Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Dehydrative Glycosylation with Cyclic Phosphonium Anhydrides

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Supporting Material

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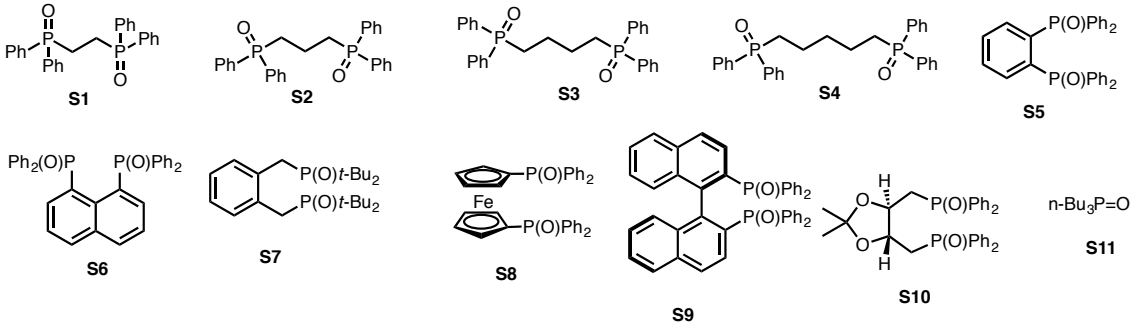
1. General Experimental Protocols

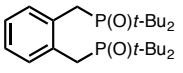
All chemicals were purchased as reagent grade and used without further purification, unless otherwise noted. Solvents were filtered through a column of activated alumina prior to use. All reactions were carried out under dry N_2 in oven-dried glassware. Trifluoromethanesulfonic anhydride was distilled from phosphorus pentoxide. TLC analyses were performed on Merck TLC plates and visualizations were performed with UV light and/or Hanessian stain and/or sulfuric acid stain (5% H_2SO_4 in MeOH). Column chromatography was performed on silica gel (230-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on Bruker/Varian 300/500 MHz instruments are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. The residual solvent reference peaks were used from published literature.[1] 2D NMR experiments were performed using standard parameters (*200 and More NMR Experiments,* S. Berger, S. Braun, Wiley-VCH, 2004). IR measurements were performed on Agilent Cary 630 FT/IR instrument and optical rotations were measured on JASCO P-1030 and are reported as an average of ten data points.

2. Synthesis of Phosphine Oxides

Phosphine oxides **S1,**[2] **S2,**[3] **S3,**[4] **S4,**[4] **S5**,[5] **S6,**[6] **S9, S10,**[7] **S11**[8] were prepared according to the published protocols. Compounds **S7** and **S8** were prepared according to the procedures described below.

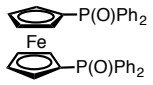


Synthesis of bis-phosphine bis-oxide (General Protocol). A solution of bis-phosphine (0.38 mmol) in THF (4 mL) was treated with 33% H_2O_2 (1.1 mL). The reaction was stirred at rt for 2 h as the reaction mixture turned from opaque to a clear solution upon completion. THF was removed by rotary evaporator and the precipitated solid was filtered, washed with cold H_2O, and dried overnight under high vacuum



S7

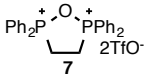
1,2-Bis(diphenylphosphie oxide)xylene (S7). Obtained as a white powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 2H), 7.11 (dd, *J* = 5.6, 3.4 Hz, 2H), 3.82 (d, *J* = 11.4 Hz, 4H), 1.20 (d, *J* = 13.2 Hz, 36H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 134.6, 134.5, 132.5, 126.5, 36.8, 36.2, 29.6, 29.1, 27.1, 26.1; IR (ATR) 3056, 2960, 2926, 2855, 1439, 1194, 1115 cm^{-1}; ^{31}P NMR (162 MHz, $CDCl_3$) δ 63.5; HRMS (ESI) *m/z* calc for $C_{24}H_{44}O_2P_2$ ($M+H^+$) 427.2895, found 427.2895.



S8

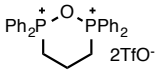
1,1'Bis(diphenylphosphine oxide)ferrocene (S8). Obtained as an orange powder: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.21 (m, 20H), 4.68 (s, 4H), 4.27 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.6, 131.3, 131.2, 128.3, 128.2, 128.1, 74.1, 74.0, 73.5, 73.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6; IR (ATR) 3484, 3098, 3052, 1439, 1168, 1123 cm^{-1}; HRMS (ESI) *m/z* calc for $C_{34}H_{28}FeO_2P_2$ ($M+Li^+$), 593.1075, found 593.1073.

3. Synthesis of Cyclic Phosphonium Anhydrides



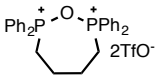
7

Phosphonium salt 7.[9] In an NMR tube a solution of **S1** (7.5 mg, 0.017 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (10 μL, 0.060 mmol, 3.5 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and characterized by NMR: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.10 – 7.54 (m, 20H), 4.46 (d, J = 7.2 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 135.6, 135.5, 135.4, 132.7, 132.6, 132.5, 123.5, 122.2, 119.3, 118.3, 117.9, 117.0, 24.9, 24.8, 24.1, 24.0; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 60.2.



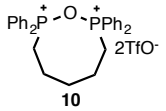
8

Phosphonium salt 8.[9] In an NMR tube a solution of **S2** (23.8 mg, 0.054 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (10.8 μL, 0.064 mmol, 1.2 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and was characterized by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.89 – 7.61 (m, 20H), 3.12 (dt, J = 11.2, 7.9 Hz, 4H), 2.04 (dt, J = 16.0, 7.9 Hz, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 135.4 (3), 131.5, 131.4 (2), 131.3, 130.1 (2), 130.0, 129.9 (2), 125.8, 122.2, 121.6, 120.8, 117.3, 113.1, 27.0, 26.8, 26.1, 25.9, 14.1, 14.0 (2); ^{31}P NMR (122 MHz, CD_2Cl_2) δ 85.4.



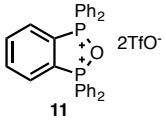
9

Phosphonium salt 9.[9] In an NMR tube a solution of **S3** (11.3 mg, 0.025 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (4.5 μL, 0.024 mmol, 1.1 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.03 – 7.61 (m, 20H), 3.84 (q, J = 5.7 Hz, 4H), 2.61 – 2.38 (m, 4H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 139.9, 135.0, 134.9, 134.8, 132.9, 132.8 (2), 130.0, 128.4, 124.1, 122.2, 120.0, 119.4, 119.3, 118.6, 117.9, 117.8, 23.4, 23.1, 22.7, 19.2; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 90.6.



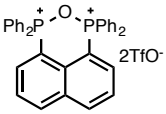
10

Phosphonium salt 10. In an NMR tube a solution of **S4** (12.6 mg, 0.027 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (5 μL, 0.029 mmol, 1.1 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.91 – 7.52 (m, 20H), 2.90 – 2.64 (m, 4H), 1.69 (m 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 135.1 (2), 131.4, 131.3, 129.9, 129.7, 125.8, 123.0, 121.6, 117.4, 113.2, 30.4, 26.0, 25.2, 19.9, 19.9; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 62.0.



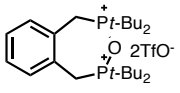
11

Phosphonium salt 11. In an NMR tube a solution of **S5** (17.0 mg, 0.036 mmol, 1.5 equiv) in anh. CD_2Cl_2 (0.4 mL) was treated with distilled triflic anhydride (8.0 μL, 0.045 mmol, 1.25 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed at 0 °C for 30 min and the reaction was characterized by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.91 – 7.80 (m, 2H), 7.72 – 7.63 (m, 4H), 7.60 – 7.38 (m, 18H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 139.3, 134.8, 134.3 (2), 134.2, 131.3, 125.7, 125.6, 124.7, 124.6, 121.3, 119.7, 118.1, 116.5, 115.4, 114.3; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 51.8.



12

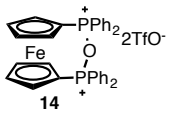
Phosphonium salt 12. In an NMR tube a solution of **S6** (25.3 mg, 0.048 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (9.6 μL, 0.057 mmol, 1.2 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.92 – 8.73 (m, 2H), 8.15 (dq, J = 26.6, 8.8, 8.3 Hz, 4H), 8.01 – 7.42 (m, 20H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 140.3, 139.4, 139.3, 139.2, 138.8, 134.8, 134.7, 134.6, 131.2, 131.1, 131.0, 128.4, 128.2, 128.1, 121.9, 117.6, 116.6, 116.5, 115.8, 115.1, 115.0, 108.3, 106.9. ^{31}P NMR (162 MHz, CD_2Cl_2) δ 68.7.



13

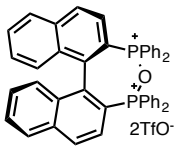
Phosphonium salt 13. In an NMR tube a solution of **S7** (26.7 mg, 0.063 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (12.6 μL, 0.075 mmol, 1.2 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.49 – 7.35 (m, 4H), 3.97 (d, J = 10.8 Hz, 2H), 1.35 (d, J = 15.6 Hz, 36H);

^{13}C NMR (75 MHz, CD_2Cl_2) δ 135.8, 131.3, 127.9, 123.6, 119.4, 115.2, 39.2, 38.6, 28.0; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 95.7.



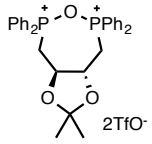
14

Phosphonium salt 14. In an NMR tube a solution of **S8** (43.9 mg, 0.075 mmol, 1 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (15.1 μL, 0.09 mmol, 1.2 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.12 – 9.59 (m, 4H), 7.27 (br s, 2H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 140.2, 134.9, 134.8, 134.7, 133.3, 133.2, 133.1, 119.2, 119.0, 118.2, 117.9, 117.4, 117.2, 82.6, 82.5, 82.4, 80.1, 80.0, 80.0; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 79.2.



(R)-**15**

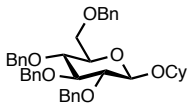
Phosphonium salt (*R*)-15. In an NMR tube a solution of **S9** (29 mg, 0.044 mmol, 1.5 equiv) in anh. CD_2Cl_2 (0.5 mL) was treated with distilled triflic anhydride (7.0 μL, 0.037 mmol, 1.25 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed and immediately characterized by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00 – 7.90 (m, 6H), 7.86 – 7.68 (m, 5H), 7.65 (d, *J* = 1.7 Hz, 5H), 7.51 – 7.41 (m, 3H), 7.38 – 7.04 (m, 8H), 7.02 – 6.87 (m, 5H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 134.9, 134.4, 133.1, 132.3, 132.2, 130.6, 130.5, 130.3, 130.1, 129.8, 129.7, 129.5, 128.6, 128.5, 128.2, 128.1, 127.8, 127.6, 126.8, 121.0, 120.7, 117.8, 117.6; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 40.8.



(R)-**16**

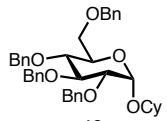
Phosphonium salt (*R*)-16. In an NMR tube a solution of **S10** (11.5 mg, 0.022 mmol, 1 equiv) in anh. CD_2Cl_2 (0.4 mL) was treated with distilled triflic anhydride (4.4 μL, 0.026 mmol, 1.2 equiv) under inert nitrogen atmosphere of a glovebox. The solution was vortexed, stirred at 0 °C for 30 min, and analyzed by NMR: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.07 – 7.73 (m, 13H), 7.73 – 7.50 (m, 7H), 4.36 – 4.21 (m, 2H), 3.96 (d, *J* = 12.3 Hz, 1H), 3.48 (td, *J* = 16.6, 16.2, 1.8 Hz, 2H), 2.98 (ddd, *J* = 15.5, 9.0, 6.2 Hz, 1H), 1.07 (s, 6H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 137.6, 137.4, 136.2, 135.3, 135.0, 132.8, 132.6, 131.8, 131.6, 131.5, 129.8, 129.7, 129.4, 129.3, 74.6, 74.5, 74.4, 74.3, 25.9; ^{31}P NMR (122 MHz, CD_2Cl_2) δ 58.4.

4. Detailed Procedures for Compounds 18-40



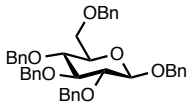
18a

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (18a). Table 1, entry 4. A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (1.26 g, 2.76 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (1.13 g, 5.54 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, the mixture was cooled to 0 °C, Tf_2O (463 μL, 2.76 mmol) was added and stirred at 0 °C for 30 min. 2,3,4,6-Tetra-*O*-benzyl-D-glucopyranoside **17** (1.00 g, 1.84 mmol) in anhydrous dichloromethane (0.8 mL) was added, stirred for 15 min at 0 °C, followed by cyclohexanol (0.383 mL, 3.68 mmol). This mixture was stirred at 0 °C for 2 h and at rt for 16 h, quenched with Et_3N, filtered, concentrated, and toluene was added to the residue and decanted. The solvent was concentrated, the crude material was triturated with chloroform and toluene and filtered to recover the phosphine oxide (1.15 g, 91%). The crude compound was purified by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **18a** (0.95 g, 83%, *α/β* = 1:1.9) as a white solid. β anomer: $[\alpha]_D^{23}$ +10 (c 0.65, $CHCl_3$); IR (ATR) 2934, 2859, 1500, 1366, 1067, 1022 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.17 (m, 20 H), 5.00 (d, J = 10.9 Hz, 1H), 4.93 (d, J = 10.9 Hz, 1H), 4.83 – 4.70 (m, 3H), 4.63 – 4.50 (m, 3H), 3.76 – 3.62 (m, 4H), 3.55 (t, J = 9.3 Hz, 1H), 3.48 – 3.43 (m, 2H), 2.04 – 1.93 (m, 2H), 1.80 – 1.74 (m, 2H), 1.56 – 1.21 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.5, 138.3, 138.1, 128.4 (2), 128.3, 128.2, 128.0, 127.9, 127.7 (2), 127.6 (2), 127.5, 102.0, 84.9, 82.3, 78.0, 77.8, 75.7, 75.0, 74.8, 74.8, 73.4, 69.2, 33.8, 32.0, 25.7, 24.1, 24.0; HRMS (ESI) *m/z* calc for $C_{40}H_{46}O_6Li$ ($M+Li^+$) 629.3455, found 629.3451.



α–**18a**

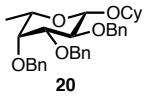
Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranoside (18a). Table 1, entry 6. A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (105 mg, 0.14 mmol) and 2,4,6-tri-*tert*-butylpyridine (69.0 mg, 0.28 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.10 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added and cooled to 0 °C, Tf_2O (64.9 μL, 0.230 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **17** (83.0 mg, 0.153 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. A solution of TBAI (0.113g, 0.306 mmol) and benzyl alcohol (15.9 μL, 0.153 mmol) in dichloromethane (3.0 mL) was then added and the reaction mixture over 45 min. The reaction mixture was stirred for 1 h, extracted (3x) with CH2Cl2, washed with NaHCO3, bride, dried (MgSO4), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **18b** (48.0 mg, 50%, only α) as a colorless oil. The analytical data is in agreement with that reported in the literature.[10]



18b

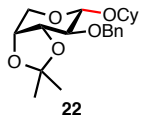
Benzyl 1,2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside (18b). Table 1, entry 5. A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (63 mg, 0.140 mmol) and 2,4,6-tri-*tert*-butylpyridine (69.0

mg, 0.280 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added and cooled to 0 °C, Tf_2O (19 µL, 0.12 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **17** (50.0 mg, 0.0900 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. Benzyl alcohol (20.0 mg, 0.18 mmol) was then added and the reaction mixture was stirred at 0 °C for 30 min, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **18b** (53.0 mg, 91%, *α/β* = 1.2/1) as a white solid. The analytical data is in agreement with that reported in the literature.[11]



20

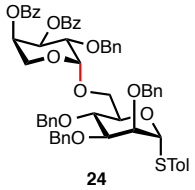
Cyclohexyl 2,3,4-tri-*O*-benzyl-6-deoxy-*β*-L-fucopyranose (20). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (91.0 mg, 0.199 mmol) and 2,4,6-tri-*tert*-butylpyridine (73.0 mg, 0.297 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added, followed by anhydrous dichloromethane (3.0 mL). This mixture was cooled to 0 °C, Tf_2O (33.0 µL, 0.199 mmol) was added and the mixture was stirred 0 °C for 30 min. A solution of 2,3,4-tri-*O*-benzyl-6-deoxy-L-fucopyranose **19**[12] (87.0 mg, 0.199 mmol) in anhydrous dichloromethane (0.8 mL) was added, the mixture was stirred at 0 °C for 15 min and a solution of cyclohexanol (10.0 µL, 0.099 mmol) in anhydrous dichloromethane (0.5 mL) was added. The reactions mixture was stirred at -20 °C for 16 h, quenched with Et_3N, diluted with EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **20** (48.0 mg, 94%, *α/β* = 1:32) as a colorless oil: $[\alpha]_D^{23}$ -0.3 (c 0.6, $CHCl_3$); IR (ATR) 2944, 2859, 1455, 1366, 1071, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.39 – 7.27 (m, 15 H), 4.98 (dd, *J* = 11.3, 5.0 Hz, 1H), 4.80 – 4.69 (m, 4H), 4.42 (d, *J* = 7.7 Hz, 1H), 3.78 (dd, *J* = 9.7, 7.7 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.54 (dd, *J* = 3.0, 1.0 Hz, 1H), 3.49 (dd, *J* = 9.7, 3.0 Hz, 1H), 3.44-3.40 (m, 1H), 1.97 – 1.90 (m, 2H), 1.76 – 1.72 (m, 2H), 1.52 – 1.20 (m, 7H), 1.15 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 139.0, 138.8, 138.7, 128.6, 128.3, 128.2(2), 128.1, 127.5(2), 127.4, 101.8, 82.8, 79.5, 76.3, 75.1, 74.4, 73.2, 70.2, 33.6, 31.8, 25.7, 24.1, 24.0, 17.0; HRMS (ESI) *m/z* calc for $C_{33}H_{40}O_5Li$ ($M+Li^+$) 523.3036, found 523.3037.



22

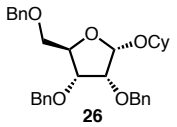
Cyclohexyl 3,4-*O*-(1-methylethylidene)-2-*O*-benzyl-α-D-arabinose (22). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (102 mg, 0.222 mmol) and 2,4,6-tri-*tert*-butylpyridine (132 mg, 0.534 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added and the reaction mixture was cooled to 0 °C, Tf_2O (37.0 µL, 0.222 mmol) was added and the mixture was stirred at 0 °C for 30 min. A solution of 2-*O*-benzyl-3,4-*O*-(1-methylethylidene)-D-arabinose **21** (50.0 mg, 0.178 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. A solution of cyclohexanol (39.0 µL, 0.356 mmol) in anhydrous dichloromethane (0.5 mL) was added and stirred at 0 °C for 30 min, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure.

Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **22** (40.0 mg, 62%, α/β = 1:3) as a white foam: $[\alpha]_D^{23}$ -41.3 (c 1.2, $CHCl_3$); IR (ATR) 2934, 2859, 1455, 1373. 1127, 1033 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 5 H), 4.85 (d, J = 11.7 Hz, 1H), 4.78 (d, J = 11.7 Hz, 1H), 4.46 (d, J = 7.2 Hz, 1H), 4.24 – 4.21 (m, 1H), 4.14 – 4.10 (m, 1H), 4.08 (dd, J = 13.1, 3.5 Hz, 1H), 3.73 (dd, J = 13.1, 3.7 Hz, 1H), 3.67 – 3.62 (m, 1H), 3.44 (t, J = 7.2 Hz, 1H), 1.93 – 1.89 (m, 2H), 1.78 – 1.72 (m, 2H), 1.54 -1.21 (m, 6H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 128.2, 128.1, 127.5, 109.8, 100.5, 79.8, 78.2, 73.5, 73.0, 62.4, 33.7, 31.7, 27.7, 26.1, 25.6, 24.1, 23.9; HRMS (ESI) *m/z* calc for $C_{21}H_{30}O_5Li$ ($M+Li^+$) 369.2254, found 369.2265.



24

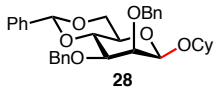
***p*-Tolyl 6-*O*-(2-*O*-benzyl-3,4-di-*O*-benzoyl-β-D-arabinopyranosyl)-2,3,4-tri-*O*-(benzyl)-α-D-mannopyranoside (24).** A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (33.0 mg, 0.0720 mmol) and 2,4,6-tri-*tert*-butylpyridine (27.0 mg, 0.107 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (12.0 µL, 0.072 mmol) was added and the mixture was stirred at 0 °C for 30 min. A solution of 3,4-*O*-benzoyl-2-*O*-benzyl-D-arabinopyranose **23a** (32.0 mg, 0.072 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C followed by a solution of *p*-tolyl 2,3,4-tri-*O*-benzyl-1-thio-α-D-mannopyranoside **23b**[13] (20.0 mg, 0.036 mmol) in anhydrous dichloromethane (0.5 mL). The reaction mixture was stirred at 0 °C for 2 h and at rt for 3 h, quenched with Et_3N, diluted with EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 20:1 to 10:1) afforded **24** (25.0 mg, 70%, α/β = 11:1) as a clear oil.: $[\alpha]_D^{23}$ -79.3 (c 0.9, $CHCl_3$); IR (ATR) 2874, 1726, 1279, 1264, 1093, 1071 cm^{-1}; H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.3, 1.4 Hz, 2H), 7.88 – 7.86 (m, 2H), 7.60 – 7.16 (m, 28H), 7.06 (d, J = 8.1 Hz, 1H), 5.74 (dd, J = 10.2, 3.5 Hz, 1H), 5.56 – 5.54 (m, 1H), 5.53 (d, J = 1.7 Hz, 1H), 5.05 (d, J = 3.3 Hz, 1H), 4.95 (d, J = 11.1 Hz, 1H), 4.75 – 4.61 (m, 6H), 4.34 – 4.30 (m, 1H), 4.16 – 3.85 (m, 7H), 3.71 (dd, J = 13.1, 2.2 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 165.3, 138.6, 138.2, 138.0 (2), 137.4, 133.1, 132.9, 131.7, 130.6, 130.0 (2), 129.9, 129.8, 129.7, 129.6, 128.4, 128.3, 128.2, 128.0 (2), 127.7 (2),127.6, 98.2, 85.8, 80.1, 76.2, 75.1, 75.0, 73.9, 72.6, 72.5, 72.1, 72.0, 70.5, 69.9, 68.0, 60.6, 21.0; HRMS (ESI) *m/z* calc for $C_{60}H_{58}O_{11}SLi$ ($M+Li^+$) 993.3861, found 993.3843.



26

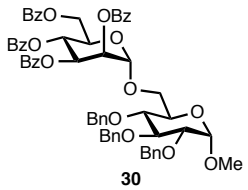
Cyclohexyl 2,3,5-tri-*O*-benzyl-α-D-ribofuranoside (26).[14] A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (40.8 mg, 0.0890 mmol) and 2,4,6-tri-*tert*-butylpyridine (52.9 mg, 0.214 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, the mixture was cooled to 0 °C, Tf_2O (18.0 µL, 0.107 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,5-tri-*O*-benzyl-D-ribofuranoside

25 (30.0 mg, 0.717 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C, followed by solution of cyclohexanol (2.2 µL, 0.210 mmol) and TBAI (52.7 mg, 0.143 mmol) in dichloromethane (3.0 mL) added over 45 min. The reaction was continued at 0 °C for 1 h, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **26** (8.0 mg, 76%, α only) as a white foam: $[\alpha]_D^{23}$ +103.6 (c 0.5, $CHCl_3$); IR (ATR) 2937, 1455, 1221, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.21 (m, 15H), 5.18 (d, J = 4.2 Hz, 1H), 4.72 (d, J = 13.2 Hz, 2H), 4.62 (d, J = 12.3 Hz, 1H), 4.54 – 4.41 (m, 3H), 4.24 (q, J = 3.9 Hz, 1H), 3.84 – 3.82 (m, 1H), 3.77 – 3.75 (m, 1H), 3.62 – 3.58 (m, 1H), 3.46 (dd, J = 10.6, 3.7 Hz, 1H), 3.37 (dd, J = 10.5, 4.2 Hz, 1H), 1.98 – 1.92 (m, 2H), 1.77 – 1.75 (m, 2H), 1.56 -1.17 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 138.2, 138.0, 128.3 (2), 128.2, 128.0 (2), 127.7, 127.6 (2), 127.5, 99.6, 80.9, 76.2, 75.5, 73.4, 72.3, 72.1, 69.9, 33.8, 31.9, 25.7, 24.6, 24.5; HRMS (ESI) *m/z* calc for $C_{32}H_{38}O_5Li$ ($M+Li^+$) 509.2880, found 509.2880.



28

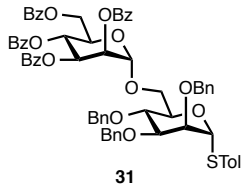
Cyclohexyl 2,3-bis-*O*-benzyl-4,6-*O*-[(*R*)-phenylmethylene]-β-D-mannopyranoside (28). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (61.0 mg, 0.133 mmol) and 2,4,6-tri-*tert*-butylpyridine (66.0 mg, 0.267 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture followed by anhydrous dichloromethane (3.0 mL). This mixture was cooled to 0 °C, Tf_2O (22.0 µL, 0.133 mmol) was added and the reaction mixture was stirred at 0 °C for 30 min. A solution of 2,3-bis-*O*-benzyl-4,6-*O*-[(*R*)-phenylmethylene]-D-mannopyranoside **27**[15] (40.0 mg, 0.089 mmol) in anhydrous dichloromethane (0.8 mL) was added via syringe, this mixture was stirred at 0 °C for 15 min, and a solution of cyclohexanol (19.0 µL, 0.178 mmol) in anhydrous dichloromethane (0.5 mL) was added. The reaction mixture was stirred at 0 °C for 2 h and at rt for 16 h, quenched with Et_3N, diluted with EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 5:1) afforded **28** (43.0 mg, 91%, α/β = 1:8) as a colorless oil: $[\alpha]_D^{23}$ -73 (c 0.45, $CHCl_3$); IR (ATR) 2937, 2863, 1459, 1221, 1093 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.28 (m, 15 H), 5.62 (s, 1H), 5.02 (d, J = 12.5 Hz, 1H), 4.91 (d, J = 12.5 Hz, 1H), 4.66 (d, J = 12.5 Hz, 1H), 4.59 – 4.57 (m, 2H), 4.30 (dd, J = 10.4, 4.8 Hz, 1H), 4.22 (t, J = 9.6 Hz, 1H), 3.95 (t, J = 10.3 Hz, 1H), 3.88 (d, J = 3.2 Hz, 1H), 3.73-3.68 (m, 1H), 3.58 (dd, J = 9.9, 3.2 Hz, 1H), 3.32 (td, J = 9.7, 4.8 Hz, 1H), 1.92 – 1.70 (m, 4H), 1.56 – 1.26 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.4, 137.6, 128.8, 128.7, 128.3, 128.2, 128.1, 127.5, 126.0, 101.4, 100.0, 78.6, 78.1, 76.2, 74.6, 72.3, 68.7, 67.5, 33.4, 31.4, 25.6, 23.7, 23.6 ; HRMS (ESI) *m/z* calc for $C_{33}H_{38}O_6Li$ ($M+Li^+$) 537.2829, found 537.2842.



30

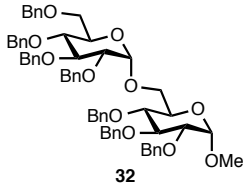
Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (30). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (98.0 mg, 0.214 mmol) and

2,4,6-tri-*tert*-butylpyridine (79.4 mg, 0.320 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added and the mixture was cooled to 0 °C, Tf_2O (36.0 µL, 0.214 mmol) was added and stirred at 0 °C for 30 min. 2,3,4,6-Tetra-*O*-benzoyl-D-mannopyranoside **29a** (128 mg, 0.215 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. Methyl 2,3,4-tri-*O*-benzyl-D-glucopyranoside **29b**[16] (50.0 mg, 0.107 mmol) in anhydrous dichloromethane (0.5 mL) was added, stirred at 0 °C for 120 min and 16 h at rt, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **30** (101 mg, 91%, α/β > 99:1) as a clear oil: $[\alpha]_D^{23}$ +7.7 (c 2, $CHCl_3$); IR (ATR) 2930, 1731, 1264, 1072, 1031 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.3, 1.4 Hz, 2H), 8.05 (dd, J = 8.3, 1.4 Hz, 2H), 7.90 – 7.92 (m, 2H), 7.84 (dd, J = 8.4, 1.4 Hz, 2H), 7.61 – 7.26 (m, 27H), 6.08 (t, J = 10.1 Hz, 1H), 5.89 (dd, J = 10.1, 3.3 Hz, 1H), 5.74 (dd, J = 3.4, 1.8 Hz, 1H), 5.17 (d, J = 1.8 Hz, 1H), 5.03 (dd, J = 11.1, 2.7 Hz, 2H), 4.85 – 4.80 (m, 2H), 4.70 (dd, J = 11.7, 3.1 Hz, 2H), 4.66 – 4.63 (m, 2H), 4.43 – 4.40 (m, 1H), 4.35 (dd, J = 12.1, 4.4 Hz, 1H), 4.05 (t, J = 9.2 Hz, 1H), 3.95 (dd, J = 11.0, 5.1 Hz, 1H), 3.89 – 3.86 (m, 1H), 3.82 (dd, J = 11.0, 1.8 Hz, 1H), 3.60 – 3.52 (m, 2H), 3.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 165.4(2), 165.3, 138.7, 138.2(2), 133.4, 133.2, 133.1, 129.9(2), 129.7(2), 129.4, 129.1, 129.0, 128.6, 128.5(2), 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6(2), 97.9, 97.8, 82.1, 80.2, 77.7, 75.7, 75.0, 73.5, 70.3, 70.0, 69.9, 68.9, 66.9, 66.7, 62.7, 55.2; HRMS (ESI) *m/z* calc for $C_{62}H_{58}O_{15}Li$ ($M+Li^+$) 1049.3937, found 1049.3922.



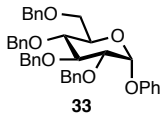
31

***p*-Tolyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (31).** A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (33.0 mg, 0.072mmol) and 2,4,6-tri-*tert*-butylpyridine (43.0 mg, 0.173 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added and cooled to 0 °C, Tf_2O (12.0 µL, 0.115 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranoside **29a** (43.0 mg, 0.072 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. A solution of *p*-tolyl 2,3,4-tris-*O*-benzyl-1-thio-α-D-mannopyranoside **23b** (20.0 mg, 0.036 mmol) in anhydrous dichloromethane (0.5 mL) was added and stirred at 0 °C for 20 min and 16 h at rt., quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) afforded **31** (33.0 mg, 80%, α/β > 99:1) as a colorless oil: $[\alpha]_D^{23}$ -17.9 (c 0.75, $CHCl_3$); IR (ATR) 2930, 1726, 1455, 1268, 1071, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, J = 8.3, 1.4 Hz, 2H), 7.90 (ddd, J = 17.2, 8.3, 1.4 Hz, 4H), 7.74 – 7.72 (m, 2H), 7.74 – 7.15 (m, 29H), 6.93 (d, J = 7.9 Hz, 2H), 5.85 (t, J = 9.5 Hz, 1H), 5.61 (dd, J = 10.0, 4.0 Hz, 1H), 5.57 (d, J = 3.2 Hz, 1H), 5.47 (d, J = 1.6 Hz, 1H), 4.95 (t, J = 3.6 Hz, 1H), 4.85 (d, J = 11.0 Hz, 1H), 4.68 (d, J = 12.3 Hz, 1H), 4.57 (d, J = 12.3 Hz, 1H), 4.52 – 4.47 (m, 4H), 4.35 (dd, J = 12.0, 4.9 Hz, 1H), 4.25 – 4.22 (m, 1H), 4.05 – 4.01 (m, 1H), 3.91 – 3.90 (m, 1H), 3.86 (t, J = 9.5 Hz, 1H), 3.73 – 3.66 (m, 3H), 2.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 165.8, 165.2, 138.3, 138.2, 137.9, 137.3, 136.3, 133.3, 132.9, 131.6, 130.6, 130.1, 129.8, 129.7, 129.7, 129.6, 129.3, 129.0, 128.4 (2), 128.3, 128.2, 128.0, 127.9, 127.7 (2), 127.6, 126.7, 122.8, 98.0, 85.3, 80.2, 76.6, 76.1 (2), 75.0 (2), 72.26, 72.0 (2), 71.8, 70.5, 66.9, 63.7, 63.4, 21.0; HRMS (ESI) *m/z* calc for $C_{68}H_{62}O_{14}SLi$ ($M+Li^+$) 1141.4022, found 1141.4006.



