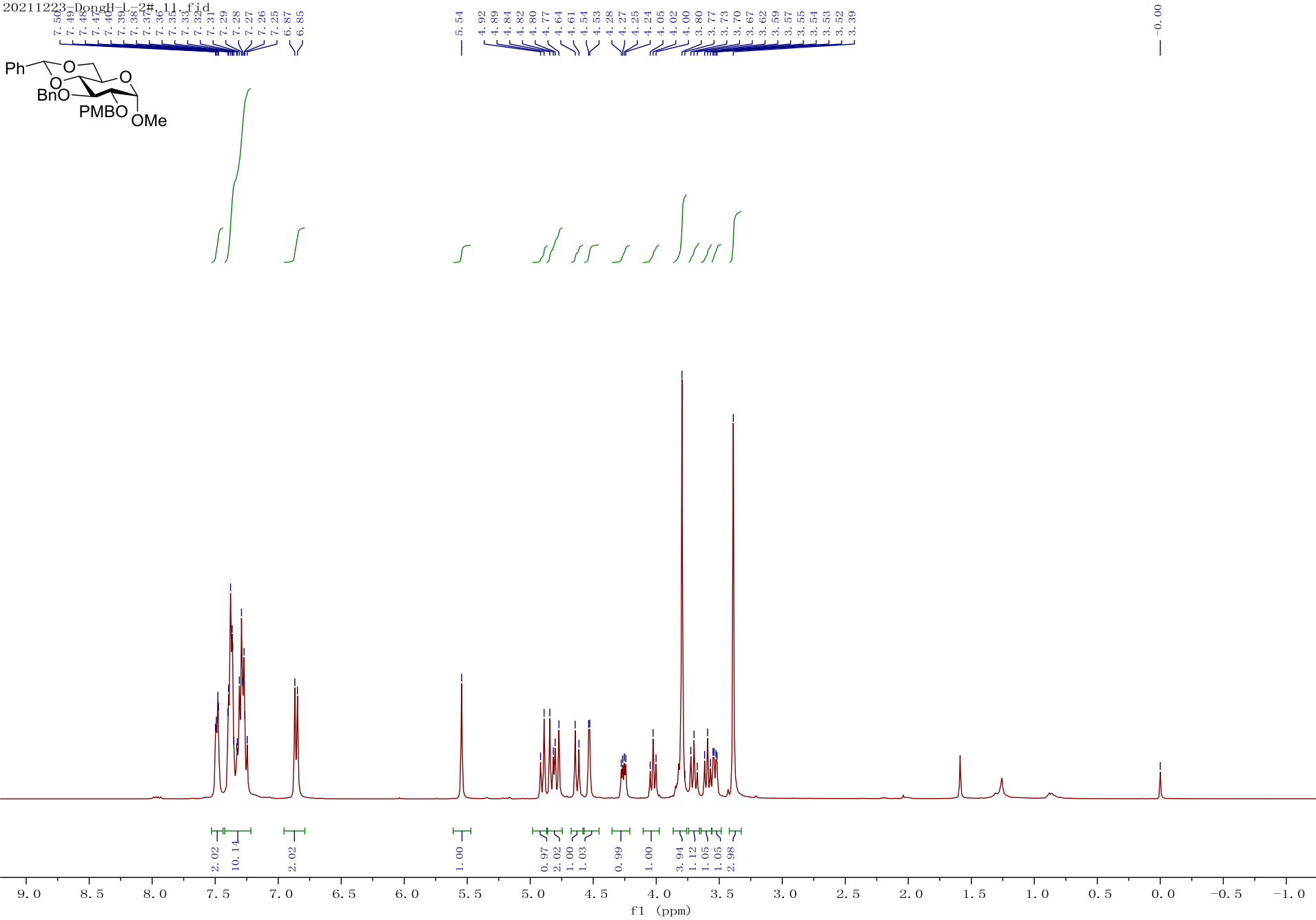


Methyl 2,4,6-tri-*O*-acetyl- α -D-mannopyranoside 30

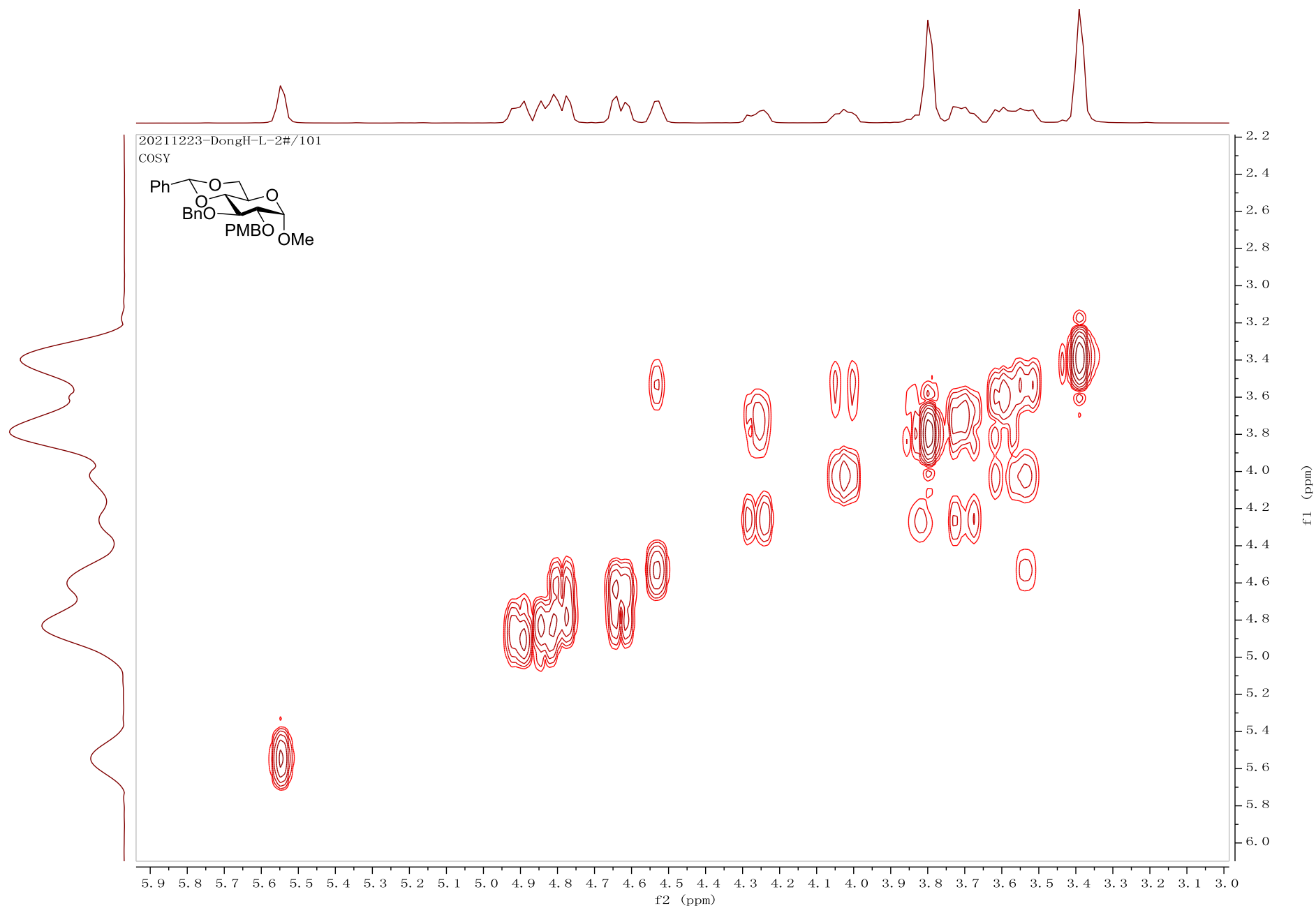
donghai-20220509-L1/1



Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside 31

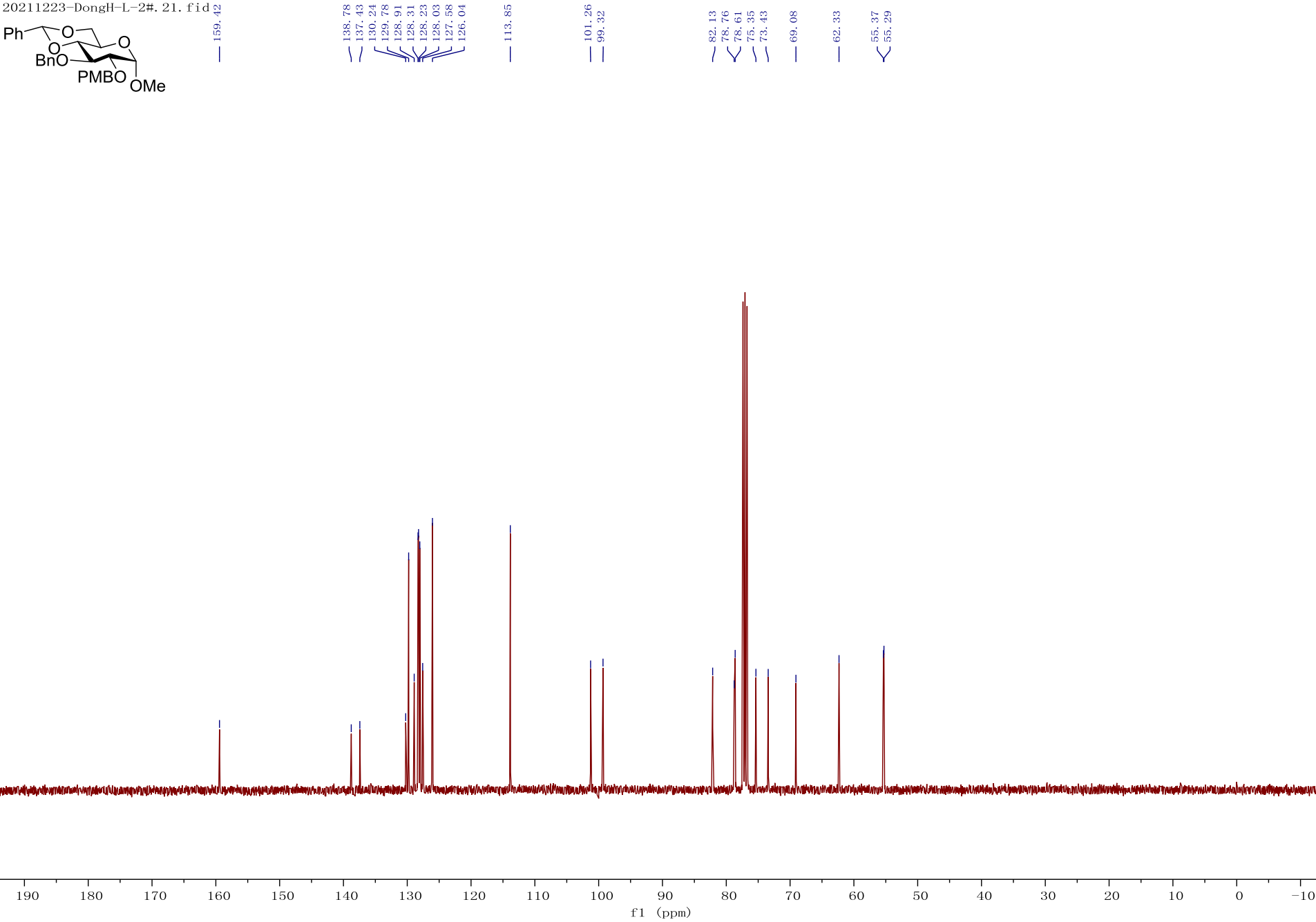
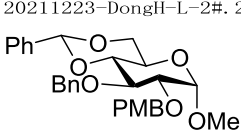


Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside 31

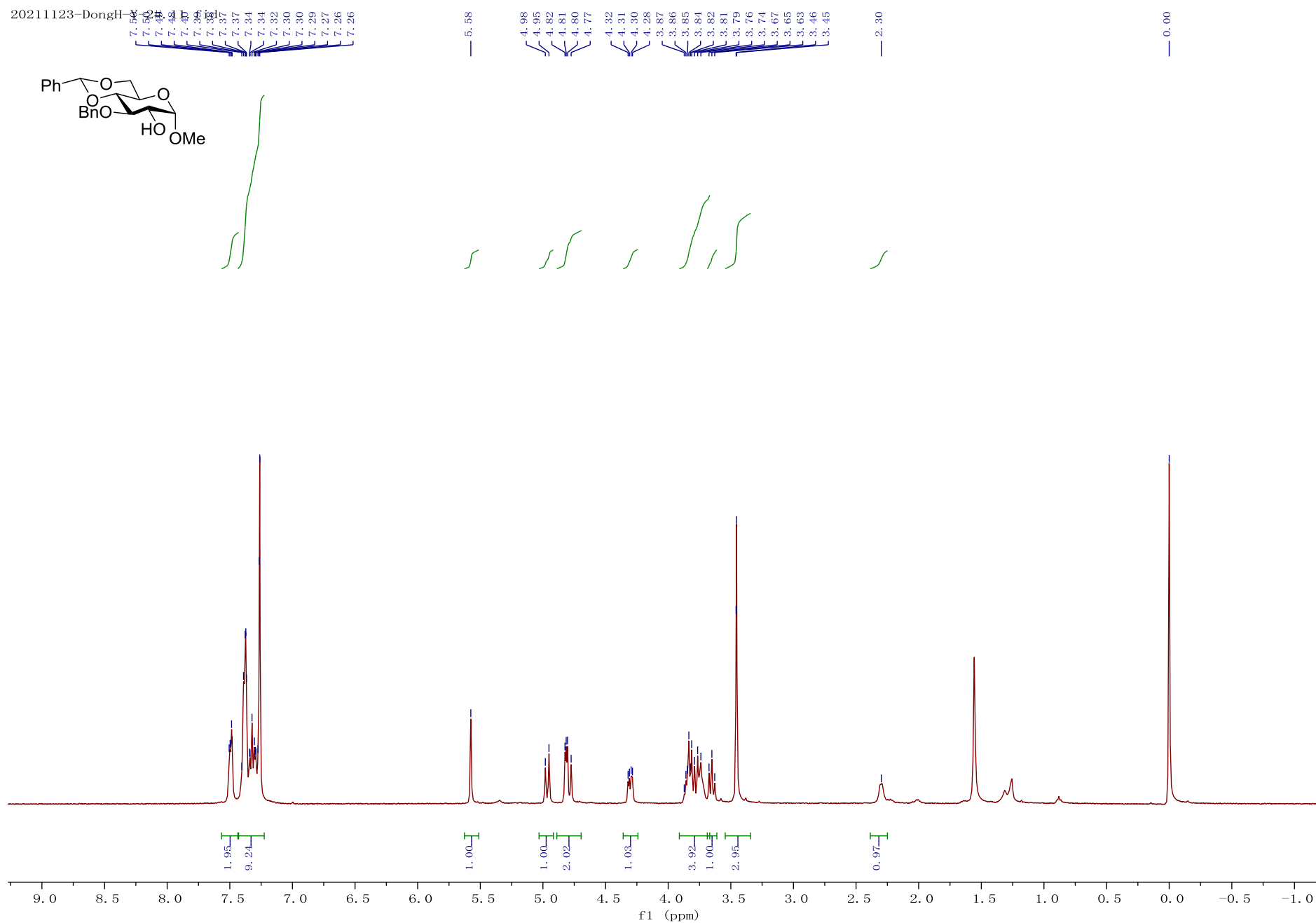


Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside 31

20211223-DongH-L-2#. 21. fid

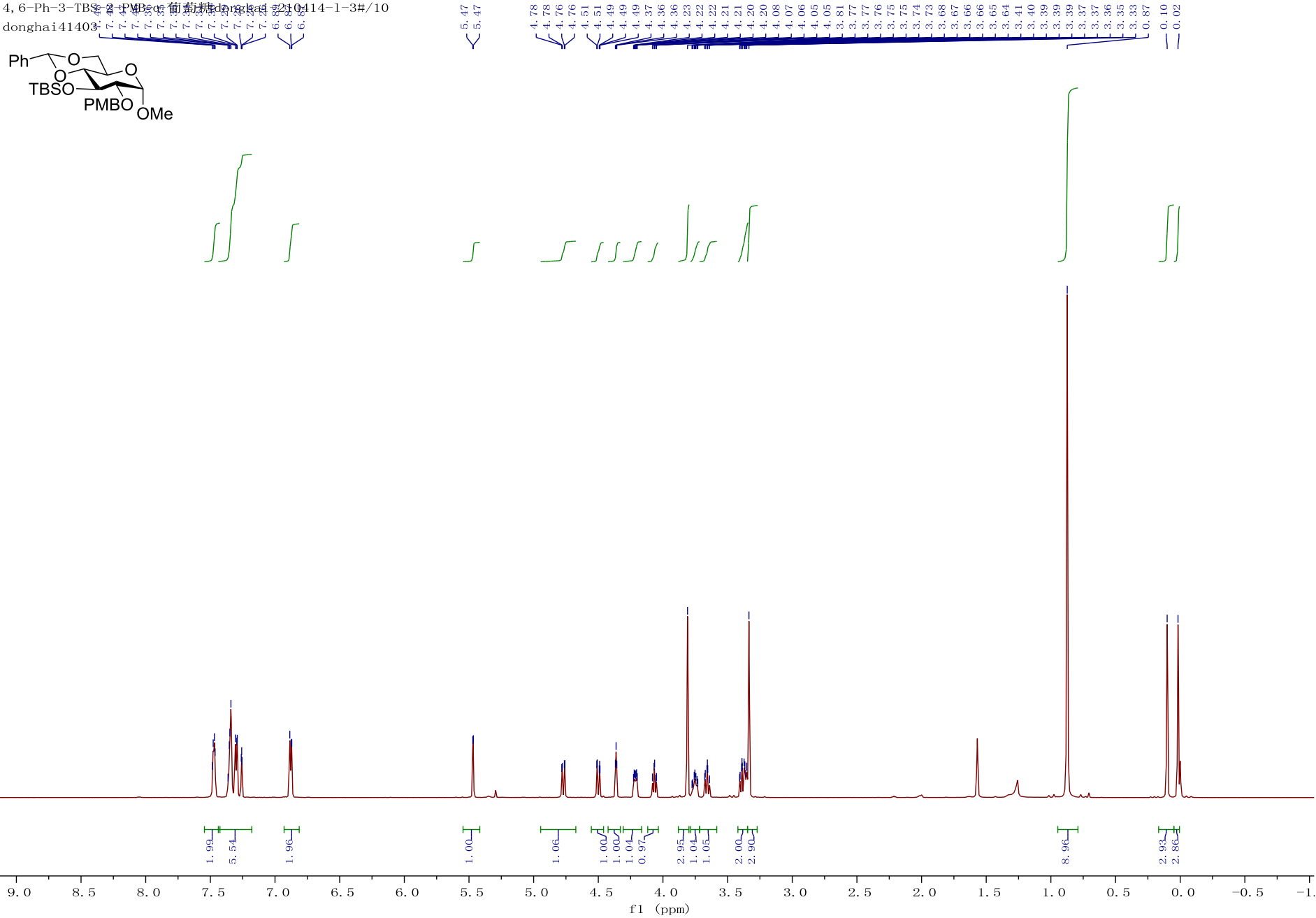
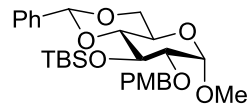


Methyl 3-*O*-benzyl-4,6-*O*-benzylidene- α -D-glucopyranoside 32

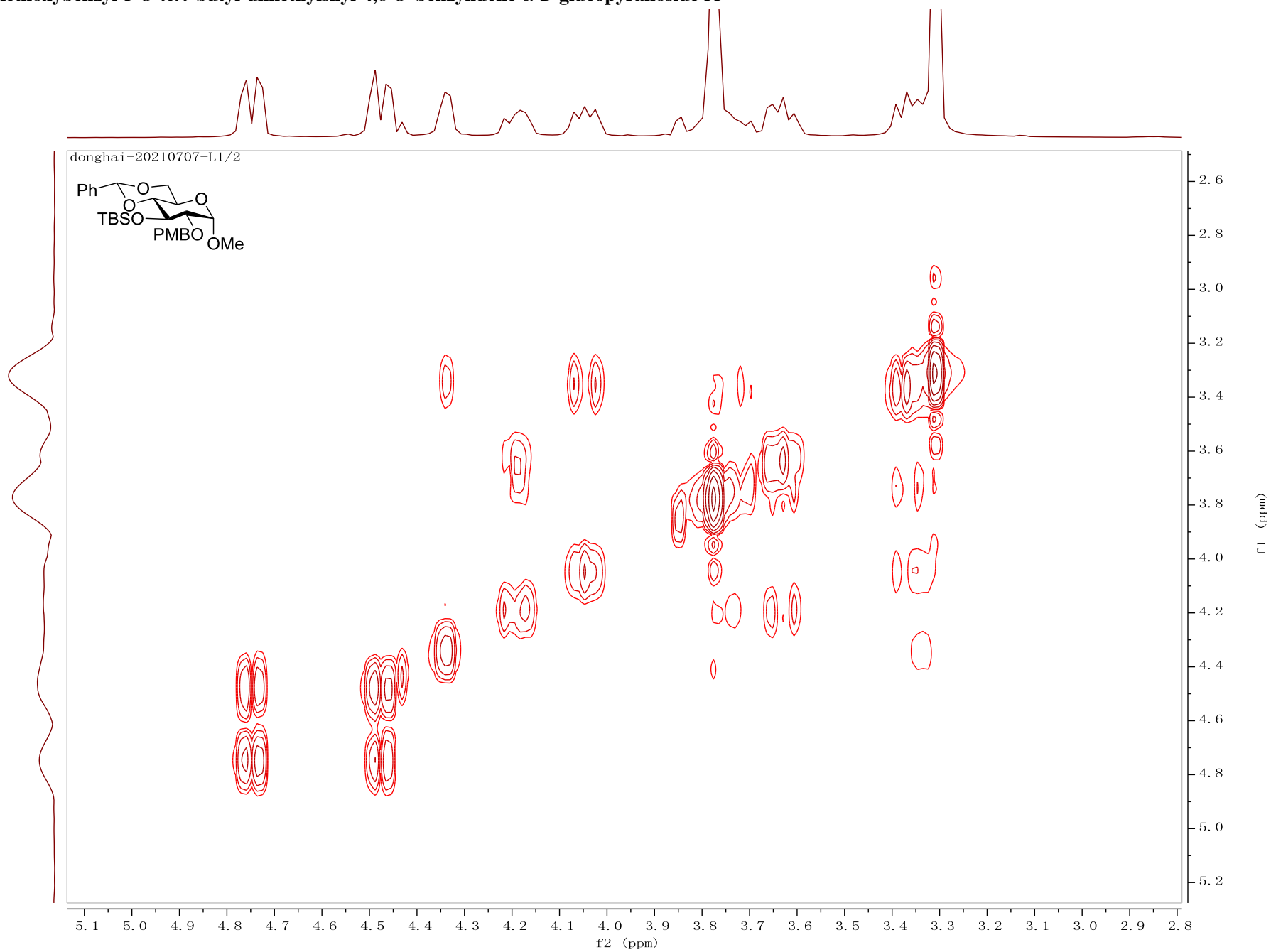


Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-*tert*-butyl-dimethylsilyl-4,6-*O*-benzylidene- α -D-glucopyranoside 33

