

One-pot Conversion Reactions of Glycosyl Boranophosphates into Glycosyl Phosphate Derivatives via Acylphosphite Intermediates

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Electronic supplementary information

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General information

All the reactions were conducted under Ar atmosphere unless otherwise noted. Dry organic solvents were prepared by appropriate procedures. ¹H NMR spectra were recorded at 300 MHz with tetramethylsilane (δ 0.0) as an internal standard in CDCl₃. ¹³C NMR spectra were recorded at 75.5 MHz with CDCl₃ (δ 77.0) as an internal standard in CDCl₃. ³¹P NMR spectra were recorded at 121.5 MHz with 85% H₃PO₄ (δ 0.0) as an external standard. COSY and HMQC were used to confirm the NMR peak assignments. Silica gel column chromatography was carried out using spherical, neutral, 63–210 or 40–50 μ m silica gel unless otherwise noted. Analytical TLC was performed on commercial glass plates bearing 0.25 mm layer of silica gel.

Experimental procedures

Boranophosphodiester-linked α -D-Man-(1-*P*-6)-D-Gal derivative¹ and boranophosphodiester-linked β -D-Glc-(1-*P*-6)-D-Glc derivative¹, and dimethylthiuram disulfide (DTD)² was prepared according to the literatures.

1. Synthesis of glycosyl phosphate derivatives

Experimental details for the reactions in Table 1.

(Entry 1)

t-Butyl diphenyl silyl chloride was added to a solution of **1** (64 mg, 50 μ mol, α : β = 96:4) and DTD (32 mg, 150 μ mol) in dry pyridine (1 mL) at rt and the mixture was allowed to stir for 2.5 h. The reaction was quenched with MeOH (1 mL). CHCl₃ (5 mL) was added to the mixture and washed with a saturated NaHCO₃ aqueous solution (5

mL) and 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined, and back-extracted with CHCl₃ (2 × 5 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in CDCl₃, and NMR yield of **2** was estimated by ³¹P NMR.

(Entry 2)

1 (64 mg, 50 μmol, α:β = 96:4) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). DTD (32 mg, 150 μmol) and 2,4,6-triisopropyl benzenesulfonyl chloride (23 mg, 75 μmol) were added successively while stirring, and the mixture was allowed to stir for 2.5 h at rt. The reaction was quenched with a saturated NaHCO₃ aqueous solution (5 mL). CHCl₃ (8 mL) and a saturated NaHCO₃ aqueous solution (3 mL) were added successively to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2 × 8 mL). The aqueous layers were separated, and back-extracted with CHCl₃ (2 × 8 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in CDCl₃, and NMR yield of **2** was estimated by ³¹P NMR.

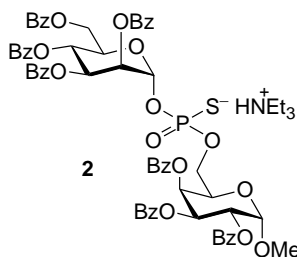
(Entry 3)

1 (63 mg, 50 μmol, α:β = 96:4) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). After adding DTD (32 mg, 150 μmol), Ac₂O (10 μL, 100 μmol) was added to the mixture at 0 °C while stirring. The mixture was warmed to rt after 5 min and allowed to stir for 2.5 h. CHCl₃ (5 mL), a saturated NaHCO₃ aqueous solution (5 mL) and MeOH (1 mL) were added successively to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined, and back-extracted with CHCl₃ (2 × 5 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in CDCl₃, and NMR yield of **2** was estimated by ³¹P NMR.

(Entry 4–6)

1 (63 mg, 50 μmol, α:β = 96:4) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). After adding a sulfurizing reagent (150 μmol, DTD for entry 4, S₈ for entry 5, 3-phenyl 1,2,4-dithiazoline 5-one (POS) for entry 6), PivCl (12 μL, 100 μmol) was added to the mixture at 0 °C while stirring. The mixture was warmed to rt after 5 min and allowed to stir for 2.5 h. The reaction was quenched with a saturated NaHCO₃ aqueous solution (5 mL) at 0 °C. CHCl₃ (5 mL) was added to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined and back-extracted with CHCl₃ (2 × 5 mL). The organic layers were combined, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was dissolved in CDCl₃, and NMR yield of **2** was estimated by ³¹P NMR. The solution was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography using CH₂Cl₂–Et₃N–MeOH (100:0.5:0.5, v/v/v) as an eluent to give **2** (as a colorless oil for Entries 4, 5, and a yellow foam for Entry 6).

Phosphorothioate diester-linked α-D-Man-(1-P-6)-D-Gal derivative (2**)**



¹H NMR (CDCl₃) δ 11.7 (br, 1H), 8.17–7.88 (m, 10H), 7.82–7.72 (m, 4H), 7.62–7.17 (m, 21H), 6.20 (t, *J* = 10.2 Hz, 0.5H), 6.11–5.86 (m, 4.5H), 5.82–5.78 (m, 1H), 5.65 (dd, *J* = 3.6, 10.8 Hz), 5.63 (dd, *J* = 3.8, 10.7 Hz)

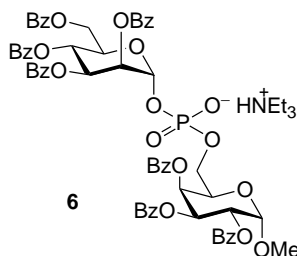
(diastereomers, 1H), 5.29–5.26 (m, 1H), 4.83–4.67 (m, 2H), 4.62–4.08 (m, 4H), 3.52, 3.50 (s, 2 × 1.5H), 3.13 (q, $J = 7.3$ Hz), 3.12 (q, $J = 7.3$ Hz) (diastereomers, 6H), 1.35 (t, $J = 7.2$ Hz, 9H).

^{13}C NMR (CDCl_3) δ 166.1, 166.0, 165.6, 165.5, 165.4, 165.3, 165.2, 165.1, 165.0 (C=O), 133.2, 133.1, 133.0, 132.9, 132.8, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 129.1, 129.0, 128.4, 128.3, 128.2, 128.1 (Ar), 97.4 (CH), 94.4 (CH, $J_{\text{P-C}} = 4.8$ Hz), 93.7 (CH, $J_{\text{P-C}} = 5.1$ Hz), 70.5 (CH, $J_{\text{P-C}} = 4.2$ Hz), 70.4 (CH, $J_{\text{P-C}} = 2.3$ Hz), 70.3 (CH), 70.1 (CH), 69.6 (CH), 69.5 (CH), 69.5 (CH), 69.3 (CH), 69.1 (CH), 68.9 (CH), 68.9 (CH), 68.7 (CH), 68.0 (CH, $J_{\text{P-C}} = 10.2$ Hz), 67.4 (CH, $J_{\text{P-C}} = 8.2$ Hz), 66.7 (CH), 66.5 (CH), 64.3 (CH_2 , $J_{\text{P-C}} = 4.0$ Hz), 63.7 (CH_2 , $J_{\text{P-C}} = 5.1$ Hz), 62.7 (CH_2), 62.5 (CH_2), 55.7 (CH_3), 55.7 (CH_3), 45.7 (CH_2), 8.6 (CH_3).

^{31}P NMR (CDCl_3) δ 57.0, 56.7.

HRMS (ESI): calcd for $\text{C}_{62}\text{H}_{52}\text{O}_{20}\text{PS}^-$ [M] $^-$: 1179.25158; found: 1179.25050.

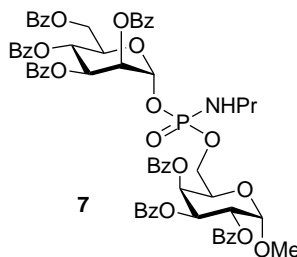
Phosphodiester-linked α -D-Man-(1-*P*-6)-D-Gal derivative (6)



1 (63 mg, 50 μmol , $\alpha:\beta = 96:4$) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). After adding CBr_4 (33 mg, 101 μmol), PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 40 min. A saturated NaHCO_3 aqueous solution (5 mL) was added to the mixture at 0 $^\circ\text{C}$. After 15 min, CHCl_3 (5 mL) was added to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2 × 5 mL). The aqueous layers were combined and back-extracted with CHCl_3 (2 × 5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2 – Et_3N – MeOH (100:1:0–100:1:2, v/v/v) as an eluent. The fractions containing **6** were collected and concentrated under reduced pressure. The residue was dissolved in CHCl_3 (5 mL) and washed with a 1 M TEAB aqueous solution (5 mL). The aqueous layer was back-extracted with CHCl_3 (2 × 5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to give **6** as a colorless foam (57 mg, 45 μmol , 90%, $\alpha:\beta = 99:1$). The ^1H and ^{31}P NMR spectra were identical to the reported data².

^1H NMR (CDCl_3) δ 12.2 (br, 1H), 8.16–7.16 (m, 35H, Ar), 6.13–5.89 (m, 4H), 5.78 (t, $J = 2.6$ Hz, 1H), 5.70 (dd, $J = 2.1, 8.1$ Hz, 1H), 5.64 (dd, $J = 3.4, 10.4$ Hz, 1H), 5.26 (d, $J = 3.6$ Hz, 1H), 4.71 (dt, $J = 2.9, 9.8$ Hz, 1H), 4.63–4.55 (m, 2H), 4.35–4.22 (m, 2H), 4.19–4.08 (m, 1H), 3.49 (s, 3H), 3.16–3.02 (m, 6H), 1.37 (t, $J = 7.2$ Hz, 9H).

Phosphoramidate-linked α -D-Man-(1-*P*-6)-D-Gal derivative (7)



1 (63 mg, 49 μmol , $\alpha:\beta = 99:1$) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was

warmed to rt after 5 min and allowed to stir for further 35 min. Propyl amine (62 μL , 750 μmol) was added to the mixture at 0 $^{\circ}\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 15 min. A 5.5 M *t*-BuOOH decane solution (100 μL , 550 μmol) was added to the mixture at 0 $^{\circ}\text{C}$. After 10 min the reaction was quenched with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL) while keeping at 0 $^{\circ}\text{C}$. CHCl_3 (5 mL) was added to the mixture, and the organic layer was separated, washed successively with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL), and a saturated NaHCO_3 aqueous solution (5 mL). The aqueous layers were combined and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on NH silica gel (100–200 mesh) using Toluene–AcOEt (100:0–80:20, v/v) as an eluent to give **7** as a colorless foam (42 mg, 35 μmol , 70%, β isomer was not detected by ^{31}P NMR).

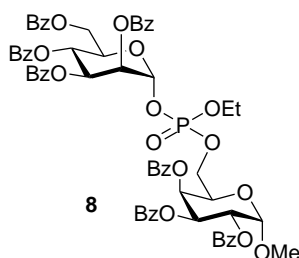
^1H NMR (CDCl_3) δ 8.15–7.92 (m, 10H), 7.86–7.72 (m, 4H), 7.64–7.16 (m, 21H), 6.21 (t, $J = 10.1$ Hz), 6.13 (t, $J = 10.1$ Hz) (diastereomers, 1H), 6.06–5.84 (m, 4H), 5.81–5.74 (m, 1H), 5.68 (dd, $J = 3.6, 10.8$ Hz), 5.64 (dd, $J = 3.6, 10.5$ Hz) (diastereomers, 1H), 5.31 (d, $J = 3.3$ Hz), 5.30 (d, $J = 3.3$ Hz) (diastereomers, 1H) 4.77–4.50 (m, 3.5H), 4.46–4.14 (m, 2.5H), 3.51, 3.47 (s, 2×1.5 H), 3.07–2.81 (m, 3H), 1.64–1.40 (m, 2H), 0.95 (t, $J = 7.4$ Hz, 1.5H), 0.84 (t, $J = 7.4$ Hz, 1.5H).

^{13}C NMR (CDCl_3) δ 166.0, 165.5, 165.4, 165.3, 165.0 (C=O), 133.7, 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2 (Ar), 97.6 (CH), 97.5 (CH), 94.5 (CH, $J_{\text{P-C}} = 5.6$ Hz), 94.3 (CH, $J_{\text{P-C}} = 5.4$ Hz), 70.5 (CH), 70.4 (CH), 69.9 (CH, $J_{\text{P-C}} = 3.6$ Hz), 69.8 (CH, $J_{\text{P-C}} = 3.3$ Hz), 69.4 (CH), 69.3 (CH), 69.0 (CH), 69.0 (CH), 68.2 (CH), 68.1 (CH), 67.7 (CH, $J_{\text{P-C}} = 7.6$ Hz), 67.4 (CH, $J_{\text{P-C}} = 10.6$ Hz), 66.0 (CH), 64.8 (CH_2 , $J_{\text{P-C}} = 4.8$ Hz), 63.9 (CH_2 , $J_{\text{P-C}} = 4.6$ Hz), 62.3 (CH_2), 62.2 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 43.2 (CH_2 , $J_{\text{P-C}} = 6.4$ Hz), 24.9 (CH_2 , $J_{\text{P-C}} = 2.6$ Hz), 24.8 (CH_2 , $J_{\text{P-C}} = 2.8$ Hz), 11.1 (CH_3), 11.0 (CH_3).

^{31}P NMR (CDCl_3) δ 8.0, 7.2.

HRMS (ESI): calcd for $\text{C}_{65}\text{H}_{61}\text{NO}_{20}\text{P}^+$ $[\text{M}+\text{H}]^+$: 1206.35191; found: 1206.35315.

Phosphotriester-linked α -D-Man-(1-P-6)-D-Gal derivative (8**)**



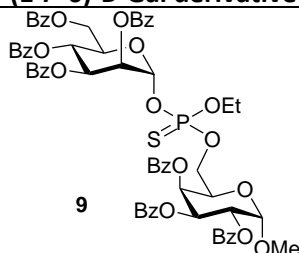
1 (63 mg, 50 μmol , $\alpha:\beta = 99:1$) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^{\circ}\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. Ethanol (29 μL , 500 μmol) was added to the mixture at 0 $^{\circ}\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 15 min. A 5.5 M *t*-BuOOH decane solution (500 μL , 2.75 mmol) was added to the mixture at 0 $^{\circ}\text{C}$ and the mixture was warmed to rt after 5 min. The mixture was allowed to stir further 5 min, and the reaction was quenched with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL) at 0 $^{\circ}\text{C}$. CHCl_3 (5 mL) was added to the mixture, and the organic layer was separated, washed successively with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL), and a saturated NaHCO_3 aqueous solution (5 mL). The aqueous layers were combined and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using Toluene–AcOEt (8:1–4:1, v/v) as an eluent to give **8** as a colorless foam (48 mg, 40 μmol , 80%, β isomer was not detected by ^{31}P NMR).

^1H NMR (CDCl_3) δ 8.14–7.92 (m, 10H), 7.85–7.72 (m, 4H), 7.63–7.31 (m, 17H), 7.30–7.17 (m, 4H), 6.19 (t, J = 10.5 Hz), 6.12 (t, J = 10.4 Hz) (diastereomers, 1H), 6.03–5.86 (m, 4H), 5.82–5.77 (m, 1H), 5.70–5.62 (m, 1H), 5.30 (d, J = 3.3 Hz, 1H), 4.76–4.60 (m, 2H), 4.59–4.49 (m, 1.5 H), 4.45–4.12 (m, 4.5 H), 3.51, 3.50 (s, $2 \times 1.5\text{H}$), 1.38 (dt, J = 0.9, 10.2 Hz, 1.5H), 1.28 (t, 1.5H, J = 7.4 Hz).

^{13}C NMR (CDCl_3) δ 166.0, 165.9, 165.5, 165.3, 165.2, 164.9 (C=O), 133.6, 133.5, 133.3, 133.2, 133.1, 133.0, 129.9, 129.8, 129.7, 129.6, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2 (Ar), 97.5 (CH), 95.3 (CH, $J_{\text{P-C}}$ = 5.4 Hz), 95.2 (CH, $J_{\text{P-C}}$ = 5.4 Hz), 70.6 (CH), 70.6 (CH), 69.6 (CH), 69.5 (CH), 69.3 (CH), 69.2 (CH), 69.1 (CH), 68.9 (CH), 68.8 (CH), 68.2 (CH), 68.1 (CH), 67.6 (CH, $J_{\text{P-C}}$ = 6.4 Hz), 67.4 (CH, $J_{\text{P-C}}$ = 7.2 Hz), 66.1 (CH_2 , $J_{\text{P-C}}$ = 4.6 Hz), 65.9 (CH), 65.9 (CH), 65.7 (CH_2 , $J_{\text{P-C}}$ = 4.6 Hz), 65.1 (CH_2 , $J_{\text{P-C}}$ = 5.7 Hz), 65.1 (CH_2 , $J_{\text{P-C}}$ = 6.0 Hz), 62.2 (CH_2), 62.2 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 16.1 (CH_3 , $J_{\text{P-C}}$ = 6.9 Hz), 15.9 (CH_3 , $J_{\text{P-C}}$ = 6.6 Hz).

^{31}P NMR (CDCl_3) δ -3.0, -3.2. HRMS (ESI): calcd for $\text{C}_{64}\text{H}_{58}\text{O}_{21}\text{P}^+$ [$\text{M}+\text{H}$] $^+$: 1193.32028; found: 1193.32141.

Phosphorothioate triester-linked α -D-Man-(1-*P*-6)-D-Gal derivative (9)



1 (63 mg, 50 μmol , $\alpha:\beta$ = 99:1) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. Ethanol (29 μL , 500 μmol) was added to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 20 min. DTD (32 mg, 150 μmol) was added to the mixture. After 30 min, CHCl_3 (5 mL) was added and the mixture was washed with saturated NaHCO_3 aqueous solutions (3×5 mL). The aqueous layers were combined, and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt –hexane (1:4–1:2, v/v) as an eluent to give **9** as a colorless foam (48 mg, 40 μmol , 79%, β isomer was not detected by ^{31}P NMR)

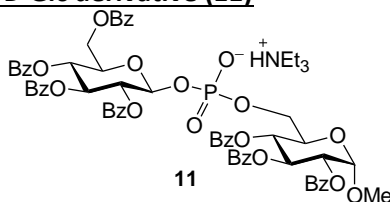
^1H NMR (CDCl_3) δ 8.14–7.93 (m, 10H), 7.85–7.72 (m, 4H), 7.62–7.32 (m, 17H), 7.31–7.17 (m, 4H), 6.21 (t, J = 10.1 Hz), 6.15 (t, J = 10.1 Hz) (diastereomers, 1H) 6.05–5.95 (m, 3H), 5.93–5.85 (m, 1H), 5.79–5.76 (m, 1H), 5.70–5.61 (m, 1H), 5.32 (d, J = 3.6 Hz), 5.30 (d, J = 3.6 Hz) (diastereomers, 1H), 4.77–4.50 (m, 3.5H), 4.45–4.11 (m, 4.5H), 3.52, 3.51 (s, $2 \times 1.5\text{H}$), 1.34 (dt, J = 0.9, 7.1 Hz), 1.30 (dt, J = 1.0, 7.1 Hz) (diastereomers, 3H).

^{13}C NMR (CDCl_3) δ 166.0, 165.9, 165.5, 165.4, 165.3, 165.2, 165.0, 164.9 (C=O), 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 130.0, 129.9, 129.8, 129.7, 129.6, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2 (Ar), 97.6 (CH), 97.5 (CH), 95.6 (CH, $J_{\text{P-C}}$ = 4.9 Hz), 95.5 (CH, $J_{\text{P-C}}$ = 4.8 Hz), 70.7 (CH), 70.6 (CH), 69.7 (CH), 69.6 (CH), 69.5 (CH), 69.4 (CH), 69.3 (CH), 69.0 (CH), 68.8 (CH), 68.3 (CH), 68.2 (CH), 67.4 (CH, $J_{\text{P-C}}$ = 2.9 Hz), 67.3 (CH, $J_{\text{P-C}}$ = 4.6 Hz), 66.2 (CH_2 , $J_{\text{P-C}}$ = 3.7 Hz), 66.1 (CH), 66.0 (CH), 65.9 (CH_2 , $J_{\text{P-C}}$ = 3.2 Hz), 65.4 (CH, $J_{\text{P-C}}$ = 5.1 Hz), 62.3 (CH_2), 62.2 (CH_2), 55.9 (CH_3), 55.8 (CH_3), 15.9 (CH_3 , $J_{\text{P-C}}$ = 7.5 Hz), 15.7 (CH_3 , $J_{\text{P-C}}$ = 7.7 Hz).

^{31}P NMR (CDCl_3) δ 67.0, 66.9.

HRMS (ESI): calcd for $\text{C}_{64}\text{H}_{58}\text{O}_{20}\text{PS}^+$ [$\text{M}+\text{H}$] $^+$: 1209.29743; found: 1209.29859.

