Supporting Information

An Inexpensive, Green Iron(III) Catalyst for the Regio/Site-Selective Acylation of Diols and Polyols

*Jian Lv, Jian-Tao Ge, Tao Luo and Hai Dong**

Key laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, School of Chemistry & Chemical Engineering, Huazhong University of Science & Technology, Luoyu Road 1037, Wuhan, 430074, PR China Tel.: +86 2787793243; Fax: +86 2787793242; E-mail: hdong@mail.hust.edu.cn

Contents

1. Experimental methods

General: All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. High resolution mass spectra (HRMS) were obtained by electrospray ionization (ESI) and Q-TOF detection. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H and ^{13}C spectra were recorded at 298K in $CDCl_3$ or CD_3OD using the residual signals from $CDCl_3$ (^{1}H: δ = 7.26 ppm; ^{13}C: δ = 77.2 ppm) and CD_3OD (^{1}H: δ = 3.31 ppm) as internal standard. ^{1}H peak assignments were made by first order analysis of the spectra, supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

General Method for Regioselective Acylation of Polyols: 1,2- and 1,3-diol reactants (100 mg) were allowed to react with acylating reagent (1.2-4.0 equiv) and *N*,*N*-Diisopropylethylamine (1.2-4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 2-8 hours in the presence of $Fe(acac)_3$ (0.1 equiv). The reaction mixture was directly purified by flash column chromatography, affording the pure selectively protected derivatives.

Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside (2).[1] Methyl-6-*O*-(tert-butyldimethylsilyl)-*α*-D-mannopyranoside **1** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (80.5 μL, 1.5 equiv) and benzoyl chloride (44.8 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (11.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2** as yellow oil (113.7 mg, 85%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.13-8.11 (m, 2H, Ar**H**), 7.63–7.58 (m, 1H, Ar**H**), 7.49–7.45 (m, 2H, Ar**H**), 5.21 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.67 (d, *J* = 1.6 Hz, 1H, **H-1**), 4.10-3.94 (m, 2H, **H-2**, **H-5**, **H-4**), 3.88-3.84 (m, 1H, **H-6a**), 3.69-3.65 (m, 1H, **H-6b**), 3.43 (s, 3H, O**CH**$_3$), 0.94 (s, 9H, Si(C**(CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.13 (s, 6H, Si(C(CH$_3$)$_3$)(**CH**$_3$)$_2$).

Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (4a).[2] Methyl-6-*O*-(tert-butyldimethylsilyl)-*β*-D-galactopyranoside **3** (140.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (118.5 μL, 1.5 equiv) and benzoyl chloride (62.8 μL, 1.2 equiv) in dry acetonitrile (1.5 mL) at room temperature for 8 h in the presence of $Fe(acac)_3$ (16.1 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **4a** as pale yellow oil (159.2 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–

8.10 (m, 2H, Ar**H**), 7.60–7.55 (m, 1H, Ar**H**), 7.46-7.42 (m, 2H, Ar**H**), 5.08 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.33–4.28 (m, 2H, **H-1, H-4**), 4.05 (dd, *J* = 10.0 Hz and 8.0 Hz, 1H, **H-2**), 3.96 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H, **H-6a**), 3.91 (dd, *J* = 10.4 Hz and 4.4 Hz, 1H, **H-6b**), 3.61–3.58 (m, 4H, **H-5,** O**CH**$_3$), 0.90 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.10 (s, 6H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$).

Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (4b).[3] Methyl-6-*O*-(tert-butyldimethylsilyl)-*β*-D-galactopyranoside **3** (86.5 mg) was allowed to react with *N*,*N*-diisopropylethylamine (73.5 μL, 1.5 equiv) and acetyl chloride (24.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 3 h in the presence of Fe(acac)$_3$ (9.9 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **4b** as pale yellow oil (81.6 mg, 83%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.82 (dd, *J* = 10.0 Hz and 2.8 Hz, **H-3**), 4.25 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.19 (d, *J* = 2.8 Hz, 1H, **H-4**), 3.97-3.87 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.57 (s, 3H, O**CH**$_3$), 3.52 (t, *J* = 5.2 Hz, 1H, **H-5**), 2.18 (s, 3H, O**Ac**), 0.89 (s, 9H, Si(C**(CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.09 (s, 6H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$).

Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (6a).[1] Methyl-6-*O*-(tert-butyldimethylsilyl)-*α*-D-galactopyranoside **5** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (84.5 μL, 1.5 equiv) and benzoyl chloride (44.8 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 7 h in the presence of Fe(acac)$_3$ (11.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **6a** as pale yellow solid (109.6 mg, 82%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.12–8.10 (m, 2H, Ar**H**), 7.59–7.54 (m, 1H, Ar**H**), 7.46–7.42 (m, 2H, Ar**H**), 5.27 (dd, *J* = 10.2 Hz and 2.6 Hz, 1H, **H-3**), 4.90 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.32 (d, *J* = 2.6 Hz, 1H, **H-4**), 4.27–4.22 (m, 1H, **H-2**), 3.97–3.84 (m, 3H, **H-5, H-6a** and **H-6b**), 3.47 (s, 3H, O**CH**$_3$), 0.90 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$).

Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (6b).[3] Methyl-6-*O*-(tert-butyldimethylsilyl)-*α*-D-galactopyranoside **5** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (84.5 μL, 1.5 equiv) and acetyl chloride (34.7 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 5 h in the presence of Fe(acac)$_3$ (11.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **6b** as pale yellow oil (96.6 mg, 85%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.04 (dd, *J* = 10.0 Hz and 2.4 Hz, **H-3**), 4.85 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.19 (d, *J* = 2.4 Hz, 1H, **H-4**), 4.08 (dd, *J* = 10.3 Hz and

3.6 Hz, 1H, **H-2**), 3.94-3.86 (m, 2H, **H-6a** and **H-6b**), 3.78-3.76 (m, 1H, **H-5**), 3.44 (s, 3H, O**CH**$_3$), 2.18 (s, 3H, O**Ac**), 0.91 (s, 9H, Si(C**(CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.10 (s, 6H, Si(C(CH$_3$)$_3$)(**CH**$_3$)$_2$).

Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (8a). Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **7** (106.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (57.5 μL, 1.2 equiv) and benzoyl chloride (38.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 6 h in the presence of Fe(acac)$_3$ (9.7 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **8a** as viscous pale yellow oil (125.1 mg, 93%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.09-8.07 (m, 2H, Ar**H**), 7.62-7.54 (m, 3H, Ar**H**), 7.45-7.41 (m, 2H, Ar**H**), 7.33-7.31 (m, 3H, Ar**H**), 5.11 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.65 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.36 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.10 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.01 (dd, *J* = 10.8 Hz and 5.2 Hz, 1H, **H-6a**), 3.93 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6b**), 3.64 (t, *J* = 4.4 Hz, 1H, **H-5**), 0.91 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.12 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 166.3, 133.3, 132.8, 131.8, 129.9, 129.6, 129.0, 128.4, 128.1, 89.1, 77.6, 68.7, 67.2, 63.7, 25.8, 18.3, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{34}O_6SSiNa$ $[M+Na]^+$: 513.1743; found: 513.1728.

Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (8b). Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **7** (95.1 mg) was allowed to react with *N*,*N*-diisopropylethylamine (51.5 μL, 1.2 equiv) and acetyl chloride (21.1 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of Fe(acac)$_3$ (8.7 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **8b** as viscous pale yellow oil (90.6 mg, 86%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.59-7.57 (m, 2H, Ar**H**), 7.30-7.27 (m, 3H, Ar**H**), 4.86 (dd, *J* = 9.6 Hz and 2.4 Hz, 1H, **H-3**), 4.58 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.23 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.99-3.89 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.56 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.15 (s, 3H, O**Ac**), 0.91 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.11 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.9, 132.8, 131.7, 129.0, 128.1, 88.8, 77.4, 76.5, 68.7, 66.9, 63.8, 25.8, 21.1, 18.2, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{20}H_{32}O_6SSiNa$ $[M+Na]^+$: 451.1587; found: 451.1588.

Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (10a). Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **9** (97.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (51.5 μL, 1.2 equiv) and benzoyl chloride (34.0 μL, 1.2 equiv) in dry

acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (8.6 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **10a** as viscous pale yellow oil (111.4 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H, Ar**H**), 7.58-7.55 (m, 1H, Ar**H**), 7.43 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.36-7.26 (m, 5H, Ar**H**), 5.02 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.34-4.31 (m, 2H, **H-1**, **H-4**), 4.13 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.01 (d, *J* = 12.8 Hz, 1H, Ph**CH$_2$**), 3.97-3.87 (m, 3H, Ph**CH$_2$**, **H-6a** and **H-6b**), 3.55 (t, *J* = 4.4 Hz, 1H, **H-5**), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.12 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.11 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 137.4, 133.3, 129.9, 129.7, 129.1, 128.7, 128.4, 127.3, 85.2, 77.7, 77.1, 68.6, 67.9, 63.3, 33.7, 25.9, 18.3, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{36}O_6SSiNa$ $[M+Na]^+$: 527.1900; found: 527.1921.

Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (10c). Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **9** (174.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (91.5 μL, 1.2 equiv) and acetyl chloride (37.5 μL, 1.2 equiv) in dry acetonitrile (1.5 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (15.4 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **10c** as viscous pale yellow oil (163.6 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.25 (m, 5H, Ar**H**), 4.76 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.25 (d, *J* = 10.0 Hz, 2H, **H-1**), 4.19 (d, *J* = 3.2 Hz, 1H, **H-4**), 4.00-3.93 (m, 2H, **H-2,** Ph**CH$_2$**), 3.91-3.84 (m, 3H, Ph**CH$_2$**, **H-6a** and **H-6b**), 3.48-3.45 (m, 1H, **H-5**), 2.15 (s, 3H, O**Ac**), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.12 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 137.4, 129.0, 128.7, 127.3, 85.1, 77.5, 76.6, 68.6, 67.7, 63.4, 33.6, 25.8, 21.1, 18.3, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{34}O_6SSiNa$ $[M+Na]^+$: 465.1743; found: 465.1740.

Methyl 3-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-mannopyranoside (12a) and **Methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-mannopyranoside (12b).[4]** Methyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside **11** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (73.5 μL, 1.2 equiv) and benzoyl chloride (49.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (12.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **12a** (110.8 mg, 81%) and **12b** (17.8 mg, 13%) as white solid. **12a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.08 (m, 2H, Ar**H**), 7.62–7.33 (m, 8H, Ar**H**), 5.63 (s, 1H, PhC**H**), 5.59 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.83 (s, 1H, **H-1**), 4.37-

4.27 (m, 3H, **H-2**, **H-4** and **H-6a**), 4.06-4.00 (m, 1H, **H-5**), 3.94 (t, *J* = 10.4 Hz, 1H, **H-6b**), 3.47 (s, 3H, O**CH**$_3$). **12b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12–8.09 (m, 2H, Ar**H**), 7.62–7.37 (m, 8H, Ar**H**), 5.66 (s, 1H, PhC**H**), 5.47 (dd, *J* = 3.6 Hz and 1.2 Hz, 1H, **H-2**), 4.84 (d, *J* = 1.2 Hz, 1H, **H-1**), 4.37-4.29 (m, 2H, **H-4** and **H-6a**), 4.06-4.01 (m, 1H, **H-5**), 3.95-3.86 (m, 2H, **H-3**, **H-6b**), 3.44 (s, 3H, O**CH**$_3$).

Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (14a) and **Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-2-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (14b).** Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*α*-D-mannopyranoside **13** (59.3 mg) was allowed to react with *N*,*N*-diisopropylethylamine (32.5 μL, 1.2 equiv) and benzoyl chloride (22.5 μL, 1.2 equiv) in dry acetonitrile (0.8 mL) at room temperature for 2 h in the presence of $Fe(acac)_3$ (5.4 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **14a** (62.5 mg, 83%) and **14b** (8.3 mg, 11%) as viscous pale yellow oil. **14a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.09 (m, 2H, Ar**H**), 7.60-7.55 (m, 3H, Ar**H**), 7.51-7.48 (m, 2H, Ar**H**), 7.46-7.42 (m, 2H, Ar**H**), 7.33-7.36 (m, 3H, Ar**H**), 5.53 (d, *J* = 1.6 Hz, 1H, **H-1**), 5.35 (dd, *J* = 9.2 Hz and 3.2 Hz, 1H, **H-3**), 4.42-4.40 (m, 1H, **H-2**), 4.30-4.21 (m, 2H, **H-4, H-5**), 3.95 (dd, *J* = 10.4 Hz and 4.4 Hz, 1H, **H-6a**), 3.91 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6b**), 0.90 (s, 9H, Si(C(**CH**$_3$)$_3$)(CH_3)$_2$), 0.09 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$)$_2$), 0.08 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 133.8, 133.4, 131.5, 129.9, 129.6, 129.1, 128.5, 127.6, 87.9, 75.1, 72.6, 70.7, 68.1, 64.3, 25.9, 18.3, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{34}O_6SSiNa$ $[M+Na]^+$: 513.1743; found: 513.1725. **14b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H, Ar**H**), 7.58-7.54 (m, 1H, Ar**H**), 7.51-7.48 (m, 2H, Ar**H**), 7.42 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.32-7.26 (m, 3H, Ar**H**), 5.62 (s, 2H, **H-1, H-2**), 4.22-4.17 (m, 1H, **H-5**), 4.15-4.07 (m, 2H, **H-3**, **H-4**), 3.98 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6a**), 3.90 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6b**), 0.92 (s, 9H, Si(C(**CH**$_3$)$_3$)(CH_3)$_2$), 0.11 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$)$_2$), 0.10 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 133.7, 133.5, 131.8, 129.9, 129.5, 129.1, 128.4, 127.7, 86.3, 73.9, 72.2, 71.0, 70.4, 64.0, 25.9, 18.3, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{34}O_6SSiNa$ $[M+Na]^+$: 513.1743; found: 513.1768.

Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (16a). Phenyl-ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **15** (102.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (63.0 μL, 1.2 equiv) and benzoyl chloride (42.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (10.7 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum

ether: 1/5), afforded compound **16a** as viscous pale yellow oil (113.8 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.10 (m, 2H, Ar**H**), 7.60-7.55 (m, 1H, Ar**H**), 7.46-7.42 (m, 2H, Ar**H**), 5.10 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.44 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.36 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.12 (t, *J* = 9.6 Hz, 1H, **H-2**), 3.96 (dd, *J* = 10.4 Hz and 5.2 Hz, 1H, **H-6a**), 3.91 (dd, *J* = 10.4 Hz and 4.0 Hz, 1H, **H-6b**), 3.62 (t, *J* = 4.8 Hz, 1H, **H-5**), 2.83-2.72 (m, 2H, SC**H**$_2$$CH_3$), 1.33 (t, *J* = 7.2 Hz, 3H, SCH**CH**$_3$), 0.89 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH_3)$_2$), 0.09 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$**)**$_2$), 0.08 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$**)**$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 133.3, 129.9, 129.7, 128.4, 86.6, 77.6, 68.6, 67.7, 63.3, 25.8, 25.6, 23.9, 18.2, 15.4, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{34}O_6SSiNa$ $[M+Na]^+$: 465.1743; found: 465.1742.

Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (16b). Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **15** (114.1 mg) was allowed to react with *N*,*N*-diisopropylethylamine (70.5 μL, 1.2 equiv) and acetyl chloride (29.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 5 h in the presence of $Fe(acac)_3$ (12.0 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **16b** as viscous pale yellow oil (110.3 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.85 (dd, *J* = 9.6 Hz and 2.4 Hz, 1H, **H-3**), 4.38 (d, *J* = 10.0 Hz, 1H, **H-1**), 4.23 (dd, *J* = 4.4 Hz and 2.4 Hz, 1H, **H-4**), 3.98-3.86 (m, 3H, **H-2, H-6a** and **H-6b**), 3.55 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.83-2.68 (m, 2H, SC**H**$_2$$CH_3$), 2.18 (s, 3H, O**Ac**), 1.34-1.30 (m, 3H, SCH**CH**$_3$), 0.89 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH_3)$_2$), 0.09 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$**)**$_2$), 0.08 (s, 3H, Si(C(CH_3)$_3$)(**CH**$_3$**)**$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 86.5, 77.4, 68.6, 67.4, 63.5, 25.8, 23.9, 21.2, 18.2, 15.4, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{16}H_{32}O_6SSiNa$ $[M+Na]^+$: 403.1587; found: 403.1574.

Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (18a).[1] Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside **17** (105.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (62.5 μL, 1.2 equiv) and benzoyl chloride (41.3 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (10.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **18a** as viscous yellow oil (121.1 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.57 (t, *J* = 7.6 Hz, 1H, Ar**H**), 7.46-7.42 (m, 2H, Ar**H**), 5.12 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.52 (d, *J* = 10.0 Hz, 1H, **H-1**), 4.34 (d, *J* = 3.2 Hz, 1H, **H-4**), 4.07 (dd, *J* = 10.0 Hz and 9.6 Hz, 1H, **H-2**), 3.93 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H, **H-6a**), 3.88 (dd, *J* = 10.4 Hz and

4.4 Hz, 1H, **H-6b**), 3.63 (dd, *J* = 5.2 Hz and 5.2 Hz, 1H, **H-5**), 3.31-3.32 (m, 1H, C**H**$(CH_3)_2$), 1.37 (s, 3H, CH(**CH₃**)$_2$), 1.35 (s, 3H, CH(**CH₃**)$_2$), 0.89 (s, 9H, Si(C(**CH₃**)**₃**)$(CH_3)_2$), 0.09(s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$), 0.08(s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$).

Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-*β*-D-galactopyranoside (18b). Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside **17** (121.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (72.5 μL, 1.2 equiv) and acetyl chloride (29.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (12.1 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **18b** as viscous pale yellow oil (123.2 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (dd, *J* = 9.6 Hz and 2.4 Hz, 1H, **H-3**), 4.45 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.21 (d, *J* = 2.4 Hz, 1H, **H-4**), 3.93-3.84 (m, 3H, **H-2**, **H-6a** and **H-6b**), 3.56-3.54 (m, 1H, **H-5**), 3.28-3.20 (m, 1H, C**H**$(CH_3)_2$), 2.18 (s, 3H, O**Ac**), 1.34 (d, *J* = 6.8 Hz, 6H, CH(**CH₃**)$_2$), 0.89 (s, 9H, Si(C(**CH₃**)**₃**)$(CH_3)_2$), 0.09 (s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$), 0.08 (s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 86.4, 77.6, 76.4, 68.4, 67.7, 63.3, 35.4, 25.8, 24.3, 24.2, 21.2, 18.2, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{17}H_{34}O_6SSiNa$ $[M+Na]^+$: 417.1743; found: 417.1742.

***p*-tolyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (20a).** *p*-tolyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **19** (110.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (58.0 μL, 1.2 equiv) and benzoyl chloride (39.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (9.7 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether 1/5), afforded compound **20a** as viscous pale yellow oil (128.9 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (m, 2H, Ar**H**), 7.57-7.53 (m, 1H, Ar**H**), 7.49 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.42 (t, *J* = 7.6 Hz, 2H, Ar**H**), 7.12 (d, *J* = 8.0 Hz, 2H, Ar**H**), 5.10 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.57 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.34 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.06-3.97 (m, 2H, **H-2** and **H-6a**), 3.92 (dd, *J* = 10.4 Hz and 4.0 Hz, 1H, **H-6b**), 3.63-3.60 (m, 1H, **H-5**), 2.35 (s, 3H, SPhC**H₃**), 0.91 (s, 9H, Si(C(**CH₃**)**₃**)$(CH_3)_2$), 0.12 (s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$), 0.10 (s, 3H, Si(C$(CH_3)_3$)(**CH₃**)$_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 138.6, 133.6, 133.4, 130.1, 129.9, 129.8, 128.5, 127.9, 89.4, 77.8, 77.3, 68.9, 67.2, 63.7, 25.9, 21.3, 18.3, -5.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{26}H_{36}O_6SSiNa$ $[M+Na]^+$: 529.1900; found: 527.1877.

***p*-tolyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (20b).** *p*-tolyl-6-

O-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **19** (98.3 mg) was allowed to react with *N*,*N*-diisopropylethylamine (51.5 μL, 1.2 equiv) and acetyl chloride (21.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 5 h in the presence of $Fe(acac)_3$ (8.7 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **20b** as viscous pale yellow oil (96.7 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.10 (d, *J* = 8.0 Hz, 2H, Ar**H**), 4.85 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.50 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.22 (d, *J* = 2.8 Hz, 1H, **H-4**), 3.97 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6a**), 3.92-3.84 (m, 2H, **H-2** and **H-6b**), 3.53 (t, *J* = 4.0 Hz, 1H, **H-5**), 2.33 (s, 3H, SPh**CH$_3$**), 2.14 (s, 3H, O**Ac**), 0.91 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.12 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 138.5, 133.5, 129.8, 127.5, 88.9, 77.3, 76.5, 68.8, 66.8, 63.8, 25.8, 21.2, 18.2, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{34}O_6SSiNa$ $[M+Na]^+$: 465.1743; found: 465.1735.

Methyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (22). Methyl-6-*O*-(*tert*-butyldimethylsilyloxy)-1-thio-*β*-D-galactopyranoside **21** (69.1 mg) was allowed to react with *N*,*N*-diisopropylethylamine (55.5 μL, 1.5 equiv) and acetyl chloride (23.0 μL, 1.5 equiv) in dry acetonitrile (0.7 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (7.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **22** as viscous pale yellow oil (64.7 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.86 (dd, *J* = 9.6 Hz and 2.8 Hz, 1H, **H-3**), 4.30-4.27 (m, 2H, **H-1, H-4**), 4.04-3.96 (m, 2H, **H-2, H-6a**), 3.91 (dd, *J* = 10.8 Hz and 4.0 Hz, 1H, **H-6b**), 3.55 (t, *J* = 4.4 Hz, 1H, **H-5**), 2.22 (s, 3H, SC**H$_3$**), 2.19 (s, 3H, S**CH$_3$**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 85.9, 77.1, 76.5, 68.9, 66.7, 63.8, 25.8, 25.6, 21.2, 18.2, 10.9, -3.6, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{15}H_{30}O_6SSiNa$ $[M+Na]^+$: 389.1430; found: 389.1442.

Allyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (24). Allyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside **23** (88.5 mg) was allowed to react with *N*,*N*-diisopropylethylamine (55.5 μL, 1.2 equiv) and benzoyl chloride (36.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (9.4 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **24** as viscous colorless oil (106.8 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-

8.08 (m, 2H, Ar**H**), 7.56-7.52 (m, 1H, Ar**H**), 7.43-7.39 (m, 2H, Ar**H**), 5.99-5.89 (m, 1H, $OCH_2C\mathbf{H}=CH_2$), 5.33-5.29 (m, 1H, $OCH_2CH=C\mathbf{H_a}H_b$), 5.22-5.19 (m, 1H, $OCH_2CH=CH_a\mathbf{H_b}$), 5.07 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.44-4.37 (m, 2H, **H-1** and $OC\mathbf{H_a}H_bCH=CH_2$), 4.26 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.15 (q, *J* = 6.4 Hz, 1H, $OCH_a\mathbf{H_b}CH=CH_2$), 4.10-4.05 (m, 1H, **H-2**), 3.95-3.85 (m, 2H, **H-6a** and H-**6b**), 3.59-3.57 (m, 2H, **H-5**), 0.89 (s, 9H, $Si(C(\mathbf{CH_3})_3)(CH_3)_2$), 0.08 (s, 6H, $Si(C(CH_3)_3)(\mathbf{CH_3})_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 133.8, 133.3, 129.9, 129.7, 128.4, 118.0, 102.3, 75.9, 74.1, 70.1, 69.4, 67.9, 62.7, 25.8, 18.3, -5.4 ppm; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{34}O_7SiNa$ $[M+Na]^+$: 461.1971; found: 461.1981.

Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (26). Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-*β*-D-galactopyranoside **25** (65.5 mg) was allowed to react with *N*,*N*-diisopropylethylamine (37.5 μL, 1.2 equiv) and benzoyl chloride (24.5 μL, 1.2 equiv) in dry acetonitrile (0.6 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (6.3 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **26** as viscous colorless oil (72.2 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12-8.10 (m, 2H, Ar**H**), 7.58-7.55 (m, 1H, Ar**H**), 7.46-7.41 (m, 2H, Ar**H**), 7.31-7.25 (m, 2H, Ar**H**), 7.11-7.03 (m, 3H, Ar**H**), 5.17 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.99 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.36-4.31 (m, 2H, **H-4** and **H-2**), 3.94-3.91 (m, 2H, **H-6a** and **H-6b**), 3.73-3.70 (m, 1H, **H-5**), 0.89 (s, 9H, $Si(C(\mathbf{CH_3})_3)(CH_3)_2$), 0.06 (s, 3H, $Si(C(CH_3)_3)(\mathbf{CH_3})_2$), 0.05 (s, 3H, $Si(C(CH_3)_3)(\mathbf{CH_3})_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 157.2, 133.4, 130.0, 129.5, 128.5, 122.9, 117.2, 101.8, 75.8, 74.5, 69.3, 68.0, 62.9, 25.8, 18.3, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{34}O_7SiNa$ $[M+Na]^+$: 497.1971; found: 497.1978.

Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-3′-*O*-benzoyl-1-*S*-*β*-D-lactoside (28a). Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-1-*S*-*β*-D-lactoside **27** (73.1 mg) was allowed to react with *N*,*N*-diisopropylethylamine (23.0 μL, 1.2 equiv) and benzoyl chloride (15.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (3.9 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **28a** as viscous colorless oil (73.6 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11-8.09 (m, 2H, Ar**H**), 7.59–7.55 (m, 3H, Ar**H**), 7.46-7.42 (m, 2H, Ar**H**), 7.29-7.26 (m, 3H, Ar**H**), 5.03 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3′**), 4.54-4.48 (m, 2H, **H-1** and **H-1′**), 4,28 (d, *J* = 2.8 Hz, 1H, **H-4′**), 4.07 (dd, *J* = 10.0 Hz and 8.0 Hz, 1H, **H-2′**), 3.95-3.94 (m, 2H, **H-6a** and **H-6b**), 3.90-3.88 (m, 2H, **H-**

6a′ and **H-6b′**), 3.69-3.65 (m, 2H, **H-5′** and **H-3**), 3.62-3.57 (m, 1H, **H-4**), 3.44-3.35 (m, 2H, **H-5** and **H-2**), 0.90 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.88 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.07 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.3, 133.4, 133.2, 131.7, 129.9, 129.6, 128.9, 128.5, 128.1, 104.4, 87.3, 80.8, 78.9, 77.4, 77.1, 76.7, 76.3, 75.9, 74.5, 71.7, 69.3, 67.6, 62.8, 62.4, 25.9, 25.8, 18.3, 18.2, -5.1, -5.2, -5.5 ppm; HRMS (ESI-TOF) m/z calcd for $C_{37}H_{58}O_{11}SSi_2Na$ $[M+Na]^+$: 789.3136; found: 789.3113.

Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-3′-*O*-acetyl-1-*S*-*β*-D-lactoside (28b). Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-1-*S*-*β*-D-lactoside **27** (77.7 mg) was allowed to react with *N*,*N*-diisopropylethylamine (24.0 μL, 1.2 equiv) and acetyl chloride (10.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (4.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **28b** as viscous colorless oil (68.6 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.55 (m, 2H, Ar**H**), 7.29-7.27 (m, 3H, Ar**H**), 4.78 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3′**), 4.53 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.43 (d, *J* = 7.6 Hz, 1H, **H-1′**), 4.16 (d, *J* = 2.8 Hz, 1H, **H-4′**), 3.94-3.87 (m, 5H, **H-2′**, **H-6a**, **H-6b**, **H-6a′** and **H-6b′**), 3.68-3.63 (m, 1H, **H-3**), 3.60-3.55 (m, 2H, **H-4** and **H-5′**), 3.44-3.34 (m, 2H, **H-2** and **H-5**), 2.18 (s, 3H, O**Ac**), 0.90 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.87 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.07 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 133.2, 131.7, 128.9, 128.1, 104.4, 87.4, 80.9, 78.9, 76.2, 75.3, 74.3, 71.7, 69.1, 67.6, 62.8, 62.6, 25.9, 25.8, 21.1, 18.3, 18.2, -5.1, -5.2, -5.6 ppm; HRMS (ESI-TOF) m/z calcd for $C_{32}H_{56}O_{11}SSi_2Na$ $[M+Na]^+$: 727.2980; found: 727.2963.

Phenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*α*-D-mannopyranoside (30).[5] Phenyl-4,6-*O*-benzylidene-1-thio-*α*-D-mannopyranoside **29** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (58.0 μL, 1.2 equiv) and benzoyl chloride (38.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (9.8 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **30** as white solid (104.4 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.59-7.42 (m, 7H, Ar**H**), 7.35-7.29 (m, 6H, Ar**H**), 5.61-5.57 (m, 3H, **H-1**, **H-3** and PhC**H**), 4.58-4.50 (m, 2H, **H-2**, **H-5**), 4.36 (t, *J* = 10.0 Hz, **H-4**), 4.26 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-6a**), 3.93-3.88 (m, 1H, **H-6b**).

Methyl-3-*O*-benzoyl-*α*-L-fucopyranoside (32a).[1] Methyl-*α*-L-fucopyranoside **31** (100 mg) was

allowed to react with *N*,*N*-diisopropylethylamine (139.5 μL, 1.5 equiv) and benzoyl chloride (97.5 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (19.8 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **32a** as pale yellow solid (126.7 mg, 80%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.15–8.13 (m, 2H, Ar**H**), 7.64–7.60 (m, 1H, Ar**H**), 7.52–7.47 (m, 2H, Ar**H**), 5.24 (dd, *J* = 10.4 Hz and 2.8 Hz, 1H, **H-3**), 4.77 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.18 (dd, *J* = 10.4 Hz and 3.6 Hz, 1H, **H-2**), 4.07 (dd, *J* = 13.2 Hz and 6.8 Hz, 1H, **H-5**), 3.98 (d, *J* = 2.8 Hz, 1H, **H-4**), 3.46 (s, 3H, O**CH**$_3$), 1.26 (d, *J* = 6.8 Hz, 3H, CH**CH**$_3$).

Methyl-3-*O*-acetyl-*α*-L-fucopyranoside (32b).[6] Methyl-*α*-L-fucopyranoside **31** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (147.0 μL, 1.5 equiv) and acetyl chloride (59.5 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 8 h in the presence of $Fe(acac)_3$ (19.8 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **32b** as pale yellow oil (93.9 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H, **H-3**), 4.80 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.04-3.95 (m, **H-2** and **H-5**), 3.86-3.85 (m, 1H, **H-4**), 3.45 (s, 3H, O**CH**$_3$), 2.18 (s, 3H, O**Ac**), 1.29 (d, *J* = 6.8 Hz, 3H, CH**CH**$_3$).

Methyl-3-*O*-benzoyl-*α*-L-rhamnopyranoside (34).[1] Methyl-*α*-L-rhamnopyranoside **33** (89.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (130.5 μL, 1.5 equiv) and benzoyl chloride (86.5 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 6 h in the presence of $Fe(acac)_3$ (17.6 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **34** as yellow oil (121.3 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–8.04 (m, 2H, Ar**H**), 7.57–7.53 (m, 1H, Ar**H**), 7.42–7.39 (m, 2H, Ar**H**), 5.23 (dd, *J* = 9.2 Hz and 3.2 Hz, 1H, **H-3**), 4.66 (s, 1H, **H-1**), 4.13–4.11 (m, 1H, **H-2**), 3.80–3.72 (m, 2H, **H-4** and **H-5**), 3.37 (s, 3H, O**CH**$_3$), 1.35 (d, *J* = 5.6 Hz, 3H, CH**CH**$_3$).

Methyl-3-*O*-benzoyl-6-deoxy-*α*-D-mannopyranoside (36). Methyl-6-deoxy-*α*-D-mannopyranoside **35** (52.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (77.0 μL, 1.5 equiv) and benzoyl chloride (51.0 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 8 h in the presence of $Fe(acac)_3$ (10.3 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **36** as viscous colorless oil (60.5 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H, Ar**H**), 7.60–7.56 (m, 1H, Ar**H**),

7.46–7.42 (m, 2H, Ar**H**), 5.26 (dd, *J* = 9.2 Hz and 2.8 Hz, 1H, **H-3**), 4.70 (s, 1H, **H-1**), 4.14 (s, 1H, **H-2**), 3.82–3.77 (m, 2H, **H-4** and **H-5**), 3.41 (s, 3H, O**CH**$_3$), 1.38 (d, *J* = 5.2 Hz, 3H, CH**CH**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 133.5, 129.8, 129.5, 128.5, 100.6, 75.5, 71.4, 69.7, 68.5, 54.9, 17.6 ppm; HRMS (ESI-TOF) m/z calcd for $C_{14}H_{18}O_6Na$ $[M+Na]^+$: 305.1001; found: 305.1004.

1,6-Anhydro-2-*O*-benzoyl-*β*-D-mannopyranoside (38). 1,6-Anhydro-*β*-D-mannopyranoside **37** (76.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (98.5 μL, 1.2 equiv) and benzoyl chloride (65.5 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (16.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **38** as viscous colorless oil (97.3 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08–8.06 (m, 2H, Ar**H**), 7.61–7.56 (m, 1H, Ar**H**), 7.47–7.43 (m, 2H, Ar**H**), 5.59 (s, 1H, **H-1**), 5.12 (dd, *J* = 5.2 Hz and 1.6 Hz, 1H, **H-2**), 4.60 (d, *J* = 5.2 Hz, 1H, **H-5**), 4.36 (d, *J* = 7.6 Hz, 1H, **H-6a**), 4.28-4.25 (m, 1H, **H-3**), 3.98-3.96 (m, 1H, **H-4**), 3.82 (dd, *J* =7.2 Hz and 5.6 Hz, **H-6b**). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 133.7, 129.9, 129.0, 128.6, 100.0, 76.6, 72.2, 70.7, 69.5, 65.3 ppm; HRMS (ESI-TOF) m/z calcd for $C_{13}H_{14}O_6Na$ $[M+Na]^+$: 289.0688; found: 289.0674.

Methyl 3,6-di-*O*-benzoyl-*β*-D-galactopyranoside (40a).[1] Methyl-*β*-D-galactopyranoside **39** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (359.0 μL, 4.0 equiv) and benzoyl chloride (237.5 μL, 4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (18.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **40a** as white solid (165.8 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.01 (m, 4H, Ar**H**), 7.58-7.52 (m, 2H, Ar**H**), 7.44-7.39 (m, 4H, Ar**H**), 5.13 (dd, *J* = 10.4 Hz and 2.8 Hz, 1H, **H-3**), 4.66-4.54 (m, 2H, **H-6a** and **H-6b**), 4.35 (d, *J* = 7.6 Hz, 1H, **H-1**), 4.23 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.06 (dd, *J* = 10.4 Hz and 7.6 Hz, 1H, **H-2**), 3.96 (t, *J* = 6.4 Hz, 1H, **H-5**), 3.57 (s, 3H, O**CH**$_3$).

Methyl 3,6-di-*O*-acetyl-*β*-D-galactopyranoside (40b).[3] Methyl-*β*-D-galactopyranoside **39** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (359.0 μL, 4.0 equiv) and acetyl chloride (145.5 μL, 4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (18.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **40b** as white solid (111.8 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.84 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.32-4.24 (m, 3H, **H-1**, **H-6a** and **H-6b**), 4.04-4.03 (m, 1H, **H-4**), 3.85-3.82 (m, 1H, **H-2**), 3.75 (t, *J* = 6.4 Hz, 1H, **H-5**), 3.58 (s, 3H, O**CH**$_3$), 2.18

(s, 3H, O**Ac**), 2.09 (s, 3H, O**Ac**).

Methyl 3,6-di-*O*-benzoyl-*α*-D-galactopyranoside (42a).[7] Methyl-*α*-D-galactopyranoside **41** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (359.0 μL, 4.0 equiv) and benzoyl chloride (237.5 μL, 4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 6 h in the presence of $Fe(acac)_3$ (18.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **42a** as colorless oil (153.3 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 7.2Hz, 2H, Ar**H**), 8.02 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.59-7.54 (m, 2H, Ar**H**), 7.43 (t, *J* = 7.6 Hz, 4H, Ar**H**), 5.33 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H, **H-3**), 4.93 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.60 (dd, *J* = 11.6 Hz and 6.0 Hz, 1H, **H-6a**), 4.51 (dd, *J* = 11.6 Hz and 6.8 Hz, 1H, **H-6b**), 4.24-4.19 (m, 3H, **H-2**, **H-4** and **H-5**), 3.47 (s, 3H, O**CH**$_3$).

Methyl 3,6-di-*O*-acetyl-*α*-D-galactopyranoside (42b).[3] Methyl-*α*-D-galactopyranoside **41** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (359.0 μL, 4.0 equiv) and acetyl chloride (145.5 μL, 4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (18.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **42b** as colorless oil (97.4 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.07 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H, **H-3**), 4.86 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.34 (dd, *J* = 11.6 Hz and 6.0 Hz, 1H, **H-6a**), 4.25 (dd, *J* = 11.6 Hz and 6.8 Hz, 1H, **H-6b**), 4.06-3.98 (m, 3H, **H-2, H-4** and **H-5**), 3.46 (s, 3H, O**CH**$_3$), 2.17 (s, 3H, O**Ac**), 2.09 (s, 3H, O**Ac**).

Methyl 3,6-di-*O*-benzoyl-*α*-D-mannopyranoside (44).[8] Methyl-*α*-D-mannopyranoside **43** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (359.0 μL, 4.0 equiv) and benzoyl chloride (237.5 μL, 4.0 equiv) in dry acetonitrile (1 mL) at room temperature for 6 h in the presence of $Fe(acac)_3$ (18.2 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **44** as colorless oil (157.5 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.05 (m, 4H, Ar**H**), 7.58-7.53 (m, 2H, Ar**H**), 7.45-7.39 (m, 4H, Ar**H**), 5.36 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.78-4.72 (m, 2H, **H-1**, **H-6a**), 4.60 (dd, *J* = 12.0 Hz and 2.0 Hz, **H-6b**), 4.18-4.17 (m, 1H, **H-2**), 4.15-4.10 (m, 1H, **H-4**), 4.02-3.97 (m, 1H, **H-5**), 3.47 (s, 3H, O**CH**$_3$).

2-Hydroxyethyl benzoate (46).[9] Ethylene glycol **45** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (337.0 μL, 1.2 equiv) and benzoyl chloride (223.0 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (57.0 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether

1/4), afforded compound **46** as colorless oil (224.9 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05-8.03 (m, 2H, Ar**H**), 7.55-7.52 (m, 1H, Ar**H**), 7.43-7.38 (m, 2H, Ar**H**), 4.43 (t, *J* = 4.8 Hz, 2H, C**H**$_2$OCOPh), 3.93 (t, *J* = 4.8 Hz, 2H, C**H**$_2$OH), 3.01 (br s, 1H, O**H**).

2-Hydroxy-2-phenylethyl benzoate (48).[9] 1-phenyl-1,2-ethanediol **47** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (151.5 μL, 1.2 equiv) and benzoyl chloride (100.2 μL, 1.2 equiv) in dry acetonitrile (1 mL) at room temperature for 8 h in the presence of $Fe(acac)_3$ (25.6 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **48** as colorless oil (142.0 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2H, Ar**H**), 7.56-7.30 (m, 8H, Ar**H**), 5.08 (dd, *J* = 5.2 Hz and 2.4 Hz, 1H, C**H**OH), 4.50 (dd, *J* = 7.6 Hz and 2.0 Hz, 1H, C**H**$_2$OCOPh), 4.41 (dd, *J* = 7.6 Hz and 5.6 Hz, 1H, C**H**$_2$OCOPh), 2.78 (br s, 1H, O**H**).

1-*O*-Benzoyl-2-propanol (50).[7] 1,2-propanediol **49** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (344.5 μL, 1.5 equiv) and benzoyl chloride (227.5 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $Fe(acac)_3$ (46.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **50** as colorless oil (210.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 7.2 Hz, 2H, Ar**H**), 7.54 (t, *J* = 7.2 Hz, 1H, Ar**H**), 7.41 (t, *J* = 7.6 Hz, 2H, Ar**H**), 4.30 (dd, *J* = 10.4 Hz and 2.8 Hz, 1H, C**H**$_2$OCOPh), 4.23–4.12 (m, 2H, C**H**$_2$OCOPh and C**H**OH), 3.09 (br s, 1H, CHO**H**), 1.27 (d, *J* = 6.4 Hz, 3H, CHC**H**$_3$).

3-Hydroxybutyl benzoate (52).[10] 1,3-butanediol **51** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (290.0 μL, 1.5 equiv) and benzoyl chloride (192.0 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 5 h in the presence of $Fe(acac)_3$ (39.5 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/8), afforded compound **52** as colorless oil (172.5 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H, Ar**H**), 7.54 (t, *J* = 7.6Hz, 1H, Ar**H**), 7.42 (t, *J* = 8.0 Hz, 2H, Ar**H**), 4.58-4.51 (m, 1H, C**H**$_2$OCOPh), 4.42–4.36 (m, 1H, C**H**$_2$OCOPh), 4.02-3.95 (m, 1H, C**H**OH), 3.22 (br s, 1H, CHO**H**), 1.96-1.81 (m, 2H, C**H**$_2$), 1.26 (d, *J* = 6.0 Hz, 3H, CHC**H**$_3$).

3-Hydroxy-3-methylbutyl benzoate (54).[11] 3-methyl-1,3-butanediol **53** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (251.5 μL, 1.5 equiv) and benzoyl chloride (166.5 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 6 h in the presence of $Fe(acac)_3$ (40.0 mg, 0.1 equiv).

The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **54** as colorless oil (188.0 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.02 (m, 2H, Ar**H**), 7.57-7.52 (m, 1H, Ar**H**), 7.43-7.39 (m, 2H, Ar**H**), 4.50 (t, *J* = 6.8 Hz, 2H, C**H**$_2$), 1.98 (t, *J* = 6.8 Hz, 2H, C**H**$_2$), 1.32 (s, 6H, (C**H**$_3$)$_2$).

2-Hydroxy-3-allyloxypropyl benzoate (56).[7] 3-(allyloxy)-1,2-propanediol **55** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (197.5 μL, 1.5 equiv) and benzoyl chloride (131.0 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 5 h in the presence of $Fe(acac)_3$ (26.8 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **56** as colorless oil (144.8 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (m, 2H, Ar**H**), 7.57-7.53 (m, 1H, Ar**H**), 7.44-7.40 (m, 2H, Ar**H**), 5.95-5.85 (m, 1H, CH_2=C**H**CH_2), 5.30-5.18 (m, 2H, C**H**$_2$=$CHCH_2$), 4.44-4.36 (m, 2H, C**H**$_2$OBz), 4.19-4.14 (m, 1H, C**H**OH), 4.03 (d, *J* = 5.2 Hz, 2H, CH_2=CHC**H**$_2$), 3.62-3.53 (m, 2H, C**H**$_2$OAllyl).

