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Supporting Information

Site-Selective Carbamoylation of Carbohydrates Catalyzed by $SnCl_2$/Me_2SnCl_2 Leading to Complementary Selectivity

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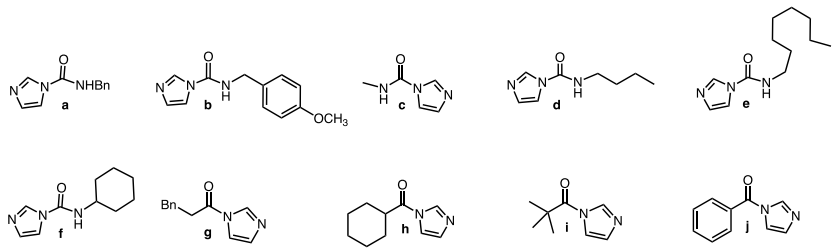
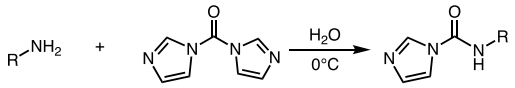
1. General experiments

General. All commercially available starting materials and solvents were of reagent grade and used without further purification. Chemical reactions were monitored with thin-layer chromatography using precoated silica gel 60 (0.25 mm thickness) plates. Flash column chromatography was performed on silica gel 60 (SDS 0.040-0.063 mm). ^{1}H NMR spectra were recorded at 298 K in $CDCl_3$, using the residual signals from $CHCl_3$ (^{1}H: = 7.26 ppm) as internal standard. ^{1}H peak assignments were made by first order analysis of the spectra, supported by standard ^{1}H-^{1}H correlation spectroscopy (COSY).

Structure of acylation reagents a – j.

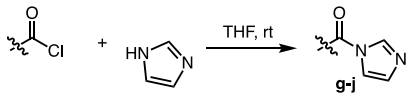


General procedure A for the synthesis of 1-carbamoylimidazoles a - f.



1-carbamoylimidazoles **a-f** were prepared based on the literature[1]: The amine (5.00 mmol) was dissolved in water (50 mL) and stirred for 15 min at 0ºC. Then *N*, *N'*- carbonyldiimidazole (CDI) (6.00 mmol) was added, and the mixture was stirred for 30 min at 0ºC. The mixture was extracted with ethyl acetate (2 × 25 mL), then the organic layers were pooled together and washed with a saturated aqueous solution of $NaHCO_3$ (2 × 25 mL) and a saturated aqueous solution of NaCl (25 mL). The organic layer was dried over Na_2SO_4, filtered and the solvent rotary evaporated. The crude residue was chromatographed over silica gel using a gradient of ethyl acetate (from 0% to 50%) in dichloromethane as the mobile phase to afford the expected 1-carbamoylimidazole **a**-**f**.

General procedure B for the synthesis of acyl imidazoles g - j.



Acyl imidazoles **g-j** were prepared based on the literature[2]: Imidazole (11.72 mmol) was dissolved in anhydrous THF (20 mL) and the corresponding acyl chloride (0.5 equiv, 5.86 mmol) was added dropwise. The reaction mixture was stirred overnight at room temperature under argon. The white precipitate of imidazolium chloride was filtered off and discarded. The solvent was removed under vacuum to give the acyl imidazolide **g-j**, which was stored under argon at 4°C and used for the acylation reactions without further purification.

General procedure C for the carbamoylation of substrates catalyzed by $SnCl_2$.

The substrate (0.1 - 0.2 mmol), $SnCl_2$ (0.1 equiv) and *N*, *N*-diisopropylethylamine (DIPEA) (0.2 equiv) were mixed in dry acetonitrile (0.5 - 1.0 mL). Then, 1-carbamoylimidazole (1.4 equiv) was added to the

mixture. After stirring vigorously at (50℃ - 70℃) for 4 - 12 hours, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography, affording the pure selectively carbamoylated derivatives.

General procedure D for the carbamoylation of substrates catalyzed by Me_2SnCl_2. The substrate (0.1 - 0.2 mmol), Me_2SnCl_2 (0.1 equiv) and DIPEA (0.2 equiv) were mixed in dry acetonitrile (0.5 - 1.0 mL). Then, 1-carbamoylimidazole (1.4 equiv) was added to the mixture. After stirring vigorously at 50℃ for 1 - 2 hours, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography, affording the pure selectively carbamoylated derivatives.

2. Figure S1-5

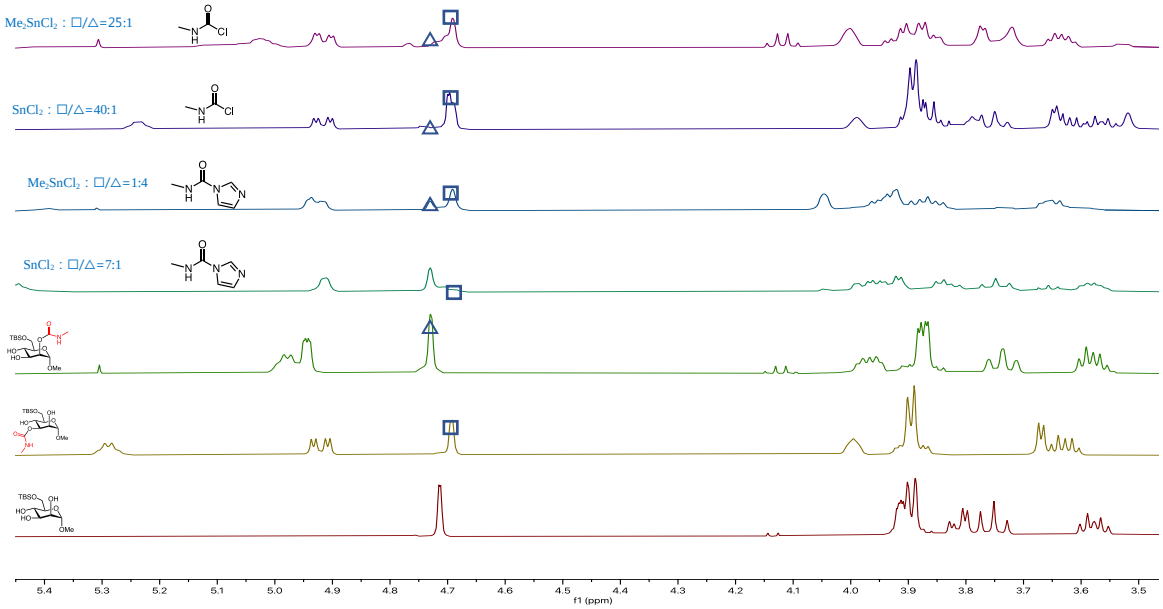


Figure S1. ^{1}H-NMR spectra of crude products with c and c' as acylation reagents

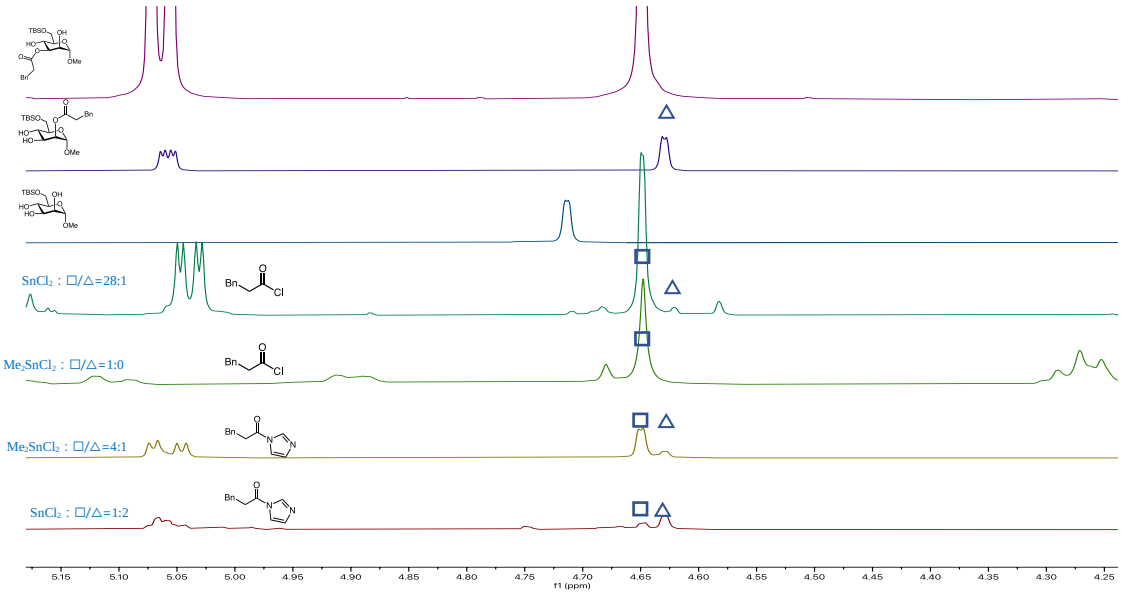


Figure S2. ^{1}HNMR spectra of crude products with g and g' as acylation reagents

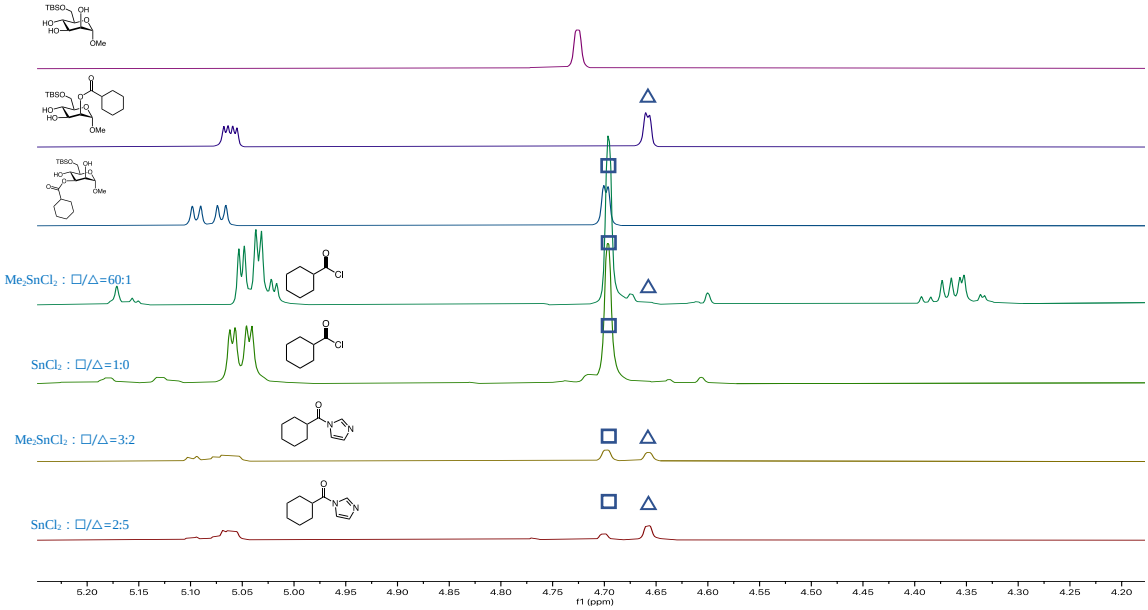


Figure S3. ^{1}HNMR spectra of crude products with h and h' as acylation reagents

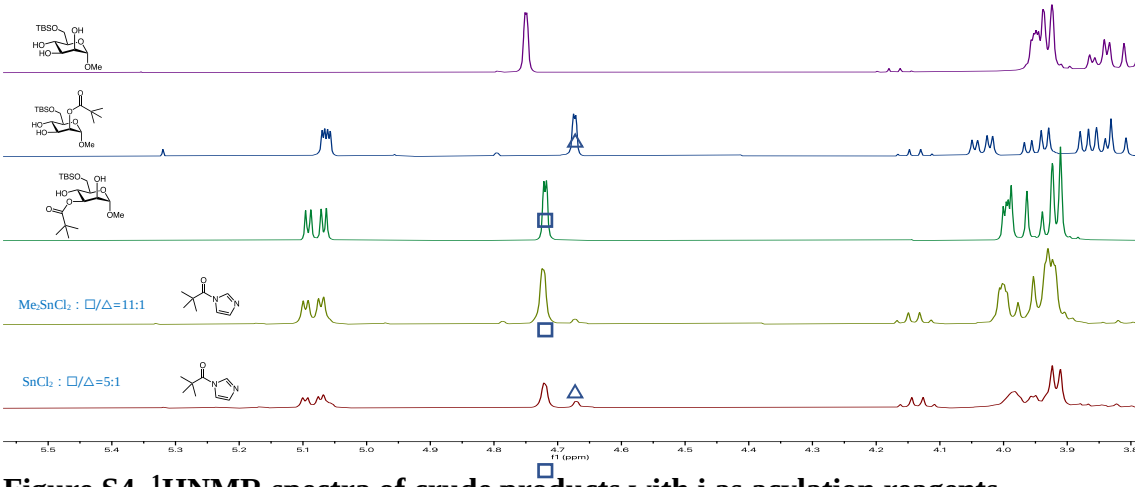


Figure S4. ^{1}HNMR spectra of crude products with i as acylation reagents

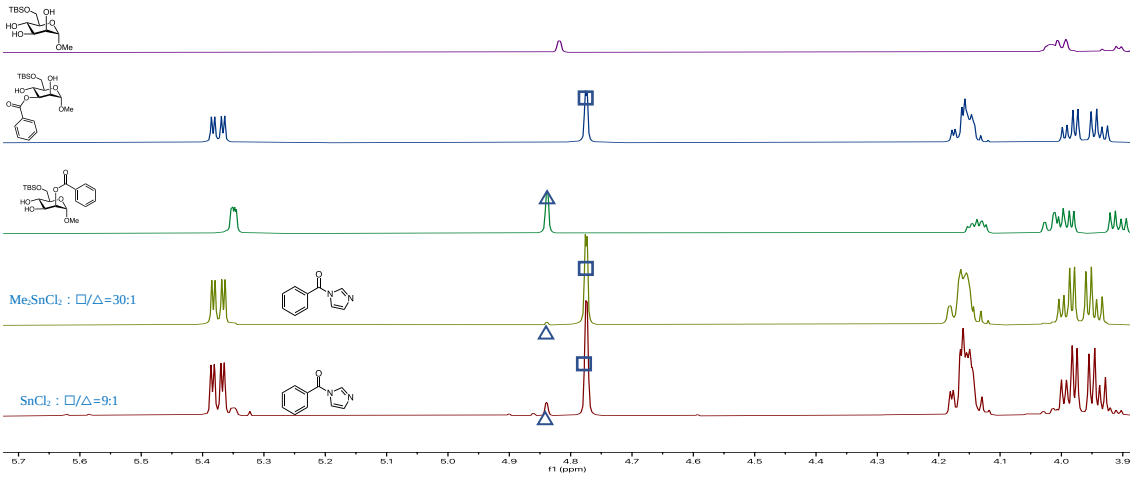
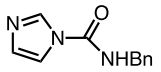
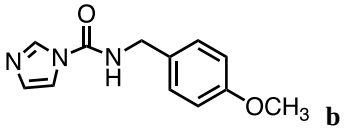


Figure S5. ^{1}HNMR spectra of crude products with j as acylation reagents

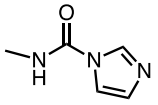
3. Preparation and characterization for the compounds

 **a**

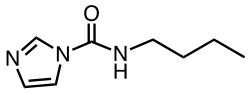
1-benzyl-carbamoylimidazole (**a**)：Following the general procedure A, a mixture of benzylamine (2.14 g, 20 mmol) and CDI (3.89 g, 24 mmol) afforded the title compound **a** as a white powder (3.635 g, 90%). *Rf* = 0.30 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ 9.08 (s, 1H), 8.28 (s, 1H), 7.71 (s, 1H), 7.40 – 7.27 (m, 5H), 7.04 (s, 1H), 4.46 (d, *J* = 5.9 Hz, 2H). NMR data were consistent with literature description.[1]

 **b**

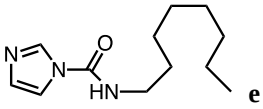
1-(4-methoxyphenyl)-carbamoylimidazole (**b**). Following the general procedure A, a mixture of 4-methoxybenzylamine (686 mg, 5.00 mmol) and CDI (973 mg, 6.00 mmol) afforded the title compound **b** as an off-white powder (982.2 mg, 85%). *Rf* = 0.24 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.74 (t, J = 5.6 Hz, 1H), 7.42 (s, 1H), 7.26 – 7.20 (m, 2H), 6.90 – 6.83 (m, 3H), 4.50 – 4.44 (m, 2H), 3.78 (s, 3H). NMR data were consistent with literature description.[3]

 **c**

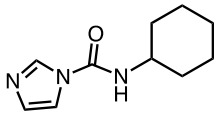
1-methyl-carbamoylimidazole (**c**). Synthesized in light of the reported reference.[4] CDI (20.0 g, 111 mmol, 1.10 equiv) and $MeNH_3Cl$ (6.82 g, 101 mmol, 1.0 equiv) were dissolved in DMF (20 mL) and acetonitrile (60 mL). The solution was stirred at room temperature for 2 h before being concentrated under an air stream to a thick oil. Flash chromatography (4% MeOH/ CH_2Cl_2) gave **c** as a white solid (12.6 g, quantitative yield). Rf = 0.24 (4% MeOH/CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 4.7 Hz, 1H), 8.26 (t, *J* = 1.2 Hz, 1H), 7.56 (t, *J* = 1.5 Hz, 1H), 7.01 (dd, *J* = 1.6, 0.9 Hz, 1H), 2.99 – 2.95 (m, 3H). NMR data were consistent with literature description.[4]

 **d**

1-butyl-carbamoylimidazole (**d**). Following the general procedure A, a mixture of butylamine (366 mg, 5.00 mmol) and CDI (973 mg, 6.00 mmol) afforded the title compound **d** as a colorless oil (715.5 mg, 85%). *Rf* = 0.35 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (t, J = 5.7 Hz, 1H), 8.28 (s, 1H), 7.61 (s, 1H), 7.00 (s, 1H), 3.41 – 3.34 (m, 2H), 1.62 – 1.55 (m, 2H), 1.41 – 1.31 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). NMR data were consistent with literature description.[1]

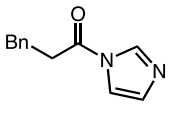
 **e**

1-octyl-carbamoylimidazole (**e**). Following the general procedure A, a mixture of octylamine (646 mg, 5.00 mmol) and CDI (973 mg, 6.00 mmol) afforded the title compound **e** as a colorless oil (268.2 mg, 24%). *Rf* = 0.27 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.00 (t, J = 5.6 Hz, 1H), 7.54 (s, 1H), 7.00 (s, 1H), 3.41 – 3.31 (m, 2H), 1.66 – 1.55 (m, 2H), 1.42 – 1.13 (m, 10H), 0.91 – 0.81 (m, 3H). NMR data were consistent with literature description.[1]



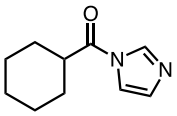
f

1-cyclohexyl-carbamoylimidazole (**f**). Following the general procedure A, a mixture of cyclohexylamine (496 mg, 5.00 mmol) and CDI (973 mg, 6.00 mmol) afforded the title compound **f** as an off-white powder (710.6 mg, 74%). *Rf* = 0.25 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (600 MHz, CDCl3) δ 8.20 (s, 1H), 7.50 (s, 1H), 7.42 (d, J = 7.8 Hz, 1H), 6.99 (s, 1H), 3.83 – 3.74 (m, 1H), 2.06 – 1.98 (m, 2H), 1.79 – 1.70 (m, 2H), 1.69 – 1.61 (m, 1H), 1.43 – 1.19 (m, 4H), 1.17 – 1.06 (m, 1H). NMR data were consistent with literature description.[1]



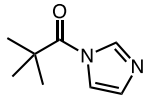
g

1-(benzylacetyl)imidazole (**g**). Following the general procedure B, a mixture of hydrocinnamoyl chloride (843 mg, 5 mmol) and imidazole (680 mg, 10 mmol) afforded the title compound **g** as a colorless oil (950 mg, 95%). *Rf* = 0.25 (ethyl acetate/petroleum ether: 1/4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 1.1 Hz, 1H), 7.45 (t, *J* = 1.5 Hz, 1H), 7.36 – 7.17 (m, 5H), 7.07 (dd, *J* = 1.7, 0.8 Hz, 1H), 3.21 – 3.06 (m, 4H).[5]



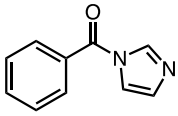
h

1-(cyclohexylcarbonyl)imidazole (**h**). Following the general procedure B, a mixture of cyclohexanecarbonyl chloride (733 mg, 5 mmol) and imidazole (680 mg, 10 mmol) afforded the title compound **h** as a colorless oil (801 mg, 90%). *Rf* = 0.20 (ethyl acetate/petroleum ether: 1/4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.50 (t, *J* = 1.5 Hz, 1H), 7.12 – 7.06 (m, 1H), 2.92 (tt, *J* = 11.5, 3.4 Hz, 1H), 2.04 – 1.81 (m, 4H), 1.80 – 1.71 (m, 1H), 1.70 – 1.58 (m, 2H), 1.46 – 1.19 (m, 3H). NMR data were consistent with literature description.[5]



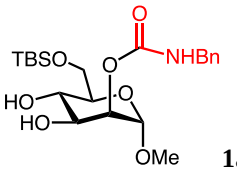
i

1-(trimethylacetyl)imidazole (**i**). Following the general procedure B, a mixture of trimethylacetyl chloride (603 mg, 5 mmol) and imidazole (680 mg, 10 mmol) afforded the title compound **i** as a colorless oil (669 mg, 88%). *Rf* = 0.25 (ethyl acetate/petroleum ether: 1/2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.60 – 7.55 (m, 1H), 7.08 – 7.05 (m, 1H), 1.47 (s, 9H). NMR data were consistent with literature description.[5]



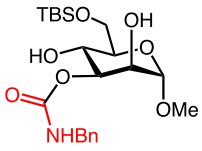
j

1-(benzoyl)imidazole (**j**). Following the general procedure B, a mixture of benzoyl chloride (703 mg, 5 mmol) and imidazole (680 mg, 10 mmol) afforded the title compound **j** as a colorless oil (826 mg, 96%). *Rf* = 0.20 (ethyl acetate/petroleum ether: 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.84 – 7.77 (m, 2H), 7.74 – 7.65 (m, 1H), 7.61 – 7.53 (m, 3H), 7.20 – 7.15 (m, 1H). NMR data were consistent with literature description.[5]



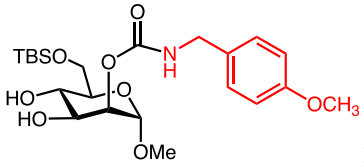
1aa

Methyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1aa**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 4 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1aa** as colorless oil (37.9 mg, 86%). R_f = 0.4 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 17.0 (c 1.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 5H), 5.37 (t, J = 6.0 Hz, 1H, N*H*), 4.97 (dd, J = 3.6, 1.6 Hz, 1H, *H*-2), 4.75 (d, J = 1.7 Hz, 1H, *H*-1), 4.43 – 4.25 (m, 2H, ArC*H*$_2$), 3.97 (dd, J = 9.4, 3.6 Hz, 1H, *H*-3), 3.86 (m, 2H, *H*-6a and *H*-6b), 3.73 (t, J = 9.6 Hz, 1H, *H*-4), 3.57 (dq, J = 10.0, 5.0 Hz, 1H, *H*-5), 3.35 (s, 3H), 0.89 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.36, 138.18, 128.65, 127.55, 127.47, 98.86, 72.83, 71.91, 70.07, 69.16, 63.80, 54.83, 45.05, 25.91, 18.31, -5.27, -5.29. HRMS (ESI) m/z calcd for $C_{21}H_{35}NO_7SiNa$ $[M + Na]^+$ 464.2080, found 464.2100.



1ba

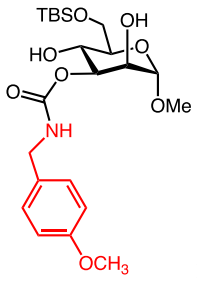
Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ba**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1ba** as colorless oil (36.2 mg, 81%). R_f = 0.6 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, CDCl3) δ 7.36 – 7.20 (m, 5H), 5.59 (t, J = 5.9 Hz, 1H), 4.96 (dd, J = 9.8, 3.2 Hz, 1H), 4.68 (d, J = 1.8 Hz, 1H), 4.36 – 4.31 (m, 2H), 4.02 – 3.98 (m, 1H), 3.95 – 3.84 (m, 3H), 3.63 (dt, J = 10.2, 5.1 Hz, 1H), 3.37 (s, 3H), 0.90 (s, 9H), 0.09 (s, 6H). NMR data were consistent with literature description.[1]



1ab

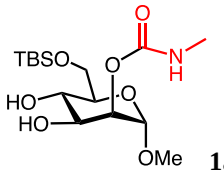
Methyl 2-*O*-(4-methoxy-benzyl) carbamoyl-6-*O*-(tert-butyldimethyl)silyl-α-D-mannopyranoside (**1ab**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(4-methoxyphenyl)-carbamoylimidazole (**b**) (32.3mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1ab** as colorless oil (40.5 mg, 86%). R_f = 0.4 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 17.6 (c 0.34, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.06 (m, 2H), 6.80 – 6.72 (m, 2H), 5.32 (t, *J* = 5.8 Hz, 1H,N*H*), 4.87 (dd, *J* = 3.6, 1.6 Hz, 1H, *H*-2), 4.65 (d, *J* = 1.6 Hz, 1H, *H*-1), 4.25 – 4.08 (m, 2H), 3.87 (dd, *J* = 9.6, 3.5 Hz, 1H, *H*-3), 3.81 – 3.72 (m, 2H, *H*-6a and *H*-6b), 3.70 (s, 3H, OC*H*$_3$), 3.62 (t, *J* = 9.5 Hz, 1H, *H*-4), 3.47 (dt, *J* = 9.7, 4.9 Hz, 1H, *H*-5), 3.26 (s, 3H, OC*H*$_3$), 0.81 (s,

9H), 0.00 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.05, 156.15, 130.14, 128.98, 114.07, 98.96, 72.63, 71.36, 70.19, 69.81, 64.13, 55.28, 54.92, 44.66, 25.86, 18.27, -5.38. HRMS (ESI) m/z calcd for $C_{22}H_{37}NO_8SiNa$ $[M + Na]^+$ 494.2186, found 494.2185.



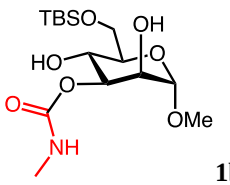
1bb

Methyl 3-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bb**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(4-methoxyphenyl)-carbamoylimidazole (**b**) (32.3mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bb** as colorless oil (38.6 mg, 82%). R_f = 0.7 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 81.4 (c 0.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 2H), 6.79 – 6.71 (m, 2H), 5.35 (t, *J* = 5.8 Hz, 1H, N*H*), 4.86 (dd, *J* = 9.7, 3.2 Hz, 1H, *H*-3), 4.59 (d, *J* = 1.8 Hz, 1H, *H*-2), 4.24 – 4.12 (m, 2H), 3.92 – 3.88 (m, 1H, *H*-2), 3.85 – 3.74 (m, 3H, *H*-4, *H*-6a and *H*-6b), 3.69 (s, 3H), 3.53 (dt, *J* = 9.8, 4.9 Hz, 1H, *H*-5), 3.48 (d, *J* = 3.4 Hz, 1H, 4-O*H*), 3.28 (s, 3H), 2.42 – 2.37 (m, 1H, 2-O*H*), 0.81 (s, 9H), -0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.08, 156.76, 130.10, 129.07, 114.08, 100.59, 75.43, 72.10, 69.56, 67.64, 63.91, 55.29, 54.90, 44.76, 25.90, 18.32, -5.40. HRMS (ESI) m/z calcd for $C_{22}H_{37}NO_8SiNa$ $[M + Na]^+$ 494.2186, found 494.2231.



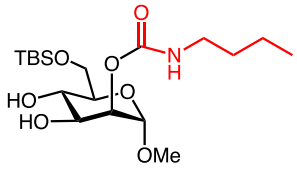
1ac

Methyl 2-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ac**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-methyl-carbamoylimidazole (**c**) (17.5 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 6 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1ac** as colorless oil (28.5 mg, 78%). R_f = 0.5 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 42.9 (c 0.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.81 (m, 2H, N*H*, *H*-2), 4.62 (d, *J* = 1.7 Hz, 1H, *H*-1), 3.86 (dd, *J* = 9.2, 4.5 Hz, 1H, *H*-3), 3.77 (dd, *J* = 5.1, 2.1 Hz, 2H, *H*-6a and *H*-6b), 3.67 – 3.58 (m, 1H, *H*-4), 3.47 (dt, *J* = 9.7, 5.0 Hz, 1H, *H*-5), 3.26 (s, 3H), 3.24 – 3.20 (m, 1H, 4-O*H*), 3.03 (d, *J* = 5.0 Hz, 1H, 3-O*H*), 2.69 (m, 2H), 0.81 (s, 9H), -0.00 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.79, 99.05, 72.48, 71.13, 70.25, 70.04, 64.25, 54.96, 27.59, 25.86, 18.28, -5.41. HRMS (ESI) m/z calcd for $C_{15}H_{31}NO_7SiNa$ $[M + Na]^+$ 388.1767, found 388.1763.



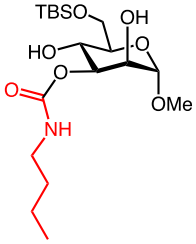
1bc

Methyl 3-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bc**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-methyl-carbamoylimidazole (**c**) (17.5 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bb** as colorless oil (29.9 mg, 82%). R_f = 0.52 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (dd, *J* = 9.7, 3.3 Hz, 1H, *H*-3), 4.60 (d, *J* = 1.8 Hz, 1H, *H*-1), 3.91 (d, *J* = 4.7 Hz, 1H, *H*-2), 3.86 – 3.75 (m, 3H, *H*-4, *H*-6a and *H*-6b), 3.59 – 3.49 (m, 1H, *H*-5), 3.29 (s, 3H), 2.77 – 2.62 (m, 3H), 0.81 (s, 9H), 0.00 (s, 6H). NMR data were consistent with literature description.[1]



1ad

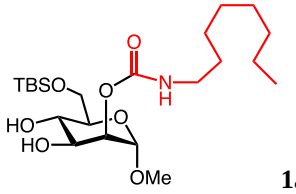
Methyl 2-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ad**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-butyl-carbamoylimidazole (**d**) (23.4 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 8 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1ad** as colorless oil 33.8 mg, 84%). R_f = 0.4 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 11.7 (c 0.3, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.01 (t, J = 6.0 Hz, 1H, N*H*), 4.93 (dd, J = 3.6, 1.7 Hz, 1H, *H*-2), 4.73 (d, J = 1.6 Hz, 1H, *H*-1), 3.96 (dd, J = 9.5, 3.6 Hz, 1H, *H*-3), 3.92 – 3.83 (m, 2H, *H*-6a and *H*-6b), 3.74 (t, J = 9.5 Hz, 1H, *H*-4), 3.58 (dt, J = 9.7, 4.9 Hz, 1H, *H*-5), 3.37 (s, 3H, OC*H*$_3$), 3.19 – 3.07 (m, 2H), 1.53 – 1.42 (m, 2H), 1.38 – 1.29 (m, 2H), 0.95 – 0.89 (m, 12H), δ 0.11 (s, 3H), 0.10 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.22, 99.02, 72.40, 71.28, 70.21, 69.79, 64.08, 54.94, 40.87, 31.82, 25.87, 19.89, 18.29, 13.71, -5.39. HRMS (ESI) m/z calcd for $C_{18}H_{37}NO_7SiNa$ $[M + Na]^+$ 430.2237, found 430.2242.



1bd

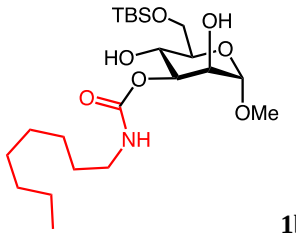
Methyl 3-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bd**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-butyl-carbamoylimidazole (**d**) (23.4 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bd** as colorless oil (32.2 mg, 79%). R_f = 0.8 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (t, J = 5.8 Hz, 1H), 4.90 (dd, J = 9.7, 3.3 Hz, 1H), 4.69 (d, J = 1.8 Hz, 1H), 3.99 (ddd, J = 5.5, 3.2, 1.7 Hz, 1H),

3.92 – 3.86 (m, 3H), 3.73 (d, J = 3.6 Hz, 1H), 3.66 – 3.56 (m, 1H), 3.37 (s, 3H), 3.21 – 3.11 (m, 2H), 2.87 (d, J = 5.8 Hz, 1H), 1.54 – 1.42 (m, 2H), 1.40 – 1.32 (m, 2H), 0.95 – 0.86 (m, 12H), 0.09 (s, 6H). NMR data were consistent with literature description.[1]



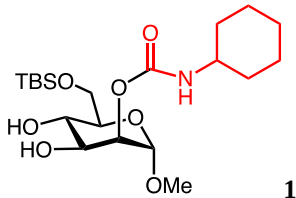
1ae

Methyl 2-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ae**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-octyl-carbamoylimidazole (**e**) (31.2 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1ae** as colorless oil 33.7 mg, 75%). R_f = 0.5 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 43.0 (c 0.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 – 4.76 (m, 2H,N*H* and *H*-2), 4.63 (d, *J* = 1.7 Hz, 1H, *H*-1), 3.86 (d, *J* = 9.6 Hz, 1H, *H*-3), 3.83 – 3.71 (m, 2H, *H*-6a and *H*-6b), 3.64 (t, *J* = 9.4 Hz, 1H, *H*-4), 3.47 (dt, *J* = 9.8, 5.0 Hz, 1H, *H*-5), 3.26 (s, 3H), 3.15 (s, 1H,4-O*H*), 3.13 – 2.97 (m, 2H), 2.94 (s, 1H, 3-O*H*), 1.42 – 1.33 (m, 2H), 1.24 – 1.10 (m, 10H), 0.84 – 0.68 (m, 12H), -0.00 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.18, 99.04, 72.38, 71.19, 70.24, 69.93, 64.14, 54.95, 41.21, 31.79, 29.77, 29.23, 29.21, 26.77, 25.87, 22.64, 18.28, 14.10, -5.39. HRMS (ESI) m/z calcd for $C_{20}H_{39}NO_7SiNa$ $[M + Na]^+$ 486.2863, found 486.2872.



1be

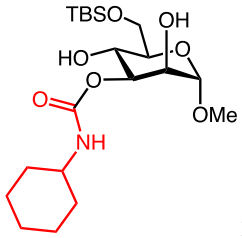
Methyl 3-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1be**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-octyl-carbamoylimidazole (**e**) (31.2 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1be** as colorless oil (34.6 mg, 77%). R_f = 0.83 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.34 (t, *J* = 5.8 Hz, 1H), 4.91 (dd, *J* = 9.7, 3.2 Hz, 1H), 4.70 (d, *J* = 1.8 Hz, 1H), 4.00 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.96 – 3.84 (m, 3H), 3.62 (dt, *J* = 9.5, 4.7 Hz, 1H), 3.38 (s, 3H), 3.20 – 3.11 (m, 2H), 1.54 – 1.43 (m, 2H), 1.35 – 1.18 (m, 10H), 0.94 – 0.83 (m, 12H), 0.10 (s, 6H). NMR data were consistent with literature description.[1]



1af

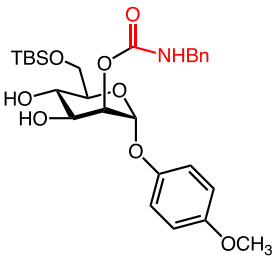
Methyl 2-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1af**). Following the general procedure C, the reaction was carried out with methyl 6-*O*-(*tert*-

butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-cyclohexyl-carbamoylimidazole (**f**) (27.0 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 4 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1af** as colorless oil 35.5 mg, 82%). R_f = 0.47 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 31.3 (c 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (dd, *J* = 3.6, 1.7 Hz, 1H, *H*-2), 4.76 (d, *J* = 8.1 Hz, 1H, N*H*), 4.63 (d, *J* = 1.7 Hz, 1H, *H*-1), 3.86 (d, *J* = 9.5 Hz, 1H, *H*-3), 3.81 – 3.71 (m, 2H), 3.64 (t, *J* = 9.5 Hz, 1H, *H*-4), 3.47 (dt, *J* = 9.7, 4.9 Hz, 1H, *H*-5), 3.42 – 3.28 (m, 1H), 3.26 (s, 3H, OC*H*$_3$), 3.18 (s, 1H, 4-O*H*), 3.00 (d, *J* = 4.8 Hz, 1H, 3-O*H*), 1.88 – 1.76 (m, 2H), 1.64 – 1.55 (m, 2H), 1.49 (dt, *J* = 12.7, 3.9 Hz, 1H), 1.34 – 1.12 (m, 2H), 1.12 – 0.95 (m, 3H), 0.81 (s, 9H), -0.00 (s, sH), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.34, 99.03, 72.33, 71.29, 70.24, 69.84, 64.06, 54.96, 50.09, 33.26, 33.15, 25.89, 25.44, 24.78, 18.30, -5.36. HRMS (ESI) m/z calcd for $C_{20}H_{39}NO_7SiNa$ $[M + Na]^+$ 456.2393, found 456.2396.



1bf

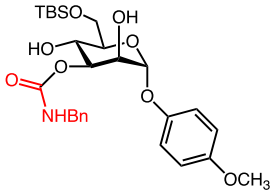
Methyl 3-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bf**). Following the general procedure D, the reaction was carried out with methyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-cyclohexyl-carbamoylimidazole (**f**) (27.0 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bf** as colorless oil (39.9 mg, 92%). R_f = 0.75 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (d, *J* = 8.1 Hz, 1H), 4.90 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.71 (d, *J* = 1.8 Hz, 1H), 4.00 (s, 1H), 3.96 – 3.84 (m, 3H), 3.72 (d, *J* = 3.4 Hz, 1H), 3.62 (dt, *J* = 9.4, 4.7 Hz, 1H), 3.55 – 3.41 (m, 1H), 3.39 (s, 3H), 2.46 (s, 1H), 1.97 – 1.89 (m, 2H), 1.75 – 1.65 (m, 2H), 1.60 (dt, *J* = 12.8, 3.7 Hz, 1H), 1.41 – 1.28 (m, 2H), 1.26 – 1.07 (m, 3H), 0.91 (s, 9H), 0.10 (s, 6H). NMR data were consistent with literature description.[1]



2a

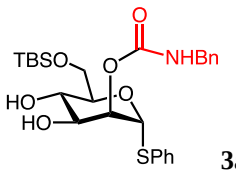
4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**2a**). Following the general procedure C, the reaction was carried out with 4-methoxyphenyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2**[1] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 5 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **2a** as colorless oil (48.0 mg, 90%). R_f = 0.45 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 22.7 (c 0.33, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.15 (m, 5H), 6.99 – 6.90 (m, 2H), 6.79 – 6.70 (m, 2H), 5.41 (d, *J* = 1.7 Hz, 1H, *H*-1), 5.37 (t, *J* = 6.0 Hz, 1H, N*H*), 5.12 (dd, *J* = 3.6, 1.8 Hz, 1H,

H-2), 4.37 – 4.21 (m, 2H, PhC*H*$_2$), 4.15 (d, *J* = 9.5 Hz, 1H, *H*-3), 3.85 – 3.76 (m, 3H, *H*-4, *H*-6a and *H*-6b), 3.74 – 3.68 (m, 4H, *H*-5 and OC*H*$_3$), 3.46 (s, 1H, 4-O*H*), 3.36 – 3.30 (m, 1H, 3-O*H*), 0.81 (s, 9H), 0.00 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.11, 155.08, 150.18, 137.89, 128.70, 127.57, 118.06, 114.54, 97.23, 72.58, 71.83, 69.98, 69.73, 64.01, 55.62, 45.18, 25.83, 18.24, -5.41, -5.43. HRMS (ESI) m/z calcd for $C_{27}H_{39}NO_8SiNa$ $[M + Na]^+$ 556.2343, found 556.2350.



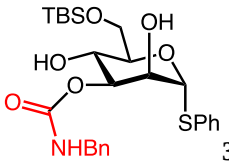
2b

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**2b**). Following the general procedure D, the reaction was carried out with 4-methoxyphenyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2**[1] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **2b** as colorless oil (35.7 mg, 67%). R_f = 0.6 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.20 (m, 5H), 7.06 – 6.96 (m, 2H), 6.85 – 6.77 (m, 2H), 5.54 (t, *J* = 5.9 Hz, 1H), 5.39 (d, *J* = 1.9 Hz, 1H), 5.21 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.38 (t, *J* = 5.4 Hz, 2H), 4.22 (s, 1H), 4.03 (td, *J* = 9.5, 2.8 Hz, 1H), 3.90 – 3.78 (m, 3H), 3.77 (s, 3H), 3.57 (d, *J* = 3.4 Hz, 1H), 2.64 (s, 1H), 0.87 (s, 9H), 0.05 (s, 6H). NMR data were consistent with literature description.[1]



3a

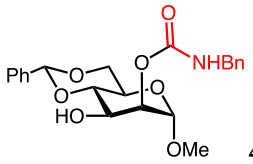
Phenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside (**3a**). Following the general procedure C, the reaction was carried out with phenyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **3**[6,7] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 5 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **3a** as colorless oil (45.7 mg, 88%). R_f = 0. 5 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 159.0 (c 0.2, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.29 – 7.13 (m, 8H), 5.48 (d, *J* = 1.6 Hz, 1H, *H*-1), 5.26 (t, *J* = 5.9 Hz, 1H, N*H*), 5.19 (dd, *J* = 3.5, 1.5 Hz, 1H, *H*-2), 4.33 – 4.16 (m, 2H, BnC*H*$_2$), 4.06 (dt, *J* = 9.8, 5.1 Hz, 1H, *H*-5), 3.91 (d, *J* = 9.6 Hz, 1H, *H*-3), 3.86 – 3.70 (m, 3H, *H*-4, *H*-6a and *H*-6b), 3.41 (s, 1H, 4-O*H*), 3.24 (s, 1H, 3-O*H*), 0.81 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.00, 137.88, 133.92, 131.82, 129.01, 128.70, 127.59, 127.41, 127.16, 86.46, 74.35, 72.31, 70.82, 70.20, 64.11, 45.19, 25.89, 18.30, -5.39. HRMS (ESI) m/z calcd for $C_{26}H_{37}NO_6SSiNa$ $[M + Na]^+$ 542.2009, found 542.2003.



3b

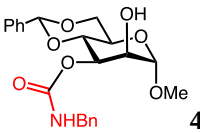
Phenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside (**3b**). Following the general procedure D, the reaction was carried out with phenyl 6-*O*-(*tert*-

butyldimethyl)silyl-α-D-mannopyranoside **3**[6,7] (48.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **3b** as colorless oil (46.2 mg, 89%). R_f = 0.6 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 124.6 (c 0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.30 – 7.14 (m, 8H), 5.44 (t, *J* = 5.9 Hz, 1H, N*H*), 5.40 (d, *J* = 1.7 Hz, 1H, *H*-1), 4.91 (dd, *J* = 9.7, 3.1 Hz, 1H, *H*-3), 4.32 – 4.21 (m, 3H, BnCH_2 and *H*-2), 4.12 (dt, *J* = 9.6, 4.8 Hz, 1H, *H*-5), 3.95 (td, *J* = 9.6, 3.3 Hz, 1H, *H*-4), 3.87 – 3.76 (m, 2H, *H*-6a and *H*-6b), 3.50 (d, *J* = 3.4 Hz, 1H, 4-O*H*), 2.69 (d, *J* = 5.7 Hz, 1H, 2-O*H*), 0.82 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.49, 137.88, 133.88, 131.56, 129.05, 128.74, 127.67, 127.52, 87.91, 75.52, 73.05, 71.07, 67.89, 63.91, 45.32, 25.91, 18.34, -5.43. HRMS (ESI) m/z calcd for $C_{26}H_{37}NO_6SSiNa$ $[M + Na]^+$ 542.2009, found 542.1960.



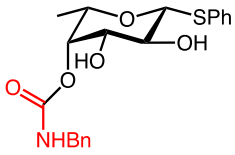
4a

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**4a**). Following the general procedure C, the reaction was carried out with phenyl methyl 4,6-*O*-benzylidene-α-D-mannopyranoside **4**[9] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 6 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **4a** as colorless oil (33.2 mg, 80%). R_f = 0.7 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 76.9 (c 0.26, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.41 (m, 2H), 7.39 – 7.19 (m, 8H), 5.57 (s, 1H, PhC*H*), 5.37 (t, *J* = 5.8 Hz, 1H, N*H*), 5.14 (dd, *J* = 3.8, 1.6 Hz, 1H, *H*-2), 4.76 (d, *J* = 1.6 Hz, 1H, *H*-1), 4.35 – 4.30 (m, 2H), 4.29 – 4.24 (m, 1H. *H*-6a), 4.21 (dd, *J* = 9.4, 3.6 Hz, 1H, *H*-3), 3.92 – 3.84 (m, 1H, *H*-4), 3.84 – 3.76 (m, 2H, *H*-5 and *H*-6b), 3.39 (s, 3H), 2.73 (s, 1H, 3-O*H*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.29, 138.31, 137.53, 129.61, 129.10, 128.70, 128.04, 128.01, 126.66, 102.65, 100.39, 79.52, 73.29, 69.15, 67.76, 63.63, 55.62, 45.64. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 438.1529, found 438.1507.



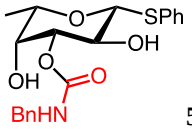
4b

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside (**4b**). Following the general procedure D, the reaction was carried out with phenyl methyl 4,6-*O*-benzylidene-α-D-mannopyranoside **4**[9] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **4b** as colorless oil (12.5 mg, 30%). R_f = 0.45 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 16.0 (c 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.11 (m, 10H), 5.51 (s, 1H, PhC*H*), 5.31 – 5.19 (m, 2H, N*H* and *H*-3), 4.74 – 4.69 (m, 1H, *H*-1), 4.37 – 4.22 (m, 3H, PhCH_2 and *H*-6b), 4.21 (s, 1H, *H*-2), 4.07 (t, *J* = 9.7 Hz, 1H, *H*-4), 3.91 (td, *J* = 9.7, 4.4 Hz, 1H, *H*-5), 3.82 (t, *J* = 10.1 Hz, 1H, *H*-6a), 3.38 (s, 3H), 2.71 (d, *J* = 4.6 Hz, 1H, 2-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.41, 138.11, 137.26, 129.07, 128.64, 128.26, 127.55, 127.51, 127.42, 127.34, 126.27, 101.97, 101.55, 71.63, 70.02, 68.83, 63.68, 55.07, 45.09, 44.55. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 438.1529, found 438.1509.



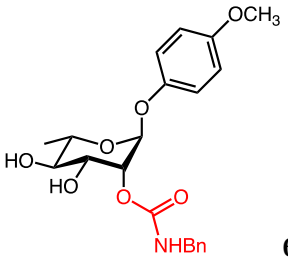
5a

Phenyl 4-*O*-benzylcarbamoyl-**β**-L-fucopyranoside (**5a**). Following the general procedure C, the reaction was carried out with phenyl **β**-L-fucopyranoside **5**[7] (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 5 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **5a** as colorless oil (27.2 mg, 70%). R_f = 0.4 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 70.0 (c 0.02, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.41 – 7.19 (m, 8H), 5.25 (t, *J* = 6.1 Hz, 1H, N*H*), 5.06 (d, *J* = 3.2 Hz, 1H, *H*-4), 4.57 (d, *J* = 9.7 Hz, 1H, *H*-1), 4.45 – 4.36 (m, 2H), 3.84 – 3.72 (m, 2H, *H*-3 and *H*-5), 3.65 (t, *J* = 9.4 Hz, 1H, *H*-2), 3.06 (s, 1H, 3-O*H*), 2.65 (s, 1H, 2-O*H*), 1.33 – 1.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.40, 128.95, 128.77, 127.98, 127.66, 127.41, 88.78, 74.08, 74.07, 73.68, 70.07, 64.89, 50.32, 45.25, 29.71, 16.75. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 412.1195, found 412.1237.



5b

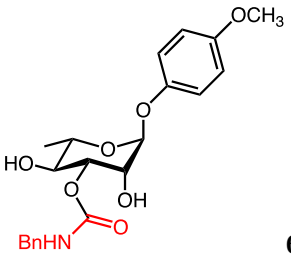
Phenyl 3-*O*-benzylcarbamoyl-**β**-L-fucopyranoside (**5b**). Following the general procedure D, the reaction was carried out with phenyl **β**-L-fucopyranoside **5**[7] (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **5b** as a white solid (32.3 mg, 83%): mp 127.3−128.5 °C. R_f = 0.6 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 16.3 (c 0.16, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 2H), 7.32 – 7.17 (m, 8H), 5.70 (t, *J* = 6.0 Hz, 1H, N*H*), 4.75 (dd, *J* = 9.6, 3.1 Hz, 1H, *H*-3), 4.55 (d, *J* = 9.7 Hz, 1H, *H*-1), 4.39 – 4.24 (m, 2H), 3.86 (t, *J* = 4.1 Hz, 1H, *H*-4), 3.77 (td, *J* = 9.7, 2.9 Hz, 1H, *H*-2), 3.67 (q, *J* = 6.4 Hz, 1H, *H*-5), 3.21 (d, *J* = 3.6 Hz, 1H, 2-O*H*), 2.49 (d, *J* = 6.0 Hz, 1H, 4-O*H*), 1.29 – 1.25 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.28, 138.05, 132.50, 132.43, 128.98, 128.67, 127.94, 127.59, 127.53, 88.81, 77.60, 74.56, 70.63, 67.62, 45.13, 16.52. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 412.1195, found 412.1280.



6a

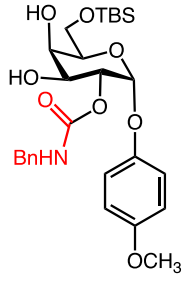
4-methoxyphenyl 2-*O*-benzylcarbamoyl-α-L-rhamnopyranoside (**6a**). Following the general procedure C, the reaction was carried out with 4-methoxyphenyl α-L-rhamnopyranoside **6**[1] (27.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 6 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **6a** as colorless oil (32.6 mg, 81%). R_f = 0.45 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ – 70.3 (c 0.32, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.13

(m, 5H), 6.99 – 6.90 (m, 2H), 6.83 – 6.76 (m, 2H), 5.68 (t, *J* = 5.9 Hz, 1H, N*H*), 5.36 (d, *J* = 1.7 Hz, 1H, *H*-1), 5.17 (dd, *J* = 3.6, 1.8 Hz, 1H, *H*-2), 4.35 (dd, *J* = 14.9, 6.4 Hz, 1H, ArCH_2), 4.25 (dd, *J* = 14.9, 5.5 Hz, 1H, ArCH_2), 4.14 (dd, *J* = 9.6, 3.6 Hz, 1H, *H*-3), 3.80 (dt, *J* = 9.5, 6.1 Hz, 1H, *H*-5), 3.75 (s, 3H, OCH_3), 3.56 (t, *J* = 9.5 Hz, 1H, *H*-4), 1.26 (s, 2H), 1.25 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.29, 155.11, 150.10, 137.89, 128.72, 127.63, 127.60, 117.95, 114.62, 97.19, 73.15, 70.10, 68.81, 55.65, 45.22, 29.72, 17.55. HRMS (ESI) m/z calcd for $C_{21}H_{25}NO_7SiNa$ $[M + Na]^+$ 426.1529, found 426.1528.



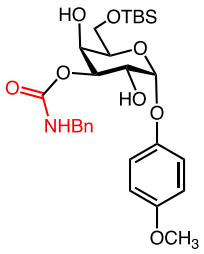
6b

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-L-rhamnopyranoside (**6b)**. Following the general procedure D, the reaction was carried out with 4-methoxyphenyl α-L-rhamnopyranoside **6**[1] (27.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 1 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **6b** as colorless oil (28.2 mg, 70%). R_f = 0.65 (ethyl acetate/petroleum ether: 2/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 5H), 7.02 – 6.91 (m, 2H), 6.85 – 6.77 (m, 2H), 5.72 (t, *J* = 6.0 Hz, 1H, N*H*), 5.34 (d, *J* = 1.8 Hz, 1H, *H*-1), 5.11 (dd, *J* = 9.8, 3.2 Hz, 1H, *H*-3), 4.40 – 4.30 (m, 2H, ArCH_2), 4.20 (t, *J* = 2.6 Hz, 1H, *H*-2), 3.81 (dt, *J* = 12.3, 6.2 Hz, 1H, *H*-5), 3.76 (s, 3H), 3.68 (t, *J* = 9.7 Hz, 1H, *H*-4), 3.39 (s, 1H, 4-O*H*), 2.90 (s, 1H, 2-O*H*), 1.30 – 1.23 (m, 3H). NMR data were consistent with literature description.[1]



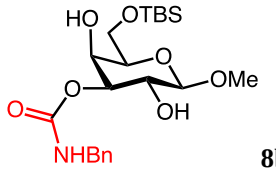
7c

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside (**7c**). Following the general procedure C, the reaction was carried out with 4-methoxyphenyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **7c** as colorless oil (45.8 mg, 86%). R_f = 0.65 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 40 (c 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.15 (m, 5H), 6.95 – 6.87 (m, 2H), 6.80 – 6.70 (m, 2H), 5.55 (d, *J* = 3.7 Hz, 1H, *H*-1), 5.27 (t, *J* = 6.0 Hz, 1H, N*H*), 5.02 (dd, *J* = 10.0, 3.8 Hz, 1H, *H*-2), 4.37 – 4.24 (m, 2H, ArCH_2), 4.14 – 4.03 (m, 2H, *H*-4 and *H*-3), 3.90 (t, *J* = 4.8 Hz, 1H, *H*-5), 3.86 – 3.76 (m, 2H, *H*-6a and *H*-6b), 3.71 (s, 3H,OCH_3), 3.42 (d, *J* = 2.3 Hz, 1H, 4-O*H*), 3.20 (d, *J* = 7.4 Hz, 1H, 3-O*H*), 0.82 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.69, 155.13, 150.75, 137.90, 128.71, 127.55, 118.22, 114.57, 96.71, 72.36, 70.29, 69.73, 68.93, 63.50, 55.66, 45.22, 29.70, 25.79, 18.22, -5.51. HRMS (ESI) m/z calcd for $C_{27}H_{39}NO_8SiNa$ $[M + Na]^+$ 556.2343, found 556.2393.



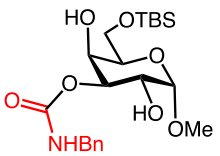
7b

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside (**7b**). Following the general procedure D, the reaction was carried out with 4-methoxyphenyl 6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **7b** as colorless oil (44.8 mg, 84%). R_f = 0.35 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 113.3 (c 0.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.10 (m, 5H), 7.01 – 6.92 (m, 2H), 6.81 – 6.69 (m, 2H), 5.64 (t, *J* = 6.0 Hz, 1H, N*H*), 5.42 (d, *J* = 3.9 Hz, 1H, *H*-1), 5.12 (dd, *J* = 10.4, 3.0 Hz, 1H, *H*-3), 4.34 – 4.28 (m, 2H, ArC*H*$_2$), 4.25 (s, 1H, *H*-4), 4.19 (td, *J* = 10.5, 3.8 Hz, 1H, *H*-2), 3.89 (d, *J* = 4.4 Hz, 1H, *H*-6a), 3.84– 3.75 (m, 2H, *H*-6b and *H*-5), 3.71 (s, 3H), 2.59 (d, *J* = 10.8 Hz, 1H, 2-O*H*), 0.82 (s, 9H), 0.01 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.57, 155.19, 150.67, 138.13, 128.66, 127.51, 118.10, 114.62, 98.81, 73.88, 69.83, 67.41, 64.01, 60.42, 55.63, 45.17, 25.78, 18.19, 14.19, -5.53, -5.55. HRMS (ESI) m/z calcd for $C_{27}H_{39}NO_8SiNa$ $[M + Na]^+$ 556.2343, found 556.2344.



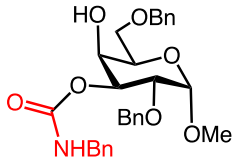
8b

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-β-D-galactopyranoside (**8b**). Following the general procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-β-D-galactopyranoside **8**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **8b** as colorless oil (38.8 mg, 88%). Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-β-D-galactopyranoside **8**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 60℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **8b** as colorless oil (31.8 mg, 72%). R_f = 0.55 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 5H), 5.71 (t, *J* = 6.0 Hz, 1H, N*H*), 4.72 (dd, *J* = 10.0, 3.1 Hz, 1H), 4.37 – 4.30 (m, 2H), 4.25 – 4.12 (m, 2H), 3.94 – 3.80 (m, 3H), 3.52 – 3.47 (m, 4H), 3.27 (s, 1H, 4-O*H*), 3.10 (s, 1H, 2-O*H*), 0.89 (s, 9H), 0.08 (s, 6H). NMR data were consistent with literature description.[1]



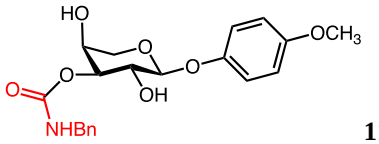
9b

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside (**9b**). Following the general procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **9**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **9b** as colorless oil (38.4 mg, 87%). Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **9**[6] (40.0 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 60℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **9b** as colorless oil (18.1 mg, 41%). R_f = 0.55 (ethyl acetate/petroleum ether: 1/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.12 (m, 5H), 5.46 (t, *J* = 6.0 Hz, 1H, N*H*), 4.86 (dd, *J* = 10.3, 3.0 Hz, 1H, *H*-3), 4.73 (d, *J* = 3.9 Hz, 1H, *H*-1), 4.31 – 4.22 (m, 2H, PhCH_2), 4.15 (d, *J* = 2.9 Hz, 1H, *H*-4), 4.03 – 3.94 (m, 1H, *H*-2), 3.86 – 3.74 (m, 2H, *H*-6a and *H*-6b), 3.67 (t, *J* = 4.6 Hz, 1H, *H*-5), 3.39 (s, 1H, 4-O*H*), 3.32 (s, 3H), 2.26 (d, *J* = 10.5 Hz, 1H, 2-O*H*), 0.81 (s, 9H), -0.00 (s, 6H). NMR data were consistent with literature description.[1]



10b

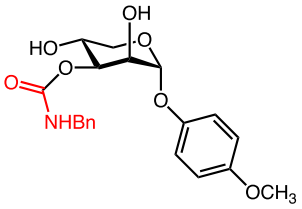
Methyl 3-*O*-benzylcarbamoyl-2,6-*O*-benzyl-α-D-galactopyranoside (**10b**). Following the general procedure D, the reaction was carried out with methyl 2,6-O-benzyl-α-D-galactopyranoside **10**[8] (37.4 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **10b** as colorless oil (47.7 mg, 94%). Following the general procedure C, the reaction was carried out with methyl 2,6-O-benzyl-α-D-galactopyranoside[8] (37.4 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 60℃ for 8 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **10b** as colorless oil (41.6 mg, 82%). R_f = 0.62 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 71.3 (c 0.15, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 15H), 5.15 (dd, *J* = 10.4, 3.1 Hz, 1H, *H*-3), 5.07 (t, *J* = 5.9 Hz, 1H, N*H*), 4.75 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.68 – 4.50 (m, 4H), 4.39 (dd, *J* = 14.9, 6.3 Hz, 1H，*H*-6a), 4.32 – 4.25 (m, 2H, *H*-4 and *H*-5), 3.98 – 3.93 (m, 2H, *H*-2 and *H*-6a), 3.77 – 3.69 (m, 2H), 3.38 (s, 3H), 3.12 (d, *J* = 2.5 Hz, 1H, 4-O*H*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.61, 138.38, 138.31, 137.38, 128.65, 128.50, 128.33, 127.92, 127.90, 127.72, 127.57, 127.50, 98.78, 74.01, 73.82, 73.37, 72.87, 70.56, 69.98, 67.85, 55.40, 45.10. HRMS (ESI) m/z calcd for $C_{29}H_{33}NO_7SiNa$ $[M + Na]^+$ 530.2155, found 530.2148.



11b

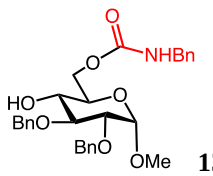
4-methoxyphenyl 3-*O*-benzylcarbamoyl-β-L-arabinopyranoside (**11b**). Following the general procedure D, the reaction was carried out with 4-methoxyphenyl β-L-arabinopyranoside **11**[1] (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **11b** as colorless oil (34.6 mg, 89%). Following the general

procedure C, the reaction was carried out with 4-methoxyphenyl β-L-arabinopyranoside **11**[1] (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 60℃ for 8 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **11b** as colorless oil (27.6 mg, 71%). R_f = 0.58 (ethyl acetate/petroleum ether: 3/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.22 (m, 5H), 7.00 (dd, *J* = 9.3, 3.1 Hz, 2H), 6.87 – 6.76 (m, 2H), 5.61 (t, *J* = 6.0 Hz, 1H,N*H*), 4.84 (dd, *J* = 9.6, 3.3 Hz, 1H, *H*-3), 4.77 (d, *J* = 7.3 Hz, 1H, *H*-1), 4.36 – 4.30 (m, 2H, PhC*H*$_2$), 4.14 – 4.07 (m, 2H, *H*-2 and *H*-5b), 4.00 (dd, *J* = 12.8, 2.8 Hz, 1H, *H*-4), 3.76 (s, 3H), 3.61 (dd, *J* = 12.8, 1.5 Hz, 1H, *H*-5a), 3.20 (s, 1H, 4-O*H*), 2.79 (s, 1H, 2-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.11, 155.64, 150.86, 137.97, 128.73, 127.62, 118.91, 117.96, 114.70, 114.58, 102.93, 75.53, 69.53, 67.26, 65.91, 55.64, 45.23. NMR data were consistent with literature description.[1]



12b

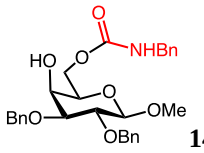
4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-D-lyxopyranoside (**12b**). Following the general procedure D, the reaction was carried out with 4-methoxyphenyl α-D-lyxopyranoside **12** (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **12b** as colorless oil (16.3 mg, 42%). Following the general procedure C, the reaction was carried out with 4-methoxyphenyl α-D-lyxopyranoside **12** (25.6 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 60℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **12b** as colorless oil (31.9 mg, 82%). R_f = 0.58 (ethyl acetate/petroleum ether: 3/1). $[\alpha]^{18}_D$ + 58.0 (c 0.05, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.20 (m, 5H), 7.04 – 6.96 (m, 2H), 6.88 – 6.79 (m, 2H), 5.39 – 5.33 (m, 2H, N*H* and *H*-1), 5.12 (dd, *J* = 9.3, 3.3 Hz, 1H, *H*-3), 4.43 – 4.38 (m, 2H, PhC*H*$_2$), 4.23 (d, *J* = 3.3 Hz, 1H, *H*-2), 4.12 (q, *J* = 7.1 Hz, 1H, *H*-4), 3.86 (dd, *J* = 11.4, 5.4 Hz, 1H, *H*-5a), 3.77 (s, 3H, OC*H*$_3$), 3.73 – 3.63 (m, 1H, *H*-5b), 3.23 (d, *J* = 5.1 Hz, 1H, 4-O*H*), 2.34 (d, *J* = 4.8 Hz, 1H, 2-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.15, 150.01, 137.70, 128.82, 127.81, 127.66, 117.68, 114.67, 98.58, 75.69, 69.55, 66.17, 63.33, 55.67, 45.43, 14.20. HRMS (ESI) m/z calcd for $C_{20}H_{23}NO_7SiNa$ $[M + Na]^+$ 412.1372, found 412.1370.



13

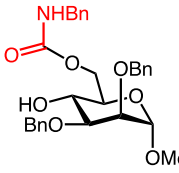
Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-glucopyranoside (**13**). Following the general procedure C, the reaction was carried out with methyl 2,3-*O*-benzyl-α-D-glucopyranoside[8] (37.4 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 70℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **13** as colorless oil (40.6 mg, 80%). R_f = 0.5 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 29.2 (c 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.22

(m, 15H), 5.18 (t, *J* = 6.0 Hz, 1H, N*H*), 4.95 (d, *J* = 11.2 Hz, 1H, BnC*H*$_2$), 4.86 – 4.75 (m, 2H, BnC*H*$_2$), 4.69 – 4.56 (m, 3H, BnC*H*$_2$, *H*-6b and *H*-1), 4.43 – 4.25 (m, 2H, BnC*H*$_2$), 4.13 (dd, *J* = 12.3, 2.1 Hz, 1H, *H*-6a), 3.82 (t, *J* = 9.2 Hz, 1H, *H*-3), 3.69 (ddd, *J* = 10.0, 3.7, 2.1 Hz, 1H, *H*-5), 3.53 – 3.38 (m, 2H, *H*-2 and *H*-4), 3.36 (s, 3H), 3.18 (d, *J* = 3.4 Hz, 1H,4-O*H*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.97, 138.78, 138.10, 138.01, 128.72, 128.52, 128.47, 128.12, 128.09, 127.94, 127.79, 127.62, 127.53, 98.48, 81.00, 79.28, 75.67, 73.34, 70.08, 69.88, 63.69, 55.31, 45.26. HRMS (ESI) m/z calcd for $C_{29}H_{33}NO_7SiNa$ [M + Na]$^+$ 530.2155, found 530.2197.



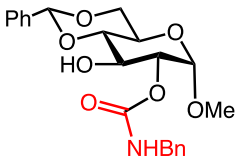
14

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-galactopyranoside (**14**). Following the general procedure C, the reaction was carried out with methyl 2,3-*O*-benzyl-α-D-galactopyranoside[8] (37.4 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 70℃ for 3 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **14** as colorless oil (47.2 mg, 93%). R_f = 0.65 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ + 28.0 (c 0.1, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 15H), 5.16 (t, *J* = 6.0 Hz, 1H, N*H*), 4.88 (d, *J* = 11.1 Hz, 1H, BnC*H*$_2$), 4.74 – 4.64 (m, 3H, BnC*H*$_2$), 4.44 – 4.28 (m, 4H, BnC*H*$_2$, *H*-6a and *H*-6b), 4.25 (d, *J* = 7.7 Hz, 1H, *H*-1), 3.94 (t, *J* = 3.0 Hz, 1H, *H*-4), 3.61 (q, *J* = 7.8 Hz, 2H, *H*-2 and *H*-5), 3.54 (s, 3H), 3.49 (dd, *J* = 9.4, 3.5 Hz, 1H, *H*-3), 2.63 (d, *J* = 2.5 Hz, 1H,4-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.35, 138.63, 138.31, 137.82, 128.73, 128.51, 128.34, 128.08, 127.96, 127.87, 127.65, 127.61, 127.56, 104.66, 80.32, 78.86, 75.14, 72.49, 72.09, 66.51, 63.49, 56.99, 45.16. HRMS (ESI) m/z calcd for $C_{29}H_{33}NO_7SiNa$ [M + Na]$^+$ 530.2155, found 530.2046.



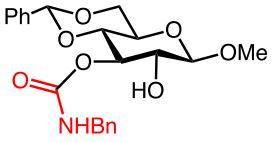
15

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-mannopyranoside (**15**). Following the general procedure C, the reaction was carried out with methyl 2,3-*O*-benzyl-α-D-mannopyranoside[8] (37.4 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 70℃ for 5 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **15** as colorless oil (36.0 mg, 71%). R_f = 0.6 (ethyl acetate/petroleum ether: 1/1). $[\alpha]^{18}_D$ – 10.8 (c 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.10 (m, 15H), 5.25 (t, *J* = 6.0 Hz, 1H, N*H*), 4.77 (d, *J* = 1.7 Hz, 1H, *H*-1), 4.71 – 4.66 (m, 2H, BnC*H*$_2$), 4.63 – 4.58 (m, 3H, BnC*H*$_2$ and *H*-6b), 4.48 – 4.25 (m, 3H, BnC*H*$_2$ and *H*-6a), 4.01 (t, *J* = 9.7 Hz, 1H, *H*-4), 3.79 (dd, *J* = 3.1, 1.7 Hz, 1H, *H*-2), 3.76 – 3.66 (m, 2H, *H*-3 and *H*-5), 3.34 (s, 3H), 3.11 (s, 1H, 4-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.01, 138.31, 138.26, 138.16, 128.67, 128.46, 128.35, 127.94, 127.73, 127.69, 127.54, 127.50, 99.43, 79.20, 74.21, 72.72, 72.25, 71.36, 66.48, 64.03, 54.89, 45.19. HRMS (ESI) m/z calcd for $C_{29}H_{33}NO_7SiNa$ [M + Na]$^+$ 530.2155, found 530.2181.



