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Supporting Information

Stereoselective β-Mannosylation via Anomeric *O*-Alkylation with L-Sugar-Derived Electrophiles

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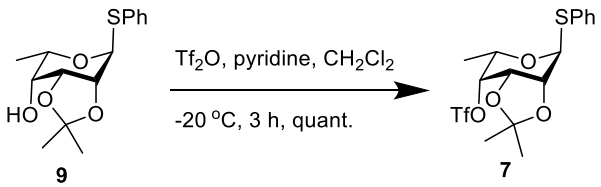
Supporting Information

General Information

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. 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.

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruker Advance-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, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants in Hertz. All ^{13}C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectra (HRMS) 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. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer.

Synthesis of L-Talose-derived Triflates

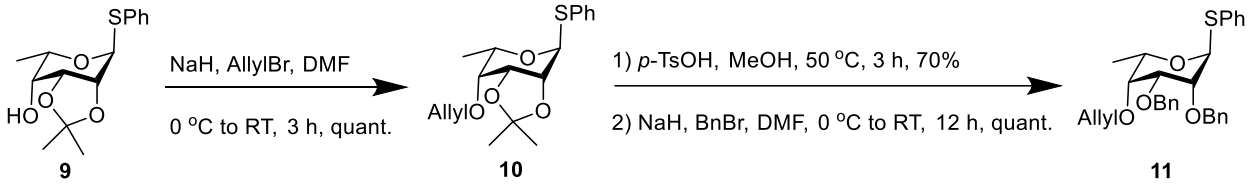


Phenyl 6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate)-2,3-*O*-(1-methyl ethylidene)-1-thio-α-L-talopyranoside (7)

To a solution of known compound phenyl 6-deoxy-2,3-*O*-(methyl ethylidene)-1-thio-α-L-talopyranoside (**9**)[1] (100 mg, 0.33 mmol) in 2 mL of methylene chloride and pyridine (0.53 mL, 6.6 mmol) cooled at -20 ℃ was added triflic anhydride (100 μL, 0.66 mmol) dropwise. The resulting mixture was stirred at -20 ℃ for 3 hours and then quenched with ice water. Organic layer was separated and washed sequentially with saturated $CuSO_4$ (2×10 mL) and water (3×20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (pure CH_2Cl_2) to afford 143 mg (quantitative) of phenyl 6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate)-2,3-*O*-(methyl ethylidene)-1-thio-α-L-talopyranoside **7** as a colorless oil.

^{1}H NMR (600 MHz,$CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.3 Hz, 2H, Ar-*H*), 7.35 – 7.28 (m, 3H, Ar-*H*), 5.66 (d, *J* = 2.3 Hz, 1H, *H1*), 4.92 (dd, *J* = 5.4, 1.5 Hz, 1H, *H4*), 4.44 – 4.39 (m, 2H, *H5*,*H3*), 4.24 (dd, *J* = 6.6, 2.4 Hz, 1H, *H2*), 1.60 (s, 3H, *isoprop*.), 1.40 (s, 3H, , *isoprop*), 1.31 (d, *J* = 6.6 Hz, 3H, *H6*).

^{13}C NMR (150 MHz, CDCl3) δ 132.48, 131.99, 129.17, 128.01, 118.52 (q, $^1J_{C\text{-}F}$ =322.5Hz), 110.97, 83.47, 82.11, 72.97, 70.33, 64.68, 25.76, 24.85, 16.55.



9 **10** **11**

Phenyl 6-deoxy-2,3-*O*-(1-methyl ethylidene)-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside (10)

To a solution of phenyl 6-deoxy-2,3-*O*-(methyl ethylidene)-1-thio-α-L-talopyranoside (**9**) (400 mg, 1.35 mmol) in 4.5 mL of *N*,*N*-dimethylformamide cooled to 0 °C was added sodium hydride (60% dispersion in mineral oil, 108 mg, 2.7 mmol) portion wise. The resulting mixture was stirred at 0 °C for 20 minutes before allyl bromide (170 μL, 2.02 mmol) was added dropwise. The reaction mixture was warmed up and stirred at ambient temperature for 3 hours. The reaction mixture was quenched with water and extracted with EtOAc (3×20 mL). Combined extracts were sequentially

washed with water (2×50 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 20/1), to afford 500mg (quantitative) of phenyl 6-deoxy-2,3-*O*-(1-methyl ethylidene)-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside **10**.

^{1}H NMR (600 MHz,$CDCl_3$) δ 7.51 – 7.48 (m, 2H, Ar-*H*), 7.28 (m, *J* = 7.0, 1.7 Hz, 2H, Ar-*H*), 7.23 (m, *J* = 6.3, 3.8, 1.1 Hz, 1H, Ar-*H*), 5.90 (m, 1H, *H2*'), 5.49 (d, *J* = 4.5 Hz, 1H, *H1*), 5.27 – 5.22 (m, 1H, *H3'*), 5.18 (d, *J* = 10.3 Hz, 1H, *H3'*), 4.38 (dd, *J* = 6.1, 4.6 Hz, 1H, *H3*), 4.28 (ddd, *J* = 12.6, 5.7, 1.1 Hz, 1H, *H1'*), 4.19 (dd, *J* = 6.6, 3.4 Hz, 1H, *H5*), 4.13 (dd, *J* = 6.1, 4.7 Hz, 1H, *H2*), 4.05 (ddd, *J* = 12.7, 6.3, 1.1 Hz, 1H, *H1'*), 3.60 – 3.55 (m, 1H, *H4*), 1.56 (s, 3H, *isoprop.*), 1.37 (s, 3H, *isoprop.*), 1.31 (d, *J* = 6.6 Hz, 3H, *H6*).
^{13}C NMR (150 MHz, CDCl3) δ 134.67, 134.01, 131.14, 128.80, 127.11, 117.81, 110.10, 82.20, 74.38, 73.87, 73.42, 73.36, 67.98, 26.62, 25.60, 15.86.

$[\alpha]_D^{22}$ = -156 ° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{29}H_{32}O_4SNa]^+$ 359.1420, found 359.1418.

Phenyl 2,3-di-*O*-benzyl-6-deoxy-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside (11)

To a solution of phenyl 6-deoxy-2,3-*O*-(1-methyl ethylidene)-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside **10** (450 mg, 1.33 mmol) in 27 mL of MeOH was added *p*-toluenesulfonic acid (74 mg, 0.39 mmol). The resulting mixture was warmed up to 50 ℃ and stirred for 3 hours before being quenched with Et_3N (0.39 mmol). Methanol was removed under reduced pressure. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 4/1) to furnish (270 mg, 0.91mmol) desired diol. The diol (270 mg, 0.91mmol) was subsequently dissolved in 3 mL of *N*,*N*-dimethylformamide and cooled to 0 ℃ for 30 minutes before NaH (60% dispersion in mineral oil, 91 mg, 2.28 mmol) was added. The resulting mixture was stirred at 0 °C for 20 minutes before benzyl bromide (250 μL, 2.0 mmol) was added dropwise. The reaction mixture was warmed up and stirred at ambient temperature for 12 hours. The reaction mixture was quenched with water and extracted with EtOAc (3×20 mL). Combined extracts were sequentially washed with water (2×50 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 10/1), to afford 600 mg

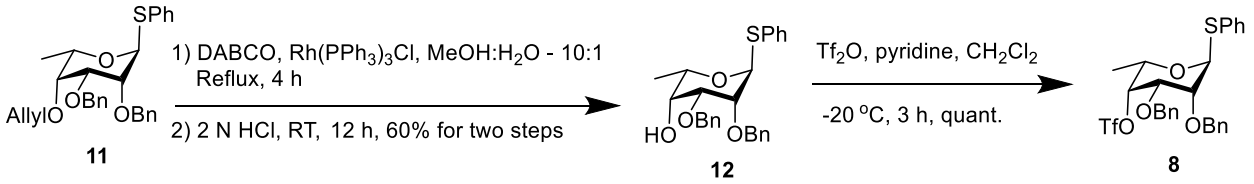
(2.29 mmol, quant) phenyl 2,3,-*O*-di-benzyl-6-deoxy-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside **11** as a pale yellow oil.

^{1}H NMR (600 MHz,$CDCl_3$) δ 7.54 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.48 – 7.41 (m, 6H, Ar-*H*), 7.41 – 7.28 (m, 7H, Ar-*H*), 6.03 (m, 1H, *H2'*), 5.81 (d, J= 4.7 Hz, 1H, *H1*), 5.39 (dd, *J* = 17.3, 1.5 Hz, 1H, *H3'*), 5.25 (d, *J* = 10.4 Hz, 1H, *H3'*), 4.92 (d, *J* = 12.6 Hz, 1H, *H1'*), 4.73 (d, *J* = 12.6 Hz, 1H, *H1'*), 4.62 (s, 2H, R-CH_2-Ph), 4.56 (dd, *J* = 12.6, 4.3 Hz, 1H, *H4*), 4.38 (d, *J* = 6.5 Hz, 1H, *H5*), 4.32 (dd, *J* = 12.8, 6.3 Hz, 1H, *H3*), 3.96 (s, 1H, RCH_2Ph), 3.82 (s, 1H, RCH_2Ar), 3.69 (s, 1H, *H2*), 1.45 (d, *J* = 6.5 Hz, 3H, *H6*).

^{13}C NMR (151 MHz, Chloroform-d) δ 138.54, 138.44, 136.00, 135.03, 130.76, 129.20, 128.43, 128.31, 127.78, 127.72, 127.49, 127.11, 116.86, 76.13, 75.33, 73.29, 72.63, 71.29, 69.23, 16.73.

$[\propto]_D^{22}$ = -56° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{18}H_{24}O_4SNa]^+$ 499.2031, found 499.2014.



Phenyl 2,3,-*O*-di-benzyl-6-deoxy-1-thio-α-L-talopyranoside (12)

To a solution of phenyl 2,3,-*O*-di-benzyl-6-deoxy-4-*O*-propen-1-yl-1-thio-α-L-talopyranoside **11** (600 mg, 1.26 mmol) in 6.3 mL MeOH and 0.6 mL H_2O was added 1,4-diazabicyclo[2.2.2]octane (DABCO) (212 mg, 1.89 mmol) and Tris(triphenylphosphine)rhodium(I) chloride ($Rh(PPh_3)_3Cl$) (233 mg, 0.252 mmol). The reaction mixture was refluxed at 80 ℃ for 4 hours followed by addition of 1.5 mL of 2 N HCl and stirred for another 12 hours at ambient temperature before being quenched with saturated $NaHCO_3$. Methanol was removed under pressure and the remaining aqueous mixture was extracted with EtOAc (3×20 mL). Combined organic extracts was sequentially washed with water (2×50 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography

(Hexanes/EtOAc = 5/1), to afford 600 mg (60% over two steps) of phenyl 2,3,-*O*-di-benzyl-6-deoxy-1-thio-α-L-talopyranoside **12** as a white solid.

^{1}H NMR (600 MHz,$CDCl_3$) δ 7.46 – 7.27 (m, 15H, Ar-*H*), 5.62 (s, 1H, *H1*), 4.74 (s, 2H, R-CH_2A-Ph), 4.59 (dd, *J* = 11.9, 2.5 Hz, 1H, R-CH_2-Ph), 4.29 – 4.26 (m, 1H, *H5*), 4.05 (s, 1H, *H2*), 3.86 (d, *J* = 10.2 Hz, 1H, *H3*), 3.73 – 3.69 (m, 1H, *H4*), 3.66 (dd, *J* = 10.3, 3.7 Hz, 1H, R-CH_2-Ph), 1.38 (dd, *J* = 6.4, 3.1 Hz, 3H, *H6*).

^{13}C NMR (150 MHz, CDCl3) δ 137.95, 137.24, 134.39, 131.36, 129.22, 128.61, 128.22, 128.16, 127.94, 127.86, 127.55, 86.46, 77.43, 74.15, 73.42, 70.54, 69.88, 69.15, 16.67.

$[\propto]_D^{22}$ = -25.8° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{26}H_{28}O_4SNa]^+$ 459.1738, found 459.1711.

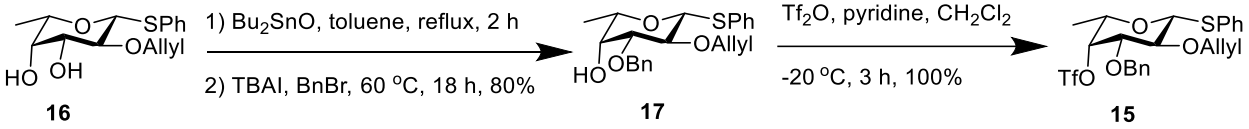
Phenyl 2,3,-*O*-di-benzyl-6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate)-1-thio-α-L-talopyranoside (8)

To a solution of phenyl 2,3,-*O*-di-benzyl-6-deoxy-1-thio-α-L-talopyranoside **12** (100 mg, 0.22 mmol) in 1.5 mL of CH_2Cl_2 and pyridine (170 μL, 2.2 mmol) cooled to -20 ℃ was added triflic anhydride(70 μL, 0.44 mmol) dropwise. The resulting mixture was stirred for 3 h at -20 ℃ before quenching with ice water. The organic layer was separated and washed with saturated $CuSO_4$ (2×50 mL), water (3×20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (pure CH_2Cl_2) to furnish 143 mg (quant.) of phenyl 2,3,-*O*-di-benzyl-6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate)-1-thio-α-L-talopyranoside **8** as a colorless solid, which is characterized below.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 – 7.35 (m, 8H, Ar-*H)*, 7.34 – 7.29 (m, 7H, Ar-*H*), 5.67 (d, *J* = 1.4 Hz, 1H, *H1*), 5.06 (dt, *J* = 2.9, 1.2 Hz, 1H, *H4*), 4.82 – 4.74 (m, 2H, R-*CH*$_2$-Ph), 4.72 (d, *J* = 12.0 Hz, 1H, R-*CH*$_2$-Ph), 4.57 (d, *J* = 12.1 Hz, 1H, R-*CH*$_2$-Ph), 4.53 (td, *J* = 6.5, 1.4 Hz, 1H, *H5*), 3.90 (dt, *J* = 3.3, 1.3 Hz, 1H, *H2*), 3.77 (t, *J* = 3.2 Hz, 1H, *H3*), 1.40 (d, *J* = 6.6 Hz, 3H, *H6)*.

^{13}C NMR (151 MHz, Chloroform-*d*) δ 137.84, 136.87, 133.48, 130.82, 129.22, 128.59, 128.10, 127.79, 127.68, 127.53, 118.60 (q, $^{1}J_{C\text{-}F}$ =319.2Hz), 86.33, 84.17, 74.04, 72.99, 71.33, 66.01, 16.60.

Synthesis of L-Fucose-derived Triflates



Phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-galactopyranoside (17)

To a solution of known compound phenyl 2-*O*-allyl-1-thio-β-L-fucopyranoside **16**[2] (670 mg, 2.26 mmol) in 20 mL of toluene was added Bu_2SnO (563 mg, 2.26 mmol). The reaction mixture was refluxed for 2 h using Dean-stark apparatus for water removal and then cooled to room temperature. Tetrabutylammonium iodide (TBAI) (88 mg, 0.226 mmol), benzyl bromide (0.4 mL, 3.39 mmol) were added and the resulting mixture was heated at 60 ℃ for 18 h. Toluene was removed under the reduced pressure. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 5/1) to afford the compound phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-galactopyranoside **17** (700 mg, 1.8 mmol, 80%) as a pale yellow oil which is characterized below.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 2H, Ar-*H*), 7.42 – 7.24 (m, 8H, Ar-*H*), 6.07 (m, 1H, *H2'*), 5.35 – 5.30 (m, 1H, *H3'*), 5.22 (d, *J* = 10.3 Hz, 1H, *H3'*), 4.74 (s, 2H, RC*H*$_2$Ph, 4.59 (dd, *J* = 9.7, 3.0 Hz, 1H, *H1*), 4.38 – 4.29 (m, 2H, *H1'*), 3.81 (s, 1H, *H3*), 3.65 (t, *J* = 9.3 Hz, 1H, *H2*), 3.56 – 3.49 (m, 2H, *H5*, *H4*), 2.64 (s, 1H, O*H*), 1.39 (d, *J* = 6.4 Hz, 3H, *H6*).

^{13}C NMR (150 MHz, CDCl3) δ 137.65, 134.70, 134.00, 131.44, 128.67, 128.32, 127.73, 127.68, 127.01, 117.06, 87.04, 82.45, 76.63, 74.14, 74.00, 71.90, 69.14, 16.62.

$[\propto]_D^{22}$ = +97.3° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{22}H_{26}O_4SNa]^+$ 409.1658, found 409.1688.

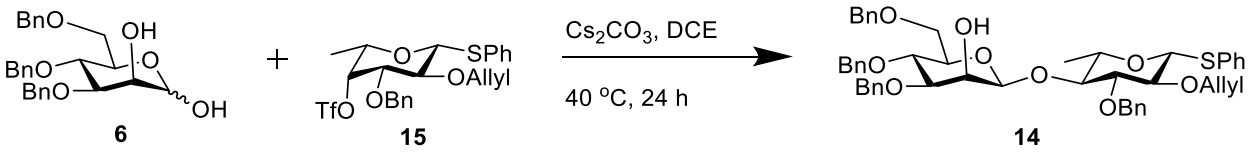
Phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-4-(1,1,1,-trifluoromethanesulfonate) -1-thio-β-L-galactopyranoside (15)

To a solution of compound phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-β-L-galactopyranoside **17** (100 mg, 0.26 mmol) in 1.5 mL of methylene chloride and pyridine (0.4 mL, 5.2 mmol) cooled to -20 ℃ for 30 min and was added triflic anhydride (87 μL, 0.52 mmol) dropwise. The resulting mixture was stirred for 3 h at -20 ℃ before quenching with water. The organic layer was washed with saturated $CuSO_4$ (2×20 mL), water (3×20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (pure CH_2Cl_2) to furnish phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-4-(1,1,1,-trifluoromethanesulfonate)-1-thio-β-L-galactopyranoside **15** (120 mg, quant.) as a colorless solid, which is characterized below.

^{1}H NMR (600 MHz, CDCl3): **δ** 7.45 – 7.42 (m, 2H), 7.30 – 7.22 (m, 4H), 7.21 – 7.15 (m, 4H), 5.83 (ddt, *J* = 16.2, 10.4, 5.8 Hz, 1H), 5.15 (m, 1H), 5.12 (m, 1H), 5.07 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.91 (d, *J* = 2.7 Hz, 1H), 4.74 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 9.3 Hz, 1H), 4.18 – 4.11 (m, 2H), 3.63 (q, *J* = 6.4 Hz, 1H), 3.50 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.43 (t, *J* = 9.4 Hz, 1H), 1.28 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 137.04, 134.55, 133.13, 132.44, 129.04, 128.58, 128.31, 128.16, 127.92, 117.61, 119.3 (q, $^1J_{C\text{-}F}$ =319.2Hz), 87.65, 85.89, 79.66, 75.79, 74.72, 73.10, 72.43, 17.14.

Anomeric *O*-Alkylation of D-Mannose Donor with L-Fucose-derived Triflate



Phenyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-β-L-glucopyranoside (14)

To a mixture of 3,4,6-tri-*O*-benzyl-D-mannopyranose **6** (576 mg, 1.28 mmol), phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-4-(1,1,1,-trifluoromethanesulfonate)-1-thio-β-L-galactopyranoside **15** (2.0 g, 3.85 mmol, 3.0 eq.) and Cs_2CO_3 (1.46 g, 4.48 mmol, 3.5 eq.) were added in 1,2-dichloroethane (16 mL). The reaction mixture was stirred at 40 ℃ for 24 h. The crude reaction mixture purified

by flash column chromatography (toluene/EtOAc= 15/1) to furnish Phenyl 3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-β-L-glucopyranoside **14** (524 mg, 0.63 mmol, 50%). The β configuration of the mannosidic linkage in **14** was assigned by measuring the $J_{(C1\text{-}H1)}$ of anomeric carbon of the mannose moiety (160.70 Hz).

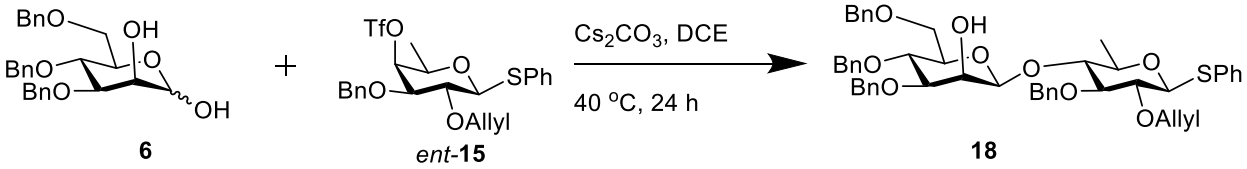
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.5 Hz, 1H, Ar-*H*), 7.46 – 7.25 (m, 24H, Ar-*H*), 6.05 (ddt, *J* = 16.4, 10.9, 5.7 Hz, 1H, *H2'*), 5.36 (d, *J* = 17.2 Hz, 1H, *H3'*), 5.26 (d, *J* = 10.4 Hz, 1H, *H3'*), 5.06 (d, *J* = 11.3 Hz, 1H, *H2mann*), 4.91 (d, *J* = 10.8 Hz, 1H, *H5mann*), 4.77 (s, 1H, *H1mann*), 4.72 (d, *J* = 11.3 Hz, 1H, *H3mann*), 4.68 (d, *J* = 10.0 Hz, 2H, R-*CH*$_2$-Ph), 4.65 – 4.59 (m, 3H, *H1gluco*, *H6mann*), 4.54 (d, *J* = 11.8 Hz, 1H, *H4mann*), 4.48 (dd, *J* = 12.1, 5.6 Hz, 1H, *H1'*), 4.30 (dd, *J* = 12.1, 6.2 Hz, 1H, *H1'*), 3.93 (d, *J* = 2.9 Hz, 1H, R-*CH*$_2$-Ph), 3.90 (t, *J* = 9.5 Hz, 1H, R-*CH*$_2$-Ph), 3.78 (t, *J* = 3.2 Hz, 2H, R-*CH*$_2$-Ph), 3.69 (t, *J* = 8.6 Hz, 1H, *H4gluco*), 3.58 – 3.52 (m, 2H, *H5gluco*, *H3gluco*), 3.43 (t, *J* = 9.3 Hz, 1H, *H2gluco*), 3.38 (ddd, *J* = 12.4, 8.5, 3.3 Hz, 2H, R-*CH*$_2$-Ph), 1.50 (d, *J* = 5.3 Hz, 3H, *H6gluco*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.51, 138.35, 138.21, 137.92, 134.61, 133.93, 131.81, 129.02, 128.69, 128.60, 128.50, 128.47, 128.28, 127.96, 127.94, 127.91, 127.72, 127.67, 127.55, 127.47, 117.66, 100.60, 87.39, 86.68, 82.13, 81.02, 80.70, 75.85, 75.36, 75.23, 74.20, 74.14, 73.63, 71.54, 69.19, 68.44, 18.33.

$[\propto]_D^{22}$ = +24.6 ° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{49}H_{54}O_9SNa]^+$ 841.3578, found 841.3600.

Anomeric *O*-Alkylation of D-Mannose Donor with D-Fucose-derived Triflate



Phenyl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-D-glucopyranoside (18)

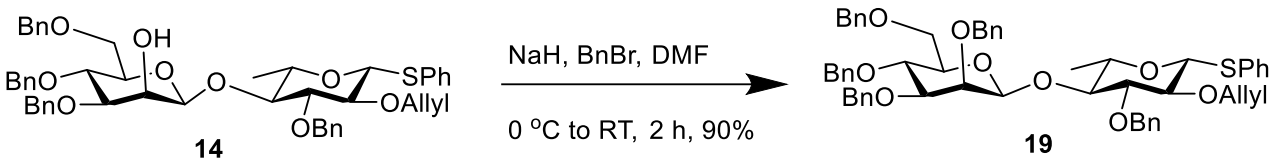
To a mixture of 3,4,6-tri-*O*-benzyl-D-mannopyranose **6** (45 mg, 0.1 mmol), phenyl 2-*O*-allyl-3-*O*-benzyl-6-deoxy-4-(1,1,1,-trifluoromethanesulfonate)-1-thio-*β*-D-galactopyranoside *ent*-**15** (prepared same as compound **15** using D-fucose) (129 mg, 0.25 mmol) and Cs_2CO_3 (98 mg, 0.30 mmol) were added in 1,2-dichloroethane (1 mL). The reaction mixture was stirred at 40 ℃ for 24 h. The crude reaction mixture purified by flash column chromatography (toluene/EtOAc= 15/1) to furnish phenyl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-D-glucopyranoside **18** (66.3 mg, 0.809 mmol, 81%). The *β* configuration of the mannosidic linkage in was assigned by measuring the $J_{(C1\text{-}H1)}$ of anomeric carbon of the mannose moiety (160.0 Hz).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.42 – 7.23 (m, 25H, Ar-*H*), 7.21 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 5.96 (ddt, *J* = 16.5, 11.0, 5.8 Hz, 1H, *H2'*), 5.27 (d, *J* = 17.2 Hz, 1H, *H3'*), 5.18 (d, *J* = 10.3 Hz, 1H, *H3'*), 5.03 (d, *J* = 10.9 Hz, 1H, *H2mann)*, 4.87 (t, *J* = 11.8 Hz, 2H, *H4mann*, R-*CH*$_2$-Ph), 4.72 (d, *J* = 11.8 Hz, 1H, R-*CH*$_2$-Ph), 4.67 – 4.59 (m, 3H, R-*CH*$_2$-Ph, *H1mann, H1gluco*), 4.54 (d, *J* = 10.8 Hz, 1H, *H3mann*), 4.45 (d, *J* = 3.0 Hz, 2H, R-*CH*$_2$-Ph), 4.36 (dd, *J* = 11.8, 5.7 Hz, 1H, *H1'*), 4.25 (dd, *J* = 11.8, 6.1 Hz, 1H, *H1'*), 4.03 (d, *J* = 2.9 Hz, 1H, *H4gluco*), 3.87 (t, *J* = 9.5 Hz, 1H, *H5mann*), 3.71 – 3.62 (m, 2H, R-*CH*$_2$-Ph), 3.59 – 3.50 (m, 3H, *H6mann, H3gluco*), 3.46 (dd, *J* = 9.6, 5.8 Hz, 1H, *H5gluco*), 3.35 (t, *J* = 8.7 Hz, 2H, *H2gluco*, R-*CH*$_2$-Ph), 2.61 (s, 1H, *OH*), 1.36 (d, *J* = 6.1 Hz, 3H, *H6-gluco*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.71, 138.33, 138.21, 137.84, 134.60, 133.80, 131.85, 128.93, 128.53, 128.40, 128.10, 127.93, 127.89, 127.74, 127.51, 117.49, 100.13, 87.40, 84.72, 81.68, 81.32, 80.78, 75.67, 75.39, 75.23, 74.31, 73.99, 73.41, 71.50, 69.03, 68.23, 18.42.

$[\propto]_D^{22}$ = -24.3 ° (c =1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{49}H_{54}O_9SNa]^+$ 841.36, found 841.34.



Phenyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside (19)

To a solution of compound phenyl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside **14** (500 mg, 0.61 mmol) in 2.0 mL *N*, *N*-dimethylformamide cooled to 0 ℃ was added sodium hydride (60% dispertion in mineral oil, 30 mg, 0.73 mmol) portion wise. The resulting mixture was stirred at 0 ℃ for 30 minutes before benzyl bromide (109 μL, 0.915 mmol) was added dropwise. The reaction mixture was warmed up and stirred at ambient temperature for 2 h and was quenched with water. The resulting mixture was extracted with EtOAc (3×20 mL). The organic layer was washed with water (2×50 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc =20/1), to afford the compound phenyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside **19** (498 mg, 0.54 mmol, 90%) as a colorless oil which is characterized below.

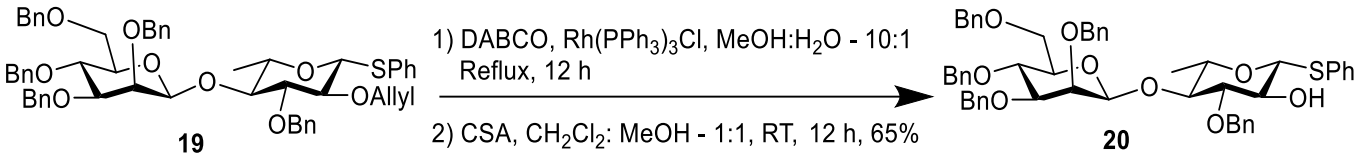
^{1}H NMR (600 MHz, Chloroform-d) δ 7.59 – 7.56 (m, 2H, Ar-*H*), 7.44 (dd, J = 7.3, 2.2 Hz, 2H, Ar-*H*), 7.36 – 7.28 (m, 21H, Ar-*H*), 7.23 (dd, J = 7.6, 1.9 Hz, 3H, Ar-*H*), 7.19 – 7.15 (m, 2H, Ar-*H*), 6.00 (ddt, J = 16.4, 10.4, 5.9 Hz, 1H, *H2'*), 5.31 (d, J = 17.2 Hz, 1H, *H3'*), 5.21 (dd, J = 10.3, 1.7 Hz, 1H, *H3'*), 4.92 (d, J = 11.5 Hz, 1H, *H4mann*), 4.87 (d, J = 10.7 Hz, 1H, *H2mann*), 4.84 (s, 2H, *H6mann*), 4.70 (d, J = 12.1 Hz, 1H, R-*CH*$_2$-Ph), 4.67 – 4.62 (m, 2H, *H1mann*, *H1gluco*), 4.59 (d, J = 5.2 Hz, 1H, R-*CH*$_2$-Ph), 4.57 (d, J = 3.9 Hz, 1H, *H5mann*), 4.41 (ddd, J = 12.1, 5.5, 1.5 Hz, 1H, *H1'*), 4.36 (d, J = 11.5 Hz, 1H, *H3mann*), 4.33 – 4.27 (m, 2H, R-*CH*$_2$-Ph), 4.24 (ddd, J = 12.0, 6.1, 1.4 Hz, 1H, *H1'*), 3.88 (t, J = 9.6 Hz, 1H, *H4gluco*), 3.80 – 3.75 (m, 2H, *H3gluco*, R-*CH*$_2$-Ph), 3.61 (d, J = 2.9 Hz, 1H, R-*CH*$_2$-Ph), 3.49 (t, J = 8.8 Hz, 1H, *H5gluco*), 3.46 – 3.42 (m, 2H, *H2gluco*, R-*CH*$_2$-Ph), 3.39 – 3.34 (m, 2H, R-*CH*$_2$-Ph), 3.22 (dd, J = 9.4, 2.9 Hz, 1H, R-*CH*$_2$-Ph), 1.48 (d, J = 5.4 Hz, 3H, *H6gluco*).

^{13}C NMR (151 MHz, Chloroform-d) δ 138.83, 138.58, 138.54, 138.33, 138.30, 134.57, 134.02, 131.69, 128.94, 128.56, 128.40, 128.36, 128.18, 128.12, 127.72, 127.69, 127.60, 127.54, 127.48,

127.43, 127.06, 117.61, 102.07, 87.41, 86.97, 83.01, 80.79, 75.86, 75.55, 75.49, 75.27, 74.76, 74.14, 73.63, 73.59, 71.69, 69.67, 18.33.

$[\propto]_D^{22}$ = +146.2° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{56}H_{60}O_9SNa]^+$ 931.3958, found 931.4012.



Phenyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside (20)

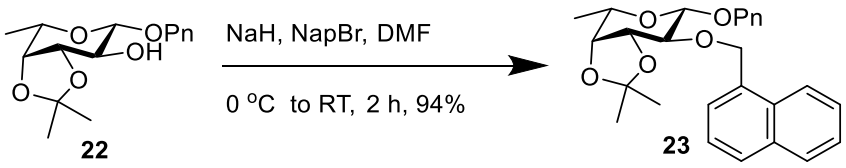
To a solution of compound phenyl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-allyl-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside **19** (530 mg, 0.58 mmol) in 3.0 mL of MeOH and 0.3 mL of H_2O (10/1) were added 1,4-diazabicyclo[2.2.2]octane (DABCO) (98 mg, 0.3 mmol), Tris(triphenylphosphine)rhodium(I) chloride ($Rh(PPh_3)_3Cl$) (21 mg, 0.023 mmol). The reaction mixture was refluxed at 80 ℃ for 12 h followed by addition of 1.5 mL of 2 N HCl and stirred for 5 minutes at room temperature to neutralize DABCO. MeOH was removed under reduced pressure. The resulting mixture was extracted with EtOAc (3×20 mL). The organic layer was washed with water (2×50 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. To the resulting crude in 2mL of CH_2Cl_2 and 2 mL of MeOH (1/1,) was added camphorsulfonic acid (13 mg, 0.058 mmol). Reaction mixture was stirred 12 h at ambient temperature and then quenched with solid $NaHCO_3$. MeOH was removed under reduced pressure. The resulting mixture was extracted with EtOAc (3×20 mL). The organic layer was washed with water (2×50 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 5/1), to afford the compound phenyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-1-thio-*β*-L-glucopyranoside **20** (327 mg, 0.37 mmol, 65% for two steps) as white solid which is characterized below.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 6.6, 3.0 Hz, 2H, Ar-*H*), 7.46 – 7.43 (m, 2H, Ar-*H*), 7.39 – 7.26 (m, 21H, Ar-*H*), 7.24 (tt, *J* = 4.8, 2.5 Hz, 3H, Ar-*H*), 7.21 – 7.19 (m, 2H, Ar-*H*), 4.95 (d, *J* = 11.6 Hz, 1H, *H2mann*), 4.89 (d, *J* = 10.7 Hz, 1H, *H5mann*), 4.84 (d, *J* = 3.1 Hz, 2H, R-*CH*$_2$-Ph), 4.70 (d, *J* = 11.9 Hz, 1H, *H6mann*), 4.66 (s, 1H, *H1mann*), 4.59 (d, *J* = 2.8 Hz, 1H, *H4mann*), 4.57 (d, *J* = 1.5 Hz, 1H, *H6mann*), 4.54 (d, *J* = 9.4 Hz, 1H, *H1gluco*), 4.40 (d, *J* = 11.7 Hz, 1H, *H3mann*), 4.32 (s, 2H, R-*CH*$_2$-Ph), 3.88 (t, *J* = 9.6 Hz, 1H, *H4gluco*), 3.82 – 3.76 (m, 2H, R-*CH*$_2$-Ph), 3.65 (d, *J* = 2.9 Hz, 1H, *H3gluco*), 3.50 (td, *J* = 8.2, 7.7, 3.1 Hz, 2H, *H5gluco*, *H2gluco*), 3.48 – 3.41 (m, 2H, R-*CH*$_2$-Ph), 3.38 (ddt, *J* = 9.8, 4.7, 2.8 Hz, 1H, R-*CH*$_2$-Ph), 3.25 (dd, *J* = 9.5, 2.9 Hz, 1H, R-*CH*$_2$-Ph), 2.50 (s, 1H, *OH*), 1.51 (d, *J* = 6.0 Hz, 3H, *H6gluco*).

