Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Data for:

Synthesis of α-D-Glc*p*-(1→3)-α-D-Gal*f*-(1→2)-α-L-Rha*p* constituent of the CPS of *Streptococcus pneumoniae* 22F. Effect of 3-*O*-substitution in 1,2-*cis* α-D-galactofuranosylation

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Allyl 3-*O*-benzoyl-2,5,6-tri-*O*-benzyl-α-D-galactofuranoside (28). To a solution of **22** (496 mg, 1.01 mmol) in dry pyridine (2 mL) cooled to 0 ºC, was added benzoyl chloride (0.24 mL, 2.02 mmol) with stirring. After 1h at room temperature, water was added and the stirring continued for 30 min. The mixture was extracted with CH_2Cl_2 (100 mL) and the organic layer was sequentially extracted with 10% HCl (100 mL), water (100 mL), saturated aq. $NaHCO_3$ (100 mL) and water (100 mL), dried (Na_2SO_4), filtered and concentrated. Column chromatography (10:1 hexane-EtOAc) of the residue gave **28** (491 mg, 82%) as a colorless syrup: R*f* 0.57 (7:3 hexane-EtOAc); $[\alpha]_D$ +43.7 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.99 (dd, 2H, *J* = 8.3, 1.3 Hz, Ar*H*), 7.59-7.16 (m, 18H, Ar*H*), 5.99 (dd, 1H, *J* = 7.4, 6.4 Hz, H-3), 5.86 (dddd, 1H, *J* = 17.1, 10.3, 6.4, 5.0 Hz, C*H*=CH_2), 5.26 (dq, 1 H, *J* = 17.1, 1.7 Hz, HC=CH_aH), 5.14 (dq, 1 H, *J* = 10.3, 1.4 Hz, HC=CH_bH), 5.01 (d, 1H, *J* = 4.4 Hz, H-1), 4.81, 4.74 (2d, 2H, *J* = 11.7 Hz, PhCH_2), 4.67, 4.62 (2d, 2H, *J* = 12.4 Hz, PhCH_2), 4.40, 4.37 (2d AB, 2H, *J* = 12.4 Hz, PhCH_2), 4.24-4.19 (m, 3 H, OCH_aH-CH=, H-2, H-4), 3.97 (ddt, 1 H, *J* = 13.0, 6.4, 1.4 Hz, OCH_bH-CH=), 3.83 (apparent q, 1H, *J* = 5.1 Hz, H-5), 3.68 (dd, 1H, *J* = 10.3, 4.7 Hz, H-6a), 3.66 (dd, 1H, *J* = 10.3, 5.1 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.6 (CO); 138.9, 138.1, 137.6 (Bn);134.1 (*C*H=CH_2); 133.1, 130.1, 129.8, 129.7, 128.4, 128.3, 128.2, 128.1, 127.84, 127.76, 127.6, 127.5, 127.4, 127.2 (Bn, Bz); 117.3 (CH=*C*H_2), 98.7 (C-1), 81.7, 80.2 (C-2, C-4), 78.8 (C-5), 75.9 (C-3); 73.3, 73.0, 72.3 (Ph*C*H_2); 69.2 (C-6), 68.1 (O*C*H_2-CH=); HRMS (ESI) calcd for (M+Na) $C_{37}H_{38}O_7Na$:617.2510. Found: 617.2534.

Allyl 2,5,6-tri-*O*-benzyl-3-*O*-pentafluorobenzoyl-α-D-galactofuranoside (29). The same procedure as described for **28** was followed starting from **22** (100 mg, 0.20 mmol) and pentafluorobenzoyl chloride (0.058 mL, 0.40 mmol). Crystallization of the crude from methanol gave **29** (95 mg, 68%): mp 67-69 ºC; R*f* 0.62 (7:3 hexane-EtOAc); $[\alpha]_D$ +31.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38-7.19 (m, 15H, Ar*H*), 5.99 (dd, 1H, *J* = 7.4, 6.7 Hz, H-3), 5.84 (dddd, 1H, *J* = 17.0, 10.4, 6.4, 5.0 Hz, C*H*=CH_2), 5.25 (dq, 1 H, *J* = 17.0, 1.7 Hz, HC=CH_aH), 5.16 (dq, 1 H, *J* = 10.4, 1.4 Hz, HC=CH_bH), 4.93 (d, 1H, *J* = 4.3 Hz, H-1), 4.73 (s, 2H, PhCH_2), 4.65, 4.61 (2d, 2H, *J* = 12.2 Hz, PhCH_2), 4.47, 4.42 (2d, 2H, *J* = 12.1 Hz, PhCH_2), 4.23 (t, 1H, *J* = 6.2 Hz, H-4), 4.17 (ddt, 1 H, *J* = 13.0, 5.0, 1.5 Hz, OCH_aH-CH=), 4.16 (dd, 1H, *J* = 7.4, 4.3 Hz, H-2), 3.92 (ddt, 1 H, *J* = 13.0, 6.4, 1.3 Hz, OCH_bH-CH=), 3.78 (dt, 1H, *J* = 5.8, 4.7 Hz, H-5), 3.72 (dd, 1H, *J* = 10.4, 4.5 Hz, H-6a), 3.69 (dd, 1H, *J* = 10.4, 4.7 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6, 138.1,

137.4 (Ar); 133.9 (*C*H=CH_2); 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.39, 127.35, 127.3 (Ar); 117.5 (CH=*C*H_2), 98.6 (C-1), 82.0, 79.7, 79.0 , 77.5; 73.2, 73.0, 72.7 (Ph*C*H_2); 69.1 (C-6), 68.2 (O*C*H_2-CH=); HRMS (ESI) calcd for (M+Na) $C_{37}H_{33}O_7F_5Na$:707.2039. Found: 707.2065.

Allyl 2,5,6-tri-*O*-benzyl-3-*O*-(4-methoxybenzoyl)-α-D-galactofuranoside (30). The same procedure as described for **28** was followed starting from **22** (176 mg, 0.36 mmol) and *p*-methoxybenzoyl chloride (0.073 mL, 0.54 mmol). Purification of the crude by column chromatography (10:1 hexane EtOAc) followed by crystallization from MeOH to yield **30** (191 mg, 85%): mp 64-66 ºC; R*f* 0.48 (7:3 hexane-EtOAc); $[\alpha]_D$ +29.4 (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (d, 2H, *J* = 9.0 Hz, Ar*H*); 7.38-7.15 (m, 15H, Ar*H*), 6.90 (d, 2H, *J* = 9.0 Hz, Ar*H*), 5.96 (dd, 1H, *J* = 7.4, 6.5 Hz, H-3), 5.86 (dddd, 1H, *J* = 17.1, 10.4, 6.4, 5.0 Hz, C*H*=CH_2), 5.25 (dq, 1 H, *J* = 17.1, 1.7 Hz, HC=CH_aH), 5.14 (dq, 1 H, *J* = 10.4, 1.4 Hz, HC=CH_bH), 5.00 (d, 1H, *J* = 4.4 Hz, H-1), 4.81, 4.74 (2d, 2H, *J* = 11.7 Hz, PhCH_2), 4.67, 4.62 (2d, 2H, *J* = 12.5 Hz, PhCH_2), 4.38 (s, 2H, PhCH_2), 4.24-4.18 (m, 3H, OCH_aH-CH=, H-2, H-4), 3.97 (ddt, 1 H, *J* = 13.0, 6.4, 1.3 Hz, OCH_bH-CH=), 3.87 (s, 3H, PMBz), 3.82 (m, 1H, H-5), 3.67 (dd, 1H, *J* = 10.4, 4.9 Hz, H-6a), 3.64 (dd, 1H, *J* = 10.4, 5.2 Hz, H-6b); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.3, 163.5 (CO, Ar); 138.9, 138.1, 137.7 (Ar); 134.2 (*C*H=CH_2); 131.9, 128.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 122.1 (Ar), 117.3 (CH=*C*H_2), 113.6 (Ar), 98.8 (C-1), 81.7, 80.4 (C-2, C-4), 78.9 (C-5), 75.7 (C-3); 73.2, 73.1, 72.2 (Ph*C*H_2); 69.3 (C-6), 68.1 (O*C*H_2-CH=), 55.5 (PMBz); HRMS (ESI) calcd for (M+Na) $C_{38}H_{40}O_8Na$:647.2615. Found: 647.2619.

Allyl 2,5,6-tri-*O*-benzyl-3-*O*-triisopropylsilyl-α-D-galactofuranoside (31). To a stirred solution of **22** (87.0 mg, 0.177 mmol) and imidazol (50.6 mg, 0.74 mmol) in anhyd DMF (1 mL), cooled to 0 ºC, was added triisopropylsilyl chloride (0.13 mL, 0.63 mmol). After 4 days at room temperature, the mixture was diluted with CH_2Cl_2 (50 mL), washed with brine (4 x 60 mL), water (1 x 60 mL), dried (Na_2SO_4), filtered and concentrated. Column chromatography (100:1, then 40:1 hexane-EtOAc) of the residue gave **31** (89 mg, 78%) as a colorless syrup: R*f* 0.65 (8:2 hexane- EtOAc); $[\alpha]_D$ +50.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.39-7.21 (m, 15H, Ar*H*), 5.83 (dddd, 1H, *J* = 17.0, 10.4, 6.5, 5.0 Hz, C*H*=CH_2), 5.22 (dq, 1 H, *J* = 17.0, 1.7 Hz, HC=CH_aH), 5.11 (dq, 1 H, *J* = 10.4, 1.5 Hz, HC=CH_bH), 4.92 (d, 1H, *J* = 4.2 Hz, H-1), 4.83, 4.67 (2d, 2H, *J* = 11.7 Hz, PhCH_2), 4.62 (t, 1H, *J* = 6.7 Hz, H-3), 4.59, 4.52 (2d, 2H, *J* = 11.4 Hz, PhCH_2),

4.54, 4.50 (2d, 2H, *J* = 12.1 Hz, PhCH_2), 4.17 (ddt, 1 H, *J* = 13.1, 5.0, 1.5 Hz, OCH_aH-CH=), 3.91 (ddt, 1 H, *J* = 13.1, 6.5, 1.4 Hz, OCH_bH-CH=), 3.88 (dd, 1H, *J* = 6.3, 4.8 Hz, H-4), 3.84 (dd, 1H, *J* = 7.0, 4.2 Hz, H-2), 3.80 (dt, 1H, *J* = 6.8, 4.5 Hz, H-5), 3.72 (dd, 1H, *J* = 10.2, 4.2 Hz, H-6a), 3.67 (dd, 1H, *J* = 10.2, 6.8 Hz, H-6b), 0.99 (m, 21H, $(CH_3)_2CH)_3Si$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.1, 138.3, 137.8 (Bn); 134.5 (*C*H=CH_2), 128.3, 128.22, 128.19, 128.12, 128.11, 127.7, 127.5, 127.4, 127.1 (Bn); 117.0 (CH=*C*H_2), 98.8 (C-1), 84.9, 83.1, 78.4, 75.1; 73.3, 73.0, 72.6 (Ph*C*H_2); 71.1 (C-6), 68.0 (O*C*H_2-CH=), 18.13, 18.10 (*C*$H_3)_2$CH)$_3$Si), 12.6 $(CH_3)_2$*C*H)$_3$Si); HRMS (ESI) calcd for (M+Na) $C_{39}H_{54}O_6SiNa$:669.3582. Found:669.3571

3-*O*-Benzoyl-2,5,6-tri-*O*-benzyl-D-galactofuranose (32). The same procedure as described for **14** was followed starting from **28** (491 mg, 0.82 mmol) and $PdCl_2$ (26.9 mg, 0.15 mmol). Column chromatography of the residue (18:1 toluene-EtOAc) gave **32** (350 mg, 77%) as a colorless syrup (α:β 10:3.5); R*f* 0.40 (5:1 toluene-EtOAc): $[\alpha]_D$ -7.9 (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.04-7.19 (m, 20H, Ar), 5.58 (dd, 0.26H, *J* = 4.8, 1.9 Hz, H-3β), 5.54 (dd, 0.74H, *J* = 4.6, 3.5 Hz, H-3α), 5.53 (bs, 0.26H, H-1β), 5.37 (d , 0.74H, *J* = 4.8 Hz, H-1α), 4.94-4.57 (m, 4H, PhCH_2), 4.55 (t, 0.26H, *J* = 4.6 Hz, H-4β), 4.53, 4.50 (2d, 1.48H, *J* = 12.0 Hz, PhCH_2), 4.49, 4.45 (2d, 0.52H, *J* = 12.0 Hz, PhCH_2), 4.26 (t, 0.74H, *J* = 4.8 Hz, H-2α), 4.21 (dd, 0.74H, *J* = 3.5, 2.6 Hz, H-4α), 4.17 (dt, 0.74H, *J* = 6.1, 2.6 Hz, H-5α), 4.10 (dd, 0.26H, *J* = 1.9, 1.3 Hz, H-2β), 3.96 (apparent q, 0.26H, *J* = 5.2 Hz, H-5β), 3.76-3.66 (m, 2H, H-6aα, H-6bα, H-6aβ, H-6bβ); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.4, 165.9 (CO); 138.4, 138.1, 138.0, 137.5, 137.4, 137.2 (Bn); 133.4, 133.3, 129.8, 129.7, 129.3, 128.5, 128.4 (x3), 128.3 (x3), 128.2 (x2), 128.1, 128.0, 127.9 (x2), 127.8 (x2), 127.7, 127.6 (x2), 127.5 (x2) (Aa); 101.3 (C-1β), 96.2 (C-1α), 87.4 (C-2β), 82.8 (C-4β), 82.7 (C-2α), 82.4 (C-4α), 79.2 (C-3α), 77.7 (C-5α); 77.58, 77,55 (C-3β, C-5β); 74.4, 73.5 (x2), 73.4, 72.1, 71.6 (Ph*C*H_2); 70.2 (C-6β), 69.2 (C-6α). HRMS (ESI) calcd for (M+Na) $C_{34}H_{34}O_7Na$:577.2197. Found: 577.2216.

Unreacted **28** was also recovered (64 mg, 13%).

2,5,6-Tri-*O*-benzyl-3-*O*-pentafluorobenzoyl-D-galactofuranose (33). The same procedure as described for **14** was followed starting from **29** (83 mg, 0.12 mmol) and $PdCl_2$ (3.9 mg, 0.022 mmol). Column chromatography (20:1 toluene-EtOAc) of the residue gave **33** (54 mg, 70%) as a colorless syrup

(α:β 10:4) which crystallized from MeOH: mp 109-112 ºC; R*f* 0.58 (5:1 toluene-EtOAc); $[\alpha]_D$ +4.4 (*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40-7.22 (m, 15H, Bn), 5.58 (dd, 0.29H, *J* = 4.7, 1.6 Hz, H-3β), 5.54 (dd, 0.71H, *J* = 4.4, 3.6 Hz, H-3α), 5.51 (bs, 0.29H, H-1β), 5.33 (dd , 0.71H, *J* = 4.8, 11.8 Hz, H-1α), 4.92-4.46 (m, 6.29 H, PhC*H*$_2$, H-4β), 4.22 (dd, 0.71H, *J* = 3.6, 2.7 Hz, H-4α), 4.18 (t, 0.71H, *J* = 4.8 Hz, H-2α), 4.07 (dt, 0.71H, *J* = 6.1, 2.7 Hz, H-5α), 4.05 (dd, 0.29H, *J* = 1.6, 1.1 Hz, H-2β), 3.92 (apparent q, 0.29H, *J* = 5.6 Hz, H-5β), 3.77-3.69 (m, 2H, H-6aα, H-6bα, H-6aβ, H-6bβ); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.2, 137.0 (Bn); 128.6, 128.4 (x2), 128.3 (x2), 128.2 (x2), 128.0 (x2), 127.9 (x2), 127.7, 127.6 (x2) (Ar); 101.2 (C-1β), 96.2 (C-1α), 87.0, 82.7, 82.6, 81.8, 81.2, 79.1, 77.4; 74.3, 73.6, 73.5, 72.3 71.7 (PhCH_2); 70.0 (C-6β), 69.8 (C-6α). HRMS (ESI) calcd for (M+Na) $C_{34}H_{29}O_7F_5Na$:667.1757. Found: 667.1763.

2,5,6-Tri-*O*-benzyl-3-*O*-(4-methoxybenzoyl)-D-galactofuranose (34). The same procedure as described for **14** was followed starting from **30** (190 mg, 0.30 mmol) and $PdCl_2$ (9.9 mg, 0.056 mmol). Column chromatography (20:1 toluene-EtOAc) of the residue gave **34** (75 mg, 43%) as colorless syrup (α:β 10:3); R*f* 0.35 (5:1 toluene-EtOAc). $[\alpha]_D$ -10.9 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.00-6.90 (m, 19H, Bn), 5.55 (dd, 0.23H, *J* = 4.8, 1.9 Hz, H-3β), 5.53 (bs, 0.23H, H-1β), 5.52 (dd, 0.77H, *J* = 4.8, 3.5 Hz, H-3α), 5.35 (bs, 0.77H, H-1α), 4.98-4.44 (m, 6.23H, PhC*H*$_2$, H-4β), 4.25 (t, 0.77H, *J* = 4.8 Hz, H-2α), 4.19 (dd, 0.77H, *J* = 3.5, 2.5 Hz, H-4α), 4.17 (dt, 0.77H, *J* = 6.2, 2.5 Hz, H-5α), 4.10 (dd, 0.23H, *J* = 1.9, 1.2 Hz, H-2β), 3.96 (dt, 0.23H, *J* = 5.5, 5.0 Hz, H-5β), 3.88 (s, 2.31H, OCH_3 α anomer), 3.87 (s, 0.69H, OCH_3 β anomer), 3.75-3.67 (m, 2H, H-6aα, H-6bα, H-6aβ, H-6bβ); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 165.6, 163.7 (CO, Ar); 138.1, 138.0, 137.4, 137.3 (Bn); 131.9, 131.8,128.5, 128.4 (x2), 128.3, 128.2 (x2), 128.0 (x2), 127.9, 127.8, 127.6 (x2), 127.5, 121.9, 121.7, 113.72, 113.70 (Ar); 101.4 (C-1β), 96.2 (C-1α), 87.5, 83.0, 82.7, 82.6, 78.9, 77.8, 77.6; 74.5, 73.5 (x2), 72.0, 71.6 (PhCH_2); 70.2 (C-6β), 70.1 (C-6α). HRMS (ESI) calcd for (M+Na) $C_{35}H_{36}O_8Na$:607.2302. Found: 607.2318.

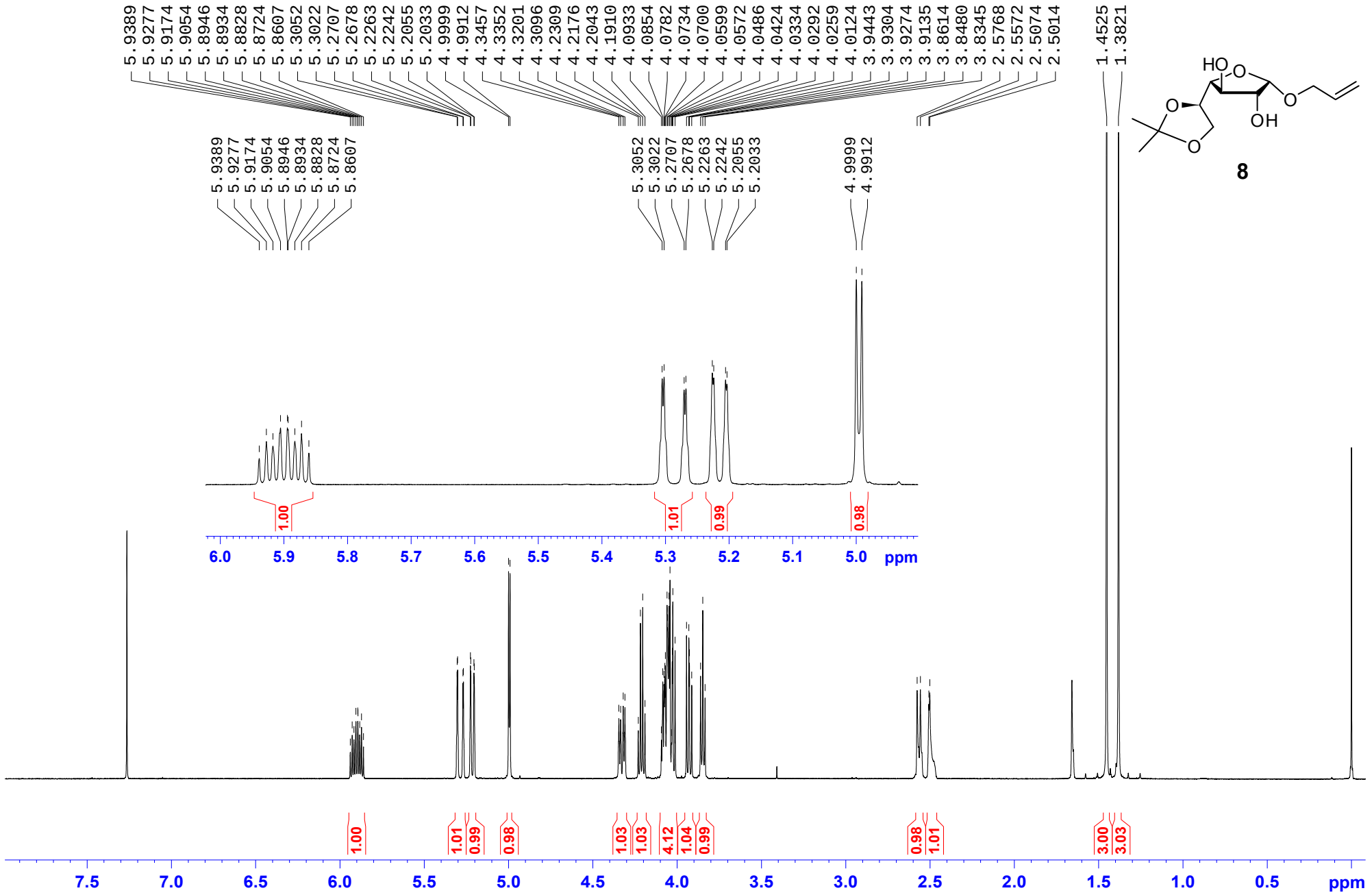
2,5,6-Tri-*O*-benzyl-3-*O*-triisopropylsilyl-D-galactofuranose (35). The same procedure as described for **14** was followed starting from **31** (77 mg, 0.12 mmol) and $PdCl_2$ (4 mg, 0.022 mmol). Column chromatography (10:1 hexane-EtOAc) of the residue gave **35** (58 mg, 80%) as a colorless syrup (α:β 7:10); R*f* 0.37 (4:1 hexane-EtOAc); $[\alpha]_D$ +5.1 (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37-7.20

(m, 15, Bn), 5.39 (d, 0.59H, *J* = 10.3 Hz, H-1β), 5.34 (dd , 0.41H, *J* = 12.2, 4.7 Hz, H-1α), 4.86-4.43 (m, 6.59H, PhC*H*$_2$, H-2β), 4.43 (t, 0.41H, *J* = 3.8 Hz, H-3α), 4.32 (dd, 0.59H, *J* = 6.1, 2.3 Hz, H-4β), 4.28 (d, 0.41H, *J* = 12.2 Hz,, OH-1α), 4.03 (dd, 0.41H, *J* = 3.3, 2.3 Hz, H-4α), 3.90 (t, 0.41H, *J* = 4.4 Hz, H-2α), 3.85-3.71 (m, 2.41H, H-3β, H-5β, H-6aα, H-5α, H-6bα), 3.67 (dd, 0.59H, *J* = 10.4, 5.2 Hz, H-6aβ), 3.62 (dd, 0.59H, *J* = 10.4, 5.8 Hz, H-6bβ), 3.50 (d, 0.59H, *J* = 10.3 Hz, OH-1β), 1.01-0.97 (m, 21H, $(CH_3)_2CH)_3Si$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.6, 138.1, 137.8, 137.5, 137.2 (Bn); 128.4 (x3), 128.3, 128.2 (x2), 128.1, 128.0, 127.9, 127.8, 127.7, 127.6 (x2), 127.5, 127.4 (Bn); 100.9 (C-1β), 96.7 (C-1α), 88.4 (C-4β), 87.8 (C-3β), 87.3 (C-2α), 85.2 (C-4α), 77.4 (C-3α), 77.2 (C-5β), 77.0 (C-5α), 75.9 (C-2β); 73.5, 73.4, 73.3, 73.2, 72.2, 71.7 (PhCH_2); 70.9 (C-6β, C-6α), 17.9 (($CH_3)_2$CH)$_3$Siα), 17.8 (($CH_3)_2$CH)$_3$Siβ), 12.1 (($CH_3)_2$CH)$_3$Siα), 11.9 (($CH_3)_2$CH)$_3$Siβ). HRMS (ESI) calcd for (M+Na) $C_{36}H_{50}O_6NaSi$: 629.3269. Found: 629.3276.

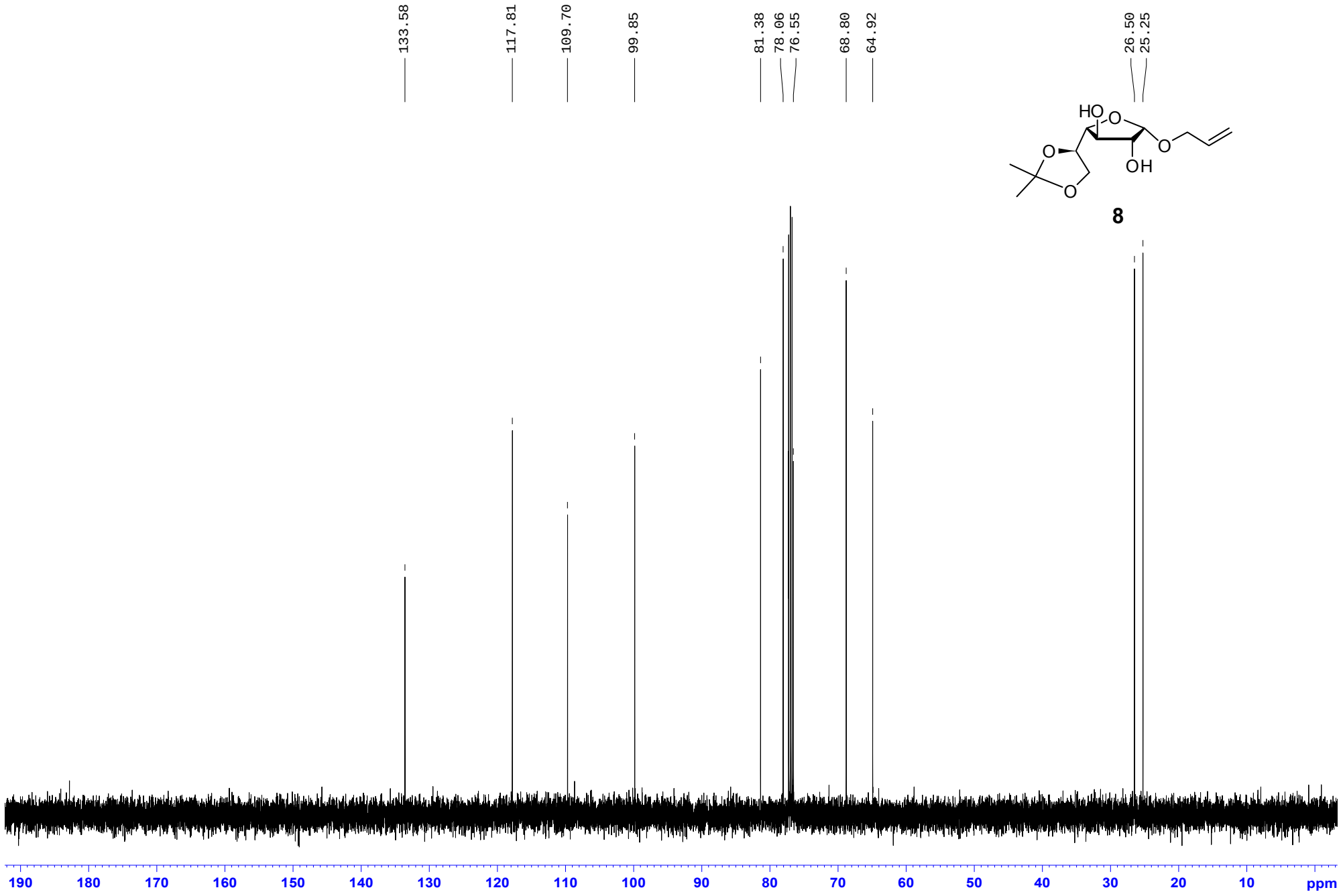
2,5,6-Tri-*O*-benzyl-3-*O*-pentafluorobenzoyl-β-D-galactofuranosyl trichloroacetimidate (25). The same procedure as described for **6** was followed starting from **33** (46 mg, 0.071 mmol); Cl_3CCN (35.8μl, 0.35 mmol) and DBU (4.2 μl, 0.028 mmol) to yield **25** (45 mg, 81 %) as a colorless syrup: R*f* 0.55 (3:1:0.04 hexane-EtOAc-TEA); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.55 (s, 1H, N*H*), 7.40-7.18 (m, 15H, Ar*H*), 6.44 (s, 1H, H-1), 5.66 (d, 1H, *J* = 4.6 Hz, H-3), 4.86-4.71 (m, 4H, PhCH_2), 4.61 (t, 1H, *J* = 4.5 Hz, H-4), 4.49 (s, 2H, PhCH_2), 4.27 (bs, 1H, H-2), 3.97 (apparent q, 1H, *J* = 5.4 Hz, H-5), 3.78-3.67 (m, 2H, H-6a, H-6b).

2,5,6-Tri-*O*-benzyl-3-*O*-(4-methoxybenzoyl)-β-D-galactofuranosyl trichloroacetimidate (26). The same procedure as described for **6** was followed starting from **34** (65.5 mg, 0.11 mmol); Cl_3CCN (56.2 μl, 0.56 mmol) and DBU (6.6 μl, 0.044 mmol) to give **26** (71.0 mg, 89 %) as a colorless syrup; R*f* 0.51 (3:1:0.04 hexane-EtOAc-TEA); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.54 (s, 1H, N*H*), 8.00, 6.90 (2d, 4H, *J* = 8.8 Hz, PMBz), 7.49-7.14 (m, 15H, Ar*H*), 6.49 (s, 1H, H-1), 5.61 (d, 1H, *J* = 3.6 Hz, H-3), 4.94-4.43 (m, 4H, PhCH_2), 4.66 (t, 1H, *J* = 4.3 Hz, H-4), 4.47 (s, 2H, PhCH_2), 4.28 (s, 1H, H-2), 4.02 (apparent q, 1H, *J* = 5.0 Hz, H-5), 3.86 (s, 3H, OCH_3), 3.80-3.64 (m, 2H, H-6a, H-6b); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 165.5 (*C*ONHCCl_3), 138.3, 138.1, 131.9, 128.5, 128.3 (x2), 128.0, 128.0, 127.9, 127.6 (x2), 127.5, 113.6 (Ar); 104.2 (C-1), 86.0, 85.8, 77.6, 77.2; 73.5, 73.4, 71.7, (PhCH_2), 70.1 (C-6), 55.4 (O*C*H_3).

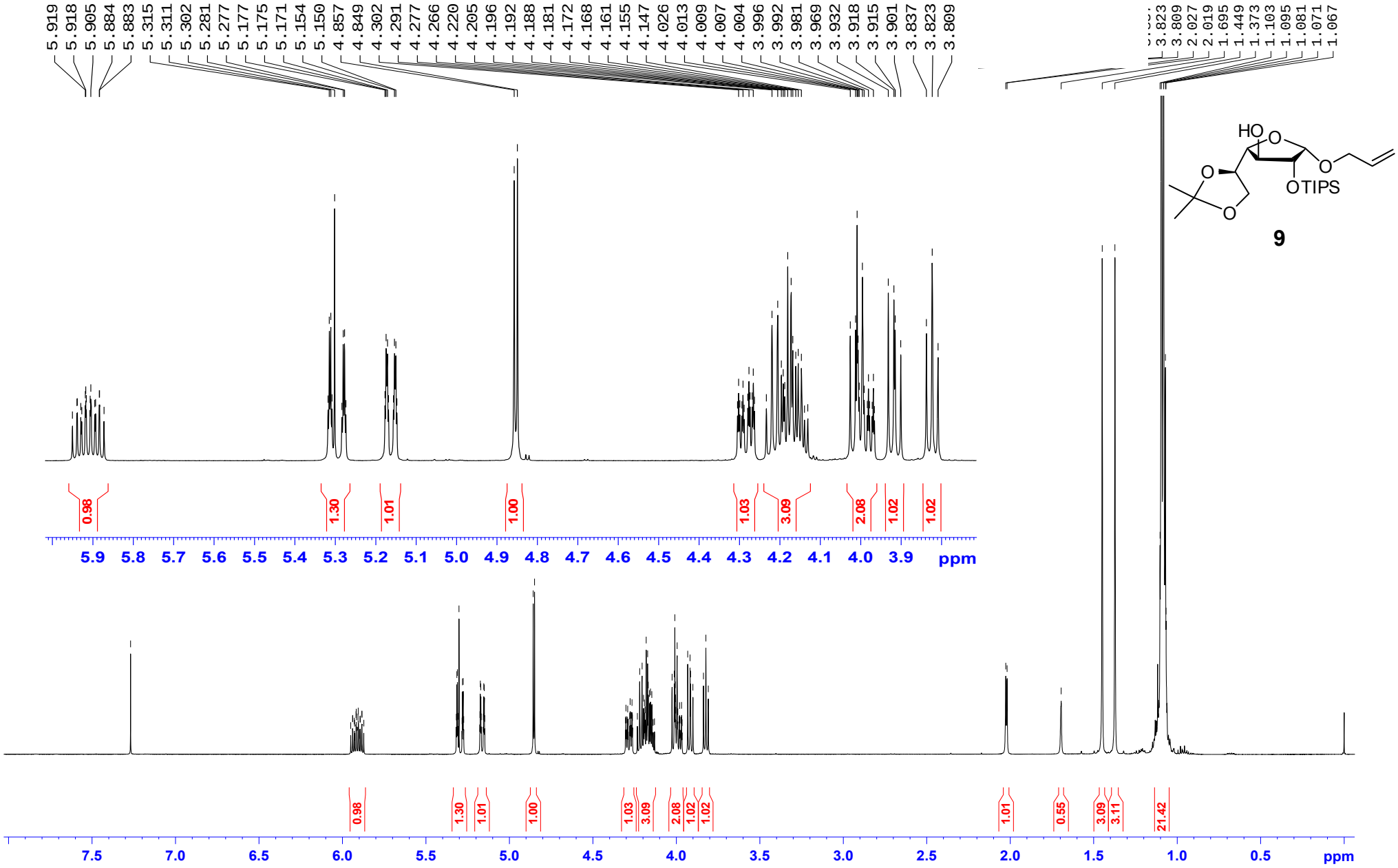
2,5,6-Tri-*O*-benzyl-3-*O*-triisopropylsilyl-β-D-galactofuranosyl trichloroacetimidate (27). The same procedure as described for **6** was followed starting from **35** (49.5 mg, 0.082 mmol); Cl_3CCN (40.9 μl, 0.41 mmol) and DBU (4.9 μl, 0.033 mmol). The concentrated was purified by column chromatography (10:1:0.1 hexane-EtOAc-TEA) to give **27** (79 mg, 80 %) as a colorless syrup; R*f* 0.56 (9:2:0.11 hexane-EtOAc-TEA); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.49 (s, 1H, N*H*), 7.36-7.21 (m, 15H, Ar*H*), 6.41 (s, 1H, H-1), 4.87-4.46 (m, 7H, PhCH_2, H-3), 4.34 (dd, 1H, *J* = 4.8, 3.4 Hz, H-4), 4.10 (d, 1H, *J* = 1.2 Hz, H-2), 3.90 (dt, 1H, *J* = 5.8, 3.2 Hz, H-5), 3.84-3.71 (m, 2H, H-6a, H-6b), 0.98-0.84 (m, 21H, $(CH_3)_2CH)_3Si$); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 161.4 (*C*ONHCCl_3), 138.3, 128.4, 128.3, 128.1 (x2), 128.0, 127.8, 127.5, 127.4 (Ar); 103.7 (C-1), 89.2, 88.1, 77.3; 73.3, 72.9, 72.2, (Ph*C*H_2), 71.0 (C-6), 17.9 ((CH_3)$_2$CH)$_3$Si), 12.1((CH_3)$_2$*C*H)$_3$Si).



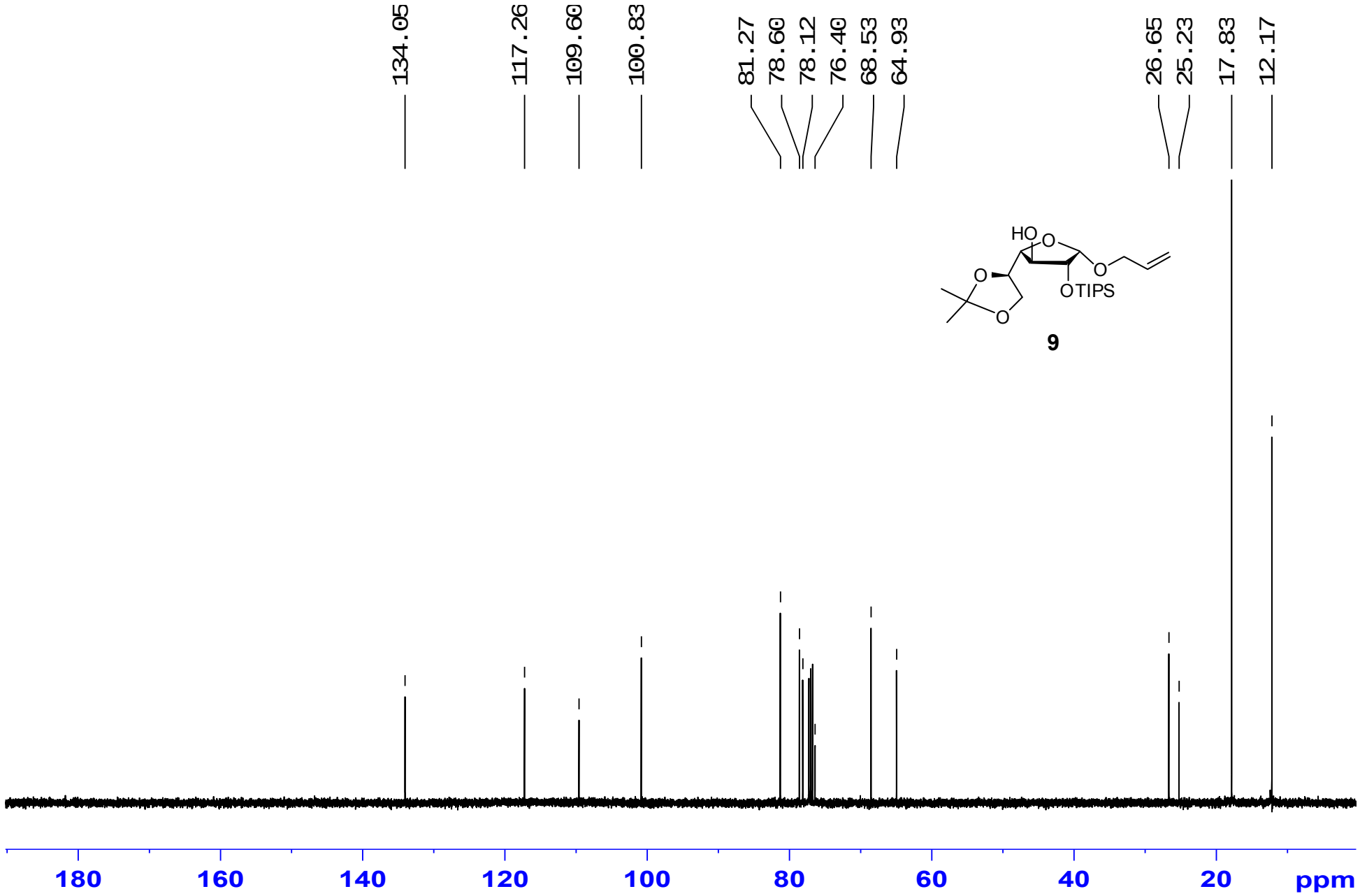
^{1}H NMR spectrum of compound **8** ($CDCl_3$; 500 MHz)



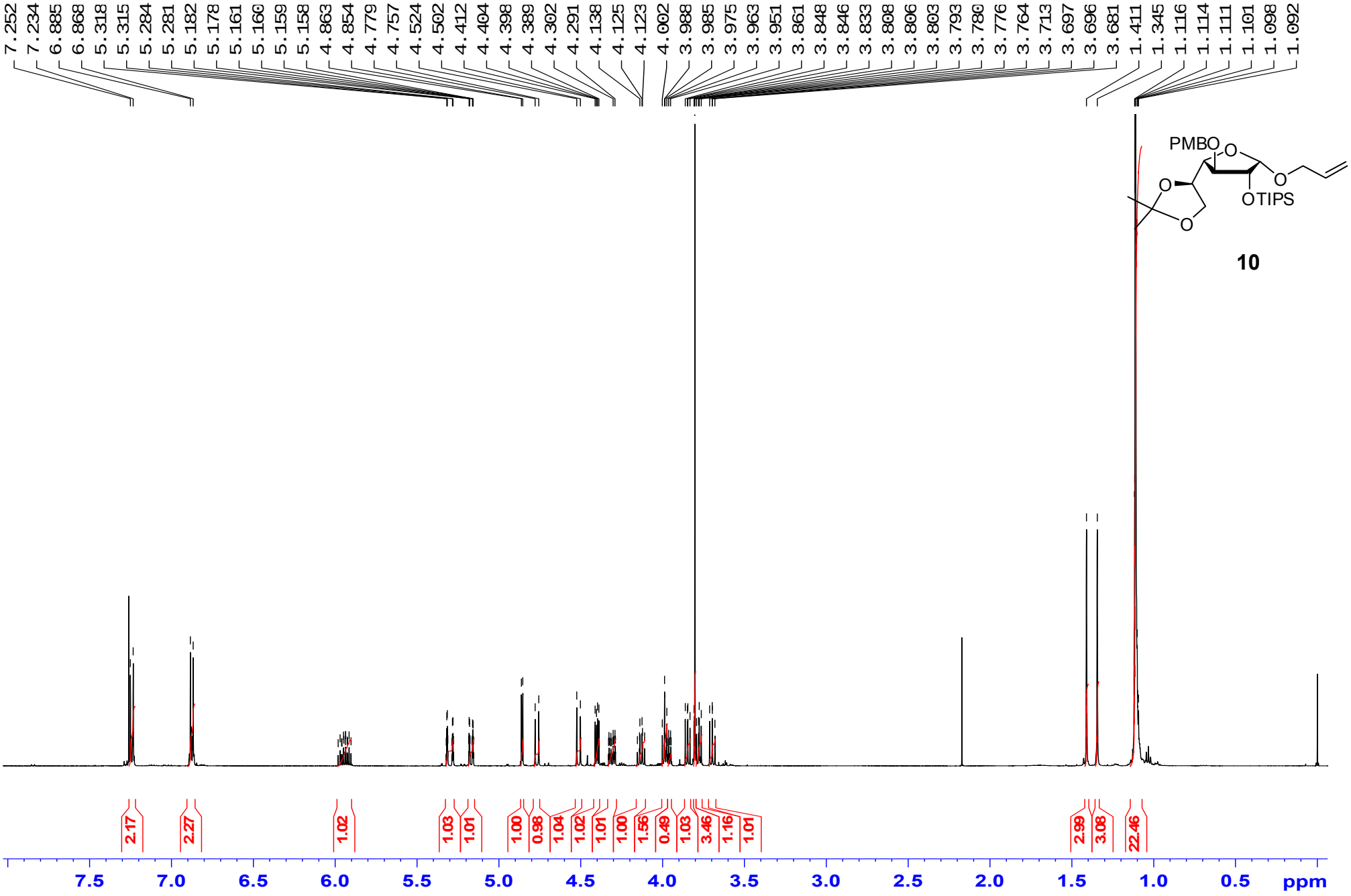
^{13}C NMR spectrum of compound **8** ($CDCl_3$; 125.8 MHz).