4, 6-Ph-3-TBS-2-PMBO 葡萄糖衍生物
donghai411403

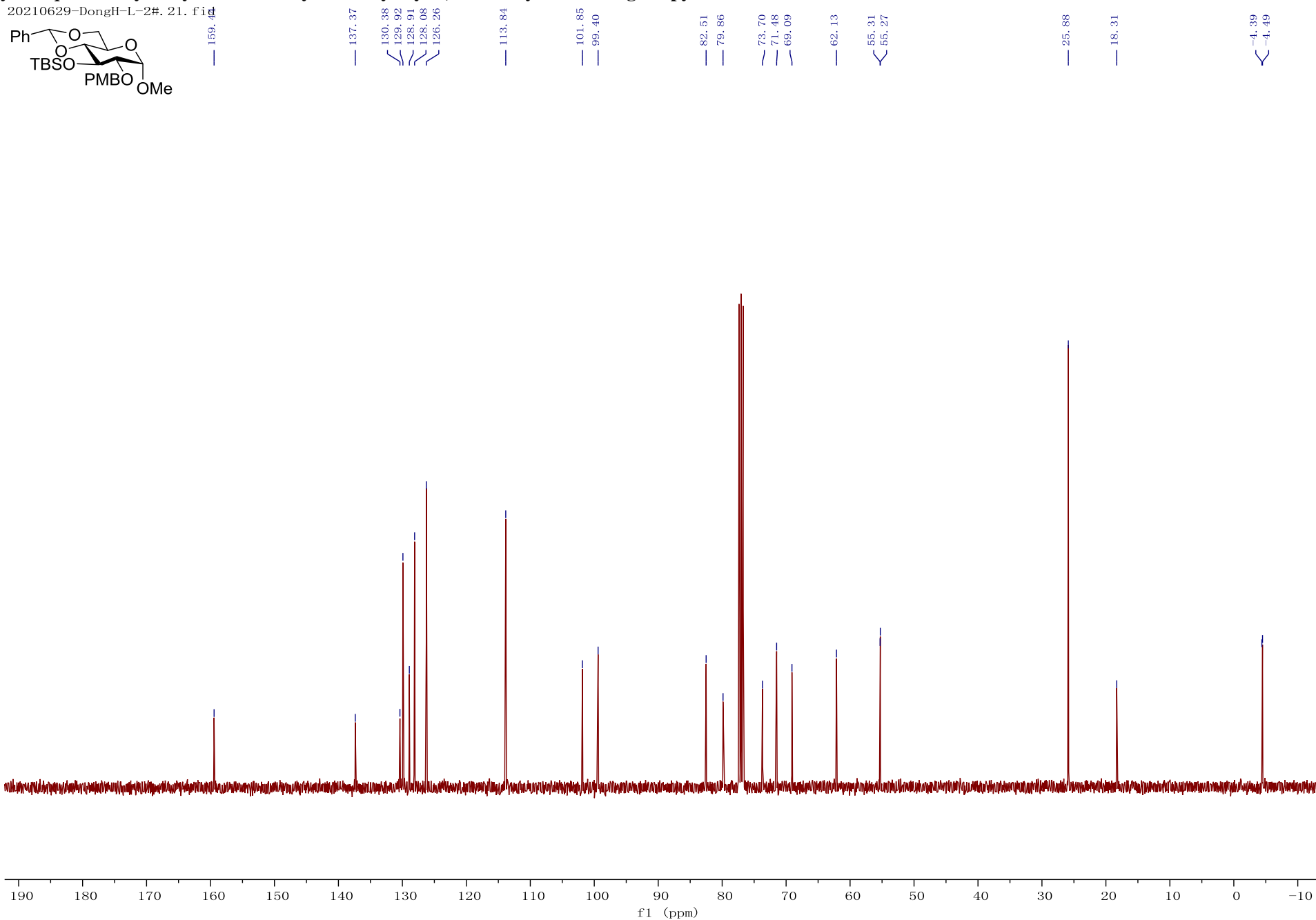


Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-*tert*-butyl-dimethylsilyl-4,6-*O*-benzylidene- α -D-glucopyranoside 33



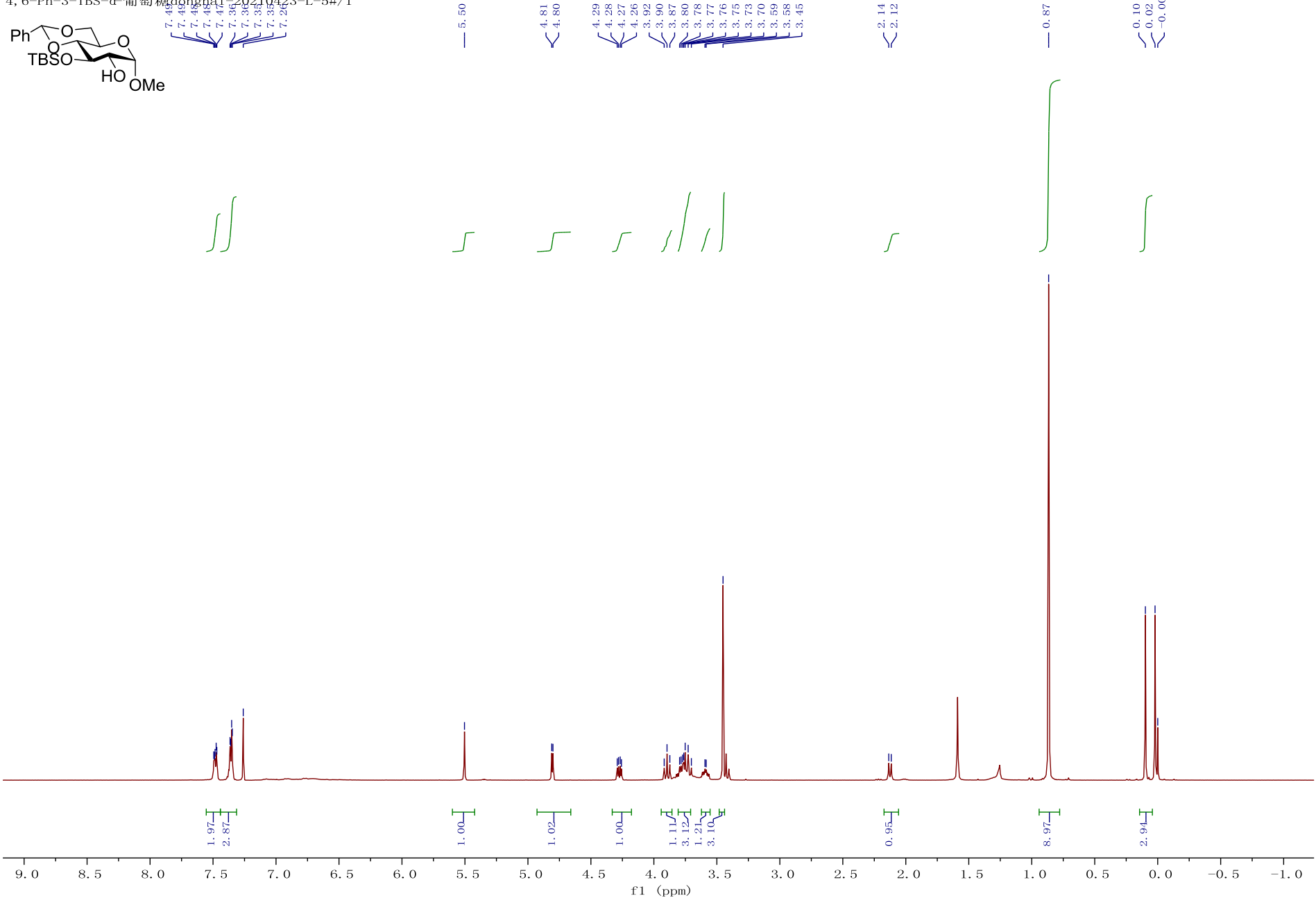
Methyl 2-*O*-*p*-methoxybenzyl-3-*O*-*tert*-butyl-dimethylsilyl-4,6-*O*-benzylidene- α -D-glucopyranoside 33

20210629-DongH-L-2#. 21. f1.d



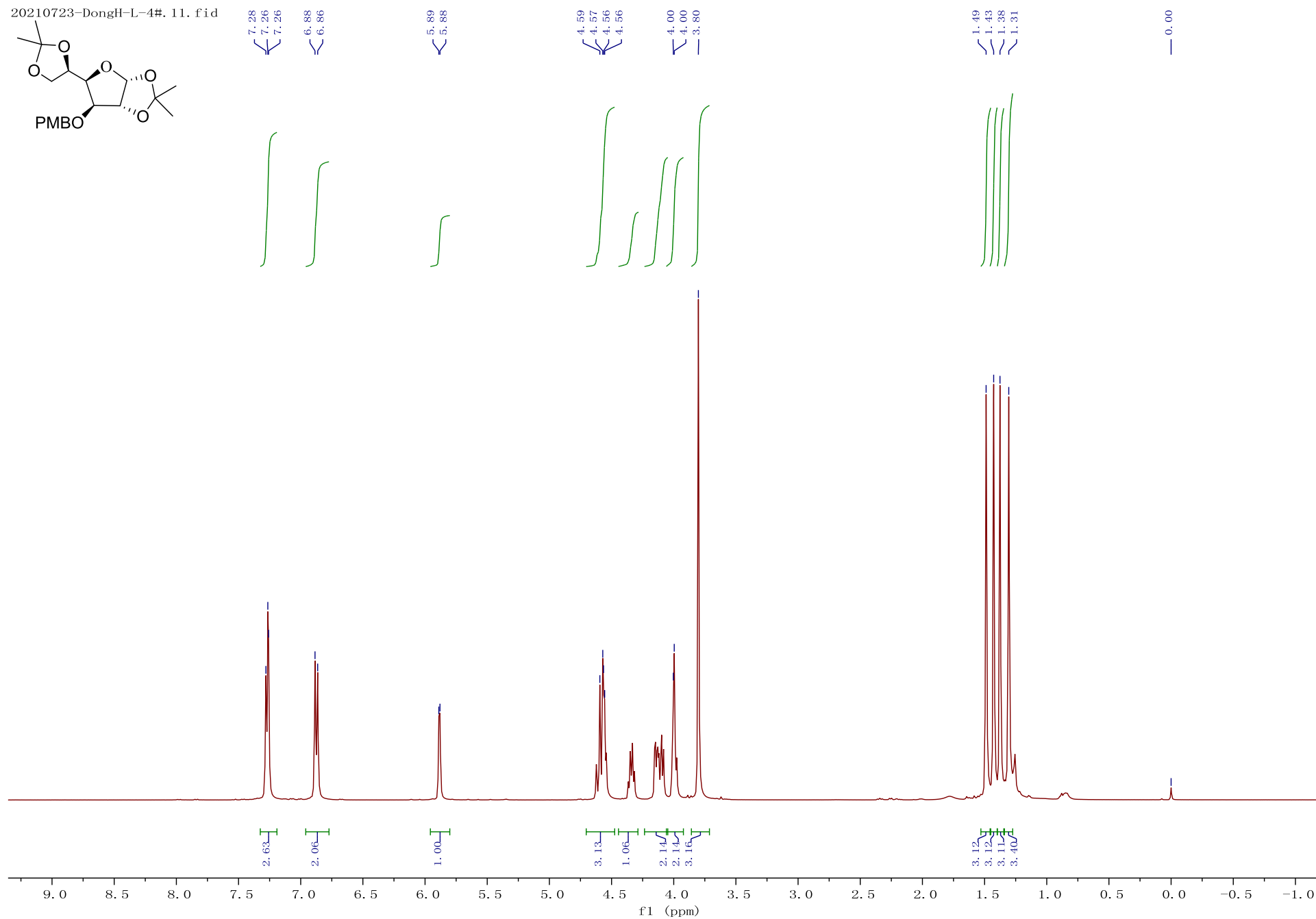
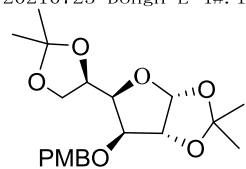
Methyl 3-*O*-*tert*-butyl-dimethylsilyl-4,6-*O*-benzylidene- α -D-glucopyranoside 34

