Synthesis of an Unusual Hexasaccharide Repeating Unit from the Cell Wall Polysaccharide of *Eubacterium saburreum* Strain T19

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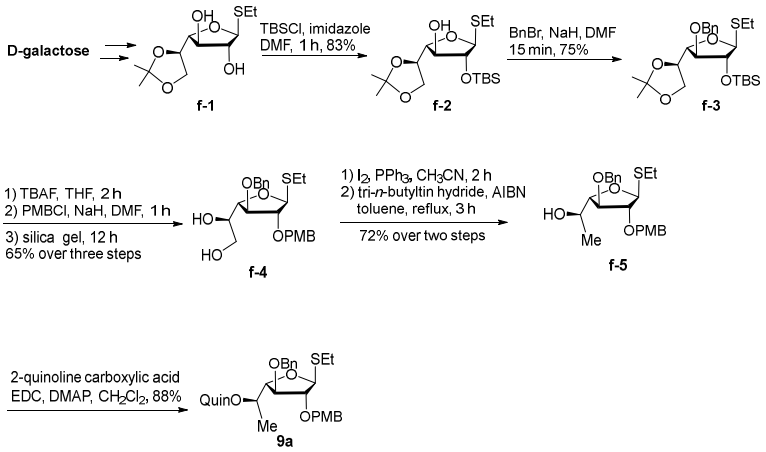
Contents of Supporting Information

1. General methods

All non-aqueous reactions were performed under a nitrogen atmosphere and monitored by thin layer chromatography (TLC) using Silica Gel GF_{254} plates with detection by charring with 10% (v/v) H_2SO_4 in EtOH or by UV detection. Solvents used in the reactions were distilled from appropriate drying agents prior to use. Silica gel (200-300 mesh) was used for column chromatography. Optical rotations were measured at 25 ± 0.3 °C for solutions in a 1.0 dm cell. High resolution mass spectra (HRMS) were acquired in the ESI mode. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal reference. Chemical shifts are expressed in ppm downfield from the internal TMS absorption. Standard splitting patterns are abbreviated: s (singlet), d (doublet), t (triplet), m (multiplet). *J* values are given in Hz.

2. Experimental procedures

Synthesis of D-Fuc*f* Donors 9a-e



Ethyl 2-*O*-*tert*-butyldimethylsilyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (f-2)

To a solution of **f-1**[1] (540 mg, 2.0 mmol) in dry DMF (20 mL) were added TBSCl (365 mg, 2.4 mmol) and imidazole (408 mg, 6.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by addition of methanol and then the mixture was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (20:1, petroleum ether-EtOAc) to afford **f-2** (628 mg, 83%) as a white solid. **f-2**: R_f = 0.5 (10:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -110.7 (*c* 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (d, *J* = 2.2 Hz, 1H), 4.32 (q, *J* = 6.6 Hz, 1H), 4.08-3.98 (m, 3H), 3.93-3.89 (m, 1H), 3.81 (s, 1H), 2.79-2.56 (m, 2H), 2.48 (s, 1H), 1.45 (s, 3H), 1.36 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H), 0.89 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.05, 89.24, 85.61, 83.44, 79.86, 75.96, 65.73, 26.79, 25.92, 25.39, 24.96, 18.17, 15.08, -4.47, -4.56; HRMS (ESI): *m/z* calcd for $C_{17}H_{34}O_5SSi$ $[M+Na]^+$: 401.1794, found: 401.1790.

Ethyl 2-*O*-*tert*-butyldimethylsilyl-3-*O*-benzyl-5,6-*O*-isopropylidene-1-thio-β-D-galactofuranoside (f-3)

To a solution of **f-2** (315 mg, 0.8 mmol) in dry DMF (16 mL) were added benzyl bromide (0.1 mL, 0.9 mmol) and NaH (48 mg, 1.2 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was stirred for 15 minutes at 0 °C. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (30:1, petroleum ether-EtOAc) to afford **f-3** (265 mg, 75%) as a colorless syrup. **f-3**: R_f = 0.6 (15:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -122.9 (*c* 0.64, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 5H), 5.14 (d, *J* = 2.3 Hz, 1H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 4.27-4.19 (m, 2H), 4.15 (t, *J* = 5.9 Hz, 1H), 3.90-3.77 (m, 2H), 3.71 (dd, *J* = 5.6, 2.4 Hz, 1H), 2.78-2.56 (m, 2H), 1.41 (s, 3H), 1.35 (s, 3H), 1.30 (t, *J* = 7.4 Hz, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.79, 128.68, 128.13, 128.08, 109.85, 90.73, 86.72, 82.46, 82.36, 76.16, 72.51, 65.77, 26.68, 25.95, 25.60, 25.56, 18.10, 15.20, -4.07, -4.67; HRMS (ESI): *m/z* calcd for $C_{24}H_{40}O_5SSi$ $[M+Na]^+$: 491.2264, found: 491.2261.

Ethyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-1-thio-β-D-galactofuranoside (f-4)

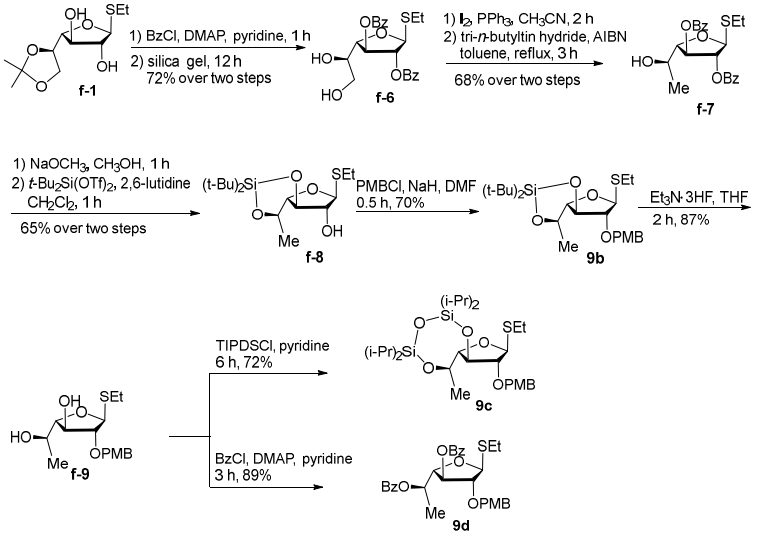
To a solution of **f-3** (372 mg, 0.8 mmol) in THF (8 mL) was added TBAF (0.8 mL, 1 M in THF). The reaction mixture was stirred at room temperature for 2 h and then it was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (5:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup (255 mg, 0.7 mmol) in dry DMF (7 mL) was added 4-methoxybenzyl chloride (0.14 mL, 1.2 mmol) at 0 °C. The mixture was stirred for 10 minutes at the same temperature. Then NaH (62 mg, 2.1 mmol, 60% in mineral oil) was added. The resulting mixture was stirred for 1 h at the same temperature. The mixture was quenched with saturated aqueous NH_4Cl, diluted with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was put on silica gel chromatography column for 12 h and eluted by petroleum ether-EtOAc (2:1) to afford **f-4** (226 mg, 65% over three steps) as a white solid. **f-4**: R_f = 0.3 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -116.4 (*c* 0.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.18 (m, 8H), 6.89 (d, *J* = 8.3 Hz, 2H), 5.36 (s, 1H), 4.62-4.53 (m, 2H), 4.49 (d, *J* = 11.7 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.19-4.15 (m, 1H), 4.06 (dd, *J* = 6.8, 2.8 Hz, 1H), 3.96 (t, *J* = 2.6 Hz, 1H), 3.80 (s, 4H), 3.67 (t, *J* = 4.9 Hz, 2H), 2.78-2.58 (m, 2H), 2.56 (d, *J* = 8.4 Hz, 1H), 2.25 (s, 1H), 1.30 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.65, 137.50, 129.92, 129.17, 128.60, 128.10, 128.03, 114.04, 114.01, 88.06, 87.74, 83.70, 81.83 , 72.48, 71.82, 71.10, 64.72, 55.41, 25.63, 15.03; HRMS (ESI): *m/z* calcd for $C_{23}H_{30}O_6S$ $[M+Na]^+$: 457.1661, found: 457.1662.

Ethyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-1-thio-β-D-fucofuranoside (f-5)

To a solution of **f-4** (360 mg, 0.9 mmol) in acetonitrile (6 mL) was added triphenylphosphine (350 mg, 1.34 mmol). The reaction mixture was cooled to -10 °C and a solution of iodine (270.2 mg, 1.07 mmol) in DMF (1 ml) was added. The resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature at the end of which time TLC indicated the reaction was complete. The reaction mixture was concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (6:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup (392 mg, 0.7 mmol) in dry toluene (6 mL) were added tri-*n*-butyltin hydride (0.3 ml, 1.1 mmol) and azodiisobutyronitrile (11 mg, 0.07 mmol). The reaction mixture was heated under reflux for 3 h at the end of which time TLC indicated the reaction was complete. Then the reaction was cooled to room temperature and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford **f-5** as a colorless syrup (271 mg, 72% over two steps). **f-5**: R_f = 0.45 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -115.4 (*c* 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 7H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.36 (d, *J* = 2.2 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 2H), 4.47 (d, *J* = 11.8 Hz, 1H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.03-3.95 (m, 2H), 3.93-3.83 (m, 2H), 3.81 (s, 3H), 2.79-2.57 (m, 2H), 2.15 (d, *J* = 6.1 Hz, 1H), 1.31 (t, *J* = 7.4 Hz, 3H), 1.21 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.61, 137.68, 129.86, 129.34, 128.54, 128.02, 127.99, 114.02, 88.20, 87.52, 84.76, 84.18, 72.33, 71.74, 67.70, 55.41, 25.46, 19.62, 15.08; HRMS (ESI): *m/z* calcd for $C_{23}H_{30}O_5S$ $[M+Na]^+$: 441.1712, found: 441.1707.

Ethyl 2-*O*-*p*-methoxybenzyl-3-*O*-benzyl-5-*O*-(2-quinolinecarbonyl)-1-thio-β-D-fucofuranoside (9a)

To a solution of **f-5** (540 mg, 1.29 mmol) in dry CH_2Cl_2 (13 mL) were added 2-quinoline carboxylic acid (670 mg, 3.87 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (1.23 g, 6.45 mmol)，and 4-dimethylaminopyridine (32 mg, 0.26 mmol). The reaction mixture was stirred for 1 h at room temperature and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (10:1, petroleum ether-EtOAc) to afford **9a** (619 mg, 88%) as a colorless syrup. **9a**: R_f = 0.50 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -95.6 (*c* 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 1H), 8.07 (s, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.80-7.73 (m, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.34-7.15 (m, 7H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.55-5.45 (m, 2H), 4.55 (d, *J* = 11.4 Hz, 2H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.36-4.30 (m, 1H), 3.98 (d, *J* = 6.1 Hz, 2H), 3.78 (s, 3H), 2.83-2.59 (m, 2H), 1.48 (d, *J* = 6.4 Hz, 3H), 1.32 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 159.51, 148.16, 147.88, 137.54, 137.19, 131.05, 130.20, 129.82, 129.52, 129.35, 128.58, 128.51, 128.11, 127.95, 127.54, 121.36, 113.93, 88.51, 87.45, 83.98, 82.59, 72.47, 71.82, 71.24, 55.40, 25.53, 16.70, 15.25; HRMS (ESI): *m/z* calcd for $C_{33}H_{35}NO_6S$ $[M+Na]^+$: 596.2083, found: 596.2085.



Ethyl 2,3-di-*O*-benzoyl-1-thio-β-D-galactofuranoside (f-6)

To a solution of **f-1**[1] (2.5 g, 9.5 mmol) in pyridine (95 mL) were added benzoyl chloride (4.4 mL, 37.9 mmol) and 4-dimethylaminopyridine (231 mg, 1.9 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The syrup was put on silica gel chromatography column for 12 h and eluted by (2:1, petroleum ether-EtOAc) to afford **f-6** as a colorless syrup (2.9 g, 72% over two steps). **f-6**: R_f = 0.3 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +149.5 (*c* 0.73, $CHCl_3$); ^{1}H NMR (400 MHz, MeOD) δ 8.09-8.00 (m, 4H), 7.60 (t, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 4H), 5.81 (d, *J* = 5.7 Hz, 1H), 5.44 (dd, *J* = 10.1, 5.8 Hz, 1H), 4.65-4.50 (m, 3H), 4.11-4.02 (m, 2H), 2.63-2.41 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, MeOD) δ 167.74, 167.53, 134.39, 134.37, 131.20, 131.14, 130.82, 130.52, 129.58, 129.48, 83.11, 72.87, 71.16, 70.32, 69.64, 65.69, 24.57, 15.05; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}O_7S$ $[M+Na]^+$: 455.1141, found: 455.1141.

Ethyl 2,3-di-*O*-benzoyl-1-thio-β-D-fucofuranoside (f-7)

To a solution of **f-6** (400 mg, 0.9 mmol) in acetonitrile (9 mL) was added triphenylphosphine (358 mg, 1.4 mmol). The reaction mixture was cooled to -10 °C, then a solution of iodine (274 mg, 1.1 mmol) in DMF (1.1 ml) was added. The resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature at the end of which time TLC indicated the reaction was complete. The reaction mixture was concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (6:1, petroleum ether-EtOAc) to afford a colorless syrup (430 mg). To a solution of the obtained syrup in dry toluene (10 mL) were added tri-*n*-butyltin hydride (0.3 ml, 1.2 mmol) and azodiisobutyronitrile (13 mg, 0.08 mmol). The reaction mixture was heated under reflux for 3 h at the end of which time TLC indicated the reaction was complete. Then the reaction was cooled to room temperature and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford **f-7** as a colorless syrup (255 mg, 68% over two steps). **f-7**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -41.7 (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.04 (m, 4H), 7.65-7.55 (m, 2H), 7.52-7.41 (m, 4H), 5.57 (s, 1H), 5.54 (d, *J* = 4.8 Hz, 1H), 5.51 (t, *J* = 1.5 Hz, 1H), 4.30 (t, *J* = 4.6 Hz, 1H), 4.25-4.15 (m, 1H), 2.86-2.65 (m, 2H), 1.36 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.92, 165.48, 133.71, 130.12, 130.01, 129.24, 129.20, 128.67, 88.23, 86.11, 83.01, 78.14, 67.24, 25.54, 19.67, 15.07; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}O_6S$ $[M+Na]^+$: 439.1192, found: 439.1185.

Ethyl 3,5-*O*-di-*tert*-butylsilylene-1-thio-β-D-fucofuranoside (f-8)

To a solution of **f-7** (450 mg, 1.08 mmol) in MeOH (10 mL) was added $NaOCH_3$ (117 mg, 2.16 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The reaction mixture was stirred for 1 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, CH_2Cl_2-MeOH) to afforded a white solid (207 mg). To a solution of the obtained white solid (207 mg, 4.13 mmol) in dry CH_2Cl_2 (10 mL) were added di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (0.4 mL, 1.3 mmol) and 2,6-lutidine (0.6 mL, 5.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. Then the reaction was quenched by addition of MeOH. The resulting mixture was diluted with CH_2Cl_2. The resulting organic solution was washed with water, aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **f-8** (244 mg, 65% over two steps) as a colorless syrup. **f-8**: R_f = 0.5 (5:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -98.6 (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.06 (d, *J* = 5.5 Hz, 1H), 4.64-4.49 (m, 1H), 4.19-4.01 (m, 3H), 2.73-2.64 (m, 2H), 1.33-1.26 (m, 6H), 1.03 (s, 9H), 1.00 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 88.75, 82.15, 75.84, 75.60, 70.30, 27.56, 27.43, 26.19, 21.62, 20.86, 16.86, 15.20; HRMS (ESI): *m/z* calcd for $C_{16}H_{32}O_4SSi$ $[M+Na]^+$: 371.1689, found: 371.1690.

Ethyl 2-*O*-*p*-methoxybenzyl-3,5-*O*-di-*tert*-butylsilylene-1-thio-β-D-fucofuranoside (9b)

To a solution of **f-8** (172 mg, 0.49 mmol) in dry DMF (5 mL) was added 4-methoxybenzyl chloride (80 μL, 0.59 mmol) at 0 °C. The mixture was stirred for 10 minutes at the same temperature and then NaH (35.28 mg, 0.88 mmol, 60% in mineral oil) was added. The resulting mixture was stirred for 0.5 h at the same temperature. The mixture was quenched with saturated aqueous NH_4Cl, diluted with

CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (30:1, petroleum ether-EtOAc) to afford **9b** as a colorless syrup (161 mg, 70%). **9b**: R_f = 0.5 (10:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -96.9 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.15 (d, *J* = 5.0 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.59-4.53 (m, 1H), 4.23-4.11 (m, 2H), 3.85-3.81 (m, 1H), 3.81 (s, 3H), 2.76-2.54 (m, 2H), 1.30-1.26 (m, 6H), 1.05 (s, 9H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.45, 129.87, 129.81, 113.91, 88.09, 87.57, 75.64, 71.93, 70.17, 55.42, 27.46, 27.38, 26.03, 21.50, 20.75, 16.81, 14.91; HRMS (ESI): *m/z* calcd for $C_{24}H_{40}O_5SSi$ $[M+Na]^+$: 491.2264, found: 491.2257.

Ethyl 2-*O*-*p*-methoxybenzyl-1-thio-β-D-fucofuranoside (f-9)

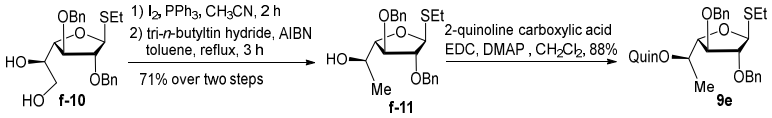
To a solution of **9b** (328 mg, 0.29 mmol) in THF (3 mL) was added triethylamine trihydrofluoride (30 μL, 0.58 mmol) slowly at 0 °C, and the resulting mixture was stirred for 2 h at the same temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford compound **f-9** as a colorless syrup (246 mg, 87%). **f-9**: R_f = 0.3 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -0.9 (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.35 (d, *J* = 2.2 Hz, 1H), 4.56 (d, *J* = 11.3 Hz, 1H), 4.51 (d, *J* = 11.3 Hz, 1H), 4.09-4.04 (m, 1H), 3.95-3.88 (m, 1H), 3.87-3.83 (m, 2H), 3.79 (s, 3H), 2.77-2.55 (m, 2H), 1.30 (t, *J* = 7.4 Hz, 3H), 1.25 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.59, 129.74, 129.38, 114.08, 89.79, 87.34, 86.44, 77.24, 71.90, 67.48, 55.41, 25.03, 19.43, 14.95; HRMS (ESI): *m/z* calcd for $C_{16}H_{24}O_5S$ $[M+Na]^+$: 351.1242, found: 351.1240.

Ethyl 2-*O*-*p*-methoxybenzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-β-D-fucofuranoside (9c)

To a solution of **f-9** (86 mg, 0.41 mmol) in dry pyridine (4 mL) were added 1,1,3,3-tetraisopropyl-1,3-dichlorosiloxane (0.67 mL, 2.1 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 6 h. Then the reaction was quenched by addition of MeOH. The resulting mixture was diluted with CH_2Cl_2. The resulting organic solution was washed with water, aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **9c** (175 mg, 72%) as a colorless syrup. **9c**: R_f = 0.5 (5:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -66.3 (*c* 0.59, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 5.24 (d, *J* = 4.3 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 4.24 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.15 (dt, *J* = 7.9, 3.9 Hz, 1H), 3.85 (t, *J* = 5.4 Hz, 1H), 3.80 (s, 3H), 3.74 (dd, *J* = 9.2, 2.6 Hz, 1H), 2.65 (ddq, *J* = 35.5, 14.3, 7.1 Hz, 2H), 1.32-1.25 (m, 6H), 1.09 (s, 6H), 1.07 (s, 6H), 1.05 (s, 4H), 1.02 (t, *J* = 5.8 Hz, 8H); HRMS (ESI): *m/z* calcd for $C_{20}H_{28}O_7$ $[M+Na]^+$: 593.2765, found: 593.2761.

Ethyl 2-*O*-*p*-methoxybenzyl-3,5-di-*O*-benzoyl-1-thio-β-D-fucofuranoside (9d)

To a solution of **f-9** (200 mg, 0.6 mmol) in pyridine (6 mL) were added benzoyl chloride (0.4 mL, 3.7 mmol) and 4-dimethylaminopyridine (15 mg, 0.12 mmol). The mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **9d** as a colorless syrup (294 mg, 89%). **9d**: R_f = 0.5 (5:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -109.3 (*c* 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, *J* = 6.5 Hz, 4H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.38-7.25 (m, 3H), 7.21-7.02 (m, 4H), 6.68 (d, *J* = 8.6 Hz, 2H), 5.47-5.38 (m, 2H), 5.36 (d, *J* = 3.8 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.36 (t, *J* = 4.6 Hz, 1H), 3.96 (t, *J* = 2.0 Hz, 1H), 3.63 (s, 3H), 2.70-2.47 (m, 2H), 1.35 (d, *J* = 6.5 Hz, 3H), 1.20 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.02, 165.71, 159.41, 133.50, 132.92, 130.23, 129.95, 129.87, 129.62, 129.48, 129.39, 128.56, 128.31, 113.91, 88.22, 88.12, 83.53, 78.04, 71.86, 69.88, 55.33, 25.53, 16.28, 15.19; HRMS (ESI): *m/z* calcd for $C_{30}H_{32}O_7S$ $[M+Na]^+$: 559.1767, found: 559.1764.



Ethyl 2,3-di-*O*-benzyl-1-thio-β-D-fucofuranoside (f-11)

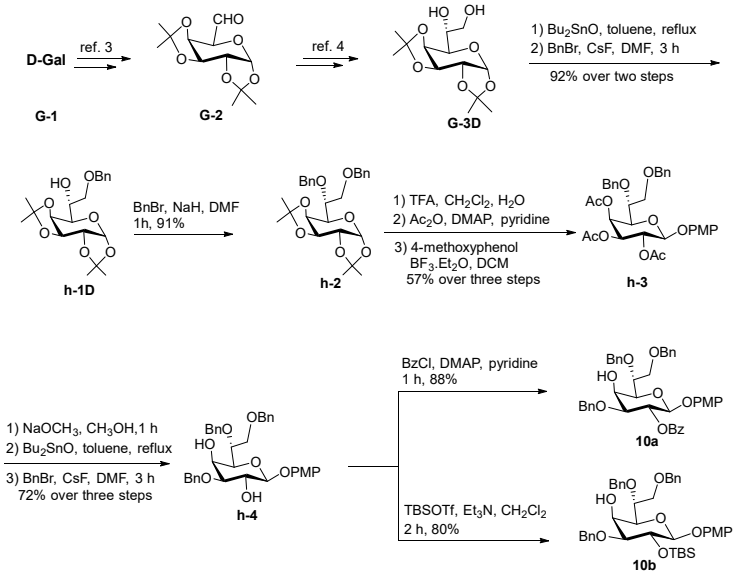
To a solution of **f-10**[2] (360 mg, 0.89 mmol) in acetonitrile (9 mL) was added triphenylphosphine (350 mg, 1.34 mmol). The reaction mixture was cooled to -10 °C, then a solution of iodine (270.2 mg, 1.07mmol) in DMF (1 ml) was added. The resulting mixture was warmed gradually to room temperature. The reaction mixture was stirred for 2 h at the same temperature at the end of which time TLC indicated the reaction was complete. The reaction mixture was concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (6:1, petroleum ether-EtOAc) to afford a colorless syrup (403 mg). To a solution of the obtained syrup in dry toluene (36 mL) were added tri-*n*-butyltin hydride (0.3 ml, 1.2 mmol) and azodiisobutyronitrile (13 mg, 0.08 mmol). The reaction mixture was heated under reflux for 3 h at the end of which time TLC indicated the reaction was complete. Then the reaction was cooled to room temperature and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford **f-11** as a colorless syrup (245 mg, 71% over two steps). **f-11**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -145.3 (*c* 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.03 (m, 10H), 5.38 (d, *J* = 2.2 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.49 (dd, *J* = 11.7, 1.5 Hz, 2H), 4.04-3.97 (m, 2H), 3.94-3.85 (m, 2H), 2.79-2.58 (m, 2H), 2.14 (d, *J* = 6.2 Hz, 1H), 1.32 (t, *J* = 7.4 Hz, 3H), 1.22 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.66, 137.33, 128.64, 128.56, 128.16, 128.14, 128.03, 128.02, 88.64, 87.49, 84.80, 84.16, 72.40, 72.09, 67.69, 25.47, 19.65, 15.08; HRMS (ESI): *m/z* calcd for $C_{22}H_{28}O_4S$ $[M+Na]^+$: 411.1606, found: 411.1605.

Ethyl 2,3-di-*O*-benzyl-5-*O*-(2-quinolinecarbonyl)-1-thio-β-D-fucofuranoside (9e)

To a solution of **f-11** (740 mg, 1.91 mmol) in dry CH_2Cl_2 (19 mL) were added 2-quinoline carboxylic acid (992 mg, 5.73 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride

(1.83 g, 9.55 mmol), and 4-dimethylaminopyridine (47 mg, 0.38 mmol). The reaction mixture was stirred for 1 h at room temperature and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (10:1, petroleum ether-EtOAc) to afford **9e** (876 mg, 88%) as a colorless syrup. **9e**: R_f = 0.50 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +107.9 (*c* 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.6 Hz, 1H), 8.06 (d, *J* = 1.0 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.79-7.72 (m, 1H), 7.67-7.59 (m, 1H), 7.31-7.16 (m, 10H), 5.54-5.46 (m, 2H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.58 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 4.37-4.32 (m, 1H), 4.02 (dd, *J* = 4.2, 1.7 Hz, 2H), 2.81-2.60 (m, 2H), 1.49 (d, *J* = 6.6 Hz, 3H), 1.33 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 148.12, 147.87, 137.49, 137.47, 137.20, 131.03, 130.21, 129.35, 128.58, 128.56, 128.51, 128.12, 128.10, 128.03, 127.96, 127.55, 121.33, 88.92, 87.40, 83.90, 82.59, 72.52, 72.15, 71.21, 25.54, 16.69, 15.23; HRMS (ESI): *m/z* calcd for $C_{32}H_{33}NO_5S$ $[M+H]^+$: 544.2157, found: 544.2156.

Synthesis of the D-Galhep*p* Acceptors 10a,b



7-*O*-Benzyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (h-1D)

To a solution of **G-3D** (500 mg, 1.72 mmol) in dry toluene (20 mL) was added Bu_2SnO (516 mg, 2.06 mmol). The reaction mixture was heated under reflux for 3 h then it was cooled to room temperature and concentrated *in vacuo*. To a solution of obtained residue in dry DMF (7 mL) were added benzyl bromide (0.24 mL, 2.06 mmol) and CsF (522.5 mg, 3.44 mmol). The reaction mixture was stirred for 3 h at 60 °C and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (5:1, petroleum ether-EtOAc) to afford **h-1D** (601 mg, 92% over two steps) as a white solid. **h-1D**: R_f = 0.3 (3:1, petroleum ether-EtOAc). Our spectroscopic data was in agreement of previously reported data.[5]

6,7-Di-*O*-benzyl-1,2:3,4-di-*O*-isopropylidene-D-*glycero*-α-D-*galacto*-heptopyranose (h-2)

To a solution of **h-1D** (235 mg, 0.62 mmol) in dry DMF (6 mL) were added benzyl bromide (0.22 mL, 1.86 mmol) and NaH (74.4 mg, 1.86 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was

warmed to room temperature and stirred for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (8:1, petroleum ether-EtOAc) to afford **h-2** (265 mg, 91%) as a colorless syrup. **h-2**: R_f = 0.3 (4:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -5.5 (*c* 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.27 (m, 10H), 5.52 (d, *J* = 4.9 Hz, 1H), 4.79 (d, *J* = 11.1 Hz, 1H), 4.68-4.56 (m, 4H), 4.52 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.29 (dd, *J* = 4.9, 2.3 Hz, 1H), 3.96 (dd, *J* = 9.2, 1.7 Hz, 1H), 3.86-3.78 (m, 2H), 3.65 (dd, *J* = 10.8, 5.3 Hz, 1H), 1.48 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.32 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 138.82, 128.35, 127.68, 127.46, 108.93, 108.78, 96.45, 76.84, 73.58, 73.40, 71.05, 70.79, 70.58, 70.15, 66.33, 26.16, 26.13, 25.17, 24.47; HRMS (ESI): *m/z* calcd for $C_{27}H_{34}O_7$ $[M+Na]^+$: 493.2203, found: 493.2198.

***p*-Methoxyphenyl 2,3,4-tri-*O*-acetyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (h-3)**

To a solution of **h-2** (718 mg, 1.5 mmol) in CH_2Cl_2 (15 mL) was added TFA (0.75 mL, 10.1 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 12 h at room temperature. Then the reaction mixture was neutralized with triethylamine and concentrated *in vacuo* to afford a residue which was directly used for the next step without further purification. To a solution of the obtained residue in pyridine (15 mL) were added acetic anhydride (1.4 mL, 15.0 mmol) and 4-dimethylaminopyridine (35 mg, 0.3 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc). To a solution of the obtained syrup (620 mg) in dry CH_2Cl_2 (14 mL) were added 4-methoxyphenol (410 mg, 3.3 mmol) and $BF_3{\cdot}Et_2O$ (0.7 mL, 5.6 mmol) at 0 °C. The resulting mixture was stirred for 2 h at room temperature. The mixture was neutralized with triethylamine, diluted with CH_2Cl_2, and then the mixture was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc) to afford **h-3** as a white solid (532 mg, 57% over three steps). **h-3**: R_f = 0.5 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -24.0 (*c* 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 5H), 7.31-7.24 (m, 5H), 6.92 (d, *J* = 9.1 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 5.72 (d, *J* = 3.4 Hz, 1H), 5.43 (dd, *J* = 10.4, 8.0 Hz, 1H), 5.13 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.94 (d, *J* = 8.0 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 4.36 (d, *J* = 11.2 Hz, 1H), 4.02 (d, *J* = 8.5 Hz, 1H), 3.82 (d, *J* = 9.1 Hz, 1H), 3.73 (s, 3H), 3.68-3.61 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.17, 170.09, 169.66, 155.56, 151.27, 138.32, 137.35, 128.65, 128.58, 128.08, 127.80, 127.46, 117.91, 114.69, 100.53, 74.54, 73.49, 71.95, 71.76, 71.51, 69.24, 67.28, 55.79, 20.93, 20.89, 20.75; HRMS (ESI): *m/z* calcd for $C_{34}H_{38}O_{11}$ $[M+Na]^+$: 645.2312, found: 645.2308.

***p*-Methoxyphenyl 3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (h-4)**

To solution of **h-3** (480 mg, 0.7 mmol) in MeOH (15 mL) was added $NaOCH_3$ (40.2 mg, 0.7 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 1 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin and filtrated. The filtrate was concentrated *in vacuo*, and the obtained residue was purified by silica gel column chromatography (10:1, CH_2Cl_2-MeOH). To a solution of the obtained syrup (340 mg) in dry toluene (20 mL) was added Bu_2SnO (204.4 mg, 0.8 mmol). The reaction mixture was heated under reflux for 3 h then it was cooled to room temperature

and concentrated *in vacuo*. To a solution of obtained residue in dry DMF (7 mL) were added benzyl bromide (0.1 mL, 0.8 mmol) and CsF (207.8 mg, 1.4 mmol). The reaction mixture was stirred for 3 h at 60 °C and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (1:1, petroleum ether-EtOAc) to afforded **h-4** (295 mg, 72% over three steps) as a colorless syrup. **h-4**: R_f = 0.5 (2:1, CH_2Cl_2-MeOH); $[\alpha]_D^{25}$ -13.1 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 15H), 6.96 (d, *J* = 9.1 Hz, 2H), 6.70 (d, *J* = 9.1 Hz, 2H), 4.76(s, 2H), 4.75 (d, *J* = 7.8 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.60 (d, *J* = 5.8 Hz, 1H), 4.57 (d, *J* = 6.6 Hz, 1H), 4.47 (d, *J* = 12.3 Hz, 1H), 4.24 (s, 1H), 4.04 (t, *J* = 8.6 Hz, 1H), 3.95 (dt, *J* = 9.0, 3.4, 2.3 Hz, 1H), 3.74 (dd, *J* = 3.8, 1.2 Hz, 1H), 3.73-3.71 (m, 4H), 3.60 (dd, *J* = 10.6, 3.4 Hz, 1H), 3.52 (dd, *J* = 9.4, 3.3 Hz, 1H), 2.47 (s, 1H), 2.37 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.31, 151.23, 138.45, 138.27, 137.87, 128.81, 128.53, 128.51, 128.30, 128.26, 128.13, 127.96, 127.68, 127.43, 118.16, 114.53, 102.03, 80.75, 75.53, 73.37, 72.86, 72.61, 72.36, 70.92, 68.39, 65.26, 55.74; HRMS (ESI): *m/z* calcd for $C_{35}H_{38}O_8$ $[M+Na]^+$: 609.2465, found: 609.2464.

_p_-Methoxyphenyl 2-_O_-benzoyl-3,6,7-tri-_O_-benzyl-D-_glycero_-β-D-_galacto_-heptopyranoside (10a)

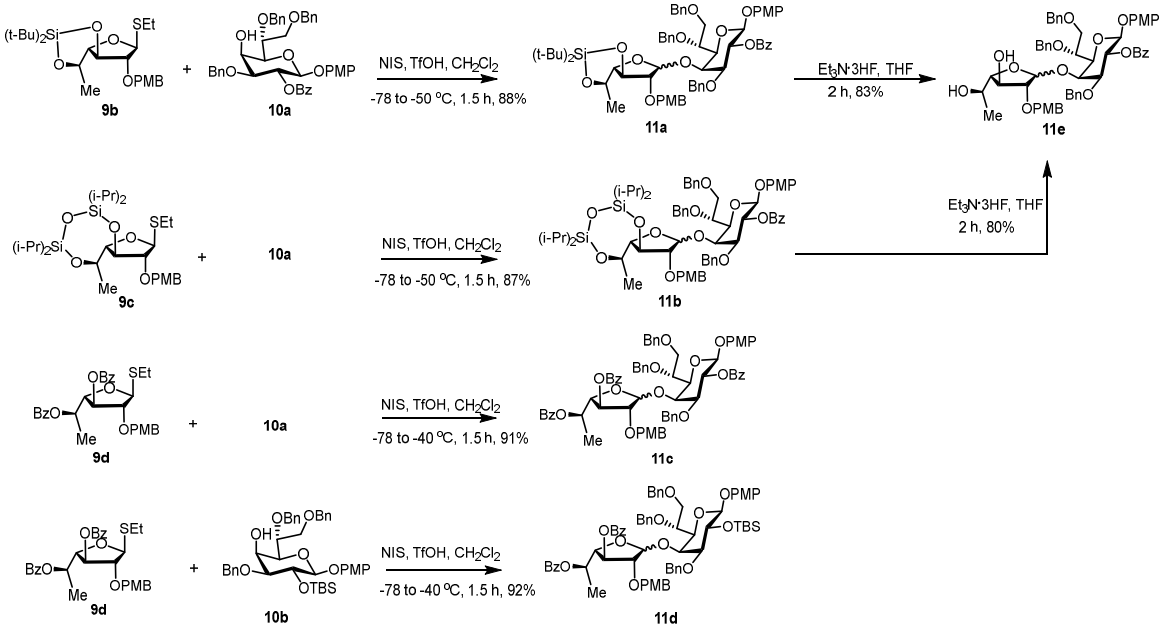
To a solution of **h-4** (450 mg, 0.8 mmol) in pyridine (8 mL) were added benzoyl chloride (0.2 mL, 1.5 mmol) and 4-dimethylaminopyridine (19 mg, 0.2 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc) to afford **10a** as a colorless syrup (486 mg, 88%). **10a**: R_f = 0.4 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +33.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.40-7.27 (m, 10H), 7.23-7.13 (m, 5H), 6.85 (d, *J* = 9.1 Hz, 2H), 6.62 (d, *J* = 9.1 Hz, 2H), 5.71 (dd, *J* = 9.7, 8.1 Hz, 1H), 4.93 (d, *J* = 8.1 Hz, 1H), 4.71 (dd, *J* = 13.8, 11.9 Hz, 2H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.35 (s, 1H), 4.06-4.02 (m, 1H), 3.82 (d, *J* = 9.1 Hz, 1H), 3.77 (dd, *J* = 10.7, 2.2 Hz, 1H), 3.74-3.64 (m, 5H), 2.57 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.56, 155.31, 151.50, 138.49, 138.32, 137.26, 133.22, 130.08, 129.99, 128.60, 128.55, 128.52, 128.49, 128.29, 128.15, 128.10, 127.98, 127.68, 127.46, 118.29, 114.46, 100.77, 78.60, 75.61, 73.43, 72.97, 72.55, 71.59, 71.22, 68.37, 65.06, 55.72; HRMS (ESI): *m/z* calcd for $C_{42}H_{42}O_9$ $[M+Na]^+$: 777.2346, found: 777.2374.

_p_-Methoxyphenyl 2-_O-tert_-butyldimethylsilyl-3,6,7-tri-_O_-benzyl-D-_glycero_-β-D-_galacto_-heptopyranoside (10b)

To a solution of **h-4** (967 mg, 1.6 mmol) in dry CH_2Cl_2 (16 mL) were added TBSOTf (0.4 ml, 1.8 mmol) and triethylamine (0.3 mL, 2.5 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature at the end of which time TLC indicated the reaction was completed. The reaction mixture was quenched with MeOH. The resulting mixture was concentrated *in vacuo.* The crude material was purified by column chromatography (10:1, petroleum ether-EtOAc) to afford **10b** as a colorless syrup (920 mg, 80%); **10b**: R_f = 0.4 (6:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -33.1 (*c* 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.18 (m, 15H), 6.93 (d, *J* = 9.1 Hz, 2H), 6.69 (d, *J* = 9.1 Hz, 2H), 4.78-4.71 (m, 2H), 4.69-4.62 (m, 2H), 4.62-4.55 (m, 2H), 4.48 (d, *J* = 12.3 Hz, 1H), 4.17 (d, *J* = 3.3 Hz, 1H), 3.99 (dd, *J* = 9.1, 7.6 Hz,

1H), 3.92 (dt, *J* = 9.3, 2.7 Hz, 1H), 3.76-3.69 (m, 5H), 3.60 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.48 (dd, *J* = 9.1, 3.3 Hz, 1H), 0.90 (s, 9H), 0.16 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.88, 151.40, 138.60, 138.42, 138.02, 128.68, 128.49, 128.27, 128.19, 128.13, 127.89, 127.62, 127.40, 117.45, 114.51, 101.83, 82.52, 75.66, 73.37, 72.85, 72.56, 72.22, 71.59, 68.52, 65.23, 55.73, 26.06, 18.39, -4.08, -4.26; HRMS (ESI): *m/z* calcd for $C_{41}H_{52}O_8Si$ [M+Na]$^+$: 723.3329, found: 723.3332.

Glycosylation of D-Fuc*f* Donors 9b-d



***p*-Methoxyphenyl 2-*O*-*p*-methoxybenzyl-3,5-*O*-di-*tert*-butylsilylene-α/β-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (11a)**

A mixture of donor **9b** (30 mg, 64 μmol), acceptor **10a** (37 mg, 53 μmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (0.6 mL) were stirred for 15 minutes at room temperature. The mixture was cooled to -78 °C, then NIS (21.6 mg, 96 μmol) and TfOH (0.6 μl, 6.4 μmol) were added. The reaction mixture was gradually warmed to -50 °C and stirred for 1.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (15:1, petroleum ether-EtOAc) to afford an inseparable mixture of α/β isomers **11a** (51 mg, α/β = 1:1.5, 88%) as a colorless syrup. **11a**: R_f = 0.4 (8:1, petroleum ether-EtOAc); Selected analytical data for α-isomer of **11a**:^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 8.5 Hz, 2H), 5.77 (dd, *J* = 10.0, 8.2 Hz, 1H), 4.93 (d, *J* = 2.3 Hz, 1H), 1.48 (d, *J* = 6.4 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 165.25, 159.33, 155.09, 151.79, 138.79, 138.58, 137.94, 132.93, 117.91, 114.44, 113.76, 104.29, 101.09, 81.19, 78.44, 72.57, 71.79, 71.39, 71.04, 70.77, 66.71, 55.72, 55.37, 21.50, 20.76, 16.95. Selected analytical data for β-isomer of **11a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 9.0 Hz, 2H), 5.94 (dd, *J* = 9.8, 8.2 Hz, 1H), 5.62 (d, *J* = 2.4 Hz, 1H), 1.18 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.25, 159.03, 155.19, 151.69, 138.51, 138.31, 137.36, 133.10, 117.83, 114.44, 113.76, 108.26, 100.89, 88.52, 80.19, 72.73, 71.86, 71.50, 70.58, 70.27, 66.86, 55.70, 55.39, 21.50, 20.74, 16.70; HRMS (ESI): *m/z* calcd for $C_{64}H_{76}O_{14}Si$ [M+Na]$^+$: 1119.4902, found: 1119.4926.

***p*-Methoxyphenyl 2-*O*-*p*-methoxybenzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α/β-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (11b)**

A mixture of fucose donor **9c** (25 mg, 43 μmol), acceptor **10a** (25 mg, 36 μmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (0.4 mL) were stirred for 15 minutes at room temperature. The mixture was cooled to -78 °C and then NIS (14.5 mg, 65 μmol) and TfOH (0.4 μl, 4.3 μmol) were added. The reaction mixture was gradually warmed to -50 °C and stirred for 1.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (20:1, petroleum ether-EtOAc) to afford **11b** (38 mg, β/α > 15:1, 87%) as colorless syrups. **11b-β**: R_f = 0.4 (10:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +52.8 (*c* 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.97 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41-7.27 (m, 12H), 7.20-7.03 (m, 5H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 9.1 Hz, 2H), 5.91 (dd, *J* = 10.1, 8.0 Hz, 1H), 5.57 (d, *J* = 2.5 Hz, 1H), 4.95 (d, *J* = 8.0 Hz, 1H), 4.90 (d, *J* = 11.6 Hz, 1H), 4.73 (d, *J* = 11.1 Hz, 1H), 4.71-4.66 (m, 3H), 4.63 (d, *J* = 12.1 Hz, 1H), 4.55-4.45 (m, 3H), 4.32-4.22 (m, 2H), 4.12-4.08 (m, 2H), 3.97-3.86 (m, 2H), 3.82-3.68 (m, 9H), 1.26 (d, *J* = 6.7 Hz, 3H), 1.11-1.06 (m, 16H), 1.05-1.01 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.27, 158.84, 155.21, 151.73, 138.72, 138.60, 137.30, 133.08, 131.13, 130.24, 129.94, 129.44, 128.51, 128.45, 128.41, 128.22, 128.04, 127.93, 127.83, 127.77, 127.59, 127.37, 118.18, 114.42, 113.51, 107.37, 101.11, 88.96, 83.06, 79.90, 74.55, 73.83, 73.36, 72.26, 72.06, 71.53, 70.98, 68.44, 64.81, 55.69, 55.35, 19.48, 17.65, 17.61, 17.51, 17.33, 17.25, 17.23, 13.75, 13.38, 13.00, 12.65; HRMS (ESI): *m/z* calcd for $C_{68}H_{86}O_{15}Si_2$ $[M+Na]^+$: 1221.5403, found: 1221.5408.

***p*-Methoxyphenyl 2-*O*-*p*-methoxybenzyl-3,5-di-*O*-benzoyl-α/β-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (11c)**

A mixture of fucose donor **9d** (233 mg, 0.43 mmol), acceptor **10a** (250 mg, 0.36 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (4 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (146 mg, 0.65 mmol) and TfOH (4 μl, 43 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **11c** (381 mg, α/β = 4:1, 91%) as colorless syrups. **11c-α**: R_f = 0.39 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +37.5 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 6.8 Hz, 2H), 7.88 (d, *J* = 6.6 Hz, 2H), 7.59-7.49 (m, 2H), 7.44-7.36 (m, 4H), 7.32 (d, *J* = 4.6 Hz, 4H), 7.30-7.27 (m, 2H), 7.25-7.22 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 4H), 7.14-7.06 (m, 4H), 6.87 (d, *J* = 9.1 Hz, 2H), 6.65 (dd, *J* = 8.9, 6.8 Hz, 4H), 6.13 (t, *J* = 7.0 Hz, 1H), 5.86 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.44-5.35 (m, 1H), 5.24 (d, *J* = 4.8 Hz, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.68 (dd, *J* = 12.0, 8.4 Hz, 2H), 4.57 (d, *J* = 12.2 Hz, 1H), 4.48 (t, *J* = 11.9 Hz, 2H), 4.44-4.37 (m, 3H), 4.32-4.25 (m, 2H), 4.23-4.14 (m, 2H), 3.81 (d, *J* = 9.2 Hz, 1H), 3.70 (s, 3H), 3.68-3.61 (m, 4H), 3.55 (dd, *J* = 11.0, 2.4 Hz, 1H), 1.64 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.06, 165.87, 154.78, 151.29, 138.22, 137.98, 137.96, 133.38, 132.79, 130.06, 129.93, 129.69, 129.57, 128.63, 128.59, 128.47, 128.31, 128.29, 127.95, 127.91, 127.83, 127.75, 127.58, 117.16, 114.52, 103.59, 102.01, 81.16, 79.59, 76.58, 76.35, 75.40, 74.93, 73.38, 72.34, 72.19, 71.80,

71.11, 70.71, 66.56, 55.76, 26.05, 18.36, 14.58, -4.20, -4.21; HRMS (ESI): *m/z* calcd for $C_{70}H_{68}O_{16}$ $[M+Na]^+$: 1187.4405, found: 1187.4407. **11c-β**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -17.7 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 2H), 8.02 (d, *J* = 7.3 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.52-7.42 (m, 3H), 7.45-7.34 (m, 4H), 7.33 (t, *J* = 4.0 Hz, 8H), 7.29 (d, *J* = 5.3 Hz, 9H), 7.23-7.06 (m, 10H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 5.87 (dd, *J* = 10.0, 8.0 Hz, 1H), 5.78 (s, 1H), 5.53-5.43 (m, 2H), 5.00 (d, *J* = 8.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.67-4.58 (m, 3H), 4.58-4.48 (m, 5H), 4.51-4.42 (m, 5H), 4.08 (d, *J* = 9.0 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.83-3.74 (m, 5H), 3.75 (s, 4H), 3.70 (s, 4H), 3.67 (d, *J* = 8.6 Hz, 4H), 1.41 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.97, 165.95, 165.33, 159.25, 155.16, 151.77, 138.49, 138.37, 137.31, 133.31, 133.15, 132.78, 130.24, 130.19, 130.17, 129.93, 129.82, 129.79, 129.75, 129.70, 128.60, 128.57, 128.50, 128.48, 128.20, 128.10, 128.08, 127.97, 127.79, 127.66, 127.37, 117.81, 114.48, 113.88, 108.05, 100.85, 86.84, 85.32, 79.85, 77.26, 76.01, 73.34, 72.77, 72.33, 71.83, 71.75, 71.63, 70.62, 67.20, 55.73, 55.31, 16.25; HRMS (ESI): *m/z* calcd for $C_{70}H_{68}O_{16}$ $[M+Na]^+$: 1187.4405, found: 1187.4404.

***p*-Methoxyphenyl 2-*O*-*p*-methoxybenzyl-3,5-di-*O*-benzoyl-α/β-D-fucofuranosyl-(1→4)-2-*O*-*tert*-butyldimethylsilyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (11d)**

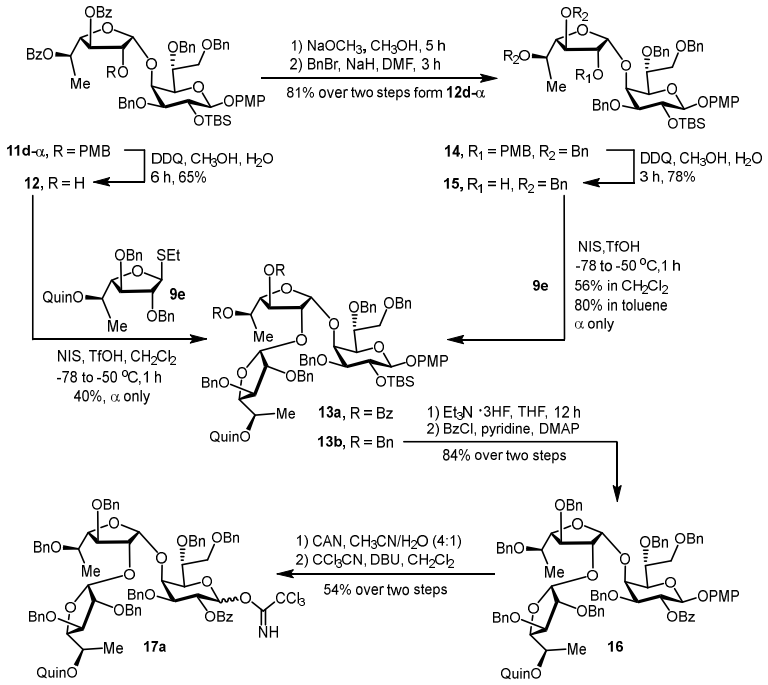
A mixture of fucose donor **9d** (239 mg, 0.45 mmol), acceptor **10b** (260 mg, 0.37 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (5 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (153 mg, 0.68 mmol) and TfOH (5 μl, 45 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 1.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **11d** (445 mg, α/β = 7:1, 92%) as colorless syrups. **11d-α**: R_f = 0.59 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +2.8 (*c* 0.39, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 6.8, 4.9 Hz, 4H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 6.3 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.30-7.18 (m, 13H), 7.14 (d, *J* = 6.6 Hz, 2H), 7.08-7.01 (m, 4H), 6.85-6.79 (m, 2H), 6.68-6.61 (m, 2H), 6.58-6.51 (m, 2H), 5.97 (t, *J* = 6.8 Hz, 1H), 5.41-5.31 (m, 1H), 5.15 (d, *J* = 4.9 Hz, 1H), 4.72 (d, *J* = 7.6 Hz, 1H), 4.68 (d, *J* = 12.8 Hz, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 4.53 (dd, *J* = 11.7, 6.1 Hz, 2H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.33 (d, *J* = 4.2 Hz, 1H), 4.30 (d, *J* = 3.7 Hz, 1H), 4.24-4.18 (m, 2H), 4.15 (d, *J* = 11.8 Hz, 1H), 4.13-4.07 (m, 3H), 3.71-3.66 (m, 4H), 3.58 (s, 3H), 3.52 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.44 (dd, *J* = 10.9, 2.4 Hz, 1H), 3.38 (dd, *J* = 9.5, 2.8 Hz, 1H), 1.55 (d, *J* = 6.4 Hz, 3H), 0.77 (s, 9H), -0.01 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.11, 165.44, 159.30, 154.55, 151.54, 138.79, 138.60, 138.41, 133.36, 132.58, 130.18, 130.00, 129.86, 129.75, 129.72, 128.51, 128.49, 128.34, 128.31, 128.26, 127.62, 127.59, 127.46, 127.42, 127.39, 117.04, 114.44, 113.74, 104.01, 101.89, 81.88, 81.83, 81.01, 77.36, 76.00, 75.27, 74.99, 73.26, 72.64, 72.34, 71.81, 71.14, 70.28, 66.69, 55.76, 55.28, 26.05, 18.35, 15.10, -4.24; HRMS (ESI): *m/z* calcd for $C_{69}H_{78}O_{15}Si$ $[M+Na]^+$: 1197.5008, found: 1197.5013. **11d-β**: R_f = 0.6 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +29.9 (*c* 0.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.9 Hz, 2H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.52-7.45 (m, 1H), 7.42-7.37 (m, 3H), 7.35-7.31 (m, 6H), 7.31-7.23 (m, 14H), 7.18-7.12 (m, 4H), 6.97 (d, *J* = 9.1 Hz, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 9.1 Hz, 2H), 5.79 (s, 1H), 5.48 (dd, *J* = 4.3, 1.6 Hz, 1H), 5.46-5.38 (m, 1H), 4.79 (d, *J* = 7.5 Hz, 1H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.63-4.56 (m, 2H), 4.55-4.49 (m, 3H), 4.48-4.42 (m, 3H), 4.31 (d, *J* = 1.6 Hz, 1H), 4.07 (dd, *J* = 9.4, 7.5 Hz, 1H), 4.02 (dt, *J* = 9.1, 2.4 Hz, 1H), 3.82-3.78 (m, 1H), 3.77 (s, 3H), 3.76-3.73 (m, 4H),

3.63 (dd, *J* = 10.7, 2.8 Hz, 1H), 3.50 (dd, *J* = 9.4, 2.5 Hz, 1H), 1.36 (d, *J* = 6.5 Hz, 3H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.94, 159.29, 154.72, 151.67, 138.58, 138.50, 137.78, 133.33, 132.79, 130.22, 130.04, 129.84, 129.81, 129.70, 129.47, 128.64, 128.56, 128.50, 128.43, 128.41, 128.20, 127.97, 127.90, 127.67, 127.62, 127.32, 117.10, 114.49, 113.88, 107.83, 102.03, 87.30, 84.79, 83.21, 77.30, 76.07, 73.37, 73.26, 72.41, 71.97, 71.89, 71.64, 71.62, 70.51, 67.26, 55.74, 55.36, 26.05, 18.36, 16.14, -4.12, -4.15; HRMS (ESI): *m/z* calcd for $C_{69}H_{78}O_{15}Si$ $[M+Na]^+$: 1197.5008, found: 1197.5007.

_p_-Methoxyphenyl 2-_O_-_p_-methoxybenzyl-α/β-D-fucofuranosyl-(1→4)-2-_O_-benzoyl-3,6,7-tri-_O_-benzyl-D-_glycero_-β-D-_galacto_-heptopyranoside (11e)

To a solution of **11a** (318 mg, 0.29 mmol) in THF (3 mL) was added triethylamine trihydrofluoride (30 μL, 0.58 mmol) slowly at 0 °C, and the resulting mixture was stirred for 2 h at the same temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford compound **11e** as colorless syrups (246 mg, α/β = 1:1.5, 83%); According to the same method above, **11e** was obtained by **11b** in 80% yield. **11e-α**: R_f = 0.35 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +27.8 (*c* 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.39-7.27 (m, 9H), 7.23-7.09 (m, 8H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.2 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 5.74 (dd, *J* = 10.2, 7.9 Hz, 1H), 4.95 (d, *J* = 4.6 Hz, 1H), 4.91 (d, *J* = 7.8 Hz, 1H), 4.85 (d, *J* = 11.5 Hz, 1H), 4.82-4.75 (m, 2H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 2H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.37 (d, *J* = 12.2 Hz, 1H), 4.29-4.23 (m, 2H), 4.18 (d, *J* = 9.3 Hz, 1H), 4.09-3.98 (m, 2H), 3.89 (t, *J* = 9.3 Hz, 1H), 3.74 (d, *J* = 9.2 Hz, 1H), 3.71-3.59 (m, 8H), 3.48 (dd, *J* = 11.1, 2.3 Hz, 1H), 1.15 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.04, 159.32, 155.20, 151.64, 138.44, 138.34, 136.94, 133.02, 130.78, 130.24, 130.16, 129.64, 128.64, 128.54, 128.36, 128.19, 128.09, 127.91, 127.87, 127.73, 127.53, 118.09, 114.48, 113.89, 103.94, 100.67, 86.36, 83.97, 78.16, 75.05, 74.63, 73.74, 73.36, 72.79, 71.69, 71.30, 71.21, 70.48, 66.33, 55.76, 55.35, 20.11; HRMS (ESI): *m/z* calcd for $C_{56}H_{60}O_{14}$ $[M+Na]^+$: 979.3881, found: 979.3881. **11e-β**: R_f = 0.3 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -46.0 (*c* 0.39, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.42-7.24 (m, 11H), 7.21-7.10 (m, 6H), 6.87 (t, *J* = 8.5 Hz, 4H), 6.64 (d, *J* = 8.8 Hz, 2H), 5.76 (dd, *J* = 10.0, 8.0 Hz, 1H), 5.64 (s, 1H), 4.96 (d, *J* = 8.0 Hz, 1H), 4.71-4.64 (m, 3H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.56 (d, *J* = 2.7 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 11.3 Hz, 1H), 4.38 (d, *J* = 11.3 Hz, 1H), 4.17 (s, 1H), 4.07-3.98 (m, 2H), 3.97-3.92 (m, 1H), 3.91-3.83 (m, 3H), 3.81-3.67 (m, 7H), 1.19 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.41, 159.50, 155.31, 151.52, 138.37, 138.36, 137.14, 133.27, 130.04, 130.00, 129.94, 129.33, 128.61, 128.56, 128.12, 128.10, 128.00, 127.92, 127.77, 127.50, 118.05, 114.49, 114.02, 107.39, 100.97, 91.25, 87.02, 79.94, 76.71, 75.97, 73.42, 72.74, 72.72, 71.89, 71.72, 71.65, 71.60, 68.14, 67.07, 55.73, 55.38, 19.43; HRMS (ESI): *m/z* calcd for $C_{56}H_{60}O_{14}$ $[M+Na]^+$: 979.3881, found: 979.3881.

Synthesis of the Left Trisaccharide Donor 17a



***p*-Methoxyphenyl 3,5-di-*O*-benzoyl-α-D-fucofuranosyl-(1→4)-2-*O*-*tert*-butyldimethylsilyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (12)**

To a solution of **11d-α** (940 mg, 0.8 mmol) in MeOH (8 mL) were added DDQ (363 mg, 1.6 mmol) and 2 drops of water at 0 ºC. The mixture was stirred under nitrogen for 2 h at room temperature. The reaction mixture was diluted with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc) to afford **12** as a white solid (548 mg, 65%). **12**: R_f = 0.5 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +4.5 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 3H), 7.34-7.26 (m, 13H), 7.13 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 9.1 Hz, 2H), 6.77-6.71 (m, 2H), 5.71 (t, *J* = 7.3 Hz, 1H), 5.46-5.36 (m, 1H), 5.06 (d, *J* = 5.0 Hz, 1H), 4.79 (d, *J* = 7.5 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.69-4.61 (m, 2H), 4.57 (d, *J* = 12.1 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.32 (d, *J* = 2.8 Hz, 1H), 4.23 (dd, *J* = 7.2, 4.5 Hz, 2H), 4.09 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.98 (dt, *J* = 9.0, 2.5 Hz, 1H), 3.81 (dd, *J* = 10.8, 2.2 Hz, 1H), 3.78 (d, *J* = 8.9 Hz, 1H), 3.75 (s, 3H), 3.61 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.44 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.29 (d, *J* = 9.8 Hz, 1H), 1.55 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 9H), 0.12 (s, 3H), 0.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.06, 165.87, 154.78, 151.29, 138.22, 137.98, 137.96, 133.38, 132.79, 130.06, 129.93, 129.69, 129.57, 128.63, 128.59, 128.47, 128.31, 128.29, 127.95, 127.91, 127.83, 127.75, 127.58, 117.16, 114.52, 103.59, 102.01, 81.16, 79.59, 76.58, 76.35, 75.40, 74.93, 73.38, 72.34, 72.19, 71.80, 71.11, 70.71, 66.56, 55.76, 26.05, 18.36, 14.58, -4.20, -4.21; HRMS (ESI): *m/z* calcd for $C_{61}H_{70}O_{14}Si$ $[M+Na]^+$: 1077.4433, found: 1077.4435.

***p*-Methoxyphenyl 2-*O*-*p*-methoxybenzyl-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-*tert*-butyldimethylsilyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (14)**

To a solution of **11d-α** (352 mg, 0.3 mmol) in MeOH (3 mL) was added $NaOCH_3$ (32 mg, 0.6 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred

for 5 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (4:1, petroleum ether-EtOAc) to afforded a white solid. To a solution of the white solid (261 mg, 0.27 mmol) in dry DMF (3 mL) were added benzyl bromide (0.26 mL, 2.18 mmol) and NaH (87.2 mg, 2.18 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (8:1, petroleum ether-EtOAc) to afford **14** (279 mg, 81% over two steps) as a colorless syrup. **14**: R_f = 0.4 (5:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +21.7 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.04 (m, 32H), 6.95 (d, *J* = 9.1 Hz, 2H), 6.73 (d, *J* = 3.4 Hz, 2H), 6.71 (d, *J* = 3.8 Hz, 2H), 5.12 (d, *J* = 4.5 Hz, 1H), 4.78 (d, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.71-4.65 (m, 1H), 4.65-4.59 (m, 3H), 4.59-4.50 (m, 4H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 12.2 Hz, 1H), 4.33 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 3.3 Hz, 1H), 4.25-4.21 (m, 1H), 4.15 (dd, *J* = 9.5, 7.4 Hz, 1H), 4.06-3.99 (m, 2H), 3.96 (dd, *J* = 6.6, 5.2 Hz, 1H), 3.82-3.71 (m, 5H), 3.70 (s, 3H), 3.65 (dd, *J* = 10.9, 1.9 Hz, 1H), 3.52 (dd, *J* = 10.8, 2.6 Hz, 1H), 3.42 (dd, *J* = 9.5, 2.8 Hz, 1H), 1.29 (d, *J* = 6.4 Hz, 3H), 0.87 (s, 9H), 0.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.24, 154.59, 151.60, 139.20, 138.49, 138.40, 138.36, 130.41, 129.83, 128.52, 128.44, 128.34, 128.20, 128.10, 127.97, 127.75, 127.73, 127.70, 127.67, 127.44, 127.37, 117.13, 114.44, 113.77, 102.62, 102.01, 83.25, 82.75, 81.50, 81.32, 76.15, 75.00, 73.60, 73.25, 72.59, 72.44, 72.09, 71.81, 71.61, 71.08, 70.40, 66.69, 55.74, 55.32, 26.07, 25.97, 18.39, 15.60, 0.14, -4.06, -4.10; HRMS (ESI): *m/z* calcd for $C_{69}H_{82}O_{13}Si$ $[M+Na]^+$: 1169.5423, found: 1169.5425.

_p_-Methoxyphenyl 3,5-di-_O_-benzyl-α-D-fucofuranosyl-(1→4)-2-_O_-_tert_-butyldimethylsilyl-3,6,7-tri-_O_-benzyl-D-_glycero_-β-D-_galacto_-heptopyranoside (15)

To a solution of **14** (306 mg, 0.27 mmol) in MeOH (3 mL) were added DDQ and 2 drops of water (122 mg, 0.54 mmol) at 0 ºC. The mixture was stirred under nitrogen for 3 h at room temperature. The reaction mixture was diluted with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc) to afford **15** as a white solid (216 mg, 78%). **15**: R_f = 0.5 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +3.9 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.35-7.27 (m, 18H), 7.26-7.21 (m, 5H), 6.94 (d, *J* = 9.1 Hz, 2H), 6.73 (d, *J* = 9.1 Hz, 2H), 4.99 (d, *J* = 4.9 Hz, 1H), 4.82-4.71 (m, 3H), 4.67-4.54 (m, 6H), 4.44 (dd, *J* = 11.8, 2.9 Hz, 2H), 4.34 (d, *J* = 2.9 Hz, 1H), 4.12 (s, 1H), 4.03 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.94 (t, *J* = 6.1 Hz, 1H), 3.91-3.86 (m, 2H), 3.86-3.76 (m, 3H), 3.75 (s, 4H), 3.61 (dd, *J* = 10.9, 2.5 Hz, 1H), 3.41 (dd, *J* = 9.5, 2.8 Hz, 1H), 1.23 (d, *J* = 6.4 Hz, 3H), 0.89 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.85, 151.35, 139.11, 138.23, 138.07, 137.80, 128.66, 128.58, 128.45, 128.36, 128.28, 128.17, 128.02, 128.00, 127.96, 127.83, 127.74, 127.64, 127.58, 127.55, 127.39, 117.24, 114.53, 103.72, 102.14, 83.36, 83.03, 80.78, 77.97, 76.45, 75.07, 73.83, 73.39, 72.36, 72.04, 71.82, 71.38, 70.88, 70.80, 66.54, 55.75, 26.07, 18.40, 15.28, -4.04, -4.12; HRMS (ESI): *m/z* calcd for $C_{61}H_{74}O_{12}Si$ $[M+Na]^+$: 1049.4848, found: 1049.4841.

***p*-Methoxyphenyl 2,3-di-*O*-benzyl-5-*O*-(2-quinolinecarbonyl)-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzoyl-α-D-fucofuranosyl-(1→4)-2-*O*-*tert*-butyldimethylsilyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (13a)**

A mixture of fucose donor **9e** (239 mg, 0.44 mmol), acceptor **12** (390 mg, 0.37 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (5 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (158 mg, 0.7 mmol) and TfOH (5 μl, 44 μmol) were added. The reaction mixture was gradually warmed to -50 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **13a** (227 mg, 40%) as a colorless syrup. **13a**: R_f = 0.55 (3:1, petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.02-7.93 (m, 2H), 7.83-7.78 (m, 1H), 7.77-7.69 (m, 5H), 7.65-7.59 (m, 1H), 7.47-7.40 (m, 3H), 7.33-7.27 (m, 12H), 7.24-7.15 (m, 9H), 7.15-7.09 (m, 3H), 7.07-6.98 (m, 4H), 6.91 (d, *J* = 9.1 Hz, 2H), 6.60 (d, *J* = 9.1 Hz, 2H), 6.03 (t, *J* = 6.8 Hz, 1H), 5.54-5.40 (m, 2H), 5.25 (d, *J* = 4.0 Hz, 1H), 5.21 (d, *J* = 4.4 Hz, 1H), 4.81 (d, *J* = 7.5 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.60-4.49 (m, 3H), 4.44 (dd, *J* = 6.8, 4.3 Hz, 1H), 4.40-4.30 (m, 3H), 4.27-4.15 (m, 5H), 4.12-4.04 (m, 2H), 4.01 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.79 (d, *J* = 9.5 Hz, 1H), 3.63 (s, 2H), 3.60 (s, 3H), 3.44 (dd, *J* = 9.4, 3.0 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 0.84 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.85, 164.55, 164.49, 154.39, 151.53, 149.14, 147.65, 138.50, 138.36, 138.22, 138.15, 137.68, 136.76, 132.78, 132.53, 131.02, 130.25, 130.14, 129.86, 129.72, 129.24, 128.60, 128.57, 128.55, 128.53, 128.48, 128.27, 128.24, 128.10, 128.00, 127.72, 127.70, 127.65, 127.57, 127.53, 127.40, 127.33, 121.57, 116.68, 114.40, 103.67, 101.74, 98.85, 84.47, 81.17, 81.07, 80.45, 79.12, 75.22, 74.80, 74.16, 74.13, 73.28, 73.12, 72.84, 71.97, 71.83, 71.80, 71.21, 69.93, 66.27, 55.52, 26.06, 18.33, 15.95, 14.27, -4.22, -4.24; HRMS (ESI): *m/z* calcd for $C_{91}H_{97}NO_{19}Si$ $[M+Na]^+$: 1558.6422, found: 1558.6411.

***p*-Methoxyphenyl 2,3-di-*O*-benzyl-5-*O*-(2-quinolinecarbonyl)-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-*tert*-butyldimethylsilyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (13b)**

Protocol a: A mixture of fucose donor **9e** (85 mg, 0.16 mmol), acceptor **15** (134 mg, 0.13 mmol), and freshly activated 4 Å molecular sieves in Cl_2Cl_2 (13 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (54 mg, 0.24 mmol) and TfOH (3 μl, 32 μmol) were added. The reaction mixture was gradually warmed to -50 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **13b** (109 mg, 56%) as a colorless syrup. **13b**: R_f = 0.5 (3:1, petroleum ether-EtOAc);

Protocol b: A mixture of fucose donor **9e** (175 mg, 0.32 mmol), acceptor **15** (278 mg, 0.27 mmol), and freshly activated 4 Å molecular sieves in toluene (25 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C and then NIS (108 mg, 0.48 mmol) and TfOH (7 μl, 64 μmol) were added. The reaction mixture was gradually warmed to -20 °C and stirred for 1 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **13b** (326 mg, 80%) as a colorless syrup. **13b**:

R_f = 0.5 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +32.7 (*c* 0.50, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 8.11-7.98 (m, 3H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.1 Hz, 2H), 7.35-7.27 (m, 8H), 7.27-7.23 (m, 9H), 7.22-7.16 (m, 6H), 7.15-7.07 (m, 8H), 7.03 (d, *J* = 6.7 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 5.60 (d, *J* = 3.9 Hz, 1H), 5.56-5.47 (m, 1H), 5.13 (d, *J* = 4.3 Hz, 1H), 4.81 (d, *J* = 7.4 Hz, 1H), 4.77-4.69 (m, 3H), 4.61-4.52 (m, 4H), 4.44-4.37 (m, 5H), 4.32-4.20 (m, 7H), 4.16-4.09 (m, 3H), 3.98 (t, *J* = 5.4 Hz, 1H), 3.79 (d, *J* = 9.6 Hz, 1H), 3.76-3.72 (m, 1H), 3.71-3.66 (m, 2H), 3.64 (s, 3H), 3.43 (dd, *J* = 9.4, 3.1 Hz, 1H), 1.49 (d, *J* = 6.4 Hz, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 0.86 (s, 9H), 0.17 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.75, 154.53, 151.81, 148.64, 147.75, 139.21, 138.83, 138.64, 138.48, 138.35, 138.09, 137.88, 137.13, 131.09, 130.07, 129.31, 128.67, 128.63, 128.57, 128.55, 128.50, 128.45, 128.35, 128.25, 128.19, 128.15, 128.13, 128.06, 127.85, 127.78, 127.77, 127.66, 127.59, 127.55, 127.44, 127.36, 127.33, 121.37, 116.79, 114.55, 104.11, 102.12, 98.85, 84.96, 83.86, 81.89, 81.47, 81.45, 80.72, 80.45, 75.77, 74.96, 74.66, 73.39, 72.94, 72.89, 72.50, 72.24, 71.83, 71.44, 70.98, 70.19, 66.29, 55.68, 26.19, 18.45, 16.43, 15.34, -4.02, -4.04; HRMS (ESI): *m/z* calcd for $C_{91}H_{101}NO_{17}Si$ $[M+Na]^+$: 1530.6737, found: 1530.6638.

_p_-Methoxyphenyl 2,3-di-_O_-benzyl-5-_O_-(2-quinolinecarbonyl)-α-D-fucofuranosyl-(1→2)-3,5-di-_O_-benzyl-α-D-fucofuranosyl-(1→4)-2-_O_-benzoyl-3,6,7-tri-_O_-benzyl-D-_glycero_-β-D-_galacto_-heptopyranoside (16)

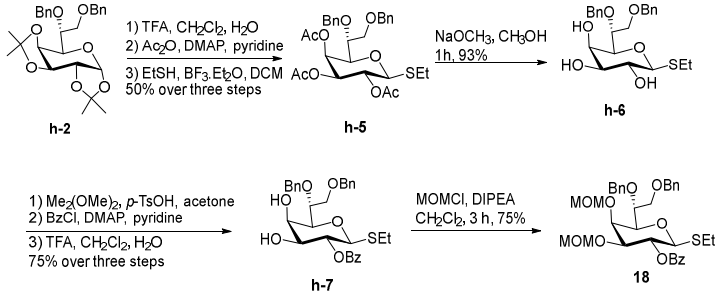
To a solution of **13b** (321 mg, 0.2 mmol) in THF (2 mL) was added triethylamine trihydrofluoride (52 μL, 1 mmol) slowly at 0 °C, and the resulting mixture was stirred for 12 h at the same temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (4:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup in pyridine (2 mL) were added benzoyl chloride (53 μL, 0.6 mmol) and 4-dimethylaminopyridine (5 mg, 0.02 mmol). The mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The syrup was purified by silica gel column chromatography (3:1, petroleum ether-EtOAc) to afford **16** as a colorless syrup (252 mg, 84% over two steps). **16**: R_f = 0.3 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +50.5 (*c* 0.44, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 8.01-7.95 (m, 2H), 7.75-7.66 (m, 2H), 7.57 (q, *J* = 7.5 Hz, 2H), 7.47-7.39 (m, 4H), 7.31 (q, *J* = 5.0 Hz, 6H), 7.25 (d, *J* = 3.7 Hz, 6H), 7.22-7.08 (m, 22H), 7.08-7.01 (m, 5H), 6.84 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.89-5.79 (m, 2H), 5.48 (p, *J* = 6.5 Hz, 1H), 5.27 (d, *J* = 3.5 Hz, 1H), 5.14 (d, *J* = 12.1 Hz, 1H), 4.97 (d, *J* = 7.9 Hz, 1H), 4.83 (d, *J* = 11.5 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.67-4.61 (m, 2H), 4.60-4.56 (m, 2H), 4.54 (d, *J* = 10.7 Hz, 2H), 4.48-4.41 (m, 3H), 4.41-4.37 (m, 2H), 4.35-4.28 (m, 3H), 4.28-4.24 (m, 1H), 4.22 (d, *J* = 7.0 Hz, 1H), 4.19-4.15 (m, 1H), 4.00-3.91 (m, 2H), 3.83 (d, *J* = 9.3 Hz, 1H), 3.79 (d, *J* = 10.9 Hz, 1H), 3.76-3.72 (m, 1H), 3.70 (d, *J* = 3.1 Hz, 1H), 3.66 (d, *J* = 3.2 Hz, 4H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.10, 164.65, 155.09, 151.53, 148.33, 147.74, 139.51, 138.94, 138.36, 138.32, 138.13, 137.99, 137.56, 137.17, 132.96, 130.95, 130.34, 130.08, 129.98, 129.28, 128.58, 128.48, 128.43, 128.40, 128.36, 128.18, 128.16, 128.06, 128.04, 127.93, 127.83, 127.78, 127.71, 127.62, 127.54, 127.51, 127.44, 127.35, 127.16, 127.06,

121.36, 117.80, 114.46, 104.26, 100.64, 99.32, 84.66, 84.41, 82.25, 81.89, 81.87, 77.71, 77.23, 76.28, 75.46, 74.76, 73.35, 72.60, 72.29, 72.24, 71.99, 71.48, 71.02, 70.69, 69.98, 66.23, 55.69, 16.14, 15.96; HRMS (ESI): *m/z* calcd for $C_{92}H_{91}NO_{18}$ $[M+Na]^+$: 1520.6134, found: 1520.6134 .

2,3-Di-*O*-benzyl-5-*O*-(2-quinolinecarbonyl)-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-α/β-D-*galacto*-heptopyranosyl trichloroacetimidate (17a)

To a solution of **16** (76 mg, 0.05 mmol) in CH_3CN/H_2O (v/v, 4:1, 1 mL) was added ceric ammonium nitrate (82 mg, 0.15 mmol). The mixture was stirred under nitrogen for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (3:1, petroleum ether-EtOAc) to afford a colorless syrup (56 mg). Then a solution of the obtained syrup (56 mg) in CH_2Cl_2 (1 mL) were added Cl_3CCN (40 μL, 0.4 mmol) and DBU (12 μL, 0.08 mmol) at 0 ºC. The resulting mixture was stirred under nitrogen for 1 h at 0 ºC. After completion of the reaction, the mixture was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to give **17a** as colorless syrups (42 mg, 54% over two steps). **17a**: R_f = 0.6 (5:1, petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.0 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.62-7.50 (m, 3H), 7.43-7.27 (m, 13H), 7.21-7.06 (m, 23H), 6.69 (d, *J* = 3.7 Hz, 1H), 5.80 (dd, *J* = 10.6, 3.7 Hz, 1H), 5.75 (d, *J* = 2.7 Hz, 1H), 5.54-5.43 (m, 1H), 5.28 (d, *J* = 3.5 Hz, 1H), 5.00 (d, *J* = 11.9 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.72-4.58 (m, 5H), 4.53-4.41 (m, 5H), 4.39-4.33 (m, 3H), 4.31-4.20 (m, 5H), 4.15 (t, *J* = 4.6 Hz, 1H), 4.07 (dd, *J* = 10.5, 2.8 Hz, 1H), 3.99 (d, *J* = 9.7 Hz, 1H), 3.93-3.87 (m, 1H), 3.82-3.69 (m, 2H), 3.57 (dd, *J* = 10.7, 2.6 Hz, 1H), 1.51 (d, *J* = 6.4 Hz, 3H), 1.10 (d, *J* = 6.3 Hz, 3H).

<u>Synthesis of D-Galhep*p* Donors 18, 22a-d</u>



Ethyl 2,3,4-tri-*O*-acetyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-5)

To a solution of **h-2** (940 mg, 2.0 mmol) in CH_2Cl_2 (20 mL) was added TFA (1 mL, 13.5 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 12 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo* to afford a residue which was directly used for the next step without further purification. To a solution of the obtained residue in pyridine (20 mL) were added acetic anhydride (1.9 mL, 20.0 mmol) and 4-dimethylaminopyridine (47 mg, 0.4 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was purified by

column chromatography on silica gel (5:1, petroleum ether-EtOAc). To a solution of the obtained syrup (804 mg, 1.4 mmol) in dry CH_2Cl_2 (14 mL) was added EtSH (0.2 mL, 2.8 mmol) slowly at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes, then $BF_3{\cdot}Et_2O$ (0.9 mL, 7.0 mmol) was added slowly and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 3 h at the same temperature at the end of which time TLC indicated that it was finished. The reaction was quenched with triethylamine and diluted with CH_2Cl_2. The organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (10:1, petroleum ether-EtOAc) to give **h-5** as a colorless syrup (560 mg, 50% over three steps). **h-5**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -26.7 (*c* 0.58, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.16 (m, 10H), 5.70 (d, *J* = 3.3 Hz, 1H), 5.18 (t, *J* = 9.9 Hz, 1H), 5.06 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.60 (d, *J* = 11.1 Hz, 1H), 4.56 (s, 2H), 4.47 (d, *J* = 10.0 Hz, 1H), 4.36 (d, *J* = 11.1 Hz, 1H), 3.87-3.78 (m, 2H), 3.67-3.55 (m, 2H), 2.65-2.54 (m, 2H), 2.05 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.18, 170.08, 169.84, 138.24, 137.36, 128.70, 128.56, 128.54, 128.04, 127.84, 127.78, 84.35, 75.43, 74.44, 73.58, 72.48, 72.03, 67.91, 67.83, 67.48, 24.73, 20.98, 20.79, 14.96; HRMS (ESI): *m/z* calcd for $C_{29}H_{36}O_9S$ $[M+Na]^+$: 583.1978, found: 583.1976.

Ethyl 6,7-di-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-6)

To a solution of **h-5** (310 mg, 0.7 mmol) in MeOH (7 mL) was added $NaOCH_3$ (39 mg, 0.7 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated to dryness. The resulting residue was purified by column chromatography (10:1, CH_2Cl_2-MeOH) to afford compound **h-6** as a white solid (282 mg, 93%). **h-6**: R_f = 0.2 (10:1, CH_2Cl_2-MeOH); $[\alpha]_D^{25}$ -35.0 (*c* 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-6.85 (m, 10H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.63 (d, *J* = 11.5 Hz, 1H), 4.55 (s, 2H), 4.29 (d, *J* = 9.6 Hz, 1H), 4.19 (s, 1H), 3.91-3.87 (m, 1H), 3.73 (dd, *J* = 10.4, 3.2 Hz, 1H), 3.70-3.60 (m, 3H), 3.60-3.52 (m, 1H), 3.31 (d, *J* = 6.1 Hz, 1H), 3.00 (s, 1H), 2.86 (d, *J* = 4.1 Hz, 1H), 2.68-2.56 (m, 2H), 1.26 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.22, 138.11, 128.62, 128.53, 128.27, 128.05, 127.81, 127.77, 86.38, 76.08, 75.01, 73.56, 73.04, 70.76, 68.96, 68.22, 24.75, 15.45; HRMS (ESI): *m/z* calcd for $C_{23}H_{30}O_6S$ $[M+Na]^+$: 457.1661, found: 457.1660.

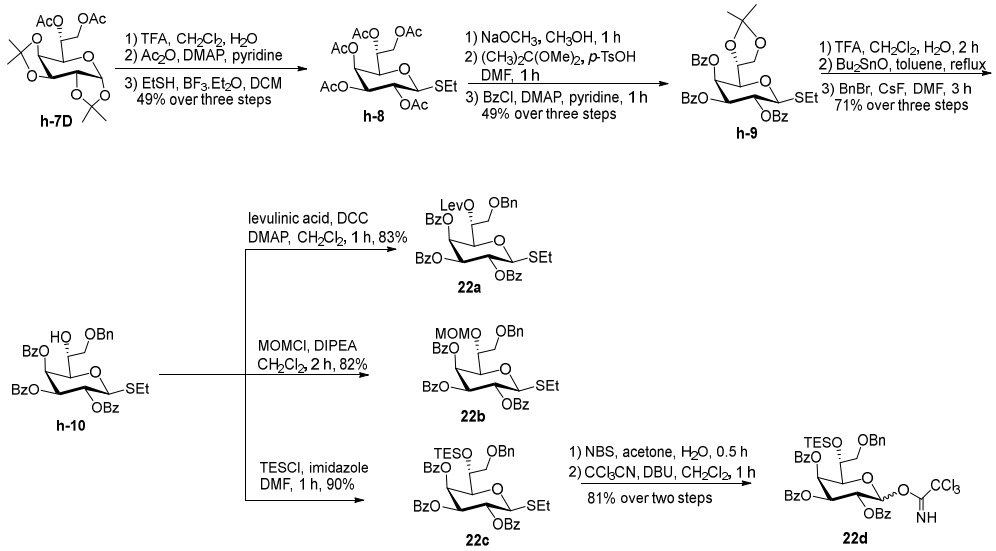
Ethyl 2-*O*-benzoyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-7)

To a solution of the **h-6** (300 mg, 0.7 mmol) in dry acetone (7 mL) were added 2,2-dimethoxypropane (0.17 mL, 1.38 mmol) and *p*-toluenesulfonic acid (13 mg, 0.07 mmol) at 0 °C. The mixture was stirred under nitrogen at room temperature. After 2 h, the reaction was quenched by addition of triethylamine. The resulting mixture was concentrated *in vacuo* to afford a residue which was directly used for the next step without further purification. To a solution of the obtained residue in pyridine (7 mL) were added benzoyl chloride (0.24 mL, 2.07 mmol) and 4-dimethylaminopyridine (17 mg, 0.14 mmol). The mixture was stirred for 3 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (7:1, petroleum ether-EtOAc). To a solution of the obtained syrup in CH_2Cl_2 (7 mL) was added TFA (0.4 mL, 4.7 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 12 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (2:1,

petroleum ether-EtOAc) to afford **h-7** as a colorless syrup (283 mg, 75% over three steps). **h-7**: R_f = 0.2 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ -22.0 (*c* 0.41, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.40-7.27 (m, 10H), 5.28 (t, *J* = 9.6 Hz, 1H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.60-4.52 (m, 3H), 4.25 (d, *J* = 3.4 Hz, 1H), 3.96 (dt, *J* = 7.7, 4.0 Hz, 1H), 3.81-3.73 (m, 2H), 3.72 (dd, *J* = 7.3, 1.0 Hz, 1H), 3.68 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.08 (s, 1H), 2.88 (s, 1H), 2.75-2.55 (m, 2H), 1.23 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.84, 138.11, 137.93, 133.41, 130.11, 129.79, 128.69, 128.58, 128.50, 128.34, 128.17, 127.89, 127.83, 83.56, 76.31, 73.98, 73.63, 73.14, 72.48, 68.74, 68.60, 24.16, 15.12; HRMS (ESI): *m/z* calcd for $C_{30}H_{34}O_7S$ $[M+Na]^+$: 561.1923, found: 561.1923.

Ethyl 2-*O*-benzoyl-3,4-di-*O*-methoxymethyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (18)

To a solution of the **h-7** (420 mg, 0.78 mmol) in dry CH_2Cl_2 (8 mL) was added chloromethyl methyl ether (0.3 mL, 3.9 mmol) slowly at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes, then *N*,*N*-diisopropylethylamine (1.36 mL, 7.8 mmol) was added slowly and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 3 h at the same temperature, at the end of which time TLC indicated that it was finished. The reaction was diluted with CH_2Cl_2. The organic solution was washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated to dryness. The crude product was purified by column chromatography (10:1, petroleum ether-EtOAc) to give **18** as a colorless syrup (386 mg, 79%). **18**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +26.7 (*c* 0.58, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39-7.27 (m, 10H), 5.56 (t, *J* = 9.9 Hz, 1H), 4.86 (d, *J* = 6.6 Hz, 1H), 4.78-4.69 (m, 3H), 4.59-4.55 (m, 4H), 4.53 (d, *J* = 5.2 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 1H), 3.96-3.87 (m, 3H), 3.76-3.68 (m, 2H), 3.43 (s, 3H), 3.18 (s, 3H), 2.70-2.55 (m, 2H), 1.21 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.51, 138.44, 138.26, 133.21, 130.03, 129.94, 128.54, 128.51, 128.49, 127.98, 127.86, 127.75, 97.94, 95.00, 84.36, 77.77, 76.82, 75.78, 73.49, 72.54, 71.56, 70.28, 67.92, 56.26, 55.78, 24.50, 14.96; HRMS (ESI): *m/z* calcd for $C_{34}H_{42}O_9S$ $[M+Na]^+$: 649.2448, found: 649.2447.



Ethyl 2,3,4,6,7-penta-*O*-acetyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-8)

To a solution of **h-7D**[6] (340 mg, 0.9 mmol) in CH_2Cl_2 (9 mL) was added TFA (0.5 mL, 6.7 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 12 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo* to afford a residue which was directly used for the next step without further purification. To a solution of the obtained residue in pyridine (9 mL) were added acetic anhydride (0.9 mL, 9.0 mmol) and 4-dimethylaminopyridine (29 mg, 0.02 mmol). The mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (5:1, petroleum ether-EtOAc). To a solution of the obtained syrup (299 mg, 0.65 mmol) in dry CH_2Cl_2 (7 mL) was added EtSH (0.1 mL, 1.3 mmol) slowly at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes, then $BF_3{\cdot}Et_2O$ (0.4 mL, 3.3 mmol) was added slowly and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 3 h at the same temperature at the end of which time TLC indicated that it was finished. The reaction was quenched with triethylamine and diluted with CH_2Cl_2. The organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (10:1, petroleum ether-EtOAc) to give **h-8** as a colorless syrup (148 mg, 49% over three steps). **h-8**: R_f = 0.3 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +127.5 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45-5.39 (m, 1H), 5.21 (t, *J* = 10.0 Hz, 1H), 5.13 (m, *J* = 9.6, 4.1, 2.4 Hz, 1H), 5.05 (dd, *J* = 10.1, 3.4 Hz, 1H), 4.49 (d, *J* = 9.9 Hz, 1H), 4.44 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.20 (dd, *J* = 12.3, 4.1 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 2.77-2.60 (m, 2H), 2.09 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.61, 170.54, 170.24, 169.69, 169.67, 84.23, 74.17, 71.95, 67.49, 67.27, 66.34, 62.36, 24.41, 20.93, 20.84, 20.76, 20.76, 20.70, 14.89; HRMS (ESI): *m/z* calcd for $C_{19}H_{28}O_{11}S$ $[M+Na]^+$: 487.1250, found: 487.1246.

Ethyl 2,3,4-tri-*O*-benzoyl-6,7-*O*-isopropylidene-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-9)

To a solution of **h-8** (557 mg, 1.2 mmol) in MeOH (12 mL) was added $NaOCH_3$ (65 mg, 1.2 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 1 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated to afford a white solid which was directly used for the next step without further purification. To a solution of the obtained residue in dry DMF (12 mL) were added 2,2-dimethoxypropane (0.17 mL, 1.4 mmol) and *p*-toluenesulfonic acid (22 mg, 0.1 mmol) at 0 °C. The mixture was stirred under nitrogen at room temperature. After 1 h, the reaction was quenched by addition of triethylamine. The resulting mixture was concentrated *in vacuo* to afford a residue which was directly used for the next step without further purification. To a solution of the obtained residue in pyridine (12 mL) were added benzoyl chloride (0.7 mL, 5.9 mmol) and 4-dimethylaminopyridine (28.8 mg, 0.2 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography on silica gel (10:1, petroleum ether-EtOAc) to afford **h-9** as a colorless syrup (356 mg, 49% over three steps). **h-9**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +154.8 (*c* 0.31, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.94 (d, *J* = 6.9 Hz, 2H), 7.77 (d, *J* = 6.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55-7.30 (m, 6H), 7.28-7.21 (m, 2H), 6.04 (d, *J* = 2.2 Hz, 1H), 5.76 (t, *J* = 9.9 Hz, 1H), 5.62 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.83 (d, *J* = 10.0 Hz, 1H),

4.29-4.17 (m, 1H), 4.16-4.02 (m, 2H), 3.84 (d, *J* = 7.9 Hz, 1H), 2.92-2.69 (m, 2H), 1.46 (s, 3H), 1.33 (t, *J* = 7.4 Hz, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.72, 165.49, 165.27, 133.56, 133.43, 133.31, 130.05, 129.94, 129.89, 129.53, 129.38, 129.09, 128.74, 128.51, 128.38, 109.98, 84.58, 78.39, 73.15, 73.13, 68.43, 68.38, 67.00, 27.17, 25.24, 24.72, 15.14; HRMS (ESI): *m/z* calcd for $C_{33}H_{34}O_9S$ $[M+Na]^+$: 629.1822, found: 629.1819.

