Supporting Information
For

Is Donor-Acceptor Hydrogen Bonding Necessary for 4,6-*O*-Benzylidene-directed β-Mannopsylation? Stereoselective Synthesis of β-*C*-Mannopyranosides and α-*C*-Glucopyranosides

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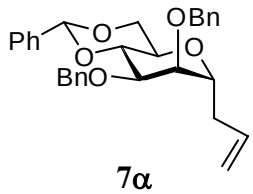
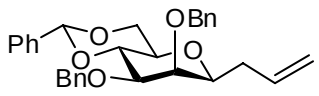
General. Unless otherwise stated ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ solution. Optical rotations were recorded in $CHCl_3$ solutions, unless otherwise stated. All organic extracts were dried over sodium sulfate, and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel.

General Procedure for Glycosylation Using the BSP/TTBP/Tf_2O System. To a stirred solution of donor (1 equiv), BSP (1.2 equiv), TTBP (1.5 equiv), and 3 Å molecular sieves in CH_2Cl_2 (0.05 M in substrate) at -60 ^{o}C under an argon atmosphere was added Tf_2O (1.2 equiv). After 30 min of stirring at -60 ^{o}C, a solution of the glycosyl acceptor (4.0 equiv) in CH_2Cl_2 (0.20 M in acceptor) was slowly added. The reaction mixture was stirred for a further 2 h at -60 ^{o} C, and then the reaction mixture was diluted with CH_2Cl_2, and the molecular sieves were filtered off and washed with saturated $NaHCO_3$ solution and brine. The organic layer was separated, dried over Na_2SO_4, and concentrated. Purification by column chromatography on silica gel, eluting with hexanes/ethyl acetate mixtures, afforded the corresponding coupled products.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-allyl-α-D-mannopyranose (7α) and 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-allyl-β-D-mannopyranose (7β).



7α

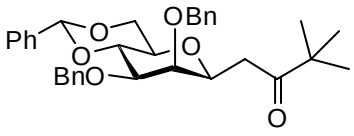


7β

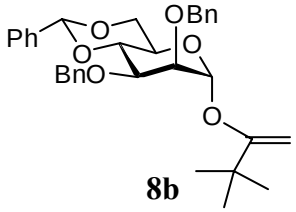
Prepared by the general procedure with a combined yield of 53.0 mg (61%, 1:8 α/β). **7α:** Colorless oil; $[\alpha]^{20}_{D}$ +10.4 (*c* = 0.25, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.5, 7.5 Hz, 2H), 7.40-7.65 (m, 13H), 5.65–5.58 (m, 2H), 5.02 (d, *J* = 10.0 Hz, 1H), 4.96 (dd, *J* = 1.5, 17.0 Hz, 1H), 4.81 (d, *J* = 12.5 Hz, 1H), 4.75 (s, 2H), 4.66 (d, *J* = 12.5 Hz, 1H), 4.28 (t, *J* = 10.0 Hz, 1H), 4.21 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.05 (t, *J* = 8.0

Hz, 1H), 3.86–3.82 (m, 2H), 3.70 (d, *J* = 1.5 Hz, 1H), 3.69-3.6 (m, 1H), 2.45–2.41 (m, 1H), 2.21–2.17 (m, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.5, 138.2, 137.7, 133.4, 128.8, 128.4, 128.3, 128.2, 127.7, 127.7, 126.0, 117.9, 101.4, 79.6, 76.3, 75.5, 72.9, 72.8, 69.2, 65.8, 33.8; ESI-HRMS calcd for $C_{30}H_{32}O_5Na$ $[M + Na]^+$, 495.2142; found, 495.2127. **7β:** Colorless oil; $[\alpha]^{20}_D$ – 20.2 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.0 Hz, 2H), 7.41-7.25 (m, 13H), 5.68–5.63 (m, 2H), 5.09–5.01 (m, 3H), 4.93 (d, *J* = 12.5 Hz, 1H), 4.77 (d, *J* = 12.5 Hz, 1H), 4.70 (d, *J* = 11.5 Hz, 1H), 4.30–4.23 (m, 2H), 3.85 (t, *J* = 5 Hz, 1H), 3.81 (d, *J* = 3.0 Hz, 1H), 3.73 (dd, *J* = 2.5, 7.0 Hz, 1H), 3.45 (dd, *J* = 7.0, 7.5 Hz, 1H), 3.41–3.36 (m, 1H), 2.45 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.27 (dd, *J* = 7.5, 14.0 Hz, 1H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.7, 138.4, 137.7, 134.2, 128.8, 128.5, 128.4, 128.3, 128.2, 127.7, 127.6, 127.5, 126.1, 117.5, 101.4, 80.8, 79.7, 79.6, 76.4, 75.0, 73.2, 71.9, 68.7, 35.5; ESI-HRMS calcd for $C_{30}H_{32}O_5Na$ $[M + Na]^+$, 495.2142; found, 495.2121. The ^{1}H-NMR data for compound **7β** do not match that reported in the literature for this compound (Terauchi, M.; Abe, H.; Matsuda, A.; Shuto, S. *Org. Lett.* **2004,** *6,* 3751-3754). It is not clear why this is at the present time.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-(3,3-dimethyl-2-oxo-butyl)-β-D-mannopyranose (8a) and (3,3-dimethyl-2buten-2-yl) 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (8b).



8a



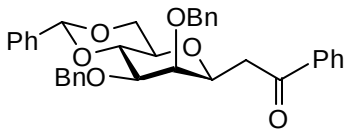
8b

Prepared by the general procedure with a combined yield of 62.0 mg (63%, 7:1 8a/8b). **8a:** Colorless oil; $[\alpha]^{20}_D$ –1.5(*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.7 (d, *J* = 3.0 Hz, 2H), 7.48(d, *J* = 7.5 Hz, 4H), 7.30–7.17 (m, 9H), 5.41 (s, 1H), 5.28 (d, *J* = 11.5 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 12.5 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.42 (t, *J* = 9.5 Hz, 1H), 4.27 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.03 (t, *J* = 6.5 Hz, 1H), 3.90 (d, *J* = 2.0 Hz, 1H), 3.72–3.66 (m, 2H), 3.43–3.36 (m, 1H), 3.00 (dd, *J* = 6.0, 17.5 Hz, 1H), 2.58 (dd, *J* = 6.0, 17.5 Hz, 1H), 1.02 (s, 9H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 211.7,

139.4, 139.2, 138.6, 128.6, 128.4, 128.3, 128.02, 127.8, 127.6, 127.5, 126.5, 101.5, 80.9, 79.9, 77.9, 75.6, 75.5, 75.4, 71.8, 68.7, 43.7, 38.2, 26.1; ESI-HRMS calcd for $C_{33}H_{38}O_6Na$ $[M + Na]^+$, 553.2560; found, 553.2552.

