Supporting Information

Stannous Chloride as a Low-toxic and Extremely Cheap Catalyst for Regio/Site-Selective Acylation with Unusually Broad Substrate Scope

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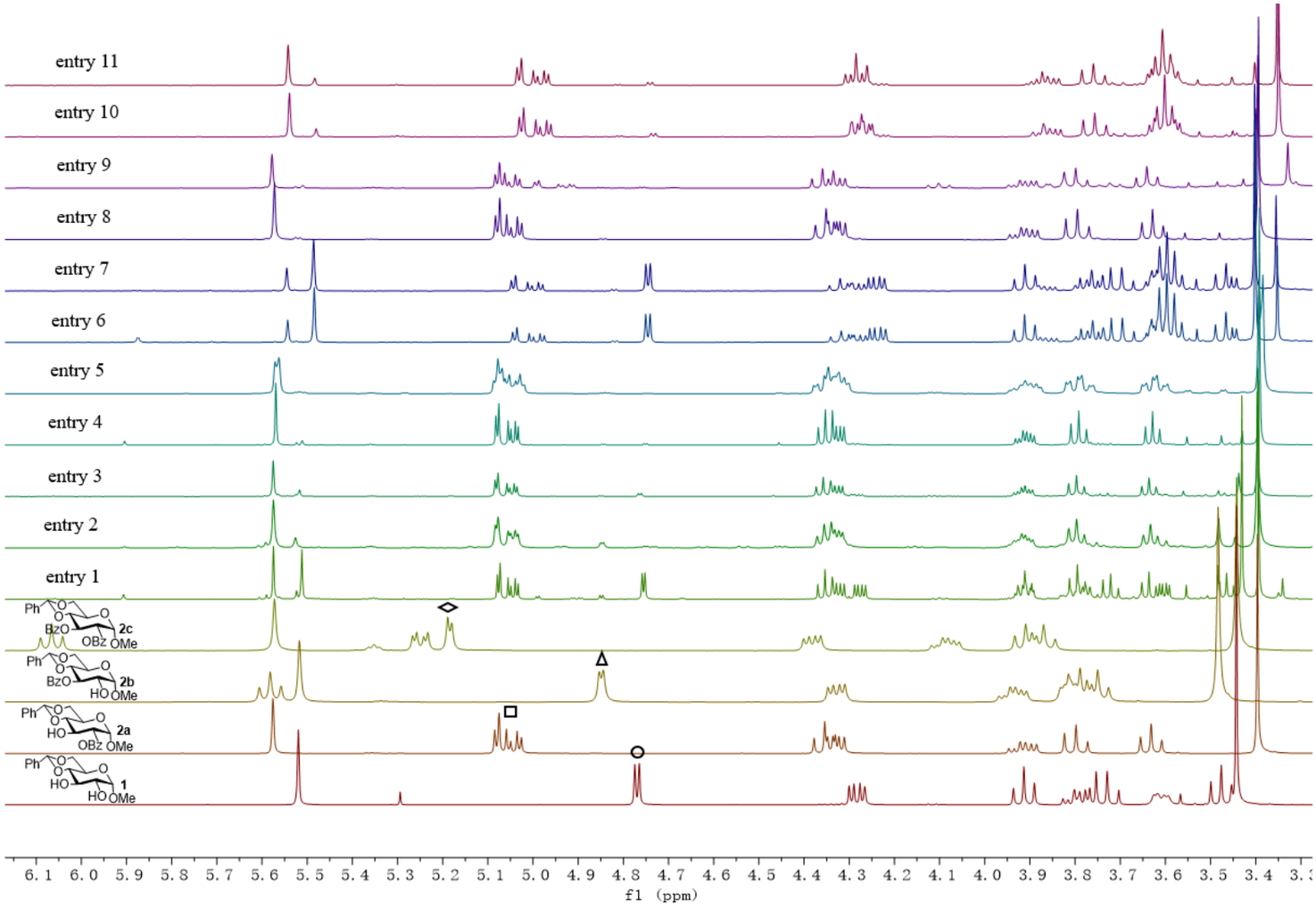
Contents

1. Experimental methods

General: all chemicals were purchased as reagent grade and used without further purification. The solvents were purified before use and CH_3CN was distilled over CaH_2. Chemical reactions were monitored by thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). Spots were visualized by UV light (254 nm) then by charring with a solution of H_2SO_4 (5%) in ethanol. ^1H NMR spectra were recorded by 400 MHz or 600 MHz (^1H) and 100 MHz (^{13}C) at 298K in $CDCl_3$ or CD_3CN using the residual signals from $CDCl_3$ (^1H: δ = 7.26 ppm; ^{13}C: δ = 77.16 ppm) and CD_3CN (^1H: δ = 1.94 ppm; ^{13}C: δ = 118.26 ppm) as internal standard. ^1H peak assignments were made by first order analysis of the spectra, supported by standard ^1H-^1H correlation spectroscopy (COSY). High-resolution mass spectra (HRMS) were obtained by TOF detection.

General procedure for the acylation of substrates: the substrate (0.1 - 0.2 mmol), $SnCl_2$ (0.05 equiv) and *N*,*N*-diisopropylethylamine (DIPEA) (1.2 - 2.5 equiv) were mixed in dry acetonitrile (0.5 - 1.0 mL). Then, acyl chloride (1.2 - 2.5 equiv) was added to the mixture. After stirring vigorously at room temperature for 0.5 - 2 hours, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography, affording the pure selectively protected derivatives.

Large-scale procedure for the benzoylation of substrates 19b and 23: the substrate (**19b**: 1.0 g, 2.3 mmol; **23**: 580 mg, 1.88 mmol), $SnCl_2$ (**19b**: 4.5 mg; **23**: 3.6 mg, 0.01 equiv) and *N*,*N*-diisopropylethylamine (DIPEA) (**19b**: 615 μL; **23**: 500 μL, 1.5 equiv) were mixed in dry acetonitrile (10.0 mL). Then, benzoyl chloride (**19b**: 405 μL; **23**: 330 μL, 1.5 equiv) was added to the mixture. After stirring vigorously at room temperature for 1 hour, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography, affording the pure selectively protected products **20b** as white solid (1.028 g, 83%) and **24** as colorless syrup (722 mg, 93%).



2. Figure S1a. ^{1}H-NMR spectra of crude reaction mixtures for Table 1.

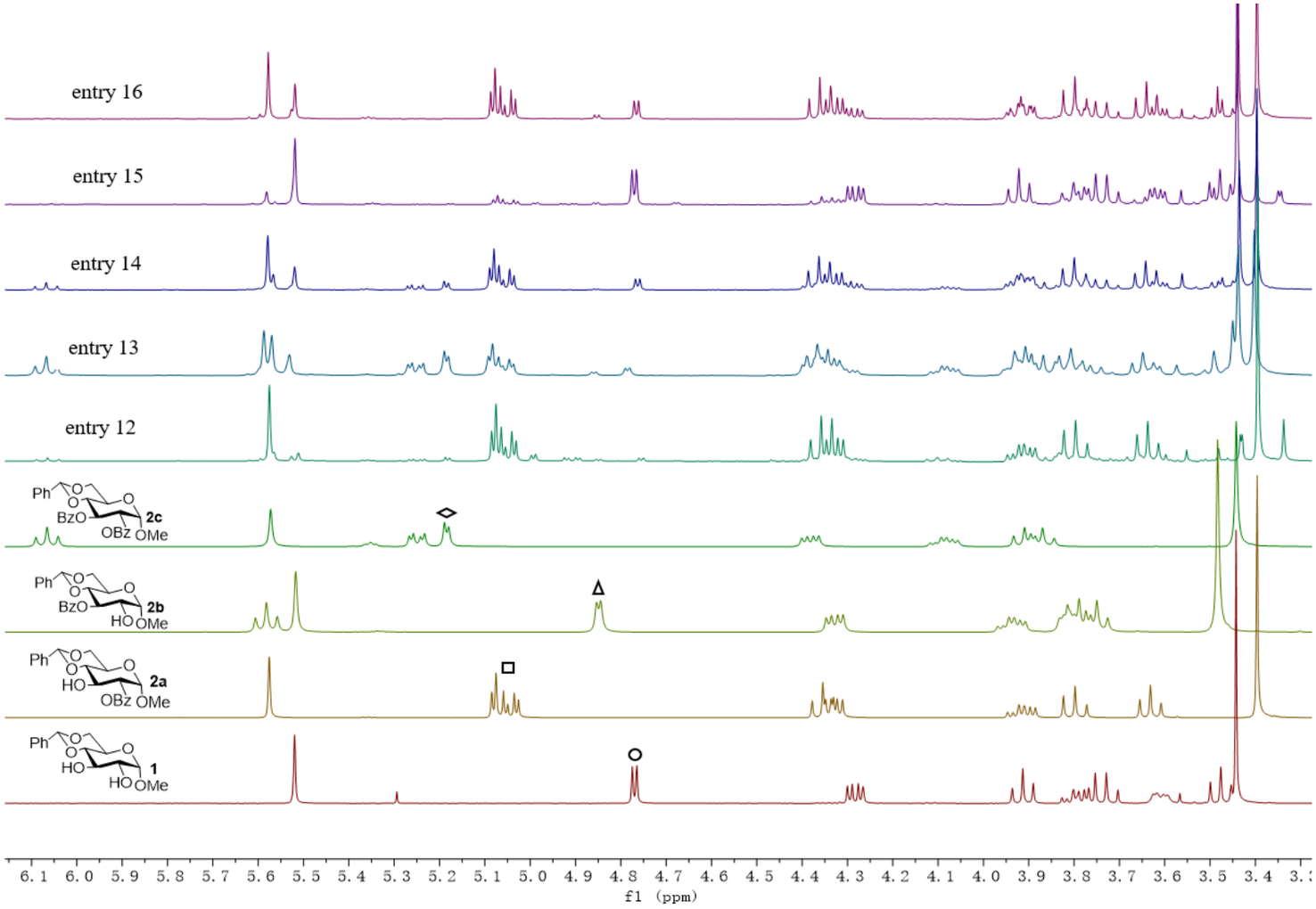


Figure S1b. ^{1}H-NMR spectra of crude reaction mixtures with various bases for Table 1.

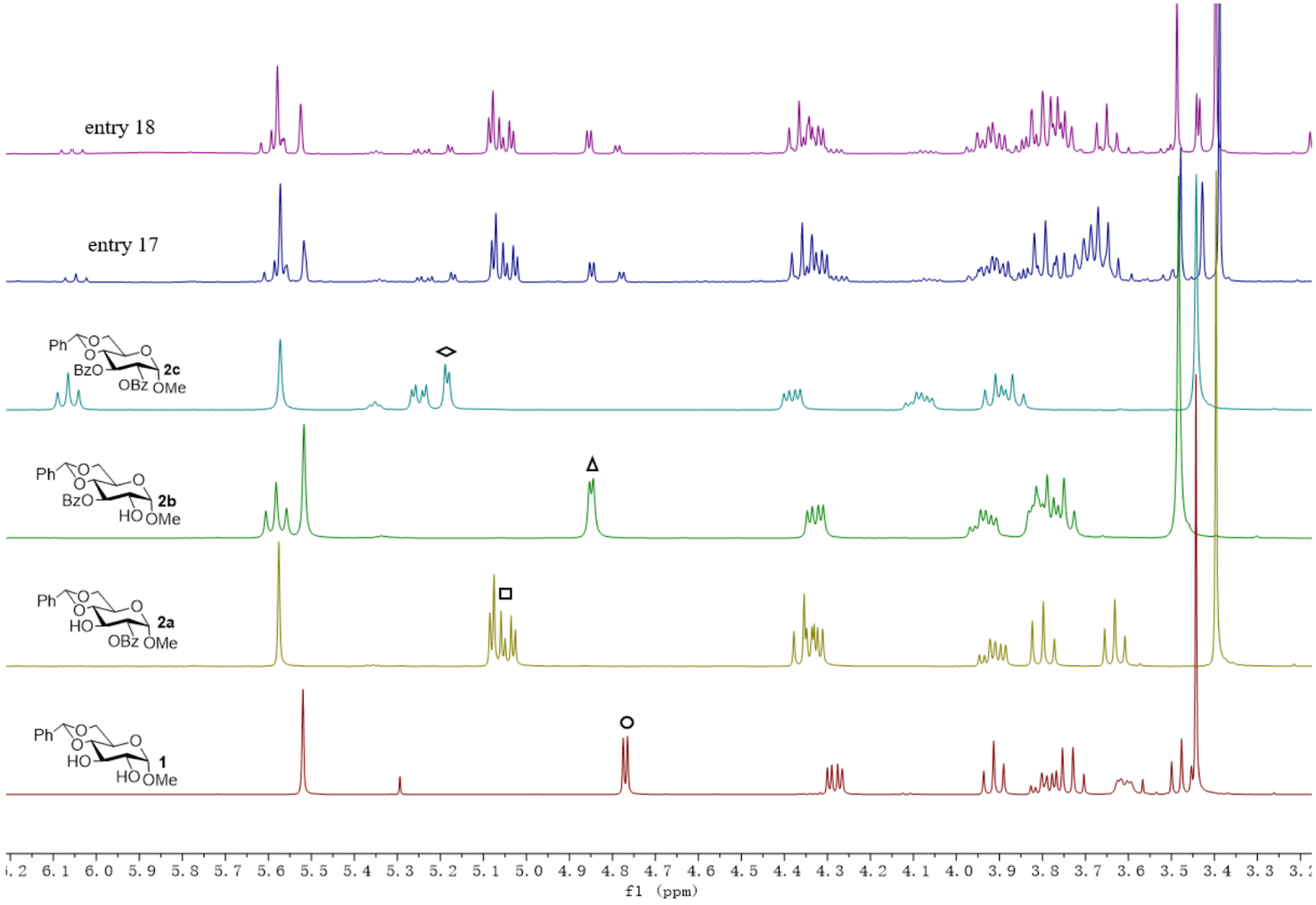


Figure S1c. ^{1}H-NMR spectra of crude reaction mixtures with Bz_2O instead of BzCl for Table 1.

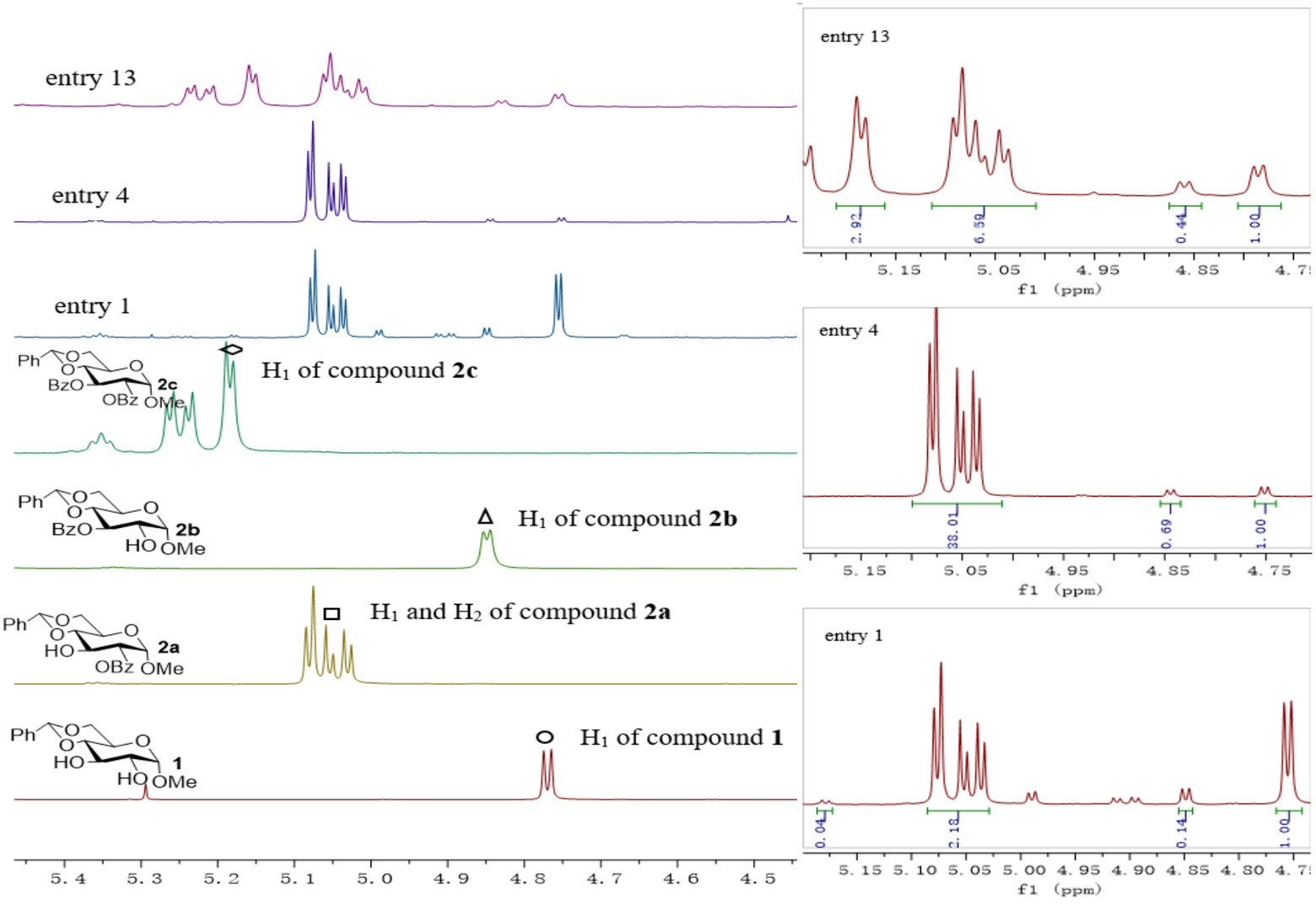
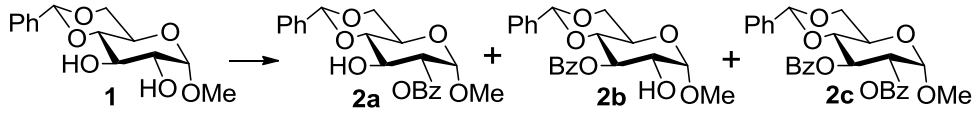


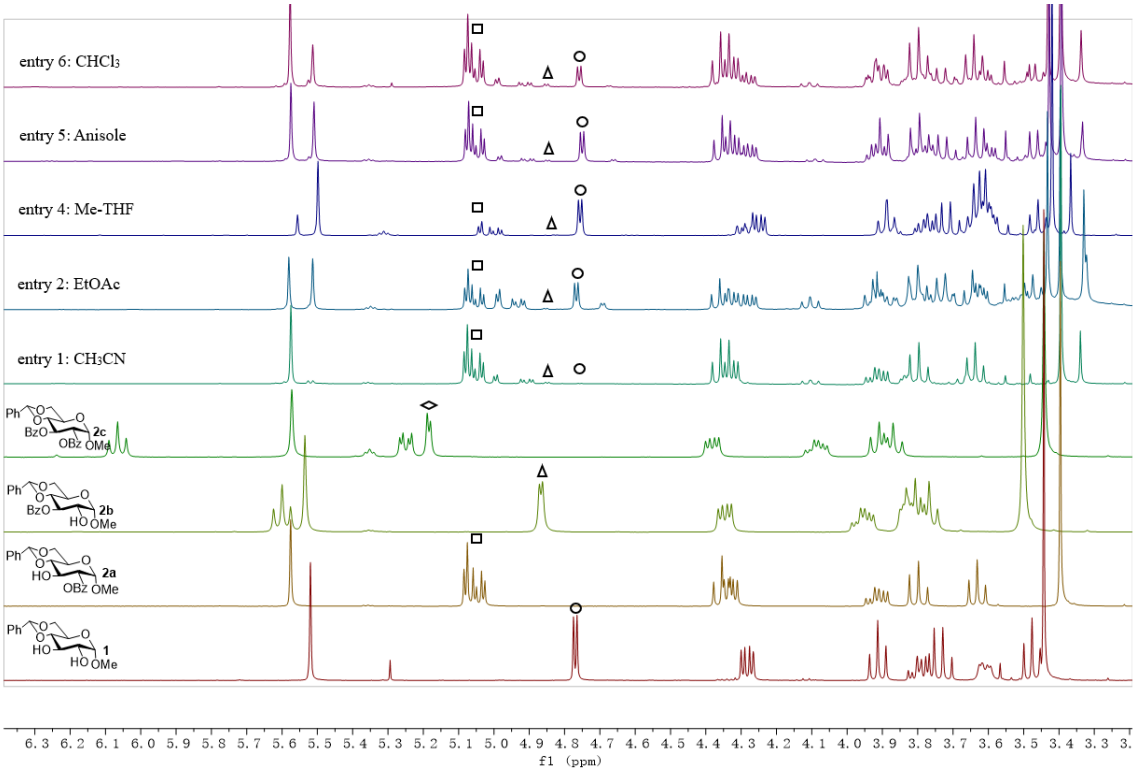
Figure S1d. Example of calculation the NMR ratio for Table 1. NMR yields was calculated in light of the ratio of the integral peak area: for example for entry **1**, H_1 and H_2 of compound **2a**/H_1 of compound **2b**/H_1 of compound **2c**/ H_1 of compound **1** = 2.18/0.14/0.04/1.00, indicating that the NMR ratio: **2a**/**2b**/**2c**/**1** = (2.18/2)/0.14/0.04/1.00 = 1.09/0.14/0.04/1.00 = 48%/6%/2%/44%.

3. Table S1. Evaluation of solvents for selective acylation of substrate 1[a]

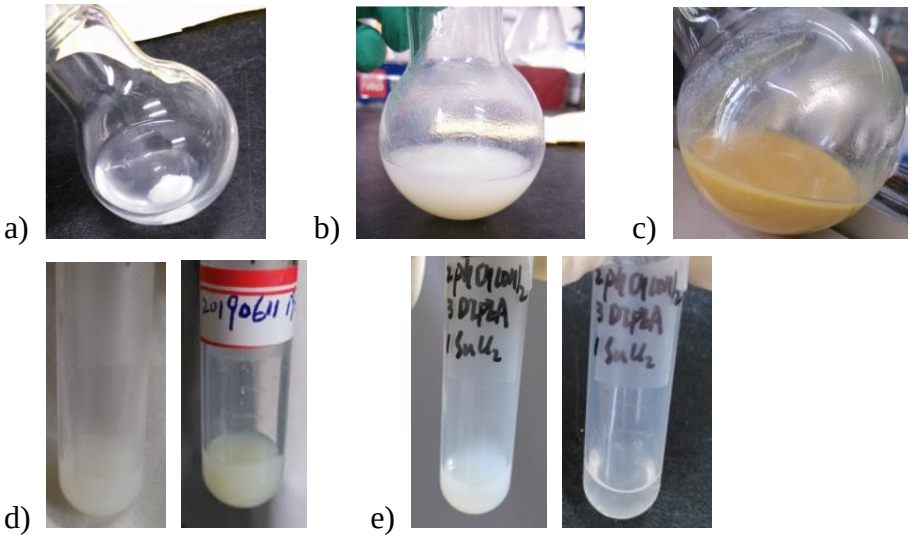


Entry	Solvent	Ratio[b] 2a/2b/ 2c/1
1	CH_3CN,1h	95/4/0/1
2	EtOAc, 4h	51/2/0/46
3	THF, 4h	<5/-/-/>95[c]
4	Me-THF, 4h	21/2/0/77
5	Anisole, 4h	60/2/0/38
6	$CHCl_3$, 4h	68/5/0/27
7	1,4-dioxane, 4h	<5/-/-/>95[c]

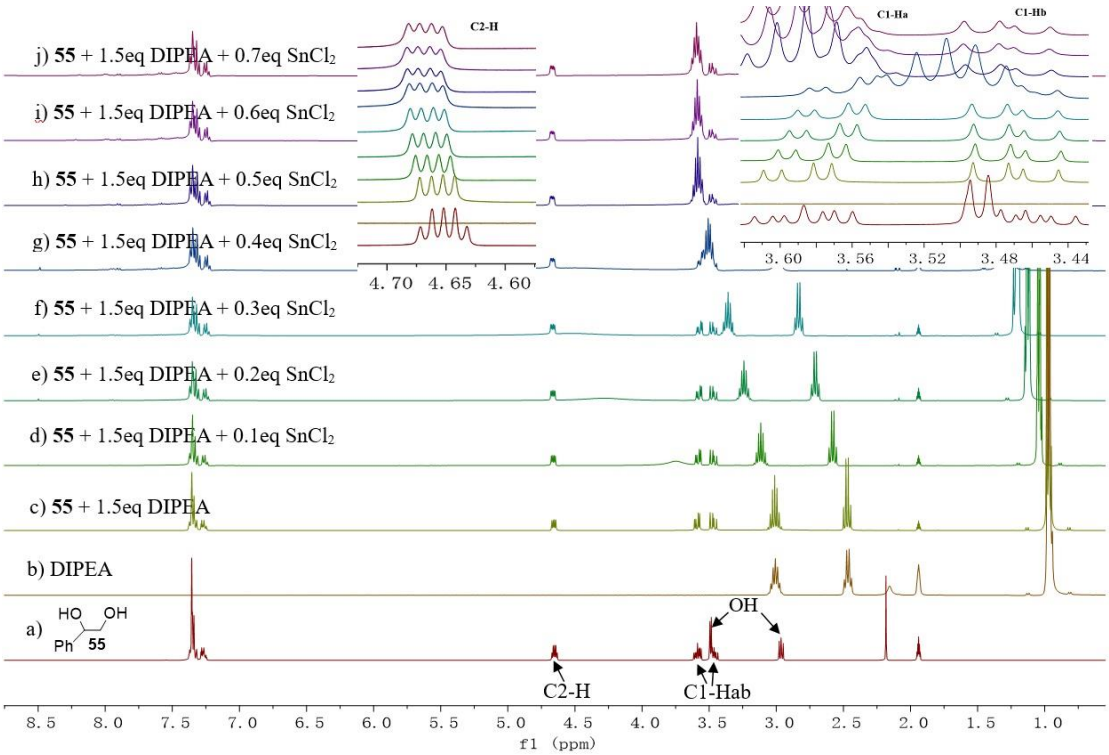
Reaction conditions: [a]Substrate **1** (0.1mmoL), DIPEA (1.5 equiv.), $SnCl_2$ (0.05 equiv.), BzCl (1.2 equiv.), solvent (0.5mL), r.t. [b]Ratios determined by ^{1}H NMR. [c]Ratios monitored by TLC.



4. Figure S2. ^{1}H-NMR spectra of crude reaction mixtures for Table S1.

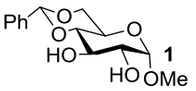
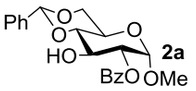
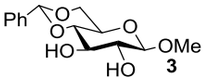
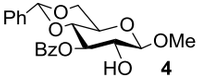
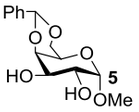
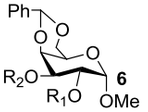
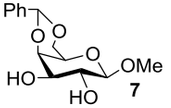
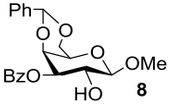
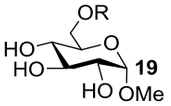
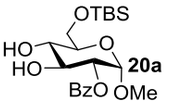
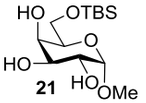
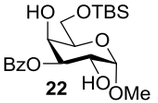
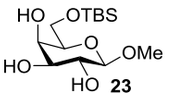
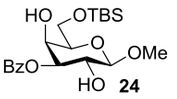
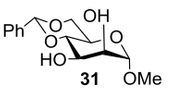
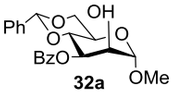
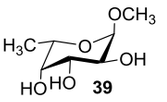
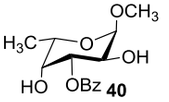
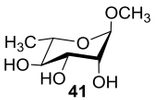
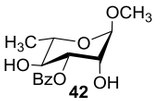


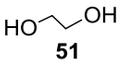
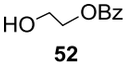
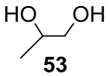
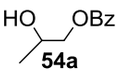
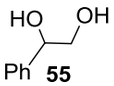
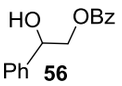
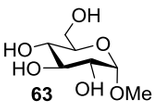
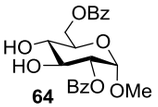
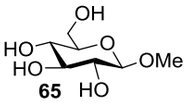
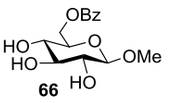
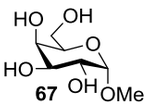
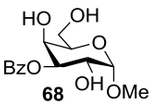
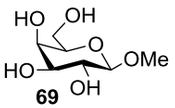
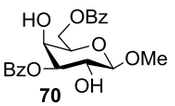
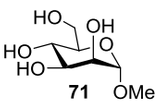
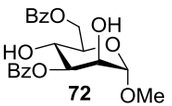
5. Figure S3. a) $SnCl_2$ (5.0 mmol) was mixed in acetonitrile (10 mL) and shaken; b) 2.5 equiv of DIPEA was added to a) and shaken slightly; c) the mixture was stirred for 10 min at rt; d) left: $SnCl_2$ and DIPEA (3.0 equiv) were mixed in acetonitrile; right: after holding for 48 h, e) left: $SnCl_2$, DIPEA (3.0 equiv) and phenylglycol (5.0 equiv) were mixed in acetonitrile; right: turned into a clear solution after holding for 4 h.



6. Figure S4. ^{1}H-NMR spectrum of compound **55** with the addition of $SnCl_2$ (from 0.1 equiv to 0.7 equiv) in the presence of 1.5 equiv of DIPEA in CD_3CN. The proton connecting C-1^o shifted to upfield and the proton connecting C-2^o shifted to downfield slightly with the addition of $SnCl_2$.

7. Table S2 Comparison of $SnCl_2$ with various reagents which are applicable to both substrates containing *cis*-diol and substrates containing *trans*-diol.

Entry	Substrate	Product	Yields ($SnCl_2$)	Yields (organotin) (stoich. amount)	Yields (organotin) (cat. amount)	Yields[8] (**fig. 1d**)	Yields[9] (**fig. 1d**)
1			92%	72%-100%[1]	92%[2]	85%	83%
2			poor	39%[3]		71%	-
3			95%, 2-OBz/3-OBz = 1.8/1	-	-	2-OBz/3-OBz = 1/1.4-2.5/1	-
4			86%	-	-	81%	-
5			83%	-	-	-	84%
6			90%	-	-	-	83%
7			95%	-	-	-	80%
8			75%	90%[1c]	-	87%	-
9			90%	-	-	-	-
10			94%	100%[1c]	-	-	94%

11	 **51**	 **52**	81%		100%[2]	-	-
12	 **53**	 **54a**	83%	67%[4]	-	-	-
13	 **55**	 **56**	84%	77%[4]	90%[2]	-	-
14	 **63**	 **64**	78%	95%[5]	-	-	-
15	 **65**	 **66**	62%	86%[6]	79%[7]	-	-
16	 **67**	 **68**	71%		84%[7]	-	-
17	 **69**	 **70**	94%	95%[5]	-	-	-
18	 **71**	 **72**	89%	90%[5]	-	-	-

1 (a) G.-J. Boons, G. H. Castle, J. A. Clase, P. Grice, S. V. Ley and C. Pinel, *Synlett*, 1993, 913; (b) G.-J. Boons, G. H. Castle, J. A. Clase, P. Grice, S. V. Ley and C. Pinel, *Synlett*, 1994, 764; (c) C. W. Holzapfel, J. M. Koekemoer and C. F. Marais, *S. Afr. J. Chem.*, 1984, **37**, 19; (d) S. David and A. Thiéffry, *J. Chem. Soc., Perkin Trans.* Ⅰ 1979, 1568; (e) D. J. Jenkins and B. V. L. Potter, *Carbohydr. Res.*, 1994, **265**, 145; (f) R. M. Manavu and H. H. Szmant, *J. Org. Chem.*, 1976, **41**, 1832.

2 T. Maki, F. lwasaki and Y. Matsumura, *Tetrahedron. Lett.*, 1998, **39**, 5601.

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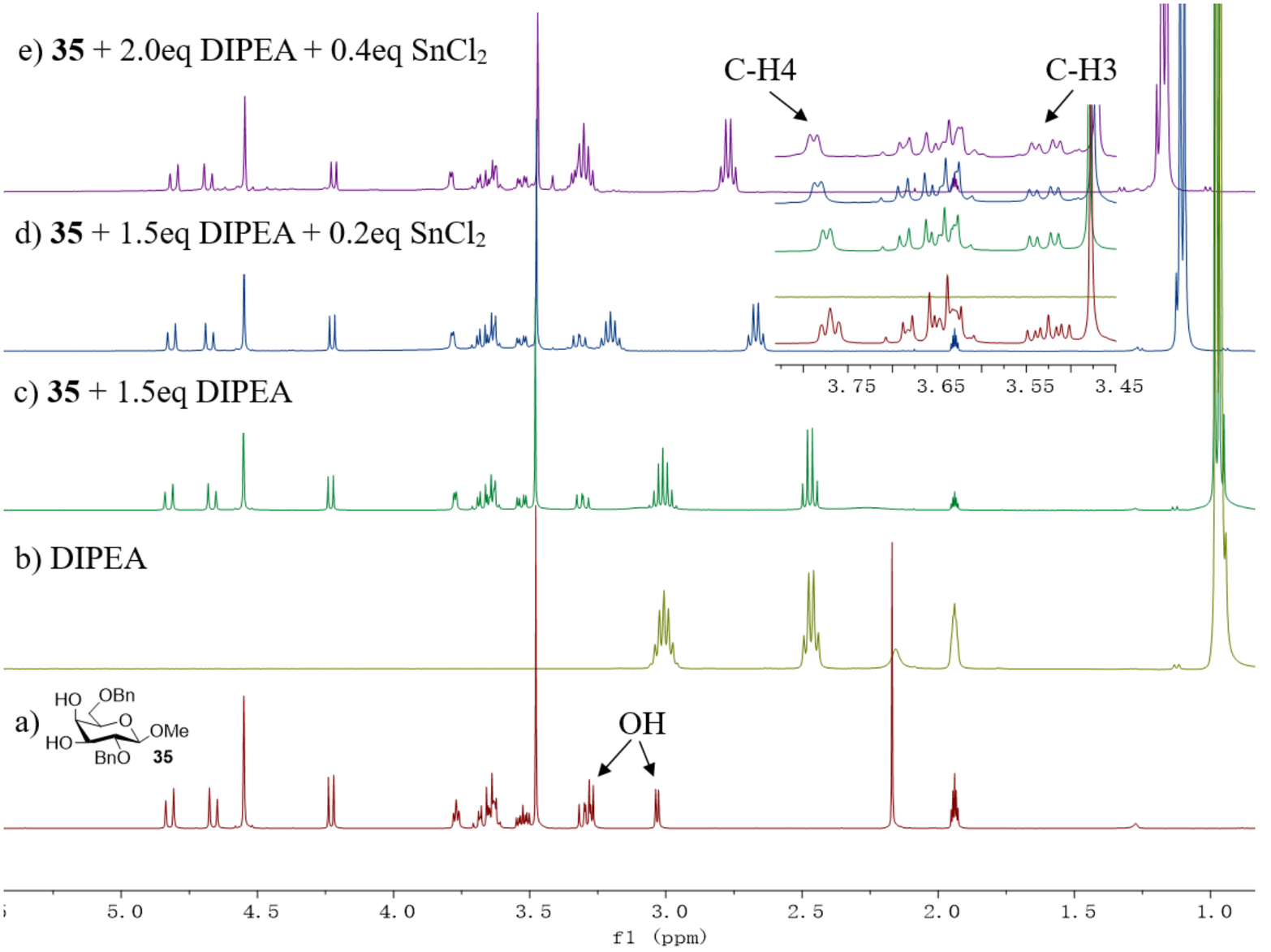
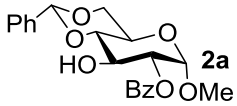


8. Figure S5. ^{1}H-NMR spectrum of compound **35** with the addition of $SnCl_2$ (from 0.2 equiv to 0.4 equiv) in the presence of DIPEA in CD_3CN. The proton connecting C-3 shifted to upfield and the proton connecting C-4 shifted to downfield slightly with the addition of $SnCl_2$.

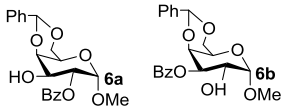
9. Characterization Data of Corresponding Compounds

Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2a).[1]



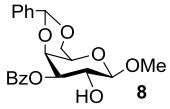
Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **2a** as white solid (35.5 mg, 92%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.11-8.09 (m, 2H), 7.61-7.38 (m, 8H), 5.58 (s, 1H), 5.08 (d, *J* = 4.0 Hz, 1H), 5.04 (dd, *J* = 9.6 Hz and 4.0 Hz, 1H), 4.38-4.31 (m, 2H), 3.92 (td, *J* = 10.0 Hz and 4.4 Hz, 1H), 3.80 (t, *J* = 10.0 Hz, 1H), 3.63 (t, *J* = 9.6 Hz, 1H), 3.40 (s, 3H).

Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-galactopyranoside (6a)[2] **and Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-galactopyranoside (6b)**.[2]



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-galactopyranoside **5** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded a mixture of compound **6a** and **6b** as colorless oil (36.7 mg, 95%, **6a**/**6b** = 65/35). **^{1}H NMR (400 MHz, $CDCl_3$)**: **6a**: δ 5.60 (s, 1H), 5.12 (d, *J* = 3.6 Hz, 1H, **H-1**), 3.43 (s, 3H, O**C**$\mathbf{H_3}$); **6b**: δ 5.53 (s, 1H), 5.00 (d, *J* = 3.6 Hz, 1H, **H-1**), 3.50 (s, 3H, O**C**$\mathbf{H_3}$).

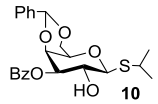
Methyl-3-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (8).[1]



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside **7** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (17.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **8** as white solid (33.2 mg, 86%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ

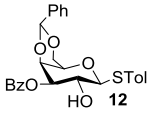
8.10-8.08 (m, 2H), 7.58-7.32 (m, 8H), 5.52 (s, 1H), 5.15 (dd, *J* = 10.0 Hz and 3.6 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.38-4.35 (m, 2H), 4.17 (dd, *J* = 10.4 Hz and 8.0 Hz, 1H), 4.09 (dd, *J* = 12.4 Hz and 1.6 Hz, 1H), 3.60-3.58 (m, 4H).

Isopropylthio-3-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (10)



Following the general procedure, the reaction was carried out with isopropylthio-4,6-*O*-benzylidene-*β*-D-galactopyranoside **9** (32.6 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv.), and BzCl (17.5 μL, 1.5 equiv.) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **10** as pale yellow oil (40.1 mg, 93%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.11-8.08 (m, 2H, Ar**H**), 7.58-7.34 (m, 8H, Ar**H**), 5.51 (s, 1H, PhC**H**), 5.19 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H, **H-3**), 4.56 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.53-4.52 (m, 1H, **H-4**), 4.35 (dd, *J* = 12.4 Hz and 1.2 Hz, 1H, **H-6a**), 4.20 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.04 (dd, *J* = 12.4 Hz and 1.6 Hz, 1H, **H-6b**), 3.62-3.61 (m, 1H, **H-5**), 3.37-3.27 (m, 1H, S**CH**$(CH_3)_2$), 1.38 (dd, *J* = 15.6 Hz and 6.8 Hz, 6H, SCH**$(CH_3)_2$**). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.5, 137.9, 133.4, 130.0, 129.8, 128.9, 128.5, 128.2, 126.3, 100.9, 86.3, 75.4, 74.1, 70.0, 69.3, 67.1, 35.3, 24.5, 24.2 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{23}H_{26}O_6SNa]^+$: 453.1342; found: 453.1344.

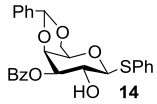
***p*-Tolyl-3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (12)**



Following the general procedure, the reaction was carried out with *p*-tolyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside **11** (37.4 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (17.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **12** as pale yellow syrup (41.6 mg, 87%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05-8.02 (m, 2H, Ar**H**), 7.61-7.35 (m, 10H, Ar**H**), 7.09-7.07 (m, 2H, Ar**H**), 5.49 (s, 1H, PhC**H**), 5.19 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.62 (d, *J* = 9.6 Hz, 1H, **H-1**), 4.49-4.48 (m, 1H, **H-4**), 4.40 (dd, *J* = 12.4 Hz and 1.2 Hz, 1H, **H-6a**), 4.10 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.04 (dd, *J* = 12.4 Hz and 1.2

Hz, 1H, **H-6b**), 3.66 (d, *J* = 0.8 Hz, 1H, **H-5**), 2.36 (s, 3H, SPH**CH**$_3$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.5, 138.6, 137.9, 134.1, 133.4, 130.1, 129.9, 129.7, 129.1, 128.5, 128.1, 126.7, 126.5, 100.9, 87.9, 75.4, 73.9, 70.0, 69.3, 65.9, 21.4 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{27}H_{26}O_6SNa]^+$: 501.1342; found: 501.1350.

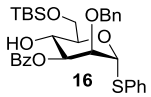
Phenyl-3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (14)



14

Following the general procedure, the reaction was carried out with phenyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside **13** (36.0 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (17.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **14** as an pale oil (41.7 mg, 90%). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.05-8.03 (m, 2H, Ar**H**), 7.72-7.70 (m, 2H, Ar**H**), 7.56-7.25 (m, 11H, Ar**H**), 5.50 (s, 1H, PhC**H**), 5.20 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.67 (d, *J* = 9.2 Hz, 1H, **H-1**), 4.50 (dd, *J* = 3.2 Hz and 0.4 Hz, 1H, **H-4**), 4.40 (dd, *J* = 12.4 Hz and 1.6 Hz, 1H, **H-6a**), 4.17 (t, *J* = 9.6 Hz, 1H, **H-2**), 4.05 (dd, *J* = 12.8 Hz and 1.6 Hz, 1H, **H-6b**), 3.68-3.67 (m, 1H, **H-5**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.5, 137.9, 133.5, 133.4, 130.8, 130.1, 129.7, 129.1, 128.5, 128.3, 128.2, 126.4, 100.8, 87.8, 75.4, 73.9, 70.0, 69.3, 65.9 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{26}H_{24}O_6SNa]^+$: 487.1186; found: 487.1193.

Phenyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-2-*O*-benzyl-1-thio-*α*-D-mannopyranoside (16)

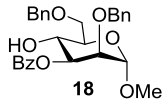


16

Following the general procedure, the reaction was carried out with phenyl-6-*O*-(tert-butyldimethylsilyl)-2-*O*-benzyl-1-thio-*α*-D-mannopyranoside **15** (86.2 mg, 0.181 mmol), DIPEA (48.0 μL, 1.5 equiv), and BzCl (25.5 μL, 1.2 equiv) in the presence of $SnCl_2$ (1.6 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/6), afforded compound **16** as colorless oil (93.5 mg, 89%). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.11-8.09 (m, 2H, Ar**H**), 7.62-7.16 (m, 13H, Ar**H**), 5.61 (d, *J* = 1.2 Hz, 1H, **H-1**), 5.37 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H, **H-3**), 4.68 (d, *J* = 12.4 Hz, 1H, PhC**H**$_2$), 4.55 (d, *J* = 12.0 Hz, 1H, PhC**H**$_2$), 4.35 (t, *J* = 9.6 Hz, 1H, **H-4**), 4.27 (t, *J* = 5.2 Hz, 1H, **H-5**), 4.24 (dd, *J* = 3.6 Hz and 2.0 Hz, 1H, **H-2**), 3.98 (d, *J* =

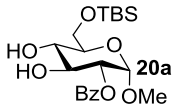
5.2 Hz, 2H, **H-6ab**), 0.93 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.12 (s, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.5, 137.6, 134.4, 133.3, 131.6, 130.0, 129.8, 129.2, 128.5, 128.4, 127.9, 127.8, 127.5, 85.8, 77.3, 74.6, 72.7, 72.6, 68.5, 64.7, 26.0, 18.4, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{32}H_{40}O_6SSiNa]^+$: 603.2207; found: 603.2210.

Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*α*-D-mannopyranoside (18)



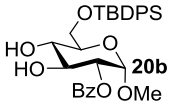
Following the general procedure, the reaction was carried out with methyl-2,6-di-*O*-benzyl-*α*-D-mannopyranoside **17** (24.4 mg, 0.065 mmol), DIPEA (17.5 μL, 1.5 equiv), and BzCl (11.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (0.6 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **18** as colorless oil (26.5 mg, 85%). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.08-8.05 (m, 2H, Ar**H**), 7.60-7.56 (m, 1H, Ar**H**), 7.46-7.19 (m, 12H, Ar**H**), 5.37 (dd, *J* = 10.0 Hz and 3.6 Hz, 1H, **H-3**), 4.80 (d, *J* = 2.0 Hz, 1H, **H-1**), 4.69-4.59 (m, 4H, **H-6ab** and PhC**H$_2$**), 4.29-4.24 (m, 1H, **H-4**), 3.95 (q, *J* = 1.6 Hz, 1H, **H-2**), 3.88-3.82 (m, 3H, **H-5** and PhC**H$_2$**), 3.40 (s, 3H, O**CH$_3$**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.7, 138.1, 137.9, 133.3, 130.0, 129.9, 128.5, 128.4, 127.8, 99.2, 75.9, 74.8, 73.8, 73.3, 71.3, 70.7, 67.7, 55.1 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{28}H_{30}O_7Na]^+$: 501.1884; found: 501.1885.

Methyl-2-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-glucopyranoside (20a).[3]



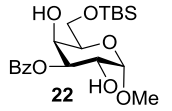
Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-glucopyranoside **19** (30.8 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **20a** as white solid (34.3 mg, 83%). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.09-8.06 (m, 2H), 7.59-7.54 (m, 1H), 7.46-7.41 (m, 2H), 4.99 (d, *J* = 3.6 Hz, 1H), 4.91 (dd, *J* = 10.0 Hz and 3.6 Hz, 1H), 4.15 (dd, *J* = 10.0 Hz and 8.4 Hz, 1H), 3.92 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H), 3.86 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H), 3.72-3.63 (m, 2H), 3.37 (s, 3H), 0.91 (s, 9H), 0.11 (s, 6H).

Methyl-2-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-*α*-D-glucopyranoside (20b).[4]



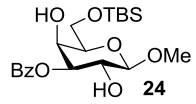
Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldiphenylsilyl)-*α*-D-glucopyranoside **19** (43.3 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **20b** as white solid (46.7 mg, 87%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.10-8.08 (m, 2H), 7.74-7.70 (m, 4H), 7.58-7.55 (m, 1H), 7.45-7.39 (m, 8H), 5.01 (d, *J* = 3.6 Hz, 1H), 4.94 (dd, *J* = 10.0 Hz and 3.6 Hz, 1H), 4.16 (dd, *J* = 9.6 Hz and 8.4 Hz, 1H), 3.97-3.89 (m, 2H), 3.76-3.69 (m, 2H), 3.33 (s, 3H), 1.08 (s, 9H).

Methyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (22).[3]



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside **21** (30.8 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **2** as white solid (37.2 mg, 90%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.11-8.09 (m, 2H), 7.57-7.53 (m, 1H), 7.45-7.41 (m, 2H), 5.26 (dd, *J* = 10.0 Hz and 2.8 Hz, 1H), 4.89 (d, *J* = 3.6 Hz, 1H), 4.31 (d, *J* = 2.8 Hz, 1H), 4.23 (dd, *J* = 10.4 Hz and 4.0 Hz, 1H), 3.95-3.82 (m, 3H), 3.45 (s, 3H), 0.89 (s, 9H), 0.09 (s, 6H).

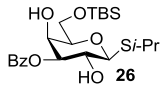
Methyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24).[3]



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (25.3 mg, 0.082 mmol), DIPEA (22.0 μL, 1.5 equiv), BzCl (14.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (0.8 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **24** as colorless syrup (32.2 mg, 95%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.11-8.09 (m, 2H), 7.58-7.54 (m, 1H),

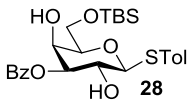
7.45-7.41 (m, 2H), 5.07 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 4.32-4.28 (m, 2H), 4.04 (dd, *J* = 10.0 Hz and 7.6 Hz, 1H), 3.96 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H), 3.89 (dd, *J* = 10.4 Hz and 4.8 Hz, 1H), 3.61-3.57 (m, 4H), 0.89 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).

Isopropylthio-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (26).[5]



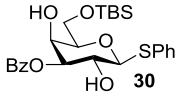
Following the general procedure, the reaction was carried out with isopropylthio-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **25** (33.4 mg, 0.1 mmol), DIPEA (25.5 μL, 1.5 equiv), and BzCl (16.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **26** as viscous yellow oil (41.6 mg, 96%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.12-8.09 (m, 2H), 7.59-7.54 (m, 1H), 7.46-7.42 (m, 2H), 5.11 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H), 4.51 (d, *J* = 9.6 Hz, 1H), 4.32 (d, *J* = 2.4 Hz, 1H), 4.06 (t, *J* = 9.6 Hz, 1H), 3.93 (dd, *J* = 10.8 Hz and 5.6 Hz, 1H), 3.87 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H), 3.62 (t, *J* = 5.2 Hz, 1H), 3.31-3.20 (m, 1H), 1.35 (d, *J* = 6.8 Hz, 6H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

***p*-Tolyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-galactopyranoside (28).**[6]



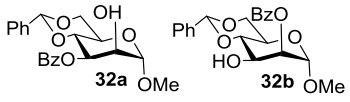
Following the general procedure, the reaction was carried out with *p*-tolyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-galactopyranoside **27** (78.8 mg, 0.2 mmol), DIPEA (52.5 μL, 1.5 equiv), and BzCl (30.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (2 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **28** as viscous yellow oil (90.6 mg, 91%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.09-8.07 (m, 2H), 7.57-7.40 (m, 5H), 7.14-7.12 (m, 2H), 5.10 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H), 4.58 (d, *J* = 9.6 Hz, 1H), 4.34 (dd, *J* = 3.2 Hz and 0.8 Hz, 1H), 4.07-3.97 (m, 2H), 3.92 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H), 3.62 (t, *J* = 4.4 Hz, 1H), 2.35 (s, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

Phenyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-galactopyranoside (30).[6]



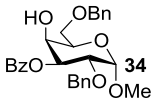
Following the general procedure, the reaction was carried out with phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-galactopyranoside **29** (27.9 mg, 0.073 mmol), DIPEA (19.5 μL, 1.5 equiv), and BzCl (10.5 μL, 1.2 equiv) in the presence of $SnCl_2$ (0.7 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **30** as a white solid (34.0 mg, 95%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.10-8.07 (m, 2H), 7.62-7.54 (m, 3H), 7.44-7.40 (m, 2H), 7.33-7.31 (m, 3H), 5.11 (dd, *J* = 9.2 Hz and 2.8 Hz, 1H), 4.64 (d, *J* = 9.6 Hz, 1H), 4.36 (dd, *J* = 3.2 Hz and 2.8 Hz, 1H), 4.09 (t, *J* = 9.6 Hz, 1H), 4.00 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H), 3.93 (dd, *J* = 10.8 Hz and 4.0 Hz, 1H), 3.64 (ddd, *J* = 5.2 Hz, 4.4 Hz, 0.8 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

Methyl-3-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (32a)[7] **and Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (32b).**[7]



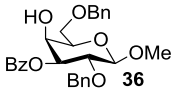
Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside **31** (28.2 mg, 0.1 mmol), DIPEA (21.5 μL, 1.2 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **32a** as white solid (29.1 mg, 75%) and **32b** as white foam (8.2 mg, 21%). **^{1}H NMR (400 MHz, $CDCl_3$)**: **32a**: δ 8.08-8.05 (m, 2H), 7.58-7.54 (m, 1H), 7.45-7.41 (m, 4H), 7.33-7.31 (m, 3H), 5.60 (s, 1H), 5.55 (dd, *J* = 10.0 and 3.2 Hz, 1H), 4.78 (d, *J* = 1.6 Hz, 1H), 4.34-4.24 (m, 3H), 4.00 (td, *J* = 10.4 Hz and 4.8 Hz, 1H), 3.91 (t, *J* = 10.0 Hz, 1H), 3.43 (s, 3H). **32b**: δ 8.12-8.09 (m, 2H), 7.63-7.59 (m, 1H), 7.53-7.46 (m, 4H), 7.39-7.37 (m, 3H), 5.66 (s, 1H), 5.47 (dd, *J* = 3.6 Hz and 1.6 Hz, 1H), 4.84 (d, *J* = 1.2 Hz, 1H), 4.37-4.32 (m, 2H), 4.06-4.01 (m, 1H), 3.95-3.86 (m, 2H), 3.44 (s, 3H).

Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*α*-D-galactopyranoside (34)



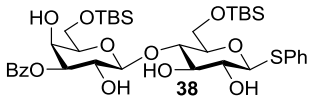
Following the general procedure, the reaction was carried out with methyl-2,6-di-*O*-benzyl-*α*-D-galactopyranoside **33** (48.6 mg, 0.13 mmol), DIPEA (34.5 μL, 1.5 equiv), and BzCl (23.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **34** as colorless oil (57.6 mg, 93%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.08-8.05 (m, 2H, Ar**H**), 7.60-7.56 (m, 1H, Ar**H**), 7.47-7.24 (m, 12H, Ar**H**), 5.46 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H, **H-3**), 4.82 (d, *J* = 3.2 Hz, 1H, **H-1**), 4.74-4.64 (m, 2H, PhC**H**$_2$), 4.61-4.53 (m, 2H, PhC**H**$_2$), 4.36 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.18 (dd, *J* = 10.4 Hz and 3.6 Hz, 1H, **H-2**), 4.03 (t, *J* = 4.8 Hz, 1H, **H-5**), 3.79-3.72 (m, 2H, **H-6ab**), 3.43 (s, 3H, O**CH**$_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.8, 138.1, 137.5, 133.2, 130.1, 129.8, 128.6, 128.5, 128.5, 128.0, 127.9, 127.9, 127.8, 98.8, 73.9, 73.5, 73.3, 73.0, 70.5, 69.5, 67.9, 55.6 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{28}H_{30}O_7Na]^+$: 501.1884; found: 501.1879.

Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*β*-D-galactopyranoside (36).[8]



Following the general procedure, the reaction was carried out with methyl-2,6-di-*O*-benzyl-*β*-D-galactopyranoside **35** (37.4 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (17.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **36** as colorless oil (43.5 mg, 91%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.02-7.99 (m, 2H), 7.60-7.56 (m, 1H), 7.45-7.29 (m, 7H), 7.23-7.14 (m, 5H), 5.13 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 4.85 (d, *J* = 11.6 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.62-4.55 (m, 2H), 4.44 (d, *J* = 7.6 Hz, 1H), 4.26 (d, *J* = 3.2 Hz, 1H), 3.88 (dd, *J* = 10.0 Hz and 7.6 Hz, 1H), 3.83-3.73 (m, 3H), 3.63 (s, 3H).

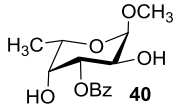
Phenyl-3'-benzoyl-6,6'-di-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-lactoside (38).[6]



Following the general procedure, the reaction was carried out with phenyl-6,6'-di-*O*-(*tert*-butyldimethylsilyl)-1-thio -*β*-D-lactoside **37** (60.7 mg, 0.1 mmol), DIPEA (19.5 μL, 1.2 equiv), and BzCl (13.0

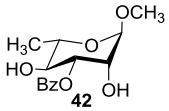
μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **38** as colorless oil (63.5 mg, 90%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10-8.08 (m, 2H), 7.59-7.55 (m, 3H), 7.46-7.42 (m, 2H), 7.29-7.26 (m, 3H), 5.02 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 4.54-4.48 (m, 2H), 4.28 (d, *J* = 2.8 Hz, 1H), 4.07 (dd, *J* = 10.0 Hz and 8.0 Hz), 3.94-3.87 (m, 4H), 3.69-3.57 (m, 3H), 3.44-3.35 (m, 2H), 0.89 (s, 9H), 0.87 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.06 (s, 6H).

Methyl-3-*O*-benzoyl-*α*-*L*-fucopyranoside (40).[9]



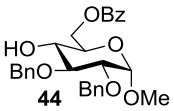
Following the general procedure, the reaction was carried out with methyl-*α*-*L*-fucopyranoside **39** (17.8 mg, 0.1 mmol), DIPEA (21.5 μL, 1.2 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **40** as a white solid (25.5 mg, 90%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.09-8.07 (m, 2H), 7.58-7.54 (m, 1H), 7.45-7.41 (m, 2H), 5.27 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.13 (dd, *J* = 10.4 Hz and 4.0 Hz, 1H), 4.08-4.03 (m, 1H), 3.97-3.96 (m, 1H), 3.45 (s, 3H), 1.30 (d, *J* = 6.4 Hz, 3H). Trace amount of *β* product was also observed by NMR due to the mixture of raw materials. *β* product δ 5.05 (dd, *J* = 10.0 Hz and 3.2 Hz, 0.08 H, **H-3**), 4.27 (d, *J* = 7.6 Hz, 0.08 H, **H-1**).

Methyl-3-*O*-benzoyl-*α*-*L*-rhamnopyranoside (42).[5]



Following the general procedure, the reaction was carried out with methyl-*α*-*L*-rhamnopyranoside **41** (26.8 mg, 0.15 mmol), DIPEA (40.0 μL, 1.5 equiv), and BzCl (26.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1.5 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/1), afforded compound **42** as colorless oil (39.7 mg, 94%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-8.04 (m, 2H), 7.58-7.53 (m, 1H), 7.43-7.40 (m, 2H), 5.24 (dd, *J* = 9.2 Hz and 3.2 Hz, 1H), 4.67 (d, *J* = 1.6 Hz, 1H), 4.12 (dd, *J* = 3.2 Hz and 2.0 Hz, 1H), 3.81-3.71 (m, 2H), 3.38 (s, 3H), 1.36 (d, *J* = 6.0 Hz, 3H).

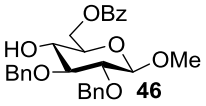
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside (44).[1]



44

Following the general procedure, the reaction was carried out with methyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside **43** (48.1 mg, 0.13 mmol), DIPEA (34.5 μL, 1.5 equiv), and BzCl (23.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1.2 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **44** as colorless oil (57.1 mg, 92%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.05-8.03 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.31 (m, 12H), 5.03 (d, *J* = 11.2 Hz, 1H), 4.81-4.76 (m, 2H), 4.69-4.61 (m, 3H), 4.53 (dd, *J* = 12.0 Hz and 1.6 Hz, 1H), 3.91-3.83 (m, 2H), 3.57-3.52 (m, 2H), 3.42 (s, 3H).

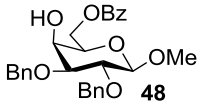
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*β*-D-glucopyranoside (46).[10]



46

Following the general procedure, the reaction was carried out with methyl-2,3-di-*O*-benzyl-*β*-D-glucopyranoside **45** (37.4 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and BzCl (17.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **46** as colorless oil (40.2 mg, 84%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.07-8.05 (m, 2H), 7.59-7.54 (m, 1H), 7.46-7.28 (m, 12H), 4.95 (dd, *J* = 11.2 Hz and 9.2 Hz, 2H), 4.73 (dd, *J* = 11.2 Hz and 7.6 Hz, 2H), 4.66-4.57 (m, 2H), 4.37 (d, *J* = 7.6 Hz, 1H), 3.59-3.41 (m, 7H), 2.66 (d, *J* = 2.4 Hz, 1H).

Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*β*-D-galactopyranoside (48).[10]

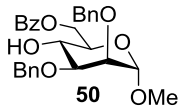


48

Following the general procedure, the reaction was carried out with methyl-2,3-di-*O*-benzyl-*β*-D-galactopyranoside **47** (48.1 mg, 0.129 mmol), DIPEA (34.5 μL, 1.5 equiv), and BzCl (23.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1.2 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **48** as colorless oil (45.2 mg, 73%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-8.04 (m, 2H), 7.61-7.56 (m, 1H), 7.48-7.28 (m, 12H), 4.91 (d, *J* = 11.2 Hz, 1H), 4.78-4.70 (m, 3H), 4.65-4.56 (m, 2H), 4.30 (d, *J* =

7.6 Hz, 1H), 3.99 (d, *J* = 2.8 Hz, 1H), 3.75 (td, *J* = 6.8 Hz and 0.8 Hz, 1H), 3.66 (dd, *J* = 9.6 Hz and 8.0 Hz, 1H), 3.57 (s, 3H), 3.54 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H).

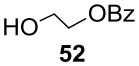
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-mannopyranoside (50).[10]



50

Following the general procedure, the reaction was carried out with methyl-2,3-di-*O*-benzyl-*α*-D-mannopyranoside **49** (53.0 mg, 0.142 mmol), DIPEA (37.5 μL, 1.5 equiv), and BzCl (25.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1.3 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **50** as colorless oil (56.4 mg, 83%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.08-8.05 (m, 2H), 7.56-7.52 (m, 1H), 7.40-7.28 (m, 12H), 4.83 (d, *J* = 1.6 Hz, 1H), 4.67-4.12 (m, 5H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.13 (t, *J* = 9.6 Hz, 1H), 3.89-3.82 (m, 2H), 3.76 (dd, *J* = 9.2 Hz and 2.8 Hz, 1H), 3.38 (s, 3H).

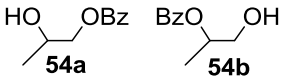
2-Hydroxyethyl-benzoate (52).[11]



52

Following the general procedure, the reaction was carried out with ethylene glycol **51** (10.5 mg, 0.17 mmol), DIPEA (36.0 μL, 1.2 equiv), and BzCl (24.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1.5 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **52** as colorless oil (22.8 mg, 81%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.07-8.04 (m, 2H), 7.58-7.54 (m, 1H), 7.46-7.42 (m, 2H), 4.47-4.44 (m, 2H), 3.96-3.94 (m, 2H).

2-Hydroxy-2-phenylethyl benzoate (54a)[12] **and 1-Hydroxy-2-phenylethyl benzoate (54b).**[12]

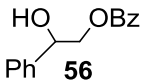


54a **54b**

Following the general procedure, the reaction was carried out with 1-phenyl-1,2-ethanediol **53** (12.8 mg, 0.168 mmol), DIPEA (35.5 μL, 1.2 equiv), and BzCl (24.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1.5 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **54a and 54b** mixture as colorless oil (28.5 mg, 94%, **54a**/**54b** = 88/12). **^{1}H NMR (400 MHz, $CDCl_3$)**: **54a**: δ 8.06-8.03 (m, 2H), 7.59-7.53 (m, 1H), 7.46-7.42 (m, 2H), 4.37-4.30 (m, 1H), 4.22-4.14 (m, 2H), 1.29-1.28 (m, 3H). **54b**: δ

8.06-8.03 (m, 2H), 7.59-7.53 (m, 1H), 7.46-7.42 (m, 2H), 5.27-5.19 (m, 1H), 3.81-3.72 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H).

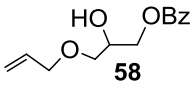
2-Hydroxy-2-phenylethyl benzoate (56).[10]



56

Following the general procedure, the reaction was carried out with 1-phenyl-1,2-ethanediol **55** (13.8 mg, 0.1 mmol), DIPEA (21.5 μL, 1.2 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/6), afforded compound **56** as colorless oil (20.3 mg, 84%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.07-8.04 (m, 2H), 7.60-7.56 (m, 1H), 7.47-7.31 (m, 7H), 5.12 (dd, *J* = 8.4 Hz and 3.6 Hz, 1H), 4.53 (dd, *J* = 11.6 Hz and 3.6 Hz, 1H), 4.43 (dd, *J* = 11.6 Hz and 8.0 Hz, 1H).

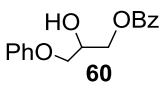
3-(Allyloxy)-2-hydroxypropyl benzoate (58).[10]



58

Following the general procedure, the reaction was carried out with 3-(allyloxy)-1,2-propanediol **57** (12.8 mg, 0.1 mmol), DIPEA (21.0 μL, 1.2 equi.), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **58** as colorless oil (20.4 mg, 89%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-8.03 (m, 2H), 7.59-7.54 (m, 1H), 7.46-7.42 (m, 2H), 5.95-5.85 (m, 1H), 5.31-5.18 (m, 2H), 4.45-4.37 (m, 2H), 4.18-4.15 (m, 1H), 4.05 (dt, *J* = 5.6 Hz and 1.6 Hz, 2H), 3.61 (dd, *J* = 10.0 Hz and 4.4 Hz, 1H), 3.55 (dd, *J* = 10.0 Hz and 6.4 Hz, 1H).

3-Phenoxypropyl benzoate (60).[10]

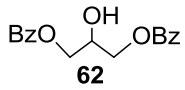


60

Following the general procedure, the reaction was carried out with 3-phenoxy-1,2-propanediol **59** (16.8 mg, 0.1 mmol), DIPEA (21.5 μL, 1.2 equiv), and BzCl (14.0 μL, 1.2 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **60** as colorless oil (23.7 mg, 87%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.07-8.05 (m, 2H),

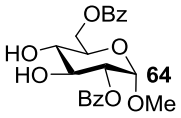
7.60-7.56 (m, 1H), 7.47-7.43 (m, 2H), 7.32-7.27 (m, 2H), 7.01-6.92 (m, 3H), 4.59-4.51 (m, 2H), 4.42-4.36 (m, 1H), 4.16-4.08 (m, 2H).

1,3-di-*O*-benzoyl-propane-2-ol (62).[8]



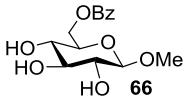
Following the general procedure, the reaction was carried out with glycerol **61** (16.9 mg, 0.184 mmol), DIPEA (81.0 μL, 2.5 equiv), and BzCl (54.0 μL, 2.5 equiv) in the presence of $SnCl_2$ (1.8 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **62** as colorless oil (43.2 mg, 78%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-8.03 (m, 4H), 7.58-7.54 (m, 2H), 7.44-7.40 (m, 4H), 4.55-4.47 (m, 4H), 4.40-4.35 (m, 1H).

Methyl-2,6-di-*O*-benzoyl-*α*-D-glucopyranoside (64).[13]



Following the general procedure, the reaction was carried out with methyl-*α*-D-glucopyranoside **63** (19.4 mg, 0.1 mmol), DIPEA (44.0 μL, 2.5 equiv), and BzCl (29.0 μL, 2.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **64** as white solid (31.4 mg, 78%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.08-8.04 (m, 4H), 7.58-7.52 (m, 2H), 7.45-7.39 (m, 4H), 5.03 (d, *J* = 3.6 Hz, 1H), 4.94 (dd, *J* = 10.0 Hz and 4.0 Hz, 1H), 4.70 (dd, *J* = 12.4 Hz and 4.8 Hz, 1H), 4.55 (dd, *J* = 12.4 Hz and 2.0 Hz, 1H), 4.18 (td, *J* = 9.6 Hz and 3.6 Hz, 1H), 3.93 (ddd, *J* = 10.0 Hz, 4.8 Hz and 2.0 Hz, 1H), 3.88 (d, *J* = 4.0 Hz, 1H), 3.60 (td, *J* = 9.6 Hz and 4.0 Hz, 1H), 3.42 (d, *J* = 3.6 Hz, 1H), 3.38 (s, 3H).

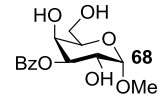
Methyl-6-*O*-benzoyl-*β*-D-glucopyranoside (66).[10]



Following the general procedure, the reaction was carried out with methyl-*β*-D-glucopyranoside **65** (38.8 mg, 0.2 mmol), DIPEA (53.0 μL, 1.5 equiv), and BzCl (35.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (2 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **66** as white solid (36.7 mg, 62%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ

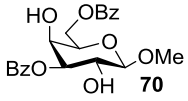
8.03-8.01 (m, 2H), 7.54-7.50 (m, 1H), 7.41-7.37 (m, 2H), 4.63-4.54 (m, 2H), 4.22 (d, *J* = 8.0 Hz, 1H), 3.62-3.56 (m, 2H), 3.52-3.47 (m, 4H), 3.43-3.38 (m, 1H).

Methyl-3-*O*-benzoyl-*α*-D-galactopyranoside (68).[14]



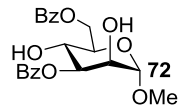
Following the general procedure, the reaction was carried out with methyl-*α*-D-galactopyranoside **67** (38.8 mg, 0.2 mmol), DIPEA (53.0 μL, 1.5 equiv), and BzCl (35.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (2 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/0), afforded compound **68** as colorless oil (42.2 mg, 71%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.10-8.07 (m, 2H), 7.59-7.55 (m, 1H), 7.46-7.42 (m, 2H), 5.27 (dd, *J* = 10.4 Hz and 3.6 Hz, 1H), 4.92 (d, *J* = 4.0 Hz, 1H), 4.29 (d, *J* = 2.8 Hz, 1H), 4.23-4.20 (m, 1H), 3.97-3.85 (m, 3H), 3.47 (s, 3H, O**CH_3**).

Methyl-3,6-di-*O*-benzoyl-*β*-D-galactopyranoside (70).[8]



Following the general procedure, the reaction was carried out with methyl-*β*-D-galactopyranoside **69** (38.8 mg, 0.2 mmol), DIPEA (88.0 μL, 2.5 equiv), and BzCl (59.0 μL, 2.5 equiv) in the presence of $SnCl_2$ (2 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/2), afforded compound **70** as white solid (75.3 mg, 94%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-7.97 (m, 4H), 7.56-7.33 (m, 6H), 5.11 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 4.61-4.52 (m, 2H), 4.32 (d, *J* = 7.6 Hz, 1H), 4.23-4.22 (m, 1H), 4.06 (dd, *J* = 10.0 Hz and 8.0 Hz), 3.93 (t, *J* = 6.4 Hz, 1H), 3.52 (s, 3H).

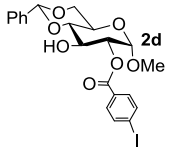
Methyl-3,6-di-*O*-benzoyl-*α*-D-mannopyranoside (72).[8]



Following the general procedure, the reaction was carried out with methyl-*α*-D-mannopyranoside **71** (38.8 mg, 0.2 mmol), DIPEA (88.0 μL, 2.5 equiv), and BzCl (59.0 μL, 2.5 equiv) in the presence of $SnCl_2$ (2 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **72** as white solid (71.4 mg, 89%). **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.06-8.01 (m, 4H), 7.55-7.34 (m, 6H), 5.33 (dd, *J* = 9.6 Hz and 3.2 Hz, 1H), 4.73 (d, *J* = 1.6 Hz, 1H), 4.68 (dd, *J* = 12.0 Hz and 6.0 Hz, 1H), 4.59 (dd, *J* = 12.0 Hz and 2.0

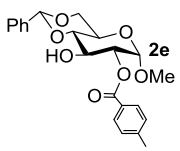
Hz, 1H), 4.16-4.10 (m, 2H), 3.98 (ddd, *J* = 9.6 Hz, 5.6 Hz and 2.0 Hz, 1H), 3.37 (s, 3H).

Methyl-2-*O*-4-iodobenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2d)



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and 4-iodobenzoyl chloride (40.0 mg, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 2 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2d** as colorless syrup (45.6 mg, 89%). R_f = 0.52 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.83-7.77 (m, 4H, Ar**H**), 7.52-7.50 (m, 2H, Ar**H**), 7.42-7.37 (m, 3H, Ar**H**), 5.57 (s, 1H, Ph**CH**-), 5.06-5.01 (m, 2H, **H-1** and **H-3**), 4.35-4.30 (m, 2H, **H-2** and **H-4**), 3.90 (td, *J* = 10.4 Hz and 4.8 Hz, 1H, **H-5**), 3.79 (t, *J* = 10.0 Hz, 1H, **H-6a**), 3.61 (t, *J* = 9.6 Hz, 1H, **H-6b**), 3.39 (s, 3H, O**CH**$_3$). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.9, 137.9, 137.1, 131.5, 129.5, 129.1, 128.5, 126.4, 102.2, 101.4, 97.8, 81.6, 74.3, 69.0, 68.9, 62.2, 55.6 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{21}H_{21}O_7INa]^+$: 535.0224; found: 535.0217.

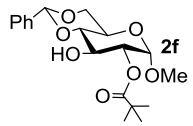
Methyl-2-*O*-4-methylbenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2e)



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and 4-methylbenzoyl chloride (20.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2e** as white powder (36.1 mg, 90%). R_f = 0.50 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 8.00-7.98 (m, 2H, Ar**H**), 7.53-7.50 (m, 2H, Ar**H**), 7.41-7.36 (m, 3H, Ar**H**), 7.26-7.24 (m, 2H, Ar**H**), 5.57 (s, 1H, Ph**CH**-), 5.07 (d, *J* = 3.6 Hz, 1H, **H-1**), 5.02 (dd, *J* = 9.6 Hz and 4.0 Hz, 1H, **H-3**), 4.37-4.35 (m, 1H, **H-4**), 4.32 (dd, *J* = 5.2 Hz and 3.6 Hz, 1H, **H-2**), 3.91 (td, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-5**), 3.80 (t, *J* = 10.4 Hz, 1H, **H-6a**), 3.63 (t, *J* = 9.2 Hz, 1H, **H-6b**), 3.39 (s, 3H, O**CH**$_3$), 2.42 (s, 3H, Ph**CH**$_3$). **^{13}C NMR**

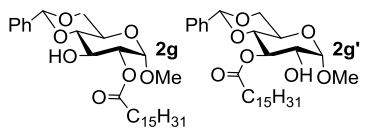
(101 MHz, $CDCl_3$): δ 166.4, 144.3, 137.1, 130.1, 129.4, 129.3, 128.5, 126.8, 126.5, 102.2, 98.0, 81.6, 74.1, 69.1, 69.0, 62.2, 55.6, 21.8 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{22}H_{24}O_7Na]^+$: 423.1414; found: 423.1414.

Methyl-2-*O*-pivaloyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2f).[15]



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (35.5 μL, 2.0 equiv), and pivaloyl chloride (25.0 μL, 2.0 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **2f** as colorless crystals (33.4 mg, 91%). R_f = 0.63 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.50-7.47 (m, 2H), 7.39-7.36 (m, 3H), 5.55 (s, 1H), 4.93 (d, *J* = 4.0 Hz, 1H), 4.74 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H), 4.29 (dd, *J* = 10.0 Hz and 4.8 Hz, 1H), 4.19 (t, *J* = 9.6 Hz, 1H), 3.85 (td, *J* = 10.0 Hz and 4.8 Hz, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.55 (t, *J* = 9.6 Hz, 1H), 3.38 (s, 3H, O**C**$\mathbf{H_3}$), 1.24 (s, 9H, C(**C**$\mathbf{H_3}$)$_3$).

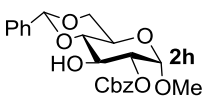
Methyl-2-*O*-palmitoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2g) and Methyl-3-*O*-palmitoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2g')



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and palmitoyl chloride (46.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **2g** as colorless syrup (36.1 mg, 69%). R_f = 0.50 (ethyl acetate/petroleum ether: 1/4); compound **2g'** as colorless syrup (12.6 mg, 24%). R_f = 0.30 (ethyl acetate/petroleum ether: 1/4) ; **2g**: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.53-7.47 (m, 2H, Ar**H**), 7.40-7.36 (m, 3H, Ar**H**), 5.55 (s, 1H, Ph**CH**-), 4.95 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.80 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H, **H-2**), 4.29 (dd, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-6a**), 4.17 (t, *J* = 9.6 Hz, 1H, **H-3**), 3.84 (td, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-5**), 3.76 (t, *J* = 10.0 Hz, 1H, **H-6b**), 3.56 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.39 (s, 3H, O**C**$\mathbf{H_3}$), 2.41 (t, *J* = 7.2 Hz, 2H), 1.68-1.57 (m, 2H), 1.26 (s, 24H), 0.88 (t, *J* = 6.8 Hz,

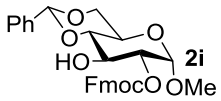
3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.7, 137.1, 129.4, 128.5, 126.4, 102.1, 97.7, 81.5, 73.5, 69.0, 68.8, 62.1, 55.5, 34.3, 34.0, 32.0, 29.8, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 25.1, 24.8, 22.8, 14.2 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{30}H_{48}O_7Na]^+$: 543.3292; found: 543.3293; **2g'**: **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.45-7.42 (m, 2H, Ar**H**), 7.38-7.33 (m, 3H, Ar**H**), 5.49 (s, 1H, Ph**CH**-), 5.34 (t, *J* = 10.0 Hz, 1H, **H-3**), 4.80 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.31 (dd, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-6a**), 3.87 (td, *J* = 10.0 Hz and 4.4 Hz, 1H, **H-5**), 3.75 (t, *J* = 10.4 Hz, 1H, **H-6b**), 3.68-3.64 (m, 1H, **H-2**), 3.59 (t, *J* = 9.6 Hz, 1H, **H-4**), 3.47 (s, 3H, O**CH$_3$**), 2.39-2.34 (m, 2H), 1.66-1.59 (m, 2H), 1.25 (s, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$):** δ 174.1, 137.2, 129.2, 128.3, 126.3, 101.6, 100.3, 78.9, 72.2, 72.0, 69.1, 62.9, 55.7, 34.6, 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.6, 29.5, 29.4, 29.2, 29.1, 25.2, 24.9, 22.8, 14.3 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{30}H_{48}O_7Na]^+$: 543.3292; found: 543.3294.

Methyl-2-*O*-benzyloxycarbonyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2h)



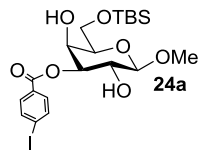
Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and benzyl chloroformate (21.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2** as colorless syrup (37.2 mg, 89%). R_f = 0.38 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.52-7.34 (m, 10H, Ar**H**), 5.54 (s, 1H, Ph**CH**-), 5.20 (s, 2H, Ph**CH$_2$**-), 5.01 (d, *J* = 3.6 Hz, 1H, **H-1**), 4.67 (dd, *J* = 9.6 Hz and 4.0 Hz, 1H, **H-2**), 4.30 (dd, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-6a**), 4.21 (td, *J* = 9.2 Hz and 2.0 Hz, 1H, **H-3**), 3.85 (td, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-5**), 3.76 (t, *J* = 10.4 Hz, 1H, **H-6b**), 3.56 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.39 (s, 3H, O**CH$_3$**), 2.68 (d, *J* = 2.8 Hz, 1H, **3-OH**). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.7, 137.0, 134.9, 129.4, 128.8, 128.7, 128.5, 128.5, 126.4, 102.2, 97.6, 81.2, 77.0, 70.3, 69.0, 68.8, 62.1, 55.6 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{22}H_{24}O_8Na]^+$: 439.1363; found: 439.1365.

Methyl-2-*O*-9-fluorenylmethyloxycarbonyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2i)



Following the general procedure, the reaction was carried out with methyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside **1** (28.2 mg, 0.1 mmol), DIPEA (26.5 μL, 1.5 equiv), and 9-fluorenylmethyl chloroformate (39.0 mg, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2i** as as colorless syrup (43.0 mg, 85%). R_f = 0.44 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.78-7.76 (m, 2H, Ar**H**), 7.66-7.61 (m, 2H, Ar**H**), 7.52-7.50 (m, 2H, Ar**H**), 7.43-7.30 (m, 7H, Ar**H**), 5.56 (s, 1H, Ph**CH**-), 5.00 (d, *J* = 4.0 Hz, 1H, **H-1**), 4.70 (dd, *J* = 9.6 Hz and 3.6 Hz, 1H, **H-2**), 4.46 (d, *J* = 7.6 Hz, 2H, **CH_2-**), 4.34-4.25 (m, 3H, **-CH-**, **H-6a** and **H-3**), 3.88 (td, *J* = 10.0 Hz and 4.8 Hz, 1H, **H-5**), 3.78 (t, *J* = 10.4 Hz, 1H, **H-6b**), 3.59 (t, *J* = 9.2 Hz, 1H, **H-4**), 3.44 (s, 3H, O**CH_3**). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.9, 143.4, 143.3, 141.5, 141.4, 137.0, 129.5, 128.5, 128.1, 127.3, 127.3, 126.5, 125.3, 120.2, 102.2, 97.6, 81.4, 77.0, 70.5, 69.0, 68.8, 62.2, 55.7, 46.8 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{29}H_{28}O_8Na]^+$: 527.1676; found: 527.1676.

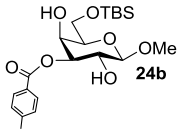
Methyl-3-*O*-4-iodobenzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24a)



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (29.9 mg, 0.1 mmol), DIPEA (26.0 μL, 1.5 equiv), and 4-iodobenzoyl chloride (38.8 mg, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/4), afforded compound **2** as pale yellow syrup (50.8 mg, 97%). R_f = 0.27 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.79 (s, 4H, Ar**H**), 5.04 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.31-4.28 (m, 2H, **H-1** and **H-4**), 4.02 (dd, *J* = 10.0 Hz and 7.6 Hz, 1H, **H-2**), 3.96 (dd, *J* = 10.8 Hz and 5.6 Hz, 1H, **H-6a**), 3.90 (dd, *J* = 10.8 Hz and 4.4 Hz, 1H, **H-6b**), 3.59-3.56 (m, 4H, **H-5** and O**CH_3**), 0.89 (s, 9H,

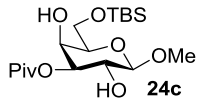
Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**), 0.08 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.0, 137.9, 131.5, 129.3, 104.5, 101.3, 76.2, 73.9, 69.5, 68.3, 63.1, 57.2, 25.9, 18.4, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{20}H_{31}O_7ISiNa$]$^+$: 561.0776; found: 561.0774.

Methyl-3-*O*-4-methylbenzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24b)



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (32.6 mg, 0.1 mmol), DIPEA (28.5 μL, 1.5 equiv), and 4-methylbenzoyl chloride (21.5 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1.0 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **24b** as colorless syrup (43.5 mg, 96%). R_f = 0.43 (ethyl acetate/petroleum ether: 1/2); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 8.00-7.98 (m, 2H, Ar**H**), 7.24-7.22 (m, 2H, Ar**H**), 5.06 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H, **H-3**), 4.31 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.28 (d, *J* = 2.8 Hz, 1H, **H-4**), 4.03 (dd, *J* = 10.0 Hz and 7.6 Hz, 1H, **H-2**), 3.96 (dd, *J* = 10.8 Hz and 6.0 Hz, 1H, **H-6a**), 3.89 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6b**), 3.61-3.58 (m, 4H, **H-5** and O**CH$_3$**), 2.40 (s, 3H, Ph**CH$_3$**), 0.89 (s, 9H, Si(C(**CH$_3$)$_3$**)(CH$_3$)$_2$), 0.08 (d, *J* = 0.4 Hz, 6H, Si(C(CH$_3$)$_3$)(**CH$_3$)$_2$**). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.5, 144.2, 130.1, 129.3, 127.0, 104.5, 75.9, 74.1, 69.7, 68.2, 63.0, 57.2, 26.0, 21.8, 18.4, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{21}H_{34}O_7SiNa$]$^+$: 449.1966; found: 449.1959.

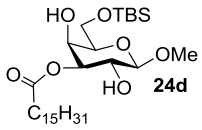
Methyl-3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24c).[3]



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (25.4 mg, 0.082 mmol), DIPEA (29.5 μL, 2.0 equiv), and pivaloyl chloride (20.5 μL, 2.0 equiv) in the presence of $SnCl_2$ (0.8 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **24c** as colorless syrup (30.9 mg, 96%). **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 4.80 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H), 4.23 (d,

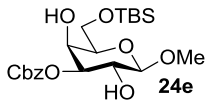
J = 7.6 Hz, 1H), 4.10 (br s, 1H), 3.92 (dd, *J* = 10.4 Hz and 5.6 Hz, 1H), 3.88-3.83 (m, 2H), 3.55 (s, 3H), 3.53-3.51 (m, 1H), 1.25 (s, 9H), 0.88 (s, 9H), 0.08 (d, *J* = 0.4 Hz, 6H).

Methyl-3-*O*-palmitoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24d)



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (31.8 mg, 0.1 mmol), DIPEA (27.5 μL, 1.5 equiv), palmitoyl chloride (47.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1 mg, 0.05 equiv) at room temperature for 1.0 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/5), afforded compound **24d** as colorless syrup (50.7 mg, 90%). R_f = 0.41 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 4.84 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.24 (d, *J* = 8.0 Hz, 1H, **H-1**), 4.16-4.15 (m, 1H, **H-4**), 3.94 (dd, *J* = 10.4 Hz and 5.2 Hz, 1H, **H-6a**), 3.90-3.85 (m, 2H, **H-6b** and **H-2**), 3.56 (s, 3H, O**CH_3**), 3.53-3.50 (m, 1H, **H-5**), 2.42 (t, *J* = 7.6 Hz, 2H), 1.69-1.61 (m, 2H), 1.24 (s, 24H), 0.89-0.85 (m, 12H), 0.09 (s, 3H), 0.08 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.8, 104.4, 75.2, 73.9, 69.6, 68.3, 63.2, 57.2, 34.4, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 25.9, 25.1, 22.8, 18.4, 14.3, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for $[C_{29}H_{58}O_7SiNa]^+$: 569.3844; found: 569.3846.

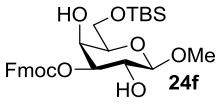
Methyl-3-*O*-benzyloxycarbonyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24e)



Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (41.5 mg, 0.135 mmol), DIPEA (36.0 μL, 1.5 equiv), and benzyl chloroformate (29.0 μL, 1.5 equiv) in the presence of $SnCl_2$ (1.2 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **24e** as colorless syrup (56.2 mg, 94%). R_f = 0.24 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 7.40-7.33 (m, 5H, Ar**H**), 5.19 (br s, 2H, Ph**CH_2**O-), 4.68 (dd, *J* = 10.0 Hz and 3.2 Hz, 1H, **H-3**), 4.25-4.22 (m, 2H, **H-1** and **H-4**), 3.94-3.86 (m, 3H, **H-2**,

H-6ab), 3.55 (s, 3H, O**CH**$_3$), 3.53-3.50 (m, 1H, **H-5**), 2.81 (d, *J* = 3.6 Hz, 1H, **4-OH**), 2.55 (d, *J* = 2.8 Hz, 1H, **3-OH**), 0.89 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.08 (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 (101 MHz, CDCl$_3$):** δ 154.8, 134.9, 128.8, 128.7, 128.6, 104.2, 79.3, 73.9, 70.3, 69.5, 67.6, 62.7, 57.2, 25.9, 18.4, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{21}H_{34}O_8SiNa$]$^+$: 465.1915; found: 465.1916.

Methyl-3-*O*-9-fluorenylmethyloxycarbonyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24f)



24f

Following the general procedure, the reaction was carried out with methyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside **23** (39.4 mg, 0.128 mmol), DIPEA (34.5 μL, 1.5 equiv), and 9-fluorenylmethyl chloroformate (49.8 mg, 1.5 equiv) in the presence of $SnCl_2$ (1.2 mg, 0.05 equiv) at room temperature for 0.5 h. The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether: 1/3), afforded compound **24f** as colorless syrup (59.8 mg, 88%). R_f = 0.29 (ethyl acetate/petroleum ether: 1/3); **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.77-7.75 (m, 2H, Ar**H**), 7.66-7.62 (m, 2H, Ar**H**), 7.43-7.30 (m, 4H, Ar**H**), 4.70 (dd, *J* = 10.4 Hz and 3.2 Hz, 1H, **H-3**), 4.49 (dd, *J* = 10.4 Hz and 7.6 Hz, 1H, -**CH**$_2$-), 4.43 (dd, *J* = 10.4 Hz and 7.2 Hz, 1H, -**CH**$_2$-), 4.30-4.23 (m, 3H, -**CH**-, **H-1** and **H-4**), 3.99-3.93 (m, 2H, **H-2** and **H-6a**), 3.89 (dd, *J* = 10.8 Hz and 4.8 Hz, 1H, **H-6b**), 3.57 (s, 3H, O**CH**$_3$), 3.54-3.51 (m, 1H, **H-5**), 0.90 (s, 9H, Si(C(**CH**$_3$**)**$_3$)(CH$_3$)$_2$), 0.10 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$), 0.09 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$**)**$_2$). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 154.9, 143.5, 143.3, 141.4, 141.4, 128.0, 127.3, 125.4, 125.4, 120.2, 104.2, 79.3, 73.9, 70.4, 69.4, 67.8, 62.8, 57.2, 46.8, 25.9, 18.4, -5.3 ppm; **HRMS (ESI-TOF):** Calculated for [$C_{28}H_{38}O_8SiNa$]$^+$: 553.2228; found: 553.2239.

10. References

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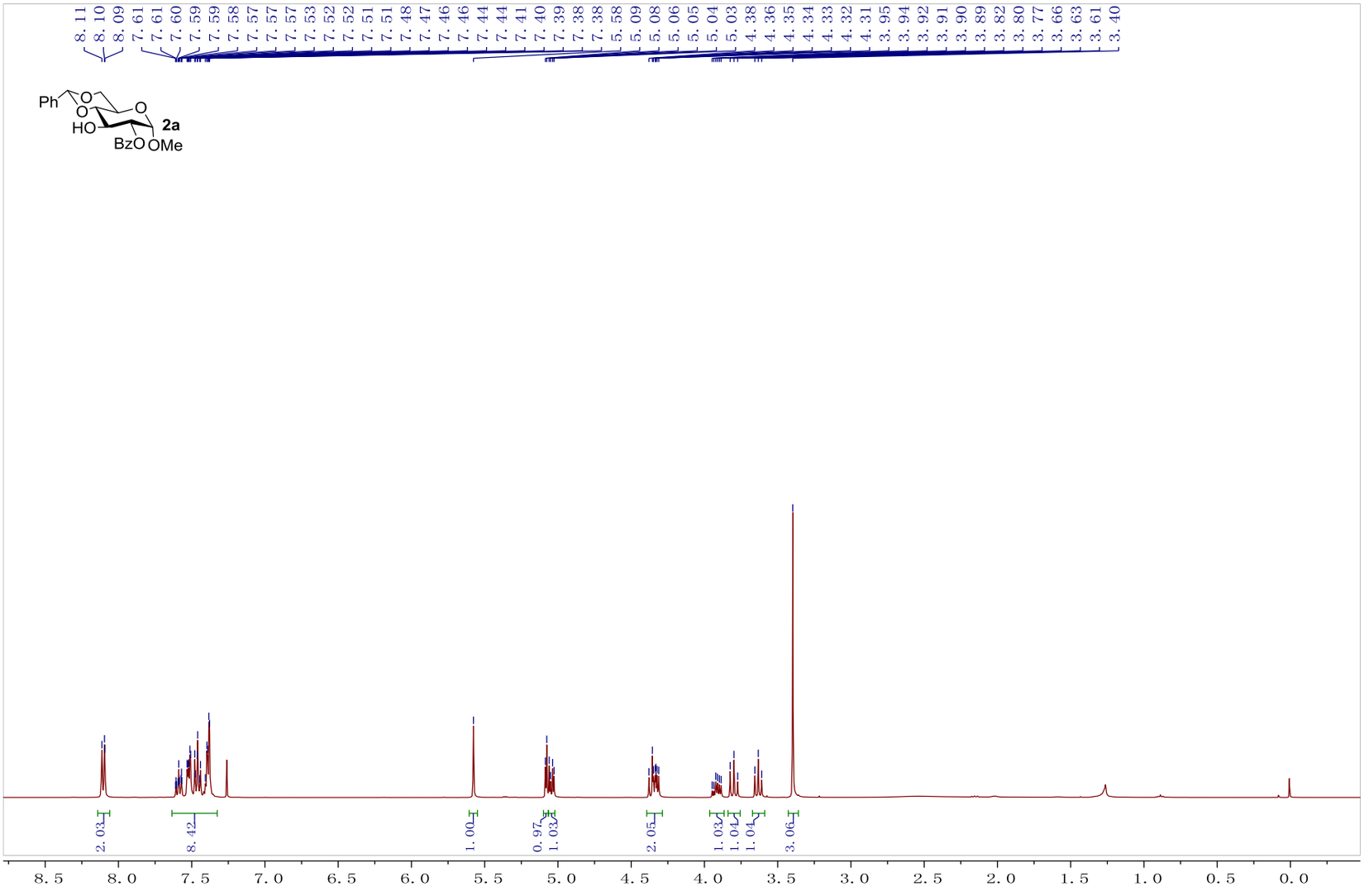
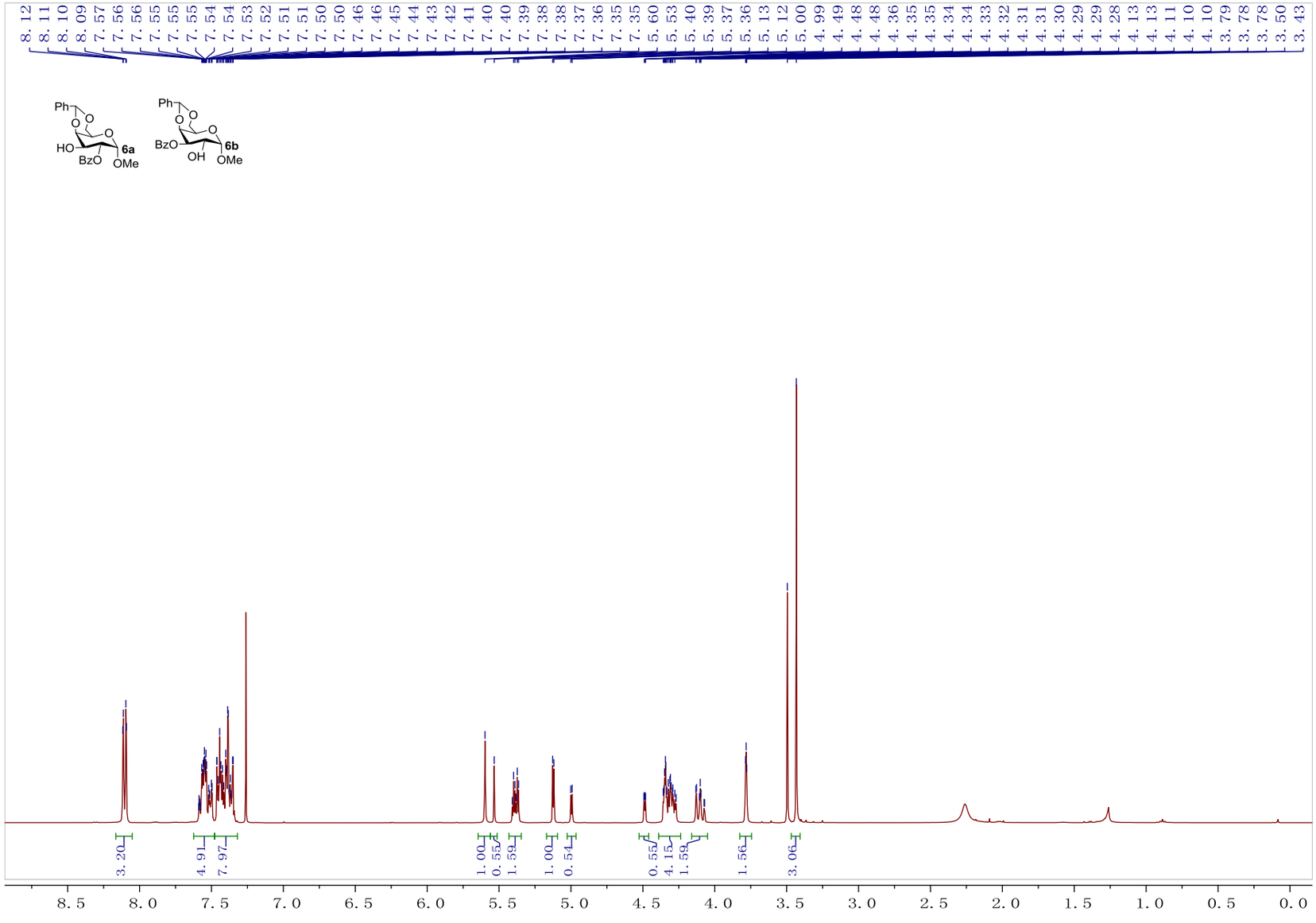
11. NMR Spectra

Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2a)

^{1}H-NMR of compound **2a** ($CDCl_3$)

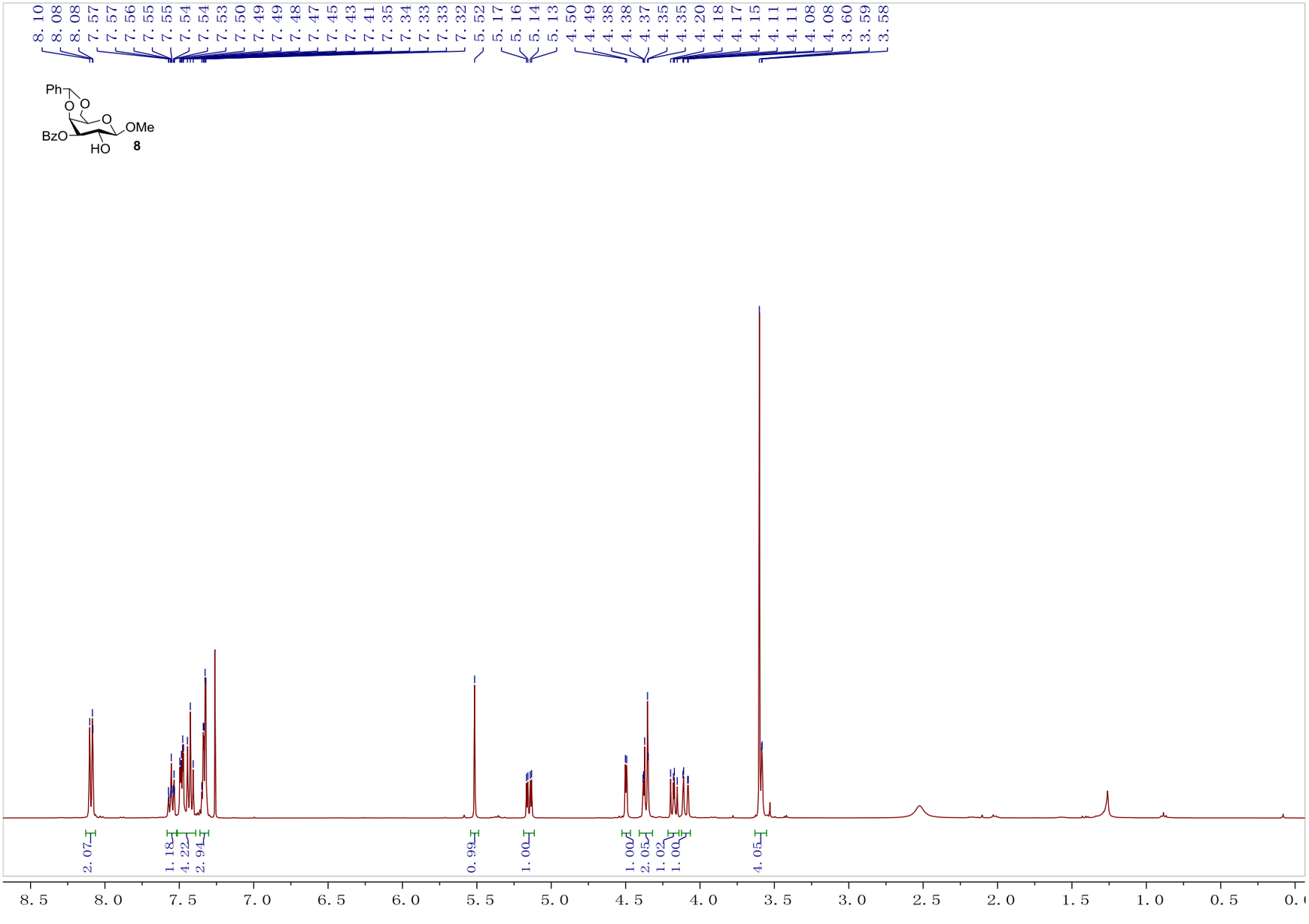


Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-galactopyranoside (6a) and Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-galactopyranoside (6b) ^{1}H-NMR of mixture of compounds **6a** and **6b** ($CDCl_3$)