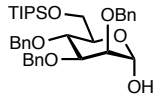
32

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (32). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (119 mg, 0.26 mmol) and 2,4,6-tri-*tert*-butylpyridine (96.0 mg, 0.39 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (44.0 μL, 0.26 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-O-benzyl-D-glucopyranoside **17** (211 mg, 0.390 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. A solution of methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **29b**[16] (60.0 mg, 0.130 mmol) in anhydrous dichloromethane (0.5 mL) was added, and the reaction mixture was stirred at 0 °C for 60 min and 16 h at rt, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chrom. on SiO_2 (Toluene:EtOAc, 10:1) afforded **32** (80.0 mg, 80%, α/β = 1:0.85) as a colorless oil. The analytical data is in agreement with that reported in the literature.[10]



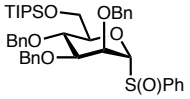
33

Phenyl 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranoside (33). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide (291 mg, 0.636 mmol) and 2,4,6-tri-*tert*-butylpyridine (236 mg, 0.954 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture, followed by anhydrous dichloromethane (3.0 mL). The reaction mixture was cooled to 0 °C, Tf_2O (107 μL, 0.636 mmol) was added and the mixture was stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **17** (347 mg, 0.637 mmol) in anhydrous dichloromethane (0.8 mL) was added, the reaction mixture was stirred for 15 min at 0 °C, followed by a solution of phenol (30.0 mg, 0.318 mmol) in anhydrous dichloromethane (0.5 mL). The reaction was continued at 0 °C for 3 h, quenched with Et_3N, the mixture was dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **33** (193 mg, 98%, *α/β* = 8:1) as a white solid: $[\alpha]_D^{23}$ +76.9 (c 1.2, $CHCl_3$); IR (ATR) 3034, 2867, 1600, 1459, 1227, 1074 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 - 6.99 (m, 25 H), 5.50 (d, J = 3.5 Hz, 1H), 5.08 (d, J = 10.7 Hz, 1H), 4.93 – 4.81 (m, 3H), 4.71 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 4.51 (d, J = 10.7 Hz, 1H), 4.42 (d, J = 12.0 Hz, 1H), 4.23 (t, J = 9.3 Hz, 1H), 3.91 – 3.89 (m, 1H), 3.83-3.80 (m, 1H), 3.77 – 3.73 (m, 2H), 3.59 (dd, J = 10.8, 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 138.0, 137.7, 137.6, 128.6, 128.4 (2), 128.3, 128.0 (2), 127.9 (2), 127.7, 124.6, 122.3, 116.8, 82.0, 79.7, 75.8, 75.1, 73.4, 73.3, 70.8, 68.2; HRMS (ESI) *m/z* calc for $C_{40}H_{40}O_6Li$ ($M+Li^+$) 623.2986, found 623.2986.



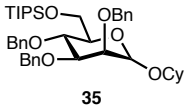
34a

2,3,4-Tri-*O*-benzyl-6-*O*-(triisopropylsilyl)-D-mannopyranose (34a). To a solution of **S20** (0.250 g, 0.350 mmol) in acetone/water (22.5:2.5 mL) at 0 °C NBS (0.0930 g, 0.520 mmol) was added in one portion. After 30 min, the reaction mixture was concentrated and the residue was dissolved in EtOAc (75 mL) and washed with saturated $Na_2S_2O_3$ (2 x 50 mL), water, brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by column chromatography on SiO_2 (Hexanes:EtOAc, 8:1) to provide **34a** (0.12 g, 57%, α/β = 93:7) as a clear oil: $[\alpha]_D^{23}$ +13.6 (c 1, $CHCl_3$); IR (ATR) 3410, 2945, 2867, 1459, 1060, 1030 cm^{-1}; α anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 - 7.29 (m, 15H), 5.24 (dd, *J* = 3.8, 1.9 Hz, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.77 (d, *J* = 12.3 Hz, 1H), 4.69 – 4.66 (m, 4H), 4.01 – 3.89 (m, 5H), 3.78 (t, *J* = 2.4 Hz, 1H), 3.47 (d, *J* = 3.7 Hz, 1H), 1.12 – 1.06 (m, 21H); α/β anomer mixture ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.7, 138.6 (3), 138.4, 138.2, 128.5, 128.4 (2), 128.3 (2), 128.1, 127.8 (2), 127.7 (3), 127.6 (2), 127.5, 93.5, 92.6, 82.8, 79.7, 77.5, 77.3, 77.1, 76.8, 76.6, 76.5, 75.5, 75.1, 75.0, 74.8, 74.6, 74.2, 73.6, 72.9, 72.6, 72.2, 63.4, 62.8, 18.1, 18.0, 12.1, 12.0; HRMS (ESI) calc for $C_{36}H_{50}O_6SiLi$ (M+Li+) 613.3538, found 613.3540.



34b

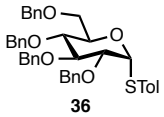
***p*-Tolyl sulfinyl 2,3,4-tri-*O*-benzyl-6-*O*-(triisopropylsilyl)-α-D-mannopyranoside (34b).** To a stirred solution of the alcohol **S20** (0.200 g, 0.280 mmol) in dry DCM (10 mL) was added *m*-CPBA (0.0500 g, 0.280 mmol) at -78 °C After 2 h 30 min the reaction mixture was quenched with aq. $NaHCO_3$ (5 mL) and diluted with DCM (15 mL) biphasic layer was separated, organic layer was washed with 5% aq. NaOH (2 x 15 mL), water, brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 5:1) to provide **34** (0.130 g, 63%) as a clear oil: $[\alpha]_D^{23}$ -51.5 (c 0.45, $CHCl_3$); IR (ATR) 2945, 2870, 1459, 1104, 1033 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.50 - 7.27 (m, 19H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.69 – 4.54 (m, 6H), 4.46 – 4.45 (m, 1H), 4.20 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.04 (t, *J* = 9.4 Hz, 1H), 3.95 – 3.88 (m, 3H), 2.42 (s, 3H), 1.04 – 1.01 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 141.6, 139.0, 138.4, 138.2, 137.8, 129.8, 128.4 (2), 128.2, 128.1, 127.9(2), 127.7 (2), 127.6, 124.4, 96.1, 79.7, 79.2, 75.2, 73.7, 72.5, 72.2, 71.9, 21.5, 18.0, 17.9, 12.0; HRMS (ESI) calc for $C_{43}H_{56}O_6SSiLi$ ($M+Li^+$) 735.3728, found 735.3726.



35

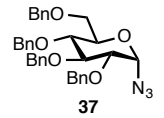
Cyclohexyl 2,3,4-tri-*O*-benzyl-6-O-(tri-isopropylsilyl)-D-mannopyranoside (35). A mixture of Diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (47.0 mg, 0.102 mmol) and 2,4,6-tri-*tert*-butylpyridine (61.0 mg, 0.247 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (17.0 µL, 0.102 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4-tri-*O*-benzyl-6-*O*-(tri-isopropylsilyl)-D-mannopyranoside **34a** (50.0 mg, 0.082 mmol) in anhydrous dichloromethane (0.8 mL)

was added and stirred for 15 min. at 0 °C. A solution of cyclohexanol (17.0 μL, 0.164 mmol) in anhydrous dichloromethane (0.5 mL) was added, stirred at 0 °C for 20 min., quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **35** (35.0 mg, 62%, *α/β* = 1:1.2) as a colorless oil: *α* isomer: $[\alpha]_D^{23}$ +25.4 (c 0.35, $CHCl_3$); IR (ATR) 2937, 2867, 1220, 1060, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) *α* isomer; *δ* 7.38 – 7.26 (m, 15 H), 4.95 (d, *J* = 1.8 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 4.68 – 4.60 (m, 4H), 3.97 – 3.93 (m, 2H), 3.88 – 3.82 (m, 2H), 3.74 – 3.70 (m, 2H), 3.60 – 3.55 (m, 1H), 1.84 – 1.76 (m, 2H), 1.68 – 1.64 (m, 2H), 1.50 – 1.47 (m, 1H), 1.31– 1.03 (m, 26H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.7, 138.6, 128.3 (2), 128.2 (2), 127.7 (2),127.6, 127.4, 95.1, 80.4, 75.6, 75.3, 75.2, 74.2, 73.6, 72.5, 72.1, 63.5, 33.2, 31.2, 25.7, 24.1, 23.9, 18.0, 12.0. *β* isomer: $[\alpha]_D^{23}$ -56.6 (c 0.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.49 – 7.47 (m, 2H), 7.32 – 7.26 (m, 13H), 4.98 (d, *J* = 12.5 Hz, 1H), 4.94 – 4.88 (m, 2H), 4.62 (d, *J* = 11.0 Hz, 1H), 4.54 (d, *J* = 11.8 Hz, 1H), 4.48 – 4.45 (m, 2H), 3.98 (dd, *J* = 10.8, 1.9 Hz, 1H), 3.90 – 3.82 (m, 3H), 3.72 – 3.67 (m, 1H), 3.50 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.26 (ddd, *J* = 9.7, 6.1, 1.9 Hz, 1H), 1.95 – 1.68 (m, 4H), 1.50 – 1.22 (m, 7H), 1.11 – 1.03 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 139.2, 138.6, 138.4, 128.3 (2), 128.1, 127.90, 127.6 (2), 127.5, 127.1, 99.4, 82.5, 76.1, 75.2, 75.0, 74.2, 73.5, 71.3, 63.3, 33.5, 31.5, 25.8, 23.9, 23.8, 18.0, 12.0; HRMS (ESI) *m/z* calc for $C_{42}H_{60}O_6SiLi$ ($M+Li^+$) 695.4320, found 695.4323.



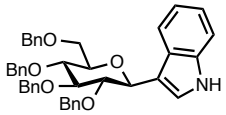
36

***p*-Tolyl 2,3,4,6-tetra-*O*-benzyl-1-thio-α-D-glucopyranoside (36).** A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide (73.0 mg, 0.16 mmol) and 2,4,6-tri-*tert*-butylpyridine (59.0 mg, 0.24 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (27.0 μL, 0.16 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **17** (87.0 mg, 0.160 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min. at 0 °C. A solution of (4-methylthio)toluene (10.0 mg, 0.0800 mmol) in anhydrous dichloromethane (0.5 mL) was added and stirred at 0 °C for 45 min, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **36** (50.0 mg, 97%, *α/β* = 6:1) as a white solid: $[\alpha]_D^{23}$ +139.8 (c 0.4, $CHCl_3$); IR (ATR) 3034, 2867, 1459, 1384, 1063 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) *δ* 7.43-7.28 (m, 22 H), 7.18 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.61 (d, *J* = 3.7 Hz, 1H), 5.03 (d, *J* = 10.8 Hz, 1H), 4.89-4.78 (m, 3H), 4.71 (d, *J* = 11.7 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.38 (ddd, *J* = 10.1, 3.9, 2.0 Hz, 1H), 3.92 – 3.90 (m, 2H), 3.80 (dd, *J* = 10.7, 3.9 Hz, 1H), 3.72-3.68 (m, 1H), 3.64 (dd, *J* = 10.6, 2.0 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 138.7, 138.2, 137.9, 137.7, 137.2, 132.1, 129.7, 128.4 (2), 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 87.4, 82.6, 79.8, 75.8, 75.1, 73.4, 72.4, 71.1, 68.6, 21.1; HRMS (ESI) *m/z* calc for $C_{41}H_{42}O_5SLi$ ($M+Li^+$) 653.2914, found 653.2906.



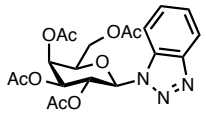
37

1-Azido-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose (37). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (63.0 mg, 0.138 mmol) and 2,4,6-tri-*tert*-butylpyridine (69.0 mg, 0.277 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture. Anhydrous dichloromethane (3.0 mL) was added and the mixture was cooled to 0 °C, Tf_2O (19.0 µL, 0.115 mmol) was added via syringe and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside **17** (50.0 mg, 0.092 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min. at 0 °C. A solution of $TMSN_3$ (24.0 µL, 0.184 mmol) in anhydrous dichloromethane (0.5 mL) was then introduced and stirred at 0 °C for 120 min and 16 h at rt, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 10:1) afforded **37** (49.0 mg, 94%, *α/β* = 12:1) as a colorless oil: $[\alpha]_D^{23}$ +75.3 (c 0.64, $CHCl_3$); IR (ATR) 2919, 2113, 1459, 1362, 1074 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.14 (m, 20H), 5.24 (d, J = 4.1 Hz, 1H), 4.95 (d, J = 10.8 Hz, 1H), 4.87 – 4.78 (m, 3H), 4.78 – 4.57 (m, 3H), 4.53 – 4.44 (m, 2H), 3.91 – 3.86 (m, 1H), 3.75 (dd, J = 10.8, 3.3 Hz, 2H), 3.68 – 3.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.7, 138.8, 138.2, 138.0, 137.8, 129.4, 128.5, 128.4, 127.9, 127.8, 88.1, 81.8, 79.4, 75.8, 75.1, 73.8, 73.5, 72.5, 68.1; HRMS (ESI) *m/z* calc for $C_{34}H_{35}N_3O_5Li$ ($M+Li^+$) 572.2737, found 572.2744.



38

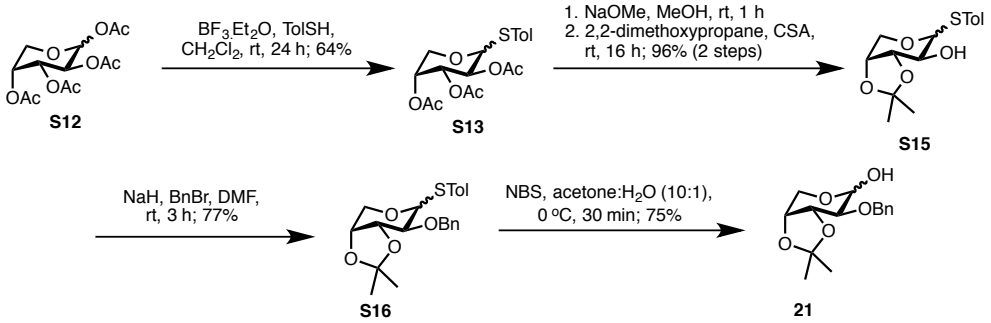
3-(2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl)-1*H*-indole (38). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (156 mg, 0.340 mmol) and 2,4,6-tri-*tert*-butylpyridine (126 mg, 0.510 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (57.0 µL, 0.34 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranoside (184 mg, 0.34 mmol) in anhydrous dichloromethane (0.8 mL) was added and stirred for 15 min at 0 °C. A solution of indole (20.0 mg, 0.170 mmol) in anhydrous dichloromethane (0.5 mL) was added, stirred at 0 °C for 60 min and 16 h at rt, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 5:1) afforded **38** (95.0 mg, 88%, α/β > 1:99) as a brown gum: $[\alpha]_D^{23}$ +137.3 (c 0.5, $CHCl_3$); IR (ATR) 3421, 2867, 1459, 1074, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.66 (dd, J = 2.5, 1.3 Hz, 1H), 7.40 -7.16 (m, 23H), 5.74 (dd, J = 5.8, 1.2 Hz, 1H), 5.08 (d, J = 10.8 Hz, 1H), 4.87 (d, J = 10.8 Hz, 1H), 4.81 (d, J = 10.7 Hz, 1H), 4.71 (d, J = 3.5 Hz, 2H), 4.68 (d, J = 12.2 Hz, 1H), 4.47 – 4.42 (m, 2H), 4.25 – 4.21 (m, 1H), 4.13 (dd, J = 9.8, 5.8 Hz, 1H), 3.84 – 3.81 (m, 1H), 3.66 (dd, J = 10.6, 3.1 Hz, 1H), 3.58 (dd, J = 10.6, 2.1 Hz, 1H), 3.37 (dt, J = 10.1, 2.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 138.4, 138.3, 138.1, 135.9, 128.4 (2), 128.3, 128.1, 128, 127.8, 127.7, 127.6 (2), 127.2, 124.6, 122.3, 120.6, 119.8, 110.9, 110.8, 82.7, 81.1, 78.4, 77.5, 77.0, 76.6 (2), 75.0, 73.50, 72.4, 71.5, 70.7, 68.9; HRMS (ESI) *m/z* calc for $C_{42}H_{41}NO_5Li$ ($M+Li^+$) 646.3146, found 646.3156.



40

1-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-benzotriazole (40). A mixture of diphenyl[4-(diphenylphosphinyl)butyl]phosphine oxide **S3** (98.0 mg, 0.214 mmol) and 2,4,6-tri-*tert*-butylpyridine (106 mg, 0.43 mmol) was azeotropically dried with PhMe (2 x 3 mL) and under high vacuum for 1 h. Freshly activated 4 Å MS (0.50 g) were added to the above mixture and further dried under high vacuum for 1 h. Anhydrous dichloromethane (3.0 mL) was added, cooled to 0 °C, Tf_2O (36.0 μL, 0.214 mmol) was added and stirred at 0 °C for 30 min. A solution of 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside **39** (50.0 mg, 0.143 mmol) in anhydrous dichloromethane (0.8 mL) was added and the mixture was stirred for 15 min. at 0 °C. A solution of benzotriazole (34.0 mg, 0.286 mmol) in anhydrous dichloromethane (0.5 mL) was introduced and the reaction mixture was stirred at 0 °C for 120 min and 16 h at rt, quenched with Et_3N, dissolved in EtOAc and washed with $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 1:1) afforded **40** (38.0 mg, 75%, α/β > 1:99) as a white foam: $[\alpha]_D^{23}$ -44.8 (c 1.6, $CHCl_3$); IR (ATR) 3027, 1752, 1373, 1216, 1063 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 7.78 (d, J = 8.3 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.44 – 7.41 (m, 1H), 6.17 (d, J = 9.2 Hz, 1H), 5.90 – 5.86 (m, 1H), 5.62 (dd, J = 3.3, 1.1 Hz, 1H), 5.33 (dd, J = 10.3, 3.2 Hz, 1H), 4.32 – 4.24 (m, 1H), 4.19 – 4.15 (m, 1H), 2.30 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 169.9, 168.7, 128.2, 124.7, 120.4, 110.9, 86.7, 73.8, 71.0, 67.1, 66.7, 61.3, 20.8, 20.6, 20.5, 20.1; HRMS (ESI) *m/z* calc for $C_{20}H_{23}N_3O_9Li$ ($M+Li^+$) 456.1595, found 456.1595.

5. Detailed Procedures for Compounds S12-S20

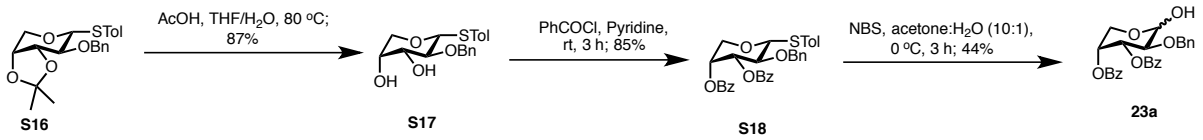


***p*-Tolyl 2,3,4-*O*-acetyl-D-arabinopyranose (S13).** To a stirred solution of **S12** (20.0 g, 62.8 mmol) in anhydrous dichloromethane (100 mL) was added $BF_3{\cdot}OEt_2$ (15.5 mL, 126 mmol) followed by 4-thiotoluene (15.6 g, 2.87 mmol). The mixture was stirred at rt for 24 h, diluted with dichloromethane (100 mL), washed with aq. $NaHCO_3$ (2 x 60 mL), water, brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 4:1) to provide **S13** (15.3 g, 64%, α/β = 81:19) as a clear oil: $[\alpha]_D^{23}$ +16 (c 1.04, $CHCl_3$); IR (ATR) 2982, 1745, 1372, 1217, 1056 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) α anomer*;* δ 7.39 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 5.46 – 5.45 (m, 0.2H, β), 5.27 – 5.22 (m, 2H), 5.08 (dd, J = 8.5, 3.4 Hz, 1H), 4.73 (d, J = 8.0 Hz, 1H), 4.15 (dd, J = 12.7, 4.1 Hz, 1H), 3.65 (dd, J = 12.8, 2.1 Hz, 1H), 2.33 (s, 3H), 2.12 (s, 1H), 2.10 (s, 7H), 2.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.2, 170 (2), 169.6, 169.4, 138.3, 138.1, 132.9, 132.8, 129.8, 129.7, 129.5, 129.4, 91.1, 87.2, 81.4, 79.9, 77.5, 77.2, 77.1, 76.6, 70.6, 68.5, 67.6, 65.4, 62.8, 21.1, 20.9 (20), 20.8(2), 20.7; HRMS (ESI) calc for $C_{18}H_{22}O_7SLi$ ($M+Li^+$) 389.1247, found 389.1245

***p*-Tolyl 2-*O*-benzyl-3,4-*O*-isopropylidene-α-D-arabinopyranose (S16).** A solution of **S13** (2.00 g, 5.23 mmol) in MeOH (60 mL) was treated with NaOMe (0.28 g, 5.23 mmol). After stirring at rt for 1 h, the mixture was quenched with DOWEX-50WX8, filtered, and concentrated. The crude material (1.3 g, 5.07 mmol) was dissolved in 2,2-dimethoxypropane (30 mL) and CSA was added (0.24 g, 1.01 mmol) and stirred at rt for 16 h, quenched with Et_3N, diluted with ethyl acetate (100 mL) and washed with saturated aq. $NaHCO_3$, water, brine, dried ($MgSO_4$), and concentrated to give **S15** as a clear oil. This compound was

subjected to the next step without purification. To a stirred solution of the alcohol **S15** (0.50 g, 1.69 mmol) in dry DMF (10 mL) NaH was added (0.120 g, 2.87 mmol) followed by benzyl bromide (0.34 mL, 2.87 mmol) at 0 °C and the mixture was stirred at rt for 3 h. Reaction mixture was quenched with ice cold water and diluted with EtOAc (100 mL). The organic phase was washed with water (2 x 60 mL), brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 5:1) to provide **S16** (0.500 g, 77%) a colorless oil: $[\alpha]_D^{23}$ +23.3 (c 0.45, $CHCl_3$); IR (ATR) 2930, 1496, 1384, 1220, 1078, 1056 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.29 (m, 8H), 7.10 (d, J = 7.8 Hz, 2H), 4.81 – 4.68 (m, 3H), 4.30 – 4.17 (m, 3H), 3.74 (dd, J = 13.0, 3.9 Hz, 1H), 3.62 – 3.59 (m, 1H), 2.33 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 137.6, 132.6, 130.2, 129.6, 128.3, 128.1, 127.8, 109.9, 86.7, 78.2, 78.1, 73.3, 72.5, 64.6, 27.8, 26.2, 21.1; HRMS (ESI) calc for $C_{22}H_{26}O_4SLi$ ($M+Li^+$) 393.1712 found 393.1712

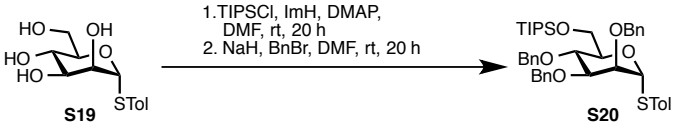
2-*O*-Benzyl-3,4-*O*-isopropylidene-D-arabinopyranose (21). To a solution of **S15** (0.100 g, 0.26 mmol) in acetone/water (10 mL, 9:1) at 0 °C NBS was added (0.0690 g, 0.39 mmol) in one portion, and after 30 min the reaction mixture was concentrated and the residue was dissolved in EtOAc (50 mL) and washed with saturated $Na_2S_2O_3$ (2 x 30 mL), water, brine, dried ($MgSO_4$) and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 1:1) to provide **21** (0.0540 g, 75%, α/β = 31:69) as a white foam: $[\alpha]_D^{23}$; IR (ATR) 2933, 2859, 1455, 1373, 1221, 1127, 1033, 1011 cm^{-1}; β – anomer: ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 - 7.29(m, 5 H), 5.17 – 5.15 (m, 1H), 4.82 (d, J = 12.0 Hz, 1H), 4.69 (d, J = 12.0 Hz, 1H), 4.40 (t, J = 6.0 Hz, 1H), 4.25 – 4.23 (m, 1H), 4.15 (dd, J = 13.1, 2.9 Hz, 1H), 3.86 (dd, J = 13.1, 1.9 Hz, 1H), 3.62 (dd, J = 6.0, 3.4 Hz, 1H), 3.01 (d, J = 5.4 Hz, 1H), 1.45 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ α/β anomers; 137.5, 128.5, 128.4, 128.0 (2), 127.8, 109.9, 109.2, 95.4, 90.9, 78.9, 75.8, 74.3, 73.0, 72.7, 72.6, 62.5, 60.0, 27.7, 27.6, 25.9, 25.8; HRMS (ESI) calc for $C_{15}H_{20}O_5Li$ ($M+Li^+$) 287.1471, found 287.1474.



***p*-Tolyl-2-*O*-benzyl-3,4-di-*O*-benzoyl-α-D-arabinopyranose (S18).** A solution of **S16** (0.900 g, 2.08 mmol) in AcOH (40 mL), H_2O (40 mL), and THF (60 mL) was stirred at 80 °C for 16 h. The reaction mixture was then concentrated and the residue was dissolved in EtOAc (100 mL), washed with water, saturated $NaHCO_3$ (2 x 75 mL), brine, dried ($MgSO_4$) and concentrated to give **S17** (0.70 g, 87%) as a white gum. To a stirred solution of the alcohol **S17** (0.700 g, 2.02 mmol) in pyridine (25 mL) was added benzoyl chloride (0.91 mL, 8.08 mmol) and the mixture was stirred at rt for 5 h. The reaction mixture was diluted with EtOAc (150 mL), washed with water (5 x 60 mL), aq. $CuSO_4$ (2 x 75 mL), water, brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 5:1) to provide **S18** (0.95 g, 85%) as a white foam: $[\alpha]_D^{23}$ -37.2 (c 0.6, $CHCl_3$); IR (ATR) 2867, 1726, 1280, 1250, 1087, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 - 7.83 (m, 4 H), 7.49 – 7.01 (m, 15H), 5.57 – 5.54 (m, 1H), 5.46 (dd, J = 7.7, 3.3 Hz, 1H), 4.85 (d, J = 6.9 Hz, 1H), 4.71 (d, J = 11.0 Hz, 1H), 4.56 (d, J = 10.9 Hz, 1H), 4.28 (dd, J = 12.5, 4.8 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.75 (dd, J = 12.5, 2.4 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 138.0, 137.5, 133.3, 132.9, 130.0, 129.9, 129.7, 129.5, 128.5, 128.4 (2), 128.1, 127.9, 87.6, 77.6, 77.1, 76.7, 76.0, 74.5, 72.5, 68.7, 21.3; HRMS (ESI) calc for $C_{33}H_{30}O_6SLi$ ($M+Li^+$) 561.1924, found 561.1933.

2-*O*-Benzyl-3,4-di-*O*-benzoyl-D-arabinopyranose (23a). To a solution of **S18** (0.450 g, 0.810 mmol) in acetone/water (40 mL, 9:1) at 0 °C NBS was added (0.220 g, 1.21 mmol) in one portion, and after 3 h the reaction mixture was concentrated, and the residue was dissolved in EtOAc (150 mL), washed with

saturated $Na_2S_2O_3$ (2 x 60 mL), water, brine, dried ($MgSO_4$), and concentrated. The resulting residue was purified by chrom. on SiO_2 (Hexanes:EtOAc, 1:1) to provide **23a** (0.160 g, 44%, α/β = 40:60) as a clear oil: $[\alpha]_D^{23}$ -162 (c 0.5, $CHCl_3$); IR (ATR) 3448, 1722, 1455, 1264, 1093, 1071 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.89 (m, 6H), 7.61 – 7.19 (m, 17H), 5.80 (dd, J = 9.1, 3.4 Hz, 1H), 5.66 – 5.64 (m, 1H), 5.60 – 5.59 (m, 0.5H), 5.45 (d, J = 3.5 Hz, 0.24H), 5.43 -5.42 (m, 1H), 4.92 – 4.88 (m, 1H), 4.80 – 4.70 (m, 3H), 4.31 (dd, J = 12.8, 2.1 Hz, 1H), 4.20 (dd, J = 13.2, 2.9 Hz, 0.6H), 4.12 (dd, J = 9.1, 3.1 Hz, 1H), 3.96 – 3.90 (m, 1.6H), 3.80 (dd, J = 13.2, 1.6 Hz, 0.64H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7 (3), 165.6, 137.8, 137.2, 133.3 (3), 133.2, 129.8 (2), 129.7 (2), 129.6, 129.5, 128.5 (2), 128.4 (2), 128.3, 128.2 (2), 127.7, 97.7, 92.0, 77.5, 77.4, 77.1, 76.7, 74.5, 74.3, 73.2, 72.2, 69.6, 69.4, 69.2, 63.6, 60.9; HRMS (ESI) calc for $C_{26}H_{24}O_7Li$ ($M+Li^+$) 455.1683, found 455.1680.



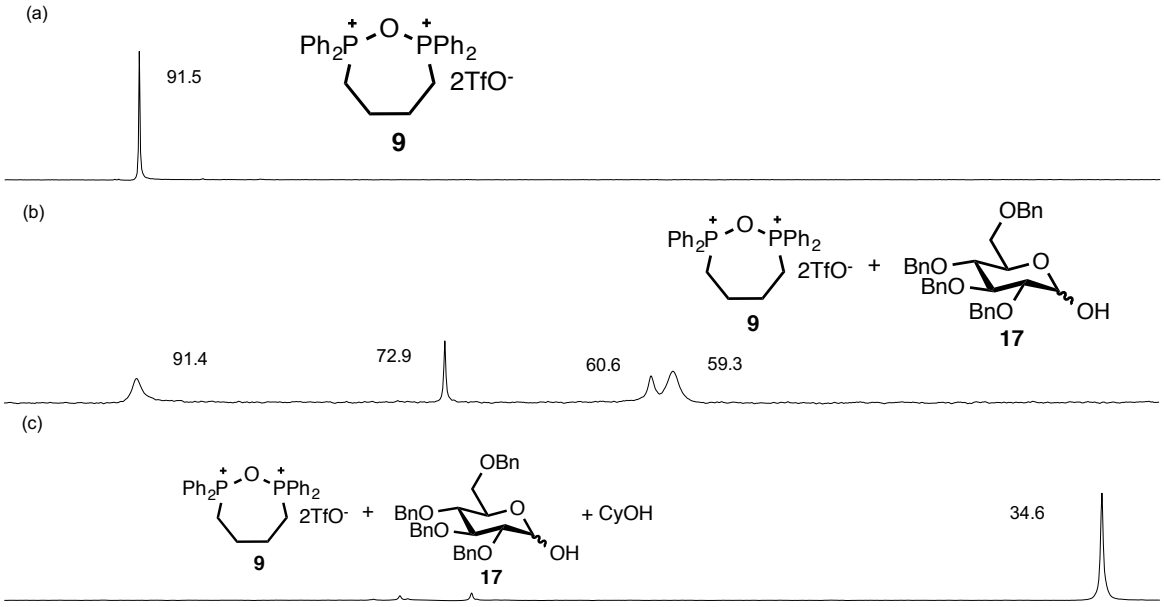
***p*-Tolyl 2,3,4-tri-*O*-benzyl-6-O-(tri-isopropylsilyl)-α-D-mannopyranoside (S20).** To a stirred solution of **S19**[17] (1.00 g, 3.49 mmol) in dry DMF (20 mL) imidazole (0.480 g, 4.19 mmol) and DMAP (0.430 g, 3.49 mmol) were added followed by TIPS-Cl (0.900 mL, 4.19 mmol) at 0 °C. The mixture was stirred at rt for 20 h, diluted with EtOAc (100 mL), washed with aq. $NaHCO_3$, water (3 x 60 mL), brine and the organic layer was dried ($MgSO_4$) and concentrated to provide crude triol. This compound was subjected to the next step without purification. To a stirred solution of the alcohol (2.0 g, 4.52 mmol) in dry DMF (20 mL) was added NaH (0.76 g, 31.6 mmol) followed by benzyl bromide (2.68 mL, 22.6 mmol) at 0 °C. The mixture was stirred at rt for 20 h, quenched with methanol/ice cold water and diluted with EtOAc (100 mL). The organic phase was washed with water (3 x 60 mL), brine and the organic layer was dried ($MgSO_4$), and concentrated. Purification by chrom. on SiO_2 (Hexanes:EtOAc, 20:1) to provided **S20** (3.00 g, 93%) as a colorless oil: $[\alpha]_D^{23}$ +71 (c 0.5, $CHCl_3$); IR (ATR) 2945, 2867, 1500, 1459, 1089, 1030 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.43-7.11 (m, 19H), 5.57 (d, J = 1.7 Hz, 1H), 5.01 (d, J = 10.8 Hz, 1H), 4.74 – 4.62 (m, 6H), 4.18 – 4.00 (m, 5H), 3.92 (dd, J = 9.2, 3.1 Hz, 1H), 2.37 (s, 3H), 1.17 – 1.09 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.4, 138.1, 137.3, 131.7, 131.3, 129.7, 128.4 (2), 128.3, 128.1, 127.9, 127.8, 127.7, 127.6 (2), 85.8, 80.2, 77.5, 77.1, 76.7, 76.6, 75.3, 74.9, 74.4, 72.1, 71.7, 63.0, 21.1, 18.1, 18.0, 12.1; HRMS (ESI) calc for $C_{43}H_{56}O_5SSiLi$ ($M+Li^+$) 719.3779, found 719.3782.