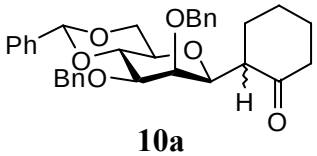
8b: Colorless oil; $[\alpha]^{20}_D$ +21.5(*c* = 0.7, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.49(d, *J* = 8.0 Hz, 2H), 7.44(d, *J* = 7.5 Hz, 2H), 7.29–7.18 (m, 9H), 5.56 (s, 1H), 5.44 (s, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.88 (d, *J* = 11.5 Hz, 1H), 4.75 (d, *J* = 12.5 Hz, 1H), 4.63–4.58(m, 2H), 4.50 (d, *J* = 2.5 Hz, 1H), 4.30–4.27(m, 2H), 4.24 (d, *J* = 2.5 Hz, 1H), 4.13–4.06 (m, 1H), 3.95 (s, 1H), 3.72 (t, *J* = 10.0 Hz, 1H), 1.11 (s, 9H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 167.5, 139.1, 138.7, 138.4, 128.6, 128.3, 128.3, 128.1, 128.0, 127.8, 127.6, 127.5, 126.5, 101.7, 96.7, 82.6, 79.5, 77.8, 76.3, 73.9, 73.4, 68.8, 65.6, 35.7, 28.1; ESI-HRMS calcd for $C_{33}H_{38}O_6Na$ $[M + Na]^+$, 553.2561; found, 553.2564.

2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-β-D-mannopyranose (9).

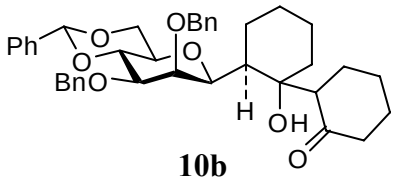


Prepared by the general procedure with a yield of 81.0 mg (80 %). Colorless oil; $[\alpha]^{20}_D$ –6.8(*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, C_6D_6) δ 7.92 (d, *J* = 6.0 Hz, 2H), 7.70(d, *J* = 7.0 Hz, 2H), 7.50(d, *J* = 7.0 Hz, 2H), 7.39(d, *J* = 7.0 Hz, 2H), 7.29–7.08 (m, 12H), 5.42 (s, 1H), 5.22 (d, *J* = 11.0 Hz, 1H), 5.00 (d, *J* = 12.5 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 11.0 Hz, 1H), 4.46(t, *J* = 9.5 Hz, 1H), 4.25 (dd, *J* = 5.0, 10.5 Hz, 1H), 4.16 (dt, *J* = 1.0, 6.5 Hz, 1H), 4.04 (d, *J* = 1.0 Hz, 1H), 3.74 (dd, *J* = 3.0, 10.0 Hz, 1H), 3.69 (t, *J* = 10 Hz, 1H), 3.44–3.39 (m, 1H), 3.32 (dd, *J* = 5.0, 17.0 Hz, 1H), 3.20 (dd, *J* = 7.0, 18.0 Hz, 1H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 196.7, 139.4, 139.0, 138.7, 132.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 127.4, 126.4, 101.5, 80.9, 79.8, 77.7, 75.8, 75.6, 73.3, 71.8, 68.7, 39.8; ESI-HRMS calcd for $C_{35}H_{34}O_6Na$ $[M + Na]^+$, 551.2428; found, 551.2382.

(2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene)-1S-1-(2-oxo-cyclohexyl)-1-deoxy-β-D-mannopyrannose (10a) and (2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-β-D-mannopyrannosyl)-1-[2-hydroxy-2-(2-oxocyclohexyl)cyclohexyl] (10b).



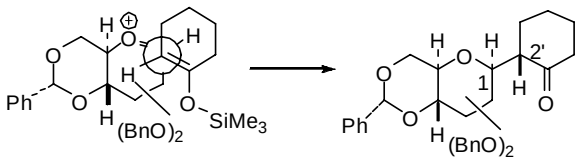
10a



10b

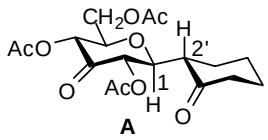
Prepared by the general procedure with a combined yield of 49.0 mg (51 %, 2:1 10a/10b).**10a :** Colorless oil; $[\alpha]^{23}_{D}$ –3.14(*c* = 0.4, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.0 Hz, 2H), 7.41–7.26 (m, 13H), 5.64 (s, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.94 (d, *J* = 13 Hz, 1H), 4.80 (d, *J* = 12.5 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.26–4.19 (m, 3H), 3.85–3.81 (m, 2H), 3.60 (d, *J* = 9.5 Hz, 1H), 3.38–3.34 (m, 1H), 2.77–2.73 (m, 1H), 2.42–2.37 (m, 1H), 2.10 (d, *J* = 1.5 Hz, 1H), 2.08 (s, 1H), 2.00–1.96 (m, 2H), 1.86–1.81 (m, 1H), 1.58–1.51 (m, 1H), 1.27–1.21 (m, 1H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 212.0, 138.7, 138.4, 137.7, 129.0, 128.7, 128.4, 128.3, 128.1, 127.8, 127.5, 126.1, 101.4, 80.7, 79.5, 78.0, 75.4, 75.1, 73.3, 71.9, 68.6, 50.1, 42.7, 31.3, 28.6, 25.0; ESI-HRMS calcd for $C_{33}H_{36}O_6Na$ $[M + Na]^+$, 529.2585; found, 529.2558.

We assign the stereochemistry of the newly formed stereodiad in **10a** as cis-anti in accordance with the work of Rovis (Frein, D. J.; Rovis, T. *Tetrahedron* **2006,** *62*, 4573). This configuration arises from a staggered anticlinal approach of the enol ether to the β-face of the oxacarbenium ion.



10a

In **10a** the $^{3}J_{H1,H2'}$ coupling constant is ~ 9.7 Hz consistent with the anti relationship of these two hydrogens in the predominant conformation. The cyclohexanone ring adopts an apparent twist boat conformation as determined by noe interactions and a strong $^{4}J_{w}$ type coupling across the carbonyl group. As such the conformation of **10a** about the newly formed C-C bond is significantly different to that reperted by Kunz for the related molecule **A** in which the $^{3}J_{1,2'}$ is 1.98 Hz.(Kunz, H.; Müller, B.; Weissmüller, J. *Carbohydr. Res.* **1987**, *171*, 25-34).

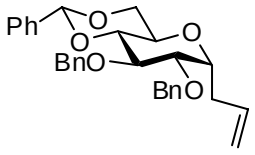


A

10b : Colorless oil; $[\alpha]^{23}_{D}$ –12.0(*c* = 0.2, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.73 (d, *J* = 7.0 Hz, 2H), 7.50–7.19 (m, 13H), 5.40 (s, 1H), 5.21 (d, *J* = 11.5 Hz, 1H), 5.03 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 12.5 Hz, 1H), 4.55 (s, 1H), 4.38 (t, *J* = 9.5 Hz, 1H), 4.22 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.98 (d, *J* = 3.0 Hz, 1H), 3.69 (t, *J* = 10.0 Hz, 1H), 3.56–3.53 (m, 1H), 3.18–3.16 (m, 1H), 2.77–2.73 (m, 1H), 2.44–2.29 (m, 2H), 2.02–2.00 (m, 1H), 1.82–1.33 (m, 14H), 1.01 (s, 1H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 210.3, 139.6, 139.2, 138.5, 128.0, 127.8, 127.6, 126.4, 101.6, 96.5, 79.5, 79.0, 78.8, 75.7, 72.4, 68.7, 67.3, 58.6, 44.1, 31.0, 29.8, 29.5, 28.8, 28.6, 25.9, 25.7, 22.3, 21.9. ESI-HRMS calcd for $C_{39}H_{46}O_7Na$ $[M + Na]^+$, 649.3141; found, 649.3080.

The stereochemistry at C2' in **10b** is assigned by analogy to **10a**. The configuration of the tertiary alcohol in **10b** remains unclear at this time.