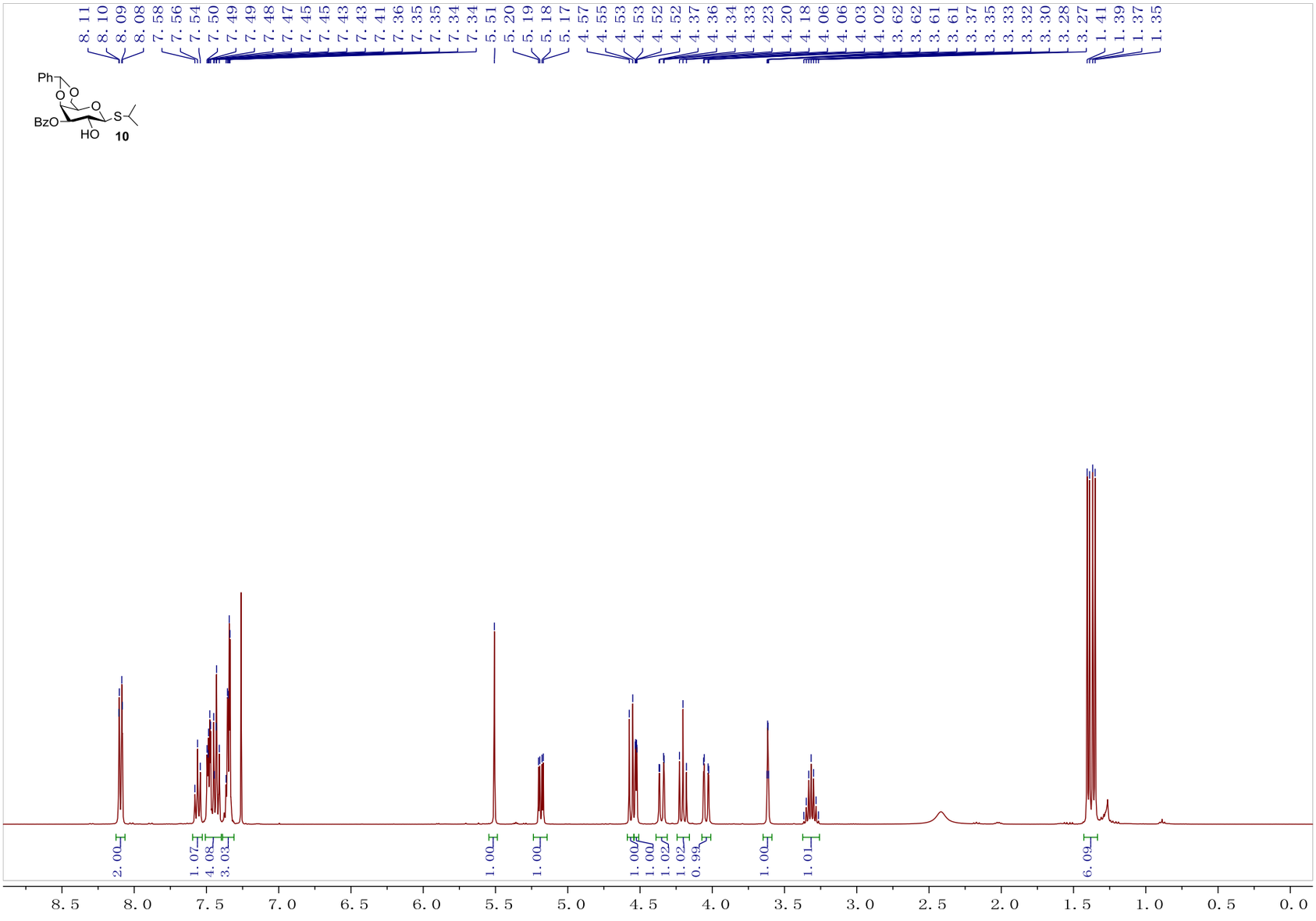
Methyl-3-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (8)

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

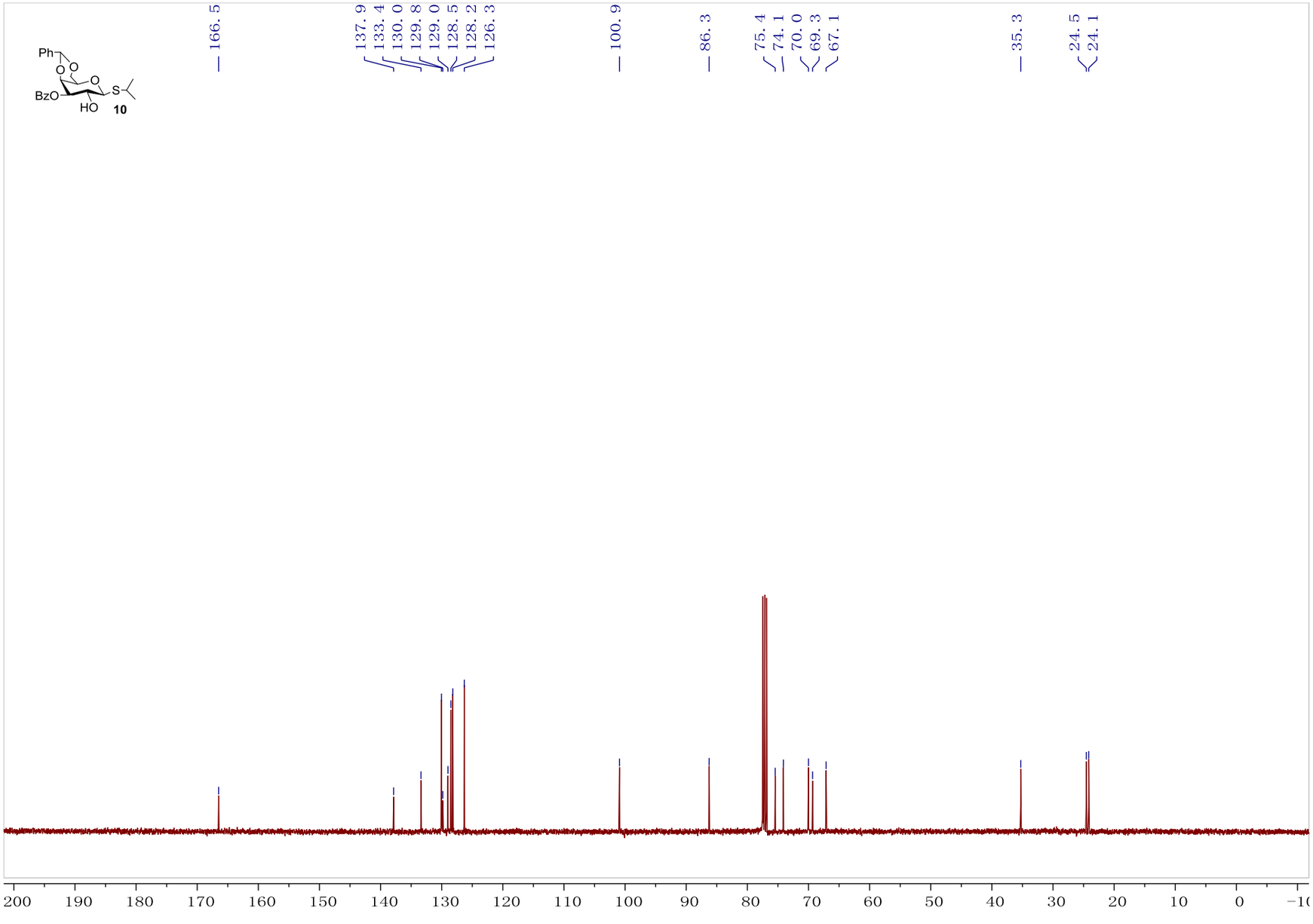


Isopropylthio-3-*O*-benzoyl-4,6-*O*-benzylidene-*β*-D-galactopyranoside (10)

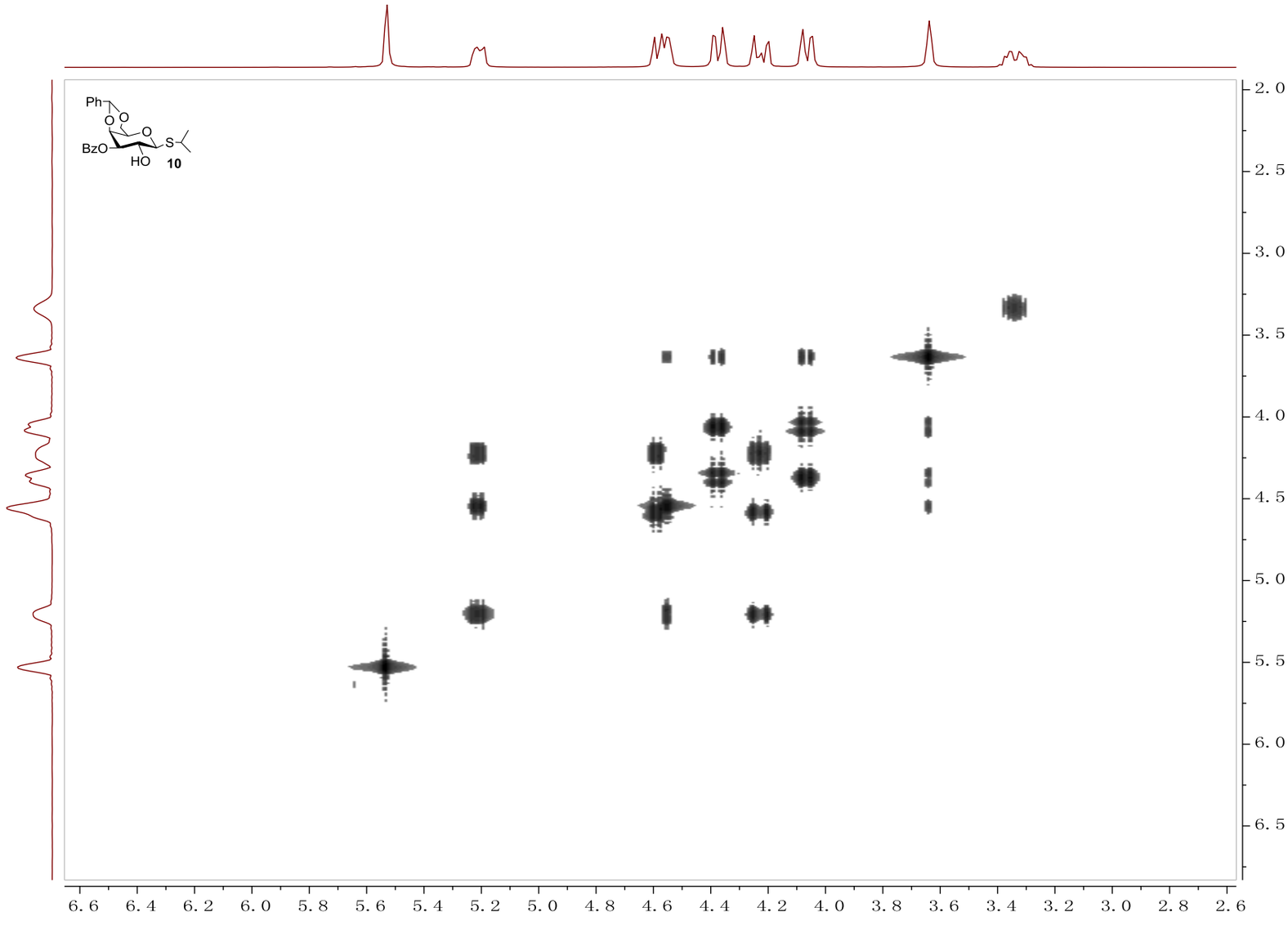
^{1}H-NMR of compound **10** ($CDCl_3$)



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

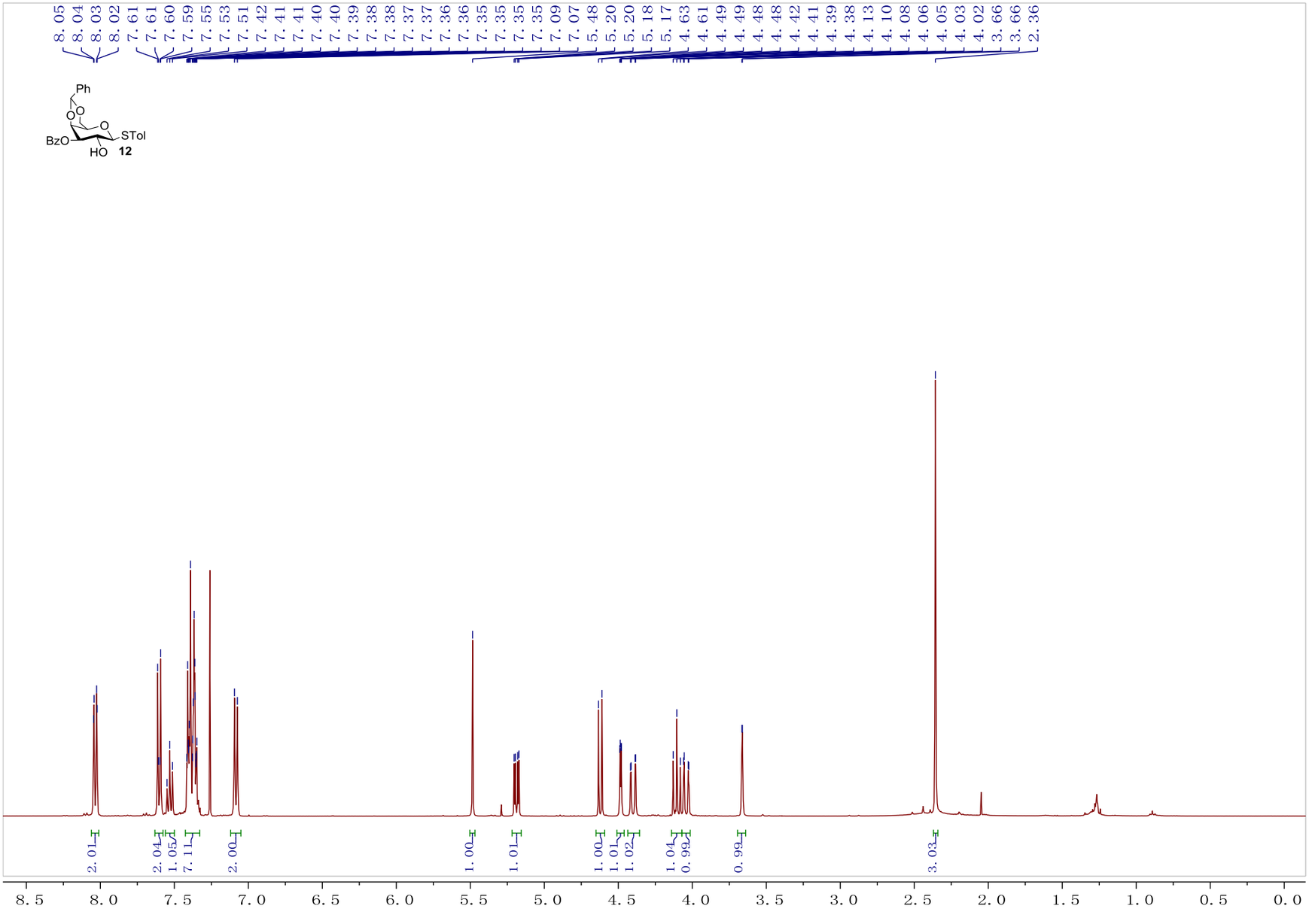


2D-COSY of compound **10** ($CDCl_3$)

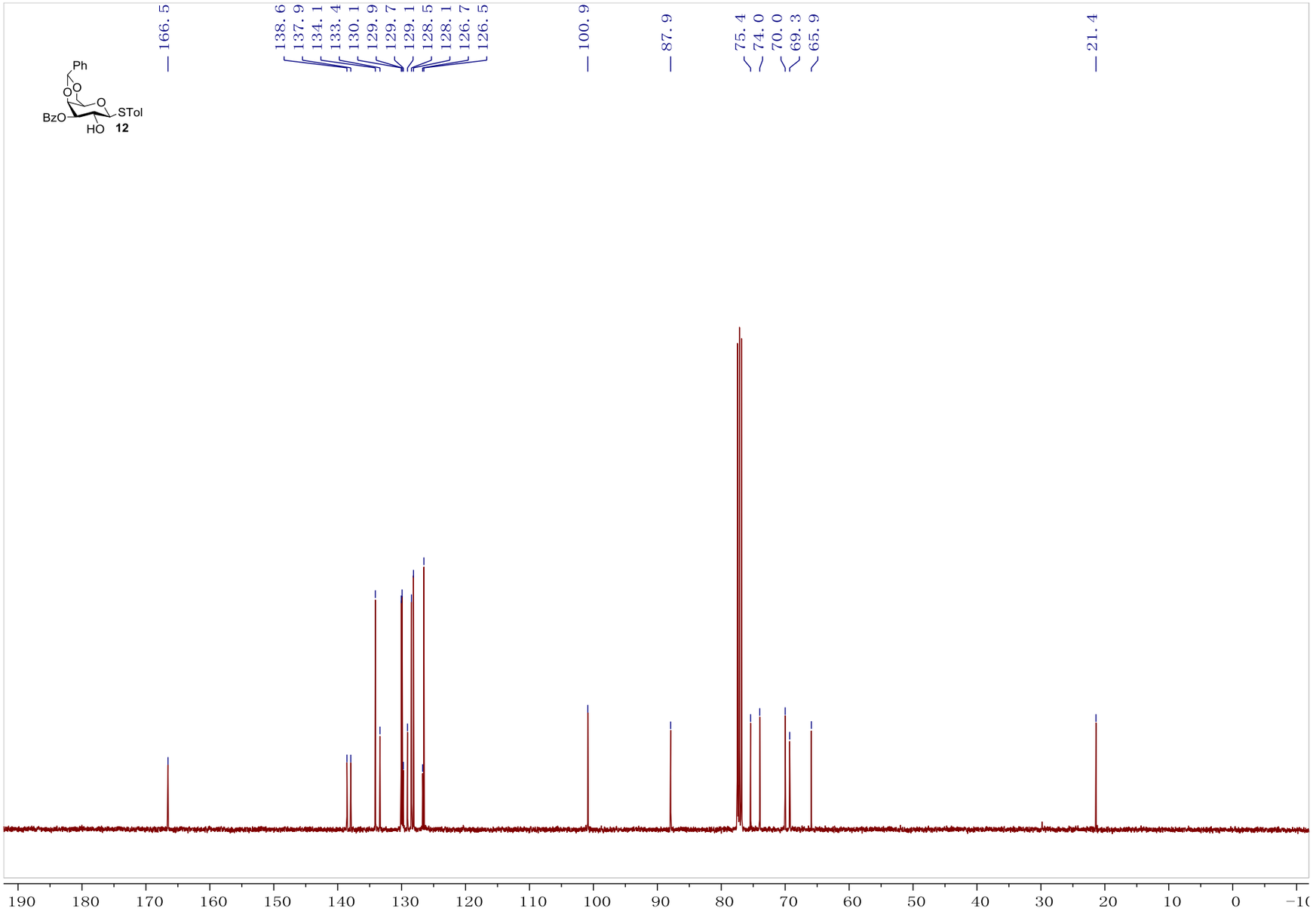


_p_-Tolyl-3-_O_-benzoyl-4,6-_O_-benzylidene-1-thio-_β_-D-galactopyranoside (12)

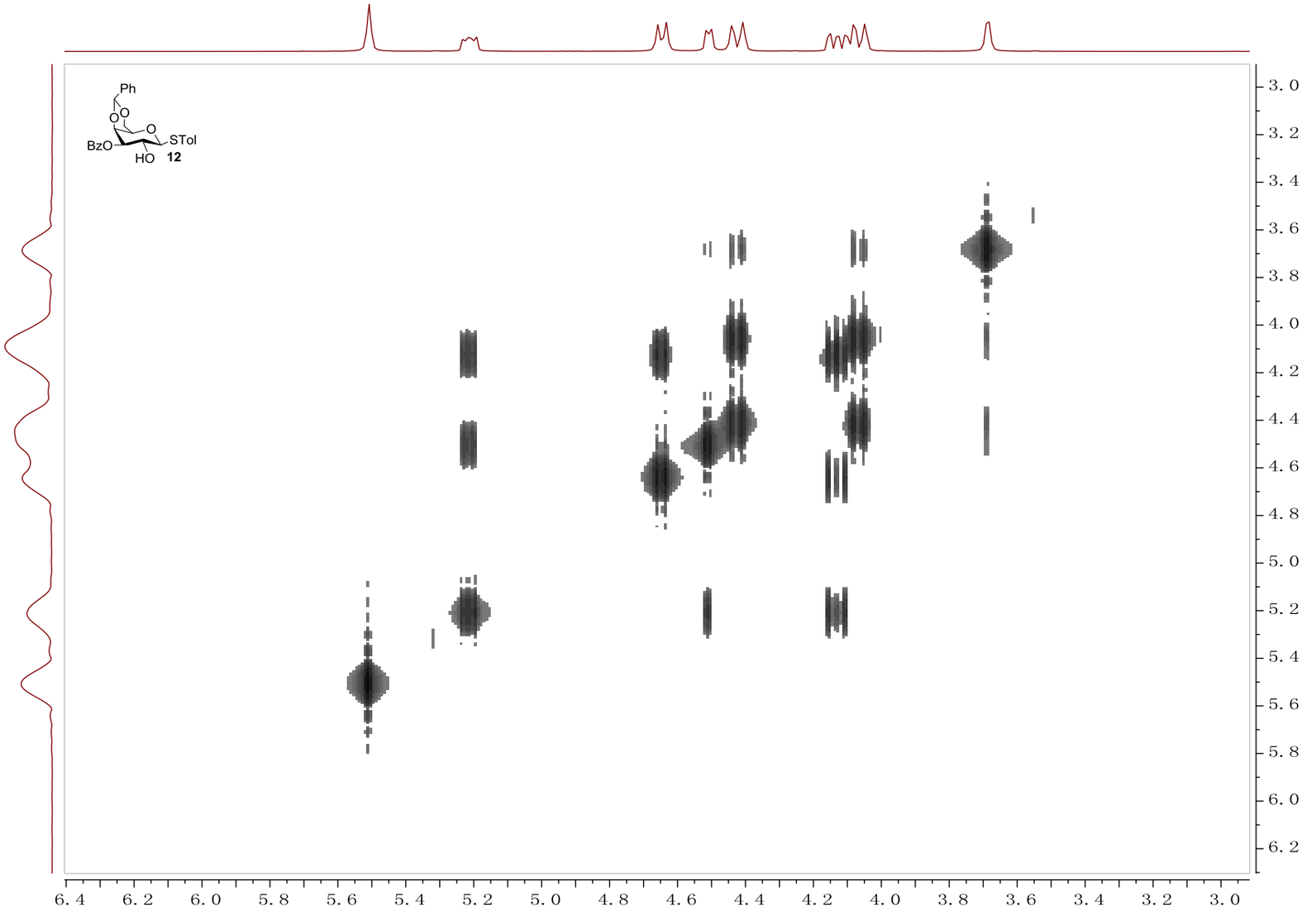
^{1}H-NMR of compound **12** ($CDCl_3$)



^{13}C-NMR of compound **12** ($CDCl_3$)

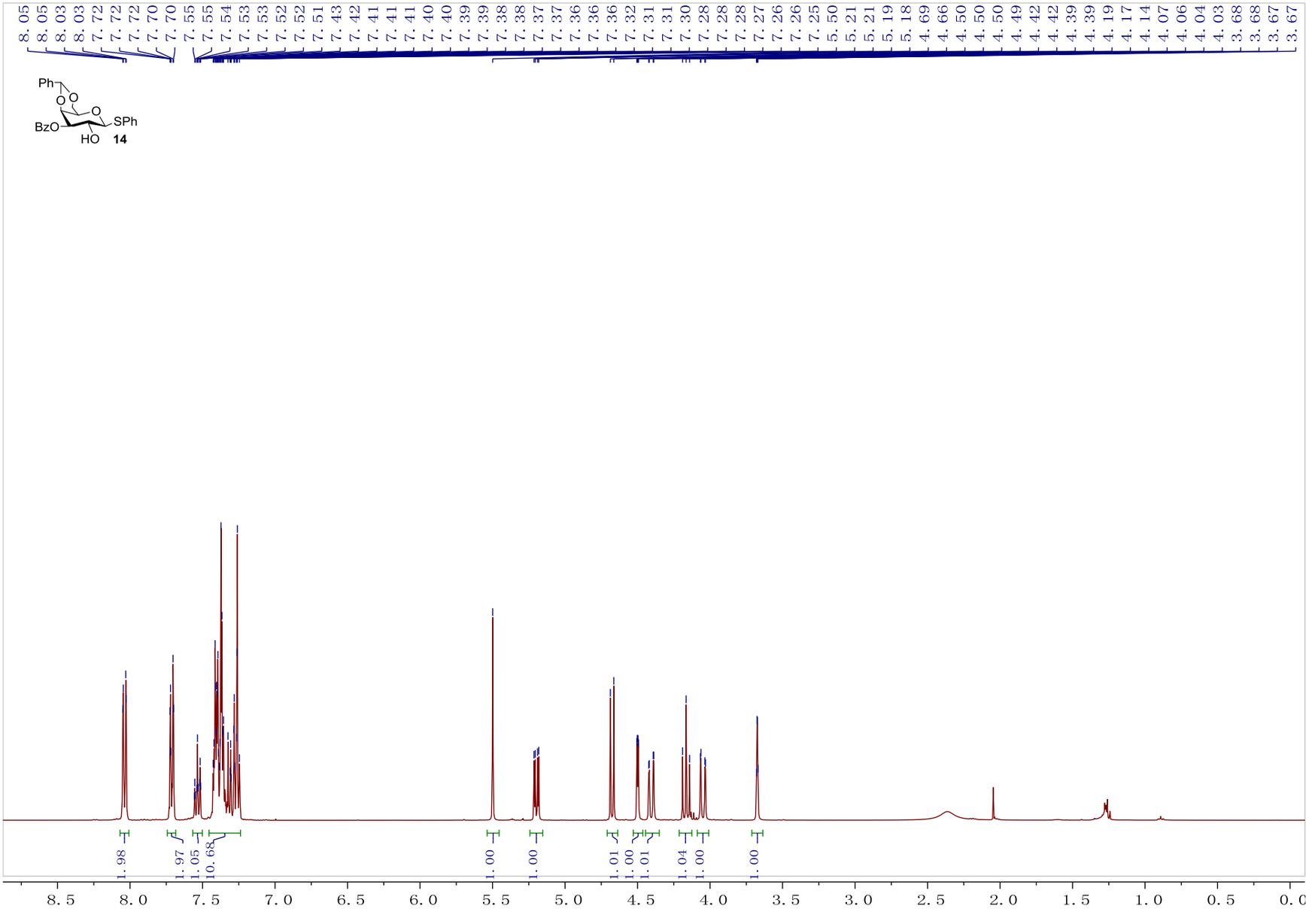


2D-COSY of compound **12** ($CDCl_3$)

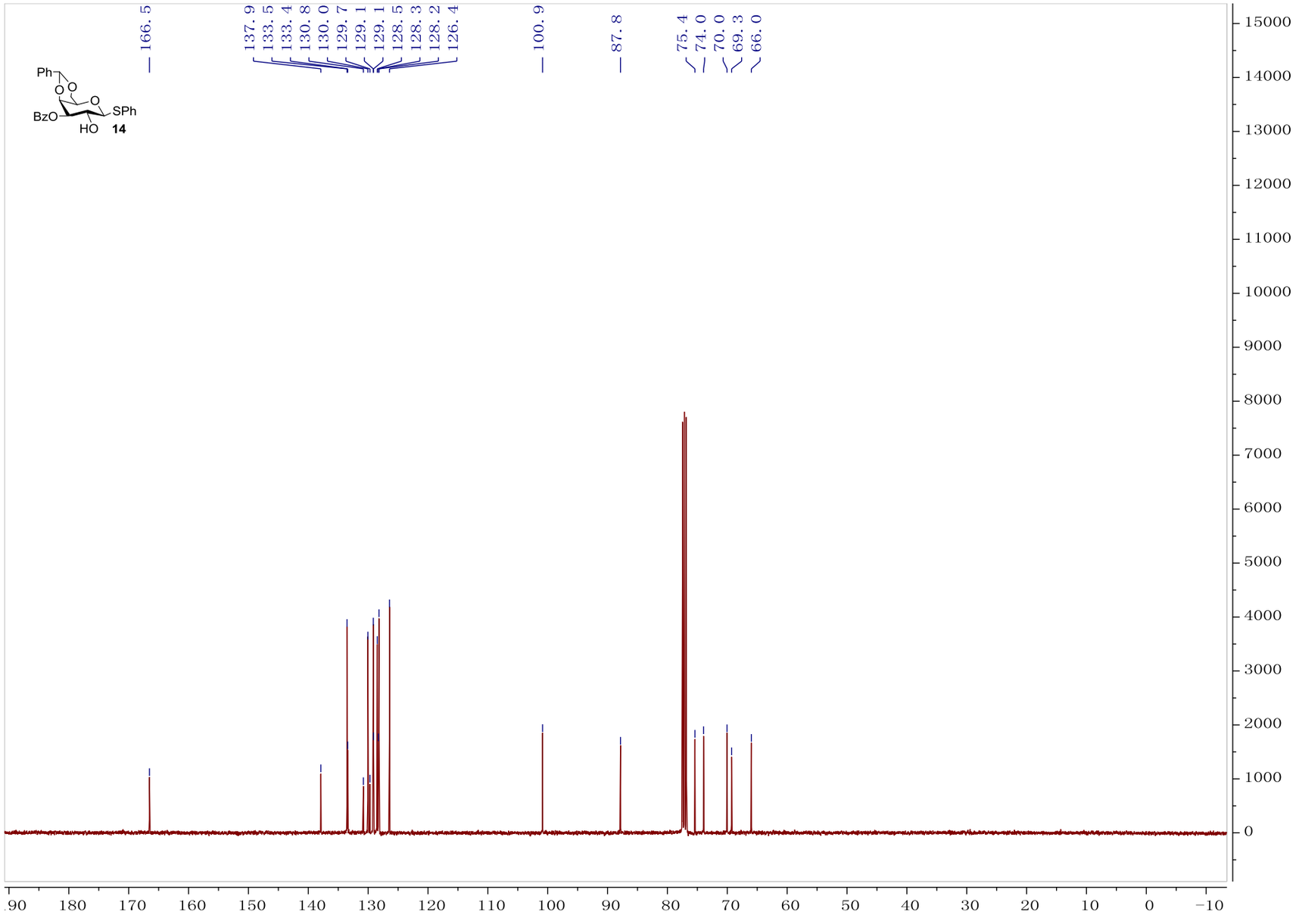


Phenyl-3-*O*-benzoyl-4,6-*O*-benzylidene-1-thio-*β*-D-galactopyranoside (14)

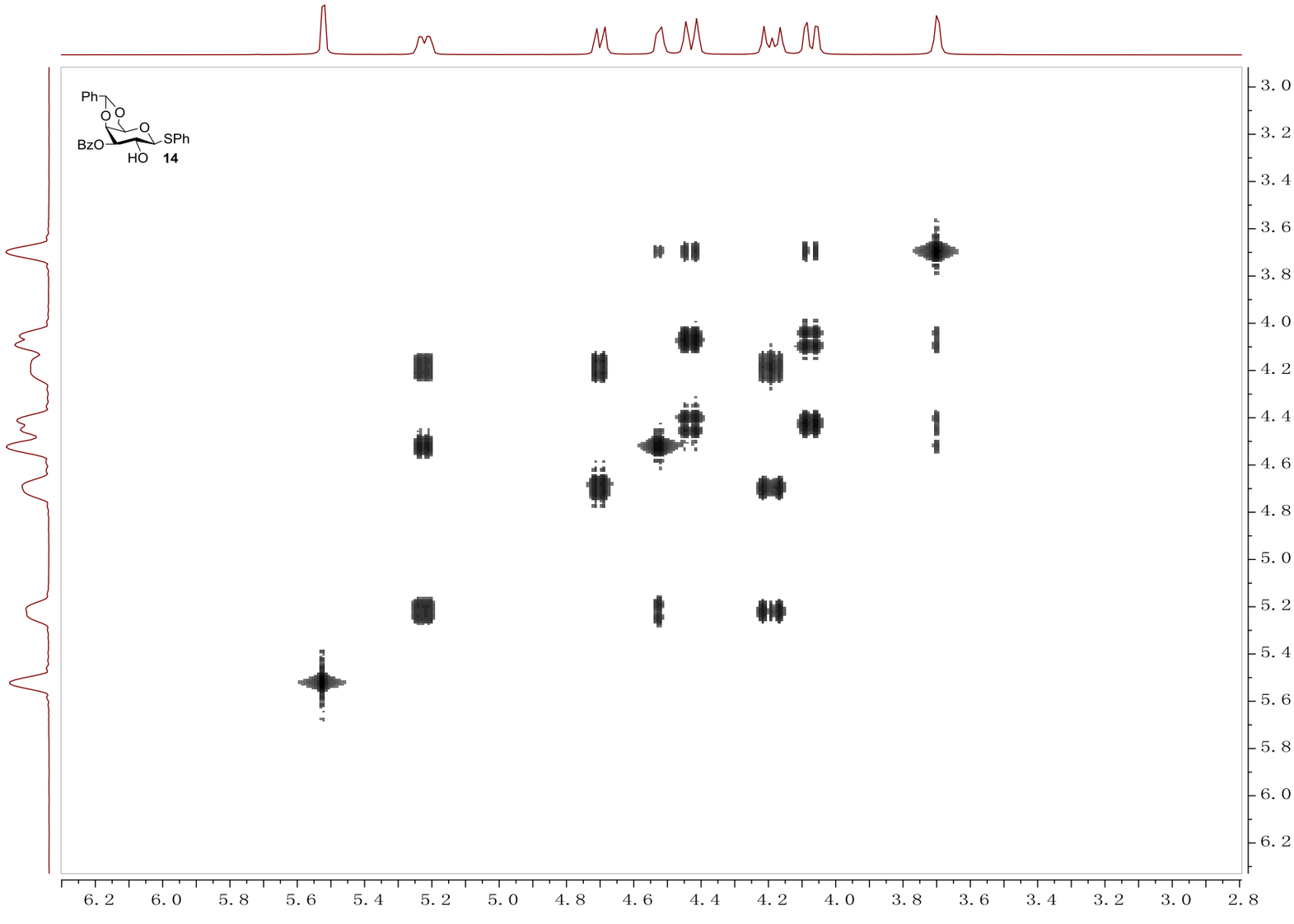
^{1}H-NMR of compound **14** ($CDCl_3$)



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

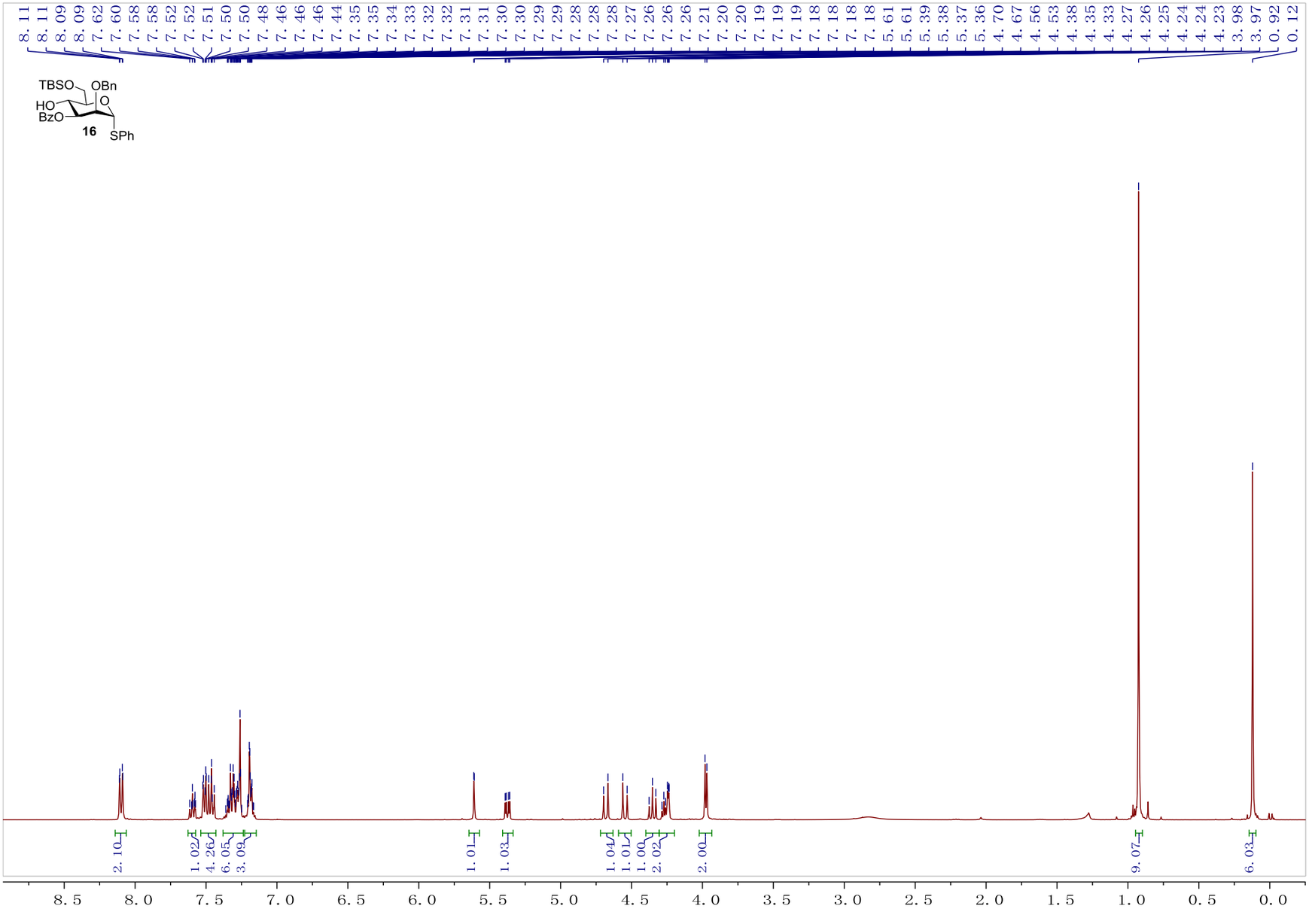


2D-COSY of compound **14** ($CDCl_3$)

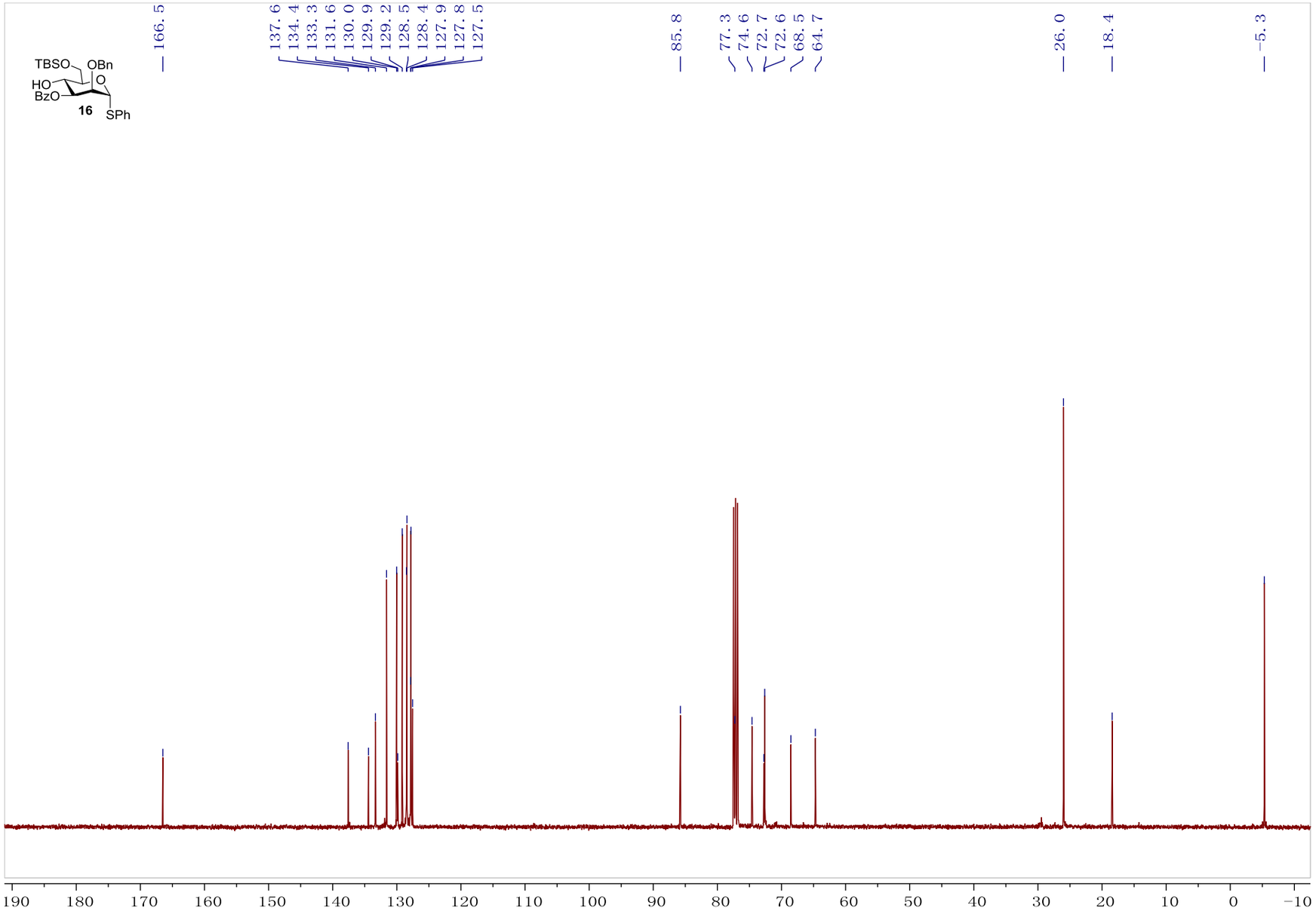


Phenyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-2-*O*-benzyl-1-thio-*α*-D-mannopyranoside (16)

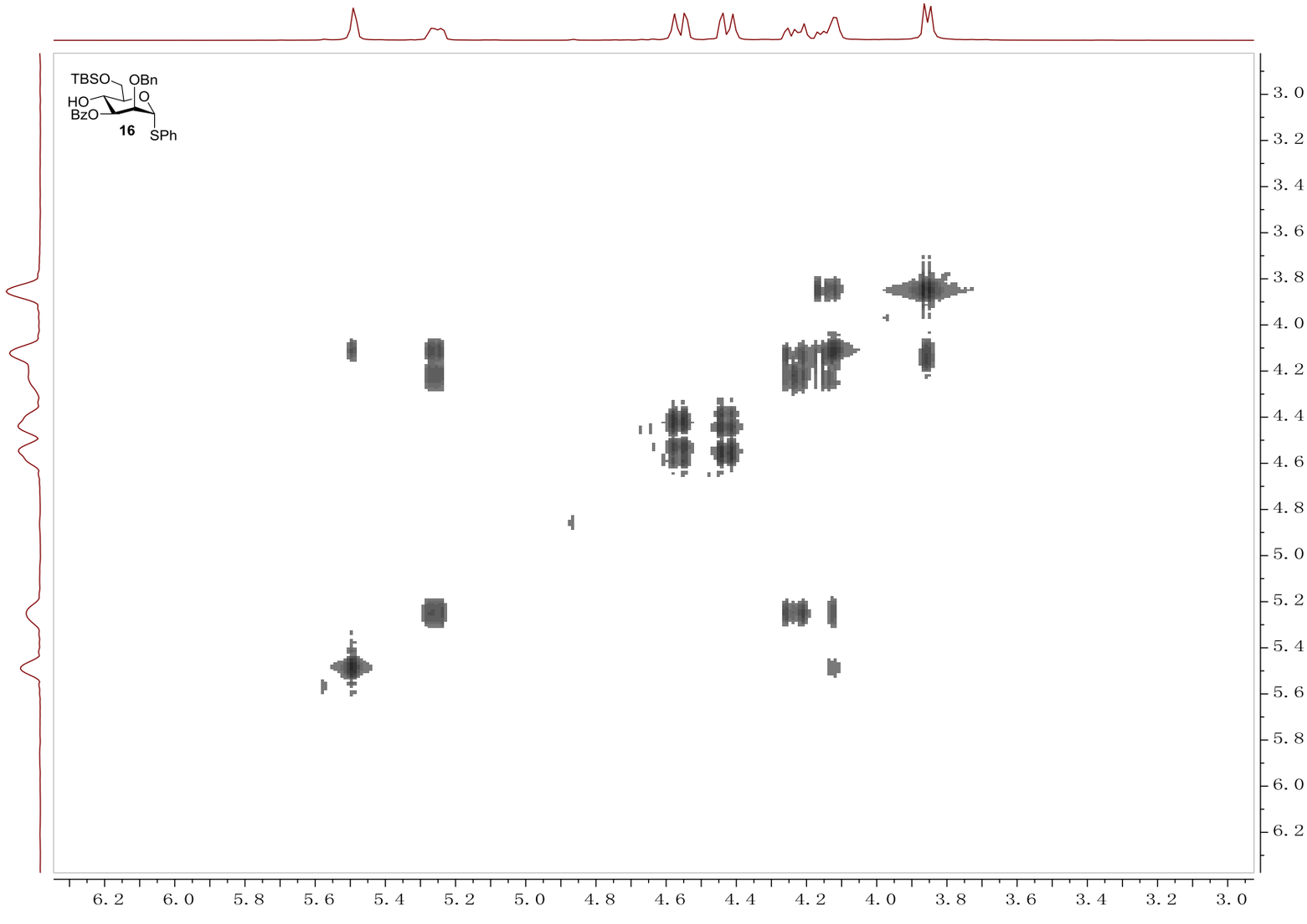
^{1}H-NMR of compound **16** ($CDCl_3$)



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

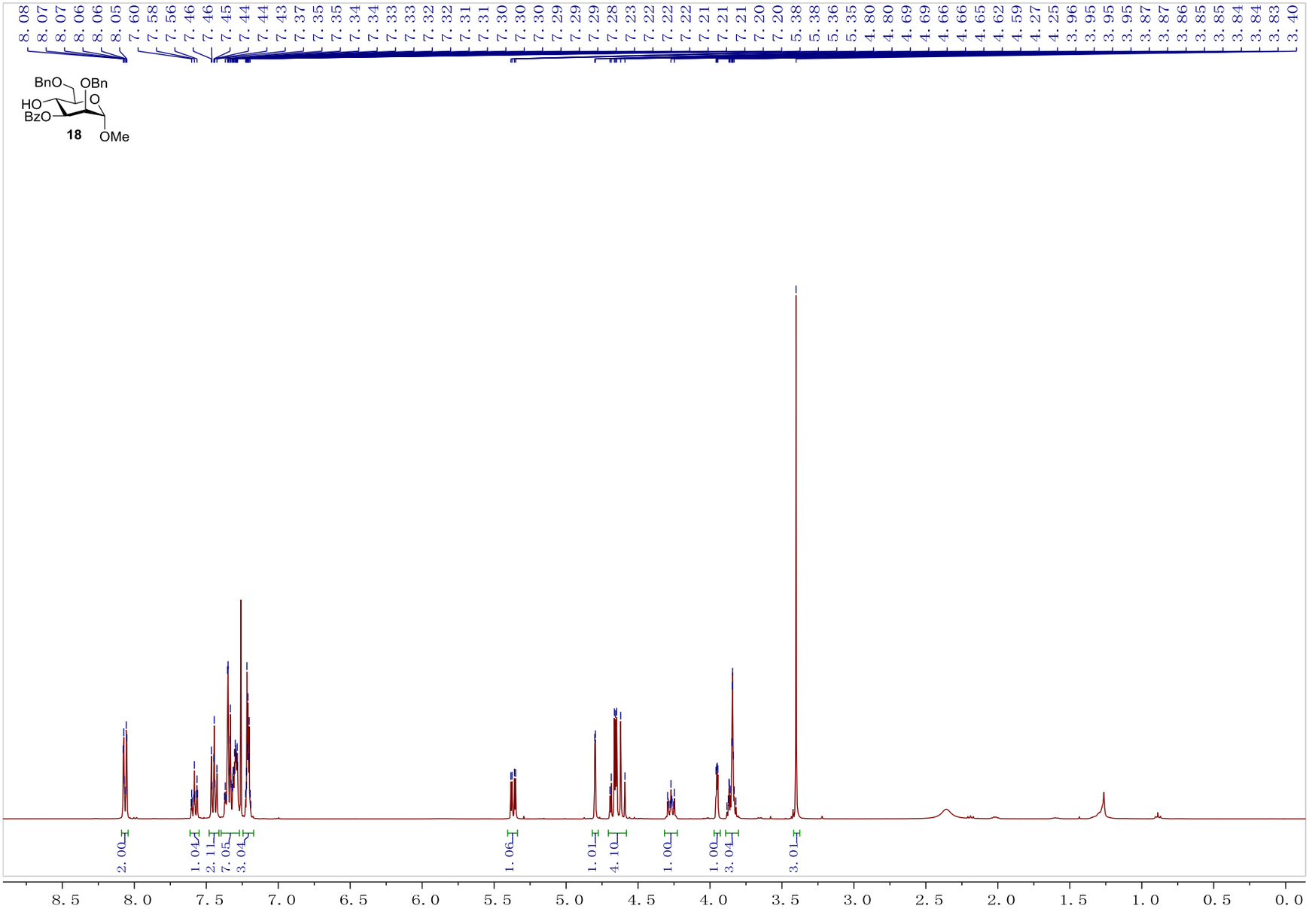


2D-COSY of compound **16** ($CDCl_3$)

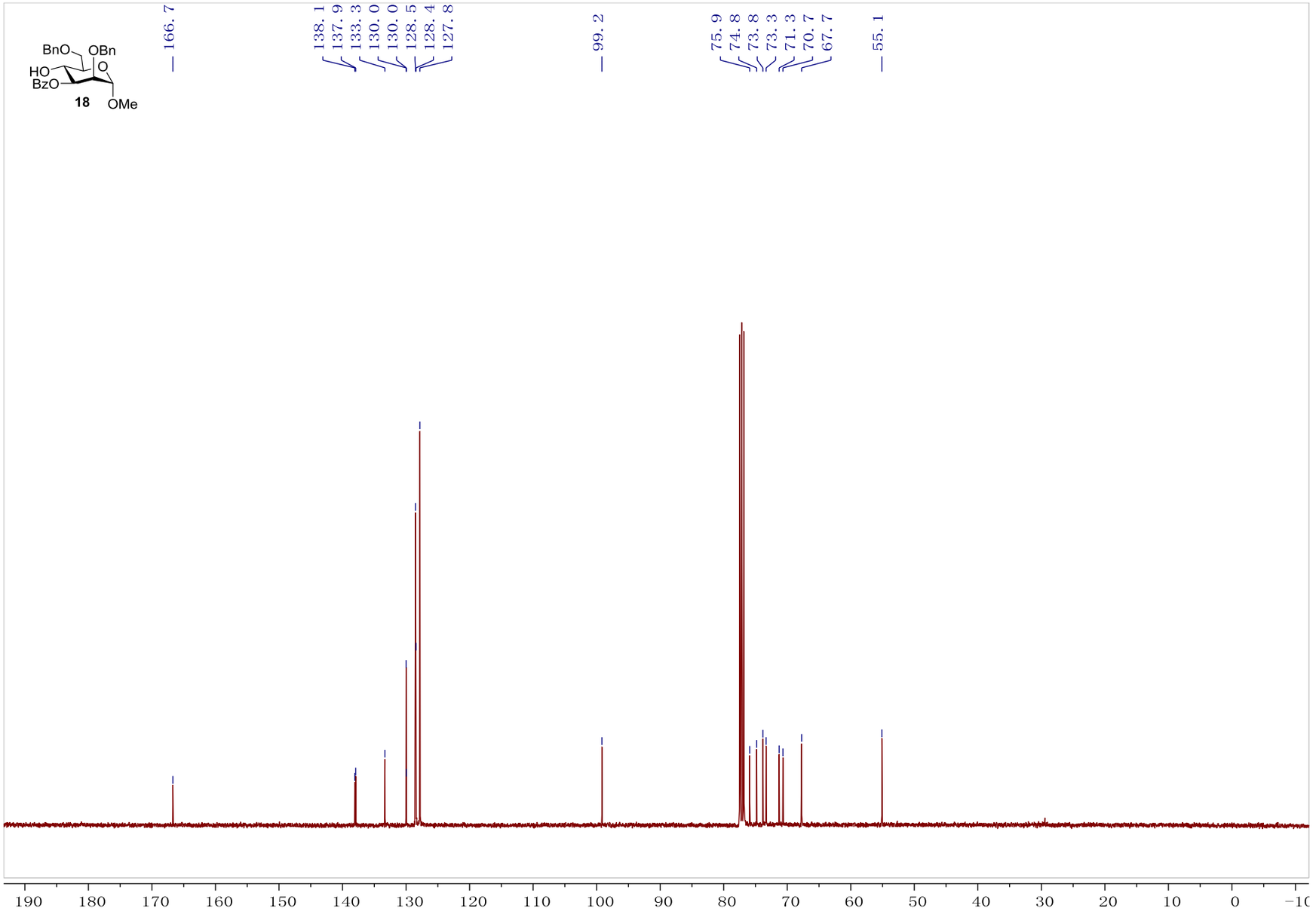


Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*α*-D-mannopyranoside (18)

