## SUPPORTING INFORMATION

# Cationic Gold(I)-Catalyzed Glycosylation with Glycosyl *N*-1,1-dimethylpropargyl Carbamate Donors

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## Materials and Methods

Proton and carbon nuclear magnetic resonance spectra ($^1$H NMR and $^{13}$C NMR) were recorded on either Bruker 600 ($^1$H NMR-600 MHz; $^{13}$C NMR 150 MHz) at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to residual protic solvent internal standard $CDCl_3$: $^1$H NMR at δ 7.26, $^{13}$C NMR at δ 77.16. Data for $^1$H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, br = broad, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet) and coupling constants in Hertz. All $^{13}$C NMR spectra were recorded with complete proton decoupling. Low resolution mass spectra (LRMS) were acquired on a Waters Acuity Premiere XE TOF LC-MS by electrospray ionization. Optical rotations were measured with Autopol-IV digital polarimeter; concentrations are expressed as g/100 mL.

All reagents and chemicals were purchased from Acros Organics, Sigma Aldrich, Fisher Scientific, Alfa Aesar, and Strem Chemicals and used without further purification. THF, methylene chloride, toluene, and diethyl ether were purified by passing through two packed columns of neutral alumina (Innovative Technology). Anhydrous DMF and benzene were purchased from Acros Organics and

Sigma-Aldrich and used without further drying. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Preparative thin layer chromatography was performed using 1 mm silica gel prep TLC plates. Flash column chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated.

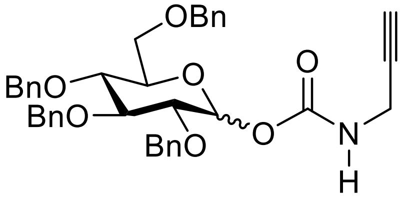
**Preparation of a solution of 3-isocyanato-1-propyne (6):**

To an ice cooled solution of propargylamine (1.2 mL, 18.0 mmol, 3.0 eq.) in methylene chloride (75 mL) was added saturated solution of $NaHCO_3$ (75 mL) and this mixture was stirred for 20 min at 0 °C. Triphosgene (1.8 g, 6.0 mmol, 1.0 eq) was added and the resulting mixture was stirred for another 20 min at 0 °C. The reaction mixture was transferred into a separatory funnel, and organic layer was separated, washed with saturated NaOH solution (40 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to afford 8 mL solution of 0.53 M 3-isocyanato-1-propyne **6** in methylene chloride (23% yield).

**Preparation of a solution 3-isocyanato-3-methyl-1-butyne (7):**

To an ice cooled solution of 1,1-dimethyl propargylamine (1.9 mL, 18.0 mmol, 3.0 eq.) in methylene chloride (75 mL) was added saturated solution of $NaHCO_3$ (75 mL) and this mixture was stirred for 20 min at 0 °C. Triphosgene (1.8 g, 6.0 mmol, 1.0 eq) was added and the resulting mixture was stirred for another 20 min at 0 °C. The reaction mixture was transferred into a separatory funnel, and organic layer was separated, washed with saturated NaOH solution (40 mL), dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to afford 11 mL solution of 0.90 M 3-isocyanato-3-methyl-1-butyne **7** in methylene chloride (55% yield).

**Synthesis of 1-*O*-(((prop-2-ynyl)amino)carbonyl)-2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (8)**



To a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (200 mg, 0.37 mmol) in dry $CH_2Cl_2$ (0.6 mL) cooled in an ice-water bath was added a solution of 3-isocyanato-1-propyne **6** in $CH_2Cl_2$ (1.04 mL, 0.53 M, 0.55 mmol, 1.5 eq), and the resulting mixture was stirred at 0 °C for 5 min. $Cs_2CO_3$ (60 mg, 0.185 mmol, 0.5 eq) was added, and the resulting mixture was stirred and slowly warmed up to room temperature. After 2 hours, the reaction mixture was directly purified by flash column chromatography (Hexane/Ethyl acetate = 8/1) to furnish 190 mg (83% yield) of compound **8** (white solid) as a mixture of anomers (α/β = 3/1). The α anomer was characterized as follows.

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 18H, ***H****Ar*), 7.21 – 7.18 (m, 2H, ***H****Ar*), 6.34 (d, *J* = 3.6 Hz, 1H, ***H***-1), 5.16 (t, *J* = 5.6 Hz, 1H, HC≡C-$CH_2$-N***H***C=O), 5.02 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.89 (dd, *J* = 12.2, 10.8 Hz, 2H, OC***H***$_2$Ar), 4.79 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 4.72 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 4.66 (d, *J* = 12.2 Hz, 1H, OC***H***$_2$Ar), 4.56 (d, *J* = 10.7 Hz, 1H, OC***H***$_2$Ar), 4.51 (d, *J* = 12.1 Hz, 1H, OC***H***$_2$Ar), 4.04 (m, 2H, HC≡C-C***H***$_2$-NHC=O), 3.98 (t, *J* = 9.3 Hz, 1H, ***H***-3), 3.90 (m, 1H, ***H***-5), 3.83 (t, *J* = 9.5 Hz, 1H, ***H***-4), 3.81 – 3.78 (m, 1H, ***H***-6a), 3.76 (dd, *J* = 9.7, 3.6 Hz, 1H, ***H***-2), 3.71 (dd, *J* = 10.9, 2.0 Hz, 1H, ***H***-6b), 2.30 (s, 1H, ***H***C≡CR).

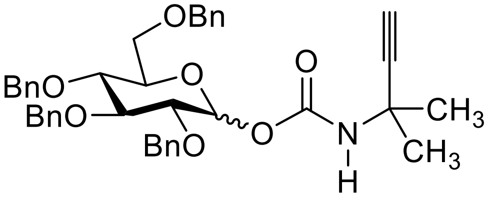
**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 154.21, 138.63, 138.13, 137.86, 137.53, 128.57, 128.48, 128.46, 128.26, 128.06, 128.03, 127.97, 127.93, 127.84, 127.79, 127.74, 91.35, 81.81, 79.24, 78.74, 77.36, 77.14, 76.93, 75.75, 75.28, 73.57, 73.21, 72.61, 72.08, 68.03, 30.90.

$[\alpha]_D^{21.6}$ **=** +50.888 (*c* = 1.0, $CHCl_3$)

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{38}H_{39}NO_7$ is 644.2624; found 644.2619.

## General Procedure for synthesis of glycosyl *N*-1,1-dimethylpropargyl carbamate donors

### 1-*O*-(((1,1-dimethyl-prop-2-ynyl)amino)carbonyl)-2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (9):



To a solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (1 g, 1.85 mmol) in dry $CH_2Cl_2$ (6 mL) cooled in an ice-water bath was added a solution of 3-isocyanato-3-methyl-1-butyne **7** in $CH_2Cl_2$ (3.11 mL, 0.90 M, 2.8 mmol, 1.5 eq), and the resulting mixture was stirred at 0 °C for 5 min.

$Cs_2CO_3$ (301 mg, 0.93 mmol, 0.5 eq) was added, and the resulting mixture was stirred and slowly warmed up to room temperature. After 2 hours, the reaction mixture was directly purified by flash column chromatography (Hexane/Ethyl acetate = 8/1) to furnish 1.1 g (94% yield) of compound **9** (white solid) as a mixture of anomers (α/β = 1.6/1). The β anomer was characterized as follows.

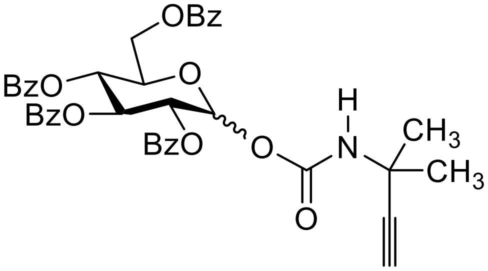
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.28 (m, 18H, $\boldsymbol{H}_{Ar}$), 7.18 (dd, *J* = 7.4, 2.2 Hz, 2H, $\boldsymbol{H}_{Ar}$), 5.61 (d, *J* = 8.2 Hz, 1H, ***H***-1), 4.95 (d, *J* = 10.9 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.91 (s, 1H, $HC{\equiv}C\text{-}C(CH_3)_2\text{-}N\boldsymbol{H}C{=}O$), 4.89 – 4.84 (t, 11.2 Hz, 2H, $OC\boldsymbol{H}_2Ar$), 4.81 (d, *J* = 11.2 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.77 (d, *J* = 11.4 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.69 (d, *J* = 12.1 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.57 (d, *J* = 10.7 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.52 (d, *J* = 12.1 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 3.83 – 3.74 (m, 4H, ***H***-3, ***H***-4, ***H***-6a, ***H***-6b), 3.61 – 3.55 (m, 2H, ***H***-2, ***H***-5), 2.38 (s, 1H, $\boldsymbol{H}\text{-}C{\equiv}CR$), 1.66 (s, 6H, $C(C\boldsymbol{H}_3)_2$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 152.11, 138.45, 138.29, 138.07, 138.01, 128.48, 128.46, 128.42, 128.39, 128.29, 94.69, 86.62, 84.92, 81.13, 77.32, 77.11, 76.89, 75.82, 75.29, 75.07, 73.49, 69.55, 68.04, 47.54, 29.12, 29.01.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.6}}$ **=** +5.3999 (*c* = 1.0, $CHCl_3$)

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{40}H_{43}NO_7$ is 672.2937; found 672.2932.

**1-*O*-(((1,1-dimethyl-prop-2-ynyl)amino)carbonyl)-2,3,4,6-tetra-*O*-benzoyl-α/β-D-glucopyranoside (10):**



Compound **10** was prepared in 99% yield as a mixture of anomers (α/β = 1/1.6) following the aforementioned general procedure. The β anomer was characterized as follows.

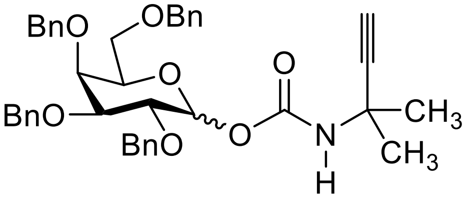
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.09 – 8.05 (m, 2H, $\boldsymbol{H}_{Ar}$), 8.00 – 7.97 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.94 – 7.91 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.87 – 7.85 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.57 – 7.49 (m, 3H, $\boldsymbol{H}_{Ar}$), 7.45 – 7.35 (m, 7H, $\boldsymbol{H}_{Ar}$), 7.31 – 7.27 (m, 2H, $\boldsymbol{H}_{Ar}$), 6.10 (d, *J* = 8.3 Hz, 1H, ***H***-1), 5.99 (t, *J* = 9.6 Hz, 1H, ***H***-3), 5.79 (t, *J* = 9.7 Hz, 1H, ***H***-4), 5.69 (t, *J* = 9.1 Hz, 1H, ***H***-2), 5.23 (s, 1H, $HC{\equiv}C\text{-}C(CH_3)_2\text{-}N\boldsymbol{H}C{=}O$), 4.65 (dd, *J* = 12.3, 2.9 Hz, 1H, ***H***-6b), 4.53 (dd, *J* = 12.3, 4.9 Hz, 1H, ***H***-6a), 4.32 (m, 1H, ***H***-5), 2.23 (s, 1H, $\boldsymbol{H}\text{-}C{\equiv}CR$), 1.52 (s, 6H, $C(C\boldsymbol{H}_3)_2$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 166.15, 165.68, 165.33, 165.15, 151.50, 133.55, 133.50, 133.33, 133.13, 129.99, 129.88, 129.80, 129.59, 128.84, 128.72, 128.66, 128.46, 128.45, 128.37, 128.35, 92.97, 86.15, 77.32, 77.10, 76.89, 72.98, 70.96, 69.58, 69.17, 62.75, 47.57, 28.89, 28.80.

$[\alpha]_D^{21.4}$ = -19.396 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{40}H_{35}NO_{11}$ is 728.2107; found 728.2096.

**1-*O*-(((1,1-dimethyl-prop-2-ynyl)amino)carbonyl)-2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside (11):**



Compound **11** was prepared in 84% yield as a mixture of anomers (α/β = 1/5) following the aforementioned general procedure. The β anomer was characterized as follows.

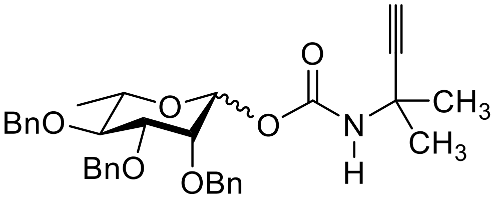
**$^1$H NMR (600 MHz, CDCl$_3$)** δ 7.50 – 7.33 (m, 20H, ***H****Ar*), 5.65 (d, *J* = 8.1 Hz, 1H, ***H***-1), 5.05 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 5.00 (s, 1H, HC≡C-C(CH$_3$)$_2$-N***H***C=O), 4.92 (d, *J* = 11.3 Hz, 1H, OC***H***$_2$Ar), 4.83 (m, 3H, OC***H***$_2$Ar), 4.72 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 4.53 (d, *J* = 11.7 Hz, 1H, OC***H***$_2$Ar), 4.49 (d, *J* = 11.7 Hz, 1H, OC***H***$_2$Ar), 4.08 (d, *J* = 2.8 Hz, 1H, ***H***-4), 4.03 – 3.98 (t, *J* = 8.9 Hz, 1H, ***H***-2), 3.79 (dd, *J* = 7.9, 5.3 Hz, 1H, ***H***-6a), 3.75 – 3.67 (m, 3H, , ***H***-3, ***H***-5, ***H***-6b), 2.41 (s, 1H, ***H***-C≡CR), 1.68 (s, 6H, C(C***H***$_3$)$_2$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 152.24, 138.73, 138.65, 138.40, 137.92, 128.53, 128.39, 128.31, 128.26, 128.07, 127.91, 127.78, 127.71, 127.66, 95.07, 86.75, 82.50, 78.33, 77.49, 77.28, 77.07, 75.31, 74.76, 73.85, 73.54, 73.24, 72.92, 69.61, 67.93, 47.54, 29.17, 29.03.

$[\alpha]_D^{21.7}$ = -4.299 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{40}H_{43}NO_7$ is 672.2937; found 672.2927.

**1-*O*-(((1,1-dimethyl-2prop-ynyl)amino)carbonyl)-2,3,4-tri-*O*-benzyl-α/β-L-rhamnopyranoside (12):**



Compound **12** was prepared in 99% yield as a mixture of anomers (α/β = 1/3.1) following the aforementioned general procedure.

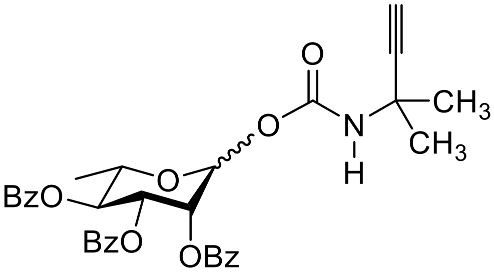
**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.51 – 7.48 (m, 2H, ***H****Ar*), 7.41 – 7.32 (m, 18H, ***H****Ar*), 6.20 (d, 0.33H, ***H***-1 α), 5.60 (d, 1H, ***H***-1 β), 5.07 – 5.04 (brs, 1H, HC≡C-C($CH_3$)$_2$-N***H***C=O), 5.04 – 4.98 (m, 1.13H, OC***H***$_2$Ar α/β), 4.94 (d, *J* = 12.2 Hz, 1H, OC***H***$_2$Ar β), 4.89 – 4.83 (m, 1.3H, OC***H***$_2$Ar α/β), 4.79 (d, *J* = 12.4 Hz, 0.34H, OC***H***$_2$Ar α), 4.74 – 4.63 (m, 4H, OC***H***$_2$Ar α/β), 3.98 (d, *J* = 2.8 Hz, 1H, ***H***-2 β), 3.94 – 3.82 (m, 1H, , ***H***-2 α, ***H***-3 α ,***H***-5 α).3.74 (t, *J* = 9.4 Hz, 0.34H, ***H***-4 α), 3.69 (t, *J* = 9.2 Hz, 1H, ***H***-4 β), 3.64 (dd, *J* = 9.4, 2.8 Hz, 1H, ***H***-3 β), 3.53 (m, 1H, ***H***-5 β), 2.41 (s, 1H, ***H***-C≡CR β), 1.65 (d, *J* = 12.8 Hz, 7H, C(C***H***$_3$)$_2$ α/β), 1.44 (d, *J* = 6.1 Hz, 3H, ***H***-6 β), 1.41 (d, *J* = 6.2 Hz, 1H, ***H***-6 α).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 152.14, 138.72, 138.60, 138.41, 138.14, 138.01, 128.53, 128.46, 128.45, 128.40, 128.23, 128.15, 128.04, 128.01, 127.82, 127.72, 127.64, 93.29, 91.97, 86.77, 86.60, 82.22, 79.99, 79.85, 79.36, 77.45, 77.24, 77.03, 75.55, 75.48, 74.82, 74.65, 73.92, 72.57, 72.52, 72.12, 69.63, 69.58, 47.46, 29.76, 29.28, 28.98, 18.17, 18.03.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.9}}$ **=** -1.3 (*c* = 1.0, $CHCl_3$)

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{33}H_{37}NO_6$ is 566.2518; found 566.2512.

**1-*O*-(((1,1-dimethyl-prop-2-ynyl)amino)carbonyl)-2,3,4-tri-*O*-benzoyl-α/β-L-rhamnopyranoside (13):**



Compound **13** was prepared in 99% yield as a mixture of anomers (α/β = 5/1) following the aforementioned general procedure. The α anomer was characterized as follows.

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 8.13 – 8.10 (m, 2H, ***H****Ar*), 7.99 – 7.96 (m, 2H, ***H****Ar*), 7.85 – 7.83 (m, 2H, ***H****Ar*), 7.66 – 7.62 (m, 1H, ***H****Ar*), 7.55 – 7.51 (m, 3H, ***H****Ar*), 7.48 – 7.44 (m, 1H, ***H****Ar*), 7.41 (t, *J* = 7.7 Hz, 2H, ***H****Ar*), 7.30 – 7.28 (m, 2H, ***H****Ar*), 6.26 (s, 1H, ***H***-1), 5.84 (br, 1H, ***H***-3), 5.72 (ovrlp, 2H, ***H***-2, ***H***-4), 5.29 (s, 1H, HC≡C-C(CH$_3$)$_2$-N***H***C=O), 4.30 (br, 1H, ***H***-5), 2.43 (s, 1H, ***H***-C≡CR), 1.72 (s, 6H, C(C***H***$_3$)$_2$), 1.42 (d, *J* = 6.2 Hz, 3H, ***H***-6).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 165.73, 165.62, 165.33, 151.22, 133.62, 133.44, 133.30, 130.01, 129.75, 129.71, 129.19, 129.15, 128.97, 128.64, 128.49, 128.35, 91.15, 86.54, 77.28, 77.06, 76.85, 71.36, 69.84, 69.82, 69.77, 68.76, 47.80, 29.08, 17.77.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.8}}$ **=** -375.96 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{33}H_{31}NO_9$ is 608.1896; found 608.1899

## General procedure (A) for cationic gold (I)-catalyzed glycosylation

A flame dried flask was charged with glycosyl donor (**9**, **11**, or **12**) (0.24 mmol, 1.2 eq.) and acceptor (**14**, **18**,[S1] **19**[S1] or **20**) (0.2 mmol, 1 eq.). The resulting mixture was azeotroped with 2 mL benzene and further dried under high vacuum for at least an hour. To this mixture, solid tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%), solid AgOTf (2.56 mg, 5 mol%) and 1 mL dry methylene chloride were added sequentially. The reaction mixture was stirred at ambient temperature for 10 min and the crude mixture was purified by flash column chromatography (Hexane/Ethyl acetate = 10/1 to 6/1) to afford desire disaccharides.

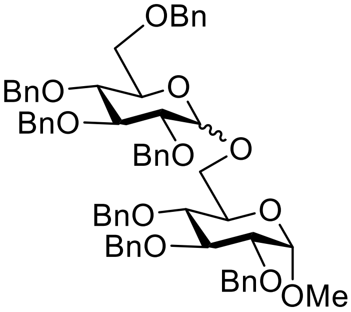
Disaccharides **15**,[S2] **22**,[S3] **23**,[S1] **24**,[S3] **25**,[S4] **26**,[S4] **27**,[S5] **28**,[S6] **29**[S6] and **30** [S5] were prepared according to the above-mentioned procedure and their spectroscopic data match with those reported in the literature.

## General procedure (B) for cationic gold (I)-catalyzed glycosylation

A flame dried flask was charged with glycosyl donor **10** or **13** (0.24 mmol, 1.2 eq) and acceptor (**14**, **18**,[S1] **19**[S1] or **20**) (0.2 mmol, 1 eq). The resulting mixture was azeotroped with 2 mL benzene and further dried under high vacuum for at least an hour. To this mixture, solid tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%), solid AgOTf (2.56 mg, 5 mol%) and 1 mL dry methylene chloride were added sequentially. The reaction mixture was stirred at ambient temperature for 10 min and the crude mixture was purified by flash column chromatography (Toluene/Ethyl acetate = 60/1 to 30/1) to afford desired disaccharides.

Disaccharides **16**,[S7] **31**,[S3] **32**, **33**,[S8] **34**,[S3] **35**, and **36**[S3] were prepared according to the above-mentioned procedure. The spectroscopic data of disaccharides **16, 31, 33, 34** and **36** match with those reported in the literature.

**Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (15):**

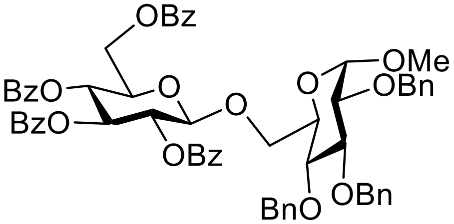


Compound **15** (192 mg, 98% yield) was prepared from donor **9** (0.24 mmol, 1.2 eq.) and acceptor **14** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.27 (m, 36H), 7.26 – 7.20 (m, 7H), 5.02 (m, 3H), 4.98 – 4.94 (m, 1H), 4.88 – 4.74 (m, 8H), 4.72 – 4.68 (m, 2H), 4.66 (d, *J* = 3.7 Hz, 1H), 4.63 (d, *J* = 2.3 Hz, 1H), 4.60 – 4.55 (m, 3H), 4.48 (dd, *J* = 19.5, 11.6 Hz, 1H), 4.40 (d, *J* = 7.8 Hz, 1H), 4.23 (dd, *J* = 10.9, 2.1 Hz, 1H), 4.06 – 3.98 (m, 2H), 3.90 – 3.85 (m, 1H), 3.82 (m, 0.49H), 3.77 (m, 1H), 3.74 – 3.65 (m, 4H), 3.64 – 3.59 (m, 1H), 3.59 – 3.52 (m, 3H), 3.48 (m, 1H), 3.40 (s, 1H), 3.38 (s, 3H).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 138.85, 138.83, 138.53, 138.49, 138.46, 138.43, 138.39, 138.35, 138.25, 138.20, 138.15, 138.10, 137.98, 128.49, 128.46, 128.44, 128.41, 128.38, 128.36, 128.32, 128.20, 128.06, 128.06, 128.02, 128.00, 127.96, 127.93, 127.89, 127.81, 127.78, 127.76, 127.70, 127.66, 127.63, 127.59, 127.55, 103.83, 98.09, 97.98, 97.29, 84.82, 82.17, 82.10, 82.01, 81.71, 80.14, 79.99, 79.77, 78.01, 77.91, 77.78, 77.62, 77.30, 77.08, 76.87, 75.77, 75.74, 75.55, 75.06, 75.05, 75.02, 74.94, 73.46, 73.44, 73.42, 73.40, 72.40, 70.37, 70.25, 69.86, 69.02, 68.58, 68.45, 66.07, 55.25, 55.20.

**Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16):**



Compound **16** (215 mg, 99% yield) was prepared from donor **10** (0.24 mmol, 1.2 eq.) and acceptor **14** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (Purified via silica gel column chromatography, Toluene/Ethyl Acetate: 60/1 to 30/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.02 – 7.99 (m, 2H, ***H**$_{Ar}$*), 7.91 (m, 4H, ***H**$_{Ar}$*), 7.84 (m, 2H, ***H**$_{Ar}$*), 7.53 (m, 2H, ***H**$_{Ar}$*), 7.43 – 7.22 (m, 23H, ***H**$_{Ar}$*), 7.08 – 7.05 (m, 2H, ***H**$_{Ar}$*), 5.91 (t, *J* = 9.63 Hz, 1H, ***H’***-3), 5.69 (t, *J* = 9.65 Hz, 1H, ***H’***-4), 5.61 (m, ***H’***-2), 4.91 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.84 (dd, *J* = 7.8, 1.2 Hz, 1H, ***H’***-1), 4.75 (d, *J* = 12.0 Hz, 1H, OC***H***$_2$Ar), 4.70 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.62 (m, 2H, ***H’***-6b, OC***H***$_2$Ar), 4.56 – 4.49 (m, 3H, ***H***-1 , ***H’***-6a, OC***H***$_2$Ar), 4.30 (d, *J* = 11.0 Hz, 1H, OC***H***$_2$Ar), 4.17 (dd, *J* = 10.6, 1.7 Hz, 1H, ***H***-6a), 4.12 (m, 1H, ***H’***-5), 3.90 (t, *J* = 9.3 Hz, 1H, **H**-3), 3.77 (dd, *J* = 10.6, 4.2 Hz, 1H, **H**-6b), 3.73 (m, 1H, ***H***-5), 3.45 (dd, *J* = 9.5, 3.7 Hz, 1H, ***H***-2), 3.42 – 3.37 (t, *J* = 9.5 Hz, 1H, ***H***-4), 3.23 (s, 3H, OC***H***$_3$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 166.12, 165.85, 165.16, 164.92, 138.79, 138.18, 138.14, 133.45, 133.27, 133.15, 133.12, 129.83, 129.76, 129.73, 129.54, 129.15, 128.77, 128.73, 128.45, 128.42, 128.34, 128.32, 128.29, 128.14, 101.33, 97.95, 81.89, 79.73, 77.38, 77.24, 77.03, 76.82, 75.56, 74.72, 73.39, 72.84, 72.19, 71.79, 69.78, 69.45, 68.30, 63.25, 55.02, 29.73.

**Isolation of 4,4-dimethyl-5-methyleneoxazolidin-2-one byproduct (17):**

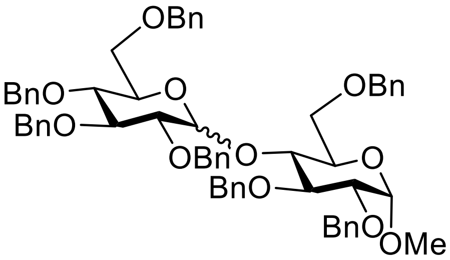
During the course of reaction, compound **17** (9.1 mg, 72% yield, TLC; $R_f$ = 0.17, Pentane:Ethyl Acetate = 3:1) was isolated using Hexane/Ethyl acetate 8/1 to 6/1 and its spectroscopic data match with that reported in the literature.[S9]

**$^{1}$H NMR (600 MHz, CDCl$_3$)** δ 5.92 (br, 1H, C(CH$_3$)$_2$-N***H***C=O), 4.66 (dd, *J* = 3.6, 1.2 Hz, 1H, ***Ha***-C=C), 4.24 (d, *J* = 3.6 Hz, 1H, ***Hb***-C=C), 1.47 (s, 6H, (C***H***$_3$)$_2$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 161.96, 155.12, 84.46, 58.30, 29.52.

**HRMS (ESI) m/z:** [M+H]$^+$ calculated for $C_6H_9NO_2$ is 128.1430; found 128.1439.

**Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (22):**

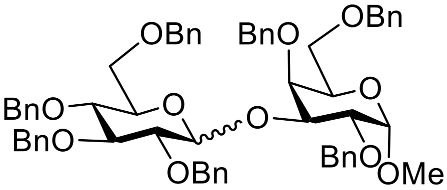


Compound **22** (188 mg, 96% yield) was prepared from donor **9** (0.24 mmol, 1.2 eq.) and acceptor **18** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate: 50/1 to 30/1) and characterized as follows:

**$^{1}$H NMR (600 MHz, CDCl$_3$)** δ 7.50 – 7.29 (m, 65H), 7.17 (dd, *J* = 7.3, 2.4 Hz, 2H), 5.78 (d, *J* = 3.6 Hz, 1H), 5.16 (s, 0.51H), 5.11 (d, *J* = 11.5 Hz, 1H), 4.94 (m, *J* = 10.2 Hz, 2H), 4.90 – 4.80 (m, 9H), 4.76 (s, 1H), 4.69 – 4.43 (m, 17H), 4.34 (d, *J* = 12.0 Hz, 1H), 4.25 – 3.88 (m, 7H), 3.84 – 3.51 (m, 15H), 3.47 (d, *J* = 2.0 Hz, 1H), 3.44 (s, 3.25H), 3.43 (s, 1.82H), 3.38 – 3.34 (m, 0.52H).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 139.59, 138.99, 138.80, 138.63, 138.61, 138.56, 138.52, 138.43, 138.34, 138.21, 138.02, 137.95, 137.87, 136.43, 134.52, 129.81, 129.05, 128.52, 128.49, 128.43, 128.39, 128.36, 128.30, 128.28, 128.18, 128.10 (d, *J* = 1.8 Hz), 128.07, 127.99, 127.90, 127.88, 127.86, 127.81, 127.78, 127.71, 127.67, 127.64, 127.61, 127.57, 127.47, 127.43, 127.39, 127.30, 127.16, 126.82, 102.54, 98.48, 97.82, 96.68, 84.91, 82.87, 82.10, 80.49, 80.26, 79.49, 78.84, 78.07, 77.68, 77.34, 77.13, 76.92, 76.63, 75.67, 75.62, 75.48, 75.19, 75.01, 74.98, 74.86, 74.49, 73.71, 73.51, 73.44, 73.40, 73.31, 73.19, 72.26, 71.01, 70.02, 69.57, 69.05 (d, *J* = 2.2 Hz), 68.18, 67.87, 55.37, 55.22.

### Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (23):

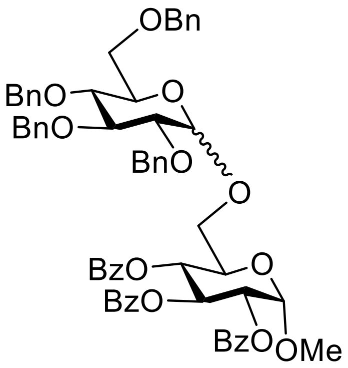


Compound **23** (187 mg, 95% yield) was prepared from donor **9** (0.24 mmol, 1.2 eq.) and acceptor **19** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1). The α anomer was characterized as follows:

**$^{1}$H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.19 (m, 33H, ***H***$_{Ar}$), 7.16 – 7.12 (m, 2H, ***H***$_{Ar}$), 5.19 (d, *J* = 3.4 Hz, 1H, ***H’***-1), 5.12 (d, *J* = 11.2 Hz, 1H, OC***H***$_2$Ar), 4.95 (d, *J* = 11.0 Hz, 1H, OC***H***$_2$Ar), 4.89 – 4.80 (m, 3H, OC***H***$_2$Ar), 4.75 (d, *J* = 3.9 Hz, 1H, ***H***-1), 4.74 – 4.71 (m, 2H, OC***H***$_2$Ar), 4.61 (dd, *J* = 11.8, 8.6 Hz, 2H, OC***H***$_2$Ar), 4.53 (d, *J* = 11.8 Hz, 1H, OC***H***$_2$Ar), 4.48 (d, *J* = 11.0 Hz, 1H, OC***H***$_2$Ar), 4.42 (dd, *J* = 11.5, 7.9 Hz, 2H, OC***H***$_2$Ar), 4.34 (d, *J* = 12.1 Hz, 1H, OC***H***$_2$Ar), 4.21 (m, 1H, ***H’***-5), 4.18 – 4.12 (m, 2H, ***H’***-3, ***H***-3), 4.03 (dd, *J* = 10.2, 3.6 Hz, 1H, ***H***-2), 3.97 (d, *J* = 2.7 Hz, 1H, ***H***-4), 3.91 (t, *J* = 6.5 Hz, 1H, ***H***-5), 3.78 (t, *J* = 9.6 Hz, 1H, ***H’***-4), 3.69 (dd, *J* = 9.8, 3.4 Hz, 1H, ***H’***-2), 3.58 – 3.53 (m, 3H, ***H’***-6b, **H**-6a, **H**-6b ), 3.46 (dd, *J* = 10.9, 2.1 Hz, 1H, ***H’***-6a), 3.37 (s, 3H, OC***H***$_3$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 138.96, 138.76, 138.67, 138.19, 138.06, 138.00, 128.53, 128.42, 128.38, 128.36, 128.29, 128.22, 128.14, 128.10, 128.08, 128.04, 127.92, 127.75, 127.73, 127.69, 127.61, 127.57, 127.45, 127.31, 98.34, 96.36, 82.19, 80.16, 77.97, 77.28, 77.07, 76.86, 76.42, 75.57, 75.52, 74.92, 74.81, 74.10, 73.45, 73.33, 73.26, 70.38, 69.21, 68.96, 68.09, 55.26.

### Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (24):

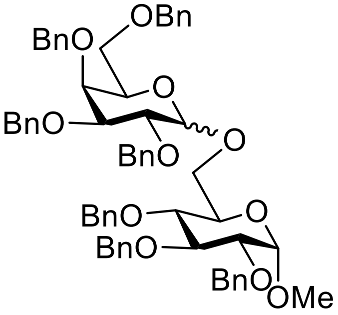


Compound **24** (175 mg, 84% yield) was prepared from donor **9** (0.24 mmol, 1.2 eq.) and acceptor **20** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1). The β anomer was characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.01 (m, 2H, $H_{Ar}$), 7.96 (m, 2H, $H_{Ar}$), 7.89 – 7.86 (m, 2H, $H_{Ar}$), 7.53 (m, 2H, $H_{Ar}$), 7.41 – 7.27 (m, 25H, $H_{Ar}$), 7.18 – 7.15 (m, 2H, $H_{Ar}$), 6.21 (dd, *J* = 10.2, 9.5 Hz, 1H, ***H***-3), 5.51 (t, *J* = 9.75 Hz, 1H, ***H***-4), 5.29 (dd, *J* = 10.2, 3.6 Hz, 1H, ***H***-2), 5.25 – 5.23 (d, *J* = 3.54 Hz, 1H, ***H***-1), 5.09 (d, *J* = 10.8 Hz, 1H, $OCH_2Ar$), 4.94 (d, *J* = 10.9 Hz, 1H, $OCH_2Ar$), 4.83 (d, *J* = 10.8 Hz, 1H, $OCH_2Ar$), 4.81 – 4.78 (m, 1H, $OCH_2Ar$), 4.71 (d, *J* = 10.8 Hz, 1H, $OCH_2Ar$), 4.57 – 4.52 (m, 2H, $OCH_2Ar$), 4.50 (d, *J* = 7.8 Hz, 1H, ***H’***-1), 4.46 (d, *J* = 12.2 Hz, 1H, $OCH_2Ar$), 4.41 (m, 1H, ***H***-5), 4.16 (dd, *J* = 11.0, 2.2 Hz, 1H, ***H***-6a), 3.84 (dd, *J* = 11.0, 7.5 Hz, 1H, ***H***-6b), 3.69 – 3.61 (m, 4H, ***H’***-3, ***H’***-4, ***H’***-6a, ***H’***-6b), 3.49 (dd, *J* = 8.9, 7.8 Hz, 1H, ***H’***-2), 3.46 – 3.44 (m, 1H, ***H’***-5), 3.41 (s, 3H, $OCH_3$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 165.85, 165.77, 165.48, 138.60, 138.47, 138.10, 138.07, 133.43, 133.37, 133.09, 104.00, 96.78, 84.55, 82.36, 77.64, 77.26, 77.05, 76.83, 75.73, 75.01, 74.88, 74.85, 73.44, 72.15, 70.49, 69.89, 68.99, 68.89, 68.63, 55.53, 29.74.

**Methyl 2,3,4,6-tetra-*O*-benzyl-α/β -D-galactopyranosyl-(1→6)- 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (25):**

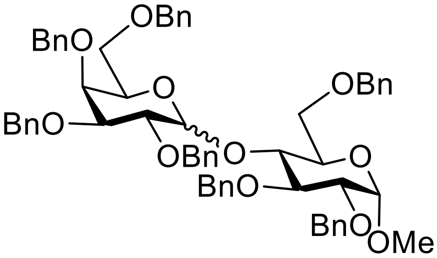


Compound **25** (193 mg, 99% yield) was prepared from donor **11** (0.24 mmol, 1.2 eq.) and acceptor **14** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.19 (m, 68H), 5.07 (d, *J* = 3.6 Hz, 1H), 5.05 – 4.97 (m, 5H), 4.94 – 4.69 (m, 14H), 4.67 – 4.61 (m, 5H), 4.60 (d, *J* = 3.6 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.52 – 4.36 (m, 5H), 4.21 (dd, *J* = 10.9, 2.1 Hz, 1H), 4.10 (dd, *J* = 9.4, 3.5 Hz, 1H), 4.07 – 3.78 (m, 11H), 3.71 – 3.61 (m, 3H), 3.60 – 3.51 (m, 6H), 3.48 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.37 (s, 2.43H), 3.36 (s, 3.1H).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 138.92, 138.90, 138.80, 138.79, 138.51, 138.45, 138.44, 138.25, 138.21, 138.08, 137.94, 128.49, 128.47, 128.44, 128.41, 128.39, 128.36, 128.35, 128.31, 128.29, 128.26, 128.20, 128.04, 128.04, 128.02, 127.94, 127.89, 127.87, 127.86, 127.77, 127.74, 127.71, 127.62, 127.58, 127.53, 127.50, 127.43, 104.26, 97.99, 97.96, 97.93, 82.35, 82.13, 82.07, 80.21, 79.89, 79.31, 78.29, 78.17, 78.03, 77.34, 77.13, 76.91, 76.57, 75.77, 75.73, 75.23, 75.12, 75.07, 74.89, 74.60, 73.58, 73.53, 73.42, 73.39, 72.92, 72.86, 72.61, 70.34, 69.96, 69.43, 68.98, 68.67, 68.60, 66.46, 55.21, 55.11.

**Methyl 2,3,4,6-tetra-*O*-benzyl-α/β -D-galactopyranosyl-(1→4)- 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (26):**

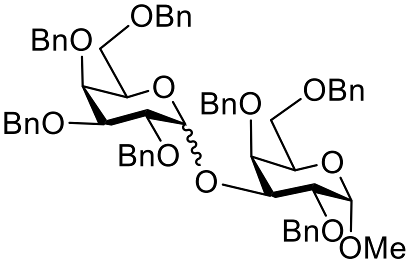


Compound **26** (171 mg, 87% yield) was prepared from donor **11** (0.24 mmol, 1.2 eq.) and acceptor **18** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.35 – 7.25 (m, 30H), 7.22 – 7.20 (m, 7H), 5.80 (d, *J* = 3.9 Hz, 1H), 5.08 (d, *J* = 10.6 Hz, 0.32H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.90 (d, *J* = 11.4 Hz, 1H), 4.86 – 4.83 (m, 1H), 4.81 – 4.54 (m, 13H), 4.46 (d, *J* = 12.3 Hz, 1H), 4.41 – 4.25 (m, 3H), 4.10 (dd, *J* = 9.6, 8.7 Hz, 1H), 4.04 – 3.97 (m, 3H), 3.96 – 3.84 (m, 4H), 3.79 – 3.62 (m, 3H), 3.61 – 3.45 (m, 4H), 3.41 (s, 3H), 3.41 (s, 1H), 3.38 – 3.33 (m, 0.54H).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 139.44, 139.09, 139.01, 138.97, 138.95, 138.80, 138.73, 138.63, 138.60, 138.59, 138.53, 138.48, 138.37, 138.26, 138.19, 138.09, 138.00, 137.88, 128.43, 128.40, 128.37, 128.34, 128.32, 128.26, 128.24, 128.19, 128.16, 128.10, 102.81, 98.45, 97.75, 97.48, 82.48, 82.05, 80.32, 80.16, 80.08, 79.20, 78.91, 77.27, 77.06, 76.85, 75.62, 75.52, 75.25, 74.80, 74.73, 74.61, 74.38, 73.84, 73.70, 73.44, 73.42, 73.07, 72.77, 72.69, 72.54, 70.03, 69.87, 69.46, 69.41, 68.68, 68.20, 68.00, 55.33, 55.13.

**Methyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (27):**



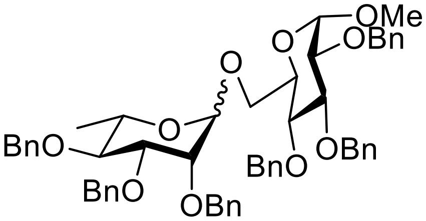
Compound **27** (174 mg, 88% yield) was prepared from donor **11** (0.24 mmol, 1.2 eq.) and acceptor **19** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1). The α anomer was characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.39 – 7.23 (m, 33H, $\boldsymbol{H}_{Ar}$), 7.17 (m, 2H, $\boldsymbol{H}_{Ar}$), 5.26 (d, *J* = 3.5 Hz, 1H, ***H'***-1), 5.02 (d, *J* = 11.4 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.97 (d, *J* = 11.4 Hz, 1H, $OC\boldsymbol{H}_2Ar$), 4.89 (d, *J* =

11.4 Hz, 1H, OC***H***$_2$Ar), 4.76 – 4.72 (m, 4H, OC***H***$_2$Ar), 4.63 (d, *J* = 3.7 Hz, 1H, ***H***-1), 4.60 (m, 2H, OC***H***$_2$Ar), 4.50 (d, *J* = 11.9 Hz, 1H, OC***H***$_2$Ar), 4.39 (m, 4H, OC***H***$_2$Ar), 4.36 (m, 1H, ***H'***-5), 4.17 (m, 2H, ***H'***-2, ***H***-3), 4.05 (dd, *J* = 10.2, 2.8 Hz, 1H, ***H'***-3), 4.00 (dd, *J* = 10.2, 3.6 Hz, 1H, ***H***-2), 3.97 (dd, *J* = 2.8, 1.4 Hz, 1H, ***H'***-4), 3.95 (dd, *J* = 2.9, 1.2 Hz, 1H, ***H***-4), 3.87 (m, 1H, ***H***-5), 3.61 – 3.53 (m, 2H, ***H'***-6a, ***H'***-6b), 3.53 – 3.45 (m, 2H, ***H***-6a, ***H***-6b), 3.31 (s, 3H, OC***H***$_3$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 139.02, 138.80, 138.70, 138.69, 138.37, 138.27, 138.12, 128.39, 128.31, 128.29, 128.23, 128.12, 128.08, 127.99, 127.86, 127.70, 127.66, 127.64, 127.58, 127.54, 127.50, 127.40, 127.27, 98.57, 97.08, 79.02, 77.28, 77.07, 76.86, 76.73, 76.19, 75.83, 75.07, 74.97, 74.88, 74.72, 74.21, 73.36, 73.31, 73.04, 72.41, 69.32, 69.22, 69.11, 68.60, 55.21.

**Methyl 2,3,4-tri-*O*-benzyl-α/β-L-rhamanopyranosyl-(1→6)-2,3,4- tri-*O*-benzyl-α-D-glucopyranoside (28):**

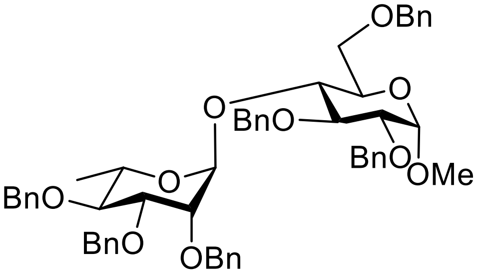


Compound **28** (180 mg, 99% yield) was prepared from donor **12** (0.24 mmol, 1.2 eq.) and acceptor **14** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL CH$_2$Cl$_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 10/1 to 6/1). The α anomer was characterized as follows:

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 7.40 – 7.21 (m, 30H, ***H***$_{Ar}$), 4.99 (dd, *J* = 18.0, 10.8 Hz, 2H, OC***H***$_2$Ar), 4.83 – 4.79 (m, 3H, OC***H***$_2$Ar), 4.75 – 4.73 (m, 2H, ***H***-1$_{\text{Rha}}$, OC***H***$_2$Ar), 4.71 – 4.65 (m, 4H, OC***H***$_2$Ar), 4.62 (d, *J* = 11.8 Hz, 1H, OC***H***$_2$Ar), 4.55 (d, *J* = 3.5 Hz, 1H, ***H***-1$_{\text{Glu}}$), 4.39 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 3.97 (t, *J* = 9.3 Hz, 1H, ***H***-3$_{\text{Glu}}$), 3.85 (m, 2H, ***H***-5$_{\text{Glu,}}$ ***H***-6a$_{\text{Glu}}$), 3.75 – 3.68 (m, 3H, ***H***-4$_{\text{Glu,}}$ ***H***-2$_{\text{Rha,}}$ ***H***-5$_{\text{Rha}}$), 3.64 (t, *J* = 9.4 Hz, 1H, ***H***-4$_{\text{Rha}}$), 3.49 (dd, *J* = 9.6, 3.5 Hz, 1H, ***H***-2$_{\text{Glu}}$), 3.46 (dd, *J* = 10.8, 5.6 Hz, 1H, ***H***-6b$_{\text{Glu}}$), 3.36 (dd, *J* = 10.1, 8.9 Hz, 1H, ***H***-3$_{\text{Rha}}$), 3.29 (s, 3H, OC***H***$_3$), 1.32 (d, *J* = 6.2 Hz, 3H, ***H***-6$_{\text{Rha}}$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 138.71, 138.56, 138.50, 138.25, 138.13, 138.08, 128.51, 128.45, 128.44, 128.41, 128.39, 128.31, 128.16, 128.11, 128.06, 127.97, 127.82, 127.74, 127.71, 127.69, 127.65, 127.60, 98.20, 97.75, 81.98, 80.60, 79.91, 79.74, 77.85, 77.25, 77.04, 76.83, 75.85, 75.53, 75.04, 74.88, 73.34, 72.73, 72.33, 69.84, 68.03, 66.03, 17.97.

**Methyl 2,3,4-tri-*O*-benzyl-α-L-rhamanopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (29):**

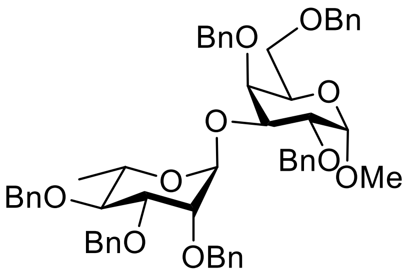


Compound **29** (158 mg, 90% yield) was prepared from donor **12** (0.24 mmol, 1.2 eq.) and acceptor **18** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 12/1 to 8/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 3H, $\boldsymbol{H}_{Ar}$), 7.35 (m, 27H, $\boldsymbol{H}_{Ar}$), 5.11 (d, *J* = 1.9 Hz, 1H, $\boldsymbol{H}$-1$_{\mathrm{Rha}}$), 5.02 (d, *J* = 10.3 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.97 (d, *J* = 11.0 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.80 (dd, *J* = 11.2, 5.5 Hz, 2H, OC$\boldsymbol{H}_2$Ar), 4.69 – 4.64 (m, 6H, OC$\boldsymbol{H}_2$Ar), 4.62 (d, *J* = 3.6 Hz, 1H, $\boldsymbol{H}$-1$_{\mathrm{Glu}}$), 4.54 (d, *J* = 12.0 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.00 (m, $\boldsymbol{H}$-5$_{\mathrm{Rha}}$), 3.88 (dd, *J* = 9.3, 3.2 Hz, 1H, $\boldsymbol{H}$-3$_{\mathrm{Rha}}$), 3.86 – 3.83 (m, 2H, $\boldsymbol{H}$-3$_{\mathrm{Glu}}$, $\boldsymbol{H}$-4$_{\mathrm{Glu}}$), 3.75 (brs, *J* = 2.6 Hz, 1H, $\boldsymbol{H}$-2$_{\mathrm{Rha}}$), 3.69 (m, 1H, $\boldsymbol{H}$-5$_{\mathrm{Glu}}$), 3.66 – 3.56 (m, 3H, $\boldsymbol{H}$-4$_{\mathrm{Rha}}$, $\boldsymbol{H}$-2$_{\mathrm{Glu}}$, $\boldsymbol{H}$-6a$_{\mathrm{Glu}}$), 3.53 – 3.49 (m, 1H, $\boldsymbol{H}$-6b$_{\mathrm{Glu}}$), 3.41 (s, 3H, OC$\boldsymbol{H}_3$), 1.13 (d, *J* = 6.2 Hz, 3H, $\boldsymbol{H}$-6$_{\mathrm{Rha}}$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 138.88, 138.67, 138.64, 138.43, 138.06, 137.95, 128.52, 128.42, 128.39, 128.31, 128.27, 128.25, 98.18, 97.94, 80.75, 80.51, 80.05, 79.78, 77.34, 77.12, 76.91, 75.59, 75.26, 75.13, 75.08, 73.57, 73.46, 72.48, 72.16, 70.06, 68.88, 68.71, 55.31, 17.91.

**Methyl 2,3,4-tri-*O*-benzyl-α-L-rhamanopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (30):**

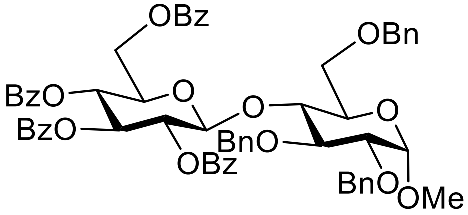


Compound **30** (164 mg, 94% yield) was prepared from donor **12** (0.24 mmol, 1.2 eq.) and acceptor **19** (0.2 mmol, 1 eq.) following the general procedure (A) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (3.52 mg, 2 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate: 10/1 to 6/1) and the α-anomer was characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.25 (m, 30H, $\boldsymbol{H}_{Ar}$), 5.32 (d, *J* = 1.6 Hz, 1H, ***H***-1$_{Rha}$), 5.00 (d, *J* = 11.1 Hz, 1H, OC***H***$_2$Ar), 4.86 (d, *J* = 11.6 Hz, 1H, OC***H***$_2$Ar), 4.69 (dd, *J* = 7.3, 3.8 Hz, 2H, ***H***-1$_{Gal,}$ OC***H***$_2$Ar), 4.62 (d, *J* = 11.8 Hz, 1H, OC***H***$_2$Ar), 4.59 – 4.52 (m, 7H, OC***H***$_2$Ar), 4.45 (d, *J* = 11.9 Hz, 1H, OC***H***$_2$Ar), 4.20 (dd, *J* = 10.2, 2.9 Hz, 1H, ***H***-3$_{Gal}$), 4.00 (dd, *J* = 10.2, 3.5 Hz, 1H, ***H***-2$_{Gal}$), 3.98 – 3.95 (m, 1H, ***H***-5$_{Gal}$), 3.89 – 3.84 (m, 4H, ***H***-2$_{Rha,}$ ***H***-3$_{Rha,}$ ***H***-5$_{Rha,}$ ***H***-4$_{Gal}$), 3.71 – 3.66 (m, 1H, ***H***-4$_{Rha}$), 3.55 (dd, *J* = 6.4, 3.9 Hz, 2H, ***H***-6a$_{Gal,}$ ***H***-6b$_{Gal}$), 3.38 (s, 3H), 1.37 (d, *J* = 6.2 Hz, 3H, ***H***-6$_{Rha}$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 138.84, 138.56, 138.52, 138.47, 138.21, 137.92, 128.47, 128.43, 128.34, 128.30, 128.27, 128.03, 127.92, 127.82, 127.76, 127.68, 127.62, 127.59, 127.54, 127.52, 127.49, 99.26, 98.12, 80.39, 79.84, 77.29, 77.07, 76.86, 75.24, 74.99, 74.92, 74.88, 73.52, 72.68, 72.21, 71.96, 69.42, 69.01, 68.96, 55.35, 18.23.

**Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (31):**

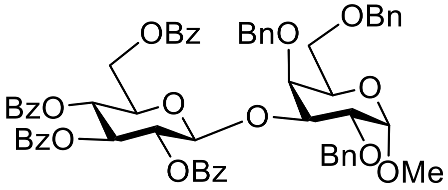


Compound **31** (216 mg, 99% yield) was prepared from donor **10** (0.24 mmol, 1.2 eq.) and acceptor **18** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate 60/1 to 30/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.01 – 7.98 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.92 – 7.90 (m, 4H, $\boldsymbol{H}_{Ar}$), 7.82 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.58 – 7.51 (m, 5H, $\boldsymbol{H}_{Ar}$), 7.47 – 7.36 (m, 12H, $\boldsymbol{H}_{Ar}$), 7.30 (m, 7H, $\boldsymbol{H}_{Ar}$), 7.22 (m, 3H, $\boldsymbol{H}_{Ar}$), 5.64 (t, *J* = 9.6 Hz, 1H, ***H’***-3), 5.58 (t, *J* = 9.6 Hz, 1H, ***H’***-4), 5.49 (dd, *J* = 9.7, 8.1 Hz, 1H, ***H’***-2), 5.10 (d, *J* = 11.2 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.83 (d, *J* = 11.2 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.80 – 4.76 (m, 3H, ***H’***-1, OC$\boldsymbol{H}_2$Ar), 4.61 (d, *J* = 12.3 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.57 (d, *J* = 3.6 Hz, 1H, ***H***-1), 4.42 (dd, *J* = 12.1, 3.4 Hz, 1H, ***H’***-6b), 4.37 (d, *J* = 12.2 Hz, 1H, OC$\boldsymbol{H}_2$Ar), 4.29 (dd, *J* = 12.0, 5.0 Hz, 1H, ***H’***-6a), 4.01 – 3.97 (t, *J* = 9.5 Hz, 1H, ***H***-4), 3.90 (t, *J* = 9.2 Hz, 1H, ***H***-3), 3.76 – 3.70 (m, 2H, ***H’***-5, ***H***-6a), 3.52 (m, 1H, ***H***-5), 3.49 (dd, *J* = 9.6, 3.7 Hz, 1H, ***H***-2), 3.45 (dd, *J* = 10.8, 1.9 Hz, 1H, ***H***-6b), 3.30 (s, 3H, OC$\boldsymbol{H}_3$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 166.06, 165.74, 165.11, 164.83, 139.27, 138.34, 137.88, 133.38, 133.35, 133.19, 132.99, 129.76, 129.69, 129.61, 129.10, 128.89, 128.85, 128.47, 128.42, 128.42, 128.36, 128.30, 128.08, 128.06, 127.77, 127.42, 127.16, 100.42, 98.51, 79.97, 78.74, 77.27, 77.06, 76.85, 75.39, 73.60, 73.16, 72.24, 71.83, 69.85, 69.46, 67.55, 63.15, 55.39.

**Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (32):**



Compound **32** (216 mg, 99% yield) was prepared from donor **10** (0.24 mmol, 1.2 eq.) and acceptor **19** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate 60/1 to 30/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.07 – 8.04 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.98 (m, 4H, $\boldsymbol{H}_{Ar}$), 7.89 – 7.85 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.56 – 7.52 (m, 2H, $\boldsymbol{H}_{Ar}$), 7.49 – 7.24 (m, 23H, $\boldsymbol{H}_{Ar}$), 7.07 – 7.03 (m, 2H, $\boldsymbol{H}_{Ar}$), 5.97 (t, *J* = 9.8 Hz, 1H, ***H***-$3_{\text{Glu}}$), 5.76 (t, *J* = 9.7 Hz, 1H, ***H***-$4_{\text{Glu}}$), 5.72 (dd, *J* = 9.9, 7.9 Hz, 1H, ***H***-$2_{\text{Glu}}$), 5.34

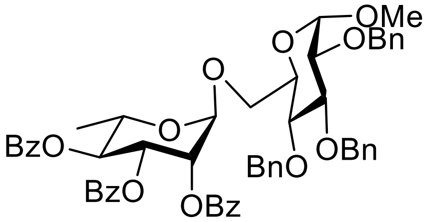
(d, *J* = 7.9 Hz, 1H, ***H***-1$_{\mathrm{Glu}}$), 5.05 (d, *J* = 11.4 Hz, 1H, OC***H***$_2$Ar), 4.69 (dd, *J* = 12.2, 3.0 Hz, 1H, ***H***-6b$_{\mathrm{Glu}}$), 4.57 (m, ovrlp, 2H, ***H***-6a$_{\mathrm{Glu,}}$ OC***H***$_2$Ar), 4.48 (dd, *J* = 12.3, 3.2 Hz, 2H, OC***H***$_2$Ar), 4.40 (d, *J* = 4.4 Hz, 1H, OC***H***$_2$Ar), 4.38 (d, *J* = 3.9 Hz, 1H, ***H***-1$_{\mathrm{Gal}}$), 4.23 (dd, *J* = 10.2, 3.0 Hz, 1H, ***H***-3$_{\mathrm{Gal}}$), 4.18 (m, 1H, ***H***-5$_{\mathrm{Glu}}$), 4.12 (d, *J* = 12.6 Hz, 1H, OC***H***$_2$Ar), 4.01 (d, *J* = 3.0 Hz, 1H, ***H***-4$_{\mathrm{Gal}}$), 3.84 – 3.78 (m, 2H, ***H***-2$_{\mathrm{Gal,}}$ ***H***-5$_{\mathrm{Gal}}$), 3.50 (dd, *J* = 9.7, 6.6 Hz, 1H, ***H***-6a$_{\mathrm{Gal}}$), 3.40 (dd, *J* = 9.7, 5.6 Hz, 1H, ***H***-6b$_{\mathrm{Gal}}$), 3.29 (s, 3H, OC***H***$_3$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 166.06, 165.83, 165.28, 165.11, 138.68, 138.30, 138.11, 133.54, 133.31, 133.29, 133.18, 129.91, 129.82, 129.78, 129.57, 129.27, 128.82, 128.77, 128.72, 128.48, 128.46, 128.36, 128.35, 128.22, 101.98, 98.58, 78.18, 77.30, 77.09, 76.88, 76.38, 75.05, 73.87, 73.40, 72.97, 72.22, 72.15, 69.72, 69.39, 69.26, 62.79, 55.18.

**$[\alpha]_{D}^{21.9}$ =** -38.3 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{62}H_{58}O_{15}$ is 1065.3673; found 1065.3663.