3-Phenoxypropyl benzoate (58).[11] 3-phenoxy-1,2-propanediol **57** (100.0 mg) was allowed to react with *N*,*N*-diisopropylethylamine (155.5 μL, 1.5 equiv) and benzoyl chloride (103.0 μL, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 7 h in the presence of $Fe(acac)_3$ (21.0 mg, 0.1 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **58** as colorless oil (123.0 mg, 76%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 2H, Ar**H**), 7.56-7.52 (m, 1H, Ar**H**), 7.43-7.38 (m, 2H, Ar**H**), 7.29-7.24 (m, 2H, Ar**H**), 6.98-6.90 (m, 3H, Ar**H**), 4.56-4.48 (m, 2H, C**H**$_2$OBz), 4.39-4.35 (m, 1H, CH_2C**H**(OH)CH_2), 4.13-4.05 (m, 2H, C**H**$_2$OPh).

2. References

(1) D. Lee, M. S. Taylor, *J. Am. Chem. Soc*., **2011**, *133*, 3724-3727.

(2) I. H. Chen, K. G. M. Kou, D. N. Le, C. M. Rathbun, V. M. Dong, *Chem. Eur. J*., **2014**, *20*, 5013-5018.

(3) B. Ren, M. Rahm, X. L. Zhang, Y. X. Zhou, H. Dong, *J. Org. Chem*., **2014**, *79*, 8134-8142.

(4) M. Adinolfi, A. Iadonisi, A. Pastore, *Tetrahedron Lett*, **2009**, *50*, 7051-7054.

(5) H. Franzyk, M. Meldal, H. Paulsen, K. J. Bock, *Chem. Soc. Perkin Trans.*, **1995**, *27*, 2883-2898.

(6) E. V. Evtushenko, *Synthetic Communications*, **2006**, *36*, 1593-1599.

(7) X. L. Zhang, B. Ren, J. T. Ge, Z. C. Pei, H. Dong, *Tetrahedron*, **2016**, *72*, 1005-1010.

(8) Z. Zhang, C. H. Wong, *Tetrahedron*, **2002**, *58*, 6513-6519.

(9) F. Iwasaka, M. Toshihide, O. Onomura, W. Nakashima, Y. Matsumura, *J. Org. Chem.*, **2000**, *65*, 996–1002.

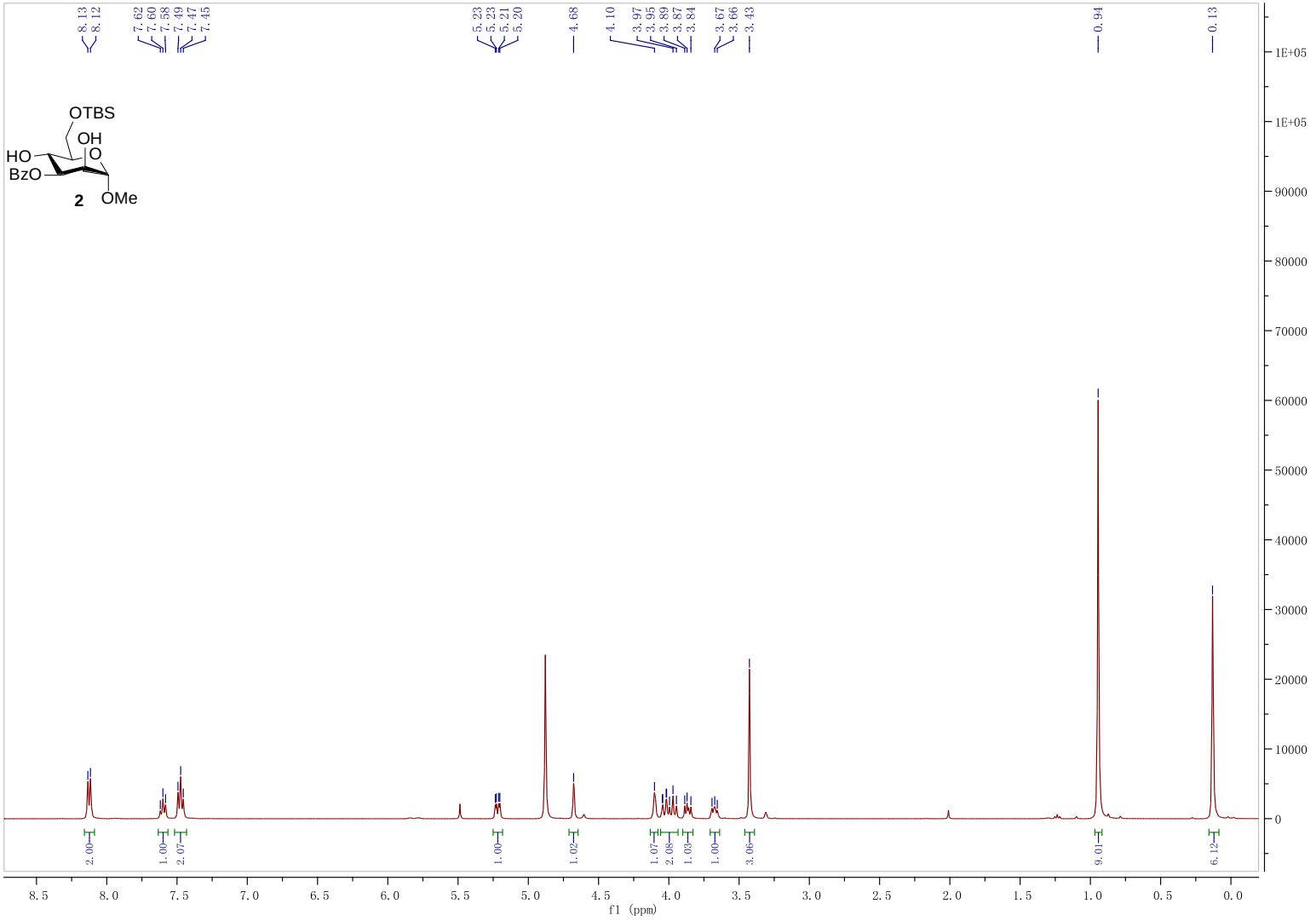
(10) D. Lee, C. L. Williamson, L. Chan, M. S. Taylor, *J. Am. Chem. Soc.*, **2012**, *134*, 8260-8267.

(11) Y. C. Lu, C. X. Hou, J. L. Ren, X. T. Xin, H. F. Xu, Y. X. Pei, H. Dong, Z. C. Pei, *Molecules*, **2016**, *21*, 641-649.

3. Copies of ^{1}H-NMR, ^{13}C-NMR and 2D-COSY

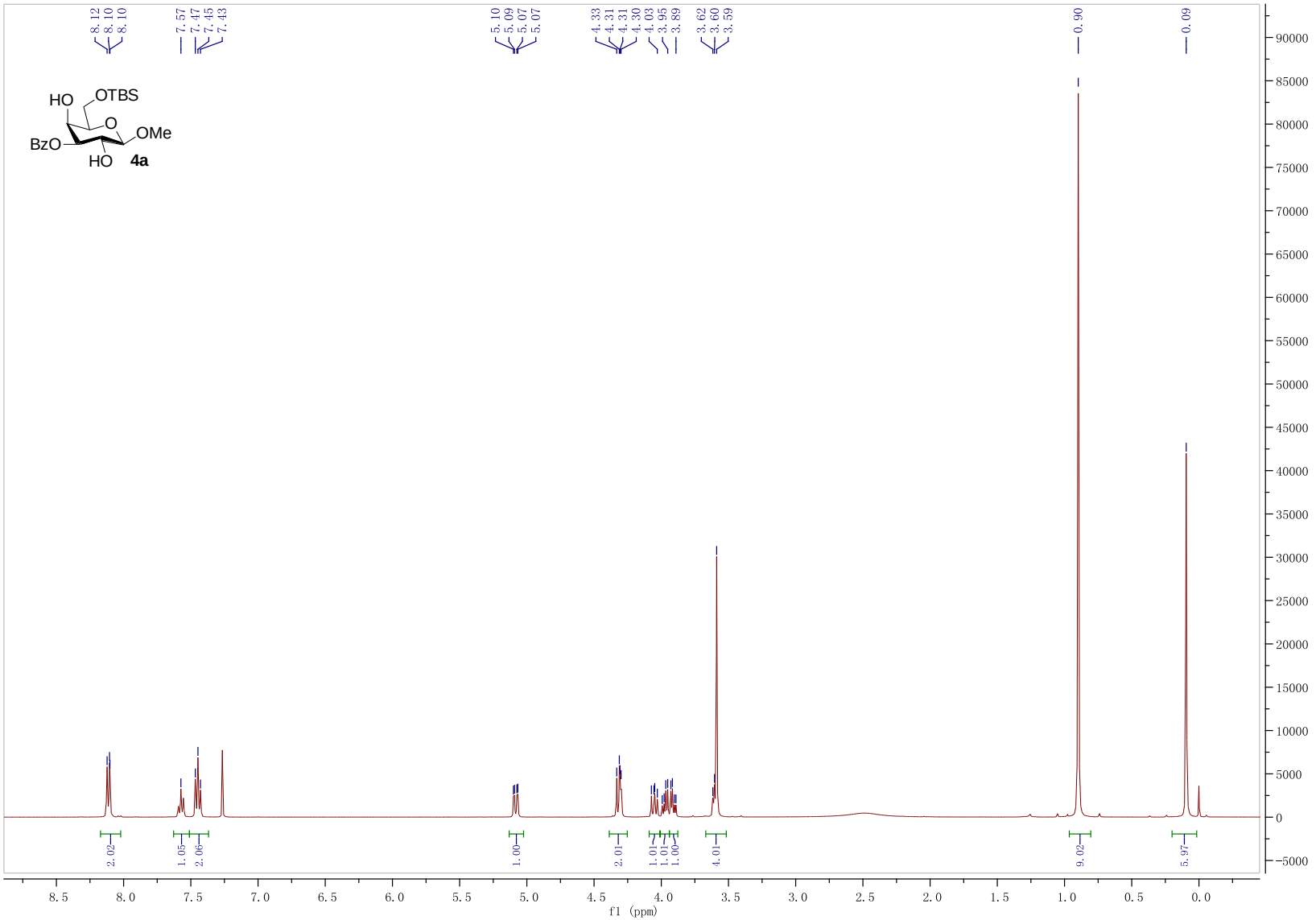
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-mannopyranoside (2)

^{1}H-NMR of compound **2** (CD_3OD)



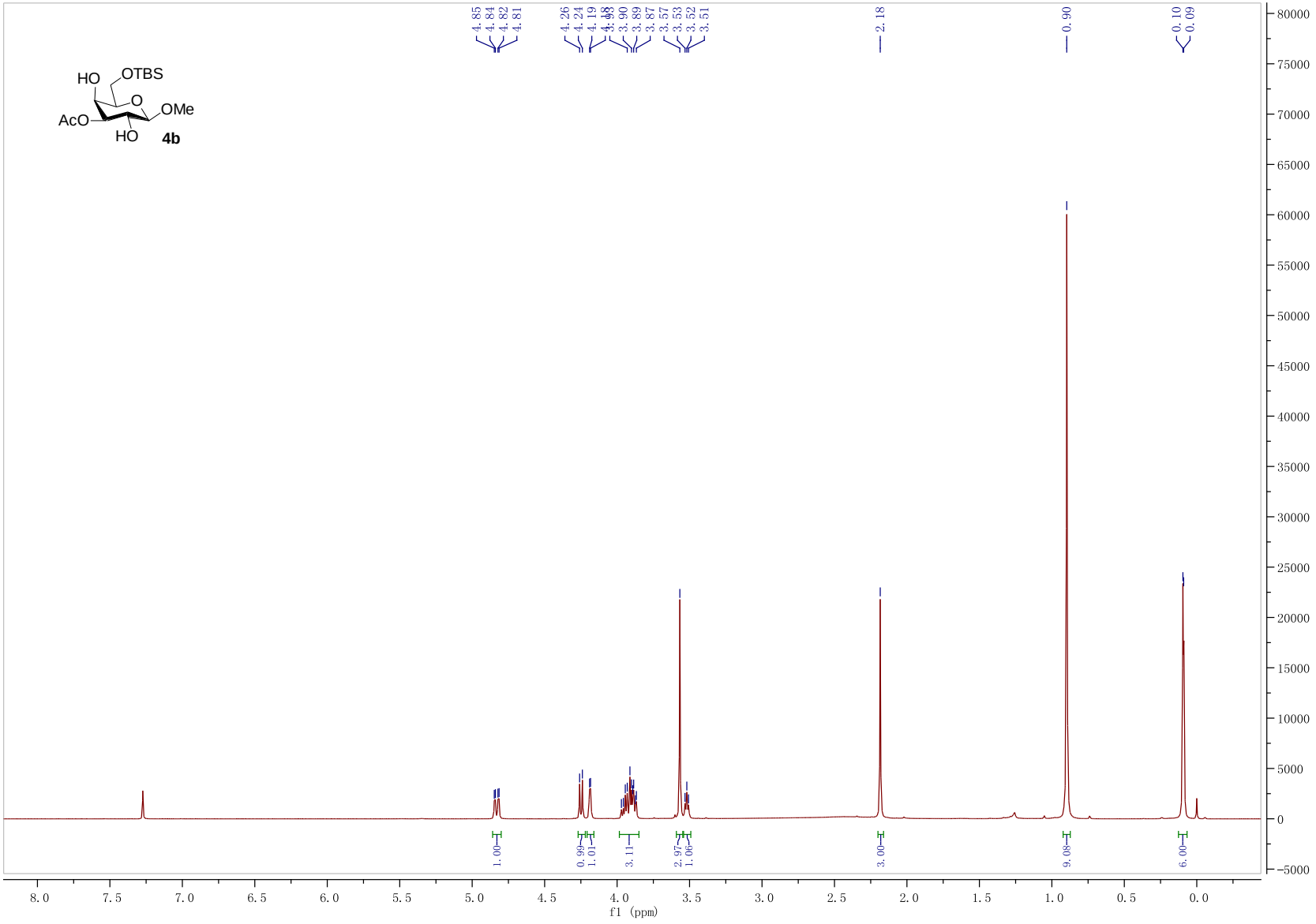
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (4a)

^{1}H-NMR of compound **4a** ($CDCl_3$)



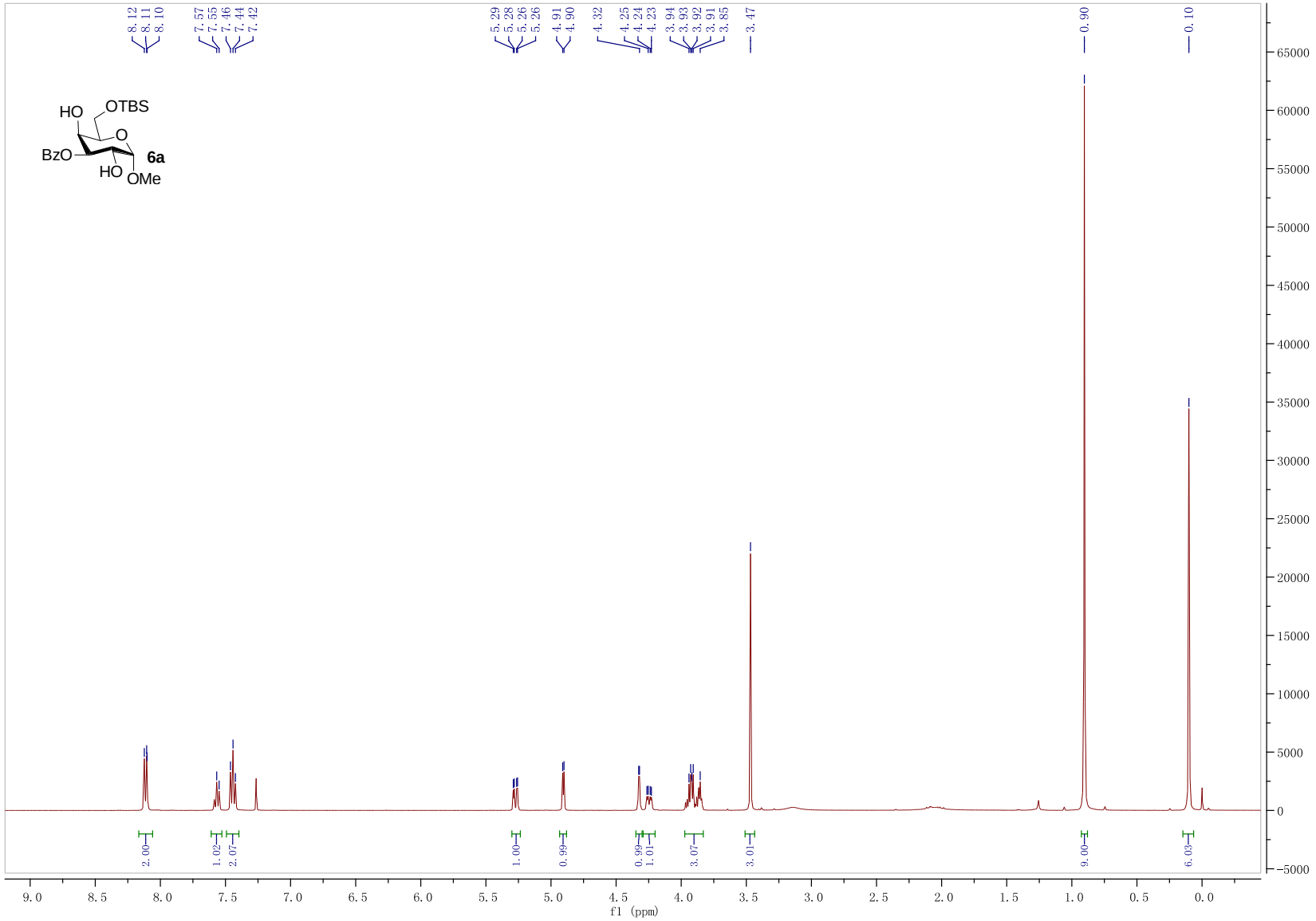
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (4b)

^{1}H-NMR of compound **4b** ($CDCl_3$)



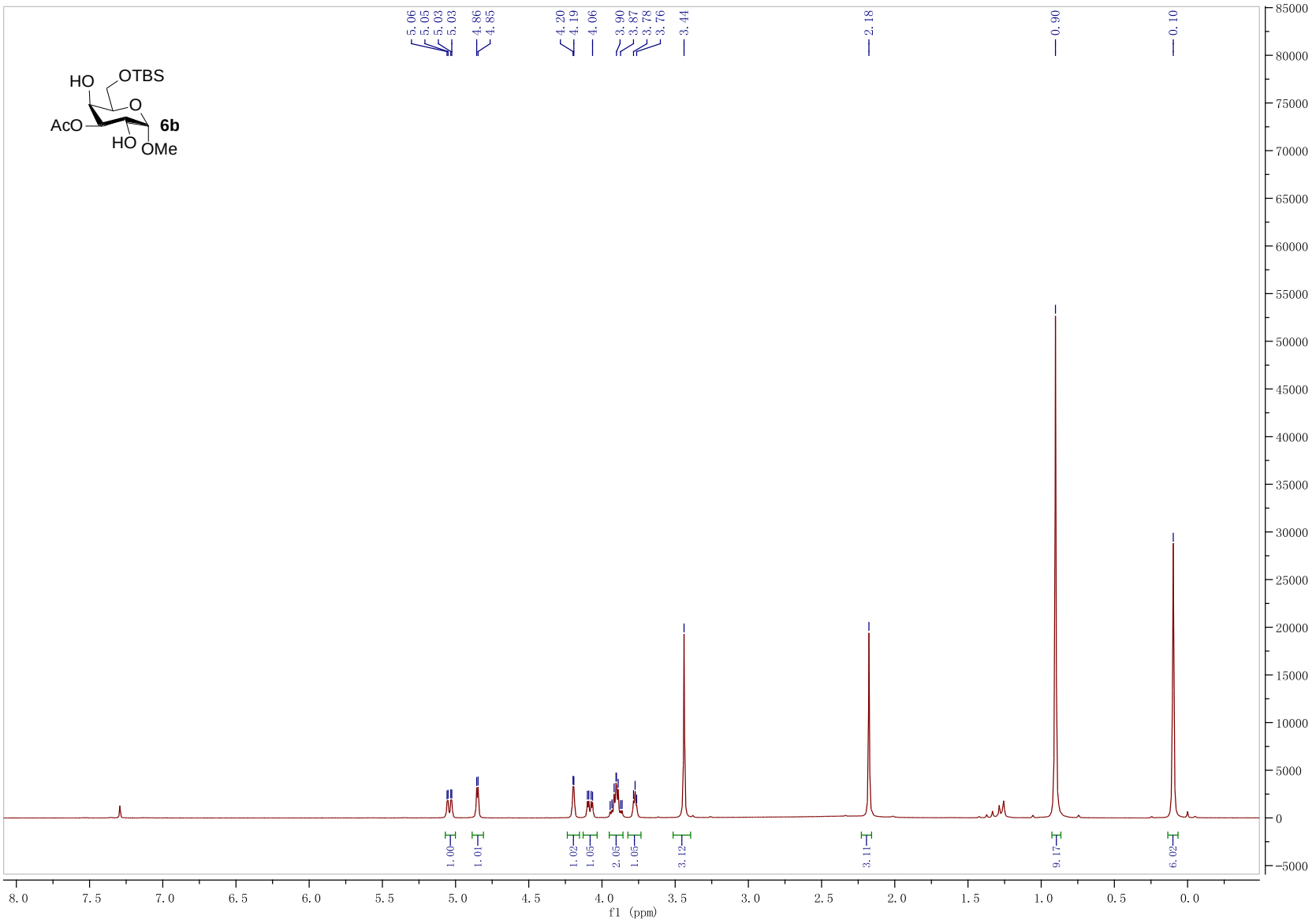
Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (6a)

^{1}H-NMR of compound **6a** ($CDCl_3$)



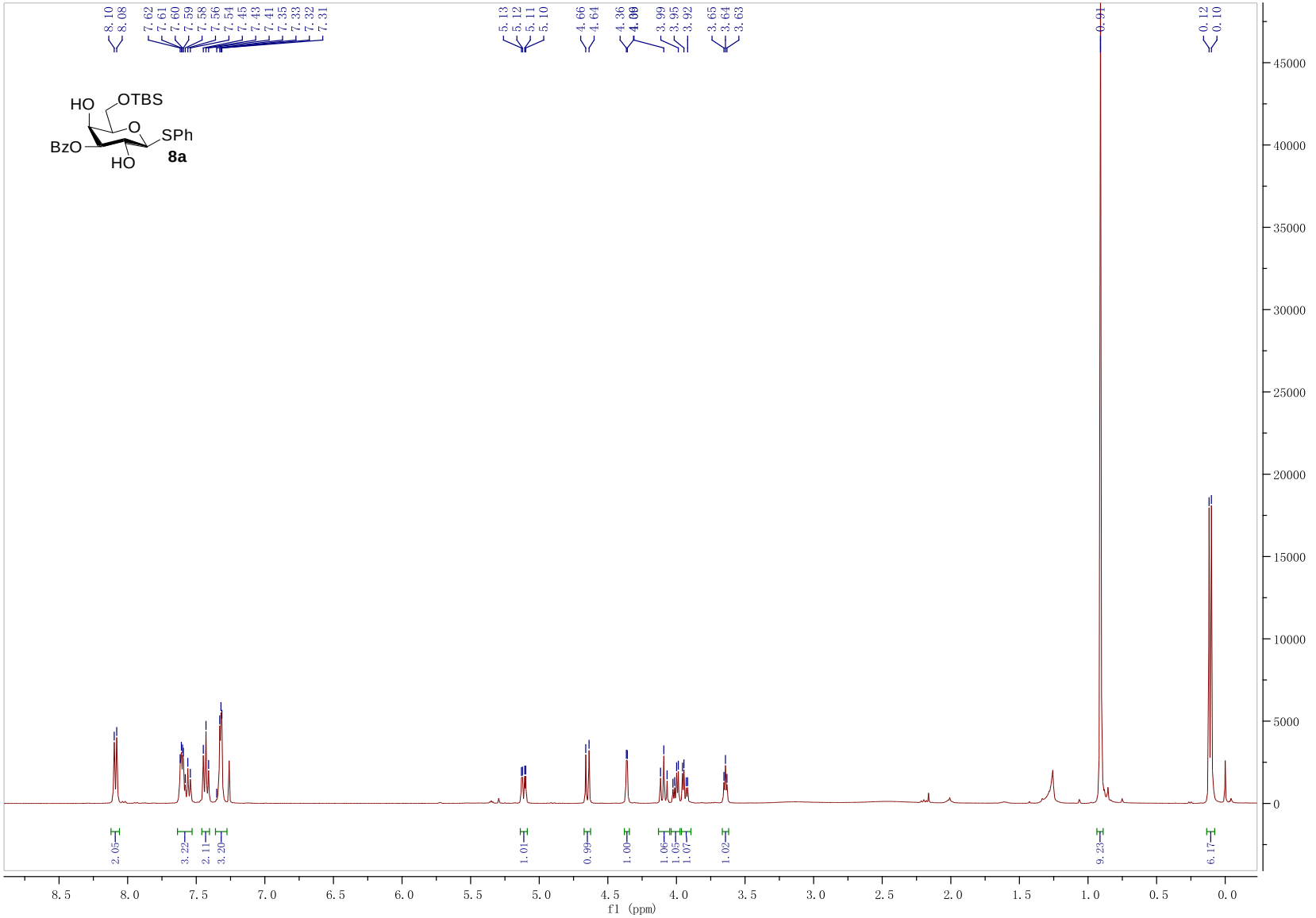
Methyl 3-*O*-acetyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (6b)

^{1}H-NMR of compound **6b** ($CDCl_3$)

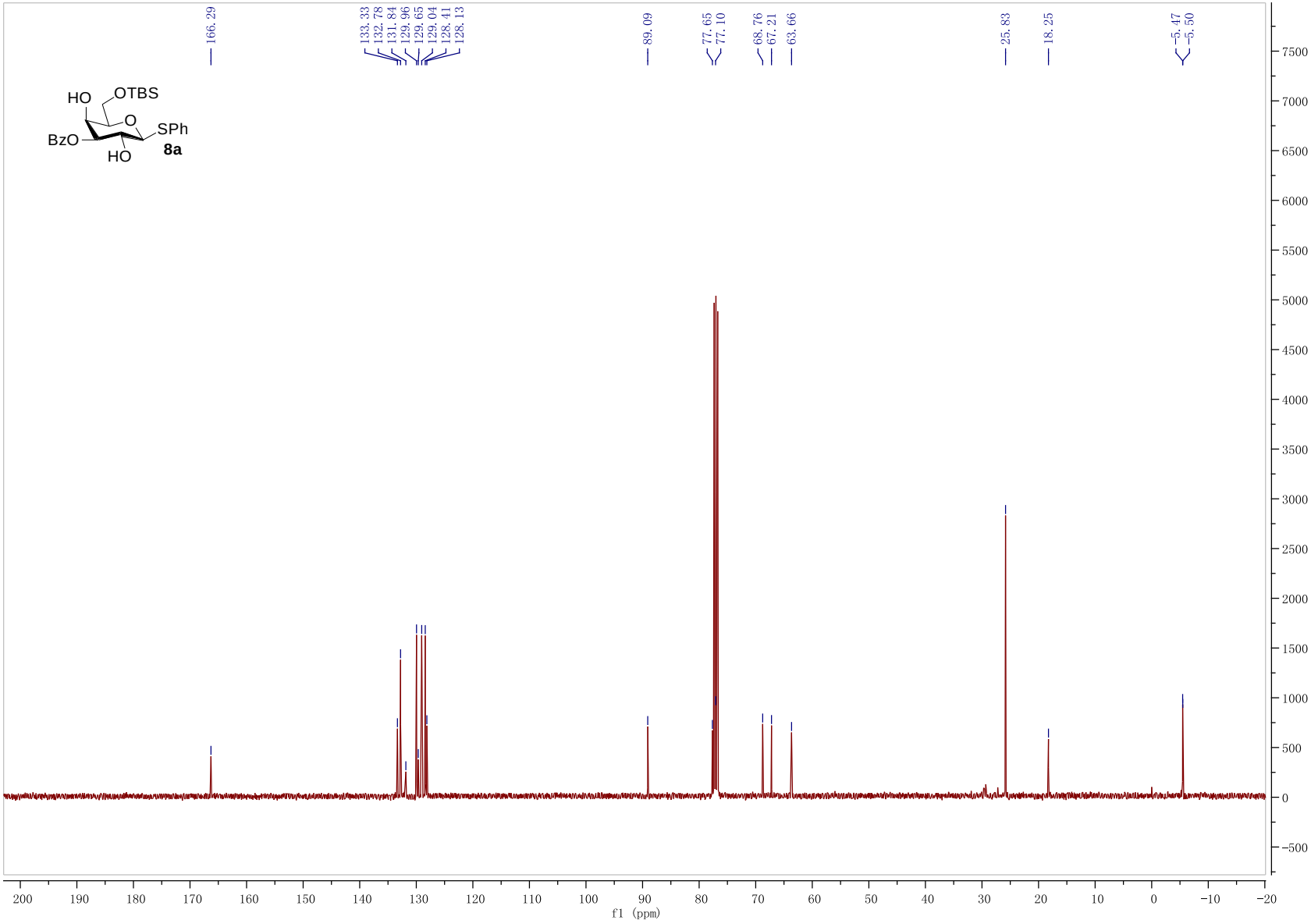


Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (8a)

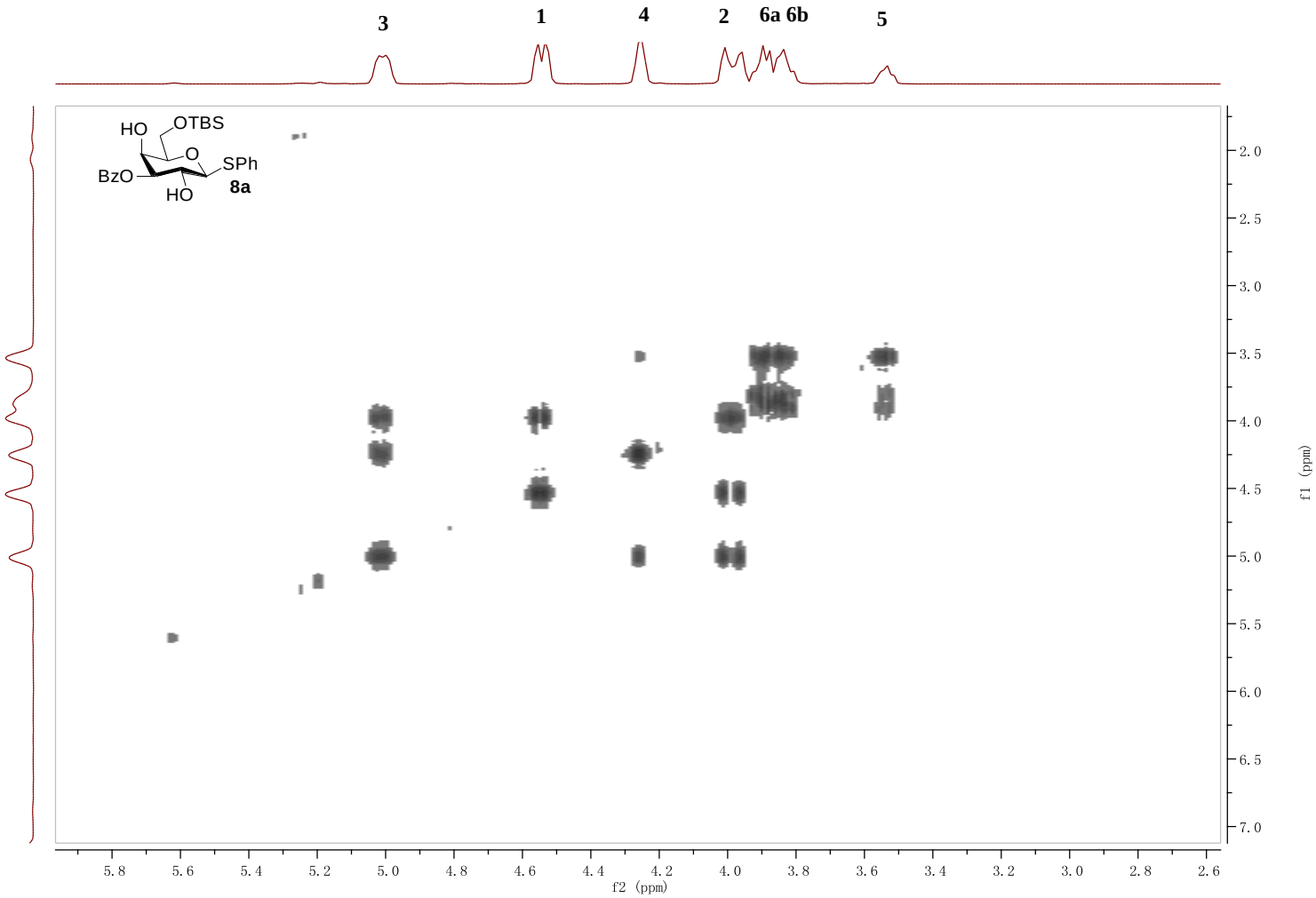
^{1}H-NMR of compound **8a** ($CDCl_3$)



^{13}C-NMR of compound **8a** ($CDCl_3$)

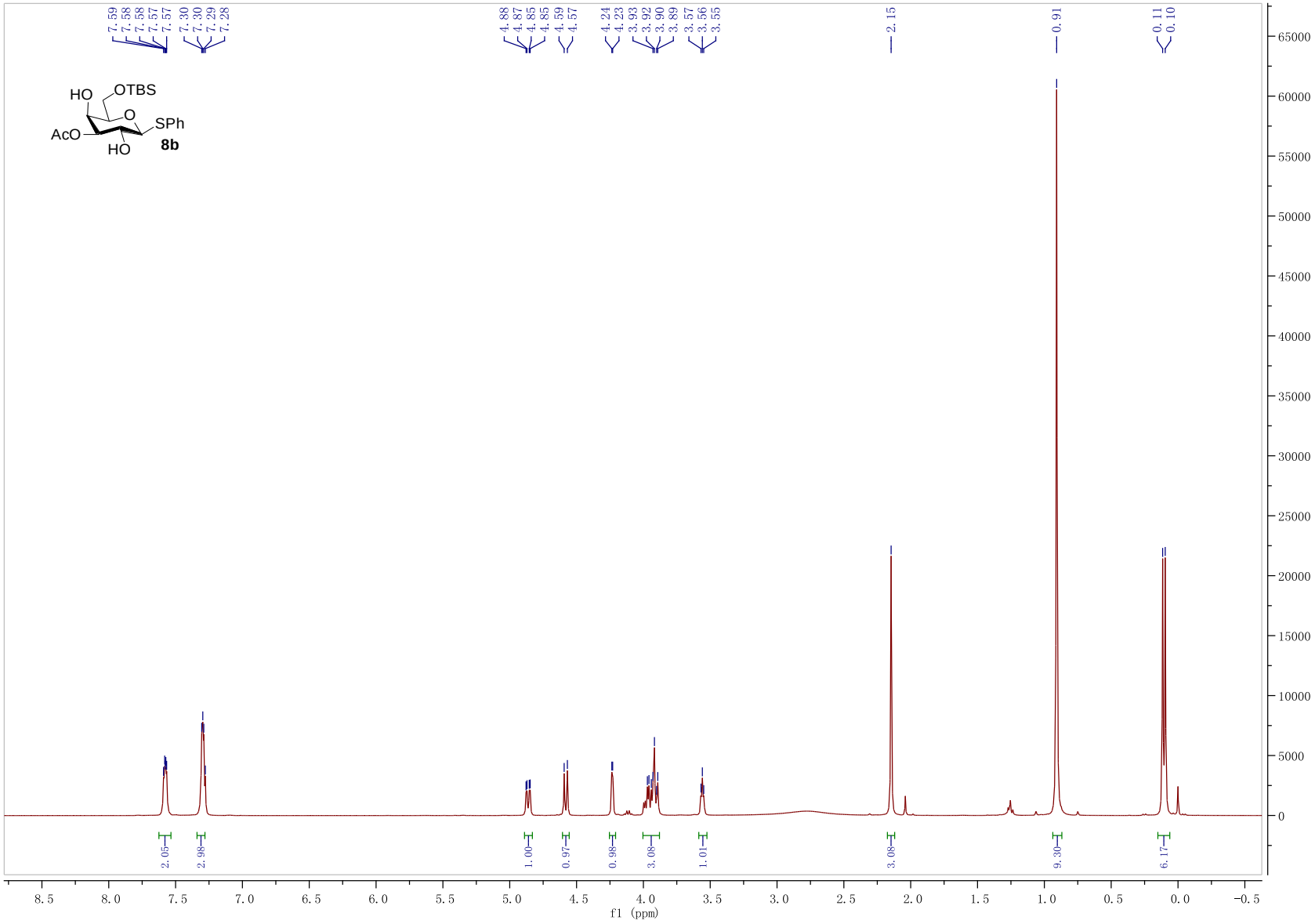


2D-COSY of compound **8a** ($CDCl_3$)

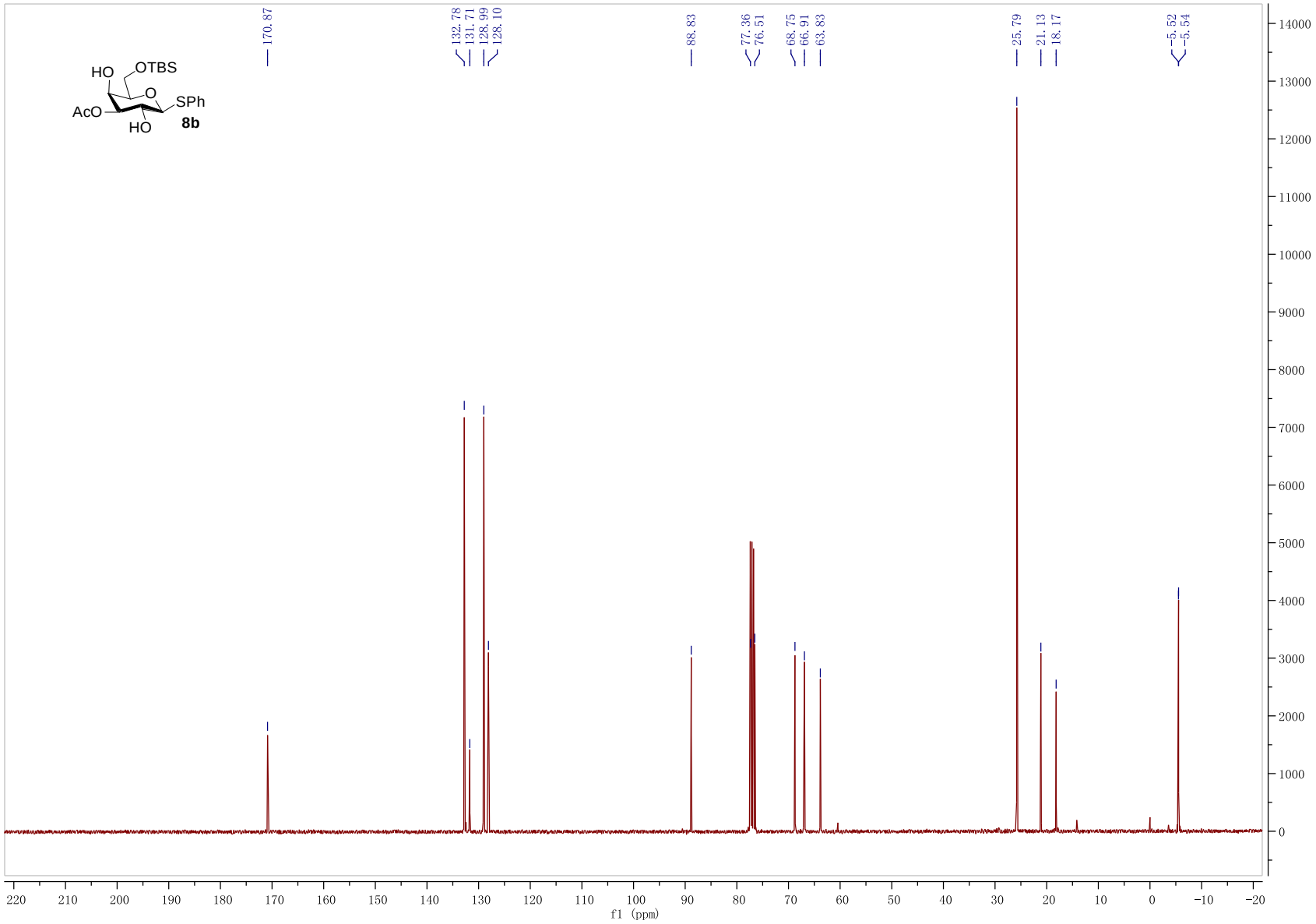


Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (8b)