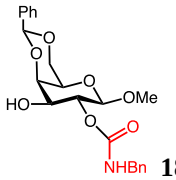
16

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**16**). Following the general procedure D, the reaction was carried out with methyl 4,6-*O*-benzylidene-α-D-glucopyranoside[8] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **16** as colorless oil (36.9 mg, 89%). mp 170.3−170.9 °C. R_f = 0.42 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 174.3 (c 0.07, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.43 (m, 2H), 7.41 – 7.21 (m, 8H), 5.51 (s, 1H, PhC*H*), 5.48 (t, *J* = 6.0 Hz, 1H, N*H*), 4.98 (d, *J* = 3.7 Hz, 1H, *H*-1), 4.72 (dd, *J* = 9.7, 3.8 Hz, 1H, *H*-2), 4.35 – 4.23 (m, 3H, PhC*H*$_2$ *H*-6a), 4.14 (td, *J* = 9.5, 3.3 Hz, 1H, *H*-3), 3.86 – 3.69 (m, 2H, *H*-5 and *H*-6b), 3.52 (t, *J* = 9.2 Hz, 1H, *H*-4), 3.38 (s, 3H), 3.00 (d, *J* = 3.4 Hz, 1H, 3-O*H*). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.92, 138.01, 137.03, 129.30, 128.70, 128.35, 127.58, 127.52, 126.36, 102.02, 98.17, 81.38, 74.27, 68.88, 62.09, 55.40, 45.15. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 438.1529, found 438.1552.



17

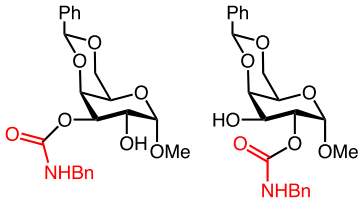
Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-glucopyranoside (**17**). Following the general procedure D, the reaction was carried out with methyl 4,6-*O*-benzylidene-β-D-glucopyranoside[9] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **17** as colorless oil (34.4 mg, 83%). R_f = 0.6 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ – 46.3 (c 0.16, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.42 – 7.33 (m, 3H), 7.30 – 7.21 (m, 5H), 5.50 (s, 1H), 5.21 (t, J = 6.0 Hz, 1H, N*H*), 5.04 (t, J = 9.3 Hz, 1H, *H*-3), 4.43 – 4.31 (m, 4H, *H*-1 and *H*-6b), 3.78 (t, J = 10.3 Hz, 1H, *H*-5), 3.66 – 3.49 (m, 6H, *H*-2, *H*-4, *H*-6a and -OC*H3*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.02, 137.88, 136.94, 129.15, 128.68, 128.29, 127.57, 127.48, 126.23, 104.65, 101.61, 78.41, 75.84, 73.87, 68.67, 66.23, 57.62, 45.22. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7SiNa$ $[M + Na]^+$ 438.1529, found 438.1549.



18

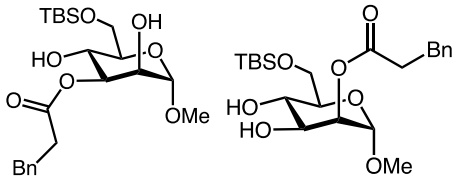
Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**18**). Following the general procedure D, the reaction was carried out with methyl 4,6-*O*-benzylidene-β-D-galactopyranoside[9] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **18** as colorless oil (37.7 mg, 91%). R_f = 0.55 (ethyl acetate/petroleum ether: 2/1). $[\alpha]^{18}_D$ + 39.1 (c 0.11, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.37 – 7.17 (m, 8H), 5.52 (s, 1H), 5.28 (t, *J* = 6.0 Hz, 1H, N*H*), 4.81 (dd, *J* = 10.2, 3.6 Hz, 1H, *H*-2), 4.44 (d, *J* = 3.6 Hz, 1H, *H*-1), 4.37 – 4.26 (m, 4H, PhC*H*$_2$ *H*-5 and *H*-4), 4.05

(dd, *J* = 12.5, 1.8 Hz, 1H, *H*-6a), 4.00 – 3.91 (m, 1H, *H*-3), 3.59 (s, 3H), 3.53 – 3.48 (m, 1H, *H*-6b), 2.63 (d, *J* = 2.6 Hz, 1H,3-O*H*). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.03, 137.98, 137.65, 129.10, 128.68, 128.20, 127.57, 127.53, 126.42, 104.04, 101.18, 74.46, 74.02, 69.09, 68.89, 66.42, 57.29, 45.10. HRMS (ESI) m/z calcd for $C_{22}H_{25}NO_7Na$ $[M + Na]^+$ 438.1529, found 438.1556.



19b **19a**

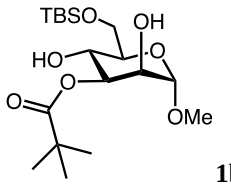
Methyl 2/3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (**19a** and **19b**). Following the general procedure D, the reaction was carried out with methyl 4,6-*O*-benzylidene-α-D-galactopyranoside[9] (28.2 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-benzyl-carbamoylimidazole (**a**) (28.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, isolated as an inseparable mixture of compound **19a** (39%) and **19b** (47%) by NMR yield.



1bg **1ag**

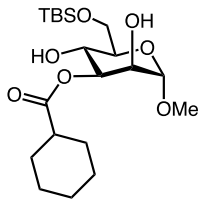
Following the general procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(benzylacetyl)imidazole (**g**)[2] (28 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bg** (35.2 mg, 80%, R_f = 0.6, ethyl acetate/petroleum ether: 1/4) and compound **1ag** (7.0 mg, 16%, R_f = 0.4, ethyl acetate/petroleum ether: 1/4) as colorless oil. Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(benzylacetyl)imidazole (**g**)[2] (28 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bg** (9.2 mg, 21%, R_f = 0.6, ethyl acetate/petroleum ether: 1/4) and compound **1ag** (27.7 mg, 63%, R_f = 0.4, ethyl acetate/petroleum ether: 1/4) as colorless oil. Methyl 3-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bg**). $[\alpha]^{18}_D$ + 70.0 (c 0.02, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 – 7.06 (m, 5H), 4.96 (dd, *J* = 9.7, 3.2 Hz, 1H，*H*-3), 4.55 (d, *J* = 1.8 Hz, 1H，*H*-1), 3.85 – 3.78 (m, 2H，*H*-4 and *H*-6a), 3.77 – 3.72 (m, 2H, *H*-2 and *H*-6b), 3.54 (dt, *J* = 10.0, 5.3 Hz, 1H, *H*-5), 3.28 (s, 3H, OC*H*$_3$), 2.90 (tt, *J* = 10.5, 5.2 Hz, 2H), 2.81 (d, *J* = 3.0 Hz, 1H, 4-O*H*), 2.73 – 2.62 (m, 2H), 1.63 (d, *J* = 5.4 Hz, 1H, 2-O*H*), 0.81 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.59, 130.15, 129.85, 128.04, 102.20, 76.12, 73.73, 70.86, 66.44, 63.11, 56.64, 37.33, 32.51, 27.18, 26.84, 19.52, -2.05. HRMS (ESI) m/z calcd for $C_{22}H_{36}NO_7Na$ $[M + Na]^+$ 463.2128, found 463.2120. Methyl 2-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ag**). $[\alpha]^{18}_D$ + 33.6 (c 0.36, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.07 (m, 5H), 4.95 (dd, *J* = 3.6, 1.7 Hz, 1H, *H*-2), 4.52 (d, *J* = 1.6 Hz, 1H, *H*-1), 3.88 – 3.68 (m, 3H, *H*-3, *H*-6a and *H*-6b), 3.62 (t, *J* = 9.4 Hz, 1H, *H*-4), 3.47

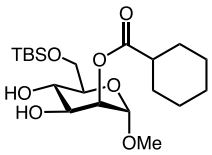
(dt, *J* = 9.8, 5.1 Hz, 1H, *H*-5), 3.24 (s, 3H), 2.99 – 2.94 (m, 1H, 4-O*H*), 2.89 – 2.81 (m, 2H), 2.65 – 2.57 (m, 2H), 1.95 (d, *J* = 5.4 Hz, 1H, 3-O*H*), 0.81 (s, 9H), 0.00 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.56, 140.17, 128.59, 128.25, 126.41, 98.52, 71.78, 70.78, 70.37, 70.03, 64.33, 55.01, 35.69, 30.87, 25.85, 18.25, -5.42, -5.45. HRMS (ESI) m/z calcd for $C_{22}H_{36}NO_7Na$ [M + Na]$^+$ 463.2128, found 463.2130.



1bh

Methyl 3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bh**). Following the procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(trimethylacetyl)imidazole (**i**) [2] (21.2 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bh** (29.0 mg, 74%, R_f = 0.55, ethyl acetate/petroleum ether: 1/4) as colorless oil. Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(trimethylacetyl)imidazole (**i**) [2] (21.2 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 6 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bh** (23.5 mg, 60%, R_f = 0.55, ethyl acetate/petroleum ether: 1/4) as colorless oil. $[\alpha]^{18}_D$ + 56.2 (c 0.26, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.96 (dd, *J* = 9.7, 3.2 Hz, 1H, *H*-3), 4.60 (d, *J* = 1.8 Hz, 1H, *H*-1), 3.88 (dd, *J* = 3.3, 1.9 Hz, 1H, *H*-2), 3.86 – 3.76 (m, 3H, *H*-4, *H*-6a and *H*-6b), 3.56 (dt, *J* = 9.8, 5.0 Hz, 1H, *H*-5), 3.29 (s, 3H), 1.15 (s, 9H), 0.80 (s, 9H), -0.00 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.71, 100.48, 74.25, 71.68, 69.29, 68.05, 64.32, 54.98, 39.08, 27.18, 27.09, 25.90, 18.33, -5.42. HRMS (ESI) m/z calcd for $C_{18}H_{36}NO_7SiNa$ [M + Na]$^+$ 415.2128, found 415.2135.

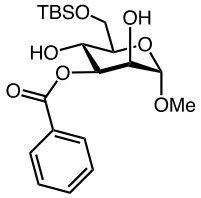




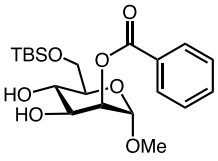
1bi **1ai**

Following the general procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(cyclohexylcarbonyl)imidazole (**h**) [2] (25 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bi** (24.2 mg, 58%, R_f = 0.4, ethyl acetate/petroleum ether: 1/2) and compound **1ai** (12.1 mg, 29%, R_f = 0.6, ethyl acetate/petroleum ether: 1/2) as colorless oil. Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(cyclohexylcarbonyl)imidazole (**h**)[2] (25 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 50℃ for 4 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bi** (18.4 mg, 44%, R_f = 0.6, ethyl acetate/petroleum ether: 1/2) and compound **1ai** (19.2 mg, 46%, R_f = 0.4, ethyl acetate/petroleum ether: 1/2) as colorless oil. Methyl 3-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bi**). $[\alpha]^{18}_D$ +

48.0 (c 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.09 (dd, *J* = 9.7, 3.2 Hz, 1H, *H*-3), 4.70 (d, *J* = 1.8 Hz, 1H, *H*-1), 4.01 – 3.84 (m, 4H, *H*-2, *H*-4, *H*-6a and *H*-6b), 3.66 (dt, *J* = 9.8, 5.0 Hz, 1H, *H*-5), 3.39 (s, 3H), 2.43 (tt, *J* = 11.3, 3.6 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.82 – 1.71 (m, 2H), 1.69 – 1.60 (m, 1H), 1.56 – 1.39 (m, 2H), 1.37 – 1.16 (m, 3H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.30, 100.53, 74.02, 71.61, 69.28, 67.94, 64.30, 55.00, 43.17, 29.13, 29.00, 25.89, 25.68, 25.38, 25.32, 18.31, -5.43. HRMS (ESI) m/z calcd for $C_{20}H_{38}NO_7SiNa$ $[M + Na]^+$ 441.2284, found 441.2307. Methyl 2-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1ai**). $[\alpha]^{18}_D$ + 10.7 (c 0.15, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (dd, *J* = 3.5, 1.7 Hz, 1H, *H*-2), 4.55 (d, *J* = 1.6 Hz, 1H, *H*-1), 3.89 (dd, *J* = 9.5, 3.5 Hz, 1H, *H*-3), 3.82 (dd, *J* = 10.6, 4.6 Hz, 1H, *H*-4), 3.76 – 3.67 (m, 2H, *H*-6a and *H*-6b), 3.47 (dt, *J* = 9.6, 4.9 Hz, 1H, *H*-5), 3.25 (s, 3H), 2.26 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.86 – 1.75 (m, 2H), 1.69 – 1.58 (m, 2H), 1.57 – 1.49 (m, 1H), 1.42 – 1.25 (m, 2H), 1.25 – 1.04 (m, 3H), 0.81 (s, 9H), 0.00 (s, 3H), -0.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.82, 98.66, 71.32, 70.91, 70.24, 70.18, 64.13, 55.01, 43.10, 29.03, 28.93, 25.85, 25.69, 25.35, 25.34, 18.26, -5.43, -5.48. HRMS (ESI) m/z calcd for $C_{20}H_{38}NO_7SiNa$ $[M + Na]^+$ 441.2284, found 441.2266.



1bj



1aj

Following the general procedure D, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(benzoyl)imidazole (**j**)[2] (24.1 mg, 0.14 mmol) in the presence of Me_2SnCl_2 (2.2 mg, 0.1 equiv) at 50℃ for 2 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bj** (34. mg, 84%, R_f = 0.5, ethyl acetate/petroleum ether: 1/4) and compound **1aj** (2.5 mg, 6%, R_f = 0.25, ethyl acetate/petroleum ether: 1/4) as colorless oil. Following the general procedure C, the reaction was carried out with 6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1** (30.8 mg, 0.1 mmol), DIPEA (3.3 μL, 0.2 equiv), and 1-(benzoyl)imidazole (**j**)[2] (24.1 mg, 0.14 mmol) in the presence of $SnCl_2$ (1.9 mg, 0.1 equiv) at 80℃ for 12 h. The reaction mixture was directly purified by flash column chromatography, afforded compound **1bj** (22.7 mg, 55%, R_f = 0.5, ethyl acetate/petroleum ether: 1/4) and compound **1aj** (2.5 mg, 6%, R_f = 0.25, ethyl acetate/petroleum ether: 1/4) as colorless oil. Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1bj**). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 2H), 7.61 – 7.55 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.36 (dd, *J* = 9.7, 3.3 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 4.18 – 4.09 (m, 2H), 3.99 – 3.88 (m, 2H), 3.74 (dt, *J* = 9.9, 5.2 Hz, 1H), 3.43 (s, 3H), 3.08 (d, *J* = 3.1 Hz, 1H), 2.08 (d, *J* = 5.8 Hz, 1H), 0.92 (s, 9H), 0.12 (s, 3H), 0.12 (s, 3H). NMR data were consistent with literature description.[10] Methyl 2-*O*-benzoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside (**1aj**). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 5.34 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.82 (d, *J* = 1.7 Hz, 1H), 4.12 (ddd, *J* = 9.1, 5.2, 3.5 Hz, 1H), 4.04 – 3.94 (m, 2H), 3.89 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.66 (dt, *J* = 9.6, 4.9 Hz, 1H), 3.41 (s, 3H), 3.05 (d, *J* = 2.1 Hz, 1H), 2.31 (d, *J* = 5.4 Hz, 1H), 0.93 (s, 9H), 0.13 (s, 6H). NMR data were consistent with literature description.[10]

4. Reference

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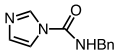
5. NMR Spectra

1-benzyl-carbamoylimidazole **a**



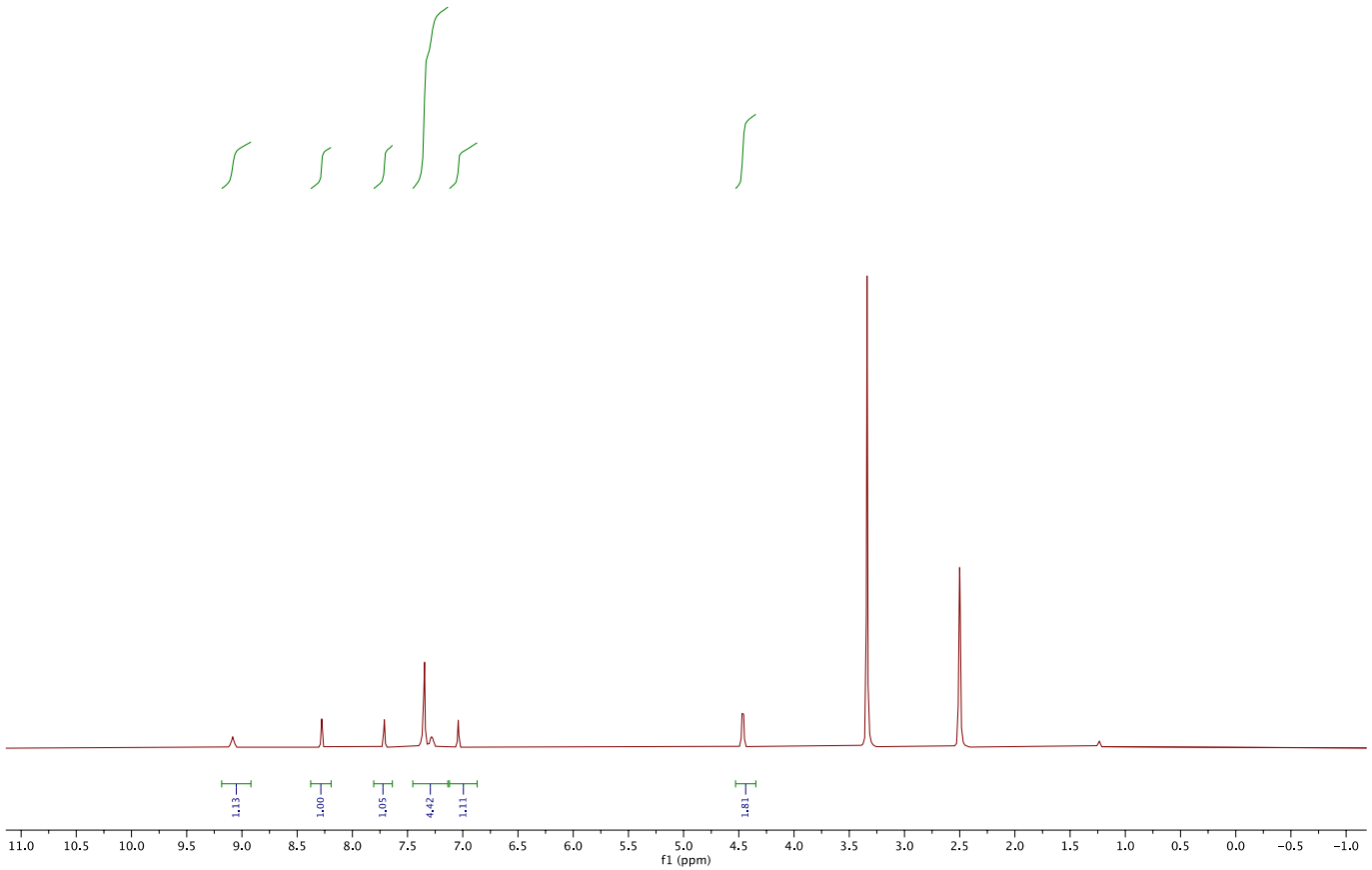
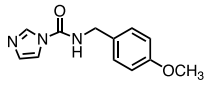


Figure S6. ^{1}H NMR spectrum (400 MHz) of **a** in $(CD_3)_2SO$

1-(4-methoxyphenyl)-carbamoylimidazole **b**



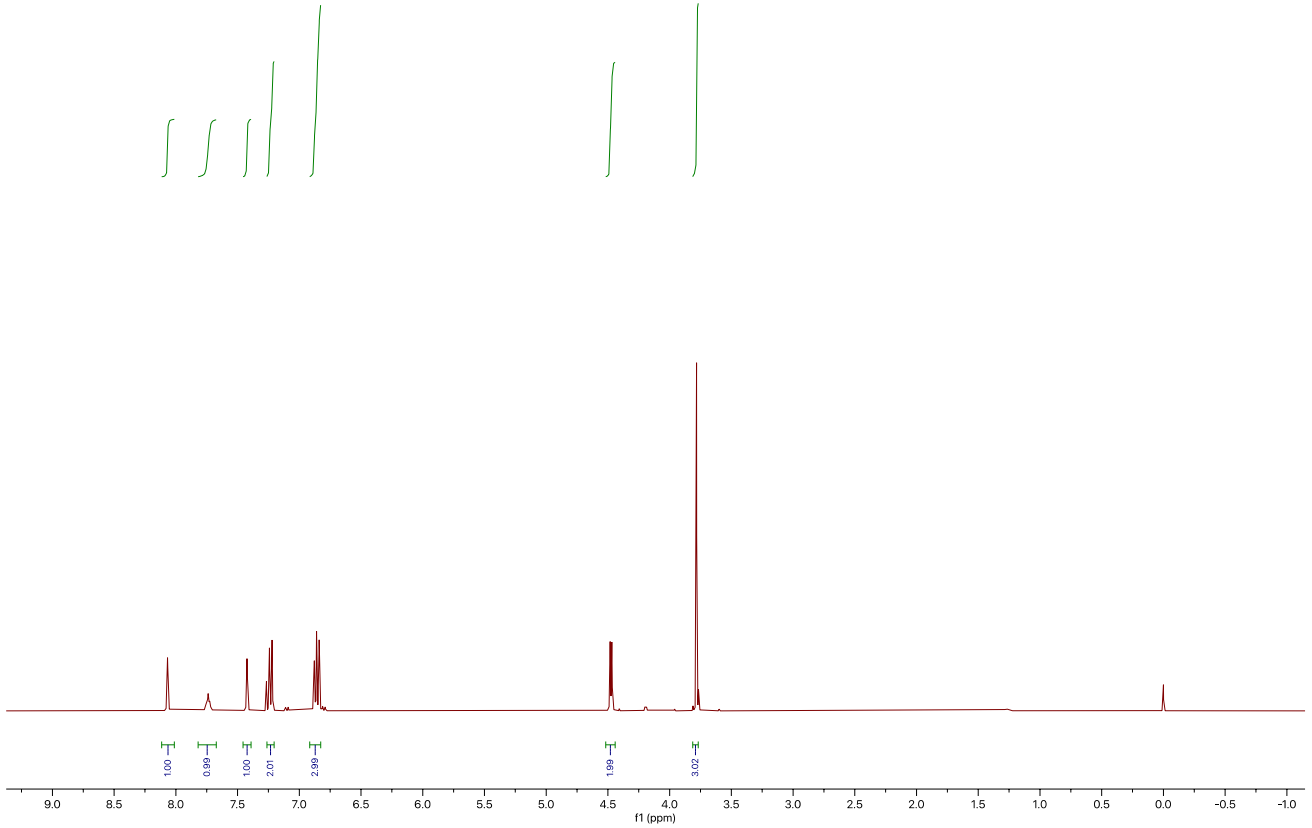
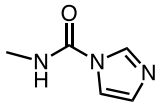


Figure S7. ^{1}H NMR spectrum (400 MHz) of **b** in $CDCl_3$

1-methyl-carbamoylimidazole **c**



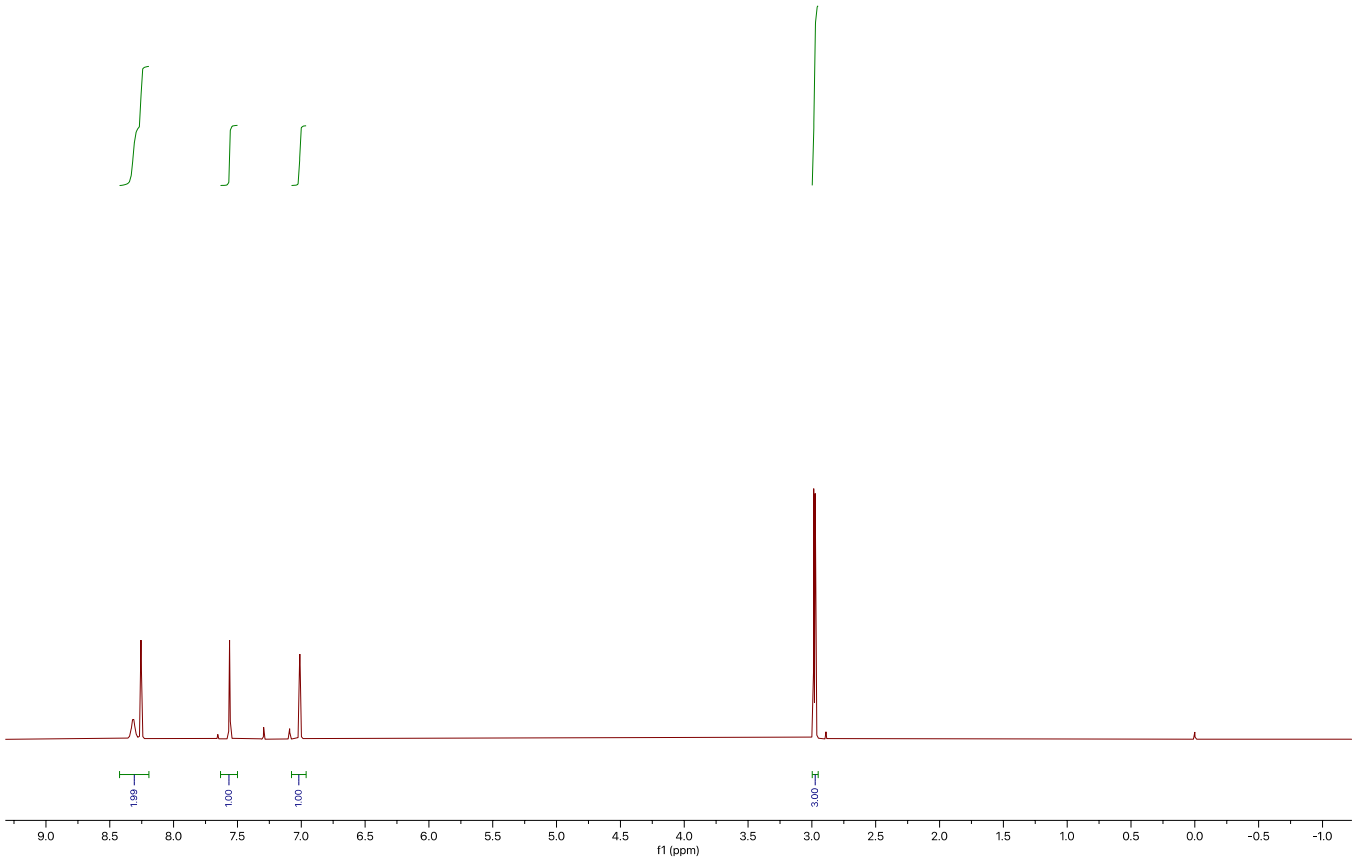


Figure S8. ^{1}H NMR spectrum (400 MHz) of **c** in $CDCl_3$

1-butyl-carbamoylimidazole **d**

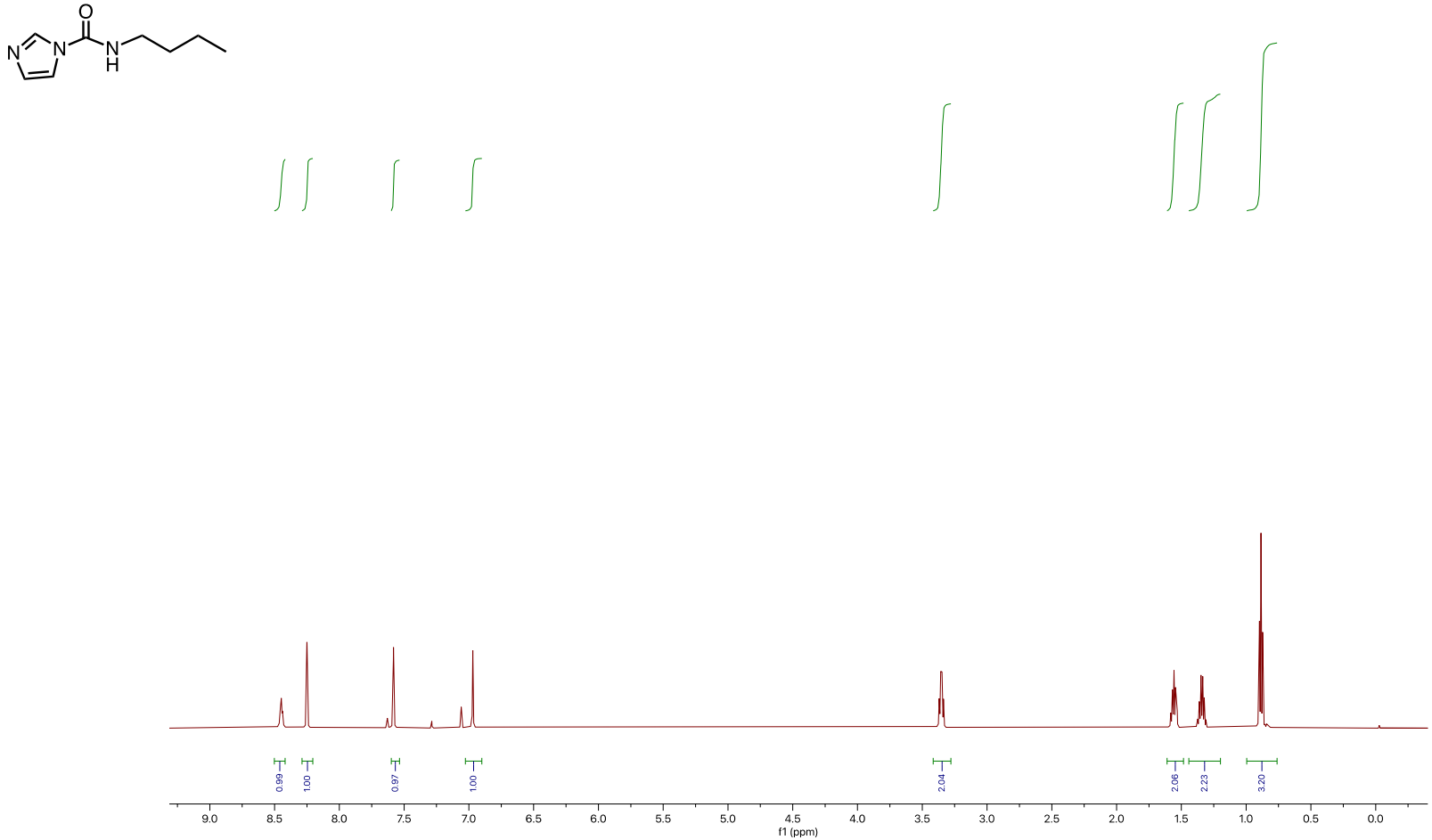
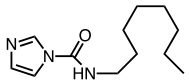


Figure S9. ^{1}H NMR spectrum (600 MHz) of **d** in $CDCl_3$

1-octyl-carbamoylimidazole **e**



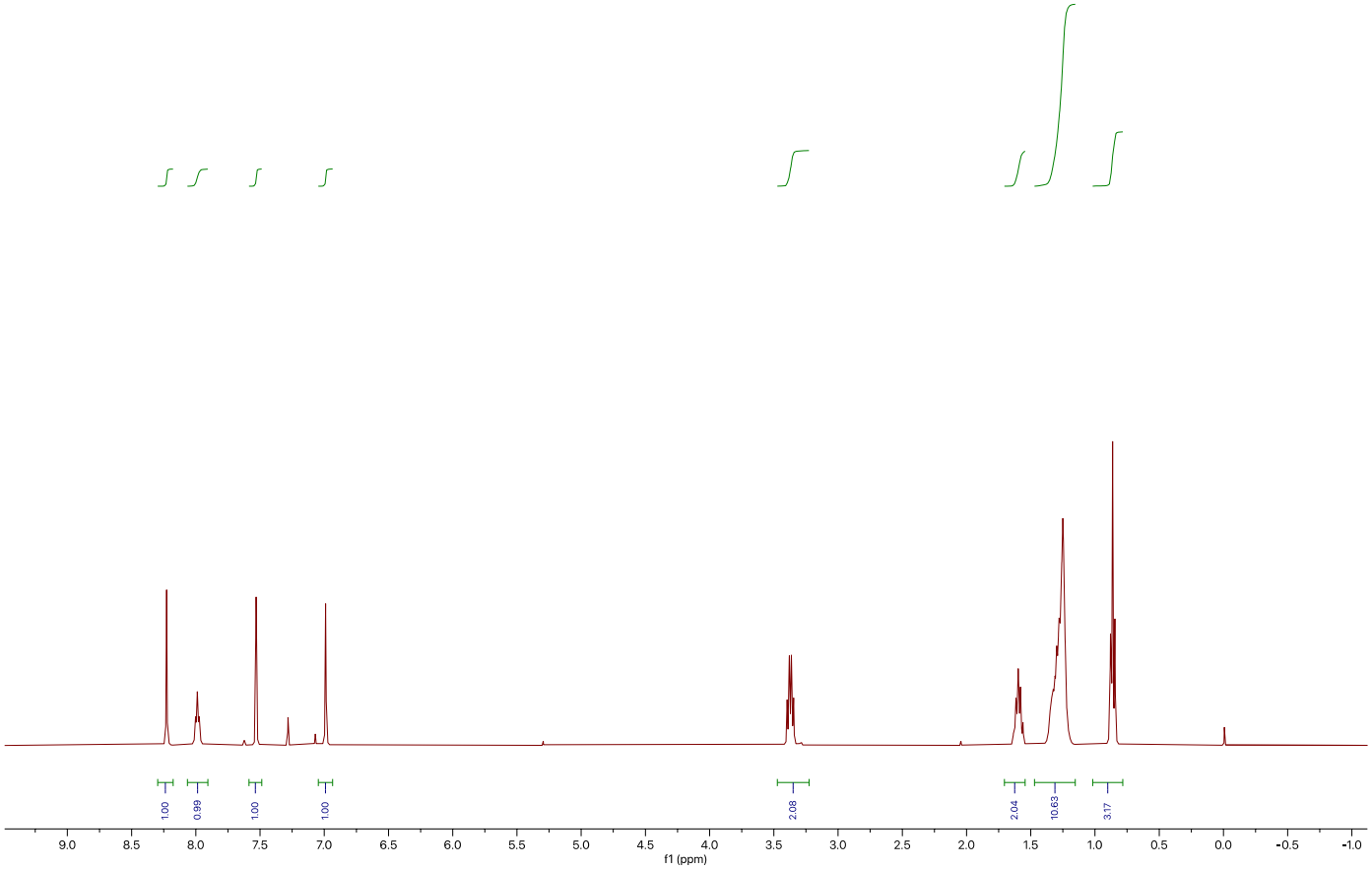
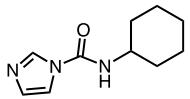


Figure S10. ^{1}H NMR spectrum (400 MHz) of **e** in $CDCl_3$

1-cyclohexyl-carbamoylimidazole **f**



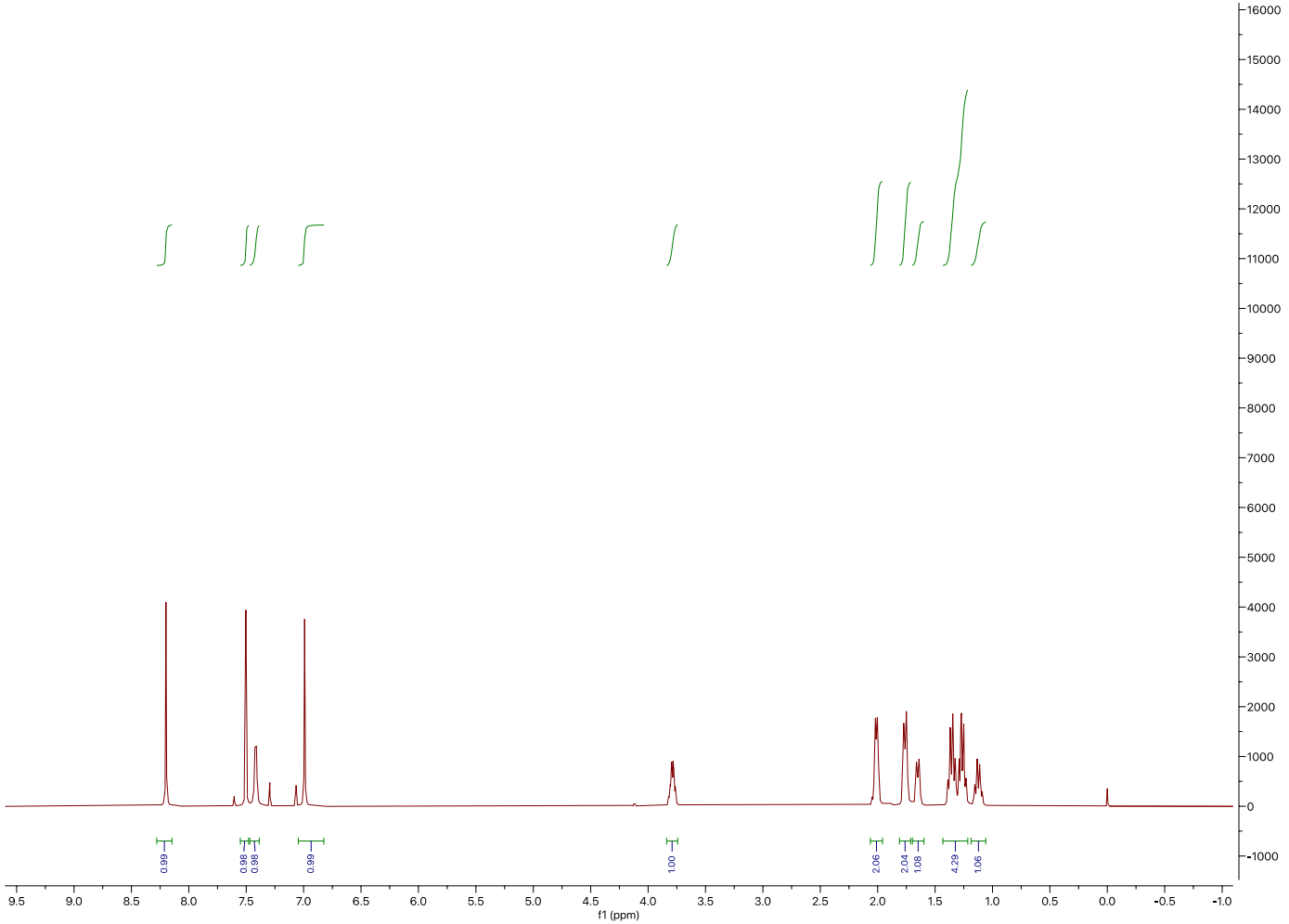


Figure S11. ^{1}H NMR spectrum (600 MHz) of **f** in $CDCl_3$

1-(phenethylcarbonyl)imidazole **g**

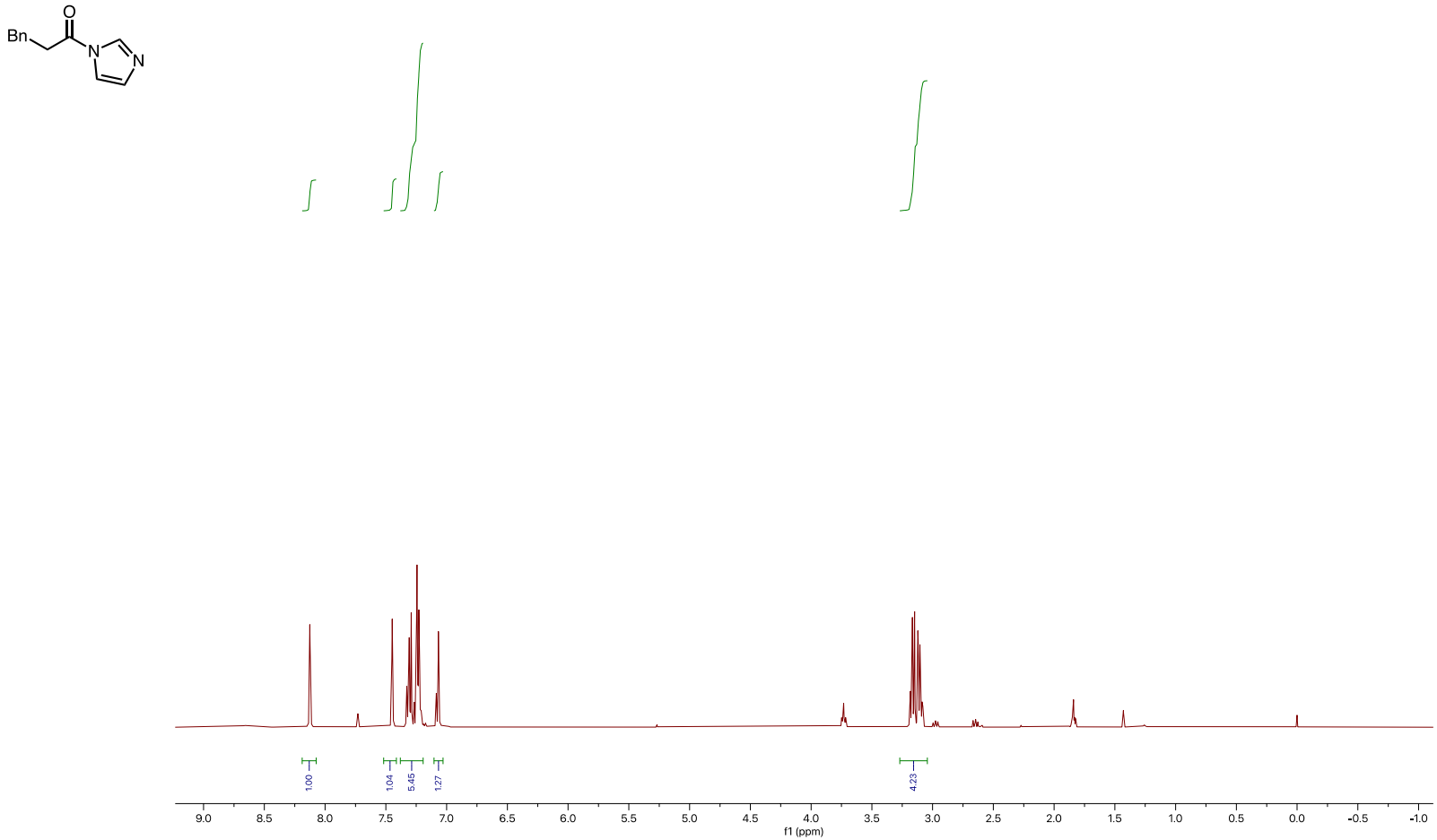
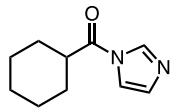


Figure S12. ^{1}H NMR spectrum (400 MHz) of **g** in $CDCl_3$

1-(cyclohexylcarbonyl)imidazole **h**



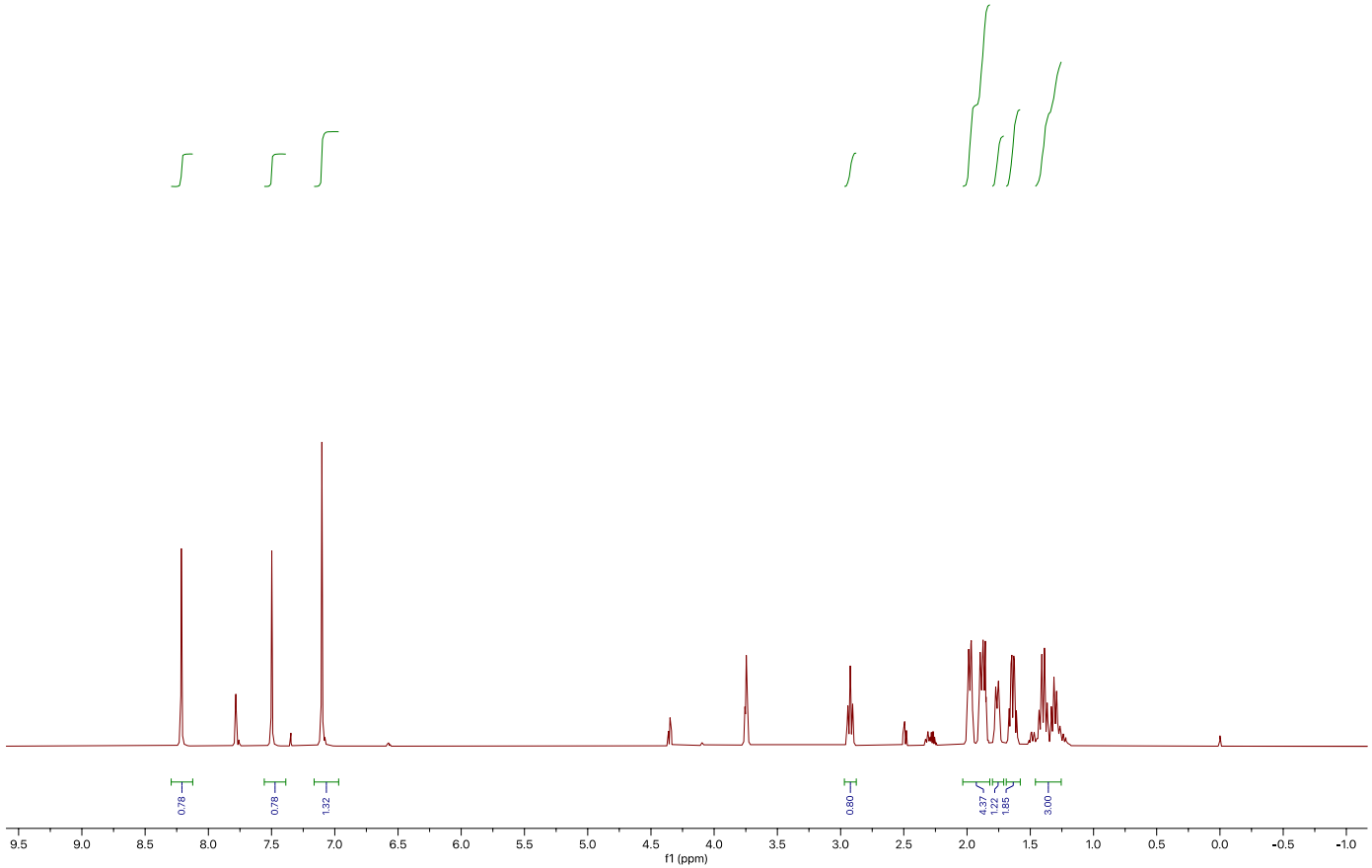
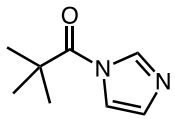


Figure S13. ^{1}H NMR spectrum (600 MHz) of **h** in $CDCl_3$

1-(trimethylacetyl) imidazole **i**



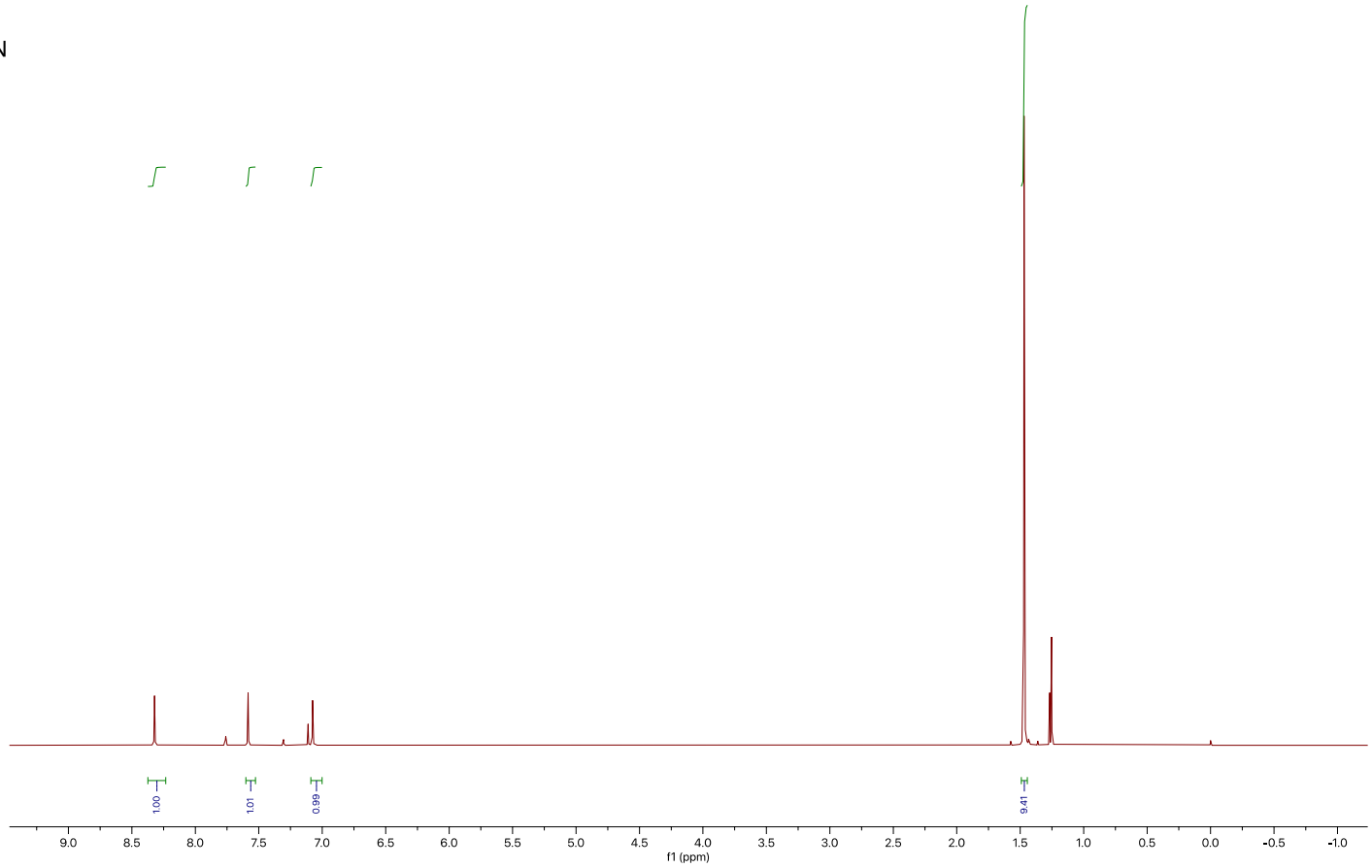
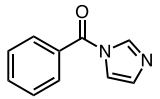


Figure S14. ^{1}H NMR spectrum (600 MHz) of **i** in $CDCl_3$

1-(benzoyl)imidazole **j**



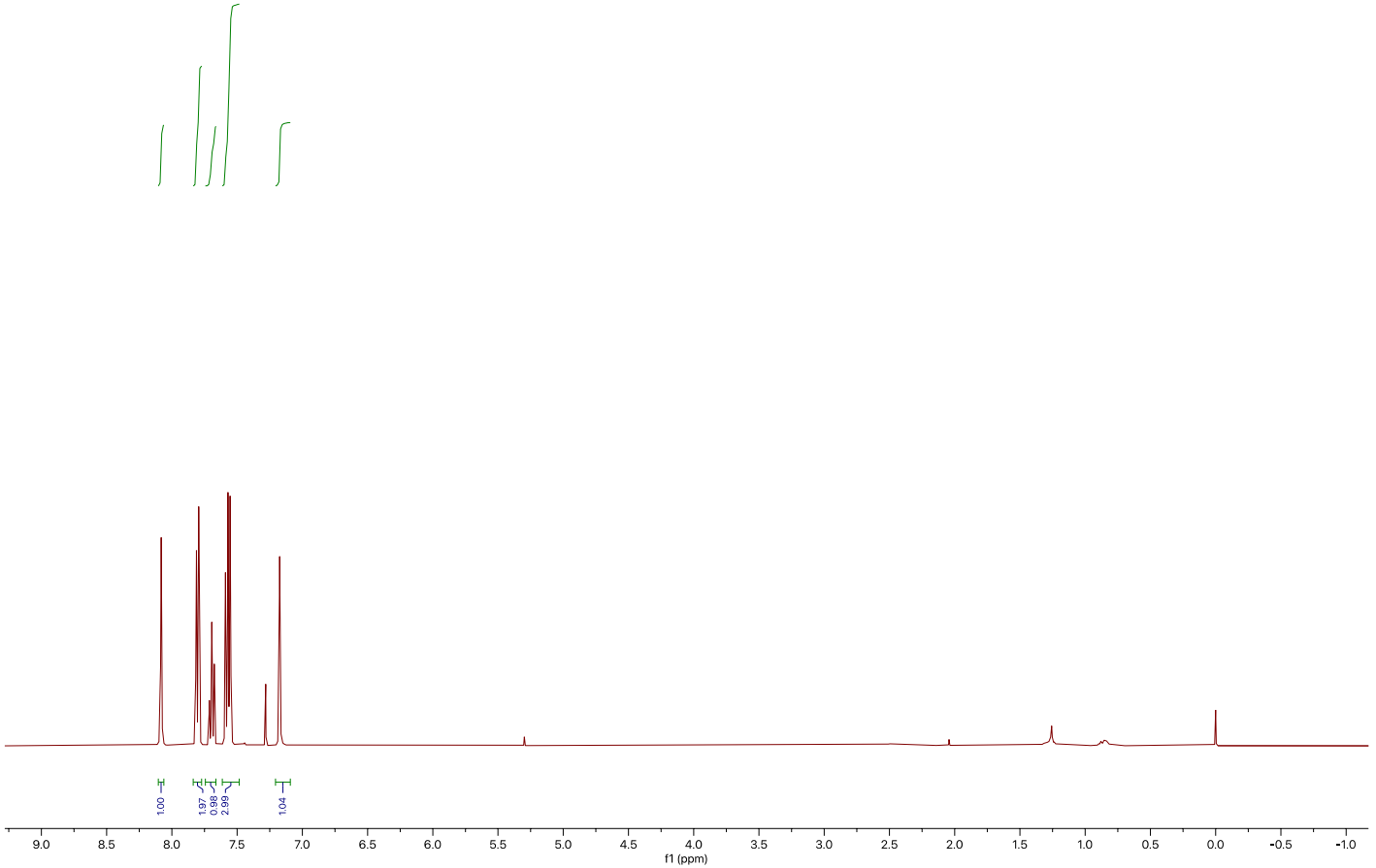


Figure S15. ^{1}H NMR spectrum (400 MHz) of **j** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1aa**

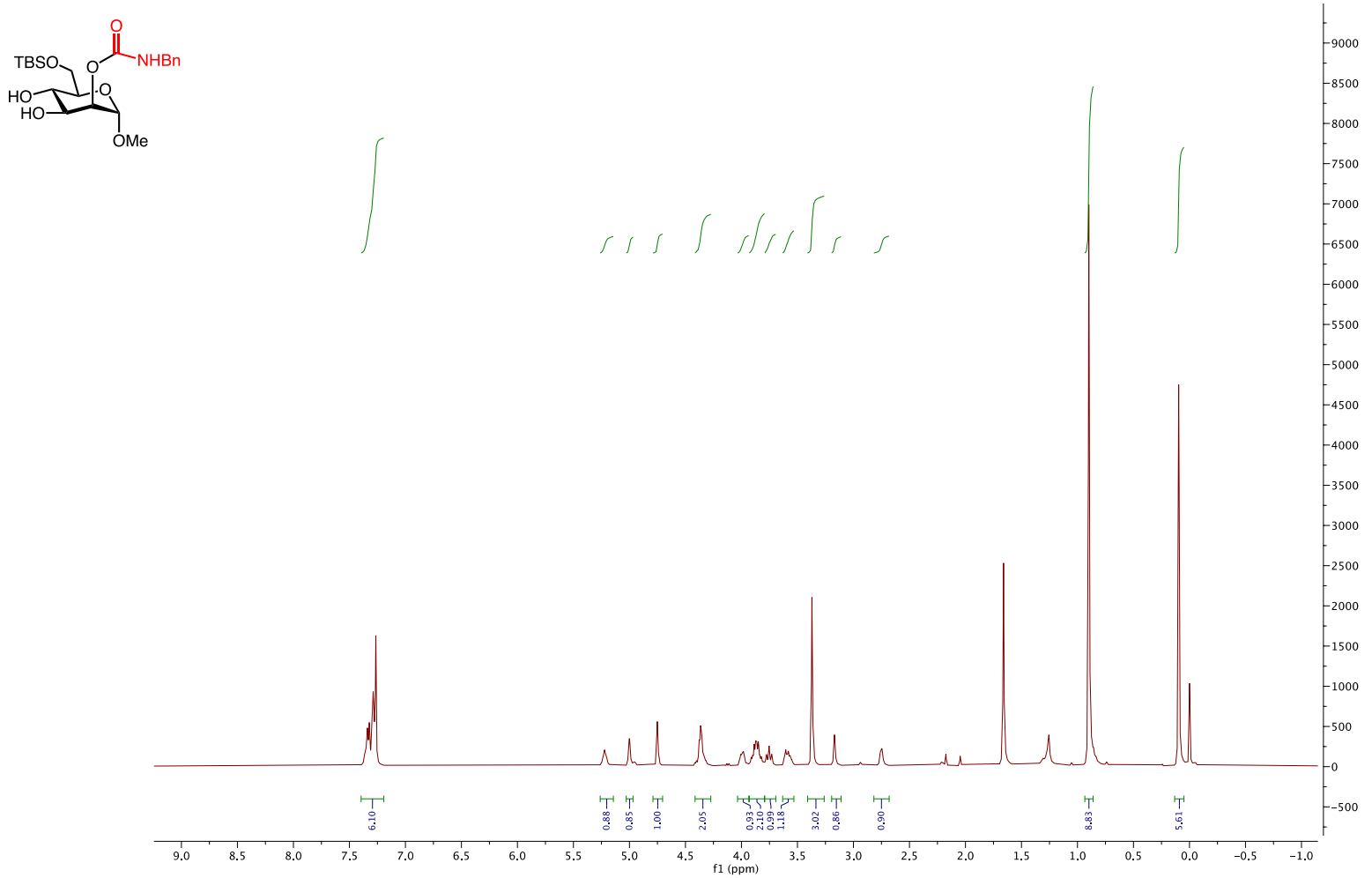


Figure S16. ^{1}H NMR spectrum (400 MHz) of **1aa** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1aa**

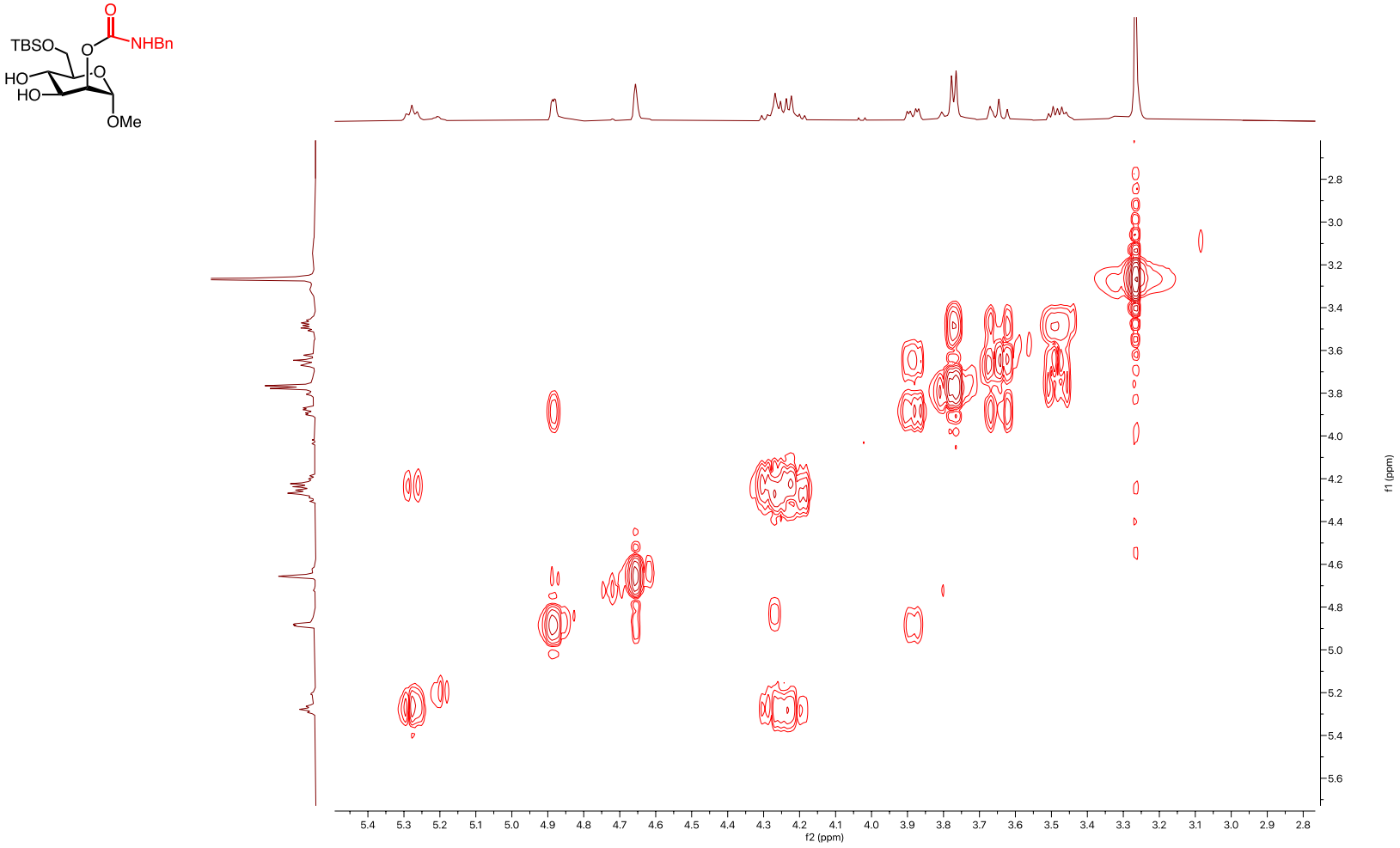


Figure S17. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1aa** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1aa**

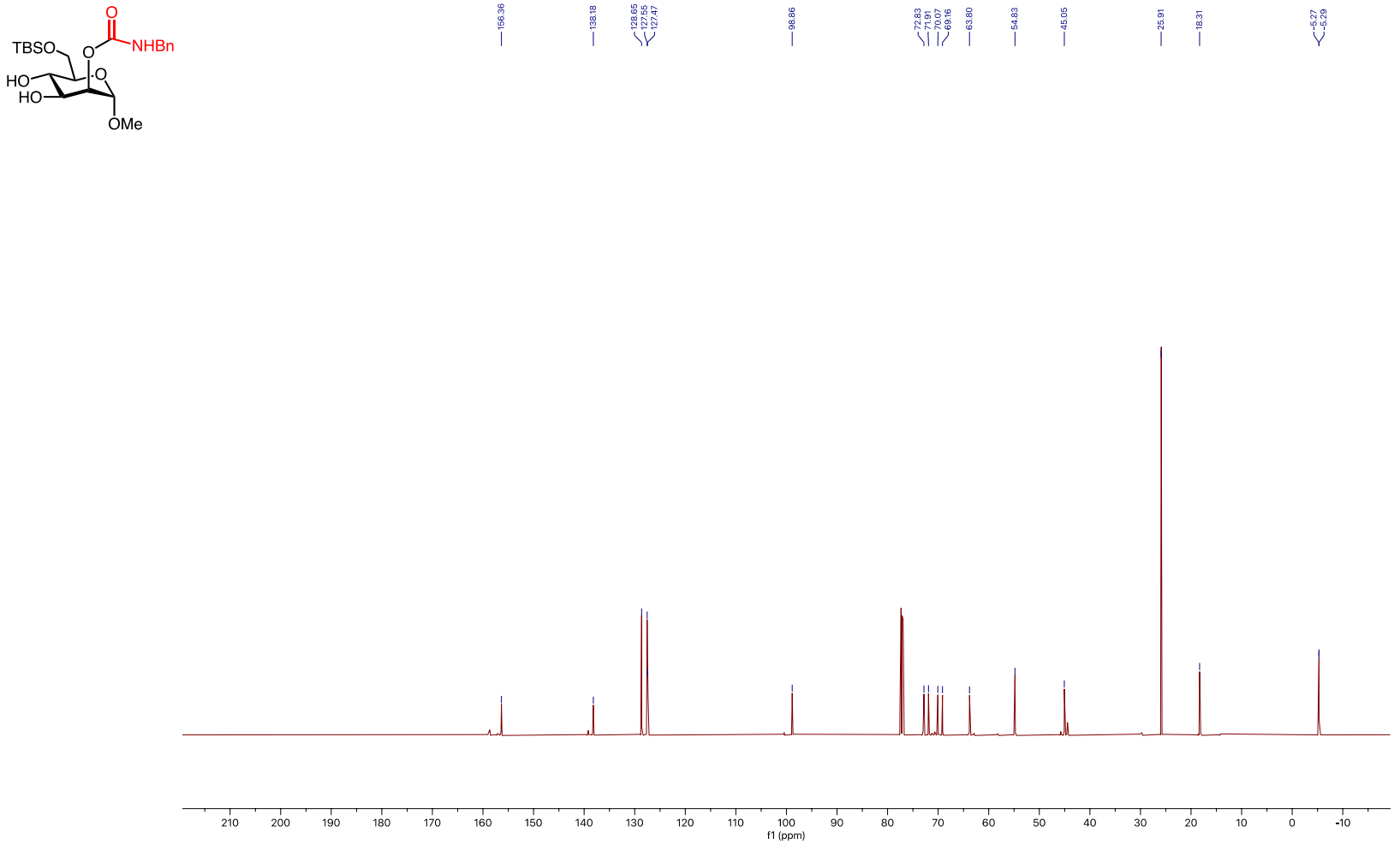


Figure S18. ^{13}C NMR spectrum (100 MHz) of **1aa** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ba**