Ethyl 2,3,4-tri-*O*-benzoyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (h-10)

To a solution of **h-9** (540 mg, 0.891 mmol) in CH_2Cl_2 (9 mL) was added TFA (0.9 mL, 12.12 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 2 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo.* The crude product was purified by column chromatography on silica gel (10:1, petroleum ether-EtOAc). To a solution of the obtained syrup in dry toluene (20 mL) was added Bu_2SnO (242.3 mg, 1.0 mmol). The reaction mixture was heated under reflux for 3 h then it was cooled to room temperature and concentrated *in vacuo*. To a solution of obtained residue in dry DMF (8 mL) were added benzyl bromide (0.1 mL, 1.0 mmol) and CsF (246.4 mg, 1.6 mmol). The reaction mixture was stirred for 3 h at 60 °C and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (3:1, petroleum ether-EtOAc) to afforded **h-10** (415 mg, 71% over three steps) as a colorless syrup. **h-10**: R_f = 0.4 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +150.9 (*c* 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.7 Hz, 2H), 7.87 (d, *J* = 6.7 Hz, 2H), 7.71 (d, *J* = 6.6 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.45-7.36 (m, 3H), 7.36-7.18 (m, 8H), 7.18-7.08 (m, 3H), 5.96 (d, *J* = 3.3 Hz, 1H), 5.74 (t, *J* = 9.9 Hz, 1H), 5.55 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.71 (d, *J* = 10.0 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 3.78-3.70 (m, 1H), 3.66 (d, *J* = 3.5 Hz, 2H), 2.64-2.60 (m, 2H), 1.17 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.62, 165.59, 137.98, 133.81, 133.44, 133.36, 130.22, 129.94, 129.87, 129.38, 129.15, 129.02, 128.75, 128.61, 128.52, 128.41, 127.97, 127.93, 84.44, 77.05, 73.74, 73.12, 70.44, 69.24, 68.65, 68.07, 24.69, 15.04; HRMS (ESI): *m/z* calcd for $C_{37}H_{36}O_9S$ $[M+Na]^+$: 679.1978, found: 679.1976.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-levulinoyl-7-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (22a)

To a solution of **h-10** (55 mg, 0.084 mmol) in dry CH_2Cl_2 (1 mL) were added levulinic acid (29 mg, 0.25 mmol), *N*,*N*-dicyclohexylcarbodiimide (51.789 mg, 0.251 mmol), and 4-dimethylaminopyridine (6 mg, 0.05 mmol). The reaction mixture was stirred for 1 h at room temperature and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (8:1, petroleum ether-EtOAc) to afford compound **22a** (54 mg, 83%) as a white solid. **22a**: R_f = 0.6 (4:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +92.7 (*c* 0.72, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.44-7.31 (m, 4H), 7.30-7.19 (m, 6H), 7.13 (dd, *J* = 14.4, 6.8 Hz, 3H), 5.85 (d, *J* = 3.4 Hz, 1H), 5.67 (t, *J* = 9.9 Hz, 1H), 5.53 (dd, *J* = 9.9, 3.4 Hz, 1H), 5.06 (d, *J* = 9.5 Hz, 1H), 4.74 (d, *J* = 9.9 Hz, 1H), 4.59-4.51 (m, 1H), 4.41 (d, *J* = 12.1 Hz, 1H), 4.30 (d, *J* = 9.4 Hz, 1H), 3.77 (dd, *J* = 11.1, 3.1 Hz, 1H), 3.61 (dd, *J* = 11.1, 2.2 Hz, 1H), 2.67-2.52 (m, 4H), 2.50-2.37 (m, 2H), 2.00 (s, 3H), 1.19 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.47, 171.60, 165.82, 165.57, 165.47, 138.05, 133.55,

133.42, 133.35, 129.93, 129.84, 129.34, 128.91, 128.68, 128.58, 128.58, 128.50, 128.38, 127.88, 127.76, 84.52, 74.22, 73.63, 72.89, 69.47, 68.39, 68.09, 67.68, 37.99, 29.84, 28.14, 24.63, 15.06; HRMS (ESI): *m/z* calcd for $C_{42}H_{42}O_{11}S$ $[M+Na]^+$: 777.2346, found: 777.2374.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-methoxymethyl-7-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside (22b)

To a solution of **h-10** (50 mg, 0.076 mmol) in dry CH_2Cl_2 (1 mL) were added chloromethyl methyl ether (23 μl, 0.304 mmol) slowly at 0 °C. The reaction mixture was stirred at 0 °C for 15 minutes, then *N*,*N*-diisopropylethylamine (66 μl, 0.38 mmol) was added slowly and the resulting mixture was warmed gradually to room temperature. The reaction mixture was stirred for 2 h at room temperature and then it was diluted with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by column chromatography (8:1, petroleum ether-EtOAc) to afford compound **22b** (44 mg, 82%) as a white solid. **22b**: R_f = 0.5 (4:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +118.6 (*c* 0.63, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.56-7.12 (m, 13H), 6.11 (d, *J* = 3.3 Hz, 1H), 5.76 (t, *J* = 9.9 Hz, 1H), 5.61 (dd, *J* = 9.9, 3.3 Hz, 1H), 4.81 (d, *J* = 9.9 Hz, 1H), 4.67-4.62 (m, 1H), 4.62-4.54 (m, 2H), 4.52-4.43 (m, 1H), 4.22 (d, *J* = 8.9 Hz, 1H), 3.88-3.82 (m, 1H), 3.81 (d, *J* = 2.9 Hz, 2H), 3.20 (s, 3H), 2.79-2.64 (m, 2H), 1.29 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.62, 165.56, 165.52, 138.16, 133.54, 133.38, 133.20, 129.96, 129.94, 129.88, 129.56, 129.43, 129.20, 128.74, 128.57, 128.48, 128.33, 127.91, 127.88, 96.87, 84.57, 75.52, 74.56, 73.75, 73.41, 68.70, 68.59, 68.27, 55.99, 24.69, 15.06; HRMS (ESI): *m/z* calcd for $C_{39}H_{40}O_{10}S$ $[M+Na]^+$: 723.2240, found: 723.2246.

Ethyl 2,3,4-tri-*O*-benzoyl-6-*O*-triethylsilyl-7-*O*-benzyl-D-*glycero*-β-D-thio-*galacto*-heptopyranoside(22c)

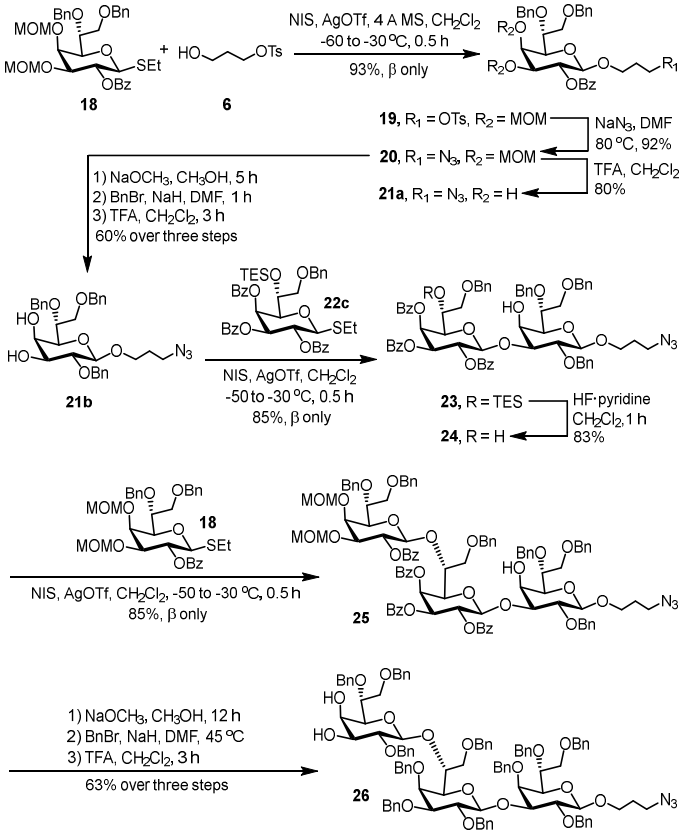
To a solution of **h-10** (231 mg, 0.35 mmol) in dry DMF (4 mL) were added TESCl (89 μL, 0.53 mmol) and imidazole (71.89 mg, 1.06 mmol) at 0 °C. The resulting mixture was warmed gradually to room temperature. The mixture was stirred for 1 h at the same temperature at the end of which time TLC indicated the reaction was complete. The reaction mixture was quenched with MeOH. Then the mixture was dissolved with CH_2Cl_2, and the resulting organic solution was washed with water and brine. The organic layer was separated and dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude material was purified by column chromatography (30:1, petroleum ether-EtOAc) to afford **22c** as a colorless syrup (244 mg, 90%). **22c**: R_f = 0.4 (15:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +122.7 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 6.8 Hz, 2H), 7.77 (d, *J* = 6.7 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (m, *J* = 11.7, 7.6 Hz, 3H), 7.44-7.27 (m, 8H), 7.26-7.20 (m, 2H), 6.09 (d, *J* = 3.2 Hz, 1H), 5.73 (t, *J* = 9.9 Hz, 1H), 5.61 (dd, *J* = 9.9, 3.2 Hz, 1H), 4.78 (d, *J* = 9.9 Hz, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.09-4.01 (m, 2H), 3.74-3.66 (m, 2H), 2.77-2.61 (m, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.52-0.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.55, 165.54, 165.47, 138.12, 133.34, 133.34, 133.12, 129.94, 129.47, 129.26, 128.63, 128.50, 128.46, 128.30, 127.99, 127.80, 84.44, 76.84, 73.68, 73.48, 71.72, 69.74, 68.76, 68.27, 24.67, 14.98, 6.89, 5.10; HRMS (ESI): *m/z* calcd for $C_{43}H_{50}O_9SSi$ $[M+Na]^+$: 793.2843, found: 793.2867.

2,3,4-Tri-*O*-benzoyl-6-*O*-triethylsilyl-7-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl

trichloroacetimidate (22d)

To a solution of **22c** (56 mg, 0.07 mmol) in acetone/H_2O (v/v, 4:1, 1 mL) was added NBS (25 mg, 0.14 mmol). The mixture was stirred under nitrogen for 15 minutes at 0 ºC. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (3:1, petroleum ether-EtOAc) to afford a colorless syrup. Then a solution of the obtained syrup in CH_2Cl_2 (1 mL) were added CCl_3CN (71 μL, 0.7 mmol) and DBU (21 μL, 0.14 mmol) at 0 ºC. The resulting mixture was stirred under nitrogen for 1 h at room temperature. After completion of the reaction, the mixture was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to give **22d** as a colorless syrup (49 mg, 81% over two steps). **22d**: R_f = 0.4 (4:1, petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.11-8.05 (m, 2H), 7.94 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.83-7.77 (m, 2H), 7.66-7.53 (m, 2H), 7.52-7.40 (m, 6H), 7.37-7.29 (m, 6H), 6.81 (d, *J* = 3.7 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 6.03 (dd, *J* = 10.7, 3.1 Hz, 1H), 5.84 (dd, *J* = 10.7, 3.7 Hz, 1H), 4.56-4.43 (m, 4H), 4.09-4.02 (m, 1H), 3.65 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.55 (dd, *J* = 10.2, 4.2 Hz, 1H), 0.76 (t, *J* = 7.9 Hz, 9H), 0.49-0.42 (m, 6H).

Synthesis of the Right Trisaccharide Acceptor 26



3-(*p*-Toluenesulfonyloxy)propyl 2-*O*-benzoyl-3,4-di-*O*-methoxymethyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (19)

A mixture of heptose donor **18** (500 mg, 0.80 mmol), acceptor **6** (221 mg, 0.96 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (13 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -60 °C and then NIS (270 mg, 0.95 mmol) and AgOTf (41 mg, 0.16

mmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 0.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **19** (591 mg, 93%) as a colorless syrup. **19**: R_f = 0.3 (4:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +149.3 (*c* 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.0 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.40-7.17 (m, 14H), 5.46 (dd, *J* = 10.3, 7.9 Hz, 1H), 4.86 (d, *J* = 6.5 Hz, 1H), 4.77 (d, *J* = 11.1 Hz, 1H), 4.71 (dd, *J* = 8.9, 6.8 Hz, 2H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.55 (d, *J* = 2.1 Hz, 1H), 4.53-4.50 (m, 2H), 4.42 (d, *J* = 7.9 Hz, 1H), 4.30 (d, *J* = 2.8 Hz, 1H), 3.99-3.85 (m, 5H), 3.75-3.67 (m, 3H), 3.42 (s, 3H), 3.41-3.34 (m, 1H), 3.16 (s, 3H), 2.42 (s, 3H), 1.82-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.39, 144.68, 138.42, 138.27, 133.25, 133.16, 130.10, 129.92, 129.86, 128.55, 127.97, 127.95, 127.90, 127.87, 127.82, 101.94, 97.99, 95.01, 77.48, 76.52, 75.81, 73.55, 72.94, 72.30, 71.64, 71.52, 67.65, 67.59, 65.02, 56.29, 55.75, 29.44, 21.72; HRMS (ESI): *m/z* calcd for $C_{42}H_{50}O_{13}S$ $[M+Na]^+$: 817.2870, found: 817.2868.

3-Azidopropyl 2-*O*-benzoyl-3,4-di-*O*-methoxymethyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (20)

To a solution of **19** (230 mg, 0.29 mmol) in dry DMF (2.9 mL) was added NaN_3 (189 mg, 2.9 mmol). The reaction mixture was warmed to 80 °C and stirred for 12 h. Then, the mixture was diluted with CH_2Cl_2, and the resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (20:1, petroleum ether-EtOAc) to afford **20** as a colorless syrup (184 mg, 92%). **20**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +14.2 (*c* 0.36, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.40-7.27 (m, 10H), 5.51 (dd, *J* = 10.3, 7.9 Hz, 1H), 4.87 (d, *J* = 6.6 Hz, 1H), 4.77 (d, *J* = 11.1 Hz, 1H), 4.72 (dd, *J* = 6.8, 6.1 Hz, 2H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.58-4.51 (m, 3H), 4.46 (d, *J* = 7.9 Hz, 1H), 4.31 (d, *J* = 2.8 Hz, 1H), 3.96-3.90 (m, 2H), 3.89 (d, *J* = 2.4 Hz, 1H), 3.79-3.68 (m, 3H), 3.43 (s, 3H), 3.41-3.34 (m, 1H), 3.25-3.11 (m, 5H), 1.80-1.64 (m, 2H); HRMS (ESI): *m/z* calcd for $C_{35}H_{43}N_3O_{10}$ $[M+Na]^+$: 688.2846, found: 688.2844; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44, 138.40, 138.19, 133.26, 130.00, 129.80, 128.57, 128.53, 128.00, 127.90, 127.81, 102.03, 97.95, 94.90, 76.34, 75.77, 73.53, 72.87, 72.21, 71.66, 71.52, 67.53, 66.12, 56.31, 55.75, 48.00, 29.02; HRMS (ESI): *m/z* calcd for $C_{35}H_{43}N_3O_{10}$ $[M+Na]^+$: 688.2846, found: 688.2844.

3-Azidopropyl 2-*O*-benzoyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (21a)

To a solution of **20** (173 mg, 0.26 mmol) in CH_2Cl_2 (2.6 mL) was added TFA (0.26 mL, 3.5 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 3 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo.* The crude product was purified by column chromatography (1:1, petroleum ether-EtOAc) to afford **21a** as a white solid (120 mg, 80%). **21a**: R_f = 0.3 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +90.1 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.41-7.15 (m, 10H), 5.21-5.15 (m, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.66 (d, *J* = 7.9 Hz, 1H), 4.63 (d, *J* = 8.5 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.20 (d, *J* = 3.4 Hz, 1H), 3.95 (m, *J* = 7.5, 3.6 Hz, 1H), 3.76 (m, *J* = 8.1, 2.9 Hz, 3H), 3.72-3.65 (m, 2H), 3.45 (m, *J* = 9.8, 7.7, 4.7 Hz, 1H), 3.22 (t, *J* = 6.6 Hz, 2H), 1.72 (m, *J* = 19.8, 14.3, 8.1, 3.9 Hz, 2H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 167.07, 138.18, 137.97, 133.51, 129.96, 129.69, 128.68, 128.58, 128.56, 128.37, 128.15, 127.96, 127.89, 101.34, 75.85, 74.28, 73.63, 73.05, 72.96, 72.77, 68.43, 68.30, 66.11, 48.02, 29.05; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}N_3O_8$ $[M+Na]^+$: 600.2322, found: 600.2318.

3-Azidopropyl 2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (21b)

To a solution of **20** (201 mg, 0.3 mmol) in MeOH (3 mL) was added $NaOCH_3$ (32 mg, 0.6 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 5 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (4:1, petroleum ether-EtOAc) to afford a white solid. To a solution of the obtained white solid (153 mg, 0.27 mmol) in dry DMF (3 mL) were added benzyl bromide (0.26 mL, 2.18 mmol) and NaH (87.2 mg, 2.18 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (8:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup (140 mg, 0.24 mmol) in CH_2Cl_2 (2.4 mL) was added TFA (0.24 mL, 3.3 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 3 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo*. The crude product was purified by column chromatography (1:1, petroleum ether-EtOAc) to afford **21b** as a white solid (102 mg, 60% over three steps). **21b**: R_f = 0.3 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +148.3 (*c* 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 10H), 4.90 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.69-4.58 (m, 3H), 4.52 (d, *J* = 12.3 Hz, 1H), 4.29 (d, *J* = 7.6 Hz, 1H), 4.16 (d, *J* = 3.3 Hz, 1H), 3.93-3.86 (m, 1H), 3.80-3.71 (m, 2H), 3.67-3.55 (m, 3H), 3.53-3.43 (m, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.91-1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.43, 138.31, 138.14, 128.70, 128.60, 128.52, 128.32, 128.10, 128.05, 128.04, 127.90, 127.81, 103.83, 79.40, 75.66, 74.79, 73.55, 73.36, 72.92, 72.67, 68.70, 67.65, 66.31, 48.42, 29.30; HRMS (ESI): *m/z* calcd for $C_{31}H_{37}N_3O_7$ $[M+Na]^+$: 586.2530, found: 586.2530.

3-Azidopropyl 2,3,4-tri-*O*-benzoyl-6-*O*-triethylsilyl-7-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (23)

A mixture of heptose donor **22c** (200 mg, 0.40 mmol), acceptor **21b** (188 mg, 0.33 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (6.7 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -60 °C and then NIS (135 mg, 0.6 mmol) and AgOTf (21 mg, 80 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 0.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **23** (285 mg, 85%) as a colorless syrup. **23**: R_f = 0.4 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +48.7 (*c* 0.54, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 2H), 7.44-7.37 (m, 4H), 7.35-7.31 (m, 5H), 7.29 (q, *J* = 2.8 Hz, 8H), 7.26-7.17 (m, 7H), 7.10-7.05 (m, 2H), 6.01 (d, *J* = 3.4 Hz, 1H), 5.75 (dd, *J* = 10.4, 7.9 Hz, 1H), 5.57 (dd, *J* = 10.4, 3.4 Hz,

1H), 5.14 (d, *J* = 8.0 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.63 (d, *J* = 12.2 Hz, 1H), 4.52 (dd, *J* = 11.8, 5.0 Hz, 2H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.37 (d, *J* = 12.1 Hz, 1H), 4.32-4.26 (m, 2H), 4.13 (d, *J* = 7.7 Hz, 1H), 4.02-3.93 (m, 3H), 3.76 (dd, *J* = 10.5, 2.1 Hz, 1H), 3.70-3.62 (m, 3H), 3.53-3.41 (m, 4H), 3.39-3.34 (m, 1H), 3.21 (t, *J* = 6.8 Hz, 2H), 1.75-1.69 (m, 2H), 0.79 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.70, 165.57, 165.52, 138.68, 138.55, 138.52, 138.32, 133.39, 133.26, 133.15, 129.98, 129.97, 129.89, 129.76, 129.26, 129.16, 128.68, 128.52, 128.49, 128.47, 128.41, 128.39, 128.30, 128.22, 127.83, 127.77, 127.73, 127.72, 127.66, 127.56, 127.22, 103.66, 102.39, 81.17, 78.96, 75.82, 74.71, 73.53, 73.51, 73.31, 72.94, 72.13, 72.03, 71.60, 70.41, 69.61, 68.94, 68.08, 67.85, 66.25, 48.30, 29.20, 6.88, 5.07; HRMS (ESI): *m/z* calcd for $C_{72}H_{81}N_3O_{16}Si$ $[M+Na]^+$: 1294.5284, found: 1294.5314.

3-Azidopropyl 2,3,4-tri-*O*-benzoyl-7-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (24)

To a solution of **23** (328 mg, 0.29 mmol) in THF (3 mL) was added hydrogen fluoride-pyridine (30 μL, 0.58 mmol) slowly at 0 °C, and the resulting mixture was stirred for 1 h at the same temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous NH_4Cl and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford compound **24** as a colorless syrup (246 mg, 83%). **24**: R_f = 0.3 (2:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +114.5 (*c* 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.33 (d, *J* = 4.3 Hz, 3H), 7.31-7.20 (m, 17H), 7.10 (d, *J* = 7.7 Hz, 2H), 5.97 (d, *J* = 3.4 Hz, 1H), 5.83 (dd, *J* = 10.4, 8.0 Hz, 1H), 5.58 (dd, *J* = 10.5, 3.4 Hz, 1H), 5.16 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.69-4.59 (m, 2H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.50 (d, *J* = 12.4 Hz, 2H), 4.40 (d, *J* = 12.1 Hz, 1H), 4.30 (d, *J* = 11.1 Hz, 1H), 4.23 (d, *J* = 3.3 Hz, 1H), 4.18 (d, *J* = 7.7 Hz, 1H), 3.95 (dt, *J* = 9.0, 3.4 Hz, 1H), 3.89 (d, *J* = 9.0 Hz, 1H), 3.81-3.75 (m, 1H), 3.73 (dd, *J* = 10.5, 2.2 Hz, 1H), 3.70-3.65 (m, 1H), 3.62 (dd, *J* = 9.8, 3.5 Hz, 2H), 3.58-3.52 (m, 2H), 3.51-3.47 (m, 2H), 3.41-3.32 (m, 1H), 3.21 (t, *J* = 6.8 Hz, 2H), 3.07 (d, *J* = 5.9 Hz, 1H), 2.64 (s, 1H), 1.78-1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 165.77, 165.56, 138.58, 138.55, 138.52, 138.13, 133.84, 133.36, 130.28, 129.86, 129.79, 129.25, 129.00, 128.81, 128.64, 128.52, 128.50, 128.46, 128.44, 128.41, 128.14, 127.90, 127.86, 127.83, 127.80, 127.76, 127.65, 127.31, 103.70, 102.18, 81.13, 79.07, 75.76, 74.79, 73.59, 73.53, 73.50, 72.96, 72.06, 71.83, 70.39, 69.10, 68.92, 68.06, 67.86, 66.30, 48.33, 29.24; HRMS (ESI): *m/z* calcd for $C_{66}H_{67}N_3O_{16}$ $[M+Na]^+$: 1180.4419, found: 1180.4418.

3-Azidopropyl 2-*O*-benzoyl-3,4-di-*O*-methoxymethyl-6,7-di-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→6)-2,3,4-tri-*O*-benzoyl-7-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (25)

A mixture of heptose donor **18** (184 mg, 0.29 mmol), acceptor **24** (250 mg, 0.24 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (5 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -60 °C and then NIS (99 mg, 0.44 mmol) and AgOTf (15 mg, 58 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 0.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column

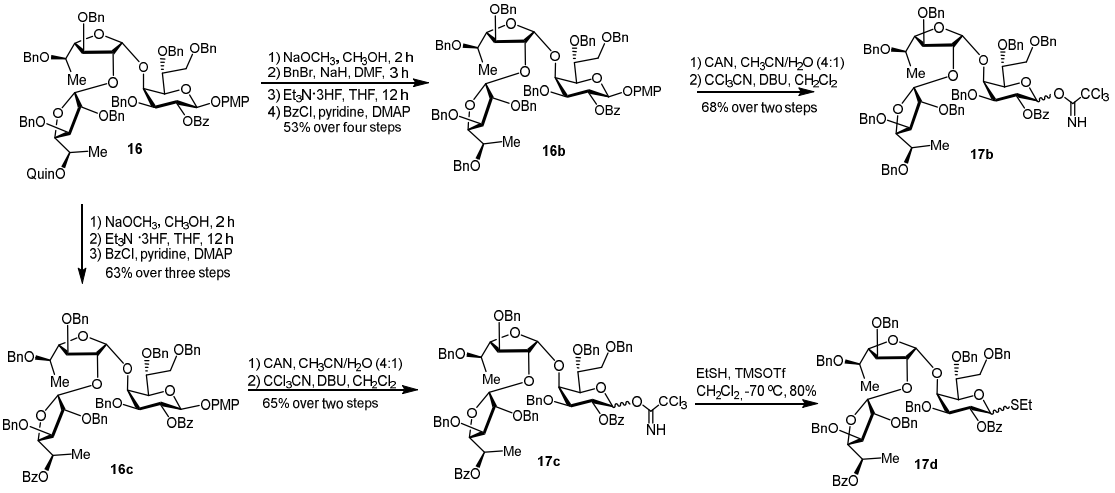
chromatography (7:1, petroleum ether-EtOAc) to afford **25** (351 mg, 85%) as a colorless syrup. **25**: R_f = 0.2 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +46.5 (*c* 0.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.7 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.49-7.12 (m, 37H), 7.08 (d, *J* = 6.5 Hz, 2H), 6.99 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.04 (d, *J* = 3.4 Hz, 1H), 5.67 (dd, *J* = 10.4, 7.8 Hz, 1H), 5.58 (dd, *J* = 10.4, 3.4 Hz, 1H), 5.43 (dd, *J* = 10.3, 7.8 Hz, 1H), 5.10 (d, *J* = 7.9 Hz, 1H), 4.78 (d, *J* = 7.9 Hz, 2H), 4.77-4.68 (m, 3H), 4.70-4.60 (m, 4H), 4.59 (d, *J* = 12.2 Hz, 2H), 4.54-4.43 (m, 3H), 4.39 (d, *J* = 11.1 Hz, 1H), 4.28-4.19 (m, 5H), 4.16 (d, *J* = 2.8 Hz, 1H), 4.12-4.04 (m, 3H), 4.01 (d, *J* = 7.8 Hz, 1H), 3.97-3.86 (m, 2H), 3.81 (dd, *J* = 10.3, 2.8 Hz, 1H), 3.67 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.65-3.54 (m, 5H), 3.50-3.35 (m, 6H), 3.36-3.26 (m, 1H), 3.22-3.08 (m, 7H), 3.02 (dd, *J* = 11.0, 2.3 Hz, 1H), 1.73-1.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.79, 165.30, 165.15, 164.59, 138.65, 138.56, 138.52, 138.50, 138.26, 138.25, 133.24, 133.11, 133.07, 132.90, 130.36, 130.32, 130.24, 129.92, 129.83, 129.79, 129.32, 129.24, 128.58, 128.47, 128.44, 128.42, 128.37, 128.23, 128.19, 127.91, 127.85, 127.75, 127.73, 127.67, 127.65, 127.40, 127.28, 127.02, 103.62, 101.99, 98.89, 97.68, 94.78, 80.39, 79.24, 76.44, 75.72, 75.50, 74.67, 73.53, 73.14, 73.13, 72.83, 72.49, 72.05, 71.91, 71.63, 70.96, 70.63, 69.16, 68.93, 67.99, 67.84, 66.25, 66.20, 56.16, 55.67, 48.33, 29.20; HRMS (ESI): *m/z* calcd for $C_{98}H_{103}N_3O_{25}$ $[M+Na]^+$: 1294.5284, found: 1294.5314.

3-Azidopropyl 2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→6)-2,3,4,7-tert-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,4,6,7-tert-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (26)

To a solution of **25** (378 mg, 0.22 mmol) in MeOH (2 mL) was added $NaOCH_3$ (36 mg, 0.66 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 12 h at the same temperature, at the end of which time TLC indicated the reaction was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the filtrate was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (EtOAc) to afforded a white solid. To a solution of the obtained white solid (258.5 mg, 0.2 mmol) in dry DMF (2 mL) were added benzyl bromide (0.38 mL, 3.2 mmol) and NaH (128 mg, 3.2 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was stirred at 45 °C for 12 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (5:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup (306 mg, 0.17 mmol) in CH_2Cl_2 (2 mL) was added TFA (0.2 mL, 2.7 mmol) dropwise, followed by 1 drop of water. The mixture was stirred under nitrogen for 3 h at room temperature. The reaction mixture was then neutralized with triethylamine and concentrated *in vacuo.* The crude product was purified by column chromatography (3:1, petroleum ether-EtOAc) to give **26** as a colorless syrup (227 mg, 63% over three steps). **26**: R_f = 0.3 (1:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +2.6 (*c* 0.37, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.00 (m, 55H), 5.18 (d, *J* = 11.9 Hz, 1H), 5.01 (d, *J* = 11.4 Hz, 1H), 4.94-4.83 (m, 3H), 4.79-4.71 (m, 3H), 4.70-4.62 (m, 4H), 4.61-4.56 (m, 5H), 4.49 (dd, *J* = 11.8, 3.0 Hz, 2H), 4.37-4.22 (m, 6H), 4.18 (dd, *J* = 13.1, 2.9 Hz, 2H), 4.06-4.01 (m, 2H), 3.91 (dt, *J* = 9.1, 2.8 Hz, 1H), 3.86-3.80 (m, 1H), 3.79-3.66 (m, 5H), 3.66-3.40 (m, 9H), 3.40-3.26 (m, 4H), 2.53 (s, 1H), 2.44 (s, 1H), 1.85-1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.52, 139.39, 139.00, 138.91, 138.66, 138.61, 138.51, 138.46, 138.43, 138.25, 138.14, 128.60, 128.53, 128.50, 128.46, 128.40, 128.31, 128.24, 128.22, 128.18, 128.17, 128.02, 127.94, 127.90, 127.89, 127.86,

127.83, 127.74, 127.70, 127.55, 127.50, 127.41, 127.40, 127.38, 127.31, 127.18, 104.81, 104.13, 99.74, 82.45, 80.58, 80.21, 79.82, 79.64, 76.20, 75.90, 75.80, 75.07, 74.76, 74.72, 74.61, 74.47, 73.62, 73.54, 73.44, 73.32, 73.19, 73.09, 72.84, 72.81, 72.63, 71.80, 68.54, 68.19, 67.68, 67.14, 66.46, 48.40, 29.22; HRMS (ESI): *m/z* calcd for $C_{101}H_{109}N_3O_{19}$ $[M+Na]^+$: 1690.7553, found: 1690.7552.

Synthesis of the Trisaccharide Donors 17b-d



***p*-Methoxyphenyl 2,3,5-tri-*O*-benzyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (16b)**

To a solution of the **16** (89 mg, 0.06 mmol) in MeOH (0.6 mL) was added $NaOCH_3$ (11 mg, 0.2 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the resulting mixture was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (4:1, petroleum ether-EtOAc) to afforded a colorless syrup. To a solution of the obtained colorless syrup (73 mg, 0.054 mmol) in dry DMF (0.6 mL) were added benzyl bromide (50 μL, 0.4 mmol) and NaH (16 mg, 0.4 mmol, 60% in mineral oil) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The reaction was quenched by addition of saturated aqueous NH_4Cl, and then the mixture was diluted with CH_2Cl_2. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (8:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the colorless syrup (72 mg, 0.05 mmol) in THF (0.5 mL) was added triethylamine trihydrofluoride (26 μL, 0.5 mmol) slowly at 0 °C, and the resulting mixture was stirred at room temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford a colorless syrup (50 mg, 0.04 mmol). To a solution of the obtained syrup in pyridine (0.4 mL) were added benzoyl chloride (23 μL, 0.2 mmol) and 4-dimethylaminopyridine (3 mg, 0.2 mmol). The mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue

was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The syrup was purified by column chromatography (8:1, petroleum ether-EtOAc) to afford **16b** as a colorless syrup (45.5 mg, 53% over two steps). **16b**: R_f = 0.3 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +58.8 (*c* 0.37, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 4H), 7.40-7.02 (m, 38H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.84 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.66 (d, *J* = 4.0 Hz, 1H), 5.22 (d, *J* = 4.2 Hz, 1H), 5.01 (d, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.81 (d, *J* = 12.2 Hz, 1H), 4.78-4.70 (m, 3H), 4.64 (dd, *J* = 16.8, 12.3 Hz, 3H), 4.59-4.53 (m, 2H), 4.49-4.34 (m, 8H), 4.31 (d, *J* = 11.1 Hz, 1H), 4.23 (d, *J* = 9.6 Hz, 1H), 4.19 (dd, *J* = 7.4, 4.0 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 1H), 3.99-3.90 (m, 3H), 3.87 (d, *J* = 9.5 Hz, 1H), 3.80 (d, *J* = 11.0 Hz, 1H), 3.75-3.61 (m, 6H), 1.16 (d, *J* = 5.4 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.10, 155.05, 151.61, 139.68, 139.49, 138.81, 138.43, 138.39, 138.04, 132.96, 130.47, 129.97, 128.59, 128.40, 128.35, 128.31, 128.23, 128.20, 127.97, 127.87, 127.82, 127.79, 127.67, 127.58, 127.49, 127.41, 127.14, 127.08, 117.50, 114.53, 103.41, 100.54, 98.64, 84.91, 84.64, 83.95, 82.36, 81.04, 79.98, 77.91, 77.74, 76.30, 75.23, 73.46, 73.00, 72.75, 72.53, 72.47, 72.32, 71.50, 70.70, 70.65, 70.64, 70.26, 66.31, 55.72, 15.76, 15.43; HRMS (ESI): *m/z* calcd for $C_{89}H_{92}O_{17}$ $[M+Na]^+$: 1455.6233, found:1455.6239.

2,3,5-Tri-*O*-benzyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-α/β-D-*galacto*-heptopyranosyl trichloroacetimidate (17b)

To a solution of **16b** (50 mg, 0.035 mmol) in CH_3CN/H_2O (v/v, 4:1, 0.5 mL) was added ceric ammonium nitrate (38 mg, 0.07 mmol). The mixture was stirred under nitrogen for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (3:1, petroleum ether-EtOAc) to afford a colorless syrup (37 mg, 0.03 mmol). To a solution of the obtained syrup (37 mg) in CH_2Cl_2 (0.6 mL) were added Cl_3CCN (31 μL, 0.3 mmol) and DBU (9 μL, 0.06 mmol) at 0 ºC. The resulting mixture was stirred under nitrogen for 1 h at 0 ºC. After completion of the reaction, the mixture was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to give **17b** as colorless syrups (35 mg, 68% over two steps). **17b**: R_f = 0.5 (5:1, petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.57-7.52 (m, 1H), 7.40 (t, *J* = 7.8 Hz, 3H), 7.36-7.28 (m, 15H), 7.24-7.14 (m, 24H), 6.63 (d, *J* = 3.7 Hz, 1H), 5.72 (dd, *J* = 10.5, 3.7 Hz, 1H), 5.64 (d, *J* = 3.4 Hz, 1H), 5.29 (d, *J* = 4.0 Hz, 1H), 4.94 (d, *J* = 11.8 Hz, 1H), 4.82 (d, *J* = 11.4 Hz, 1H), 4.71-4.65 (m, 4H), 4.62 (d, *J* = 12.1 Hz, 2H), 4.58-4.52 (m, 3H), 4.47 (dd, *J* = 14.4, 3.6 Hz, 2H), 4.43-4.36 (m, 4H), 4.33-4.25 (m, 3H), 4.22-4.18 (m, 2H), 4.12-4.06 (m, 2H), 3.98-3.89 (m, 2H), 3.82 (t, *J* = 8.6 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 1H), 3.60 (dd, *J* = 10.9, 2.6 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.06 (d, *J* = 6.4 Hz, 3H).

***p*-Methoxyphenyl 2,3-di-*O*-benzyl-5-*O*-benzoyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (16c)**

To a solution of **16** (201 mg, 0.13 mmol) in MeOH (1 mL) was added $NaOCH_3$ (16 mg, 0.3 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 2 h at the same temperature, at the end of which time TLC indicated it was finished. The reaction

was quenched with Amberlite IR120 H^+ resin, after filtration, and the resulting mixture was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (4:1, petroleum ether-EtOAc) to afforded a colorless syrup. To a solution of the colorless syrup (157 mg, 0.12 mmol) in THF (1 mL) was added triethylamine trihydrofluoride (62 μL, 1.2 mmol) slowly at 0 °C, and the resulting mixture was stirred at room temperature. The mixture was stirred at the end of which time TLC indicated the reaction was complete. The mixture was dissolved with CH_2Cl_2. The resulting organic solution was concentrated to dryness. The crude material was purified by column chromatography (5:1, petroleum ether-EtOAc) to afford a colorless syrup. To a solution of the obtained syrup (116 mg, 0.1 mmol) in pyridine (1 mL) were added benzoyl chloride (58 mL, 0.5 mmol) and 4-dimethylaminopyridine (5 mg, 0.04 mmol). The mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with MeOH, concentrated *in vacuo*. The residue was dissolved with CH_2Cl_2. The resulting organic solution was washed with water and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The syrup was purified by column chromatography (7:1, petroleum ether-EtOAc) to afford **16c** as a colorless syrup (118 mg, 63% over three steps). **16c**: R_f = 0.3 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +46.5 (*c* 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (t, *J* = 8.5 Hz, 3H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47-7.39 (m, 6H), 7.36-7.27 (m, 11H), 7.23 (d, *J* = 11.6 Hz, 9H), 7.20-7.12 (m, 11H), 7.08-7.00 (m, 4H), 6.89-6.81 (m, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 5.87 (d, *J* = 3.9 Hz, 1H), 5.82 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.41-5.30 (m, 1H), 5.27 (d, *J* = 3.4 Hz, 1H), 5.15 (d, *J* = 12.2 Hz, 1H), 4.97 (d, *J* = 8.0 Hz, 1H), 4.83 (d, *J* = 11.4 Hz, 1H), 4.77 (d, *J* = 12.2 Hz, 1H), 4.63 (d, *J* = 11.3 Hz, 2H), 4.60-4.53 (m, 4H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.45-4.37 (m, 4H), 4.35-4.29 (m, 2H), 4.26 (t, *J* = 6.8 Hz, 1H), 4.18 (d, *J* = 10.9 Hz, 1H), 4.15-4.09 (m, 2H), 3.99-3.92 (m, 2H), 3.84 (d, *J* = 9.4 Hz, 1H), 3.81-3.73 (m, 2H), 3.67 (d, *J* = 4.9 Hz, 5H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.19 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.95, 165.08, 155.16, 151.58, 139.61, 139.01, 138.51, 138.38, 138.16, 138.05, 137.72, 132.92, 132.80, 130.74, 130.44, 129.98, 129.86, 128.59, 128.52, 128.42, 128.36, 128.23, 128.16, 128.10, 128.00, 127.85, 127.80, 127.75, 127.62, 127.54, 127.47, 127.42, 127.35, 127.14, 127.04, 117.88, 114.51, 104.67, 100.71, 99.18, 84.91, 84.58, 82.50, 82.08, 81.92, 77.29, 76.27, 75.54, 73.68, 73.39, 72.88, 72.68, 72.31, 72.26, 72.03, 71.54, 71.12, 70.74, 70.00, 66.29, 55.73, 16.18, 16.04; HRMS (ESI): *m/z* calcd for $C_{89}H_{90}O_{18}Si$ $[M+Na]^+$: 1469.6025, found: 1469.6027.

2,3-Di-*O*-benzyl-5-*O*-benzoyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-α/β-D-*galacto*-heptopyranosyl trichloroacetimidate (17c)

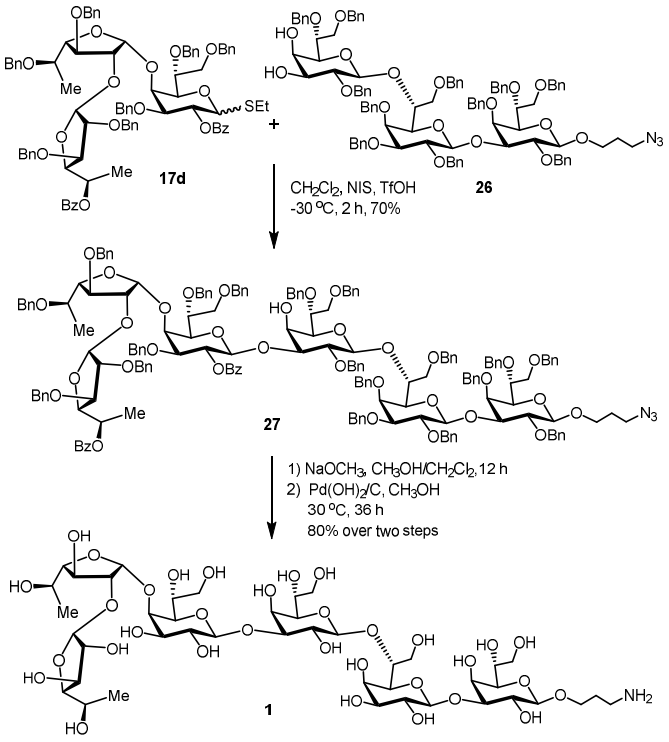
To a solution of **16c** (80 mg, 0.055 mmol) in CH_3CN/H_2O (v/v, 4:1, 1.1 mL) was added ceric ammonium nitrate (60 mg, 0.11 mmol). The mixture was stirred under nitrogen for 1 h at room temperature. The reaction mixture was diluted with CH_2Cl_2. The organic solution was washed with saturated aqueous $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (3:1, petroleum ether-EtOAc) to afford a colorless syrup (59 mg, 0.044 mmol). Then Cl_3CCN (45 μL, 0.44 mmol) and DBU (13.2 μL, 0.044 mmol) were added to a solution of the obtained syrup (56 mg) in CH_2Cl_2 (0.98 mL) at 0 ºC. The resulting mixture was stirred under nitrogen for 1 h at 0 ºC. After completion of the reaction, the mixture was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **17c** as colorless syrups (53 mg, 65% over two steps). **17c**: R_f = 0.4 (5:1, petroleum ether-EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.02 (d, *J* = 6.7 Hz, 2H), 7.93 (d, *J* = 6.8 Hz, 2H), 7.58-7.51 (m, 1H), 7.45-7.36 (m, 4H), 7.30 (dd, *J* = 12.4, 5.5 Hz, 11H),

7.24-7.06 (m, 25H), 6.69 (d, *J* = 3.7 Hz, 1H), 5.82 (dd, *J* = 10.5, 3.8 Hz, 1H), 5.75 (d, *J* = 3.7 Hz, 1H), 5.44-5.34 (m, 1H), 5.27 (d, *J* = 3.4 Hz, 1H), 4.98 (d, *J* = 11.9 Hz, 1H), 4.87 (d, *J* = 11.4 Hz, 1H), 4.71-4.61 (m, 4H), 4.57 (dd, *J* = 10.8, 7.5 Hz, 2H), 4.50 (d, *J* = 7.8 Hz, 1H), 4.48-4.44 (m, 2H), 4.40 (d, *J* = 11.4 Hz, 2H), 4.35 (d, *J* = 4.4 Hz, 2H), 4.30-4.20 (m, 4H), 4.15-4.10 (m, 2H), 4.07 (dd, *J* = 10.5, 2.9 Hz, 1H), 3.99 (dd, *J* = 7.2, 4.8 Hz, 1H), 3.91 (dd, *J* = 6.5, 4.5 Hz, 1H), 3.81-3.72 (m, 2H), 3.57 (dd, *J* = 10.9, 2.7 Hz, 1H), 1.42 (d, *J* = 6.4 Hz, 3H), 1.11 (d, *J* = 6.4 Hz, 3H).

Ethyl 2,3-di-*O*-benzyl-5-*O*-benzoyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-α/β-D-thio-*galacto*-heptopyranoside (17d)

A mixture of **17c** (119 mg, 0.08 mmol), EtSH (29 μL, 0.4 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (1.3 mL) were stirred for 15 minutes at -78 °C and then TMSOTf (1 μl, 8 μmol) was added. The reaction mixture was gradually warmed to -70 °C and stirred for 0.5 h at the same temperature. Then, the mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford an inseparable mixture of α/β isomers **17d** (89 mg, α/β = 1:1, 80%) as a colorless syrup. **17d**: R_f = 0.6 (4:1, petroleum ether-EtOAc); Selected analytical data for of **17d**; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03-7.96 (m, 4H), 7.94 (d, *J* = 7.8 Hz, 3H), 7.56 (q, *J* = 8.0 Hz, 2H), 7.48-7.39 (m, 7H), 7.38-7.23 (m, 35H), 7.23-7.07 (m, 35H), 7.00 (d, *J* = 7.0 Hz, 4H), 5.99 (d, *J* = 4.3 Hz, 1H), 5.82 (dd, *J* = 5.1, 2.6 Hz, 2H), 5.69 (dd, *J* = 10.5, 5.9 Hz, 1H), 5.54 (t, *J* = 9.8 Hz, 1H), 5.38-5.32 (m, 1H), 5.32-5.29 (m, 1H), 5.28 (d, *J* = 2.8 Hz, 1H), 5.25 (d, *J* = 3.1 Hz, 1H), 5.20 (d, *J* = 12.1 Hz, 1H), 5.05 (d, *J* = 11.9 Hz, 1H), 4.92 (d, *J* = 11.4 Hz, 1H), 4.89 (d, *J* = 11.4 Hz, 1H), 4.81 (d, *J* = 12.1 Hz, 1H), 4.70-4.62 (m, 4H), 4.62-4.53 (m, 6H), 4.52-4.45 (m, 6H), 4.45-4.39 (m, 5H), 4.39-4.33 (m, 5H), 4.32-4.21 (m, 6H), 4.18 (d, *J* = 10.8 Hz, 1H), 4.15-4.11 (m, 2H), 4.07 (t, *J* = 3.9 Hz, 1H), 3.98 (t, *J* = 2.8 Hz, 1H), 3.94 (d, *J* = 9.4 Hz, 1H), 3.90-3.85 (m, 2H), 3.84 (dd, *J* = 10.5, 3.0 Hz, 1H), 3.81-3.76 (m, 3H), 3.72-3.64 (m, 4H), 3.60 (dd, *J* = 10.9, 3.0 Hz, 1H), 3.56 (dd, *J* = 9.6, 3.1 Hz, 1H), 2.62-2.53 (m, 2H), 2.47-2.38 (m, 2H), 1.39 (d, *J* = 6.4 Hz, 6H), 1.17 (t, *J* = 7.4 Hz, 3H), 1.13-1.04 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.02, 165.92, 165.74, 165.24, 139.56, 139.46, 139.34, 138.57, 138.54, 138.48, 138.38, 138.31, 138.23, 138.09, 137.90, 137.70, 133.07, 132.99, 132.86, 130.88, 130.66, 130.62, 130.32, 130.19, 130.05, 130.03, 129.87, 129.85, 128.56, 128.51, 128.49, 128.45, 128.40, 128.38, 128.35, 128.27, 128.21, 128.19, 128.17, 128.15, 128.13, 128.08, 128.00, 127.94, 127.87, 127.84, 127.80, 127.78, 127.71, 127.62, 127.47, 127.45, 127.40, 127.29, 127.27, 127.25, 127.09, 127.00, 126.85, 105.22, 104.62, 99.38, 99.30, 85.03, 84.85, 84.72, 84.39, 84.37, 83.18, 82.40, 82.35, 82.28, 81.92, 78.02, 76.37, 76.15, 75.99, 75.85, 75.72, 75.55, 74.99, 74.61, 73.81, 73.70, 73.46, 73.03, 72.28, 72.24, 72.06, 72.03, 71.83, 71.26, 71.12, 70.88, 70.48, 70.30, 69.60, 68.78, 67.21, 66.75, 24.36, 23.50, 16.35, 16.22, 16.12, 15.93, 14.27, 14.19; HRMS (ESI): *m/z* calcd for $C_{84}H_{88}O_{16}S$ $[M+Na]^+$: 1407.5691, found: 1407.5695.

Completion of Total Synthesis of 1



3-Azidopropyl 2,3-di-*O*-benzyl-5-*O*-benzoyl-α-D-fucofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-fucofuranosyl-(1→4)-2-*O*-benzoyl-3,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,6,7-tri-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→6)-2,3,4,7-tetra-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-2,4,6,7-tetra-*O*-benzyl-D-*glycero*-β-D-*galacto*-heptopyranoside (27)

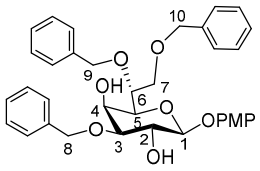
A mixture of trisaccharide donor **17d** (64 mg, 0.046 mmol), acceptor **26** (60 mg, 0.038 mmol), and freshly activated 4 Å molecular sieves in CH_2Cl_2 (0.8 mL) were stirred for 15 minutes at room temperature. The suspension was cooled to -78 °C, then NIS (21 mg, 0.09 mmol) and TfOH (1 μl, 5 μmol) were added. The reaction mixture was gradually warmed to -30 °C and stirred for 2 h at the same temperature. The mixture was quenched with triethylamine, diluted with CH_2Cl_2 and filtered. The filtrate was concentrated *in vacuo*. The obtained residue was purified by silica gel column chromatography (10:1, petroleum ether-EtOAc) to afford **27** (77 mg, 70%) as a colorless syrup. **27**: R_f = 0.5 (3:1, petroleum ether-EtOAc); $[\alpha]_D^{25}$ +21.58 (*c* 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.91-7.87 (m, 2H), 7.53-7.44 (m, 3H), 7.43-7.35 (m, 4H), 7.35-7.27 (m, 15H), 7.25-7.08 (m, 64H), 7.08-6.92 (m, 7H), 6.85-6.80 (m, 3H), 6.10 (d, *J* = 4.2 Hz, 1H), 5.63 (dd, *J* = 10.2, 8.0 Hz, 1H), 5.33-5.27 (m, 2H), 5.25 (d, *J* = 12.1 Hz, 1H), 5.18 (d, *J* = 11.8 Hz, 1H), 4.95-4.86 (m, 3H), 4.86-4.78 (m, 3H), 4.77-4.67 (m, 3H), 4.66-4.64 (m, 2H), 4.64-4.58 (m, 6H), 4.58-4.52 (m, 5H), 4.52-4.43 (m, 6H), 4.41-4.35 (m, 2H), 4.35-4.30 (m, 3H), 4.30-4.21 (m, 8H), 4.19 (d, *J* = 6.0 Hz, 2H), 4.17-4.10 (m, 3H), 4.01-3.97 (m, 2H), 3.93-3.86 (m, 2H), 3.82-3.72 (m, 6H), 3.72-3.67 (m, 2H), 3.65-3.56 (m, 4H), 3.53 (dd, *J* = 10.3, 3.1 Hz, 1H), 3.48-3.37 (m, 5H), 3.37-3.32 (m, 2H), 3.32-3.22 (m, 6H), 2.81 (s, 1H), 1.86-1.71 (m, 2H), 1.34 (d, *J* = 6.4 Hz, 3H), 1.11 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.07, 165.34, 139.58, 139.50, 139.38, 139.35, 138.99, 138.97, 138.77, 138.69, 138.64, 138.51, 138.40, 138.31, 138.29, 137.94, 137.86, 137.54, 133.01, 132.83, 130.43, 130.10, 130.05, 129.82, 128.54, 128.48, 128.45, 128.40, 128.35, 128.33, 128.29, 128.24, 128.20, 128.14, 128.11, 128.05, 128.01, 127.96, 127.89, 127.86, 127.81, 127.74, 127.72, 127.66, 127.60, 127.58,

127.54, 127.51, 127.46, 127.39, 127.34, 127.31, 127.26, 127.16, 127.03, 127.01, 126.91, 105.14, 104.57, 104.07, 103.07, 99.52, 98.70, 85.02, 84.81, 83.27, 82.47, 82.41, 82.38, 82.03, 80.35, 80.02, 79.78, 78.94, 76.61, 76.07, 75.90, 75.79, 75.70, 75.49, 75.06, 74.74, 74.63, 73.76, 73.52, 73.38, 73.14, 73.12, 73.00, 72.93, 72.81, 72.52, 72.40, 72.12, 72.02, 71.95, 71.86, 71.79, 71.31, 71.27, 70.75, 69.62, 69.03, 68.15, 67.83, 67.07, 66.45, 65.64, 48.40, 29.22, 16.32, 16.29; HRMS (ESI): *m/z* calcd for $C_{183}H_{191}N_3O_{35}$ $[M+Na]^+$: 3013.3156, found: 3013.3154.

4-Aminopropyl α-D-fucofuranosyl-(1→2)-α-D-fucofuranosyl-(1→4)-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→6)-D-*glycero*-β-D-*galacto*-heptopyranosyl-(1→3)-D-*glycero*-β-D-*galacto*-heptopyranoside (1)

To a solution of **27** (30 mg, 0.01 mmol) in MeOH/CH_2Cl_2 (v/v, 1:1, 0.1 mL) was added $NaOCH_3$ (3 mg, 0.05 mmol) at 0 °C, and the resulting mixture was warmed gradually to room temperature. The mixture was stirred for 12 h at the same temperature, at the end of which time TLC indicated the reaction was finished. The reaction was quenched with Amberlite IR120 H^+ resin. After filtration, the resulting mixture was concentrated to dryness. The obtained residue was purified by silica gel column chromatography (4:1, petroleum ether-EtOAc) to afforded a colorless syrup. To a solution of the obtained syrup in MeOH (1 mL) was added 80% $Pd(OH)_2/C$ (20 mg, 0.11 mmol), and the reaction mixture was stirred under a hydrogen atmosphere at 30 °C. The mixture was stirred for 36 h at the same temperature. The reaction mixture was filtered and the filtrate was concentrated *in vacuo.* The obtained residue was purified by Sephadex LH-20 column (H_2O) to afford **1** (9 mg, 80% over two steps) as a white solid. $[\alpha]_D^{25}$ +7.9 (*c* 0.12, H_2O); ^1H NMR (600 MHz, D_2O) δ 5.25 (d, *J* = 4.6 Hz, 1H), 5.17 (d, *J* = 4.0 Hz, 1H), 4.64 (q, *J* = 7.8, 7.1 Hz, 3H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.39-4.24 (m, 4H), 4.20-4.07 (m, 5H), 4.07-3.96 (m, 3H), 3.97-3.86 (m, 5H), 3.87-3.77 (m, 5H), 3.77-3.60 (m, 13H), 3.57-3.53 (m, 3H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.03-1.97 (m, 2H), 1.27 (d, *J* = 6.5 Hz, 2H), 1.24 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (150 MHz, D_2O) δ 101.99, 101.90, 99.79, 98.87, 97.99, 97.78, 82.17, 81.28, 80.45, 80.28, 78.90, 75.72, 73.97, 72.29, 71.68, 70.54, 70.41, 70.24, 69.88, 69.25, 69.21, 69.14, 68.77, 68.35, 67.29, 67.03, 66.02, 65.97, 65.28, 65.21, 65.17, 64.76, 64.71, 63.14, 60.34, 60.19, 60.07, 56.94, 35.13, 24.33, 16.14, 15.45; HRMS (ESI): *m/z* calcd for $C_{43}H_{77}NO_{33}$ $[M+H]^+$: 1136.4456, found: 1136.4453.

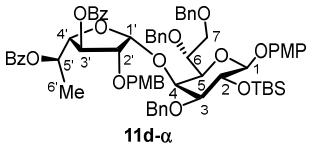
Table 1. NMR spectra of compound **h-4**



h-4

position	^1H (ppm)	^{13}C (ppm)	^1H-^1H COSY	HMBC (H→C)
1	4.75 (d, 8.0 Hz, 1H)	102.03	H-2	C-3
2	4.04 (t, 8.6 Hz, 1H)	70.92	H-1, H-3	C-1, C-3, C-4
3	3.52 (dd, 9.4, 3.3 Hz, 1H)	80.75	H-2, H-4	C-1, C-2, C-4, C-8
4	4.24 (s, 1H)	65.26	H-3, H-5	C-2, C-3
5	4.72 (m, 1H)	72.61	H-4, H-6	C-4, C-6, C-7
6	3.95 (dt, 9.0, 3.4, 2.3 Hz, 1H)	75.53	H-5, H-7a, H-7b	C-4, C-5, C-9
7	3.74 (dd, 3.8, 1.2 Hz, H-7a)	68.39	H-6	C-5, C-6, C-10
	3.60 (dd, 10.0, 3.4 Hz, H-7b)			

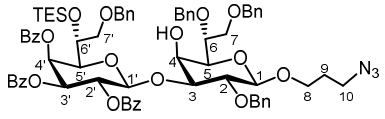
Table 2. NMR spectra of compound **11d-α**



11d-α

position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.72 (d, 7.6 Hz, 1H)	101.89	H-2	C-3
2	4.12 (m, 1H)	71.81	H-1, H-3	C-1, C-3, C-4
3	3.38 (dd, 9.5, 2.8 Hz, 1H)	81.88	H-2, H-4	C-1, C-2, C-4
4	4.22 (m, 1H)	76.00	H-3, H-5	C-2, C-3, C-1'
5	3.69 (m, 1H)	72.64	H-4, H-6	C-1, C-3
6	3.11 (m, 1H)	74.99	H-5, H-7a, H-7b	C-4, C-5
7	3.52 (dd, 10.9, 1.9 Hz, H-7a) 3.60 (dd, 10.9, 2.4 Hz, H-7b)	66.69	H-6	C-5, C-6
1'	5.15 (d, 4.9 Hz, 1H)	104.01	H-2'	C-3', C-4', C-4
2'	4.21 (m, 1H)	81.83	H-1', H-3'	C-1', C-3'
3'	5.97 (t, 6.8 Hz, 1H)	75.27	H-2' , H-4'	C-1', C-2', C-5'
4'	4.09 (m, 1H)	81.01	H-3', H-5'	C-1', C-2', C-3'
5'	5.37 (m, 1H)	71.14	H-4', H-6'	C-3', C-4', C-6'
6'	1.55 (d, 6.4 Hz, 3H)	15.10	H-5'	C-5'

Table 3. NMR spectra of compound **23**

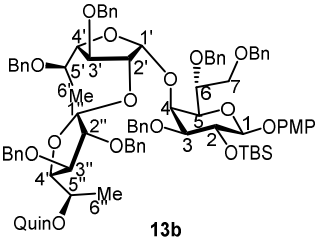


23

position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.13 (d, 7.7 Hz, 1H)	103.66	H-2	C-3, C-5, C-8
2	3.50 (m, 1H)	78.96	H-1, H-3	C-1, C-3
3	3.63 (m, 1H)	81.17	H-2, H-4	C-2, C-4, C-1'
4	4.28 (m, 1H)	67.85	H-3, H-5	C-2, C-5
5	3.48 (m, 1H)	72.13	H-4, H-6	C-1, C-4, C-6, C-7
6	4.00 (m, 1H)	75.82	H-5, H-7a, H-7b	C-4, C-5, C-7
7	3.76 (dd, 10.5, 2.1 Hz, H-7a) 3.66 (dd, 10.9, 2.4 Hz, H-7b)	68.94	H-6	C-6
8	3.37 (m, H-8a) 3.68 (m, H-8b)	66.25	H-9	C-1, C-9, C-10

9	1.72 (m, H-9a, H-9b)	29.20	H-8, H-10	C-8, C-10
10	3.21 (t, 7.7 Hz, 2H)	48.30	H-9	C-8, C-9
1'	5.14 (d, 8.0 Hz, 1H)	102.39	H-2'	C-2', C-3', C-3
2'	5.75 (dd, 10.4, 7.9 Hz, 1H)	70.41	H-1', H-3'	C-1', C-3'
3'	5.57 (dd, 10.4, 3.4 Hz, 1H)	72.02	H-2' , H-4'	C-1', C-2', C-4', C-5'
4'	6.01 (d, 3.4 Hz, 1H)	68.08	H-3', H-5'	C-2', C-3',C-6'
5'	3.96 (m, 1H)	73.53	H-4', H-6'	C-1', C-6'
6'	3.97 (m, 1H)	69.61	H-5', H-7'	C-4', C-5', C-7'
7'	3.45 (m, H-7'a)	71.60	H-6'	C-5', C-6'
	3.47 (m, H-7'b)			

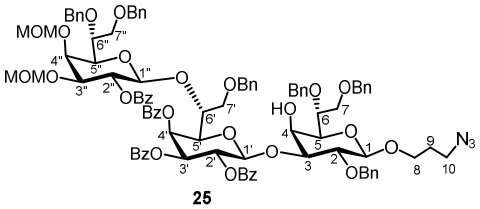
Table 4. NMR spectra of compound **13b**



13b

position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.81 (d, 7.4 Hz, 1H)	102.12	H-2	C-3, C-5
2	4.26 (m, 1H)	71.83	H-1, H-3	C-3, C-4
3	3.43 (dd, 9.4, 3.1 Hz, 1H)	81.47	H-2, H-4	C-2, C-4, C-5
4	4.41 (m, 1H)	74.66	H-3, H-5	C-2, C-3, C-1'
5	3.79 (m, 1H)	72.24	H-4, H-6	C-1, C-3, C-6, C-7
6	4.23 (m, 1H)	74.96	H-5, H-7a, H-7b	C-5, C-7
7	3.66 m (H-7a)	66.29	H-6	C-5, C-6
	3.68 m (H-7b)			
1'	5.13 (d, 4.3 Hz, 1H)	104.11	H-2'	C-3', C-4', C-4
2'	4.24 (m, 1H)	80.45	H-1', H-3'	C-3', C-1"
3'	4.29 (m, 1H)	80.72	H-2', H-4'	C-1', C-2', C-4', C-5'
4'	3.98 (t, 5.4 Hz, 1H)	83.86	H-3', H-5'	C-1', C-3', C-5', C-6'
5'	3.74 (m, 1H)	75.77	H-4', H-6'	C-4', C-6'
6'	1.31 (d, 6.6 Hz, 3H)	15.32	H-5'	C-4', C-5'
1"	5.60 (d, 3.9 Hz, 1H)	98.85	H-2"	C-2', C-2"
2"	4.13 (m, 1H)	84.96	H-1", H-3"	C-1",C-3"
3"	4.25 (m, 1H)	81.89	H-2", H-4"	C-2", C-4"
4"	4.22 (m, 1H)	81.45	H-3", H-5"	C-3", C-5", C-6"
5"	5.52 (m, 1H)	75.77	H-4", H-6"	C-4", C-6"
6"	1.49 (d, 6.4 Hz, 3H)	16.43	H-5"	C-4", C-5"

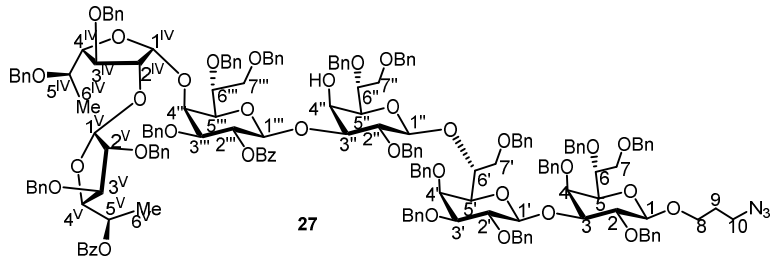
Table 5. NMR spectra of compound **25**



25

position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.01 (d, 7.8 Hz, 1H)	103.62	H-2	C-2, C-5, C-8
2	3.45 (m, 1H)	79.24	H-1, H-3	C-1, C-3
3	3.60 (m, 1H)	80.39	H-2, H-4	C-2, C-1'
4	4.23 (m, 1H)	67.84	H-3, H-5	C-6
5	3.47 (m, 1H)	72.05	H-4, H-6	C-4
6	3.93 (m, 1H)	75.72	H-5, H-7a, H-7b	C-5, C-7
7	3.67 (dd, 10.5, 2.3 Hz, H-7a)	68.93	H-6, H-8	C-6
	3.60 (m, H-7b)			
8	3.63 (m, H-8a)	66.26	H-9	C-1, C-9
	3.33 (m, H-8b)			
9	1.68 (m, H-9a, H-9b)	48.36	H-8, H-10	C-8, C-10
10	3.18 (m, H-10a, H-10b)	29.22	H-9	C-9
1'	5.10 (d, 7.9 Hz, 1H)	101.99	H-2'	C-3', C-3
2'	5.67 (dd, 10.4, 7.8 Hz, 1H)	70.63	H-1', H-3'	C-1', C-3'
3'	5.58 (dd, 10.4, 3.4 Hz, 1H)	71.63	H-2' , H-4'	C-2'
4'	6.04 (d, 3.4 Hz, 1H)	66.25	H-3', H-5'	C-2'
5'	3.89 (m, 1H)	72.83	H-4', H-6'	C-4', C-6'
6'	4.09 (d, 3.4 Hz, 1H)	72.83	H-5', H-7'	C-5', C-7', C-1"
7'	3.59 (m, H-7'a)	69.16	H-6'	C-6'
	3.39 (m, H-7'b)			
1"	4.78 (d, 7.9 Hz, 1H)	98.89	H-2"	C-6', C-5"
2"	5.43 (dd, 10.3, 7.8 Hz, 1H)	71.91	H-1", H-3"	C-1", C-3"
3"	3.81 (dd, 10.3, 2.8 Hz, 1H)	76.44	H-2", H-4"	C-2"
4"	4.16 (d, 2.8 Hz, 1H)	72.05	H-3", H-5"	C-2", C-3"
5"	3.57 (m, 1H)	72.49	H-4", H-6"	C-4", C-6"
6"	3.16 (m, 1H)	75.50	H-5", H-7"	C-5", C-7"
7"	3.11 (m, H-7"a)	66.20	H-6"	C-6"
	3.02 (m, H-7"b)			

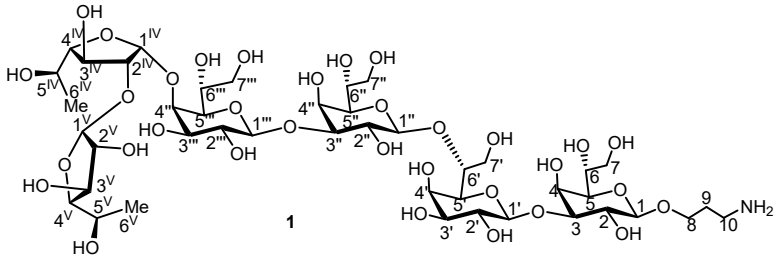
Table 6. NMR spectra of compound **27**



position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	3.98 (d, 7.4 Hz, 1H)	103.07	H-2	C-2
2	3.76 (m, 1H)	71.79	H-1, H-3	C-3
3	3.68 (m, 1H)	76.61	H-2, H-4	C-2, C-4, C-5, C-1'
4	4.23 (m, 1H)	72.12	H-3, H-5	C-2, C-5
5	3.41 (m, 1H)	72.52	H-4, H-6	C-1, C-4, C-6
6	3.90 (m, 1H)	73.38	H-5, H-7a, H-7b	C-5
7	3.76 (m, H-7a)	65.64	H-6	C-6
	3.60 (m, H-7b)			
8	3.68 (m, H-8a)	66.45	H-9	C-1, C-9, C-10
	3.34 (m, H-8b)			
9	1.77 (m, H-9a, H-9b)	48.64	H-8, H-10	C-8, C-10
10	3.29 (m, H-10a, H-10b)	29.22	H-9	C-8, C-9
1'	4.82 (d, 7.04 Hz, 1H)	104.57	H-2'	C-2', C-3
2'	3.79 (m, 1H)	79.78	H-1', H-3'	C-3', C-1'
3'	3.32 (m, 1H)	82.41	H-2' , H-4'	C-1', C-2', C-4'
4'	4.24 (m, 1H)	73.14	H-3', H-5'	C-5', C-2'
5'	3.68 (m, 1H)	72.52	H-4', H-6'	C-4',C-6'
6'	4.14 (m, 1H)	75.79	H-5', H-7'	C-5', C-1"
7'	3.62 (m, H-7'a)	67.07	H-6'	C-6'
	3.41 (m, H-7'b)			
1"	4.54 (d, 7.8 Hz, 1H)	98.70	H-2"	C-6', C-2"
2"	3.44 (m, 1H)	78.94	H-1", H-3"	C-1", C-3"
3"	3.45 (m, 1H)	82.47	H-2", H-4"	C-2", C4", C-1'"
4"	4.19 (m, 1H)	67.83	H-3", H-5"	C-2"
5"	3.35 (m, 1H)	71.95	H-4", H-6"	C-1", C-4", C-6", C-7"
6"	3.77 (m, 1H)	75.49	H-5", H-7"	C-7"
7"	3.37 (m, H-7"a)	69.03	H-6"	C-6"
	3.26 (m, H-7"b)			
1'"	4.80 (d, 7.6 Hz, 1H)	103.07	H-2'"	C-4'",C-2'", C-3"
2'"	5.63 (dd, 10.2, 8.8 Hz, 1H)	71.79	H-1'", H-3'"	C-1'", C-3'"
3'"	3.53 (dd, 10.3, 3.1 Hz, 1H)	76.61	H-2'", H-4'"	C-2'", C-4'"
4'"	4.55 (m, 1H)	72.12	H-3'", H-5'"	C-3'", C-5'",C-1^{IV}
5'"	3.64 (m, 1H)	72.52	H-4'", H-6'"	C-4'", C-6'"

6'''	3.77 (m, 1H)	73.38	H-5''', H-7'''	C-5''', C-7'''
7'''	3.26 (m, H-7'''a, H-7'''b)	65.64	H-6'''	C-6'''
1^{IV}	5.29 (d, 3.6 Hz, 1H)	105.14	H-2^{IV}	C-2^{IV}, C-4^{IV}
2^{IV}	4.48 (m, 1H)	74.63	H-1^{IV}, H-3^{IV}	C-1^{IV}, C-1^{V}, C-3^{IV}
3^{IV}	3.98 (m, 1H)	83.27	H-2^{IV}, H-4^{IV}	C-1^{IV}, C-2^{IV}, C-4^{IV}
4^{IV}	3.90 (m, 1H)	84.81	H-3^{IV}, H-5^{IV}	C-1^{IV}, C-3^{IV}, C-5^{IV}
5^{IV}	3.74 (m, 1H)	76.07	H-4^{IV}, H-6^{IV}	C-4^{IV}
6^{IV}	1.11 (d, 6.2 Hz, 3H)	16.32	H-5^{IV}	C-4^{IV}, C-5^{IV}
1^{V}	6.09 (d, 4.2 Hz, 1H)	99.52	H-2^{V}	C-2^{IV}, C-2^{V},C-3^{V}
2^{V}	4.49 (m, 1H)	85.02	H-1^{V}, H-3^{V}	C-1^{V}
3^{V}	4.25 (m, 1H)	82.03	H-2^{V}, H-4^{V}	C-2^{V}, C-4^{V}, C-5^{V}
4^{V}	4.17 (m, 1H)	82.38	H-3^{V}, H-5^{V}	C-1^{V}, C-3^{V}, C-5^{V}, C-6^{V}
5^{V}	5.31 (m, 1H)	73.76	H-4^{V}, H-6^{V}	C-3^{V}, C-4^{V}, C-6^{V}
6^{V}	1.34 (d, 6.4 Hz, 3H)	16.29	H-5^{V}	C-4^{V}, C-5^{V}

Table 7. NMR spectra of compound **1**



Position	^{1}H (ppm)	^{13}C (ppm)	^{1}H-^{1}H COSY	HMBC (H→C)
1	4.48 (d, 7.9 Hz, 1H)	98.87	H-2	C-3, C-8
2	3.68 (m, 1H)	69.21	H-1, H-3	C-1, C-3
3	3.55 (m, 1H)	80.28	H-2, H-4	C-1, C-4, C-1'
4	4.34 (m, 1H)	64.76	H-3, H-5	C-3, C-5
5	3.53 (m, 1H)	65.97	H-4, H-6	C-6
6	3.93 (m, 1H)	70.54	H-5, H-7a, H-7b	C-5
7	3.83 (m, H-7a, H-7b)	60.35	H-6	-
8	4.03 (m, H-8a)	65.22	H-9	C-1, C-9, C-10
	3.79 (m, H-8b)			
9	2.00 (m, 2H)	24.33	H-8, H-10	C-8, C-10
10	3.14 (t, 6.9 Hz, 2H)	35.13	H-9	C-9
1'	4.64 (d, 7.1 Hz, 1H)	97.99	H-2'	C-3
2'	3.57 (m, 1H)	68.77	H-1', H-3'	C-1'
3'	3.70 (m, 1H)	67.29	H-4'	C-2', C-4', C-5'
4'	4.13 (m, 1H)	64.71	H-5'	C-2'
5'	3.89 (m, 1H)	66.02	H-4', H-6'	-
6'	4.09 (m, 1H)	72.29	H-5', H-7'	C-7',C-1''
7'	3.96 (m, H-7'a)	56.94	H-6'	C-6'

	3.71 (m, H-7'b)			
1"	4.65 (d, 7.8 Hz, 1H)	101.90	H-2"	C-6'
2"	3.73 (m, 1H)	69.14	H-1", H-3"	C-1", C-3", C-4"
3"	3.80 (m, 1H)	80.45	H-2", H-4"	C-1'"
4"	4.32 (m, 1H)	64.68	H-3", H-5"	C-5", C-3'", C-2"
5"	3.81 (m, 1H)	67.04	H-4"	C-6"
6"	3.69 (m, 1H)	70.24	H-7"	C-5"
7"	3.74 (m, H-7"a, H-7"b)	60.07	H-6"	-
1'"	4.62 (d, 7.8 Hz, 1H)	97.78	H-2'"	C-3"
2'"	3.64 (m, 1H)	68.35	H-1'", H-3'"	C-1'", C-3'"
3'"	3.62 (m, 1H)	70.41	H-2'", H-4'"	C-4'", C-5'",C-1^{IV}
4'"	4.14 (m, 1H)	75.73	H-3'", H-5'"	C-5'", C-6'"
5'"	3.91 (m, 1H)	68.18	H-4'", H-6'"	C-3'"
6'"	4.01 (m, 1H)	69.88	H-5'", H-7'"	C-5'"
7'"	3.67 (m, H-7'"a, H-7'"b)	60.19	H-6'"	C-6'"
1^{IV}	5.25 (d, 4.6 Hz, 1H)	99.79	H-2^{IV}	C-3^{IV}, C-4^{IV}, C-4'"
2^{IV}	4.28 (m, 1H)	78.90	H-1^{IV}, H-3^{IV}	C-1^{V}, C-3^{IV}
3^{IV}	4.38 (m, 1H)	69.25	H-2^{IV}, H-4^{IV}	C-2^{IV}
4^{IV}	3.72 (m, 1H)	81.28	H-3^{IV}, H-5^{IV}	C-3^{IV}, C-6^{IV}
5^{IV}	3.93 (m, 1H)	63.14	H-4^{IV}, H-6^{IV}	C-4^{IV}, C-6^{IV}
6^{IV}	1.27 (d, 6.5 Hz, 3H)	16.14	H-5^{IV}	C-4^{IV}, C-5^{IV}
1^{V}	5.17 (d, 4.0 Hz, 1H)	101.99	H-2^{V}	C-3^{V}, C-2^{V},C-4^{V}
2^{V}	4.16 (m, 1H)	71.68	H-1^{V}, H-3^{V}	C-1^{V}, C-3^{V}
3^{V}	4.15 (m, 1H)	73.97	H-2^{V}, H-4^{V}	C-5^{V}, C-2^{V}
4^{V}	3.66 (m, 1H)	82.17	H-3^{V}, H-5^{V}	C-2^{V}
5^{V}	3.95 (m, 1H)	65.28	H-4^{V}, H-6^{V}	C-4^{V}, C-6^{V}
6^{V}	1.24 (d, 6.6 Hz, 3H)	15.45	H-5^{V}	C-4^{V}, C-5^{V}

3. References

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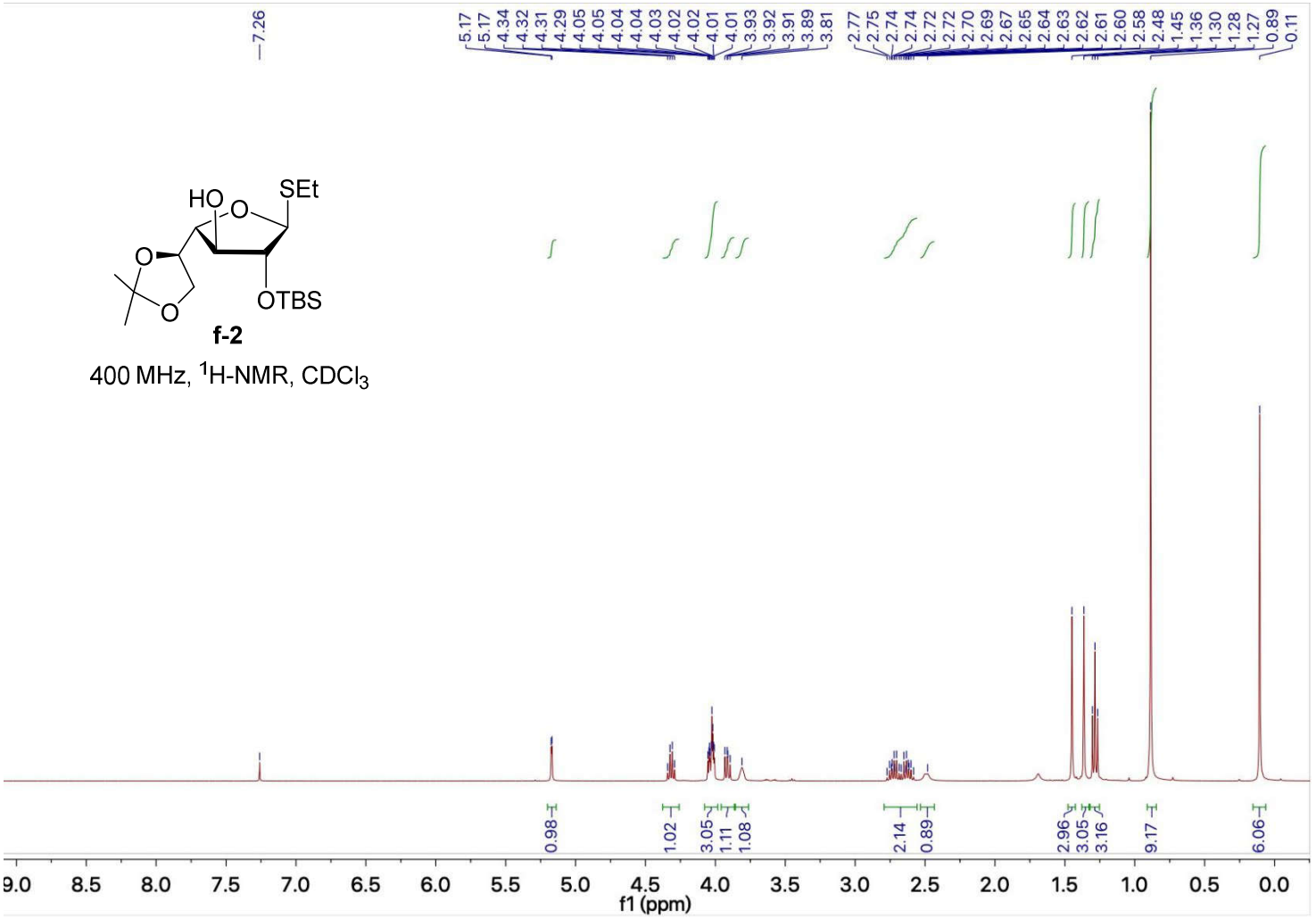
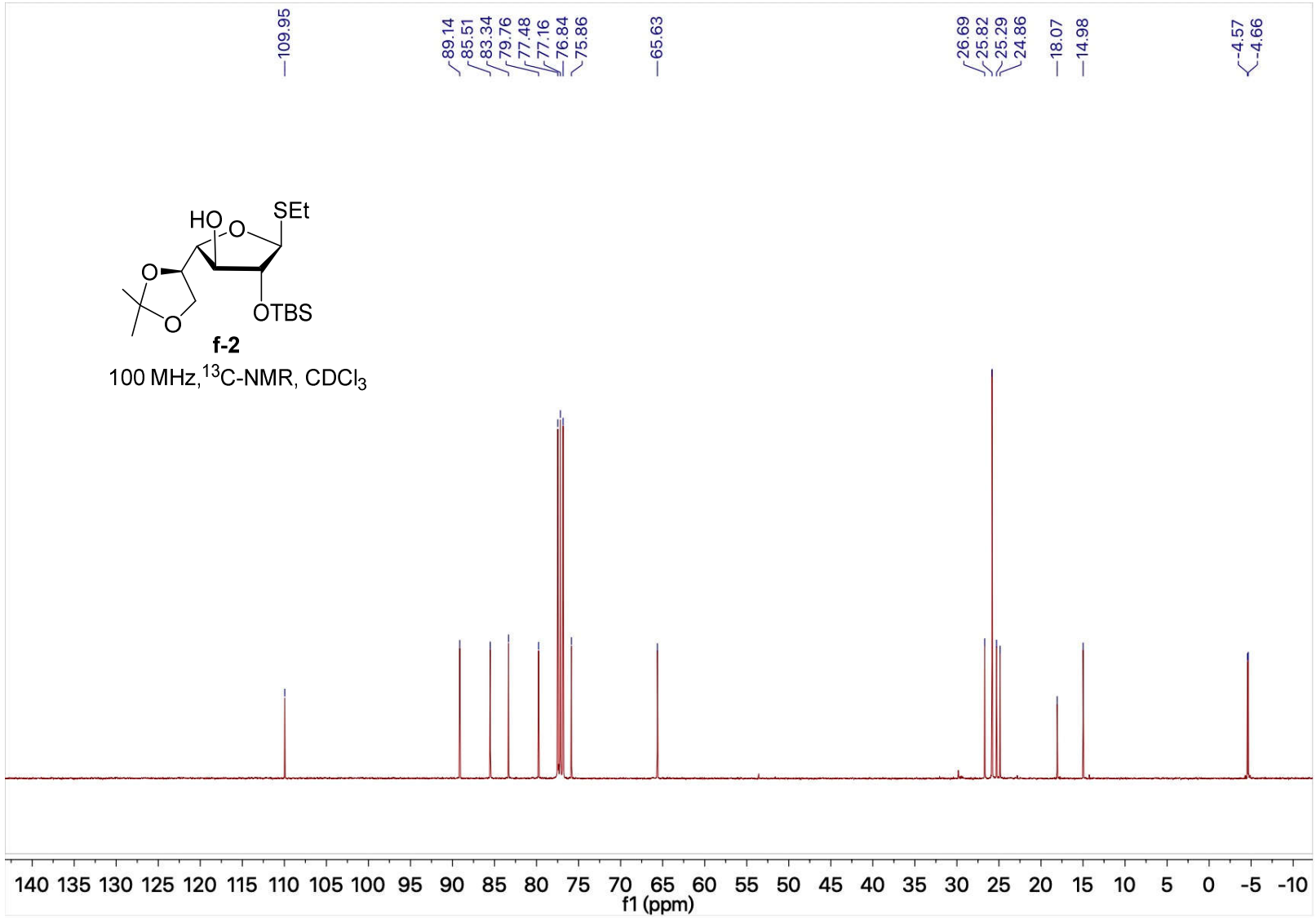
4. Copies of ^{1}H and ^{13}C NMR spectra