4, 6-Ph-3-TBS- α -葡萄糖 donghai-20210423-L-5#/1



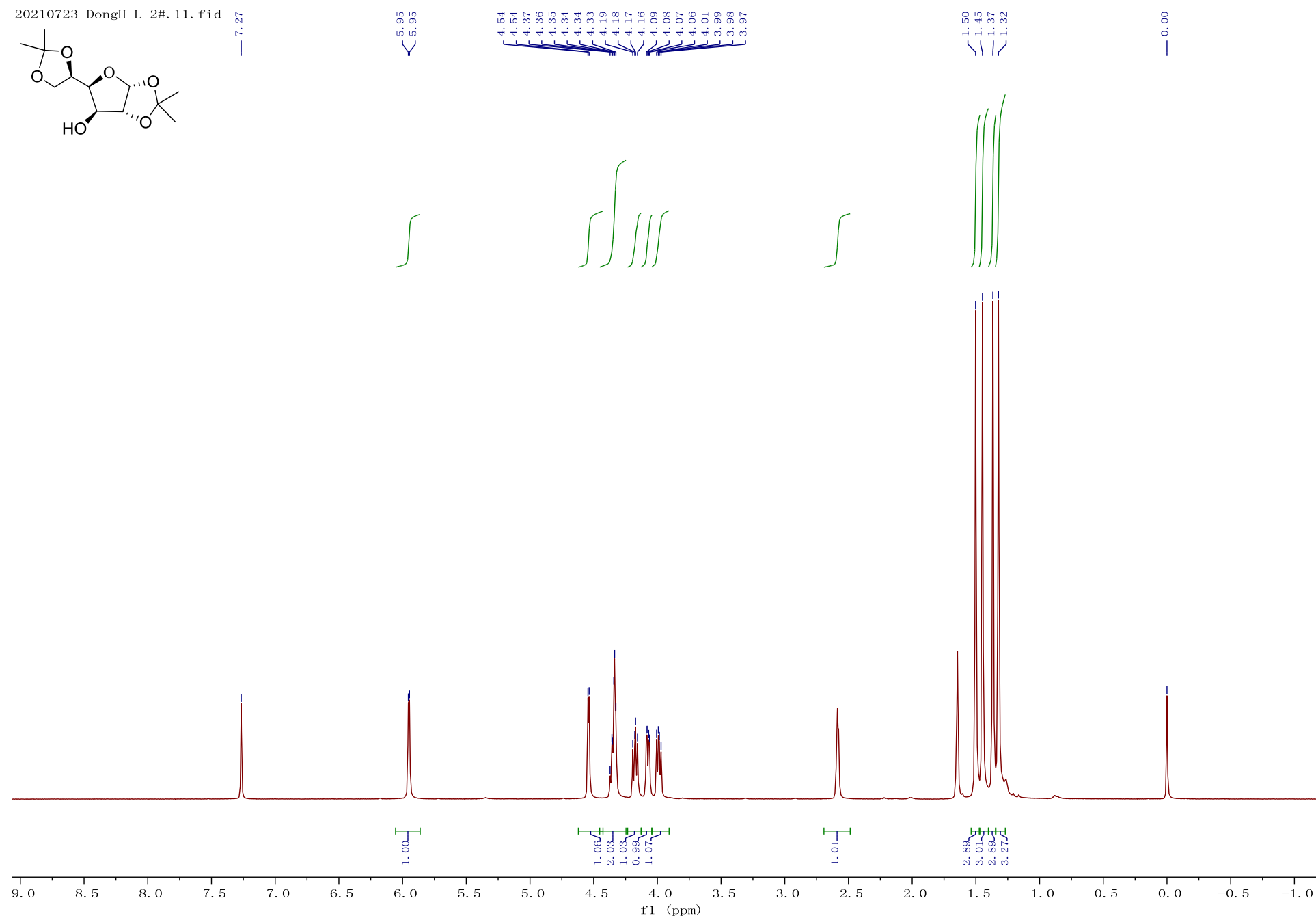
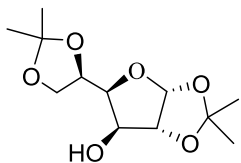
1,2:5,6-Di-*O*-isopropylidene-3-*O*-*p*-methoxybenzyl- α -D-glucufuranose 35

20210723-DongH-L-4#. 11. fid



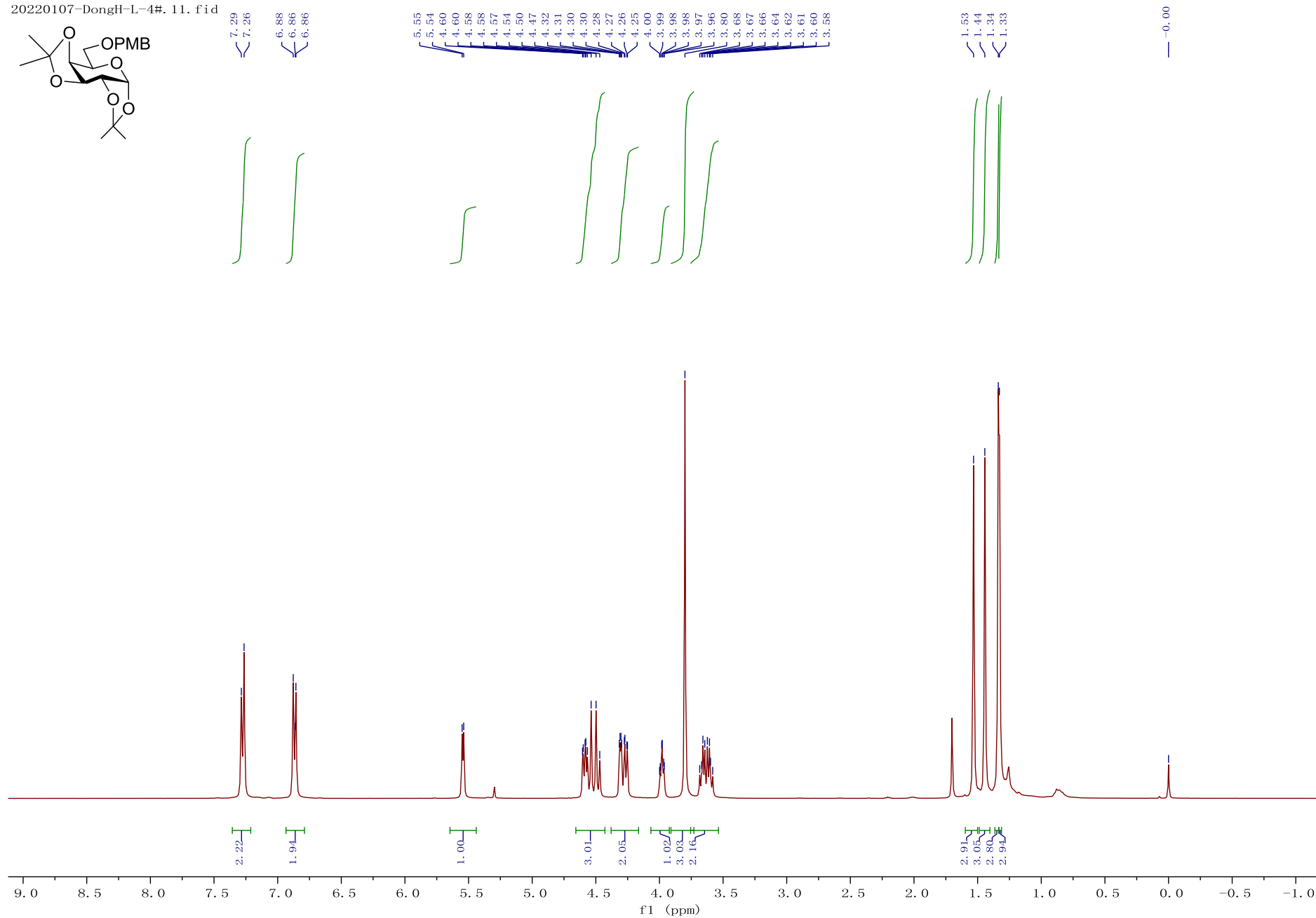
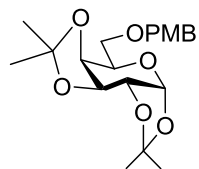
1,2:5,6-Di-*O*-isopropylidene- α -D-glucofuranose 36

20210723-DongH-L-2#. 11. fid



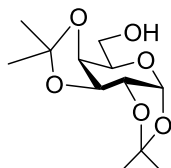
1,2:3,4-Di-*O*-isopropylidene-6-*O*-(*p*-methoxybenzyl)- α -D-galactopyranose 37

20220107-DongH-L-4#. 11. fid



1,2:3,4-Di-*O*-isopropylidene- α -D-galactopyranose 38

20220107-DongH-L-7#. 11. fid



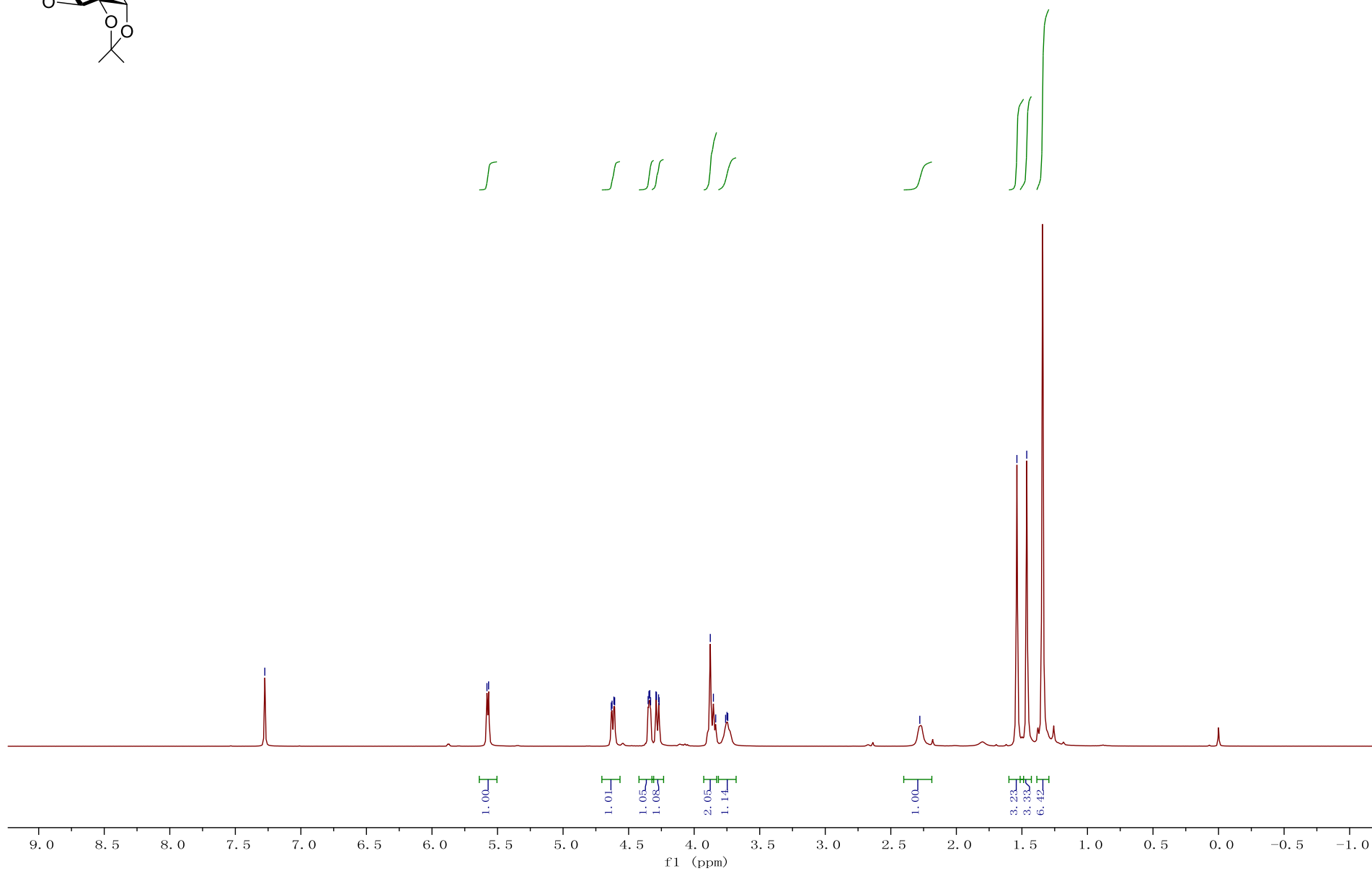
7.28

5.58
5.57

4.63
4.63
4.61
4.61
4.35
4.35
4.34
4.33
4.29
4.29
4.27
4.27
3.88
3.85
3.84
3.76
3.75
3.74