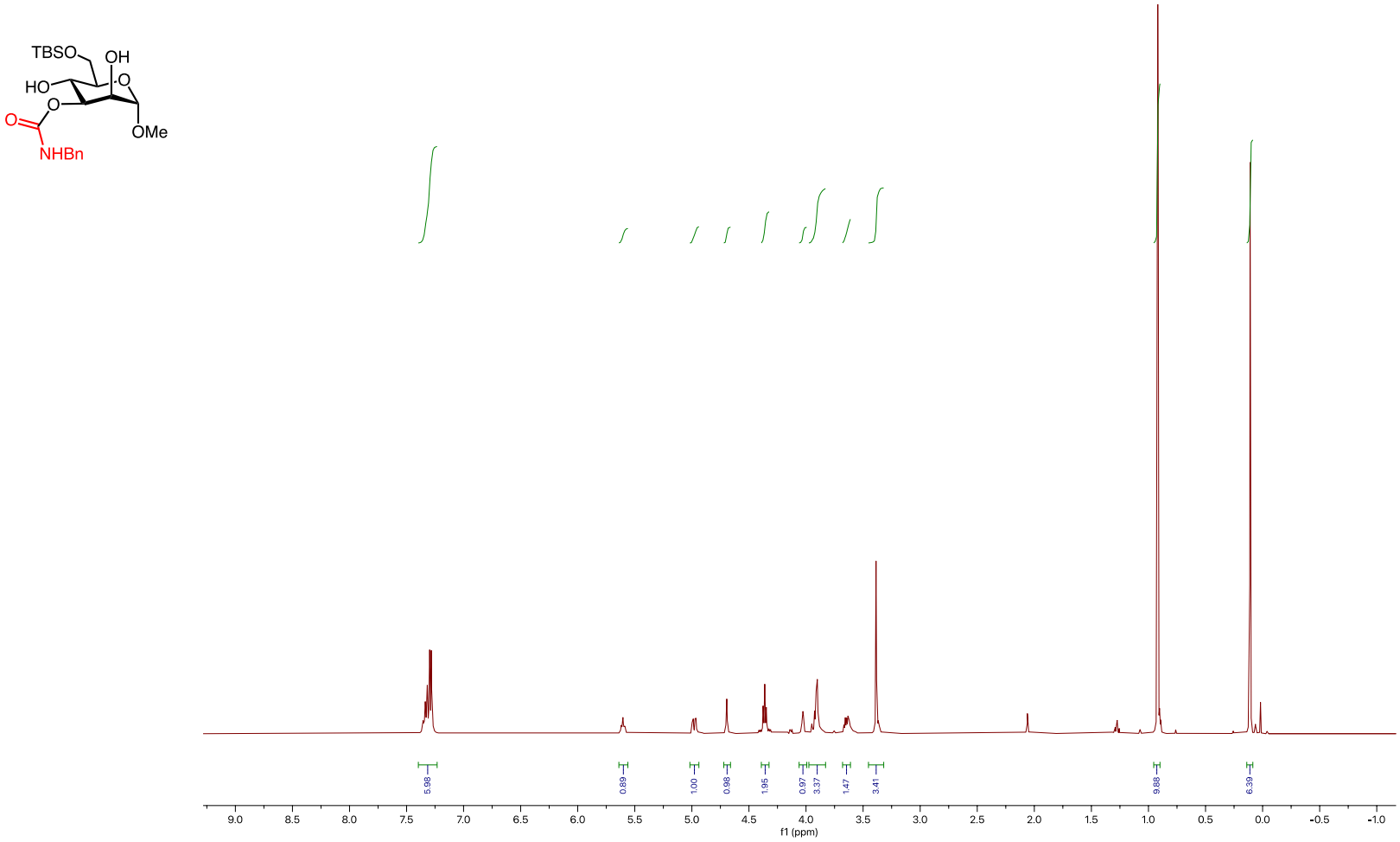


Figure S19. ^{1}H NMR spectrum (400 MHz) of **1ba** in $CDCl_3$

Methyl 2-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ab**

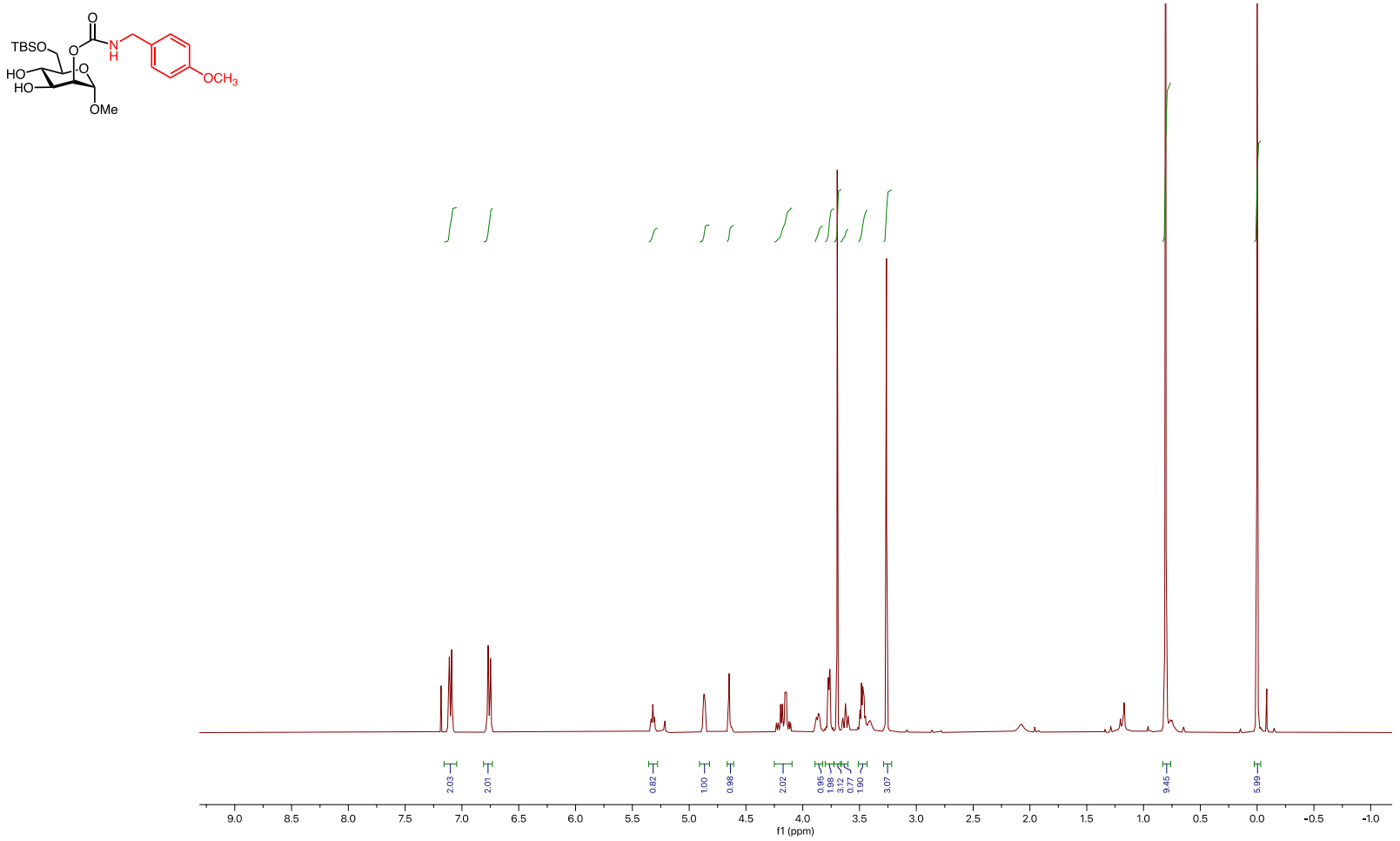


Figure S20. ^{1}H NMR spectrum (400 MHz) of **1ab** in $CDCl_3$

Methyl 2-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ab**

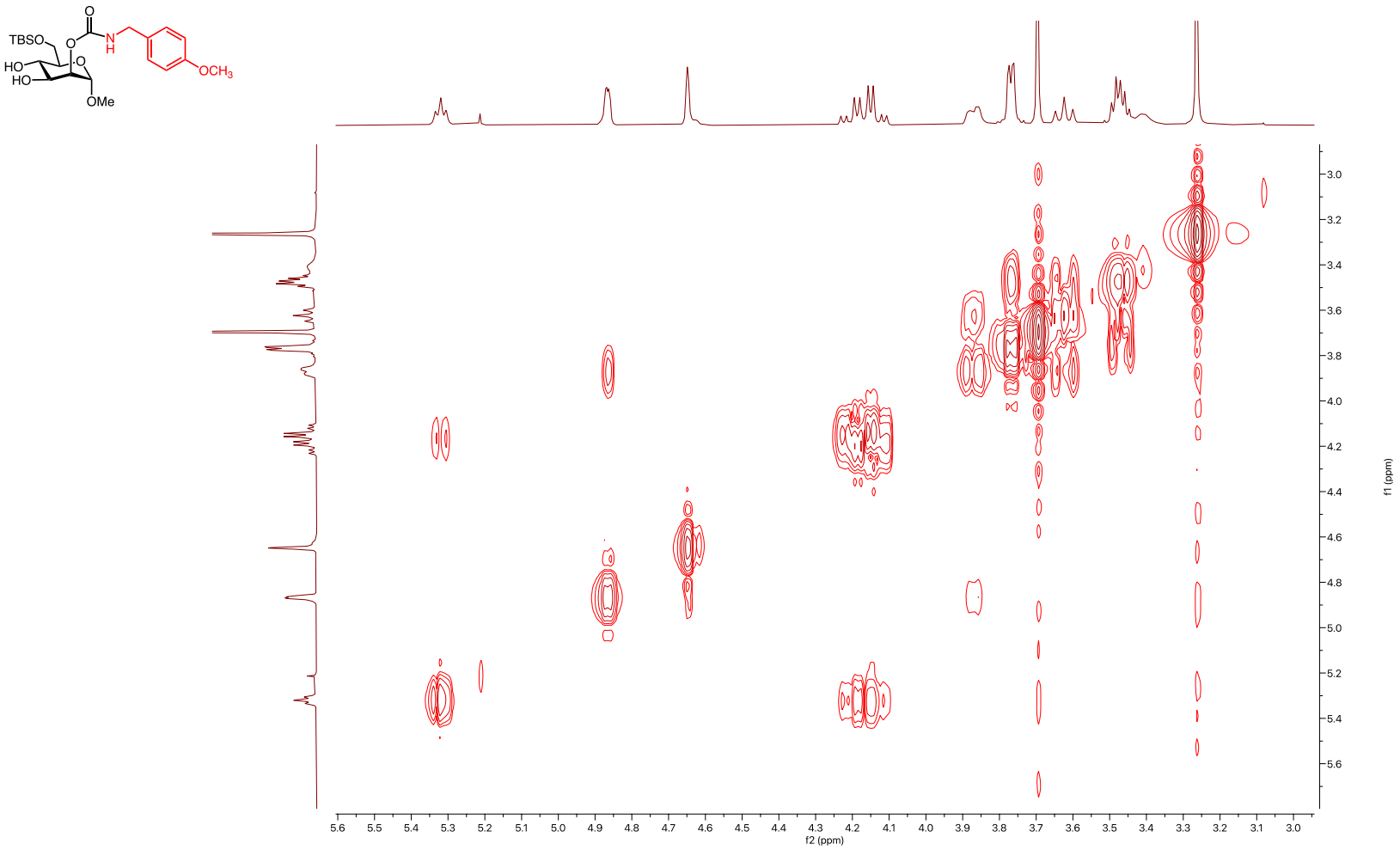


Figure S21. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ab** in $CDCl_3$

Methyl 2-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ab**

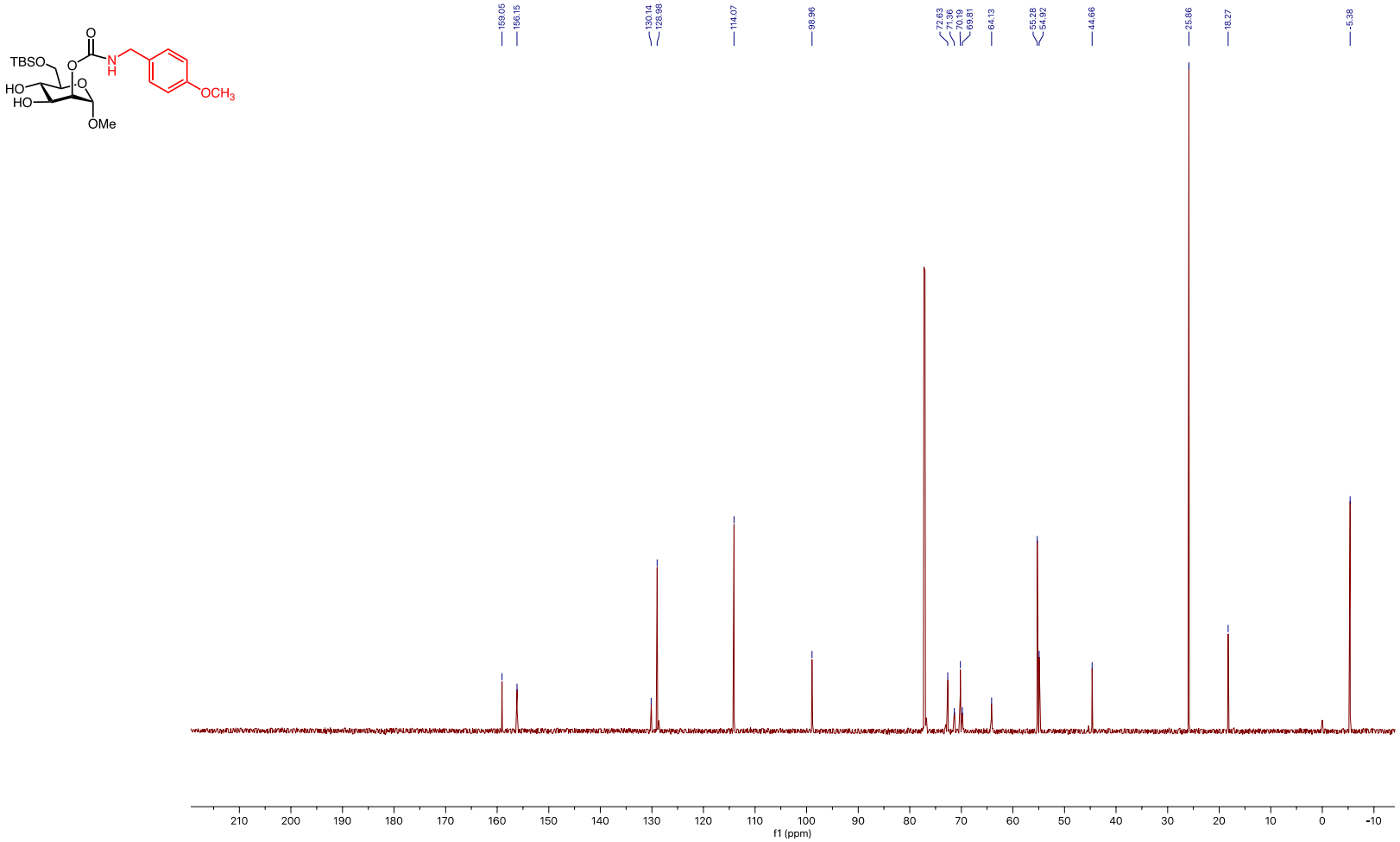


Figure S22. ^{13}C NMR spectrum (100 MHz) of **1ab** in $CDCl_3$

Methyl 3-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bb**

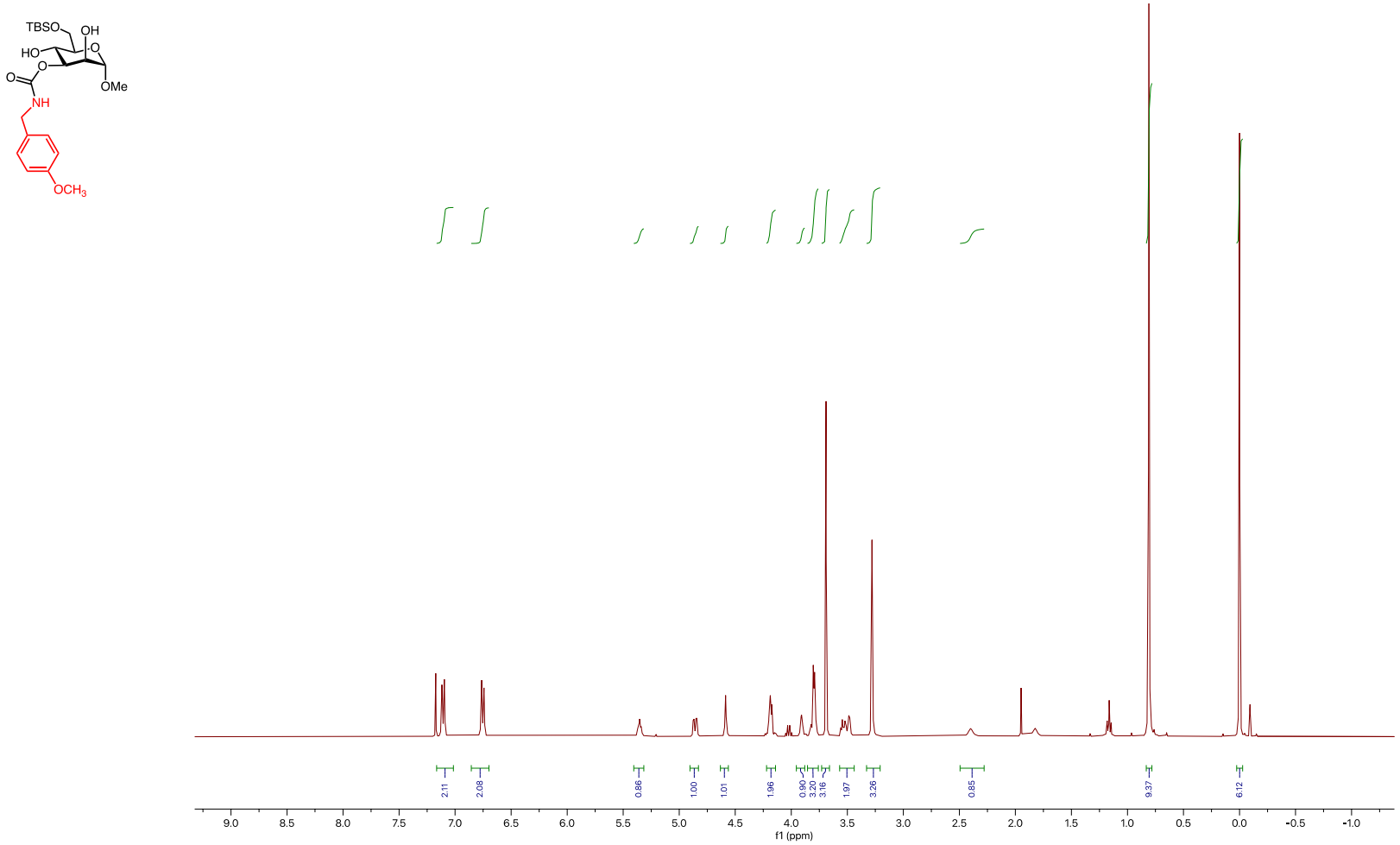


Figure S23. ^{1}H NMR spectrum (400 MHz) of **1bb** in $CDCl_3$

Methyl 3-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bb**

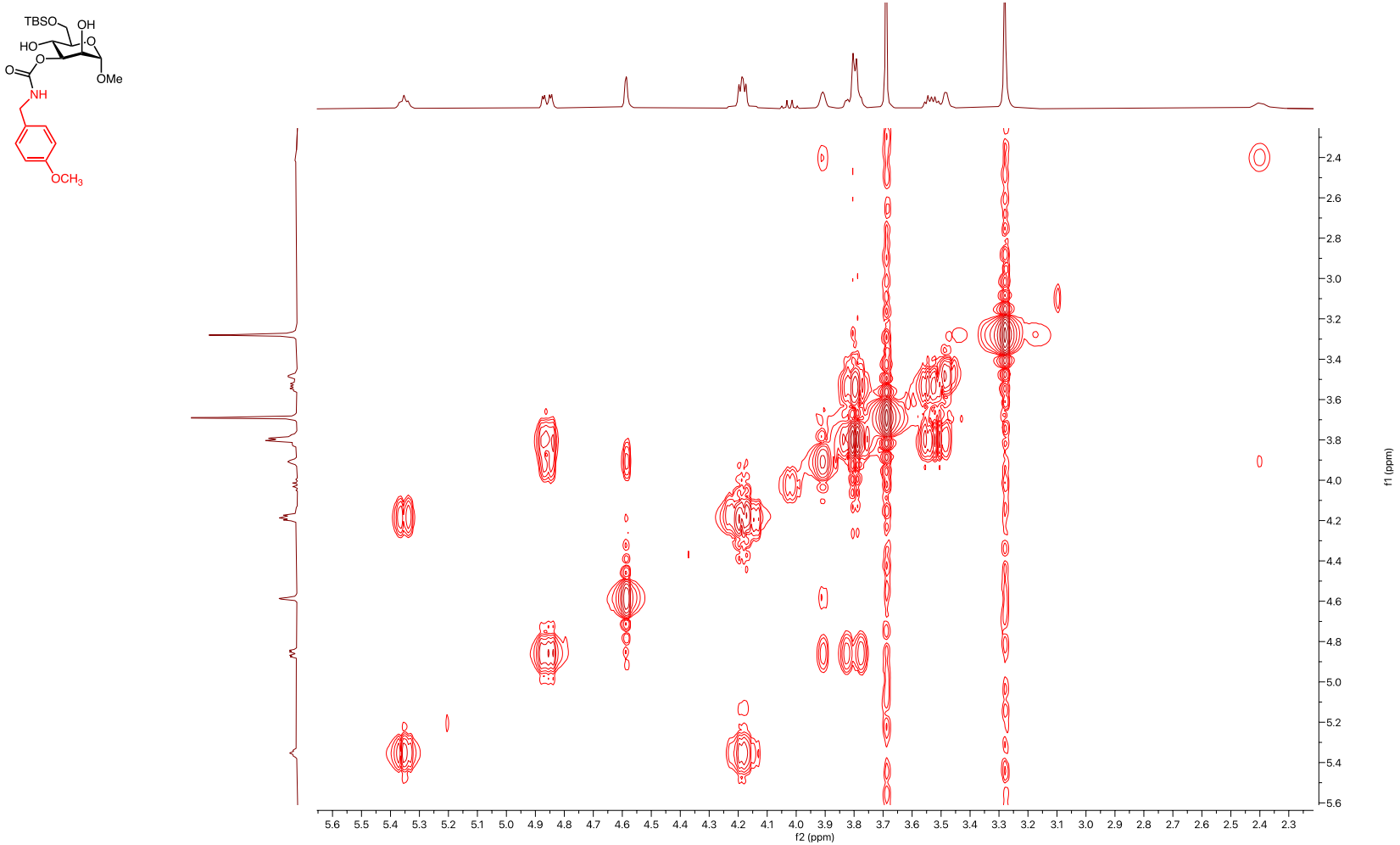


Figure S24. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1bb** in $CDCl_3$

Methyl 3-*O*-(4-methoxy-benzyl)carbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bb**

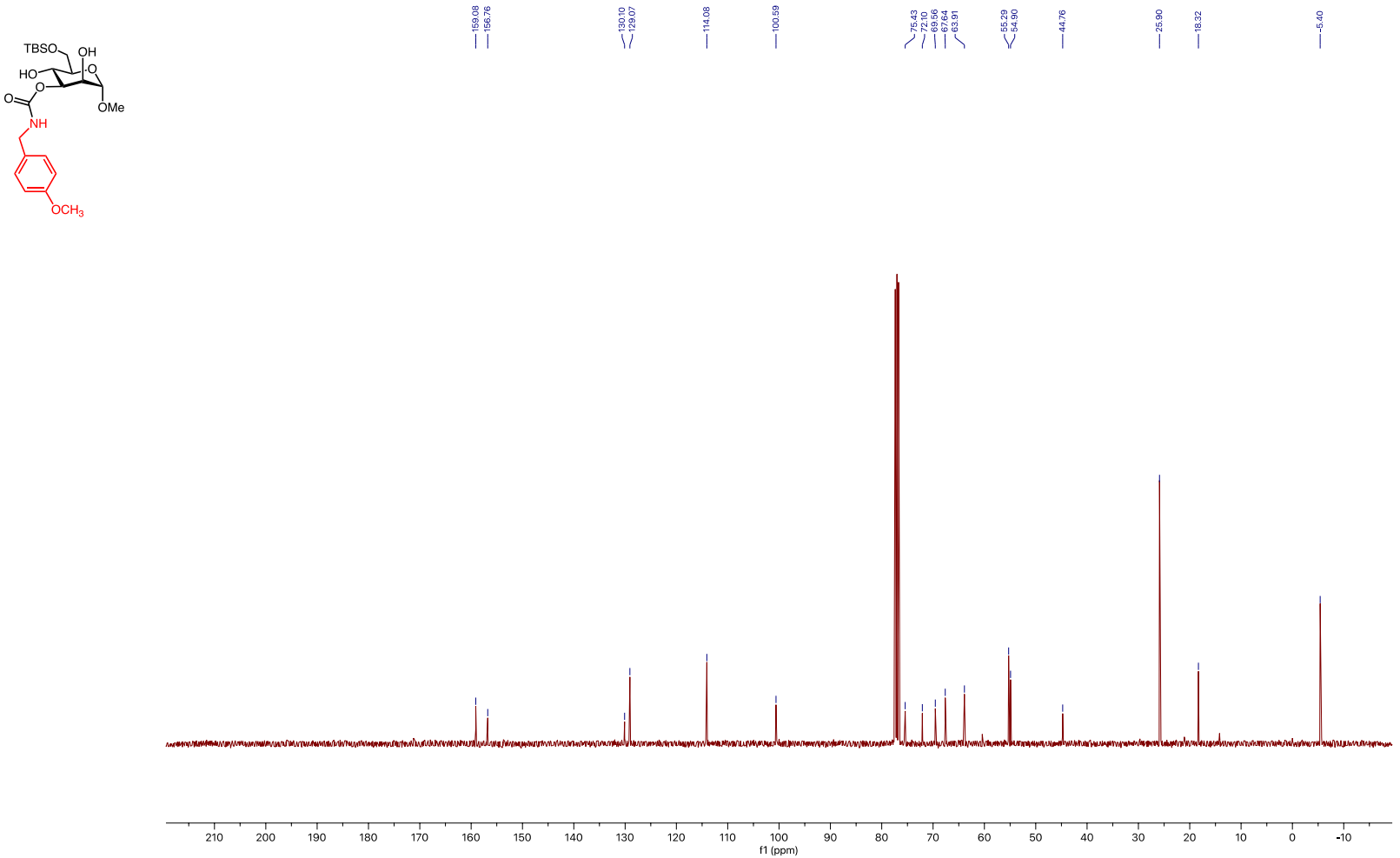
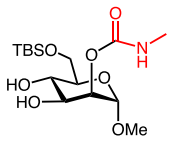


Figure S25. ^{13}C NMR spectrum (100 MHz) of **1bb** in $CDCl_3$

Methyl 2-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ac**



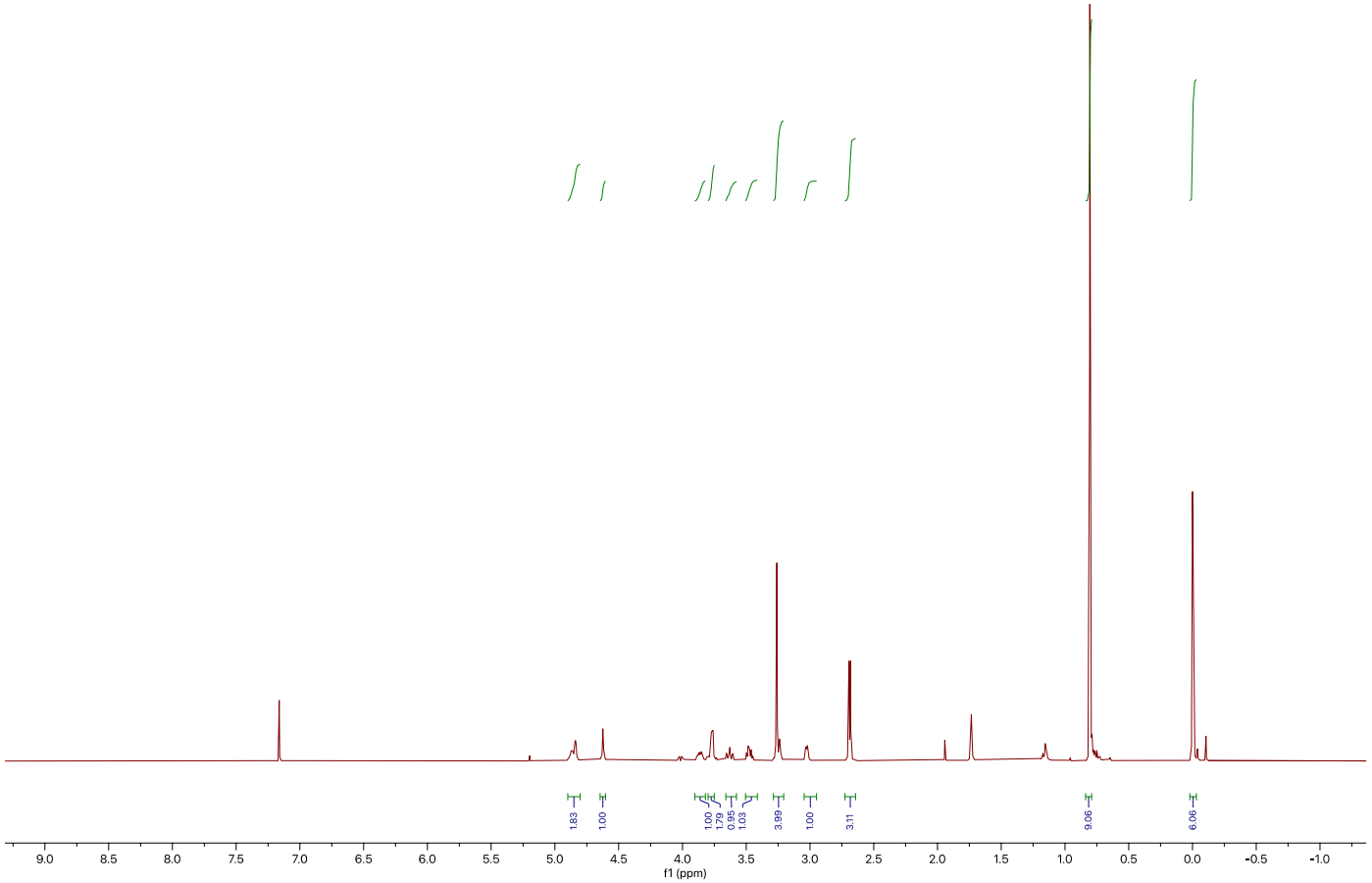


Figure S26. ^{1}H NMR spectrum (400 MHz) of **1ac** in $CDCl_3$

Methyl 2-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ac**

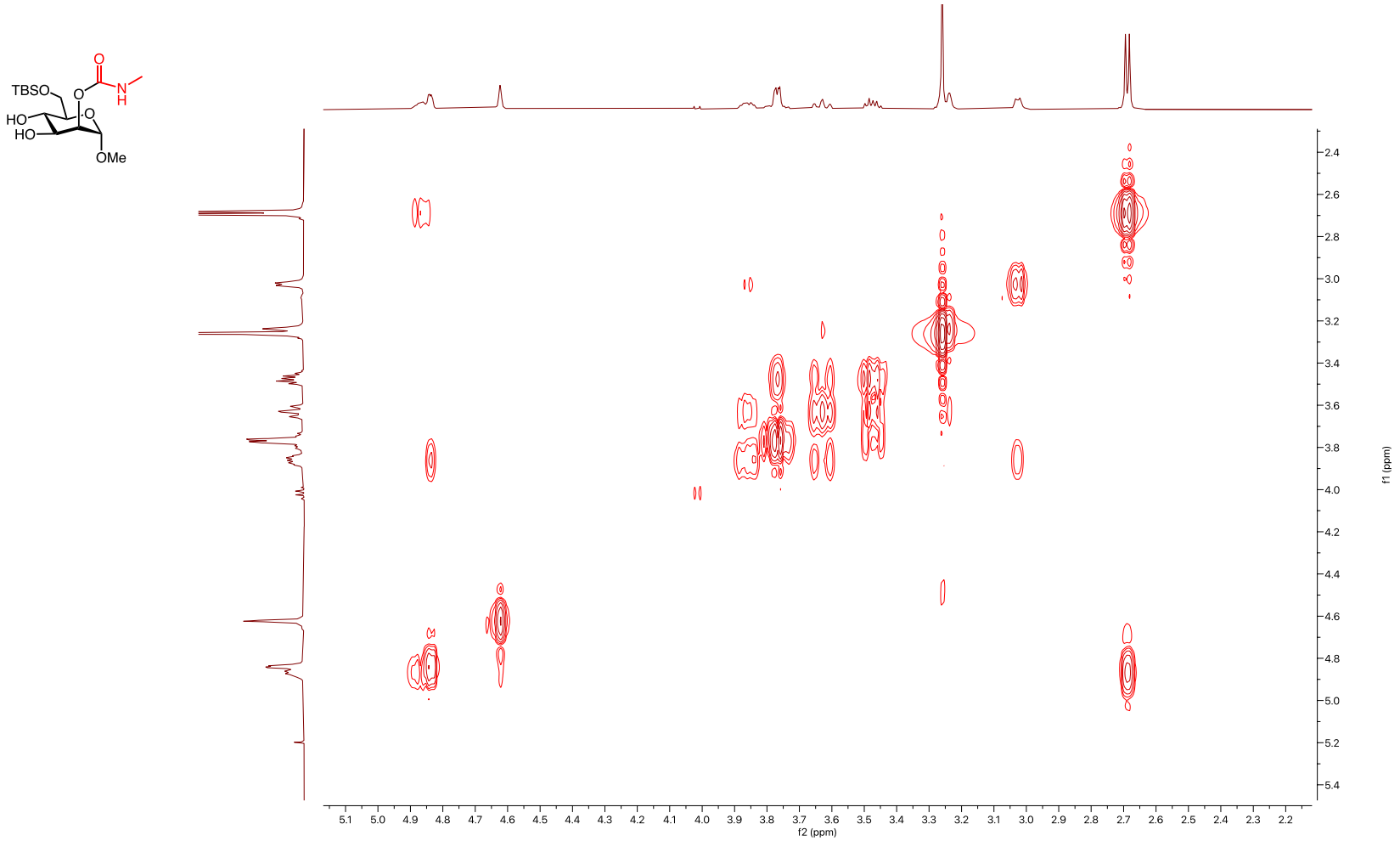


Figure S27. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ac** in $CDCl_3$

Methyl 2-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ac**

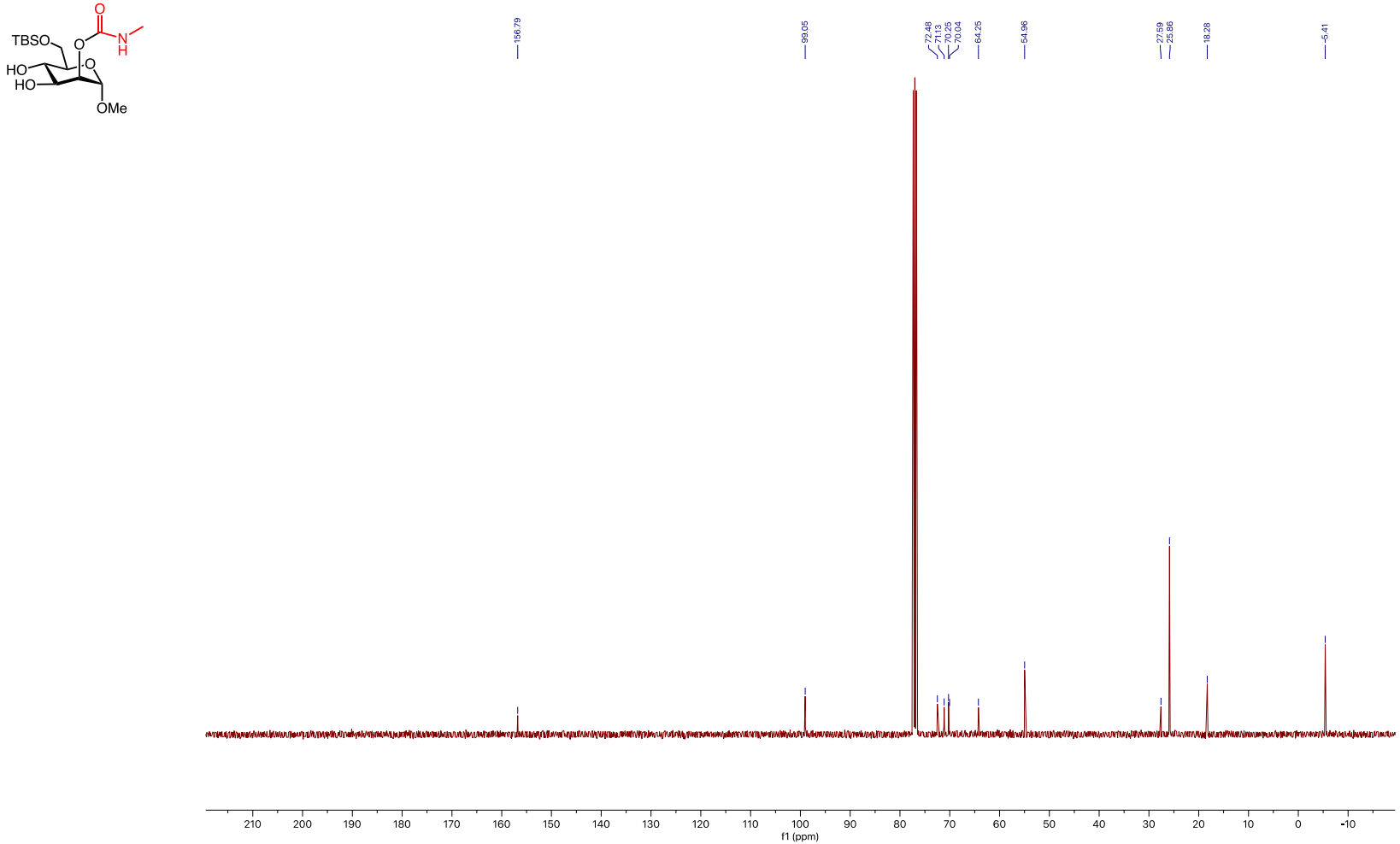


Figure S28. ^{13}C NMR spectrum (100 MHz) of **1ac** in $CDCl_3$

Methyl 3-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bc**

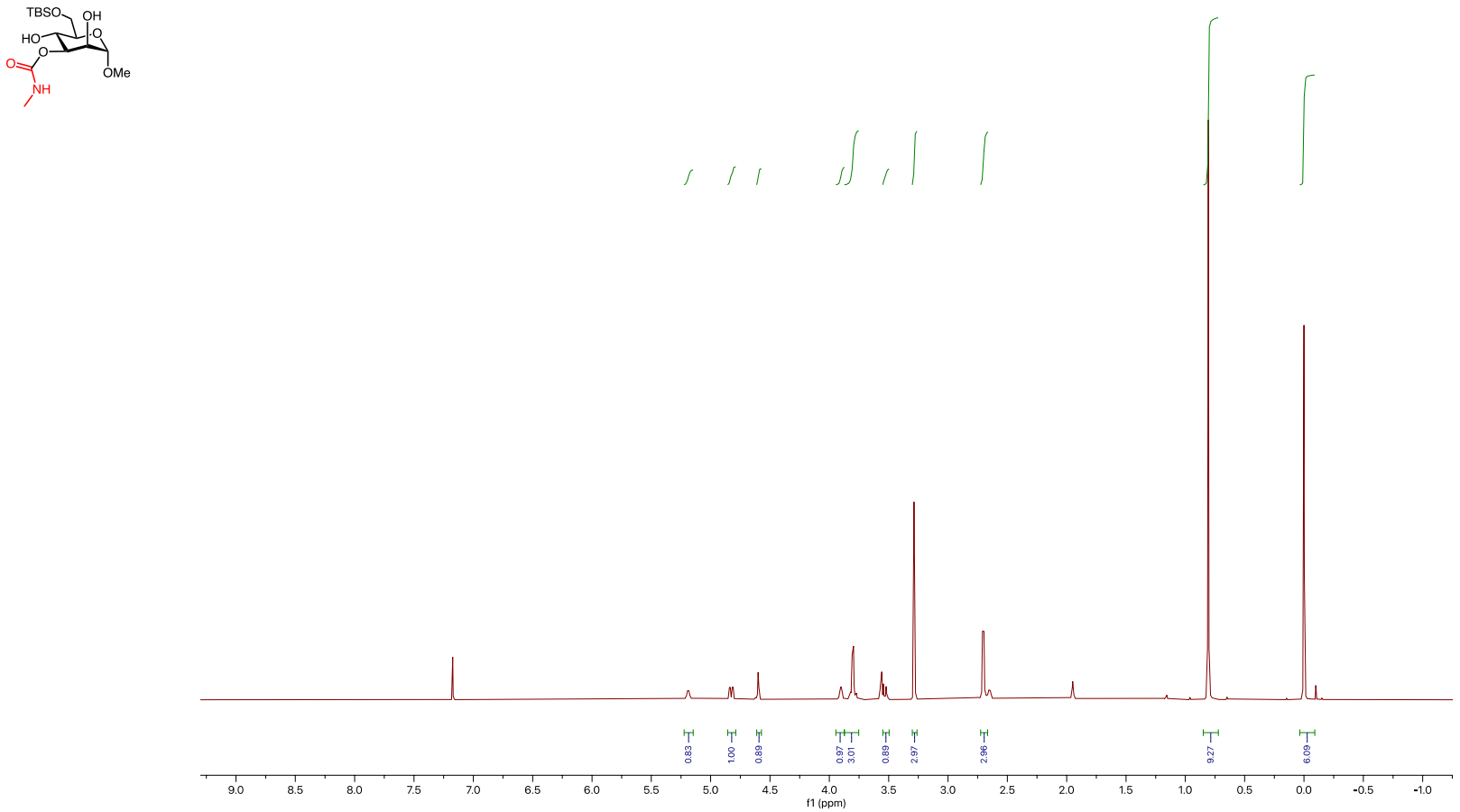


Figure S29. ^{1}H NMR spectrum (400 MHz) of **1bc** in $CDCl_3$

Methyl 3-*O*-methylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bc**

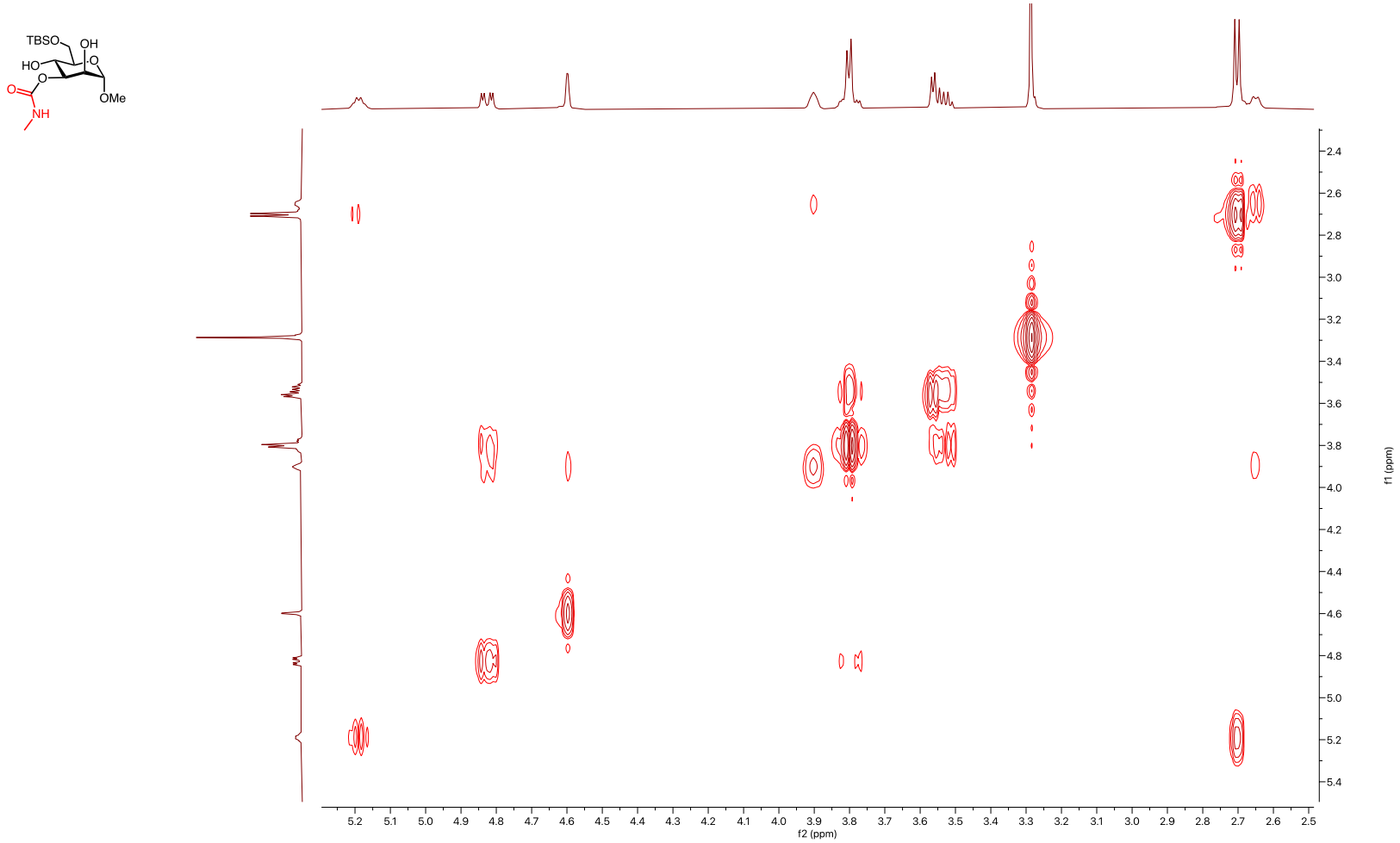


Figure S30. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1bc** in $CDCl_3$

Methyl 2-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ad**

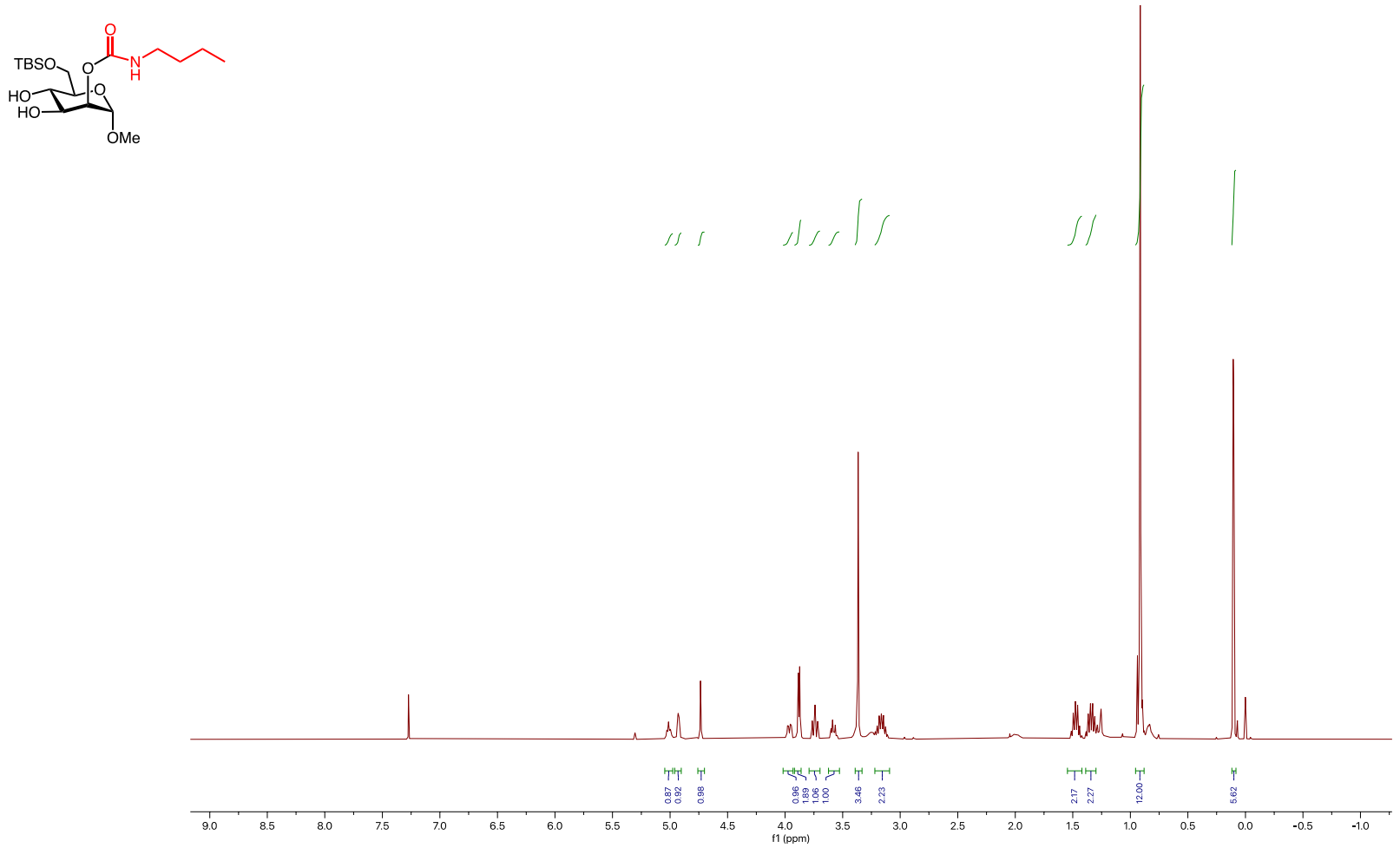


Figure S31. ^{1}H NMR spectrum (400 MHz) of **1ad** in $CDCl_3$

Methyl 2-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ad**

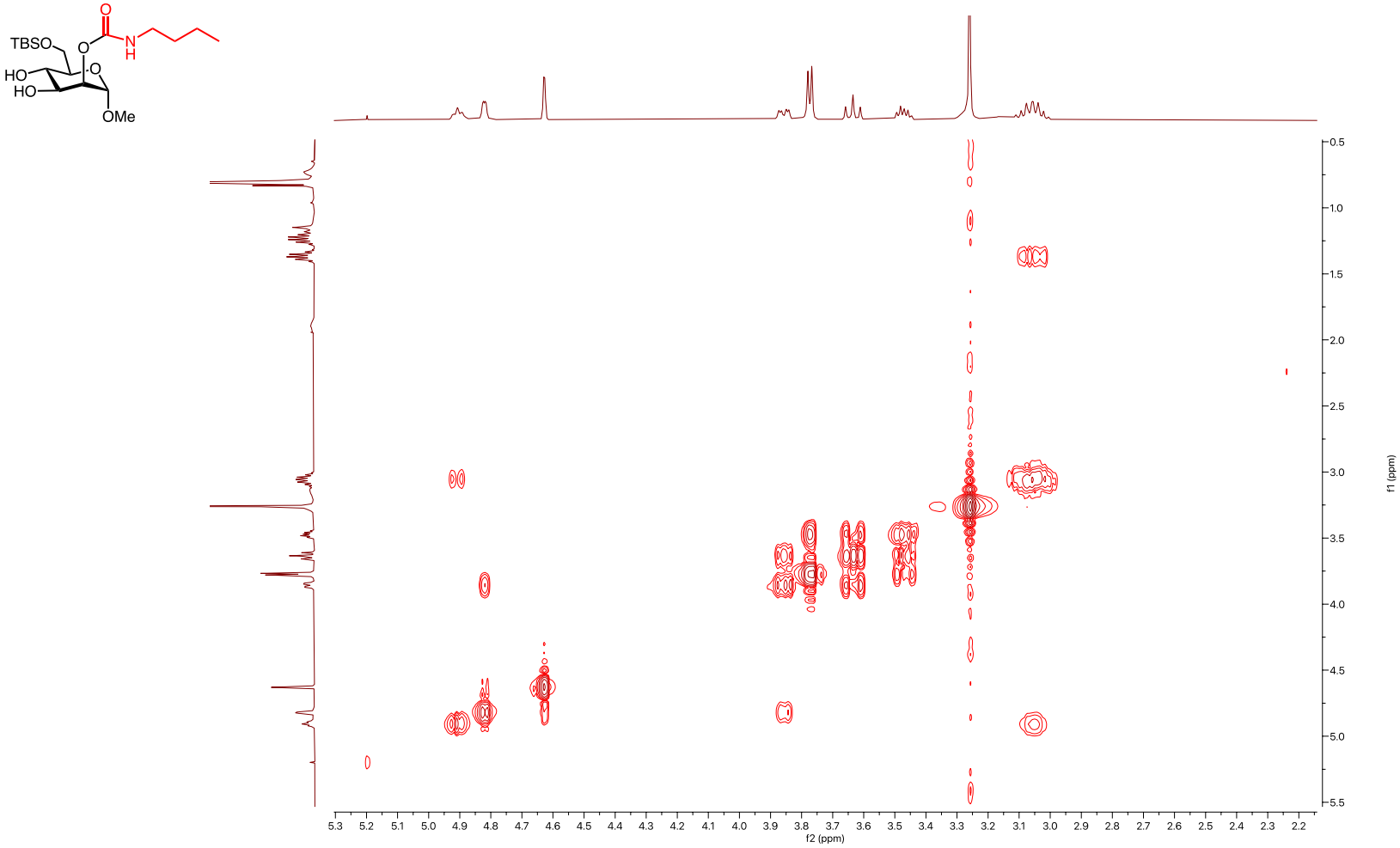


Figure S32. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ad** in $CDCl_3$

Methyl 2-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ad**

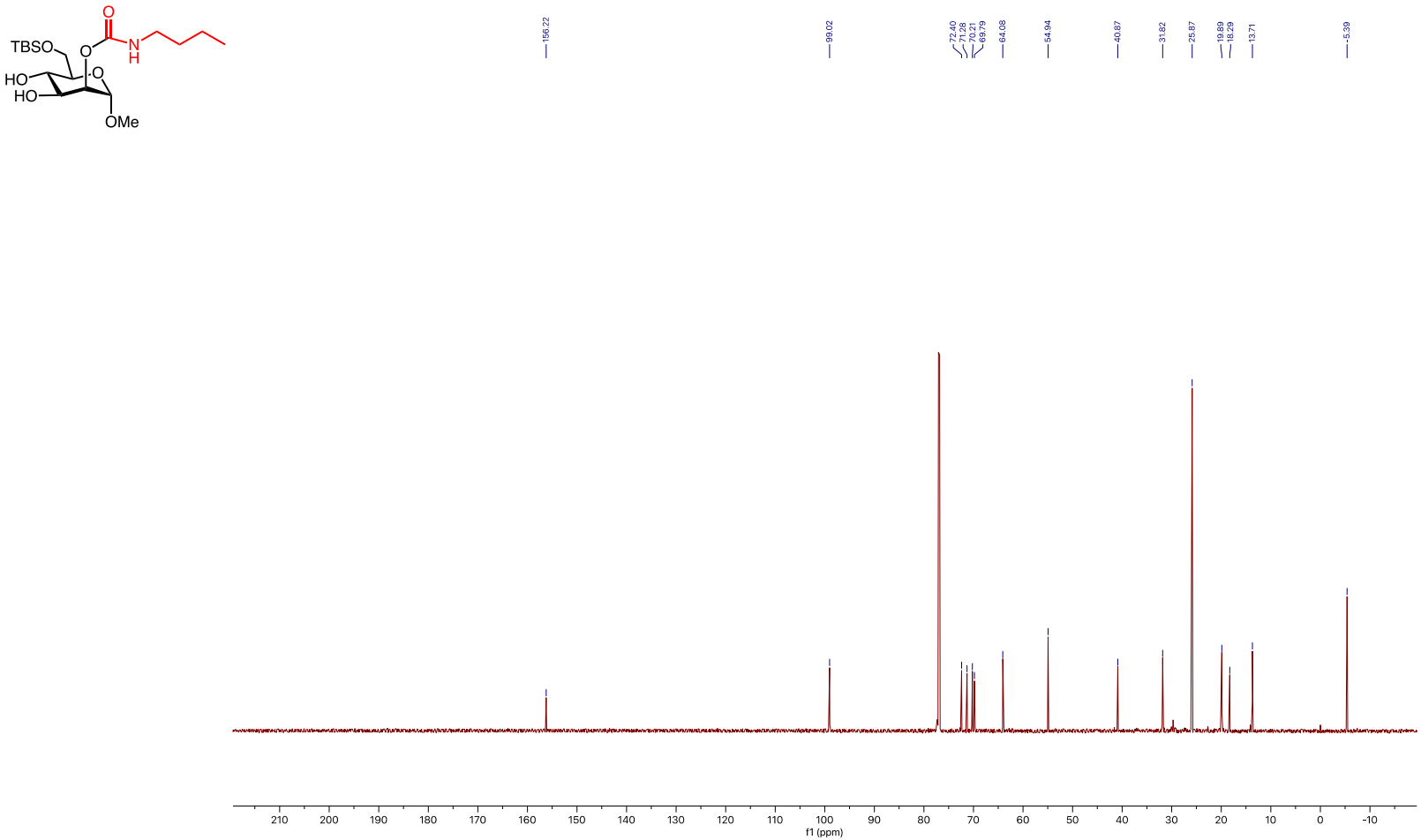


Figure S33. ^{13}C NMR spectrum (100 MHz) of **1ad** in $CDCl_3$

Methyl 3-*O*-butylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bd**

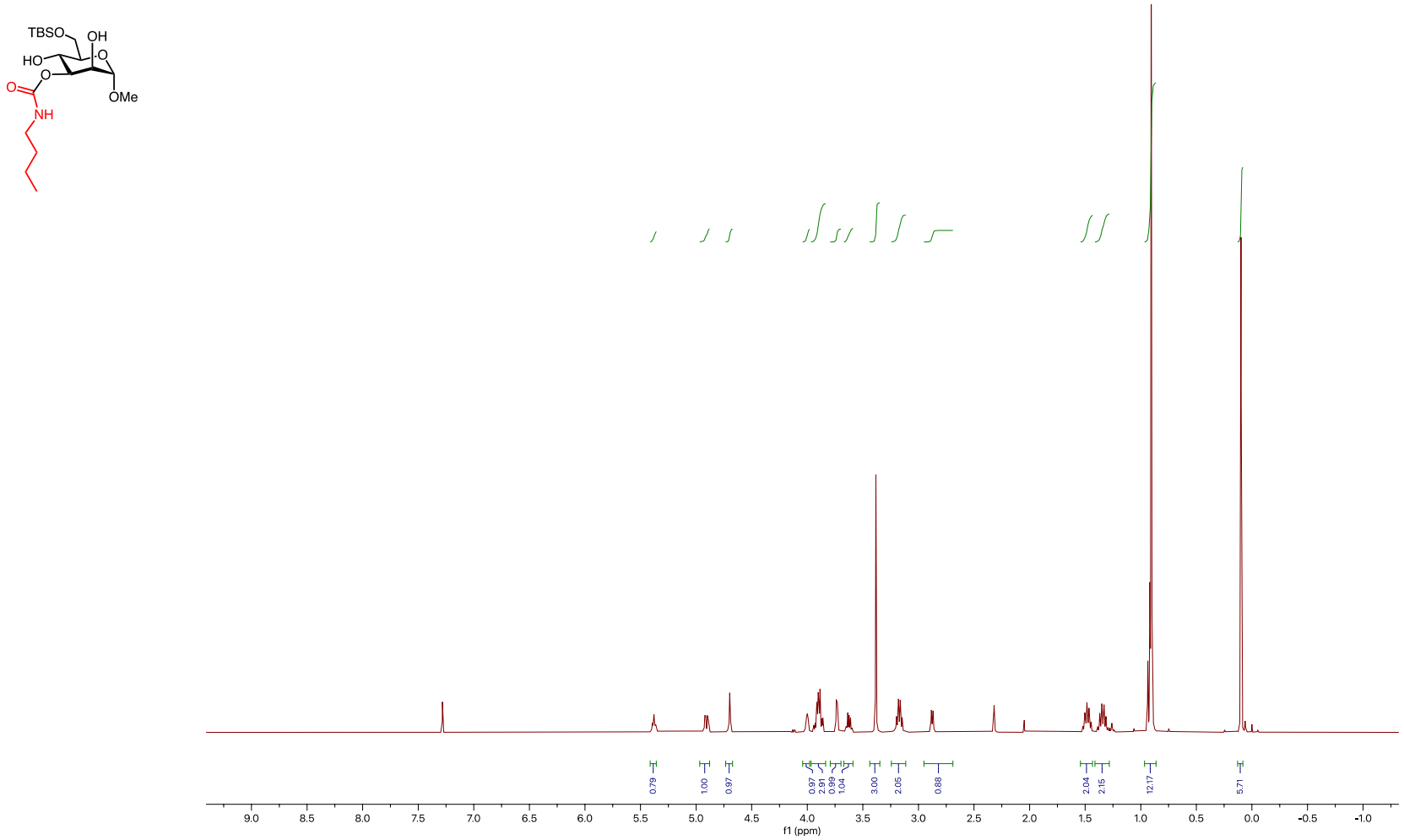


Figure S34. ^{1}H NMR spectrum (400 MHz) of **1bd** in $CDCl_3$

Methyl 2-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ae**

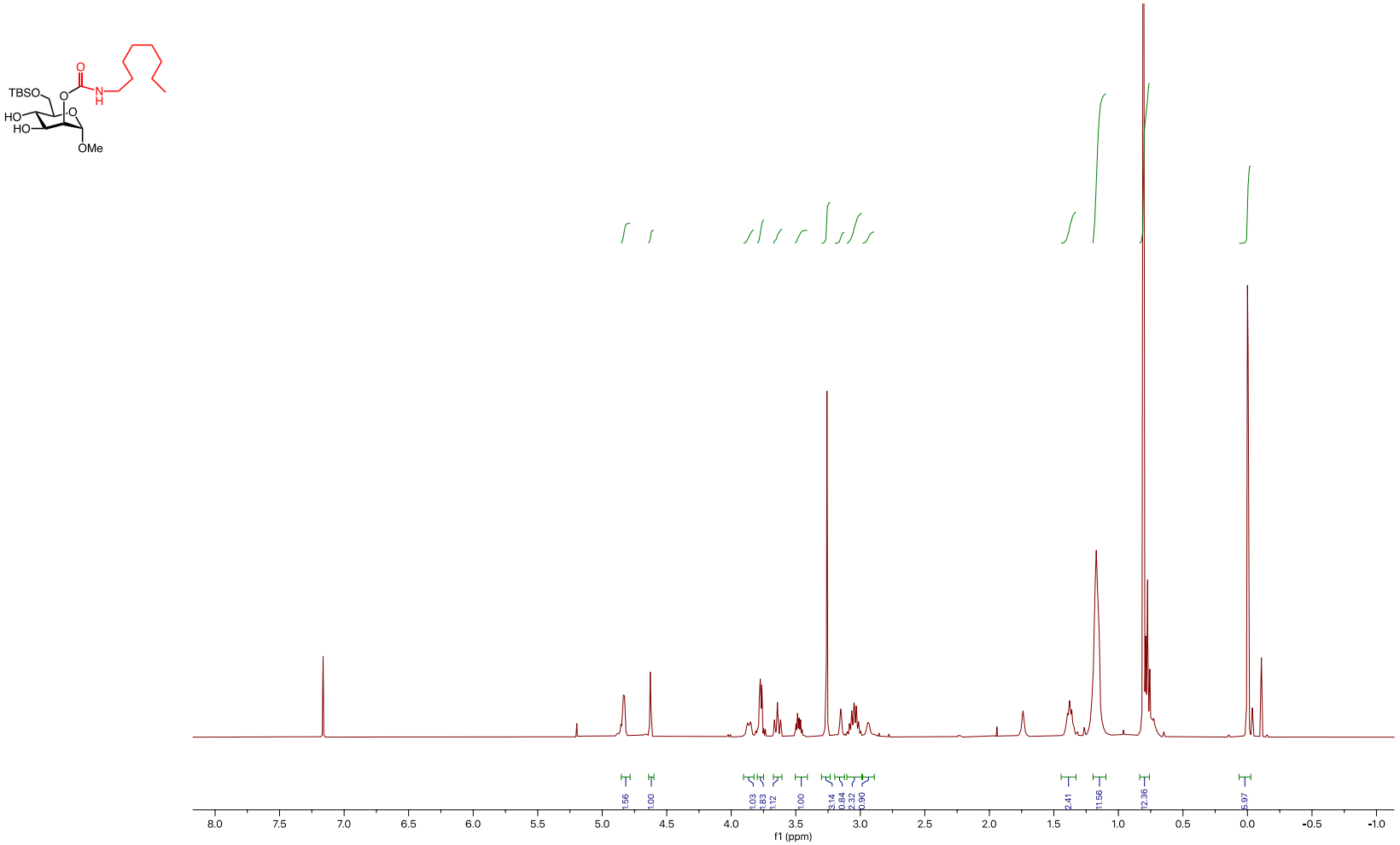


Figure S35. ^{1}H NMR spectrum (400 MHz) of **1ae** in $CDCl_3$

Methyl 2-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ae**

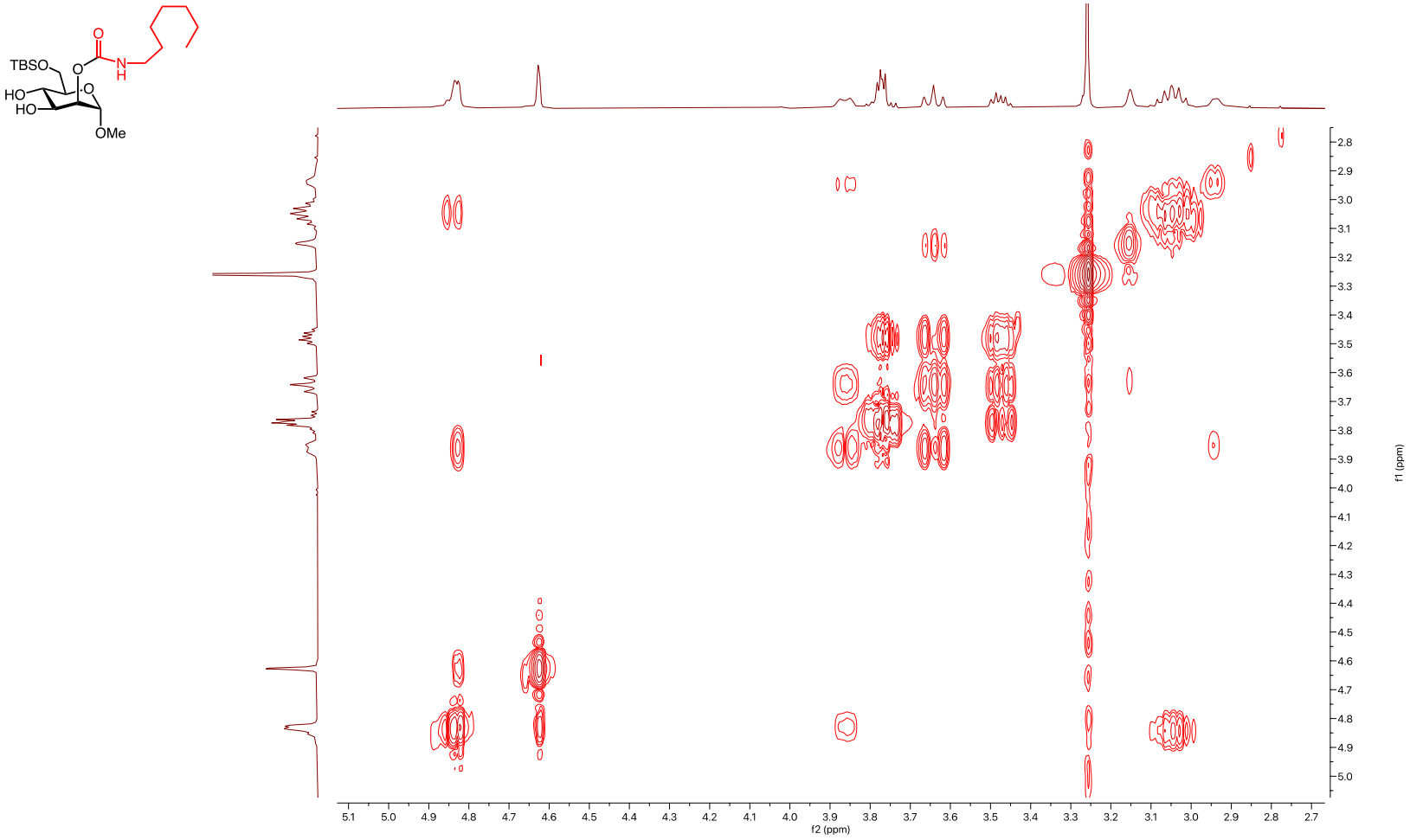


Figure S36. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ae** in $CDCl_3$

Methyl 2-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ae**

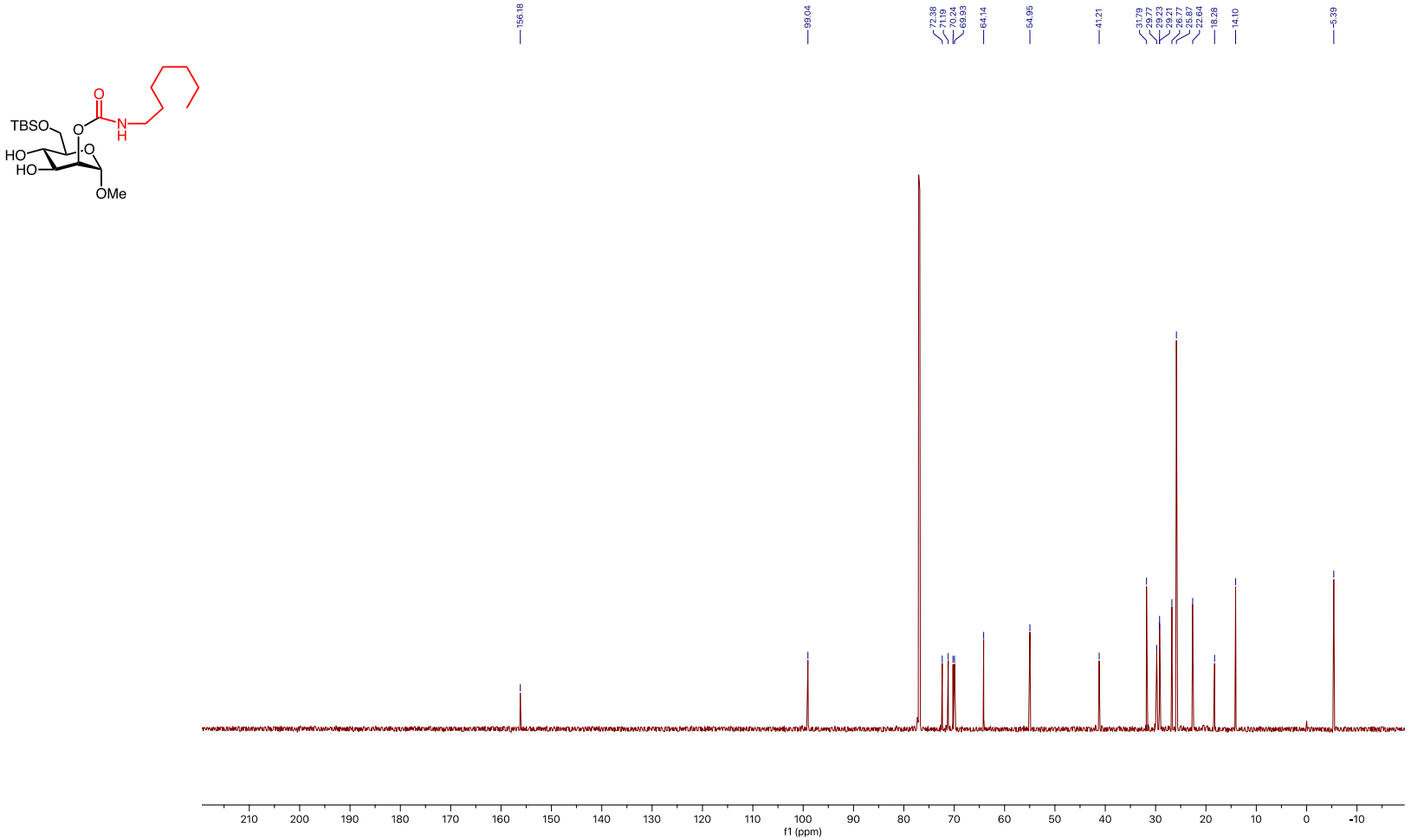


Figure S37. ^{13}C NMR spectrum (100 MHz) of **1ae** in $CDCl_3$

Methyl 3-*O*-octylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1be**

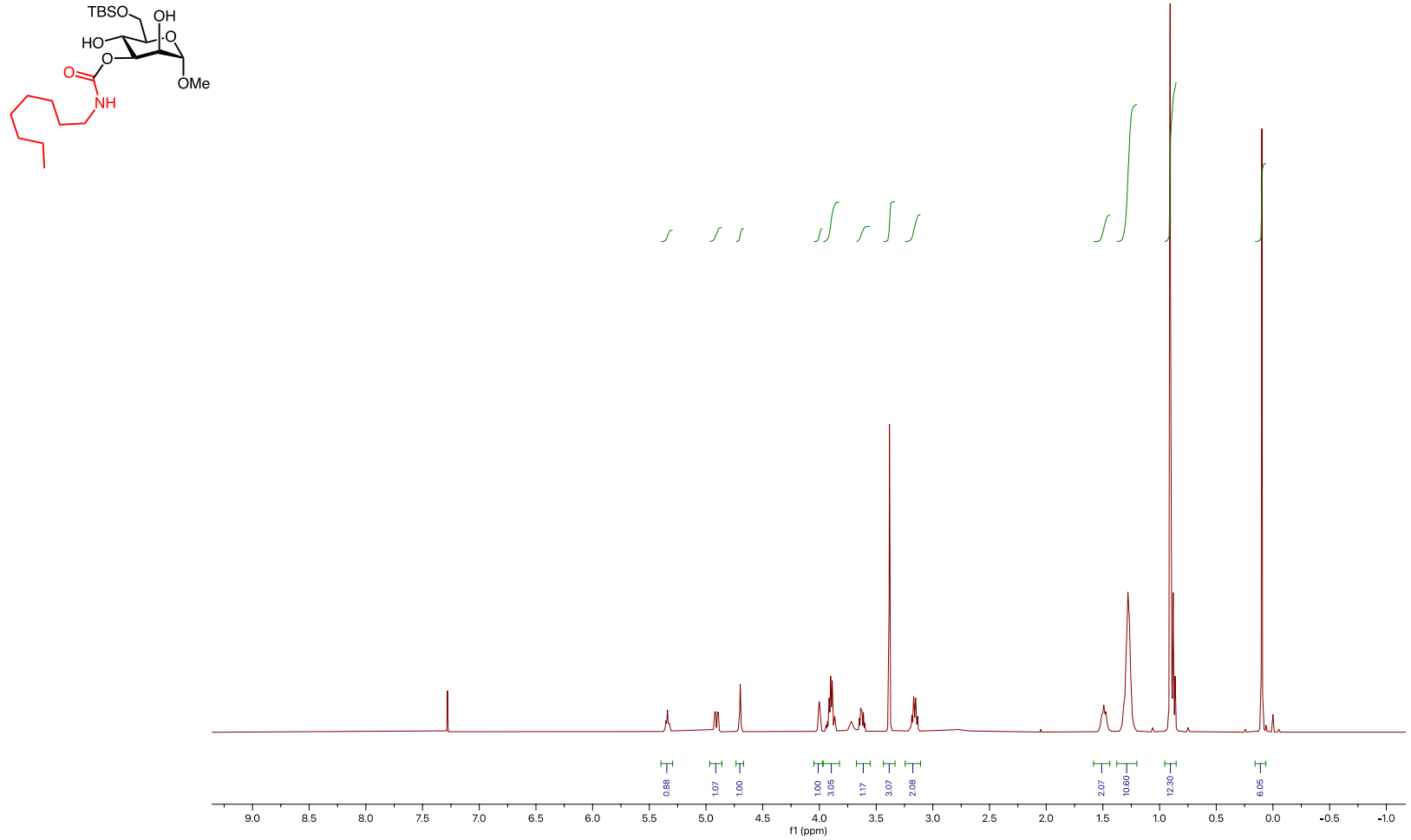
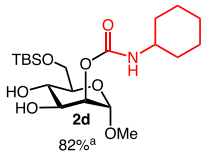