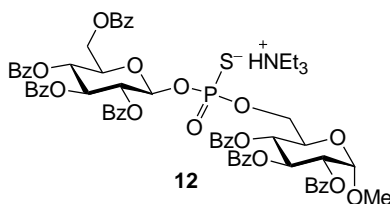
Phosphodiester-linked β -D-Glc-(1-P-6)-D-Glc derivative (11)



10 (63 mg, 50 μ mol, α : β =2:98) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). After adding CBr_4 (34 mg, 101 μ mol), PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 40 min. Water (0.5 mL) and triethylamine (0.5 mL) were added concurrently to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 30 min, and CHCl_3 (5 mL), a 1 M TEAB buffer (5 mL) were added successively to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2×5 mL). The aqueous layers were separated, and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2 - Et_3N - MeOH (100:1:0-100:1:2, v/v/v) as an eluent. The fractions containing **11** were collected and concentrated under reduced pressure. The residue was dissolved in CHCl_3 (5 mL) and washed with a 1 M TEAB aqueous solution (5 mL). The aqueous layer was back-extracted with CHCl_3 (5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to give **11** as a slightly yellow foam (54 mg, 43 μ mol, 86%, α : β = 2:98). The ^1H and ^{31}P NMR spectra were identical to the reported data².

^1H NMR (CDCl_3) δ 12.2 (br, 1H), 8.13-7.18 (m, 35H, Ar), 5.98 (t, J = 9.5 Hz, 1H), 5.87 (t, J = 9.8 Hz, 1H), 5.76-5.66 (m, 2H), 5.55 (dd, J = 8.0, 9.5 Hz, 1H), 5.23 (t, J = 9.8 Hz, 1H), 5.03-4.95 (m, 2H), 4.61 (dd, J = 3.2, 12.2 Hz, 1H), 4.40 (dd, J = 5.6, 12.3 Hz, 1H), 4.26-4.18 (m, 1H), 4.05-3.87 (m, 3H), 3.33 (s, 3H), 3.01-2.88 (m, 6H), 1.23 (t, J = 7.5 Hz, 9H).

Phosphorothioate diester-linked β -D-Glc-(1-P-6)-D-Glc derivative (12)



10 (63 mg, 50 μ mol, α : β =2:98) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). After adding POS (15 mg, 75 μ mol), PivCl (12 μ L, 100 μ mol) was added to the mixture at -30 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. Water (0.5 mL) and triethylamine (0.5 mL) were added concurrently to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 2.5 h. CHCl_3 (5 mL), a 1 M TEAB buffer (5 mL) were added successively to the mixture. The organic layer was separated, and washed with 1 M TEAB aqueous solutions (2×5 mL). The aqueous layers were separated, and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on NH silica gel (100-200 mesh) using CH_2Cl_2 -pyridine- MeOH (100:1:2-100:1:8) and CH_2Cl_2 - Et_3N - MeOH (100:1:4-100:1:8) as an eluent. The fractions containing **12** were collected and concentrated under reduced pressure. The residue was dissolved in AcOEt (5 mL) and washed with 1 M TEAB aqueous solutions (6×5 mL). The aqueous layers were combined, and back-extracted with AcOEt (5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure to give **12** as a yellow foam (58 mg, 45 μ mol, 91%, α : β = 1:99).

^1H NMR (CDCl_3) δ 12.0 (br, 1H), 8.12-7.79 (m, 14.5H), 7.62-7.23 (m, 20.5H), 6.03 (t, J = 9.6 Hz, 0.5H), 5.96-5.82

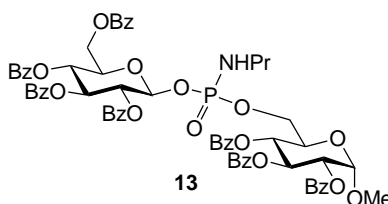
(m, 2.5H), 5.74–5.54 (m, 2H), 5.41 (t, $J = 9.6$ Hz, 0.5H), 5.18–5.10 (m, 1H), 4.99–4.90 (m, 1H), 4.81 (dd, $J = 3.6, 10.2$ Hz, 0.5H), 4.65–4.53 (m, 1H), 4.46 (dd, $J = 5.1, 12.3$ Hz), 4.37 (dd, $J = 4.7, 12.2$ Hz) (diastereomers, 1H), 4.30–4.09 (m, 2.5H), 4.05–3.93 (m, 1H), 3.69 (t, $J = 7.4$), 3.66 (t, $J = 7.5$ Hz) (diastereomers, 0.5H), 3.39, 3.31 (s, 2×1.5 H), 2.92 (q, $J = 7.3$ Hz, 6H), 1.19 (t, $J = 7.4$ Hz, 9H).

^{13}C NMR (CDCl_3) δ 166.1, 166.0, 165.8, 165.7, 165.6, 165.2, 165.1, 165.0 (C=O), 133.3, 133.2, 133.1, 133.0, 132.9, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 128.2 (Ar), 96.9 (CH, $J_{\text{P-C}} = 4.0$ Hz), 96.6 (CH, $J_{\text{P-C}} = 4.2$ Hz), 96.5 (CH), 96.1 (CH), 73.3 (CH), 73.2 (CH), 72.4 (CH), 72.2 (CH), 72.0 (CH), 71.8 (CH), 71.7 (CH), 70.9 (CH), 70.7 (CH), 69.6 (CH), 69.4 (CH), 69.1 (CH), 69.1 (CH), 68.7 (CH), 68.6 (CH), 68.5 (CH), 68.4 (CH), 65.0 (CH, $J_{\text{P-C}} = 4.5$ Hz), 64.6 (CH, $J_{\text{P-C}} = 4.3$ Hz), 63.0 (CH_2), 62.9 (CH_2), 55.4 (CH_3), 55.2 (CH_3), 45.4 (CH_2), 8.4 (CH_3).

^{31}P NMR (CDCl_3) δ 58.4, 58.1.

HRMS (ESI): calcd for $\text{C}_{62}\text{H}_{52}\text{O}_{20}\text{PS}^-$ $[\text{M}]^-$: 1179.25158; found: 1179.25052.

Phosphoramidate-linked β -D-Glc-(1-P-6)-D-Glc derivative (13)



10 (63 mg, 50 μmol , $\alpha:\beta = 2:98$) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. Propyl amine (62 μL , 750 μmol) was added to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 15 min. A 5.5 M *t*-BuOOH decane solution (100 μL , 550 μmol) was added to the mixture at 0 $^\circ\text{C}$. After 10 min, the reaction was quenched with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL) while keeping at 0 $^\circ\text{C}$. CHCl_3 (5 mL) was added to the mixture and the organic layer was separated, washed with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL), and a saturated NaHCO_3 aqueous solution (5 mL). The aqueous layers were combined and back-extracted with CHCl_3 (2×5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using Toluene–AcOEt–pyridine (100:0:0.5–75:25:0.5, v/v/v) as an eluent to give **13** as a colorless oil (42 mg, 35 μmol , 70%, $\alpha:\beta = 1:99$).

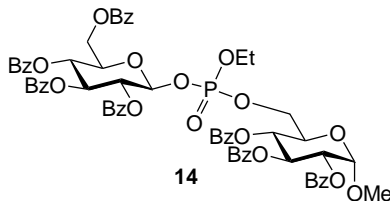
^1H NMR (CDCl_3) δ 8.08–7.80 (m, 14H), 7.59–7.26 (m, 21H), 6.10 (t, $J = 9.9$ Hz), 6.02 (t, $J = 9.8$ Hz) (diastereomers, 1H), 5.90 (t, $J = 9.8$ Hz, 1H), 5.74–5.57 (m, 2H), 5.52 (t, $J = 9.8$ Hz), 5.44 (dd, $J = 7.9, 9.8$ Hz) (diastereomers, 1H), 5.30–5.15 (m), 5.09–4.99 (m) (diastereomers, 3H), 4.68–4.58 (m, 1H), 4.51–4.41 (m, 1H), 4.33–4.10 (m), 4.02–3.91 (m, 4H), 3.38, 3.31 (s, diastereomers, 3H), 2.88–2.56 (m, 3H), 1.46–1.08 (m, 2H), 0.75 (t, $J = 7.4$ Hz), 0.57 (t, $J = 7.5$ Hz) (diastereomers, 3H).

^{13}C NMR (CDCl_3) δ 166.0, 165.9, 165.7, 165.6, 165.5, 165.3, 165.1, 165.0, 164.9 (C=O), 133.5, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.2, 129.0, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3 (Ar), 96.9 (CH), 96.7 (CH), 96.0 (CH, $J_{\text{P-C}} = 5.7$ Hz), 95.9 (CH, $J_{\text{P-C}} = 4.8$ Hz), 72.9 (CH), 72.8 (CH), 72.6 (CH), 72.5 (CH), 71.8 (CH), 71.7 (CH), 70.3 (CH), 69.0 (CH), 68.8 (CH), 68.5 (CH), 68.0 (CH, $J_{\text{P-C}} = 9.4$ Hz), 64.9 (CH_2), 64.8 (CH_2), 64.7 (CH_2), 62.6 (CH_2), 62.6 (CH_2), 55.6 (CH_3), 55.4 (CH_3), 43.0 (CH_2), 42.8 (CH_2), 24.5 (CH_2 , $J_{\text{P-C}} = 6.6$ Hz), 10.9 (CH_3), 10.7 (CH_3).

^{31}P NMR δ 9.3, 8.3.

HRMS (ESI): calcd for $\text{C}_{65}\text{H}_{61}\text{NO}_{20}\text{P}^+$ $[\text{M}+\text{H}]^+$: 1206.35191; found: 1206.35238.

Phosphotriester-linked β -D-Glc-(1-P-6)-D-Glc derivative (14)



10 (63 mg, 50 μ mol, α : β =2:98) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^{\circ}$ C while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. EtOH (88 μ L, 1.5 mmol) was added to the mixture at 0 $^{\circ}$ C, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 15 min. A 5.5 M *t*-BuOOH decane solution (500 μ L, 2.75 mmol) was added to the mixture at 0 $^{\circ}$ C and the mixture was allowed to stir for 5 min. CHCl_3 (5 mL) was added to the mixture while keeping at 0 $^{\circ}$ C and the mixture was washed with a saturated NaHCO_3 aqueous solution (2.5 mL) and a 10% $\text{Na}_2\text{S}_2\text{O}_3$ aqueous solution (2.5 mL) twice, and a saturated NaHCO_3 aqueous solution (5 mL). The aqueous layers were combined, and back extracted with CHCl_3 (2 \times 5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using Toluene–AcOEt–pyridine (89:11:0.1–80:20:0.1, v/v/v) as an eluent to give **14** as a colorless oil (43 mg, 36 μ mol, 72%, α : β = 3:97)

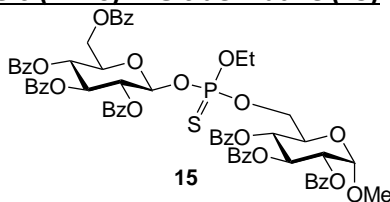
^1H NMR (CDCl_3) δ 8.10–7.78 (m, 14H), 7.61–7.23 (m, 21H), 6.14–6.05 (m, 0.5H), 5.99 (t, J = 9.5 Hz, 0.5H), 5.91 (dd, J = 2.9, 9.5 Hz), 5.88 (dd, J = 2.6, 9.5 Hz) (diastomers, 1H), 5.74–5.53 (m, 2.5H), 5.43 (t, J = 9.8 Hz, 0.5H), 5.21–4.94 (m, 3H), 4.67–4.57 (m, 1H), 4.52–4.40 (m, 1H), 4.31–3.77 (m, 6H), 3.39, 3.30 (s, 2 \times 1.5H), 1.17 (t, J = 7.2 Hz, 1.5H), 0.95 (t, J = 6.6 Hz, 1.5H).

^{13}C NMR (CDCl_3) δ 165.9, 165.7, 165.6, 165.5, 165.1, 165.0, 164.9, 164.8 (C=O), 133.6, 133.5, 133.3, 133.2, 133.1, 129.9, 129.8, 129.7, 129.6, 129.4, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3 (Ar), 96.8 (CH), 96.6 (CH), 96.5 (CH), 96.5 (CH) 73.0 (CH), 72.9 (CH), 72.4 (CH), 71.9 (CH), 71.6 (CH), 71.5 (CH), 70.3 (CH), 70.2 (CH), 68.9 (CH), 68.7 (CH), 68.0 (CH, $J_{\text{P-C}}$ = 8.8 Hz), 67.9 (CH, $J_{\text{P-C}}$ = 8.8 Hz), 66.2 (CH_2 , $J_{\text{P-C}}$ = 5.5 Hz), 66.0 (CH_2 , $J_{\text{P-C}}$ = 4.4 Hz), 64.8 (CH_2 , $J_{\text{P-C}}$ = 6.1 Hz), 64.8 (CH_2 , $J_{\text{P-C}}$ = 5.5 Hz), 62.5 (CH_2), 55.6 (CH_3), 55.4 (CH_3), 15.7 (CH_3 , $J_{\text{P-C}}$ = 7.2 Hz), 15.5 (CH_3 , $J_{\text{P-C}}$ = 7.2 Hz).

^{31}P NMR (CDCl_3) δ -2.4, -2.7.

HRMS (ESI): calcd for $\text{C}_{64}\text{H}_{58}\text{O}_{21}\text{P}^+$ [$\text{M}+\text{H}$] $^+$: 1193.32028; found: 1193.32106.

Phosphorothioate triester-linked β -D-Glc-(1-P-6)-D-Glc derivative (15)



10 (63 mg, 50 μ mol, α : β =2:98) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^{\circ}$ C while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. Ethanol (29 μ L, 500 μ mol) was added to the mixture at 0 $^{\circ}$ C, and the mixture was warmed to rt after 5 min. The mixture was allowed to stir for further 15 min. DTD (32 mg, 150 μ mol) was added to the mixture and the mixture was allowed to stir for 15 min. CHCl_3 (5 mL) was added to the mixture at 0 $^{\circ}$ C and the mixture was washed with saturated NaHCO_3 aqueous solutions (3 \times 5 mL). The aqueous layers were combined, and back-extracted with CHCl_3 (2 \times 5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by

silica gel column chromatography using AcOEt–hexane (1:4–1:2, v/v) as an eluent to give **15** as a colorless foam (48 mg, 40 μ mol, 80%, α : β = 1:99)

^1H NMR (CDCl_3) δ 8.10–7.79 (m, 21H), 7.61–7.26 (m, 14H), 6.12–5.88 (m, 2H), 5.80–5.56 (m, 3H), 5.43 (t, J = 9.8 Hz, 0.5H), 5.21–5.15 (m, 0.5H), 5.07–4.91 (m, 2H), 4.64–4.55 (m, 1H), 4.50–4.42 (m, 1H), 4.32–3.74 (m, 6H), 3.39, 3.30 (s, $2 \times 1.5\text{H}$), 1.14 (t, J = 7.4 Hz, 1.5H), 0.92 (t, J = 7.1 Hz, 1.5H).

^{13}C NMR (CDCl_3) δ 166.0, 165.9, 165.7, 165.6, 165.1, 165.0, 164.8 (C=O), 133.6, 133.5, 133.4, 133.3, 133.2, 133.1, 133.0, 130.0, 129.9, 129.8, 129.6, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2 (Ar), 97.0 (CH, $J_{\text{P-C}}$ = 3.2 Hz), 96.8 (CH), 96.4 (CH), 73.1 (CH), 73.0 (CH), 72.6 (CH), 71.9 (CH), 71.7 (CH), 71.3 (CH, $J_{\text{P-C}}$ = 10.3 Hz), 71.3 (CH, $J_{\text{P-C}}$ = 10.0 Hz), 70.4 (CH), 70.3 (CH), 69.1 (CH), 69.1 (CH), 68.9 (CH), 68.0 (CH, $J_{\text{P-C}}$ = 2.4 Hz), 67.9 (CH, $J_{\text{P-C}}$ = 10.0 Hz), 67.9 (CH, $J_{\text{P-C}}$ = 9.4 Hz), 66.4 (CH_2 , $J_{\text{P-C}}$ = 4.6 Hz), 66.2 (CH_2 , $J_{\text{P-C}}$ = 4.0 Hz), 65.1 (CH_2 , $J_{\text{P-C}}$ = 5.7 Hz), 64.8 (CH_2 , $J_{\text{P-C}}$ = 5.7 Hz), 62.7 (CH_2), 62.6 (CH_2), 55.5 (CH_3), 55.3 (CH_3), 15.5 (CH_3 , $J_{\text{P-C}}$ = 8.3 Hz), 15.3 (CH_3 , $J_{\text{P-C}}$ = 8.0 Hz).

^{31}P NMR (CDCl_3) δ 68.5, 67.8.

HRMS (ESI): calcd for $\text{C}_{64}\text{H}_{58}\text{O}_{20}\text{PS}^+$ $[\text{M}+\text{H}]^+$: 1209.29743; found: 1209.29847.

2. Reaction monitoring by ^{31}P NMR

2-1 Formation of the acylphosphite **4**

1 (63 mg, 50 μ mol, α : β = 96:4) was dissolved in pyridine- d_5 (1 mL). PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. After 5 min the mixture was warmed to rt, and the mixture (0.75 mL) was transferred into a NMR tube. The formation of the acylphosphite **4** (δ 131.8, 131.1 ppm) was confirmed by ^{31}P NMR (Figure S1).

2-2 Formation of the phosphodiester via the acylphosphite

1 (63 mg, 50 μ mol, α : β = 96:4) was dissolved in pyridine- d_5 (1 mL). After adding CBr_4 (33 mg, 99 μ mol), PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. After 5 min the mixture was warmed to rt, and the mixture (0.75 mL) was transferred into a NMR tube. The formation of the acylphosphite **4** (δ 131.7, 131.1 ppm) was confirmed by ^{31}P NMR (Figure S2). After 30 min, a saturated NaHCO_3 aqueous solution (0.1 mL) was added into the NMR tube and the formation of the phosphodiester (δ 2.0 ppm) was confirmed by ^{31}P NMR (Figure S3).

2-3 Hydrolysis of the acylphosphite **4**

1 (63 mg, 50 μ mol, α : β = 99:1) was dried by repeated coevaporation with dry pyridine and dissolved in dry pyridine (1 mL). PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. The mixture was warmed to rt after 5 min and allowed to stir for further 35 min. A saturated NaHCO_3 aqueous solution (4 mL) was added to the mixture at 0 $^\circ\text{C}$ and CHCl_3 (5 mL) was added to the mixture immediately (ca. 10 s later). The organic layer was separated, and washed with saturated NaHCO_3 aqueous solutions (3×5 mL). The aqueous layers were combined and back-extracted with CHCl_3 (5 mL). The organic layers were combined, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was dissolved in CDCl_3 and a ^{31}P NMR spectrum was recorded (Figure S4).

2-4 Formation of the phosphoramidite **S2**

1 (63 mg, 50 μ mol, α : β = 99:1) was dissolved in pyridine- d_5 (1 mL). PivCl (12 μ L, 100 μ mol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. After 5 min the mixture was warmed to rt and allowed to stir for further 40 min. Propyl amine (62 μ L, 750 μ mol) was added to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 5 min. The mixture (0.75 mL) was transferred into a NMR tube and the formation of the phosphoramidite **S2** (δ 144.4, 141.0 ppm) was confirmed.

2-5 Formation of the phosphite triester **S3**

1 (63 mg, 50 μmol , $\alpha:\beta = 99:1$) was dissolved in pyridine- d_5 (1 mL). PivCl (12 μL , 100 μmol) was added to the mixture at 0 $^\circ\text{C}$ while stirring. After 5 min the mixture was warmed to rt and allowed to stir for further 40 min. MeOH (20 μL , 500 μmol) was added to the mixture at 0 $^\circ\text{C}$, and the mixture was warmed to rt after 7 min. The mixture (0.75 mL) was transferred into a NMR tube and the formation of the phosphite triester **S3** (δ 133.4, 132.0 ppm) was confirmed.

References for Supporting Information

- 1 Sato, K.; Oka, N.; Fujita, S.; Matsumura, F.; Wada, T. *J. Org. Chem.* **2010**, *75*, 2147.
- 2 Song, Q.; Wang, Z.; Sanghvi, Y. S. *Nucleosides, Nucleotides Nucleic Acids* **2003**, *22*, 629.