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14.98
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HO
O
SEt
O
O
OTBS
f-2
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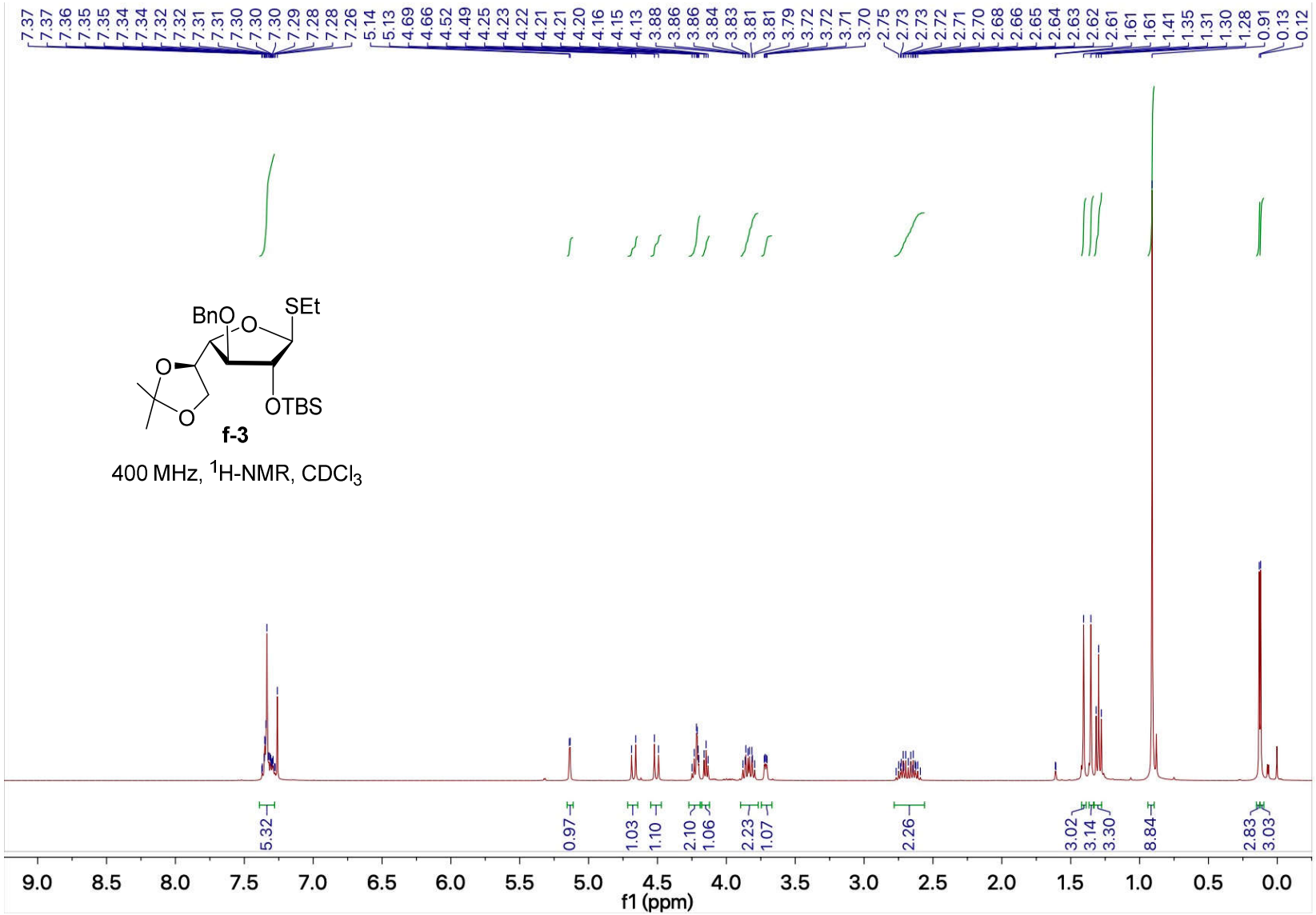
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SEt
O
O
OTBS
f-3
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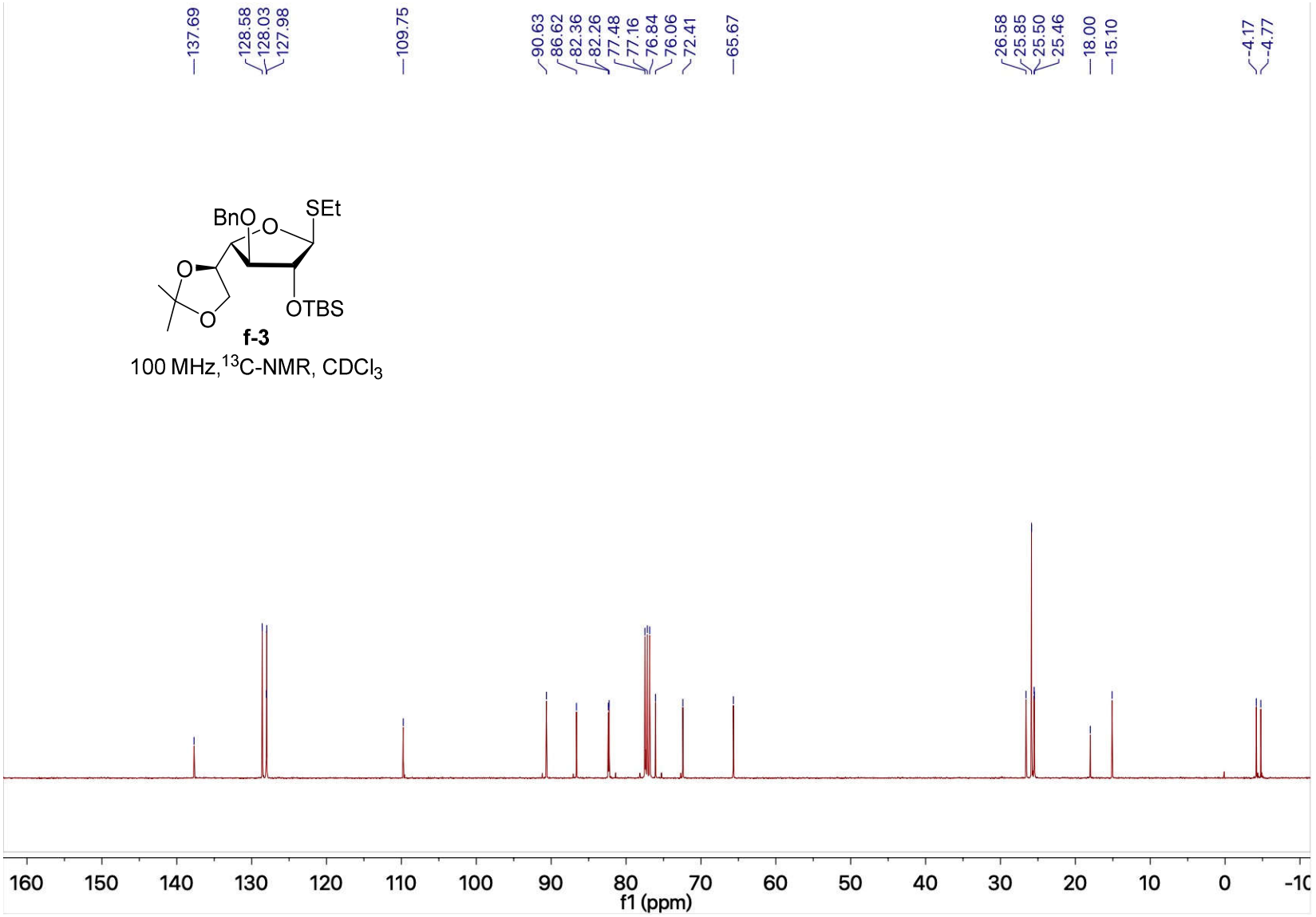
f1 (ppm)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f-3
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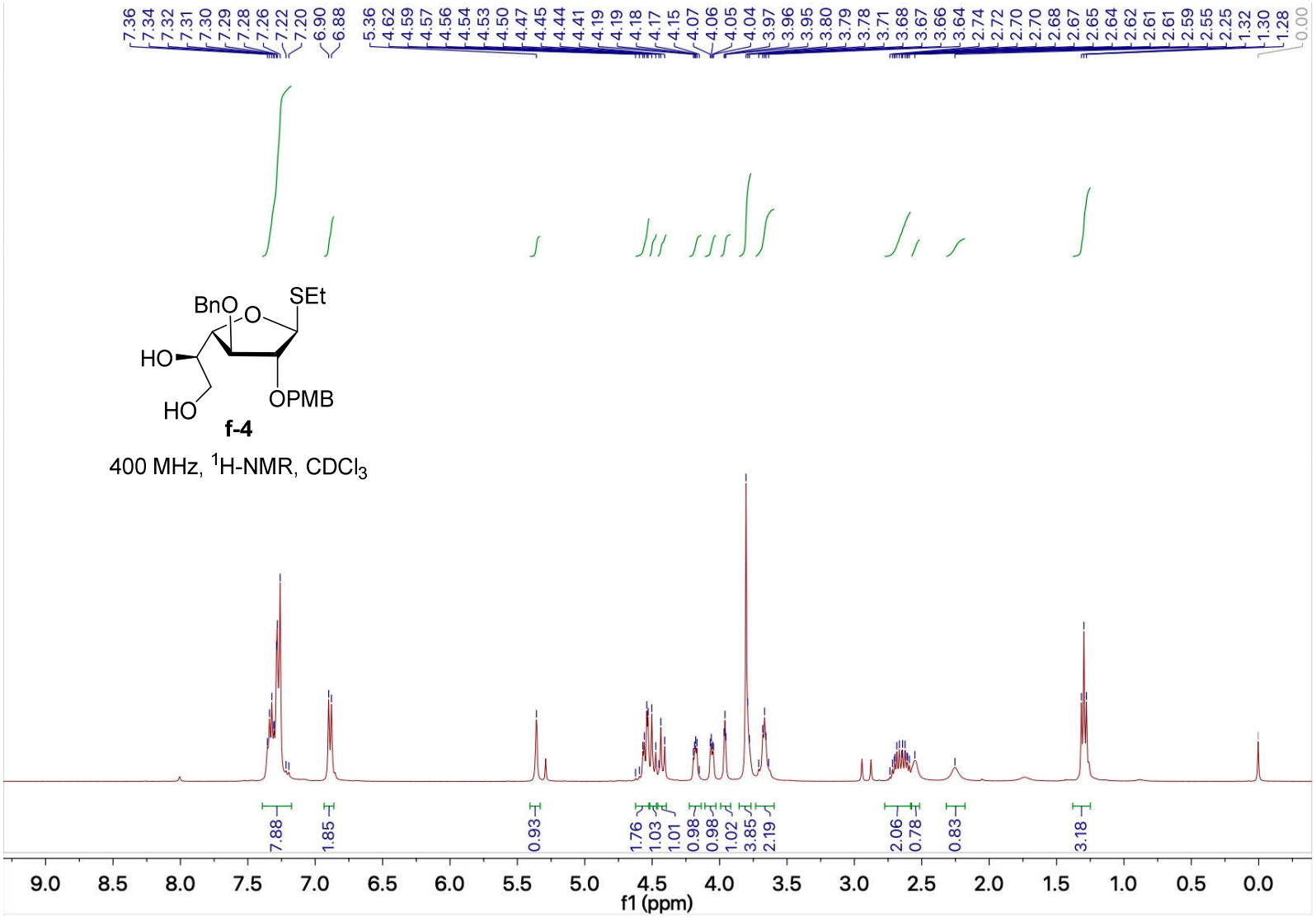
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HO
HO
OPMB
f-4
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1.01
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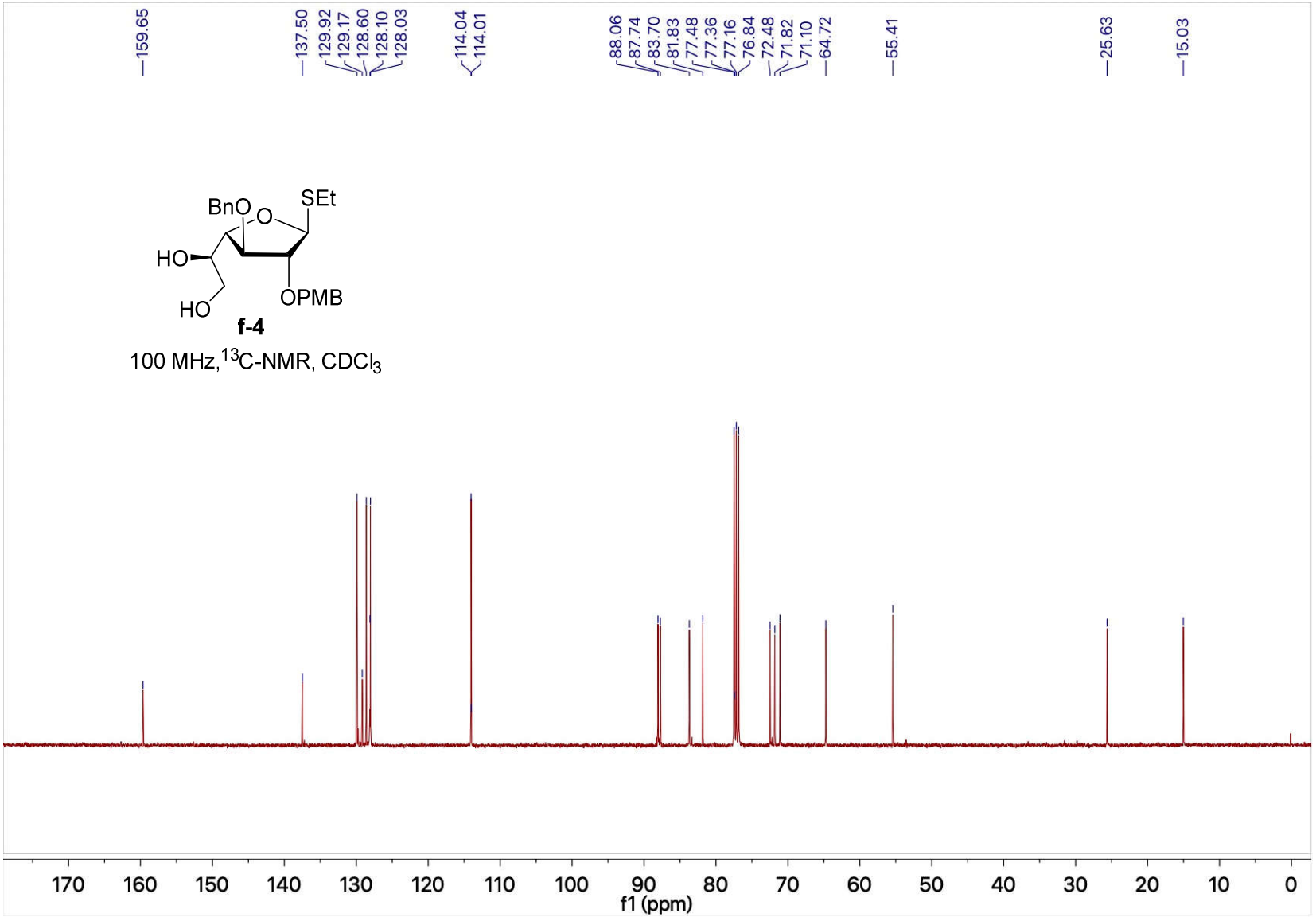
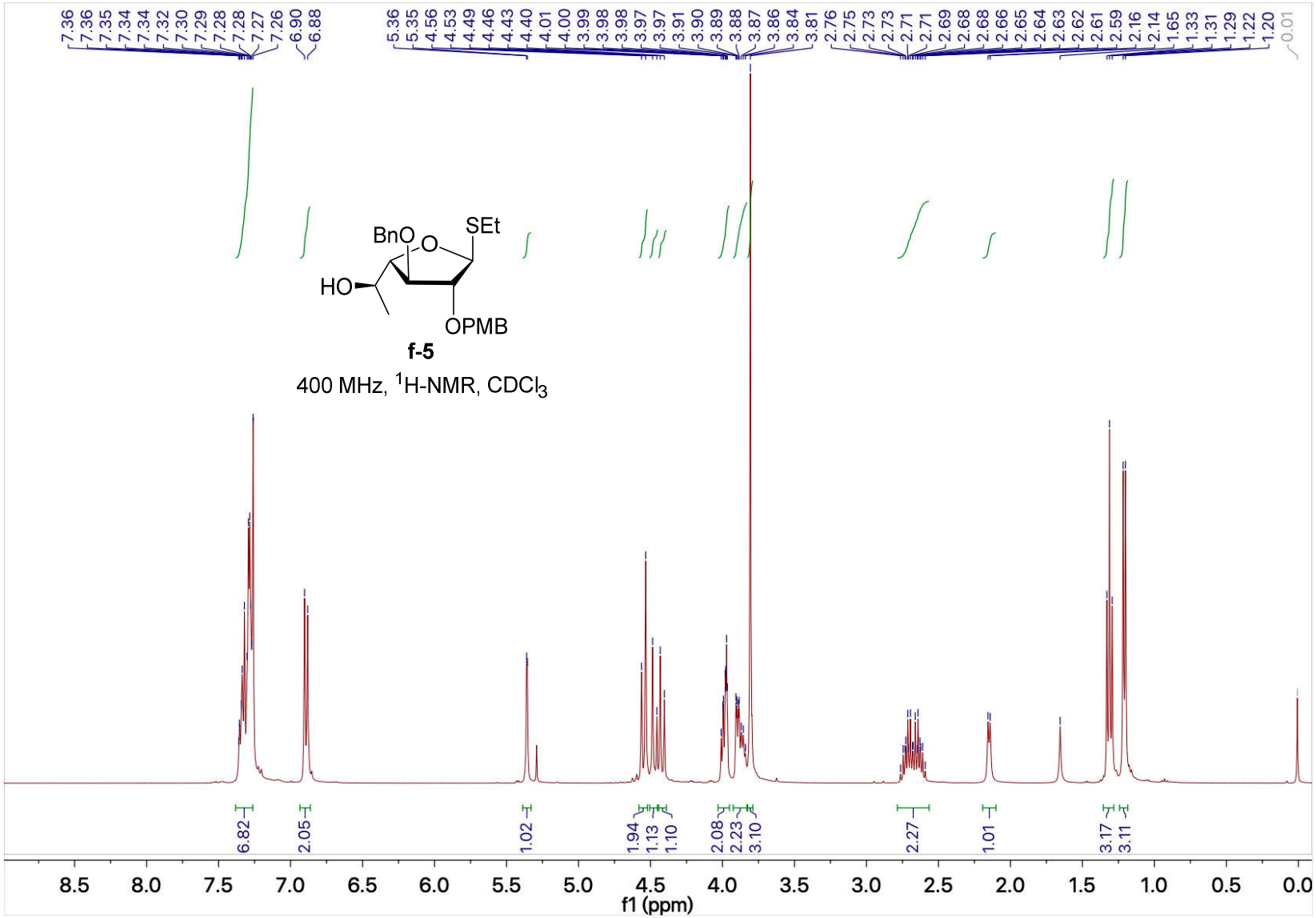
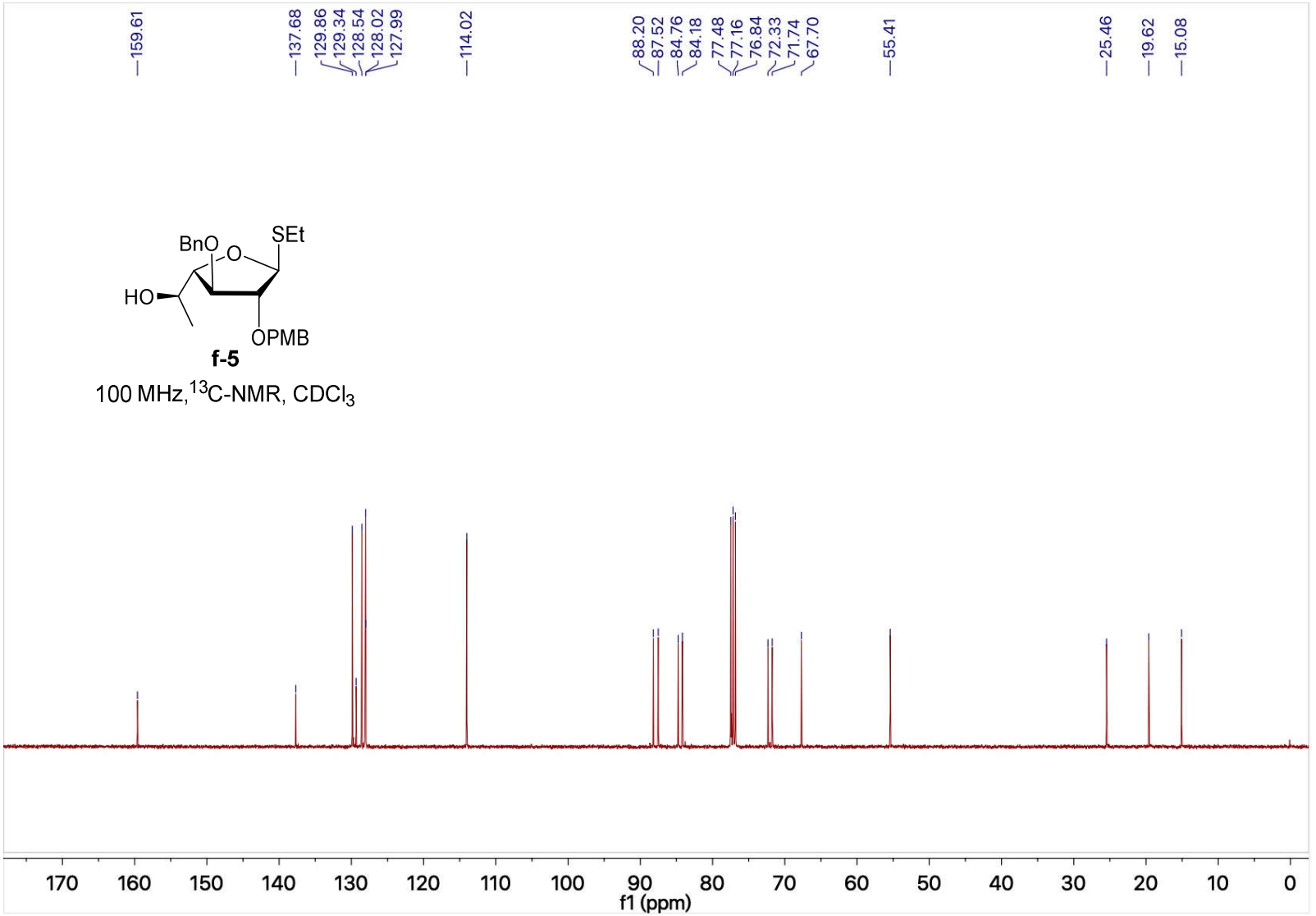
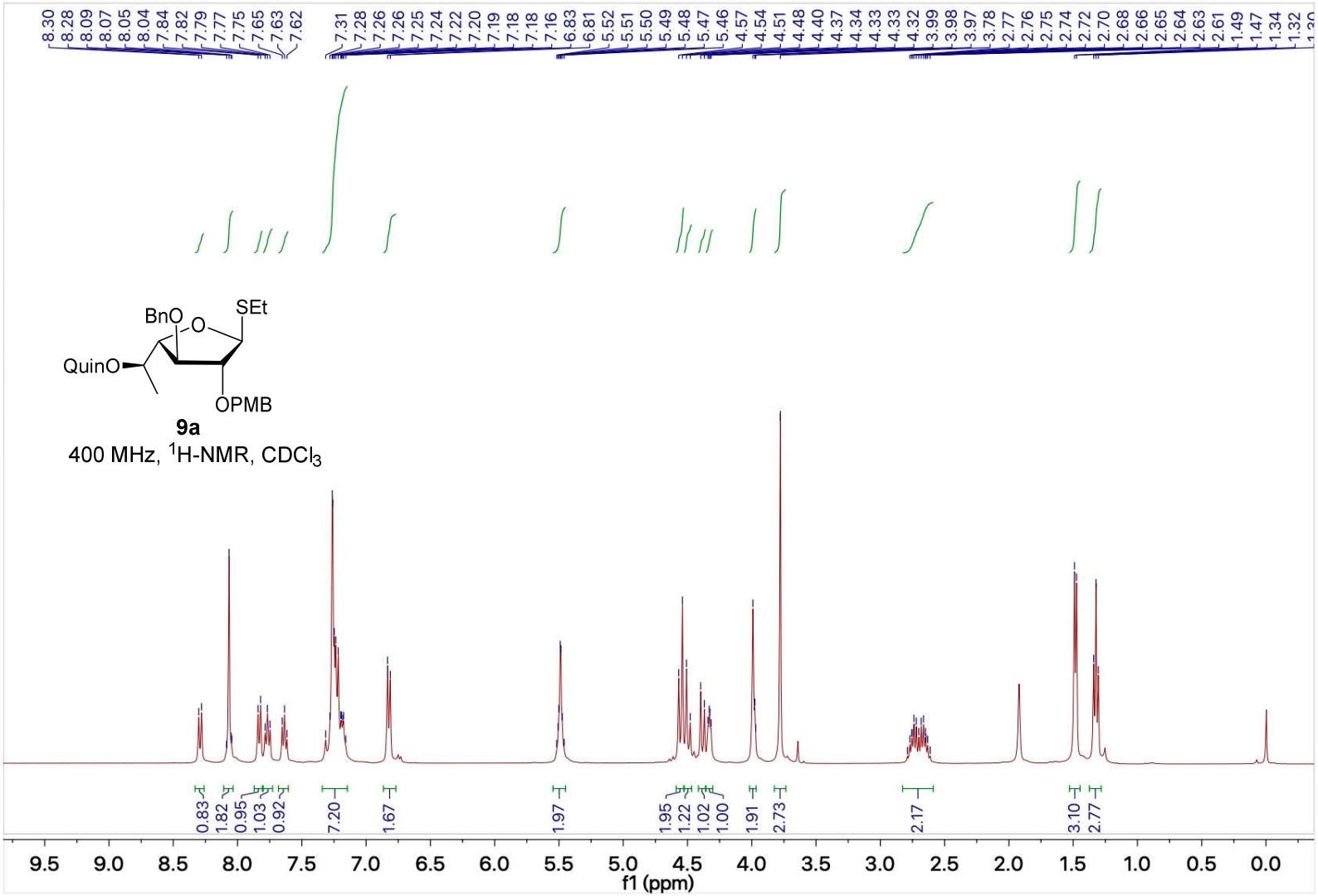
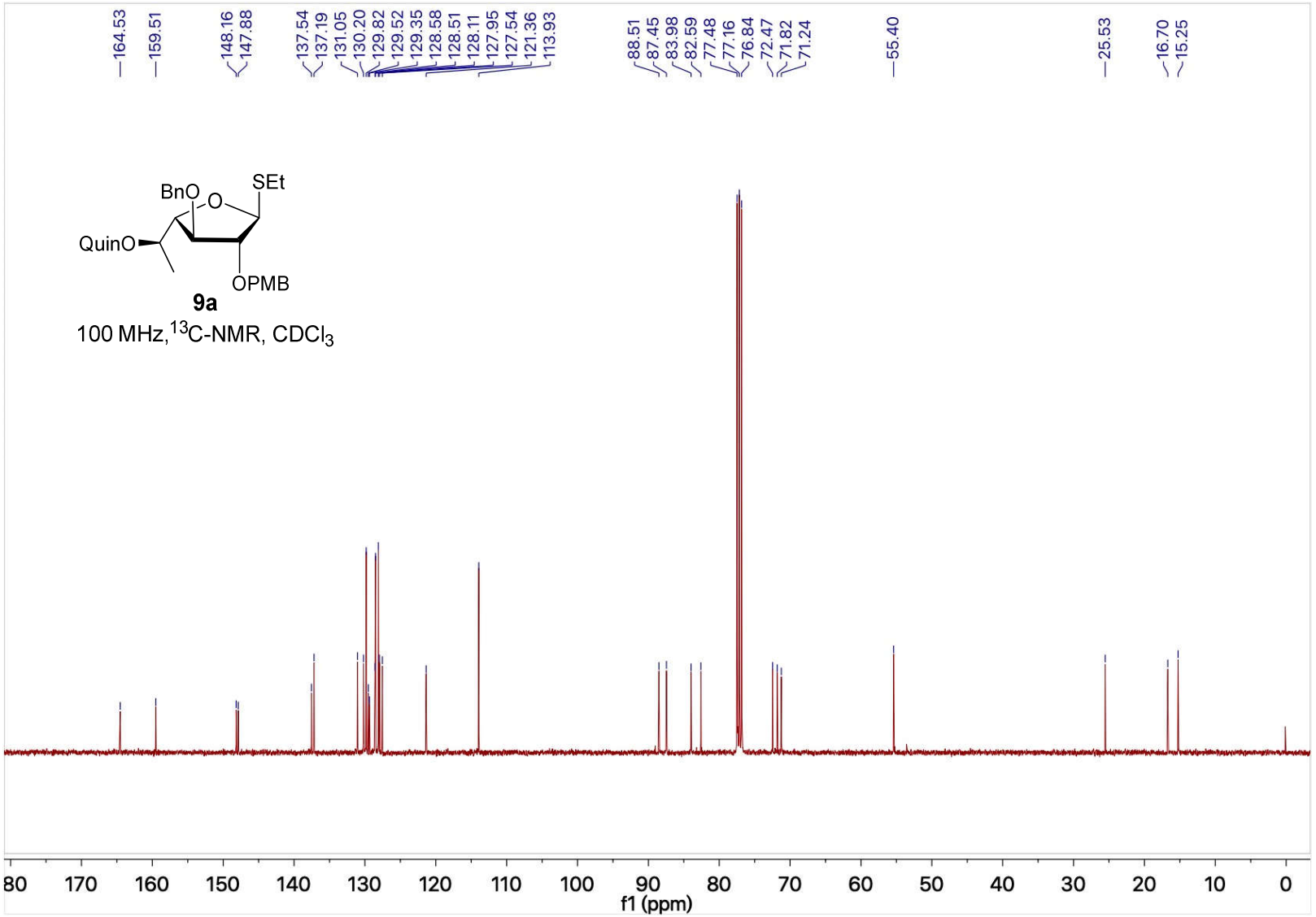
2.19
2.06
0.78
0.83
3.18
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

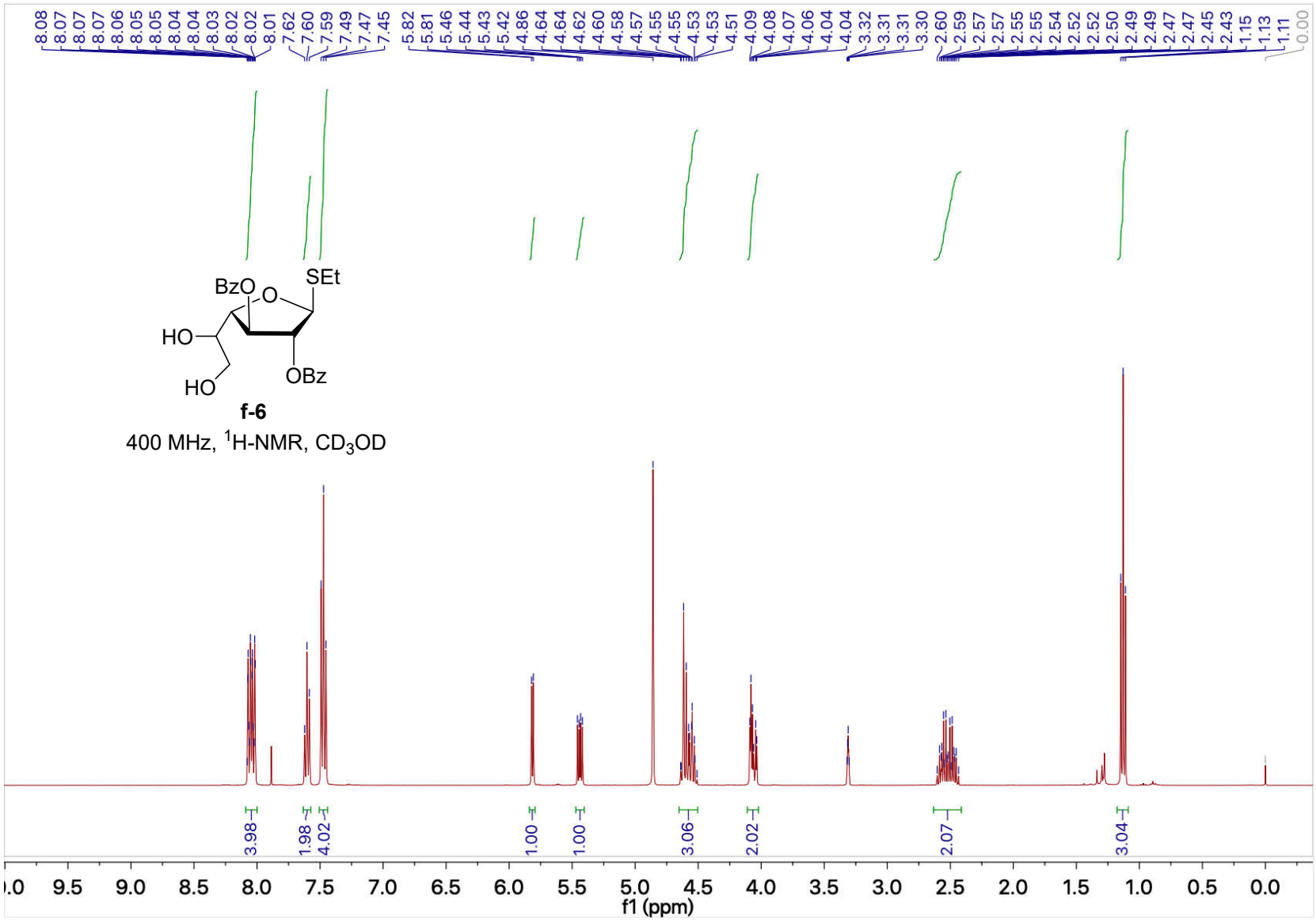

159.65
137.50
129.92
129.17
128.60
128.10
128.03
114.04
114.01
88.06
87.74
83.70
81.83
77.48
77.36
77.16
76.84
72.48
71.82
71.10
64.72
55.41
25.63
15.03
BnO
O
SEt
HO
HO
OPMB
f-4
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

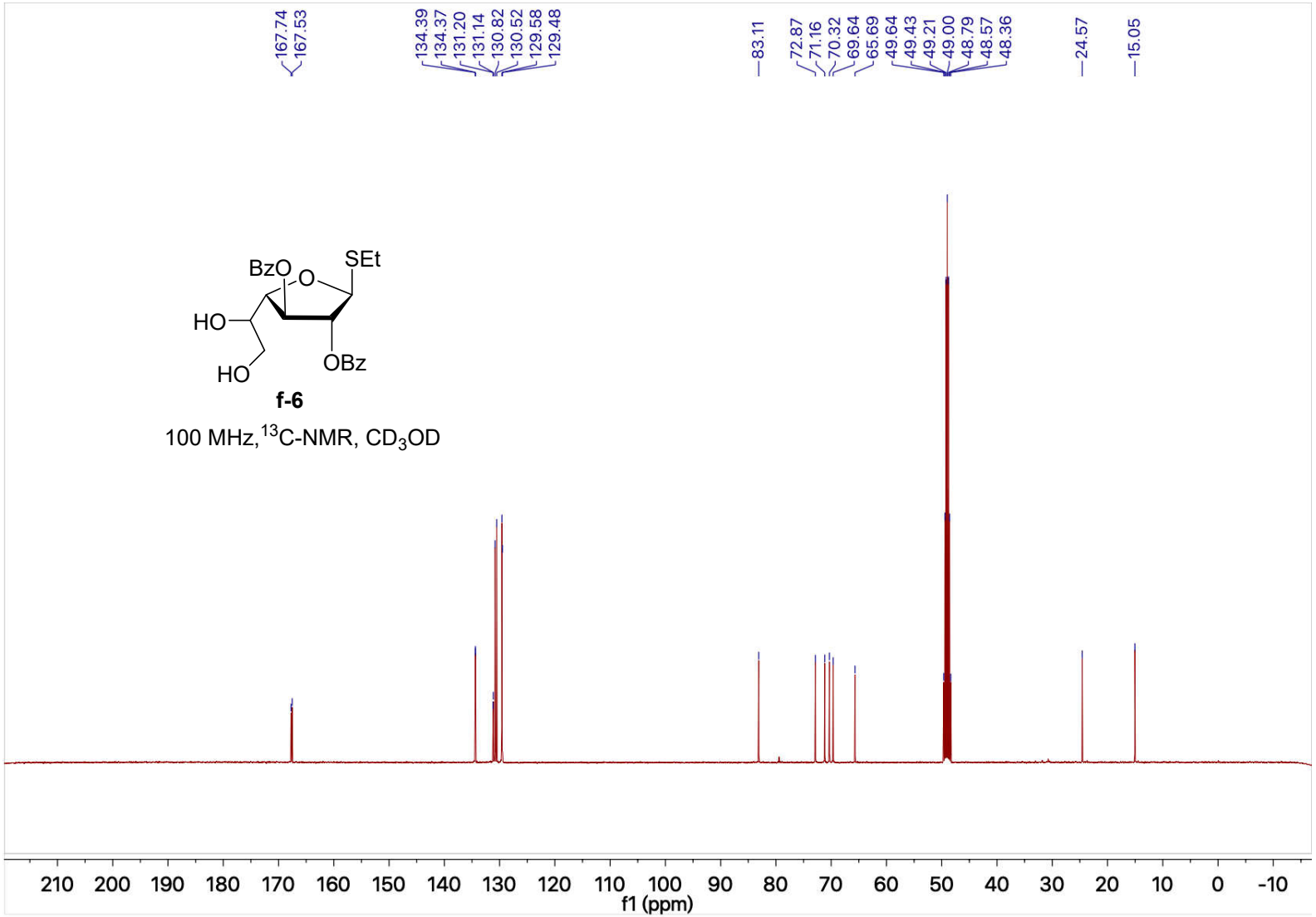

BnO
O
SEt
HO
OPMB
f-5
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

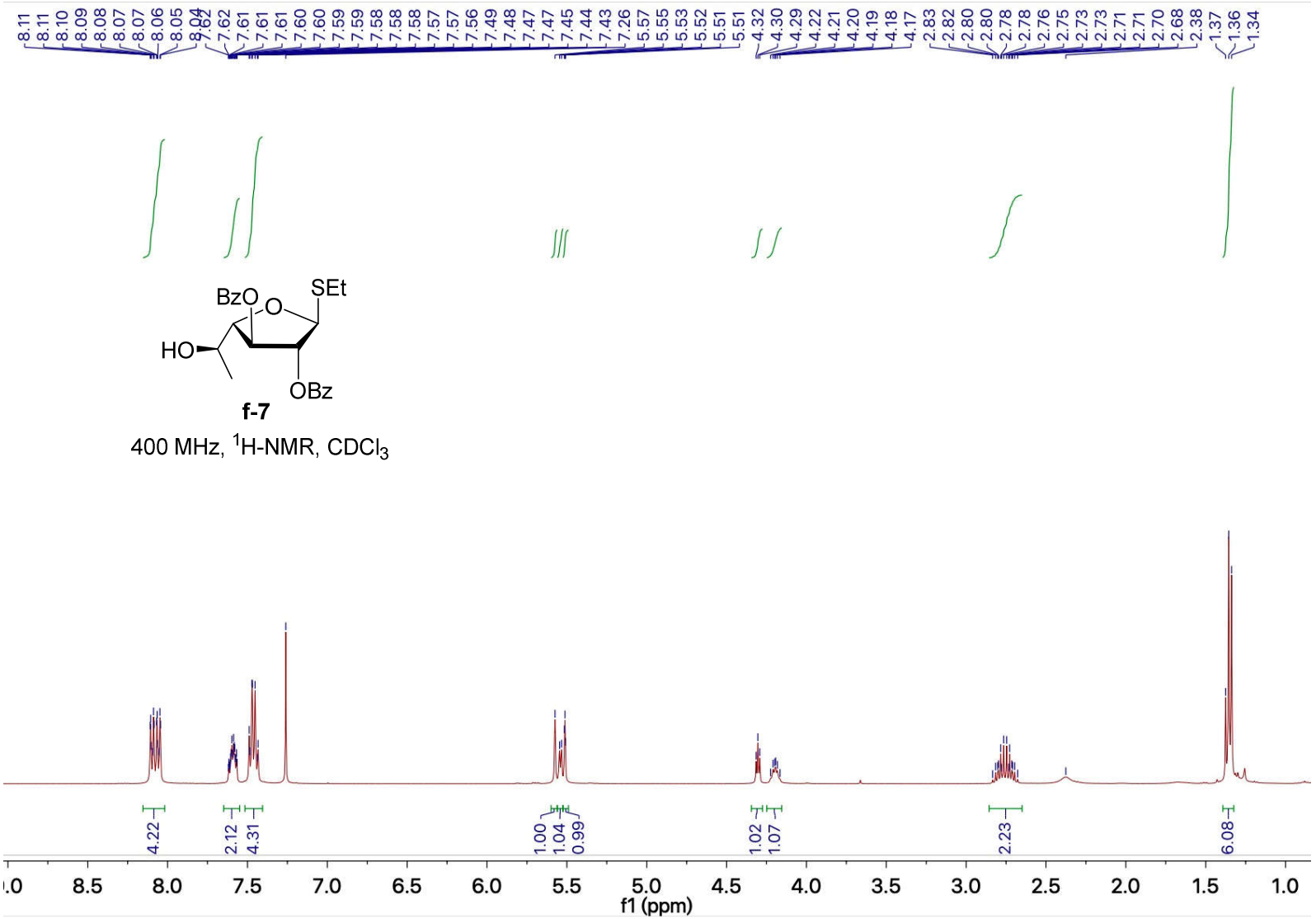

159.61
137.68
129.86
129.34
128.54
128.02
127.99
114.02
88.20
87.52
84.76
84.18
77.48
77.16
76.84
72.33
71.74
67.70
55.41
25.46
19.62
15.08
BnO
O
SEt
HO
OPMB
f-5
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
O
SEt
QuinO
OPMB
9a
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)


164.53
159.51
148.16
147.88
137.54
137.19
131.05
130.20
129.82
129.52
129.35
128.58
128.51
128.11
127.95
127.54
121.36
113.93
88.51
87.45
83.98
82.59
77.48
77.16
76.84
72.47
71.82
71.24
55.40
25.53
16.70
15.25
BnO
O
SEt
QuinO
OPMB
9a
100 MHz, 13C-NMR, CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

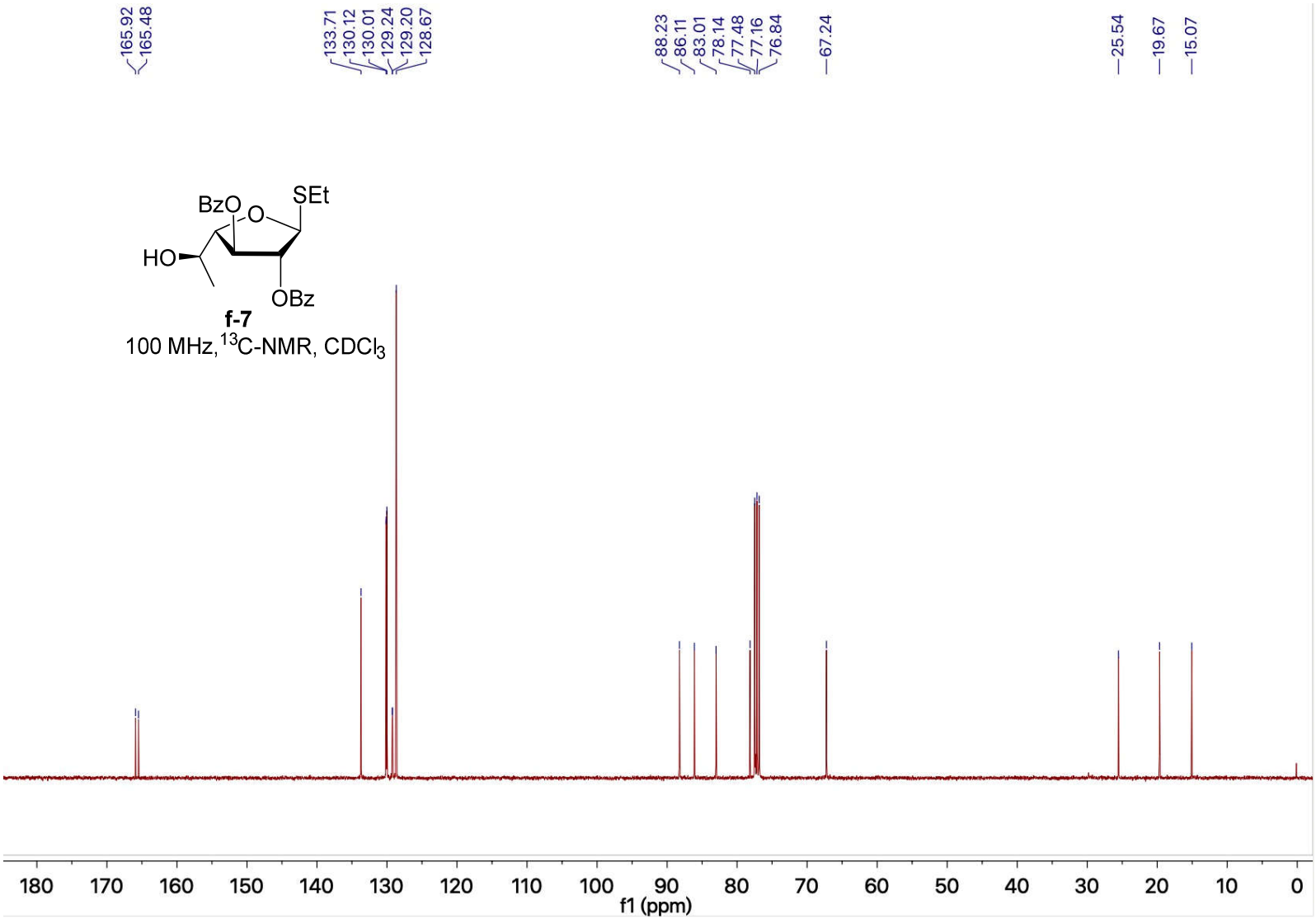

BzO
O
SEt
HO
HO
OBz
f-6
400 MHz, ^{1}H-NMR, CD_3OD
f1 (ppm)

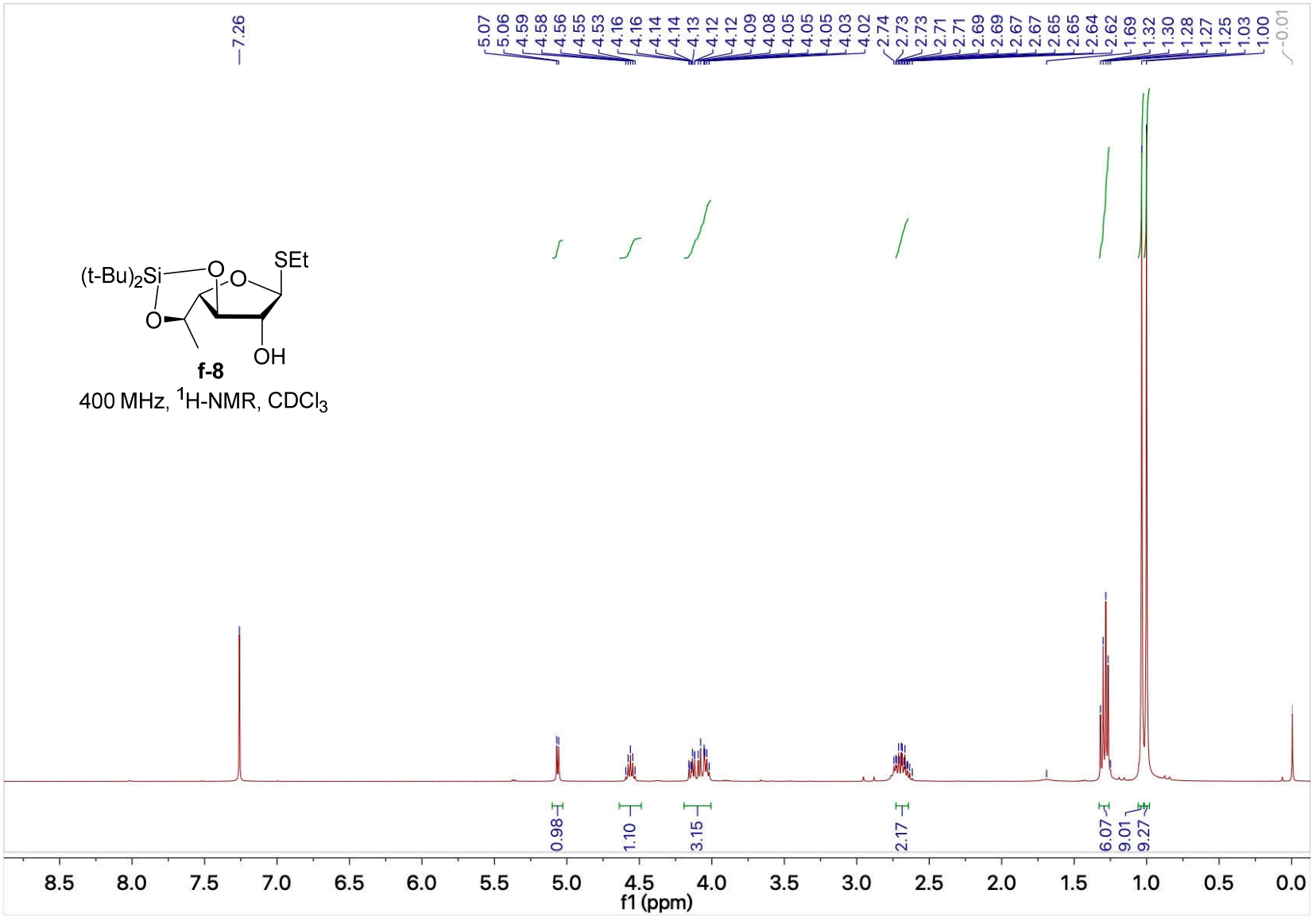

167.74
167.53
134.39
134.37
131.20
131.14
130.82
130.52
129.58
129.48
83.11
72.87
71.16
70.32
69.64
65.69
49.64
49.43
49.21
49.00
48.79
48.57
48.36
24.57
15.05
BzO
O
SEt
HO
HO
OBz
f-6
100 MHz, 13C-NMR, CD3OD
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

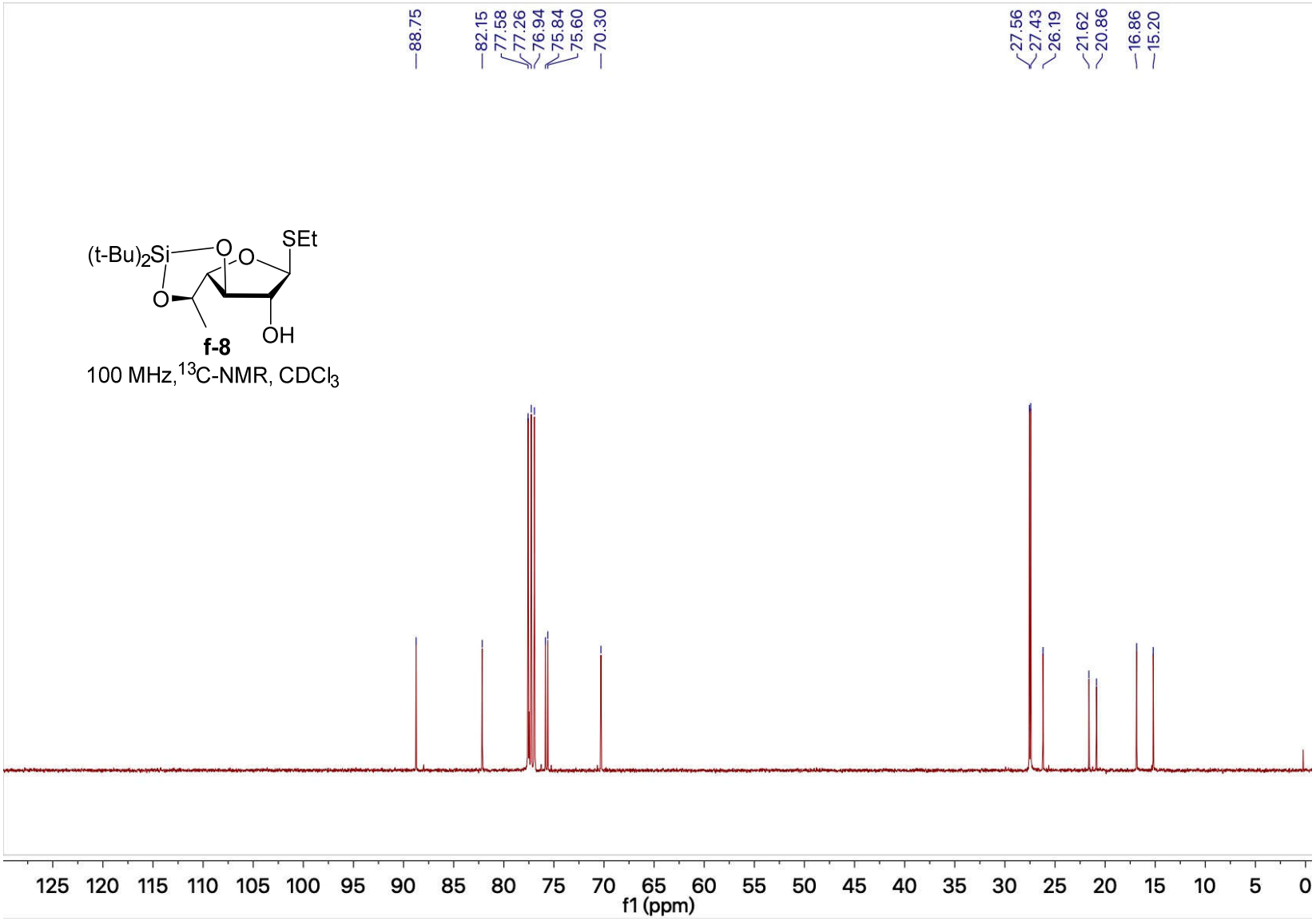


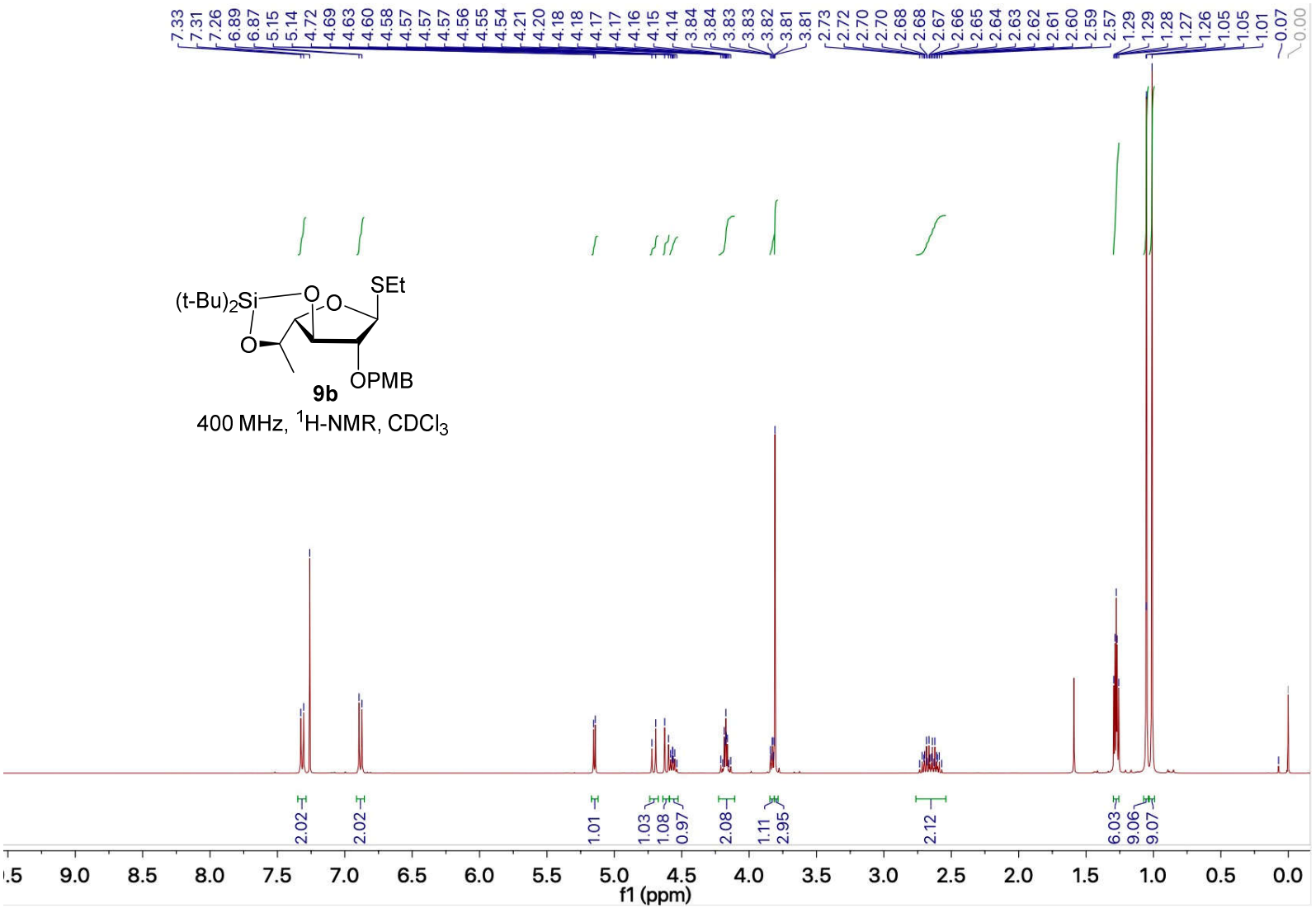
f-7

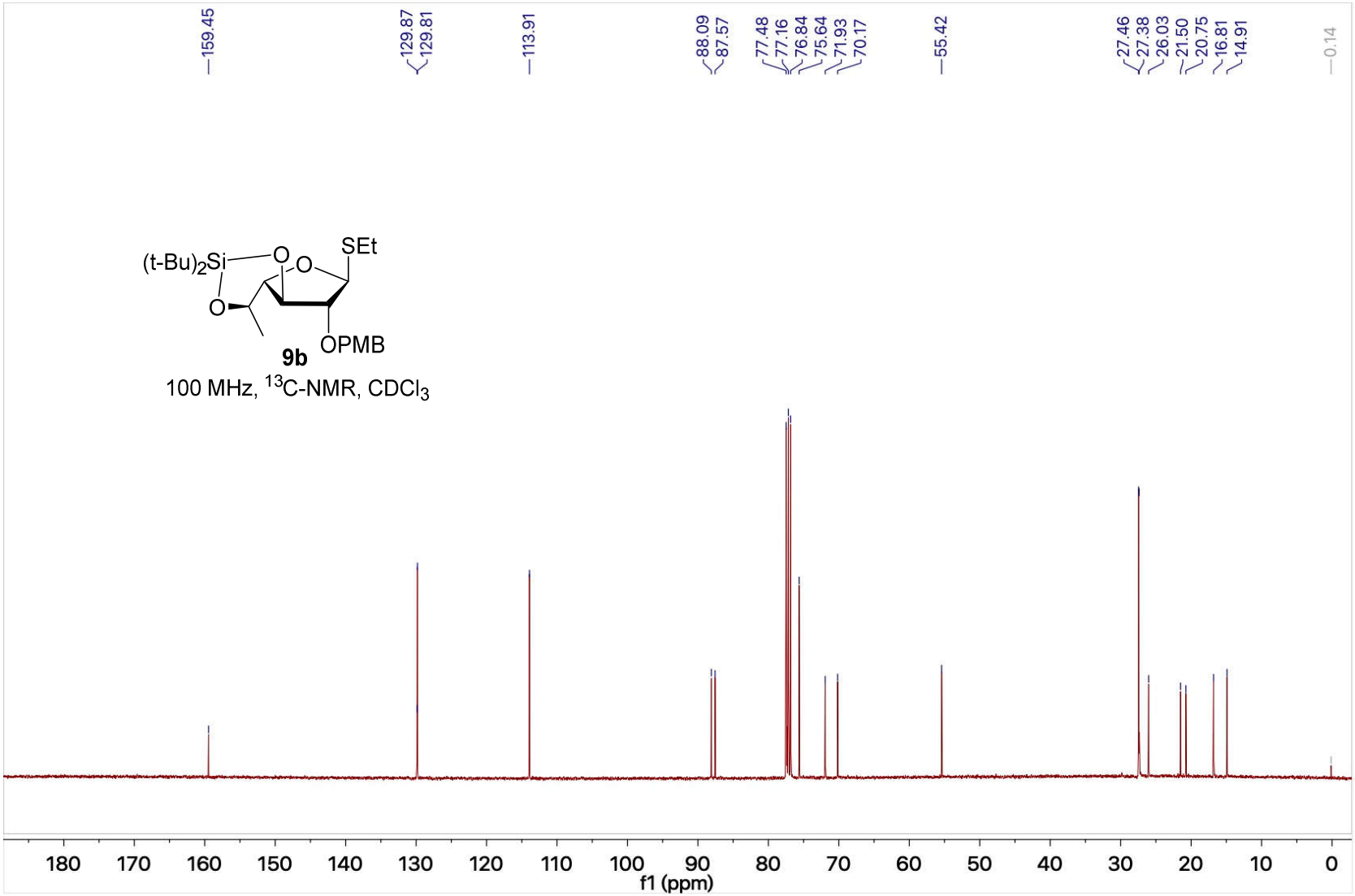
400 MHz, ^{1}H-NMR, $CDCl_3$

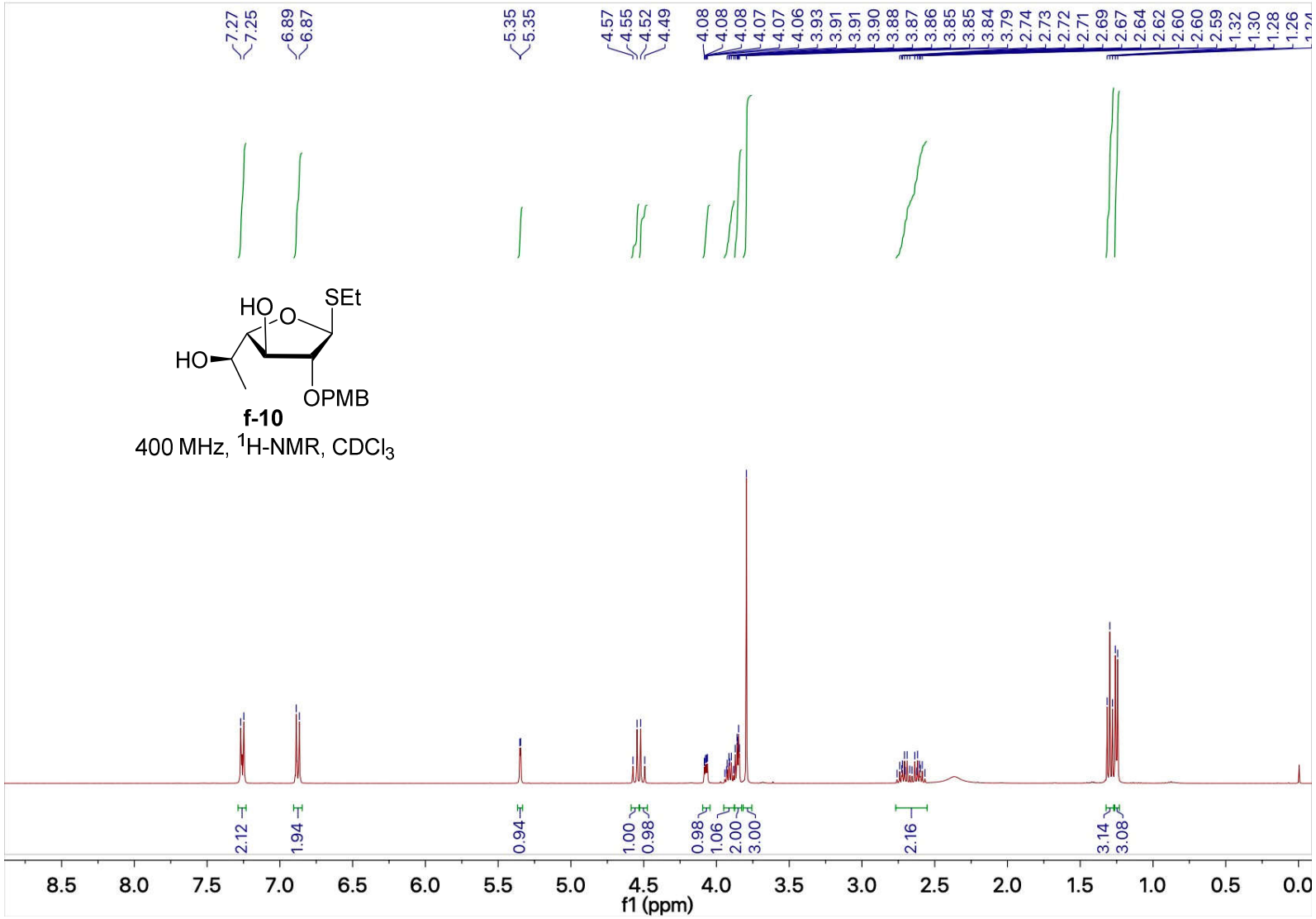

165.92
165.48
133.71
130.12
130.01
129.24
129.20
128.67
88.23
86.11
83.01
78.14
77.48
77.16
76.84
67.24
25.54
19.67
15.07
BzO
O
SEt
HO
OBz
f-7
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

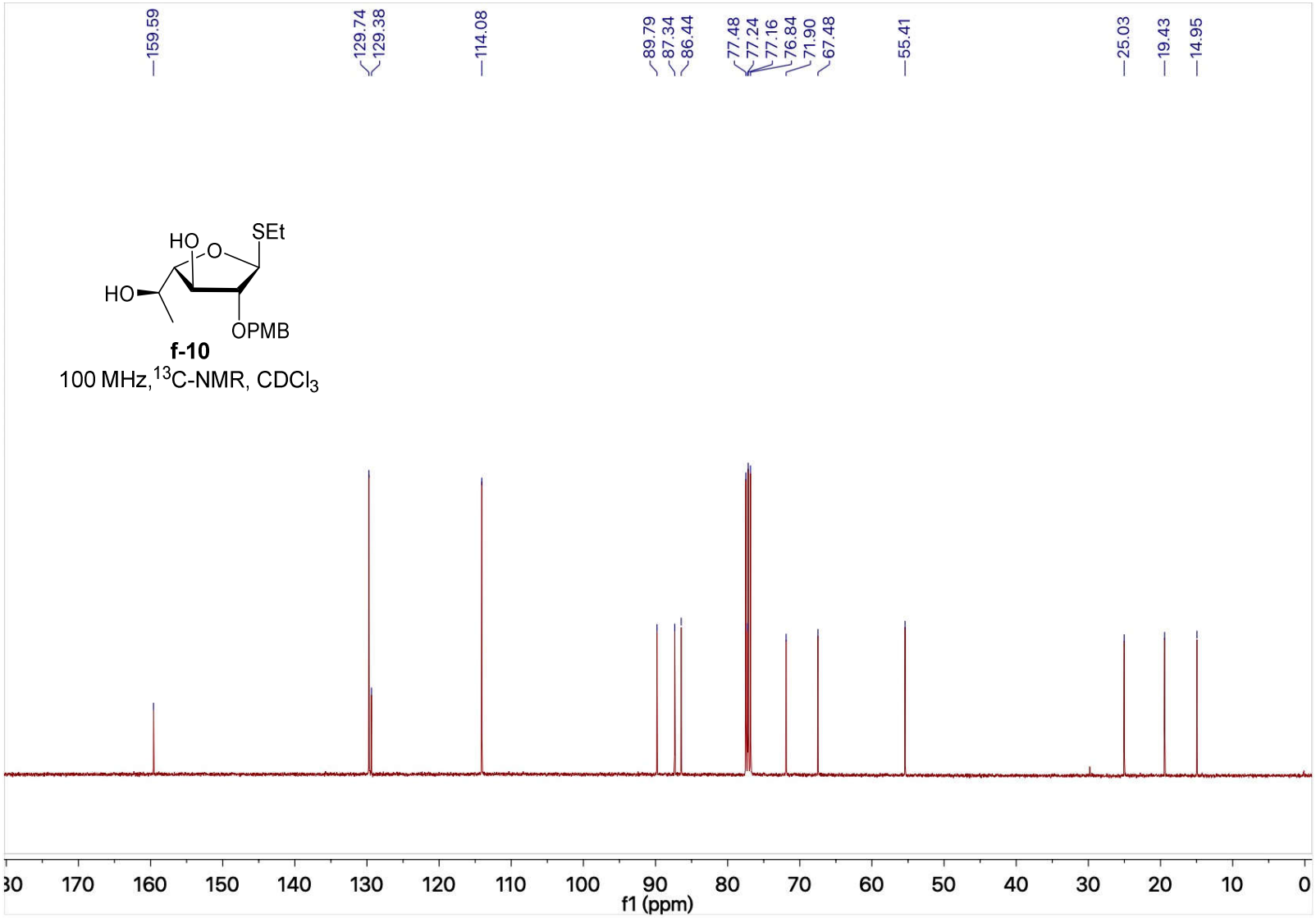

(t-Bu)2Si
O
O
SEt
O
OH
f-8
400 MHz, 1H-NMR, CDCl3
7.26
5.07
5.06
4.59
4.58
4.56
4.55
4.53
4.16
4.14
4.14
4.13
4.12
4.12
4.09
4.08
4.05
4.05
4.05
4.03
4.02
2.74
2.73
2.73
2.71
2.71
2.69
2.69
2.67
2.67
2.65
2.65
2.64
2.62
1.69
1.32
1.30
1.28
1.27
1.25
1.03
1.00
0.01
0.98
1.10
3.15
2.17
6.07
9.01
9.27
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

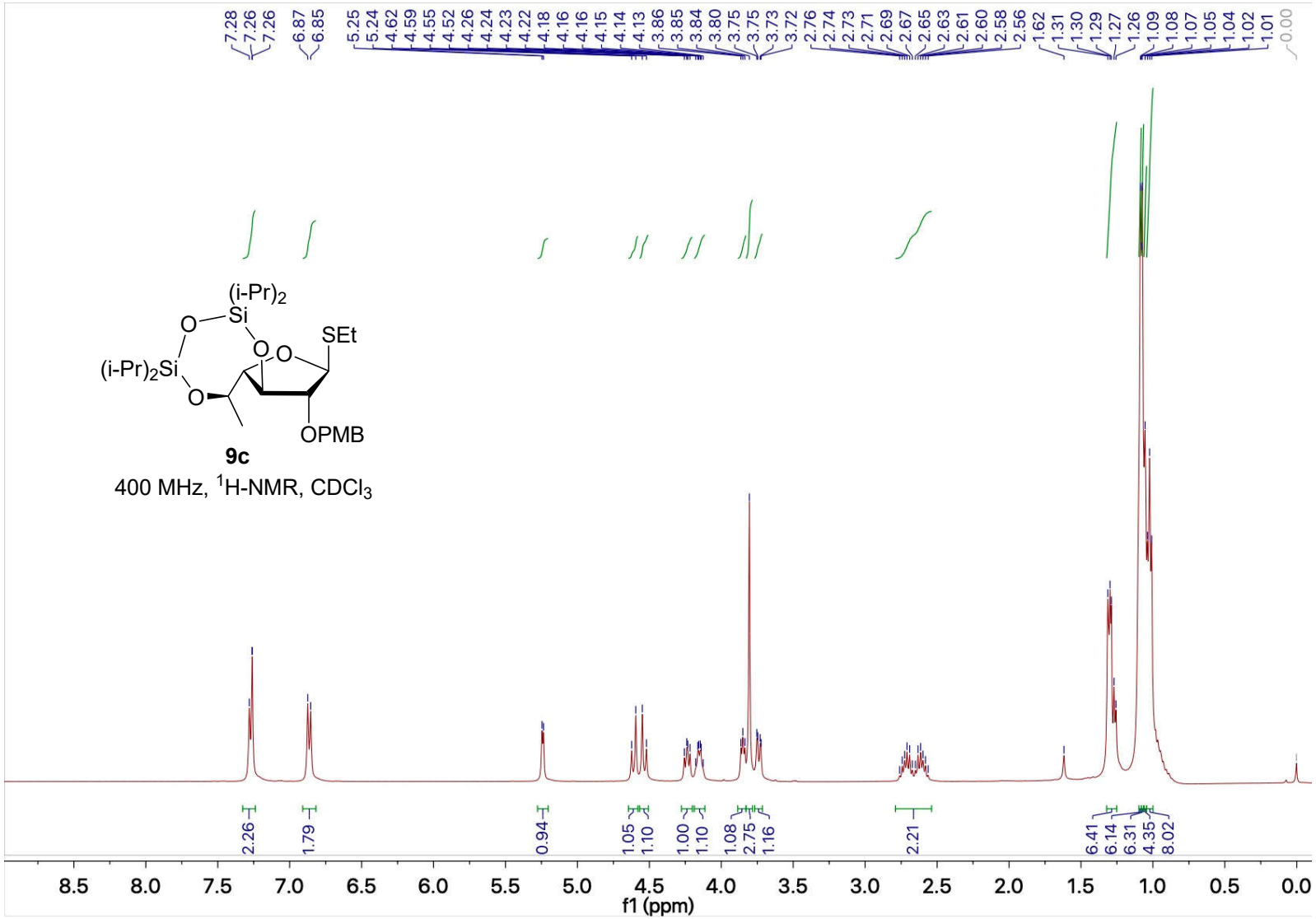

88.75
82.15
77.58
77.26
76.94
75.84
75.60
70.30
27.56
27.43
26.19
21.62
20.86
16.86
15.20
(t-Bu)2Si
O
O
O
SEt
OH
f-8
100 MHz, 13C-NMR, CDCl3
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

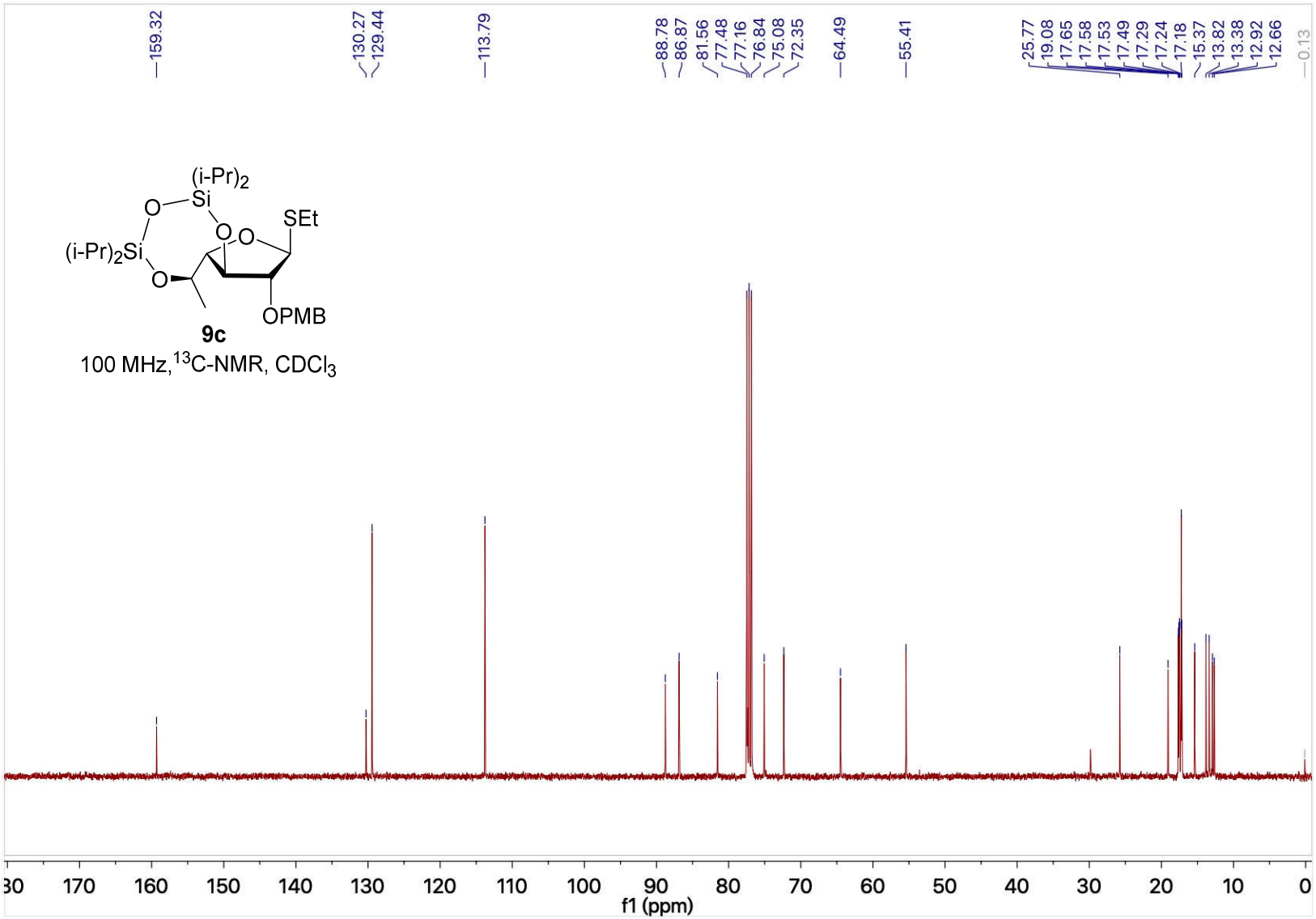

(t-Bu)2Si
O
O
O
SEt
OPMB
9b
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

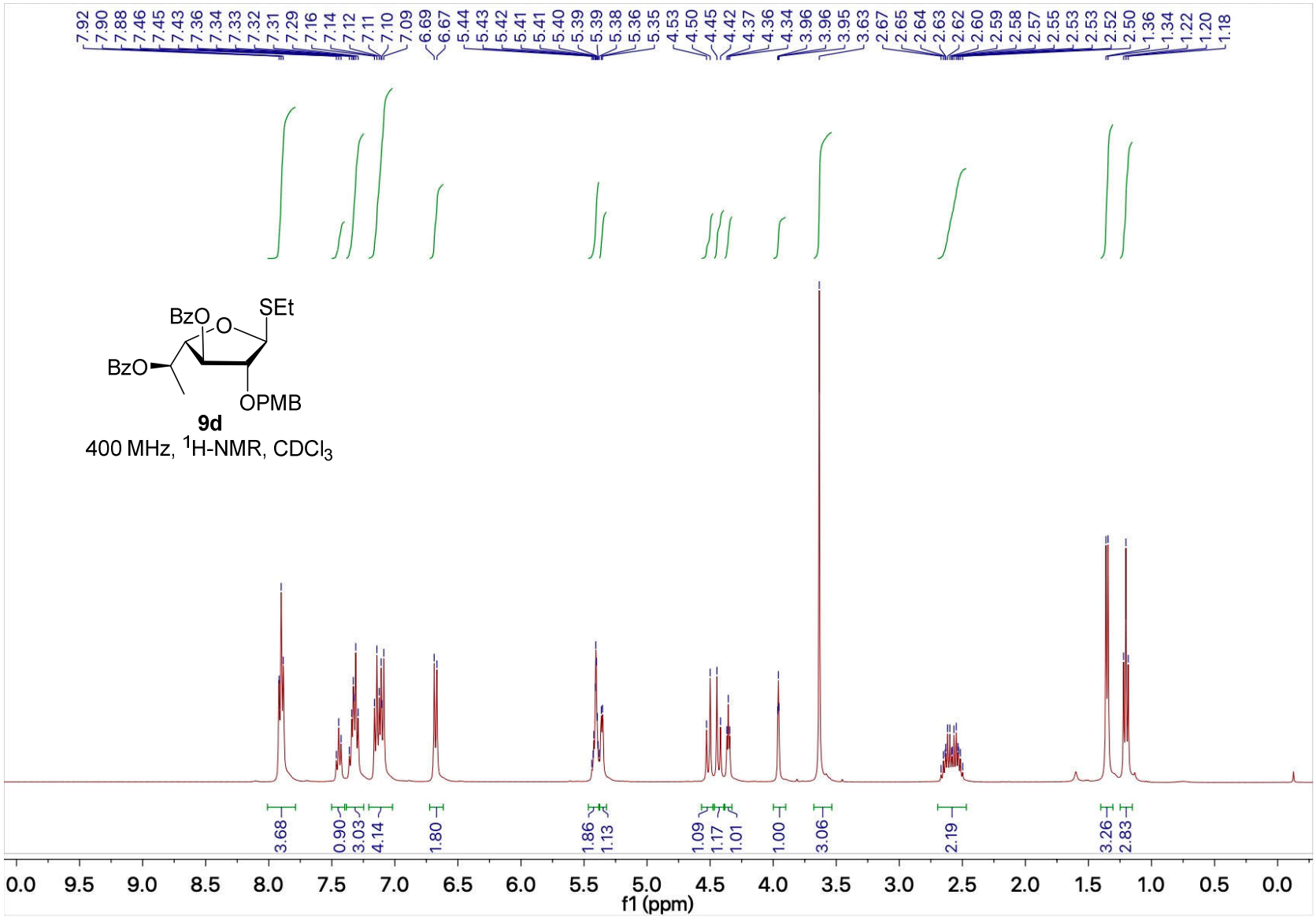

159.45
129.87
129.81
113.91
88.09
87.57
77.48
77.16
76.84
75.64
71.93
70.17
55.42
27.46
27.38
26.03
21.50
20.75
16.81
14.91
0.14
(t-Bu)2Si
O
O
O
SEt
OPMB
9b
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

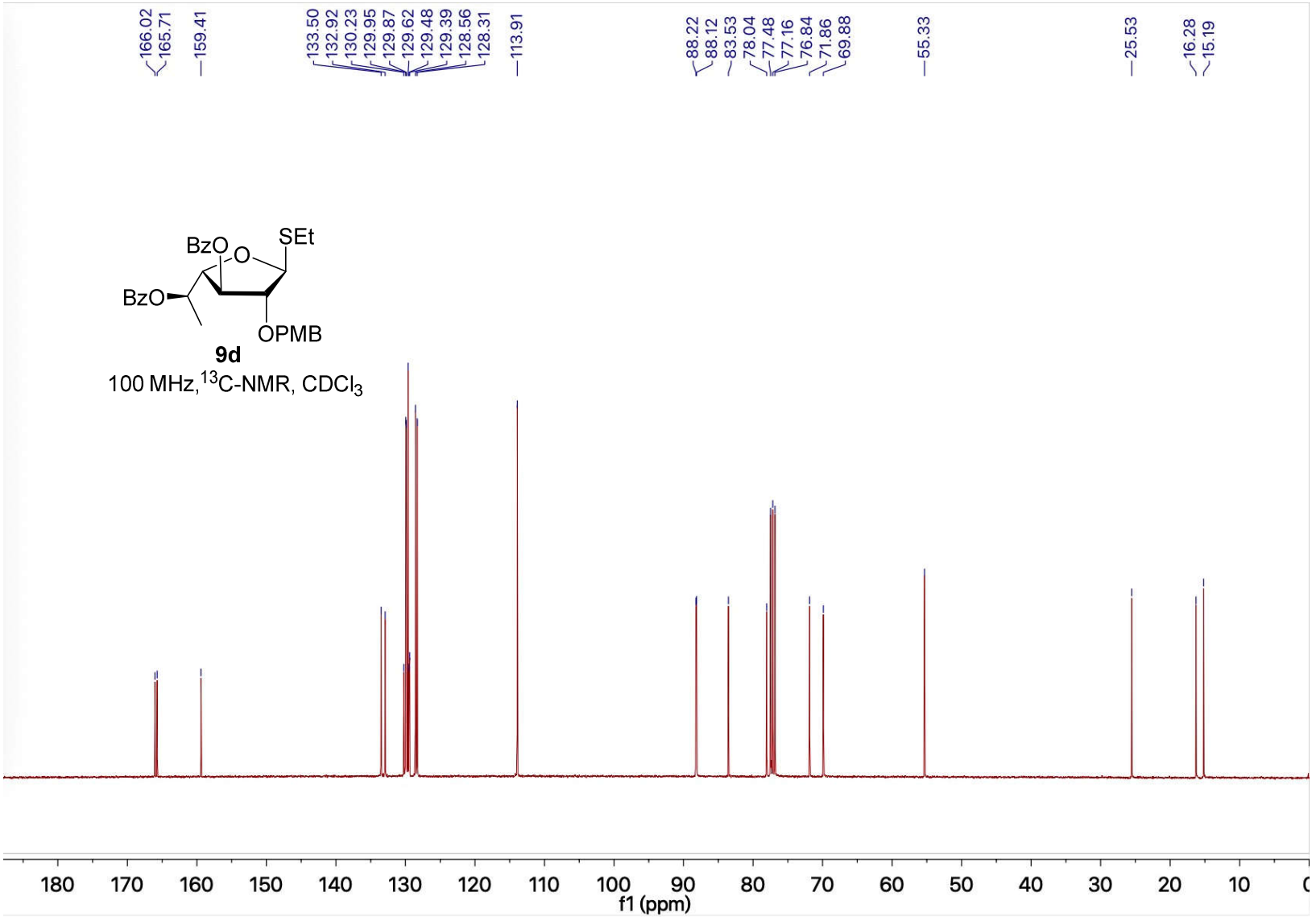

HO
O
SEt
HO
OPMB
f-10
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

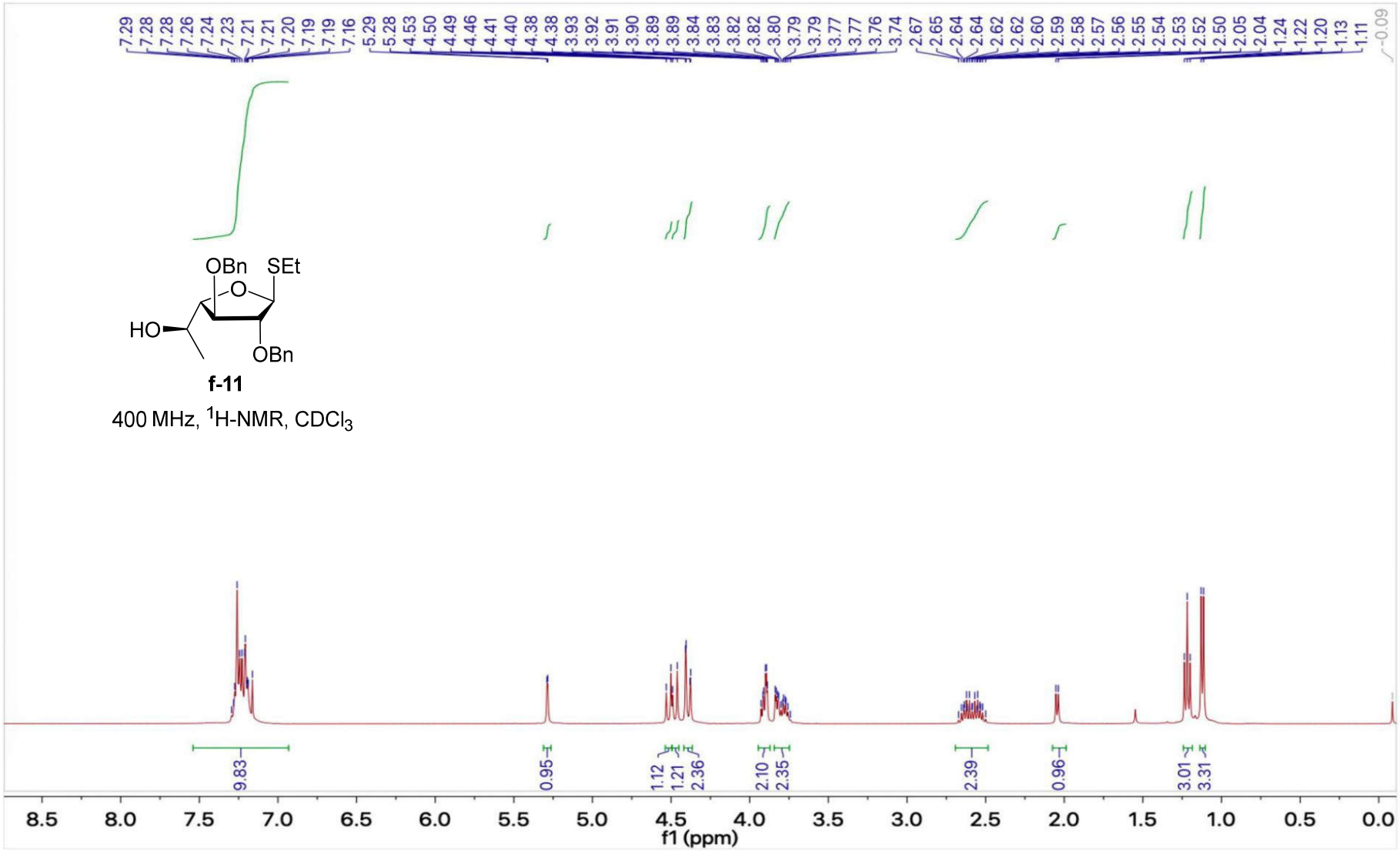

159.59
129.74
129.38
114.08
89.79
87.34
86.44
77.48
77.24
77.16
76.84
71.90
67.48
55.41
25.03
19.43
14.95
HO
O
SEt
HO
OPMB
f-10
100 MHz, 13C-NMR, CDCl3
f1 (ppm)


(i-Pr)2
Si
O
O
O
SEt
(i-Pr)2Si
O
OPMB
9c
400 MHz, 1H-NMR, CDCl3
f1 (ppm)


159.32
130.27
129.44
113.79
88.78
86.87
81.56
77.48
77.16
76.84
75.08
72.35
64.49
55.41
25.77
19.08
17.65
17.58
17.53
17.49
17.29
17.24
17.18
15.37
13.82
13.38
12.92
12.66
0.13
(i-Pr)2
Si
O
O
O
SEt
(i-Pr)2Si
O
OPMB
9c
100 MHz, 13C-NMR, CDCl3
f1 (ppm)

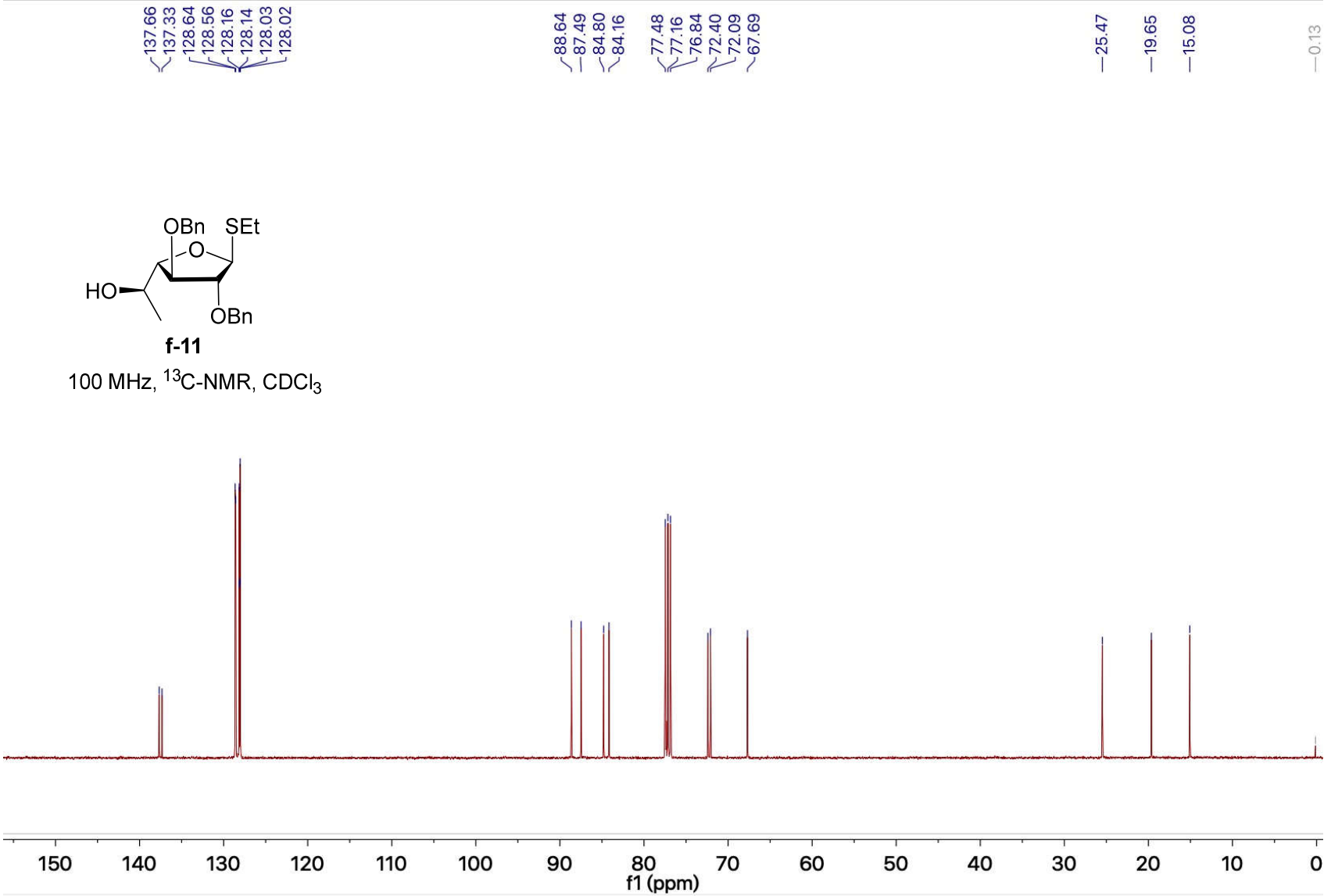

7.92 7.90 7.88 7.46 7.45 7.43 7.36 7.34 7.33 7.32 7.31 7.29 7.16 7.14 7.12 7.11 7.10 7.09 6.69 6.67 5.44 5.43 5.42 5.41 5.41 5.40 5.39 5.39 5.38 5.36 5.35 4.53 4.50 4.45 4.42 4.37 4.36 4.34 3.96 3.96 3.95 3.63 2.67 2.65 2.64 2.63 2.62 2.60 2.59 2.58 2.57 2.55 2.53 2.53 2.52 2.50 1.36 1.34 1.22 1.20 1.18
BzO
O
SEt
BzO
OPMB
9d
400 MHz, ^{1}H-NMR, $CDCl_3$
3.68 0.90 3.03 4.14 1.80 1.86 1.13 1.09 1.17 1.01 1.00 3.06 2.19 3.26 2.83
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.02
165.71
159.41
133.50
132.92
130.23
129.95
129.87
129.62
129.48
129.39
128.56
128.31
113.91
88.22
88.12
83.53
78.04
77.48
77.16
76.84
71.86
69.88
55.33
25.53
16.28
15.19
BzO
O
SEt
BzO
OPMB
9d
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