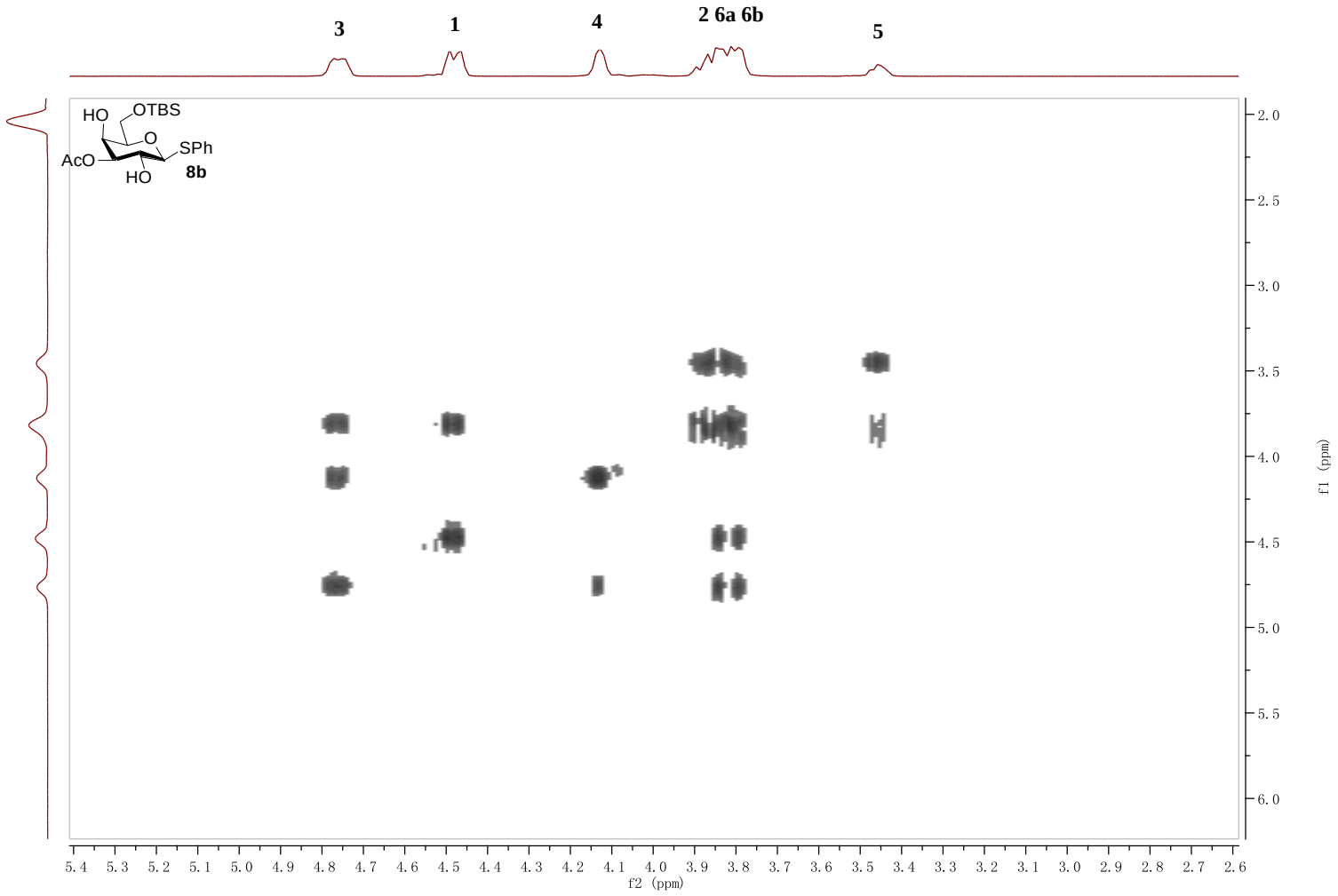
^{1}H-NMR of compound **8b** ($CDCl_3$)



^{13}C-NMR of compound **8b** ($CDCl_3$)

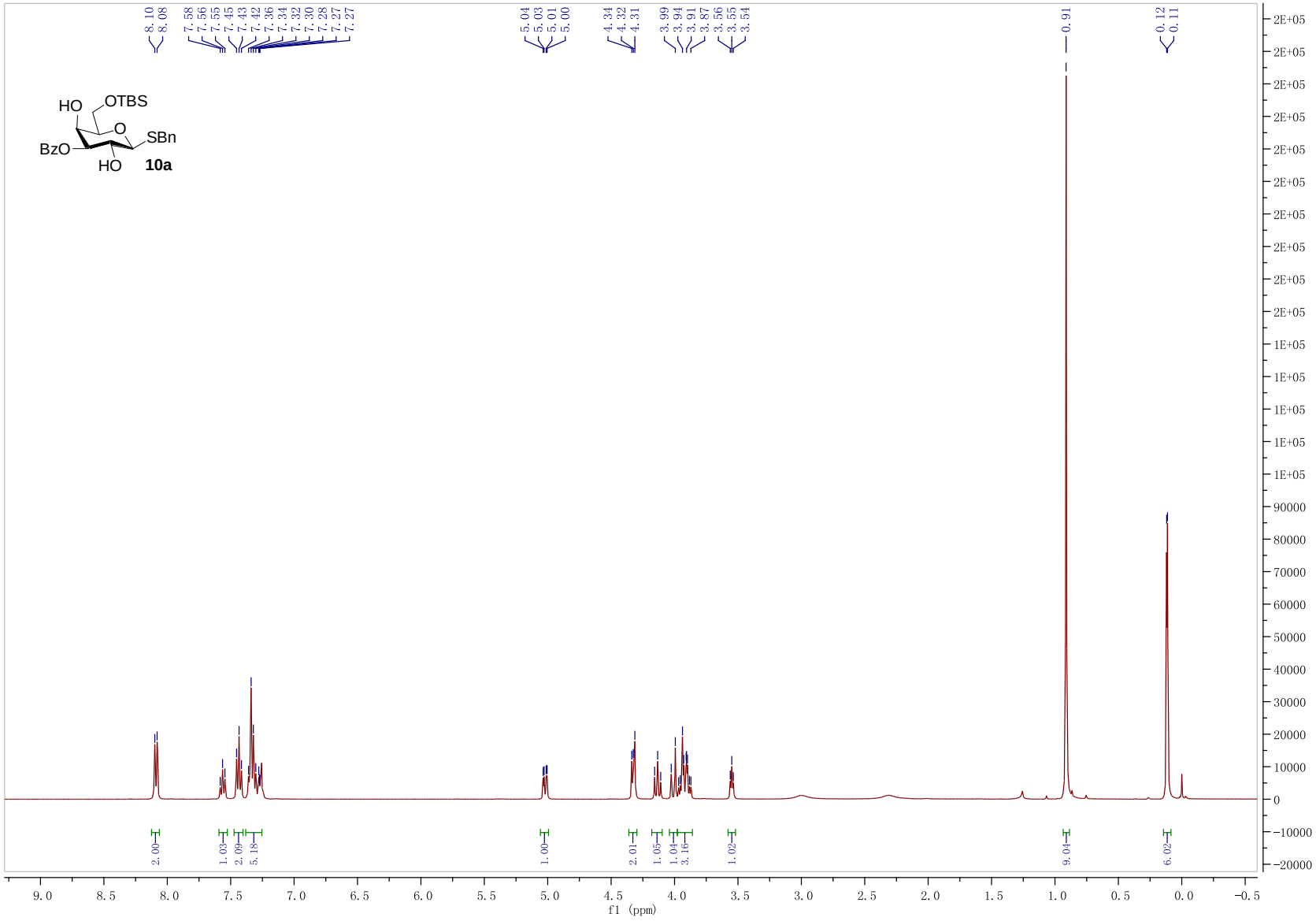


2D-COSY of compound **8b** ($CDCl_3$)

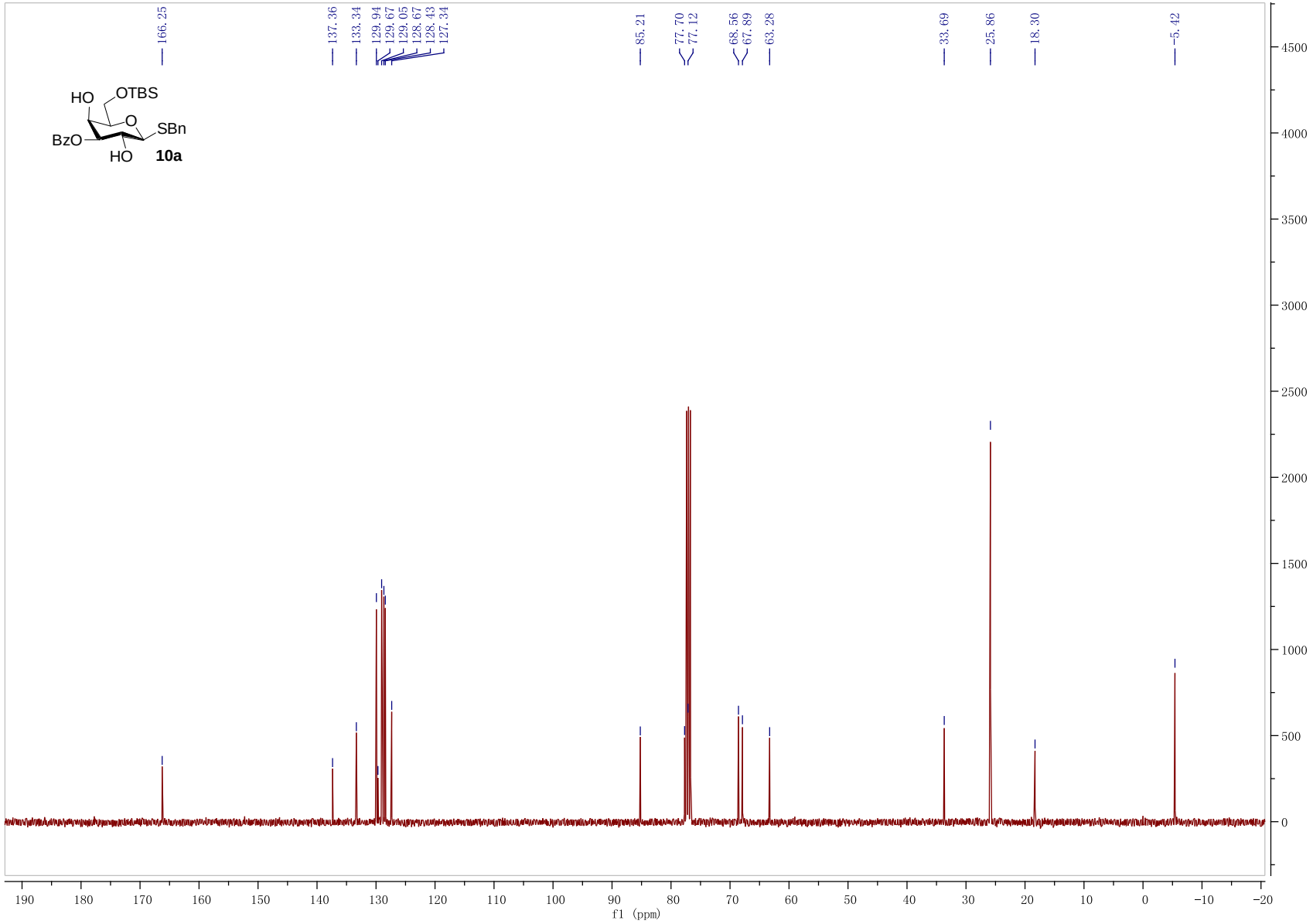


Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (10a)

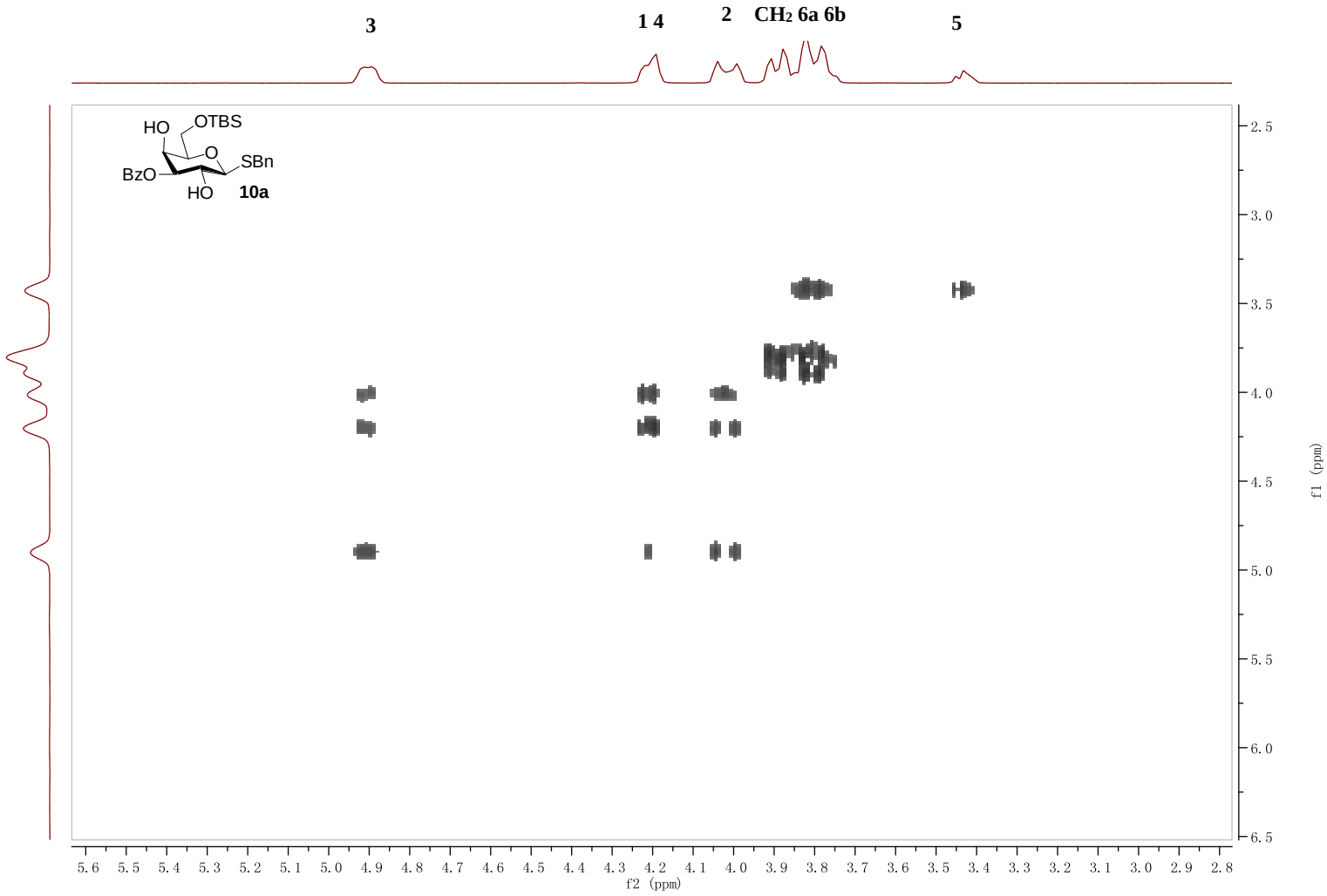
^{1}H-NMR of compound **10a** ($CDCl_3$)



^{13}C-NMR of compound **10a** ($CDCl_3$)

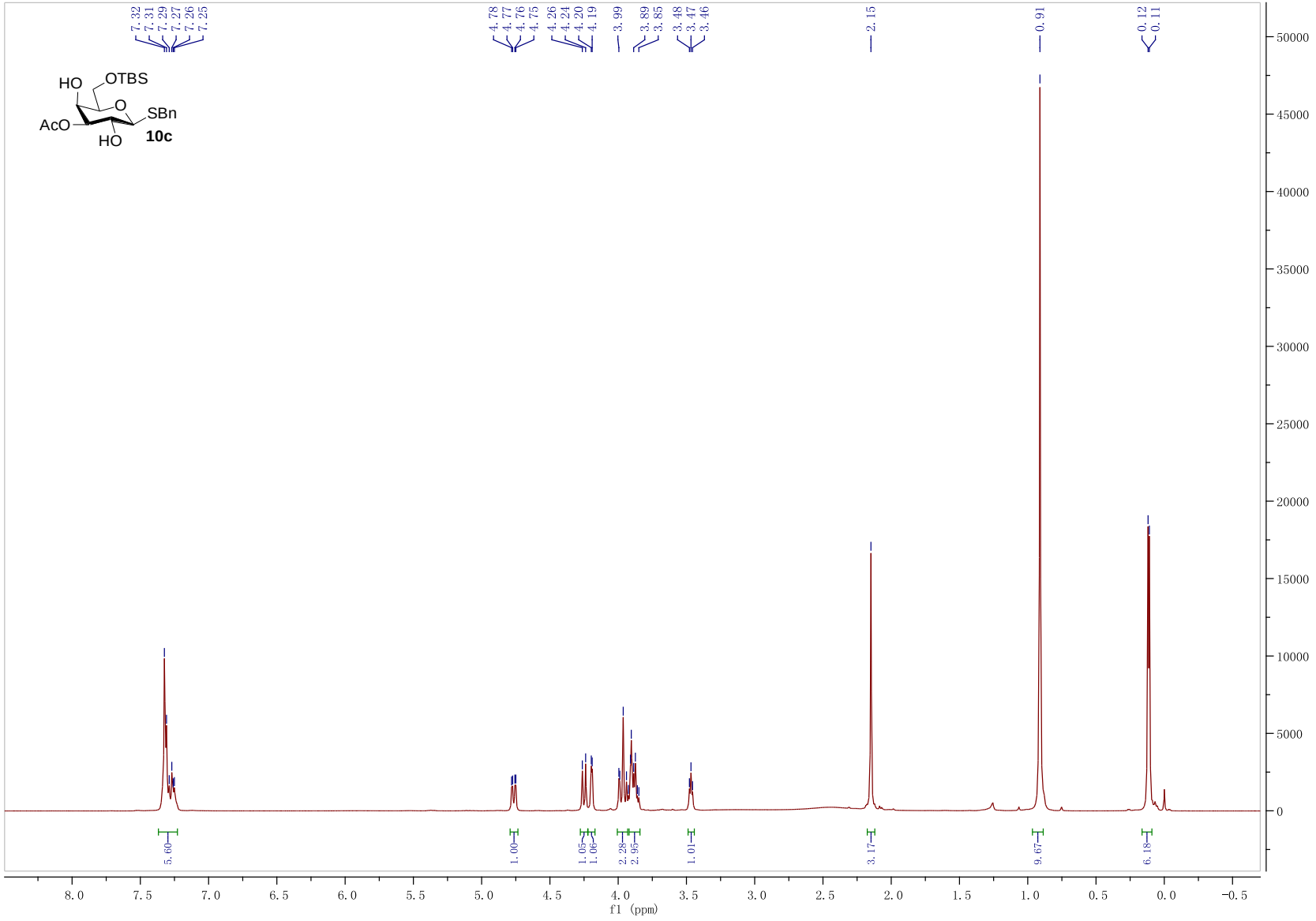


2D-COSY of compound **10a** ($CDCl_3$)

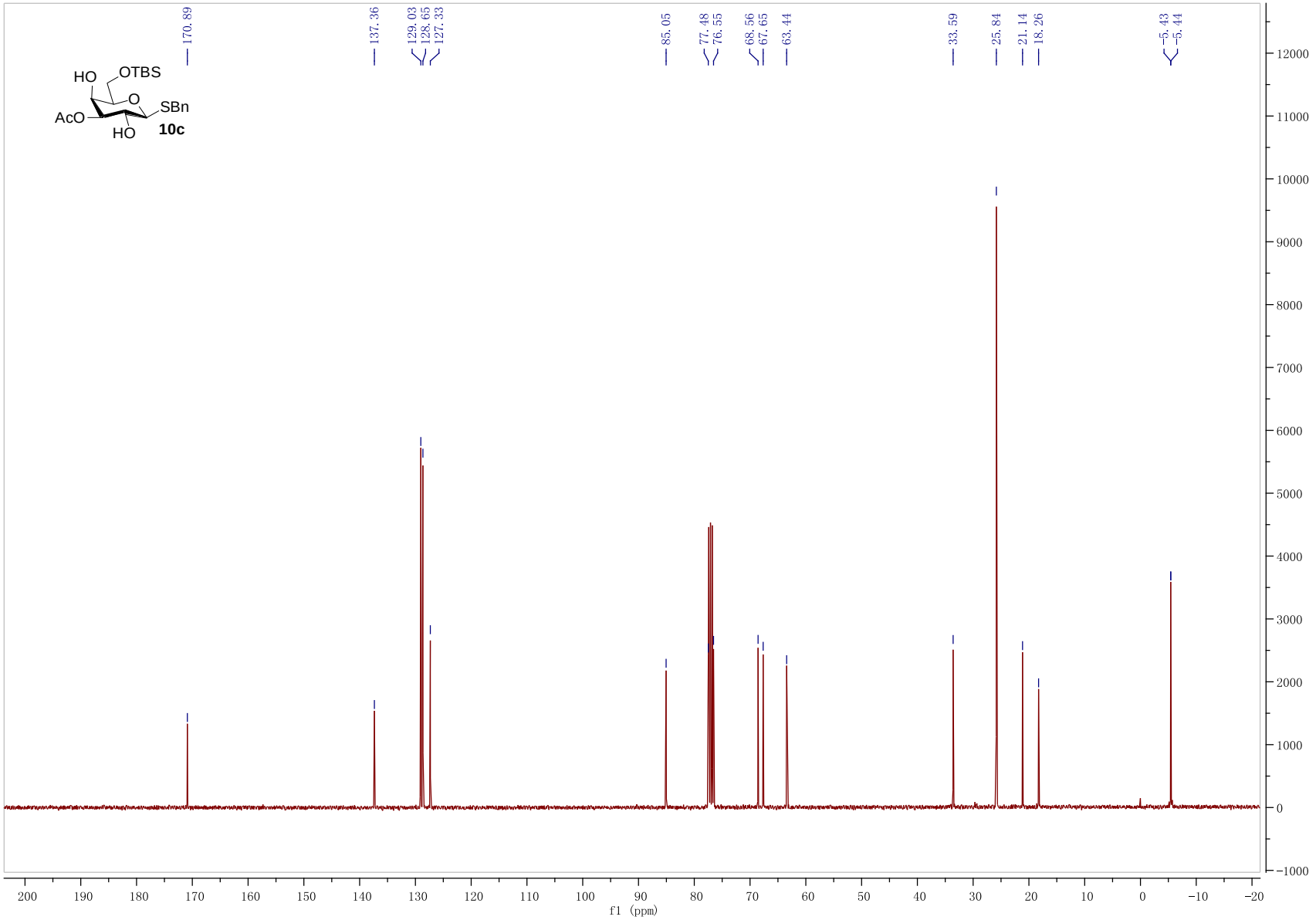


Benzyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (10c)

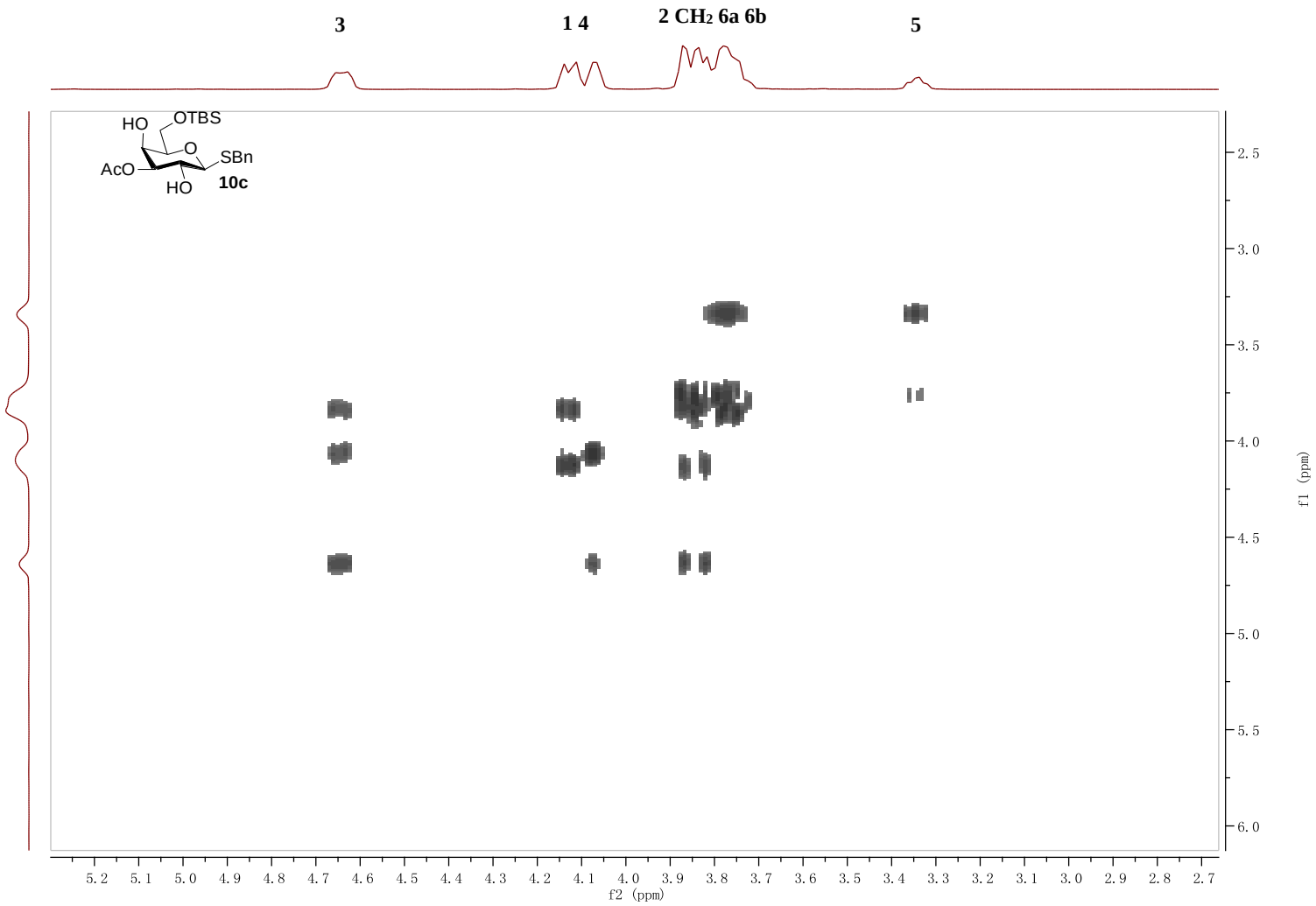
^{1}H-NMR of compound **10c** ($CDCl_3$)



^{13}C-NMR of compound **10c** ($CDCl_3$)

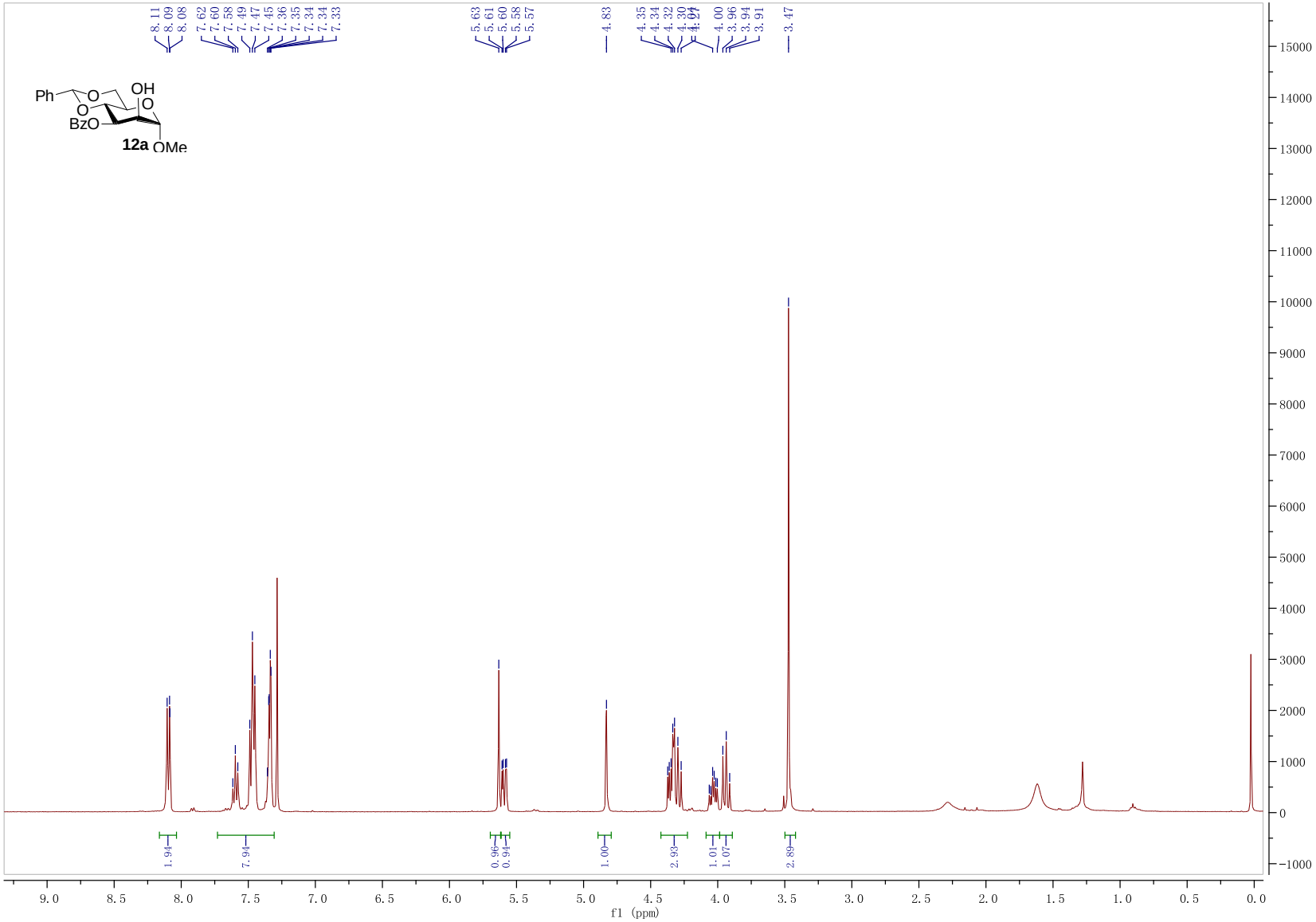


2D-COSY of compound **10c** ($CDCl_3$)



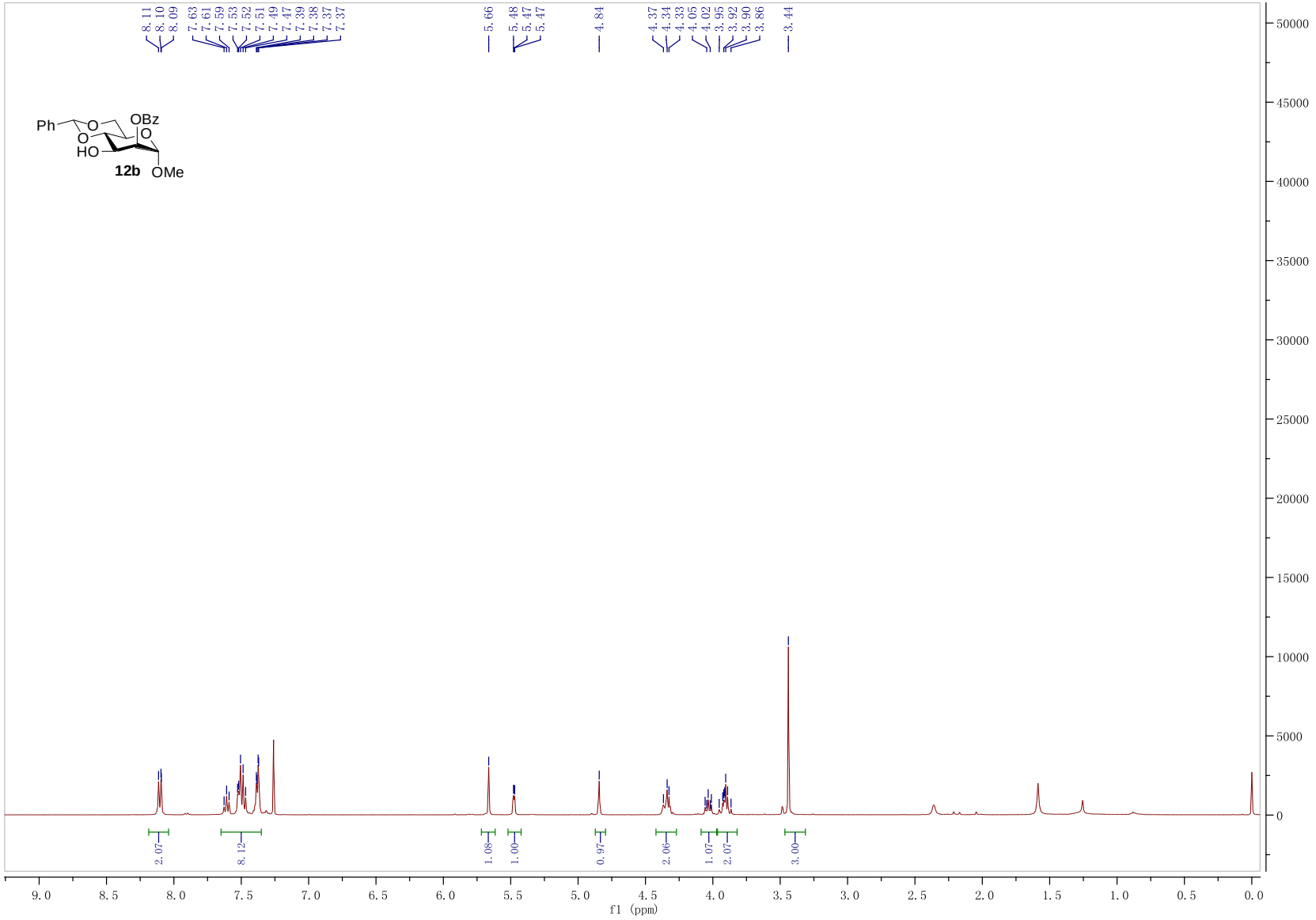
Methyl 3-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-mannopyranoside (12a)

^{1}H-NMR of compound **12a** ($CDCl_3$)



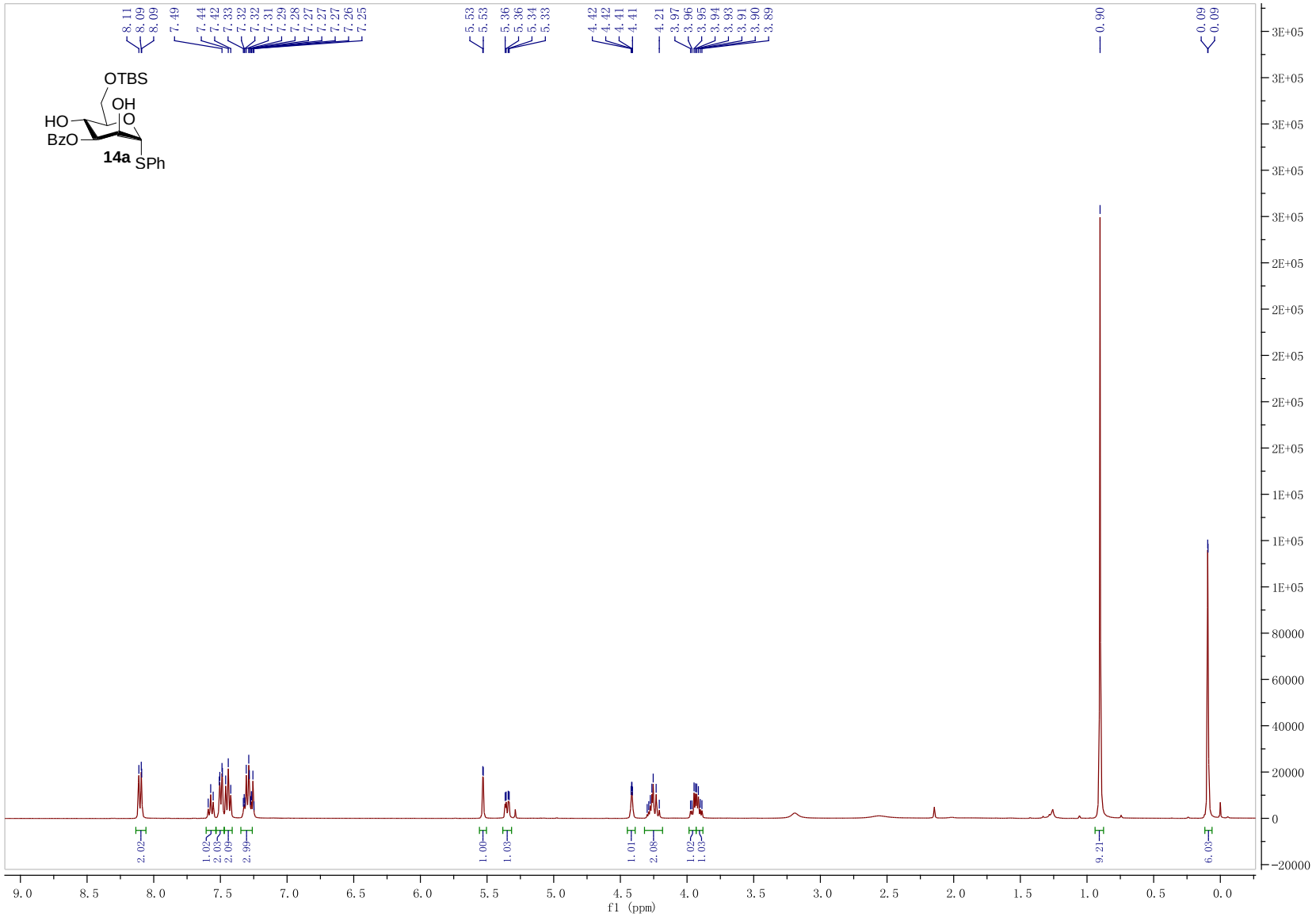
Methyl 2-*O*-benzoyl-4, 6-*O*-benzylidene-*α*-D-mannopyranoside (12b)

^{1}H-NMR of compound **12b** ($CDCl_3$)

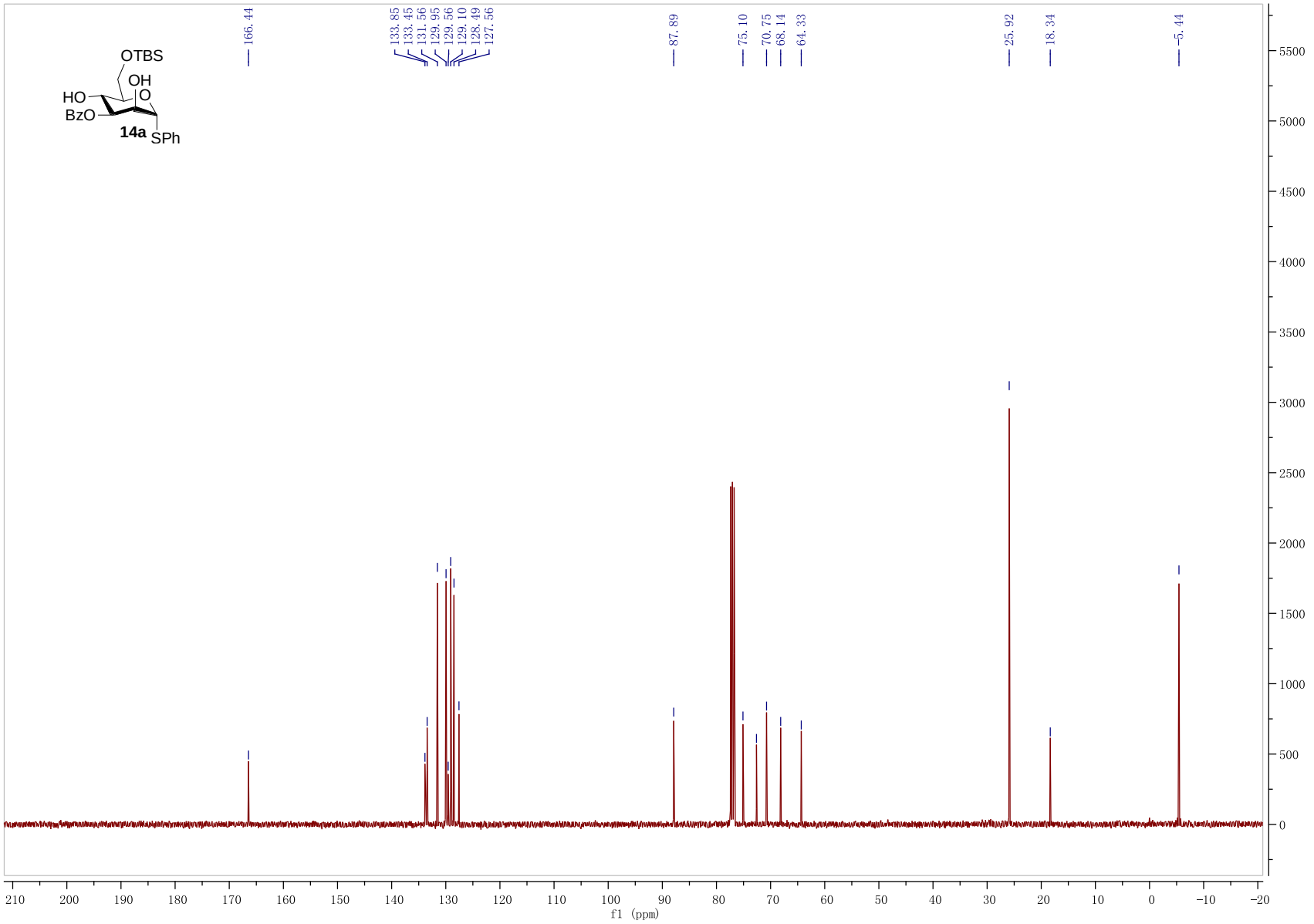


Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (14a)

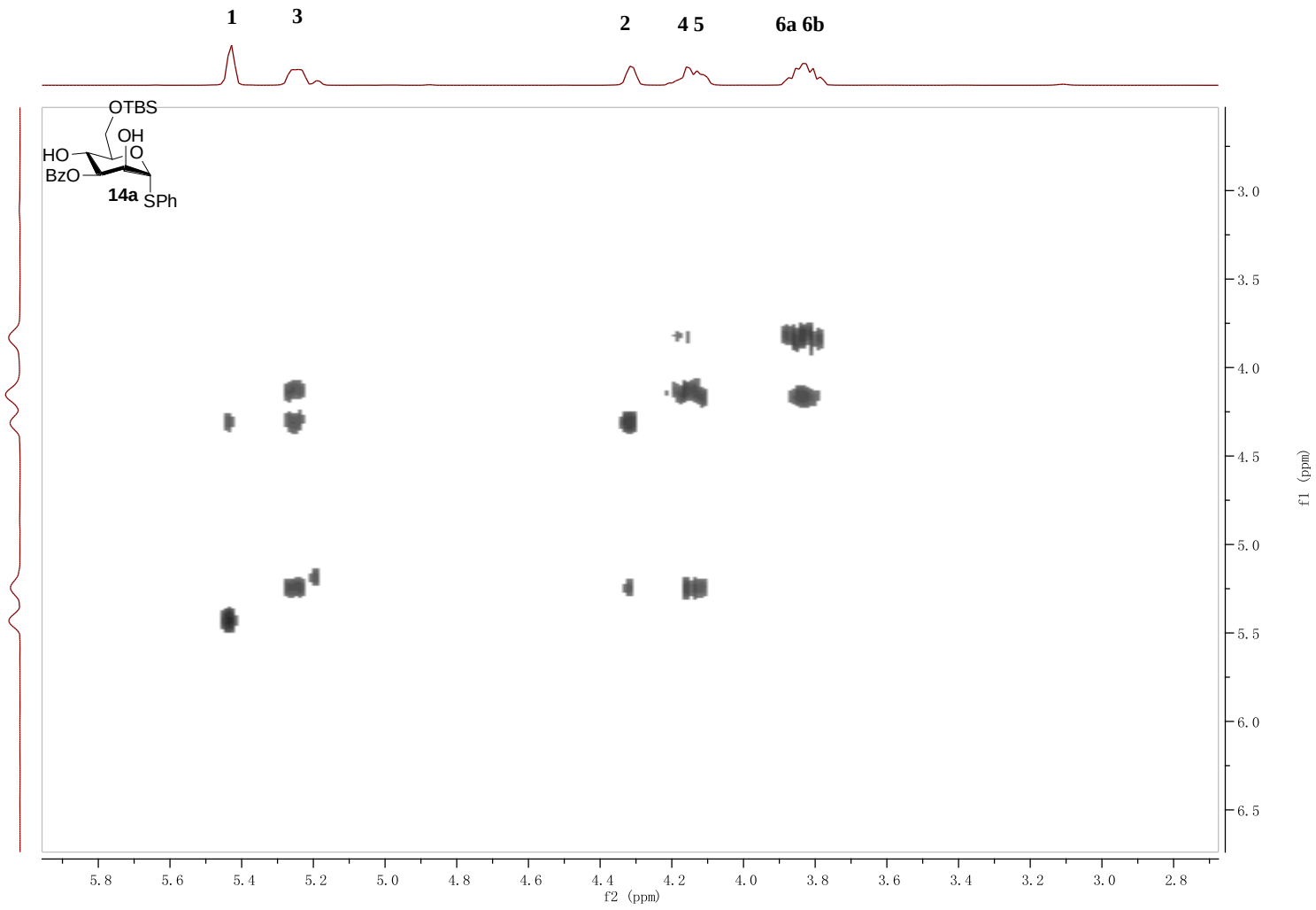
^{1}H-NMR of compound **14a** ($CDCl_3$)