**Methyl 2,3,4,-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (33):**



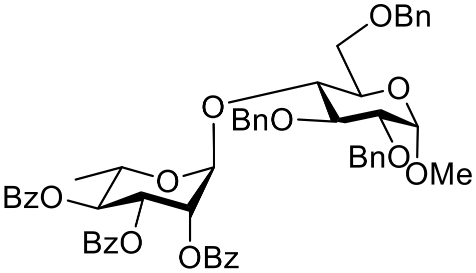
Compound **33** (190 mg, 99% yield) was prepared from the donor **13** (0.24 mmol, 1.2 eq.) and acceptor **14** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL CH$_2$Cl$_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate: 60/1 to 30/1) and characterized as follows:

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 8.12 – 8.09 (m, 2H, ***H***$_{Ar}$), 8.00 – 7.98 (m, 2H, ***H***$_{Ar}$), 7.84 – 7.81 (m, 2H, ***H***$_{Ar}$), 7.65 – 7.62 (m, 1H, ***H***$_{Ar}$), 7.56 – 7.49 (m, 3H, ***H***$_{Ar}$), 7.45 – 7.39 (m, 7H, ***H***$_{Ar}$), 7.37 – 7.33 (m, 8H, ***H***$_{Ar}$), 7.29 – 7.26 (m, 5H, ***H***$_{Ar}$), 5.82 (dd, *J* = 10.1, 3.5 Hz, 1H, ***H***-3$_{\mathrm{Rha}}$), 5.68 – 5.64 (m, 2H, ***H***-2$_{\mathrm{Rha,}}$ ***H***-4$_{\mathrm{Rha}}$), 5.05 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.99 (d, *J* = 11.2 Hz, 1H, OC***H***$_2$Ar), 4.96 (d, *J* = 1.7 Hz, 1H, ***H***-1$_{\mathrm{Rha}}$), 4.88 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.85 (d, *J* = 12.1 Hz, 1H, OC***H***$_2$Ar), 4.73 (d, *J* = 12.0 Hz, 1H, OC***H***$_2$Ar), 4.68 (d, *J* = 3.6 Hz, 1H, ***H***-1$_{\mathrm{Glu}}$), 4.65 (d, *J* = 11.2 Hz, 1H, OC***H***$_2$Ar), 4.22 – 4.16 (m, 1H, ***H***-5$_{\mathrm{Rha}}$), 4.07 (dd, *J* = 9.6, 8.8 Hz, 1H, ***H***-3$_{\mathrm{Glu}}$), 3.98 (dd, *J*

= 11.0, 1.8 Hz, 1H, ***H***-6b$_{\text{Glu}}$), 3.89 (m, 1H, ***H***-5$_{\text{Glu}}$), 3.67 – 3.61 (m, 2H, ***H***-2$_{\text{Glu,}}$ ***H***-6a$_{\text{Glu}}$), 3.54 (dd, *J* = 10.1, 8.8 Hz, 1H, ***H***-4$_{\text{Glu}}$), 3.49 (s, 3H, OC***H***$_3$), 1.33 (d, *J* = 6.2 Hz, 3H, ***H***-6$_{\text{Rha}}$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 165.81, 165.45, 165.44, 138.71, 138.16, 133.45, 133.33, 133.06, 129.91, 129.76, 129.68, 129.45, 129.29, 129.23, 128.58, 128.50, 128.48, 128.43, 128.27, 128.15, 127.99, 127.97, 127.93, 127.81, 127.63, 98.01, 97.93, 82.21, 80.15, 77.83, 77.24, 77.03, 76.82, 75.81, 75.16, 73.48, 71.79, 70.71, 70.11, 69.91, 67.06, 66.68, 55.33, 17.61.

**Methyl 2,3,4,-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (34):**

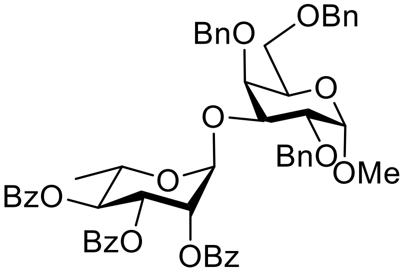


Compound **34** (178 mg, 96% yield) was prepared from donor **13** (0.24 mmol, 1.2 eq.) and acceptor **18** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL CH$_2$Cl$_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate: 60/1 to 30/1) and characterized as follows:

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 8.09 – 8.07 (m, 2H, ***H****$_{Ar}$*), 7.93 – 7.91 (m, 2H, ***H****$_{Ar}$*), 7.89 – 7.87 (m, 2H, ***H****$_{Ar}$*), 7.63 – 7.60 (m, 1H, ***H****$_{Ar}$*), 7.57 – 7.54 (m, 1H, ***H****$_{Ar}$*), 7.51 – 7.47 (m, 2H, ***H****$_{Ar}$*), 7.47 – 7.44 (m, 1H, ***H****$_{Ar}$*), 7.44 – 7.41 (m, 4H, ***H****$_{Ar}$*), 7.37 – 7.35 (m, 3H, ***H****$_{Ar}$*), 7.32 – 7.30 (m, 6H, ***H****$_{Ar}$*), 7.23 – 7.20 (m, 2H, ***H****$_{Ar}$*), 7.19 – 7.13 (m, 4H, ***H****$_{Ar}$*), 5.80 (dd, *J* = 10.2, 3.4 Hz, 1H, ***H***-3$_{\text{Rha}}$), 5.62 (t, *J* = 10.1 Hz, 1H, ***H***-4$_{\text{Rha}}$), 5.59 (dd, *J* = 3.4, 1.7 Hz, 1H, ***H***-2$_{\text{Rha}}$), 5.26 – 5.22 (m, 2H, ***H***-1$_{\text{Rha,}}$ OC***H***$_2$Ar), 4.87 (d, *J* = 11.1 Hz, 1H, OC***H***$_2$Ar), 4.79 (d, *J* = 12.1 Hz, 1H, OC***H***$_2$Ar), 4.67 (d, *J* = 10.9 Hz, 1H, OC***H***$_2$Ar), 4.65 (d, *J* = 2.5 Hz, 1H, ***H***-1$_{\text{Glu}}$), 4.63 – 4.55 (m, 2H, OC***H***$_2$Ar), 4.39 (m, 1H, ***H***-5$_{\text{Rha}}$), 4.04 (t, *J* = 9.3 Hz, 1H, ***H***-4$_{\text{Glu}}$), 4.00 (t, *J* = 9.2 Hz, 1H, ***H***-3$_{\text{Glu}}$), 3.91 (dd, *J* = 11.2, 2.9 Hz, 1H, ***H***-6b$_{\text{Glu}}$), 3.87 (m, 1H, ***H***-5$_{\text{Glu}}$), 3.76 (dd, *J* = 11.2, 1.9 Hz, 1H, ***H***-6a$_{\text{Glu}}$), 3.67 (dd, *J* = 9.2, 3.5 Hz, 1H, ***H***-2$_{\text{Glu}}$), 3.43 (s, 3H, OC***H***$_3$), 0.90 (d, *J* = 6.2 Hz, 3H, ***H***-6$_{\text{Rha}}$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 165.77, 165.70, 138.70, 137.94, 137.72, 133.47, 133.26, 133.18, 129.90, 129.71, 129.68, 129.40, 129.20, 128.57, 128.51, 128.40, 128.33, 128.28, 128.21, 128.17, 128.02, 127.91, 127.50, 127.44, 127.30, 98.01, 97.03, 80.30, 79.75, 77.25, 77.04, 76.83, 75.56, 74.79, 73.39, 73.28, 71.72, 71.27, 70.06, 69.97, 68.25, 67.04, 55.33, 29.73, 17.16.

**Methyl 2,3,4,-tri-*O*-benzoyl-α-L-rhamnopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (35):**



Compound **35** (174 mg, 94% yield) was prepared from donor **13** (0.24 mmol, 1.2 eq.) and acceptor **19** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Toluene/Ethyl Acetate: 60/1 to 30/1) and characterized as follows:

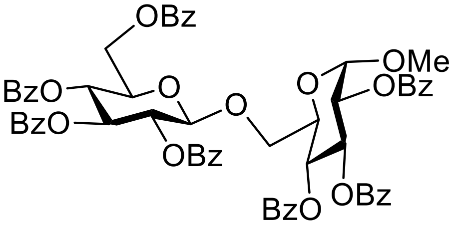
**$^1$H NMR (600 MHz, CDCl$_3$)** δ 8.11 – 8.09 (m, 2H, ***H***$_{Ar}$), 7.97 – 7.94 (m, 2H, ***H***$_{Ar}$), 7.89 – 7.86 (m, 2H, ***H***$_{Ar}$), 7.66 – 7.62 (m, 1H, ***H***$_{Ar}$), 7.54 (m, 4H, ***H***$_{Ar}$), 7.45 – 7.29 (m, 18H, ***H***$_{Ar}$), 7.24 – 7.20 (m, 1H, ***H***$_{Ar}$), 5.97 (dd, *J* = 10.0, 3.4 Hz, 1H, ***H***-3$_{\text{Rha}}$), 5.94 (dd, *J* = 3.4, 1.8 Hz, 1H, ***H***-2$_{\text{Rha}}$), 5.71 (t, *J* = 9.9 Hz, 1H, ***H***-4$_{\text{Rha}}$), 5.57 (d, *J* = 1.7 Hz, 1H, ***H***-1$_{\text{Rha}}$), 5.16 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 4.94 (d, *J* = 12.1 Hz, 1H, OC***H***$_2$Ar), 4.83 (d, *J* = 11.5 Hz, 1H, OC***H***$_2$Ar), 4.67 (d, *J* = 12.1 Hz, 1H, *OC**H**$_2$Ar*), 4.61 (d, *J* = 3.6 Hz, 1H, ***H***-1$_{\text{Gal}}$), 4.57 (d, *J* = 11.8 Hz, 1H, OC***H***$_2$Ar), 4.49 (d, *J* = 11.8 Hz, 1H, OC***H***$_2$Ar), 4.29 (m, 2H, ***H***-5$_{\text{Rha,}}$ ***H***-3$_{\text{Gal}}$), 4.15 (dd, *J* = 10.1, 3.6 Hz, 1H, ***H***-2$_{\text{Gal}}$), 4.04 – 3.99 (m, 2H, ***H***-4$_{\text{Gal,}}$ ***H***-5$_{\text{Gal}}$), 3.63 (m, 2H, ***H***-6a, ***H***-6b$_{\text{Gal}}$), 3.36 (s, 3H, OC***H***$_3$), 1.41 (d, *J* = 6.2 Hz, 3H, ***H***-6$_{\text{Rha}}$).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 165.74, 165.51, 165.33, 138.44, 138.16, 137.90, 133.37, 133.35, 133.09, 129.92, 129.74, 129.55, 129.31, 128.58, 128.53, 128.48, 128.46, 128.37, 128.35, 128.31, 127.92, 127.88, 127.85, 99.14, 98.43, 77.35, 77.29, 77.08, 76.87, 76.00, 75.23, 73.64, 73.62, 71.99, 70.60, 69.88, 69.38, 69.00, 67.48, 55.45, 29.75, 17.95.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.5}}$ = +0.037 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** $[M+H]^+$ calculated for $C_{55}H_{54}O_{13}$ is 923.3642; found 923.3634.

**Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (36):**

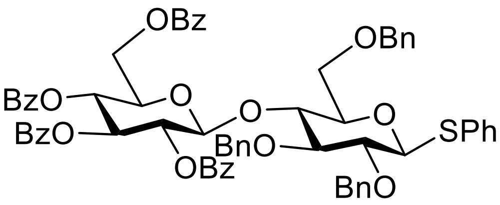


Compound **36** (207 mg, 95% yield) was prepared from donor **10** (0.24 mmol, 1.2 eq.) and acceptor **20** (0.2 mmol, 1 eq.) following the general procedure (B) using tris(2,4-di-tert-butylphenyl)phosphite gold(I) (1.76 mg, 1 mol%) and solid AgOTf (2.56 mg, 5 mol%) in 1 mL $CH_2Cl_2$ at room temperature for 10 minutes (purified via silica gel column chromatography, Hexane/Ethyl Acetate 8/1 to 6/1) and characterized as follows:

**$^1$H NMR (600 MHz, $CDCl_3$)** δ 8.03 (m, 4H, ***H****Ar*), 7.98 – 7.96 (m, 2H, ***H****Ar*), 7.94 – 7.92 (m, 2H, ***H****Ar*), 7.91 – 7.89 (m, 2H, ***H****Ar*), 7.88 – 7.85 (m, 2H, ***H****Ar*), 7.84 – 7.82 (m, 2H, ***H****Ar*), 7.57 (m, 1H, ***H****Ar*), 7.54 – 7.49 (m, 4H, ***H****Ar*), 7.46 – 7.34 (m, 12H, ***H****Ar*), 7.32 – 7.28 (m, 4H, ***H****Ar*), 6.12 (t, *J* = 9.8 Hz, 1H, ***H***-3), 5.98 (t, *J* = 9.7 Hz, 1H, ***H'***-3), 5.71 (t, *J* = 9.7 Hz, 1H, ***H'***-4), 5.62 (dd, *J* = 9.8, 7.9 Hz, 1H, ***H'***-2), 5.37 (dd, *J* = 10.3, 9.4 Hz, 1H, ***H***-4), 5.14 (dd, *J* = 10.2, 3.6 Hz, 1H, ***H***-2), 5.03 (d, *J* = 7.9 Hz, 1H, ***H'***-1), 4.99 (d, *J* = 3.6 Hz, 1H, ***H***-1), 4.66 (dd, *J* = 12.1, 3.2 Hz, 1H, ***H'***-6b), 4.50 (dd, *J* = 12.2, 5.1 Hz, 1H, ***H'***-6a), 4.27 (m, 1H, ***H***-5), 4.20 (m, 1H, ***H'***-5), 4.17 – 4.14 (m, 1H, ***H***-6a), 3.84 (dd, *J* = 11.5, 7.6 Hz, 1H, ***H***-6b), 3.14 (s, 3H, $OCH_3$).

**$^{13}$C NMR (151 MHz, $CDCl_3$)** δ 166.14, 165.84, 165.73, 165.68, 165.45, 165.20, 165.19, 133.48, 133.36, 133.28, 133.17, 133.09, 101.79, 96.45, 77.32, 77.11, 76.90, 72.83, 72.29, 72.00, 71.87, 70.33, 69.66, 69.63, 68.96, 68.76, 63.01, 55.06, 29.74.

**Phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (38):**



Compound **38** was prepared in 88% yield (β only) from glycosyl donor **10** and acceptor **37**[S10] following the aforementioned general procedure (B) for cationic gold (I)-catalyzed glycosylation, except that the reaction was stirred for 30 minutes.

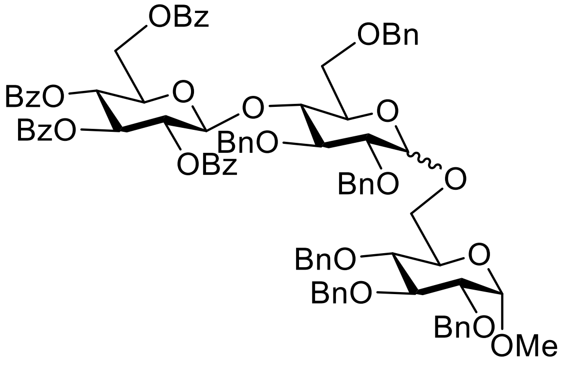
**$^{1}$H NMR (600 MHz, CDCl$_3$)** δ 8.00 – 7.97 (m, 2H, ***H****Ar*), 7.94 – 7.91 (m, 2H, ***H****Ar*), 7.91 – 7.88 (m, 2H, ***H****Ar*), 7.84 – 7.81 (m, 2H, ***H****Ar*), 7.57 – 7.17 (m, 32H, ***H****Ar*), 5.75 (t, *J* = 9.7 Hz, 1H, ***H'***-3), 5.61 (t, *J* = 9.7 Hz, 1H, ***H'***-4), 5.52 (dd, *J* = 9.9, 8.1 Hz, 1H, ***H'***-2), 5.16 (d, *J* = 11.1 Hz, 1H, OC***H***$_2$Ar), 5.02 (d, *J* = 8.1 Hz, 1H, ***H'***-1), 4.80 – 4.68 (m, 4H, OC***H***$_2$Ar), 4.58 (d, *J* = 9.9 Hz, 1H, ***H***-1), 4.47 (d, *J* = 11.9 Hz, 1H, OC***H***$_2$Ar), 4.42 (dd, *J* = 12.1, 3.3 Hz, 1H, ***H'***-6a), 4.29 (dd, *J* = 12.1, 5.0 Hz, 1H, ***H'***-6b), 4.11 (t, *J* = 9.4 Hz, 1H, ***H***-4), 3.80 (m, 1H, ***H'***-5), 3.73 (dd, *J* = 11.1, 3.5 Hz, 1H, ***H***-6b), 3.68 (t, *J* = 8.9 Hz, 1H, ***H***-3), 3.64 (dd, *J* = 11.1, 1.7 Hz, 1H, ***H***-6a), 3.45 (dd, *J* = 9.9, 8.7 Hz, 1H, ***H***-2), 3.28 (m, 1H, ***H***-5).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 166.05, 165.79, 165.11, 164.88, 138.84, 138.16, 138.06, 133.65, 133.48, 133.44, 133.26, 133.05, 132.09, 129.80, 129.78, 129.74, 129.61, 129.01, 128.90, 128.85, 128.82, 128.73, 128.57, 128.43, 128.34, 128.32, 128.24, 128.18, 128.12, 128.04, 127.78, 127.53, 127.50, 127.36, 100.51, 87.53, 84.61, 80.30, 78.50, 77.29, 77.08, 76.87, 75.56, 75.52, 73.53, 73.14, 72.26, 72.02, 69.77, 67.90, 63.07, 29.75.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.7}}$ **=** -9.4 (*c* = 1.0, CHCl$_3$)

**HRMS (ESI) m/z:** [M+Na]$^+$ calculated for $C_{67}H_{60}O_{14}S$ is 1143.3601; found 1143.3556.

**Methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-α/β-D-glucopyranosyl-(1→6)-2,3,4-tetra-*O*-benzyl-α-D-glucopyranoside (39).**



To a mixture of disaccharide donor **38** (66 mg, 0.06 mmol), methyl 2,3,4-tetra-*O*-benzyl-α-D-glucopyranoside (23 mg, 0.05 mmol) and freshly activated 4Å molecular sieves (65 mg) was added dry $CH_2Cl_2$ (0.5 mL), and the resulting solution was stirred at ambient temperature for 20 min then cooled down to -40º C and stirred for another 20 min. *N*-Iodosuccinimide (NIS) (17 mg, 0.075 mmol) and triflic acid (TfOH) (0.44 µL, 5 µmol) were added and the reaction mixture was stirred at -40 °C for 15 minutes before being quenched with $Et_3N$ (0.15 eq.). The mixture was filtered through celite and the organic solution was sequentially washed with saturated $Na_2S_2O_3$, water, and brine, dried over anhydrous $Na_2SO_4$, filtered and concentrated. The crude residue was purified by Prep TLC (Hexane/Ethyl acetate = 2/1) to afford 64 mg of trisaccharide **39** (87% yield) as an inseparable anomeric mixture (α:β = 1.3:1).

**$^1$H NMR (600 MHz, CDCl$_3$)** δ 7.97 (dd, *J* = 8.0, 1.4 Hz, 4H, ***H***$_{Ar}$), 7.95 – 7.92 (m, 2H, ***H***$_{Ar}$), 7.91 – 7.86 (m, 6H, *H*$_{Ar}$), 7.81 (m, 4H, ***H***$_{Ar}$), 7.58 – 7.14 (m, 84H, ***H***$_{Ar}$), 5.72 (t, *J* = 9.7 Hz, 1H, ***H”***-3 (α)), 5.66 – 5.54 (ovrlp, 3H, ***H”***-3(β), ***H”***-4(α and β)), 5.54 – 5.46 (ovrlp, 2H, ***H”***-2 (α and β), 5.08 (d, *J* = 11.1 Hz, 1H, OC***H***$_2$Ar, (α)), 5.05 (d, *J* = 11.2 Hz, 1H, OC***H***$_2$Ar, (β)), 5.00 – 4.96 (m, 3H, ***H”***-1 (α), OC***H***$_2$Ar (β)), 4.95 (d, *J* = 10.8 Hz, 1H, OC***H***$_2$Ar (β)), 4.90 – 4.84 (m, 3H, ***H’***-1 (β), OC***H***$_2$Ar (β)), 4.79 (m, 8H, OC***H***$_2$Ar (α and β)), 4.76 (d, *J* = 8.0 Hz, 1H, ***H”***-1 (β)), 4.73 – 4.67 (m, 4H, OC***H***$_2$Ar (α and β)), 4.65 (m, 3H, OC***H***$_2$Ar (α and β)), 4.62 (d, *J* = 10.0 Hz, 1H, OC***H***$_2$Ar(α)), 4.60 – 4.56 (m, 3H, ***H’***-1 (α), OC***H***$_2$Ar (α and β)), 4.54 (d, *J* = 11.9 Hz, 1H, OC***H***$_2$Ar (β)), 4.48 (d, *J* = 11.2 Hz, 1H, OC***H***$_2$Ar (α)), 4.42 (dd, *J* = 3.4, 1.8 Hz, 1H, ***H”***-6b (α)), 4.41 – 4.39 (m, 2H, ***H”***-6b (β)), 4.38 – 4.34 (m, 3H, ***H***-1 (α), OC***H***$_2$Ar (α and β)), 4.28 (dd, *J* = 12.1, 4.9 Hz, 1H, ***H”***-6a (α)), 4.26 – 4.22 (m, 3H, ***H***-1 (β) ***H”***-6a (β)), 4.08 (dd, *J* = 11.0, 2.0 Hz, 1H, ***H***-6a (α)), 4.06 – 4.02 (m, 1H, ***H***-5 (β)), 3.99 (m, 2H, ***H’***-4 (α), ***H’***-4 (β)), 3.94 (t, *J* = 9.3 Hz, 1H, ***H***-3, (α)), 3.85 (t, *J* = 9.2 Hz, 1H, ***H’***-3 (β)), 3.80 (m, 1H, ***H’***-5 (α)), 3.74-3.70 (m, 4H, ***H”***-3 (α), ***H”***-5 (β)), ***H***-3 (β), ***H***-6a (β)), 3.69 – 3.66 (m, 2H, ***H’***-3 (α), ***H’***-6a (β)), 3.66 – 3.63 (m, 1H, ***H***-5 (α)), 3.62 – 3.56 (m, 2H, ***H***-6b (α), ***H’***-6b (β)), 3.54 (dd, *J* = 11.1, 1.6 Hz, 1H, ***H***-6b (β)), 3.52 – 3.49 (m, 2H, ***H’***-2 (α), ***H’***-6b (α)), 3.48 – 3.39 (m, 5H, ***H’***-2 (β) ***H***-4 (α), ***H***-2 (β), ***H***-4 (β), ***H’***-6a (α) ), 3.37 (dd, *J* = 9.6, 3.6 Hz, 1H, ***H***-2, (α), ), 3.32 (s, 4H, OC*H*$_3$ (α)), 3.27 (s, 3H, OC*H*$_3$ (β)), 3.15 (m, 1H, ***H’***-5 (β)).

**$^{13}$C NMR (151 MHz, CDCl$_3$)** δ 166.04, 166.02, 165.75, 165.71, 165.09, 165.08, 164.86, 164.71, 139.24, 138.92, 138.79, 138.76, 138.50, 138.38, 138.32, 138.26, 138.16, 138.10, 138.09, 137.93, 133.43, 133.39, 133.35, 133.22, 133.19, 133.00, 132.97, 129.76, 129.69, 129.60, 129.57, 103.75, 100.43, 100.40, 98.01, 97.60, 97.20, 82.66, 82.14, 81.98, 81.47, 80.01, 79.72, 79.46, 78.89, 77.92, 77.79, 77.26, 77.05, 76.84, 75.72, 75.69, 75.25, 75.15, 74.94, 74.88, 74.87, 74.41, 73.60, 73.44, 73.38, 73.19, 73.18, 73.09, 72.87, 72.26, 72.21, 71.94, 71.77, 70.29, 69.95, 69.85, 69.68, 69.59, 68.47, 67.76, 67.51, 66.18, 63.11, 63.01, 55.21, 55.08, 29.73.

$[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{21.7}}$ **=** -121.77 (*c* = 1.0, $CHCl_3$)

**HRMS (ESI) m/z:** $[M+Na]^+$ calculated for $C_{89}H_{86}O_{20}$ is 1497.5610 found 1497.5515.

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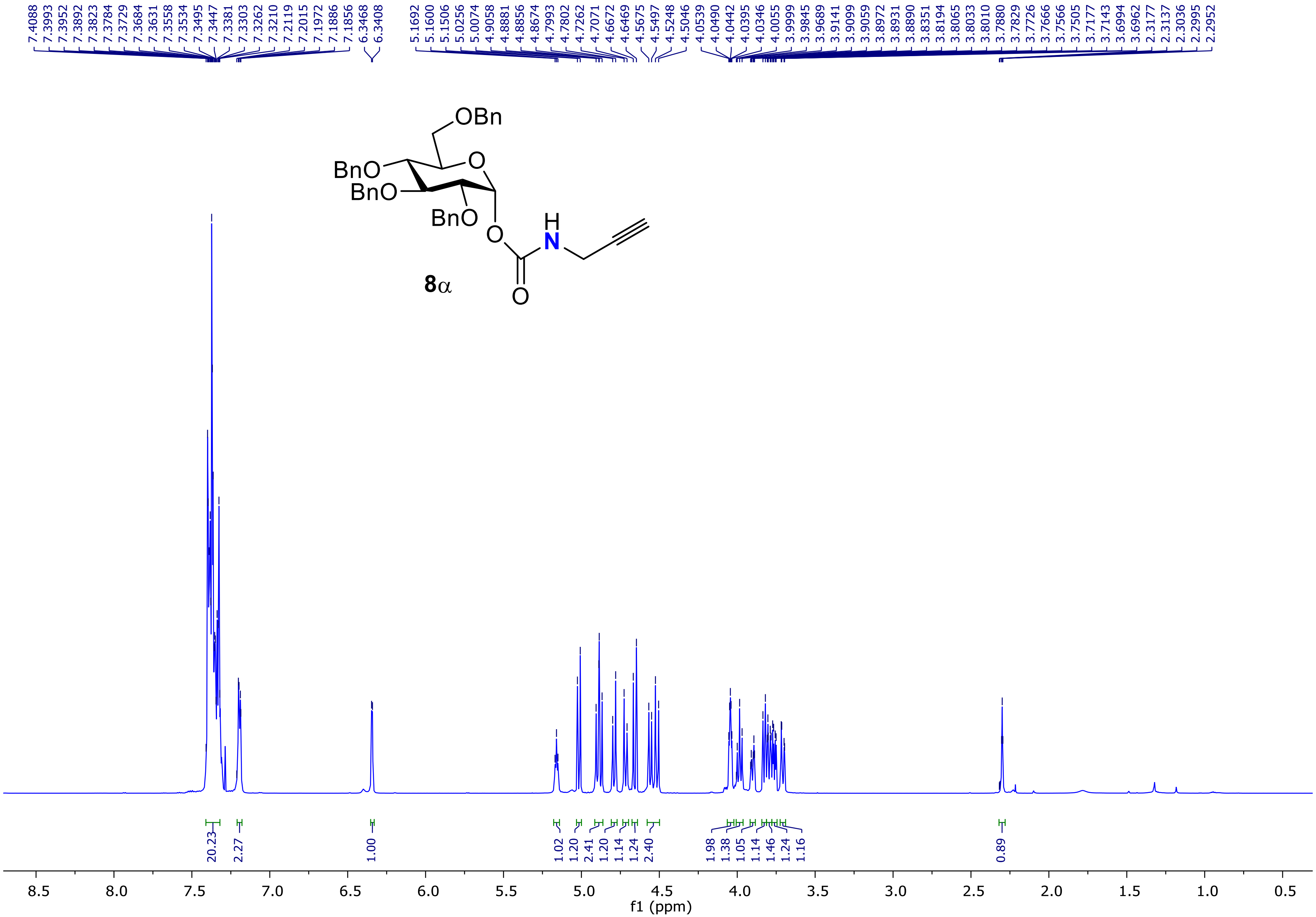

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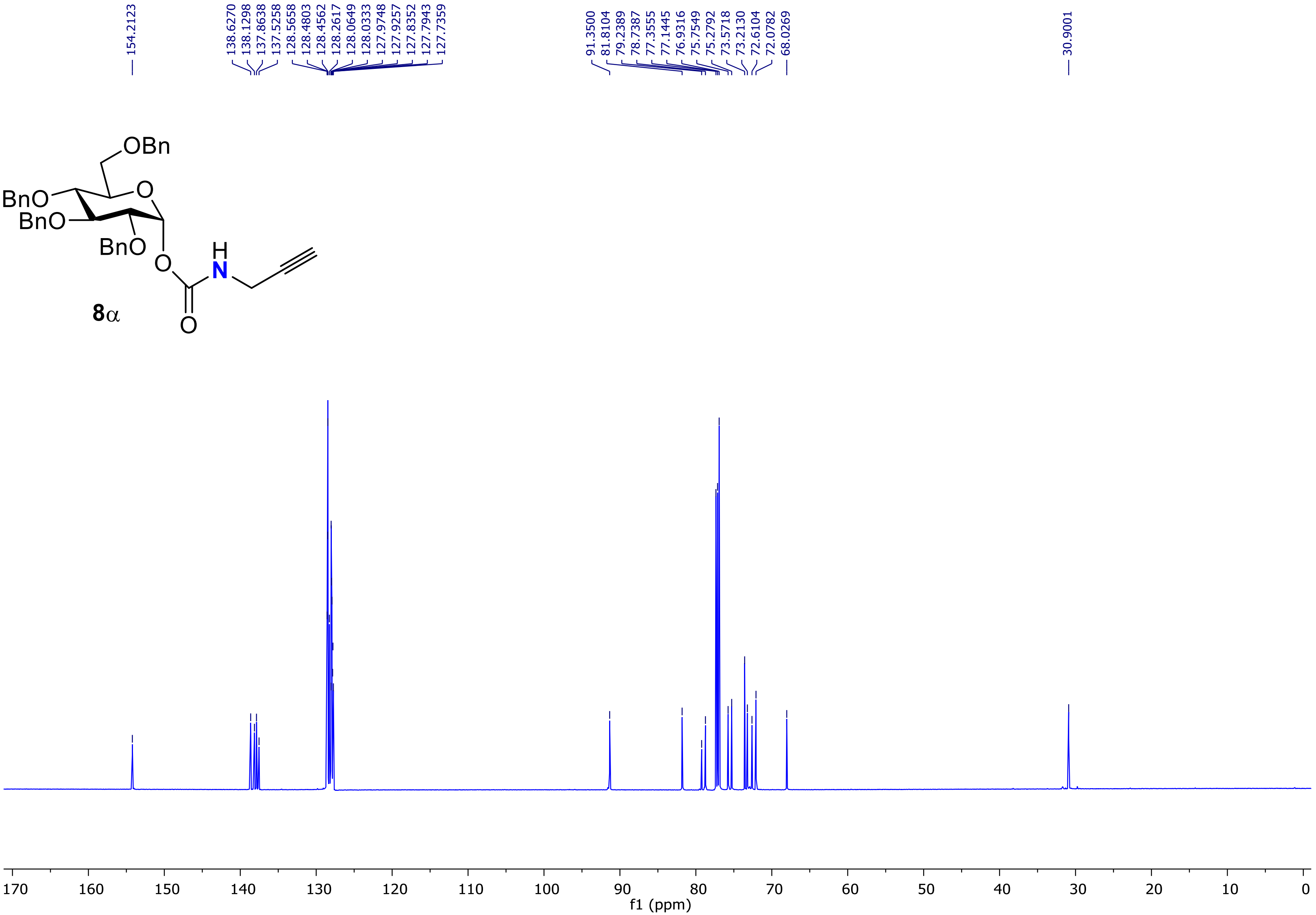
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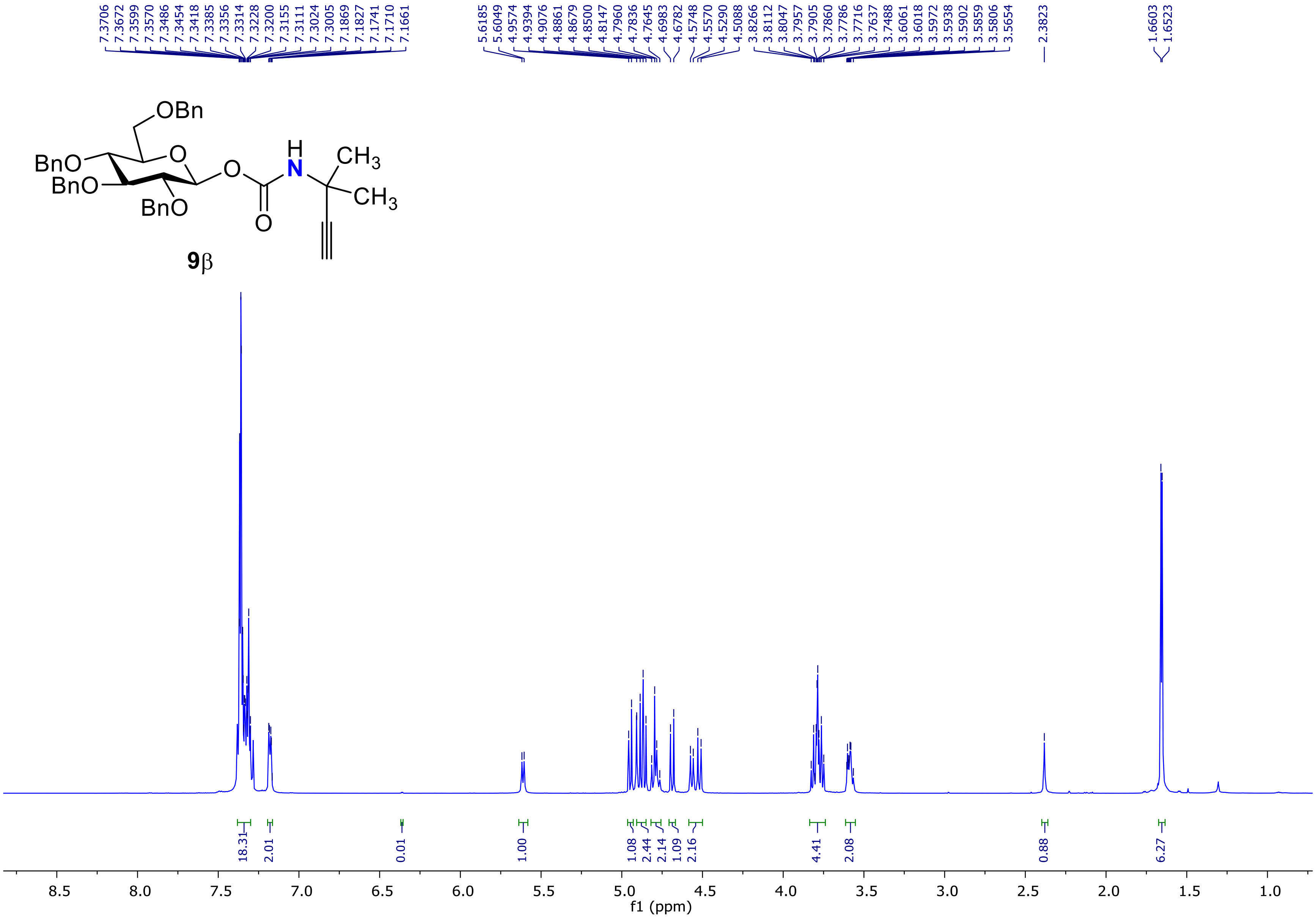
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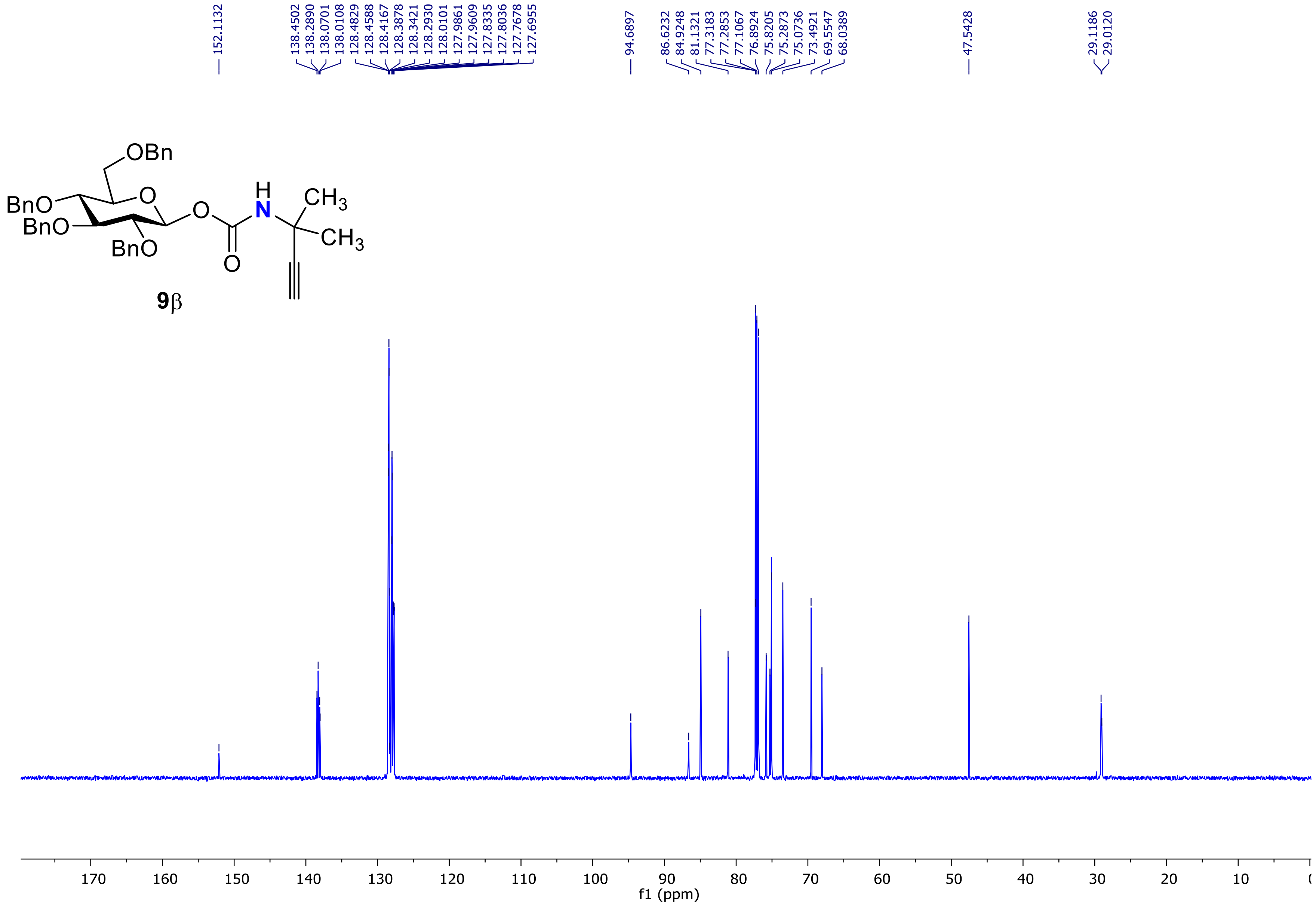
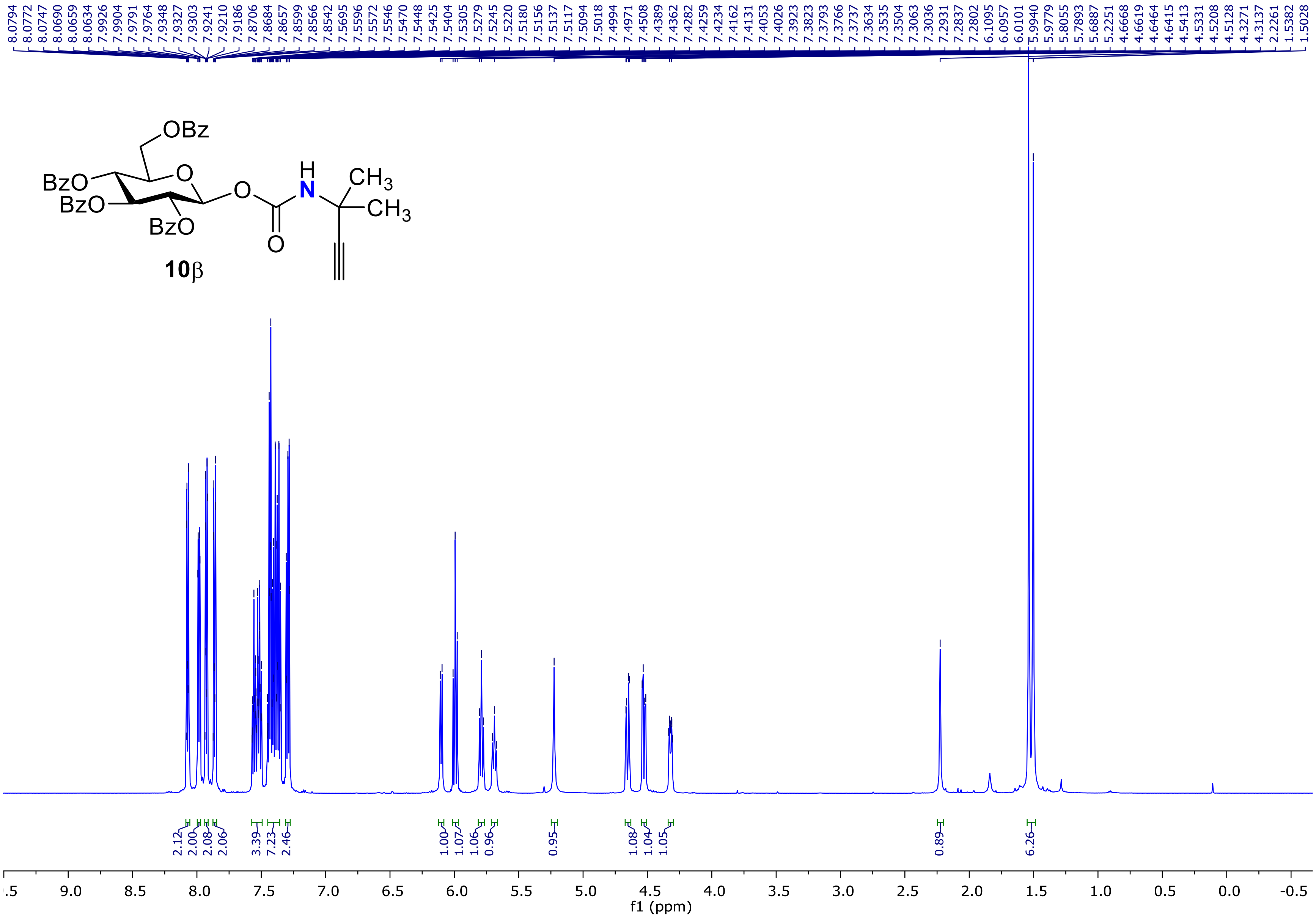
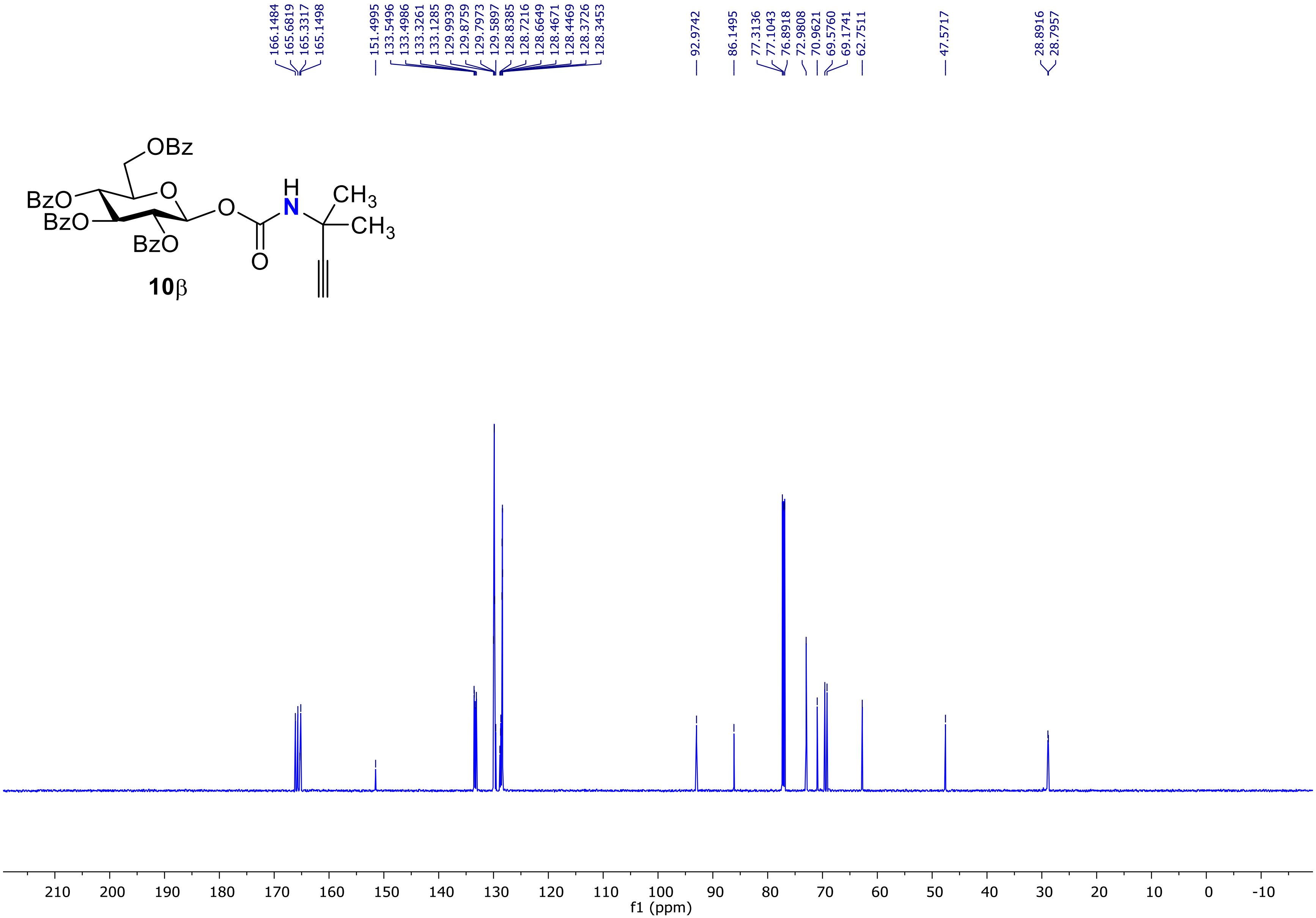
2.3823
1.6603
1.6523
OBn
BnO
BnO
BnO
O
O
H
N
CH3
CH3
O
9β
18.31
2.01
0.01
1.00
1.08
2.44
2.14
1.09
2.16
4.41
2.08
0.88
6.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

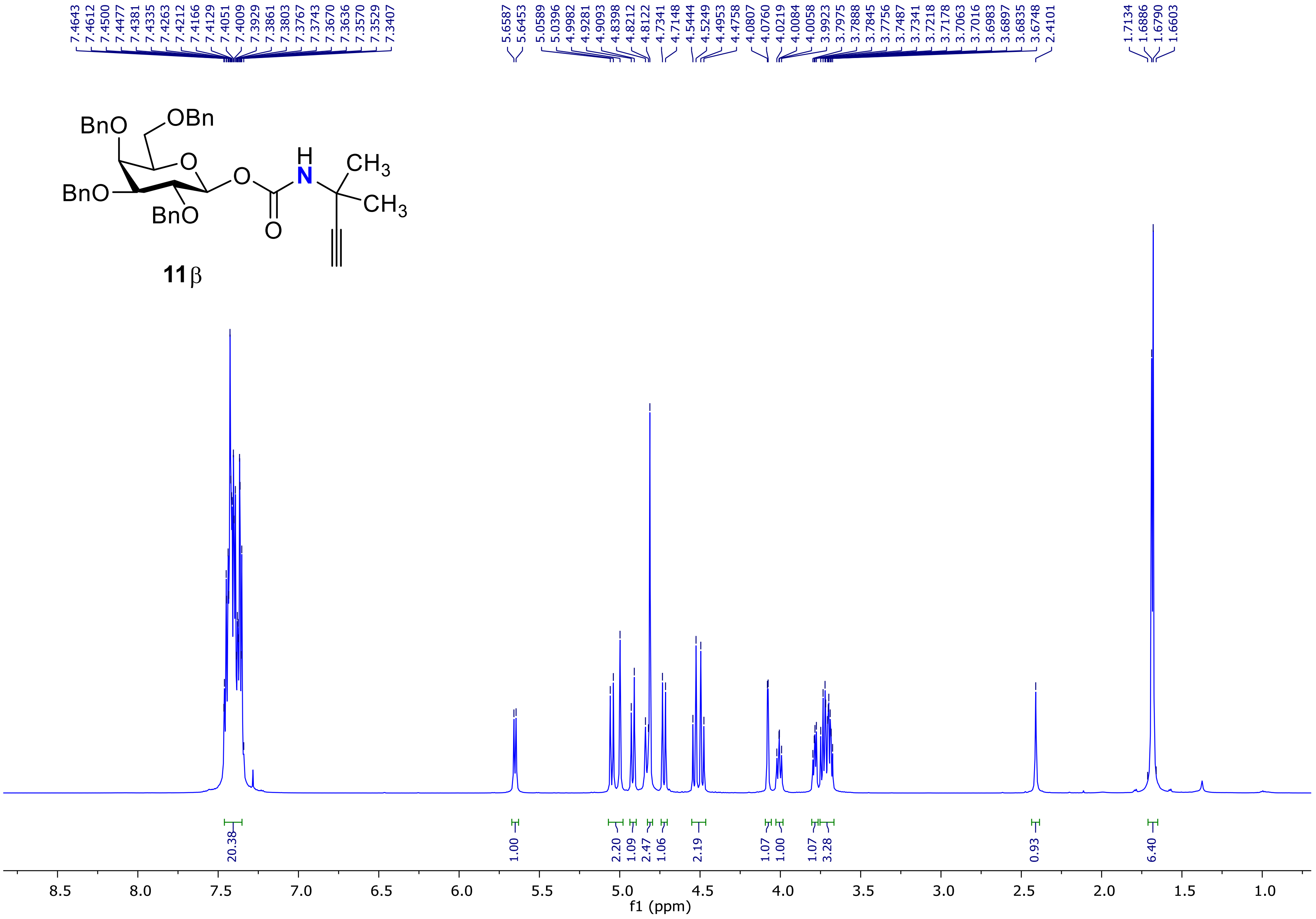

152.1132
138.4502
138.2890
138.0701
138.0108
128.4829
128.4588
128.4167
128.3878
128.3421
128.2930
128.0101
127.9861
127.9609
127.8335
127.8036
127.7678
127.6955
94.6897
86.6232
84.9248
81.1321
77.3183
77.2853
77.1067
76.8924
75.8205
75.2873
75.0736
73.4921
69.5547
68.0389
47.5428
29.1186
29.0120
OBn
BnO
BnO
BnO
O
O
H
N
CH3
CH3
O
9β
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


8.0794
8.0772
8.0747
8.0690
8.0659
8.0634
7.9926
7.9904
7.9791
7.9764
7.9348
7.9327
7.9303
7.9241
7.9210
7.9186
7.8706
7.8684
7.8657
7.8599
7.8566
7.8542
7.5695
7.5596
7.5572
7.5546
7.5470
7.5448
7.5425
7.5404
7.5305
7.5279
7.5245
7.5220
7.5180
7.5156
7.5137
7.5117
7.5094
7.5018
7.4994
7.4971
7.4508
7.4389
7.4362
7.4282
7.4259
7.4234
7.4162
7.4131
7.4053
7.4026
7.3923
7.3823
7.3793
7.3766
7.3737
7.3634
7.3535
7.3504
7.3063
7.3036
7.2931
7.2837
7.2802
6.1095
6.0957
6.0101
5.9940
5.9779
5.8055
5.7893
5.6887
5.2251
4.6668
4.6619
4.6464
4.6415
4.5413
4.5331
4.5208
4.5128
4.3271
4.3137
2.2261
1.5382
1.5028
OBz
BzO
O
BzO
BzO
O
H
N
CH3
CH3
O
10β
2.12
2.00
2.08
2.06
3.39
7.23
2.46
1.00
1.07
1.06
0.96
0.95
1.08
1.04
1.05
0.89
6.26
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

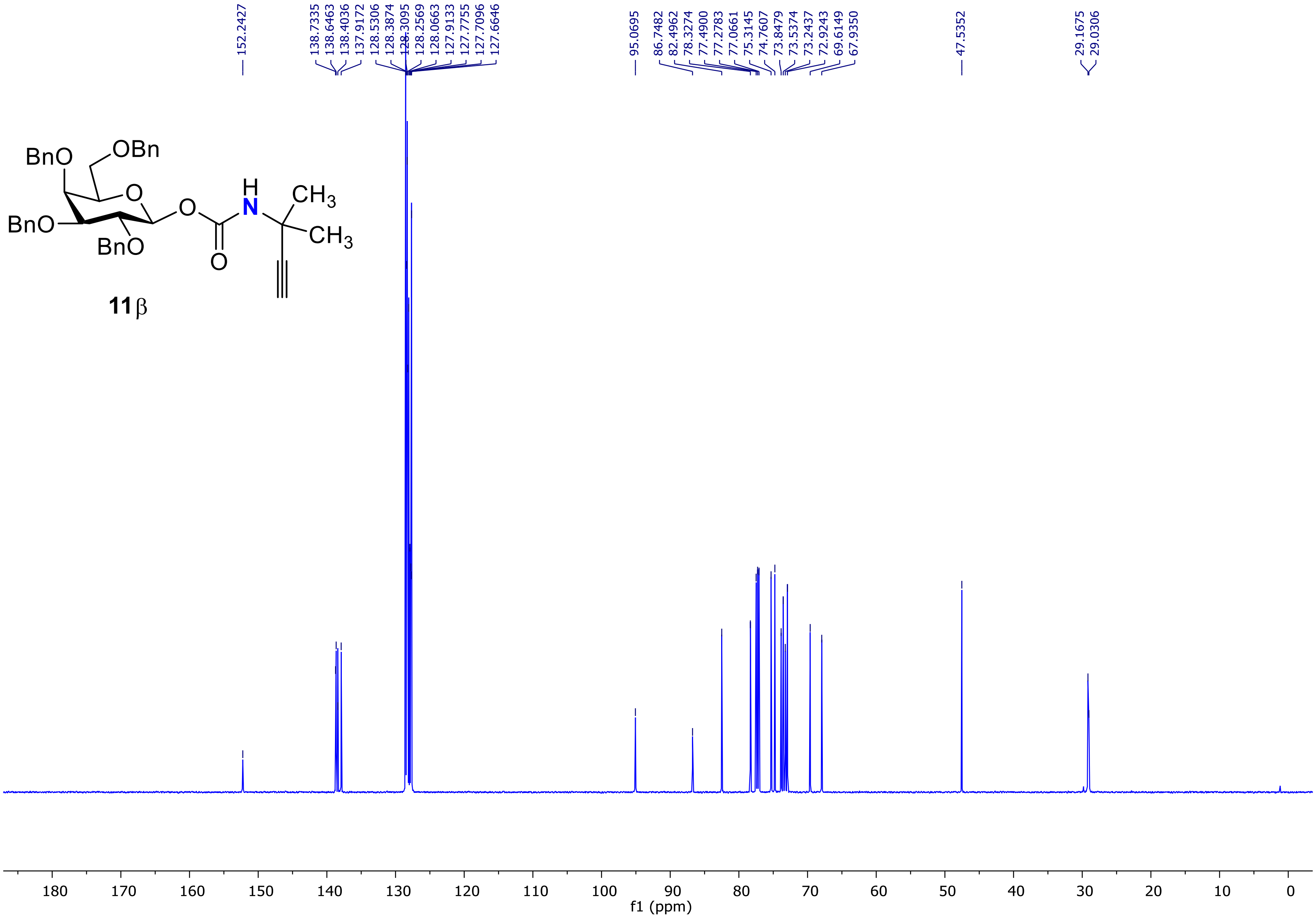

OBz
BzO
BzO
BzO
O
O
H
N
CH3
CH3
O

**10**β

166.1484
165.6819
165.3317
165.1498
151.4995
133.5496
133.4986
133.3261
133.1285
129.9939
129.8759
129.7973
129.5897
128.8385
128.7216
128.6649
128.4671
128.4469
128.3726
128.3453
92.9742
86.1495
77.3136
77.1043
76.8918
72.9808
70.9621
69.5760
69.1741
62.7511
47.5717
28.8916
28.7957
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

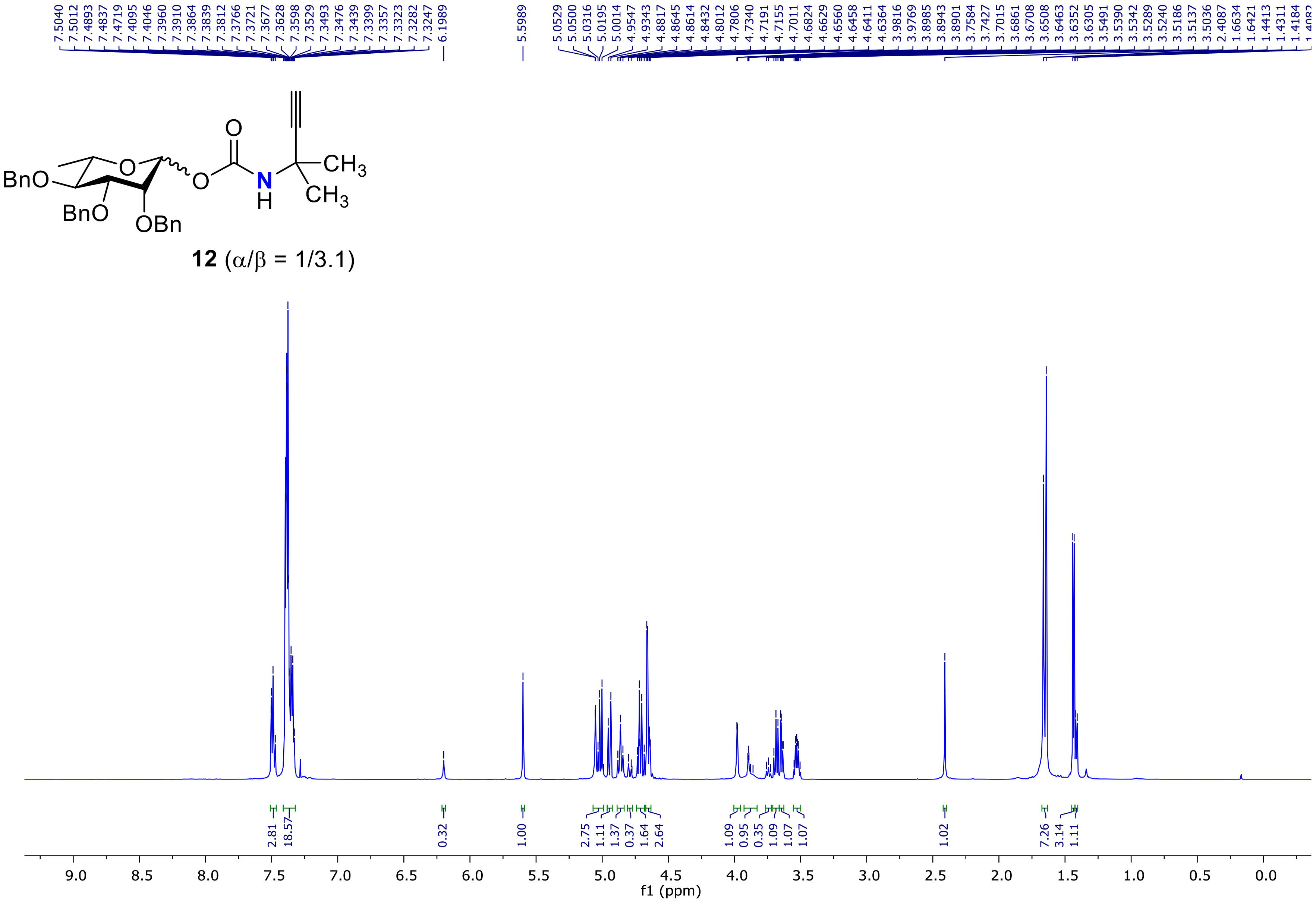

7.4643
7.4612
7.4500
7.4477
7.4381
7.4335
7.4263
7.4212
7.4166
7.4129
7.4051
7.4009
7.3929
7.3861
7.3803
7.3767
7.3743
7.3670
7.3636
7.3570
7.3529
7.3407
5.6587
5.6453
5.0589
5.0396
4.9982
4.9281
4.9093
4.8398
4.8212
4.8122
4.7341
4.7148
4.5444
4.5249
4.4953
4.4758
4.0807
4.0760
4.0219
4.0084
4.0058
3.9923
3.7975
3.7888
3.7845
3.7756
3.7487
3.7341
3.7218
3.7178
3.7063
3.7016
3.6983
3.6897
3.6835
3.6748
2.4101
1.7134
1.6886
1.6790
1.6603
BnO
OBn
O
BnO
BnO
O
H
N
$CH_3$
$CH_3$
O
20.38
1.00
2.20
1.09
2.47
1.06
2.19
1.07
1.00
1.07
3.28
0.93
6.40
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