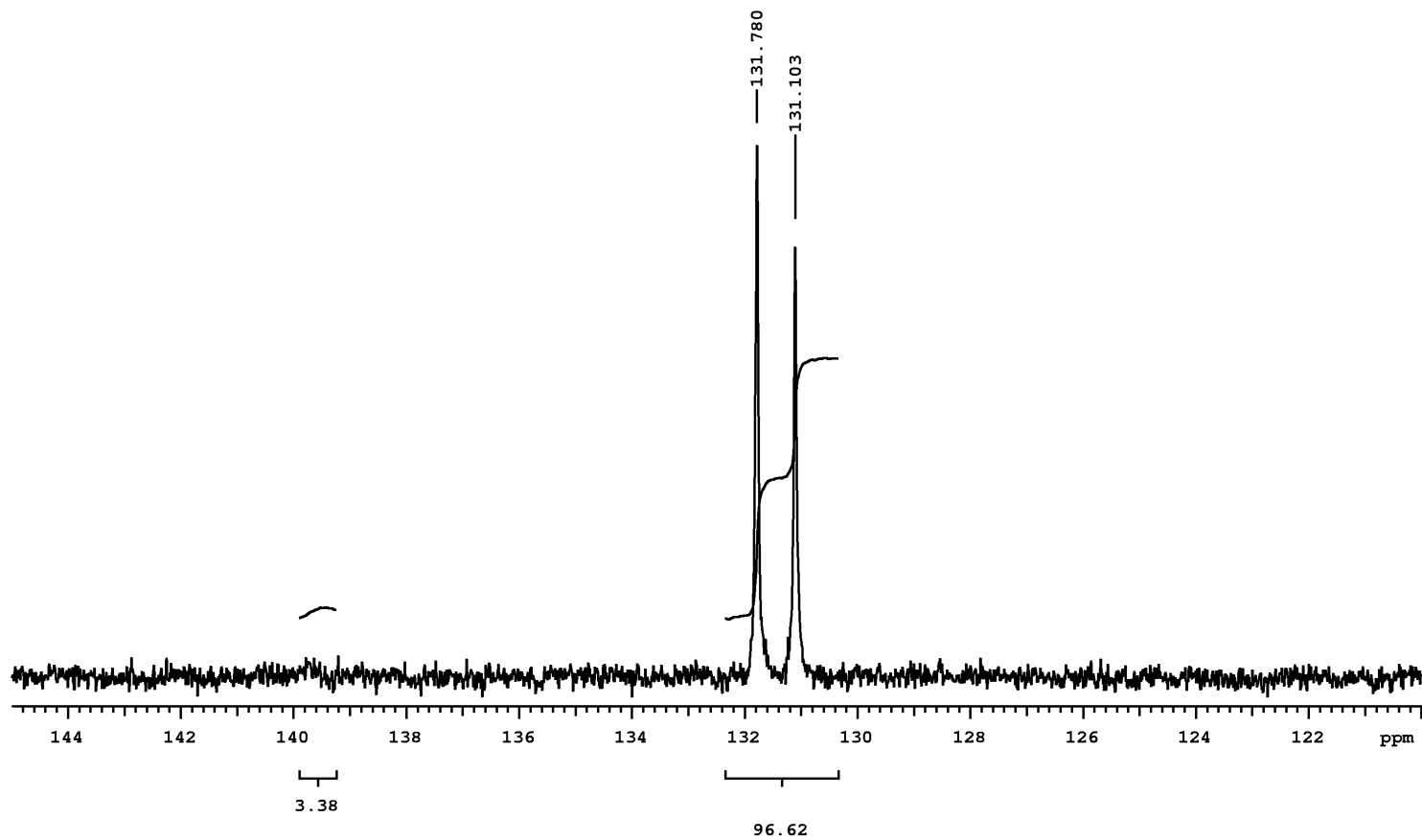
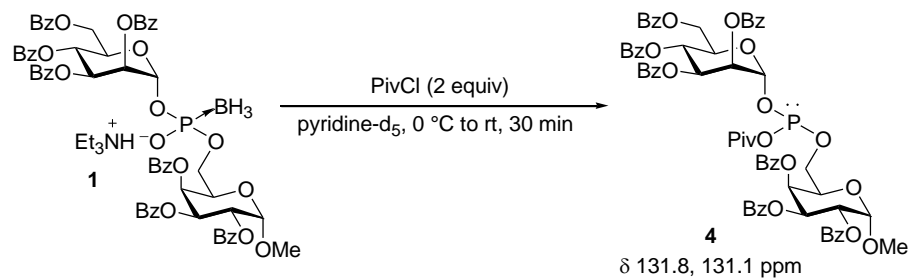


Figure S1.

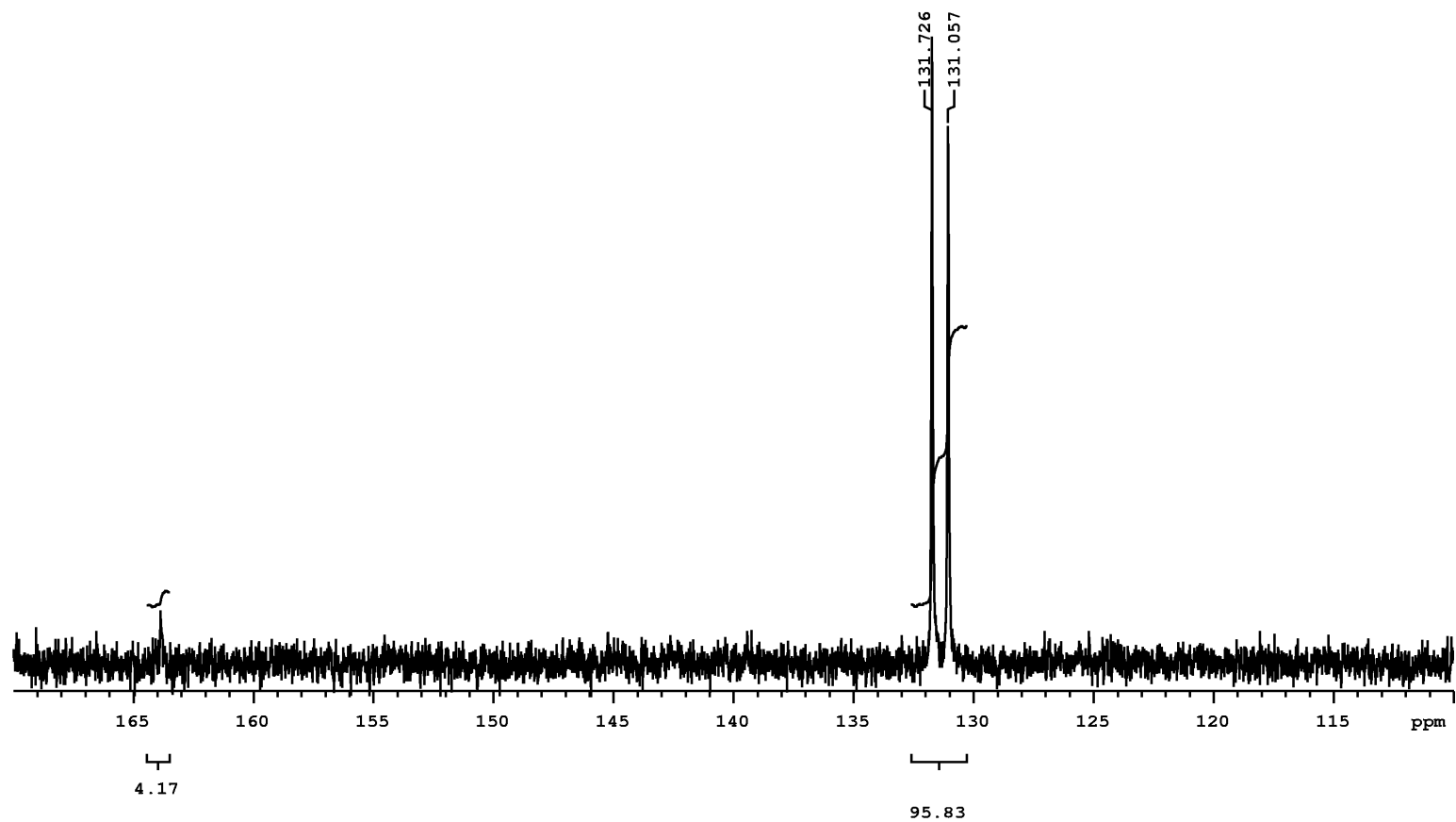
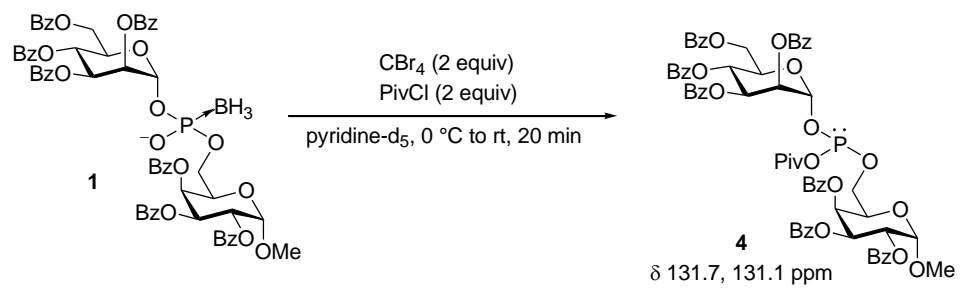


Figure S2.

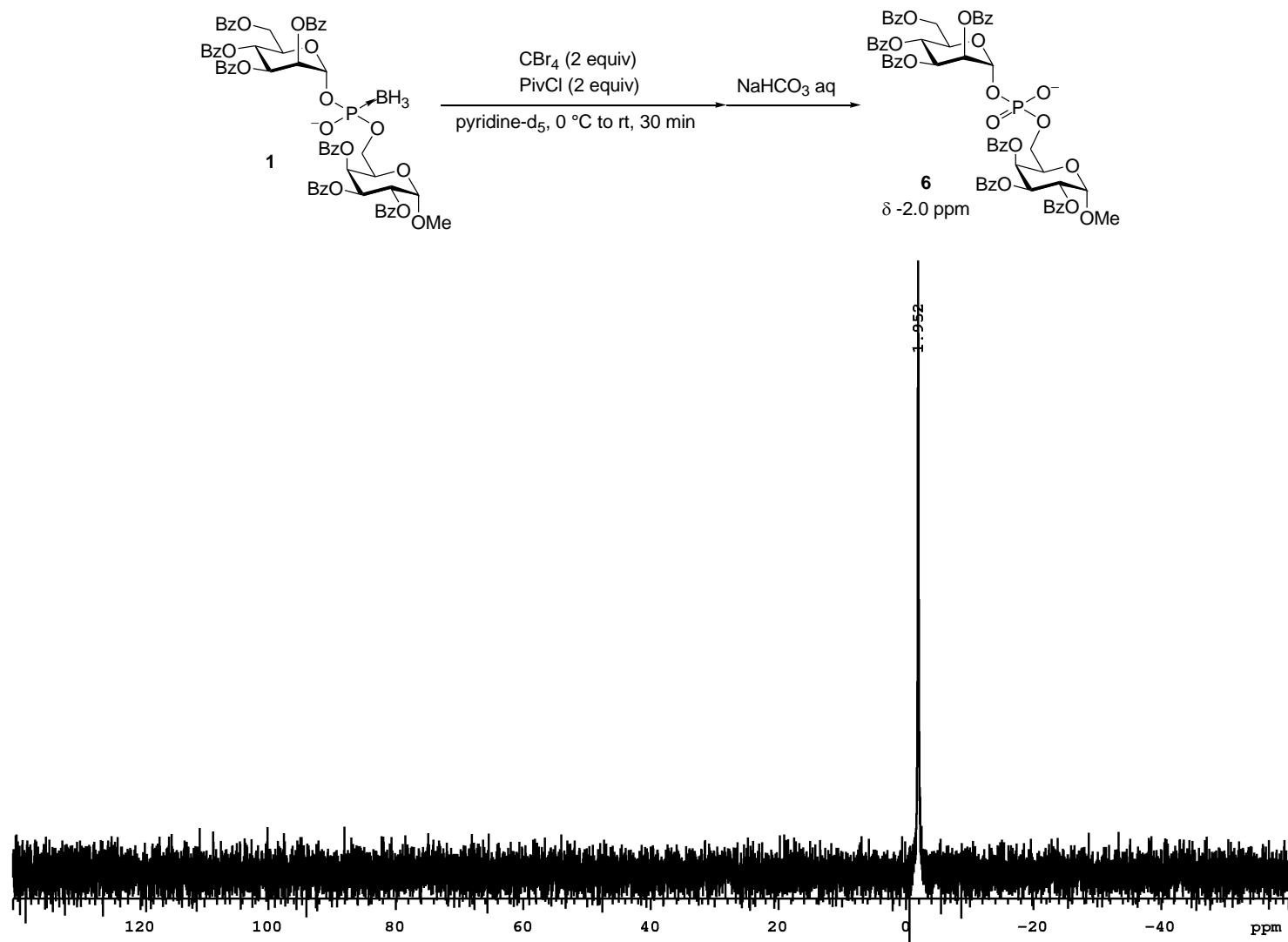


Figure S3.

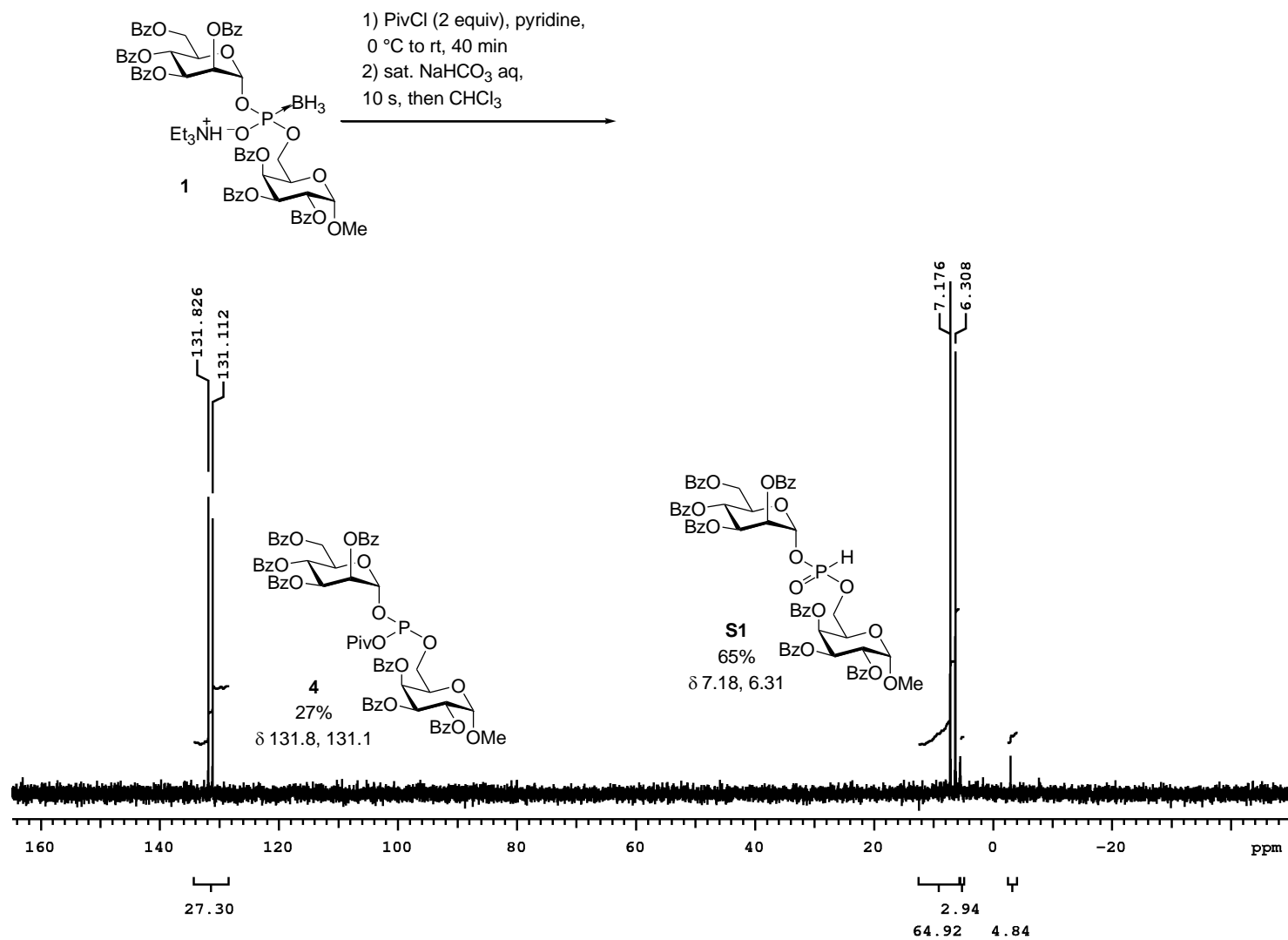


Figure S4.

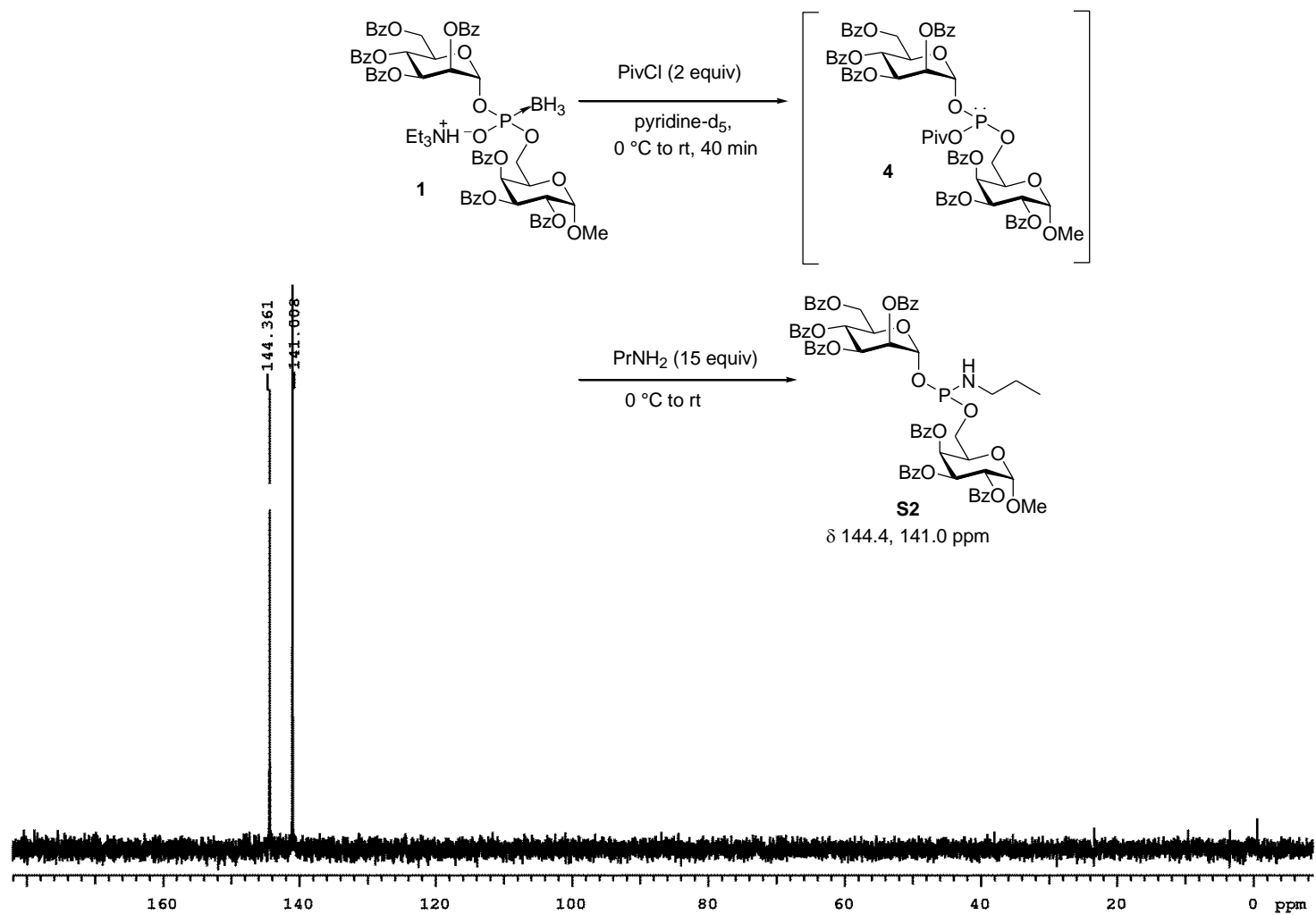


Figure S5.