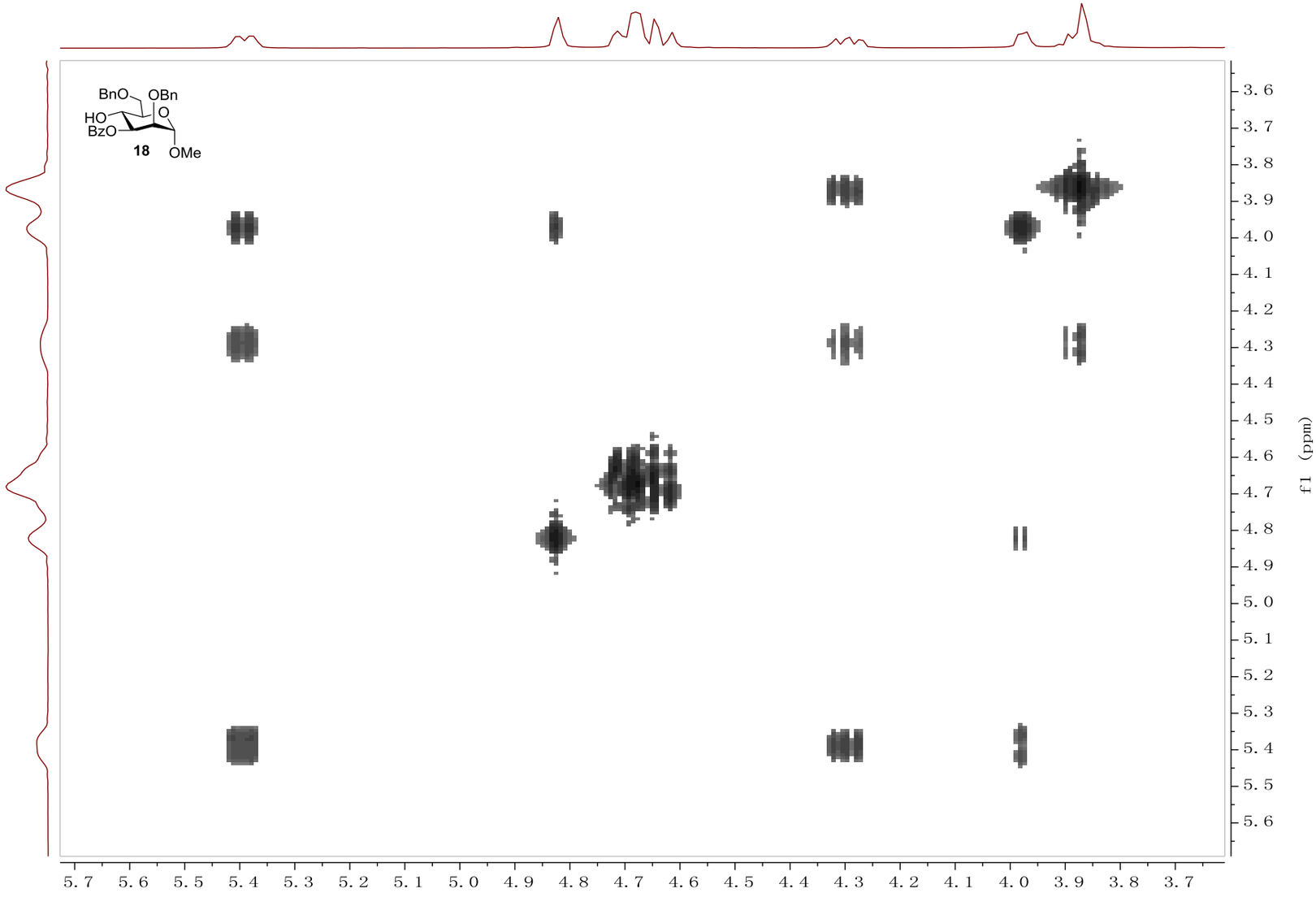
^{1}H-NMR of compound **18** ($CDCl_3$)



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

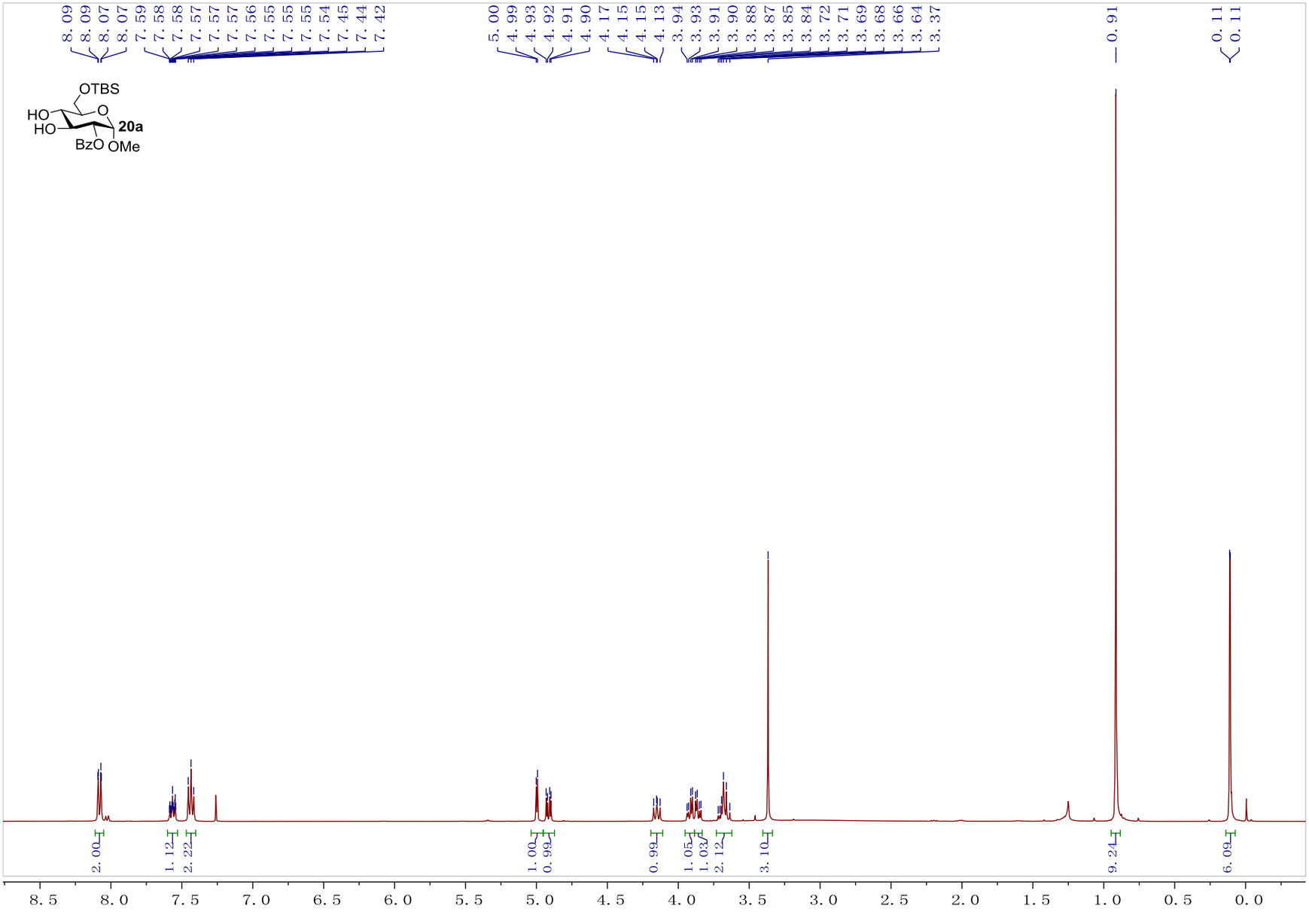


2D-COSY of compound **18** ($CDCl_3$)



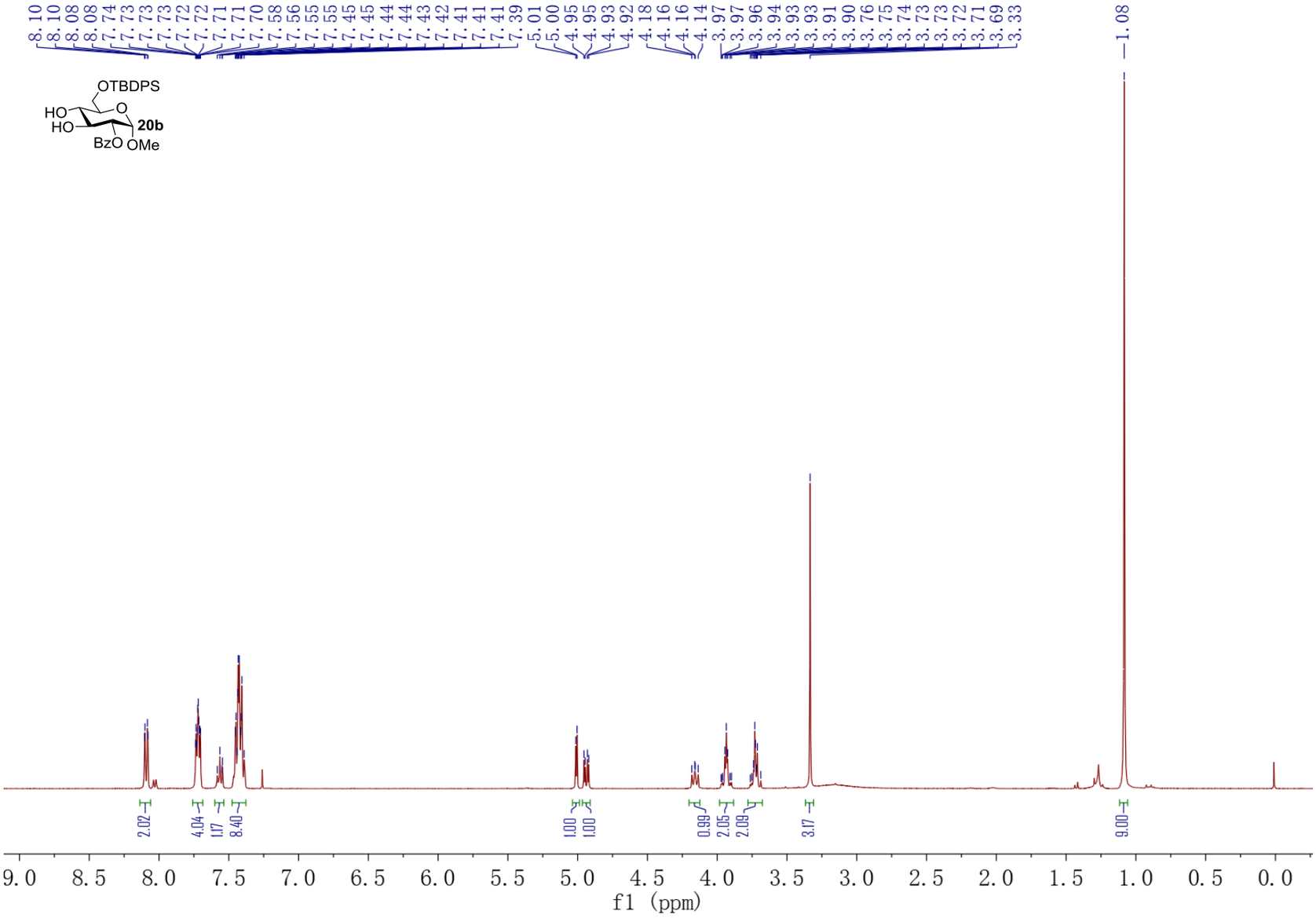
Methyl-2-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-glucopyranoside (20a)

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



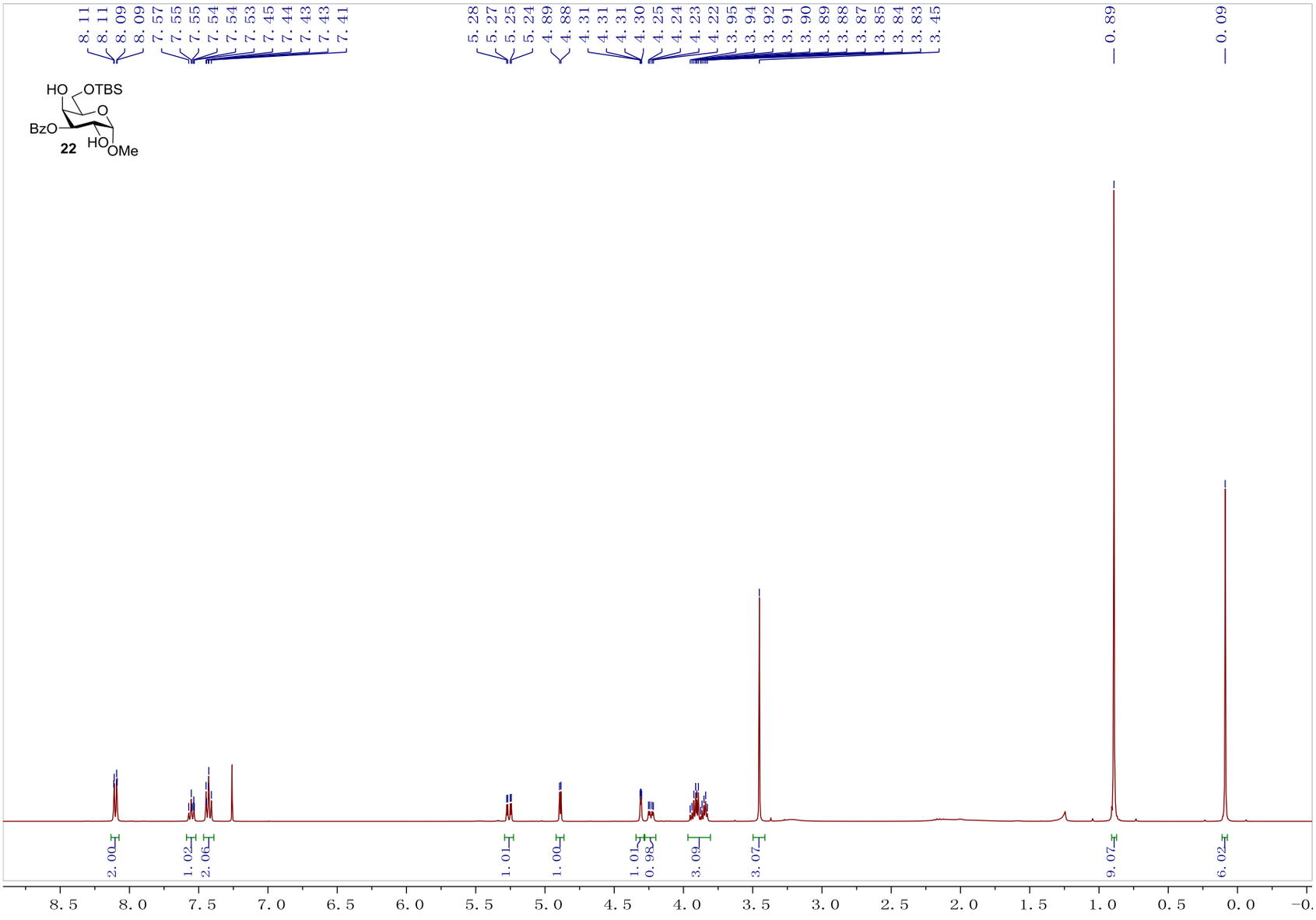
Methyl-2-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-*α*-D-glucopyranoside (20b)

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



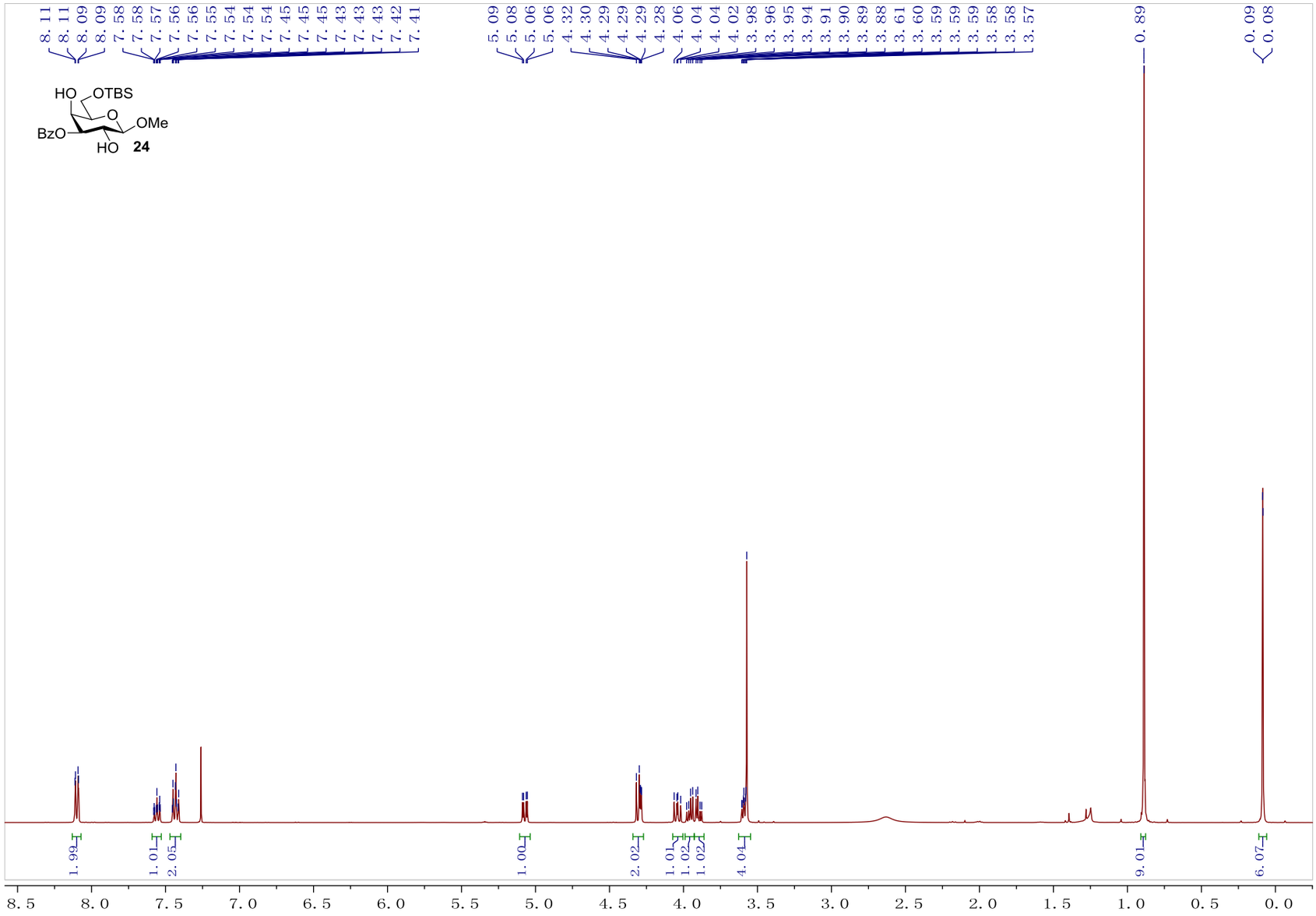
Methyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*α*-D-galactopyranoside (22)

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



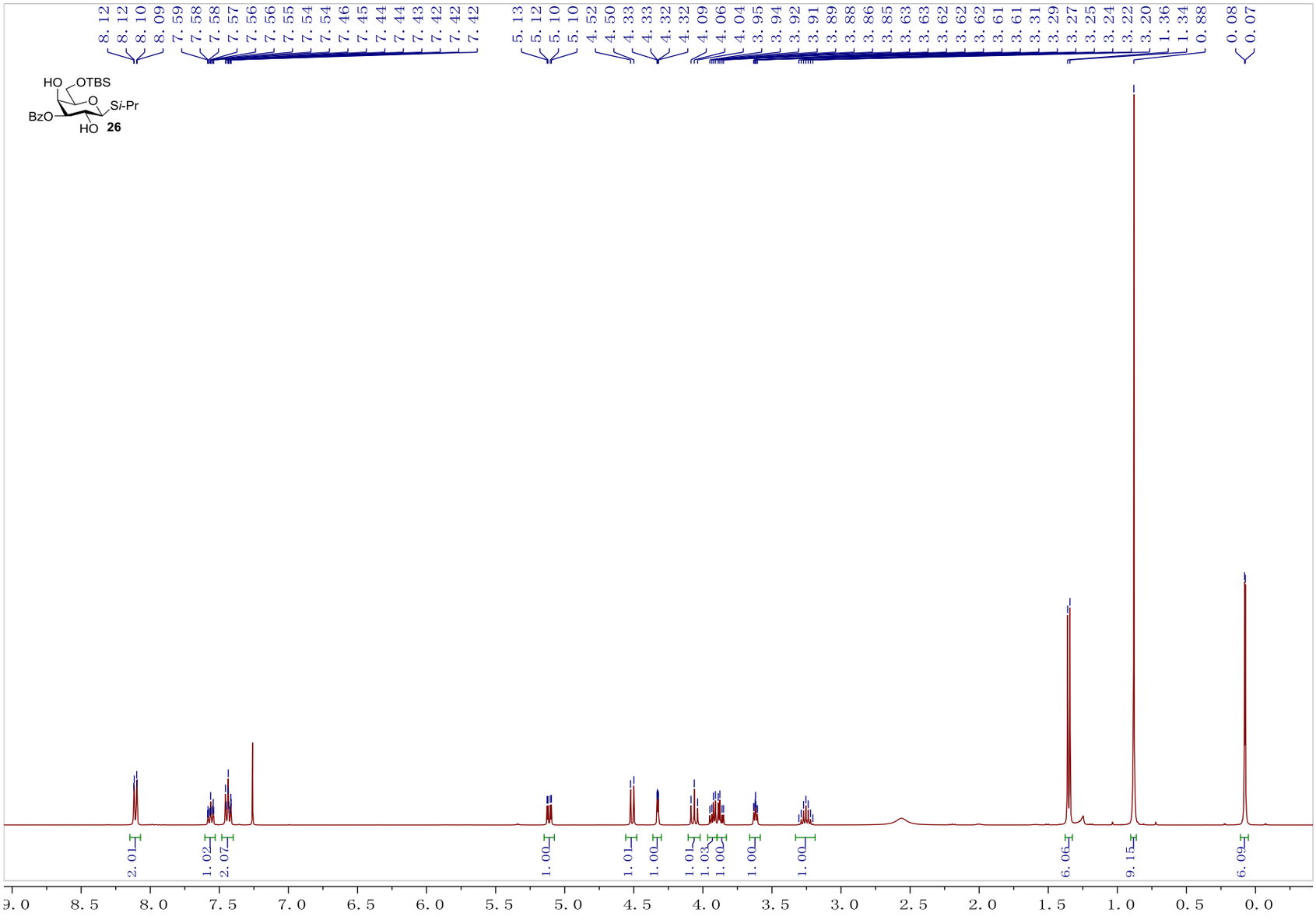
Methyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24)

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



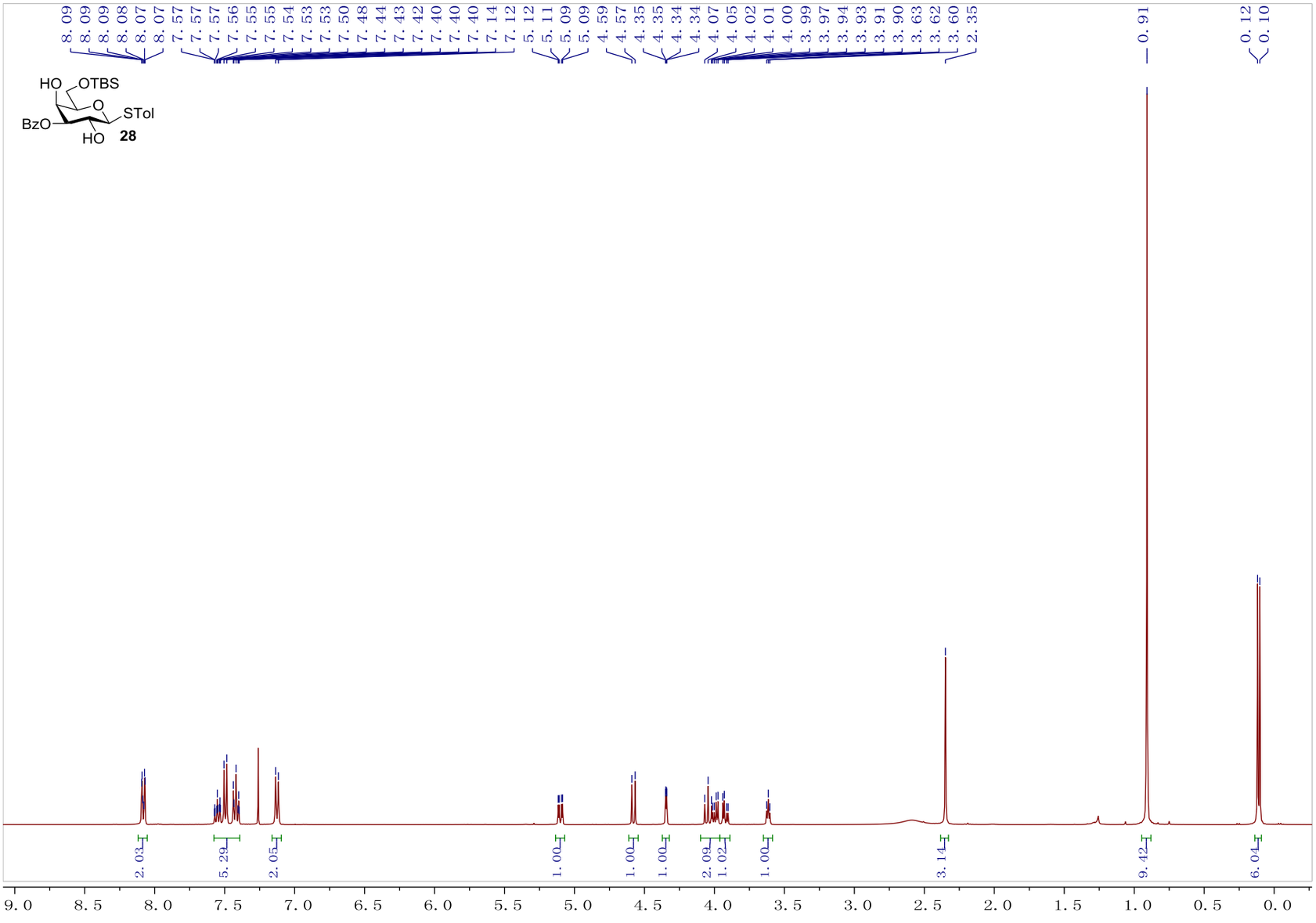
Isopropylthio-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (26)

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



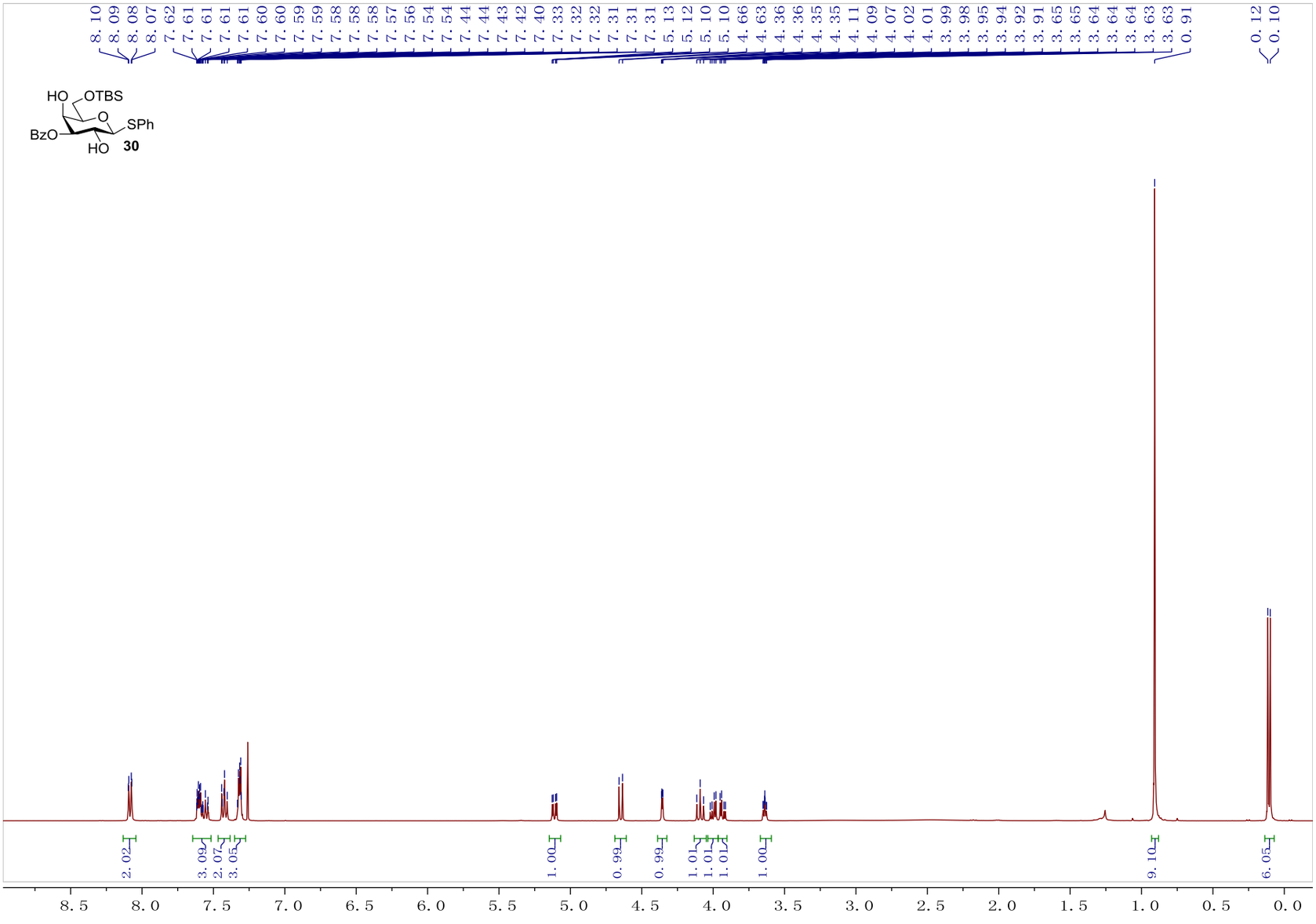
_p_-Tolyl-3-_O_-benzoyl-6-_O_-(_tert_-butyldimethylsilyl)-1-thio-_β_-D-galactopyranoside (28)

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



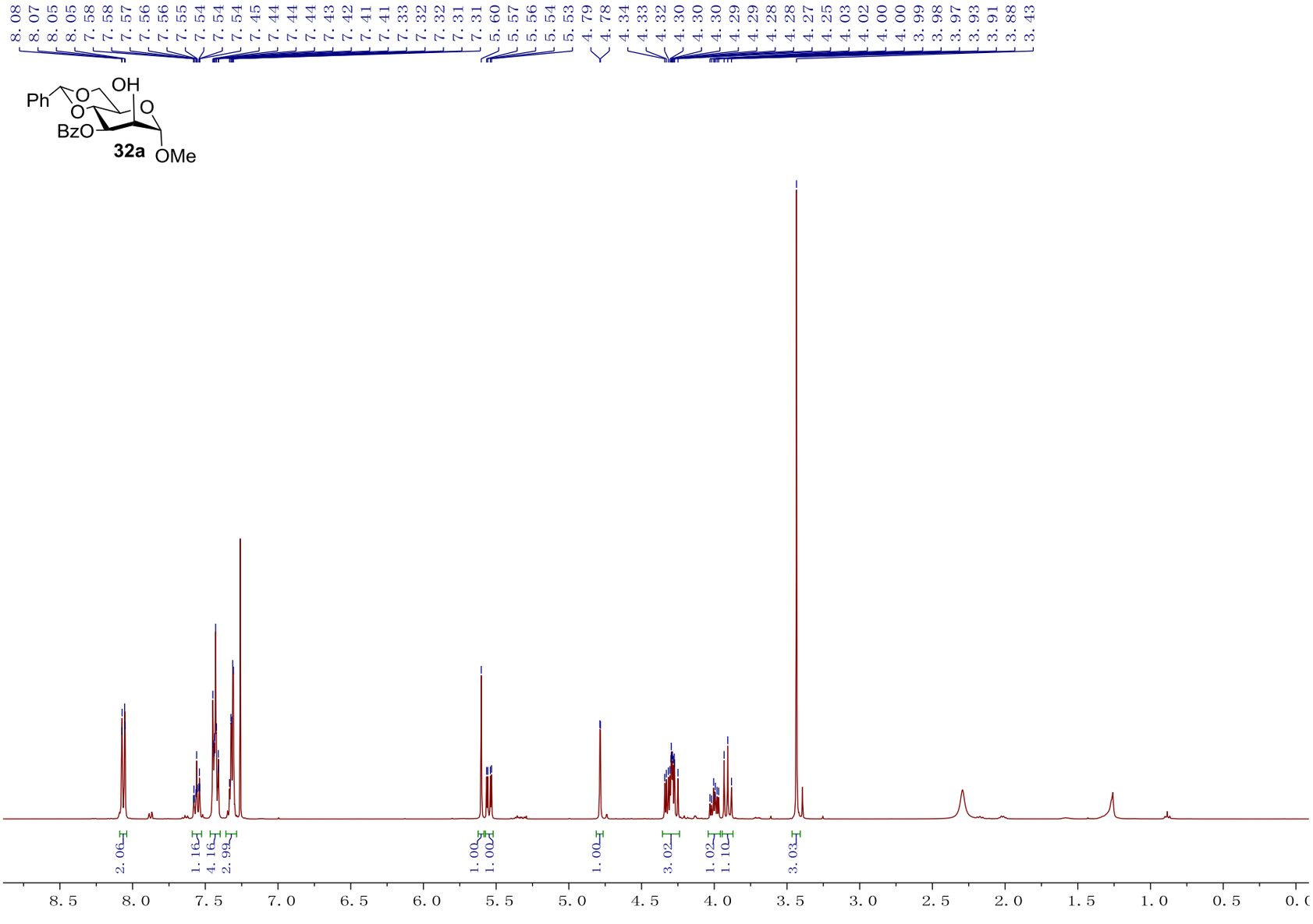
Phenyl-3-*O*-benzoyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-galactopyranoside (30)

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



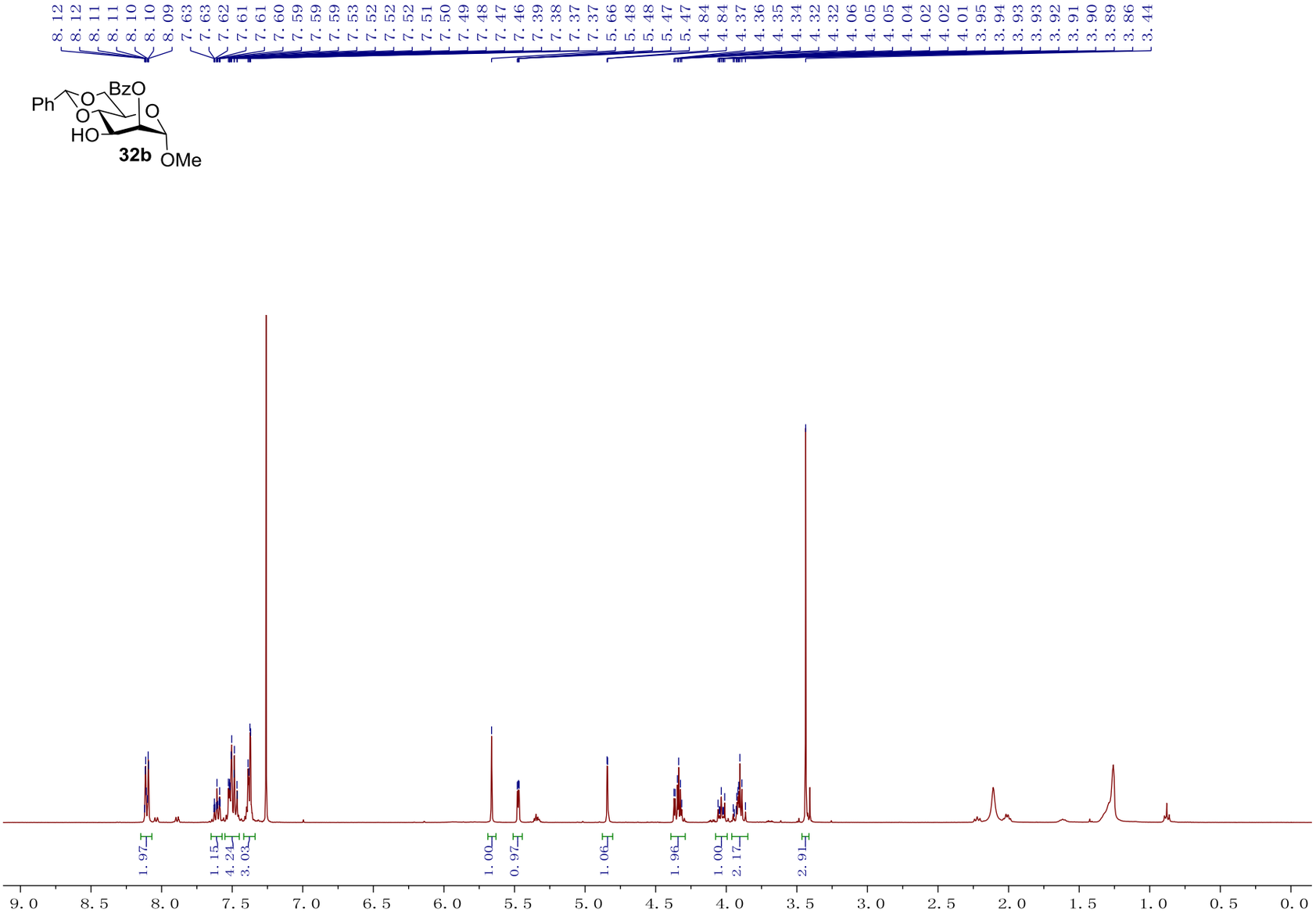
Methyl-3-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (32a)

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



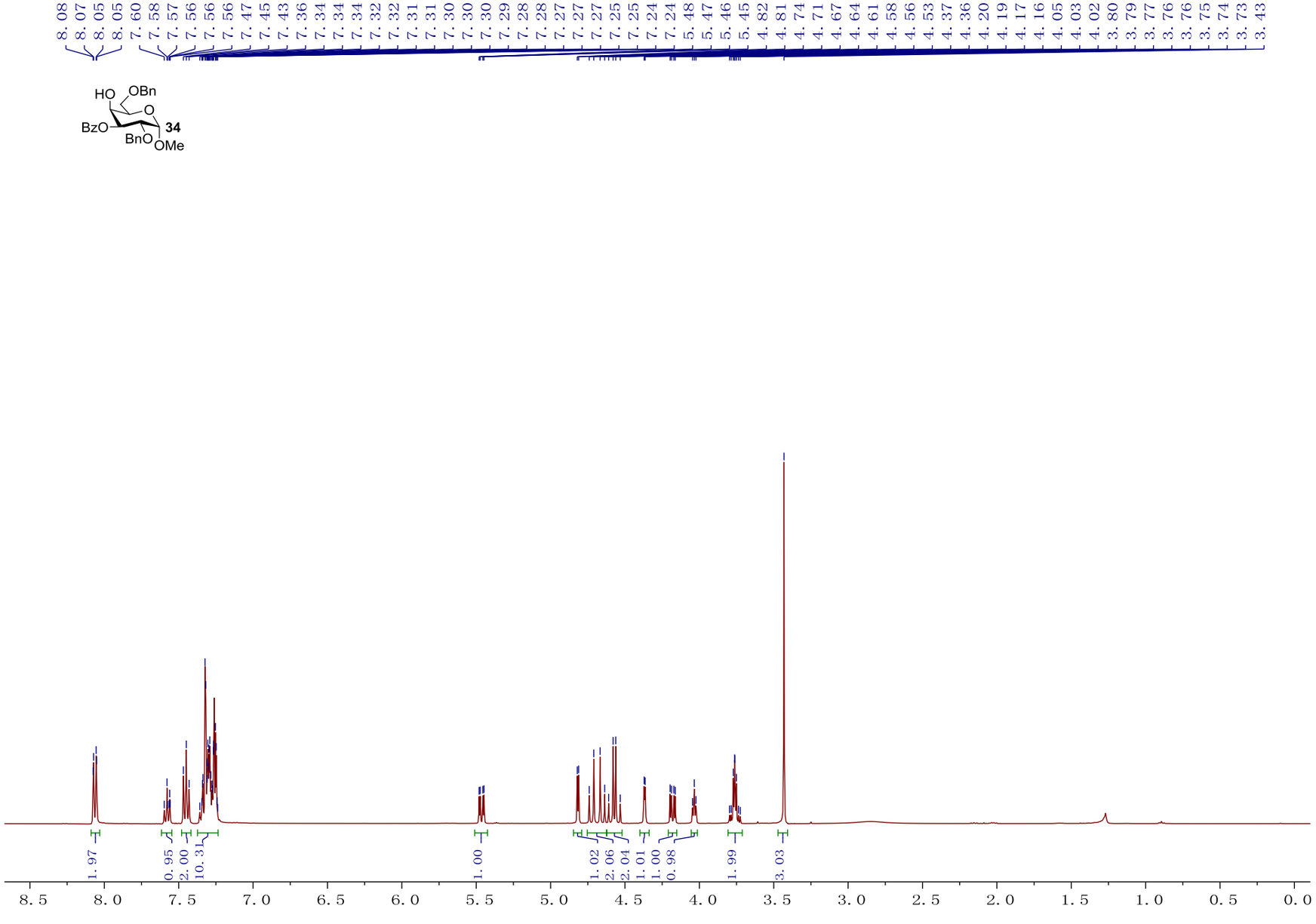
Methyl-2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-mannopyranoside (32b)

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

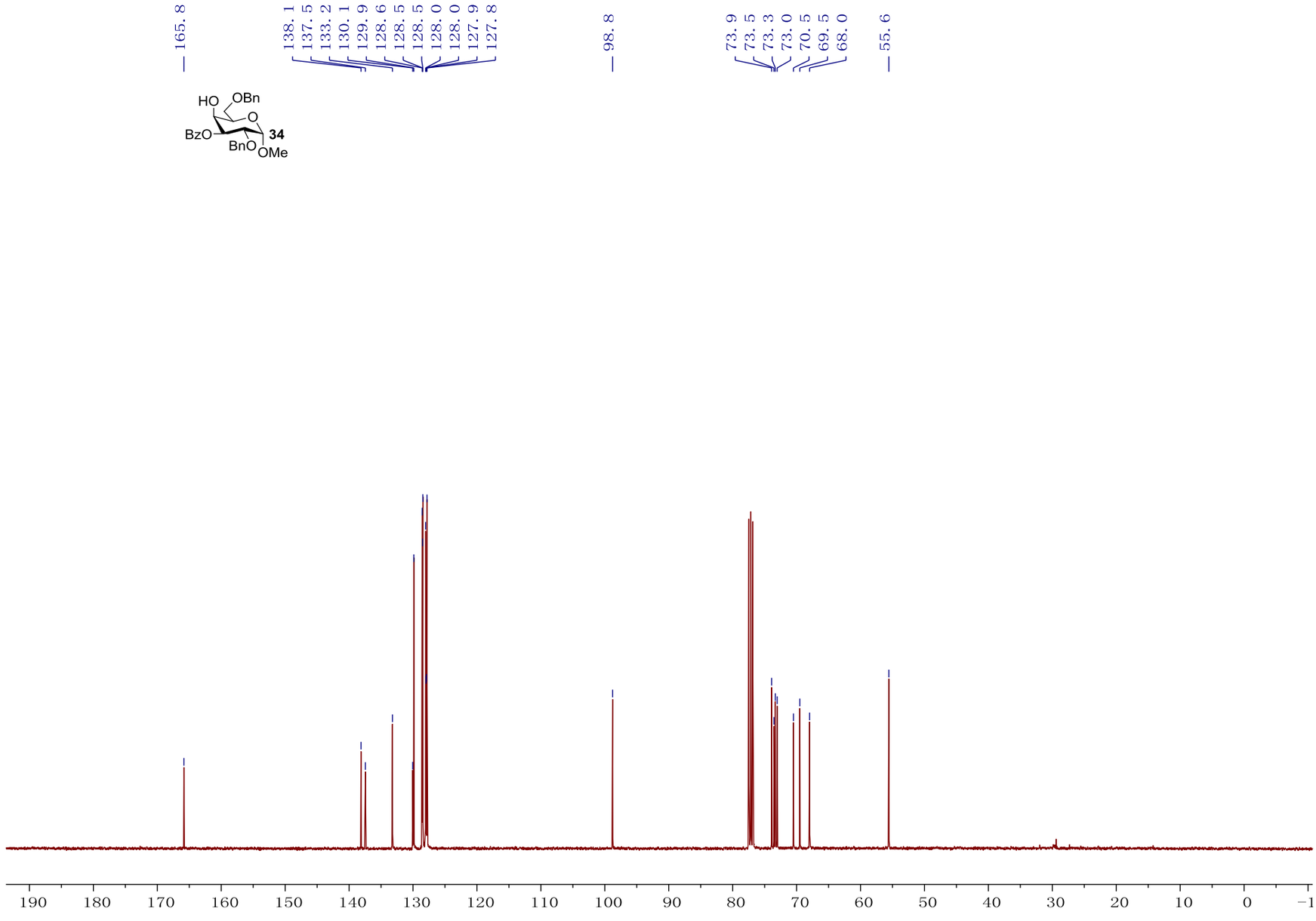


Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*α*-D-galactopyranoside (34)

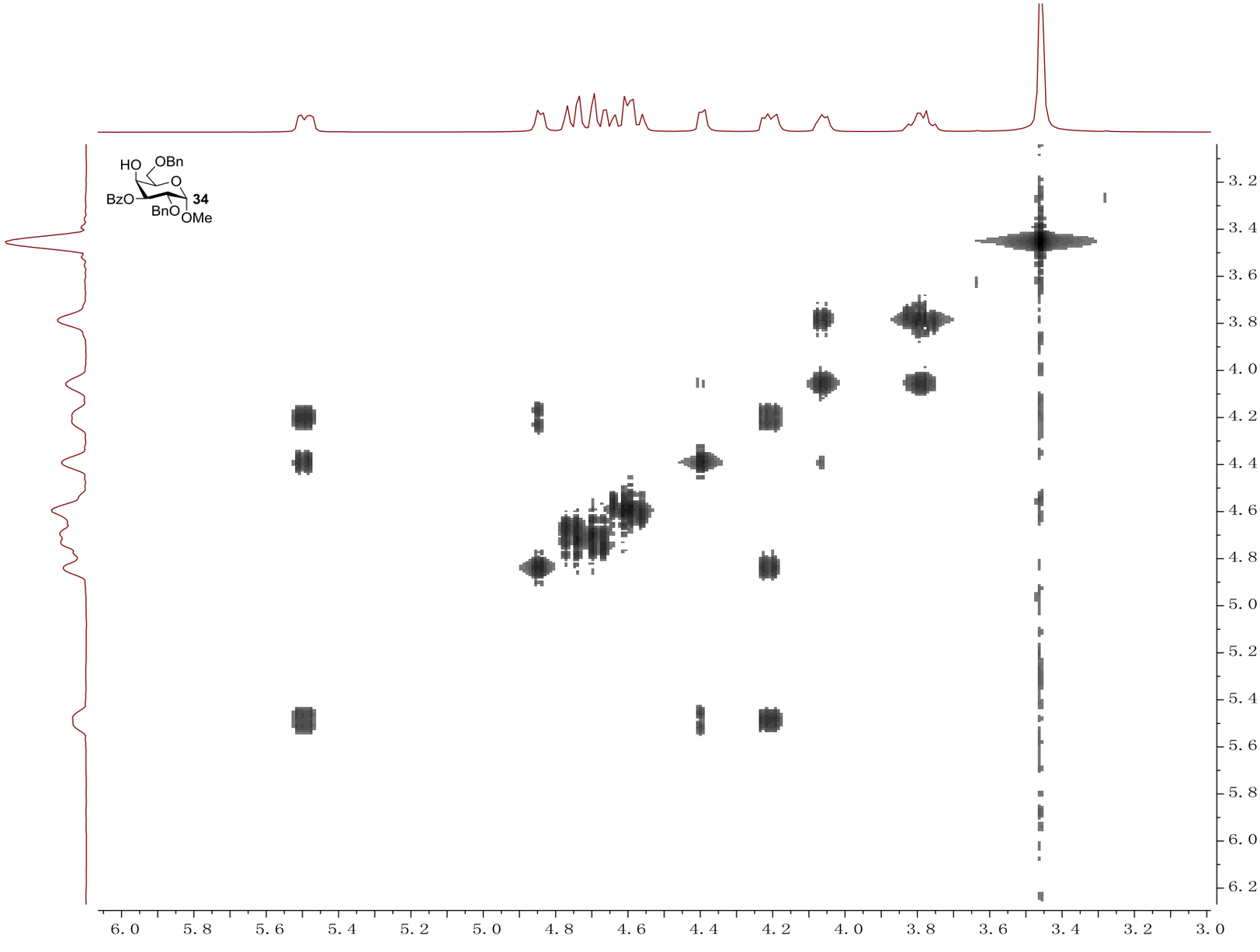
^{1}H-NMR of compound **34** ($CDCl_3$)



^{13}C-NMR of compound **34** ($CDCl_3$)