**11**β

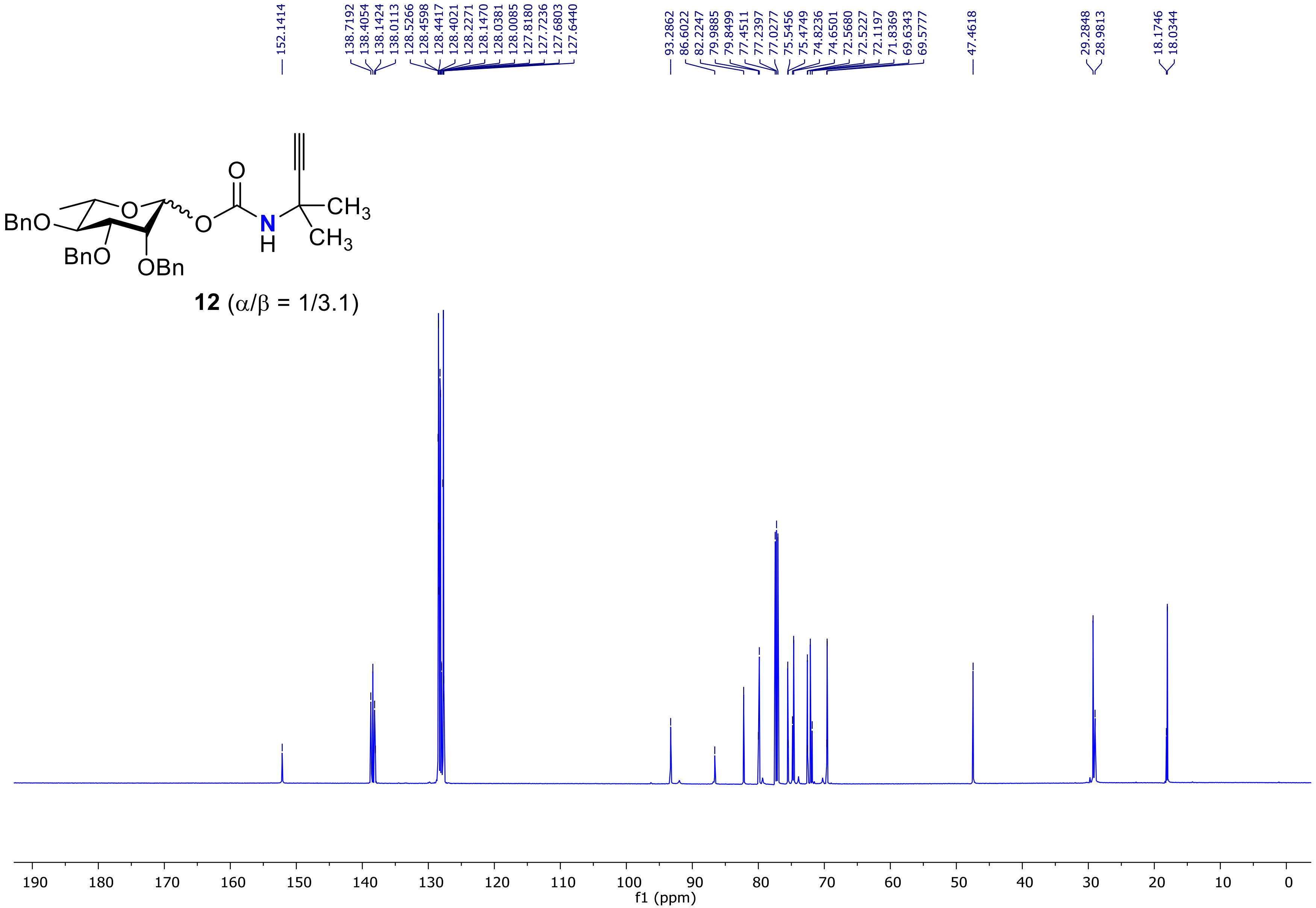

BnO
OBn
O
BnO
BnO
O
H
N
CH3
CH3
O

**11**β

152.2427
138.7335
138.6463
138.4036
137.9172
128.5306
128.3874
128.3095
128.2569
128.0663
127.9133
127.7755
127.7096
127.6646
95.0695
86.7482
82.4962
78.3274
77.4900
77.2783
77.0661
75.3145
74.7607
73.8479
73.5374
73.2437
72.9243
69.6149
67.9350
47.5352
29.1675
29.0306
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

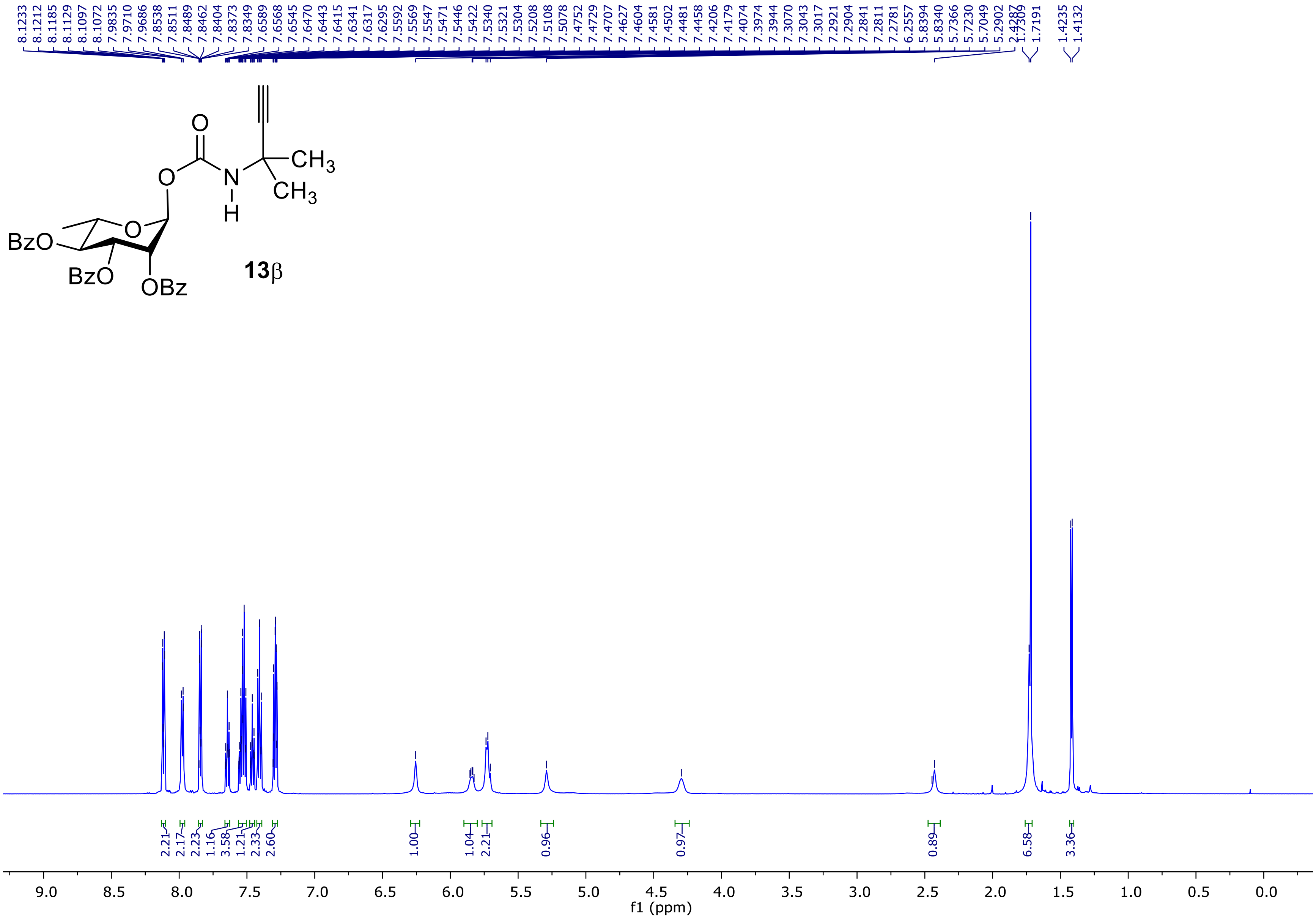

7.5040
7.5012
7.4893
7.4837
7.4719
7.4095
7.4046
7.3960
7.3910
7.3864
7.3839
7.3812
7.3766
7.3721
7.3677
7.3628
7.3598
7.3529
7.3493
7.3476
7.3439
7.3399
7.3357
7.3323
7.3282
7.3247
6.1989
5.5989
5.0529
5.0500
5.0316
5.0195
5.0014
4.9547
4.9343
4.8817
4.8645
4.8614
4.8432
4.8012
4.7806
4.7340
4.7191
4.7155
4.7011
4.6824
4.6629
4.6560
4.6458
4.6411
4.6364
3.9816
3.9769
3.8985
3.8943
3.8901
3.7584
3.7427
3.7015
3.6861
3.6708
3.6508
3.6463
3.6352
3.6305
3.5491
3.5390
3.5342
3.5289
3.5240
3.5186
3.5137
3.5036
2.4087
1.6634
1.6421
1.4413
1.4311
1.4184
1.4082
BnO
O
O
O
N
H
CH3
CH3
BnO
OBn
2.81
18.57
0.32
1.00
2.75
1.11
1.37
0.37
1.64
2.64
1.09
0.95
0.35
1.09
1.07
1.07
1.02
7.26
3.14
1.11
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

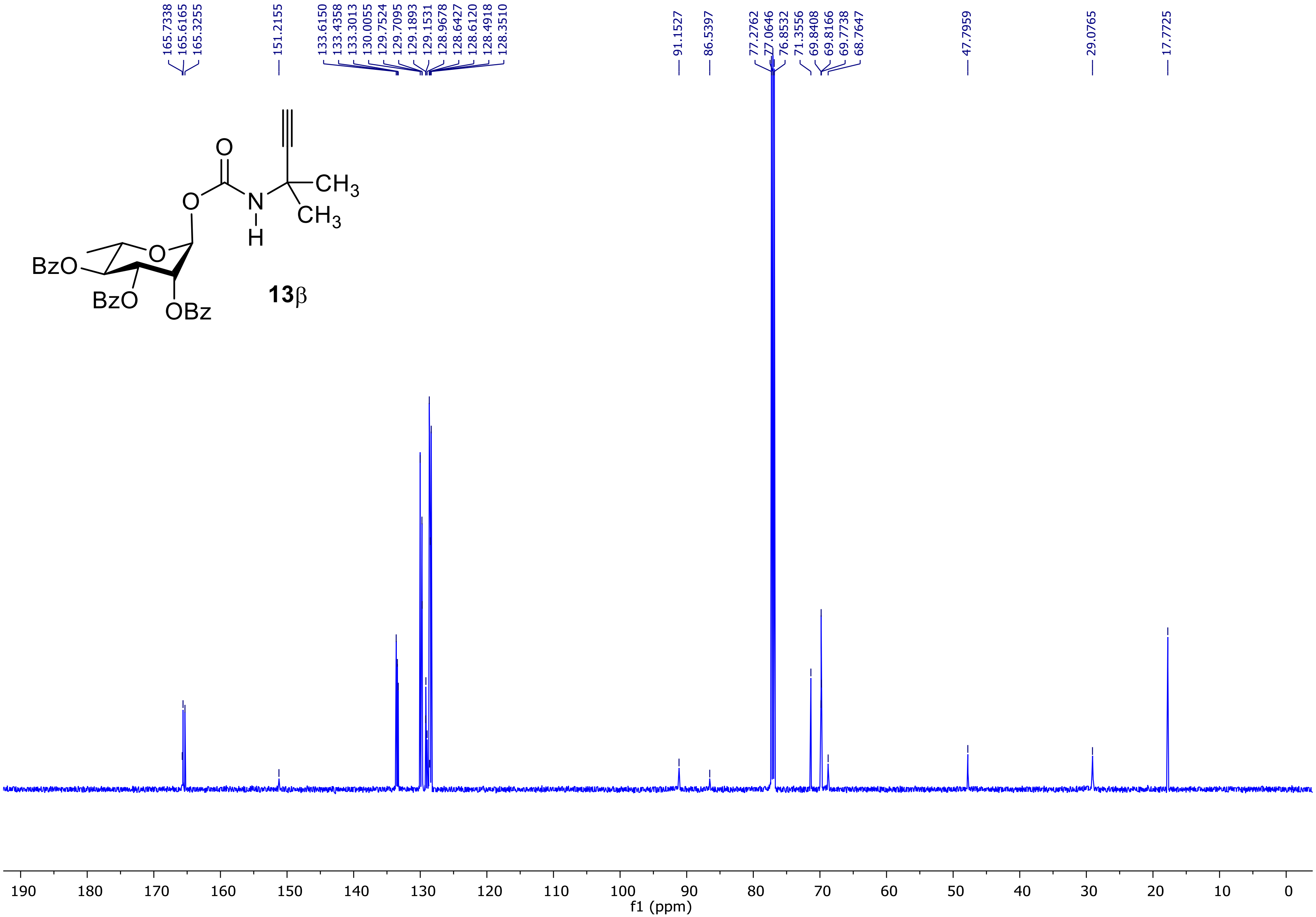
**12** (α/β = 1/3.1)



152.1414
138.7192
138.4054
138.1424
138.0113
128.5266
128.4598
128.4417
128.4021
128.2271
128.1470
128.0381
128.0085
127.8180
127.7236
127.6803
127.6440
93.2862
86.6022
82.2247
79.9885
79.8499
77.4511
77.2397
77.0277
75.5456
75.4749
74.8236
74.6501
72.5680
72.5227
72.1197
71.8369
69.6343
69.5777
47.4618
29.2848
28.9813
18.1746
18.0344
BnO
BnO
OBn
O
O
O
N
H
CH3
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

**12** (α/β = 1/3.1)


8.1233
8.1212
8.1185
8.1129
8.1097
8.1072
7.9835
7.9710
7.9686
7.8538
7.8511
7.8489
7.8462
7.8404
7.8373
7.8349
7.6589
7.6568
7.6545
7.6470
7.6443
7.6415
7.6341
7.6317
7.6295
7.5592
7.5569
7.5547
7.5471
7.5446
7.5422
7.5340
7.5321
7.5304
7.5208
7.5108
7.5078
7.4752
7.4729
7.4707
7.4627
7.4604
7.4581
7.4502
7.4481
7.4458
7.4206
7.4179
7.4074
7.3974
7.3944
7.3070
7.3043
7.3017
7.2921
7.2904
7.2841
7.2811
7.2781
6.2557
5.8394
5.8340
5.7366
5.7230
5.7049
5.2902
2.4287
1.7309
1.7191
1.4235
1.4132
O
O
N
H
$CH_3$
$CH_3$
O
BzO
BzO
OBz
**13**β
2.21
2.17
2.23
1.16
3.58
1.21
2.33
2.60
1.00
1.04
2.21
0.96
0.97
0.89
6.58
3.36
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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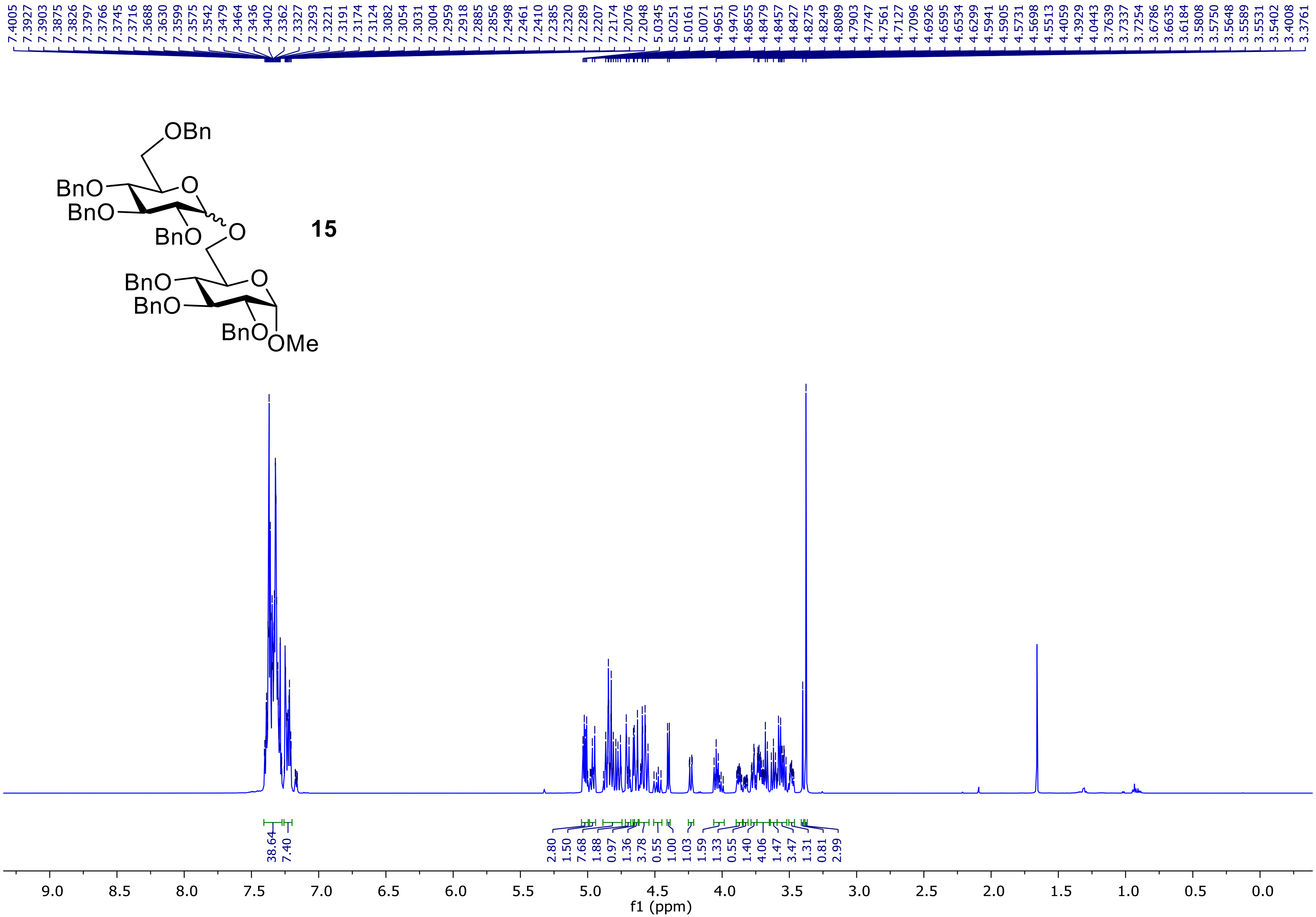
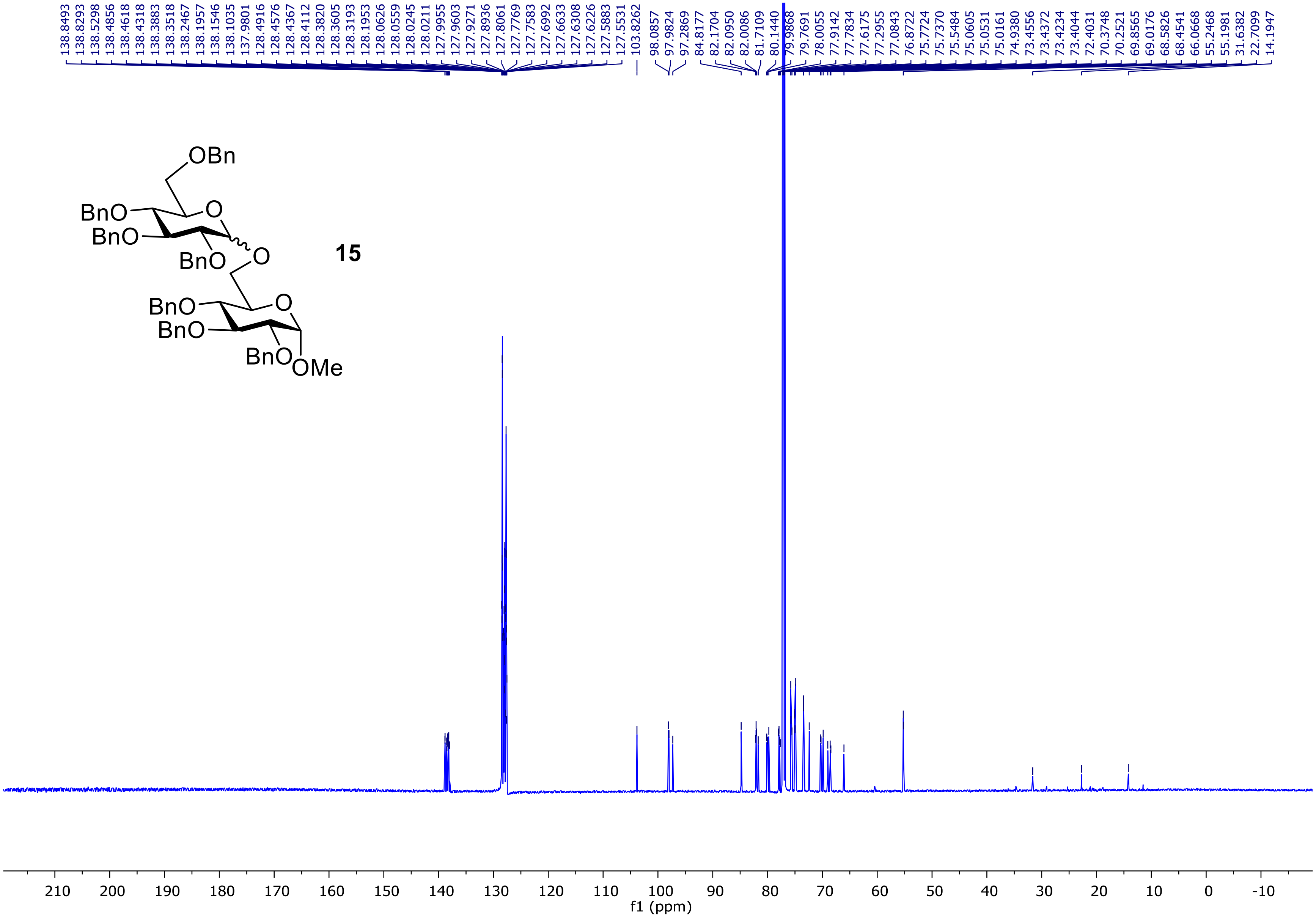
165.6165
165.3255
151.2155
133.6150
133.4358
133.3013
130.0055
129.7524
129.7095
129.1893
129.1531
128.9678
128.6427
128.6120
128.4918
128.3510
91.1527
86.5397
77.2762
77.0646
76.8532
71.3556
69.8408
69.8166
69.7738
68.7647
47.7959
29.0765
17.7725
O
O
N
H
CH3
CH3
BzO
O
BzO
OBz
13β
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.4005
7.3927
7.3903
7.3875
7.3826
7.3797
7.3766
7.3745
7.3716
7.3688
7.3630
7.3599
7.3575
7.3542
7.3479
7.3464
7.3436
7.3402
7.3362
7.3327
7.3293
7.3221
7.3191
7.3174
7.3124
7.3082
7.3054
7.3031
7.3004
7.2959
7.2918
7.2885
7.2856
7.2498
7.2461
7.2410
7.2385
7.2320
7.2289
7.2207
7.2174
7.2076
7.2048
5.0345
5.0251
5.0161
5.0071
4.9651
4.9470
4.8655
4.8479
4.8457
4.8427
4.8275
4.8249
4.8089
4.7903
4.7747
4.7561
4.7127
4.7096
4.6926
4.6595
4.6534
4.6299
4.5941
4.5905
4.5731
4.5698
4.5513
4.4059
4.3929
4.0443
3.7639
3.7337
3.7254
3.6786
3.6635
3.6184
3.5808
3.5750
3.5648
3.5589
3.5531
3.5402
3.4008
3.3761
OBn
BnO
O
BnO
BnO
O
BnO
O
BnO
BnO
OMe
38.64
7.40
2.80
1.50
7.68
1.88
0.97
1.36
3.78
0.55
1.00
1.03
1.59
1.33
0.55
1.40
4.06
1.47
3.47
1.31
0.81
2.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**15**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138.3883
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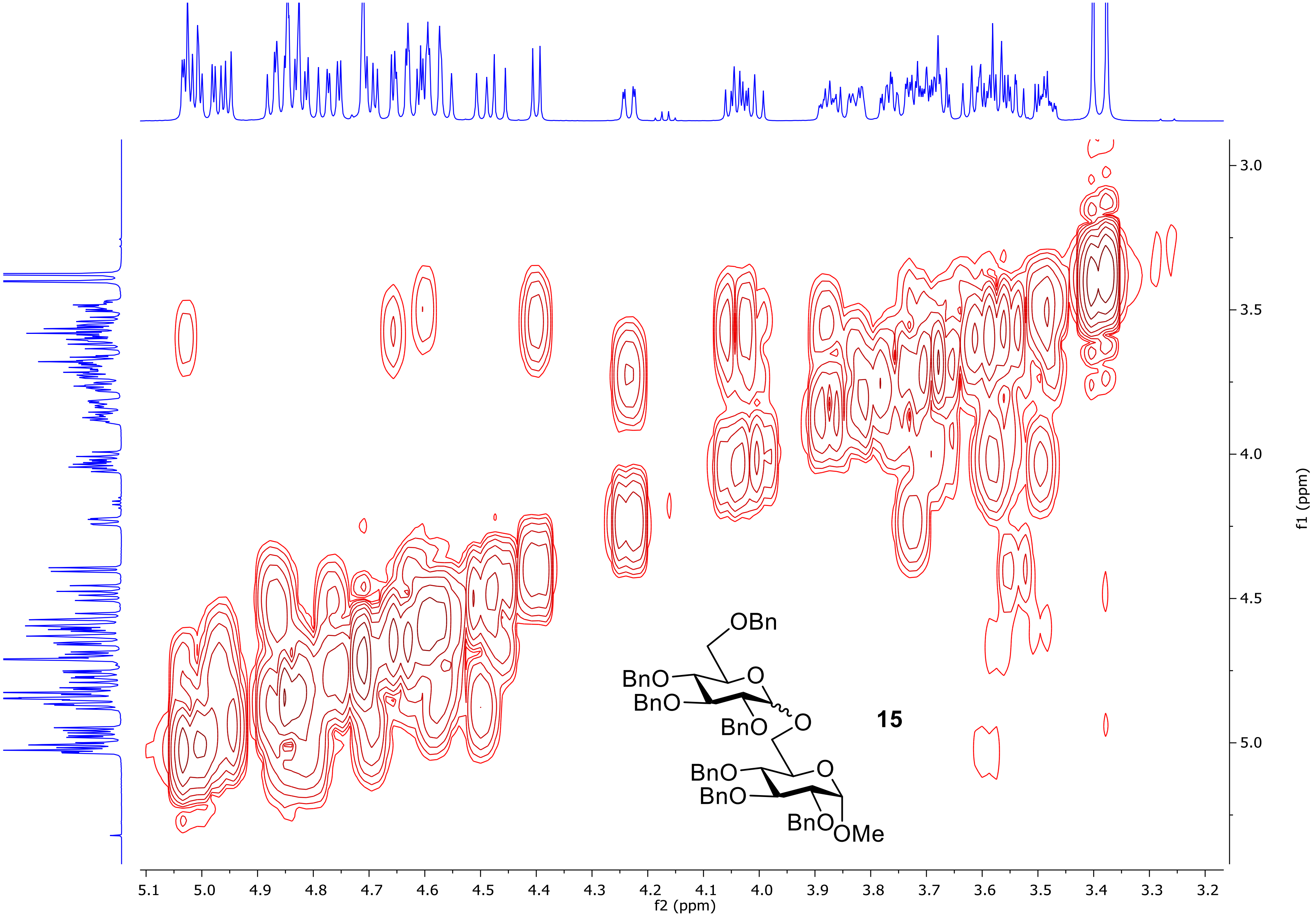
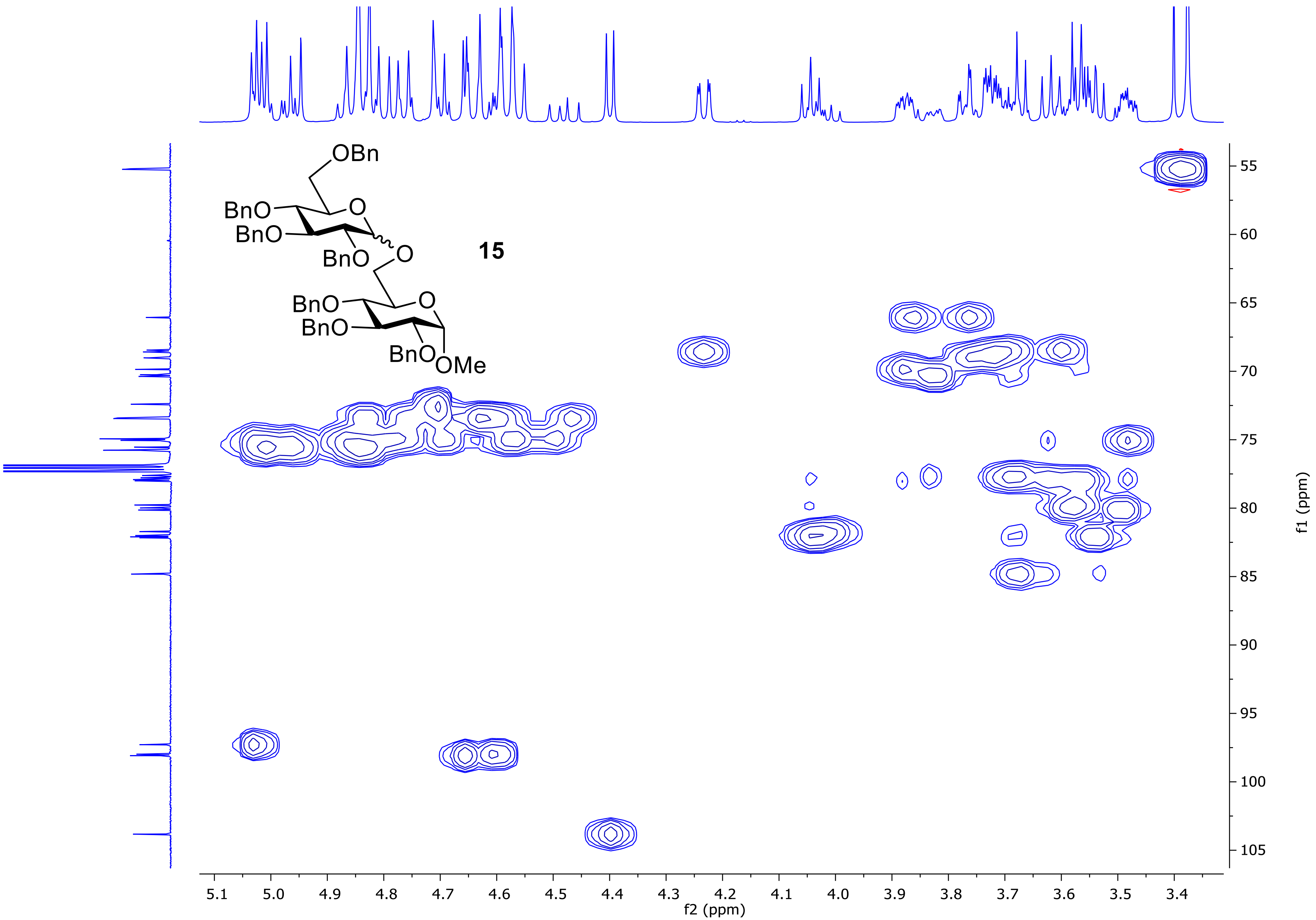
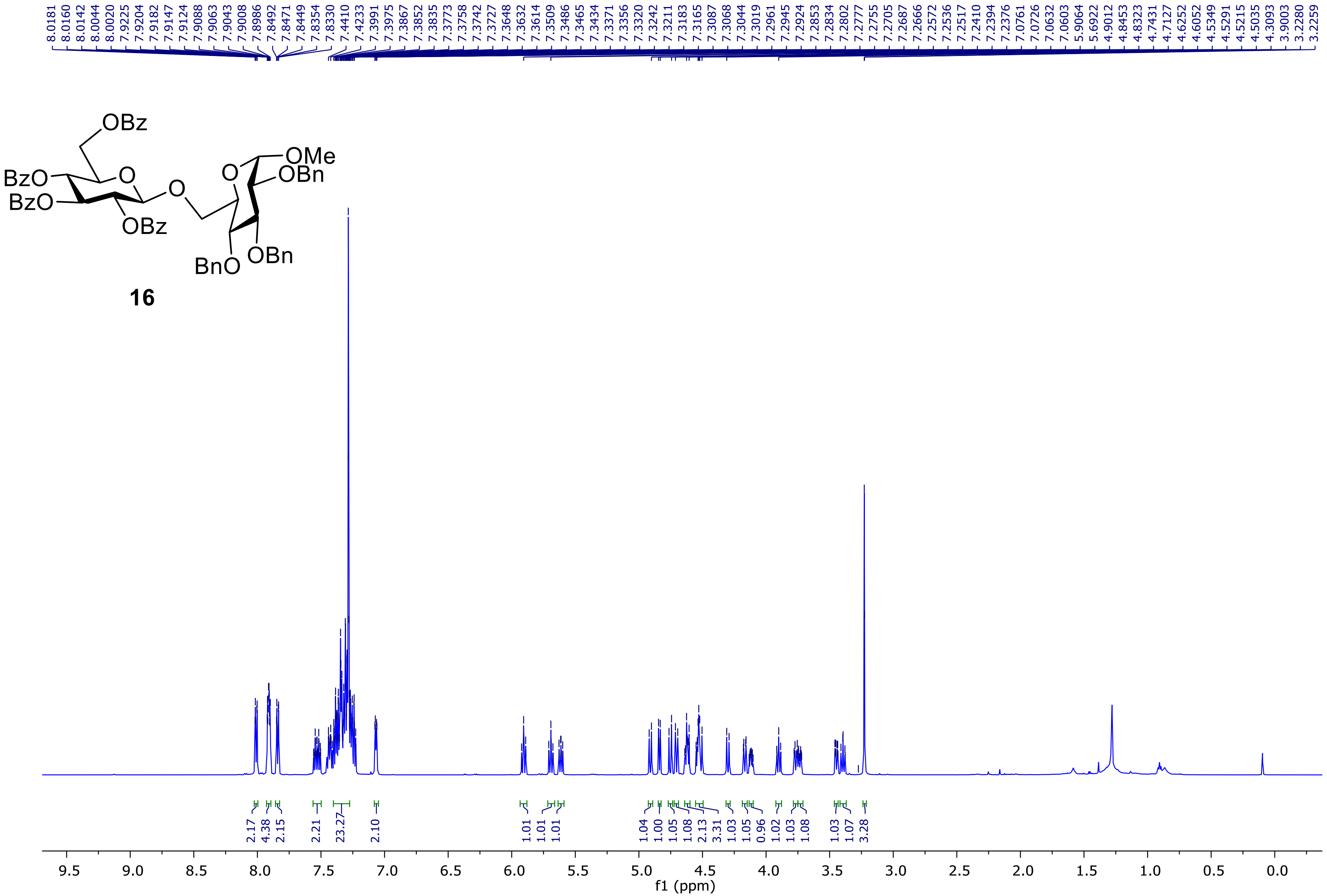
138.2467
138.1957
138.1546
138.1035
137.9801
128.4916
128.4576
128.4367
128.4112
128.3820
128.3605
128.3193
128.1953
128.0626
128.0559
128.0245
128.0211
127.9955
127.9603
127.9271
127.8936
127.8061
127.7769
127.7583
127.6992
127.6633
127.6308
127.6226
127.5883
127.5531
103.8262
98.0857
97.9824
97.2869
84.8177
82.1704
82.0950
82.0086
81.7109
80.1440
79.9868
79.7691
78.0055
77.9142
77.7834
77.6175
77.2955
77.0843
76.8722
75.7724
75.7370
75.5484
75.0605
75.0531
75.0161
74.9380
73.4556
73.4372
73.4234
73.4044
72.4031
70.3748
70.2521
69.8565
69.0176
68.5826
68.4541
66.0668
55.2468
55.1981
31.6382
22.7099
14.1947
OBn
BnO
O
BnO
BnO
O
BnO
O
BnO
BnO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**15**

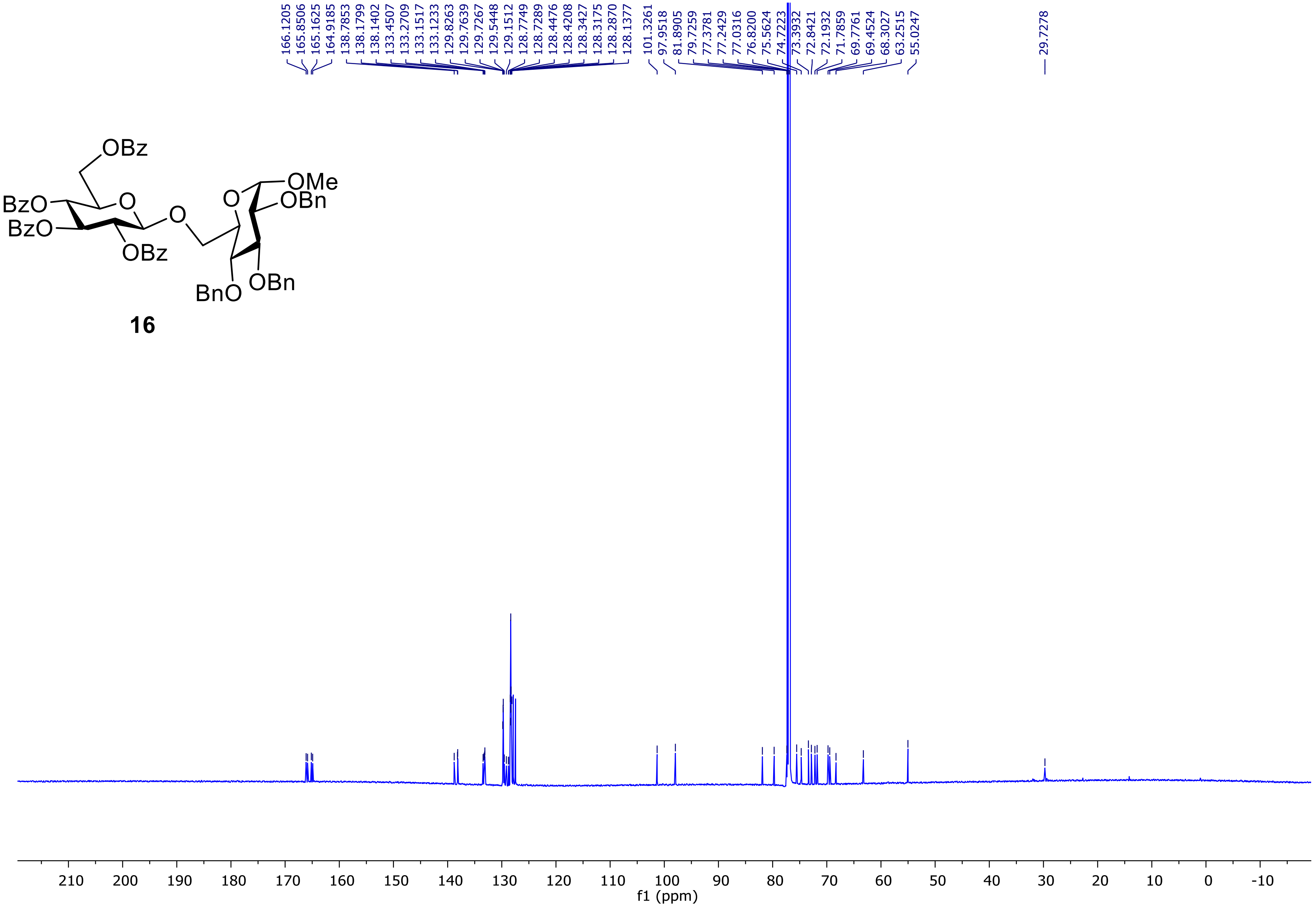

OBn
BnO
BnO
O
BnO
O
BnO
BnO
O
BnO
OMe
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f2 (ppm)
3.0
3.5
4.0
4.5
5.0
f1 (ppm)

**15**

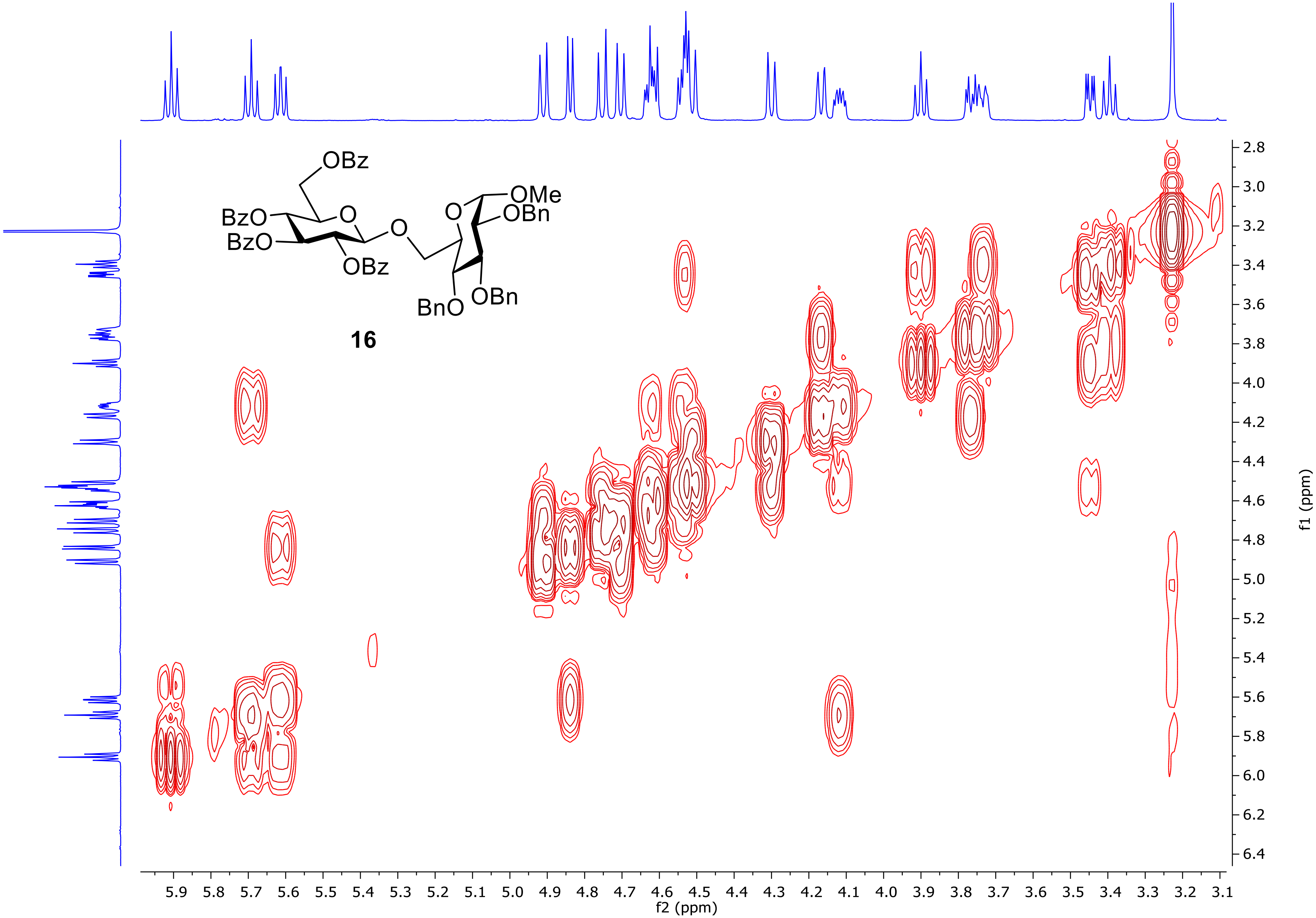

OBn
BnO
BnO
BnO
O
O
BnO
BnO
O
BnO
OMe
15
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)


8.0181
8.0160
8.0142
8.0044
8.0020
7.9225
7.9204
7.9182
7.9147
7.9124
7.9088
7.9063
7.9043
7.9008
7.8986
7.8492
7.8471
7.8449
7.8354
7.8330
7.4410
7.4233
7.3991
7.3975
7.3867
7.3852
7.3835
7.3773
7.3758
7.3742
7.3727
7.3648
7.3632
7.3614
7.3509
7.3486
7.3465
7.3434
7.3371
7.3356
7.3320
7.3242
7.3211
7.3183
7.3165
7.3087
7.3068
7.3044
7.3019
7.2961
7.2945
7.2924
7.2853
7.2834
7.2802
7.2777
7.2755
7.2705
7.2687
7.2666
7.2572
7.2536
7.2517
7.2410
7.2394
7.2376
7.0761
7.0726
7.0632
7.0603
5.9064
5.6922
4.9012
4.8453
4.8323
4.7431
4.7127
4.6252
4.6052
4.5349
4.5291
4.5215
4.5035
4.3093
3.9003
3.2280
3.2259
OBz
BzO
BzO
O
OBz
O
O
OMe
OBn
BnO
OBn
2.17
4.38
2.15
2.21
23.27
2.10
1.01
1.01
1.01
1.04
1.00
1.05
1.08
2.13
3.31
1.03
1.05
0.96
1.02
1.03
1.08
1.03
1.07
3.28
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

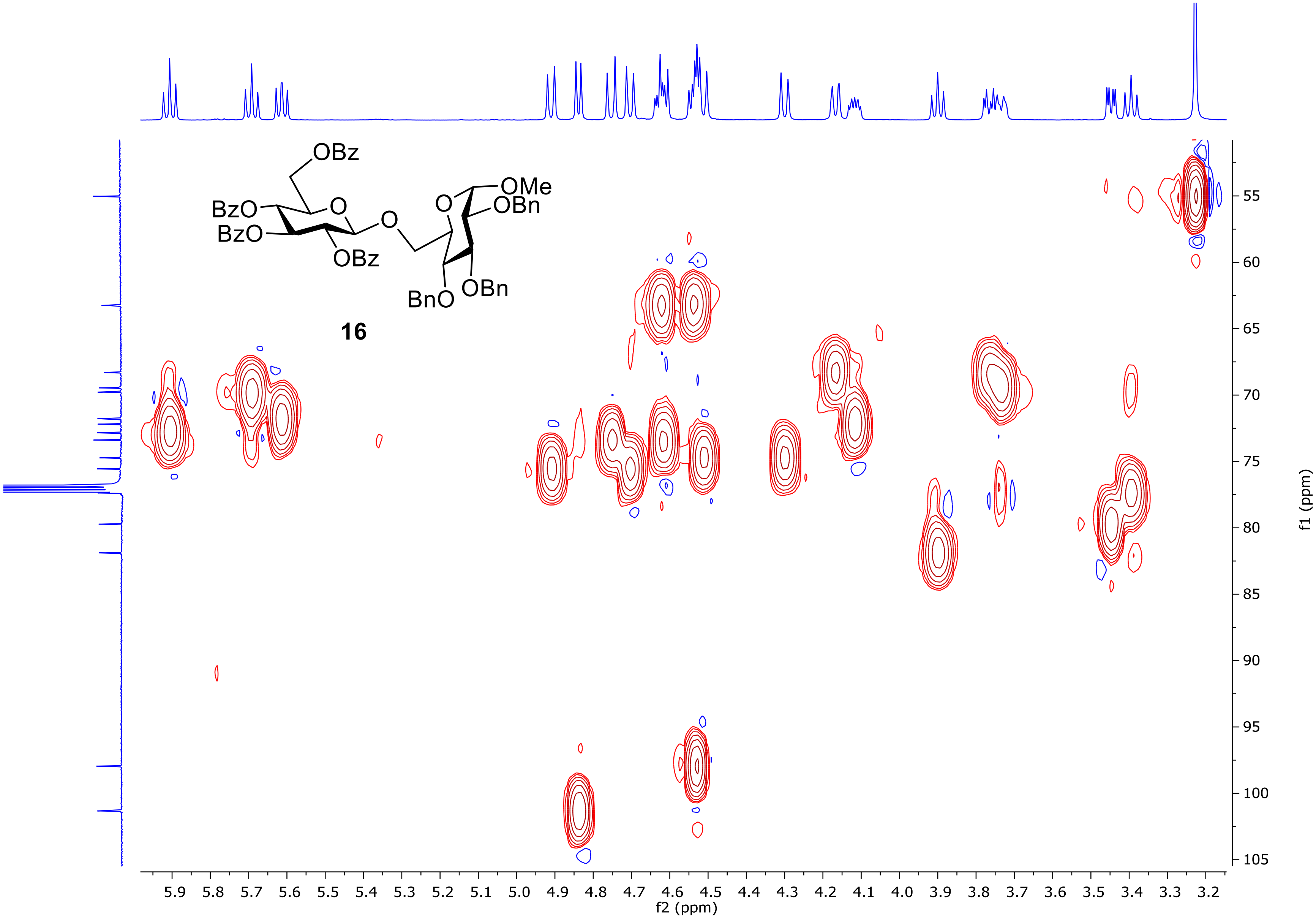
**16**


166.1205
165.8506
165.1625
164.9185
138.7853
138.1799
138.1402
133.4507
133.2709
133.1517
133.1233
129.8263
129.7639
129.7267
129.5448
129.1512
128.7749
128.7289
128.4476
128.4208
128.3427
128.3175
128.2870
128.1377
101.3261
97.9518
81.8905
79.7259
77.3781
77.2429
77.0316
76.8200
75.5624
74.7223
73.3932
72.8421
72.1932
71.7859
69.7761
69.4524
68.3027
63.2515
55.0247
29.7278
OBz
BzO
BzO
O
OBz
O
O
OMe
OBn
BnO
OBn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

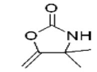
**16**



OBz
BzO
BzO
O
OBz
O
O
OMe
OBn
BnO
OBn
16
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f2 (ppm)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
6.4
f1 (ppm)

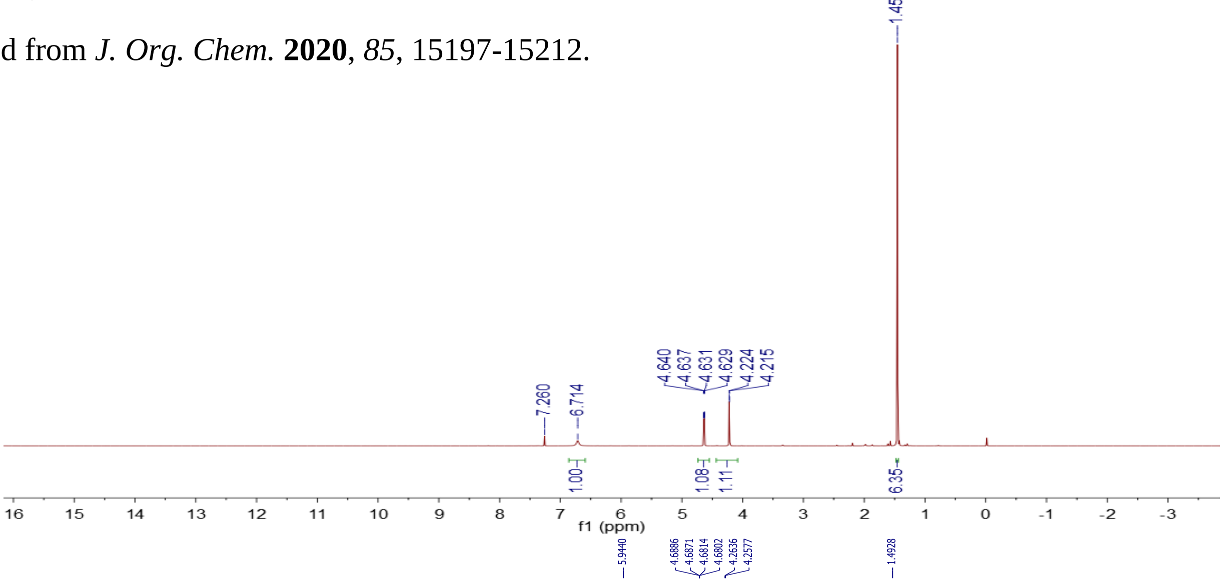

OBz
BzO
BzO
O
OBz
O
O
OMe
OBn
BnO
OBn
16
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)

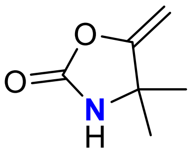
cf-644



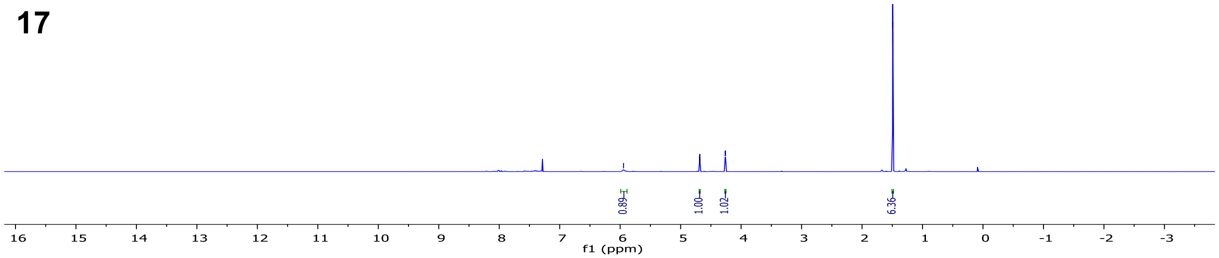
$^1$H NMR (400 MHz, $CDCl_3$)

Reported from *J. Org. Chem.* **2020**, *85*, 15197-15212.