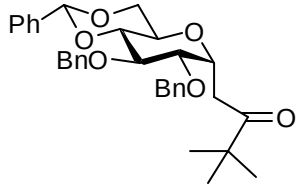
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-α-D-glucopyranose (12).



Prepared by the general procedure with a yield of 49.0 mg (54 %). Colorless oil; $[\alpha]^{22}_{D}$ +1.5 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 2.0, 7.5 Hz, 2H), 7.33–7.26 (m, 13H), 5.81–5.75 (m, 1H), 5.58 (s, 1H), 5.16–5.09 (m, 2H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.82 (d, *J* = 11.5 Hz, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.65(d, *J* = 12.0 Hz,

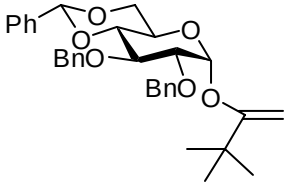
1H), 4.26–4.24 (m, 1H), 4.09 (dd, *J* = 7.5, 13.5 Hz, 1H), 3.90–3.87 (m, 1H), 3.77 (dd, *J* = 6.0, 8.5 Hz, 1H), 3.69–3.65 (m, 3H), 2.54 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 138.7, 138.2, 137.5, 134.3, 128.9, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 126.0, 117.3, 101.2, 82.8, 79.5, 78.8, 74.9, 74.9, 73.6, 69.5, 63.5, 30.7; ESI-HRMS calcd for $C_{30}H_{32}O_5Na$ $[M + Na]^+$, 495.2142; found, 495.2134.

2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-(3,3-dimethyl-2-oxo-butyl)-α-D-glucopyranose (13a).



Prepared by the general procedure with a yield of 20.0 mg (22 %). Colorless oil; $[\alpha]^{20}_D$ +11.16(*c* = 0.6, $CHCl_3$); ^{1}H NMR (500 MHz, C_6D_6) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.54(d, *J* = 7.5 Hz, 2H), 7.38–7.14 (m, 11H), 5.45 (s, 1H), 5.24 (dd, *J* = 6.0, 12.5 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.00 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 11.0 Hz, 1H), 4.54(d, *J* = 11.0 Hz, 1H), 4.27 (dd, *J* = 5.0, 10.0 Hz, 1H), 3.90 (t, *J* = 9.0 Hz, 1H), 3.81 (dd, *J* = 6.0, 9.0 Hz, 1H), 3.74–3.69 (m, 1H), 3.64 (dd, *J* = 9.0, 9.5 Hz, 1H), 3.57 (t, *J* = 10.0 Hz, 1H), 2.93 (dd, *J* = 6.0, 16.5 Hz, 1H), 2.61 (dd, *J* = 6.5, 16.5 Hz, 1H), 0.96 (s, 9H); ^{13}C NMR (125.9 MHz, C_6D_6) δ 210.3, 139.2, 138.3, 138.2, 128.8, 128.3, 128.3, 128.1, 128.0, 127.8, 127.6, 126.3, 101.3, 82.8, 79.3, 78.5, 74.3, 73.6, 71.8, 69.4, 65.0, 43.9, 34.4, 25.8; ESI-HRMS calcd for $C_{33}H_{38}O_6Na$ $[M + Na]^+$, 553.2561; found, 553.2563.

(3,3-Dimethyl-2-buten-2-yl) 2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-α-D-glucopyranoside (13b).

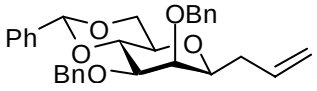


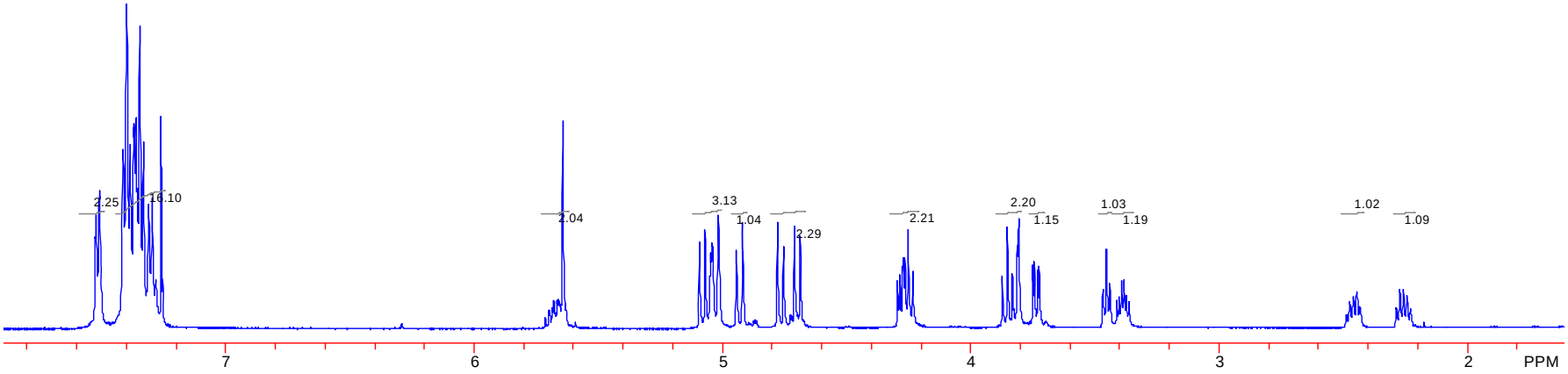
Prepared by the general procedure with a yield of 30.0 mg (33 %). Colorless oil; $[\alpha]^{20}_D$ +11.69(*c* = 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 1.5, 7.5 Hz, 2H),

7.40–7.26 (m, 13H), 5.57 (s, 1H), 5.32 (d, J = 3.5 Hz, 1H), 4.94 (d, J = 11.5 Hz, 1H), 4.87 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.67 (d, J = 12.0 Hz, 1H), 4.26 (dd, J = 5.0, 10.0 Hz, 1H), 4.21 (d, J = 2.5 Hz, 1H), 4.11 (d, J = 2.5 Hz, 1H), 4.08 (dd, J = 9.0, 9.5 Hz, 1H), 3.82–3.77 (m, 1H), 3.70 (d, J = 10.5 Hz, 1H), 3.67–3.63 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (125.9 MHz, $CDCl_3$) δ 168.9, 138.8, 137.4, 128.9, 128.4, 128.3, 128.3, 128.0, 127.6, 127.6, 126.0, 101.2, 94.9, 82.2, 82.1, 79.6, 78.5, 75.3, 73.0, 69.2, 63.0, 36.2, 28.3; ESI-HRMS calcd for $C_{33}H_{38}O_6Na$ $[M + Na]^+$, 553.2561; found, 553.2553.