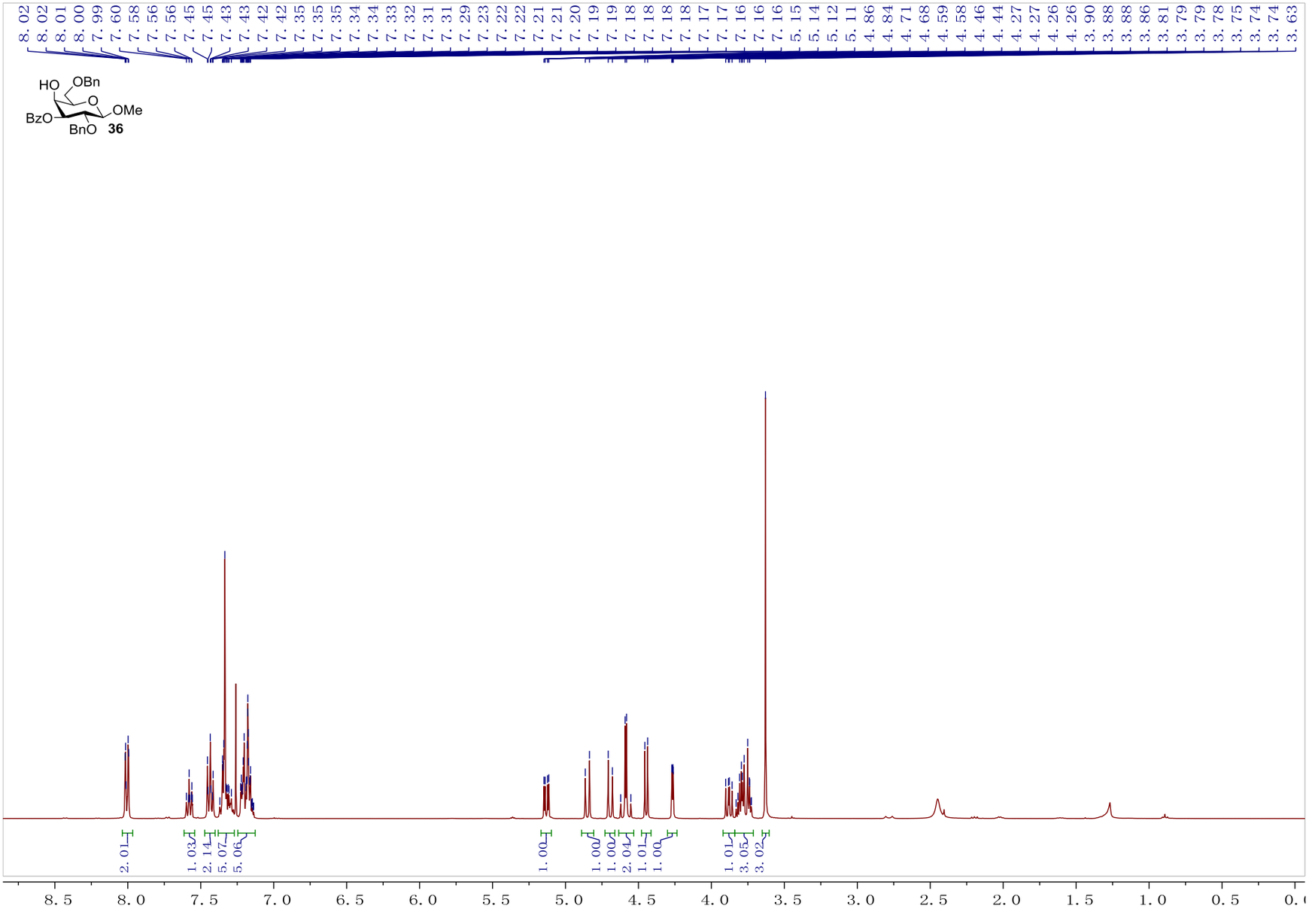


2D-COSY of compound **34** ($CDCl_3$)



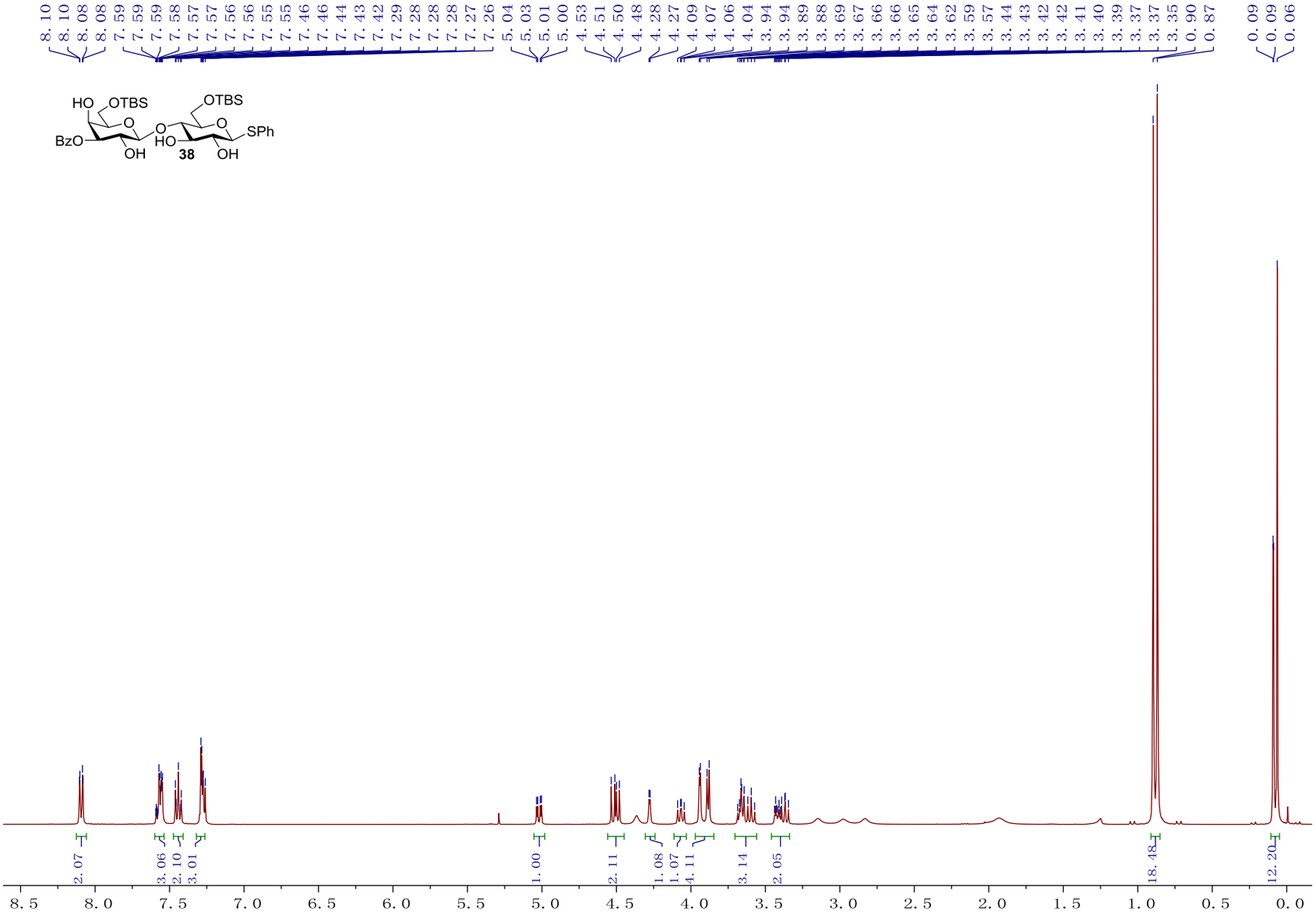
Methyl-3-*O*-benzoyl-2,6-di-*O*-benzyl-*β*-D-galactopyranoside (36)

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



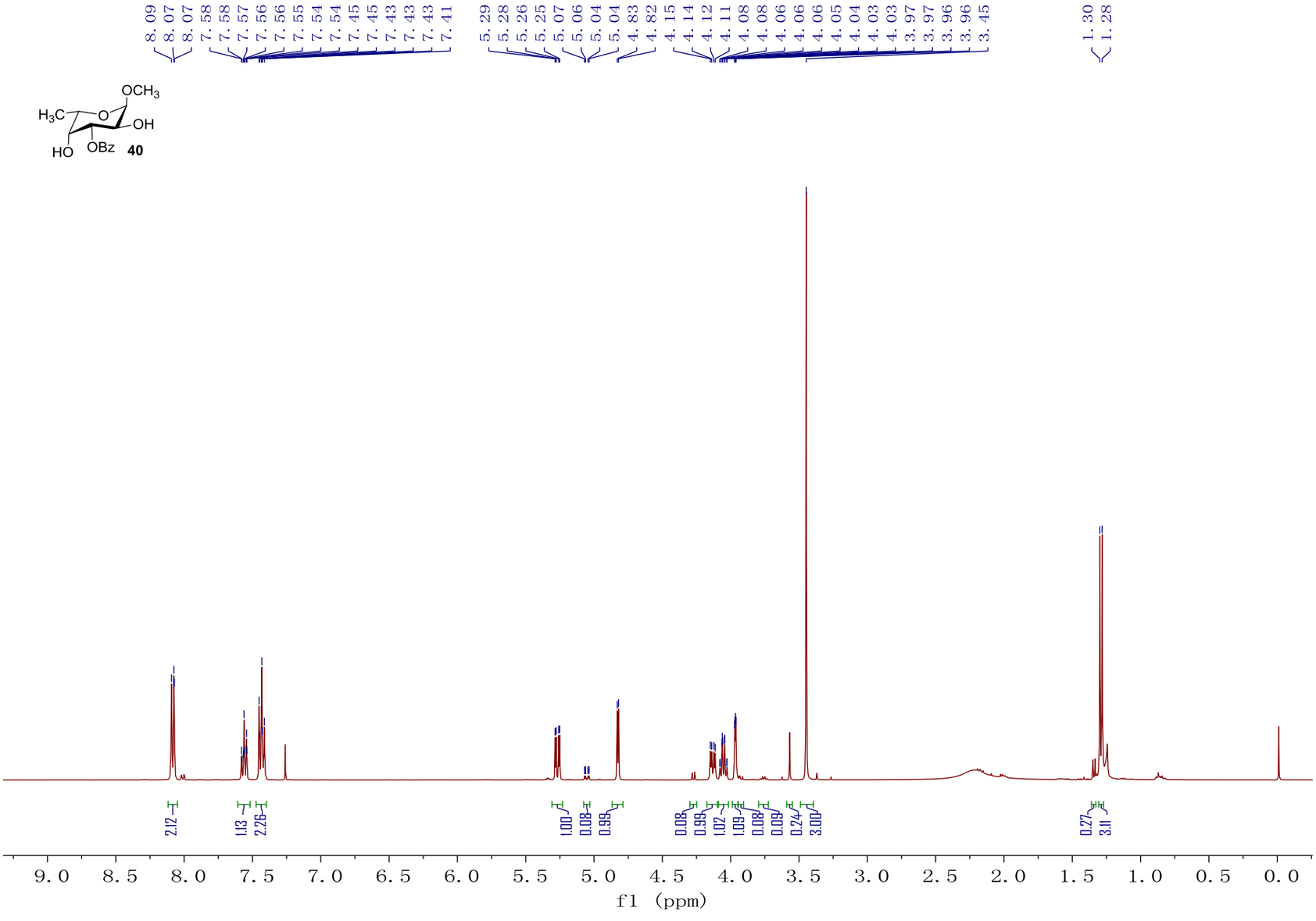
Phenyl-3'-benzoyl-6,6'-di-*O*-(*tert*-butyldimethylsilyl)-1-thio-*β*-D-lactoside (38)

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



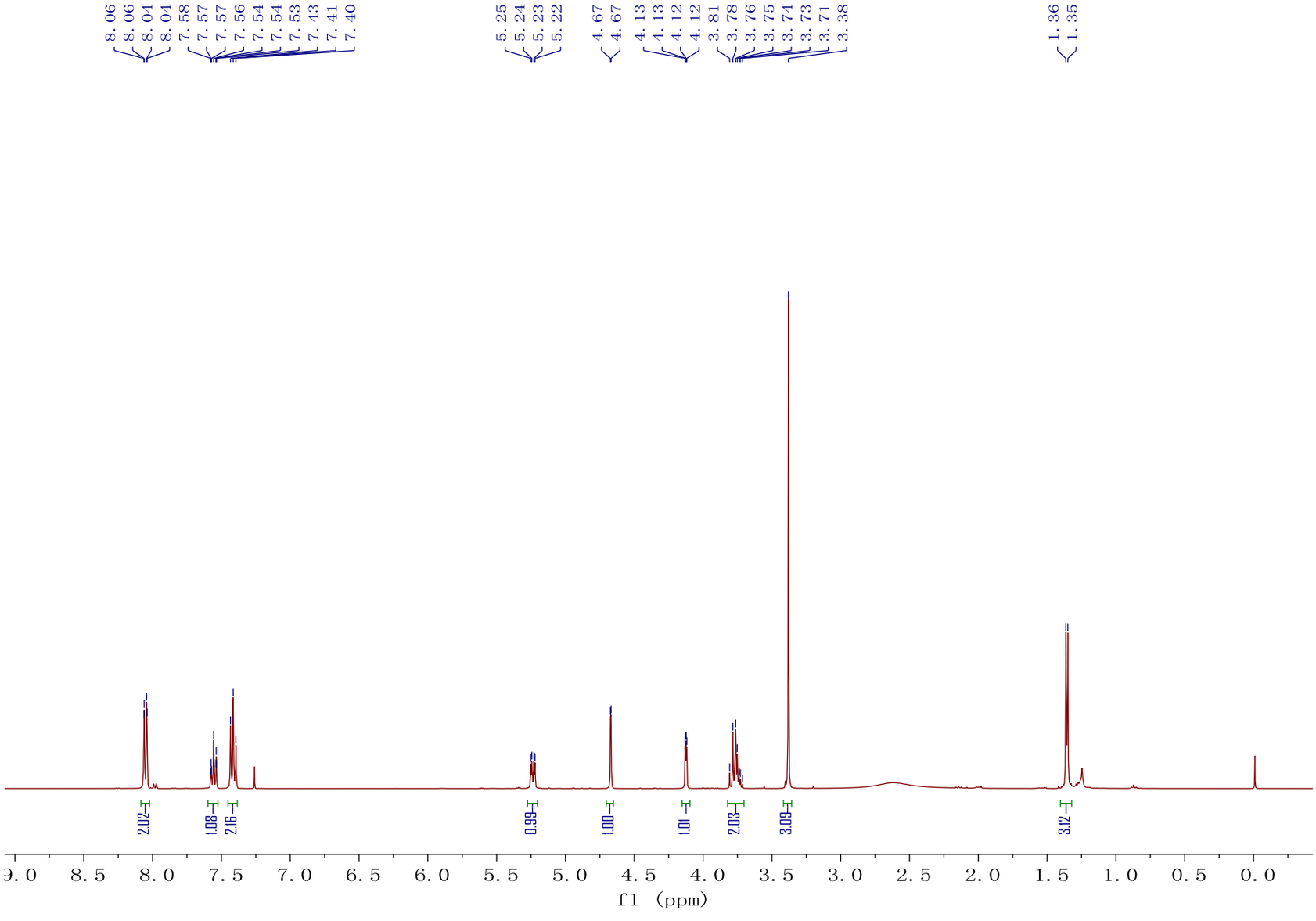
Methyl-3-*O*-benzoyl-*α*-*L*-fucopyranoside (40)

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



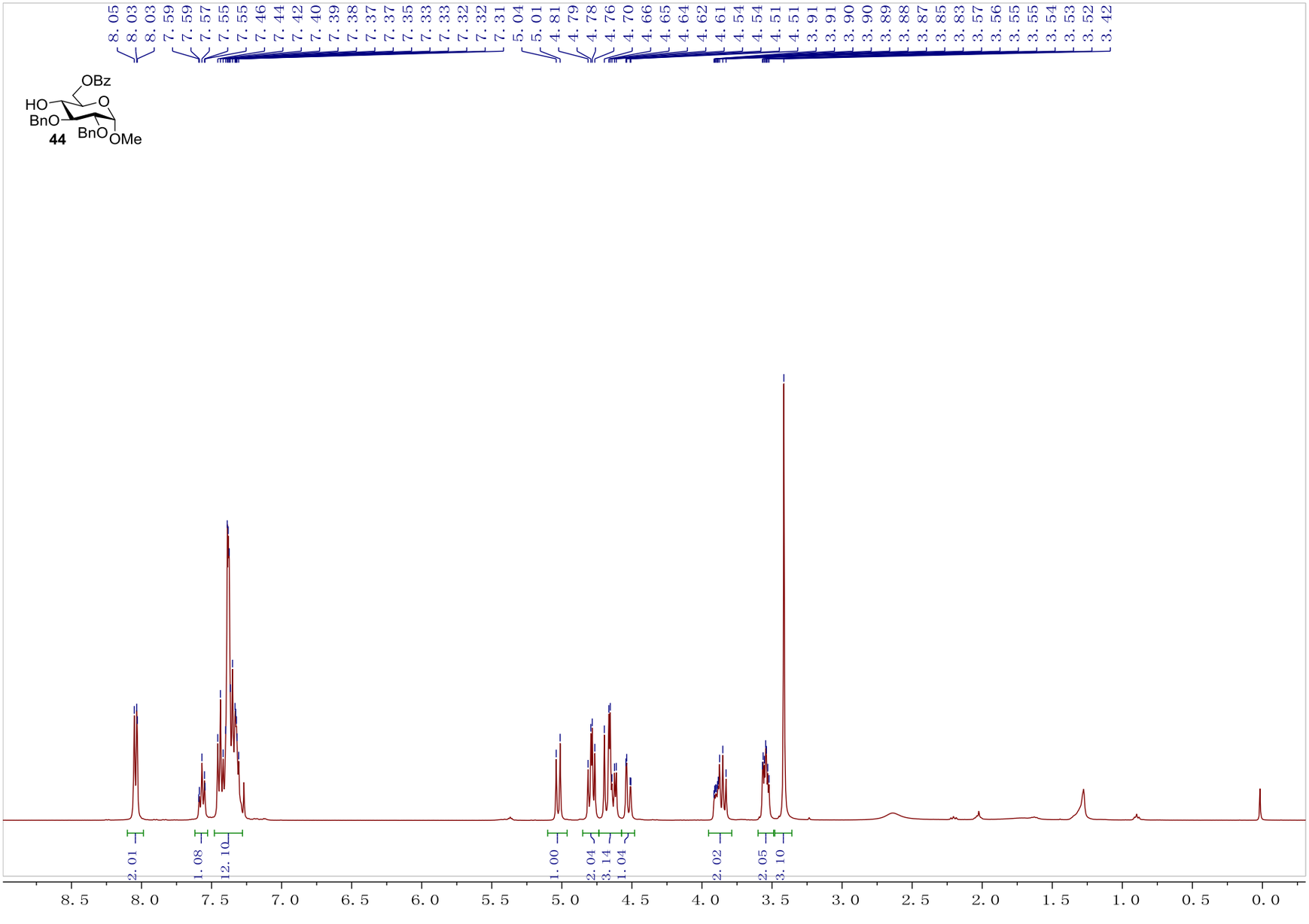
Methyl-3-*O*-benzoyl-*α*-*L*-rhamnopyranoside (42)

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



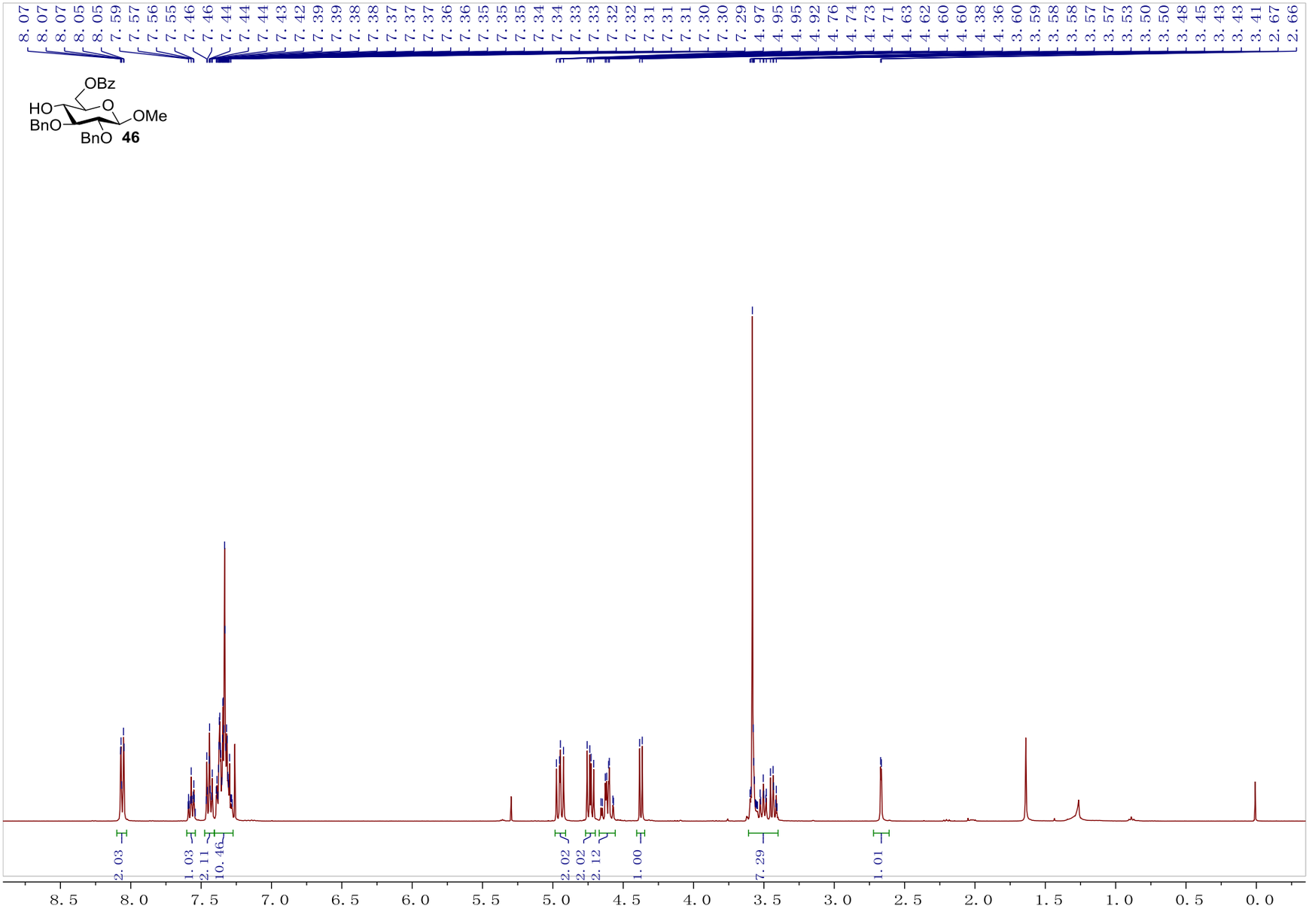
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-glucopyranoside (44)

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



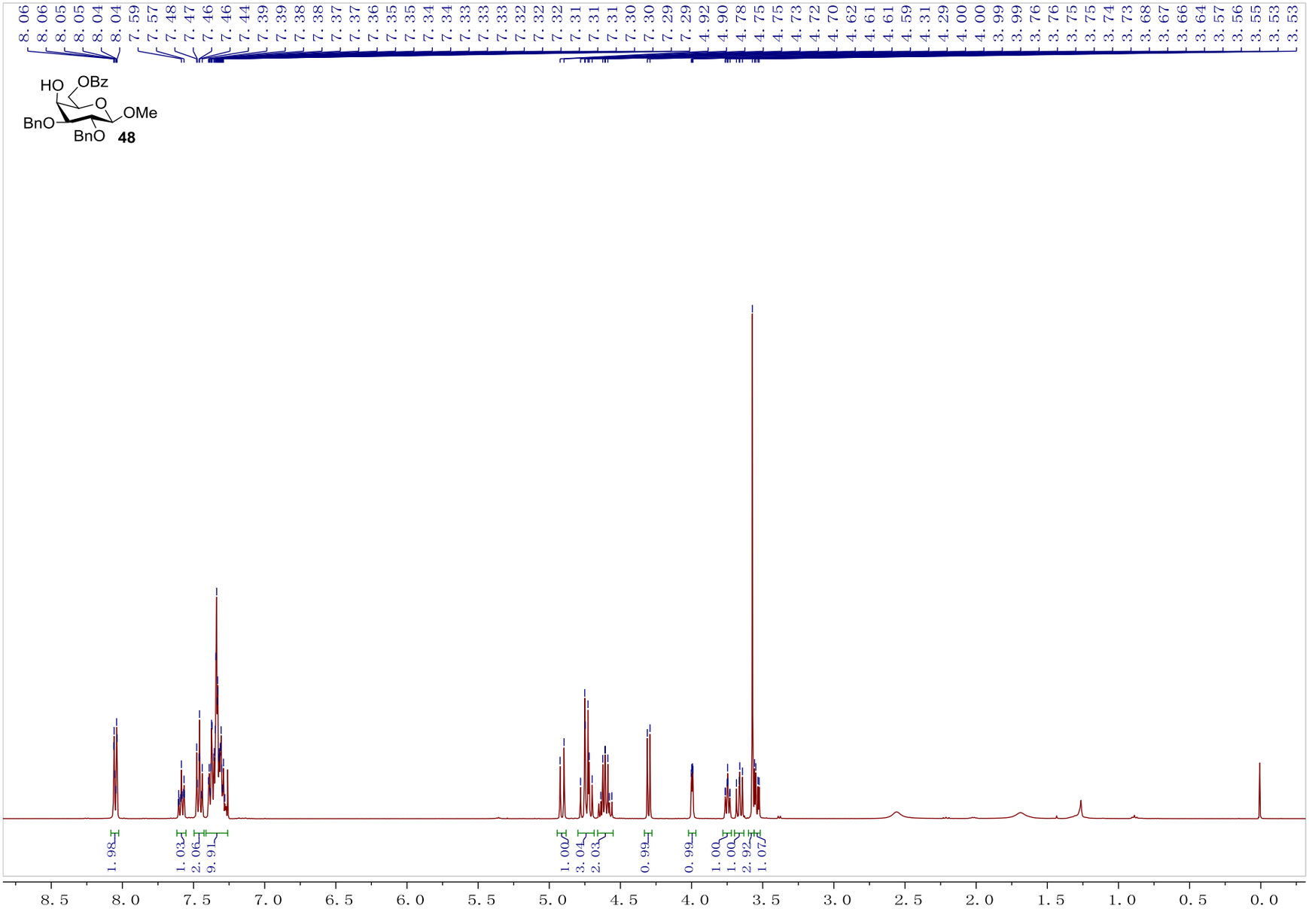
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*β*-D-glucopyranoside (46)

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



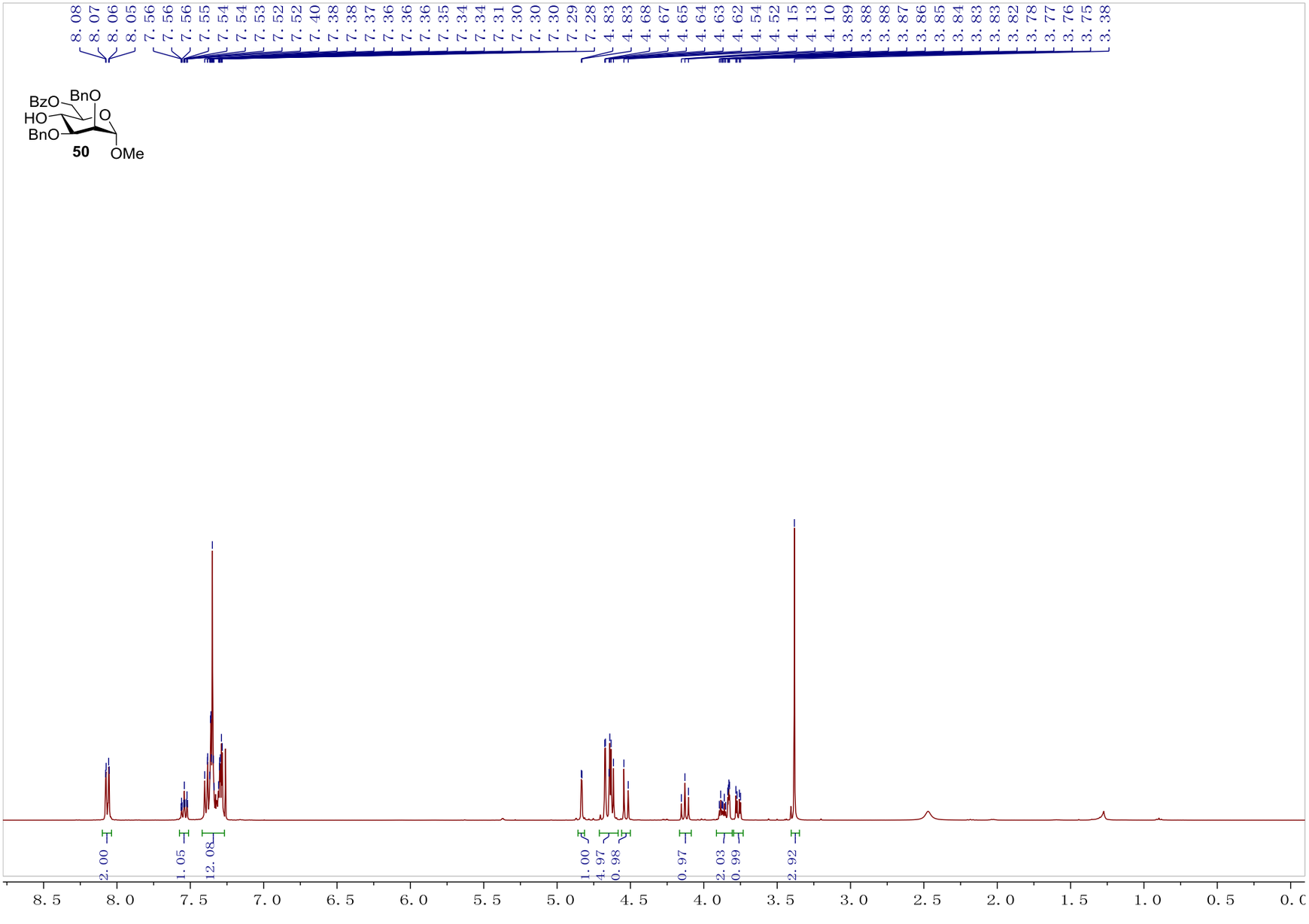
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*β*-D-galactopyranoside (48)

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



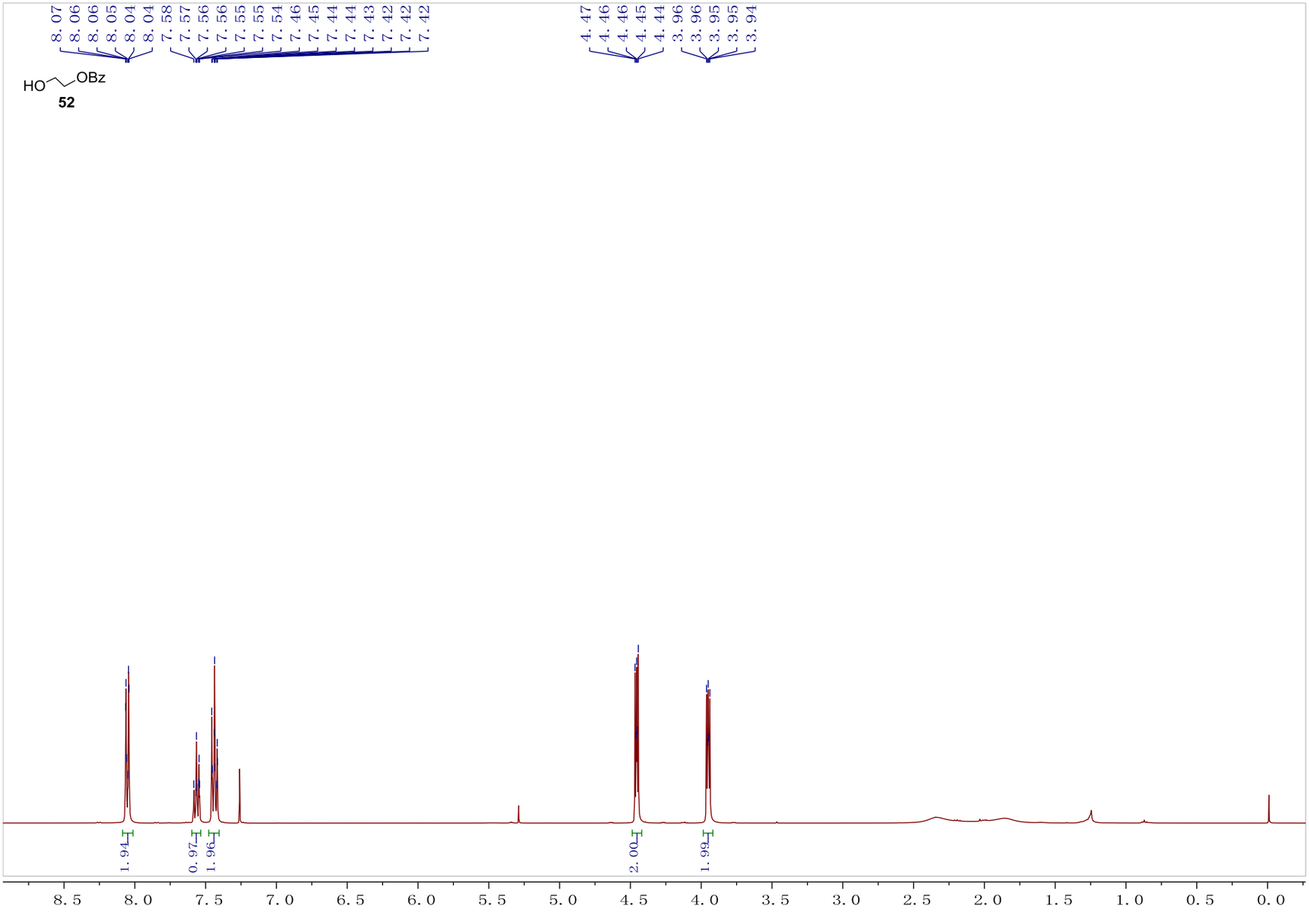
Methyl-6-*O*-benzoyl-2,3-di-*O*-benzyl-*α*-D-mannopyranoside (50)

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



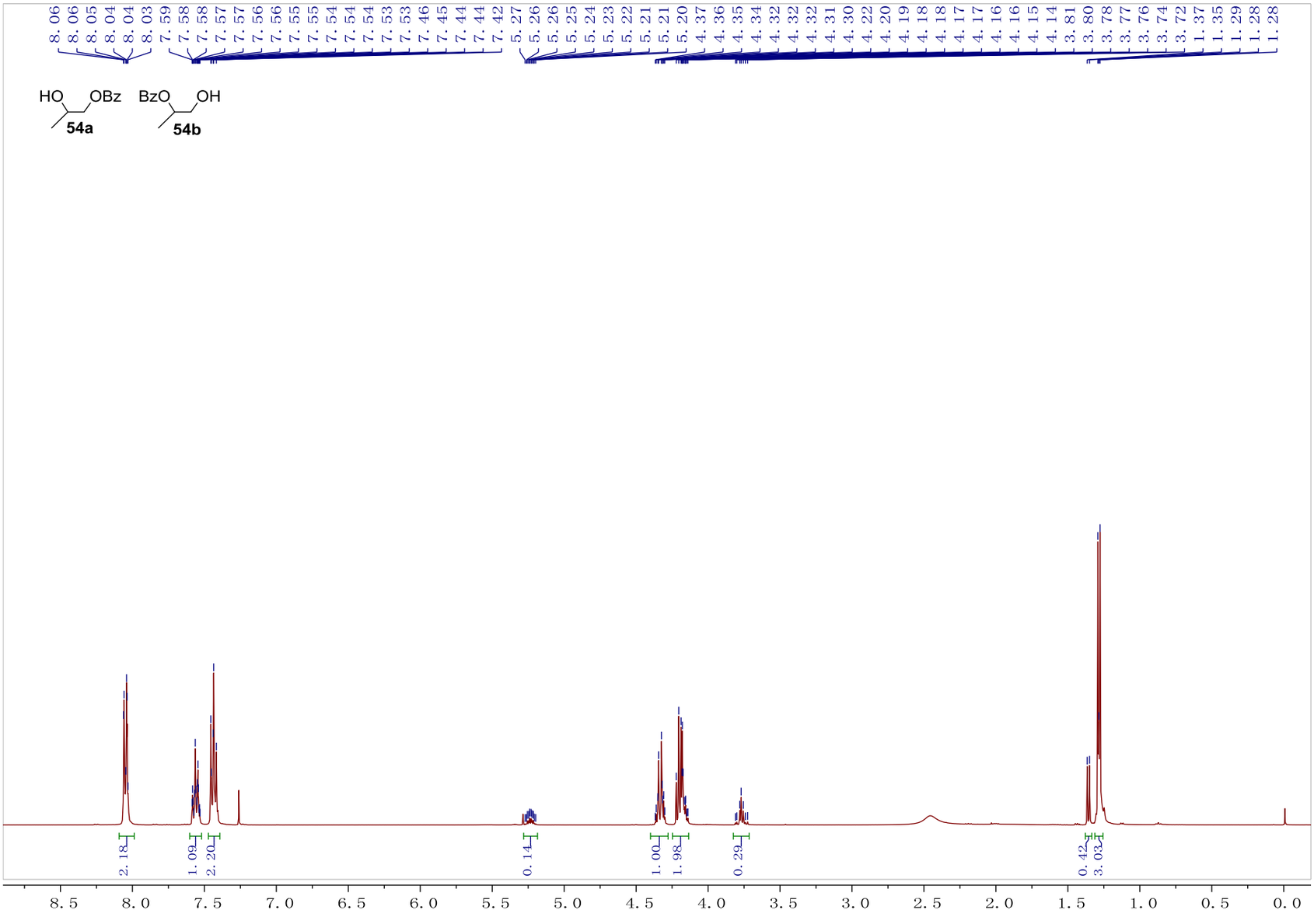
2-Hydroxyethyl-benzoate (52)

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



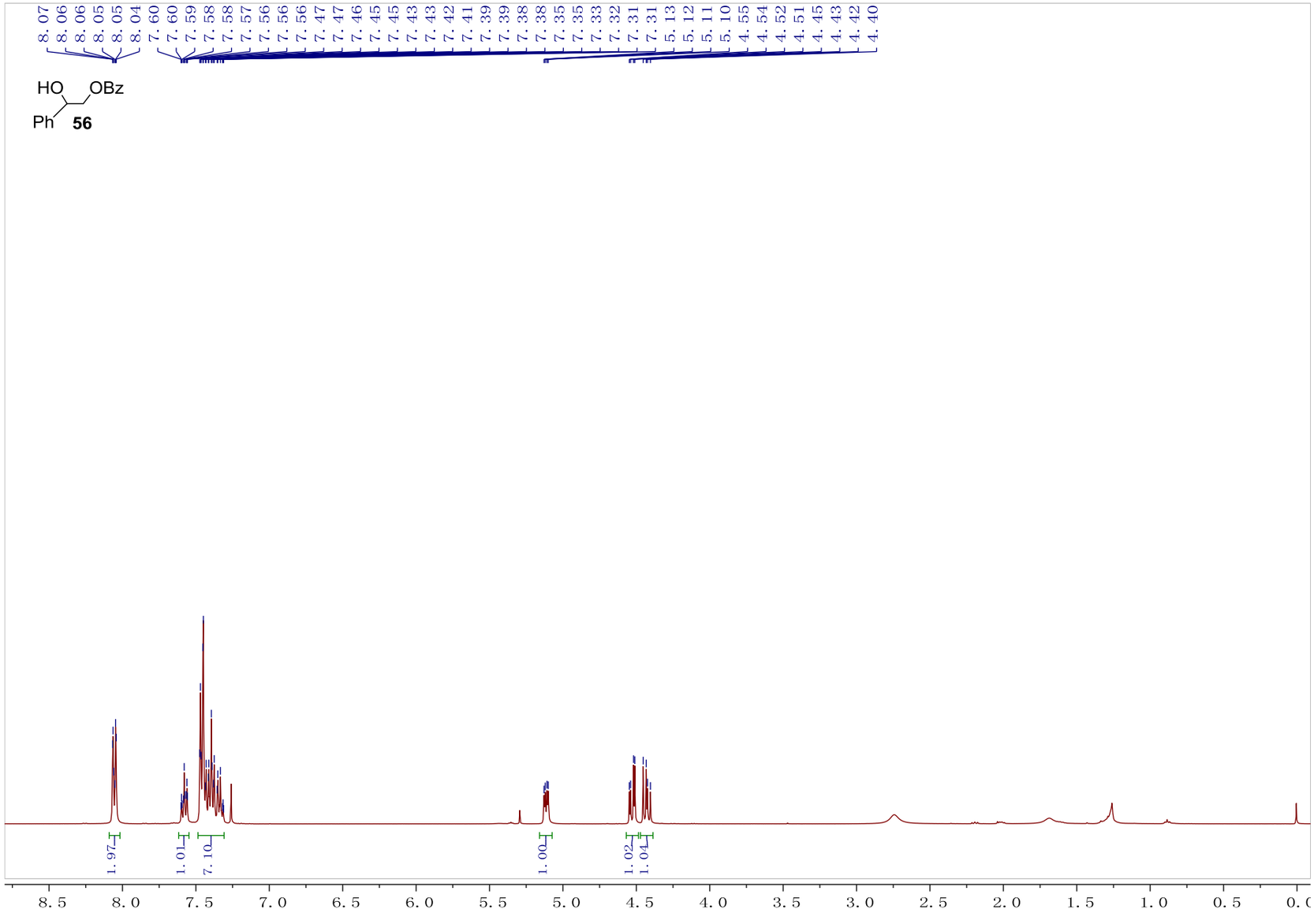
2-Hydroxy-2-phenylethyl benzoate (54a) and 1-Hydroxy-2-phenylethyl benzoate (54b)

^{1}H-NMR of mixture of compounds **54a** and **54b** ($CDCl_3$)



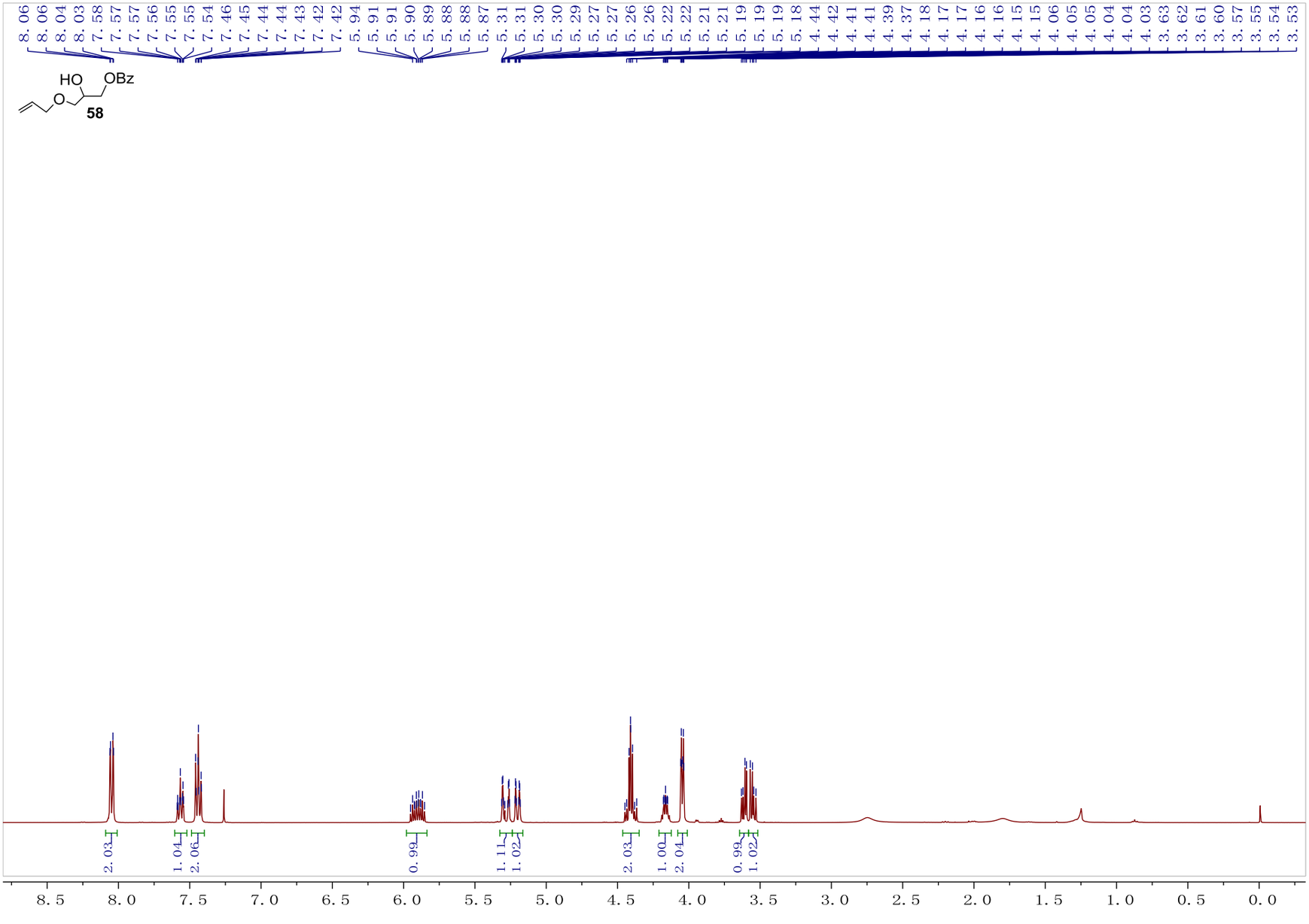
2-Hydroxy-2-phenylethyl benzoate (56)

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



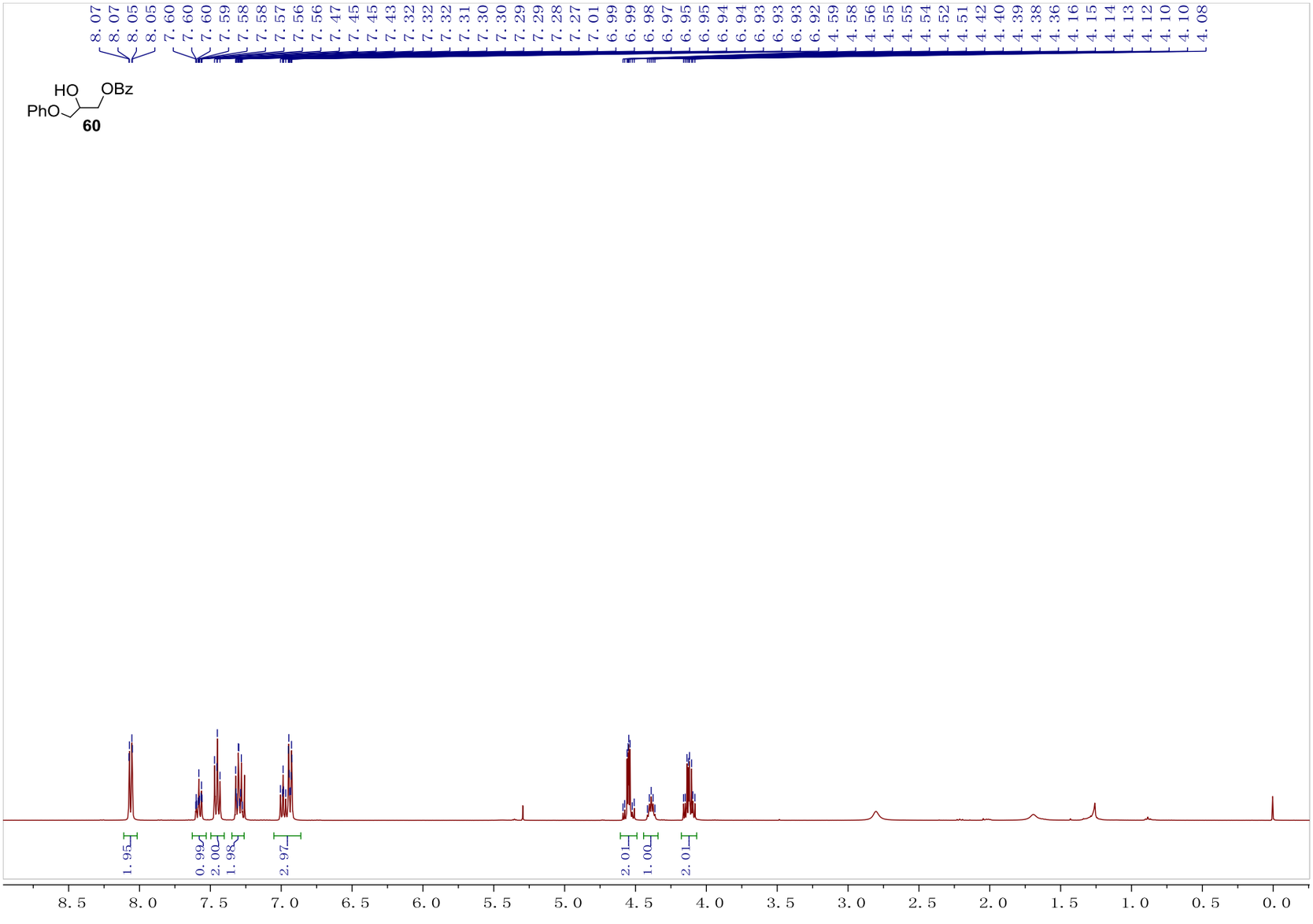
3-(Allyloxy)-2-hydroxypropyl benzoate (58)