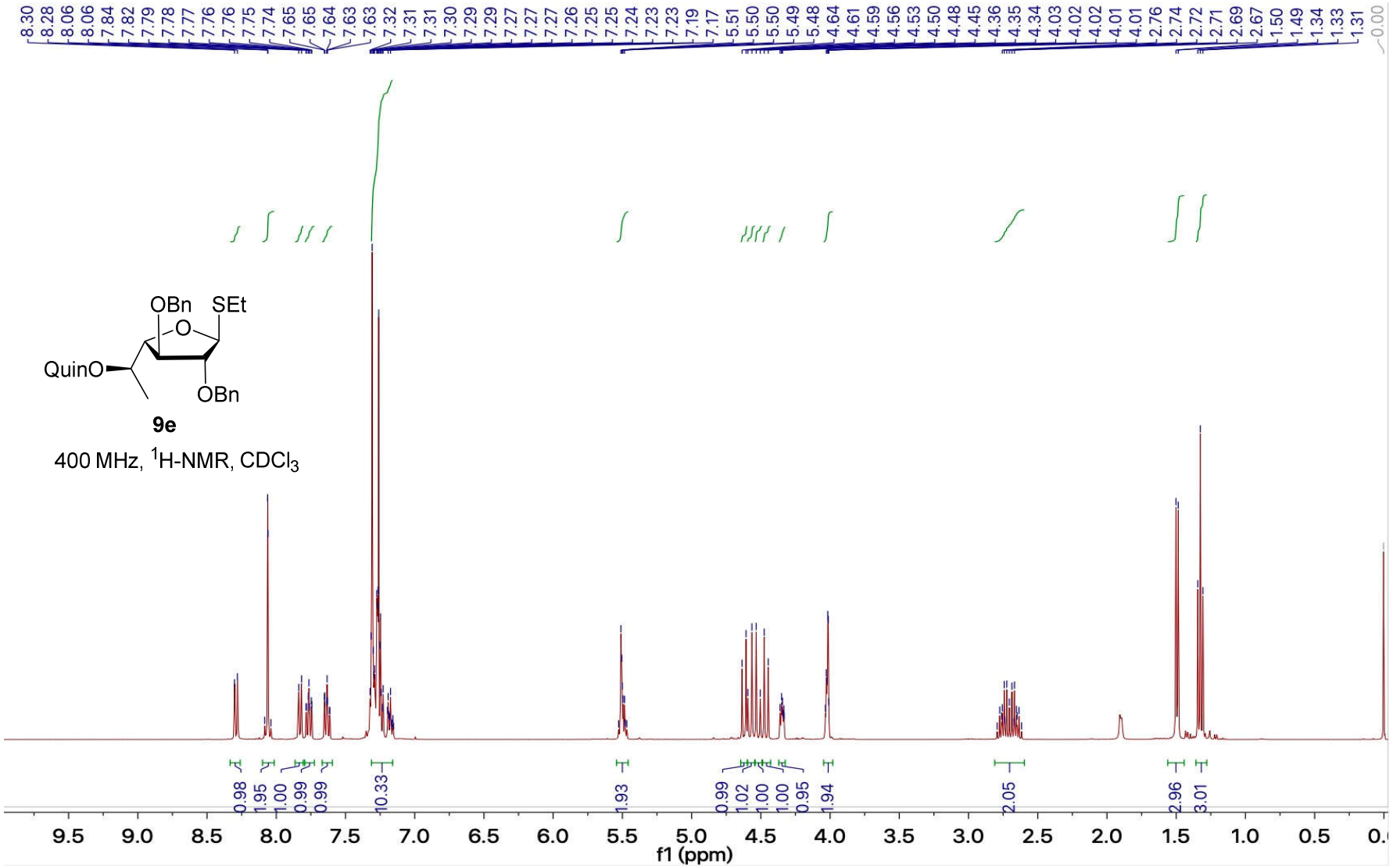
f-11

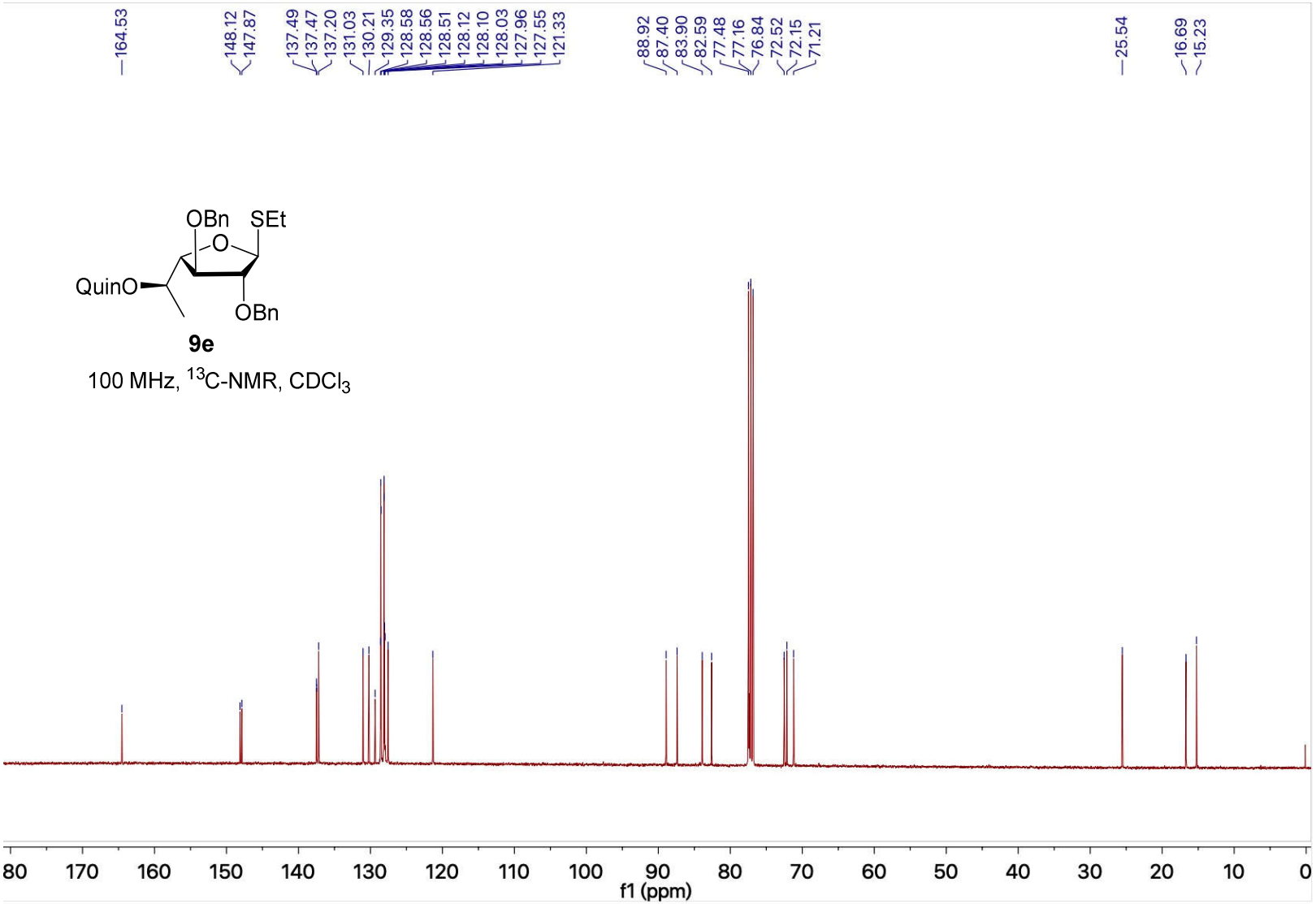
400 MHz, ^{1}H-NMR, $CDCl_3$

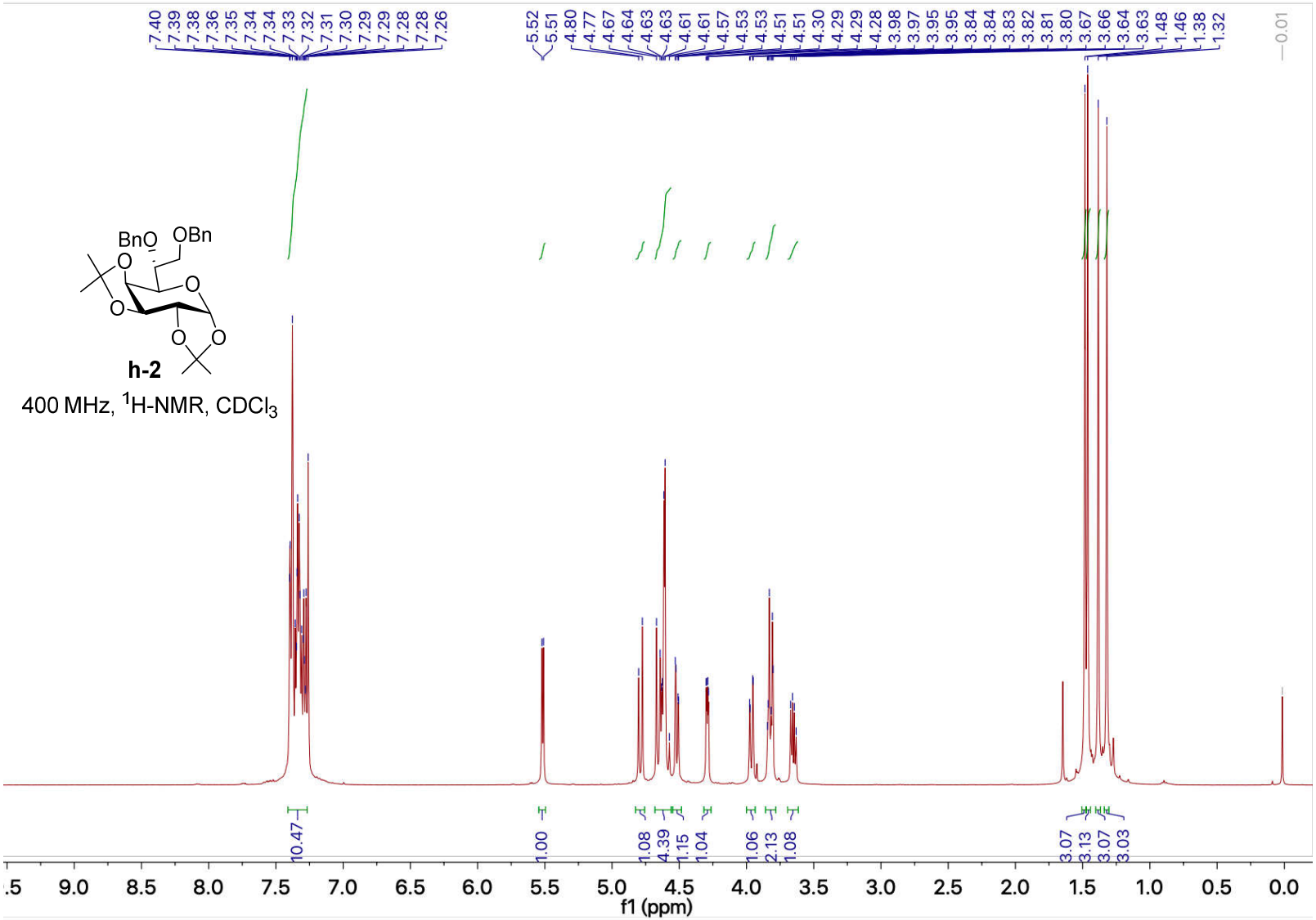


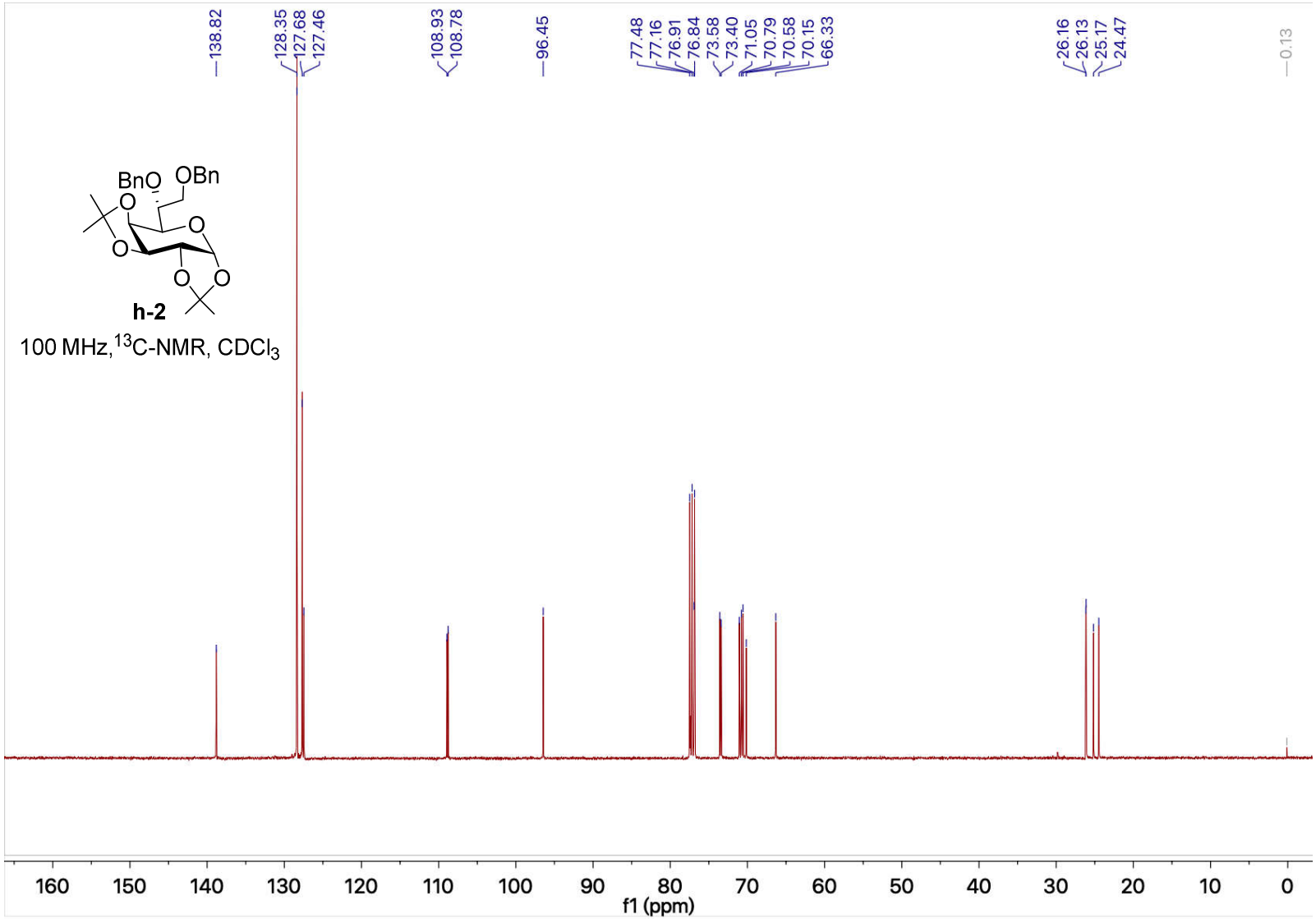
f-11

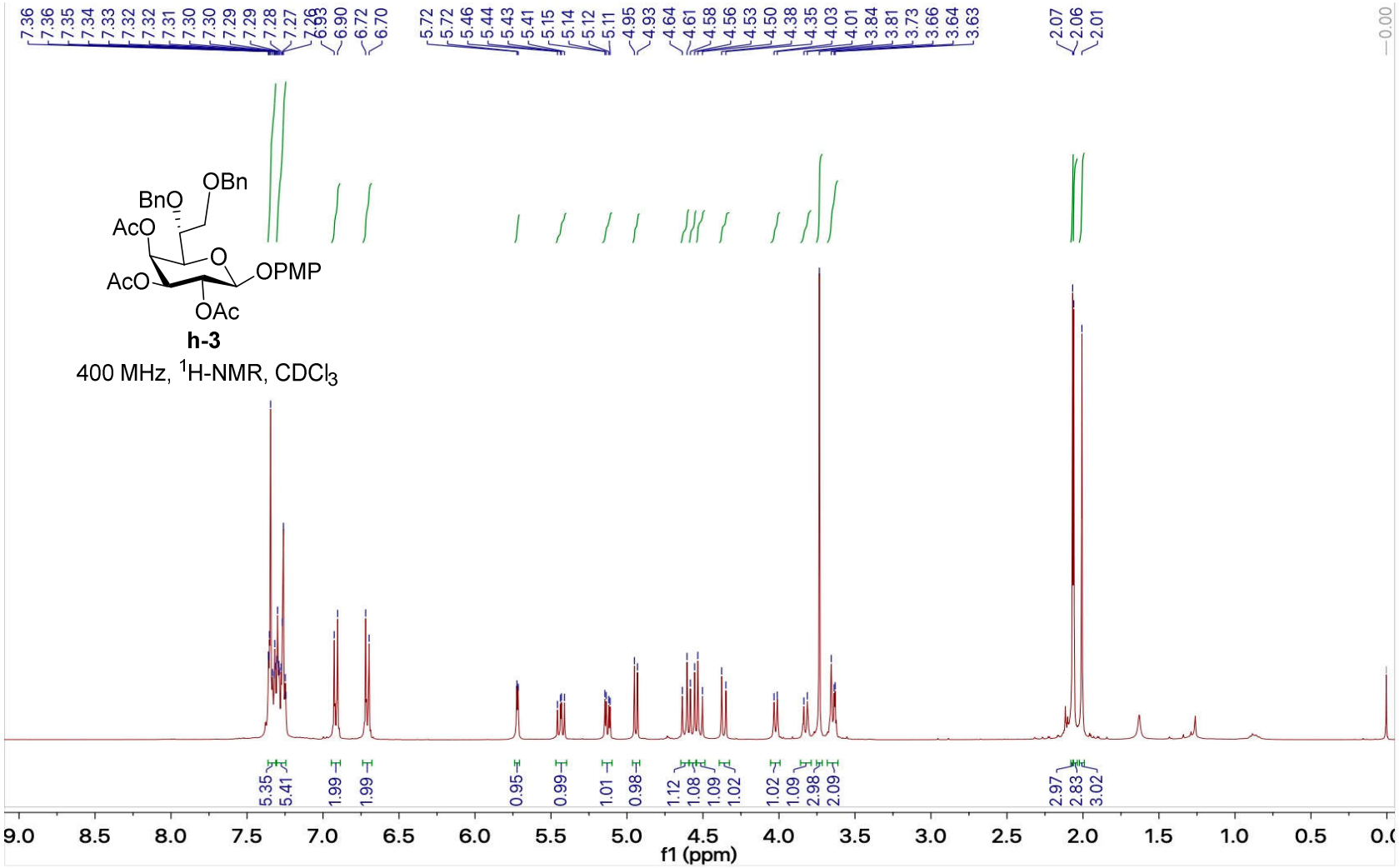
100 MHz, ^{13}C-NMR, $CDCl_3$

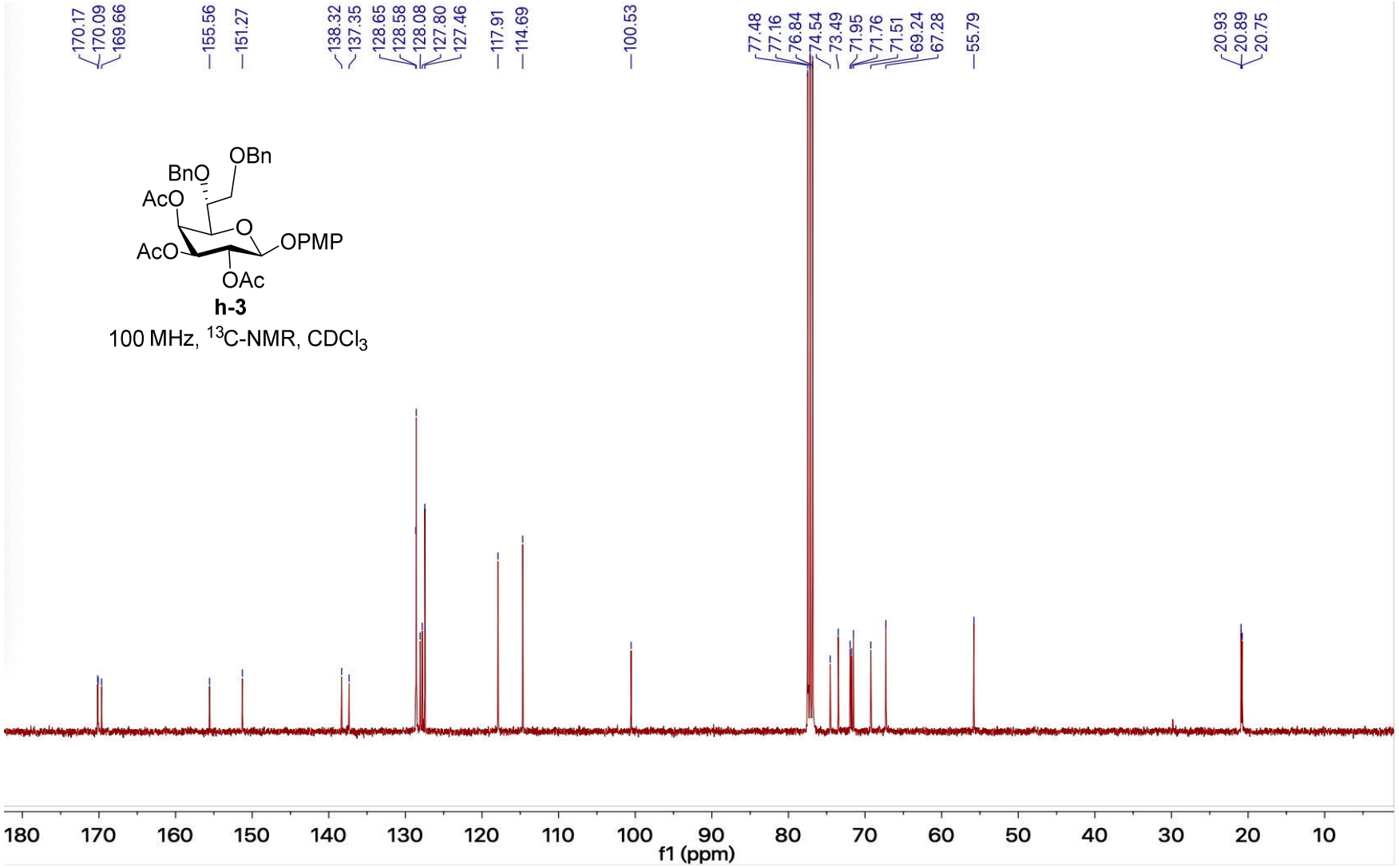

OBn
SEt
O
QuinO
OBn
9e
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

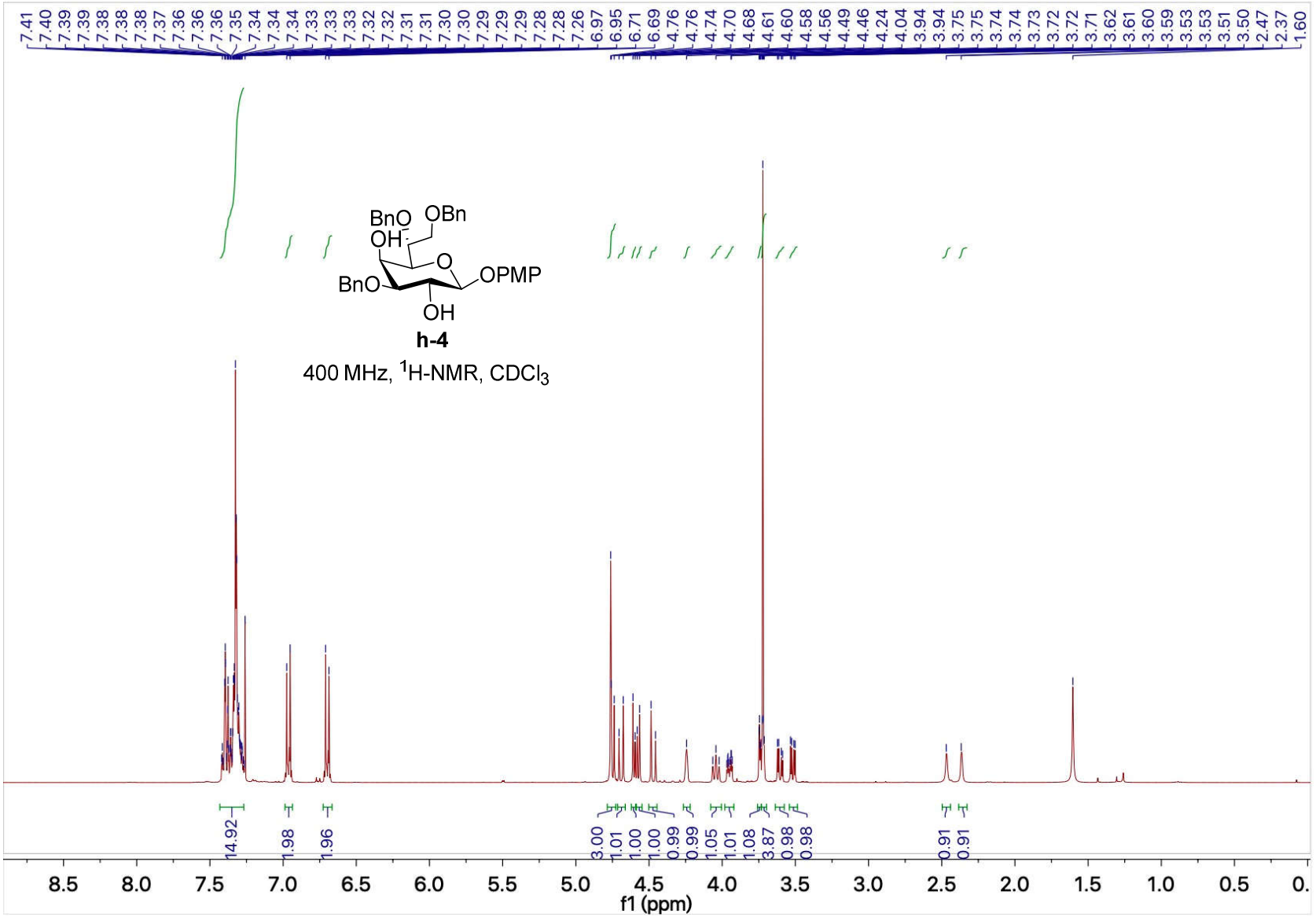

164.53
148.12
147.87
137.49
137.47
137.20
131.03
130.21
129.35
128.58
128.56
128.51
128.12
128.10
128.03
127.96
127.55
121.33
88.92
87.40
83.90
82.59
77.48
77.16
76.84
72.52
72.15
71.21
25.54
16.69
15.23
OBn
SEt
O
QuinO
OBn
9e
100 MHz, 13C-NMR, CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

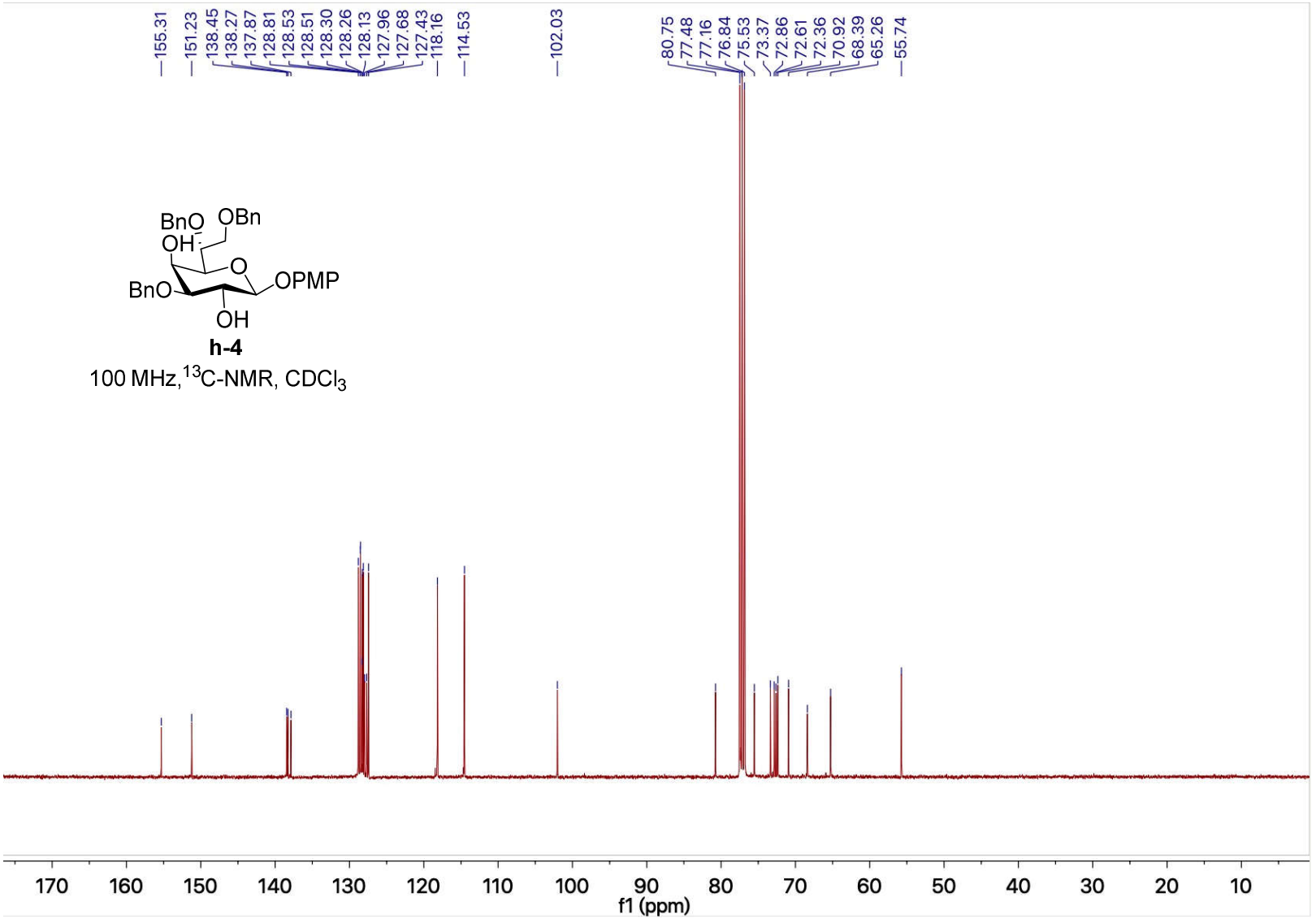

BnO
OBn
h-2
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

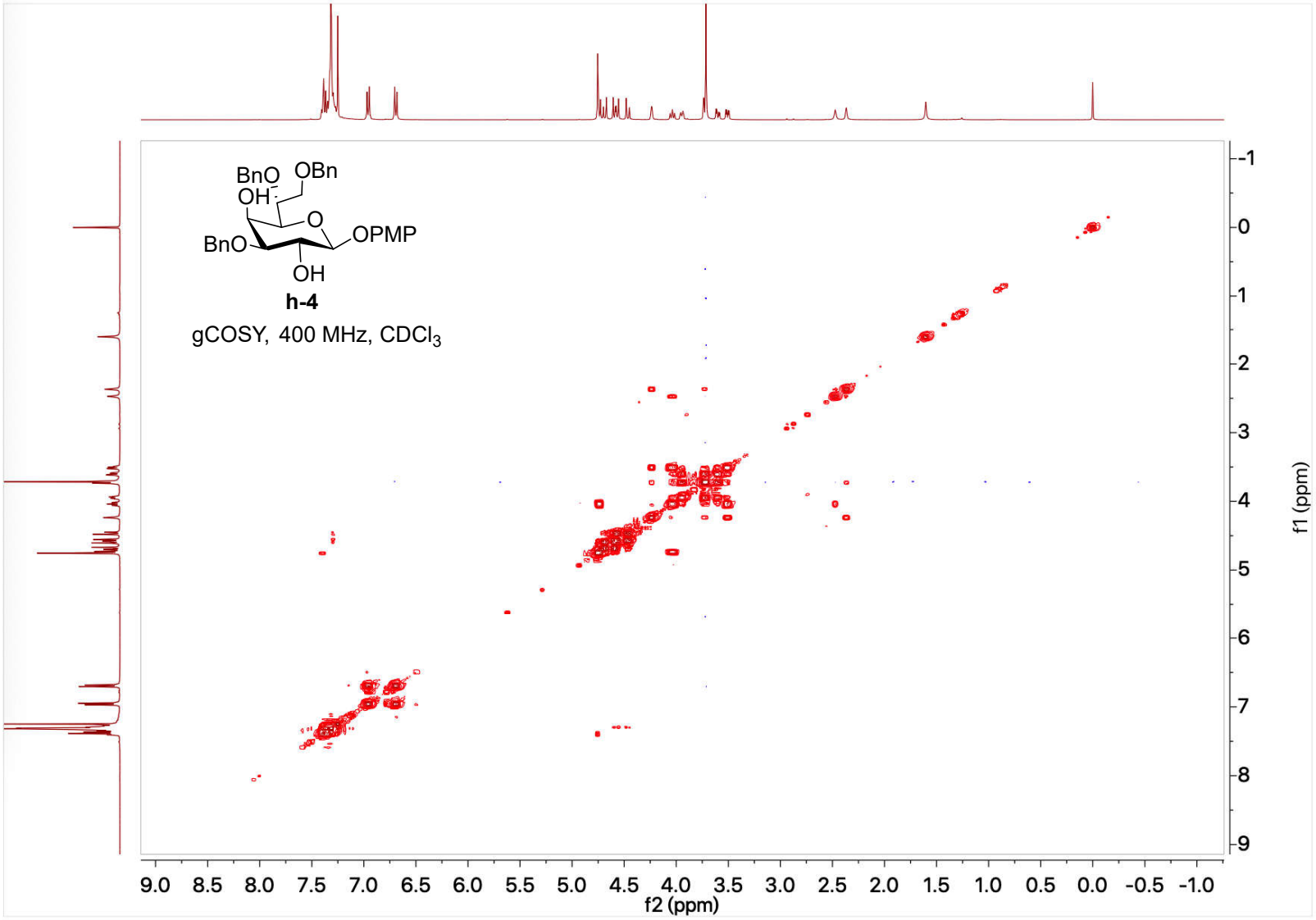

138.82
128.35
127.68
127.46
108.93
108.78
96.45
77.48
77.16
76.91
76.84
73.58
73.40
71.05
70.79
70.58
70.15
66.33
26.16
26.13
25.17
24.47
0.13
BnO
OBn
h-2
100 MHz, 13C-NMR, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

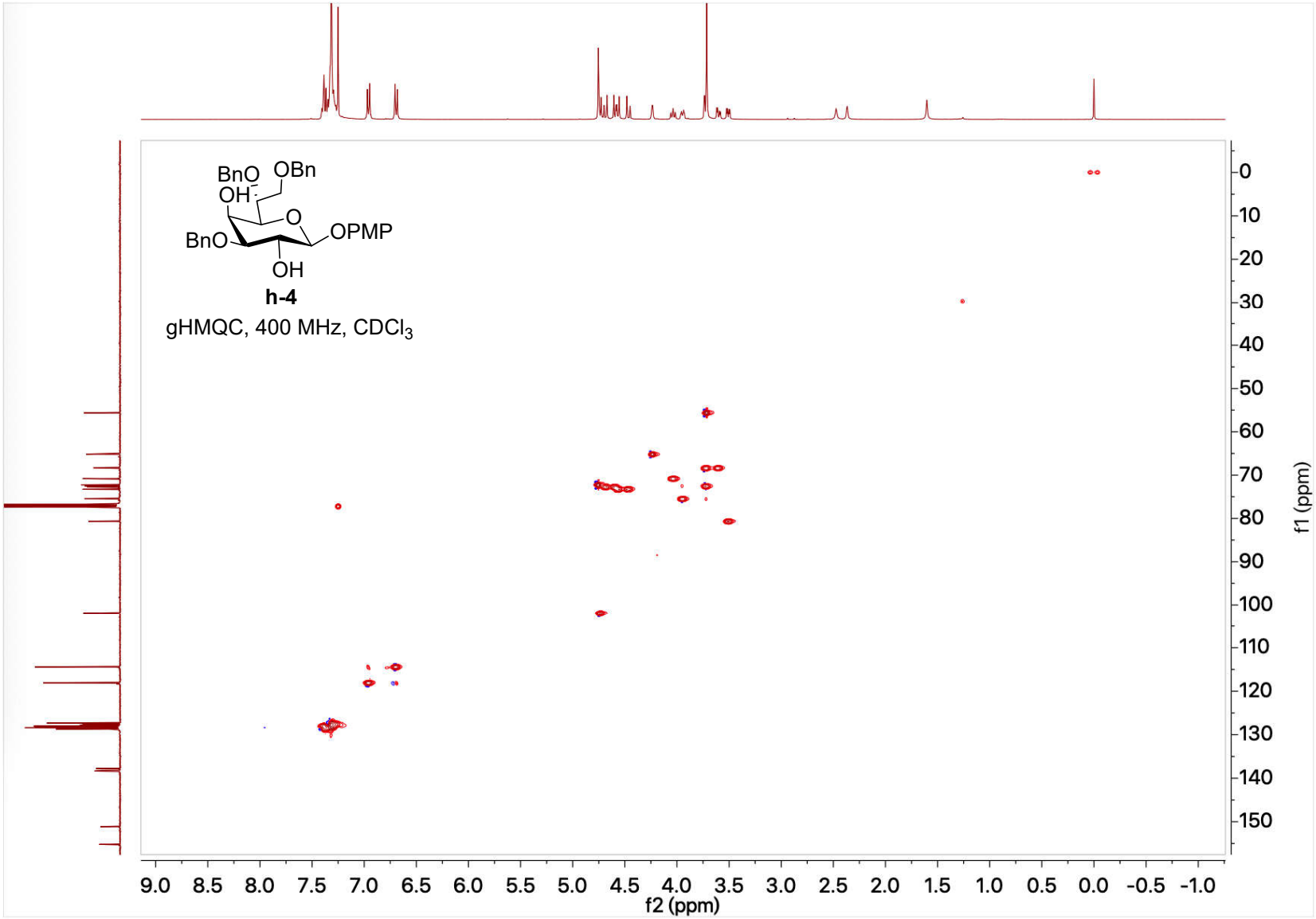

OBn
BnO
AcO
O
OPMP
AcO
OAc
h-3
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

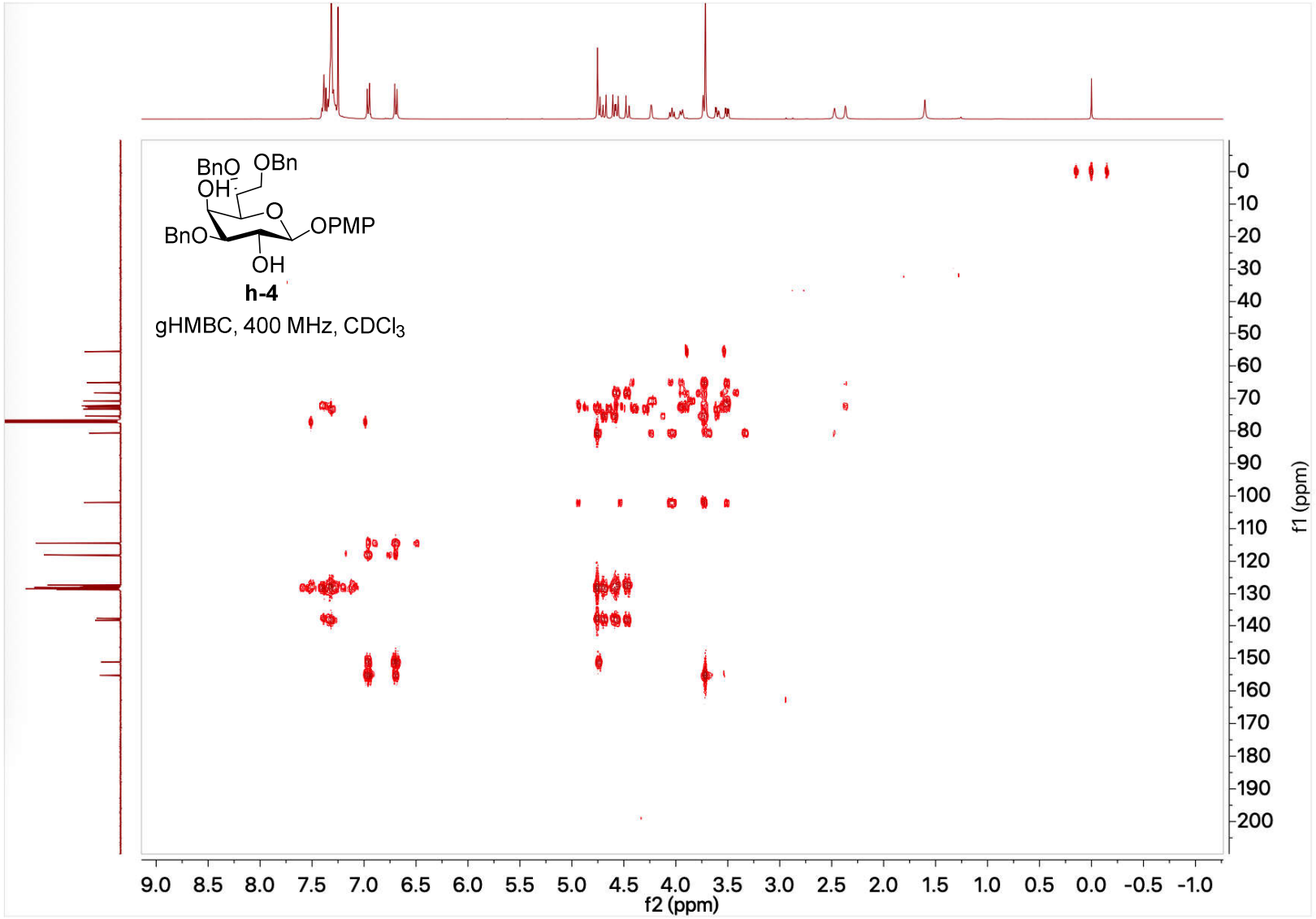

170.17
170.09
169.66
155.56
151.27
138.32
137.35
128.65
128.58
128.08
127.80
127.46
117.91
114.69
100.53
77.48
77.16
76.84
74.54
73.49
71.95
71.76
71.51
69.24
67.28
55.79
20.93
20.89
20.75
OBn
BnO
AcO
O
OPMP
AcO
OAc
h-3
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

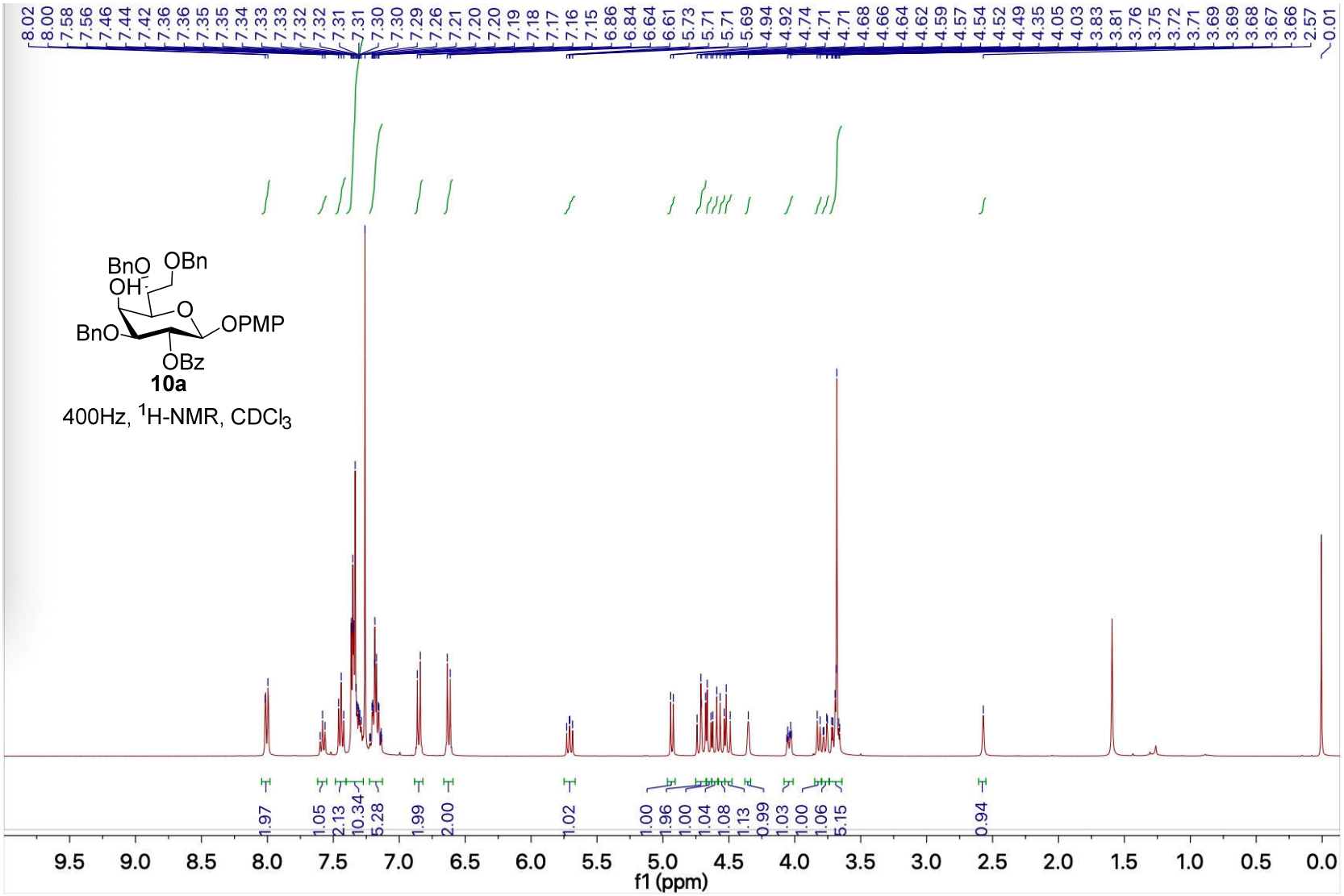

BnO
OBn
OH
O
OPMP
BnO
OH
h-4
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

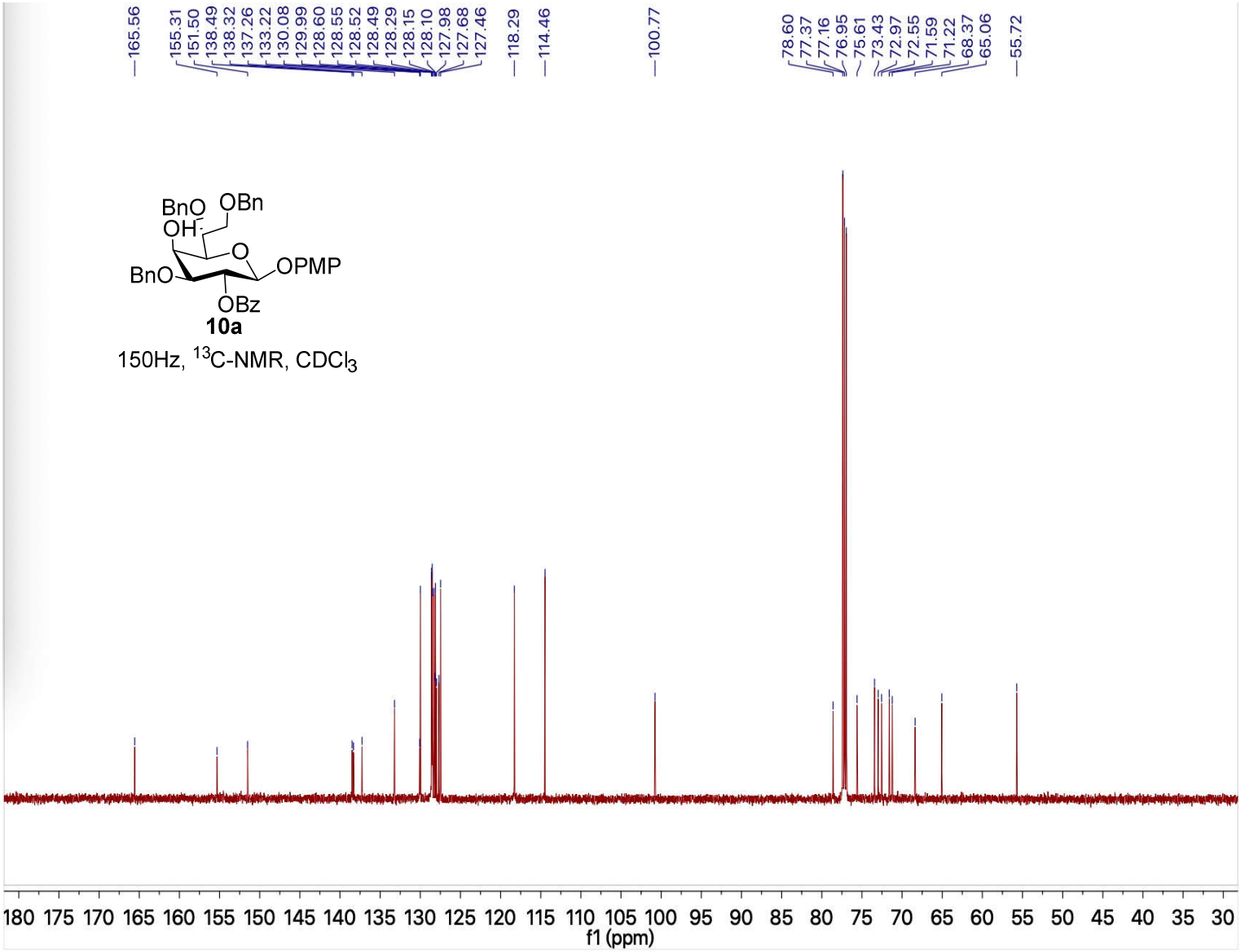

155.31
151.23
138.45
138.27
137.87
128.81
128.53
128.51
128.30
128.26
128.13
127.96
127.68
127.43
118.16
114.53
102.03
80.75
77.48
77.16
76.84
75.53
73.37
72.86
72.61
72.36
70.92
68.39
65.26
55.74
BnO
OBn
OH
O
OPMP
BnO
OH
h-4
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


BnO
OBn
OH
O
OPMP
BnO
OH
h-4
gCOSY, 400 MHz, CDCl3
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 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)


BnO
OBn
OH
O
OPMP
BnO
OH
h-4
gHMQC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OBn
OH
O
OPMP
BnO
OH
h-4
gHMBC, 400 MHz, CDCl3
f1 (ppm)
f2 (ppm)


BnO
OBn
OH
O
OPMP
BnO
OBz
10a
400Hz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)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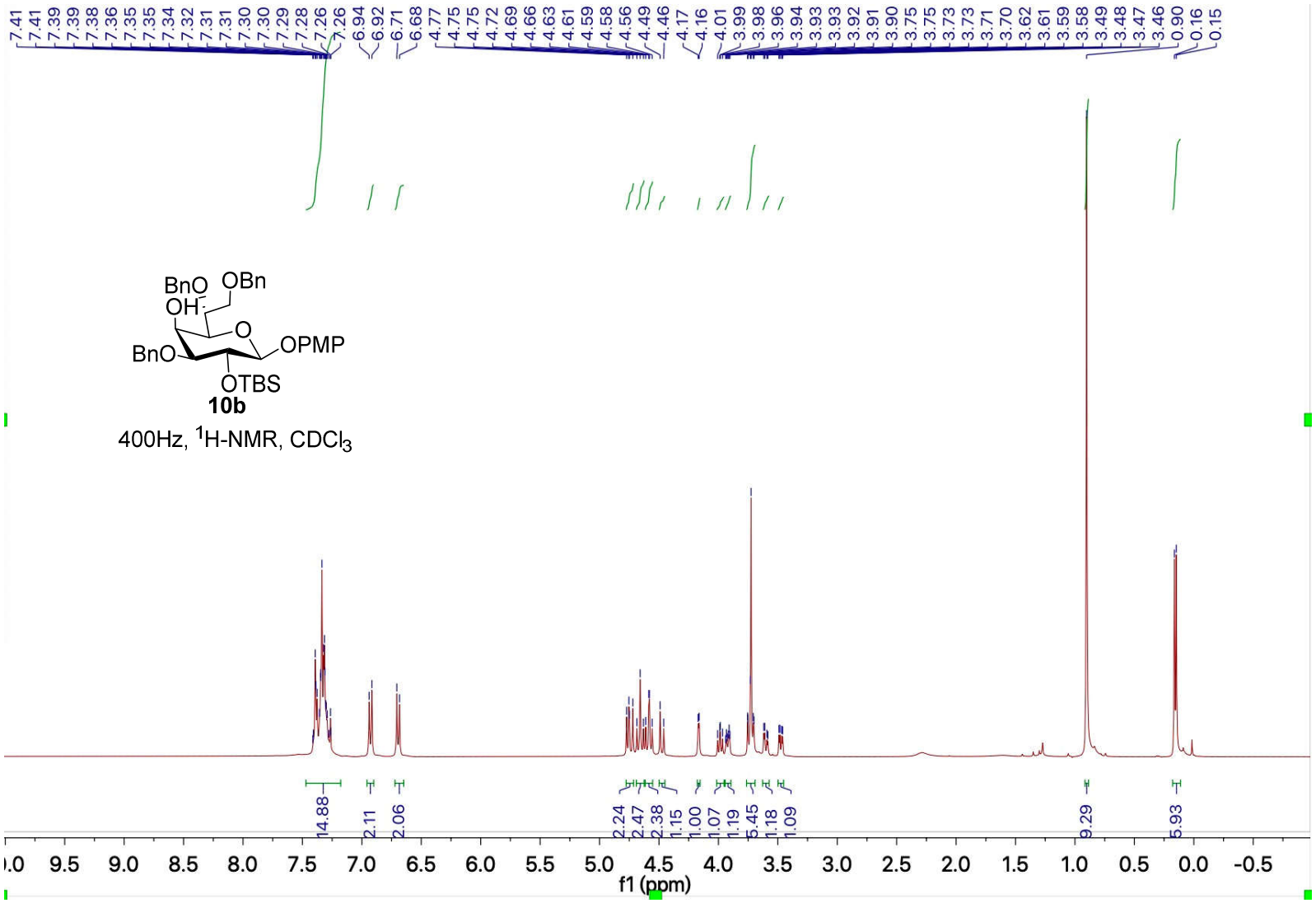
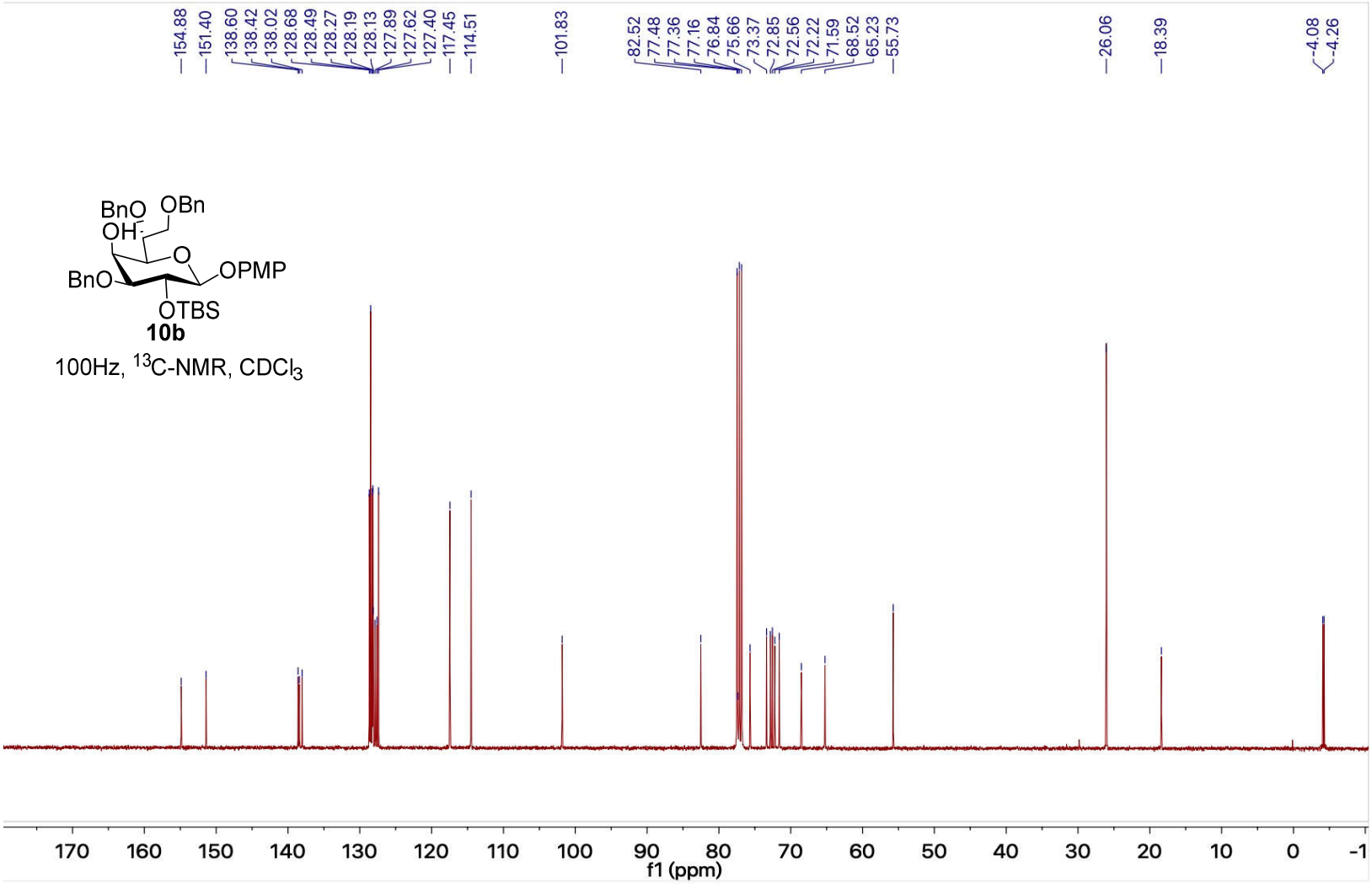
155.31
151.50
138.49
138.32
137.26
133.22
130.08
129.99
128.60
128.55
128.52
128.49
128.29
128.15
128.10
127.98
127.68
127.46
118.29
114.46
100.77
78.60
77.37
77.16
76.95
75.61
73.43
72.97
72.55
71.59
71.22
68.37
65.06
55.72
BnO
OBn
OH
O
OPMP
BnO
OBz
10a
150Hz, 13C-NMR, CDCl3
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30
f1 (ppm)


BnO
OBn
OH
O
OPMP
BnO
OTBS
10b
400Hz, 1H-NMR, CDCl3
f1 (ppm)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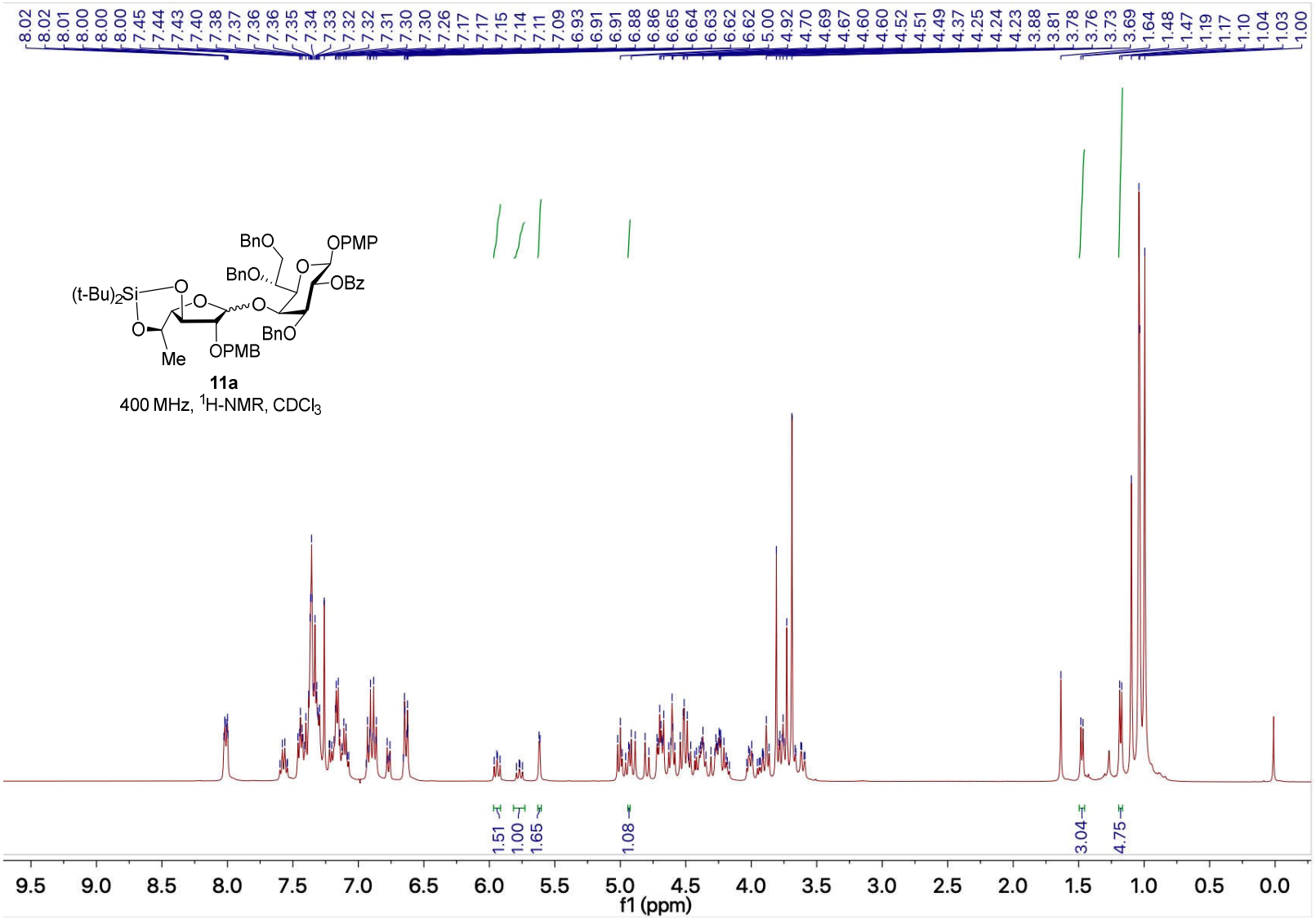
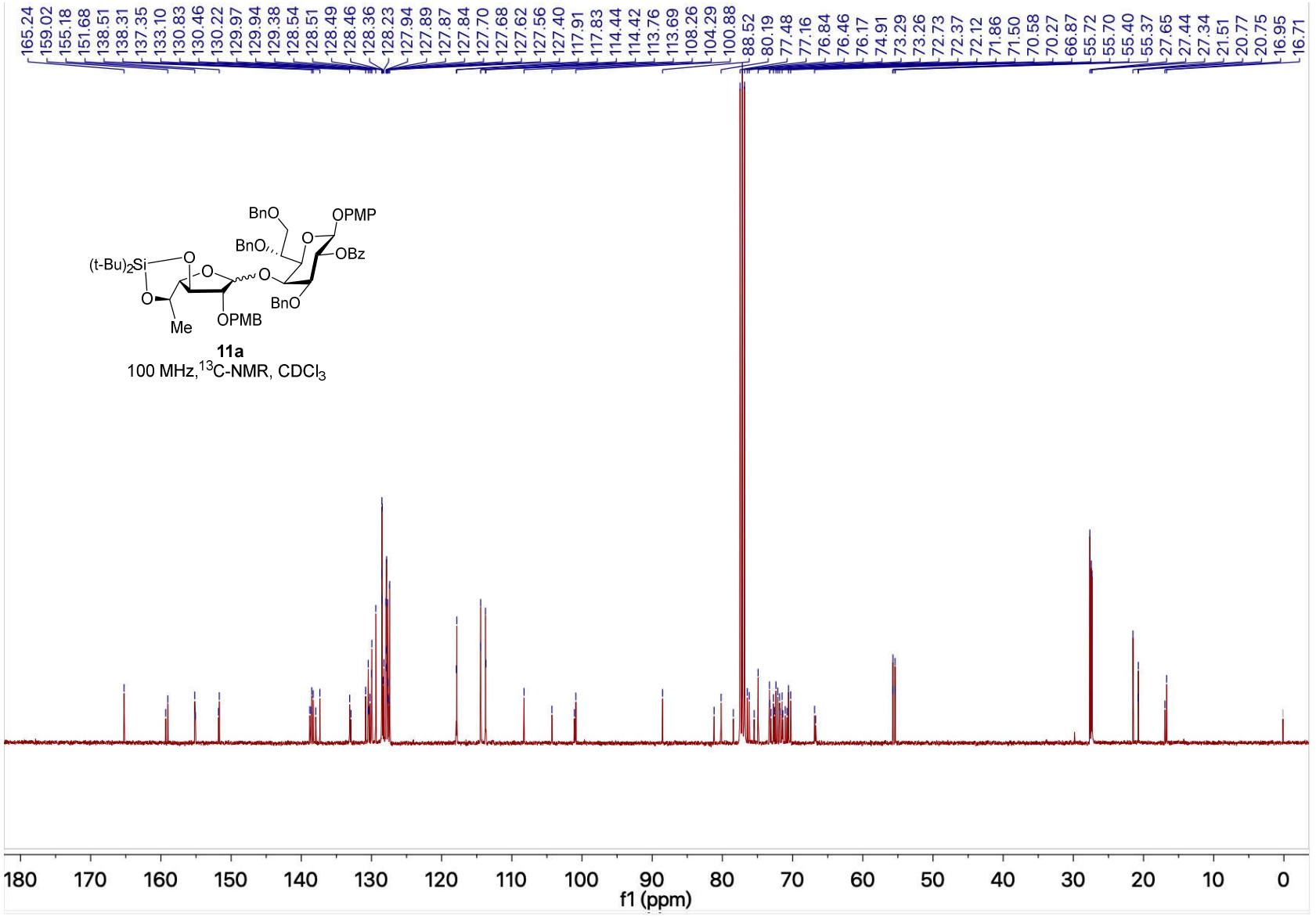
151.40
138.60
138.42
138.02
128.68
128.49
128.27
128.19
128.13
127.89
127.62
127.40
117.45
114.51
101.83
82.52
77.48
77.36
77.16
76.84
75.66
73.37
72.85
72.56
72.22
71.59
68.52
65.23
55.73
26.06
18.39
-4.08
-4.26
BnO
OBn
OH
O
OPMP
BnO
OTBS
10b
100Hz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


BnO
OPMP
BnO
O
OBz
(t-Bu)2Si
O
O
O
O
BnO
Me
OPMB
11a
400 MHz, 1H-NMR, CDCl3
1.51
1.00
1.65
1.08
3.04
4.75
f1 (ppm)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155.18
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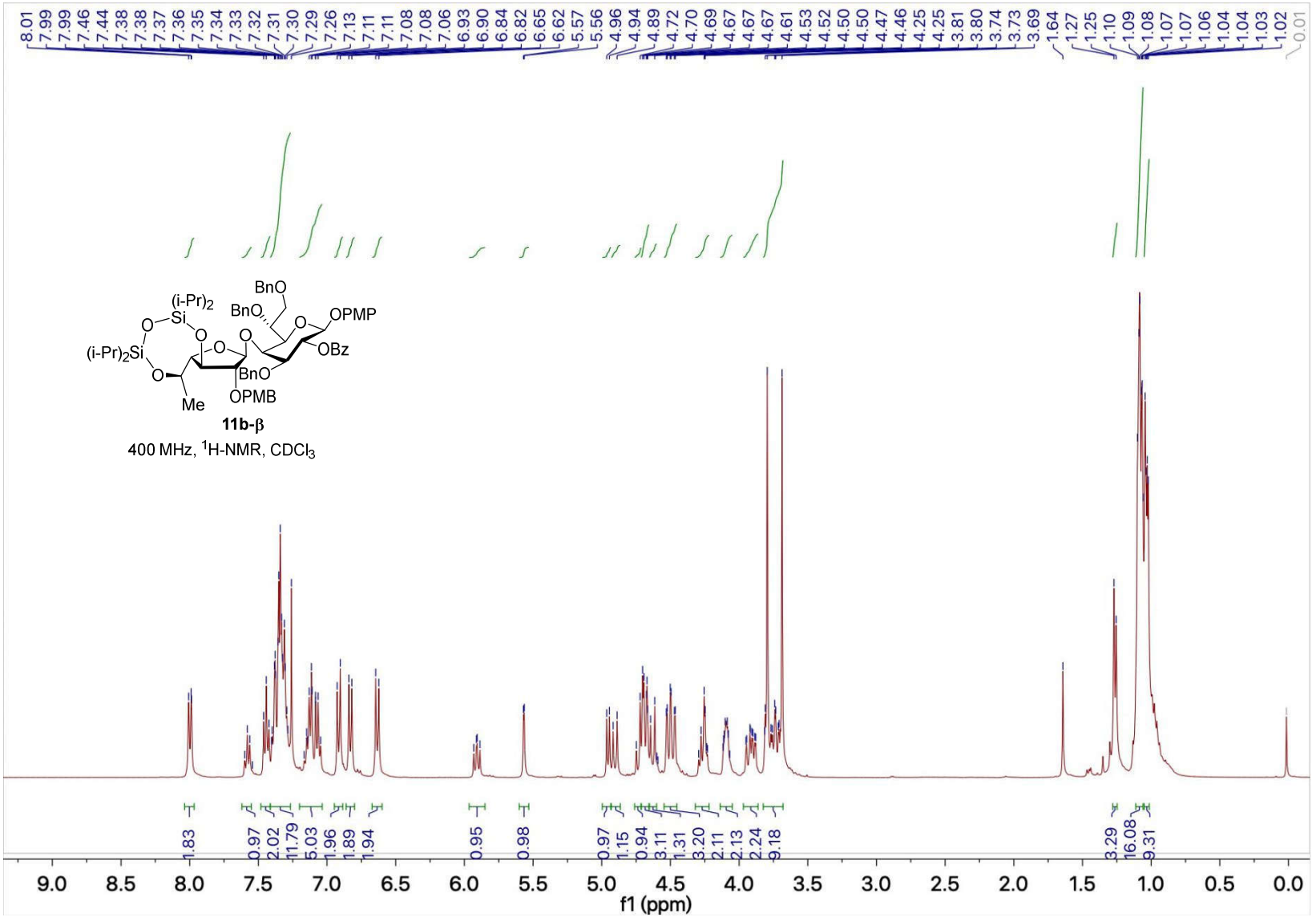
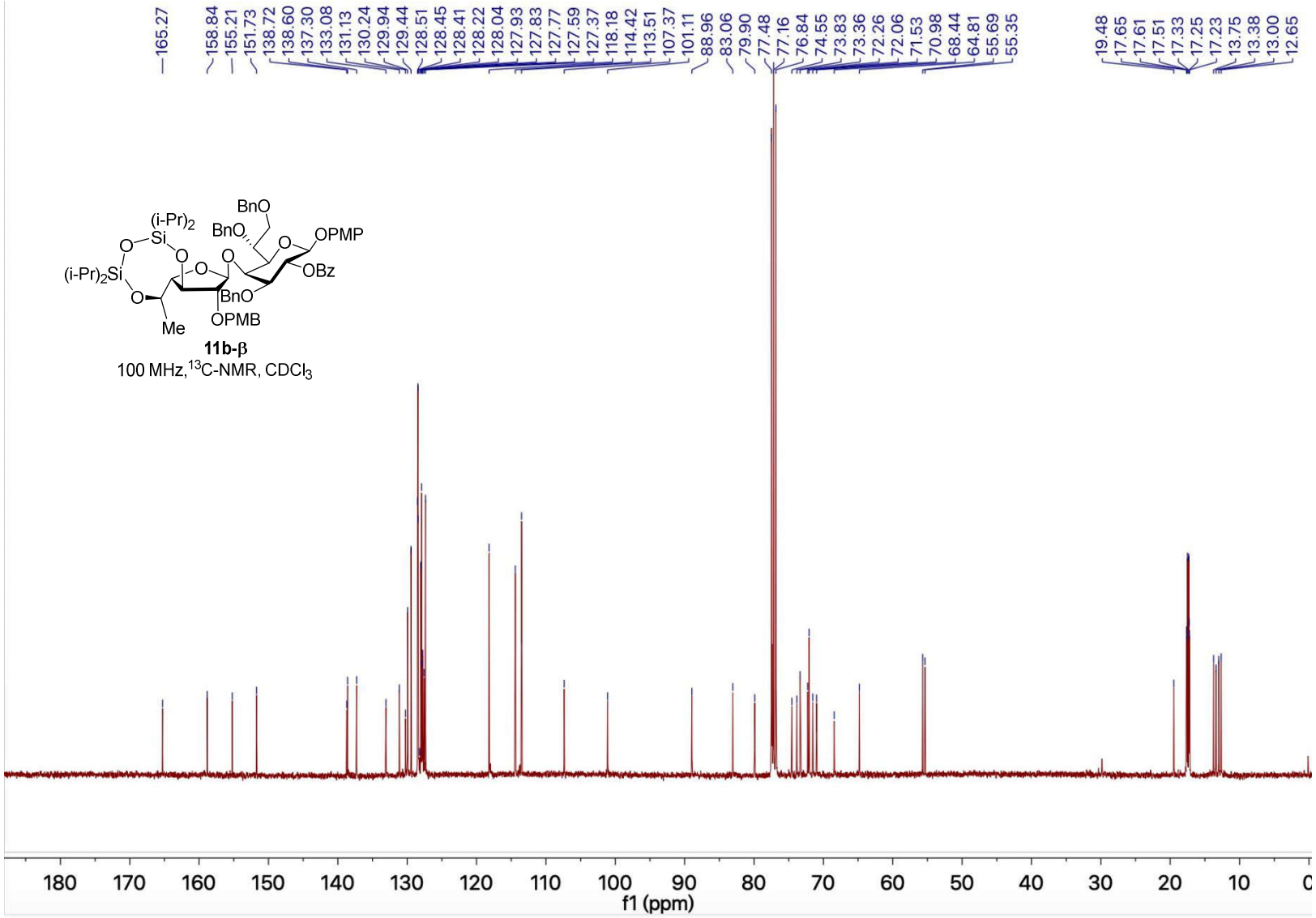
138.31
137.35
133.10
130.83
130.46
130.22
129.97
129.94
129.38
128.54
128.51
128.49
128.46
128.36
128.23
127.94
127.89
127.87
127.84
127.70
127.68
127.62
127.56
127.40
117.91
117.83
114.44
114.42
113.76
113.69
108.26
104.29
100.88
88.52
80.19
77.48
77.16
76.84
76.46
76.17
74.91
73.29
73.26
72.73
72.37
72.12
71.86
71.50
70.58
70.27
66.87
55.72
55.70
55.40
55.37
27.65
27.44
27.34
21.51
20.77
20.75
16.95
16.71
BnO
OPMP
BnO
OBz
(t-Bu)2Si
O
O
O
O
O
BnO
Me
OPMB
11a
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