^{13}C-NMR of compound **14a** ($CDCl_3$)

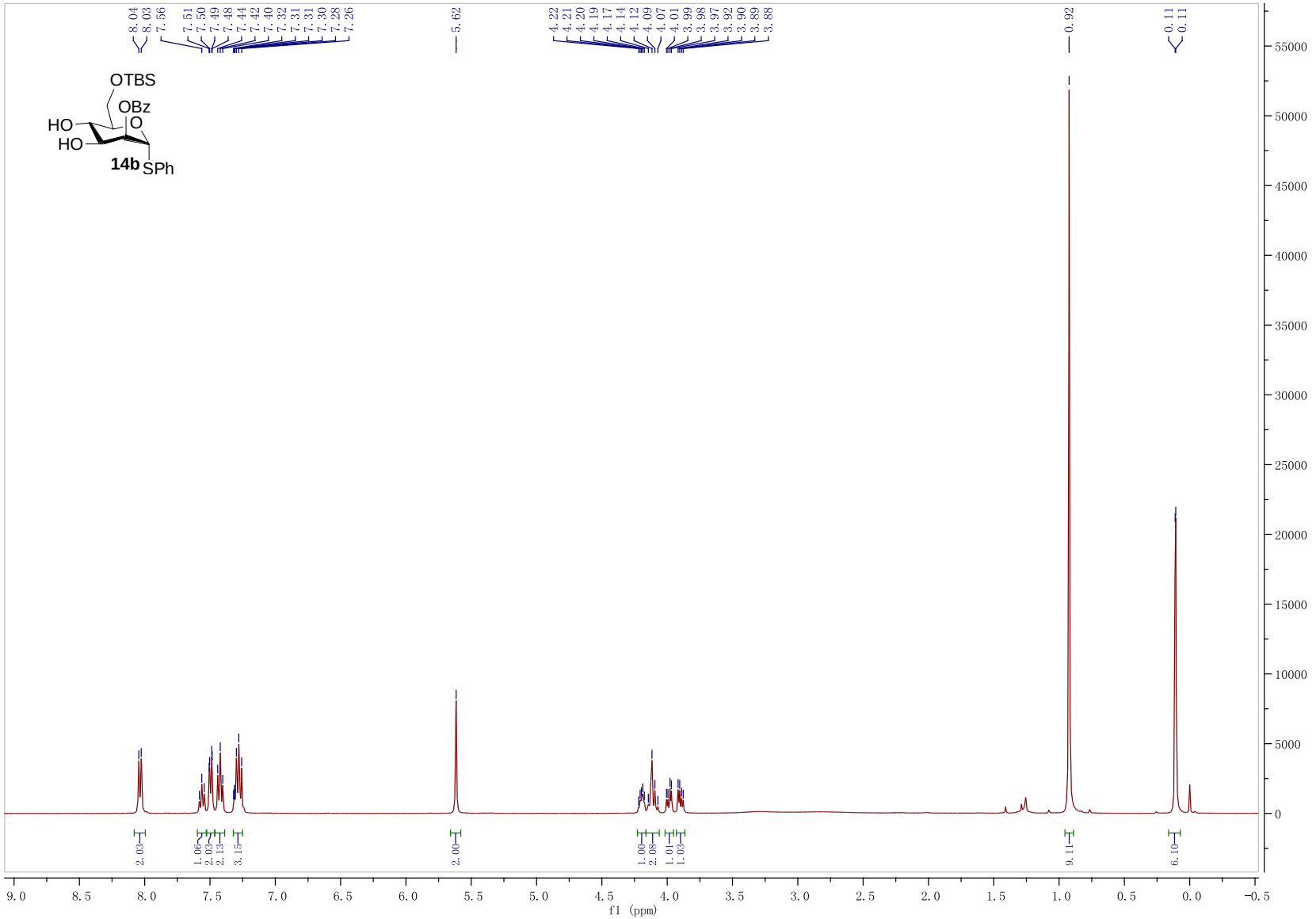


2D-COSY of compound **14a** ($CDCl_3$)

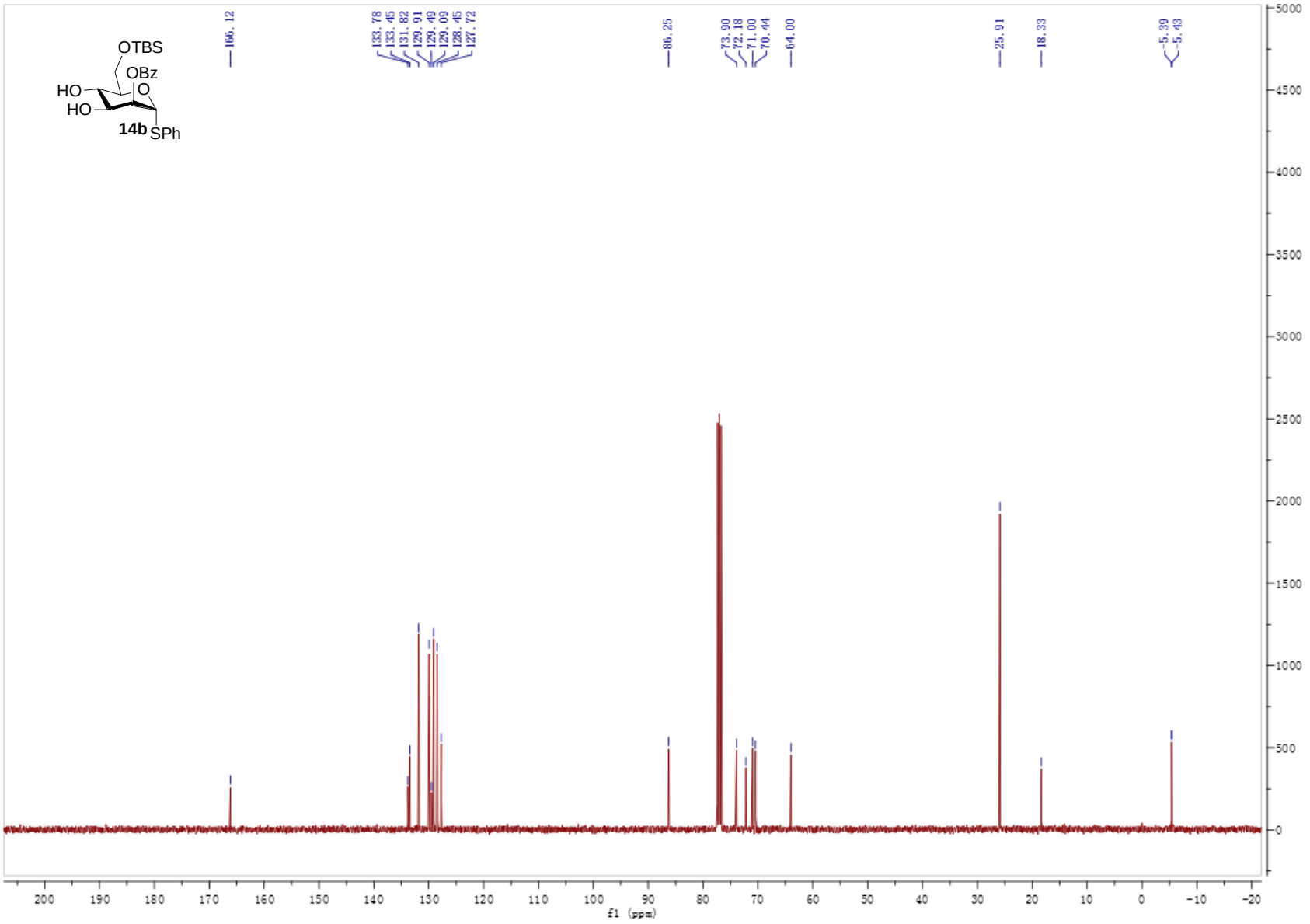


Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-2-*O*-benzoyl-1-thio-*α*-D-mannopyranoside (14b)

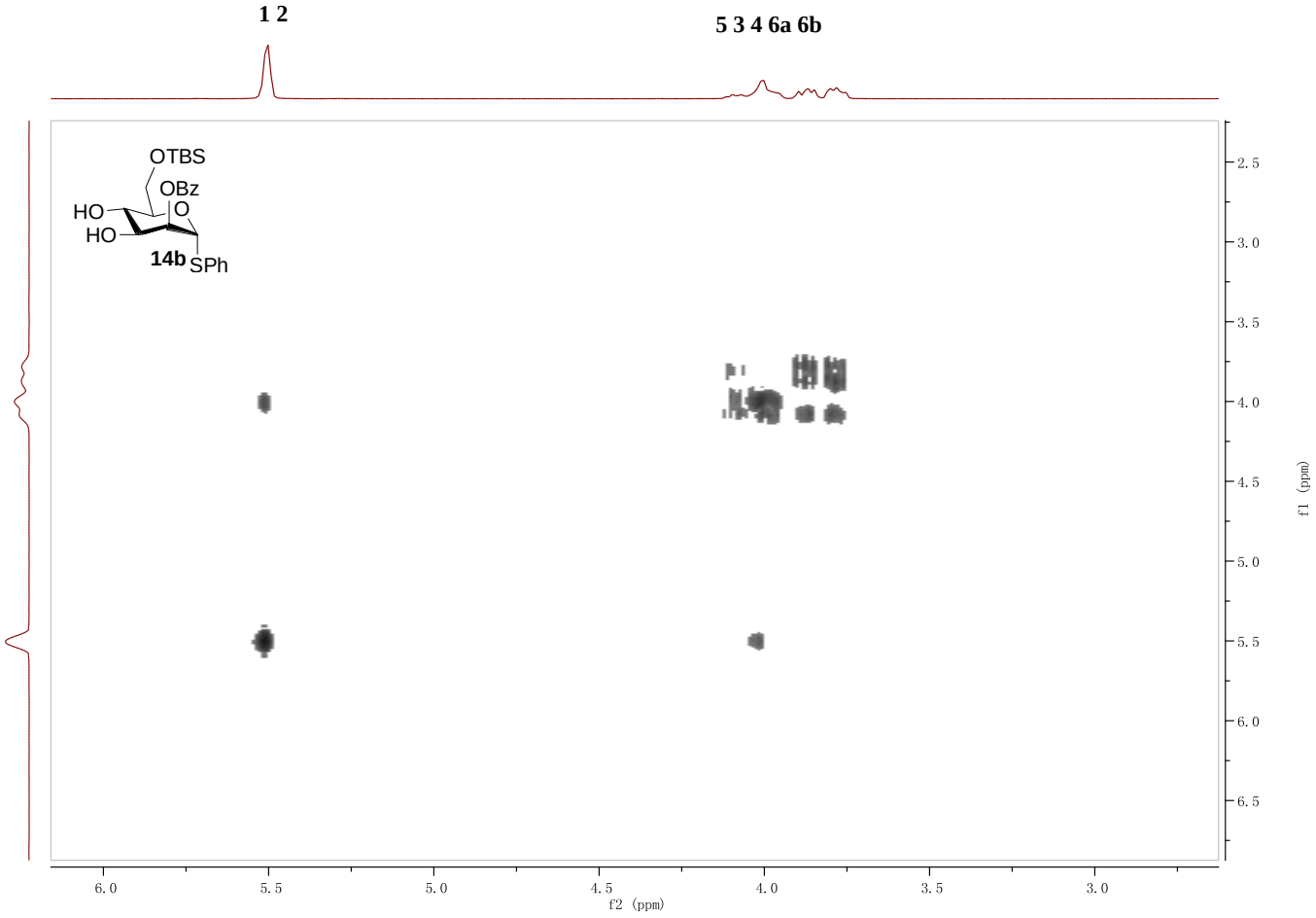
^{1}H-NMR of compound **14b** ($CDCl_3$)



^{13}C-NMR of compound **14b** ($CDCl_3$)

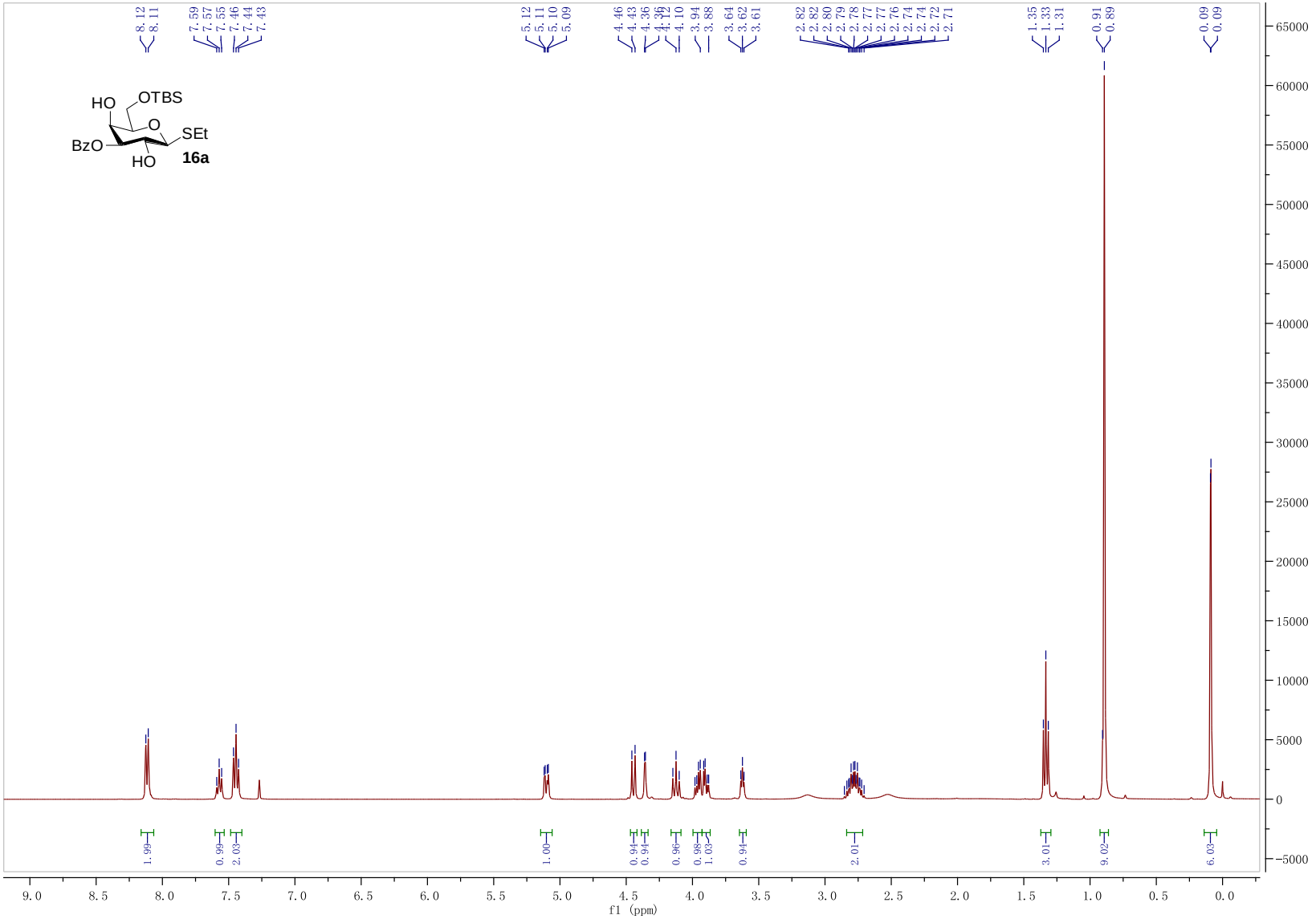


2D-COSY of compound **14b** ($CDCl_3$)

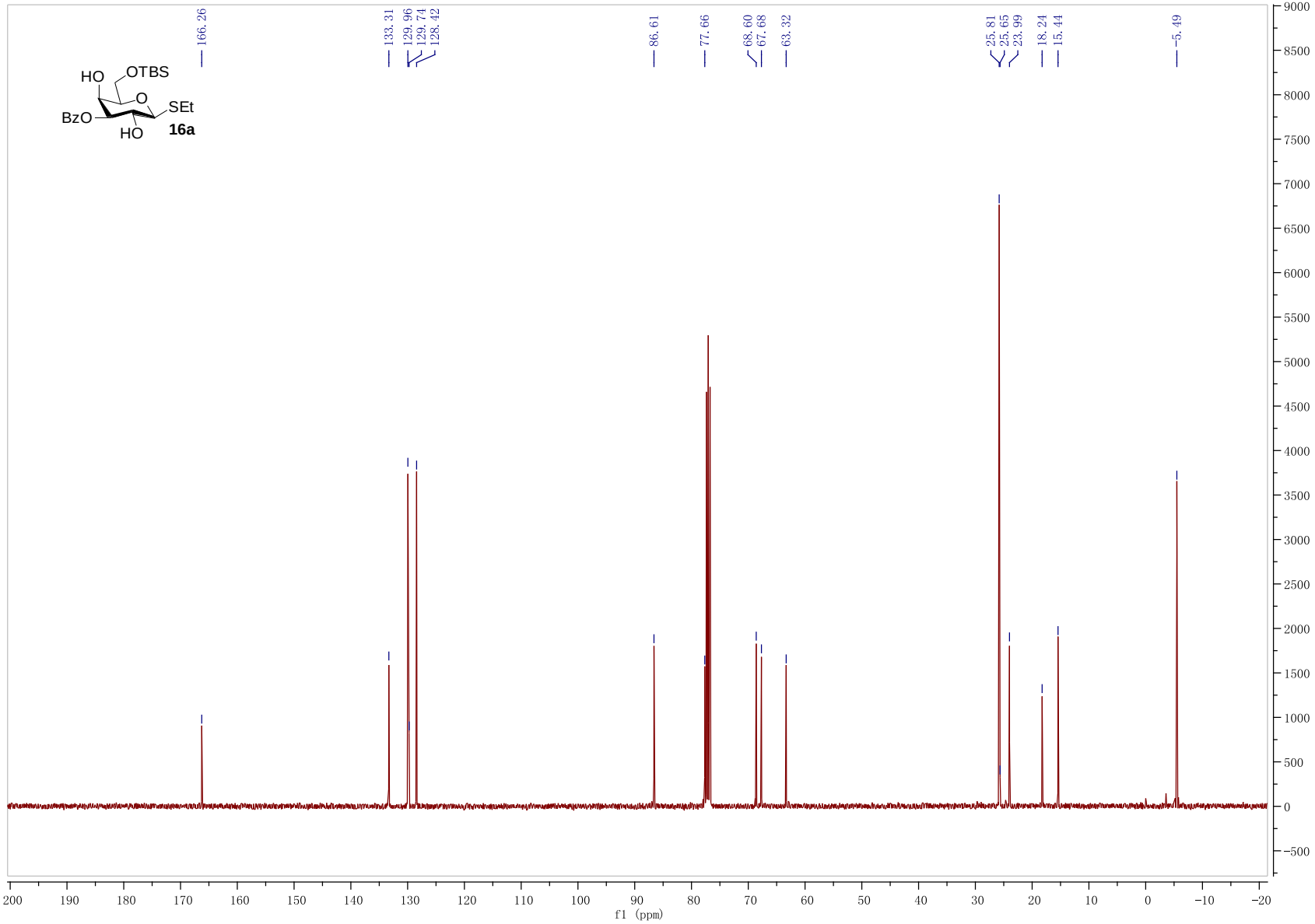


Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (16a)

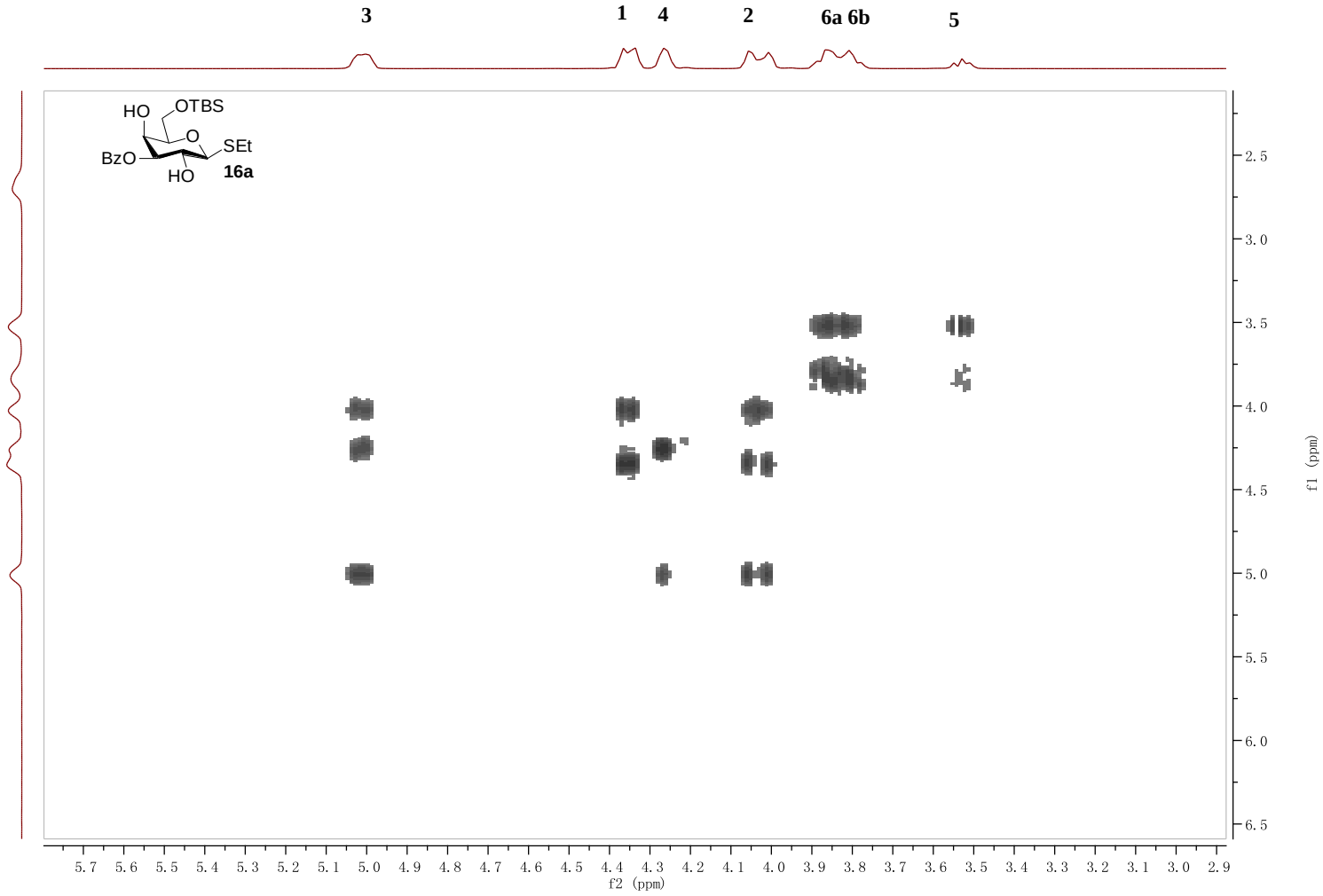
^{1}H-NMR of compound **16a** ($CDCl_3$)



^{13}C-NMR of compound **16a** ($CDCl_3$)

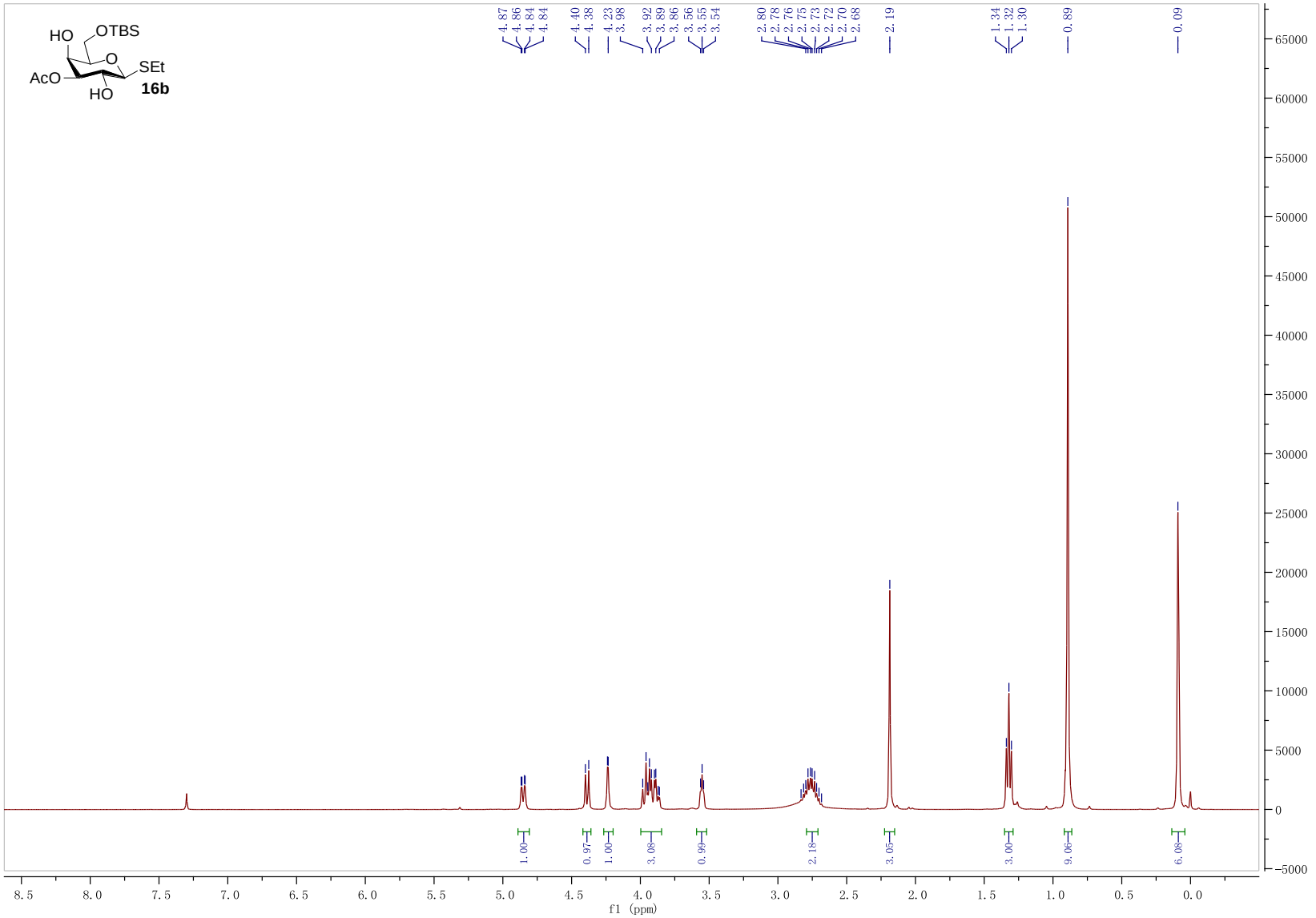


2D-COSY of compound **16a** ($CDCl_3$)



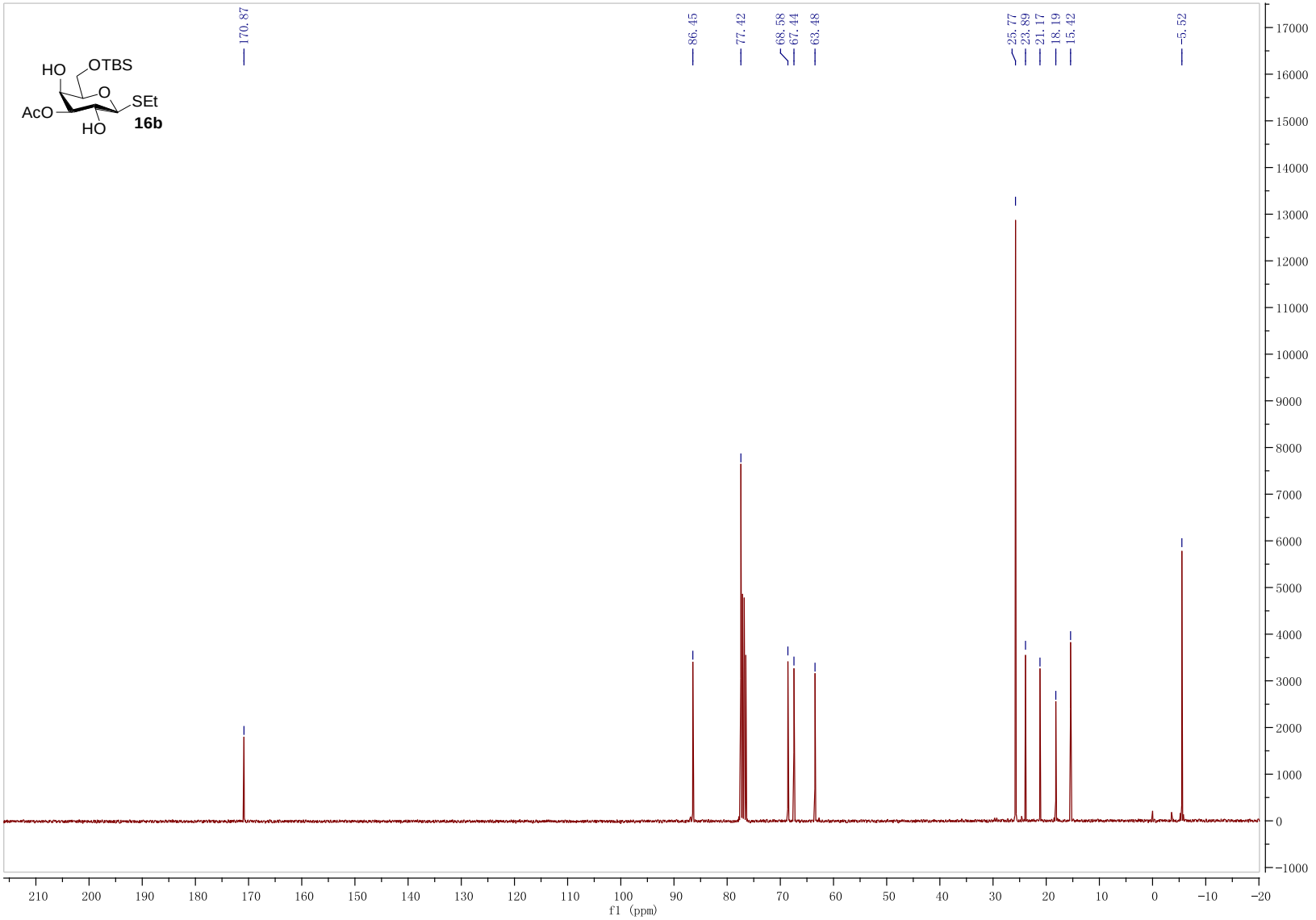
Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (16b)

^{1}H-NMR of compound **16b** ($CDCl_3$)



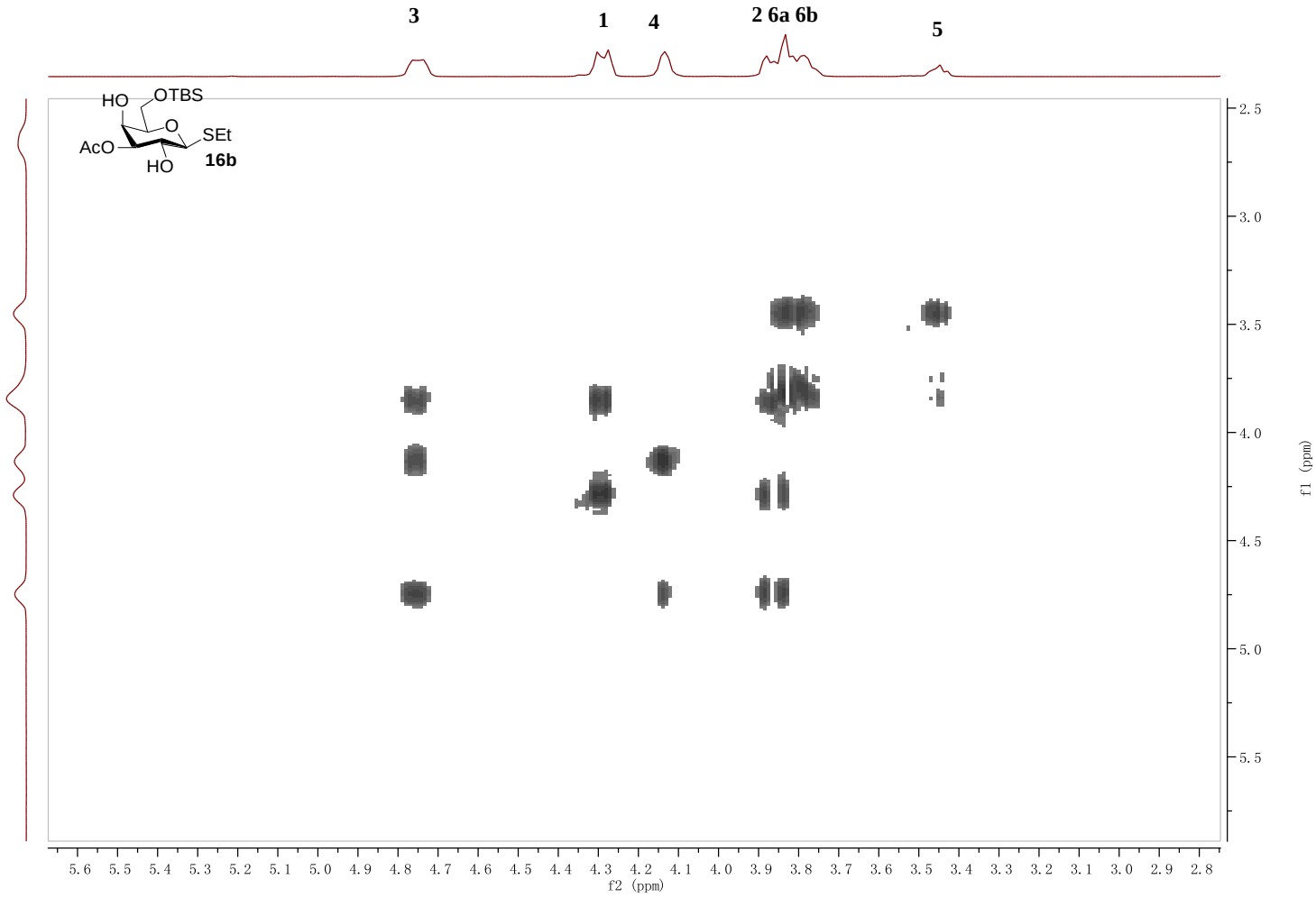
Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (16b)

^{13}C-NMR of compound **16b** ($CDCl_3$)



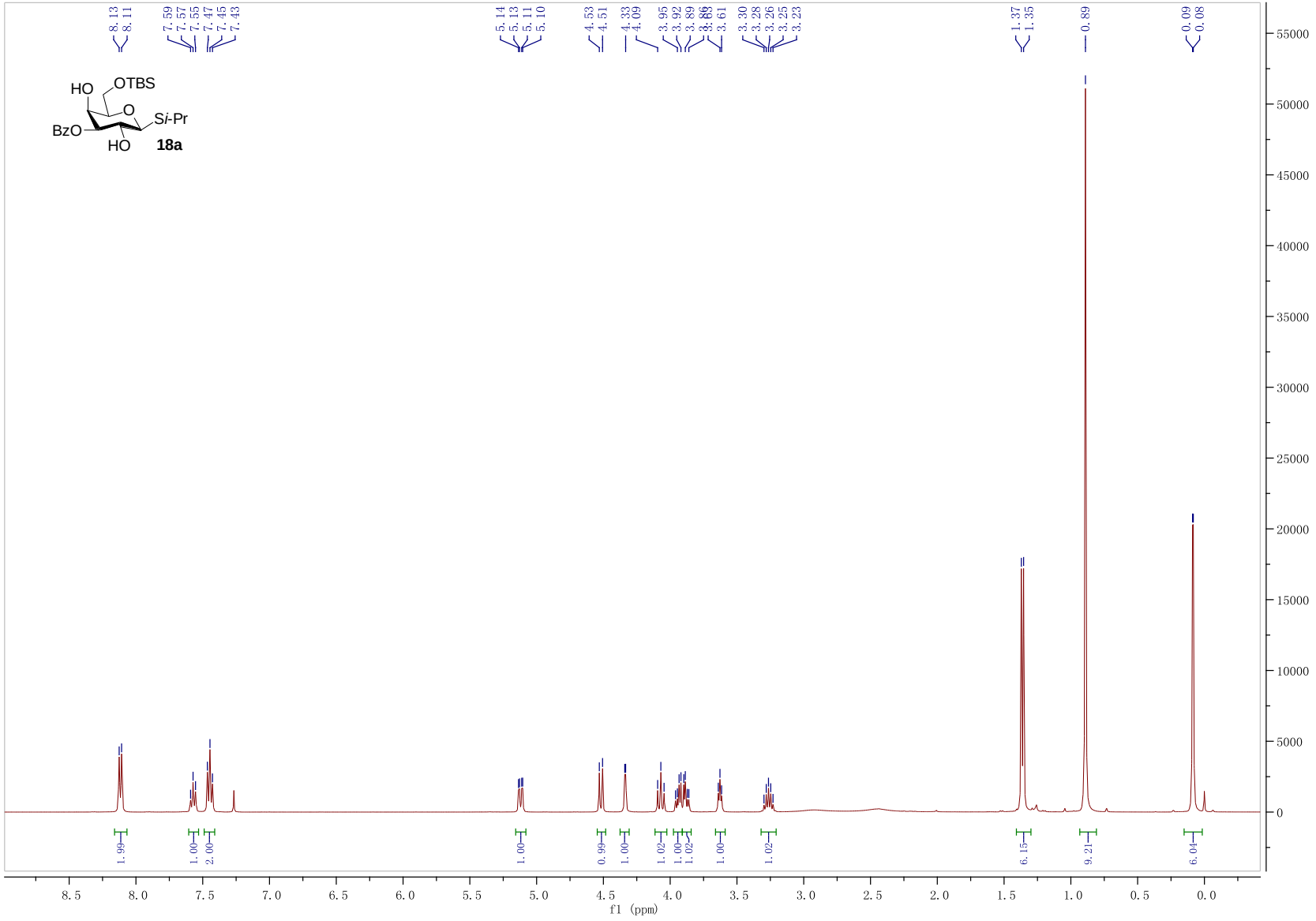
Ethyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (16b)

2D-COSY of compound **16b** ($CDCl_3$)



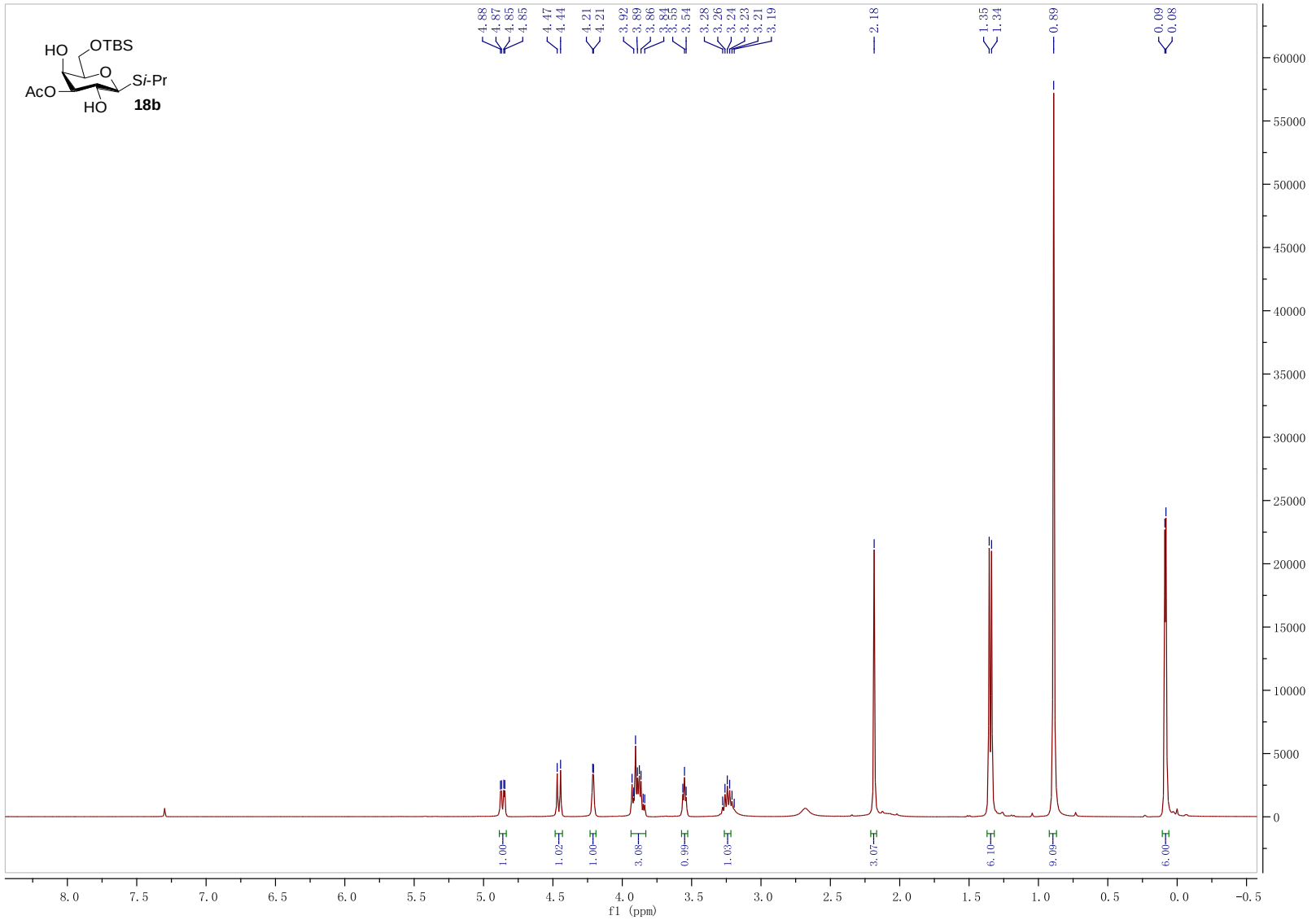
Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (18a)