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



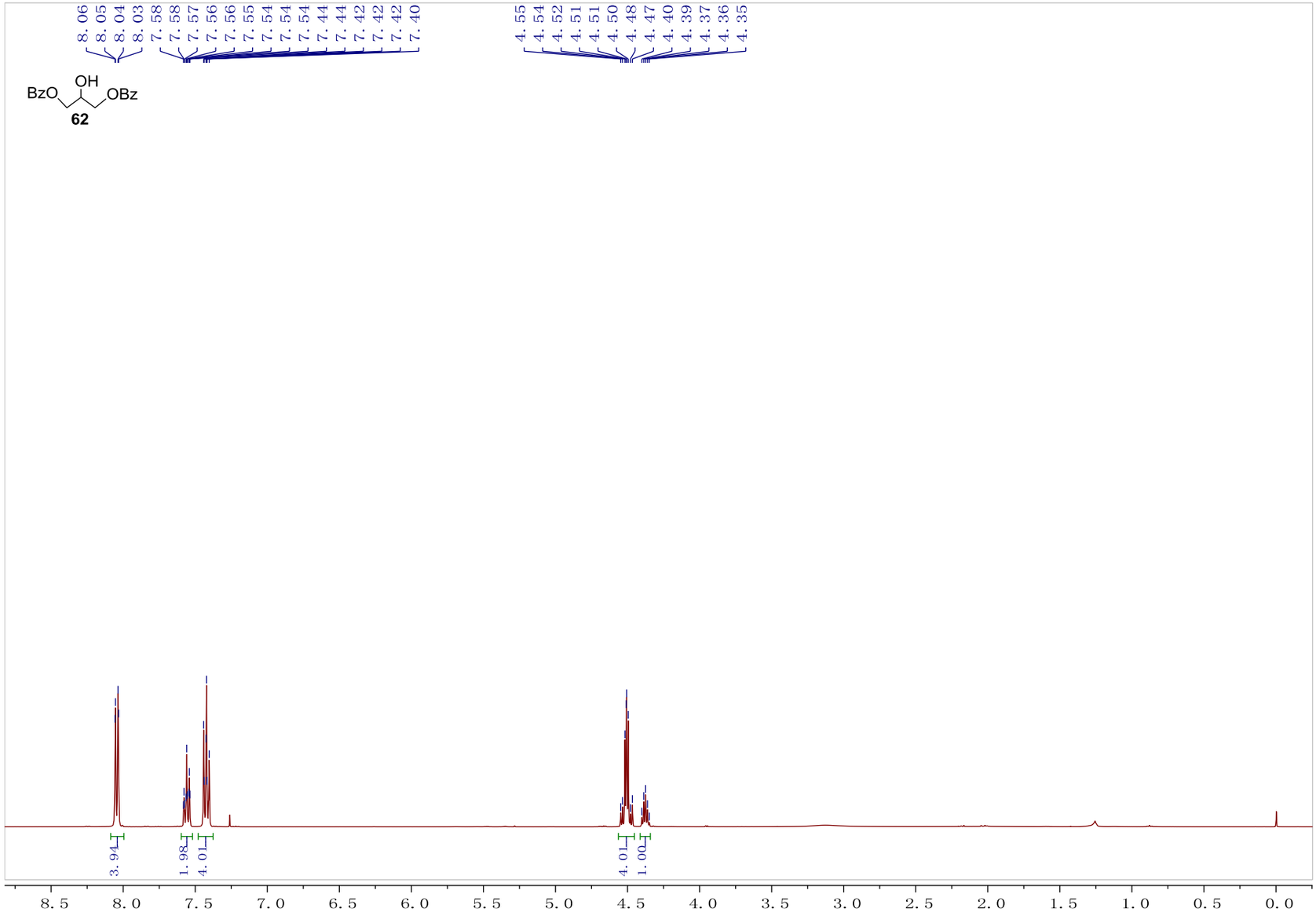
3-Phenoxypropyl benzoate (60)

^{1}H-NMR of compound **60** ($CDCl_3$)



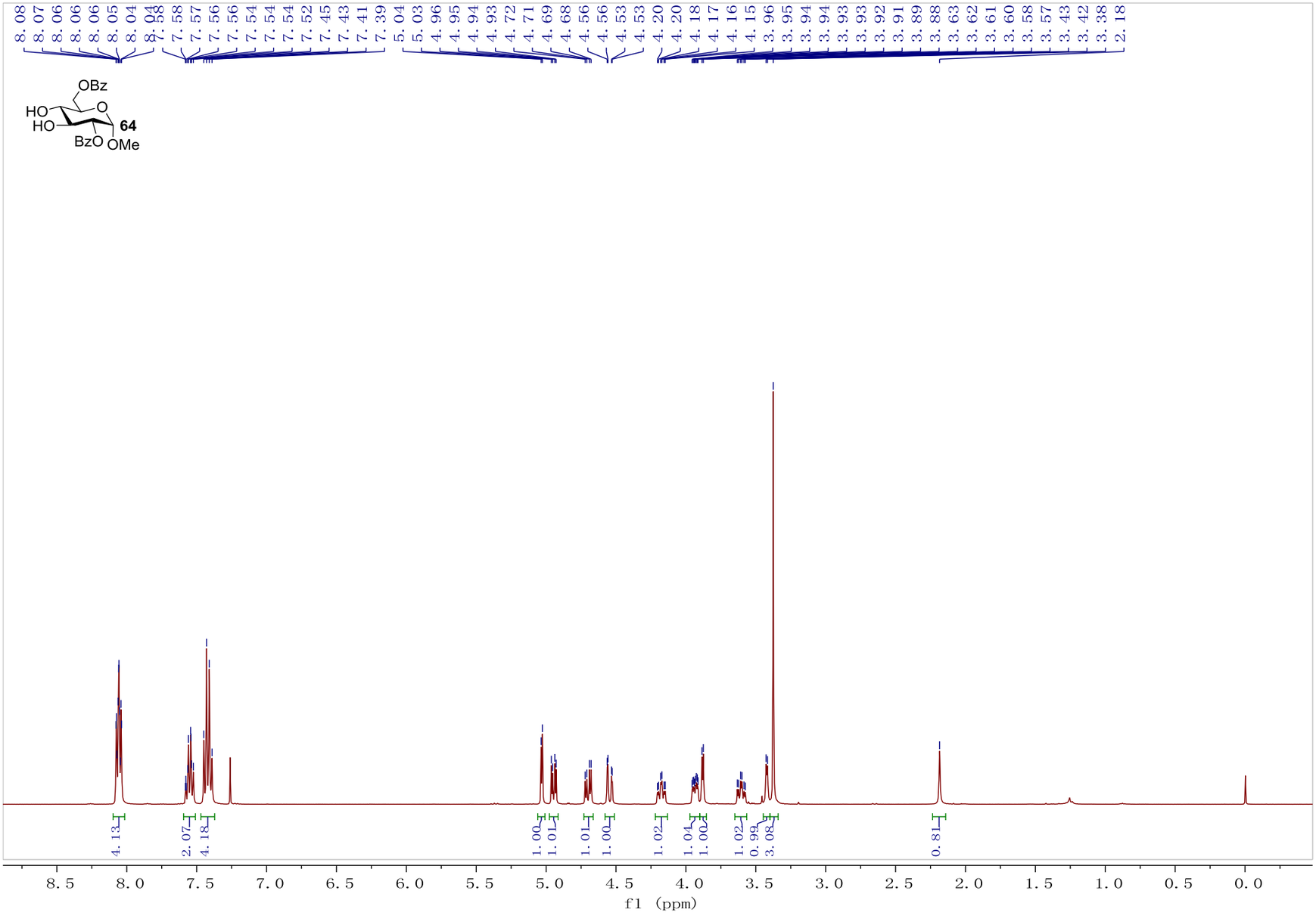
1,3-di-*O*-benzoyl-propane-2-ol (62)

^{1}H-NMR of compound **62** ($CDCl_3$)



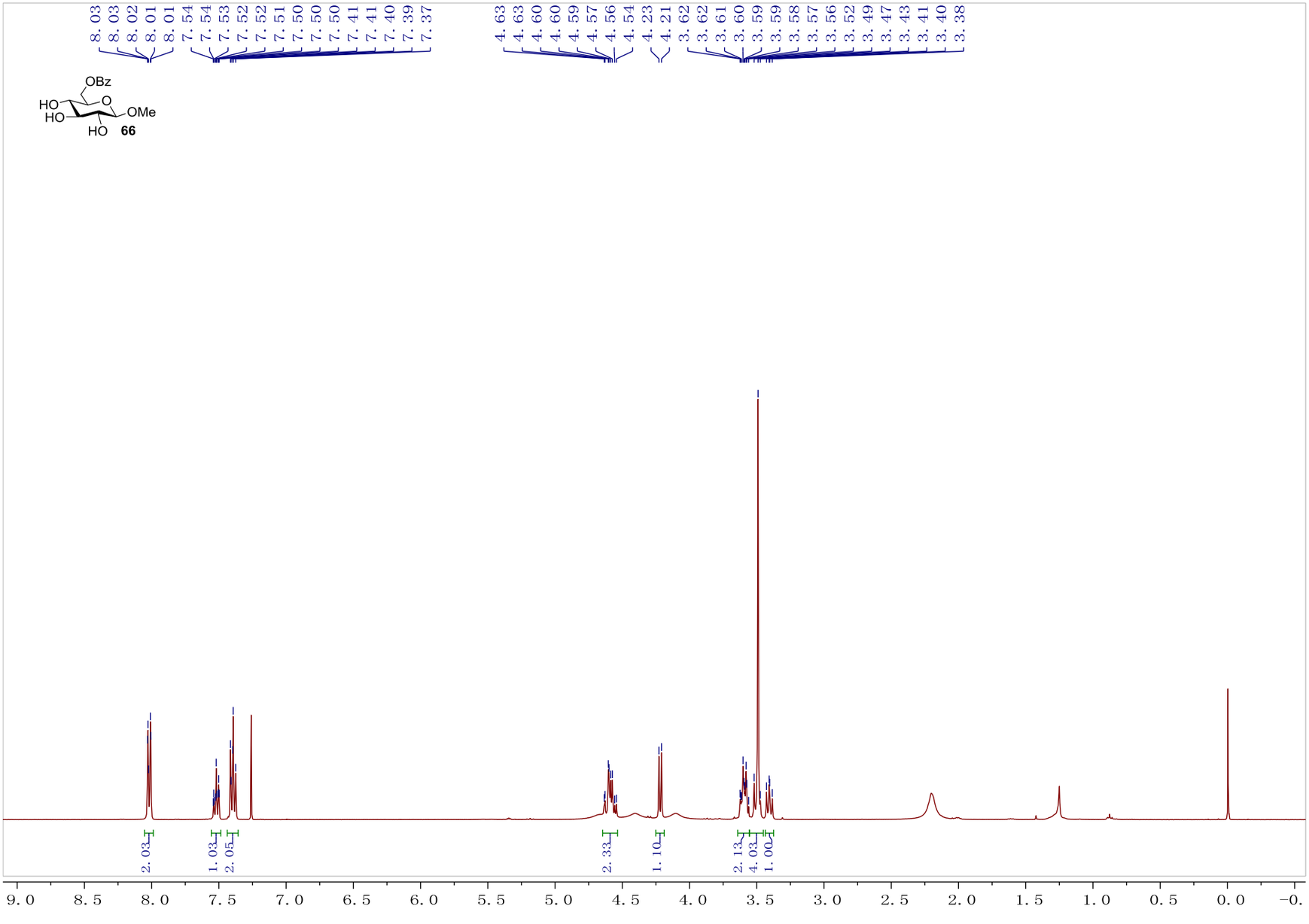
Methyl-2,6-di-*O*-benzoyl-*α*-D-glucopyranoside (64)

^{1}H-NMR of compound **64** ($CDCl_3$)



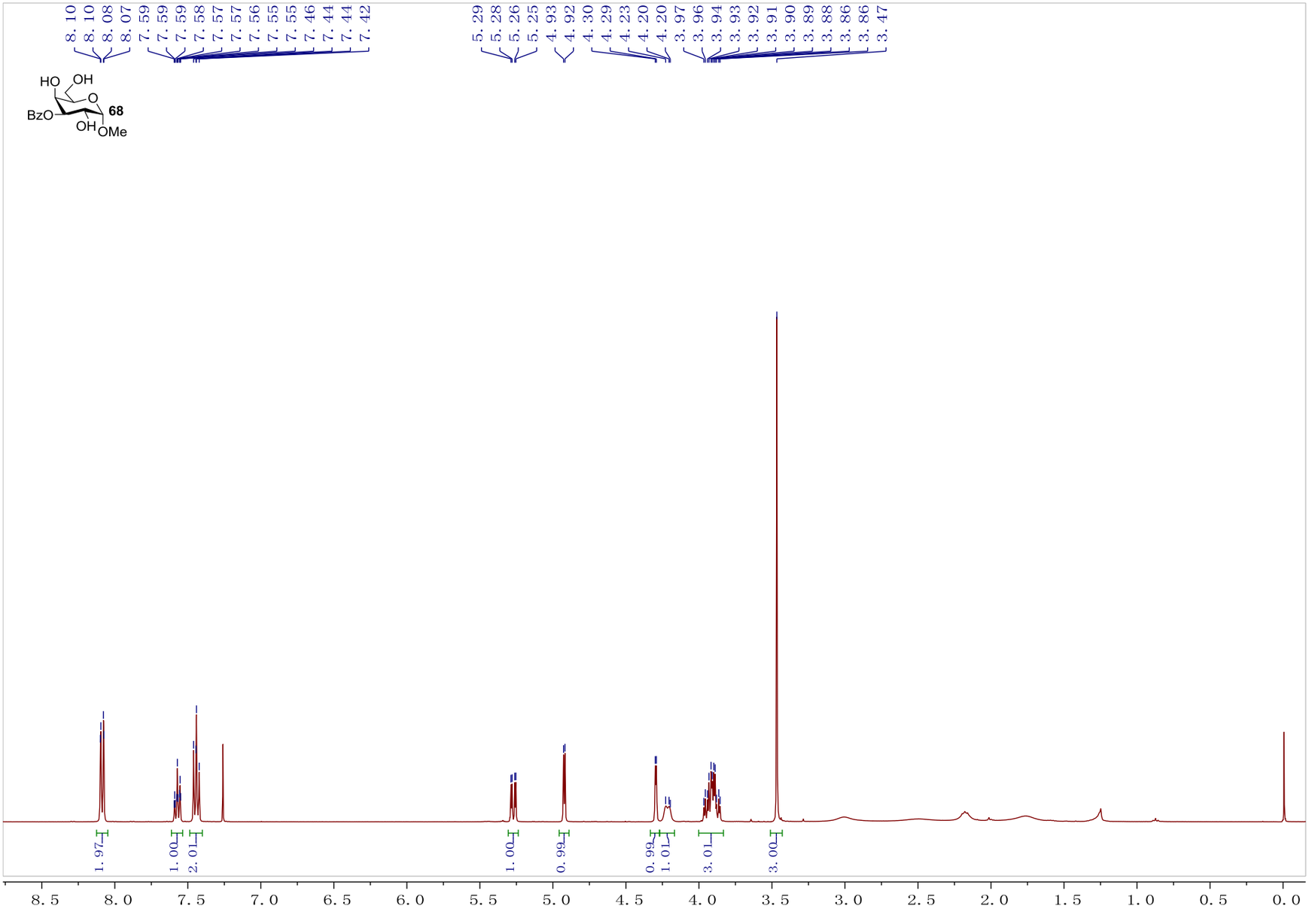
Methyl-6-*O*-benzoyl-*β*-D-glucopyranoside (66)

^{1}H-NMR of compound **66** ($CDCl_3$)



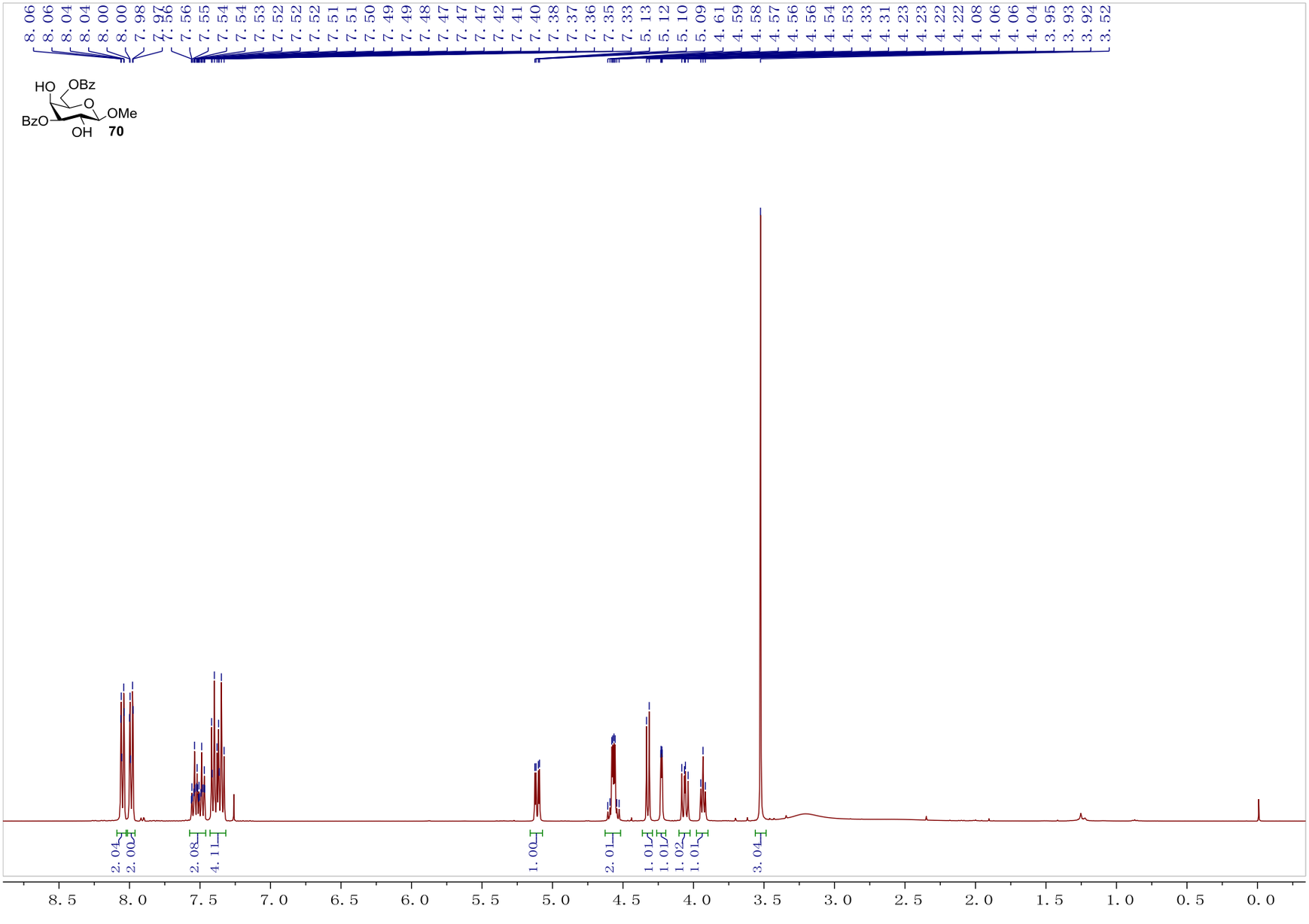
Methyl-3-*O*-benzoyl-*α*-D-galactopyranoside (68)

^{1}H-NMR of compound **68** ($CDCl_3$)



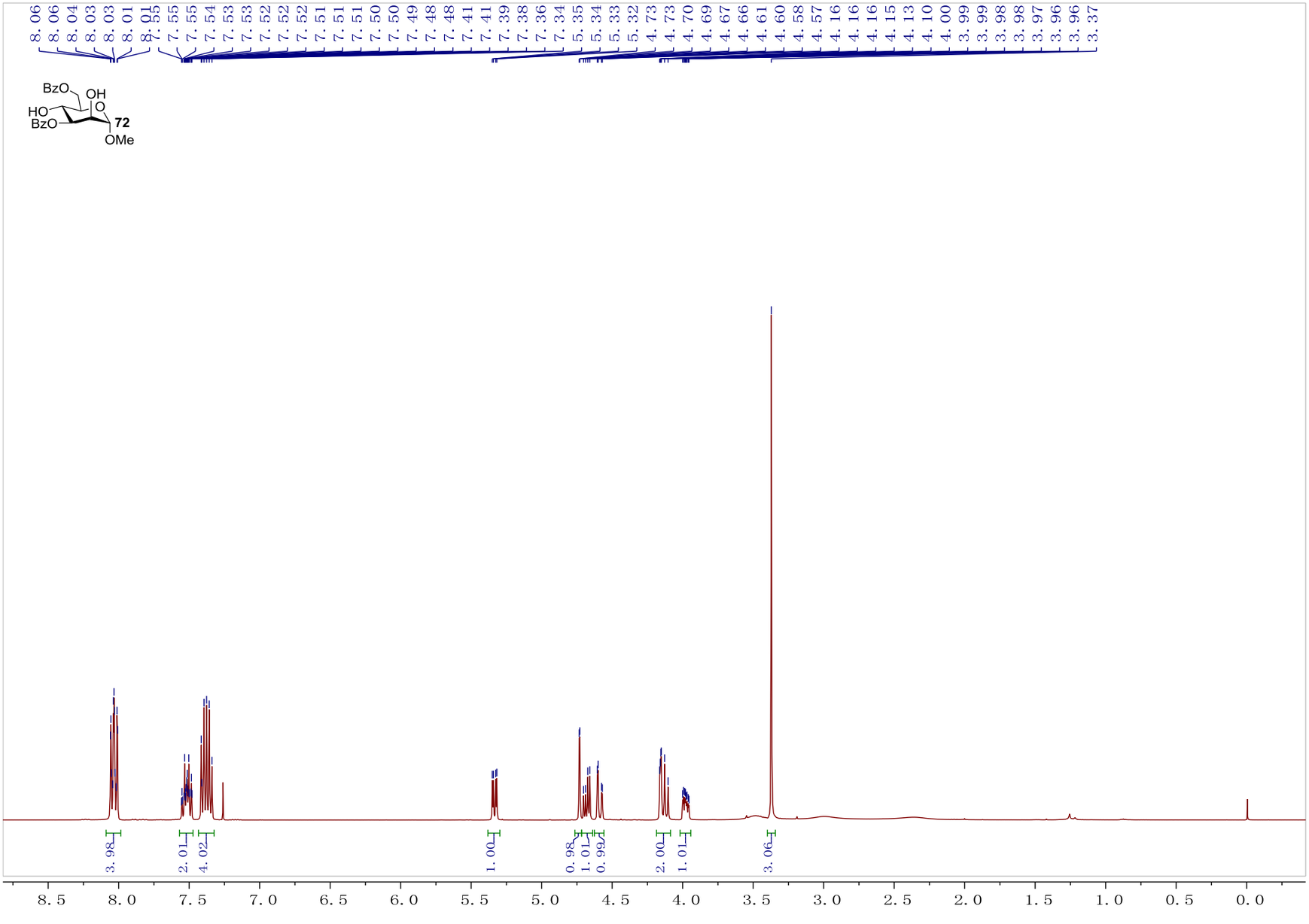
Methyl-3,6-di-*O*-benzoyl-*β*-D-galactopyranoside (70)

^{1}H-NMR of compound **70** ($CDCl_3$)



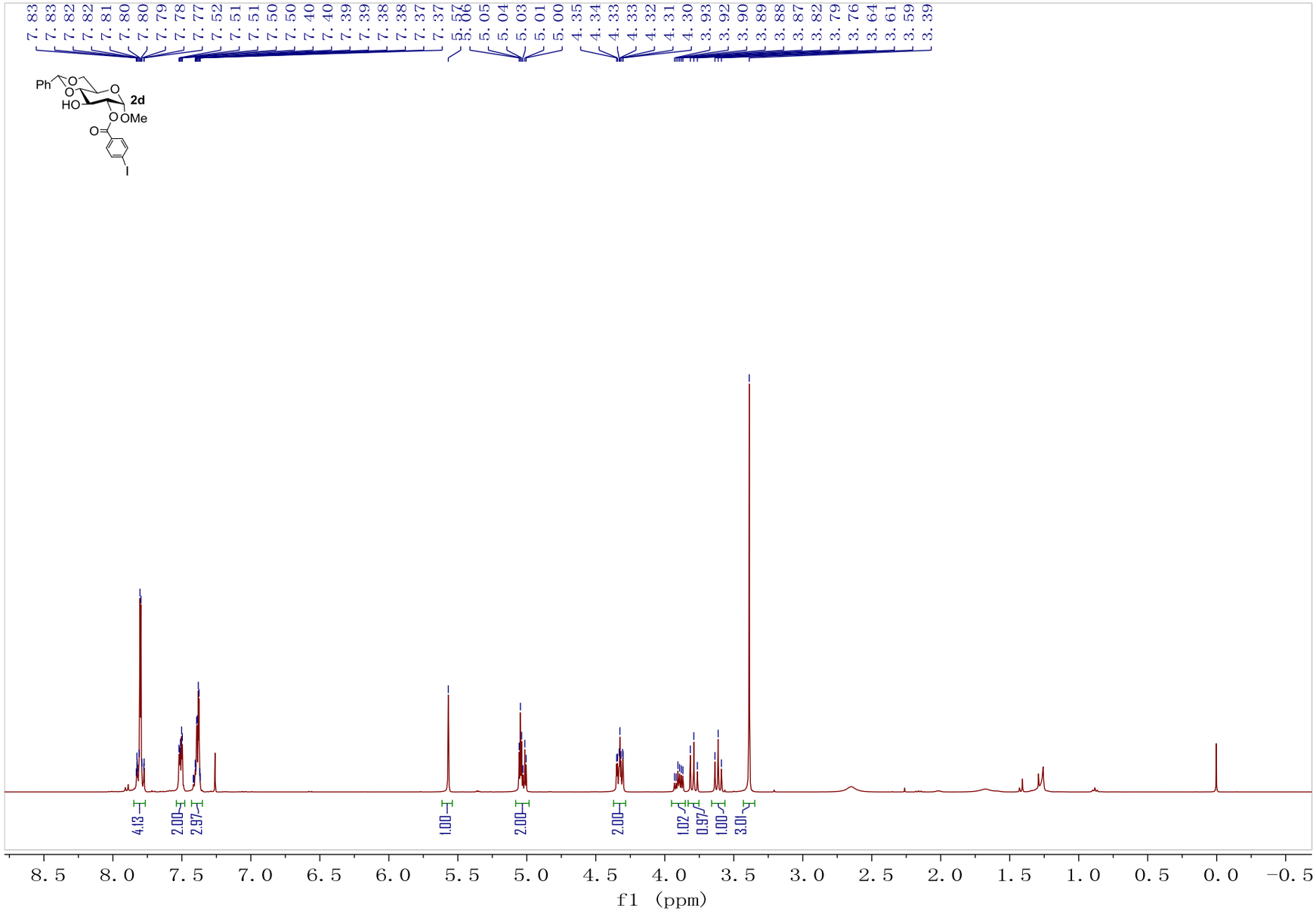
Methyl-3,6-di-*O*-benzoyl-*α*-D-mannopyranoside (72)

^{1}H-NMR of compound **72** ($CDCl_3$)

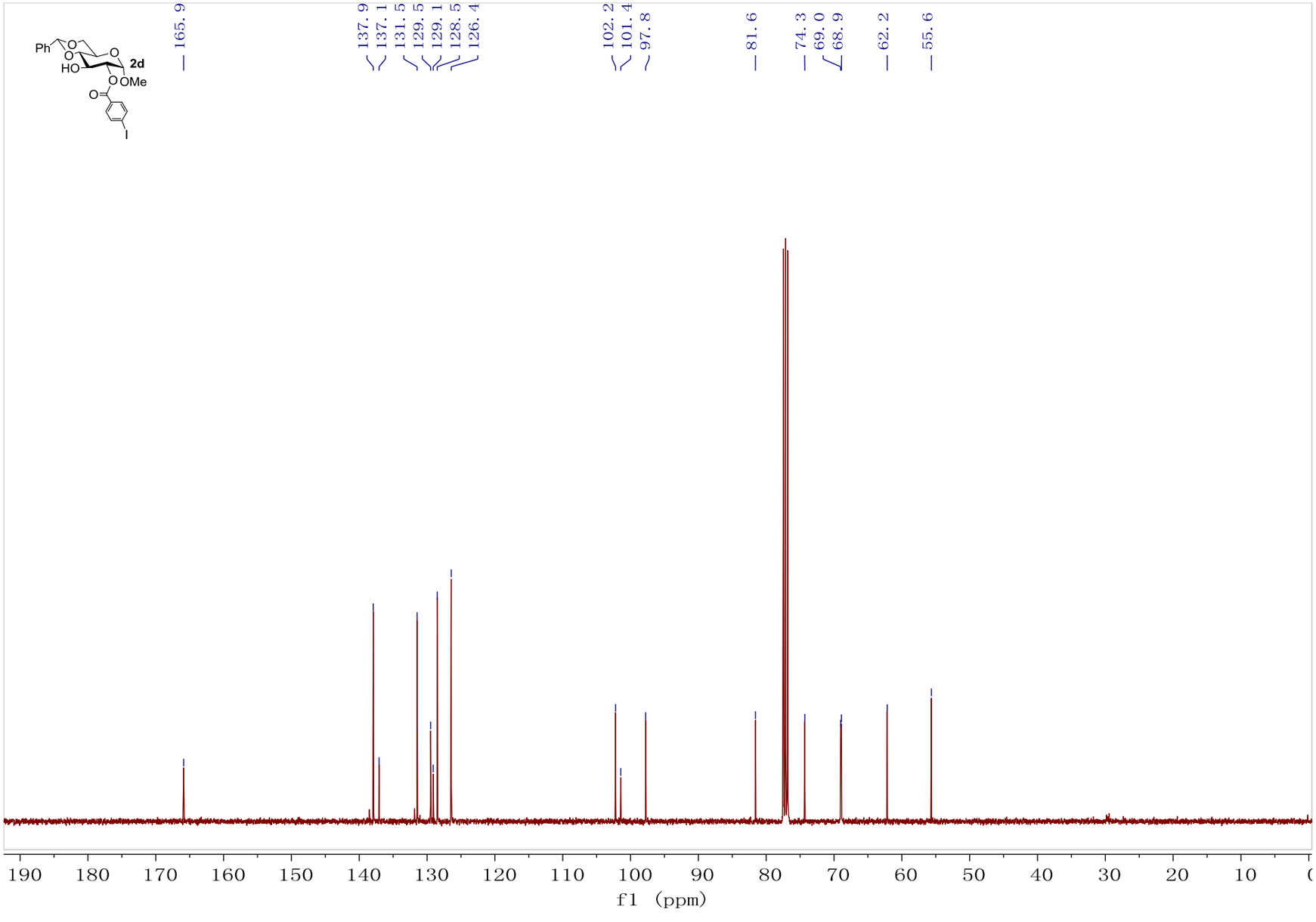


Methyl-2-*O*-4-iodobenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2d)

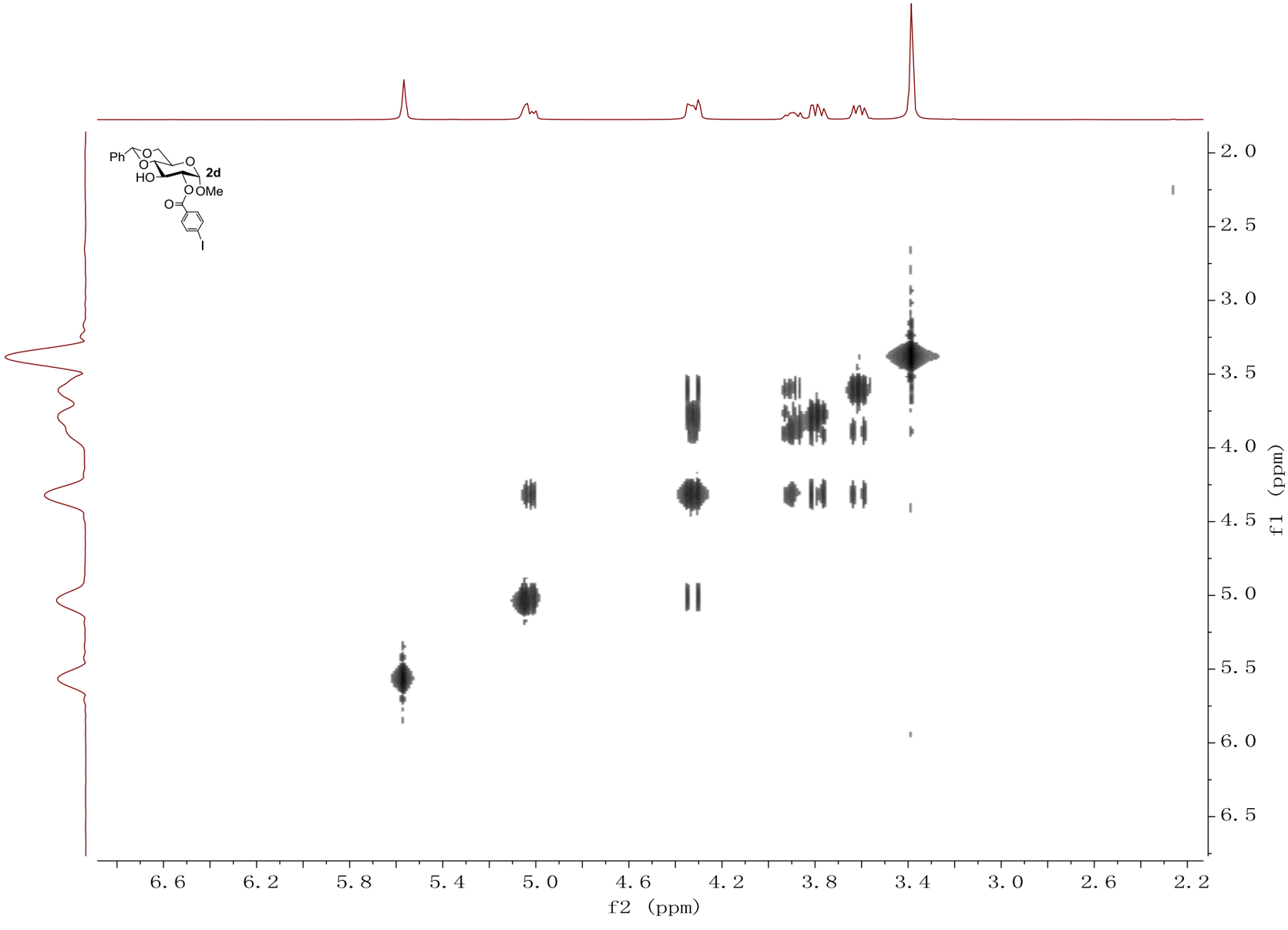
^{1}H-NMR of compound **2d** ($CDCl_3$)



^{13}C-NMR of compound **2d** ($CDCl_3$)

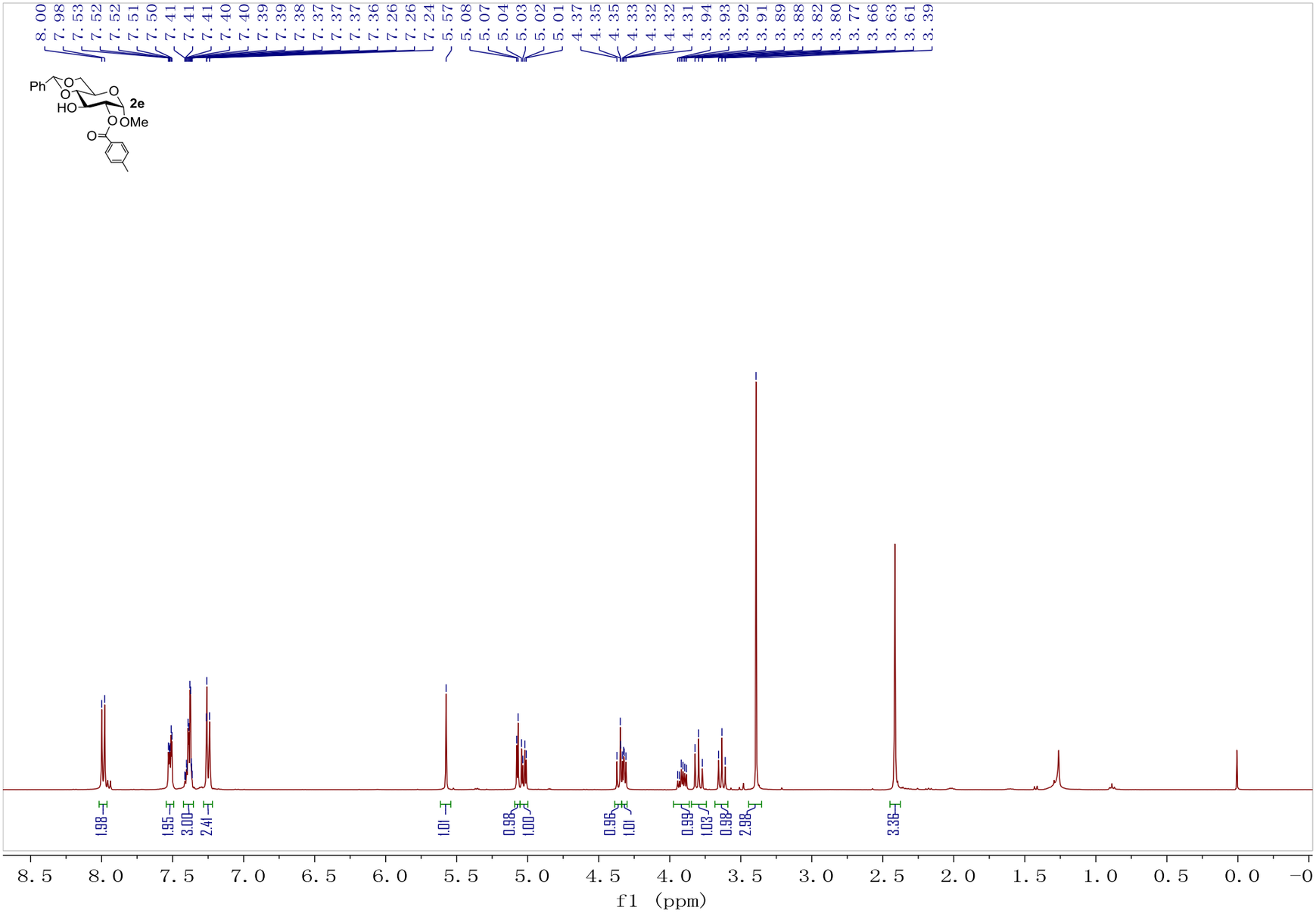


2D-COSY of compound **2d** ($CDCl_3$)

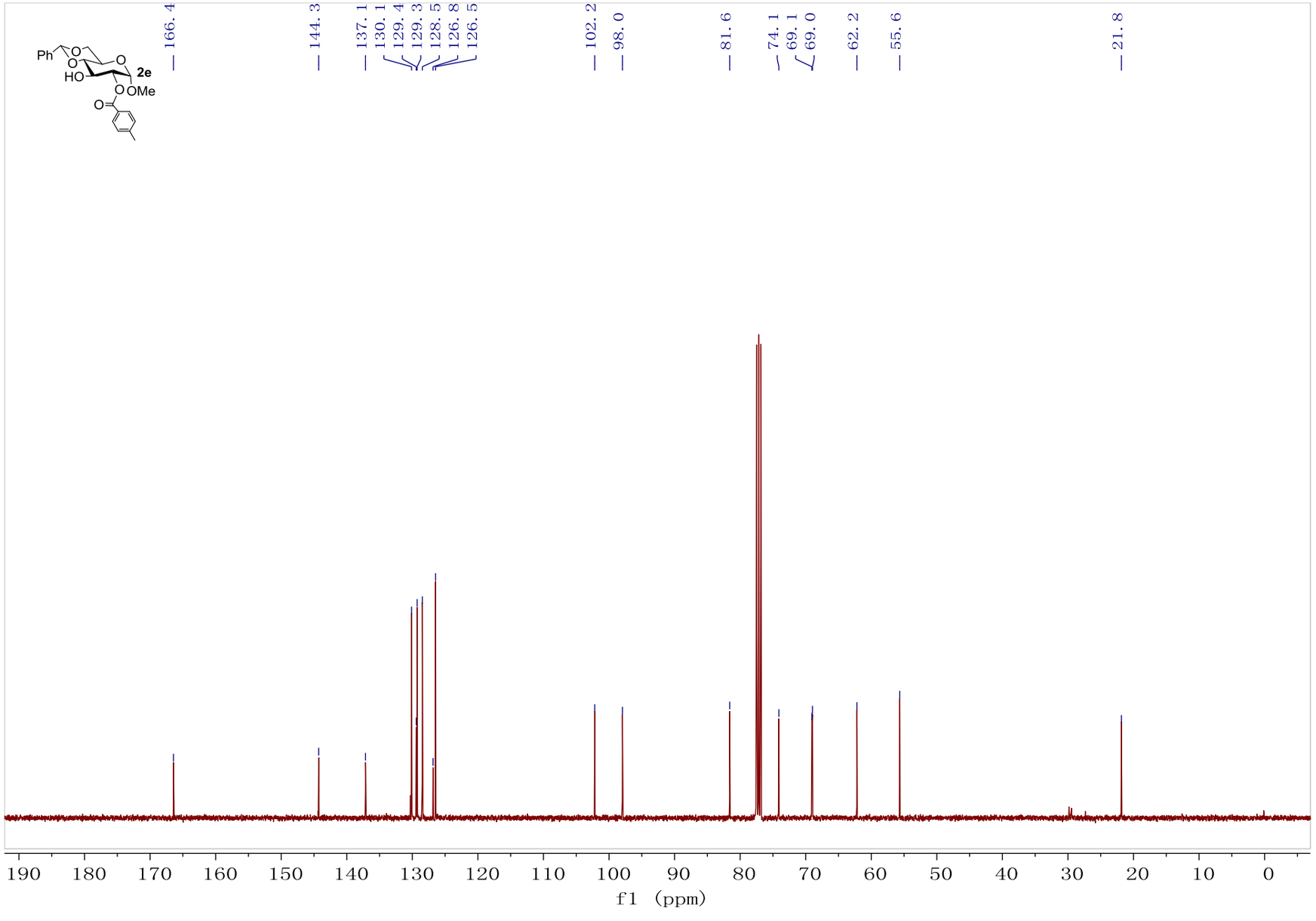


Methyl-2-*O*-4-methylbenzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2e)

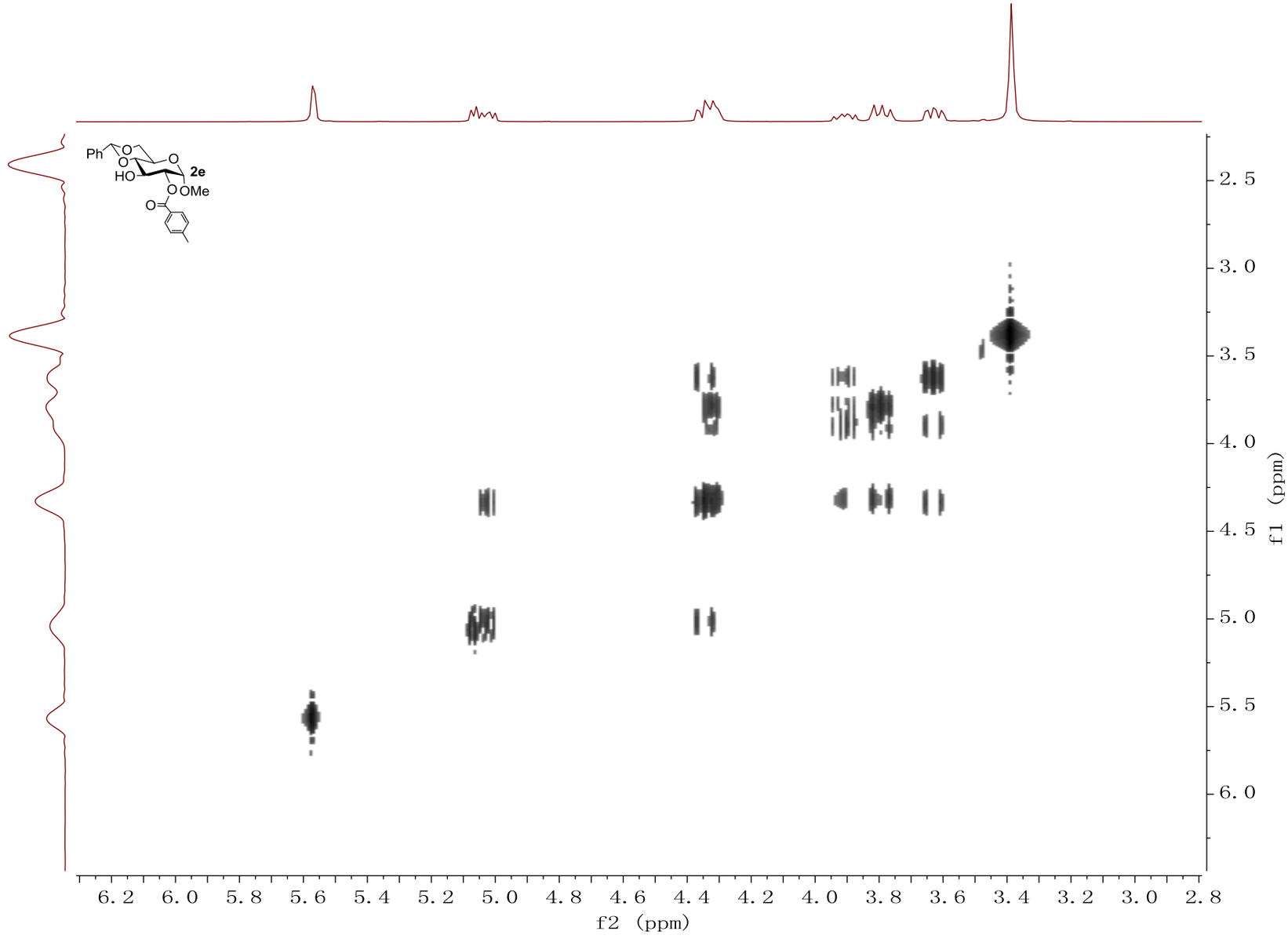
^{1}H-NMR of compound **2e** ($CDCl_3$)



^{13}C-NMR of compound **2e** ($CDCl_3$)

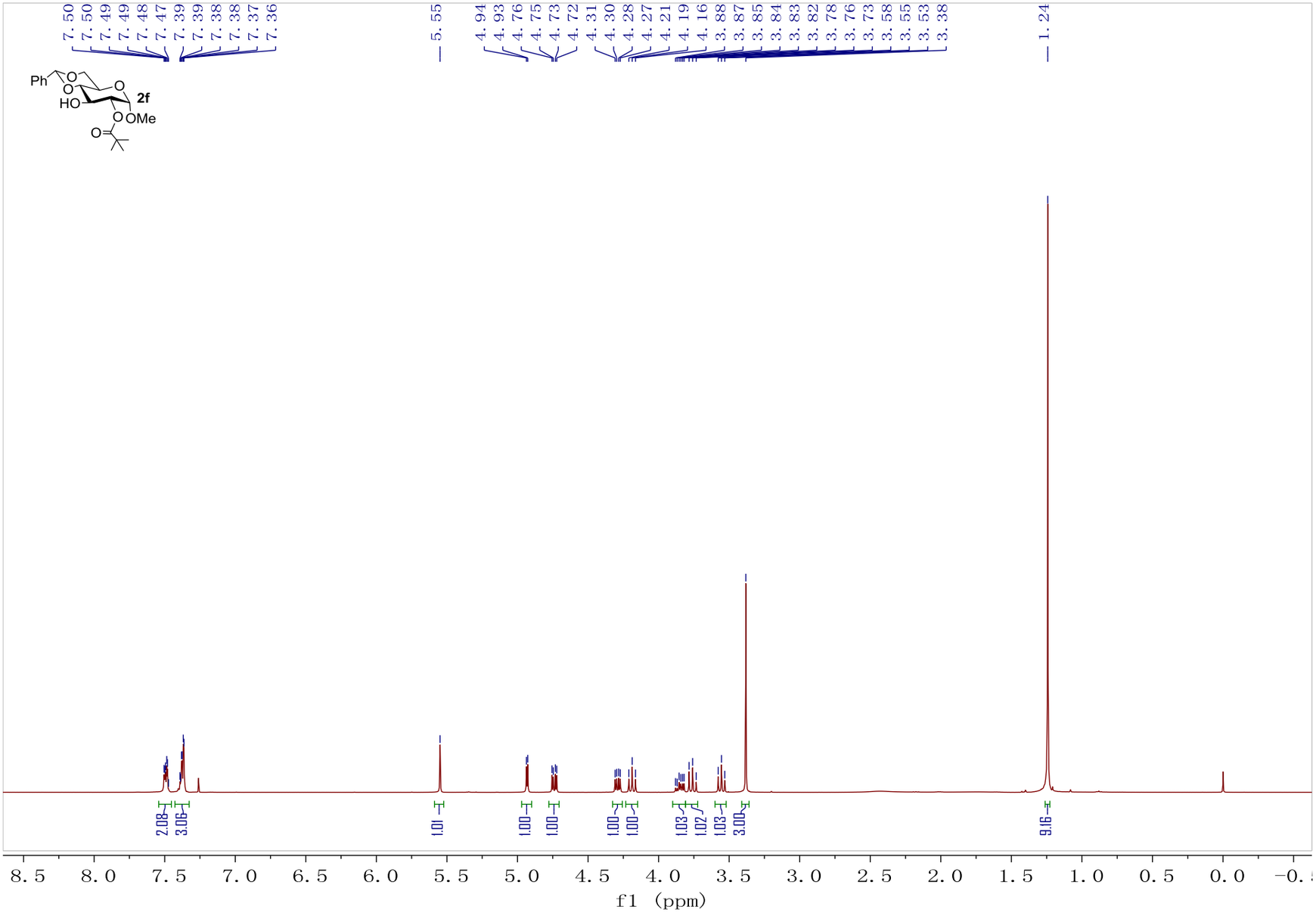


2D-COSY of compound **2e** ($CDCl_3$)