11b-β
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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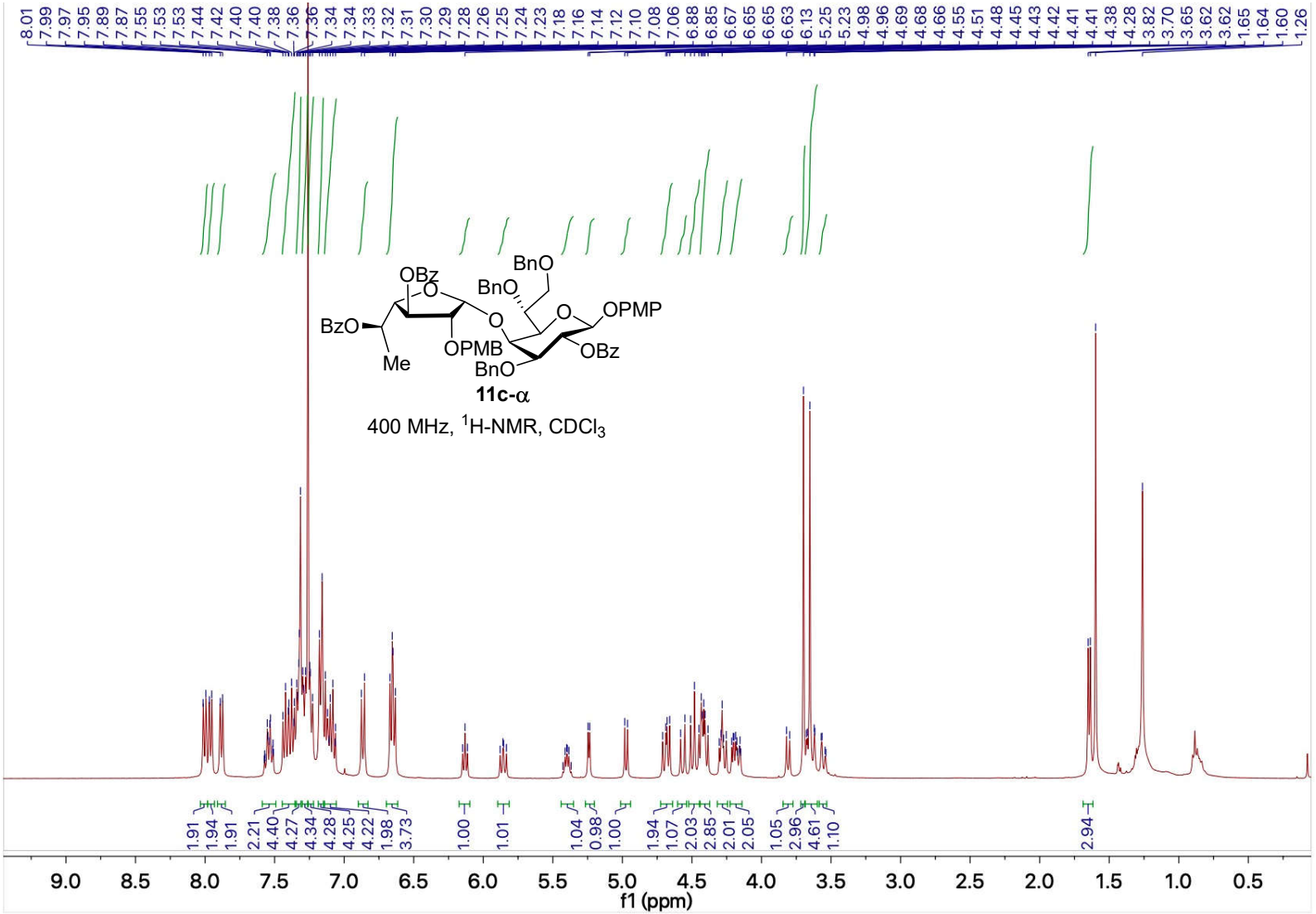
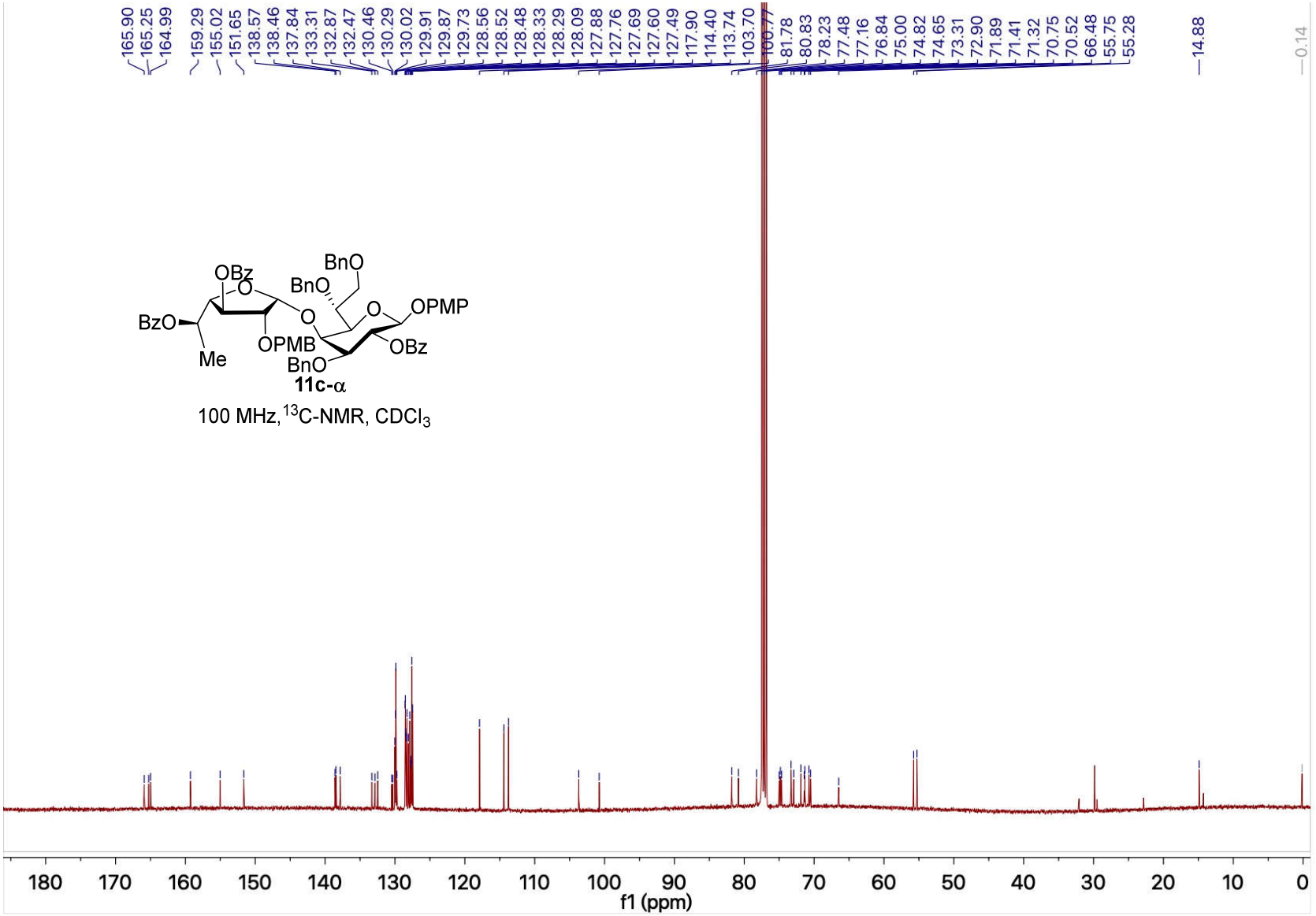
158.84
155.21
151.73
138.72
138.60
137.30
133.08
131.13
130.24
129.94
129.44
128.51
128.45
128.41
128.22
128.04
127.93
127.83
127.77
127.59
127.37
118.18
114.42
113.51
107.37
101.11
88.96
83.06
79.90
77.48
77.16
76.84
74.55
73.83
73.36
72.26
72.06
71.53
70.98
68.44
64.81
55.69
55.35
19.48
17.65
17.61
17.51
17.33
17.25
17.23
13.75
13.38
13.00
12.65
BnO
(i-Pr)2
Si
BnO
OPMP
(i-Pr)2Si
OBz
BnO
OPMB
Me
11b-β
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBz
BnO
BnO
BzO
OPMP
OPMB
OBz
Me
BnO
11c-α
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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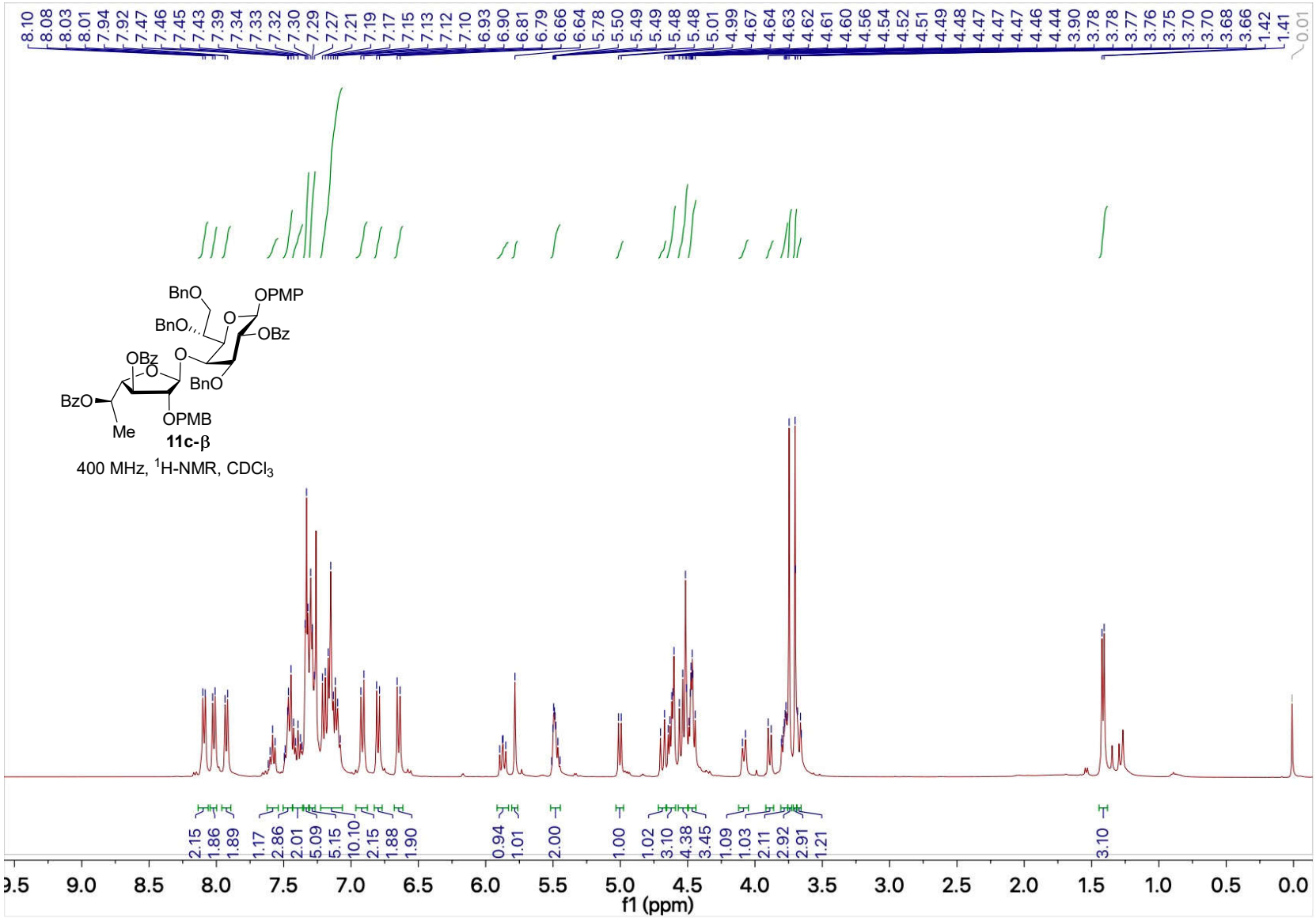
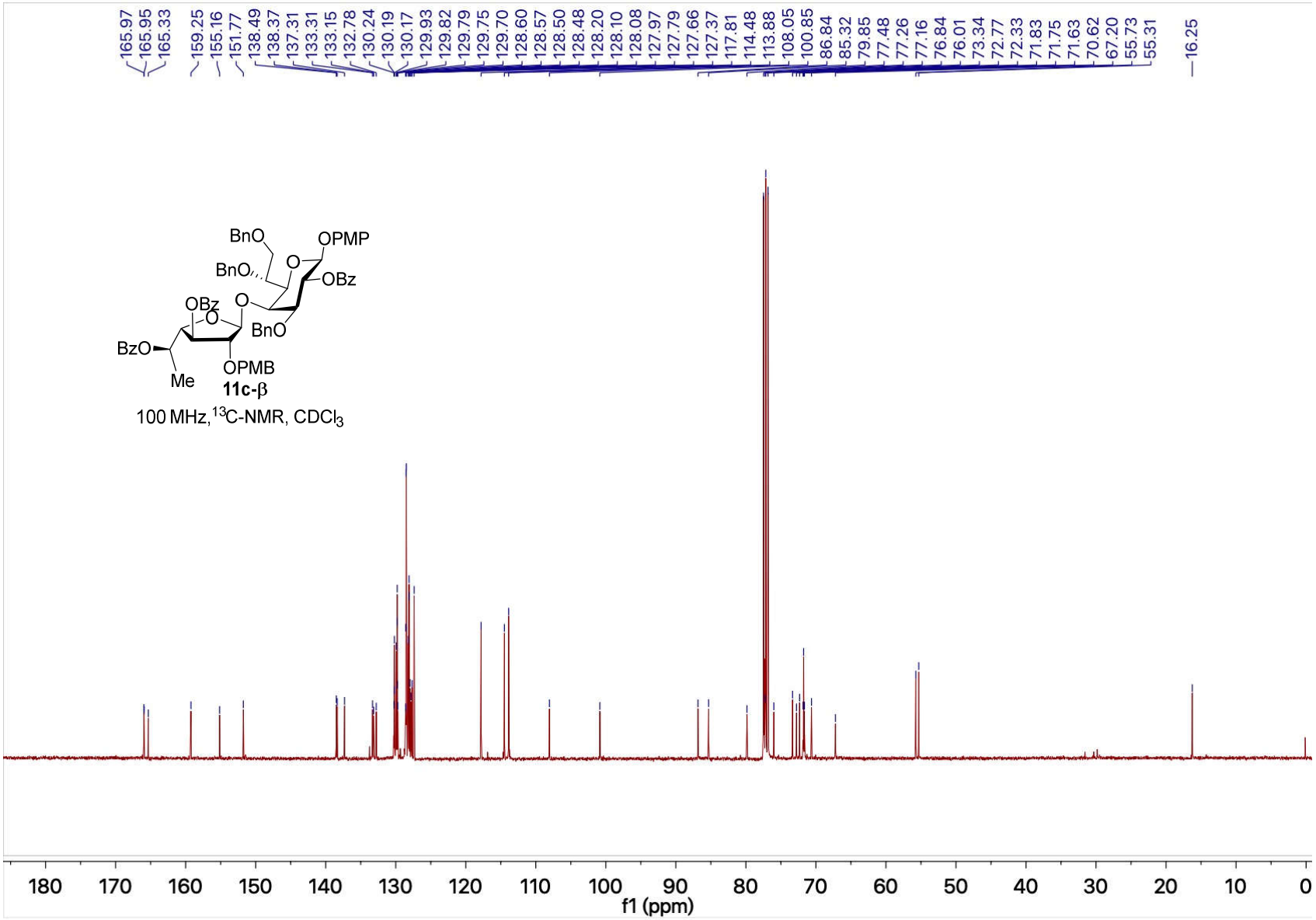
133.31
132.87
132.47
130.46
130.29
130.02
129.91
129.87
129.73
128.56
128.52
128.48
128.33
128.29
128.09
127.88
127.76
127.69
127.60
127.49
117.90
114.40
113.74
103.70
100.77
81.78
80.83
78.23
77.48
77.16
76.84
75.00
74.82
74.65
73.31
72.90
71.89
71.41
71.32
70.75
70.52
66.48
55.75
55.28
14.88
0.14
OBz
BnO
BnO
O
O
O
OPMP
BzO
OPMB
OBz
Me
BnO
11c-α
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
OPMP
BnO
O
OBz
OBz
O
O
BnO
BzO
OPMB
Me
11c-β
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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165.95
165.33
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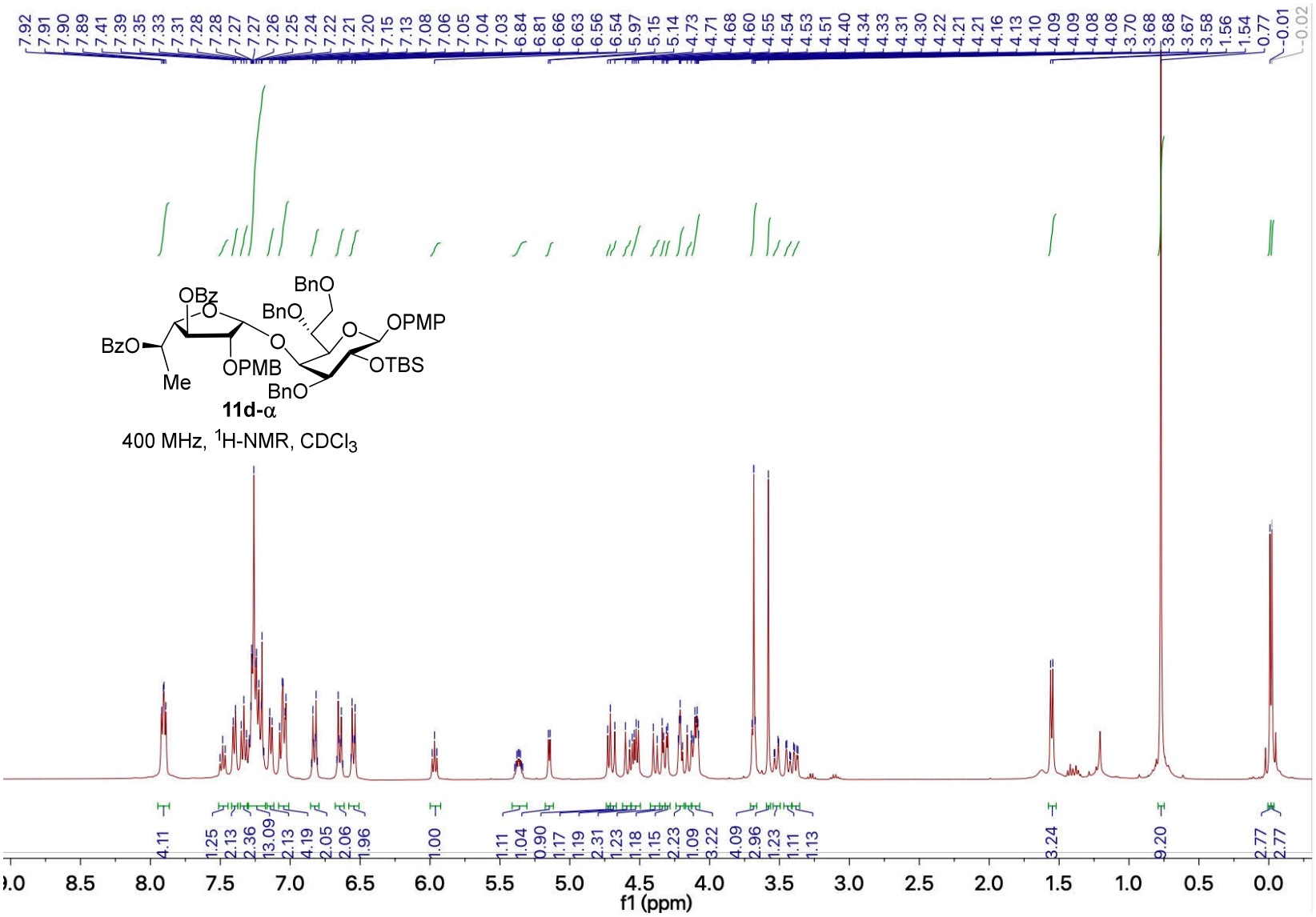
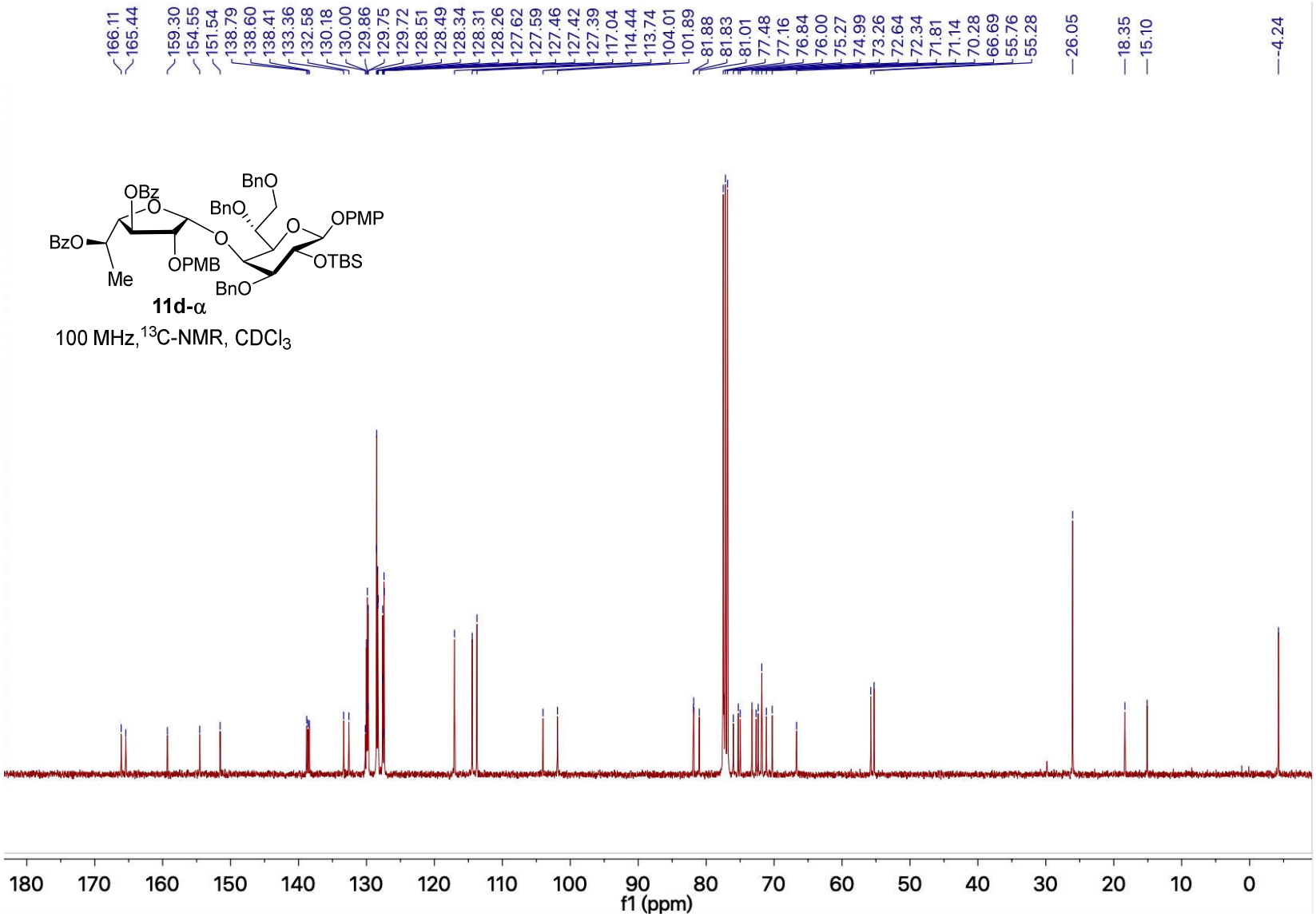
155.16
151.77
138.49
138.37
137.31
133.31
133.15
132.78
130.24
130.19
130.17
129.93
129.82
129.79
129.75
129.70
128.60
128.57
128.50
128.48
128.20
128.10
128.08
127.97
127.79
127.66
127.37
117.81
114.48
113.88
108.05
100.85
86.84
85.32
79.85
77.48
77.26
77.16
76.84
76.01
73.34
72.77
72.33
71.83
71.75
71.63
70.62
67.20
55.73
55.31
16.25
BnO
OPMP
BnO
O
OBz
OBz
O
O
BnO
BzO
OPMB
Me
11c-β
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBz
BnO
BnO
OPMP
BzO
OPMB
OTBS
Me
BnO
11d-α
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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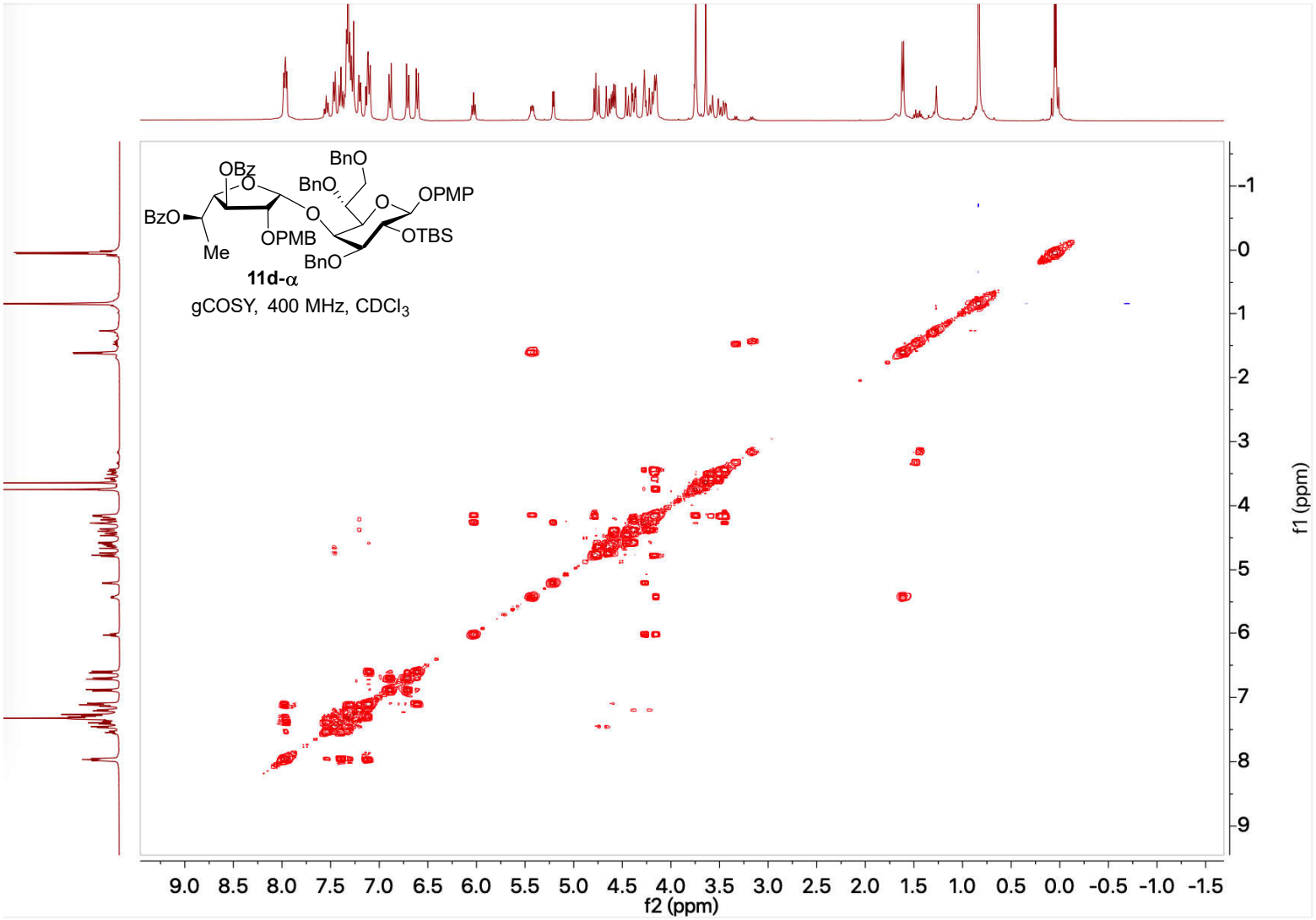
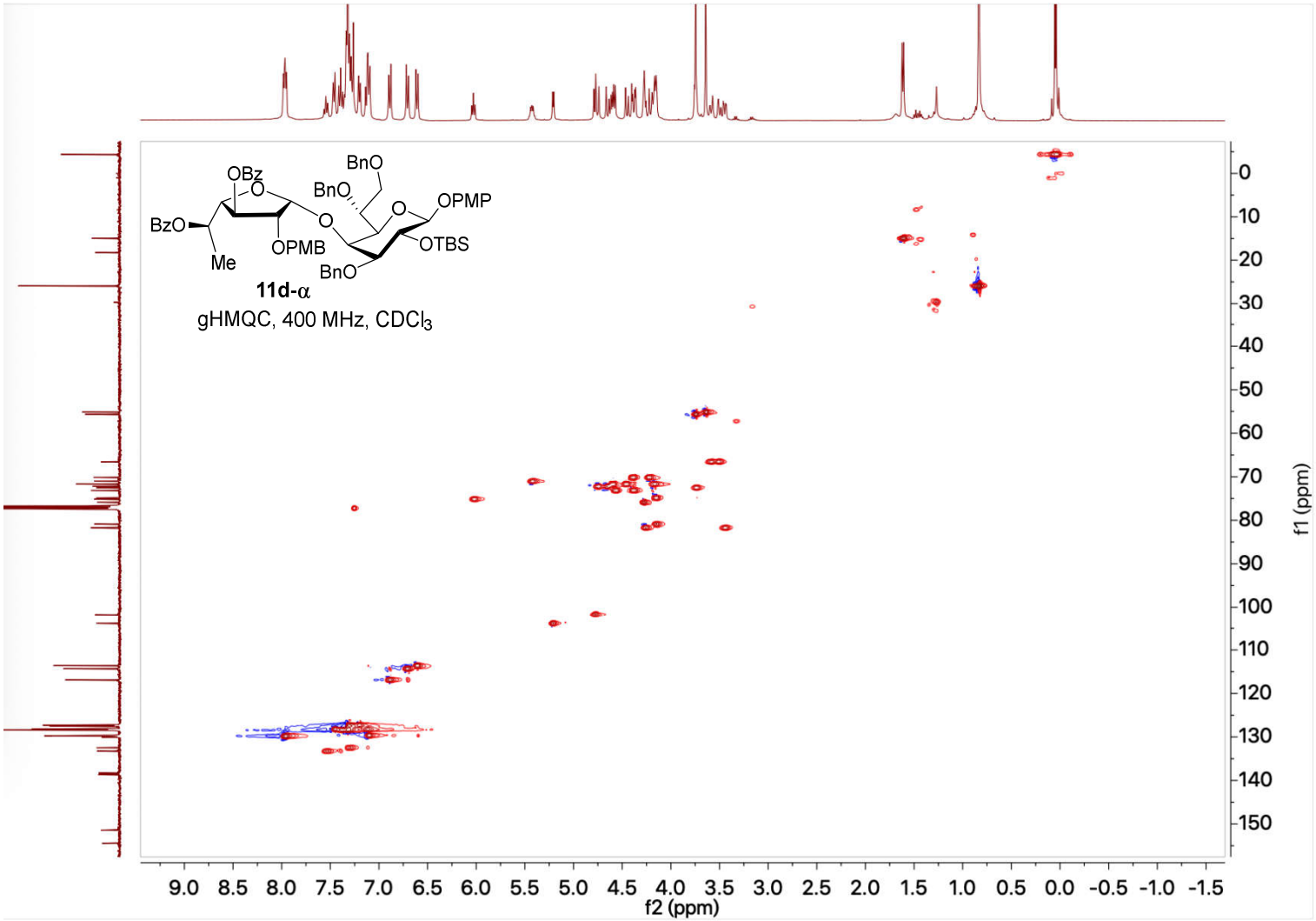
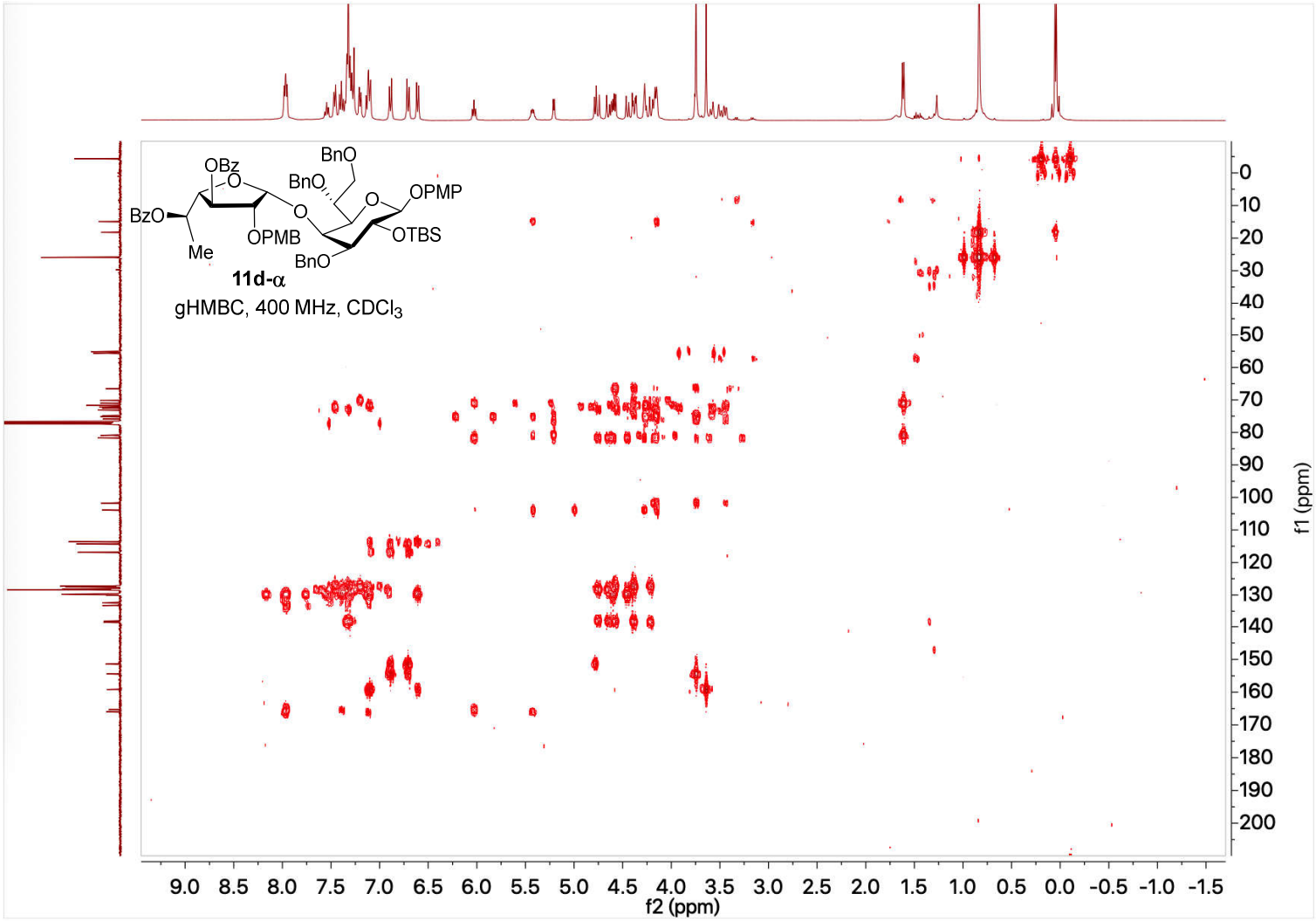
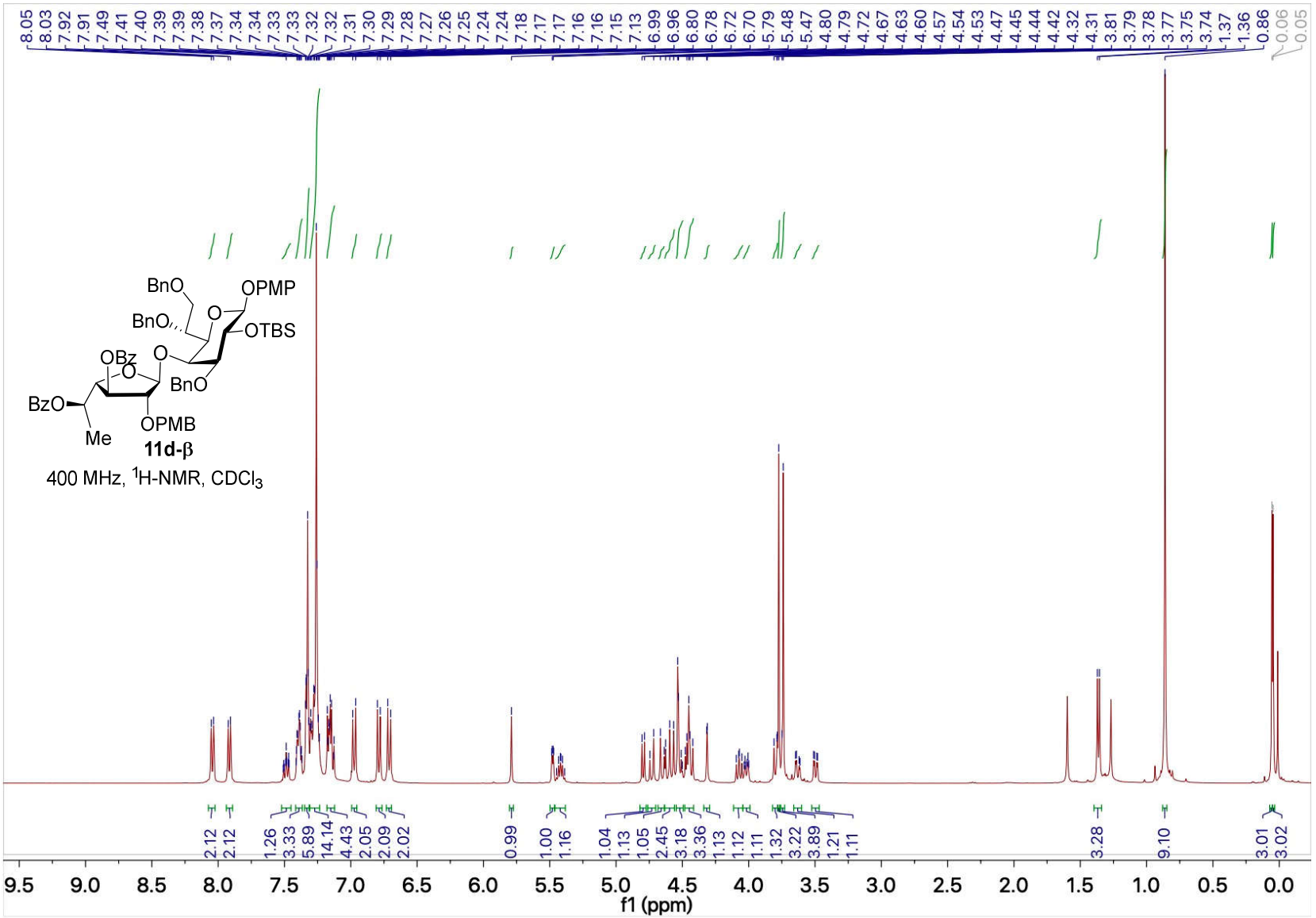
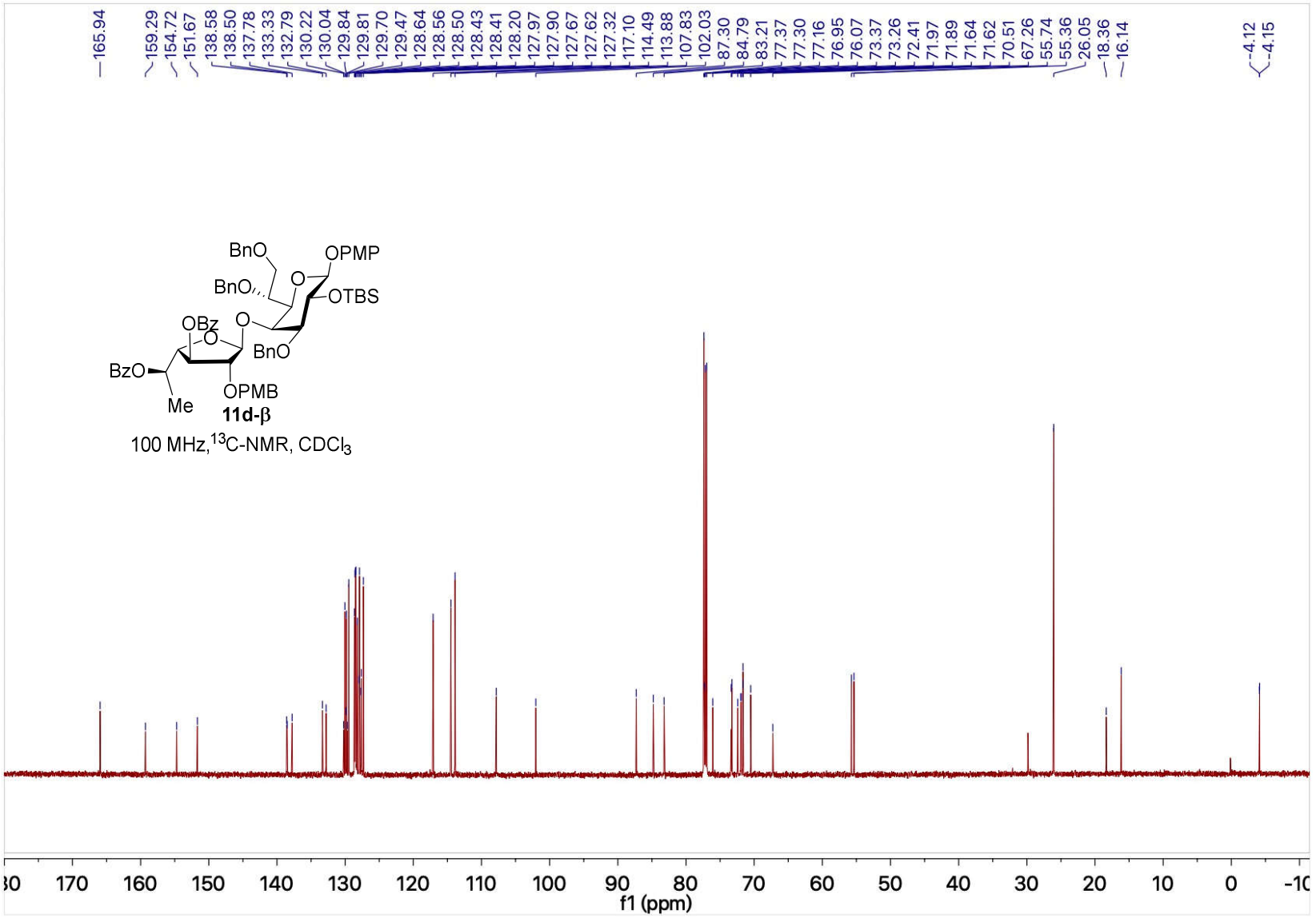
130.18
130.00
129.86
129.75
129.72
128.51
128.49
128.34
128.31
128.26
127.62
127.59
127.46
127.42
127.39
117.04
114.44
113.74
104.01
101.89
81.88
81.83
81.01
77.48
77.16
76.84
76.00
75.27
74.99
73.26
72.64
72.34
71.81
71.14
70.28
66.69
55.76
55.28
26.05
18.35
15.10
-4.24
OBz
BnO
BnO
OPMP
BzO
OPMB
OTBS
Me
BnO
11d-α
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBz
BnO
BnO
OPMP
BzO
OPMB
OTBS
Me
BnO
11d-α
gCOSY, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)


OBz
BnO
BnO
OPMP
BzO
OPMB
OTBS
Me
BnO
11d-α
gHMQC, 400 MHz, CDCl3
f1 (ppm)
f2 (ppm)


OBz
BnO
BnO
OPMP
BzO
OPMB
OTBS
Me
BnO
11d-α
gHMBC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)


BnO
OPMP
BnO
O
OTBS
OBz
O
O
BnO
BzO
OPMB
Me
11d-β
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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133.33
132.79
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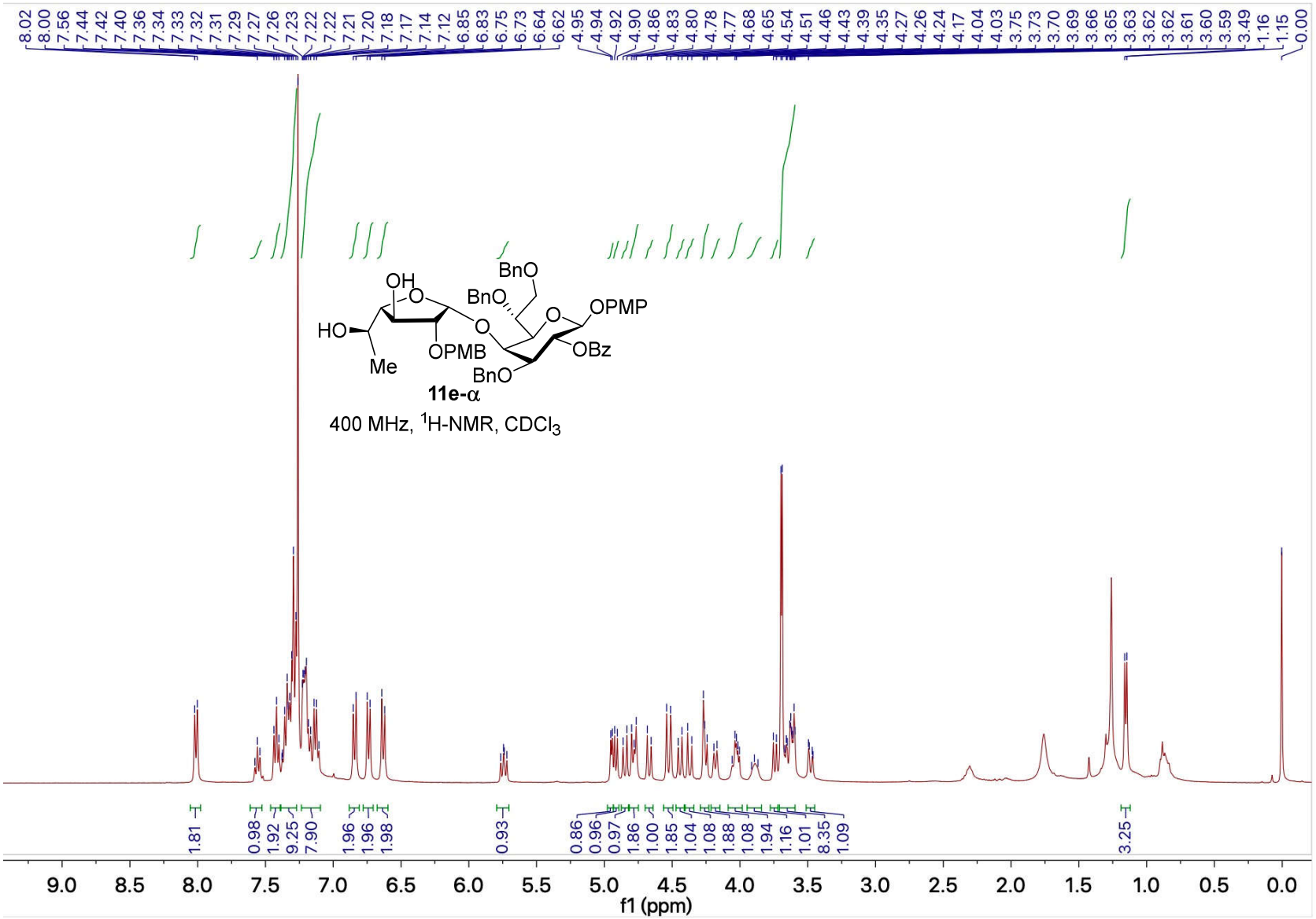
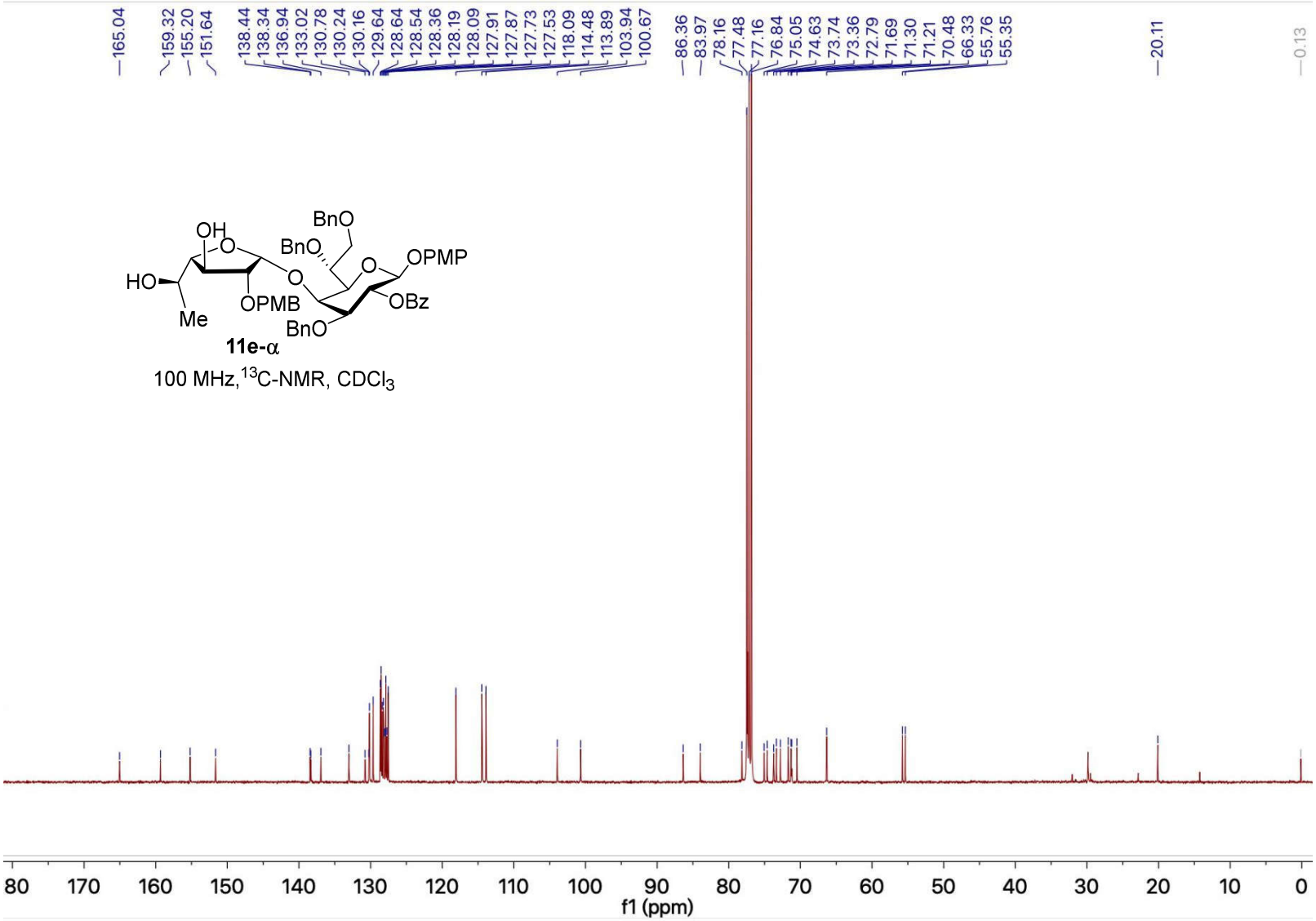
130.04
129.84
129.81
129.70
129.47
128.64
128.56
128.50
128.43
128.41
128.20
127.97
127.90
127.67
127.62
127.32
117.10
114.49
113.88
107.83
102.03
87.30
84.79
83.21
77.37
77.30
77.16
76.95
76.07
73.37
73.26
72.41
71.97
71.89
71.64
71.62
70.51
67.26
55.74
55.36
26.05
18.36
16.14
-4.12
-4.15
BnO
OPMP
BnO
O
OTBS
OBz
O
O
BnO
BzO
Me
OPMB
11d-β
100 MHz,13C-NMR, CDCl3
f1 (ppm)


11e-α
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)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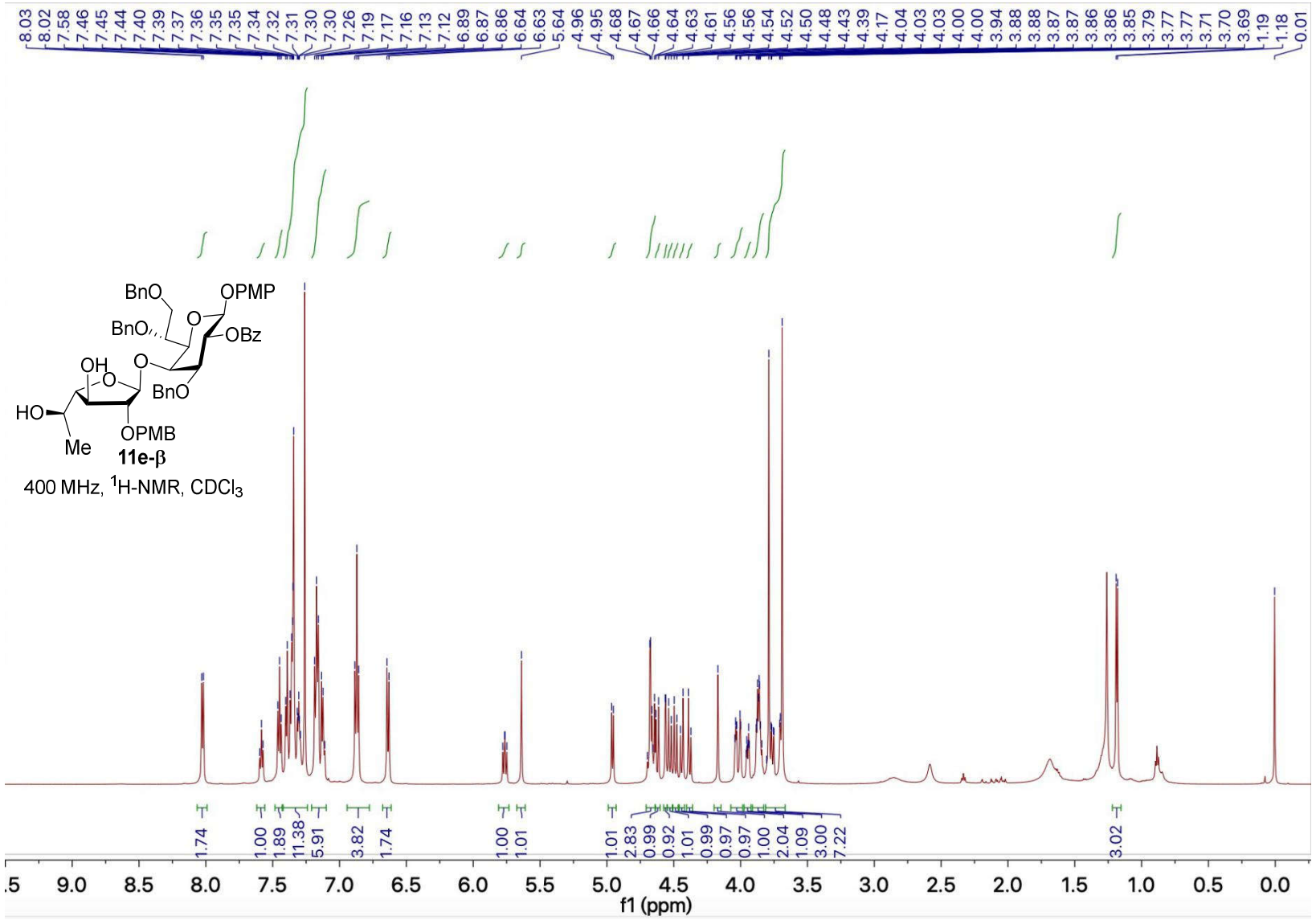
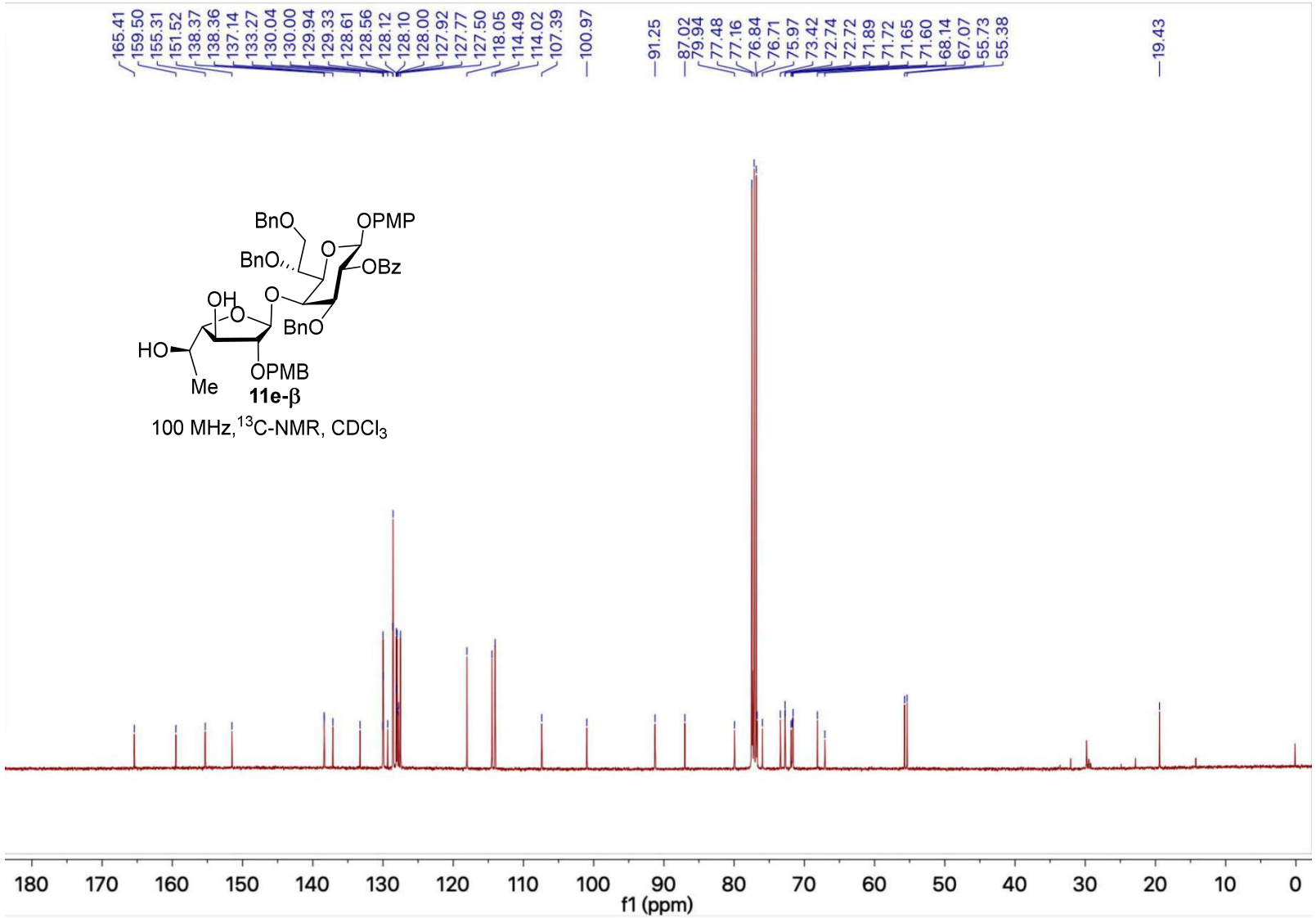
159.32
155.20
151.64
138.44
138.34
136.94
133.02
130.78
130.24
130.16
129.64
128.64
128.54
128.36
128.19
128.09
127.91
127.87
127.73
127.53
118.09
114.48
113.89
103.94
100.67
86.36
83.97
78.16
77.48
77.16
76.84
75.05
74.63
73.74
73.36
72.79
71.69
71.30
71.21
70.48
66.33
55.76
55.35
20.11
0.13
OH
O
BnO
BnO
O
OPMP
HO
O
OPMB
OBz
Me
BnO
11e-α
100 MHz, 13C-NMR, CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


BnO
OPMP
BnO
O
OBz
OH
O
O
BnO
HO
OPMB
Me
11e-β
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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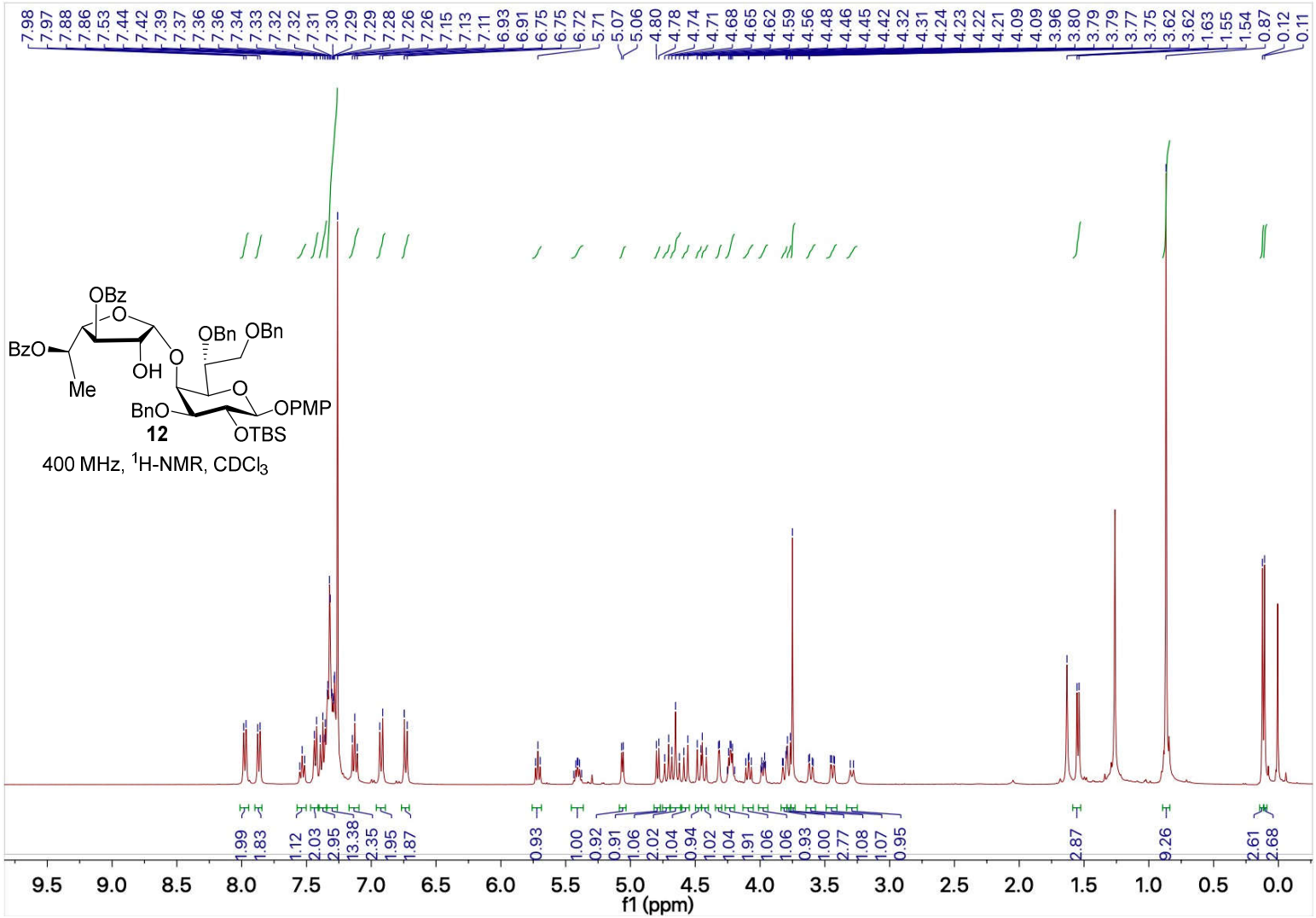
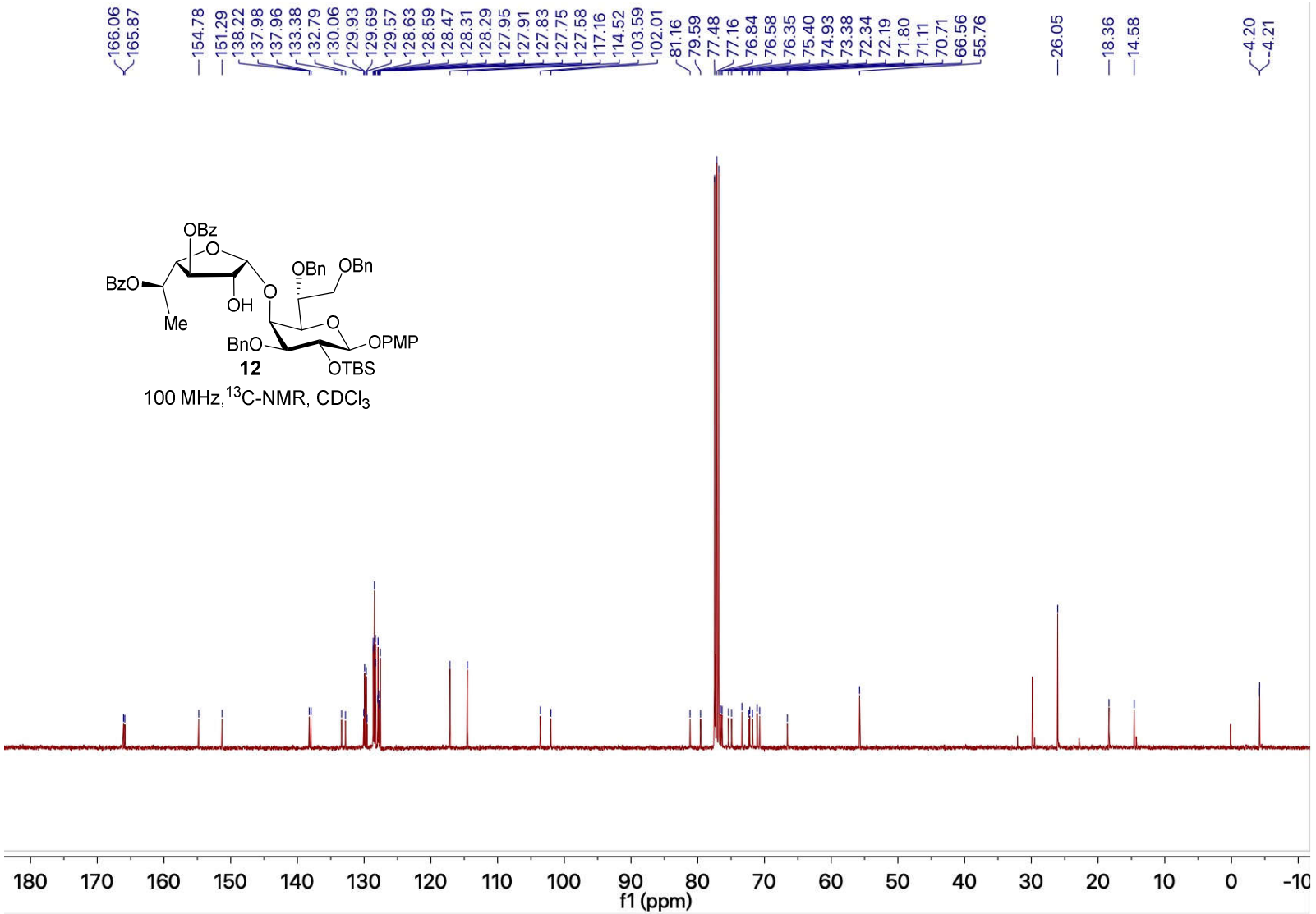
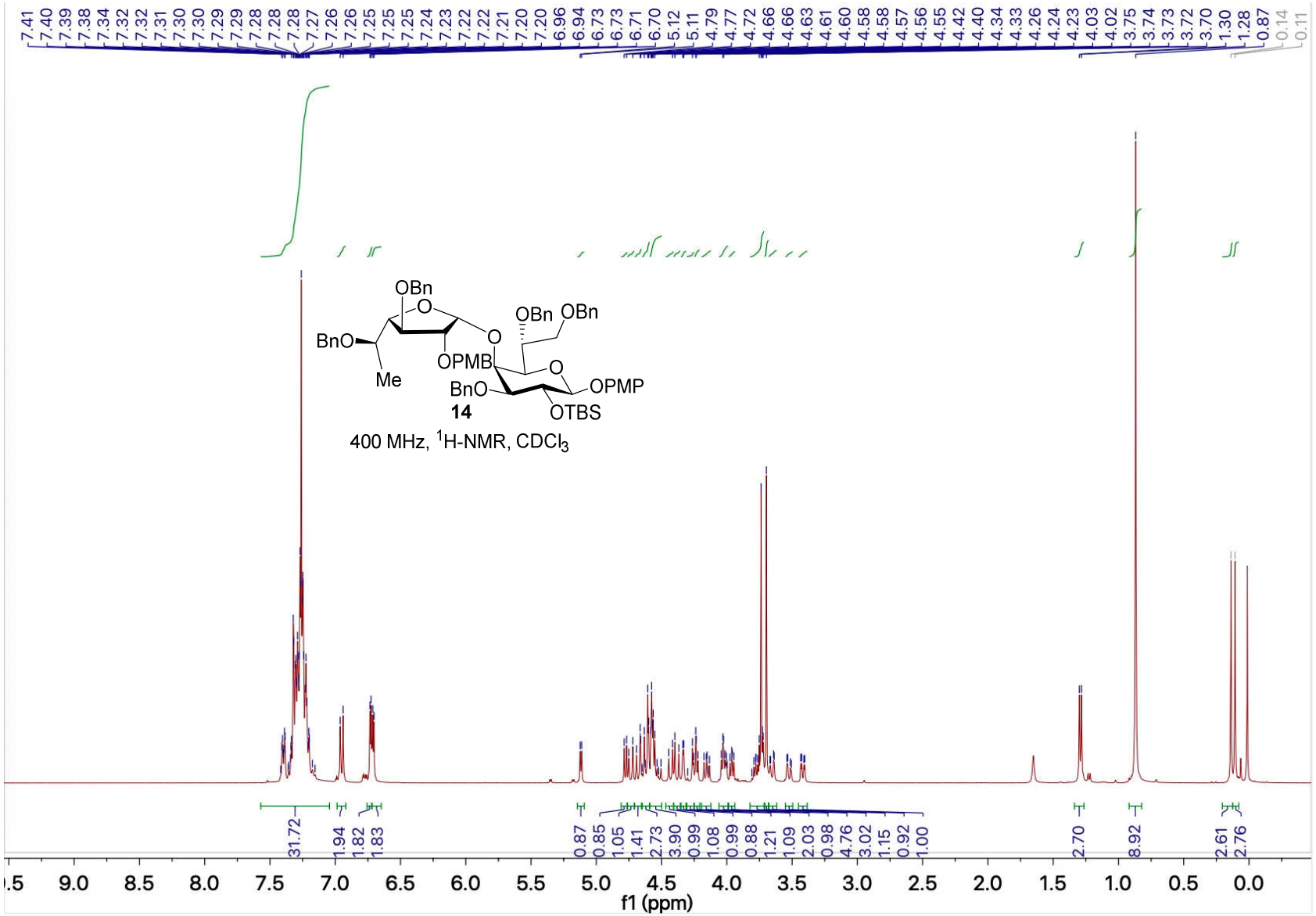
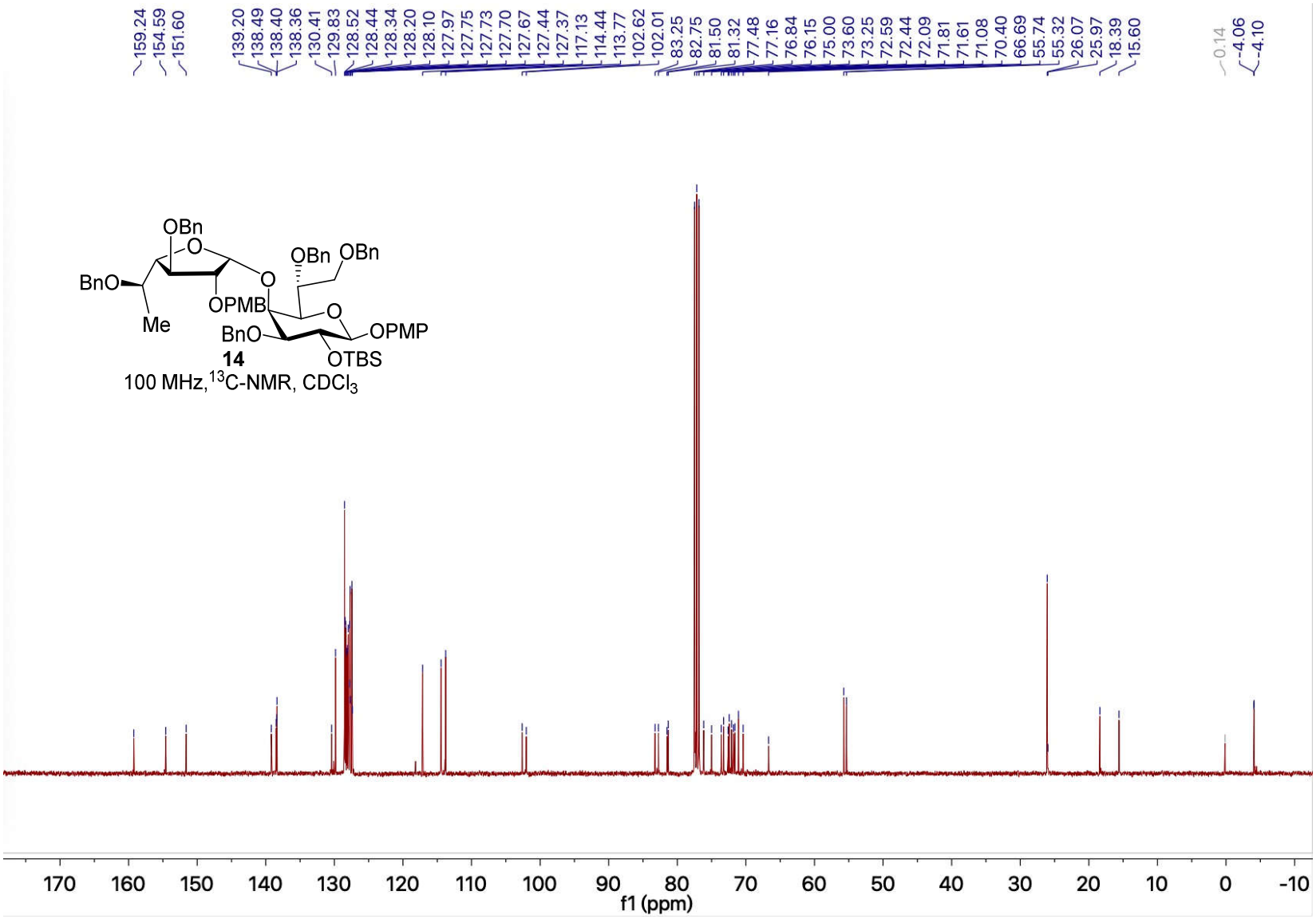
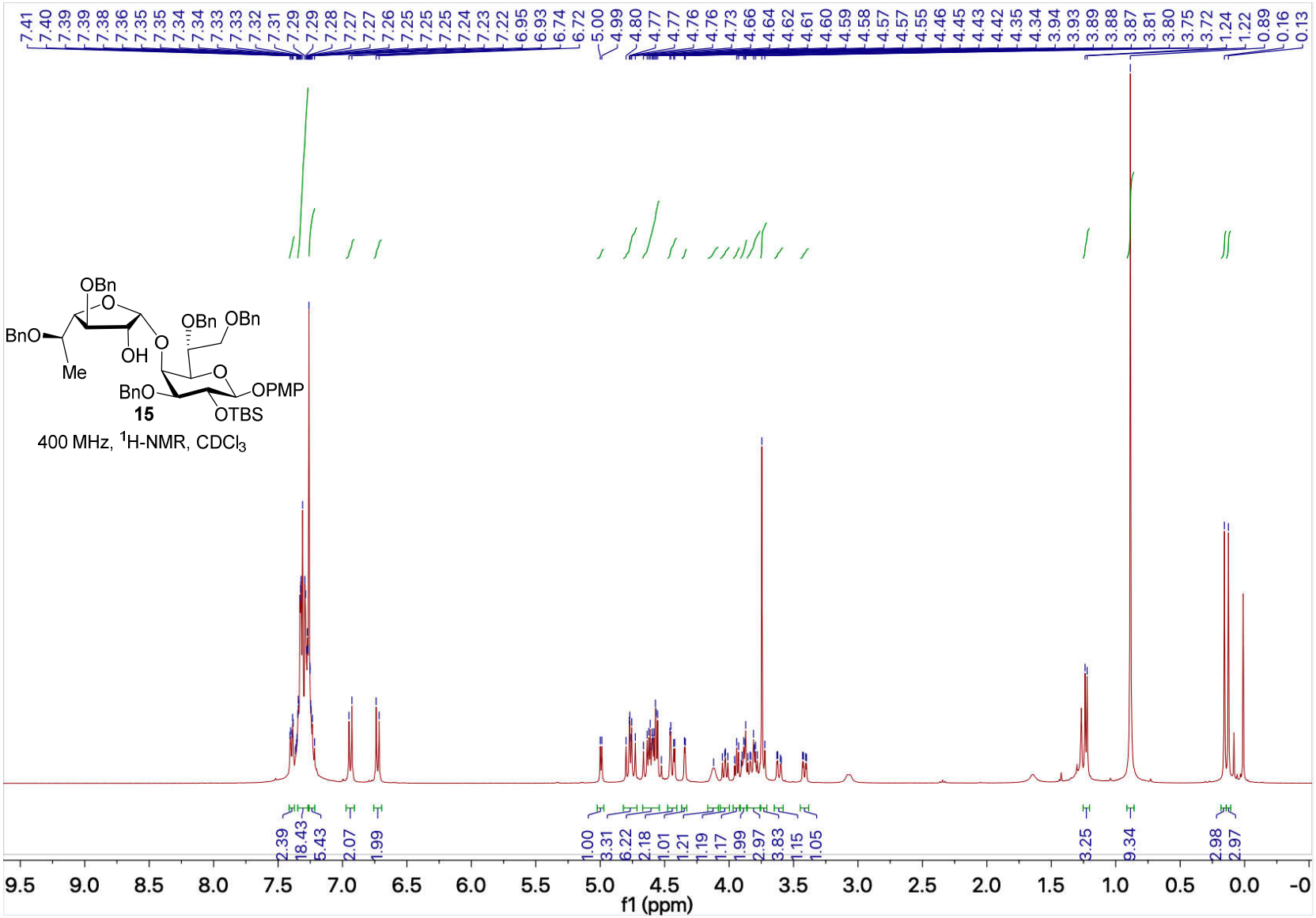
159.50
155.31
151.52
138.37
138.36
137.14
133.27
130.04
130.00
129.94
129.33
128.61
128.56
128.12
128.10
128.00
127.92
127.77
127.50
118.05
114.49
114.02
107.39
100.97
91.25
87.02
79.94
77.48
77.16
76.84
76.71
75.97
73.42
72.74
72.72
71.89
71.72
71.65
71.60
68.14
67.07
55.73
55.38
19.43
BnO
OPMP
O
BnO
OBz
OH
O
O
BnO
HO
OPMB
Me
11e-β
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

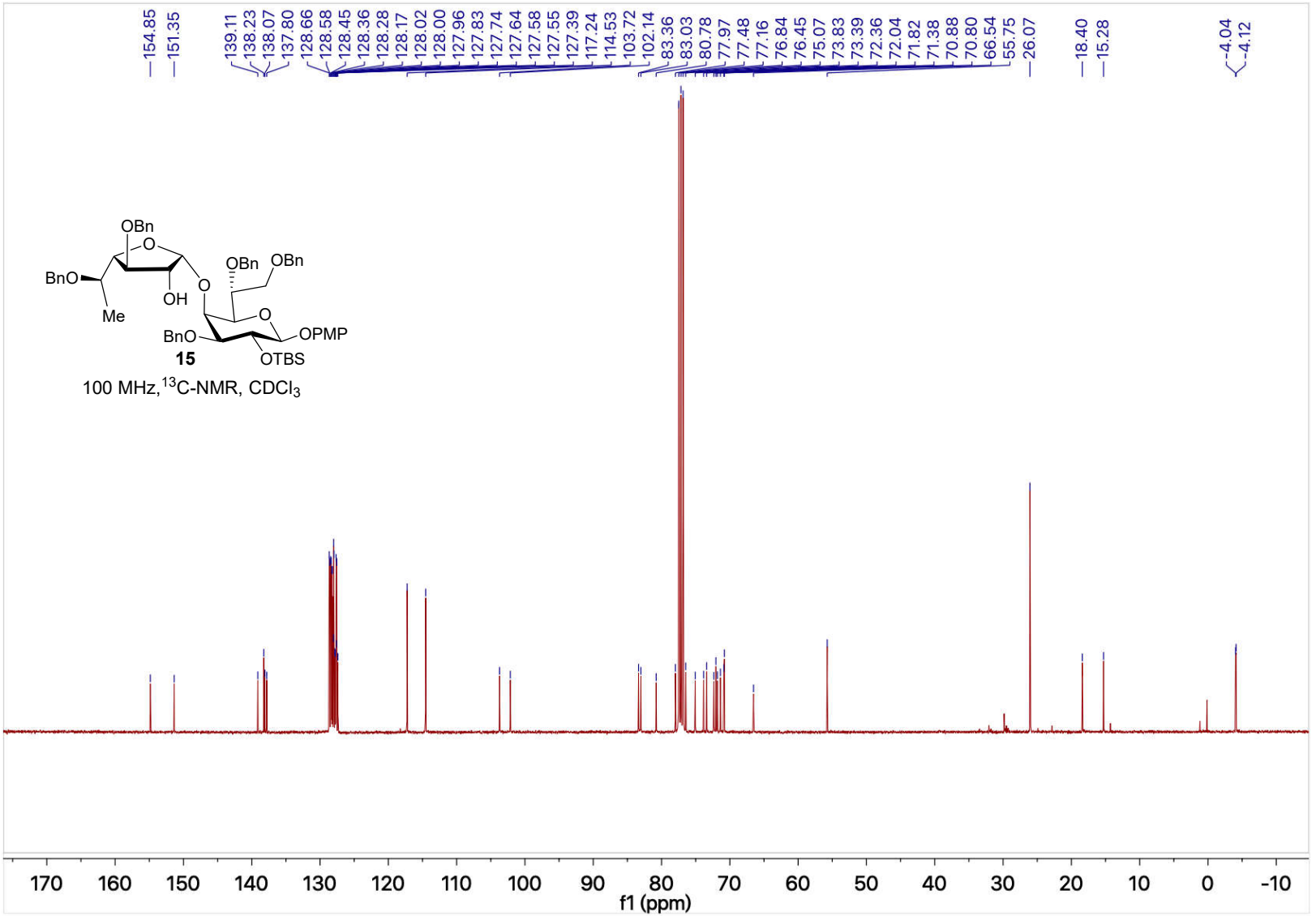

OBz
BzO
OBn OBn
OH
Me
BnO
OPMP
OTBS
12
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

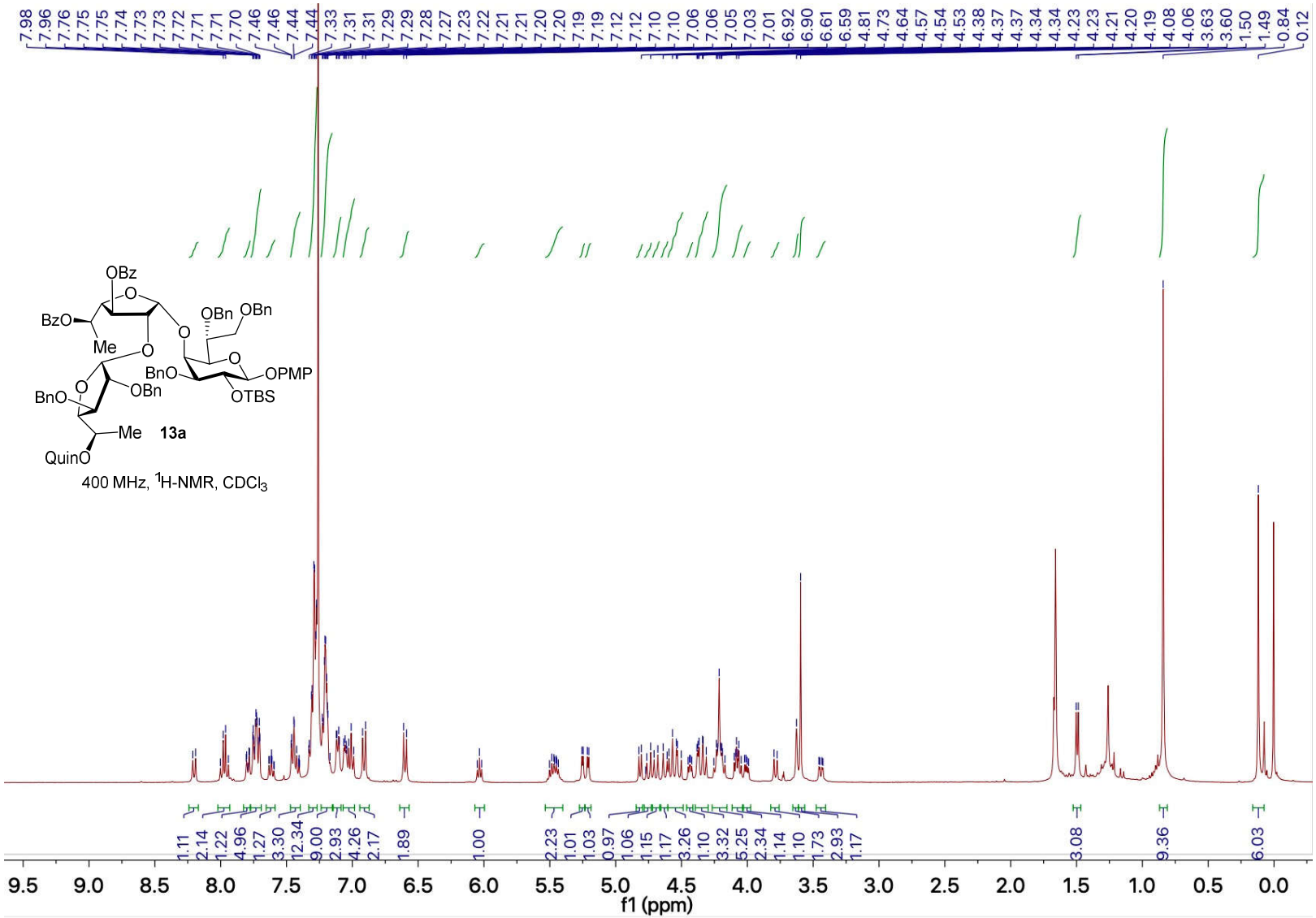

166.06
165.87
154.78
151.29
138.22
137.98
137.96
133.38
132.79
130.06
129.93
129.69
129.57
128.63
128.59
128.47
128.31
128.29
127.95
127.91
127.83
127.75
127.58
117.16
114.52
103.59
102.01
81.16
79.59
77.48
77.16
76.84
76.58
76.35
75.40
74.93
73.38
72.34
72.19
71.80
71.11
70.71
66.56
55.76
26.05
18.36
14.58
-4.20
-4.21
OBz
BzO
Me
OH
OBn
OBn
BnO
OPMP
OTBS
12
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

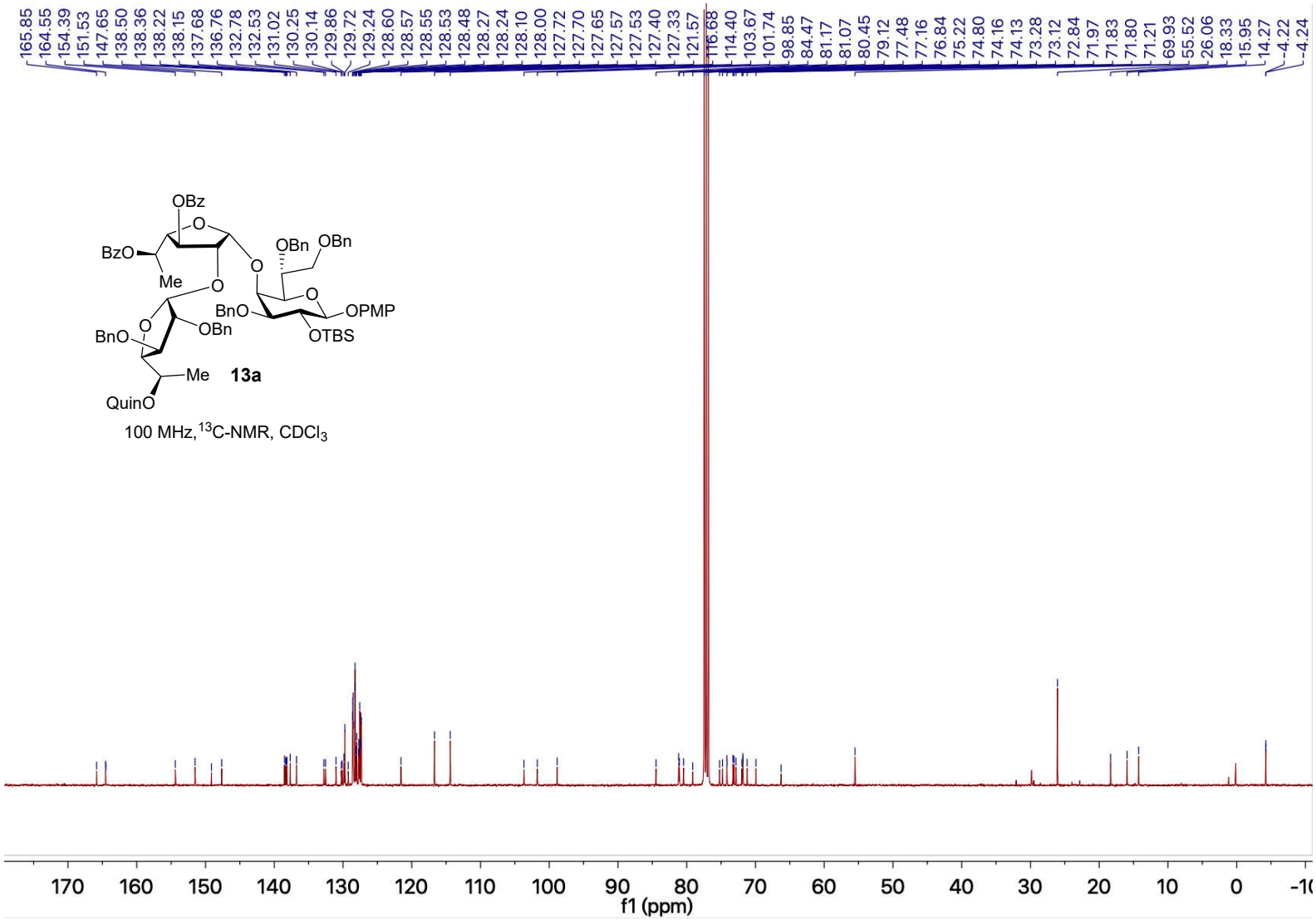

OBn
BnO
OPMB
Me
BnO
OBn OBn
O
O
OPMP
OTBS
14
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

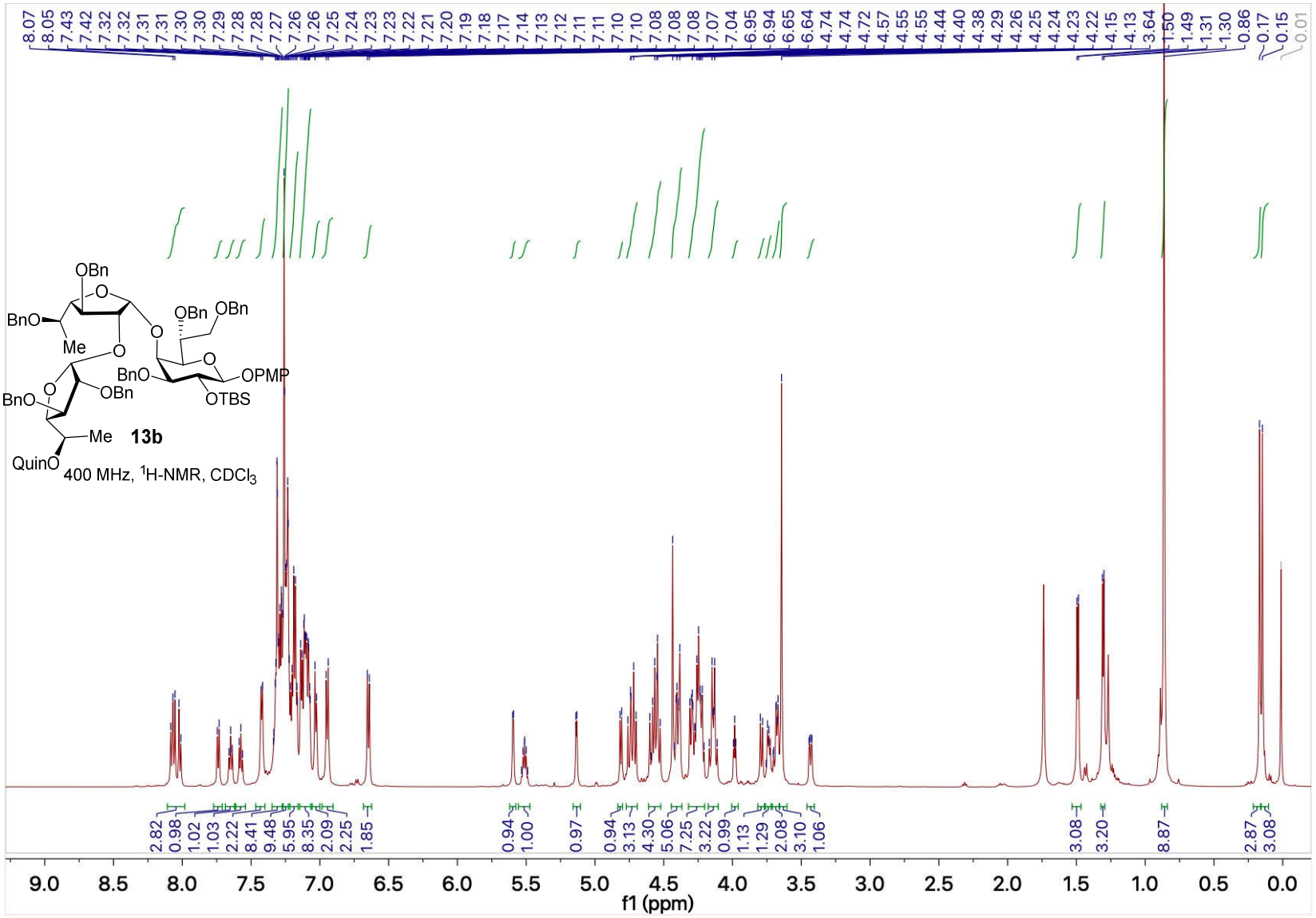

159.24
154.59
151.60
139.20
138.49
138.40
138.36
130.41
129.83
128.52
128.44
128.34
128.20
128.10
127.97
127.75
127.73
127.70
127.67
127.44
127.37
117.13
114.44
113.77
102.62
102.01
83.25
82.75
81.50
81.32
77.48
77.16
76.84
76.15
75.00
73.60
73.25
72.59
72.44
72.09
71.81
71.61
71.08
70.40
66.69
55.74
55.32
26.07
25.97
18.39
15.60
0.14
-4.06
-4.10
OBn
O
OBn
OBn
BnO
O
OPMB
O
Me
BnO
OPMP
14
OTBS
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

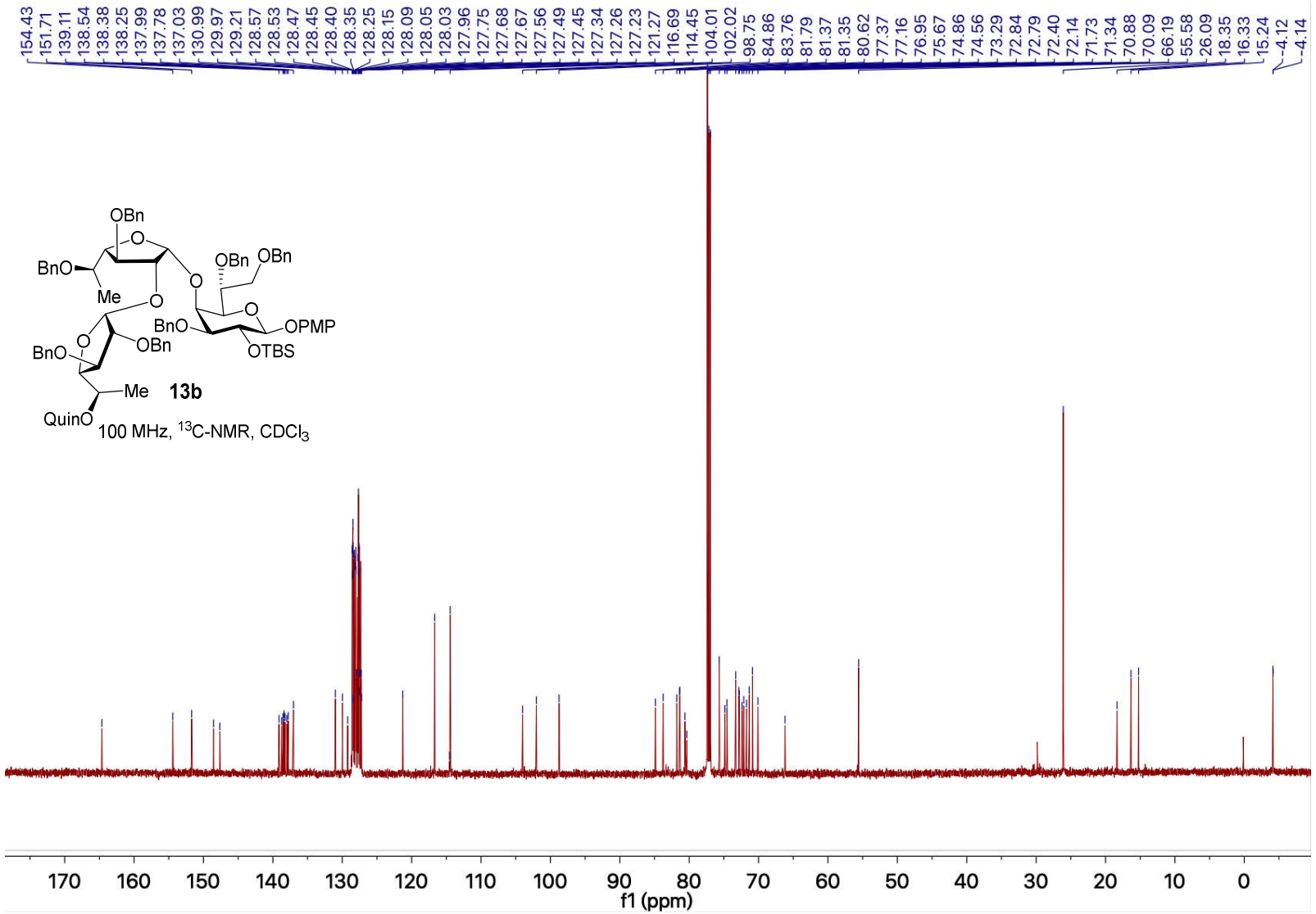

OBn
O
BnO
OBn OBn
OH
O
Me
O
BnO
OPMP
15
OTBS
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

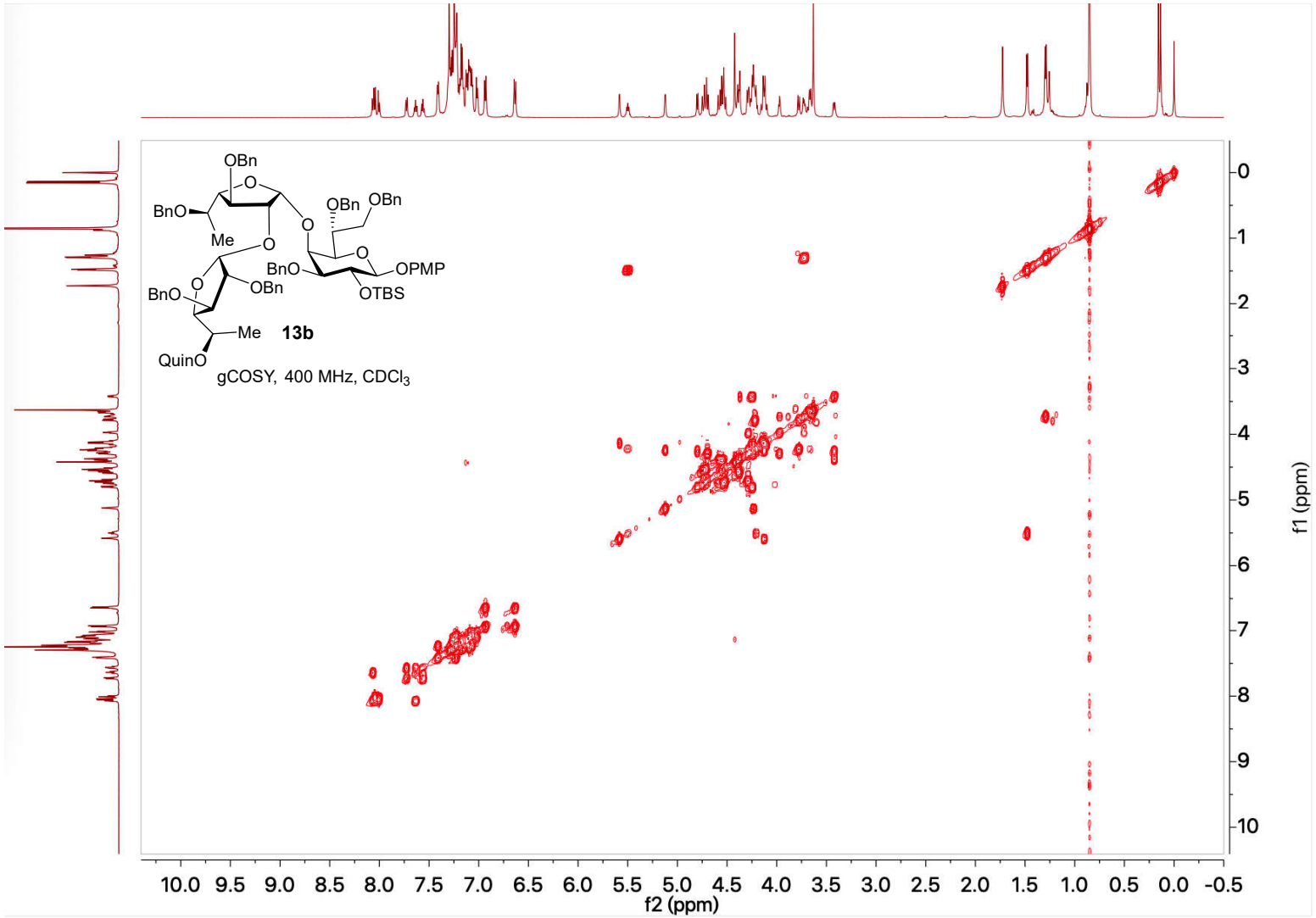

154.85
151.35
139.11
138.23
138.07
137.80
128.66
128.58
128.45
128.36
128.28
128.17
128.02
128.00
127.96
127.83
127.74
127.64
127.58
127.55
127.39
117.24
114.53
103.72
102.14
83.36
83.03
80.78
77.97
77.48
77.16
76.84
76.45
75.07
73.83
73.39
72.36
72.04
71.82
71.38
70.88
70.80
66.54
55.75
26.07
18.40
15.28
-4.04
-4.12
OBn
O
BnO
OH
Me
O
OBn
OBn
O
BnO
OPMP
OTBS
15
100 MHz, ^{13}C-NMR, $CDCl_3$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

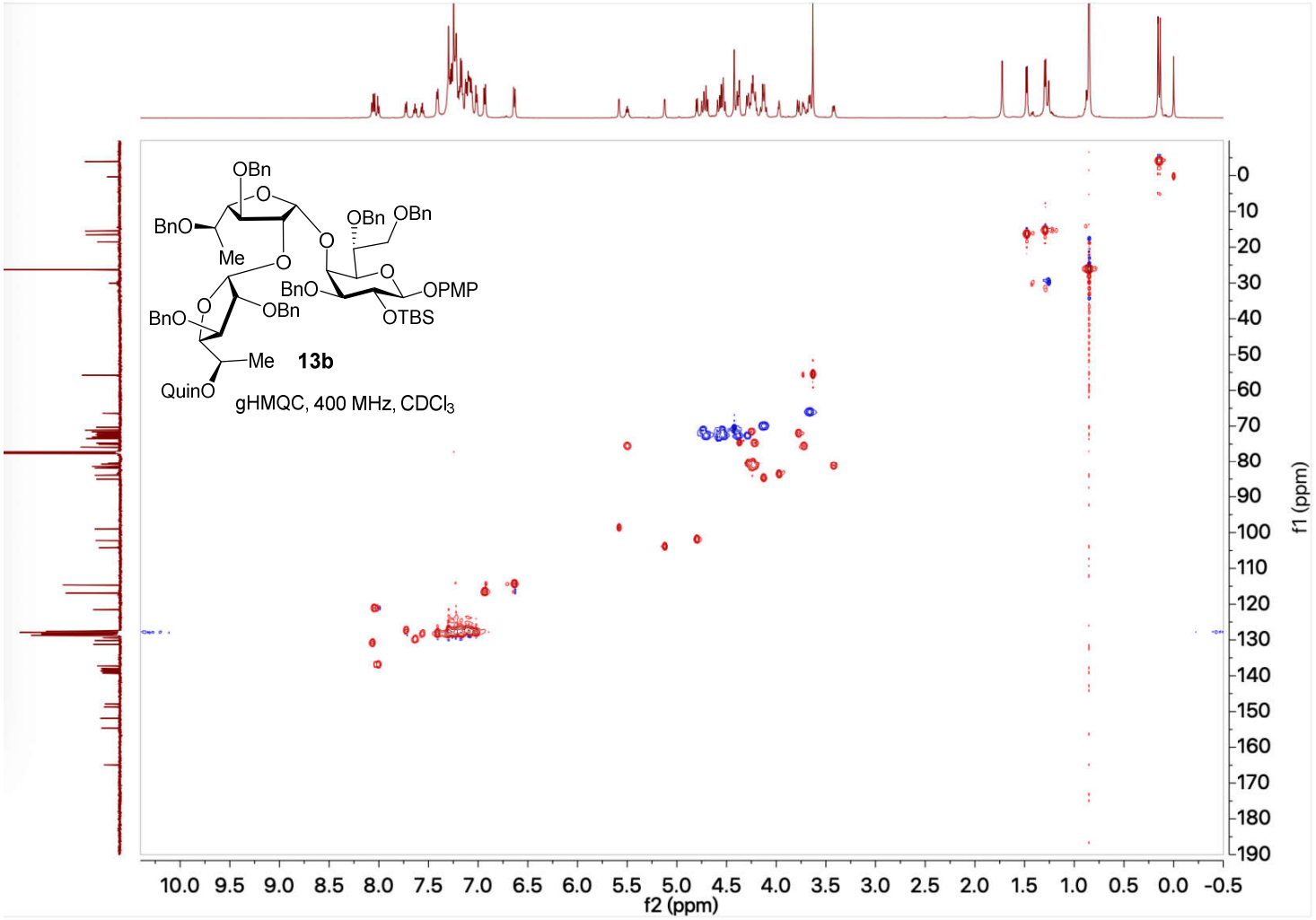

OBz
BzO
Me
OBn OBn
BnO
OPMP
OTBS
BnO
OBn
Me
QuinO
13a
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