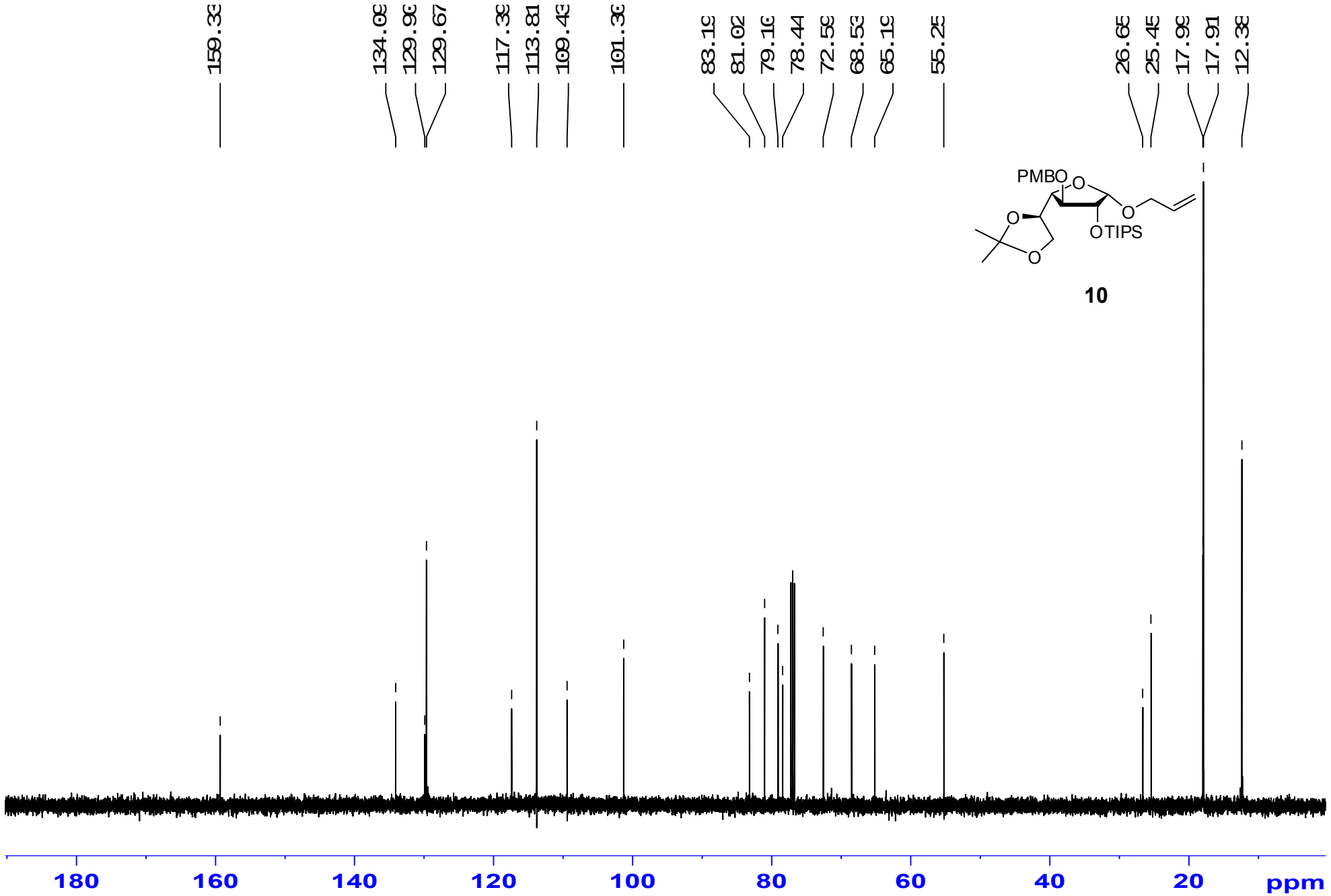
^{1}H NMR spectrum of compound **9** ($CDCl_3$; 500 MHz)



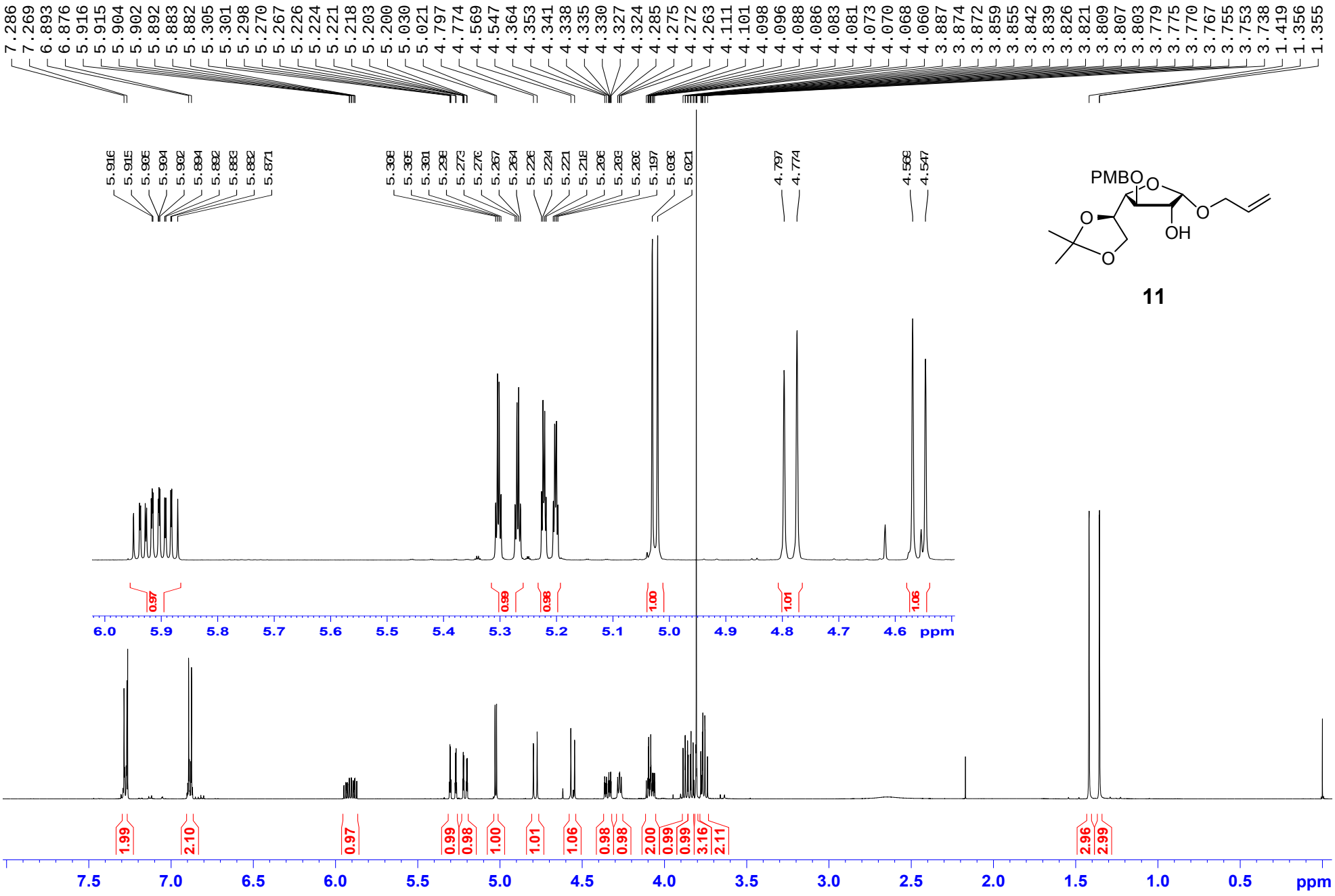
^{13}C NMR spectrum of compound **9** ($CDCl_3$; 125.8 MHz).



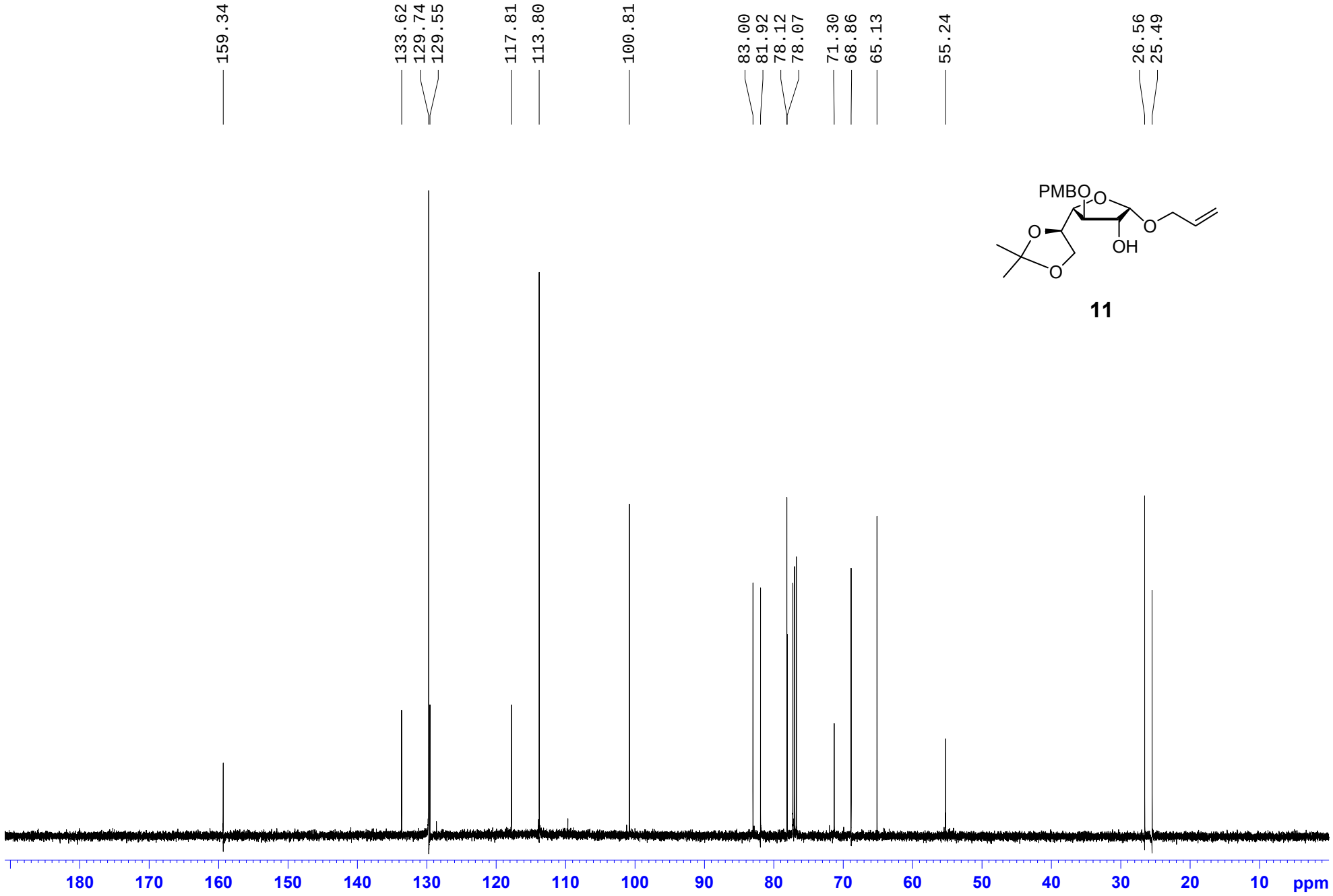
^{1}H NMR spectrum of compound **10** ($CDCl_3$; 500 MHz)



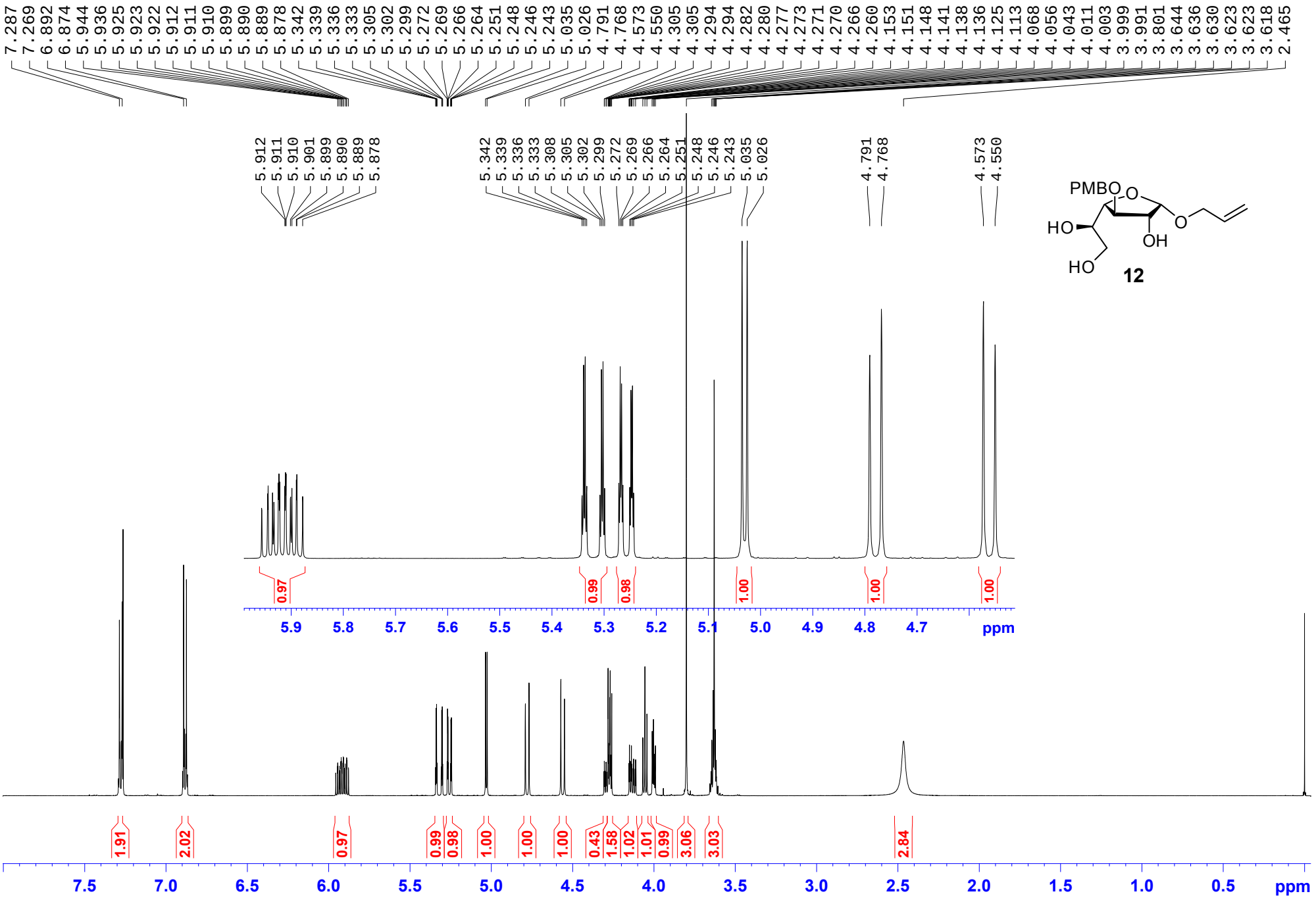
^{13}C NMR spectrum of compound **10** ($CDCl_3$; 125.8 MHz).



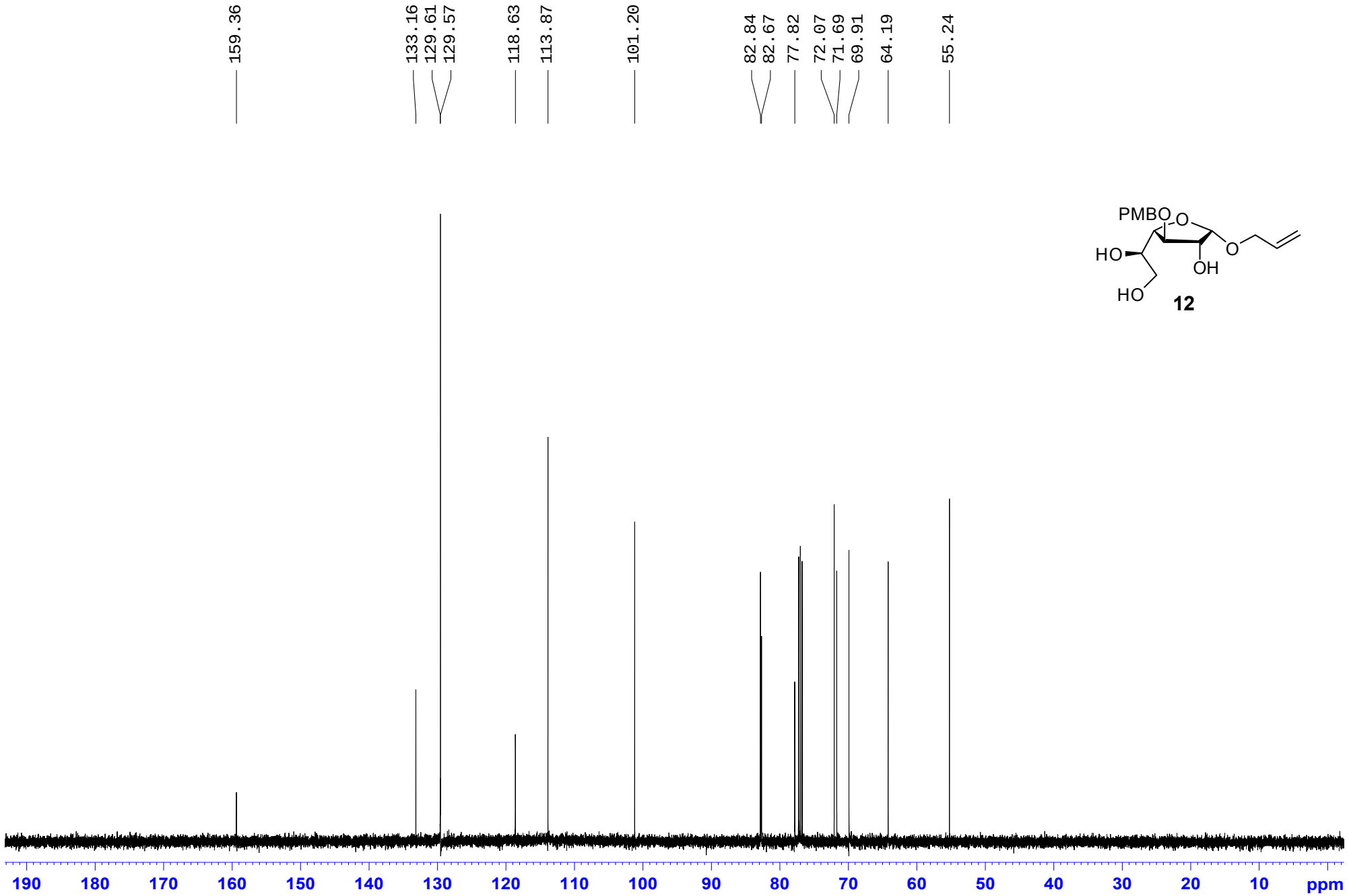
^{1}H NMR spectrum of compound **11** ($CDCl_3$; 500 MHz)



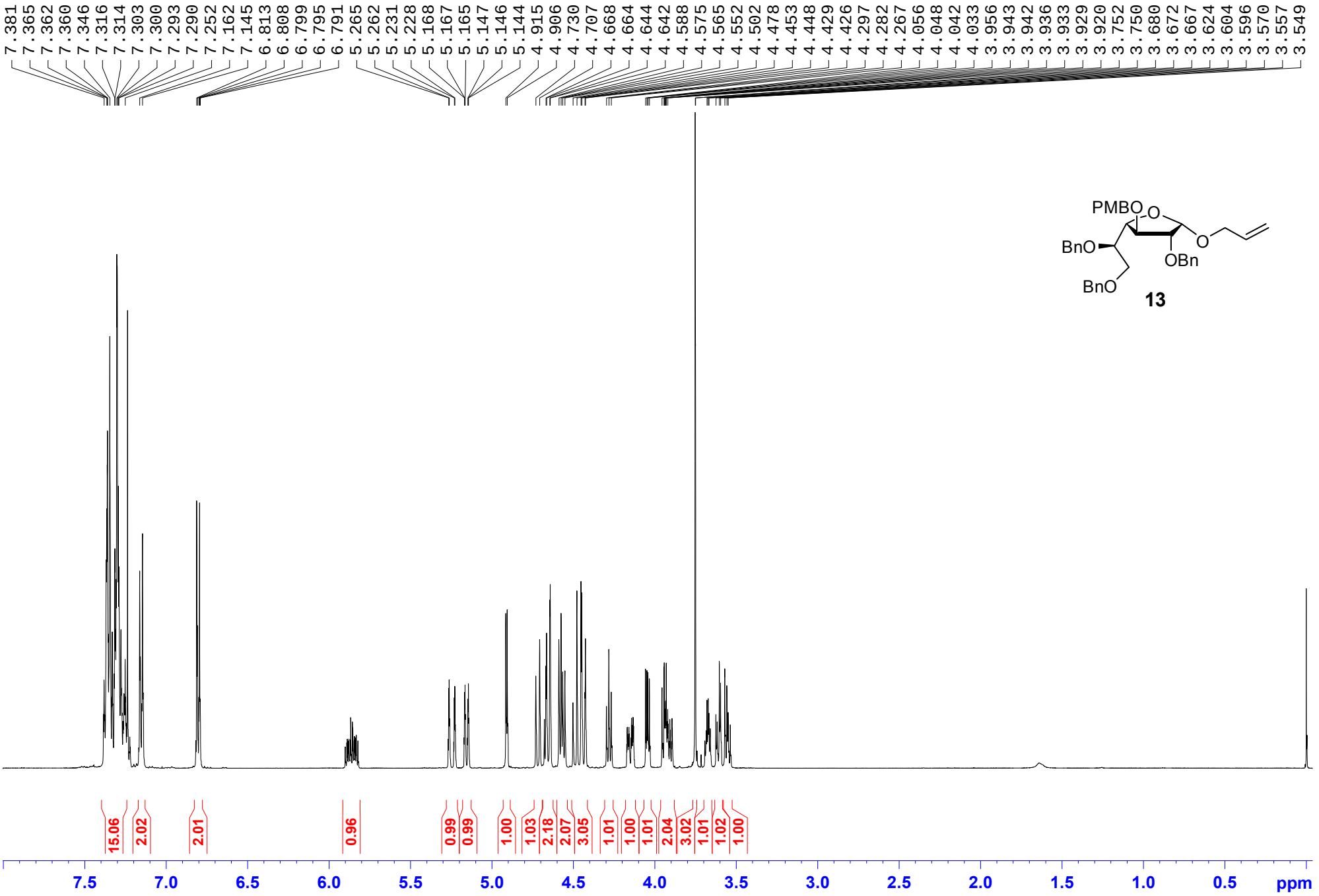
^{13}C NMR spectrum of compound **11** ($CDCl_3$; 125.8 MHz).



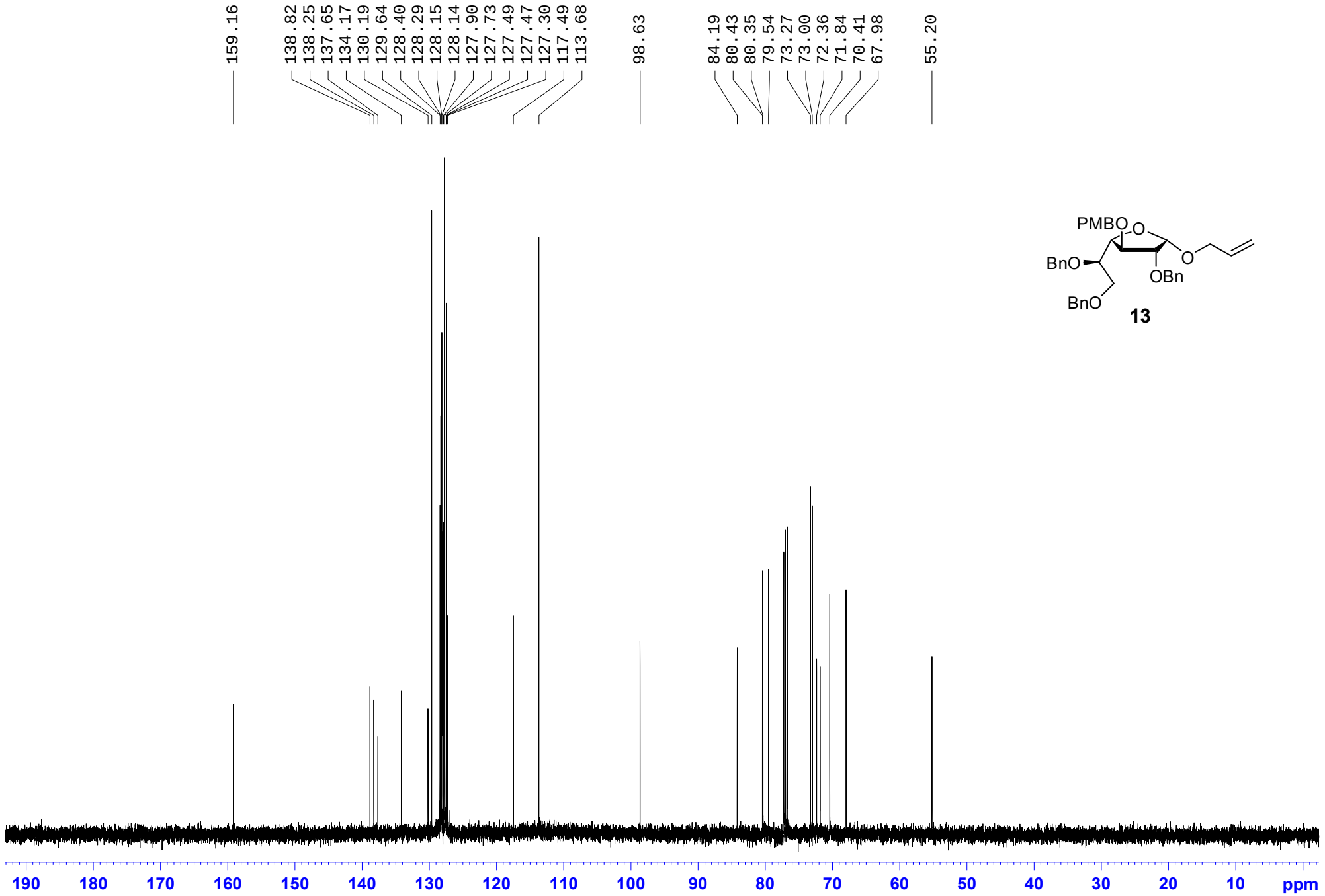
^{1}H NMR spectrum of compound **12** ($CDCl_3$; 500 MHz)



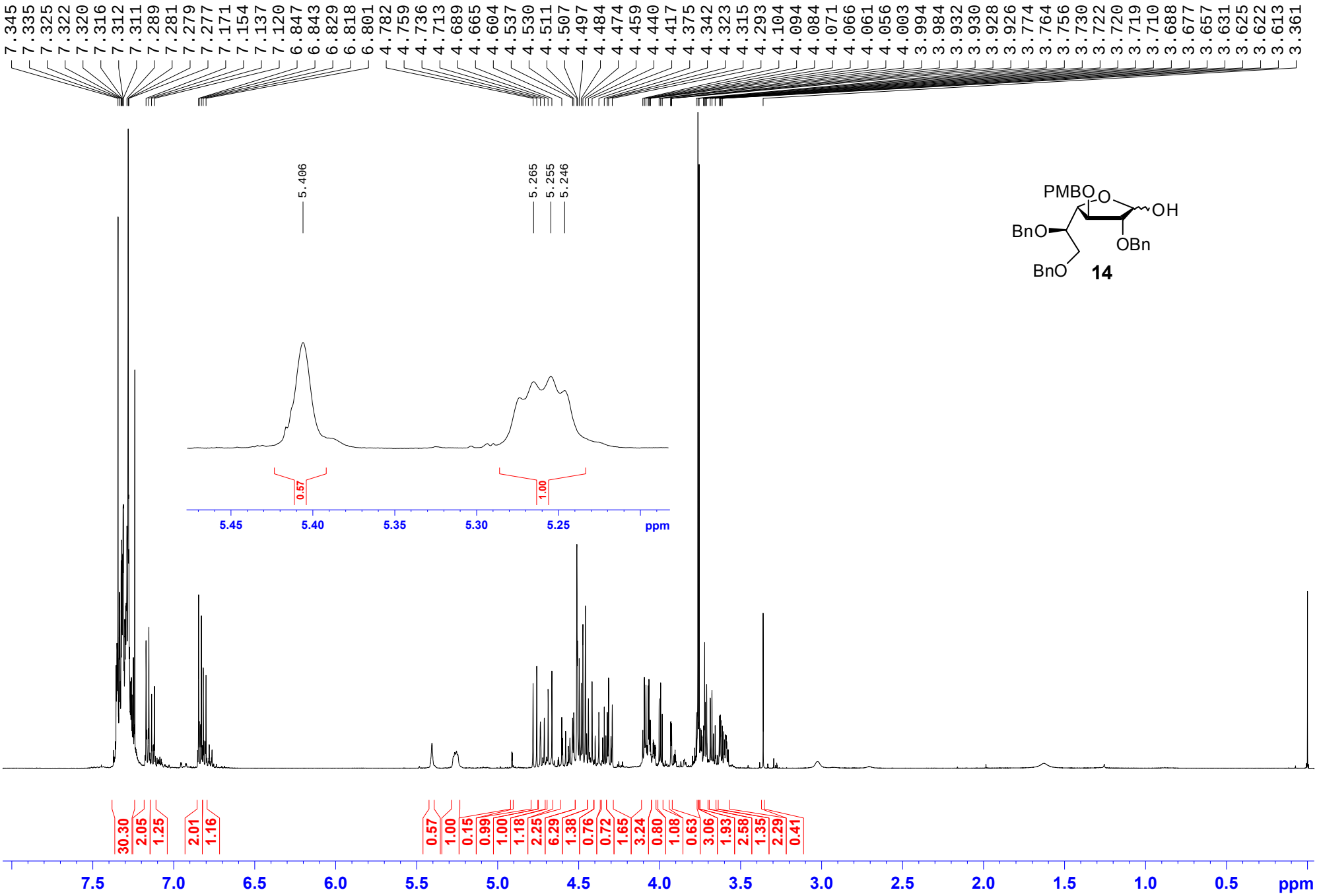
^{13}C NMR spectrum of compound **12** ($CDCl_3$; 125.8 MHz).



^{1}H NMR spectrum of compound **13** ($CDCl_3$; 500 MHz)



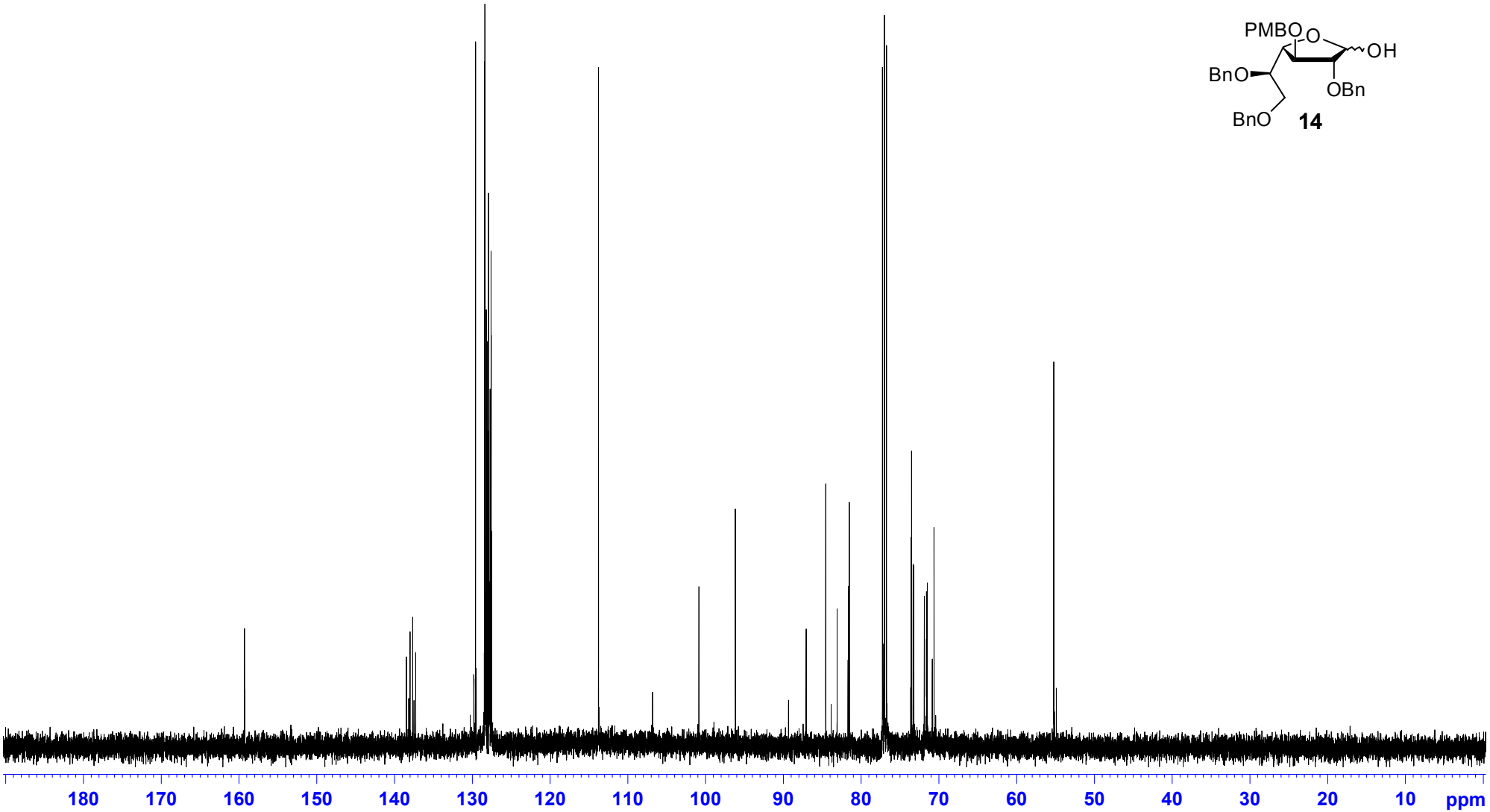
^{13}C NMR spectrum of compound **13** ($CDCl_3$; 125.8 MHz).