Figure S38. ^{1}H NMR spectrum (400 MHz) of **1be** in $CDCl_3$

Methyl 2-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1af**



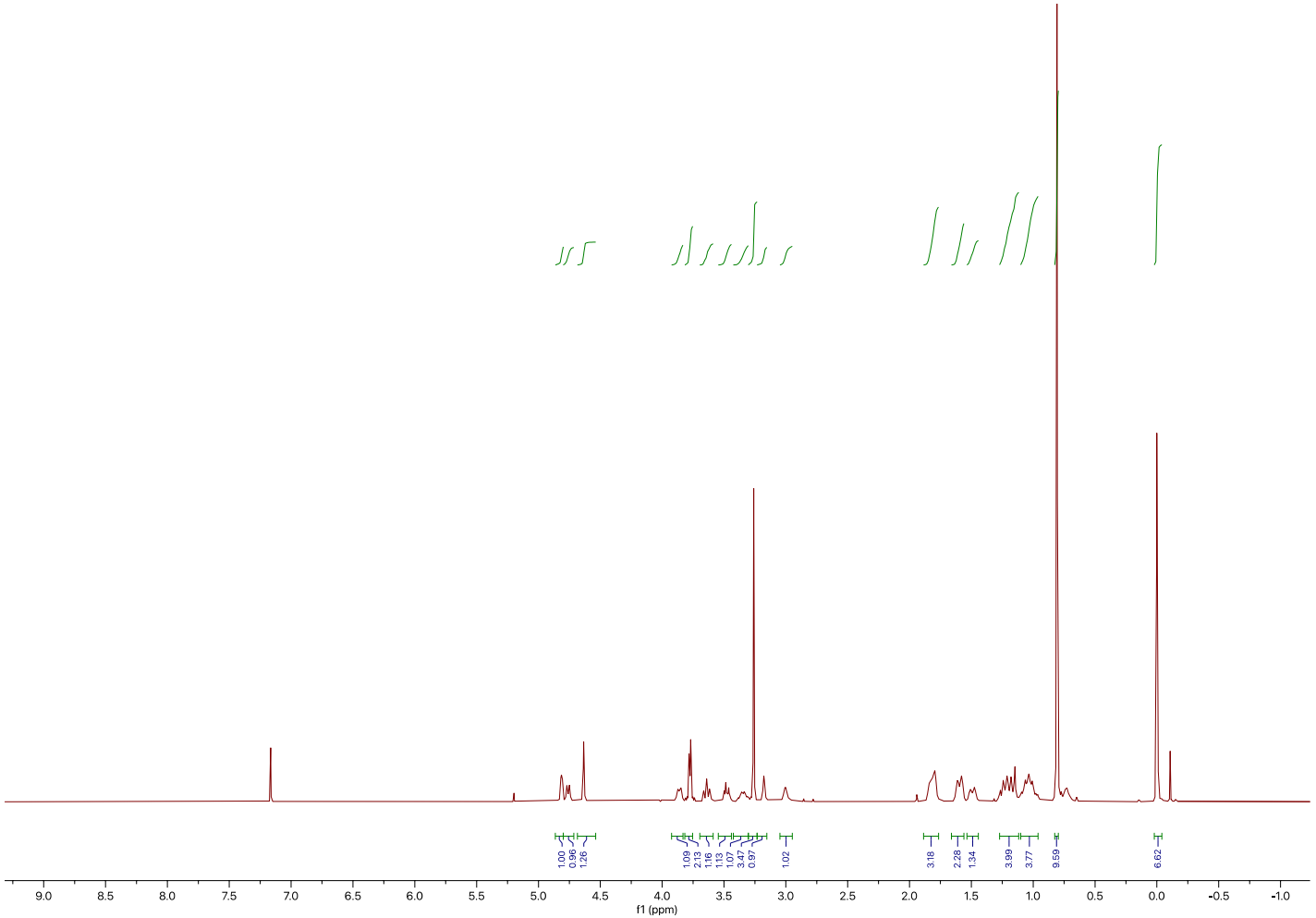


Figure S39. ^{1}H NMR spectrum (400 MHz) of **1af** in $CDCl_3$

Methyl 2-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1af**

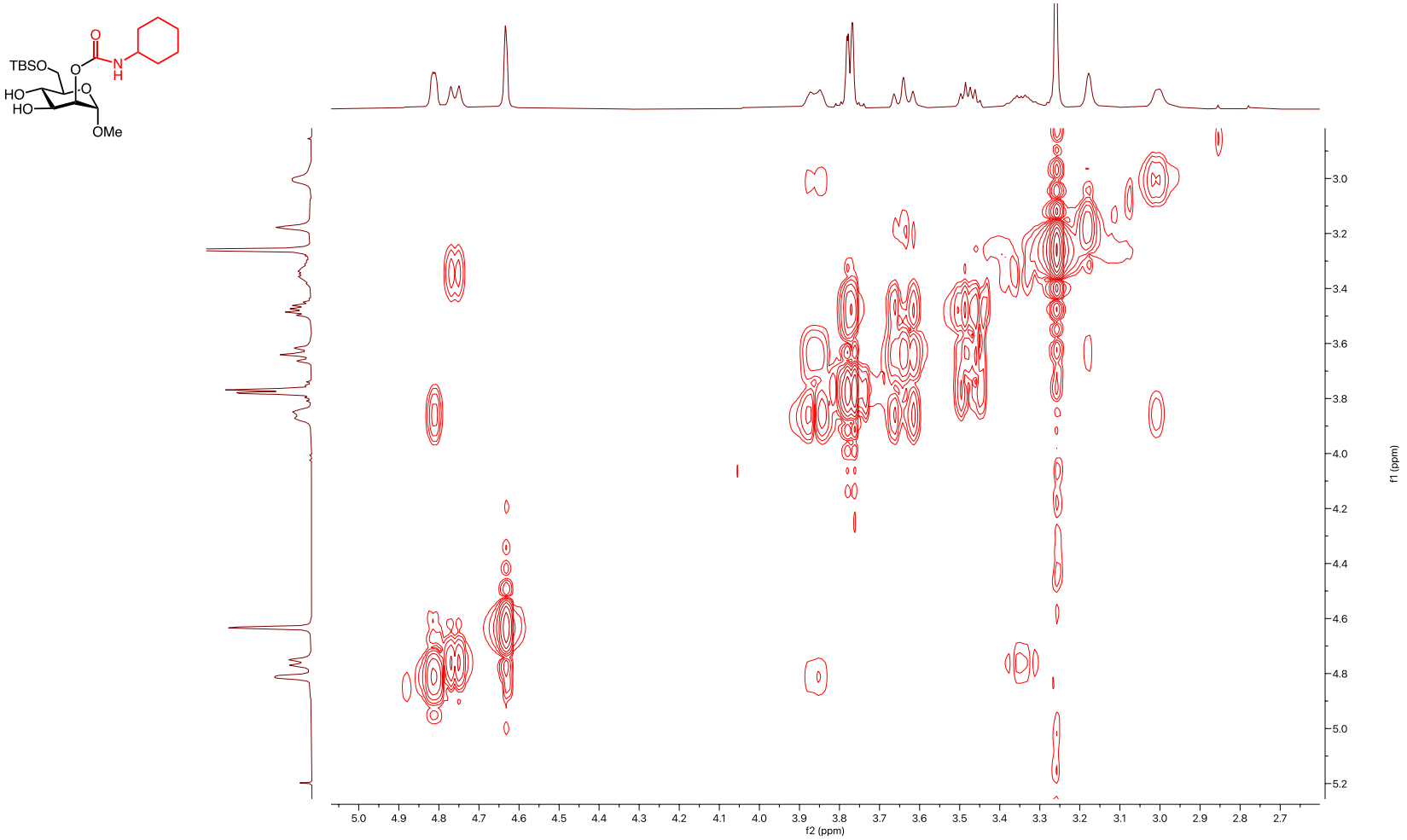


Figure S40. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1af** in $CDCl_3$

Methyl 2-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1af**

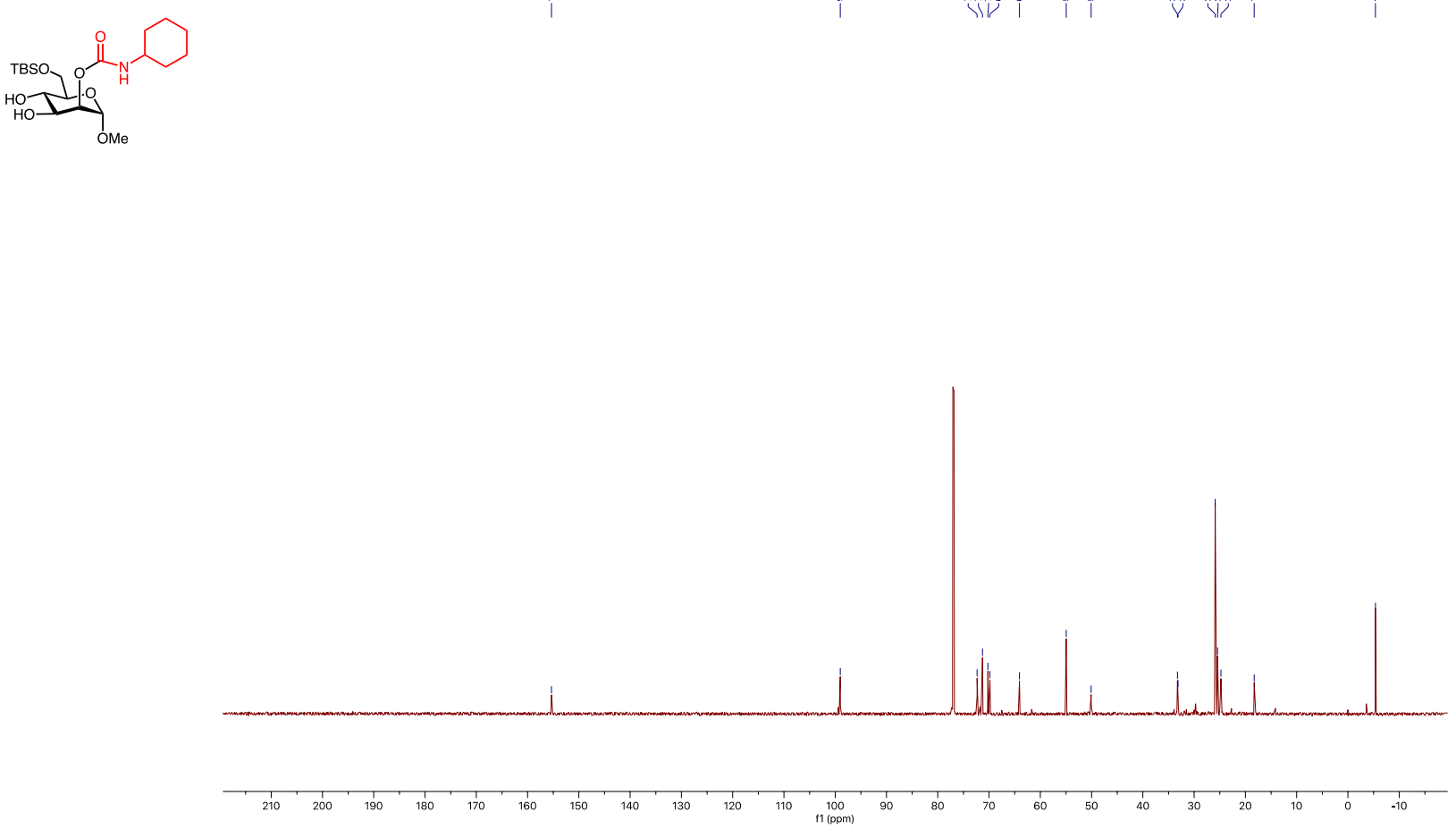


Figure S41. ^{13}C NMR spectrum (100 MHz) of **1af** in $CDCl_3$

Methyl 3-*O*-cyclohexylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bf**

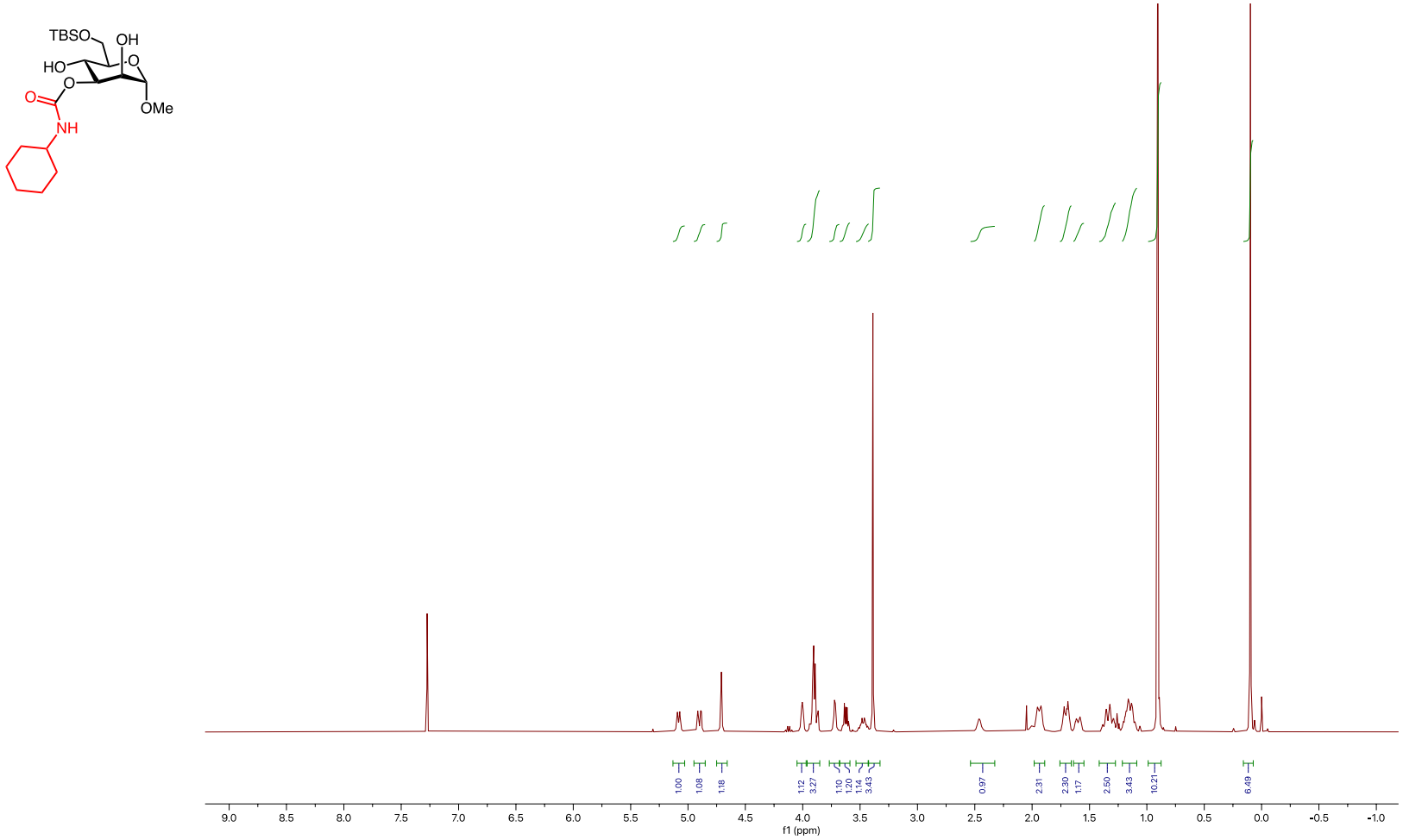
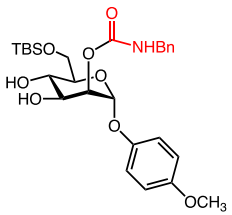


Figure S42. ^{1}H NMR spectrum (400 MHz) of **1bf** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2a**



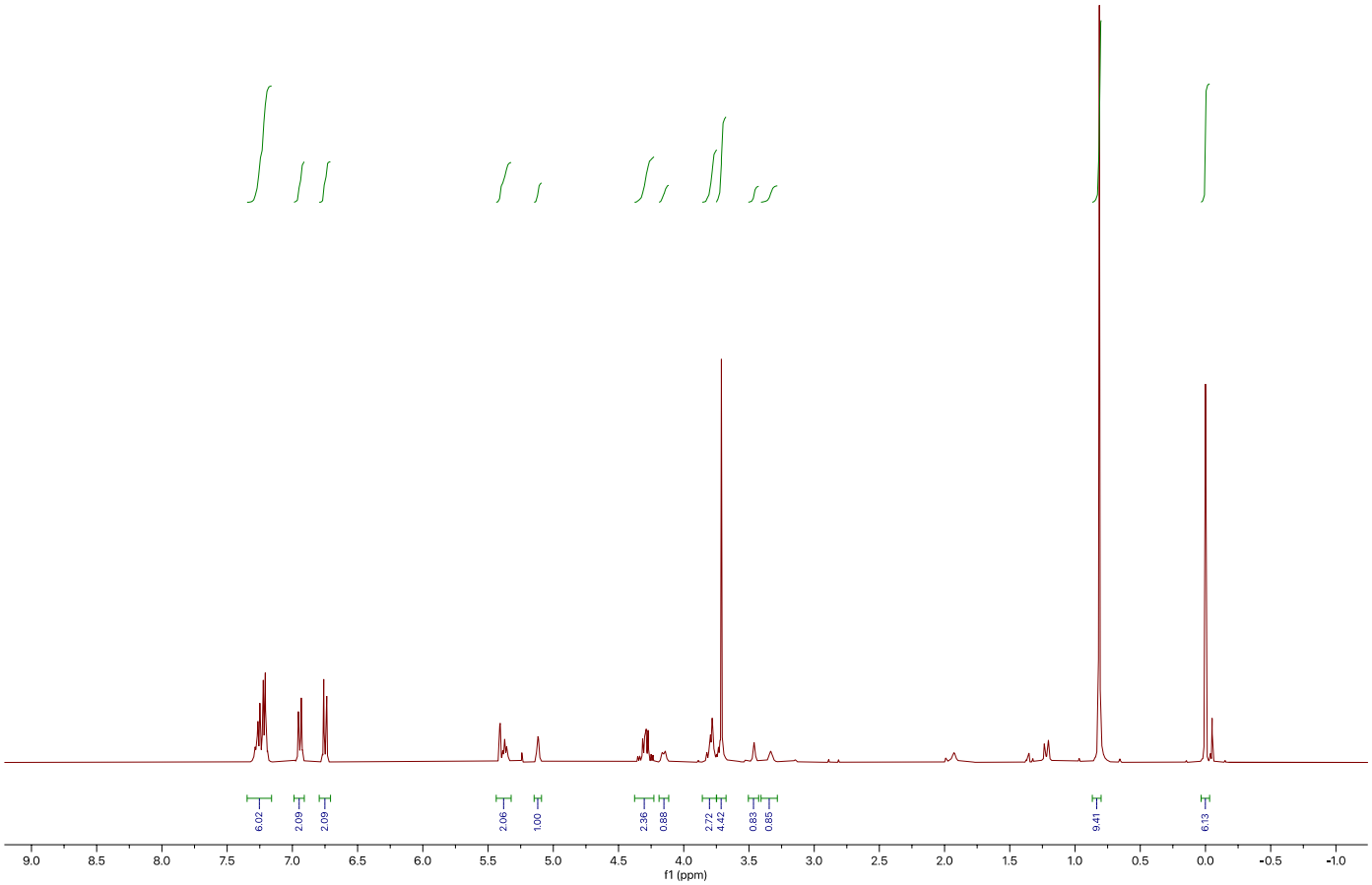


Figure S43. ^{1}H NMR spectrum (400 MHz) of **2a** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2a**

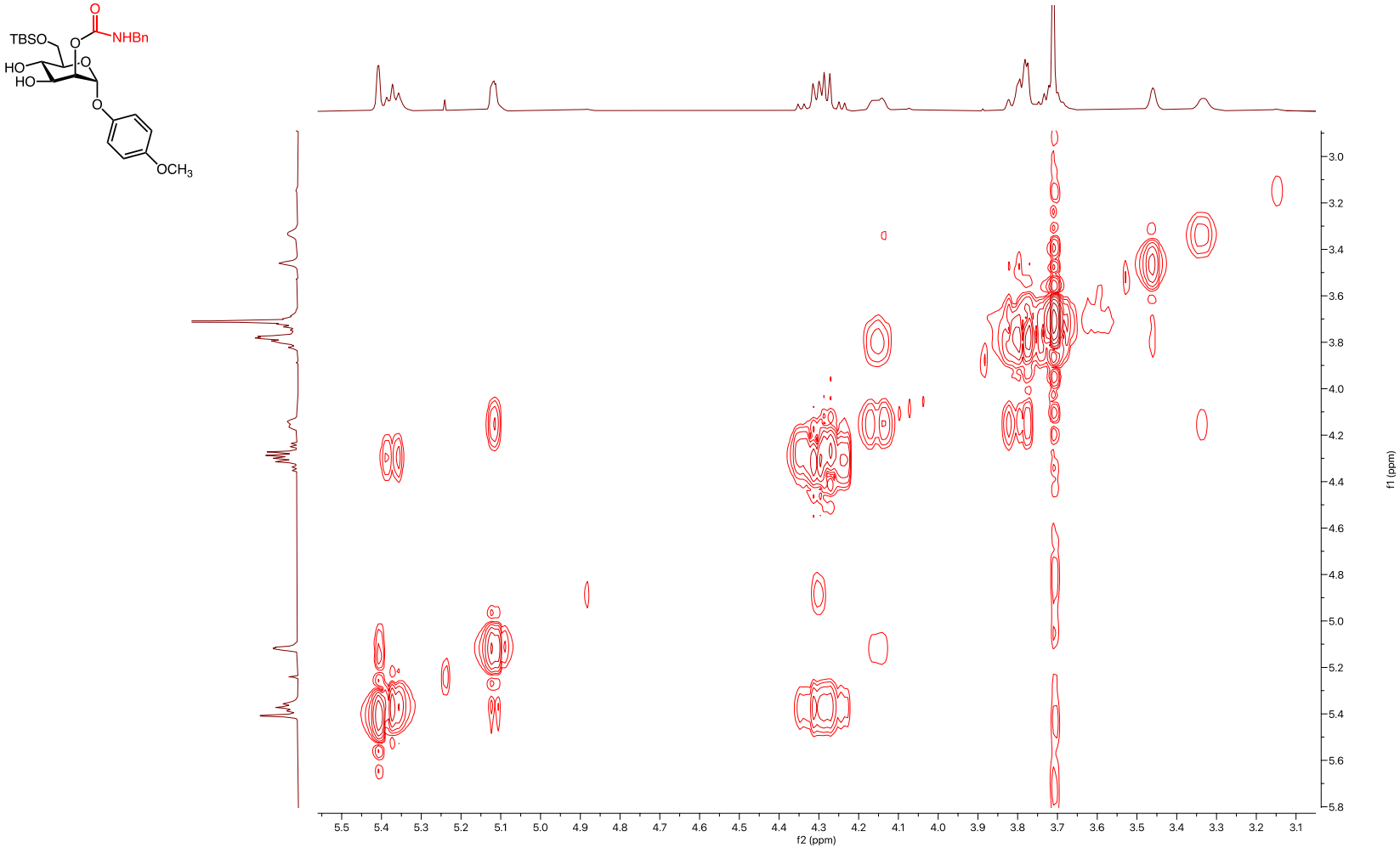


Figure S44. ^{1}H-^{1}H COSY spectrum (400 MHz) of **2a** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2a**

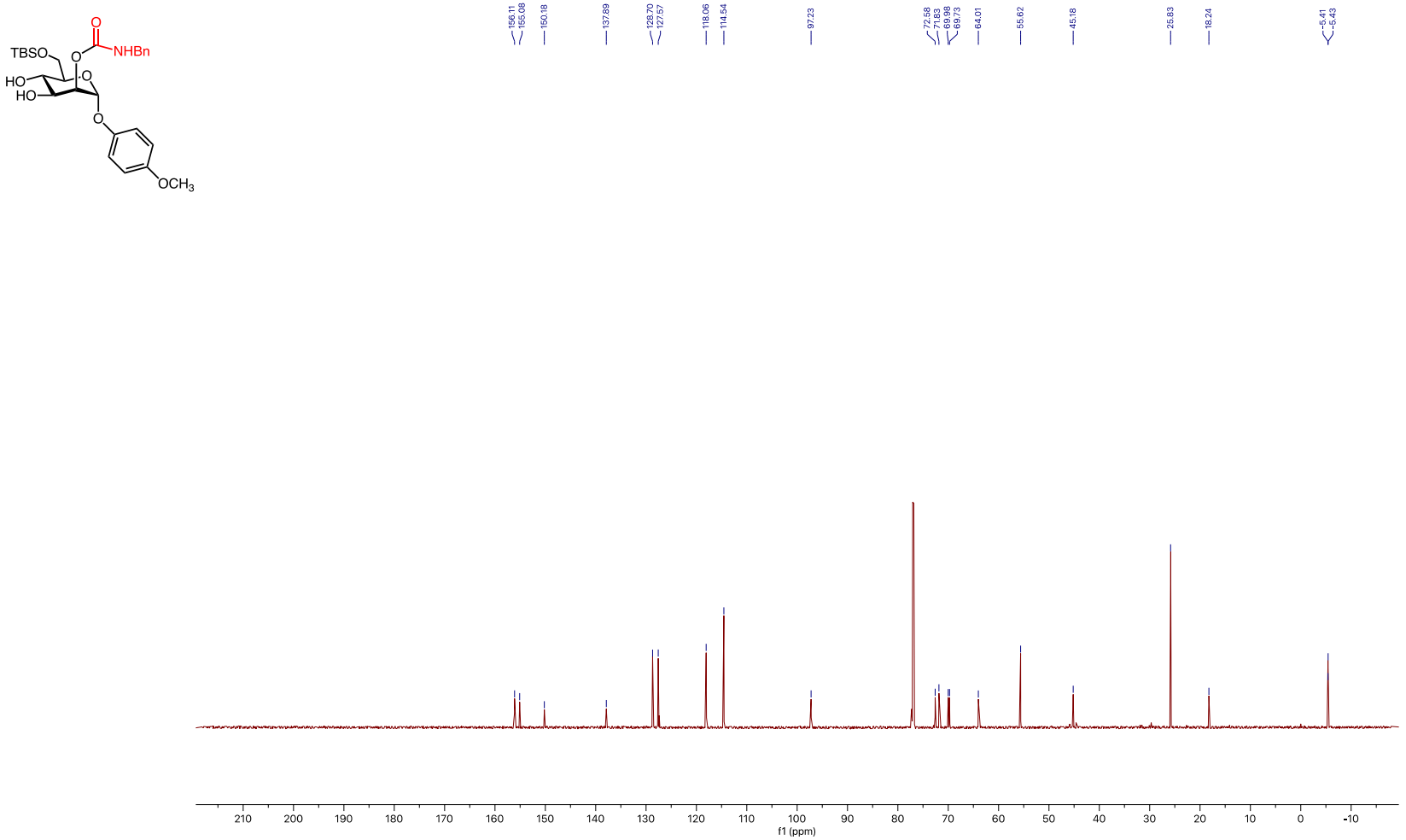


Figure S45. ^{13}C NMR spectrum (100 MHz) of **2a** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **2b**

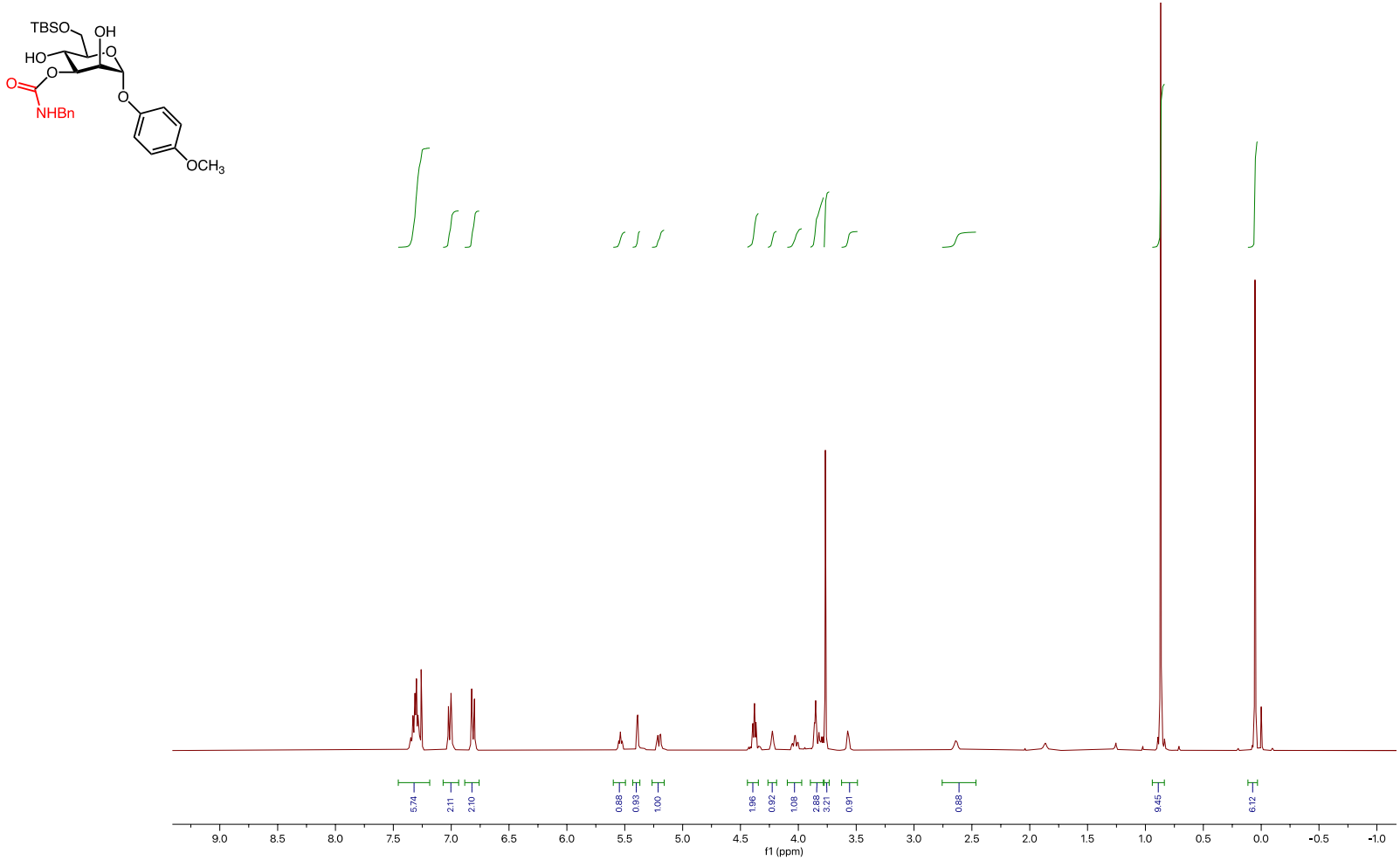
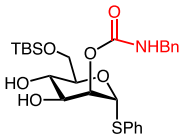


Figure S46. ^{1}H NMR spectrum (400 MHz) of **1bf** in $CDCl_3$

Phenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3a**



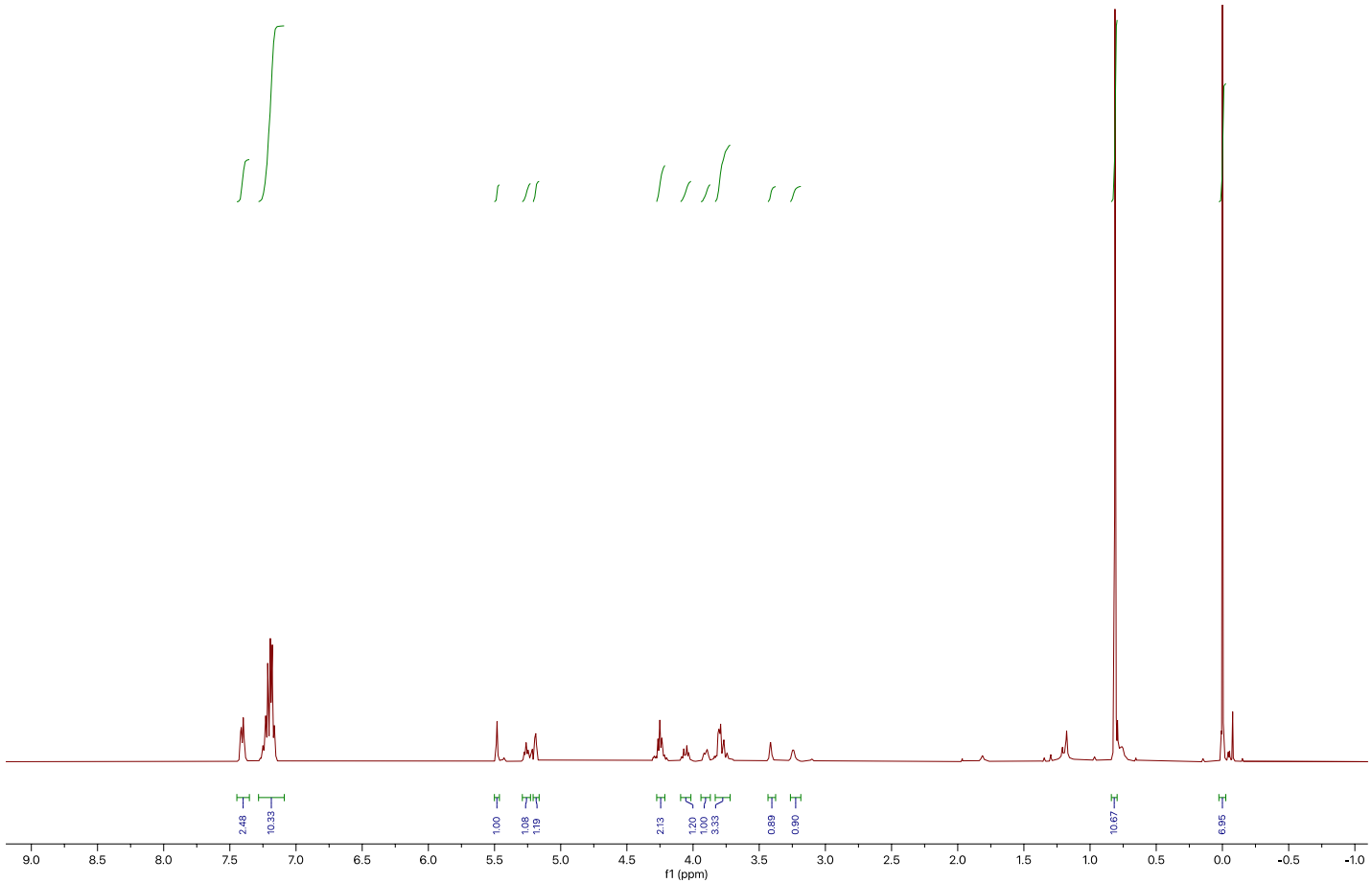


Figure S47. ^{1}H NMR spectrum (400 MHz) of **3a** in $CDCl_3$

Phenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3a**

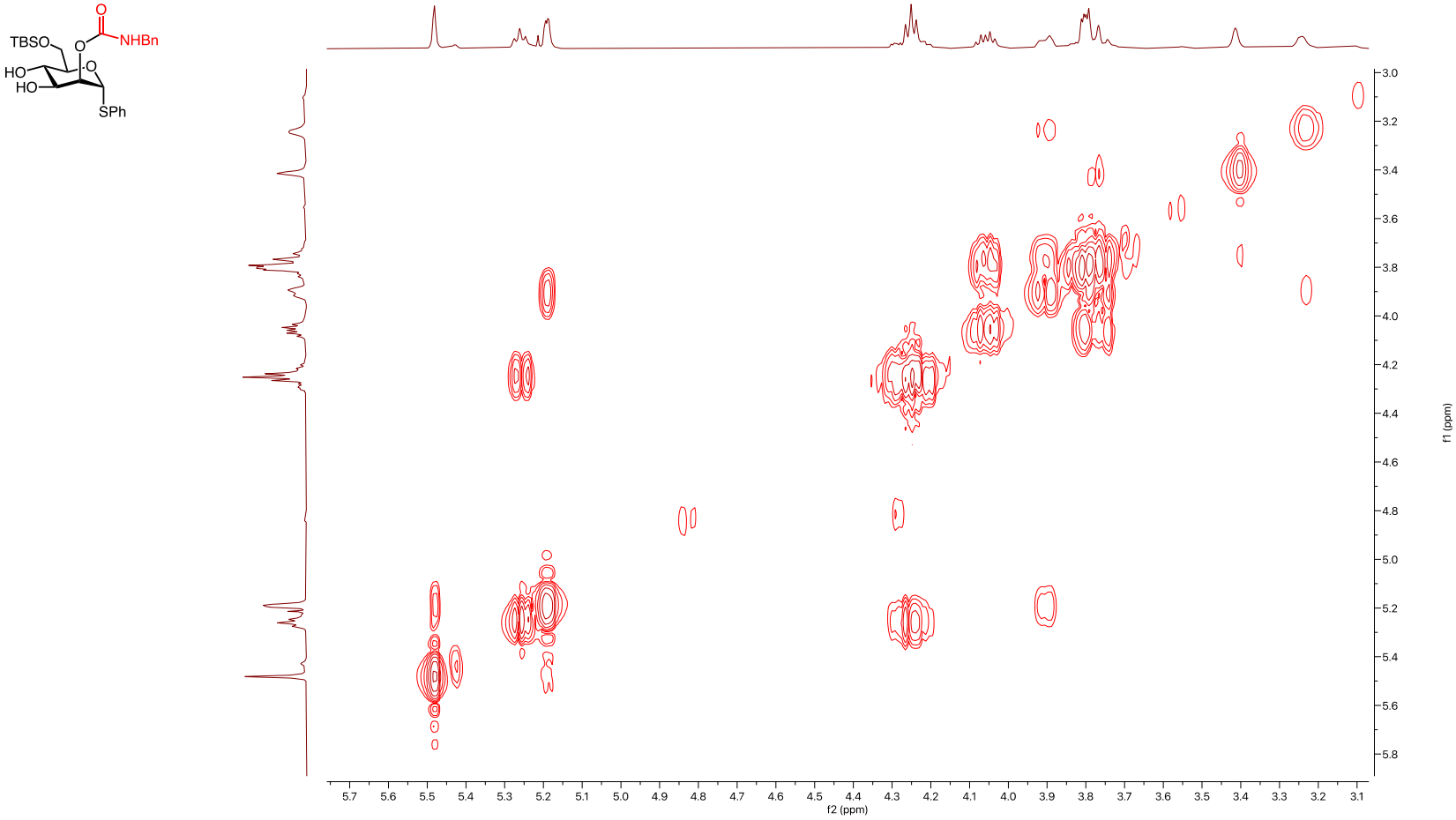
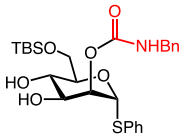


Figure S48. ^{1}H-^{1}H COSY spectrum (400 MHz) of **3a** in $CDCl_3$

Phenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3a**



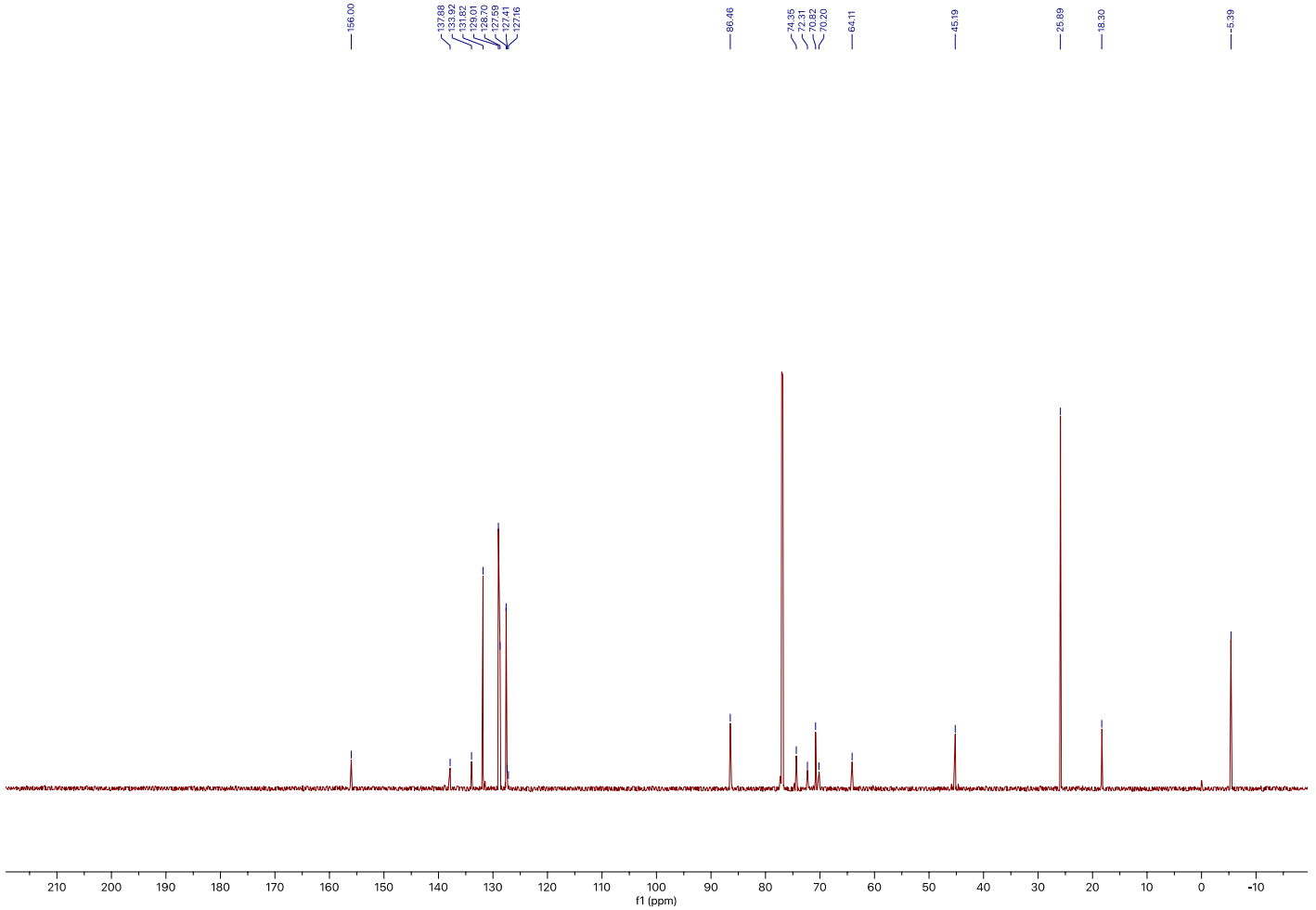


Figure S49. ^{13}C NMR spectrum (100 MHz) of **3a** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3b**

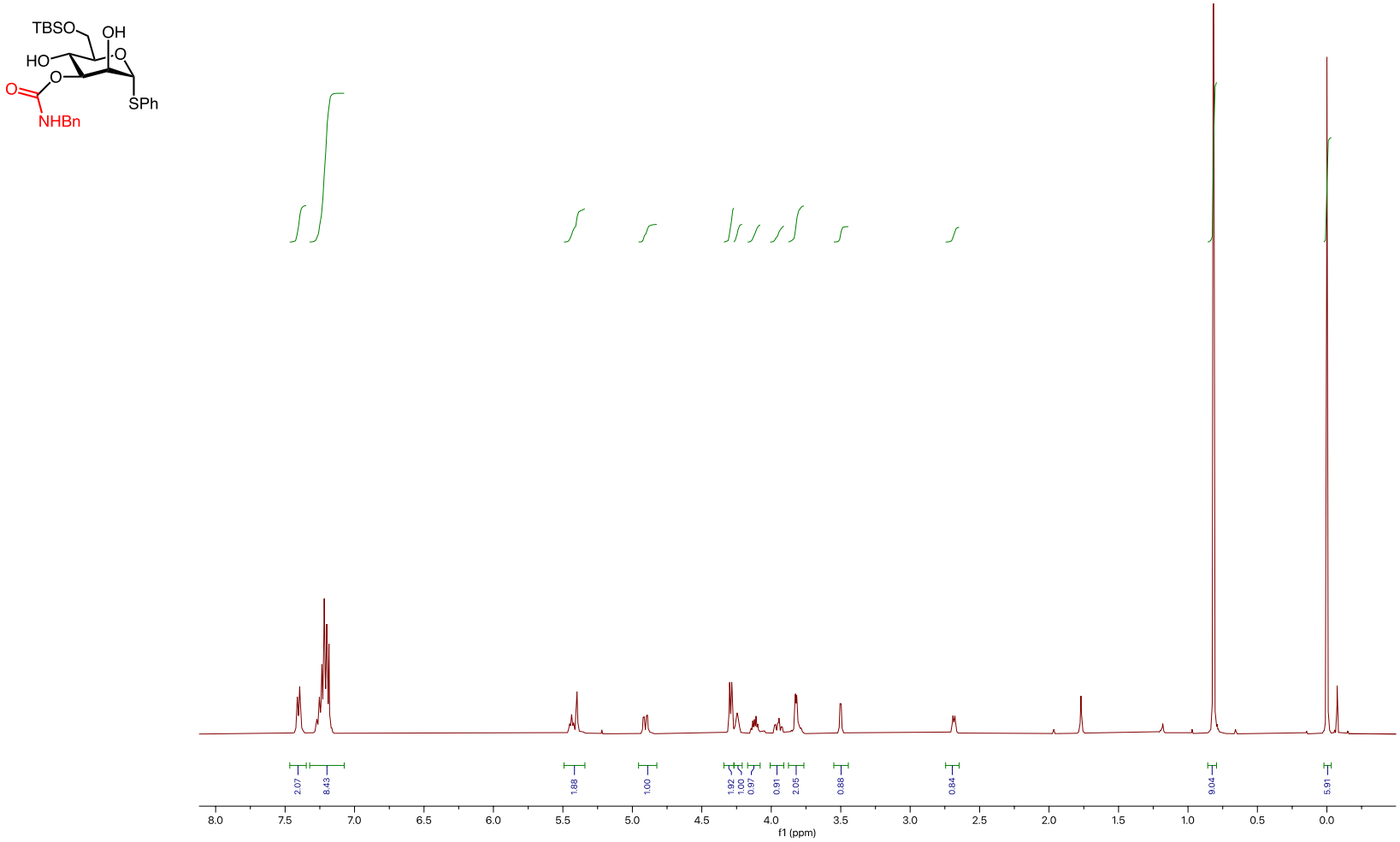
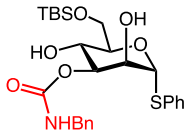


Figure S50. ^{1}H NMR spectrum (400 MHz) of **3b** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3b**



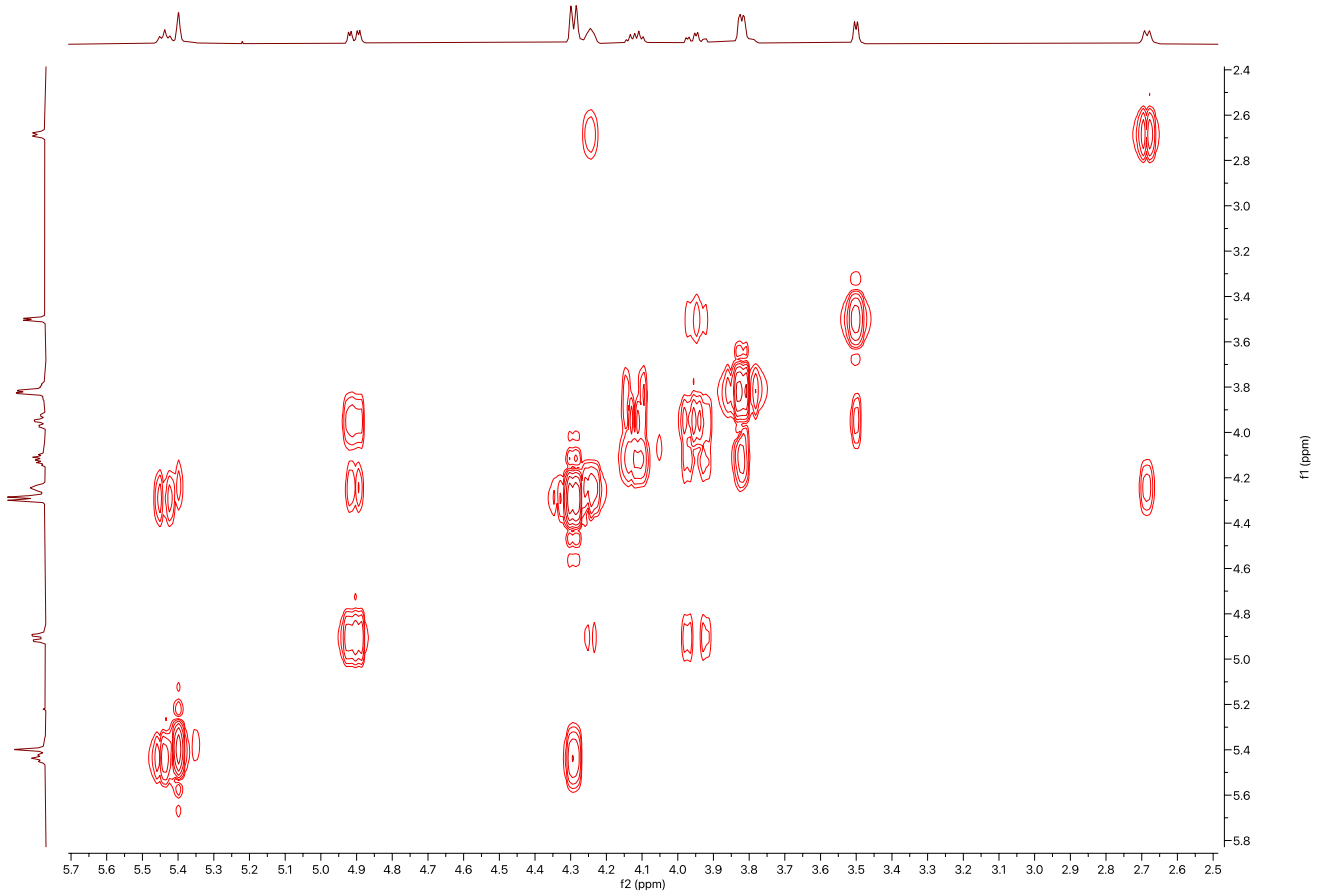


Figure S51. ^{1}H-^{1}H COSY spectrum (400 MHz) of **3b** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-1-thio-α-D-mannopyranoside **3b**

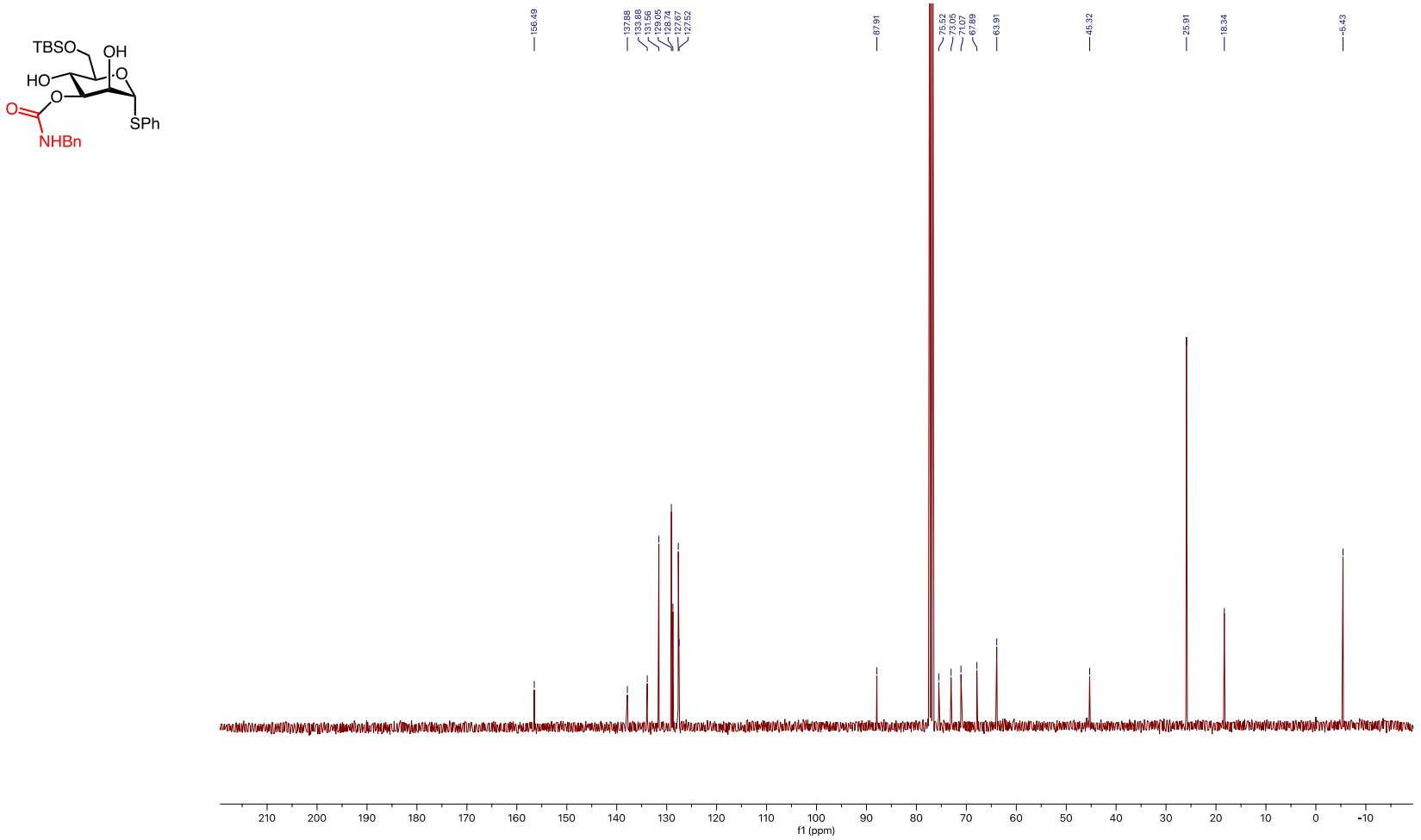


Figure S52. ^{13}C NMR spectrum (100 MHz) of **3b** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4a**

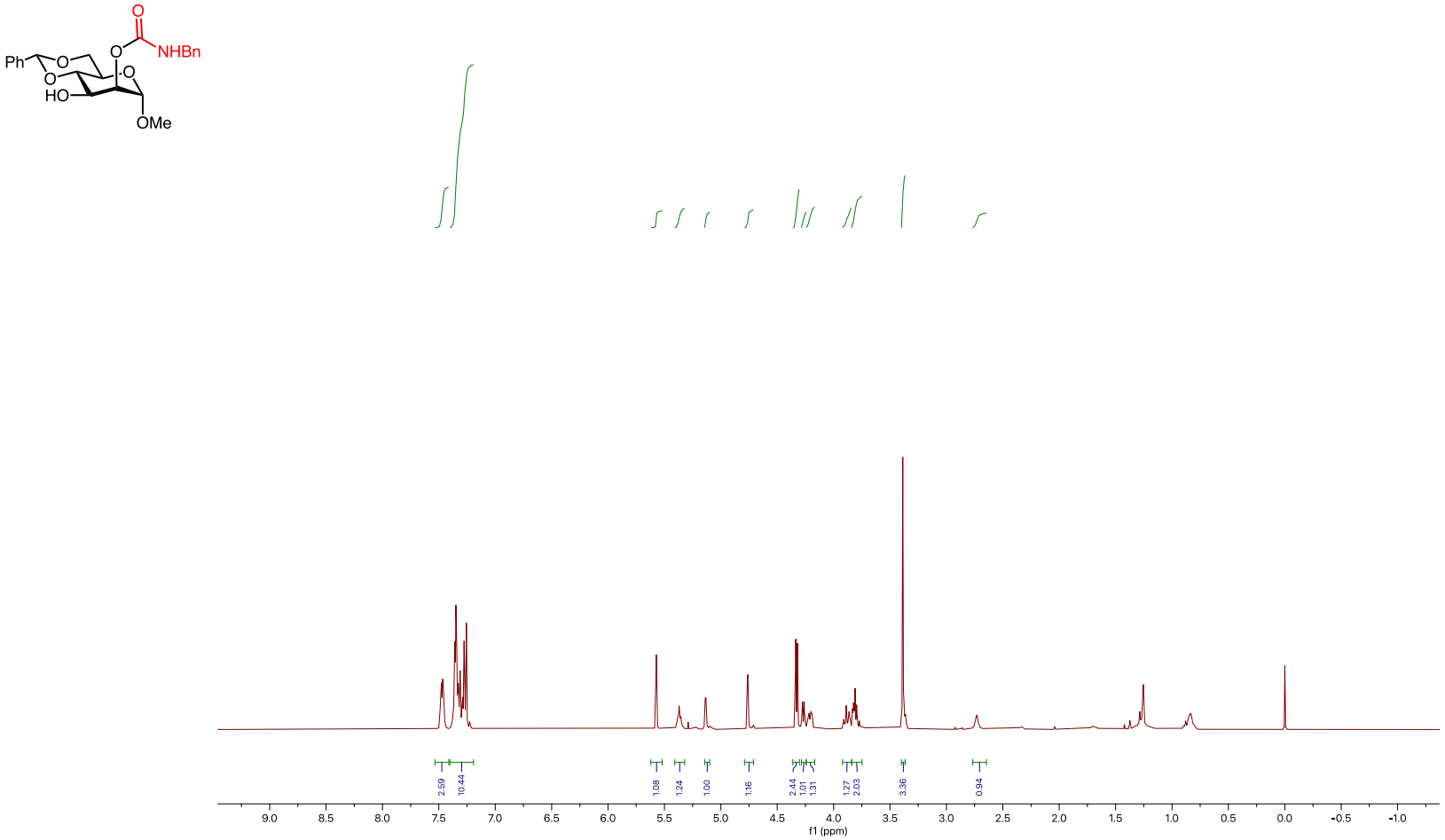


Figure S53. ^{1}H NMR spectrum (400 MHz) of **4a** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4a**

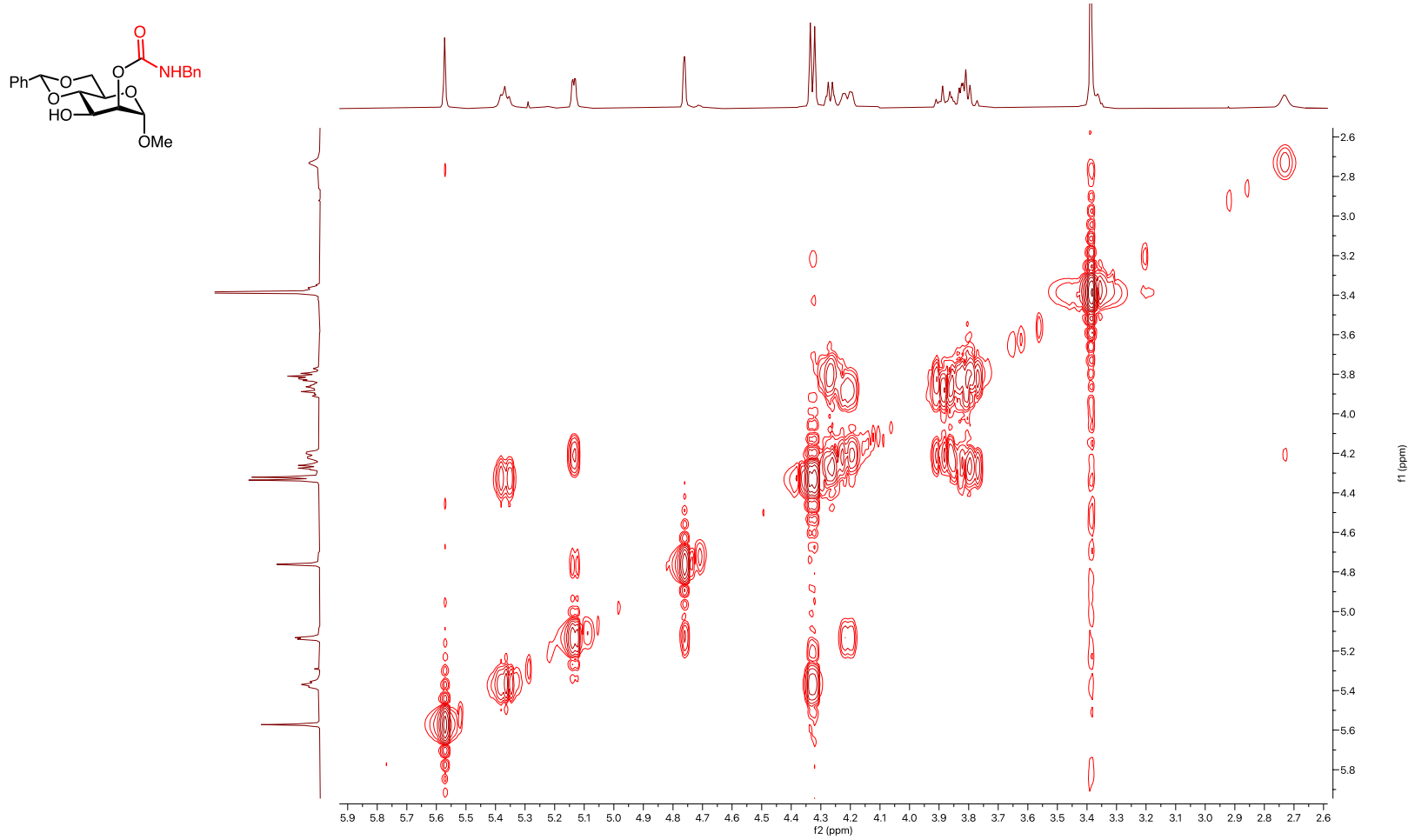


Figure S54. ^{1}H-^{1}H COSY spectrum (400 MHz) of **4a** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4a**