^{13}C NMR (151 MHz, Chloroform-d) δ 138.88, 138.65, 138.58, 138.32, 132.83, 131.78, 129.11, 128.55, 128.40, 128.36, 128.23, 128.17, 128.13, 127.74, 127.69, 127.61, 127.50, 127.45, 127.24, 102.18, 88.33, 86.23, 82.97, 80.76, 75.89, 75.82, 75.26, 75.15, 74.75, 73.80, 73.72, 73.61, 73.07, 71.69, 69.70, 18.39.

$[\alpha]_D^{22}$ = +117.8° (c =1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{53}H_{56}O_9SNa]^+$ 891.3645, found 891.3621.



4-Penten-1-yl 6-deoxy-3,4-*O*-(1-methylethylidene)-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside (23)

To a solution of 4-penten-1-yl 6-deoxy-3,4-*O*-(1-methylethylidene)-*β*-L-galactopyranoside **22**[3] (3.7 g, 13.59 mmol) in 25.0 mL of *N*,*N*-dimethylformamide cooled to 0 °C was added sodium hydride (60% dispersion in mineral oil, 815 mg, 20.83 mmol) portion wise. The resulting mixture was stirred at 0 °C for 20 minutes before 2-(bromomethyl)naphthalene (3.6 g, 16.30 mmol) was added portion wise. The reaction mixture was warmed up and stirred at ambient temperature for 2 hours. The reaction mixture was quenched with methanol and extracted with EtOAc (3×20 mL). Combined extracts were sequentially washed with water (2×20 mL) and brine (20 mL), dried over

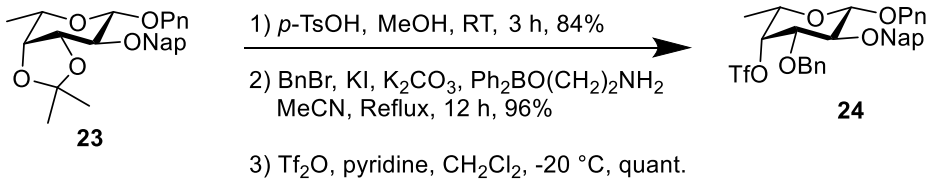
anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 10/1), to afford 5.2 g (12.6 mmol, 94%) of 4-penten-1-yl 6-deoxy-3,4-*O*-(1-methylethylidene)-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside **23.**

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 1H, Ar-*H*), 7.84 – 7.81 (m, 3H, Ar-*H*), 7.55 (dd, *J* = 8.4, 1.6 Hz, 1H, Ar-*H*), 7.49 – 7.44 (m, 2H, Ar-*H*), 5.86 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.06 (dt, *J* = 17.0, 1.7 Hz, 1H, *H5'*), 5.03 (s, 1H, *H5'*), 5.01 – 4.96 (m, 2H, -R*CH*$_2$Nap), 4.30 (d, *J* = 8.1 Hz, 1H, *H1*), 4.16 (dd, *J* = 7.2, 5.5 Hz, 1H, *H3*), 4.01 – 3.94 (m, 2H, *H1'*), 3.81 (qd, *J* = 6.6, 2.1 Hz, 1H, *H5*), 3.53 (dt, *J* = 9.4, 6.8 Hz, 1H, *H4*), 3.44 (dd, *J* = 8.1, 7.2 Hz, 1H, *H2*), 2.25 – 2.20 (m, 2H, *H3'*), 1.80 (dddd, *J* = 14.5, 9.5, 7.4, 3.7 Hz, 2H, *H2'*), 1.40 (d, *J* = 6.6 Hz, 3H, *H6*), 1.35 (s, 3H, *H-isoprop*.), 1.31 (s, 3H, *H-isoprop*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.23, 136.01, 133.32, 133.05, 127.97, 127.69, 126.90, 126.38, 125.95, 125.75, 114.97, 109.62, 102.91, 79.59, 79.29, 76.55, 73.70, 69.07, 68.74, 30.37, 29.04, 27.91, 26.49, 16.66

$[\propto]_D^{22}$ = +183.2° (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{25}H_{32}O_5Na]^+$ 435.22, found 435.21.



4-Penten-1-yl 3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside

To a solution of 4-penten-1-yl 6-deoxy-3,4-*O*-(1-methylethylidene)-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside **23** (4.5 g, 10.9 mmol) in 36 mL of MeOH was added *p*-toluenesulfonic acid monohydrate (622 mg, 3.27 mmol). The resulting mixture was stirred at room temperature for 3 hours before being quenched with Et_3N (3.27 mmol). Methanol was removed under reduced pressure. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 2/1) to furnish (3.25 g, 9.07 mmol) desired diol. The diol (2.13 g, 5.94 mmol) was subsequently dissolved in 30 mL of CH_3CN. Benzyl bromide (1.0 mL, 8.91 mmol), potassium iodide (986 mg,

5.94 mmol), potassium carbonate (901 mg, 6.53 mmol) and 2-aminoethyl diphenylborinate (134 mg, 0.594 mmol) were added and the reaction mixture was refluxed for 12 hours. Reaction mixture was filtered and extracted with EtOAc (3×20 mL). Combined extracts were sequentially washed with water (2×50 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 5/1), to afford of 4-penten-1-yl 3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside (2.65 g, 5.7 mmol, 96%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 4H, Ar-*Hnap*), 7.55 (dd, *J* = 8.3, 1.6 Hz, 1H, Ar-*Hnap)*, 7.52 – 7.47 (m, 2H, *Ar-Hnap*), 7.40 – 7.31 (m, 5H, Ar-*Hbenzyl*), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.13 (d, *J* = 11.2 Hz, 1H*, H5'*), 5.07 (dd, *J* = 17.1, 1.8 Hz, 1H, *H5*'), 5.01 (dd, *J* = 10.1, 1.8 Hz, 1H, R*CH₂nap*), 4.95 (d, *J* = 11.3 Hz, 1H, R-C*H₂nap*), 4.77 (s, 2H, R-C*H₂*Ph), 4.39 (d, *J* = 7.8 Hz, 1H, *H1*), 4.02 (dt, *J* = 9.5, 6.4 Hz, 1H, *H4*), 3.81 – 3.77 (m, 1H, *H1'*), 3.72 (t, *J* = 9.4, 7.8 Hz, 1H, *H2*), 3.66 – 3.52 (m, 3H, *H5,H3,H1'*), 2.52 (d, *J* = 3.1 Hz, 1H, O*H*), 2.23 (ddddd, *J* = 9.5, 6.8, 5.4, 2.9, 1.4 Hz, 2H, *H3'*), 1.87 – 1.76 (m, 2H, *H2'*), 1.39 (d, *J* = 6.5 Hz, 3H, *H6*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.24, 138.06, 136.27, 133.40, 133.06, 128.55, 128.07, 128.01, 127.94, 127.89, 127.74, 126.80, 126.38, 126.03, 125.85, 114.95, 103.63, 80.97, 78.89, 75.26, 72.40, 70.01, 69.55, 69.20, 30.36, 29.07, 16.47.

$[\alpha]_D^{22}$ = +74.1° (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{29}H_{34}O_5Na]^+$ 485.24, found 485.23.

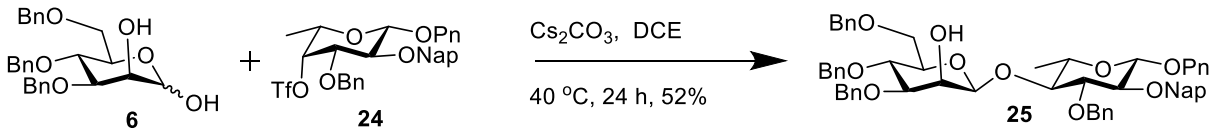
4-Penten-1-yl 3-*O*-benzyl-6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside (24)

To a solution of 4-penten-1-yl 3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside (270 mg, 0.6 mmol) in 2 mL methylene chloride and pyridine (73 µL, 0.9 mmol) cooled at -20 ℃ was added triflic anhydride (0.12 mL, 0.72 mmol) dropwise. The resulting mixture was stirred at -20 ℃ for 3 hours and then quenched with water. Organic layer was separated and washed sequentially with saturated $CuSO_4$ (2×20 mL) and water (3×20 mL), Dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (pure CH_2Cl_2) to afford 4-penten-1-yl 3-*O*-benzyl-6-deoxy-4-*O*-(1,1,1-

trifluoromethanesulfonate-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside **24** (356 mg, 0.59 mmol, quant.) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (dt, *J* = 7.1, 3.8 Hz, 1H, Ar-*Hnap*), 7.80 – 7.75 (m, 3H, Ar-*Hnap*), 7.49 – 7.45 (m, 2H, Ar-*Hnap*), 7.44 (dd, *J* = 8.4, 1.7 Hz, 1H, Ar-*H*), 7.40 – 7.35 (m, 2H, Ar-*H*), 7.31 – 7.26 (m, 3H, Ar-*H*), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.06 (d, *J* = 11.1 Hz, 1H, *H5'*), 5.04 – 5.00 (m, 1H, R-*CH$_2$-nap*), 5.00 – 4.98 (m, 1H, *H4*), 4.98 – 4.95 (m, 1H, R-*CH$_2$*-Ph), 4.90 (dd, *J* = 11.4, 4.7 Hz, 2H*, H5'*, R-*CH$_2$*-Ph), 4.68 (d, *J* = 11.8 Hz, 1H, R-*CH$_2$-nap*), 4.39 (d, *J* = 7.7 Hz, 1H, *H1*), 3.96 (dt, *J* = 9.5, 6.4 Hz, 1H, *H1'*), 3.74 – 3.67 (m, 2H, *H5*, *H2*), 3.62 (dd, *J* = 9.8, 3.0 Hz, 1H, *H3*), 3.55 (dt, *J* = 9.5, 6.8 Hz, 1H, *H1'*), 2.18 (dqt, *J* = 8.0, 6.6, 1.4 Hz, 2H, *H3'*), 1.78 (dddd, *J* = 16.3, 13.1, 8.2, 6.8 Hz, 2H, *H2'*), 1.37 (d, *J* = 6.4 Hz, 3H, *H6*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.05, 137.31, 135.85, 133.42, 133.13, 128.51, 128.21, 128.16, 128.07, 128.01, 127.79, 126.87, 126.29, 126.13, 125.98, 118.61(q, $^{1}J_{C\text{-}F}$ =319.2Hz), 115.16, 103.64, 86.08, 78.48, 77.95, 75.62, 73.42, 69.76, 68.49, 30.28, 28.99, 16.76.



4-Penten-1-yl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside (25)

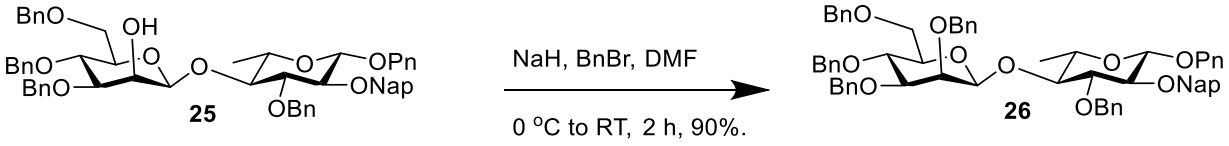
To a mixture of 3,4,6-tri-*O*-benzyl-D-mannopyranose **6** (612 mg, 1.36 mmol), 4-penten-1-yl 3-*O*-benzyl-6-deoxy-4-*O*-(1,1,1-trifluoromethanesulfonate)-2-*O*-naphthalenylmethyl-*β*-L-galactopyranoside **24** (2.44 g, 4.10 mmol) and Cs_2CO_3 (1.55 g, 4.76 mmol) were added in 1,2-dichloroethane (17.0 mL). The reaction mixture was stirred at 40 ℃ for 24 h. The crude reaction mixture was purified by flash column chromatography (Hexanes/EtOAc =5/1) to furnish 4-Penten-1-yl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside (643 mg, 0.71 mmol, 52%). The *β* configuration of the mannosidic linkage in **25** was assigned by measuring the $J_{(C1\text{-}H1)}$ of anomeric carbon of the mannose moiety (160.35 Hz).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.77 (m, 4H, Ar-*H*nap), 7.52 – 7.47 (m, 3H, Ar-*H*nap), 7.36 – 7.19 (m, 20H Ar-*H*), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.15 (d, *J* = 11.2 Hz, 1H, *H5'*), 5.10 – 5.05 (m, 1H, *H5'*), 5.05 – 5.00 (m, 2H, *H2mann*, R-*CH*$_2$-*nap*), 4.91 (d, *J* = 11.2 Hz, 1H, R-*CH*$_2$*nap*), 4.85 (d, *J* = 10.8 Hz, 1H, *H4mann*), 4.72 (s, 1H, *H1mann*), 4.65 (d, *J*=3.5 Hz, 1H, R-*CH*$_2$-Ph), 4.63 (d, J=2.7 Hz, 1H, *H3 mann*), 4.59 (d, *J* = 2.8 Hz, 1H, *H5mann*), 4.57 (d, *J* = 1.7 Hz, 2H, *H6mann*), 4.55 (s, 1H, R-*CH*$_2$-Ph), 4.50 (d, *J* = 11.7 Hz, 1H, R-*CH*$_2$-Ph), 4.45 (d, *J* = 7.8 Hz, 1H, *H1gluco*), 4.01 (dt, *J* = 9.6, 6.4 Hz, 1H, *H3gluco*), 3.88 – 3.86 (m, 1H, *H1'*), 3.84 (d, *J* = 9.5 Hz, 1H, *H1'*), 3.74 (dd, *J* = 11.1, 4.6 Hz, 1H, R-*CH*$_2$-Ph), 3.70 (dd, *J* = 11.1, 2.0 Hz, 1H, R-*CH*$_2$-Ph), 3.66 – 3.59 (m, 2H, R-*CH*$_2$-Ph), 3.52 – 3.47 (m, 3H, *H5gluco*, R-*CH*$_2$-Ph), 3.32 (ddd, *J* = 9.3, 7.4, 2.5 Hz, 2H, R-*CH*$_2$-Ph), 2.27 – 2.20 (m, 2H, *H3'*), 1.83 (dq, *J* = 13.5, 6.7 Hz, 2H, *H2'*), 1.42 (d, *J* = 5.4 Hz, 3H, *H6gluco*)

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.72, 138.49, 138.30, 137.98, 135.92, 133.42, 133.13, 128.64, 128.53, 128.48, 128.30, 128.08, 127.99, 127.91, 127.87, 127.84, 127.80, 127.75, 127.65, 127.55, 127.10, 126.43, 126.17, 126.02, 115.12, 103.57, 100.63, 84.64, 82.47, 82.21, 81.14, 75.88, 75.39, 75.33, 74.92, 74.21, 73.69, 71.65, 70.77, 69.56, 69.21, 68.54, 30.41, 29.15, 18.07.

$[\alpha]_D^{22}$ = +113.2° (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{56}H_{62}O_{10}Na]^+$ 917.43, found 917.42.



4-Penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside (26)

To a solution of compound 4-penten-1-yl 3,4,6-tri-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside **25** (60 mg, 0.073 mmol) in 0.25 mL *N*,*N*-dimethylformamide cooled to 0 ℃ was added sodium hydride (60% dispertion in mineral oil, 4 mg, 0.088 mmol) portionwise. The resulting mixture was stirred at 0 ℃ for 30 minutes before benzyl bromide (13 μL, 0.11 mmol) was added dropwise. The reaction mixture was warmed

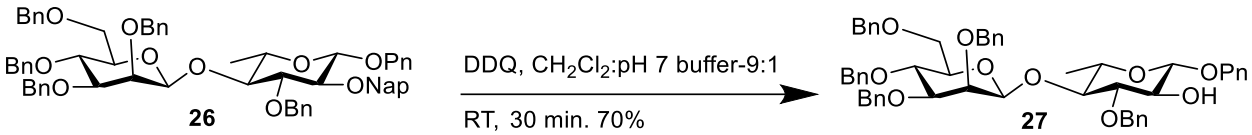
up and stirred at ambient temperature for 2 h and was quenched with water. The resulting mixture was extracted with CH_2Cl_2 (3×10 mL). The organic layer was washed with water (2×10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 10/1), to afford the compound 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside **26** (60 mg, 0.066 mmol, 90%) as a colorless oil which is characterized below.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 – 7.83 (m, 1H, Ar-*H*nap), 7.82 – 7.76 (m, 3H, Ar-*H*nap), 7.51 – 7.48 (m, 3H, Ar-*H*), 7.44 (dd, *J* = 7.5, 2.0 Hz, 2H, Ar-*H*), 7.37 – 7.28 (m, 16H, *Ar-H*), 7.23 (td, *J* = 5.5, 2.4 Hz, 4H, *Ar-H*), 7.10 (dd, *J* = 7.4, 2.1 Hz, 2H, *Ar-H*), 5.88 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.14 (d, *J* = 11.3 Hz, 1H, *H5'*), 5.10 – 5.06 (m, 1H, *H5'*), 5.02 (dq, *J* = 10.2, 1.4 Hz, 1H, R-*CH*$_2$-nap), 4.96 (d, *J* = 11.4 Hz, 1H, *H4mann*), 4.90 (d, *J* = 11.3 Hz, 1H, R-*CH*$_2$-nap), 4.88 (d, *J* = 3.5 Hz, 1H, *H2mann*), 4.85 (d, *J* = 2.3 Hz, 1H, R-*CH*$_2$-Ph), 4.71 (d, *J* = 12.1 Hz, 1H, *H1mann*), 4.64 (s, 1H, R-*CH*$_2$-Ph), 4.58 (d, *J* = 2.3 Hz, 1H, *H3mann*), 4.56 (d, *J* = 3.6 Hz, 1H, *H1gluco*), 4.49 – 4.45 (m, 1H, *H5mann*), 4.37 (s, 1H, R-*CH*$_2$-Ph), 4.33 – 4.27 (m, 2H, *H6mann*), 4.02 (dt, *J* = 9.6, 6.4 Hz, 1H, *H3gluco*), 3.89 (t, *J* = 9.6 Hz, 1H, R-CH$_2$-Ph), 3.80 (dd, *J* = 11.3, 5.2 Hz, 1H, R-CH$_2$-Ph), 3.75 (dd, *J* = 11.2, 1.9 Hz, 1H, R-*CH*$_2$-Ph), 3.66 – 3.60 (m, 2H, R-*CH*$_2$-Ph), 3.53 – 3.46 (m, 2H, *H2gluco*, R-*CH*$_2$-Ph), 3.43 (dq, *J* = 7.6, 3.1 Hz, 2H, *H5gluco*, R-*CH*$_2$-Ph), 3.36 (ddd, *J* = 9.8, 5.2, 1.9 Hz, 1H, *H1'*), 3.22 (dd, *J* = 9.4, 2.9 Hz, 1H, *H1'*), 2.24 (dddd, *J* = 12.4, 8.4, 6.4, 3.2 Hz, 2H, *H3'*), 1.84 (dq, *J* = 13.8, 6.8 Hz, 2H, *H2'*), 1.46 (d, *J* = 5.7 Hz, 3H, *H6gluco*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 138.98, 138.78, 138.73, 138.48, 138.42, 138.17, 135.97, 133.40, 133.10, 128.56, 128.46, 128.41, 128.25, 128.23, 128.19, 128.05, 127.81, 127.77, 127.65, 127.58, 127.52, 127.21, 127.05, 126.40, 126.14, 125.98, 115.10, 103.59, 102.24, 84.94, 83.09, 82.33, 81.38, 75.94, 75.58, 75.31, 74.86, 74.83, 73.79, 73.70, 71.75, 71.14, 69.70, 69.49, 30.41, 29.13, 18.13

$[\propto]_D^{22}$ = +88.3^o (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{63}H_{68}O_{10}Na]^+$ 1007.48, found 1007.47.



4-Penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-*β*-L-glucopyranoside (27)

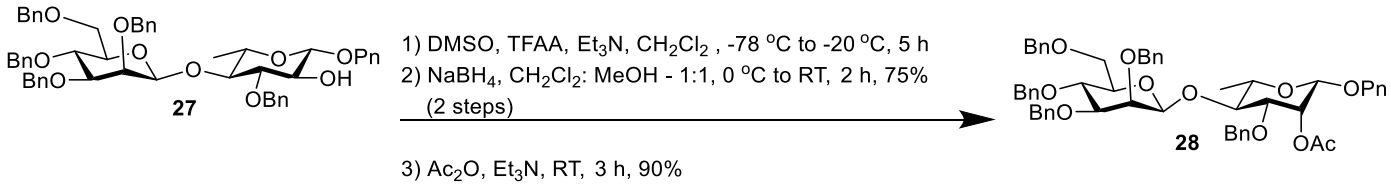
To a solution of compound 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-2-*O*-naphthalenylmethyl-*β*-L-glucopyranoside **26** (60 mg, 0.061mmol) in 0.6 mL of dichloromethane and pH 7 buffer (9/1, v/v) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (17 mg, 0.073mmol). The resulting mixture was stirred at room temperature for 30 minutes before quenching with $Na_2S_2O_3$ aqueous solution. The reaction mixture was extracted with EtOAc (3×10 mL). The organic layer was washed with water (2×10 mL), brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 3/1), to afford the compound 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-*β*-L-glucopyranoside **27** (36 mg, 0.042 mmol, 70%) as a colourless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.4, 2.1 Hz, 2H, Ar-*H*), 7.37 – 7.28 (m, 19H, Ar-*H*), 7.26 – 7.21 (m, 5H, Ar-*H*), 5.87 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.09 (dq, *J* = 17.2, 1.7 Hz, 1H, *H5'*), 5.03 (dt, *J* = 10.2, 1.6 Hz, 1H, *H5'*), 4.96 (d, *J* = 11.6 Hz, 1H, *H5mann*), 4.88 (d, *J* = 10.8 Hz, 1H, *H2mann*), 4.85 (d, *J* = 4.9 Hz, 2H, R-*CH*$_2$-Ph), 4.70 (d, *J* = 12.0 Hz, 1H, R-*CH*$_2$-Ph), 4.67 (s, 1H, *H1mann*), 4.57 (dd, *J* = 11.4, 6.6 Hz, 2H, *H3mann*, R-*CH*$_2$-Ph), 4.41 (d, *J* = 11.6 Hz, 1H, *H4mann*), 4.33 (d, *J* = 1.7 Hz, 2H, *H6mann*), 4.28 (d, *J* = 7.7 Hz, 1H, *H1gluco*), 3.97 (dt, *J* = 9.7, 6.6 Hz, 1H, *H3gluco*), 3.90 (t, *J* = 9.6 Hz, 1H, R-*CH*$_2$-Ph), 3.78 (qd, *J* = 11.2, 3.6 Hz, 2H, R-*CH*$_2$-Ph), 3.67 (d, *J* = 2.9 Hz, 1H, *H1'*), 3.60 – 3.52 (m, 2H, *H1', H2gluco*), 3.46 – 3.42 (m, 3H, R-*CH*$_2$-Ph, *H5gluco*), 3.38 (ddd, *J* = 9.9, 5.2, 2.0 Hz, 1H, *H4gluco*), 3.27 (dd, *J* = 9.5, 2.9 Hz, 1H, R-*CH*$_2$-Ph), 2.39 (d, *J* = 2.3 Hz, 1H, *OH*), 2.23 – 2.17 (m, 2H, *H3'*), 1.79 (dq, *J* = 14.3, 7.1 Hz, 2H, *H2'*), 1.46 (d, *J* = 5.4 Hz, 3H, *H6gluco*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 139.02, 138.85, 138.68, 138.47, 138.42, 138.24, 128.60, 128.48, 128.45, 128.41, 128.21, 128.19, 127.81, 127.77, 127.73, 127.67, 127.56, 127.53, 127.38, 115.09, 102.64, 102.29, 84.79, 83.05, 81.25, 75.91, 75.29, 75.24, 75.05, 74.83, 73.98, 73.80, 73.68, 71.77, 71.46, 69.72, 69.55, 30.35, 28.85, 18.14.

$[\propto]_D^{22}$ = +104.5° (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{52}H_{60}O_{10}Na]^+$ 867.42, found 867.41.



4-Penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-*β*-L-rhamnopyranoside (28)

Dimethyl sulfoxide (42 µL, 0.60 mmol) was added to 1.7 mL of dry dichloromethane and the solution was cooled to -78 ℃. Trifluoroacetic anhydride (72 µL, 0.51 mmol) was added dropwise and the mixture was allowed to react for 15 minutes. Next, a solution of 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-3-*O*-benzyl-6-deoxy-*β*-L-glucopyranoside (150 mg, 0.17 mmol) in dry dichloromethane (1.7 mL) was added. The reaction mixture was stirred at -78 ℃ for 3 hours before Et_3N (107 µL, 0.76 mmol) was added. The reaction temperature was allowed to rise to -20℃ over 2 hours and then to room temperature before being quenched with water. The resulting mixture was extracted with CH_2Cl_2 (3×10 mL). The organic layer was sequentially washed with saturated aq. $NaHCO_3$ (1x 5 mL), water (2×10 mL), and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated.

The residue was dissolved in 1.8 mL of MeOH/CH_2Cl_2 (1:1, v/v) and the solution was cooled to 0 ℃. $NaBH_4$ (13 mg, 0.34 mmol) was added and the resulting mixture was stirred at 0 ℃ for 30 minutes. The reaction was quenched with water and the mixture was extracted with EtOAc (3×10 mL). The organic layer was washed with water (2×10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography (Hexanes/EtOAc = 2/1), to afford the axial alcohol (80 mg, 0.094 mmol, 75%).

To a solution of this axial alcohol (80 mg, 0.094 mmol) in 1 mL of Et_3N was added acetic anhydride (11 µL, 0.11 mmol). The reaction mixture was stirred at room temperature for 3 hours. The solvent was removed under pressure and crude mixture was purified through flash column

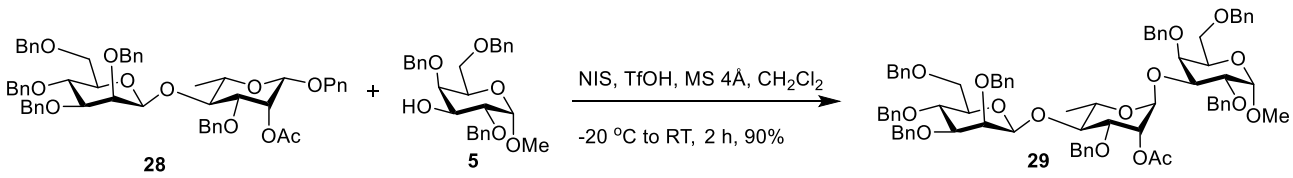
chromatography (Hexanes:EtoAc= 5:1) to afford 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-*β*-L-rhamnopyranoside **28** (75 mg, 0.084 mmol, 90%) as a colorless oil.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.47 – 7.43 (m, 2H, Ar-*H*), 7.36 – 7.25 (m, 20H, Ar-*H*), 7.24 – 7.21 (m, 2H, Ar-*H*), 7.15 (dd, *J* = 7.3, 2.2 Hz, 1H, Ar-*H*), 5.84 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H, *H4'*), 5.60 (dd, *J* = 3.4, 1.0 Hz, 1H, *H4rhamno*), 5.05 (d, *J* = 17.2 Hz, 1H, *H5'*), 5.02 – 4.99 (m, 1H, *H5'*), 4.88 (d, *J* = 10.9 Hz, 1H,R-*CH*$_2$-Ph), 4.84 (d, *J* = 4.9 Hz, 1H, *H2mann*), 4.70 (d, *J* = 1.9 Hz, 1H, R-*CH*$_2$-Ph), 4.68 (d, *J* = 3.1 Hz, 1H, *H4mann*), 4.63 (s, 1H, *H1mann*), 4.58 (d, *J* = 1.4 Hz, 1H, *H3mann*), 4.56 (d, *J* = 2.5 Hz, 1H, *H5mann*), 4.52 (d, *J* = 1.1 Hz, 1H, *H1rhamno)*, 4.42 – 4.35 (m, 2H, *H6mann)*, 4.09 (d, *J* = 10.8 Hz, 1H, *H2rhamno*), 3.94 – 3.89 (m, 1H, *H1'*), 3.88 (d, *J* = 9.6 Hz, 1H, *H1'*), 3.77 (dd, *J* = 8.0, 3.3 Hz, 2H, R-*CH*$_2$-Ph), 3.59 (t, *J* = 9.3 Hz, 1H, *H3rhamno*), 3.54 – 3.48 (m, 1H, R-*CH*$_2$-Ph), 3.45 – 3.38 (m, 2H, R-*CH*$_2$-Ph), 3.32 (dd, *J* = 9.5, 2.9 Hz, 1H, R-*CH*$_2$-Ph), 2.20 (s, 3H, R-*OAc*), 2.16 – 2.11 (m, 2H, *H3'*), 1.77 – 1.69 (m, 2H, *H2'*), 1.50 (d, *J* = 6.1 Hz, 3H, *H6 rhamno*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.89, 139.17, 138.70, 138.56, 138.40, 138.25, 137.73, 128.61, 128.51, 128.43, 128.40, 128.19, 128.11, 128.03, 127.99, 127.83, 127.72, 127.59, 127.55, 114.98, 102.31, 98.78, 83.03, 80.67, 78.85, 75.96, 75.19, 74.83, 74.19, 73.85, 73.73, 71.81, 71.72, 71.44, 69.84, 69.31, 67.93, 30.18, 28.75, 21.28, 18.15

$[\propto]_D^{22}$ = - 64.3^{o} (c=1.0, $CHCl_3$)

ESILRMS: Calculated for $[C_{54}H_{62}O_{11}Na]^+$ 909.43, found 909.42.



Methyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-β-L-rhamnopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside (29)

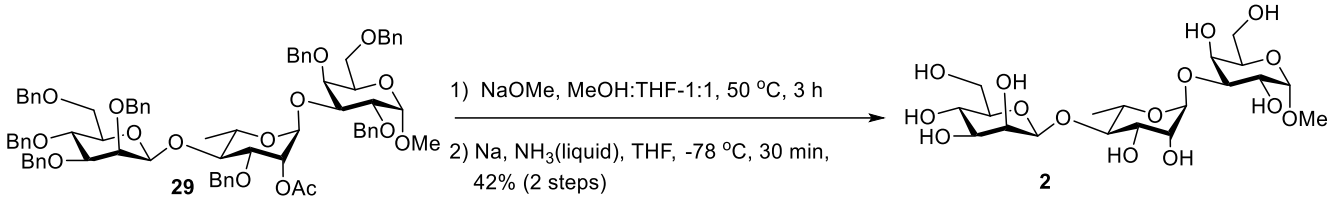
To a mixture of 4-penten-1-yl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-*β*-L-rhamnopyranoside **28** (40 mg, 0.045 mmol), D-galactose derived C-3 alcohol **5** (17 mg, 0.037 mmol), molecular sieves (40 mg) were added in CH_2Cl_2 (0.4 mL) and the reaction mixture was cooled to -20 ℃ and stirred for 10 min. *N*-Iodosuccinimide (NIS) (20 mg, 0.089 mmol) and Triflic acid (TfOH) (0.58 μL, 6.66 µmol added at -20 ℃. After stirring at -20 ℃ for 5 min. the reaction mixture was placed in an ice bath (0 ℃) and stirred for 1 h. Temperature of the reaction mixture was increased to room temperature and stirred for another 1 h. The progress of the reaction was monitored by TLC (Hexanes:EtOAc =2:1) and after the 1 h, it was completed. The reaction mixture was quenched with Et_3N (0.18 eq.) and filtered. The organic layer was washed with saturated $Na_2S_2O_3$ (2×5 mL), water (2×5 mL), brine (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude residue was purified by preparative thin layer chromatography (Hexanes/EtOAc = 2/1), to afford the compound methyl 2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2-*O*-acetyl-3-*O*-benzyl-β-L-rhamnopyranosyl-(1→3)-2,4,6-tri-*O*-benzyl-α-D-galactopyranoside **29** (42 mg, 0.033 mmol, 90%) as a colorless oil. The *α* configuration of the rhamnosidic linkage in **29** was assigned by measuring the $J_{(C1\text{-}H1)}$ of anomeric carbon of the rhamnose moiety (170.80 Hz).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 – 7.23 (m, 32H, Ar-*H*), 7.21 – 7.18 (m, 2H, Ar-*H*), 7.17 – 7.09 (m,5H, Ar-*H*), 7.07 – 7.03 (m, 1H, Ar-*H*), 5.57 (dd, *J* = 3.3, 1.8 Hz, 1H, *H4rhamno*), 5.25 (d, *J* = 1.9 Hz, 1H, *H1Gal*), 4.89 (d, *J* = 11.0 Hz, 1H, R-*CH*$_2$-Ph), 4.85 (d, *J* = 10.9 Hz, 1H, R-*CH*$_2$-Ph), 4.76 (t, *J* = 12.3 Hz, 2H, R-*CH*$_2$-Ph), 4.70 – 4.66 (m, 2H, H1mann, R-*CH*$_2$-Ph), 4.65 – 4.61 (m, 3H, R-*CH*$_2$-Ph), 4.58 (d, *J* = 4.2 Hz, 1H, *H1rhamno*), 4.55 (d, *J* = 3.2 Hz, 1H, R-*CH*$_2$-Ph), 4.53 (d, *J* = 5.3 Hz, 1H, R-*CH*$_2$-Ph), 4.50 (d, *J* = 6.3 Hz, 1H, R-*CH*$_2$-Ph), 4.43 (d, *J* = 11.9 Hz, 1H, R-*CH*$_2$-Ph), 4.31 – 4.23 (m, 2H, *H6Gal*, R-*CH*$_2$-Ph), 4.19 (dd, *J* = 10.1, 3.0 Hz, 1H, R-*CH*$_2$-Ph), 4.07 (d, *J* = 10.9 Hz, 1H, *H2mann*), 4.03 (dd, *J* = 10.1, 3.5 Hz, 1H, *H3Gal*), 3.97 (t, *J* = 6.6 Hz, 1H, R-*CH*$_2$-Ph), 3.91 (dd, *J* = 9.5, 6.2 Hz, 1H, *H5rhamno*), 3.88 – 3.86 (m, 1H, *H5Gal*), 3.83 (t, *J* = 9.5 Hz, 1H, *H5mann*), 3.78 (d, *J* = 3.4 Hz, 1H, *H3rhamno*), 3.76 (d, *J* = 3.7 Hz, 2H, *H4mann*, R-*CH*$_2$-Ph), 3.65 (d, *J* = 3.0 Hz, 1H, *H6Gal*), 3.62 (t, *J* = 9.5 Hz, 1H, *H6Gal*), 3.55 – 3.49 (m, 2H, *H2Gal*, *H3mann*), 3.39 (s, 1H, *H2 rhamno*), 3.35 (s, 3H, R-*OMe*), 3.26 (dd, *J* = 9.5, 2.9 Hz, 1H, *H4Gal*), 2.11 (s, 3H, R-*OAc*), 1.46 (d, *J* = 6.2 Hz, 3H, *H6rhamno*).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.15, 138.92, 138.64, 138.49, 138.43, 138.30, 138.03, 137.86, 137.80, 128.48, 128.44, 128.33, 128.31, 128.03, 127.99, 127.97, 127.94, 127.88, 127.85, 127.83, 127.71, 127.59, 127.53, 127.43, 127.26, 102.74, 99.27, 98.07, 82.65, 79.14, 78.15, 77.55, 75.80, 75.37, 75.18, 75.05, 74.64, 74.15, 73.78, 73.59, 73.56, 72.92, 71.62, 71.43, 69.79, 69.18, 68.71, 68.50, 68.21, 55.41, 21.11, 18.19.

$[\propto]_D^{22}$ = +23.1° (c=1.0, $CHCl_3$)

ESIHRMS: Calculated for $[C_{77}H_{84}O_{16}Na]^+$ 1287.5759, found 1287.5735.



Methyl *β*-D-mannopyranosyl-(1→4)-β-L-rhamnopyranosyl-(1→ 3)-α-D-galactopyranoside (2)

To a solution of trisaccharide **29** (24 mg, 0.023 mmol) in 0.25 mL of methanol:THF (1/1, v/v) was added NaOMe (4 µL, 0.023 mmol). The resulting mixture was heated at 50 ℃ for 3 h before the solvent was removed under reduced pressure. The residue was dried under high vaccum.

A 100 mL three-necked round-bottom flask containing a glass stir bar was equipped with a "U" shape condenser (for cooling ammonia gas) and cooled at −78 °C under argon. After acetone and dry ice were added into the "U" shape condenser, liquid ammonia (∼5 mL) was collected in the three-necked flask. A piece of sodium metal (10 mg, 0.34 mmol) was added to the flask and stirred for 15 min. Extra sodium was added until the solution remained dark blue in color. A solution of above-mentioned residue (deacetylated trisaccharide) (24 mg, 0.02 mmol) in 1 mL of THF was added and the resulting mixture was stirred at −78 °C for 30 min before being quenched with solid NH_4Cl. The reaction mixture was slowly warmed to room temperature, and liquid ammonia and THF were removed by air flow. The residue was desalted using size-exclusion chromatography (Bio-Gel P-2 Media, eluted with water) to furnish 5 mg (0.008 mmol, 42%) of desired methyl *β*-D-mannopyranosyl-(1→4)-β-L-rhamnopyranosyl-(1→ 3)-α-D-galactopyranoside **2**.

^{1}H NMR (600 MHz, Deuterium Oxide) δ 4.88 (d, *J* = 2.4 Hz, 1H), 4.78 – 4.74 (m, 1H), 3.97 – 3.92 (m, 3H), 3.86 (ddd, *J* = 9.5, 3.4, 2.1 Hz, 1H), 3.82 (dq, *J* = 9.1, 2.4 Hz, 3H), 3.78 – 3.73 (m, 2H), 3.61 (dddd, *J* = 26.2, 19.1, 8.2, 3.0 Hz, 5H), 3.55 – 3.51 (m, 1H), 3.46 (td, *J* = 9.7, 2.1 Hz, 1H), 3.31 (s, 3H), 3.27 – 3.23 (m, 1H), 1.22 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (151 MHz, Deuterium Oxide) δ 102.27, 100.60, 99.30, 79.46, 77.62, 76.16, 72.98, 70.74, 70.54, 70.30, 70.12, 69.00, 67.84, 67.37, 66.73, 61.08, 60.95, 54.97, 36.87, 31.33, 16.89.

ESILRMS: $[M-H]^-$ Calculated for $[C_{19}H_{33}O_{15}]^-$ 501.19; found 501.18.

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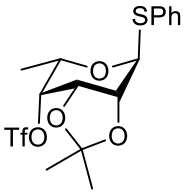
[1] T. G. Frihed, C. M. Pedersen, M. Bols, *Eur. J. Org. Chem.*, **2014**, 7924-7939.

[2] S. Ueno, S. Horito, *Carbohydrate Research*, **2011**, *346*, 2091-2097.

[3] S. Ahadi, S. I. Awan, D. B. Werz, *Chem. Eur. J.* **2020**, *26*, 6264-6270.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TfO
O

7

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77.09
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72.97
70.33
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25.77
24.87
16.56
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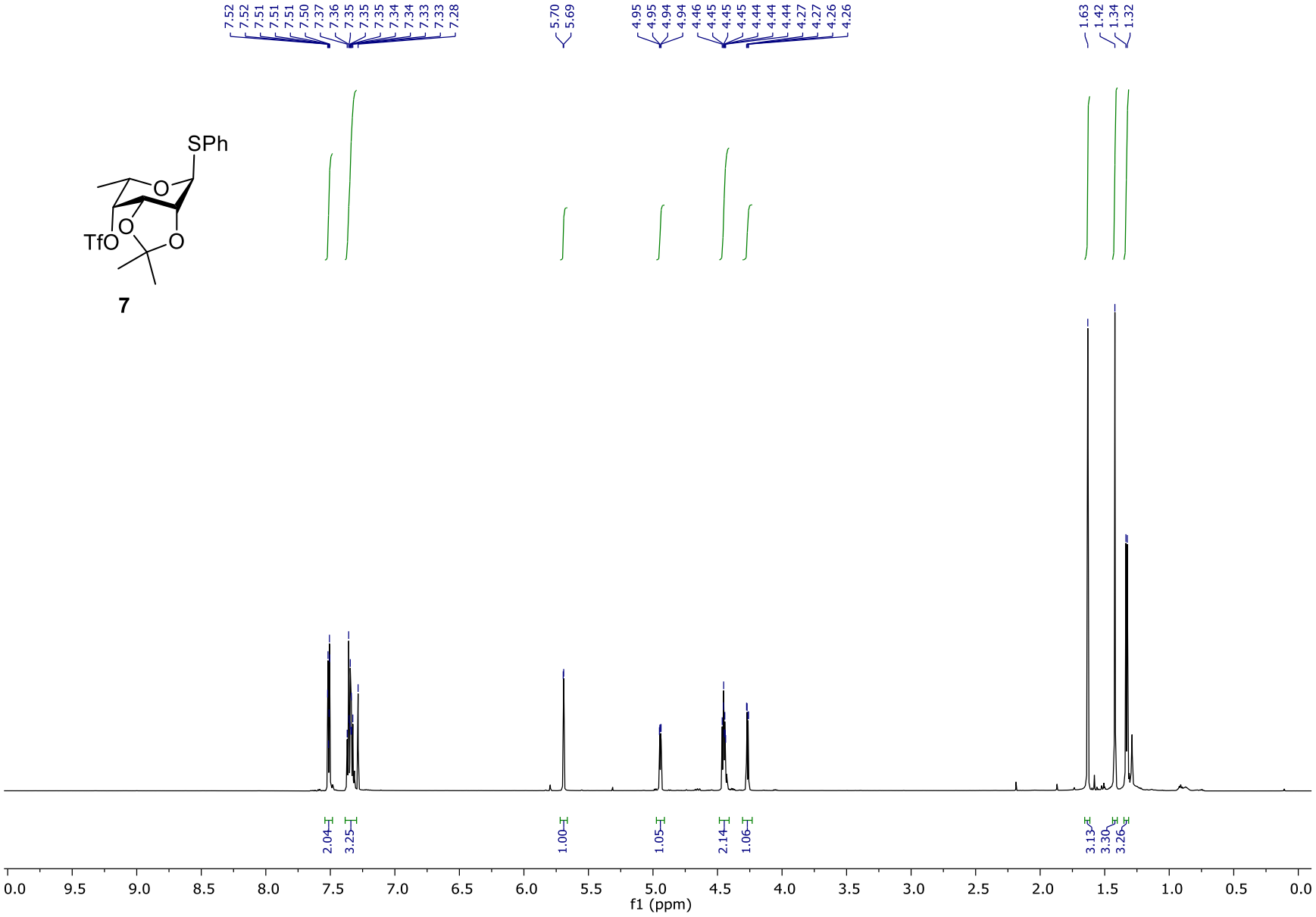
f1 (ppm)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4.94
4.94
4.46
4.45
4.45
4.45
4.44
4.44
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4.27
4.26
4.26
1.63
1.42
1.34
1.32
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O
TfO
O
7
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1.05
2.14
1.06
3.13
3.30
3.26
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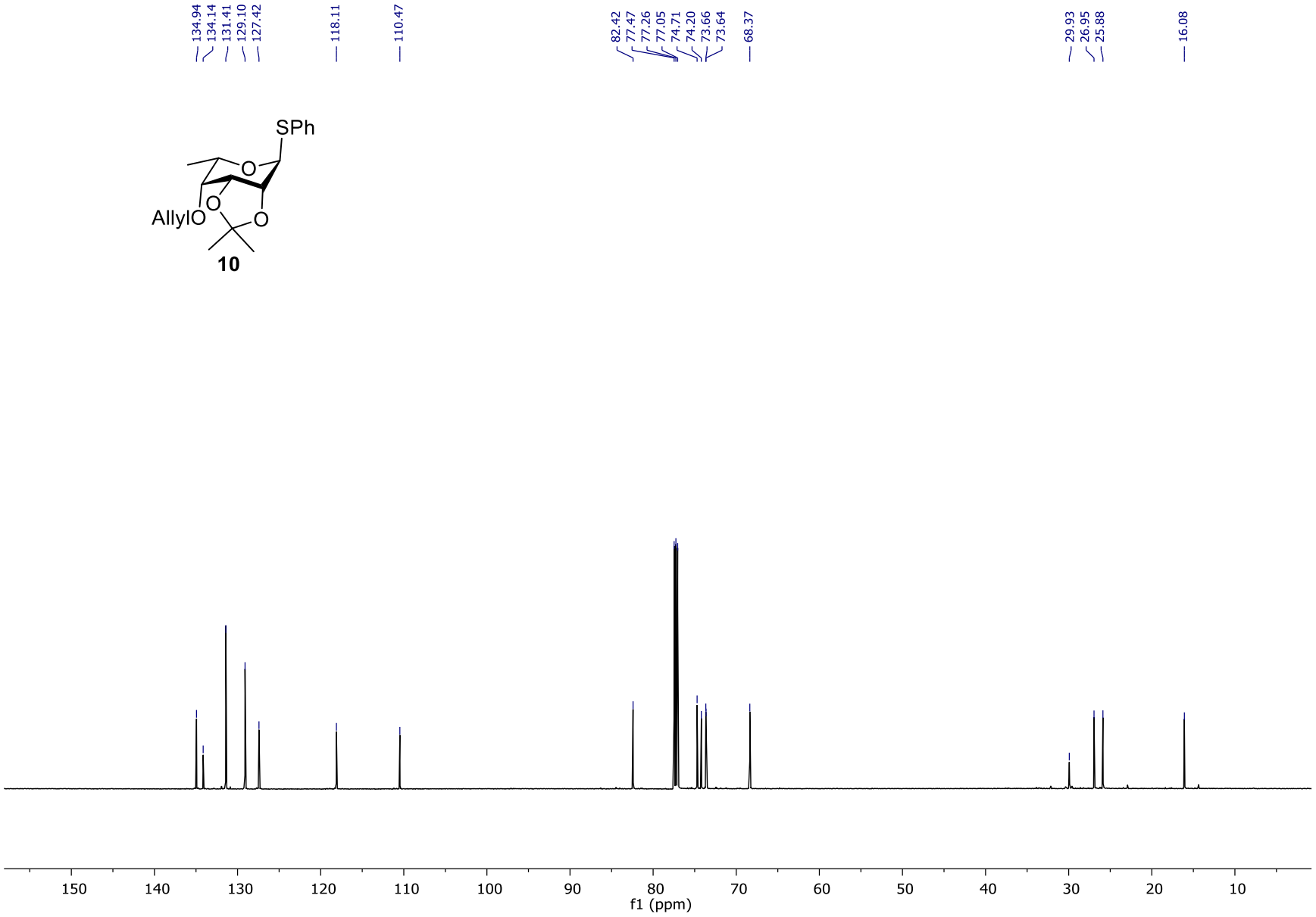
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74.20
73.66
73.64
68.37
29.93
26.95
25.88
16.08
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O
AllylO
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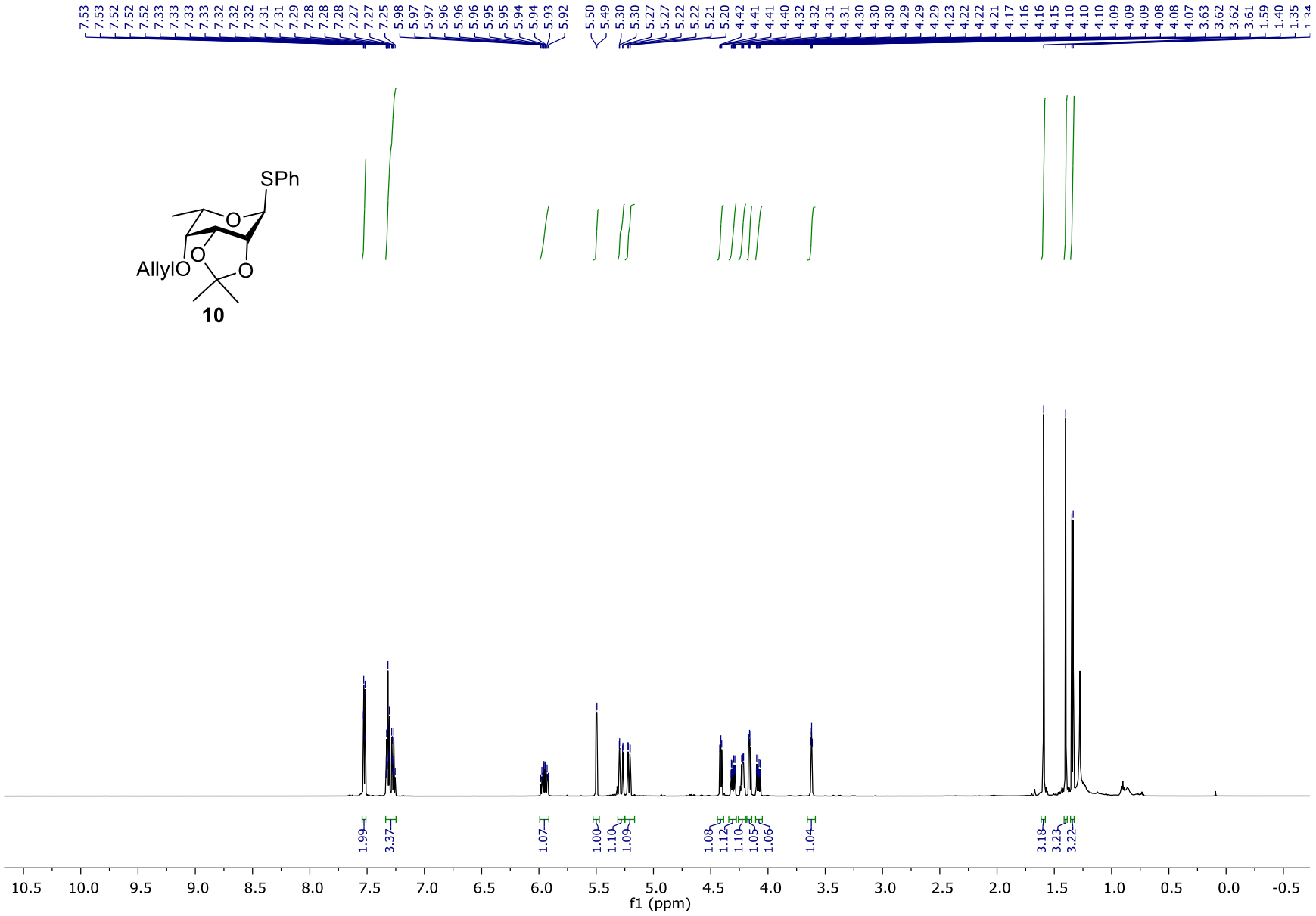
f1 (ppm)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5.50 5.49 5.30 5.30 5.27 5.22 5.22 5.21 5.20 4.42 4.41 4.41 4.40 4.32 4.32 4.31 4.31 4.30 4.30 4.30 4.29 4.29 4.29 4.23 4.22 4.22 4.21 4.17 4.16 4.16 4.15 4.10 4.10 4.10 4.09 4.09 4.09 4.08 4.08 4.07 3.63 3.62 3.62 3.61 1.59 1.40 1.35
1.99 3.37 1.07 1.00 1.10 1.09 1.08 1.12 1.10 1.05 1.06 1.04 3.18 3.23 3.22
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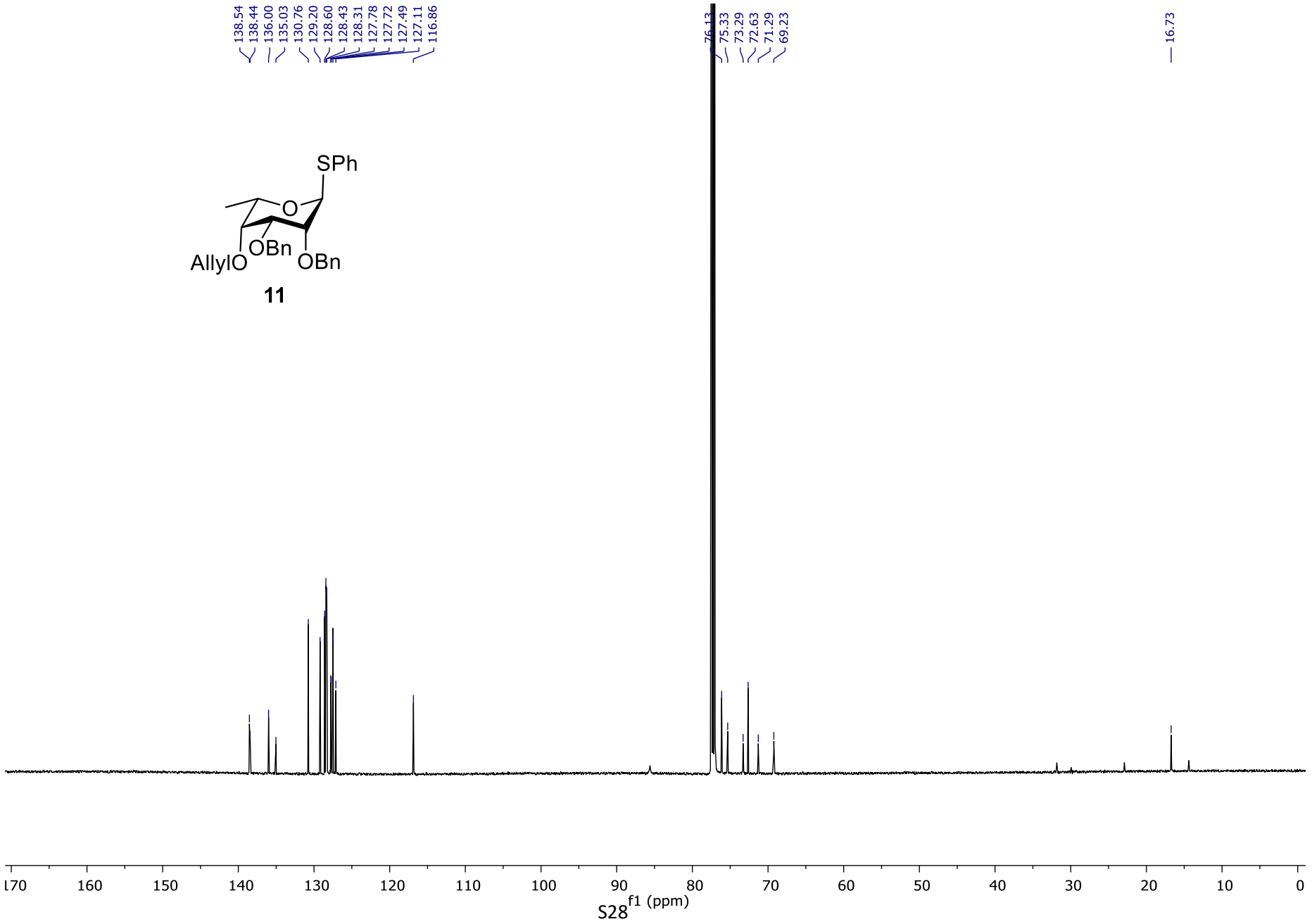
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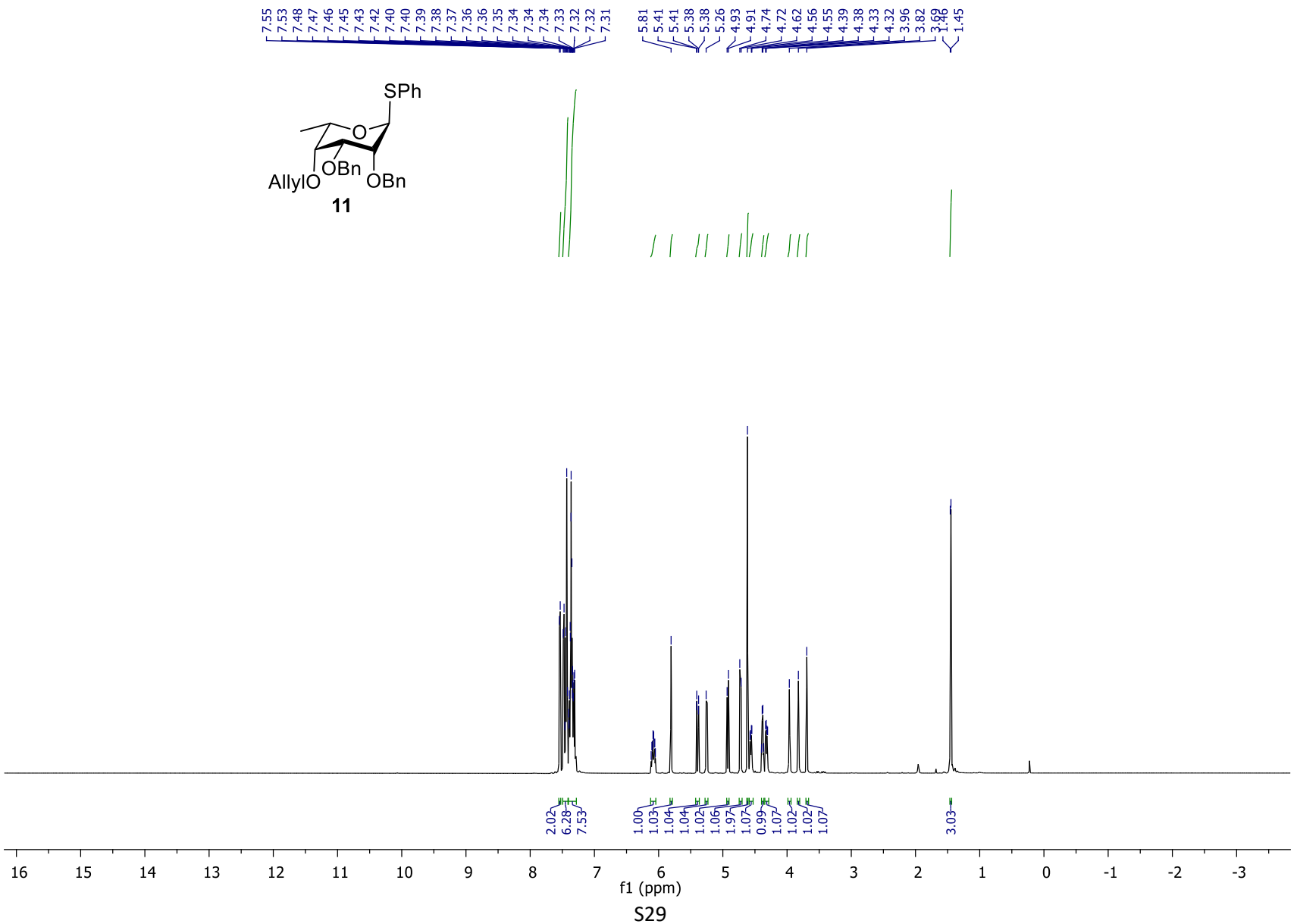
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AllylO
OBn
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1.02
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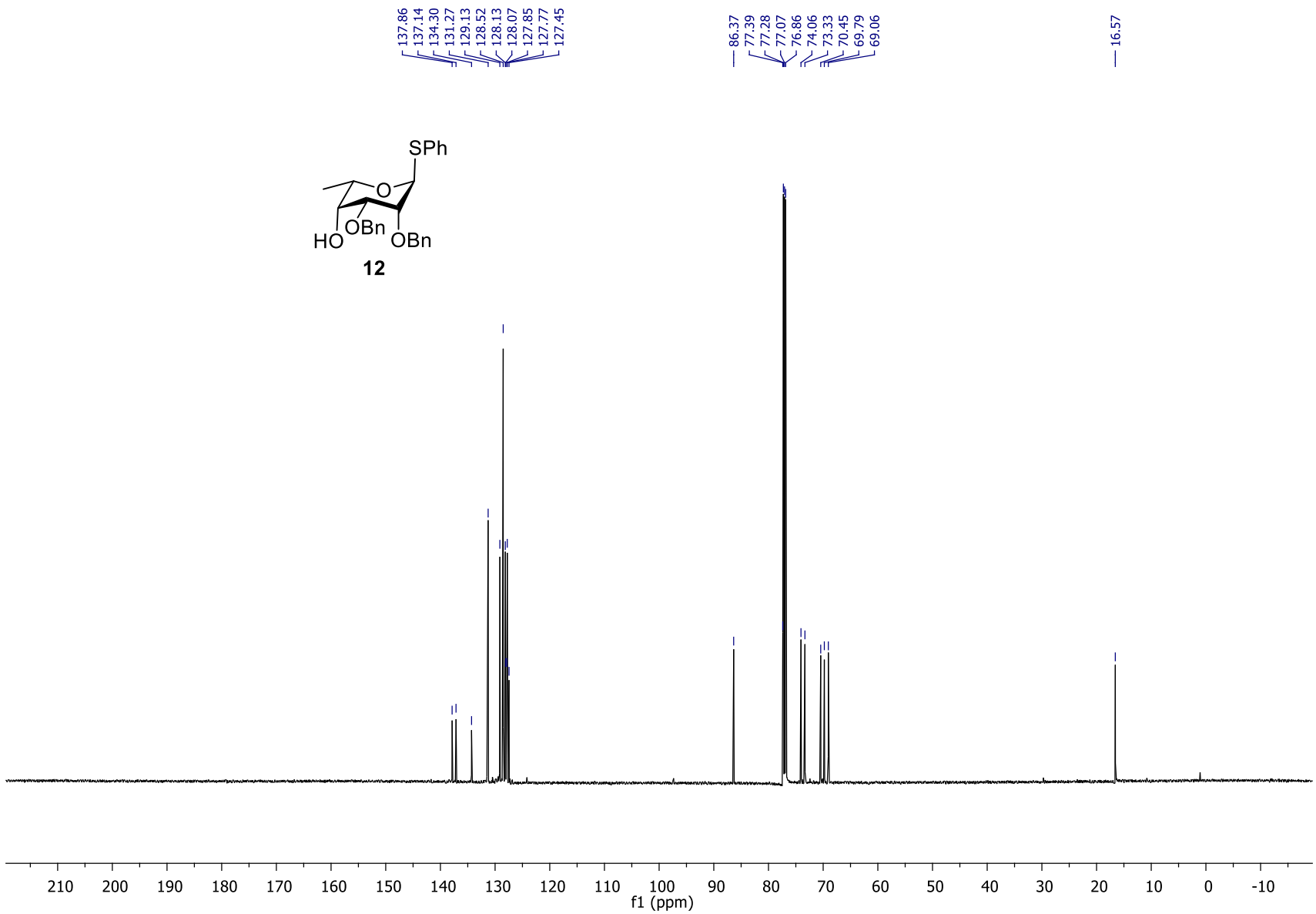
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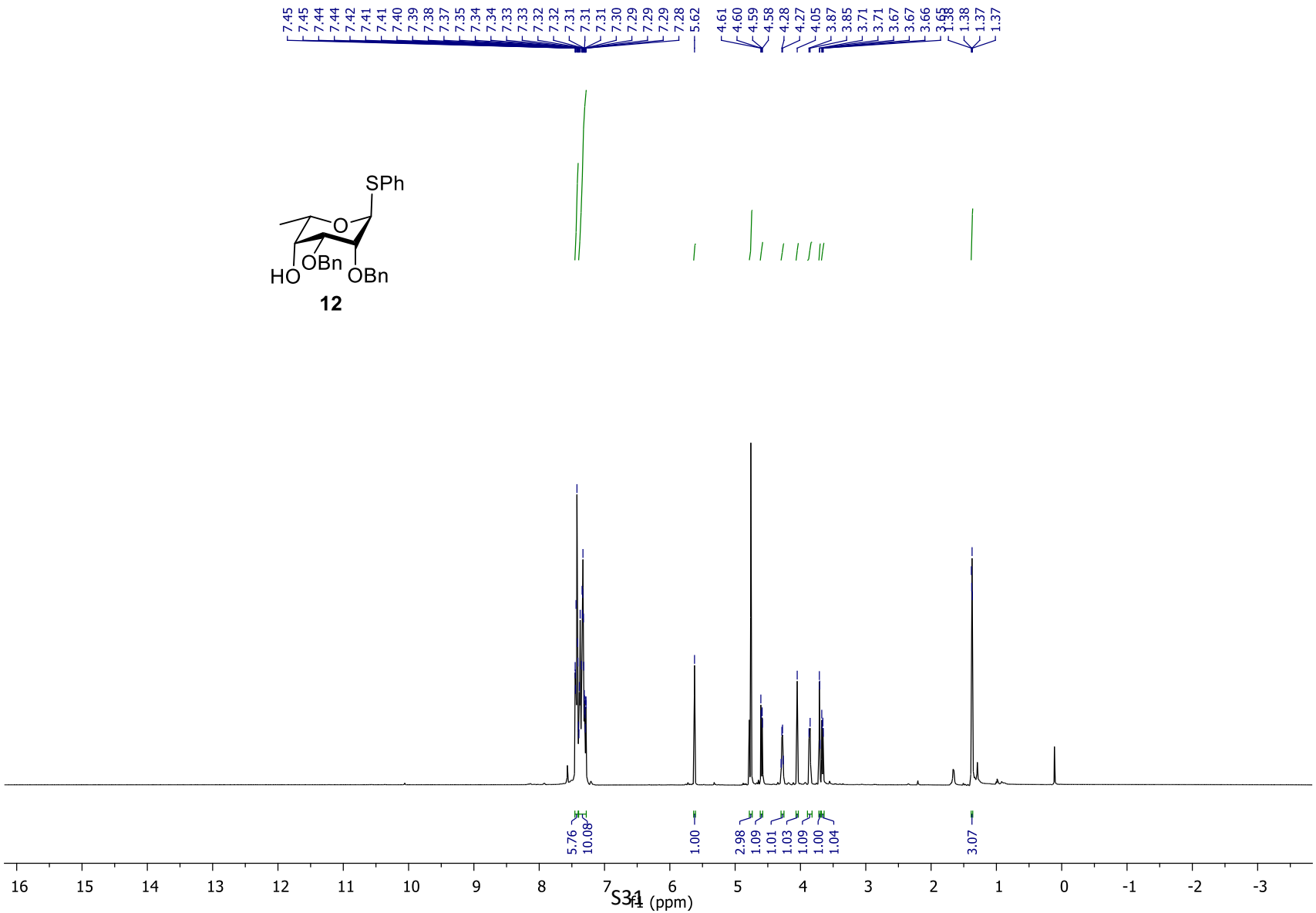
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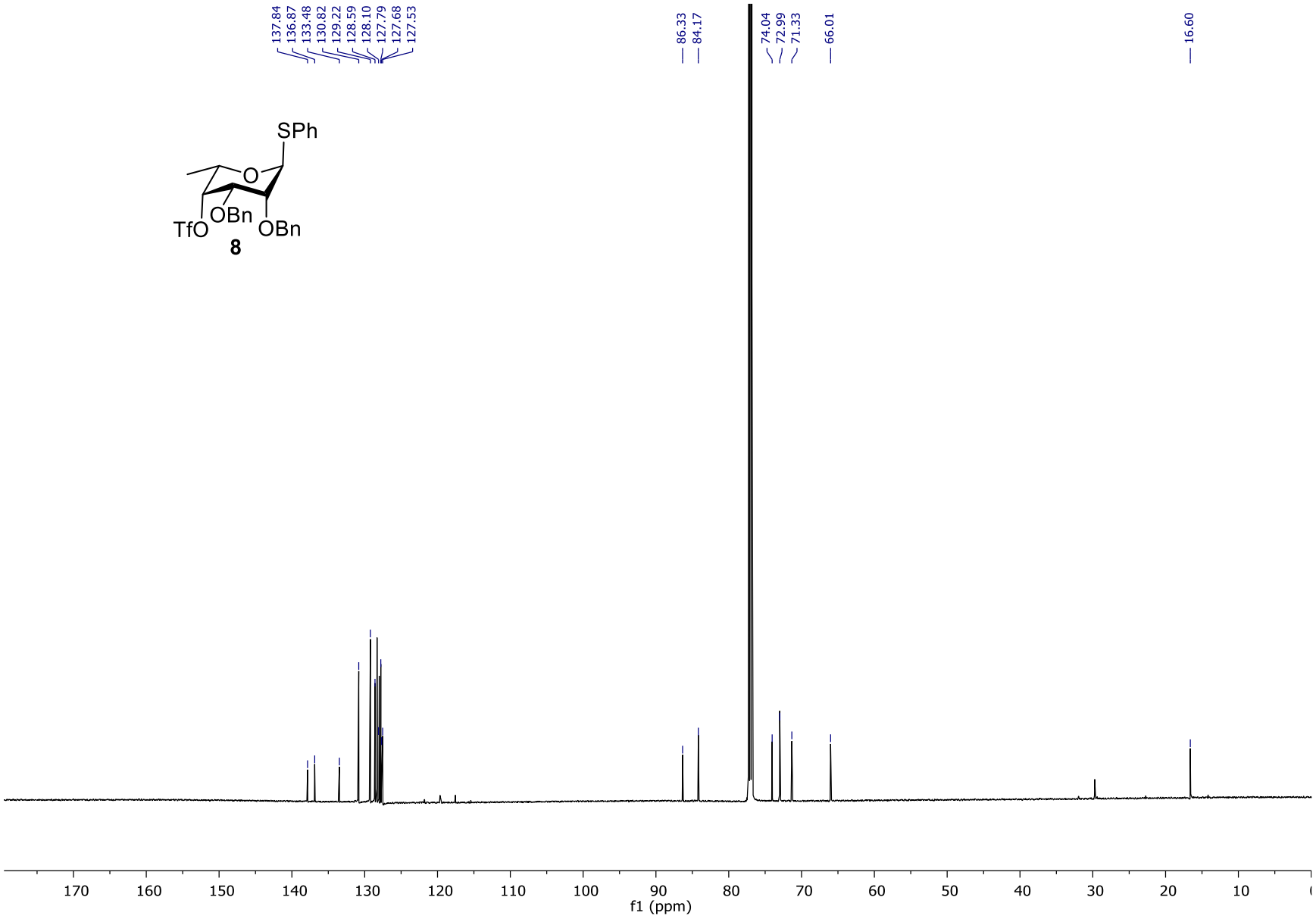
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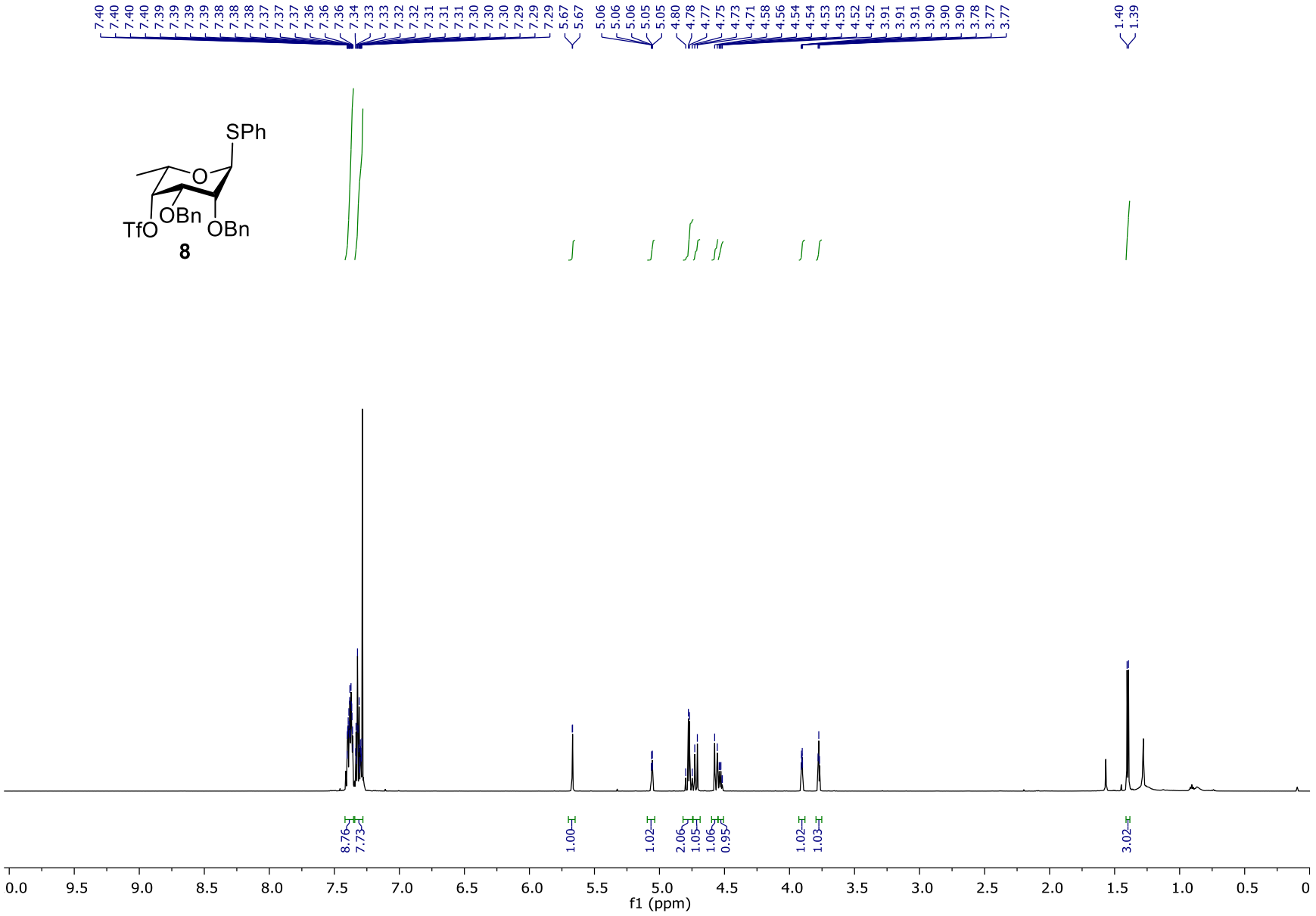
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5.67 5.67
5.06 5.06 5.06 5.05 5.05
4.80 4.78 4.77 4.75 4.73 4.71 4.58 4.56 4.54 4.54 4.54 4.53 4.53 4.52 4.52 4.52
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f1 (ppm)