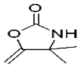




**17**

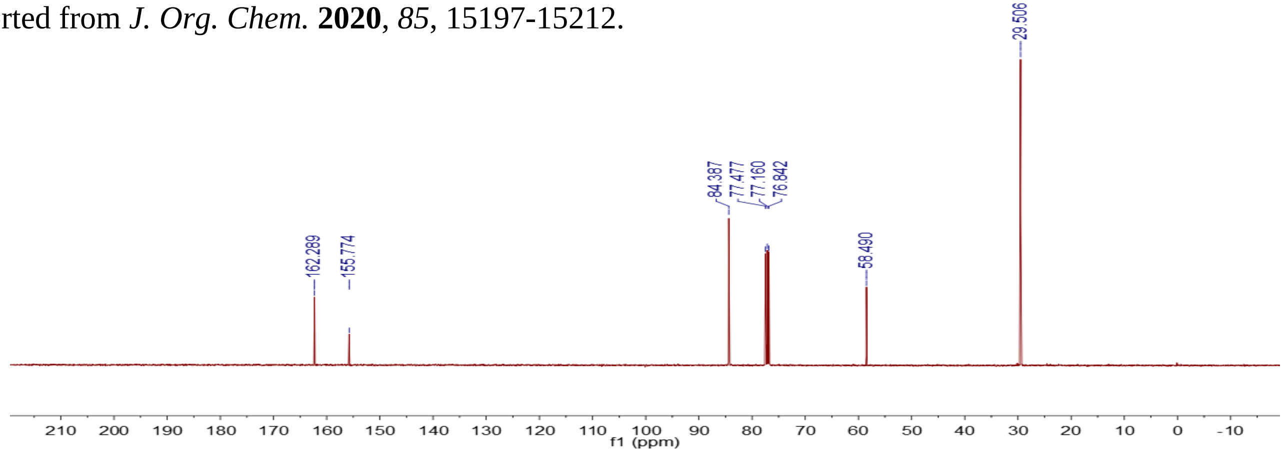


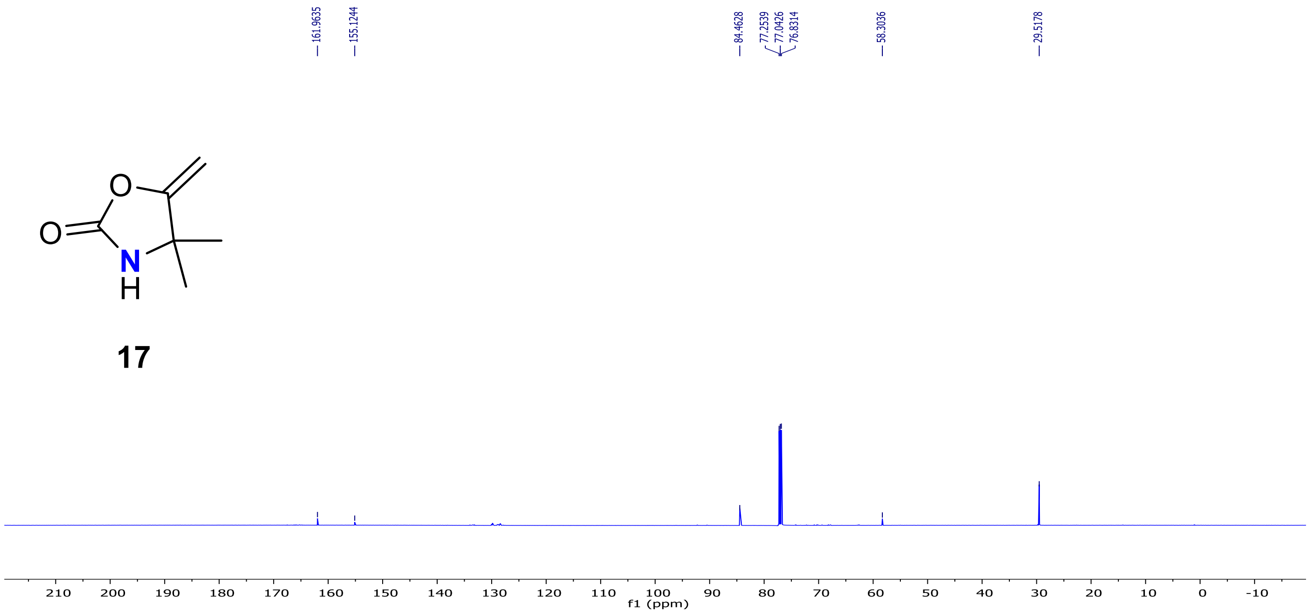
cf-644

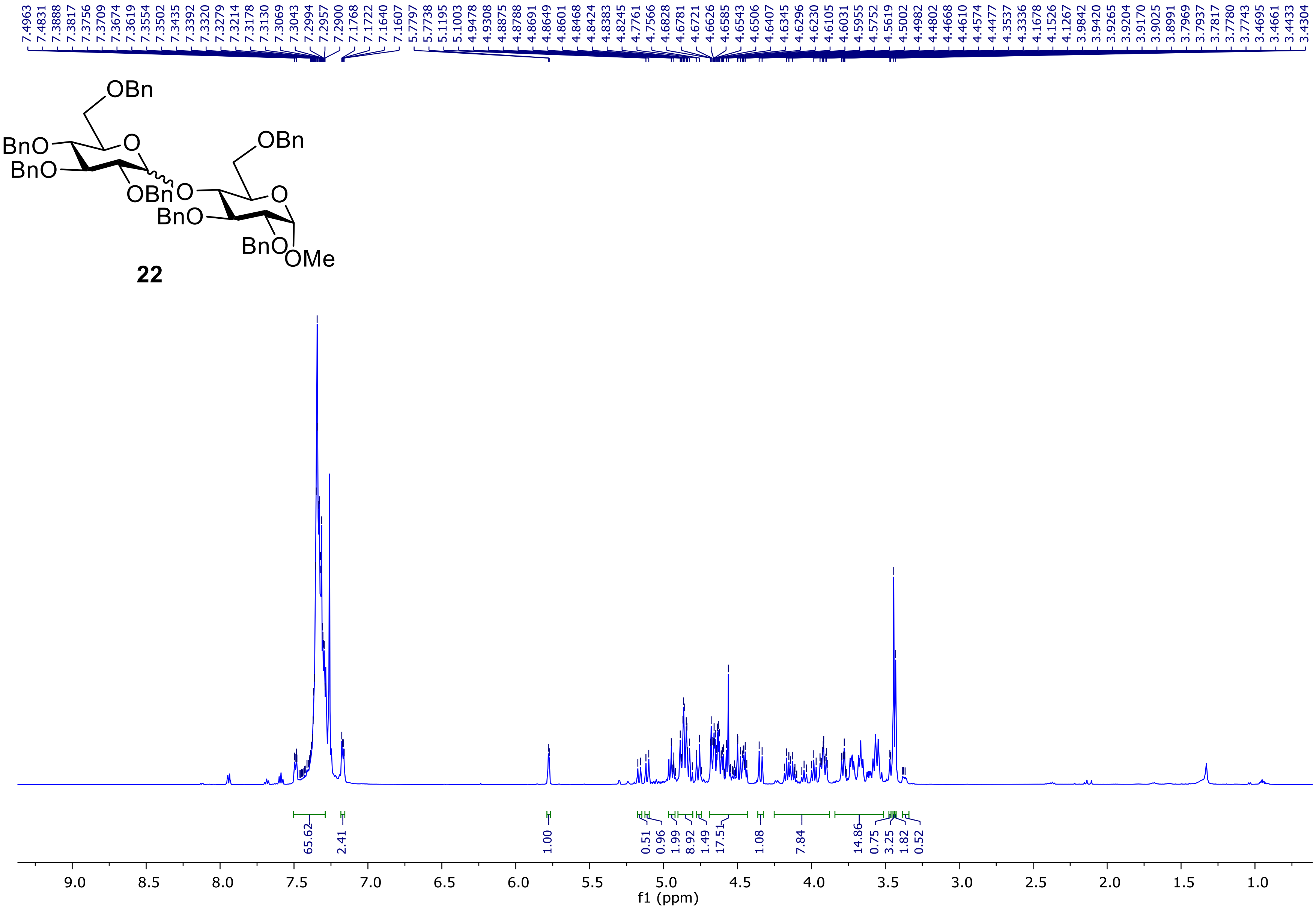


$^{13}C$ NMR (100 MHz, $CDCl_3$)

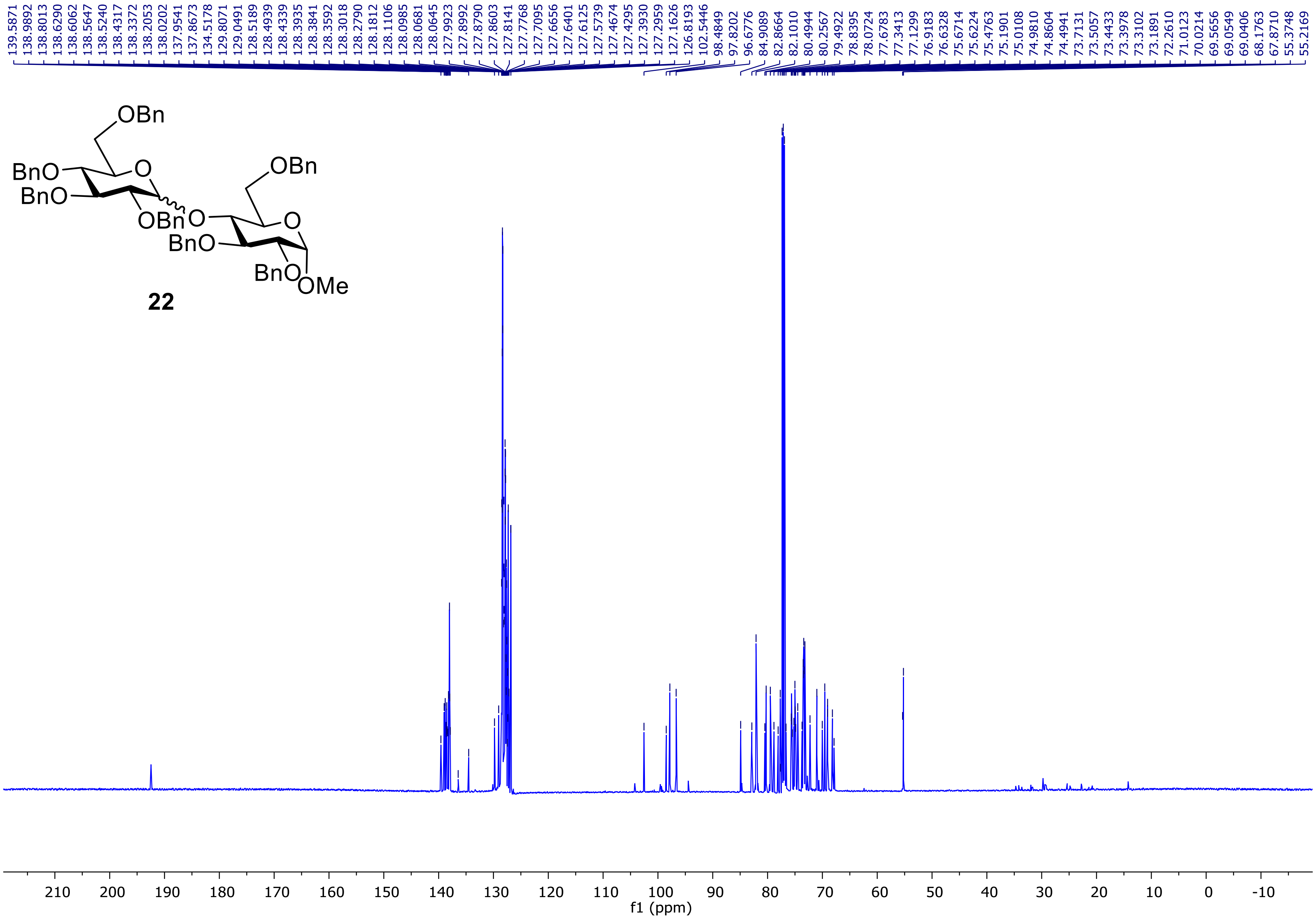
Reported from *J. Org. Chem.* **2020**, *85*, 15197-15212.



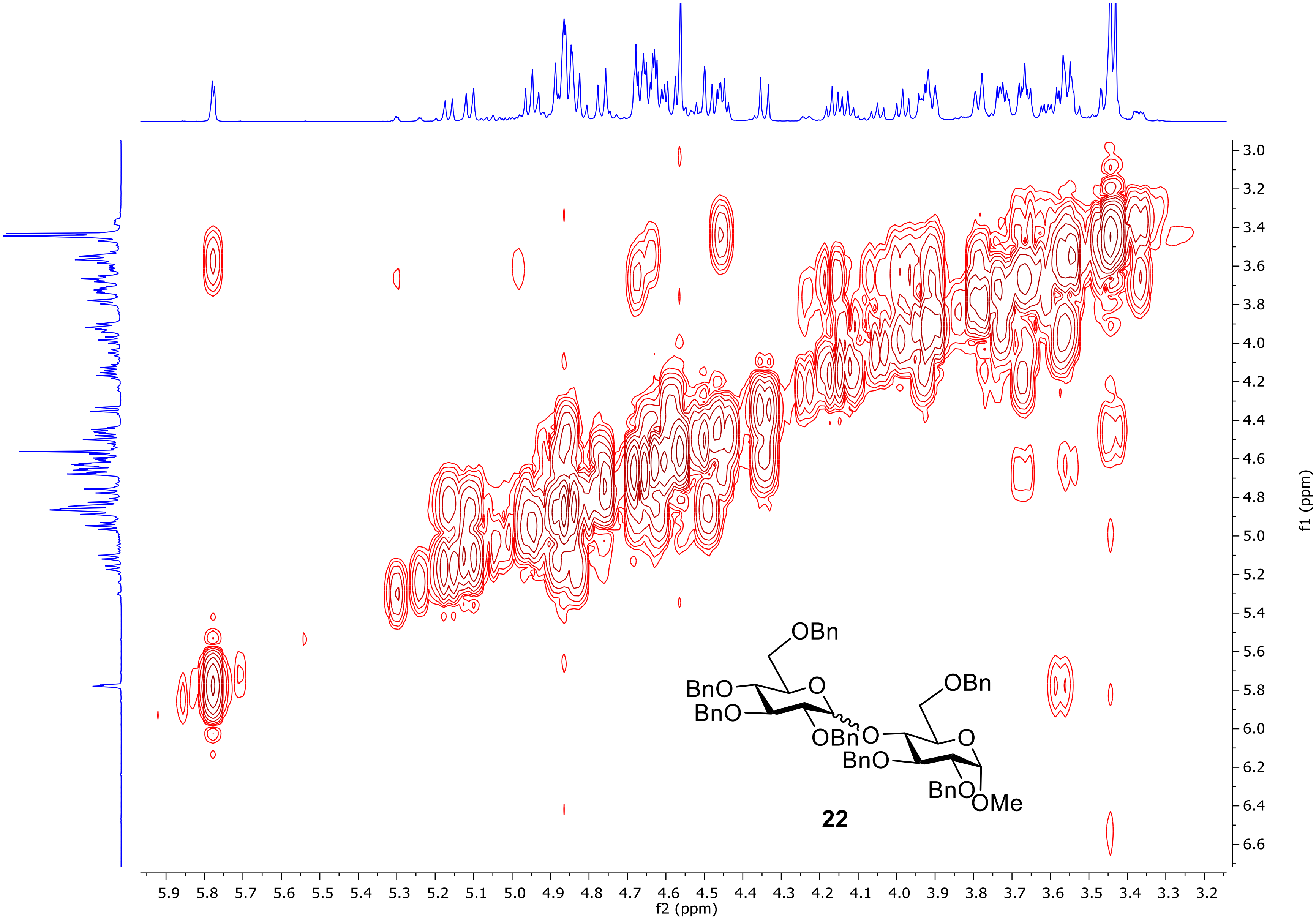



7.4963
7.4831
7.3888
7.3817
7.3756
7.3709
7.3674
7.3619
7.3554
7.3502
7.3435
7.3392
7.3320
7.3279
7.3214
7.3178
7.3130
7.3069
7.3043
7.2994
7.2957
7.2900
7.1768
7.1722
7.1640
7.1607
5.7797
5.7738
5.1195
5.1003
4.9478
4.9308
4.8875
4.8788
4.8691
4.8649
4.8601
4.8468
4.8424
4.8383
4.8245
4.7761
4.7566
4.6828
4.6781
4.6721
4.6626
4.6585
4.6543
4.6506
4.6407
4.6345
4.6296
4.6230
4.6105
4.6031
4.5955
4.5752
4.5619
4.5002
4.4982
4.4802
4.4668
4.4610
4.4574
4.4477
4.3537
4.3336
4.1678
4.1526
4.1267
3.9842
3.9420
3.9265
3.9204
3.9170
3.9025
3.8991
3.7969
3.7937
3.7817
3.7780
3.7743
3.4695
3.4661
3.4433
3.4304
OBn
BnO
BnO
O
OBn
O
OBn
O
BnO
BnO
OMe
65.62
2.41
1.00
0.51
0.96
1.99
8.92
1.49
17.51
1.08
7.84
14.86
0.75
3.25
1.82
0.52
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

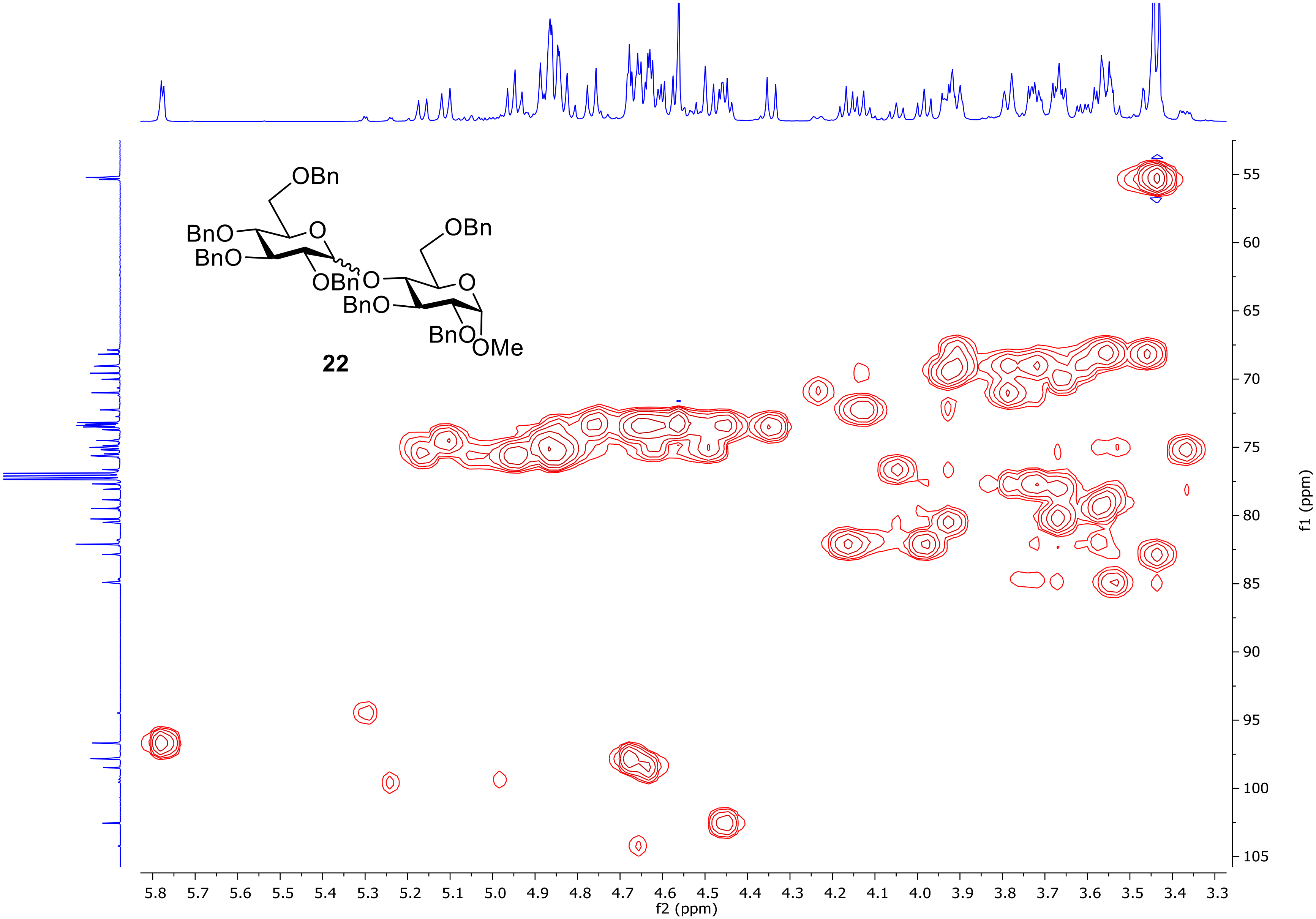
**22**


139.5871
138.9892
138.8013
138.6290
138.6062
138.5647
138.5240
138.4317
138.3372
138.2053
138.0202
137.9541
137.8673
134.5178
129.8071
129.0491
128.5189
128.4939
128.4339
128.3935
128.3841
128.3592
128.3018
128.2790
128.1812
128.1106
128.0985
128.0681
128.0645
127.9923
127.8992
127.8790
127.8603
127.8141
127.7768
127.7095
127.6656
127.6401
127.6125
127.5739
127.4674
127.4295
127.3930
127.2959
127.1626
126.8193
102.5446
98.4849
97.8202
96.6776
84.9089
82.8664
82.1010
80.4944
80.2567
79.4922
78.8395
78.0724
77.6783
77.3413
77.1299
76.9183
76.6328
75.6714
75.6224
75.4763
75.1901
75.0108
74.9810
74.8604
74.4941
73.7131
73.5057
73.4433
73.3978
73.3102
73.1891
72.2610
71.0123
70.0214
69.5656
69.0549
69.0406
68.1763
67.8710
55.3748
55.2169
OBn
BnO
BnO
O
OBn
O
OBn
O
BnO
BnO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

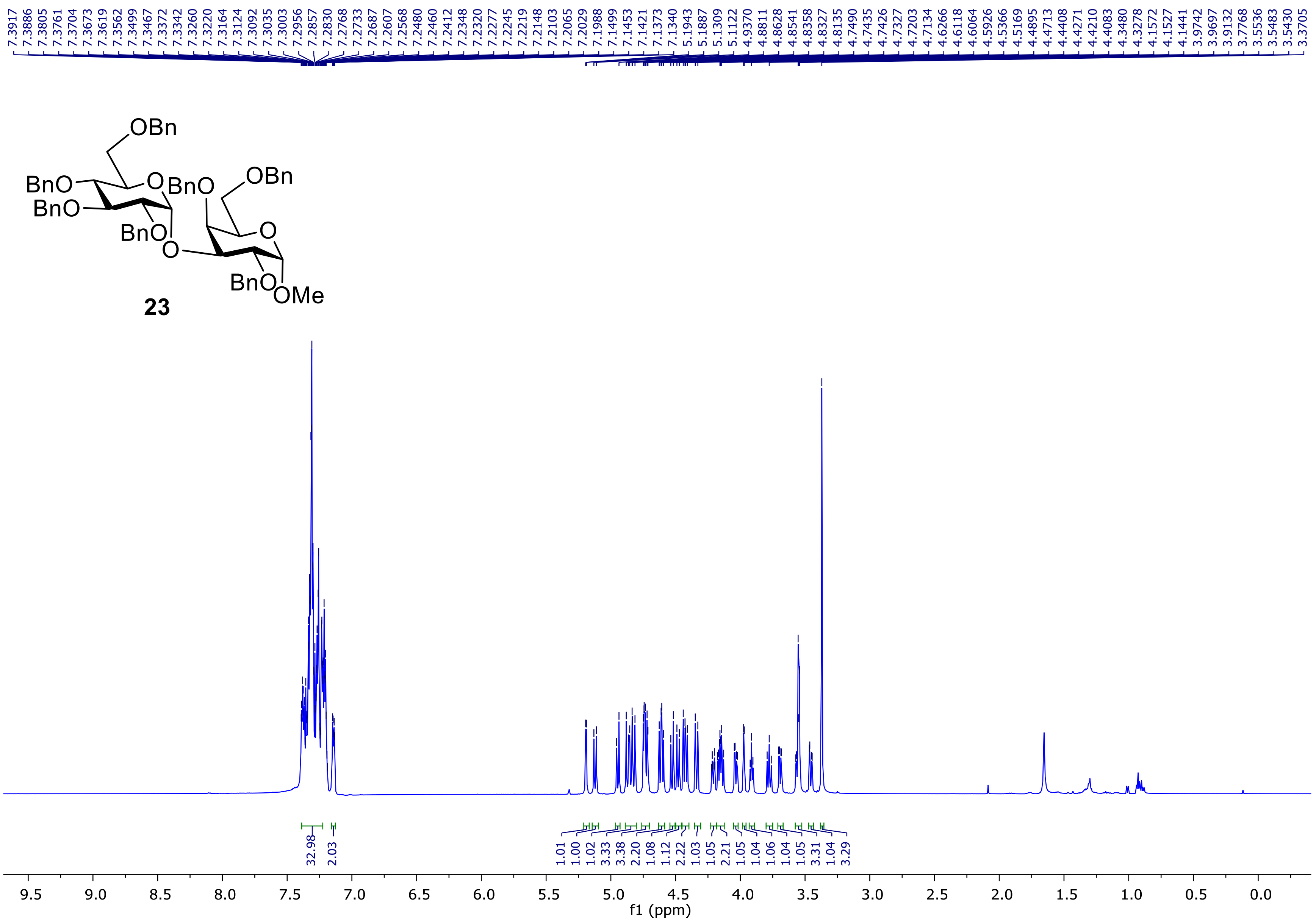
**22**


OBn
BnO
BnO
O
OBn
O
OBn
O
BnO
BnO
OMe
5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3 3.2
f2 (ppm)
3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4 6.6
f1 (ppm)

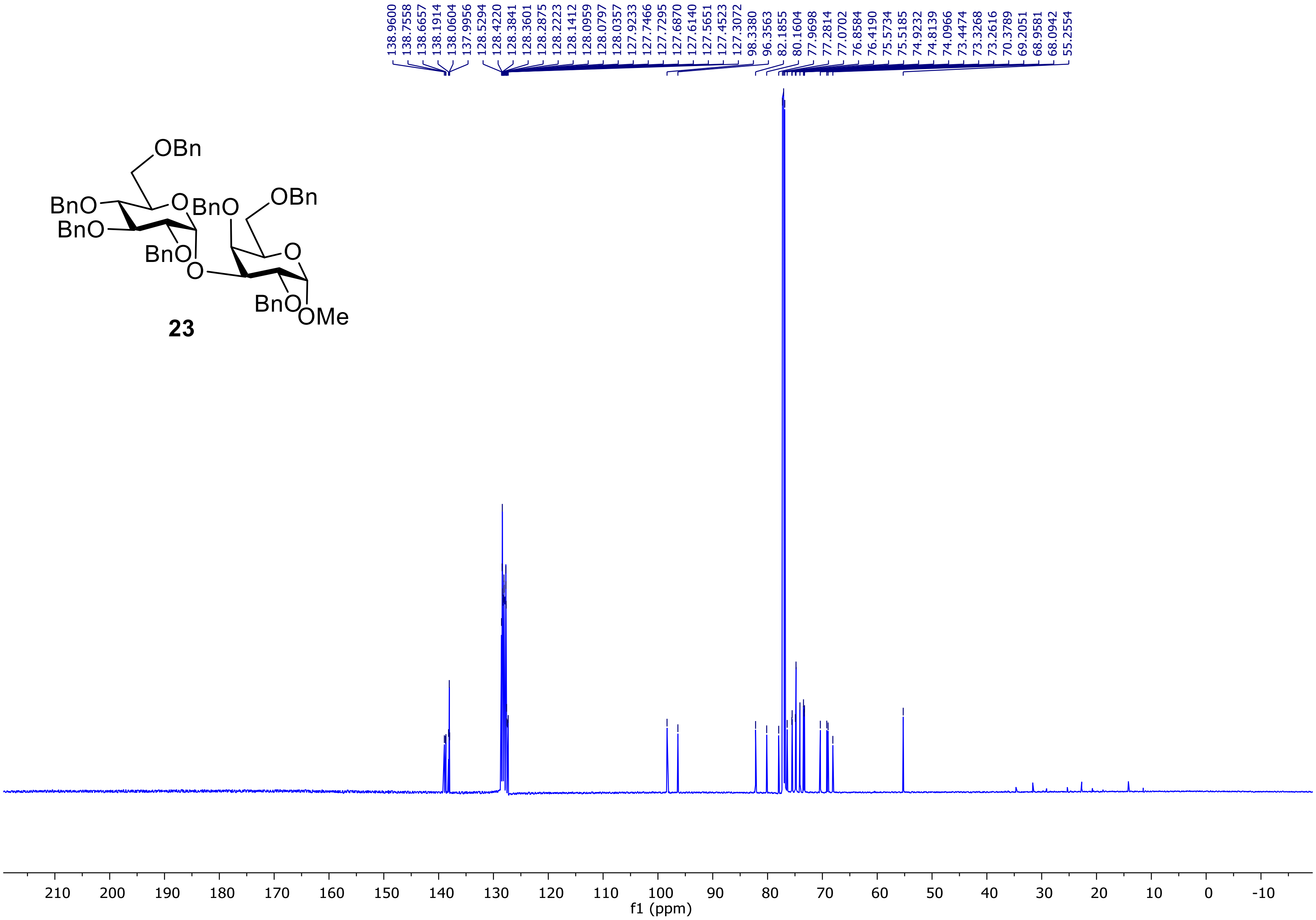
**22**


OBn
BnO
BnO
O
OBn
O
OBn
O
BnO
BnO
OMe
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)

**22**

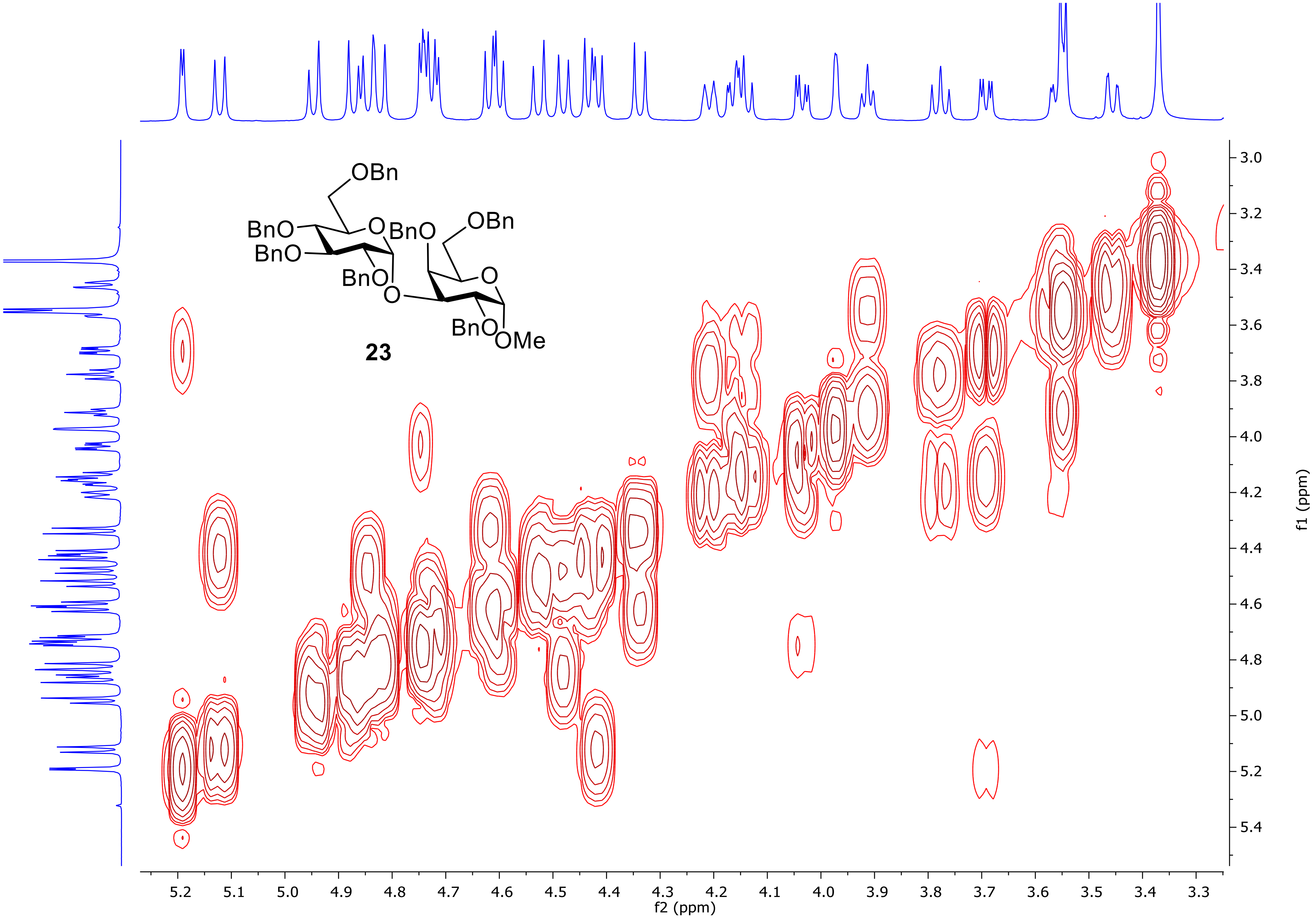

7.3917
7.3886
7.3805
7.3761
7.3704
7.3673
7.3619
7.3562
7.3499
7.3467
7.3372
7.3342
7.3260
7.3220
7.3164
7.3124
7.3092
7.3035
7.3003
7.2956
7.2857
7.2830
7.2768
7.2733
7.2687
7.2607
7.2568
7.2480
7.2460
7.2412
7.2348
7.2320
7.2277
7.2245
7.2219
7.2148
7.2103
7.2065
7.2029
7.1988
7.1499
7.1453
7.1421
7.1373
7.1340
5.1943
5.1887
5.1309
5.1122
4.9370
4.8811
4.8628
4.8541
4.8358
4.8327
4.8135
4.7490
4.7435
4.7426
4.7327
4.7203
4.7134
4.6266
4.6118
4.6064
4.5926
4.5366
4.5169
4.4895
4.4713
4.4408
4.4271
4.4210
4.4083
4.3480
4.3278
4.1572
4.1527
4.1441
3.9742
3.9697
3.9132
3.7768
3.5536
3.5483
3.5430
3.3705
OBn
BnO
O
BnO
OBn
BnO
BnO
O
O
BnO
OMe
32.98
2.03
1.01
1.00
1.02
3.33
3.38
2.20
1.08
1.12
2.22
1.03
1.05
2.21
1.05
1.04
1.06
1.04
1.05
3.31
1.04
3.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**23**


OBn
BnO
O
BnO
BnO
OBn
BnO
O
O
BnO
OMe

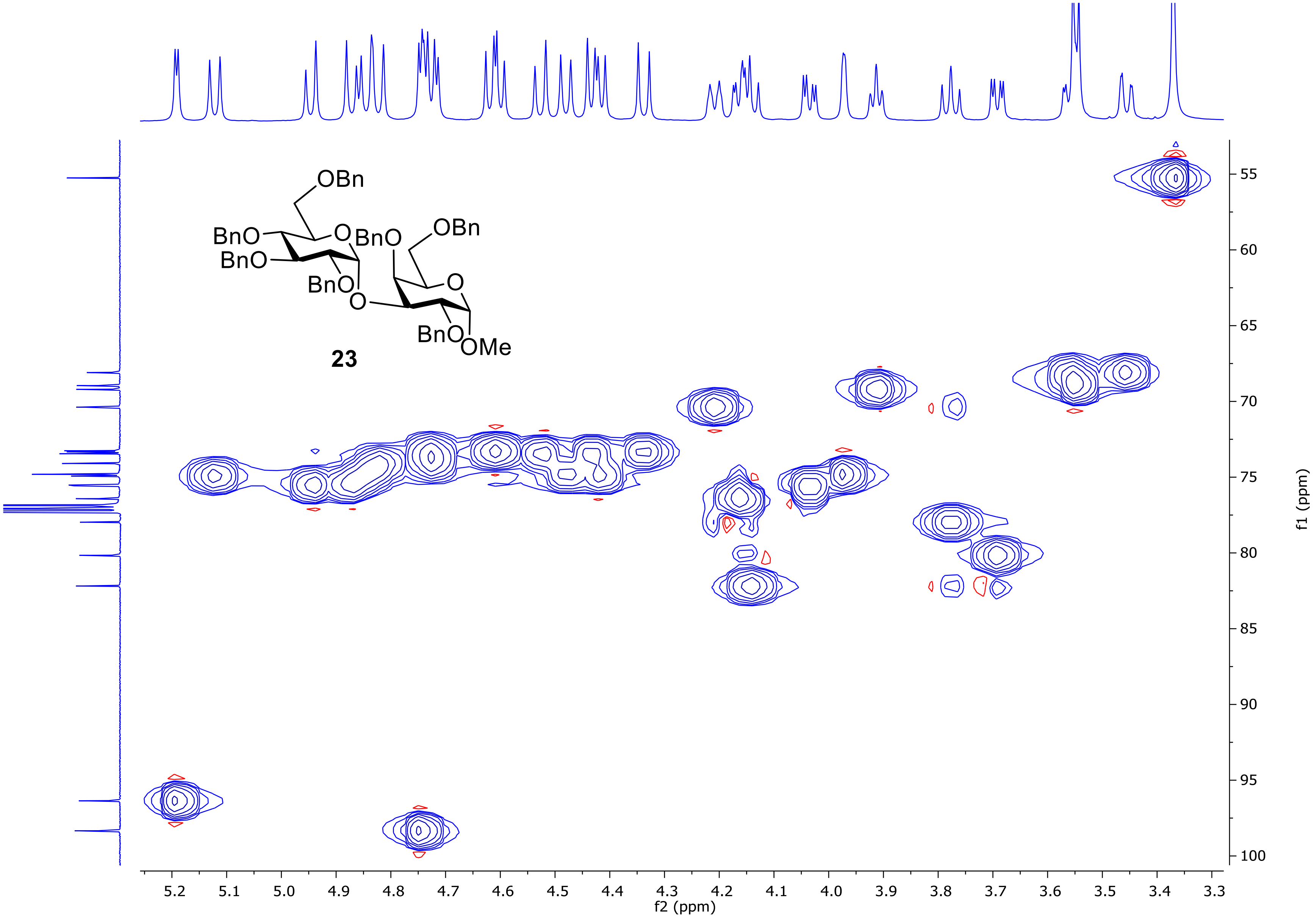
**23**

138.9600
138.7558
138.6657
138.1914
138.0604
137.9956
128.5294
128.4220
128.3841
128.3601
128.2875
128.2223
128.1412
128.0959
128.0797
128.0357
127.9233
127.7466
127.7295
127.6870
127.6140
127.5651
127.4523
127.3072
98.3380
96.3563
82.1855
80.1604
77.9698
77.2814
77.0702
76.8584
76.4190
75.5734
75.5185
74.9232
74.8139
74.0966
73.4474
73.3268
73.2616
70.3789
69.2051
68.9581
68.0942
55.2554
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



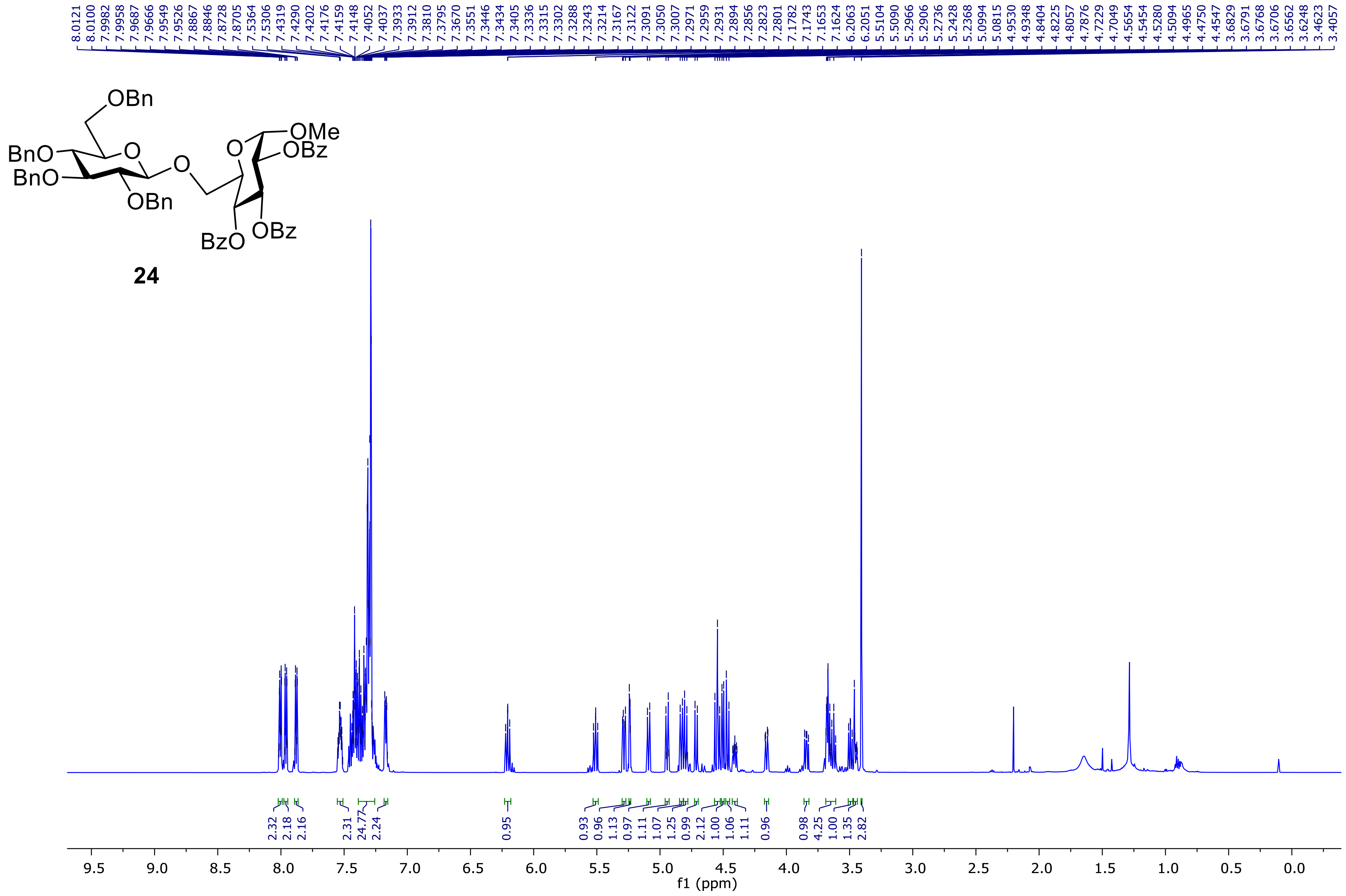
**23**

OBn
BnO
BnO
O
BnO
BnO
OBn
O
O
BnO
OMe
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
f1 (ppm)

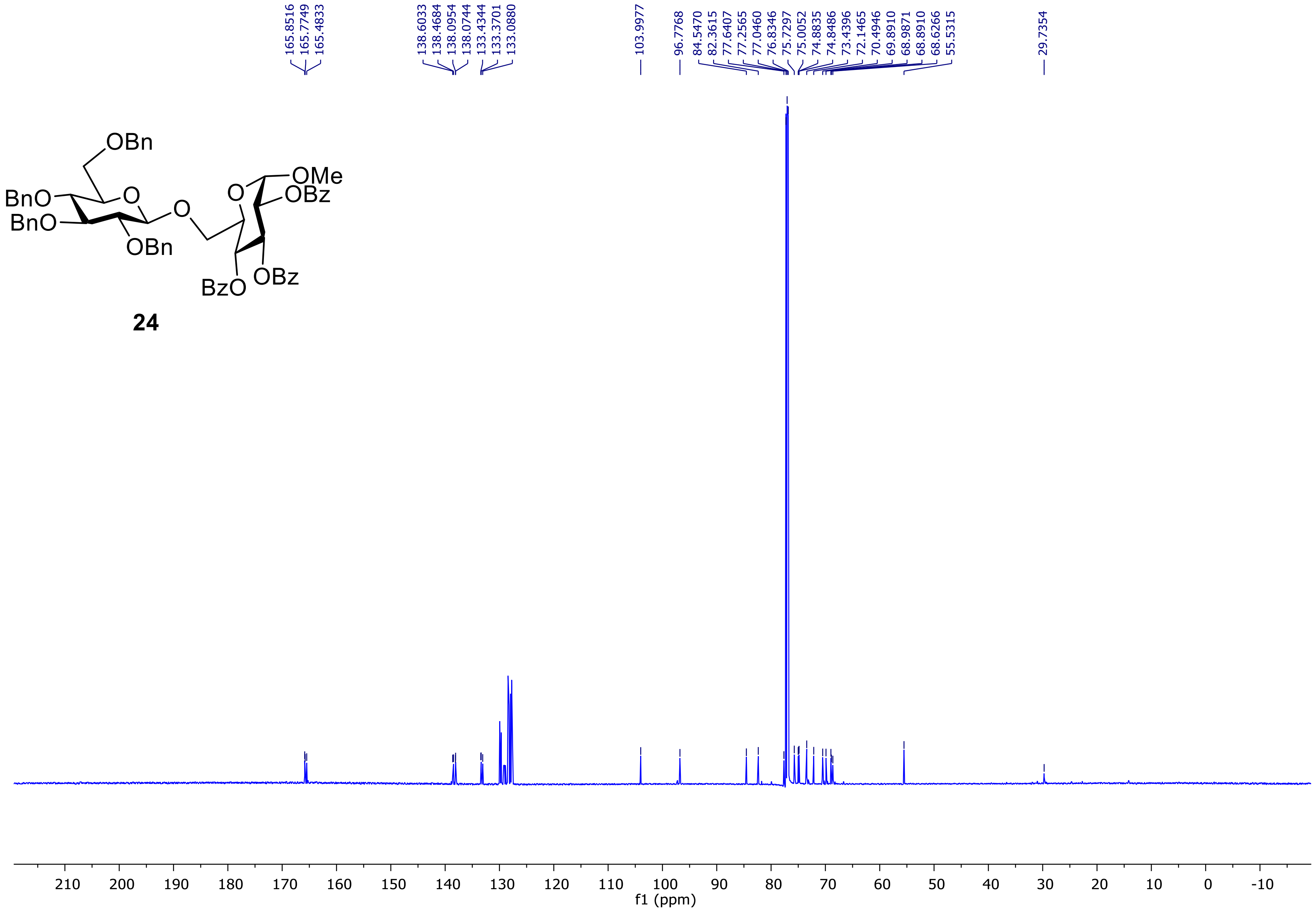


**23**

OBn
BnO
BnO
O
BnO
BnO
O
OBn
BnO
O
BnO
OMe
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)

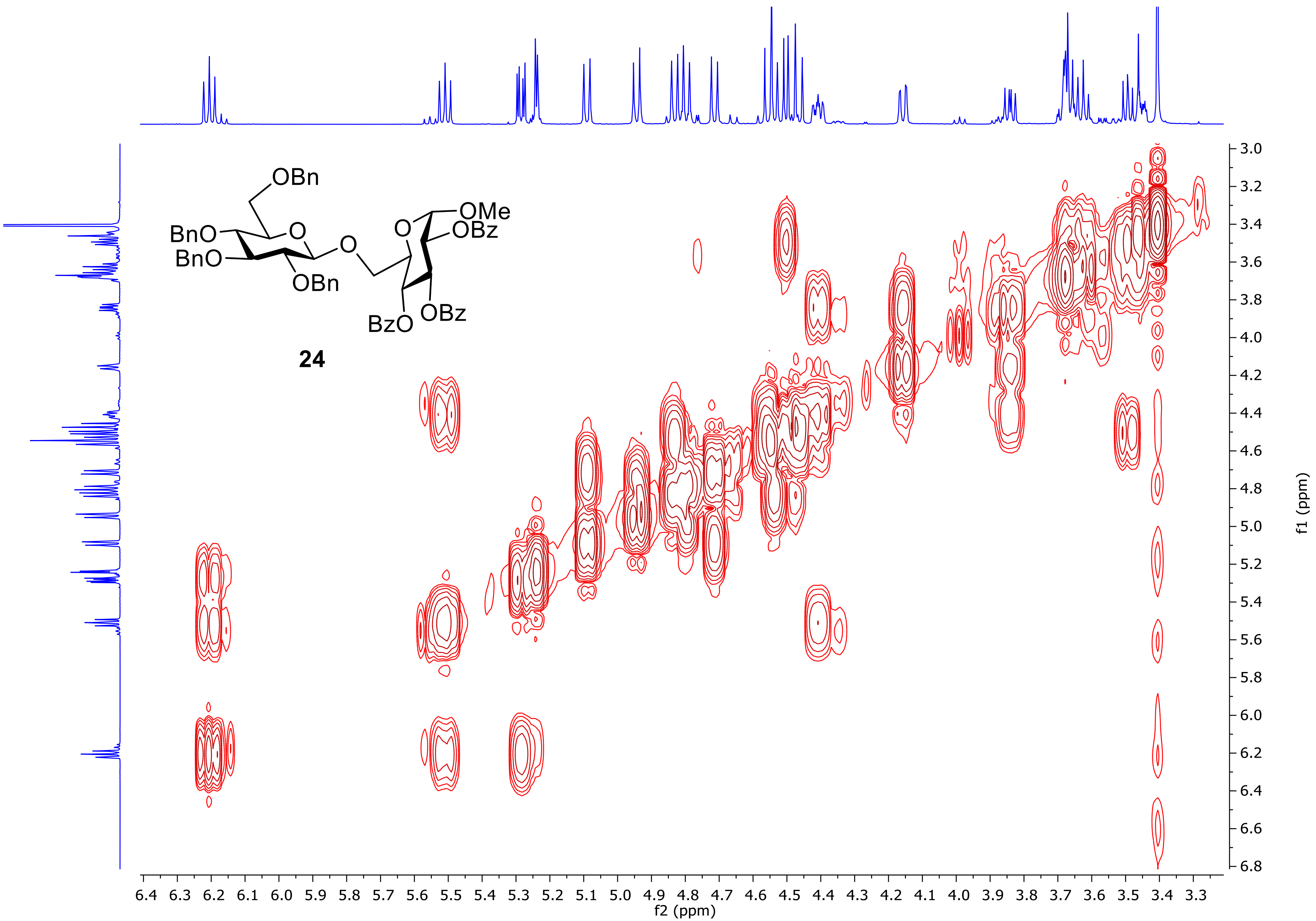

8.0121
8.0100
7.9982
7.9958
7.9687
7.9666
7.9549
7.9526
7.8867
7.8846
7.8728
7.8705
7.5364
7.5306
7.4319
7.4290
7.4202
7.4176
7.4159
7.4148
7.4052
7.4037
7.3933
7.3912
7.3810
7.3795
7.3670
7.3551
7.3446
7.3434
7.3405
7.3336
7.3315
7.3302
7.3288
7.3243
7.3214
7.3167
7.3122
7.3091
7.3050
7.3007
7.2971
7.2959
7.2931
7.2894
7.2856
7.2823
7.2801
7.1782
7.1743
7.1653
7.1624
6.2063
6.2051
5.5104
5.5090
5.2966
5.2906
5.2736
5.2428
5.2368
5.0994
5.0815
4.9530
4.9348
4.8404
4.8225
4.8057
4.7876
4.7229
4.7049
4.5654
4.5454
4.5280
4.5094
4.4965
4.4750
4.4547
3.6829
3.6791
3.6768
3.6706
3.6562
3.6248
3.4623
3.4057
OBn
BnO
O
O
O
OMe
OBz
BnO
OBn
BzO
OBz
2.32
2.18
2.16
2.31
24.77
2.24
0.95
0.93
0.96
1.13
0.97
1.11
1.07
1.25
0.99
2.12
1.00
1.06
1.11
0.96
0.98
4.25
1.00
1.35
2.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**24**

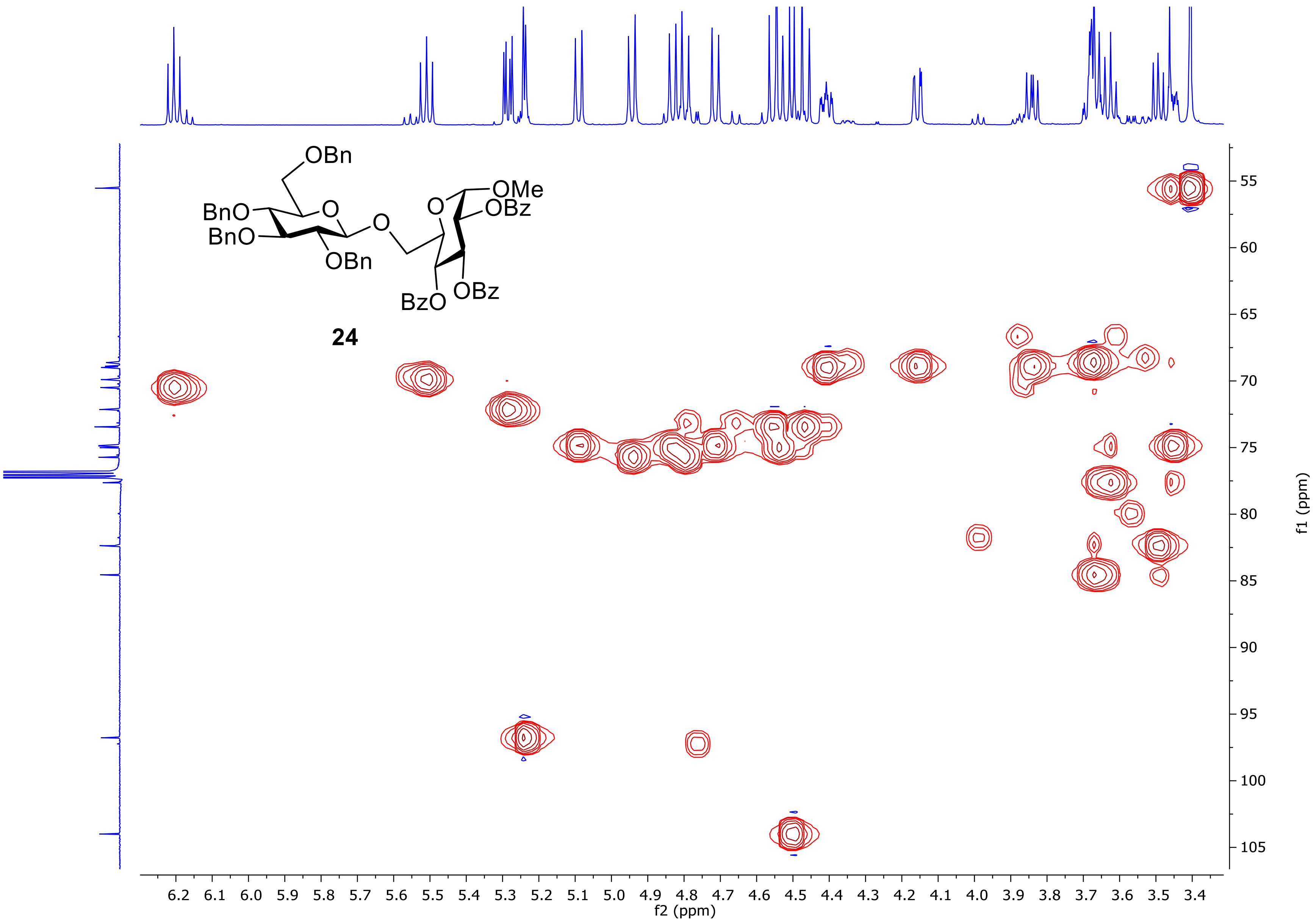


**24**

165.8516
165.7749
165.4833
138.6033
138.4684
138.0954
138.0744
133.4344
133.3701
133.0880
103.9977
96.7768
84.5470
82.3615
77.6407
77.2565
77.0460
76.8346
75.7297
75.0052
74.8835
74.8486
73.4396
72.1465
70.4946
69.8910
68.9871
68.8910
68.6266
55.5315
29.7354
OBn
BnO
BnO
O
OBn
O
O
OMe
OBz
BzO
OBz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

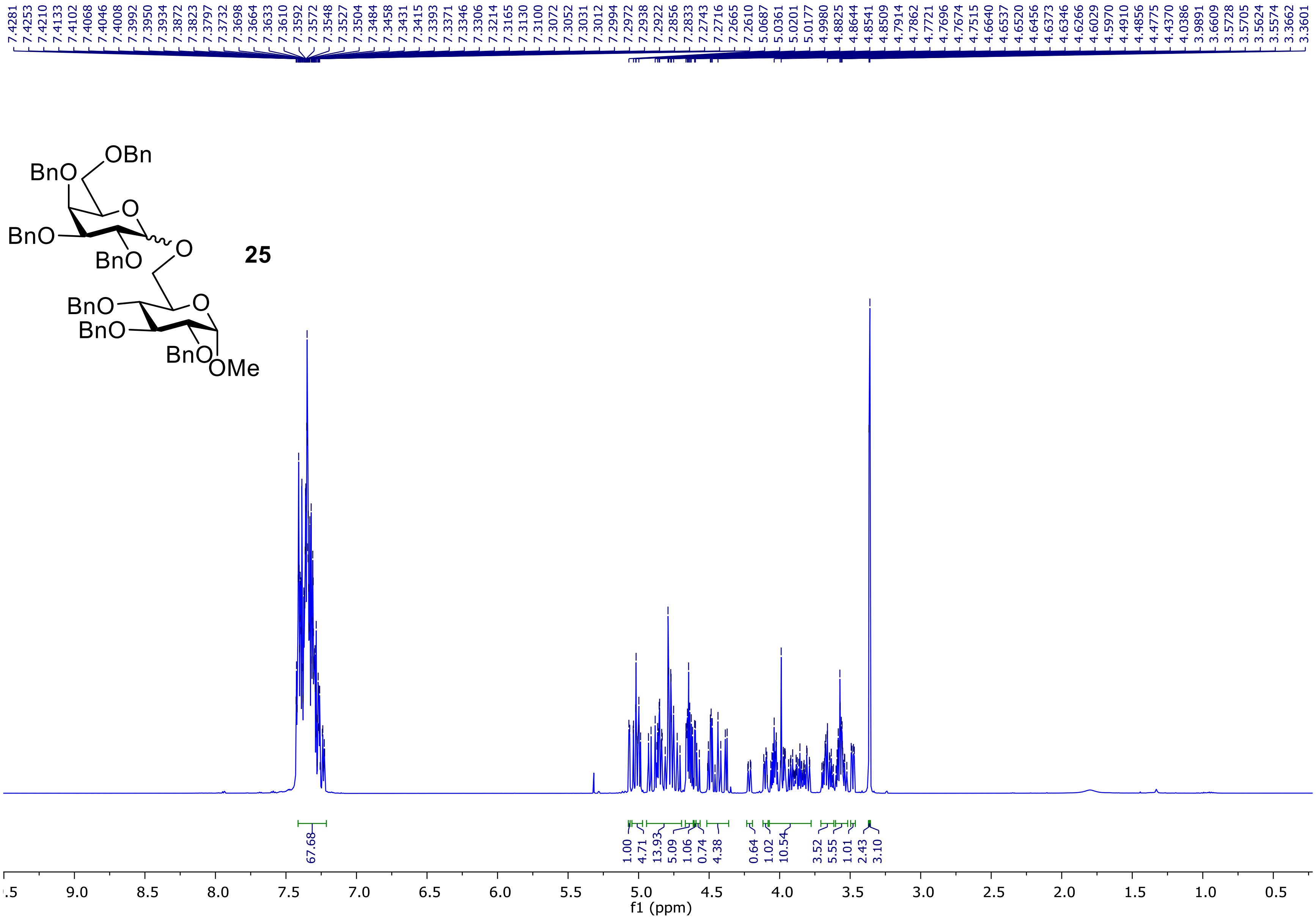

OBn
BnO
BnO
O
OBn
O
O
OMe
OBz
BzO
OBz
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.3
f2 (ppm)
3.0 3.2 3.4 3.6 3.8 4.0 4.2 4.4 4.6 4.8 5.0 5.2 5.4 5.6 5.8 6.0 6.2 6.4 6.6 6.8
f1 (ppm)

**24**



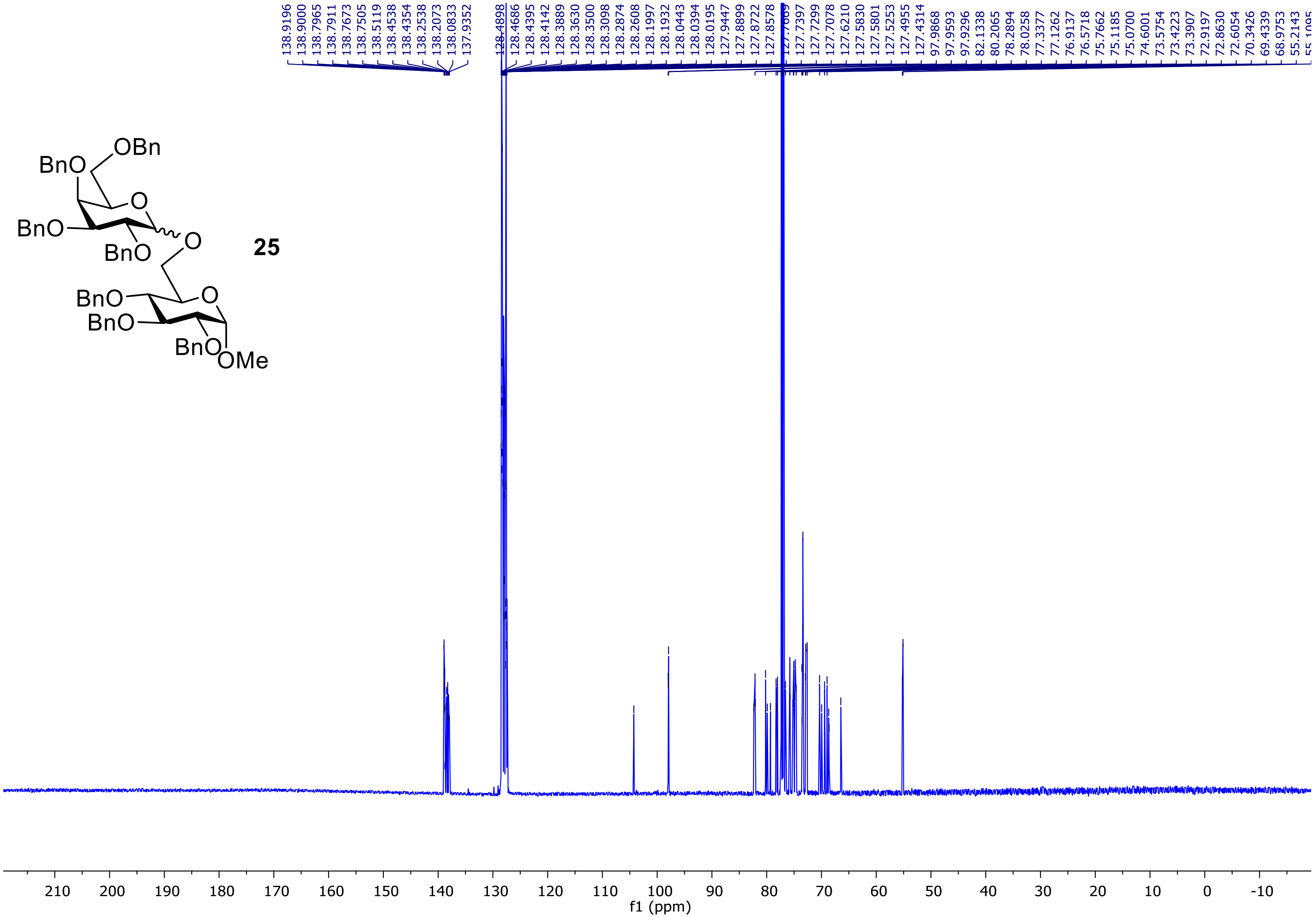
**24**

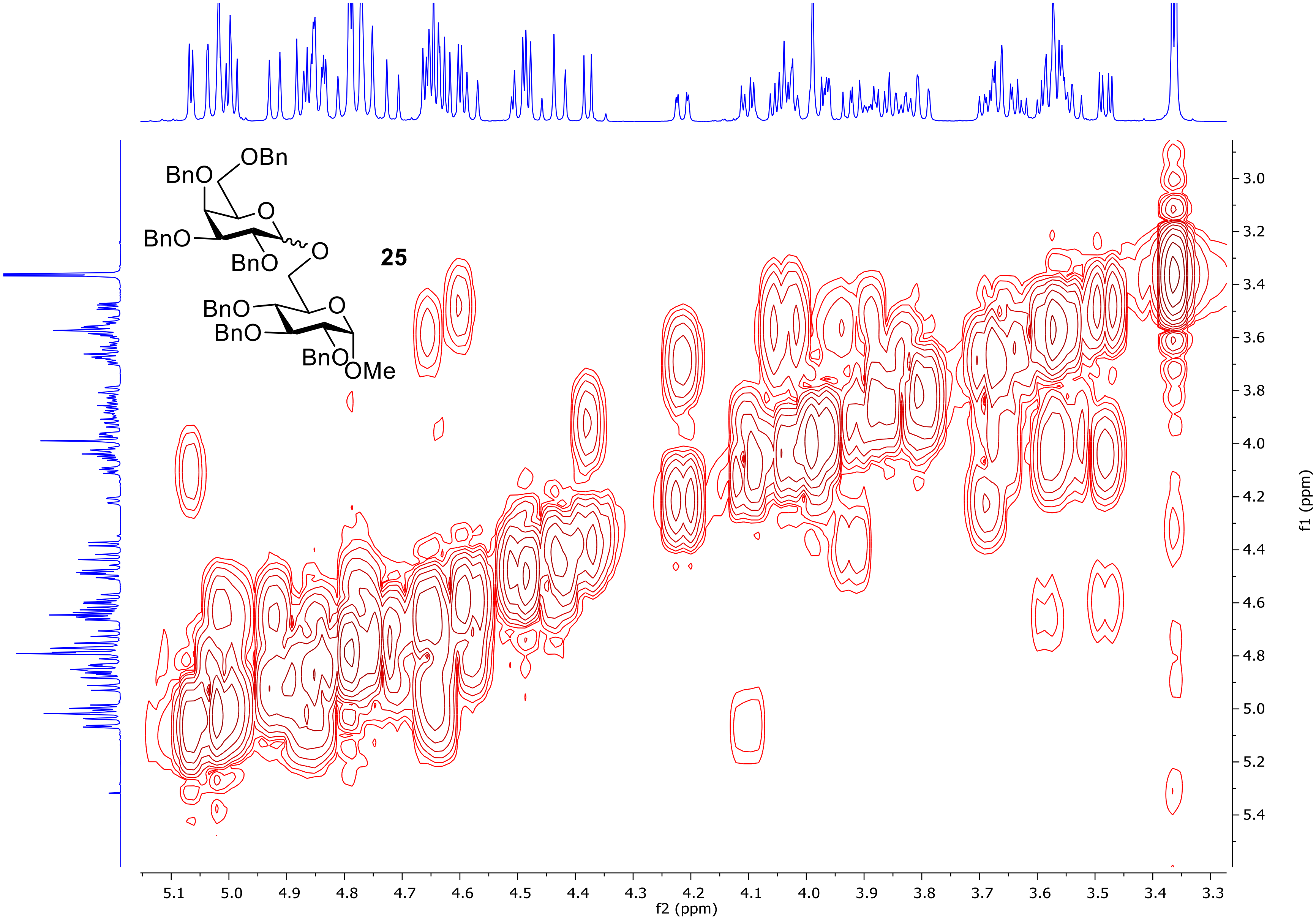
OBn
BnO
BnO
O
OBn
O
O
OMe
OBz
OBz
BzO
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)