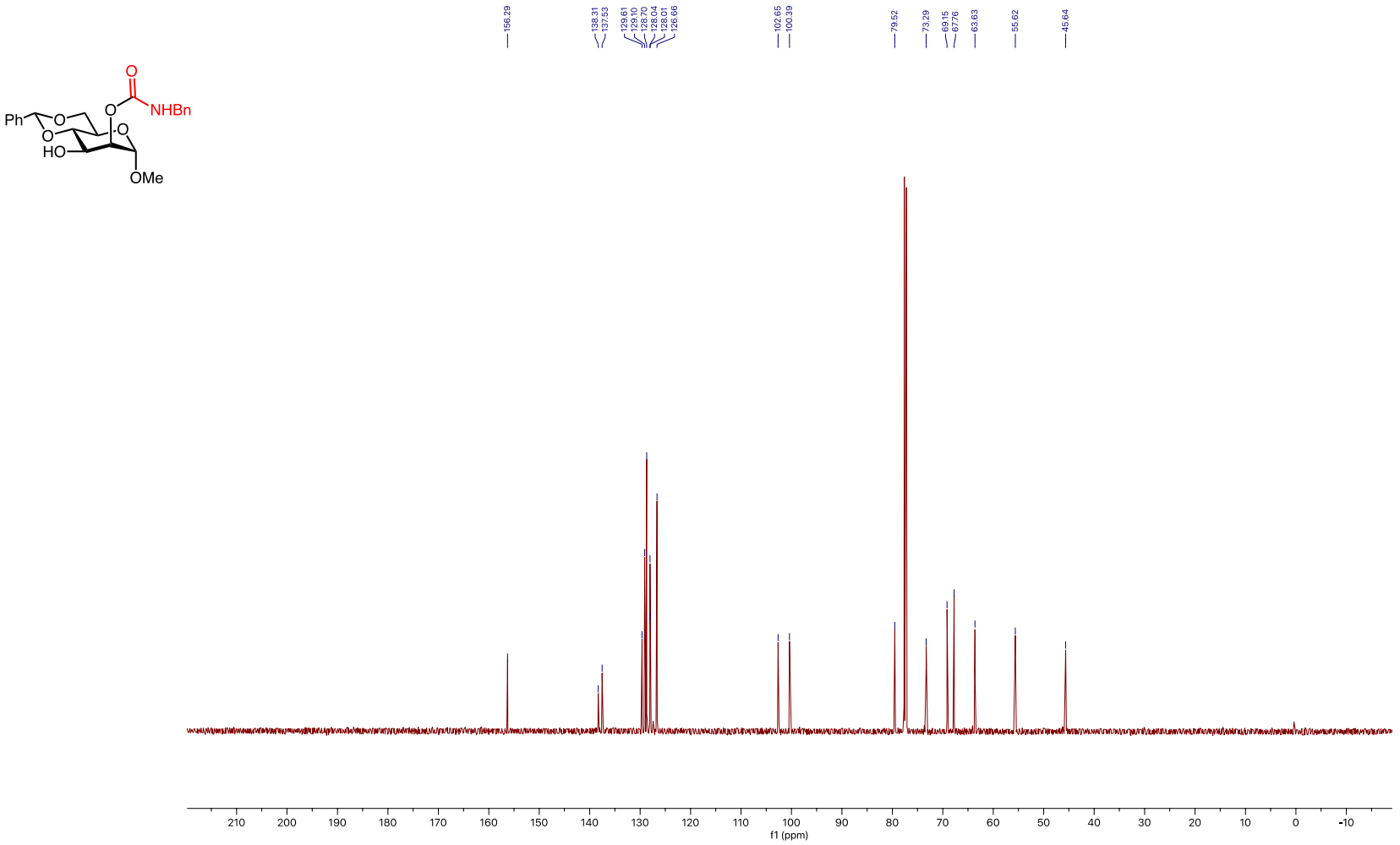
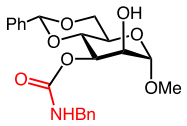


Figure S55. ^{13}C NMR spectrum (100 MHz) of **4a** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4b**



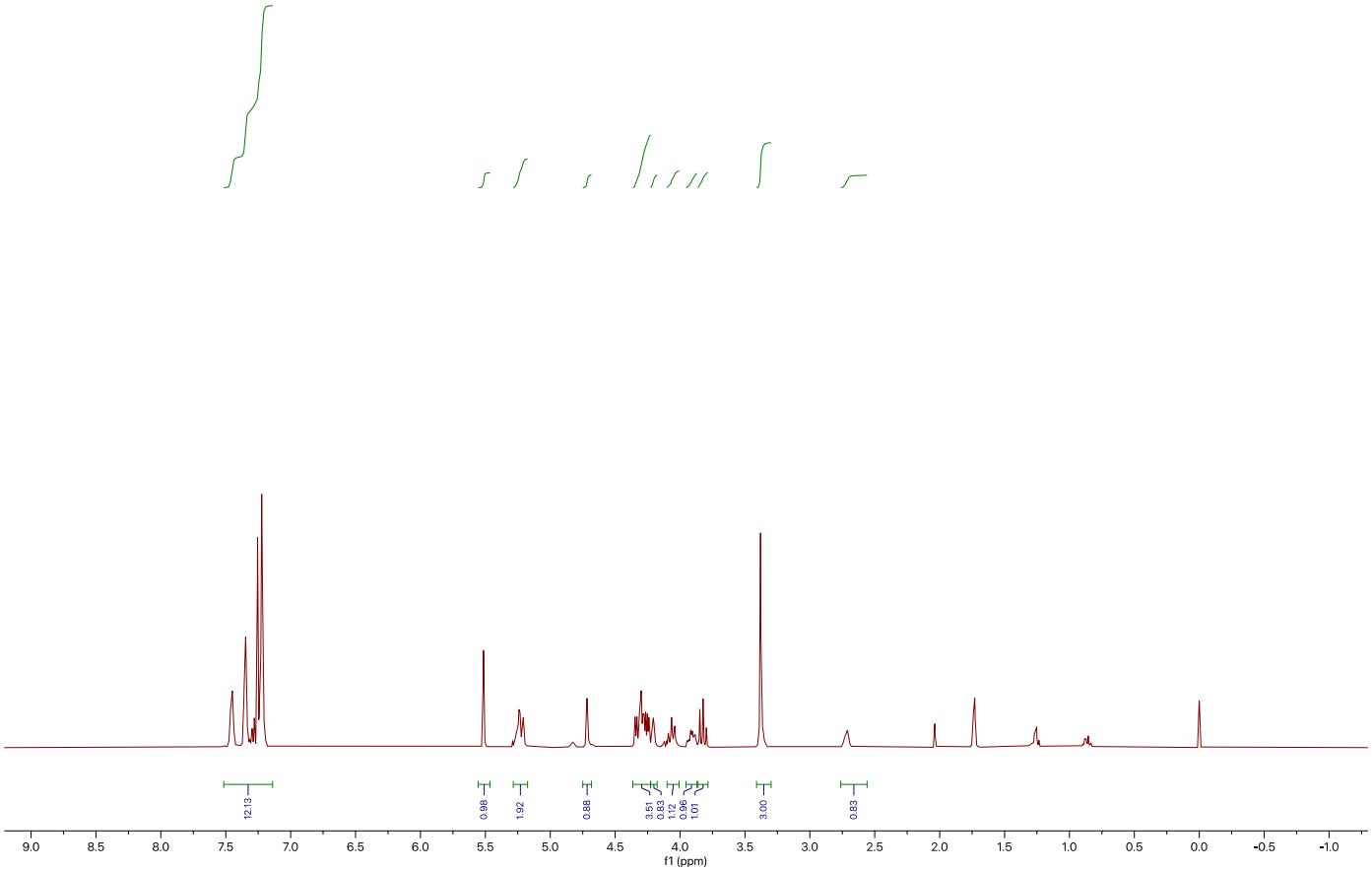


Figure S56. ^{1}H NMR spectrum (400 MHz) of **4b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4b**

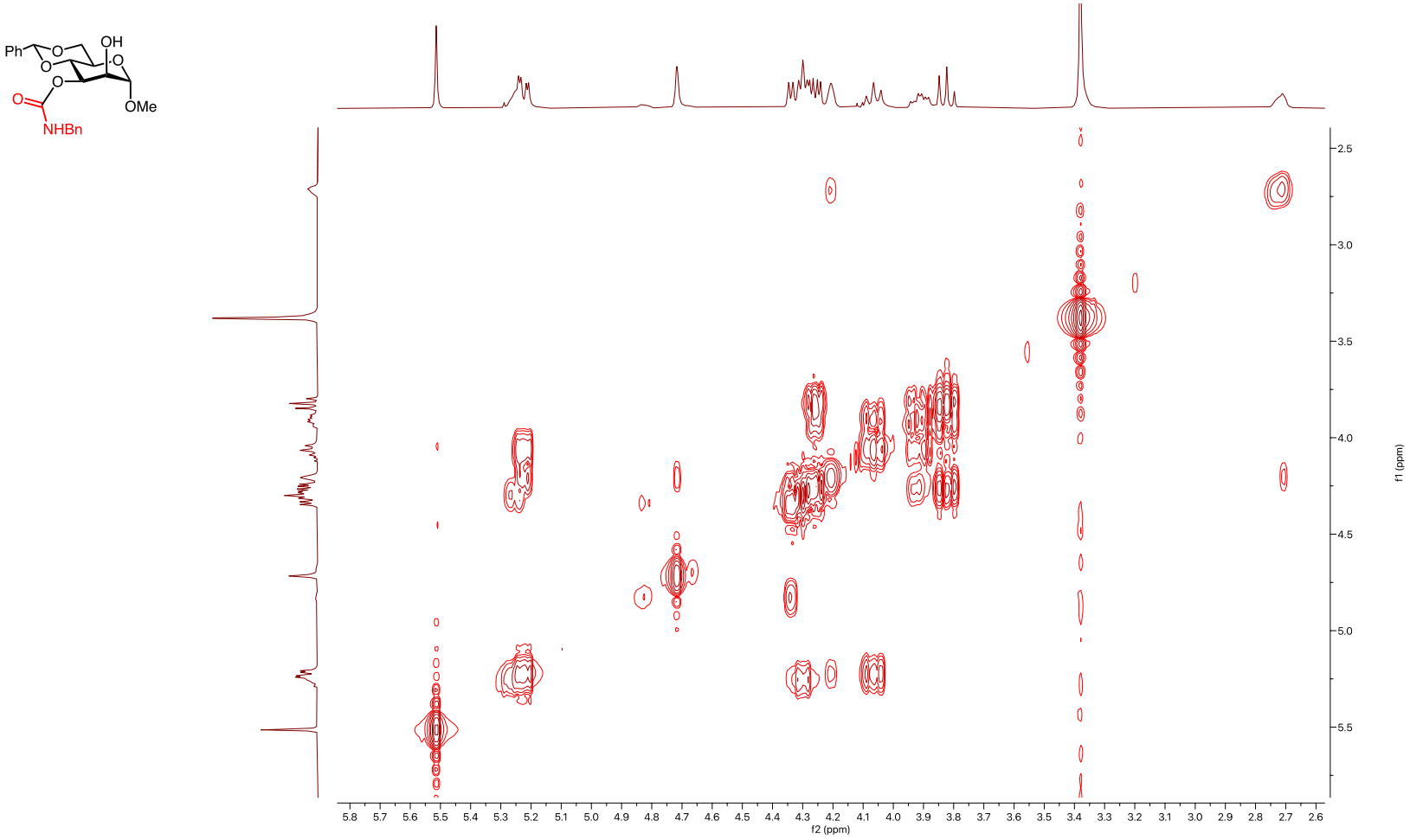


Figure S57. ^{1}H-^{1}H COSY spectrum (400 MHz) of **4b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-mannopyranoside **4b**

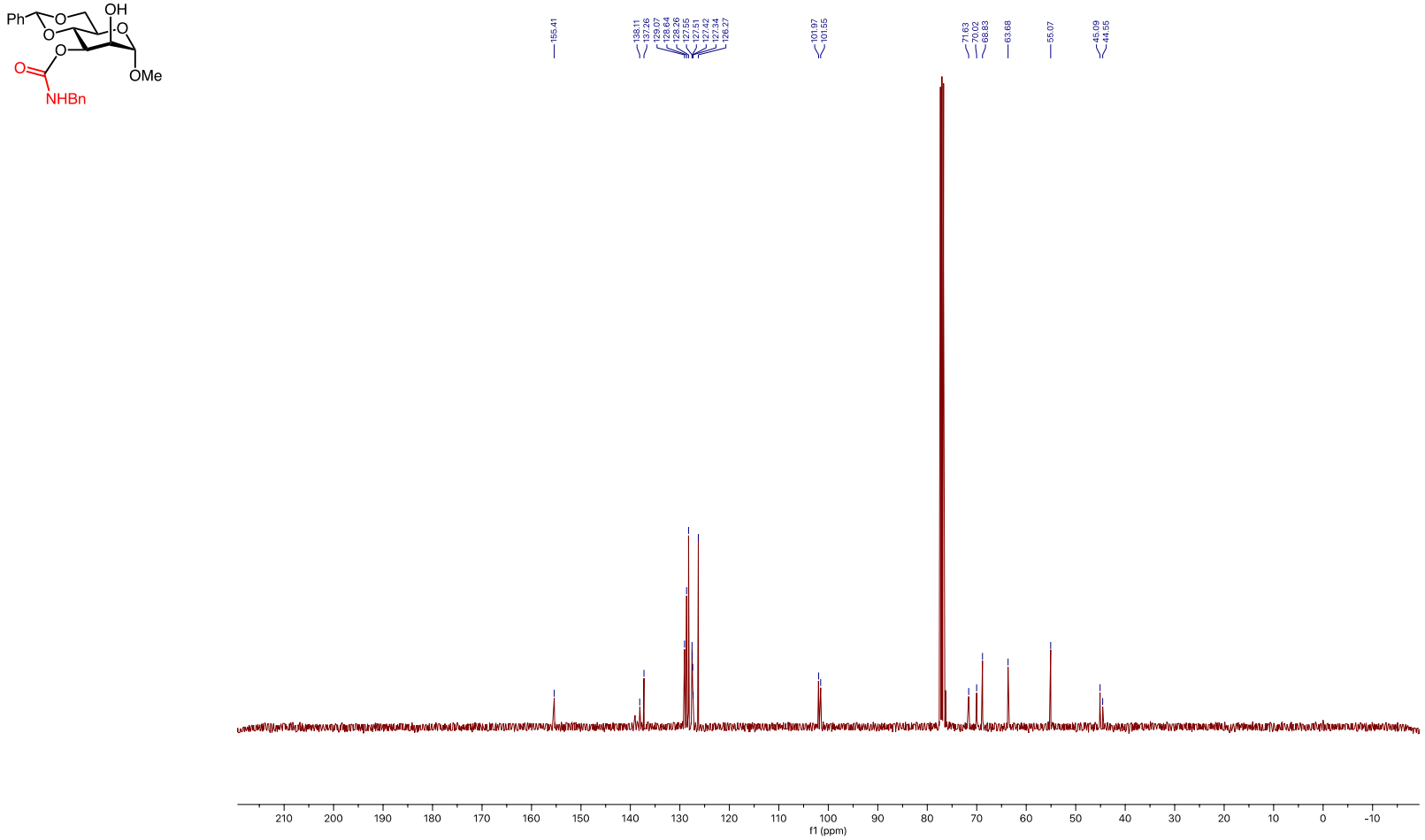


Figure S58. ^{13}C NMR spectrum (100 MHz) of **4b** in $CDCl_3$

Phenyl 4-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5a**

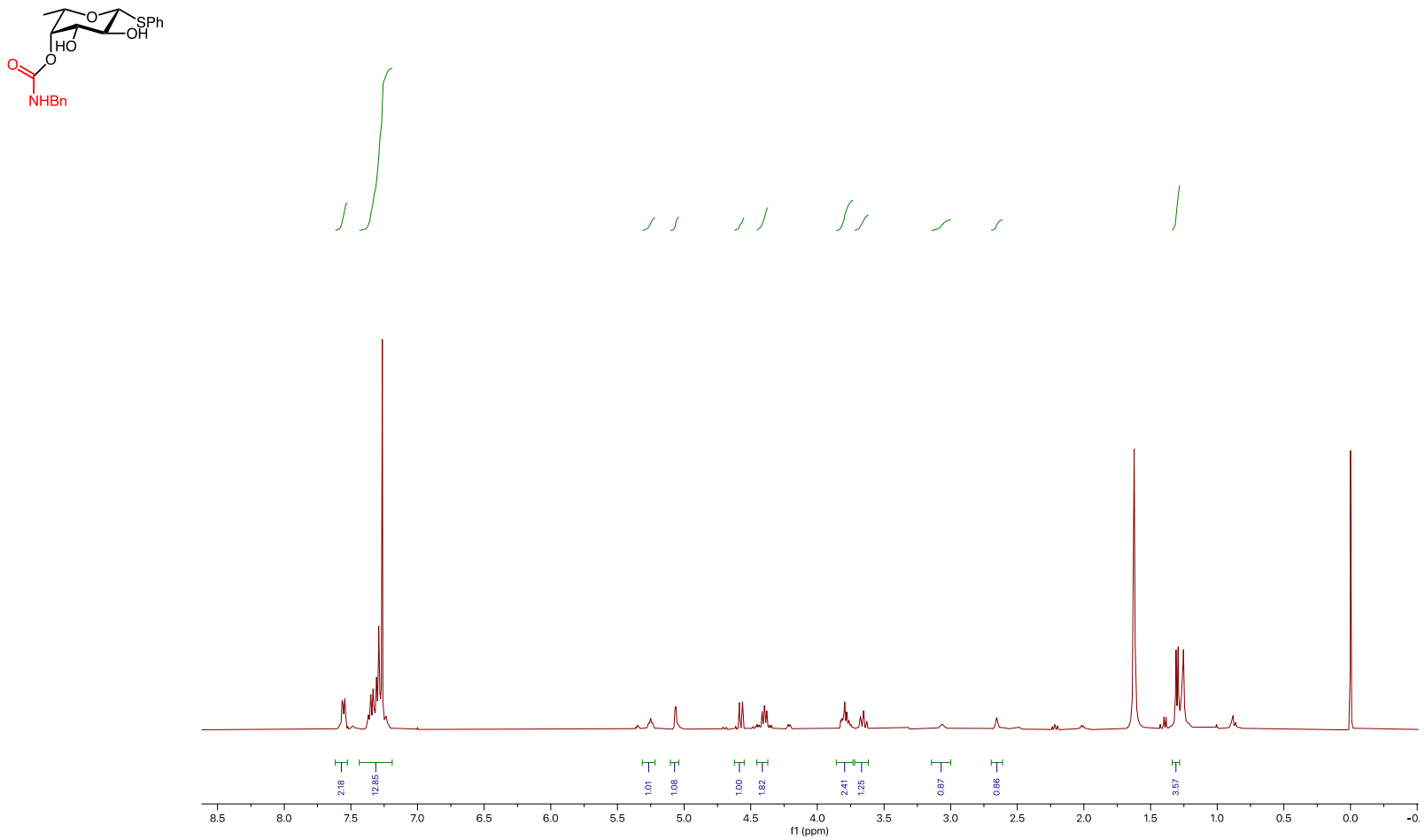
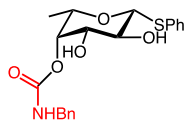


Figure S59. ^{1}H NMR spectrum (400 MHz) of **5a** in $CDCl_3$

Phenyl 4-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5a**



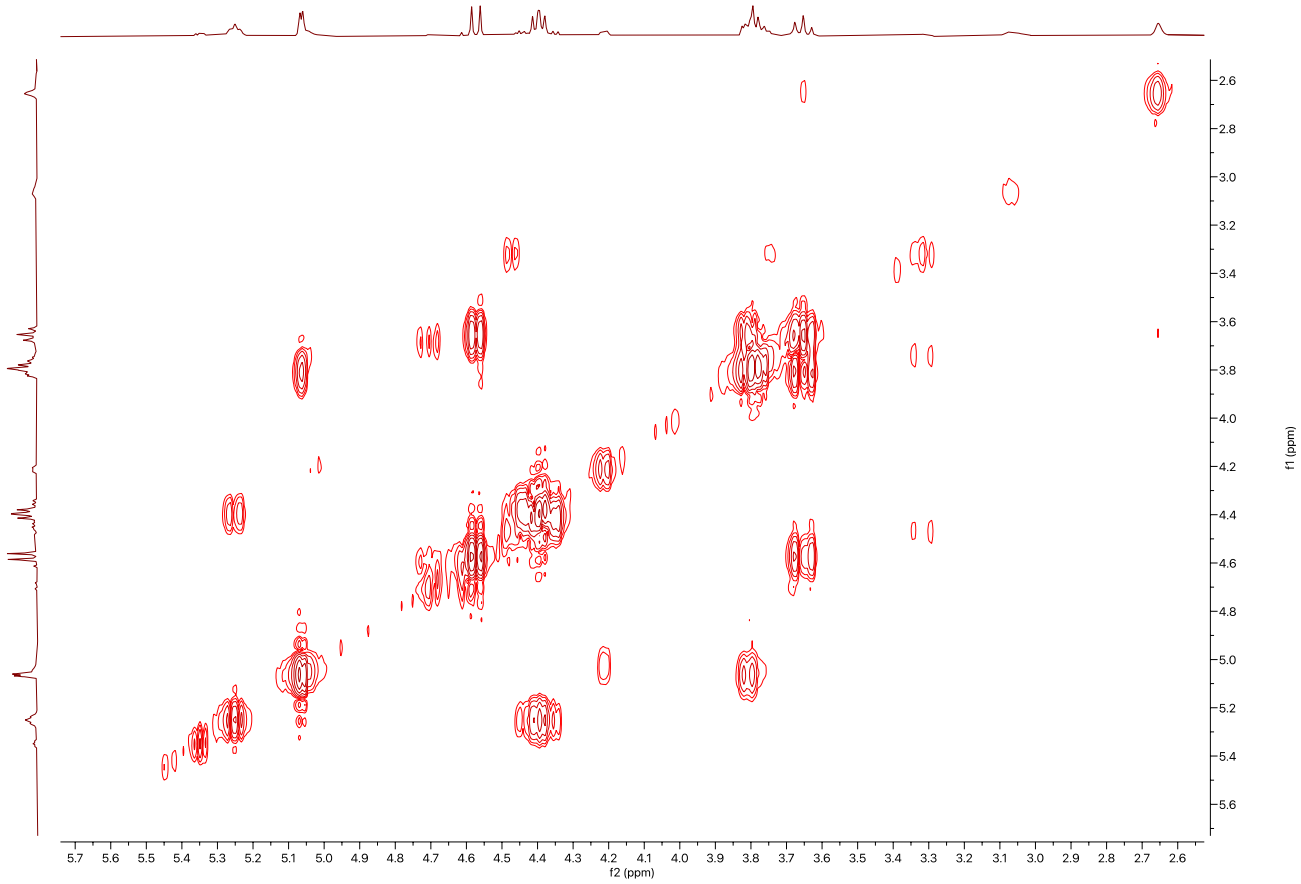


Figure S60. ^{1}H-^{1}H COSY spectrum (400 MHz) of **5a** in $CDCl_3$

Phenyl 4-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5a**

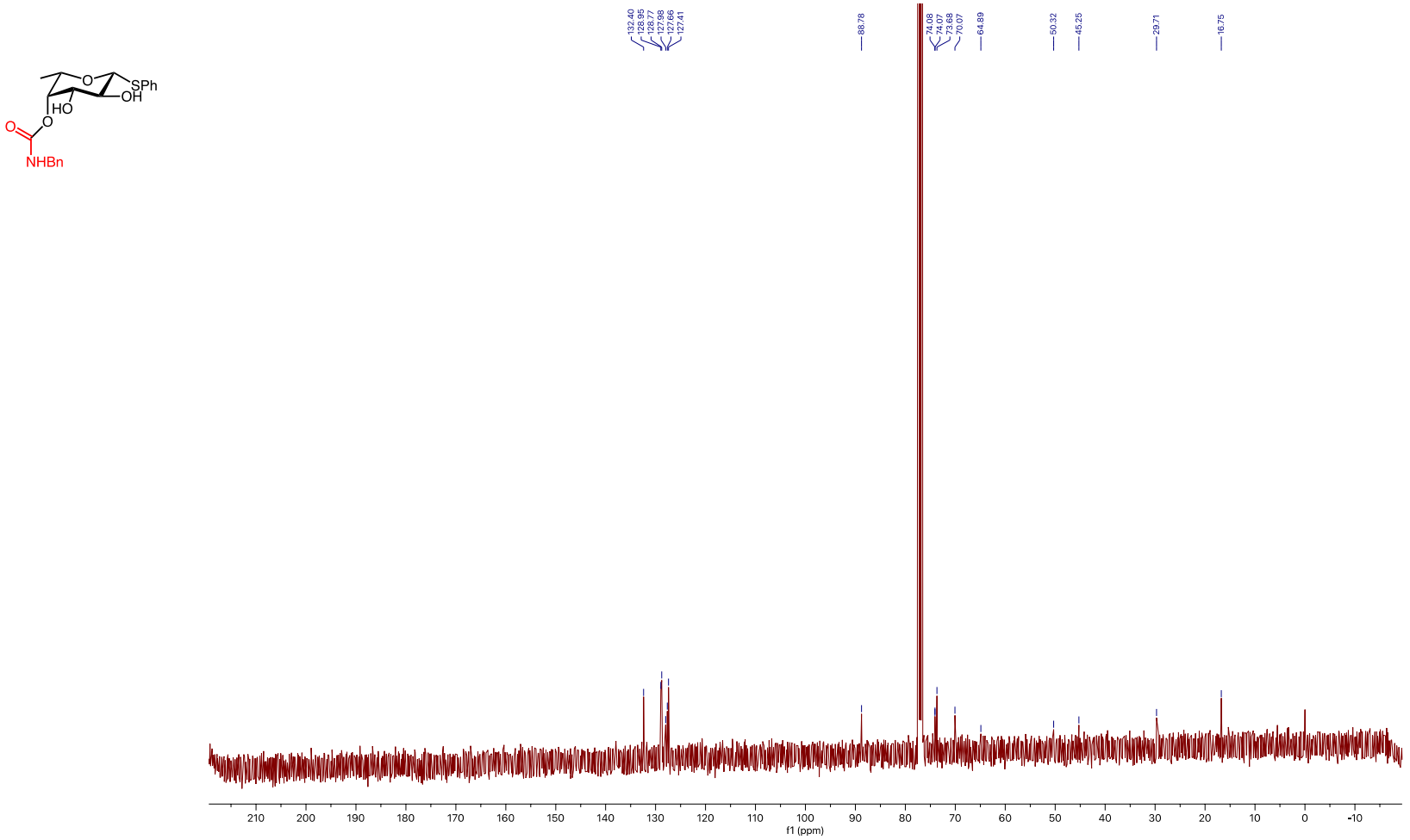
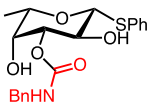


Figure S61. ^{13}C NMR spectrum (100 MHz) of **5a** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5b**



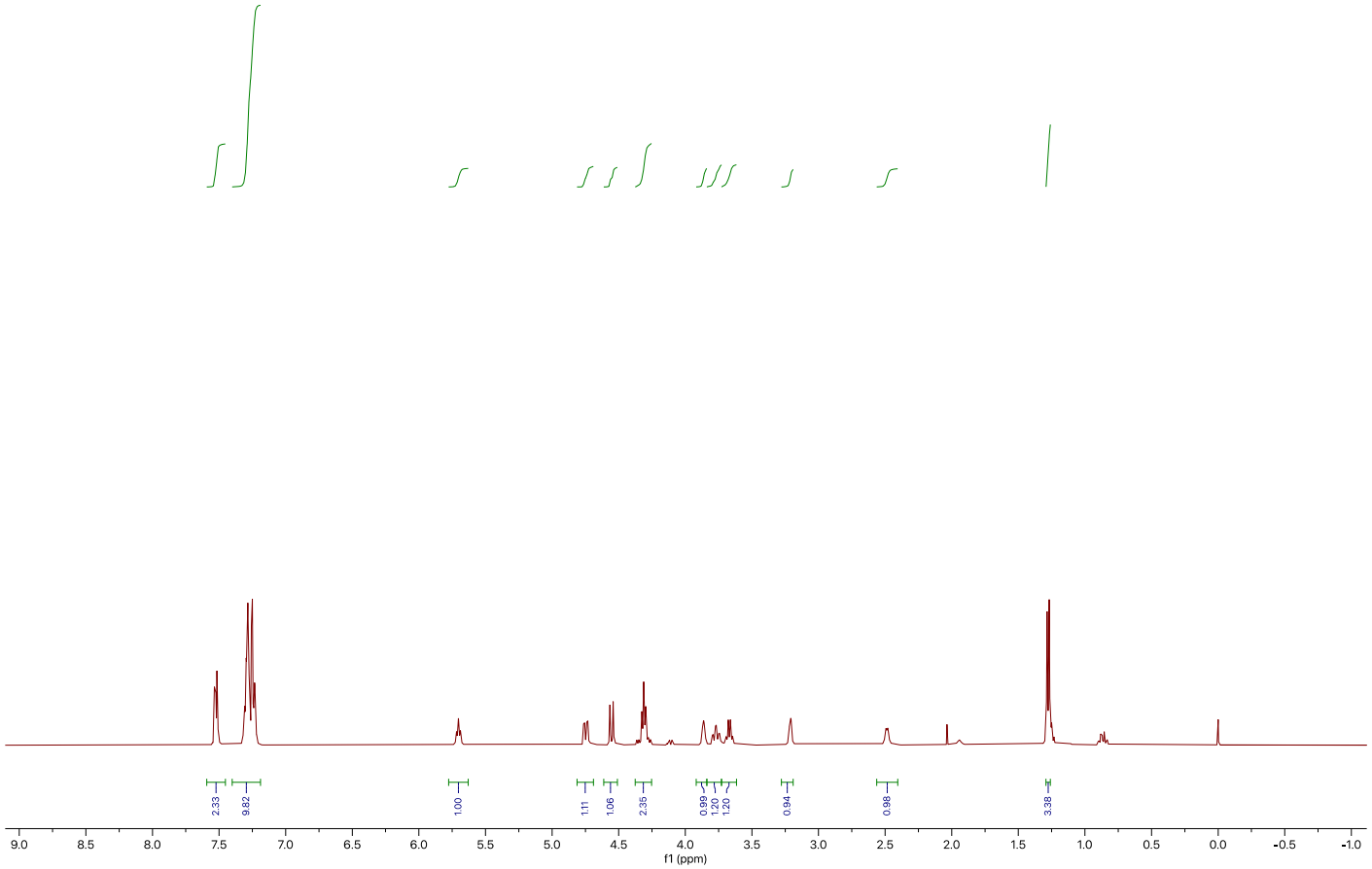


Figure S62. ^{1}H NMR spectrum (400 MHz) of **5b** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5b**

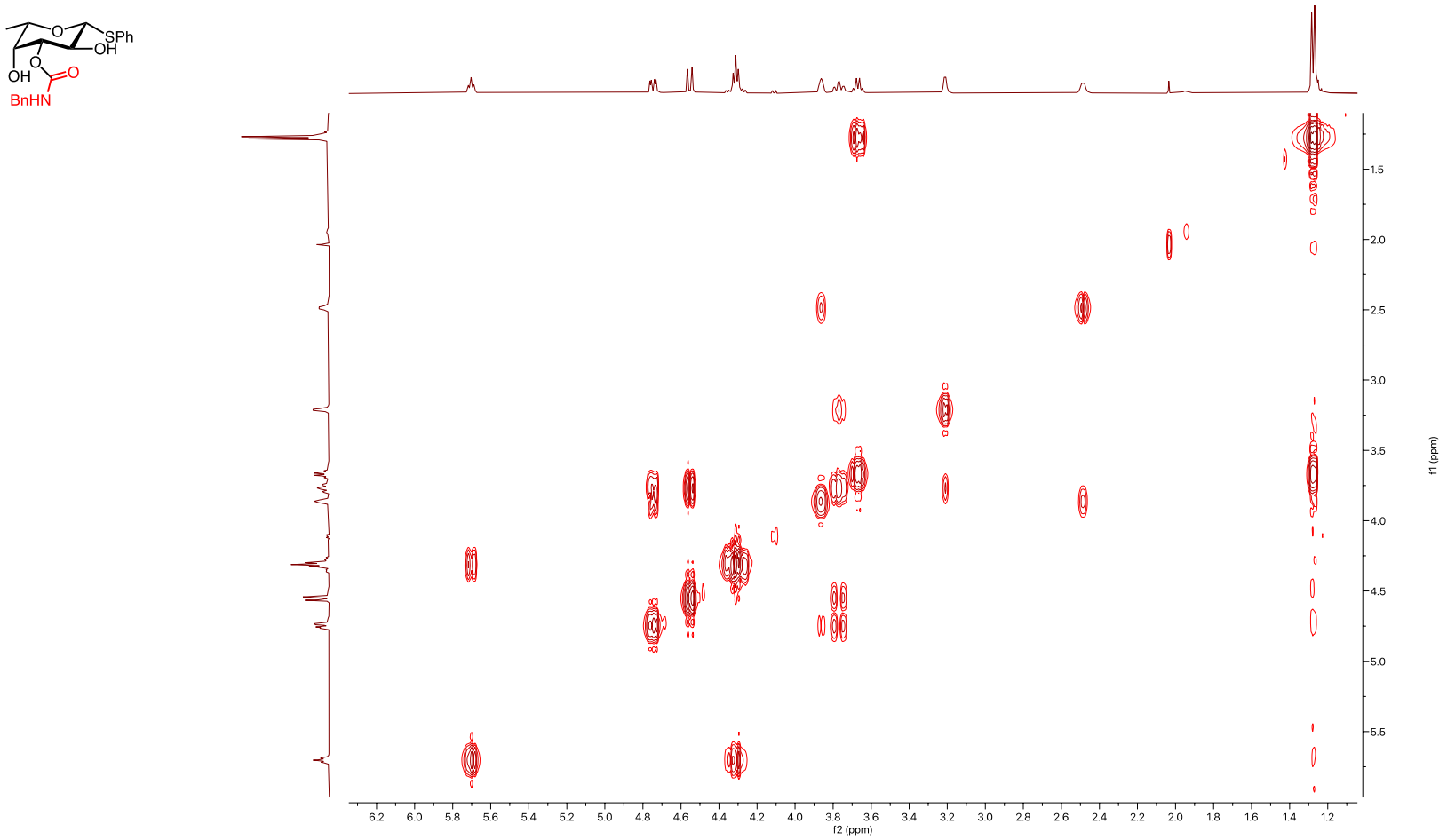


Figure S63. ^{1}H-^{1}H COSY spectrum (400 MHz) of **5b** in $CDCl_3$

Phenyl 3-*O*-benzylcarbamoyl-**β**-L-fucopyranoside **5b**

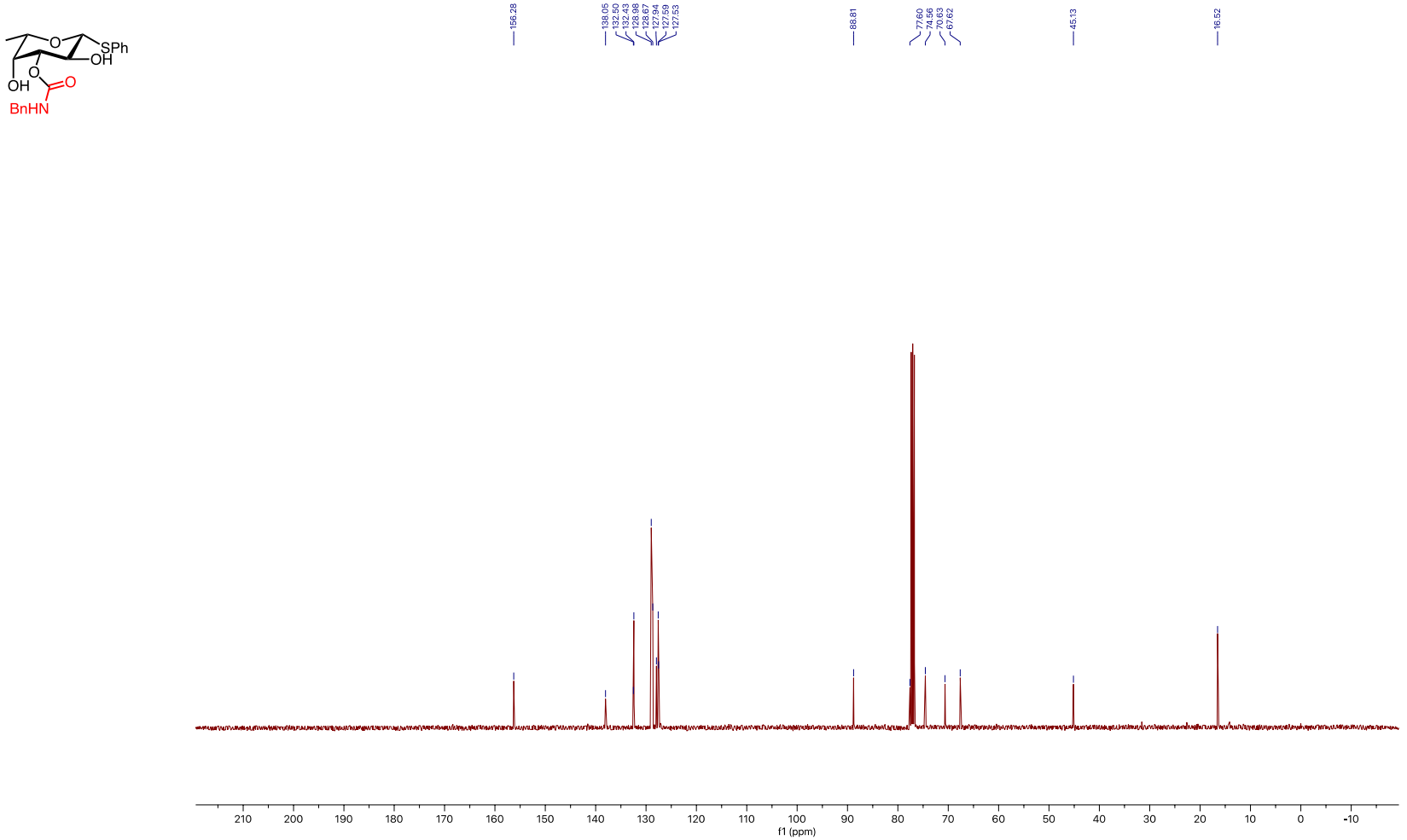


Figure S64. ^{13}C NMR spectrum (100 MHz) of **5b** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-α-L-rhamnopyranoside **6a**

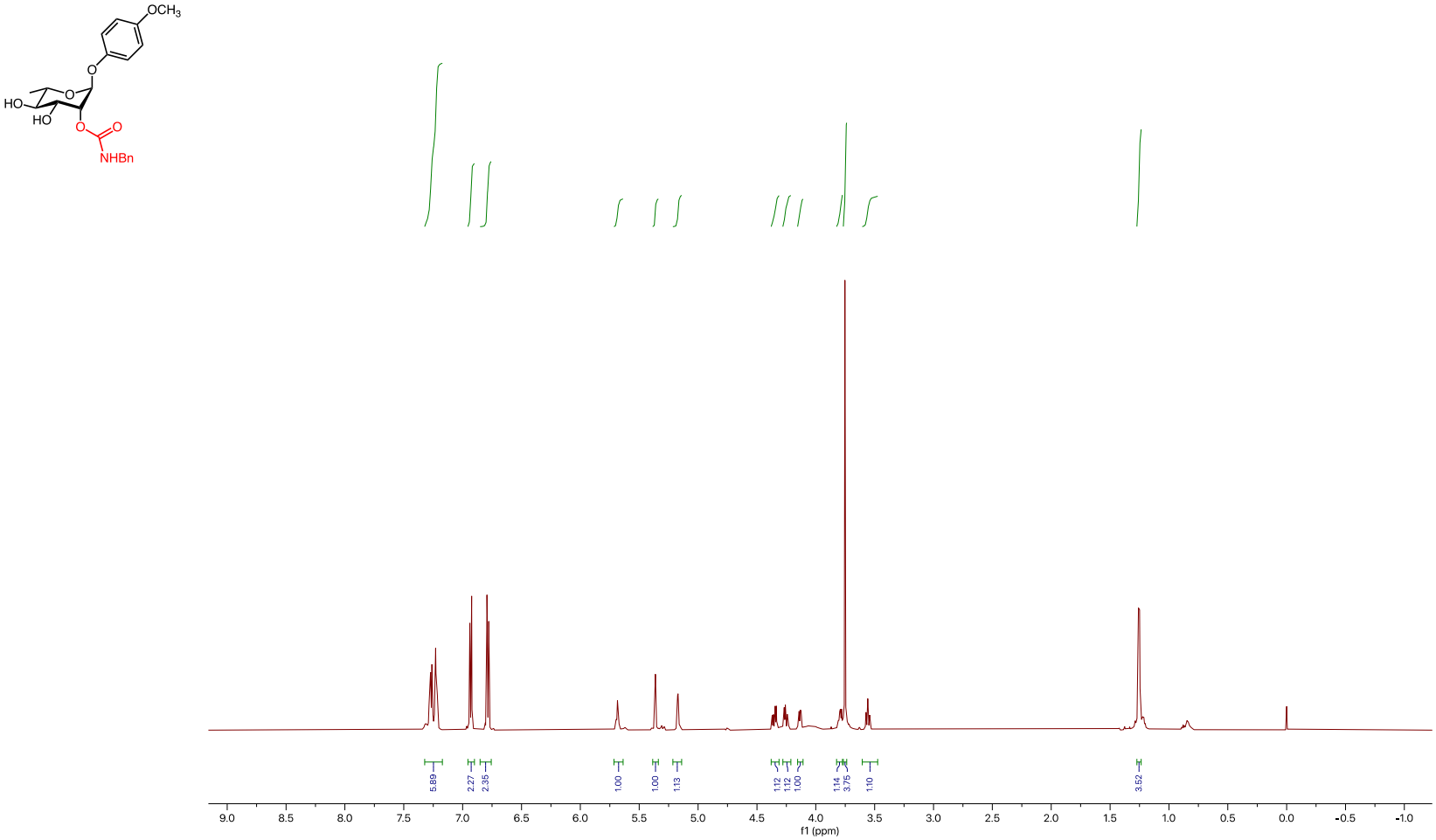


Figure S65. ^{1}H NMR spectrum (600 MHz) of **6a** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-α-L-rhamnopyranoside **6a**

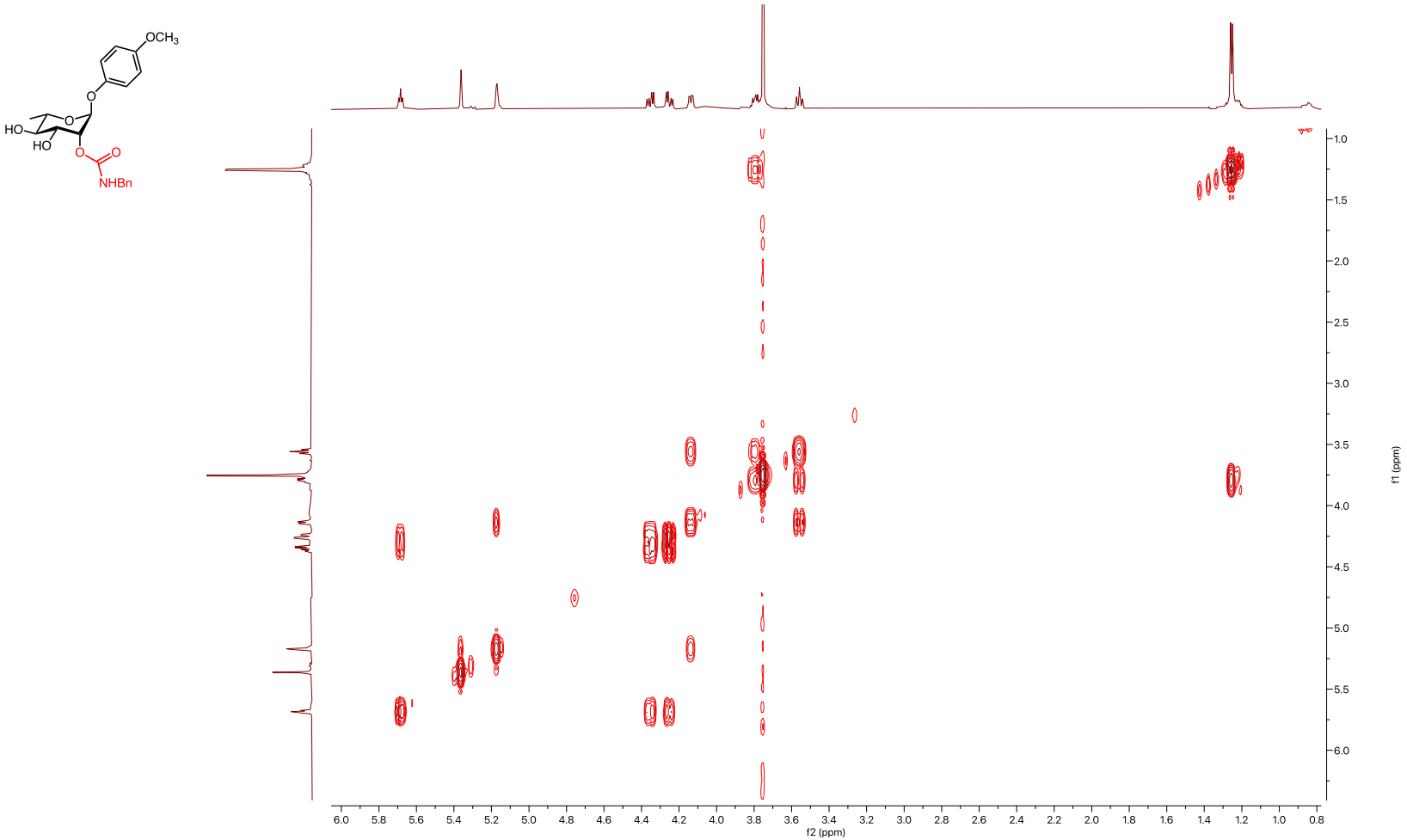


Figure S66. ^{1}H-^{1}H COSY spectrum (600 MHz) of **6a** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-α-L-rhamnopyranoside **6a**

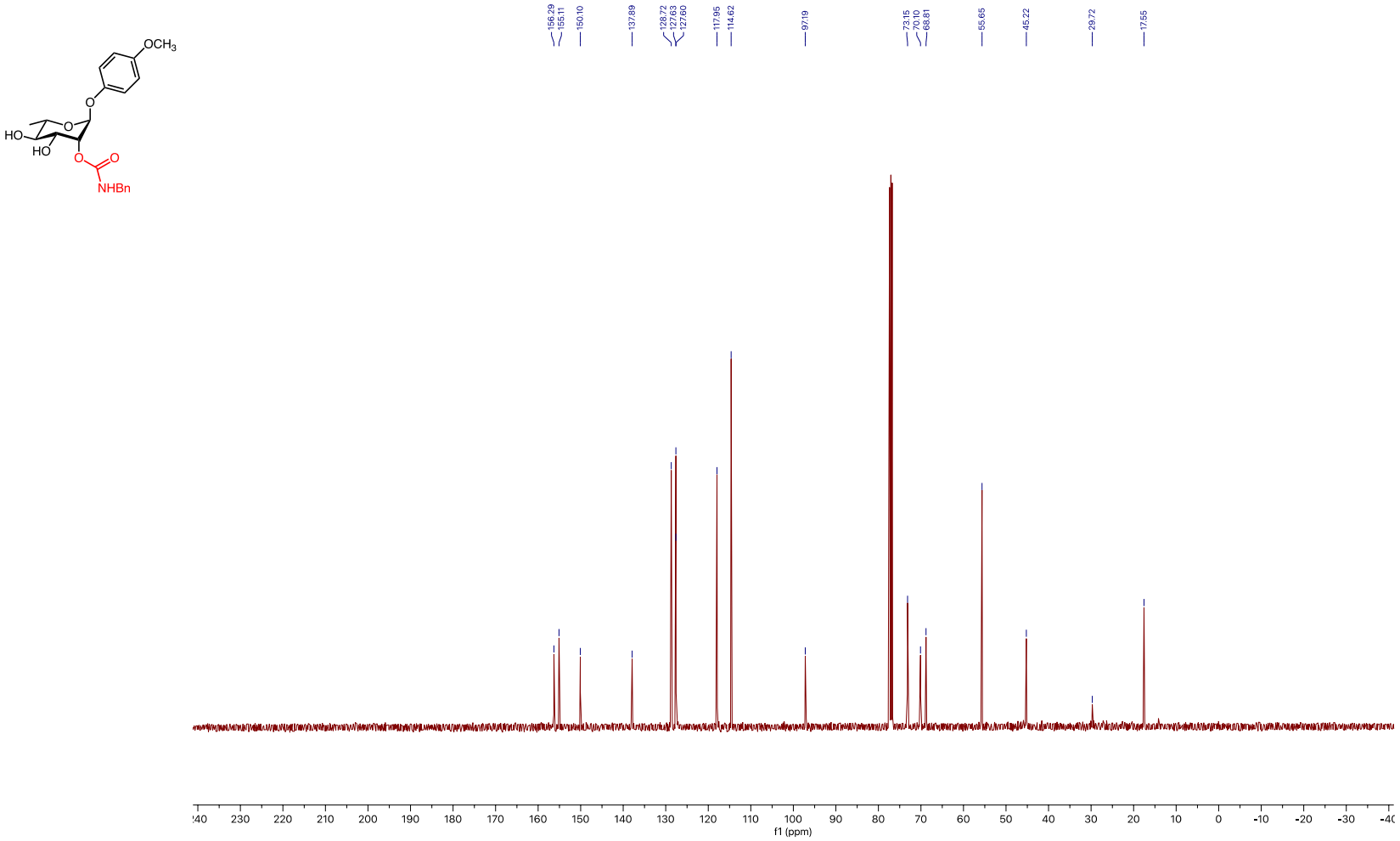


Figure S67. ^{13}C NMR spectrum (100 MHz) of **6a** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-L-rhamnopyranoside **6b**

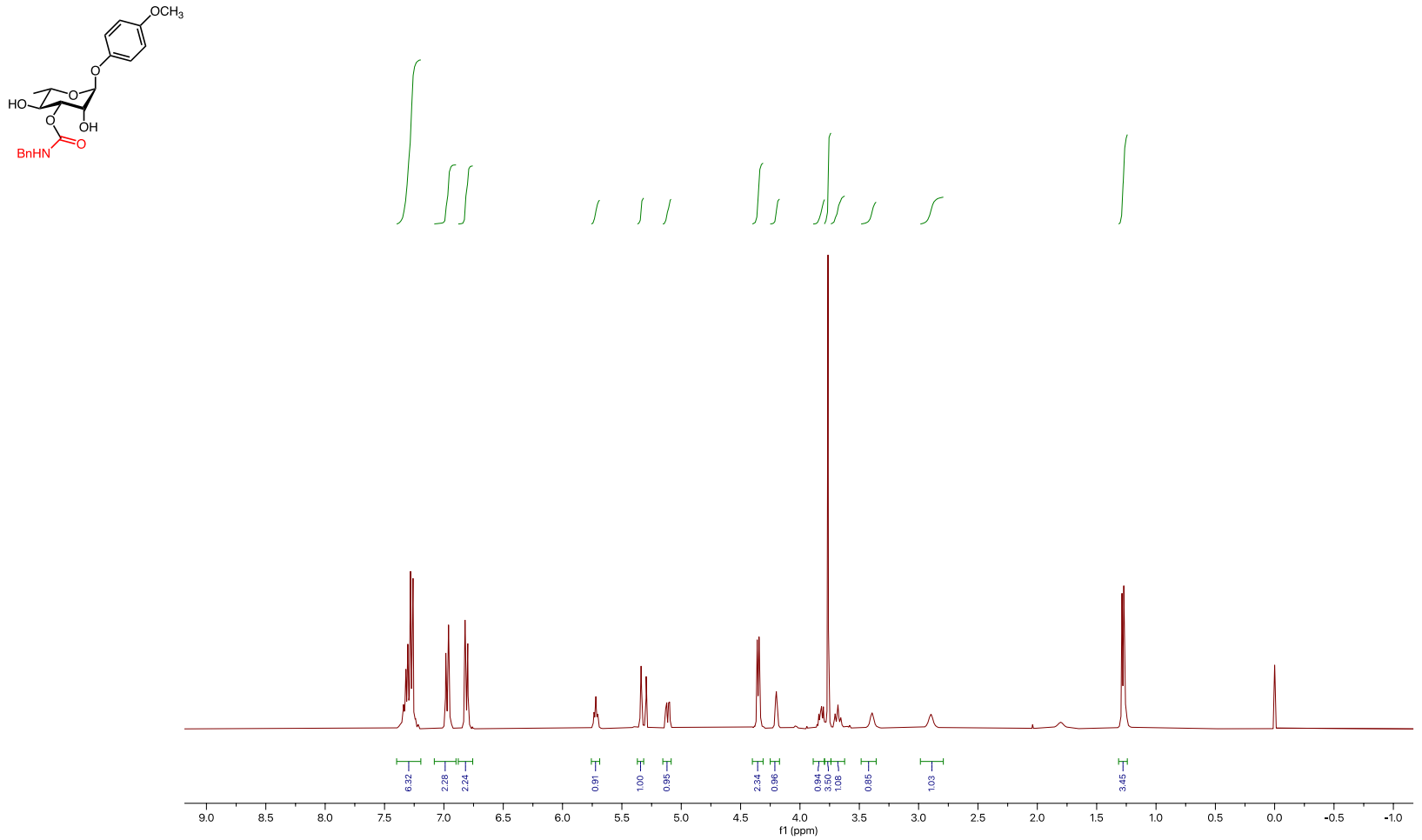


Figure S68. ^{1}H NMR spectrum (400 MHz) of **6b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-L-rhamnopyranoside **6b**

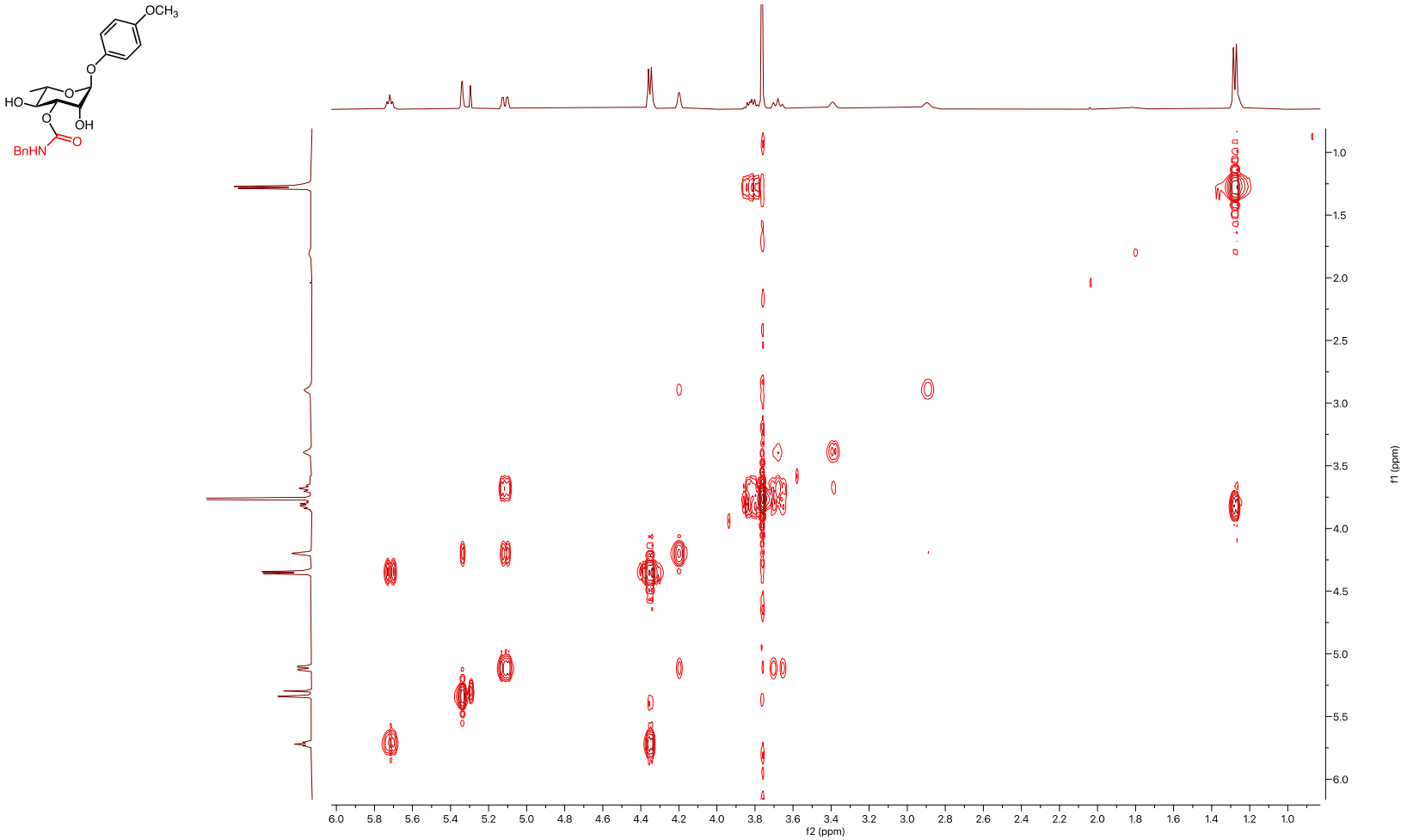


Figure S69. ^{1}H-^{1}H COSY spectrum (400 MHz) of **6b** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7c**

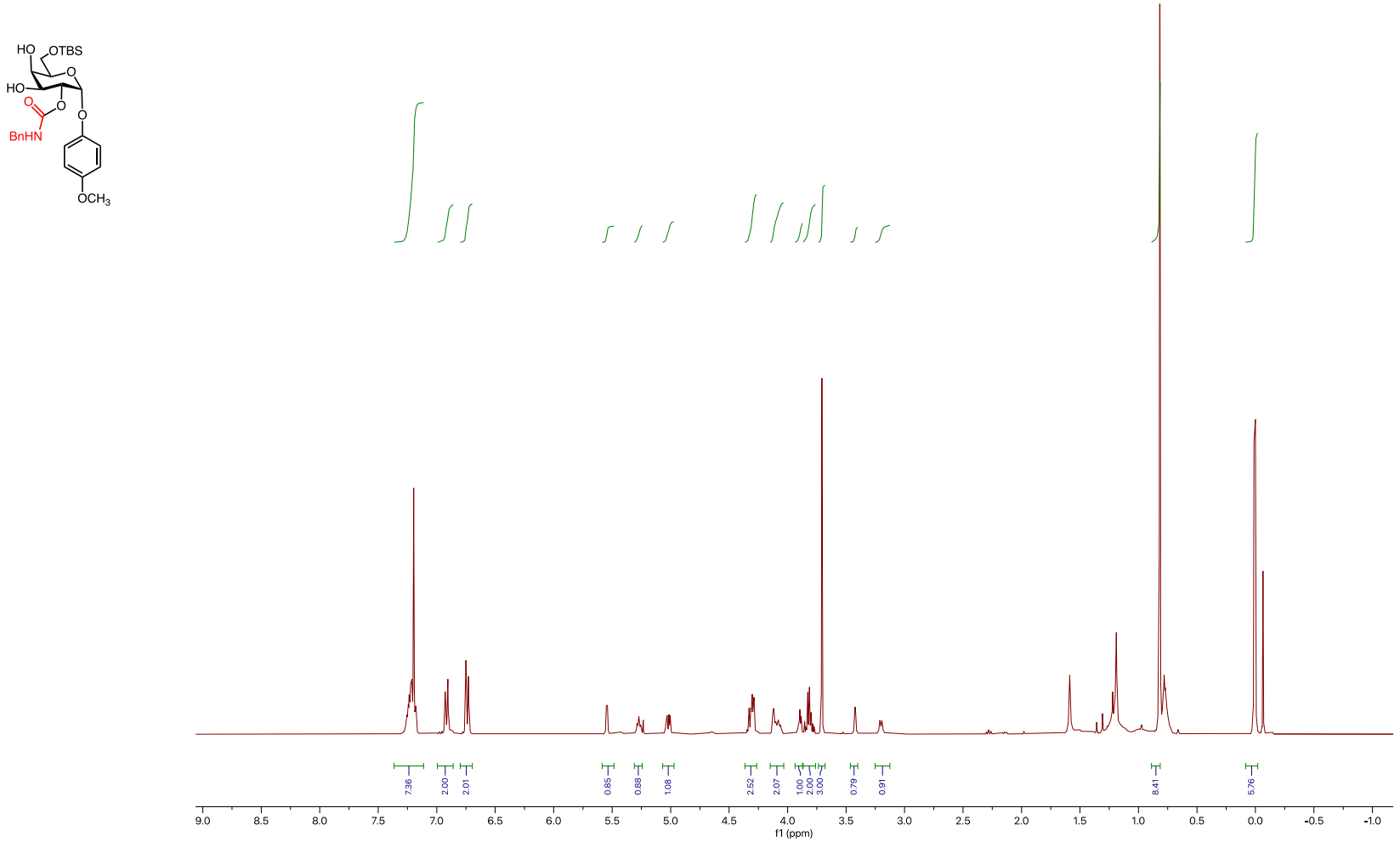


Figure S70. ^{1}H NMR spectrum (400 MHz) of **7c** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7c**

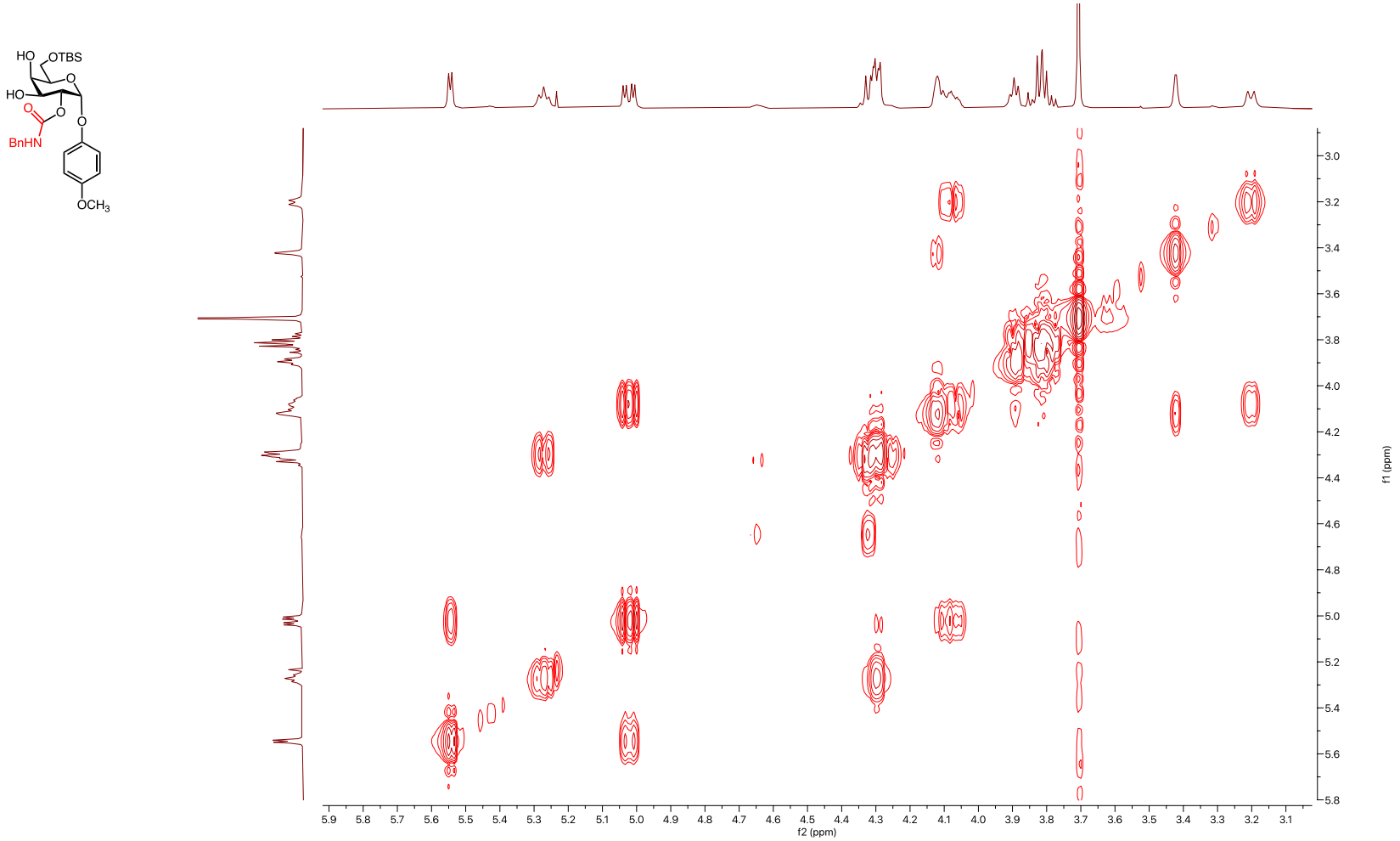


Figure S71. ^{1}H-^{1}H COSY spectrum (400 MHz) of **7c** in $CDCl_3$

4-methoxyphenyl 2-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7c**

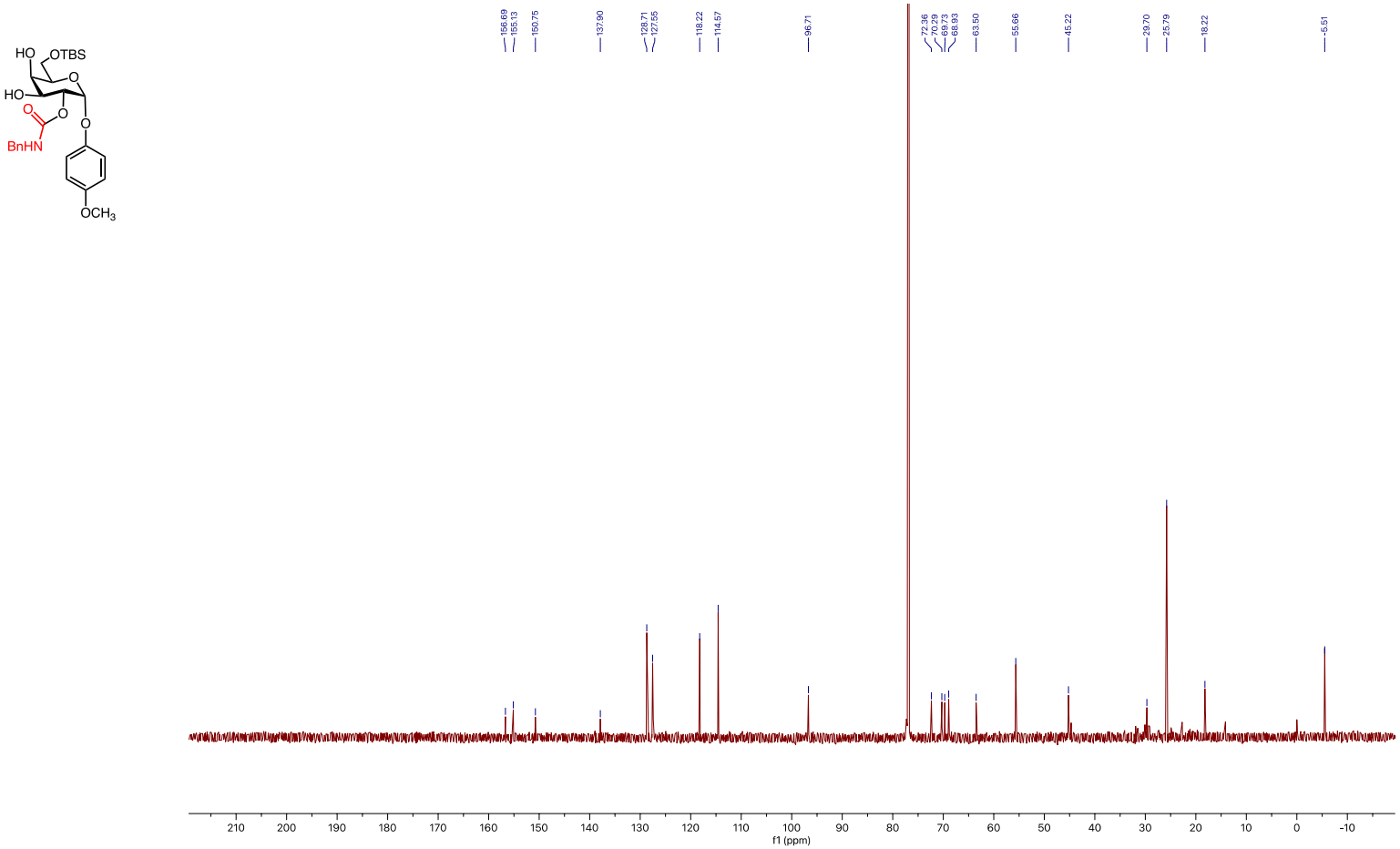


Figure S72. ^{13}C NMR spectrum (100 MHz) of **7c** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7b**