^{1}H-NMR of compound **18a** ($CDCl_3$)

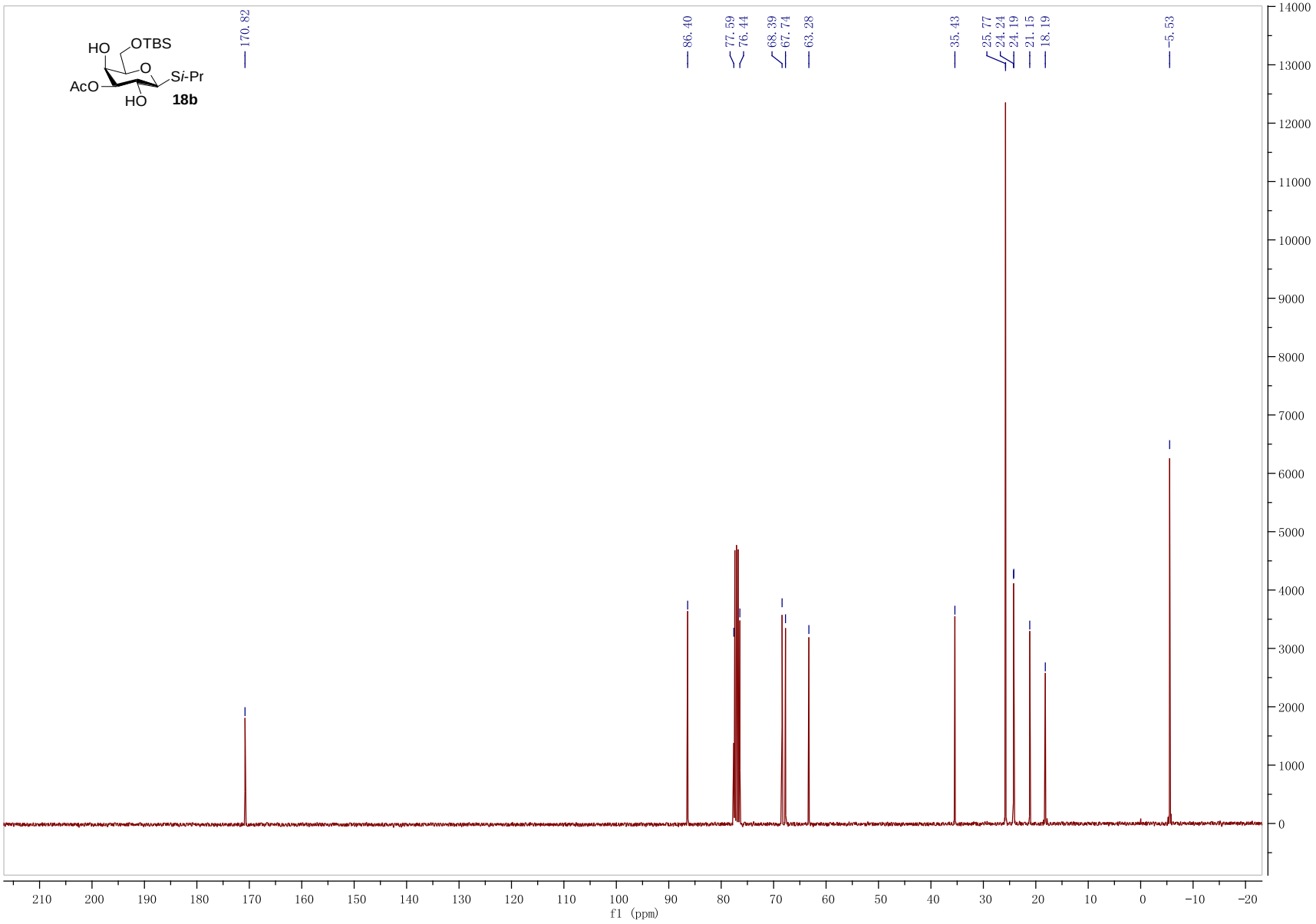


Isopropylthio-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-*β*-D-galactopyranoside (18b)

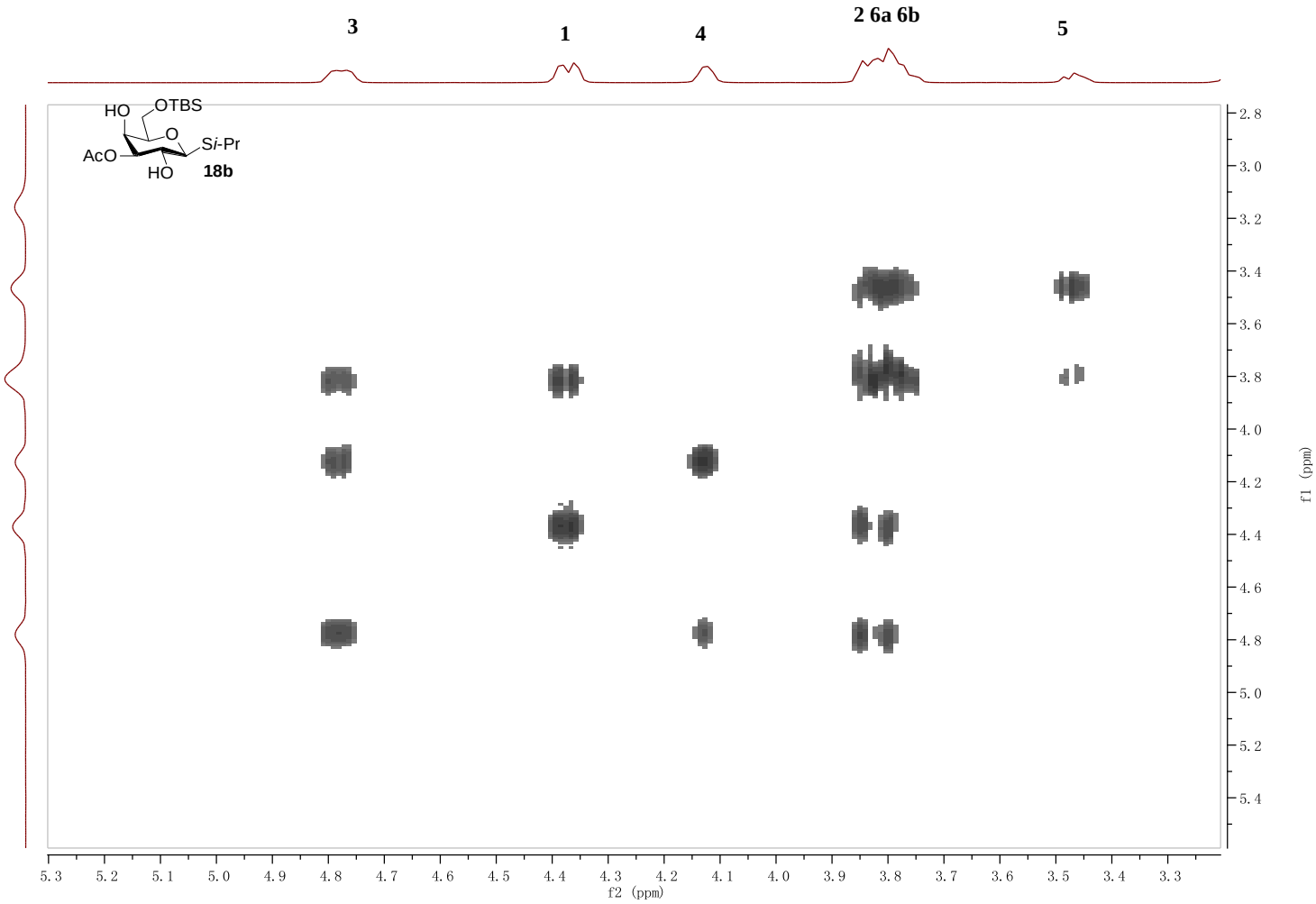
^{1}H-NMR of compound **18b** ($CDCl_3$)



^{13}C-NMR of compound **18b** ($CDCl_3$)

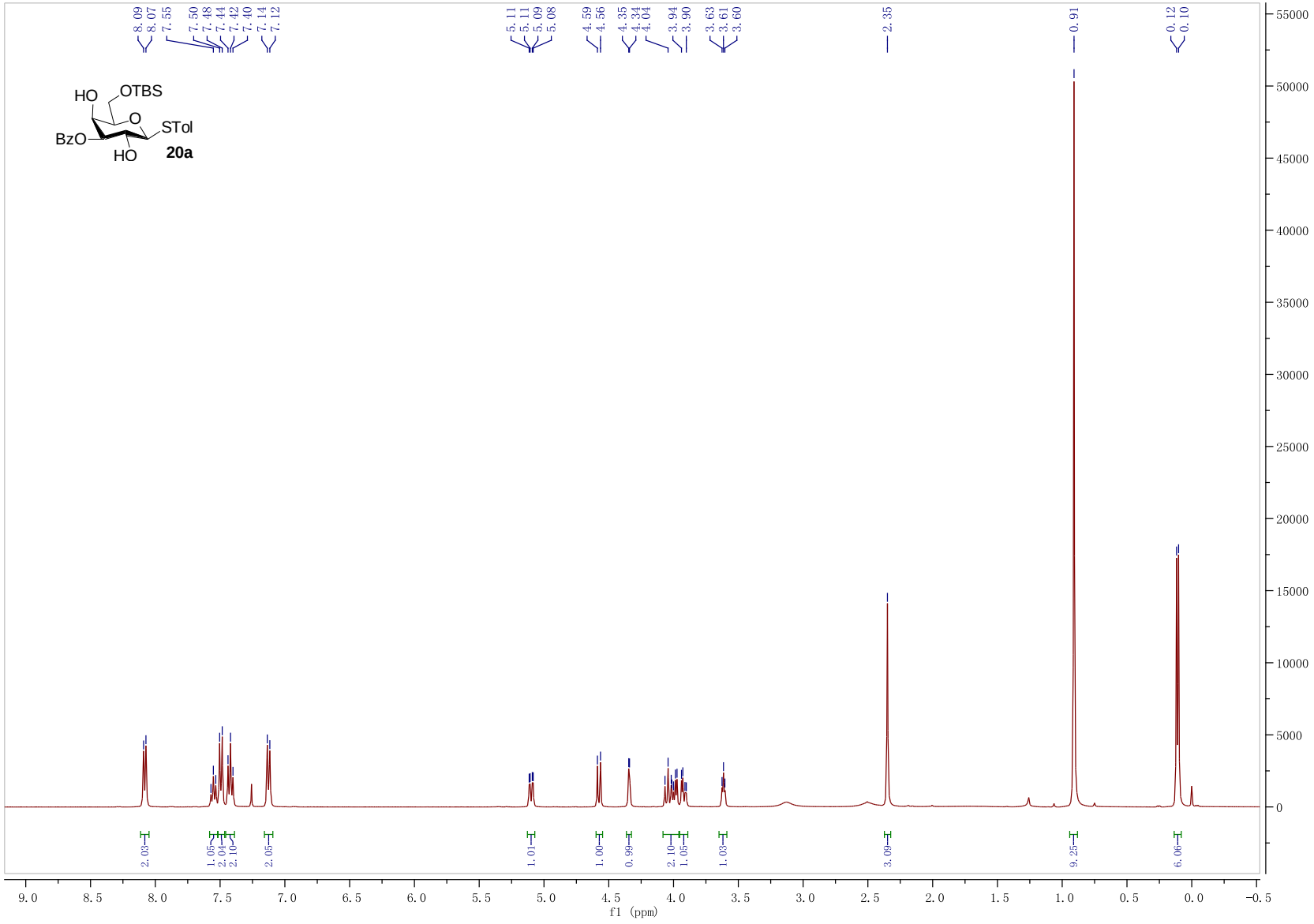


2D-COSY of compound **18b** ($CDCl_3$)

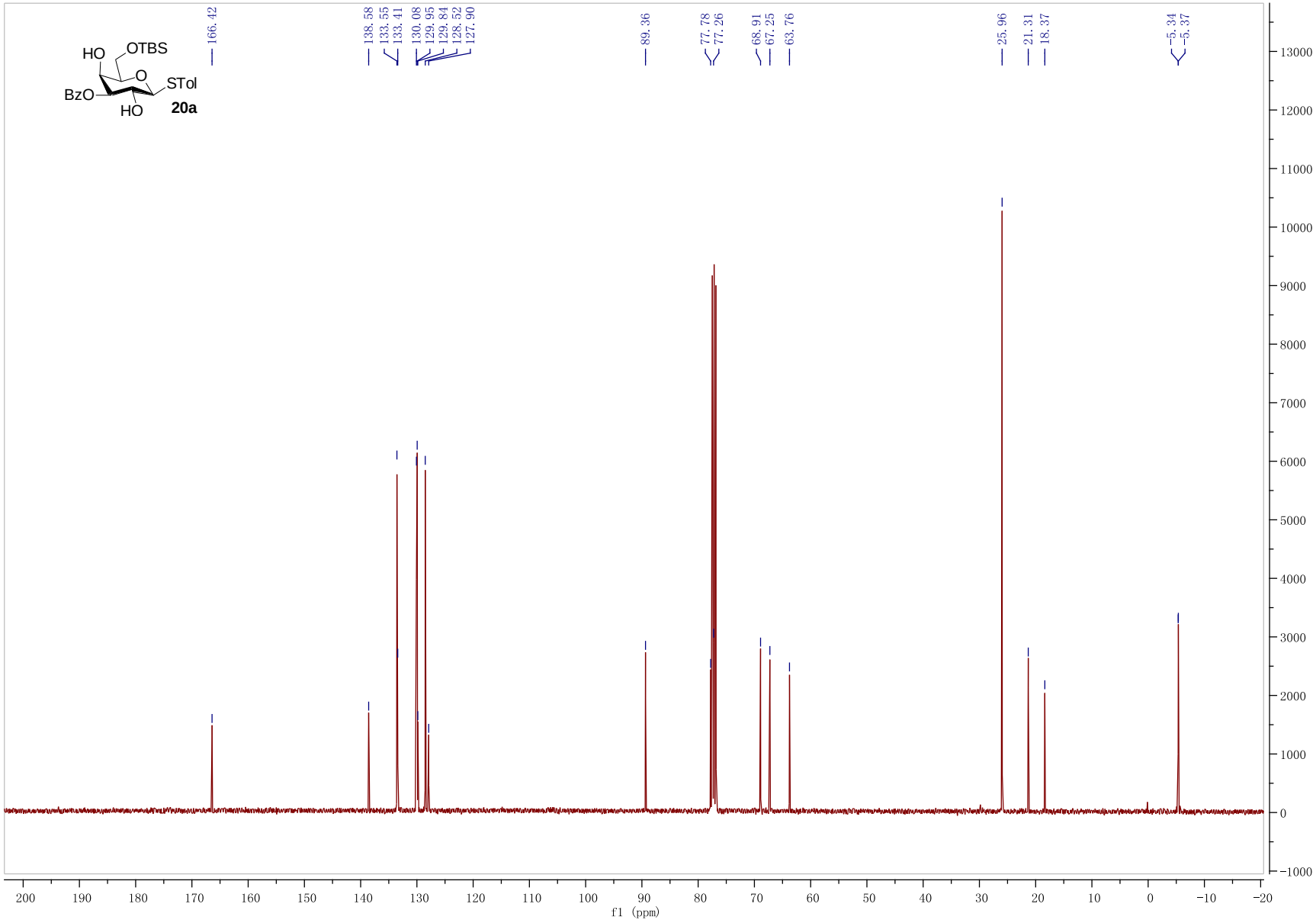


***p*-tolyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-1-thio-*β*-D-galactopyranoside (20a)**

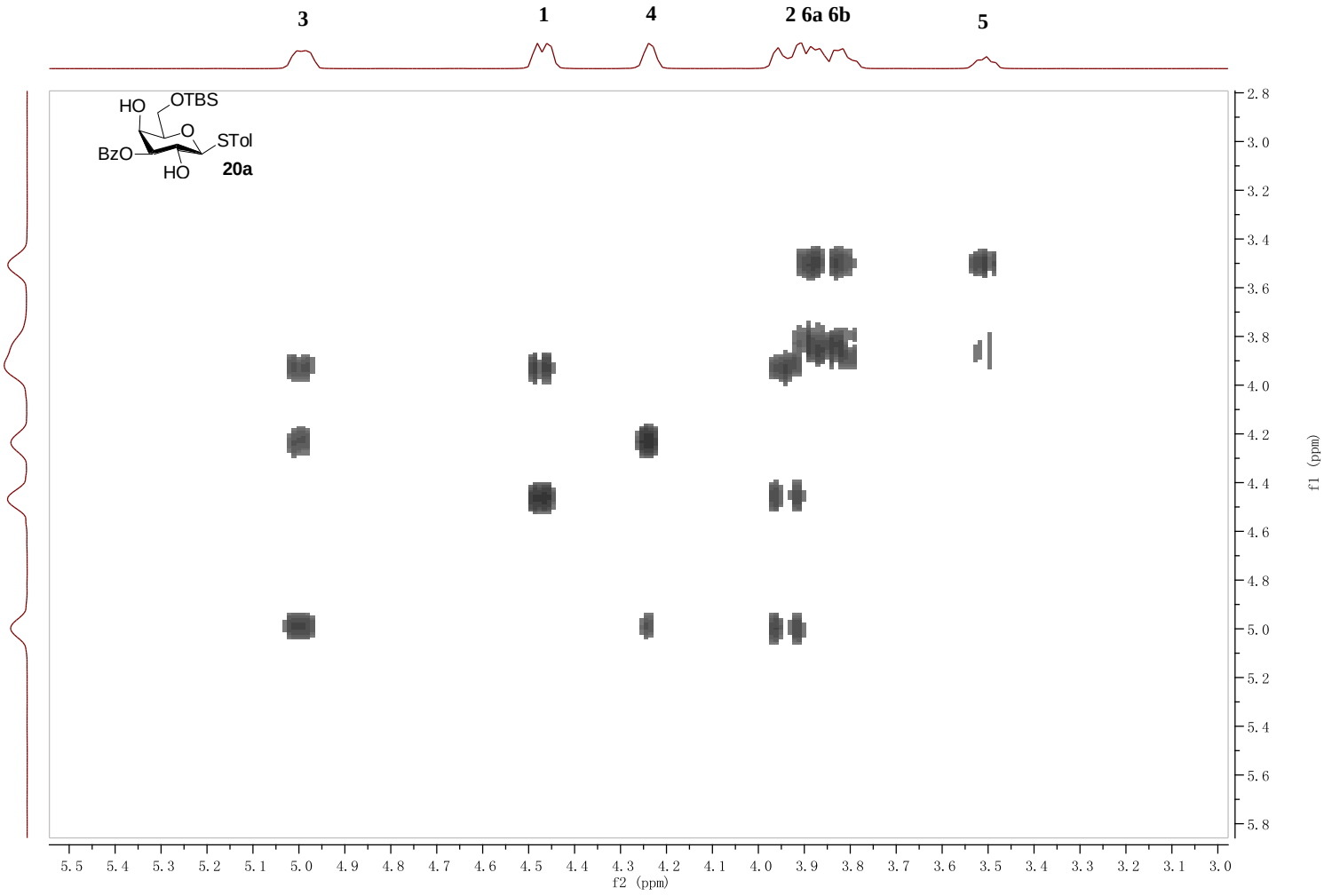
^{1}H-NMR of compound **20a** ($CDCl_3$)



^{13}C-NMR of compound **20a** ($CDCl_3$)

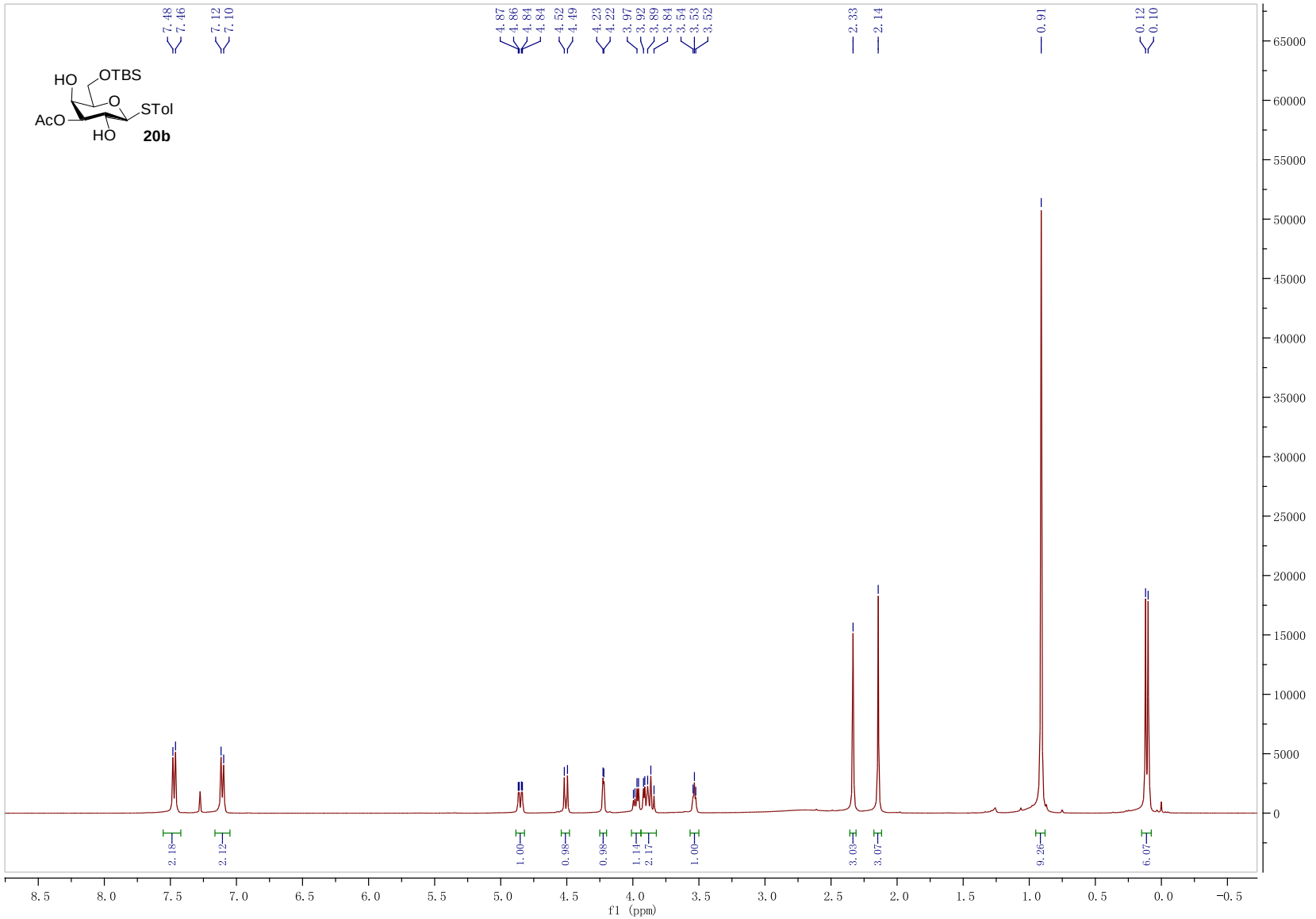


2D-COSY of compound **20a** ($CDCl_3$)

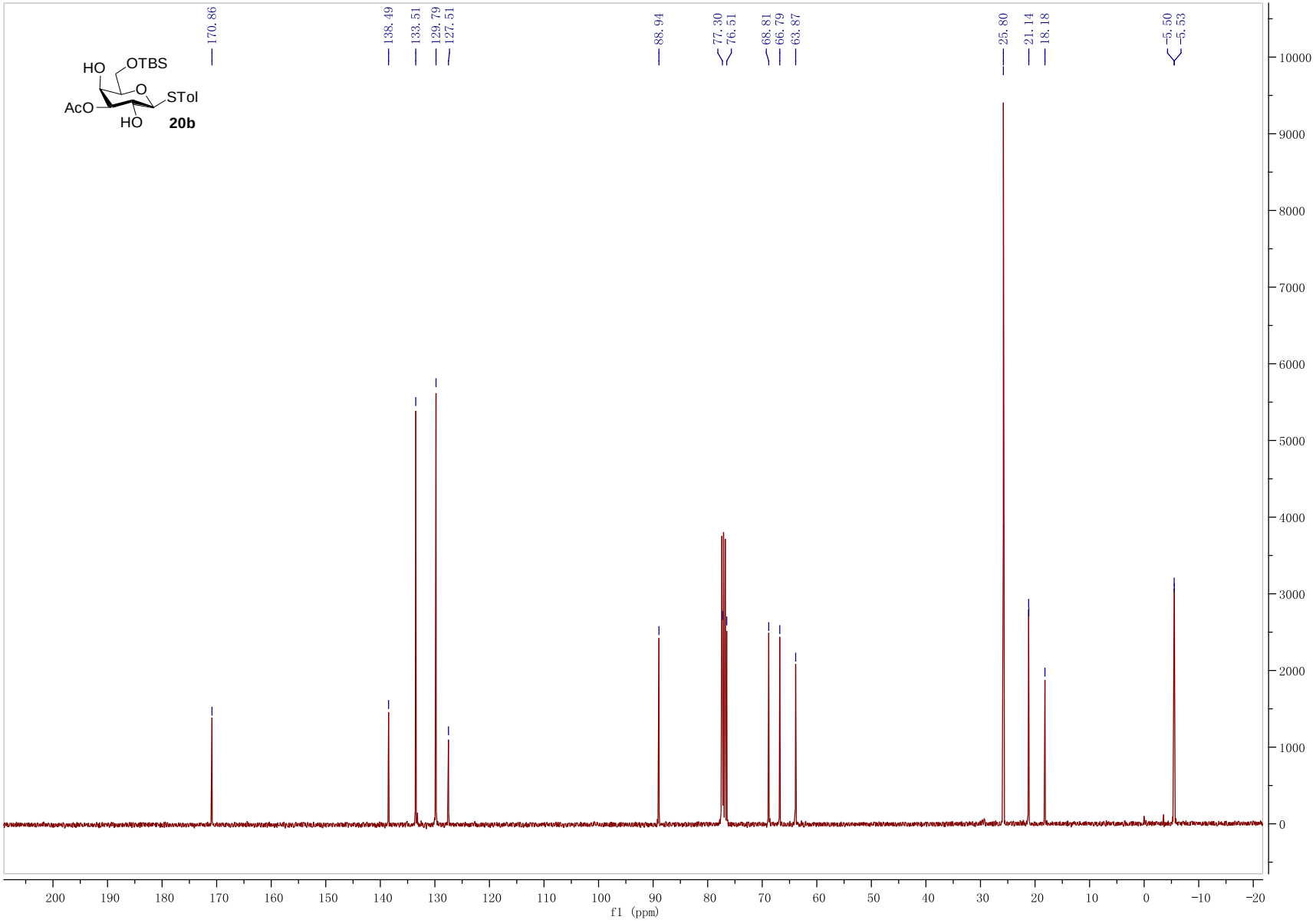


***p*-tolyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (20b)**

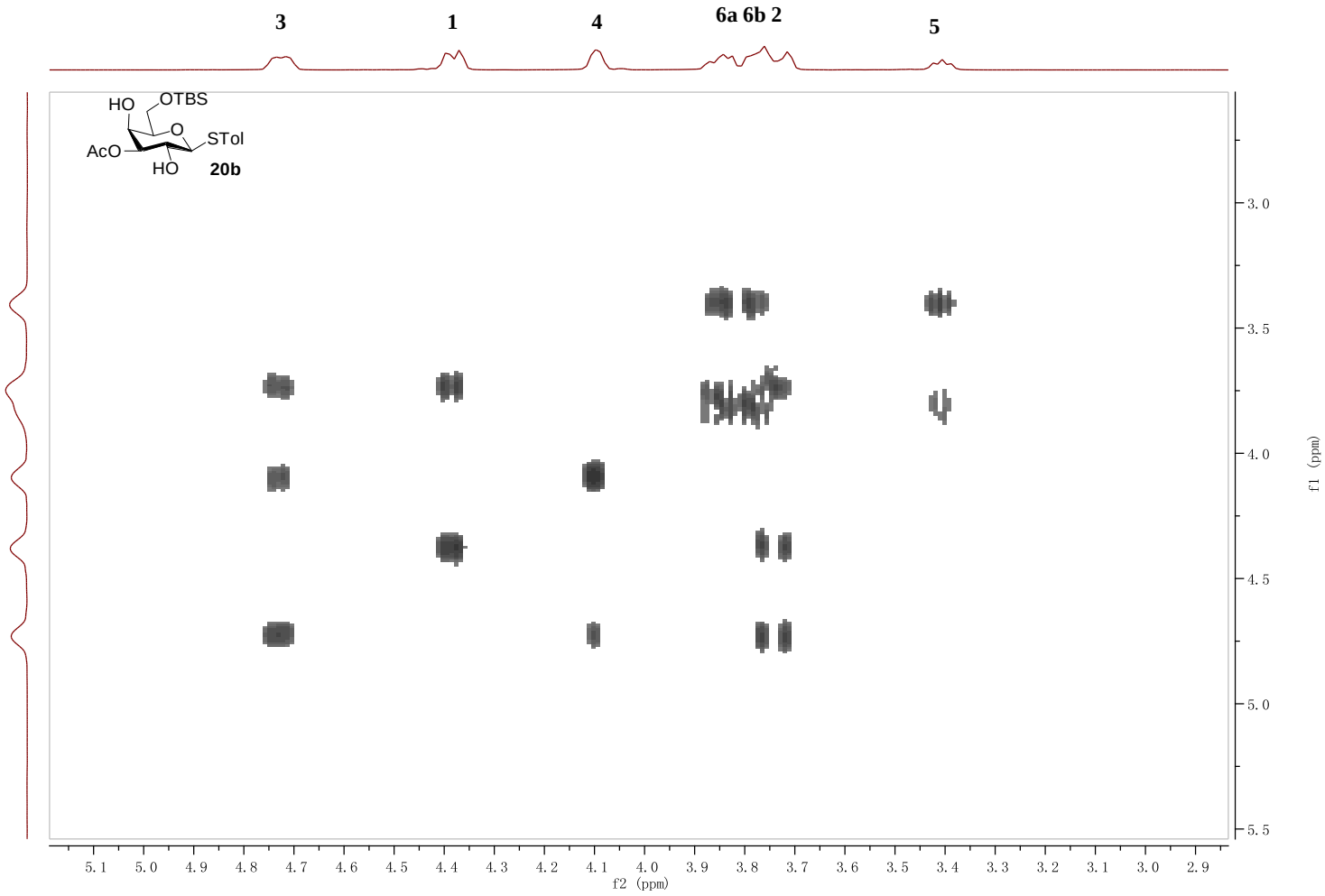
^{1}H-NMR of compound **20b** ($CDCl_3$)



^{13}C-NMR of compound **20b** ($CDCl_3$)

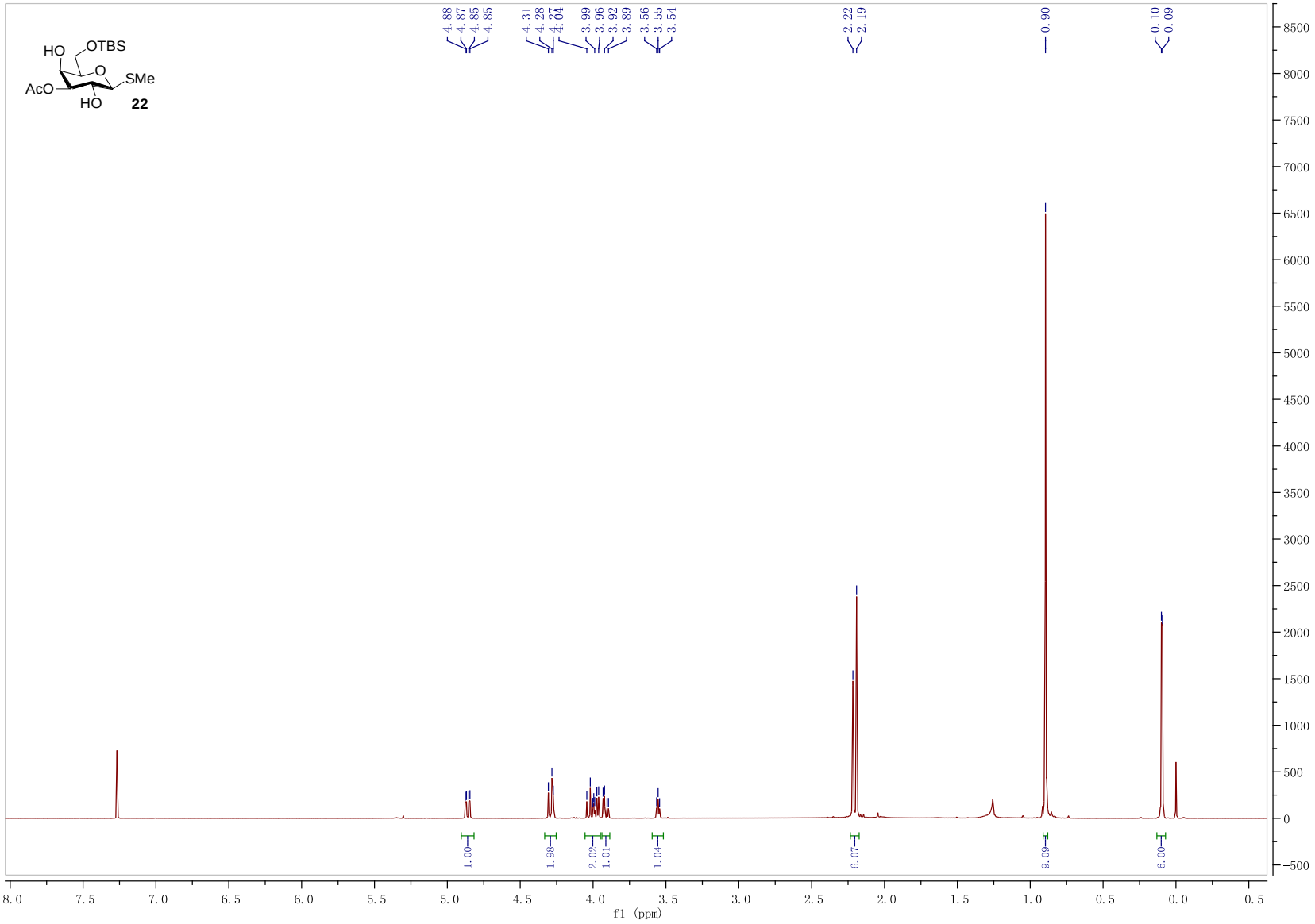


2D-COSY of compound **20b** ($CDCl_3$)

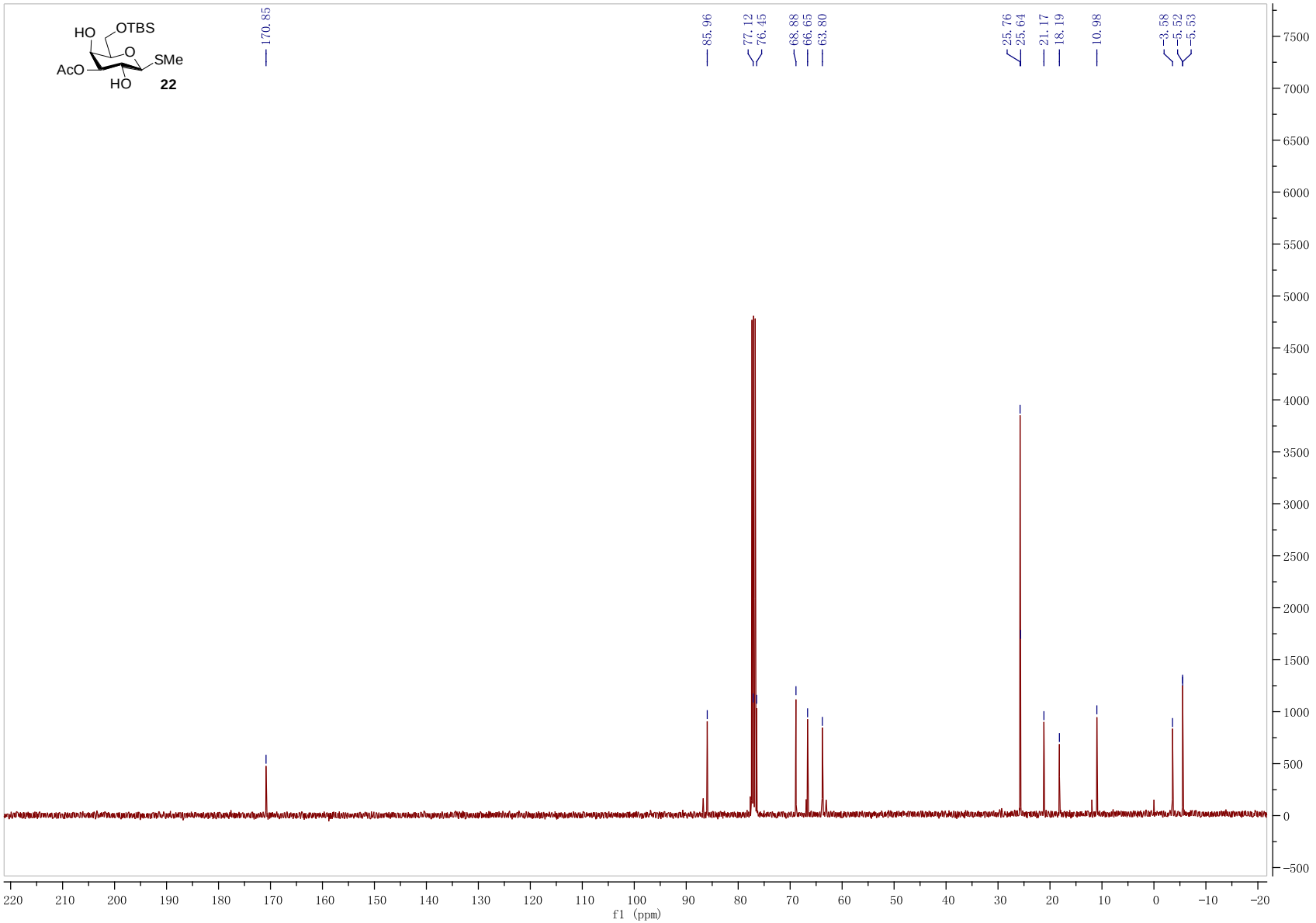


Methyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-acetyl-1-thio-*β*-D-galactopyranoside (22)

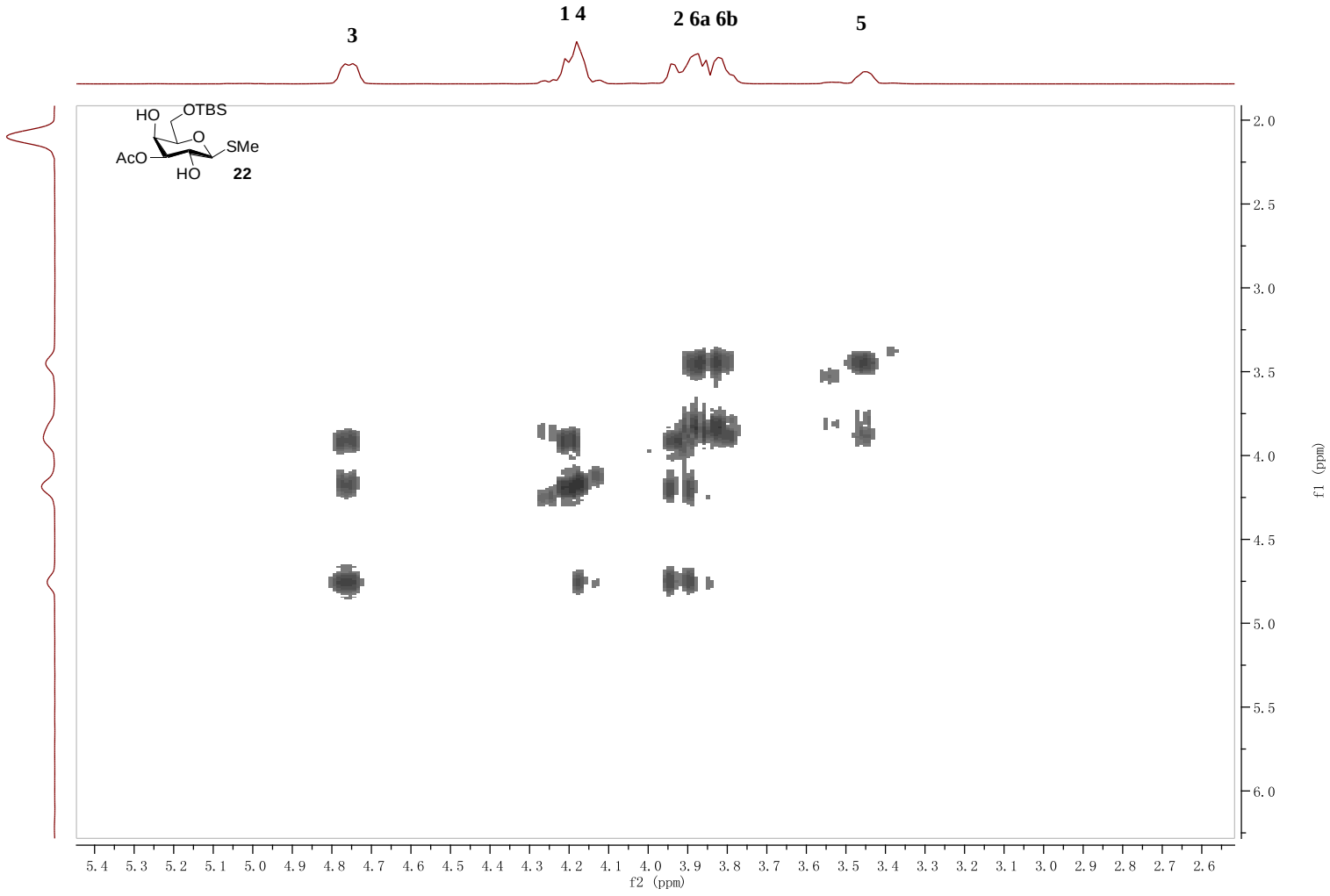
^{1}H-NMR of compound **22** ($CDCl_3$)