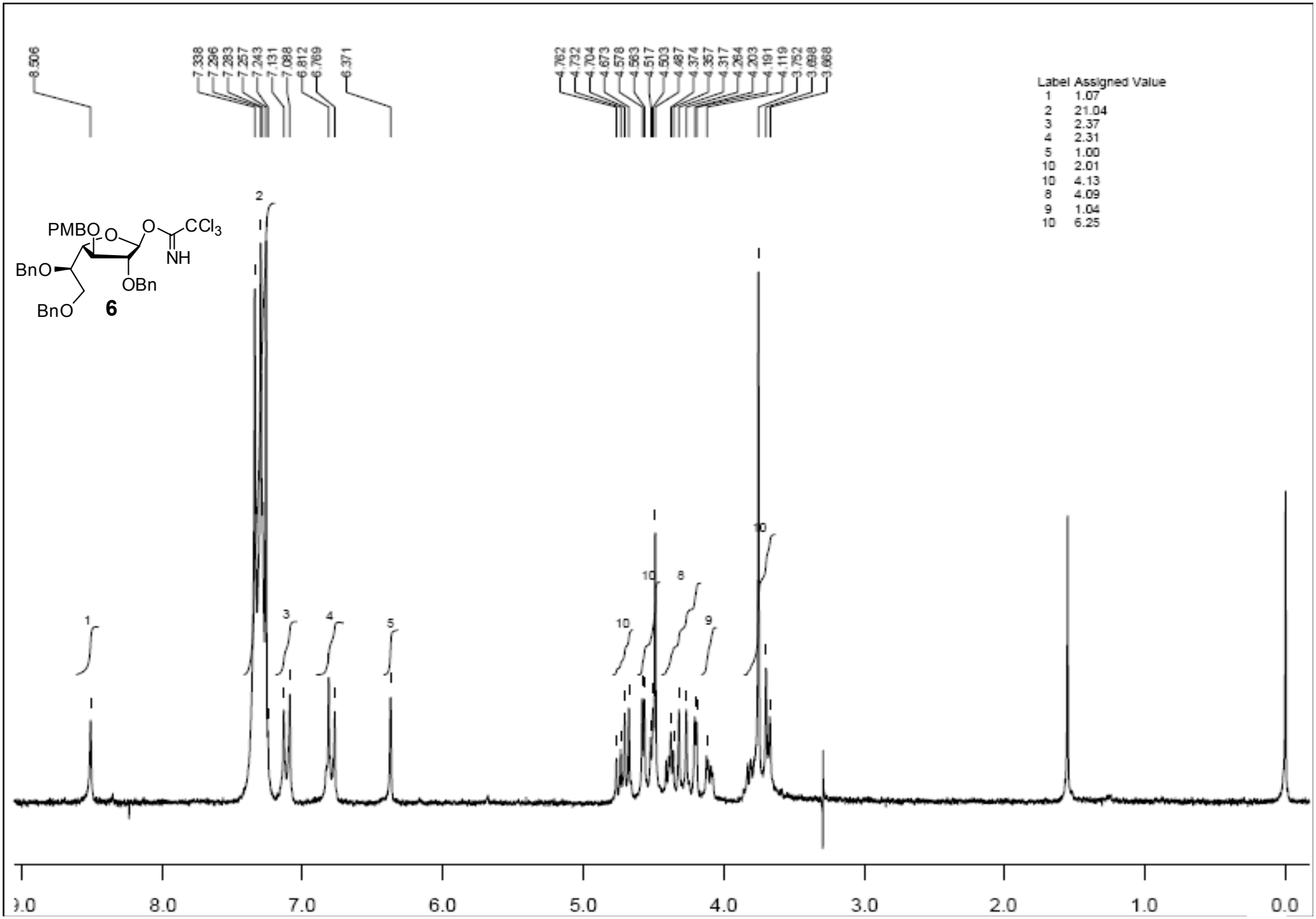
^{1}H NMR spectrum of compound **14** ($CDCl_3$; 500 MHz)

159.30 138.48 138.01 137.67 137.28 129.80 129.58 129.50 128.46 128.44 128.42 128.39 128.38 128.35 128.31 128.20 128.10 128.00 127.91 127.82 127.81 127.79 127.76 127.71 127.63 127.59 127.58 127.53 127.50 113.78 113.77 106.81 100.86 96.17 89.34 87.07 84.55 83.85 83.09 81.69 81.60 81.52 77.09 73.62 73.58 73.51 73.32 73.21 71.88 71.60 71.59 71.49 70.85 70.62 55.23 55.21 54.89

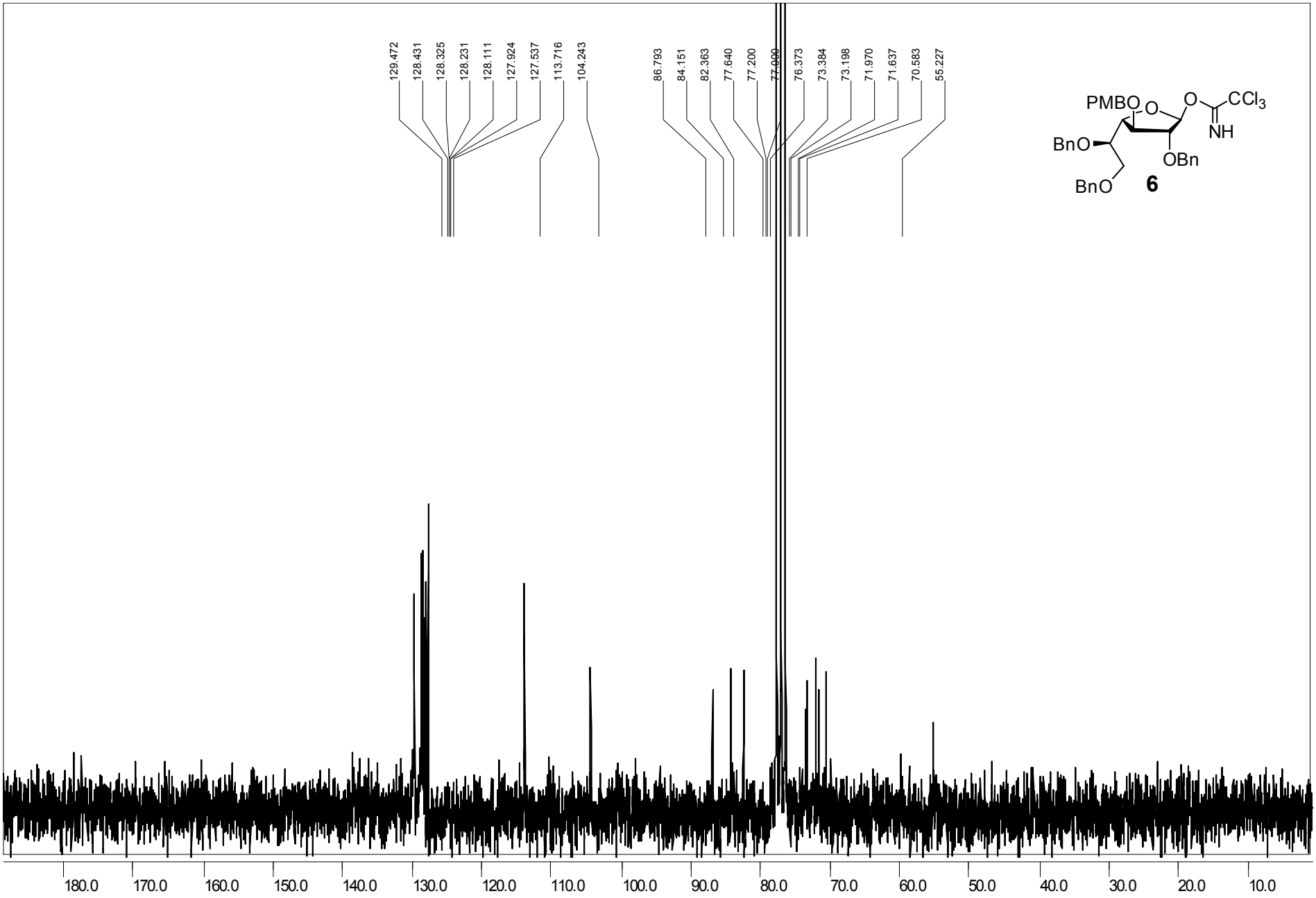
14



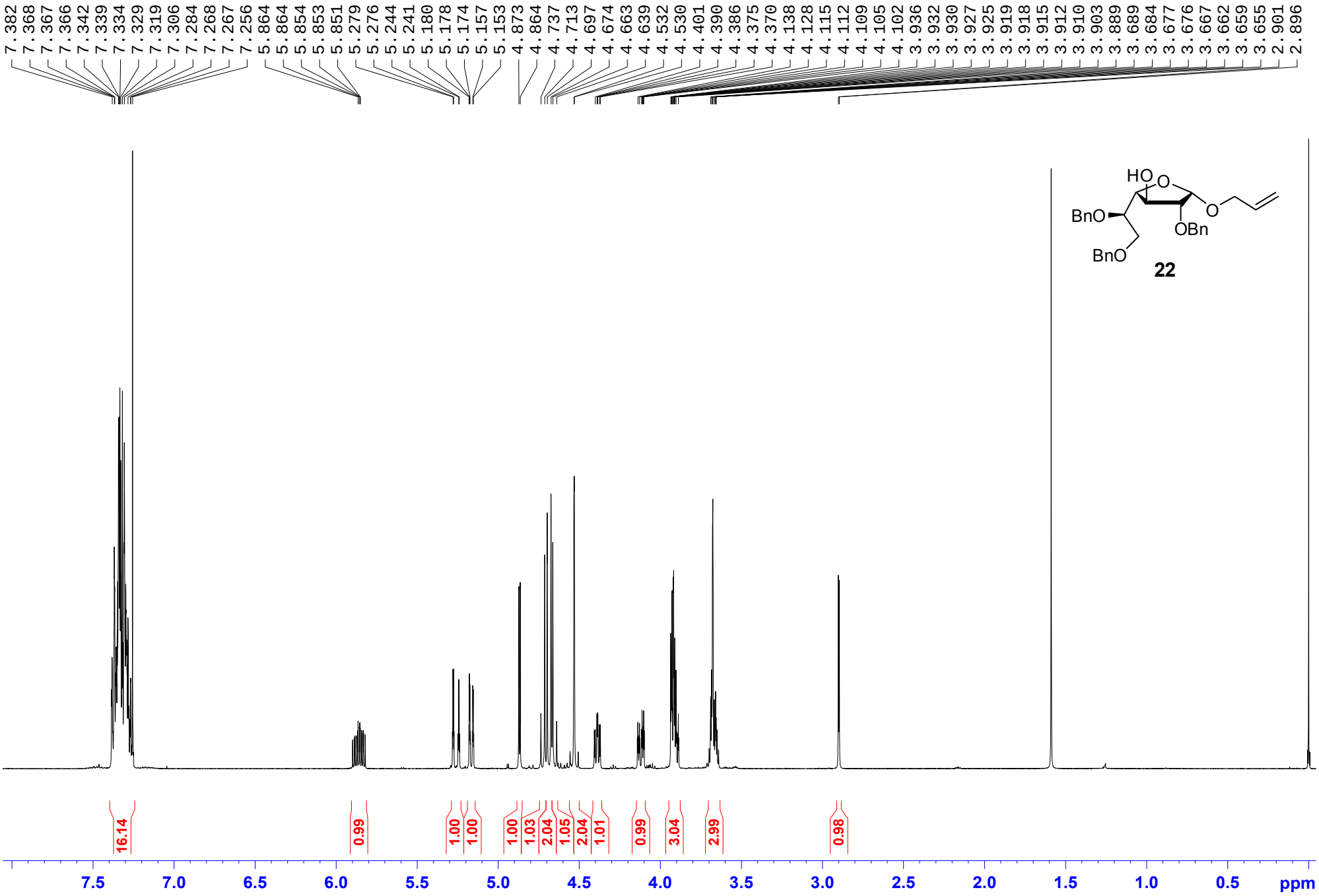
^{13}C NMR spectrum of compound **14** ($CDCl_3$; 125.8 MHz).



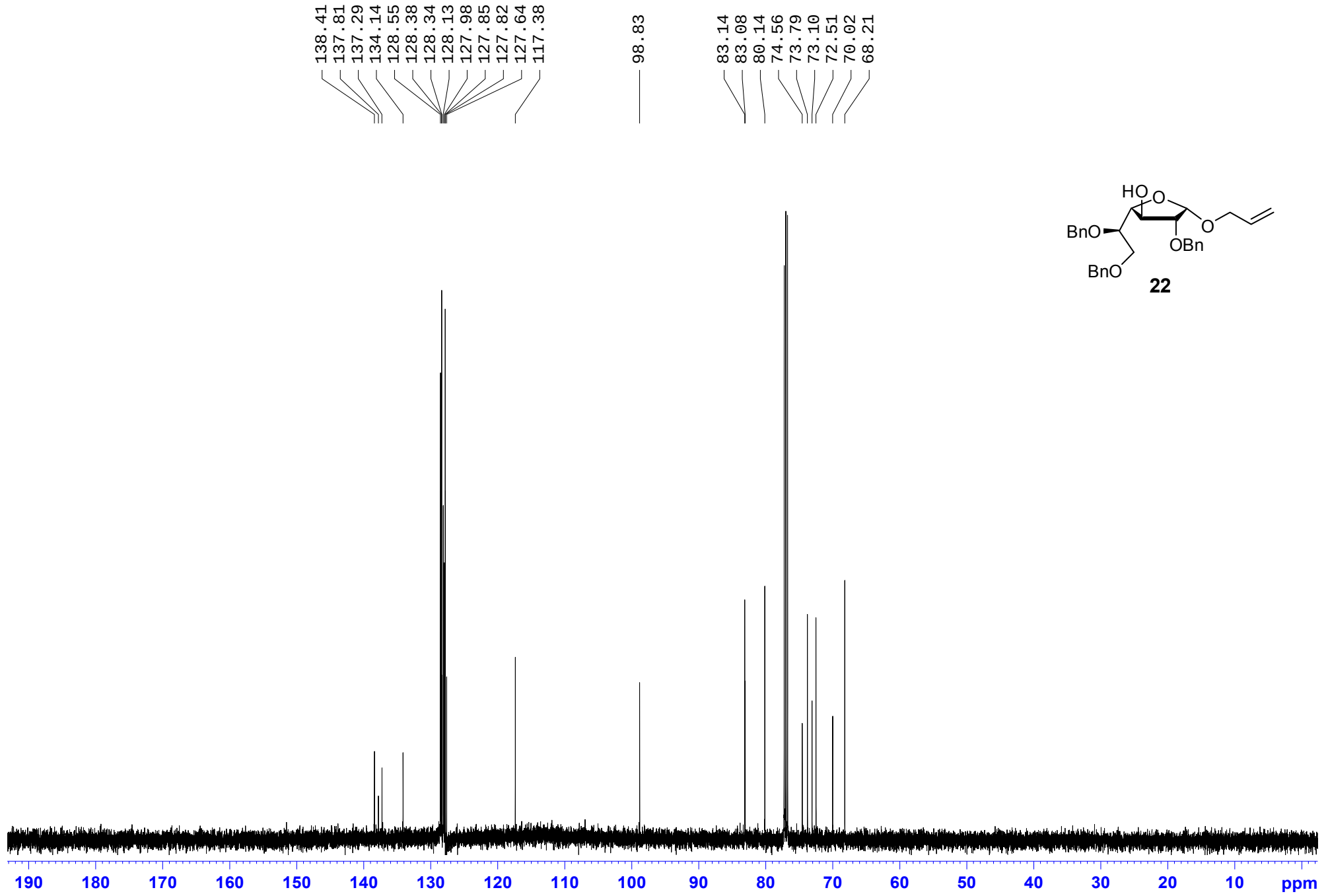
^{1}H NMR spectrum of compound **6** ($CDCl_3$; 200 MHz)



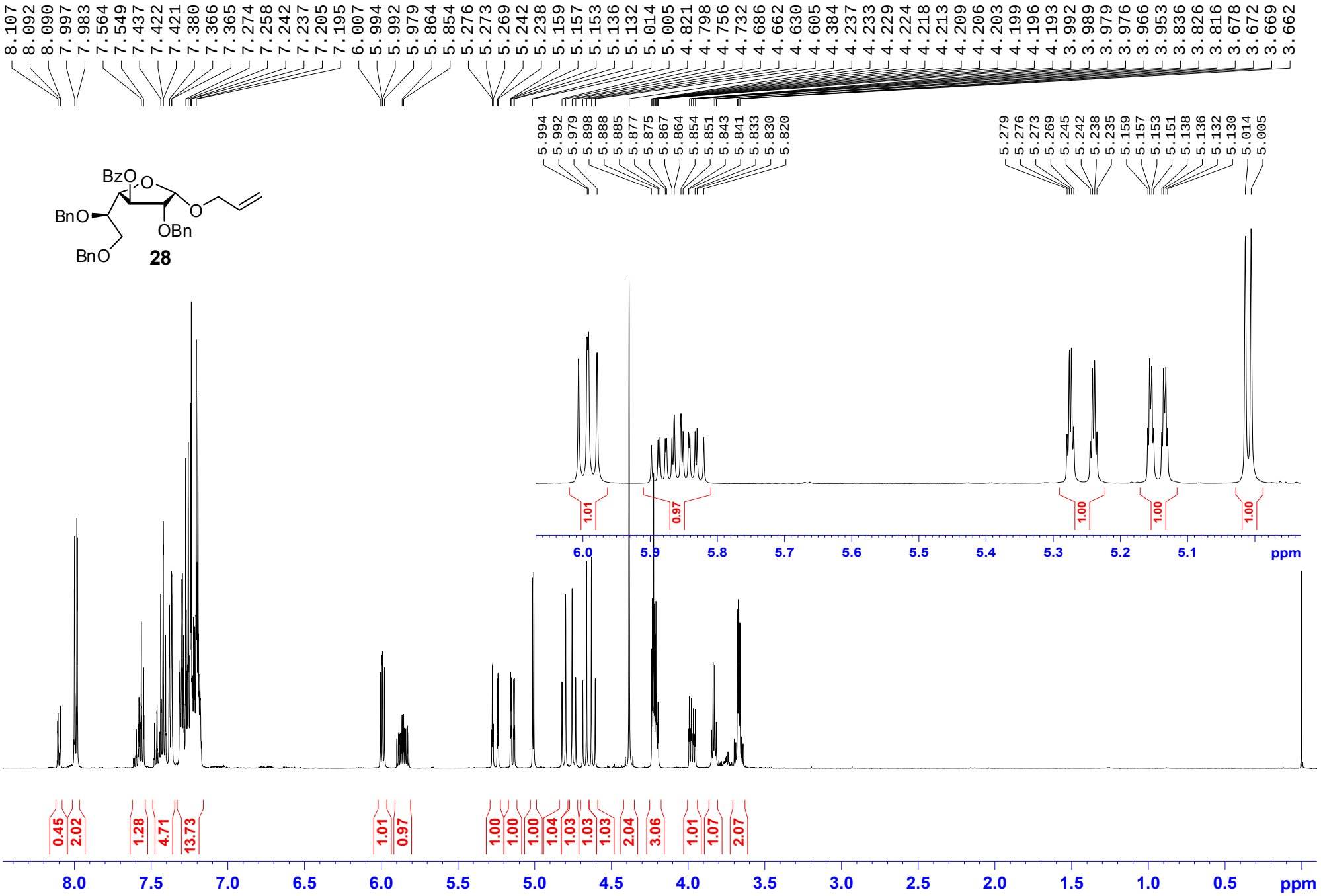
^{13}C NMR spectrum of compound **6** ($CDCl_3$; 50.3 MHz).



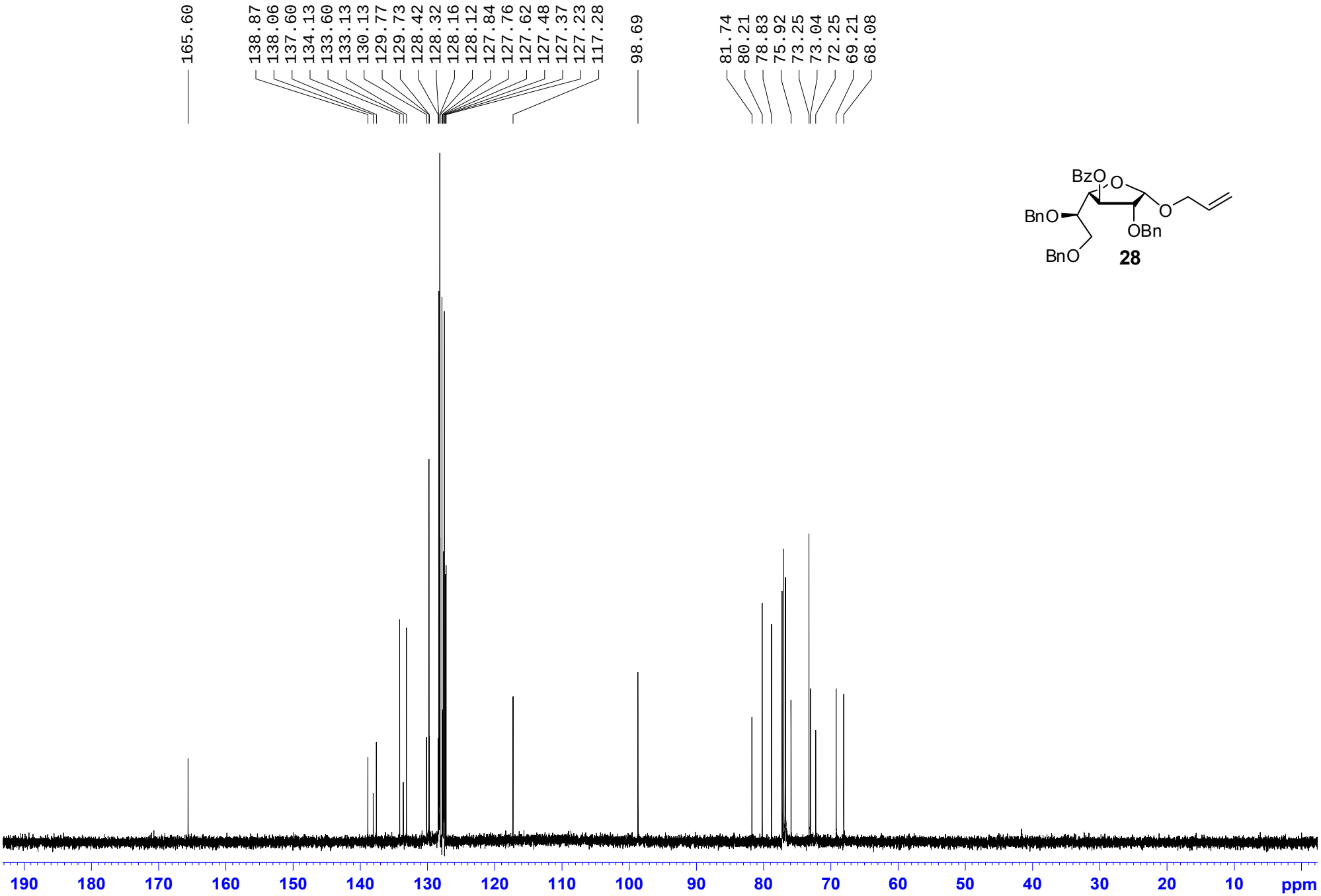
^{1}H NMR spectrum of compound **22** ($CDCl_3$; 500 MHz)



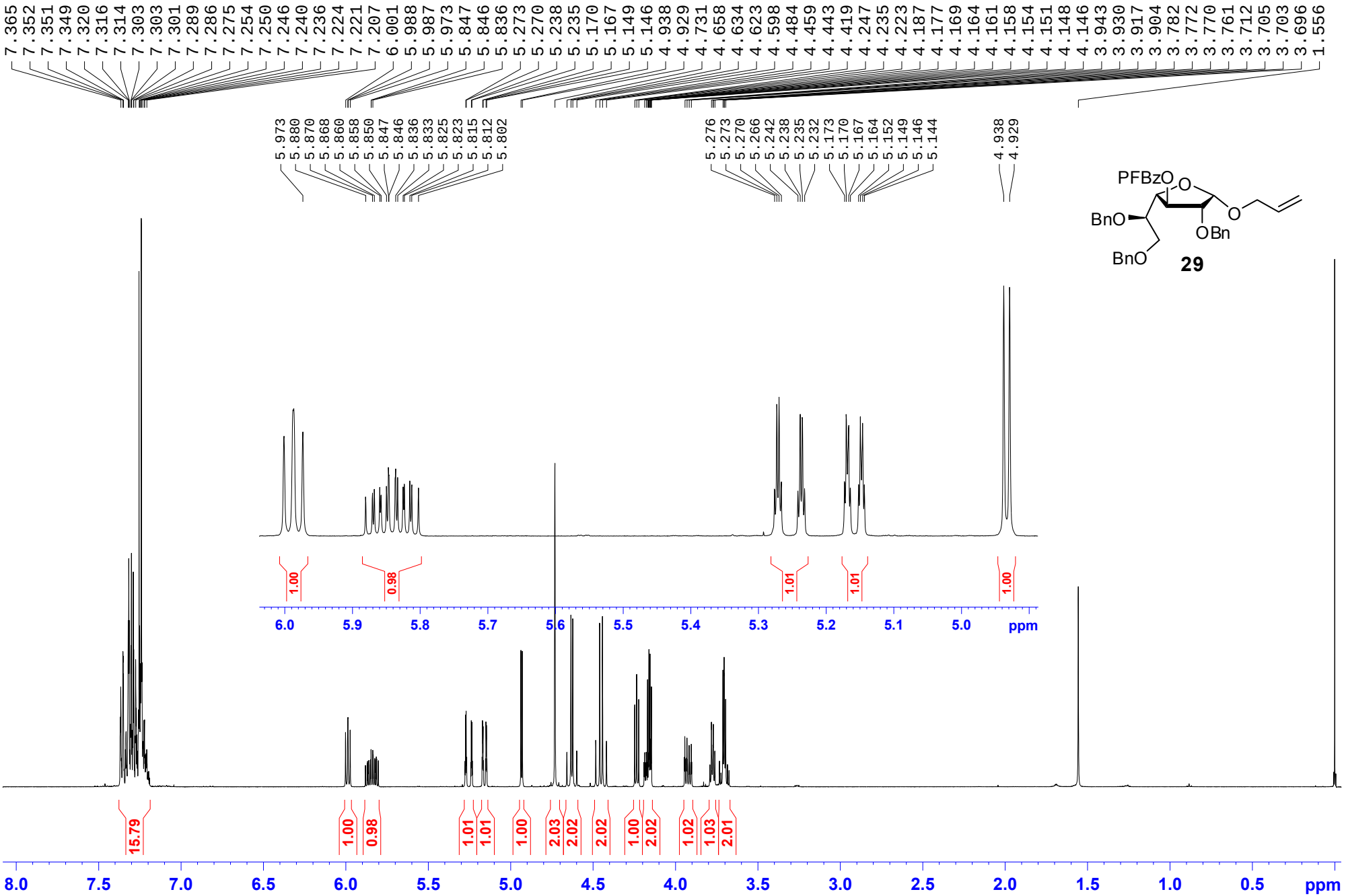
^{13}C NMR spectrum of compound **22** ($CDCl_3$; 125.8 MHz).



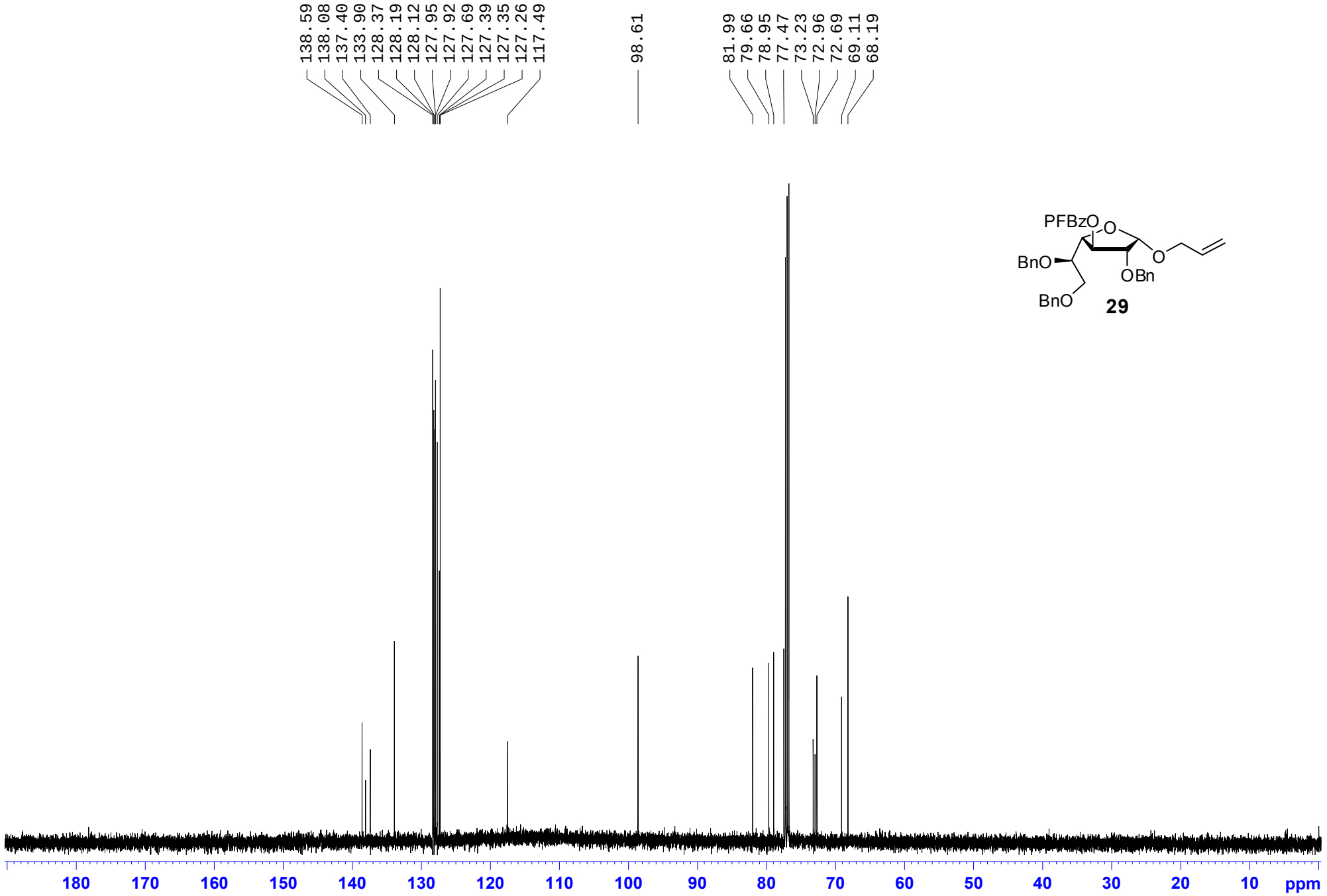
^{1}H NMR spectrum of compound **28** ($CDCl_3$; 500 MHz)



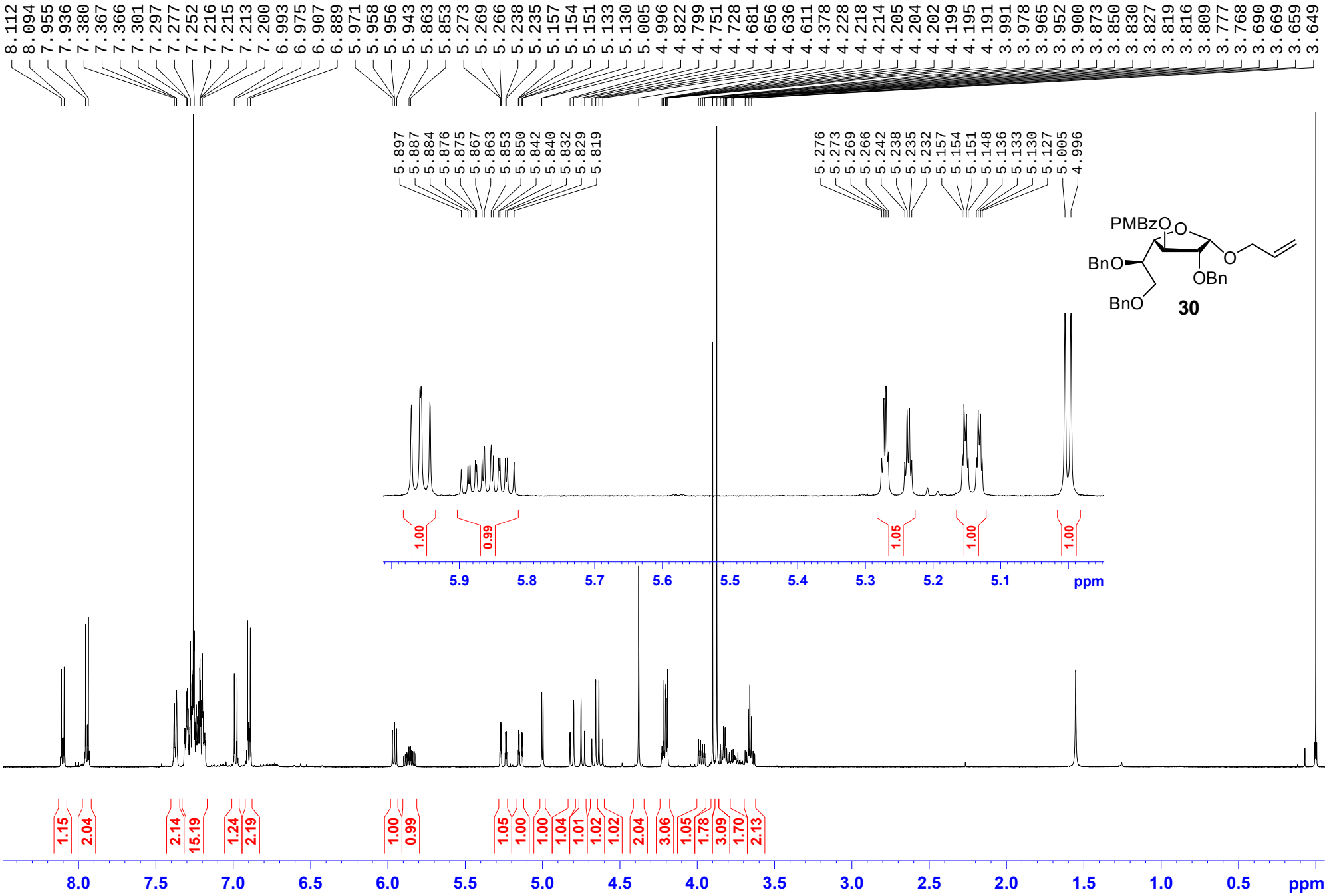
^{13}C NMR spectrum of compound **28** ($CDCl_3$; 125.8 MHz).



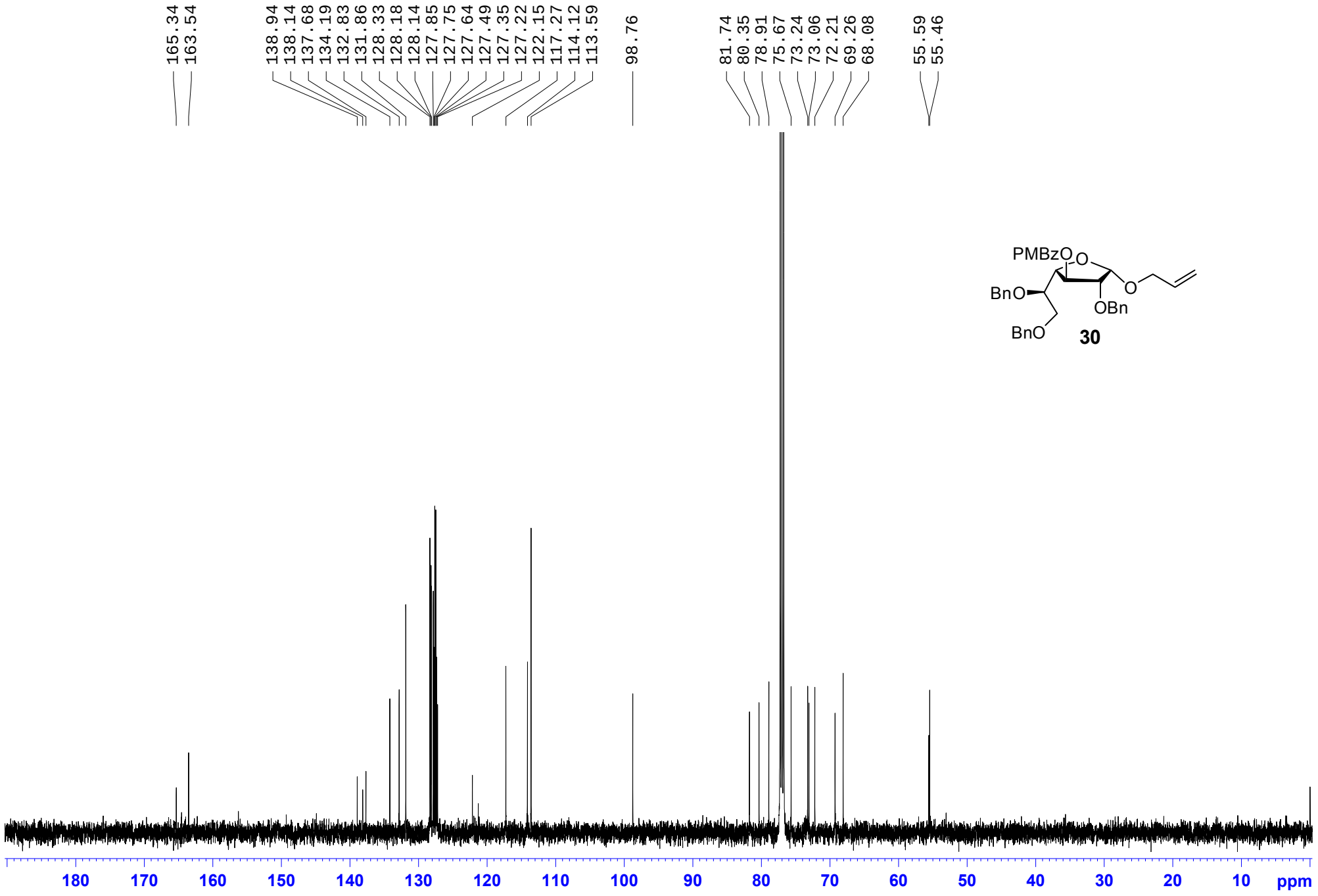
^{1}H NMR spectrum of compound **29** ($CDCl_3$; 500 MHz)



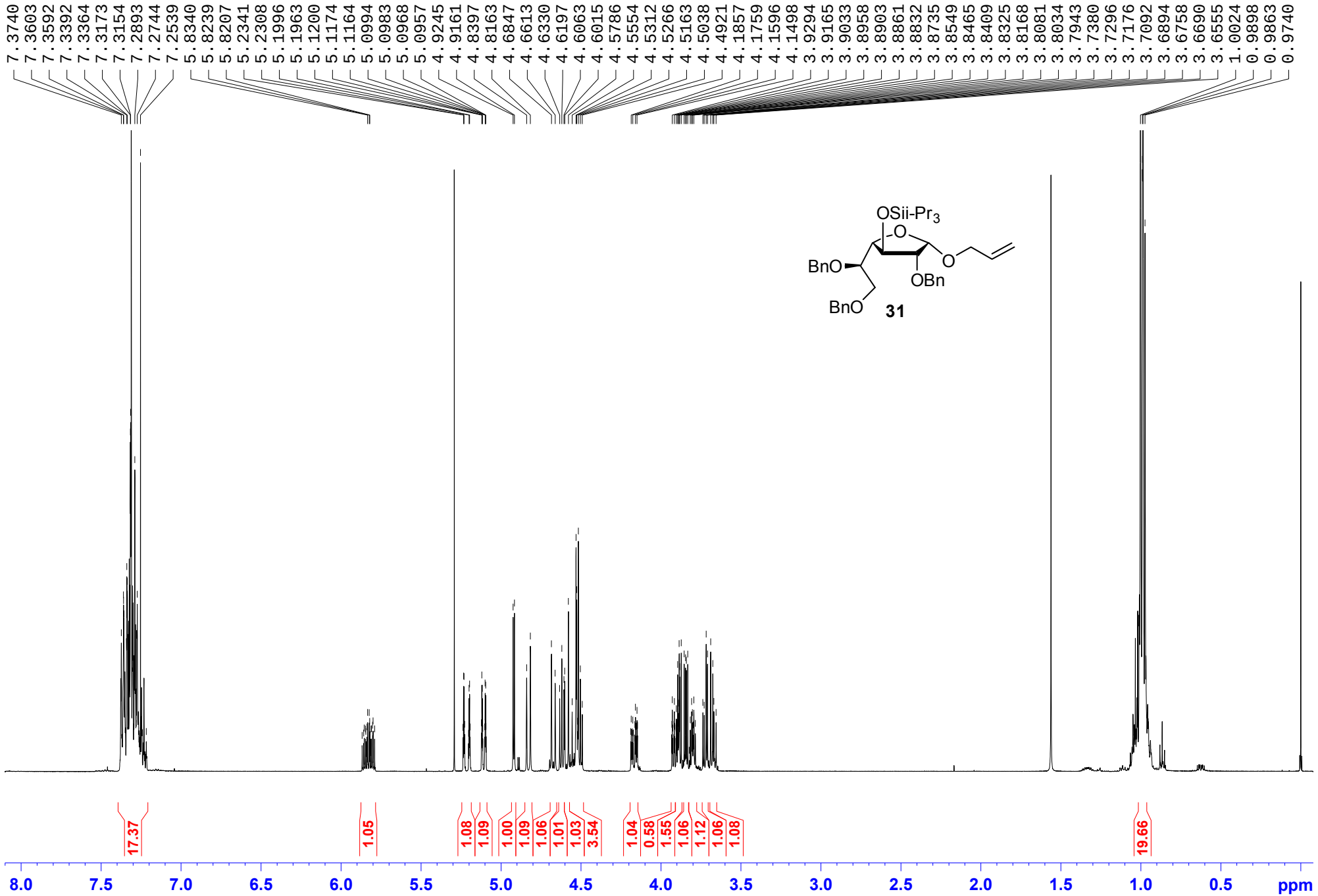
^{13}C NMR spectrum of compound **29** ($CDCl_3$; 125.8 MHz).