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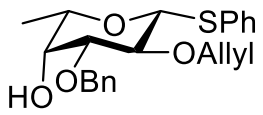

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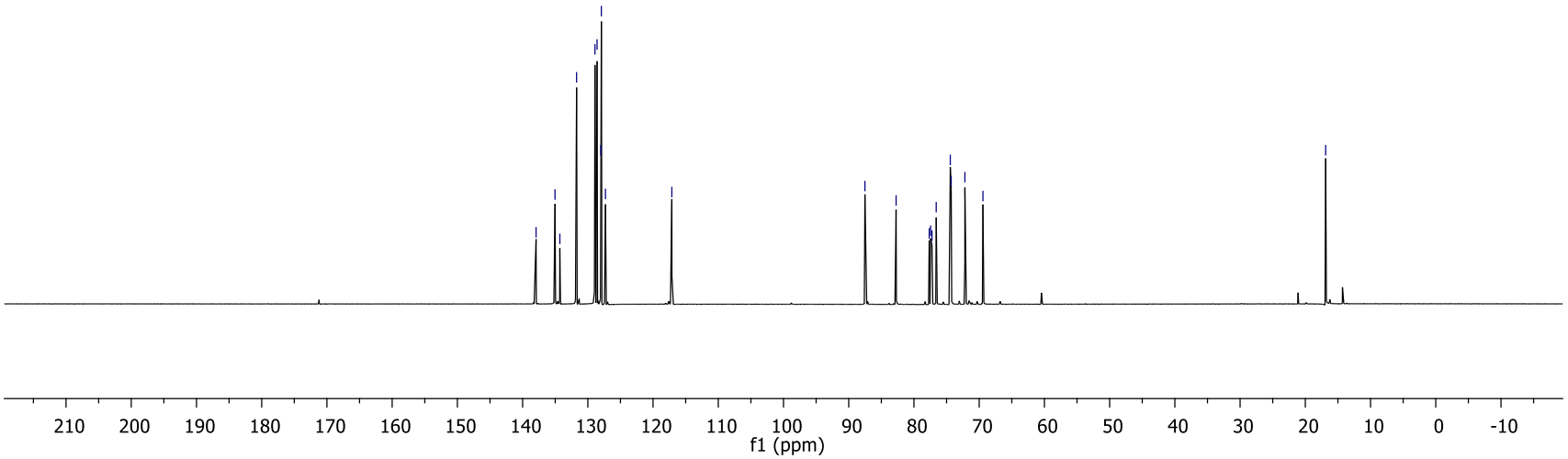

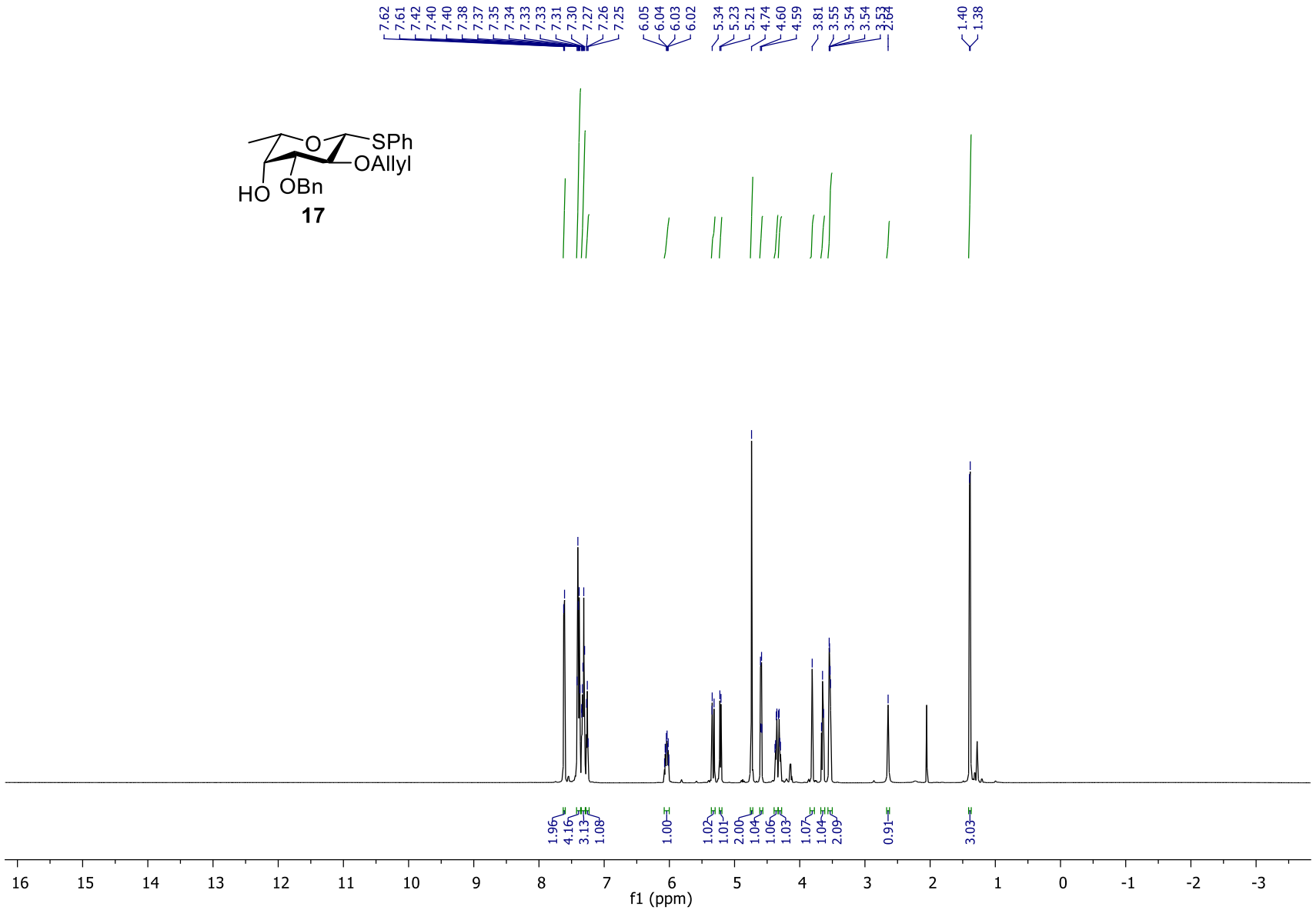
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7.26
7.25
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6.04
6.03
6.02
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3.54
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3.53
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1.38
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OAllyl
HO
OBn
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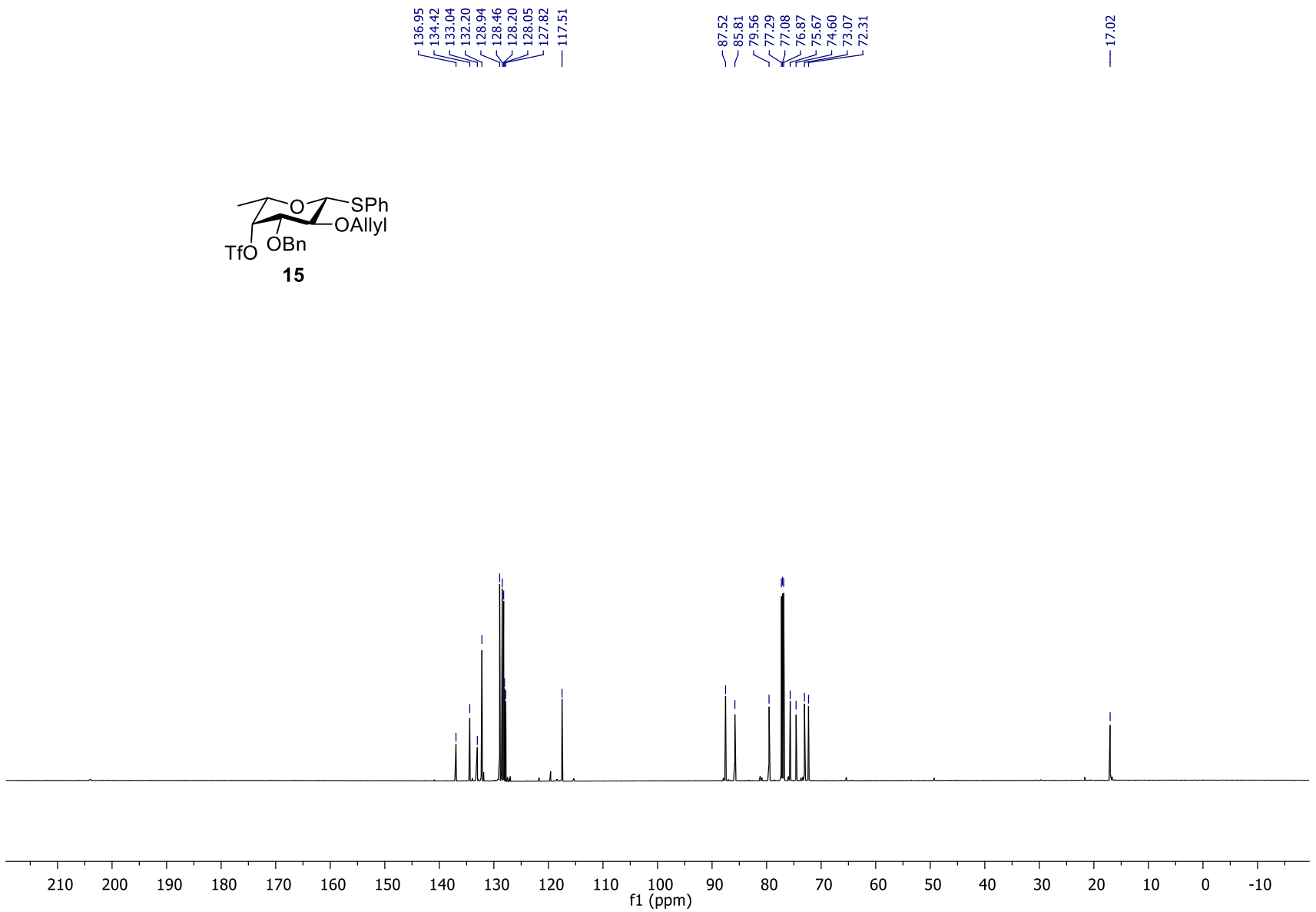
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TfO
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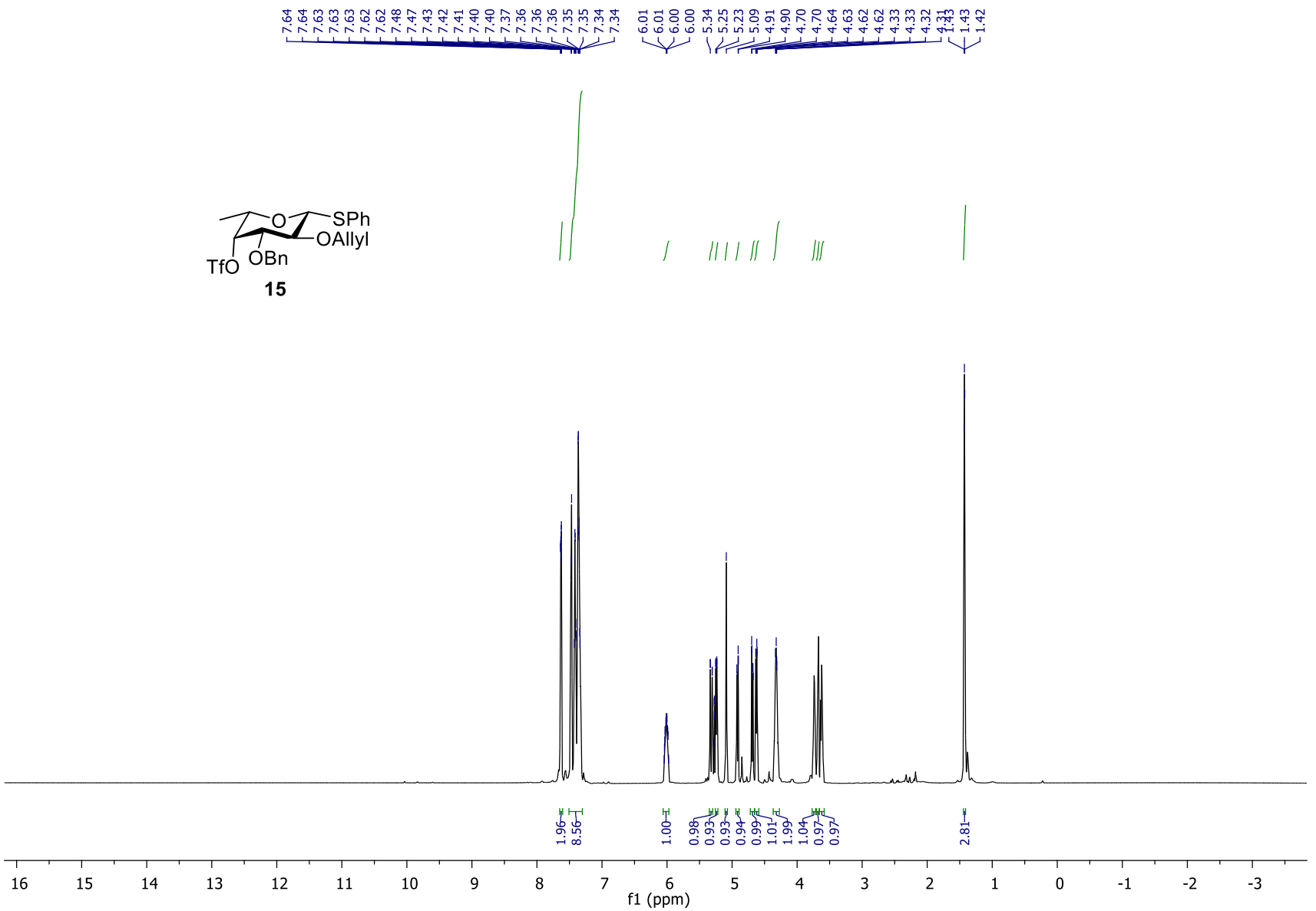
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TfO
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0.97
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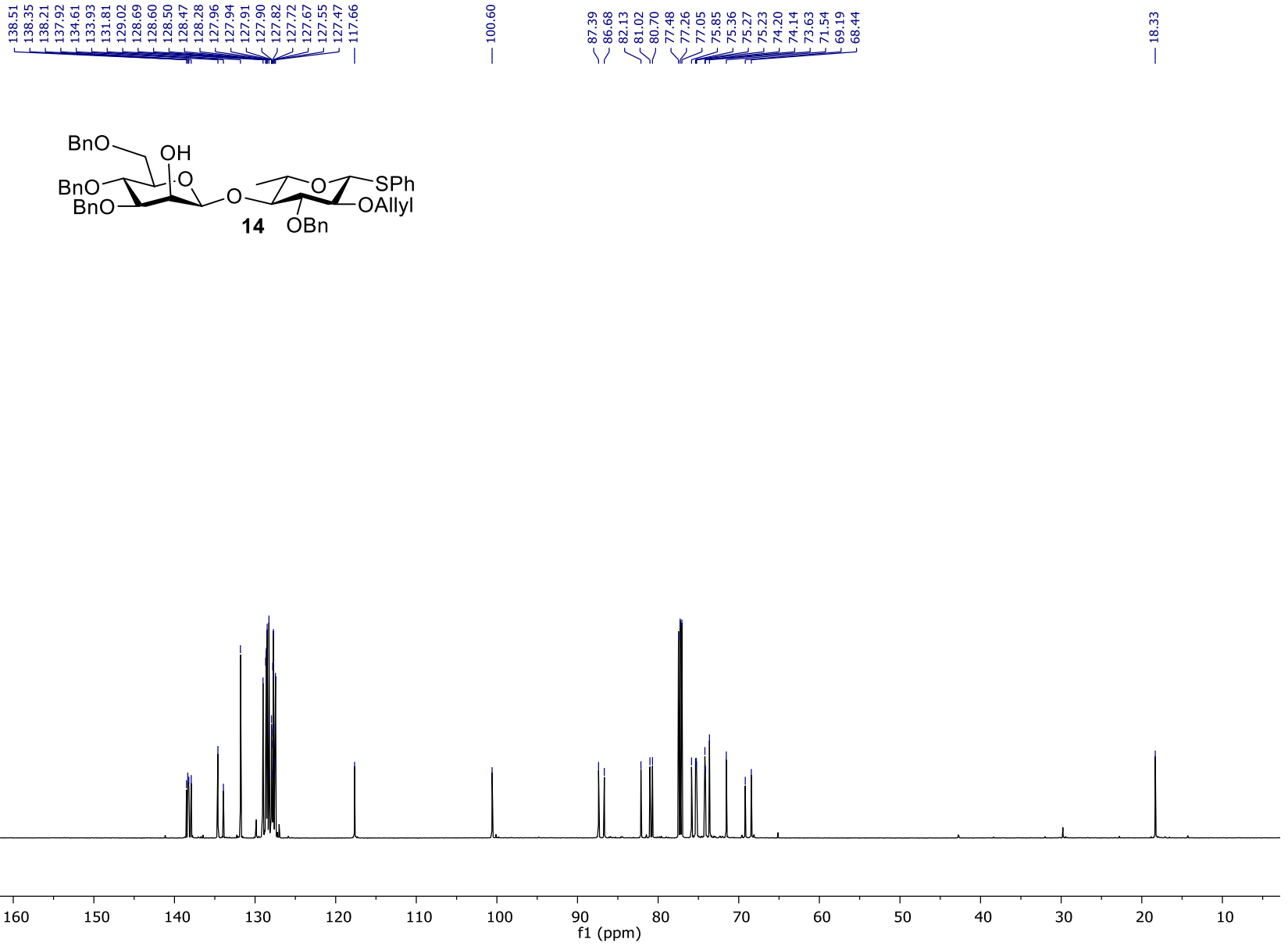
f1 (ppm)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BnO
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O
SPh
OAllyl
OBn
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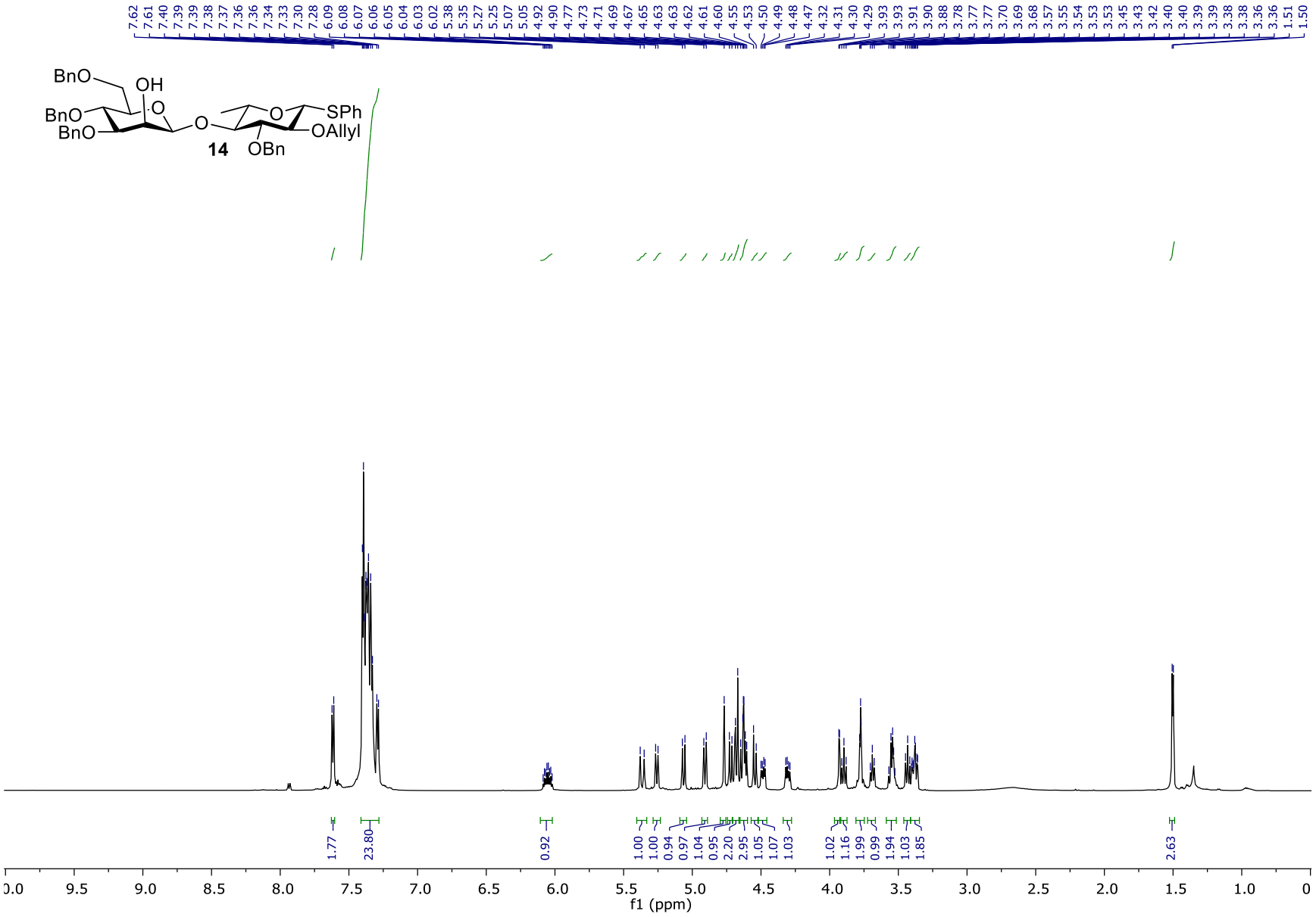
f1 (ppm)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BnO
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BnO
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1.00
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0.95
2.20
2.95
1.05
1.07
1.03
1.02
1.16
1.99
0.99
1.94
1.03
1.85
2.63
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9.0
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8.0
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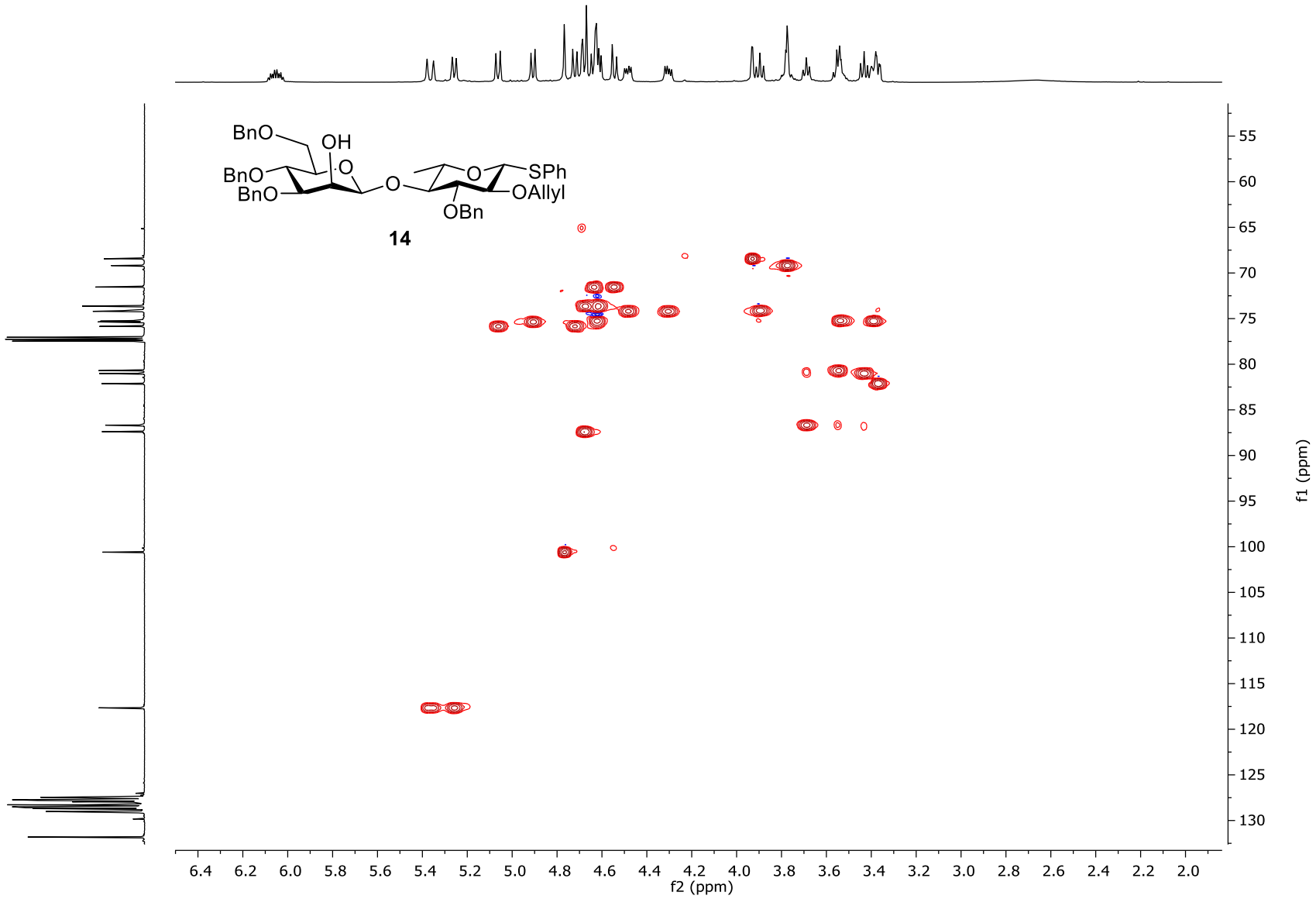
f1 (ppm)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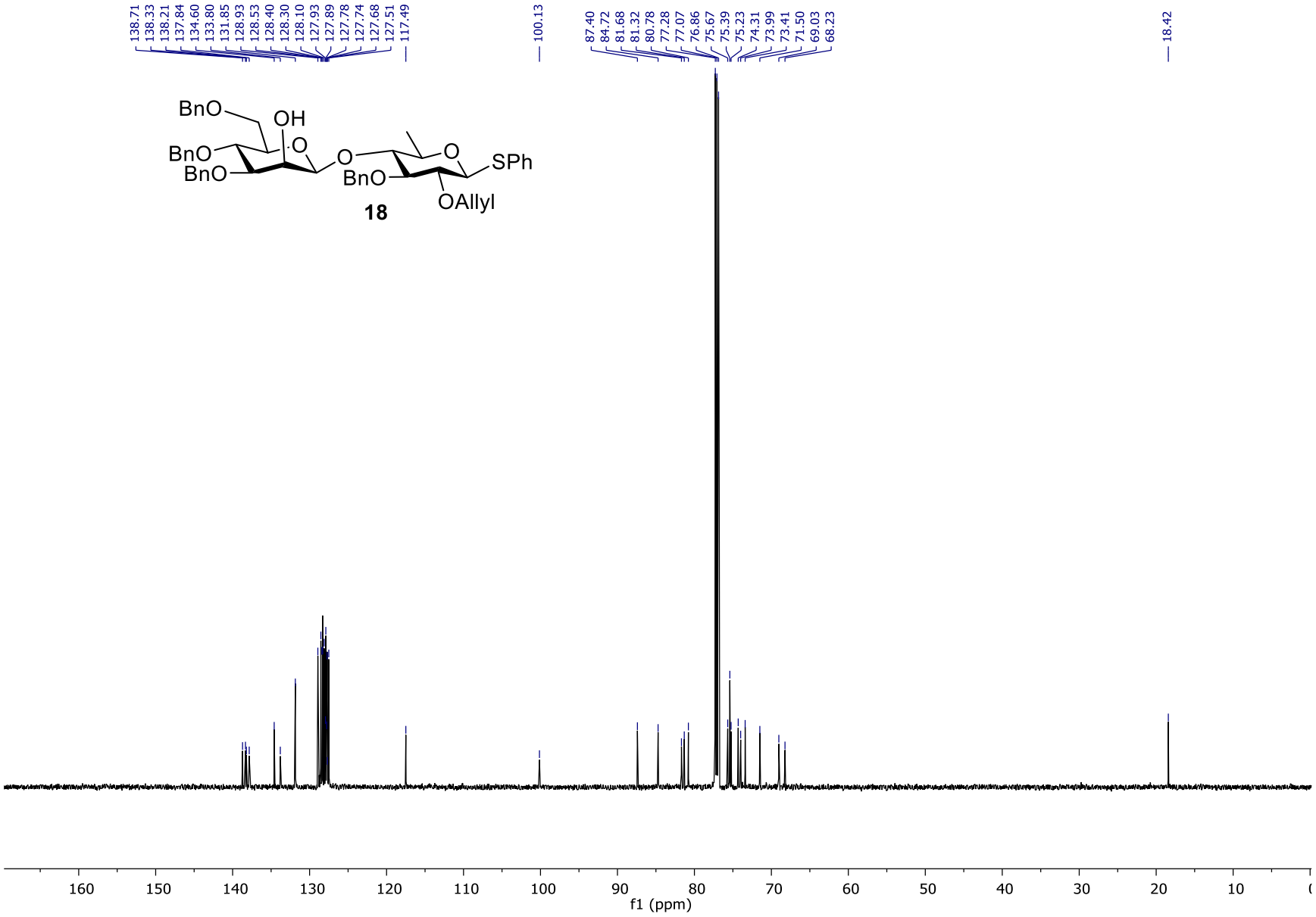
OH
BnO
BnO
O
O
O
SPh
OAllyl
OBn
14
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
f1 (ppm)
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f2 (ppm)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133.80
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128.40
128.30
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127.93
127.89
127.78
127.74
127.68
127.51
117.49
100.13
87.40
84.72
81.68
81.32
80.78
77.28
77.07
76.86
75.67
75.39
75.23
74.31
73.99
73.41
71.50
69.03
68.23
18.42
BnO
OH
BnO
BnO
O
O
O
BnO
SPh
OAllyl
18
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140
130
120
110
100
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80
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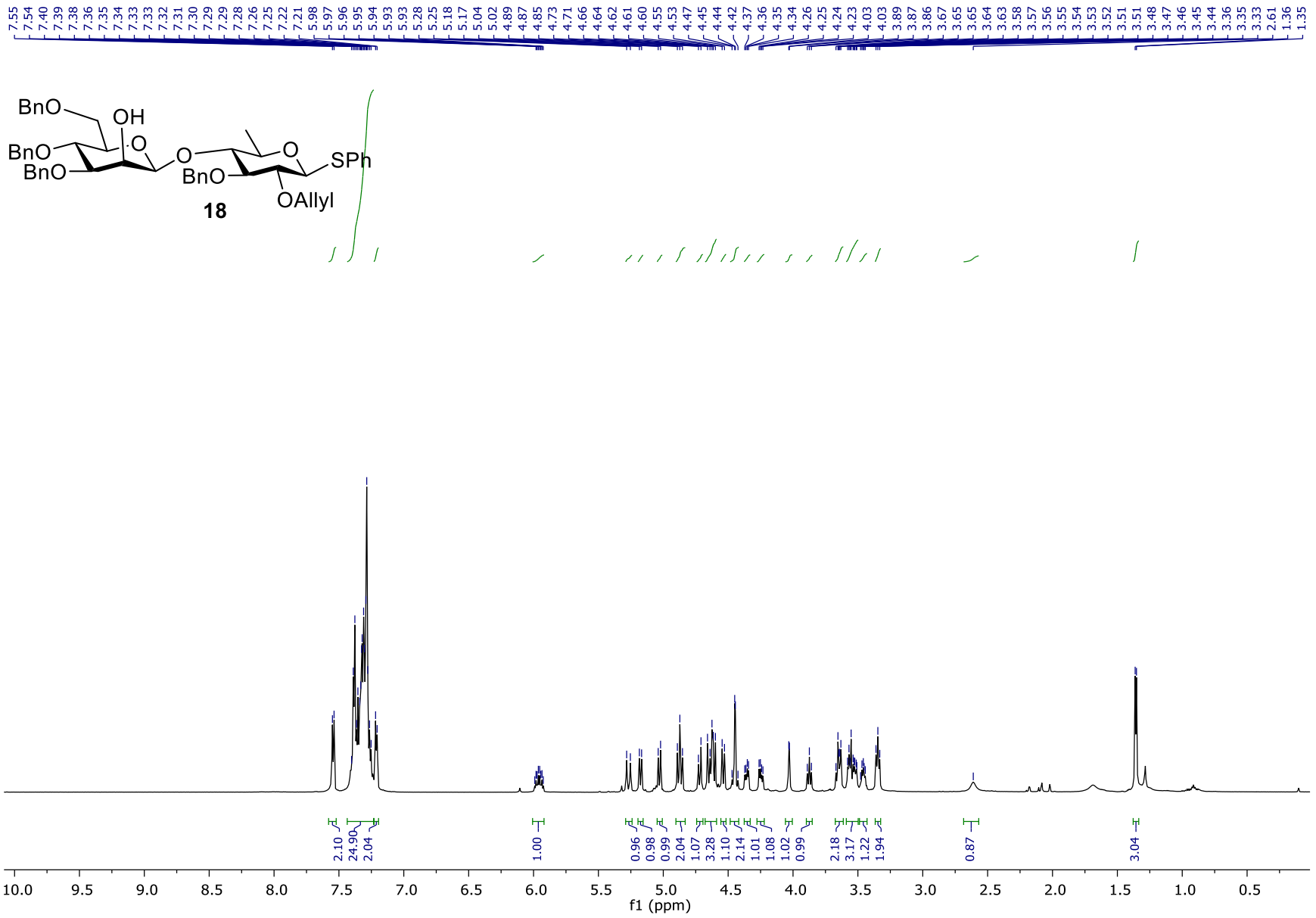
60
50
40
30
20
10
f1 (ppm)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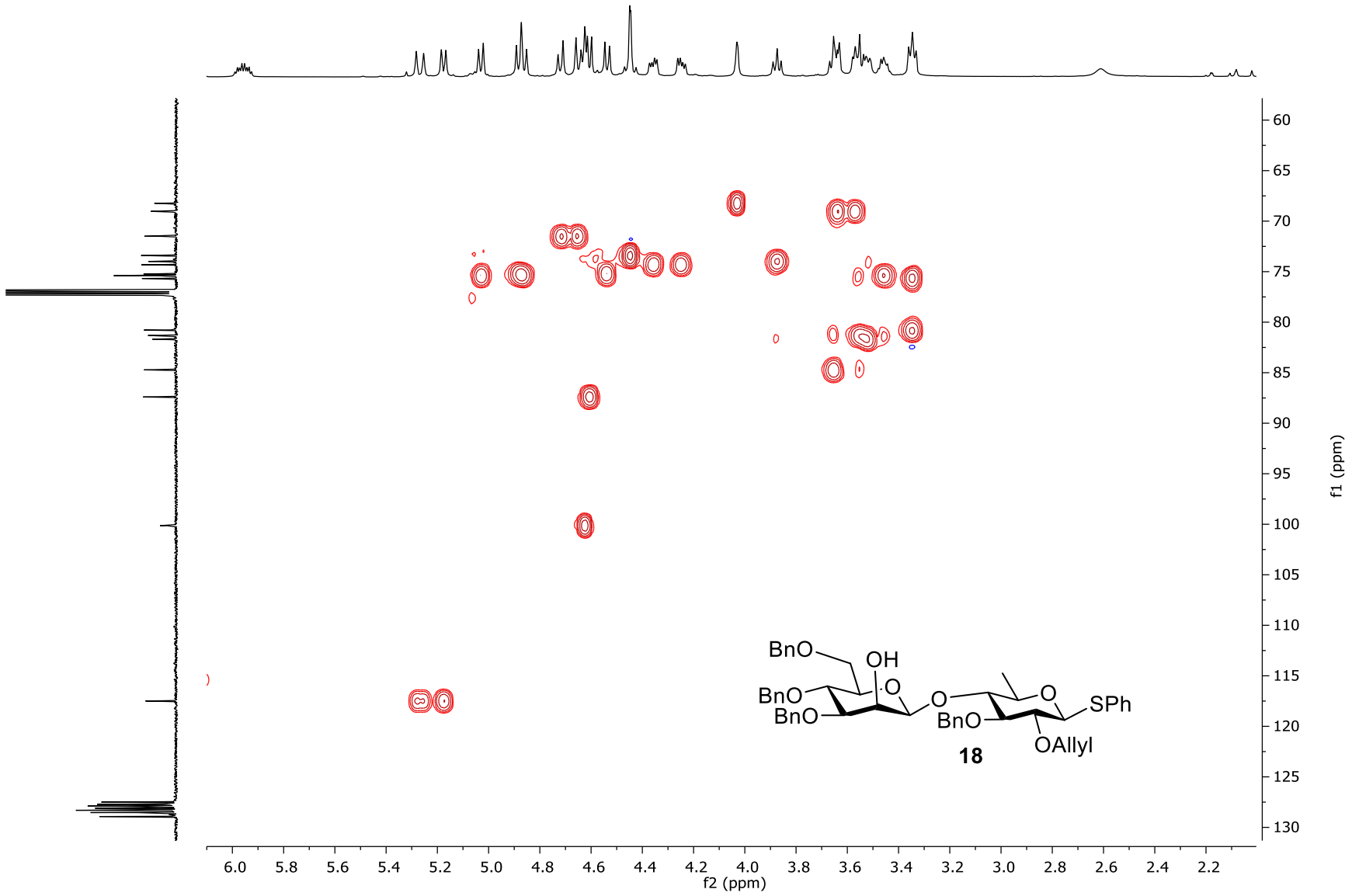
BnO
OH
O
BnO
BnO
O
BnO
O
SPh
OAllyl
18
2.10 24.90 2.04 1.00 0.96 0.98 0.99 2.04 1.07 3.28 1.10 2.14 1.01 1.08 1.02 0.99 2.18 3.17 1.22 1.94 0.87 3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