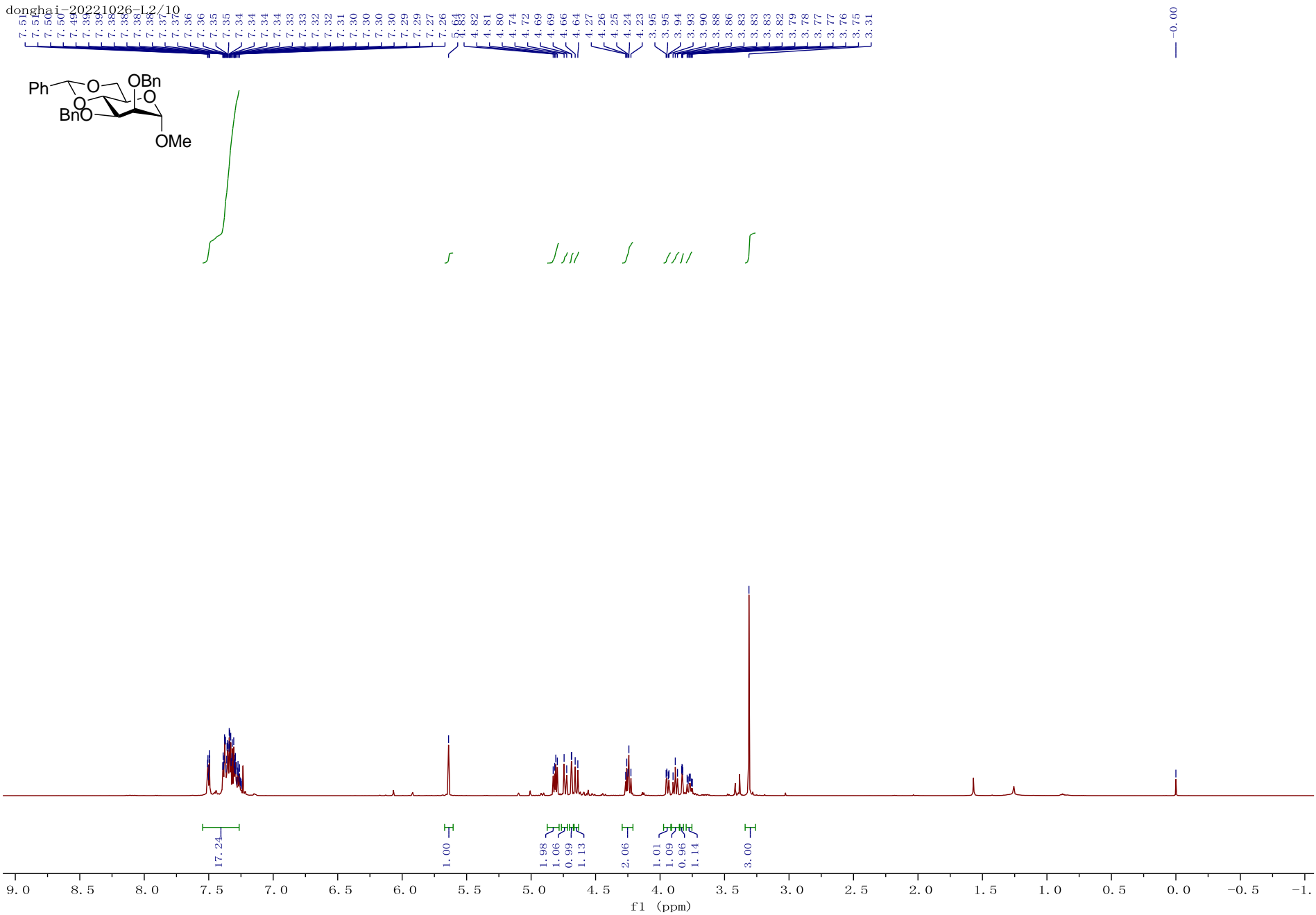
— 2.28

1.54
1.46



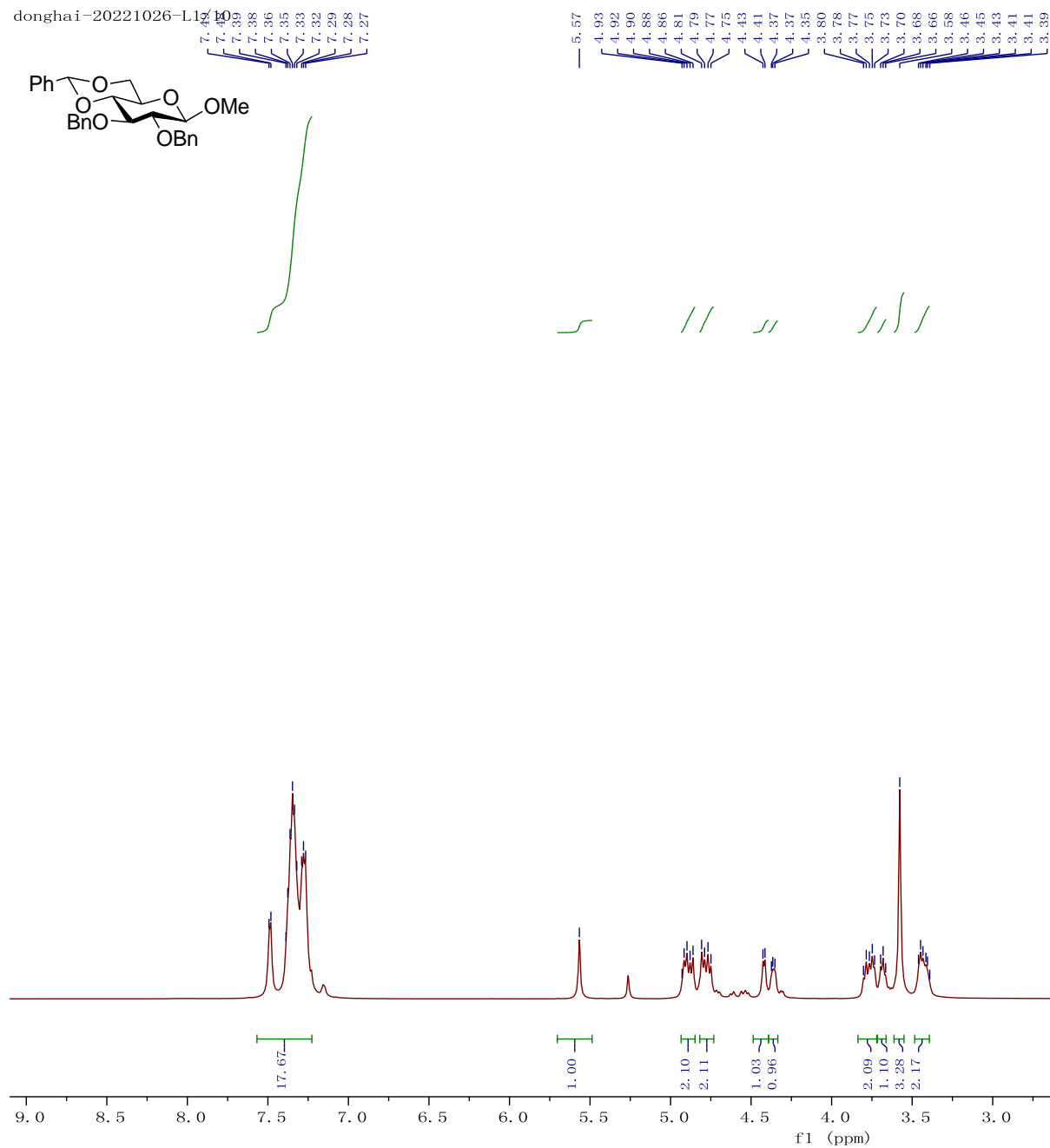
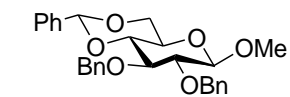
S60

Methyl 2,3-di-O-benzyl-4,6-O-benzylidene- α -D-mannopyranoside 39

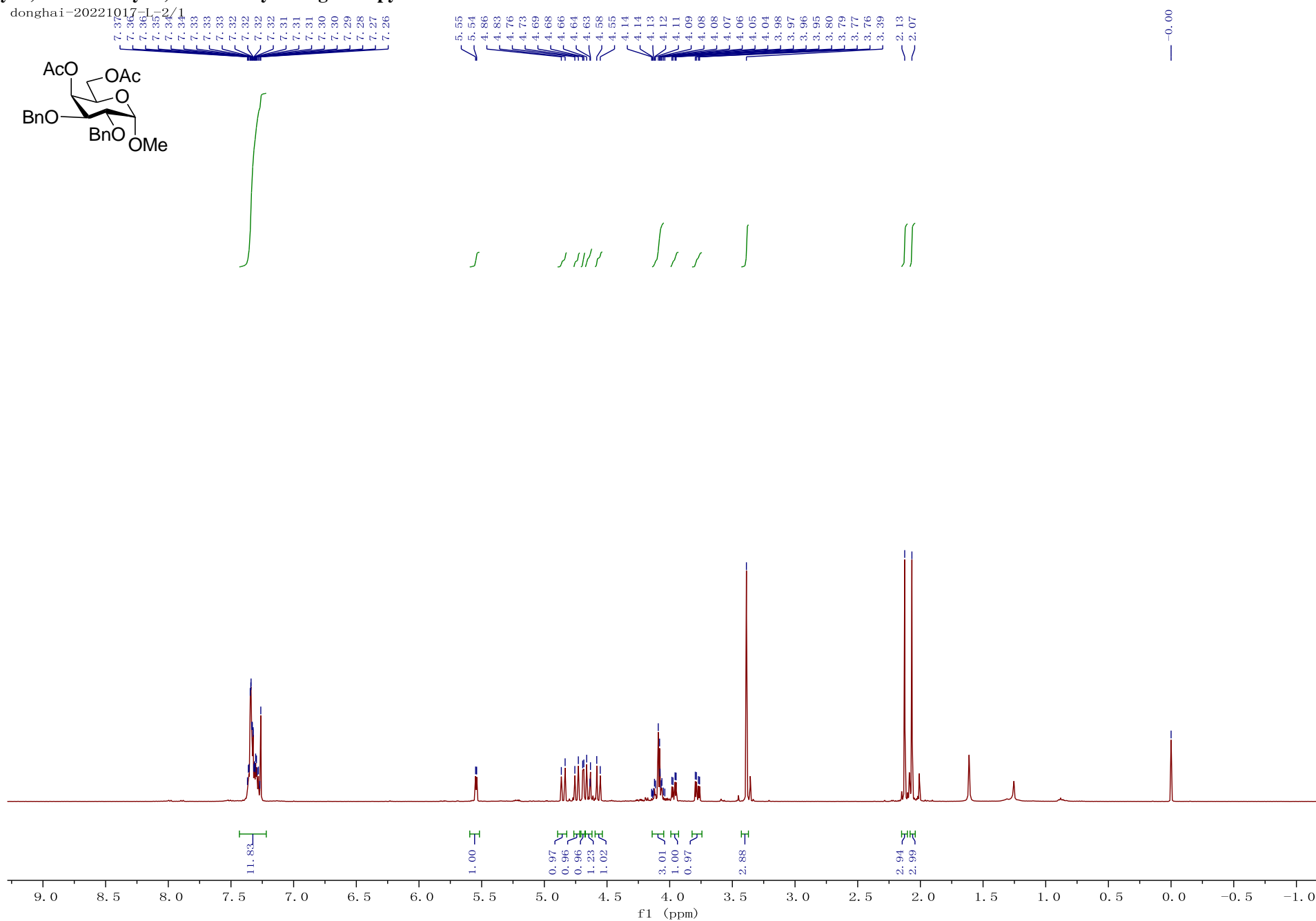


Methyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene- β -D-glucopyranoside 40