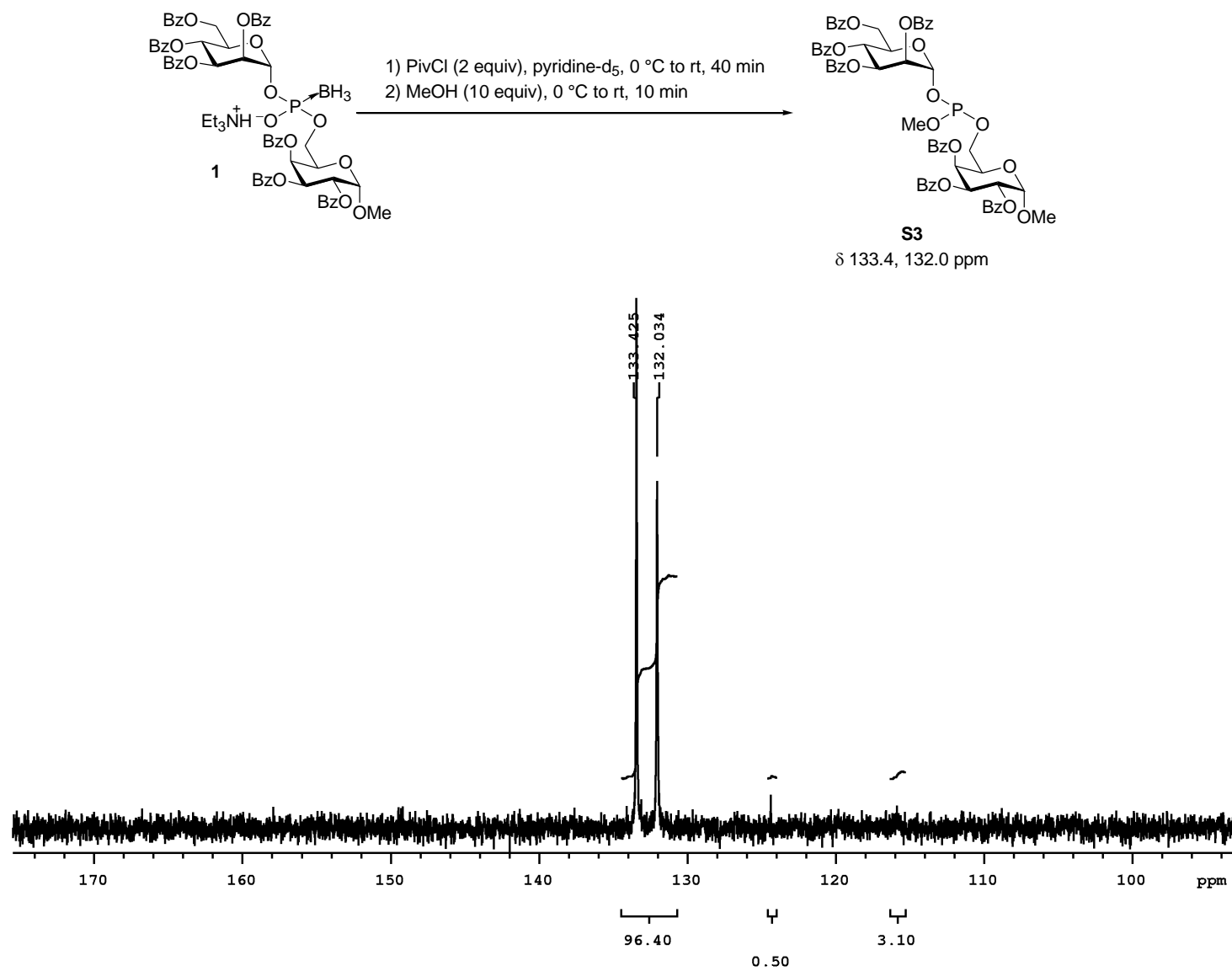
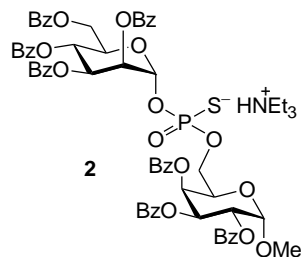
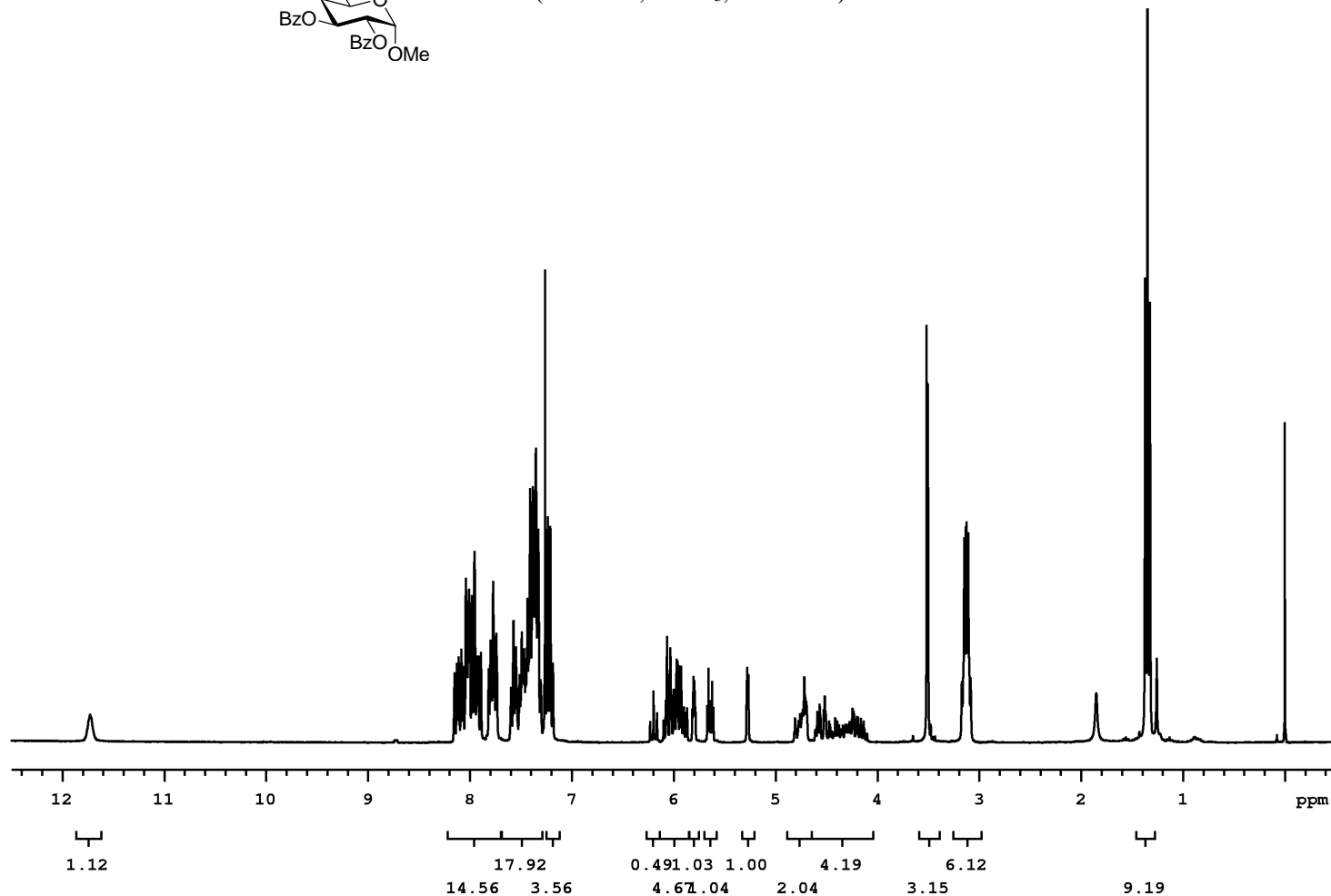


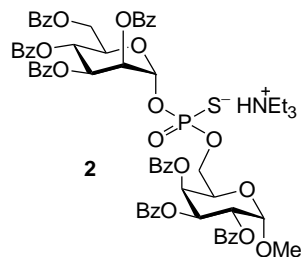
Figure S6.

^1H , ^{13}C , ^{31}P NMR spectra

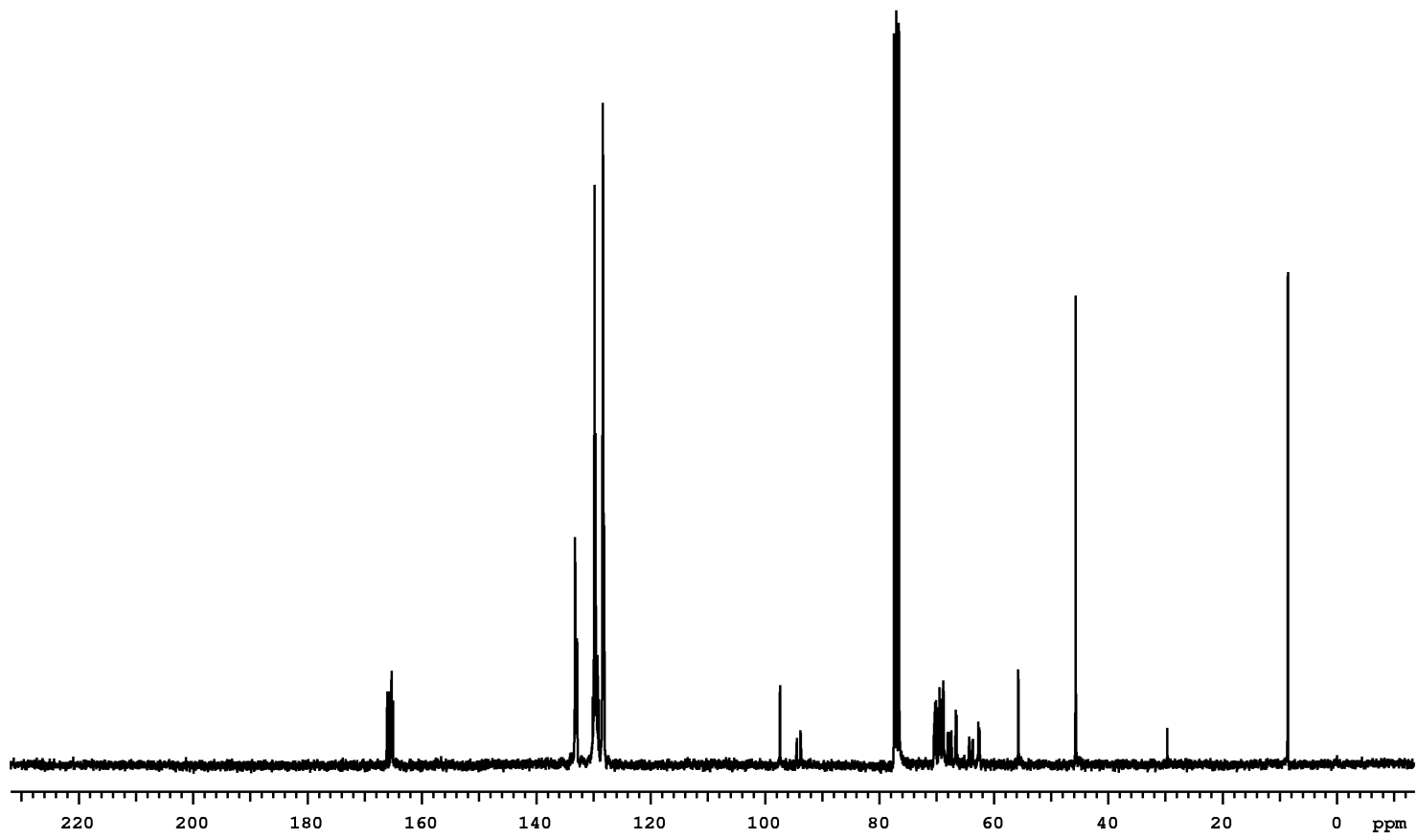


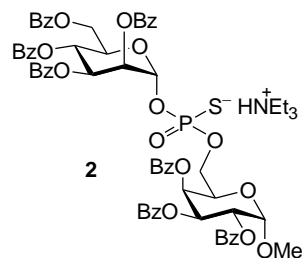
(^1H NMR, CDCl_3 , 300 MHz)



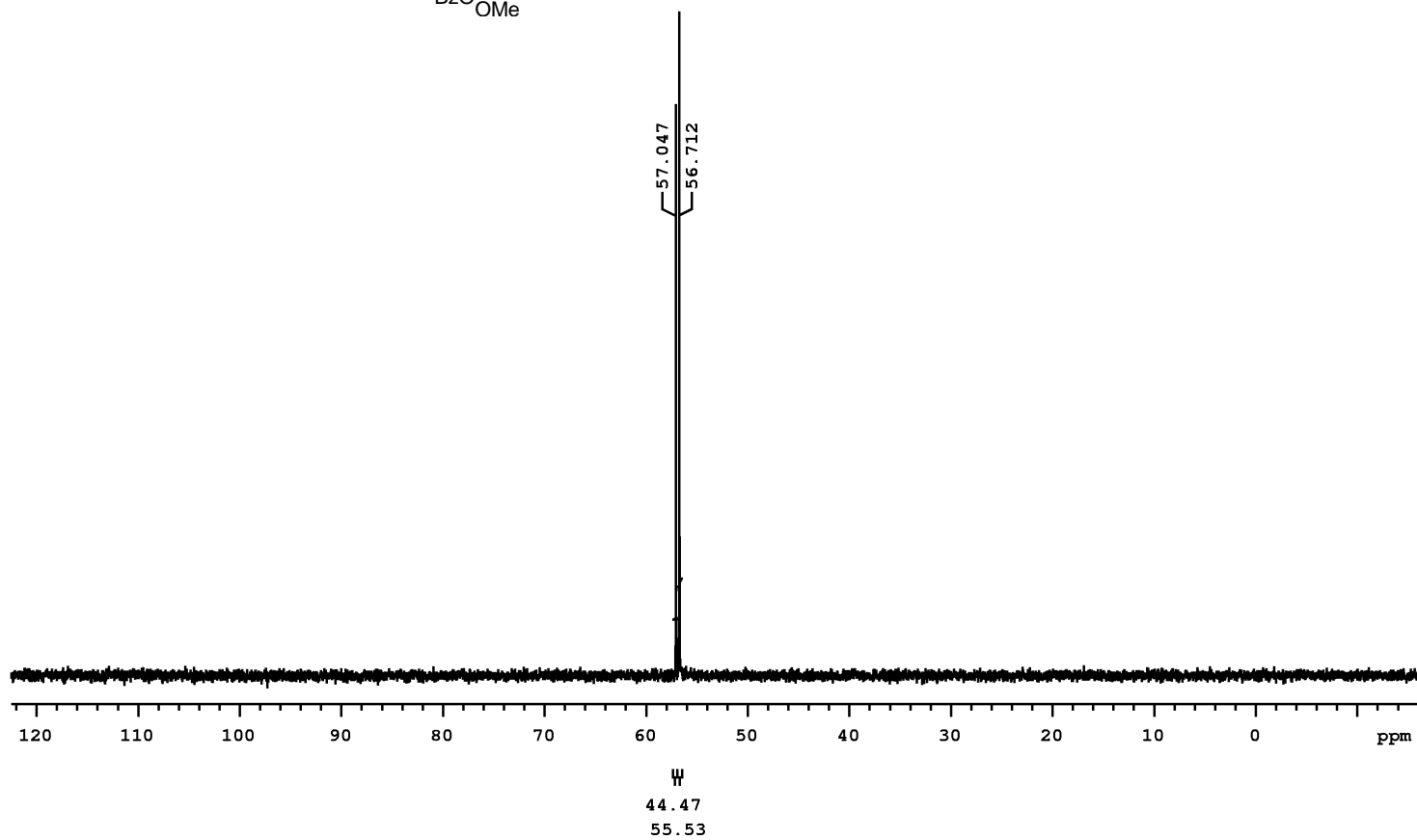


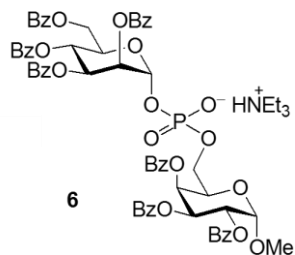
(¹³C NMR, CDCl₃, 75.5 MHz)



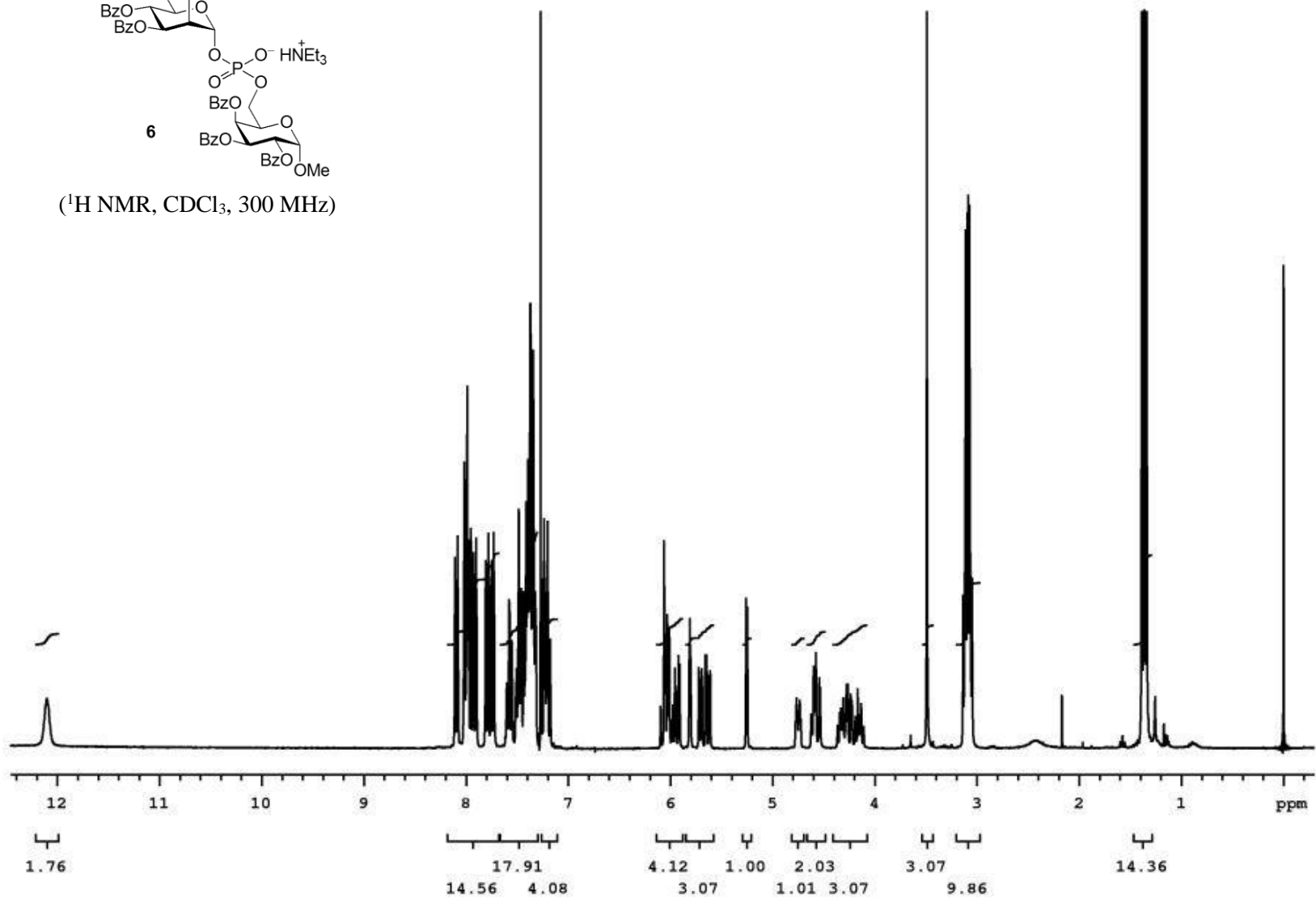


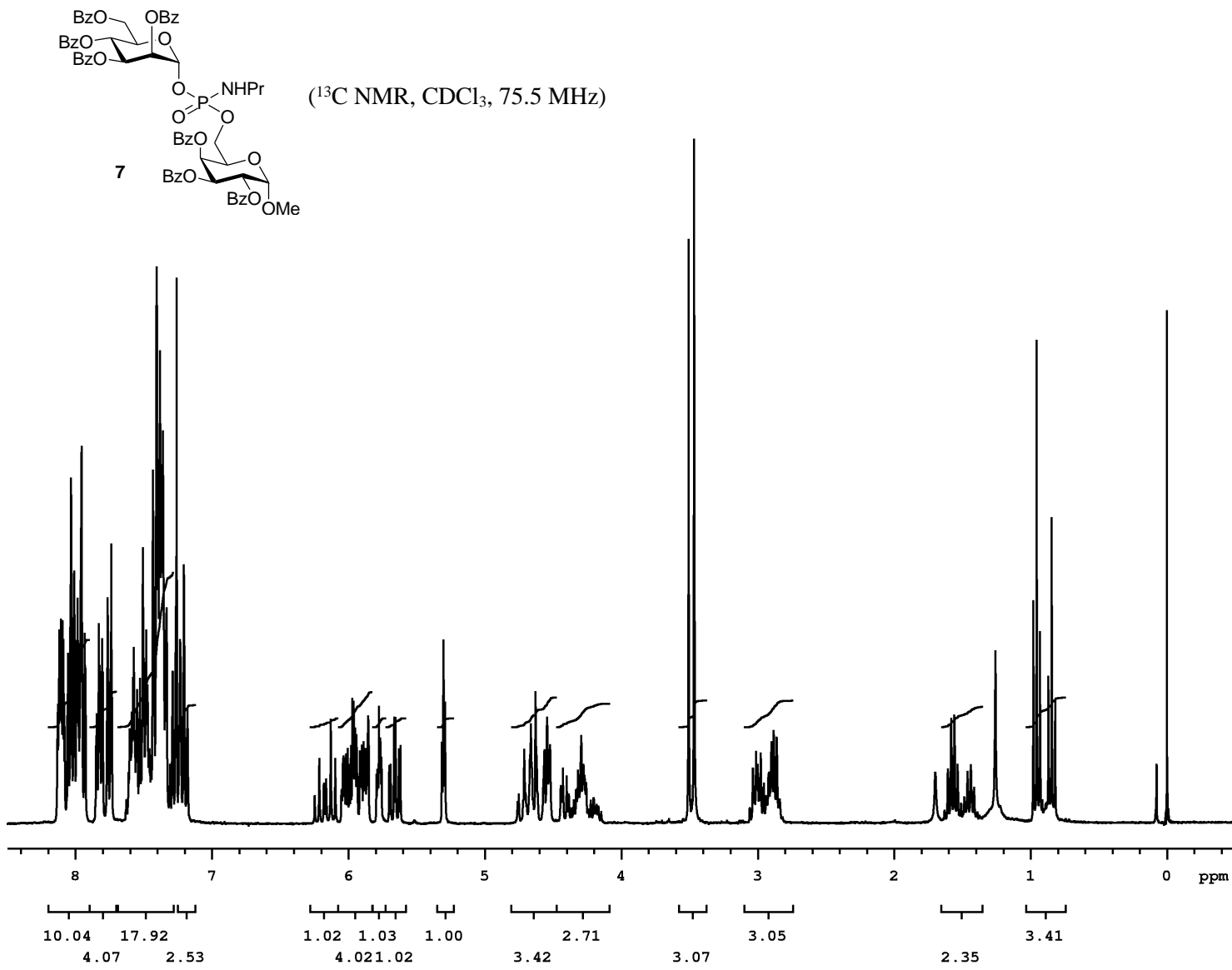
(³¹P NMR, CDCl₃, 121.5 MHz)