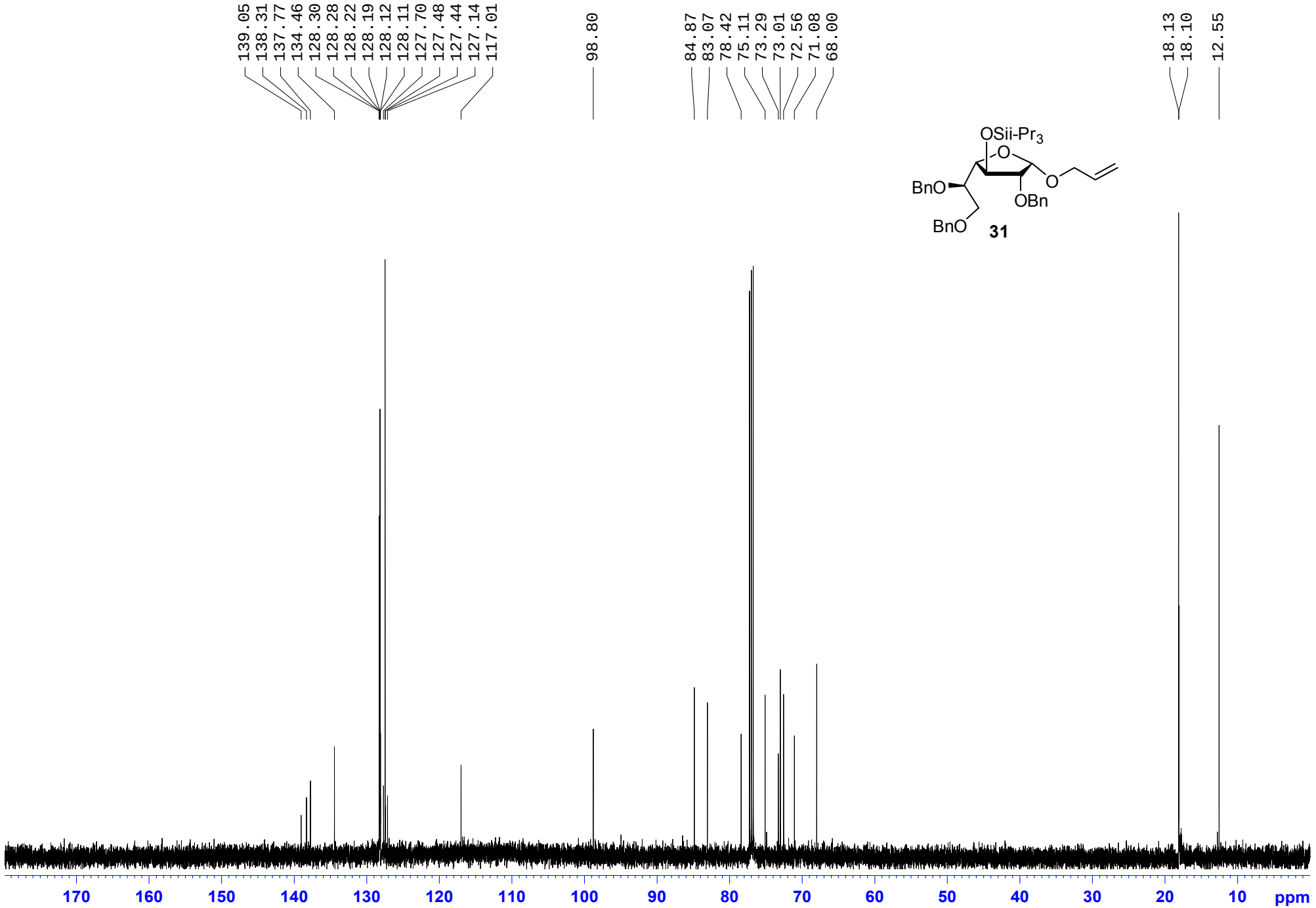
^{1}H NMR spectrum of compound **30** ($CDCl_3$; 500 MHz)



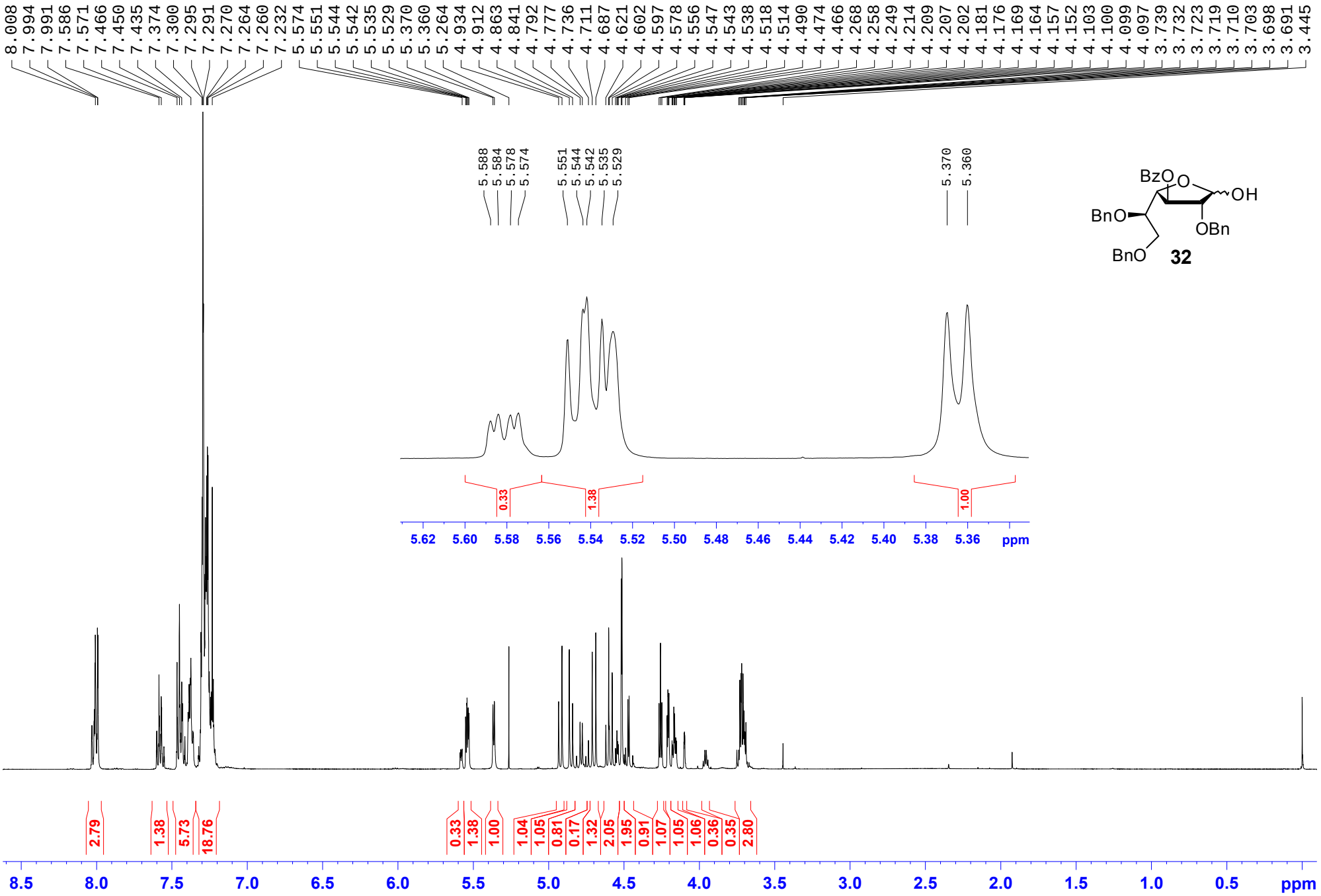
^{13}C NMR spectrum of compound **30** ($CDCl_3$; 125.8 MHz).



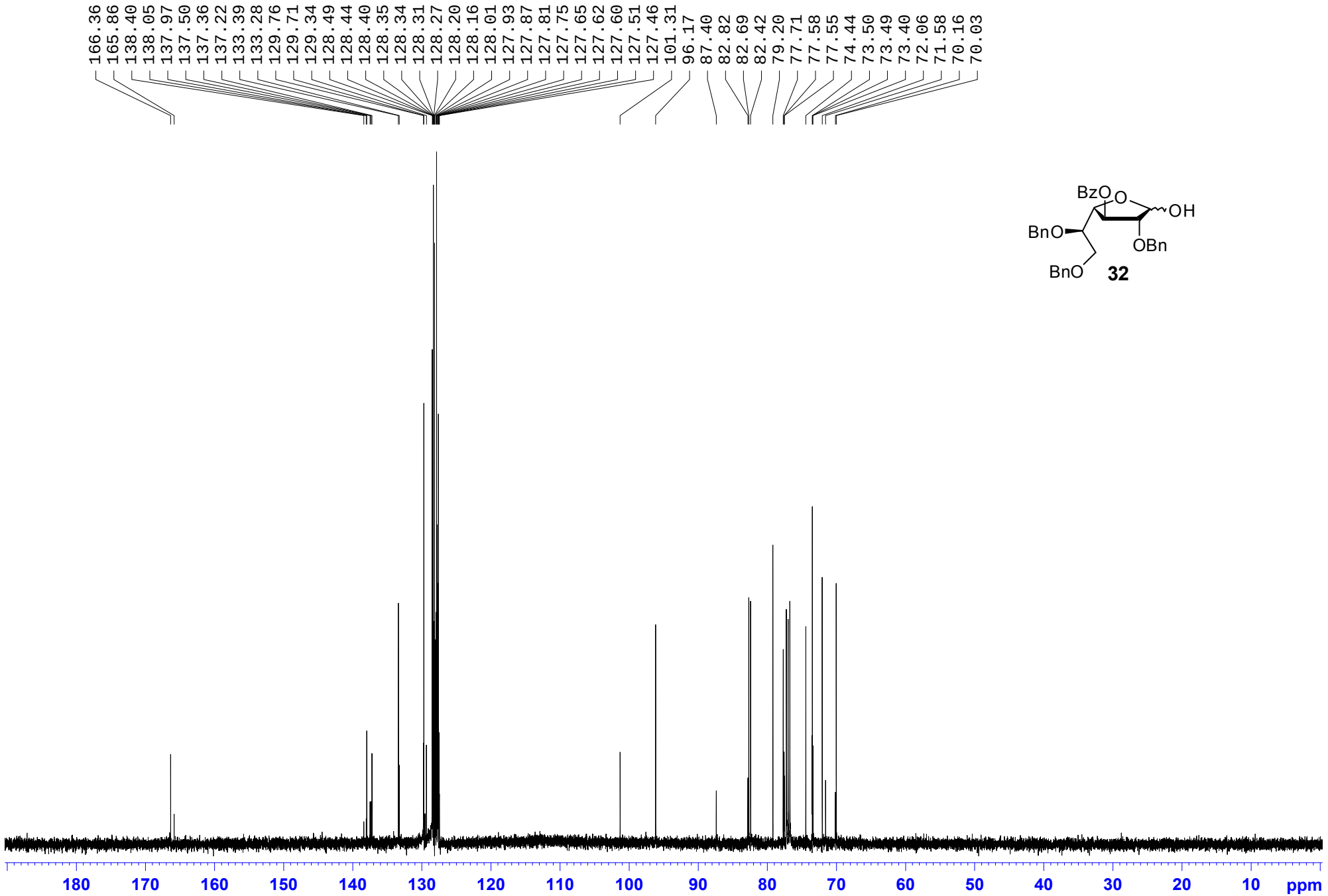
^{1}H NMR spectrum of compound **31** ($CDCl_3$; 500 MHz)



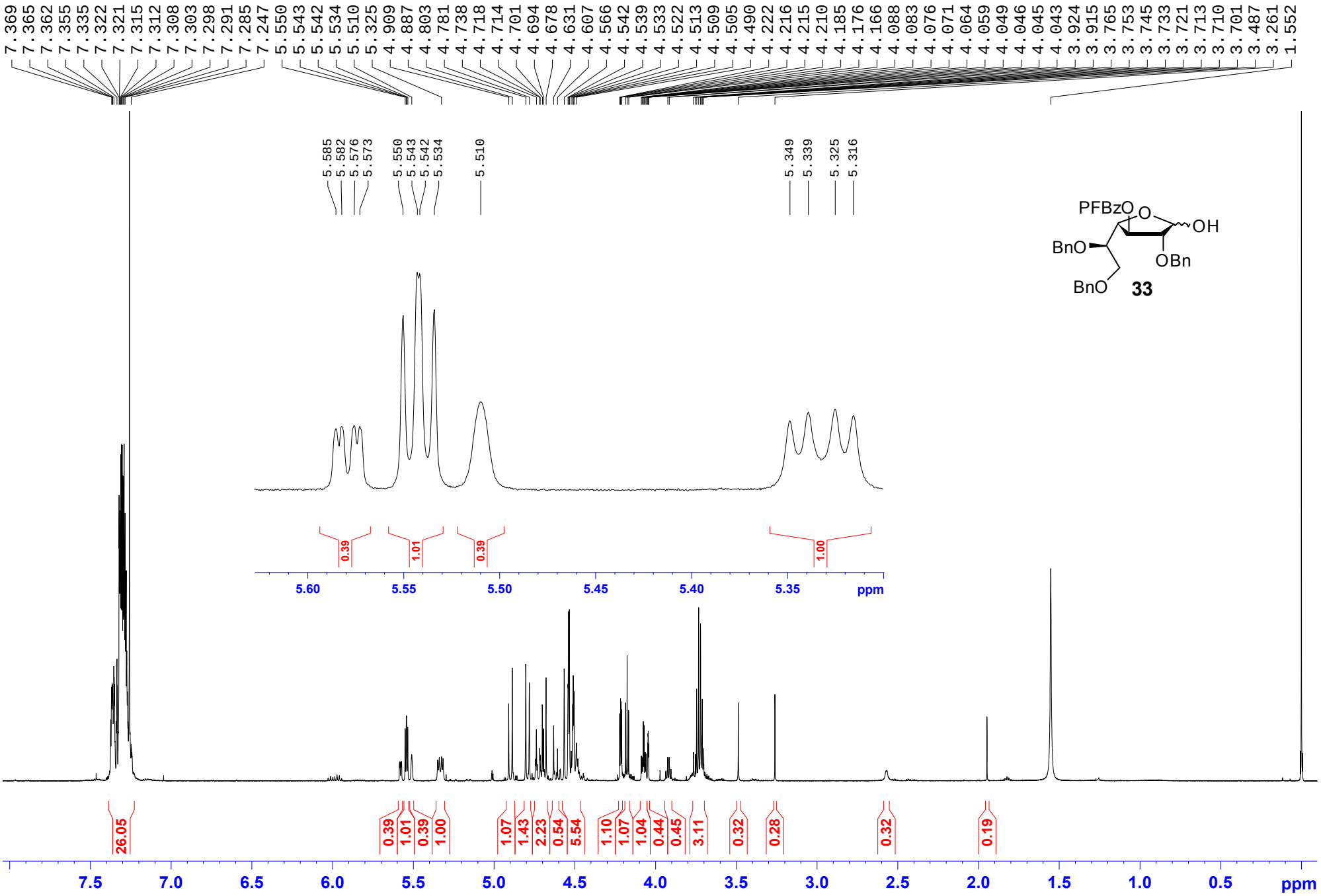
^{13}C NMR spectrum of compound **31** ($CDCl_3$; 125.8 MHz).



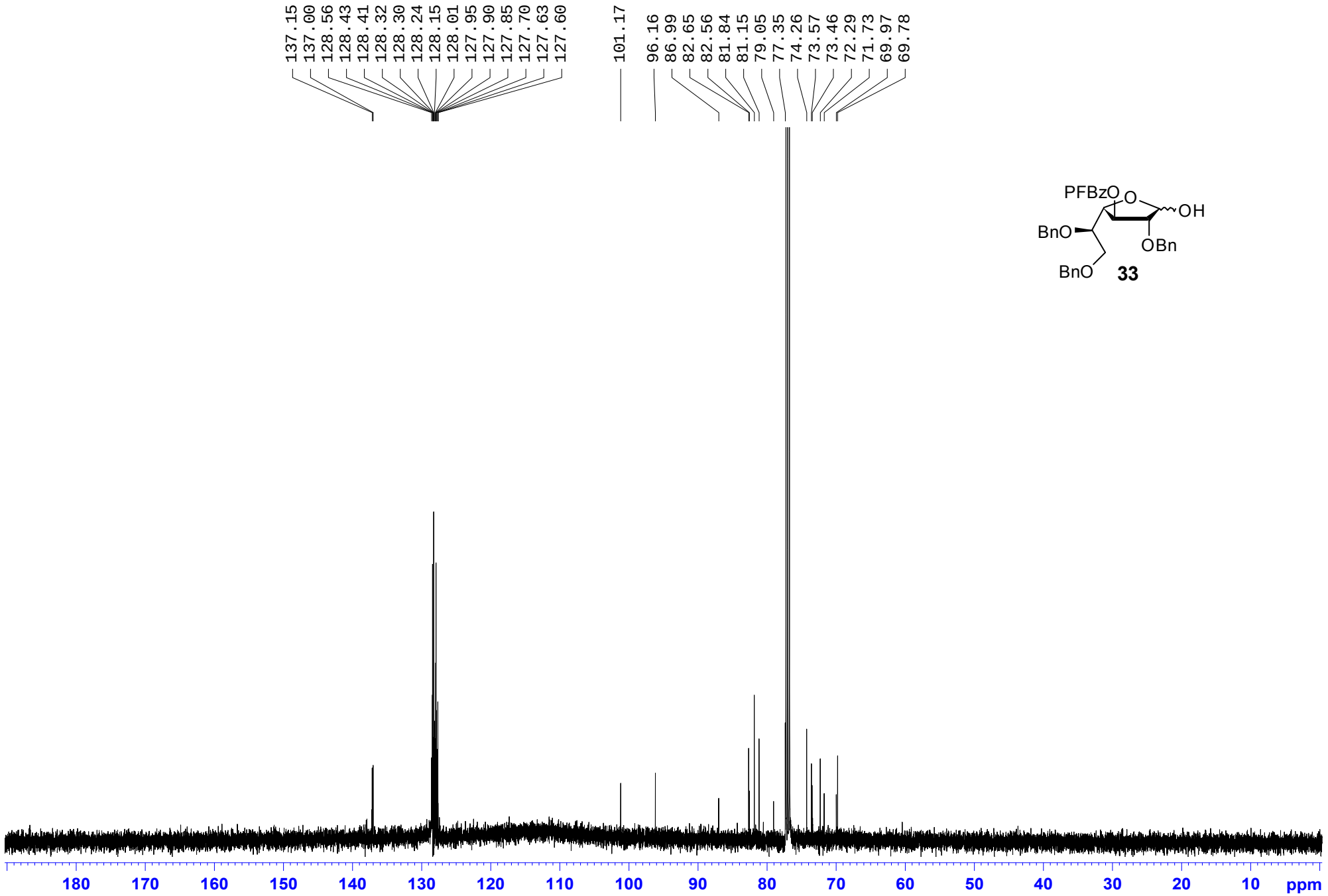
^{1}H NMR spectrum of compound **32** ($CDCl_3$; 500 MHz)



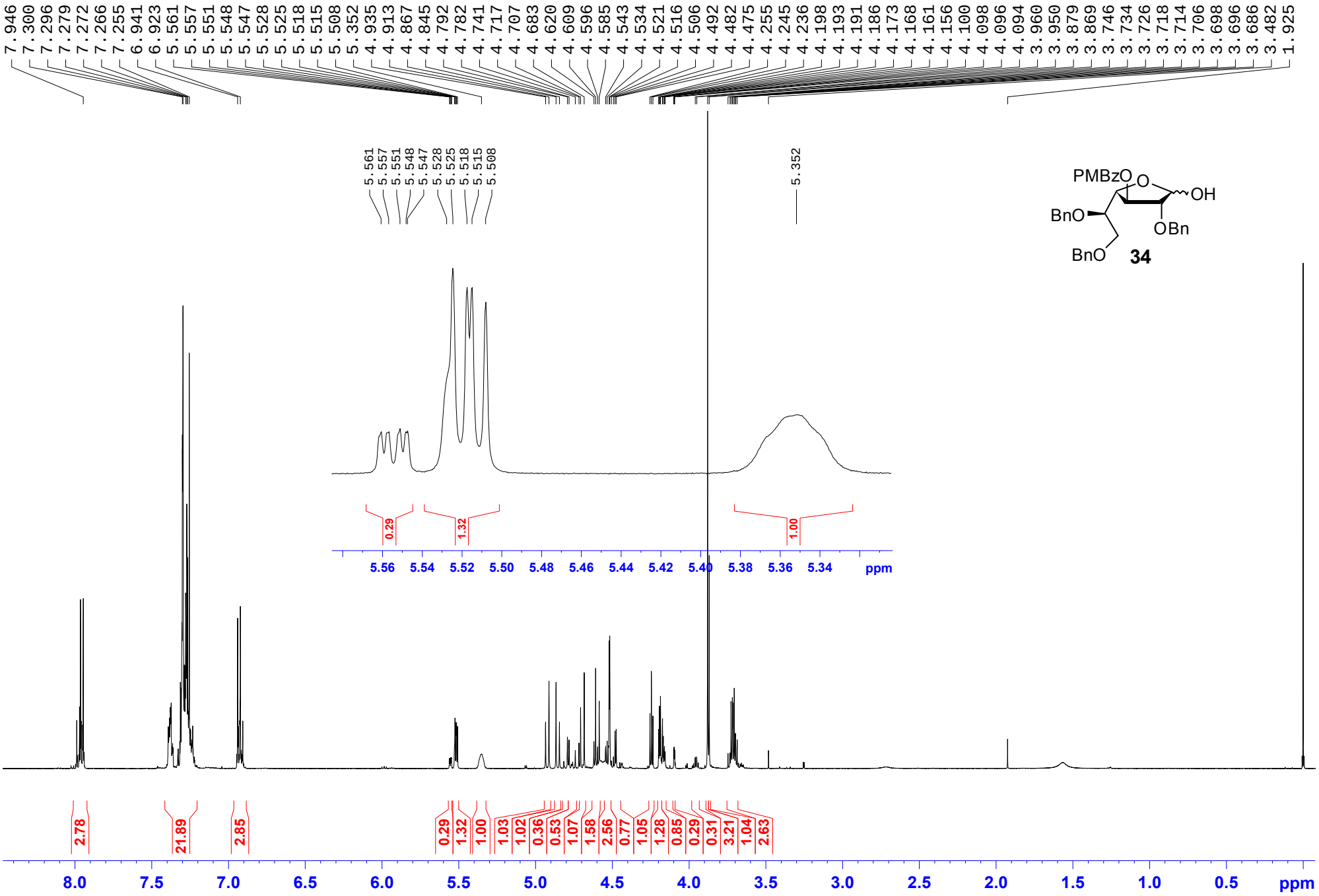
^{13}C NMR spectrum of compound **32** ($CDCl_3$; 125.8 MHz).



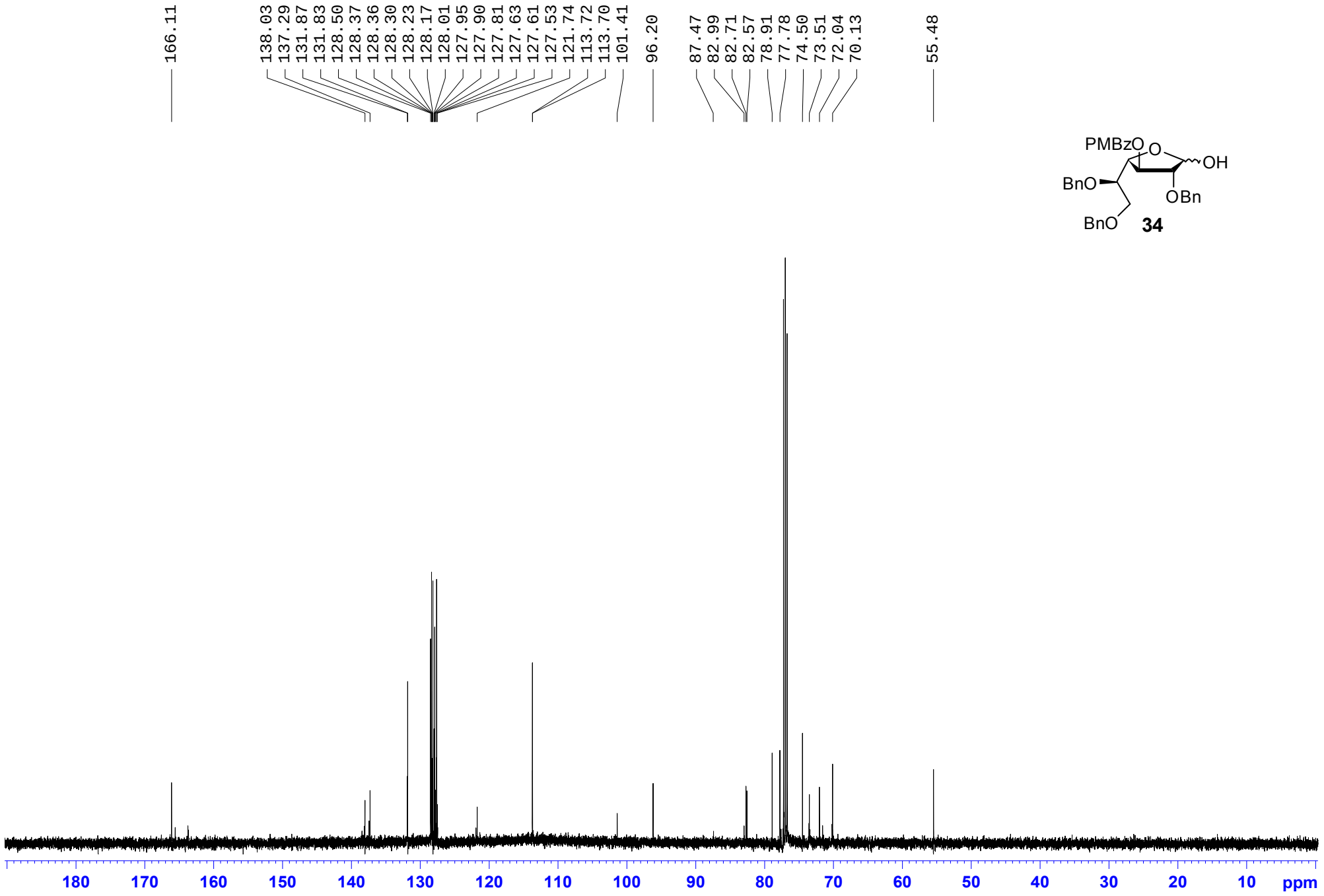
^{1}H NMR spectrum of compound **33** ($CDCl_3$; 500 MHz)



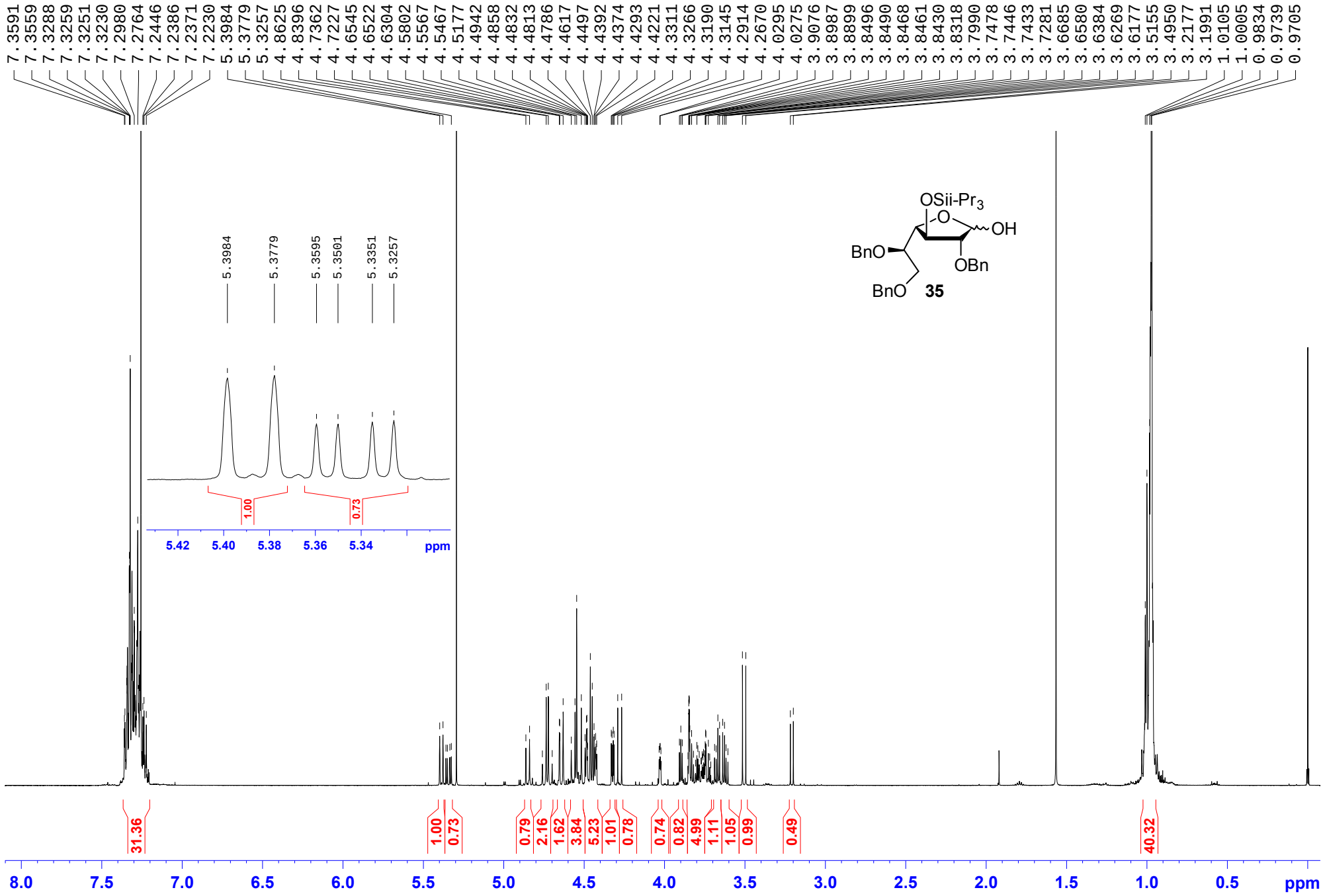
^{13}C NMR spectrum of compound **33** ($CDCl_3$; 125.8 MHz).



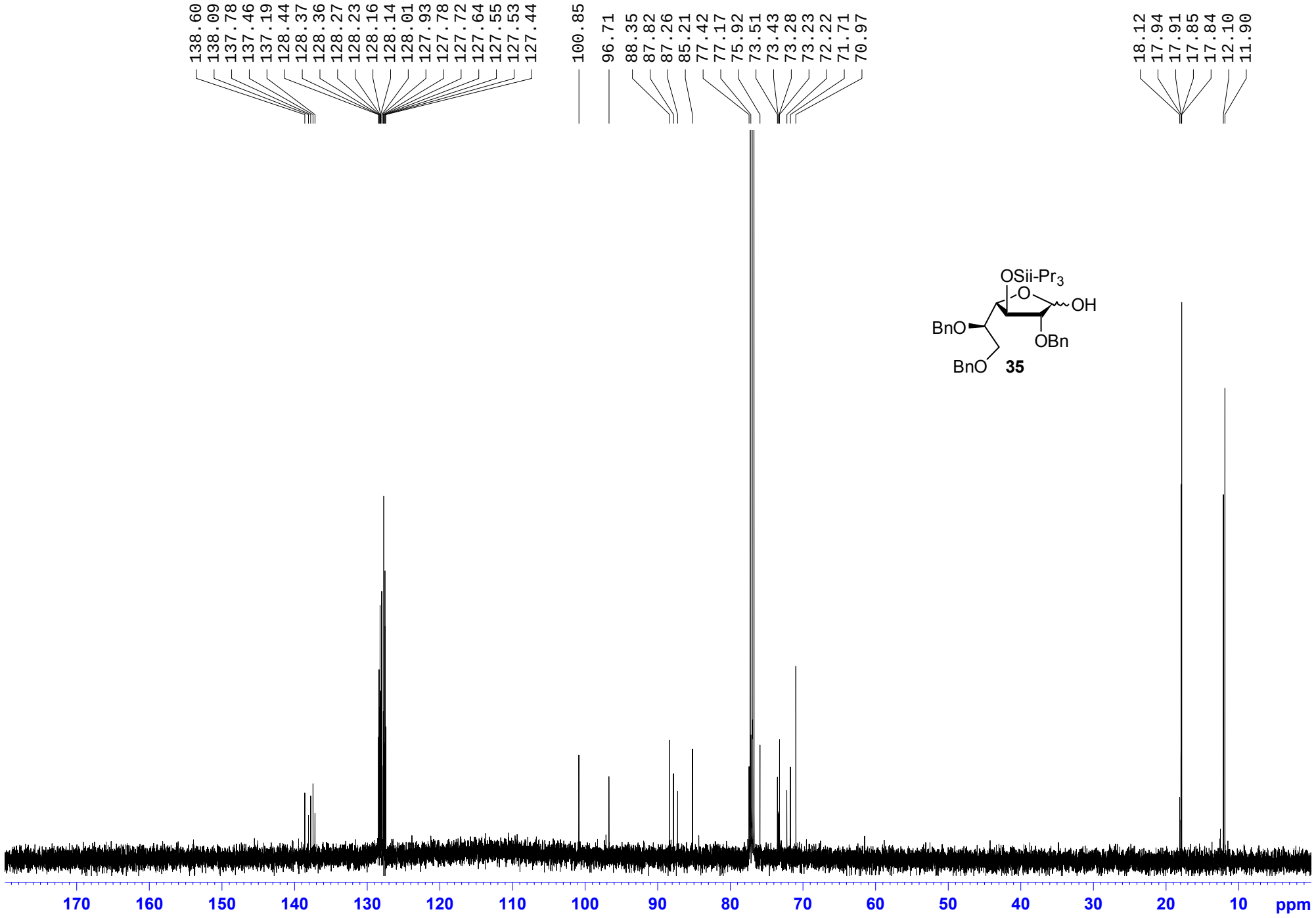
^{1}H NMR spectrum of compound **34** ($CDCl_3$; 500 MHz)



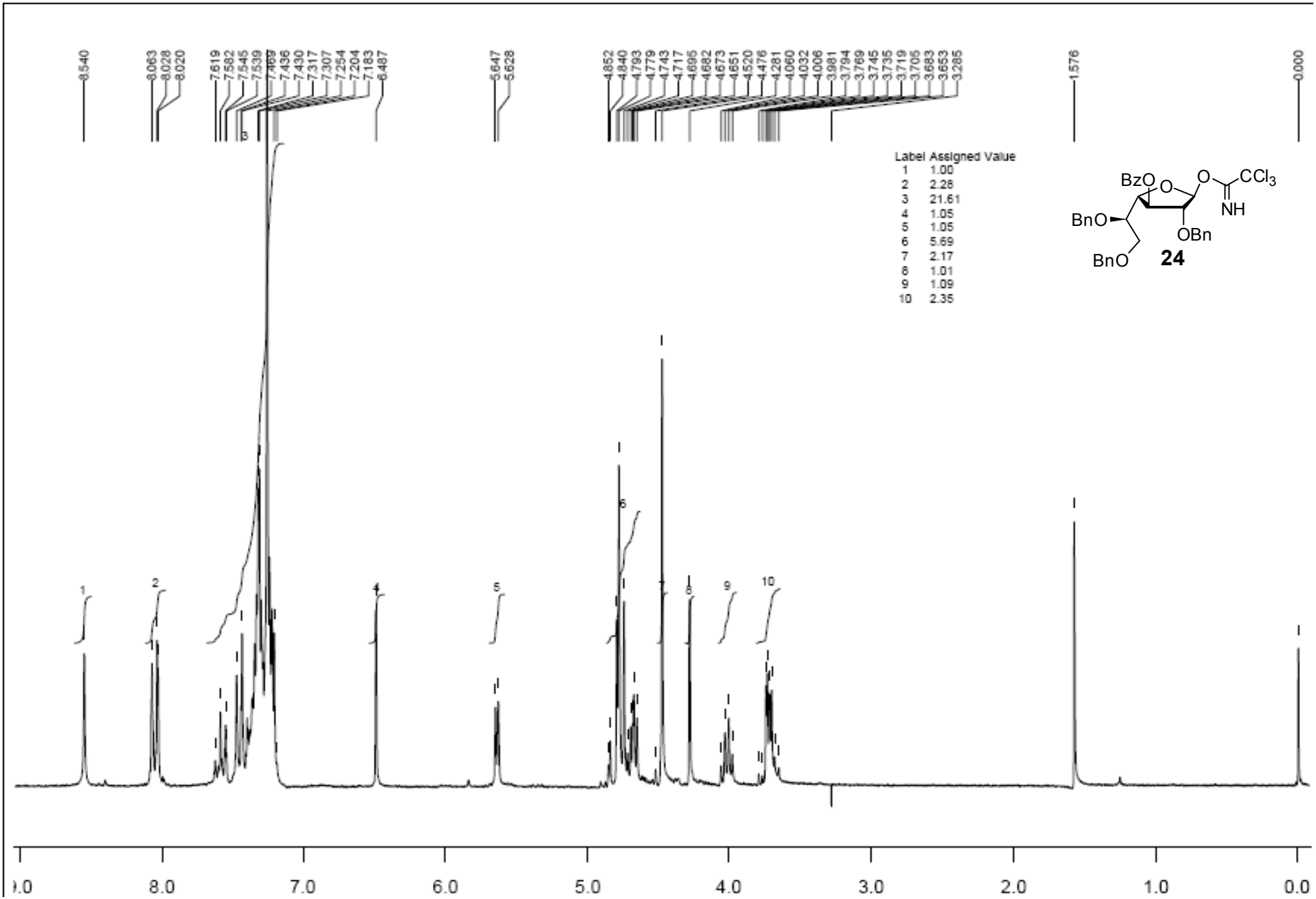
^{13}C NMR spectrum of compound **34** ($CDCl_3$; 125.8 MHz).