6. ^{31}P NMR of Anhydride 9 and 17.

Fig 1a. ^{31}P NMR of **9** in CD_2Cl_2

Fig. 1b. ^{31}P NMR of a mixture of anhydride **9** (1 equiv) and **17** (1 equiv) in CD_2Cl_2 30 min at rt

Fig 1c. As Fig. 1b followed by 1 equiv of cyclohexanol, 30 min at rt



7. References

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* **2010,** *29*, 2176-2179.
2. Petersson, M. J.; Loughlin, W. A.; Jenkins, I. D., *Chem. Commun.* **2008**, 4493-4494.
3. Lin, Y.; Bernardi, D.; Doris, E.; Taran, F., *Synlett* **2009,** *2009*, 1466-1470.
4. Calcagno, P.; Kariuki, B. M.; Kitchin, S. J.; Robinson, J. M. A.; Philp, D.; Harris, K. D. M., *Chem. Eur. J.* **2000,** *6*, 2338-2349.
5. Farrer, N. J.; McDonald, R.; Piga, T.; McIndoe, J. S., *Polyhedron* **2010,** *29*, 254-261.
6. Xu, H.; Xie, G.; Han, C.; Zhang, Z.; Deng, Z.; Zhao, Y.; Yan, P.; Liu, S., *Org. Electron.* **2012,** *13*, 1516-1525.
7. Sugiura, M.; Sato, N.; Sonoda, Y.; Kotani, S.; Nakajima, M., *Chem. Asian J.* **2010,** *5*, 478-481.
8. Hilliard, C. R.; Bhuvanesh, N.; Gladysz, J. A.; Blumel, J., *Dalton Trans.* **2012,** *41*, 1742-1754.
9. Elson, K. E.; Jenkins, I. D.; Loughlin, W. A., *Aust. J. Chem.* **2004,** *57*, 371-376.
10. Nagai, H.; Sasaki, K.; Matsumura, S.; Toshima, K., *Carbohydr. Res.* **2005,** *340*, 337-353.
11. Hotha, S.; Kashyap, S., *J. Am. Chem. Soc.* **2006,** *128*, 9620-9621.
12. Jalsa, N. K., *Tetrahedron Lett.* **2011,** *52*, 6587-6590.
13. Cancogni, D.; Lay, L., *Synlett* **2014,** *25*, 2873-2878.
14. Motoko, H.; Yoko, M.; Akiko, S.; Shinkiti, K.; Yoshika, S.; Aya, M., *Bull. Chem. Soc. Jap.* **2001,** *74*, 1679-1694.
15. Poláková, M.; Roslund, M. U.; Ekholm, F. S.; Saloranta, T.; Leino, R., *Eur. J. Org. Chem.* **2009,** *2009*, 870-888.
16. Viuff, A. H.; Besenbacher, L. M.; Kamori, A.; Jensen, M. T.; Kilian, M.; Kato, A.; Jensen, H. H., *Org. Biomol. Chem.* **2015,** *13*, 9637-9658.
17. Bruneau, A.; Roche, M.; Hamze, A.; Brion, J.-D.; Alami, M.; Messaoudi, S., *Chem. Eur. J.* **2015,** *21*, 8375-8379.

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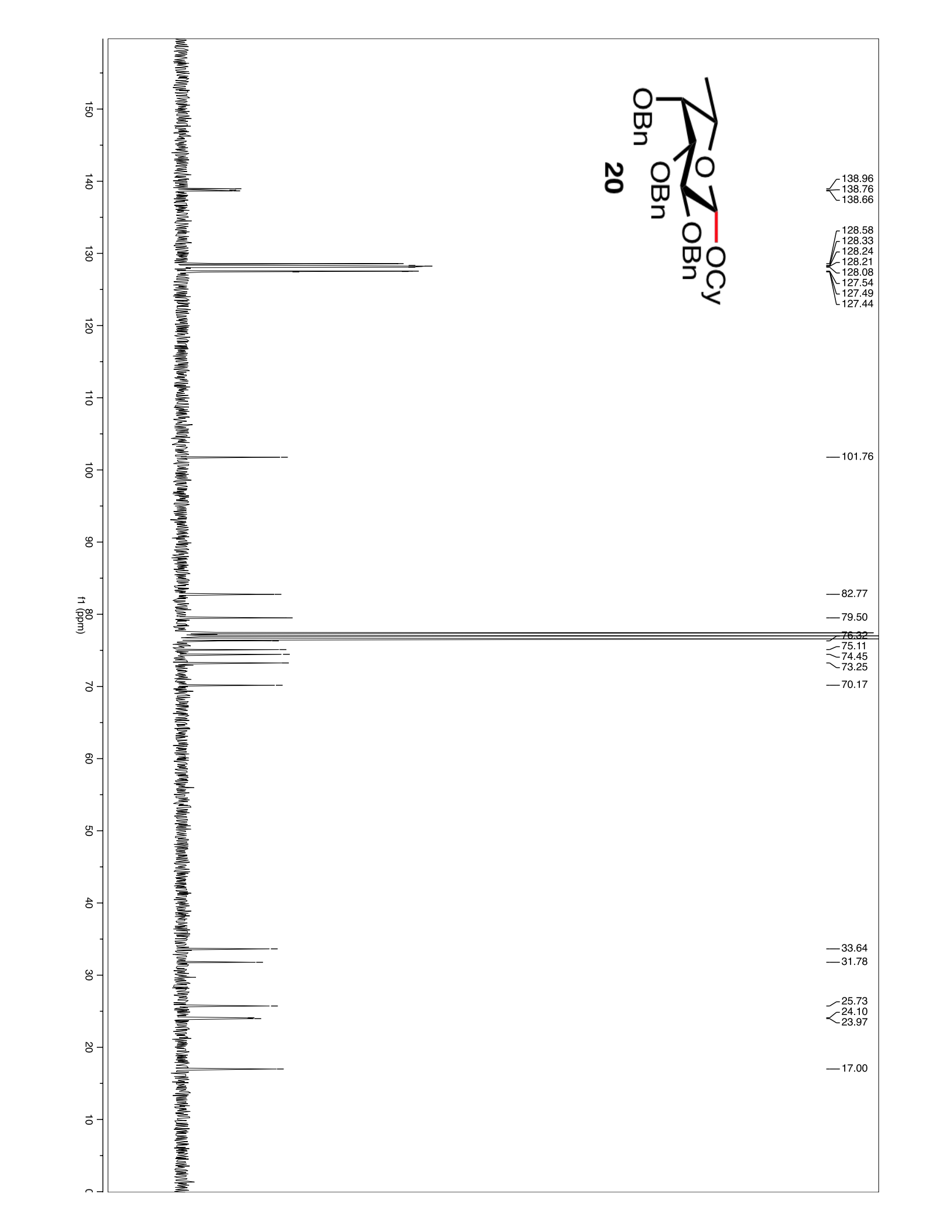
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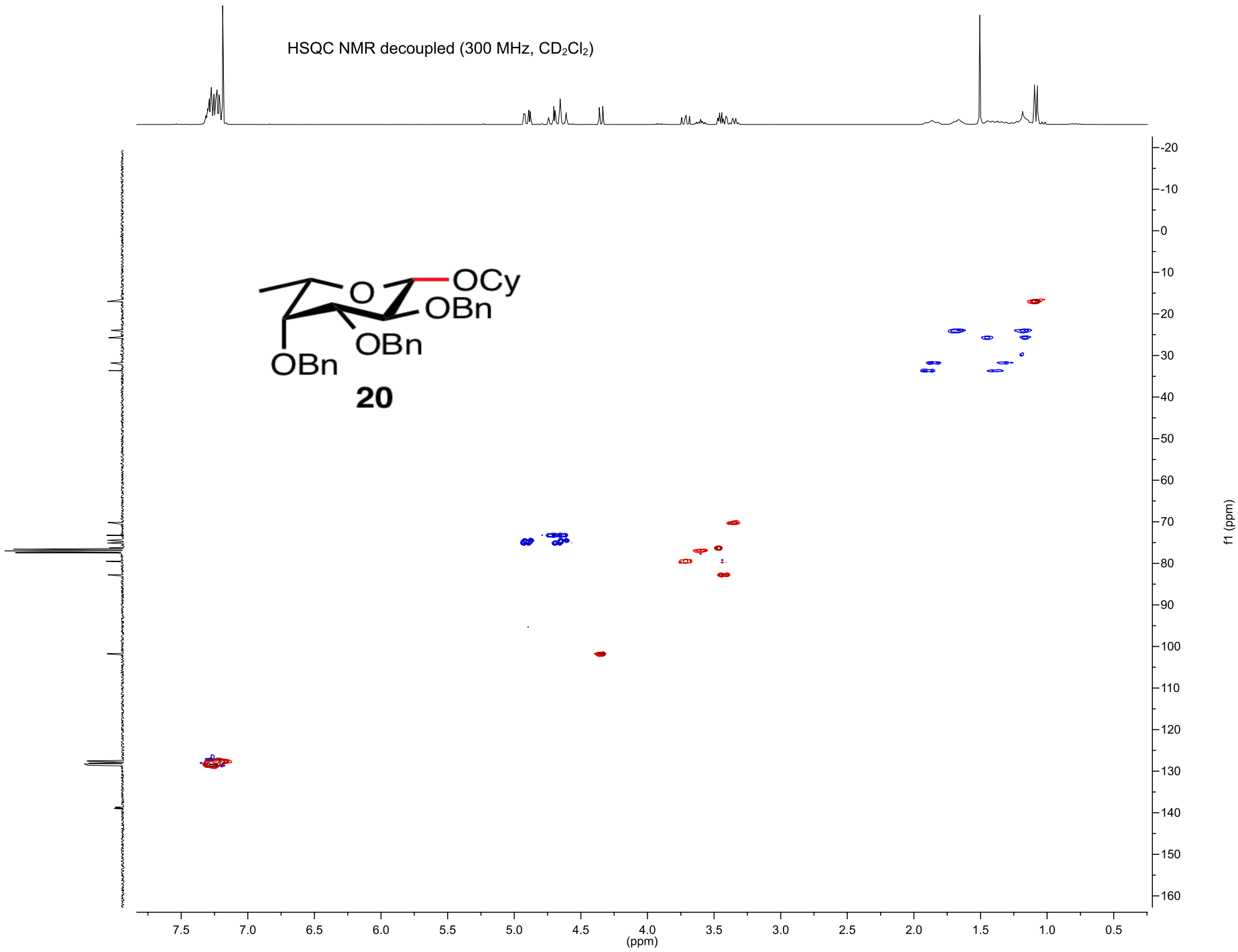
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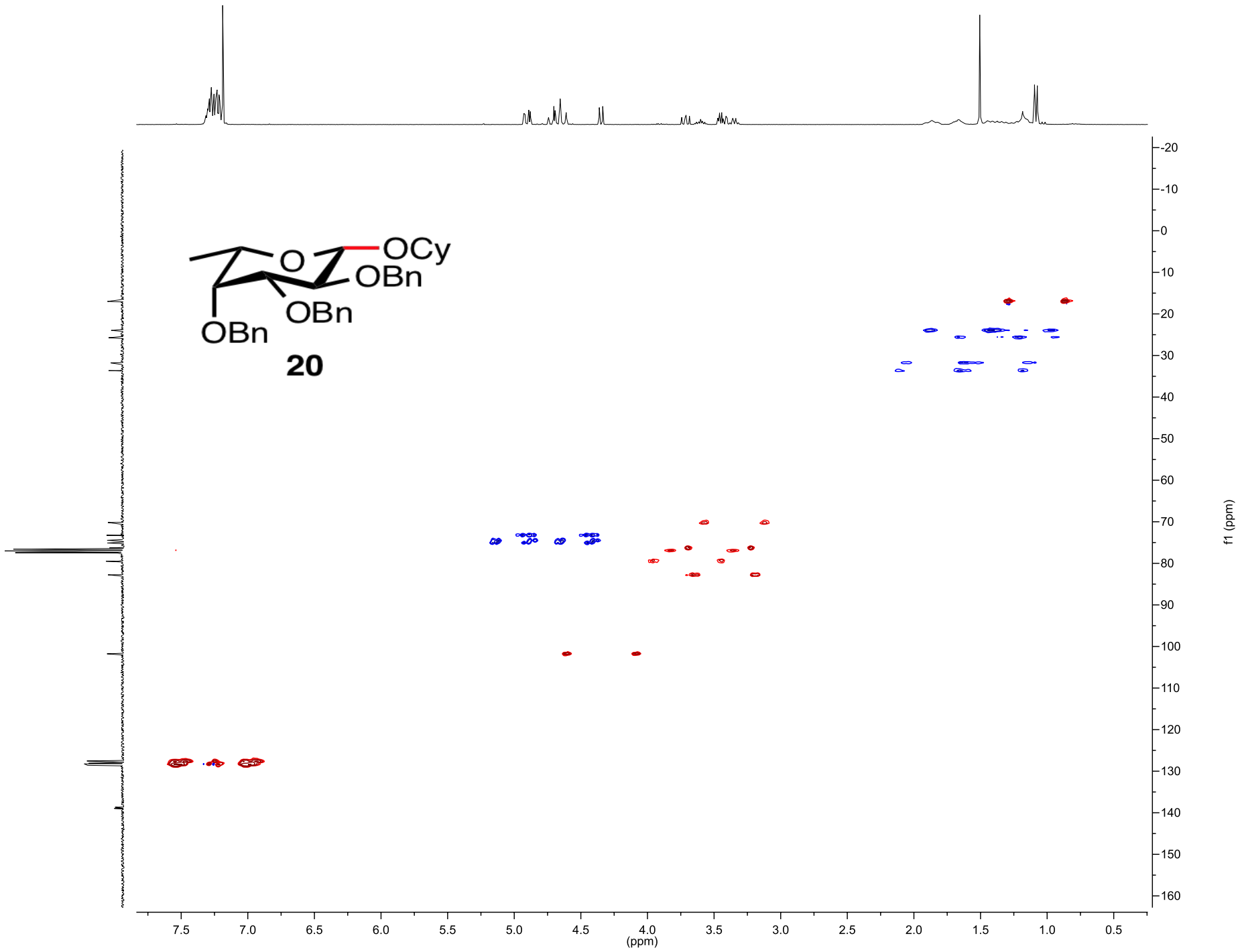
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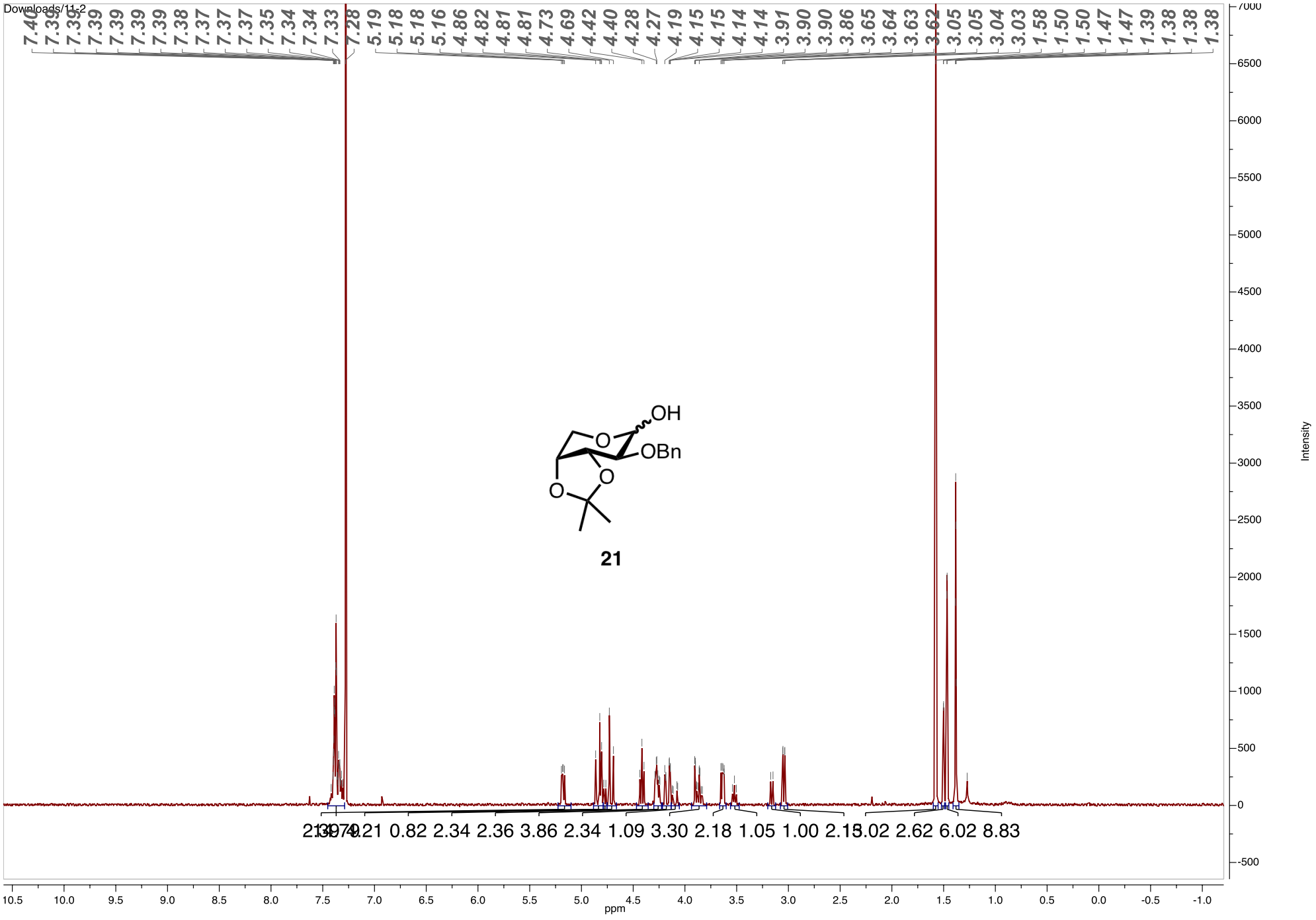
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Intensity
ppm

DRR-04-39C
DRR-04-39C, 13C in CDCl3

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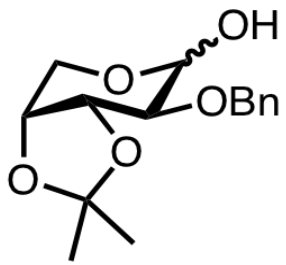

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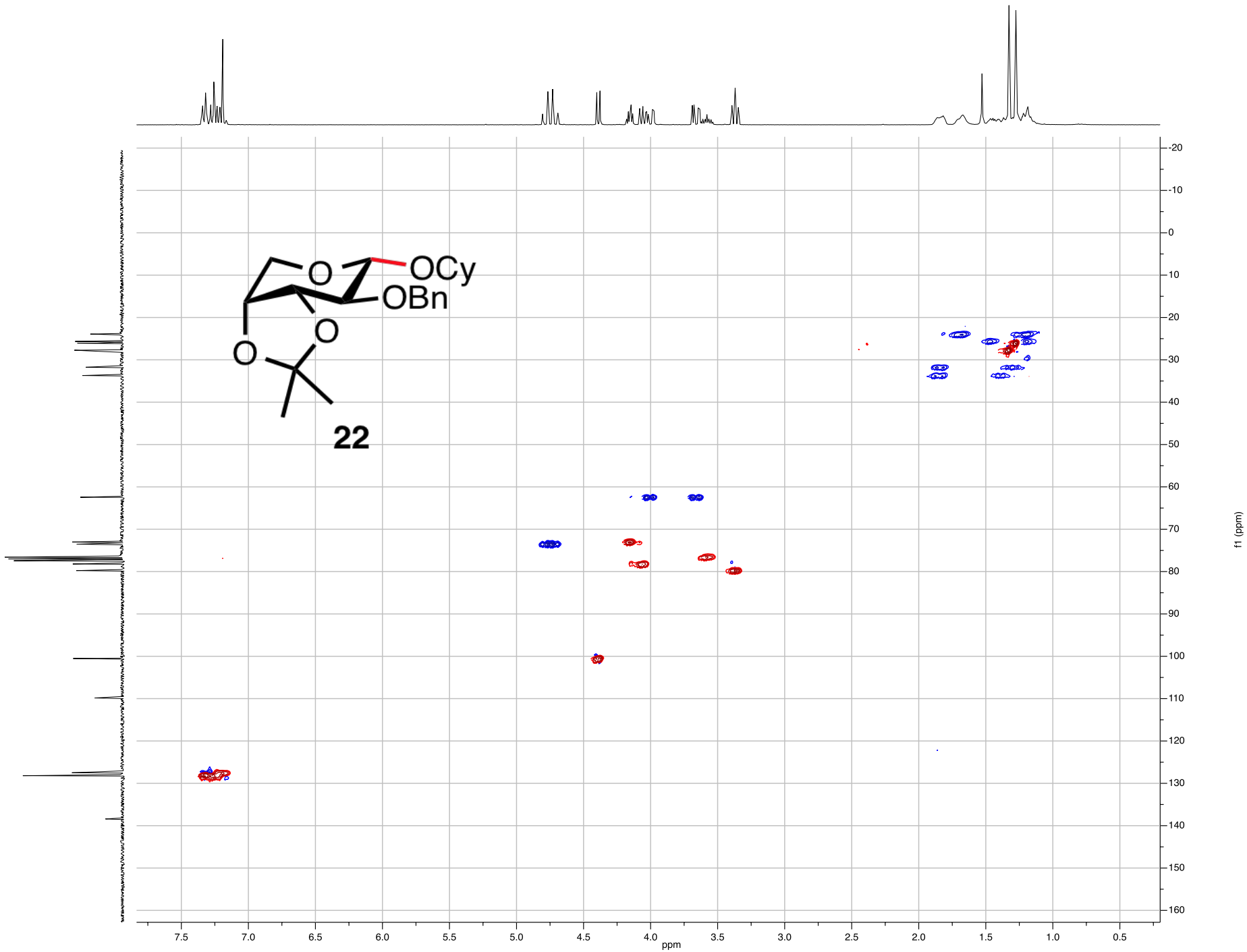
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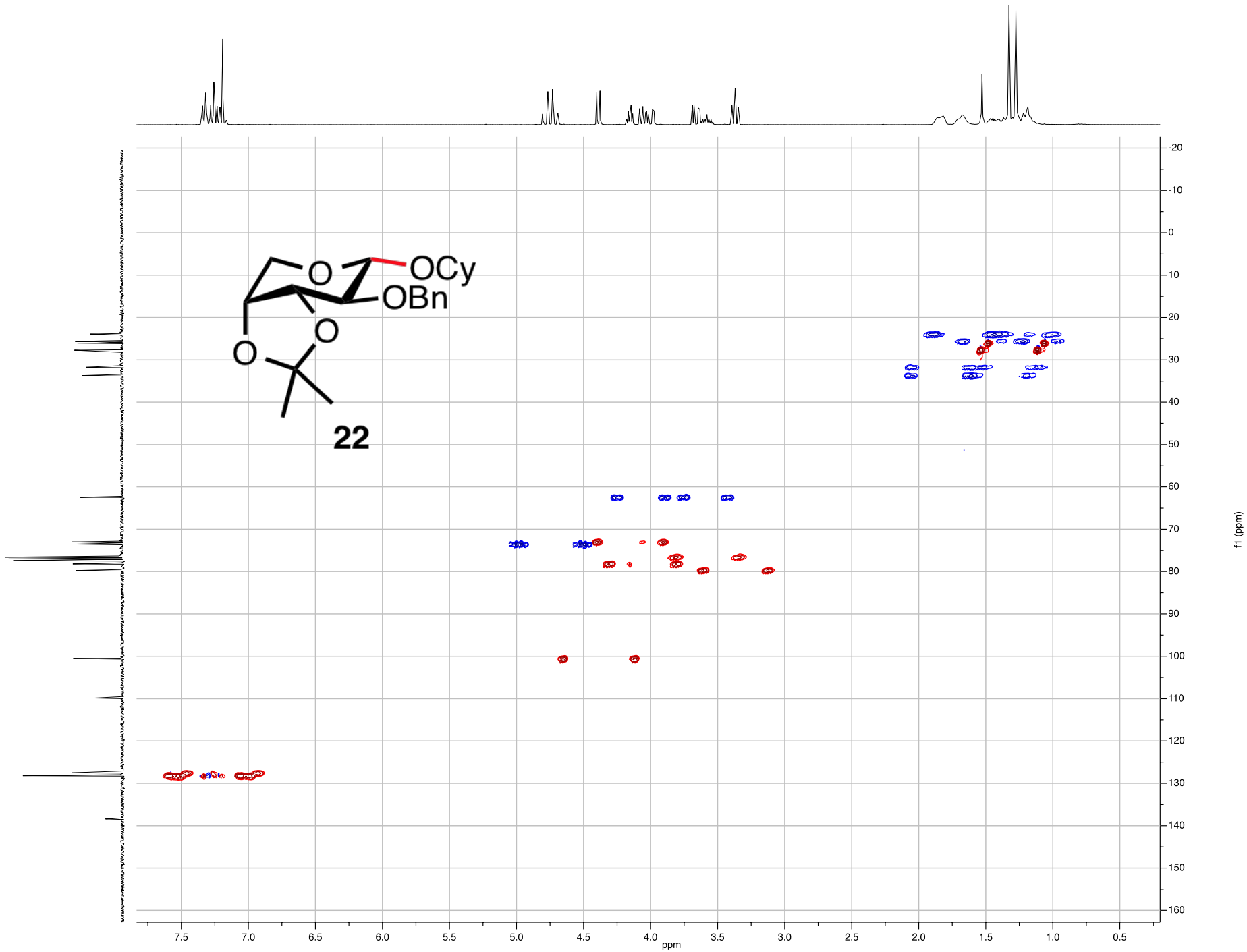
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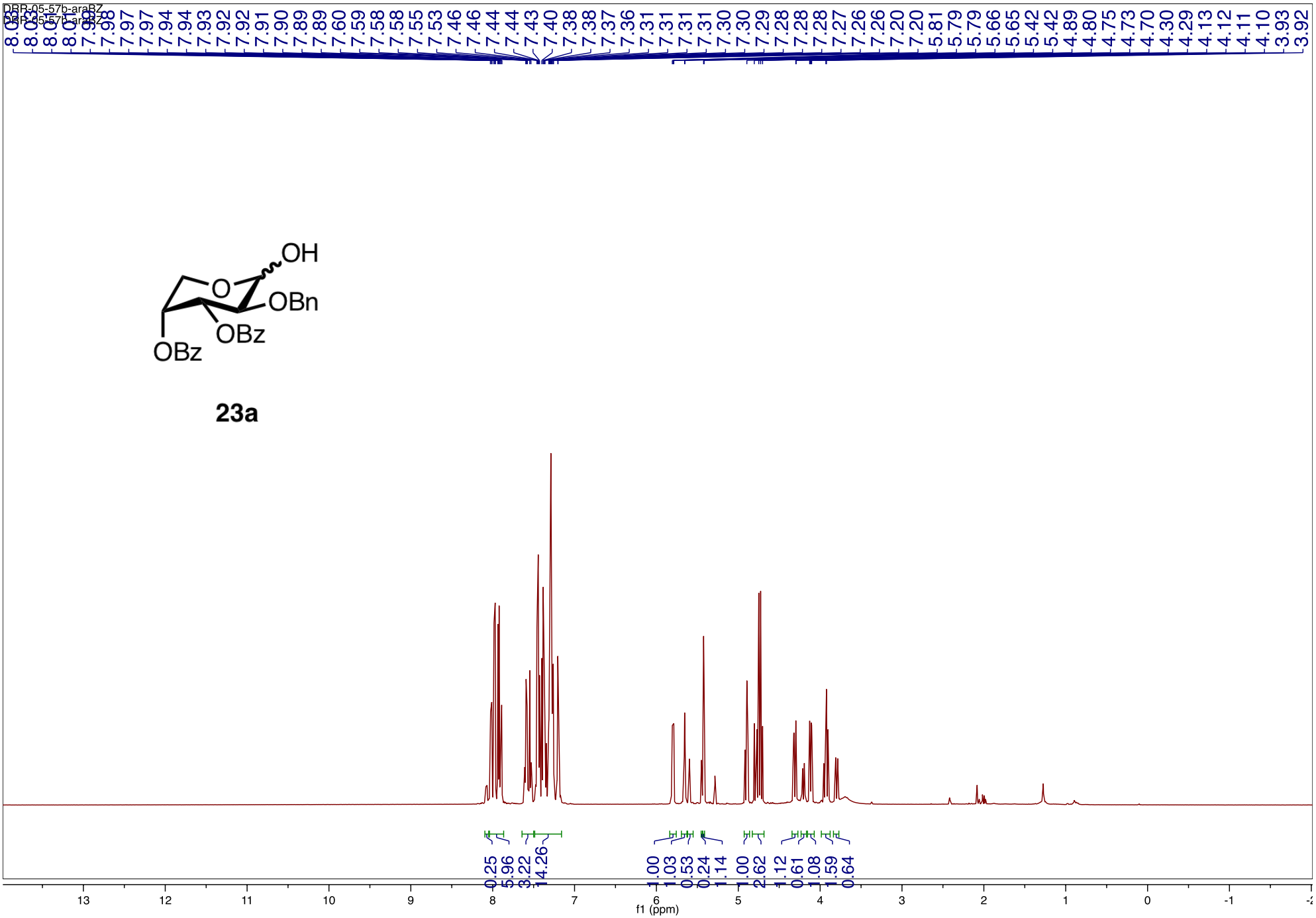
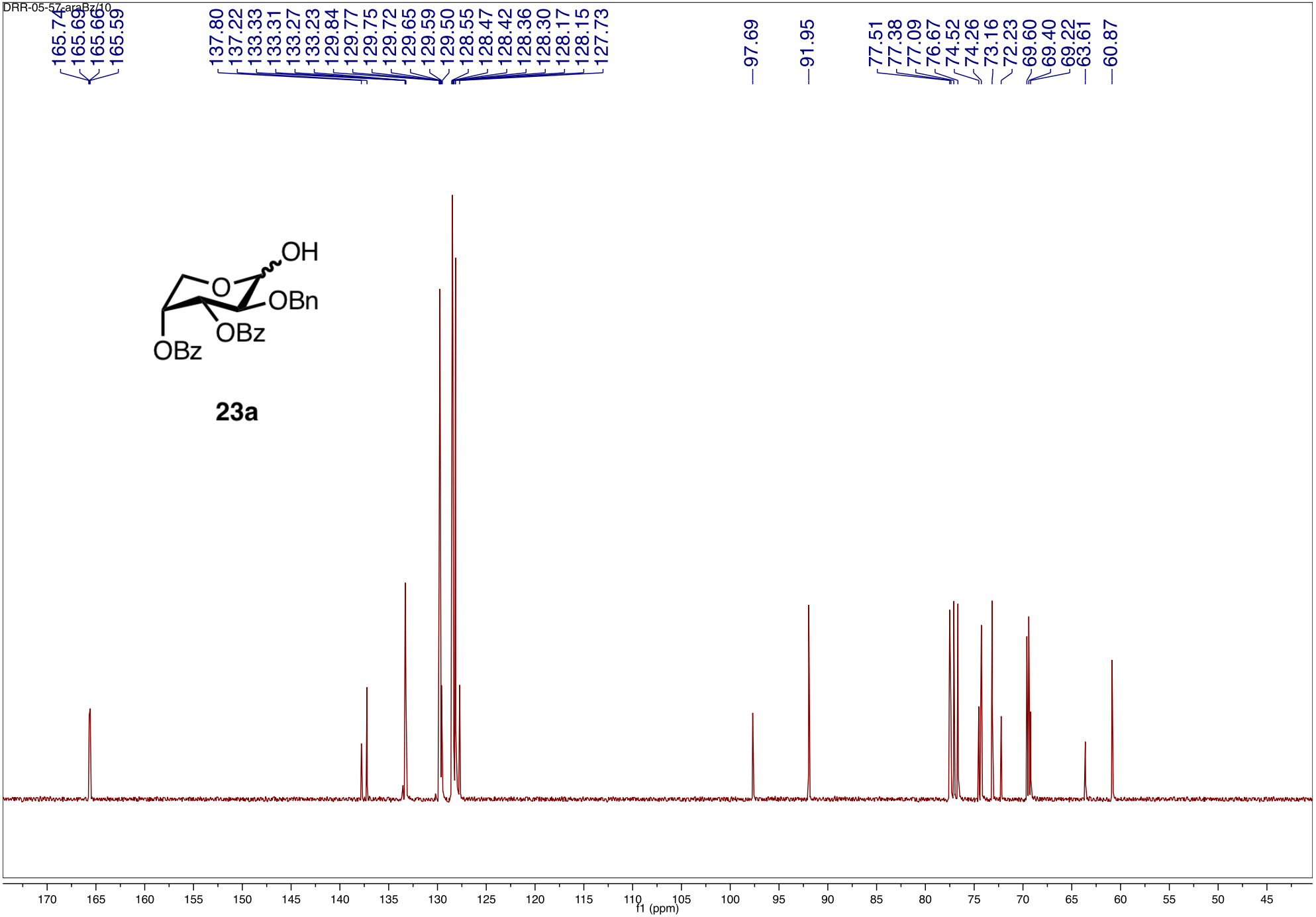
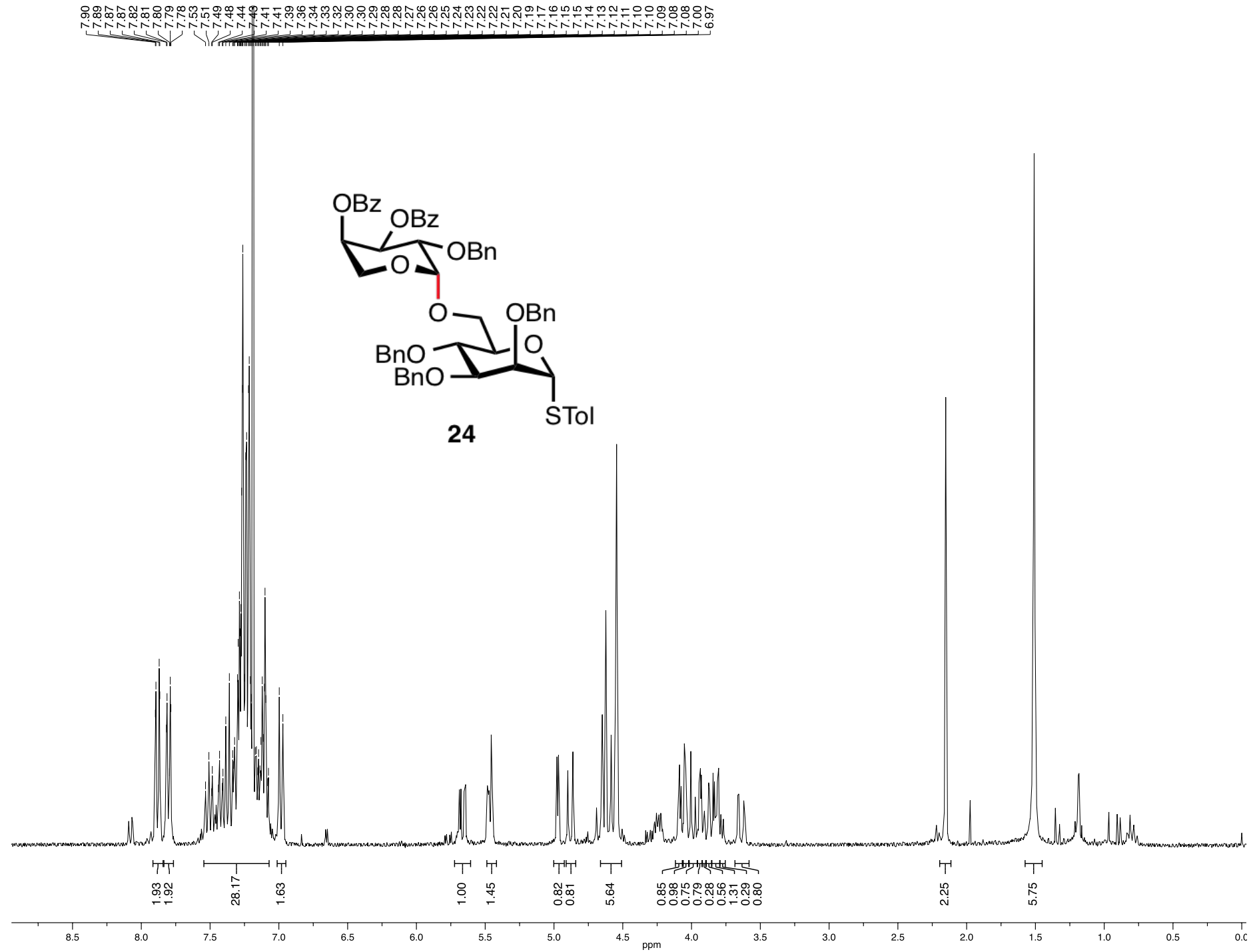
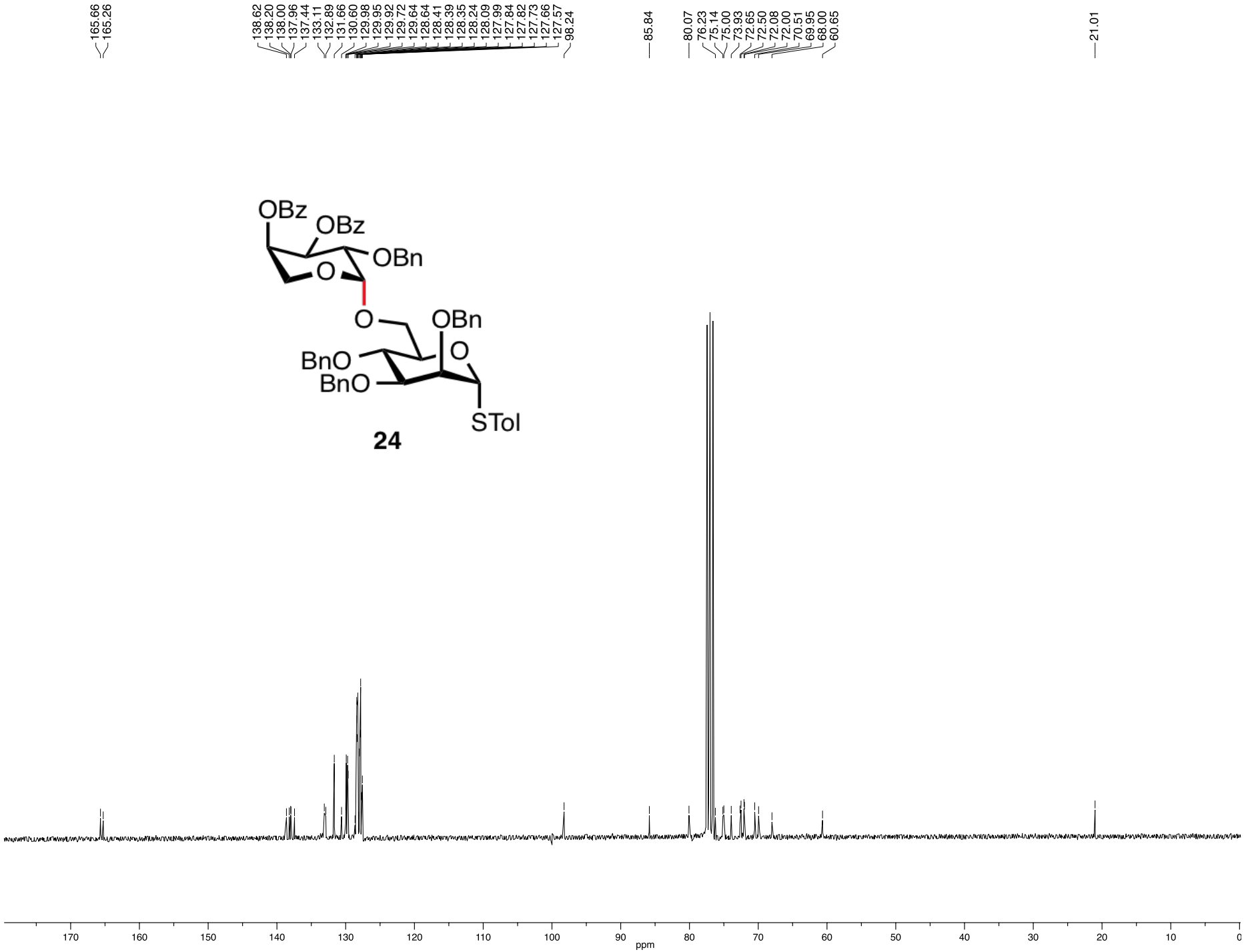
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