^{13}C-NMR of compound **22** ($CDCl_3$)

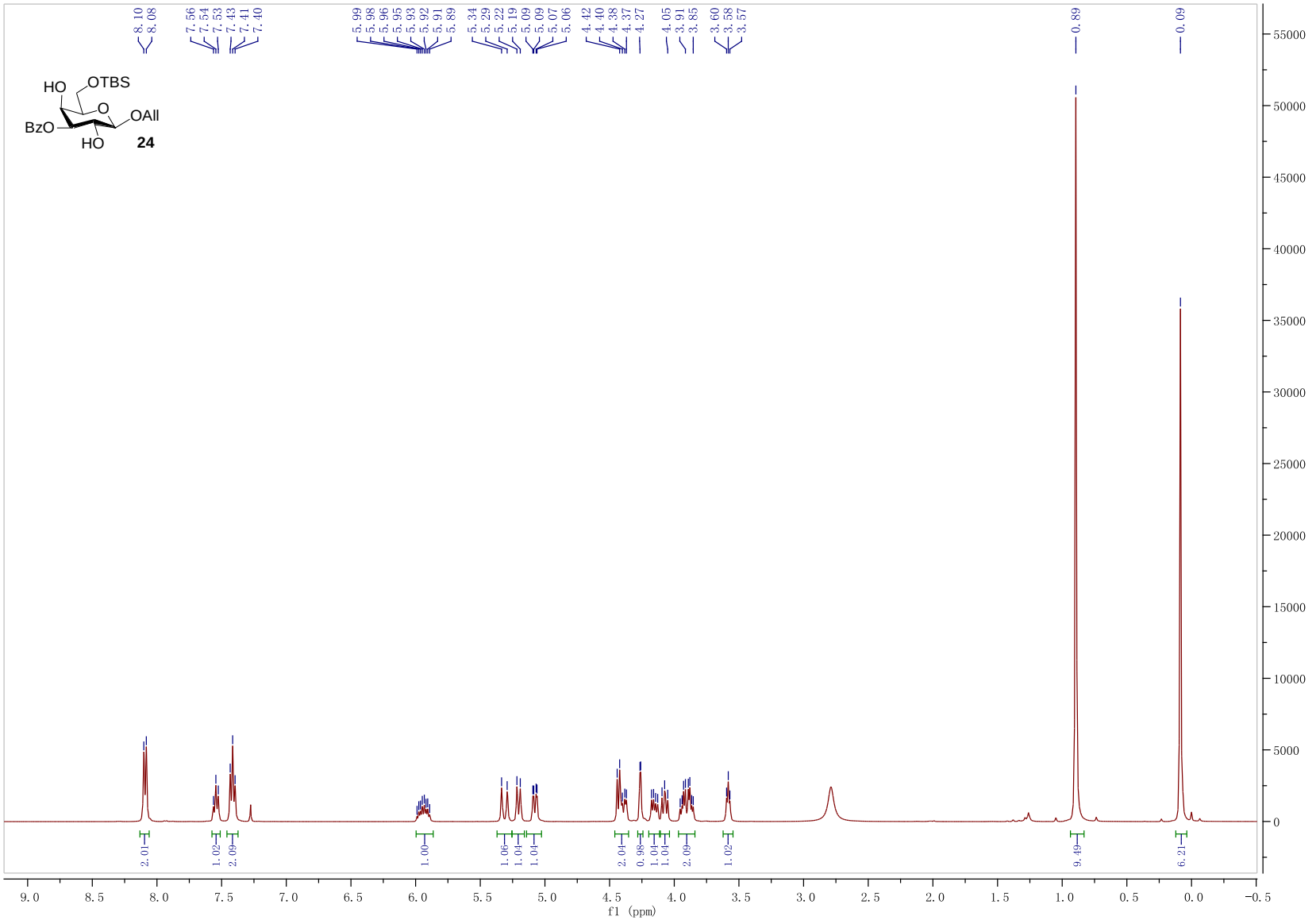


2D-COSY of compound **22** ($CDCl_3$)

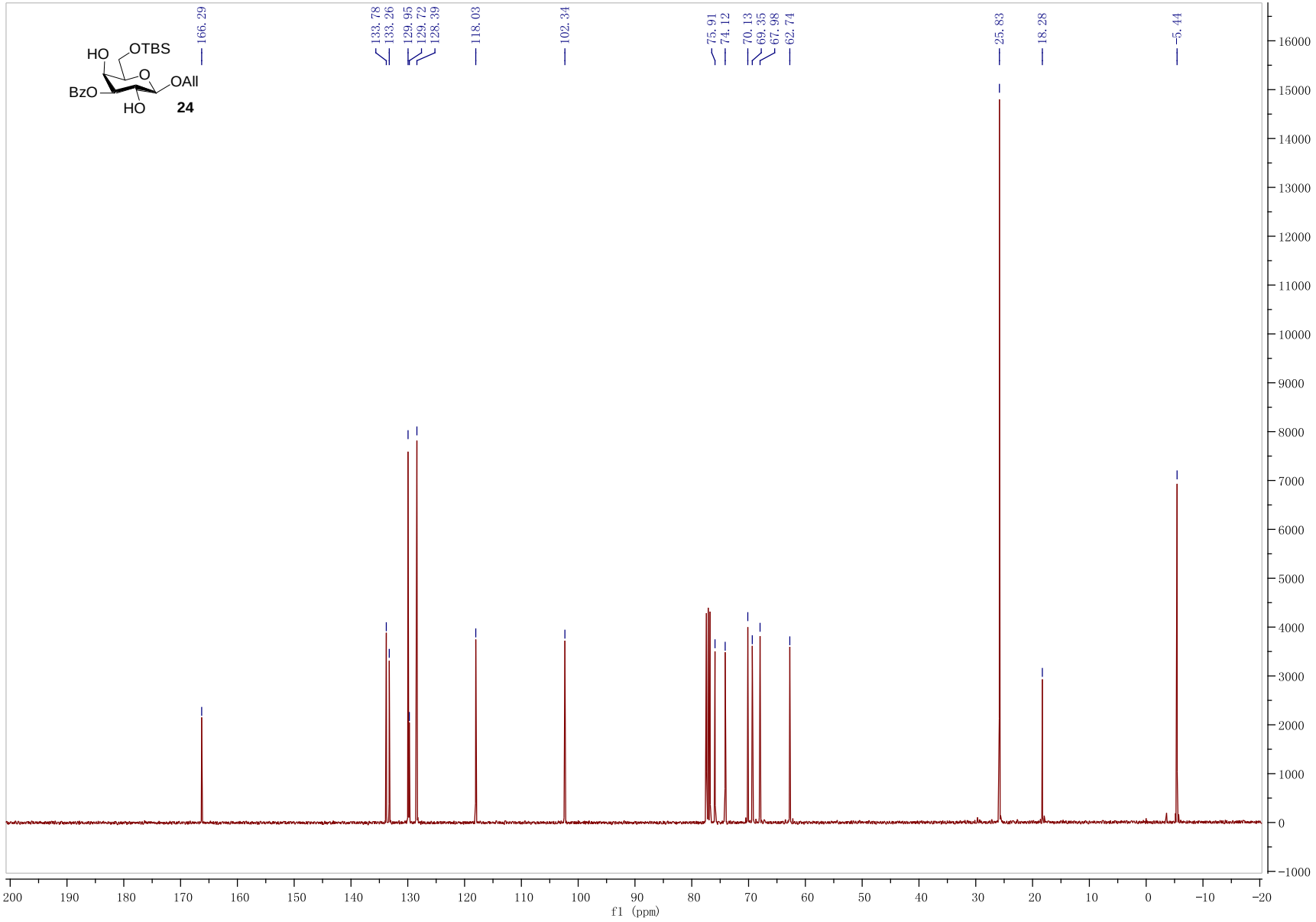


Allyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (24)

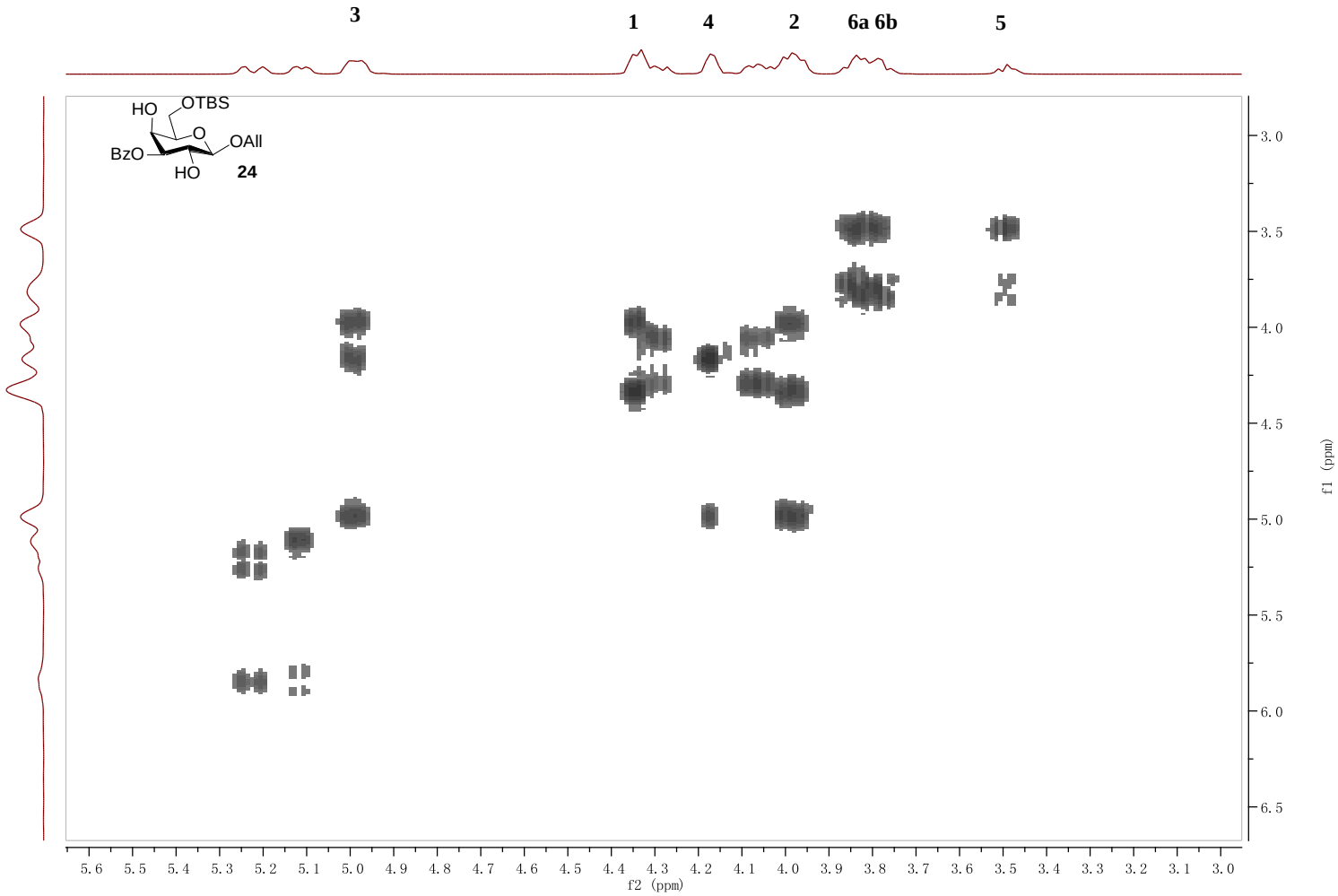
^{1}H-NMR of compound **24** ($CDCl_3$)



^{13}C-NMR of compound **24** ($CDCl_3$)

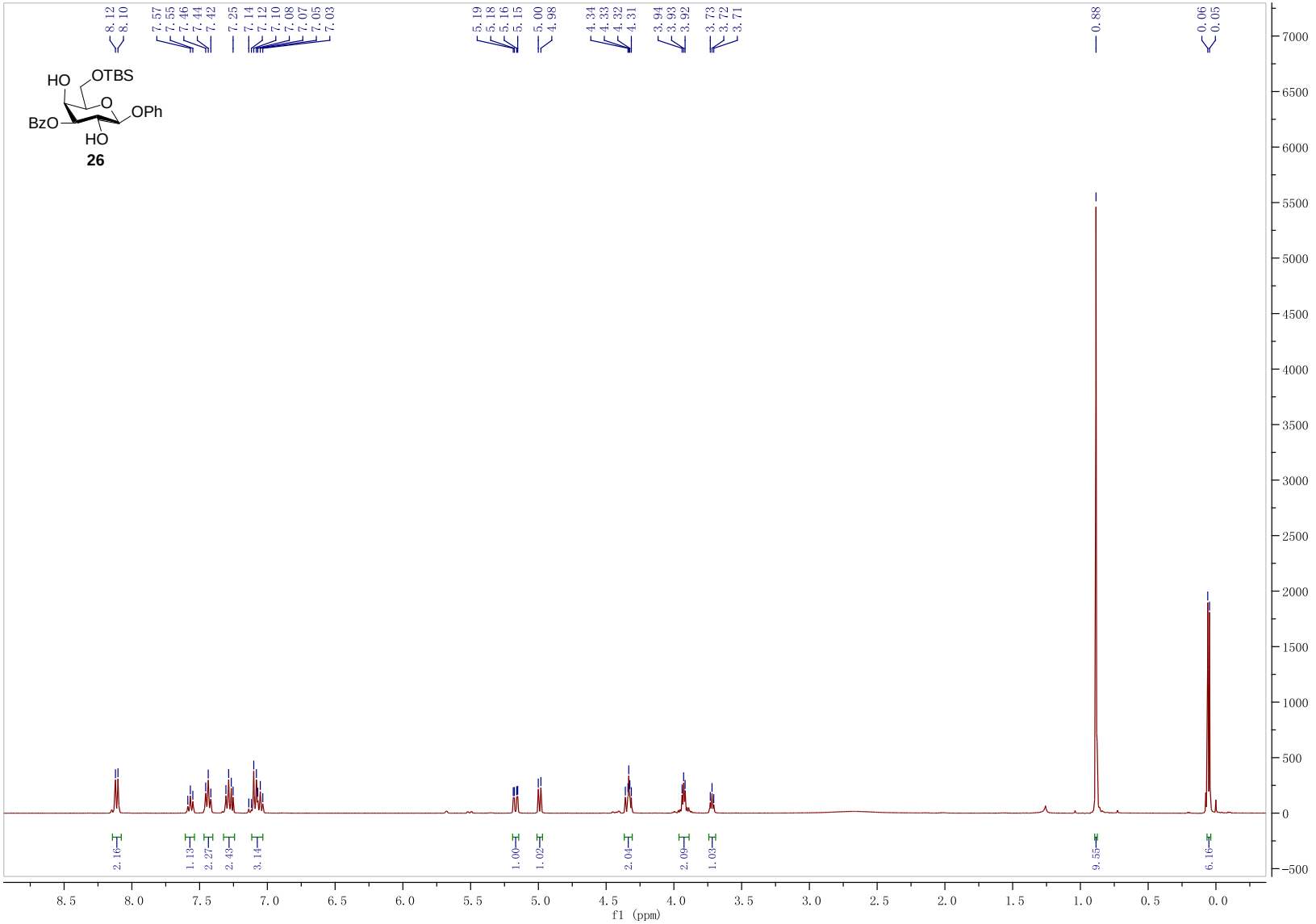


2D-COSY of compound **24** ($CDCl_3$)



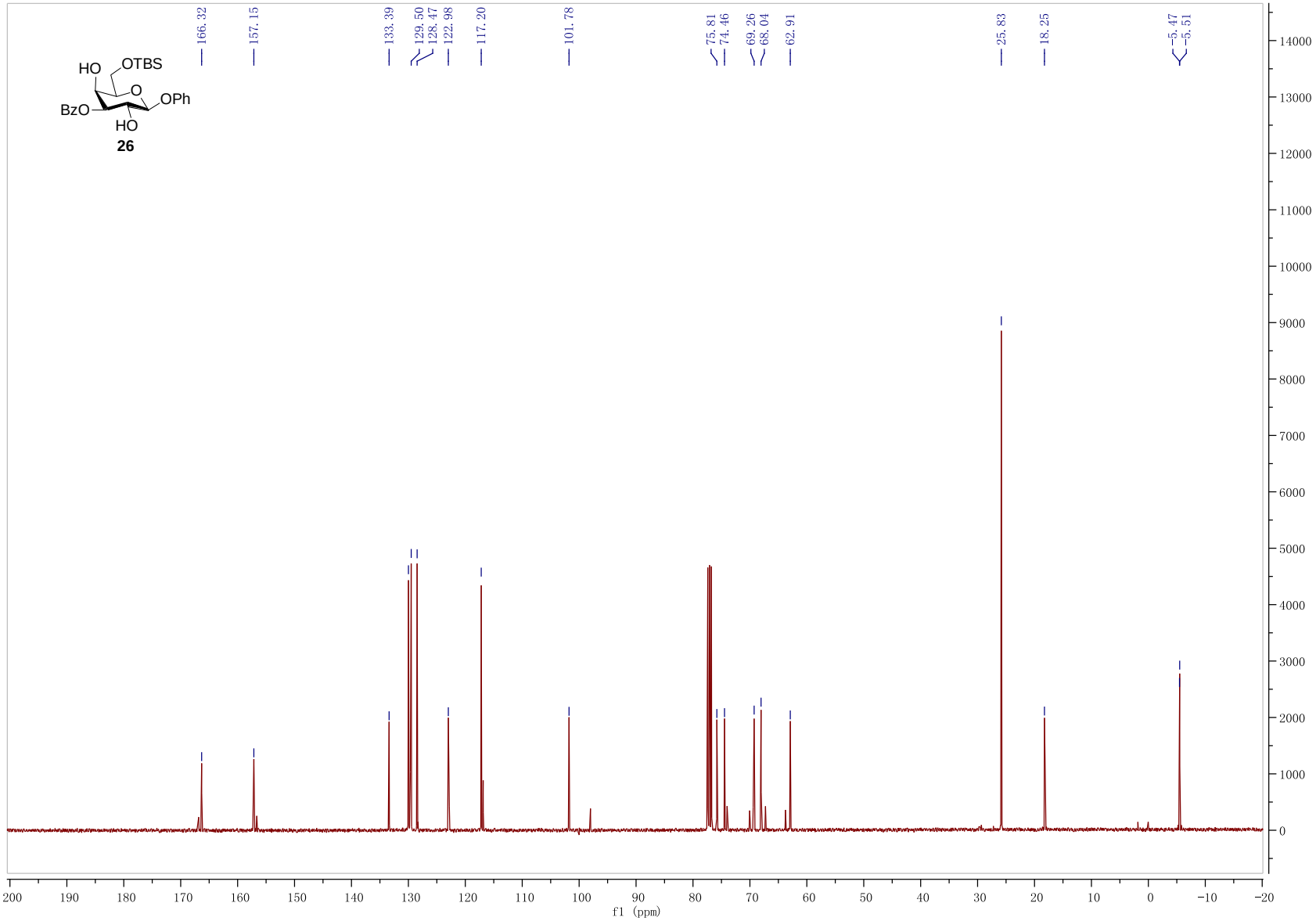
Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (26)

^{1}H-NMR of compound **26** ($CDCl_3$)

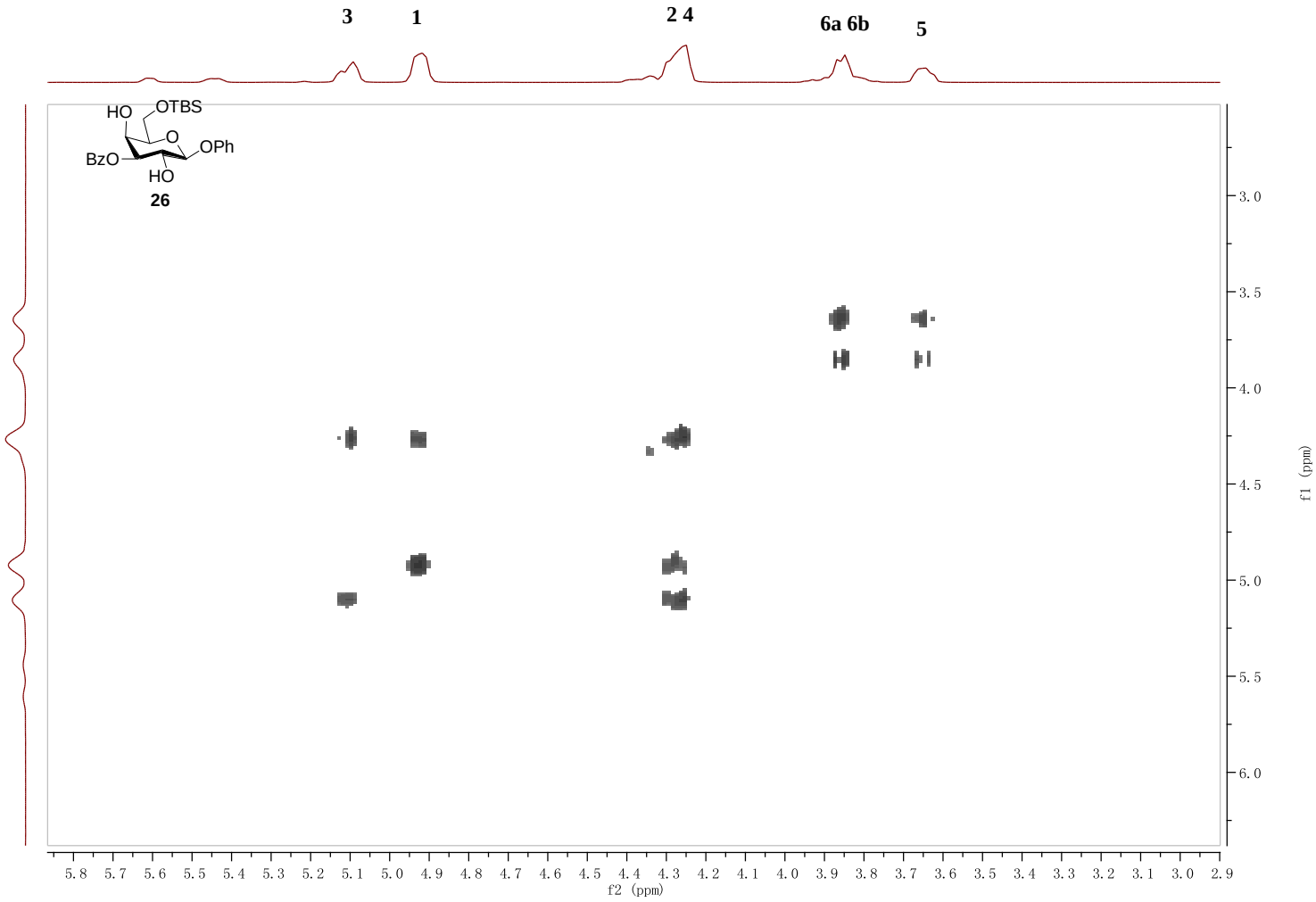


Phenyl-6-*O*-(*tert*-butyldimethylsilyloxy)-3-*O*-benzoyl-*β*-D-galactopyranoside (26)

^{13}C-NMR of compound **26** ($CDCl_3$)

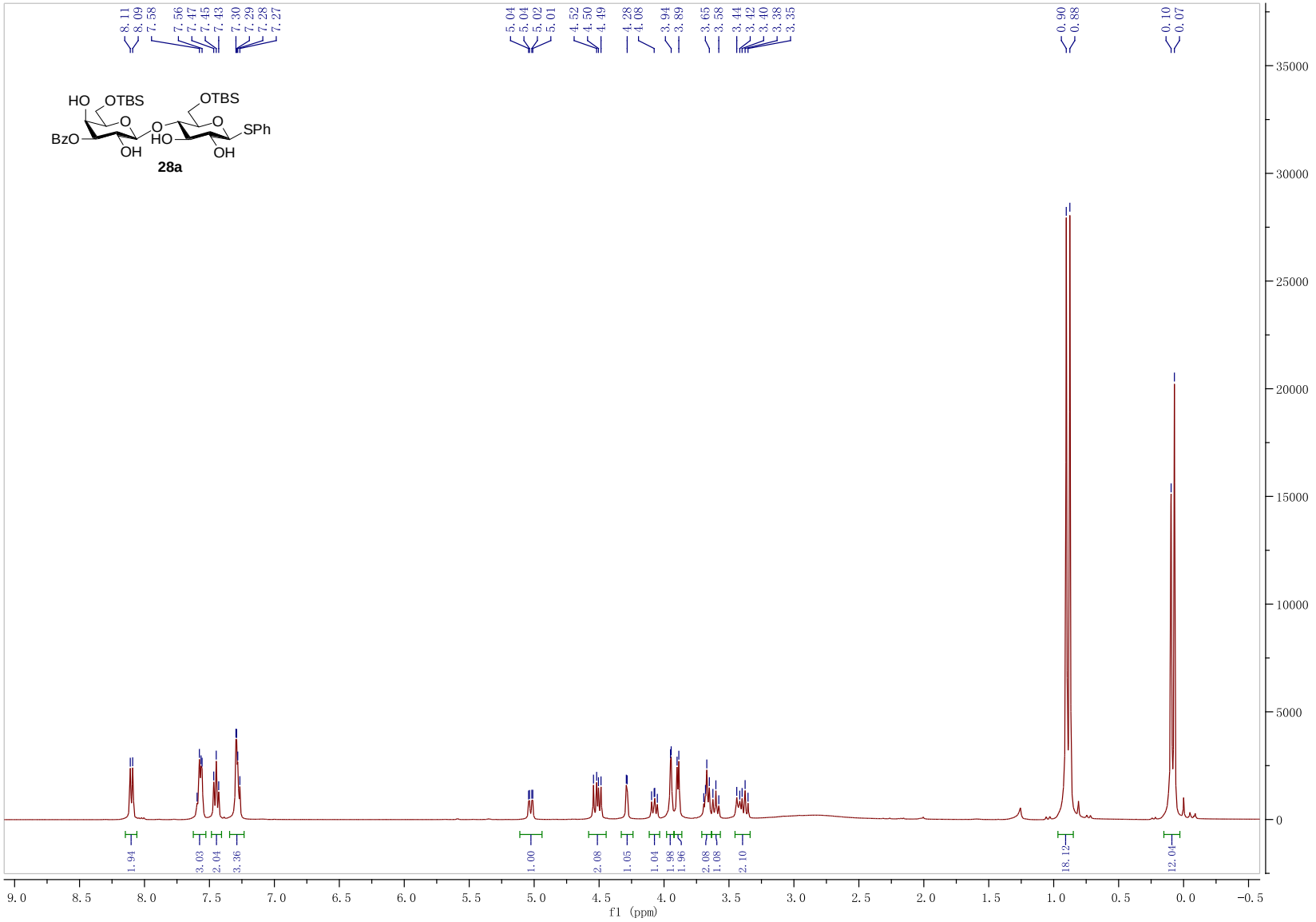


2D-COSY of compound **26** ($CDCl_3$)

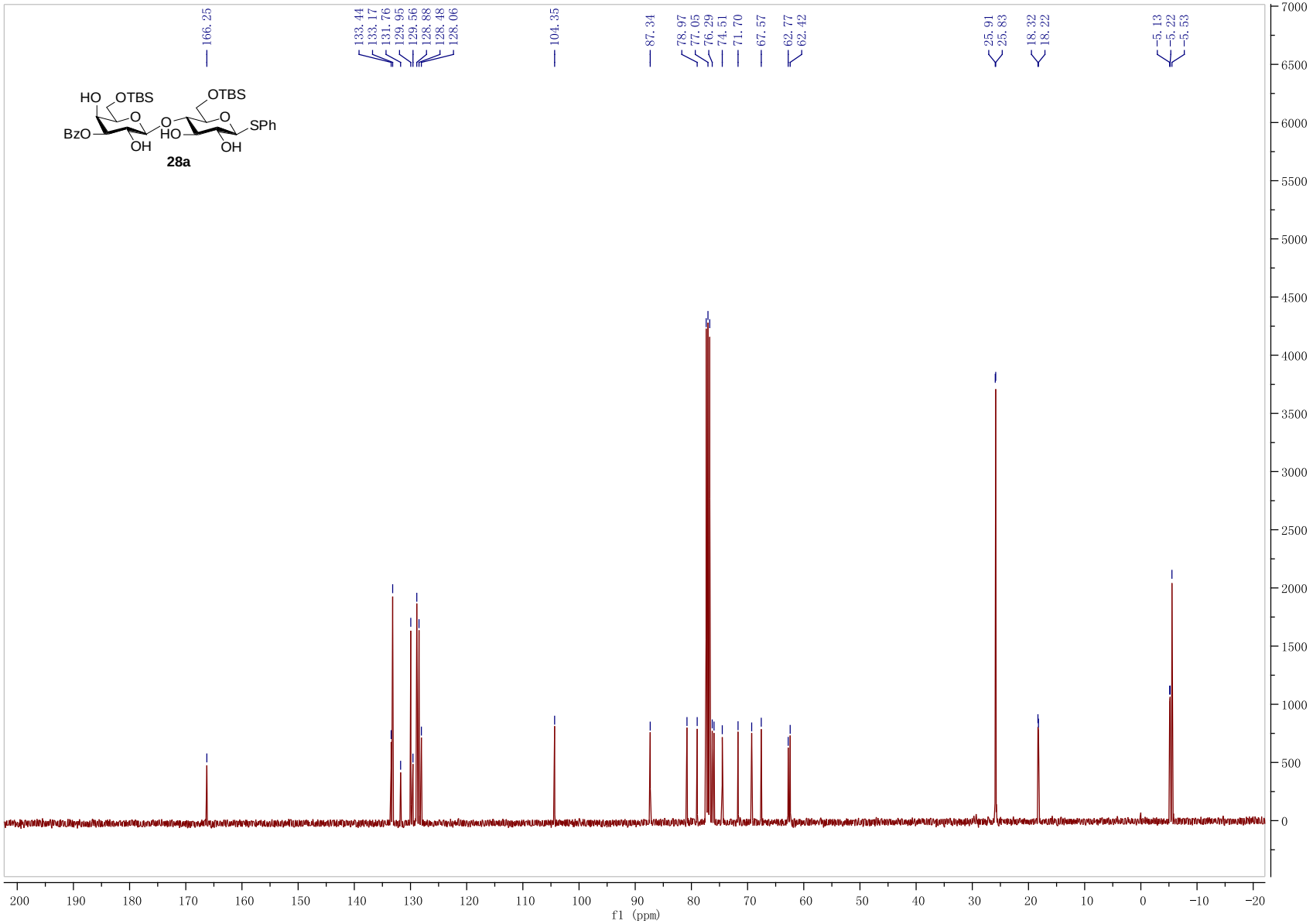


Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-3′-*O*-benzoyl-1-*S*-*β*-D-lactoside (28a)

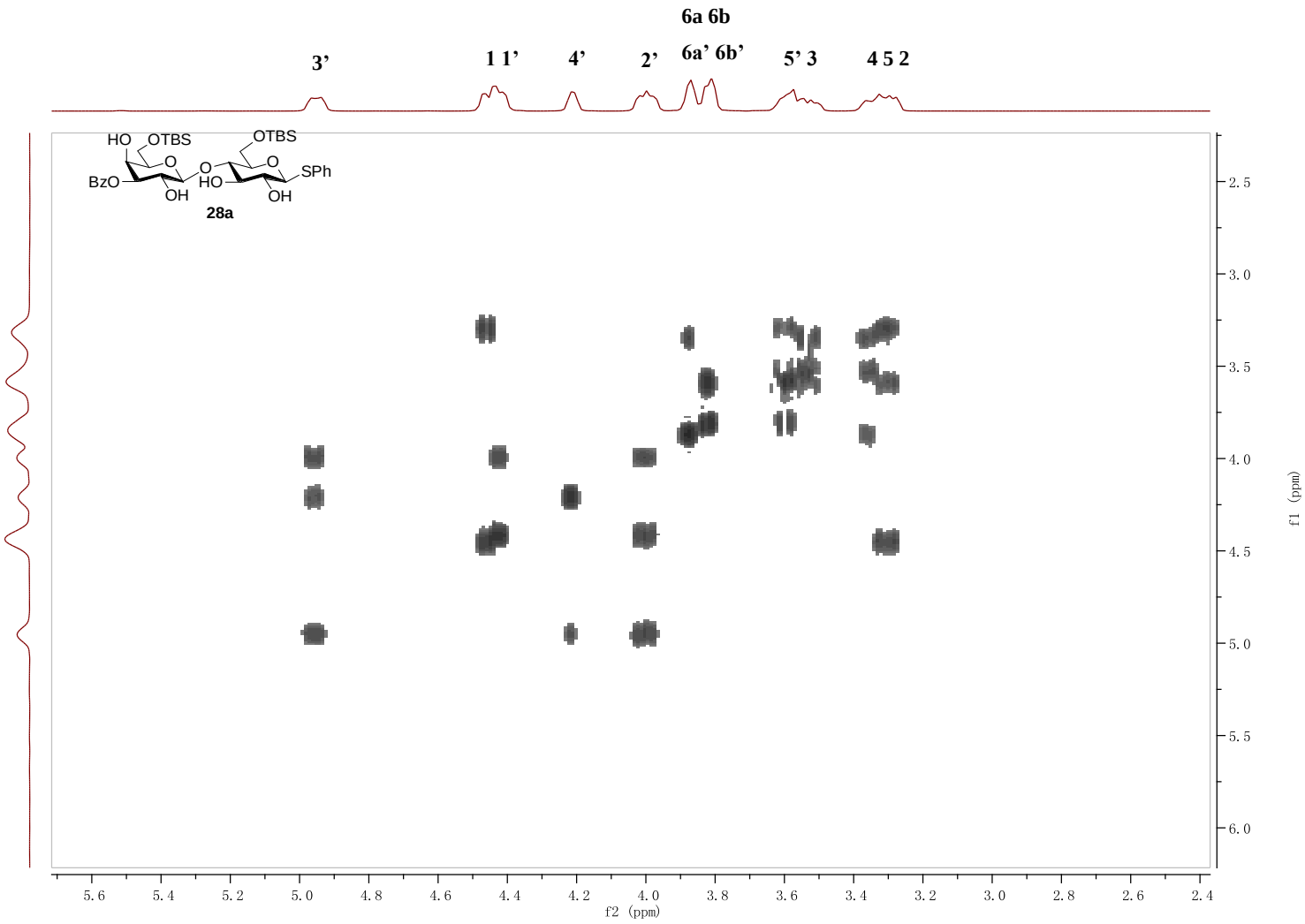
^{1}H-NMR of compound **28a** ($CDCl_3$)



^{13}C-NMR of compound **28a** ($CDCl_3$)

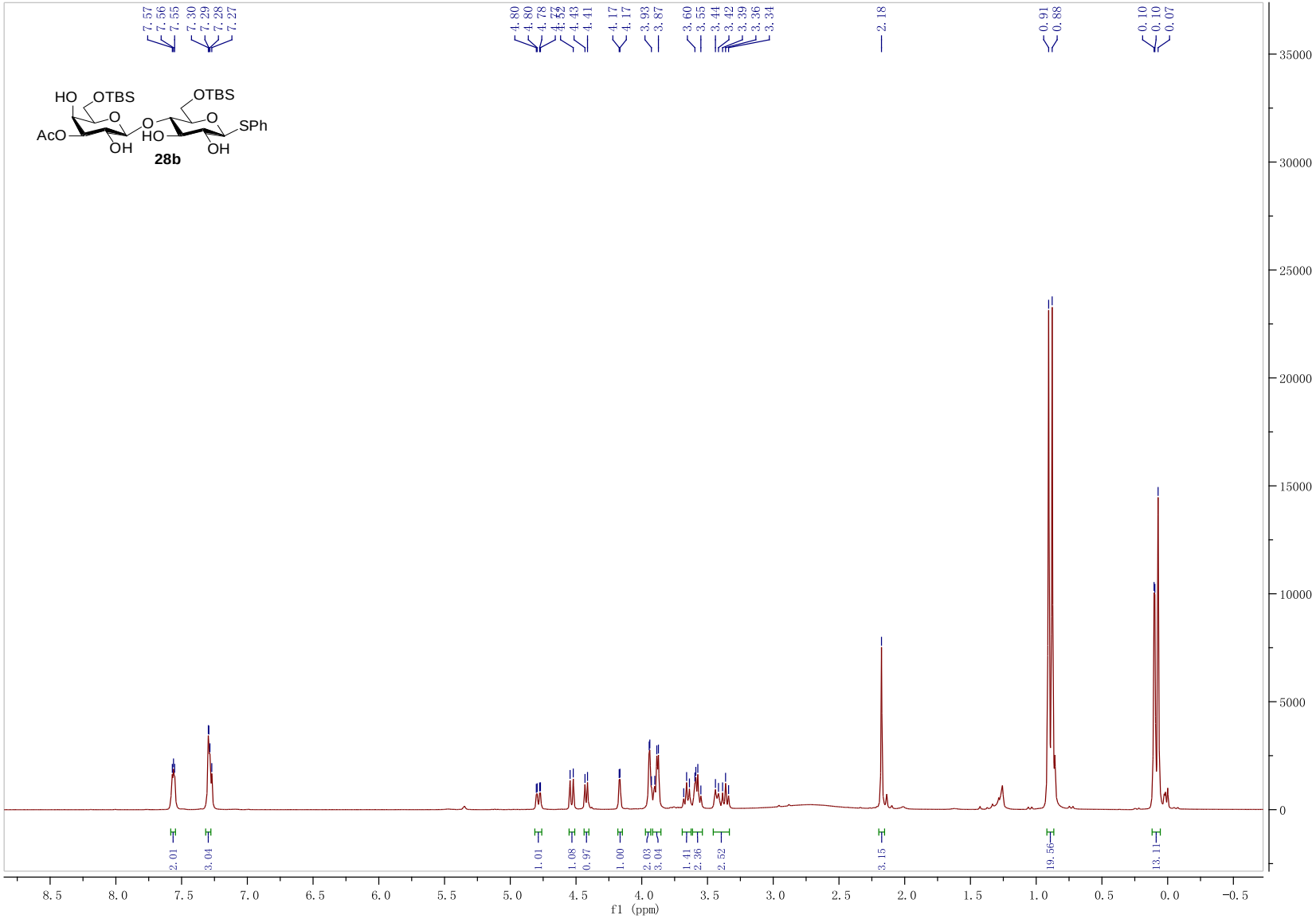


2D-COSY of compound **28a** ($CDCl_3$)

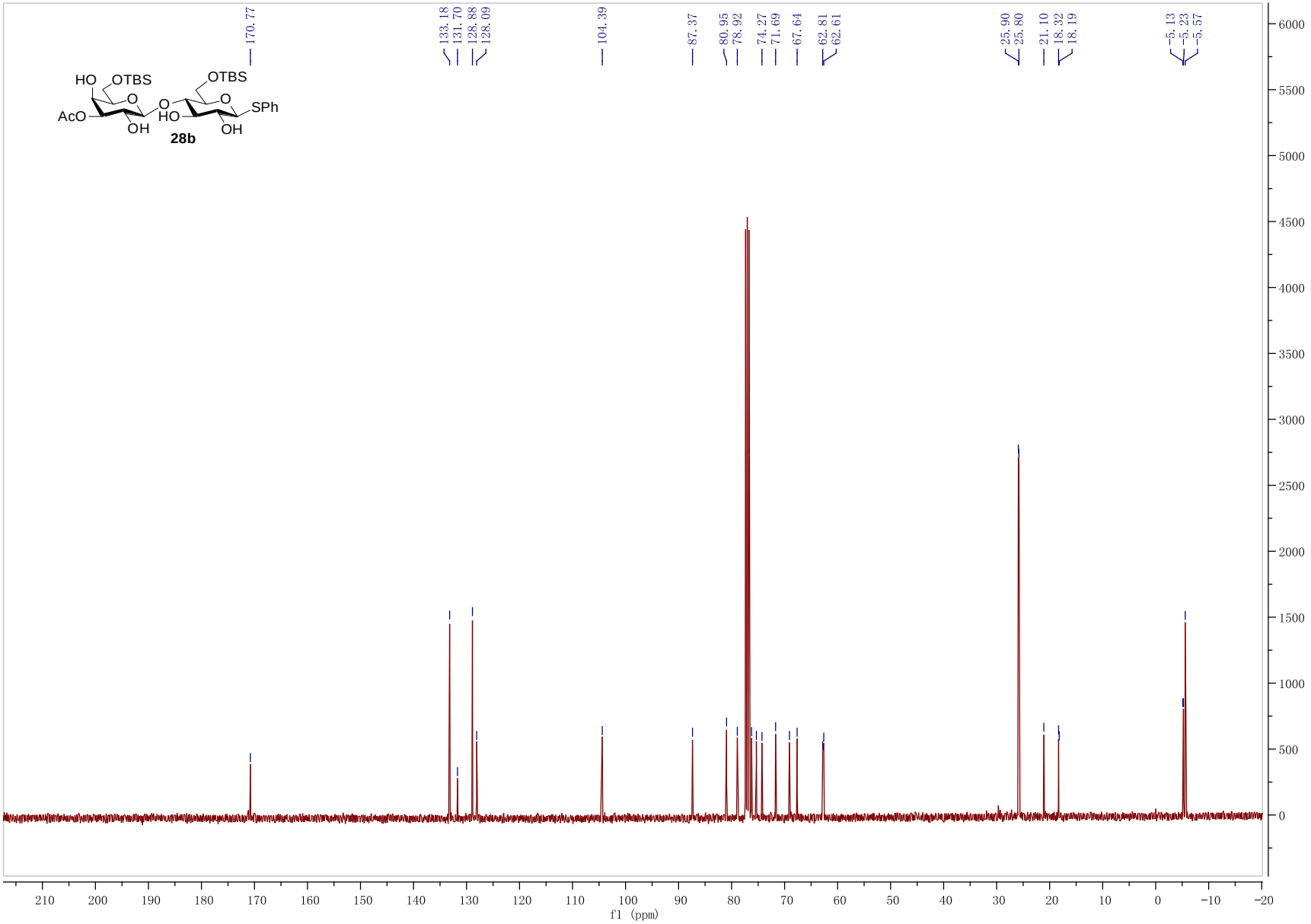


Phenyl-6,6′-di-*O*-(tert-butyldimethylsilyl)-3′-*O*-acetyl-1-*S*-*β*-D-lactoside (28b)

