Supporting Information

Intramolecular 1,8- versus 1,6-Hydrogen Atom Transfer between Pyranose Units in a (1→4)-Disaccharide Model Promoted by Alkoxyl Radicals. Conformational and Stereochemical Requirements

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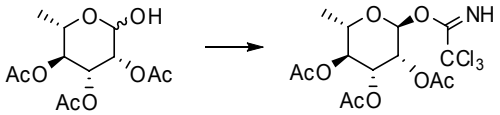
General Methods. Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were recorded in film unless otherwise stated. NMR spectra were determined at 500 MHz for ^1H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063 – 0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagents for TLC analysis were conducted with 0.5% vanillin in H_2SO_4 – EtOH (4:1) and further heating until development of color.

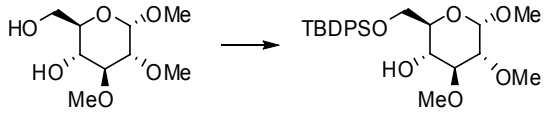


20S **21S**

2,3,4-Tri-*O*-acetyl-1-*O*-(2,2,2-trichloroethanimidoyl)-α-L-rhamnopyranose (21S).[1,2] To a solution of **20S**[3] (532 mg, 1.834 mmol) in dry CH_2Cl_2 (10.2 mL) were added trichloroacetonitrile (919 μL, 9.172 mmol) and NaH (17.5 mg, 2.384 mmol) under nitrogen and the mixture stirred at room temperature for 1 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 25:75) to give trichloroacetimidate **21S** (580 mg, 1.339 mmol, 73%) as a colorless oil: $[\alpha]_D$ –43.8 (*c*, 0.42); IR 3324, 2988, 1748, 1681, 1372, 1222, 1049 cm^{-1}; ^1H NMR δ_H 1.26 (3H, d, J = 6.2 Hz), 1.99 (3H, s), 2.06 (3H, s), 2.18 (3H, s), 4.08 (1H, dddd, J = 9.9, 6.2, 6.2, 6.2 Hz), 5.16 (1H, dd, J = 10.0, 10.0 Hz),

(1) Numbers ending in S refer to products only cited in the Supporting Information.
(2) Wang, J.; Li, J.; Tuttle, D.; Takemoto, J. Y.; Chang, C.-W. T. *Org. Lett*. **2002**, *4*, 3997–4000.
(3) Gurjar, M. K.; Mainkar, A. S. *Tetrahedron* **1992**, *48*, 6729–6738.

5.35 (1H, dd, J = 10.2, 3.5 Hz), 5.44 (1H, dd, J = 3.4, 2.0 Hz), 6.19 (1H, d, J = 1.9 Hz), 8.72 (1H, s); ^{13}C NMR δ_C 17.4 (CH_3), 20.6 (CH_3), 20.7 (2 × CH_3), 68.1 (CH), 68.8 (CH), 69.3 (CH), 70.3 (CH), 90.6 (C), 94.7 (CH), 159.9 (C), 169.7 (C), 169.8 (2 × C); MS m/z (rel intensity) 273 (M^+ – C_2HCl_3NO, 34), 230 (22), 157 (48), 111 (100); HRMS calcd for $C_{12}H_{17}O_7$ 273.0974, found 273.0974. Anal. Calcd for $C_{14}H_{18}Cl_3NO_8$: C, 38.69; H, 4.17; N, 3.22. Found: C, 38.56; H, 4.07; N, 3.55.

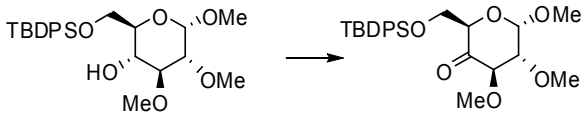


22S **23S**

Methyl 6-*O*-[*tert*-Butyl(diphenyl)silyl]-2,3-di-*O*-methyl-α-D-glucopyranoside (23S). To a solution of diol **22S**[4] (714 mg, 3.22 mmol) in dry DMF (12.5 mL) were added imidazole (657 mg, 9.66 mmol) and TBDPSCl (0.9 mL, 3.54 mmol) under nitrogen at 0 ^{o}C and the mixture stirred at room temperature for 2 h. The reaction mixture was concentrated under reduced pressure and the residue poured into ice-water and extracted with Et_2O. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 80:20) to give the alcohol **23S** (1.47 g, 3.19 mmol, 98%) as an oil: $[\alpha]_D$ +143 (c, 0.348); IR 3349, 2932, 1468, 1428, 1143, 1059 cm^{-1}; ^{1}H NMR δ_H 1.06 (9H, s), 2.68 (1H, br s) 3.39 (3H, s), 3.21 (1H, dd, J = 9.4, 3.6 Hz), 3.47 (1H, dd, J = 9.3, 9.3 Hz), 3.51 (3H, s), 3.56 (1H, dd, J = 9.3, 9.3 Hz), 3.64 (3H, s), 3.64 (1H, ddd, J = 9.2, 4.5, 4.5 Hz), 3.86 (1H, dd, J = 10.8, 4.6 Hz), 3.88 (1H, dd, J = 10.8, 4.4 Hz), 4.82 (1H, d, J = 3.5 Hz), 7.37 – 7.45 (6H, m), 7.68 – 7.72 (4H, m); ^{13}C NMR δ_C 19.2 (C), 26.7 (3 × CH_3), 55.0 (CH_3), 58.5 (CH_3), 61.2 (CH_3), 64.4 (CH_2), 70.6 (CH), 71.7 (CH), 81.7 (CH), 82.8 (CH), 97.3 (CH), 127.7 (4 × CH), 129.7 (2 × CH), 133.1 (2 × C), 135.6 (4 × CH); MS m/z (rel

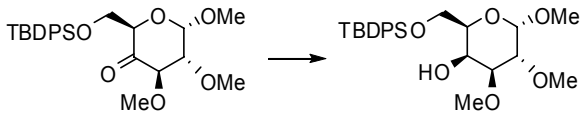
(4) Weiler, L.; Nicoll-Griffith, D. *Tetrahedron* **1991**, *47*, 2733–2750. Trimnell, D.; Doane, W. M.; Russell, C. R.; Rist, C. E. *Carbohydr. Res.* **1969**, *11*, 497–507.

intensity) 371 ($M^+ - C_5H_{13}O$, 5), 339 (6), 293 (2), 241 (18), 199 (100); HRMS calcd for $C_{20}H_{23}O_5Si$ 371.1314, found 371.1318. Anal. Calcd for $C_{25}H_{36}O_6Si$: C, 65.19; H, 7.88. Found: C, 65.18; H, 7.99.



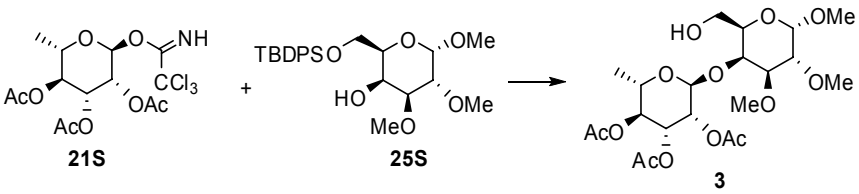
23S **24S**

Methyl 6-*O*-[*tert*-Butyl(diphenyl)silyl]-2,3-di-*O*-methyl-α-D-*xylo*-hexopyranosid-4-ulose (24S). To a solution of alcohol **23S** (1 g, 2.17 mmol) in dry Et_2O (24 mL) containing DMSO (1.1 mL, 15.2 mmol), pyridine (175 μL, 2.17 mmol), and DCC (2.23 g, 10.8 mmol) was added TFA (167 μL, 2.17 mmol) under nitrogen at 0 °C. The reaction mixture was stirred at room temperature for 2 h. Alter this time oxalic acid (390 mg, 4.34 mmol) was added at 0 °C and the stirring continued at room temperature for 0.5 h. The reaction mixture was filtered over Celite poured into brine and extracted with Et_2O. The organic extracts were dried over Na_2SO_4 anhydro and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 70:30) to give ketone **24S** (784 mg, 1.69 mmol, 79%) as a colorless oil: $[\alpha]_D$ +52.8 (*c*, 0.718); IR 3049, 2931, 2857, 1735, 1428, 1112, 1053 cm^{-1}; ^1H NMR δ_H 1.04 (9H, s), 3.52 (1H, dd, *J* = 9.9, 3.4 Hz), 3.54 (3H, s), 3.56 (3H, s), 3.58 (3H, s), 3.89 (1H, dd, *J* = 11.3, 6.5 Hz), 4.08 (1H, d, *J* = 9.9 Hz), 4.08 (1H, dd, *J* = 13.0, 3.1 Hz), 4.19 (1H, dd, *J* = 6.5, 3.2 Hz), 5.03 (1H, d, *J* = 3.4 Hz), 7.36 – 7.45 (6H, m), 7.68 – 7.69 (4H, m); ^{13}C NMR δ_C 19.2 (C), 26.7 (3 × CH_3), 55.8 (CH_3), 59.6 (CH_3), 60.2 (CH_3), 61.9 (CH_2), 74.1 (CH), 82.5 (CH), 84.4 (CH), 97.5 (CH), 127.6 (4 × CH), 129.7 (2 × CH), 133.2 (C), 133.3 (C), 135.6 (2 × CH), 135.6 (2 × CH), 202.1 (C); MS *m*/*z* (rel intensity) 427 ($M^+ - CH_3O$, <1), 369 (54), 255 (55), 199 (54), 101 (100); HRMS calcd for $C_{24}H_{31}O_5Si$ 427.1941, found 427.1941. Anal. Calcd for $C_{25}H_{34}O_6Si$: C, 65.47; H, 7.47. Found: C, 65.52; H, 7.45.



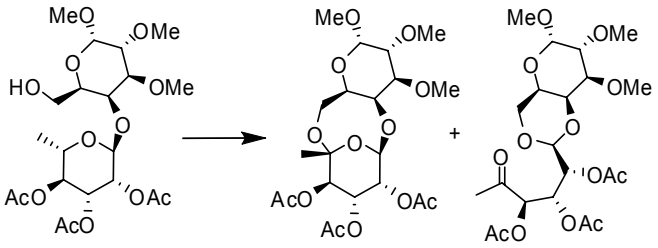
24S **25S**

Methyl 6-*O*-[*tert*-Butyl(diphenyl)silyl]-2,3-di-*O*-methyl-α-D-galactopyranoside (25S). To a solution of ketone **24S** (837 mg, 1.827 mmol) in EtOH/H_2O (6.8 mL, 9/1), was added $NaBH_4$ (125 mg, 3.289 mmol) and the mixture stirred at room temperature for 1 h. After this time the mixture was cooled to 0 ^oC, solid NH_4Cl was added and the stirring was continued for 1 h. The mixture was then filtered over Celite and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 85:15) to give the alcohol **25S** (575 mg, 1.25 mmol, 68%) and the alcohol **23S** (297 mg, 0.646 mmol, 35%) described previously. Compound **25S**: $[\alpha]_D$ +80.6 (*c*, 0.32); IR 3478, 3071, 2932, 1428, 1104, 1050 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.07 (9H, s), 2.54 (1H, br s) 3.38 (3H, s), 3.50 (3H, s), 3.51 (3H, s), 3.51 (1H, dd, J = 9.5, 3.2 Hz), 3.59 (1H, dd, J = 9.8, 3.7 Hz), 3.76 (1H, ddd, J = 5.8, 5.8, 0.8 Hz), 3.86 (1H dd, J = 10.3, 5.6 Hz), 3.94 (1H, dd, J = 10.6, 6.1 Hz), 4.17 (1H, dd, J = 3.2, 1.1 Hz), 4.87 (1H, d, J = 3.4 Hz), 7.36 – 7.45 (6H, m), 7.68 – 7.71 (4H, m); ^{13}C NMR δ_C 19.2 (C), 26.8 (3 × CH_3), 55.1 (CH_3), 57.7 (CH_3), 58.9 (CH_3), 63.4 (CH_2), 66.6 (CH), 69.7 (CH), 77.5 (CH), 79.3 (CH), 97.7 (CH), 127.7 (6 × CH), 129.7 (2 × CH), 133.2 (C), 133.3 (C), 135.6 (2 × CH); MS *m*/*z* (rel intensity) 371 (M^+ – $C_5H_{13}O$, 4), 339 (14), 311 (12), 255 (13), 237 (100); HRMS calcd for $C_{20}H_{23}O_5Si$ 371.1315, found 371.1318. Anal. Calcd for $C_{25}H_{36}O_6Si$: C, 65.19; H, 7.88. Found: C, 65.12; H, 7.86.



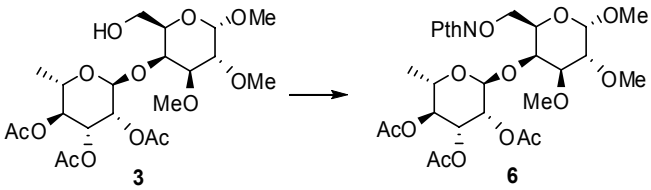
Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (3). To a solution of trichloroacetimidate **21S** (450 mg, 1.083 mmol) and alcohol **25S** (217 mg, 0.472 mmol) in dry CH_2Cl_2 (9 mL) containing molecular sieves 3Å (217 mg) was added a solution of TMSOTf (4.3 μL, 0.024 mmol) in dry CH_2Cl_2 (215 μL) under nitrogen at 0 ^oC and the mixture stirred at this temperature for 1.5 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 anhydrous and concentrated under reduced pressure. To the residue in dry THF (12.2 mL) was added a 1M solution of Bu_4NF/THF (1.2 mL, 1.18 mmol) under nitrogen and the mixture stirred at room temperature for 19 h. After this time the solvent was evaporated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 30:70) to give the disaccharide **3** (209 mg, 0.423 mmol, 90%.) as a crystalline solid: mp 154.5–156.2 ^oC (from *n*-hexane–acetone); $[\alpha]_D$ +27.0 (*c*, 0.315); IR 3486, 2937, 2840, 1748, 1372, 1224, 1046 cm^{-1}; ^1H NMR δ_H 1.23 (3H, d, *J* = 6.3 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.14 (3H, s), 3.42 (3H, s), 3.47 (3H, s), 3.53 (3H, s), 3.56 (1H, dd, *J* = 10.1, 2.9 Hz), 3.64 (1H, dd, *J* = 10.1, 3.5 Hz), 3.66 (1H, m), 3.80 – 3.86 (2H, m), 3.98 (1H, dddd, *J* = 9.7, 6.2, 6.2, 6.2 Hz), 4.11 (1H, dd, *J* = 2.6, 0 Hz), 4.87 (1H, d, *J* = 3.5 Hz), 5.05 (1H, d, *J* = 1.9 Hz), 5.07 (1H, dd, *J* = 9.9, 9.9 Hz), 5.31 (1H, dd, *J* = 10.0, 3.3 Hz), 5.47 (1H, dd, *J* = 3.3, 2.0 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.5 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 58.7 (CH_3), 59.2 (CH_3), 62.0 (CH_2), 67.5 (CH), 69.0 (CH), 69.8 (CH), 69.9 (CH), 70.9 (CH), 75.1 (CH), 78.0 (CH), 79.8 (CH), 98.1 (CH), 99.7 (CH), 169.8 (C), 169.9 (C), 170.0 (C); MS (FAB) *m/z* 517

(M^+ + Na, 4), 495 (3), 273 (100); HRMS calcd for $C_{21}H_{34}O_{13}Na$ 517.1897, found 517.1905. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.19; H, 6.95.