DBR-05-57b-araBZ
OH
O
OBn
OBz
OBz
23a
f1 (ppm)

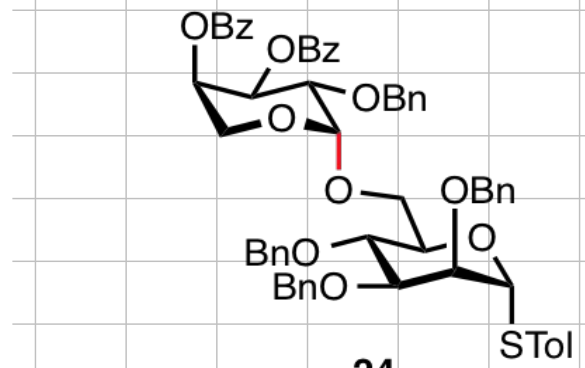
DRR-05-57-araBz/10



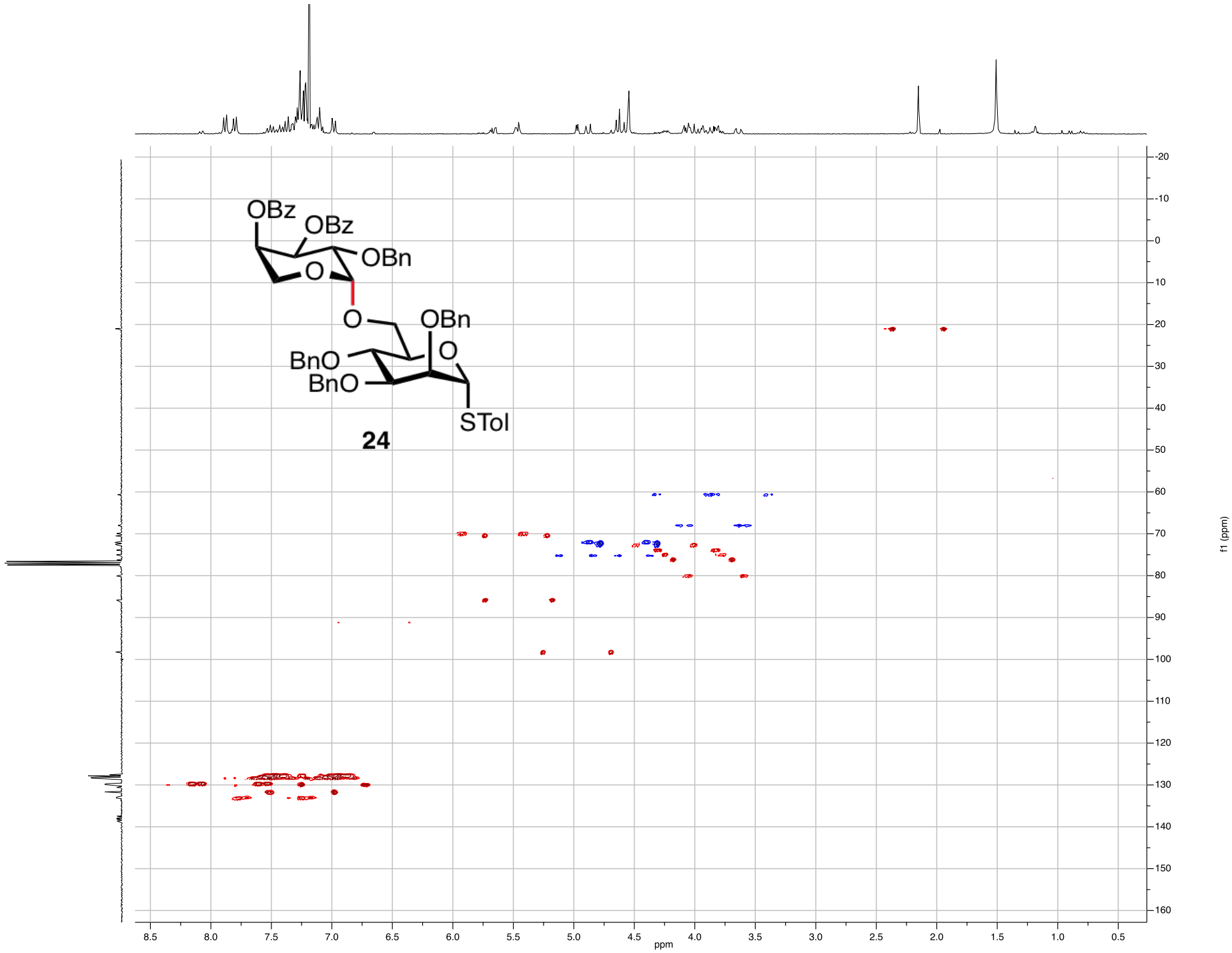

7.90 7.89 7.87 7.87 7.82 7.81 7.80 7.79 7.78 7.53 7.51 7.49 7.48 7.44 7.43 7.41 7.41 7.39 7.36 7.34 7.33 7.32 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.17 7.16 7.15 7.15 7.14 7.13 7.12 7.11 7.10 7.10 7.09 7.08 7.08 7.00 6.97
OBz
OBz
OBn
O
O
OBn
BnO
BnO
O
STol
24
1.93 1.92 28.17 1.63 1.00 1.45 0.82 0.81 5.64 0.85 0.98 0.75 0.79 0.28 0.56 1.31 0.29 0.80 2.25 5.75
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
ppm

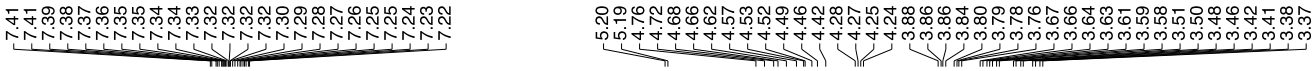

165.66
165.26
138.62
138.20
138.00
137.96
137.44
133.11
132.89
131.66
130.60
129.98
129.95
129.92
129.72
129.64
128.64
128.41
128.39
128.35
128.24
128.09
127.99
127.84
127.82
127.73
127.66
127.57
98.24
85.84
80.07
76.23
75.14
75.00
73.93
72.65
72.50
72.08
72.00
70.51
69.95
68.00
60.65
21.01
OBz
OBz
OBn
O
O
OBn
BnO
BnO
O
STol
24
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

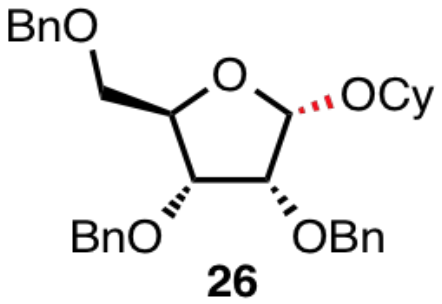
HSQC NMR decoupled (300 MHz, CD_2Cl_2)



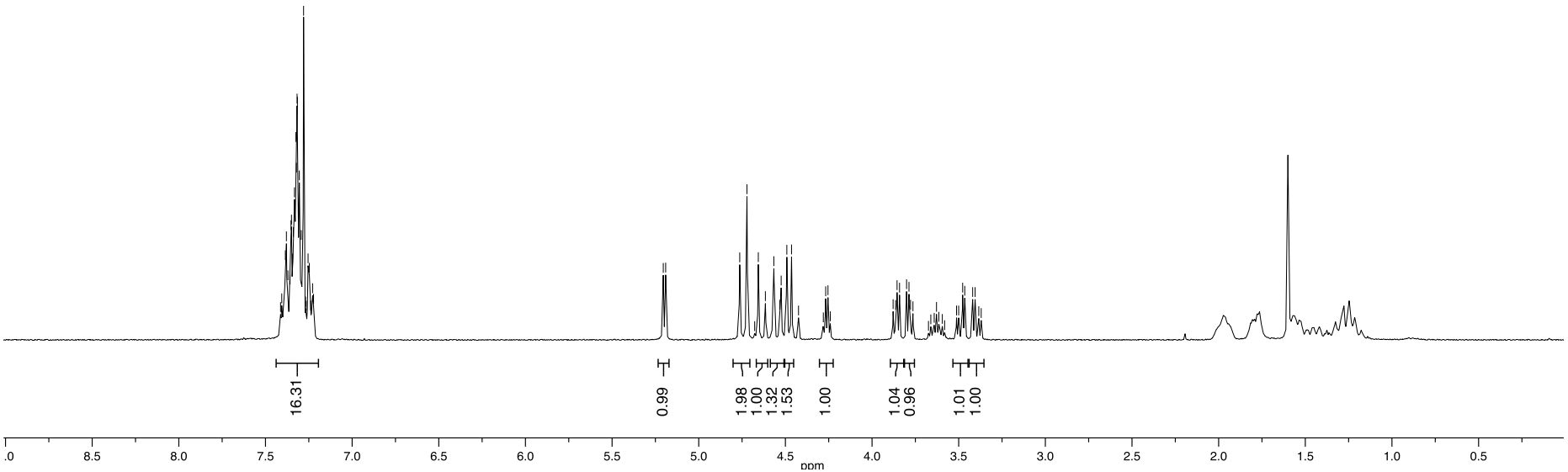
24

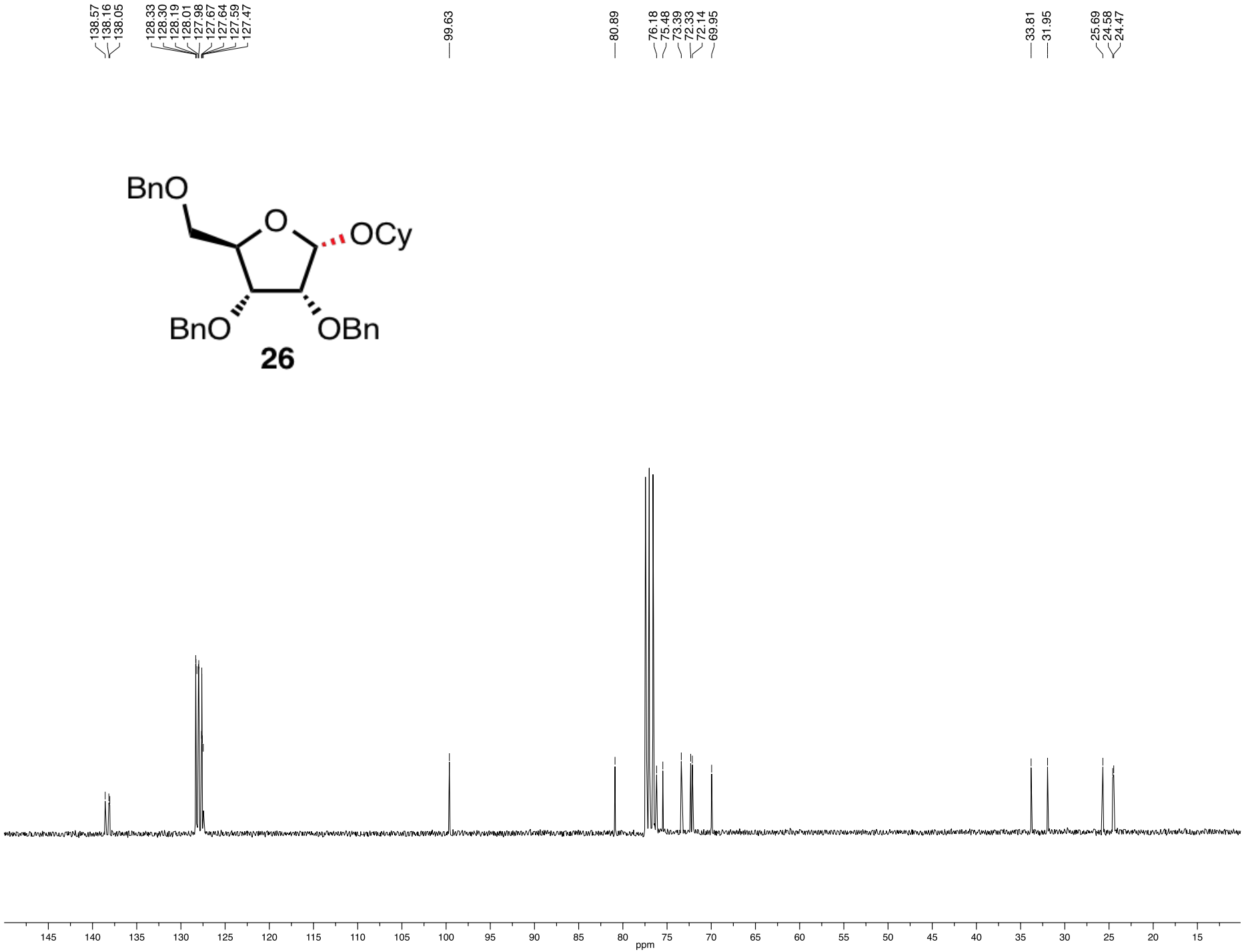

OBz
OBz
OBn
O
O
OBn
BnO
O
BnO
STol
24
ppm
f1 (ppm)

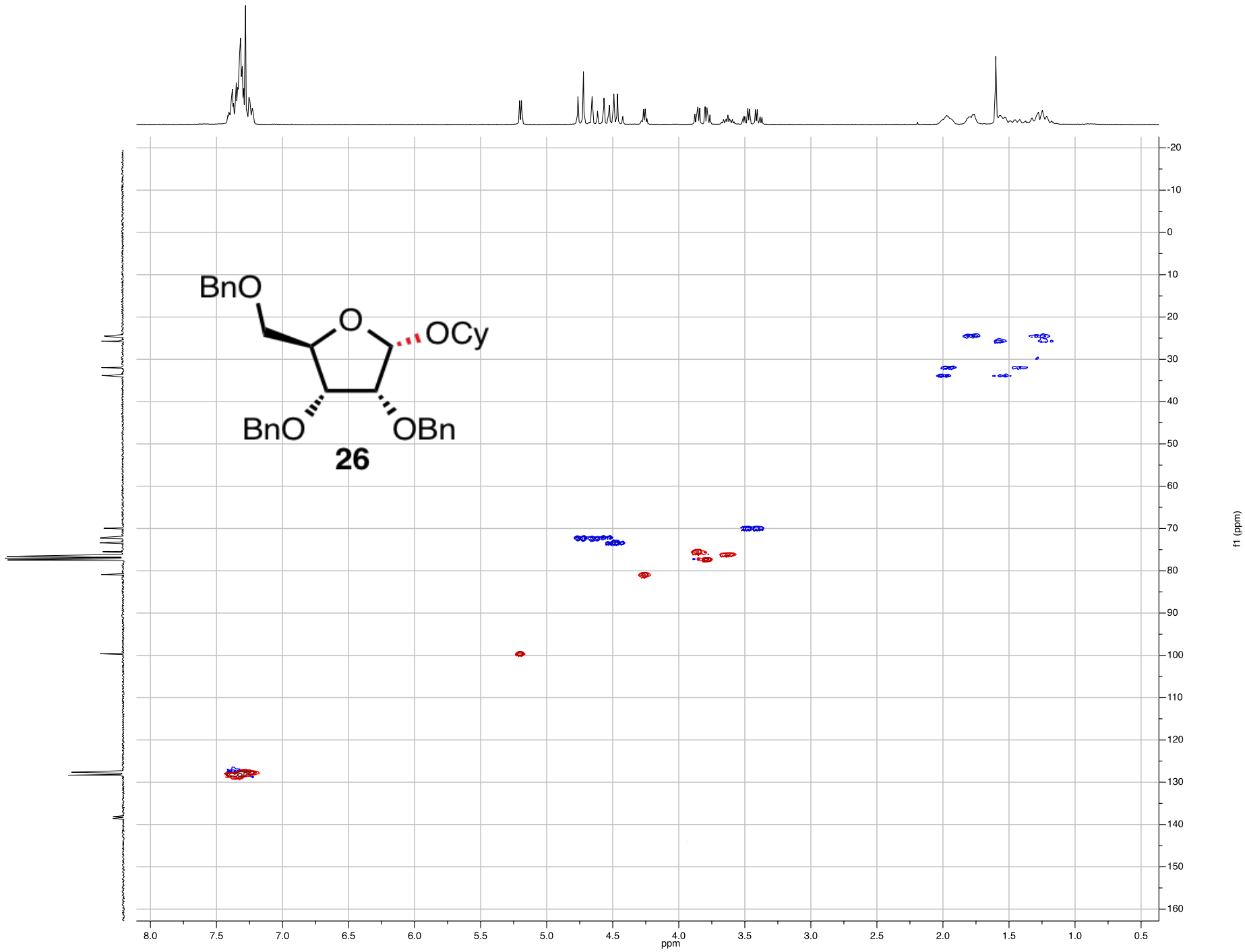

7.41
7.41
7.39
7.38
7.37
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.32
7.32
7.30
7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.23
7.22
5.20
5.19
4.76
4.72
4.68
4.66
4.62
4.57
4.53
4.52
4.49
4.46
4.42
4.28
4.27
4.25
4.24
3.88
3.86
3.86
3.84
3.80
3.79
3.78
3.76
3.67
3.66
3.64
3.63
3.61
3.59
3.58
3.51
3.50
3.48
3.46
3.42
3.41
3.38
3.37

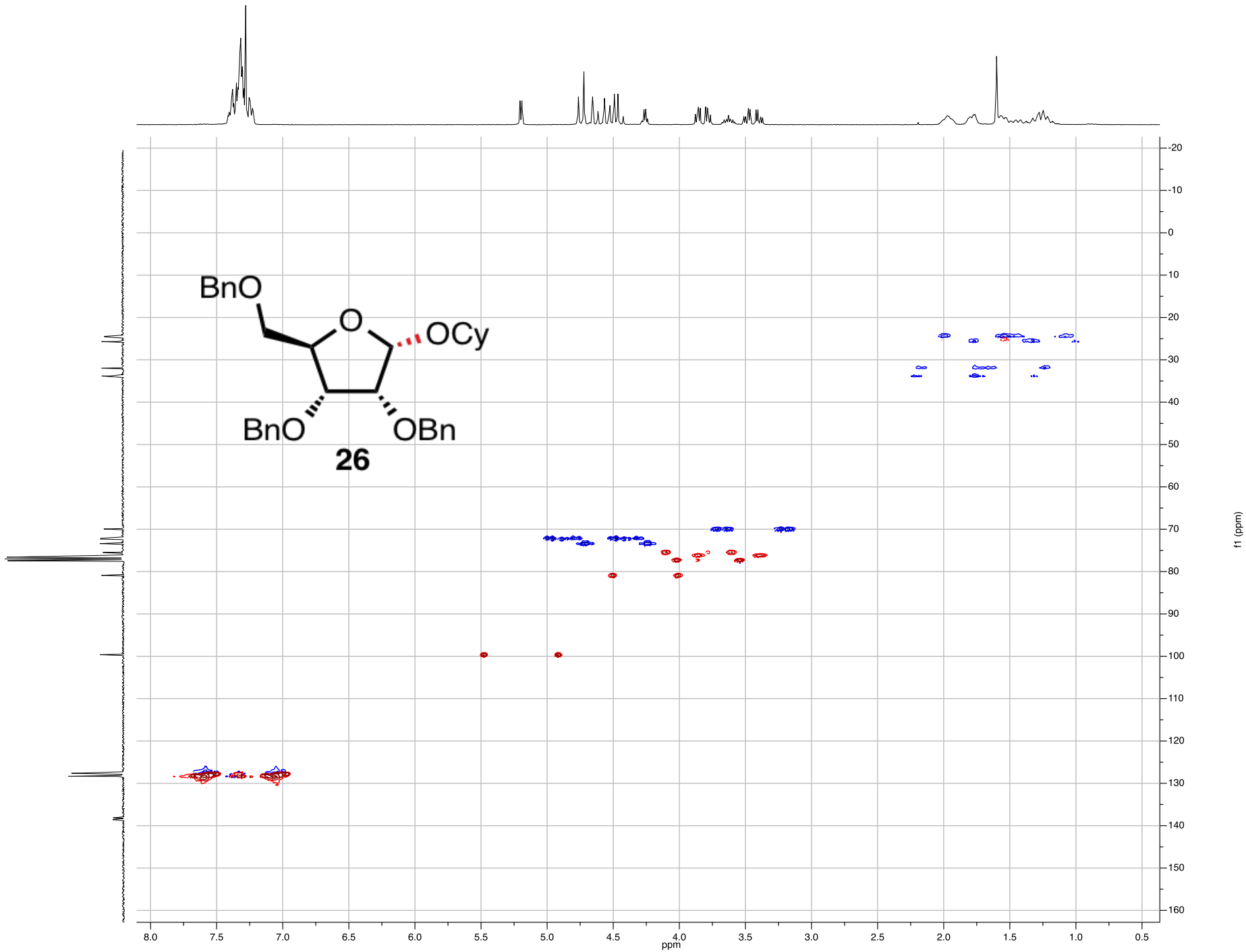

BnO
O
OCy
BnO
OBn

26


16.31
0.99
1.98
1.00
1.32
1.53
1.00
1.04
0.96
1.01
1.00
.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
ppm

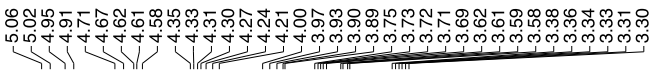

138.57
138.16
138.05
128.33
128.30
128.19
128.01
127.98
127.67
127.64
127.59
127.47
99.63
80.89
76.18
75.48
73.39
72.33
72.14
69.95
33.81
31.95
25.69
24.58
24.47
BnO
O
OCy
BnO
OBn
26
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
ppm

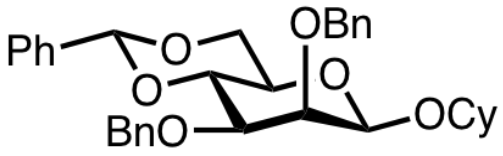

BnO
O
OCy
BnO
OBn
26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


BnO
O
OCy
BnO
OBn
26
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
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

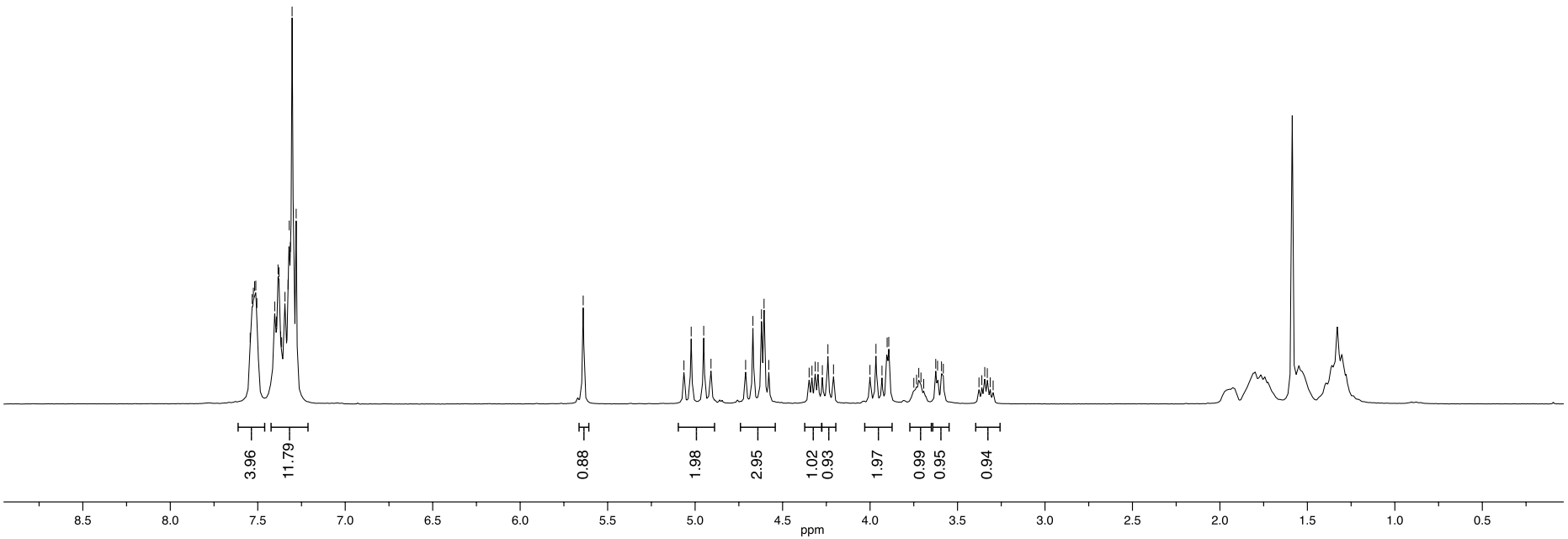

7.54
7.53
7.53
7.52
7.51
7.51
7.40
7.39
7.38
7.38
7.37
7.36
7.34
7.33
7.32
7.31
7.30
7.28