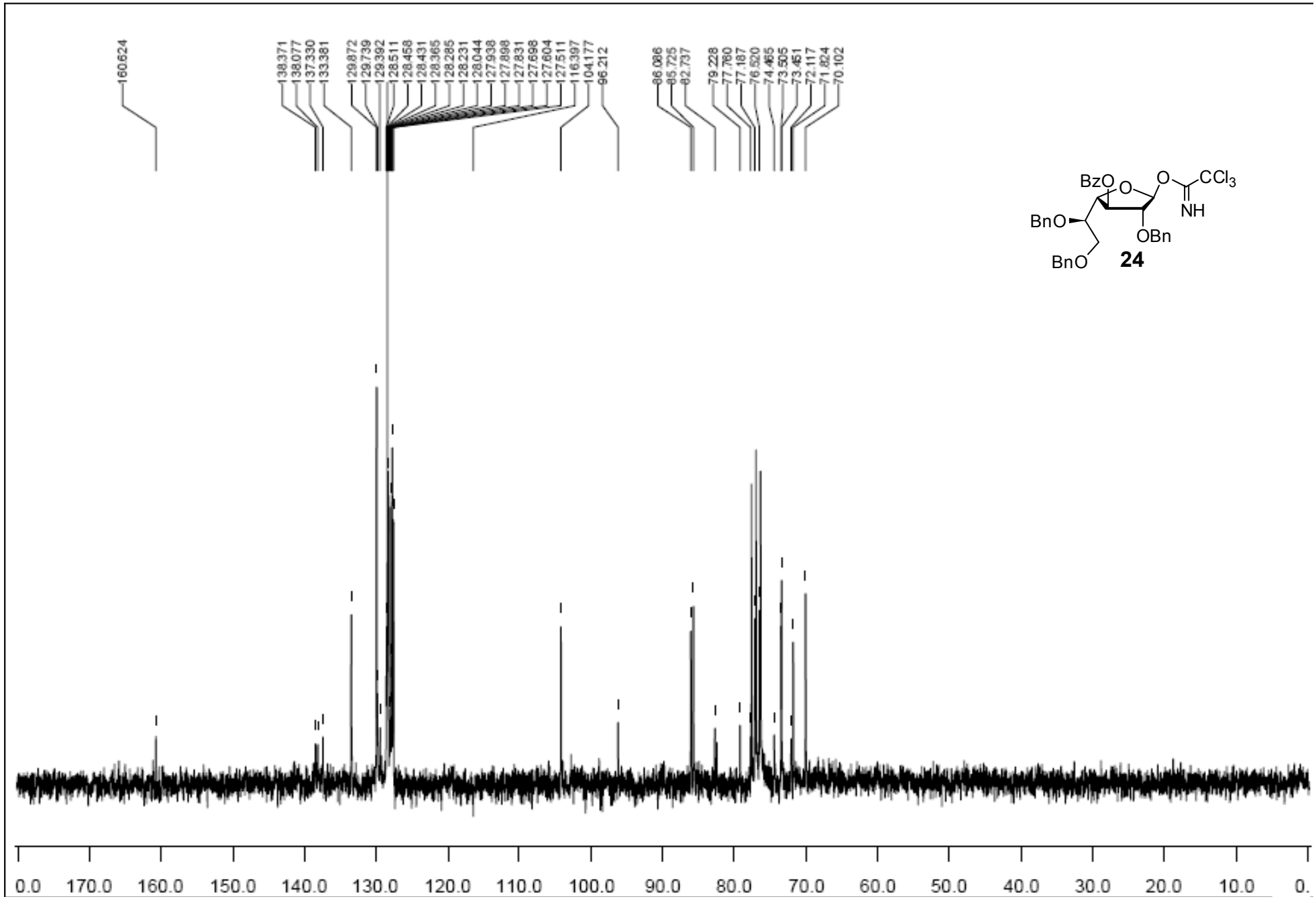
^{1}H NMR spectrum of compound **35** ($CDCl_3$; 500 MHz)



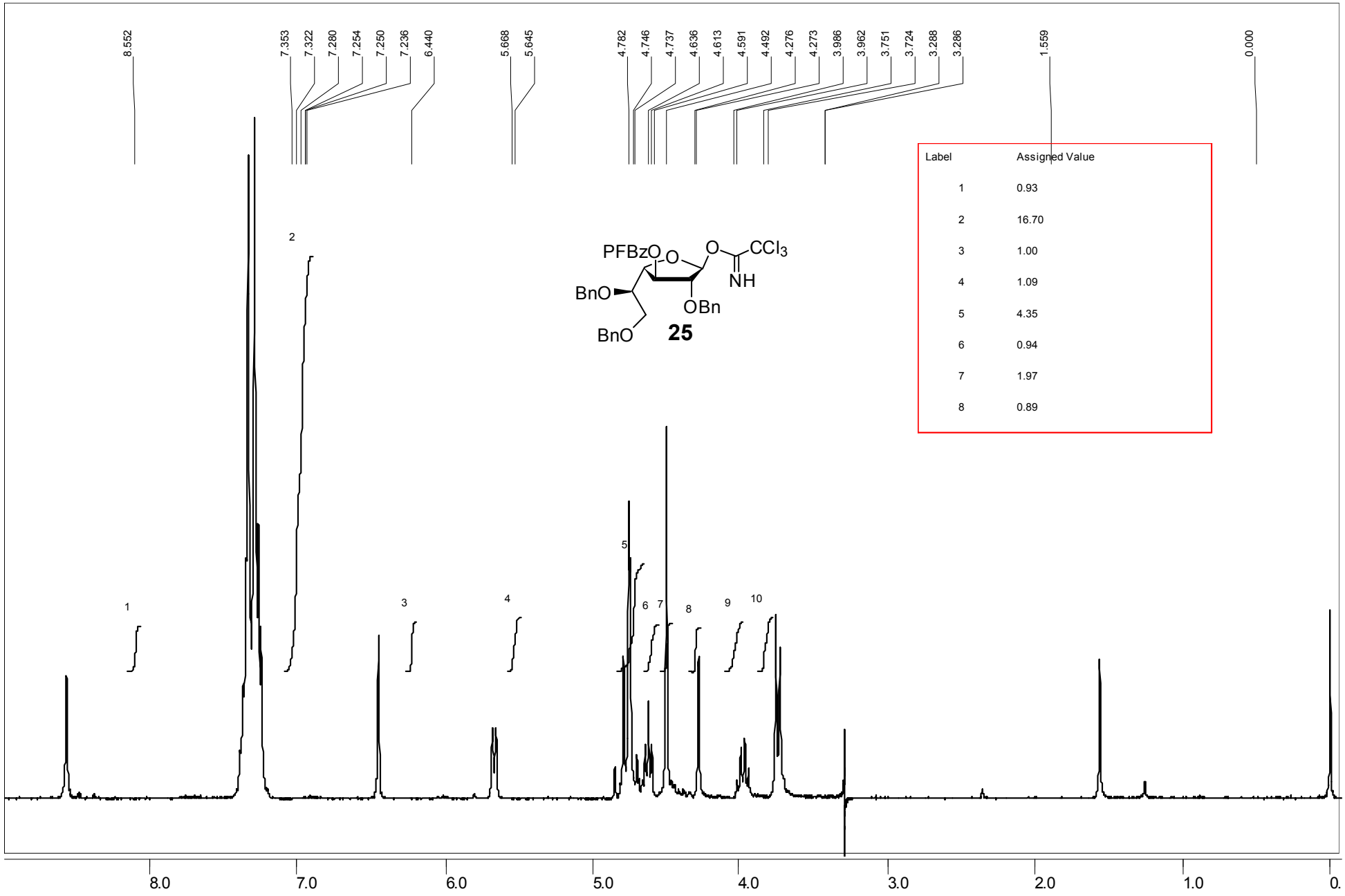
^{13}C NMR spectrum of compound **35** ($CDCl_3$; 125.8 MHz).



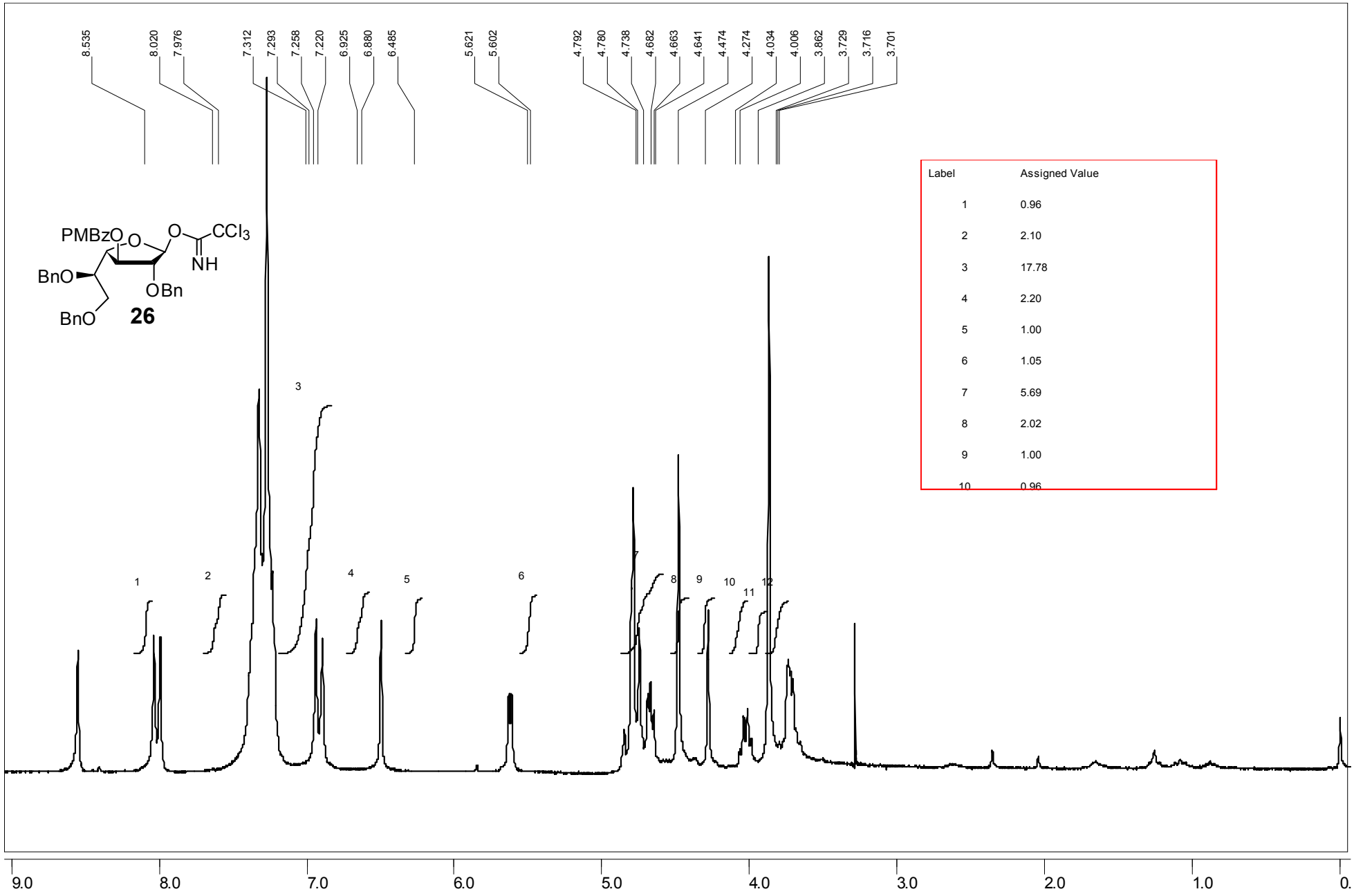
^{1}H NMR spectrum of compound **24** ($CDCl_3$; 200 MHz)



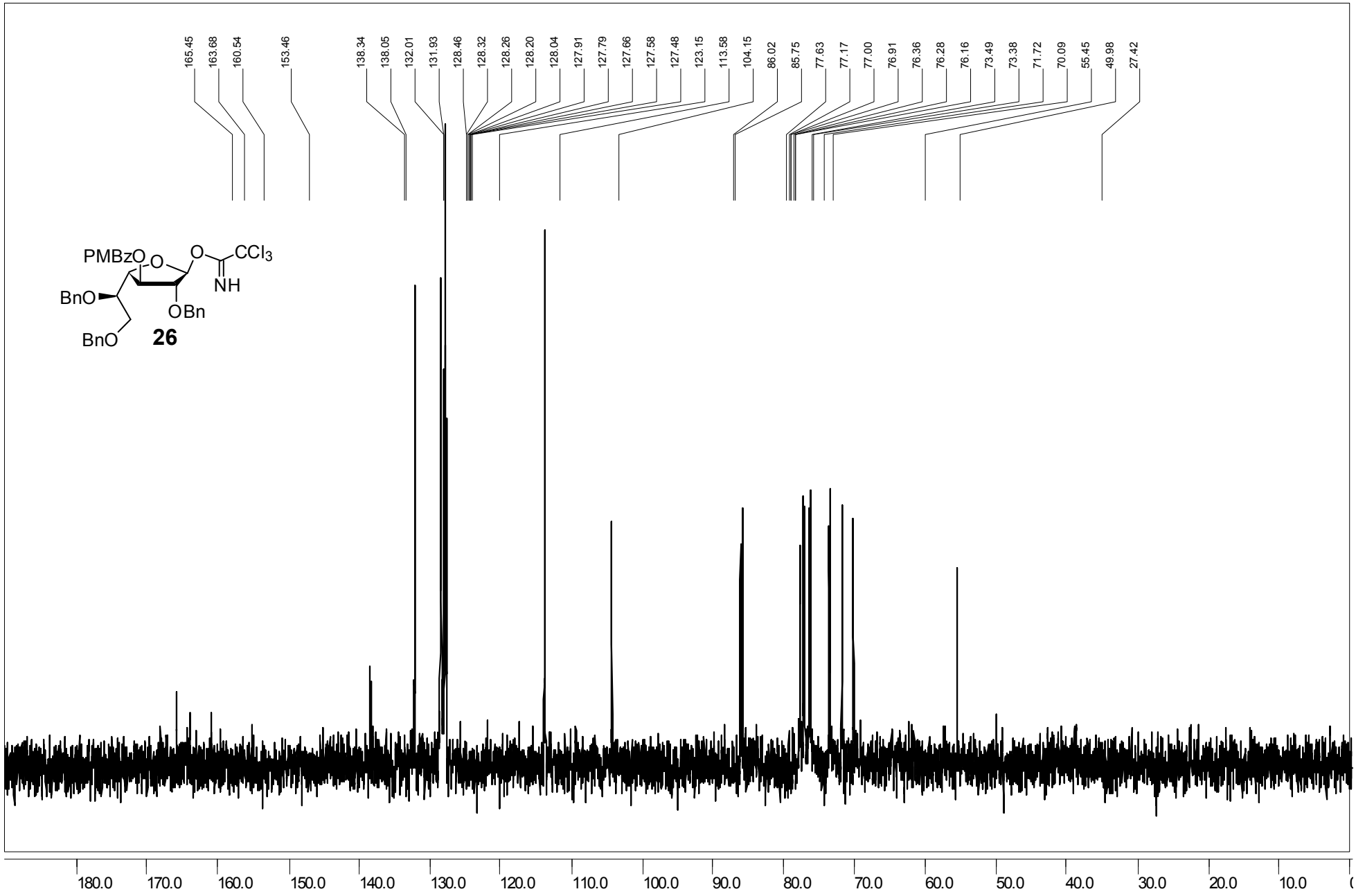
^{13}C NMR spectrum of compound **24** ($CDCl_3$; 50.3 MHz).



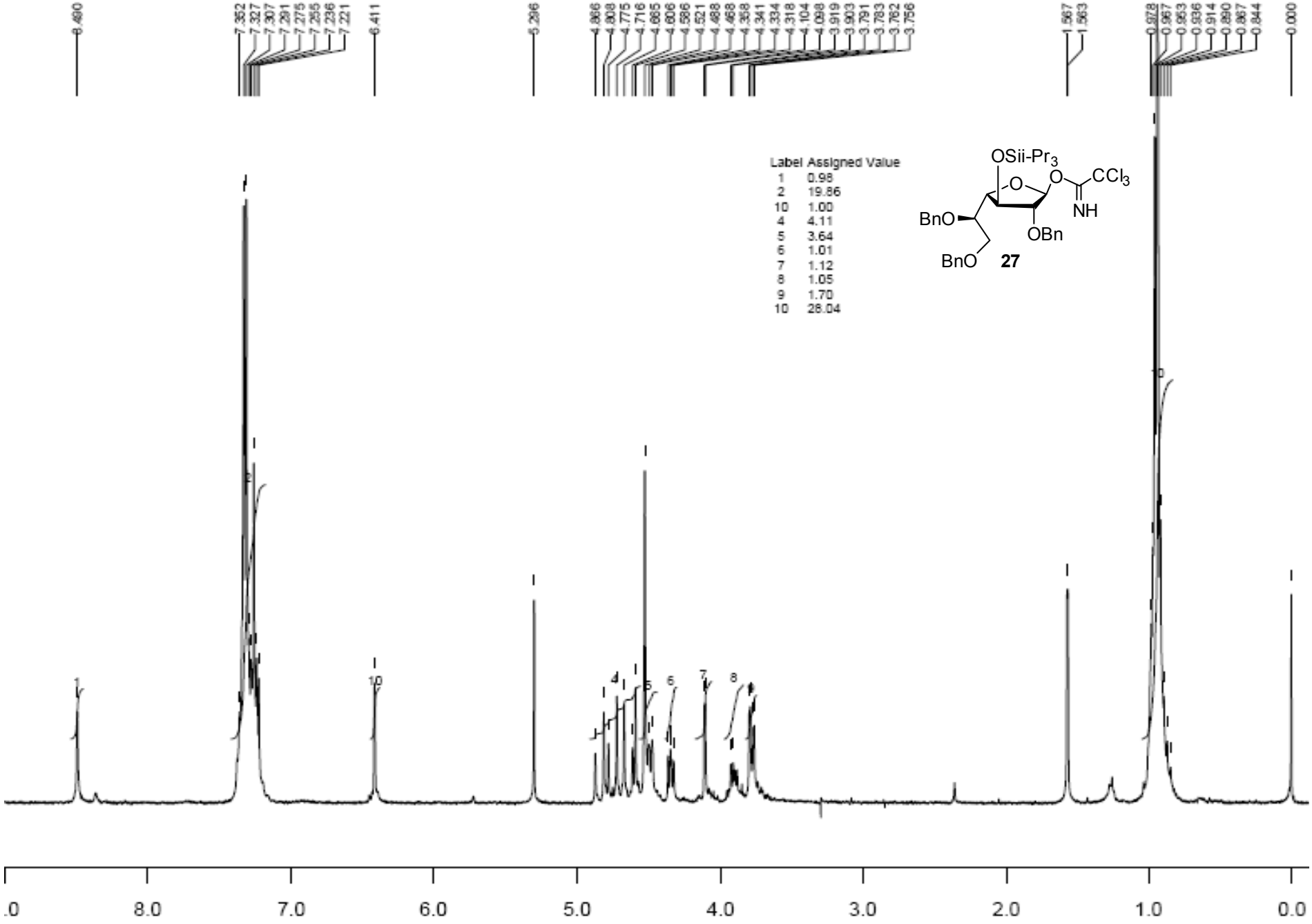
^{1}H NMR spectrum of compound **25** ($CDCl_3$; 200 MHz)



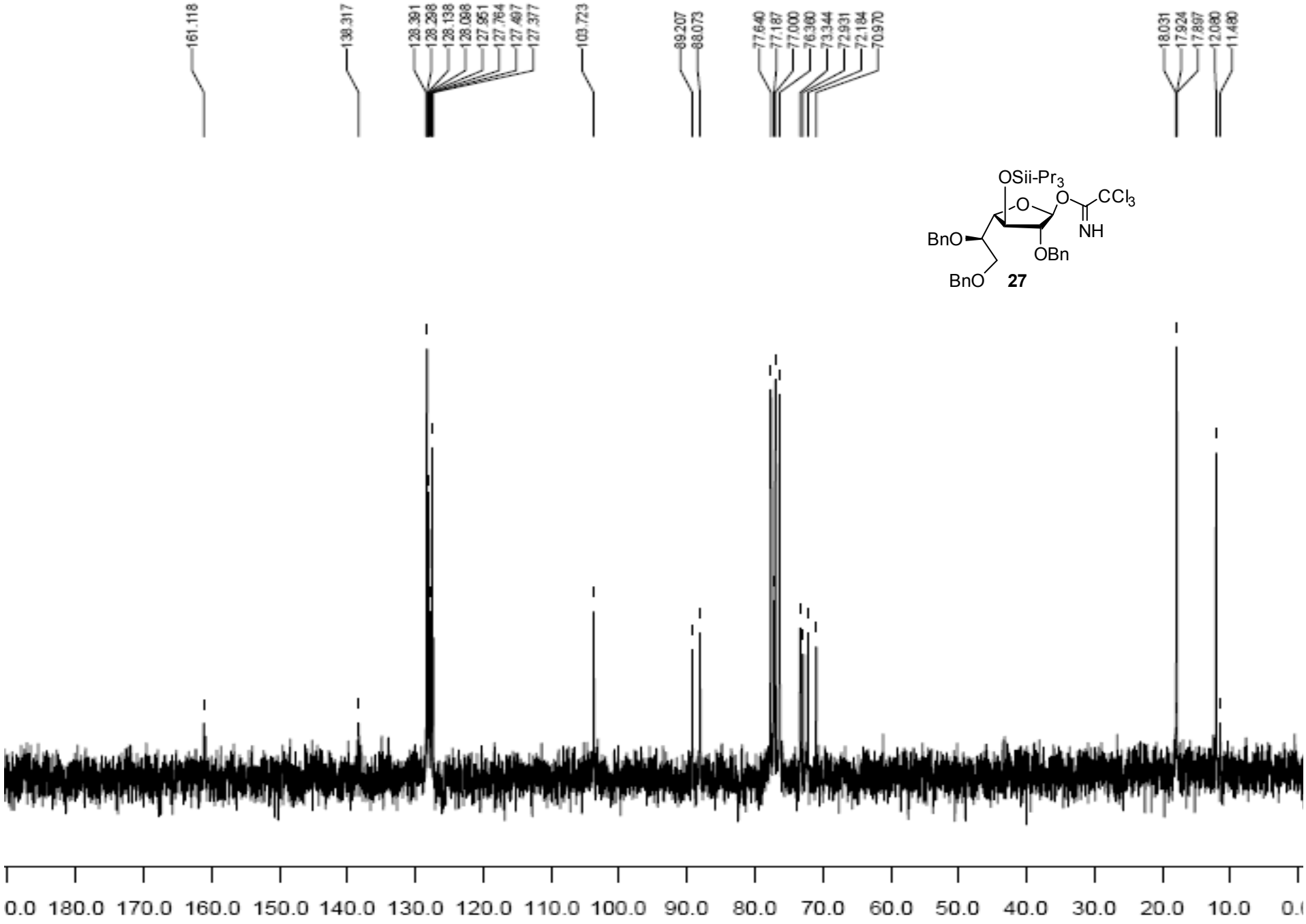
^{1}H NMR spectrum of compound **26** ($CDCl_3$; 200 MHz)



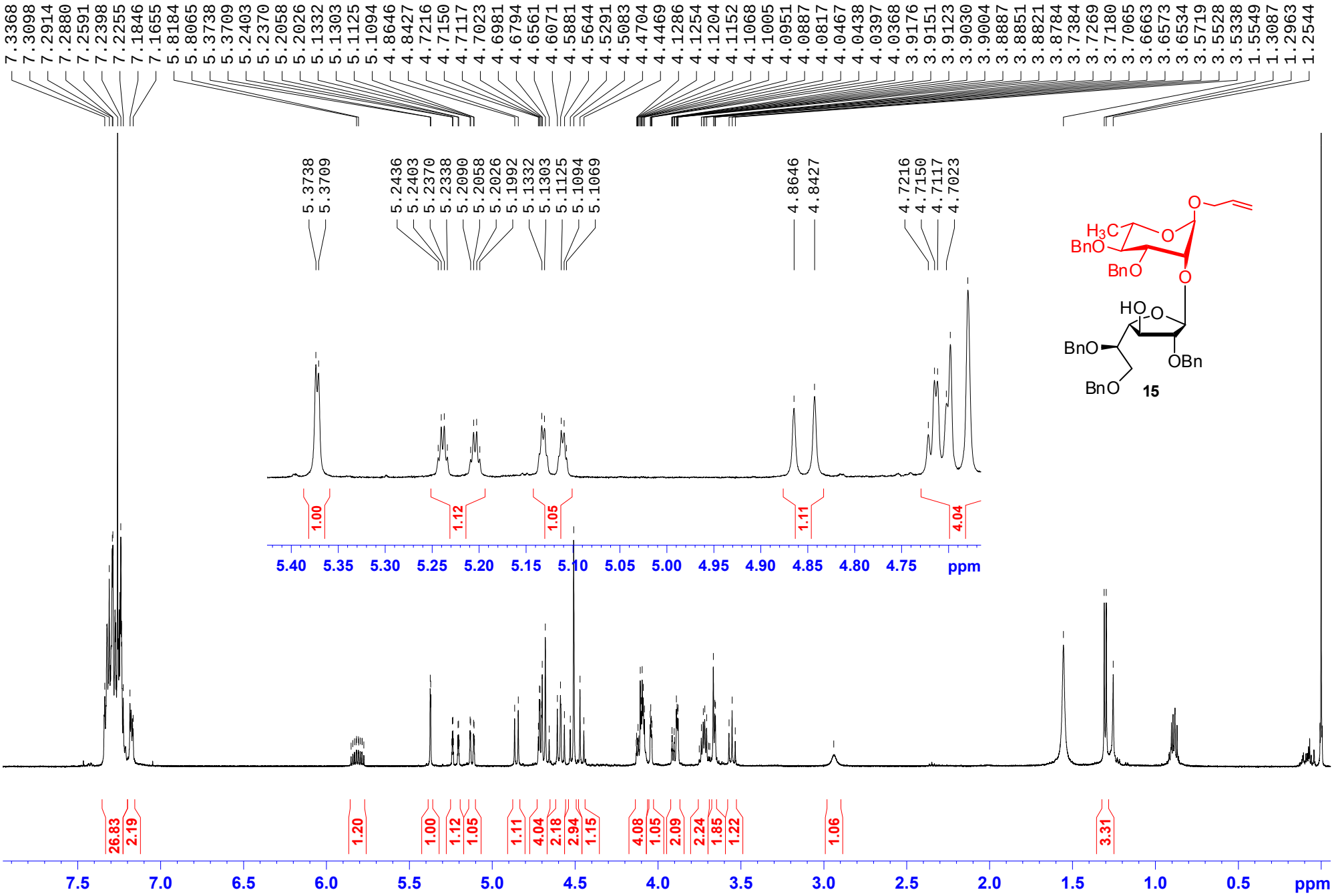
^{13}C NMR spectrum of compound **26** ($CDCl_3$; 50.3 MHz).



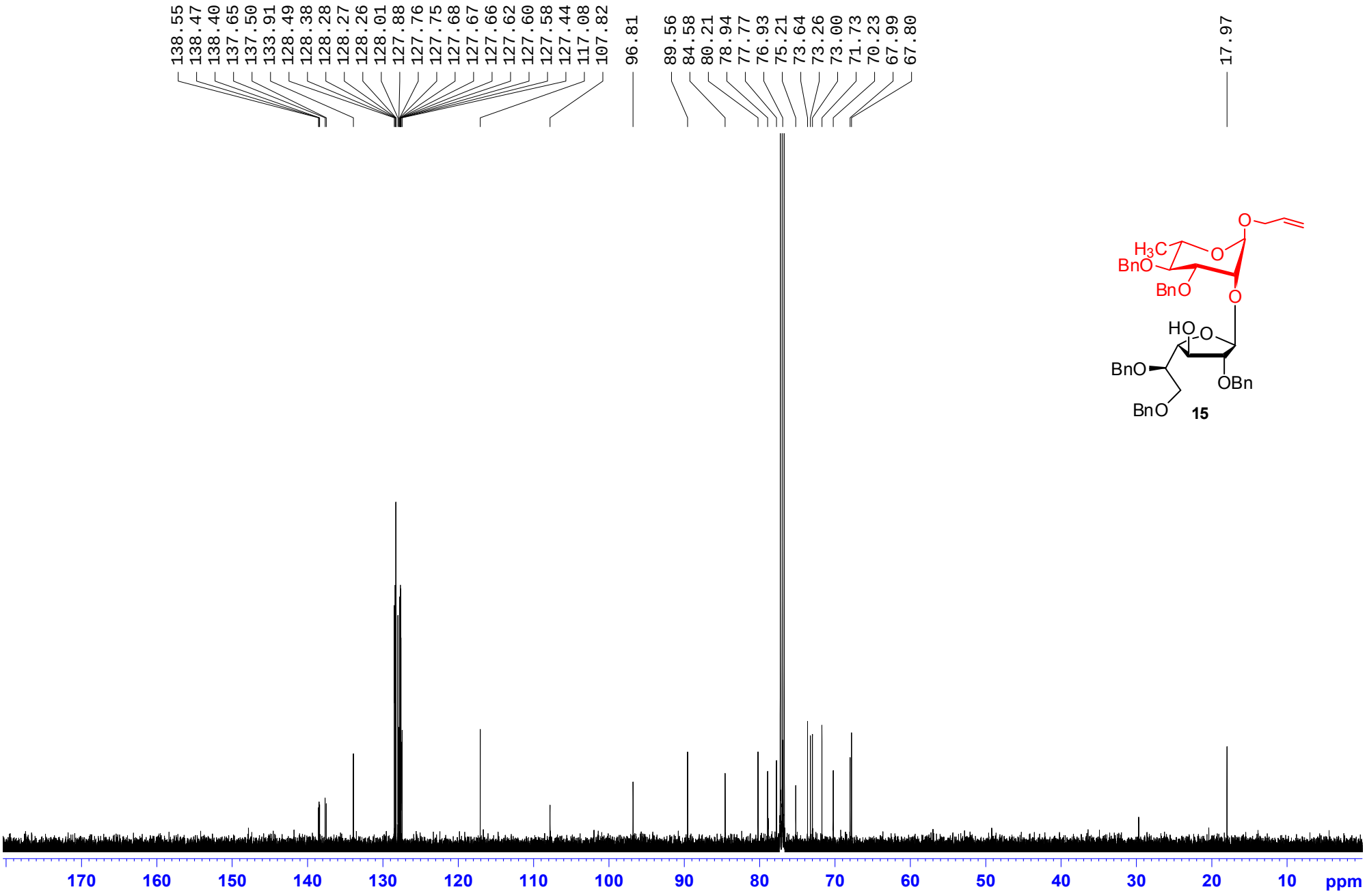
^{1}H NMR spectrum of compound **27** ($CDCl_3$; 200 MHz)



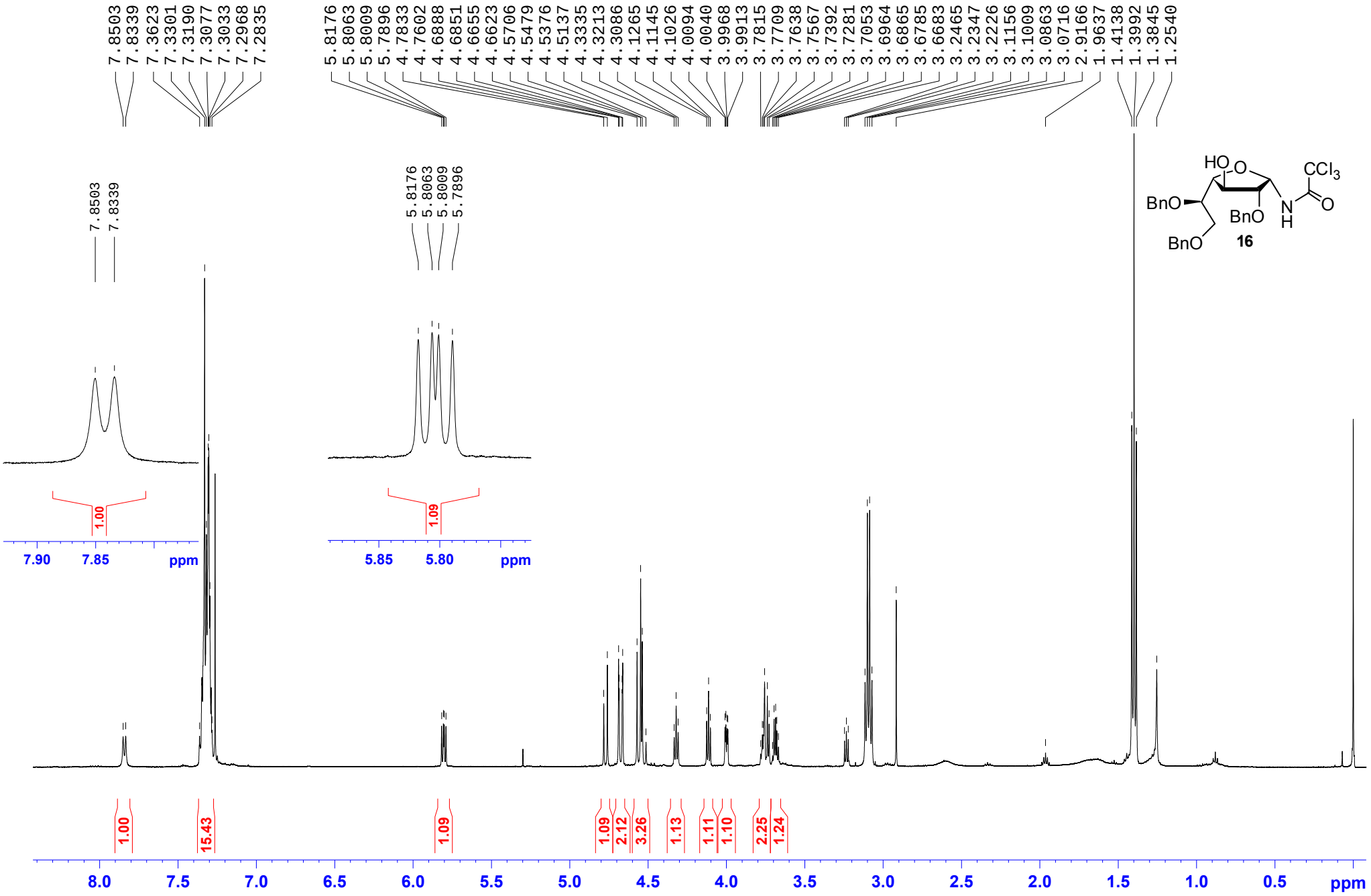
^{13}C NMR spectrum of compound **27** ($CDCl_3$; 50.3 MHz).



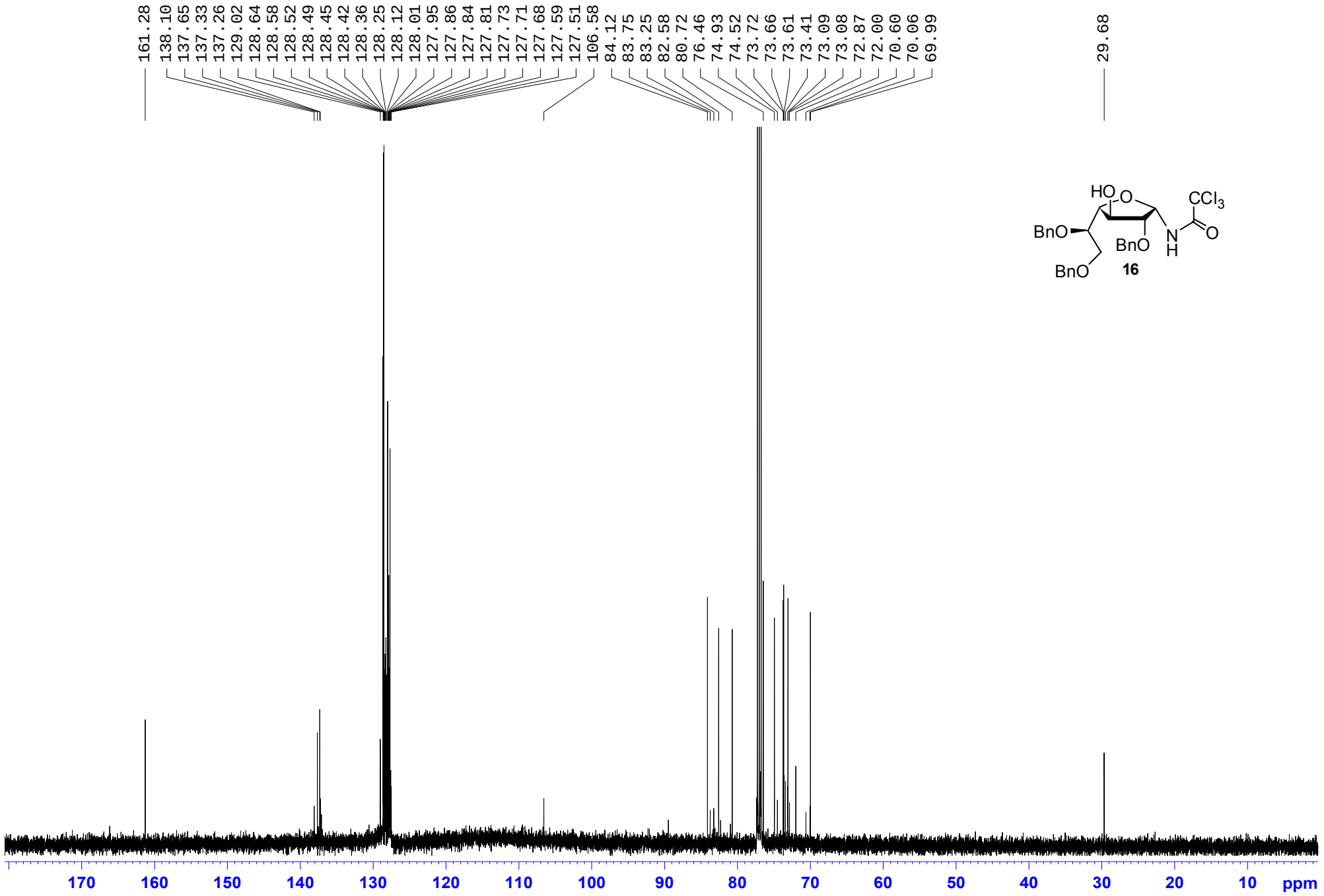
^{1}H NMR spectrum of compound **15** ($CDCl_3$; 500 MHz)



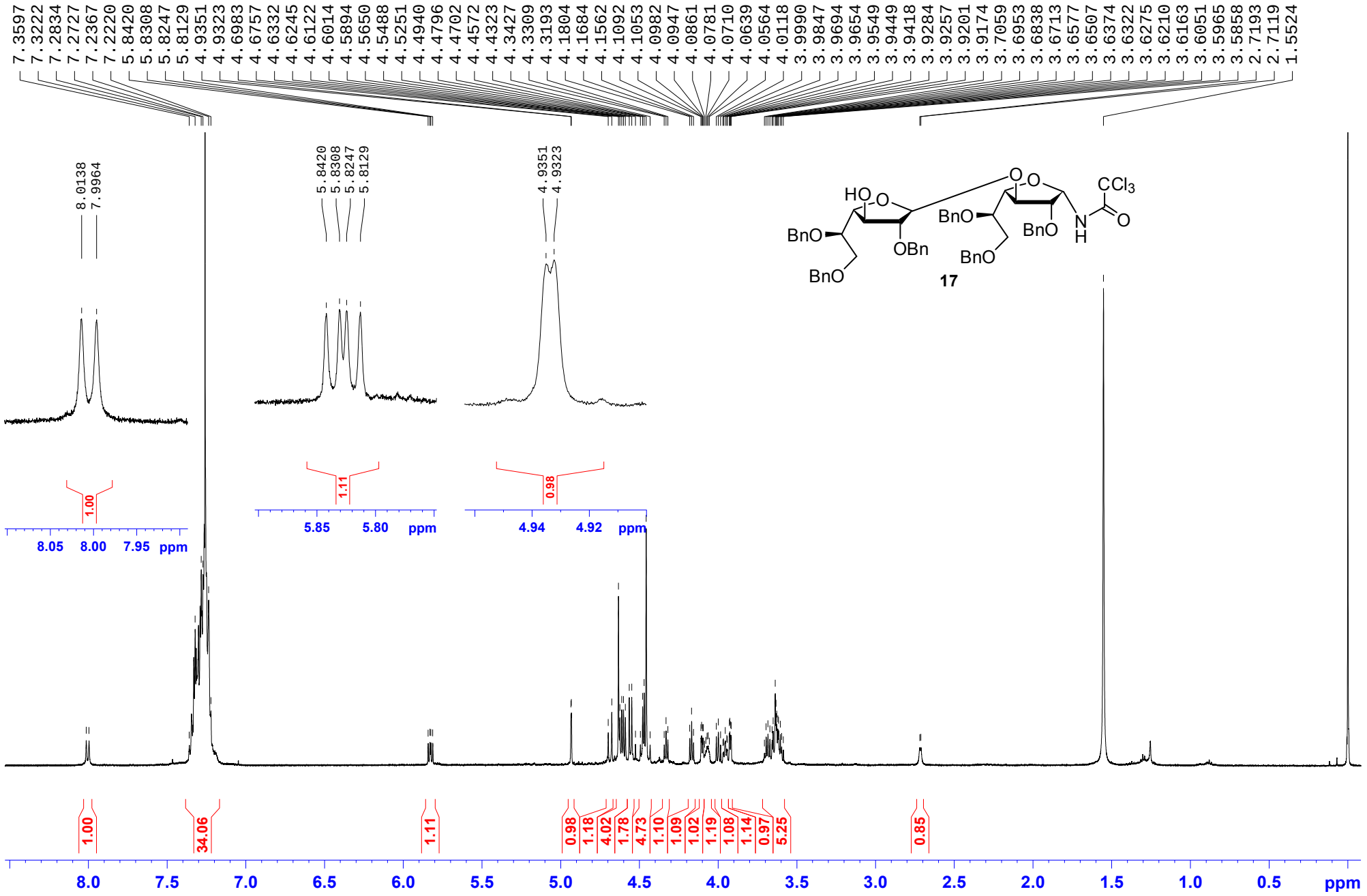
^{13}C NMR spectrum of compound **15** ($CDCl_3$; 125.8 MHz)