2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-β-D-mannopyranose (7β)

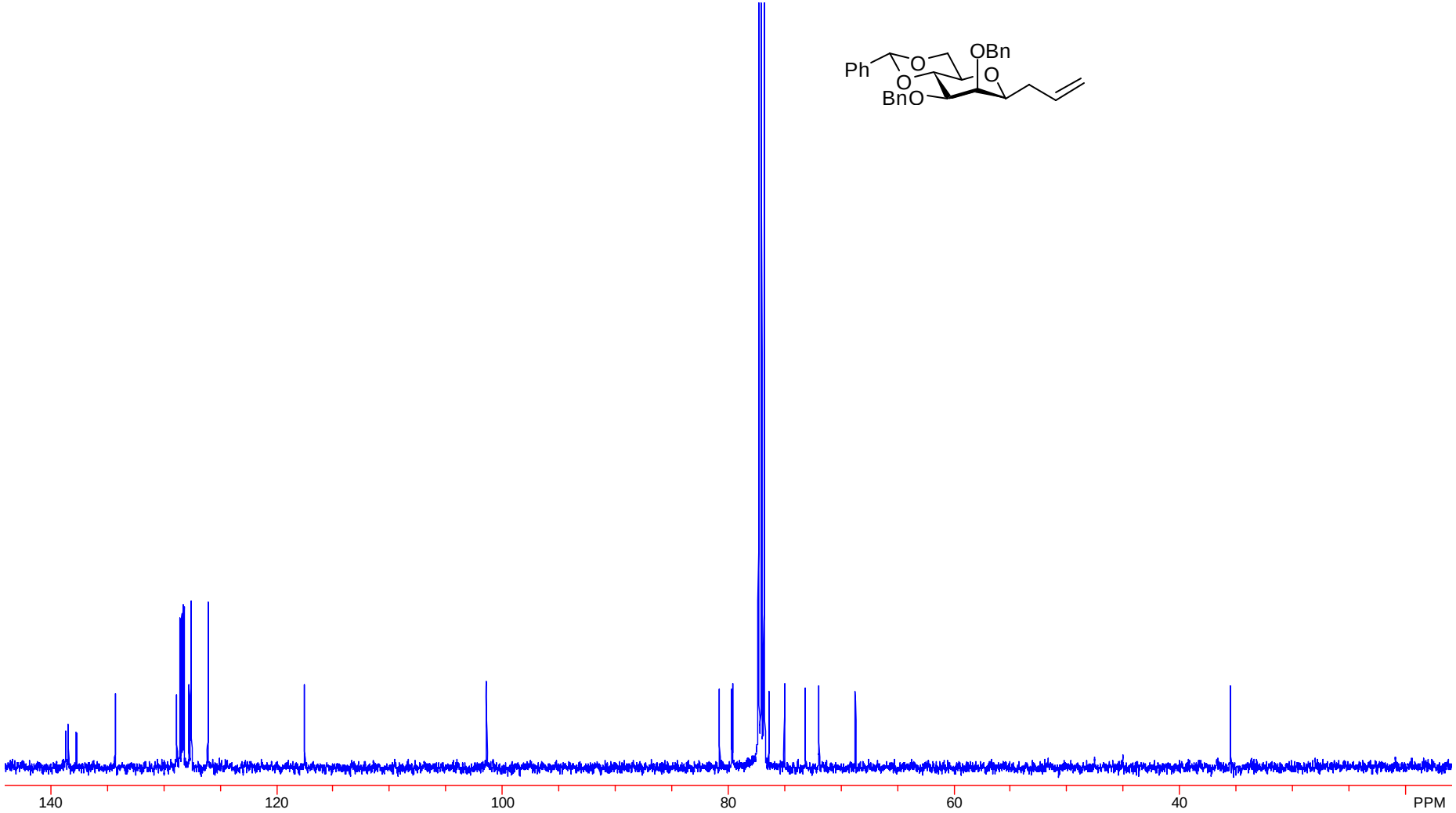
^{1}H NMR (500 MHz, $CDCl_3$)





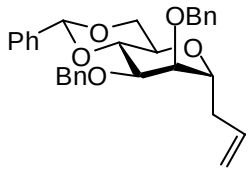
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-β-D-mannopyranose (7β)

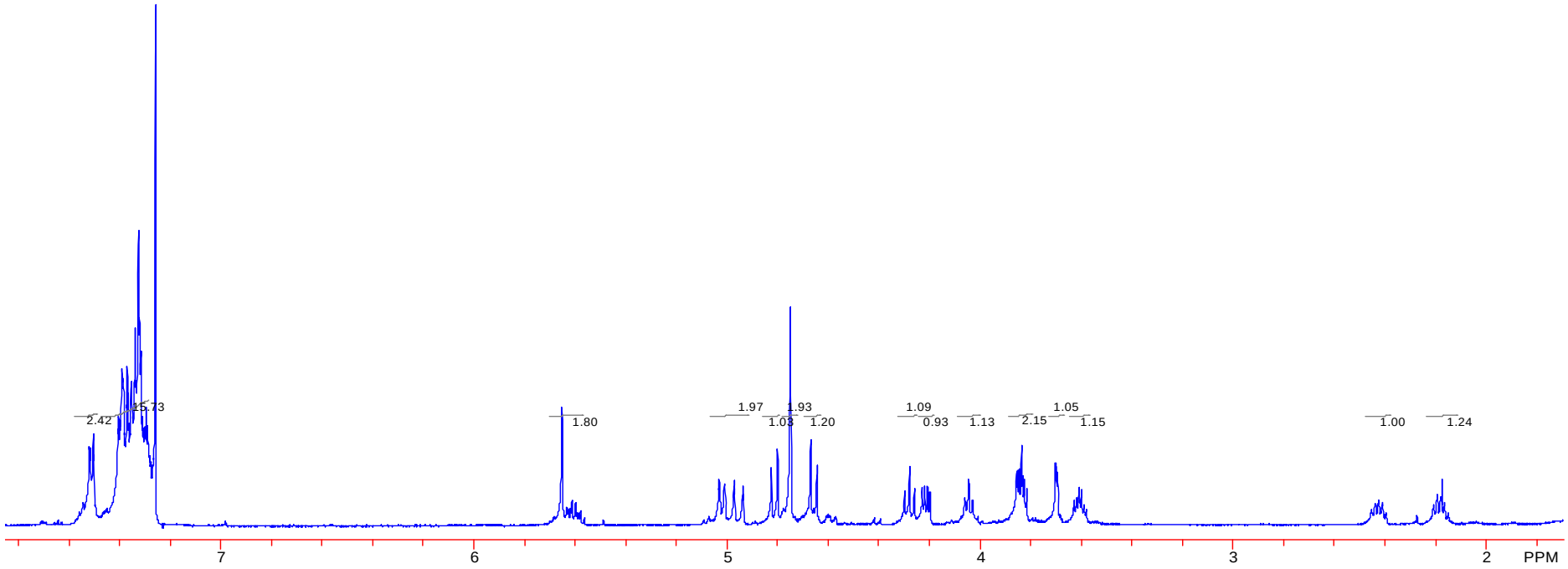
^{13}C NMR (125.9 MHz, $CDCl_3$)



2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-allyl-α-D-mannopyranose (7α)

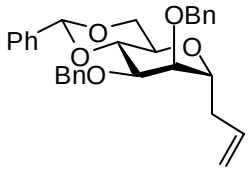
^{1}H NMR (500 MHz, $CDCl_3$)





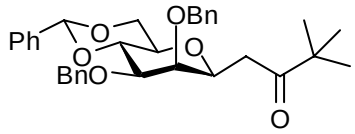
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-α-D-mannopyranose (7α)

^{13}C NMR (125.9 MHz, $CDCl_3$)