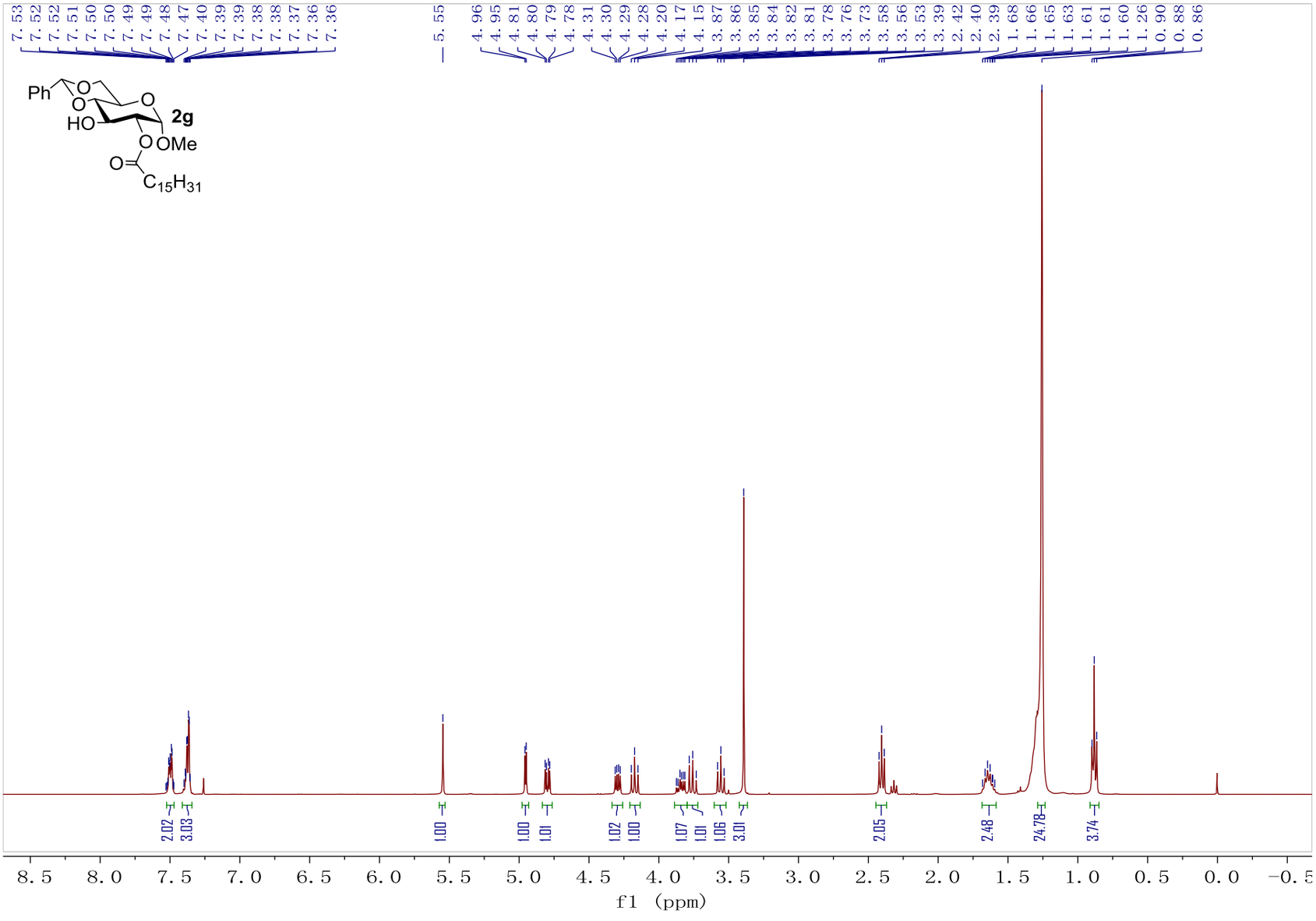
Methyl-2-*O*-pivaloyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2f)

^{1}H-NMR of compound **2f** ($CDCl_3$)

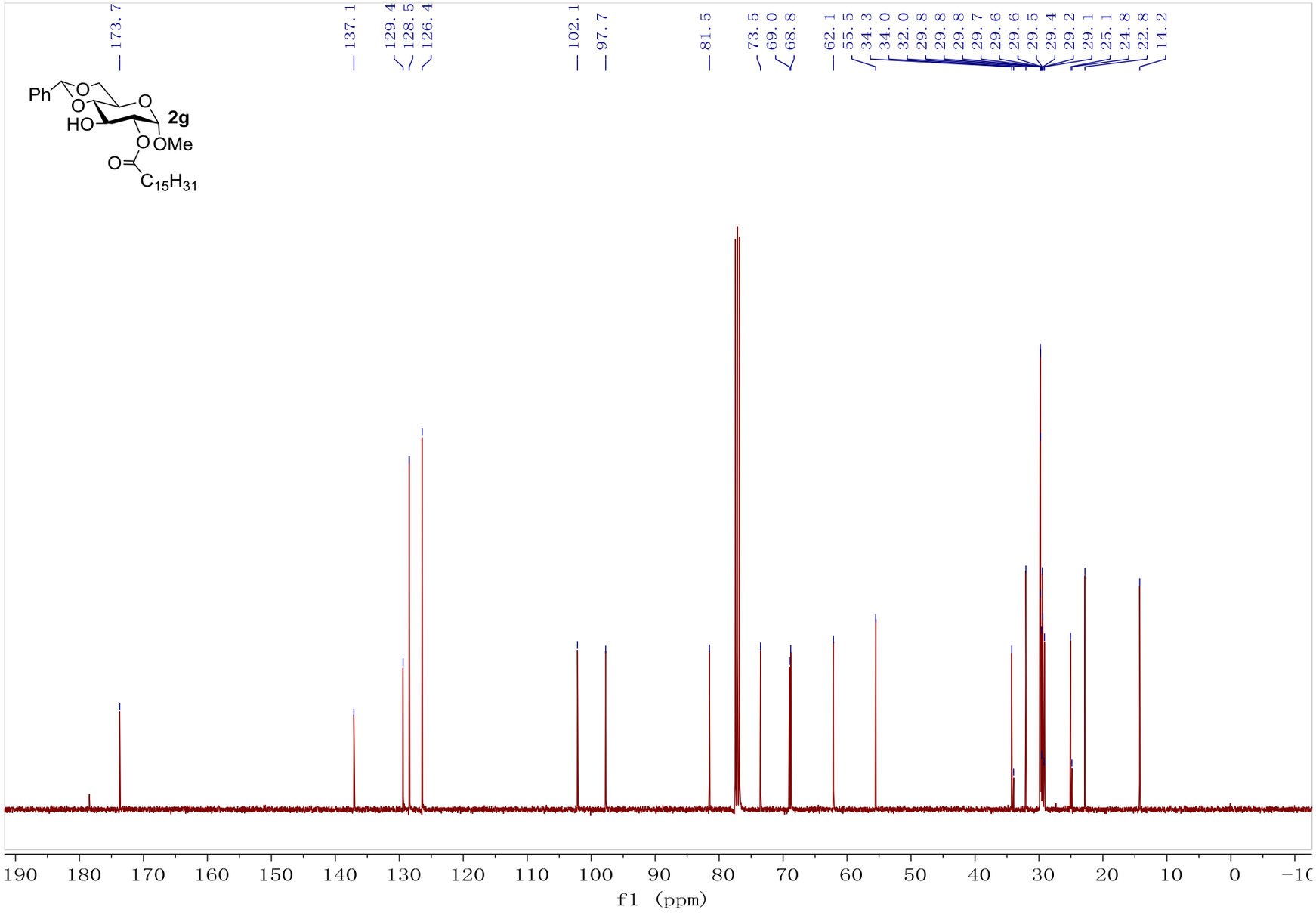


Methyl-2-*O*-palmitoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2g)

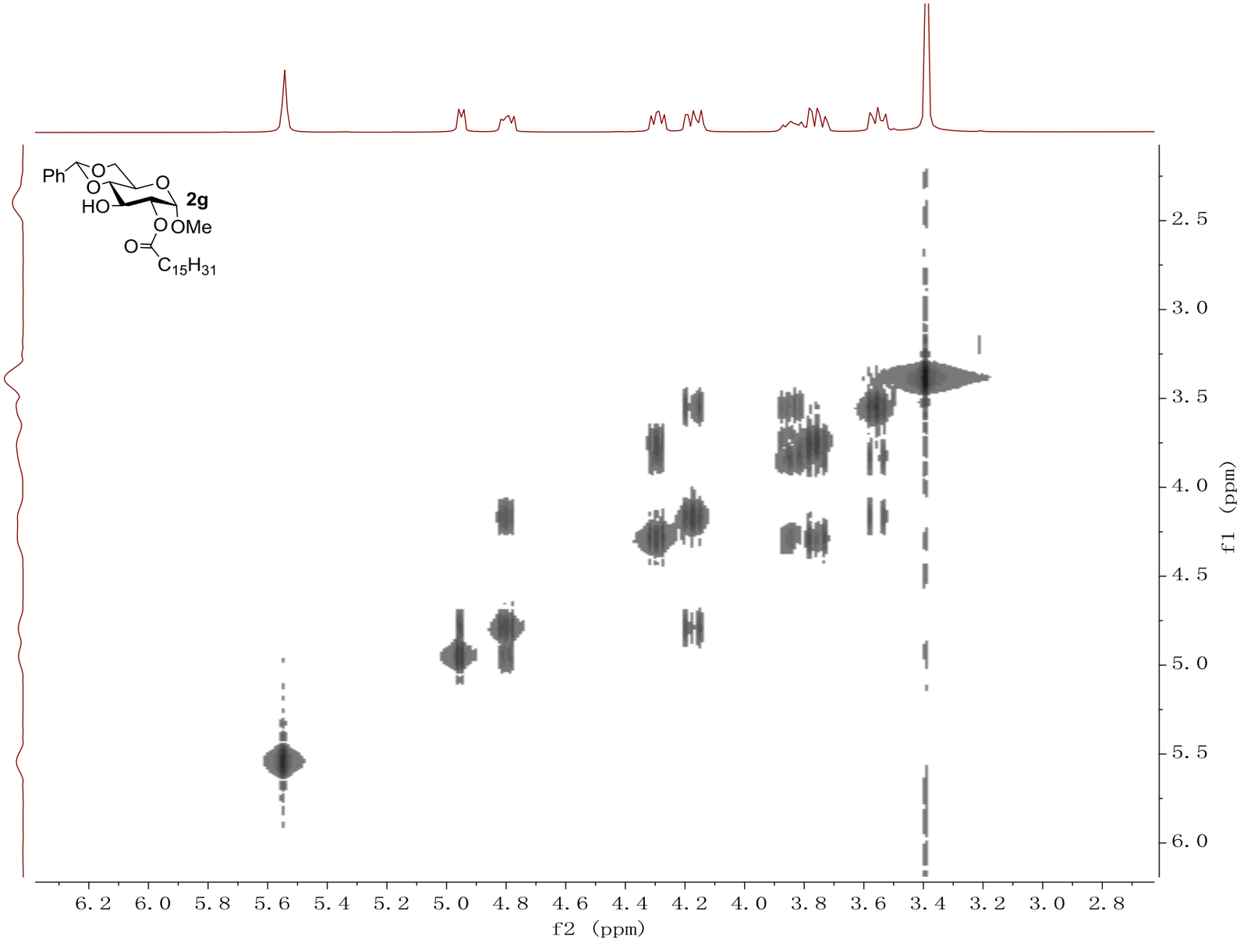
^{1}H-NMR of compound **2g** ($CDCl_3$)



^{13}C-NMR of compound **2g** ($CDCl_3$)

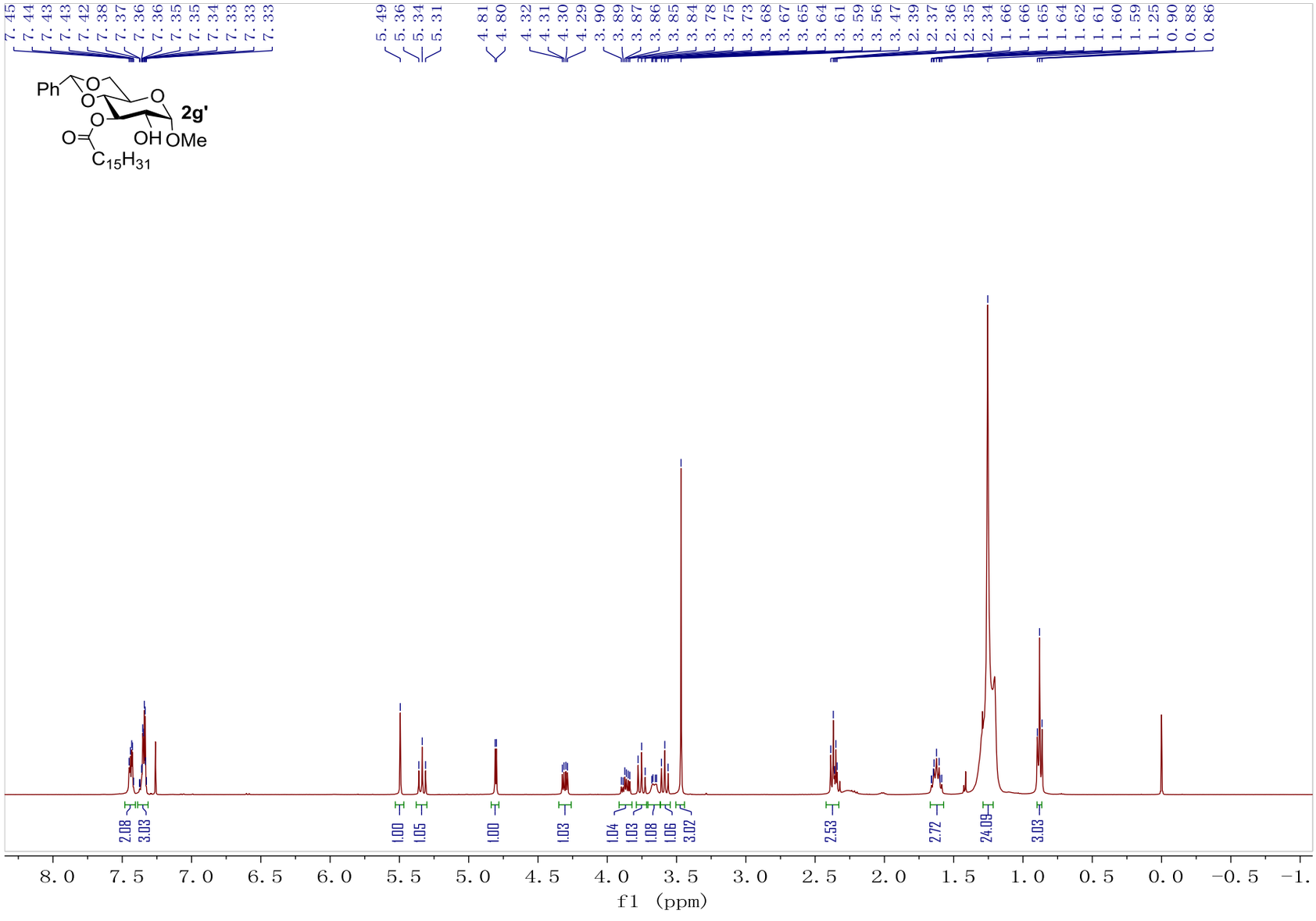


2D-COSY of compound **2g** ($CDCl_3$)

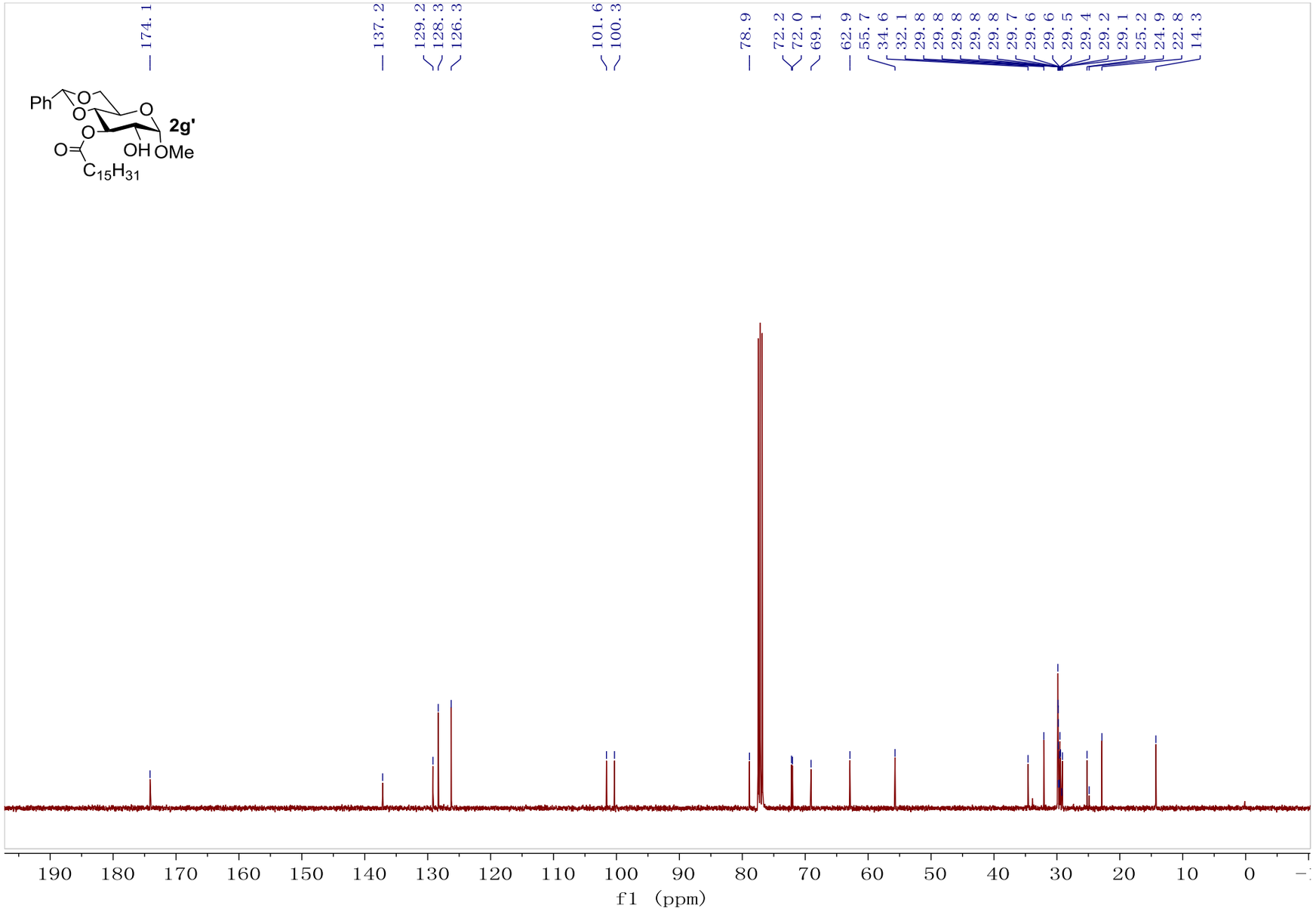


Methyl-3-*O*-palmitoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2g')

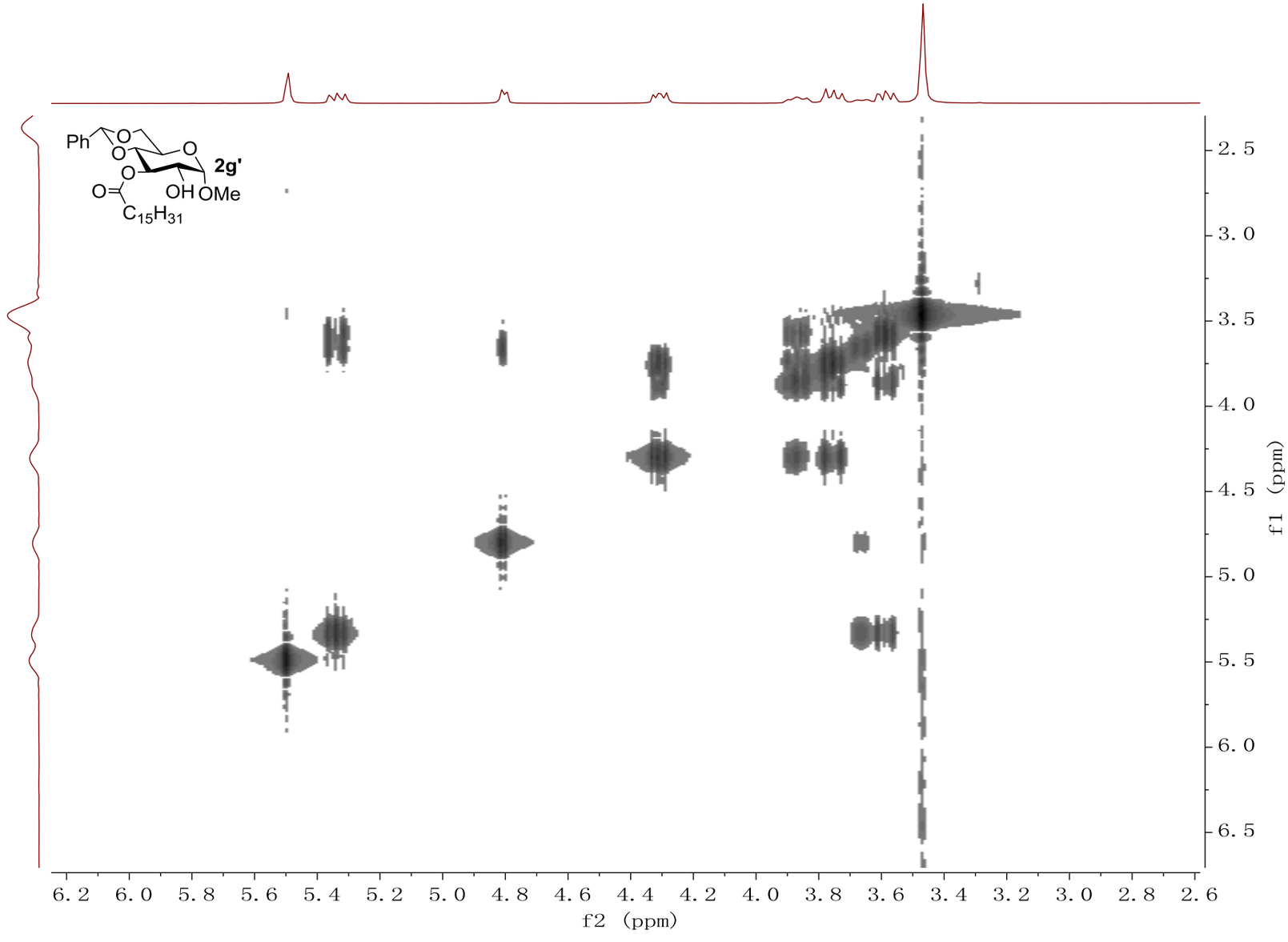
^{1}H-NMR of compound **2g'** ($CDCl_3$)



^{13}C-NMR of compound **2g'** ($CDCl_3$)

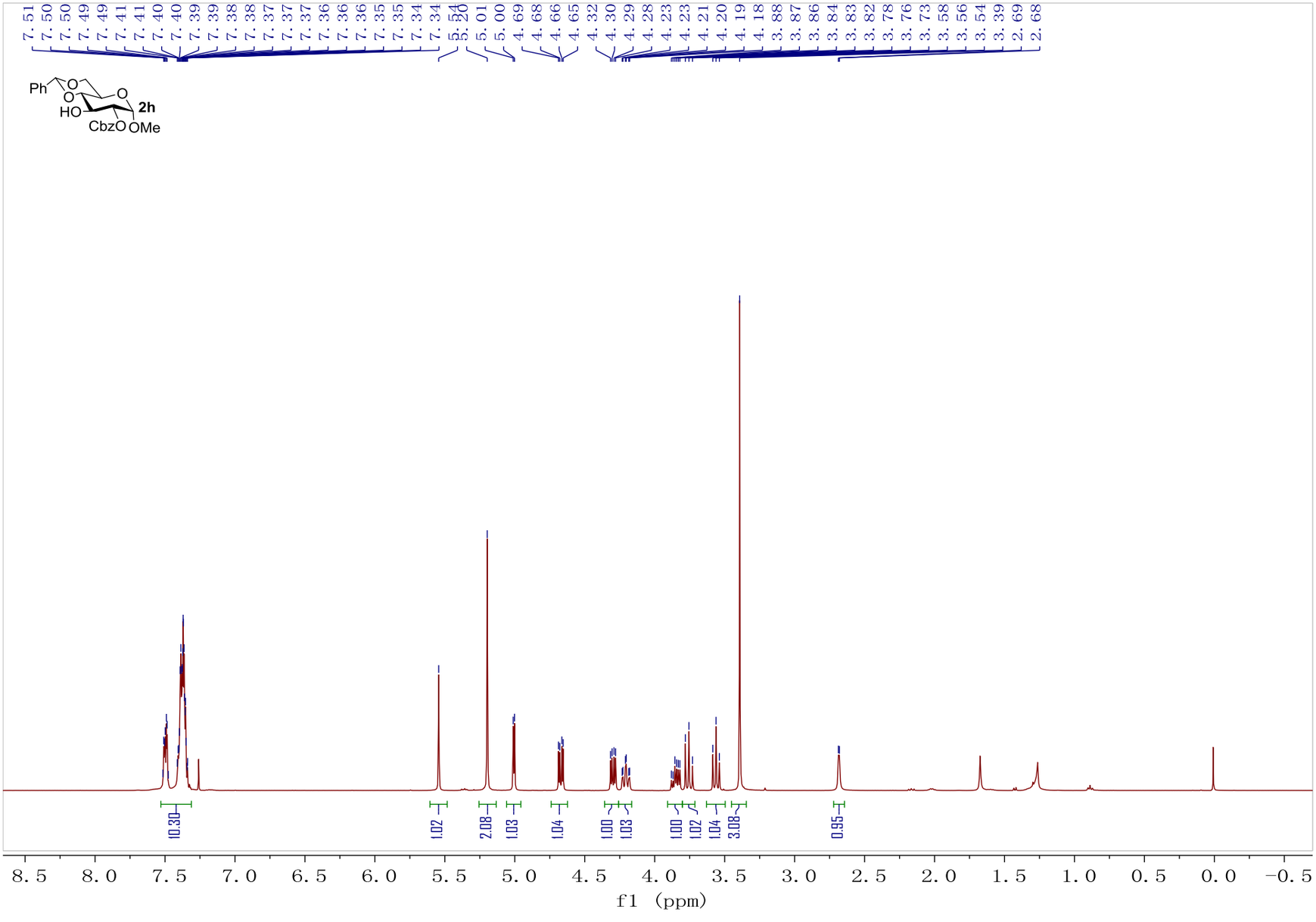


2D-COSY of compound **2g'** ($CDCl_3$)

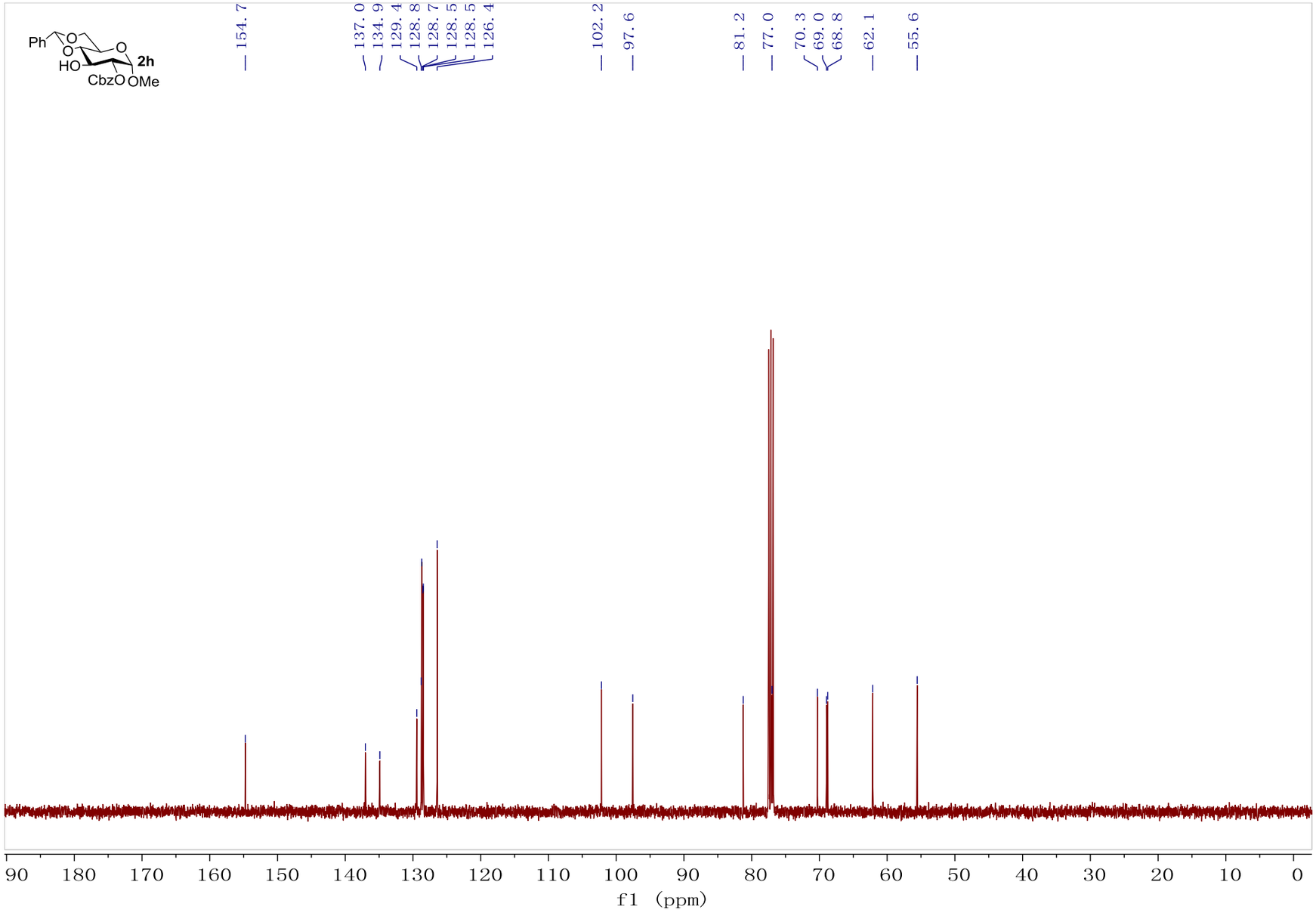


Methyl-2-*O*-benzyloxycarbonyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2h)

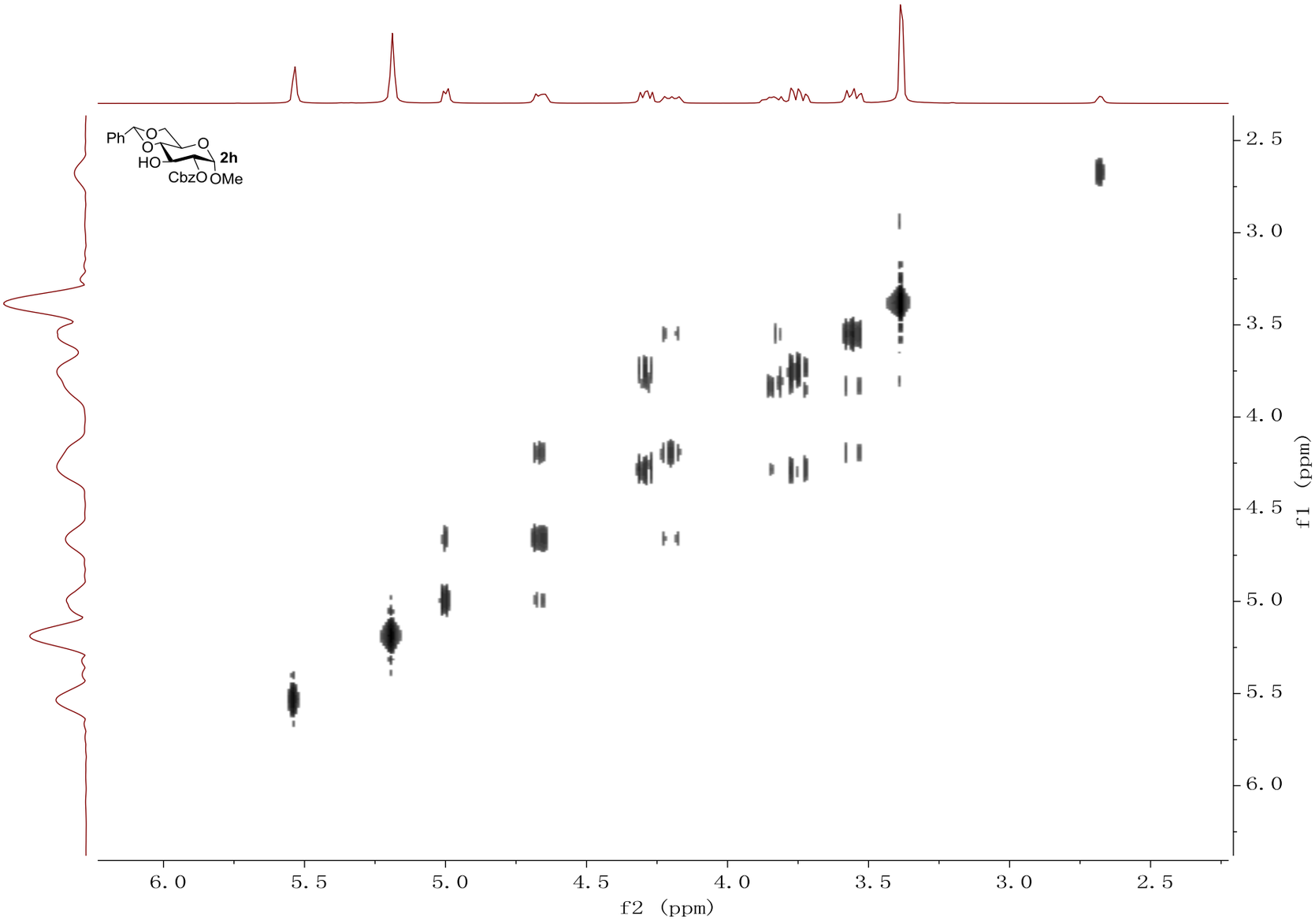
^{1}H-NMR of compound **2h** ($CDCl_3$)



^{13}C-NMR of compound **2h** ($CDCl_3$)

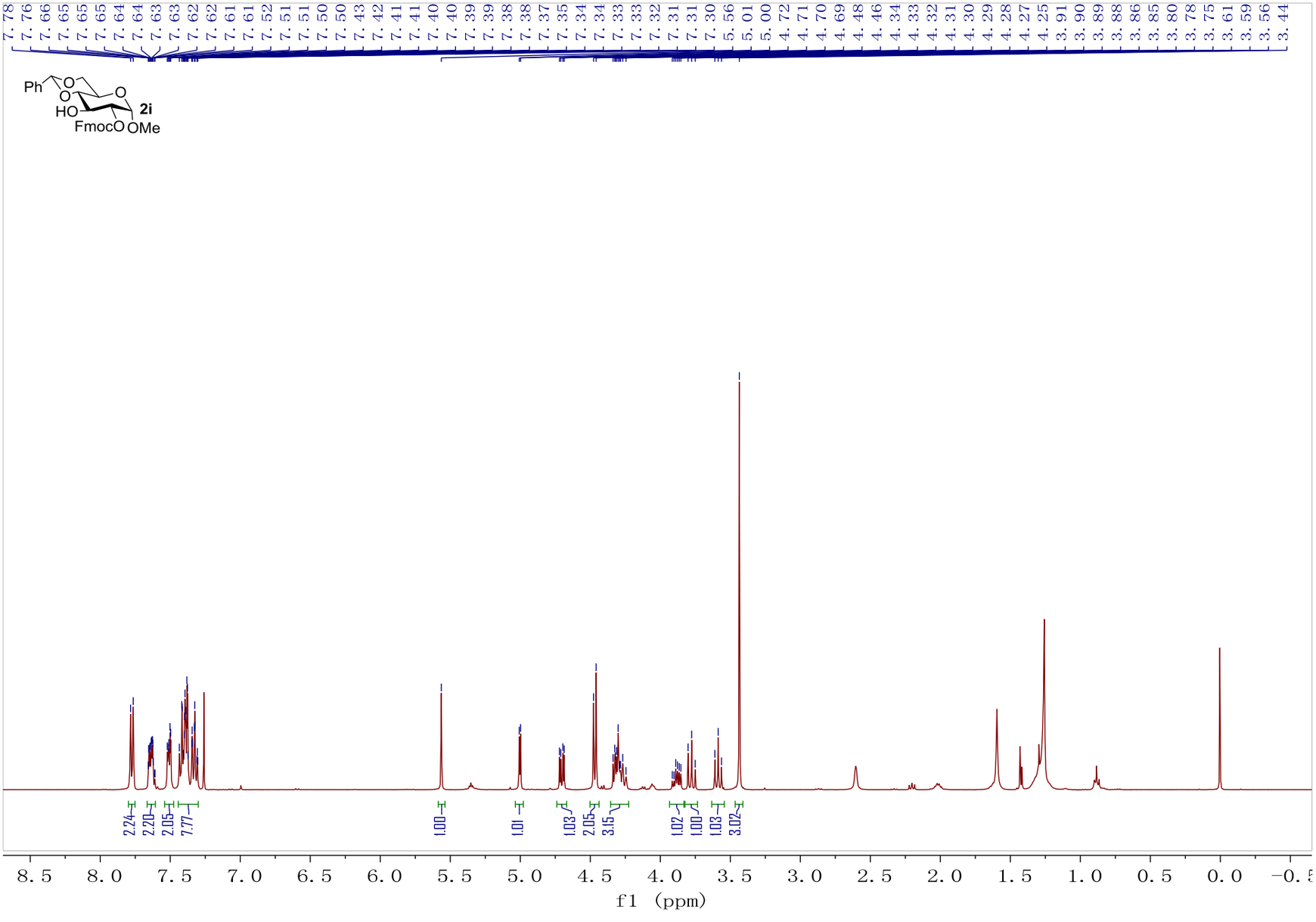


2D-COSY of compound **2h** ($CDCl_3$)

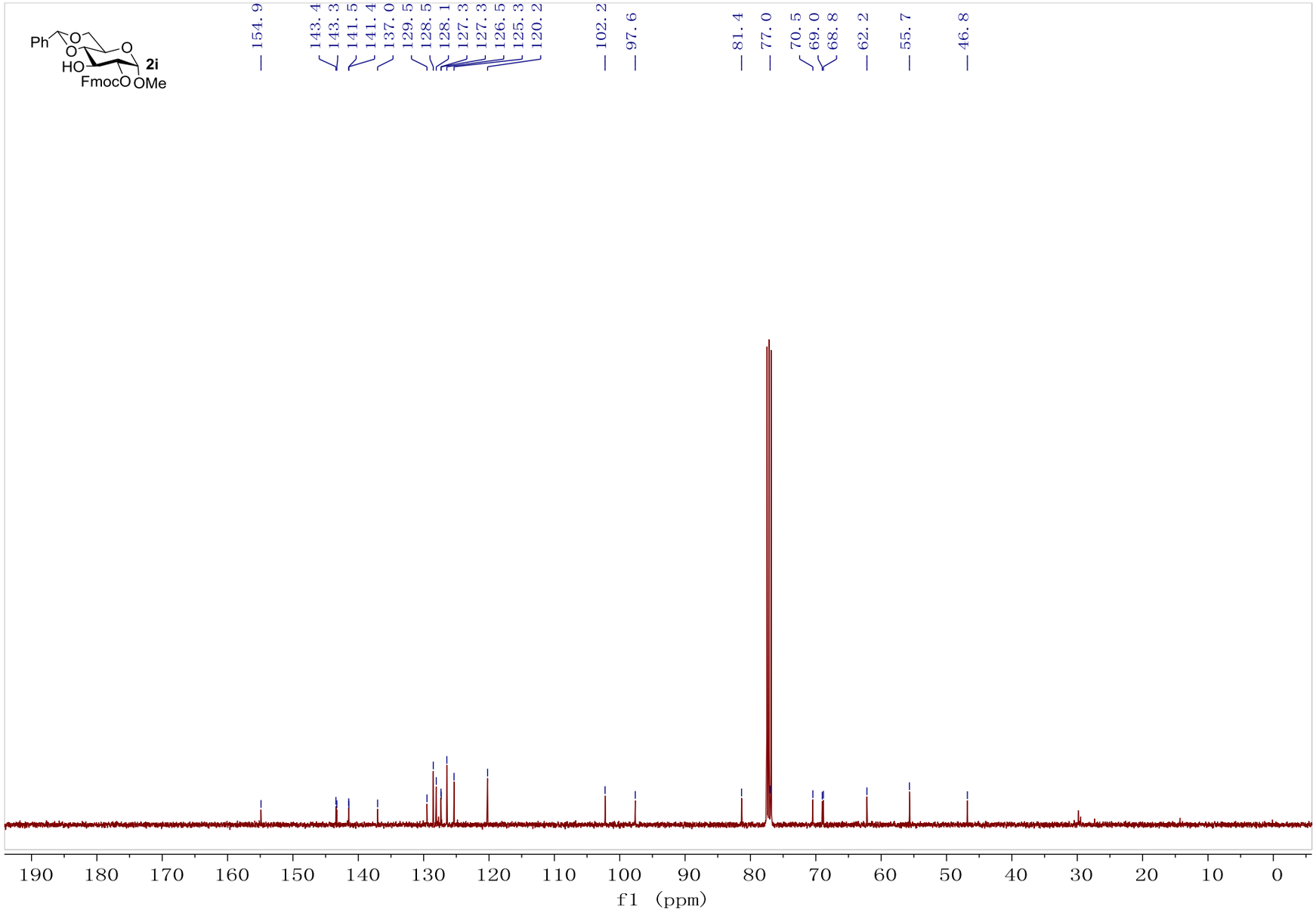


Methyl-2-*O*-9-fluorenylmethyloxycarbonyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside (2i)

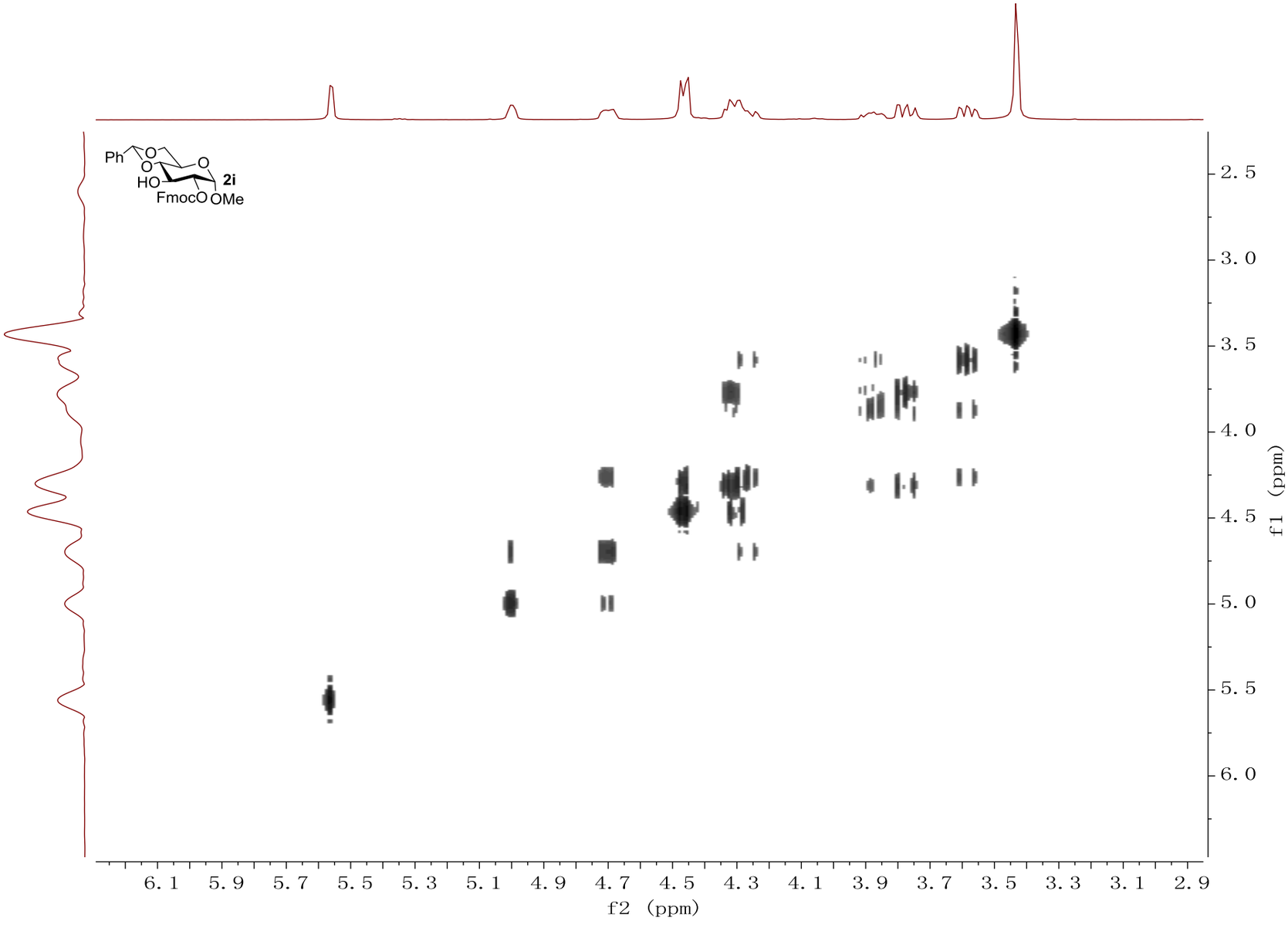
^{1}H-NMR of compound **2i** ($CDCl_3$)



^{13}C-NMR of compound **2i** ($CDCl_3$)

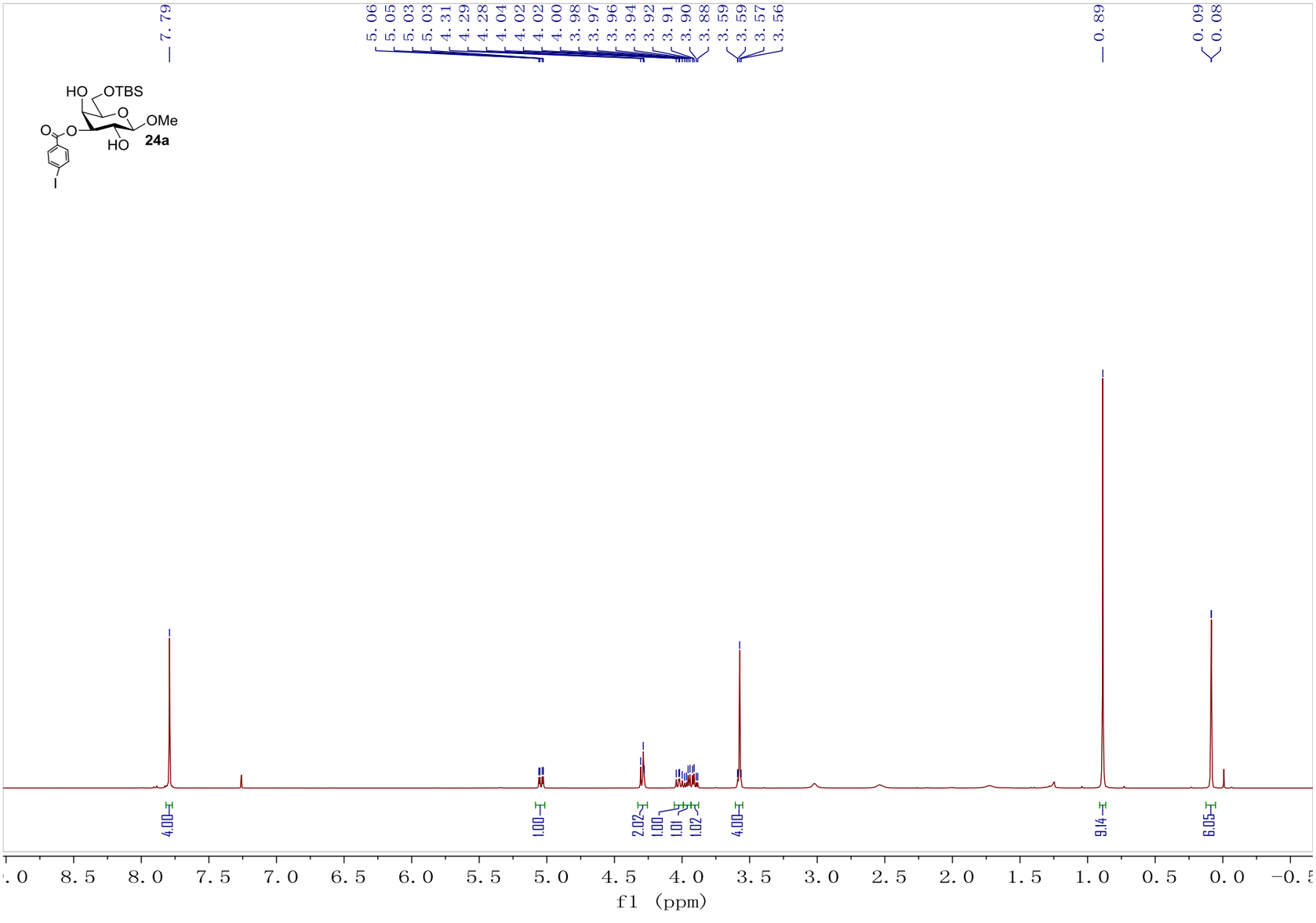


2D-COSY of compound **2i** ($CDCl_3$)

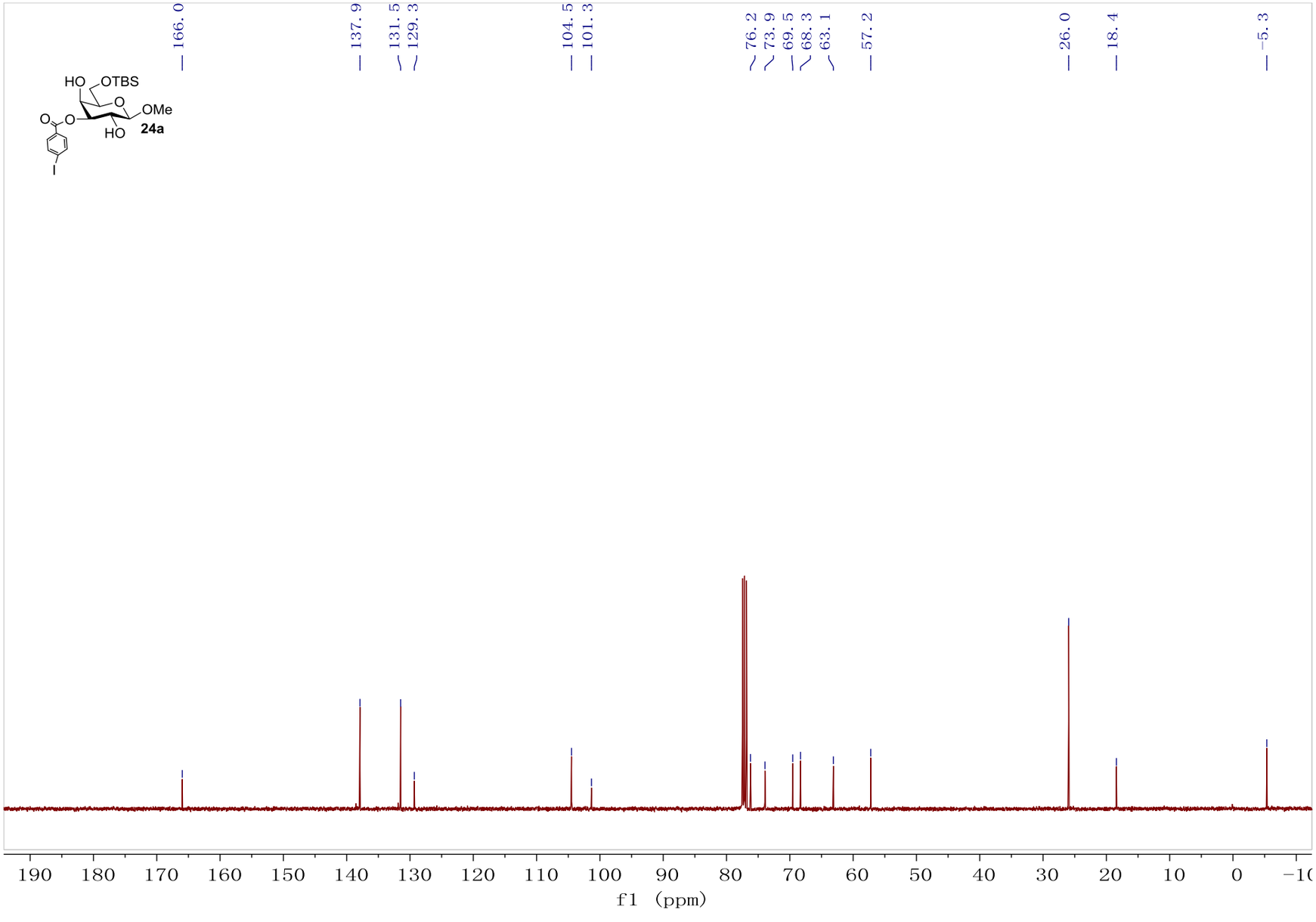


Methyl-3-*O*-4-iodobenzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24a)