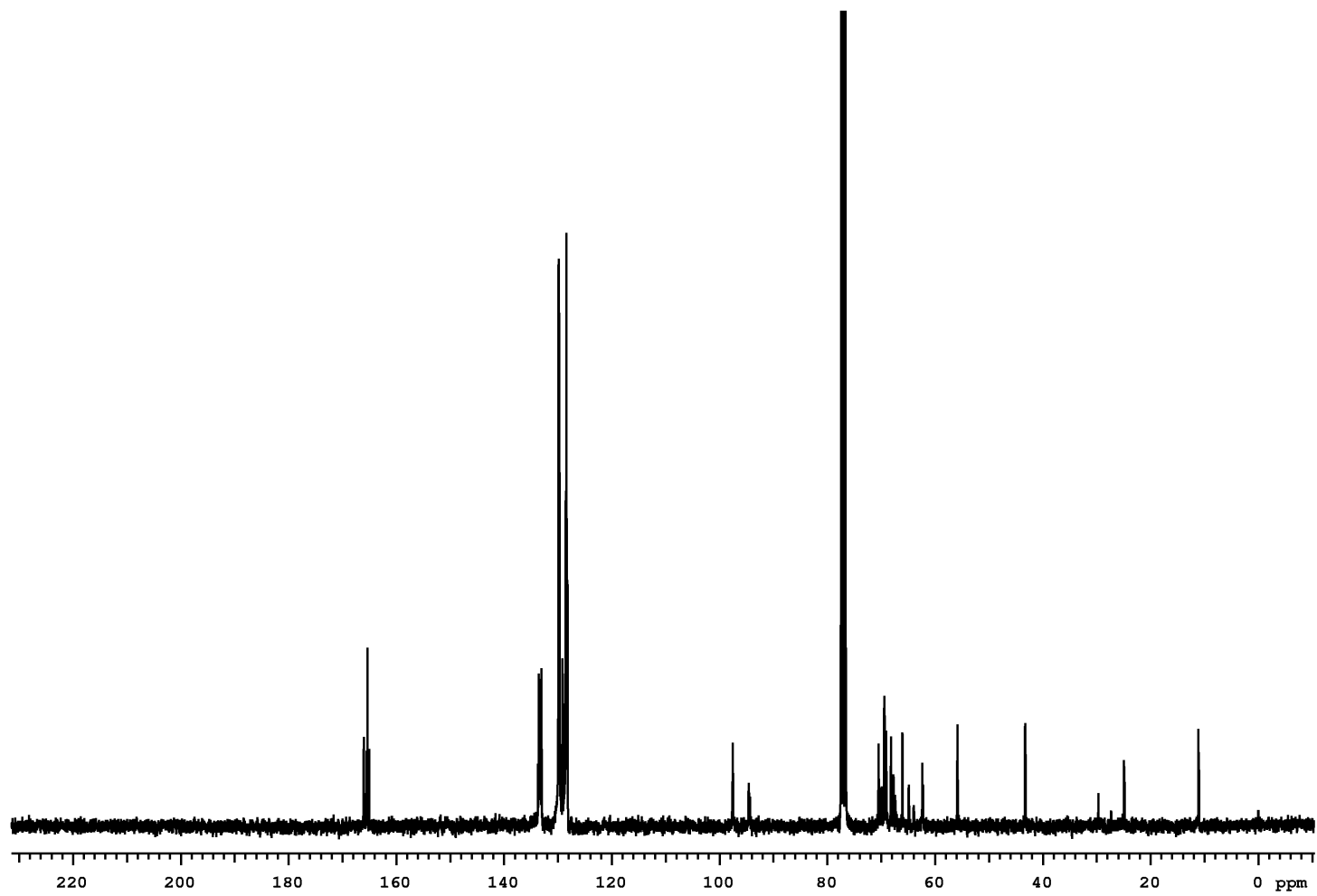


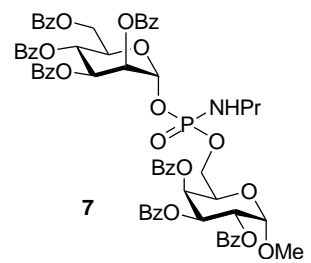


(¹H NMR, CDCl₃, 300 MHz)

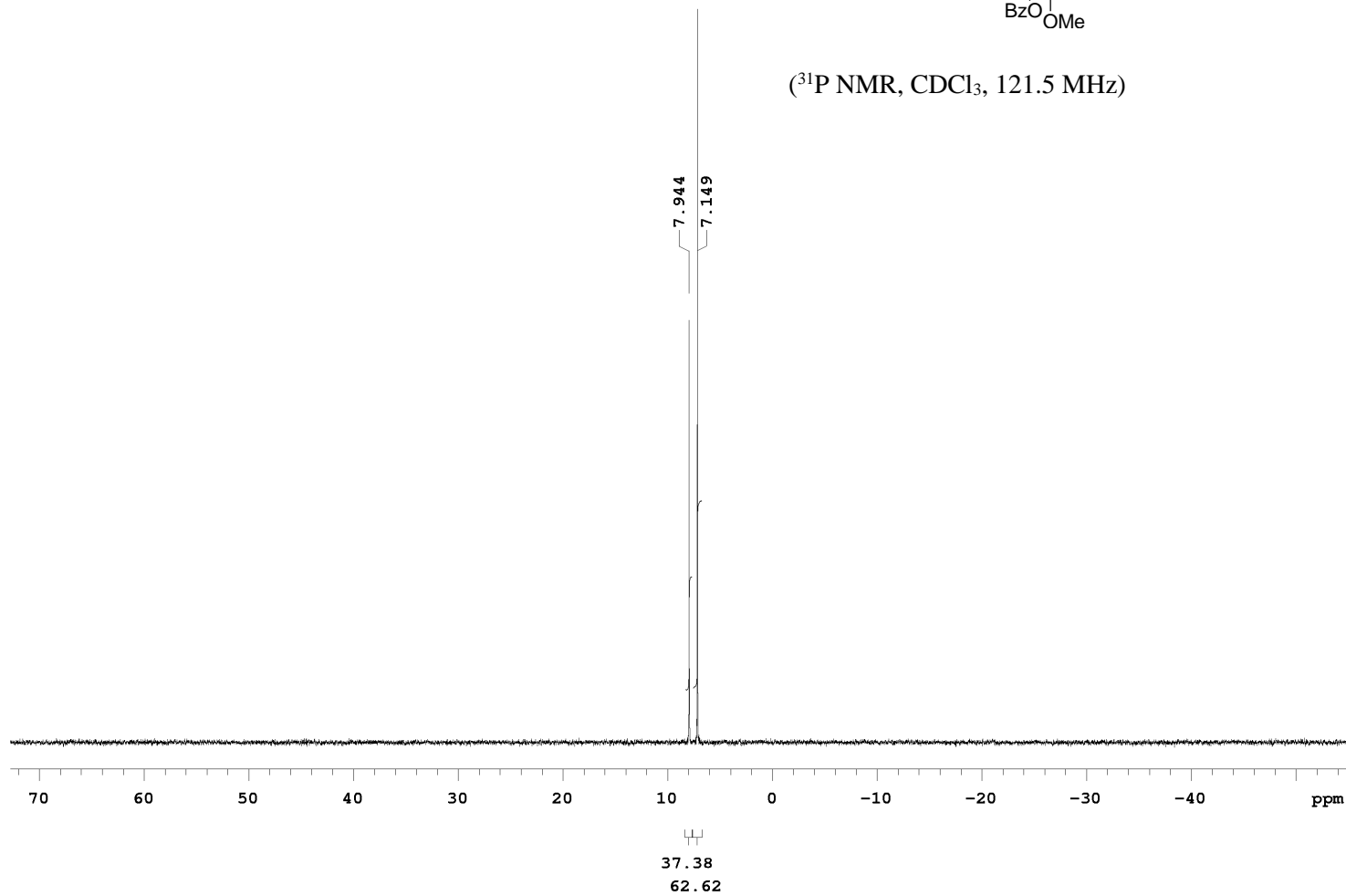


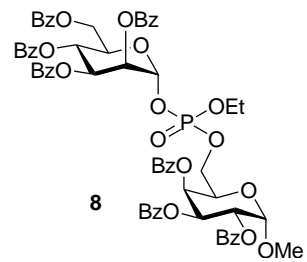




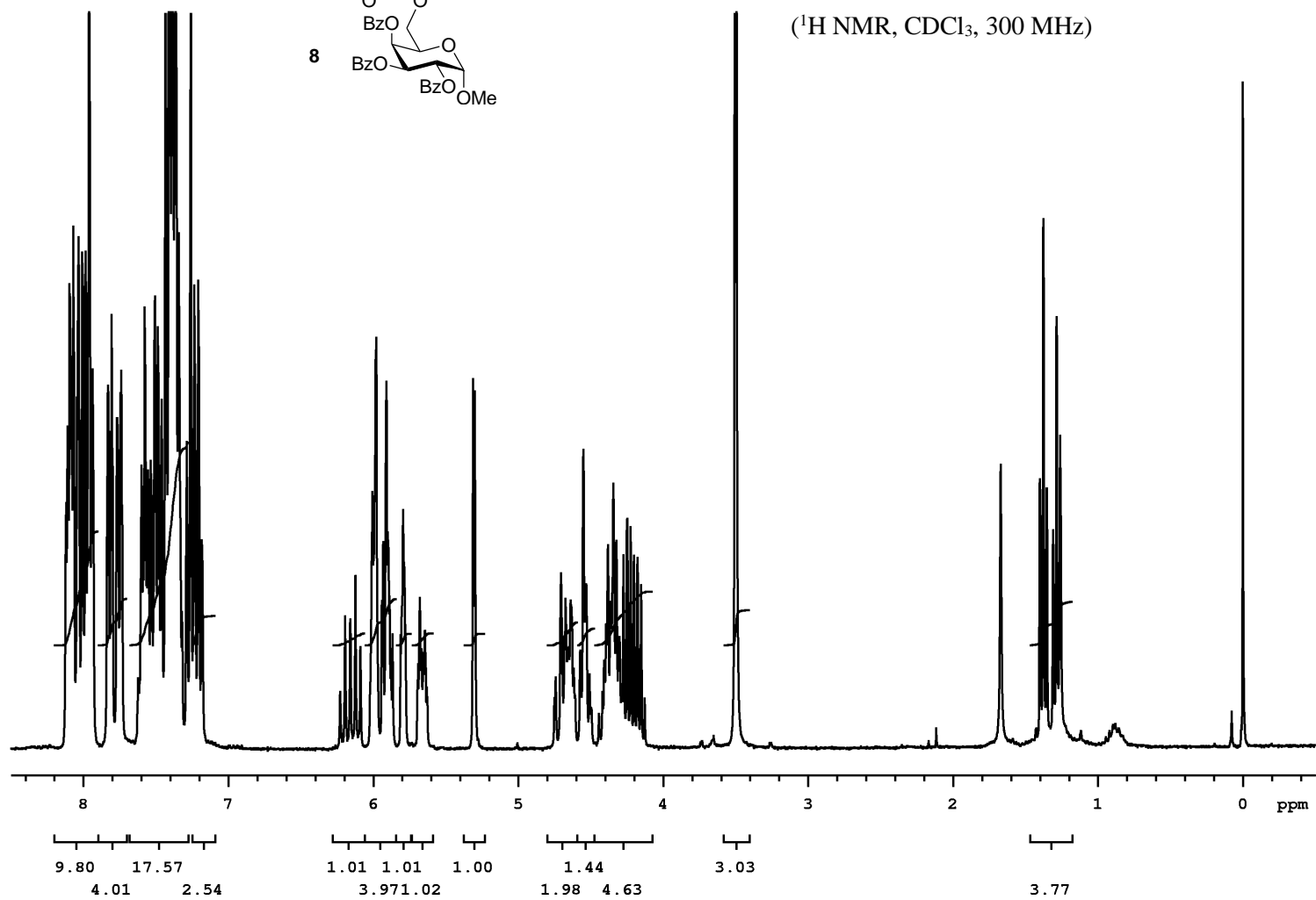


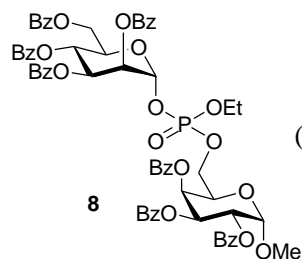
(³¹P NMR, CDCl₃, 121.5 MHz)



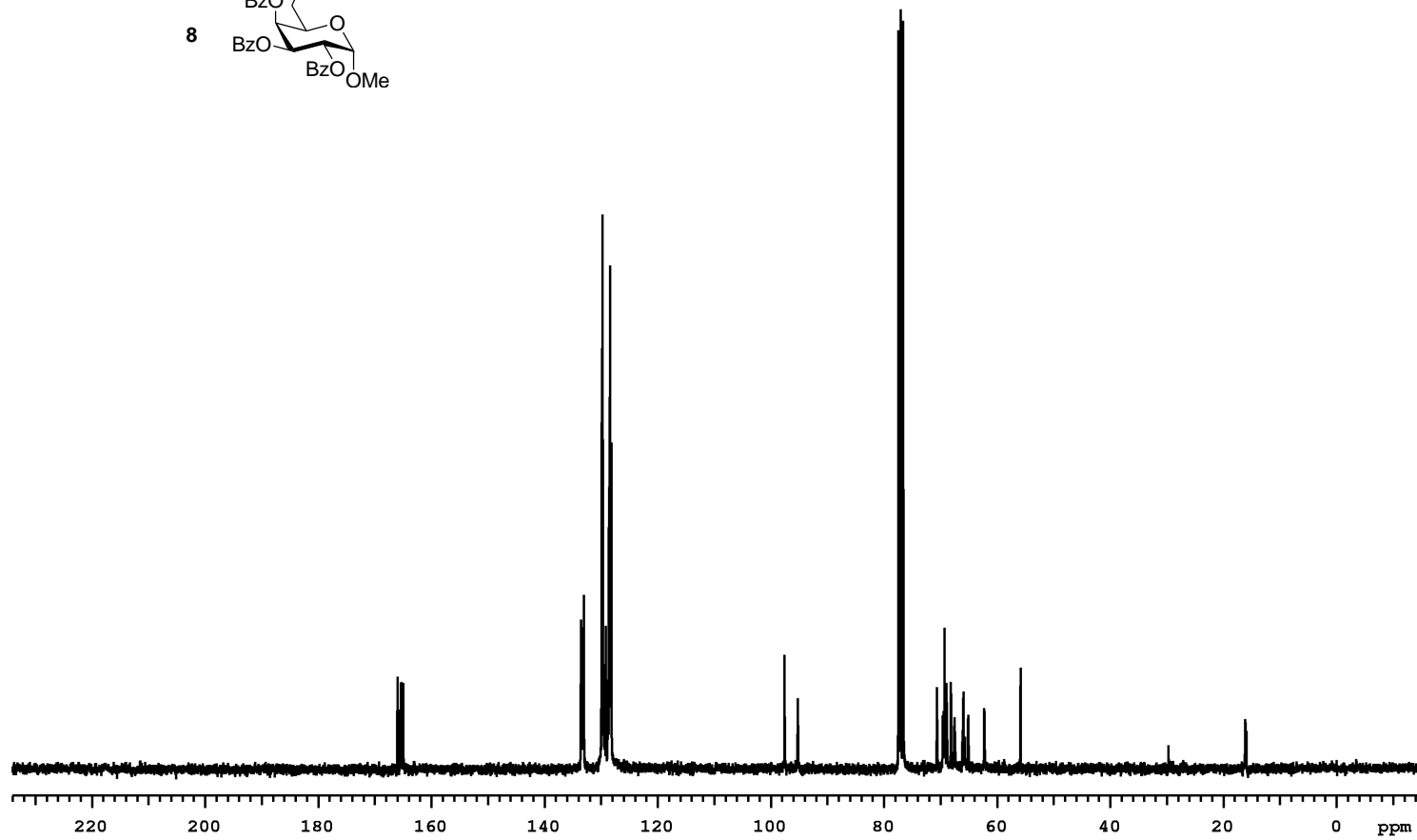


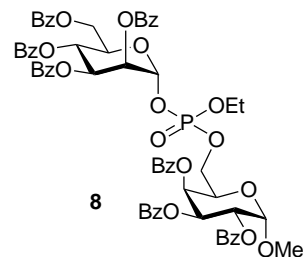
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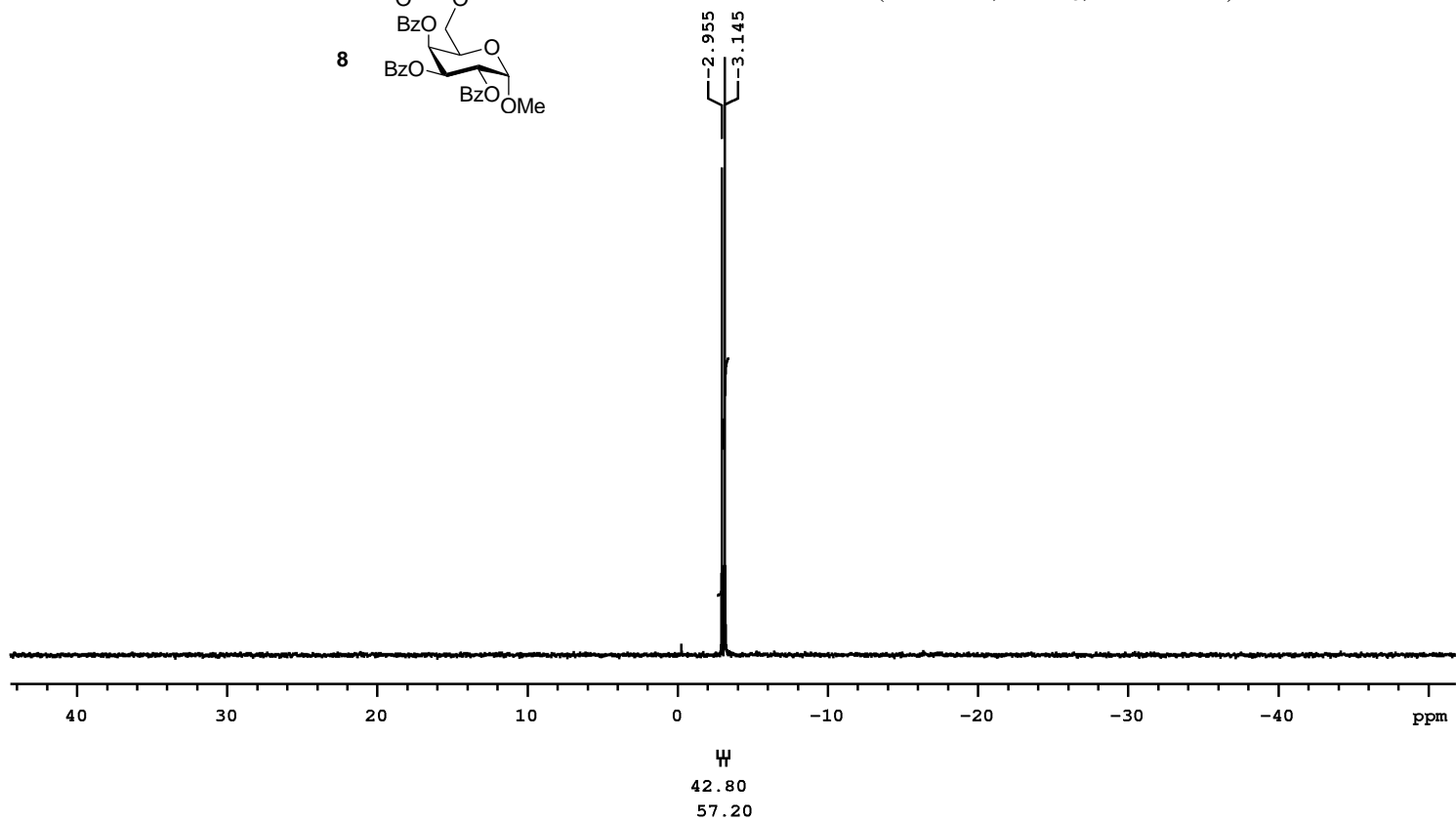