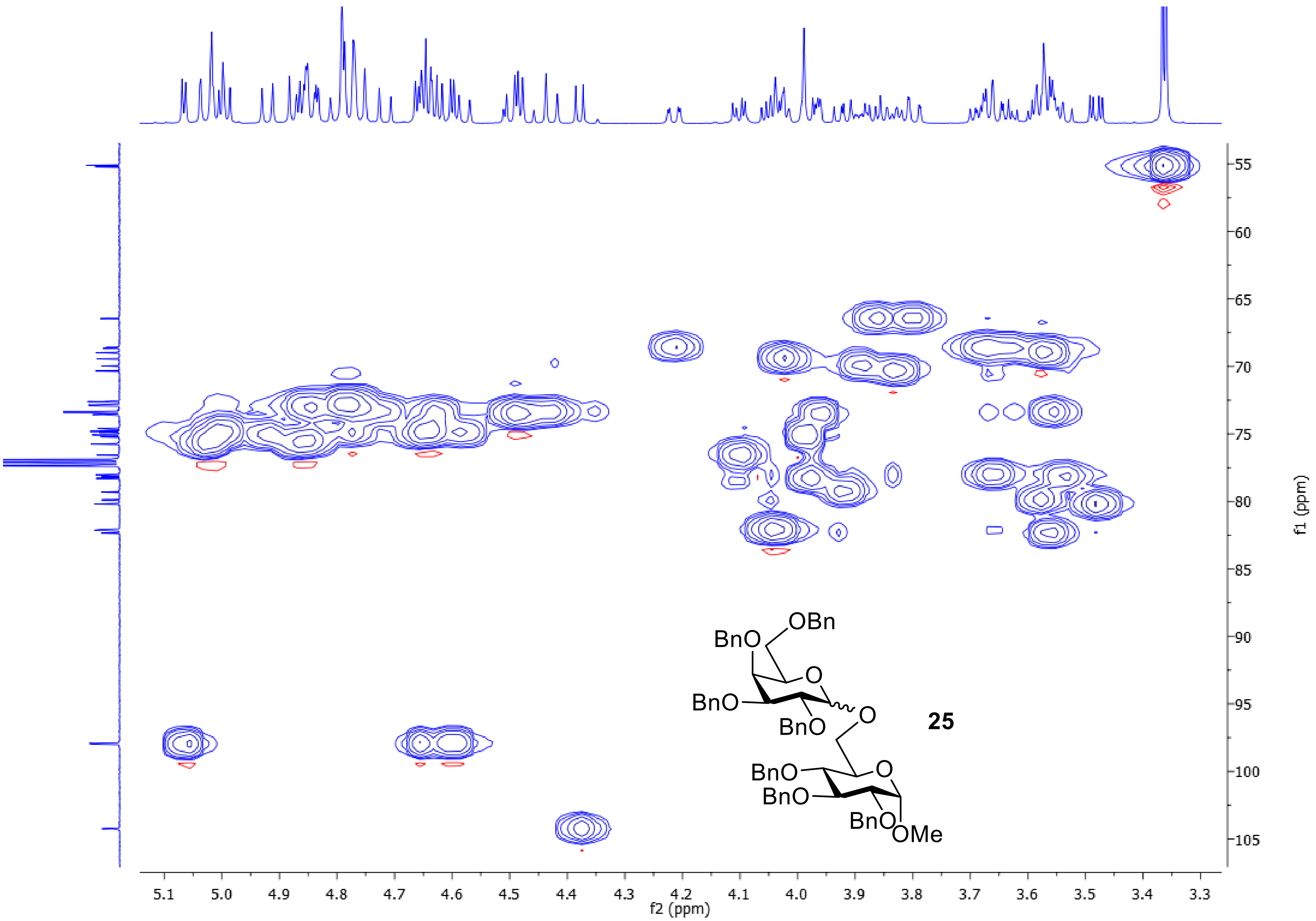


**25**

7.4281
7.4253
7.4210
7.4133
7.4102
7.4068
7.4046
7.4008
7.3992
7.3950
7.3934
7.3872
7.3823
7.3797
7.3732
7.3698
7.3664
7.3633
7.3610
7.3592
7.3572
7.3548
7.3527
7.3504
7.3484
7.3458
7.3431
7.3415
7.3393
7.3371
7.3346
7.3306
7.3214
7.3165
7.3130
7.3100
7.3072
7.3052
7.3031
7.3012
7.2994
7.2972
7.2938
7.2922
7.2856
7.2833
7.2743
7.2716
7.2665
7.2610
5.0687
5.0361
5.0201
5.0177
4.9980
4.8825
4.8644
4.8541
4.8509
4.7914
4.7862
4.7721
4.7696
4.7674
4.7515
4.6640
4.6537
4.6520
4.6456
4.6373
4.6346
4.6266
4.6029
4.5970
4.4910
4.4856
4.4775
4.4370
4.0386
3.9891
3.6609
3.5728
3.5705
3.5624
3.5574
3.3662
3.3601
OBn
BnO
O
BnO
BnO
O
BnO
BnO
O
BnO
OMe
67.68
1.00
4.71
13.93
5.09
1.06
0.74
4.38
0.64
1.02
10.54
3.52
5.55
1.01
2.43
3.10
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

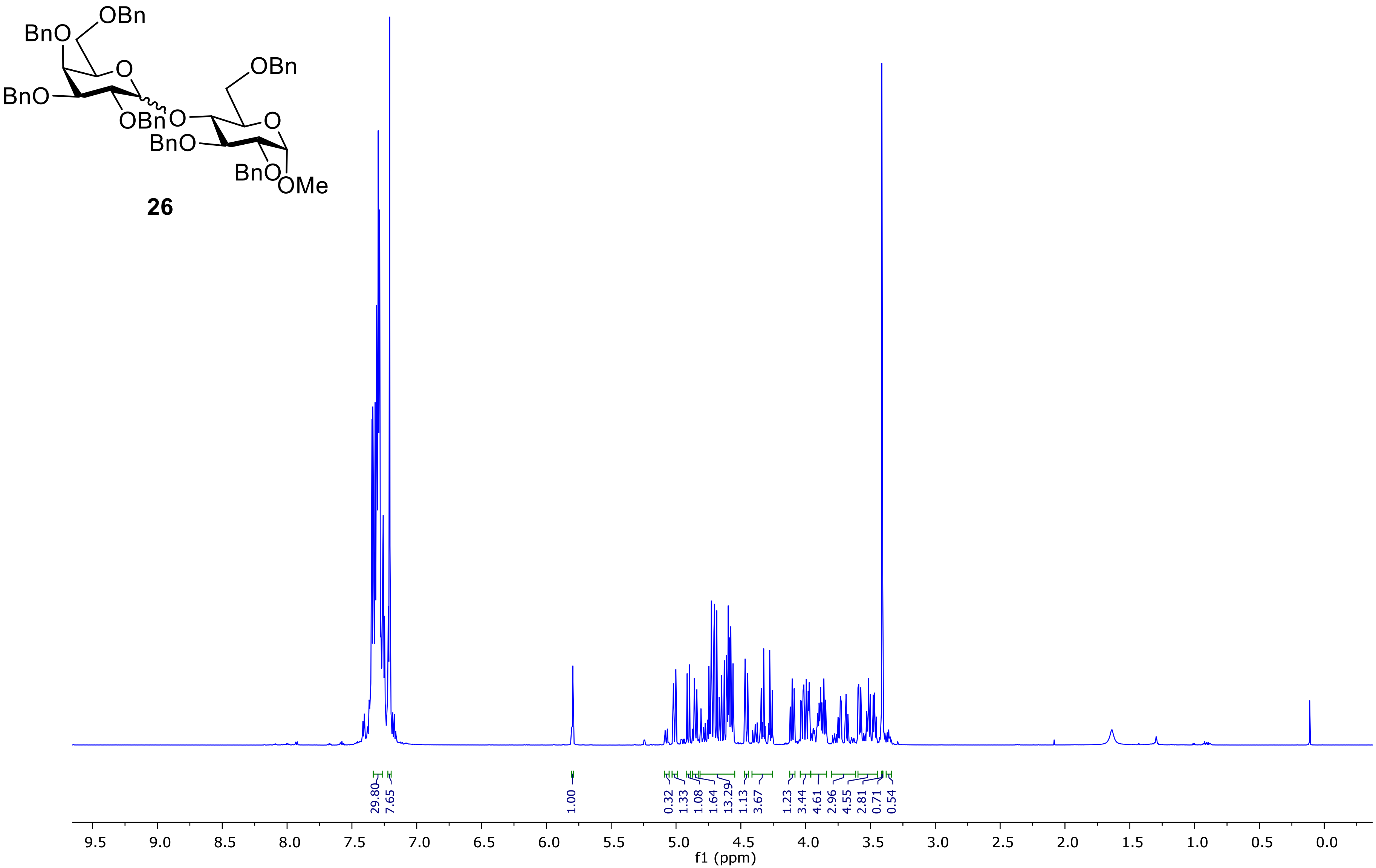

25
138.9196
138.9000
138.7965
138.7911
138.7673
138.7505
138.5119
138.4538
138.4354
138.2538
138.2073
138.0833
137.9352
128.4898
128.4686
128.4395
128.4142
128.3889
128.3630
128.3500
128.3098
128.2874
128.2608
128.1997
128.1932
128.0443
128.0394
128.0195
127.9447
127.8899
127.8722
127.8578
127.7669
127.7397
127.7299
127.7078
127.6210
127.5830
127.5801
127.5253
127.4955
127.4314
97.9868
97.9593
97.9296
82.1338
80.2065
78.2894
78.0258
77.3377
77.1262
76.9137
76.5718
75.7662
75.1185
75.0700
74.6001
73.5754
73.4223
73.3907
72.9197
72.8630
72.6054
70.3426
69.4339
68.9753
55.2143
55.1095
OBn
BnO
O
BnO
BnO
O
BnO
O
BnO
BnO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBn
BnO
O
BnO
O
BnO
25
BnO
O
BnO
BnO
OMe
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
f1 (ppm)



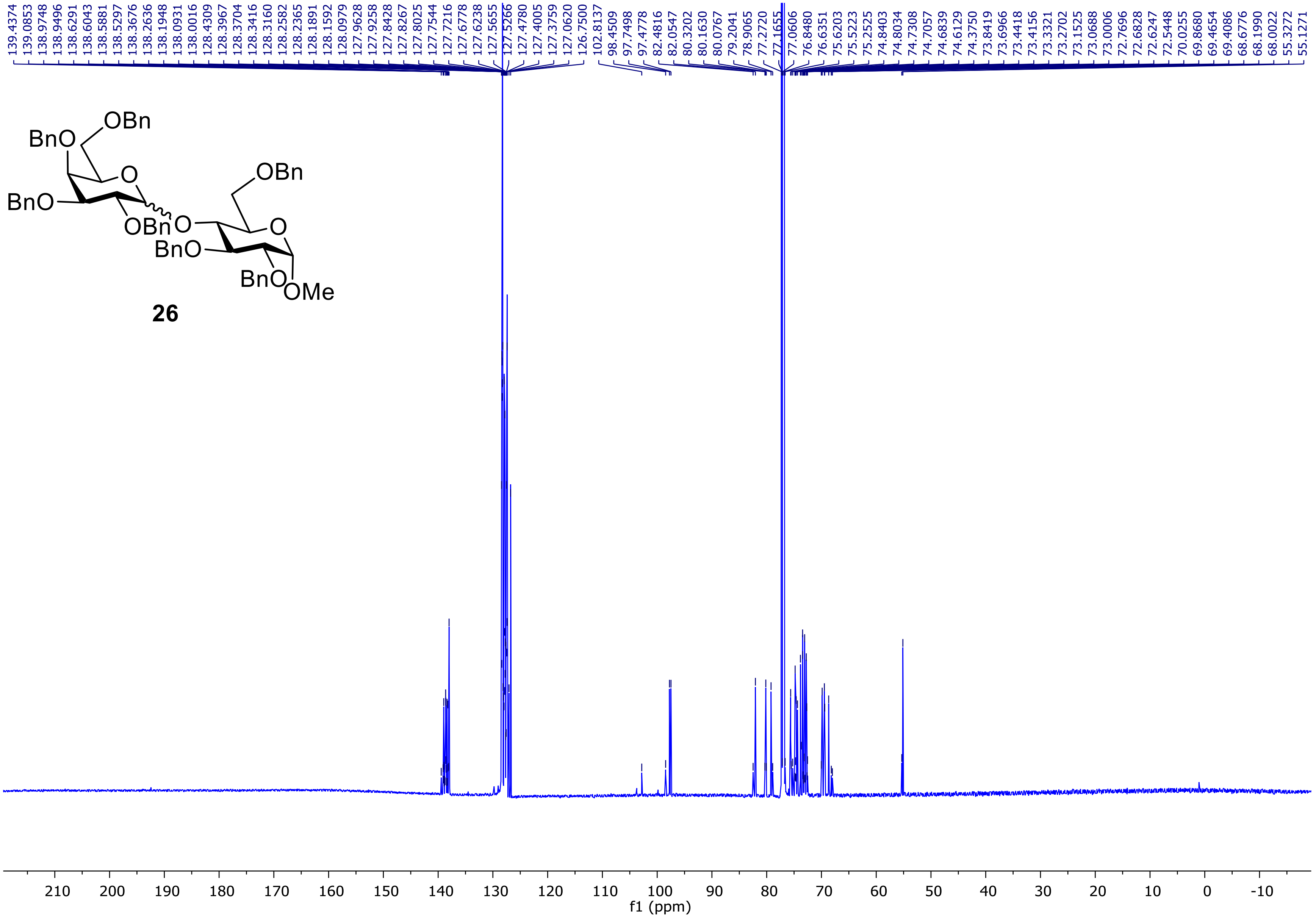
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)
OBn
BnO
O
BnO
BnO
O
BnO
BnO
O
BnO
OMe

**25**

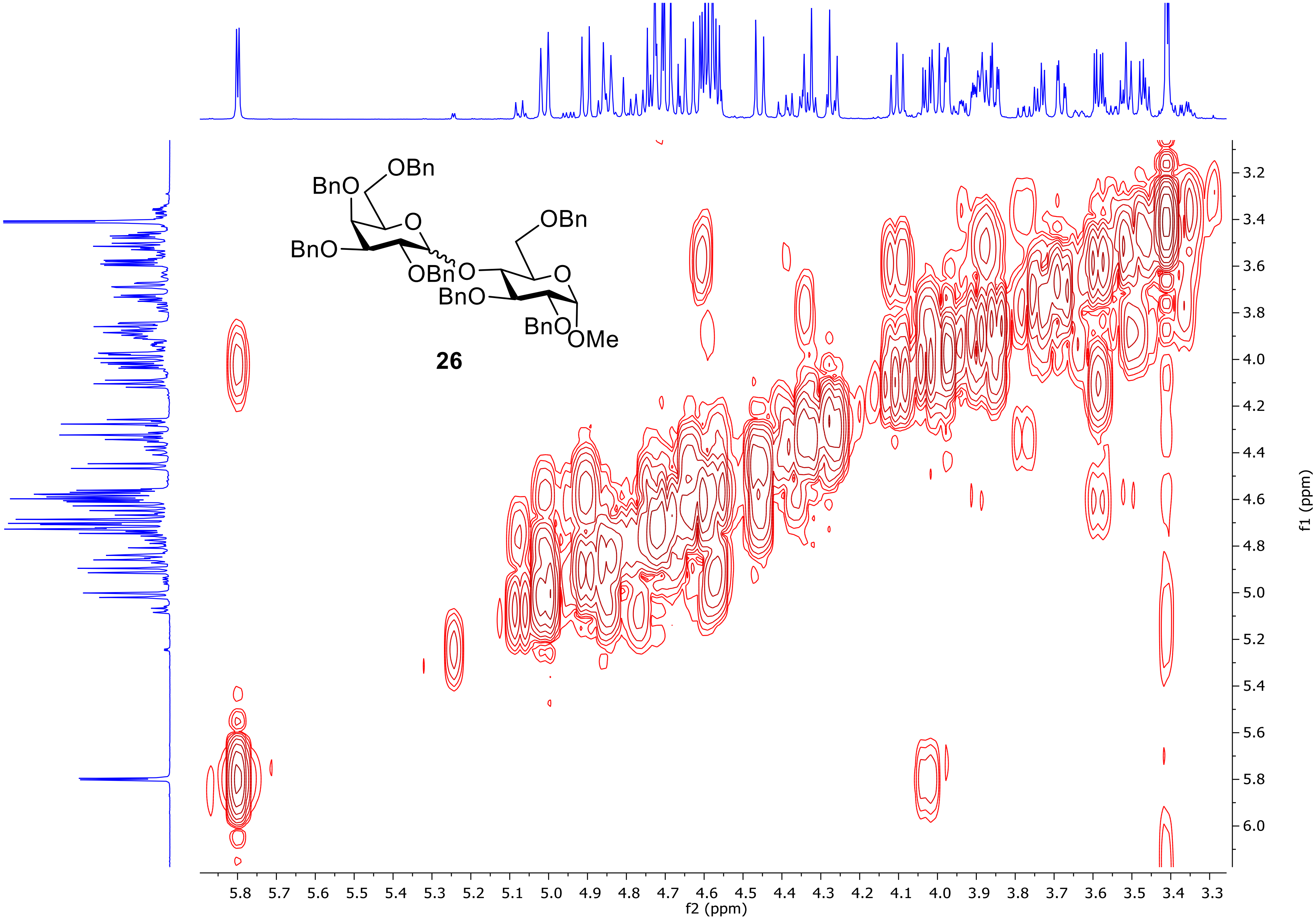

OBn
BnO
O
OBn
BnO
OBn
O
O
BnO
BnO
OMe

**26**

29.80
7.65
1.00
0.32
1.33
1.08
1.64
13.29
1.13
3.67
1.23
3.44
4.61
2.96
4.55
2.81
0.71
0.54
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

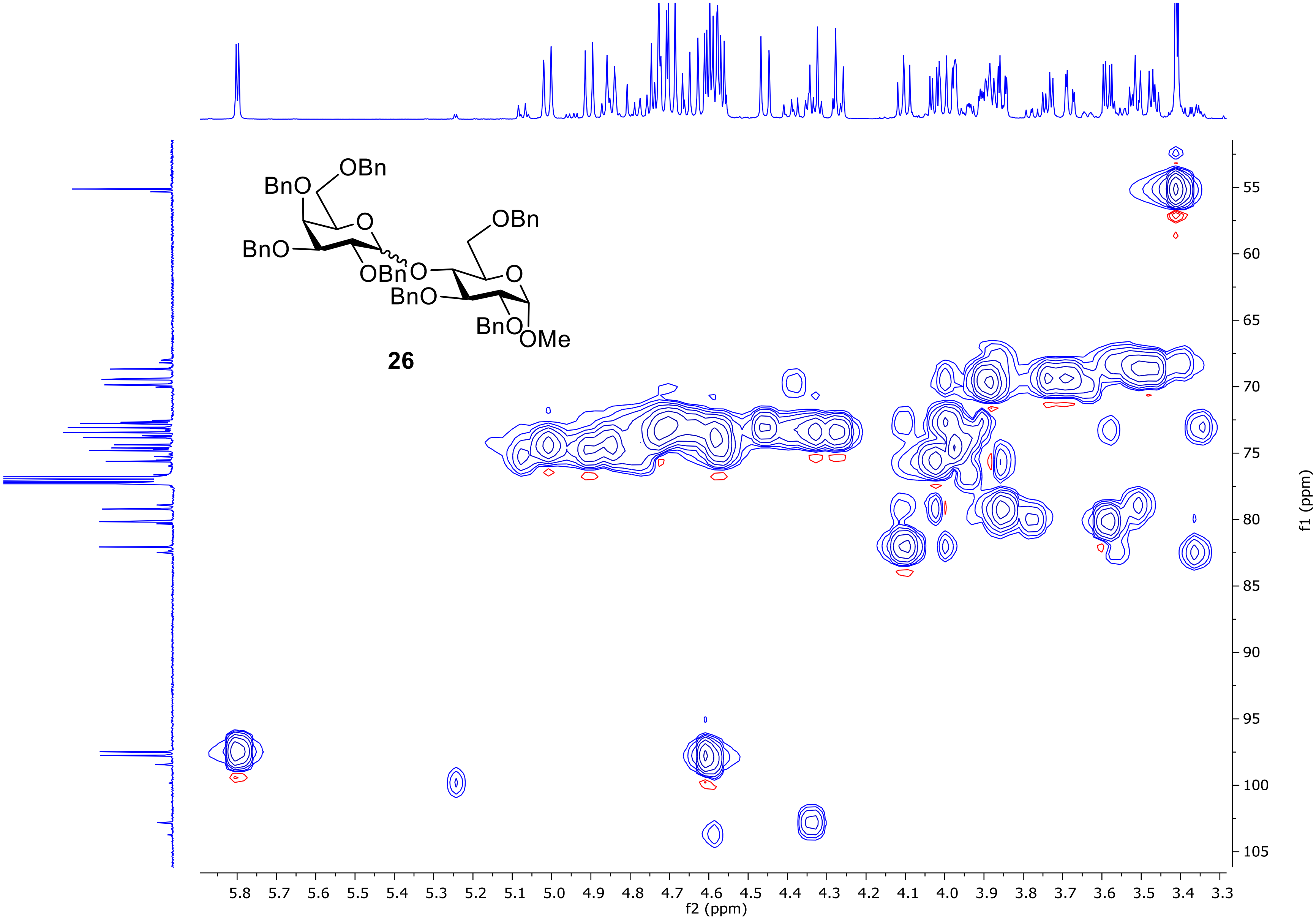

26

139.4374
139.0853
138.9748
138.9496
138.6291
138.6043
138.5881
138.5297
138.3676
138.2636
138.1948
138.0931
138.0016
128.4309
128.3967
128.3704
128.3416
128.3160
128.2582
128.2365
128.1891
128.1592
128.0979
127.9628
127.9258
127.8428
127.8267
127.8025
127.7544
127.7216
127.6778
127.6238
127.5655
127.5266
127.4780
127.4005
127.3759
127.0620
126.7500
102.8137
98.4509
97.7498
97.4778
82.4816
82.0547
80.3202
80.1630
80.0767
79.2041
78.9065
77.2720
77.1655
77.0606
76.8480
76.6351
75.6203
75.5223
75.2525
74.8403
74.8034
74.7308
74.7057
74.6839
74.6129
74.3750
73.8419
73.6966
73.4418
73.4156
73.3321
73.2702
73.1525
73.0688
73.0006
72.7696
72.6828
72.6247
72.5448
70.0255
69.8680
69.4654
69.4086
68.6776
68.1990
68.0022
55.3272
55.1271
OBn
BnO
O
BnO
OBn
O
OBn
O
BnO
BnO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



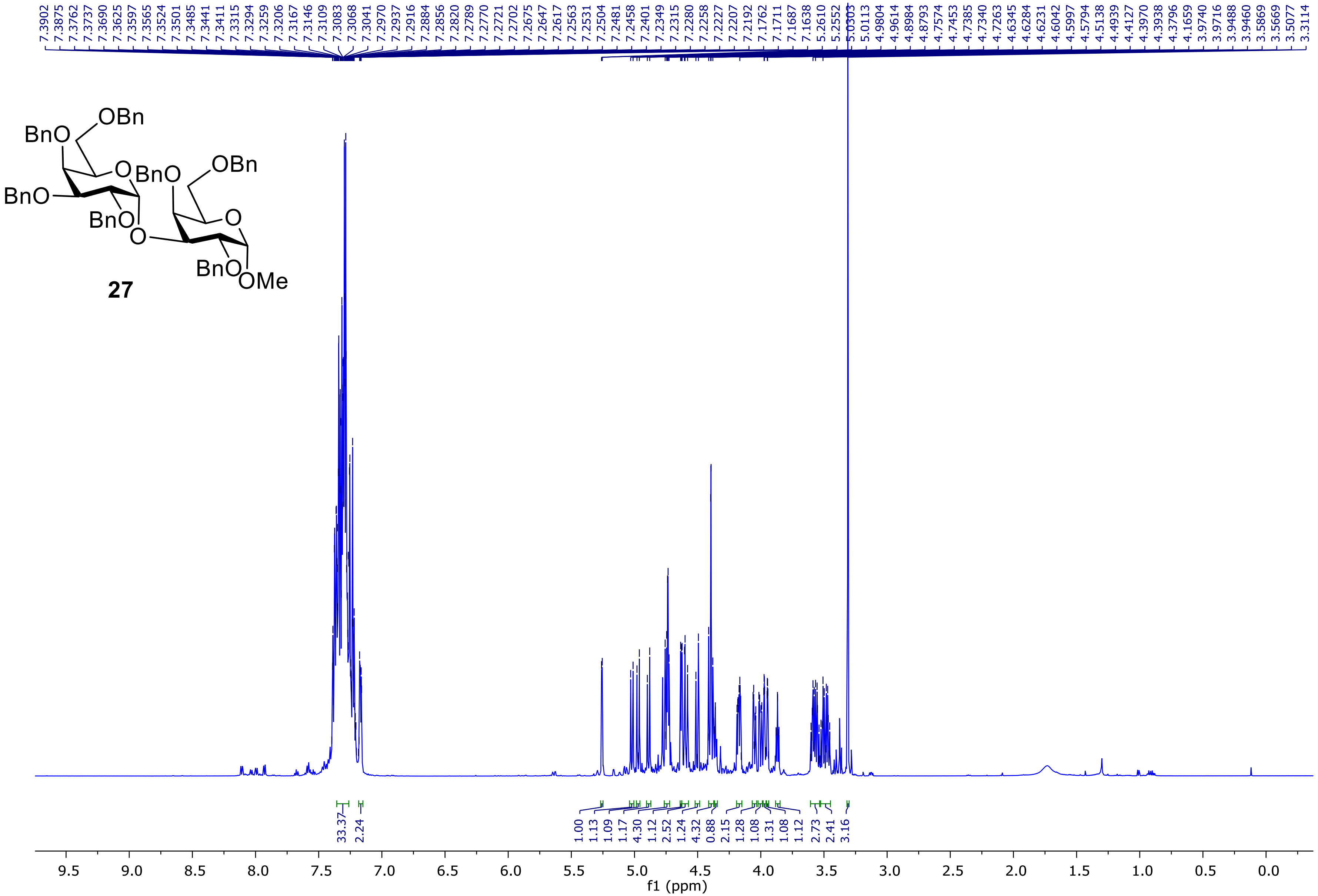
**26**

OBn
BnO
O
BnO
OBn
O
OBn
O
BnO
BnO
OMe
f2 (ppm)
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f1 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0



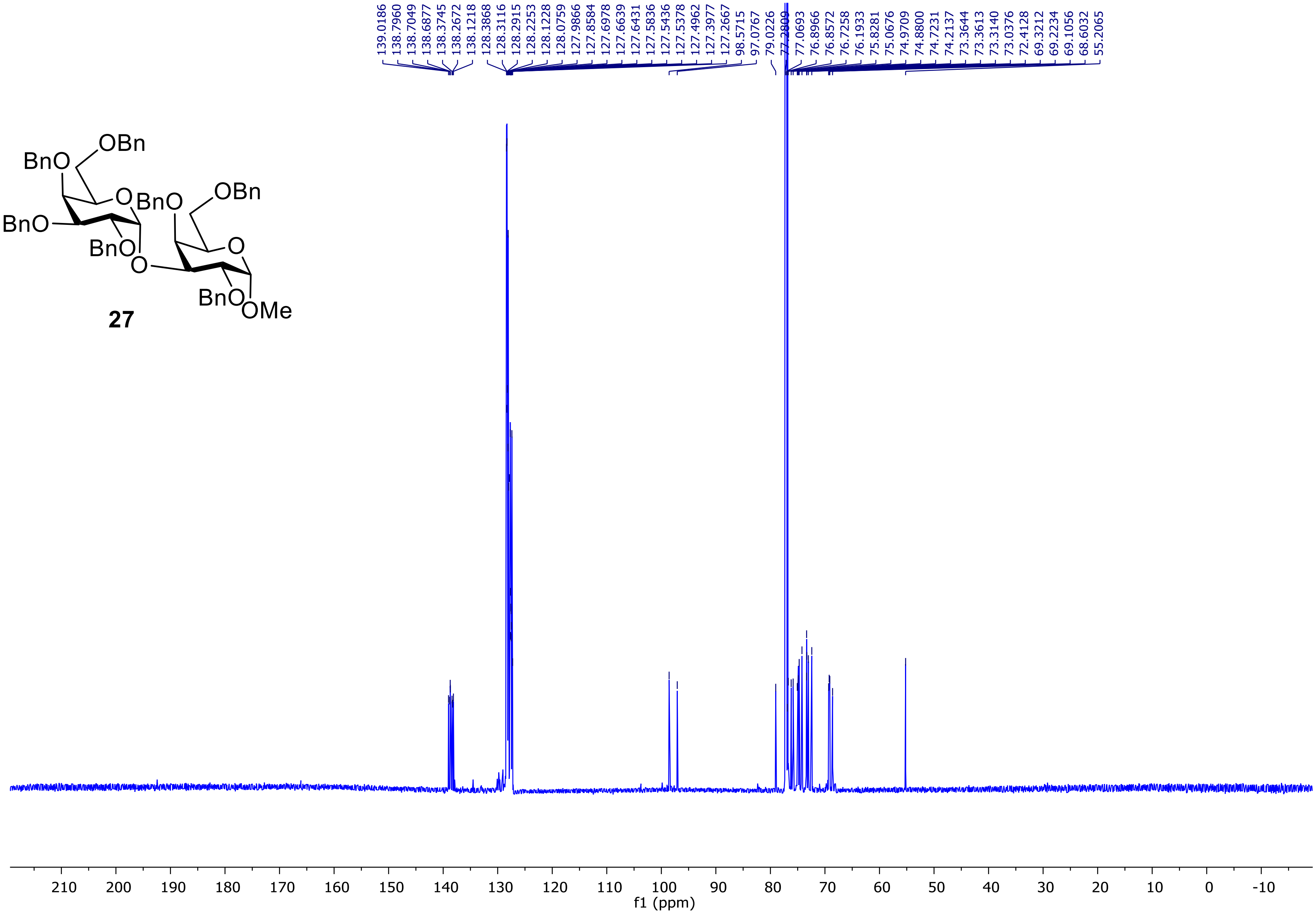
**26**

OBn
BnO
O
BnO
OBn
O
OBn
O
BnO
BnO
OMe
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)



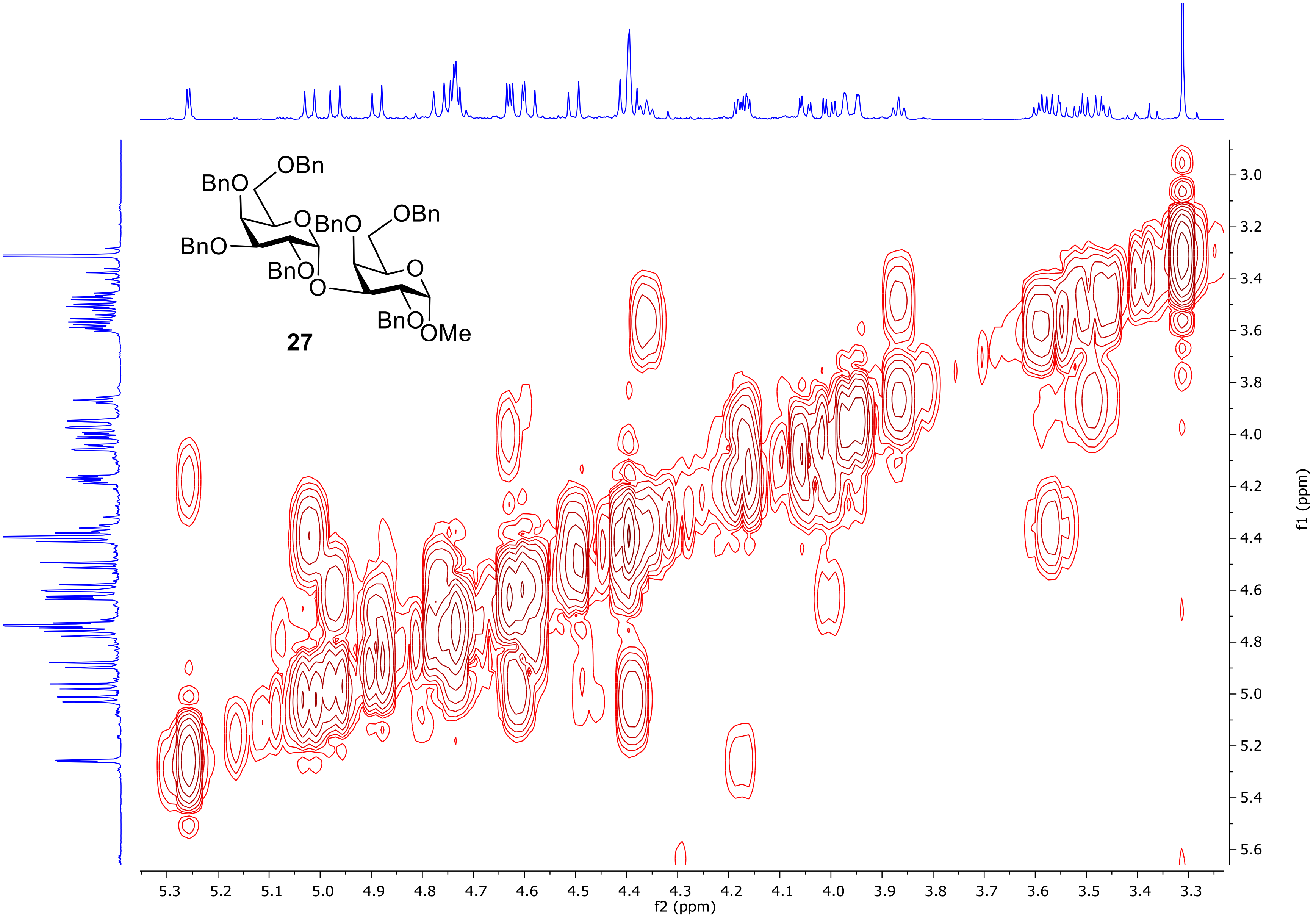
**27**

OBn
BnO
O
BnO
OBn
BnO
BnO
O
O
BnO
OMe
7.3902
7.3875
7.3762
7.3737
7.3690
7.3625
7.3597
7.3565
7.3524
7.3501
7.3485
7.3441
7.3411
7.3315
7.3294
7.3259
7.3206
7.3167
7.3146
7.3109
7.3083
7.3068
7.3041
7.2970
7.2937
7.2916
7.2884
7.2856
7.2820
7.2789
7.2770
7.2721
7.2702
7.2675
7.2647
7.2617
7.2563
7.2531
7.2504
7.2481
7.2458
7.2401
7.2349
7.2315
7.2280
7.2258
7.2227
7.2207
7.2192
7.1762
7.1711
7.1687
7.1638
5.2610
5.2552
5.0303
5.0113
4.9804
4.9614
4.8984
4.8793
4.7574
4.7453
4.7385
4.7340
4.7263
4.6345
4.6284
4.6231
4.6042
4.5997
4.5794
4.5138
4.4939
4.4127
4.3970
4.3938
4.3796
4.1659
3.9740
3.9716
3.9488
3.9460
3.5869
3.5669
3.5077
3.3114
33.37
2.24
1.00
1.13
1.09
1.17
4.30
1.12
2.52
1.24
4.32
0.88
2.15
1.28
1.08
1.31
1.08
1.12
2.73
2.41
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

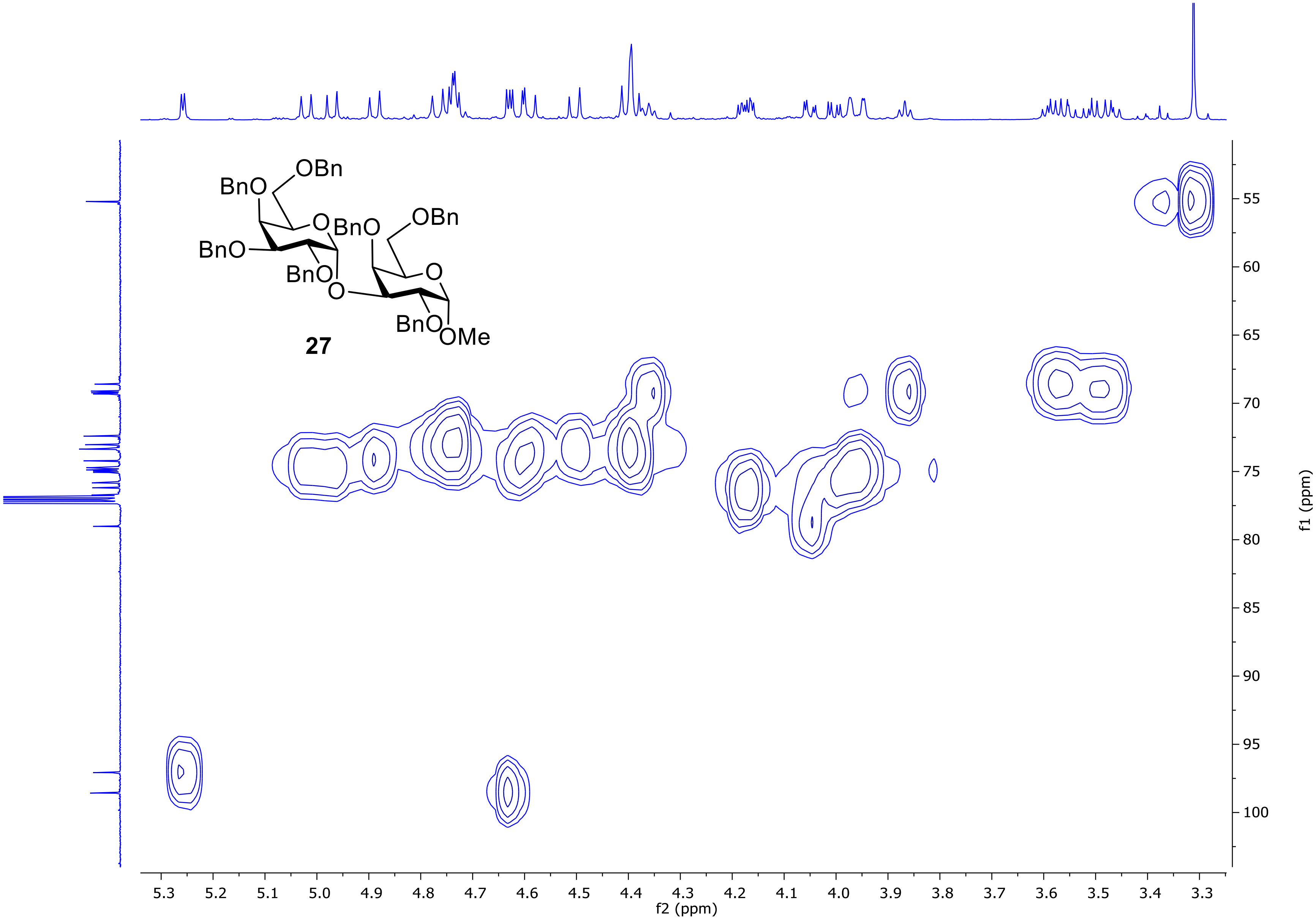

OBn
BnO
O
BnO
BnO
BnO
O
OBn
O
BnO
OMe

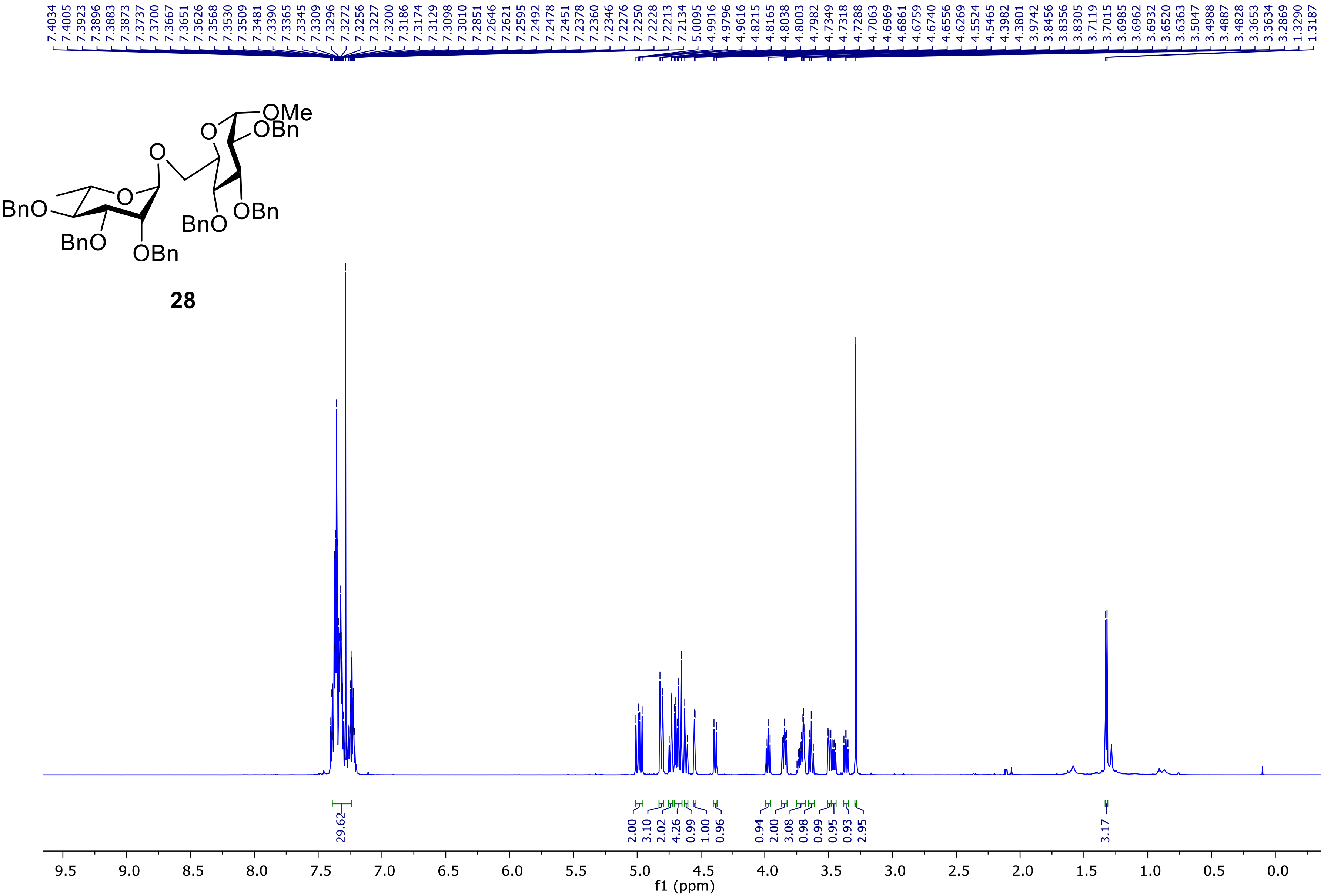
**27**

139.0186
138.7960
138.7049
138.6877
138.3745
138.2672
138.1218
128.3868
128.3116
128.2915
128.2253
128.1228
128.0759
127.9866
127.8584
127.6978
127.6639
127.6431
127.5836
127.5436
127.5378
127.4962
127.3977
127.2667
98.5715
97.0767
79.0226
77.2809
77.0693
76.8966
76.8572
76.7258
76.1933
75.8281
75.0676
74.9709
74.8800
74.7231
74.2137
73.3644
73.3613
73.3140
73.0376
72.4128
69.3212
69.2234
69.1056
68.6032
55.2065
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBn
BnO
O
BnO
BnO
BnO
OBn
O
O
BnO
OMe
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
f1 (ppm)

**27**

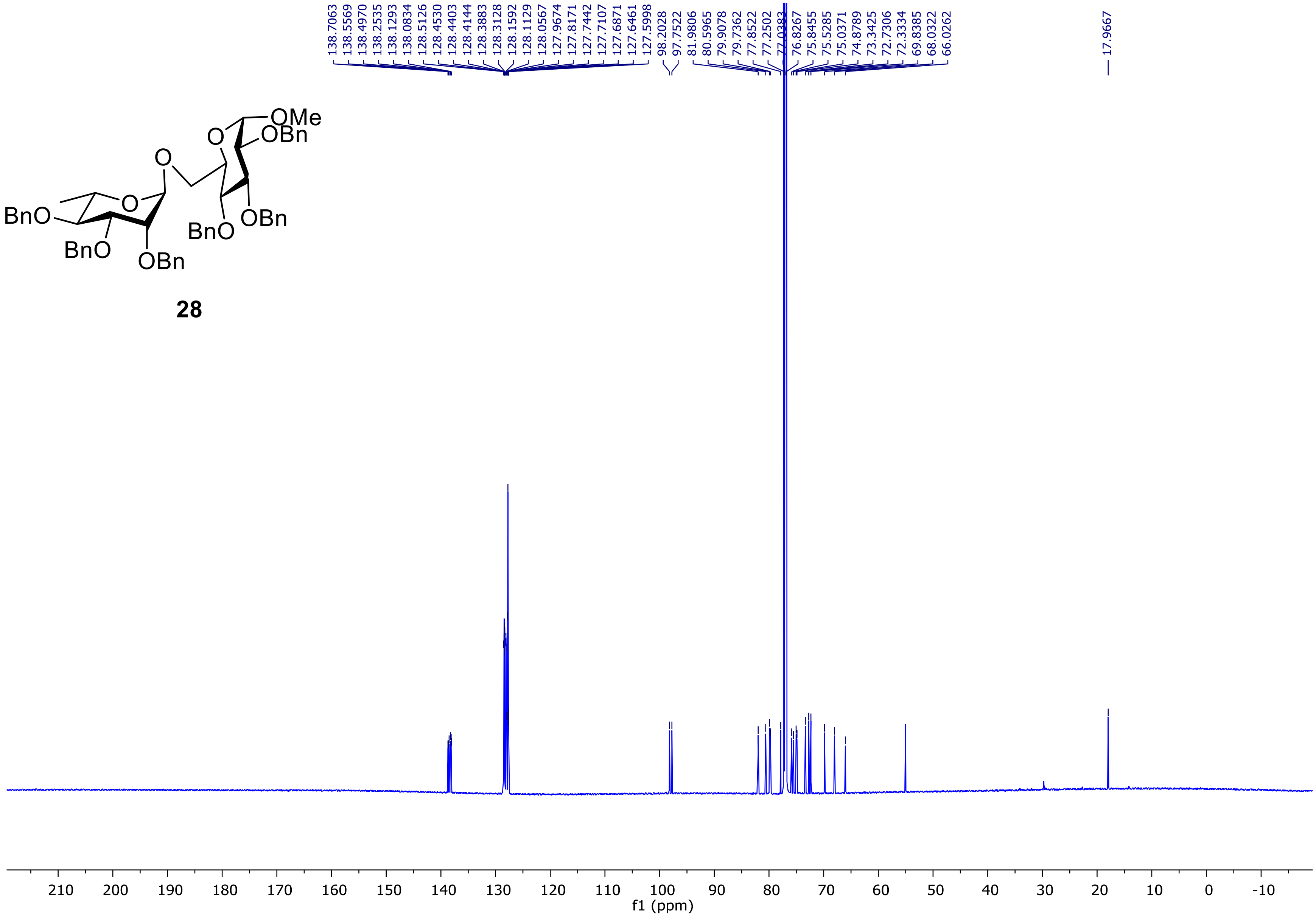

BnO
OBn
O
BnO
BnO
BnO
O
BnO
OBn
O
BnO
OMe
27
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)

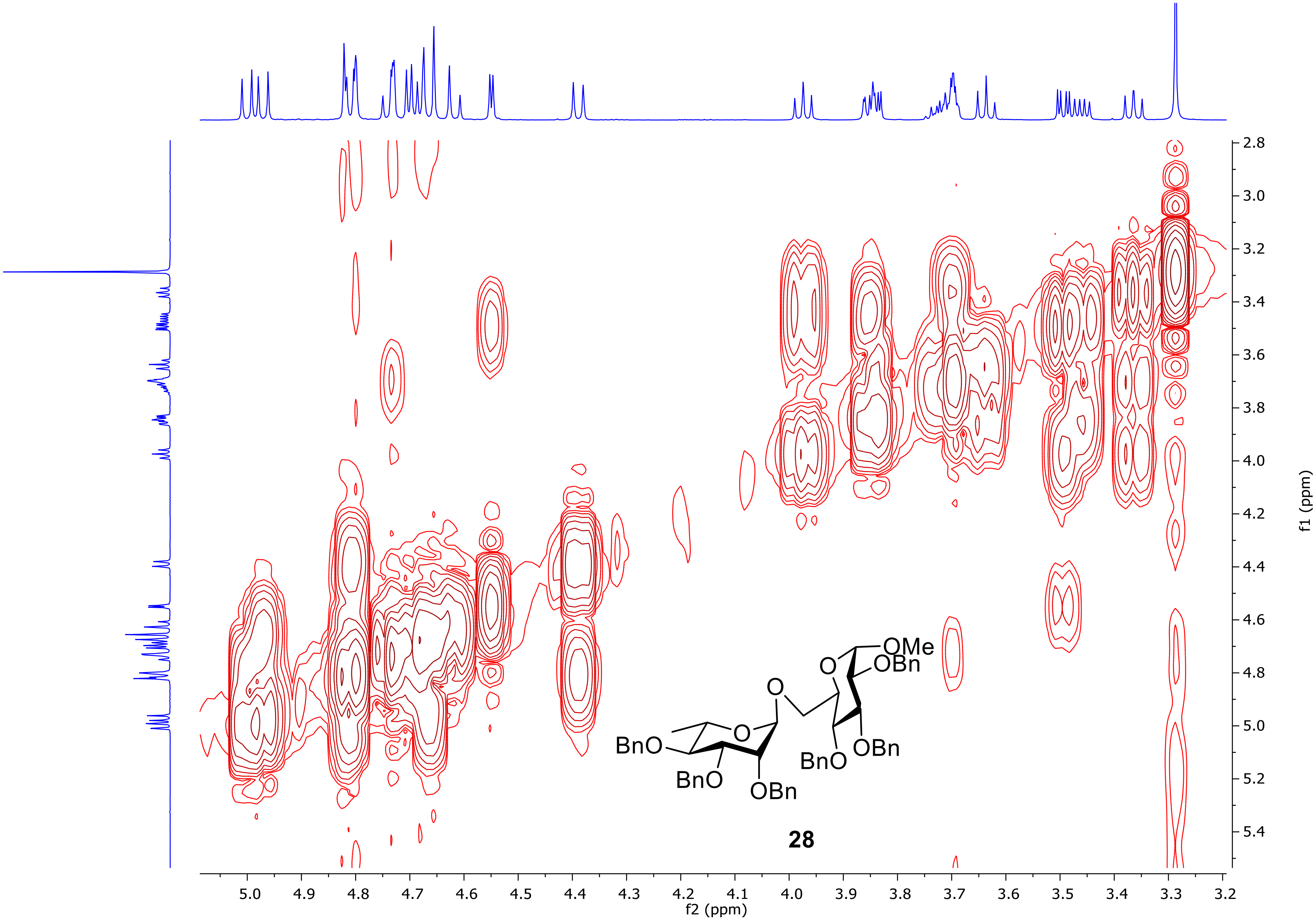

7.4034
7.4005
7.3923
7.3896
7.3883
7.3873
7.3737
7.3700
7.3667
7.3651
7.3626
7.3568
7.3530
7.3509
7.3481
7.3390
7.3365
7.3345
7.3309
7.3296
7.3272
7.3256
7.3227
7.3200
7.3186
7.3174
7.3129
7.3098
7.3010
7.2851
7.2646
7.2621
7.2595
7.2492
7.2478
7.2451
7.2378
7.2360
7.2346
7.2276
7.2250
7.2228
7.2213
7.2134
5.0095
4.9916
4.9796
4.9616
4.8215
4.8165
4.8038
4.8003
4.7982
4.7349
4.7318
4.7288
4.7063
4.6969
4.6861
4.6759
4.6740
4.6556
4.6269
4.5524
4.5465
4.3982
4.3801
3.9742
3.8456
3.8356
3.8305
3.7119
3.7015
3.6985
3.6962
3.6932
3.6520
3.6363
3.5047
3.4988
3.4887
3.4828
3.3653
3.3634
3.2869
1.3290
1.3187
OMe
O
OBn
O
BnO
O
BnO
OBn
BnO
OBn
29.62
2.00
3.10
2.02
4.26
0.99
1.00
0.96
0.94
2.00
3.08
0.98
0.99
0.95
0.93
2.95
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**28**

OMe
O
OBn
O
BnO
O
BnO
OBn
BnO
OBn
OBn

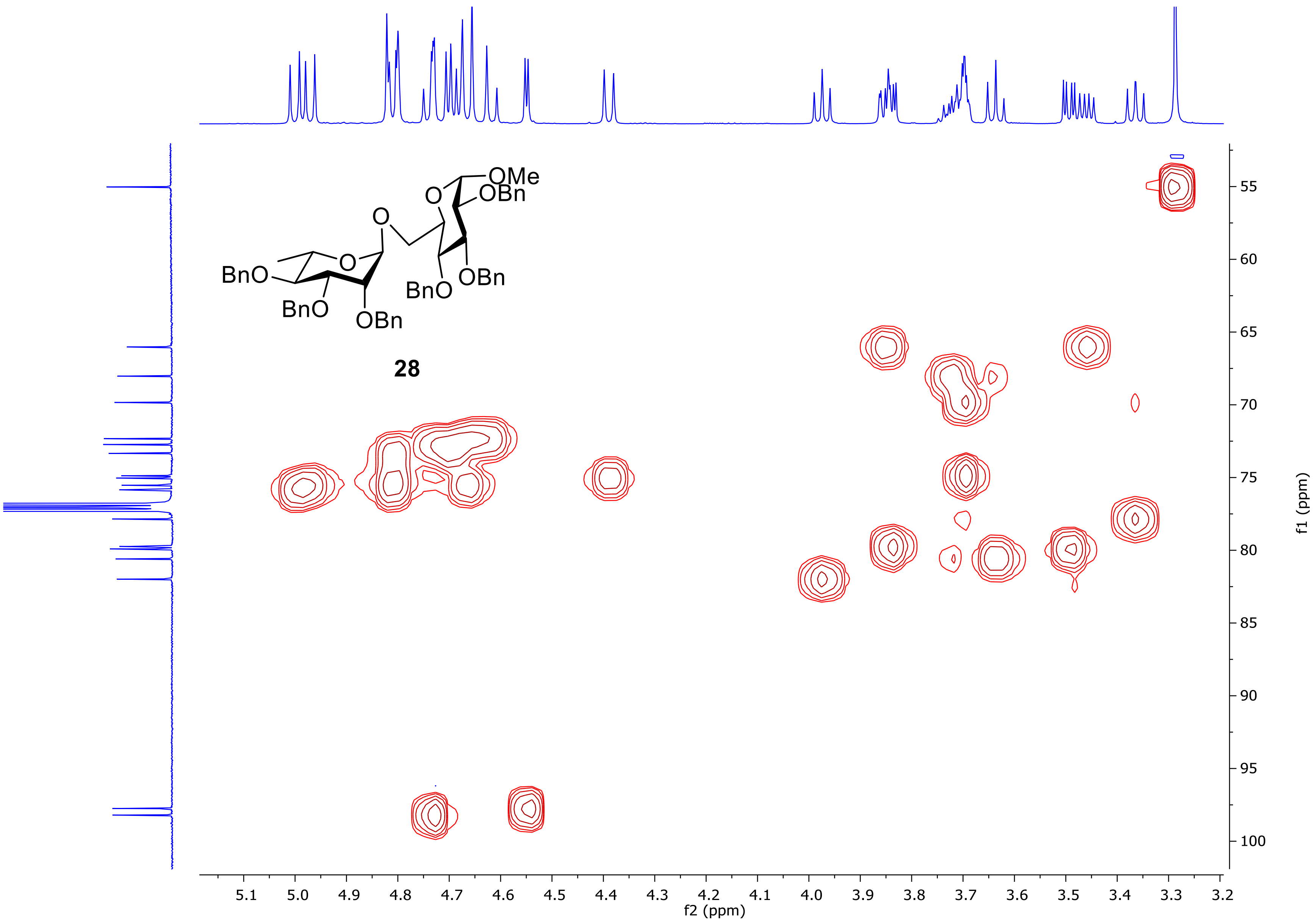
**28**

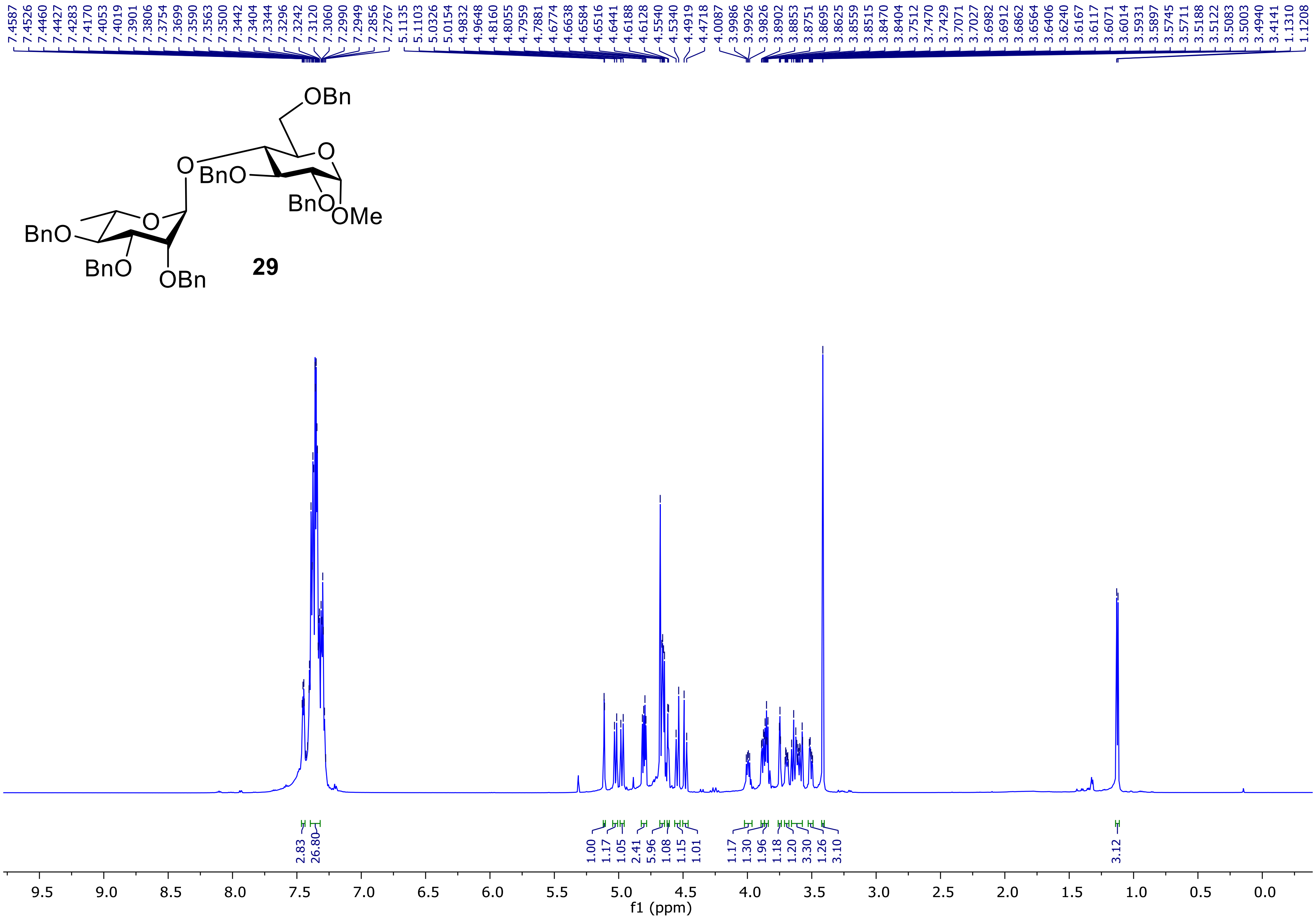

138.7063
138.5569
138.4970
138.2535
138.1293
138.0834
128.5126
128.4530
128.4403
128.4144
128.3883
128.3128
128.1592
128.1129
128.0567
127.9674
127.8171
127.7442
127.7107
127.6871
127.6461
127.5998
98.2028
97.7522
81.9806
80.5965
79.9078
79.7362
77.8522
77.2502
77.0383
76.8267
75.8455
75.5285
75.0371
74.8789
73.3425
72.7306
72.3334
69.8385
68.0322
66.0262
17.9667
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