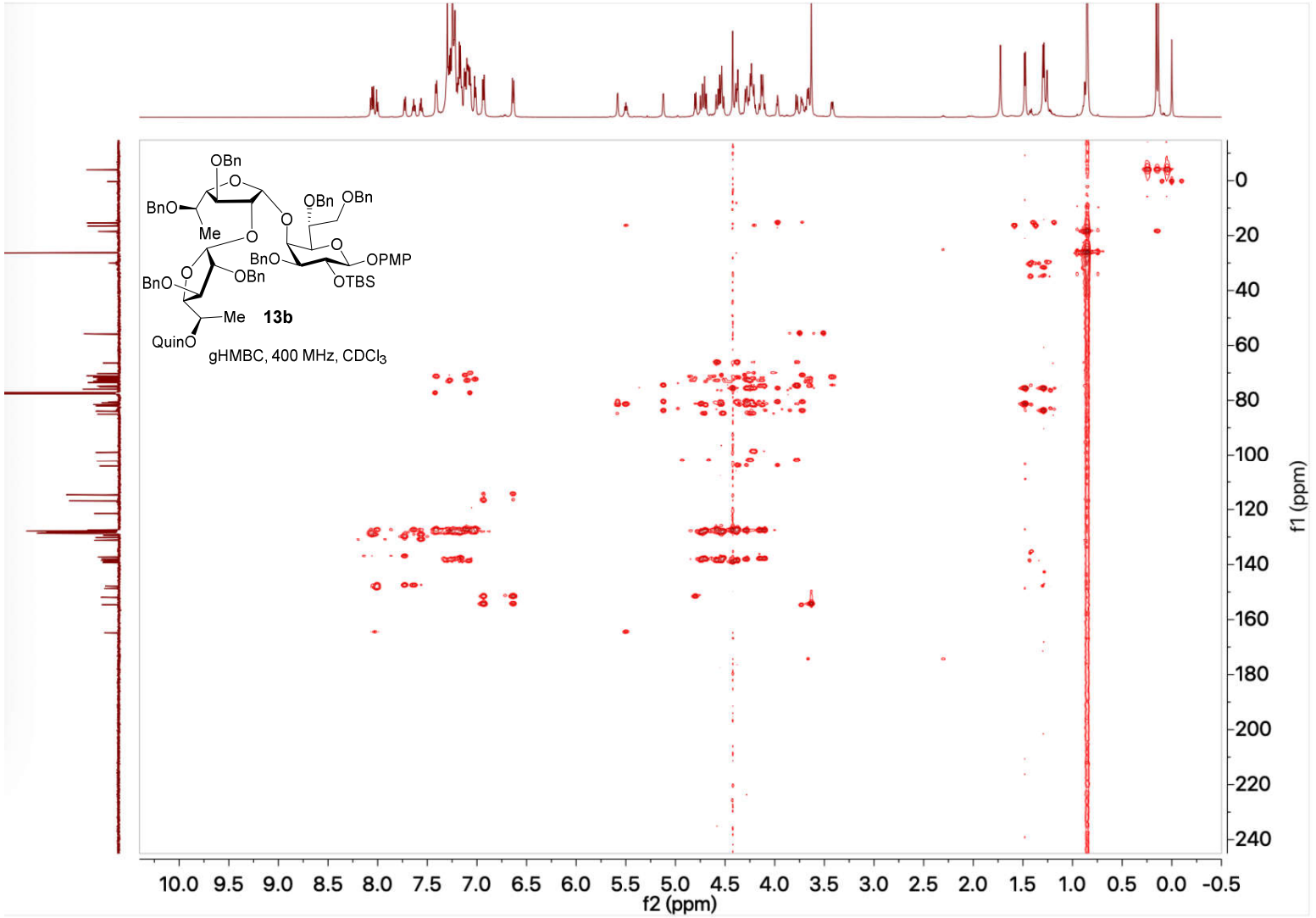

165.85
164.55
154.39
151.53
147.65
138.50
138.36
138.22
138.15
137.68
136.76
132.78
132.53
131.02
130.25
130.14
129.86
129.72
129.24
128.60
128.57
128.55
128.53
128.48
128.27
128.24
128.10
128.00
127.72
127.70
127.65
127.57
127.53
127.40
127.33
121.57
116.68
114.40
103.67
101.74
98.85
84.47
81.17
81.07
80.45
79.12
77.48
77.16
76.84
75.22
74.80
74.16
74.13
73.28
73.12
72.84
71.97
71.83
71.80
71.21
69.93
55.52
26.06
18.33
15.95
14.27
-4.22
-4.24
OBz
BzO
Me
OBn
OBn
BnO
OPMP
OTBS
BnO
OBn
Me
QuinO
13a
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

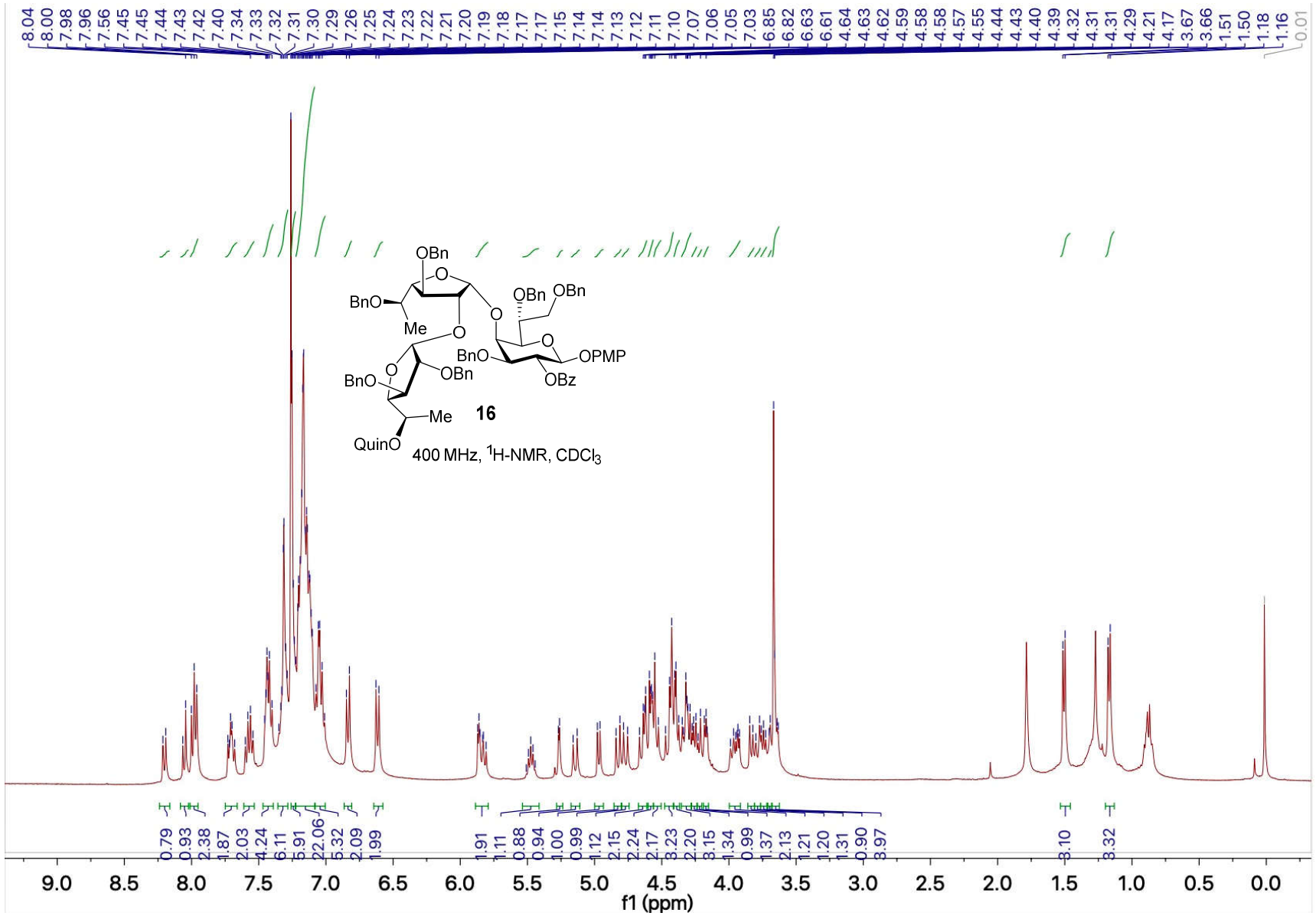

13b
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

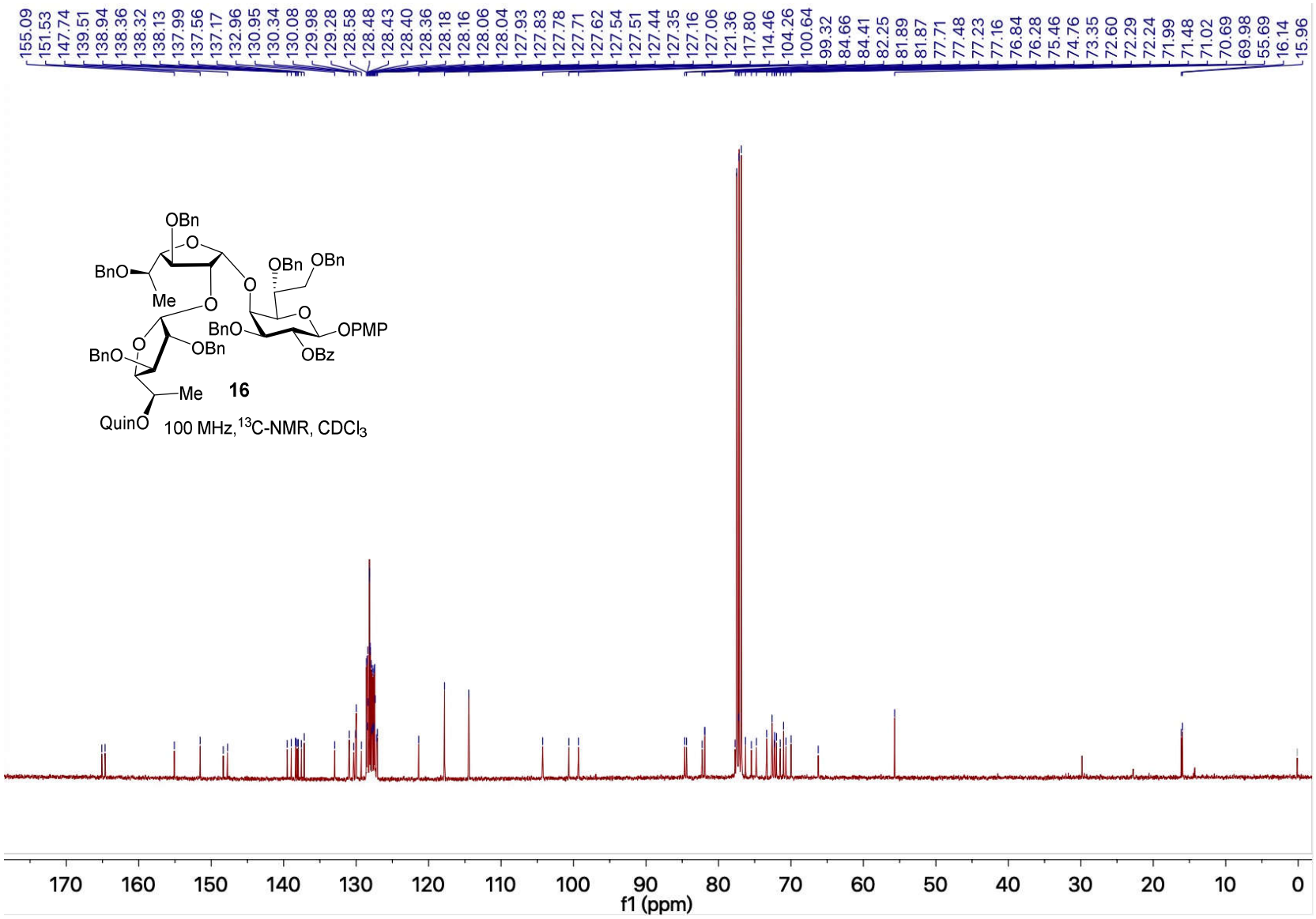

154.43
151.71
139.11
138.54
138.38
138.25
137.99
137.78
137.03
130.99
129.97
129.21
128.57
128.53
128.47
128.45
128.40
128.35
128.25
128.15
128.09
128.05
128.03
127.96
127.75
127.68
127.67
127.56
127.49
127.45
127.34
127.26
127.23
121.27
116.69
114.45
104.01
102.02
98.75
84.86
83.76
81.79
81.37
81.35
80.62
77.37
77.16
76.95
75.67
74.86
74.56
73.29
72.84
72.79
72.40
72.14
71.73
71.34
70.88
70.09
66.19
55.58
26.09
18.35
16.33
15.24
-4.12
-4.14
OBn
BnO
Me
OBn
OBn
OBn
BnO
OPMP
OTBS
BnO
OBn
Me
13b
QuinO
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

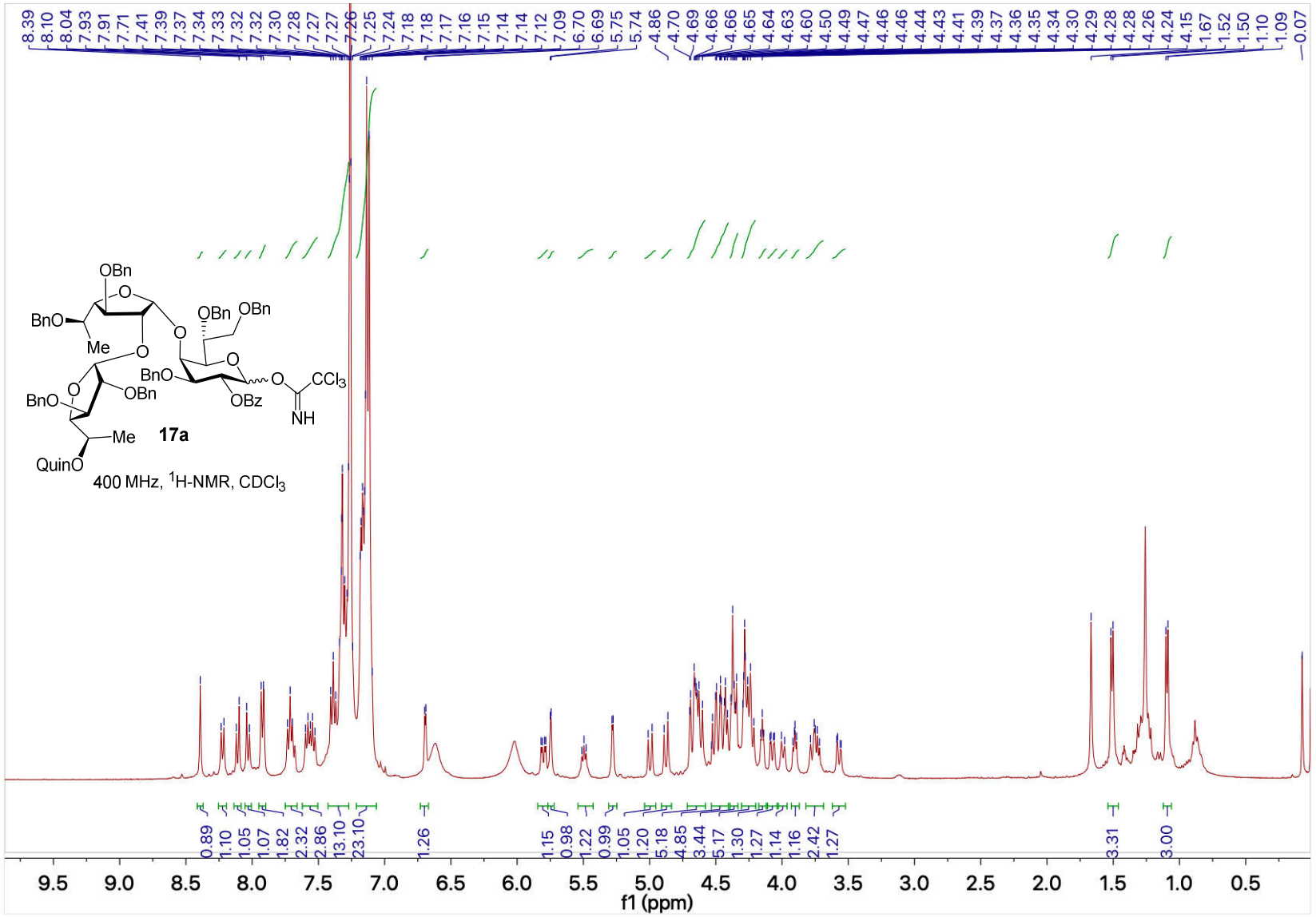

OBn
BnO
Me
OBn OBn
BnO
OPMP
OTBS
BnO
OBn
Me
QuinO
13b
gCOSY, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

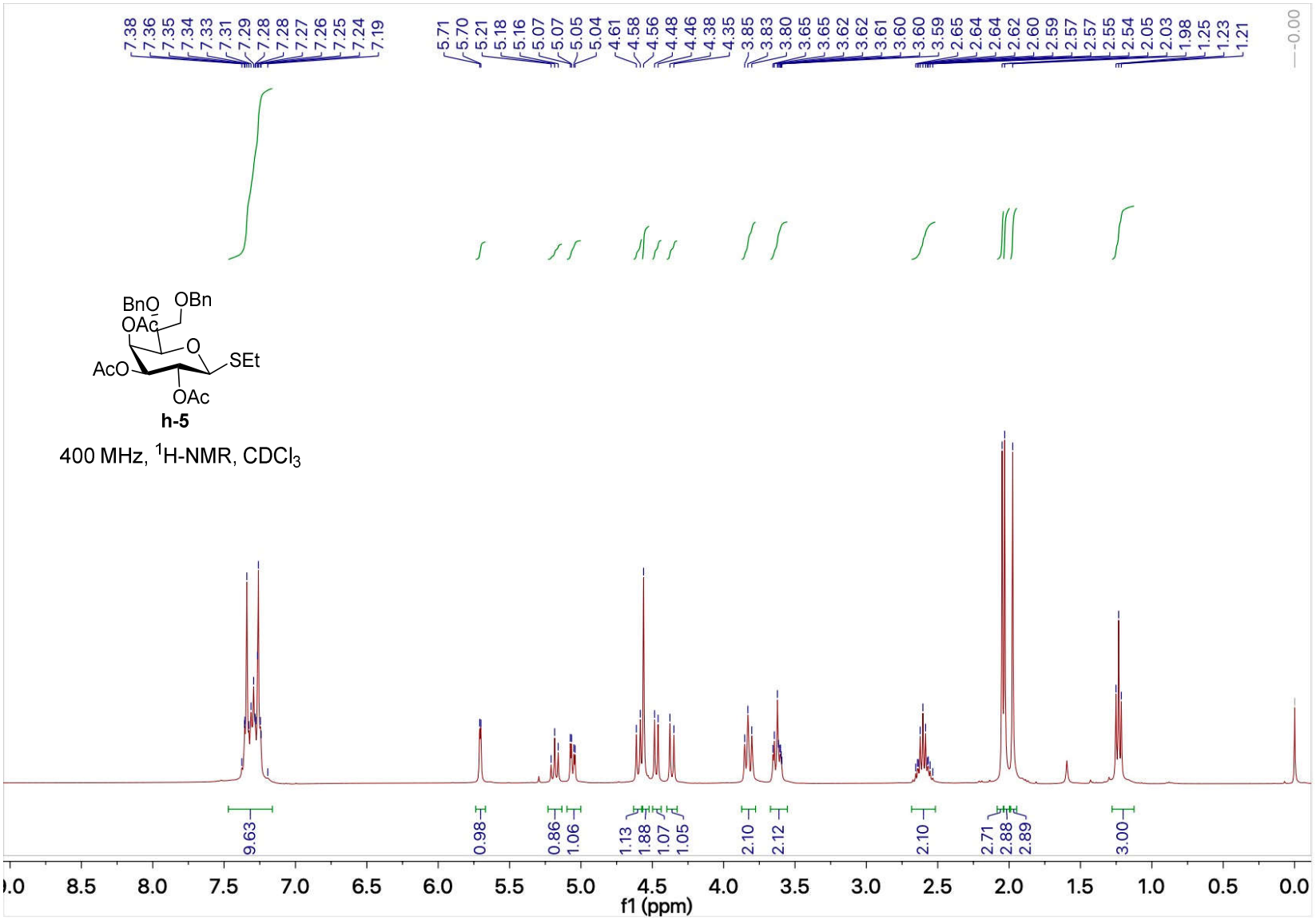

OBn
BnO
Me
OBn OBn
O
BnO
OPMP
OTBS
BnO
OBn
Me
QuinO
13b
gHMQC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

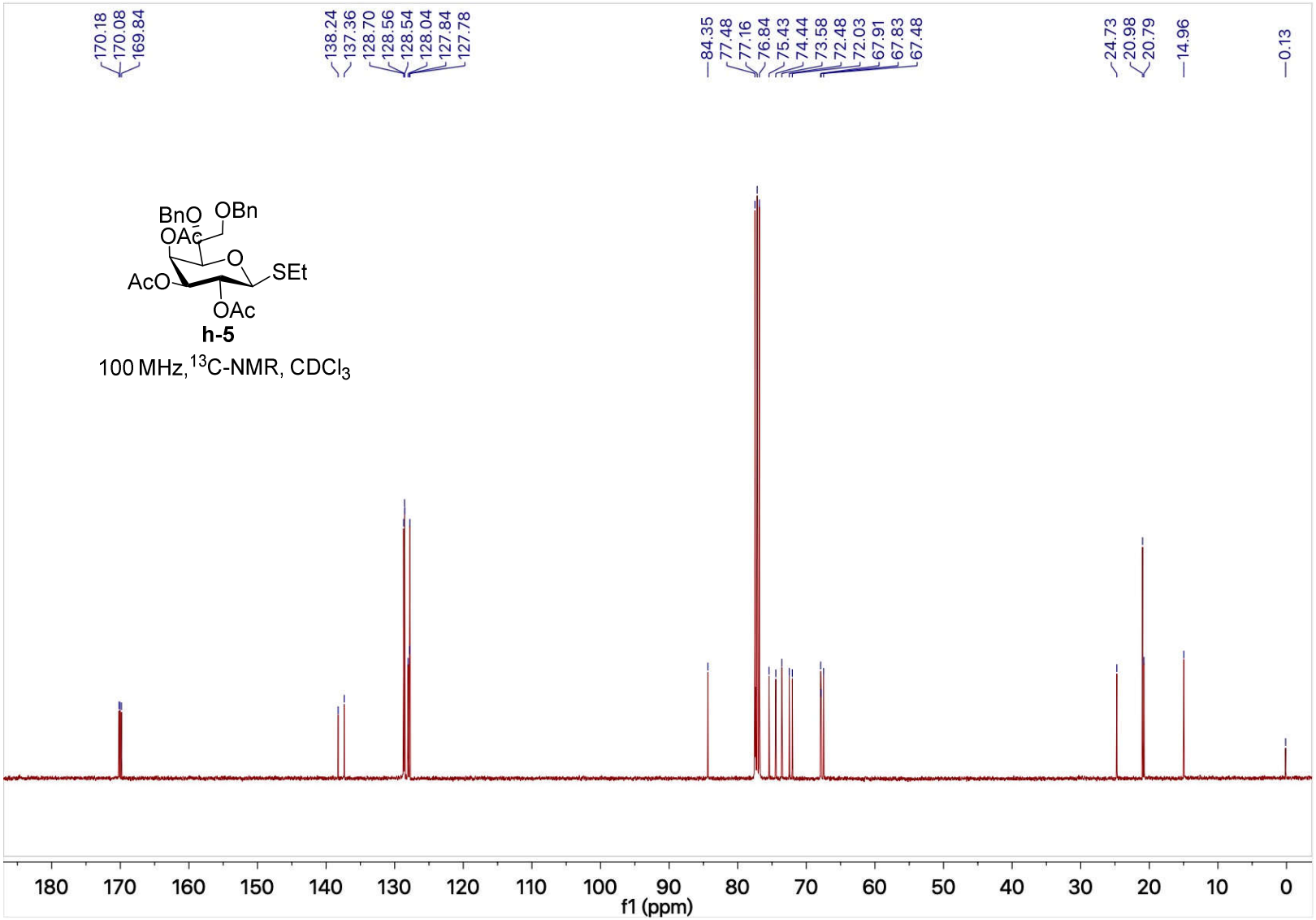

OBn
BnO
Me
OBn OBn
BnO
OPMP
OTBS
BnO
OBn
Me
QuinO
13b
gHMBC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

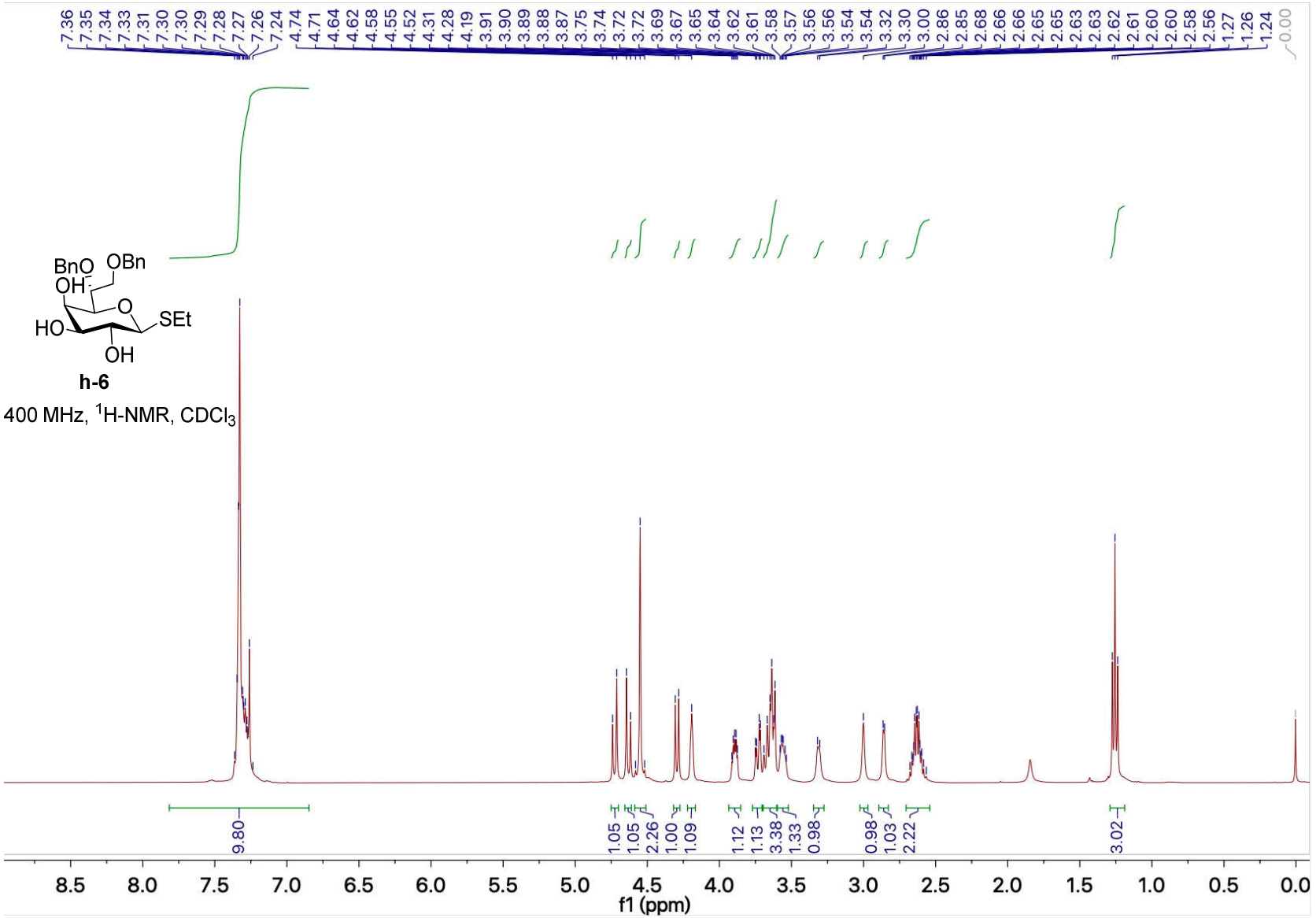

OBn
BnO
Me
O
OBn OBn
O
BnO
OPMP
OBz
BnO
OBn
Me
QuinO
16
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

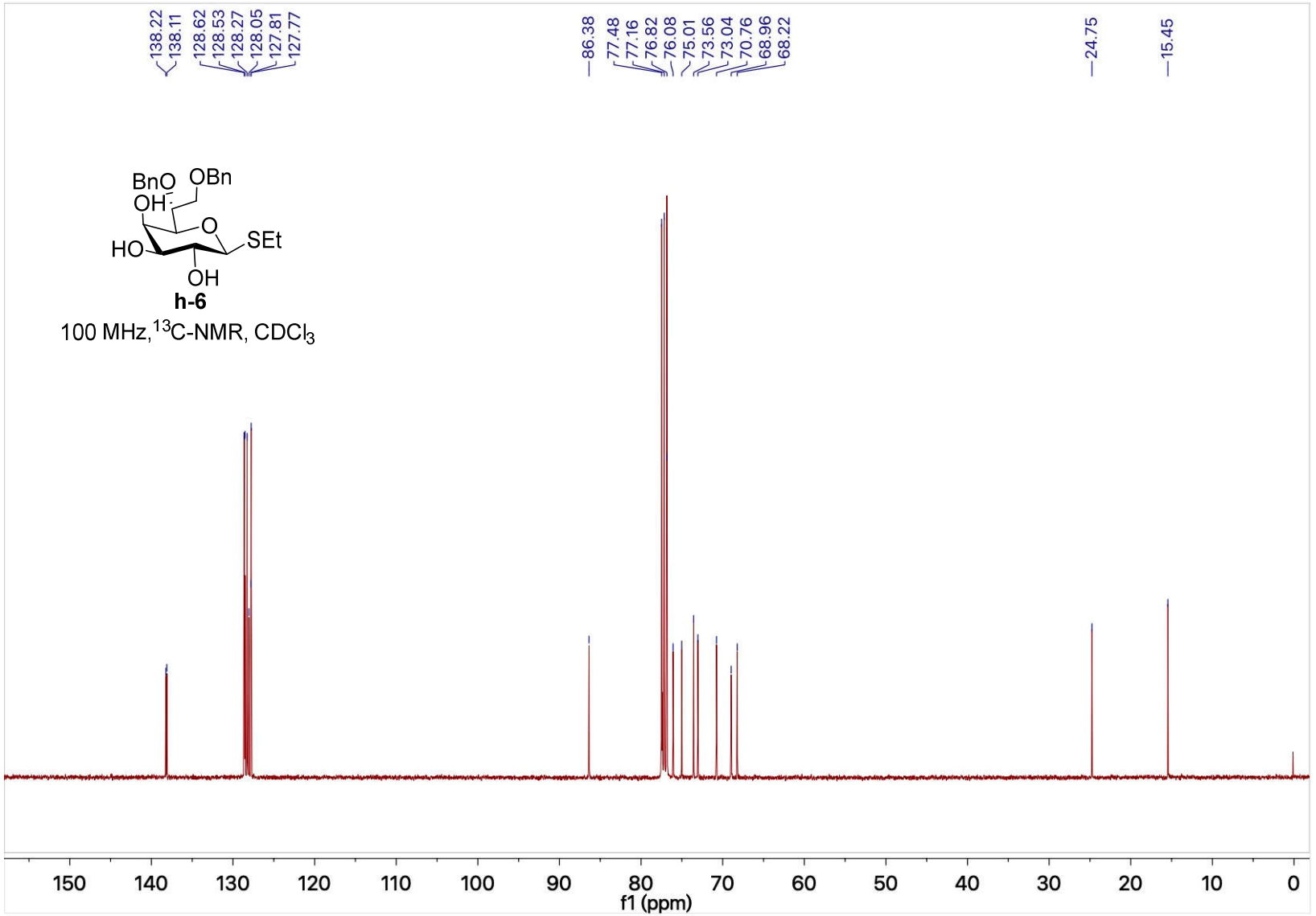

155.09
151.53
147.74
139.51
138.94
138.36
138.32
138.13
137.99
137.56
137.17
132.96
130.95
130.34
130.08
129.98
129.28
128.58
128.48
128.43
128.40
128.36
128.18
128.16
128.06
128.04
127.93
127.83
127.78
127.71
127.62
127.54
127.51
127.44
127.35
127.16
127.06
121.36
117.80
114.46
104.26
100.64
99.32
84.66
84.41
82.25
81.89
81.87
77.71
77.48
77.23
77.16
76.84
76.28
75.46
74.76
73.35
72.60
72.29
72.24
71.99
71.48
71.02
70.69
69.98
55.69
16.14
15.96
OBn
BnO
Me
OBn OBn
BnO
OPMP
OBz
BnO
OBn
Me
QuinO
16
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

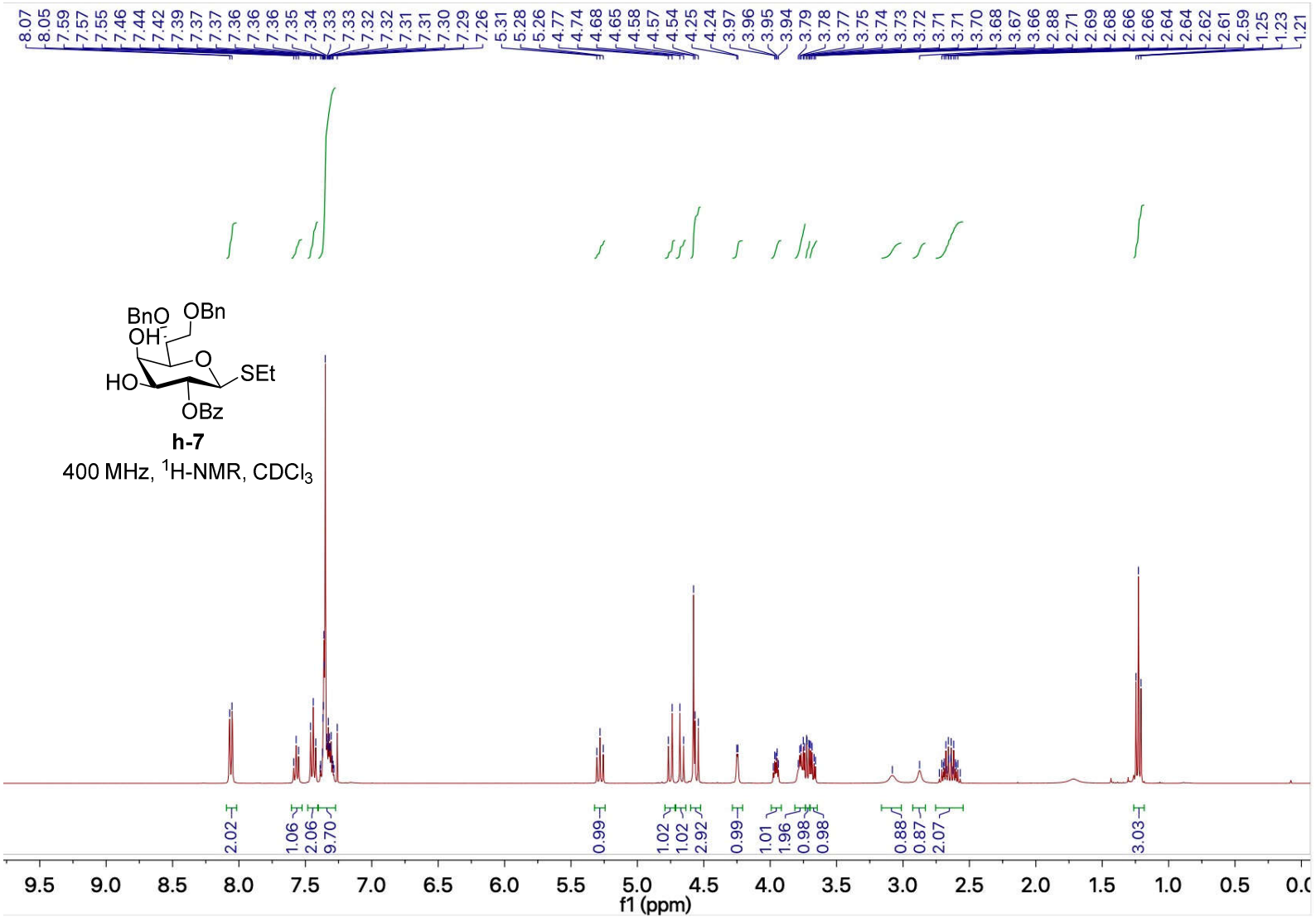

17a
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

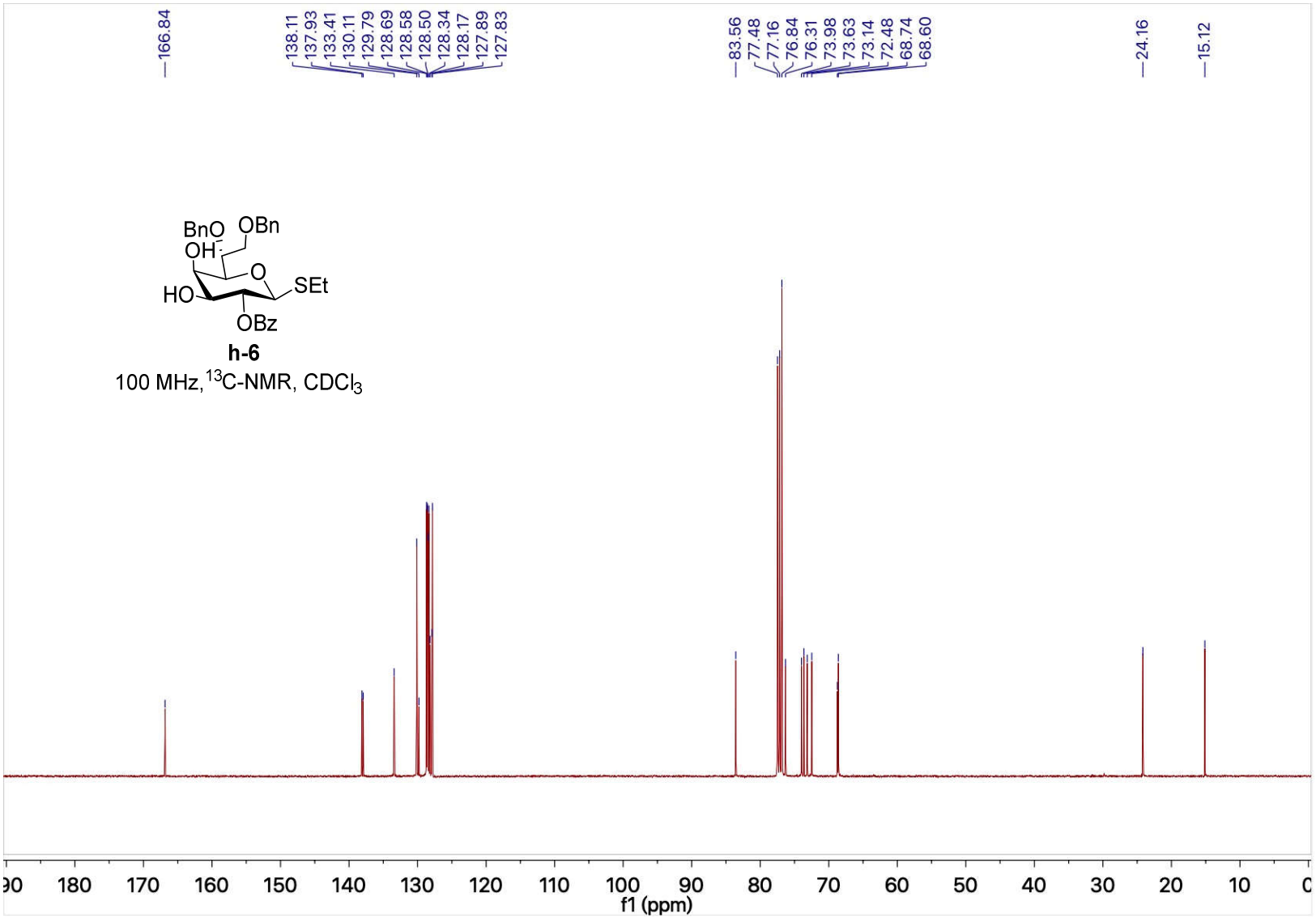

7.38
7.36
7.35
7.34
7.33
7.31
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.19
5.71
5.70
5.21
5.18
5.16
5.07
5.07
5.05
5.04
4.61
4.58
4.56
4.48
4.46
4.38
4.35
3.85
3.83
3.80
3.65
3.65
3.62
3.62
3.61
3.60
3.60
3.59
2.65
2.64
2.64
2.62
2.60
2.59
2.57
2.57
2.55
2.54
2.05
2.03
1.98
1.25
1.23
1.21
0.00
BnO
OBn
OAc
O
AcO
SEt
OAc
h-5
400 MHz, 1H-NMR, CDCl3
9.63
0.98
0.86
1.06
1.13
1.88
1.07
1.05
2.10
2.12
2.10
2.71
2.88
2.89
3.00
f1 (ppm)

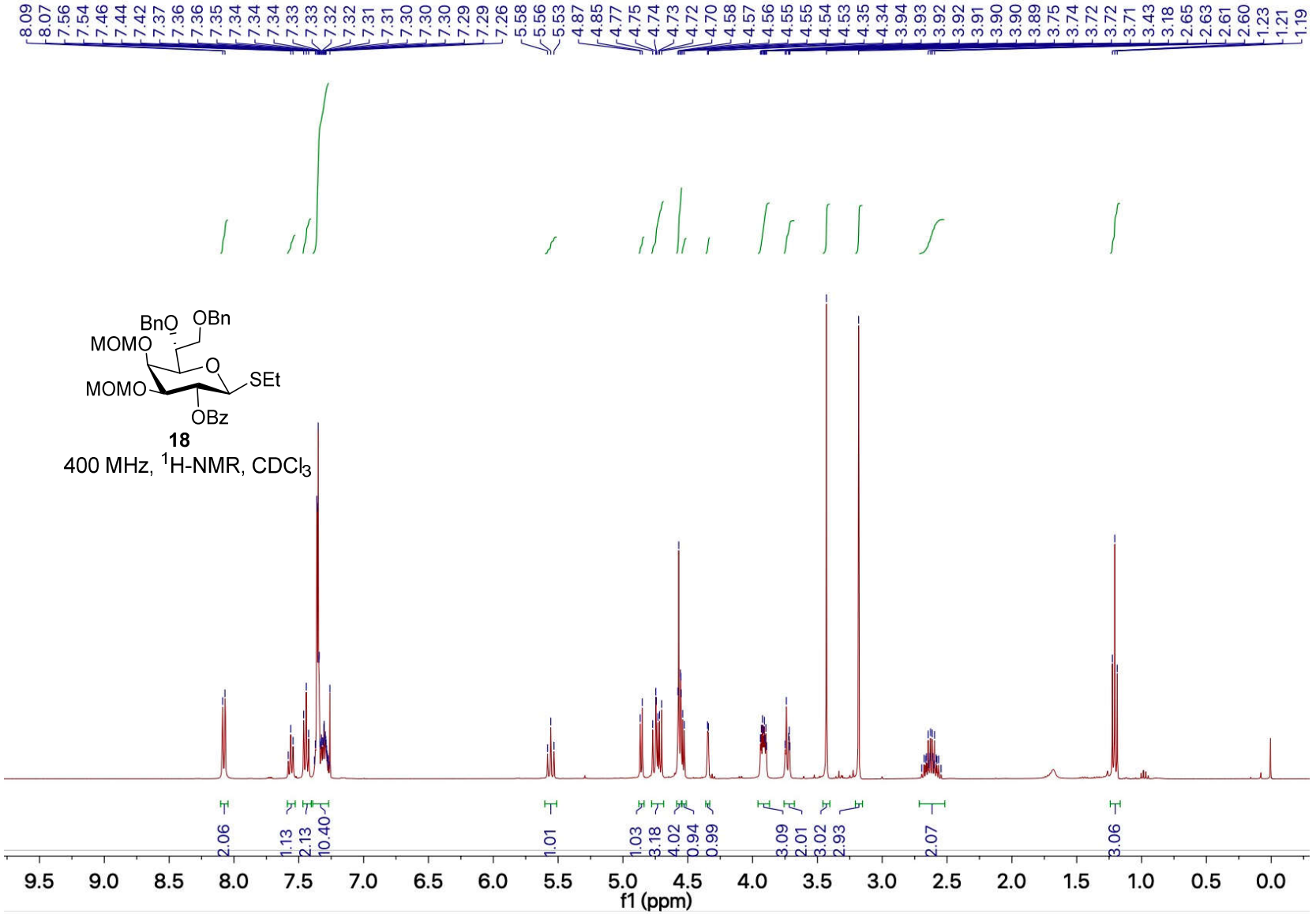

170.18
170.08
169.84
138.24
137.36
128.70
128.56
128.54
128.04
127.84
127.78
84.35
77.48
77.16
76.84
75.43
74.44
73.58
72.48
72.03
67.91
67.83
67.48
24.73
20.98
20.79
14.96
0.13
BnO
OBn
OAc
O
SEt
AcO
OAc
h-5
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

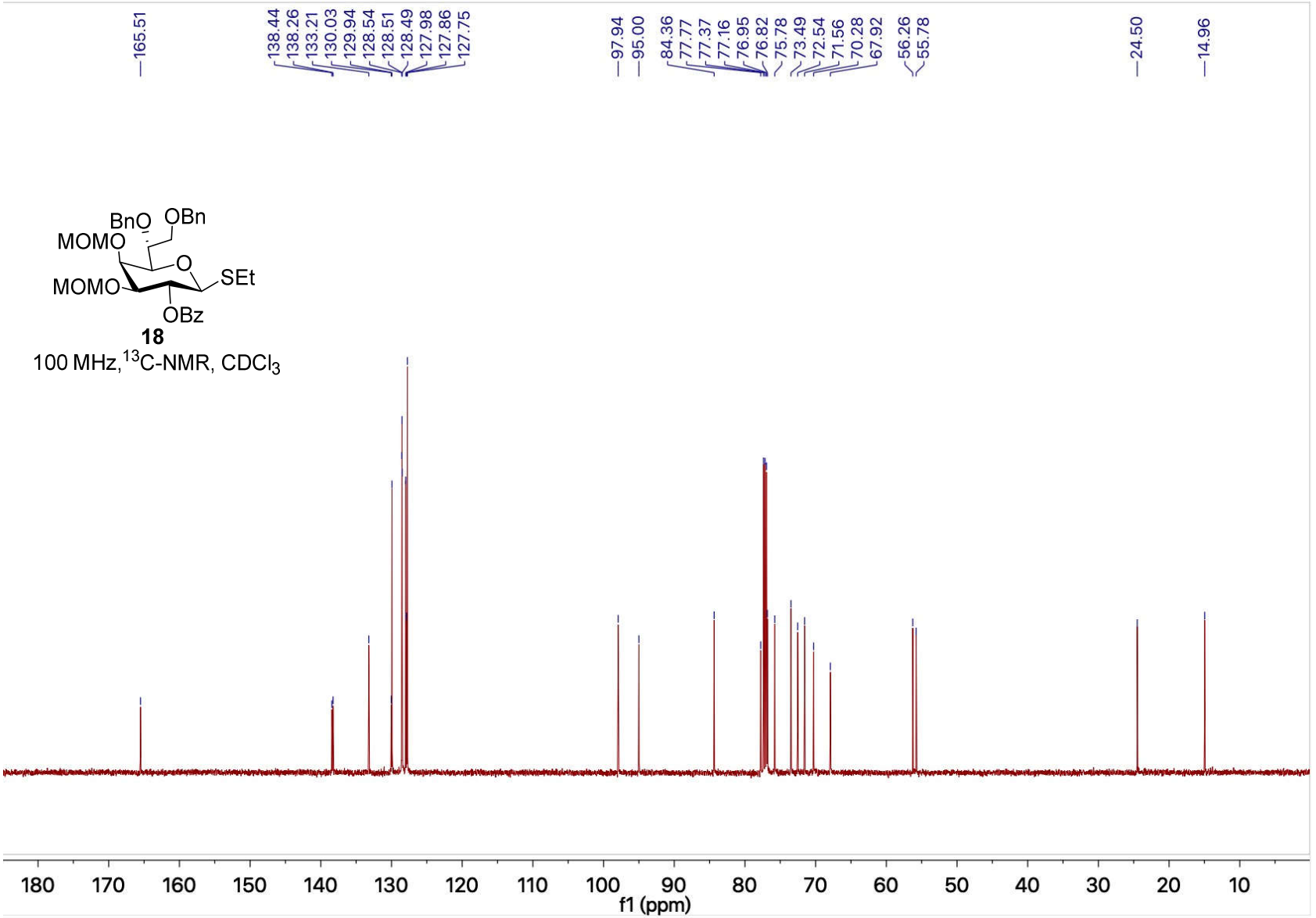

BnO
OBn
OH
O
SEt
HO
OH
h-6
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)


138.22
138.11
128.62
128.53
128.27
128.05
127.81
127.77
86.38
77.48
77.16
76.82
76.08
75.01
73.56
73.04
70.76
68.96
68.22
24.75
15.45
BnO
OBn
OH
O
HO
SEt
OH
h-6
100 MHz, 13C-NMR, CDCl3
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.07 8.05 7.59 7.57 7.55 7.46 7.44 7.42 7.39 7.37 7.37 7.36 7.36 7.36 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.26
5.31 5.28 5.26 4.77 4.74 4.68 4.65 4.58 4.57 4.54 4.25 4.24 3.97 3.96 3.95 3.94 3.79 3.78 3.77 3.75 3.74 3.73 3.72 3.71 3.71 3.70 3.68 3.67 3.66 2.88 2.71 2.69 2.68 2.66 2.66 2.64 2.64 2.62 2.61 2.59 1.25 1.23 1.21
BnO
OBn
OH
O
SEt
HO
OBz
h-7
400 MHz, ^{1}H-NMR, $CDCl_3$
2.02 1.06 2.06 9.70 0.99 1.02 1.02 2.92 0.99 1.01 1.96 0.98 0.98 0.88 0.87 2.07 3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.84
138.11
137.93
133.41
130.11
129.79
128.69
128.58
128.50
128.34
128.17
127.89
127.83
83.56
77.48
77.16
76.84
76.31
73.98
73.63
73.14
72.48
68.74
68.60
24.16
15.12
BnO
OBn
OH
O
SEt
HO
OBz
h-6
100 MHz, 13C-NMR, CDCl3
f1 (ppm)


8.09 8.07 7.56 7.54 7.46 7.44 7.42 7.37 7.36 7.36 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.26 5.58 5.56 5.53 4.87 4.85 4.77 4.75 4.74 4.73 4.72 4.70 4.58 4.57 4.56 4.55 4.55 4.54 4.53 4.35 4.34 3.94 3.93 3.92 3.92 3.91 3.90 3.90 3.89 3.75 3.74 3.72 3.72 3.71 3.43 3.18 2.65 2.63 2.61 2.60 1.23 1.21 1.19
BnO
OBn
MOMO
O
SEt
MOMO
OBz
18
400 MHz, 1H-NMR, CDCl3
2.06 1.13 2.13 10.40 1.01 1.03 3.18 4.02 0.94 0.99 3.09 2.01 3.02 2.93 2.07 3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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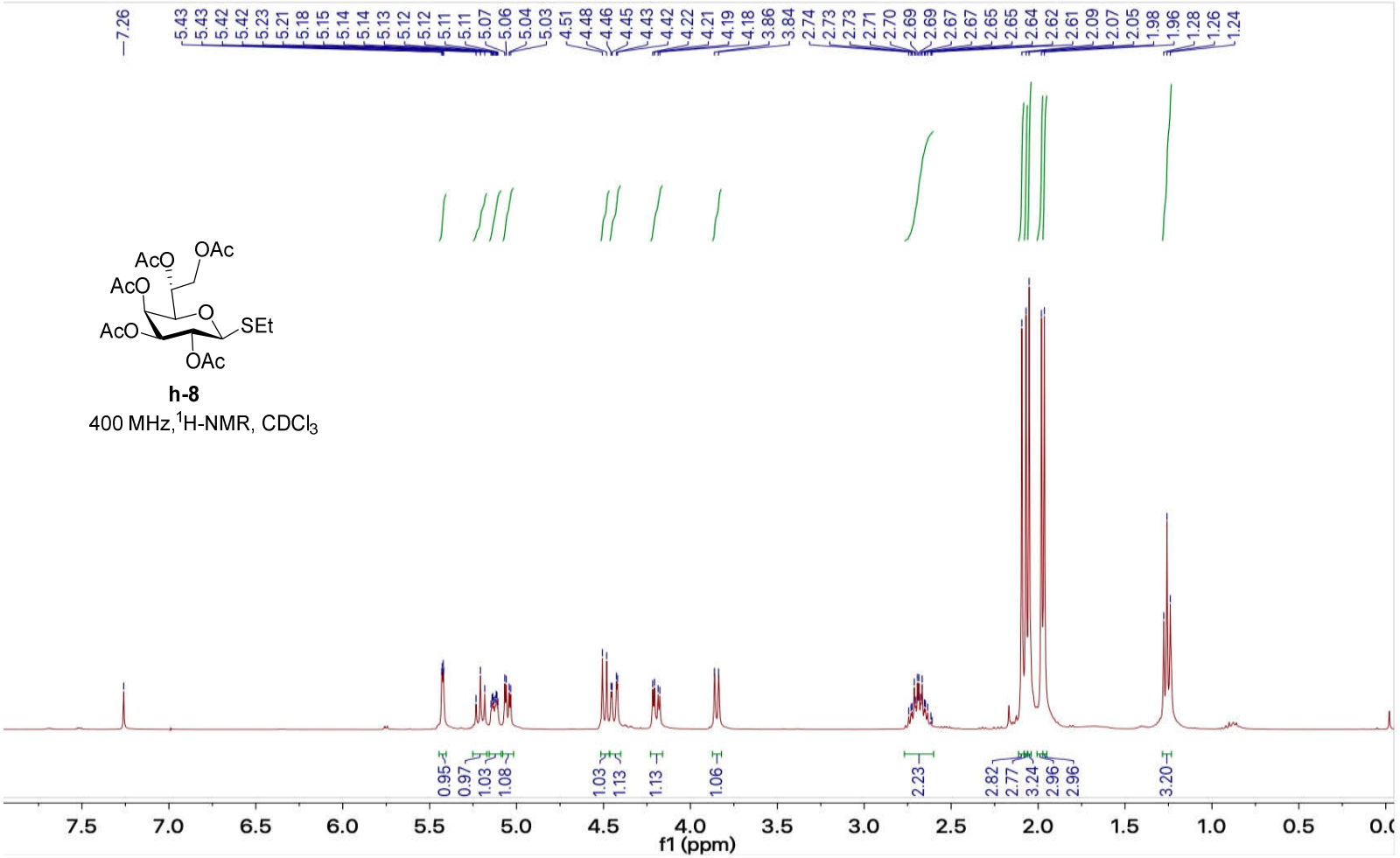
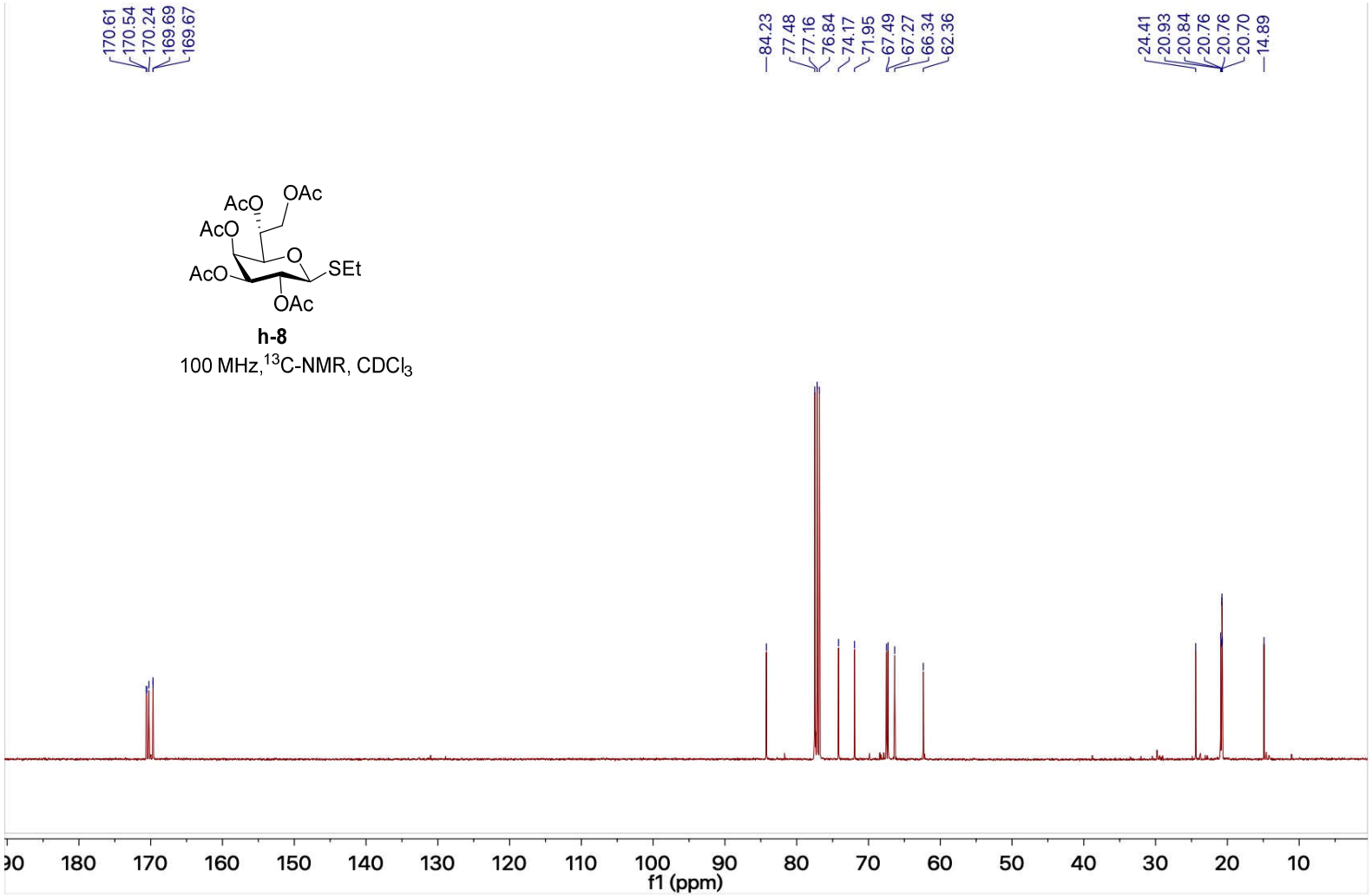
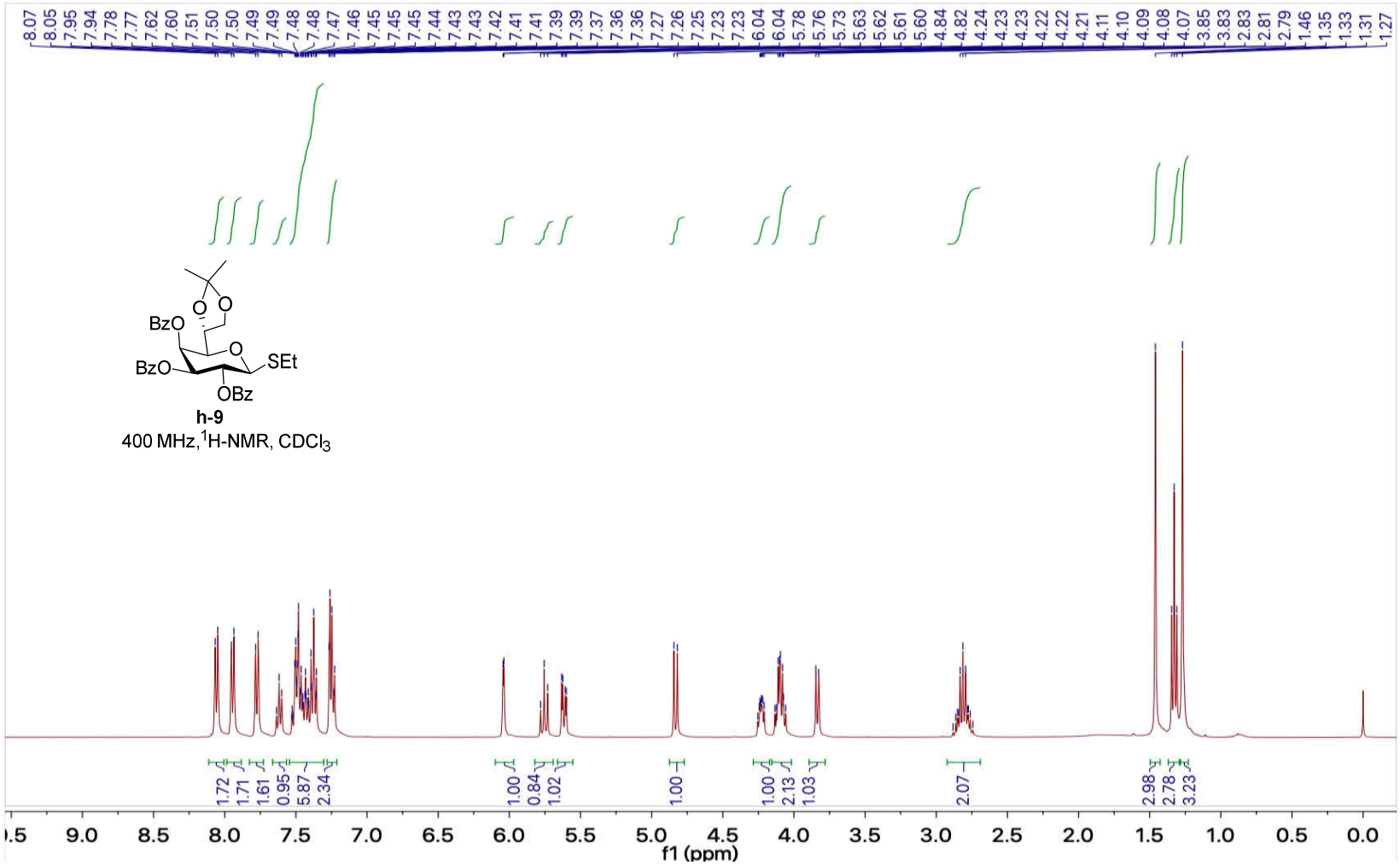
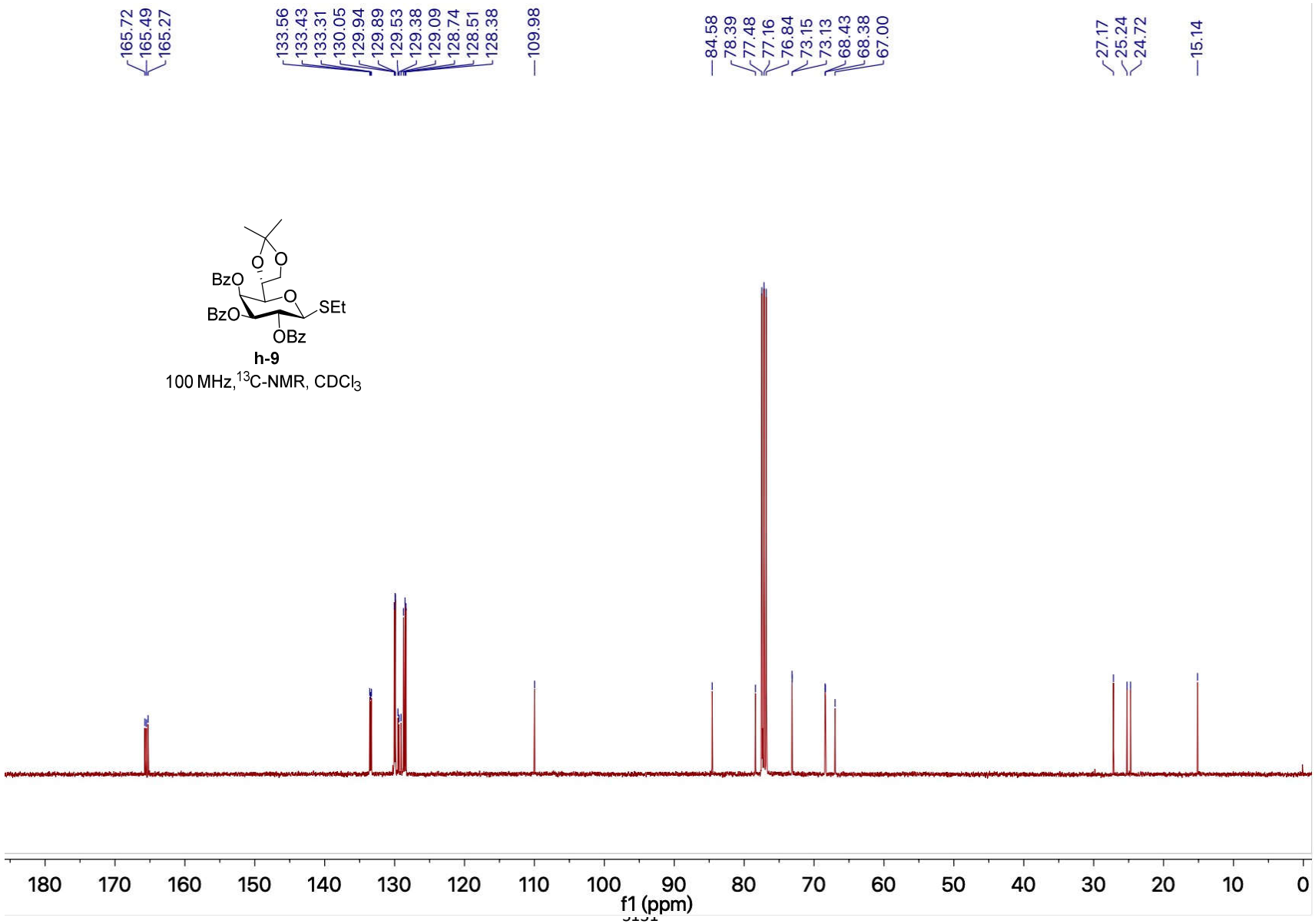
138.44
138.26
133.21
130.03
129.94
128.54
128.51
128.49
127.98
127.86
127.75
97.94
95.00
84.36
77.77
77.37
77.16
76.95
76.82
75.78
73.49
72.54
71.56
70.28
67.92
56.26
55.78
24.50
14.96
BnO
OBn
MOMO
O
SEt
MOMO
OBz
18
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


AcO
OAc
AcO
O
AcO
SEt
OAc
h-8
400 MHz, 1H-NMR, CDCl3
f1 (ppm)


170.61
170.54
170.24
169.69
169.67
84.23
77.48
77.16
76.84
74.17
71.95
67.49
67.27
66.34
62.36
24.41
20.93
20.84
20.76
20.76
20.70
14.89
AcO
OAc
AcO
O
AcO
SEt
OAc
h-8
100 MHz, 13C-NMR, CDCl3
f1 (ppm)


BzO
BzO
OBz
SEt
h-9
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)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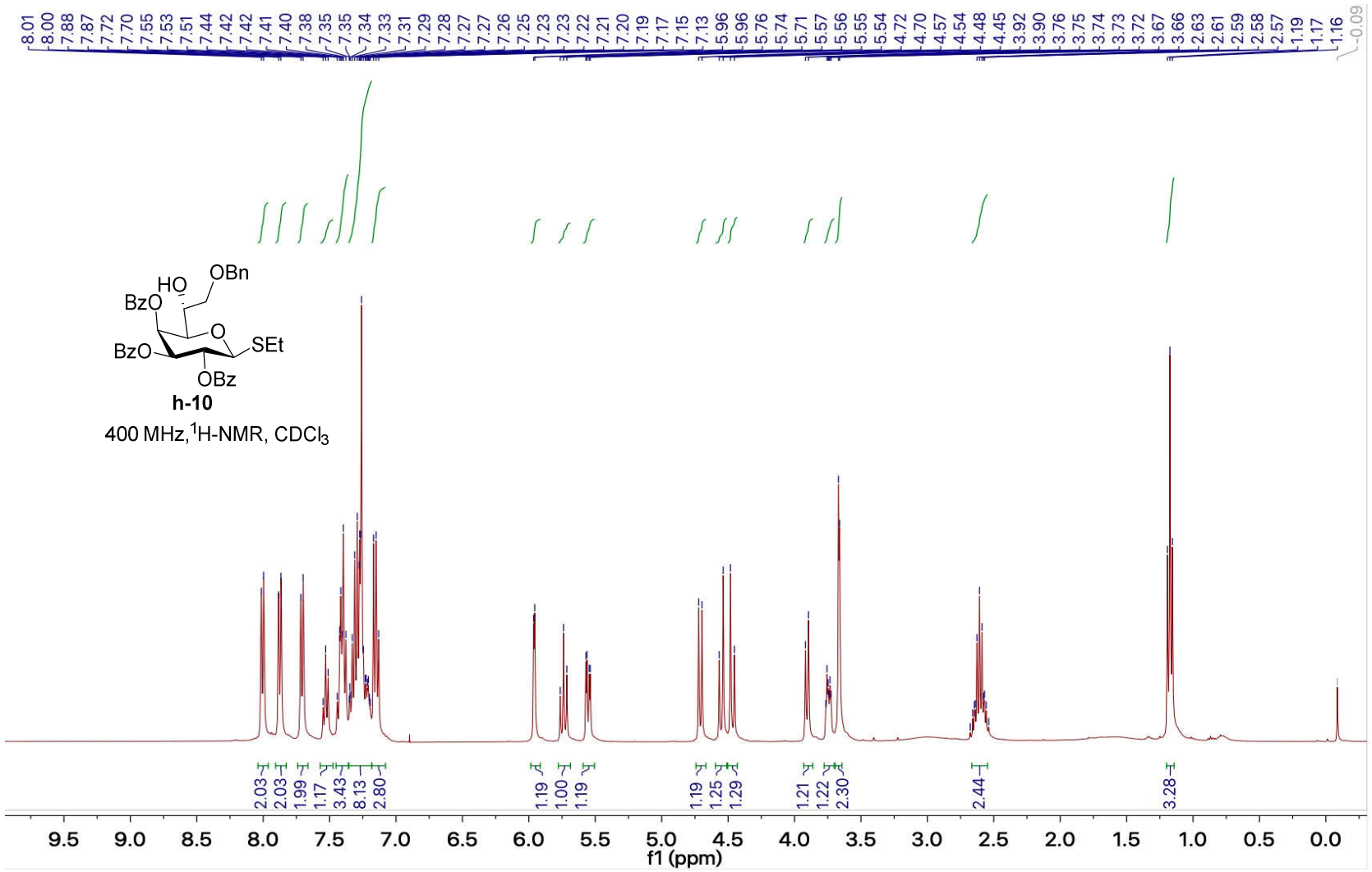
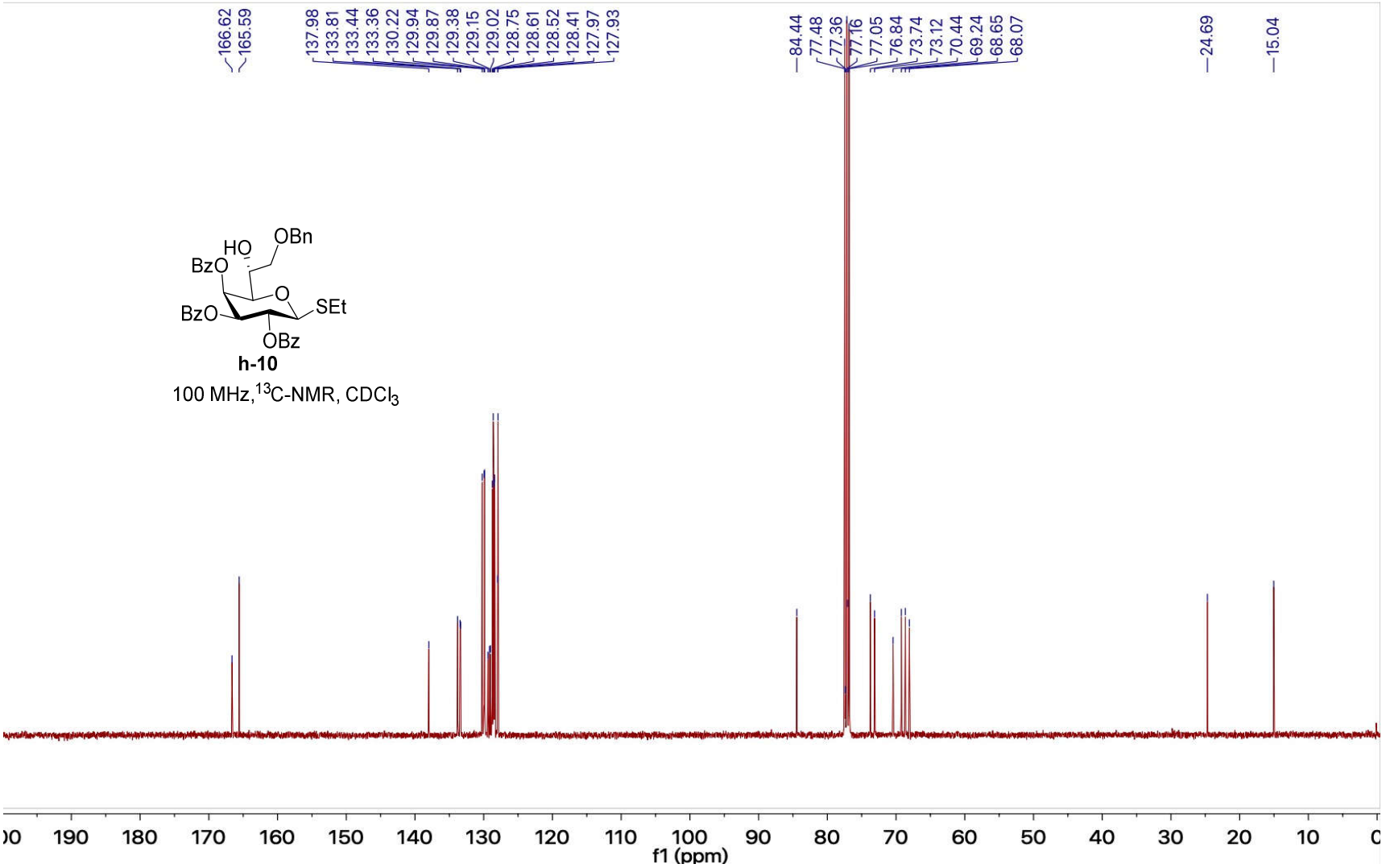
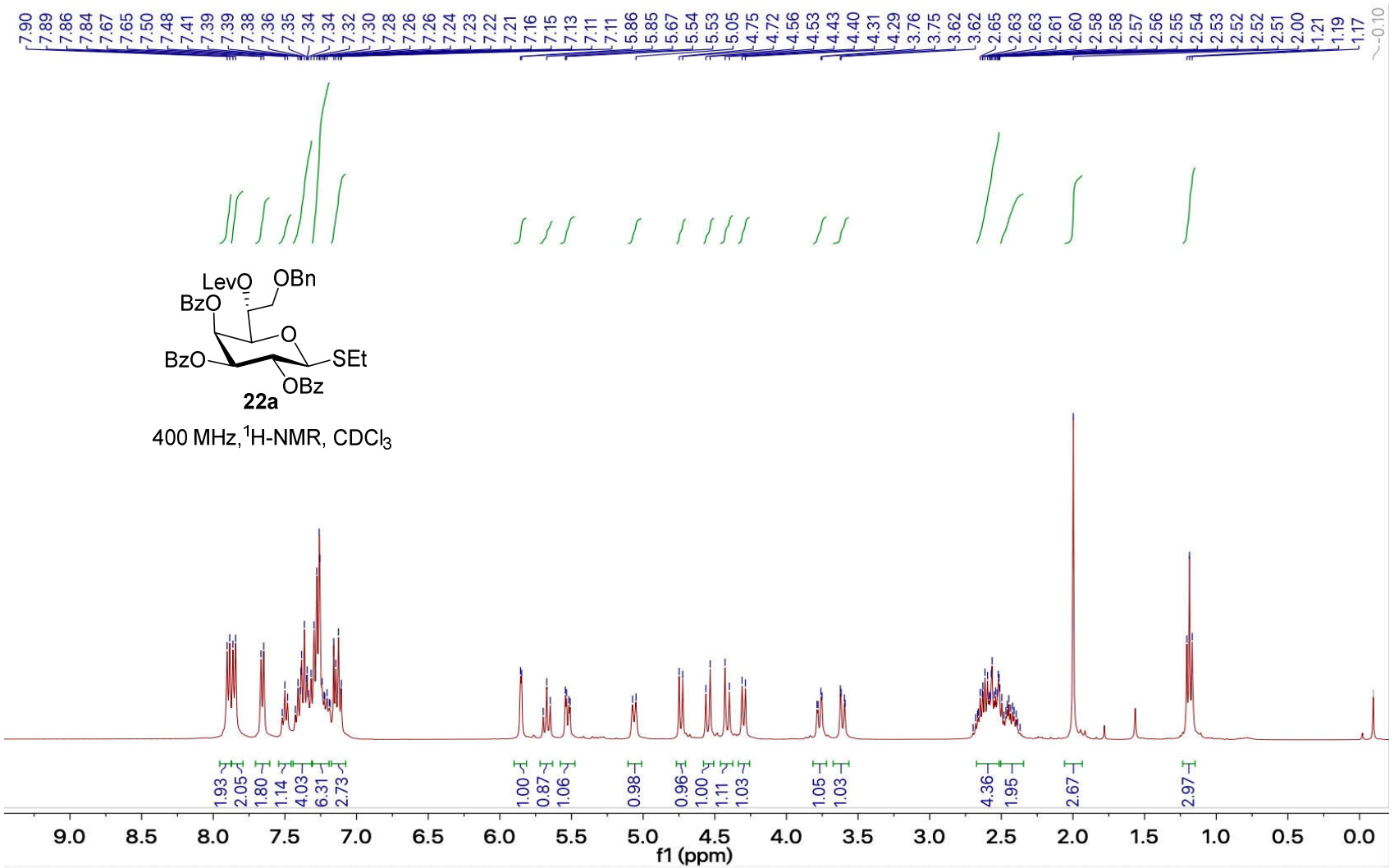
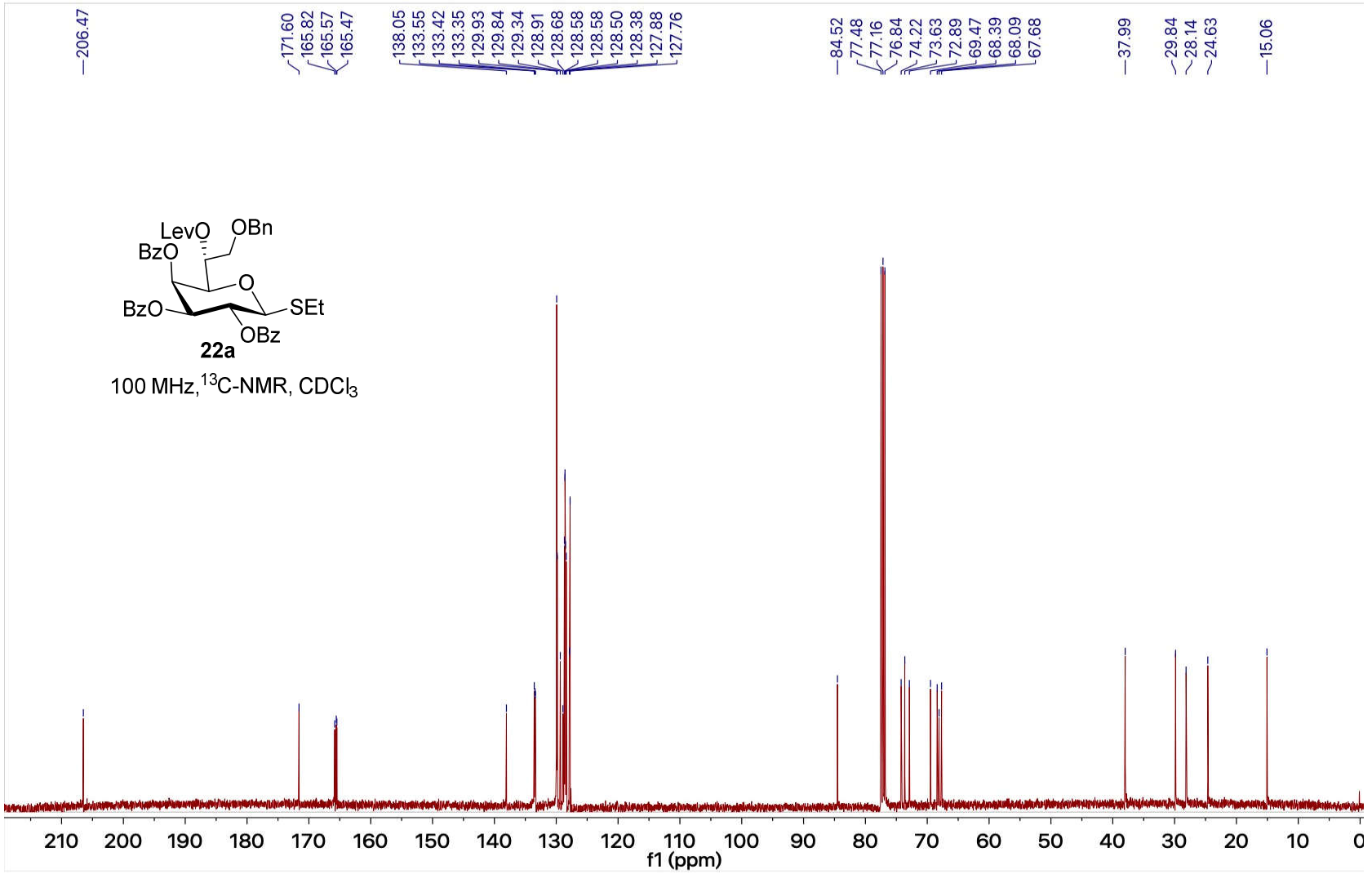
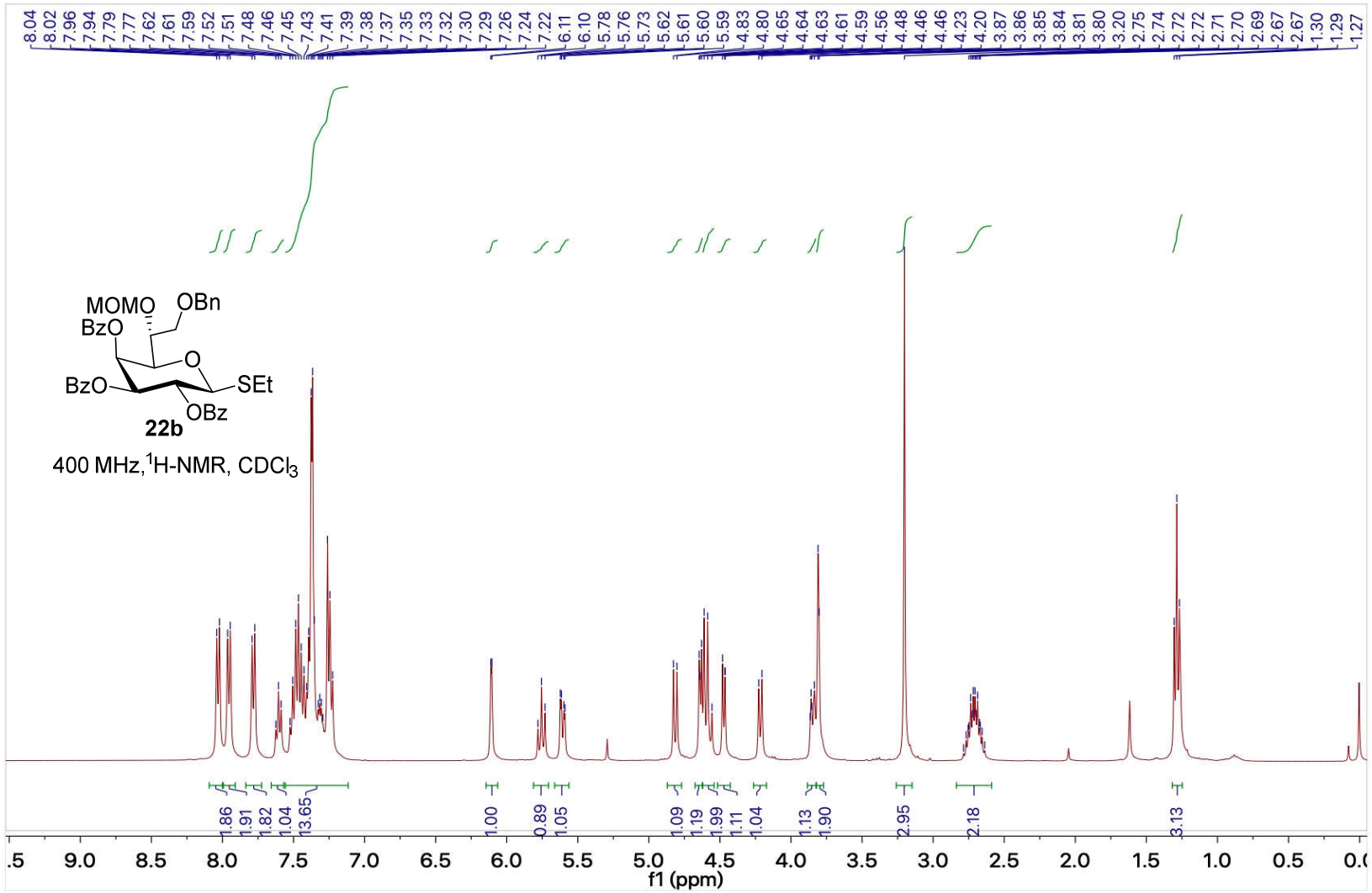
165.49
165.27
133.56
133.43
133.31
130.05
129.94
129.89
129.53
129.38
129.09
128.74
128.51
128.38
109.98
84.58
78.39
77.48
77.16
76.84
73.15
73.13
68.43
68.38
67.00
27.17
25.24
24.72
15.14
BzO
BzO
OBz
SEt
h-9
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