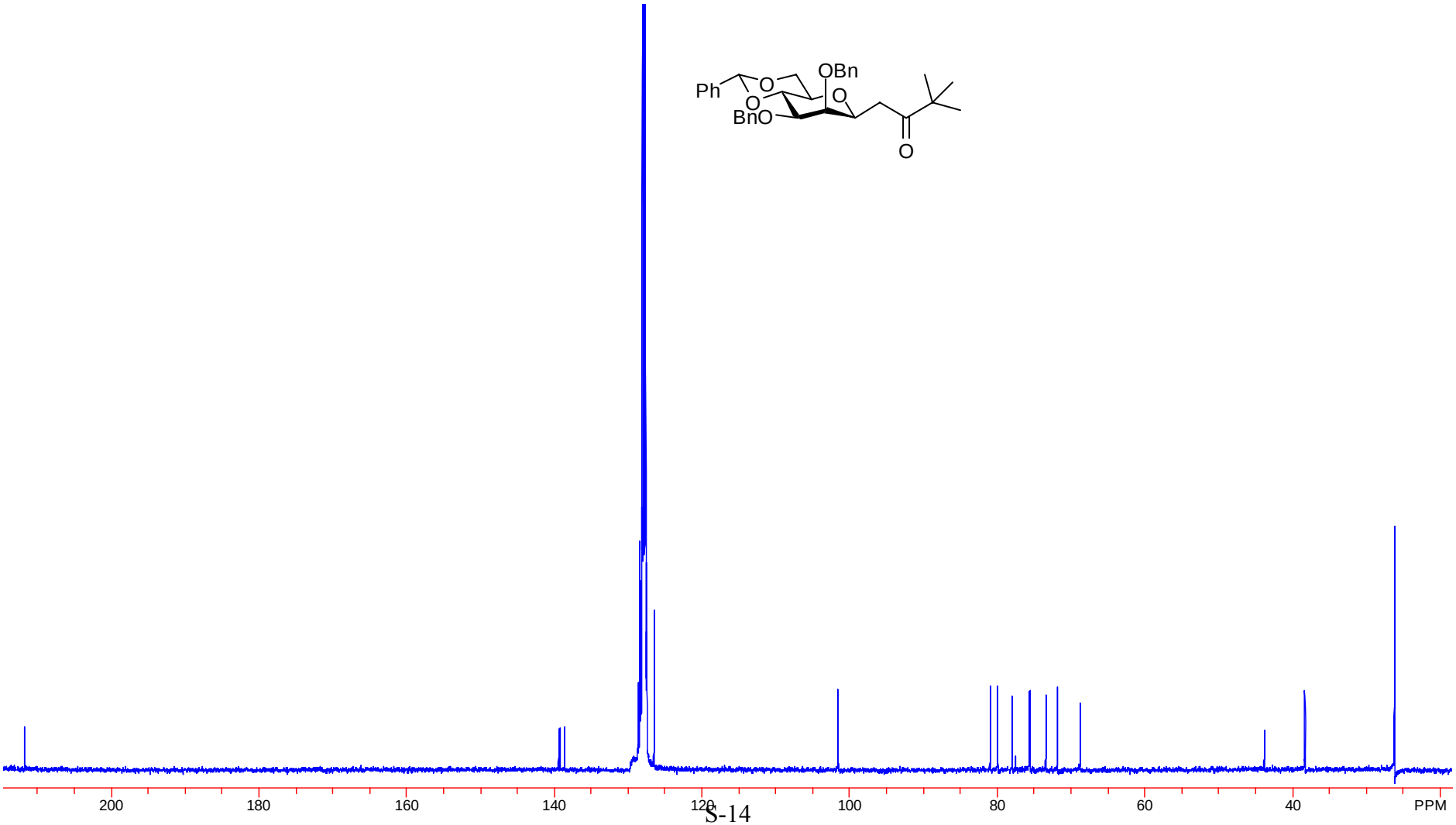
2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-(3,3-dimethyl-2-oxo-butyl)-β-D-mannopyranose (8a)

^{1}H NMR (500 MHz, C_6D_6)



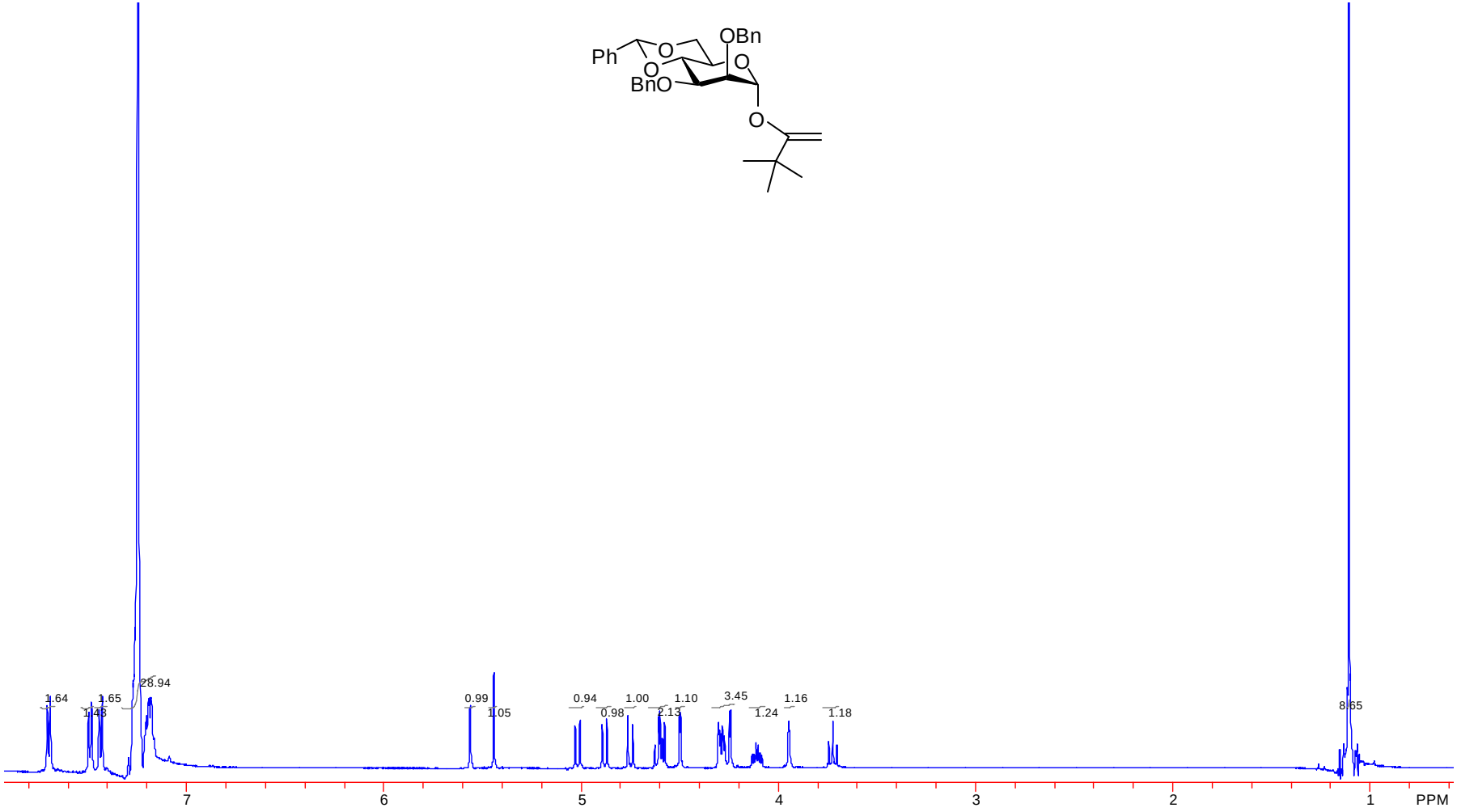
2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-(3,3-dimethyl-2-oxo-butyl)-β-D-mannopyranose (8a)