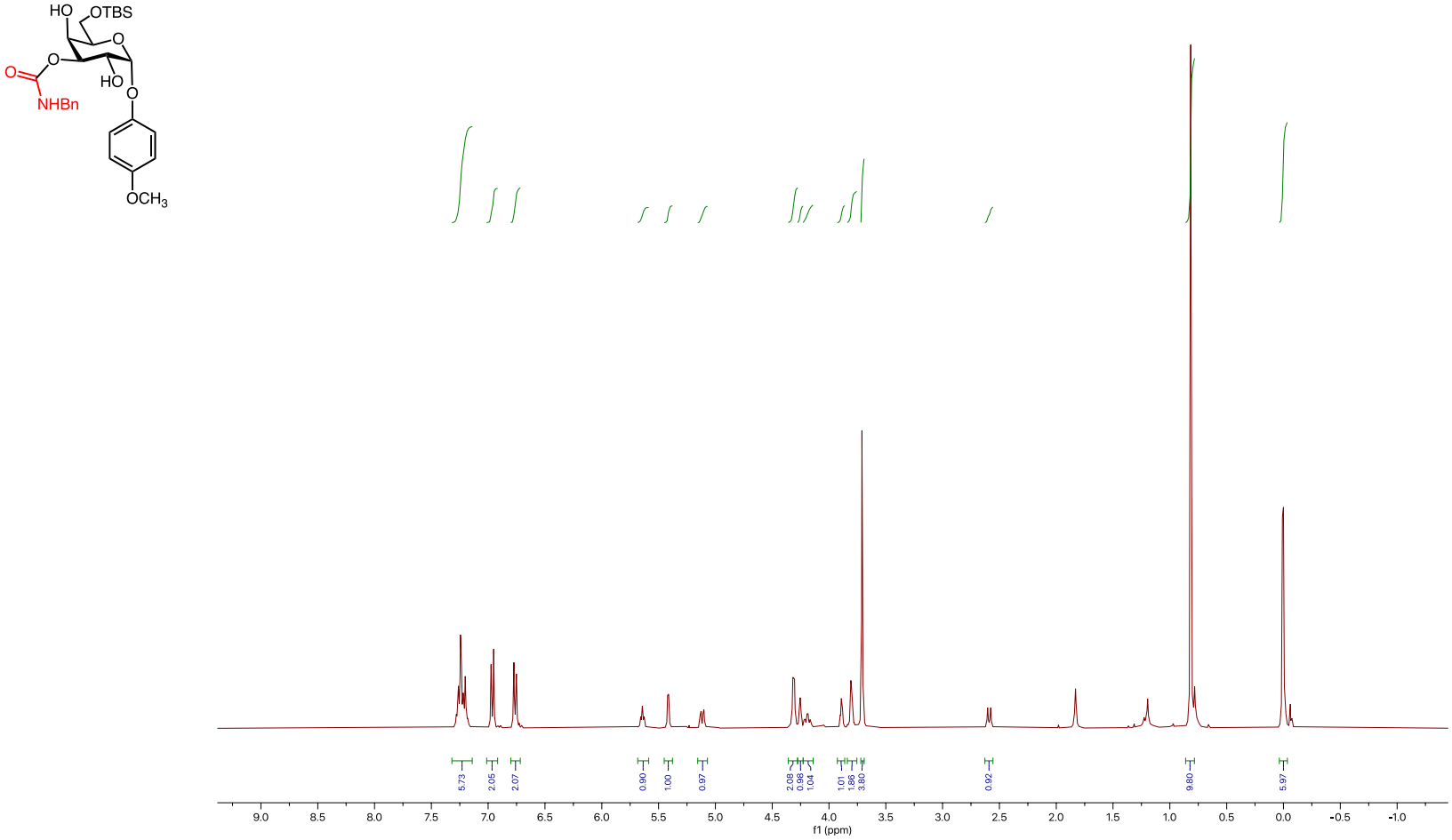


Figure S73. ^{1}H NMR spectrum (400 MHz) of **7b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7b**

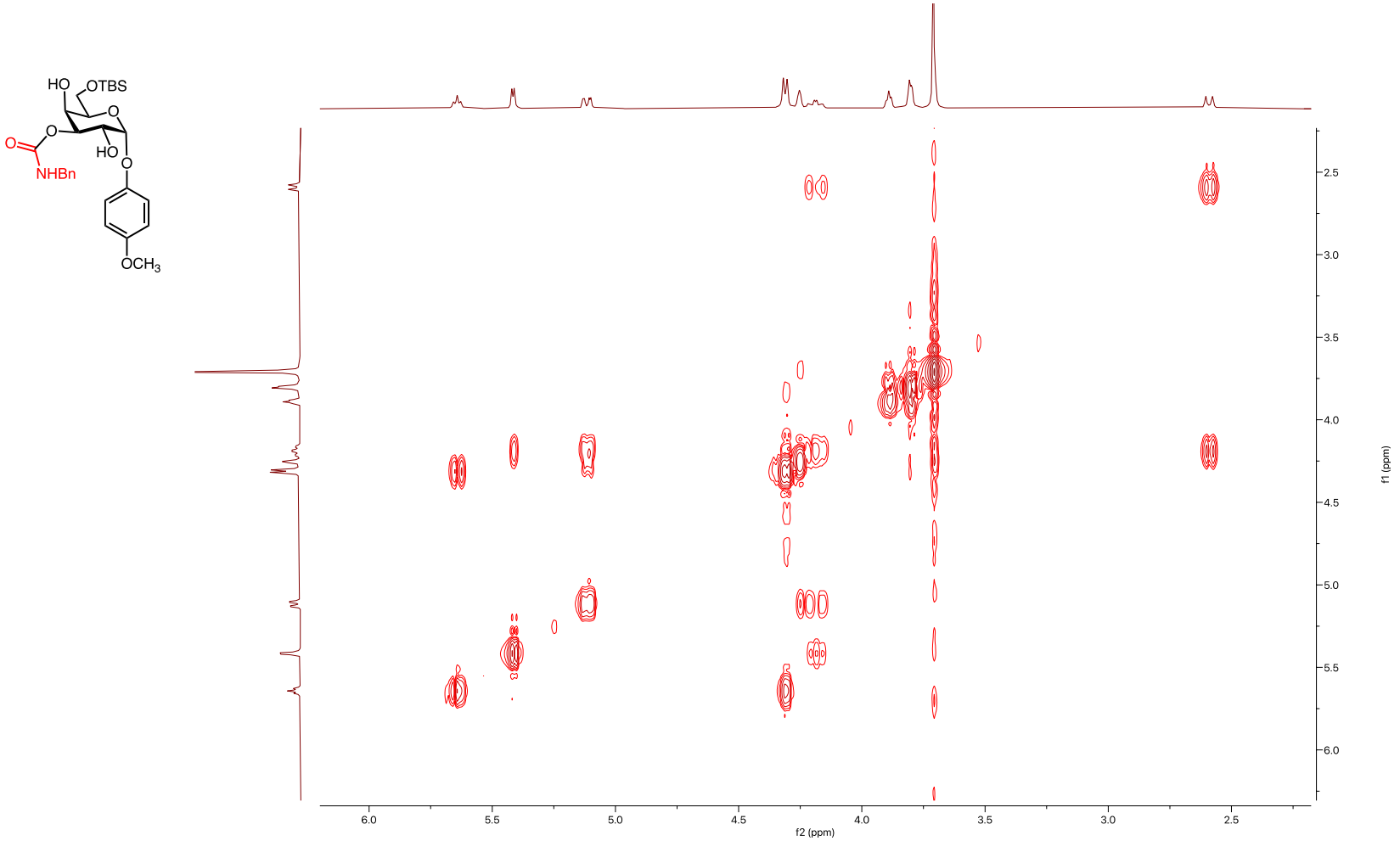


Figure S74. ^{1}H-^{1}H COSY spectrum (400 MHz) of **7b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **7b**

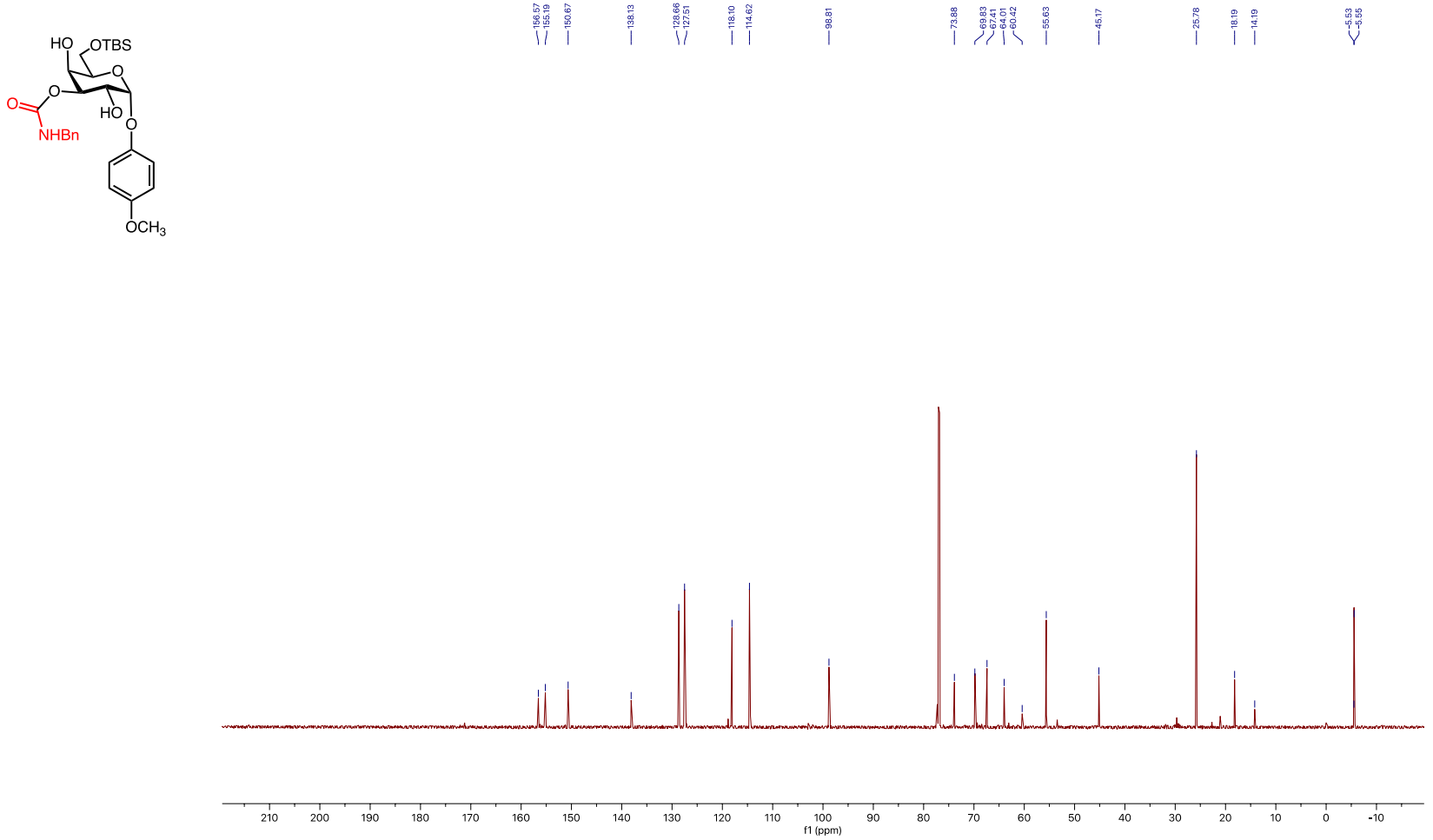


Figure S75. ^{13}C NMR spectrum (100 MHz) of **7b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-β-D-galactopyranoside **8b**

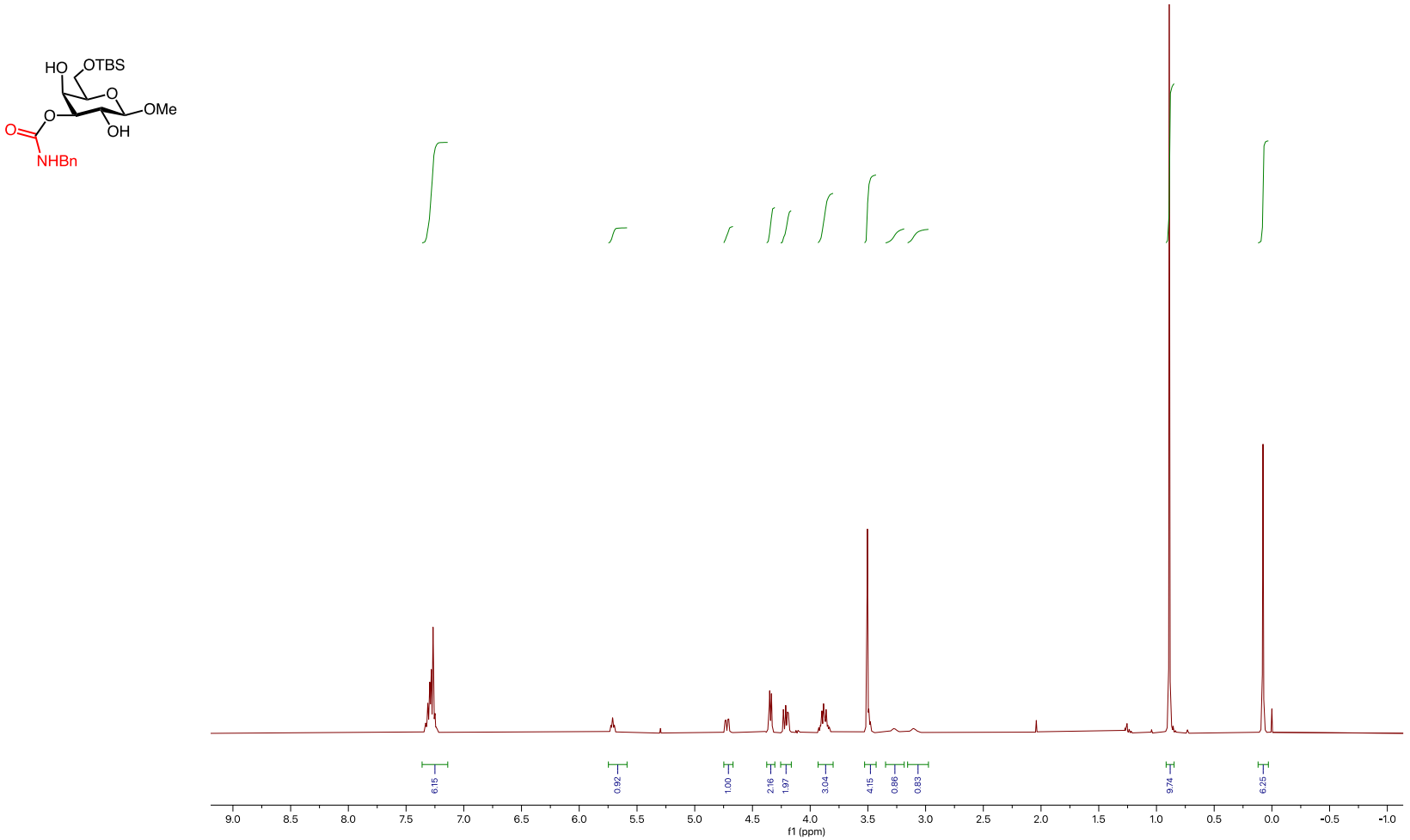


Figure S76. ^{1}H NMR spectrum (400 MHz) of **8b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-β-D-galactopyranoside **9b**

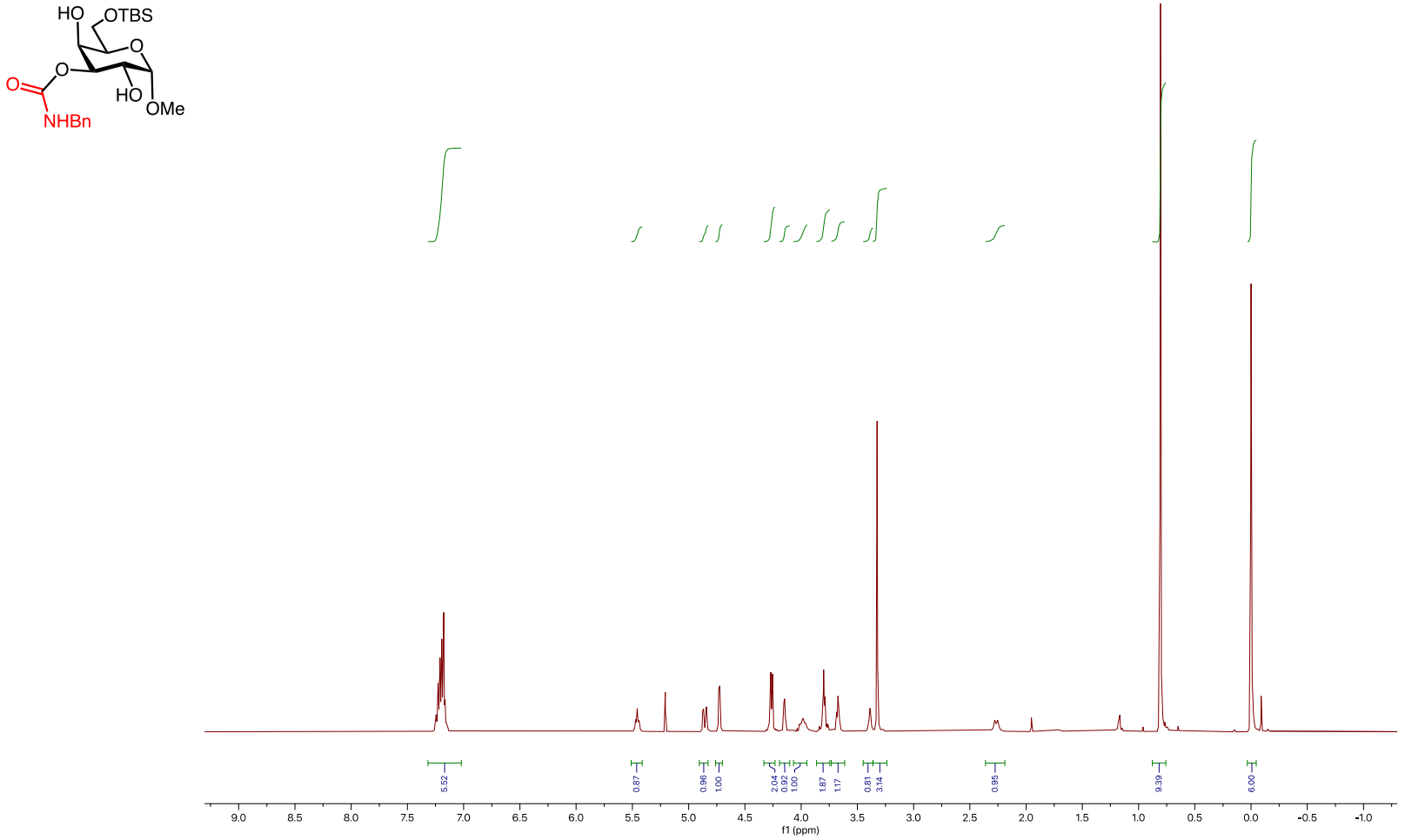


Figure S77. ^{1}H NMR spectrum (400 MHz) of **9b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-galactopyranoside **9b**

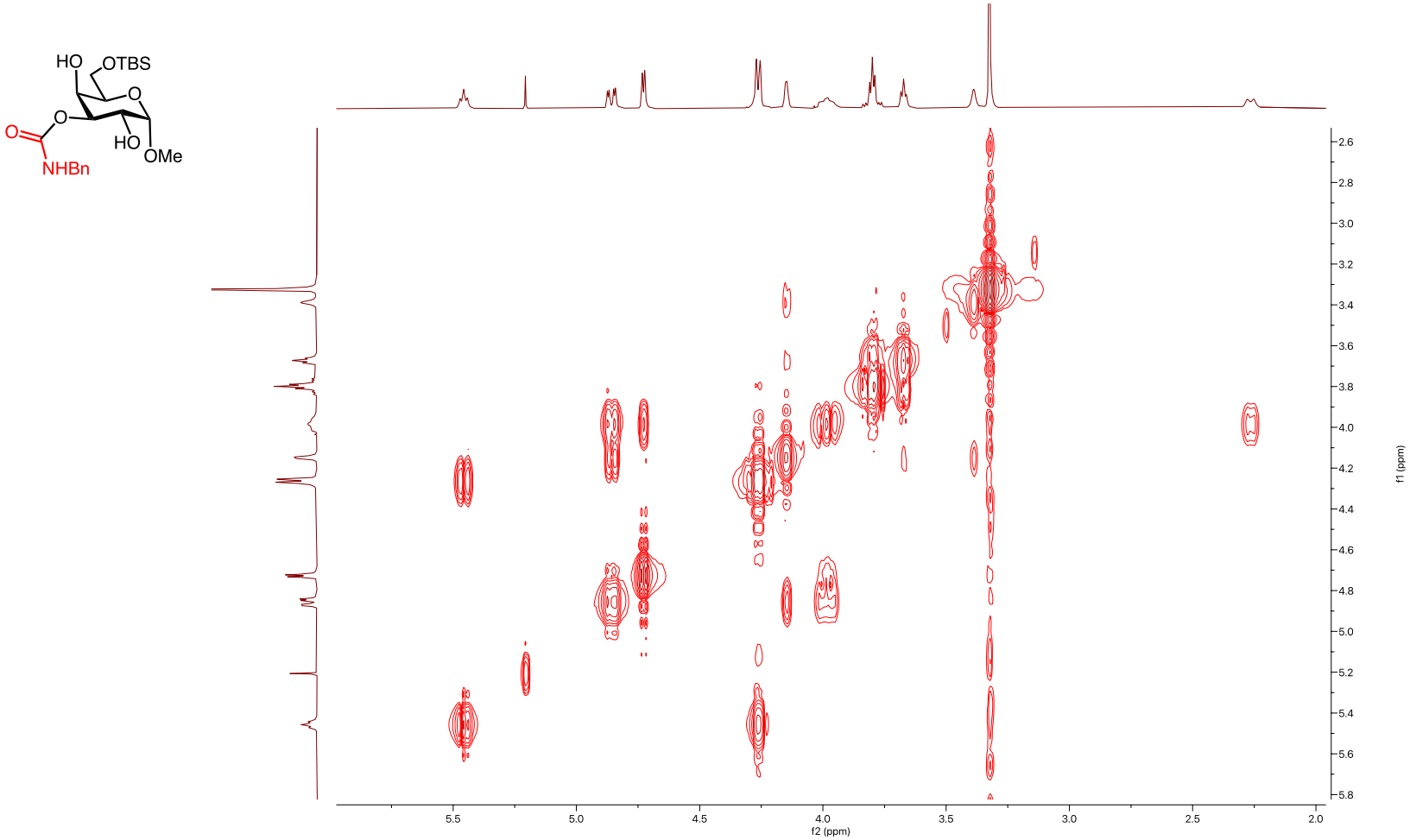
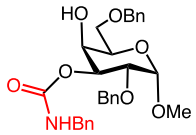


Figure S78. ^{1}H-^{1}H COSY spectrum (400 MHz) of **9b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-2,6-*O*-benzyl-α-D-galactopyranoside **10b**



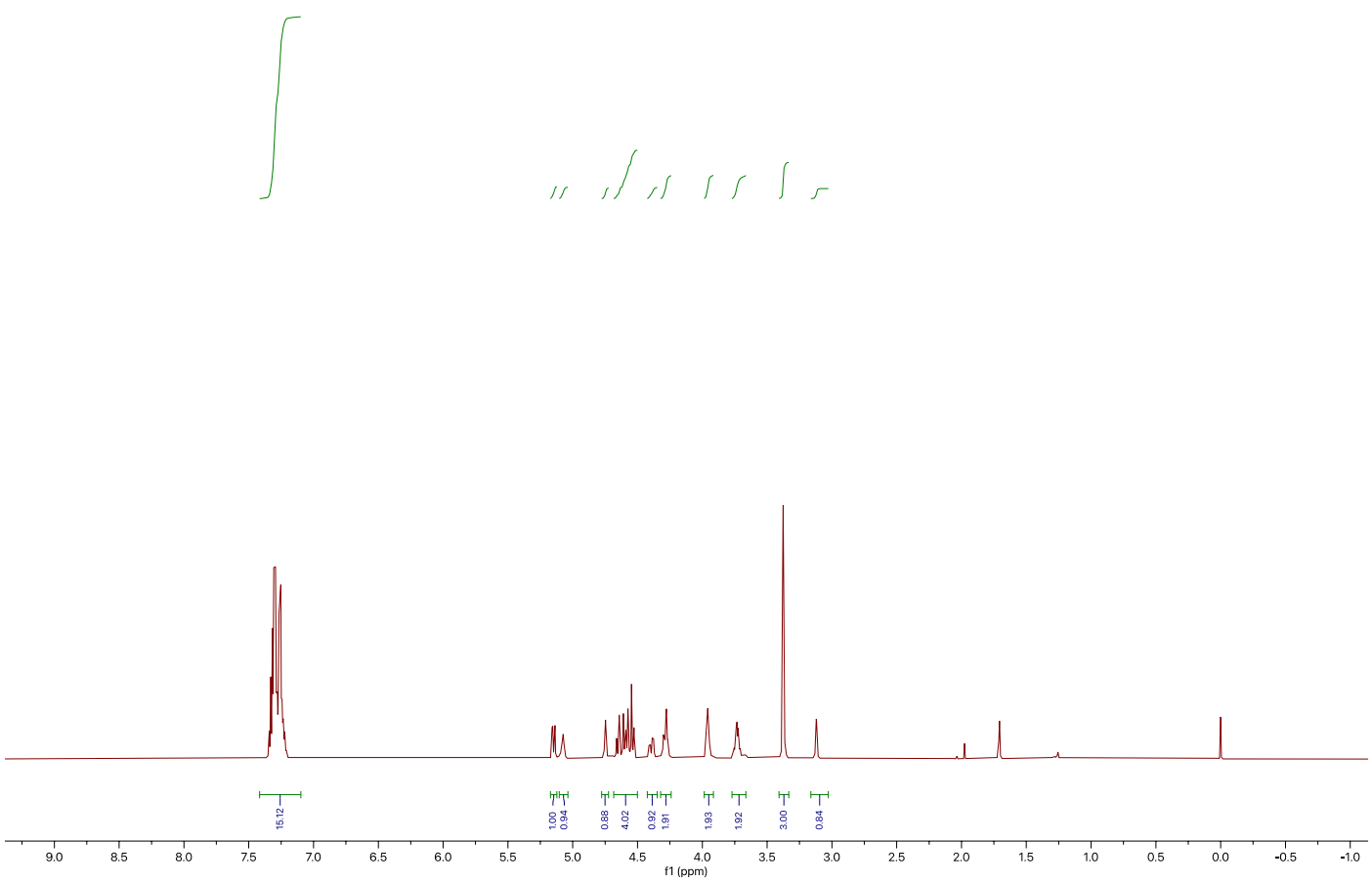
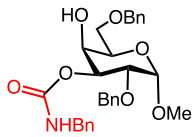


Figure S79. ^{1}H NMR spectrum (600 MHz) of **10b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-2,6-*O*-benzyl-α-D-galactopyranoside **10b**



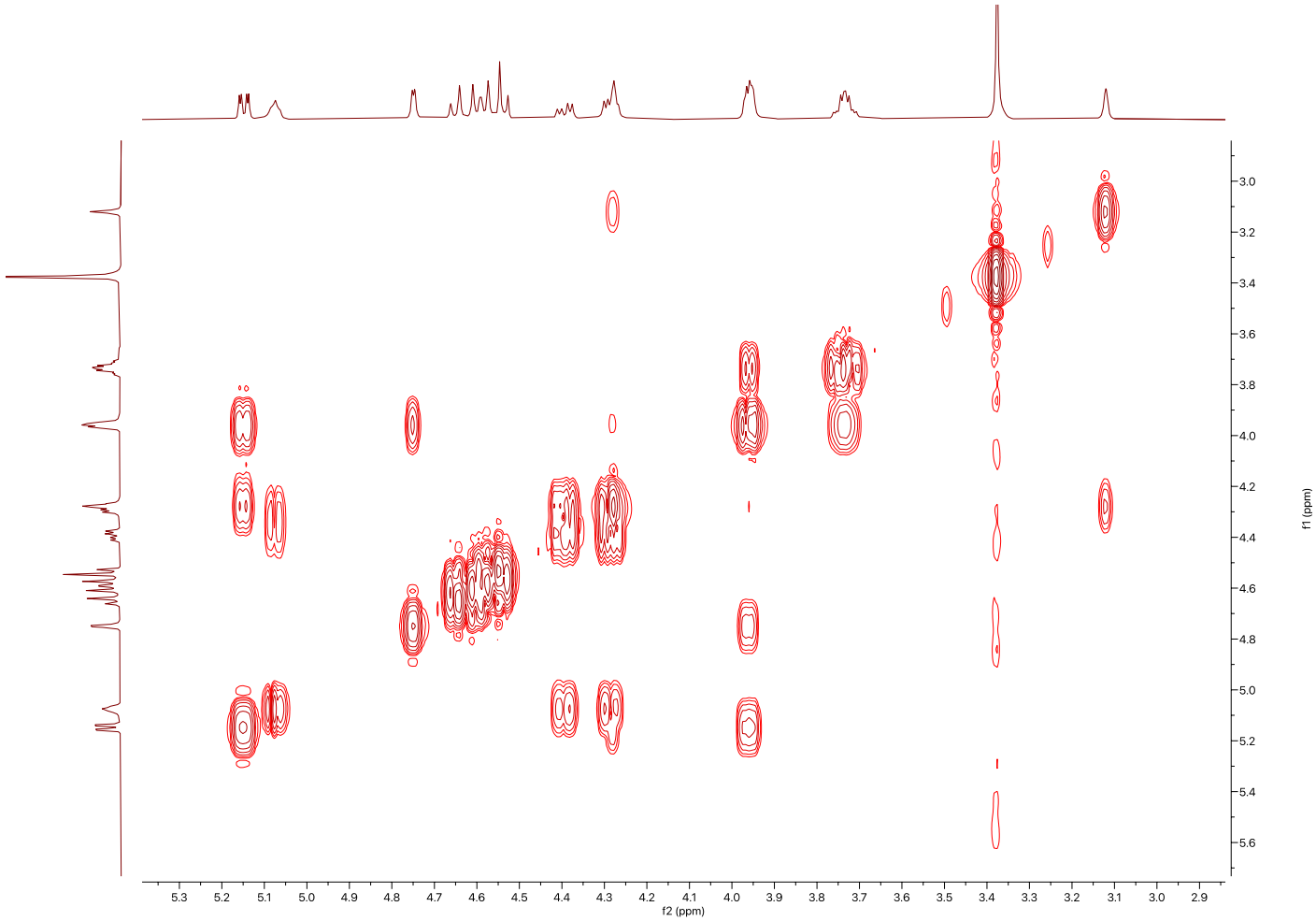


Figure S80. ^{1}H-^{1}H COSY spectrum (600 MHz) of **10b** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-2,6-*O*-benzyl-α-D-galactopyranoside **10b**

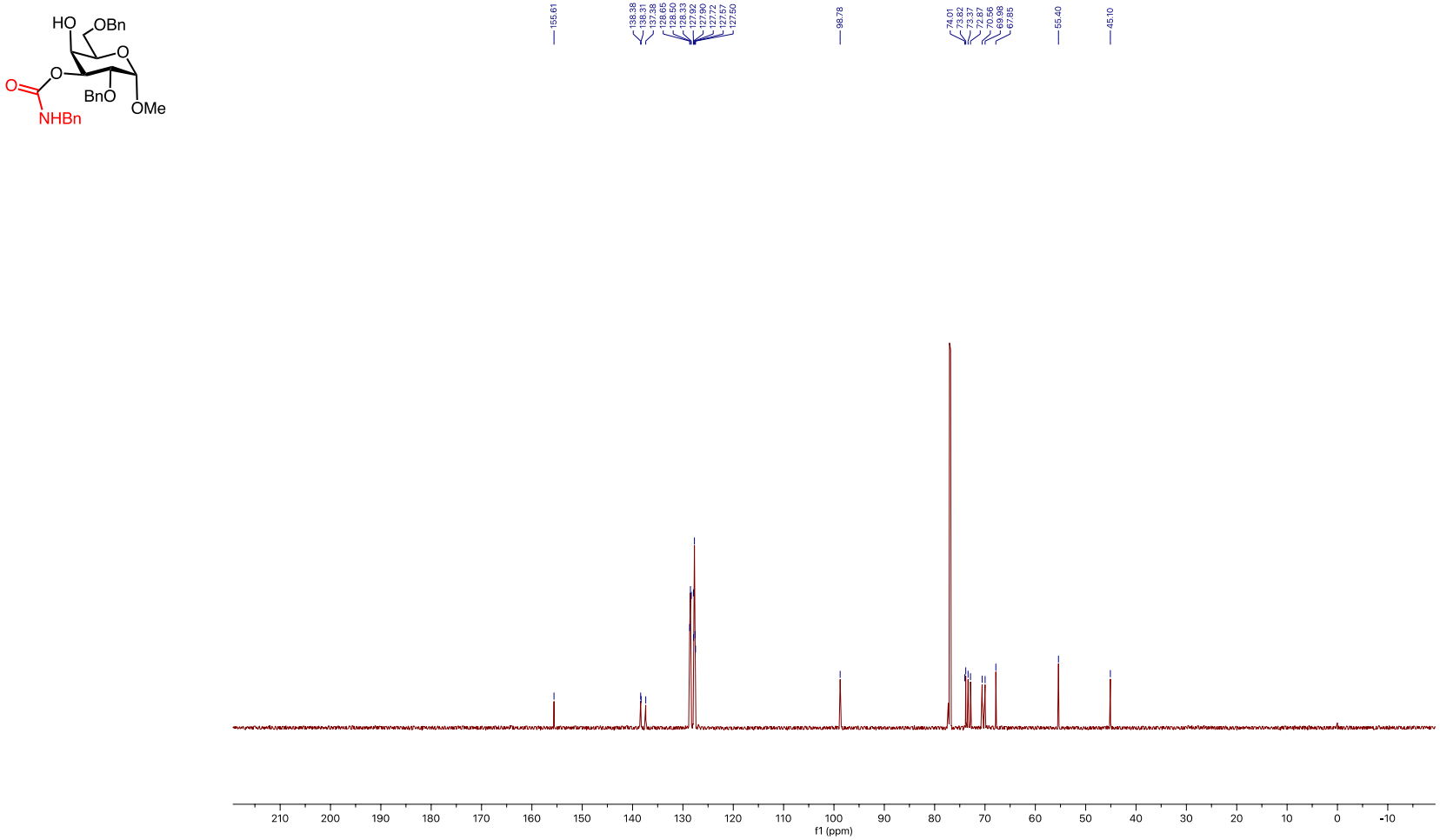


Figure S81. ^{13}C NMR spectrum (100 MHz) of **10b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-β-L-arabinopyranoside **11b**

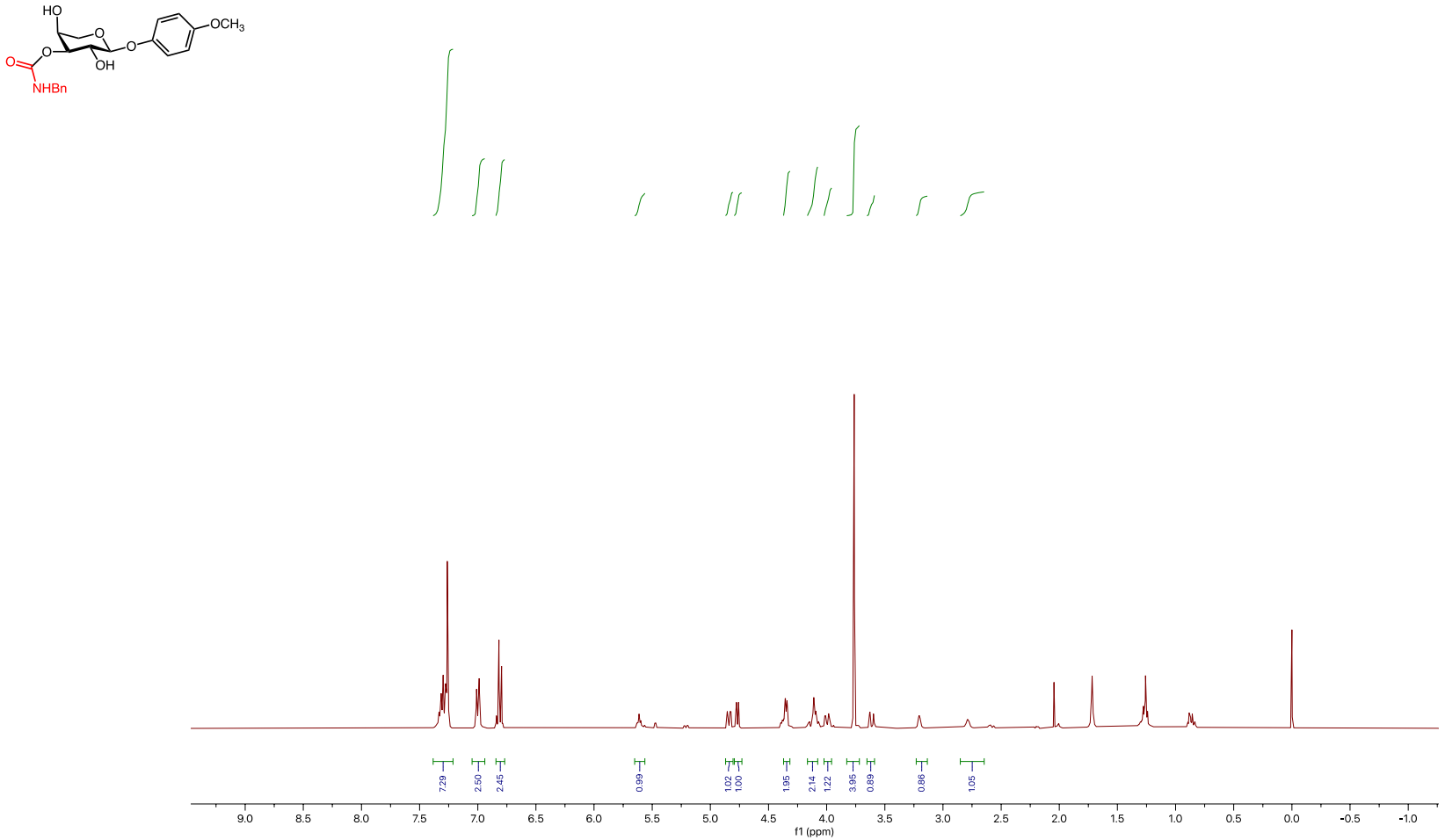


Figure S82. ^{1}H NMR spectrum (400 MHz) of **11b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-β-L-arabinopyranoside **11b**

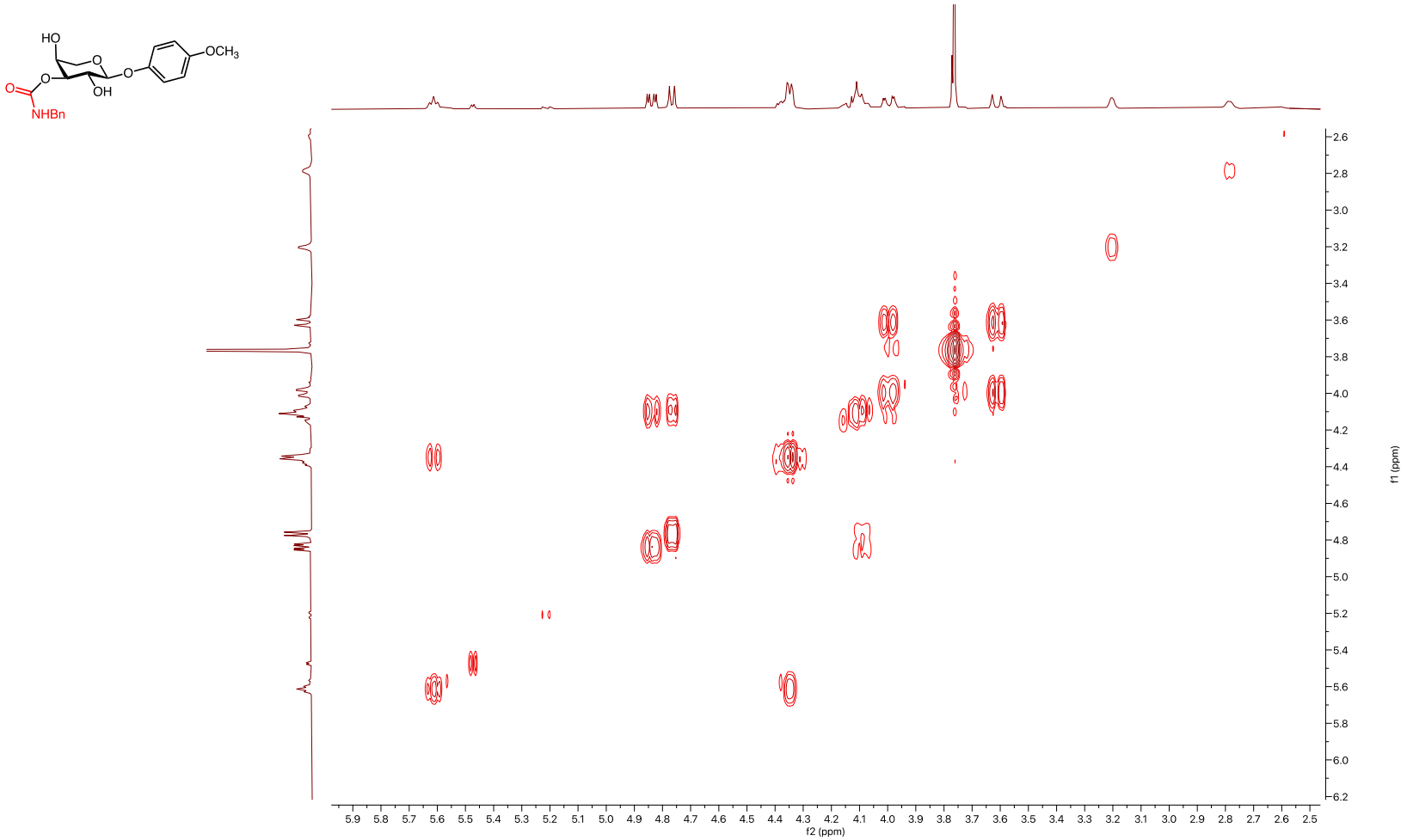


Figure S83. ^{1}H-^{1}H COSY spectrum (400 MHz) of **11b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-β-L-arabinopyranoside **11b**

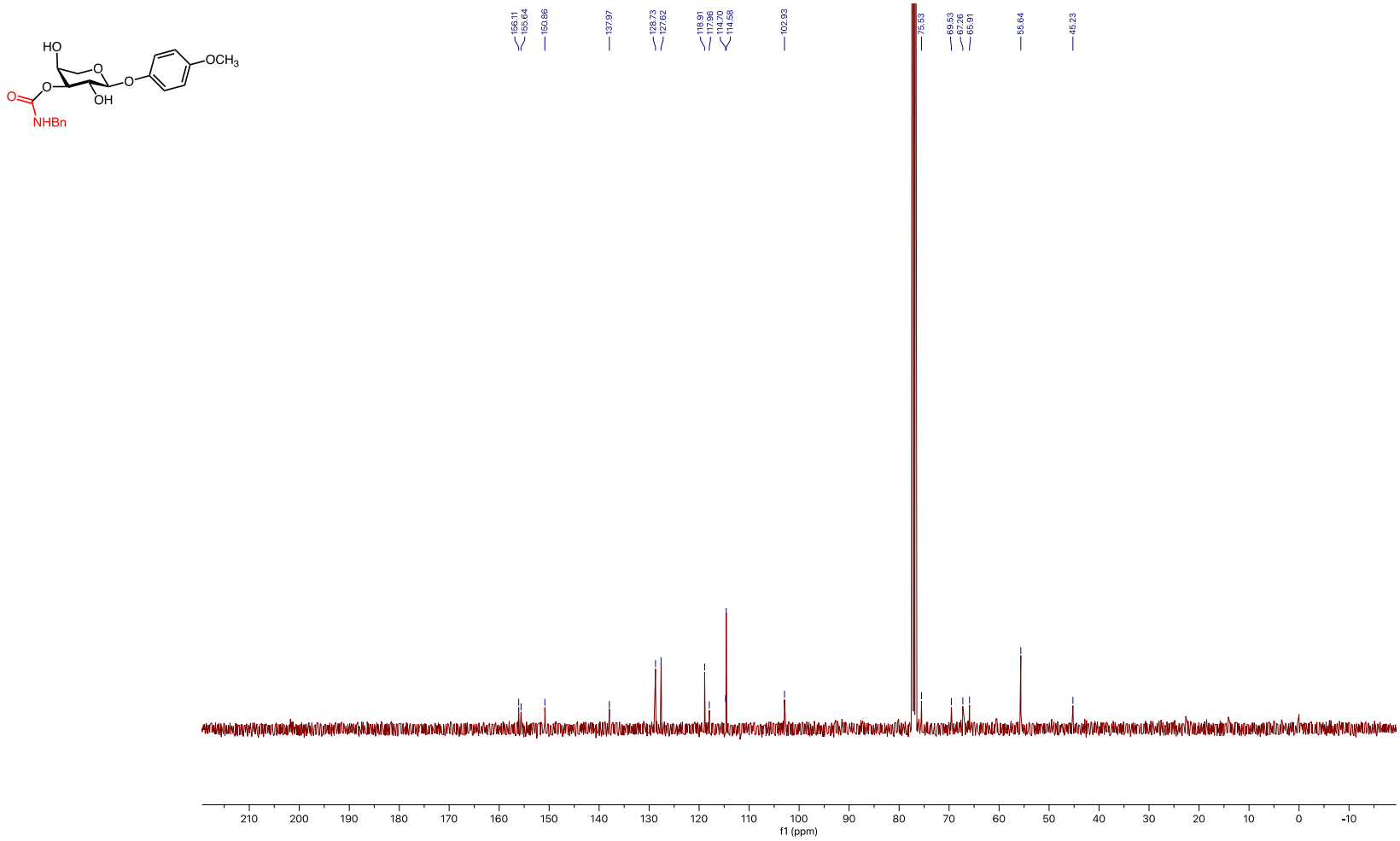


Figure S84. ^{13}C NMR spectrum (100 MHz) of **11b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-D-lyxopyranoside **12b**

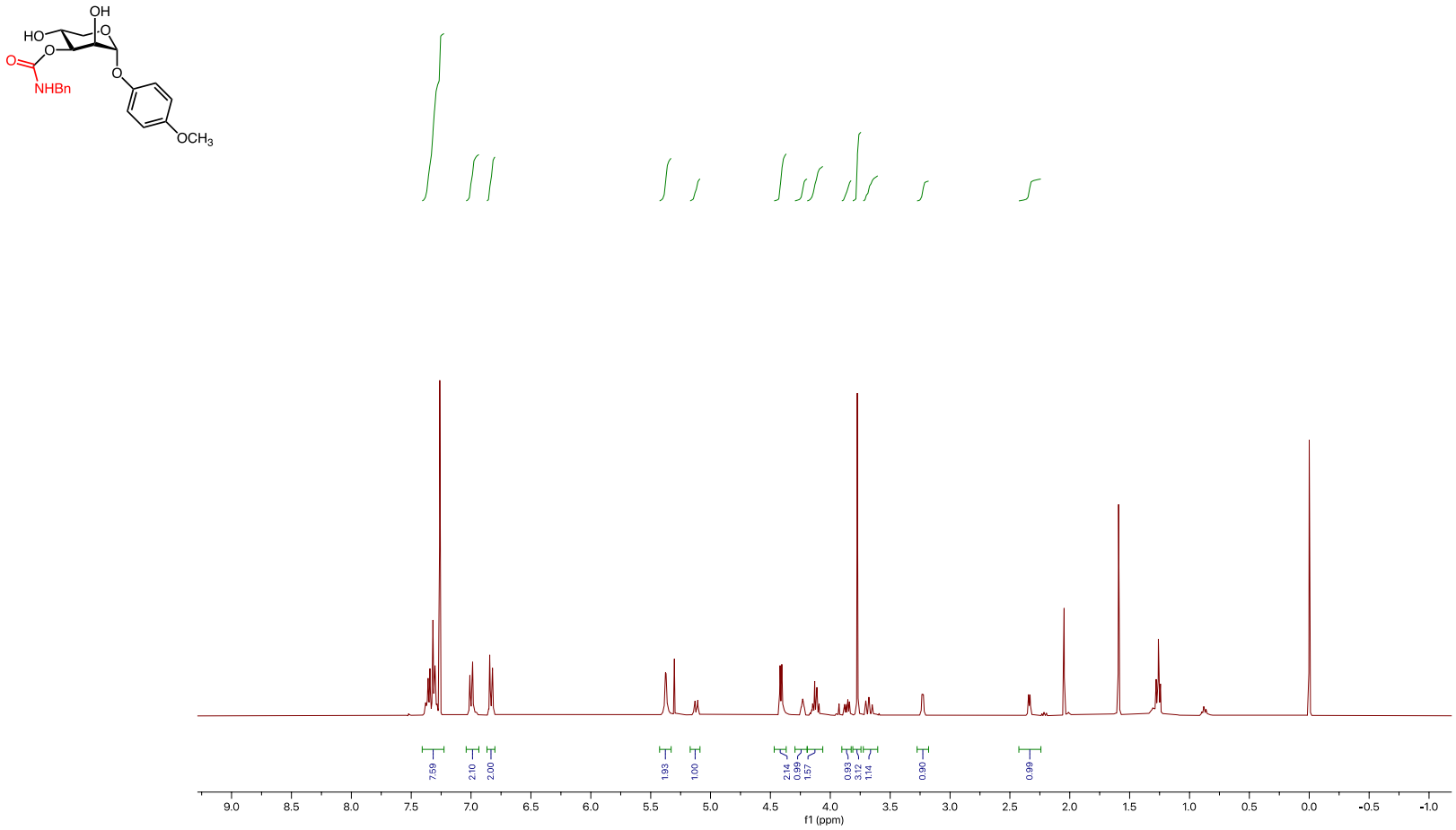


Figure S85. ^{1}H NMR spectrum (400 MHz) of **12b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-D-lyxopyranoside **12b**

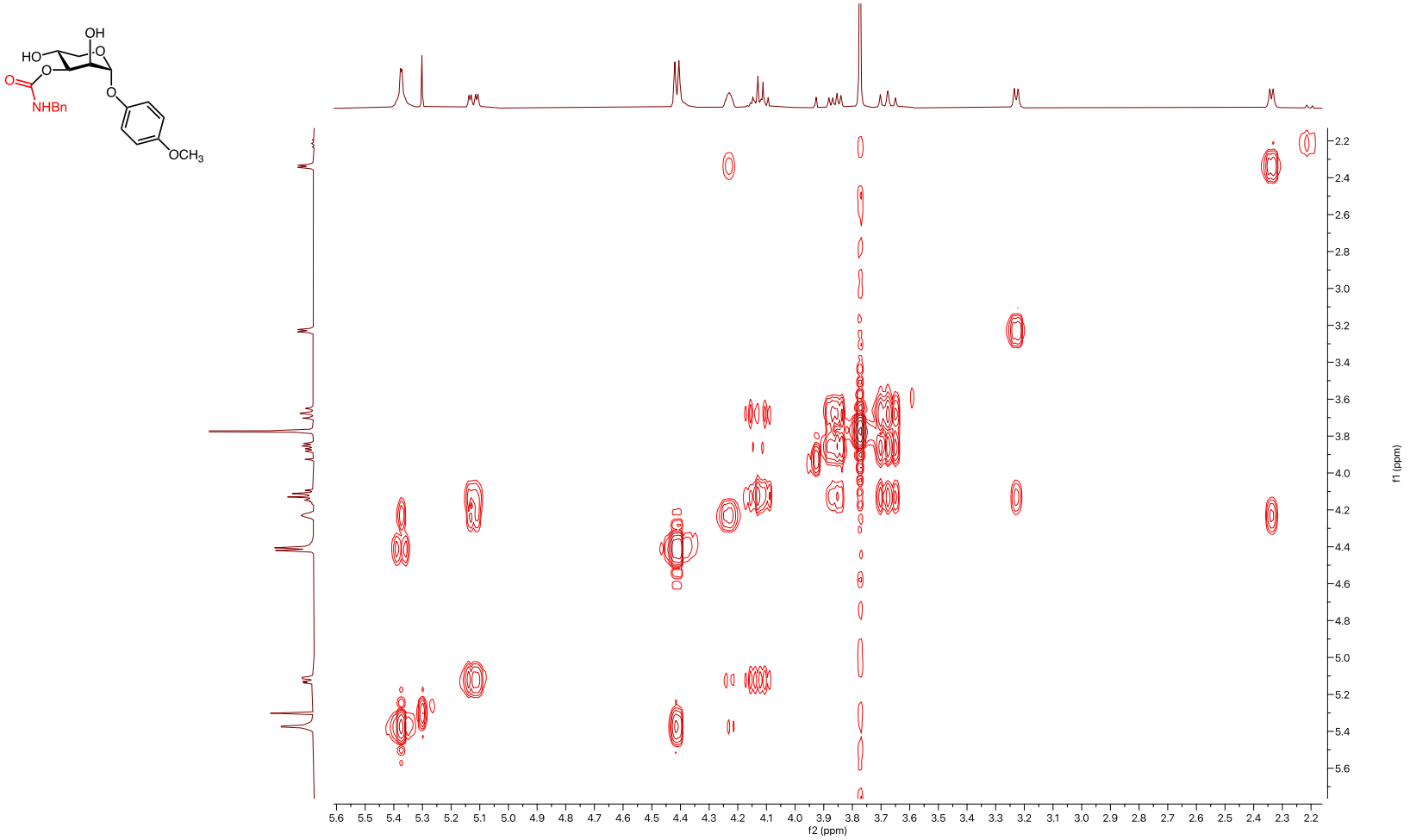


Figure S86. ^{1}H-^{1}H COSY spectrum (400 MHz) of **12b** in $CDCl_3$

4-methoxyphenyl 3-*O*-benzylcarbamoyl-α-D-lyxopyranoside **12b**

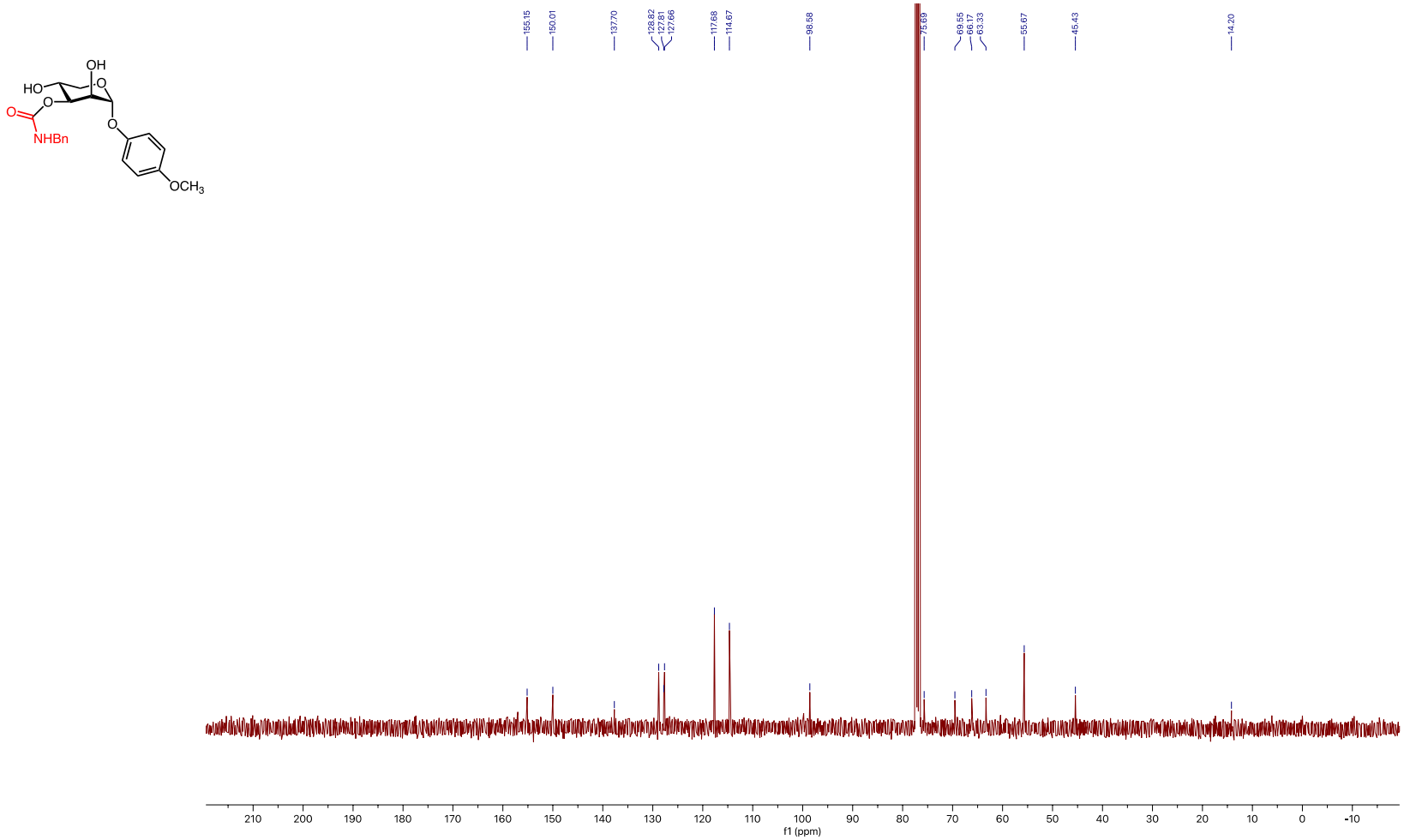
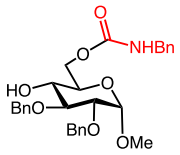


Figure S87. ^{13}C NMR spectrum (100 MHz) of **12b** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-glucopyranoside **13**



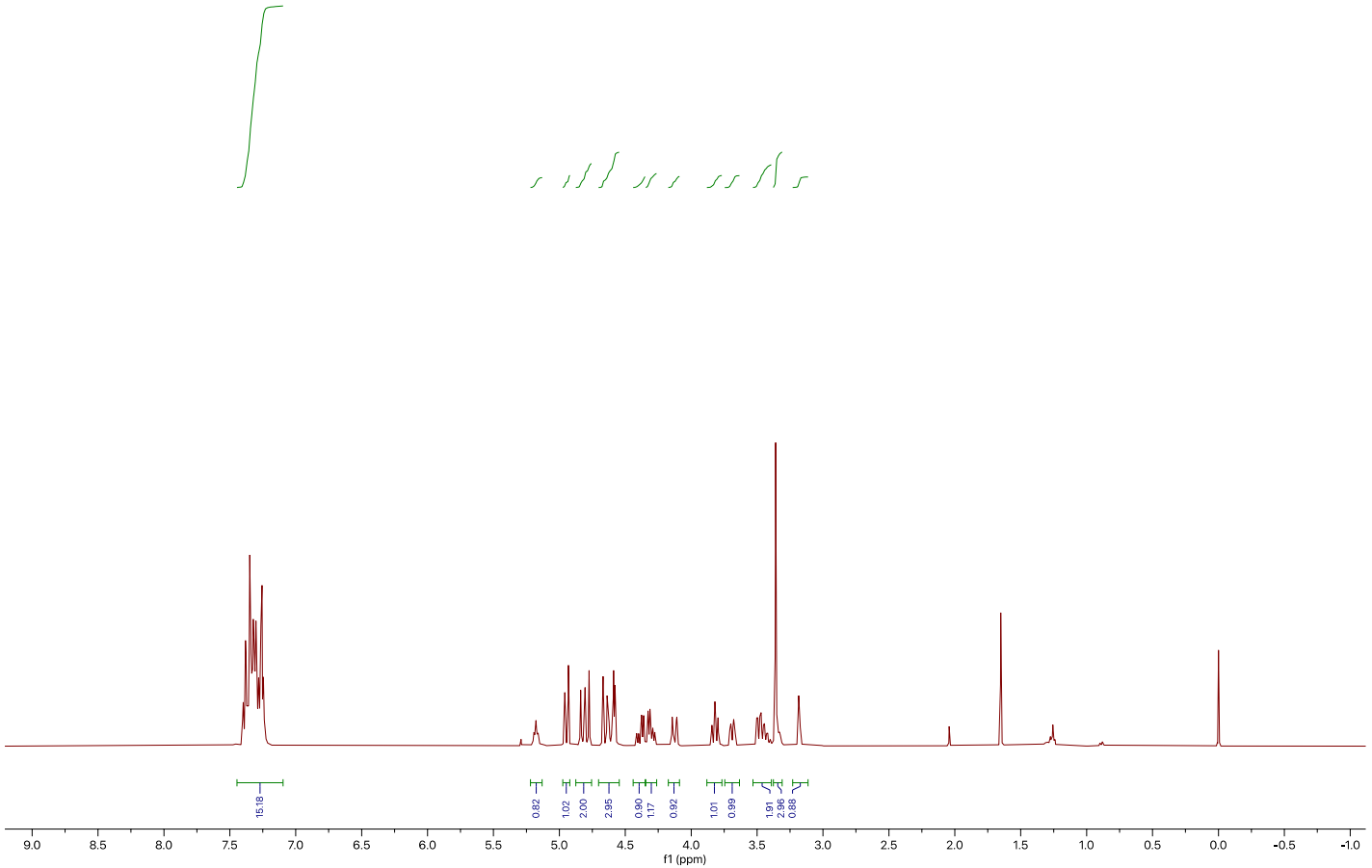


Figure S88. ^{1}H NMR spectrum (400 MHz) of **13** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-glucopyranoside **13**

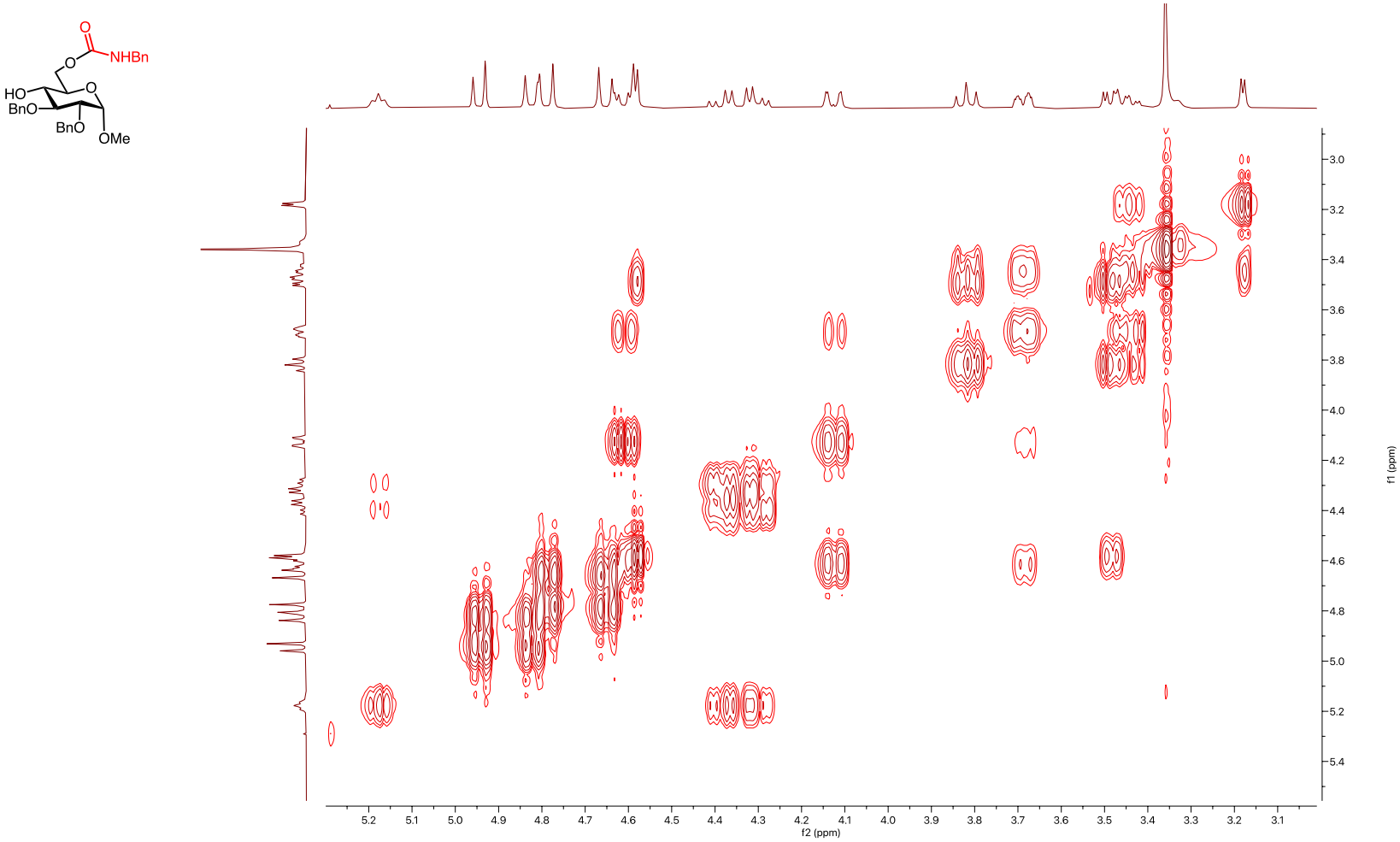


Figure S89. ^{1}H-^{1}H COSY spectrum (400 MHz) of **13** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-glucopyranoside **13**

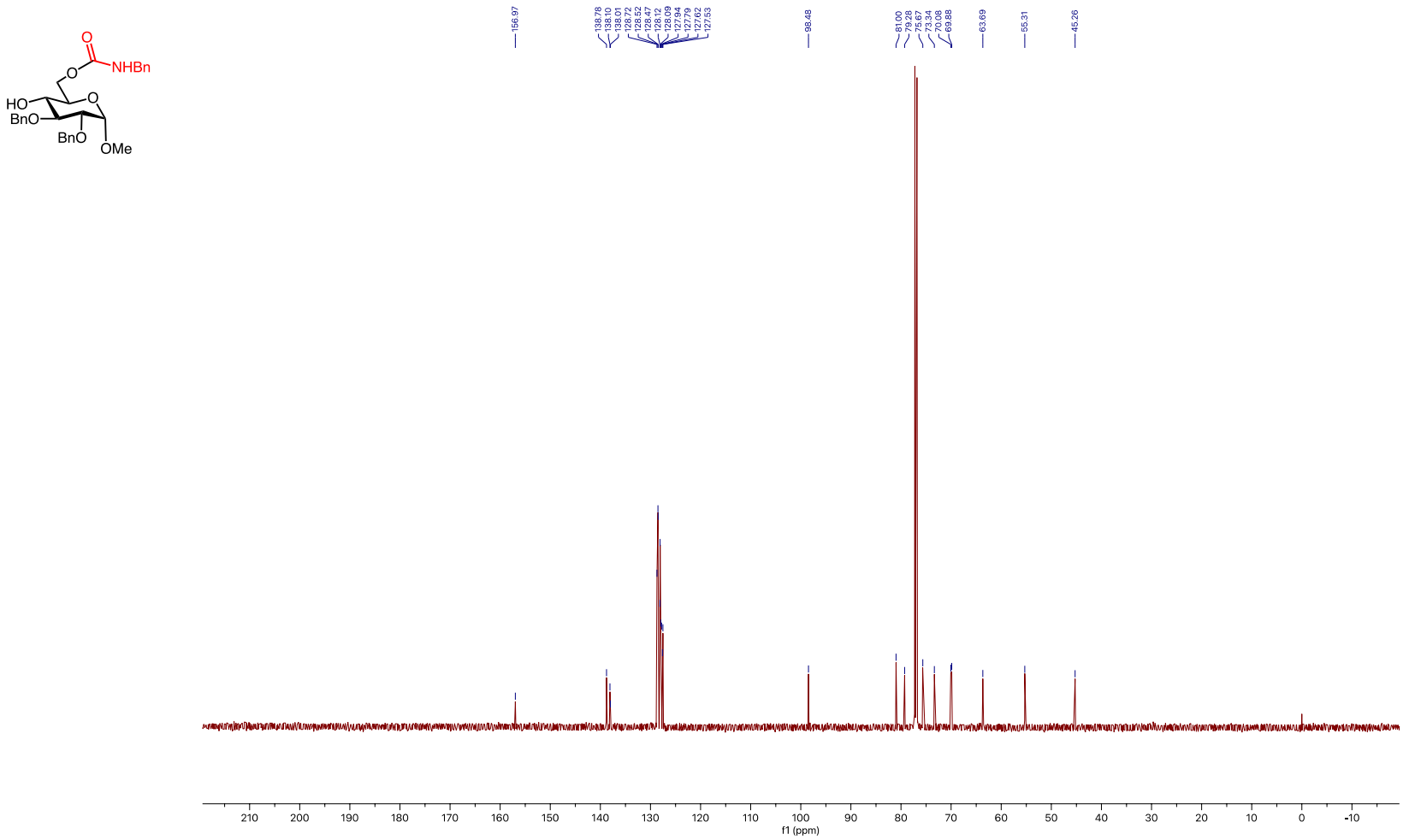


Figure S90. ^{13}C NMR spectrum (100 MHz) of **13** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-galactopyranoside **14**