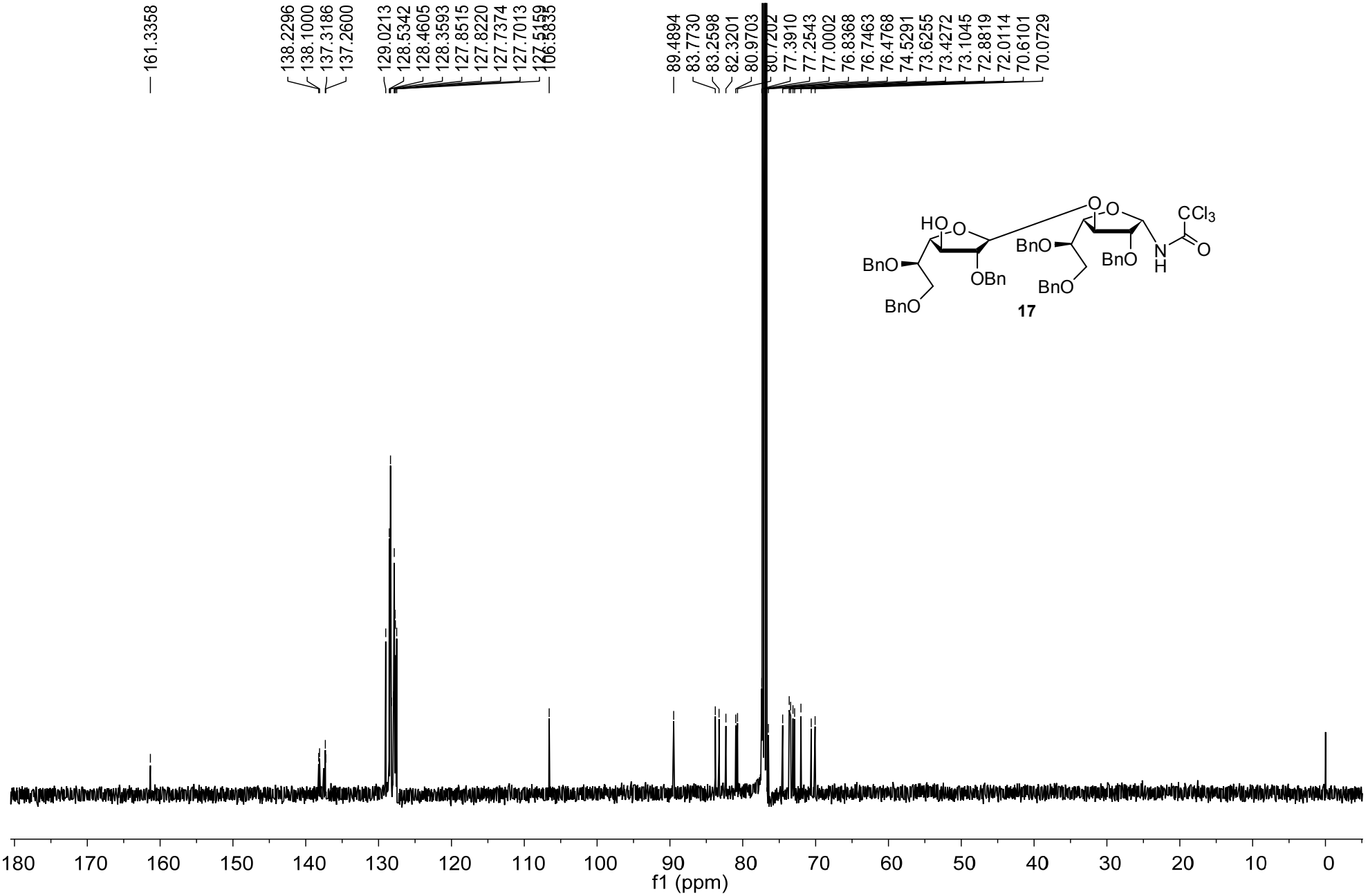
^{1}H NMR spectrum of compound **16** ($CDCl_3$; 500 MHz)



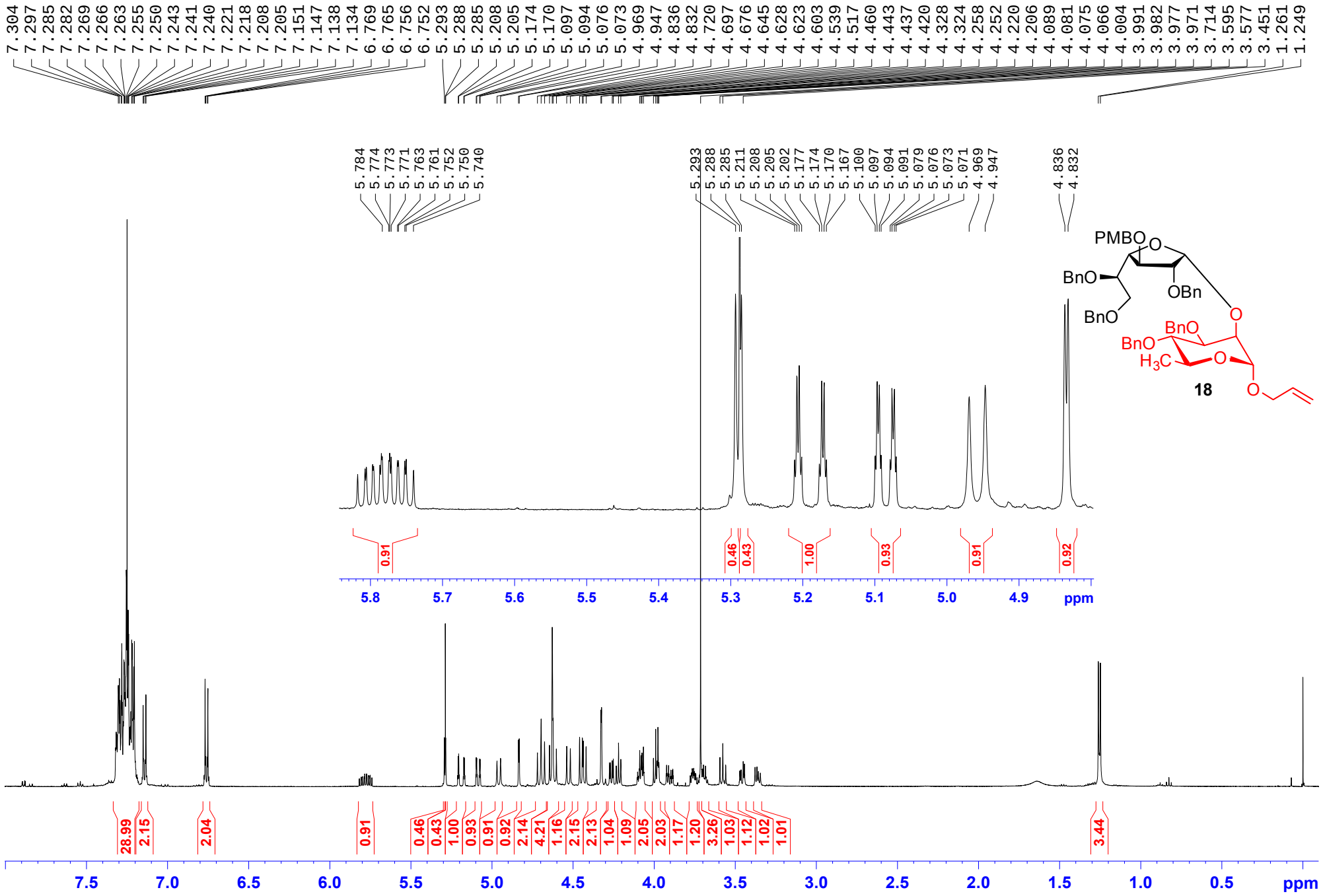
^{13}C NMR spectrum of compound **16** ($CDCl_3$; 125.8 MHz)



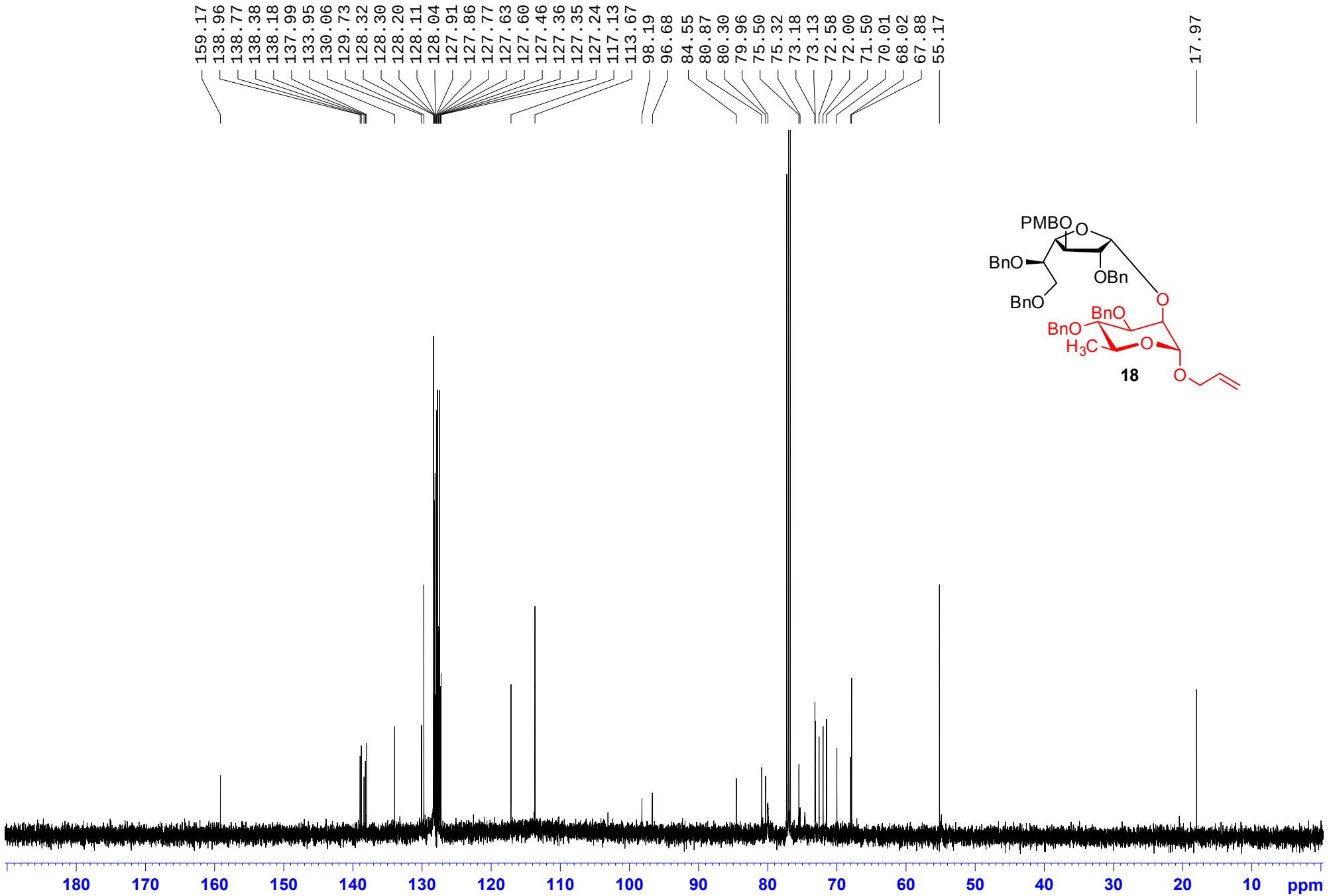
^{1}H NMR spectrum of compound **17** ($CDCl_3$; 500 MHz)



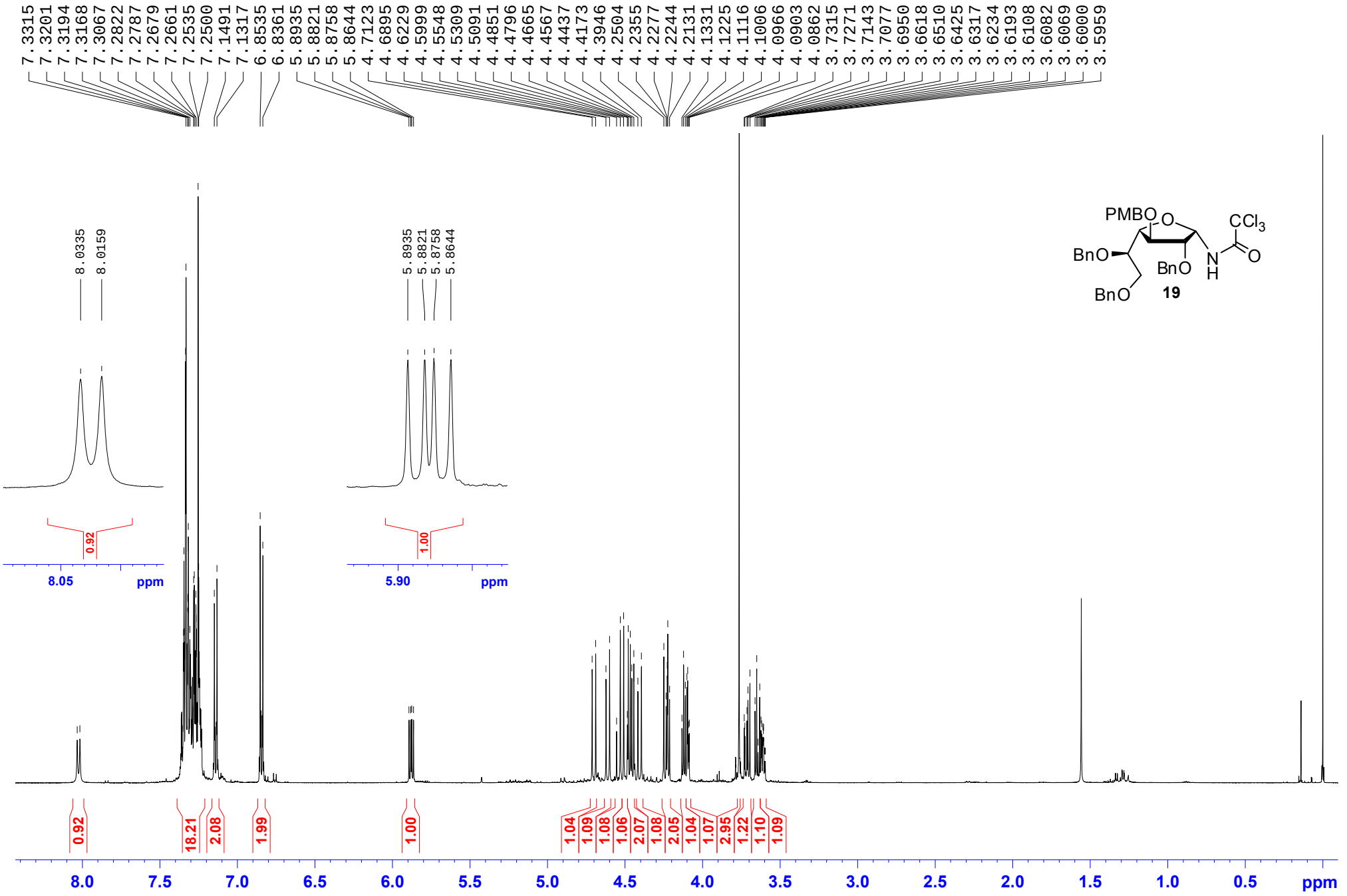
^{13}C NMR spectrum of compound **17** ($CDCl_3$; 125.8 MHz)



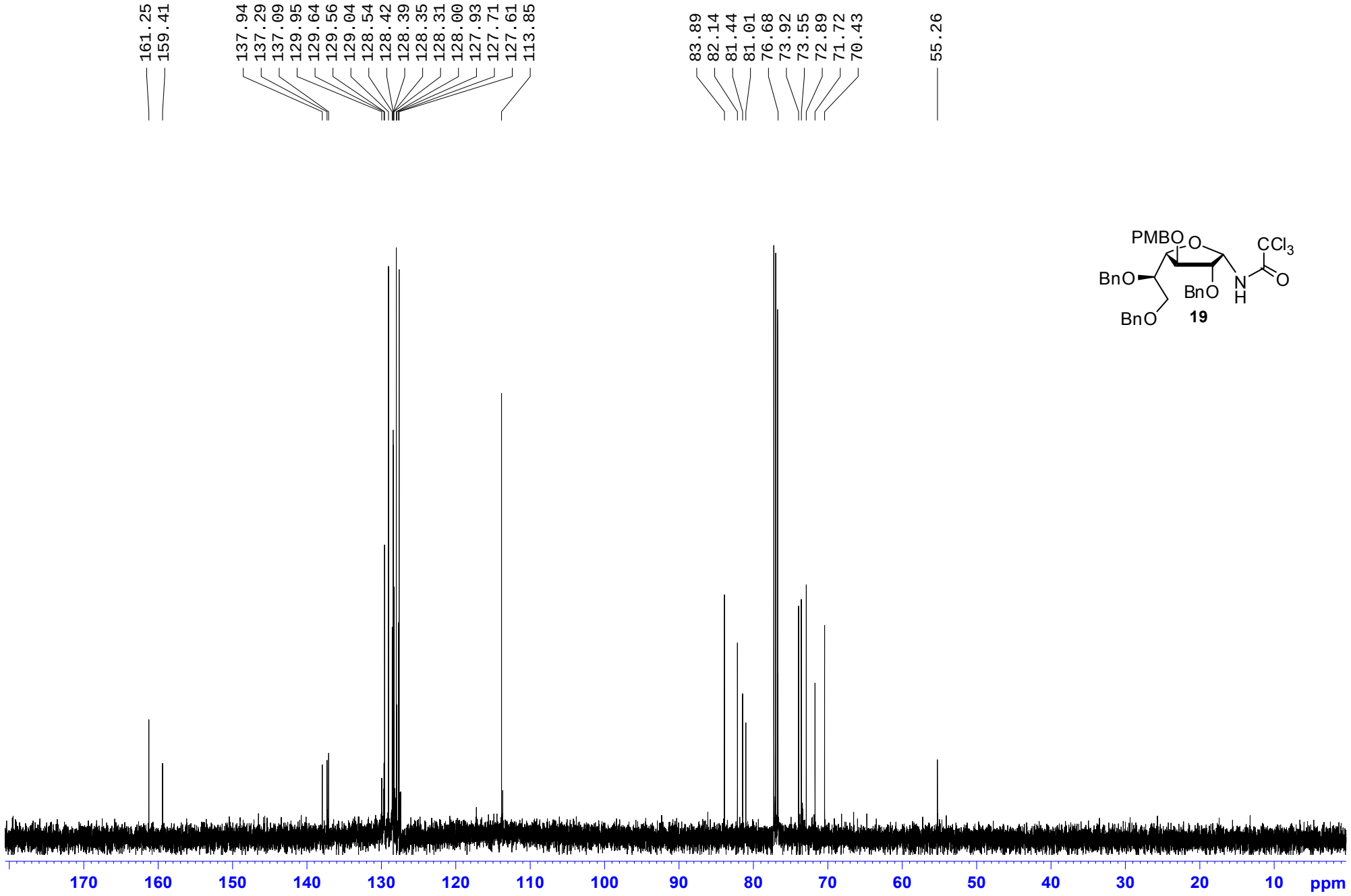
^{1}H NMR spectrum of compound **18** ($CDCl_3$; 500 MHz)



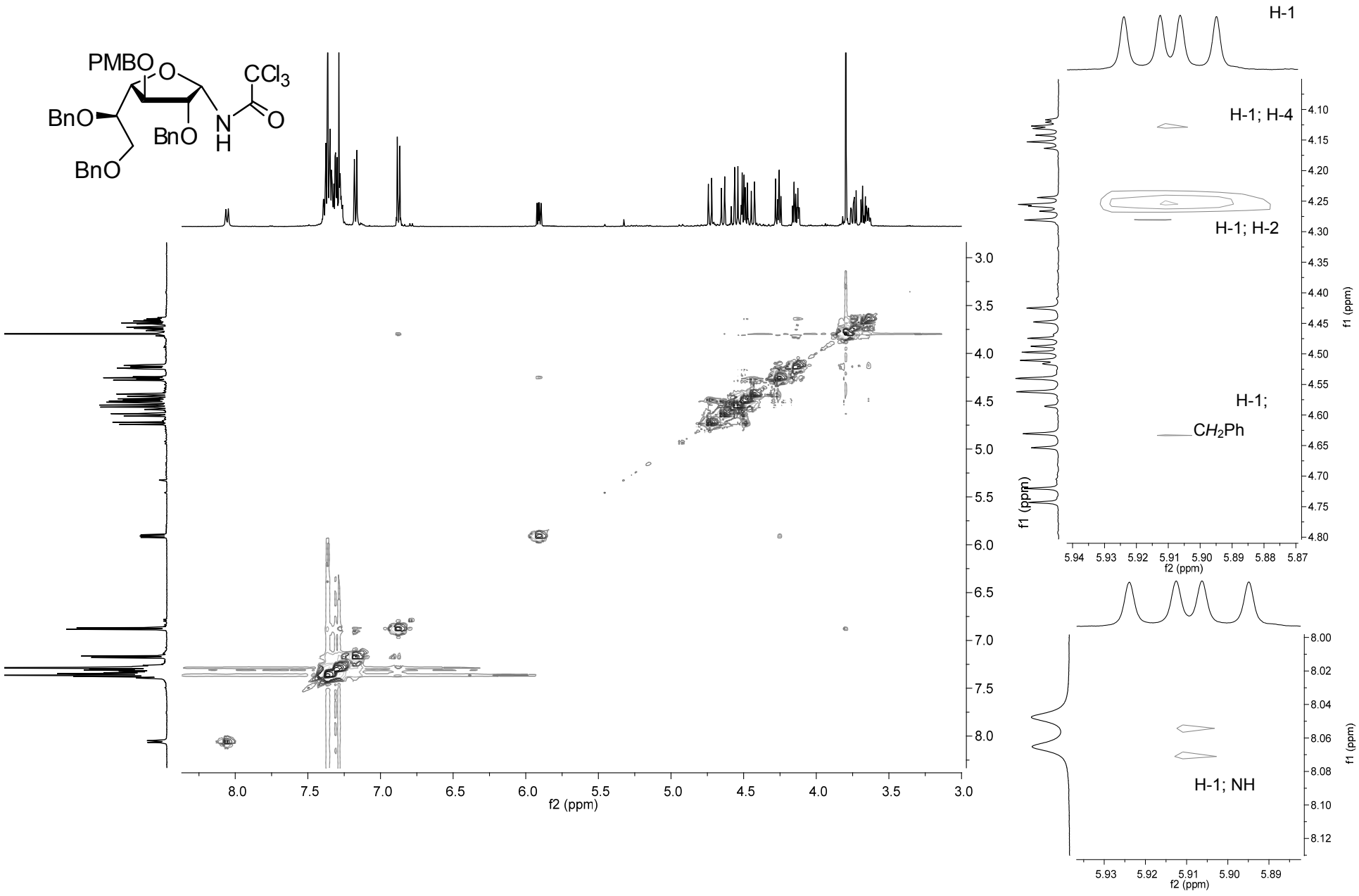
^{13}C NMR spectrum of compound **18** ($CDCl_3$; 125.8 MHz).



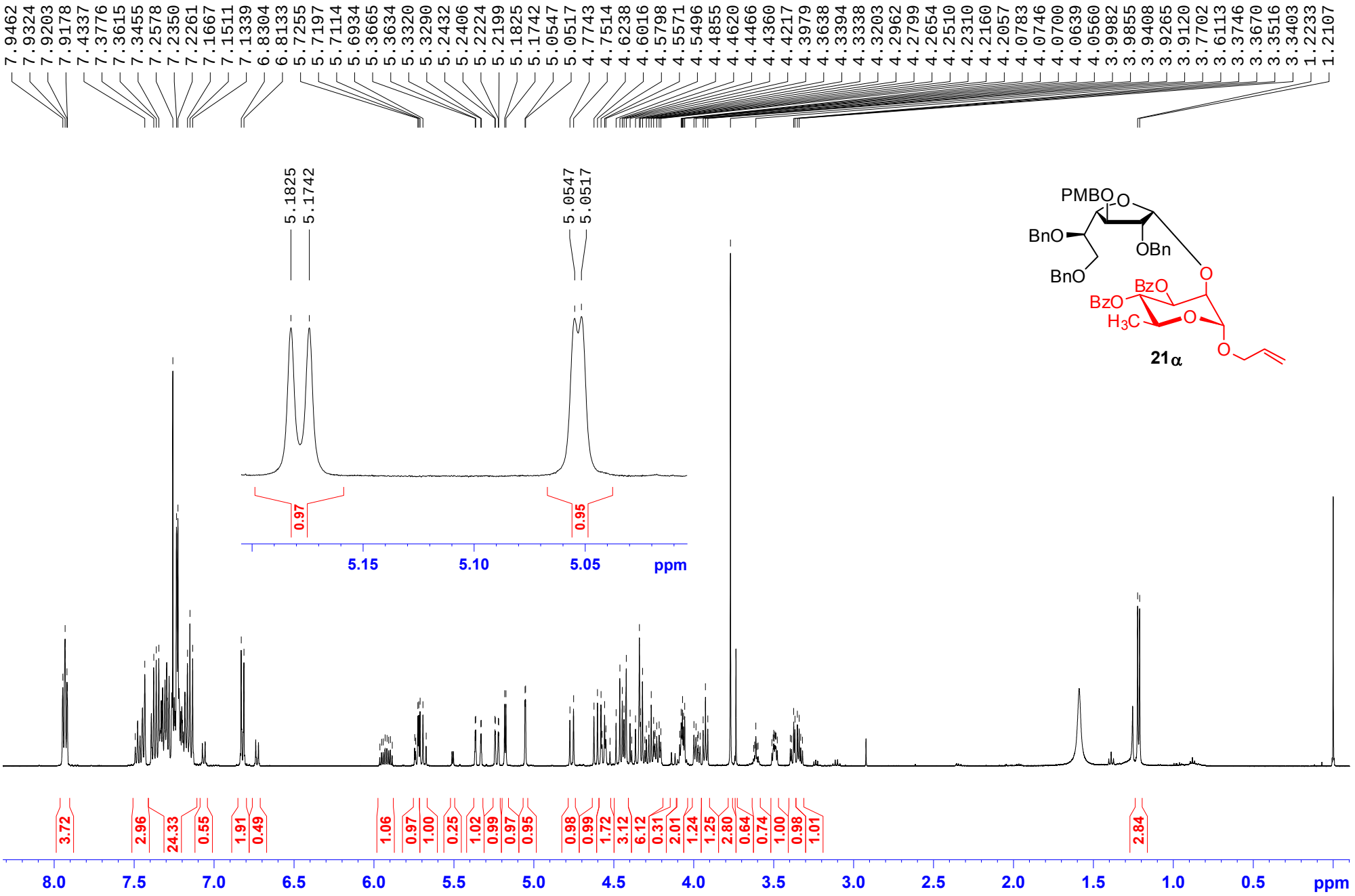
^{1}H NMR spectrum of compound **19** ($CDCl_3$; 500 MHz)



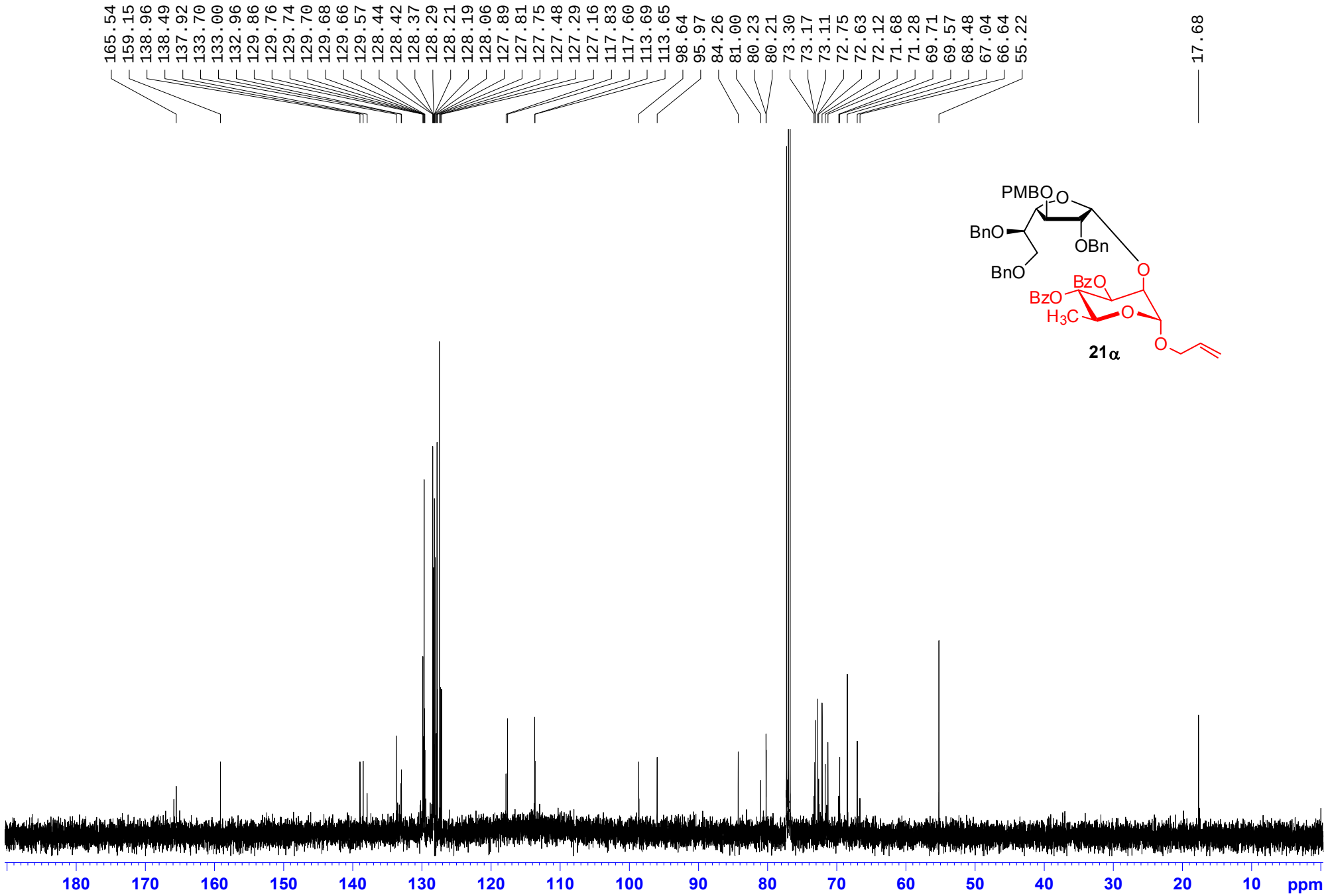
^{13}C NMR spectrum of compound **19** ($CDCl_3$; 125.8 MHz)



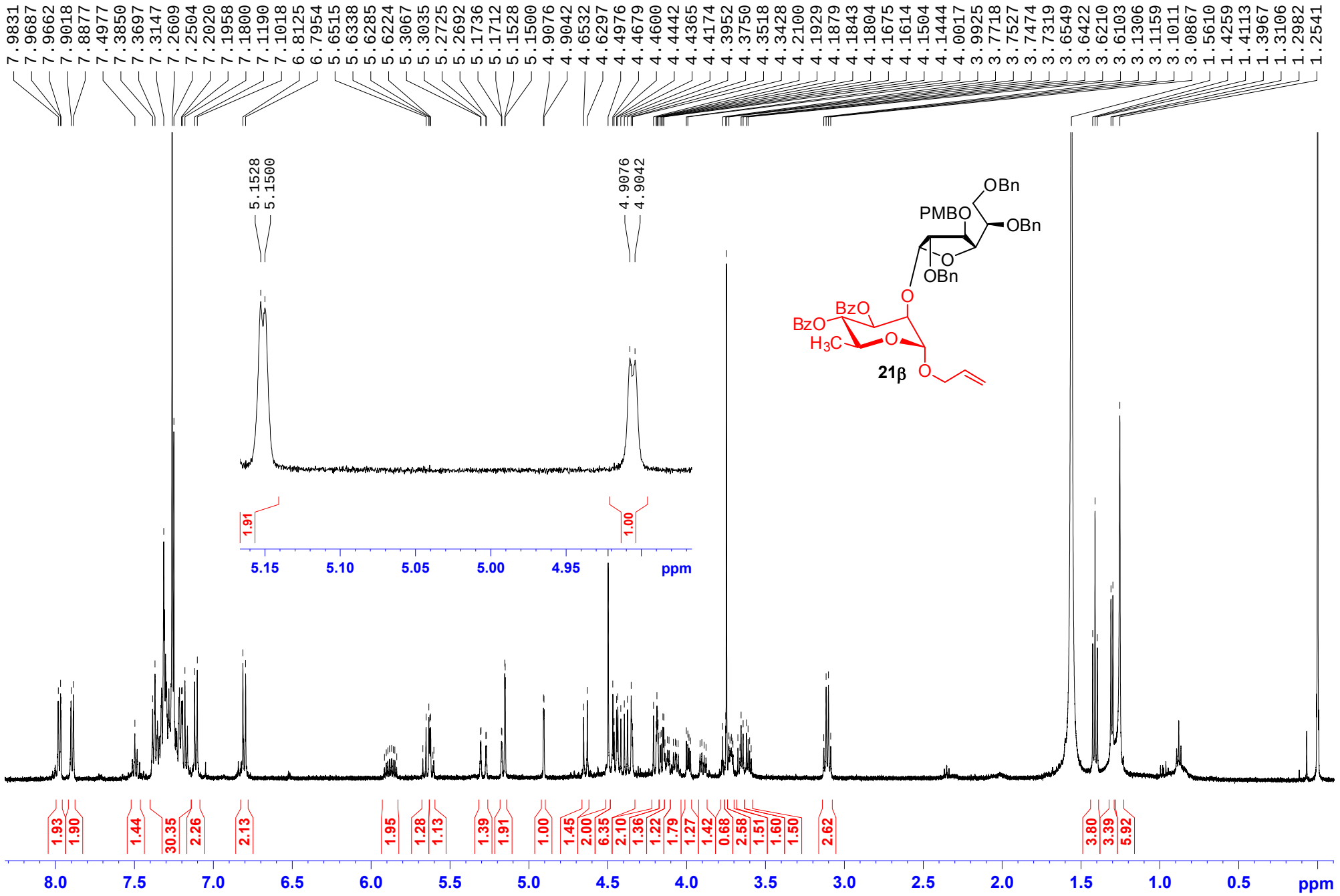
NOESY spectrum of compound **19** ($CDCl_3$; 500 MHz)



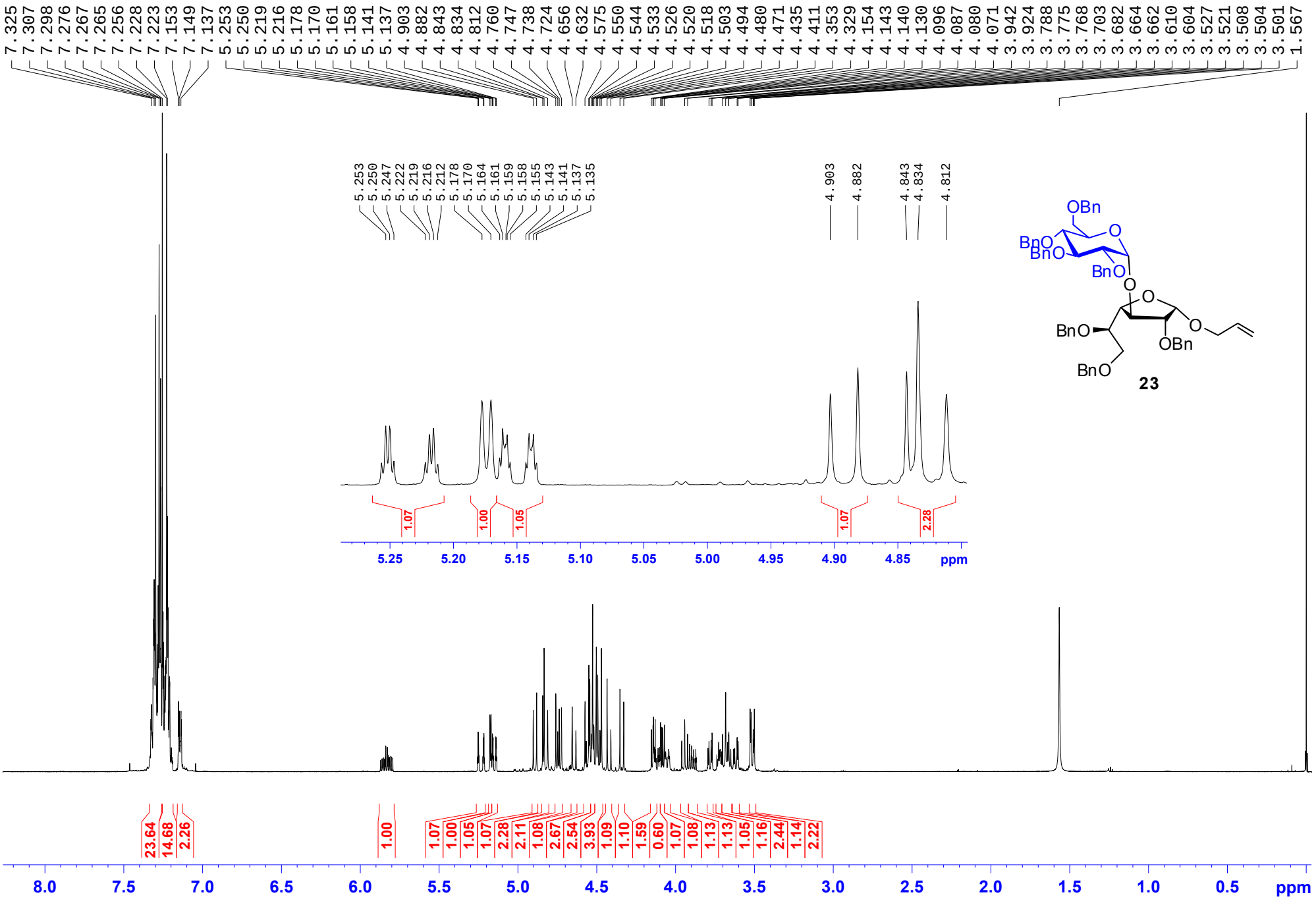
^{1}H NMR spectrum of compound **21**α ($CDCl_3$; 500 MHz)



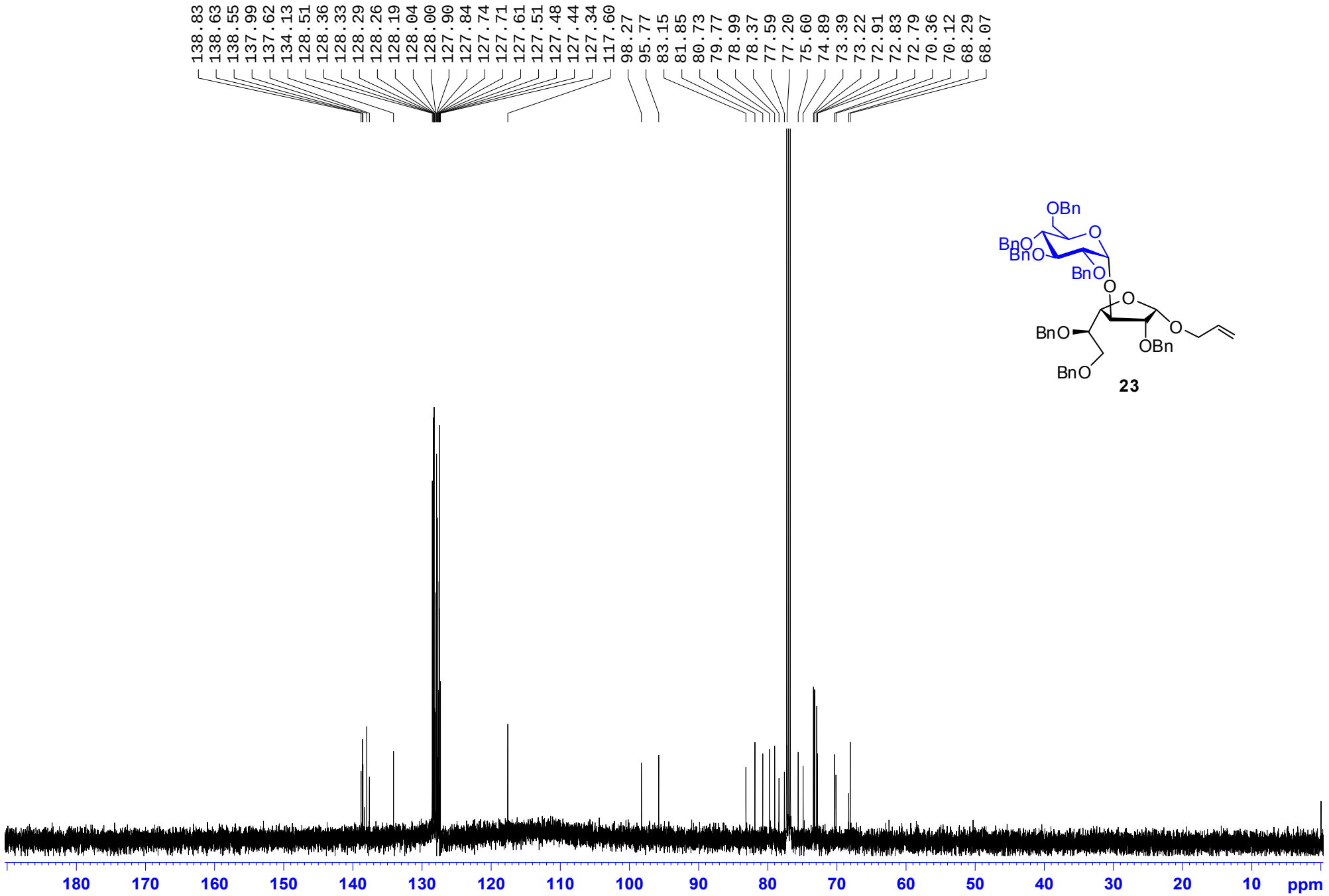
^{13}C NMR spectrum of compound **21α** ($CDCl_3$; 125.8 MHz).