^{13}C NMR (125.9 MHz, C_6D_6)



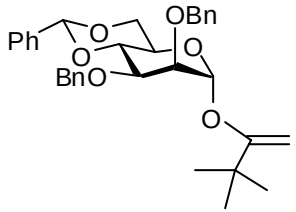
(3,3-dimethyl-2buten-2-yl) 2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-α-D-mannopyranoside (8b)

^{1}H NMR (500 MHz, C_6D_6)



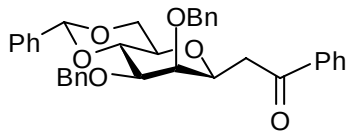
(3,3-dimethyl-2buten-2-yl) 2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-α-D-mannopyranoside (8b)

^{13}C NMR (125.9 MHz, C_6D_6)



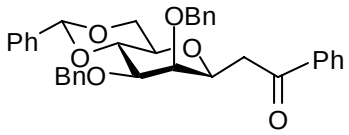
2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-β-D-mannopyranose (9)

^{1}H NMR (500 MHz, C_6D_6)



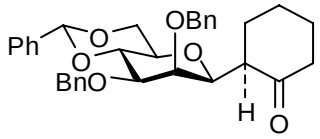
2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-deoxy-1-(2-oxo-2-phenylethyl)-β-D-mannopyranose (9)

^{13}C NMR (125.9 MHz, C_6D_6)



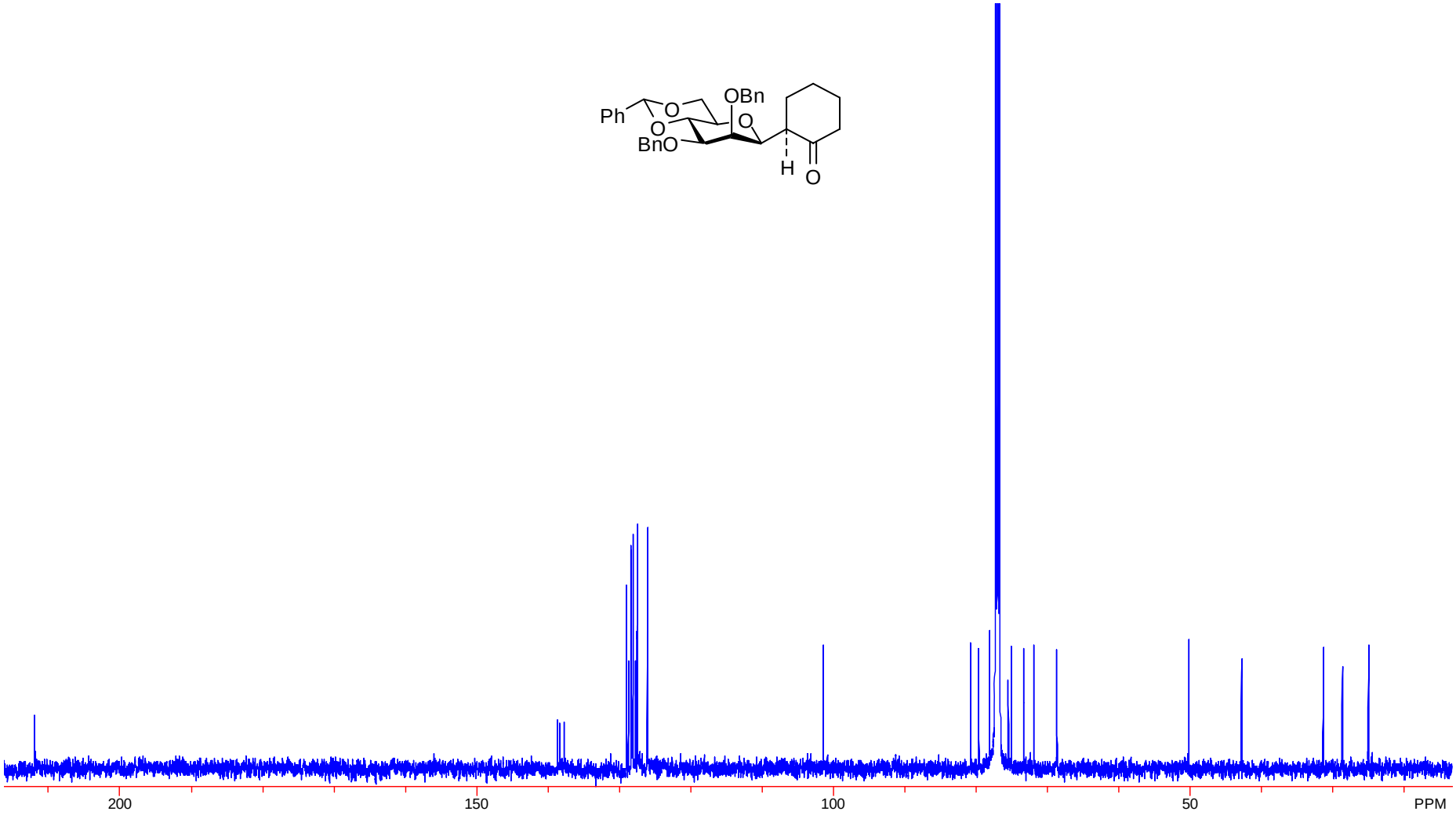
(2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene)-1S-1-(2-oxo-cyclohexyl)-1-deoxy-β-D-mannopyrannose (10a)

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



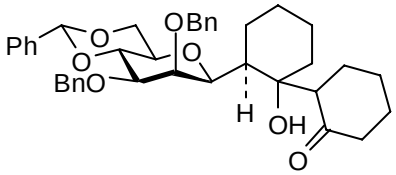
(2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene)-1S-1-(2-oxo-cyclohexyl)-1-deoxy-β-D-mannopyrannose (10a)

^{13}C NMR (125.9 MHz, $CDCl_3$)



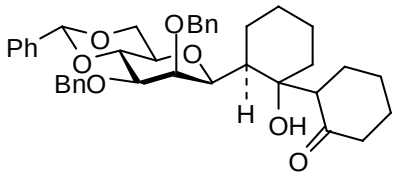
(2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyrannosyl)-1-[2-hydroxy-2-(2-oxocyclohexyl)cyclohexyl] (10b)

^{1}H NMR (500 MHz, C_6D_6)



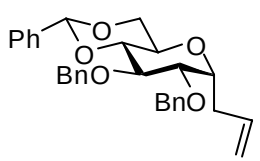
(2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-β-D-mannopyrannosyl)-1-[2-hydroxy-2-(2-oxocyclohexyl)cyclohexyl] (10b)

^{13}C NMR (125.9 MHz, C_6D_6)



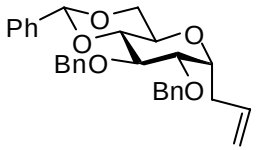
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-α-D-glucopyranose (12)