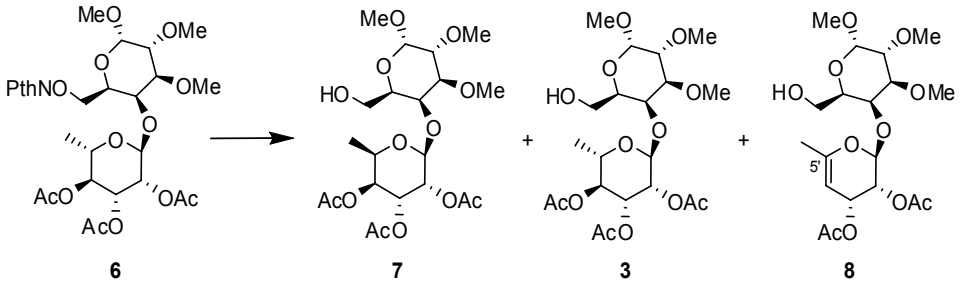
Oxidative HAT of 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (3). A solution of alcohol **3** (29 mg, 0.059 mmol) in dry CH_2Cl_2 (2.3 mL) containing DIB (32 mg, 0.1 mmol) and iodine (15 mg, 0.059 mmol) under nitrogen in the dark was heated at reflux temperature for 1.5 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the residue (hexanes–EtOAc, 25:75) gave methyl 5',6-anhydro-(2',3',4'-tri-*O*-acetyl-6'-deoxy-α-L-*lyxo*-hexos-5'-ulopyranosyl)-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**4**) (25.5 mg, 0.052 mmol, 88%), and methyl (1*S*)-4,6-*O*-(2',3',4'-tri-*O*-acetyl-6'-deoxy-α-L-*lyxo*-hexos-5'-ulosylidene)-2,3-di-*O*-methyl-α-D-galactopyranoside (**5**) (3 mg, 0.006 mmol, 10%). Compound **4**: crystalline solid, mp 216.5–217.4 °C (from *n*-hexane–acetone); $[\alpha]_D$ +98.1 (*c*, 0.27); IR 2933, 2838, 1755, 1372, 1224, 1049 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.37 (3H, s), 1.95 (3H, s), 2.08 (3H, s), 2.15 (3H, s), 3.39 (3H, s), 3.43 (3H, s), 3.48 (1H, dd, *J* = 10.1, 3.2 Hz), 3.52 (3H, s), 3.54 (1H, m), 3.67 (1H, dd, *J* = 10.1, 3.7 Hz), 3.91 (1H, dd, *J* = 13.2, 2.1 Hz), 4.08 (1H, dd, *J* = 13.2, 1.6 Hz), 4.17 (1H, br d, *J* = 3.2 Hz), 4.85 (1H, d, *J* = 1.6 Hz), 4.95 (1H, d, *J* = 3.7 Hz), 5.36 (1H, d, *J* = 10.6 Hz), 5.58 (1H, dd, *J* = 3.2, 1.6 Hz), 5.63 (1H, dd, *J* = 10.6, 3.2 Hz); ^{13}C NMR (100.6 MHz) δ_C

20.6 (2 × CH_3), 20.8 (CH_3), 21.9 (CH_3), 55.4 (CH_3), 58.1 (CH_3), 59.1 (CH_3), 63.6 (CH_2), 66.3 (CH), 66.7 (CH), 69.6 (CH), 70.7 (CH), 73.8 (CH), 77.1 (CH), 78.4 (CH), 98.0 (CH), 98.1 (CH), 100.4 (C), 169.6 (C), 169.8 (C), 170.5 (C); MS (FAB) *m/z* (rel intensity) 515 (M^+ + Na, 8, 493 (8), 491 (7), 461 (40), 154 (100); HRMS calcd for $C_{21}H_{32}O_{13}Na$ 515.1741, found 515.1755. Anal. Calcd for $C_{21}H_{32}O_{13}$: C, 51.22; H, 6.55. Found: C, 51.44; H, 6.33. Compound **5**: $[\alpha]_D$ +54.2 (*c*, 0.31); IR 2923, 2836, 1748, 1372, 1218, 1049 cm^{-1}; ^1H NMR δ_H 2.04 (3H, s), 2.07 (3H, s), 2.17 (3H, s), 2.22 (3H, s), 3.41 (3H, s), 3.43 (3H, s), 3.52 (3H, s), 3.54 (1H, m), 3.59 (1H, dd, *J* = 10.0, 3.1 Hz), 3.62 (1H, dd, *J* = 10.0, 3.1 Hz), 3.81 (1H, dd, *J* = 12.5, 1.7 Hz), 4.10 (1H, dd, *J* = 3.1, 1.1 Hz), 4.12 (1H, dd, *J* = 12.5, 1.5 Hz), 4.73 (1H, d, *J* = 4.2 Hz), 4.91 (1H, d, *J* = 3.1 Hz), 5.26 (1H, dd, *J* = 7.5, 4.2 Hz), 5.43 (1H, d, *J* = 1.9 Hz), 5.90 (1H, dd, *J* = 7.5, 1.9 Hz). ^{13}C NMR δ_C 20.5 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 26.5 (CH_3), 55.6 (CH_3), 57.0 (CH_3), 59.0 (CH_3), 62.3 (CH), 68.0 (CH), 69.0 (CH_2), 69.8 (CH), 73.0 (CH), 76.3 (CH), 76.7 (CH), 77.0 (CH), 98.4 (CH), 99.0 (CH), 169.3 (C), 169.7 (C), 170.1 (C), 201.7 (C). MS *m/z* (rel intensity) 492 (M^+, 1), 449 (>1), 363 (7), 233 (12), 75 (100); HRMS calcd for $C_{21}H_{32}O_{13}$ 492.1843, found 492.1859. Anal. Calcd for $C_{21}H_{32}O_{13}$: C, 51.22; H, 6.55. Found: C, 51.14; H, 6.78.



Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-galactopyranoside (6). DEAD (278 μL, 1.77 mmol) was added dropwise to a stirred solution of the alcohol **3** (350 mg, 0.708 mmol), *N*-hydroxyphthalimide (388 mg, 1.77 mmol) and PPh_3 (464 mg, 1.77 mmol) in dry THF

(7.7 mL) under nitrogen at 0 °C and the resulting solution was stirred at this temperature for 1.5 h. The reaction was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes–EtOAc, 80:20) to give *N*-phthalimide **6** (380 mg, 0.595 mmol, 84%) as an amorphous solid: $[\alpha]_D$ +17.5 (*c*, 0.245); IR 2939, 2835, 1791, 1735, 1372, 1225, 1044 cm^{-1}; ^1H NMR δ_H 1.15 (3H, d, *J* = 6.3 Hz), 1.97 (3H, s), 2.04 (3H, s), 2.12 (3H, s), 3.44 (3H, s), 3.48 (3H, s), 3.52 (3H, s), 3.59 (1H, dd, *J* = 10.1, 2.7 Hz), 3.66 (1H, dd, *J* = 10.1, 3.5 Hz), 3.95 (1H, dddd, *J* = 9.9, 6.3, 6.3, 6.3 Hz), 4.13 (1H, ddd, *J* = 6.1, 6.1, 0 Hz), 4.33 (1H, dd, *J* = 11.1, 5.9 Hz), 4.36 (1H, dd, *J* = 11.1, 6.2 Hz), 4.40 (1H, dd, *J* = 1.1, 0 Hz), 4.87 (1H, d, *J* = 3.5 Hz), 5.05 (1H, dd, *J* = 9.9, 9.9 Hz), 5.07 (1H, d, *J* = 1.5 Hz), 5.29 (1H, dd, *J* = 10.1, 3.3 Hz), 5.50 (1H, dd, *J* = 3.0, 2.1 Hz), 7.76 (2H, m), 7.84 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 17.3 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.8 (CH_3), 58.6 (CH_3), 59.3 (CH_3), 67.3 (CH), 67.6 (CH), 69.1 (CH), 69.9 (CH), 70.8 (CH), 75.0 (CH), 77.4 (CH_2), 77.6 (CH), 79.6 (CH), 98.4 (CH), 99.3 (CH), 123.6 (2 × CH), 128.8 (2 × C), 134.6 (2 × CH), 163.5 (2 × C), 169.8 (C), 169.9 (C), 170.0 (C); MS (FAB) *m/z* (rel intensity) 663 (M^+ + H + Na, 3), 662 (9), 273 (28), 55 (100); HRMS calcd for $C_{29}H_{38}NNaO_{15}$ 663.2139, found 663.2166. Anal. Calcd for $C_{29}H_{37}NO_{15}$: C, 54.46; H, 5.83; N, 2.19. Found: C, 54.10; H, 5.78; N, 2.38.



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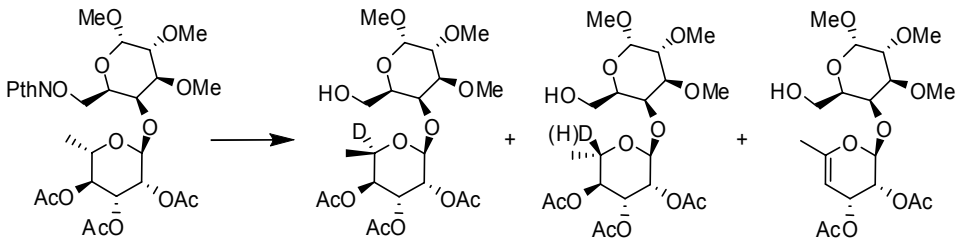
Reductive HAT of Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-galactopyranoside (6). Method A: Using *n*-Bu_3SnH and AIBN. A solution of phthalimide **6** (95 mg, 0.149 mmol) in dry benzene (11.2 mL) containing *n*-Bu_3SnH (40 μL, 0.149 mmol) and AIBN (2.4 mg, 0.015 mmol) was heated at reflux temperature for 1.5 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 50:50 → 30:70) to give methyl 2,3-di-*O*-acetyl-4,6-dideoxy-β-D-*erythro*-hex-4-enopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**8**) (3.5 mg, 0.008 mmol, 5%), the alcohol **3** (16.5 mg, 0.033 mmol, 22%), previously described, and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**7**) (38.2 mg, 0.077 mmol, 52%) as colorless oils. Compound **8**: $[\alpha]_D$ −33.8 (*c*, 0.29); IR 3468, 2935, 2834, 1747, 1682, 1372, 1247, 1049 cm^{-1}; ^1H NMR (400 MHz) δ_H 1.83 (3H, s), 2.05 (3H, s), 2.10 (3H, s), 2.21 (1H, dd, *J* = 9.8, 7.5 Hz), 3.41 (3H, s), 3.50 (3H, s), 3.51 (3H, s), 3.57 – 3.58 (2H, m), 3.60 – 3.75 (2H, m), 3.82 (1H, ddd, *J* = 6.6, 6.6, 1.3 Hz), 4.24 (1H, dd, *J* = 1.1, 1.1 Hz), 4.66 (1H, br d, *J* = 3.7 Hz), 4.85 (1H, d, *J* = 1.6 Hz), 5.25 (1H, dd, *J* = 5.0, 5.0 Hz), 5.30 (1H, d, *J* = 5.3 Hz), 5.51 (1H, ddd, *J* = 5.3, 3.7, 1.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 19.5 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3),

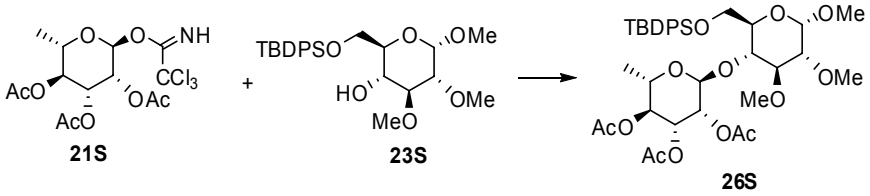
58.7 (CH_3), 59.1 (CH_3), 61.4 (CH_2), 64.1 (CH), 66.0 (CH), 69.6 (CH), 73.4 (CH), 78.0 (CH), 79.6 (CH), 95.1 (CH), 97.9 (CH), 98.4 (CH), 151.1 (C), 169.9 (C), 170.2 (C); MS *m*/*z* (rel intensity) 435 (M^+ + H, <1), 402 (<1), 374 (1), 212 (11), 88 (100); HRMS calcd for $C_{19}H_{31}O_{11}$ 435.1866, found 435.1877. Anal. Calcd for $C_{19}H_{30}O_{11}$: C, 52.53; H, 6.96. Found: C, 52.23; H, 6.90. Compound **7**: crystalline solid, mp 153.2–154.9 °C (from *n*-hexane–acetone); $[\alpha]_D$ +60.0 (*c*, 0.53); IR 3506, 2940, 2840, 1748, 1372, 1222, 1045 cm^{-1}; ^1H NMR δ_H 1.19 (3H, d, *J* = 6.4 Hz), 2.03 (3H, s), 2.13 (3H, s), 2.17 (3H, s), 3.23 (1H, m, 3.39 (3H, s), 3.47 (1H, dd, *J* = 10.1, 3.5 Hz), 3.48 (3H, s), 3.49 (3H, s), 3.57 (1H, dd, *J* = 10.1, 3.0 Hz), 3.63 (1H, m), 3.77 – 3.83 (2H, m), 4.15 (1H, dddd, *J* = 6.5, 6.5, 6.5, 1.3 Hz), 4.19 (1H, br d, *J* = 3.1 Hz), 4.81 (1H, d, *J* = 3.5 Hz), 4.83 (1H, dd, *J* = 3.7, 1.4 Hz), 4.94 (1H, d, *J* = 8.3 Hz), 5.04 (1H, dd, *J* = 8.3, 3.5 Hz), 5.34 (1H, dd, *J* = 3.6, 3.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 15.715 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.4 (CH_3), 58.4 (CH_3), 59.1 (CH_3), 60.2 (CH_2), 67.9 (CH), 68.4 (CH), 68.8 (CH), 69.0 (CH), 70.100 (CH), 73.3 (CH), 78.0 (CH), 79.2 (CH), 97.9 (CH), 99.8 (CH), 168.9 (C), 169.5 (C), 169.8 (C); MS (FAB) *m/z* (rel intensity) 518 (M^+ + H + Na, 6), 517 (21), 391 (32), 273 (63), 73 (100); HRMS calcd for $C_{21}H_{35}NaO_{13}$ 518.1975, found 518.1984. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.15; H, 6.89.