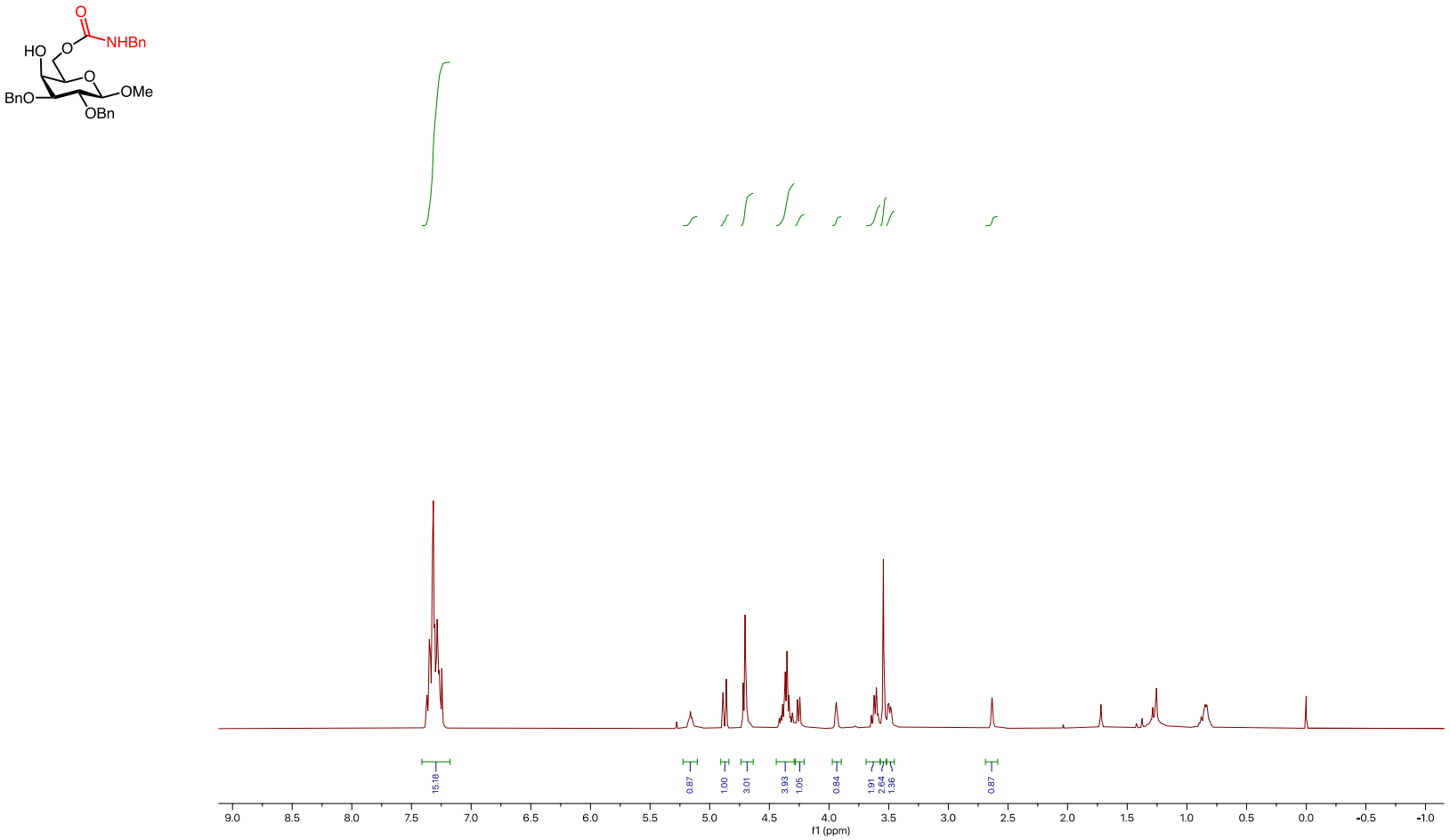


Figure S91. ^{1}H NMR spectrum (400 MHz) of **13** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-galactopyranoside **14**

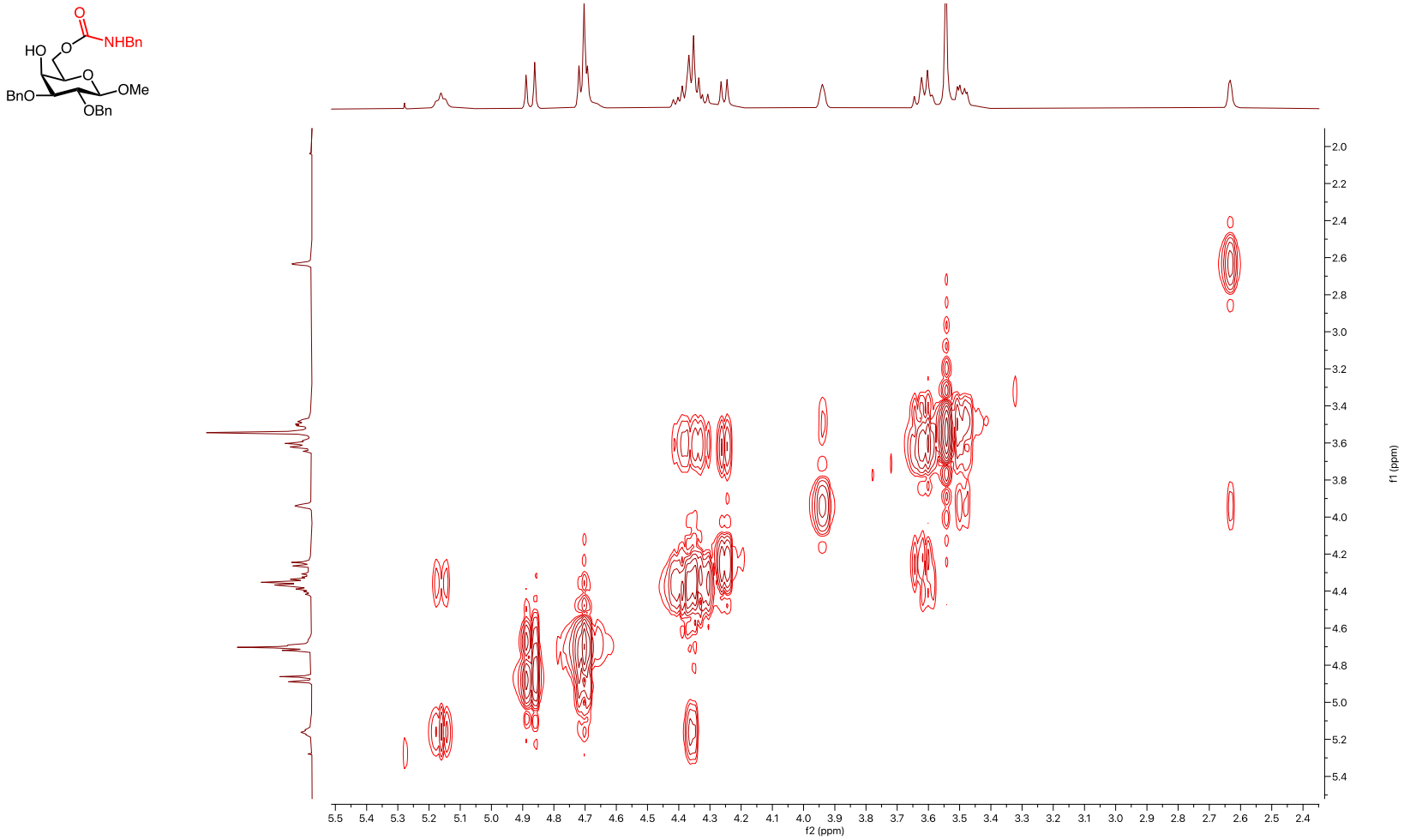


Figure S92. ^{1}H-^{1}H COSY spectrum (400 MHz) of **14** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-galactopyranoside **14**

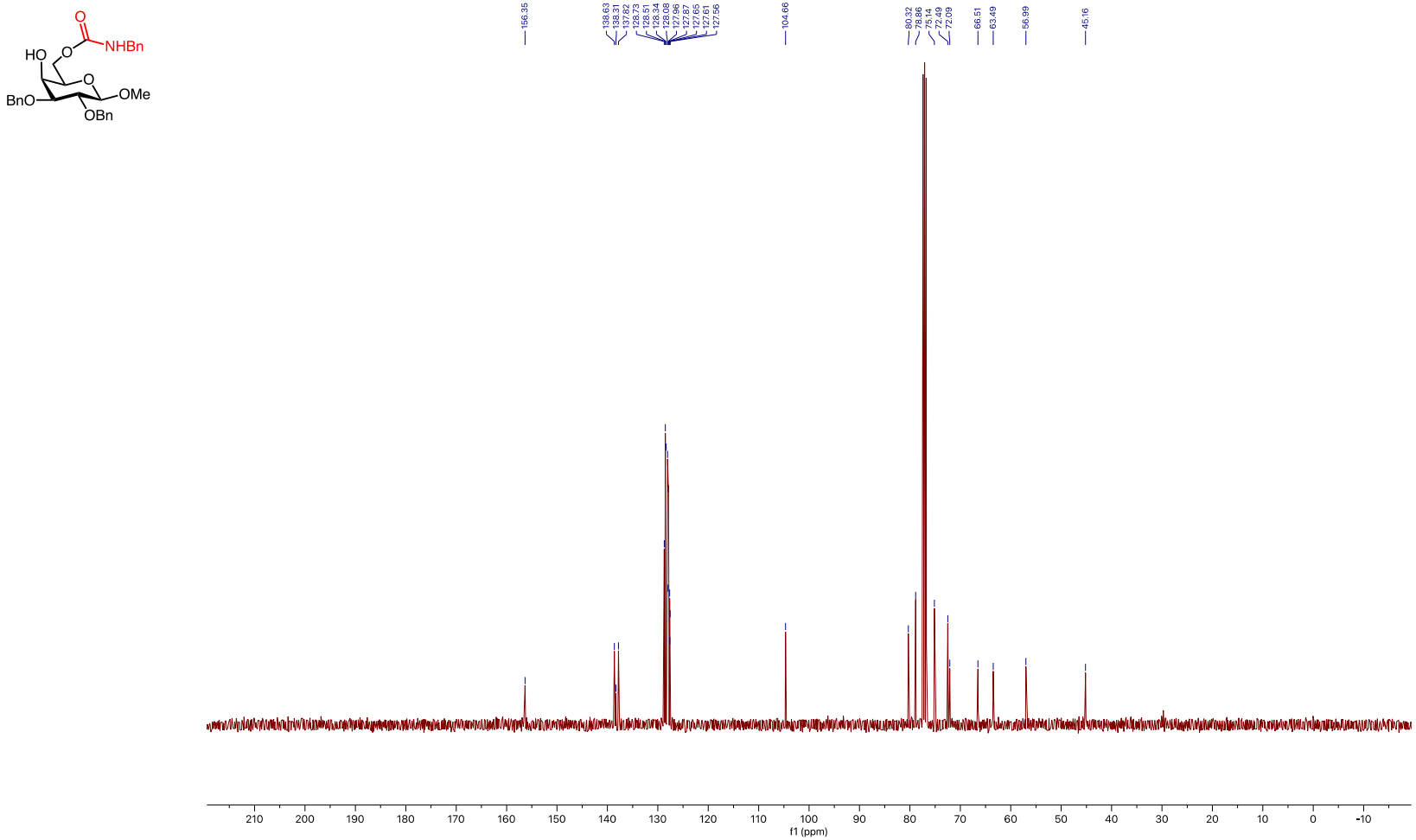
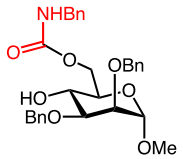


Figure S93. ^{13}C NMR spectrum (100 MHz) of **14** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-mannopyranoside **15**



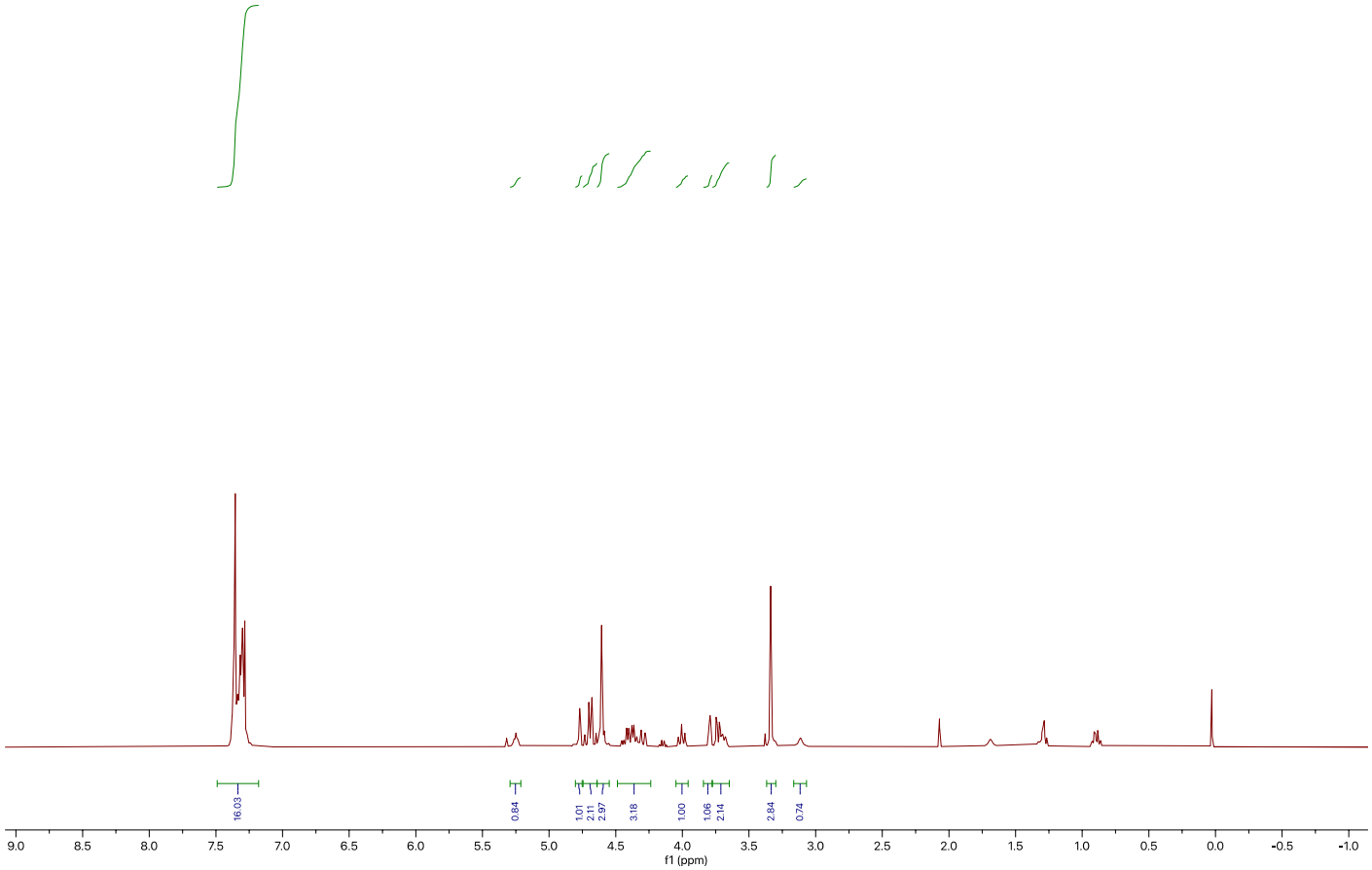
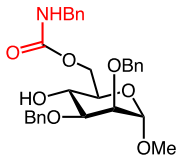


Figure S94. ^{1}H NMR spectrum (400 MHz) of **15** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-mannopyranoside **15**



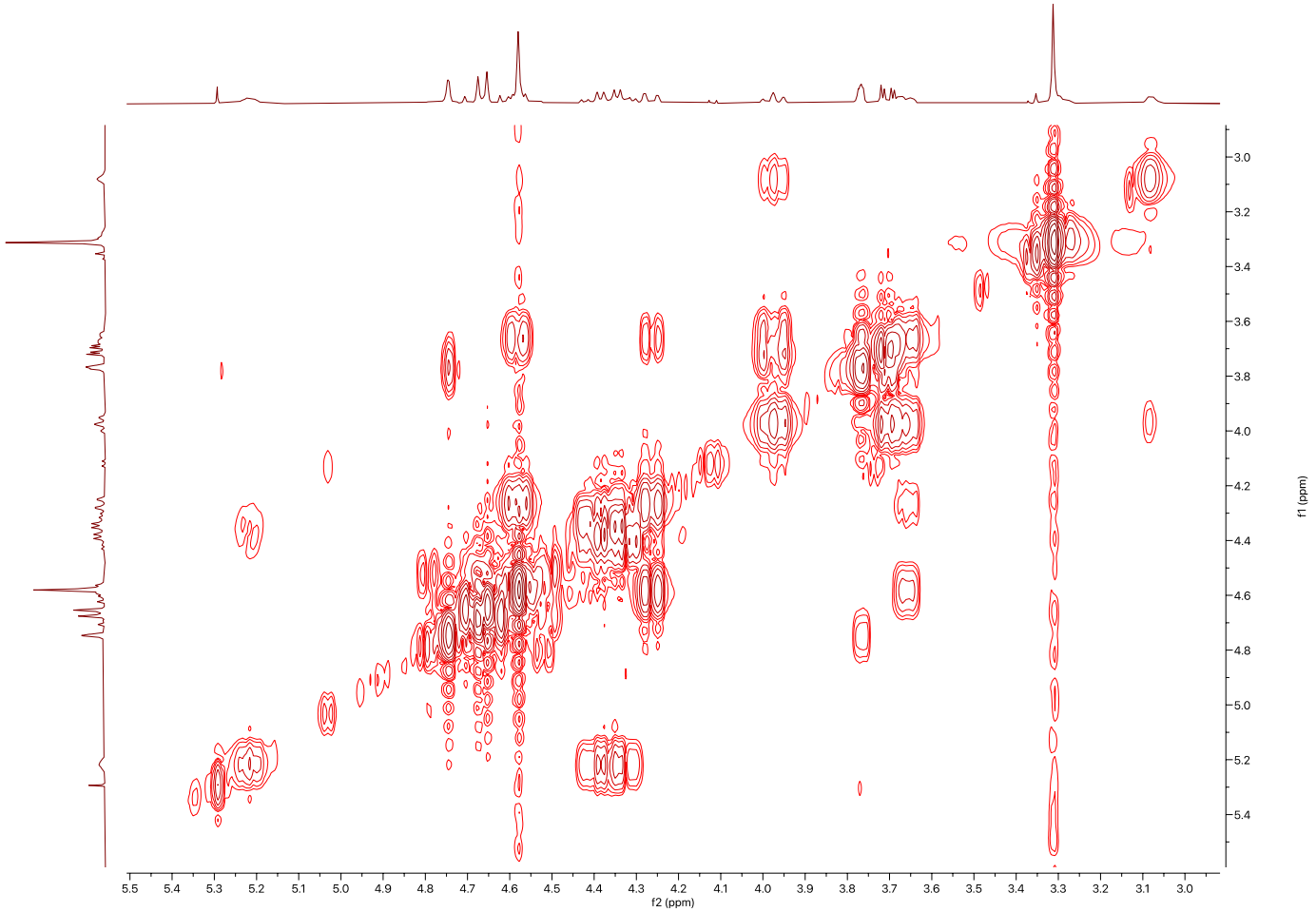


Figure S95. ^{1}H-^{1}H COSY spectrum (400 MHz) of **15** in $CDCl_3$

Methyl 6-*O*-benzylcarbamoyl-2,3-*O*-benzyl-α-D-mannopyranoside **15**

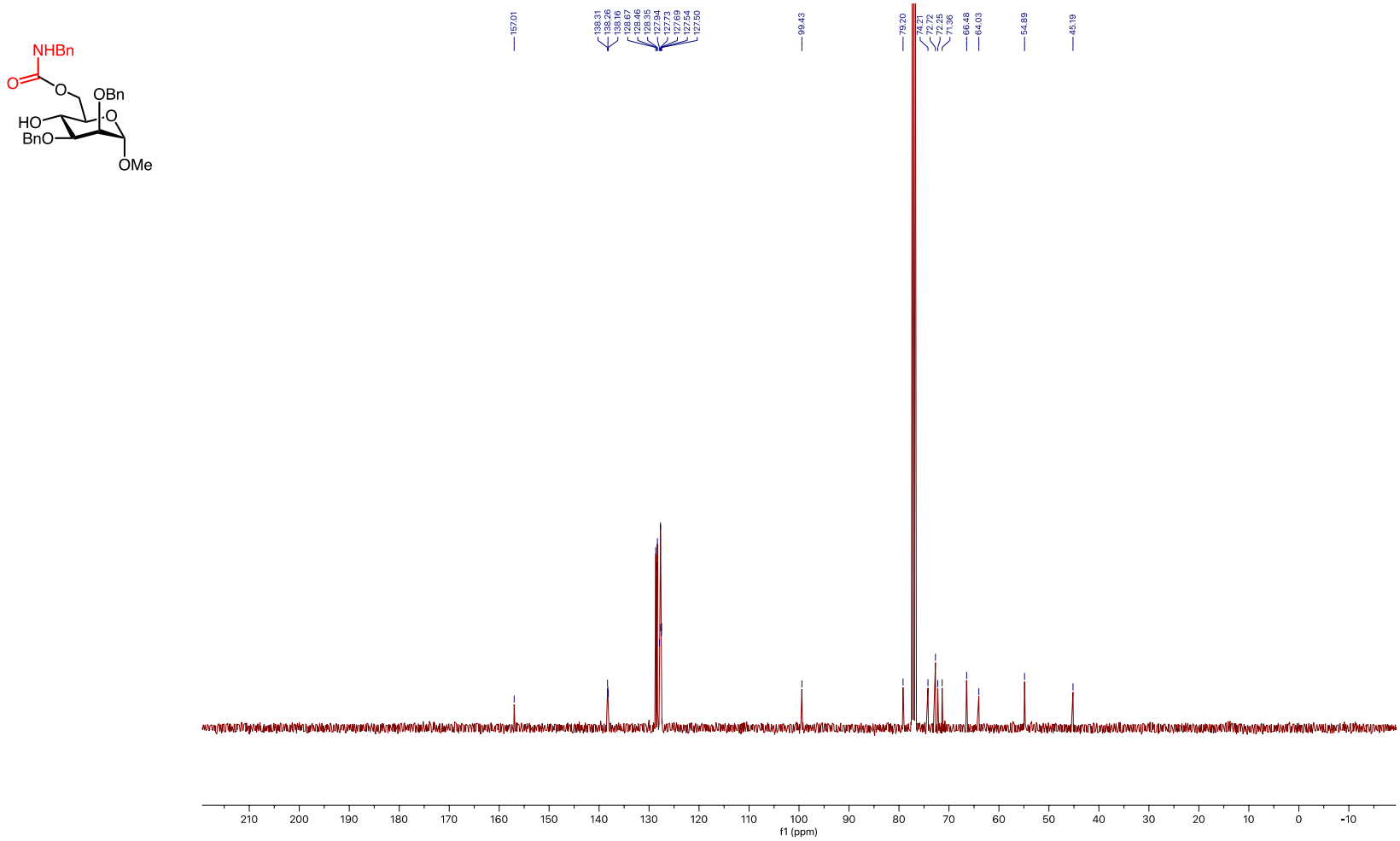
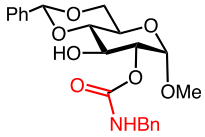


Figure S96. ^{13}C NMR spectrum (100 MHz) of **15** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-glucopyranoside **16**



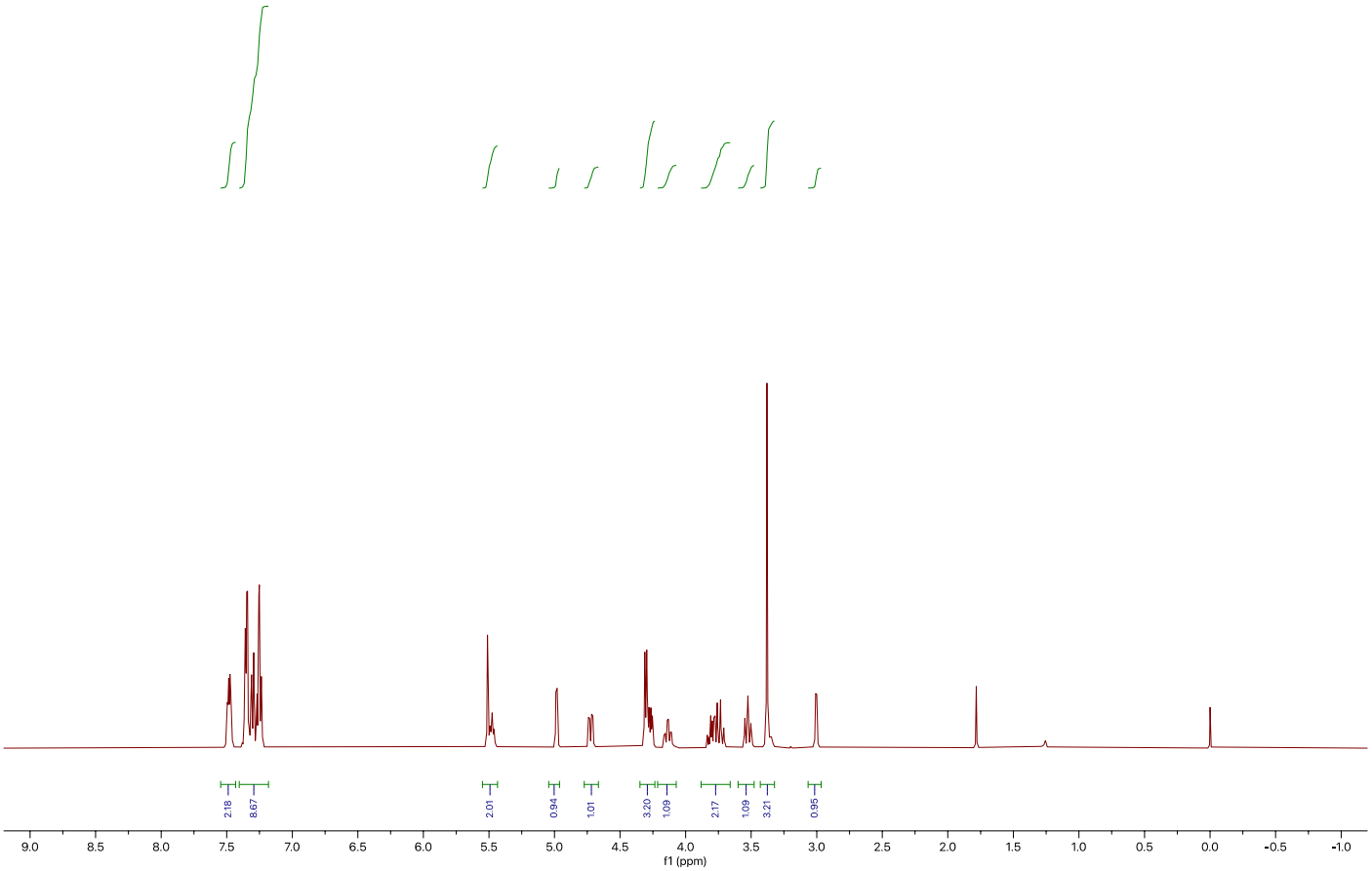


Figure S97. ^{1}H NMR spectrum (400 MHz) of **16** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-glucopyranoside **16**

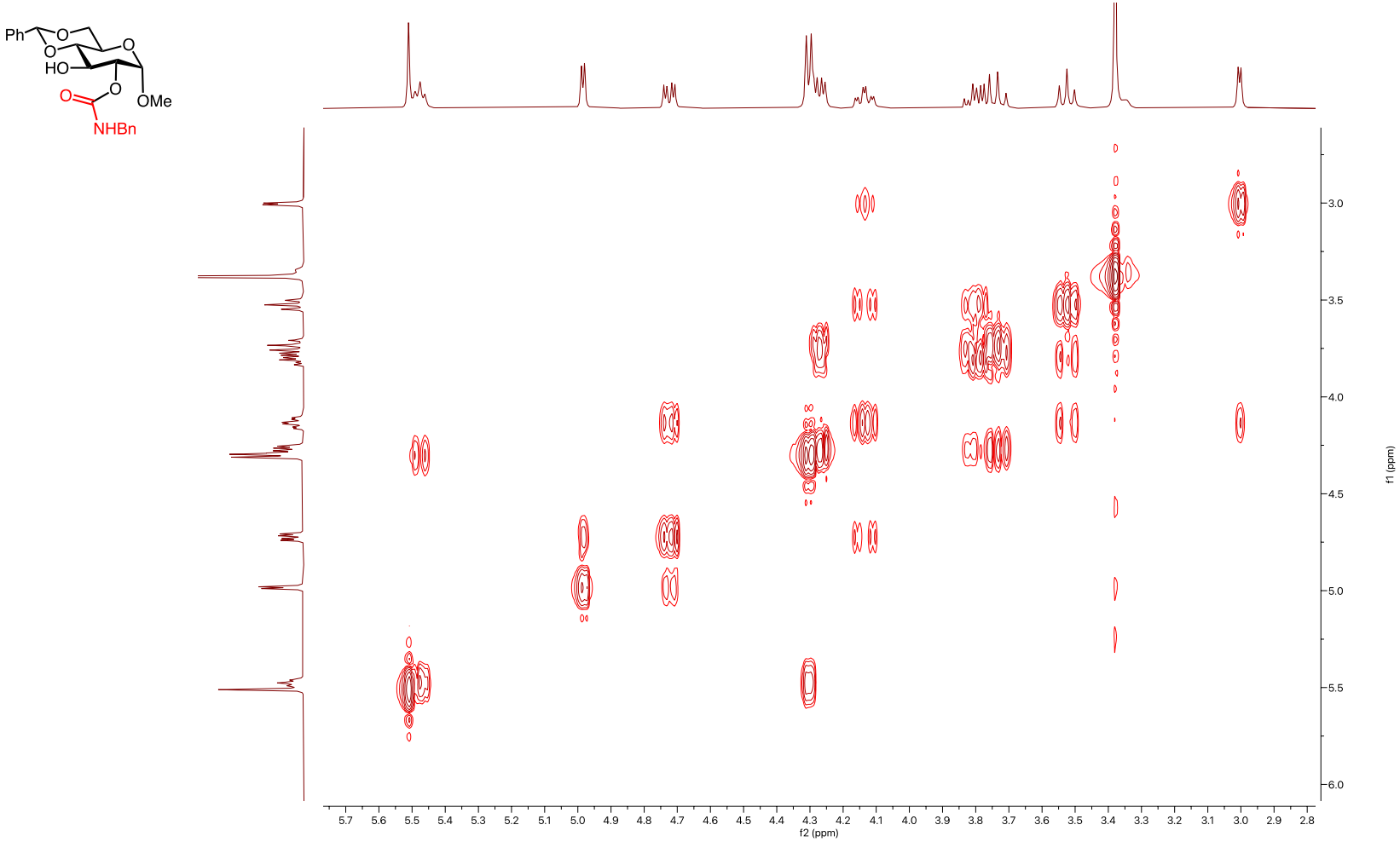


Figure S98. ^{1}H-^{1}H COSY spectrum (400 MHz) of **16** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-glucopyranoside **16**

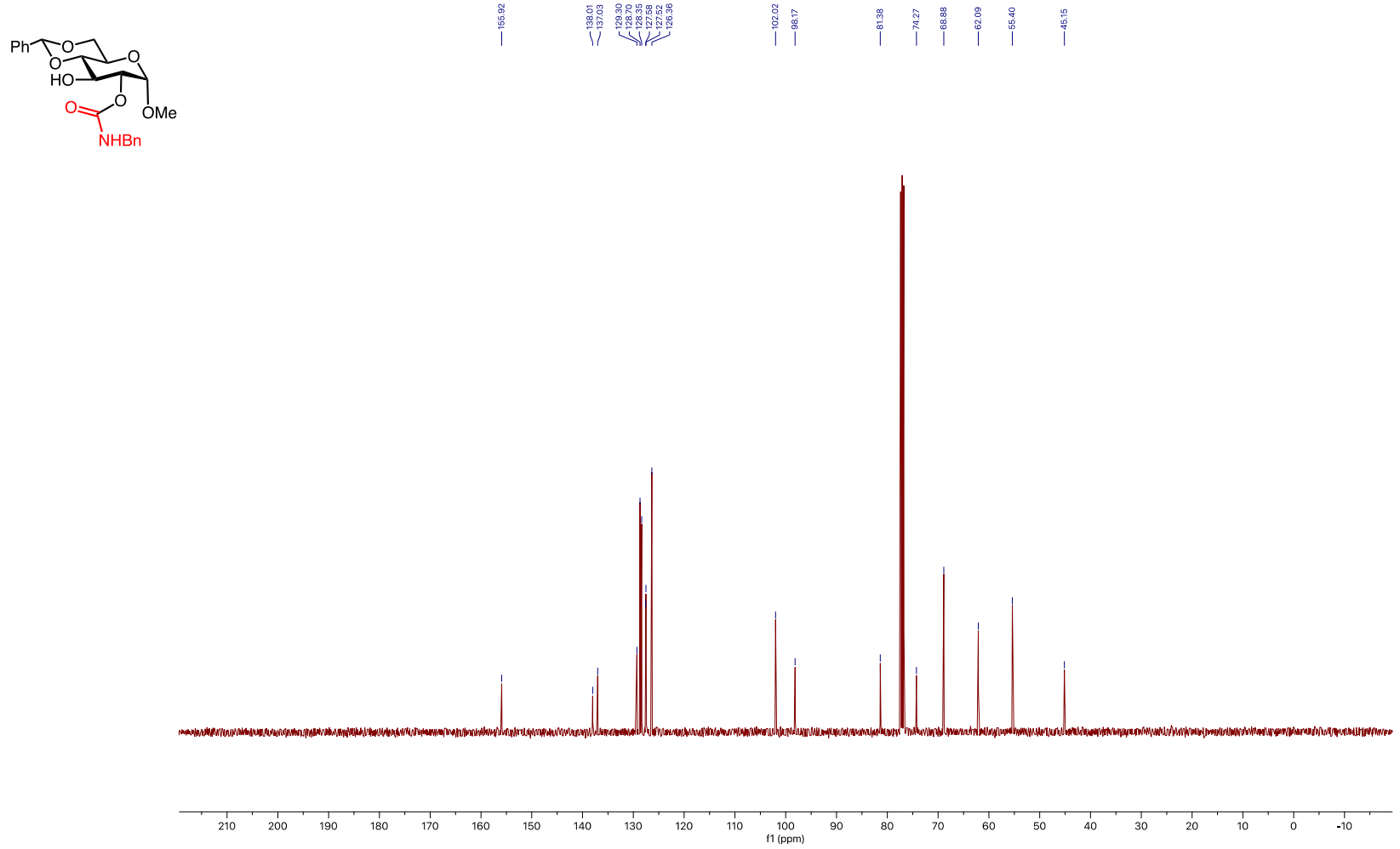
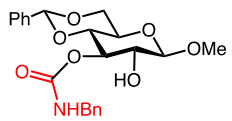


Figure S99. ^{13}C NMR spectrum (100 MHz) of **16** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-glucopyranoside **17**



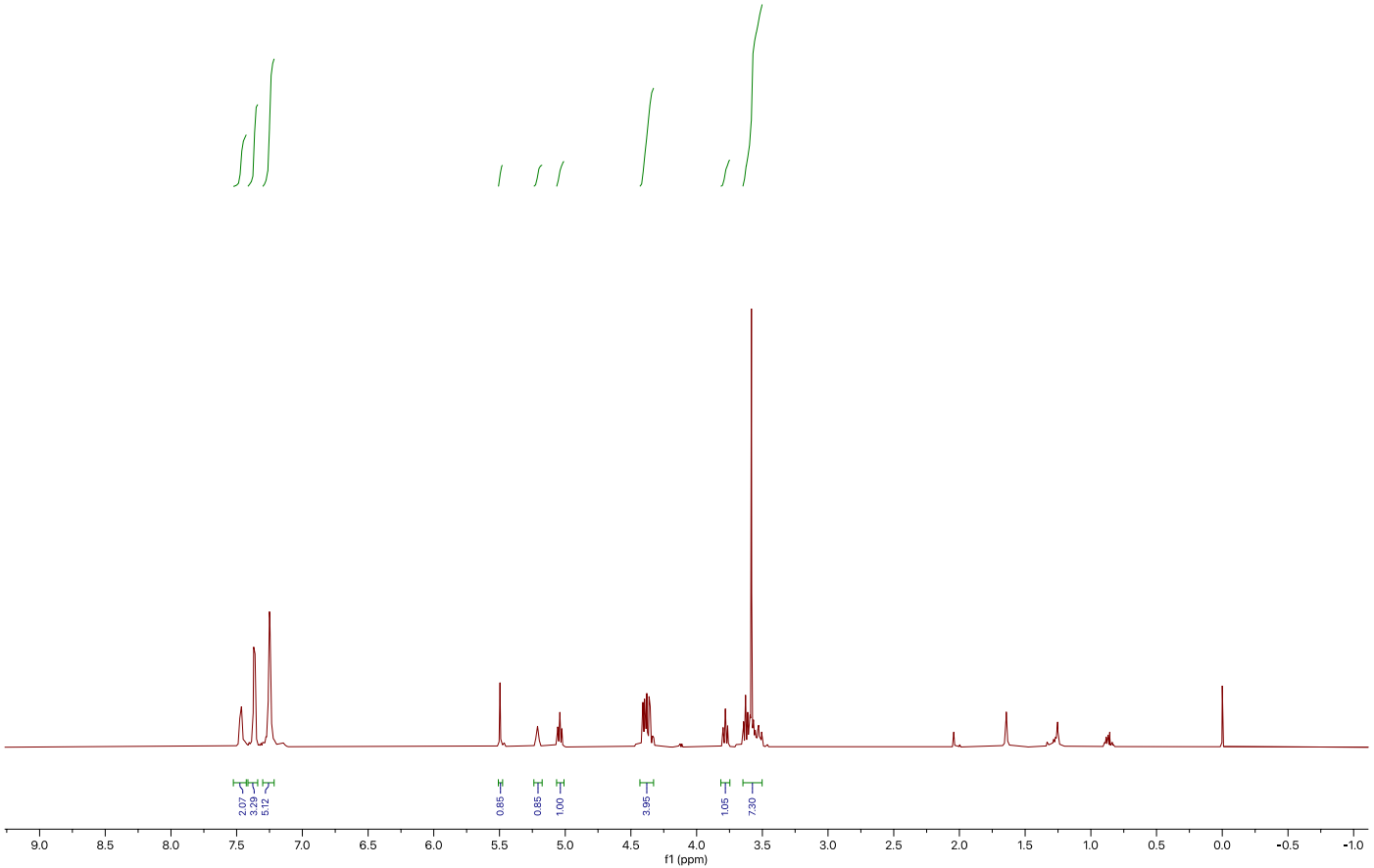


Figure S100. ^{1}H NMR spectrum (600 MHz) of **17** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-glucopyranoside **17**

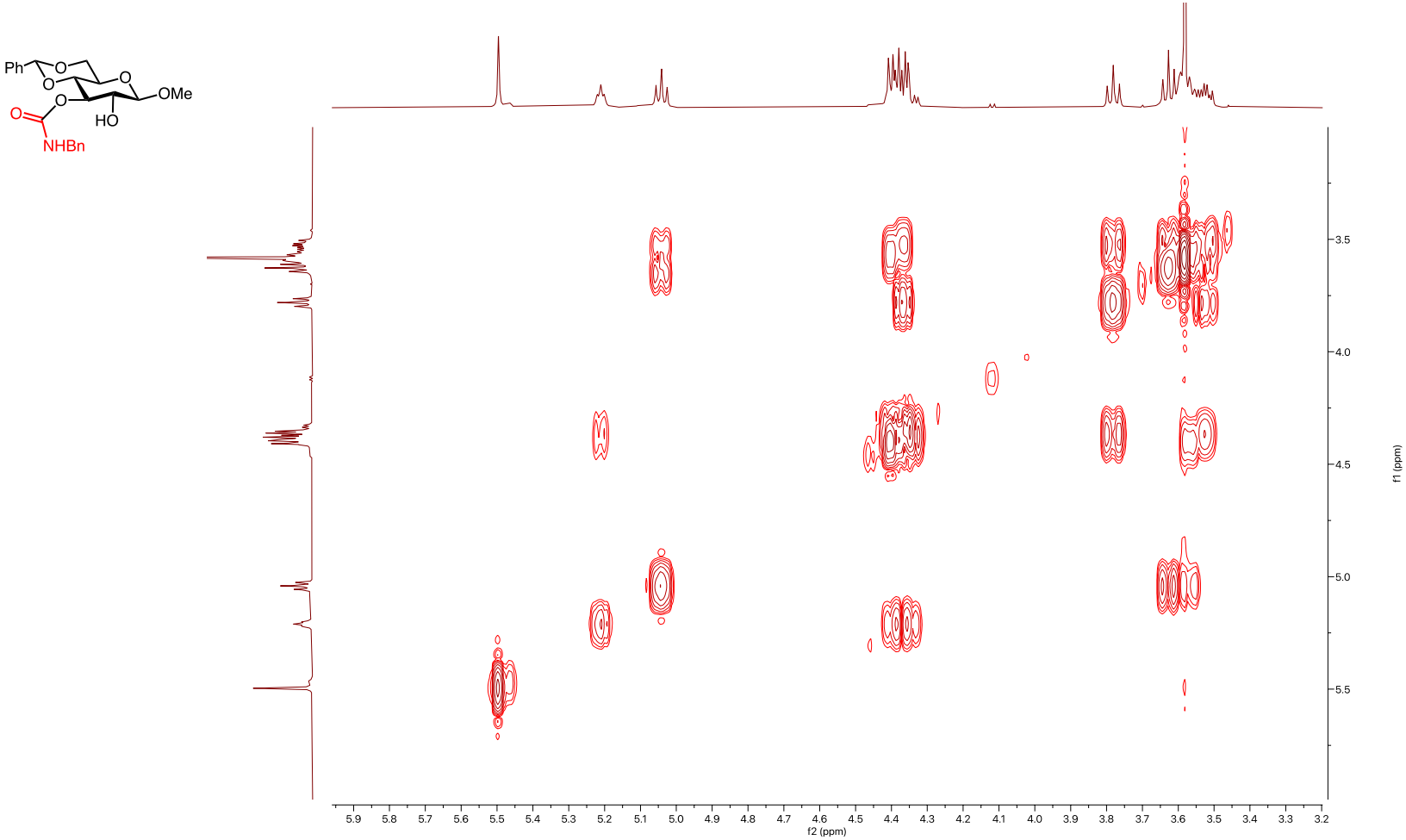


Figure S101. ^{1}H-^{1}H COSY spectrum (600 MHz) of **17** in $CDCl_3$

Methyl 3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-glucopyranoside **17**

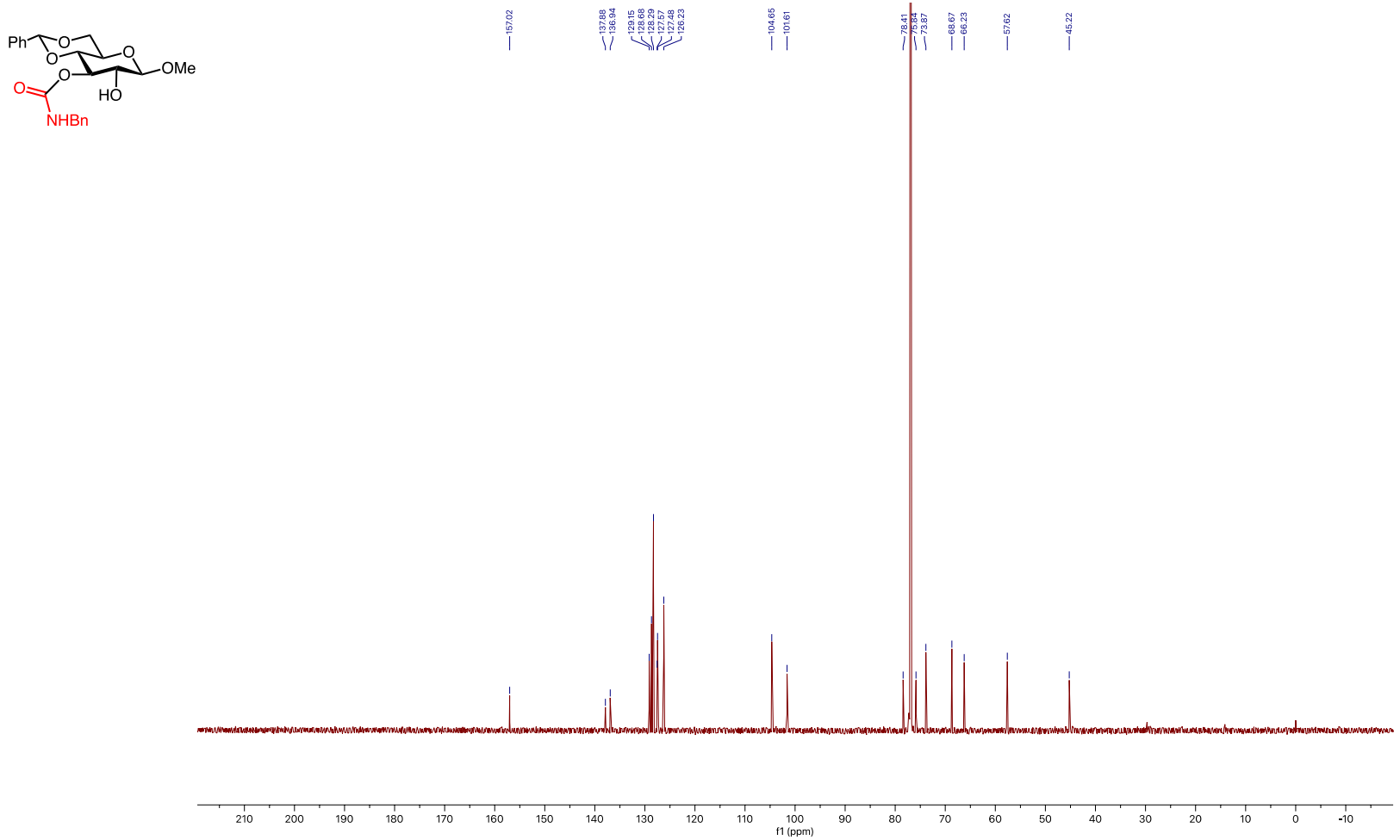
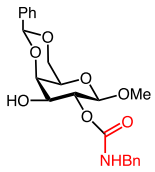


Figure S102. ^{13}C NMR spectrum (100 MHz) of **17** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-galactopyranoside **18**



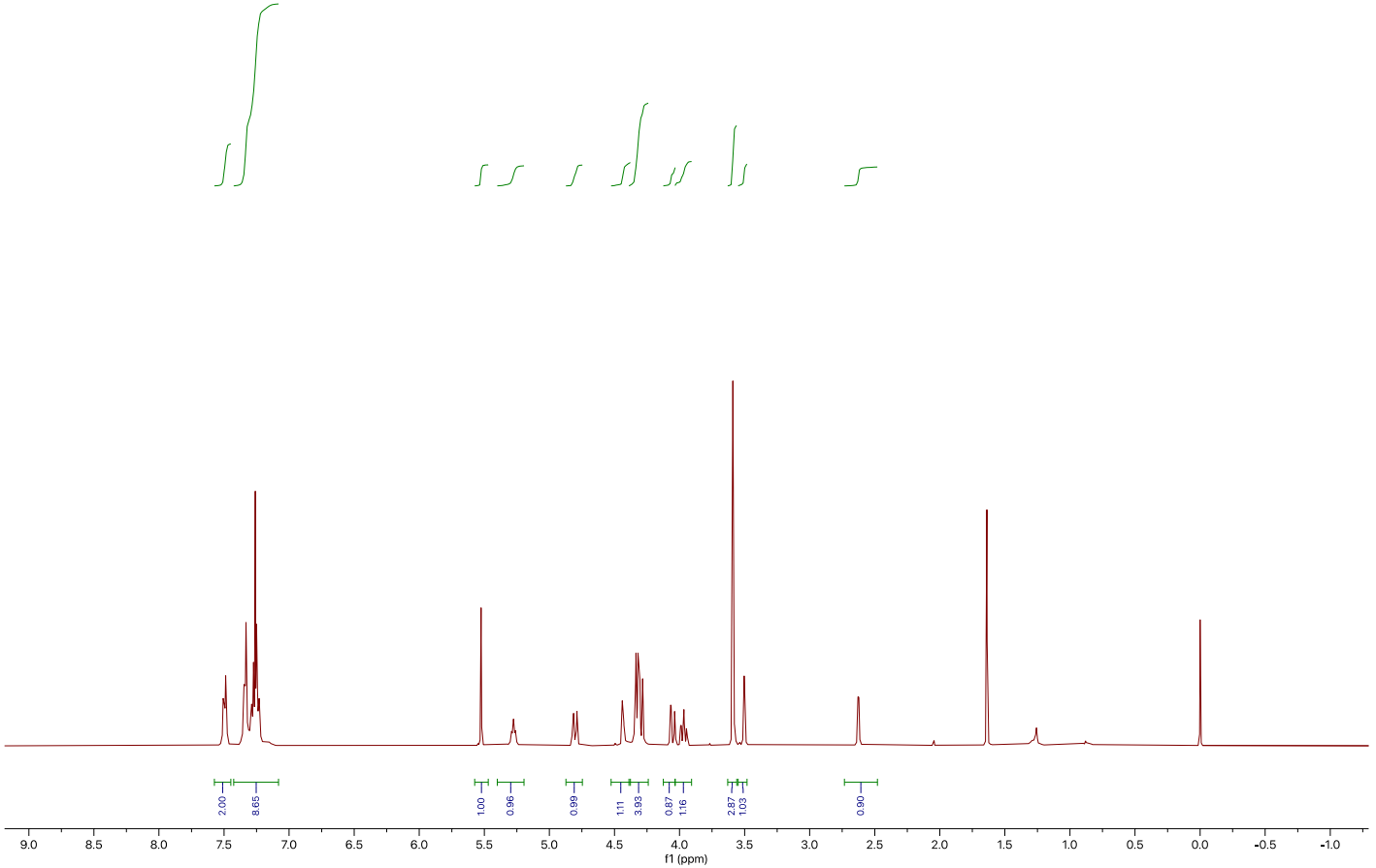


Figure S103. ^{1}H NMR spectrum (400 MHz) of **18** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-galactopyranoside **18**

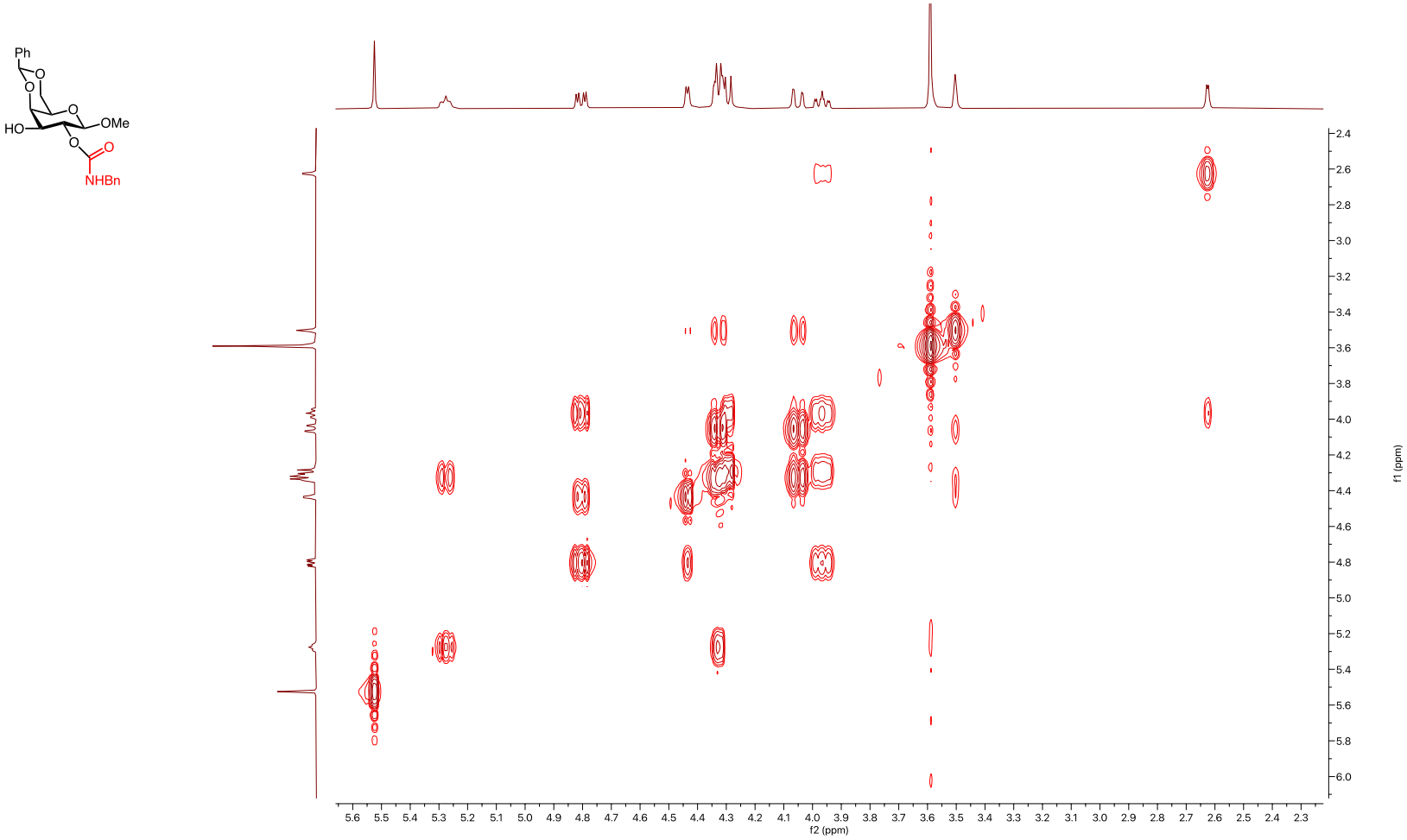


Figure S104. ^{1}H-^{1}H COSY spectrum (400 MHz) of **18** in $CDCl_3$

Methyl 2-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-β-D-galactopyranoside **18**

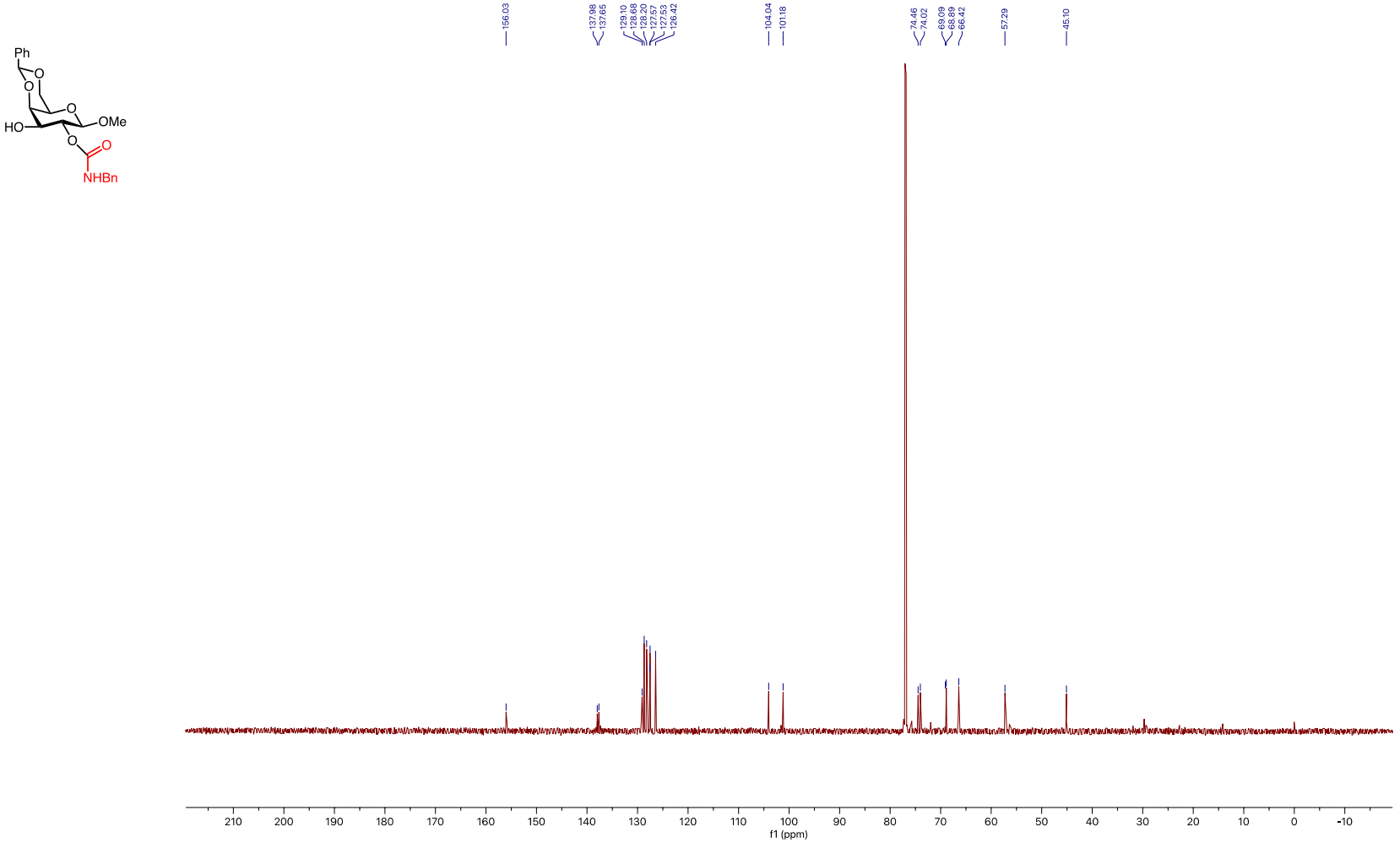


Figure S105. ^{13}C NMR spectrum (100 MHz) of **18** in $CDCl_3$

Methyl 2/3-*O*-benzylcarbamoyl-4,6-*O*-benzylidene-α-D-galactopyranoside **19a** and **19b**-**Me_2SnCl_2**

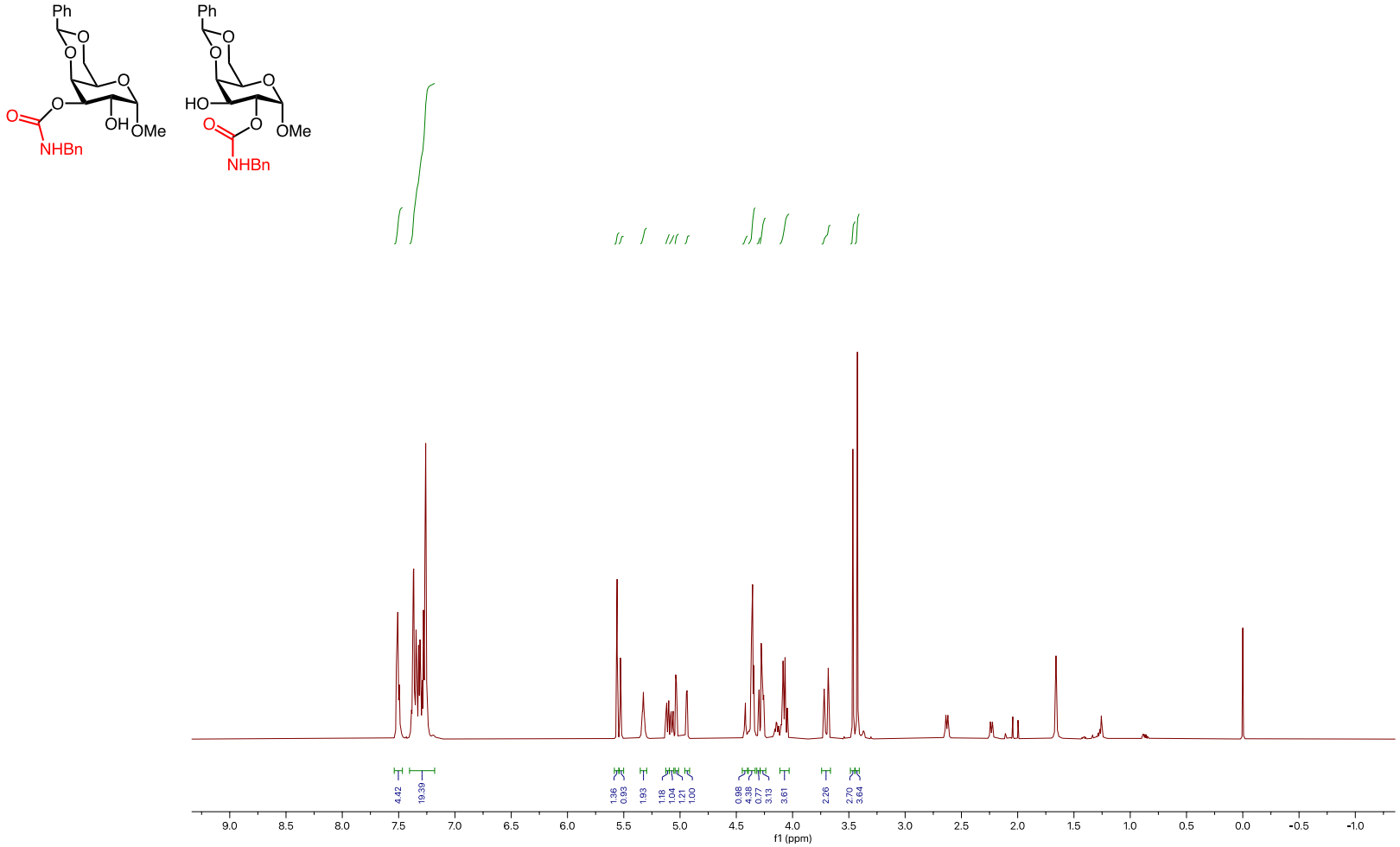


Figure S106. ^{1}H NMR spectrum (600 MHz) of **19a** and **19b** in $CDCl_3$

Methyl 2/3-O-benzylcarbamoyl-4,6-O-benzylidene-α-D-galactopyranoside **19a** and **19b** - **Me_2SnCl_2**

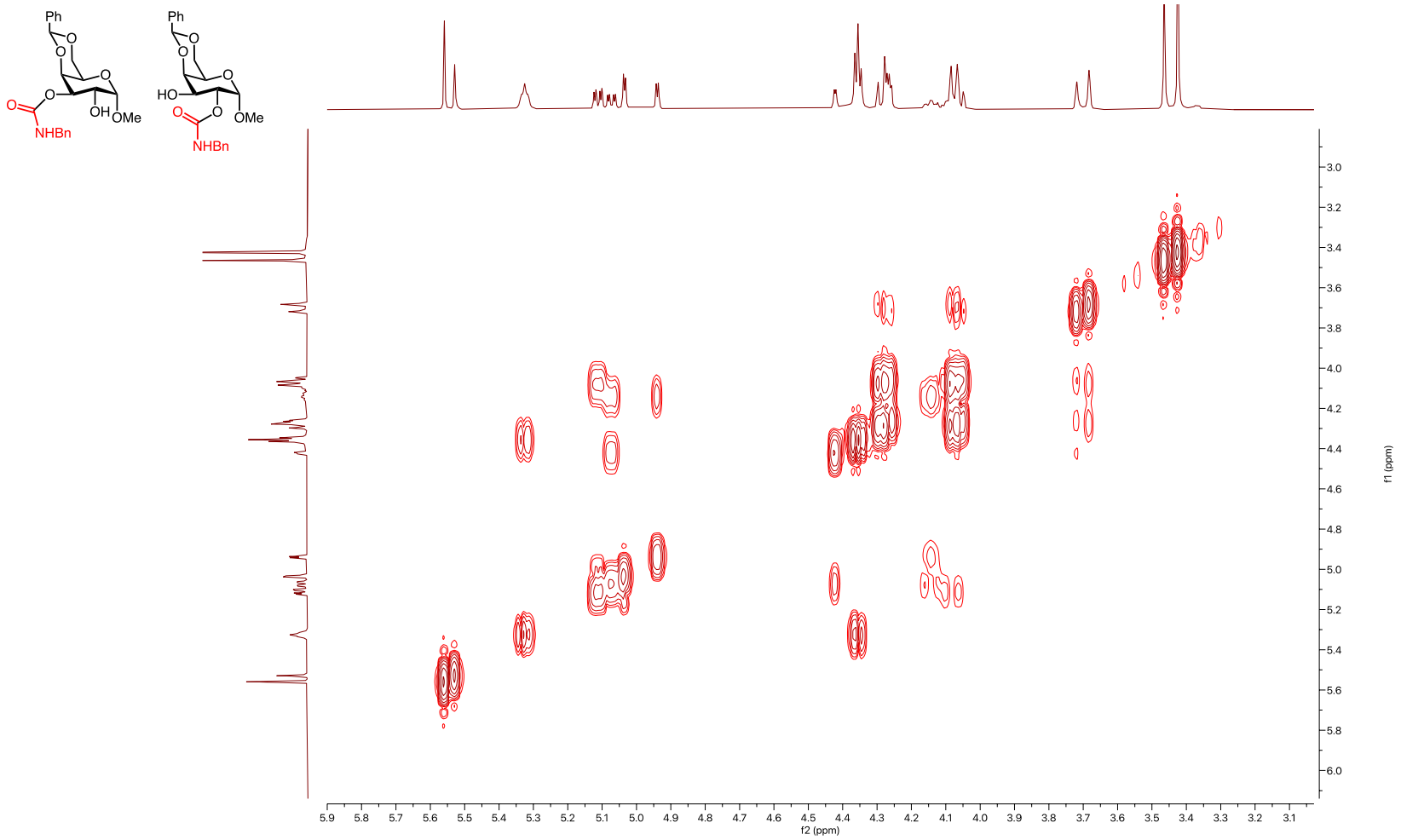


Figure S107. ^{1}H-^{1}H COSY spectrum (600 MHz) of **19a** and **19b** in $CDCl_3$

Methyl 2/3-O-benzylcarbamoyl-4,6-O-benzylidene-α-D-galactopyranoside **19a** and **19b** - **$SnCl_2$**