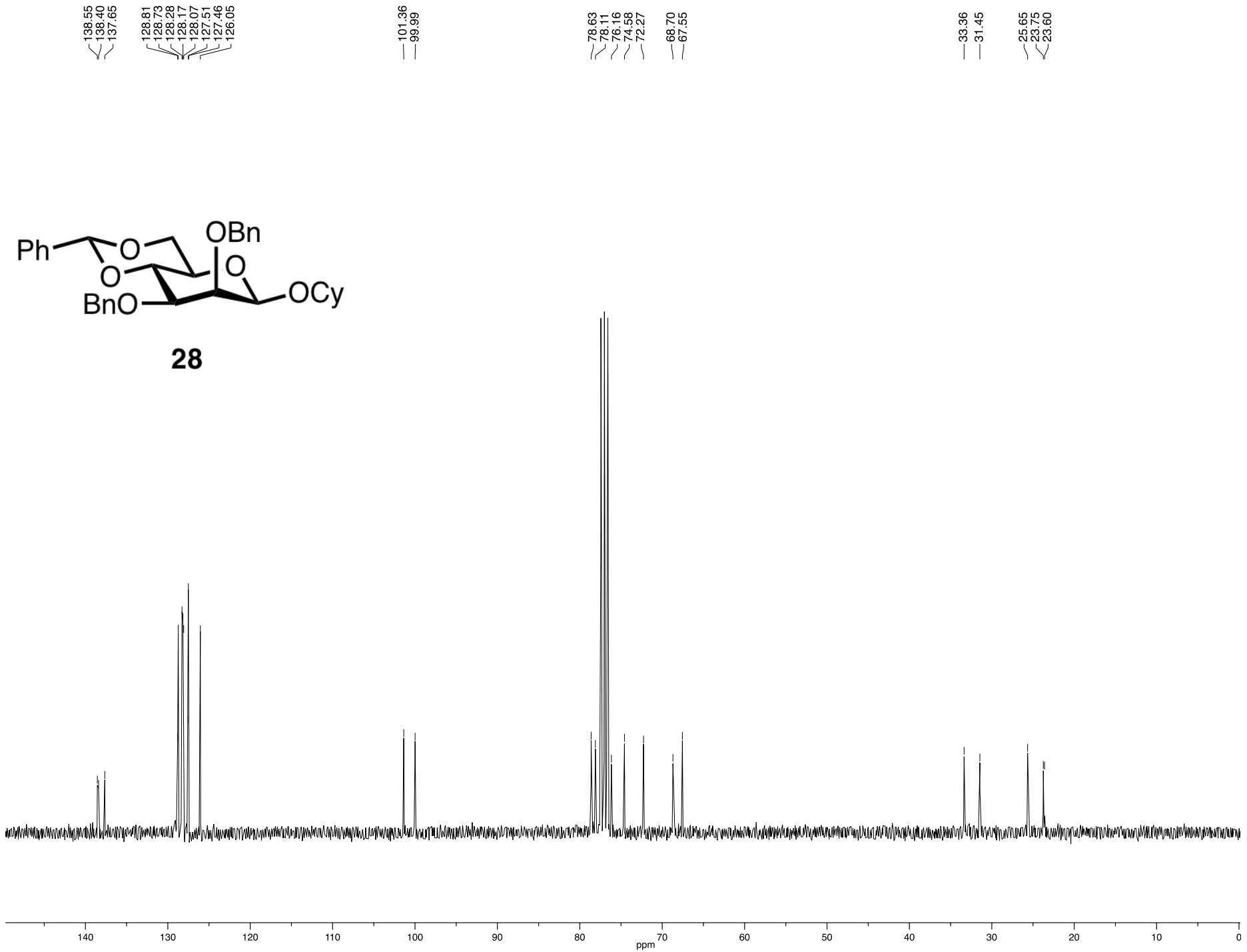

5.64

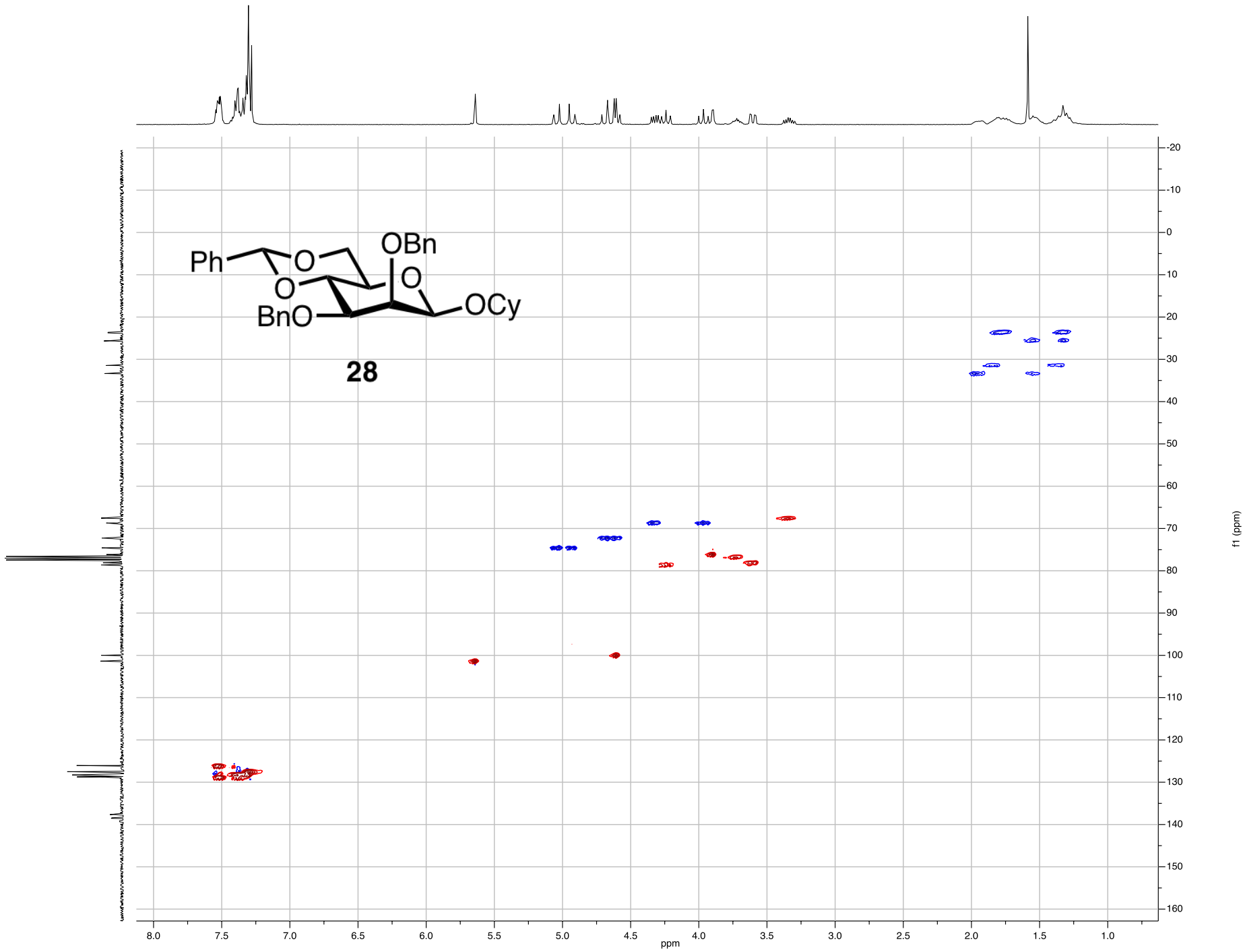

5.06
5.02
4.95
4.91
4.71
4.67
4.62
4.61
4.58
4.35
4.33
4.31
4.30
4.27
4.24
4.21
4.00
3.97
3.93
3.90
3.89
3.75
3.73
3.72
3.71
3.69
3.62
3.61
3.59
3.58
3.38
3.36
3.34
3.33
3.31
3.30

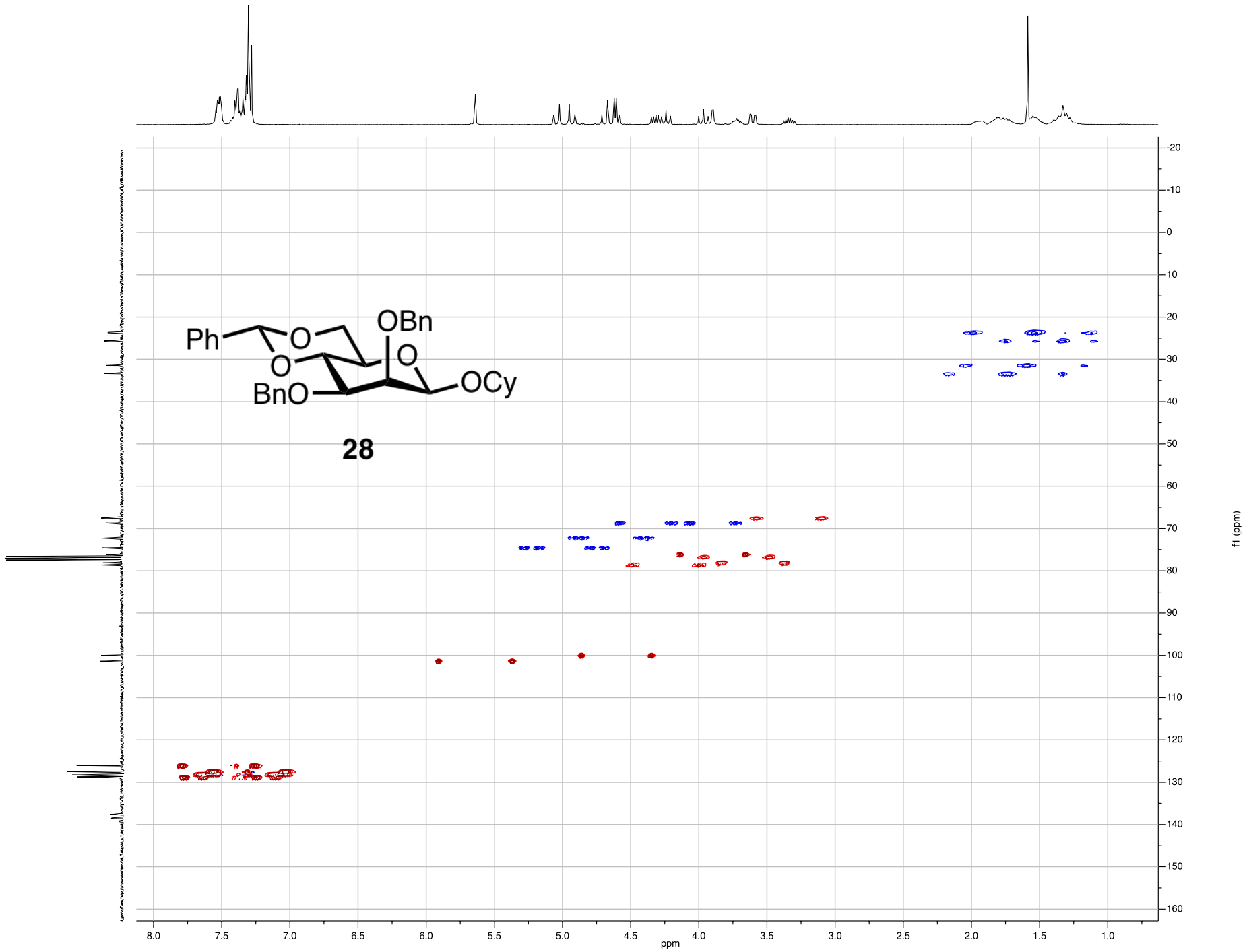

Ph
O
OBn
O
O
BnO
OCy

28

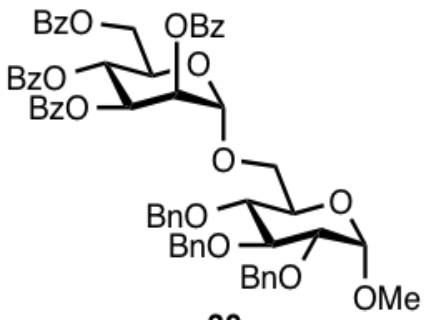

3.96
11.79
0.88
1.98
2.95
1.02
0.93
1.97
0.99
0.95
0.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


138.55
138.40
137.65
128.81
128.73
128.28
128.17
128.07
127.51
127.46
126.05
101.36
99.99
78.63
78.11
76.16
74.58
72.27
68.70
67.55
33.36
31.45
25.65
23.75
23.60
Ph
O
O
OBn
O
BnO
OCy
28
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

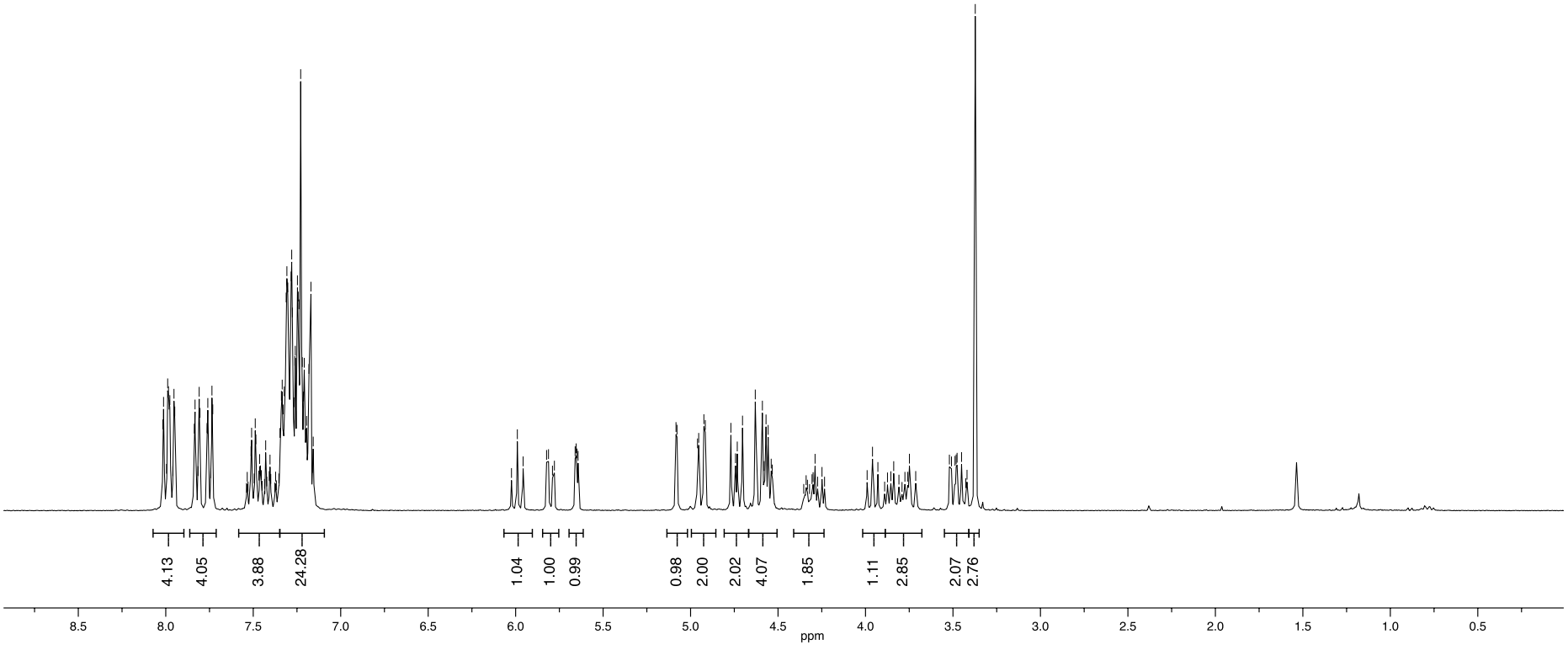

Ph
O
OBn
O
O
BnO
OCy
28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


Ph
O
OBn
O
O
BnO
OCy
28
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
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

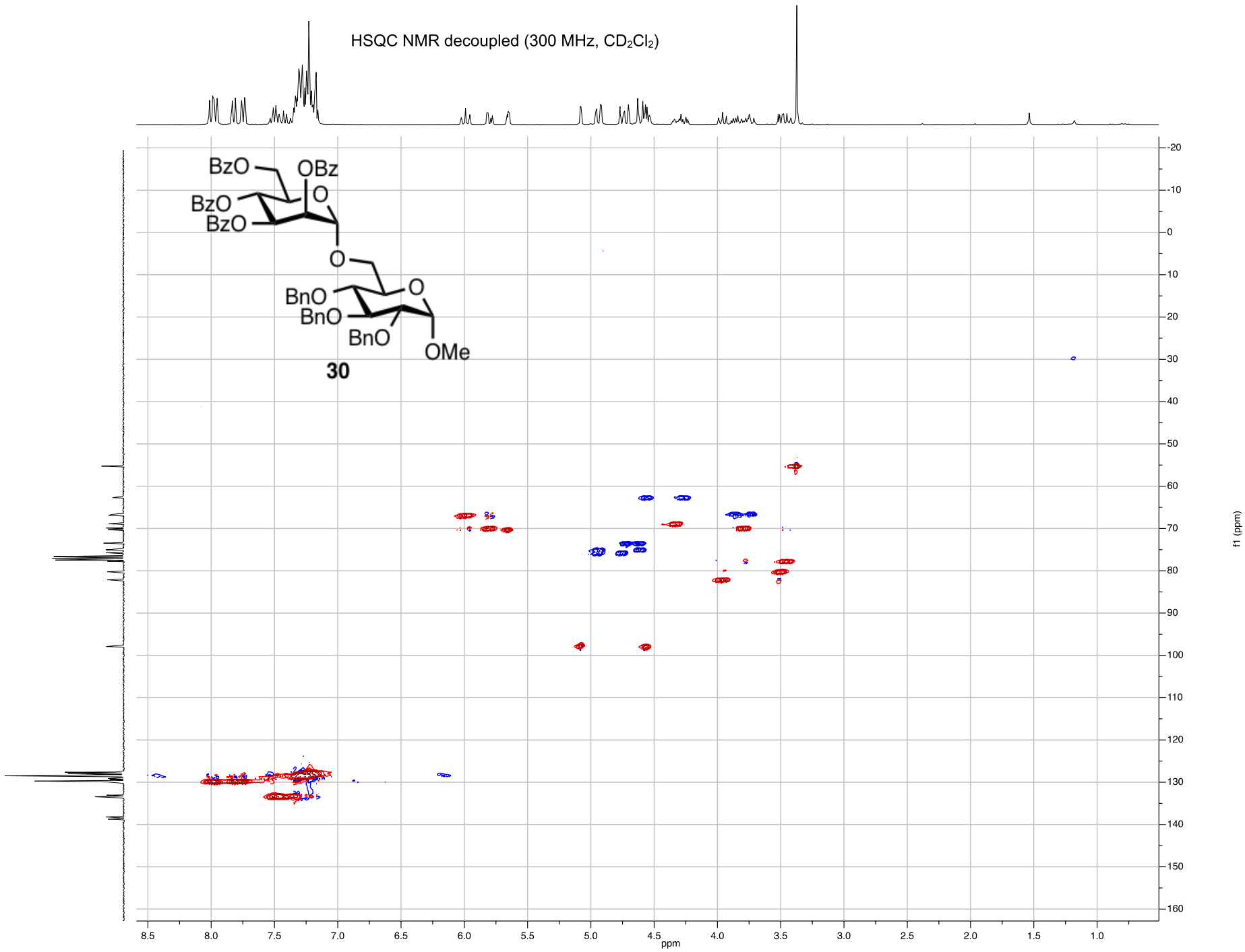

8.02 8.01 8.00 7.99 7.98 7.98 7.98 7.96 7.95 7.95 7.84 7.83 7.82 7.81 7.80 7.76 7.76 7.74 7.74 7.73 7.51 7.51 7.49 7.48 7.47 7.46 7.46 7.45 7.43 7.40 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.30 7.28 7.28 7.28 7.27 7.26 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.21 7.21 7.20 7.19 7.18 7.17 7.16 7.16 6.02 5.99 5.96 5.82 5.81 5.79 5.78 5.66 5.65 5.64 5.08 5.08 4.96 4.95 4.92 4.92 4.77 4.74 4.73 4.70 4.63 4.59 4.58 4.57 4.56 4.54 4.53 4.29 4.25 3.99 3.96 3.93 3.84 3.75 3.52 3.51 3.49 3.48 3.48 3.45 3.42 3.37

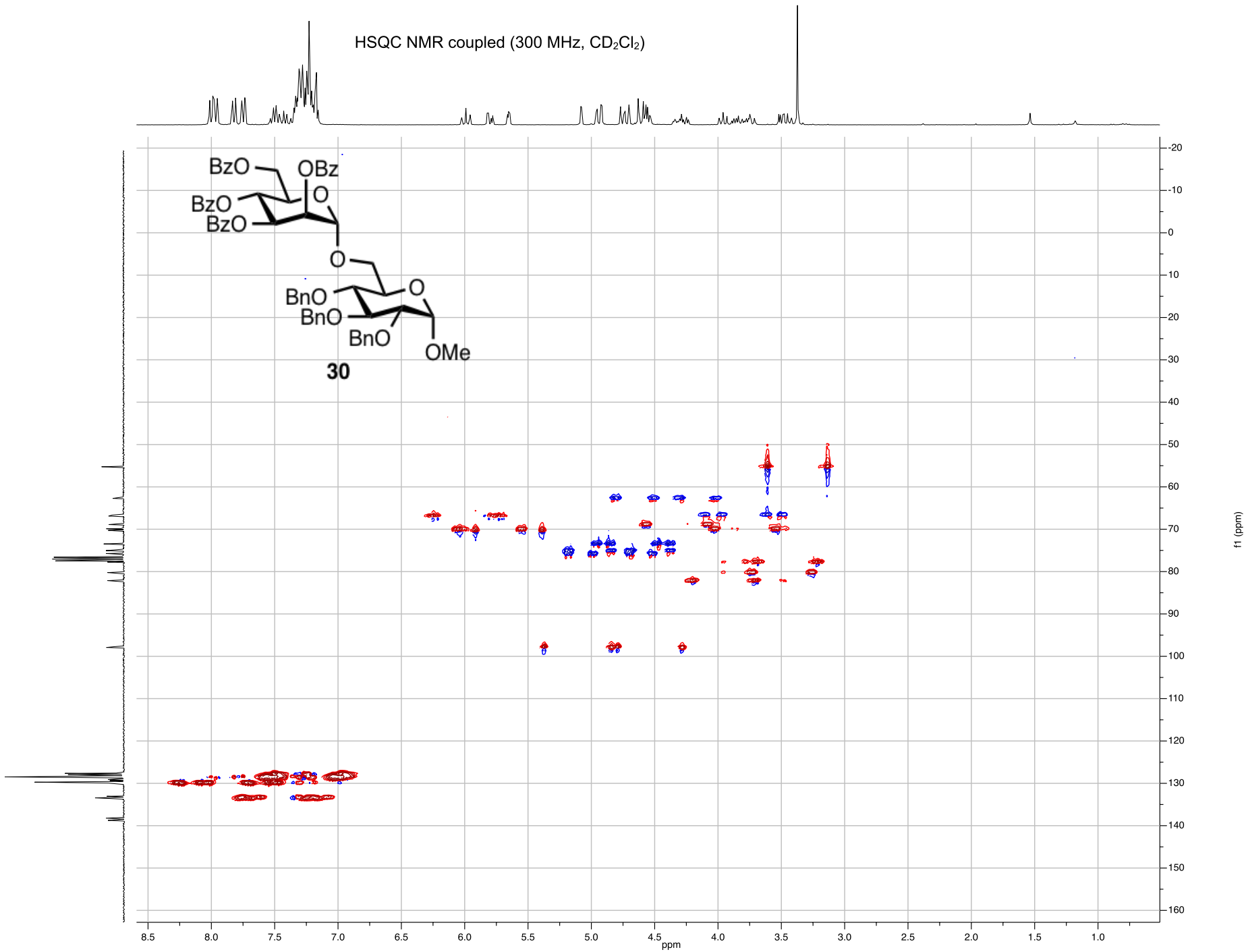

BzO
OBz
O
BzO
BzO
O
O
BnO
BnO
BnO
OMe

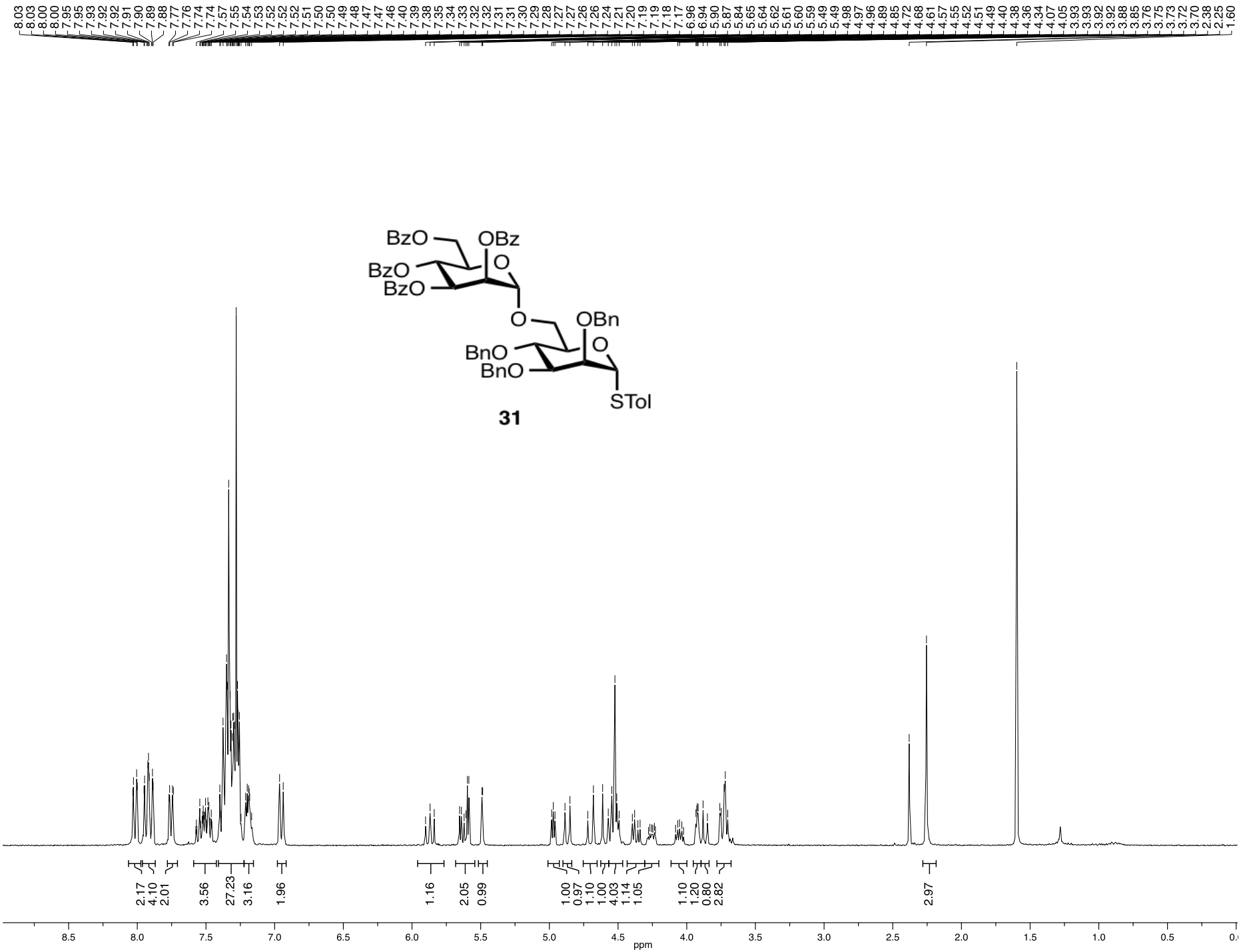
30

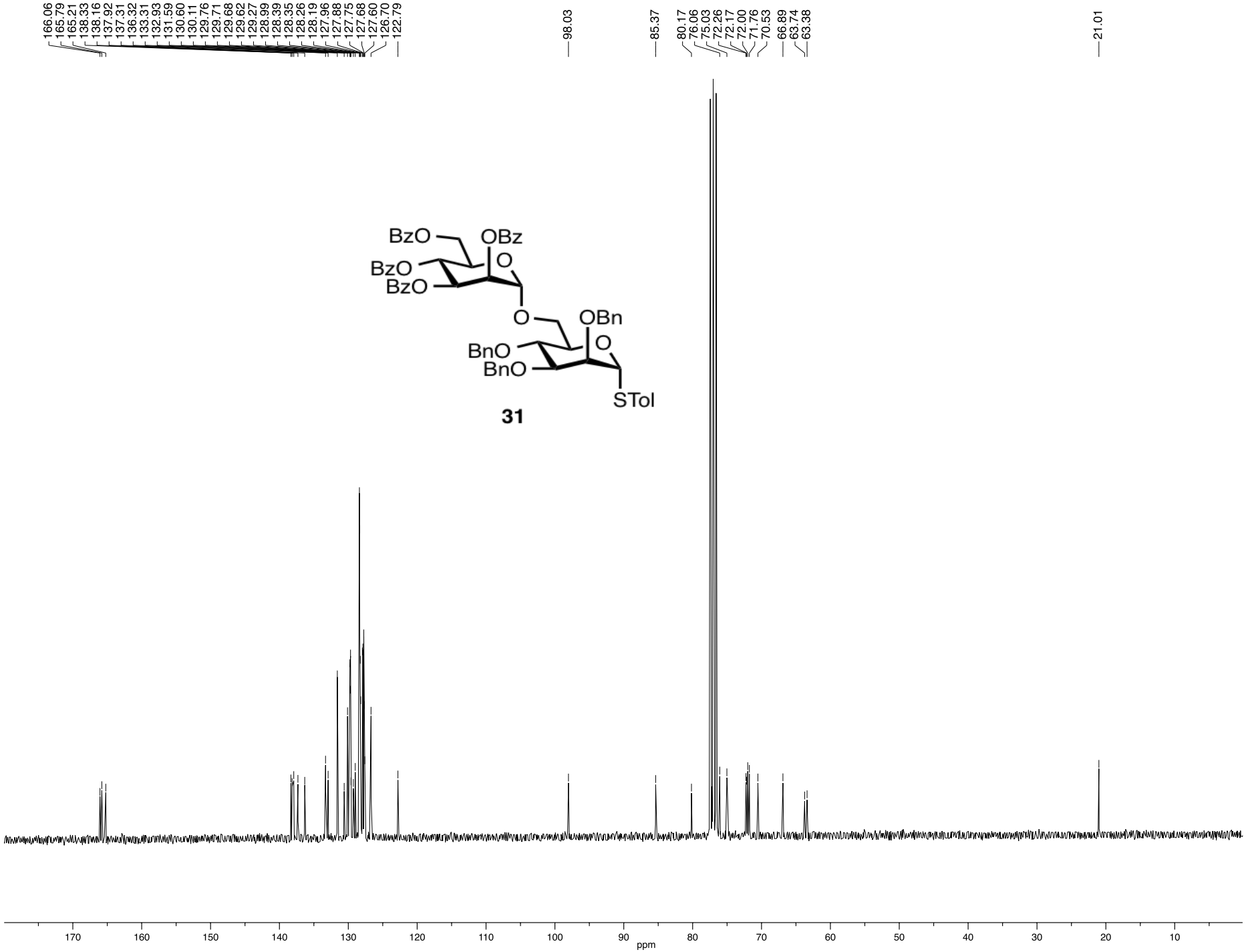

4.13
4.05
3.88
24.28
1.04
1.00
0.99
0.98
2.00
2.02
4.07
1.85
1.11
2.85
2.07
2.76
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