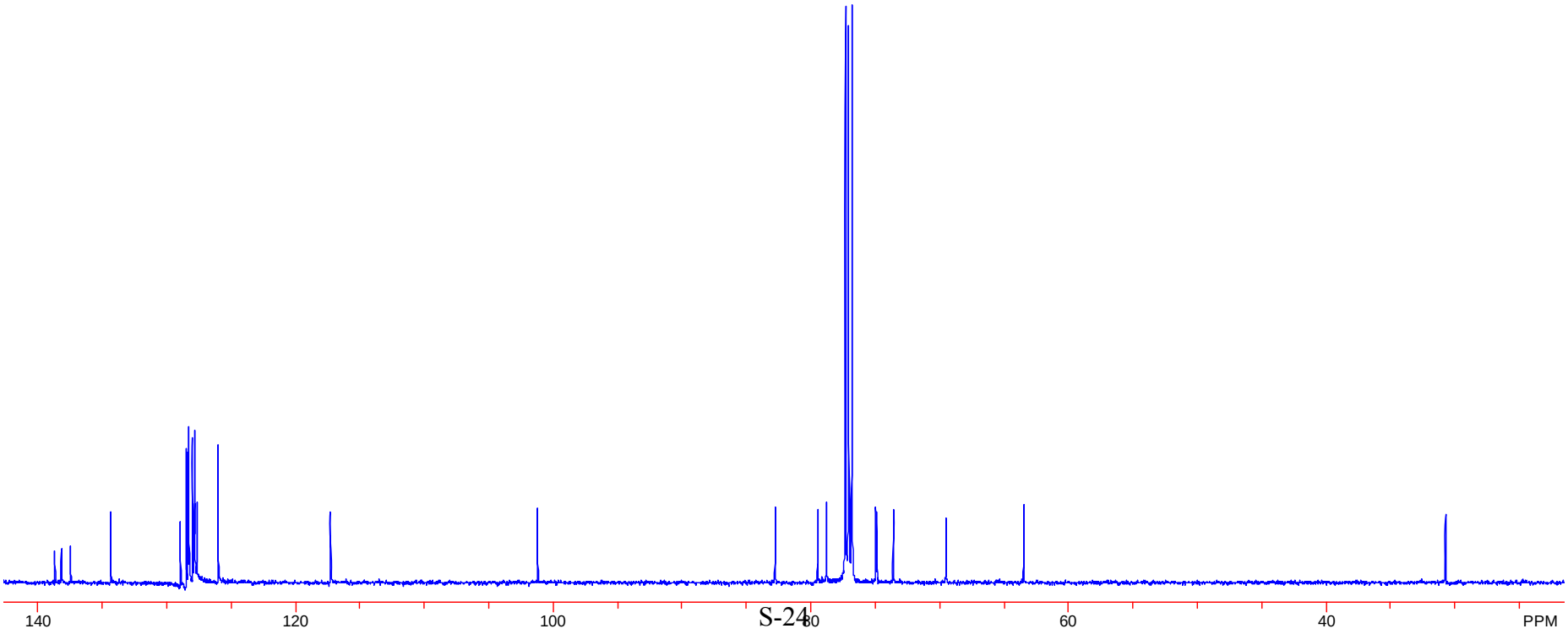
^{1}H NMR (500 MHz, $CDCl_3$)



2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-allyl-α-D-glucopyranose (12)

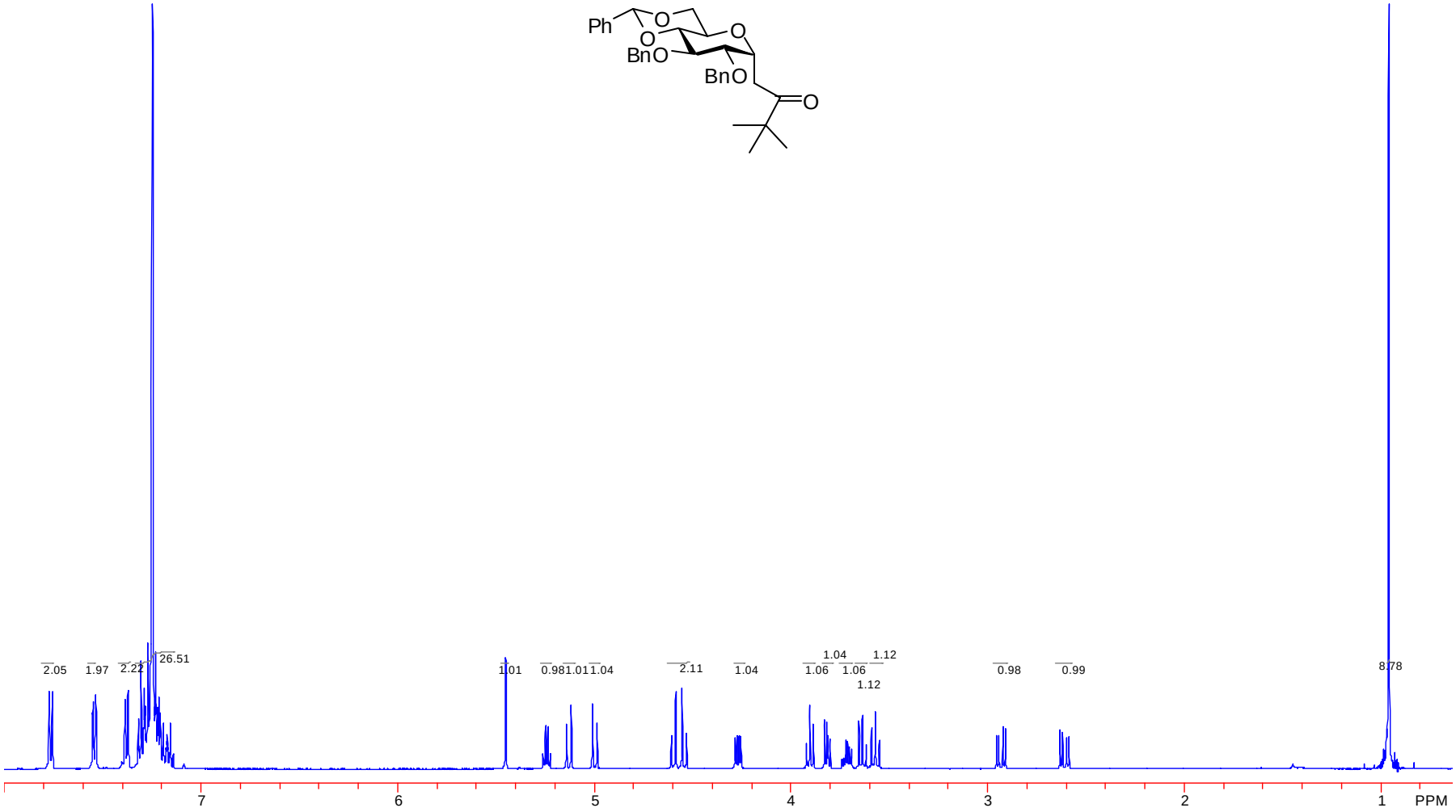
^{13}C NMR (125.9 MHz, $CDCl_3$)