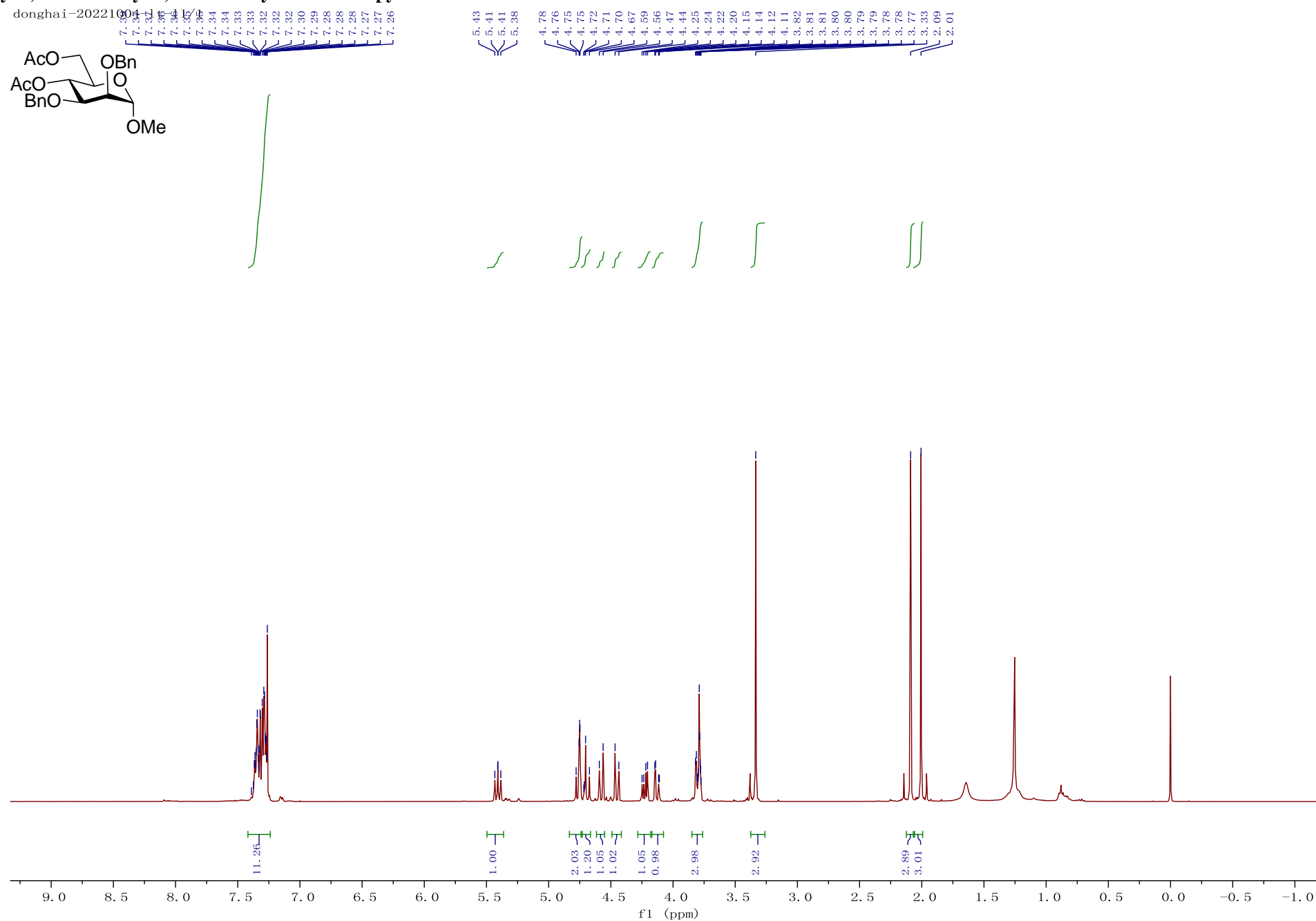
donghai-20221026-L13-10



Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-acetyl- α -D-galactopyranoside 41

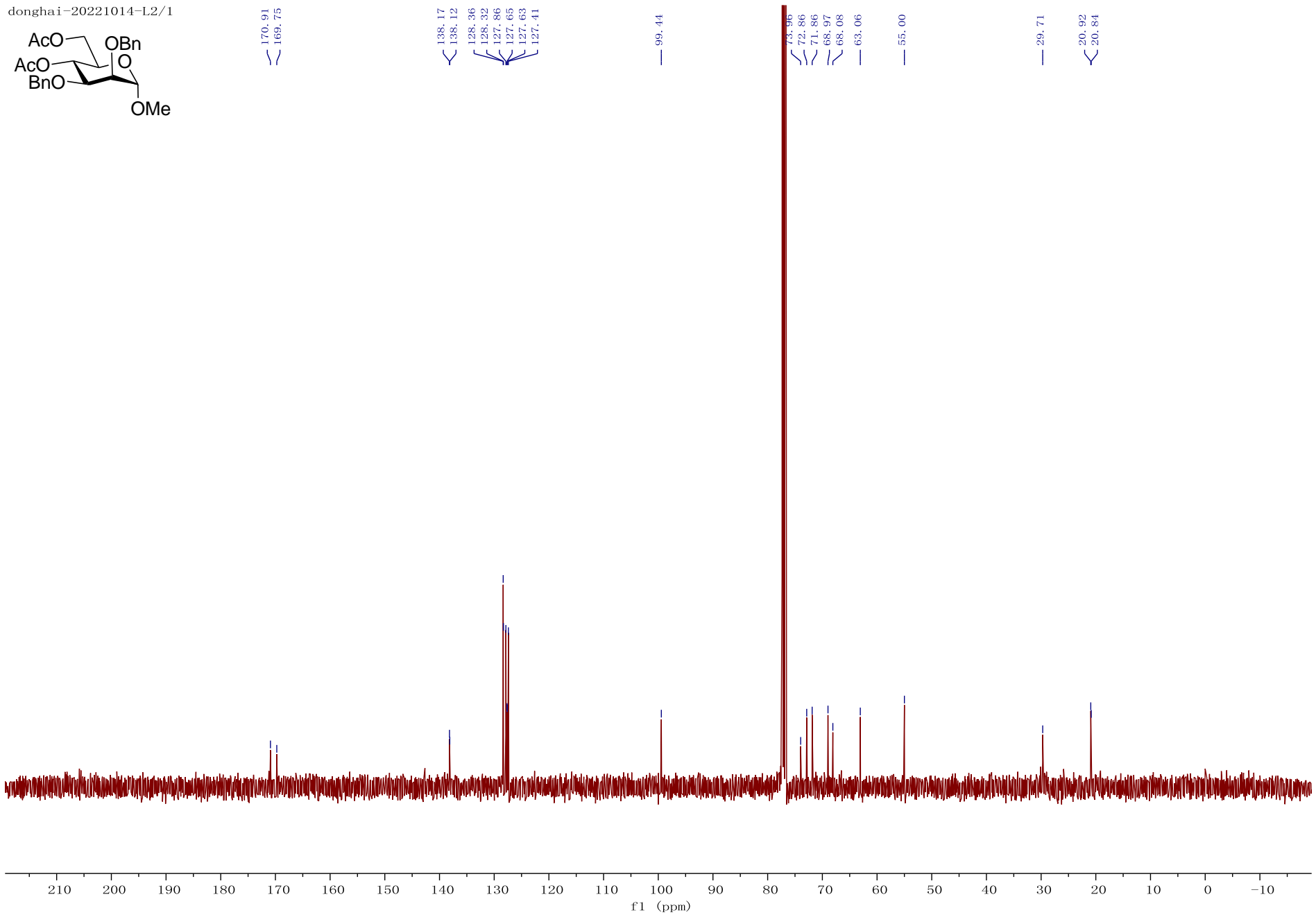
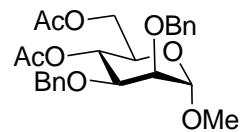


Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-acetyl- α -D-mannopyranoside 42