f2 (ppm)
f1 (ppm)
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BnO
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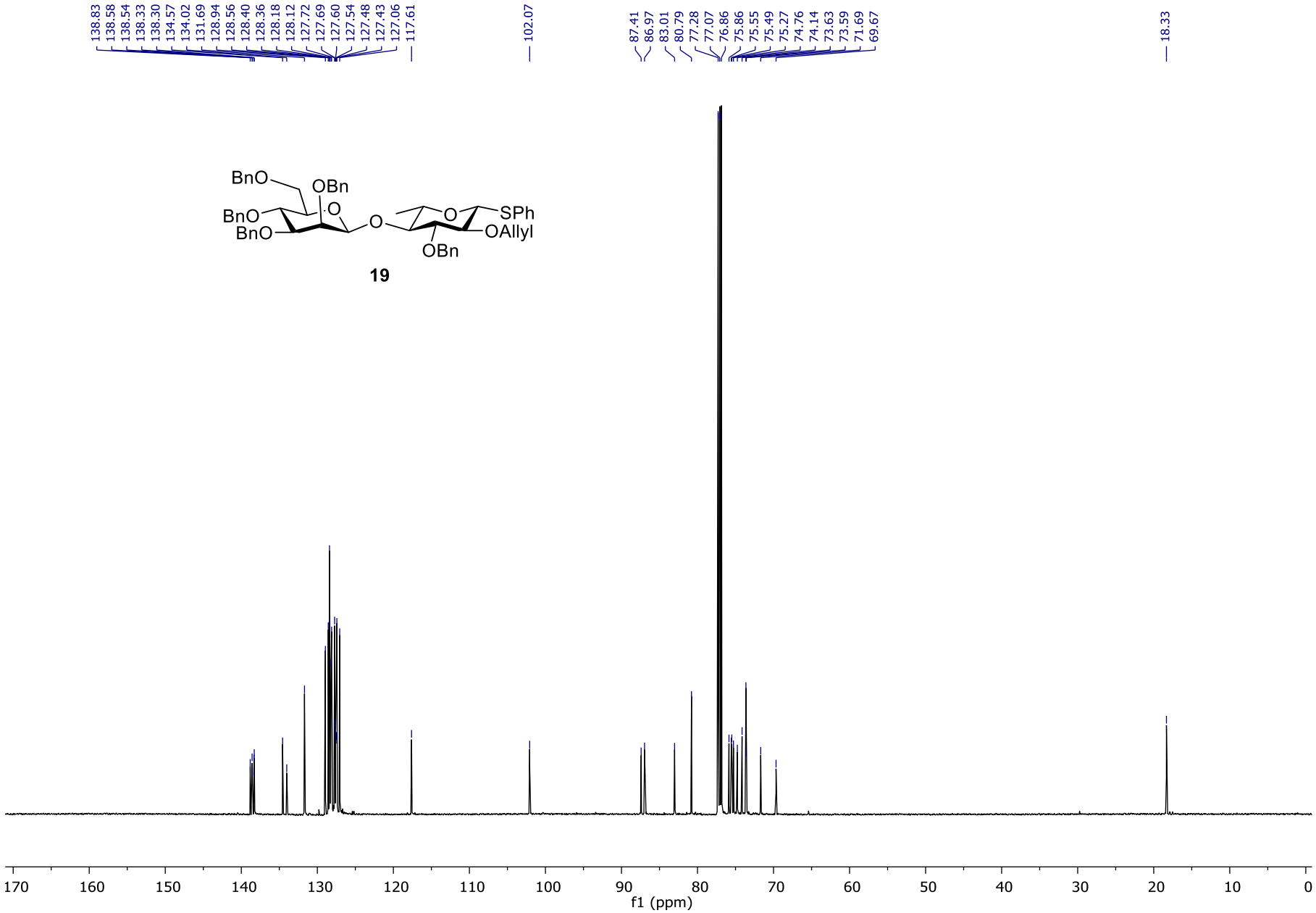
O
BnO
O
SPh
OAllyl
18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128.56
128.40
128.36
128.18
128.12
127.72
127.69
127.60
127.54
127.48
127.43
127.06
117.61
102.07
87.41
86.97
83.01
80.79
77.28
77.07
76.86
75.86
75.55
75.49
75.27
74.76
74.14
73.63
73.59
71.69
69.67
18.33
BnO
OBn
BnO
BnO
O
O
O
SPh
OAllyl
OBn
19
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130
120
110
100
90
80
70
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50
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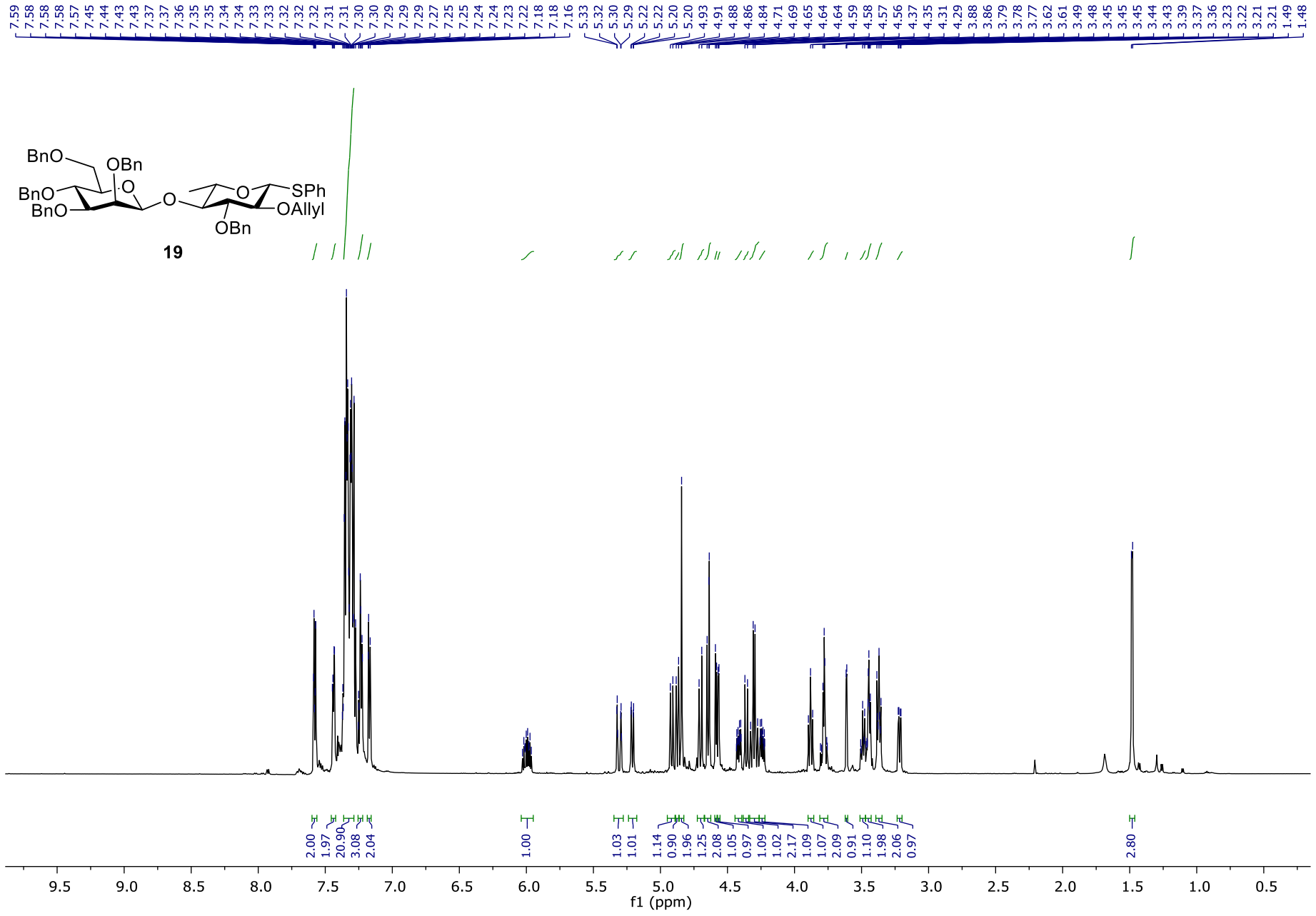
30
20
10
0
f1 (ppm)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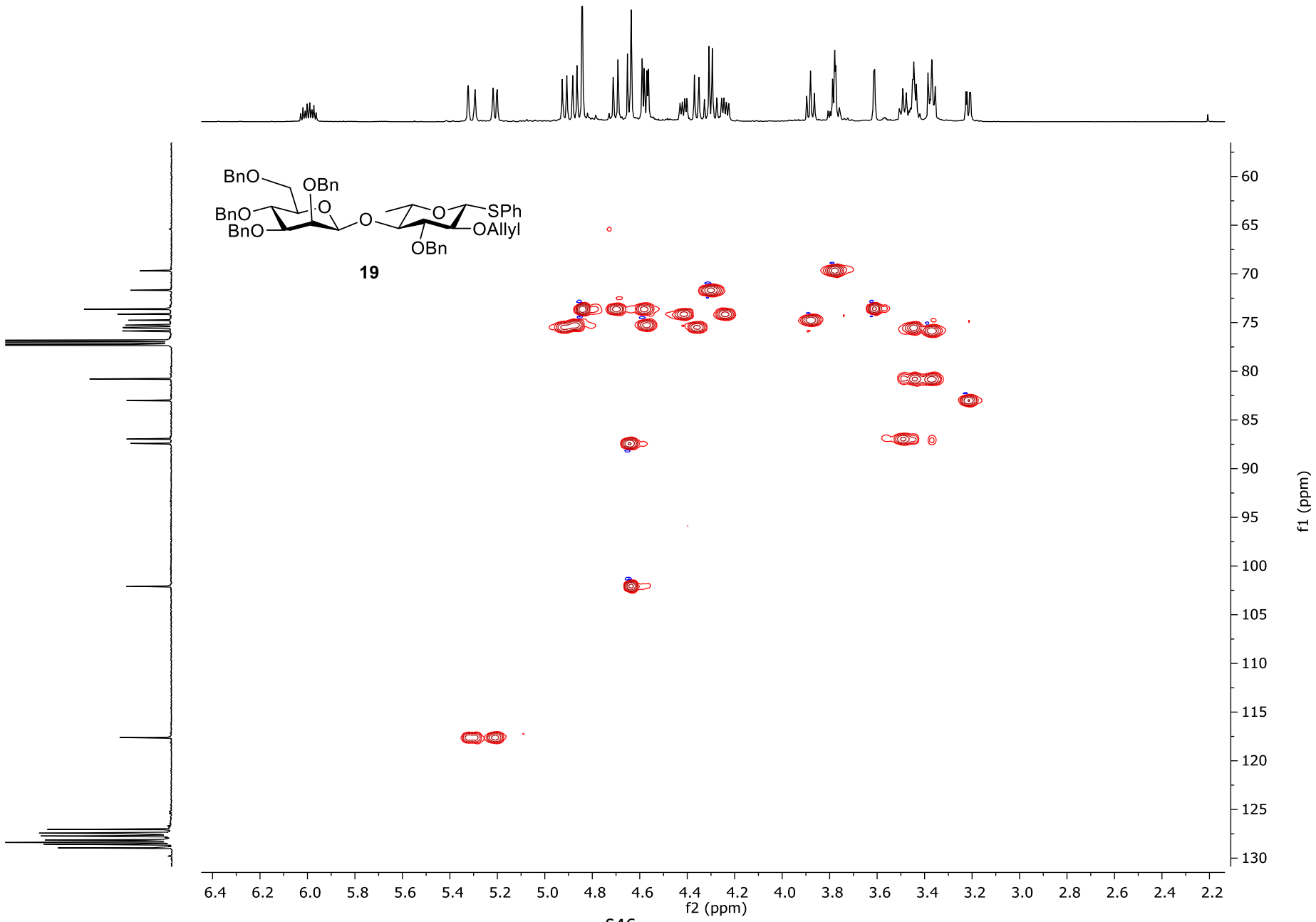
BnO
O
O
SPh
OAllyl
OBn
19
f1 (ppm)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OBn
BnO
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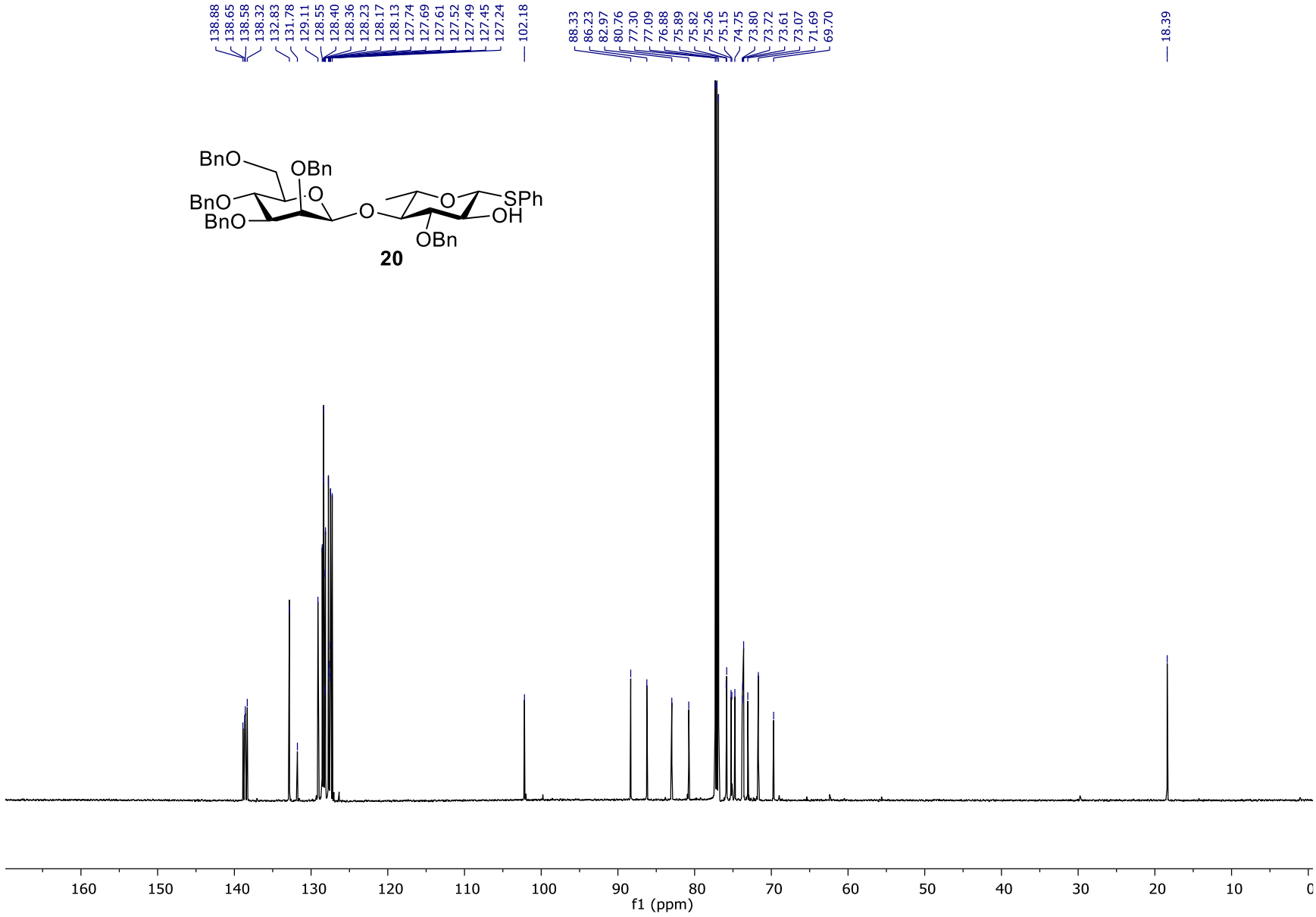
BnO
O
O
SPh
OAllyl
OBn
19
f2 (ppm)
f1 (ppm)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127.61
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127.49
127.45
127.24
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80.76
77.30
77.09
76.88
75.89
75.82
75.26
75.15
74.75
73.80
73.72
73.61
73.07
71.69
69.70
18.39
BnO
OBn
BnO
O
BnO
O
O
SPh
OH
OBn
20
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150
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130
120
110
100
90
80
70
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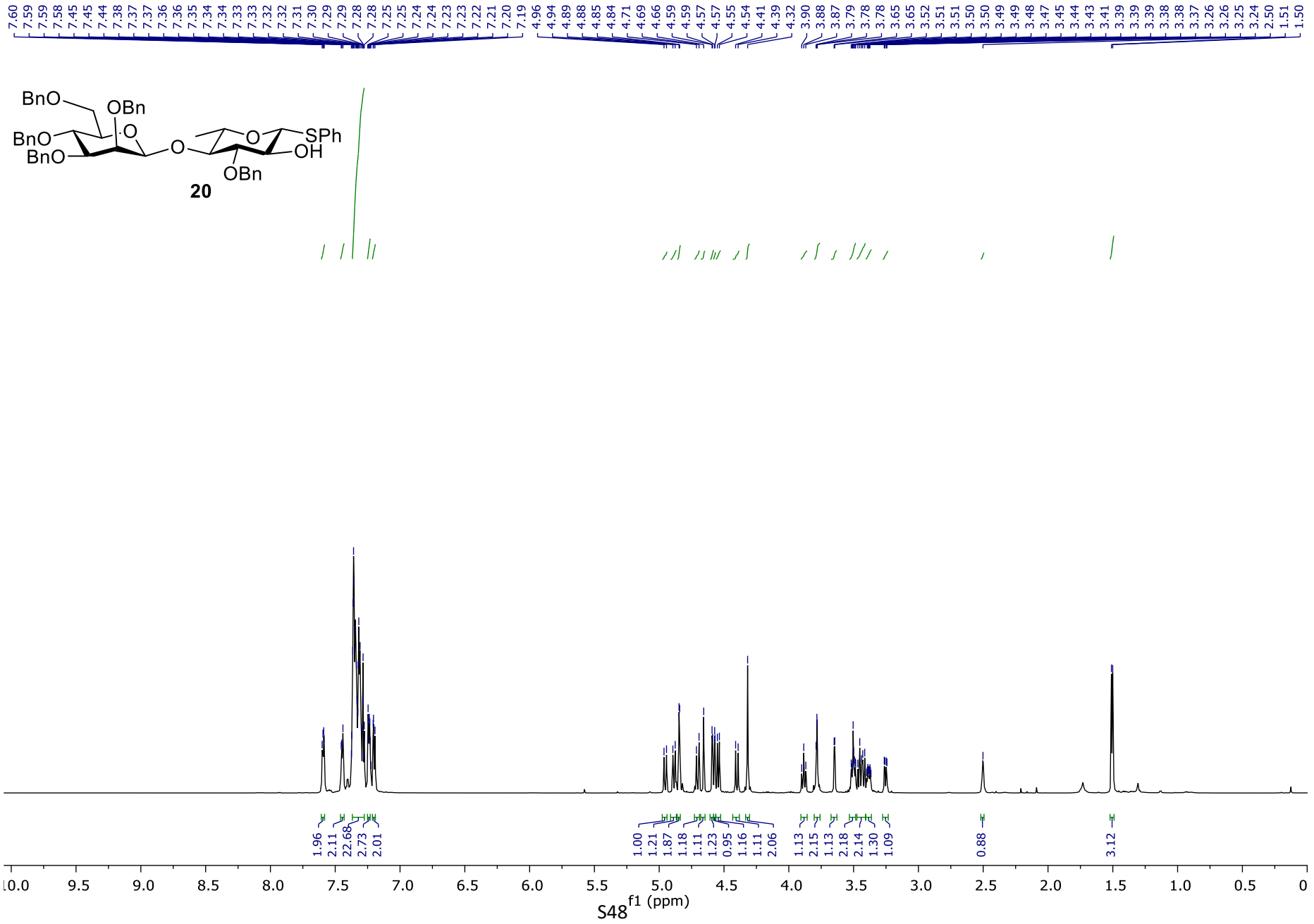
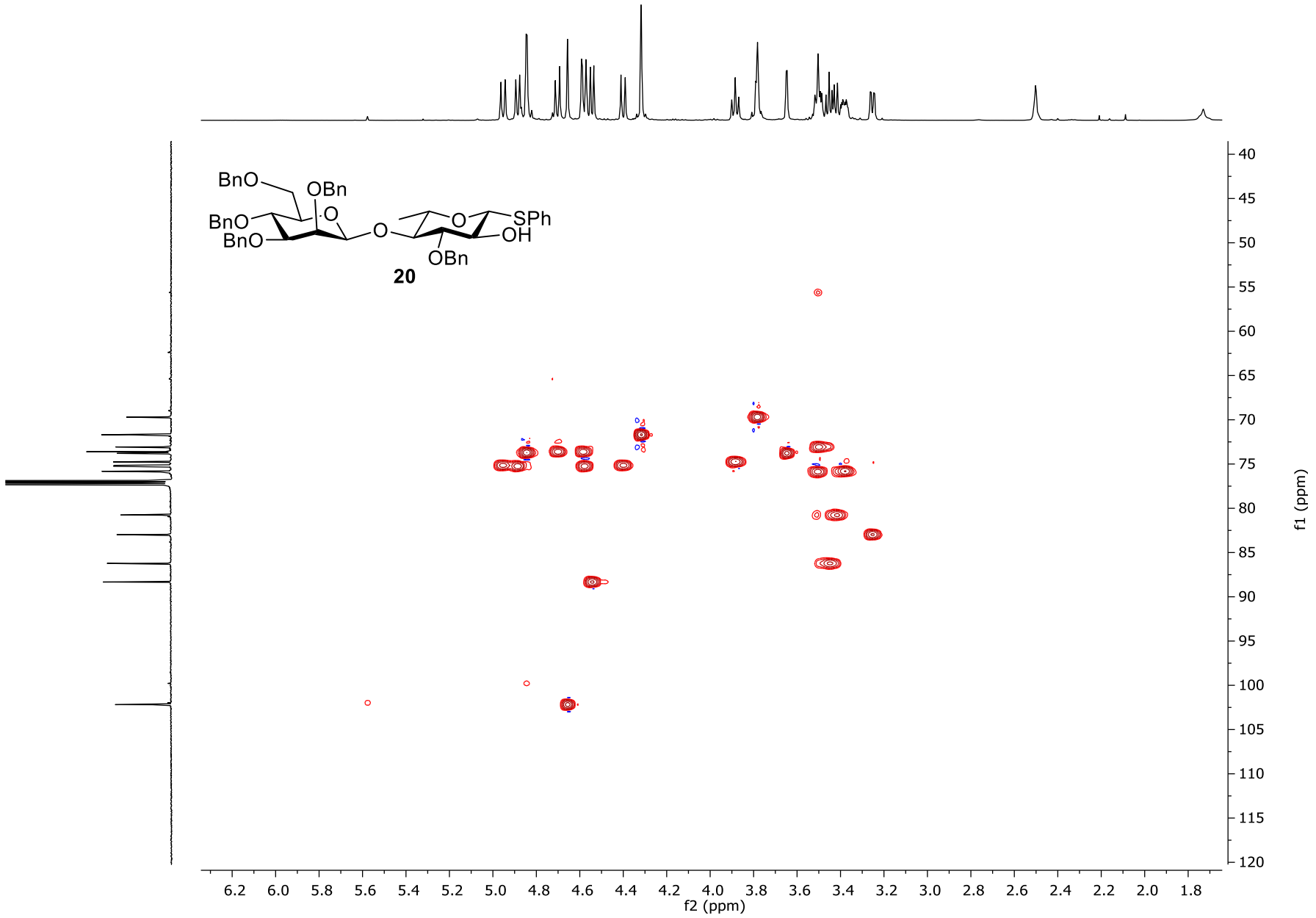
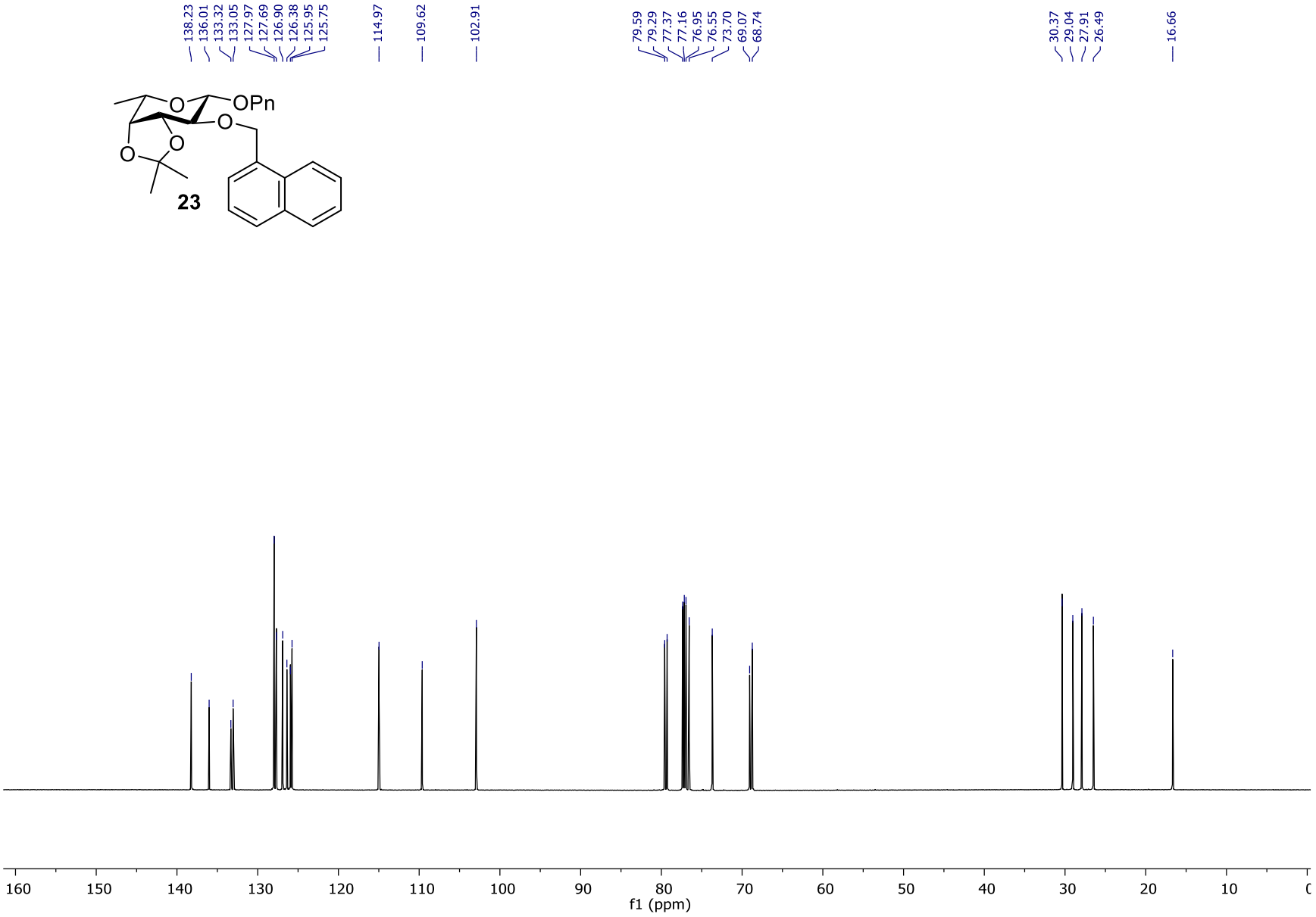
50
40
30
20
10
0
f1 (ppm)