Method B: Using *n*-Bu_3SnD and AIBN. A solution of phthalimide **6** (90 mg, 0.141 mmol) in dry benzene (10.6 mL) containing *n*-Bu_3SnD (38 μL, 0.141 mmol) and AIBN (2.3 mg, 0.014 mmol) was heated at reflux temperature for 1 h. After this time another

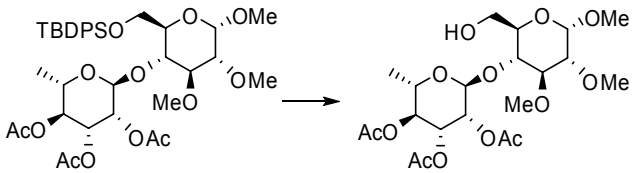
portion of *n*-Bu_3SnD (38 μL, 0.141 mmol) and AIBN (2.3 mg, 0.014 mmol) were added and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 50:50 → 30:70) to give the olefin **8** (9 mg, 0.021 mmol, 15%), previously described, methyl 2,3,4-tri-*O*-acetyl-α-L-[5-$^2H_1$]rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**10**) (12.6 mg, 0.025 mmol, 18%, $^1H/^2H$ ratio, 7:3), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-D-(5-$^2H_1$)gulopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-galactopyranoside (**9**) (31.2 mg, 0.063 mmol, 45%) as colorless oils. Compound **10**: ^1H NMR δ_H 1.22 (3H, s), 1.23 (3H, d, *J* = 6.6 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.14 (3H, s), 3.42 (3H, s), 3.47 (3H, s), 3.54 (3H, s), 3.56 (1H, dd, *J* = 10.1, 2.9 Hz), 3.64 (1H, dd, *J* = 10.1, 3.5 Hz), 3.66 (1H, m), 3.80 – 3.86 (2H, m), 3.98 (1H, dddd, *J* = 10.0, 6.3, 6.3, 6.3 Hz), 4.12 (1H, dd, *J* = 2.7, 0 Hz), 4.88 (1H, d, *J* = 3.5 Hz), 5.05 (1H, d, *J* = 2.1 Hz), 5.071 (1H, dd, *J* = 10.0 Hz), 5.073 (1H, dd, *J* = 9.8, 9.8 Hz), 5.31 (1H, dd, *J* = 10.0, 3.3 Hz), 5.47 (1H, dd, *J* = 3.3, 2.1 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.350 (CH_3), 17.489 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.4 (CH_3), 58.8 (CH_3), 59.3 (CH_3), 62.0 (CH_2), 67.5 (CH), 69.0 (CH), 69.8 (CH), 69.9 (CH), 70.869 (CH), 70.932 (CH), 75.1 (CH), 78.0 (CH), 79.8 (CH), 98.1 (CH), 99.7 (CH), 169.8 (C), 170.0 (C), 170.0 (C); MS (FAB) *m/z* (rel intensity) 519 (M^+ + Na + H, 7), 518 (26), 517 (5), 274 (46), 273 (27), 73 (100); HRMS calcd for $C_{21}H_{34}{}^2H_1NaO_{13}$ 519.2038, found 519.2042. Compound **9**: ^1H NMR δ_H 1.18 (3H, s), 2.02 (3H, s), 2.12 (3H, s), 2.16 (3H, s), 3.24 (1H, m, 3.38 (3H, s), 3.46 (1H, dd, *J* = 10.1, 3.5 Hz), 3.47 (3H, s), 3.48 (3H, s), 3.56 (1H, dd, *J* = 10.1, 3.0 Hz), 3.63 (1H, m), 3.76 – 3.82 (2H, m), 4.19 (1H, dd, *J* = 3.0, 0 Hz), 4.80 (1H, d, *J* = 3.5 Hz), 4.81 (1H, d,

J = 3.7 Hz), 4.94 (1H, d, J = 8.3 Hz), 5.03 (1H, dd, J = 8.3, 3.5 Hz), 5.33 (1H, dd, J = 3.6, 3.6 Hz); ^{13}C NMR (100.6 MHz) δ_C 15.576 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.7 (CH_3), 55.4 (CH_3), 58.4 (CH_3), 59.0 (CH_3), 60.2 (CH_2), 67.9 (CH), 68.4 (CH), 69.0 (CH), 70.036 (CH), 73.3 (CH), 78.0 (CH), 79.2 (CH), 97.9 (CH), 99.8 (CH), 168.8 (C), 169.5 (C), 169.8 (C); MS (FAB) *m/z* (rel intensity) 519 (M^+ + H + Na, 2), 518 (7), 355 (10), 274 (27), 73 (100); HRMS calcd for $C_{21}H_{34}{}^2H_1NaO_{13}$ 519.2038, found 519.2014.



Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-6-*O*-[*tert*-butyl(diphenyl)silyl]-2,3-di-*O*-methyl-α-D-glucopyranoside (26S). To a solution of trichloroacetimidate **21S** (425 mg, 0.981 mmol) and methyl 6-*O*-[*tert*-butyl(diphenyl)silyl]-2,3-di-*O*-methyl-α-D-glucopyranoside (**23S**) (205 mg, 0.446 mmol) in dry CH_2Cl_2 (8.5 mL) containing molecular sieves 3Å (205 mg) was added a solution of TMSOTf (0.89 μL, 0.0049 mmol) in dry CH_2Cl_2 (45 μL) under nitrogen at 0 ^oC and the mixture stirred at this temperature for 2 h. After this time another portion of TMSOTf (0.89 μL, 0.0049 mmol) in dry CH_2Cl_2 (45 μL) was added, and the stirring continued for an additional 1 h. The reaction mixture was poured into a saturated solution of $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 anhydrous and concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 85:15) to give the disaccharide **26S** (324 mg, 0.443 mmol, 99%) as a colorless oil: $[\alpha]_D$ +23.5 (*c*, 0.31); IR 2936, 2858, 1748, 1372, 1224, 1047 cm^{-1}; ^{1}H NMR (400 MHz) δ_H 1.03 (9H, s), 1.23 (3H, d, J = 6.1 Hz), 1.98 (3H, s), 2.05 (3H, s), 2.06 (3H, s), 3.24 (1H, dd, J = 9.5, 3.7 Hz), 3.32 (3H, s), 3.52

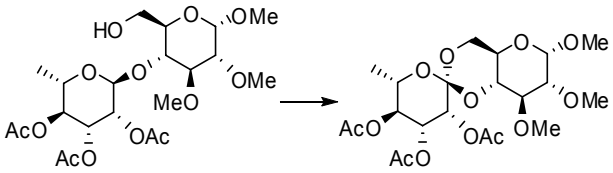
(1H, dd, J = 9.3, 9.3 Hz), 3.52 (3H, s), 3.57 (1H, m), 3.61 (3H, s), 3.82 (1H, dd, J = 11.9, 1.6 Hz), 3.86 (1H, dd, J = 9.5, 9.5 Hz), 3.88 (1H, dd, J = 11.9, 2.9 Hz), 4.20 (1H, dddd, J = 9.8, 6.1, 6.1, 6.1 Hz), 4.77 (1H, d, J = 3.7 Hz), 5.06 (1H, d, J = 1.6 Hz), 5.08 (1H, dd, J = 9.9, 9.9 Hz), 5.22 (1H, dd, J = 3.4, 1.9 Hz), 5.26 (1H, dd, J = 9.8, 3.4 Hz), 7.32 – 7.42 (6H, m), 7.62 – 7.65 (2H, m), 7.69 – 7.72 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 17.1 (CH_3), 19.3 (C), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 26.7 (3 × CH_3), 54.9 (CH_3), 58.5 (CH_3), 60.6 (CH_3), 62.7 (CH_2), 66.5 (CH), 69.3 (CH), 70.0 (CH), 70.9 (CH), 71.0 (CH), 74.9 (CH), 81.1 (CH), 82.6 (CH), 96.9 (CH), 97.6 (CH), 127.3 (2 × CH), 127.5 (2 × CH), 129.4 (CH), 129.5 (CH), 133.3 (C), 133.5 (C), 135.5 (2 × CH), 135.9 (2 × CH), 169.8 (C), 169.9 (C), 170.0 (C); MS m/z (rel intensity) 675 ($M^+ - C_4H_9$, 7), 555 (1), 273 (100), 153 (82); HRMS calcd for $C_{33}H_{43}O_{13}Si$ 675.2473, found 675.2469. Anal. Calcd for $C_{37}H_{52}O_{13}Si$: C, 60.64; H, 7.15. Found: C, 60.81; H, 7.01.



26S **11**

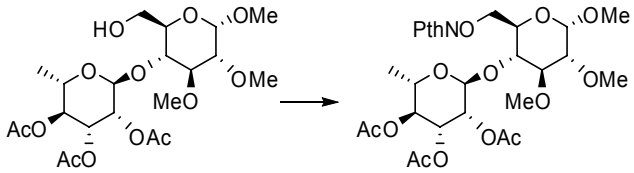
Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (11). To a solution of compound **26S** (470 mg, 0.642 mmol) in dry THF (16.4 mL) was added a solution 1M of Bu_4NF/THF (1.6 mL, 1.6 mmol), and the mixture stirred at room temperature for 19 h. The reaction mixture was concentrated under reduced pressure and the residue purified by column chromatography (hexanes–EtOAc, 50:50 → 25:75) to give the alcohol **11** (217 mg, 0.439 mmol, 68%) as an amorphous solid: $[\alpha]_D$ +44.7 (c, 0.235); IR 3502, 2917, 2848, 1748, 1372, 1225, 1046 cm^{-1}; ^{1}H NMR δ_H 1.21 (3H, d, J = 6.3 Hz), 1.88 (1H, br s) 1.99 (3H, s), 2.04 (3H, s), 2.13 (3H, s), 3.23 (1H, dd, J = 9.5, 3.7 Hz), 3.41 (3H, s), 3.50 (3H, s), 3.51 (1H, dd, J

= 9.0, 9.0 Hz), 3.59 (3H, s), 3.63 (1H, ddd, *J* = 9.8, 2.4, 2.4 Hz), 3.67 (1H, dd, *J* = 10.0, 8.7 Hz), 3.79 (1H, dd, *J* = 12.2, 2.6 Hz), 3.84 (1H, dd, *J* = 12.2, 1.9 Hz), 4.13 (1H, dddd, *J* = 9.8, 6.3, 6.3, 6.3 Hz), 4.82 (1H, d, *J* = 3.7 Hz), 4.96 (1H, d, *J* = 1.6 Hz), 5.08 (1H, dd, *J* = 10.0, 10.0 Hz), 5.16 (1H, dd, *J* = 3.4, 1.8 Hz), 5.24 (1H, dd, *J* = 10.0, 3.4 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.2 (CH_3), 58.7 (CH_3), 60.7 (CH_3), 61.0 (CH_2), 66.8 (CH), 69.2 (CH), 70.2 (CH), 70.5 (CH), 70.9 (CH), 75.4 (CH), 81.2 (CH), 82.6 (CH), 97.4 (CH), 98.0 (CH), 170.0 (C), 170.2 (C), 170.5 (C); MS *m*/*z* (rel intensity) 434 (M^+ – $C_2H_4O_2$, 3), 374 (1), 359 (1), 273 (50), 88 (100); HRMS calcd for $C_{19}H_{30}O_{11}$ 434.1788, found 434.1794. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.16; H, 6.84.



Oxidative HAT of Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (11). A solution of alcohol **11** (28 mg, 0.057 mmol) in dry CH_2Cl_2 (2.3 mL) containing DIB (46.6 mg, 0.145 mmol) and iodine (14.5 mg, 0.057 mmol) under nitrogen was irradiated with two 80 W tungsten–filament lamps at room temperature for 4 h. The reaction mixture was then poured into 10% aqueous $Na_2S_2O_3$ and extracted with CH_2Cl_2, dried over Na_2SO_4, and concentrated. Chromatotron chromatography of the reaction residue (hexanes–EtOAc, 60:40) gave methyl (1*R*)-4,6-*O*-(2,3,4-tri-*O*-acetyl-D-rhamnopyranosylidene)-2,3-di-*O*-methyl-α-D- glucopyranoside (**12**) (22.1 mg, 0.045 mmol, 79%) as a crystalline solid: mp 194.2–195.6 °C (from *n*-hexane–EtOAc); $[\alpha]_D$ +40.6 (*c*, 0.315); IR 2916, 2839, 1754, 1373, 1222, 1092, 1044 cm^{-1}; ^{1}H NMR δ_H 1.28 (3H, d, *J* = 6.3 Hz), 1.95 (3H, s), 2.04 (3H, s), 2.16 (3H, s), 3.23 (1H, dd,

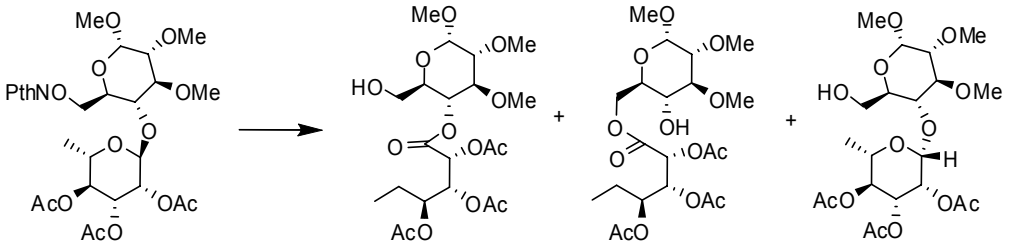
J = 8.9, 3.7 Hz), 3.40 (3H, s), 3.53 (3H, s), 3.55 (1H, dd, *J* = 9.3, 9.3 Hz), 3.58 (1H, dd, *J* = 9.3, 9.3 Hz), 3.64 (3H, s), 3.74 – 3.79 (2H, m), 3.88 (1H, dd, *J* = 9.9, 5.1 Hz), 3.98 (1H, dd, *J* = 10.4, 10.4 Hz), 4.80 (1H, d, *J* = 3.7 Hz), 5.09 (1H, dd, *J* = 9.9, 9.9 Hz), 5.27 (1H, dd, *J* = 10.1, 3.5 Hz), 5.37 (1H, d, *J* = 3.5 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.5 (CH_3), 20.6 (CH_3), 20.76 (CH_3), 20.79 (CH_3), 55.3 (CH_3), 59.6 (CH_3), 61.2 (CH_3), 61.6 (CH), 62.9 (CH_2), 68.4 (CH), 69.6 (CH), 70.0 (CH), 70.6 (CH), 73.5 (CH), 79.5 (CH), 81.4 (CH), 98.6 (CH), 108.1 (C), 169.7 (C), 169.89 (C), 169.94 (C); MS *m*/*z* (rel intensity) 492 (M^+, 1), 461 (3), 304 (44), 262 (27), 88 (100); HRMS calcd for $C_{21}H_{32}O_{13}$ 492.1843, found 492.1827. Anal. Calcd for $C_{21}H_{32}O_{13}$: C, 51.22; H, 6.55. Found: C, 51.23; H, 6.39.