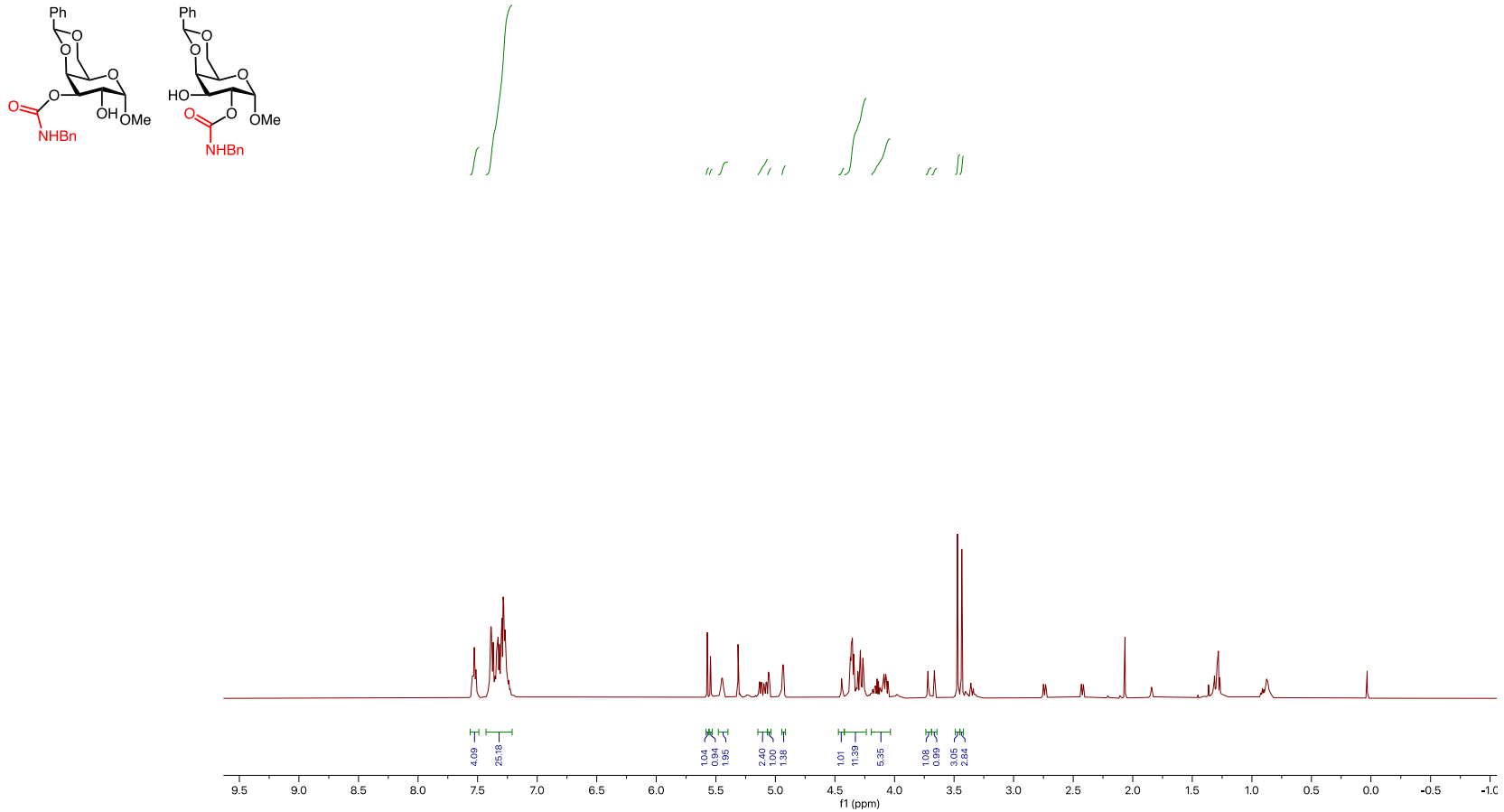


Figure S108. ^{1}H NMR spectrum (600 MHz) of **19a** and **19b** in $CDCl_3$

Methyl 2-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ag**

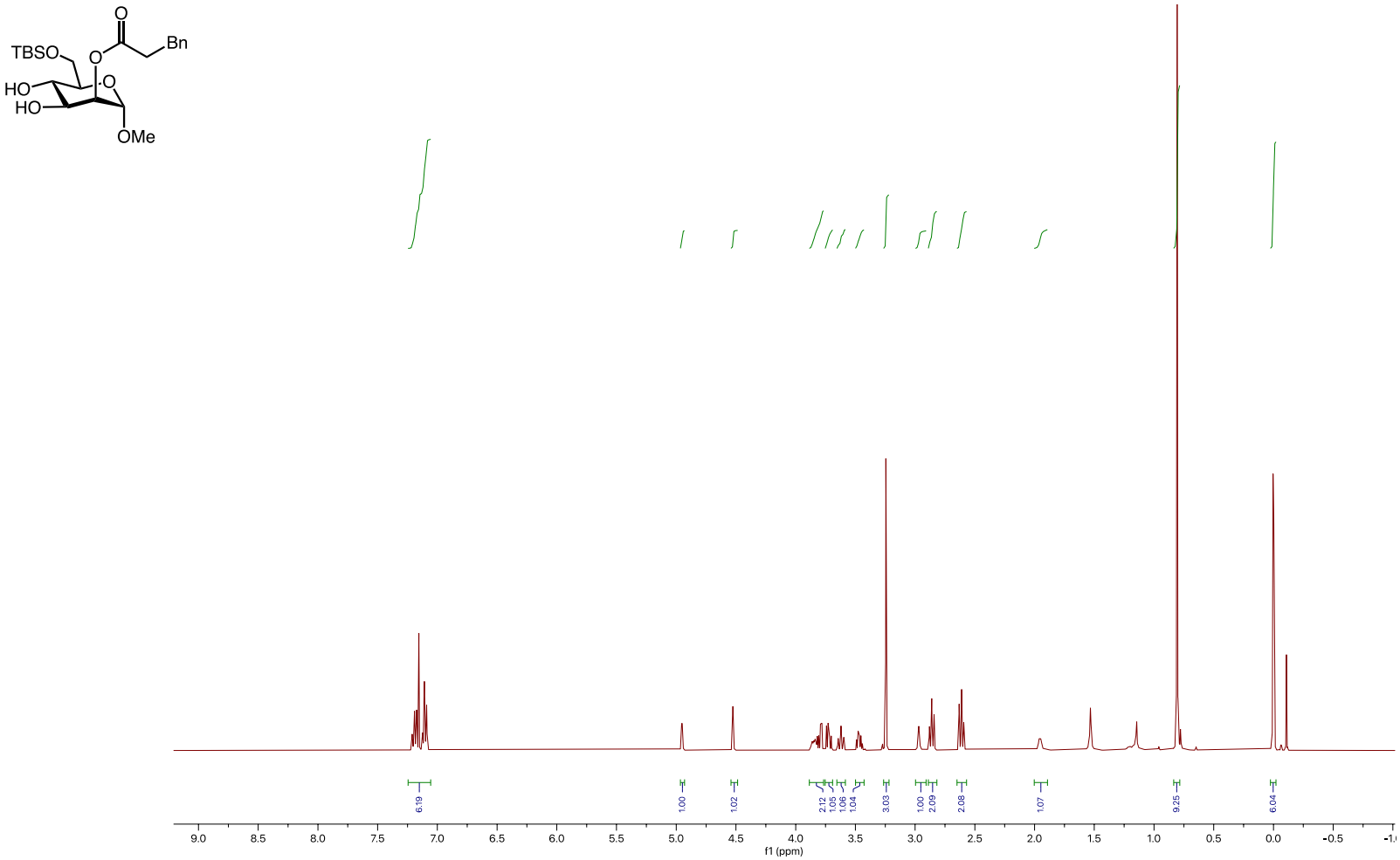


Figure S109. ^{1}H NMR spectrum (400 MHz) of **1ag** in $CDCl_3$

Methyl 2-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ag**

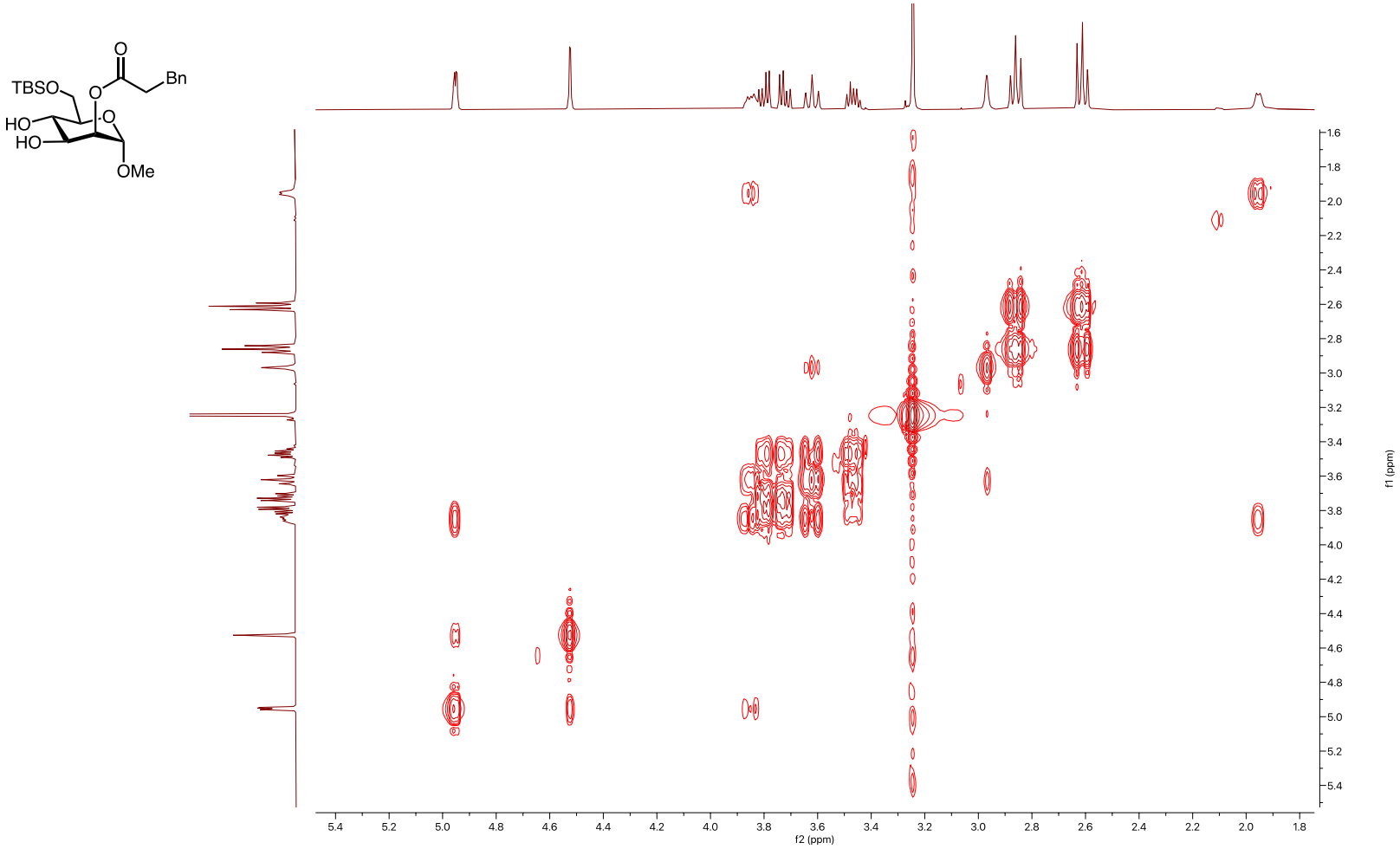
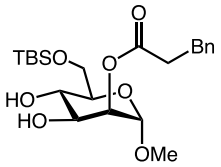


Figure S110. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ag** in $CDCl_3$

Methyl 2-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ag**



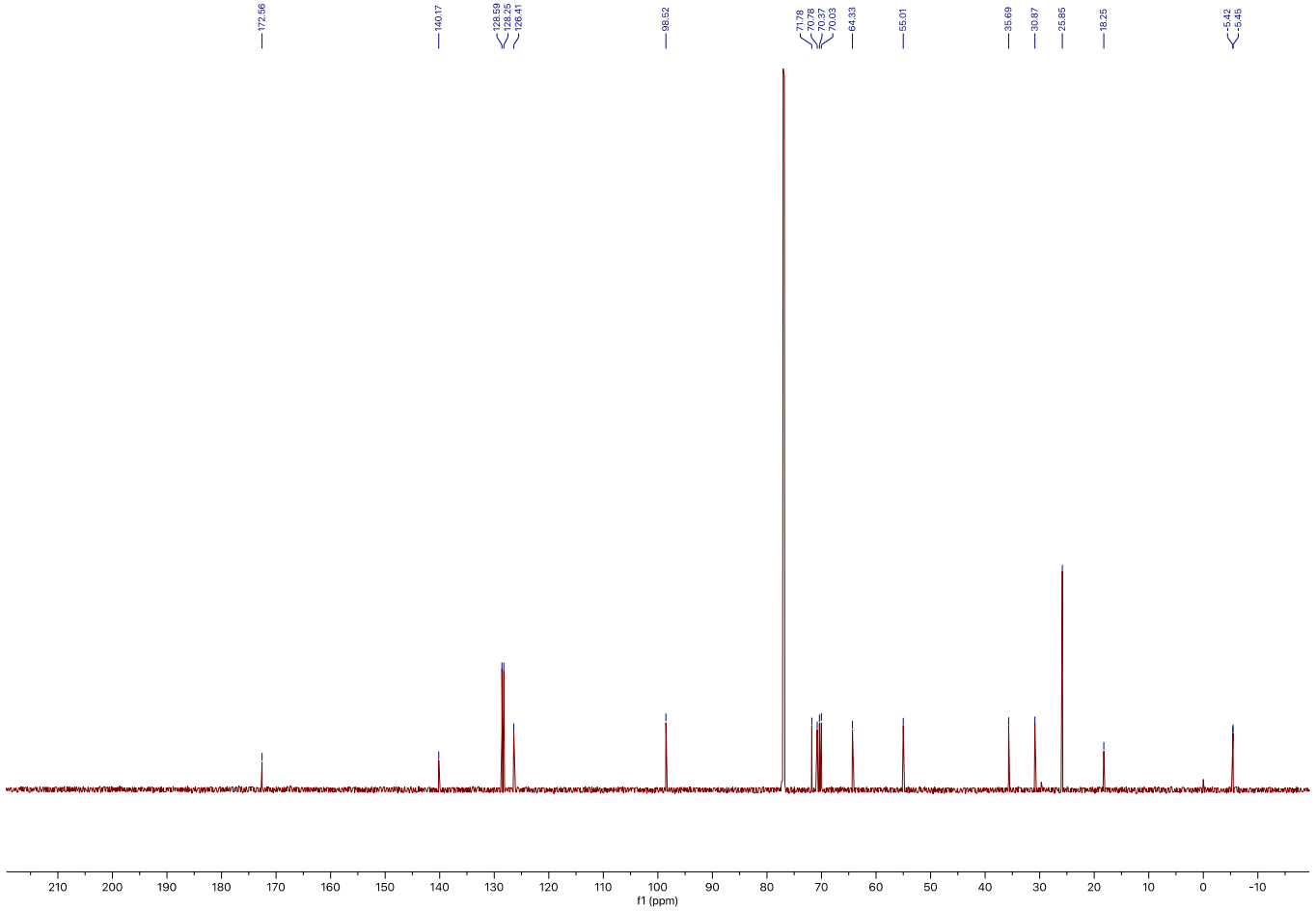
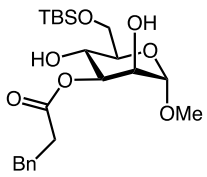


Figure S111. ^{13}C NMR spectrum (100 MHz) of **1ag** in $CDCl_3$

Methyl 3-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bg**



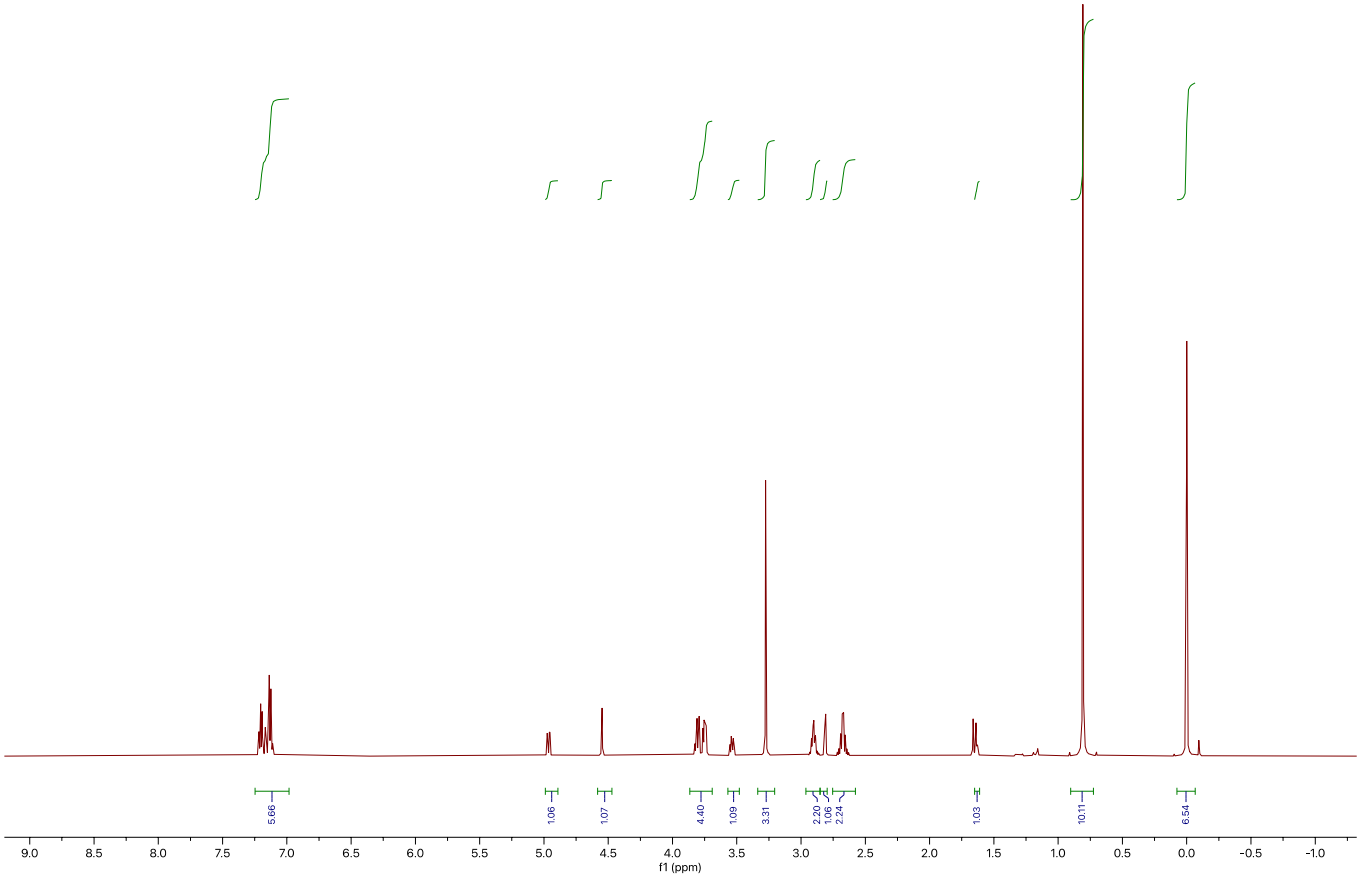


Figure S112. ^{1}H NMR spectrum (600 MHz) of **1bg** in $CDCl_3$

Methyl 3-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bg**

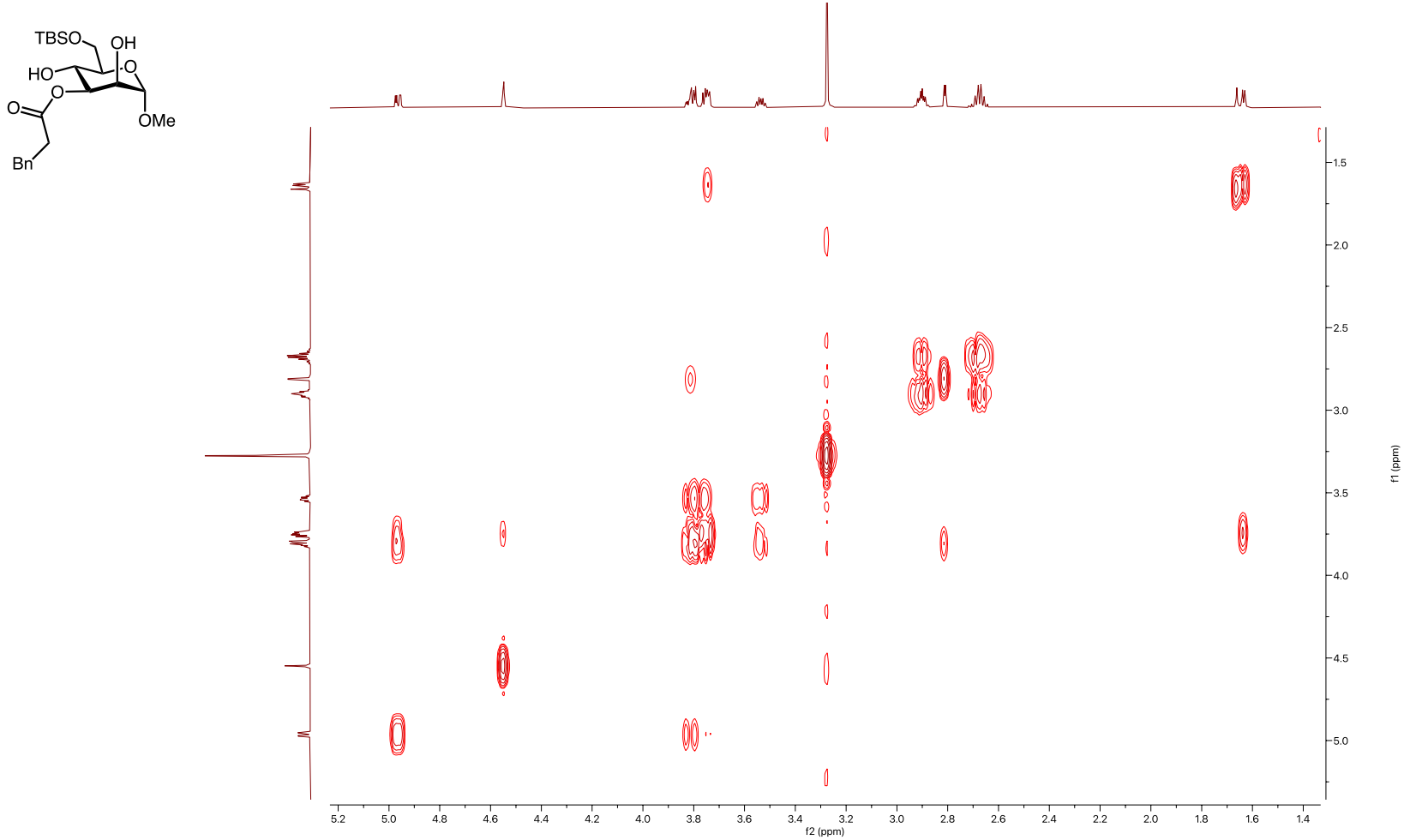


Figure S113. ^{1}H-^{1}H COSY spectrum (600 MHz) of **1bg** in $CDCl_3$

Methyl 3-*O*-benzylacetyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bg**

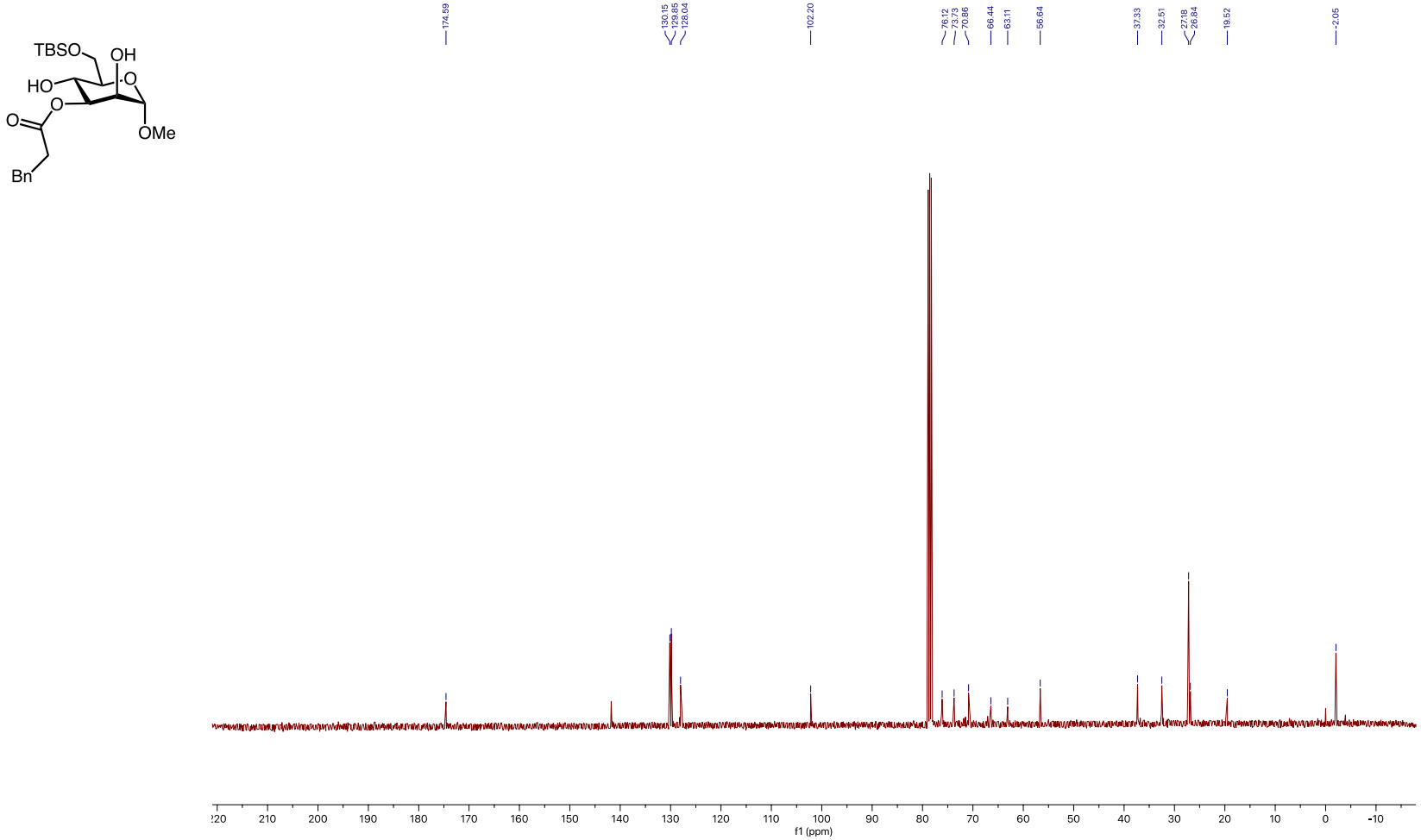


Figure S114. ^{13}C NMR spectrum (100 MHz) of **1bg** in $CDCl_3$

Methyl 3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bh**

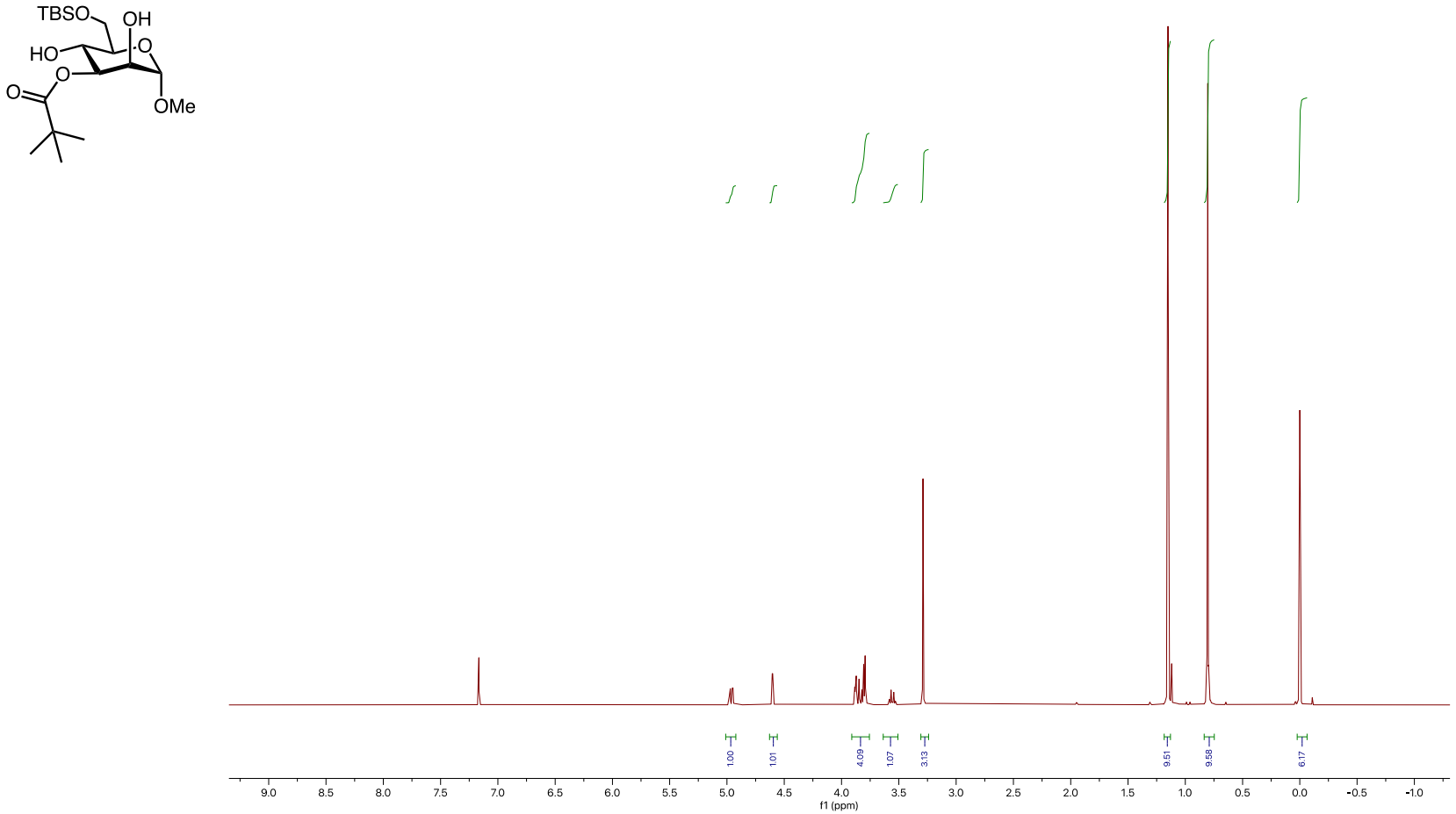


Figure S115. ^{1}H NMR spectrum (400 MHz) of **1bh** in $CDCl_3$

Methyl 3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bh**

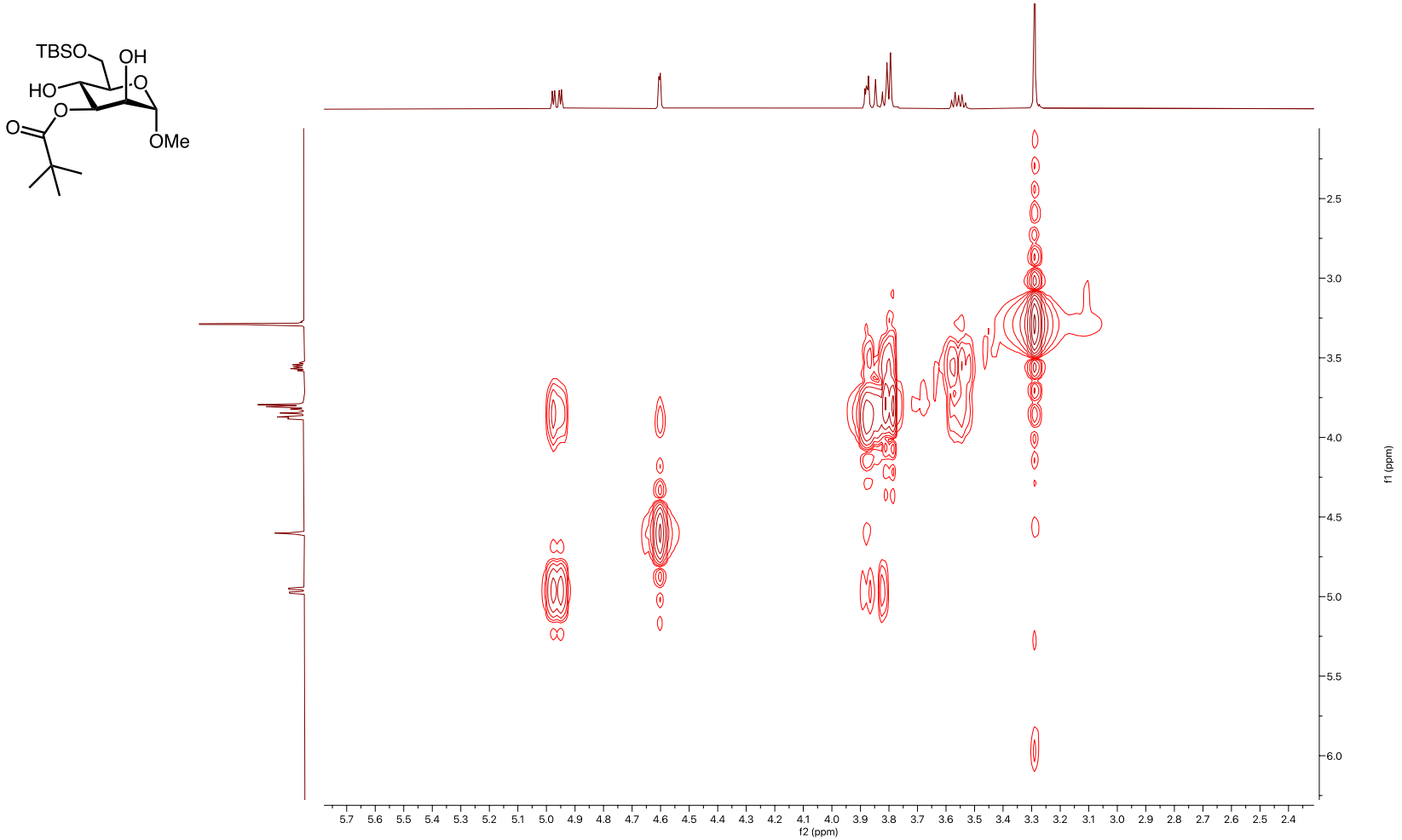


Figure S116. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1bh** in $CDCl_3$

Methyl 3-*O*-pivaloyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bh**

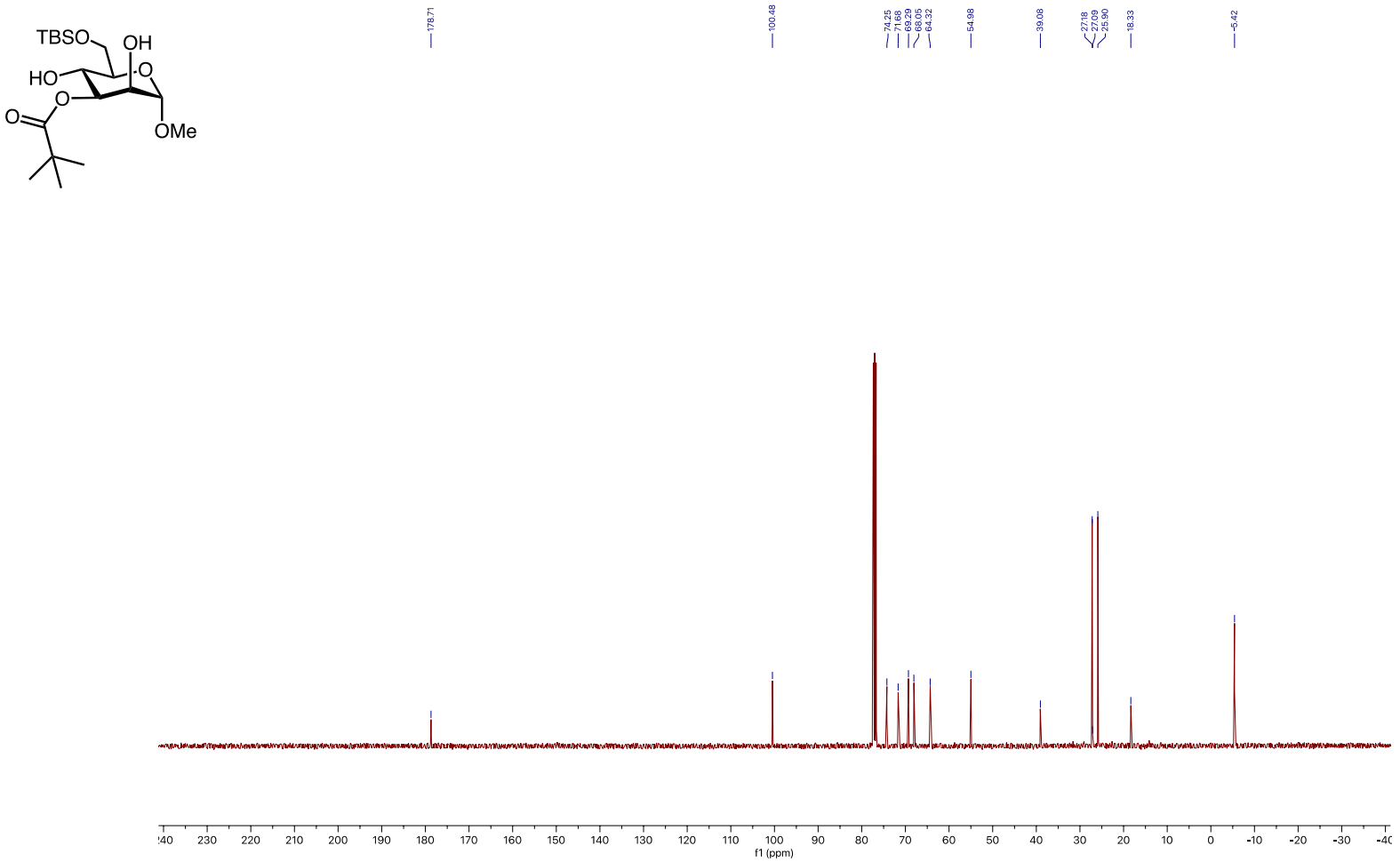
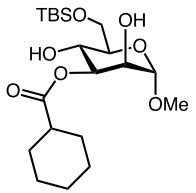


Figure S117. ^{13}C NMR spectrum (100 MHz) of **1bh** in $CDCl_3$

Methyl 3-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bi**



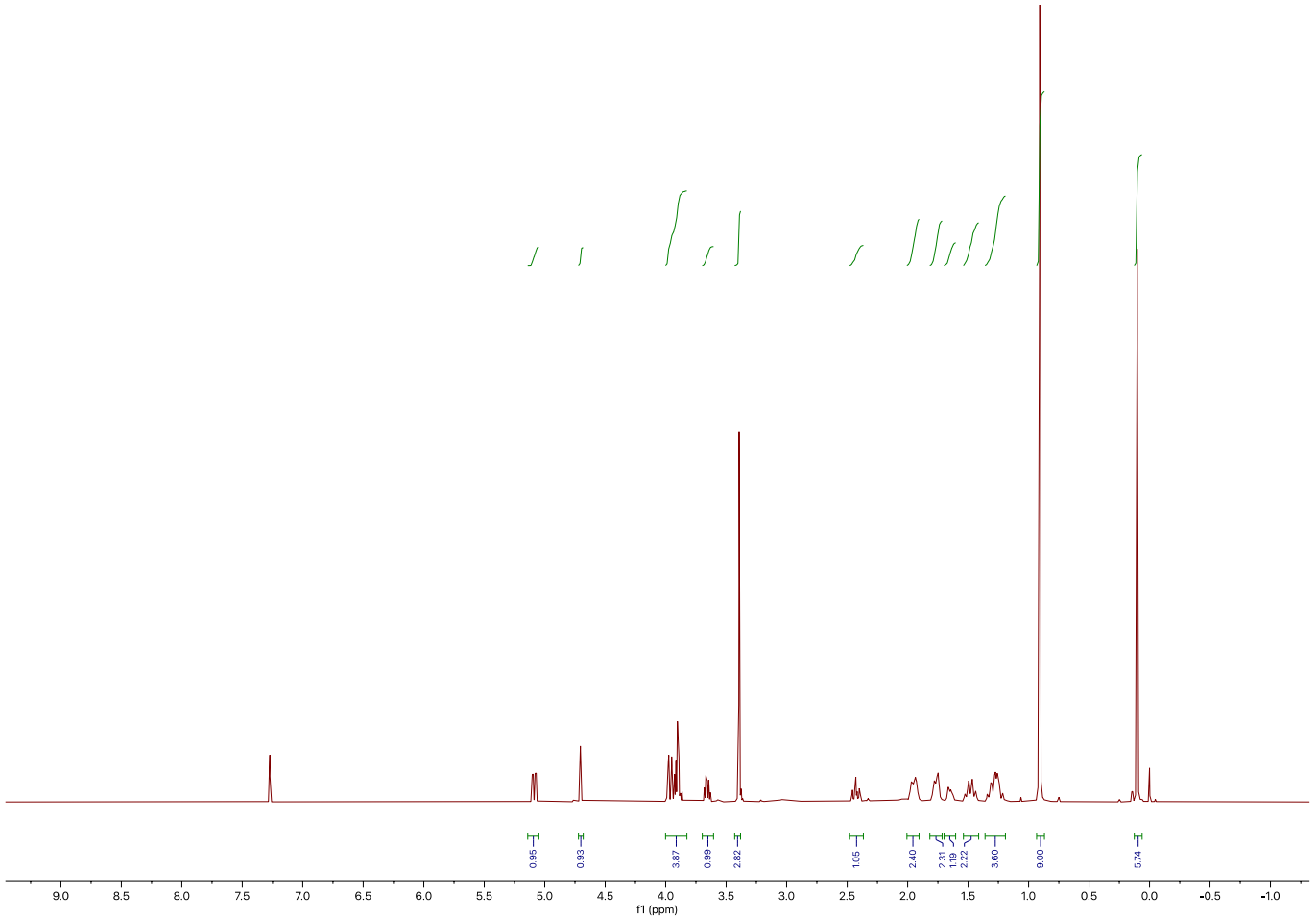


Figure S118. ^{1}H NMR spectrum (400 MHz) of **1bi** in $CDCl_3$

Methyl 3-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bi**

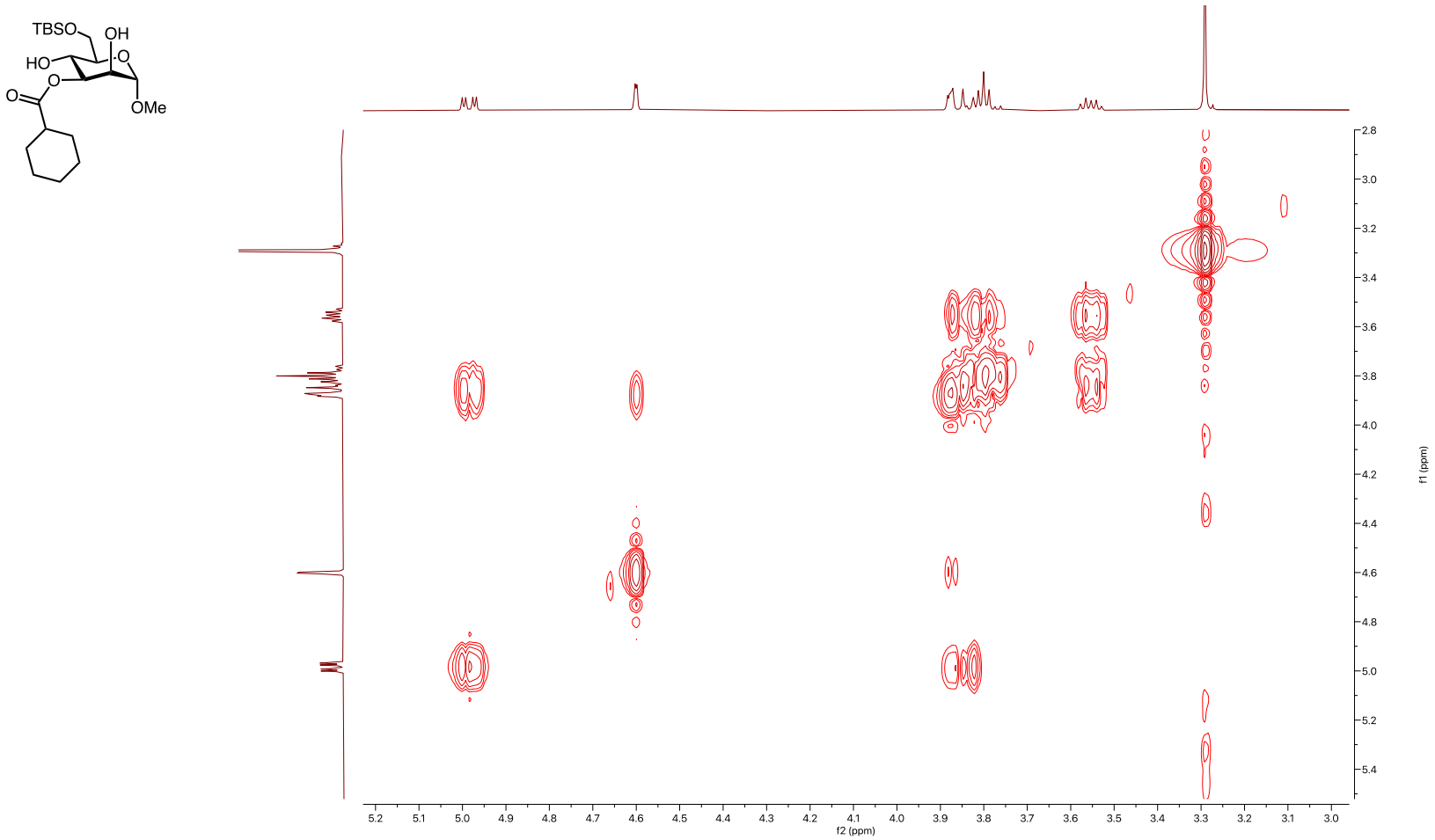


Figure S119. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1bi** in $CDCl_3$

Methyl 3-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bi**

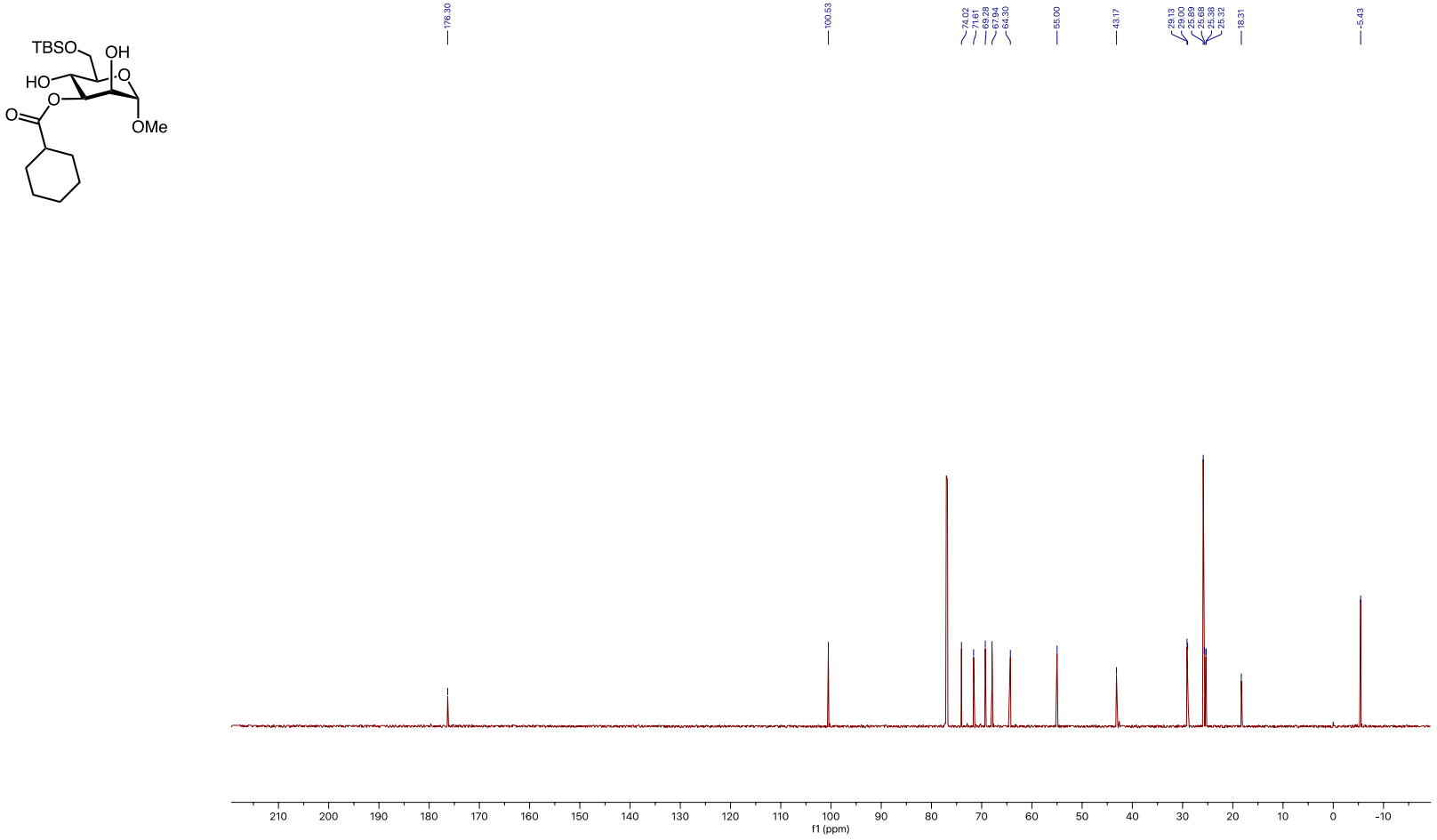


Figure S120. ^{13}C NMR spectrum (100 MHz) of **1bi** in $CDCl_3$

Methyl 2-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ai**

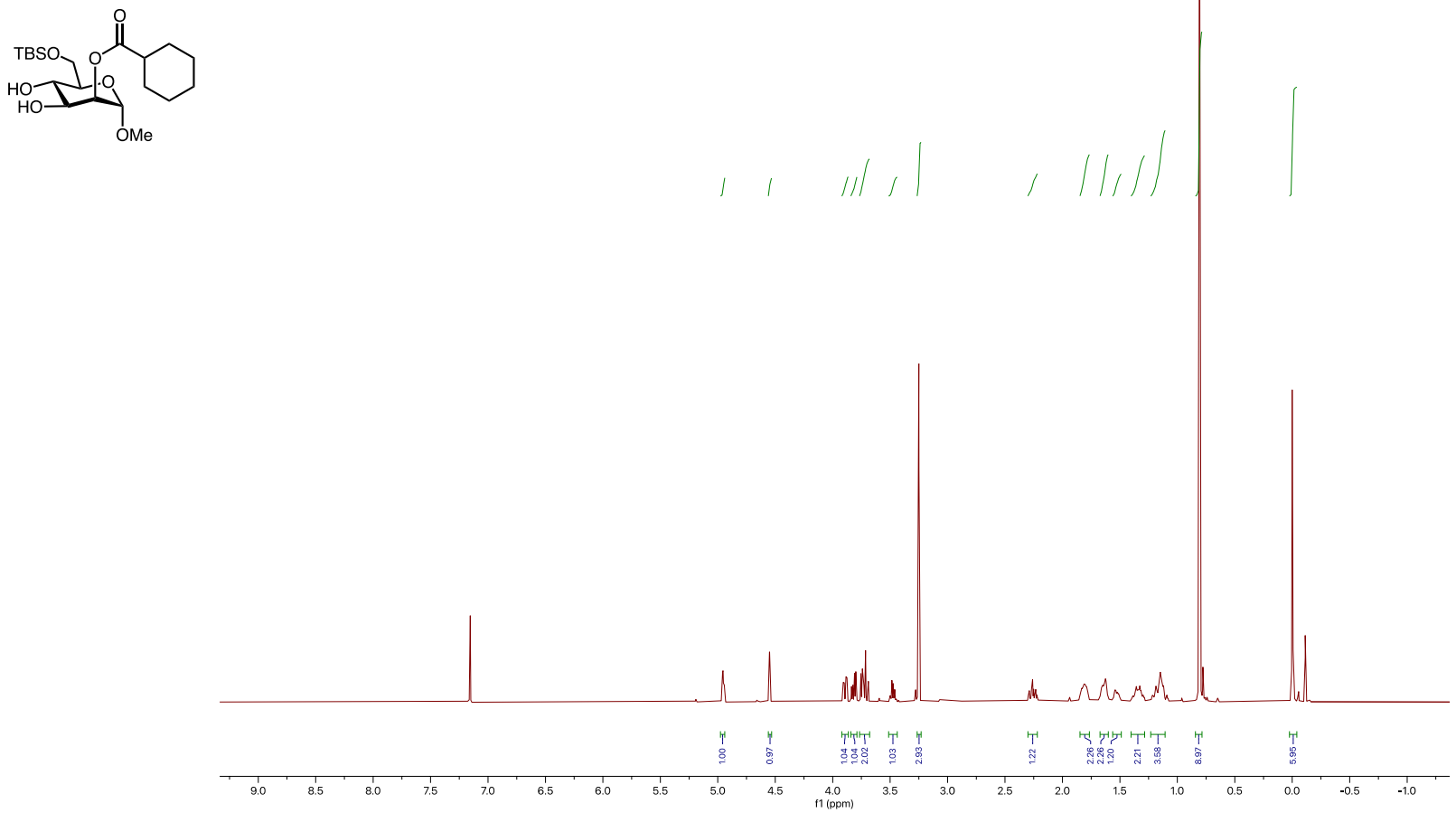


Figure S121. ^{1}H NMR spectrum (400 MHz) of **1ai** in $CDCl_3$

Methyl 2-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ai**

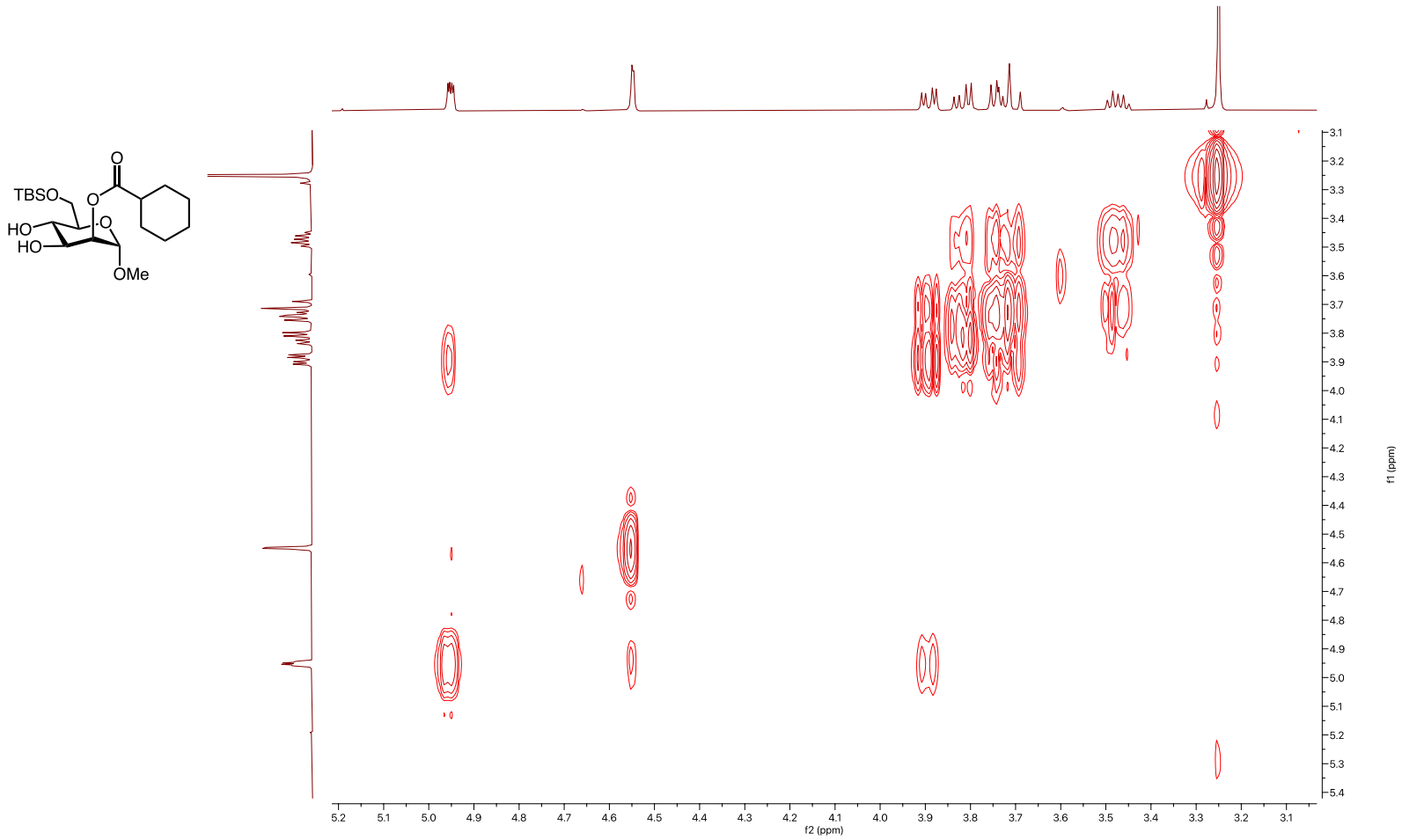


Figure S122. ^{1}H-^{1}H COSY spectrum (400 MHz) of **1ai** in $CDCl_3$

Methyl 2-*O*-cyclohexanecarbonyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1ai**

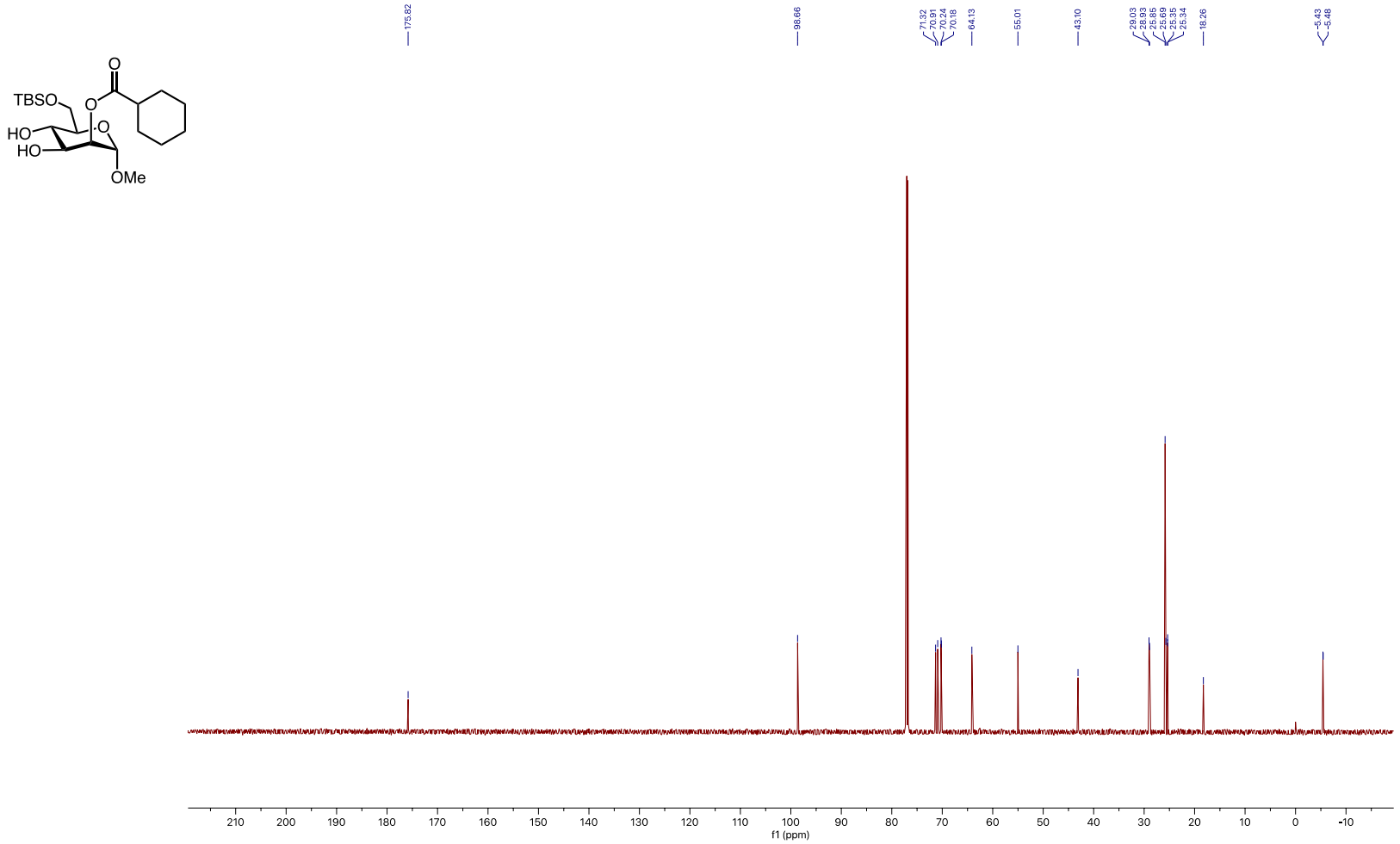
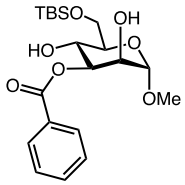


Figure S123. ^{13}C NMR spectrum (100 MHz) of **1ai** in $CDCl_3$

Methyl 3-*O*-benzoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1bj**



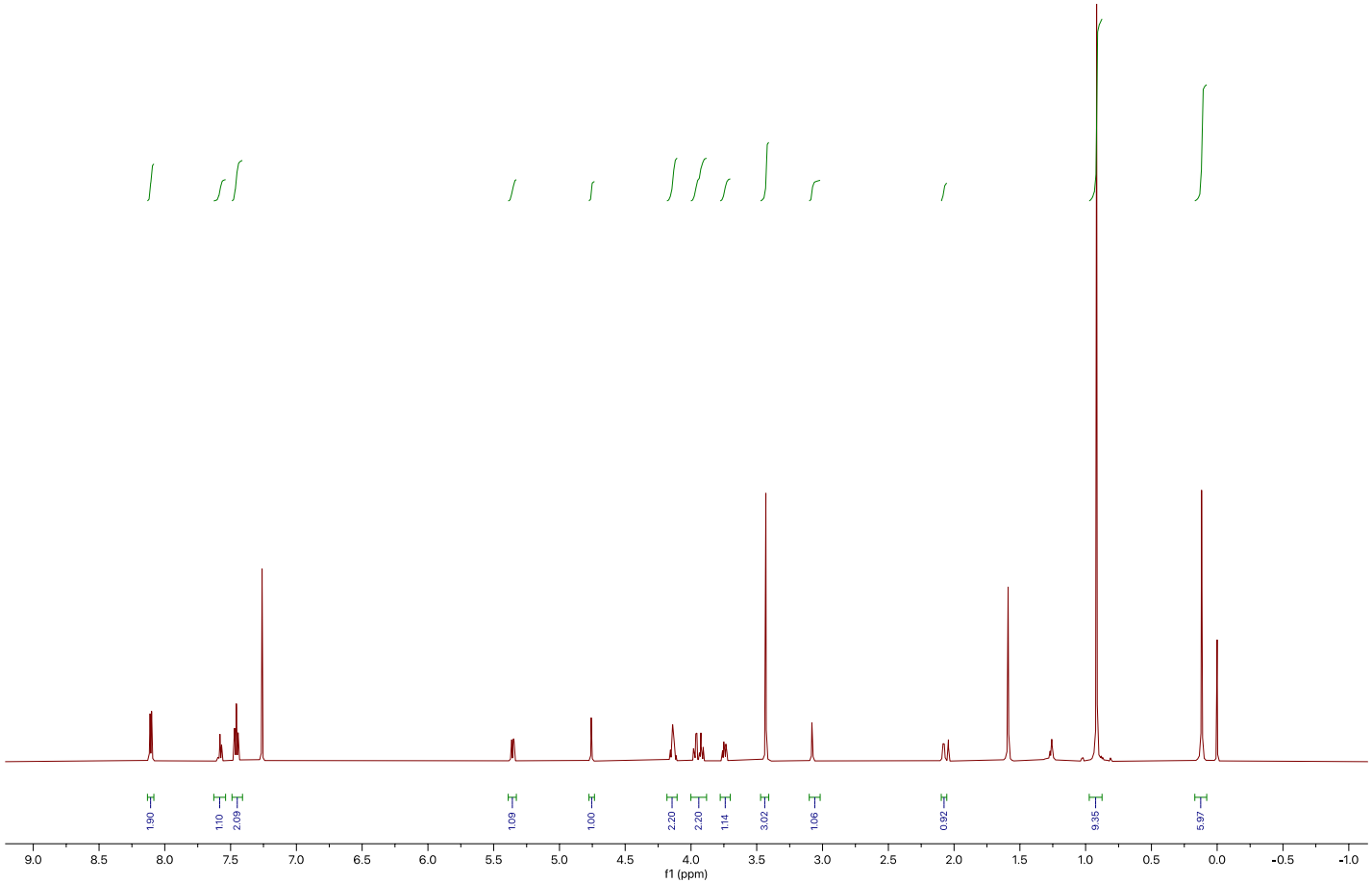
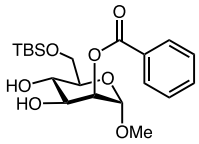


Figure S124. ^{1}H NMR spectrum (600 MHz) of **1bj** in $CDCl_3$

Methyl 2-*O*-benzoyl-6-*O*-(*tert*-butyldimethyl)silyl-α-D-mannopyranoside **1aj**



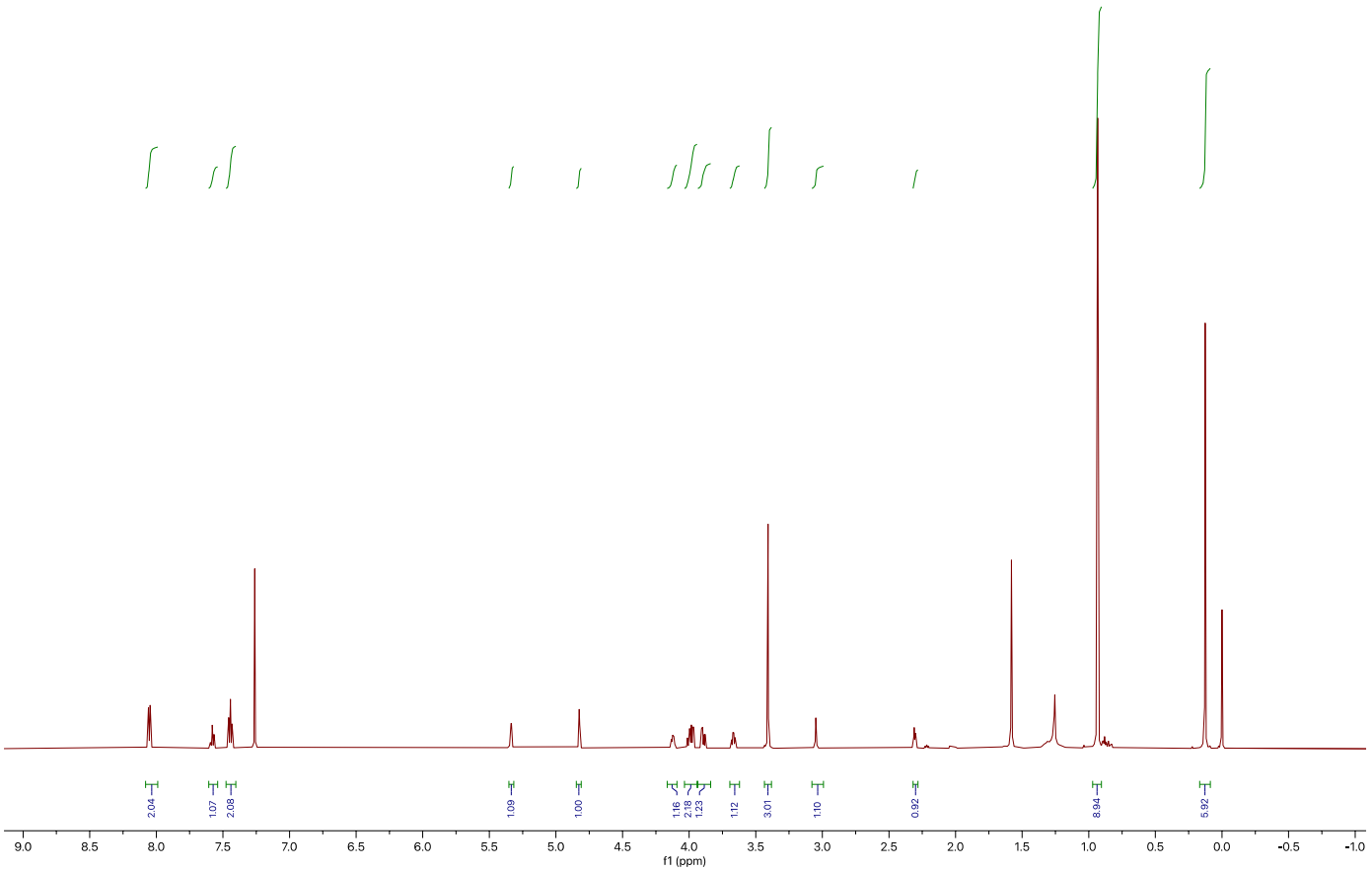


Figure S125. ^{1}H NMR spectrum (600 MHz) of **1aj** in $CDCl_3$