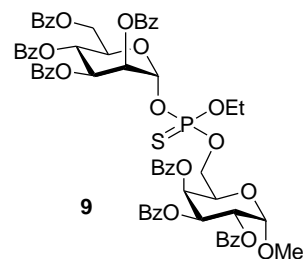
(¹³C NMR, CDCl₃, 75.5 MHz)



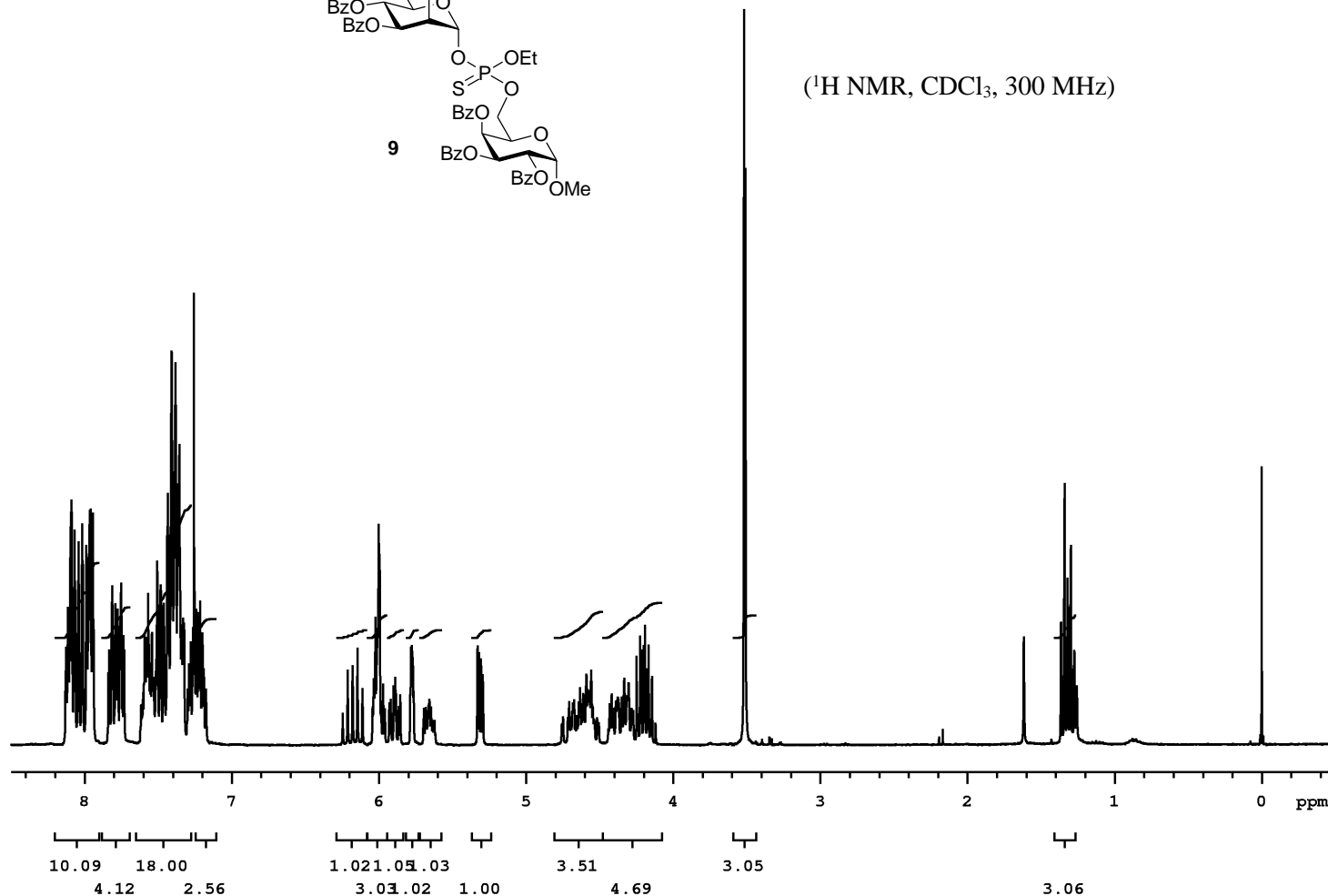


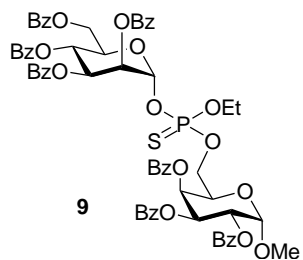
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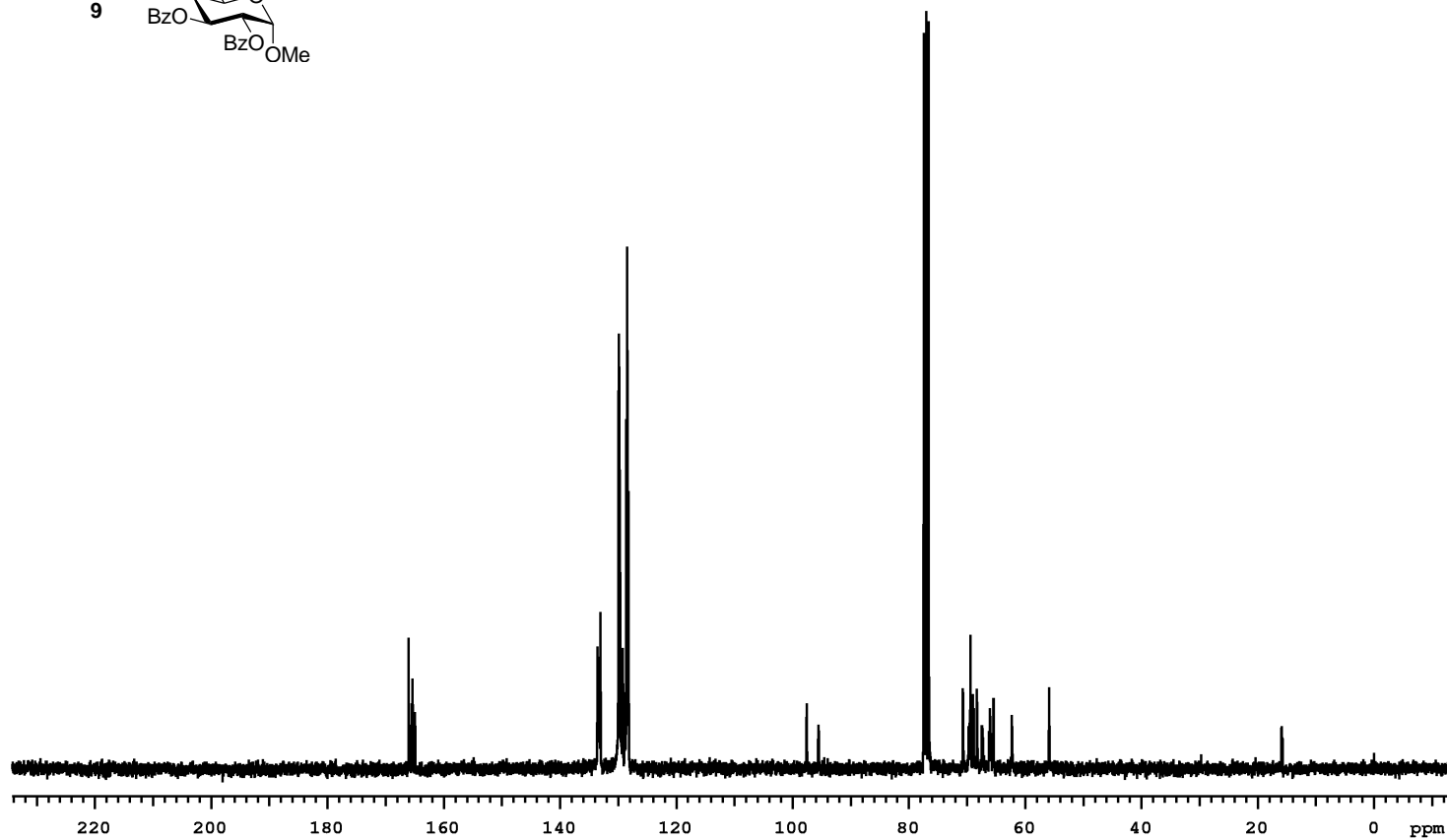


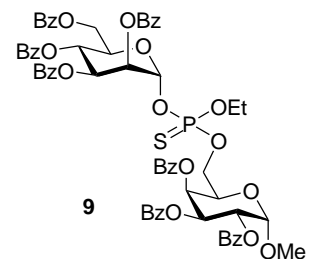
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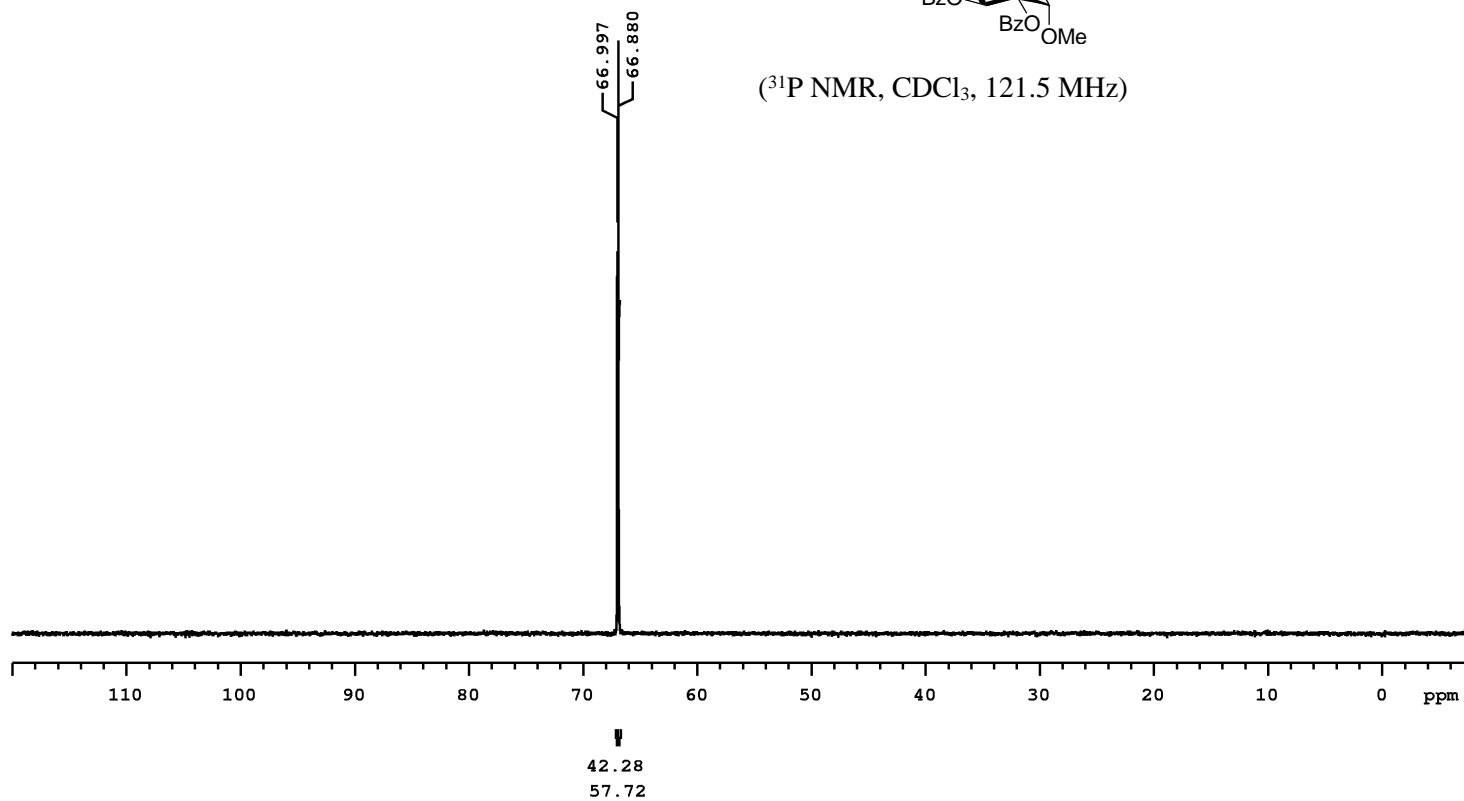


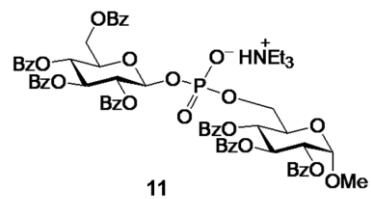
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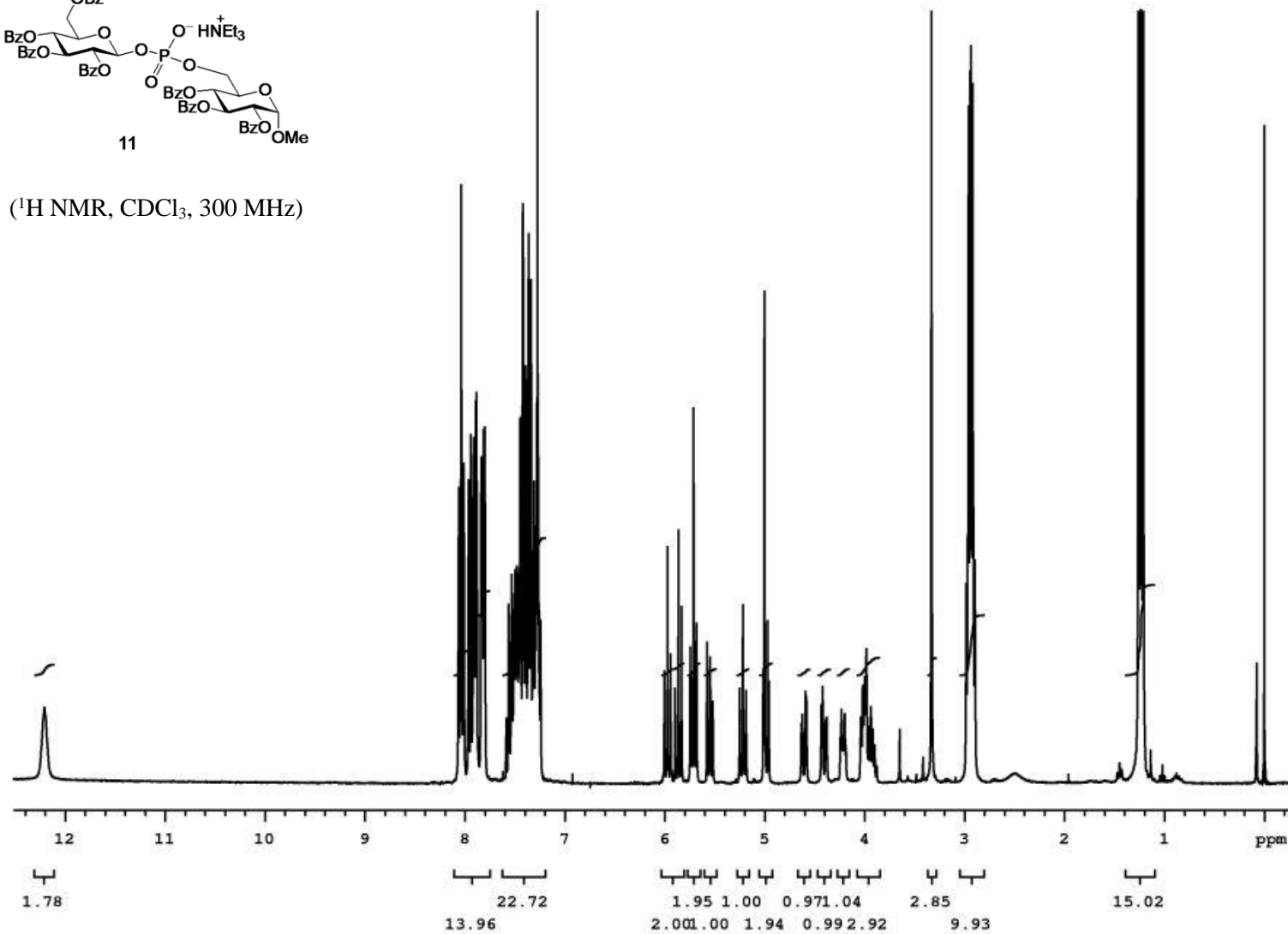


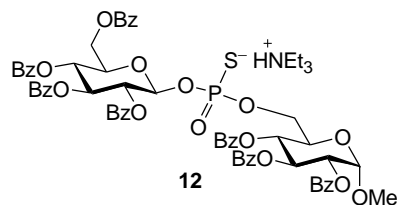
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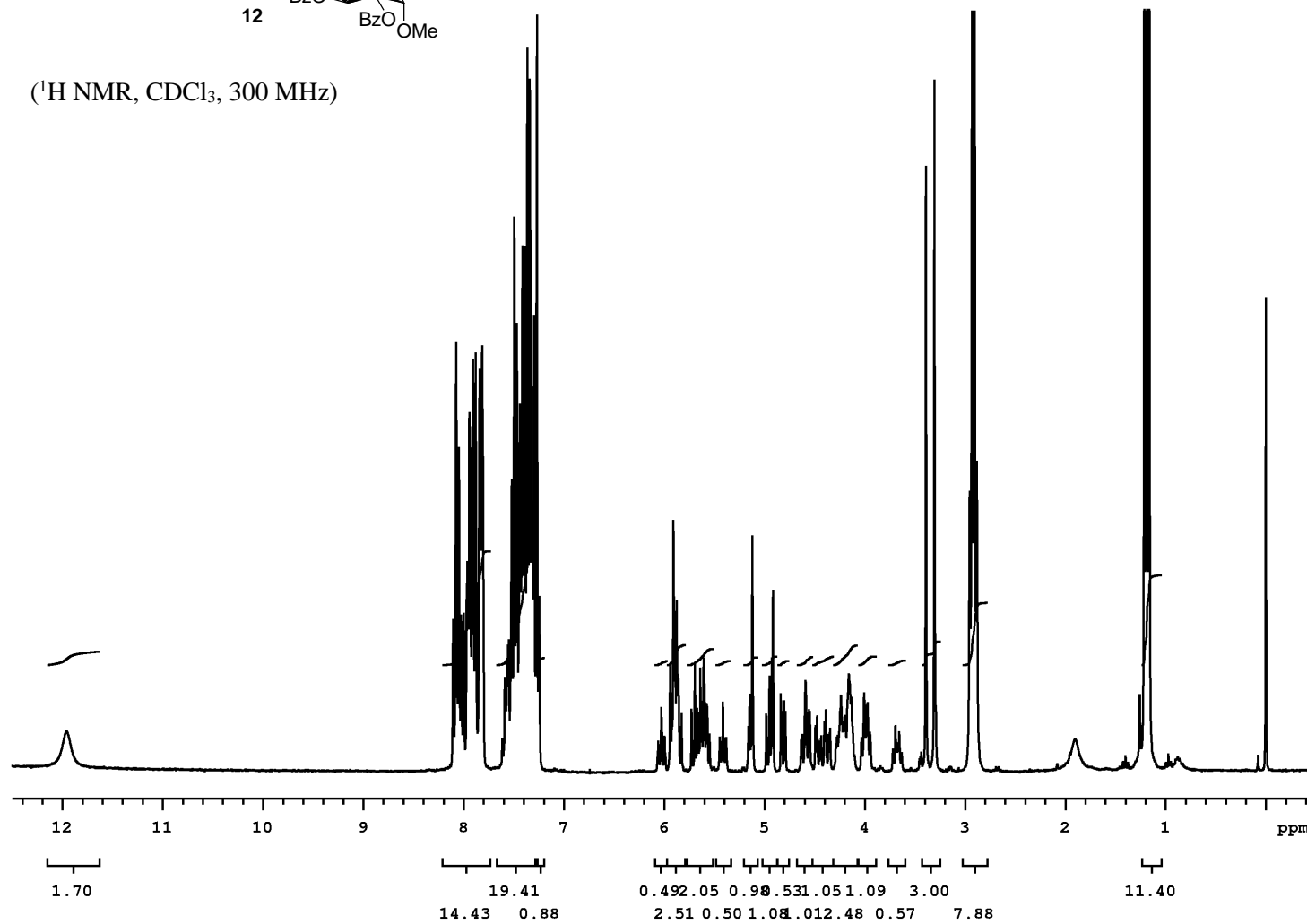