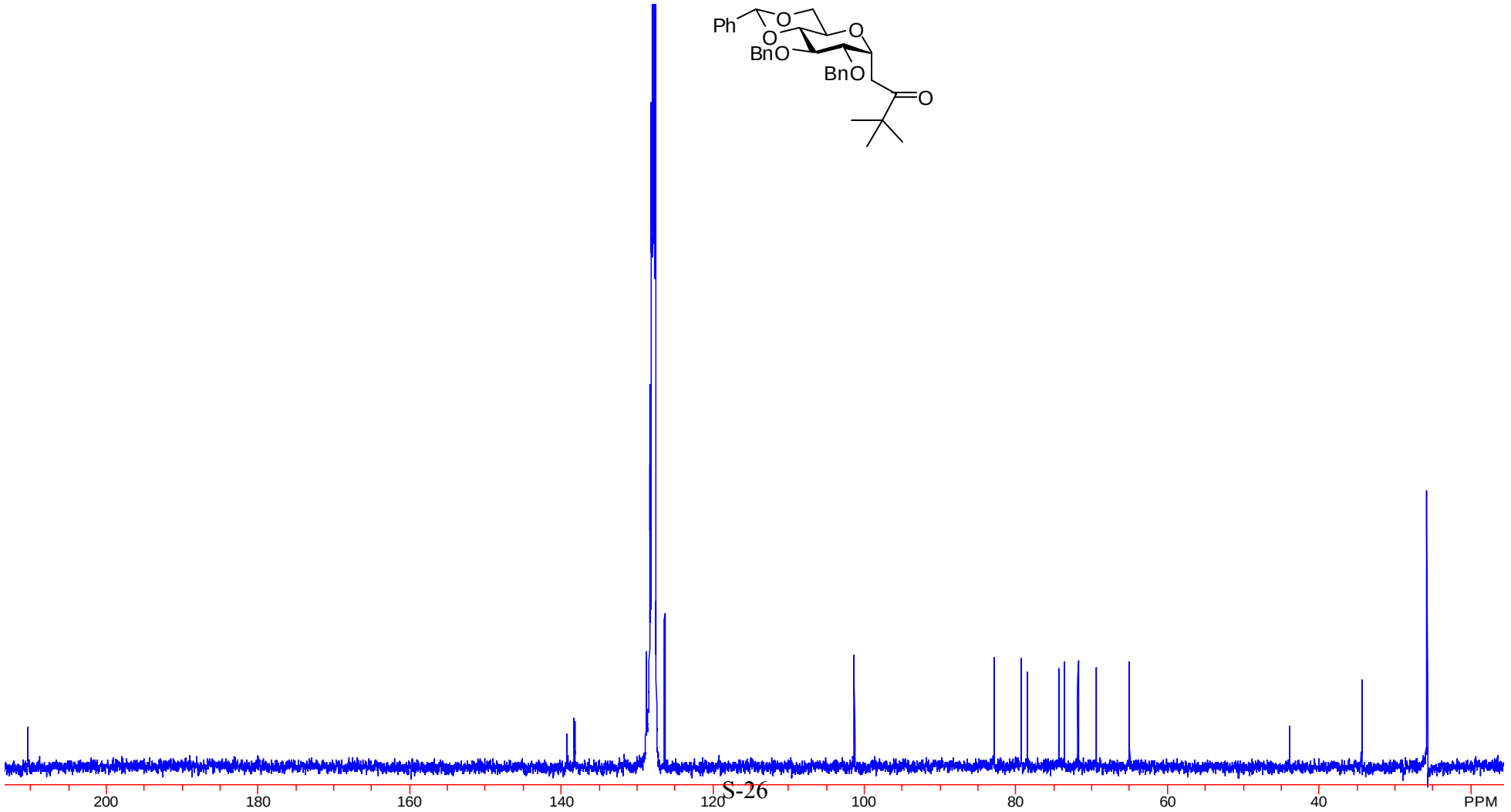
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-(3,3-dimethyl-2-oxo-butyl)-α-D-glucopyranose (13a)

^{1}H NMR (500 MHz, C_6D_6)



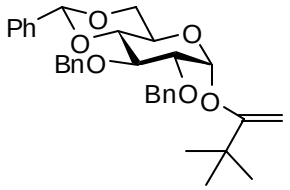
2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-1-deoxy-1-(3,3-dimethyl-2-oxo-butyl)-α-D-glucopyranose (13a)

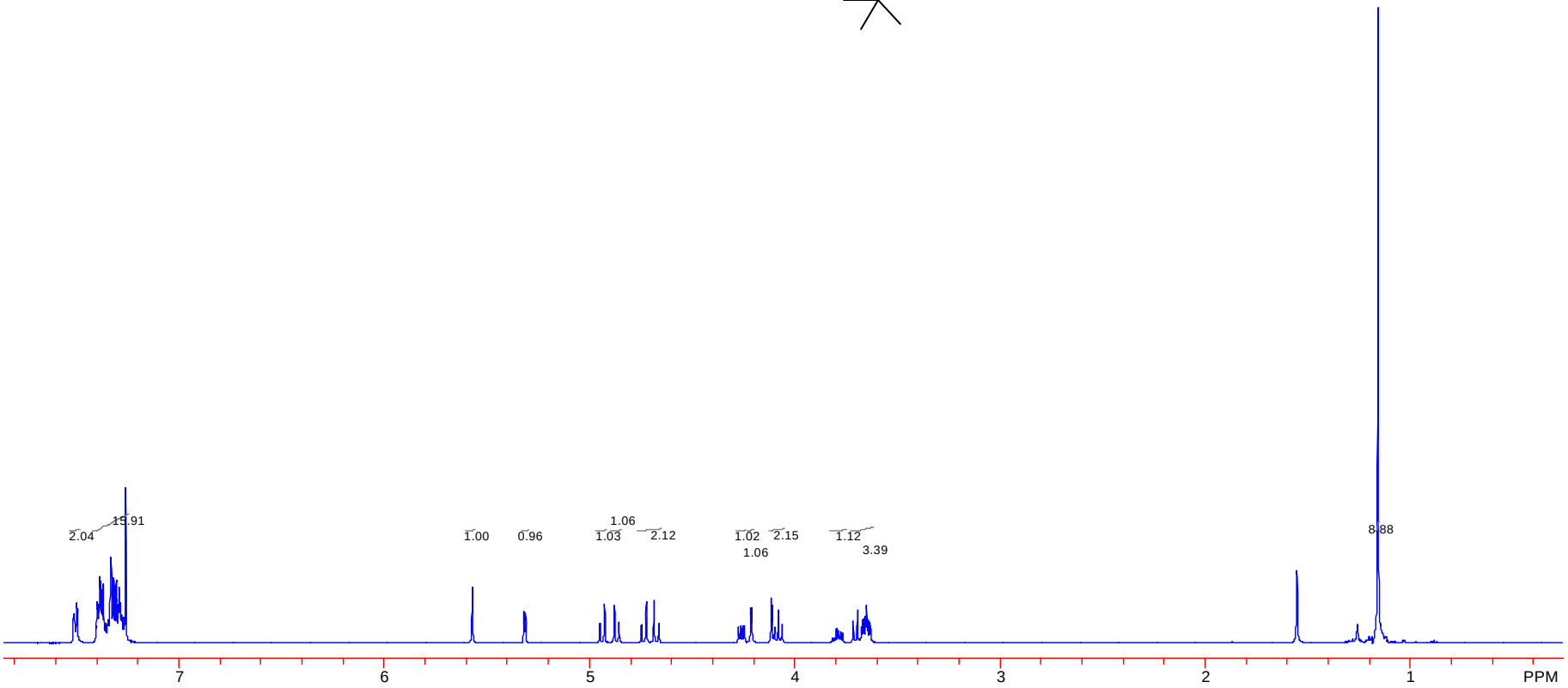
^{13}C NMR (125.9 MHz, C_6D_6)



3,3-Dimethyl-2-buten-2-yl) 2,3-Di-*O*-benzyl-4,*6*-*O*-benzylidene-α-D-glucopyranoside (13b)

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





3,3-Dimethyl-2-buten-2-yl) 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (13b)

^{13}C NMR (125.9 MHz, C_6D_6)