11 **13**

Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (13). DEAD (131 μL, 0.835 mmol) was added dropwise to a stirred solution of the alcohol **11** (165 mg, 0.334 mmol), *N*-hydroxyphthalimide (136 mg, 0.835 mmol) and PPh_3 (219 mg, 0.835 mmol) in dry THF (3.6 mL) under nitrogen at 0 °C and the resulting solution was stirred at this temperature for 1 h. The reaction was quenched with water and extracted with $CHCl_3$. The combined extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography (hexanes–EtOAc, 70:30) to give *N*-phthalimide **13** (200 mg, 0.313 mmol, 94%) as a colorless oil: $[\alpha]_D$ +48.1 (*c*, 0.21); IR 2938, 1738, 1372, 1226, 1084, 1046 cm^{-1}; ^{1}H NMR δ_H 1.24 (3H, d, *J* = 6.3 Hz), 1.96 (3H, s), 2.05 (3H, s), 2.17 (3H, s), 3.34 (1H, dd, *J* = 9.6, 3.5 Hz), 3.44 (3H, s), 3.50 (3H,

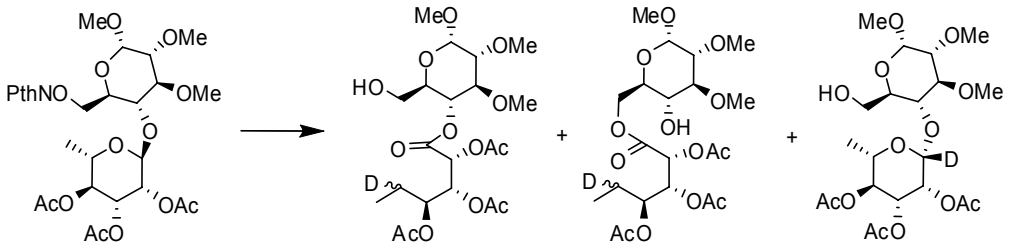
s), 3.54 (1H, dd, J = 9.4, 9.4 Hz), 3.60 (3H, s), 3.82 (1H, ddd, J = 10.1, 2.0, 2.0 Hz), 4.01 (1H, dd, J = 9.8, 9.8 Hz), 4.17 (1H, dddd, J = 10.0, 6.3, 6.3, 6.3 Hz), 4.34 (1H, dd, J = 10.3, 2.4 Hz), 4.46 (1H, dd, J = 10.3, 2.1 Hz), 4.87 (1H, d, J = 3.5 Hz), 5.12 (1H, dd, J = 9.7, 9.7 Hz), 5.24 (1H, d, J = 3.5 Hz), 5.25 (1H, dd, J = 9.1, 3.5 Hz), 5.40 (1H, s), 7.73 (2H, m), 7.77 (2H, m); ^{13}C NMR (100.6 MHz) δ_C 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 55.5 (CH_3), 58.6 (CH_3), 60.3 (CH_3), 66.7 (CH), 68.9 (CH), 69.3 (CH), 69.9 (CH), 71.0 (CH), 75.1 (CH), 75.3 (CH_2), 80.8 (CH), 81.9 (CH), 97.3 (CH), 98.1 (CH), 123.4 (2 × CH), 128.8 (2 × C), 134.4 (2 × CH), 163.0 (2 × C), 170.0 (C), 170.1 (C), 170.5 (C); MS (FAB) *m/z* (rel intensity) 662 (M^+ + Na, 4), 661 (16), 286 (16), 273 (100); HRMS calcd for $C_{29}H_{36}NO_{15}Na$ 661.1983, found 661.1957. Anal. Calcd for $C_{29}H_{37}NO_{15}$: C, 54.46; H, 5.83; N, 2.19. Found: C, 54.58; H, 5.52; N, 2.03.



Reductive HAT of Methyl 2,3,4-Tri-*O*-acetyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-6-*O*-phthalimido-α-D-glucopyranoside (13). Method A: Using *n*-Bu$_3$SnH and AIBN. A solution of phthalimide **13** (110 mg, 0.172 mmol) in dry benzene (12.9 mL) containing *n*-Bu$_3$SnH (46 μL, 0.172 mmol) and AIBN (3 mg, 0.017 mmol) was heated at reflux temperature for 1 h. After this time another portion of *n*-Bu$_3$SnH (46 μL, 0.172 mmol) and AIBN (3 mg, 0.017 mmol) were added, and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed

with *n*-hexane and the combined more polar extracts were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 60:40 → 50:50) to give methyl 6-*O*-(2,3,4-tri-*O*-acetyl-5,6-dideoxy-L-*lyxo*-hexonoyl)-2,3-di-*O*-methyl-α-D-glucopyranoside **15** (3.7 mg, 0.007 mmol, 4%), methyl 4-*O*-(2,3,4-tri-*O*-acetyl-5,6-dideoxy-L-*lyxo*-hexonoyl)-2,3-di-*O*-methyl-α-D-glucopyranoside **14** (41.2 mg, 0.083 mmol, 48%), starting alcohol **11** (6.5 mg, 0.013 mmol, 8%) and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-mannopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside **16** (7.8 mg, 0.016 mmol, 9%) as colorless oils. Compound **15**: $[\alpha]_D$ +40.7 (*c*, 0.29); IR 3488, 2938, 1748, 1373, 1220, 1063 cm^{-1}; ^1H NMR δ_H 0.91 (3H, t, *J* = 7.2 Hz), 1.58 – 1.64 (2H, m), 2.08 (3H, s), 2.11 (3H, s), 2.13 (3H, s), 3.00 (1H, br s) 3.21 (1H, dd, *J* = 9.2, 3.4 Hz), 3.43 (3H, s), 3.44 – 3.47 (2H, m), 3.51 (3H, s), 3.64 (3H, s), 3.75 (1H, ddd, *J* = 7.6, 3.8, 1.9 Hz), 4.20 (1H, dd, *J* = 11.8, 1.9 Hz), 4.54 (1H, dd, *J* = 11.8, 4.2 Hz), 4.82 (1H, d, *J* = 3.4 Hz), 5.14 (1H, d, *J* = 6.9 Hz), 5.23 (1H, ddd, *J* = 7.6, 6.1, 3.8 Hz), 5.40 (1H, dd, *J* = 7.2, 3.8 Hz); ^{13}C NMR (100.6 MHz) δ_C 9.5 (CH_3), 20.4 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 23.7 (CH_2), 55.3 (CH_3), 58.7 (CH_3), 61.3 (CH_3), 64.5 (CH_2), 69.0 (CH), 69.7 (CH), 69.8 (CH), 71.1 (CH), 72.0 (CH), 81.7 (CH), 82.5 (CH), 97.6 (CH), 167.6 (C), 169.6 (C), 170.1 (C), 170.5 (C); MS *m*/*z* (rel intensity) 463 (M^+ – C_2H_7, 1), 431 (2), 403 (1), 365 (16), 231 (34), 101 (22), 88 (100); HRMS calcd for $C_{19}H_{27}O_{13}$ 463.1452, found 463.1444. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.22; H, 6.83. Compound **14**: $[\alpha]_D$ +54.8 (*c*, 0.155); IR 3500, 2938, 1748, 1373, 1220, 1048 cm^{-1}; ^1H NMR δ_H 0.91 (3H, t, *J* = 7.4 Hz), 1.61 (2H, q, *J* = 7.4 Hz), 2.06 (3H, s), 2.11 (3H, s), 2.13 (3H, s), 3.32 (1H, dd, *J* = 9.6, 3.6 Hz), 3.43 (3H, s), 3.49 (3H, s), 3.51 (3H, s), 3.59 – 3.70 (3H, m), 3.63 (1H, dd, *J* = 9.6, 9.6 Hz), 4.87 (1H, d, *J* = 3.6 Hz), 4.91 (1H, dd, *J* = 9.6, 9.6 Hz), 5.15 (1H, d, *J* = 6.5 Hz), 5.20 (1H, ddd, *J* = 6.4, 6.4, 4.4 Hz), 5.42 (1H, dd, *J* = 6.5, 4.2 Hz); ^{13}C NMR (100.6 MHz) δ_C 9.435 (CH_3),

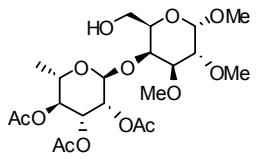
20.4 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 23.6 (CH_2), 55.4 (CH_3), 58.9 (CH_3), 60.1 (CH_3), 60.8 (CH_2), 69.4 (CH), 70.3 (CH), 71.0 (CH), 71.3 (CH), 72.034 (CH), 79.6 (CH), 81.5 (CH), 97.4 (CH), 167.4 (C), 169.6 (C), 170.1 (C), 170.2 (C); MS *m*/*z* (rel intensity) 463 ($M^+ - C_2H_7$, <1), 434 (1), 403 (1), 231 (23), 101 (11), 88 (100); HRMS calcd for $C_{19}H_{27}O_{13}$ 463.1452, found 463.1455. Anal. Calcd for $C_{21}H_{34}O_{13}$: C, 51.01; H, 6.93. Found: C, 51.12; H, 6.96. Compound **16**: ^{1}H NMR analysis revealed that the product was contaminated with small amounts of alcohols **11** and **14**. ^{1}H NMR δ_H 1.28 (3H, d, *J* = 6.5 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.15 (3H, s), 3.19 (1H, dd, *J* = 9.5, 3.8 Hz), 3.39 (3H, s), 3.50 (3H, s), 3.51 – 3.58 (2H, m), 3.59 (3H, s), 3.64 – 3.72 (3H, m), 3.81 – 3.89 (1H, m), 4.80 (1H, d, *J* = 3.4 Hz), 4.98 (1H, d, *J* = 0.8 Hz), 5.01 (1H, dd, *J* = 10.3, 2.7 Hz), 5.03 (1H, dd, *J* = 10.3, 10.3 Hz), 5.46 (1H, dd, *J* = 2.7, 0.8 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.2 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.2 (CH_3), 59.0 (CH_3), 61.3 (CH_3), 61.9 (CH_2), 69.0 (CH), 69.9 (CH), 70.4 (CH), 70.602 (CH), 70.9 (CH), 75.9 (CH), 82.3 (CH), 82.7 (CH), 97.6 (CH), 98.8 (CH), 169.8 (C), 170.0 (C), 170.1 (C).



Method B: Using *n*-Bu$_3$SnD and AIBN. A solution of phthalimide **13** (106 mg, 0.166 mmol) in dry benzene (12.4 mL) containing *n*-Bu_3SnD (45 μL, 0.166 mmol) and AIBN (2.7 mg, 0.017 mmol) was heated at reflux temperature for 2 h. After this time another portion of *n*-Bu_3SnD (45 μL, 0.166 mmol) and AIBN (2.7 mg, 0.017 mmol) were added, and heating at reflux was continued for an additional 1 h. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue was dissolved in CH_3CN, washed with *n*-hexane and the combined more polar extracts

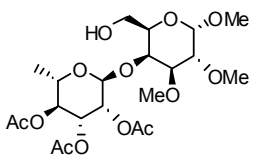
were concentrated under reduced pressure. The residue was purified by column chromatography (hexanes–EtOAc, 60:40 → 50:50) to give methyl 6-*O*-(2,3,4-tri-*O*-acetyl-5,6-dideoxy-L-(5-$^2H_1$)*lyxo*-hexonoyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (**18**) (29.7 mg, 0.06 mmol, 36%), methyl 4-*O*-(2,3,4-tri-*O*-acetyl-5,6-dideoxy-L-(5-$^2H_1$)*lyxo*-hexonoyl)-2,3-di-*O*-methyl-α-D-glucopyranoside **17** (23.1 mg, 0.047 mmol, 28%), compound **11** (5.9 mg, 0.012 mmol, 7%), and methyl 2,3,4-tri-*O*-acetyl-6-deoxy-β-L-(1-$^2H_1$)mannopyranosyl-(1→4)-2,3-di-*O*-methyl-α-D-glucopyranoside (**19**) (5.9 mg, 0.012 mmol, 7%) as colorless oils. Compound **18**: ^{1}H NMR δ_H 0.89 (3H, d, J = 7.3 Hz), 1.59 (1H, dddd, J = 8.0, 8.0, 8.0, 8.0 Hz), 2.07 (3H, s), 2.10 (3H, s), 2.12 (3H, s), 3.04 (1H, br s) 3.20 (1H, dd, J = 9.5, 3.4 Hz), 3.42 (3H, s), 3.43 – 3.46 (2H, m), 3.50 (3H, s), 3.63 (3H, s), 3.74 (1H, ddd, J = 7.5, 3.9, 2.0 Hz), 4.19 (1H, dd, J = 12.0, 2.0 Hz), 4.53 (1H, dd, J = 12.0, 4.2 Hz), 4.81 (1H, d, J = 3.5 Hz), 5.13 (1H, d, J = 7.1 Hz), 5.21 (1H, dd, J = 8.2, 3.7 Hz), 5.39 (1H, dd, J = 7.2, 3.7 Hz); ^{13}C NMR (100.6 MHz) δ_C 9.3 (CH_3), 20.4 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 23.3 (CH, t, J_{CD} = 20.0 Hz), 55.3 (CH_3), 58.6 (CH_3), 61.3 (CH_3), 64.5 (CH_2), 69.0 (CH), 69.7 (CH), 69.8 (CH), 71.1 (CH), 71.9 (CH), 81.7 (CH), 82.5 (CH), 97.6 (CH), 167.6 (C), 169.6 (C), 170.1 (C), 170.5 (C); MS *m*/*z* (rel intensity) 464 (M^+ – C_2H_5D, <1), 432 (1), 403 (1), 366 (10), 232 (17), 101 (35), 88 (100); HRMS calcd for $C_{19}H_{28}O_{13}$, 464.1530, found 464.1510. Compound **17**: ^{1}H NMR δ_H 0.90 (3H, d, J = 7.6 Hz), 1.59 (1H, m), 2.07 (3H, s), 2.12 (3H, s), 2.14 (3H, s), 2.41 (1H, br s) 3.32 (1H, dd, J = 9.5, 3.4 Hz), 3.44 (3H, s), 3.50 (3H, s), 3.51 (3H, s), 3.59 – 3.69 (3H, m), 3.64 (1H, dd, J = 9.5, 9.5 Hz), 4.88 (1H, d, J = 3.4 Hz), 4.91 (1H, dd, J = 9.5, 9.5 Hz), 5.16 (1H, d, J = 6.5 Hz), 5.20 (1H, dd, J = 8.4, 4.2 Hz), 5.42 (1H, dd, J = 6.5, 4.2 Hz); ^{13}C NMR (100.6 MHz) δ_C 9.360 (CH_3), 20.4 (CH_3), 20.6 (CH_3), 20.8 (CH_3), 23.4 (CH, t, J_{CD} = 19.0 Hz), 55.4 (CH_3), 58.9 (CH_3), 60.2 (CH_3), 60.9 (CH_2), 69.4 (CH), 70.3 (CH), 71.0 (CH), 71.4 (CH), 72.044 (CH), 79.7 (CH), 81.6 (CH), 97.5

(CH), 167.5 (C), 169.6 (C), 170.1 (C), 170.3 (C); MS *m*/*z* (rel intensity) 464 (M^+ – C_2H_5D, <1), 435 (2), 404 (1), 232 (25), 101 (17), 88 (100); HRMS calcd for $C_{19}H_{28}O_{13}$ 464.1530, found 464.1544. Compound **19**: ^{1}H NMR analysis revealed that the product was contaminated with small amounts of alcohols **11** and **17**. ^{1}H NMR δ_H 1.28 (3H, d, *J* = 6.1 Hz), 1.99 (3H, s), 2.05 (3H, s), 2.16 (3H, s), 3.19 (1H, dd, *J* = 9.5, 3.4 Hz), 3.40 (3H, s), 3.50 (3H, s), 3.51 – 3.58 (2H, m), 3.59 (3H, s), 3.64 – 3.72 (3H, m), 3.80 – 3.89 (1H, m), 4.80 (1H, d, *J* = 3.4 Hz), 5.01 (1H, dd, *J* = 10.3, 3.0 Hz), 5.03 (1H, dd, *J* = 10.3, 10.3 Hz), 5.46 (1H, d, *J* = 2.7 Hz); ^{13}C NMR (100.6 MHz) δ_C 17.2 (CH_3), 20.6 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 55.2 (CH_3), 58.9 (CH_3), 61.3 (CH_3), 62.0 (CH_2), 68.9 (CH), 69.9 (CH), 70.4 (CH), 70.570 (CH), 70.9 (CH), 75.9 (CH), 82.3 (CH), 82.7 (CH), 97.7 (CH), 169.8 (C), 170.0 (C), 170.1 (C).