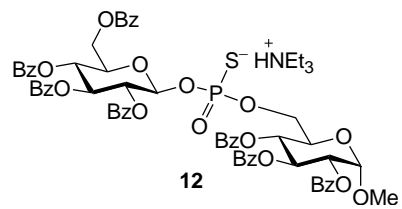
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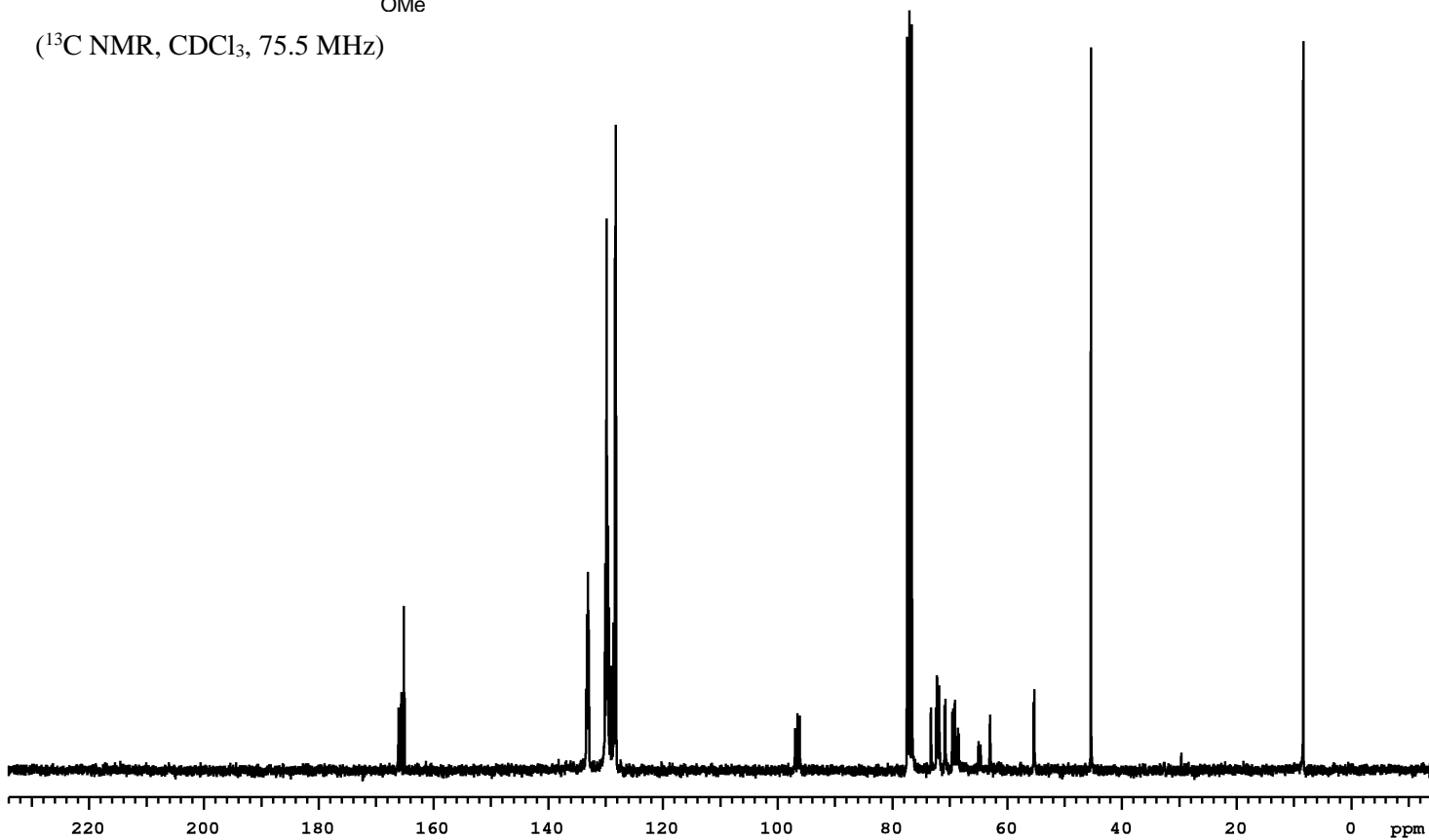


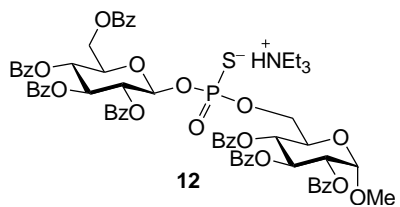
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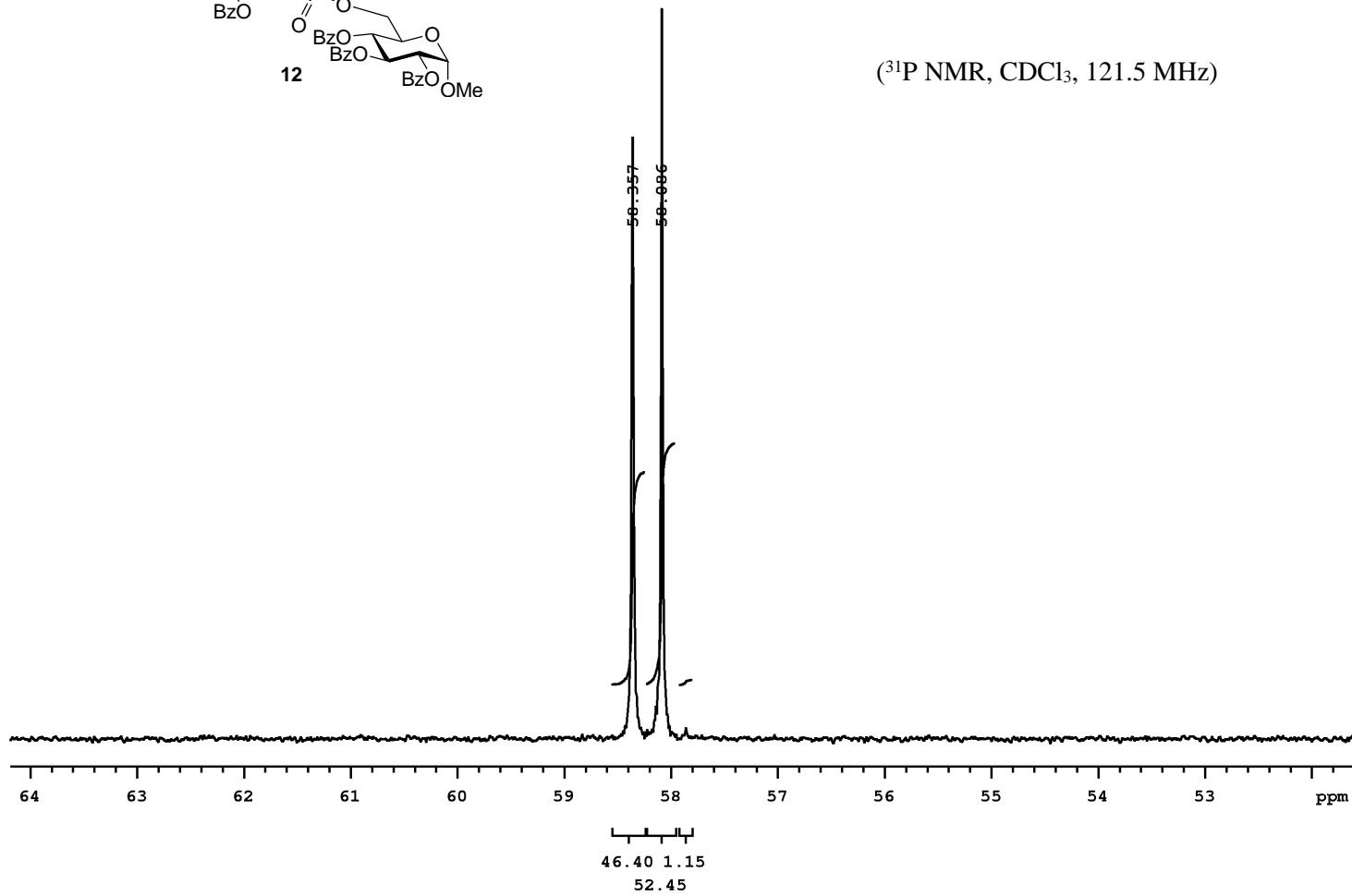


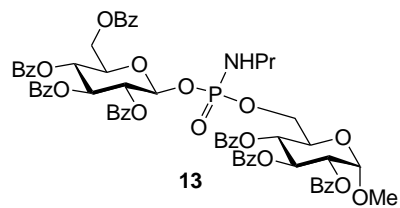
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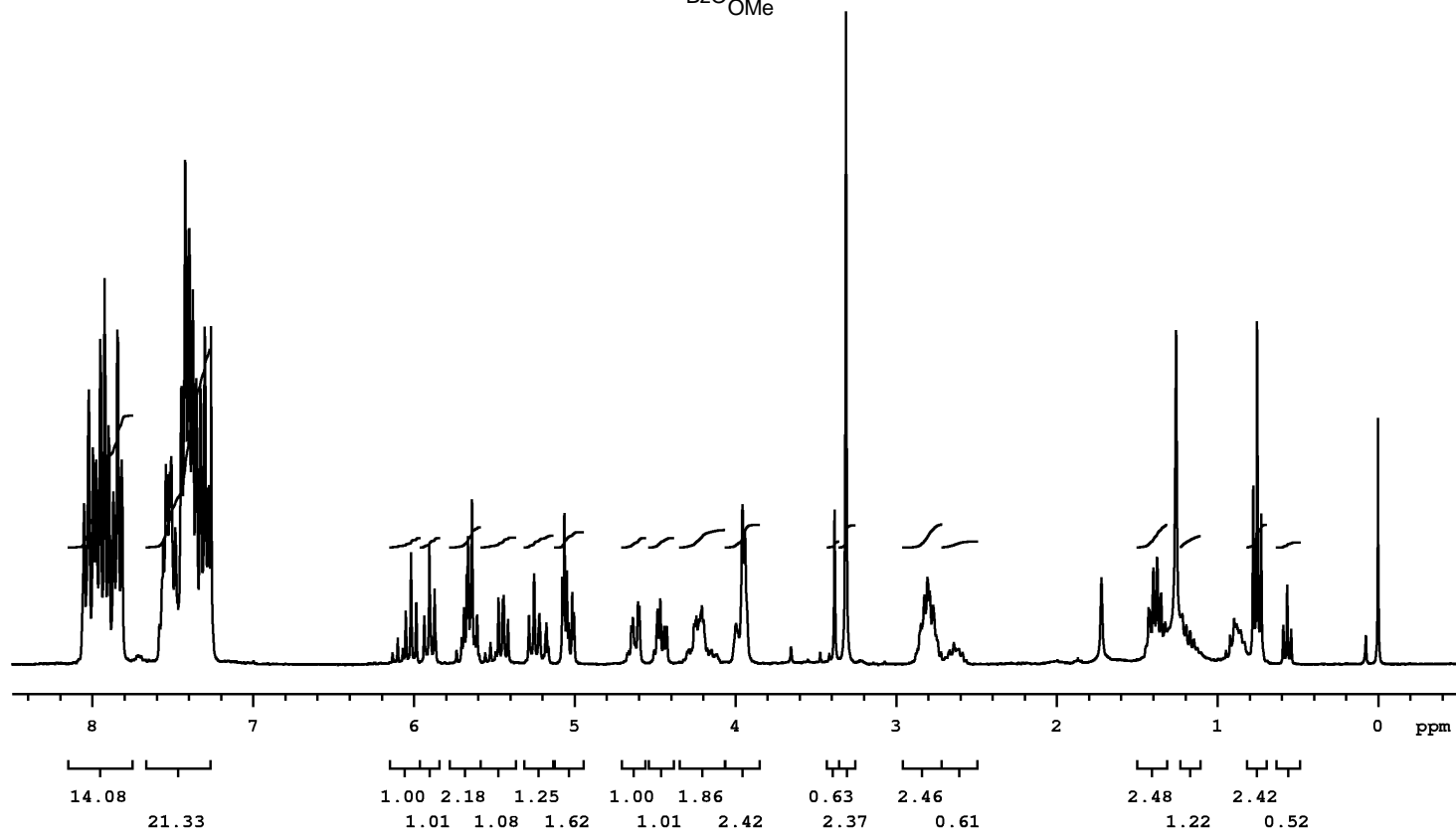


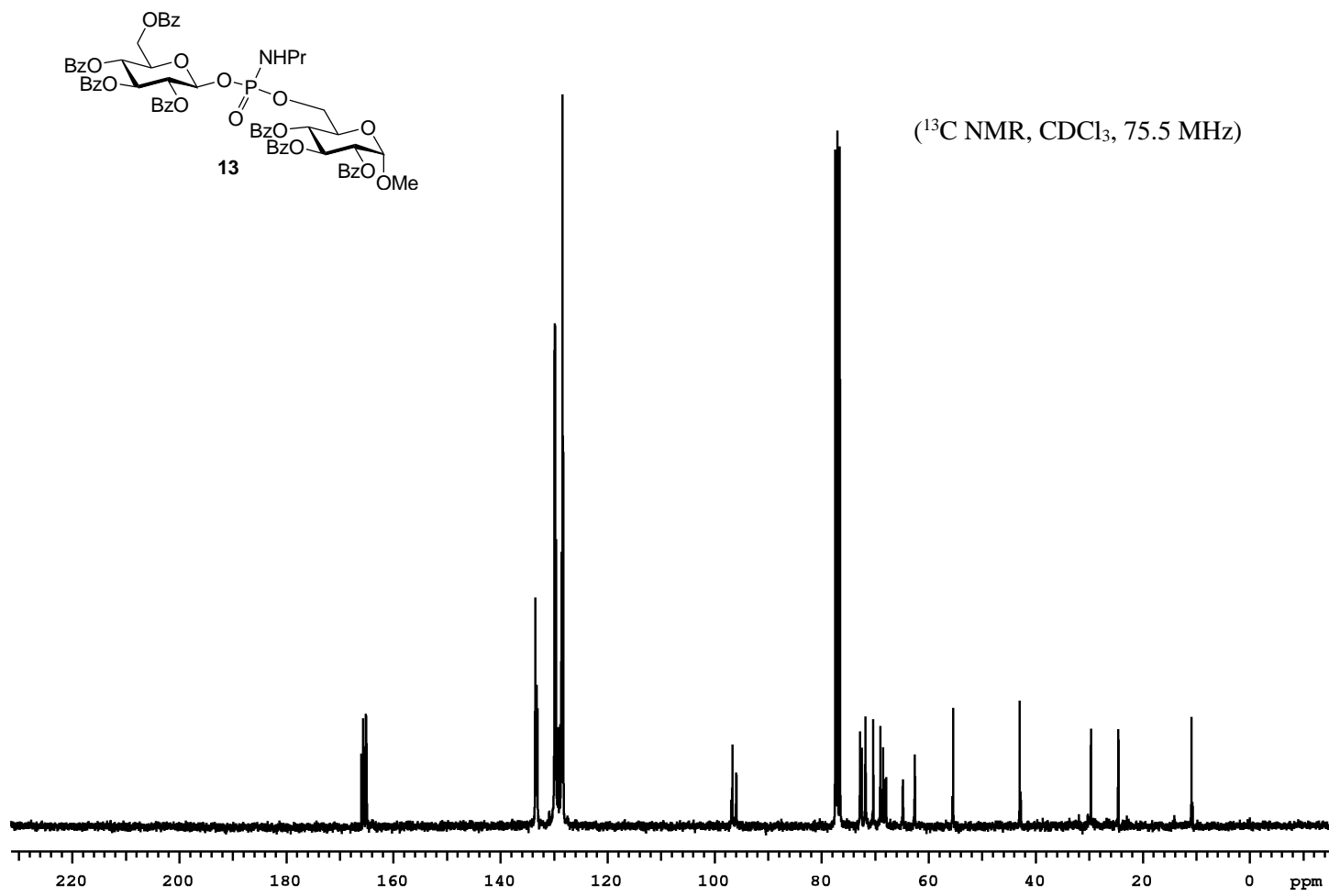
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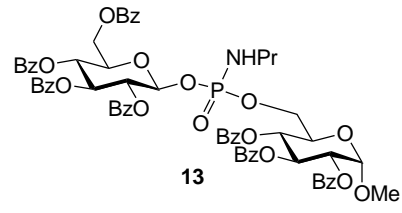




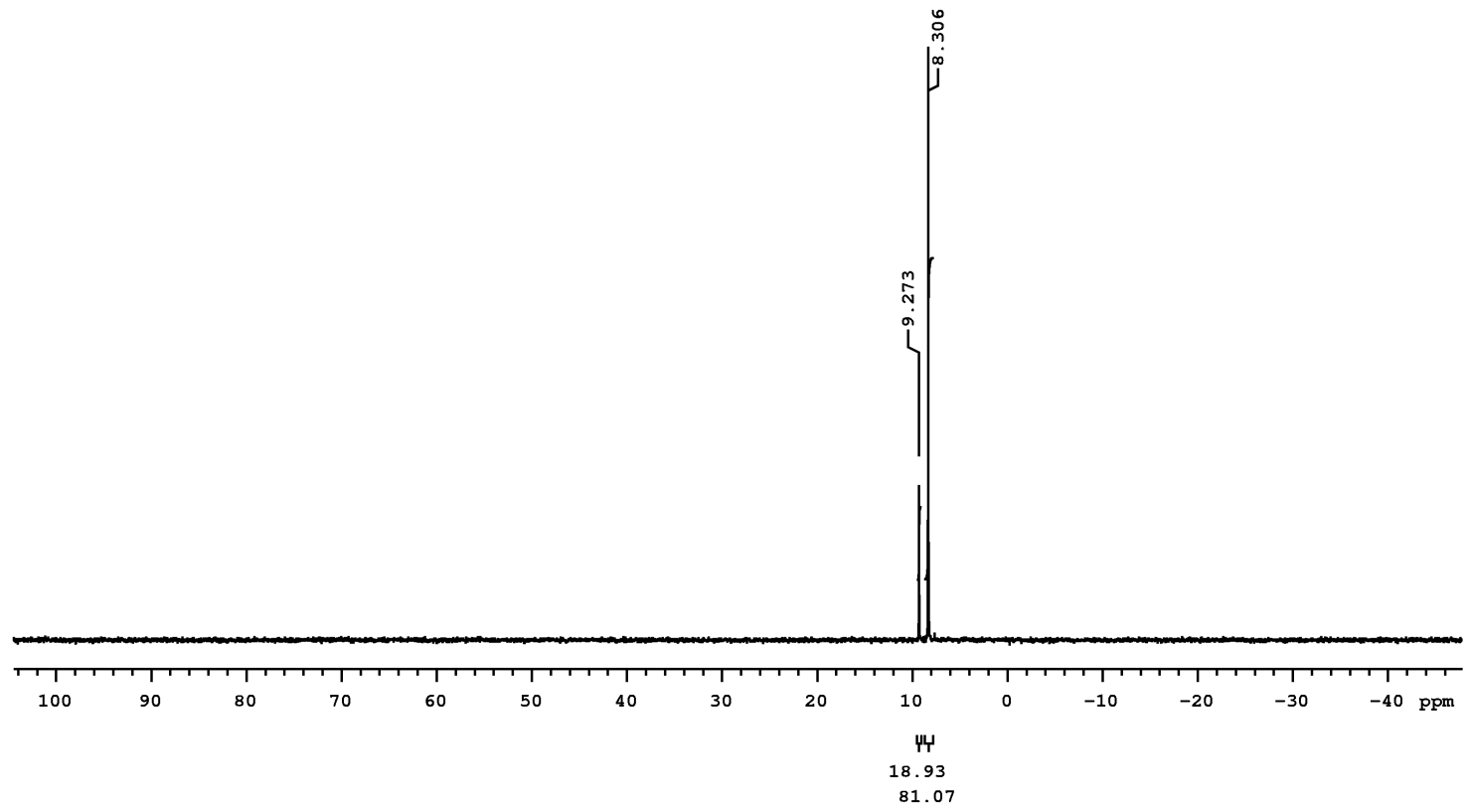
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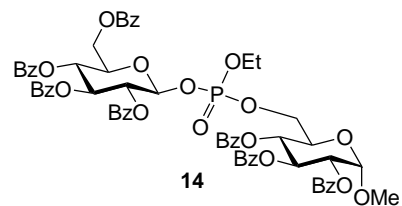