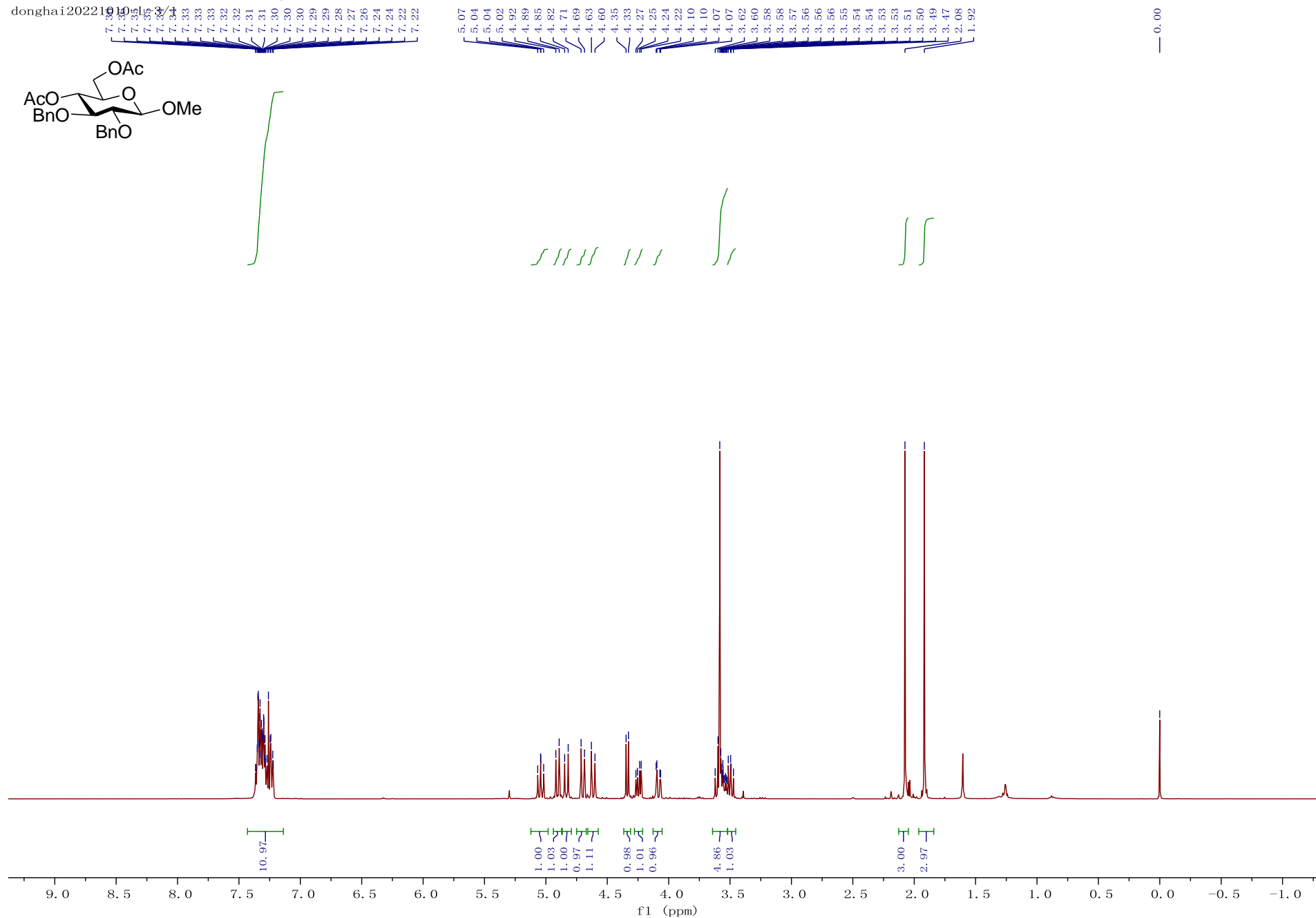


Methyl 2,3-di-O-benzyl-4,6-di-O-acetyl- α -D-mannopyranoside 42

donghai-20221014-L2/1

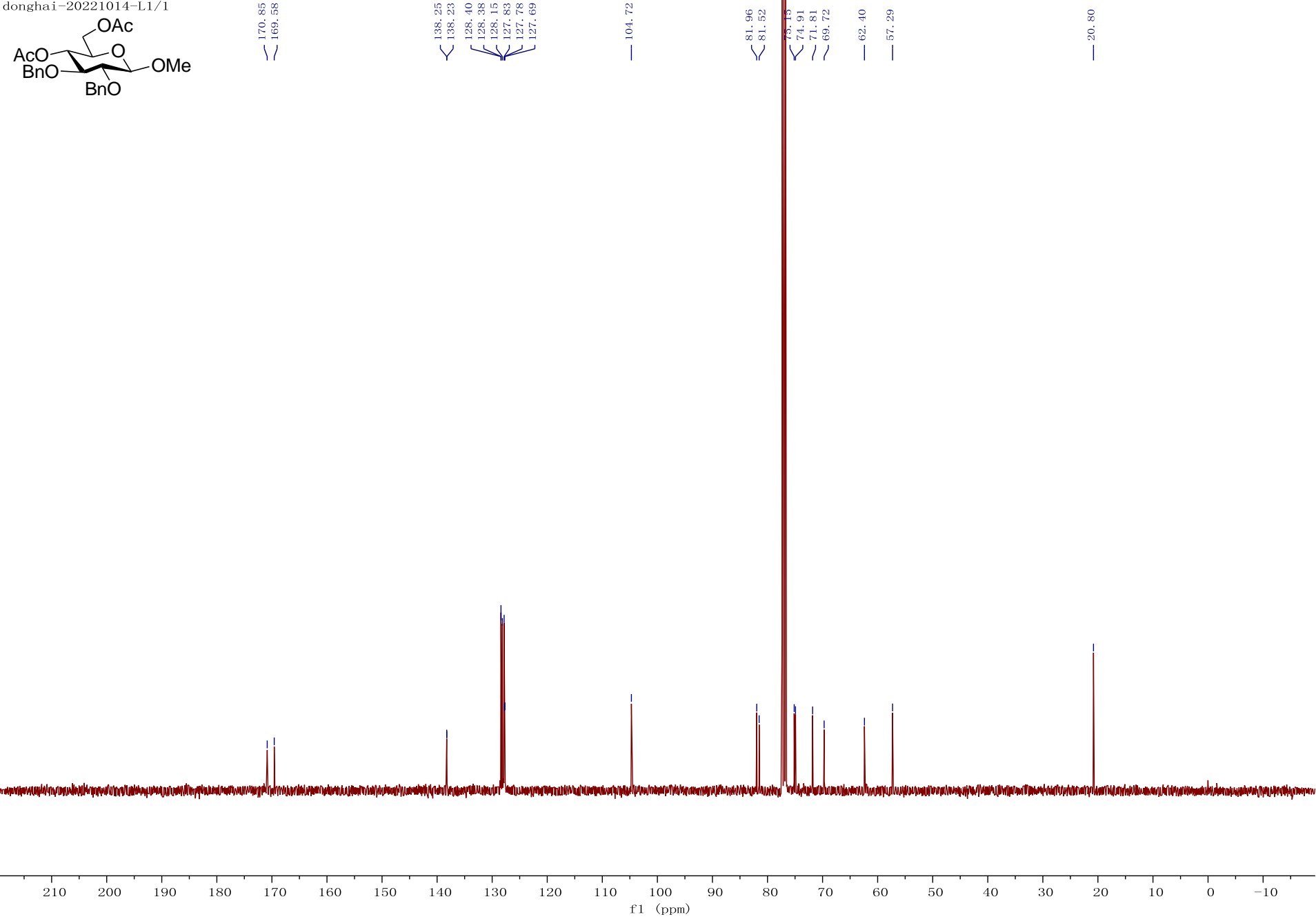
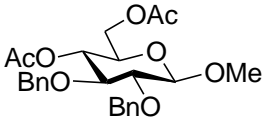


Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-acetyl- β -D-glucopyranoside 43