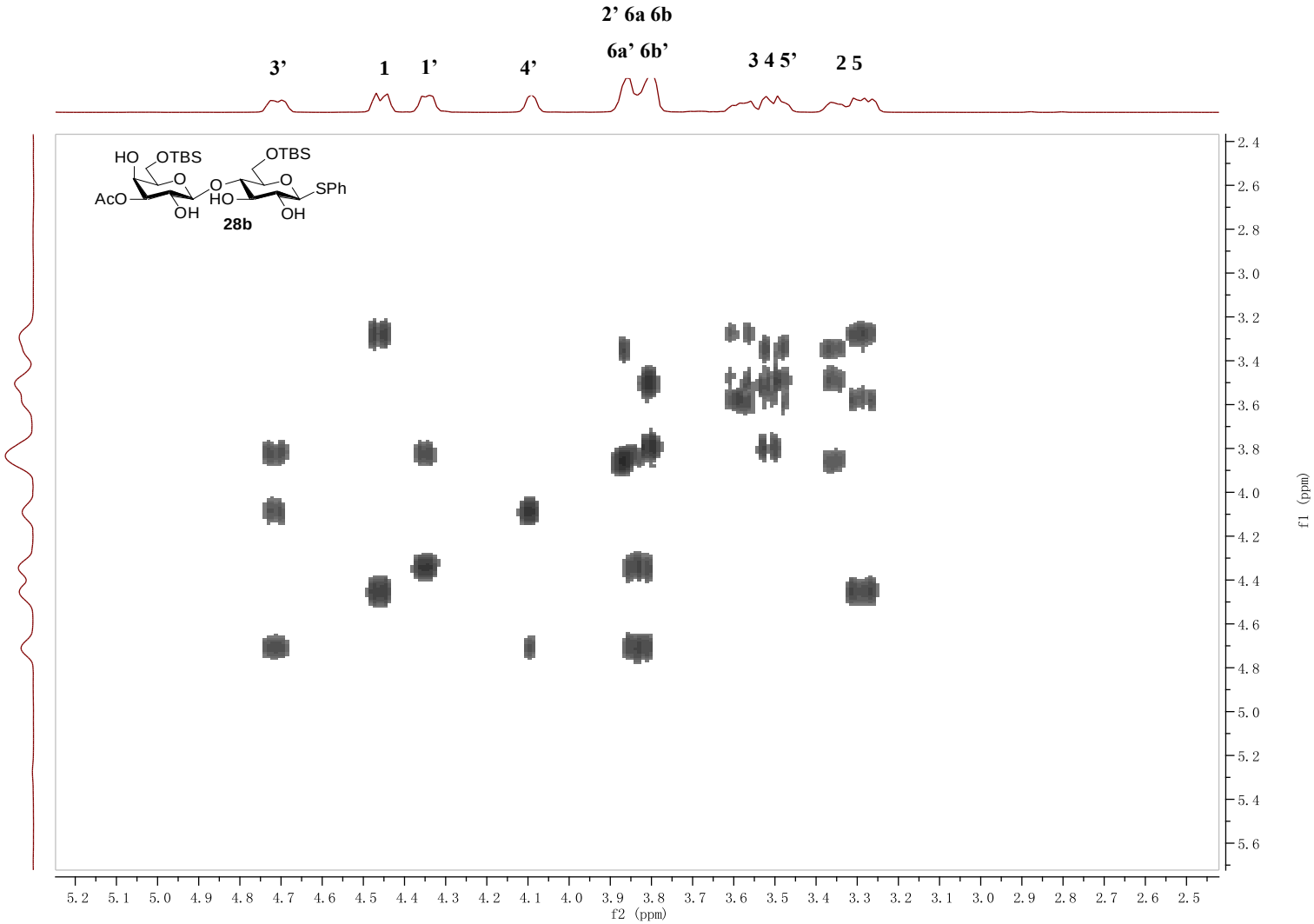
^{1}H-NMR of compound **28b** ($CDCl_3$)



^{13}C-NMR of compound **28b** ($CDCl_3$)

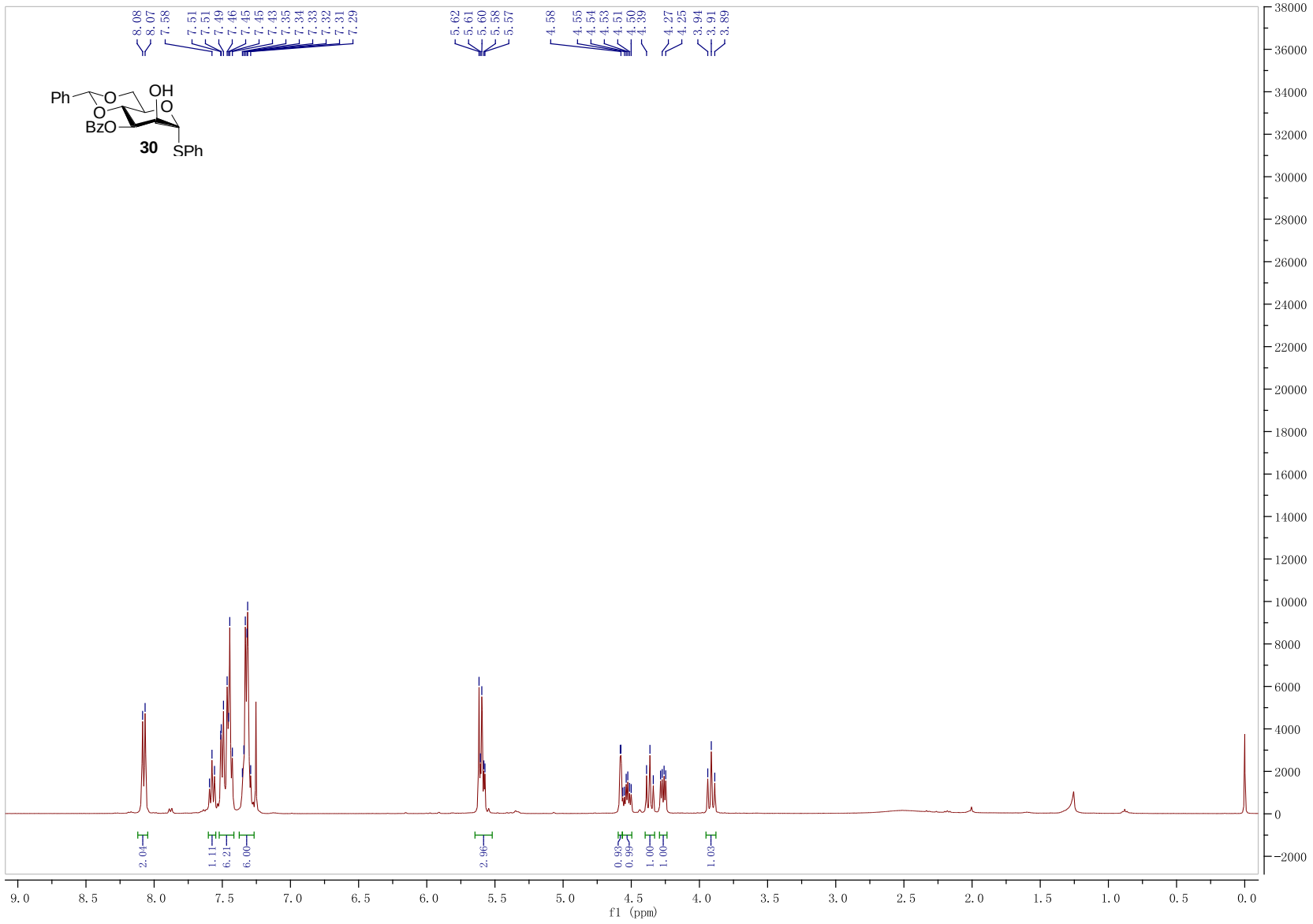


2D-COSY of compound **28b** ($CDCl_3$)



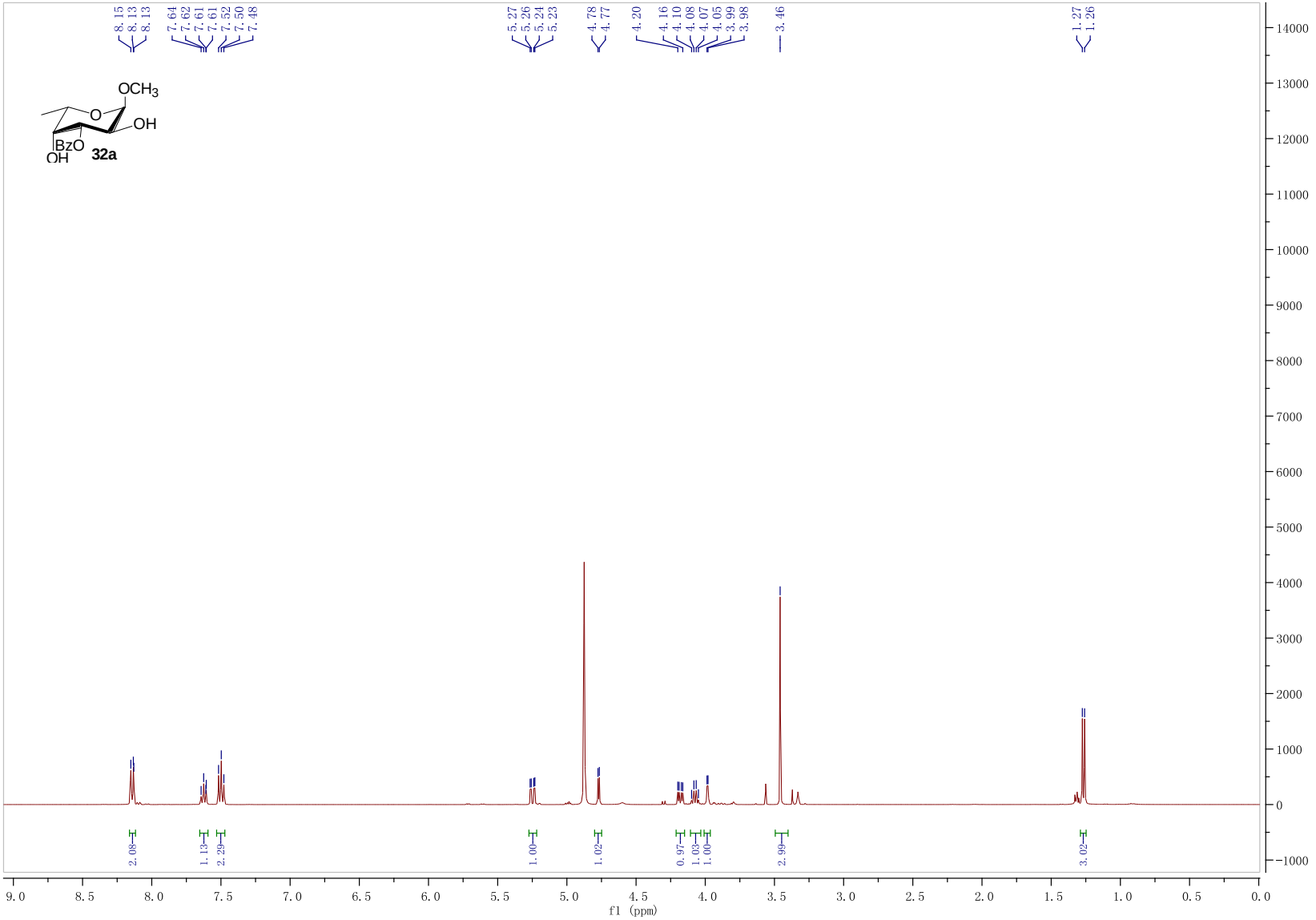
Phenyl 3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*α*-D-mannopyranoside (30)

^{1}H-NMR of compound **30** ($CDCl_3$)



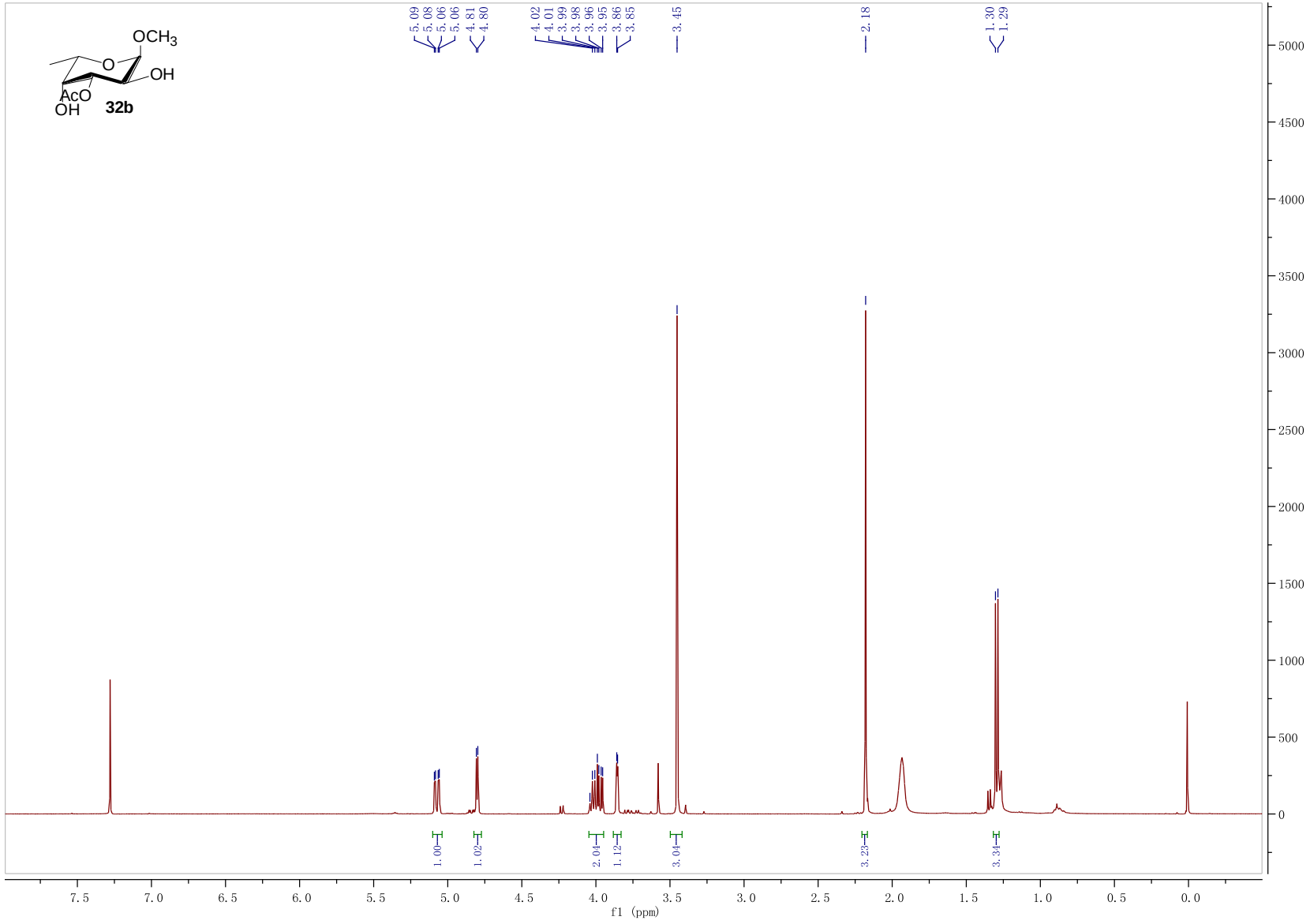
Methyl-3-*O*-benzoyl-*α*-L-fucopyranoside (32a)

^{1}H-NMR of compound **32a** (CD_3OD)



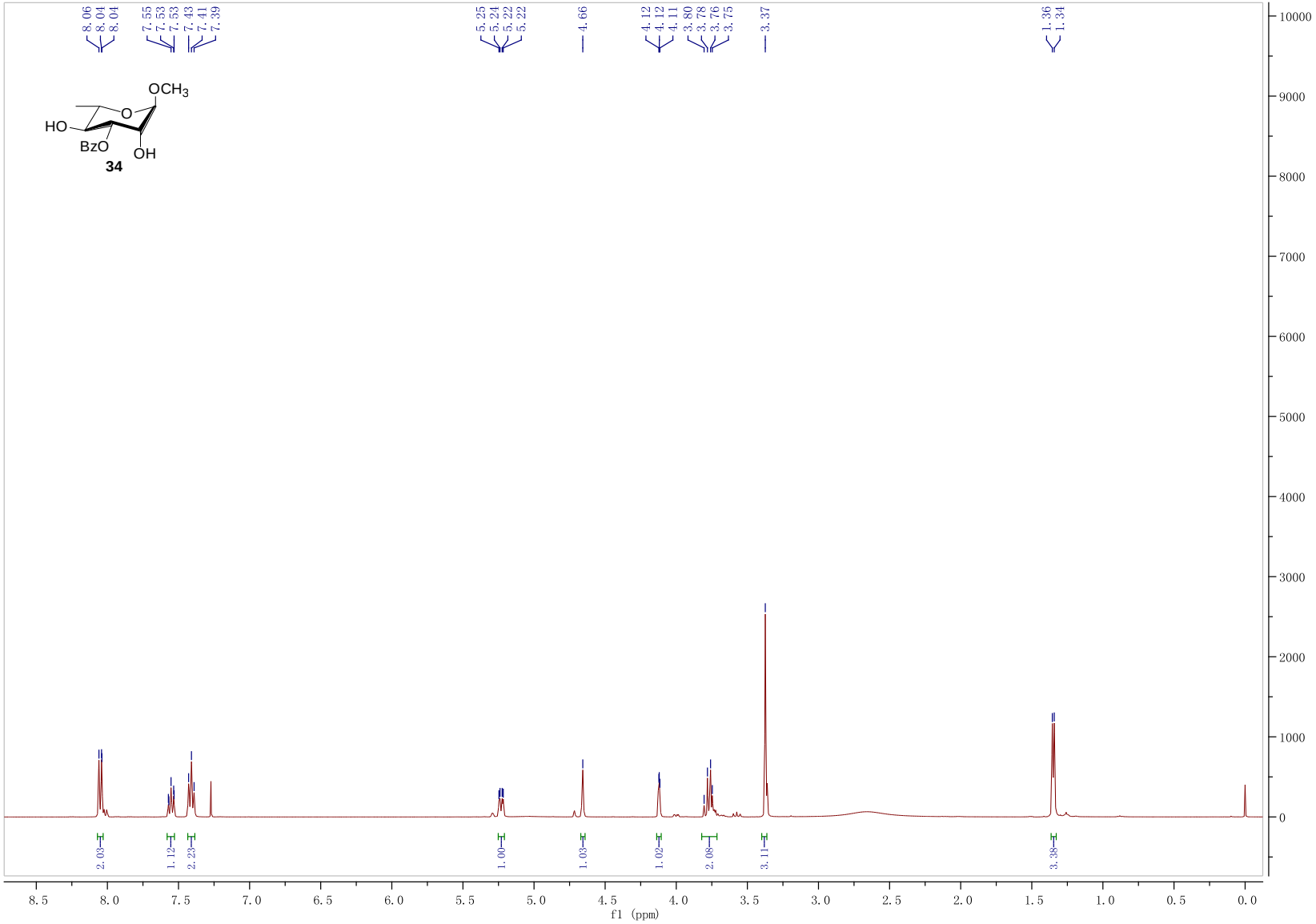
Methyl-3-*O*-acetyl-*α*-L-fucopyranoside (32b)

^{1}H-NMR of compound **32b** ($CDCl_3$)



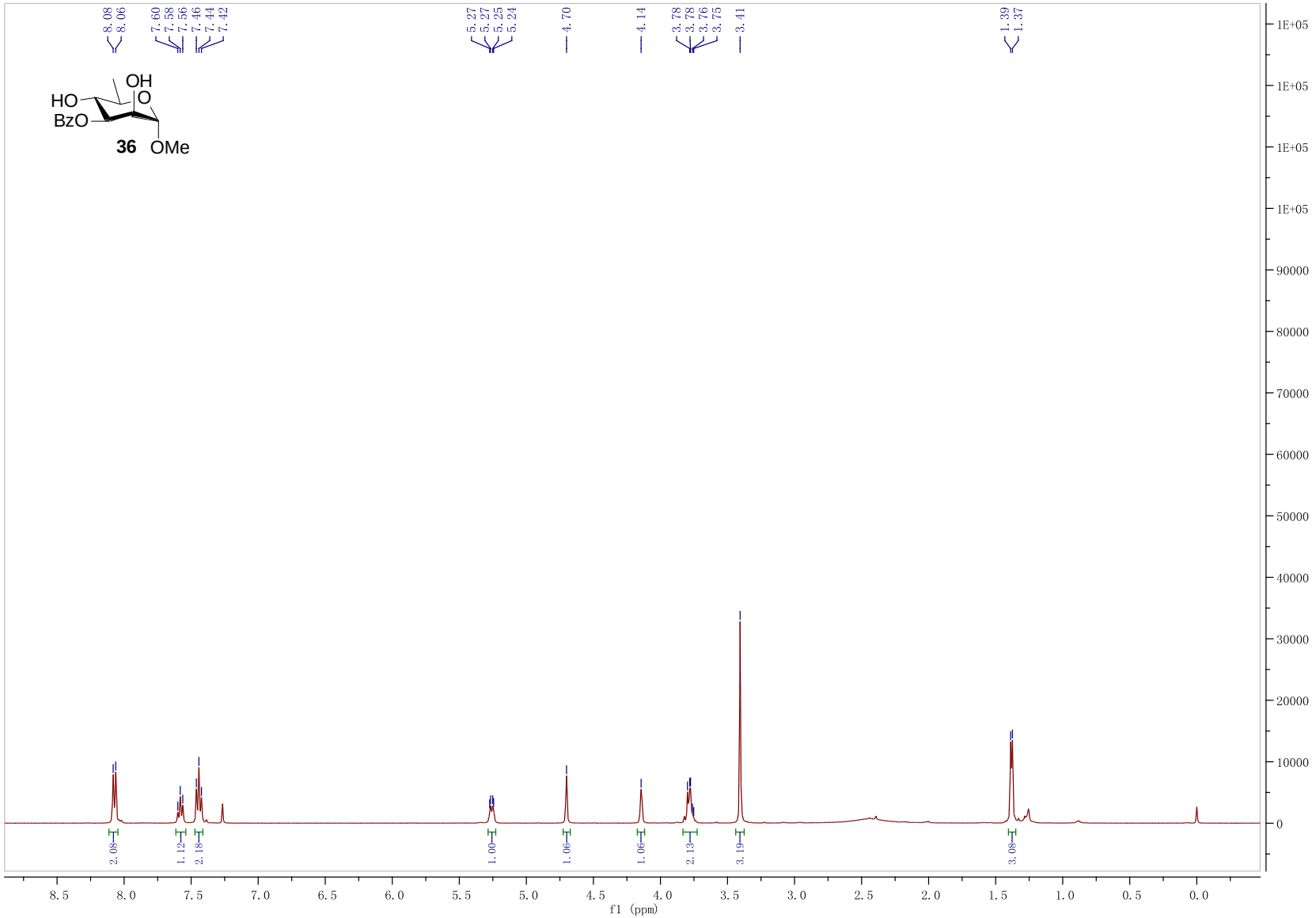
Methyl-3-*O*-benzoyl-*α*-L-rhamnopyranoside (34)

^{1}H-NMR of compound **34** ($CDCl_3$)

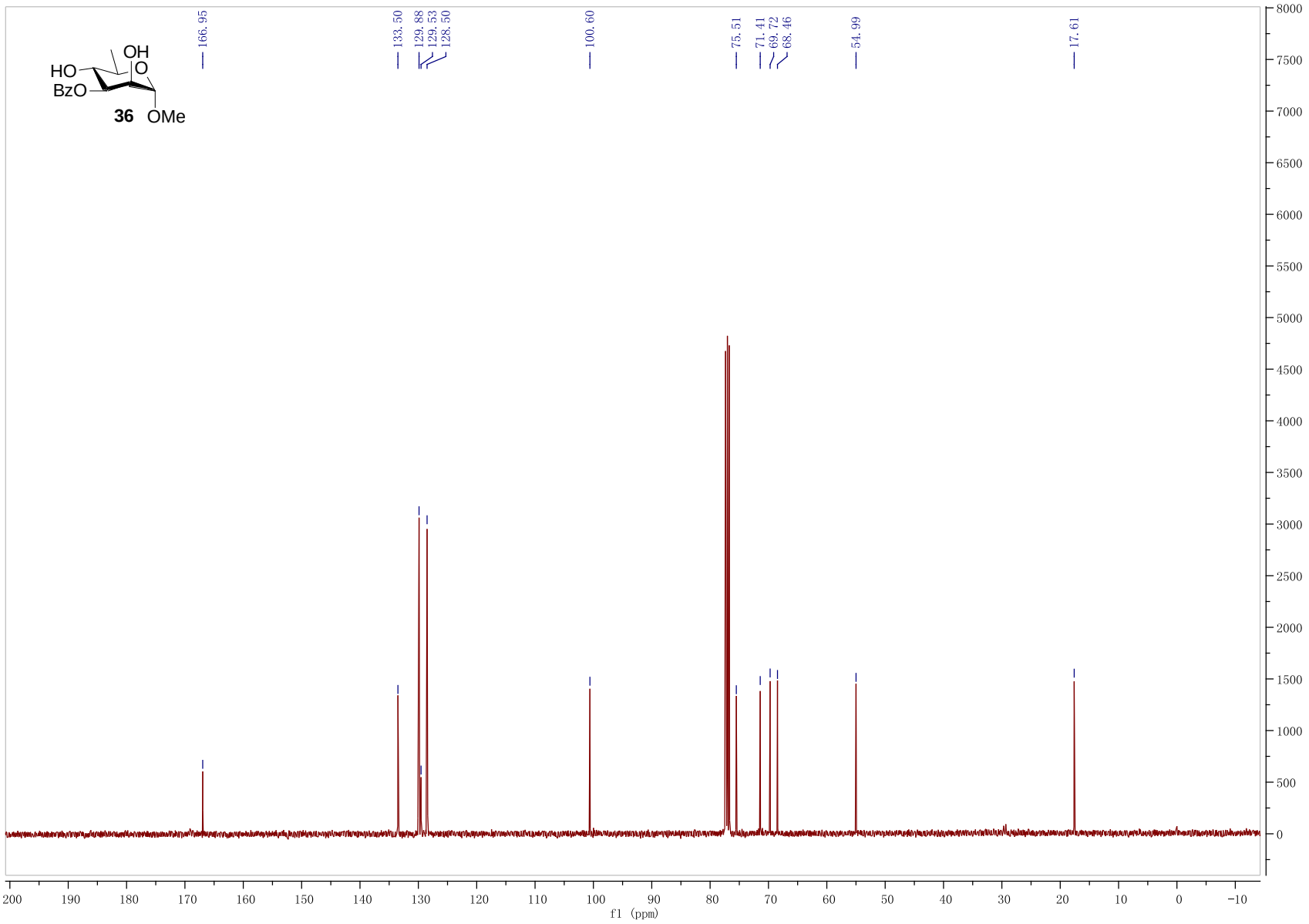


Methyl-3-*O*-benzoyl-6-Deoxy-*α*-D-mannopyranoside (36)

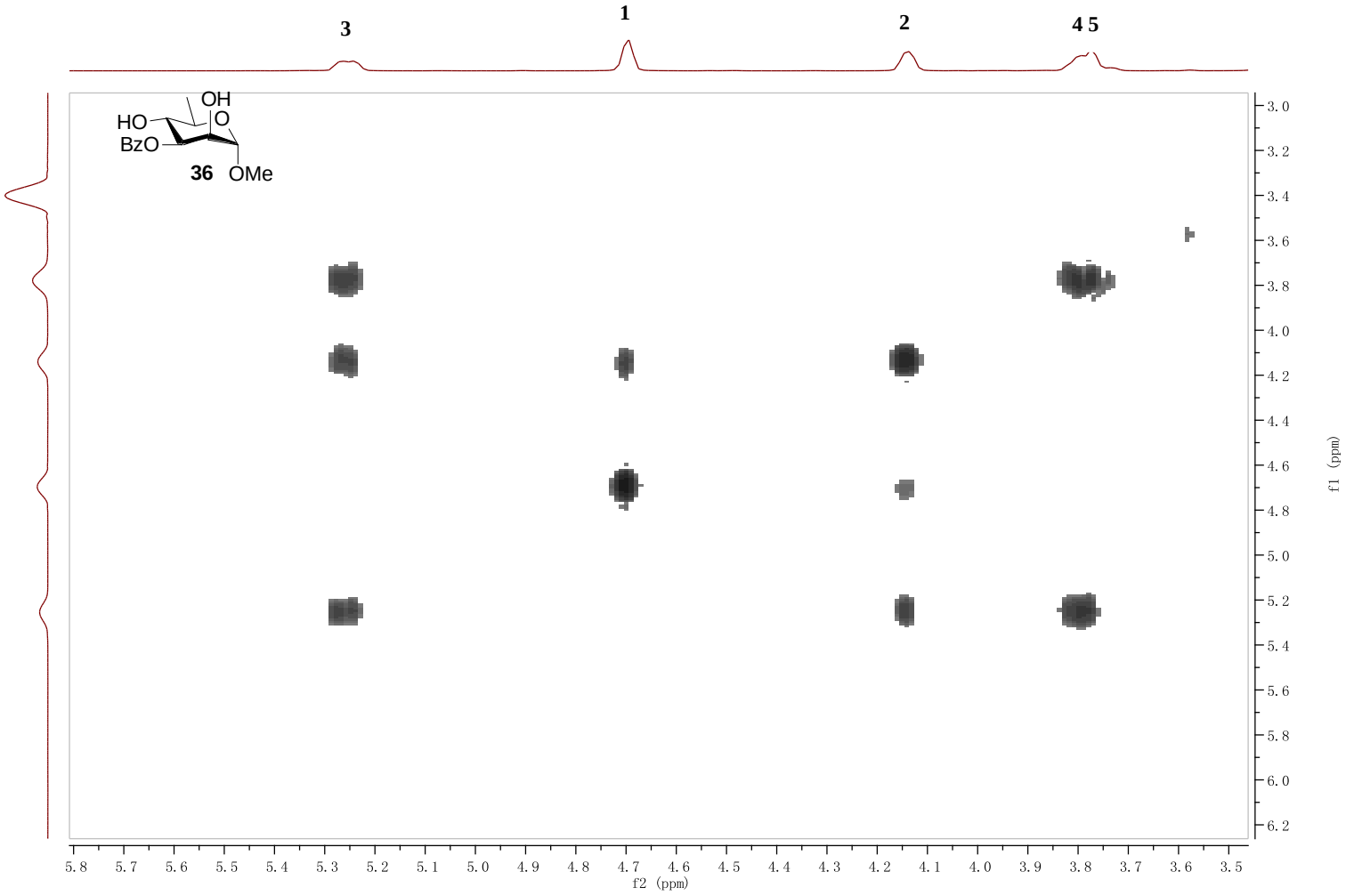
^{1}H-NMR of compound **36** ($CDCl_3$)



^{13}C-NMR of compound **36** ($CDCl_3$)

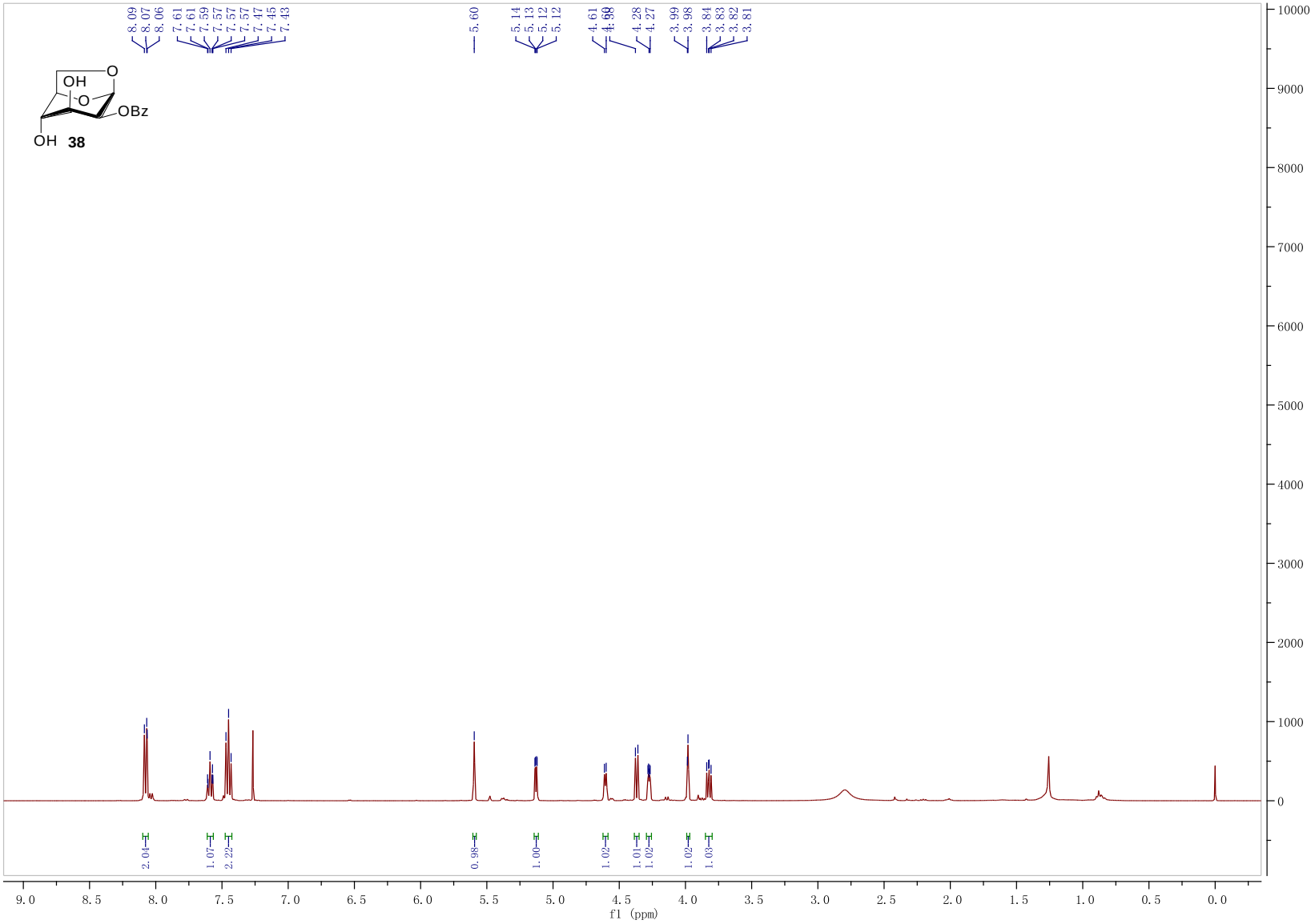


2D-COSY of compound **36** ($CDCl_3$)

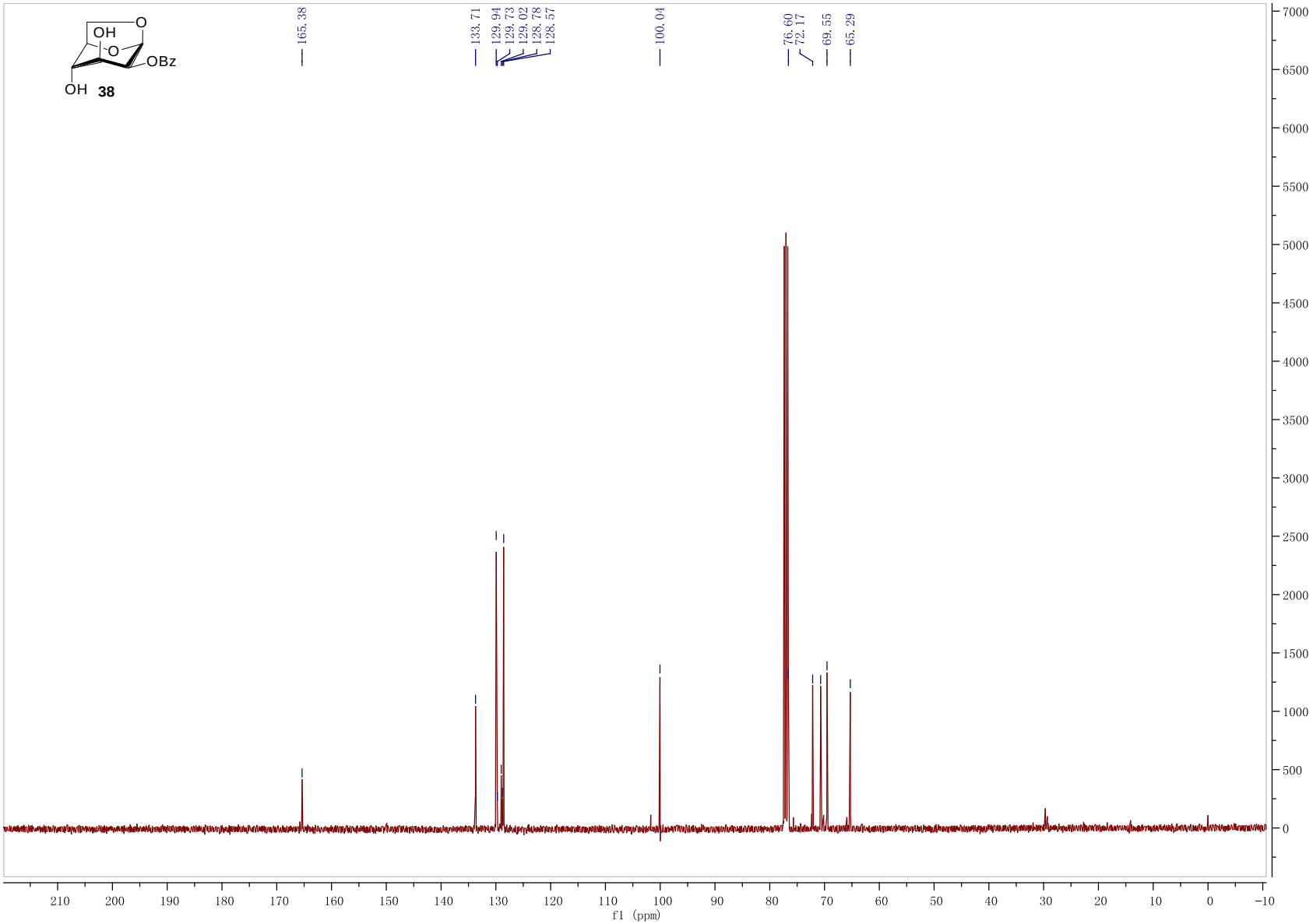


1,6-Anhydro-2-*O*-benzoyl-*β*-D-mannopyranoside (38)

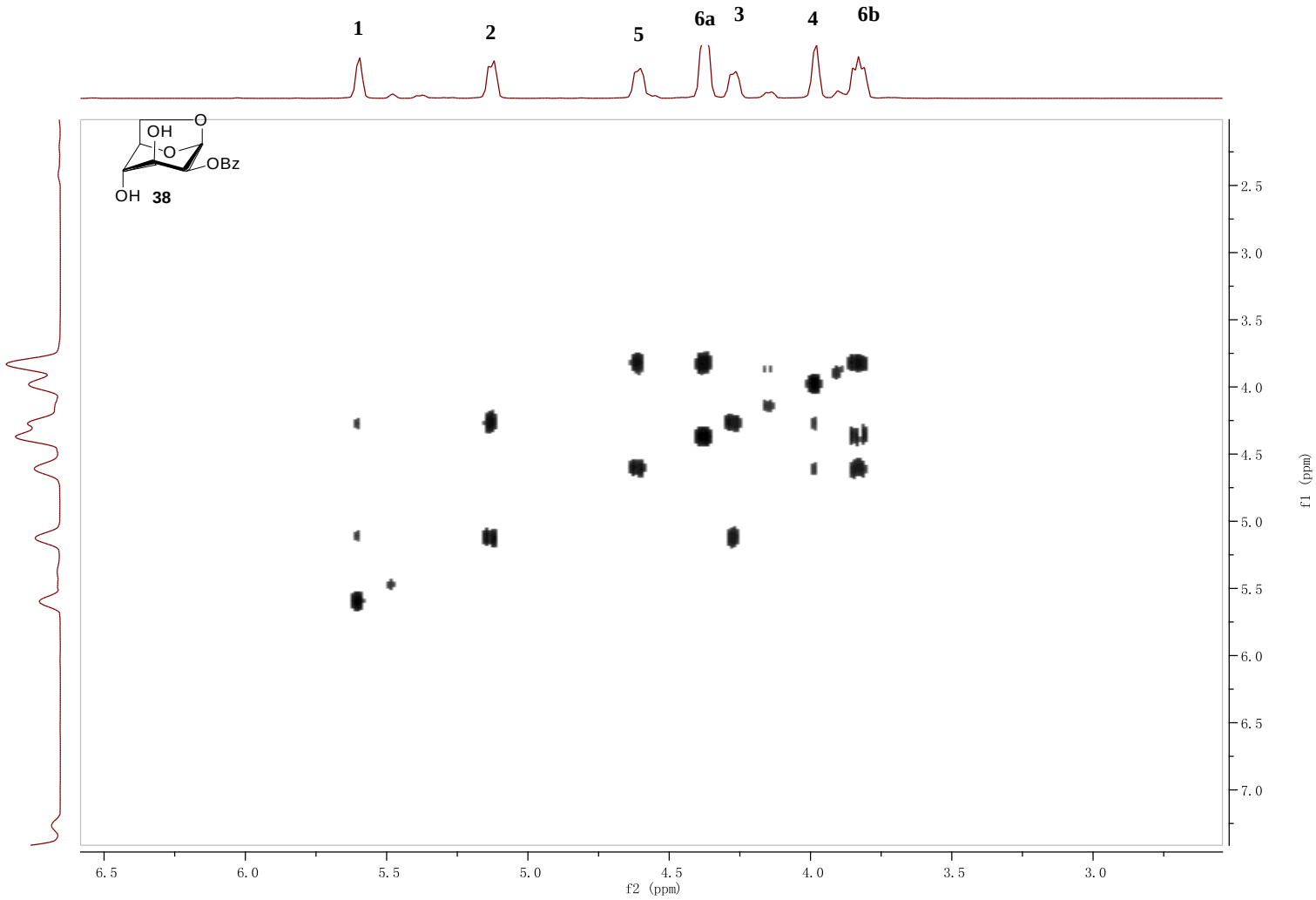
^{1}H-NMR of compound **38** ($CDCl_3$)



^{13}C-NMR of compound **38** ($CDCl_3$)