7.60 7.59 7.59 7.58 7.45 7.45 7.44 7.38 7.37 7.37 7.36 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.25 7.24 7.24 7.23 7.23 7.22 7.21 7.20 7.19 4.96 4.94 4.89 4.88 4.85 4.84 4.71 4.69 4.66 4.59 4.59 4.57 4.57 4.55 4.54 4.41 4.39 4.32 3.90 3.88 3.87 3.79 3.78 3.78 3.65 3.65 3.52 3.51 3.51 3.50 3.50 3.49 3.49 3.48 3.47 3.45 3.44 3.43 3.41 3.39 3.39 3.39 3.38 3.38 3.37 3.26 3.26 3.25 3.24 2.50 1.51 1.50
BnO
OBn
BnO
O
BnO
O
O
SPh
OH
OBn
20
1.96 2.11 22.68 2.73 2.01 1.00 1.21 1.87 1.18 1.11 1.23 0.95 1.16 1.11 2.06 1.13 2.15 1.13 2.18 2.14 1.30 1.09 0.88 3.12
10.0 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
f1 (ppm)


BnO
OBn
BnO
O
BnO
O
O
SPh
OH
OBn
20
f2 (ppm)
f1 (ppm)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133.32
133.05
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127.69
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126.38
125.95
125.75
114.97
109.62
102.91
79.59
79.29
77.37
77.16
76.95
76.55
73.70
69.07
68.74
30.37
29.04
27.91
26.49
16.66
OPn
O
O
O
O
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140
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120
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100
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80
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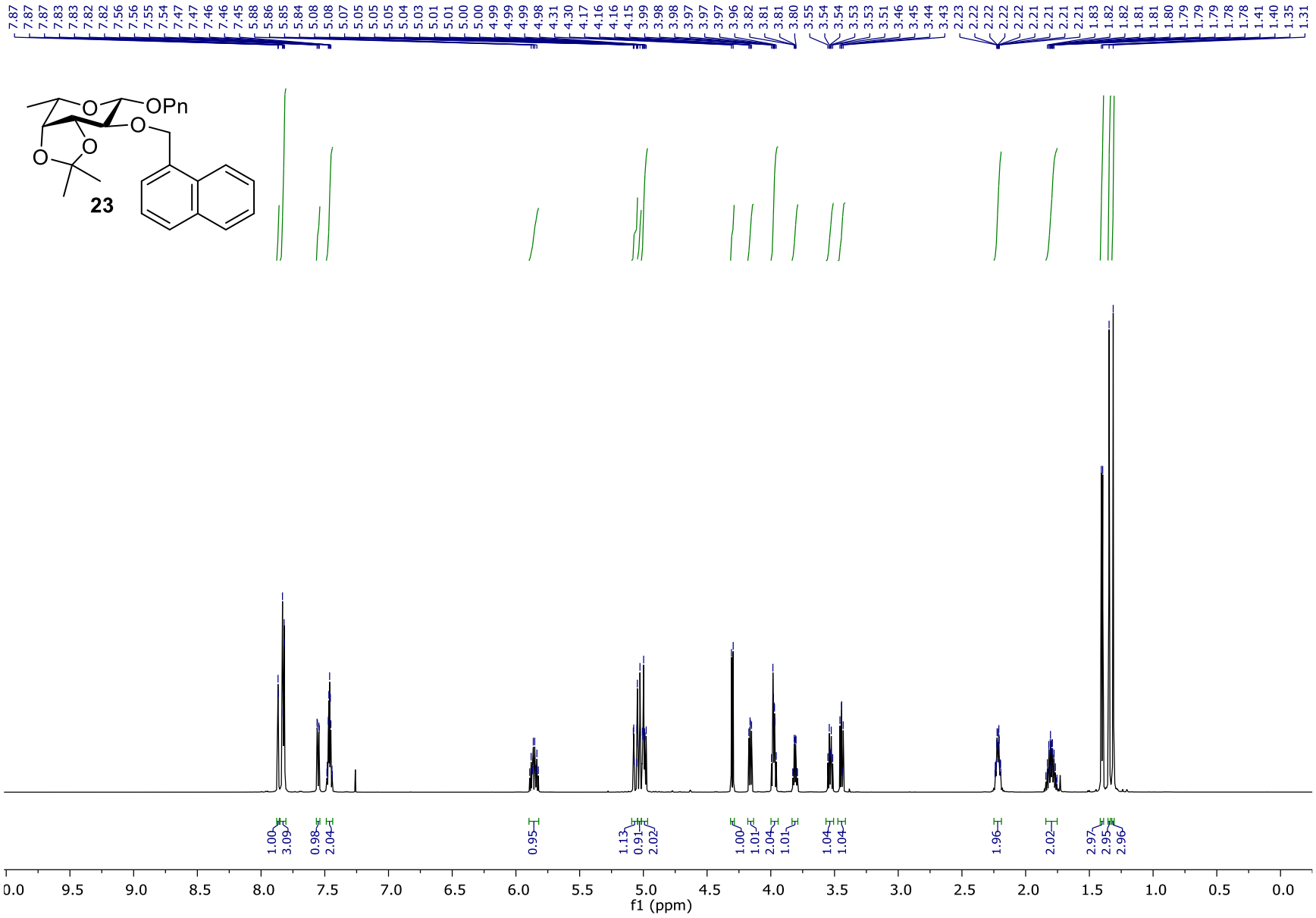
60
50
40
30
20
10
f1 (ppm)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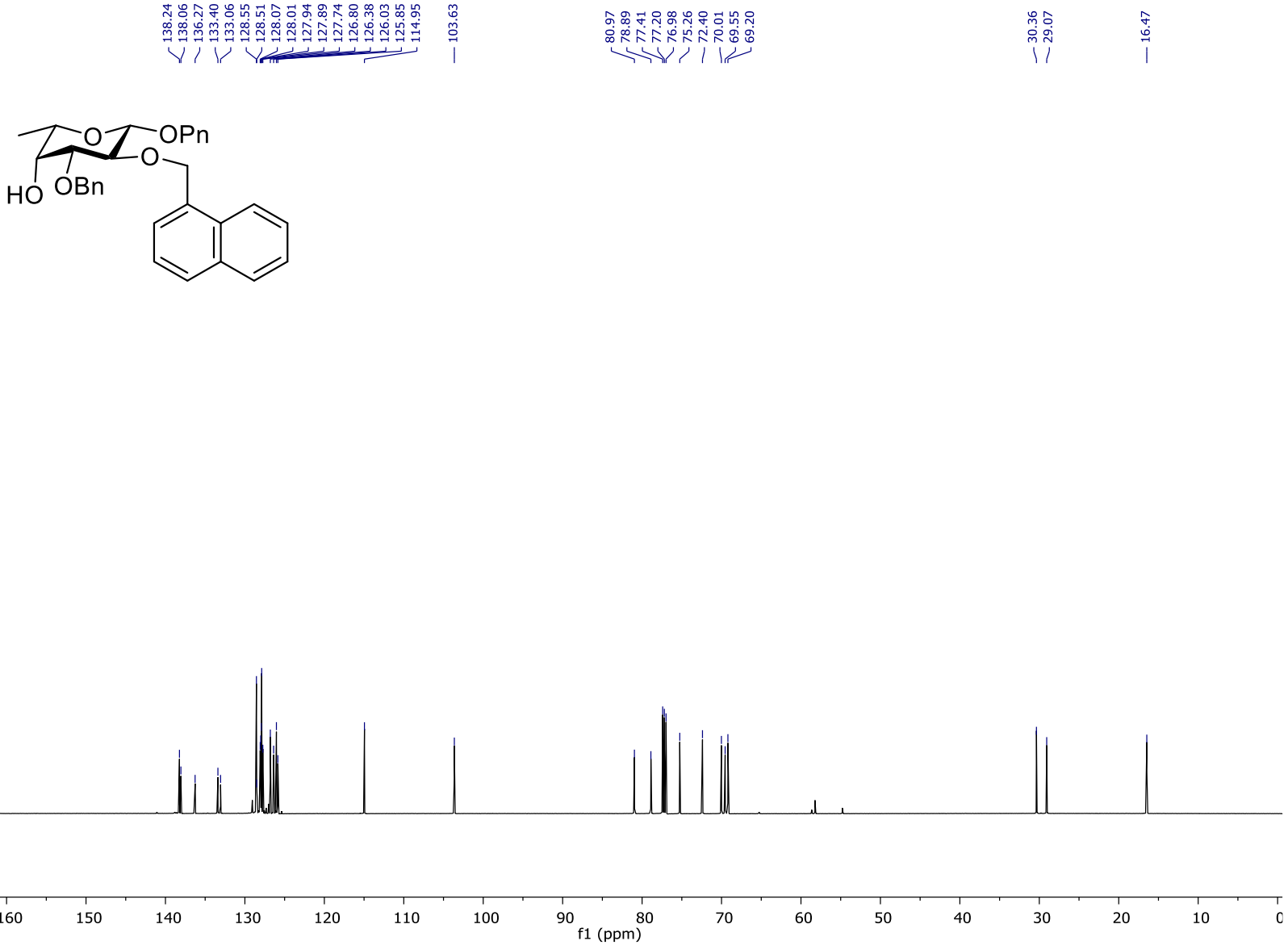
OPn
O
O
O
O
23
1.00 3.09 0.98 2.04 0.95 1.13 0.91 2.02 1.00 1.01 2.04 1.01 1.04 1.04 1.96 2.02 2.97 2.95 2.96
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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126.80
126.38
126.03
125.85
114.95
103.63
80.97
78.89
77.41
77.20
76.98
75.26
72.40
70.01
69.55
69.20
30.36
29.07
16.47
O
OPn
O
HO
OBn
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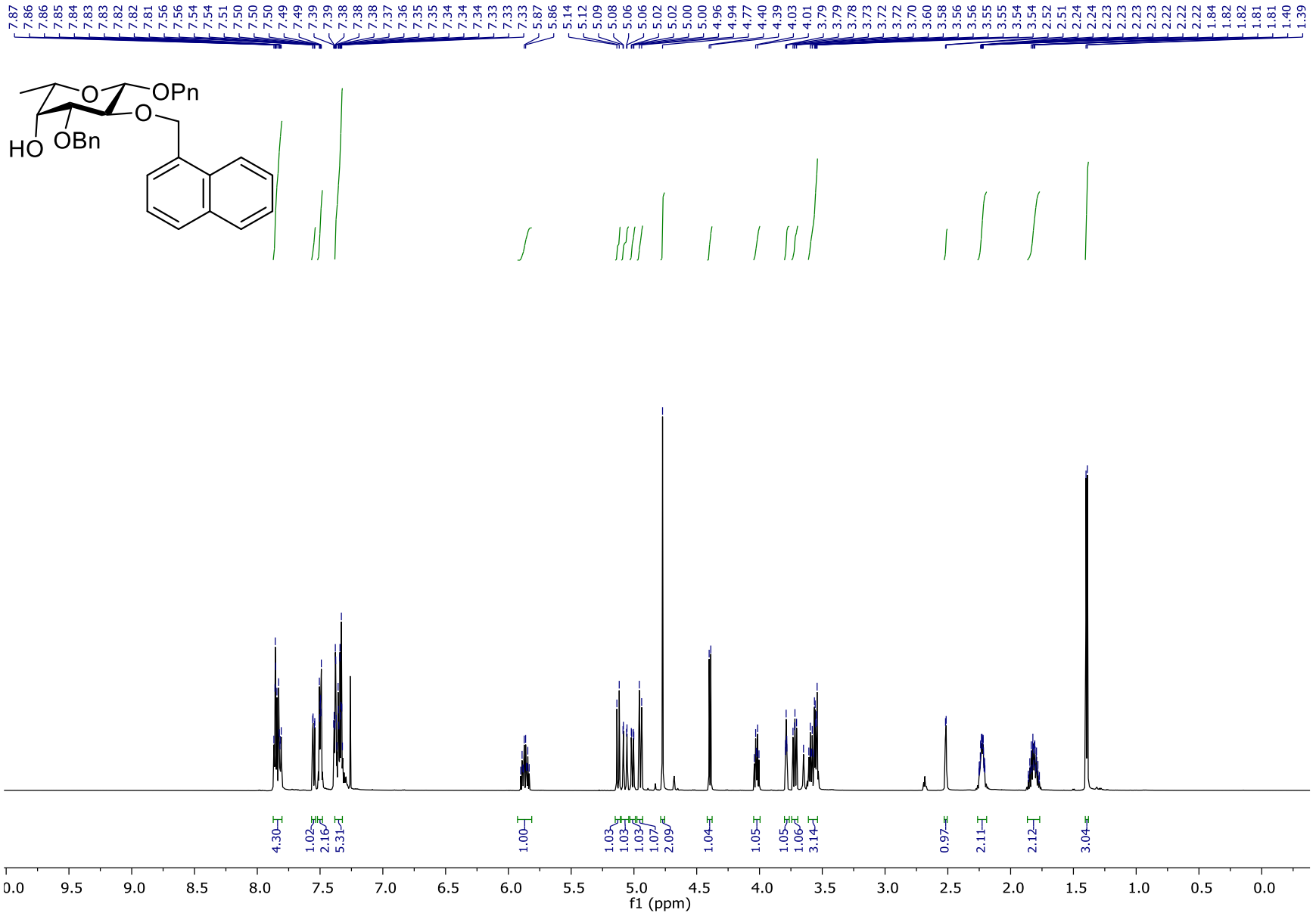
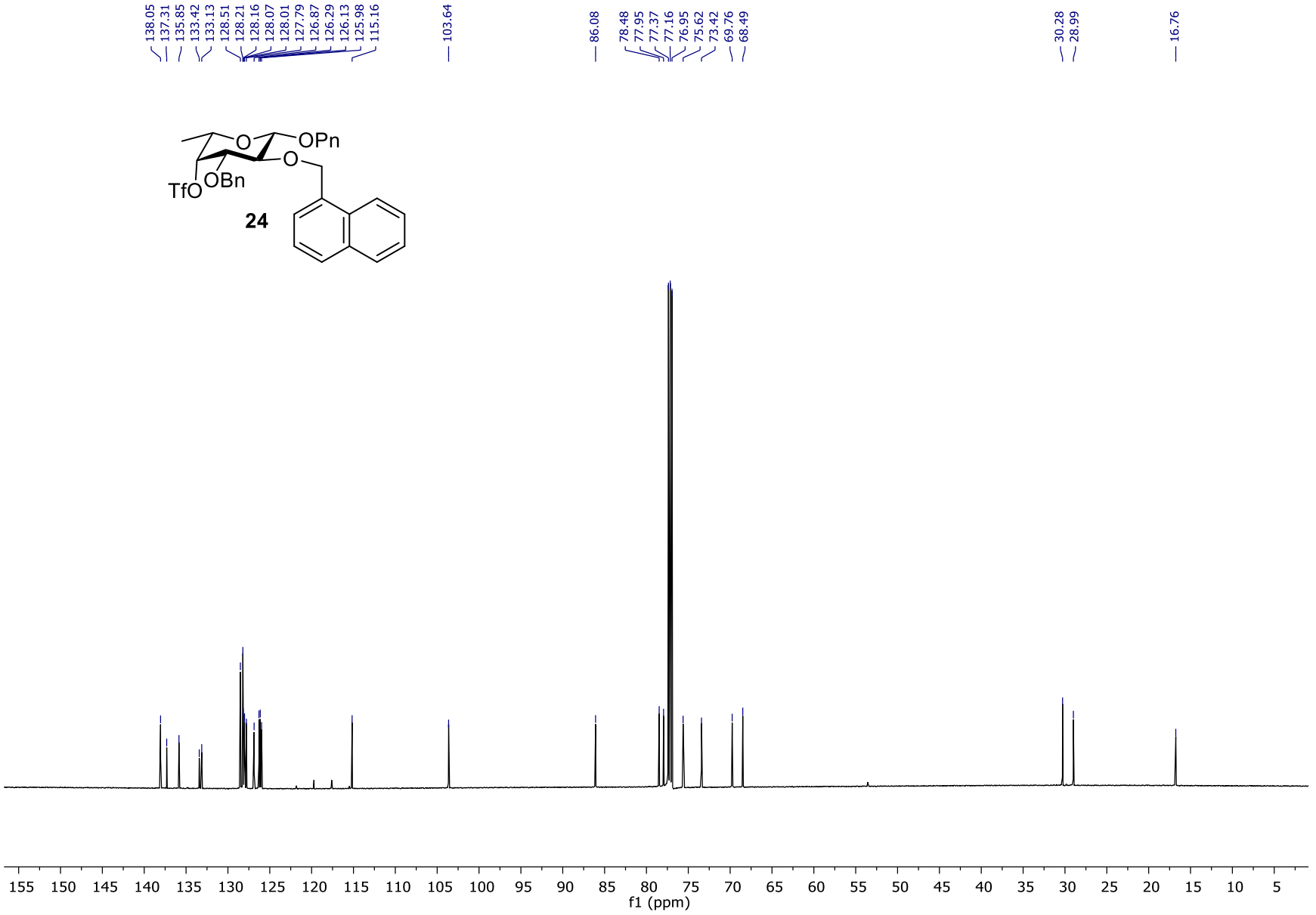
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.87 7.86 7.86 7.85 7.84 7.83 7.83 7.82 7.82 7.81 7.56 7.56 7.54 7.54 7.51 7.50 7.50 7.50 7.49 7.49 7.39 7.38 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 5.87 5.86 5.14 5.12 5.09 5.08 5.06 5.06 5.02 5.02 5.00 5.00 4.96 4.94 4.77 4.40 4.39 4.03 4.01 3.79 3.79 3.78 3.73 3.72 3.72 3.70 3.60 3.58 3.56 3.56 3.55 3.55 3.54 3.54 2.52 2.51 2.24 2.24 2.23 2.23 2.23 2.23 2.22 2.22 2.22 1.84 1.82 1.82 1.81 1.81 1.40 1.39
OPn
O
O
HO
OBn
4.30
1.02
2.16
5.31
1.00
1.03
1.03
1.03
1.07
2.09
1.04
1.05
1.05
1.06
3.14
0.97
2.11
2.12
3.04
0.0 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)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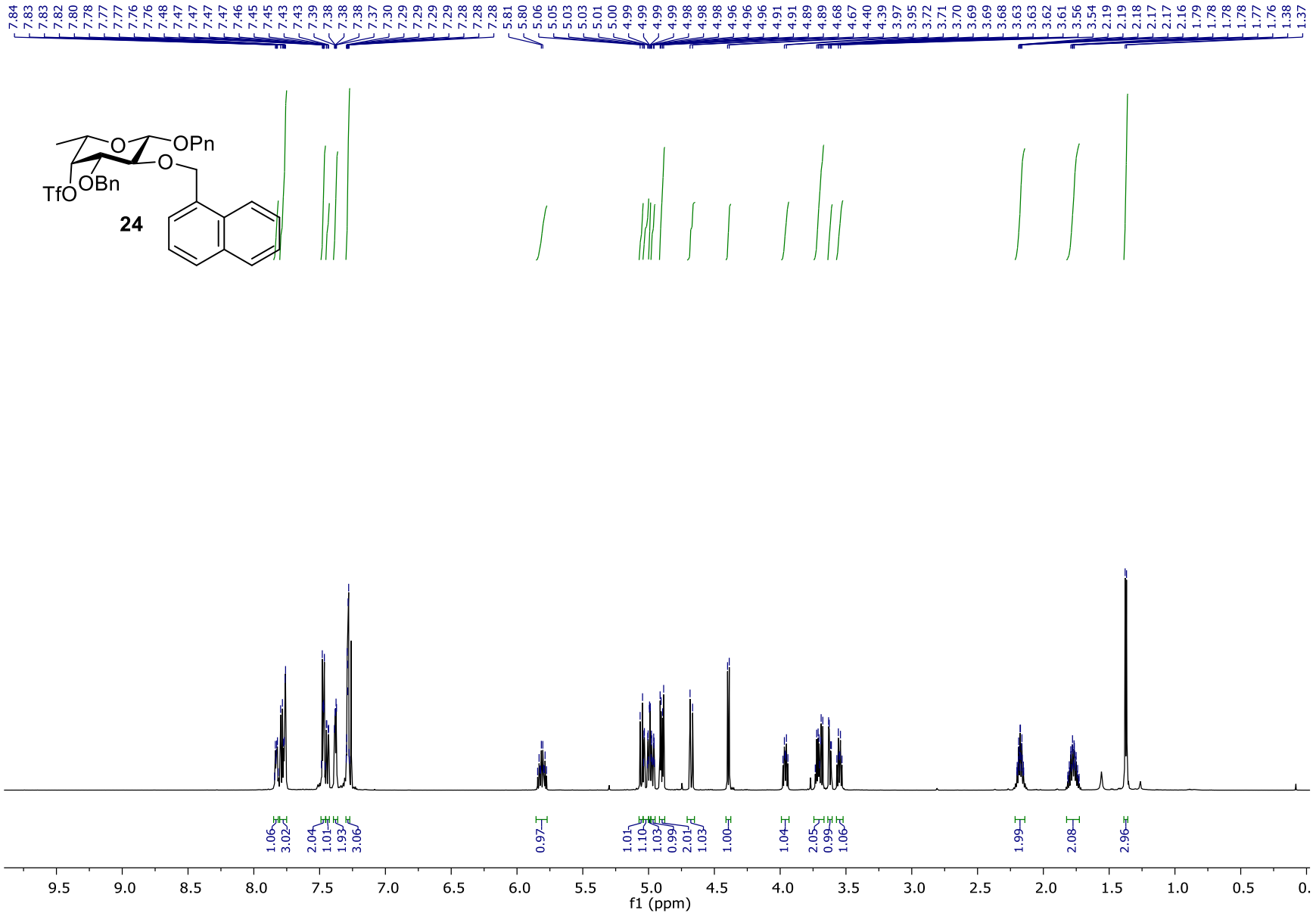
126.29
126.13
125.98
115.16
103.64
86.08
78.48
77.95
77.37
77.16
76.95
75.62
73.42
69.76
68.49
30.28
28.99
16.76
OPn
O
O
TfO
OBn
24
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)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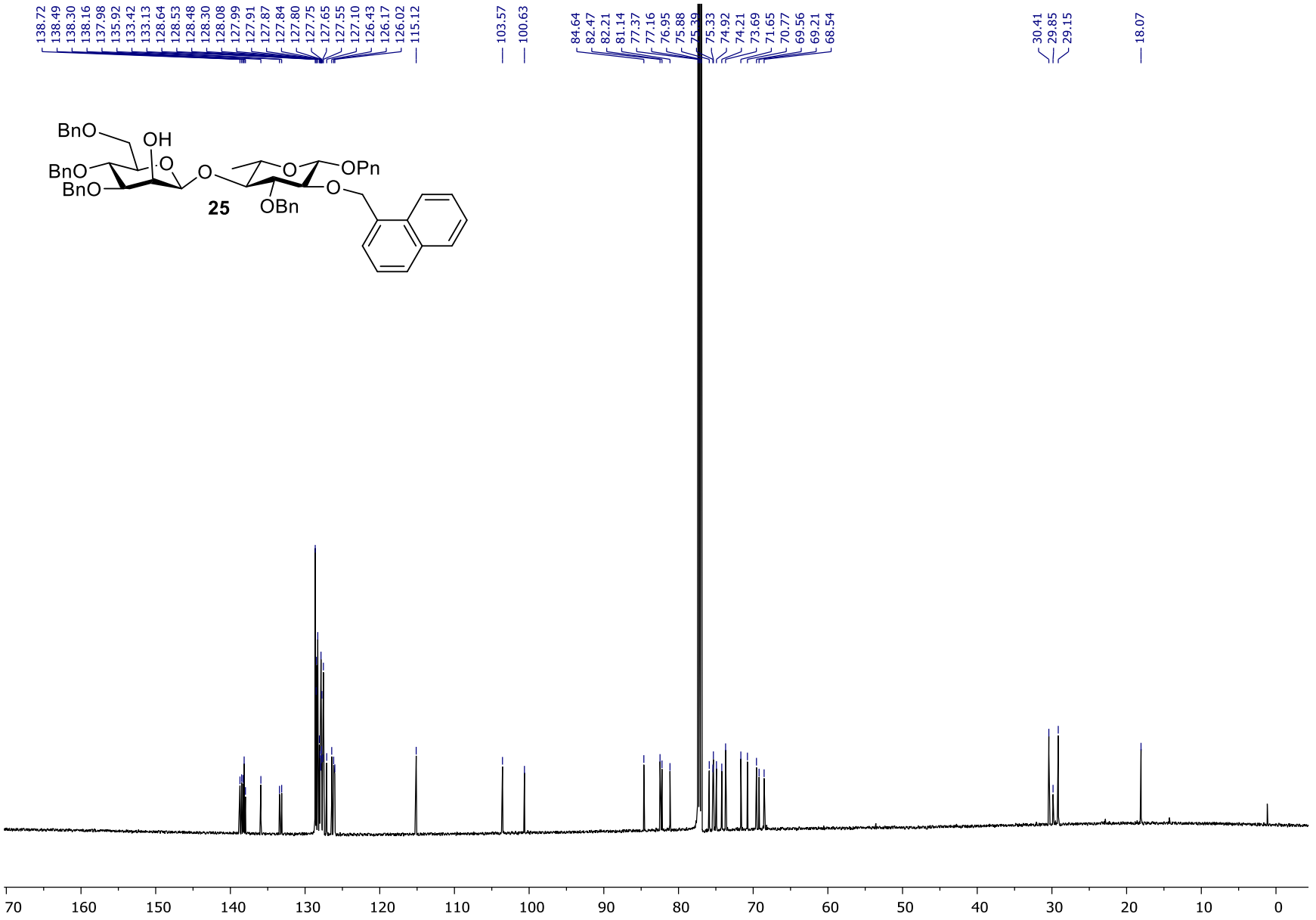
5.81 5.80 5.06 5.05 5.03 5.03 5.01 5.00 4.99 4.99 4.99 4.99 4.98 4.98 4.98 4.96 4.96 4.96 4.91 4.89 4.89 4.68 4.67 4.40 4.39 3.97 3.95 3.72 3.71 3.70 3.69 3.69 3.68 3.63 3.63 3.62 3.61 3.56 3.54 2.19 2.19 2.18 2.17 2.17 2.16 1.79 1.78 1.78 1.78 1.77 1.76 1.38 1.37
O
OPn
O
TfO
OBn
24
1.06 3.02 2.04 1.01 1.93 3.06 0.97 1.01 1.10 1.03 0.99 2.01 1.03 1.00 1.04 2.05 0.99 1.06 1.99 2.08 2.96
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.
f1 (ppm)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128.08
127.99
127.91
127.87
127.84
127.80
127.75
127.65
127.55
127.10
126.43
126.17
126.02
115.12
103.57
100.63
84.64
82.47
82.21
81.14
77.37
77.16
76.95
75.88
75.39
75.33
74.92
74.21
73.69
71.65
70.77
69.56
69.21
68.54
30.41
29.85
29.15
18.07
BnO
OH
BnO
BnO
O
O
O
OPn
O
OBn
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10
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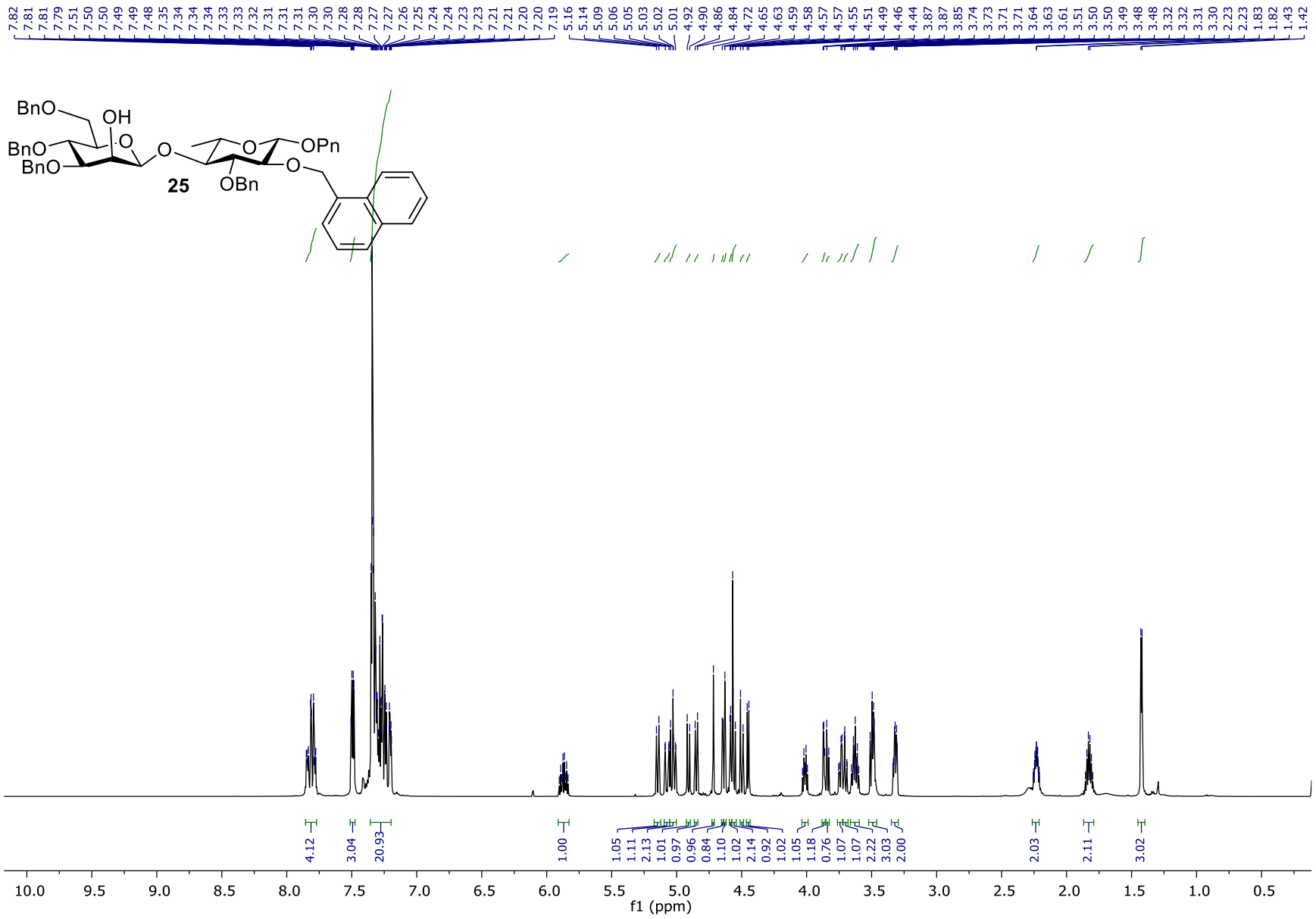
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BnO
OH
BnO
BnO
O
O
O
OPn
O
OBn
25
4.12
3.04
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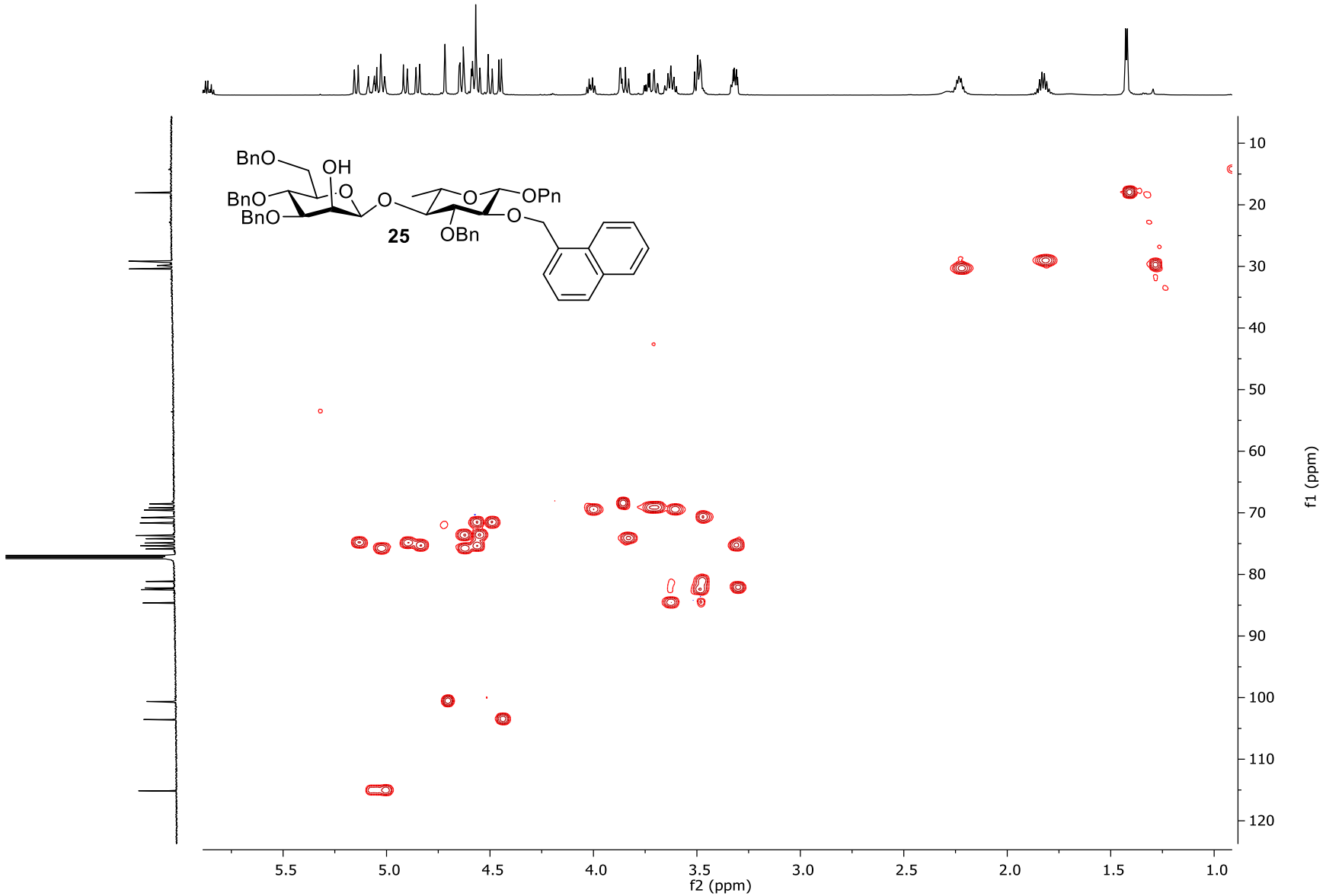
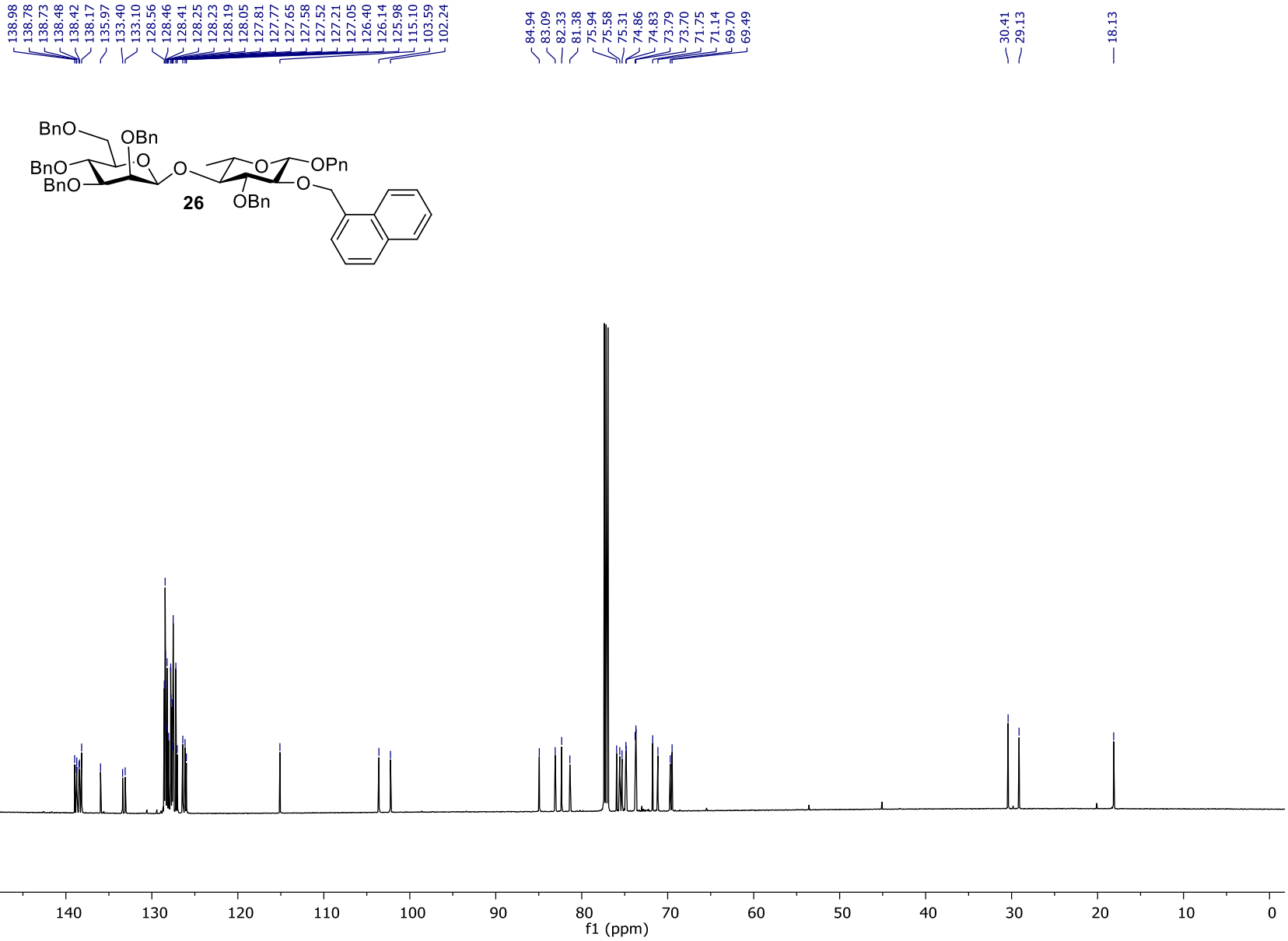
1.00
1.05
1.11
2.13
1.01
0.97
0.96
0.84
1.10
1.02
2.14
0.92
1.02
1.05
1.18
0.76
1.07
1.07
2.22
3.03
2.00
2.03
2.11
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