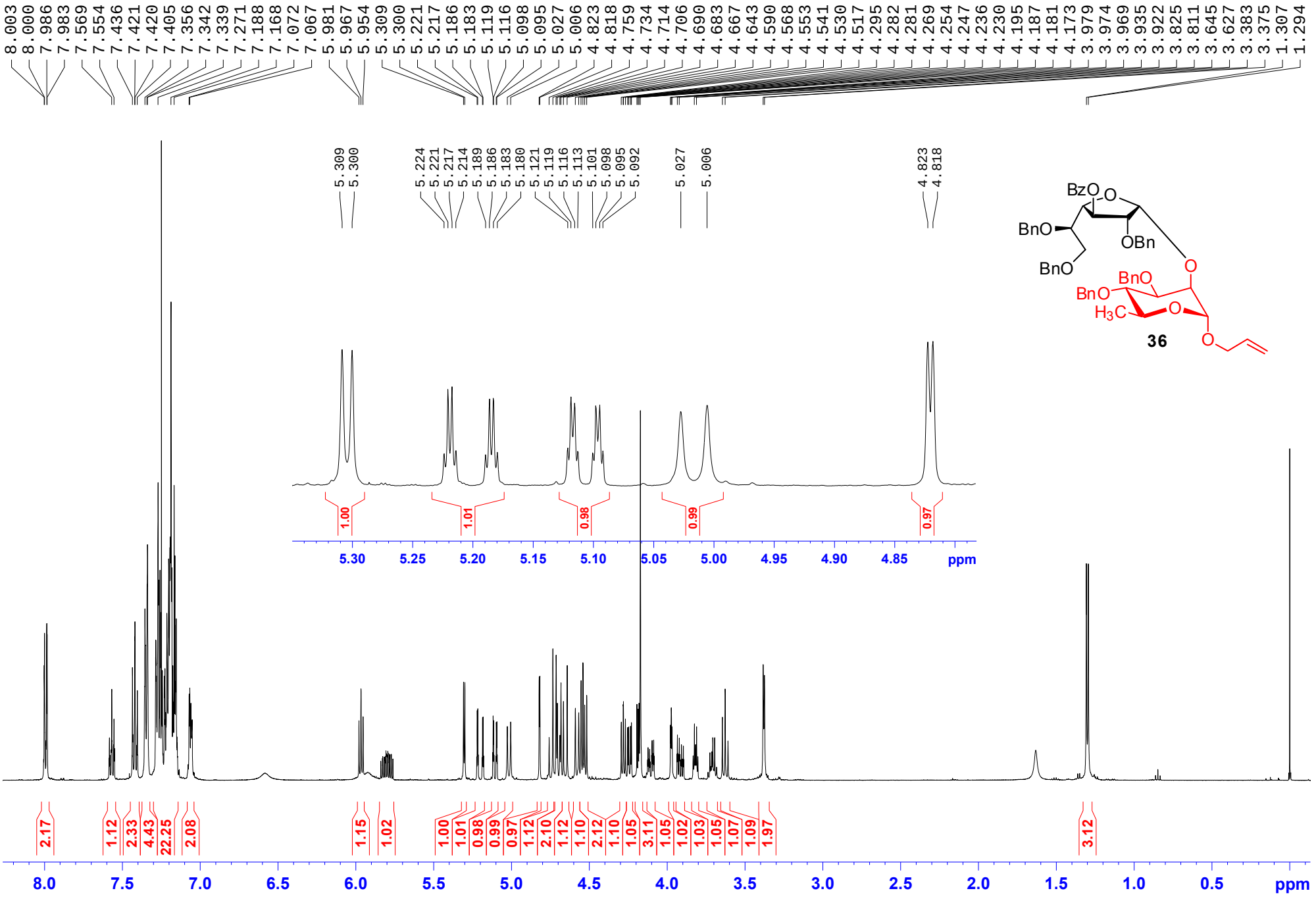
^{1}H NMR spectrum of compound **21β** ($CDCl_3$; 500 MHz).



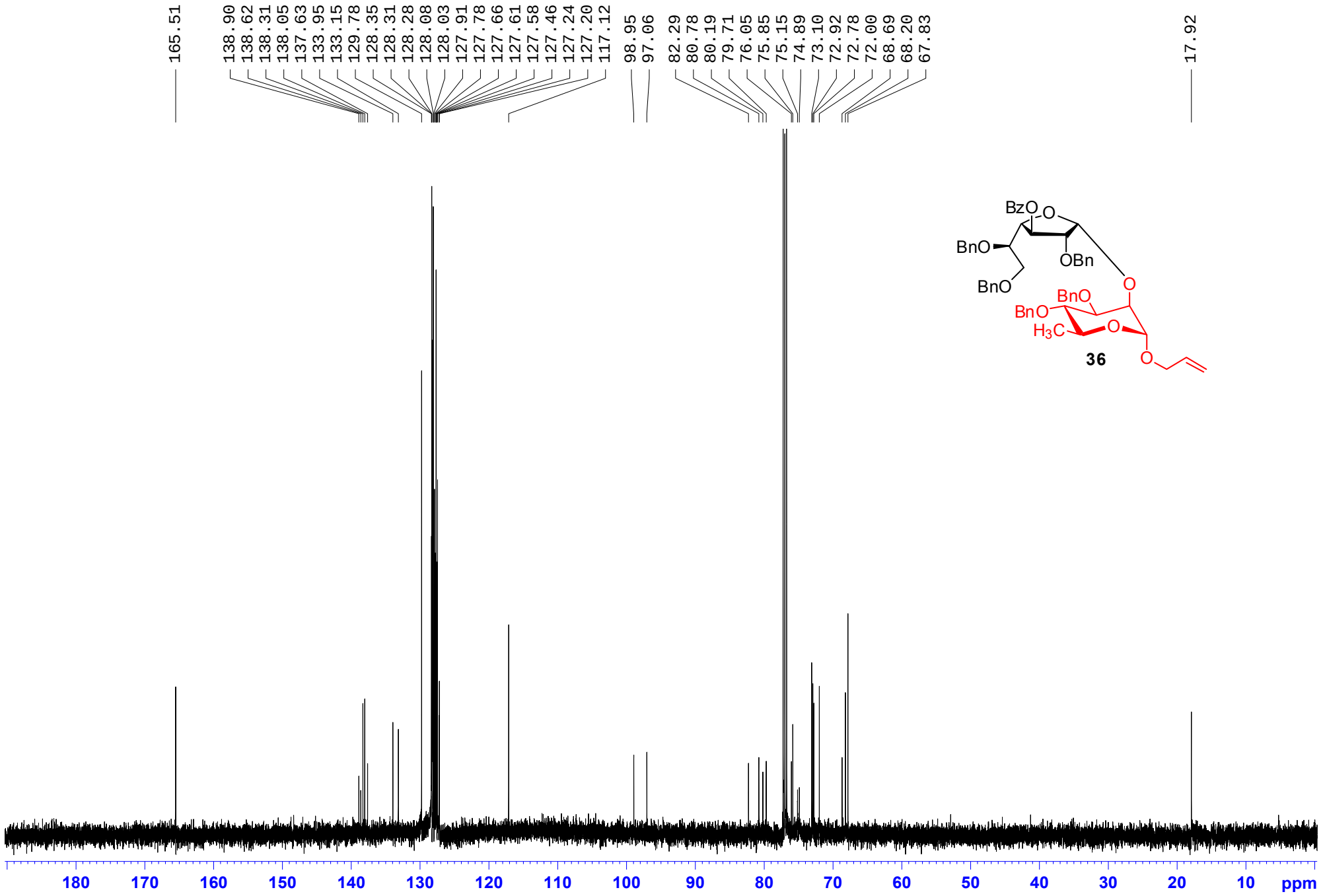
^{1}H NMR spectrum of compound **23** ($CDCl_3$; 500 MHz)



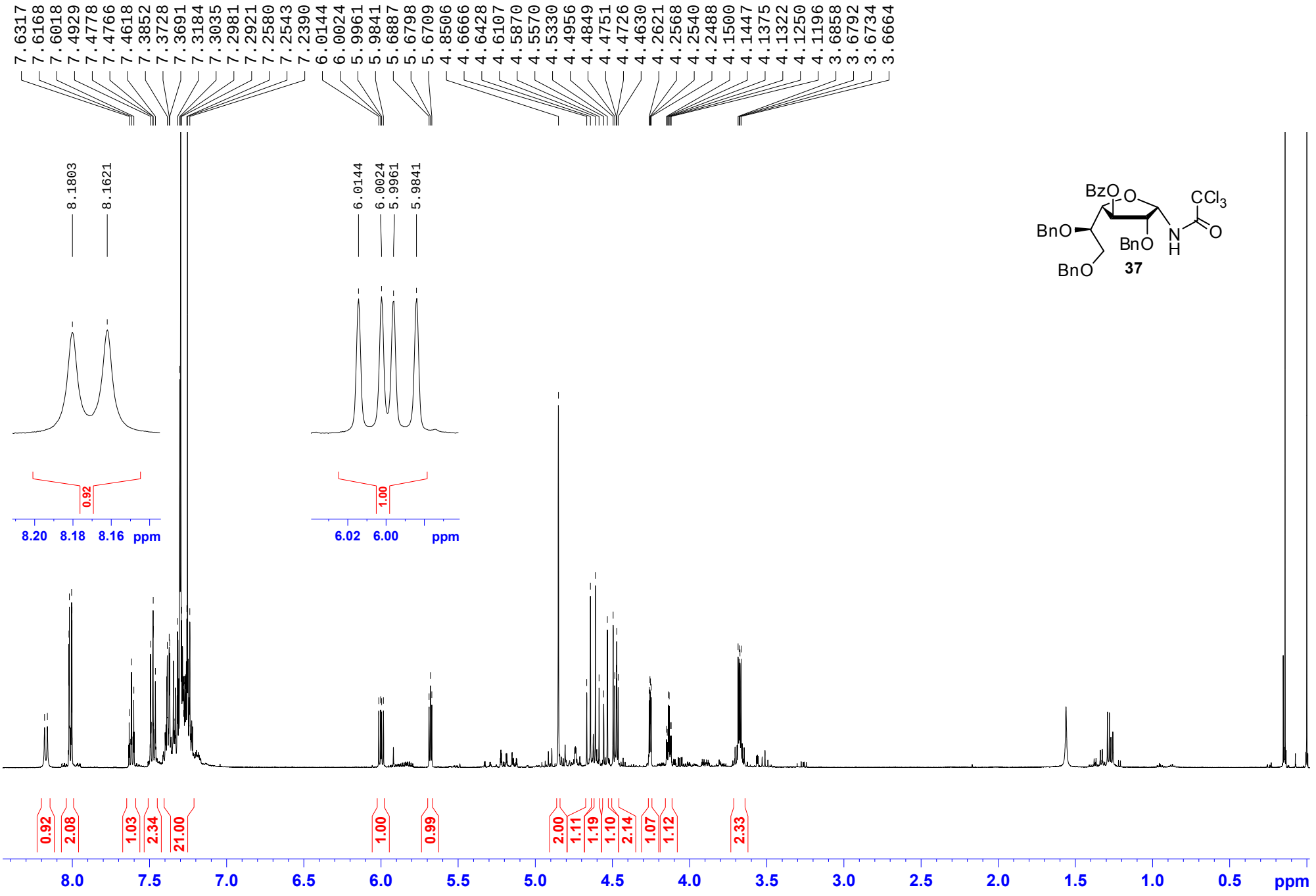
^{13}C NMR spectrum of compound **23** ($CDCl_3$; 125.8 MHz).



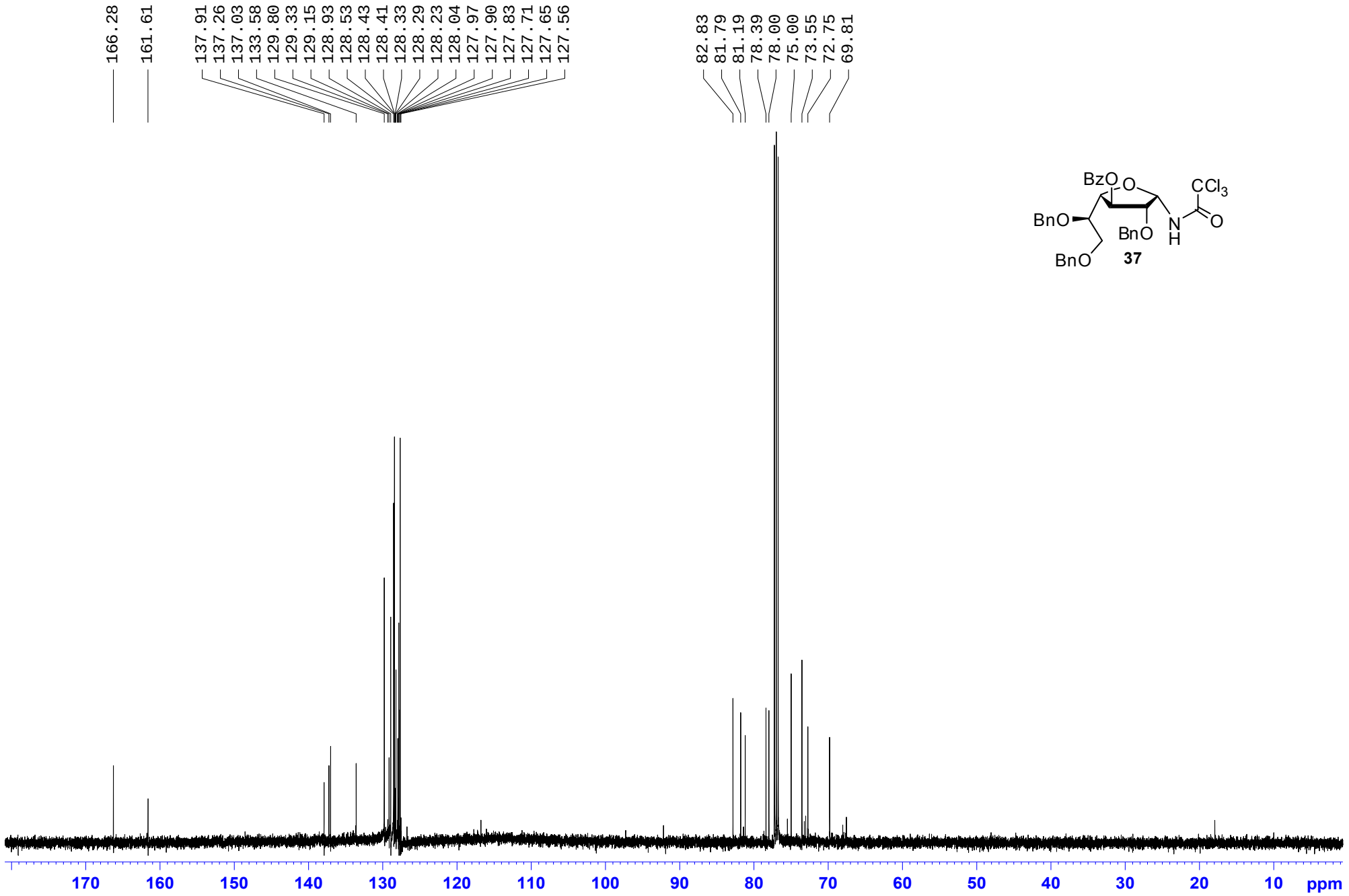
^{1}H NMR spectrum of compound **36** ($CDCl_3$; 500 MHz)



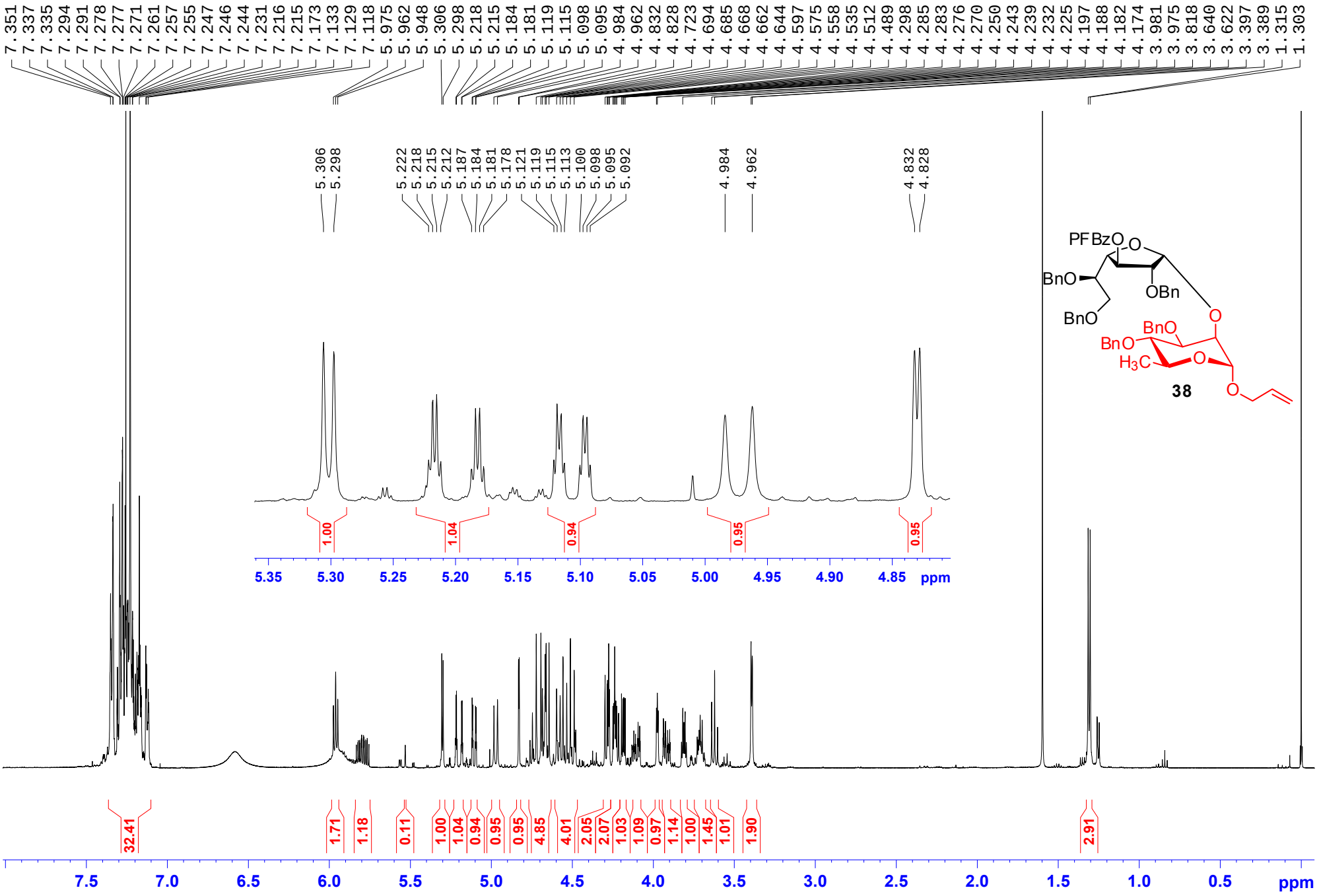
^{13}C NMR spectrum of compound **36** ($CDCl_3$; 125.8 MHz).



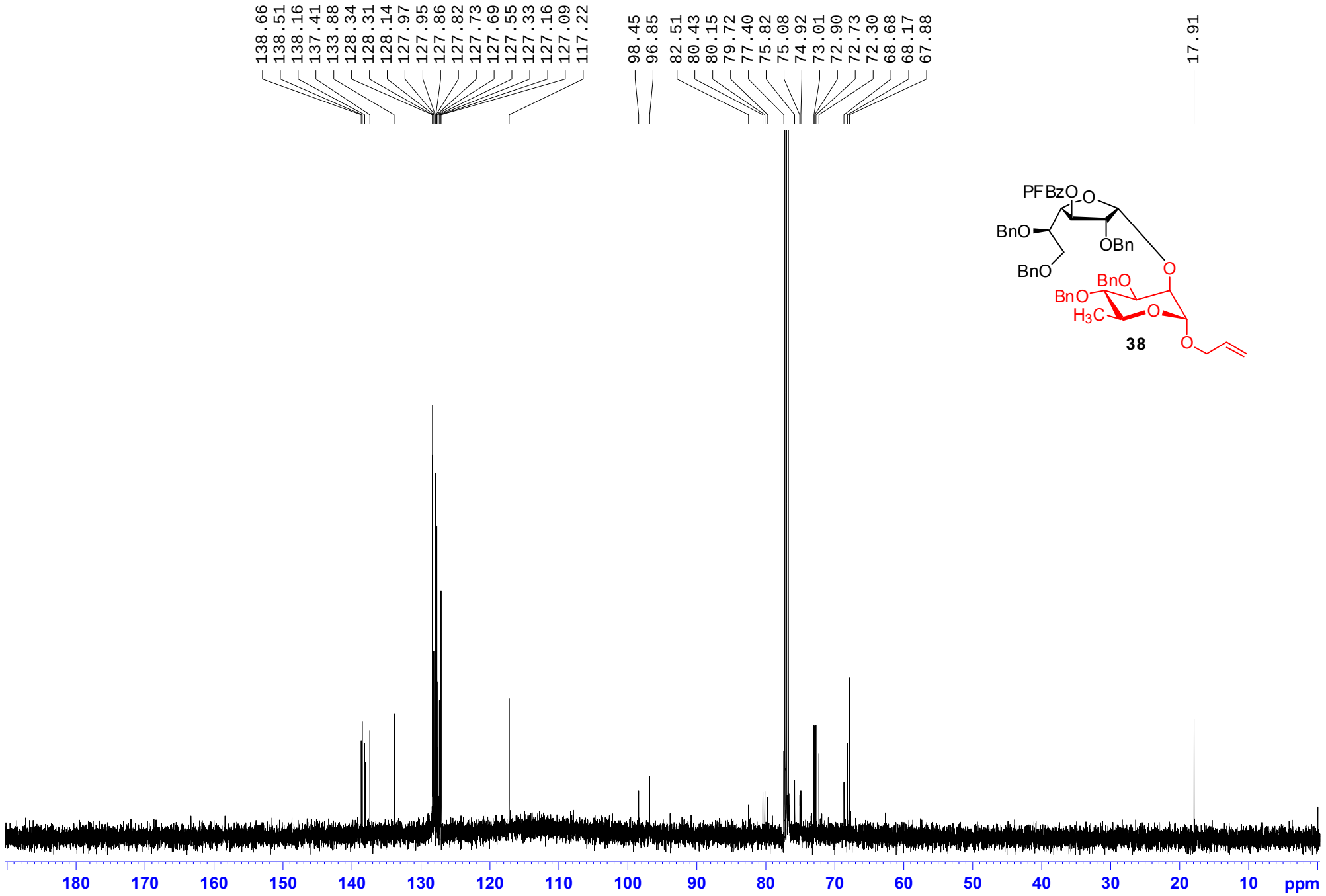
^{1}H NMR spectrum of compound **37** ($CDCl_3$; 500 MHz)



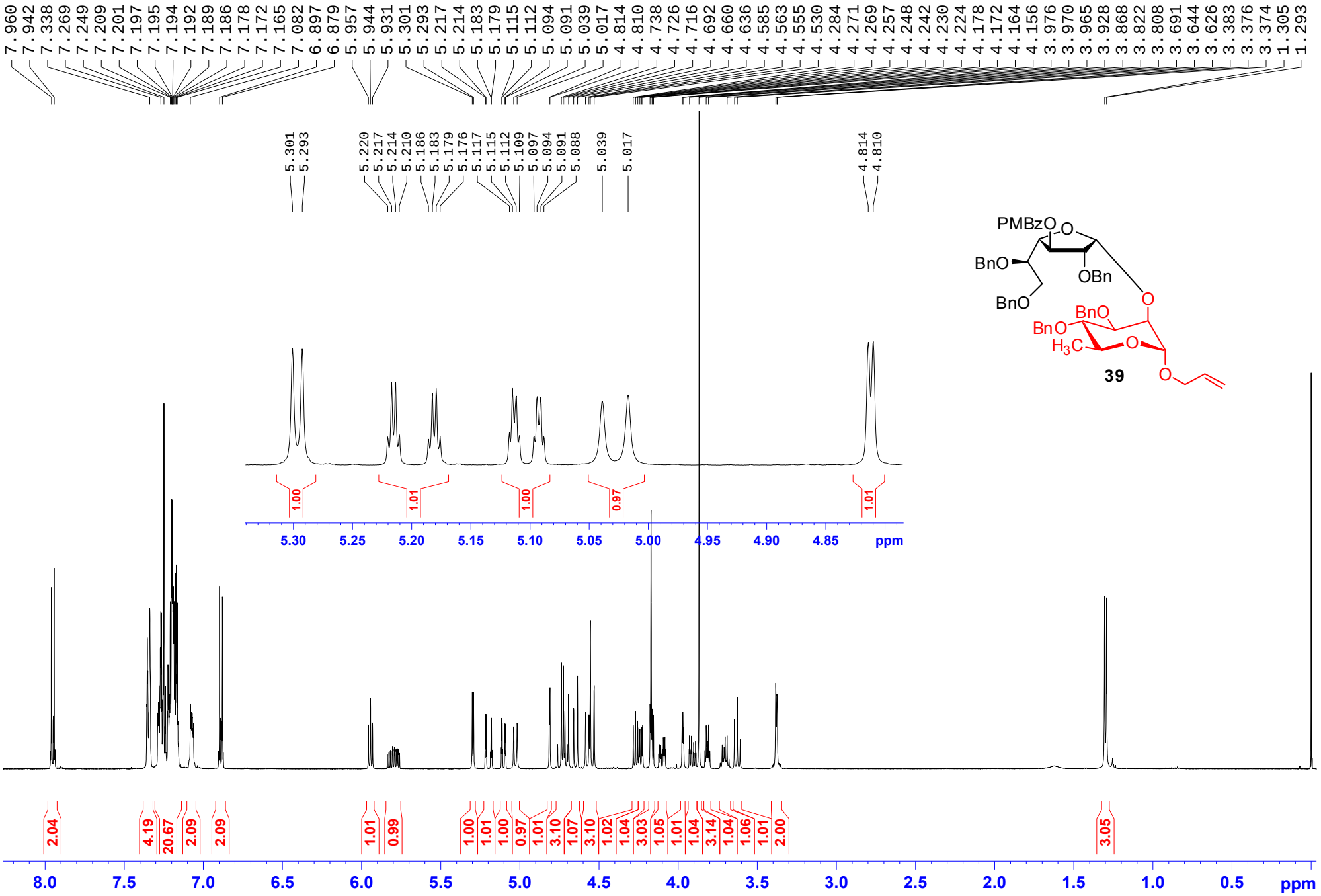
^{13}C NMR spectrum of compound **37** ($CDCl_3$; 125.8 MHz)



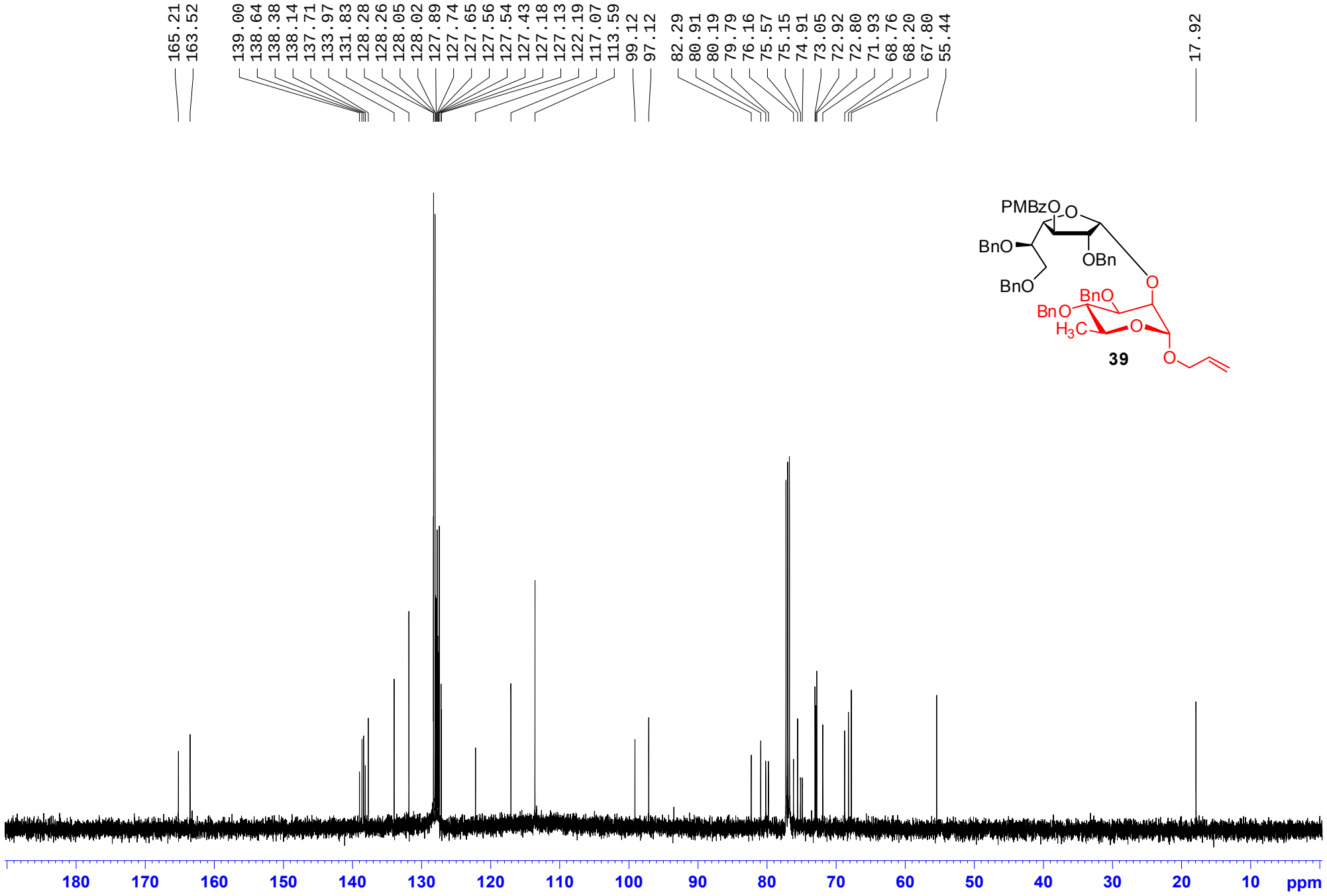
^{1}H NMR spectrum of compound **38** ($CDCl_3$; 500 MHz)



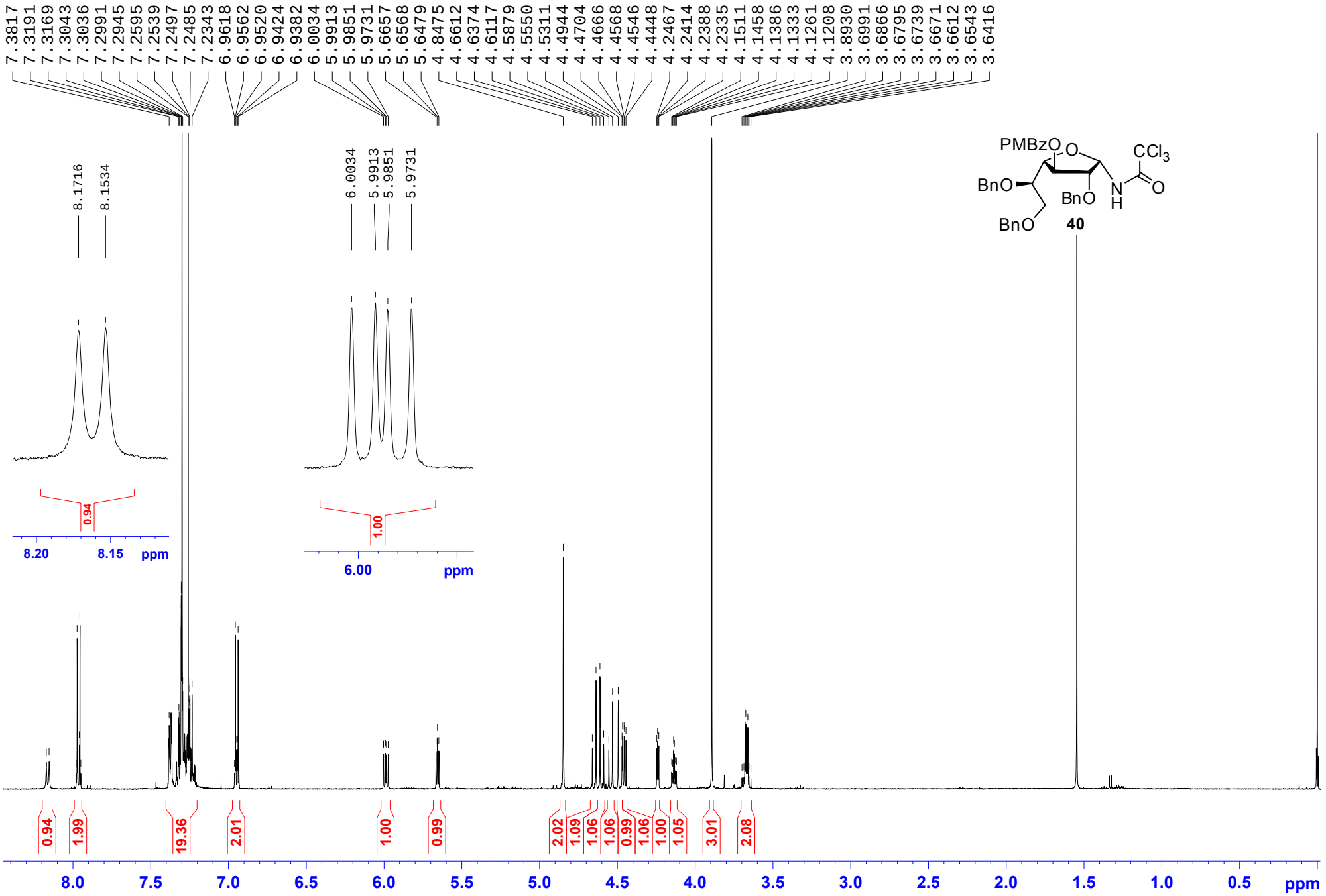
^{13}C NMR spectrum of compound **38** ($CDCl_3$; 125.8 MHz).



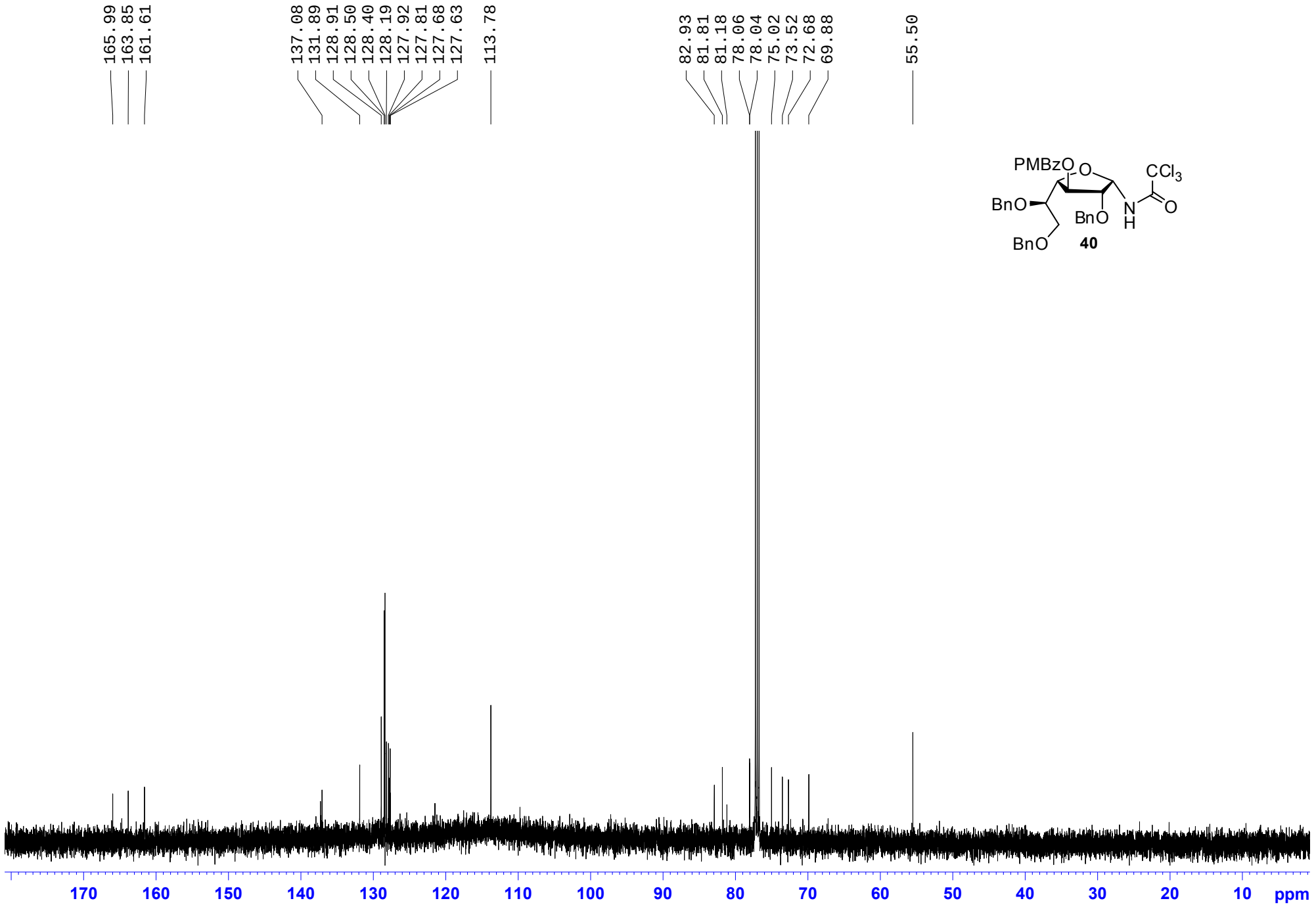
^{1}H NMR spectrum of compound **39** ($CDCl_3$; 500 MHz)



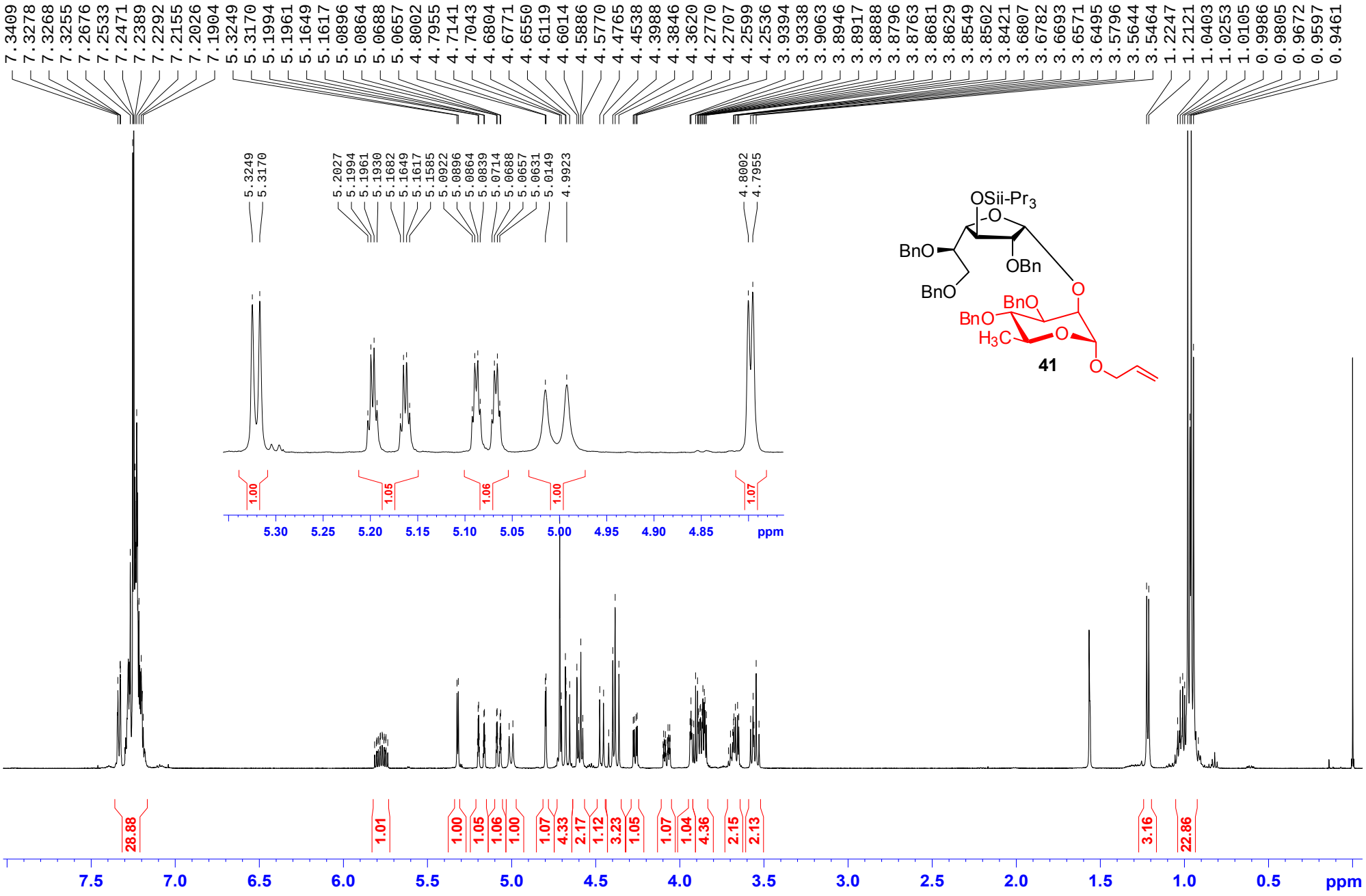
^{13}C NMR spectrum of compound **39** ($CDCl_3$; 125.8 MHz).