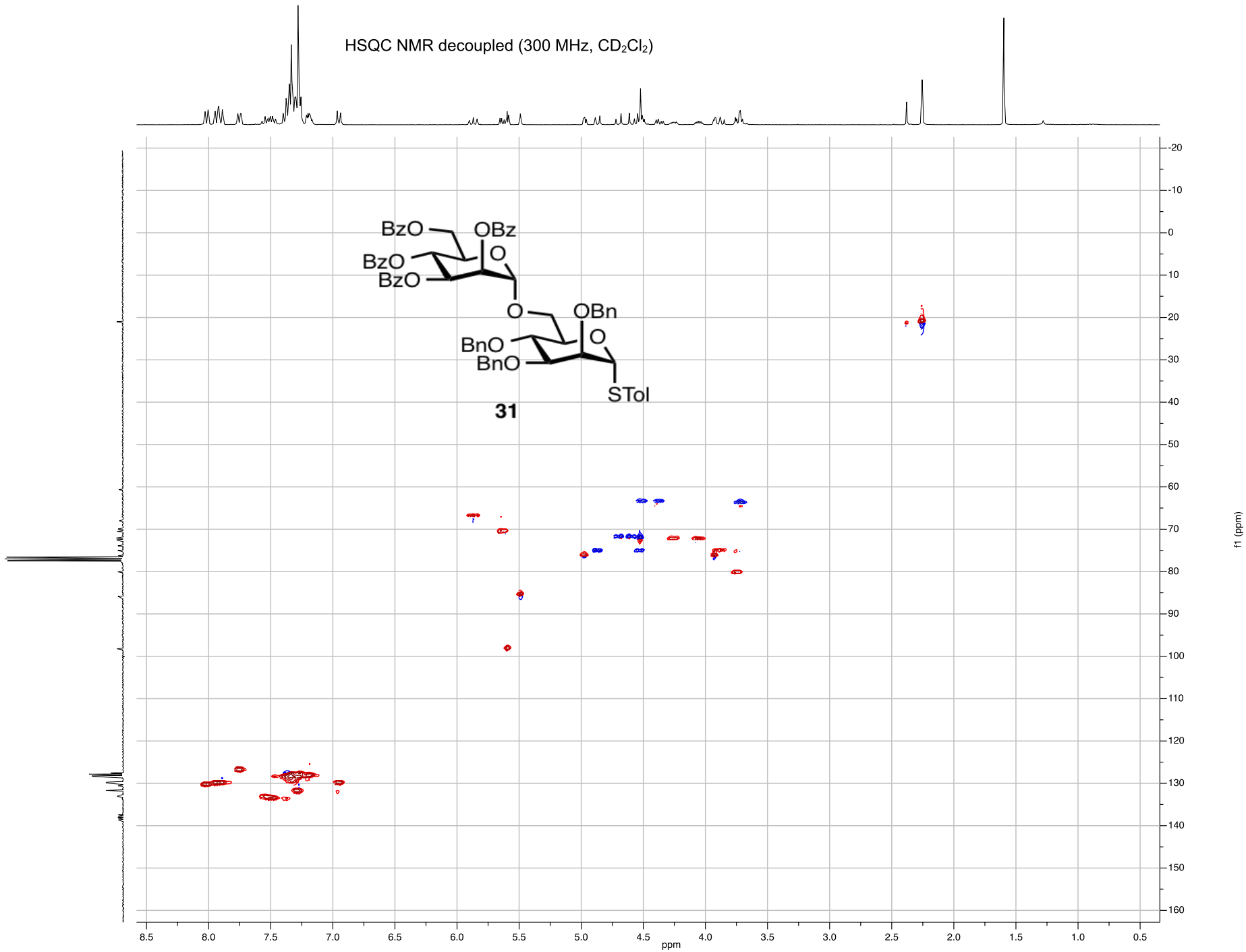
166.11
165.44
165.26
138.74
138.21
138.18
133.43
133.15
133.05
129.95
129.86
129.72
129.36
129.11
129.00
128.57
128.48
128.45
128.40
128.31
128.12
127.97
127.89
127.78
127.64
127.60
97.92
97.75
82.14
80.23
75.74
75.05
73.47
70.28
69.98
69.89
68.90
66.89
66.66
62.71
55.25
BzO
BzO
BzO
OBz
O
O
BnO
BnO
BnO
O
O
OMe
30
ppm

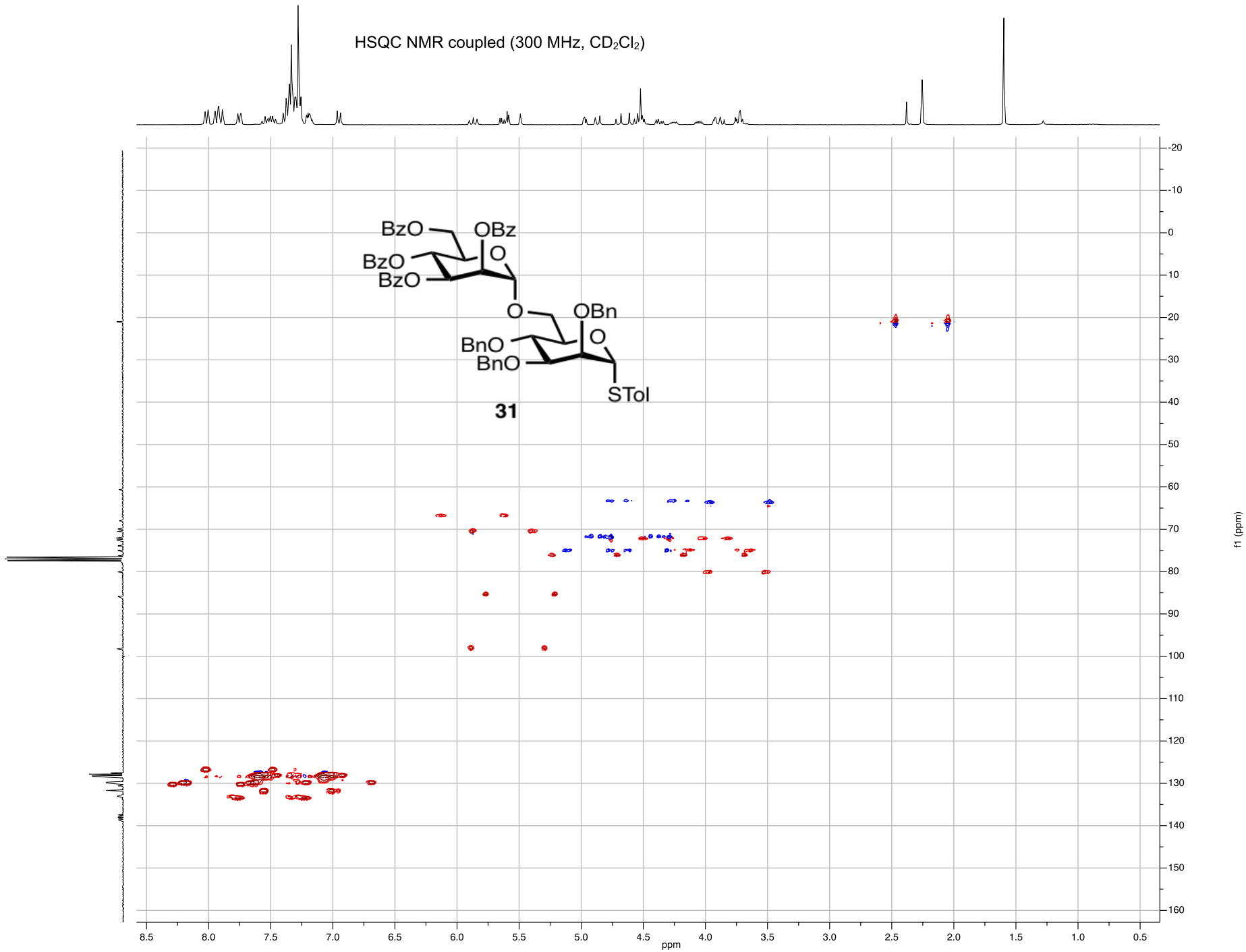

HSQC NMR decoupled (300 MHz, CD_2Cl_2)
BzO
OBz
O
BzO
BzO
O
BnO
O
BnO
BnO
OMe
30
f1 (ppm)
ppm

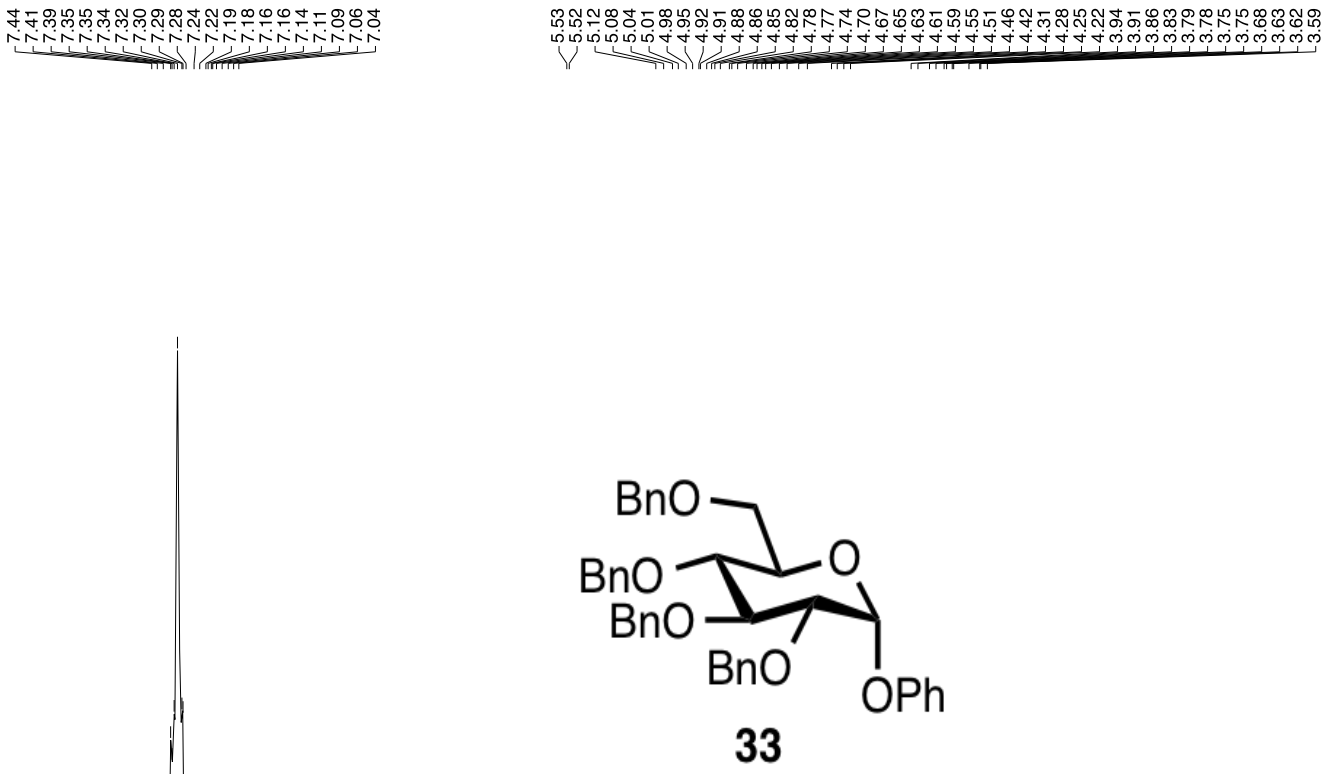

HSQC NMR coupled (300 MHz, CD_2Cl_2)
BzO
OBz
O
BzO
BzO
O
O
BnO
BnO
BnO
OMe
30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
f1 (ppm)


8.03 8.03 8.00 8.00 7.95 7.95 7.93 7.92 7.92 7.91 7.90 7.89 7.88 7.77 7.76 7.74 7.74 7.57 7.55 7.54 7.53 7.52 7.52 7.52 7.51 7.50 7.50 7.49 7.48 7.47 7.47 7.46 7.40 7.39 7.38 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.27 7.26 7.26 7.24 7.21 7.20 7.19 7.19 7.18 7.17 6.96 6.94 5.90 5.87 5.84 5.65 5.64 5.62 5.61 5.60 5.59 5.49 5.49 4.98 4.97 4.96 4.89 4.85 4.72 4.68 4.61 4.57 4.55 4.52 4.51 4.49 4.40 4.38 4.36 4.34 4.07 4.05 3.93 3.93 3.92 3.92 3.88 3.85 3.76 3.75 3.73 3.72 3.70 2.38 2.25 1.60
BzO
OBz
BzO
O
BzO
O
OBn
BnO
O
BnO
STol
31
2.17 4.10 2.01 3.56 27.23 3.16 1.96 1.16 2.05 0.99 1.00 0.97 1.10 1.00 4.03 1.14 1.05 1.10 1.20 0.80 2.82 2.97
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
ppm

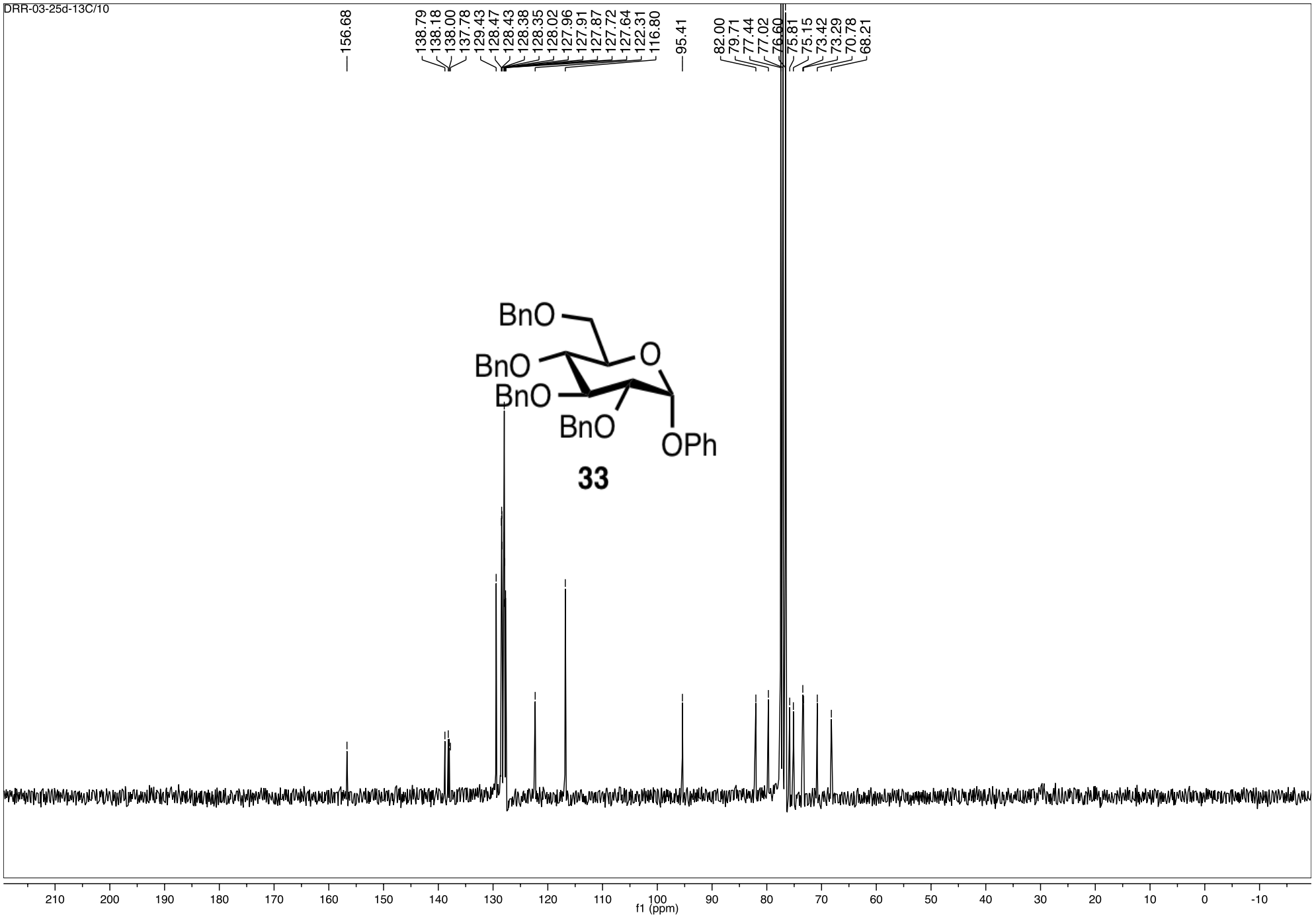

166.06
165.79
165.21
138.33
138.16
137.92
137.31
136.32
133.31
132.93
131.59
130.60
130.11
129.76
129.71
129.68
129.62
129.27
128.99
128.39
128.35
128.26
128.19
127.96
127.88
127.75
127.68
127.60
126.70
122.79
98.03
85.37
80.17
76.06
75.03
72.26
72.17
72.00
71.76
70.53
66.89
63.74
63.38
21.01
BzO
OBz
O
BzO
BzO
O
OBn
O
BnO
BnO
STol
31
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

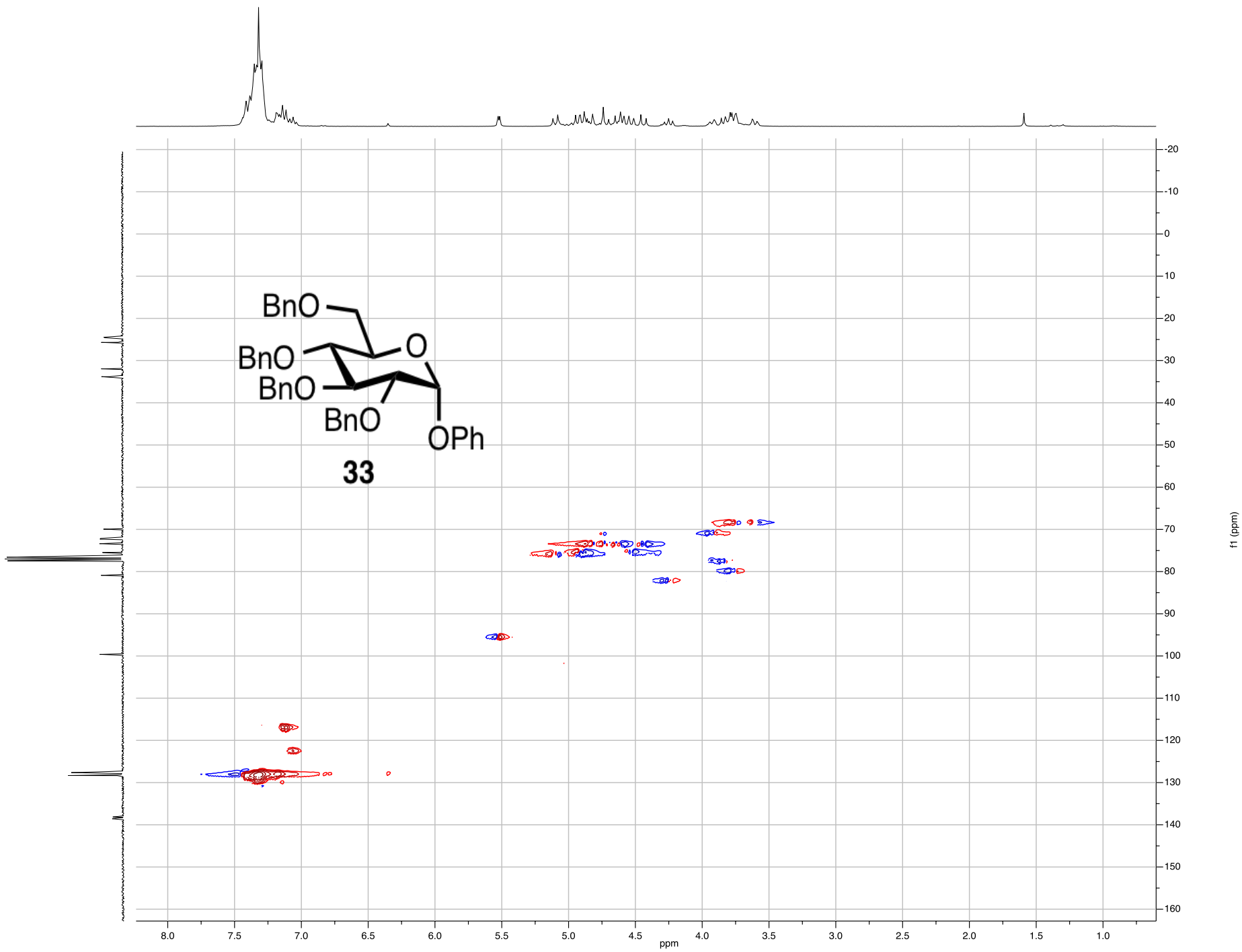

HSQC NMR decoupled (300 MHz, CD_2Cl_2)
BzO
OBz
O
BzO
BzO
O
OBn
O
BnO
BnO
STol
31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)

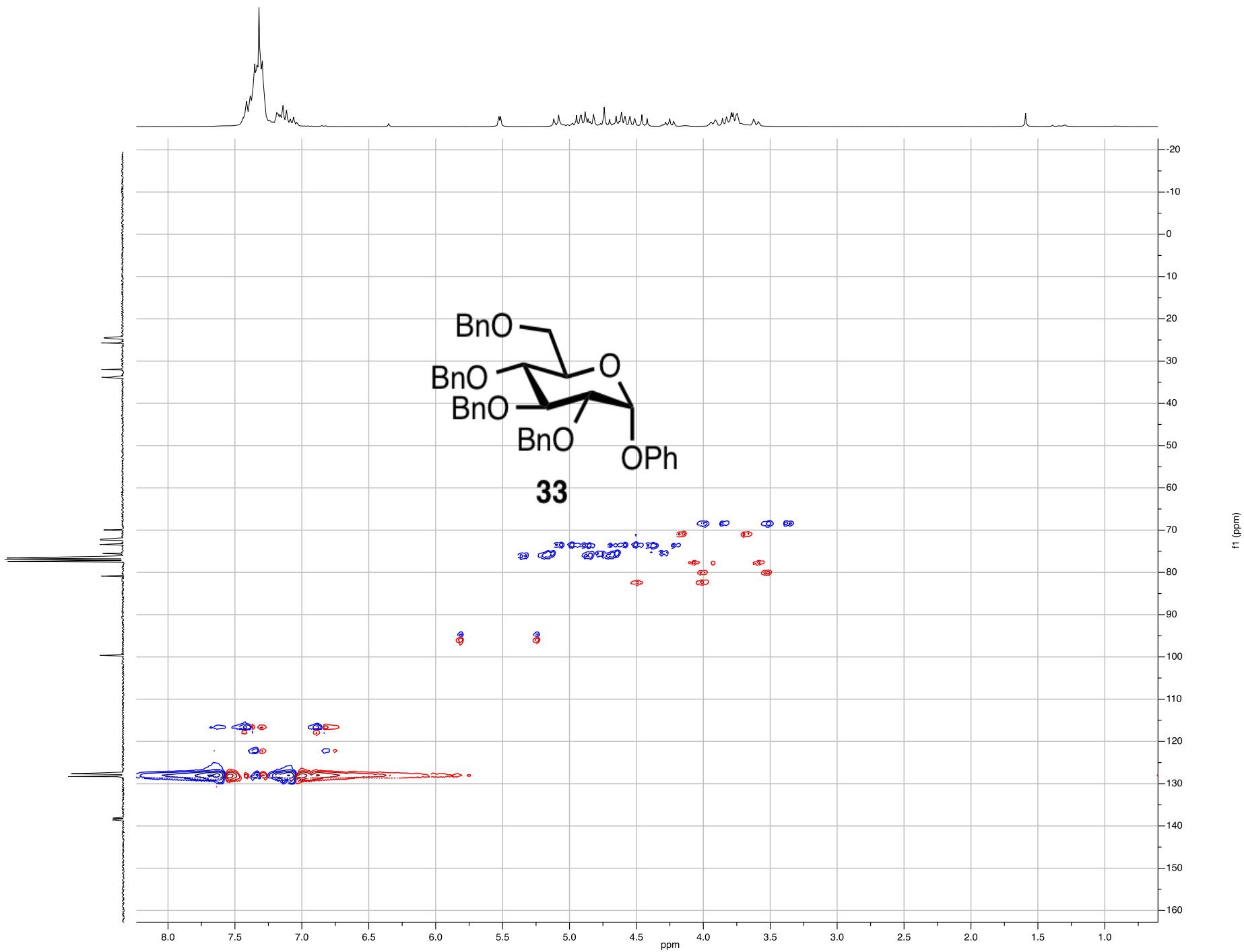

HSQC NMR coupled (300 MHz, CD_2Cl_2)
BzO
OBz
O
BzO
BzO
O
OBn
O
BnO
BnO
STol
31
ppm
f1 (ppm)

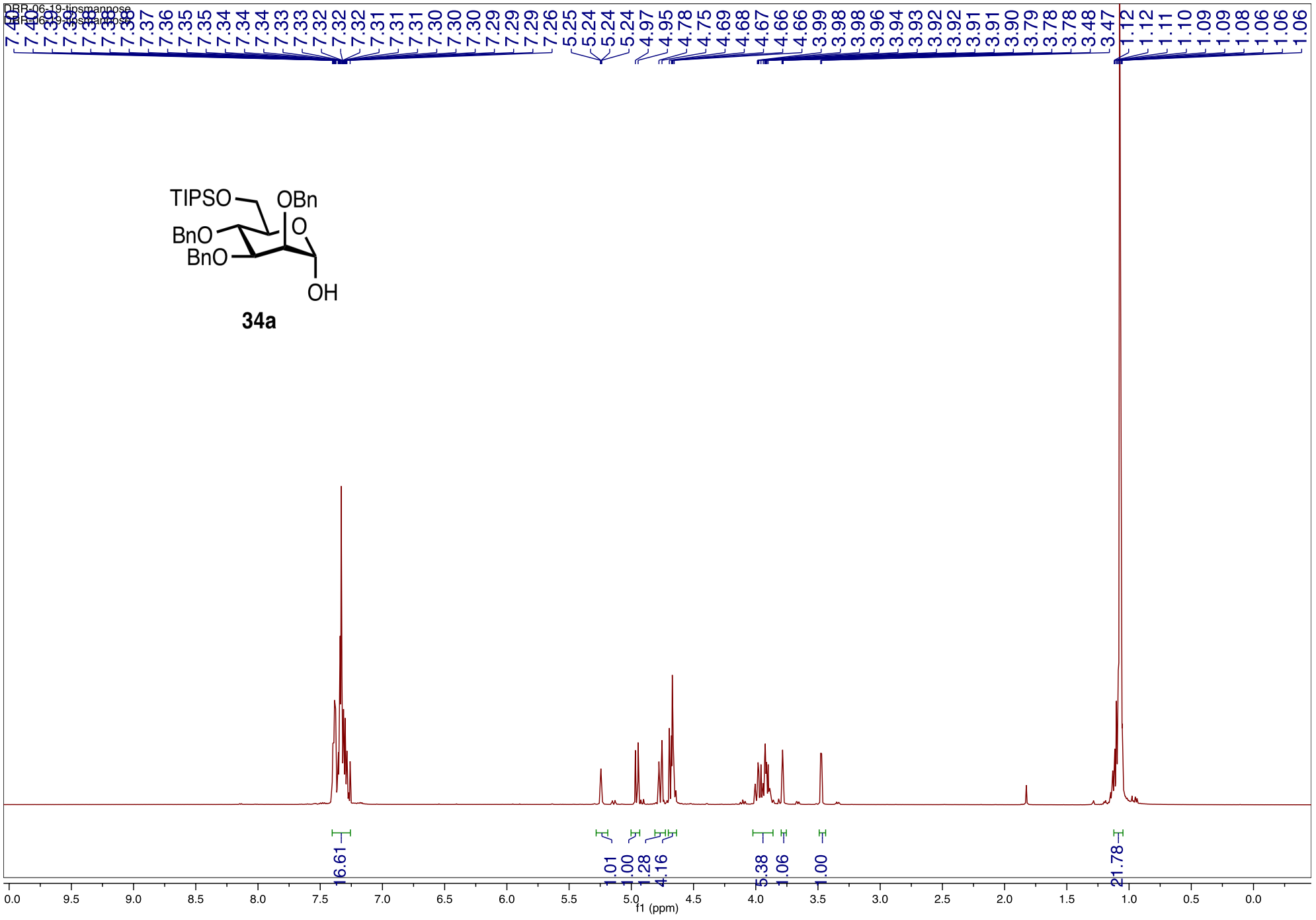

7.44
7.41
7.39
7.35
7.35
7.34
7.32
7.30
7.29
7.28
7.24
7.22
7.19
7.18
7.16
7.16
7.14
7.11
7.09
7.06
7.04
5.53
5.52
5.12
5.08
5.04
5.01
4.98
4.95
4.92
4.91
4.88
4.86
4.85
4.82
4.78
4.77
4.74
4.70
4.67
4.65
4.63
4.61
4.59
4.55
4.51
4.46
4.42
4.31
4.28
4.25
4.22
3.94
3.91
3.86
3.83
3.79
3.78
3.75
3.75
3.68
3.63
3.62
3.59
BnO
BnO
BnO
BnO
O
OPh
33
23.72
5.01
0.81
1.12
1.23
1.86
1.21
1.71
0.97
0.83
0.81
0.99
3.33
0.83
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
ppm

DRR-03-25d-13C/10

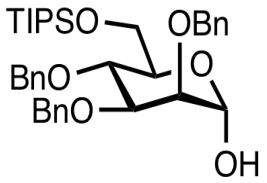



BnO
BnO
BnO
BnO
O
OPh
33
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


BnO
BnO
BnO
BnO
O
OPh
33
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
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


DRR-06-19-tipsmannose
C6H6-06-19-tipsmannose
TIPSO
OBn
BnO
O
BnO
OH
34a
f1 (ppm)

DRR-06-19-tipsmannose/10

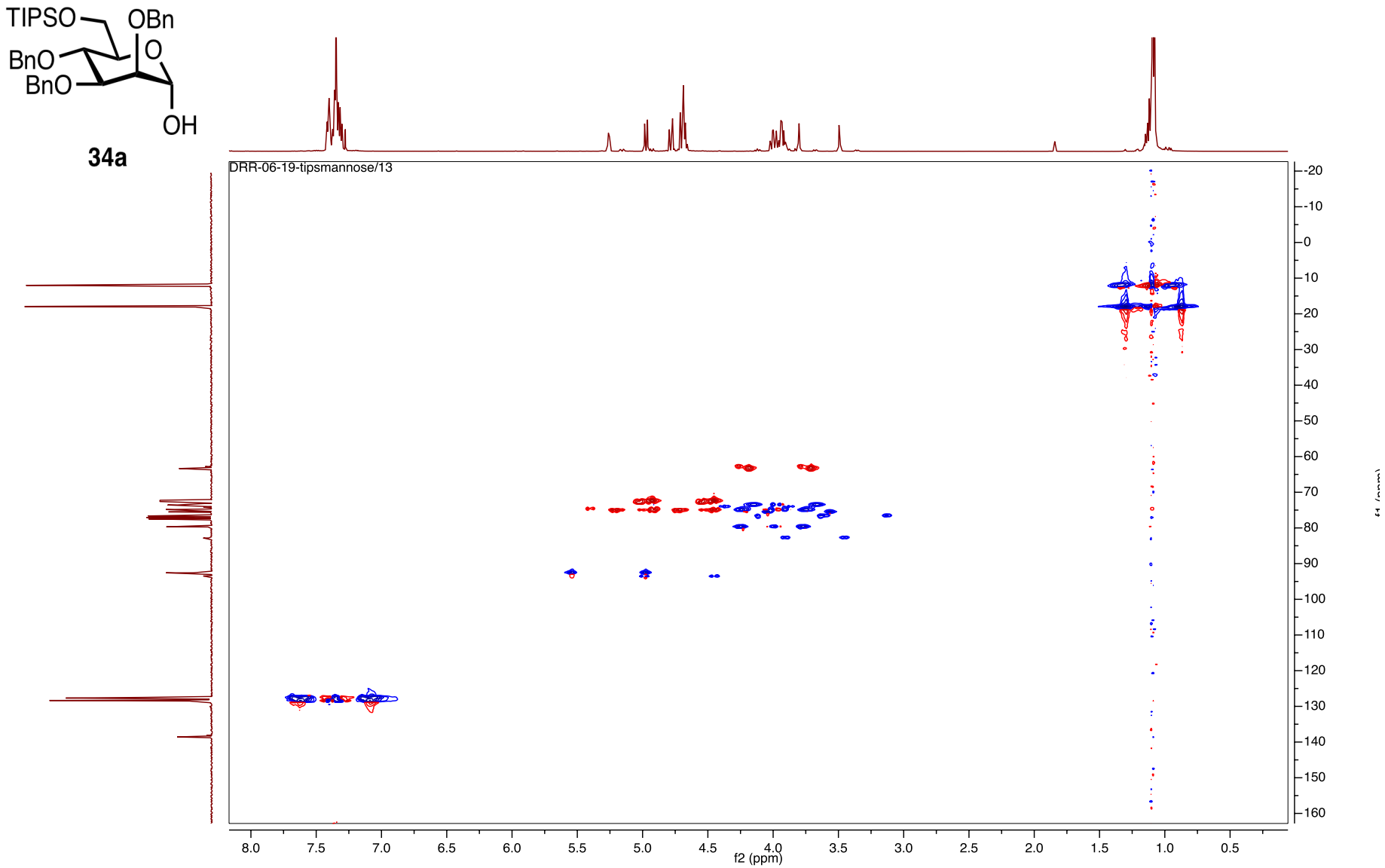


34a

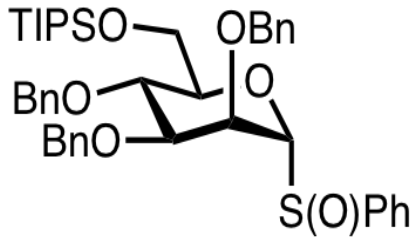
138.73 138.62 138.58 138.56 138.42 138.16 128.52 128.42 128.35 128.33 128.26 128.05 127.82 127.75 127.71 127.70 127.67 127.58 127.55 127.48 93.47 92.58 82.82 79.68 77.48 77.27 77.06 76.78 76.64 76.47 75.51 75.08 75.00 74.85 74.63 74.18 73.57 72.90 72.61 72.23 63.36 62.80 18.06 18.00 12.07 12.02