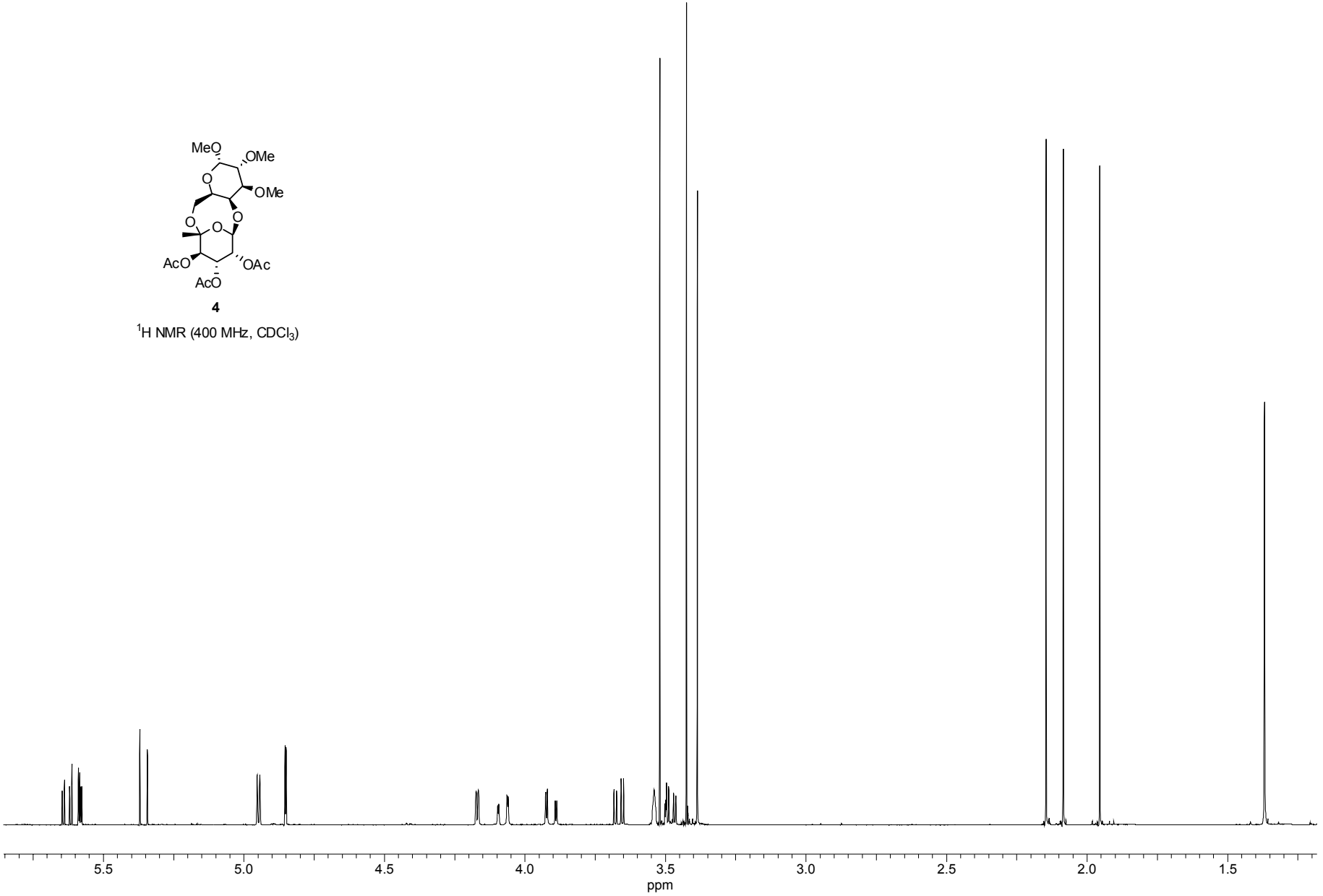
3

^{1}H NMR (500 MHz, $CDCl_3$)



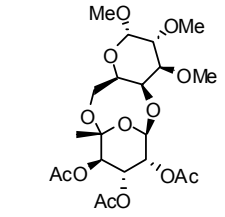
3

^{13}C NMR (100.6 MHz, $CDCl_3$)



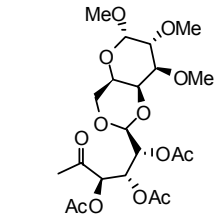
4

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



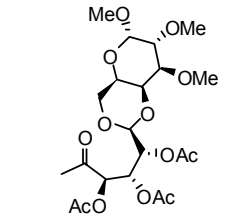
4

^{13}C NMR (100.6 MHz, $CDCl_3$)



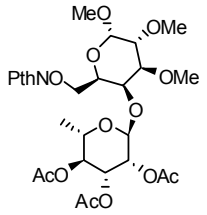
5

^{1}H NMR (500 MHz, $CDCl_3$)



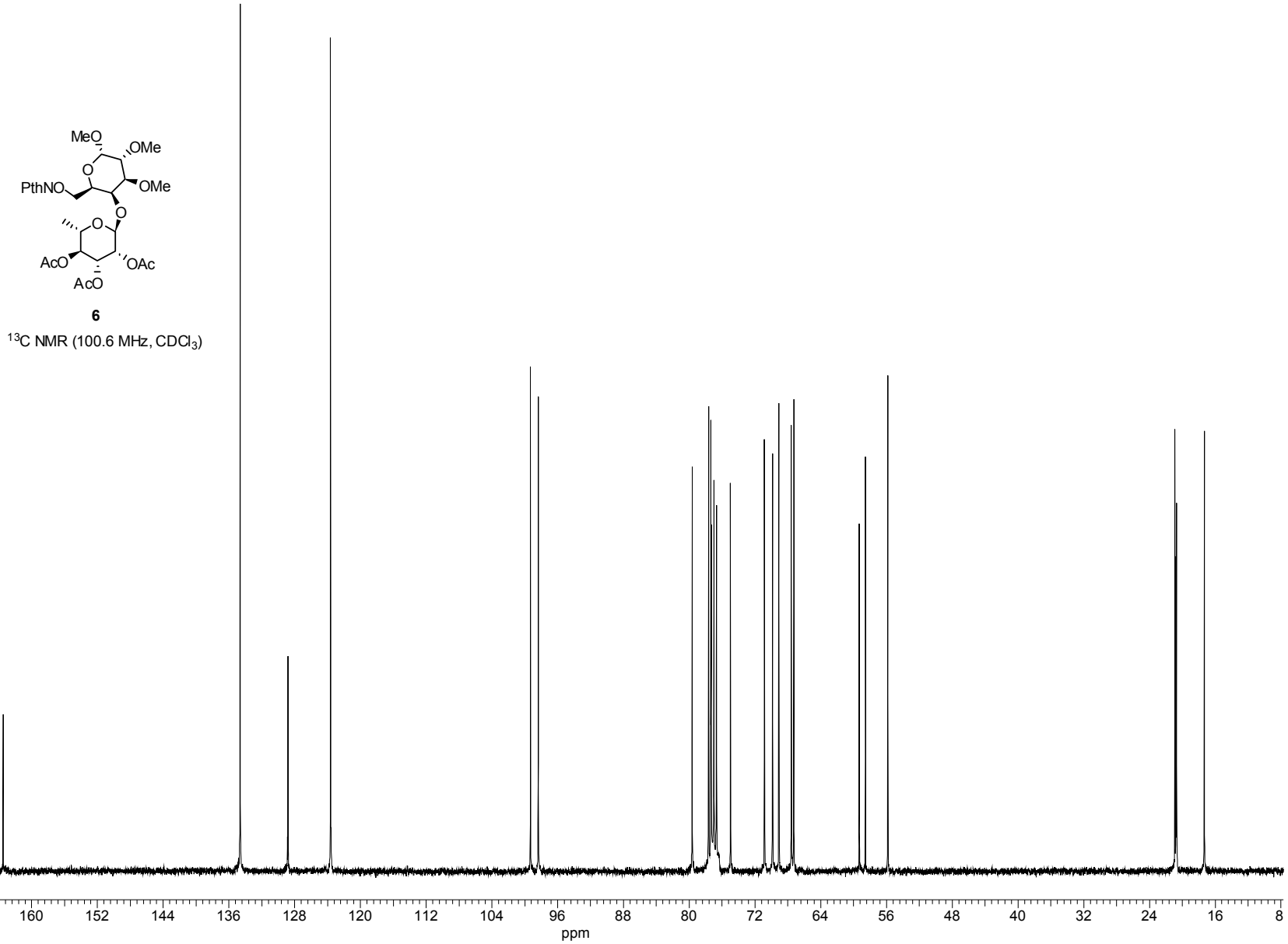
5

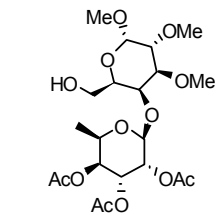
^{13}C NMR (125.7 MHz, $CDCl_3$)



6

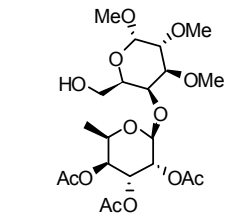
^{1}H NMR (500 MHz, $CDCl_3$)


MeO
OMe
PthNO
OMe
O
O
AcO
OAc
AcO
6
^{13}C NMR (100.6 MHz, $CDCl_3$)
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
ppm



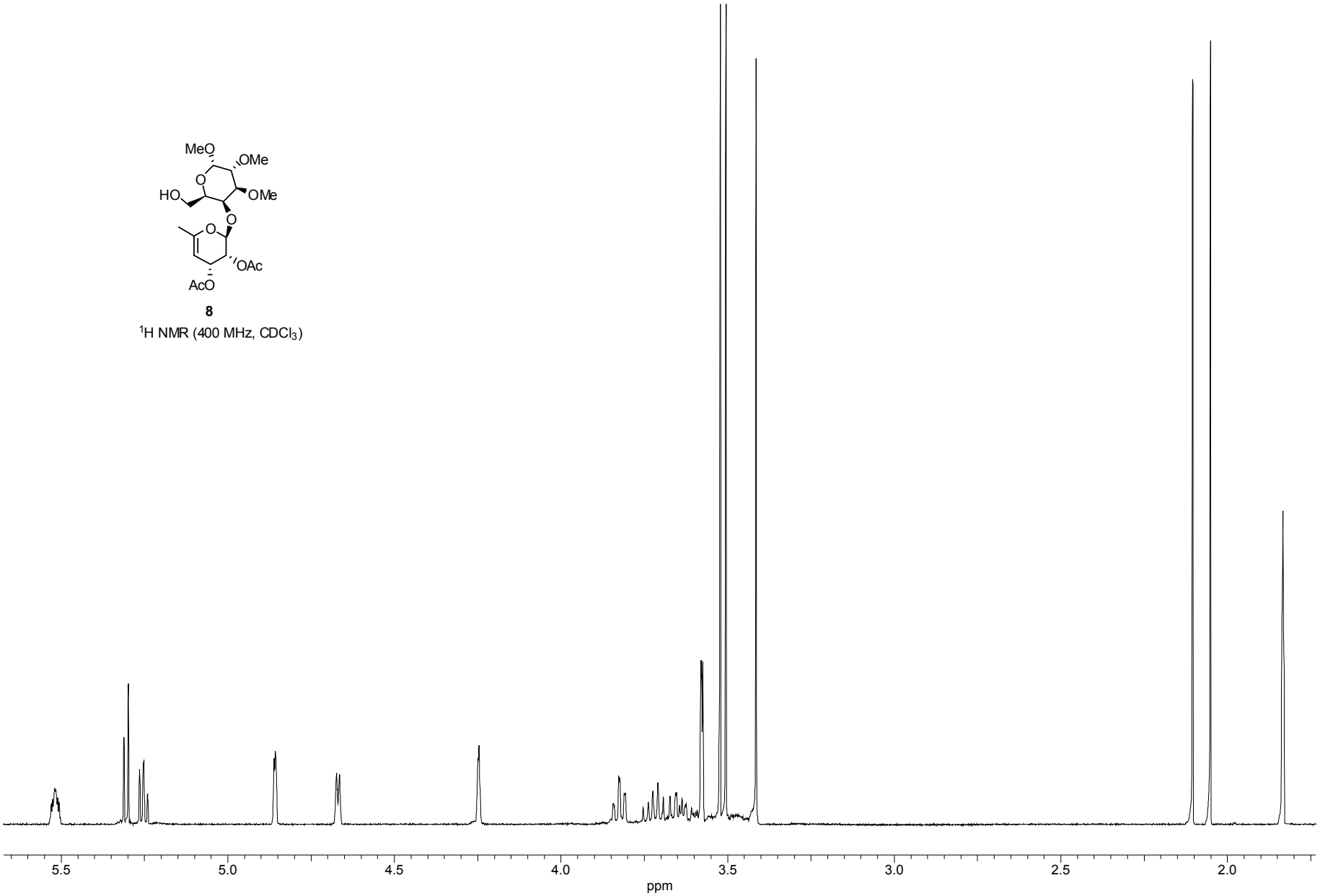
7

^{1}H NMR (500 MHz, $CDCl_3$)



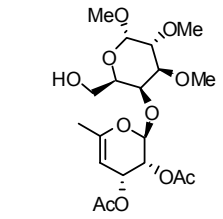
7

^{13}C NMR (100.6 MHz, $CDCl_3$)