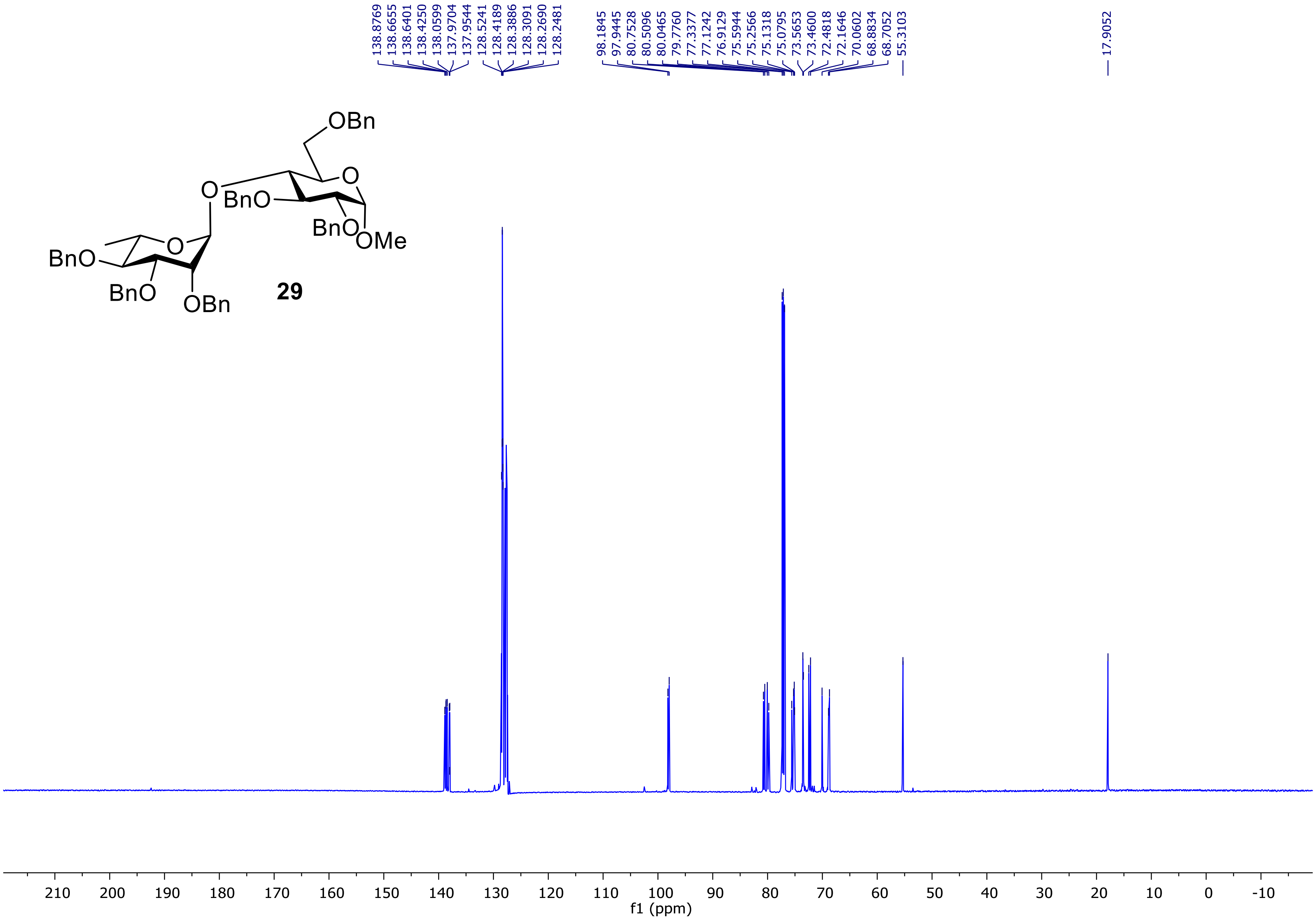
f2 (ppm)
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f1 (ppm)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
O
OMe
OBn
O
O
BnO
BnO
OBn
BnO
OBn

**28**


OMe
OBn
O
O
O
BnO
BnO
OBn
BnO
OBn
28
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)


7.4587
7.4526
7.4460
7.4427
7.4283
7.4170
7.4053
7.4019
7.3901
7.3806
7.3754
7.3699
7.3590
7.3563
7.3500
7.3442
7.3404
7.3344
7.3296
7.3242
7.3120
7.3060
7.2990
7.2949
7.2856
7.2767
5.1135
5.1103
5.0326
5.0154
4.9832
4.9648
4.8160
4.8055
4.7959
4.7881
4.6774
4.6638
4.6584
4.6516
4.6441
4.6188
4.6128
4.5540
4.5340
4.4919
4.4718
4.0087
3.9986
3.9926
3.9826
3.8902
3.8853
3.8751
3.8695
3.8625
3.8559
3.8515
3.8470
3.8404
3.7512
3.7470
3.7429
3.7071
3.7027
3.6982
3.6912
3.6862
3.6564
3.6406
3.6240
3.6167
3.6117
3.6071
3.6014
3.5931
3.5897
3.5745
3.5711
3.5188
3.5122
3.5083
3.5003
3.4940
3.4141
1.1310
1.1208
OBn
O
O
BnO
BnO
OMe
O
BnO
BnO
OBn
2.83
26.80
1.00
1.17
1.05
2.41
5.96
1.08
1.15
1.01
1.17
1.30
1.96
1.18
1.20
3.30
1.26
3.10
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

**29**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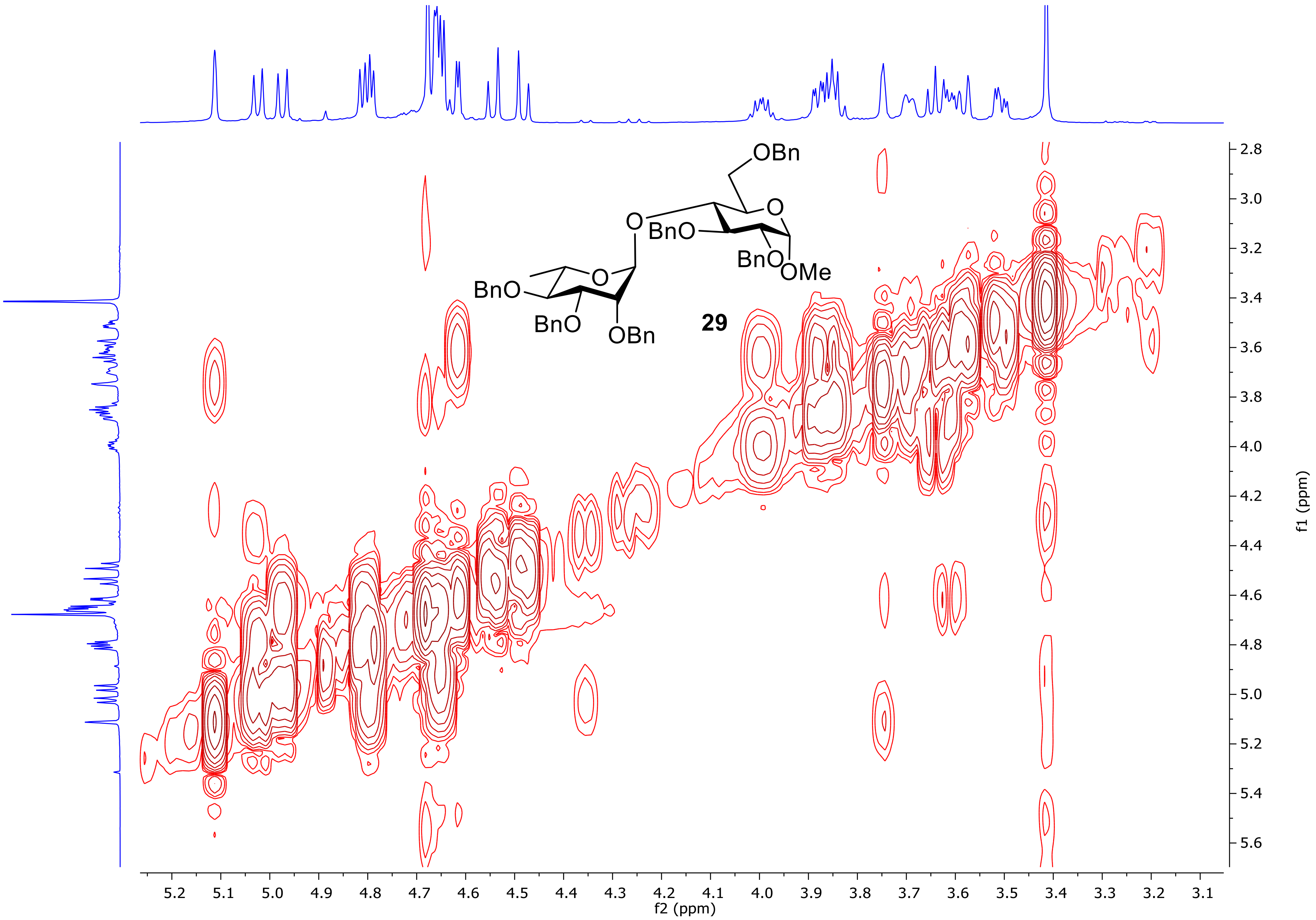
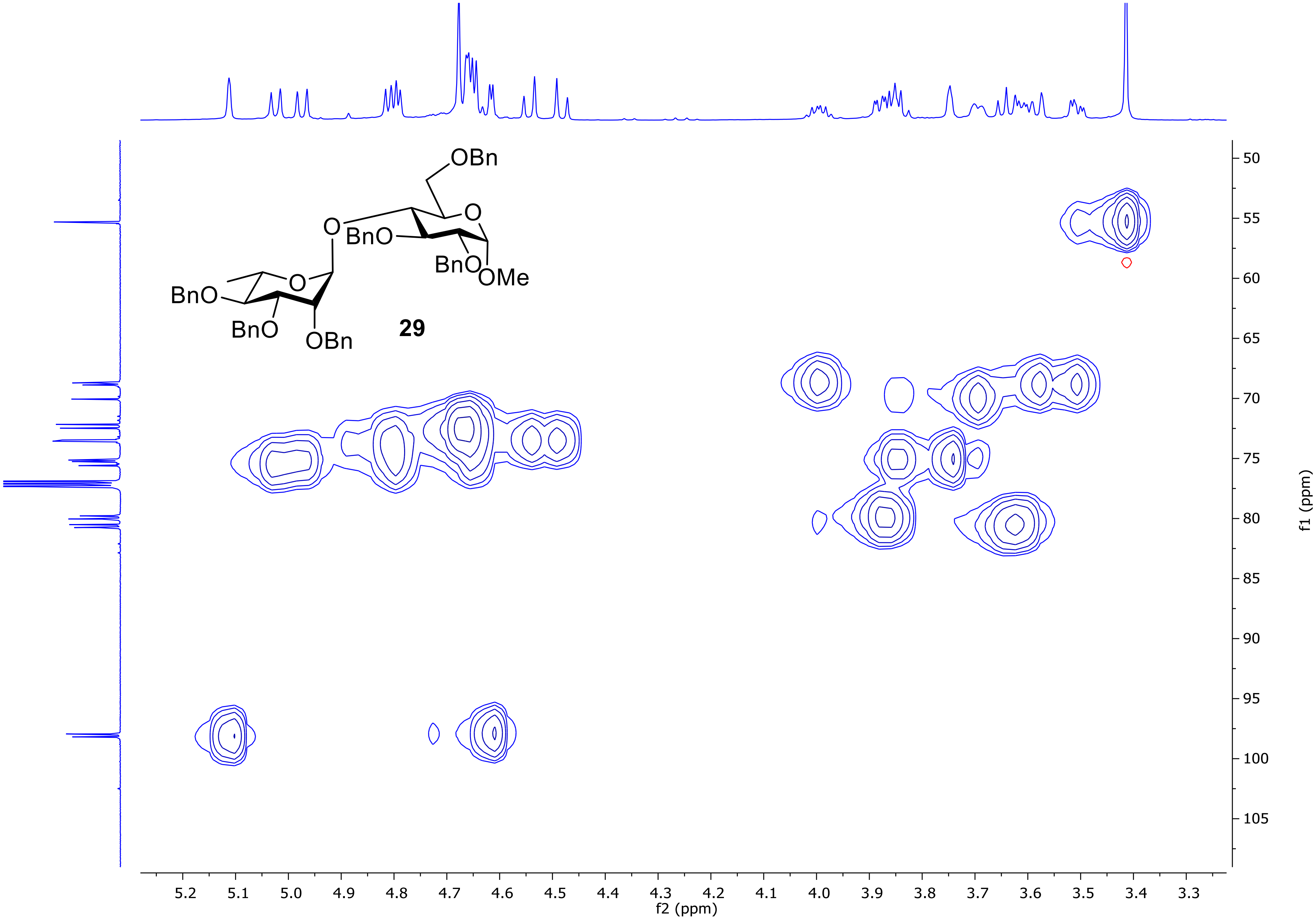
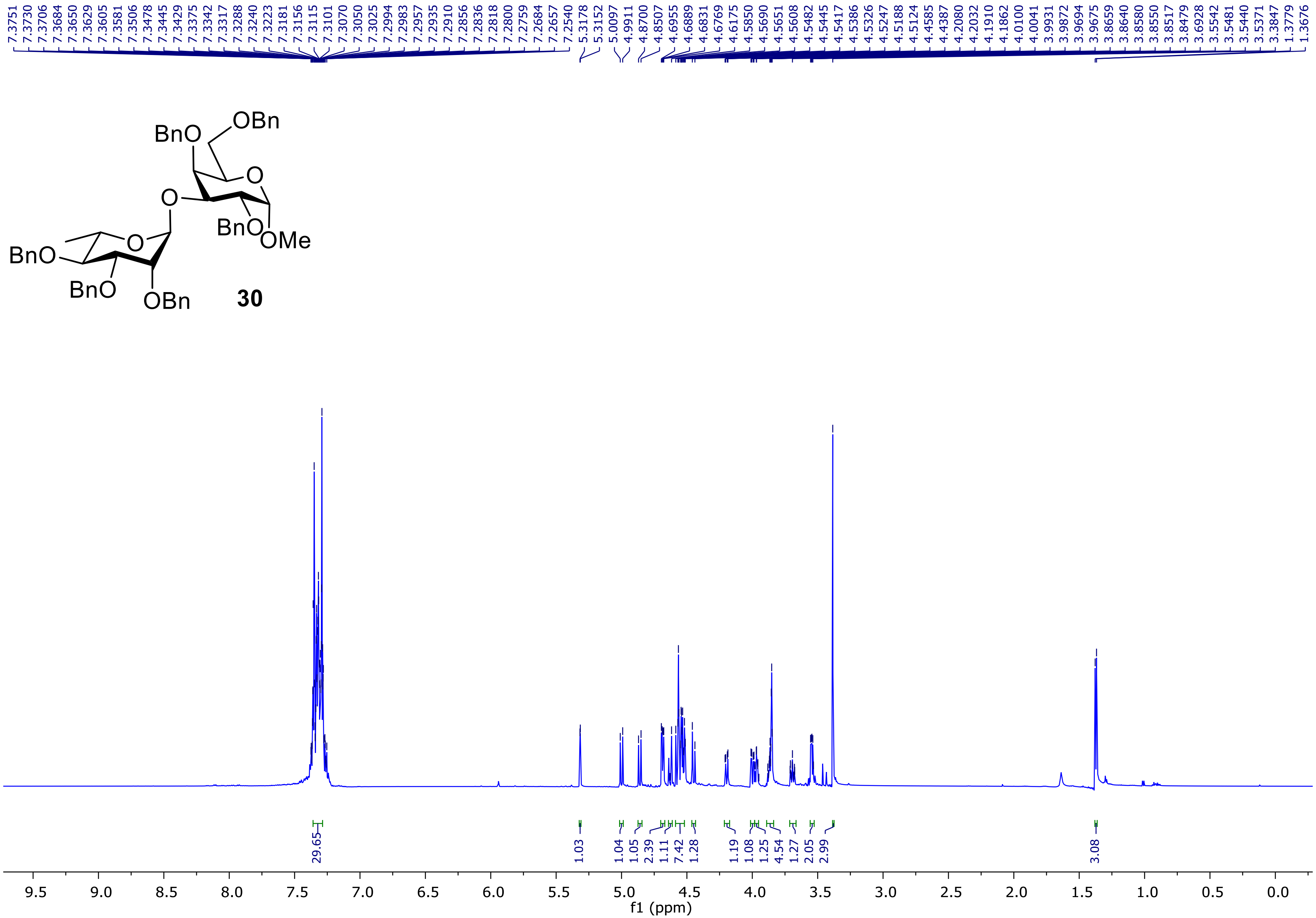
138.6655
138.6401
138.4250
138.0599
137.9704
137.9544
128.5241
128.4189
128.3886
128.3091
128.2690
128.2481
98.1845
97.9445
80.7528
80.5096
80.0465
79.7760
77.3377
77.1242
76.9129
75.5944
75.2566
75.1318
75.0795
73.5653
73.4600
72.4818
72.1646
70.0602
68.8834
68.7052
55.3103
17.9052
OBn
O
O
BnO
BnO
OMe
BnO
O
BnO
OBn
29
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBn
O
BnO
BnO
OMe
BnO
O
O
BnO
OBn
29
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f2 (ppm)
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
f1 (ppm)

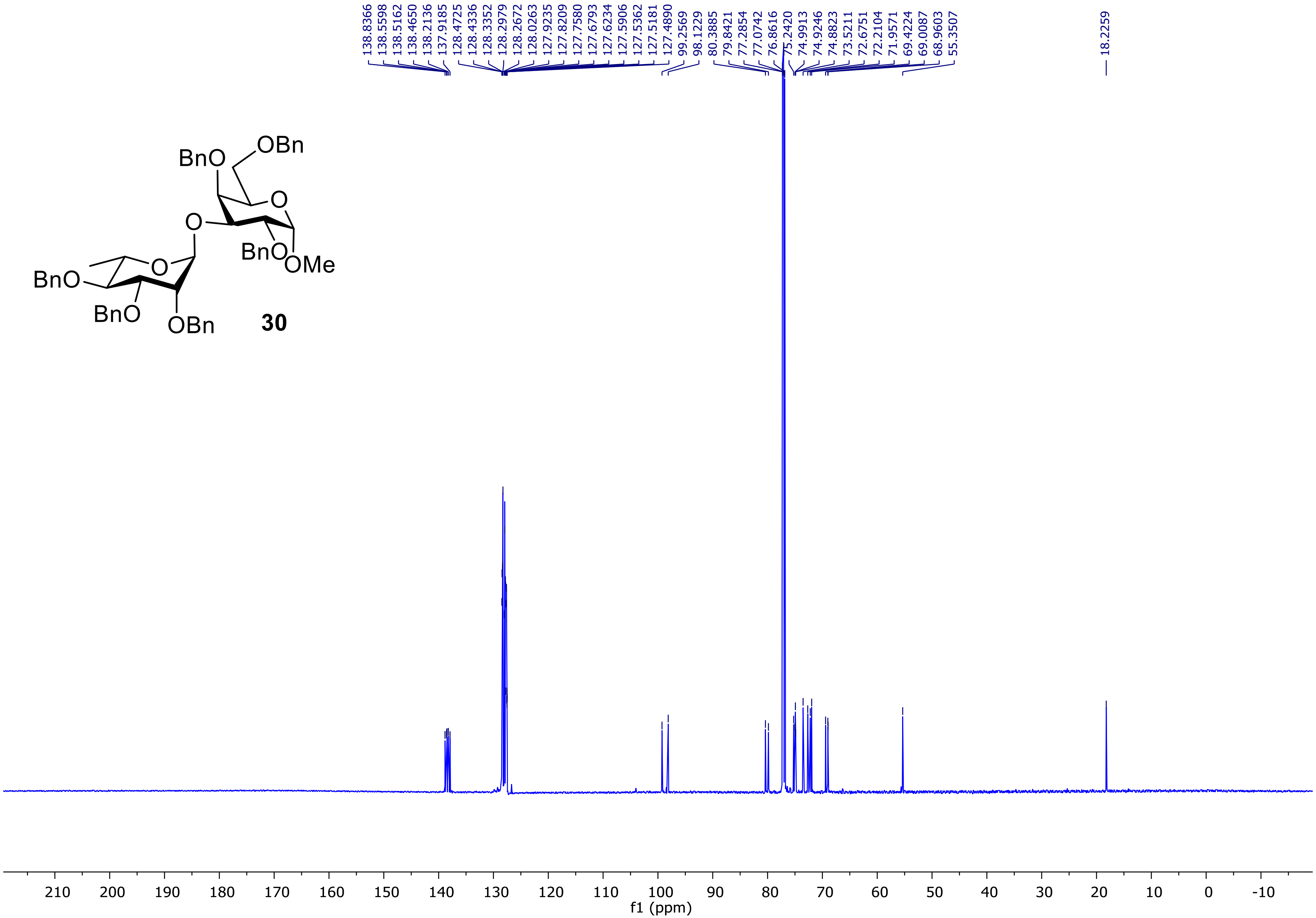


OBn
O
O
BnO
BnO
OMe
BnO
O
BnO
OBn
29
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
50
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)



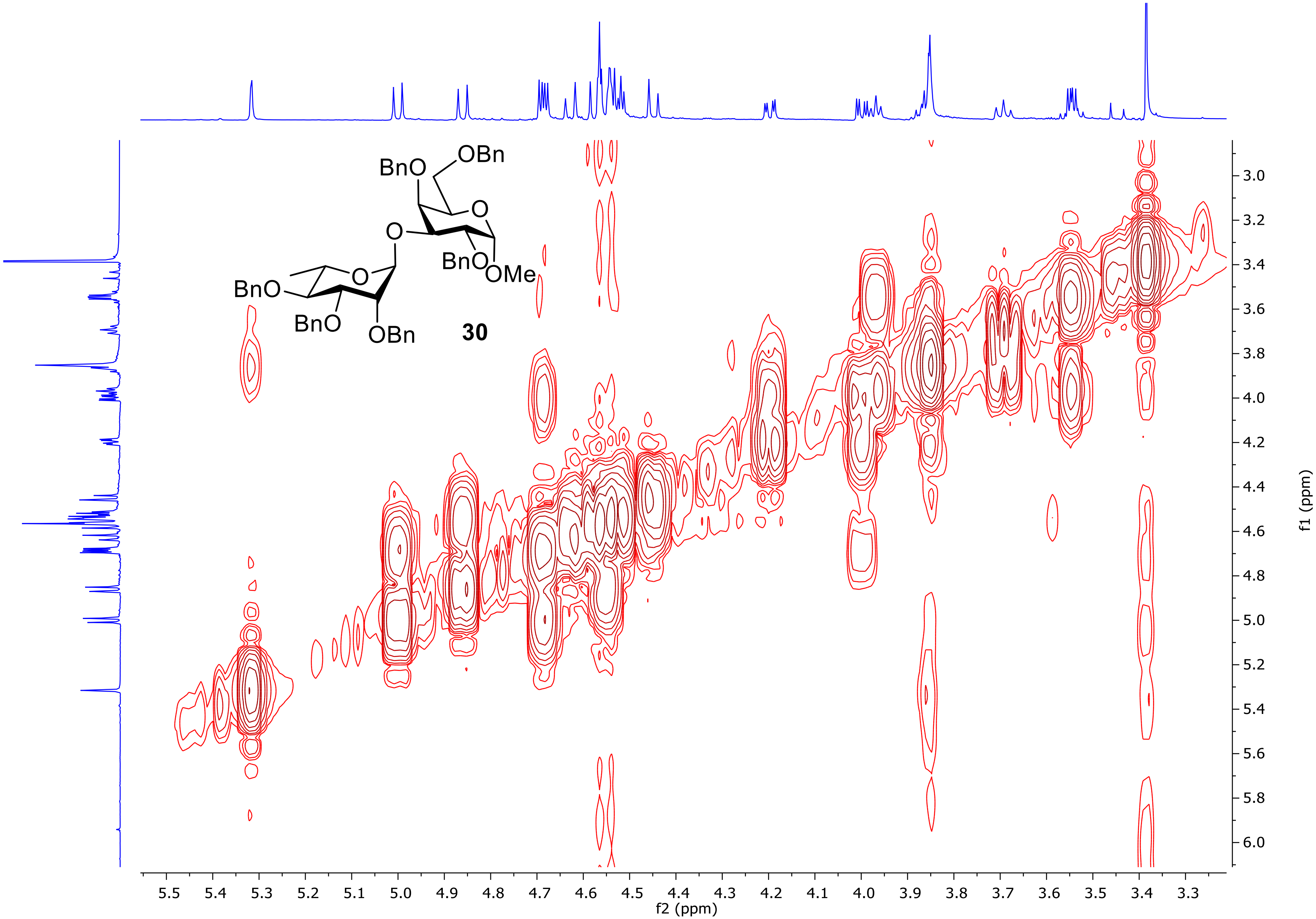
30

7.3751
7.3730
7.3706
7.3684
7.3650
7.3629
7.3605
7.3581
7.3506
7.3478
7.3445
7.3429
7.3375
7.3342
7.3317
7.3288
7.3240
7.3223
7.3181
7.3156
7.3115
7.3101
7.3070
7.3050
7.3025
7.2994
7.2983
7.2957
7.2935
7.2910
7.2856
7.2836
7.2818
7.2800
7.2759
7.2684
7.2657
7.2540
5.3178
5.3152
5.0097
4.9911
4.8700
4.8507
4.6955
4.6889
4.6831
4.6769
4.6175
4.5850
4.5690
4.5651
4.5608
4.5482
4.5445
4.5417
4.5386
4.5326
4.5247
4.5188
4.5124
4.4585
4.4387
4.2080
4.2032
4.1910
4.1862
4.0100
4.0041
3.9931
3.9872
3.9694
3.9675
3.8659
3.8640
3.8580
3.8550
3.8517
3.8479
3.6928
3.5542
3.5481
3.5440
3.5371
3.3847
1.3779
1.3676
OBn
BnO
O
O
BnO
OMe
O
BnO
BnO
OBn
29.65
1.03
1.04
1.05
2.39
1.11
7.42
1.28
1.19
1.08
1.25
4.54
1.27
2.05
2.99
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


138.8366
138.5598
138.5162
138.4650
138.2136
137.9185
128.4725
128.4336
128.3352
128.2979
128.2672
128.0263
127.9235
127.8209
127.7580
127.6793
127.6234
127.5906
127.5362
127.5181
127.4890
99.2569
98.1229
80.3885
79.8421
77.2854
77.0742
76.8616
75.2420
74.9913
74.9246
74.8823
73.5211
72.6751
72.2104
71.9571
69.4224
69.0087
68.9603
55.3507
18.2259
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

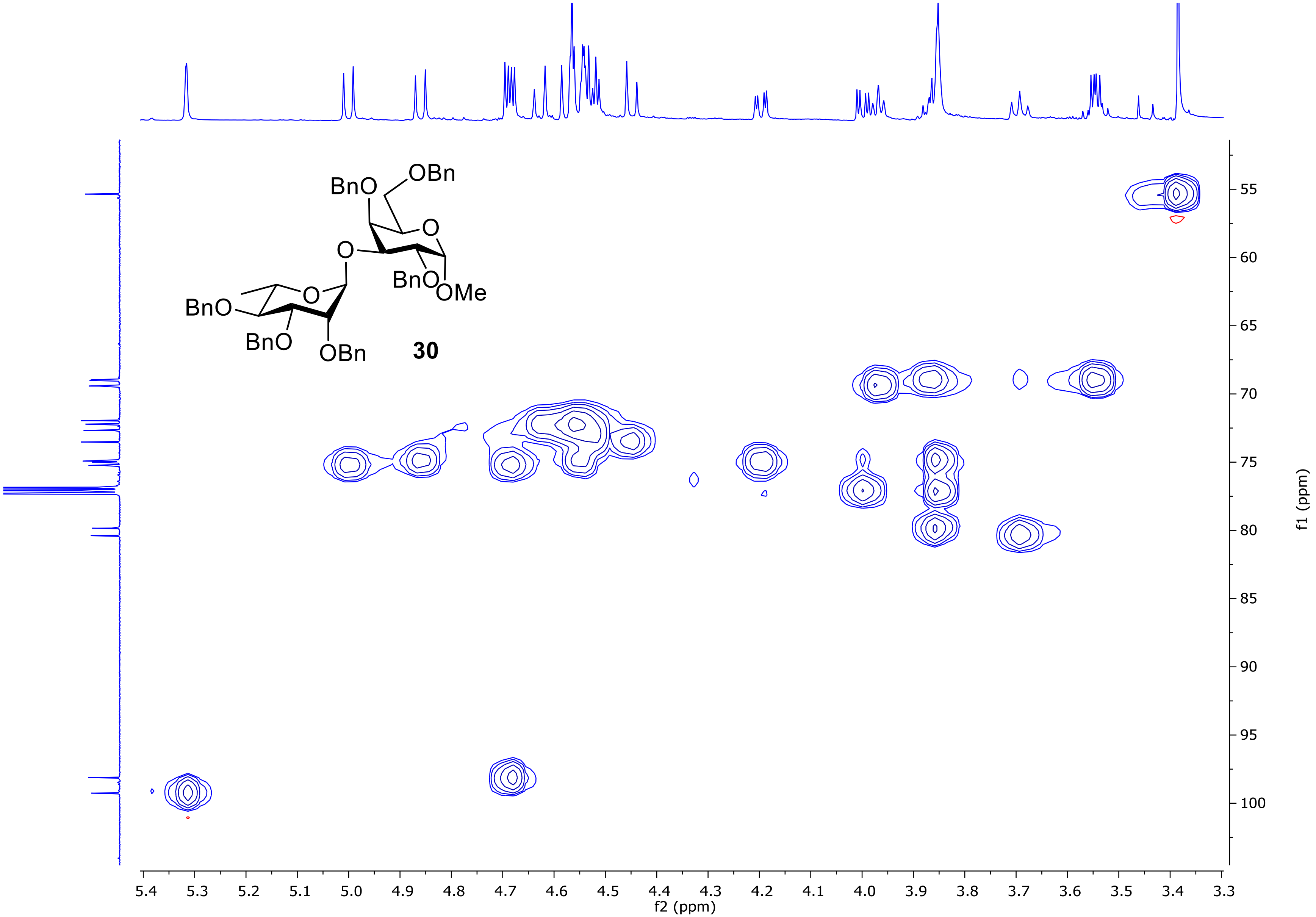
OBn
BnO
O
O
BnO
OMe
BnO
O
BnO
OBn

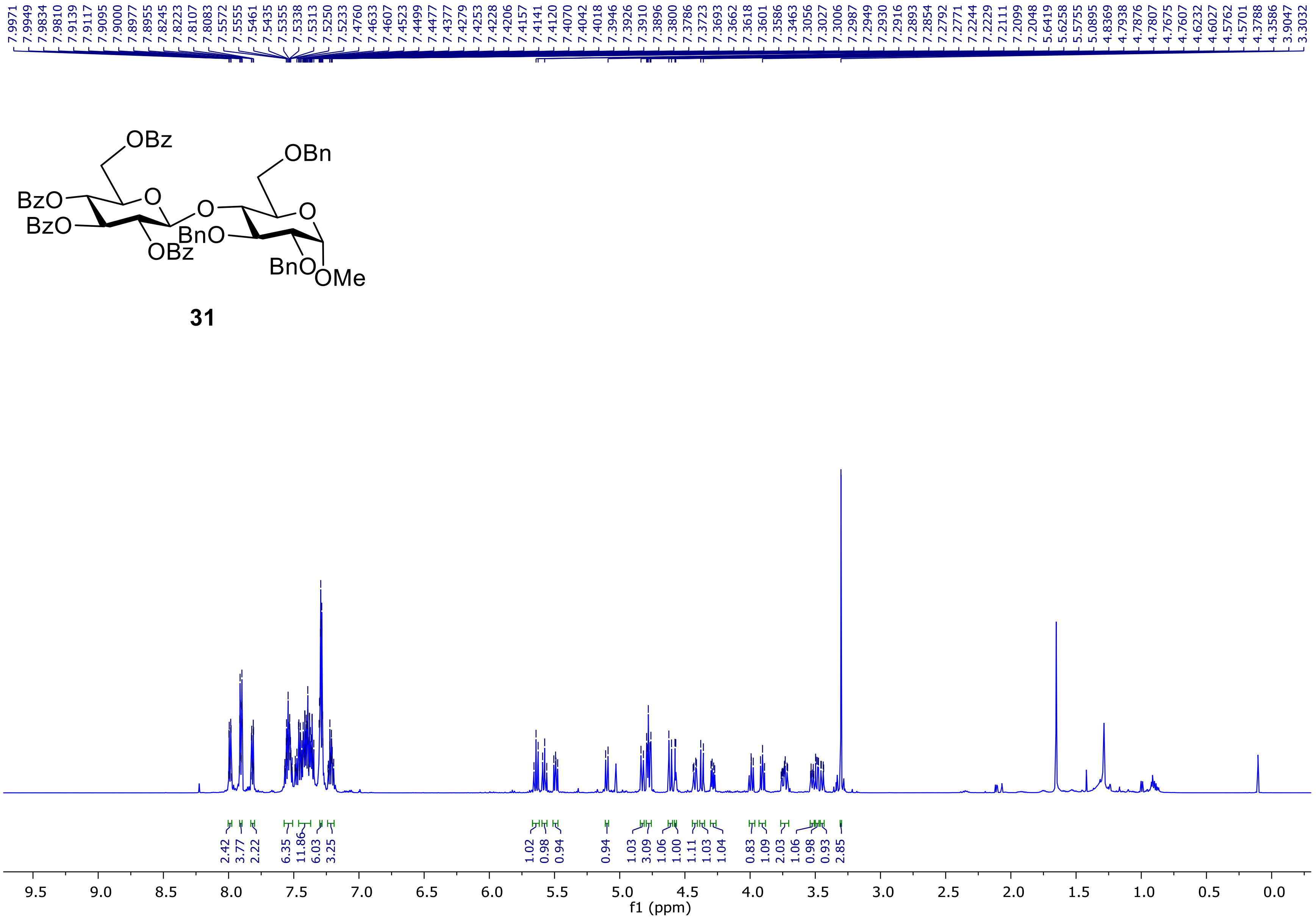
**30**

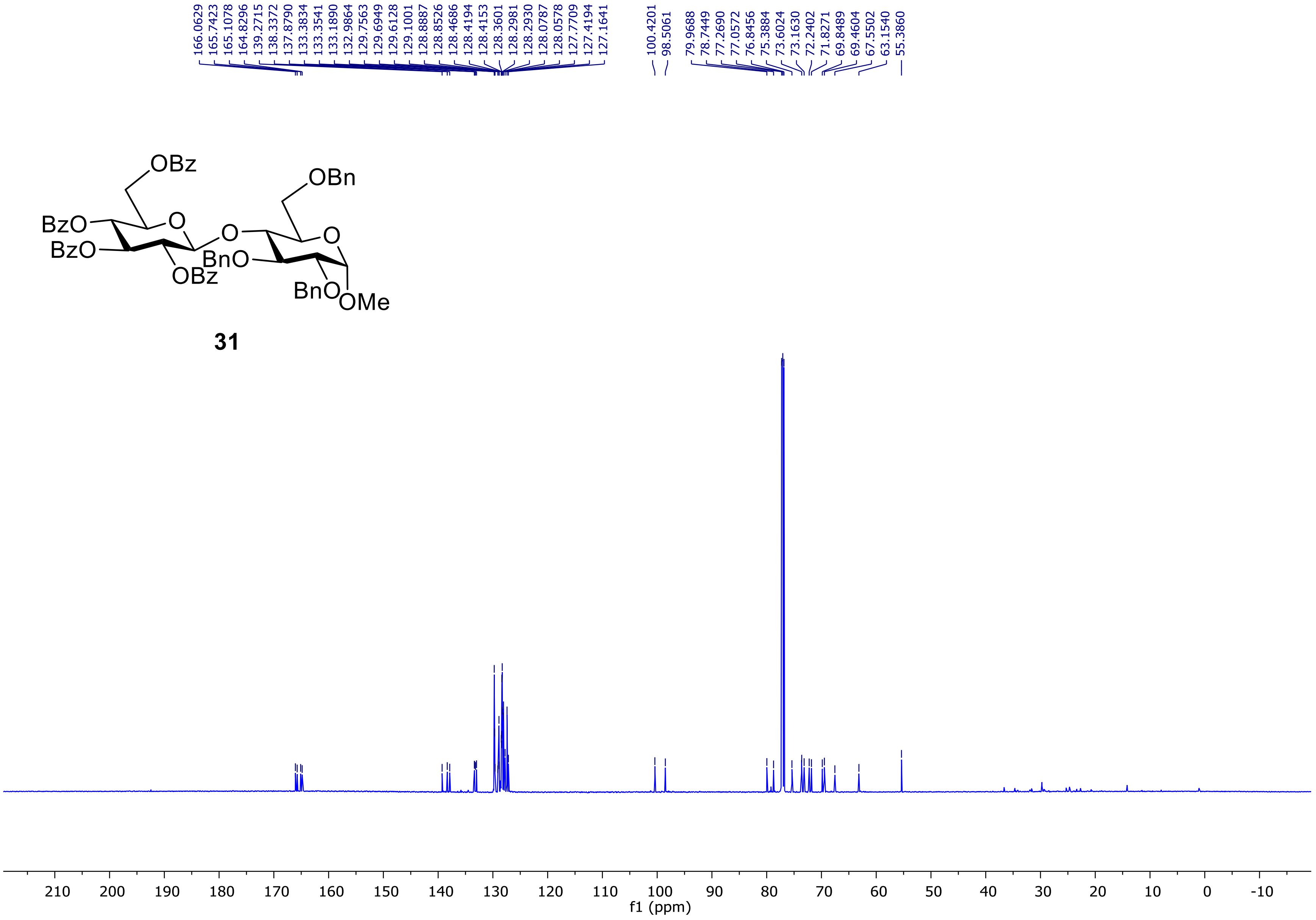


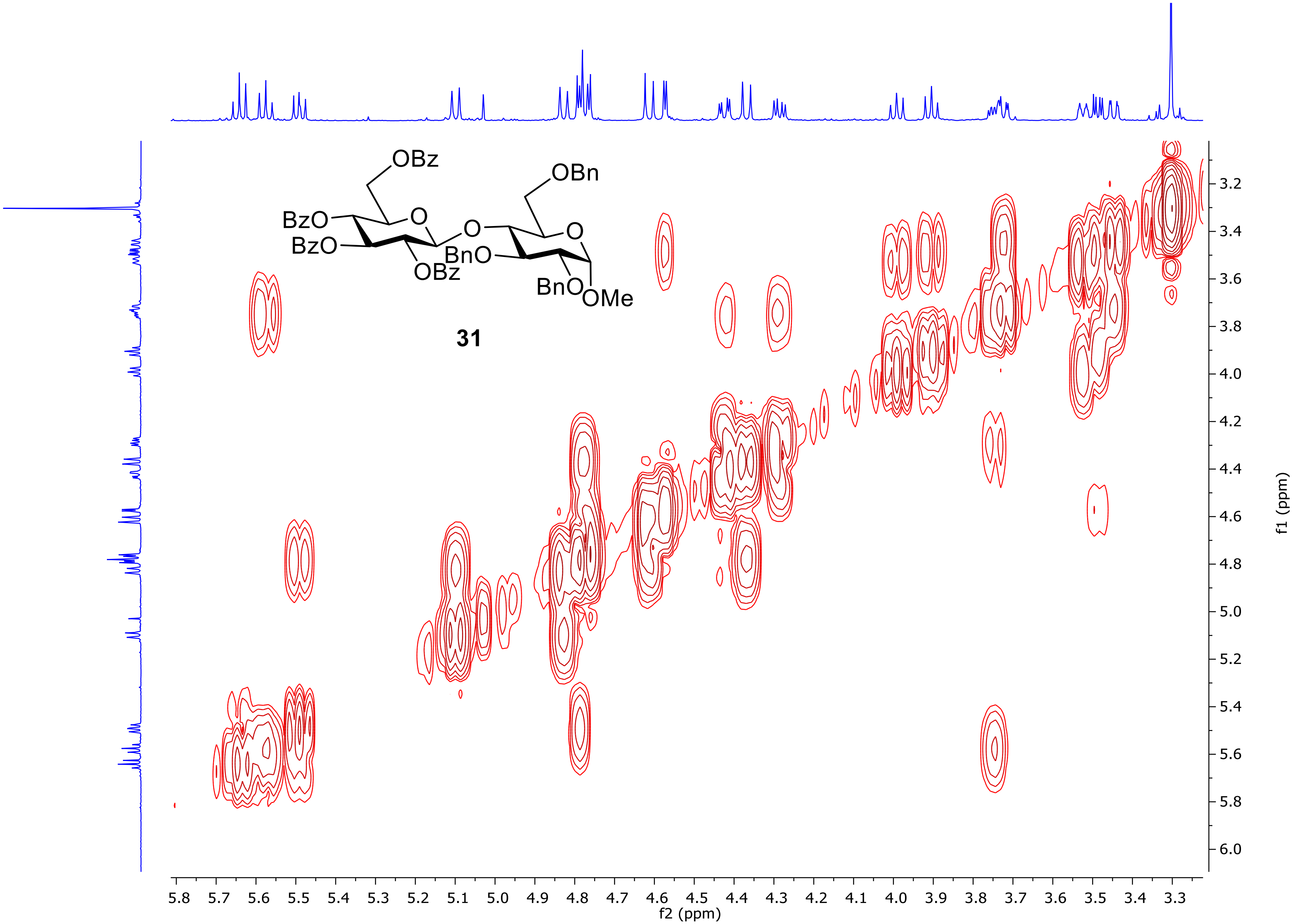
**30**

BnO
OBn
O
BnO
OMe
O
BnO
O
BnO
OBn
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
f1 (ppm)

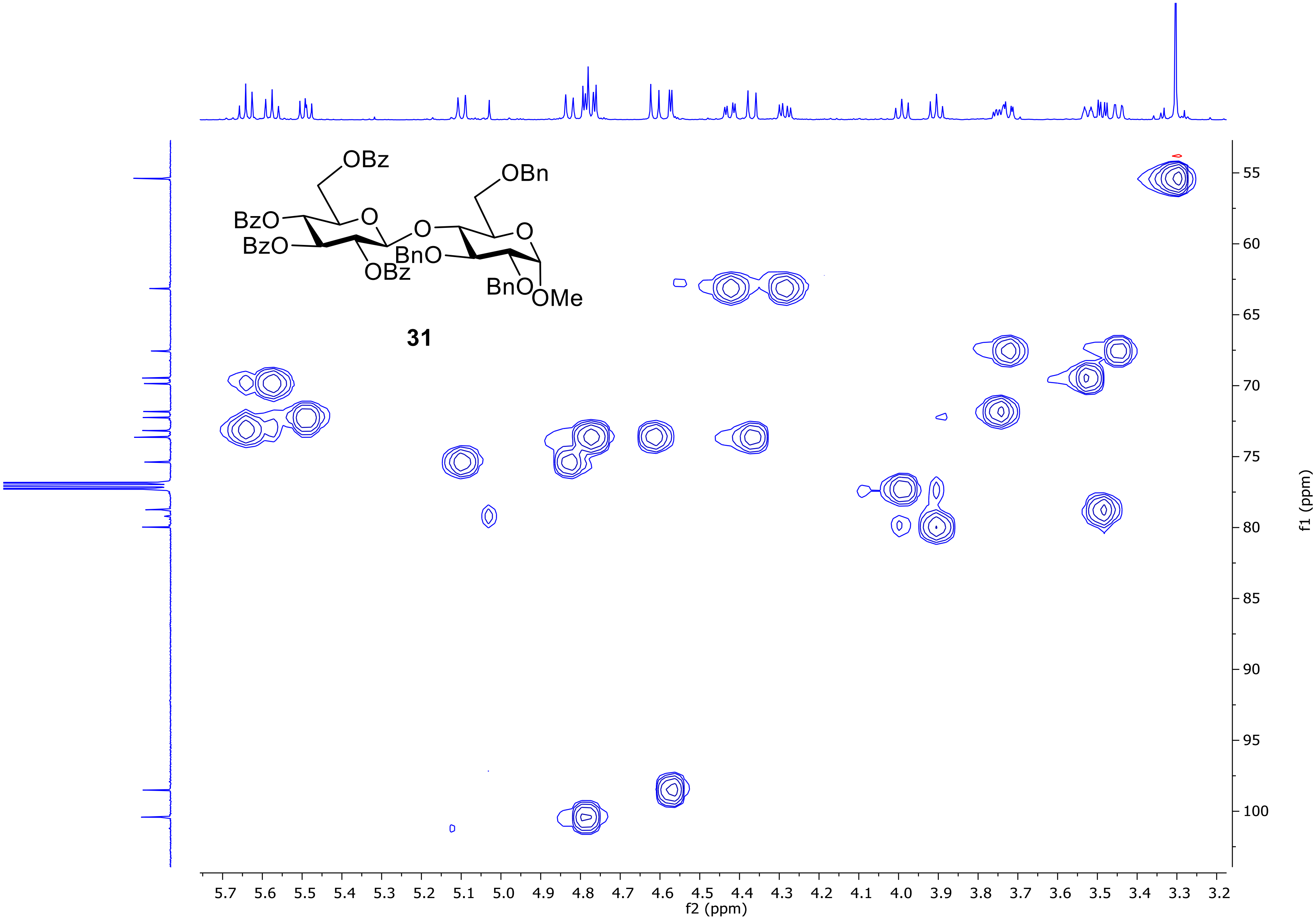

BnO
OBn
O
O
BnO
OMe
BnO
O
BnO
OBn
30
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)


7.9971
7.9949
7.9834
7.9810
7.9139
7.9117
7.9095
7.9000
7.8977
7.8955
7.8245
7.8223
7.8107
7.8083
7.5572
7.5555
7.5461
7.5435
7.5355
7.5338
7.5313
7.5250
7.5233
7.4760
7.4633
7.4607
7.4523
7.4499
7.4477
7.4377
7.4279
7.4253
7.4228
7.4206
7.4157
7.4141
7.4120
7.4070
7.4042
7.4018
7.3946
7.3926
7.3910
7.3896
7.3800
7.3786
7.3723
7.3693
7.3662
7.3618
7.3601
7.3586
7.3463
7.3056
7.3027
7.3006
7.2987
7.2949
7.2930
7.2916
7.2893
7.2854
7.2792
7.2771
7.2244
7.2229
7.2111
7.2099
7.2048
5.6419
5.6258
5.5755
5.0895
4.8369
4.7938
4.7876
4.7807
4.7675
4.7607
4.6232
4.6027
4.5762
4.5701
4.3788
4.3586
3.9047
3.3032
OBz
OBn
BzO
O
O
O
BzO
BnO
OBz
BnO
OMe
31
2.42
3.77
2.22
6.35
11.86
6.03
3.25
1.02
0.98
0.94
0.94
1.03
3.09
1.06
1.00
1.11
1.03
1.04
0.83
1.09
2.03
1.06
0.98
0.93
2.85
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

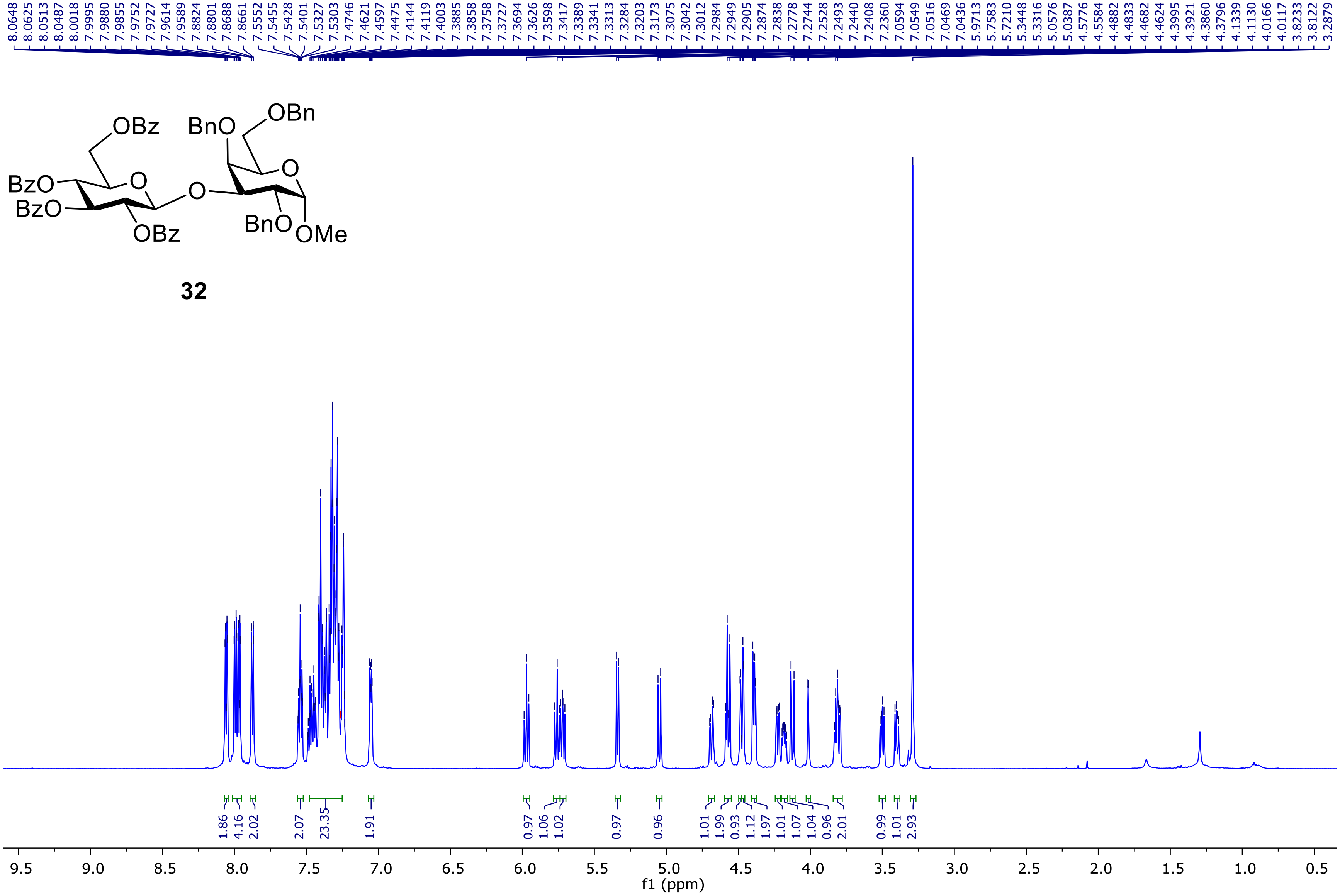

166.0629
165.7423
165.1078
164.8296
139.2715
138.3372
137.8790
133.3834
133.3541
133.1890
132.9864
129.7563
129.6949
129.6128
129.1001
128.8887
128.8526
128.4686
128.4194
128.4153
128.3601
128.2981
128.2930
128.0787
128.0578
127.7709
127.4194
127.1641
100.4201
98.5061
79.9688
78.7449
77.2690
77.0572
76.8456
75.3884
73.6024
73.1630
72.2402
71.8271
69.8489
69.4604
67.5502
63.1540
55.3860
OBz
BzO
O
BzO
OBz
O
OBn
BnO
O
BnO
OMe
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OBz
BzO
BzO
O
O
OBz
OBn
BnO
O
BnO
OMe
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
f1 (ppm)

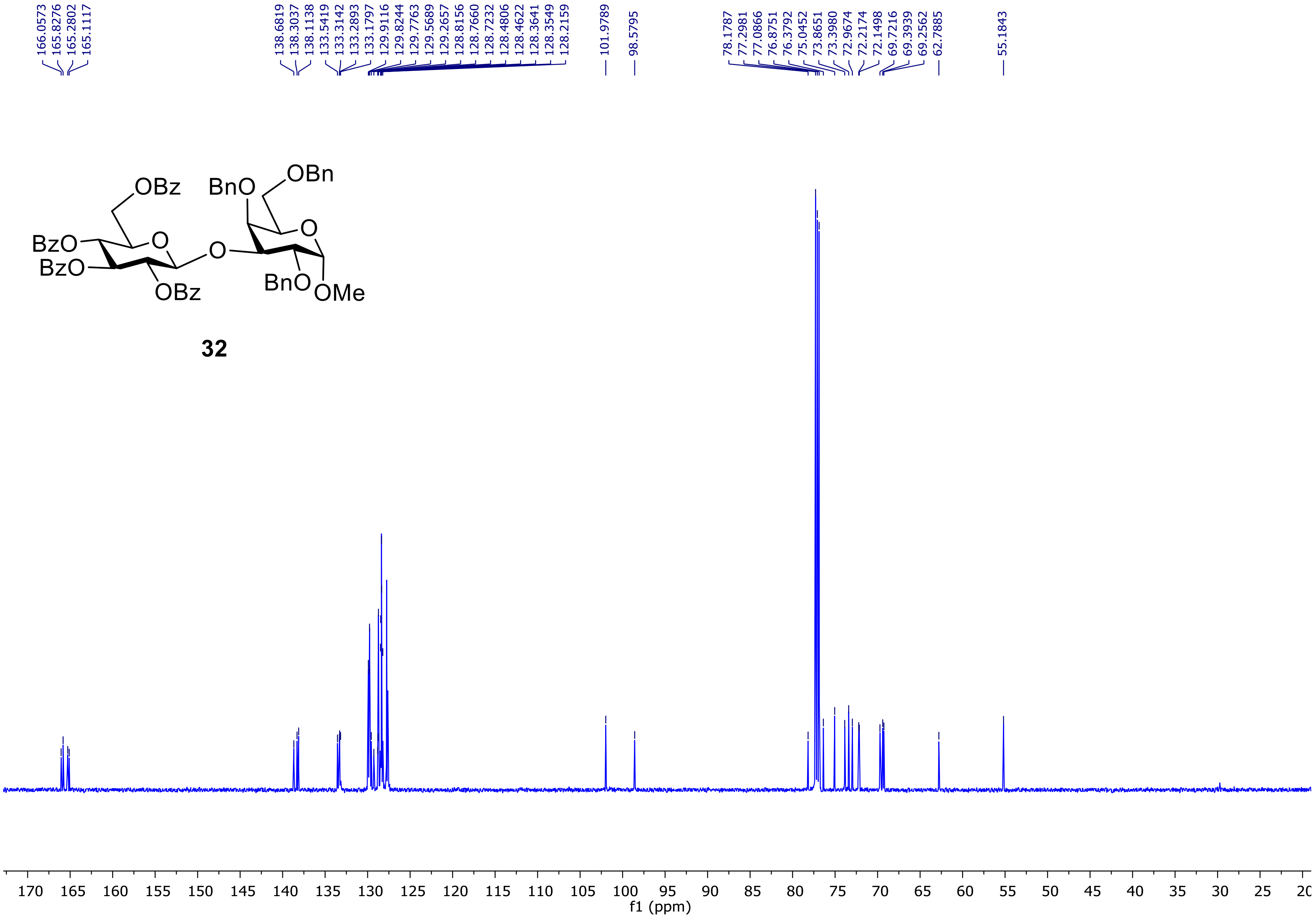
**31**

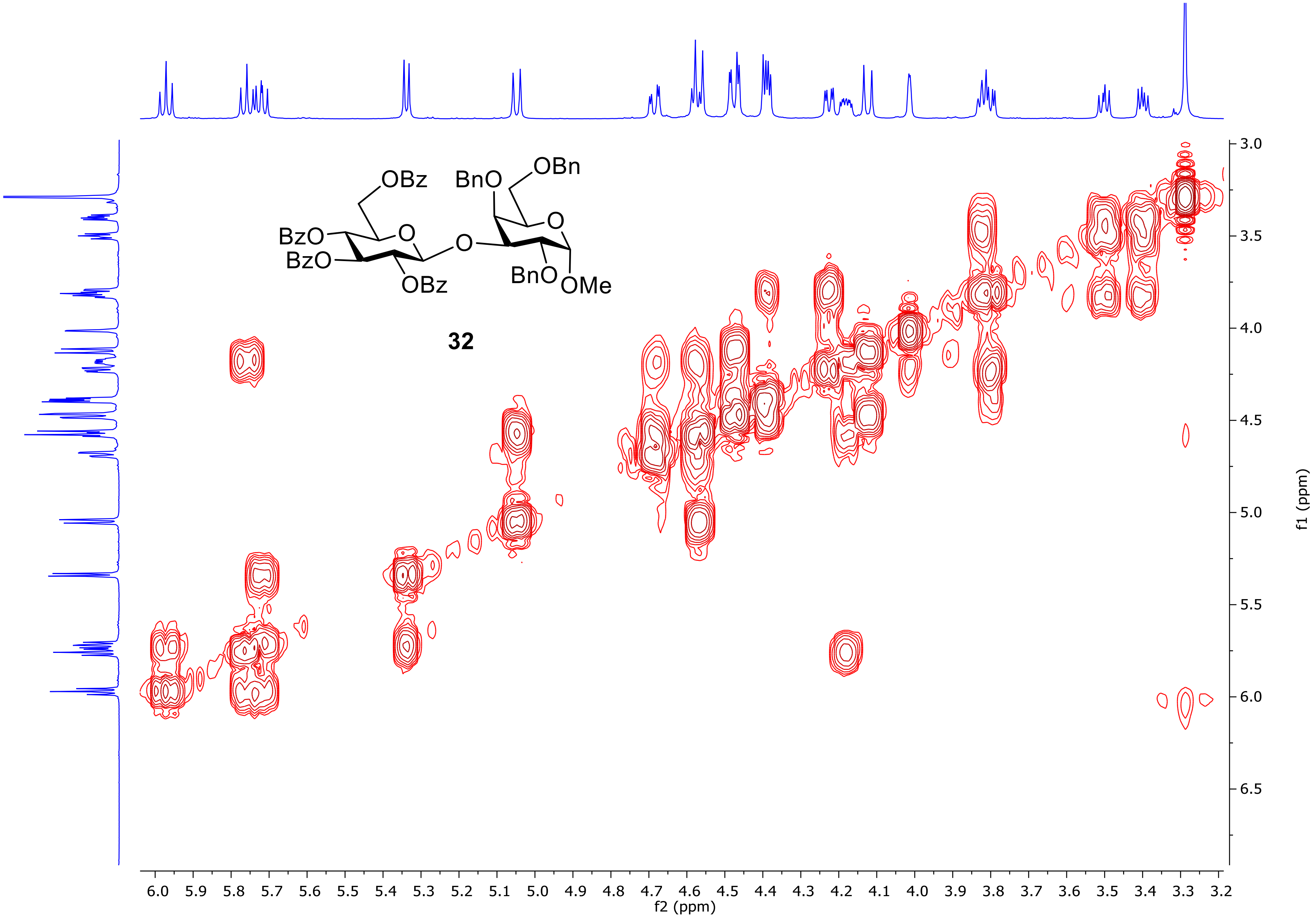

OBz
BzO
BzO
O
OBz
O
OBn
BnO
O
BnO
OMe
f1 (ppm)
55
60
65
70
75
80
85
90
95
100
f2 (ppm)
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2