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

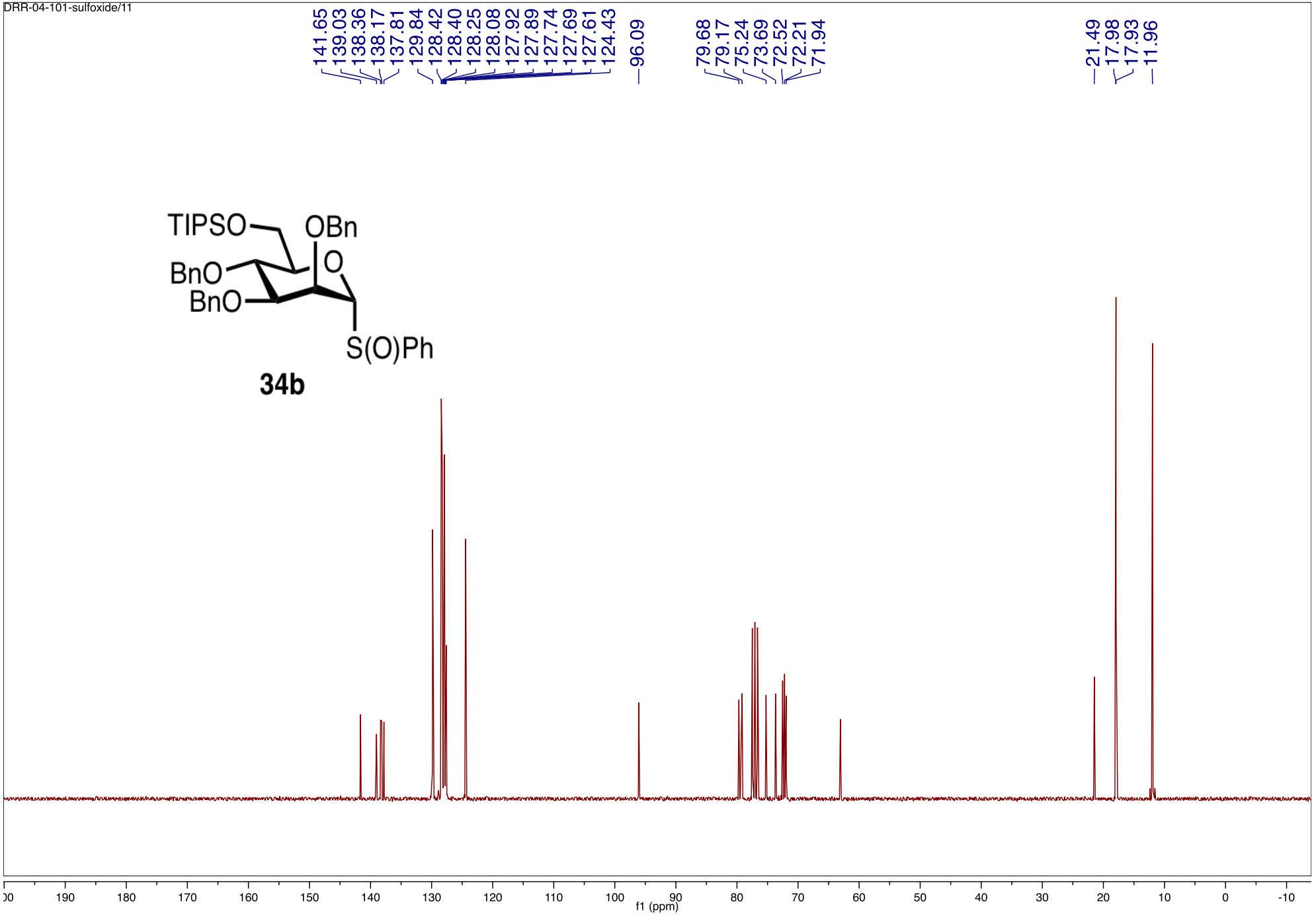

TIPSO
OBn
O
BnO
BnO
OH
34a
DRR-06-19-tipsmannose/13
f2 (ppm)

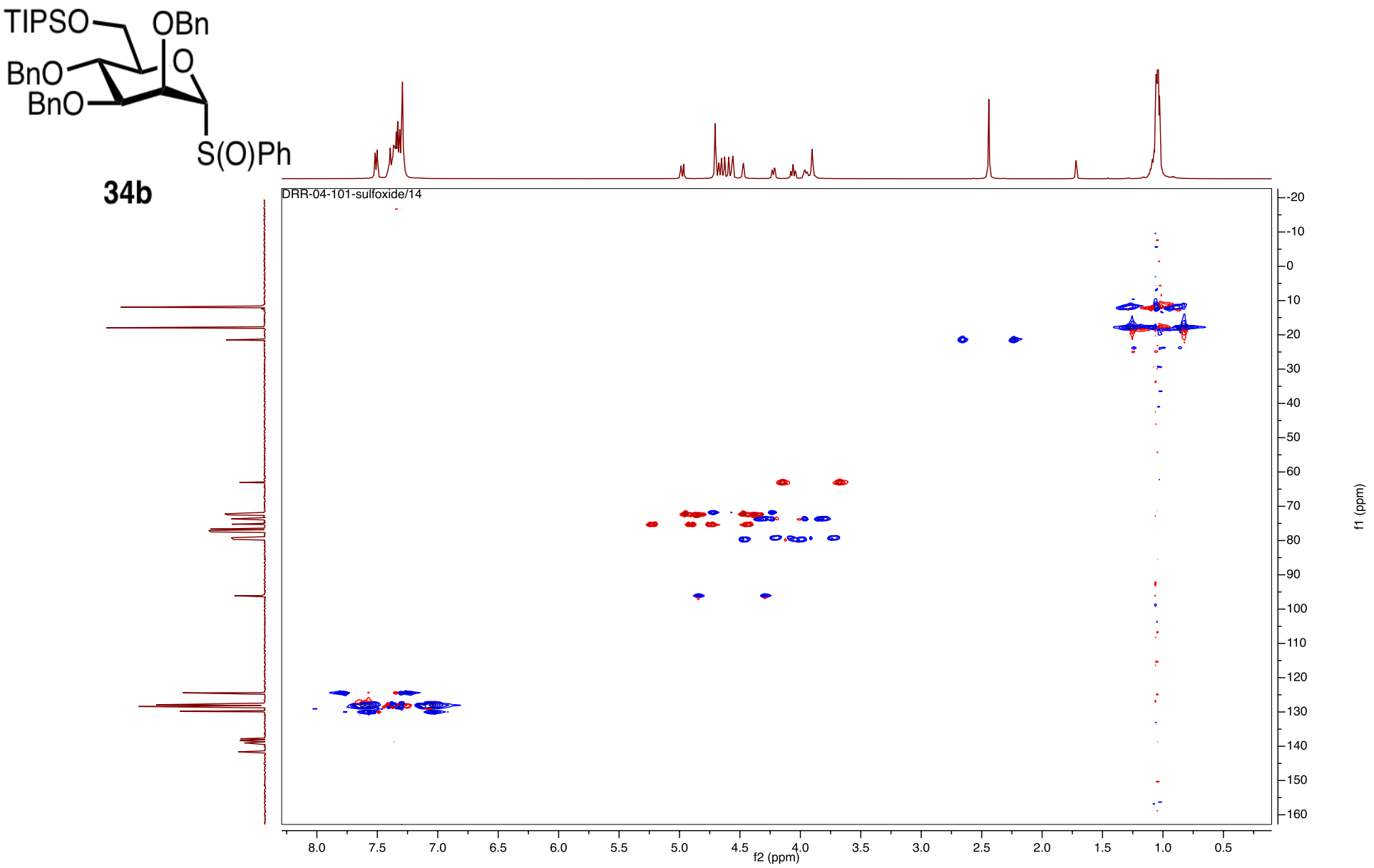
DRR-04-101-mannosulfoxide
DRR-04-101-mannosulfoxide

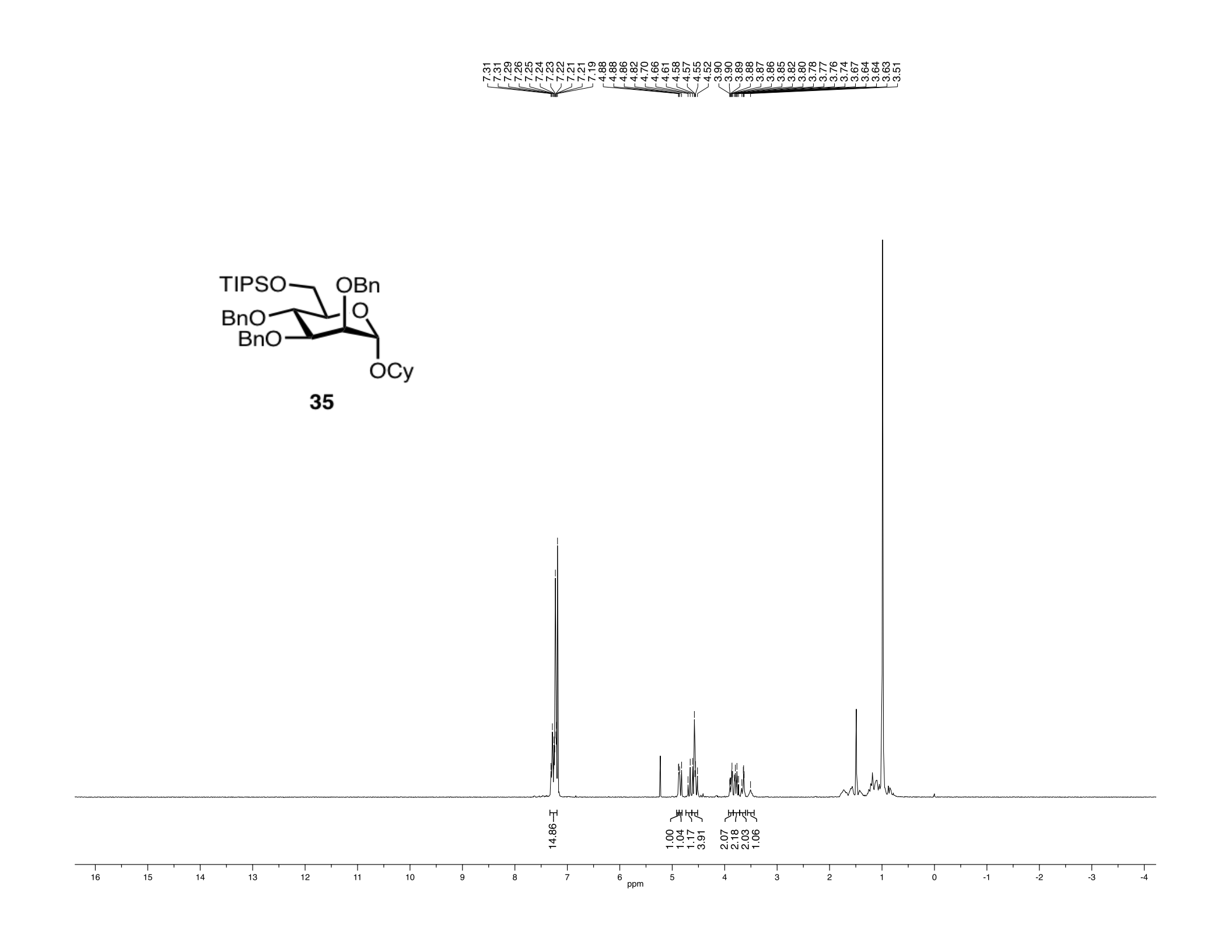


34b

DRR-04-101-sulfoxide/11

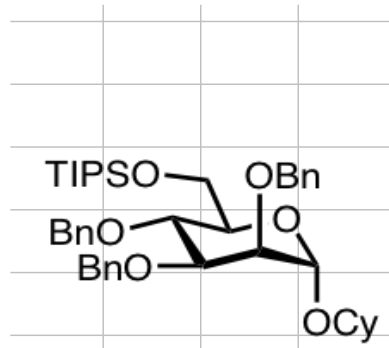



TIPSO
OBn
O
BnO
BnO
S(O)Ph
34b
DRR-04-101-sulfoxide/14
f2 (ppm)
f1 (ppm)


7.31
7.31
7.29
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.19
4.88
4.88
4.86
4.82
4.70
4.66
4.61
4.58
4.57
4.55
4.52
3.90
3.90
3.89
3.88
3.87
3.86
3.85
3.82
3.80
3.78
3.77
3.76
3.74
3.67
3.64
3.64
3.63
3.51
TIPSO
OBn
BnO
O
BnO
OCy
35
14.86
1.00
1.04
1.17
3.91
2.07
2.18
2.03
1.06
16
15
14
13
12
11
10
9
8
7
6
ppm
5
4
3
2
1
0
-1
-2
-3
-4

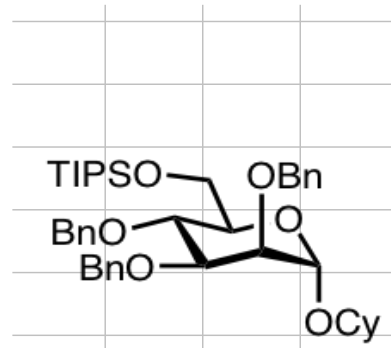
TIPSO
BnO
BnO
OBn
O
OCy
35
128.34
128.30
128.23
128.16
127.74
127.66
127.45
80.45
75.61
75.35
75.21
74.16
73.61
72.50
72.14
18.02
12.01
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140

HSQC NMR decoupled (300 MHz, CD_2Cl_2)

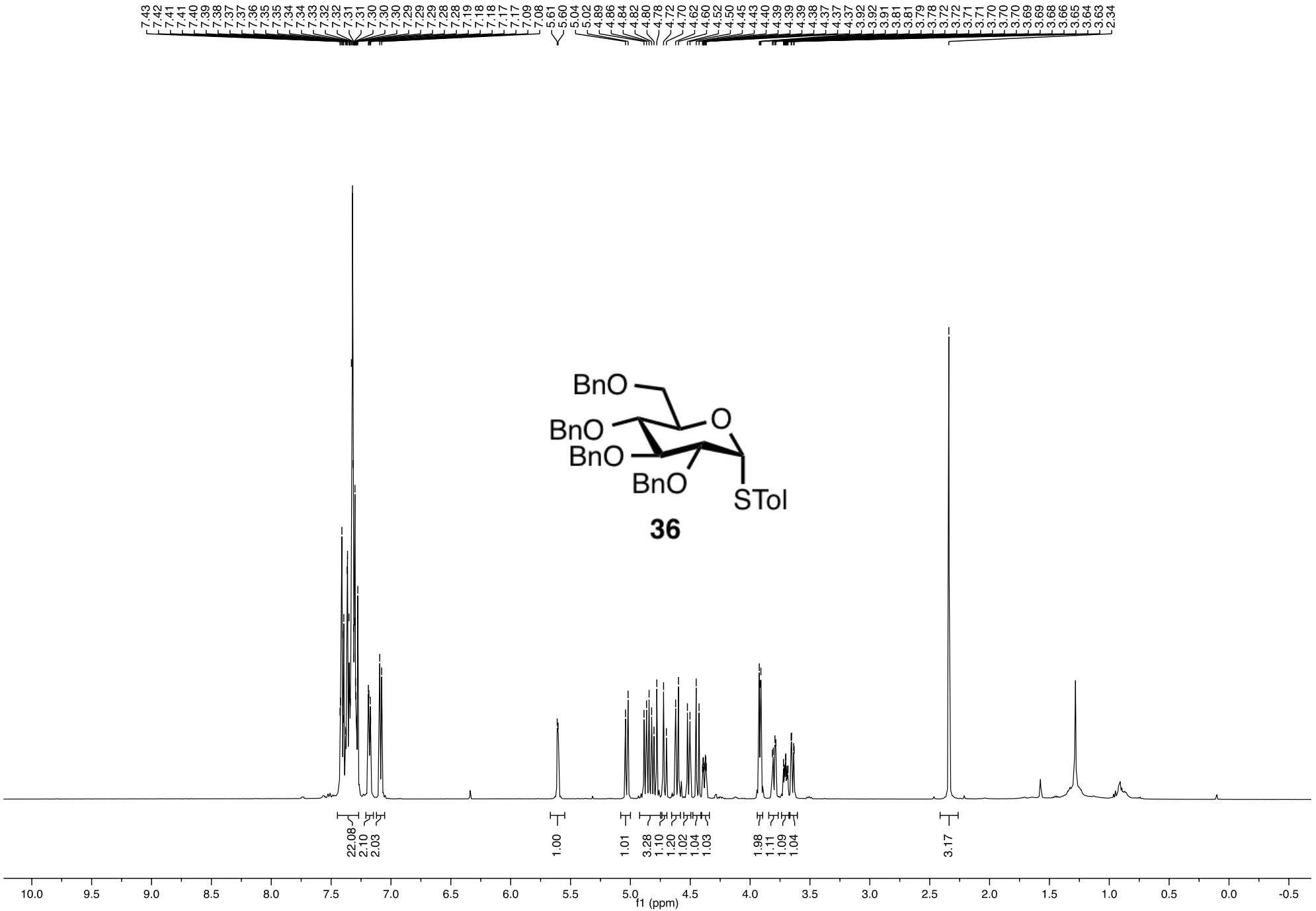


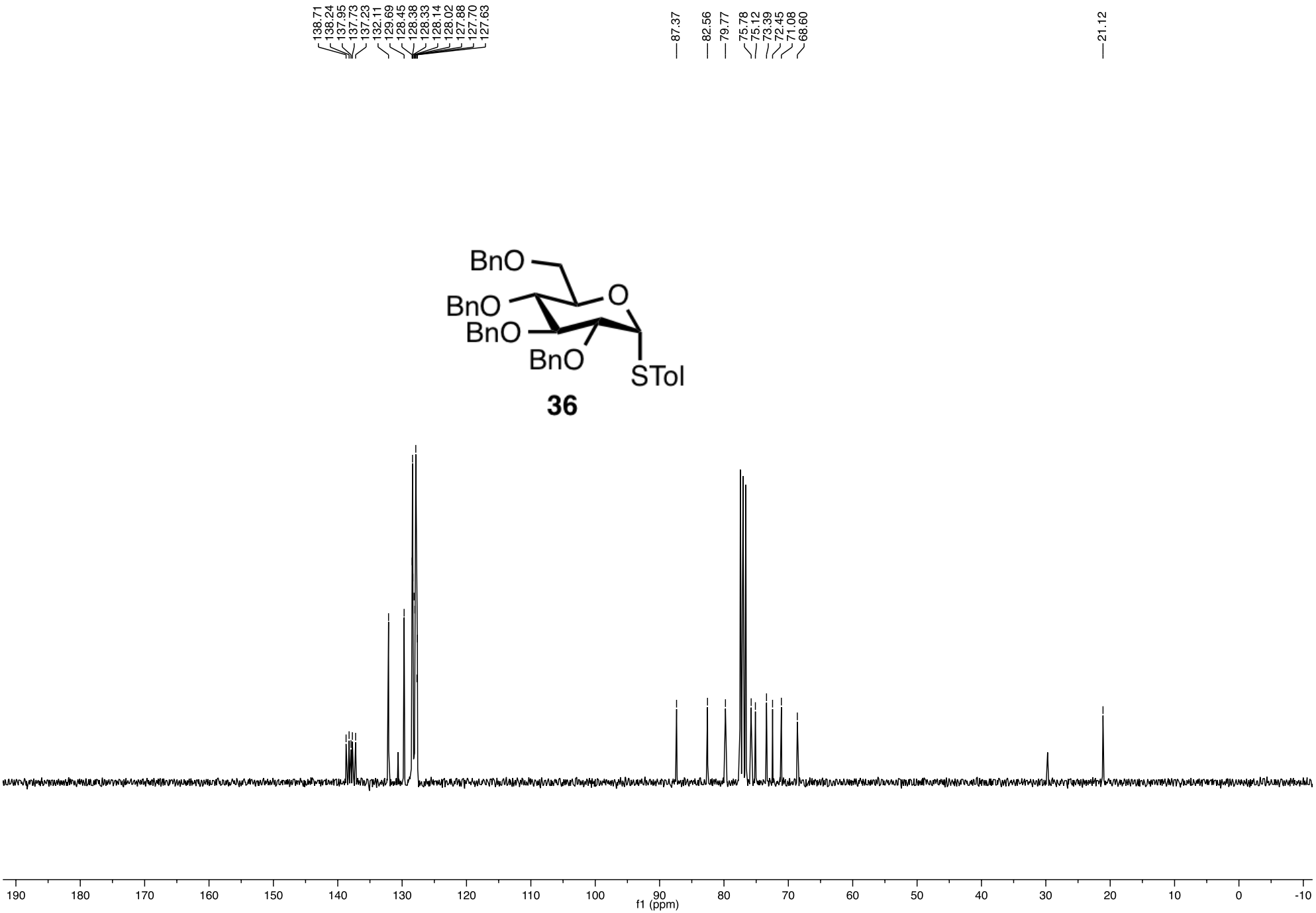
35

HSQC NMR coupled (300 MHz, CD_2Cl_2)

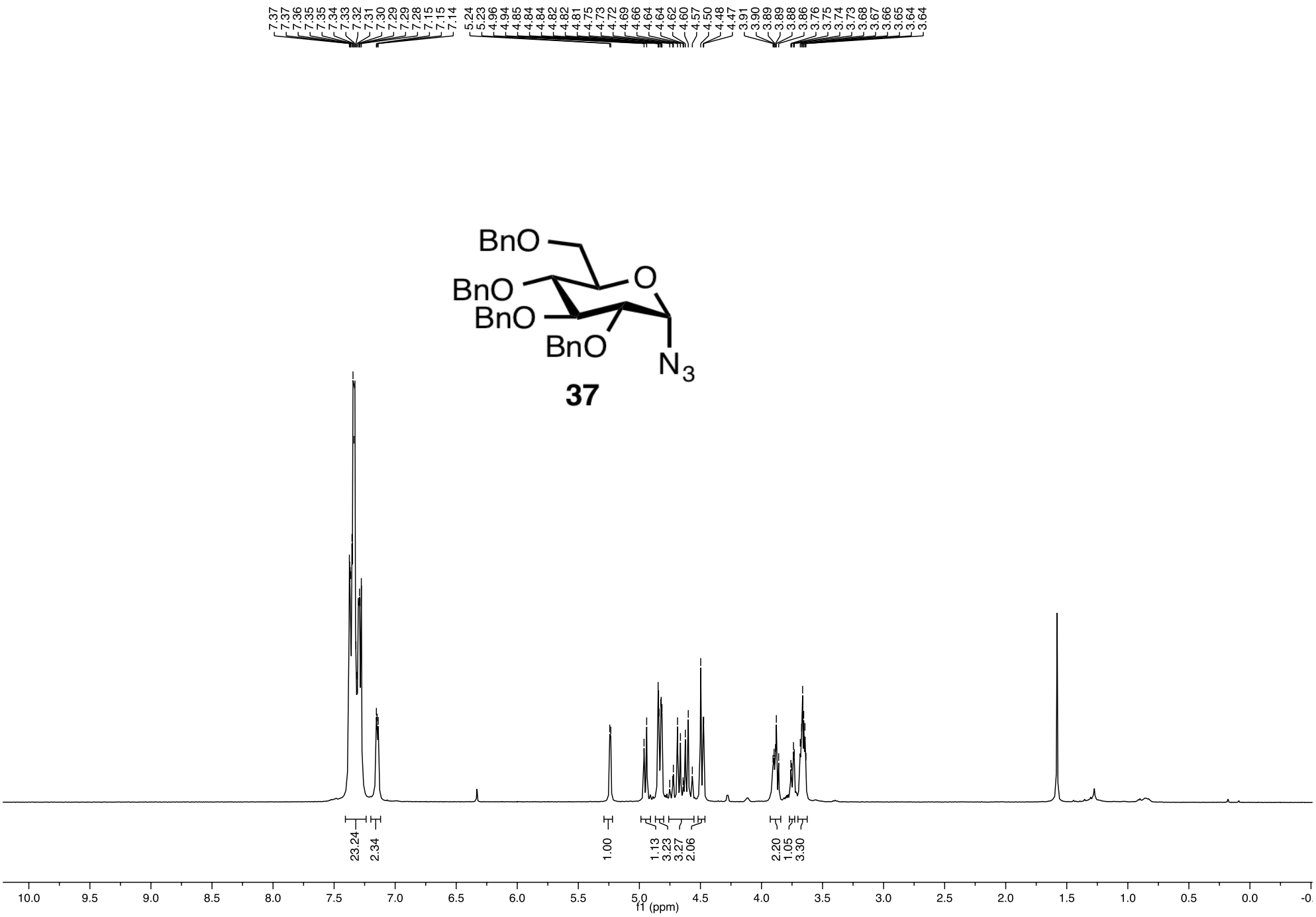


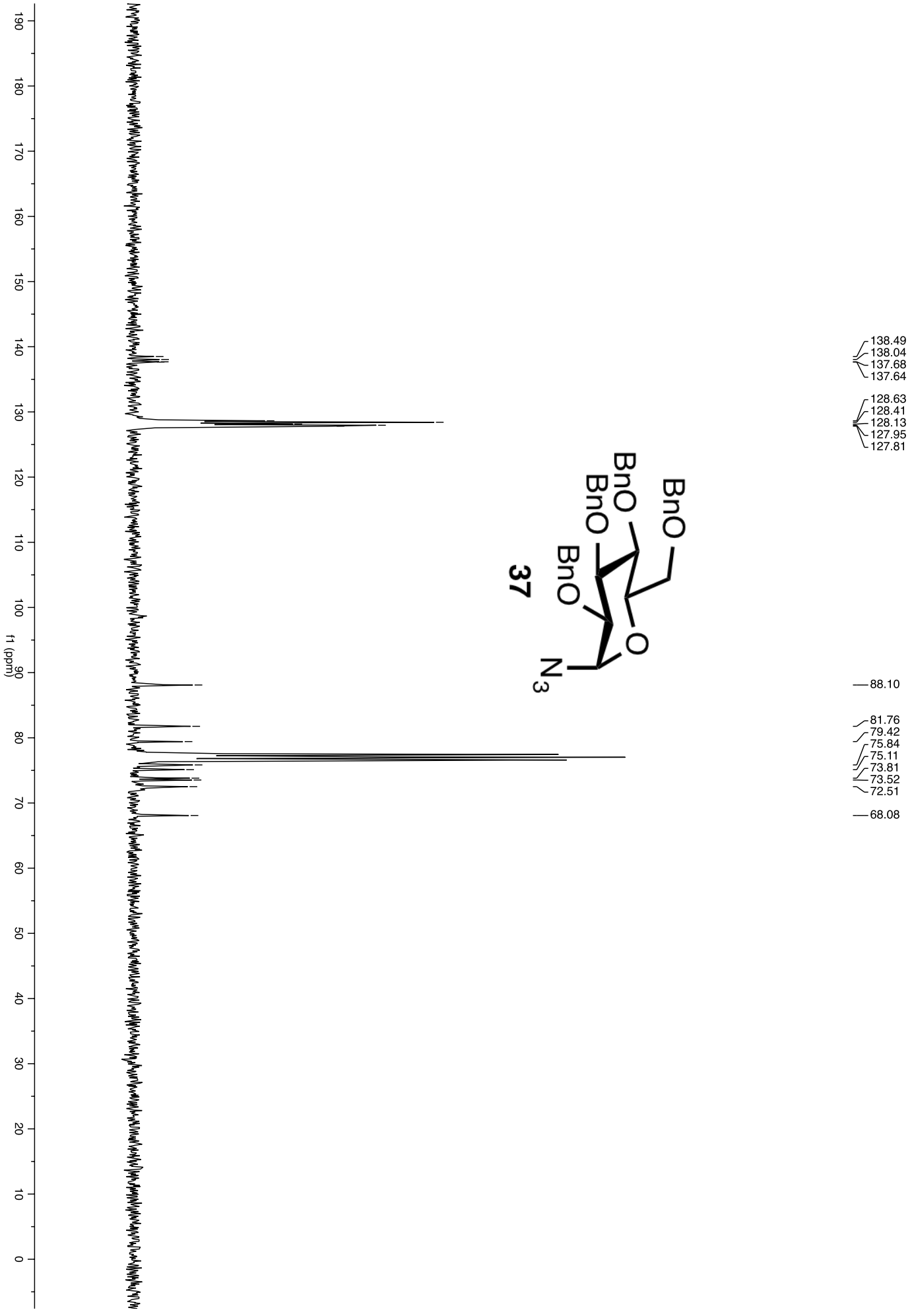
35

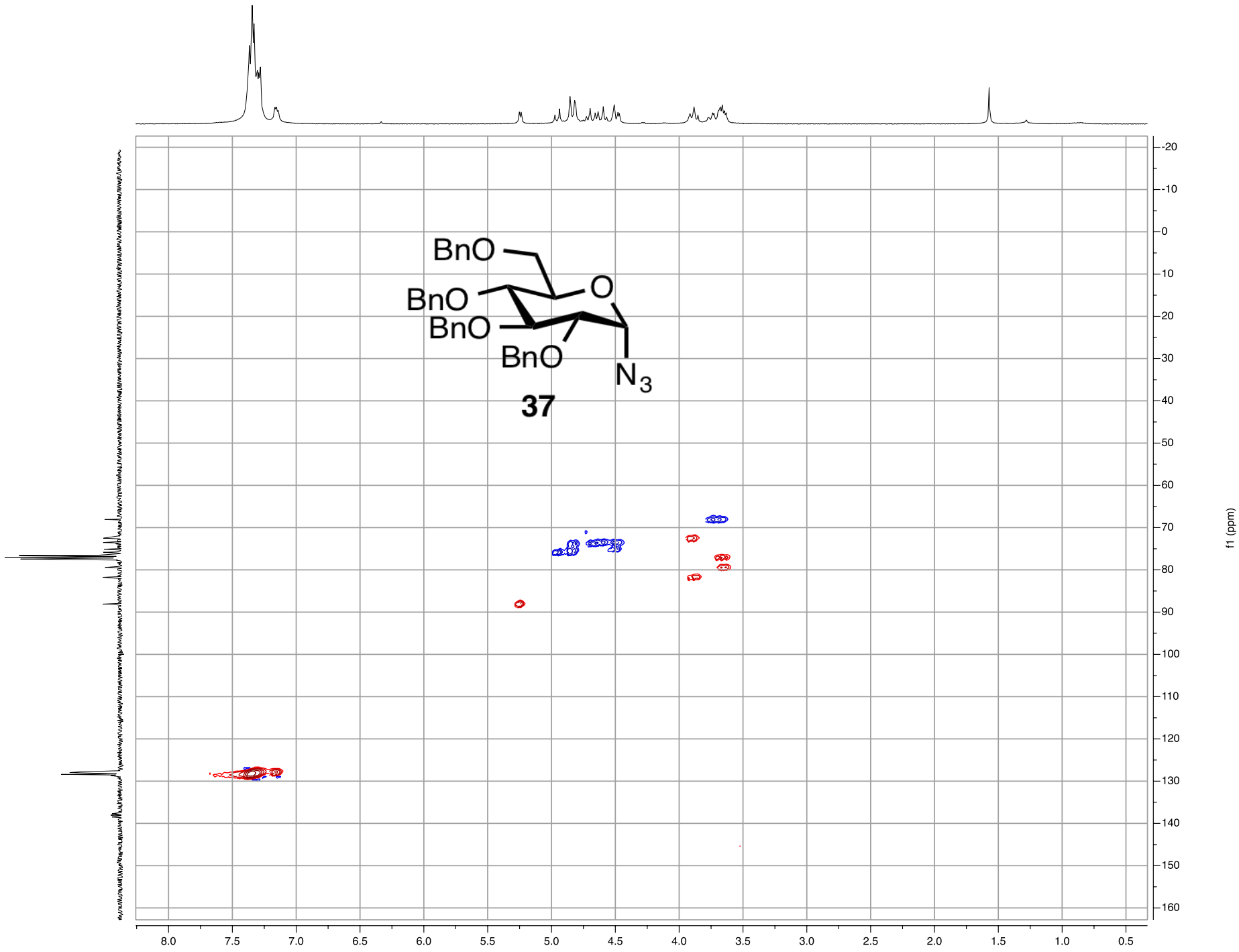

7.43 7.42 7.41 7.41 7.40 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.19 7.18 7.18 7.17 7.17 7.09 7.08 5.61 5.60 5.04 5.02 4.89 4.86 4.84 4.82 4.80 4.78 4.72 4.70 4.62 4.60 4.52 4.50 4.45 4.43 4.40 4.39 4.39 4.39 4.38 4.37 4.37 4.37 3.92 3.92 3.91 3.81 3.81 3.79 3.78 3.72 3.72 3.71 3.71 3.70 3.70 3.70 3.69 3.69 3.68 3.66 3.65 3.64 3.63 2.34
BnO
BnO
BnO
BnO
O
STol
36
22.08
2.10
2.03
1.00
1.01
3.28
1.10
1.20
1.02
1.04
1.03
1.98
1.11
1.09
1.04
3.17
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 0.0 -0.5
f1 (ppm)


138.71
138.24
137.95
137.73
137.23
132.11
129.69
128.45
128.38
128.33
128.14
128.02
127.88
127.70
127.63
87.37
82.56
79.77
75.78
75.12
73.39
72.45
71.08
68.60
21.12
BnO
BnO
BnO
BnO
O
STol
36
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