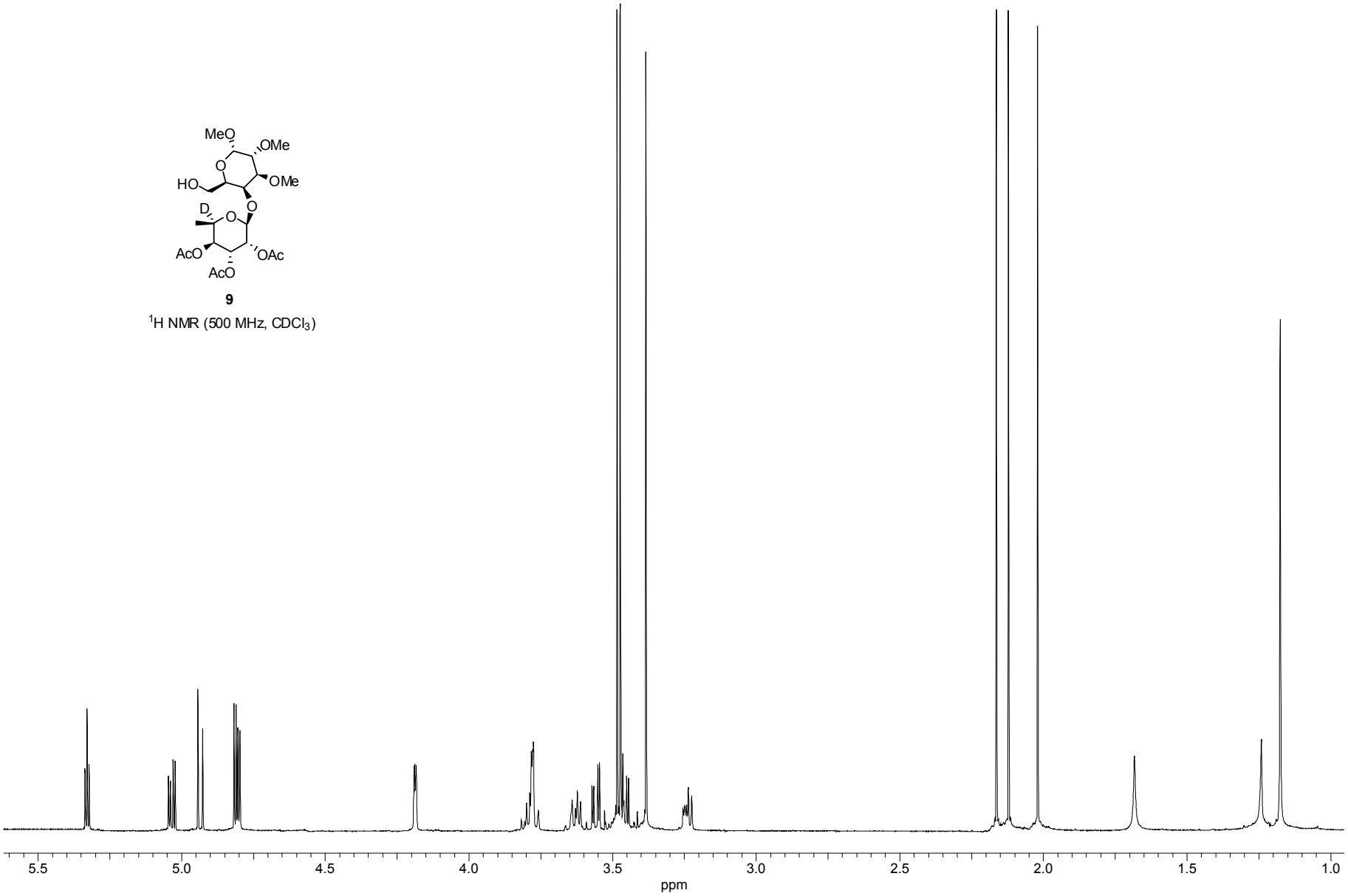
8

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



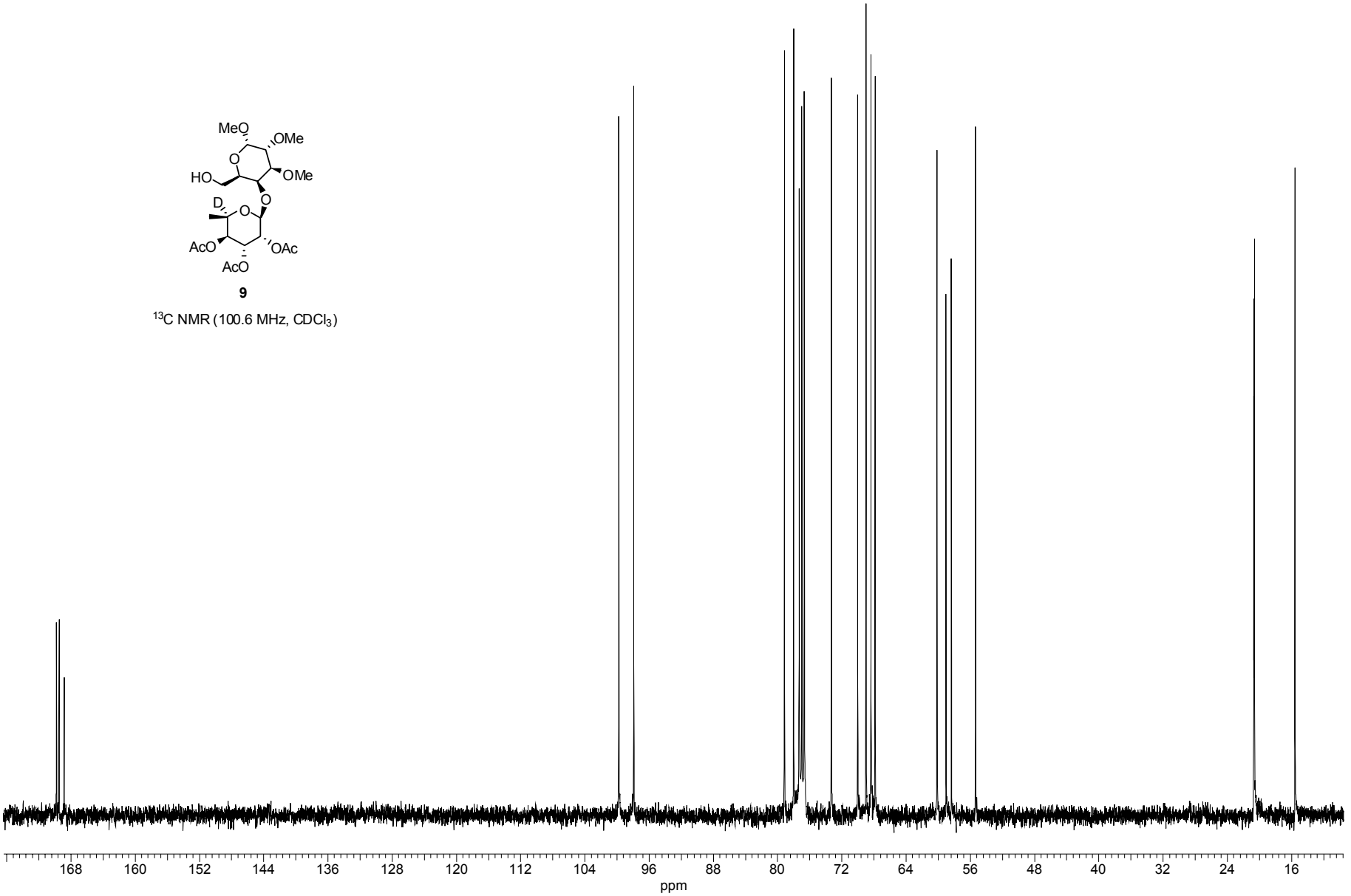
8

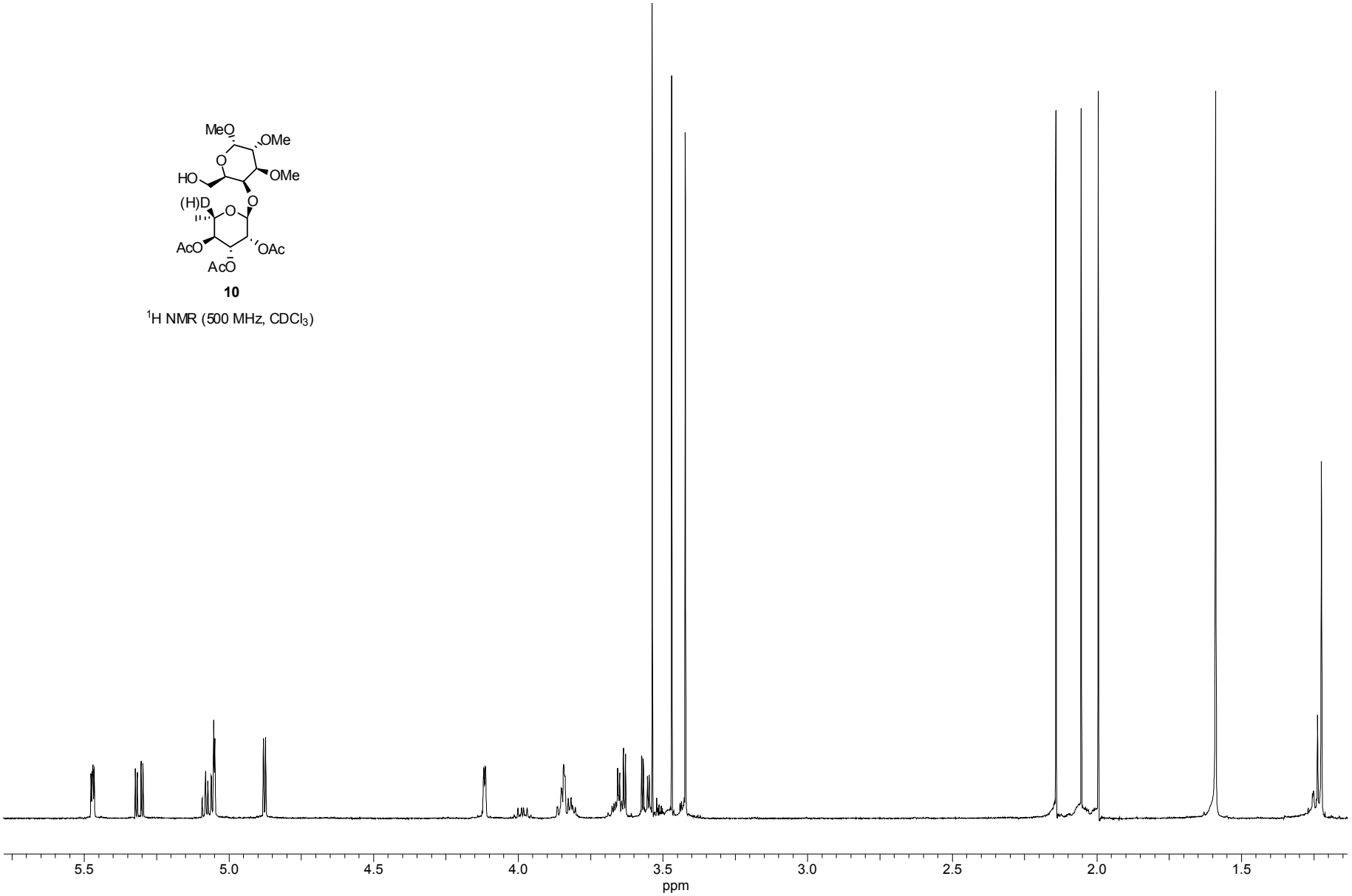
^{13}C NMR (100.6 MHz, $CDCl_3$)

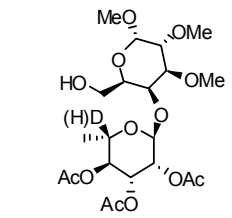


9

^{1}H NMR (500 MHz, $CDCl_3$)

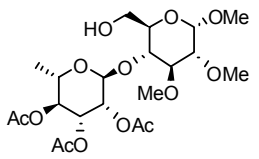

MeO
OMe
O
HO
OMe
D
O
O
AcO
OAc
AcO
9
13C NMR (100.6 MHz, CDCl3)
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
ppm


MeO
OMe
HO
OMe
(H)D
O
AcO
OAc
AcO
10
^{1}H NMR (500 MHz, $CDCl_3$)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm



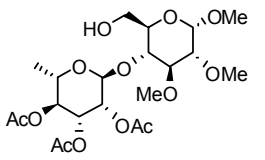
10

^{13}C NMR (100.6 MHz, $CDCl_3$)



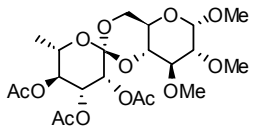
11

^{1}H NMR (500 MHz, $CDCl_3$)



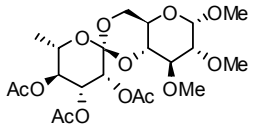
11

^{13}C NMR (100.6 MHz, $CDCl_3$)



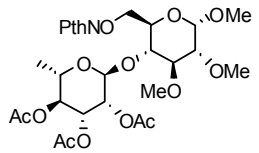
12

^{1}H NMR (500 MHz, $CDCl_3$)