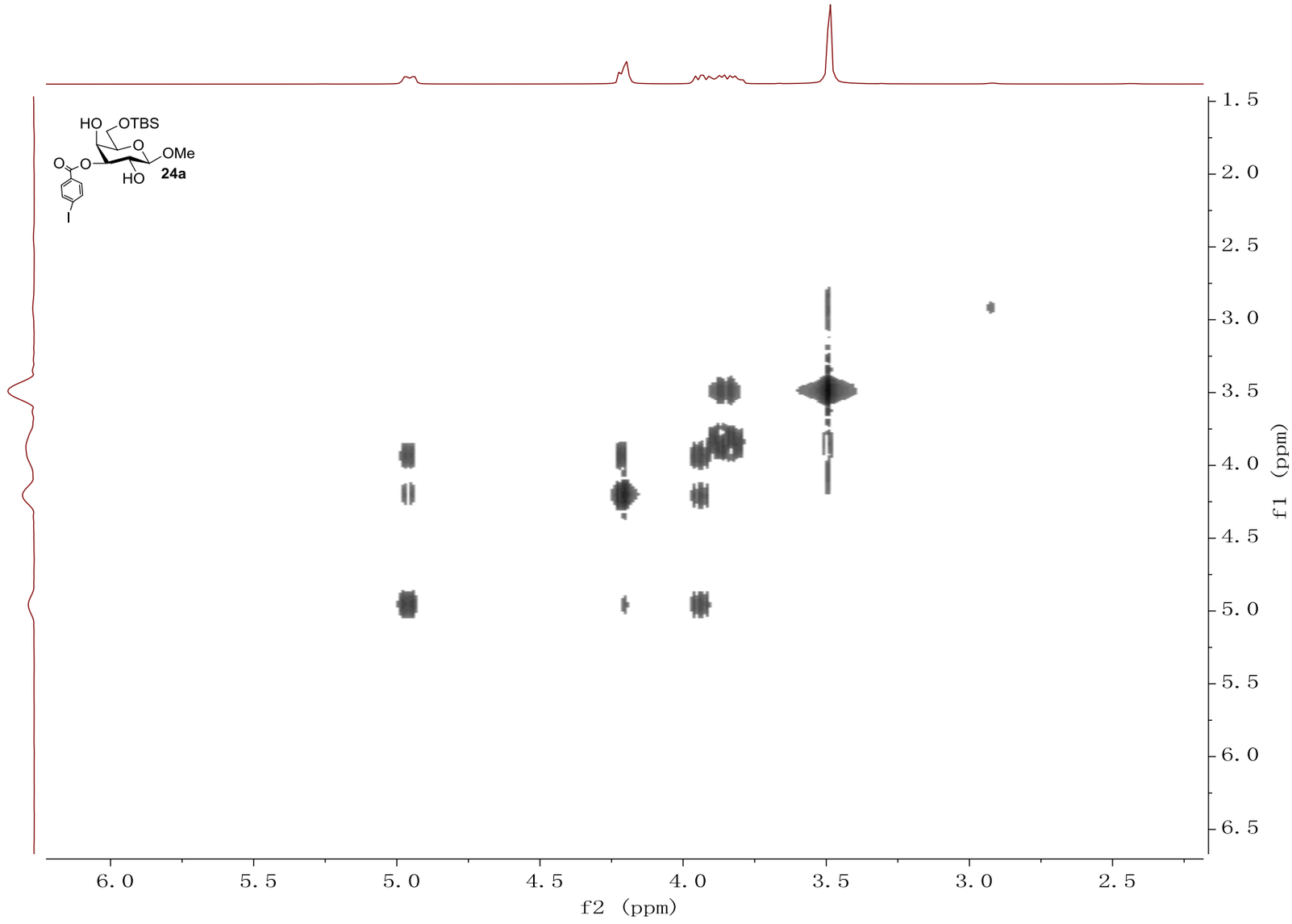
^{1}H-NMR of compound **24a** ($CDCl_3$)



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

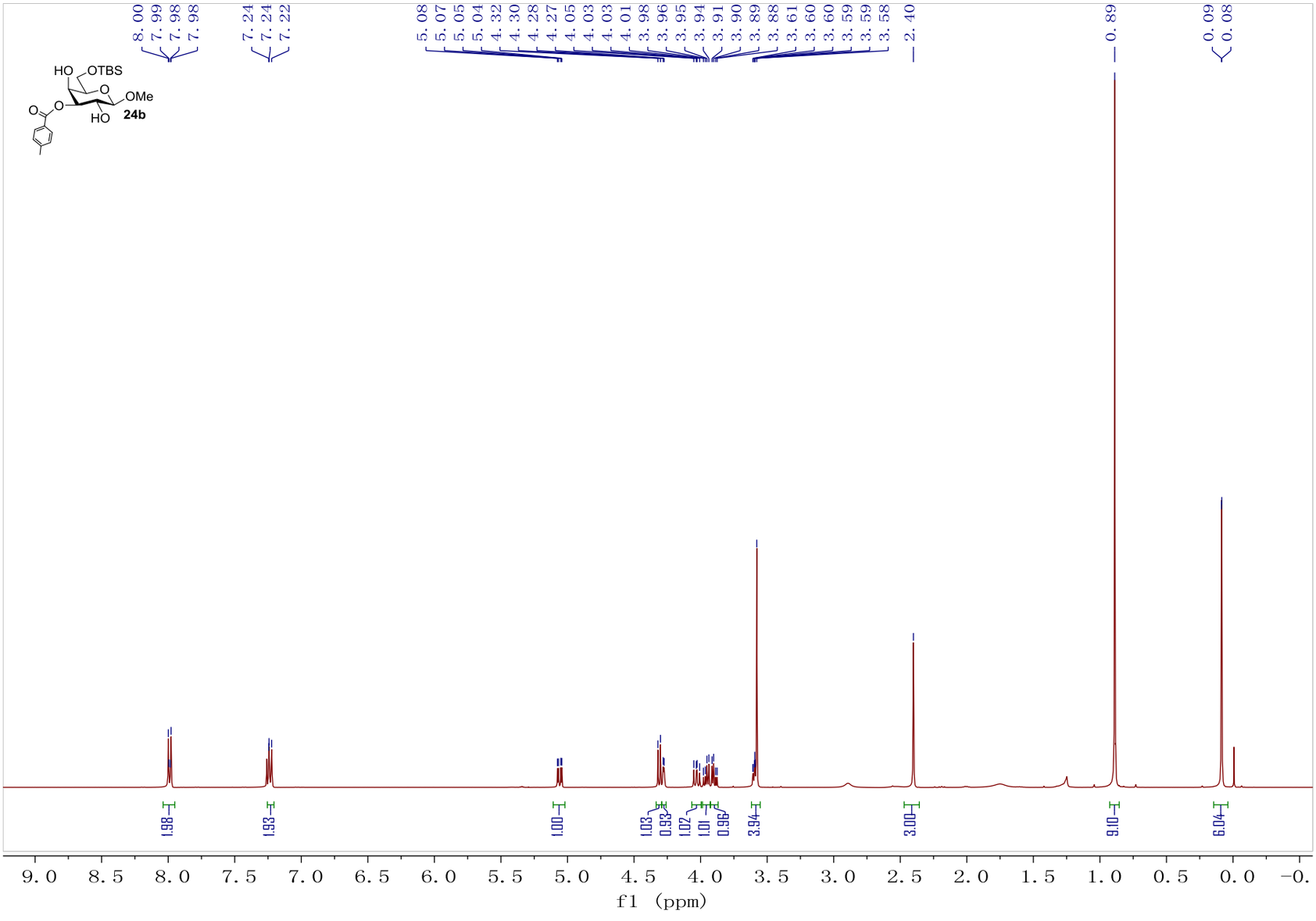


2D-COSY of compound **24a** ($CDCl_3$)

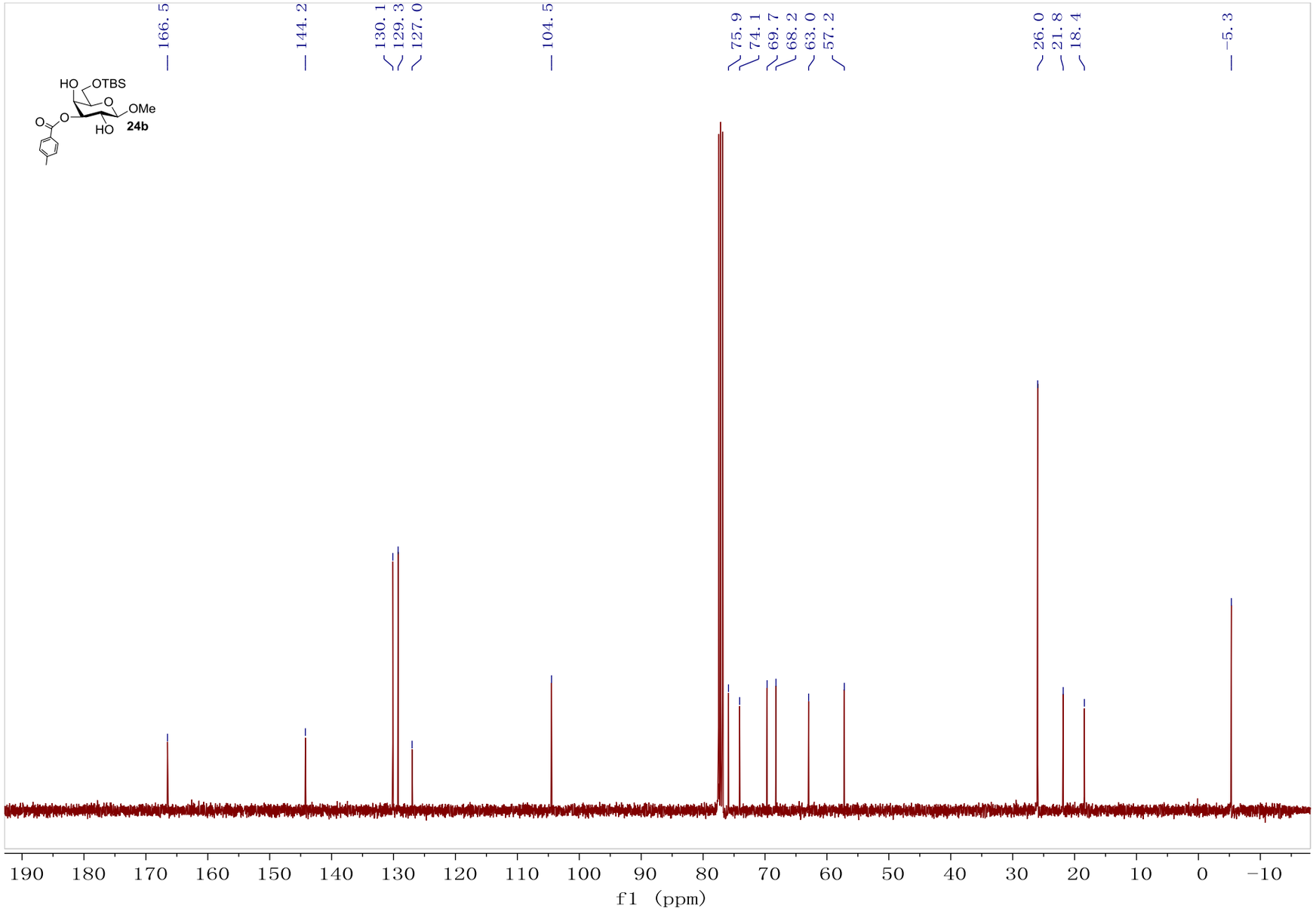


Methyl-3-*O*-4-methylbenzoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24b)

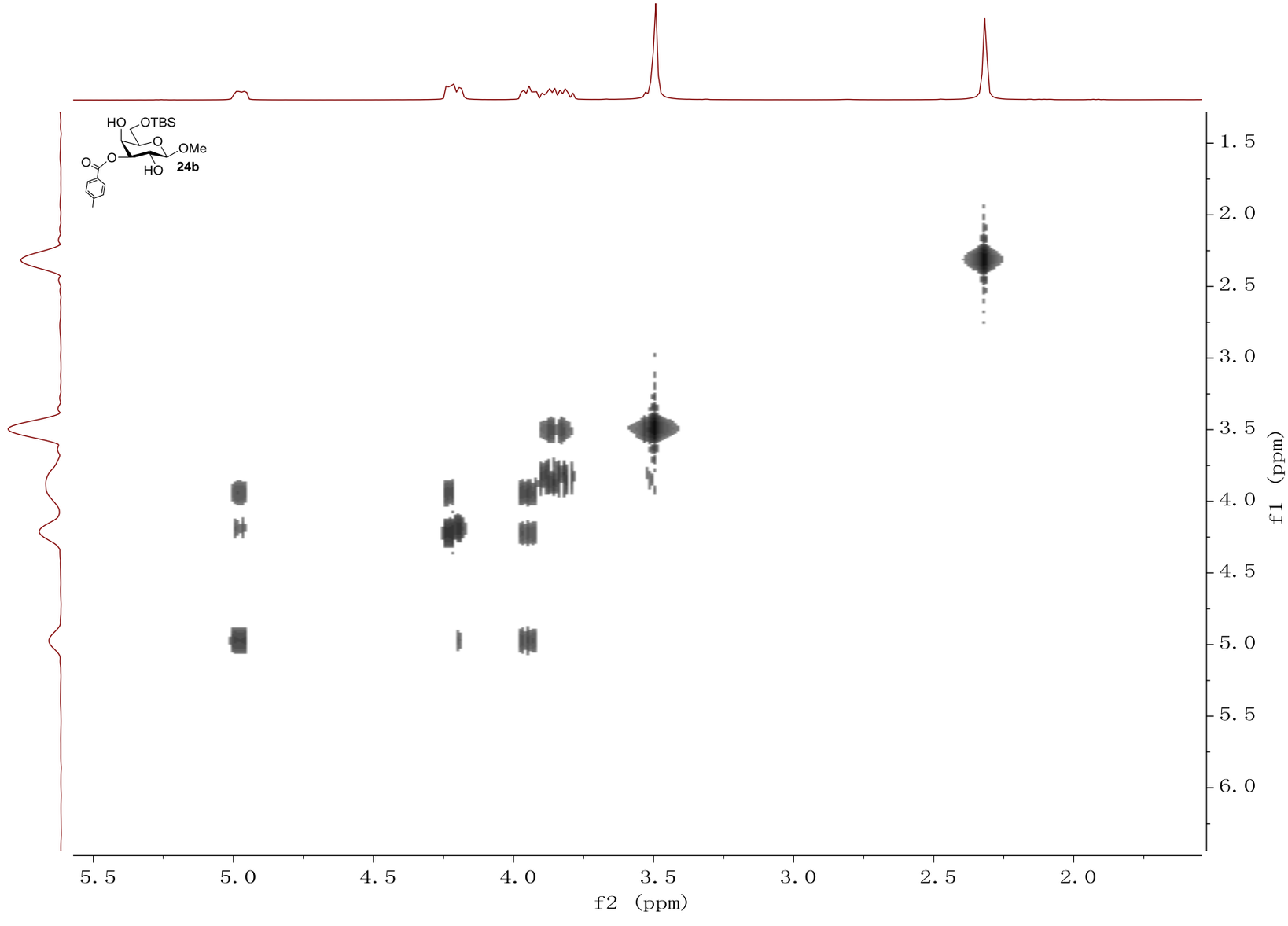
^{1}H-NMR of compound **24b** ($CDCl_3$)



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

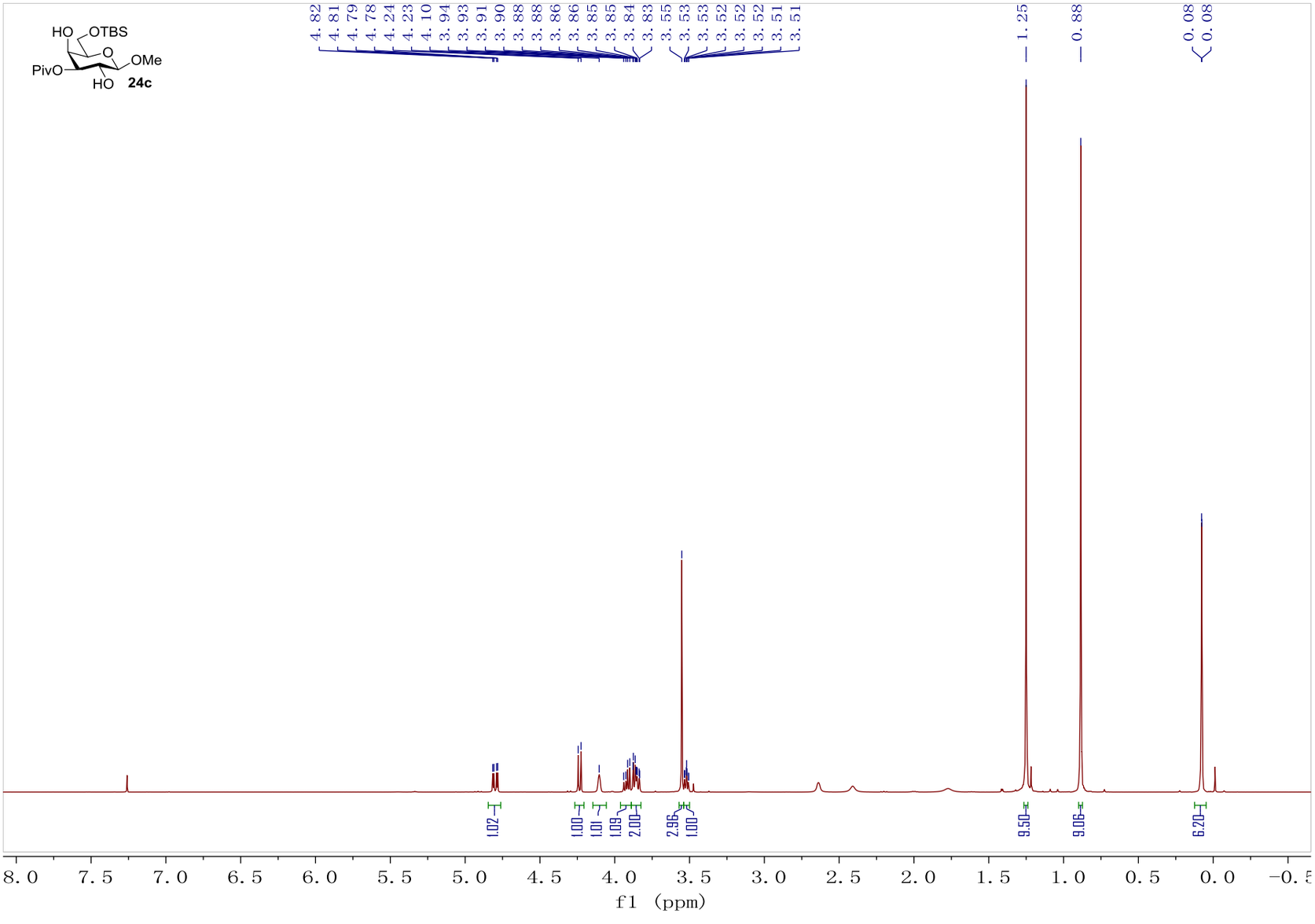


2D-COSY of compound **24b** ($CDCl_3$)



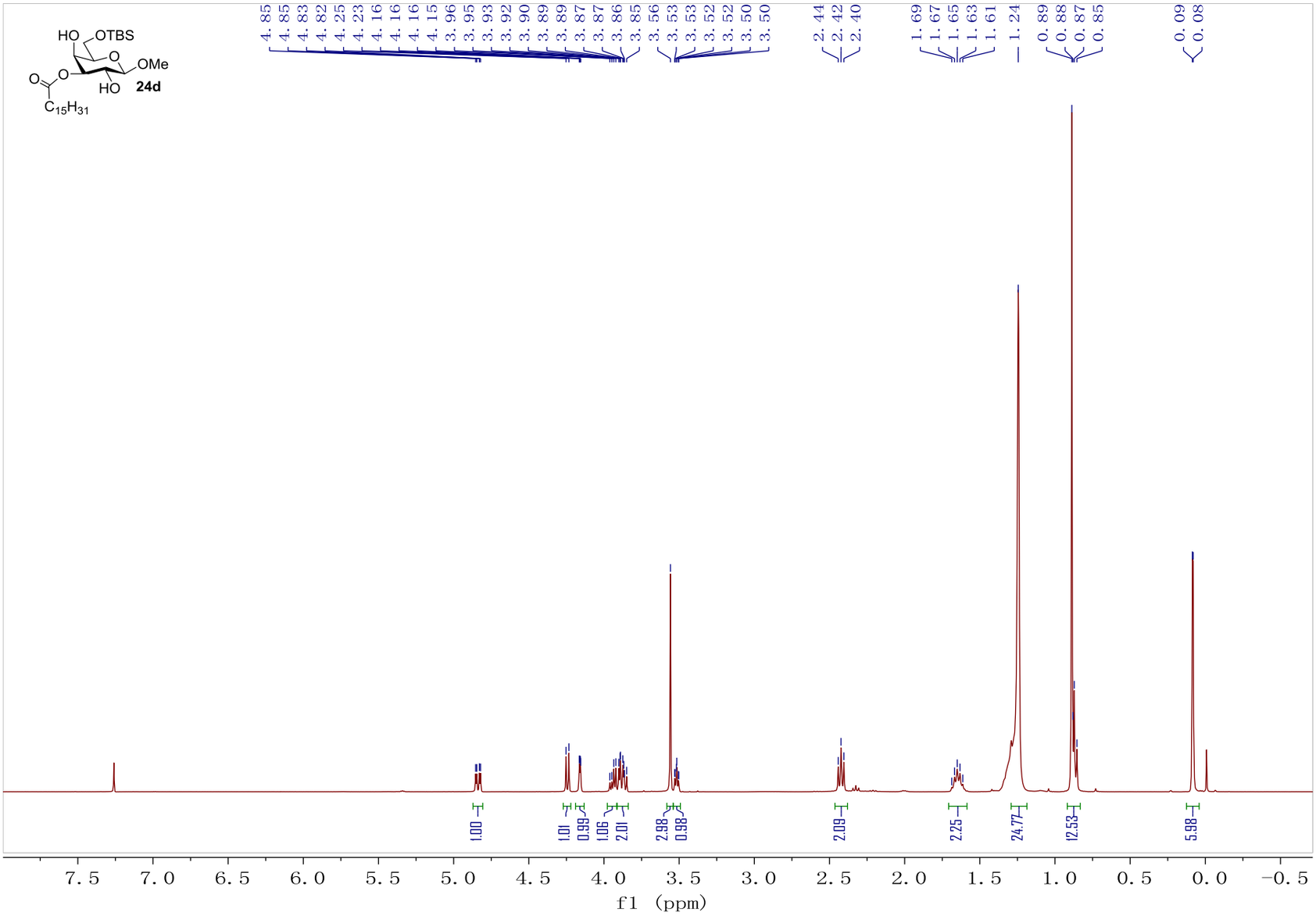
Methyl-3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24c)

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

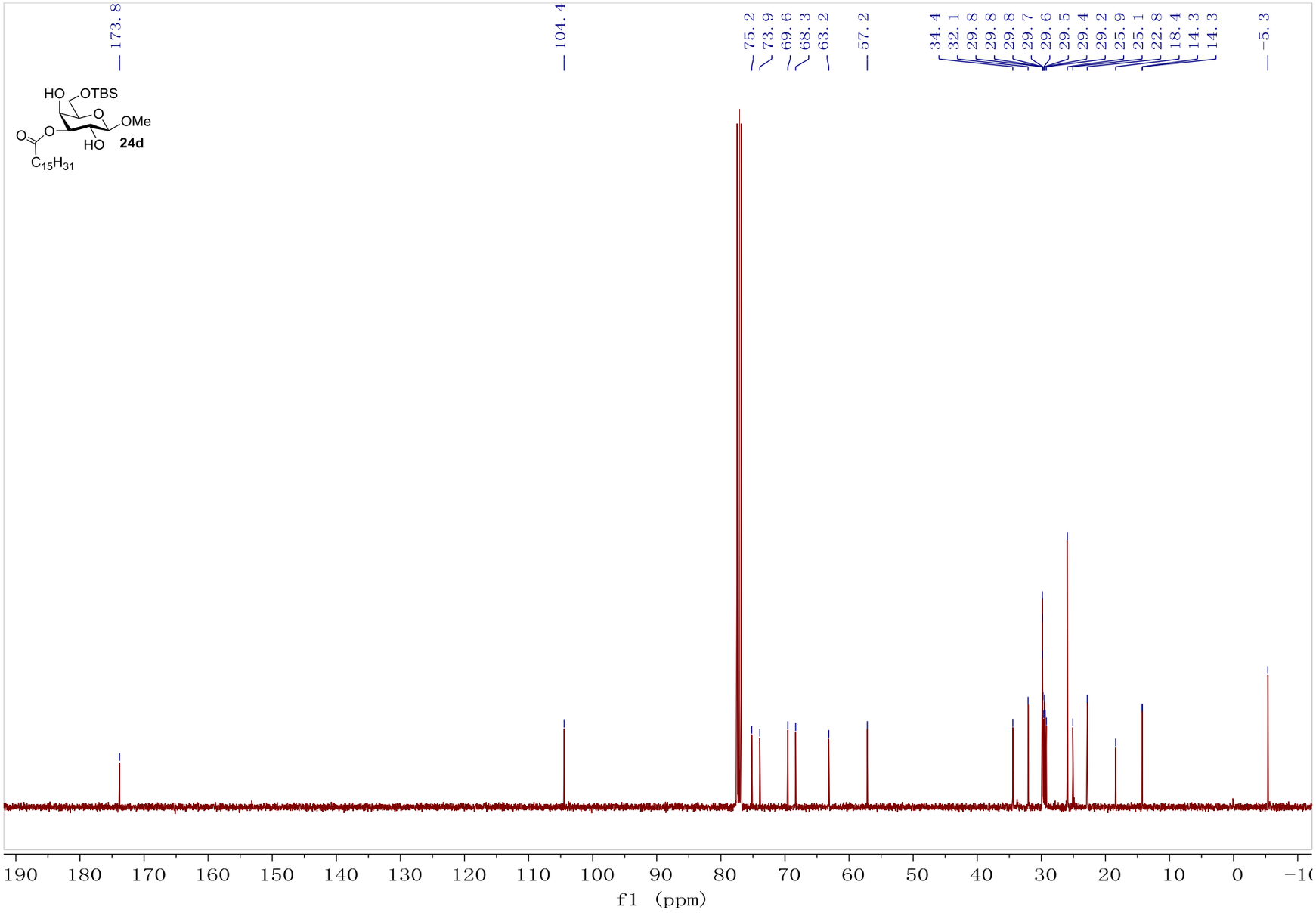


Methyl-3-*O*-palmitoyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24d)

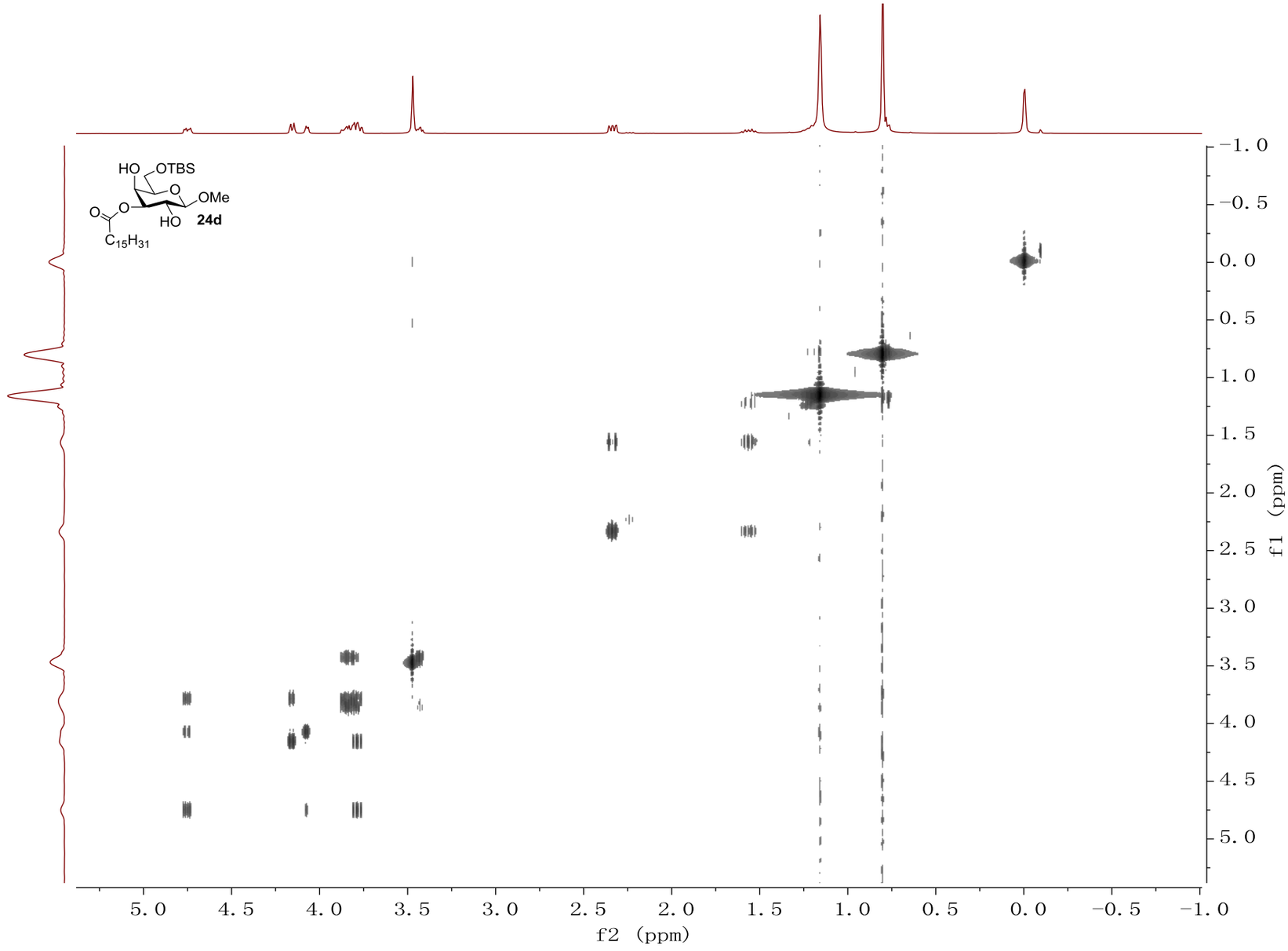
^{1}H-NMR of compound **24d** ($CDCl_3$)



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

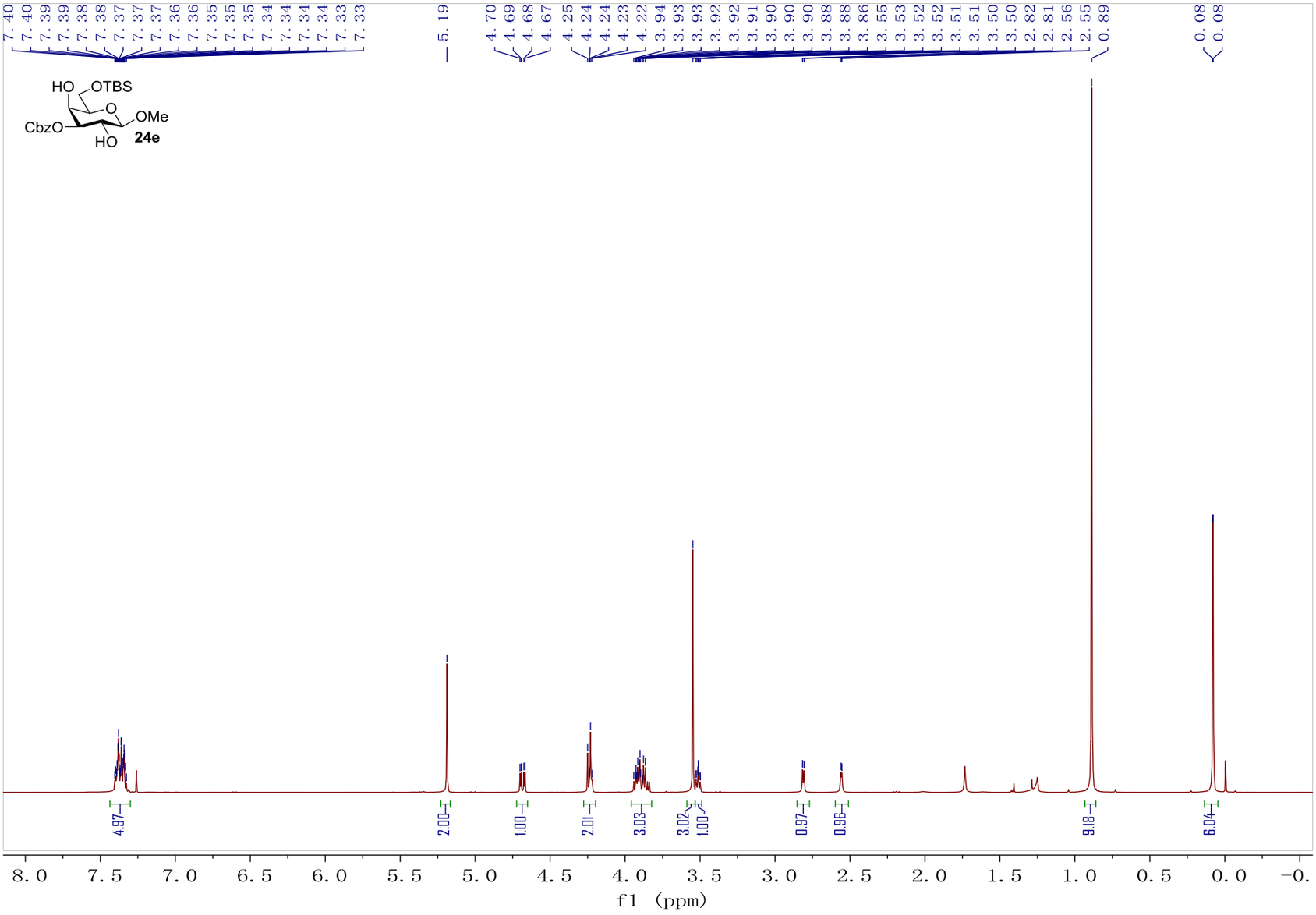


2D-COSY of compound **24d** ($CDCl_3$)

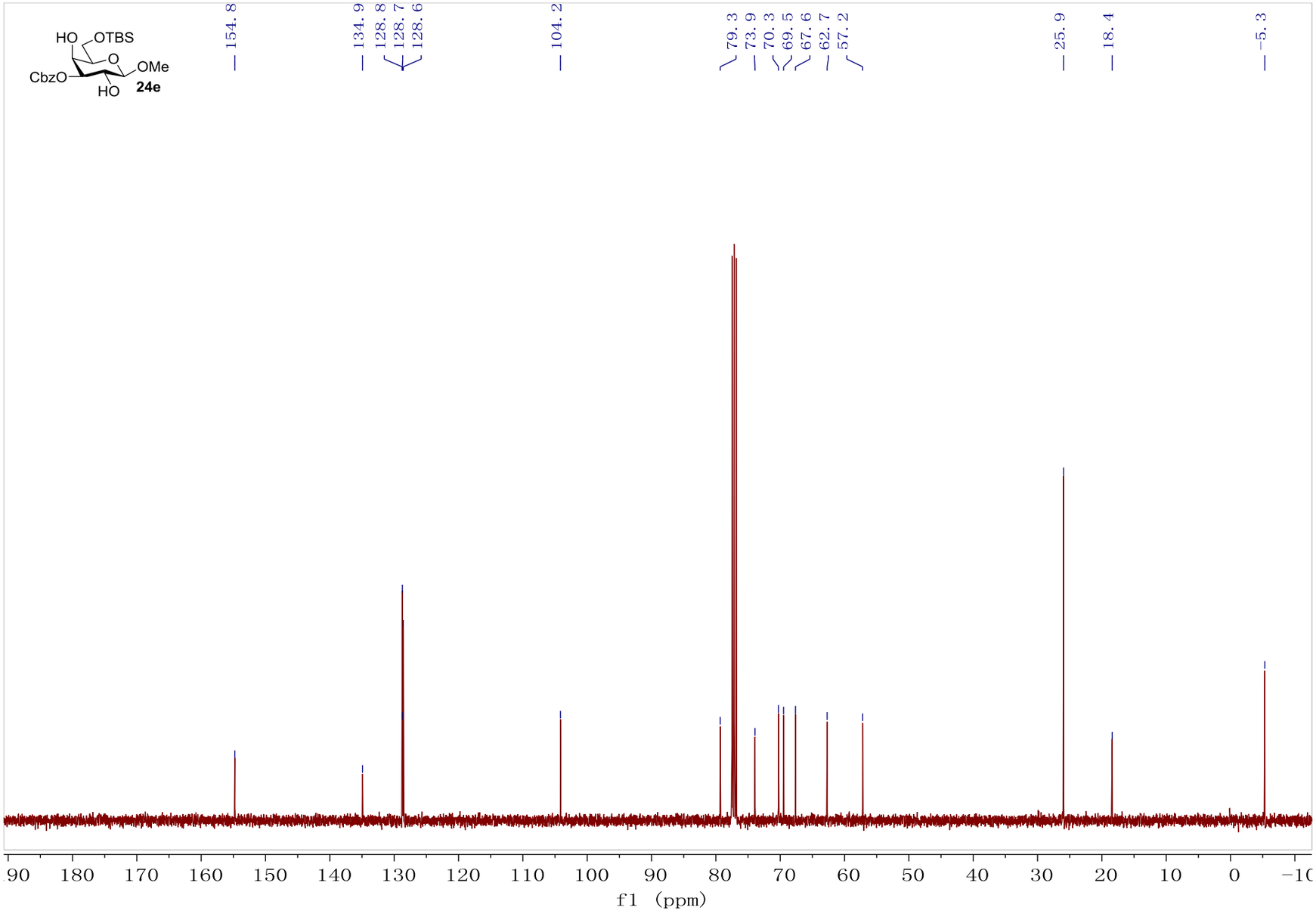


Methyl-3-*O*-benzyloxycarbonyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24e)

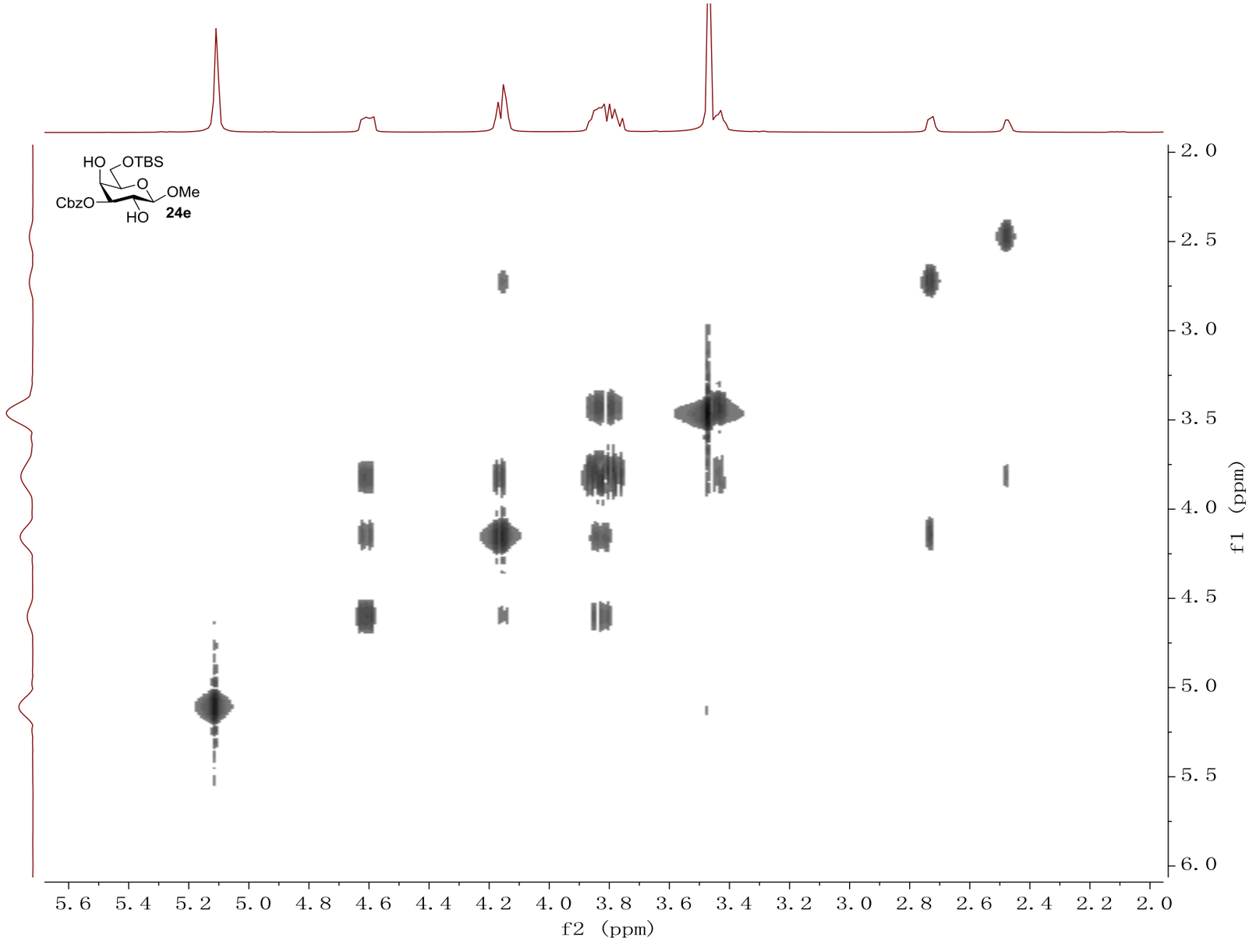
^{1}H-NMR of compound **24e** ($CDCl_3$)



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

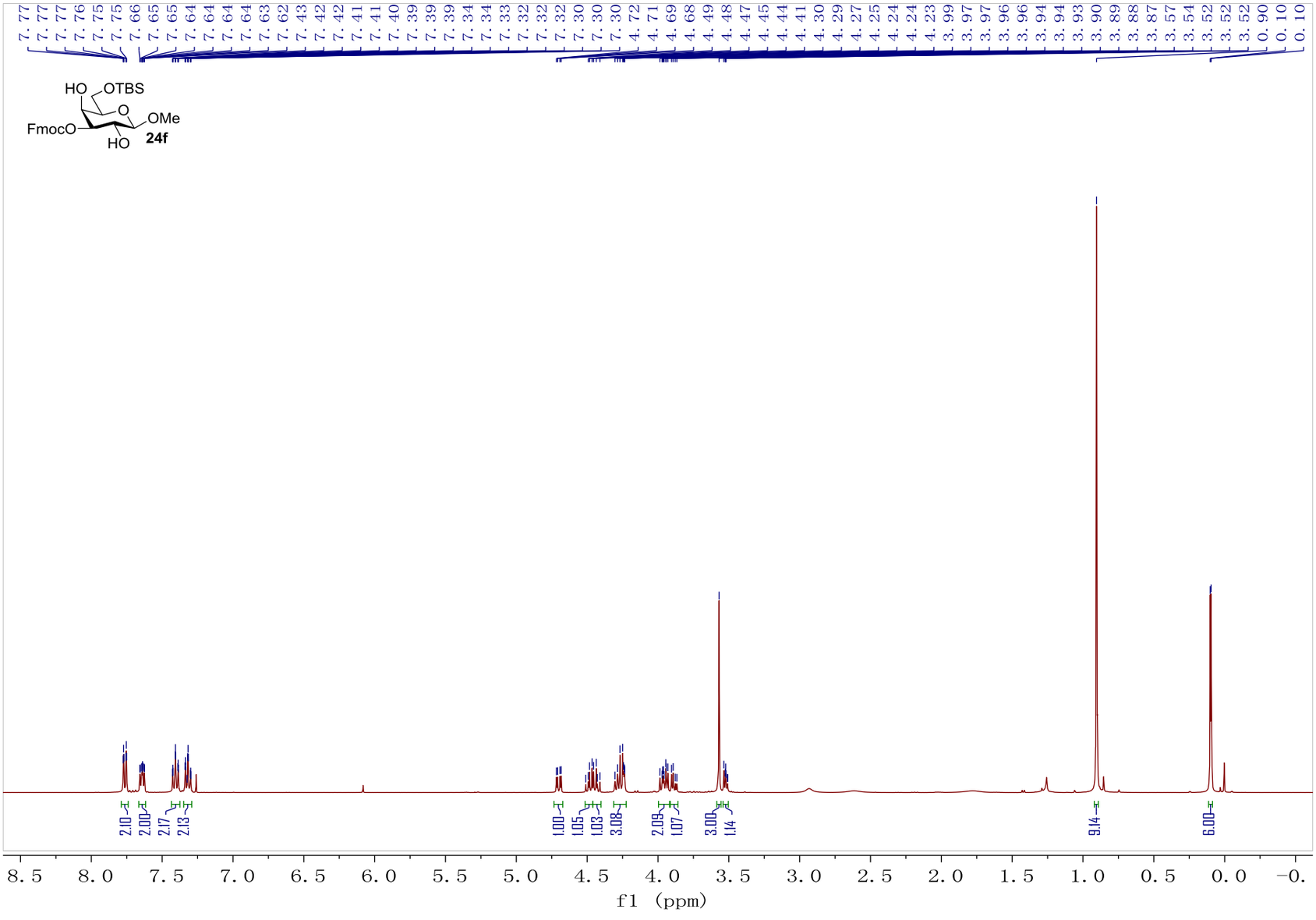


2D-COSY of compound **24e** ($CDCl_3$)

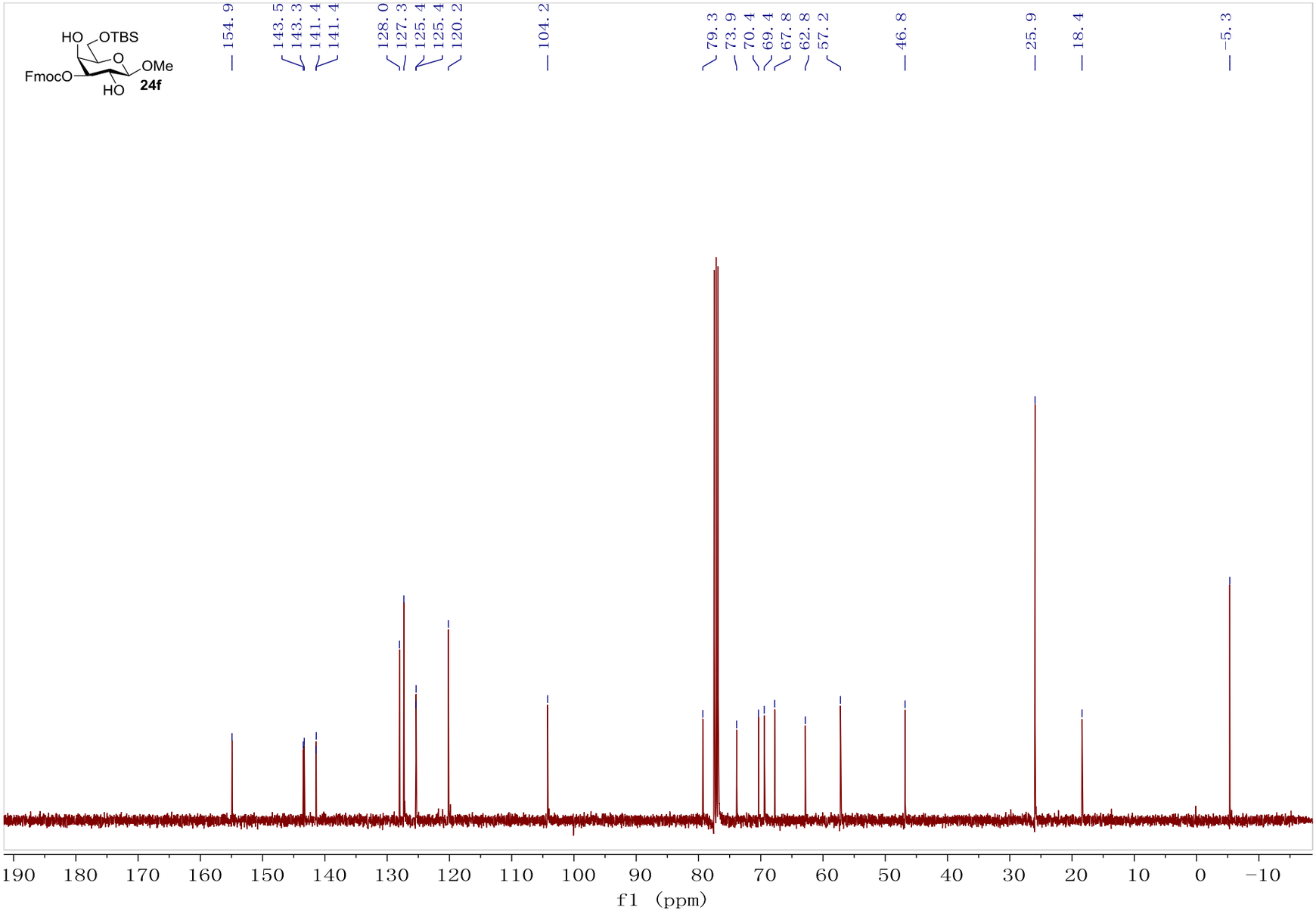


Methyl-3-*O*-9-fluorenylmethyloxycarbonyl-6-*O*-(*tert*-butyldimethylsilyl)-*β*-D-galactopyranoside (24f)

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



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



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