BnO
OH
BnO
BnO
O
O
O
OPn
O
OBn
25
f2 (ppm)
f1 (ppm)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125.98
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102.24
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82.33
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75.58
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O
OPn
O
OBn
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50
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30
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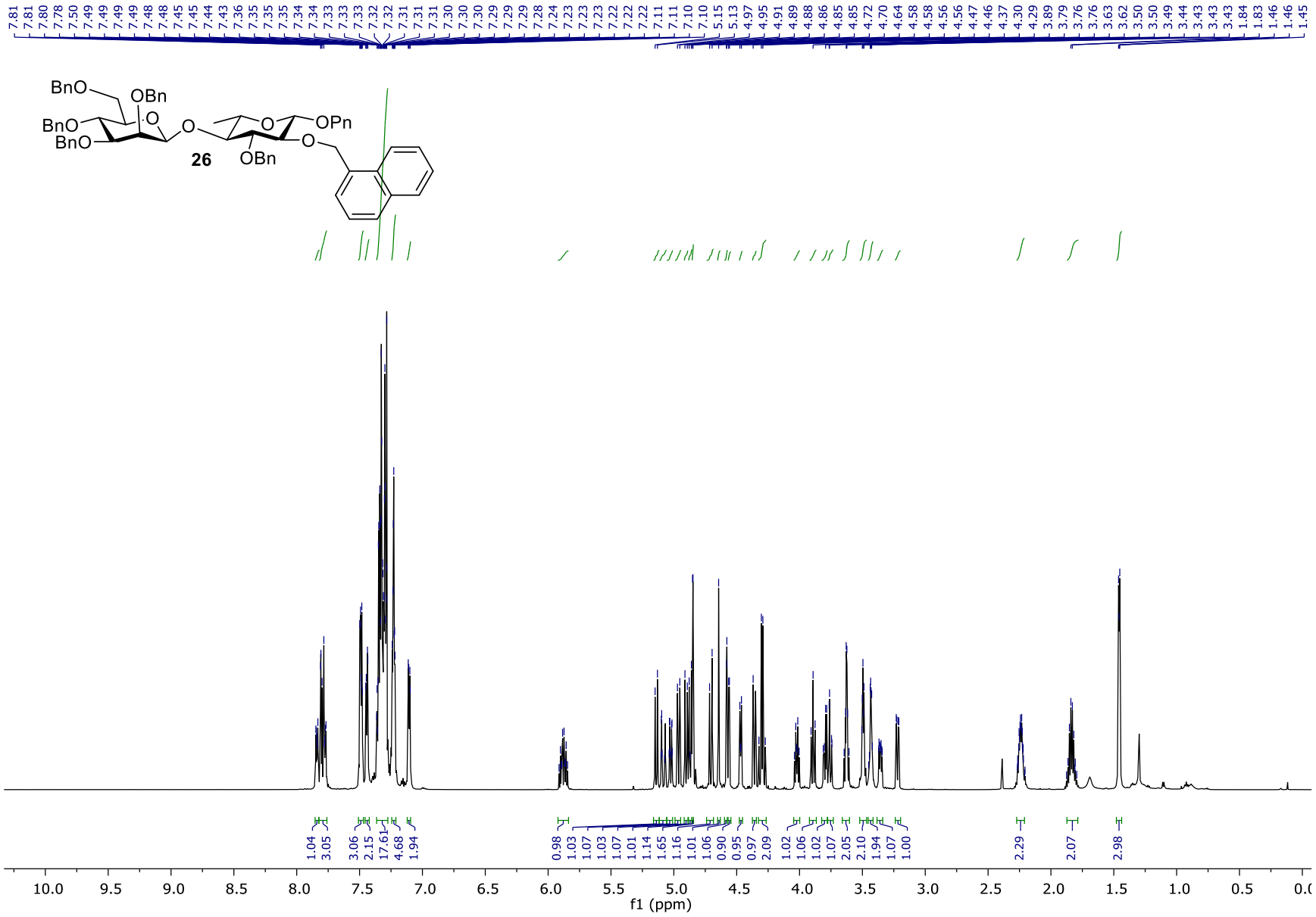
10
0
f1 (ppm)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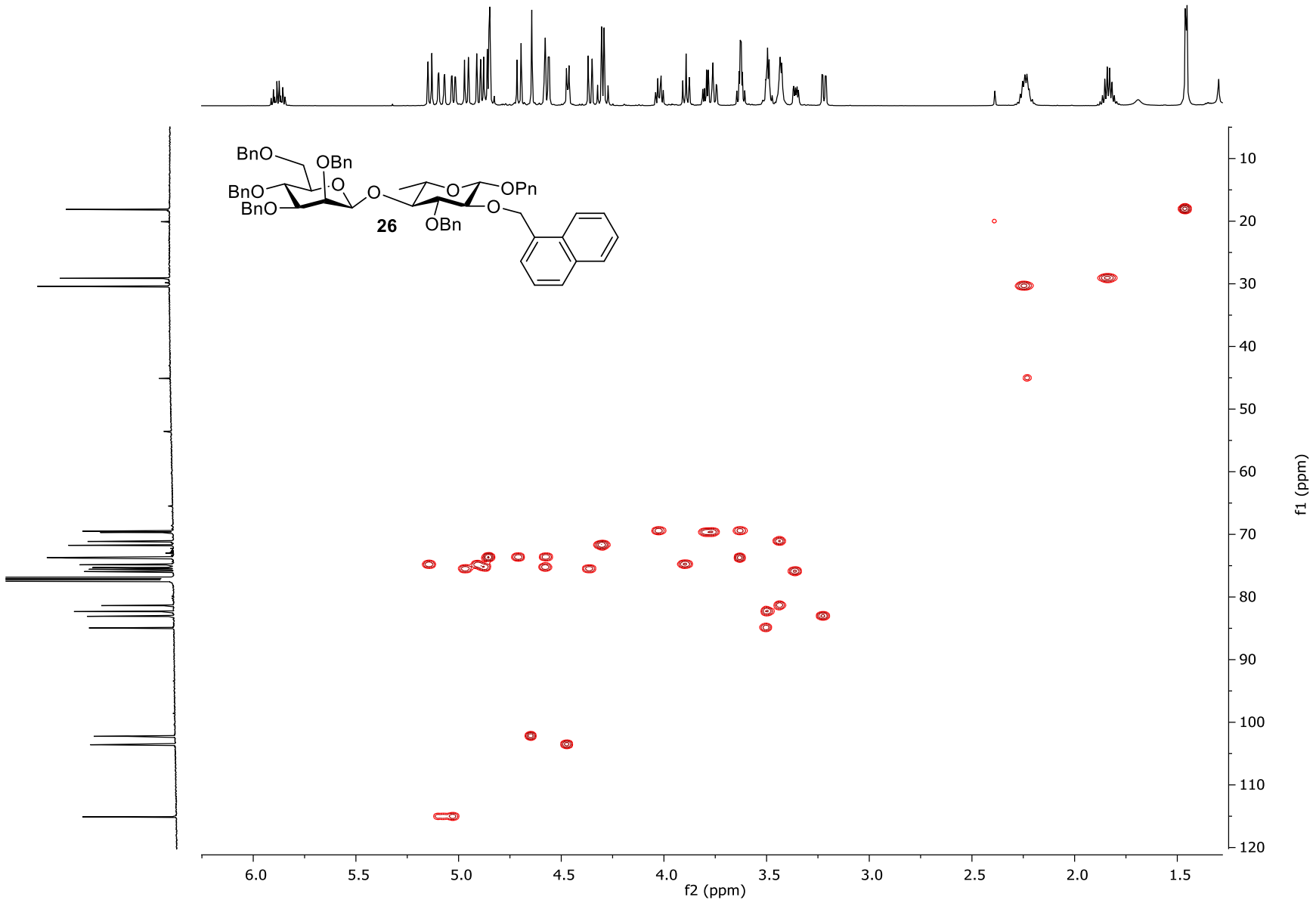
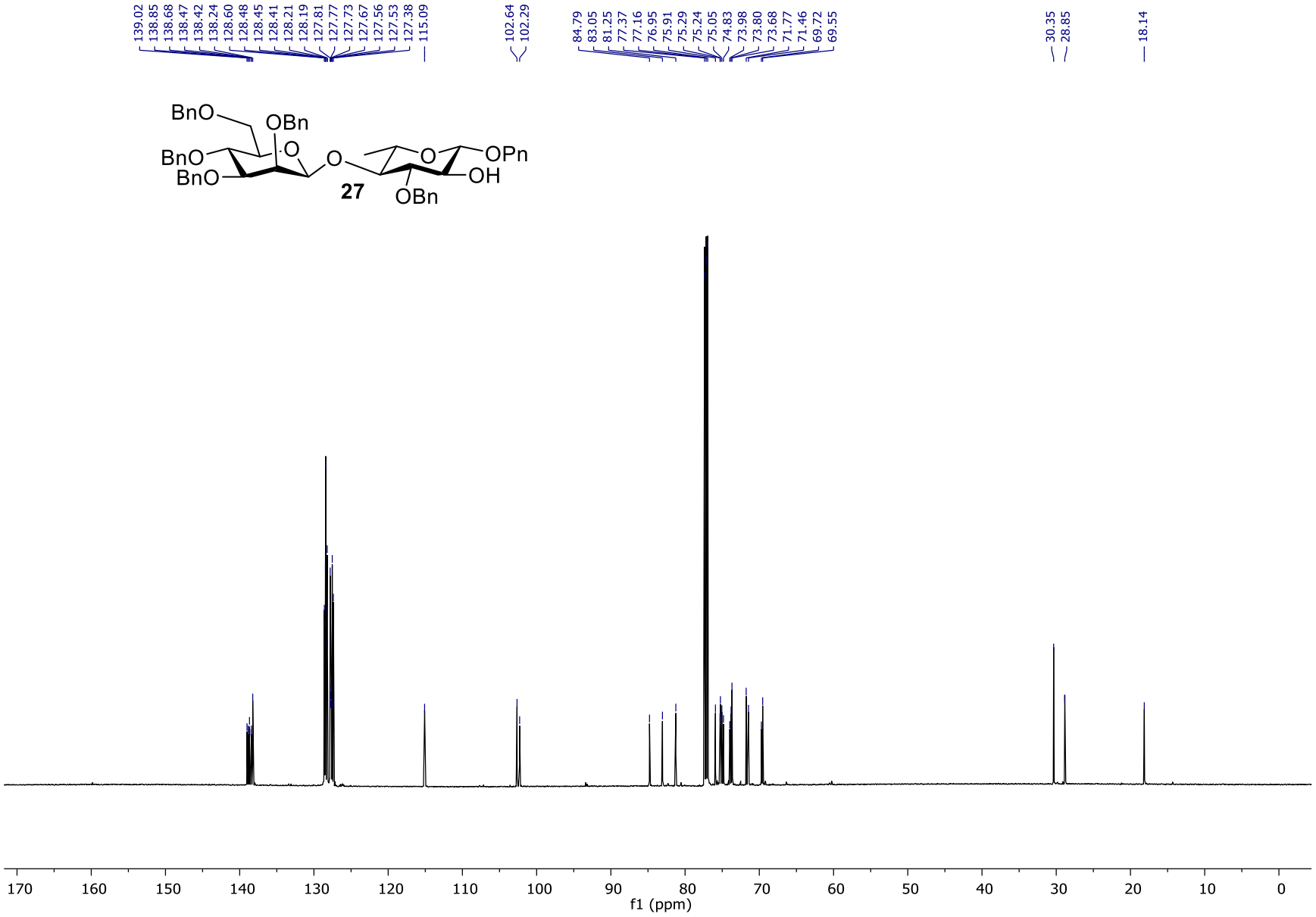
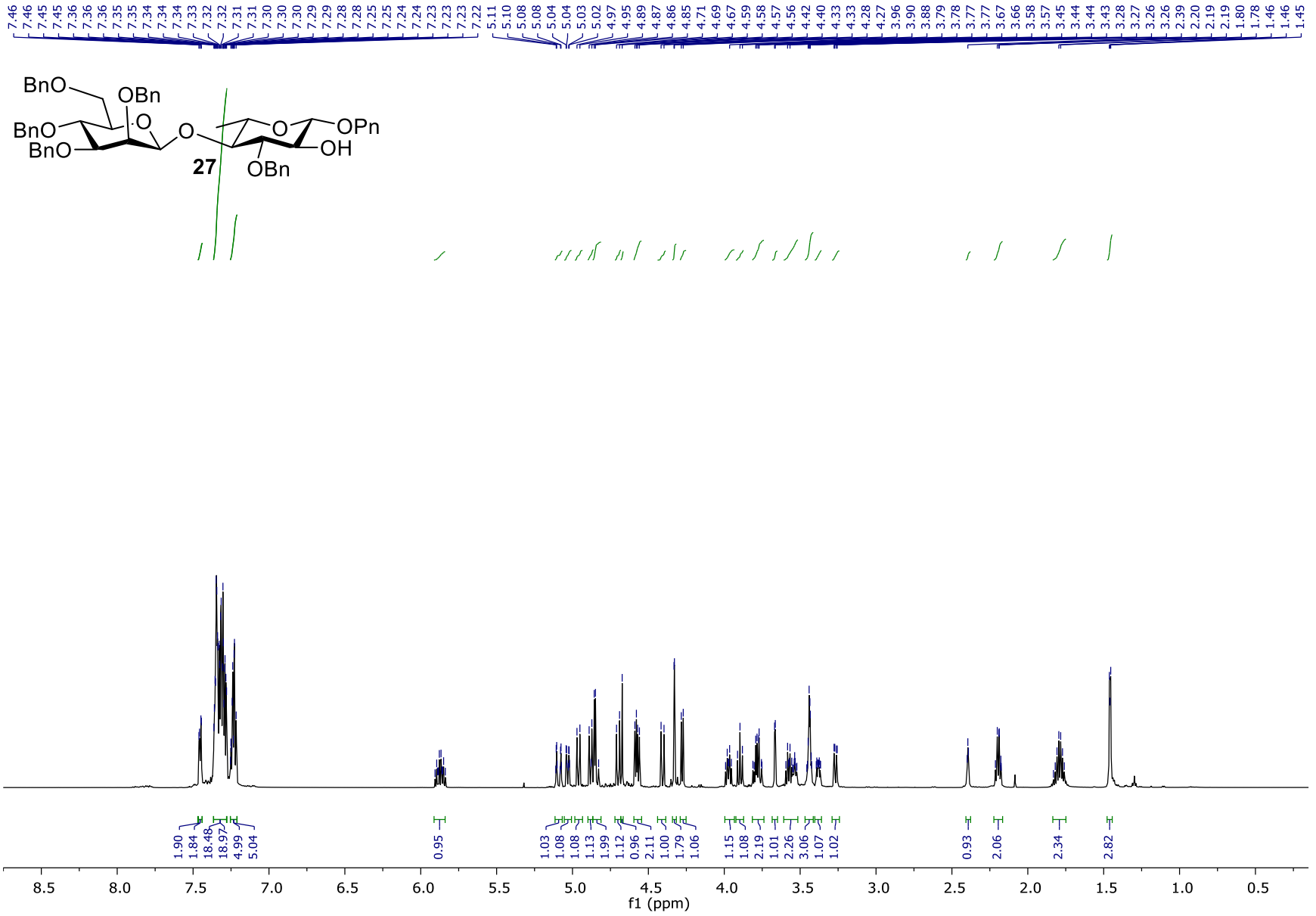
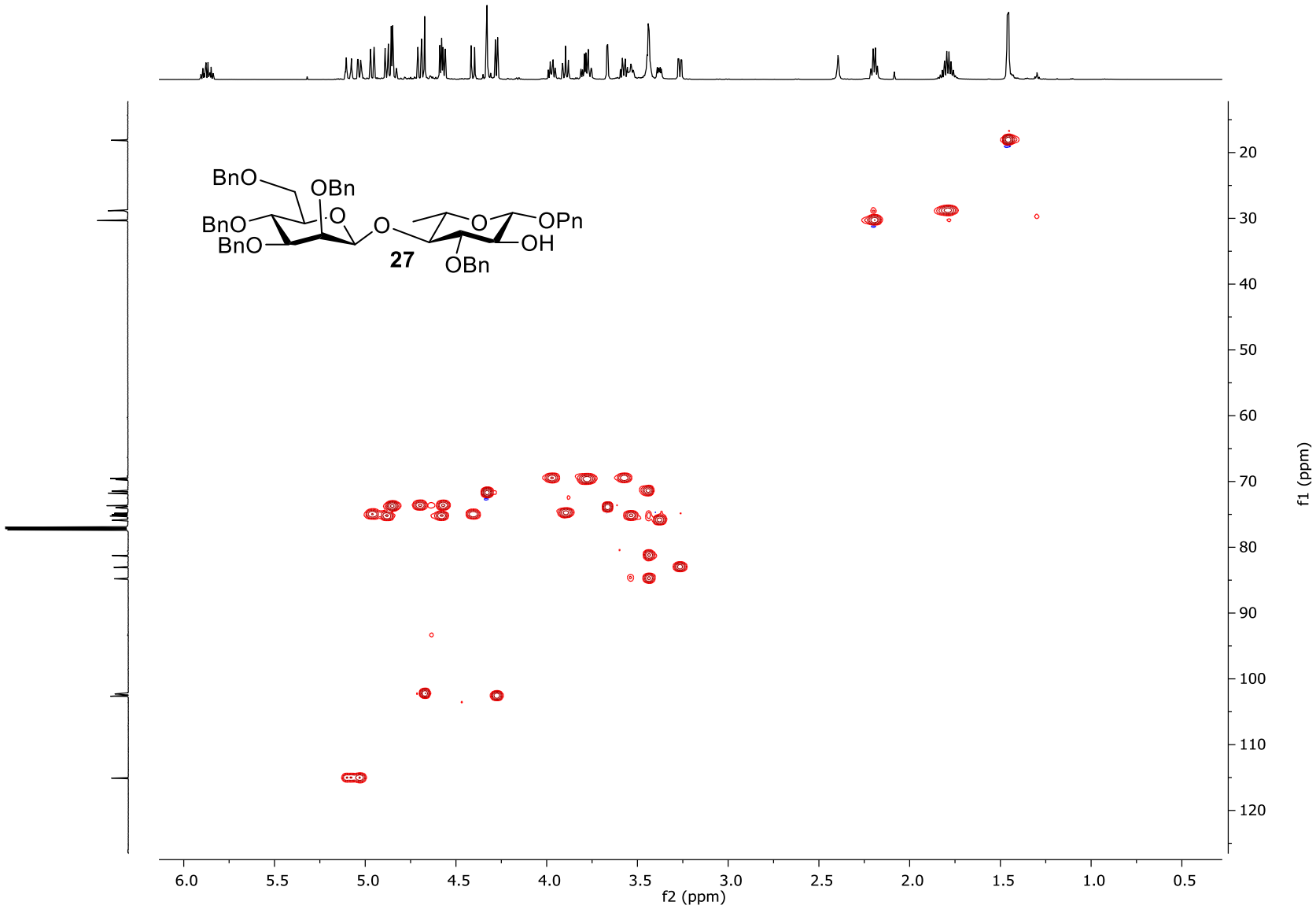
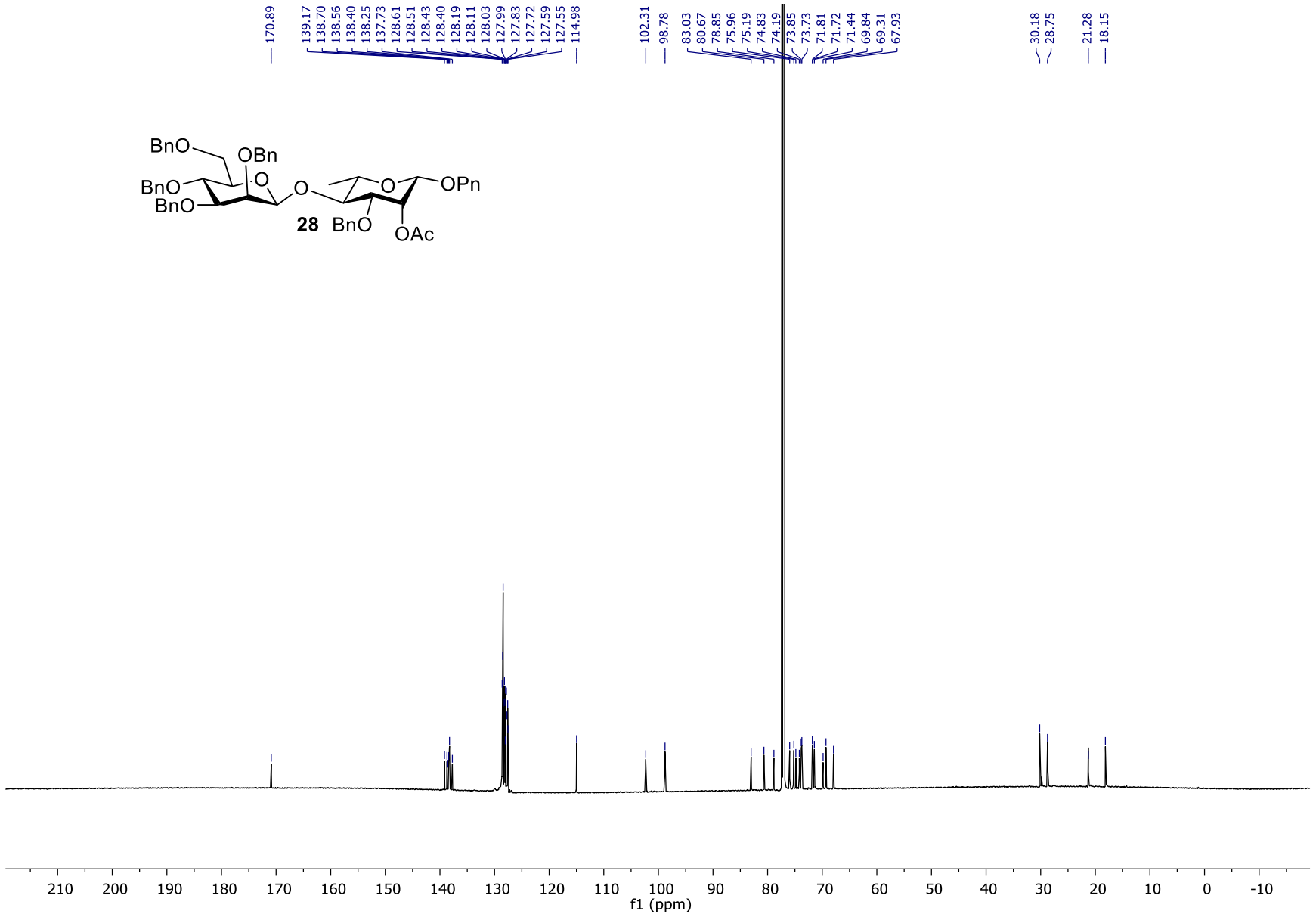
BnO
OBn
BnO
BnO
O
O
O
O
OPn
O
OBn
26
1.04 3.05 3.06 2.15 17.61 4.68 1.94 0.98 1.03 1.07 1.03 1.07 1.01 1.14 1.65 1.16 1.01 1.06 0.90 0.95 0.97 2.09 1.02 1.06 1.02 1.07 2.05 2.10 1.94 1.07 1.00 2.29 2.07 2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