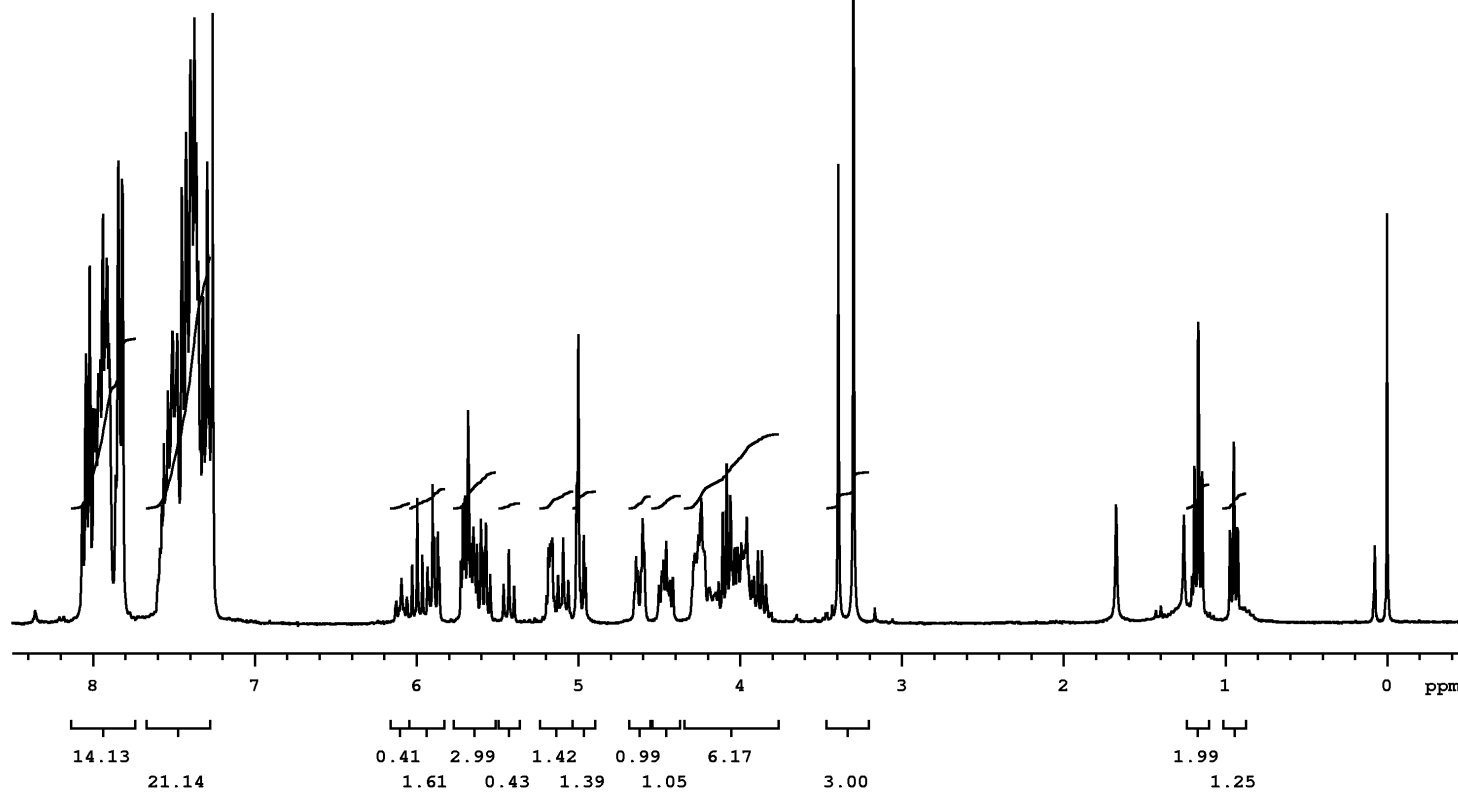


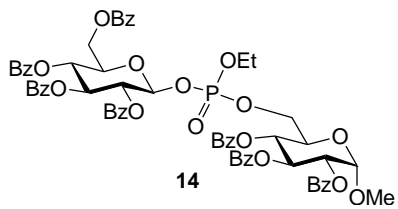
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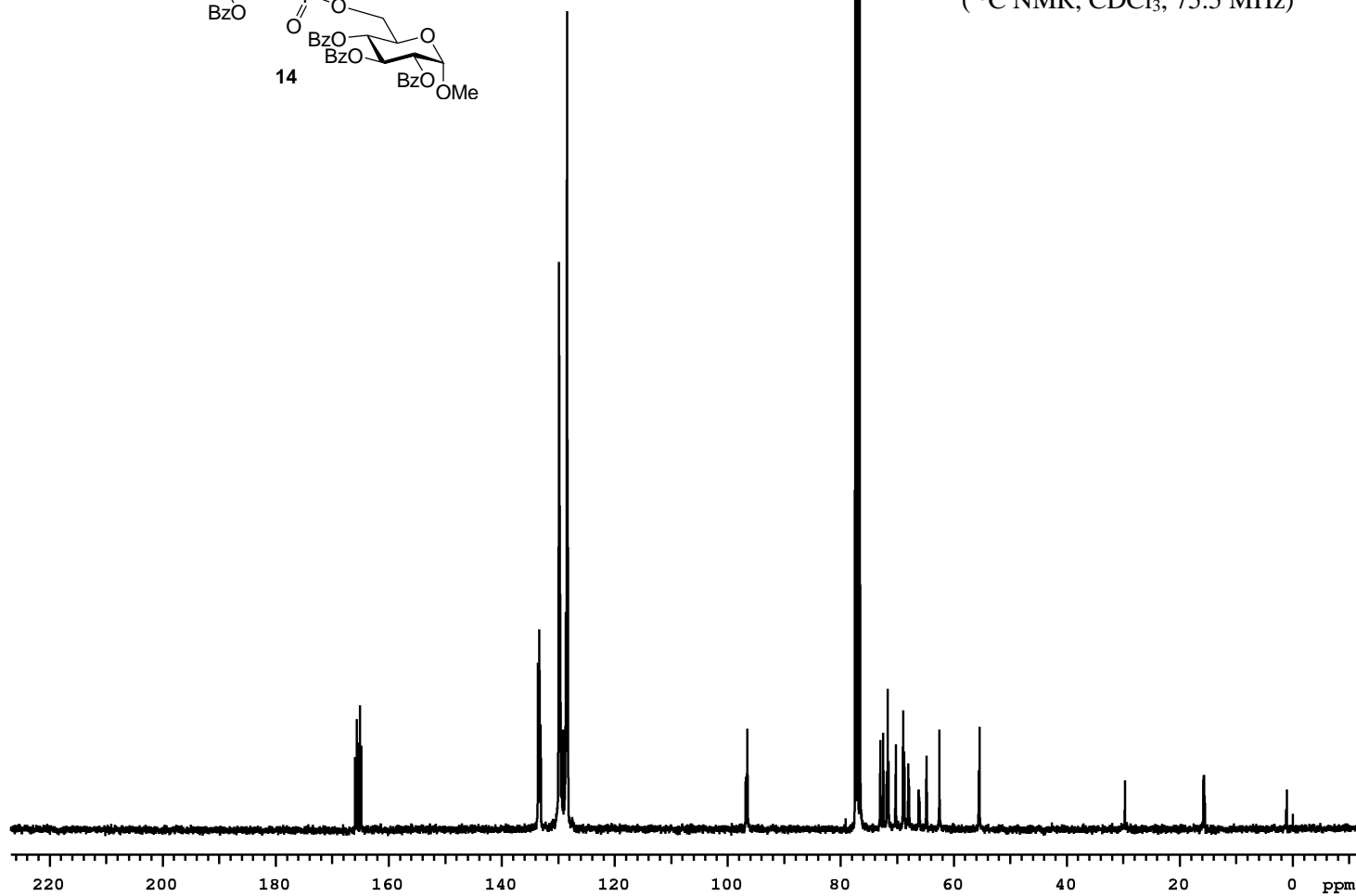


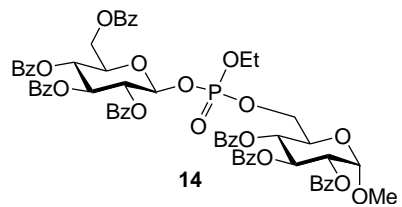
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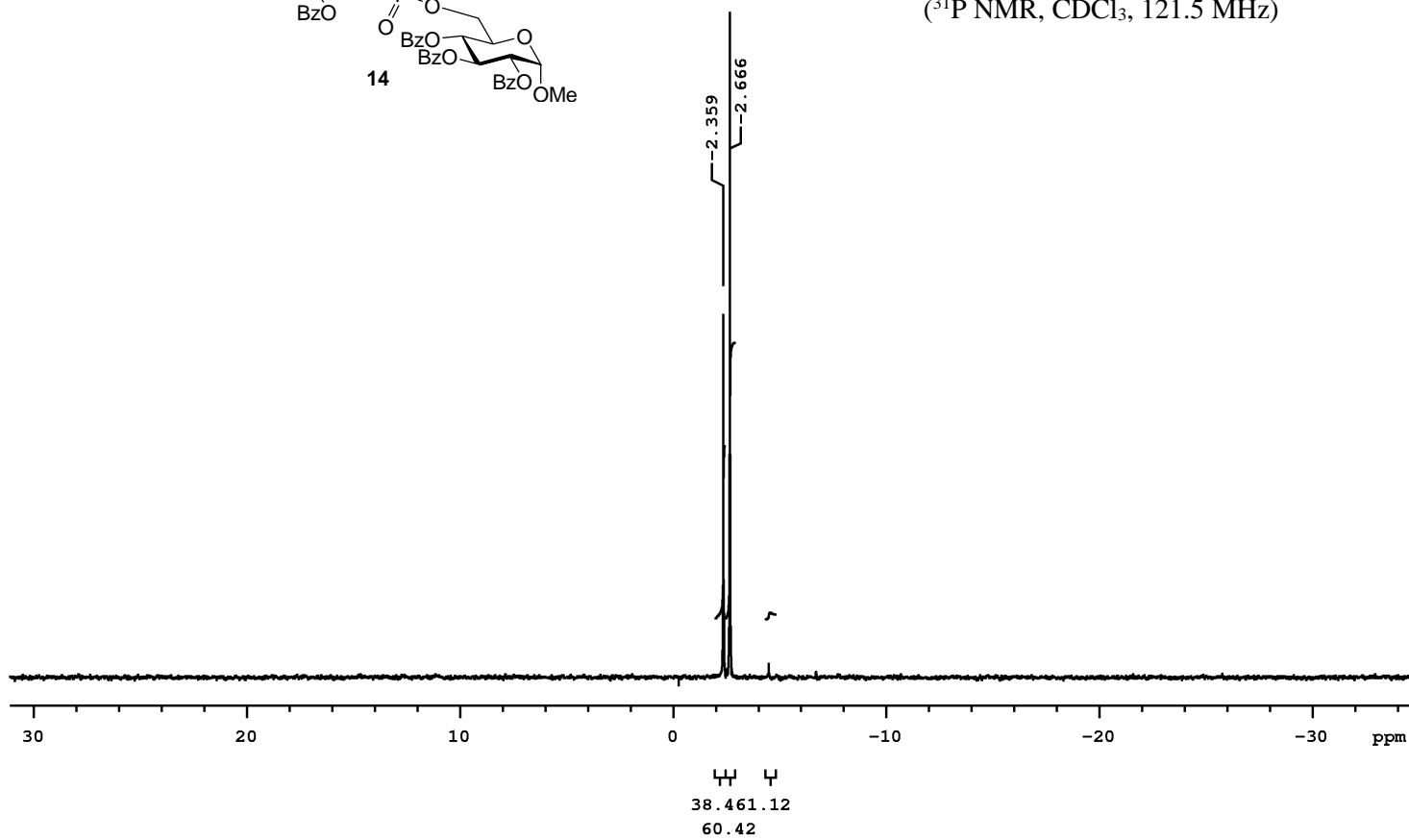


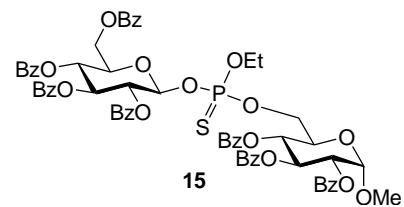
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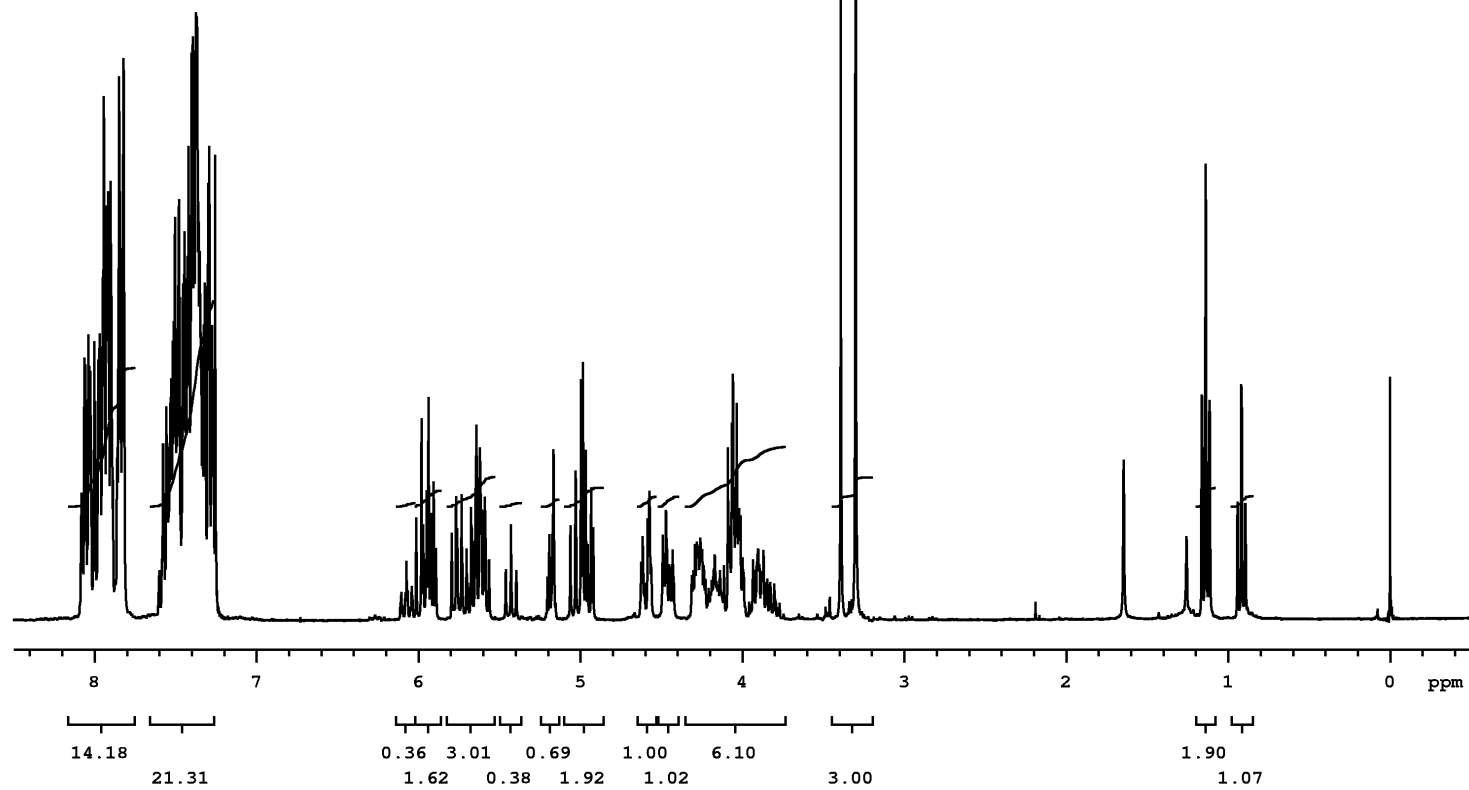


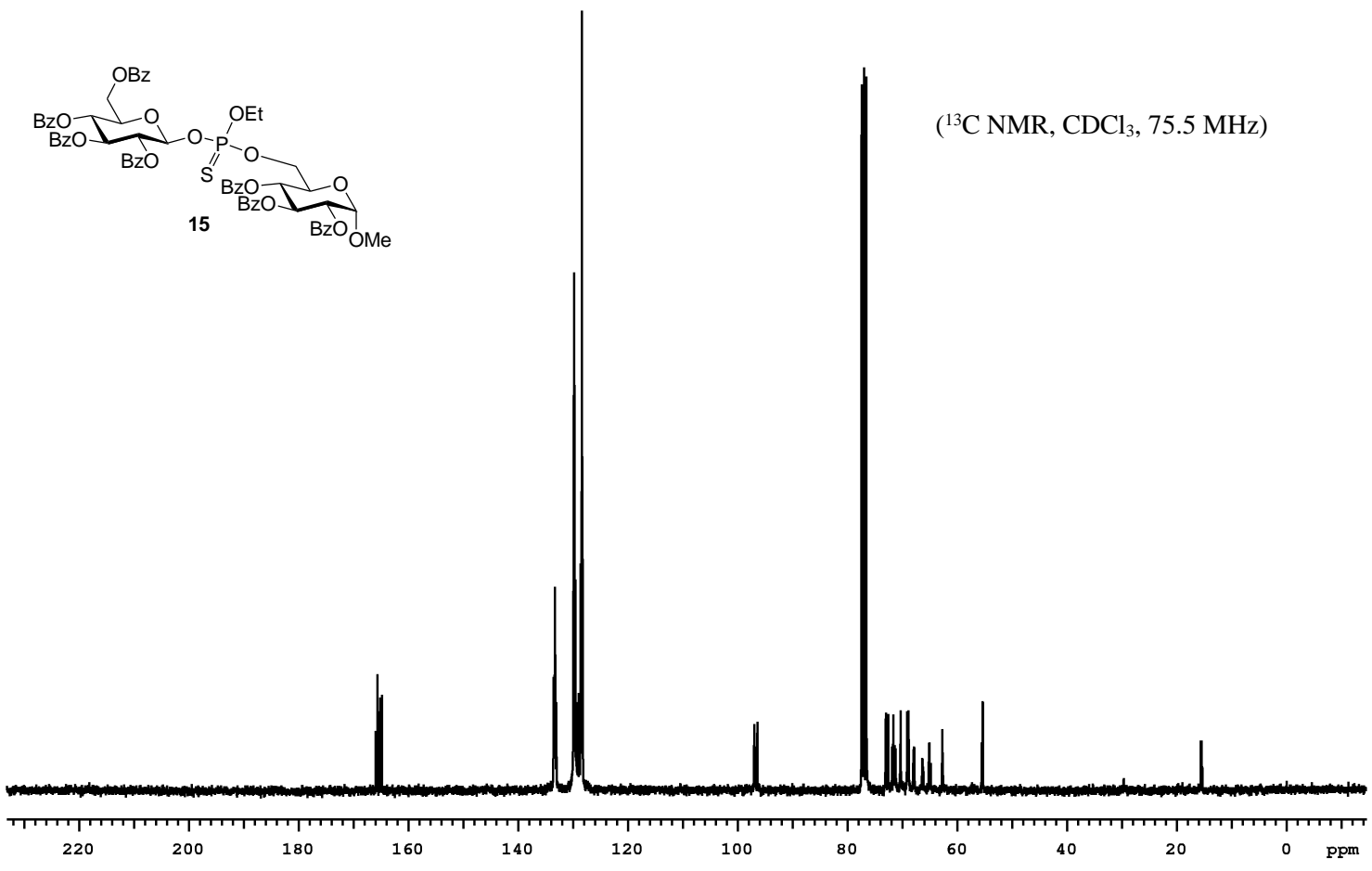
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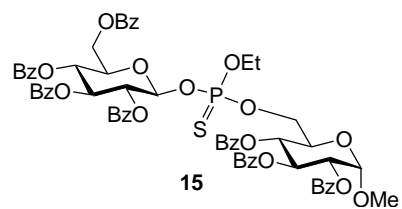




(¹H NMR, CDCl₃, 300 MHz)







(³¹P NMR, CDCl₃, 121.5 MHz)