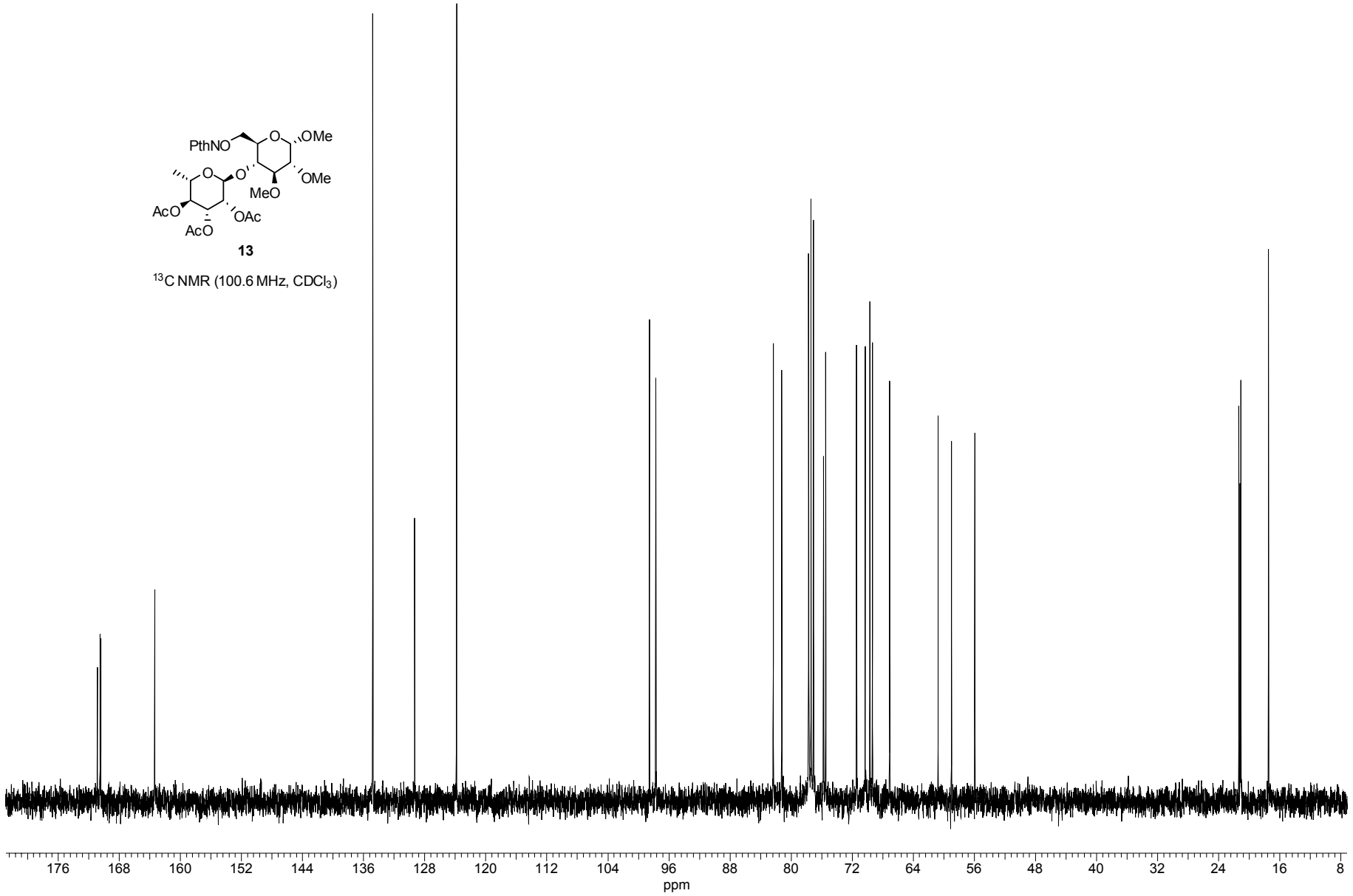
12

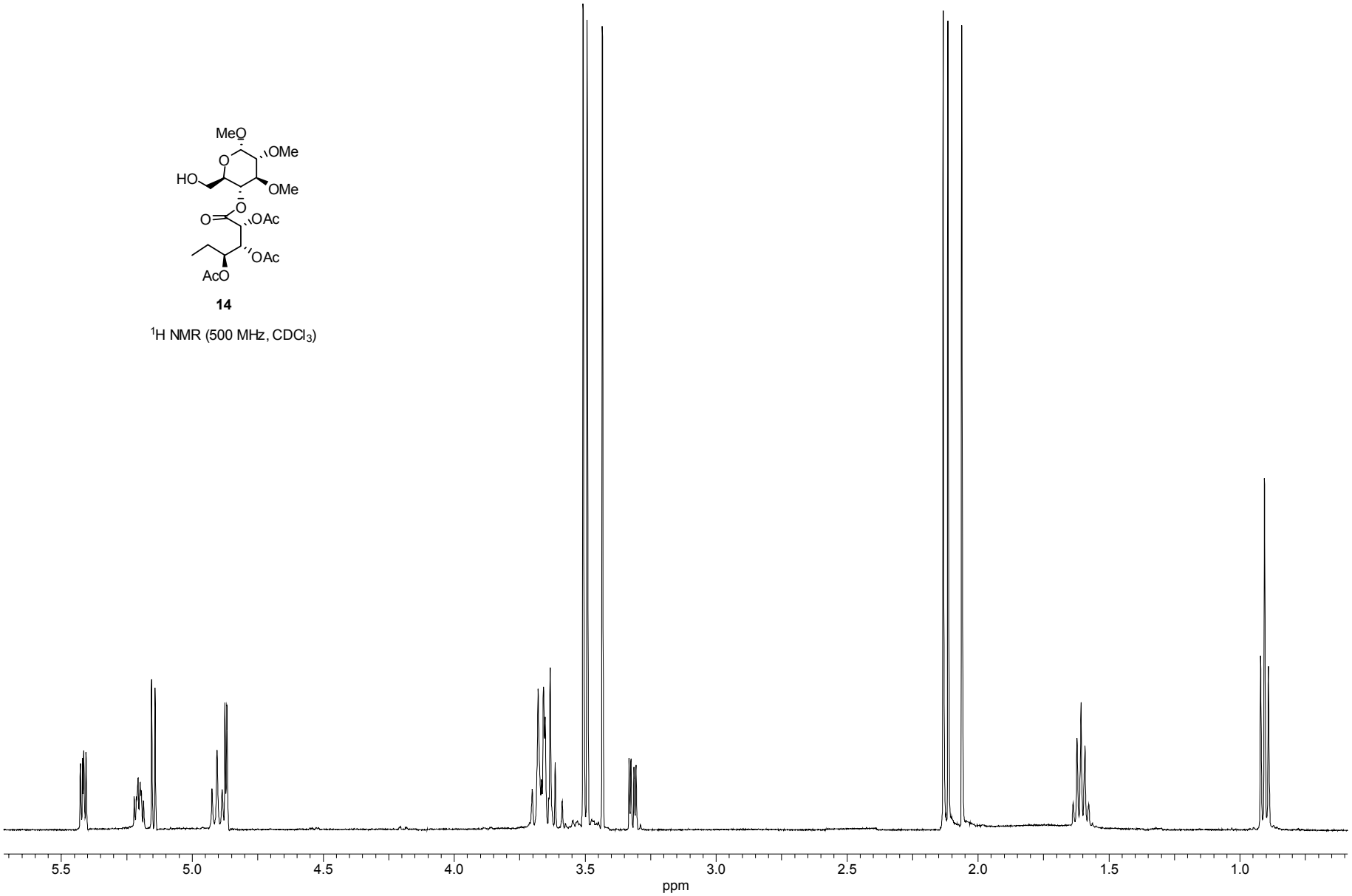
^{13}C NMR (100.6 MHz, $CDCl_3$)

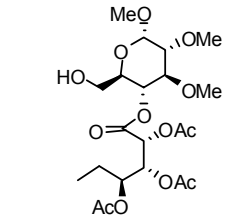


13

^{1}H NMR (500 MHz, $CDCl_3$)

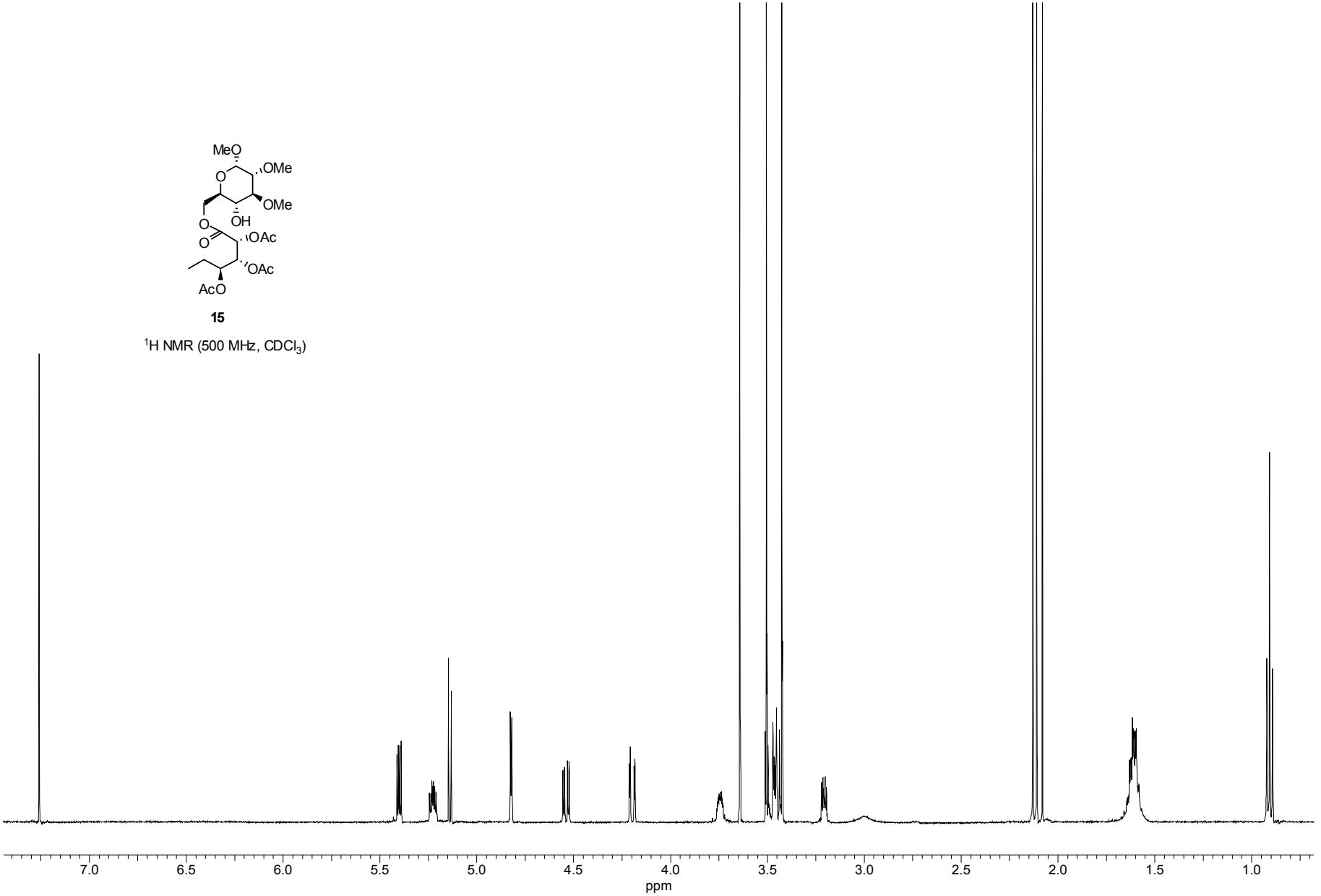

PthNO
OMe
OMe
MeO
AcO
OAc
AcO
13
^{13}C NMR (100.6 MHz, $CDCl_3$)
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
ppm


MeO
OMe
HO
OMe
O
OAc
OAc
AcO
14
1H NMR (500 MHz, CDCl3)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



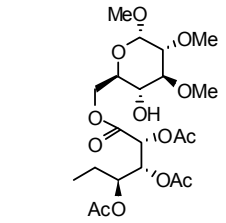
14

^{13}C NMR (100.6 MHz, $CDCl_3$)



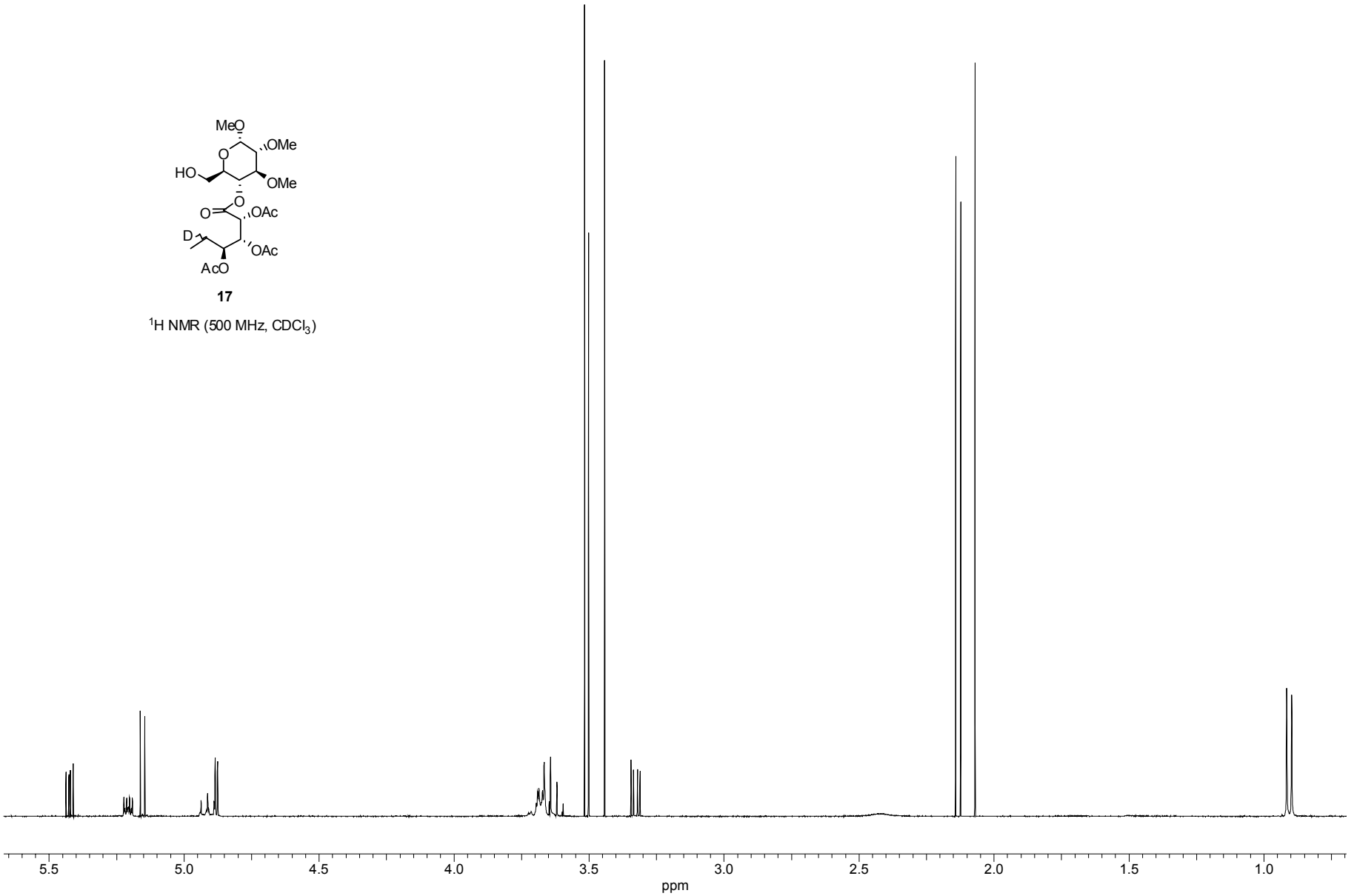
15

^{1}H NMR (500 MHz, $CDCl_3$)



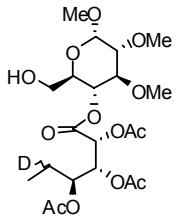
15

^{13}C NMR (100.6 MHz, $CDCl_3$)



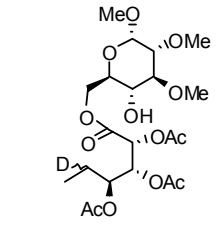
17

^{1}H NMR (500 MHz, $CDCl_3$)