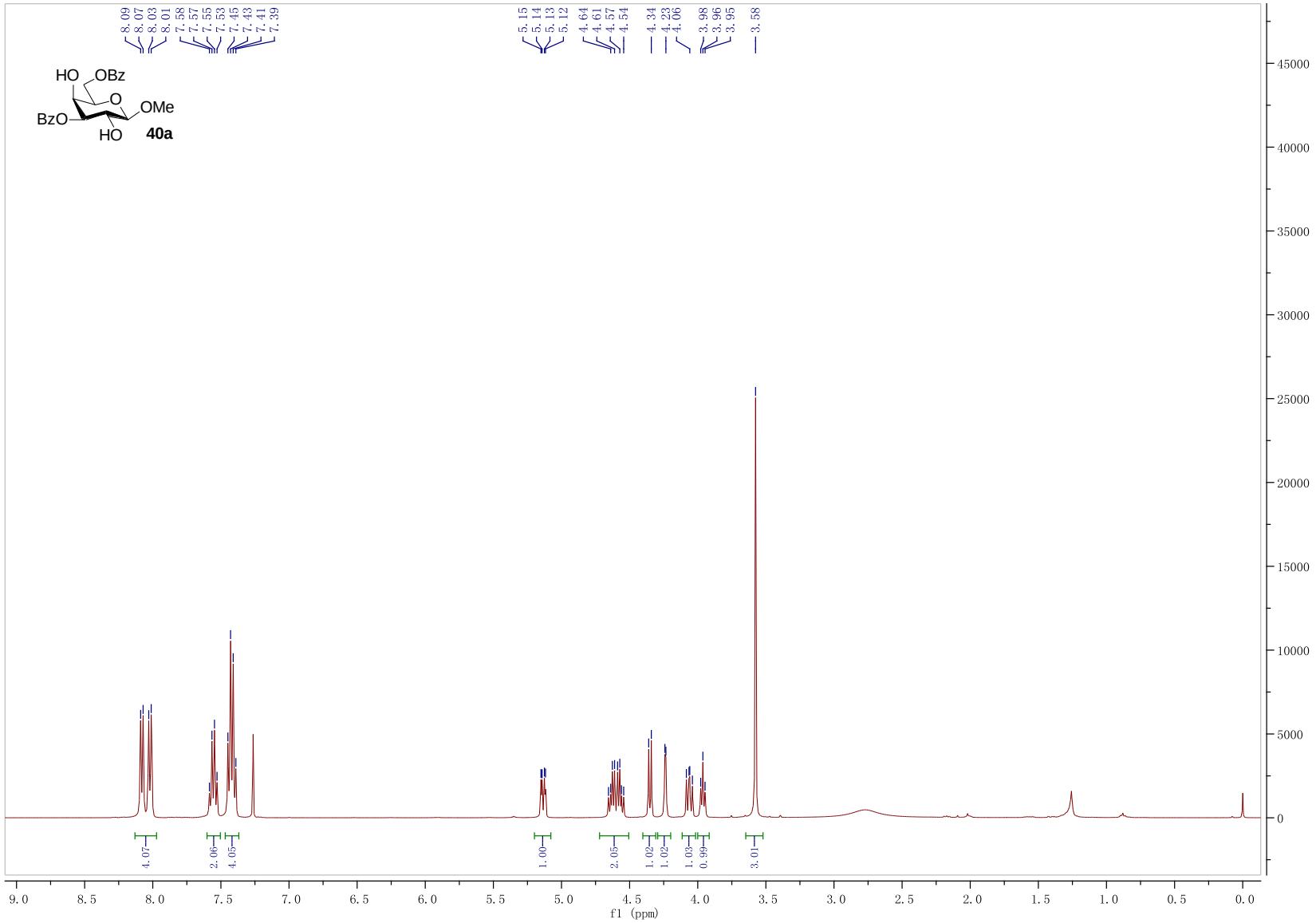


2D-COSY of compound **38** ($CDCl_3$)



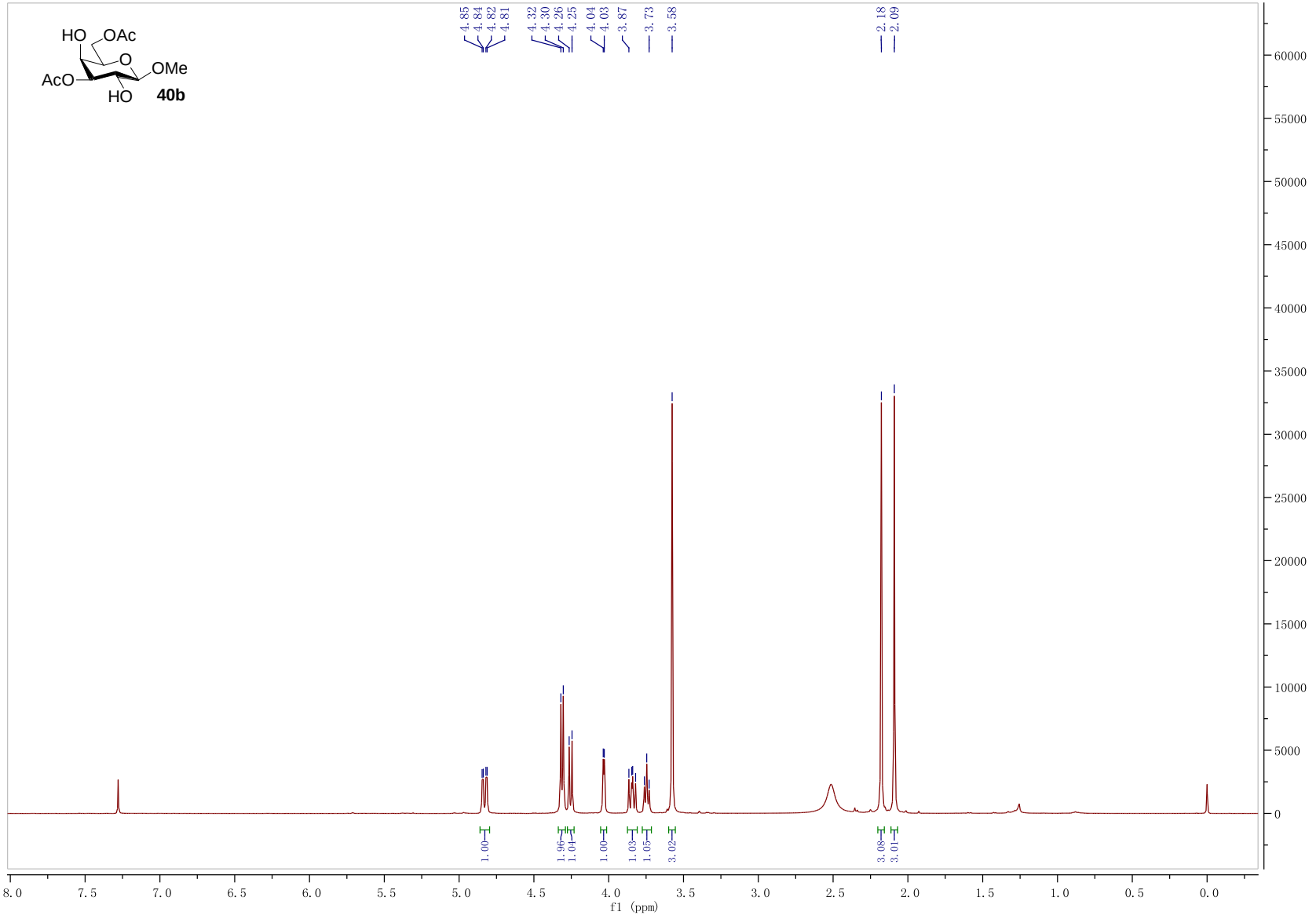
Methyl 3,6-di-*O*-benzoyl-*β*-D-galactopyranoside (40a)

^{1}H-NMR of compound **40a** ($CDCl_3$)



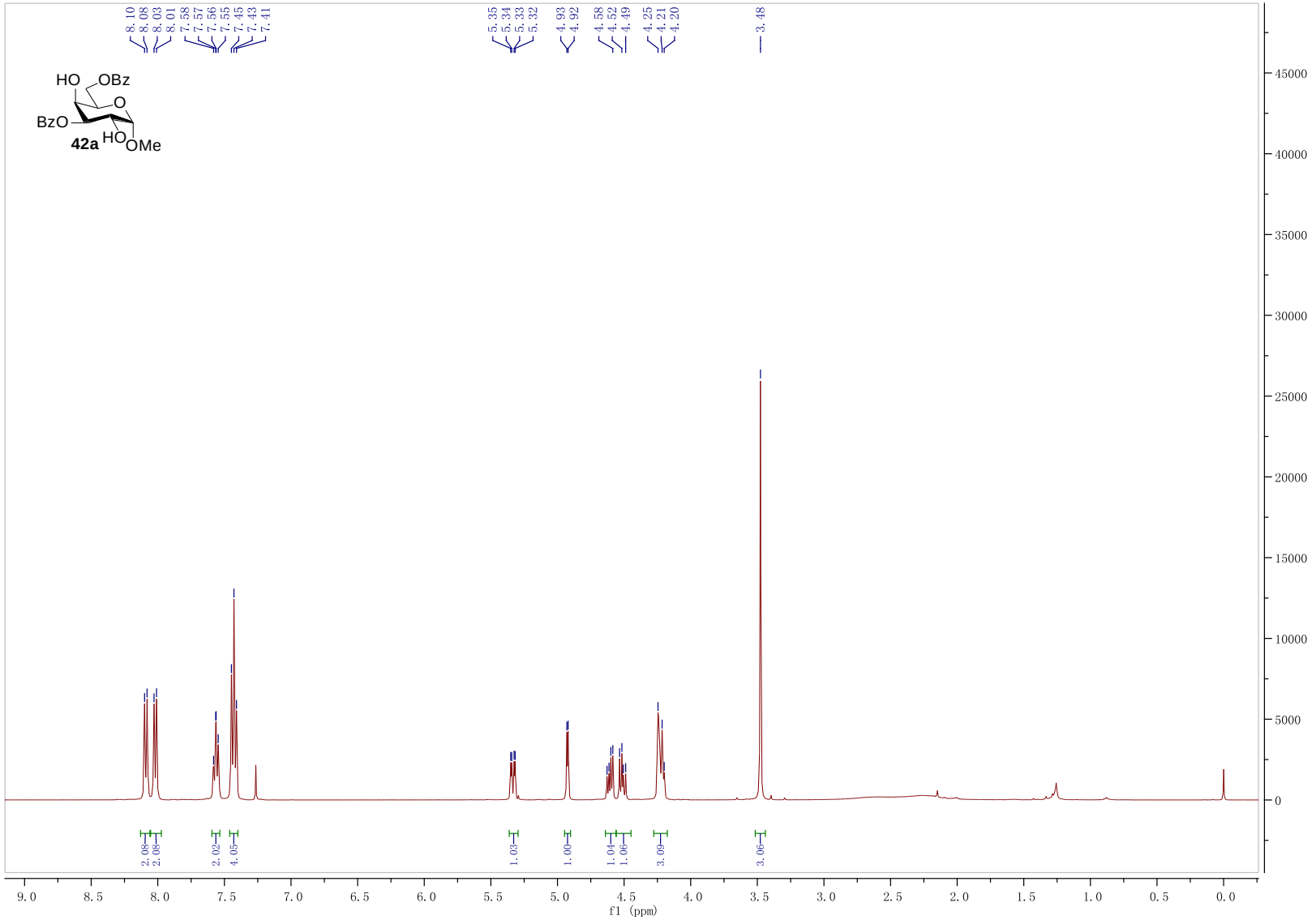
Methyl 3,6-di-*O*-acetyl-*β*-D-galactopyranoside (40b)

^{1}H-NMR of compound **40b** ($CDCl_3$)



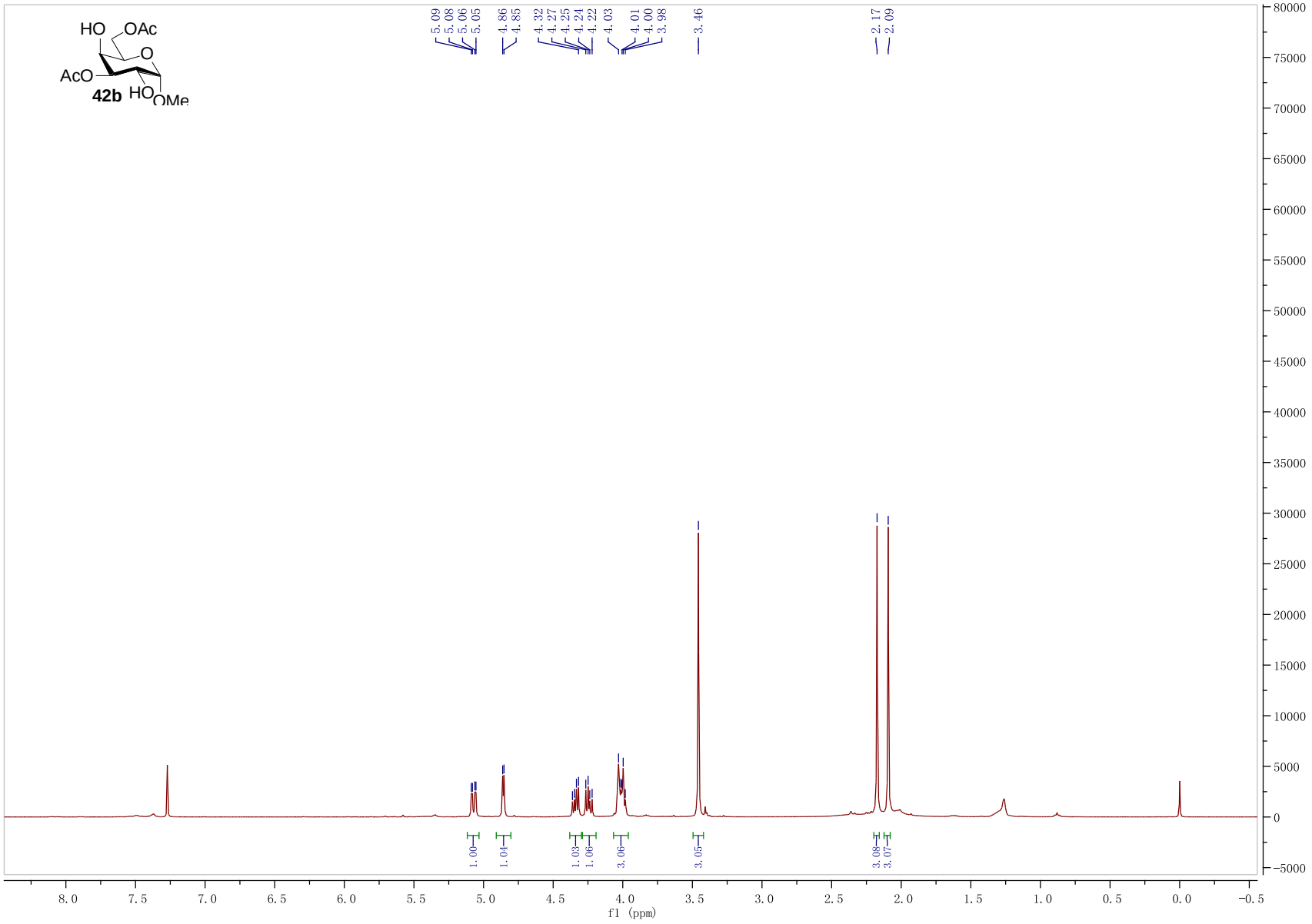
Methyl 3,6-di-*O*-benzoyl-*α*-D-galactopyranoside (42a)

^{1}H-NMR of compound **42a** ($CDCl_3$)



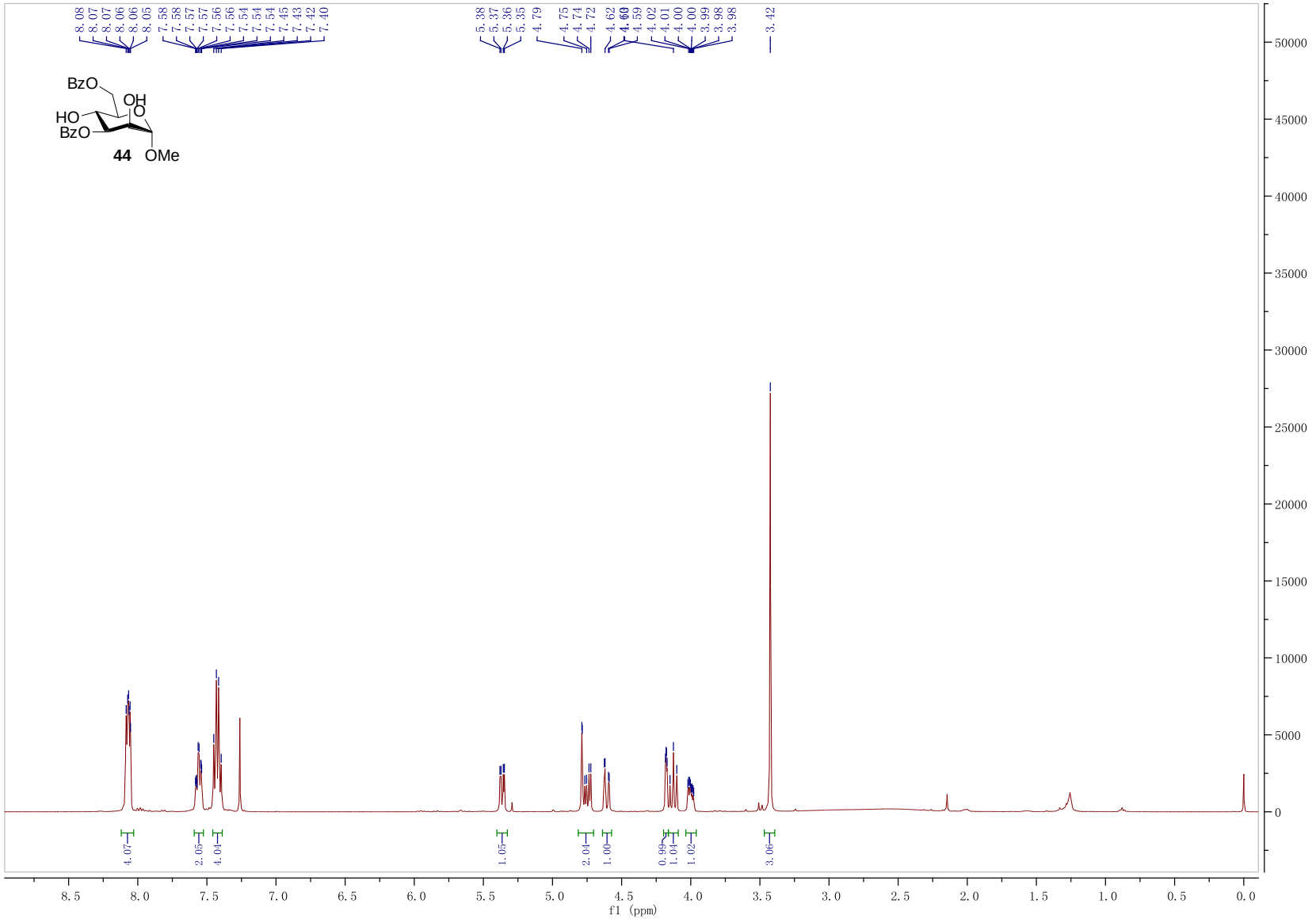
Methyl 3,6-di-*O*-acetyl-*α*-D-galactopyranoside (42b)

^{1}H-NMR of compound **42b** ($CDCl_3$)



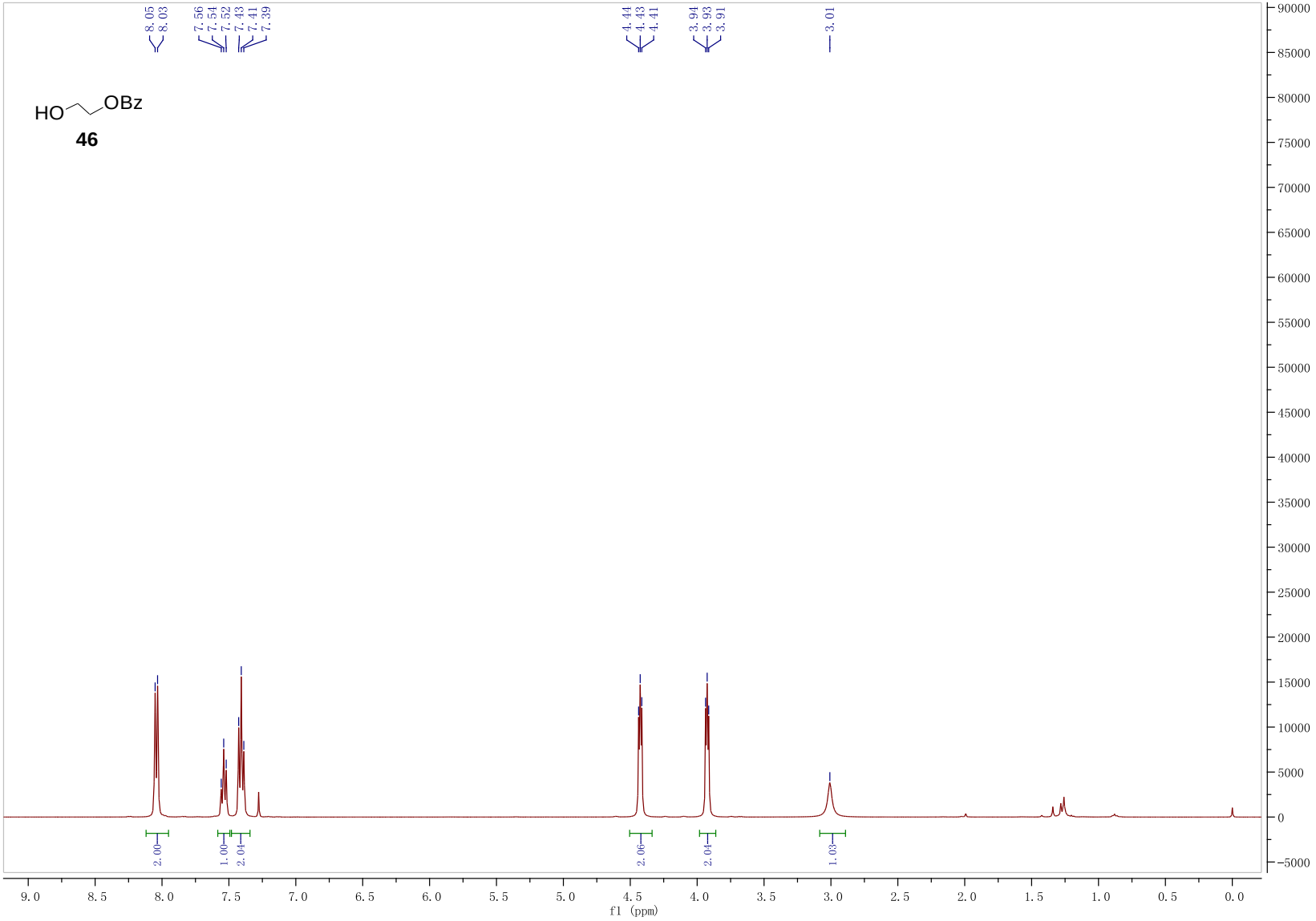
Methyl 3,6-di-*O*-benzoyl-*α*-D-mannopyranoside (44)

^{1}H-NMR of compound **44** ($CDCl_3$)



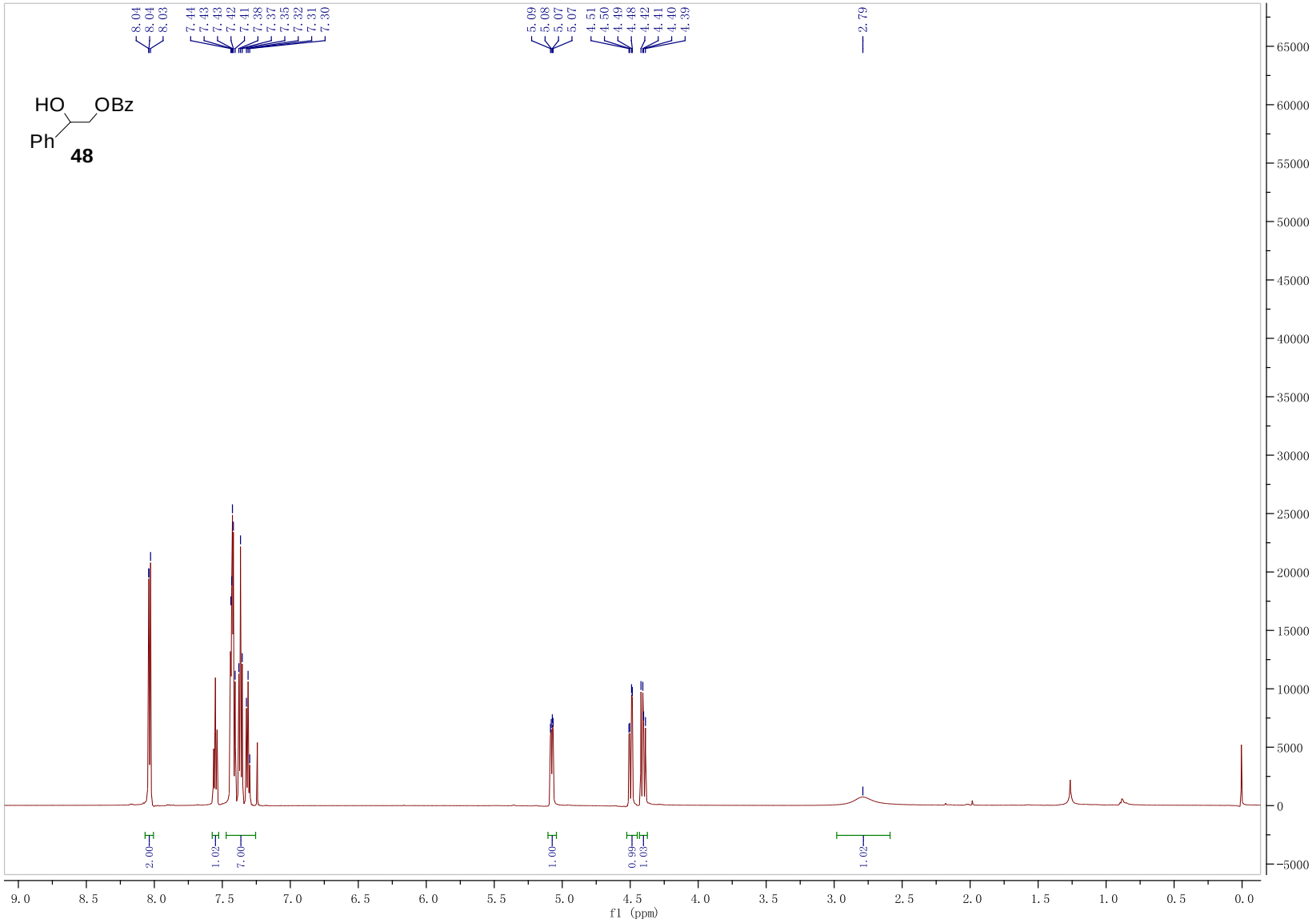
2-Hydroxyethyl benzoate (46)

^{1}H-NMR of compound **46** ($CDCl_3$)



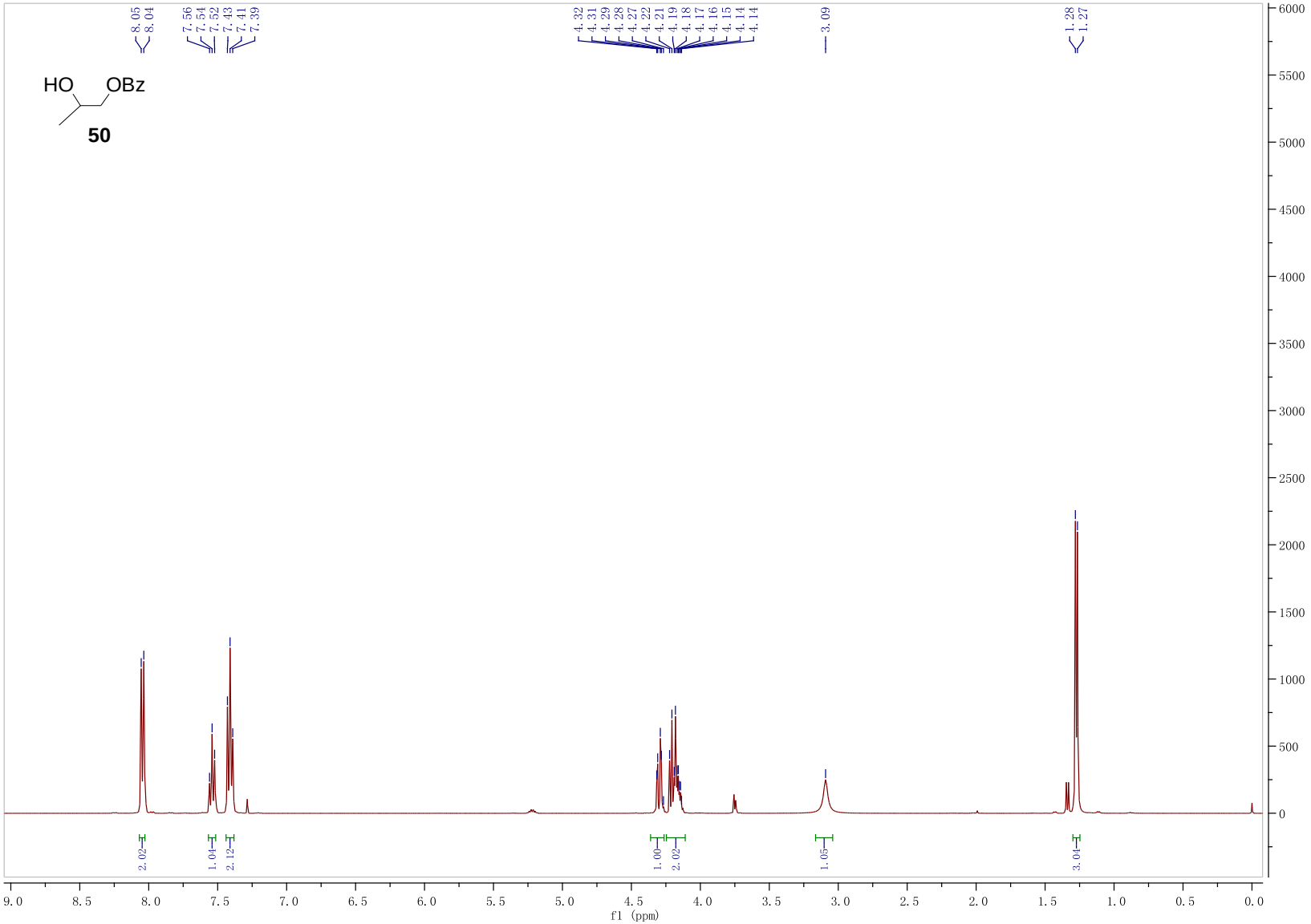
2-Hydroxy-2-phenylethyl benzoate (48)

^{1}H-NMR of compound **48** ($CDCl_3$)



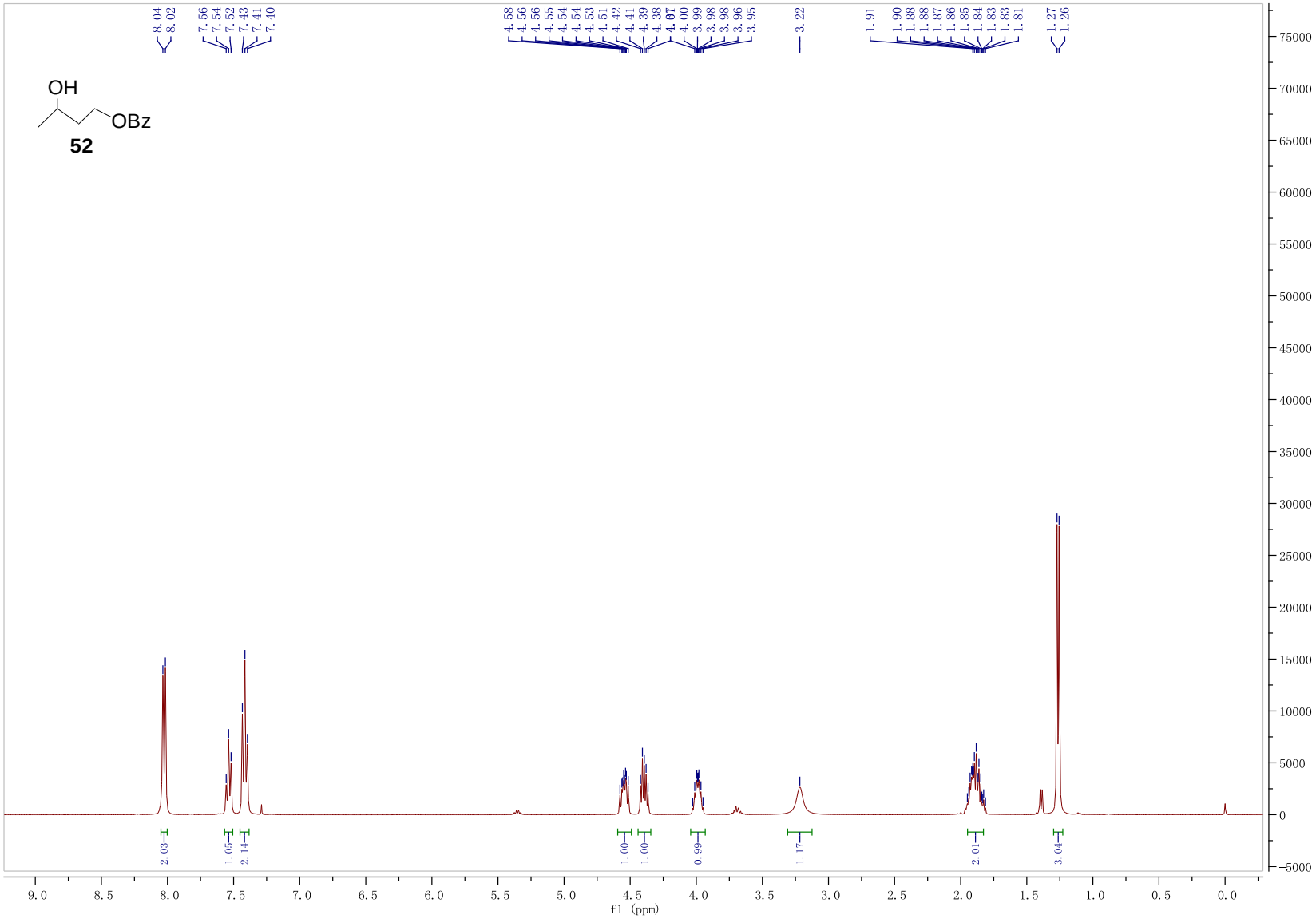
1-*O*-Benzoyl-2-propanol (50)

^{1}H-NMR of compound **50** ($CDCl_3$)



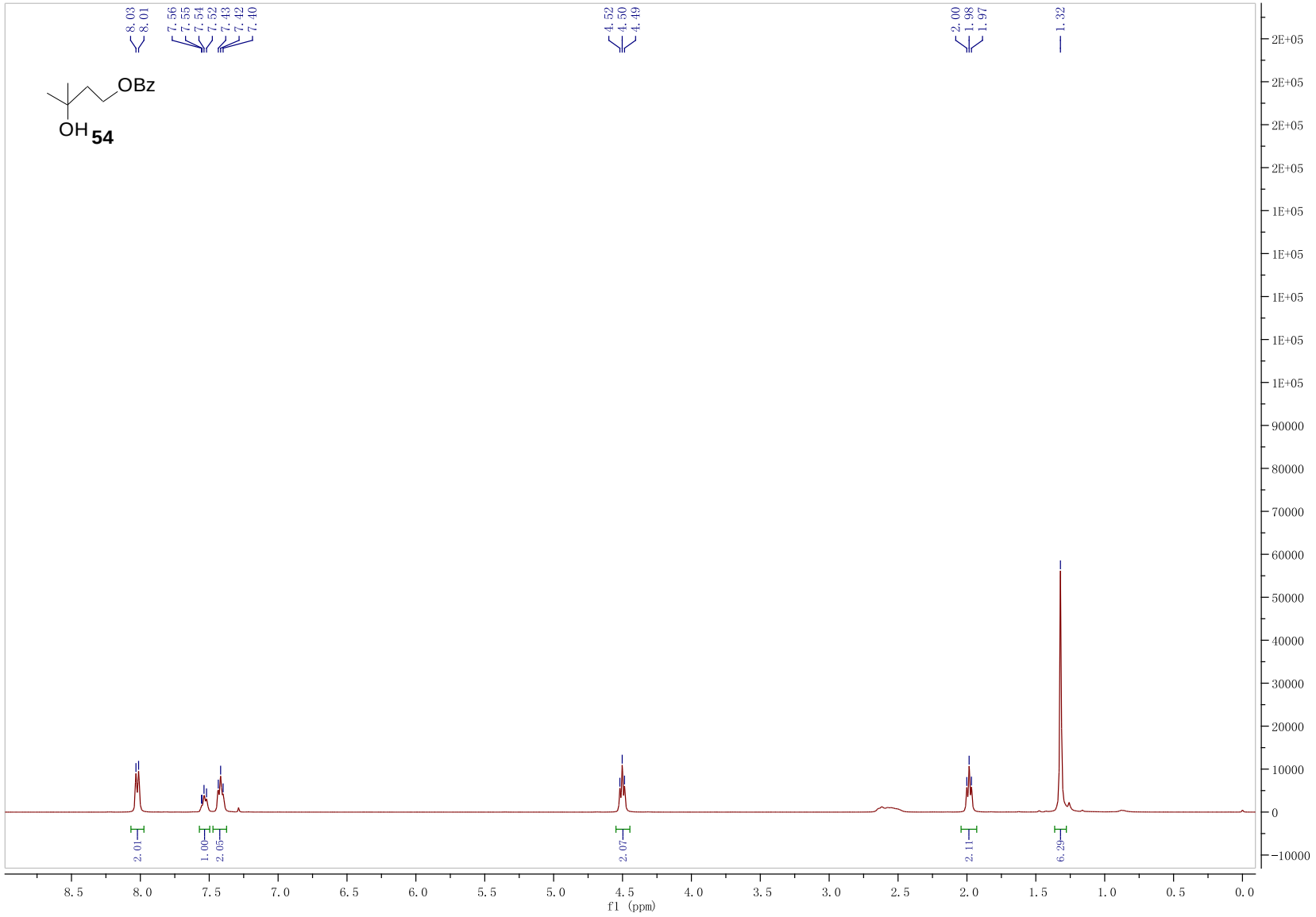
3-Hydroxybutyl benzoate (52)

^{1}H-NMR of compound **52** ($CDCl_3$)



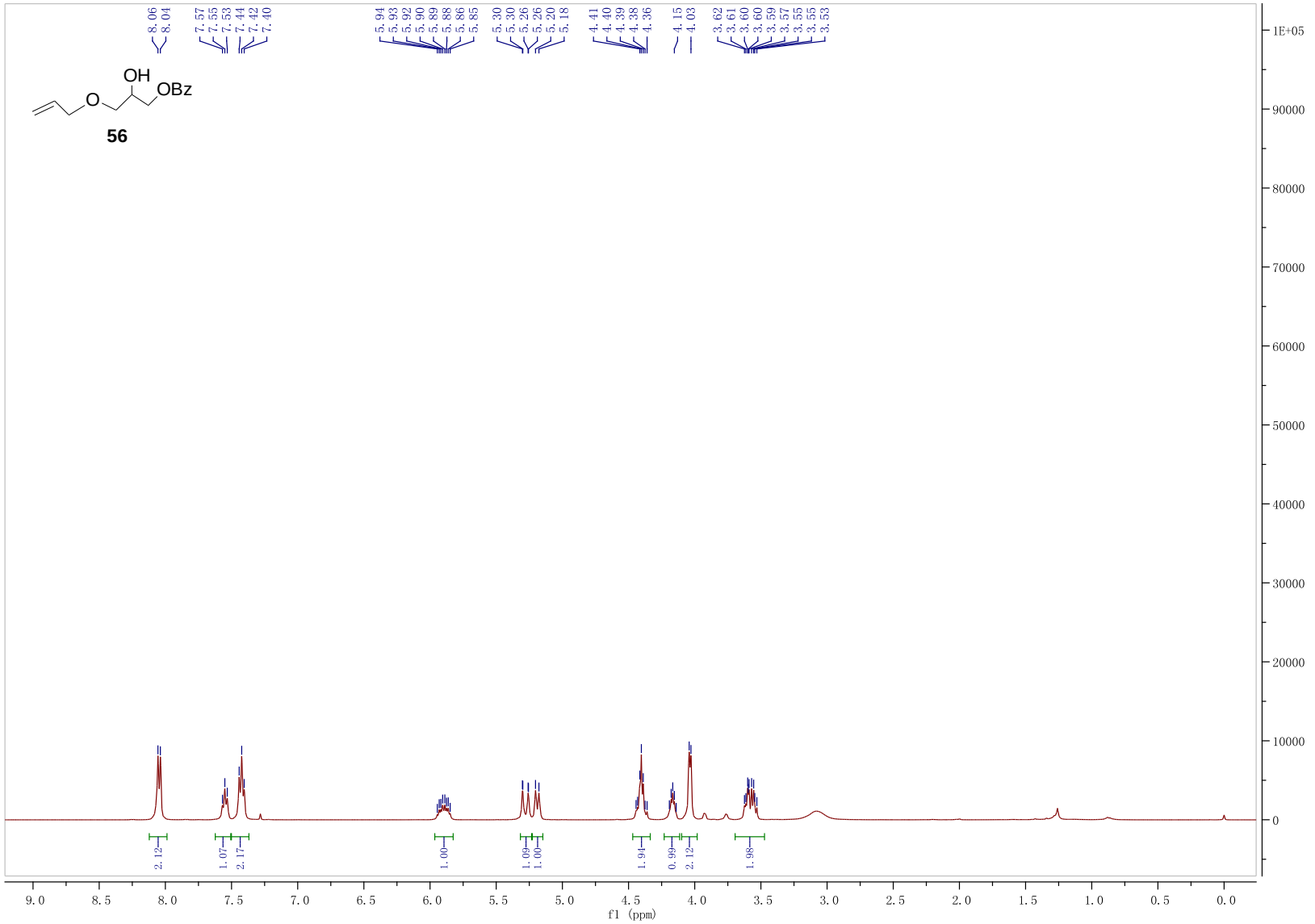
3-Hydroxy-3-methylbutyl benzoate (54)

^{1}H-NMR of compound **54** ($CDCl_3$)



2-Hydroxy-3-allyloxypropyl benzoate (56)

^{1}H-NMR of compound **56** ($CDCl_3$)



3-Phenoxypropyl benzoate (58)

^{1}H-NMR of compound **58** ($CDCl_3$)