**31**

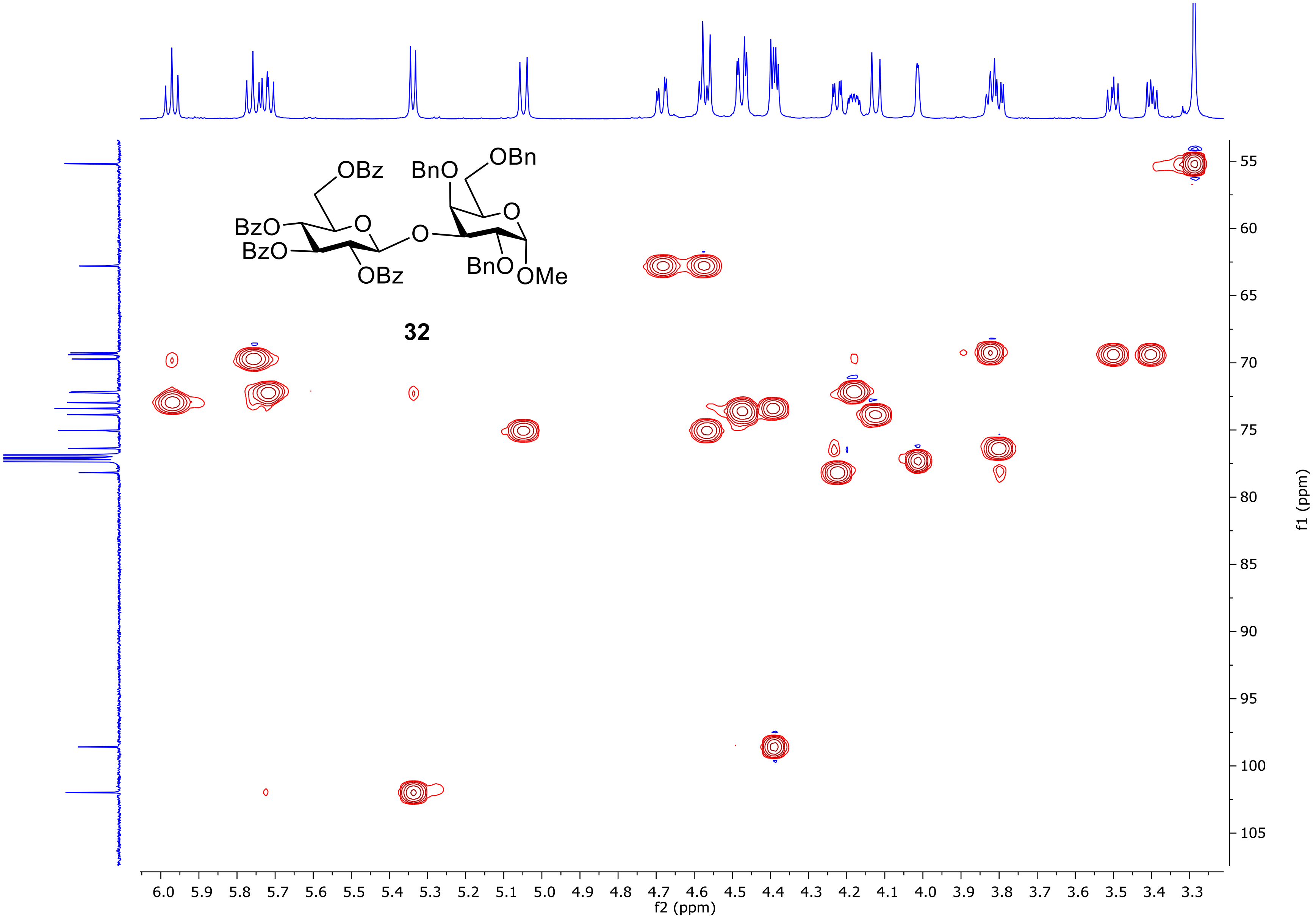

8.0648
8.0625
8.0513
8.0487
8.0018
7.9995
7.9880
7.9855
7.9752
7.9727
7.9614
7.9589
7.8824
7.8801
7.8688
7.8661
7.5552
7.5455
7.5428
7.5401
7.5327
7.5303
7.4746
7.4621
7.4597
7.4475
7.4144
7.4119
7.4003
7.3885
7.3858
7.3758
7.3727
7.3694
7.3626
7.3598
7.3417
7.3389
7.3341
7.3313
7.3284
7.3203
7.3173
7.3075
7.3042
7.3012
7.2984
7.2949
7.2905
7.2874
7.2838
7.2778
7.2744
7.2528
7.2493
7.2440
7.2408
7.2360
7.0594
7.0549
7.0516
7.0469
7.0436
5.9713
5.7583
5.7210
5.3448
5.3316
5.0576
5.0387
4.5776
4.5584
4.4882
4.4833
4.4682
4.4624
4.3995
4.3921
4.3860
4.3796
4.1339
4.1130
4.0166
4.0117
3.8233
3.8122
3.2879
OBz
BnO
OBn
BzO
O
O
O
BzO
OBz
BnO
OMe
1.86
4.16
2.02
2.07
23.35
1.91
0.97
1.06
1.02
0.97
0.96
1.01
1.99
0.93
1.12
1.97
1.01
1.07
1.04
0.96
2.01
0.99
1.01
2.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

**32**

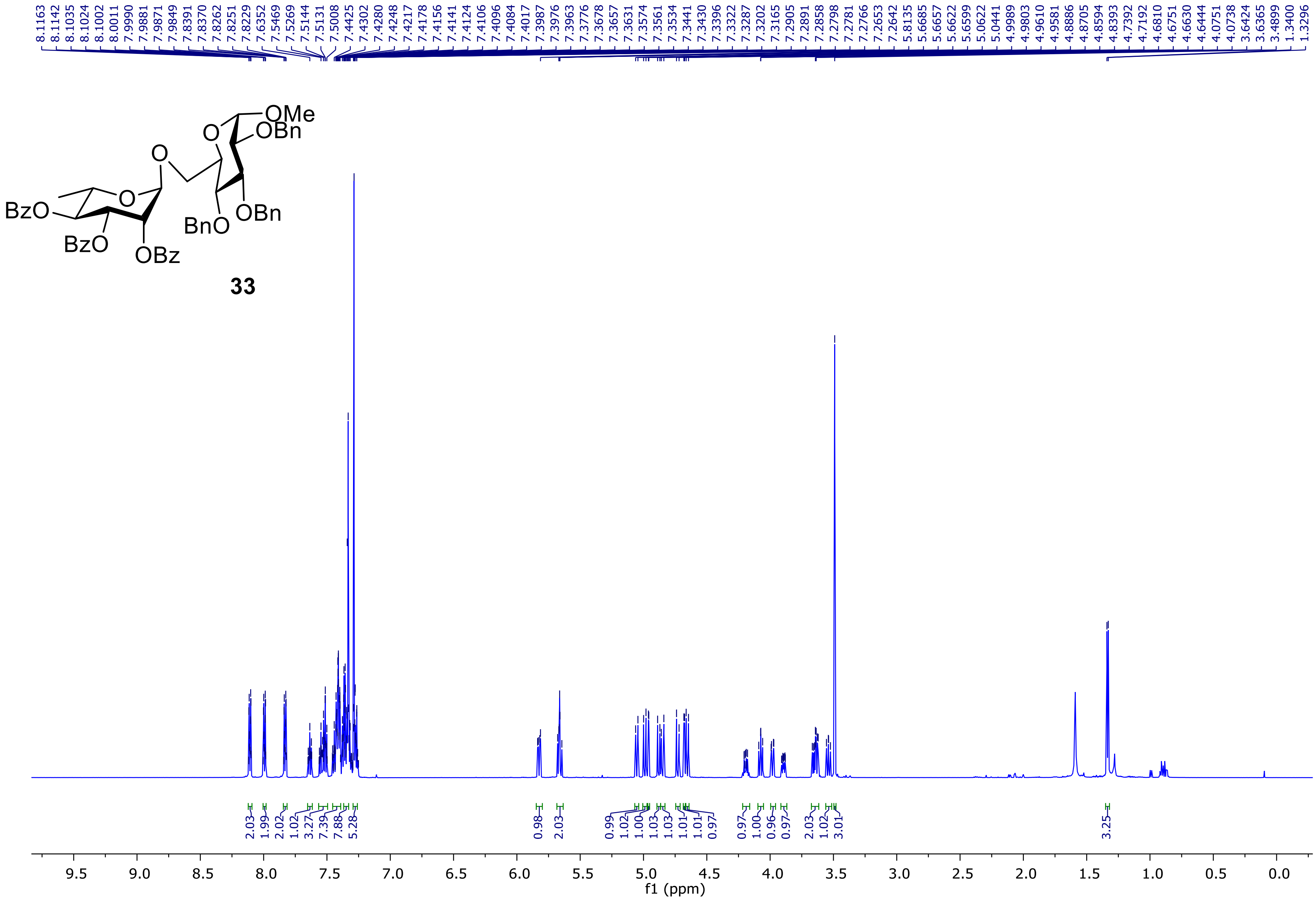

166.0573
165.8276
165.2802
165.1117
138.6819
138.3037
138.1138
133.5419
133.3142
133.2893
133.1797
129.9116
129.8244
129.7763
129.5689
129.2657
128.8156
128.7660
128.7232
128.4806
128.4622
128.3641
128.3549
128.2159
101.9789
98.5795
78.1787
77.2981
77.0866
76.8751
76.3792
75.0452
73.8651
73.3980
72.9674
72.2174
72.1498
69.7216
69.3939
69.2562
62.7885
55.1843
OBz
BzO
BzO
O
O
OBz
BnO
OBn
O
BnO
OMe
32
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
f1 (ppm)


OBz
BzO
BzO
O
OBz
O
BnO
OBn
O
BnO
OMe
f2 (ppm)
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f1 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5

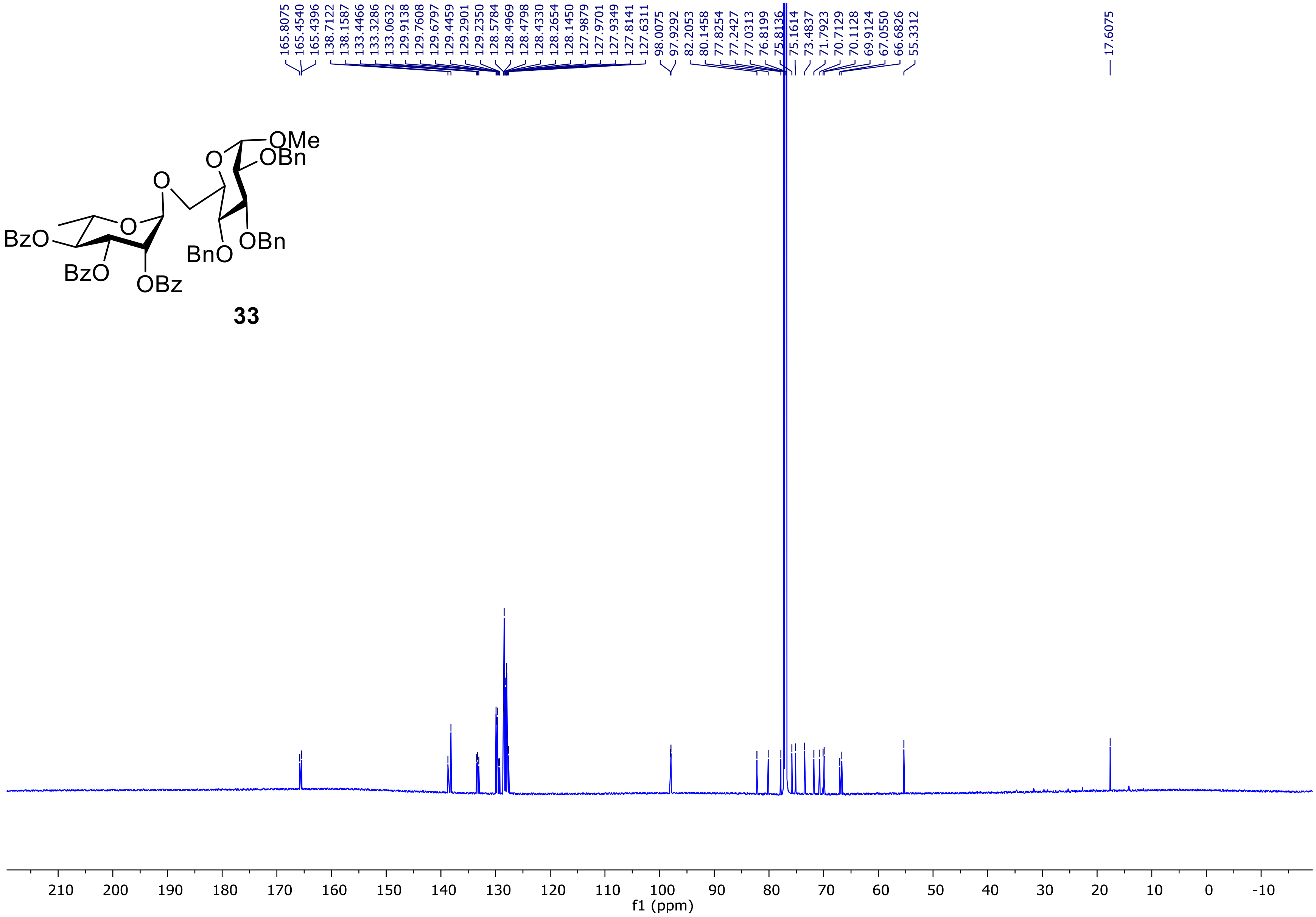
**32**


OBz
BnO
OBn
BzO
BzO
O
O
O
OBz
BnO
OMe
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)

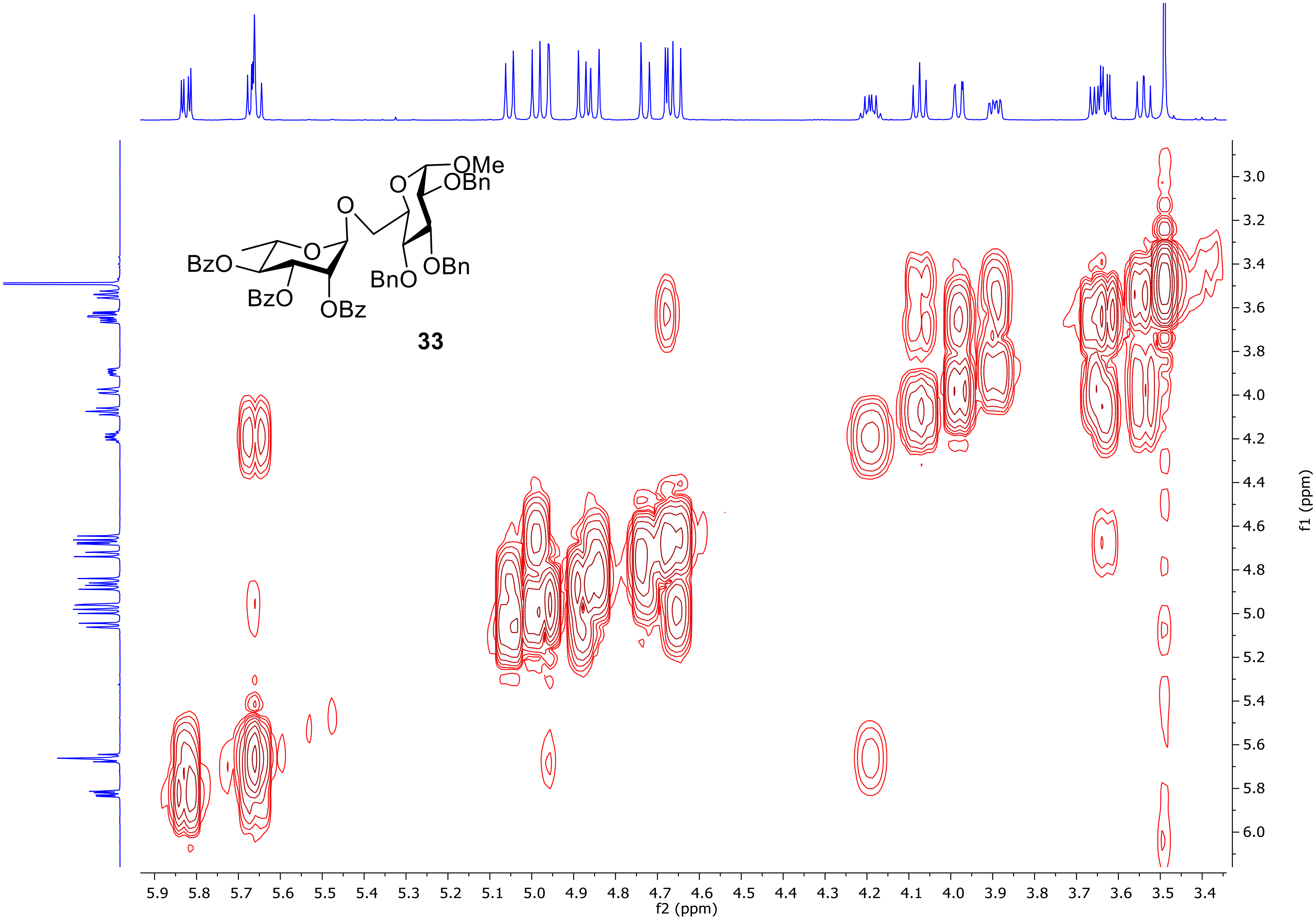
**32**


8.1163
8.1142
8.1035
8.1024
8.1002
8.0011
7.9990
7.9881
7.9871
7.9849
7.8391
7.8370
7.8262
7.8251
7.8229
7.6352
7.5469
7.5269
7.5144
7.5131
7.5008
7.4425
7.4302
7.4280
7.4248
7.4217
7.4178
7.4156
7.4141
7.4124
7.4106
7.4096
7.4084
7.4017
7.3987
7.3976
7.3963
7.3776
7.3678
7.3657
7.3631
7.3574
7.3561
7.3534
7.3441
7.3430
7.3396
7.3322
7.3287
7.3202
7.3165
7.2905
7.2891
7.2858
7.2798
7.2781
7.2766
7.2653
7.2642
5.8135
5.6685
5.6657
5.6622
5.6599
5.0622
5.0441
4.9989
4.9803
4.9610
4.9581
4.8886
4.8705
4.8594
4.8393
4.7392
4.7192
4.6810
4.6751
4.6630
4.6444
4.0751
4.0738
3.6424
3.6365
3.4899
1.3400
1.3296
OMe
OBn
O
O
O
BzO
BzO
OBz
BnO
OBn
2.03
1.99
2.02
1.02
3.27
7.39
7.88
5.28
0.98
2.03
0.99
1.02
1.00
1.03
1.03
1.01
1.01
0.97
0.97
1.00
0.96
0.97
2.03
1.02
3.01
3.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

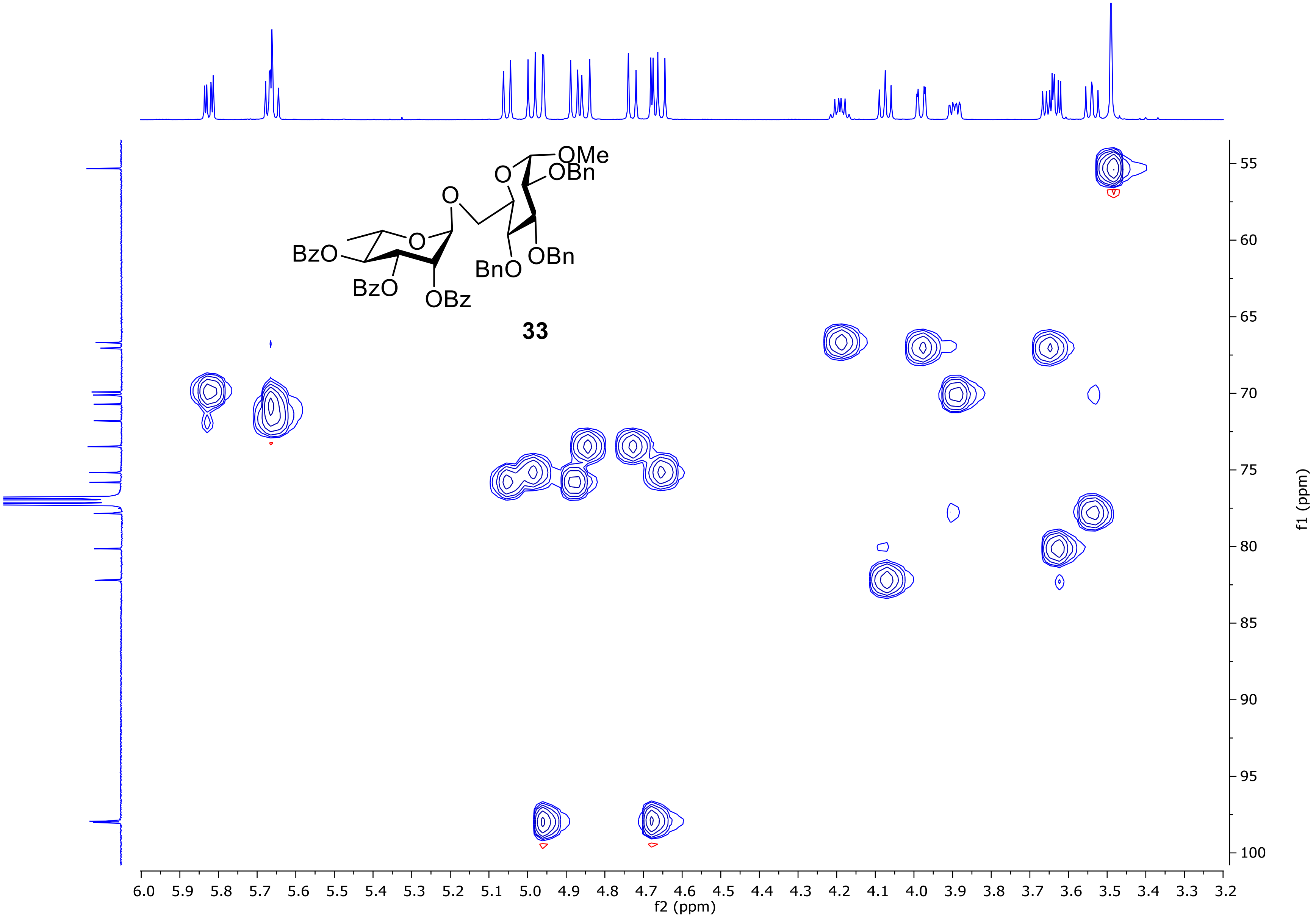
**33**


165.8075
165.4540
165.4396
138.7122
138.1587
133.4466
133.3286
133.0632
129.9138
129.7608
129.6797
129.4459
129.2901
129.2350
128.5784
128.4969
128.4798
128.4330
128.2654
128.1450
127.9879
127.9701
127.9349
127.8141
127.6311
98.0075
97.9292
82.2053
80.1458
77.8254
77.2427
77.0313
76.8199
75.8136
75.1614
73.4837
71.7923
70.7129
70.1128
69.9124
67.0550
66.6826
55.3312
17.6075
OMe
O
OBn
O
BzO
BzO
OBz
BnO
OBn
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**33**

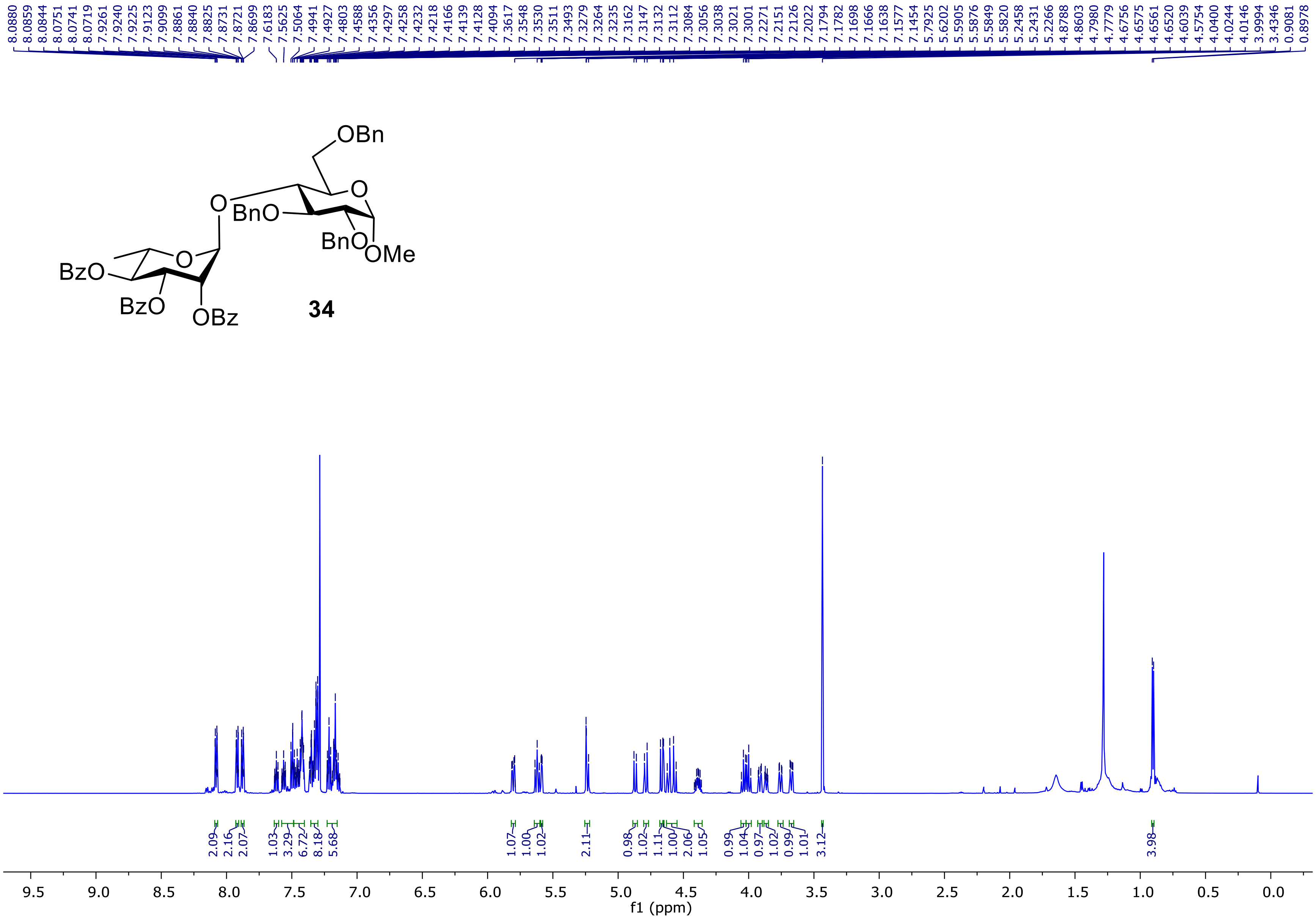

OMe
OBn
O
O
BzO
O
BnO
OBn
BzO
OBz
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
f1 (ppm)

**33**

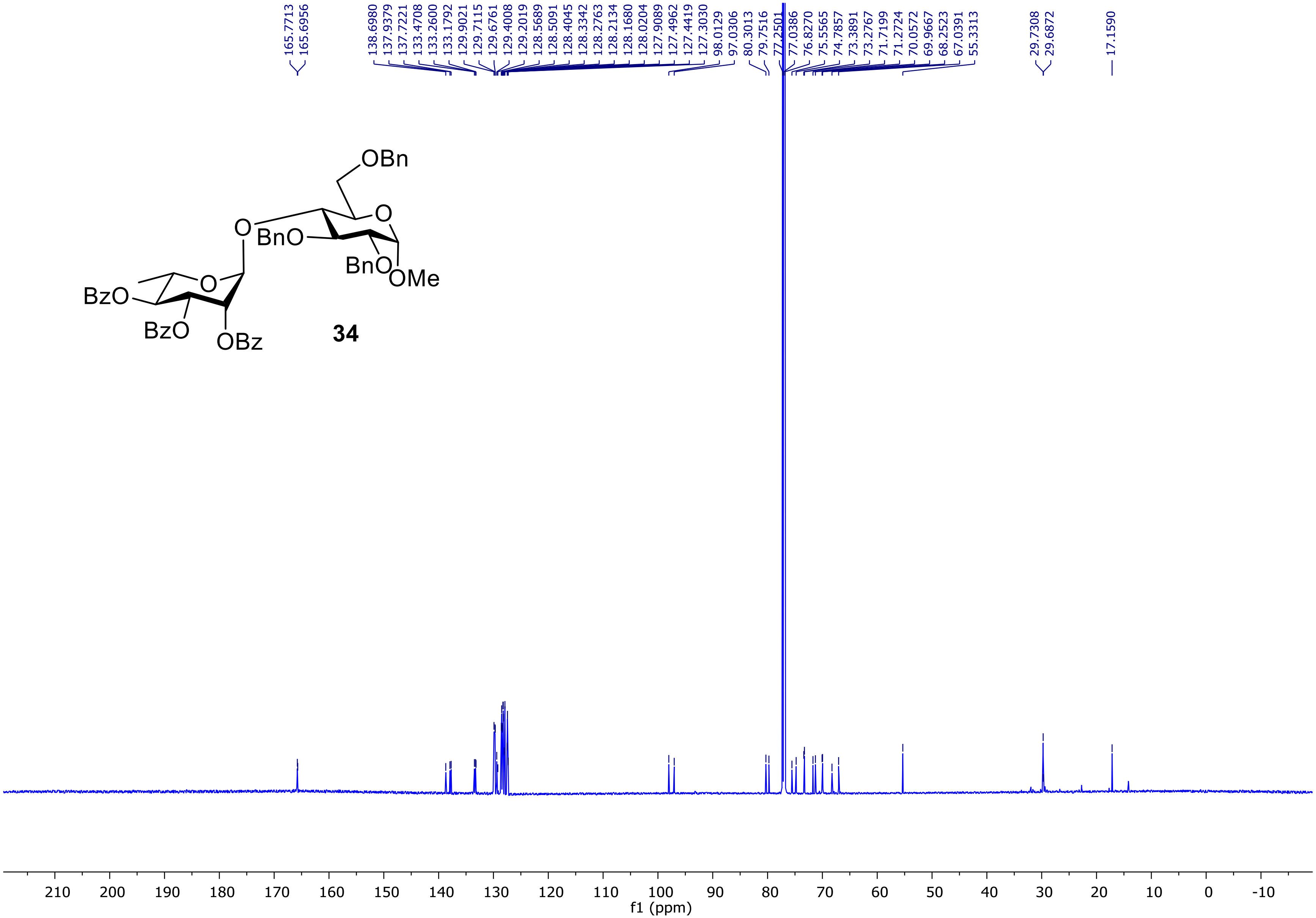


33

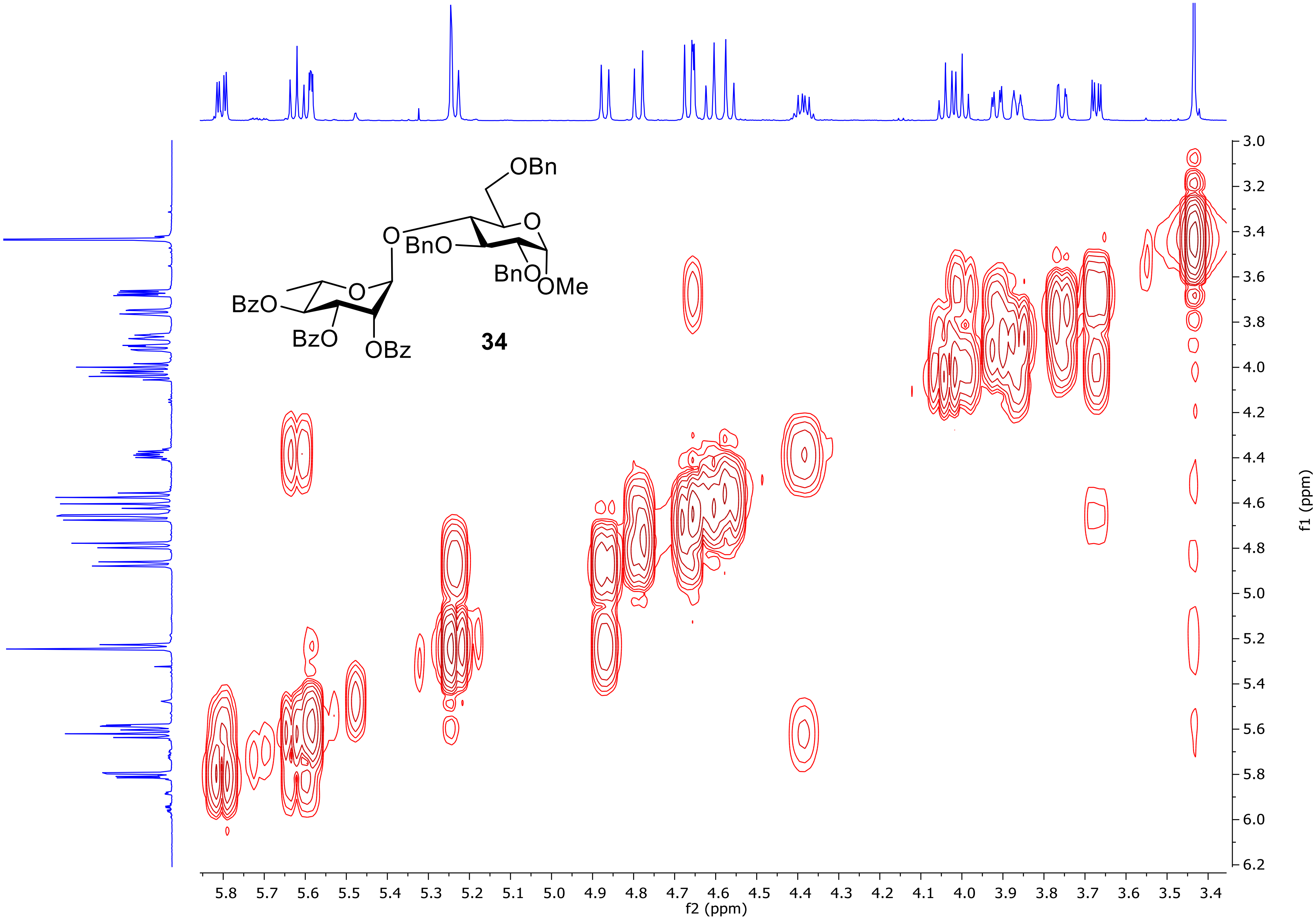
OMe
OBn
O
O
BzO
BzO
OBz
BnO
OBn
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)


8.0880
8.0859
8.0844
8.0751
8.0741
8.0719
7.9261
7.9240
7.9225
7.9123
7.9099
7.8861
7.8840
7.8825
7.8731
7.8721
7.8699
7.6183
7.5625
7.5064
7.4941
7.4927
7.4803
7.4588
7.4356
7.4297
7.4258
7.4232
7.4218
7.4166
7.4139
7.4128
7.4094
7.3617
7.3548
7.3530
7.3511
7.3493
7.3279
7.3264
7.3235
7.3162
7.3147
7.3132
7.3112
7.3084
7.3056
7.3038
7.3021
7.3001
7.2271
7.2151
7.2126
7.2022
7.1794
7.1782
7.1698
7.1666
7.1638
7.1577
7.1454
5.7925
5.6202
5.5905
5.5876
5.5849
5.5820
5.2458
5.2431
5.2266
4.8788
4.8603
4.7980
4.7779
4.6756
4.6575
4.6561
4.6520
4.6039
4.5754
4.0400
4.0244
4.0146
3.9994
3.4346
0.9081
0.8978
OBn
O
O
BnO
BnO
OMe
BzO
O
BzO
OBz
2.09
2.16
2.07
1.03
3.29
6.72
8.18
5.68
1.07
1.00
1.02
2.11
0.98
1.02
1.11
1.00
2.06
1.05
0.99
1.04
0.97
1.02
0.99
1.01
3.12
3.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

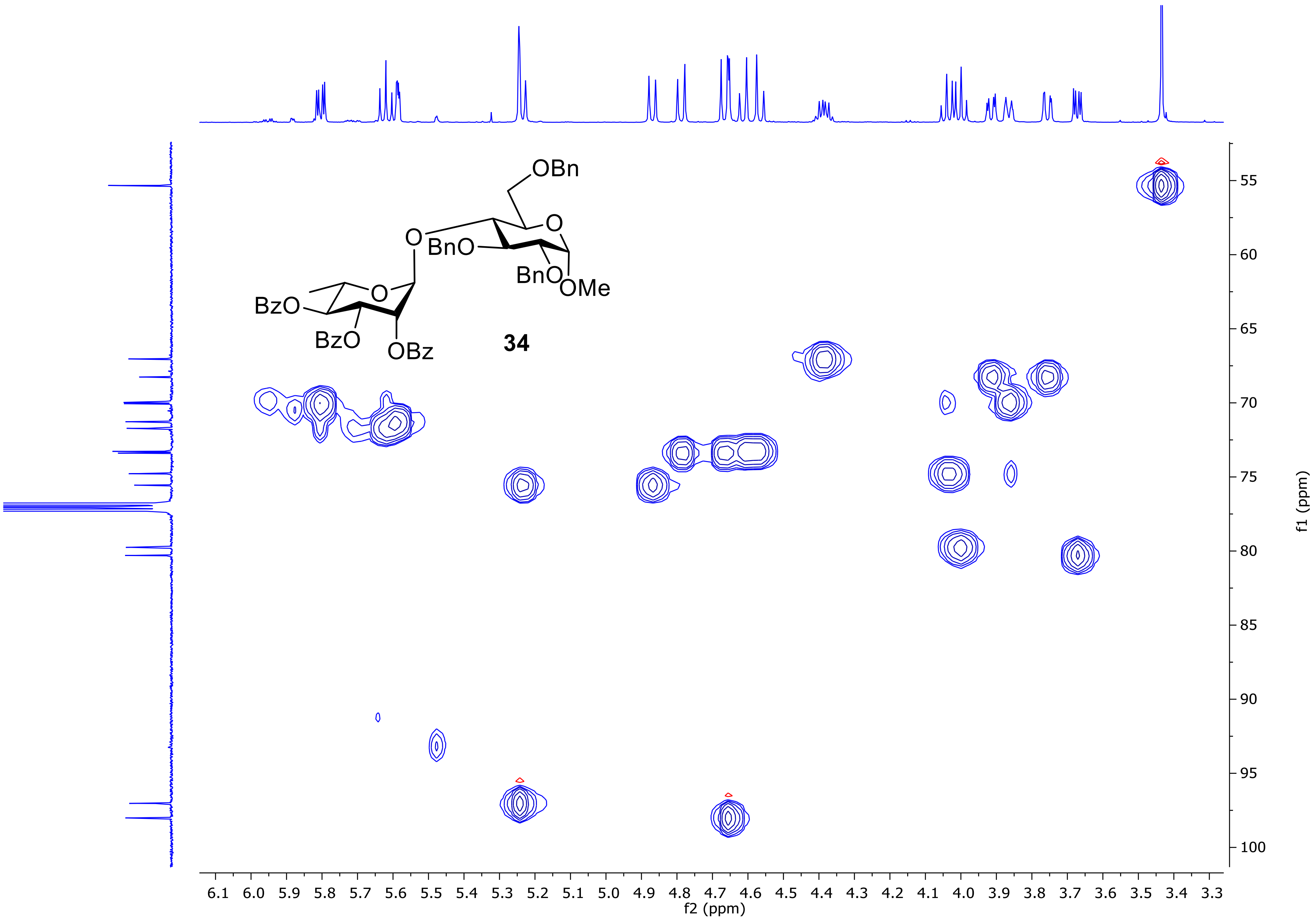
**34**

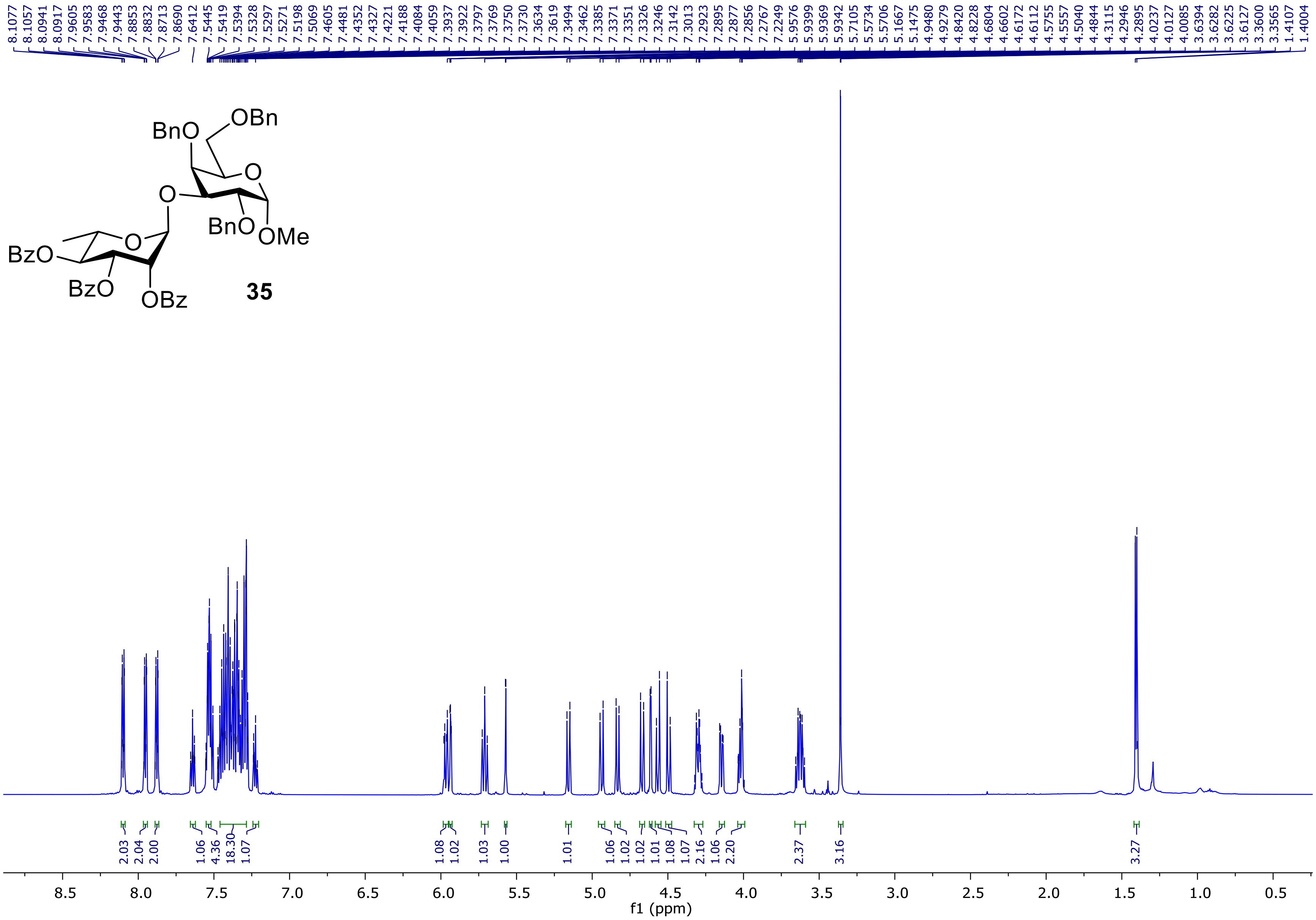

165.7713
165.6956
138.6980
137.9379
137.7221
133.4708
133.2600
133.1792
129.9021
129.7115
129.6761
129.4008
129.2019
128.5689
128.5091
128.4045
128.3342
128.2763
128.2134
128.1680
128.0204
127.9089
127.4962
127.4419
127.3030
98.0129
97.0306
80.3013
79.7516
77.2501
77.0386
76.8270
75.5565
74.7857
73.3891
73.2767
71.7199
71.2724
70.0572
69.9667
68.2523
67.0391
55.3313
29.7308
29.6872
17.1590
OBn
O
O
BnO
BnO
OMe
BzO
O
BzO
OBz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

**34**

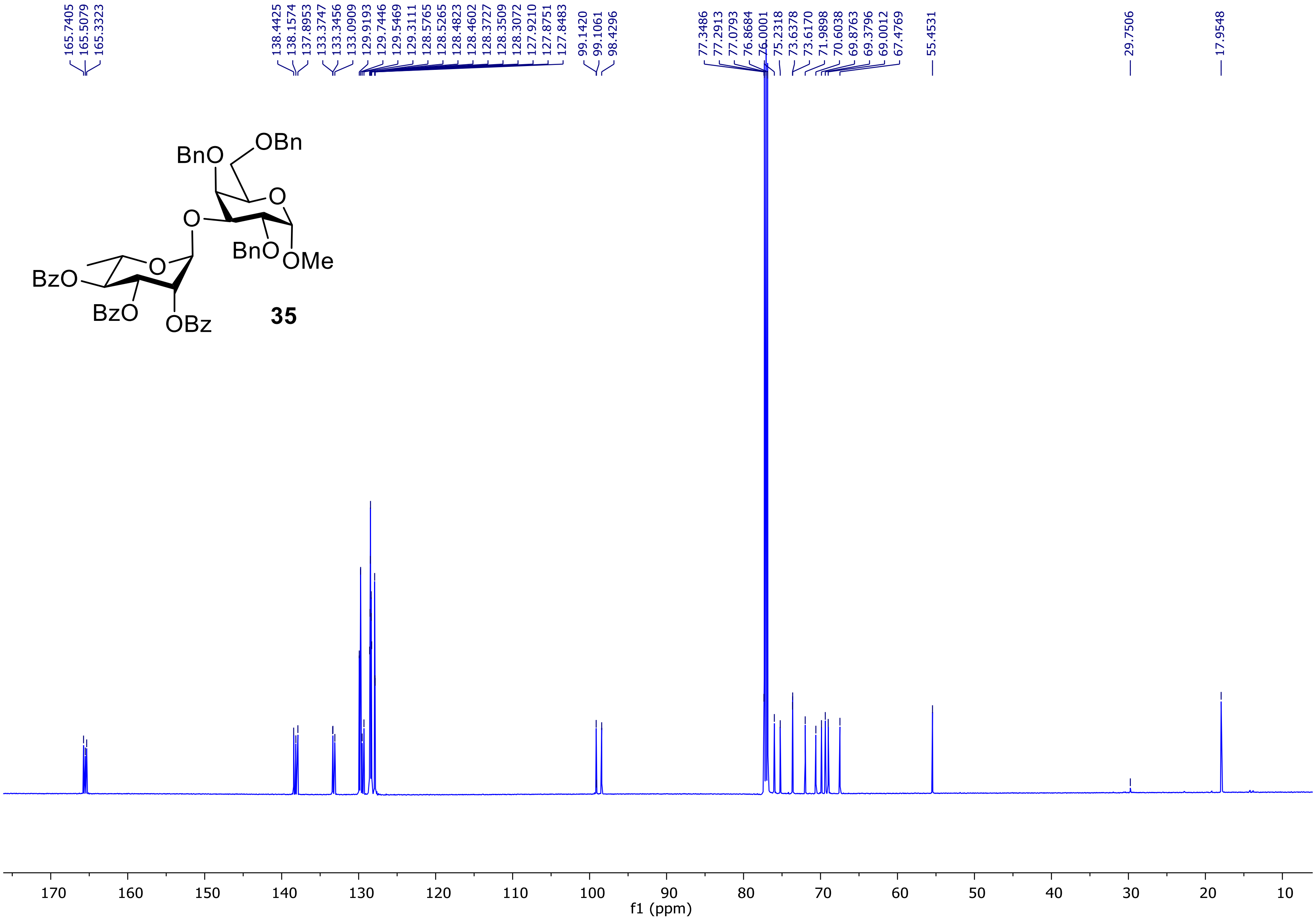

OBn
O
O
BnO
BnO
OMe
O
BzO
BzO
OBz
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
f2 (ppm)

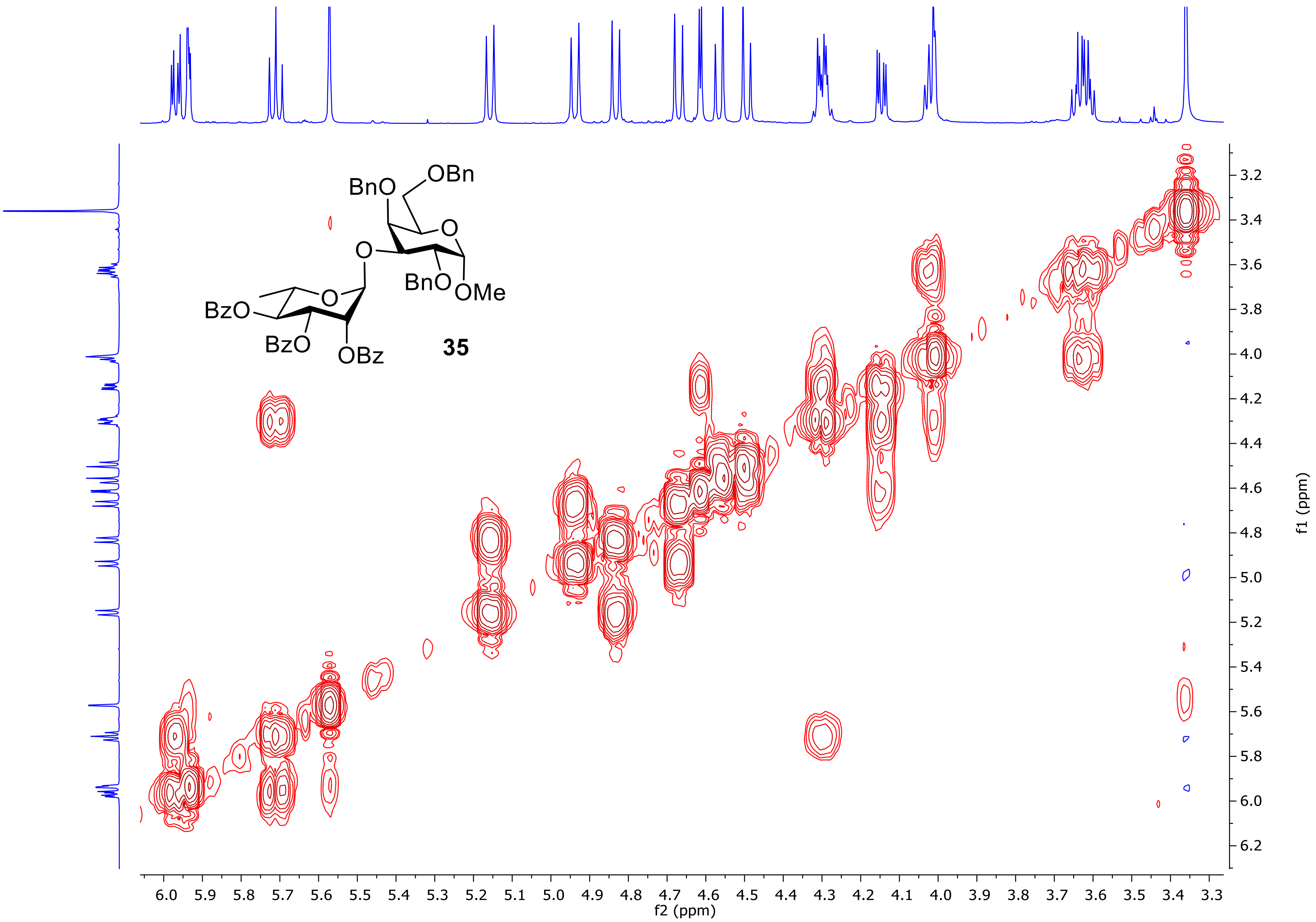
**34**


**34**
OBn
O
O
BnO
BnO
OMe
BzO
O
BzO
OBz
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
f1 (ppm)


8.1077
8.1057
8.0941
8.0917
7.9605
7.9583
7.9468
7.9443
7.8853
7.8832
7.8713
7.8690
7.6412
7.5445
7.5419
7.5394
7.5328
7.5297
7.5271
7.5198
7.5069
7.4605
7.4481
7.4352
7.4327
7.4221
7.4188
7.4084
7.4059
7.3937
7.3922
7.3797
7.3769
7.3750
7.3730
7.3634
7.3619
7.3494
7.3462
7.3385
7.3371
7.3351
7.3326
7.3246
7.3142
7.3013
7.2923
7.2895
7.2877
7.2856
7.2767
7.2249
5.9576
5.9399
5.9369
5.9342
5.7105
5.5734
5.5706
5.1667
5.1475
4.9480
4.9279
4.8420
4.8228
4.6804
4.6602
4.6172
4.6112
4.5755
4.5557
4.5040
4.4844
4.3115
4.2946
4.2895
4.0237
4.0127
4.0085
3.6394
3.6282
3.6225
3.6127
3.3600
3.3565
1.4107
1.4004
OBn
BnO
O
O
BnO
OMe
BzO
O
BzO
OBz
2.03
2.04
2.00
1.06
4.36
18.30
1.07
1.08
1.02
1.03
1.00
1.01
1.06
1.02
1.02
1.01
1.08
1.07
2.16
1.06
2.20
2.37
3.16
3.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

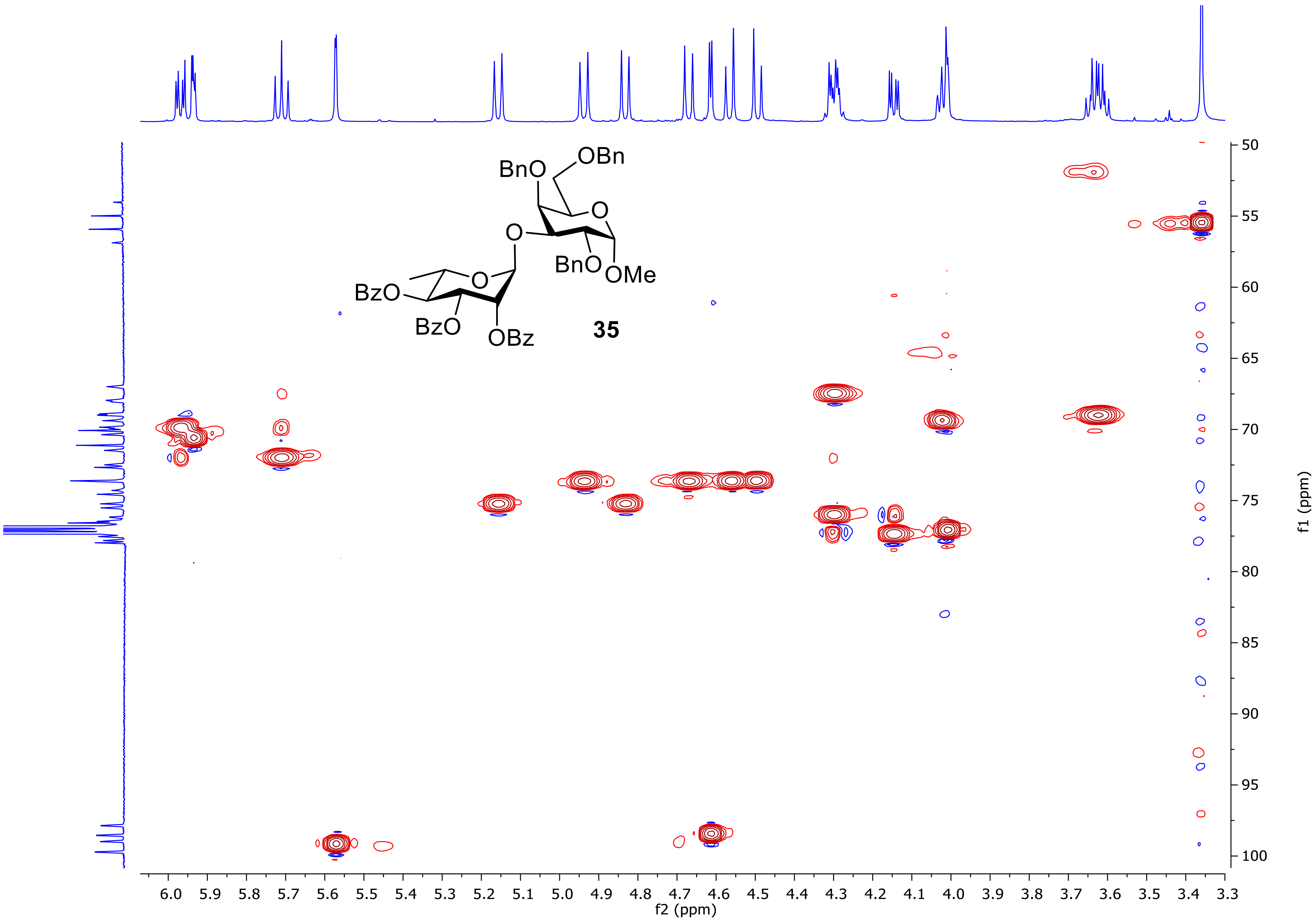
**35**


165.7405
165.5079
165.3323
138.4425
138.1574
137.8953
133.3747
133.3456
133.0909
129.9193
129.7446
129.5469
129.3111
128.5765
128.5265
128.4823
128.4602
128.3727
128.3509
128.3072
127.9210
127.8751
127.8483
99.1420
99.1061
98.4296
77.3486
77.2913
77.0793
76.8684
76.0001
75.2318
73.6378
73.6170
71.9898
70.6038
69.8763
69.3796
69.0012
67.4769
55.4531
29.7506
17.9548
BnO
OBn
O
O
BnO
OMe
BzO
O
BzO
OBz
35
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