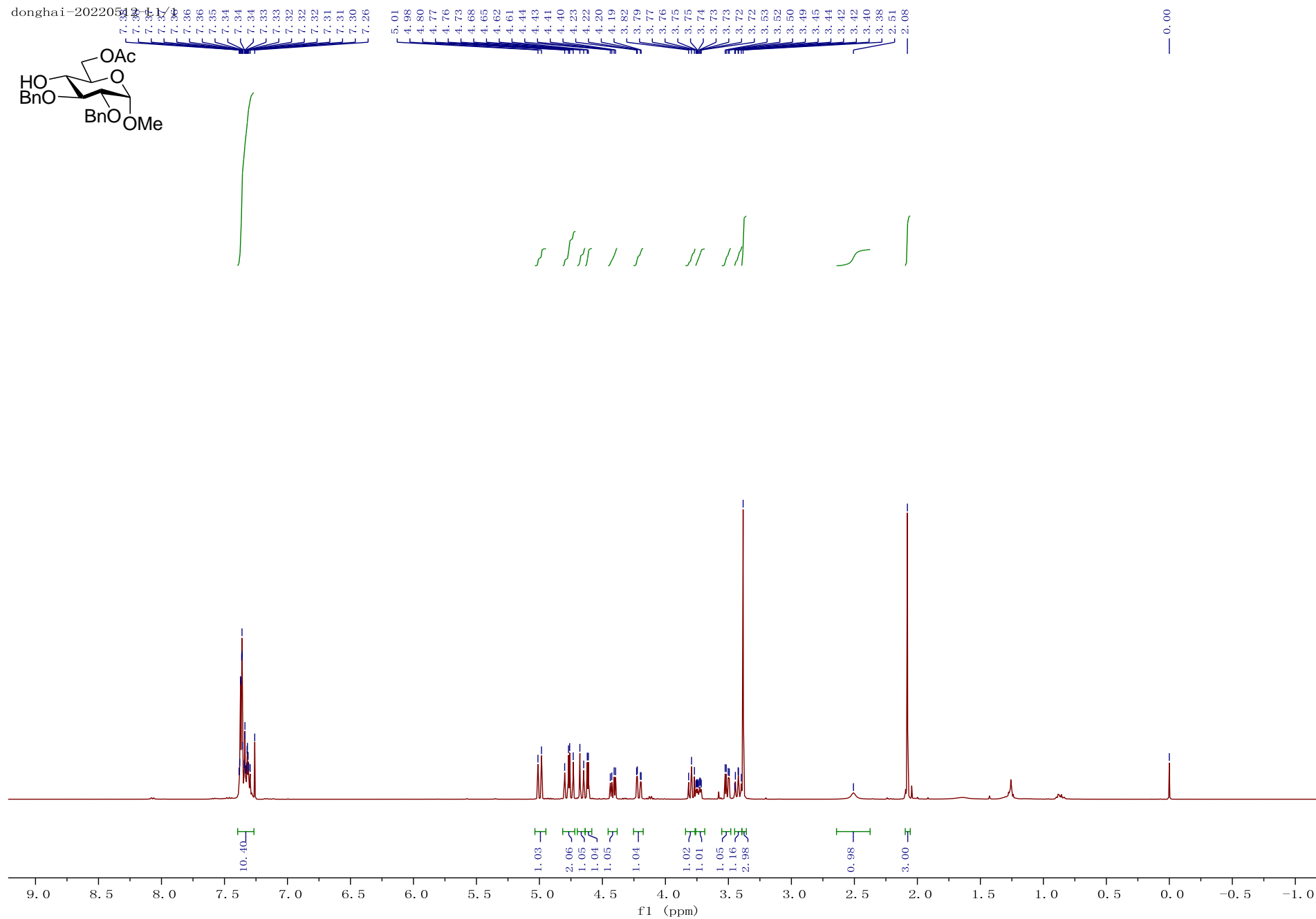


Methyl 2,3-di-O-benzyl-4,6-di-O-acetyl-β-D-glucopyranoside 43

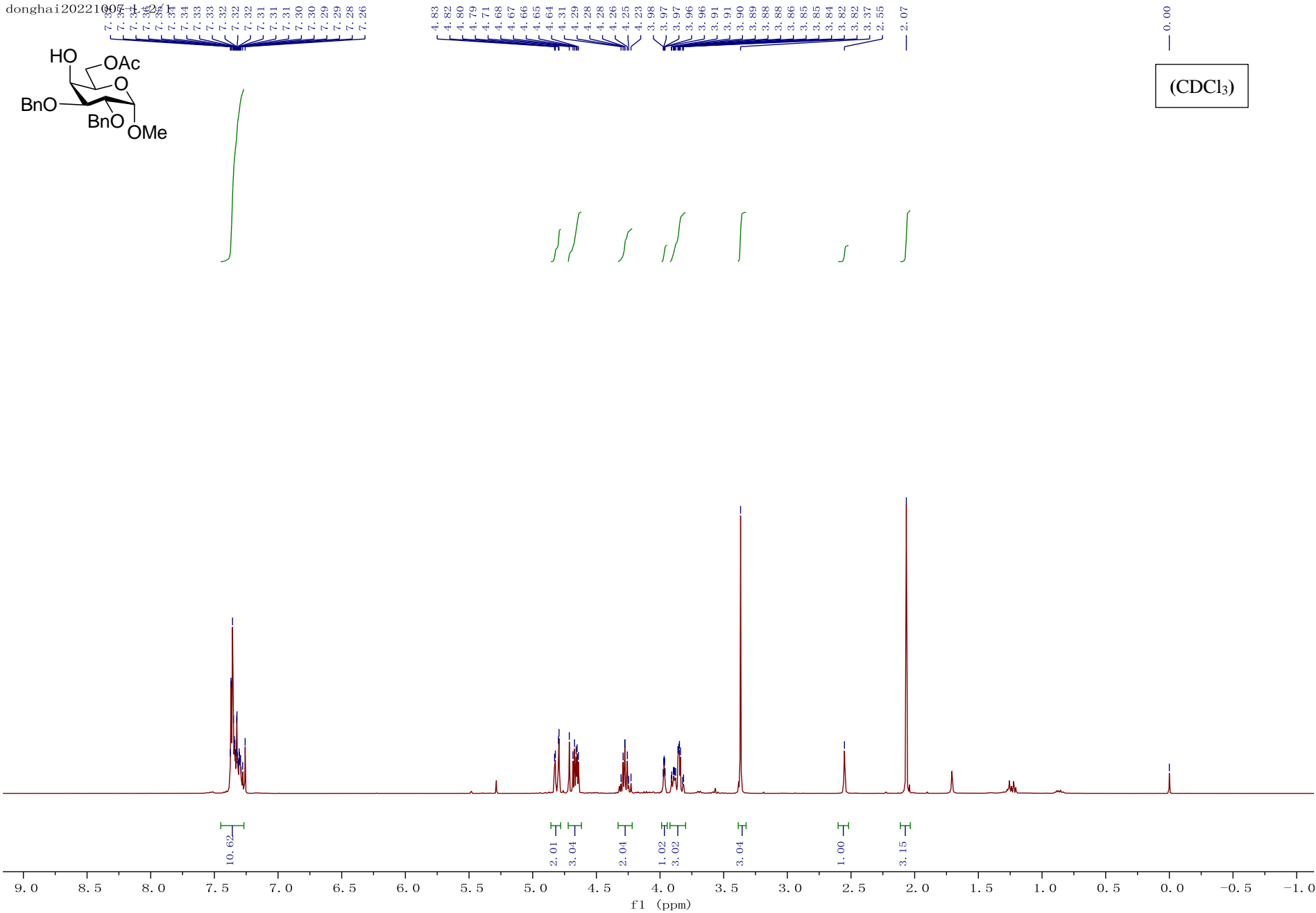
donghai-20221014-L1/1



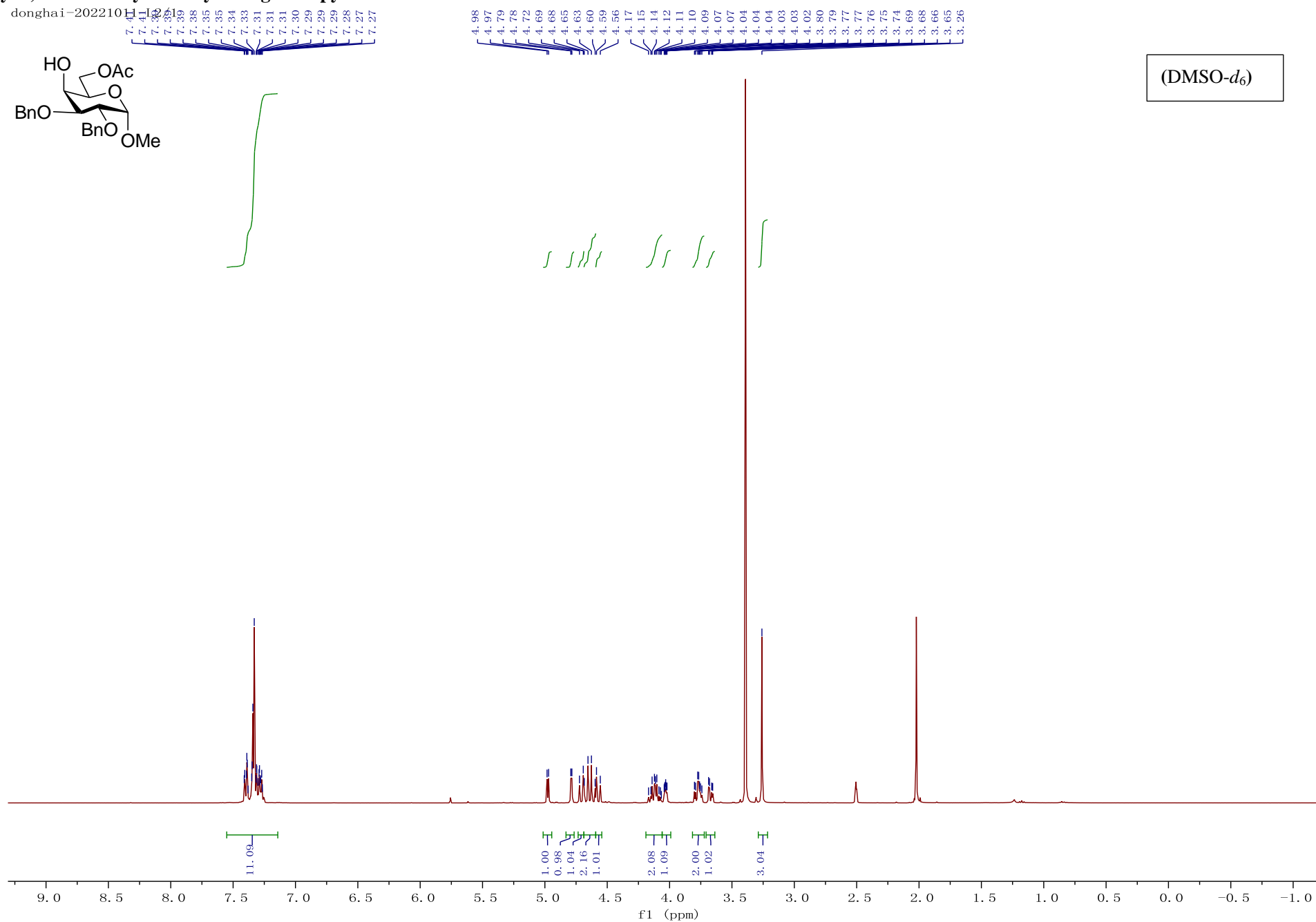
Methyl 2,3-di-*O*-benzyl-6-acetyl- α -D-glucopyranoside 44



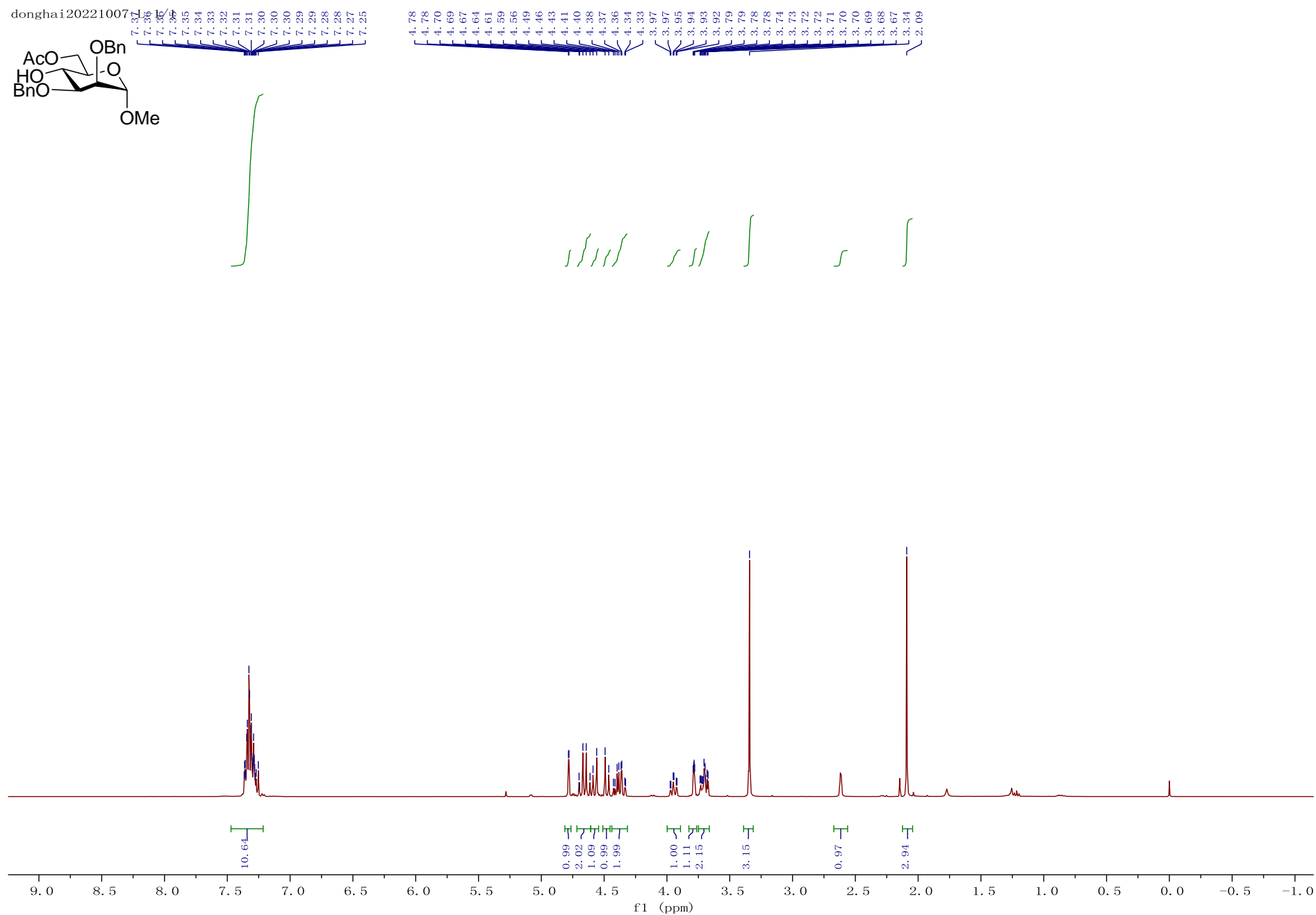
Methyl 2,3-di-O-benzyl-6-acetyl- α -D-galactopyranoside 45



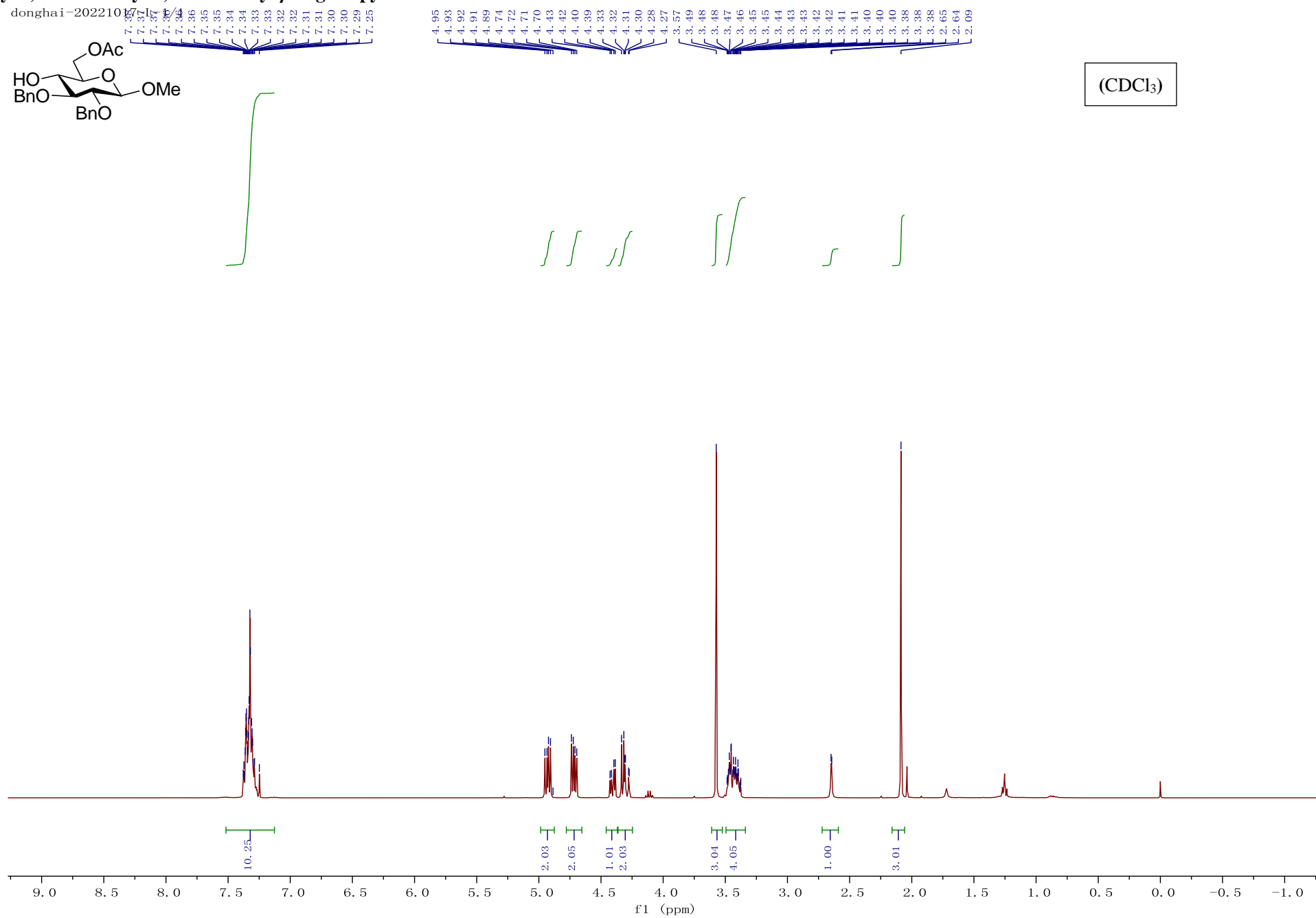
Methyl 2,3-di-*O*-benzyl-6-acetyl- α -D-galactopyranoside 45



Methyl 2,3-di-*O*-benzyl-6-acetyl- α -D-mannopyranoside 46



Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-acetyl- β -D-glucopyranoside 47



Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-acetyl- β -D-glucopyranoside 47