HSQC NMR decoupled (300 MHz,
BnO
BnO
BnO
BnO
O
STol
36
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
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


7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.29
7.28
7.15
7.15
7.14
5.24
5.23
4.96
4.94
4.85
4.84
4.84
4.82
4.82
4.81
4.75
4.73
4.72
4.69
4.66
4.64
4.64
4.62
4.60
4.57
4.50
4.48
4.47
3.91
3.90
3.89
3.89
3.88
3.86
3.76
3.75
3.74
3.73
3.68
3.67
3.66
3.65
3.64
3.64
BnO
BnO
BnO
BnO
O
N3
37
23.24
2.34
1.00
1.13
3.23
3.27
2.06
2.20
1.05
3.30
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
0.0
f1 (ppm)


f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
138.49
138.04
137.68
137.64
128.63
128.41
128.13
127.95
127.81
88.10
81.76
79.42
75.84
75.11
73.81
73.52
72.51
68.08
BnO
BnO
BnO
BnO
O
N3
37


BnO
BnO
BnO
BnO
O
N3
37
f1 (ppm)
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
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


8.01
7.85
7.83
7.59
7.58
7.58
7.57
7.33
7.32
7.30
7.30
7.29
7.28
7.26
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.12
7.11
7.10
7.10
7.05
7.05
7.02
7.02
7.01
7.00
7.00
6.99
6.98
6.97
5.67
5.67
5.65
5.65
5.02
4.98
4.81
4.77
4.75
4.72
4.68
4.64
4.63
4.61
4.60
4.57
4.40
4.37
4.33
4.18
4.15
4.12
4.07
4.05
4.04
4.02
3.77
3.75
3.74
3.71
3.61
3.60
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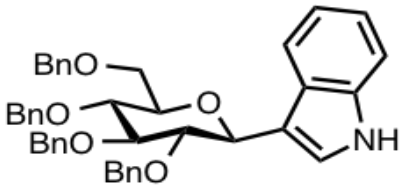
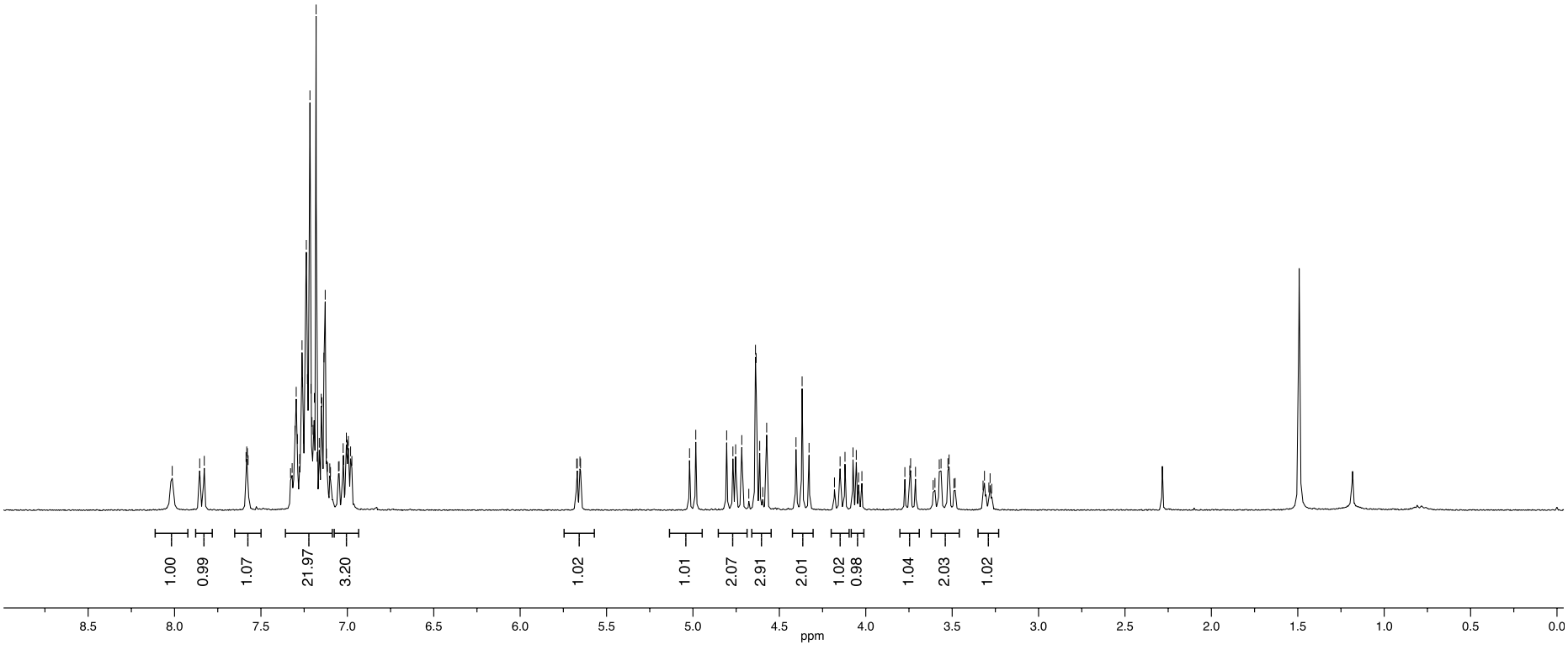
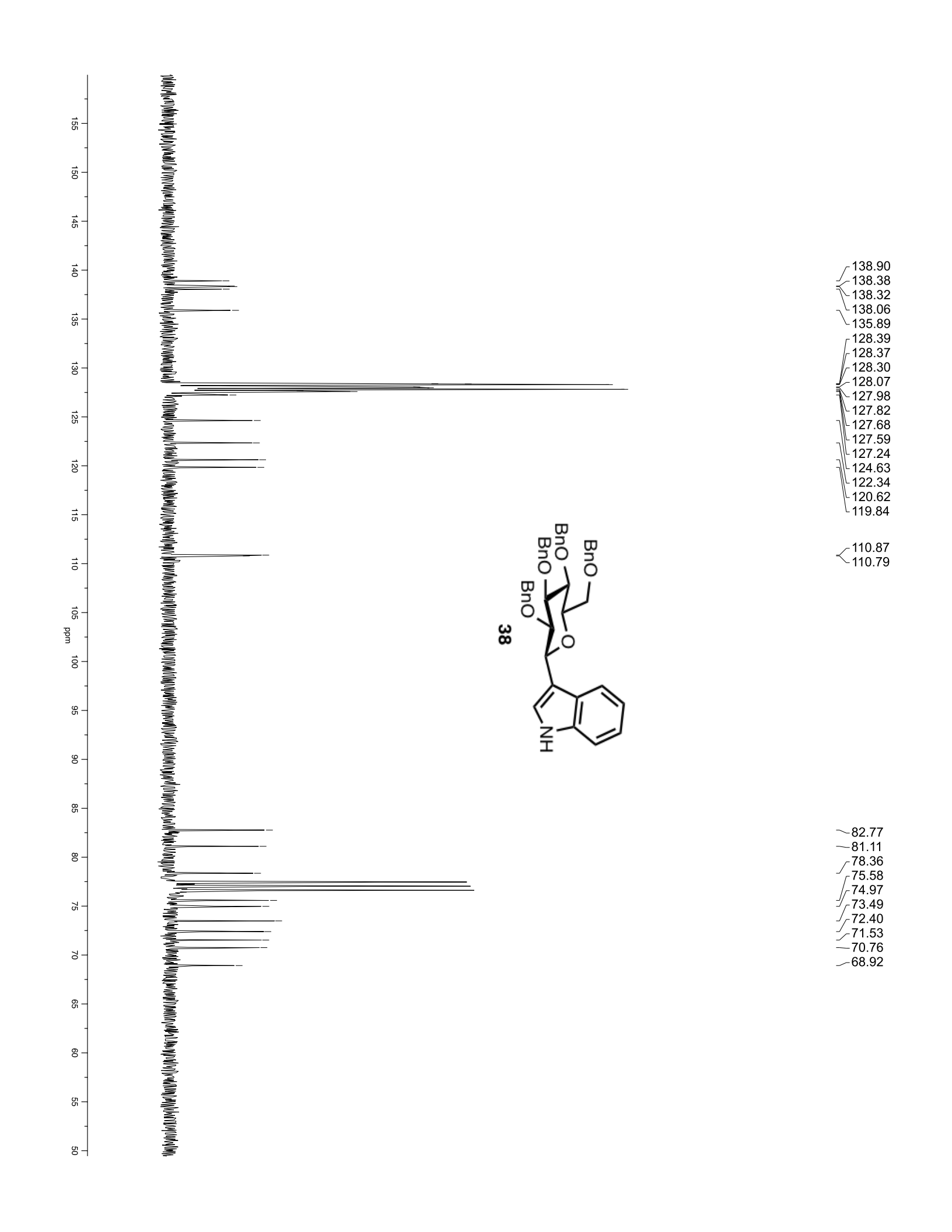
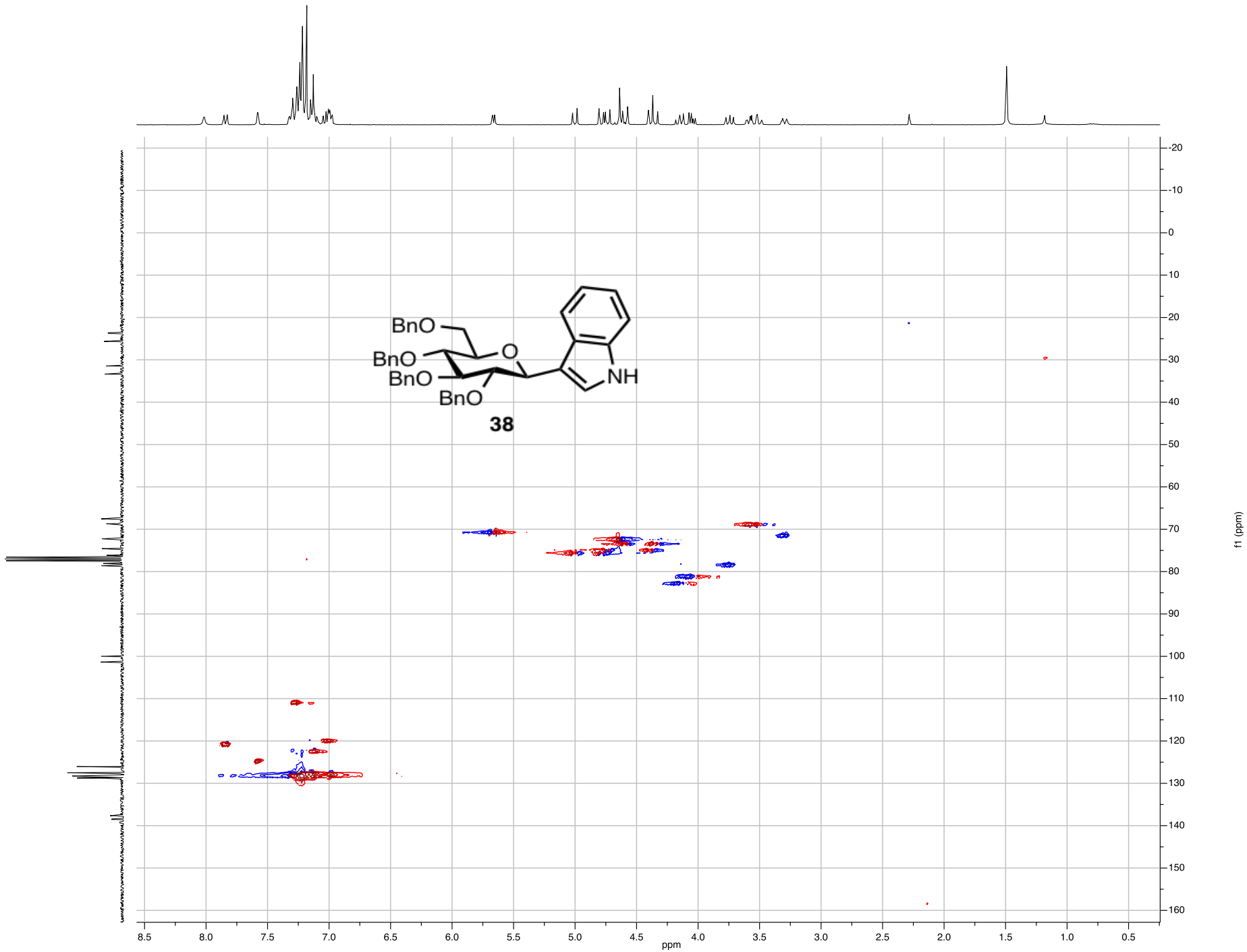
3.48
3.32
3.31
3.29
3.28
3.27

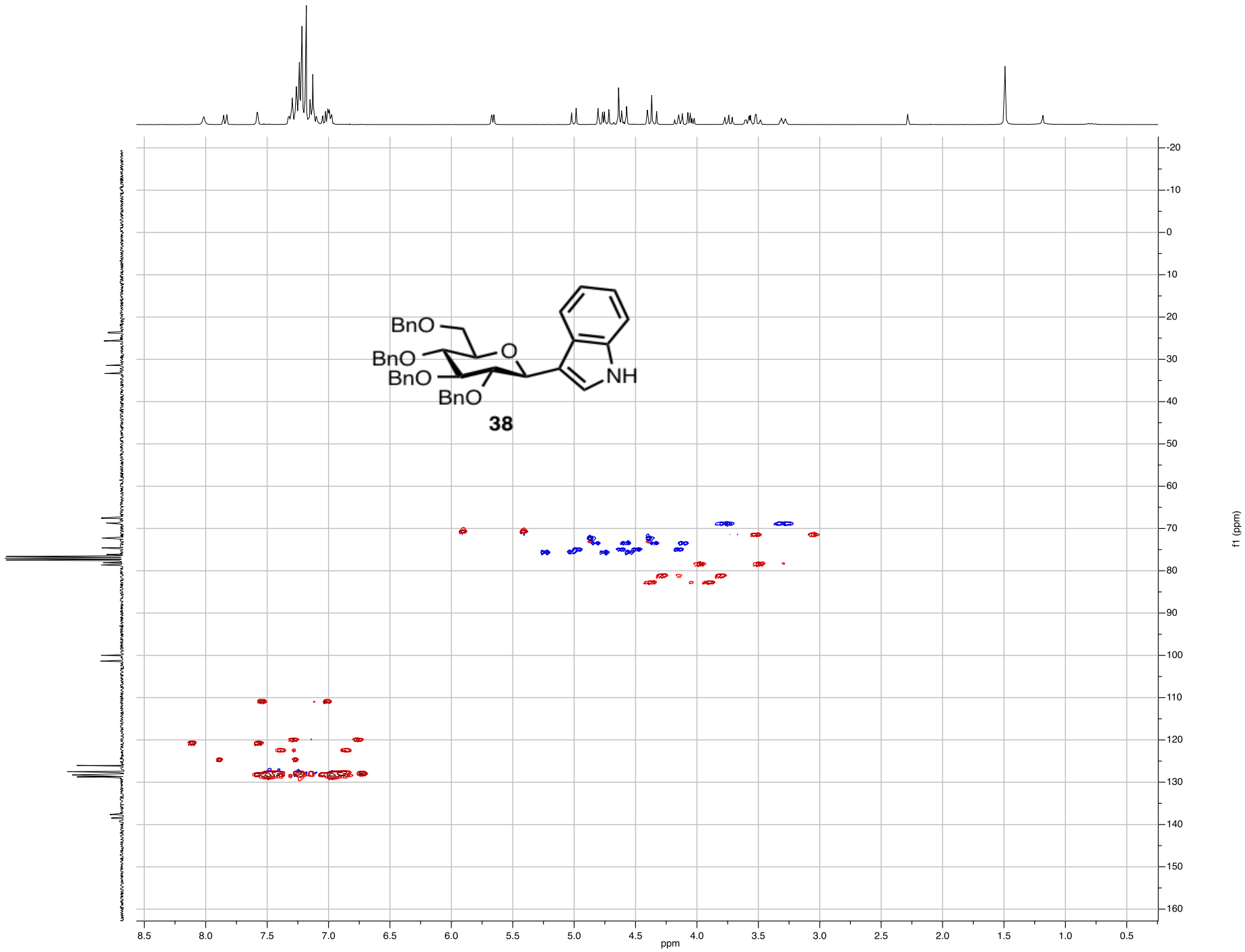

BnO
BnO
BnO
BnO
O
NH

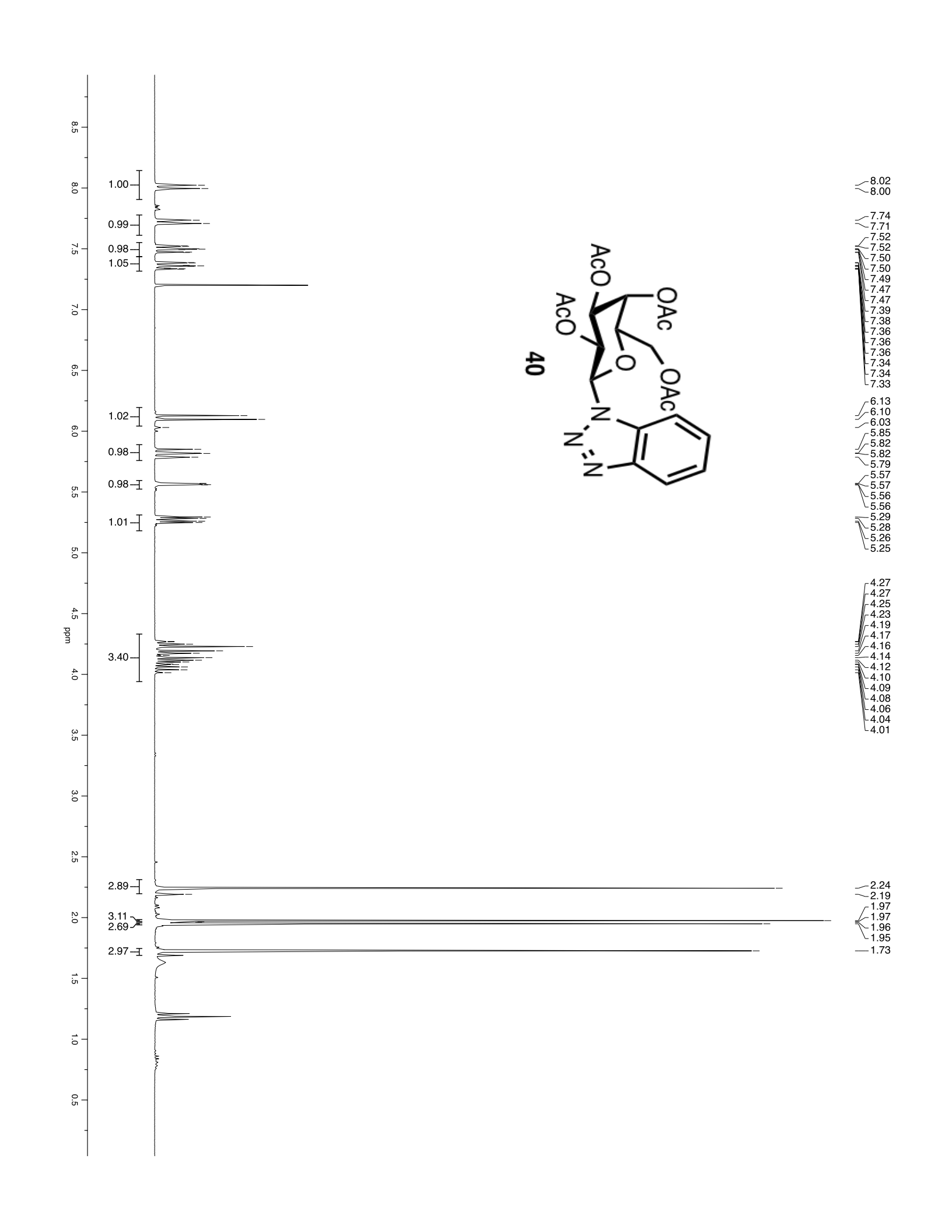
38


1.00
0.99
1.07
21.97
3.20
1.02
1.01
2.07
2.91
2.01
1.02
0.98
1.04
2.03
1.02
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
ppm


138.90
138.38
138.32
138.06
135.89
128.39
128.37
128.30
128.07
127.98
127.82
127.68
127.59
127.24
124.63
122.34
120.62
119.84
110.87
110.79
82.77
81.11
78.36
75.58
74.97
73.49
72.40
71.53
70.76
68.92
BnO
BnO
BnO
BnO
O
NH
38
ppm


BnO
BnO
BnO
BnO
O
NH
38
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
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


BnO
BnO
BnO
BnO
O
NH
38
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
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)


40
AcO
AcO
OAc
OAc
O
N
N
N
1.00
0.99
0.98
1.05
1.02
0.98
0.98
1.01
3.40
2.89
3.11
2.69
2.97
8.02
8.00
7.74
7.71
7.52
7.52
7.50
7.50
7.49
7.47
7.47
7.39
7.38
7.36
7.36
7.36
7.34
7.34
7.33
6.13
6.10
6.03
5.85
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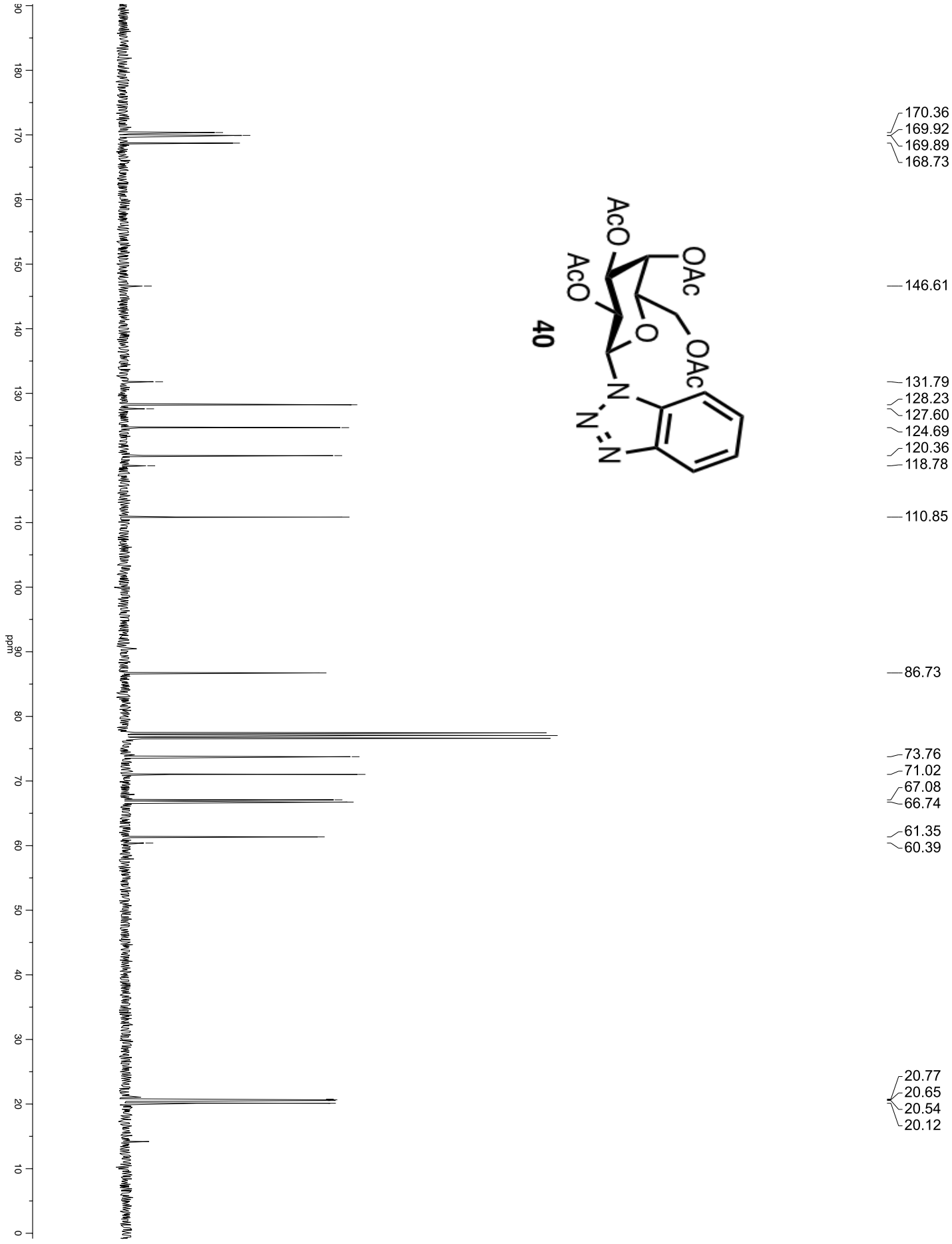
5.82
5.79
5.57
5.57
5.56
5.56
5.29
5.28
5.26
5.25
4.27
4.27
4.25
4.23
4.19
4.17
4.16
4.14
4.12
4.10
4.09
4.08
4.06
4.04
4.01
2.24
2.19
1.97
1.97
1.96
1.95
1.73
ppm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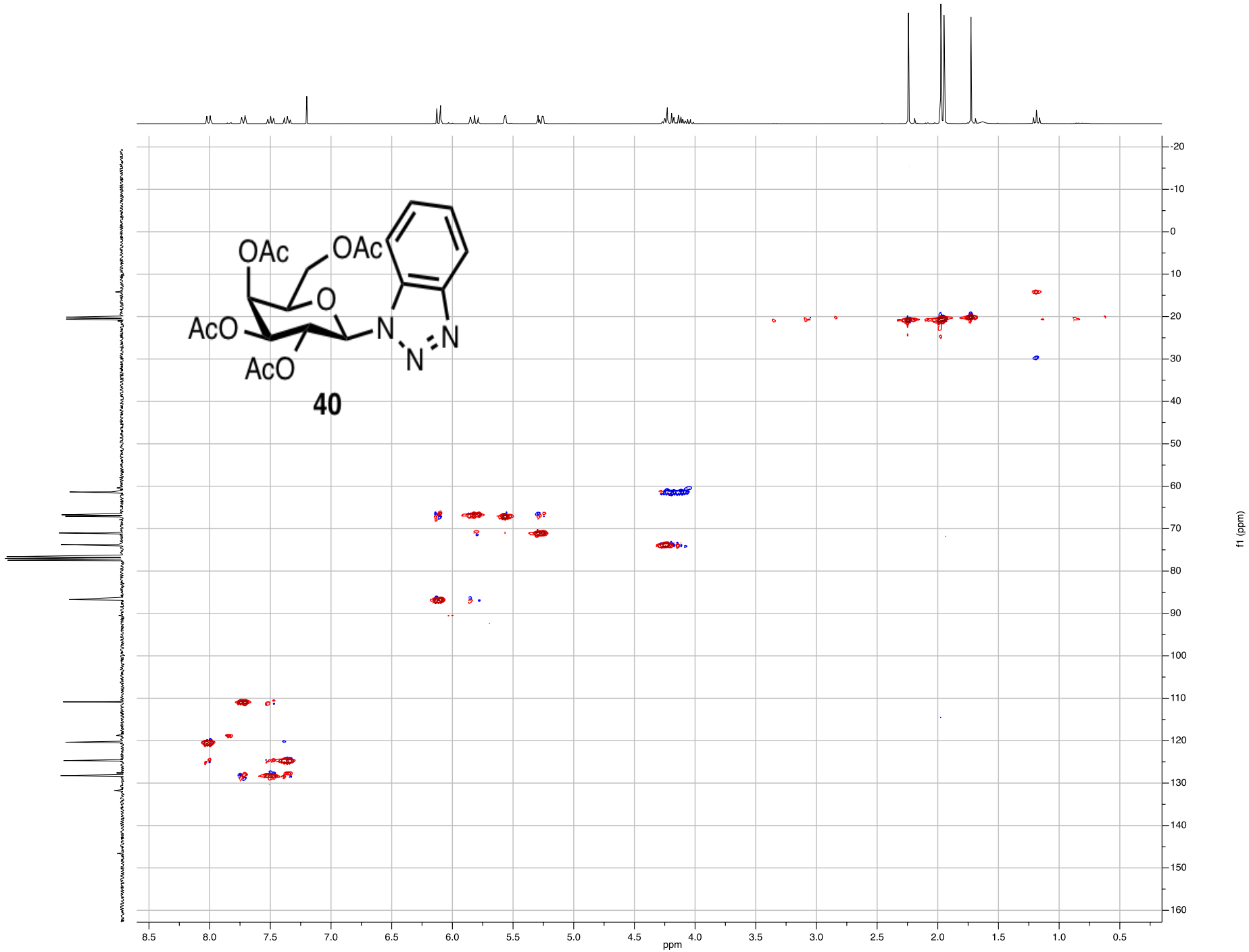
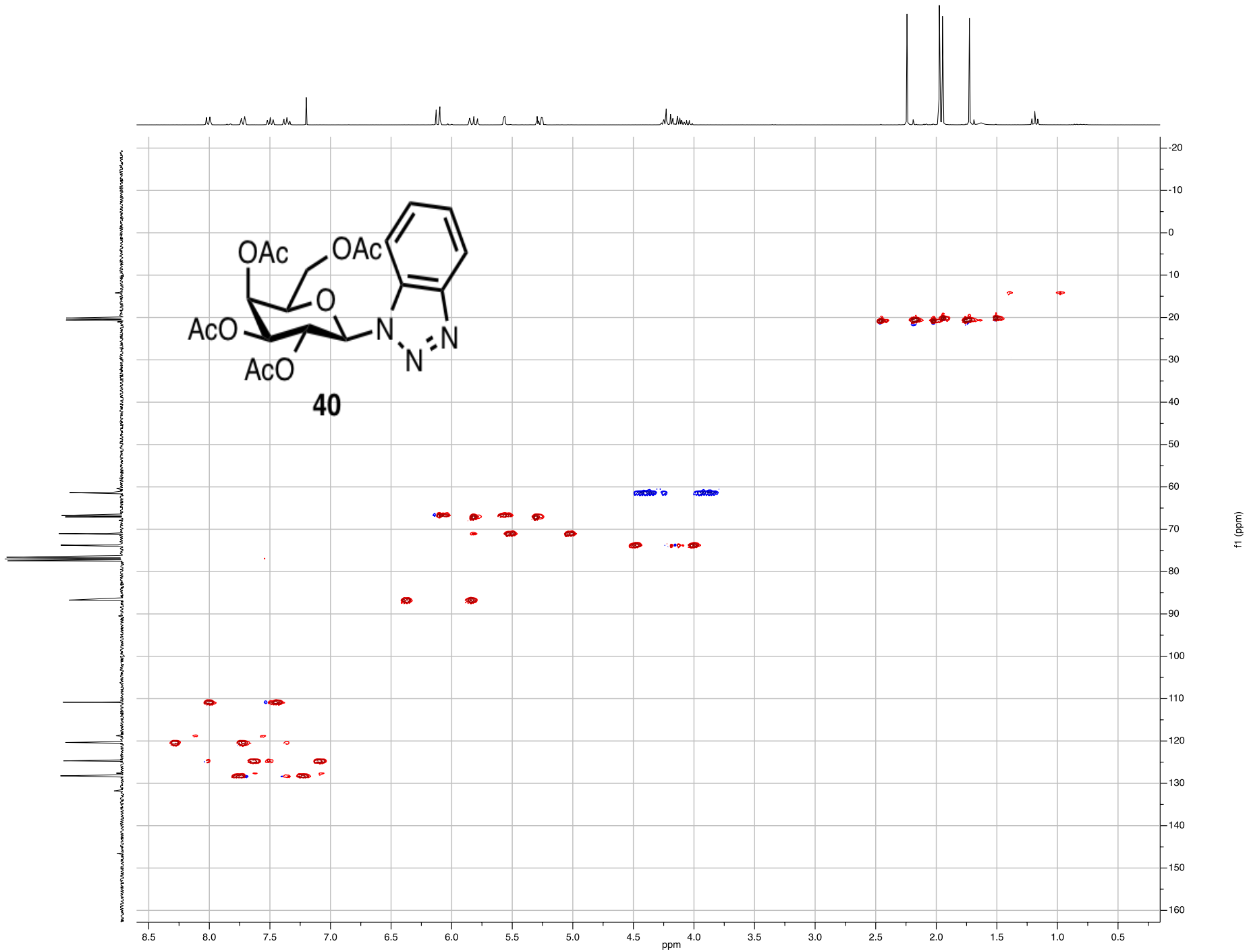
169.92
169.89
168.73
146.61
131.79
128.23
127.60
124.69
120.36
118.78
110.85
86.73
73.76
71.02
67.08
66.74
61.35
60.39
20.77
20.65
20.54
20.12
AcO
AcO
OAc
OAc
O
N
N
N
40
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
90


OAc
OAc
O
AcO
AcO
N
N
N
40
ppm
f1 (ppm)


OAc
OAc
O
AcO
AcO
N
N
N
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
0.5
ppm
-20
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
f1 (ppm)