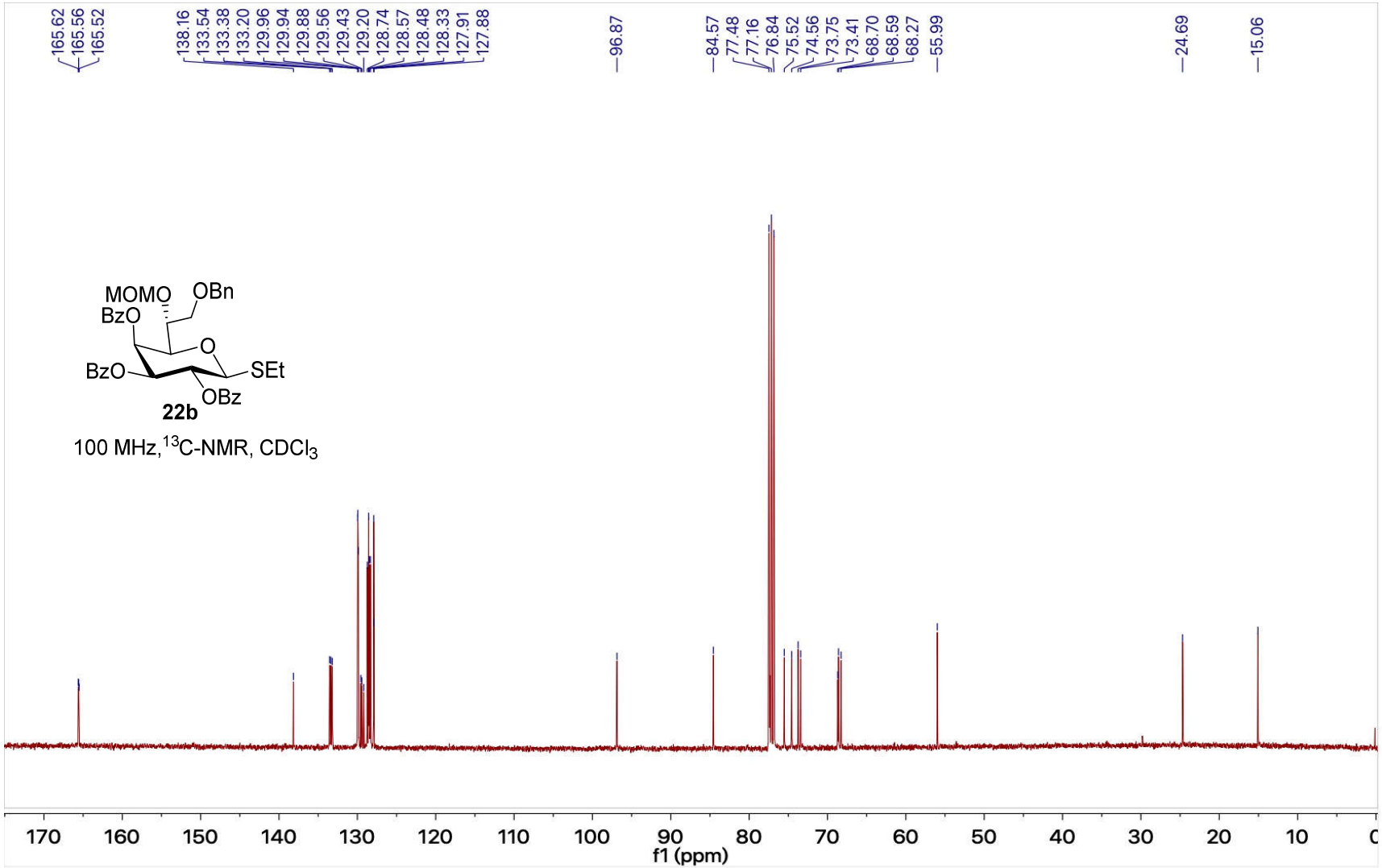

HO
OBn
BzO
O
SEt
BzO
OBz
h-10
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

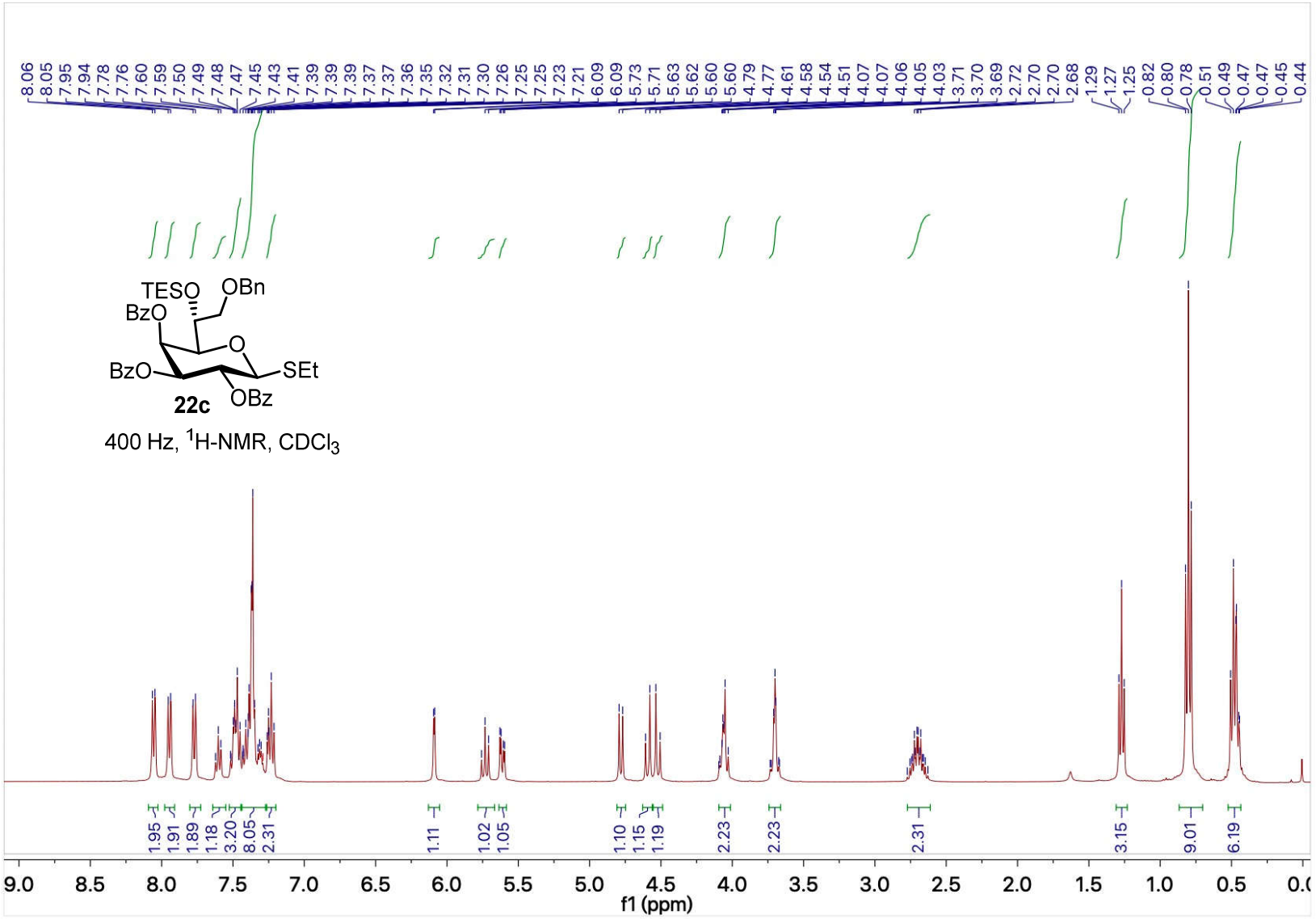

166.62
165.59
137.98
133.81
133.44
133.36
130.22
129.94
129.87
129.38
129.15
129.02
128.75
128.61
128.52
128.41
127.97
127.93
84.44
77.48
77.36
77.16
77.05
76.84
73.74
73.12
70.44
69.24
68.65
68.07
24.69
15.04
HO
OBn
BzO
O
SEt
BzO
OBz
h-10
100 MHz, 13C-NMR, CDCl3
f1 (ppm)

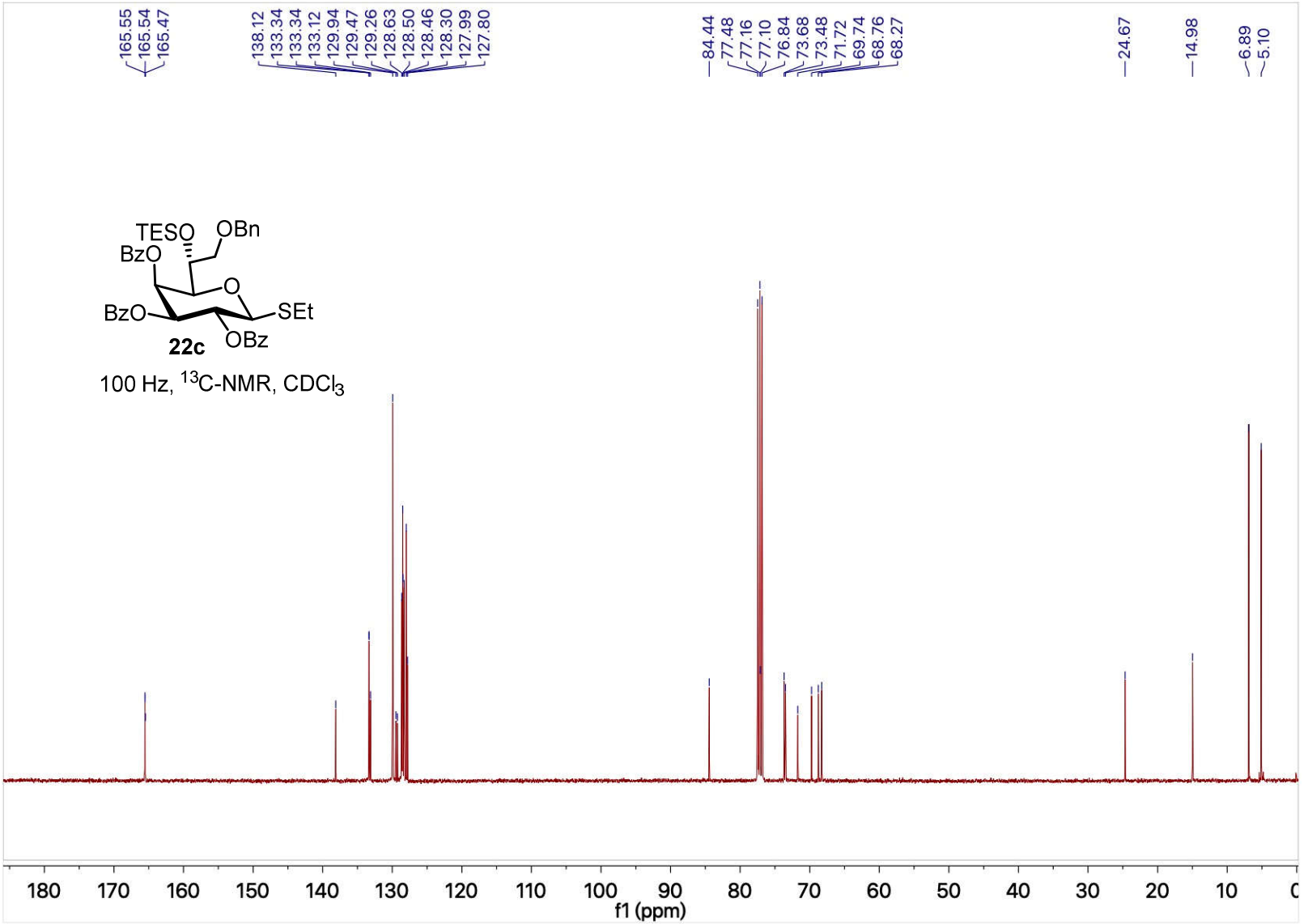

LevO
OBn
BzO
O
BzO
SEt
OBz
22a
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

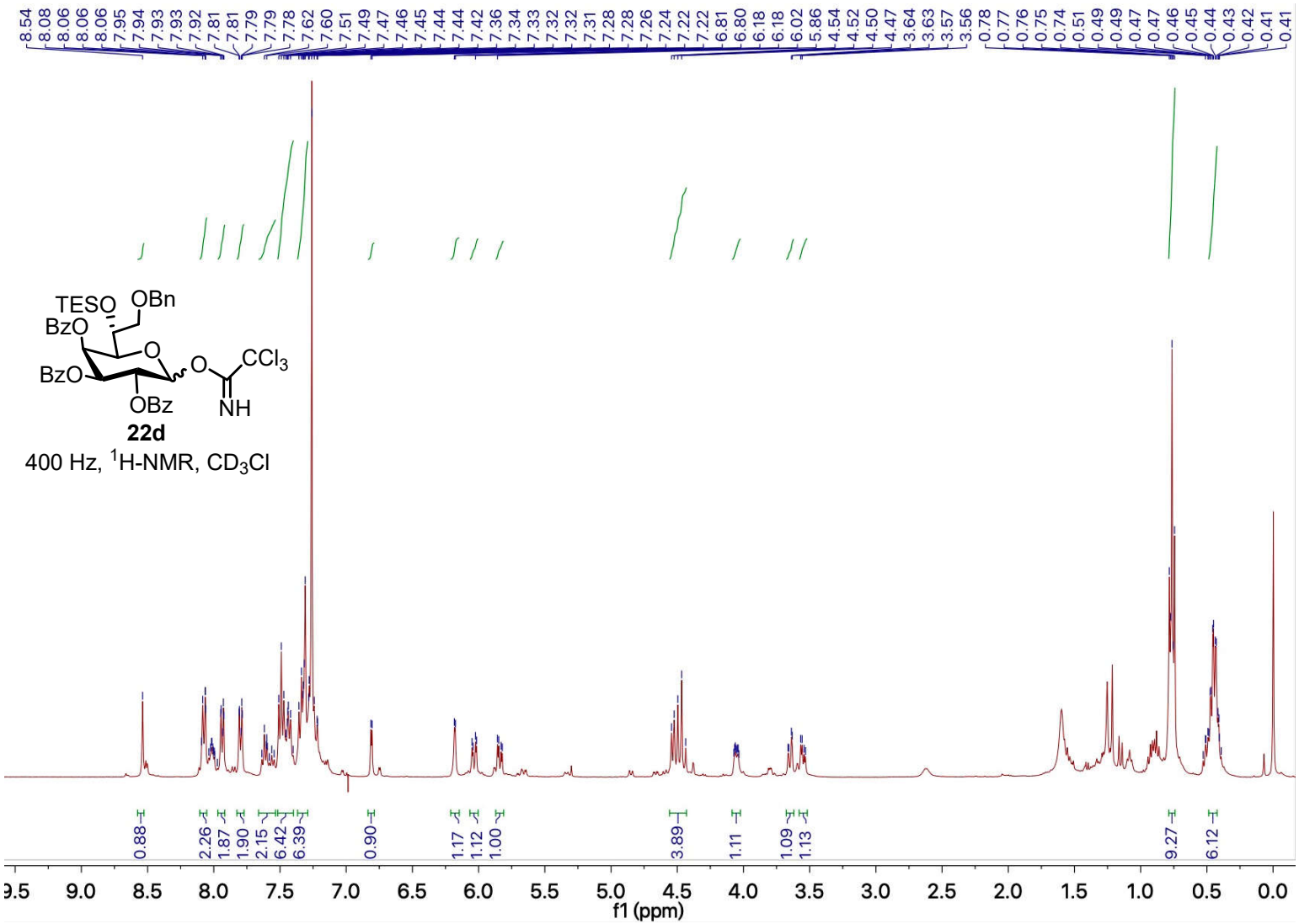

206.47
171.60
165.82
165.57
165.47
138.05
133.55
133.42
133.35
129.93
129.84
129.34
128.91
128.68
128.58
128.58
128.50
128.38
127.88
127.76
84.52
77.48
77.16
76.84
74.22
73.63
72.89
69.47
68.39
68.09
67.68
37.99
29.84
28.14
24.63
15.06
LevO
OBn
BzO
O
BzO
SEt
OBz
22a
100 MHz, 13C-NMR, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

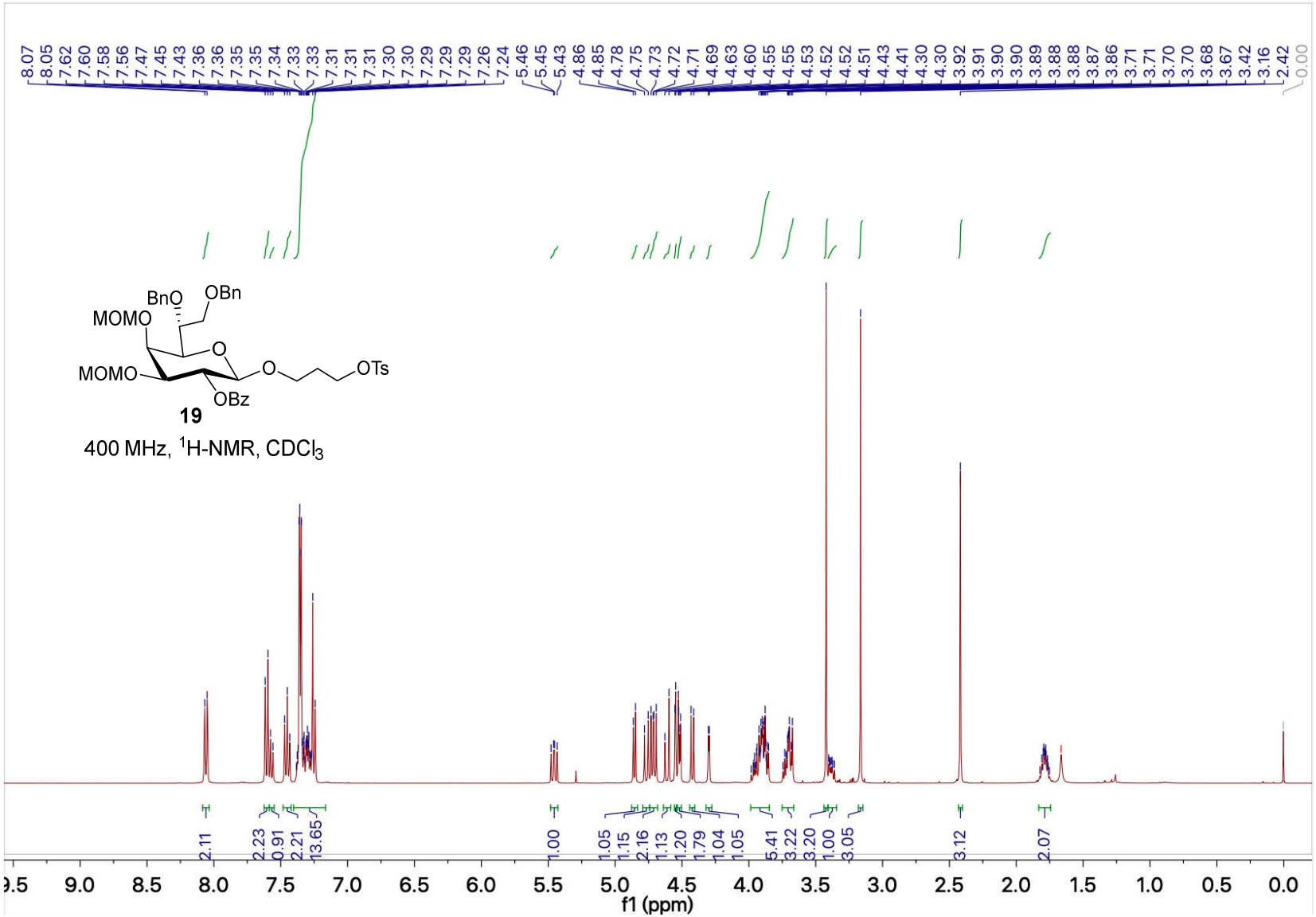

MOMO
OBn
BzO
O
BzO
SEt
OBz
22b
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

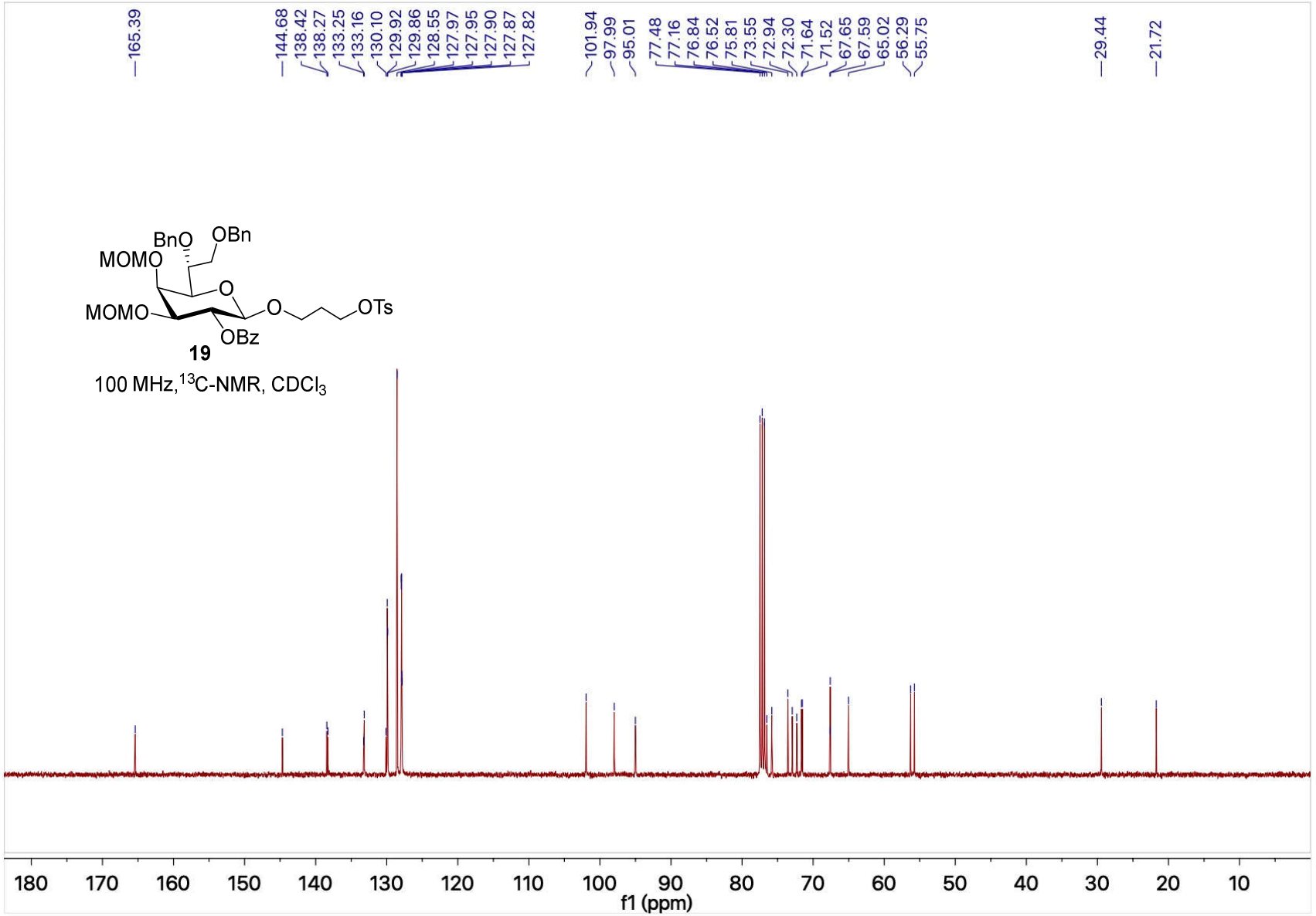

165.62
165.56
165.52
138.16
133.54
133.38
133.20
129.96
129.94
129.88
129.56
129.43
129.20
128.74
128.57
128.48
128.33
127.91
127.88
96.87
84.57
77.48
77.16
76.84
75.52
74.56
73.75
73.41
68.70
68.59
68.27
55.99
24.69
15.06
MOMO
OBn
BzO
O
BzO
SEt
OBz
22b
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

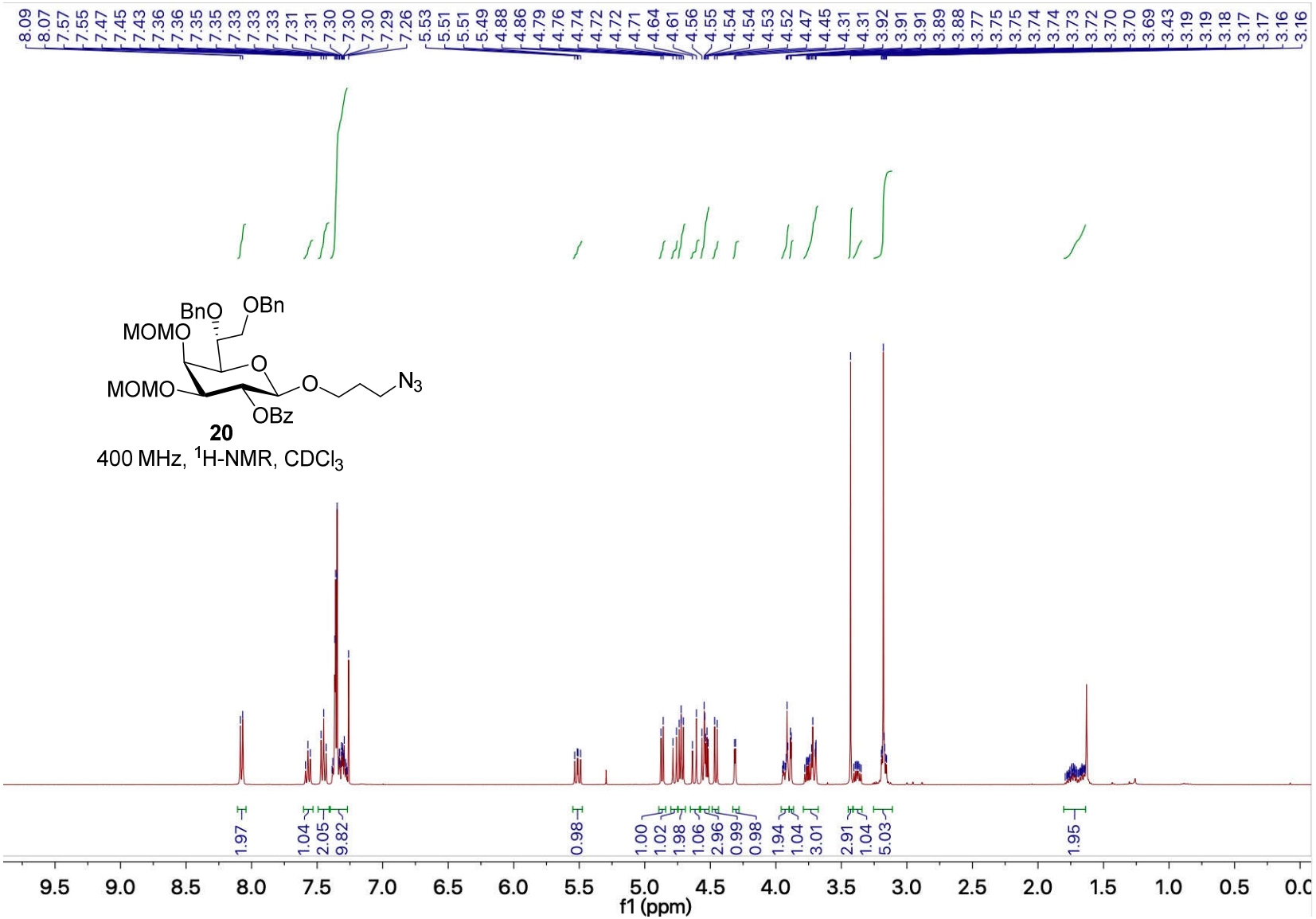

TESO
OBn
BzO
O
BzO
SEt
OBz
22c
400 Hz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

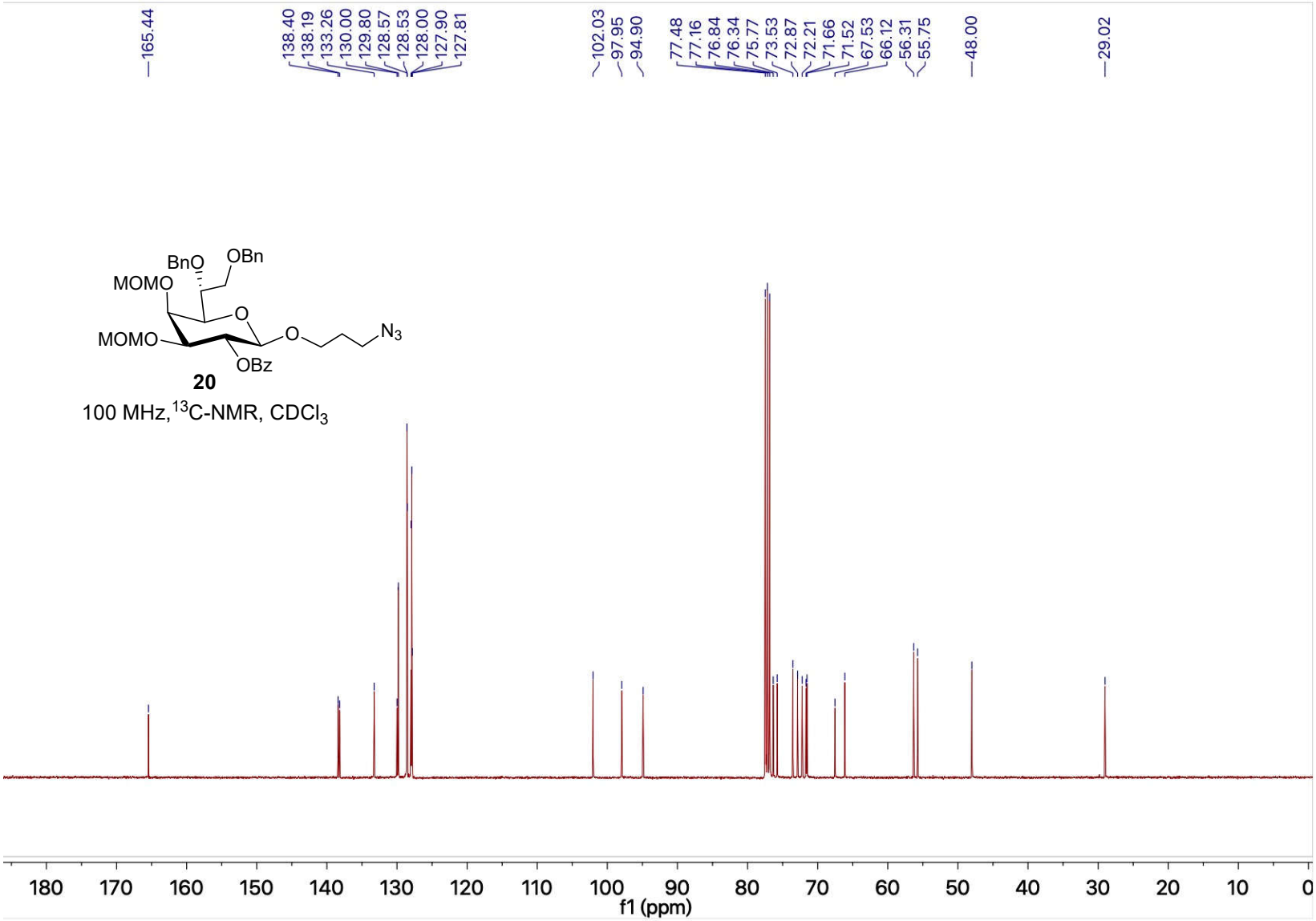

165.55
165.54
165.47
138.12
133.34
133.34
133.12
129.94
129.47
129.26
128.63
128.50
128.46
128.30
127.99
127.80
84.44
77.48
77.16
77.10
76.84
73.68
73.48
71.72
69.74
68.76
68.27
24.67
14.98
6.89
5.10
TESO
OBn
BzO
O
BzO
SEt
OBz
22c
100 Hz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


TESO
OBn
BzO
O
O
CCl3
BzO
OBz
NH
22d
400 Hz, 1H-NMR, CD3Cl
f1 (ppm)


BnO
OBn
MOMO
O
MOMO
O
OTs
OBz
19
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)


165.39
144.68
138.42
138.27
133.25
133.16
130.10
129.92
129.86
128.55
127.97
127.95
127.90
127.87
127.82
101.94
97.99
95.01
77.48
77.16
76.84
76.52
75.81
73.55
72.94
72.30
71.64
71.52
67.65
67.59
65.02
56.29
55.75
29.44
21.72
BnO
OBn
MOMO
O
MOMO
O
OTs
OBz
19
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


BnO
OBn
MOMO
O
MOMO
O
N3
OBz
20
400 MHz, 1H-NMR, CDCl3
f1 (ppm)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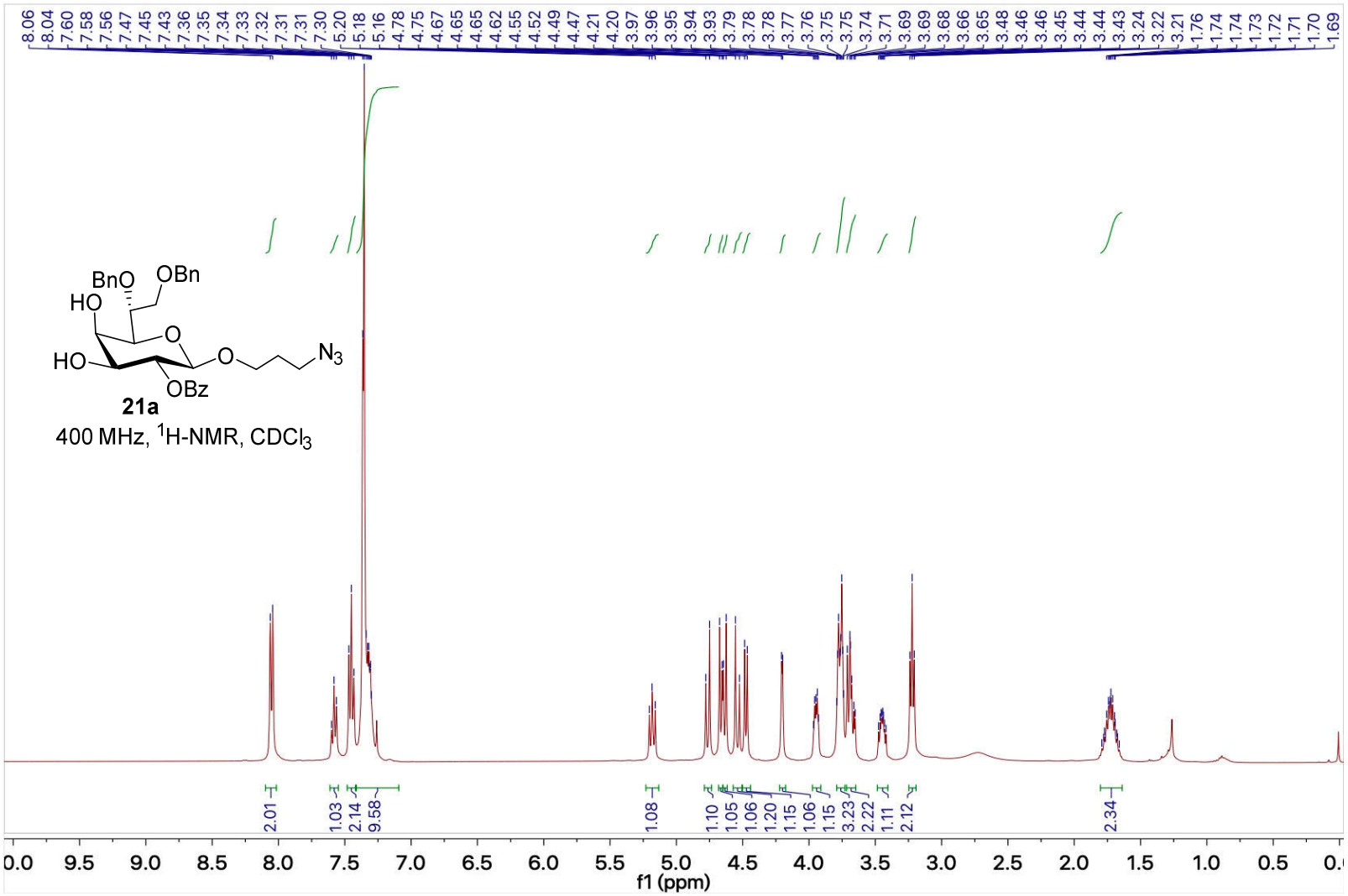
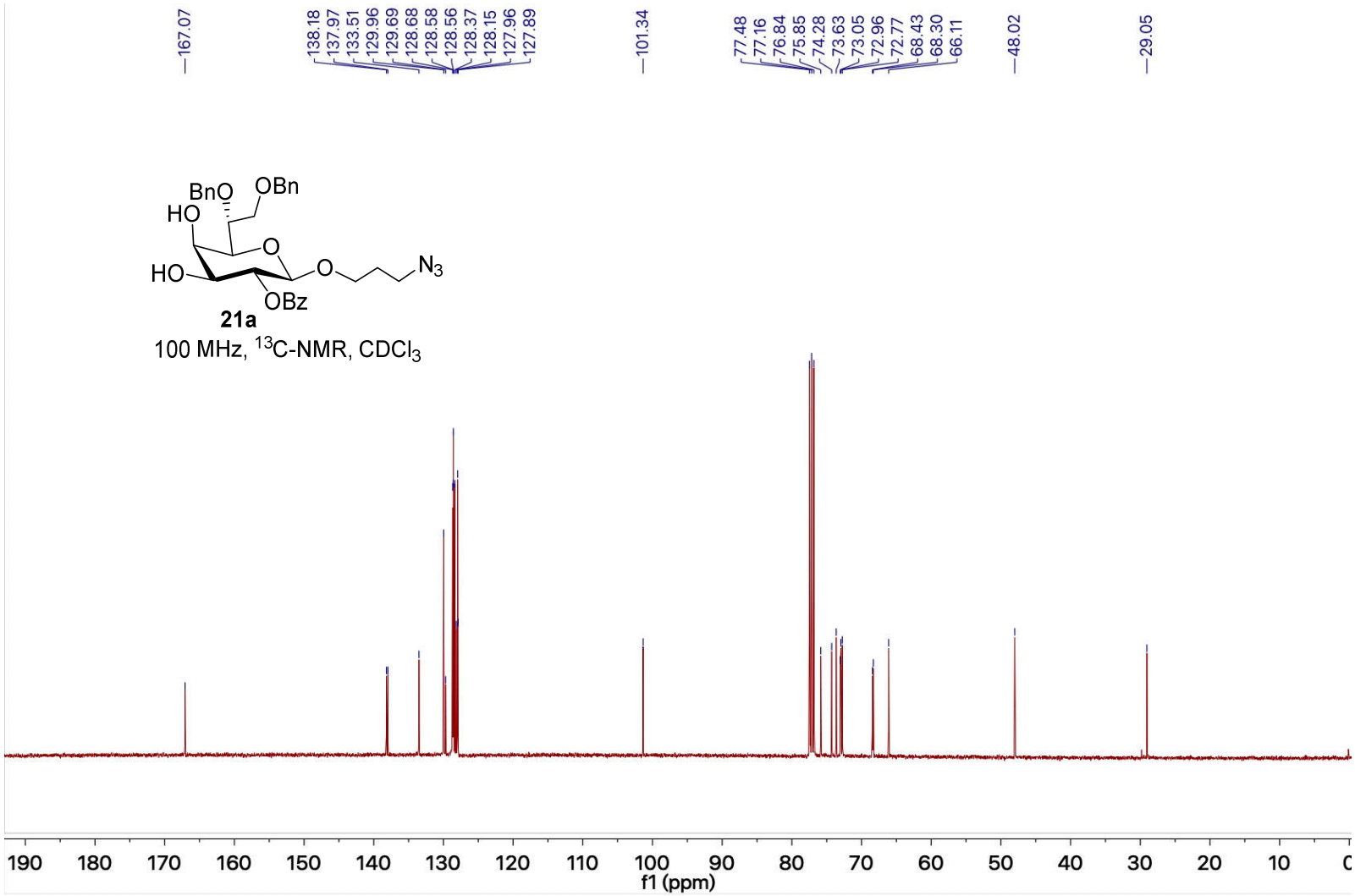
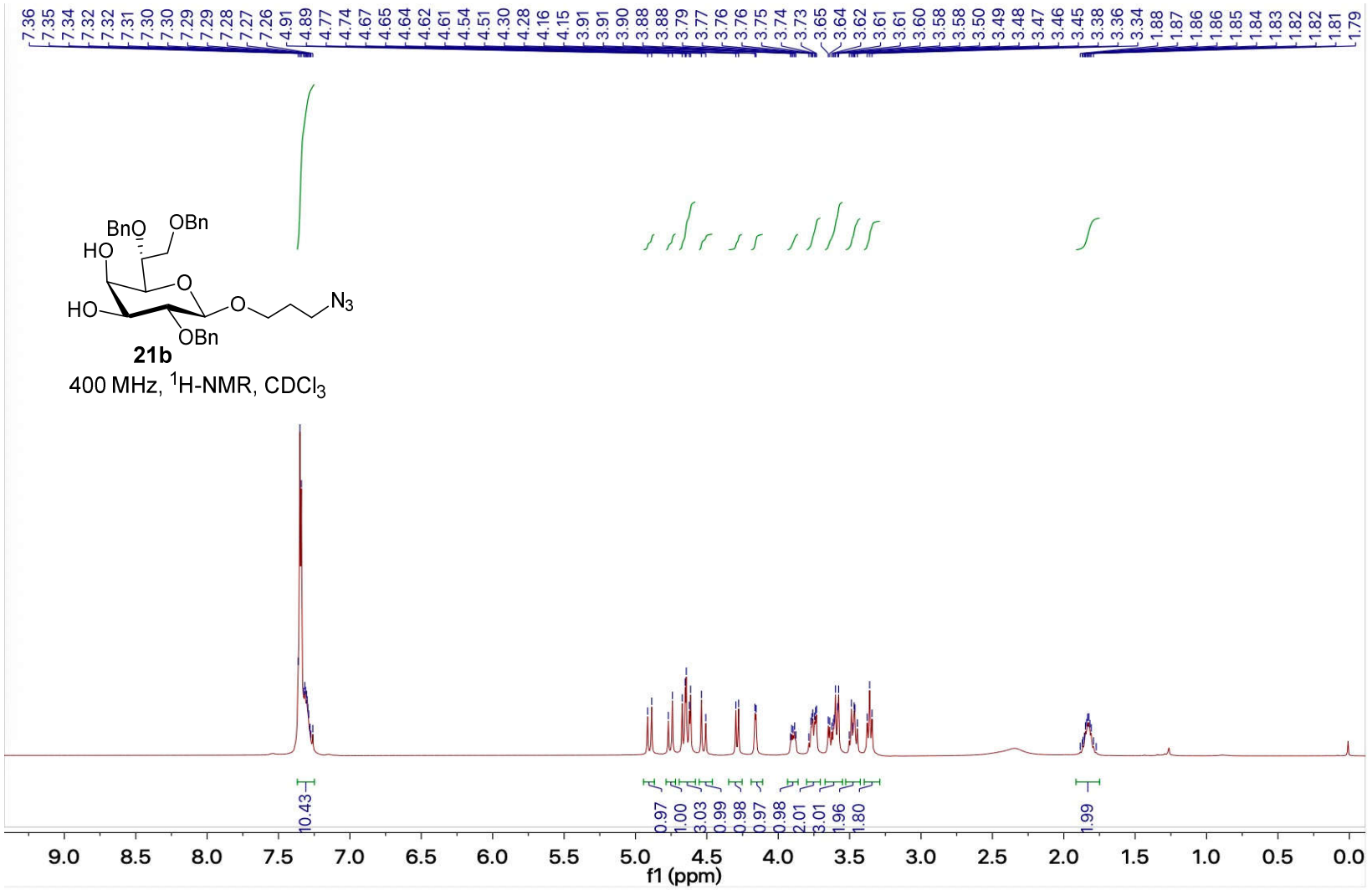
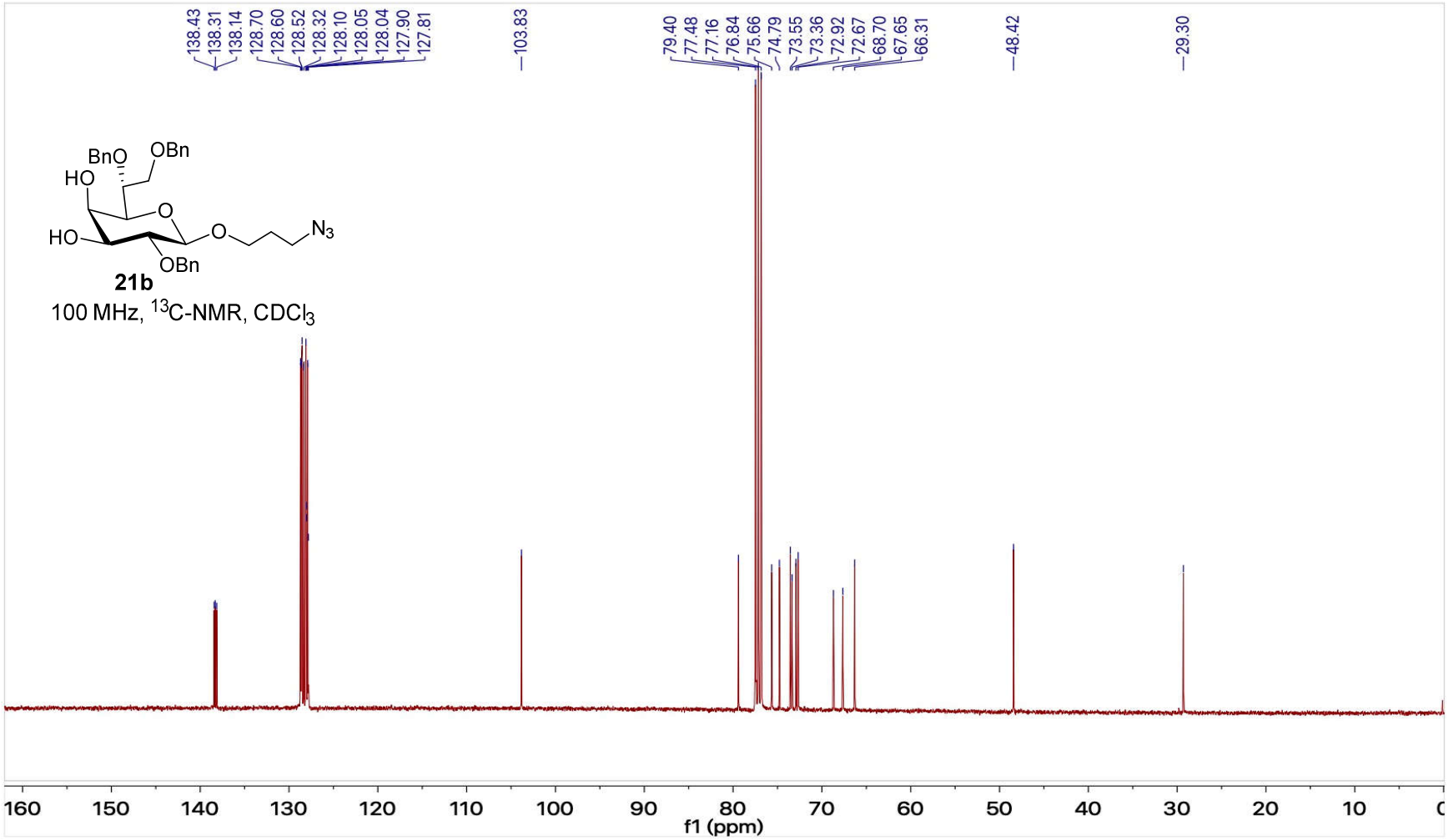
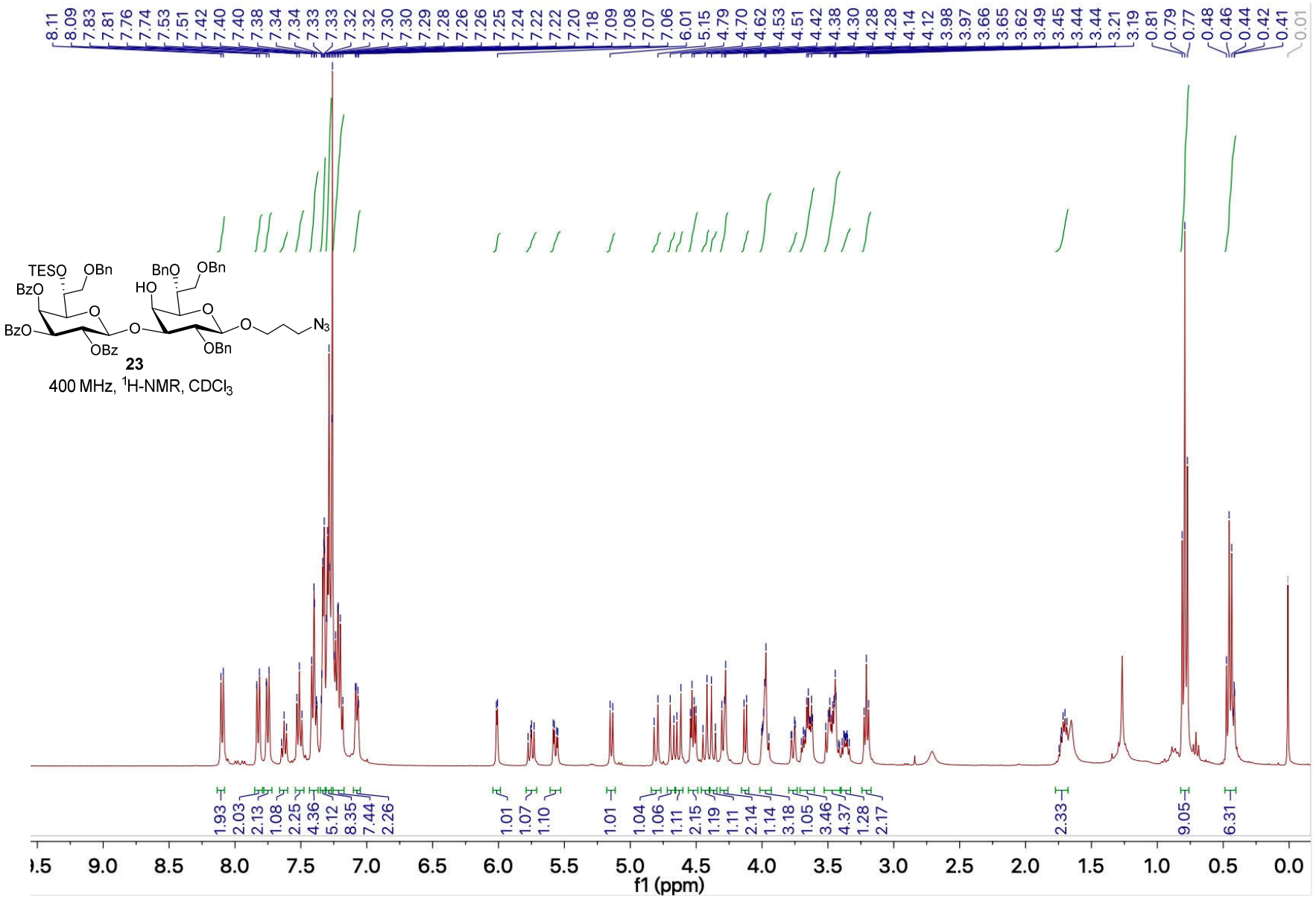
138.40
138.19
133.26
130.00
129.80
128.57
128.53
128.00
127.90
127.81
102.03
97.95
94.90
77.48
77.16
76.84
76.34
75.77
73.53
72.87
72.21
71.66
71.52
67.53
66.12
56.31
55.75
48.00
29.02
BnO
OBn
MOMO
O
MOMO
O
N3
OBz
20
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

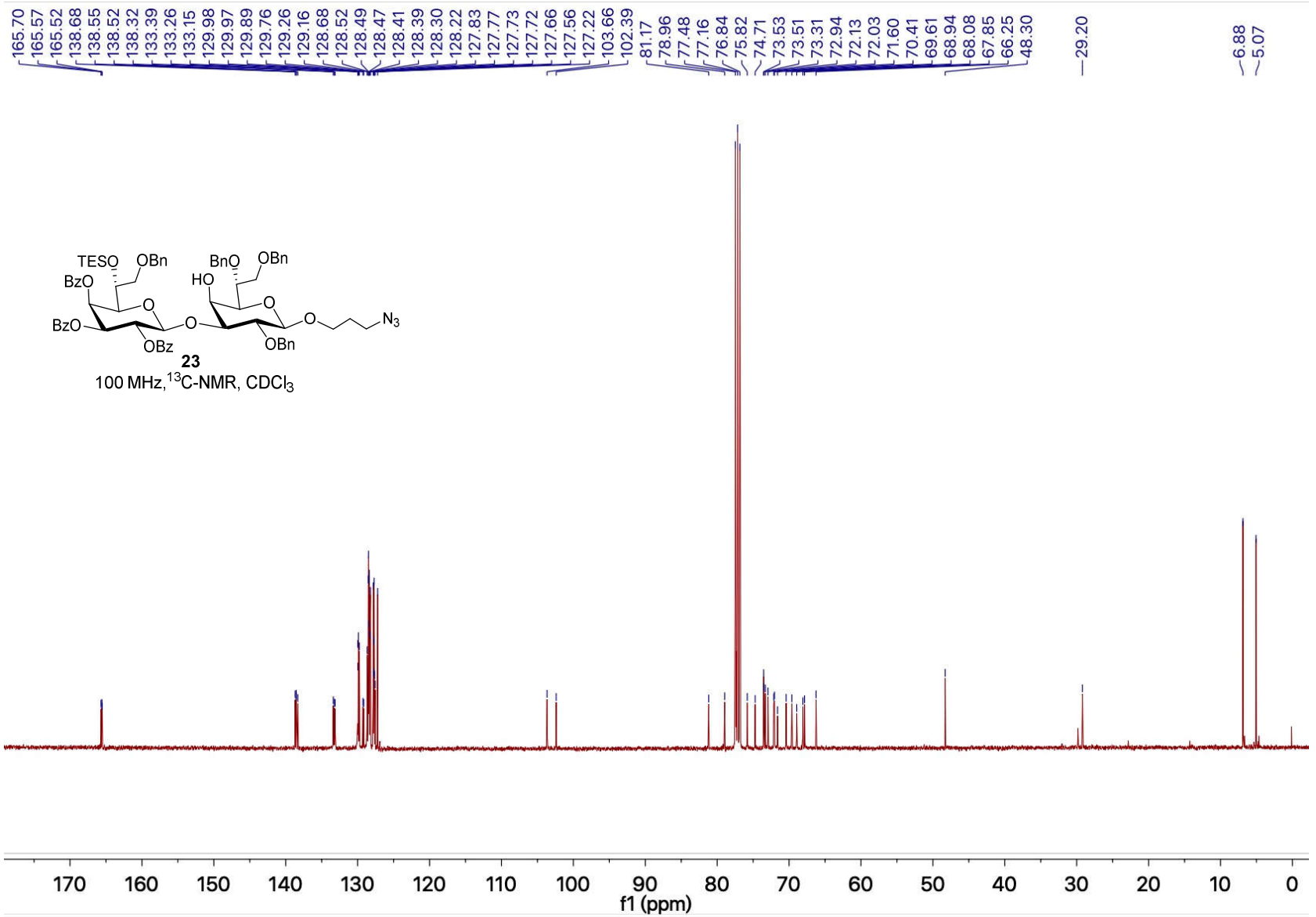

BnO
OBn
HO
O
HO
O
N3
OBz
21a
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

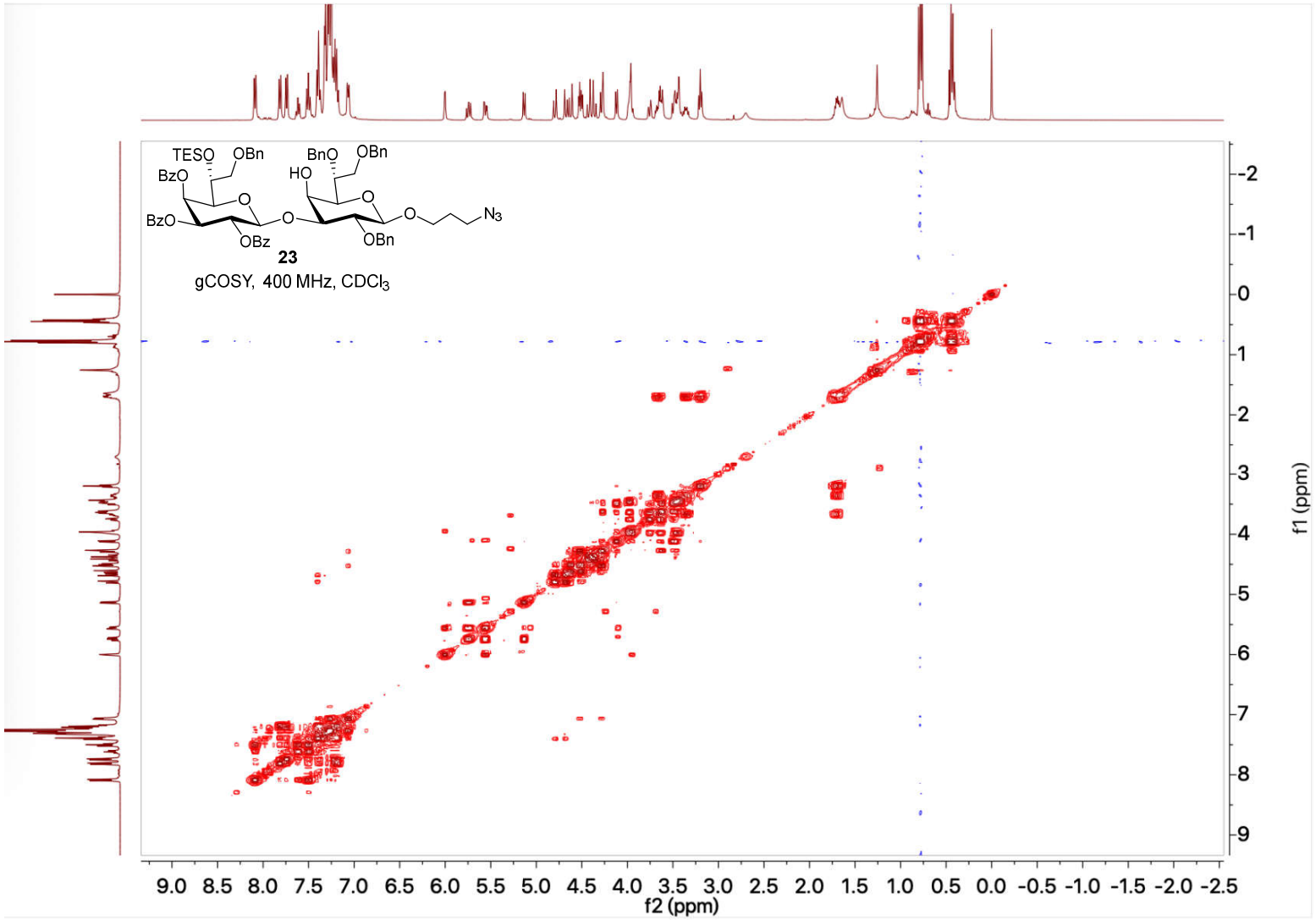

167.07
138.18
137.97
133.51
129.96
129.69
128.68
128.58
128.56
128.37
128.15
127.96
127.89
101.34
77.48
77.16
76.84
75.85
74.28
73.63
73.05
72.96
72.77
68.43
68.30
66.11
48.02
29.05
BnO
OBn
HO
O
HO
O
N3
OBz
21a
100 MHz, 13C-NMR, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

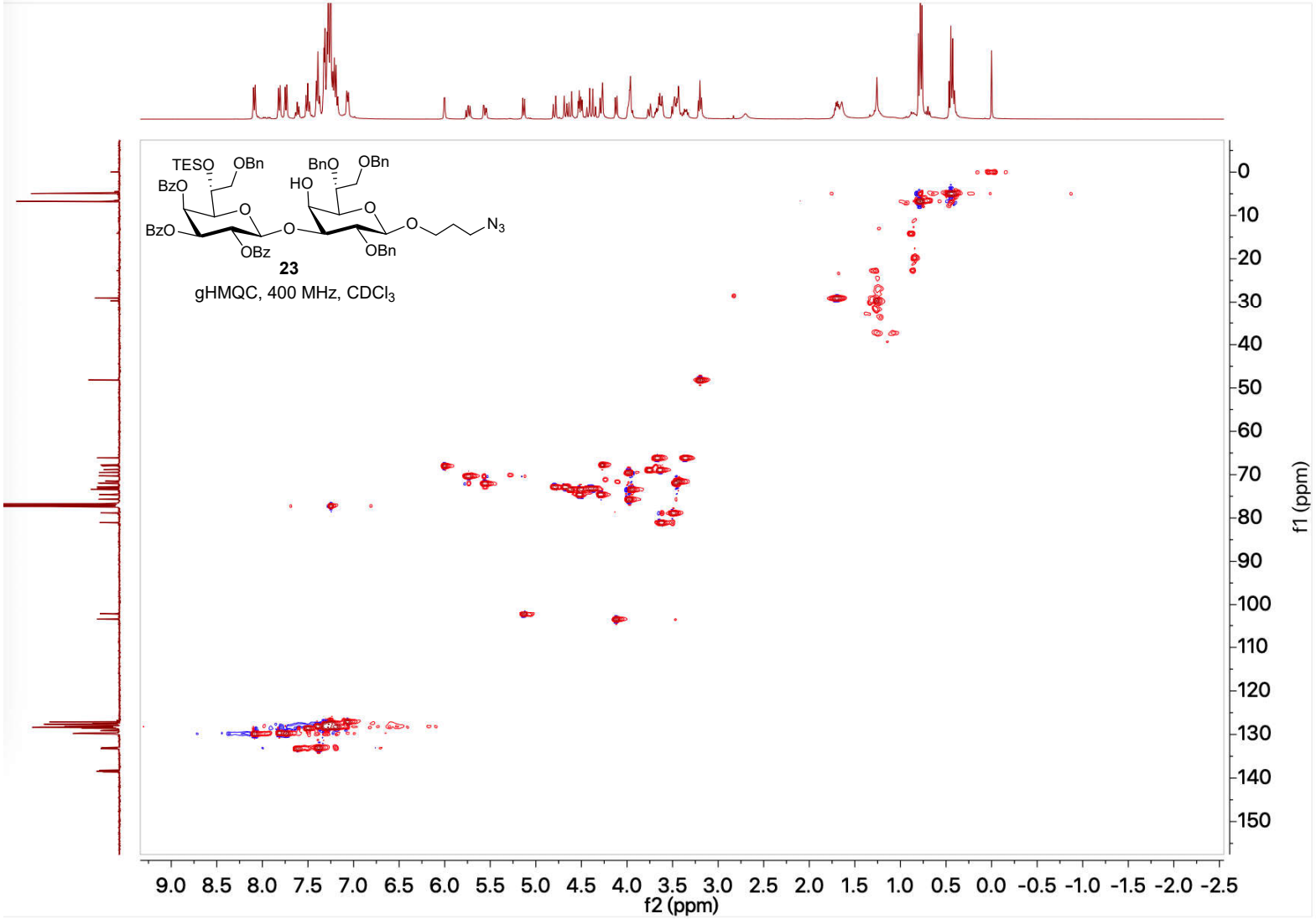

BnO
OBn
HO
O
HO
O
N3
OBn
21b
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

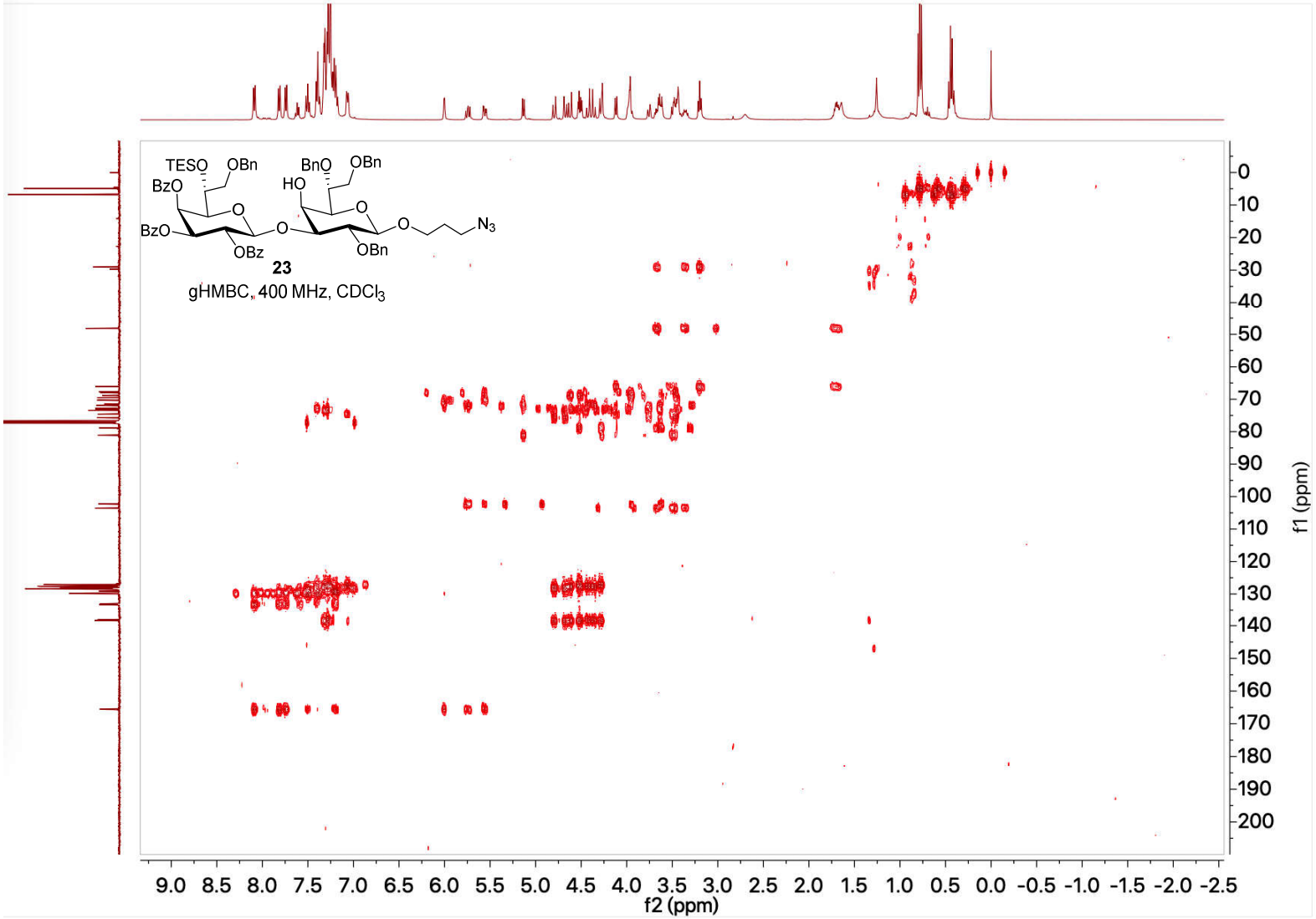

138.43
138.31
138.14
128.70
128.60
128.52
128.32
128.10
128.05
128.04
127.90
127.81
103.83
79.40
77.48
77.16
76.84
75.66
74.79
73.55
73.36
72.92
72.67
68.70
67.65
66.31
48.42
29.30
BnO
OBn
HO
O
HO
O
N3
OBn
21b
100 MHz, 13C-NMR, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

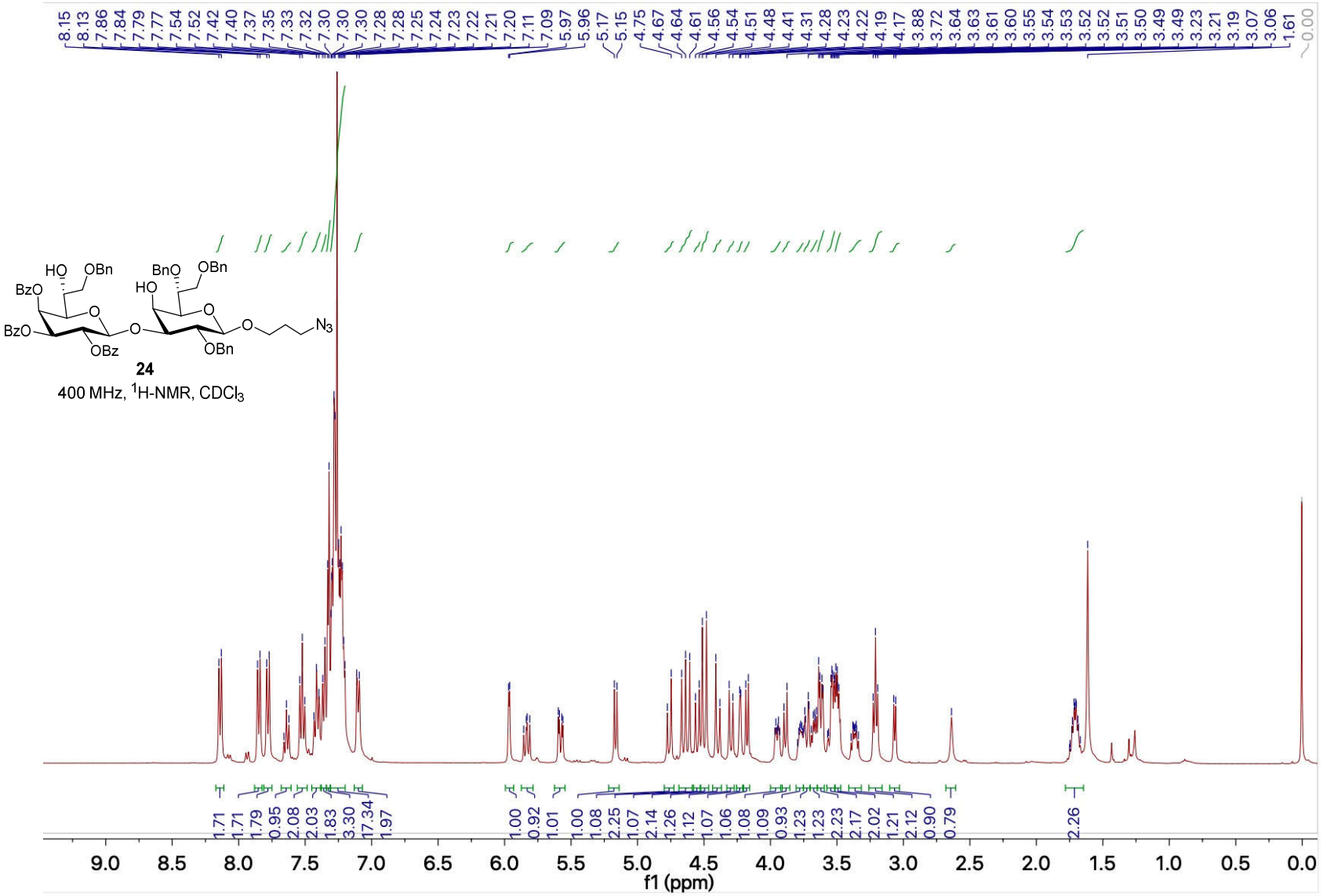

TESO
OBn
BzO
BnO
OBn
HO
BzO
OBz
OBn
N3
23
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

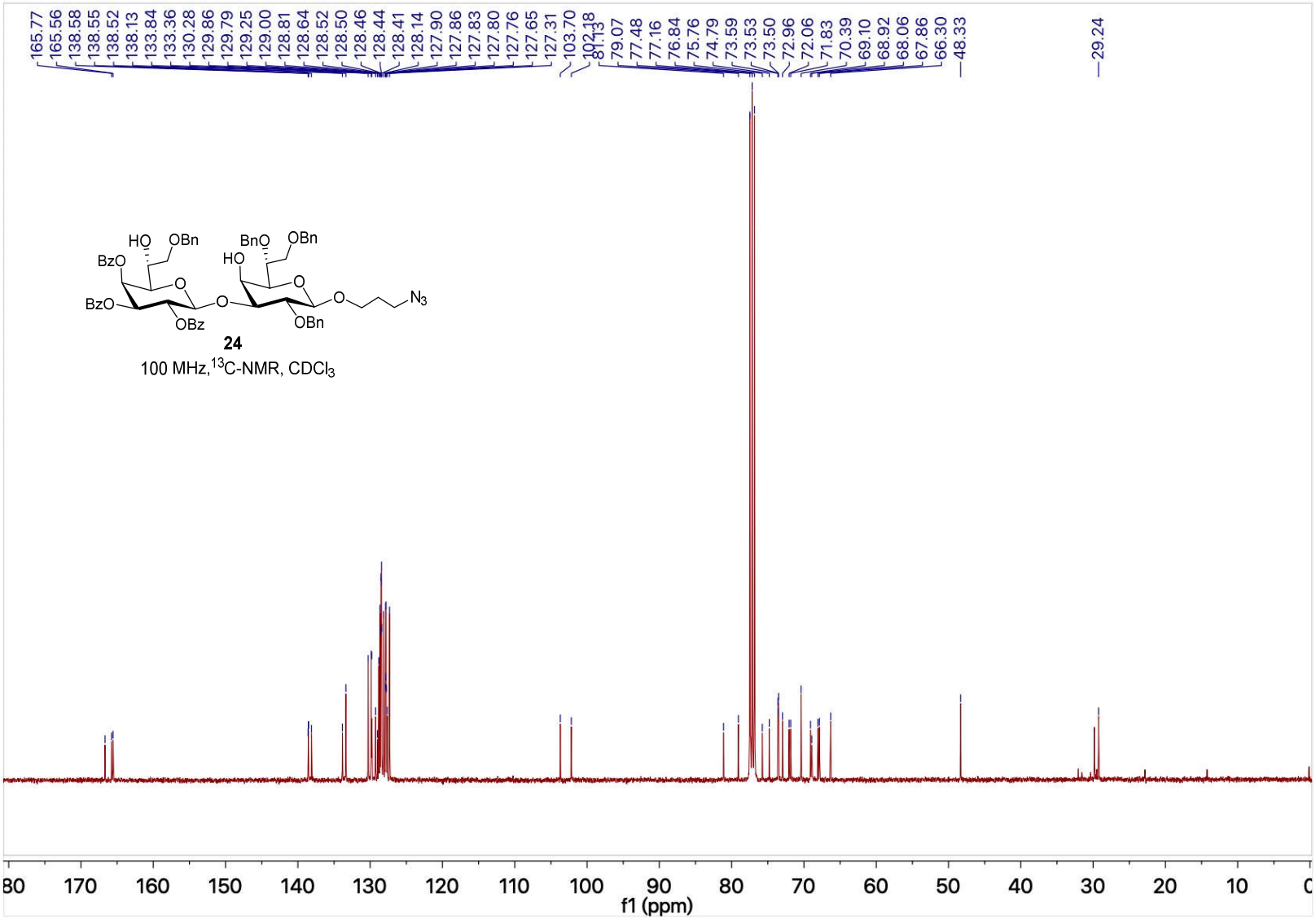

165.70
165.57
165.52
138.68
138.55
138.52
138.32
133.39
133.26
133.15
129.98
129.97
129.89
129.76
129.26
129.16
128.68
128.52
128.49
128.47
128.41
128.39
128.30
128.22
127.83
127.77
127.73
127.72
127.66
127.56
127.22
103.66
102.39
81.17
78.96
77.48
77.16
76.84
75.82
74.71
73.53
73.51
73.31
72.94
72.13
72.03
71.60
70.41
69.61
68.94
68.08
67.85
66.25
48.30
29.20
6.88
5.07
TESO
OBn
BzO
O
BzO
O
OBz
BnO
OBn
HO
O
O
N3
OBn
23
100 MHz, 13C-NMR, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

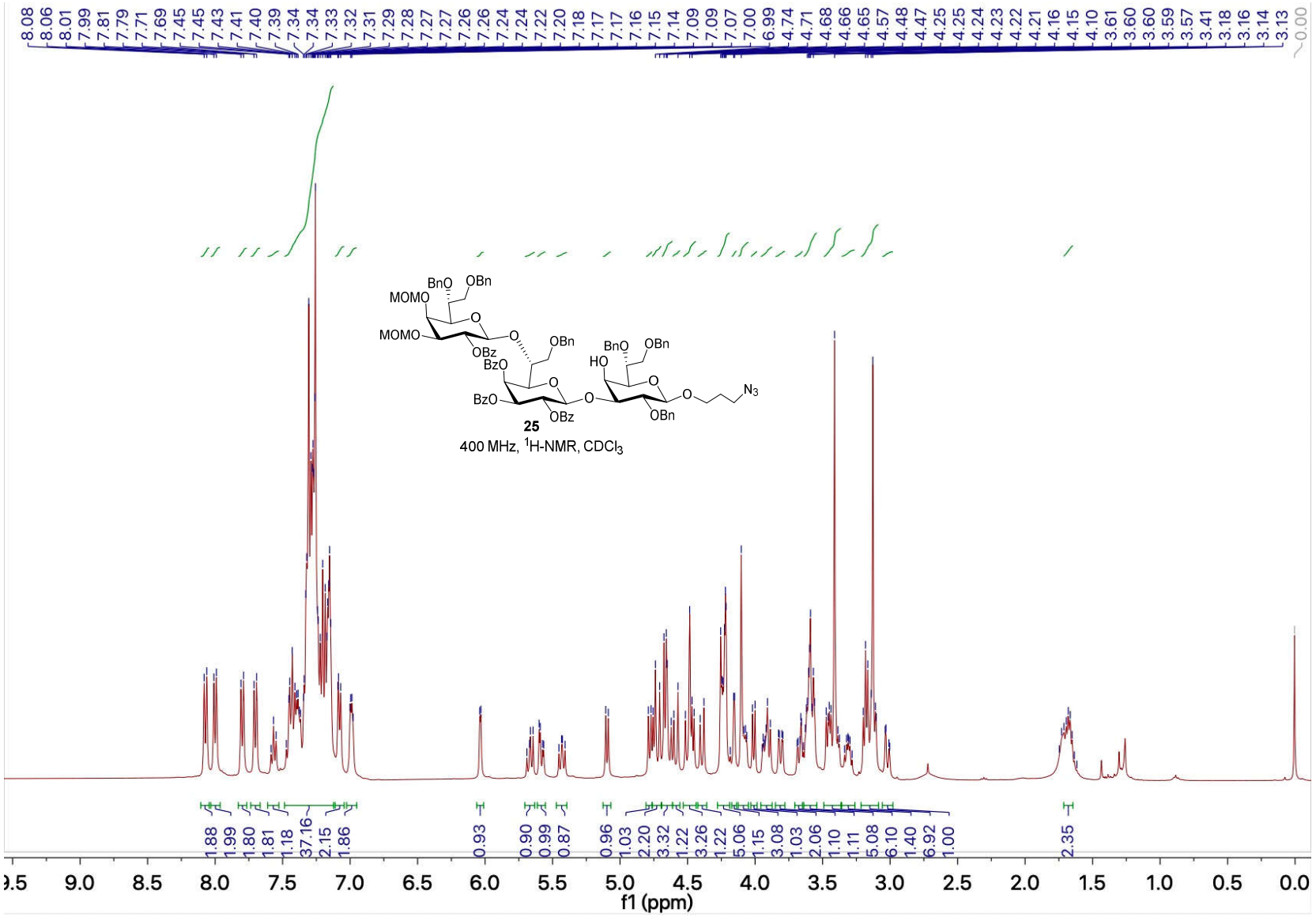

TESO
OBn
BzO
BnO
OBn
HO
BzO
OBz
OBn
N3
23
gCOSY, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

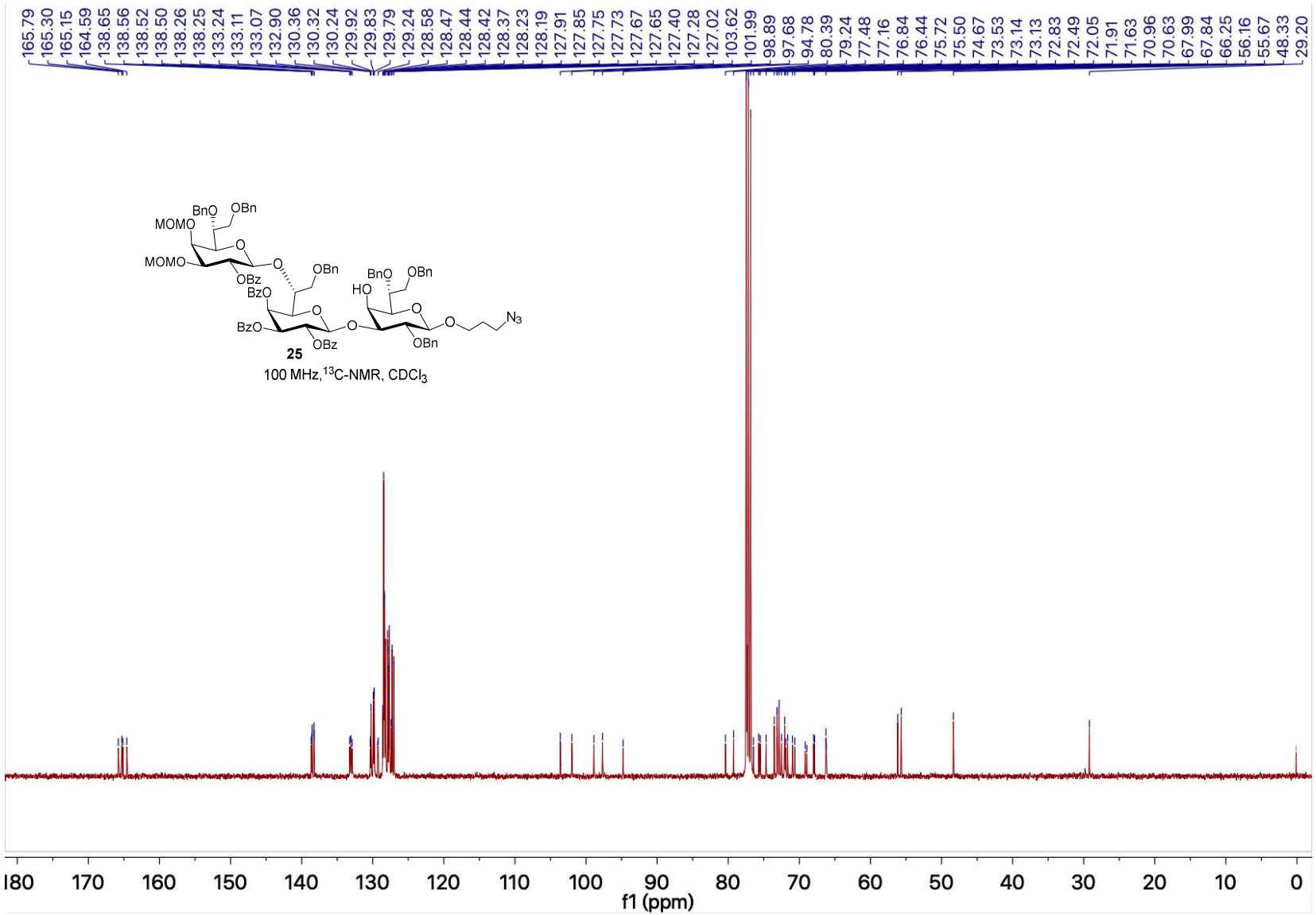

TESO
OBn
BnO
OBn
BzO
HO
O
O
BzO
O
O
N3
OBz
OBn
23
gHMQC, 400 MHz, CDCl3
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 -2.5
f2 (ppm)

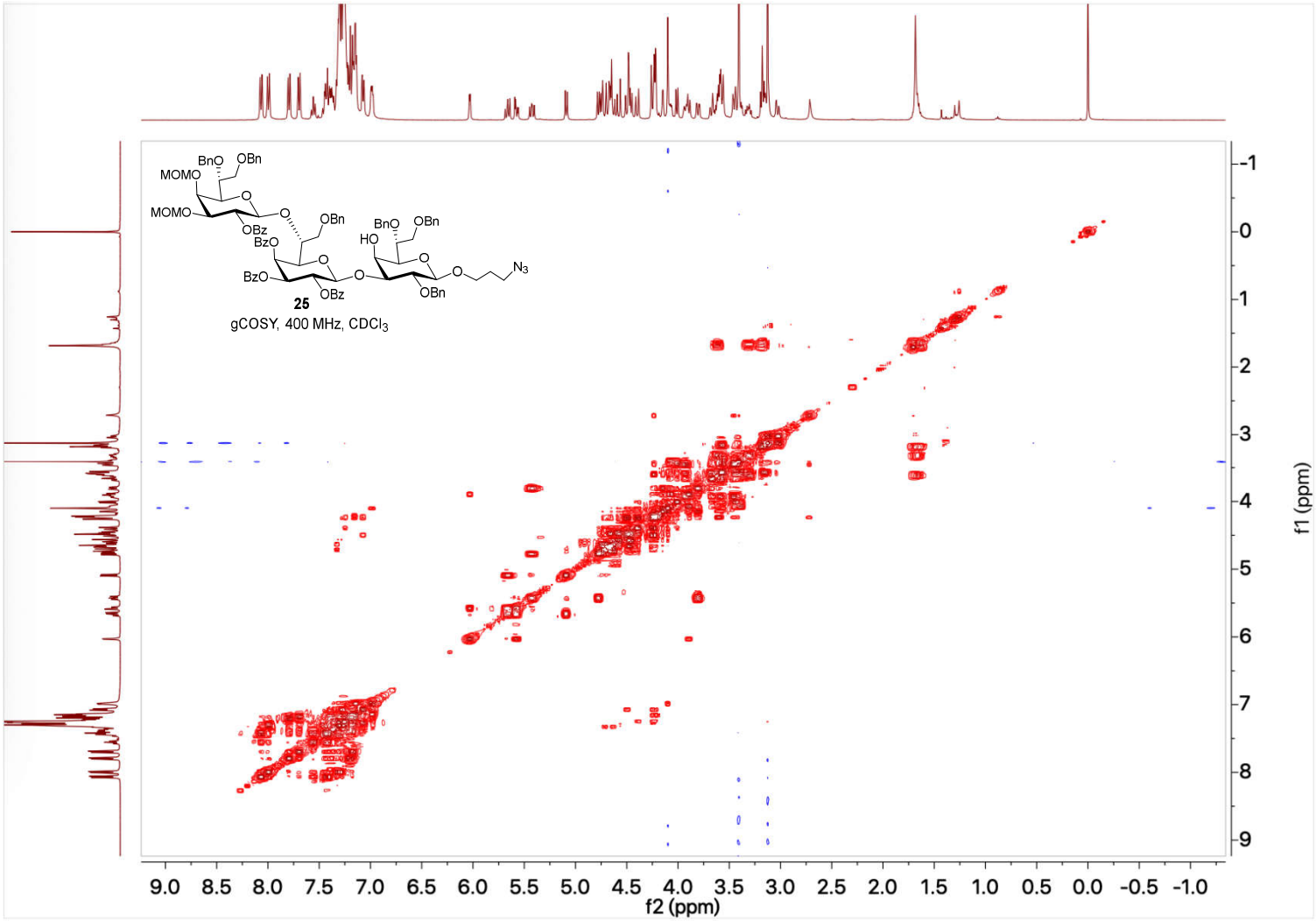

TESO
OBn
BzO
BnO
OBn
HO
BzO
OBz
OBn
N3
23
gHMBC, 400 MHz, CDCl3
f1 (ppm)
f2 (ppm)