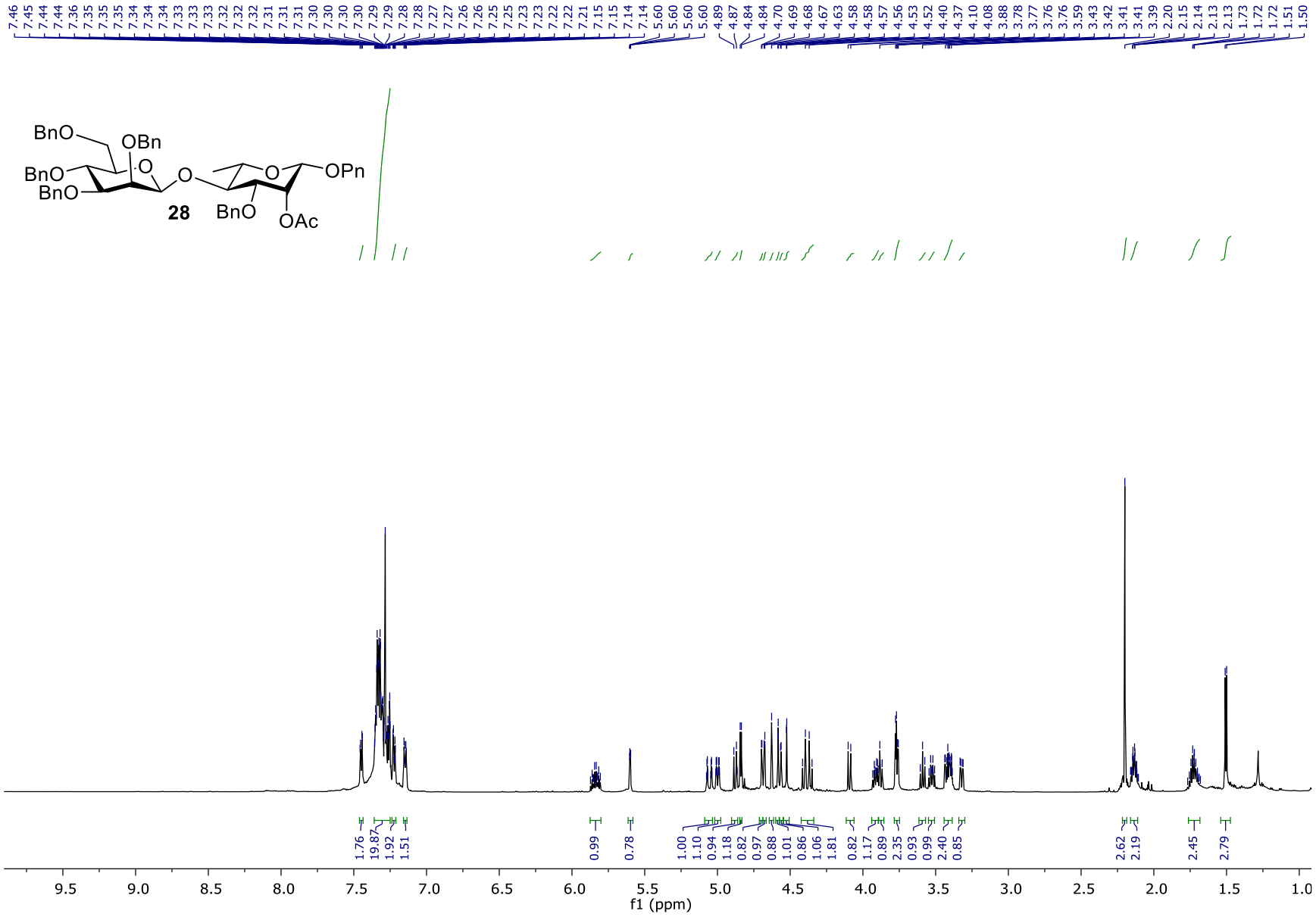

BnO
OBn
BnO
BnO
O
O
O
O
OPn
OBn
26
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)

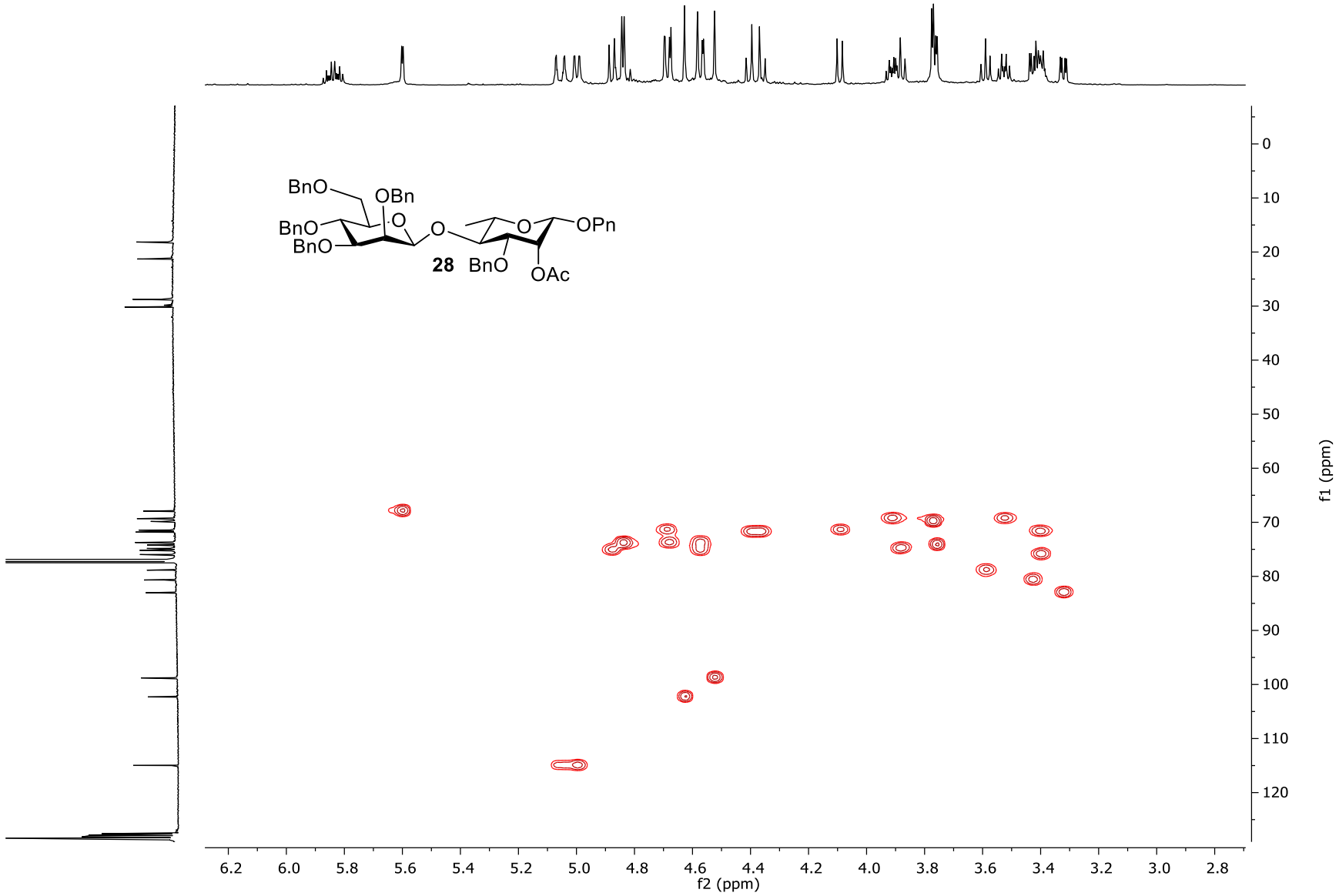

139.02
138.85
138.68
138.47
138.42
138.24
128.60
128.48
128.45
128.41
128.21
128.19
127.81
127.77
127.73
127.67
127.56
127.53
127.38
115.09
102.64
102.29
84.79
83.05
81.25
77.37
77.16
76.95
75.91
75.29
75.24
75.05
74.83
73.98
73.80
73.68
71.77
71.46
69.72
69.55
30.35
28.85
18.14
BnO
OBn
BnO
BnO
O
O
O
OPn
OH
OBn
27
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

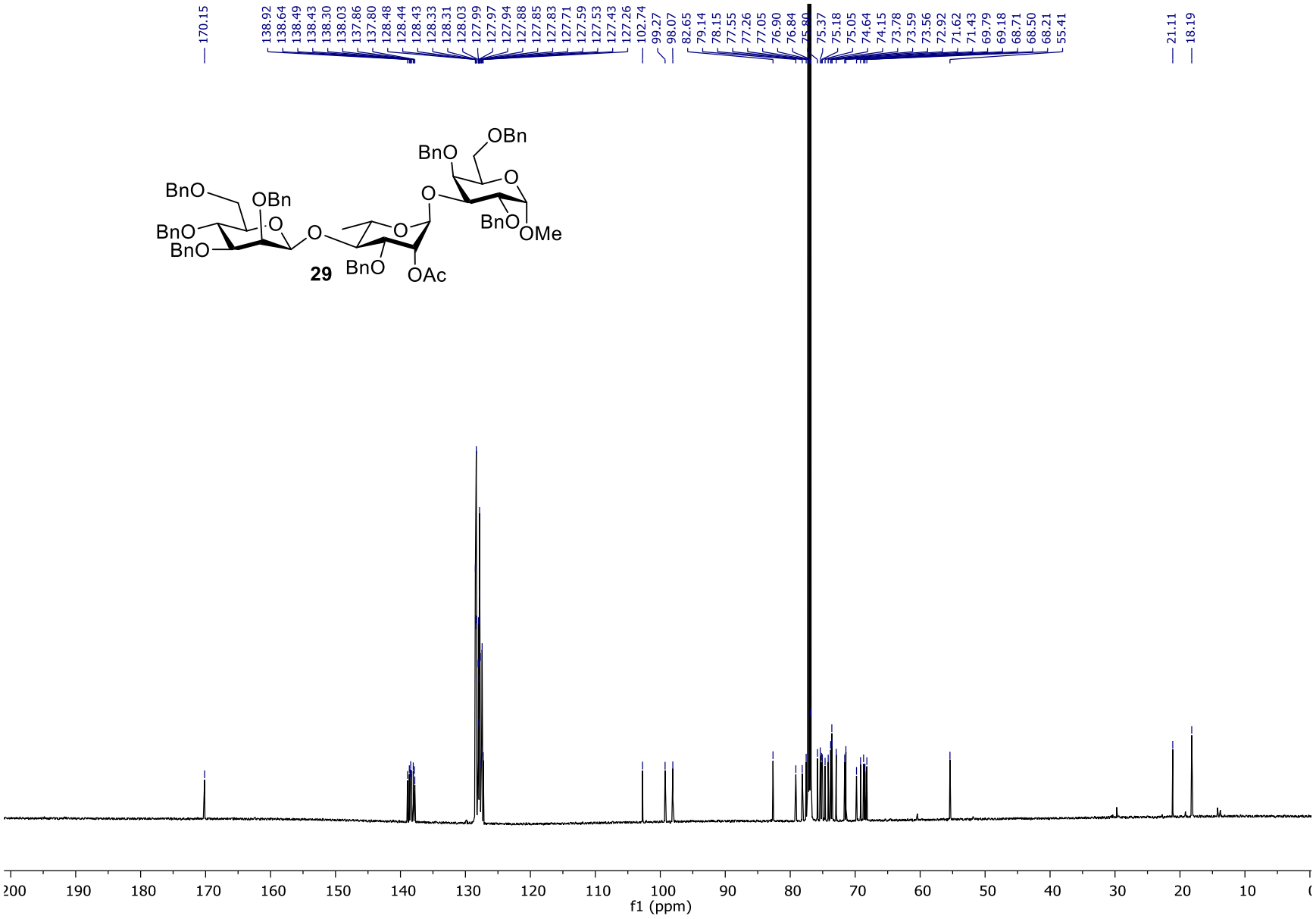

7.46 7.46 7.45 7.45 7.36 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.28 7.28 7.25 7.24 7.24 7.23 7.23 7.23 7.22 5.11 5.10 5.08 5.08 5.04 5.04 5.03 5.02 4.97 4.95 4.89 4.87 4.86 4.85 4.71 4.69 4.67 4.59 4.58 4.57 4.56 4.42 4.40 4.33 4.33 4.28 4.27 3.96 3.90 3.88 3.79 3.78 3.77 3.77 3.67 3.66 3.58 3.57 3.45 3.44 3.43 3.28 3.27 3.26 3.26 2.39 2.20 2.19 2.19 1.80 1.78 1.46 1.46 1.45
BnO
OBn
BnO
O
O
O
OPn
BnO
OH
27
OBn
1.90 1.84 18.48 18.97 4.99 5.04 0.95 1.03 1.08 1.08 1.13 1.99 1.12 0.96 2.11 1.00 1.79 1.06 1.15 1.08 2.19 1.01 2.26 3.06 1.07 1.02 0.93 2.06 2.34 2.82
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)

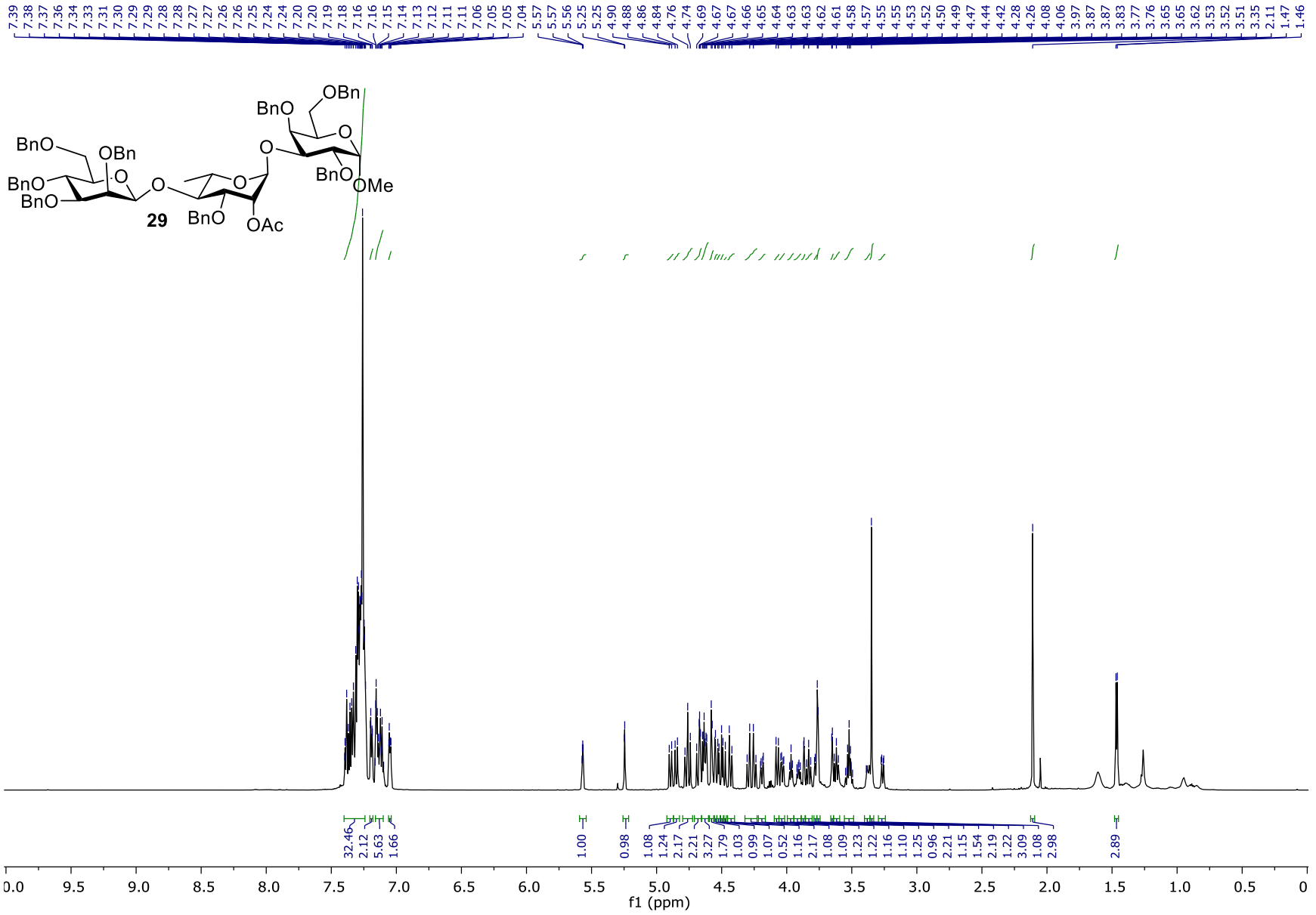

BnO
OBn
BnO
O
O
O
OPn
BnO
OH
27
OBn
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
20
30
40
50
60
70
80
90
100
110
120

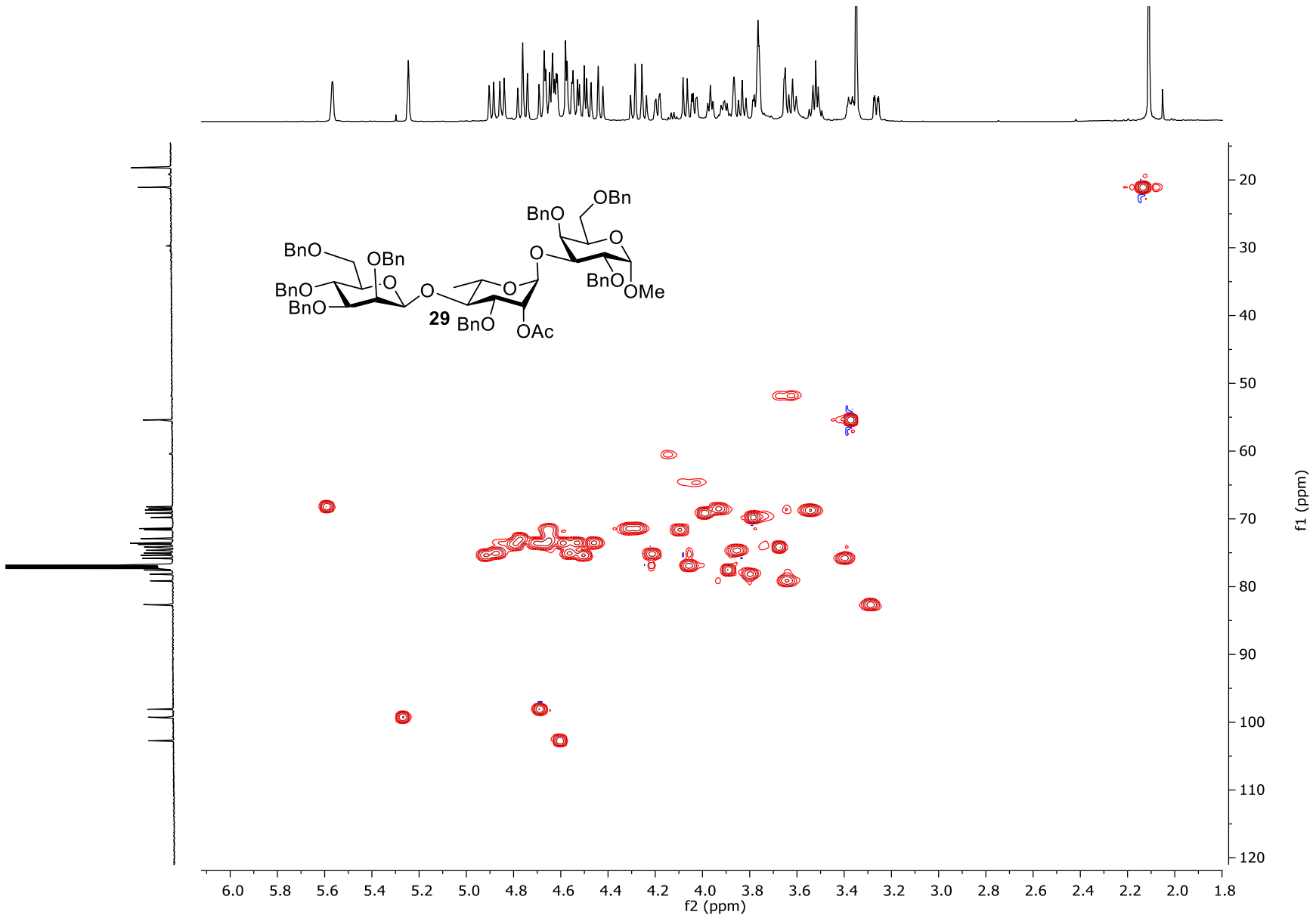

170.89
139.17
138.70
138.56
138.40
138.25
137.73
128.61
128.51
128.43
128.40
128.19
128.11
128.03
127.99
127.83
127.72
127.59
127.55
114.98
102.31
98.78
83.03
80.67
78.85
75.96
75.19
74.83
74.19
73.85
73.73
71.81
71.72
71.44
69.84
69.31
67.93
30.18
28.75
21.28
18.15
BnO
OBn
BnO
BnO
O
O
O
OPn
28
BnO
OAc
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)

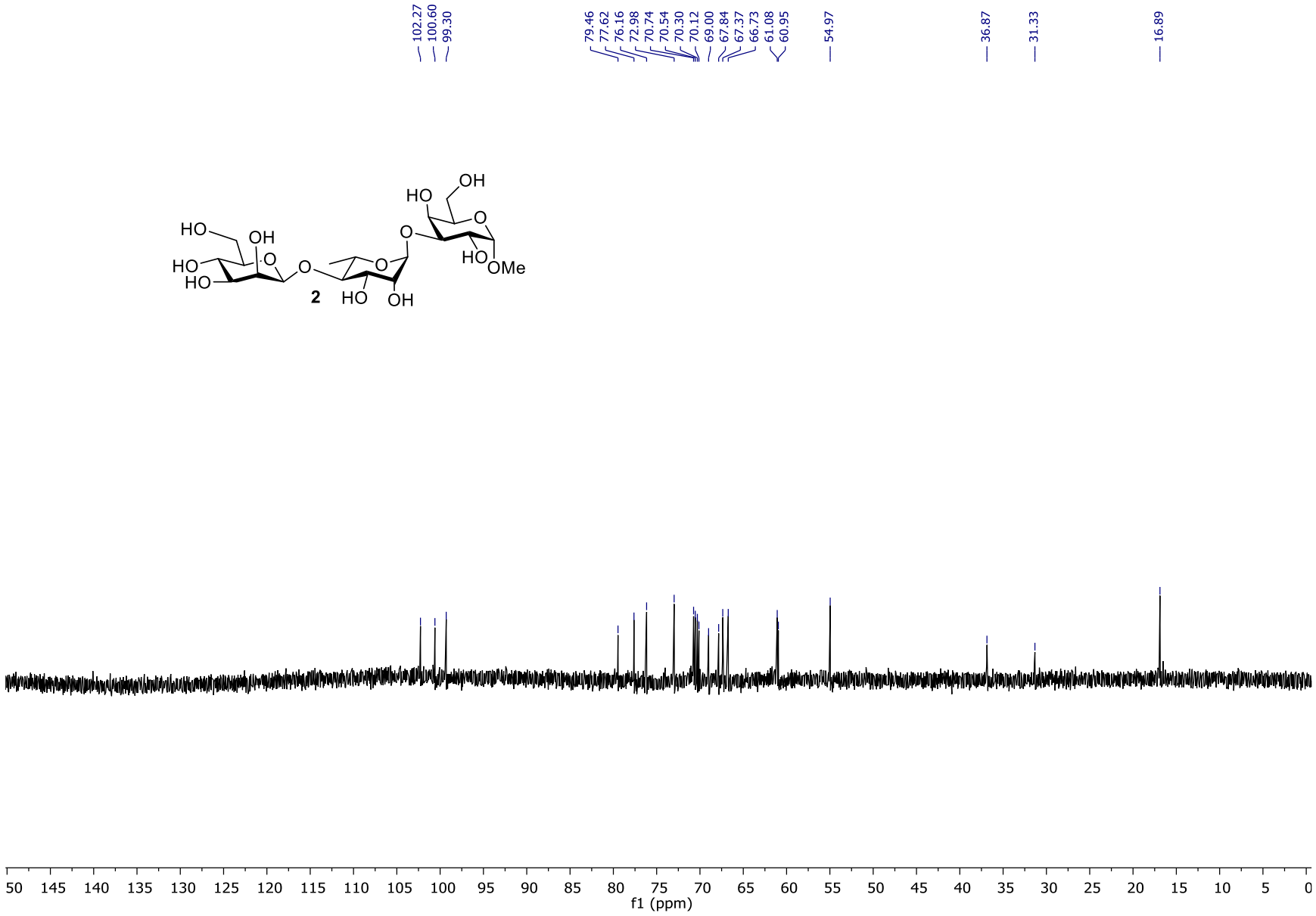

BnO
OBn
BnO
BnO
O
O
O
OPn
BnO
OAc
28
f1 (ppm)

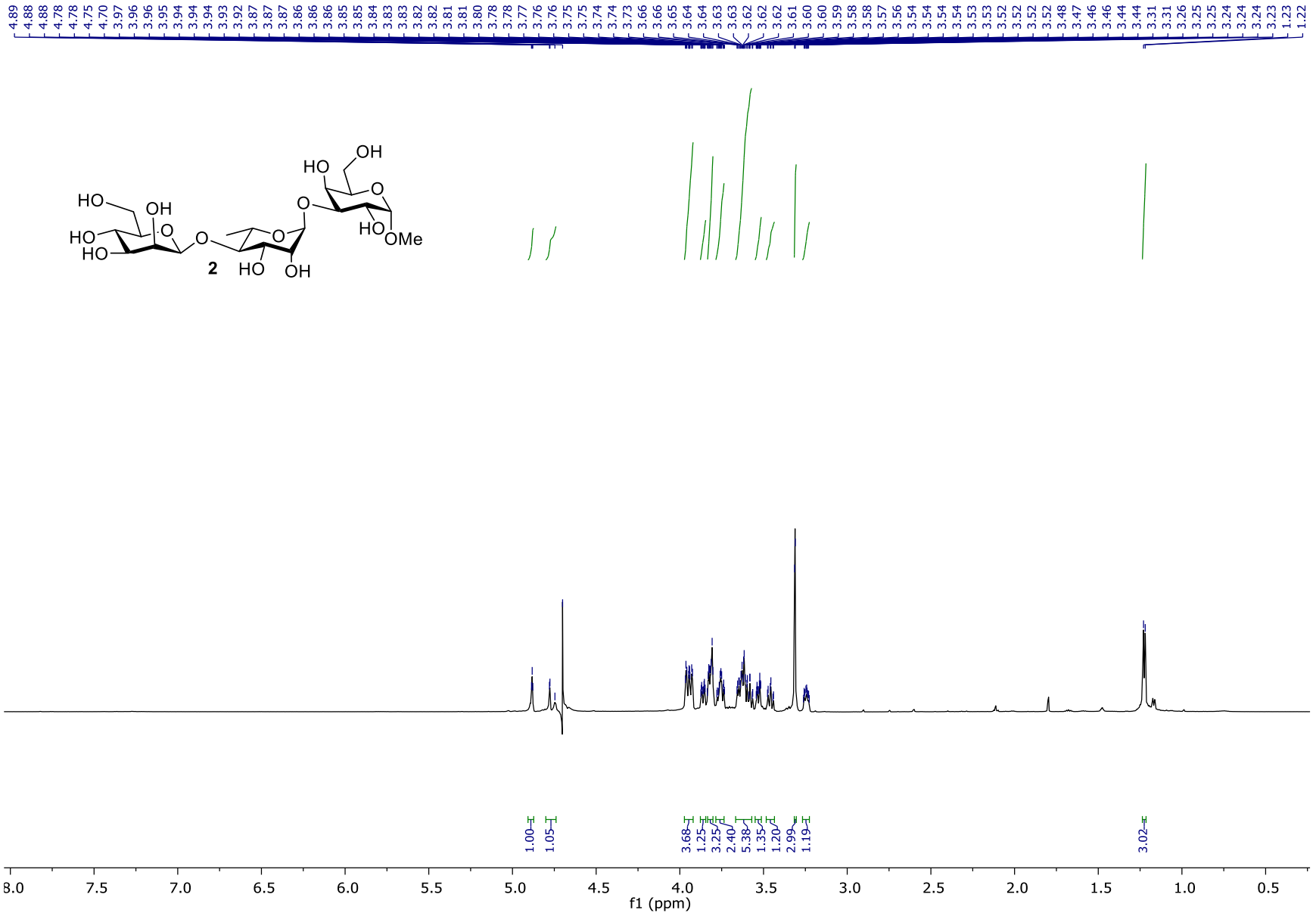

BnO
OBn
BnO
BnO
O
O
O
OPn
28
BnO
OAc
f2 (ppm)
f1 (ppm)


170.15
138.92
138.64
138.49
138.43
138.30
138.03
137.86
137.80
128.48
128.44
128.43
128.33
128.31
128.03
127.99
127.97
127.94
127.88
127.85
127.83
127.71
127.59
127.53
127.43
127.26
102.74
99.27
98.07
82.65
79.14
78.15
77.55
77.26
77.05
76.90
76.84
75.80
75.37
75.18
75.05
74.64
74.15
73.78
73.59
73.56
72.92
71.62
71.43
69.79
69.18
68.71
68.50
68.21
55.41
21.11
18.19
BnO
OBn
BnO
BnO
O
O
O
O
BnO
OBn
O
BnO
OMe
BnO
OAc
29
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.39 7.38 7.37 7.36 7.34 7.33 7.31 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.26 7.25 7.24 7.24 7.20 7.20 7.19 7.18 7.16 7.16 7.15 7.14 7.13 7.12 7.11 7.11 7.06 7.05 7.05 7.04 5.57 5.57 5.56 5.25 5.25 4.90 4.88 4.86 4.84 4.76 4.74 4.69 4.67 4.67 4.66 4.65 4.64 4.63 4.63 4.62 4.61 4.58 4.57 4.55 4.55 4.53 4.52 4.50 4.49 4.47 4.44 4.42 4.28 4.26 4.08 4.06 3.97 3.87 3.87 3.83 3.77 3.76 3.65 3.65 3.62 3.53 3.52 3.51 3.35 2.11 1.47 1.46
BnO
OBn
BnO
BnO
O
O
BnO
OBn
O
BnO
OMe
O
O
BnO
OAc
29
32.46 2.12 5.63 1.66 1.00 0.98 1.08 1.24 2.17 2.21 3.27 1.79 1.03 0.99 1.07 0.52 1.16 2.17 1.08 1.09 1.23 1.22 1.16 1.10 1.25 0.96 2.21 1.15 1.54 2.19 1.22 3.09 1.08 2.98 2.89
0.0 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
f1 (ppm)


BnO
OBn
BnO
BnO
O
O
O
29
BnO
OAc
BnO
OBn
O
BnO
OMe
f2 (ppm)
f1 (ppm)


102.27
100.60
99.30
79.46
77.62
76.16
72.98
70.74
70.54
70.30
70.12
69.00
67.84
67.37
66.73
61.08
60.95
54.97
36.87
31.33
16.89
HO
OH
HO
HO
O
O
HO
OH
O
O
HO
OH
O
HO
OMe
2
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


4.89 4.88 4.88 4.78 4.78 4.75 4.70 3.97 3.96 3.96 3.95 3.94 3.94 3.94 3.93 3.92 3.87 3.87 3.87 3.86 3.86 3.86 3.85 3.85 3.84 3.83 3.83 3.82 3.82 3.81 3.81 3.80 3.78 3.78 3.77 3.76 3.76 3.75 3.75 3.74 3.74 3.73 3.66 3.66 3.65 3.64 3.64 3.63 3.63 3.62 3.62 3.62 3.61 3.60 3.60 3.59 3.58 3.58 3.57 3.56 3.54 3.54 3.54 3.54 3.53 3.53 3.52 3.52 3.52 3.52 3.48 3.47 3.46 3.46 3.44 3.44 3.31 3.31 3.26 3.25 3.25 3.24 3.24 3.24 3.23 1.23 1.22
HO
OH
HO
HO
O
O
O
O
HO
OH
O
HO
OMe
2
HO
OH
1.00 1.05 3.68 1.25 3.25 2.40 5.38 1.35 1.20 2.99 1.19 3.02
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)