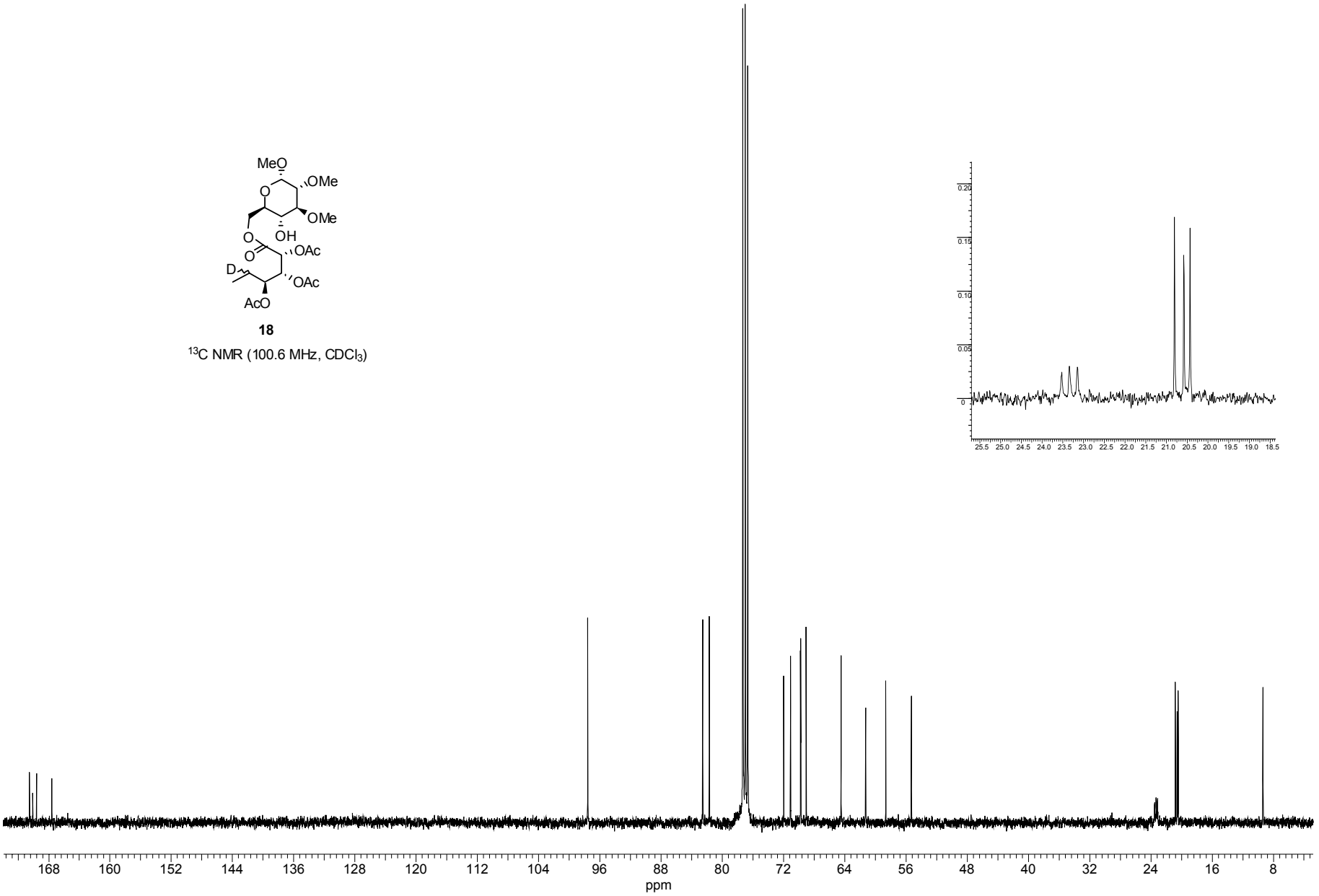
17

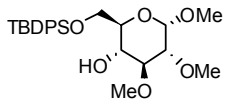
^{13}C NMR (100.6 MHz, $CDCl_3$)



18

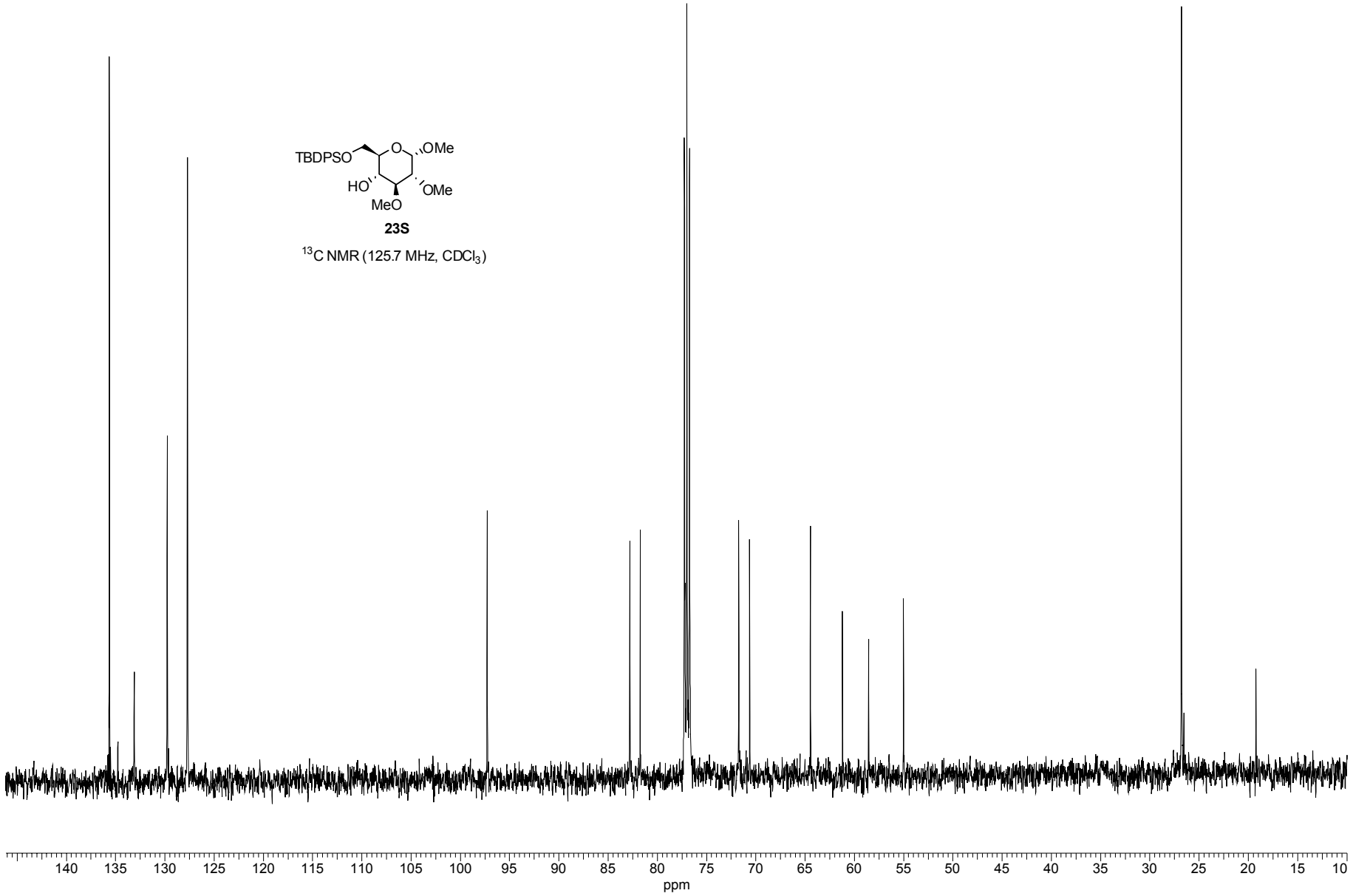
^{1}H NMR (500 MHz, $CDCl_3$)

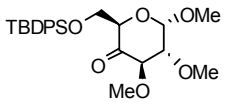

MeO
OMe
OMe
OH
OAc
OAc
AcO
D
O
O
O
18
13C NMR (100.6 MHz, CDCl3)
ppm



23S

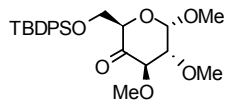
^{1}H NMR (500 MHz, $CDCl_3$)


TBDPSO
O
OMe
HO
OMe
MeO
23S
13C NMR (125.7 MHz, CDCl3)
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
ppm



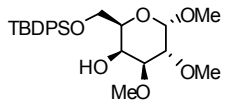
24S

^{1}H NMR (500 MHz, $CDCl_3$)



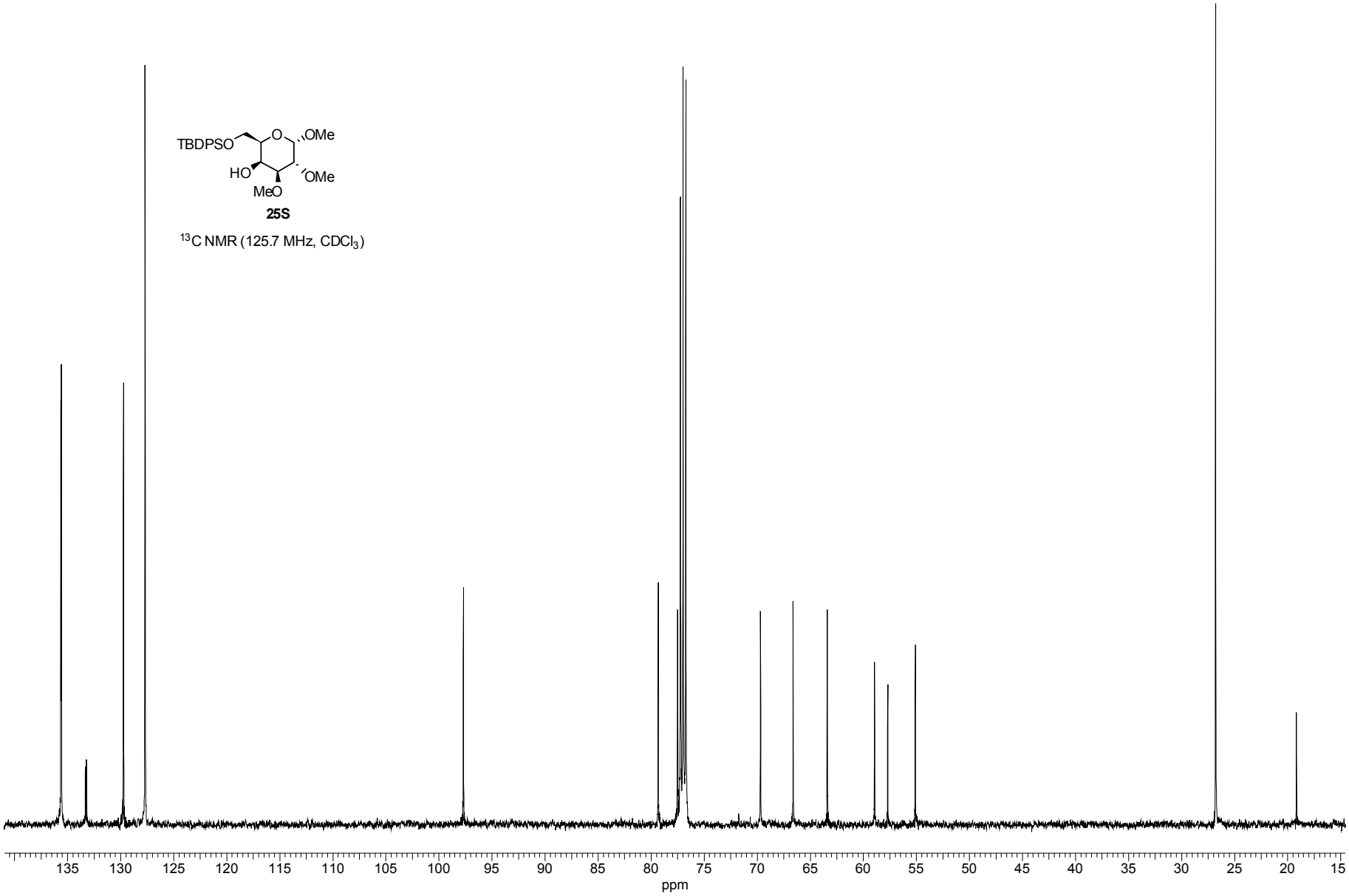
24S

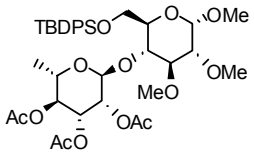
^{13}C NMR (125.7 MHz, $CDCl_3$)



25S

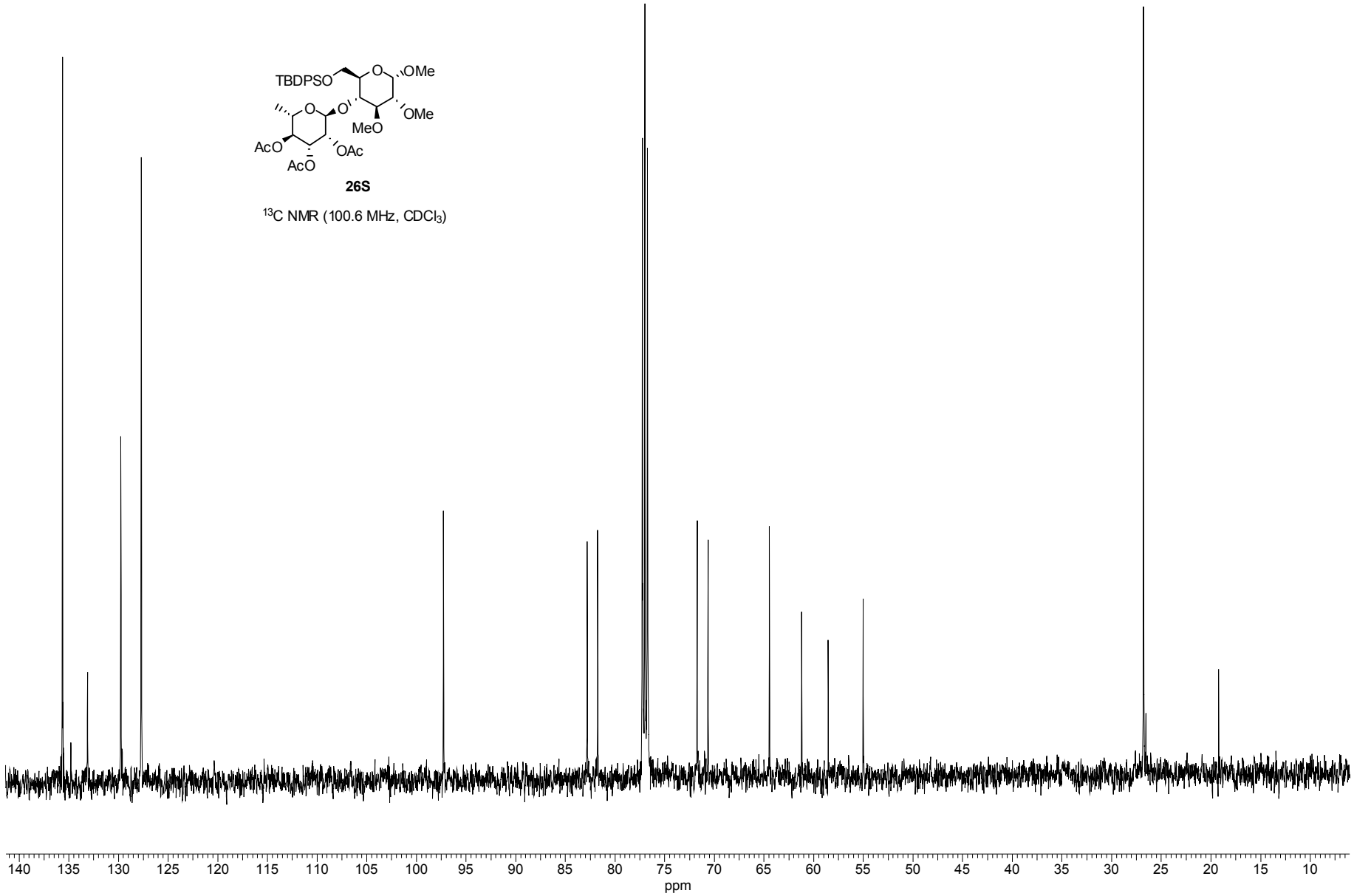
^{1}H NMR (400 MHz, $CDCl_3$)


TBDPSO
O
OMe
HO
OMe
MeO
25S
^{13}C NMR (125.7 MHz, $CDCl_3$)
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



26S

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


TBDPSO
O
OMe
O
O
OMe
MeO
AcO
OAc
AcO
26S
13C NMR (100.6 MHz, CDCl3)
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
ppm