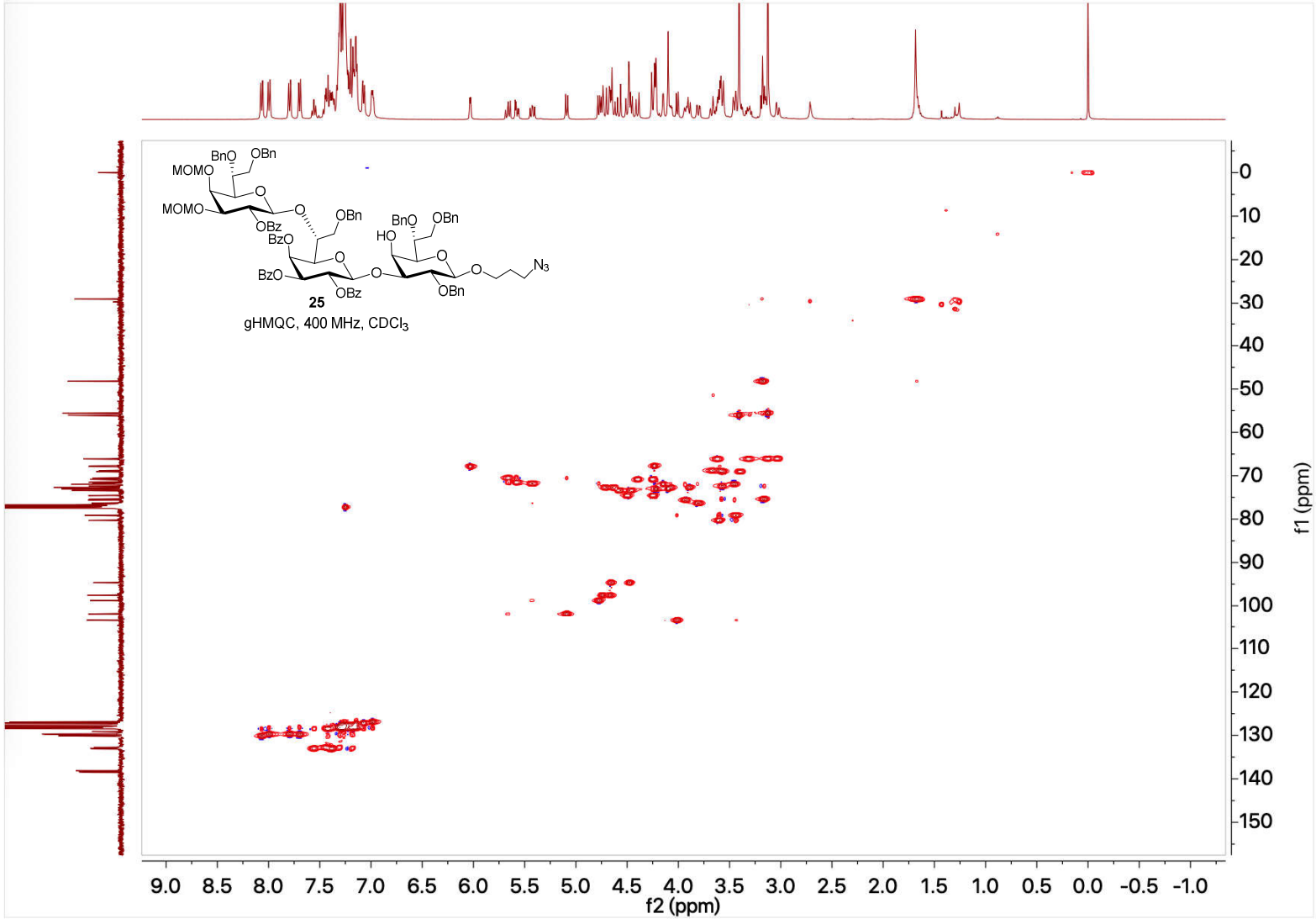

24
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

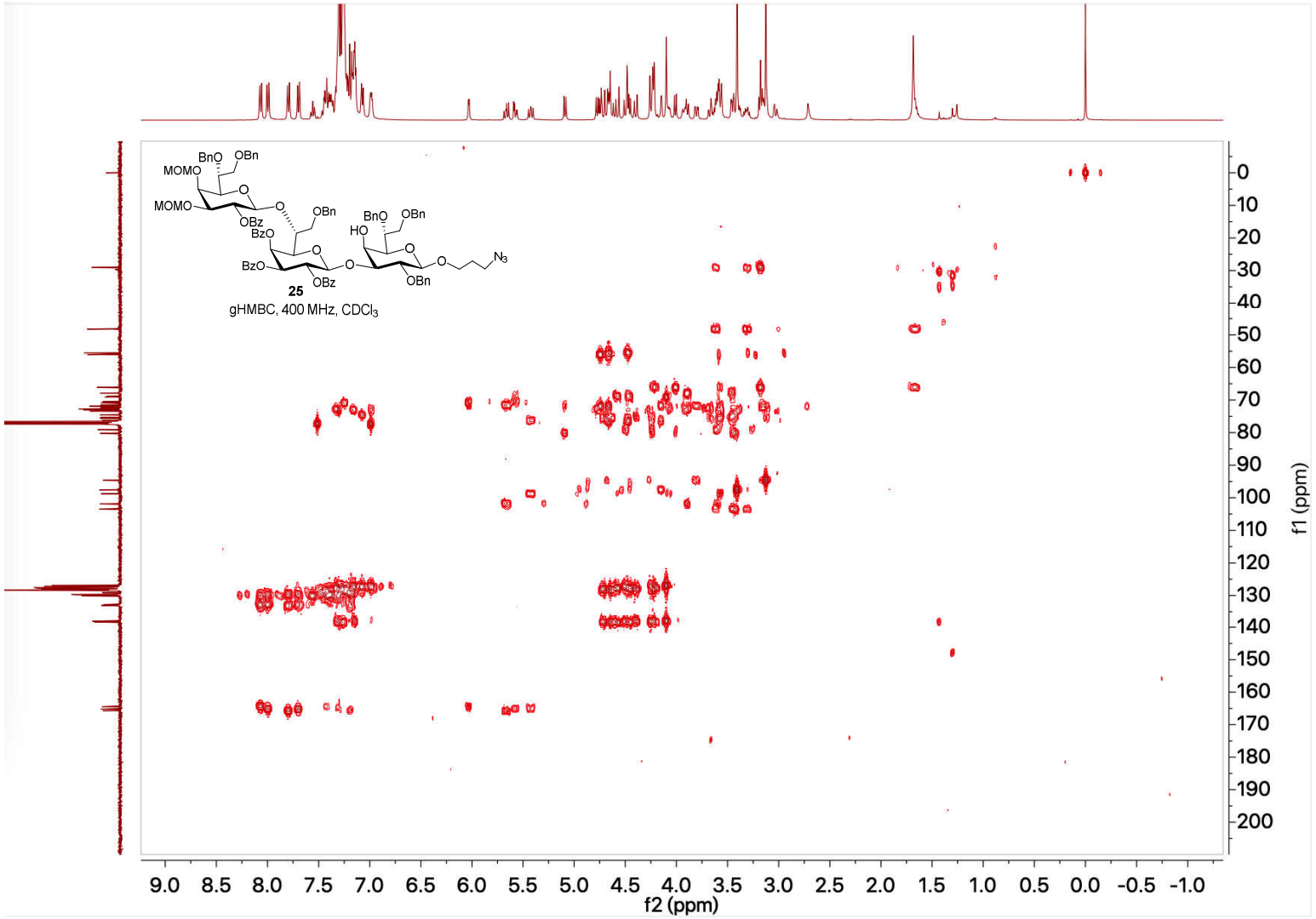

165.77
165.56
138.58
138.55
138.52
138.13
133.84
133.36
130.28
129.86
129.79
129.25
129.00
128.81
128.64
128.52
128.50
128.46
128.44
128.41
128.14
127.90
127.86
127.83
127.80
127.76
127.65
127.31
103.70
102.18
81.13
79.07
77.48
77.16
76.84
75.76
74.79
73.59
73.53
73.50
72.96
72.06
71.83
70.39
69.10
68.92
68.06
67.86
66.30
48.33
29.24
HO
OBn
BnO
OBn
BzO
HO
O
O
BzO
O
O
N3
OBz
OBn
24
100 MHz,13C-NMR, CDCl3
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

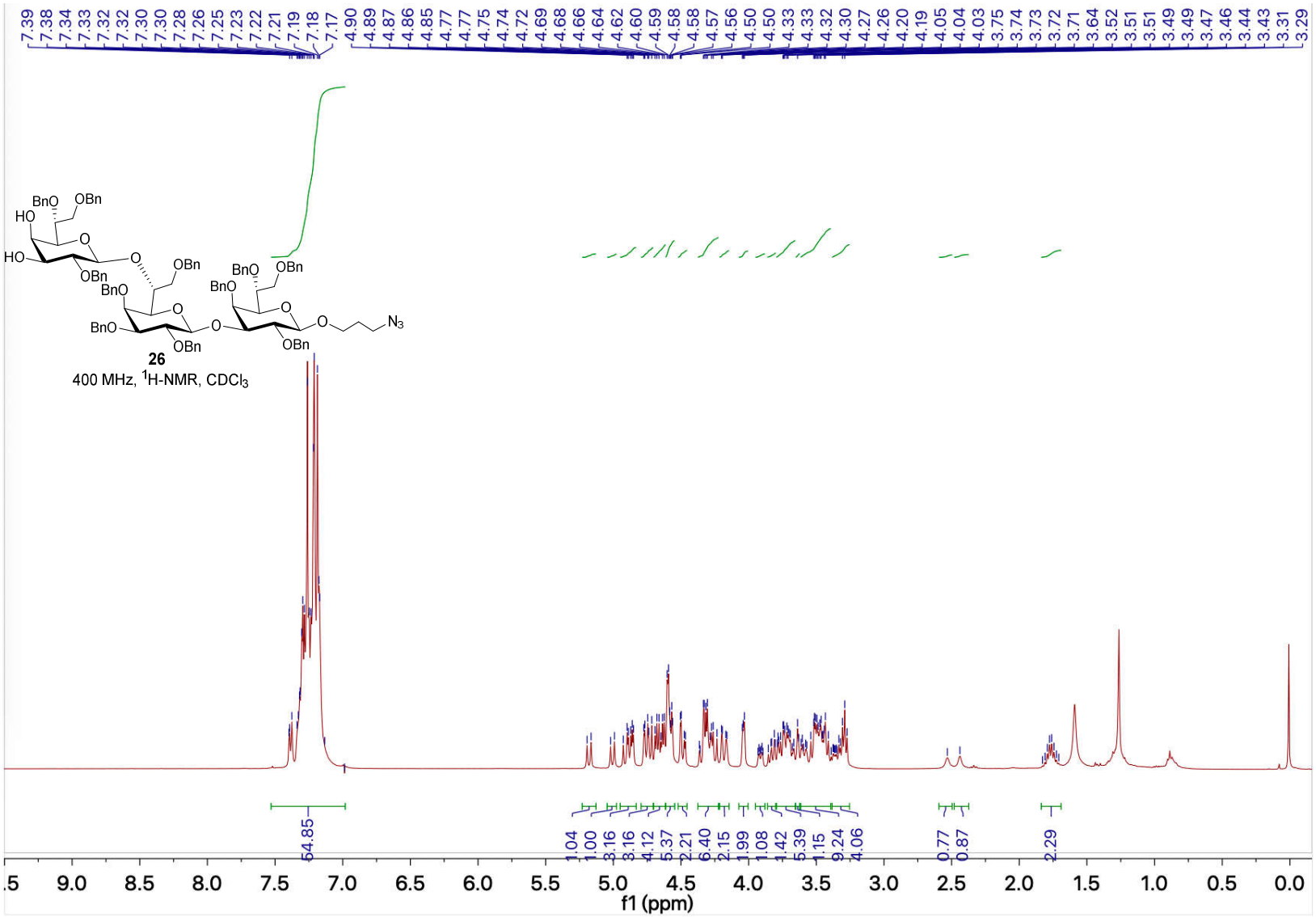

25
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

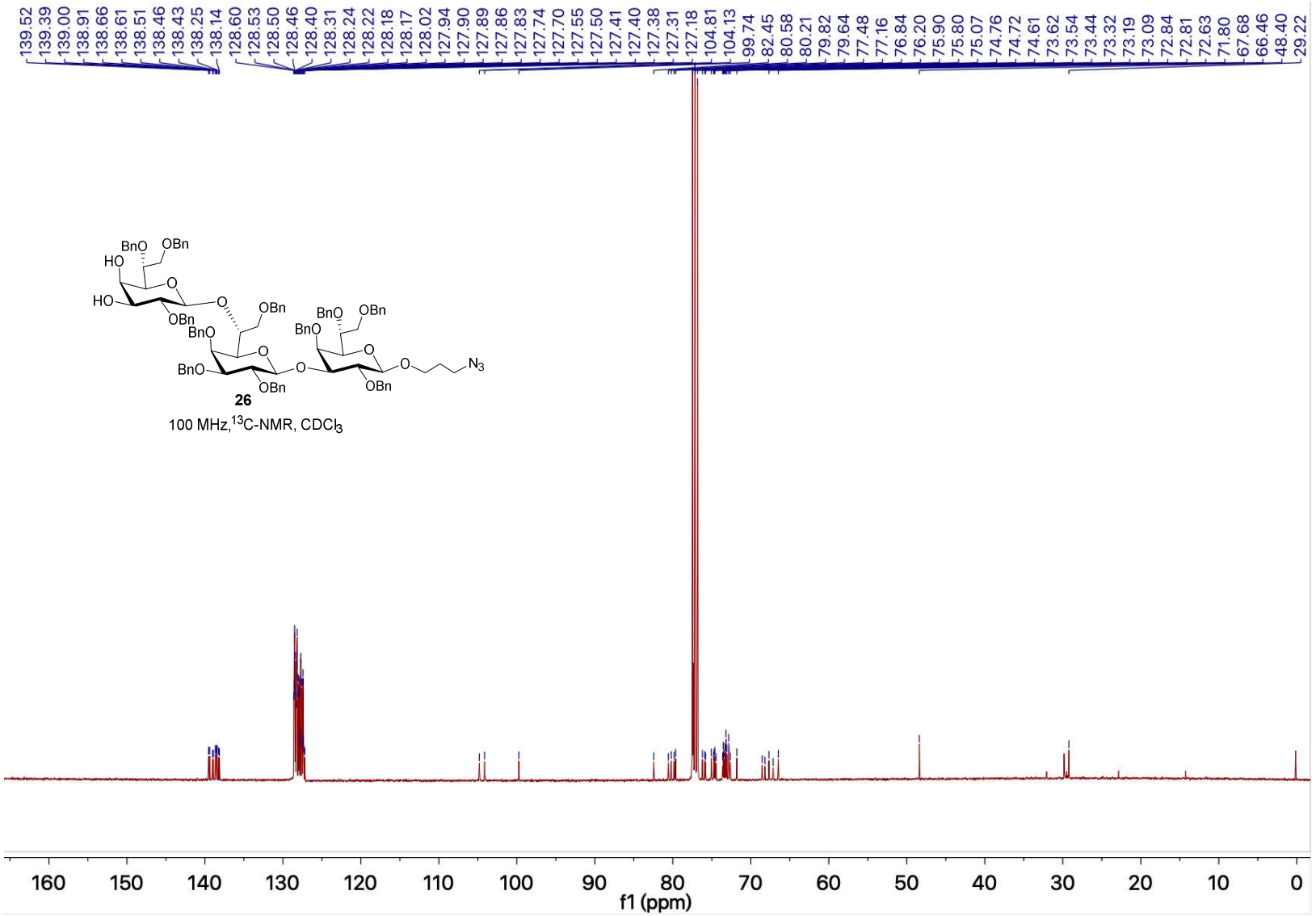

165.79
165.30
165.15
164.59
138.65
138.56
138.52
138.50
138.26
138.25
133.24
133.11
133.07
132.90
130.36
130.32
130.24
129.92
129.83
129.79
129.24
128.58
128.47
128.44
128.42
128.37
128.23
128.19
127.91
127.85
127.75
127.73
127.67
127.65
127.40
127.28
127.02
103.62
101.99
98.89
97.68
94.78
80.39
79.24
77.48
77.16
76.84
76.44
75.72
75.50
74.67
73.53
73.14
73.13
72.83
72.49
72.05
71.91
71.63
70.96
70.63
67.99
67.84
66.25
56.16
55.67
48.33
29.20
MOMO
BnO
OBn
MOMO
OBz
BzO
OBn
BzO
OBz
HO
BnO
OBn
OBn
N3
25
100 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

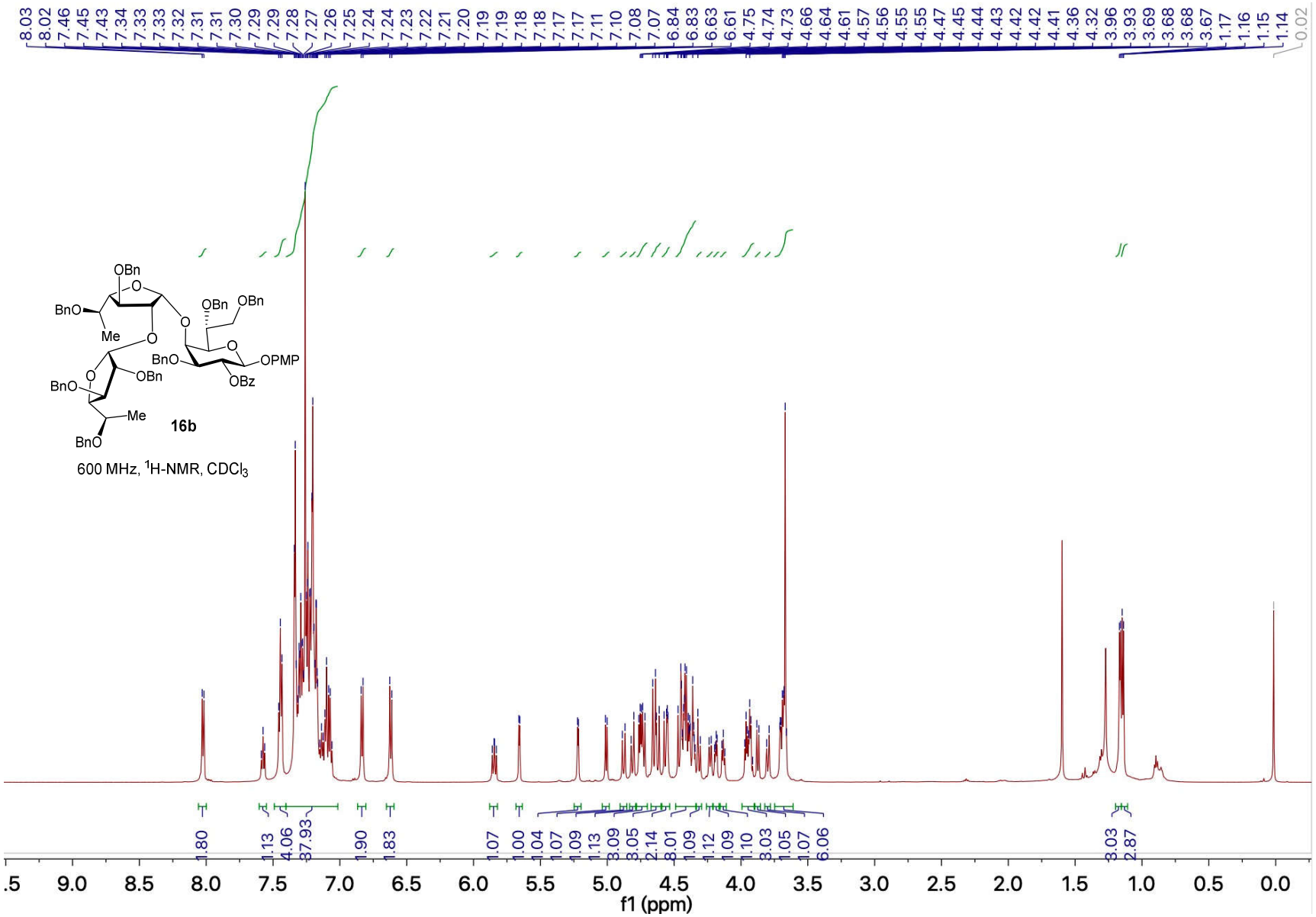

BnO
OBn
MOMO
MOMO
OBz
BzO
OBn
BnO
OBn
HO
BzO
OBz
O
N3
OBn
25
gCOSY, 400 MHz, CDCl3
f1 (ppm)
f2 (ppm)
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
-1 0 1 2 3 4 5 6 7 8 9

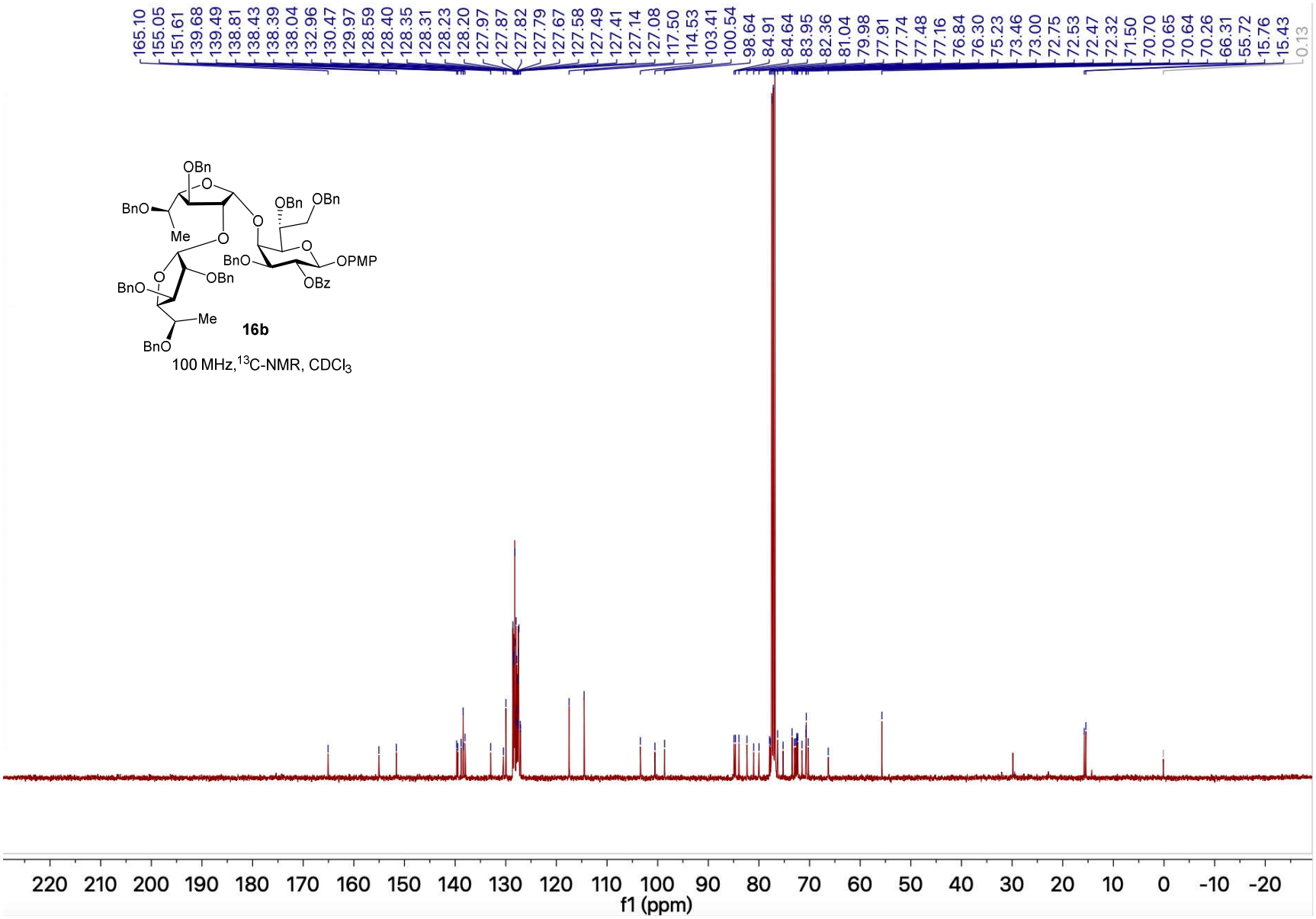

BnO
OBn
MOMO
O
MOMO
O
OBn
OBz
BzO
BzO
O
OBz
HO
BnO
OBn
O
O
N3
OBn
25
gHMQC, 400 MHz, CDCl3
f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)

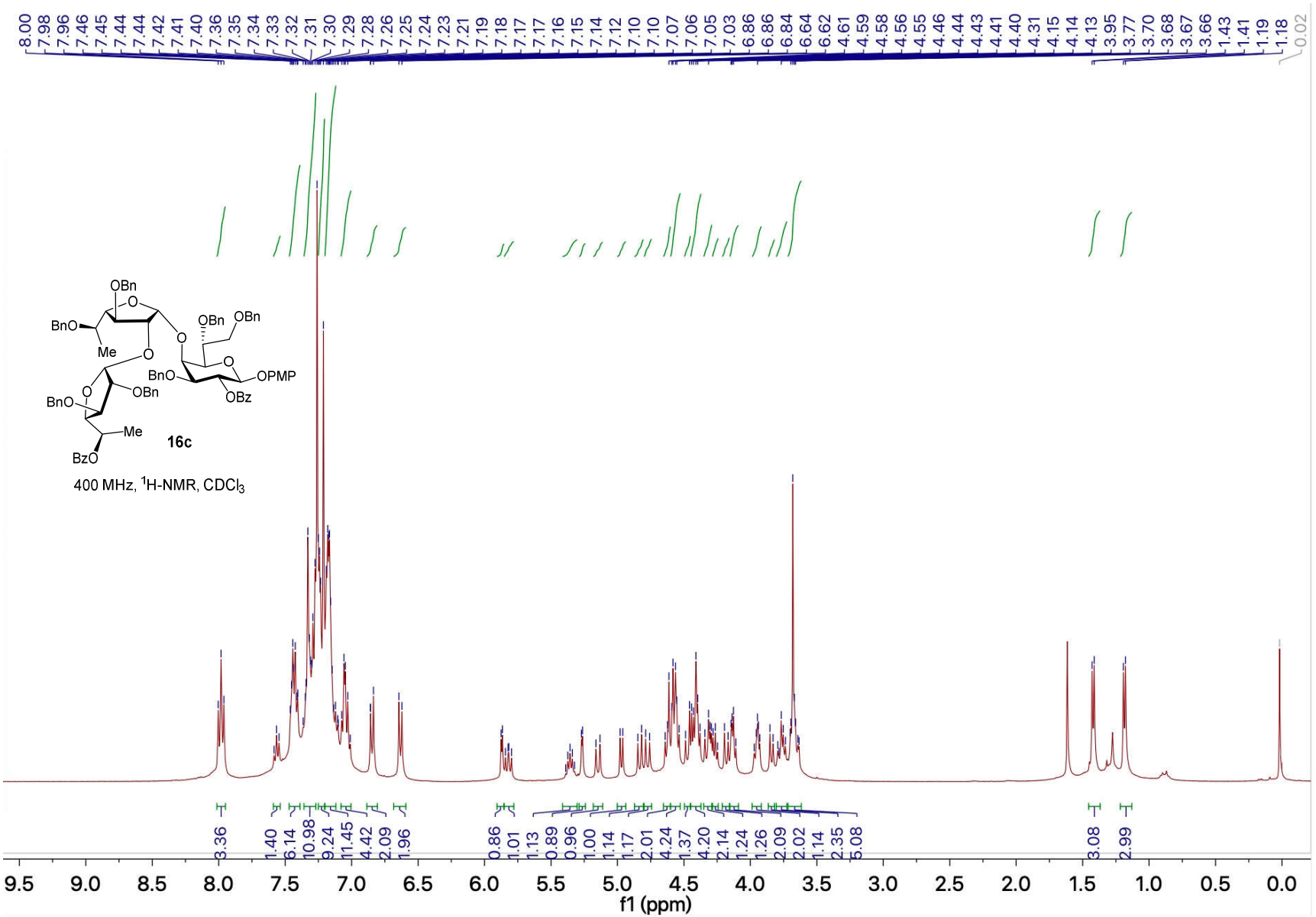

BnO
OBn
MOMO
O
MOMO
OBz
BzO
OBn
BnO
OBn
HO
O
BzO
O
O
N3
BzO
OBz
OBn
25
gHMBC, 400 MHz, CDCl3
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)

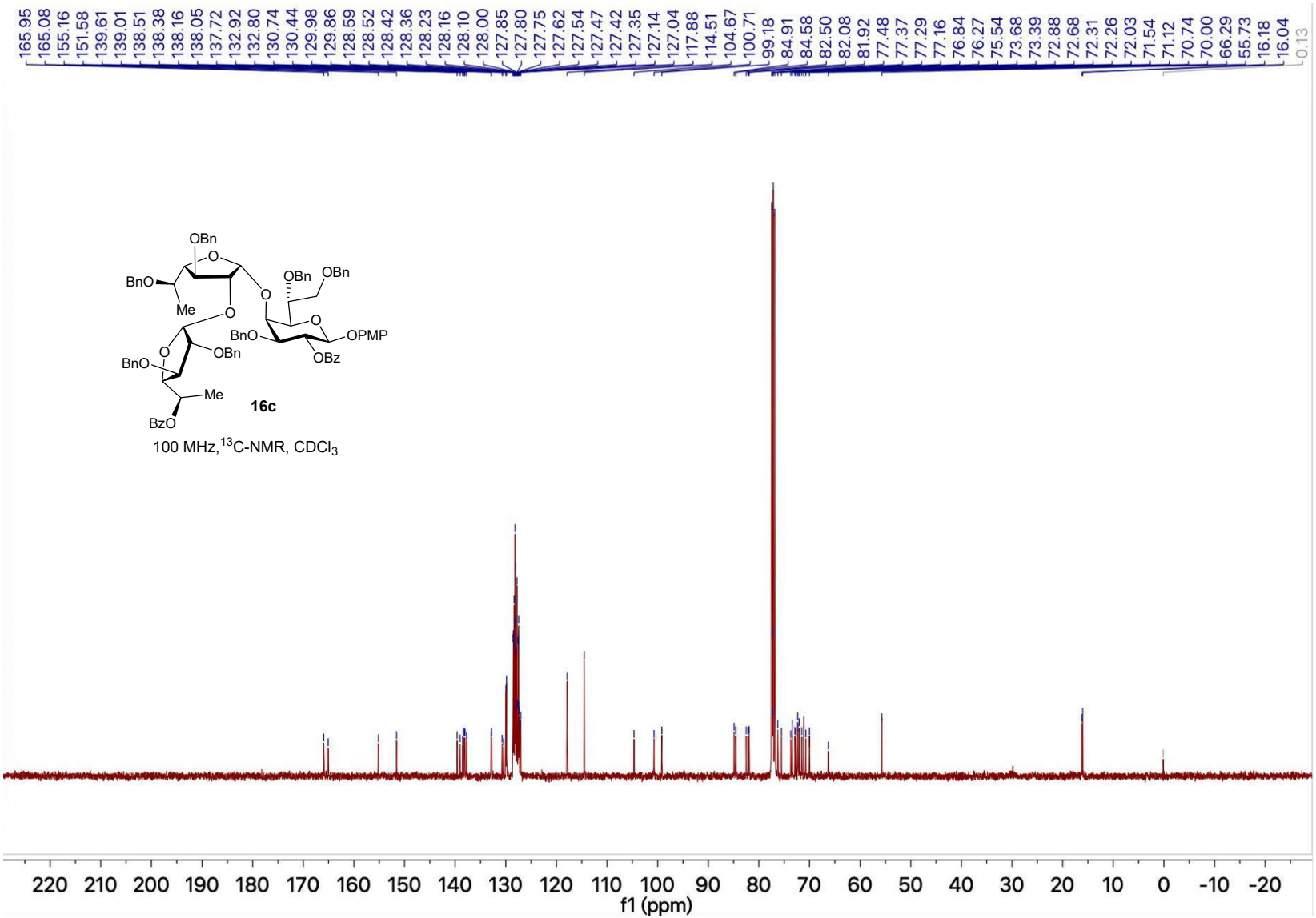

26
400 MHz, 1H-NMR, CDCl3
f1 (ppm)

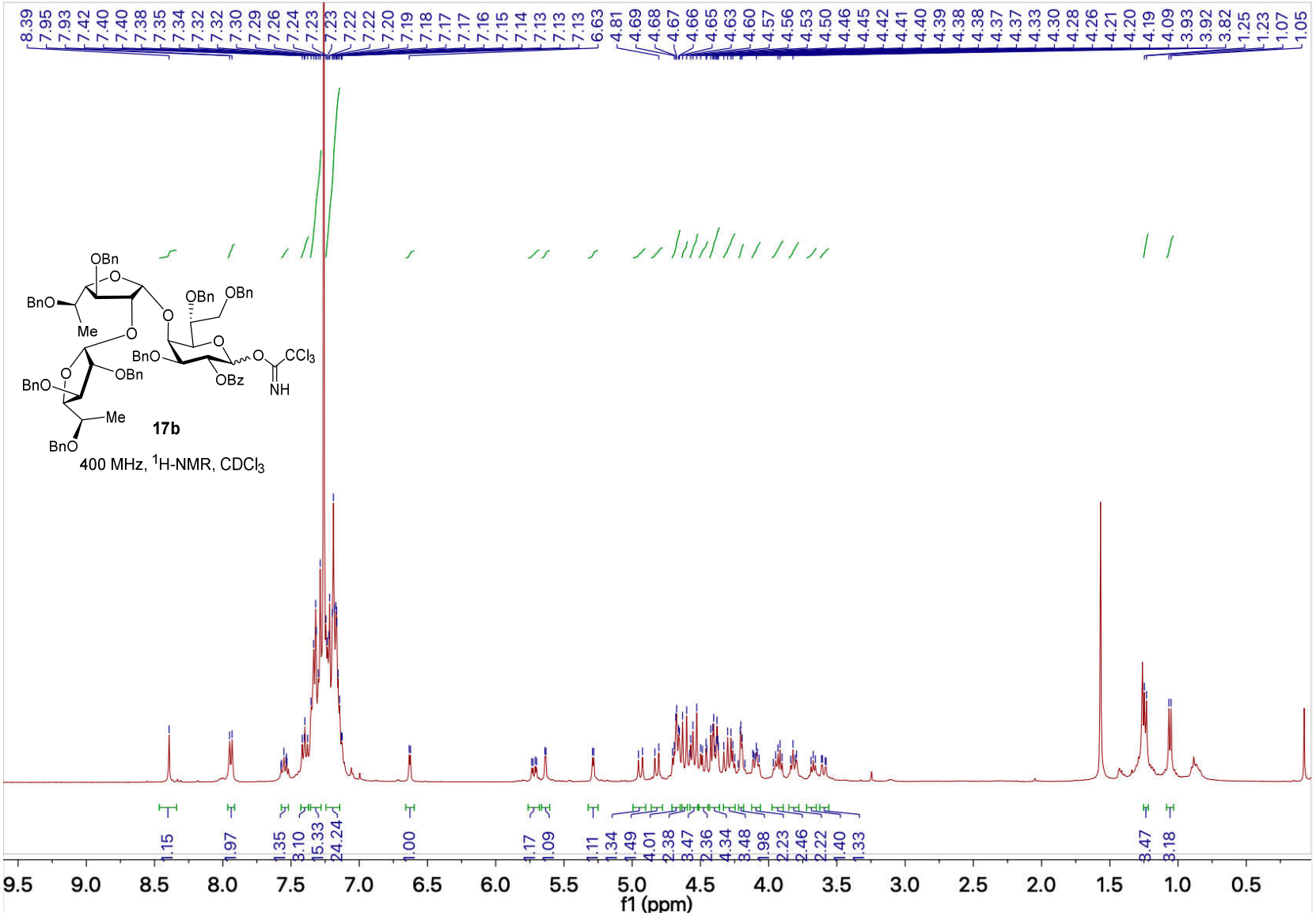

139.52
139.39
139.00
138.91
138.66
138.61
138.51
138.46
138.43
138.25
138.14
128.60
128.53
128.50
128.46
128.40
128.31
128.24
128.22
128.18
128.17
128.02
127.94
127.90
127.89
127.86
127.83
127.74
127.70
127.55
127.50
127.41
127.40
127.38
127.31
127.18
104.81
104.13
99.74
82.45
80.58
80.21
79.82
79.64
77.48
77.16
76.84
76.20
75.90
75.80
75.07
74.76
74.72
74.61
73.62
73.54
73.44
73.32
73.19
73.09
72.84
72.81
72.63
71.80
67.68
66.46
48.40
29.22
BnO
OBn
HO
O
HO
OBn
BnO
OBn
BnO
O
BnO
OBn
O
BnO
OBn
BnO
OBn
O
O
N3
OBn
26
100 MHz,13C-NMR, CDCl3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

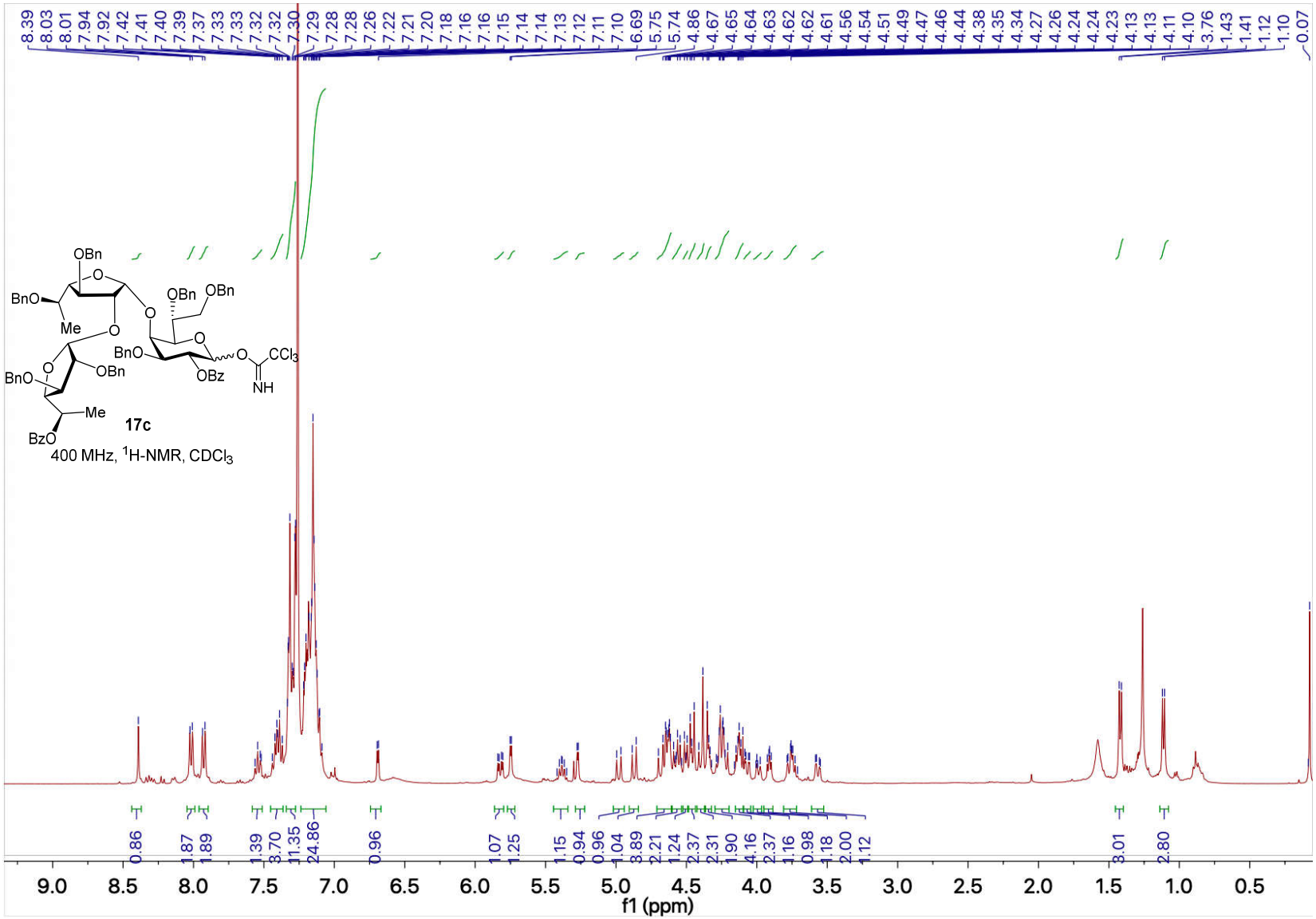

16b
600 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

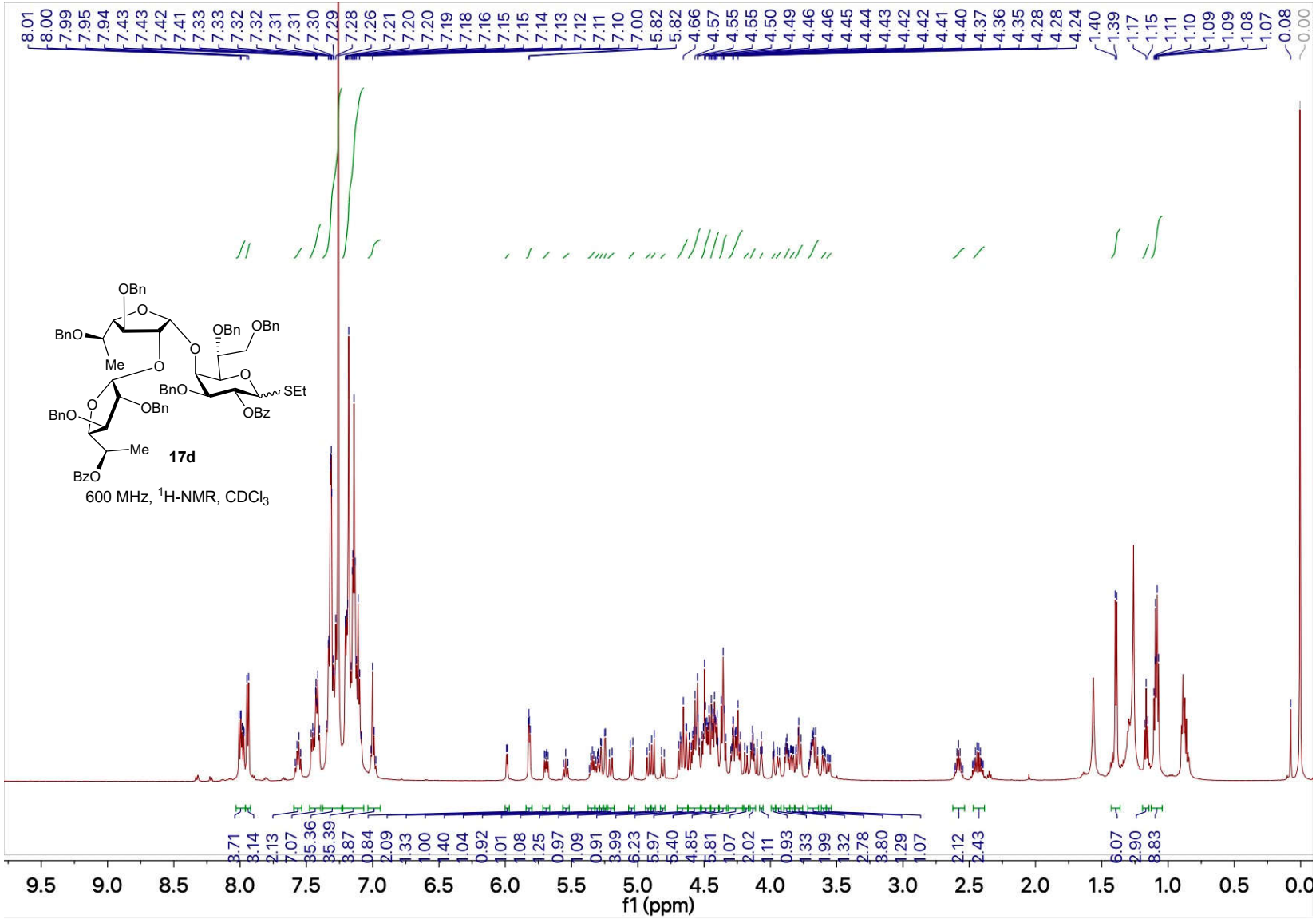

165.10
155.05
151.61
139.68
139.49
138.81
138.43
138.39
138.04
132.96
130.47
129.97
128.59
128.40
128.35
128.31
128.23
128.20
127.97
127.87
127.82
127.79
127.67
127.58
127.49
127.41
127.14
127.08
117.50
114.53
103.41
100.54
98.64
84.91
84.64
83.95
82.36
81.04
79.98
77.91
77.74
77.48
77.16
76.84
76.30
75.23
73.46
73.00
72.75
72.53
72.47
72.32
71.50
70.70
70.65
70.64
70.26
66.31
55.72
15.76
15.43
0.13
OBn
BnO
Me
O
OBn
OBn
BnO
OPMP
OBz
16b
100 MHz, 13C-NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

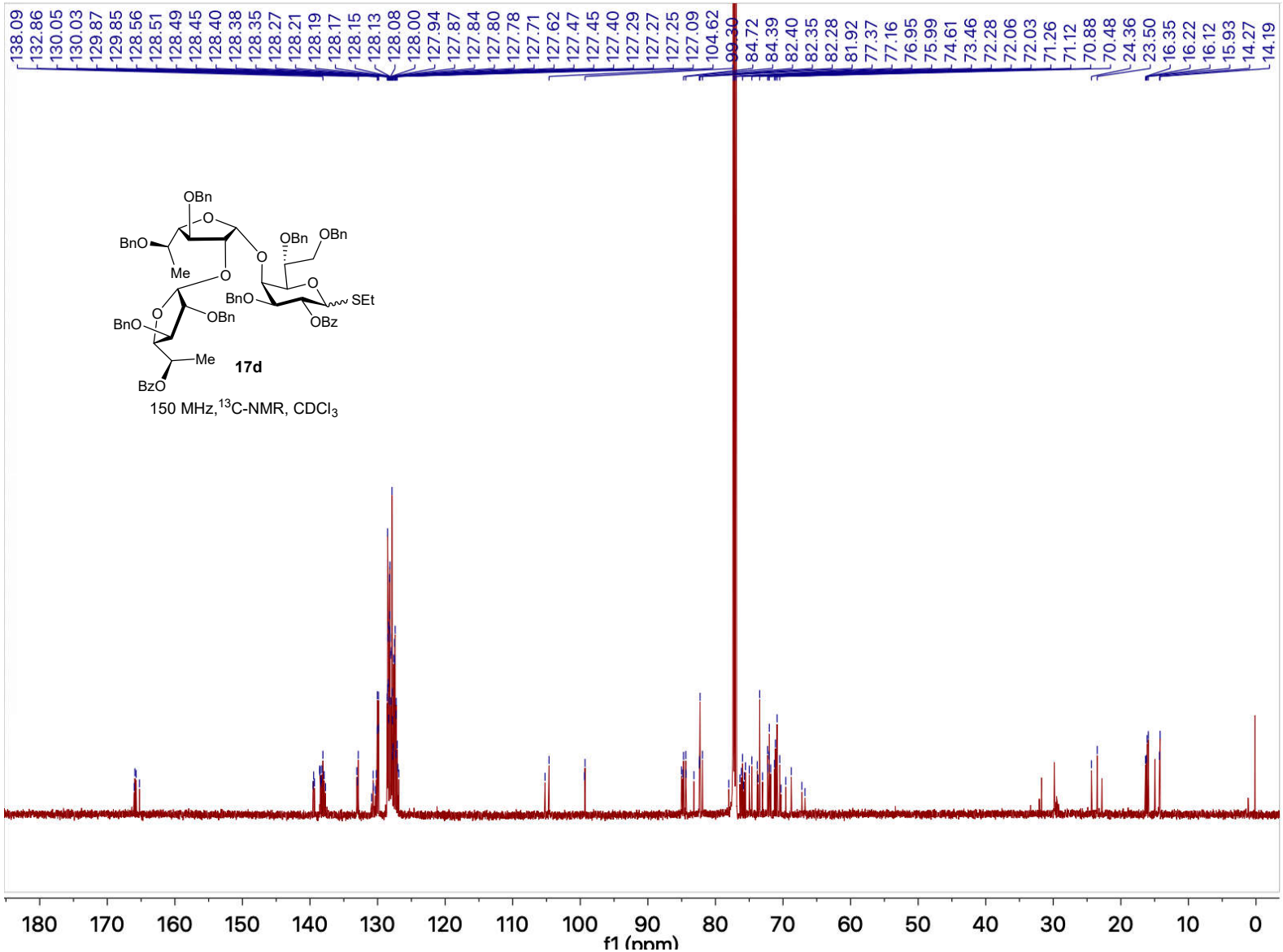

16c
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

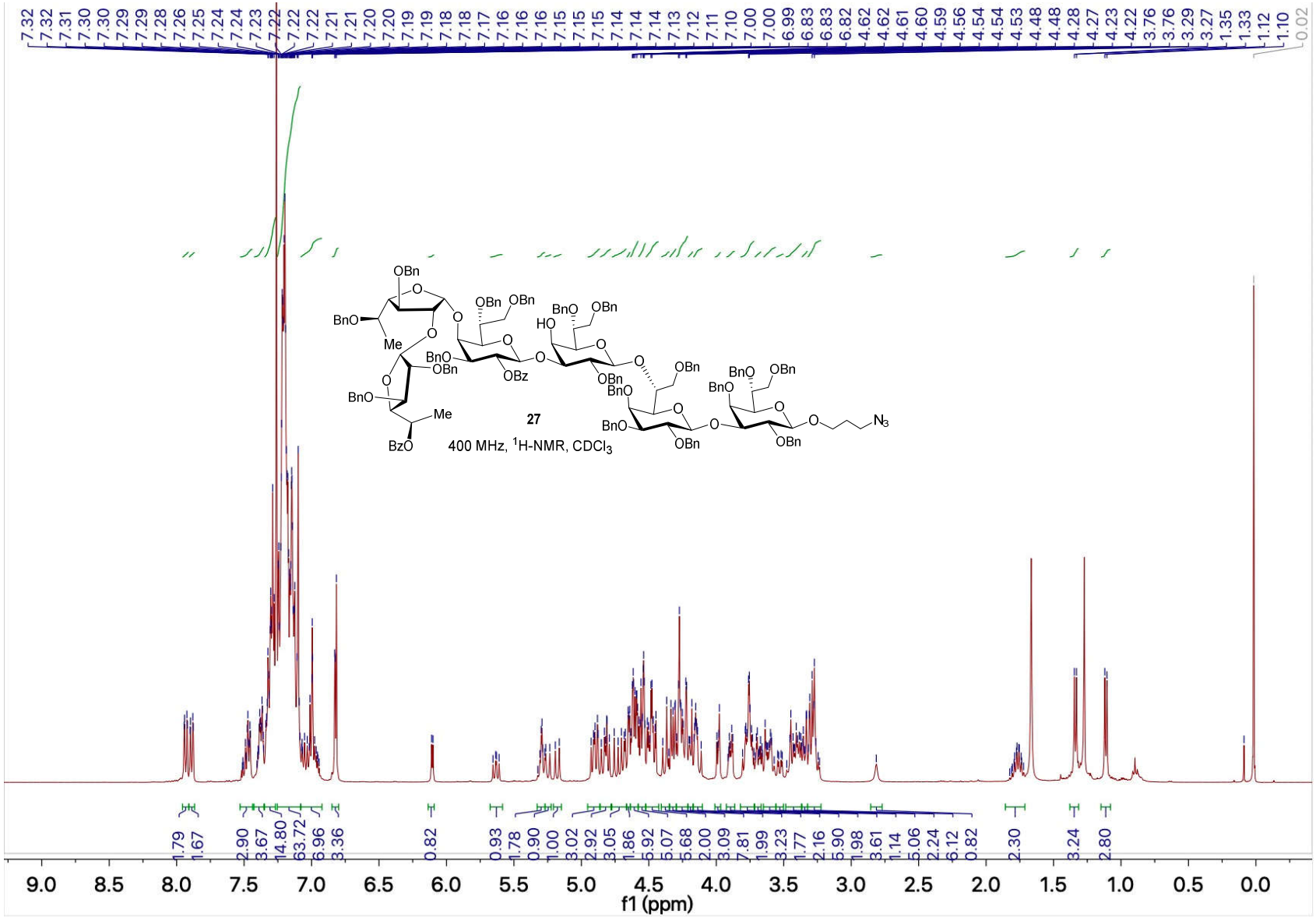

165.95
165.08
155.16
151.58
139.61
139.01
138.51
138.38
138.16
138.05
137.72
132.92
132.80
130.74
130.44
129.98
129.86
128.59
128.52
128.42
128.36
128.23
128.16
128.10
128.00
127.85
127.80
127.75
127.62
127.54
127.47
127.42
127.35
127.14
127.04
117.88
114.51
104.67
100.71
99.18
84.91
84.58
82.50
82.08
81.92
77.48
77.37
77.29
77.16
76.84
76.27
75.54
73.68
73.39
72.88
72.68
72.31
72.26
72.03
71.54
71.12
70.74
70.00
66.29
55.73
16.18
16.04
0.13
OBn
BnO
Me
OBn
OBn
BnO
OPMP
OBz
BnO
OBn
Me
BzO
16c
100 MHz, 13C-NMR, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

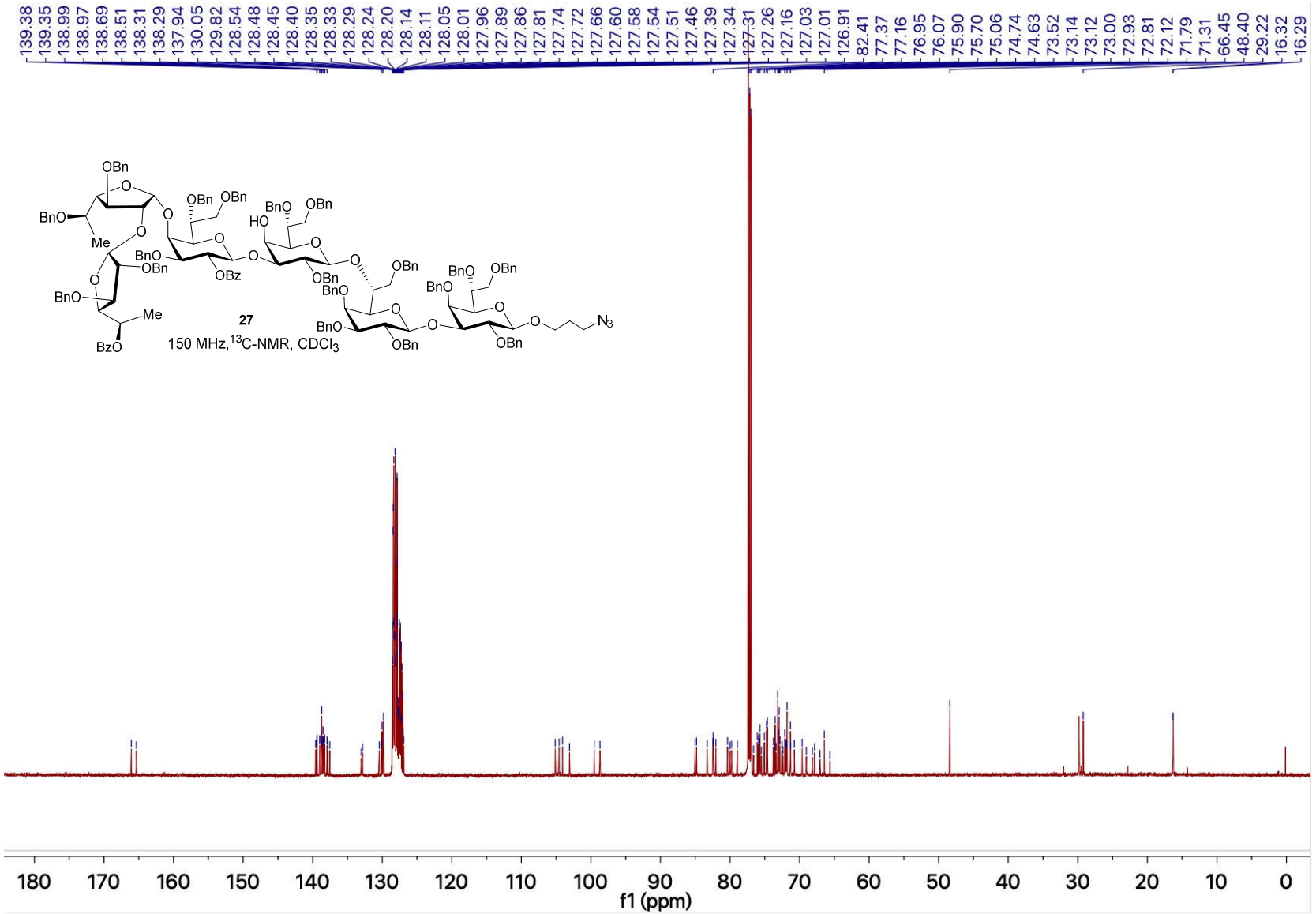

17b
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

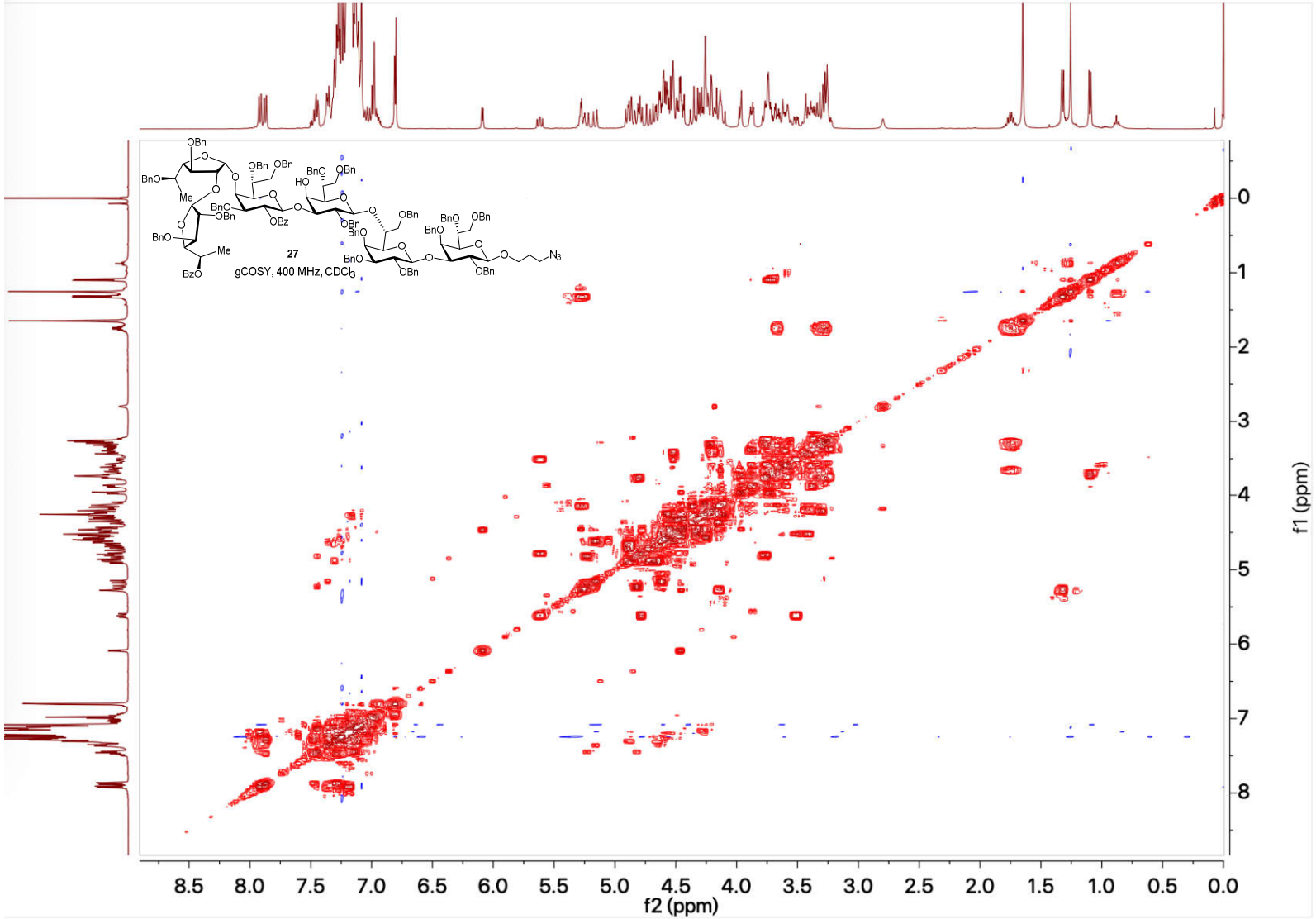

17c
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

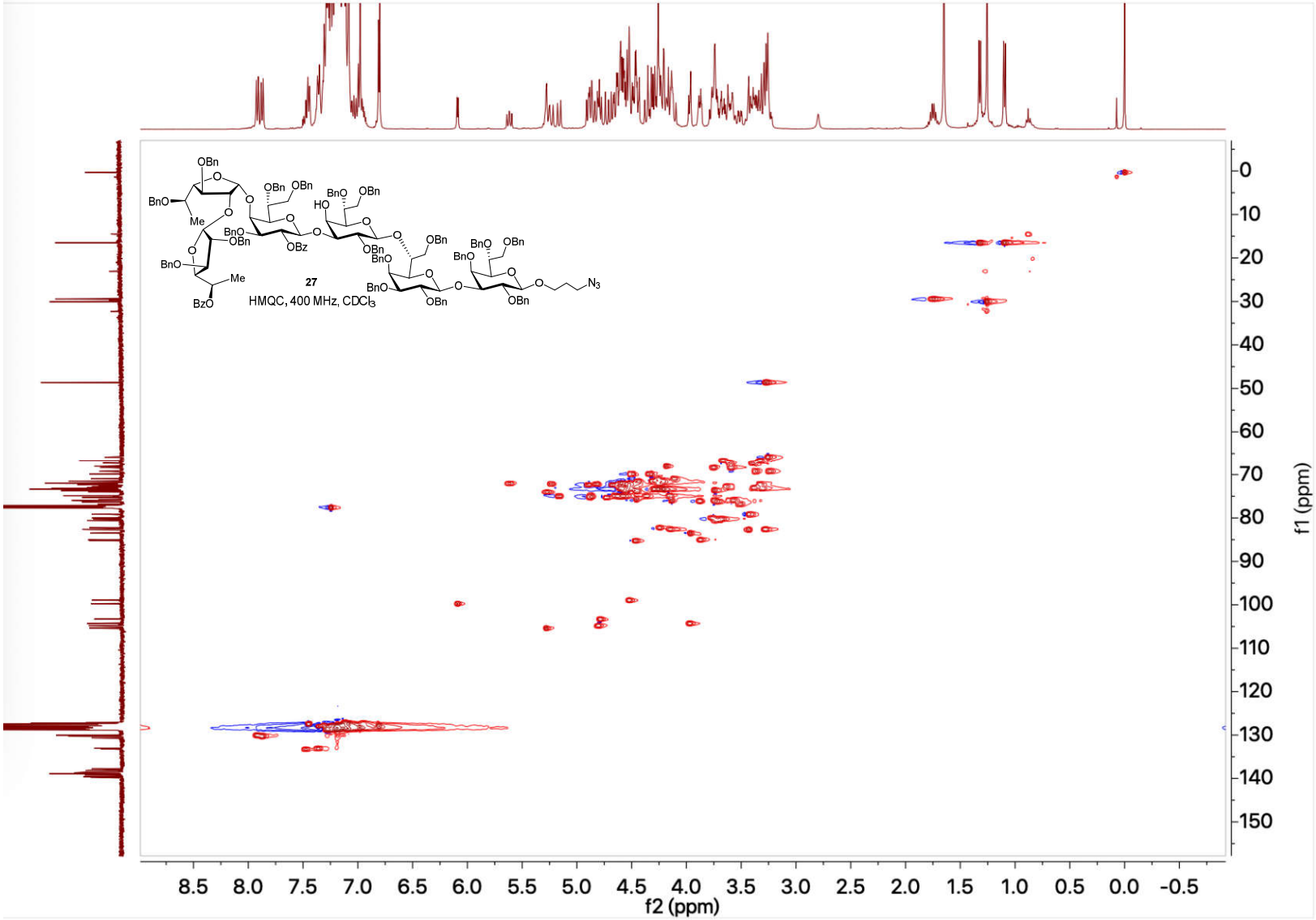

17d
600 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

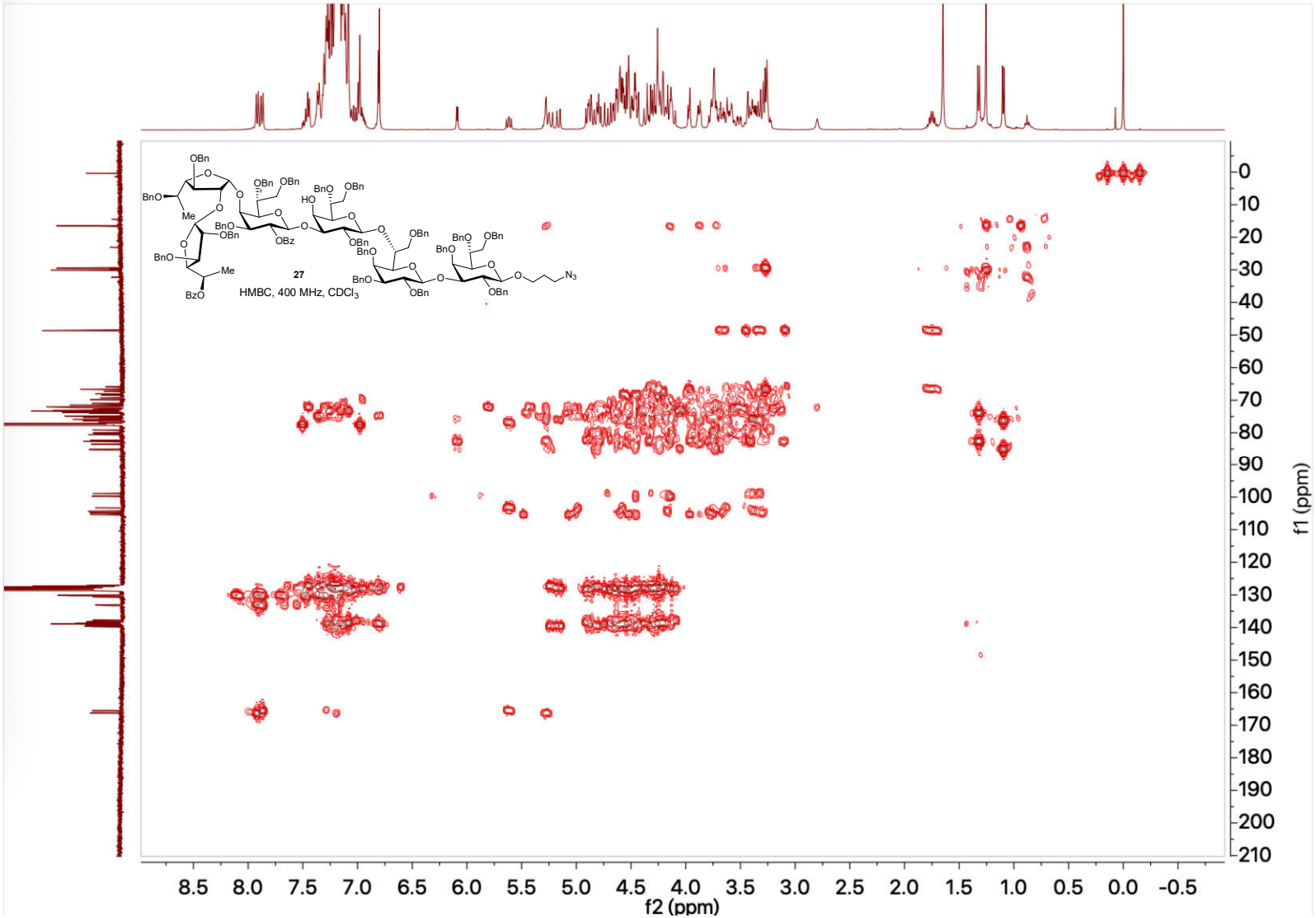

138.09
132.86
130.05
130.03
129.87
129.85
128.56
128.51
128.49
128.45
128.40
128.38
128.35
128.27
128.21
128.19
128.17
128.15
128.13
128.08
128.00
127.94
127.87
127.84
127.80
127.78
127.71
127.62
127.47
127.45
127.40
127.29
127.27
127.25
127.09
104.62
99.30
84.72
84.39
82.40
82.35
82.28
81.92
77.37
77.16
76.95
75.99
74.61
73.46
72.28
72.06
72.03
71.26
71.12
70.88
70.48
24.36
23.50
16.35
16.22
16.12
15.93
14.27
14.19
OBn
BnO
Me
O
OBn
OBn
BnO
SEt
OBz
BnO
OBn
Me
BzO
17d
150 MHz, ^{13}C-NMR, $CDCl_3$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

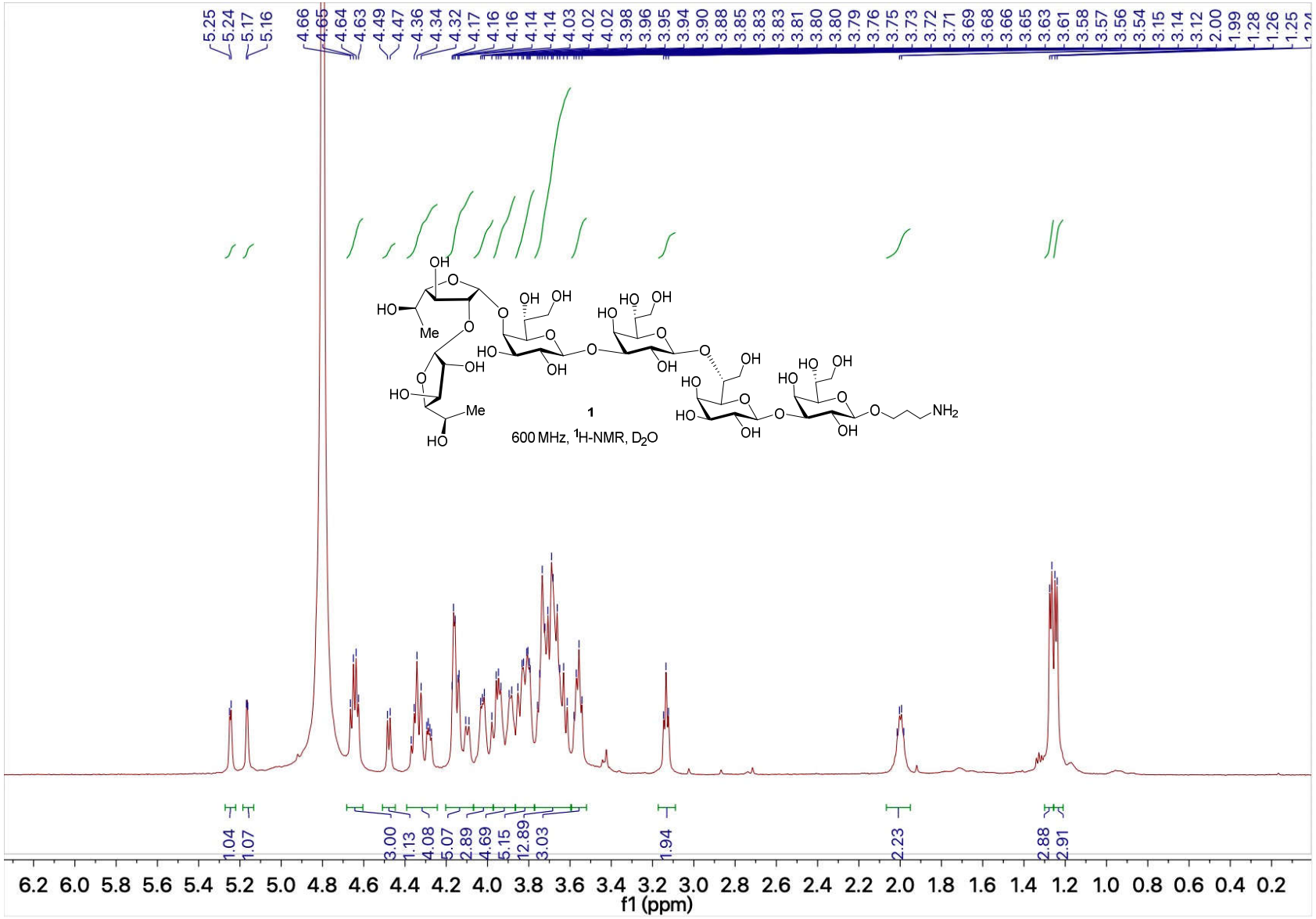

27
400 MHz, ^{1}H-NMR, $CDCl_3$
f1 (ppm)

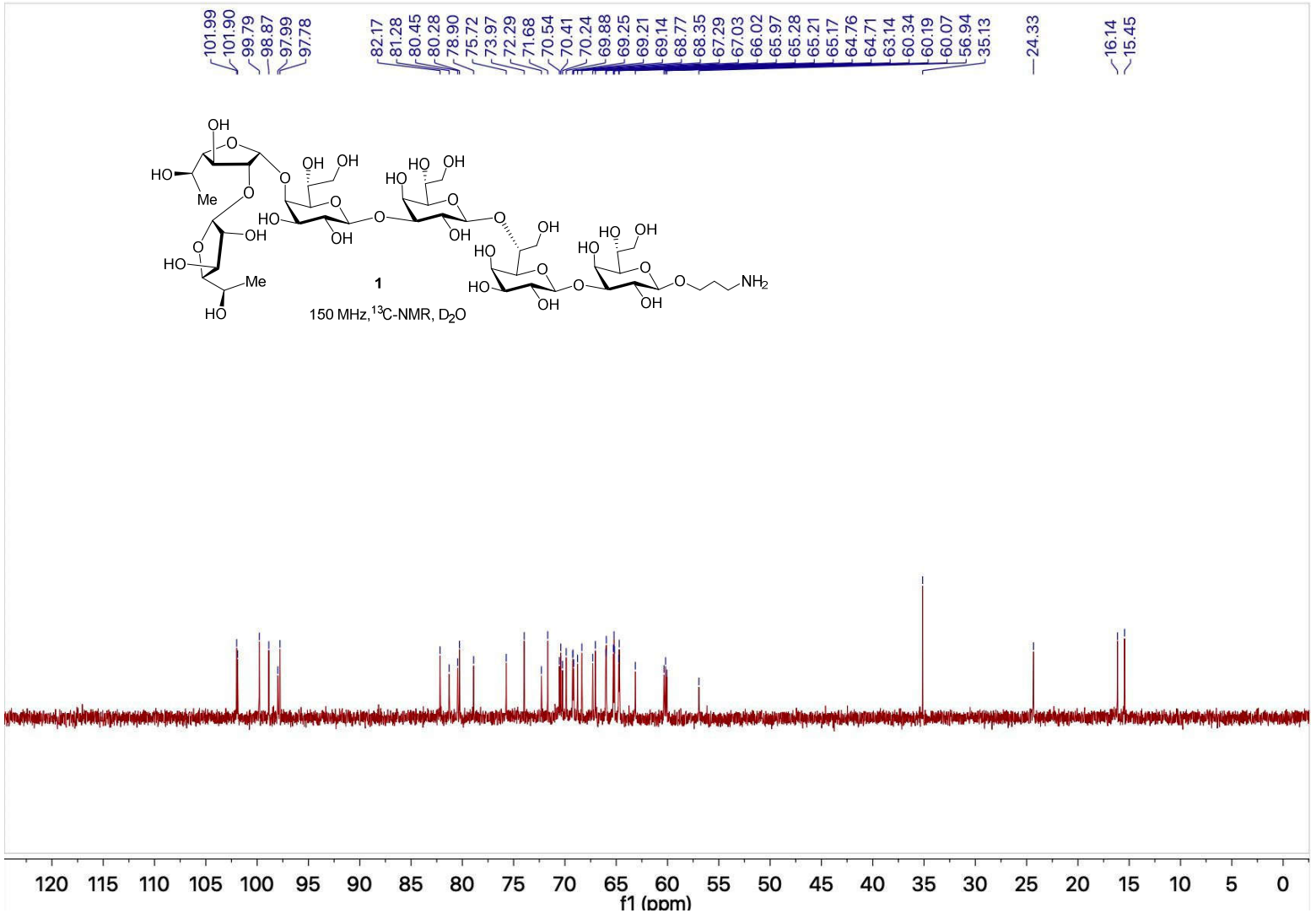

139.38
139.35
138.99
138.97
138.69
138.51
138.31
138.29
137.94
130.05
129.82
128.54
128.48
128.45
128.40
128.35
128.33
128.29
128.24
128.20
128.14
128.11
128.05
128.01
127.96
127.89
127.86
127.81
127.74
127.72
127.66
127.60
127.58
127.54
127.51
127.46
127.39
127.34
127.31
127.26
127.16
127.03
127.01
126.91
82.41
77.37
77.16
76.95
76.07
75.90
75.70
75.06
74.74
74.63
73.52
73.14
73.12
73.00
72.93
72.81
72.12
71.79
71.31
66.45
48.40
29.22
16.32
16.29
27
150 MHz, 13C-NMR, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

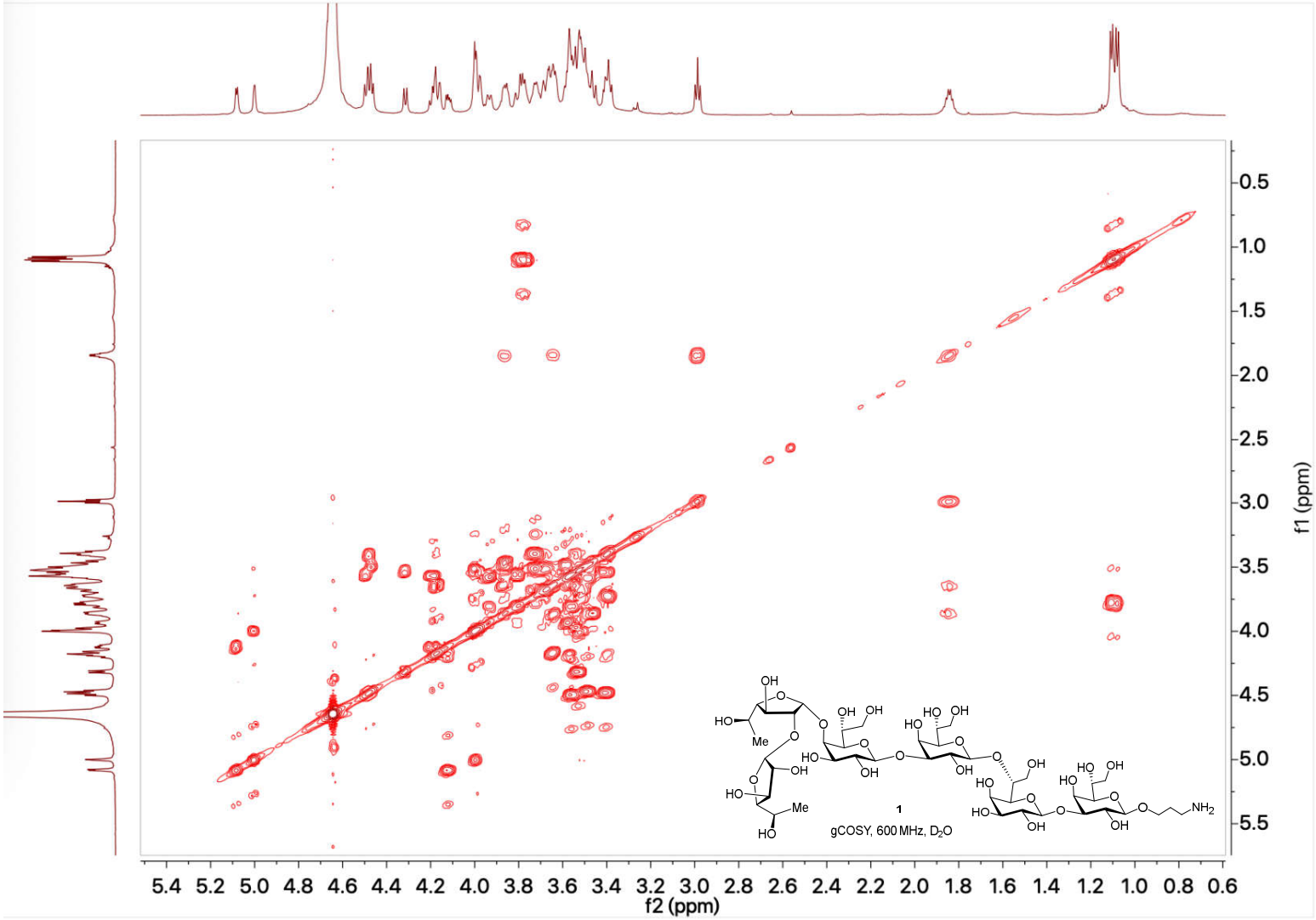

27
gCOSY, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

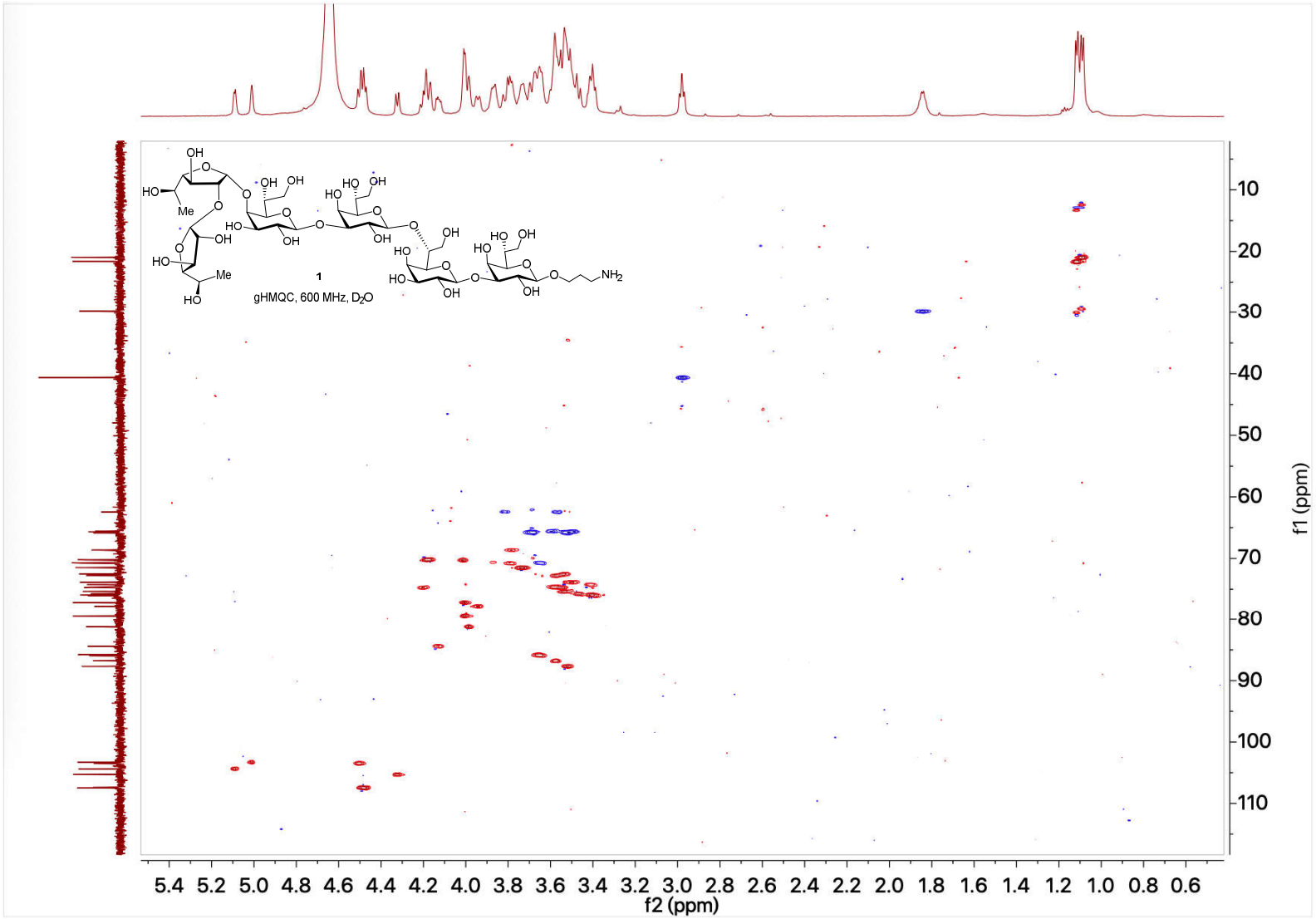

27
HMQC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

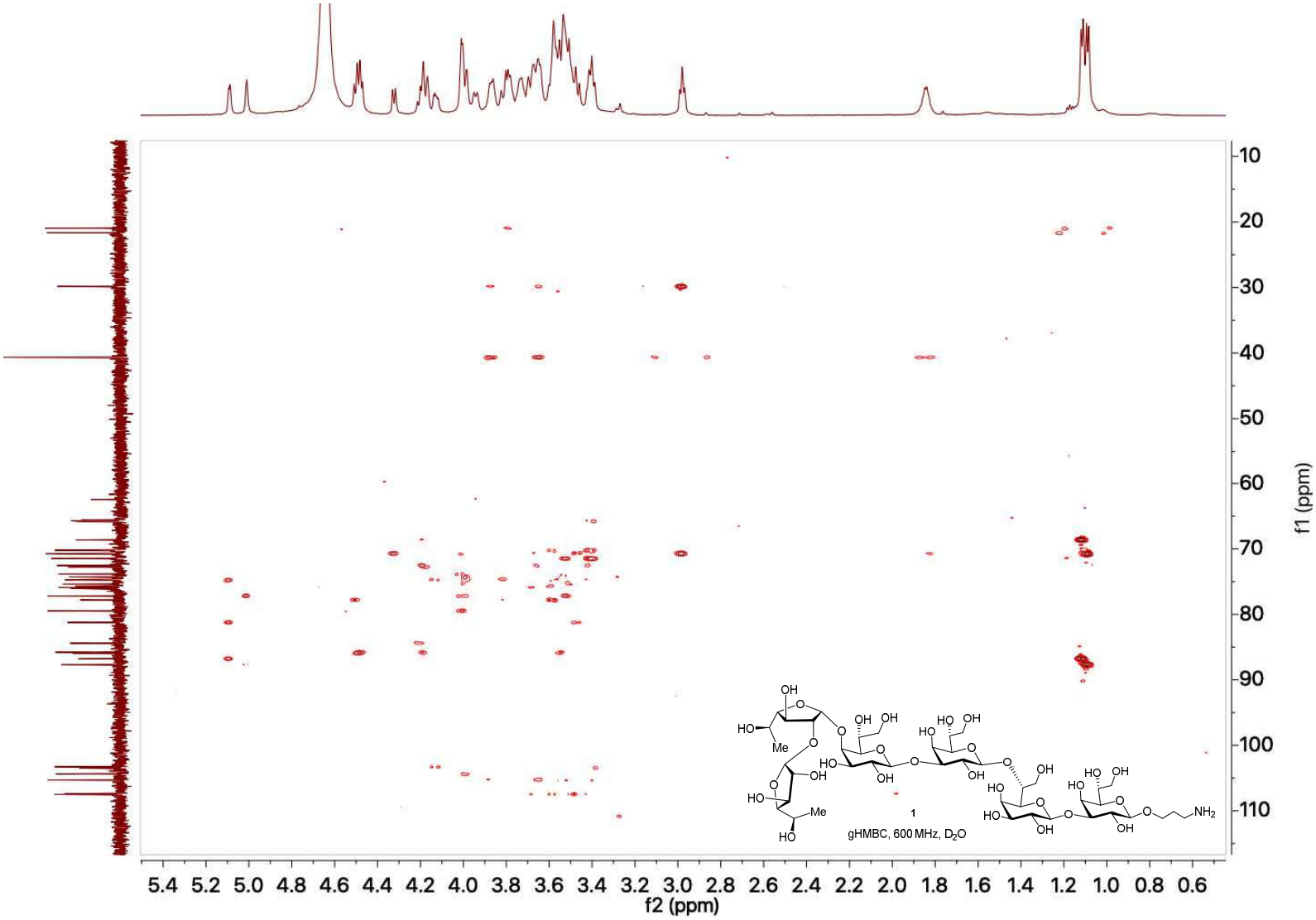

27
HMBC, 400 MHz, CDCl3
f2 (ppm)
f1 (ppm)

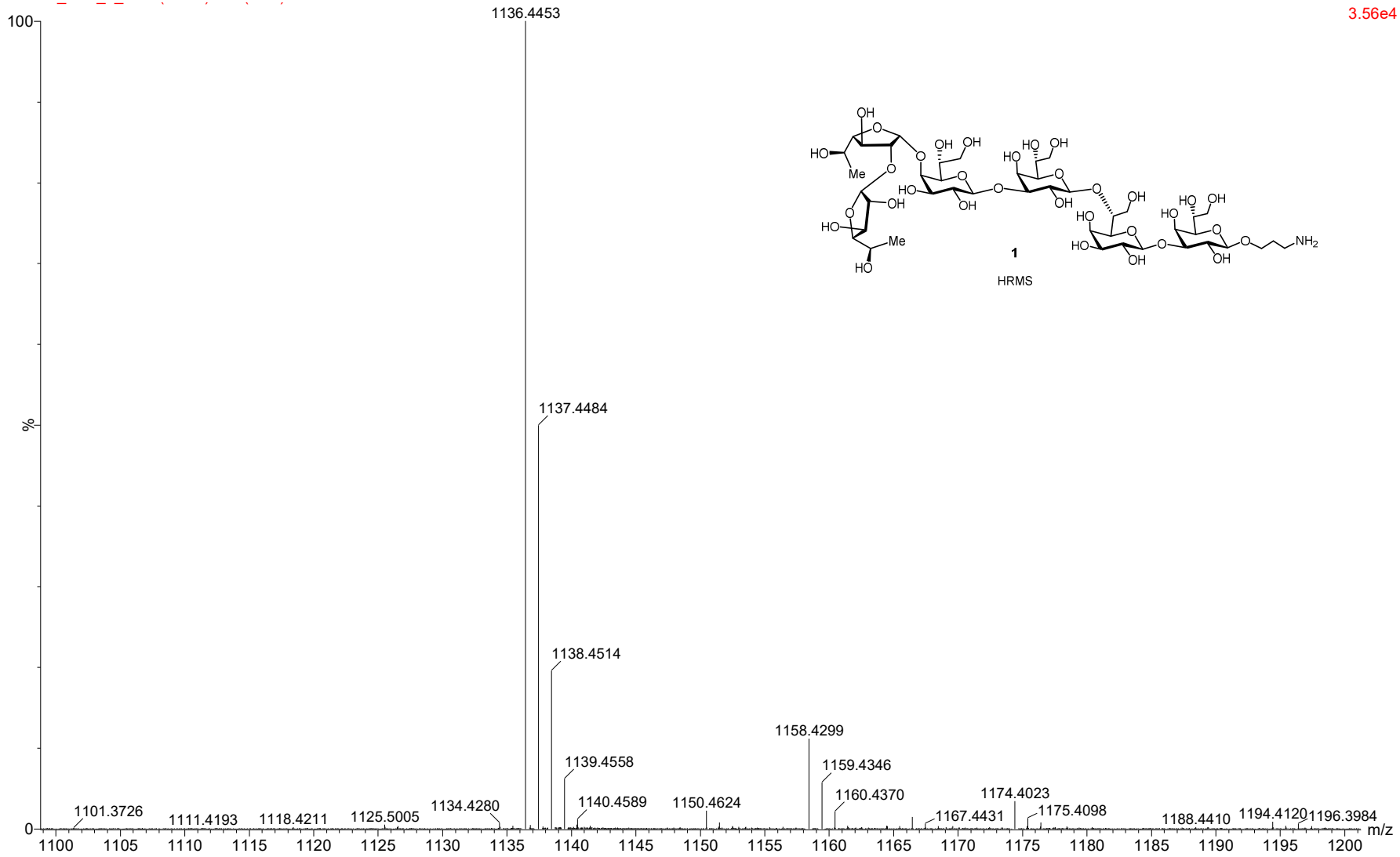

1
600 MHz, ^{1}H-NMR, D_2O
f1 (ppm)


101.99
101.90
99.79
98.87
97.99
97.78
82.17
81.28
80.45
80.28
78.90
75.72
73.97
72.29
71.68
70.54
70.41
70.24
69.88
69.25
69.21
69.14
68.77
68.35
67.29
67.03
66.02
65.97
65.28
65.21
65.17
64.76
64.71
63.14
60.34
60.19
60.07
56.94
35.13
24.33
16.14
15.45
1
150 MHz, 13C-NMR, D2O
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


f1 (ppm)
f2 (ppm)
1
gCOSY, 600 MHz, D2O


1
gHMQC, 600 MHz, D2O
5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
f2 (ppm)
10 20 30 40 50 60 70 80 90 100 110
f1 (ppm)


f2 (ppm)
f1 (ppm)
gHMBC, 600 MHz, D2O
1


3.56e4
100
%
0
1136.4453
1137.4484
1138.4514
1158.4299
1139.4558
1159.4346
1160.4370
1174.4023
1140.4589
1150.4624
1134.4280
1175.4098
1101.3726
1111.4193
1118.4211
1125.5005
1167.4431
1188.4410
1194.4120
1196.3984
m/z
1100
1105
1110
1115
1120
1125
1130
1135
1140
1145
1150
1155
1160
1165
1170
1175
1180
1185
1190
1195
1200
1
HRMS