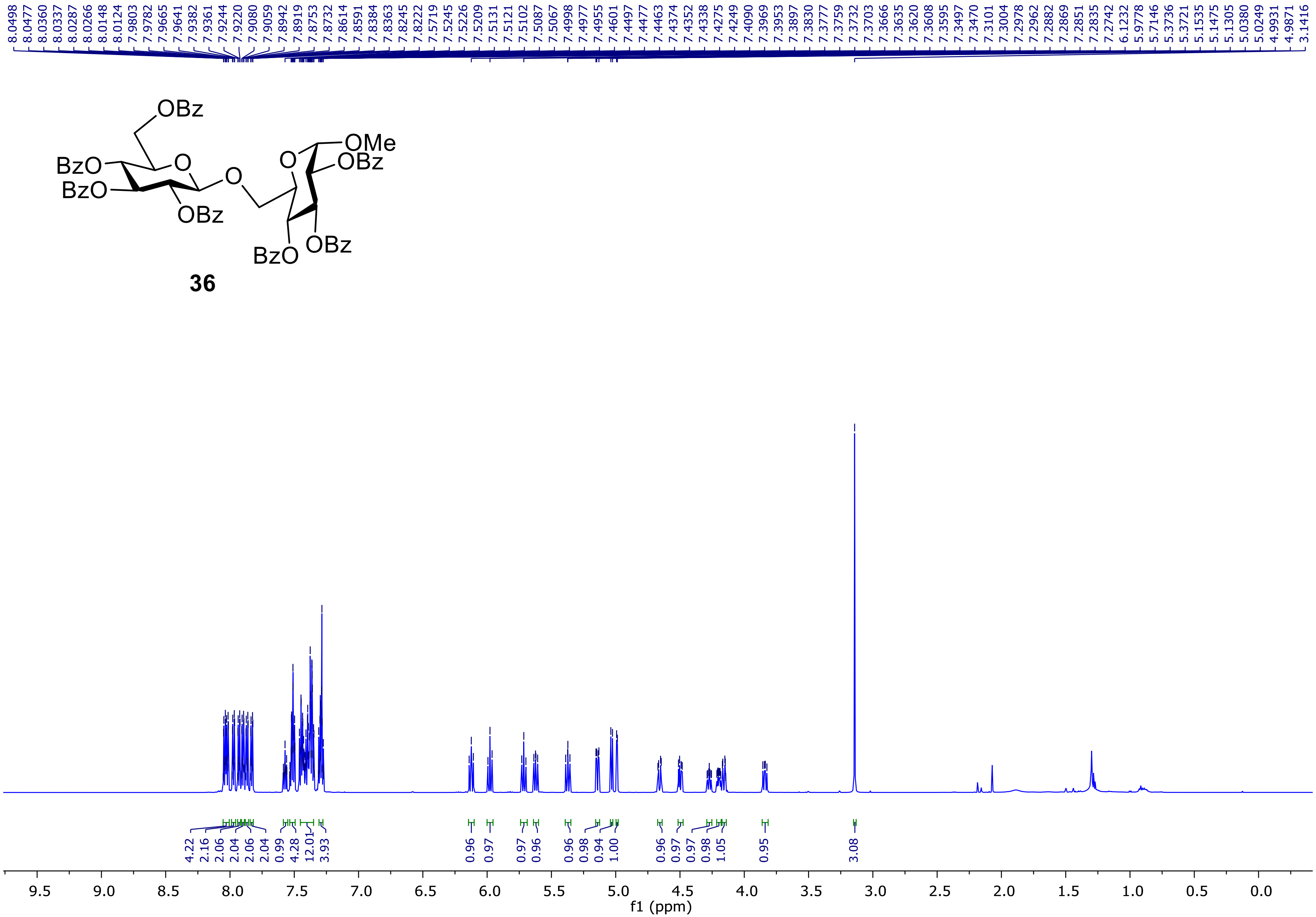


**35**

BnO
OBn
O
O
BnO
OMe
BzO
O
BzO
OBz
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)

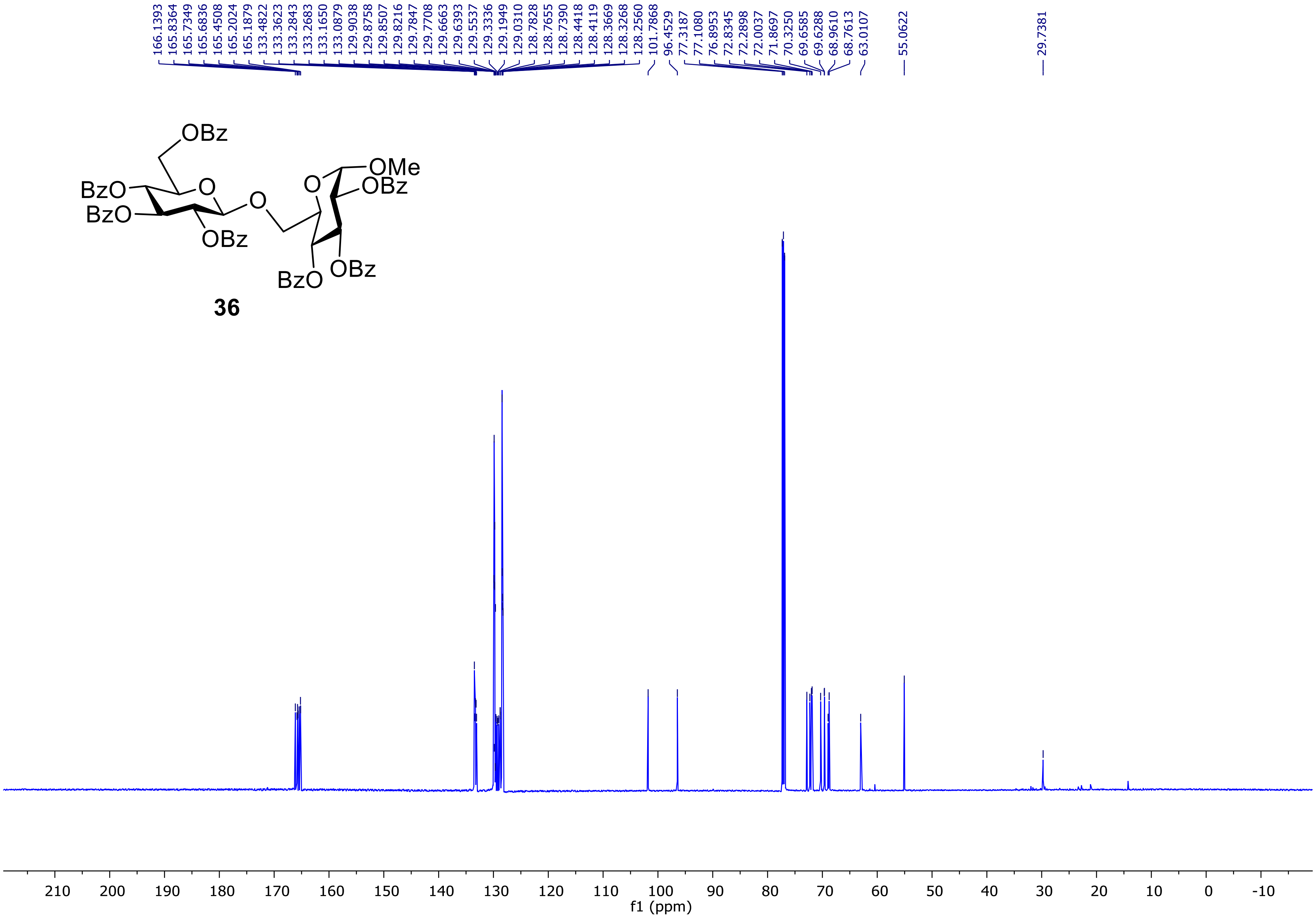

BnO
OBn
O
O
BzO
O
BnO
OMe
BzO
OBz
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
50
55
60
65
70
75
80
85
90
95
100
f1 (ppm)

**35**


OBz
BzO
O
BzO
OBz
O
O
OMe
OBz
BzO
OBz

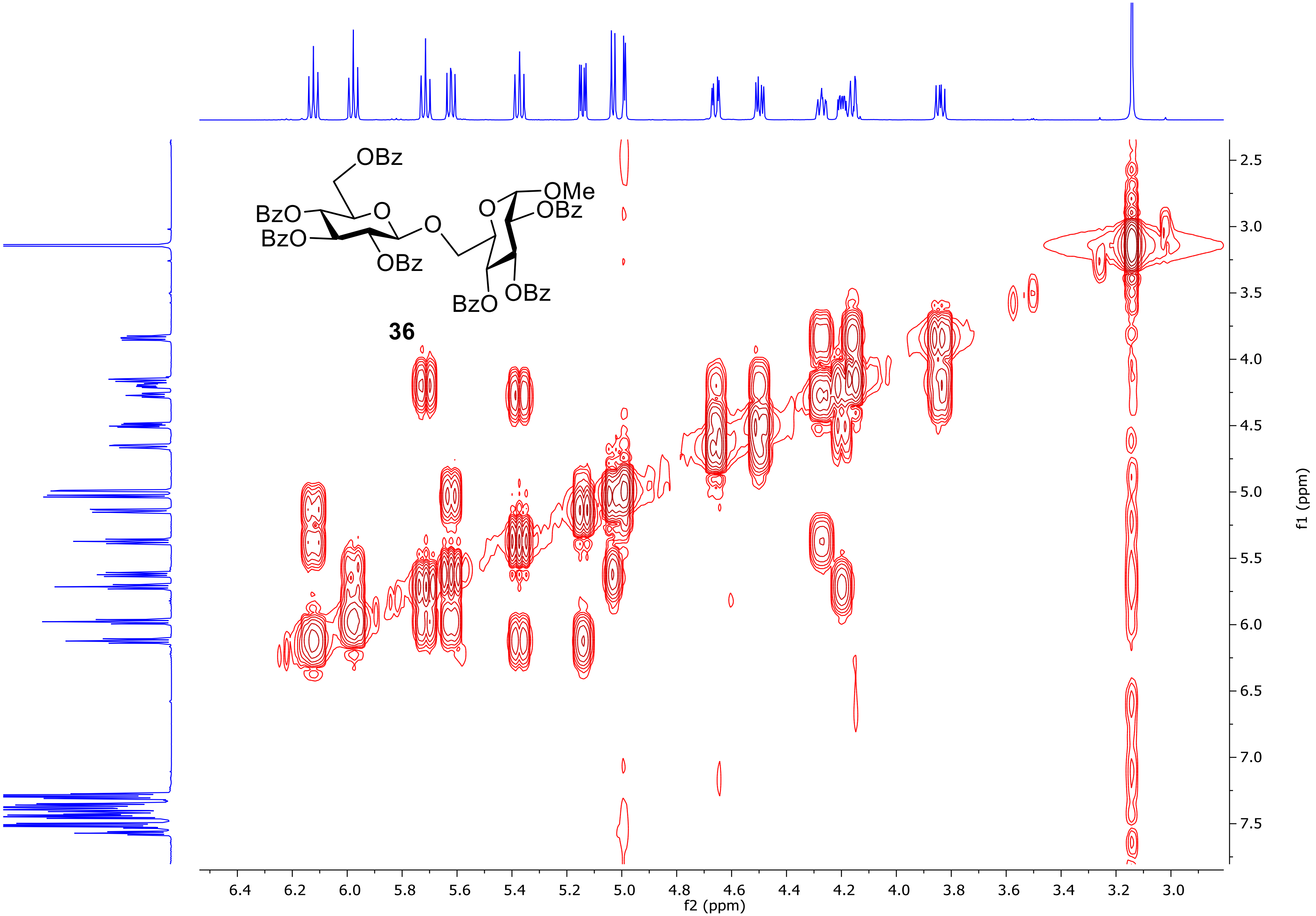
**36**

8.0498
8.0477
8.0360
8.0337
8.0287
8.0266
8.0148
8.0124
7.9803
7.9782
7.9665
7.9641
7.9382
7.9361
7.9244
7.9220
7.9080
7.9059
7.8942
7.8919
7.8753
7.8732
7.8614
7.8591
7.8384
7.8363
7.8245
7.8222
7.5719
7.5245
7.5226
7.5209
7.5131
7.5121
7.5102
7.5087
7.5067
7.4998
7.4977
7.4955
7.4601
7.4497
7.4477
7.4463
7.4374
7.4352
7.4338
7.4275
7.4249
7.4090
7.3969
7.3953
7.3897
7.3830
7.3777
7.3759
7.3732
7.3703
7.3666
7.3635
7.3620
7.3608
7.3595
7.3497
7.3470
7.3101
7.3004
7.2978
7.2962
7.2882
7.2869
7.2851
7.2835
7.2742
6.1232
5.9778
5.7146
5.3736
5.3721
5.1535
5.1475
5.1305
5.0380
5.0249
4.9931
4.9871
3.1416
4.22
2.16
2.06
2.04
2.06
2.04
0.99
4.28
12.01
3.93
0.96
0.97
0.97
0.96
0.96
0.98
0.94
1.00
0.96
0.97
0.97
0.98
1.05
0.95
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OBz
BzO
O
O
OMe
OBz
BzO
OBz
O
BzO
OBz

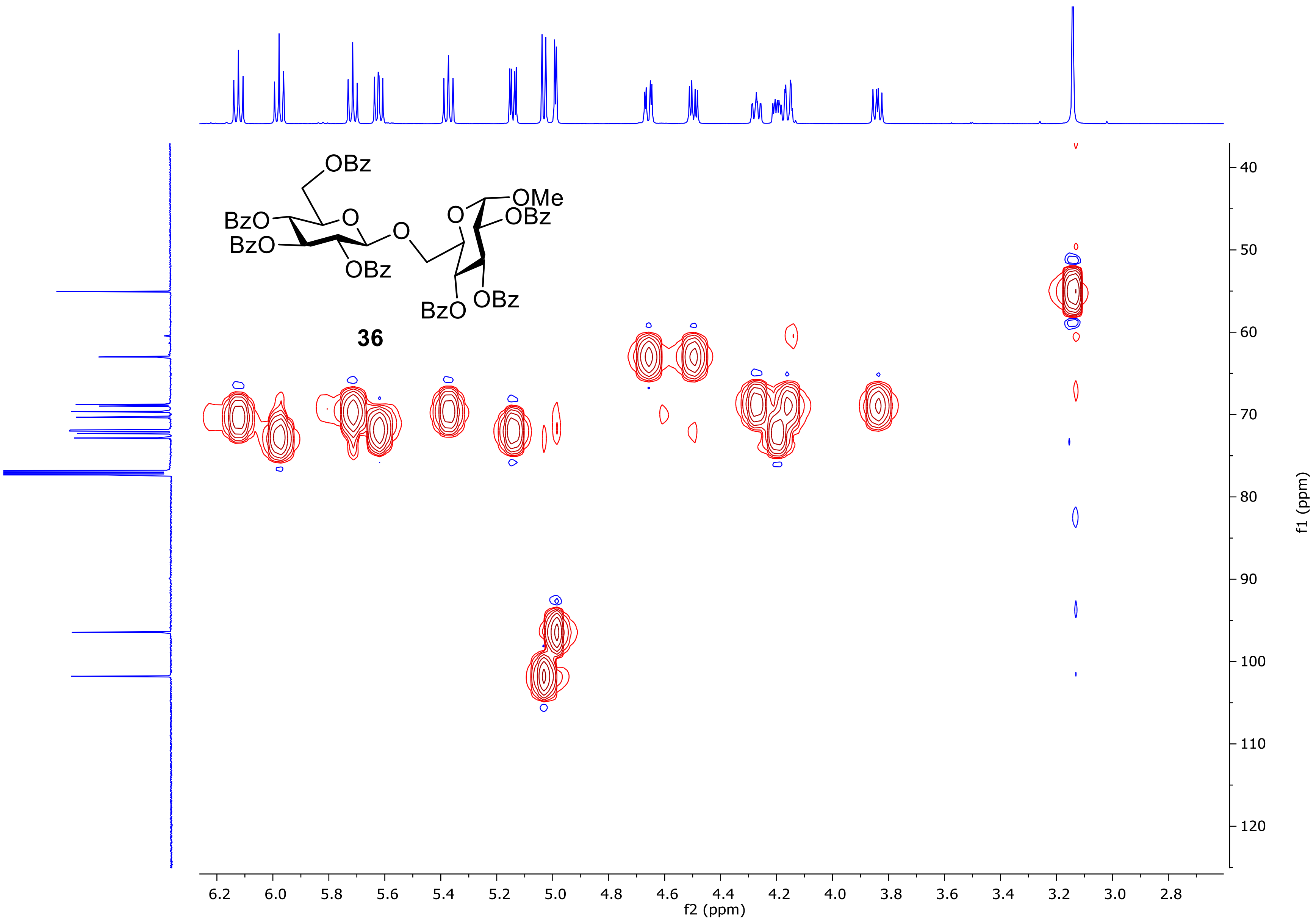
**36**

166.1393
165.8364
165.7349
165.6836
165.4508
165.2024
165.1879
133.4822
133.3623
133.2843
133.2683
133.1650
133.0879
129.9038
129.8758
129.8507
129.8216
129.7847
129.7708
129.6663
129.6393
129.5537
129.3336
129.1949
129.0310
128.7828
128.7655
128.7390
128.4418
128.4119
128.3669
128.3268
128.2560
101.7868
96.4529
77.3187
77.1080
76.8953
72.8345
72.2898
72.0037
71.8697
70.3250
69.6585
69.6288
68.9610
68.7613
63.0107
55.0622
29.7381
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



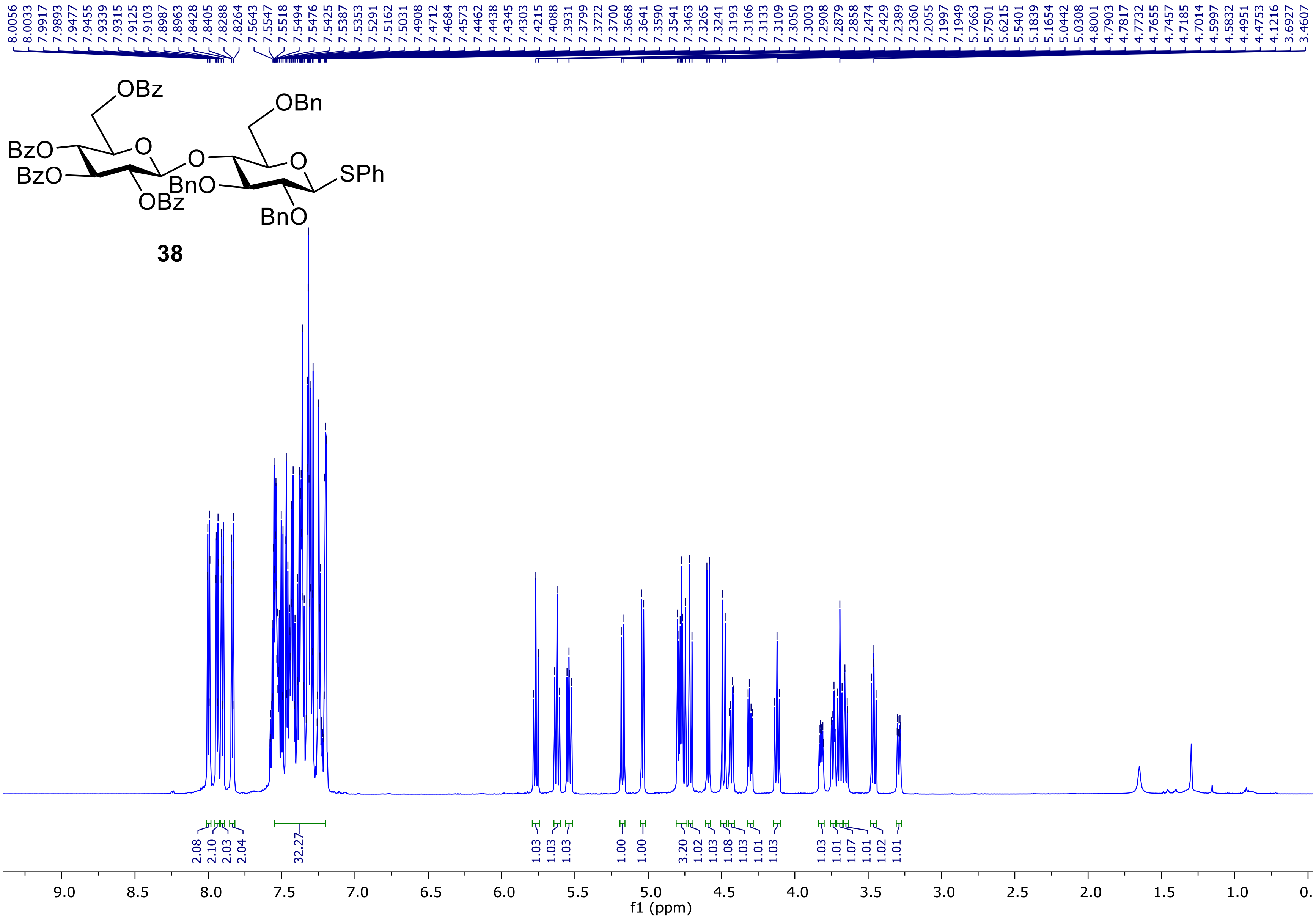
OBz
BzO
BzO
O
OBz
O
O
OMe
OBz
BzO
OBz
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
f2 (ppm)
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

**36**

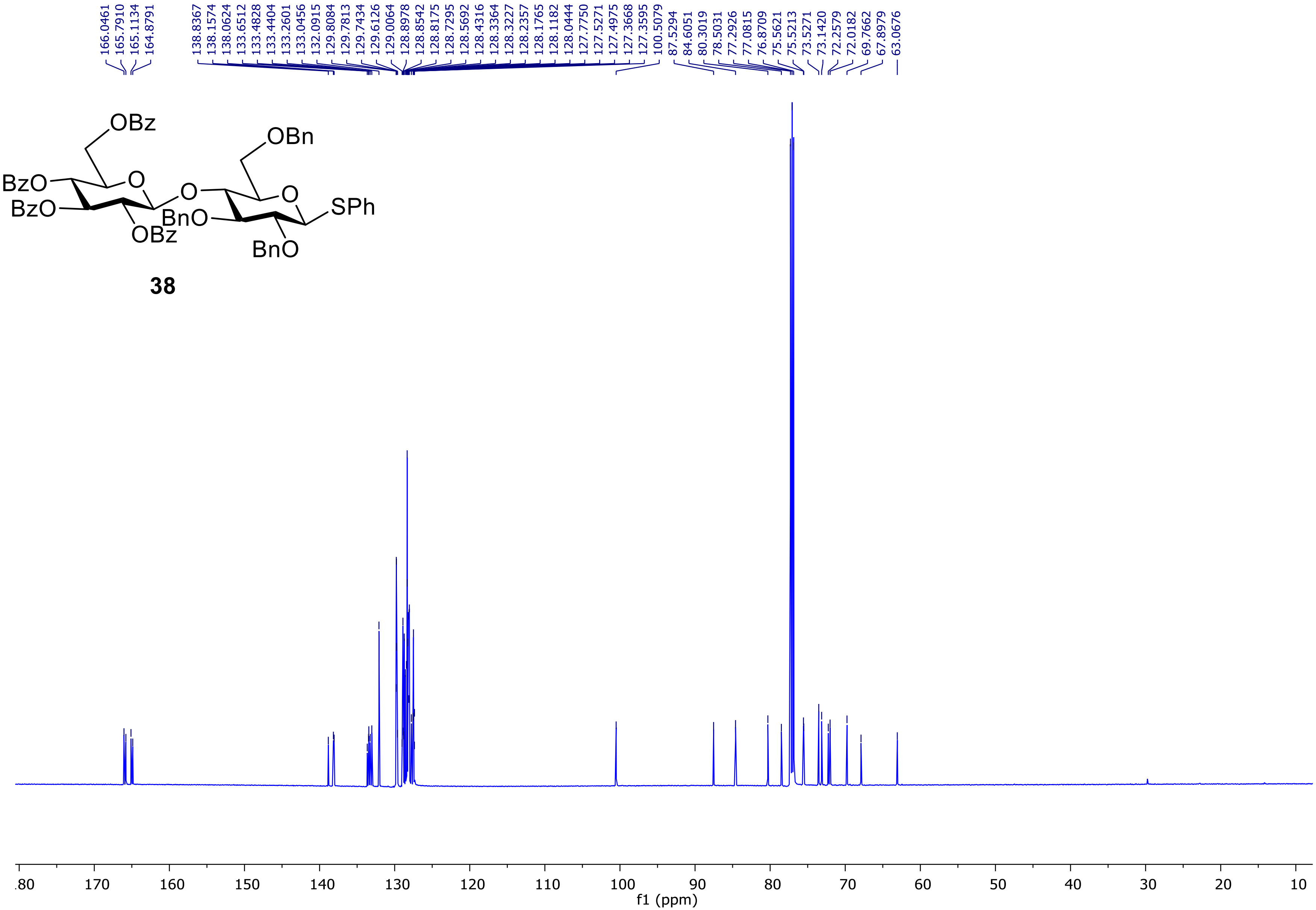


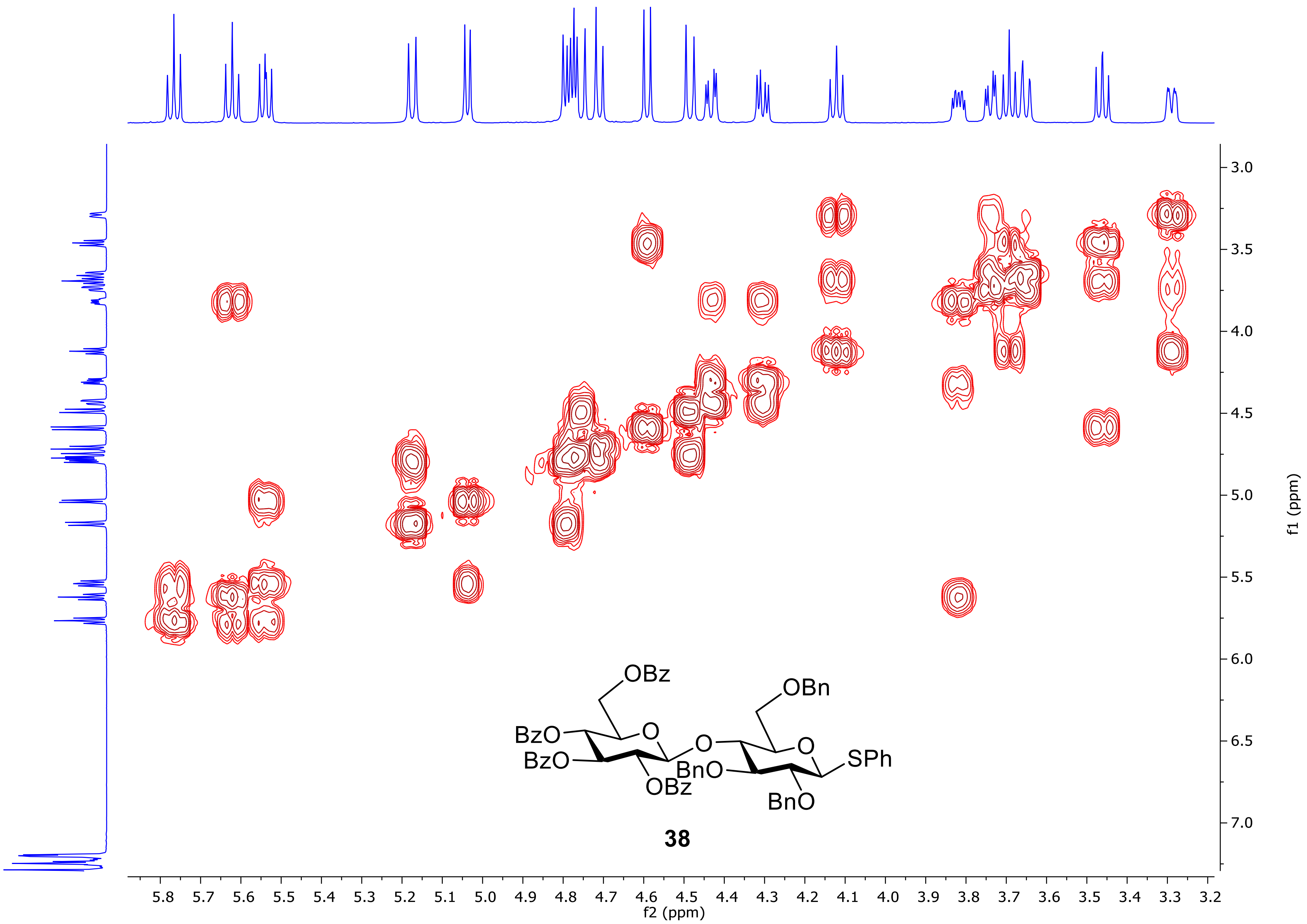
**36**

OBz
BzO
O
O
OMe
OBz
BzO
OBz
BzO
OBz
f2 (ppm)
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f1 (ppm)
40
50
60
70
80
90
100
110
120

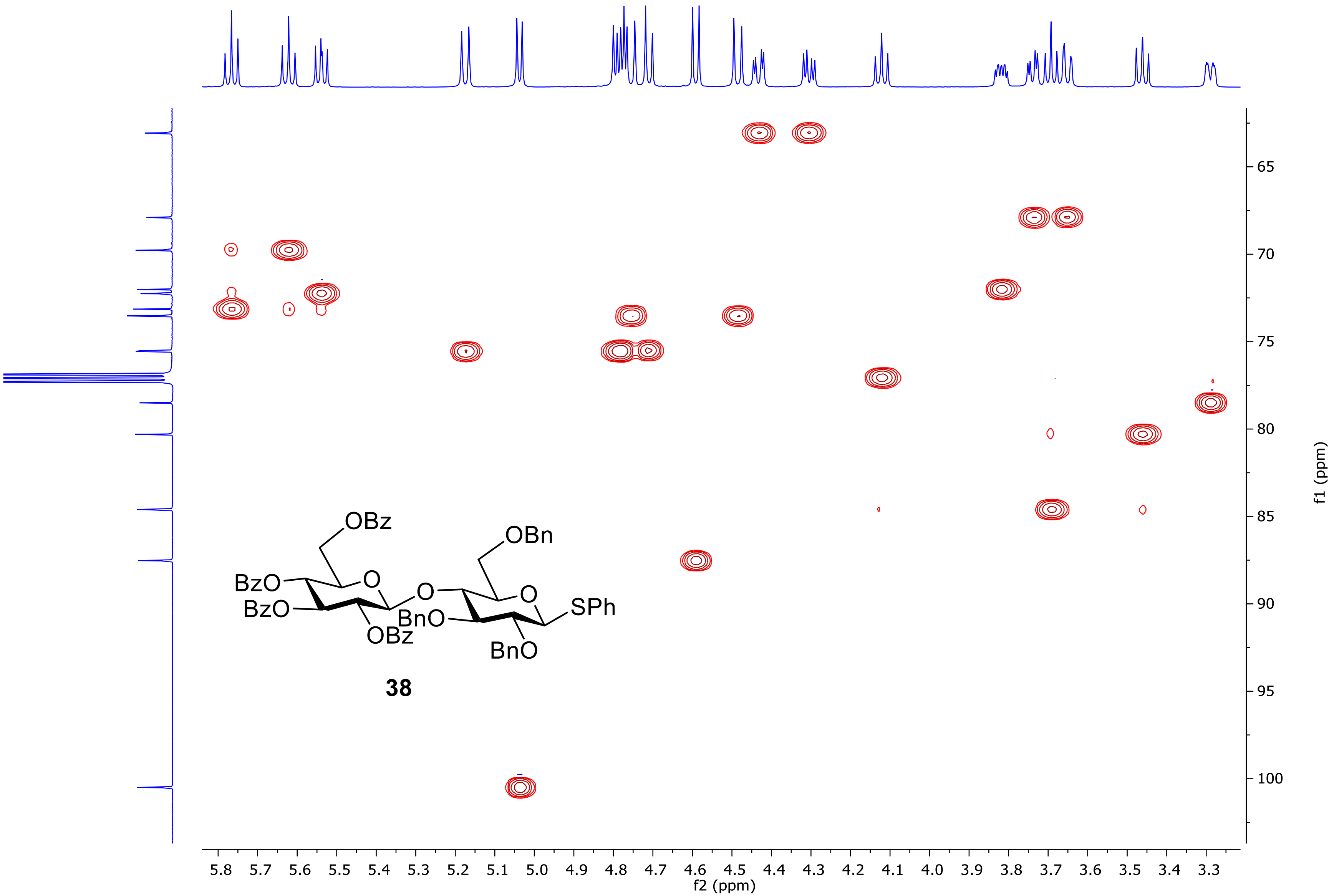

8.0056
8.0033
7.9917
7.9893
7.9477
7.9455
7.9339
7.9315
7.9125
7.9103
7.8987
7.8963
7.8428
7.8405
7.8288
7.8264
7.5643
7.5547
7.5518
7.5494
7.5476
7.5425
7.5387
7.5353
7.5291
7.5162
7.5031
7.4908
7.4712
7.4684
7.4573
7.4462
7.4438
7.4345
7.4303
7.4215
7.4088
7.3931
7.3799
7.3722
7.3700
7.3668
7.3641
7.3590
7.3541
7.3463
7.3265
7.3241
7.3193
7.3166
7.3133
7.3109
7.3050
7.3003
7.2908
7.2879
7.2858
7.2474
7.2429
7.2389
7.2360
7.2055
7.1997
7.1949
5.7663
5.7501
5.6215
5.5401
5.1839
5.1654
5.0442
5.0308
4.8001
4.7903
4.7817
4.7732
4.7655
4.7457
4.7185
4.7014
4.5997
4.5832
4.4951
4.4753
4.1216
3.6927
3.4607
OBz
OBn
BzO
O
O
O
SPh
BzO
BnO
OBz
BnO
2.08
2.10
2.03
2.04
32.27
1.03
1.03
1.03
1.00
1.00
3.20
1.02
1.03
1.08
1.03
1.01
1.03
1.03
1.01
1.07
1.01
1.02
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)

**38**

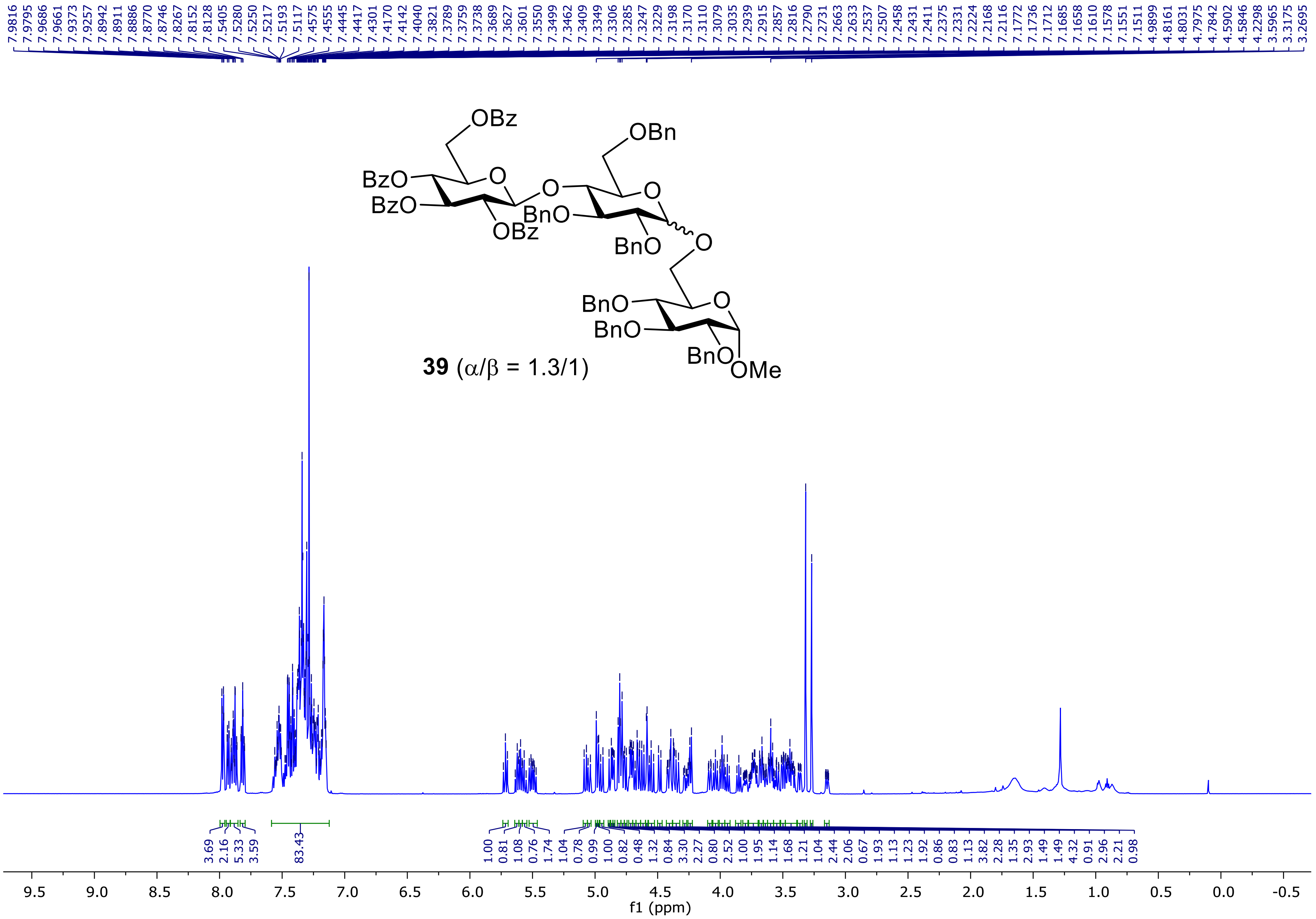

**38**
166.0461
165.7910
165.1134
164.8791
138.8367
138.1574
138.0624
133.6512
133.4828
133.4404
133.2601
133.0456
132.0915
129.8084
129.7813
129.7434
129.6126
129.0064
128.8978
128.8542
128.8175
128.7295
128.5692
128.4316
128.3364
128.3227
128.2357
128.1765
128.1182
128.0444
127.7750
127.5271
127.4975
127.3668
127.3595
100.5079
87.5294
84.6051
80.3019
78.5031
77.2926
77.0815
76.8709
75.5621
75.5213
73.5271
73.1420
72.2579
72.0182
69.7662
67.8979
63.0676
OBz
BzO
BzO
O
OBz
O
OBn
O
BnO
BnO
SPh
.80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OBz
BzO
BzO
O
O
OBz
OBn
O
BnO
SPh
BnO
f2 (ppm)
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f1 (ppm)
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0

**38**

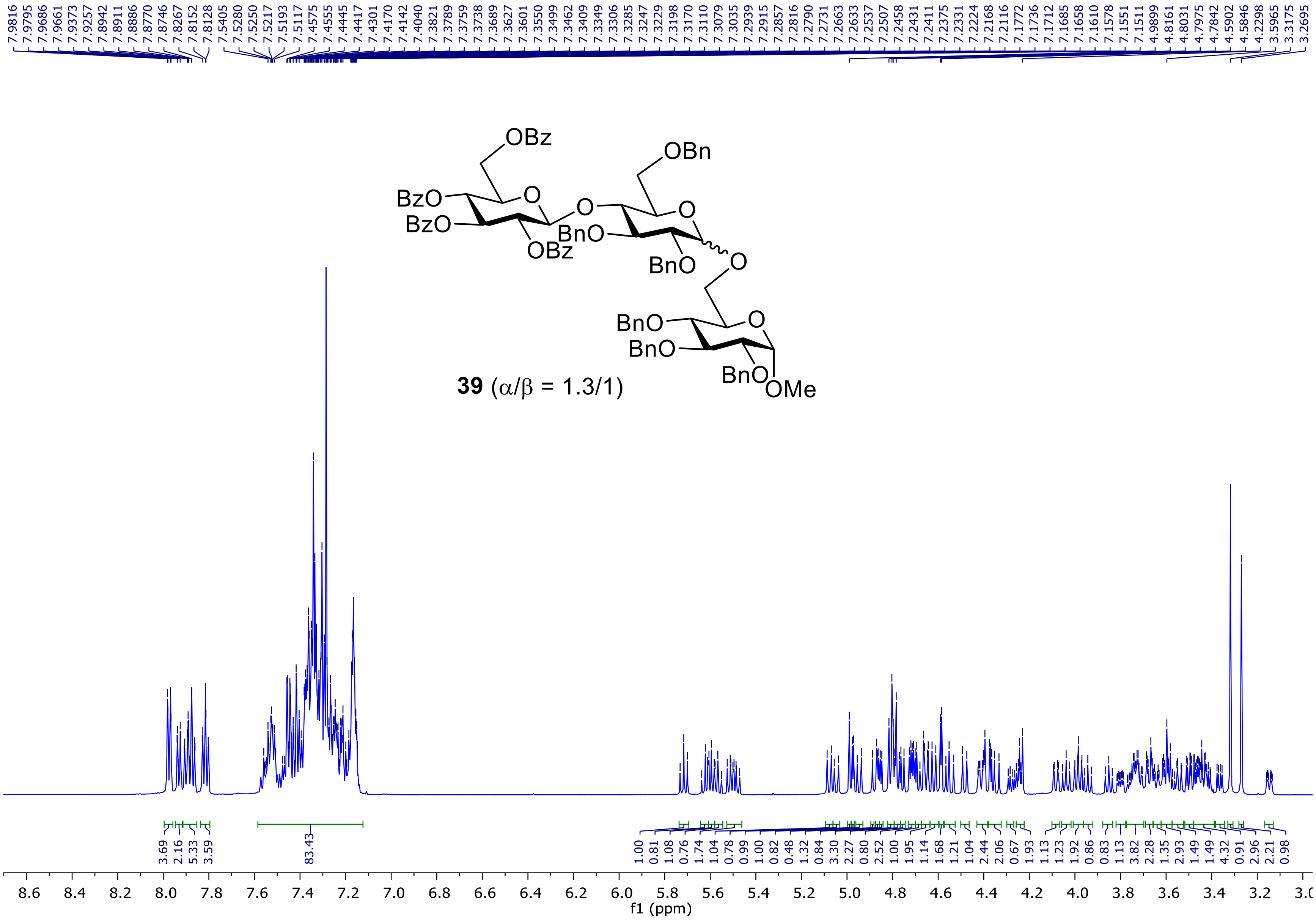

OBz
BzO
BzO
O
OBz
O
OBn
BnO
O
SPh
BnO
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
f2 (ppm)
65
70
75
80
85
90
95
100
f1 (ppm)

**38**

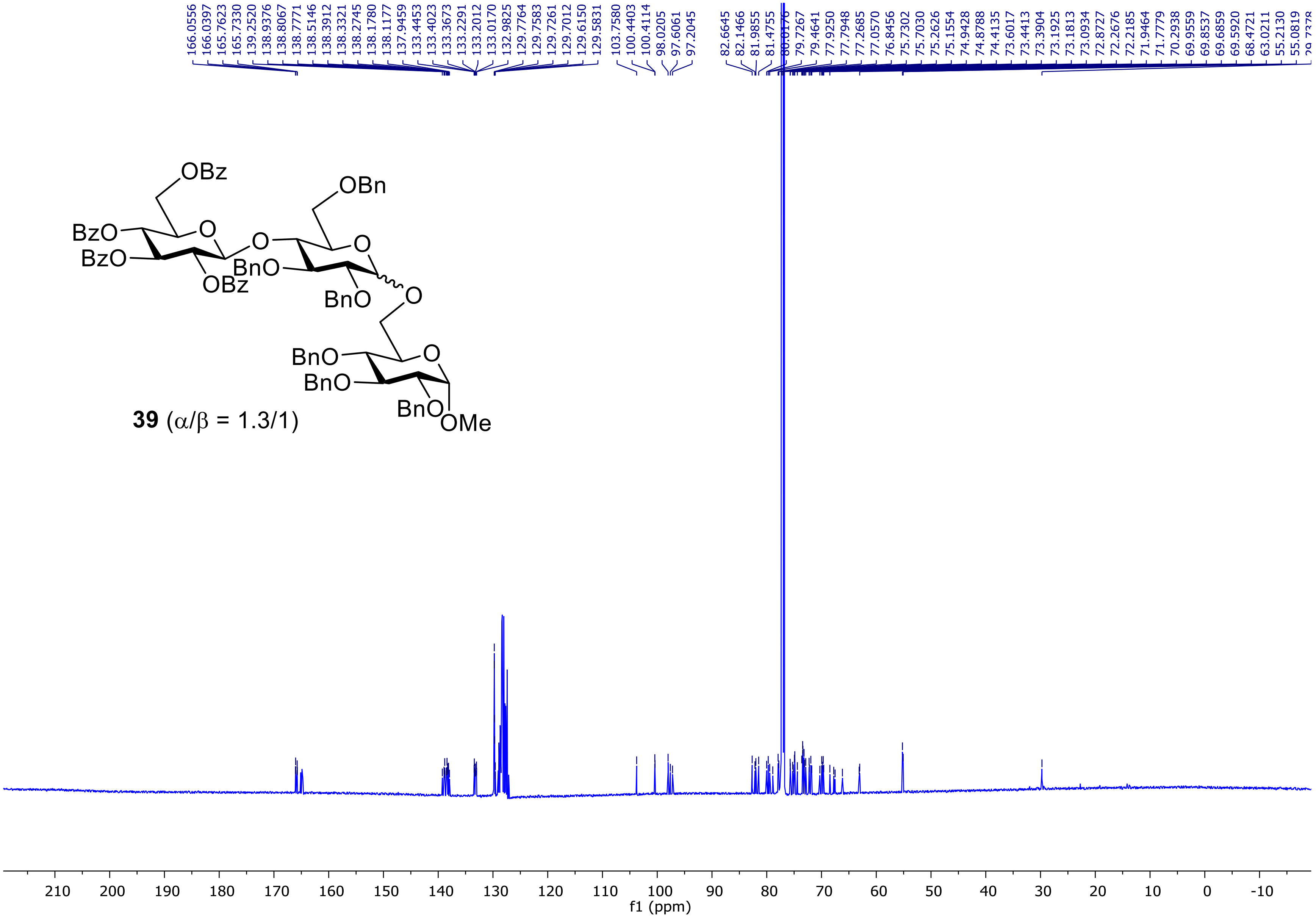


**39** (α/β = 1.3/1)

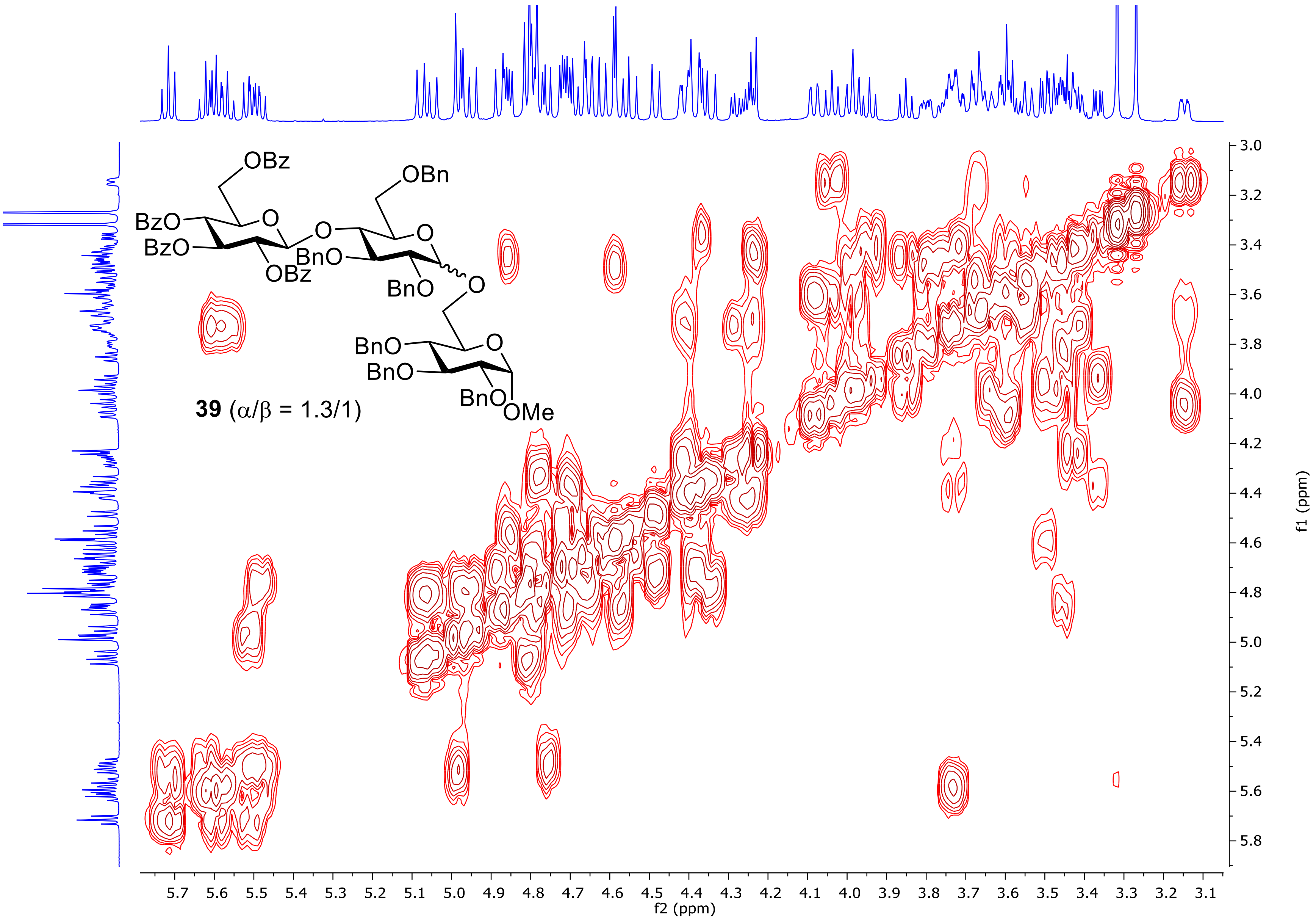
7.9816
7.9795
7.9686
7.9661
7.9373
7.9257
7.8942
7.8911
7.8886
7.8770
7.8746
7.8267
7.8152
7.8128
7.5405
7.5280
7.5250
7.5217
7.5193
7.5117
7.4575
7.4555
7.4445
7.4417
7.4301
7.4170
7.4142
7.4040
7.3821
7.3789
7.3759
7.3738
7.3689
7.3627
7.3601
7.3550
7.3499
7.3462
7.3409
7.3349
7.3306
7.3285
7.3247
7.3229
7.3198
7.3170
7.3110
7.3079
7.3035
7.2939
7.2915
7.2857
7.2816
7.2790
7.2731
7.2663
7.2633
7.2537
7.2507
7.2458
7.2431
7.2411
7.2375
7.2331
7.2224
7.2168
7.2116
7.1772
7.1736
7.1712
7.1685
7.1658
7.1610
7.1578
7.1551
7.1511
4.9899
4.8161
4.8031
4.7975
4.7842
4.5902
4.5846
4.2298
3.5965
3.3175
3.2695
OBz
BzO
BzO
O
OBz
O
OBn
BnO
O
BnO
O
BnO
BnO
O
BnO
OMe
3.69
2.16
5.33
3.59
83.43
1.00
0.81
1.08
0.76
1.74
1.04
0.78
0.99
1.00
0.82
0.48
1.32
0.84
3.30
2.27
0.80
2.52
1.00
1.95
1.14
1.68
1.21
1.04
2.44
2.06
0.67
1.93
1.13
1.23
1.92
0.86
0.83
1.13
3.82
2.28
1.35
2.93
1.49
1.49
4.32
0.91
2.96
2.21
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


7.9816
7.9795
7.9686
7.9661
7.9373
7.9257
7.8942
7.8911
7.8886
7.8770
7.8746
7.8267
7.8152
7.8128
7.5405
7.5280
7.5250
7.5217
7.5193
7.5117
7.4575
7.4555
7.4445
7.4417
7.4301
7.4170
7.4142
7.4040
7.3821
7.3789
7.3759
7.3738
7.3689
7.3627
7.3601
7.3550
7.3499
7.3462
7.3409
7.3349
7.3306
7.3285
7.3247
7.3229
7.3198
7.3170
7.3110
7.3079
7.3035
7.2939
7.2915
7.2857
7.2816
7.2790
7.2731
7.2663
7.2633
7.2537
7.2507
7.2458
7.2431
7.2411
7.2375
7.2331
7.2224
7.2168
7.2116
7.1772
7.1736
7.1712
7.1685
7.1658
7.1610
7.1578
7.1551
7.1511
4.9899
4.8161
4.8031
4.7975
4.7842
4.5902
4.5846
4.2298
3.5965
3.3175
3.2695
OBz
BzO
O
BzO
OBz
O
OBn
O
BnO
BnO
O
BnO
BnO
O
BnO
OMe
3.69
2.16
5.33
3.59
83.43
1.00
0.81
1.08
0.76
1.74
1.04
0.78
0.99
1.00
0.82
0.48
1.32
0.84
3.30
2.27
0.80
2.52
1.00
1.95
1.14
1.68
1.21
1.04
2.44
2.06
0.67
1.93
1.13
1.23
1.92
0.86
0.83
1.13
3.82
2.28
1.35
2.93
1.49
4.32
0.91
2.96
2.21
0.98
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
f1 (ppm)

**39** (α/β = 1.3/1)

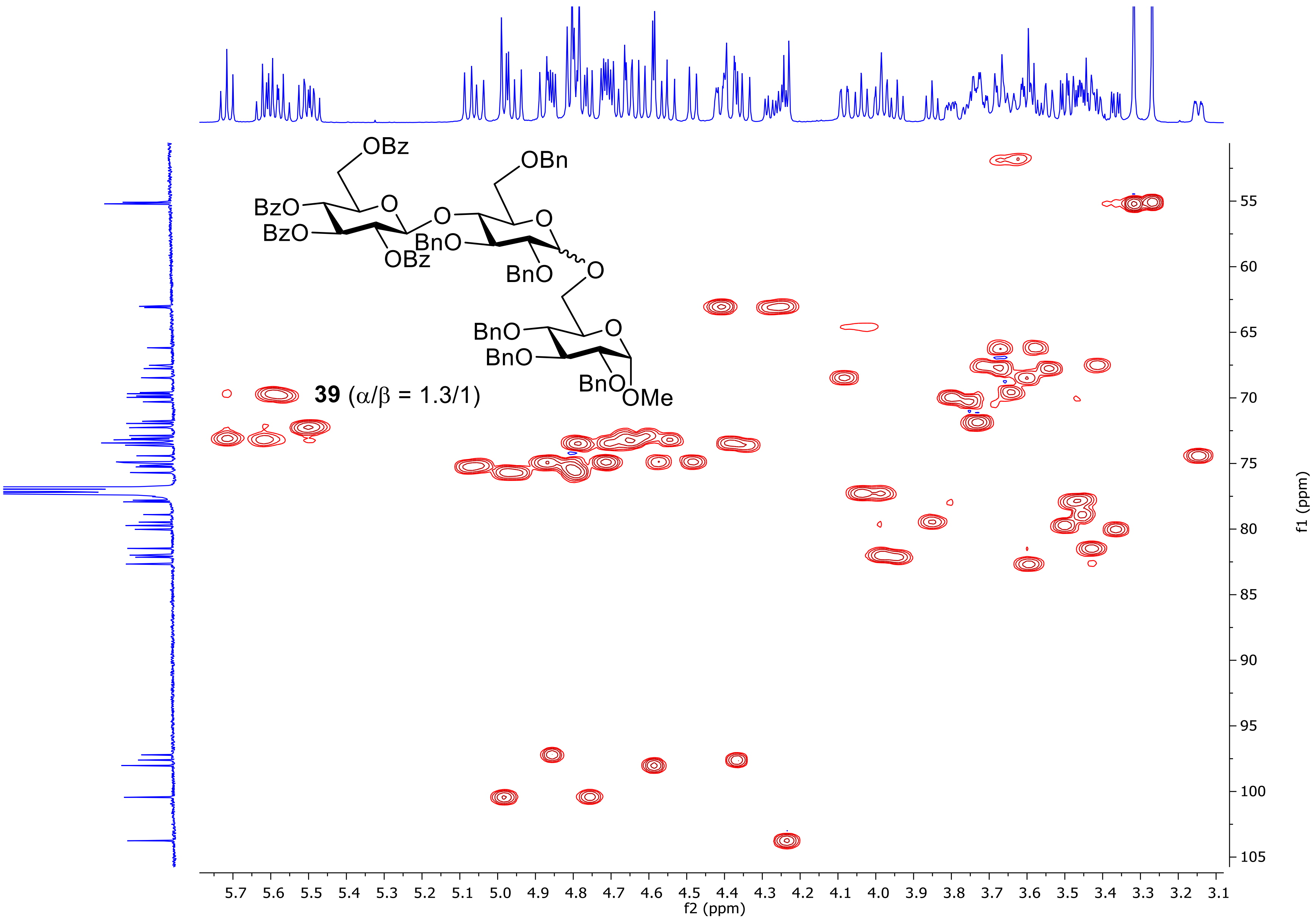

**39** (α/β = 1.3/1)

166.0556
166.0397
165.7623
165.7330
139.2520
138.9376
138.8067
138.7771
138.5146
138.3912
138.3321
138.2745
138.1780
138.1177
137.9459
133.4453
133.4023
133.3673
133.2291
133.2012
133.0170
132.9825
129.7764
129.7583
129.7261
129.7012
129.6150
129.5831
103.7580
100.4403
100.4114
98.0205
97.6061
97.2045
82.6645
82.1466
81.9855
81.4755
80.0176
79.7267
79.4641
77.9250
77.7948
77.2685
77.0570
76.8456
75.7302
75.7030
75.2626
75.1554
74.9428
74.8788
74.4135
73.6017
73.4413
73.3904
73.1925
73.1813
73.0934
72.8727
72.2676
72.2185
71.9464
71.7779
70.2938
69.9559
69.8537
69.6859
69.5920
68.4721
63.0211
55.2130
55.0819
29.7378
OBz
BzO
O
BzO
OBz
O
OBn
O
BnO
BnO
O
BnO
BnO
O
BnO
OMe
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



**39** (α/β = 1.3/1)

OBz
BzO
BzO
OBz
O
O
OBn
O
BnO
BnO
O
O
BnO
BnO
O
BnO
OMe
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f2 (ppm)
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
f1 (ppm)



**39** (α/β = 1.3/1)

OBz
BzO
O
BzO
OBz
O
OBn
O
BnO
BnO
O
BnO
O
BnO
BnO
OMe
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
f2 (ppm)
55
60
65
70
75
80
85
90
95
100
105
f1 (ppm)