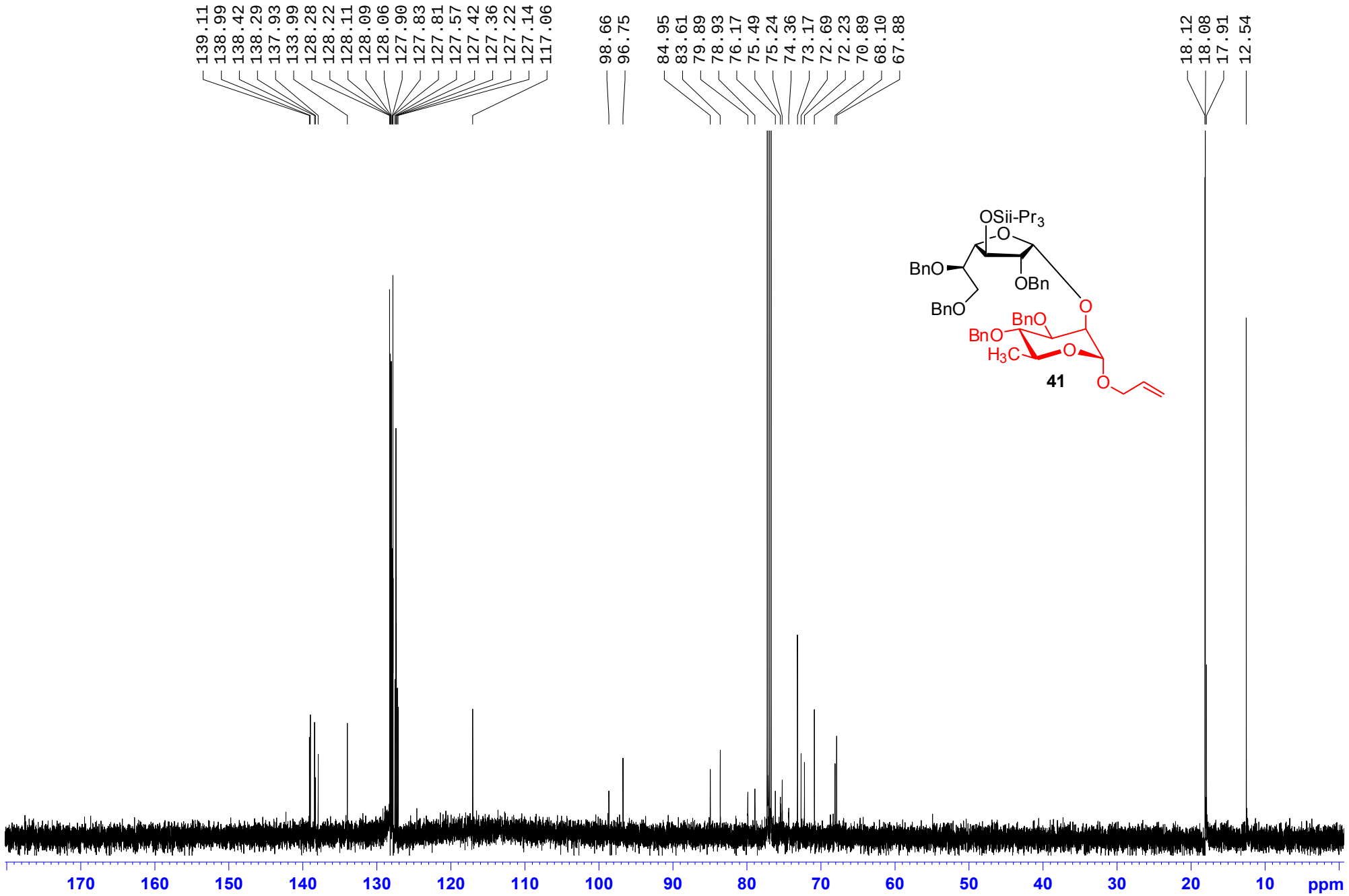
^{1}H NMR spectrum of compound **40** ($CDCl_3$; 500 MHz)



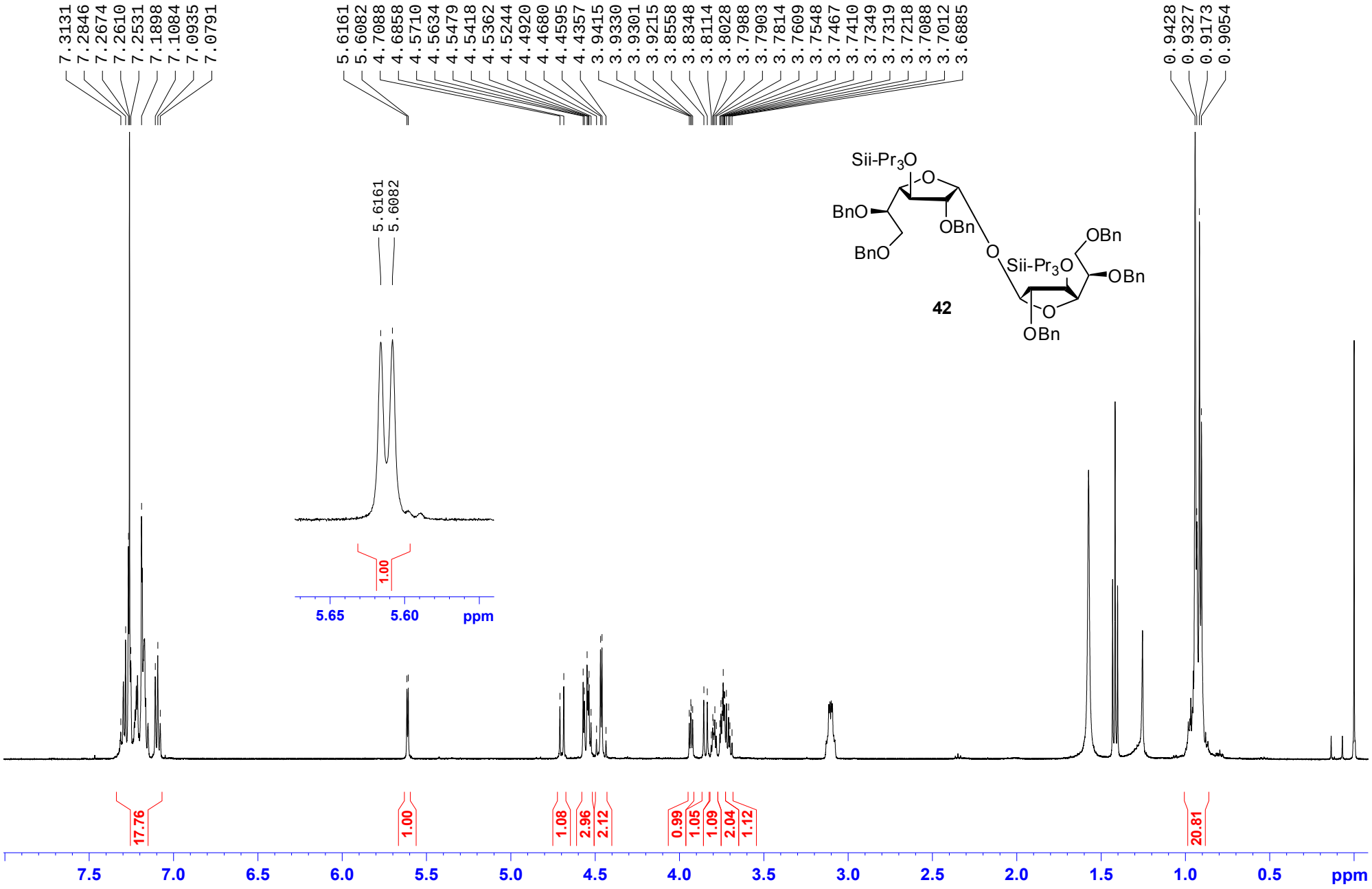
^{13}C NMR spectrum of compound **40** ($CDCl_3$; 125.8 MHz)



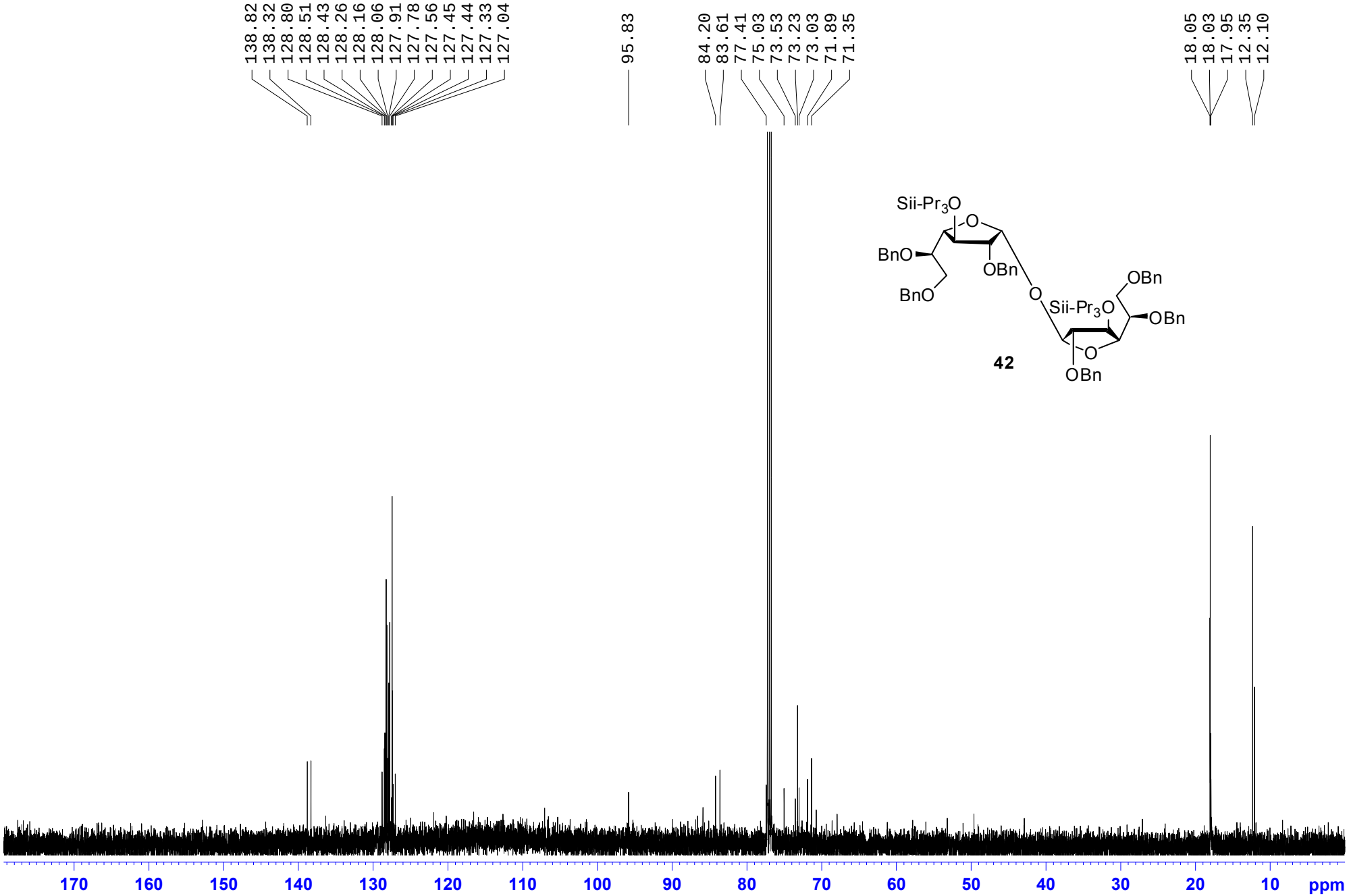
^{1}H NMR spectrum of compound **41** ($CDCl_3$; 500 MHz)



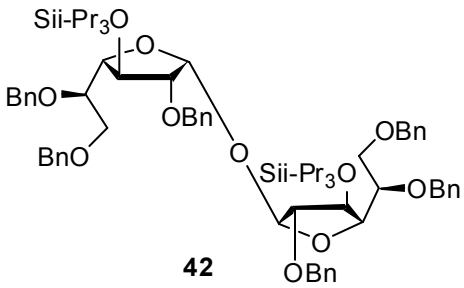
^{13}C NMR spectrum of compound **41** ($CDCl_3$; 125.8 MHz).



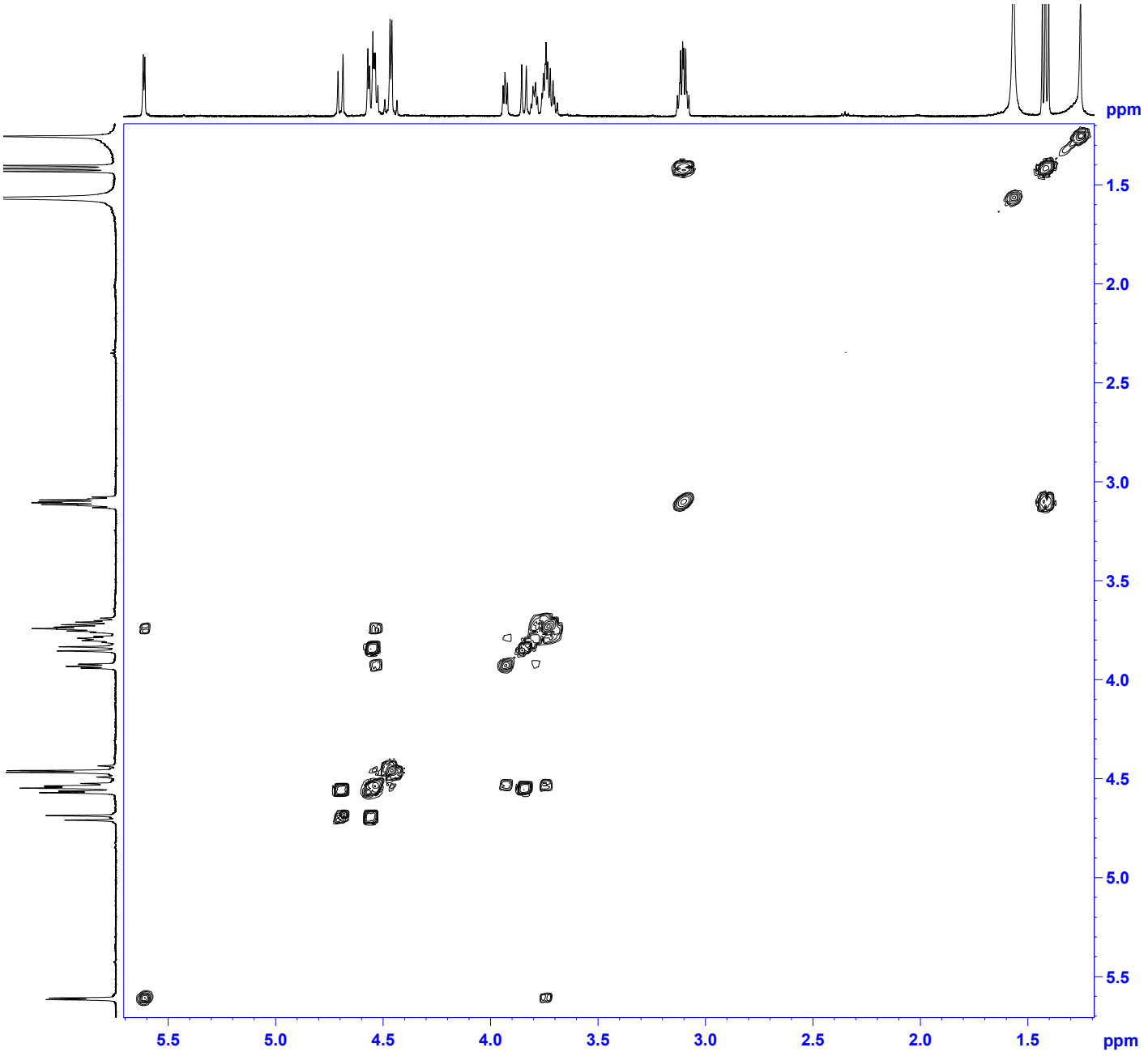
^{1}H NMR spectrum of compound **42** ($CDCl_3$; 500 MHz)



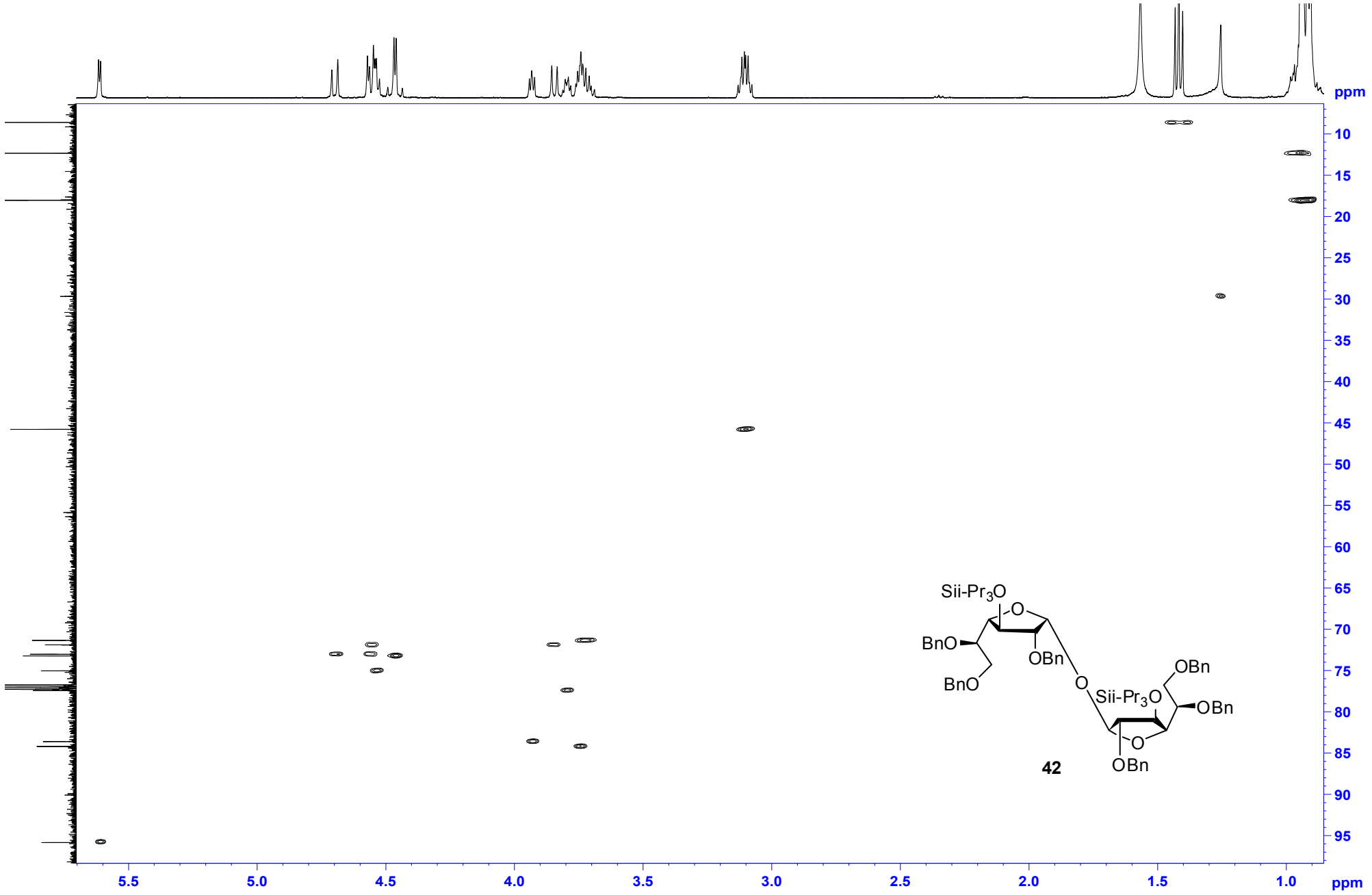
^{13}C NMR spectrum of compound **42** ($CDCl_3$; 125.8 MHz)



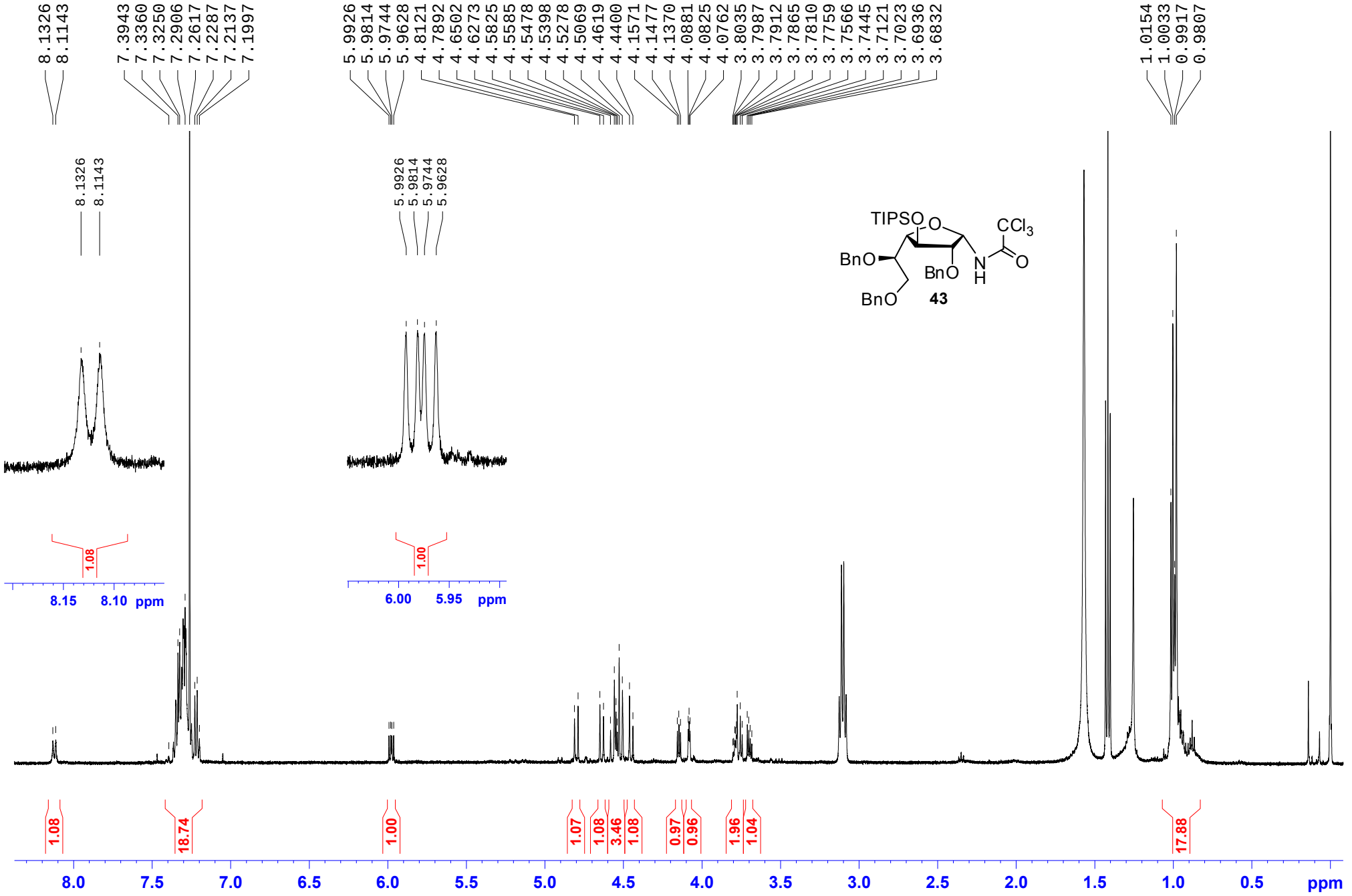
42



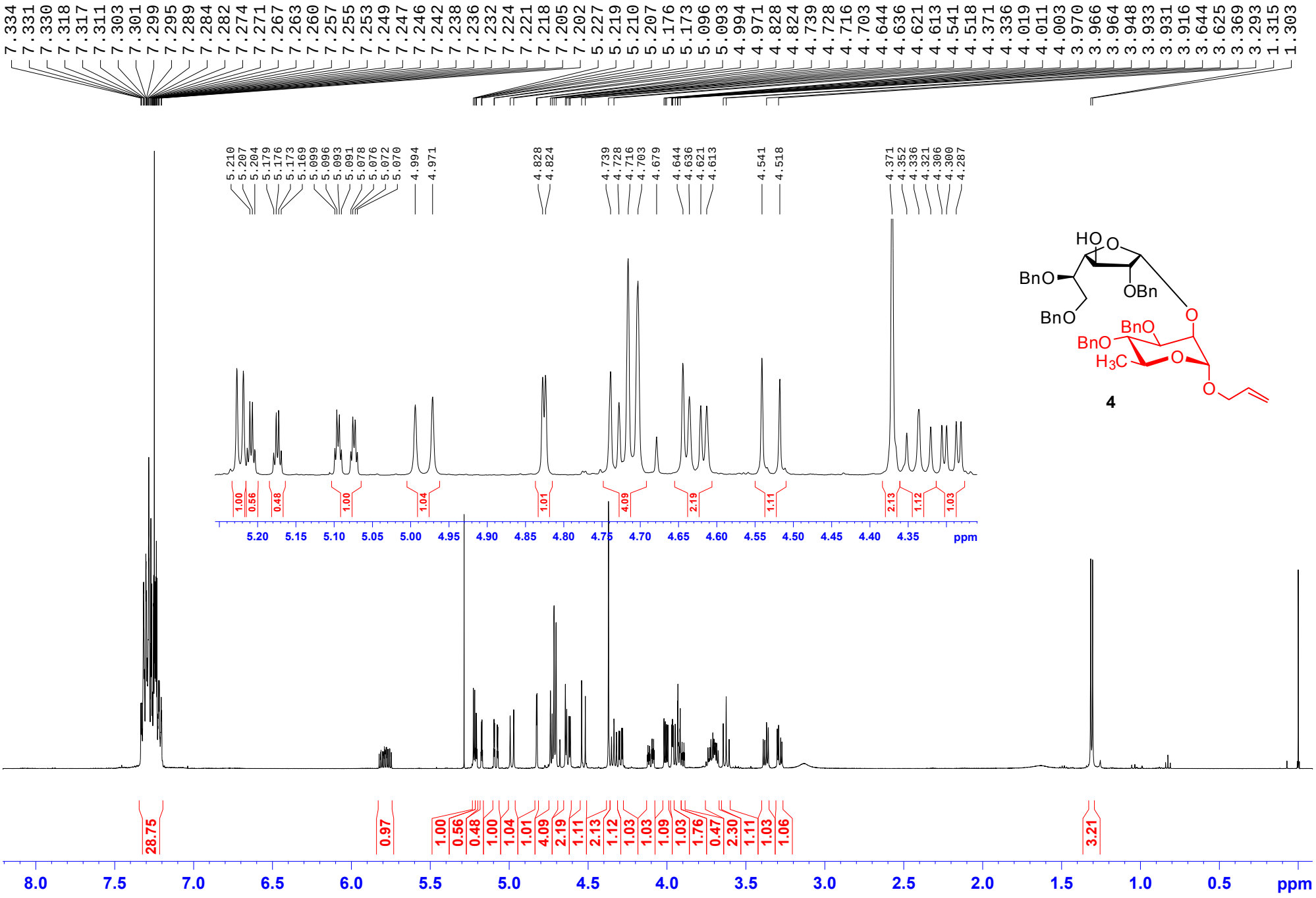
COSY spectrum of compound **42** ($CDCl_3$; 500 MHz)



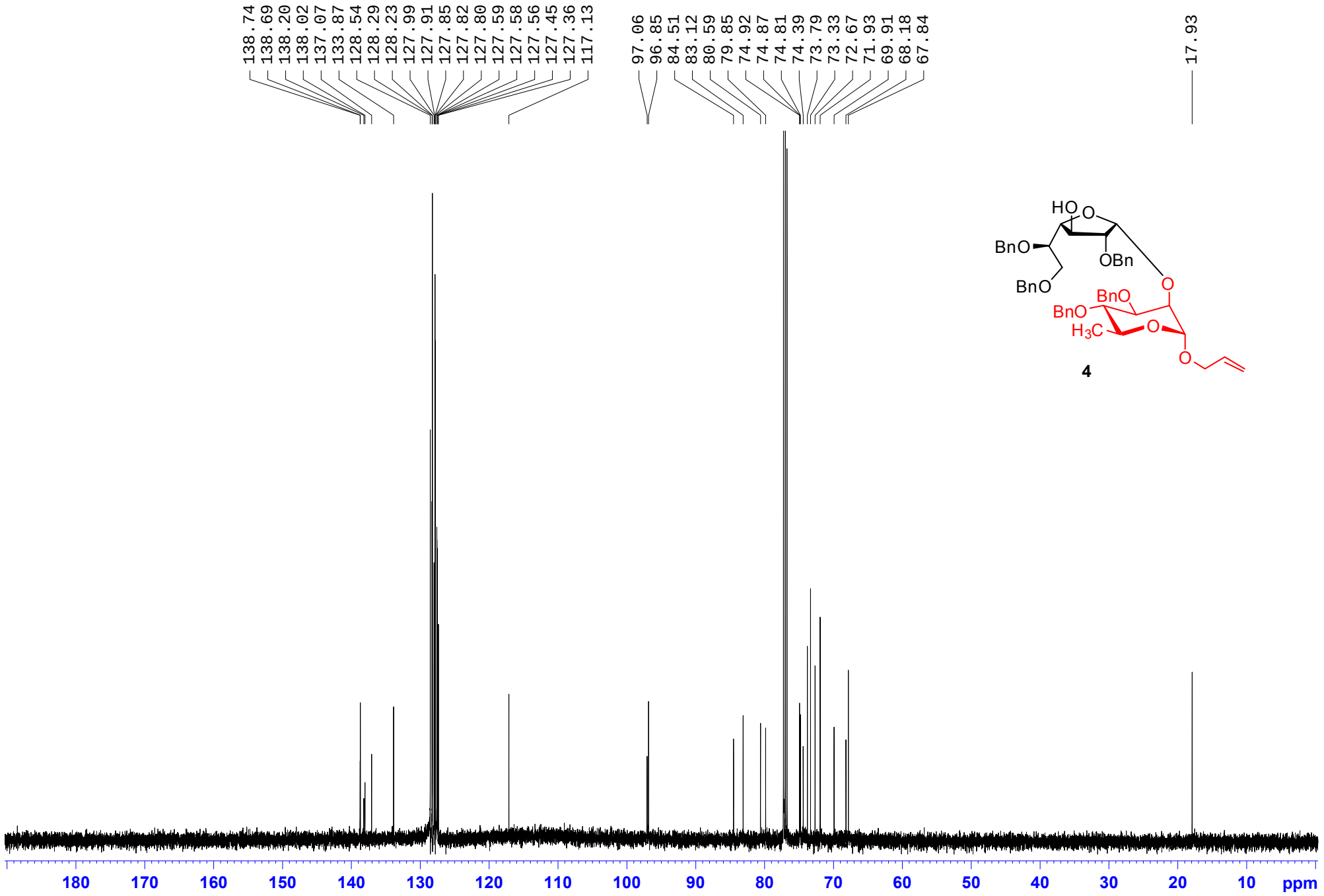
HSQC spectrum of compound **42** ($CDCl_3$; 500 MHz)



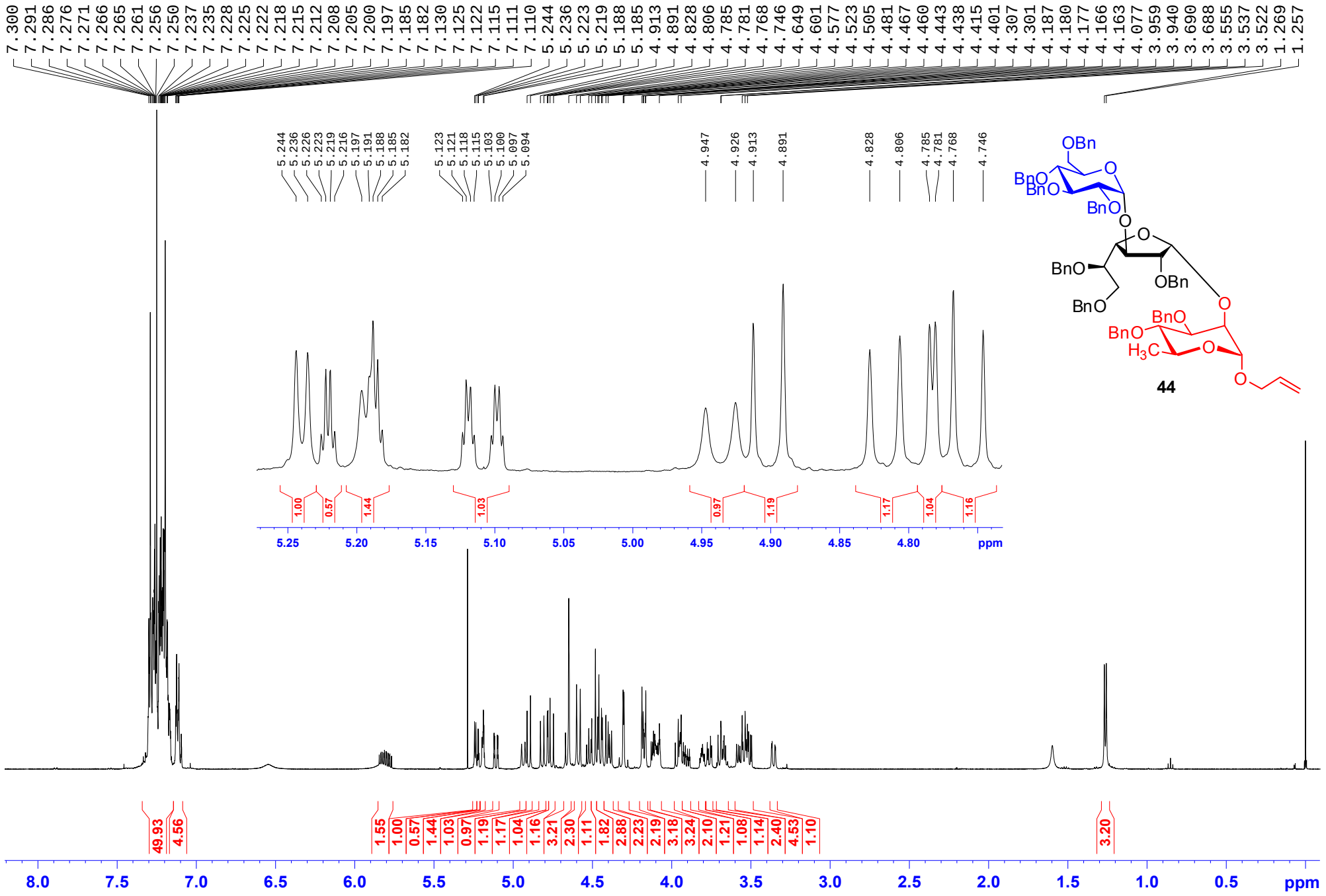
^{1}H NMR spectrum of compound **43** ($CDCl_3$; 500 MHz)



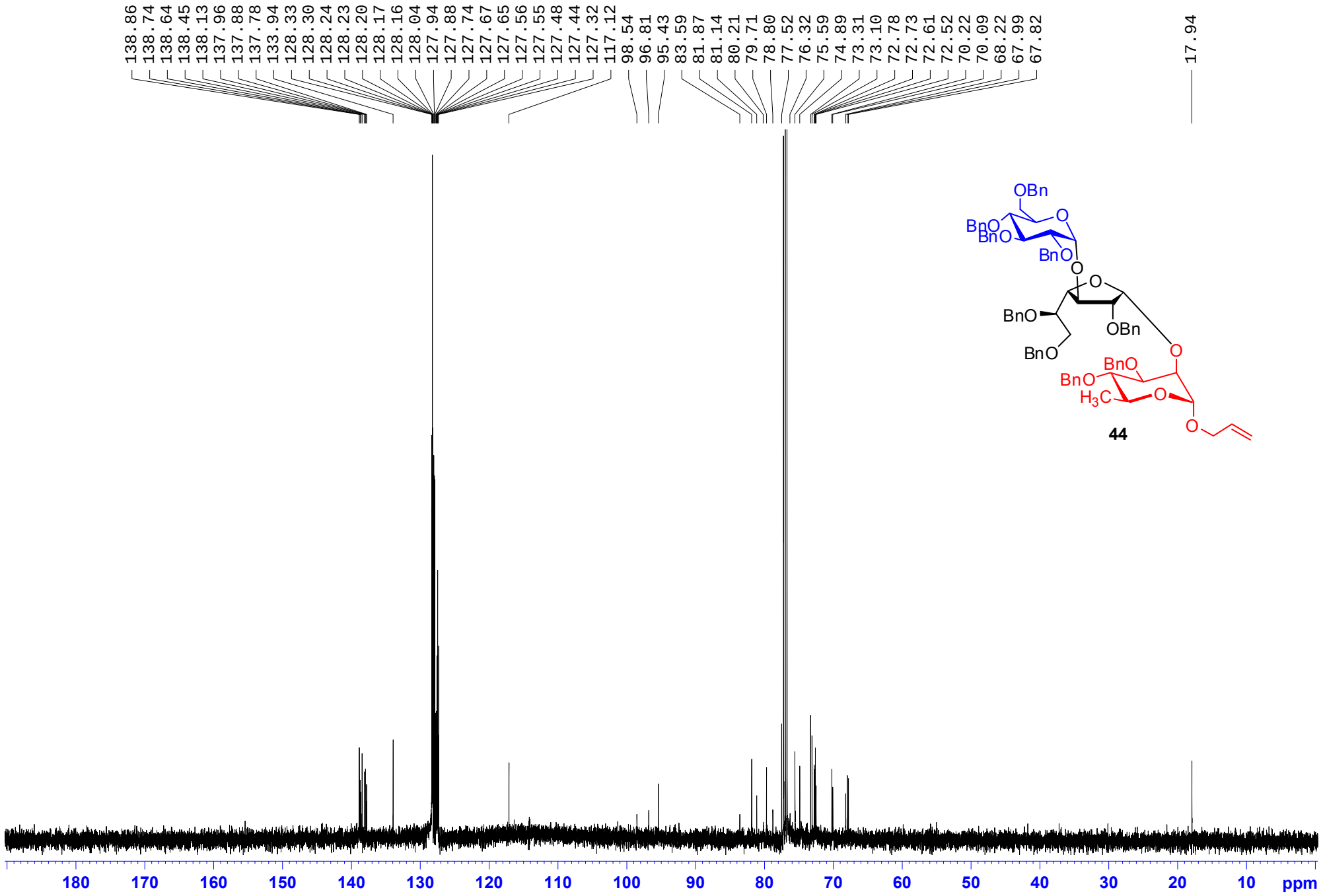
^{1}H NMR spectrum of compound **4** ($CDCl_3$; 500 MHz)



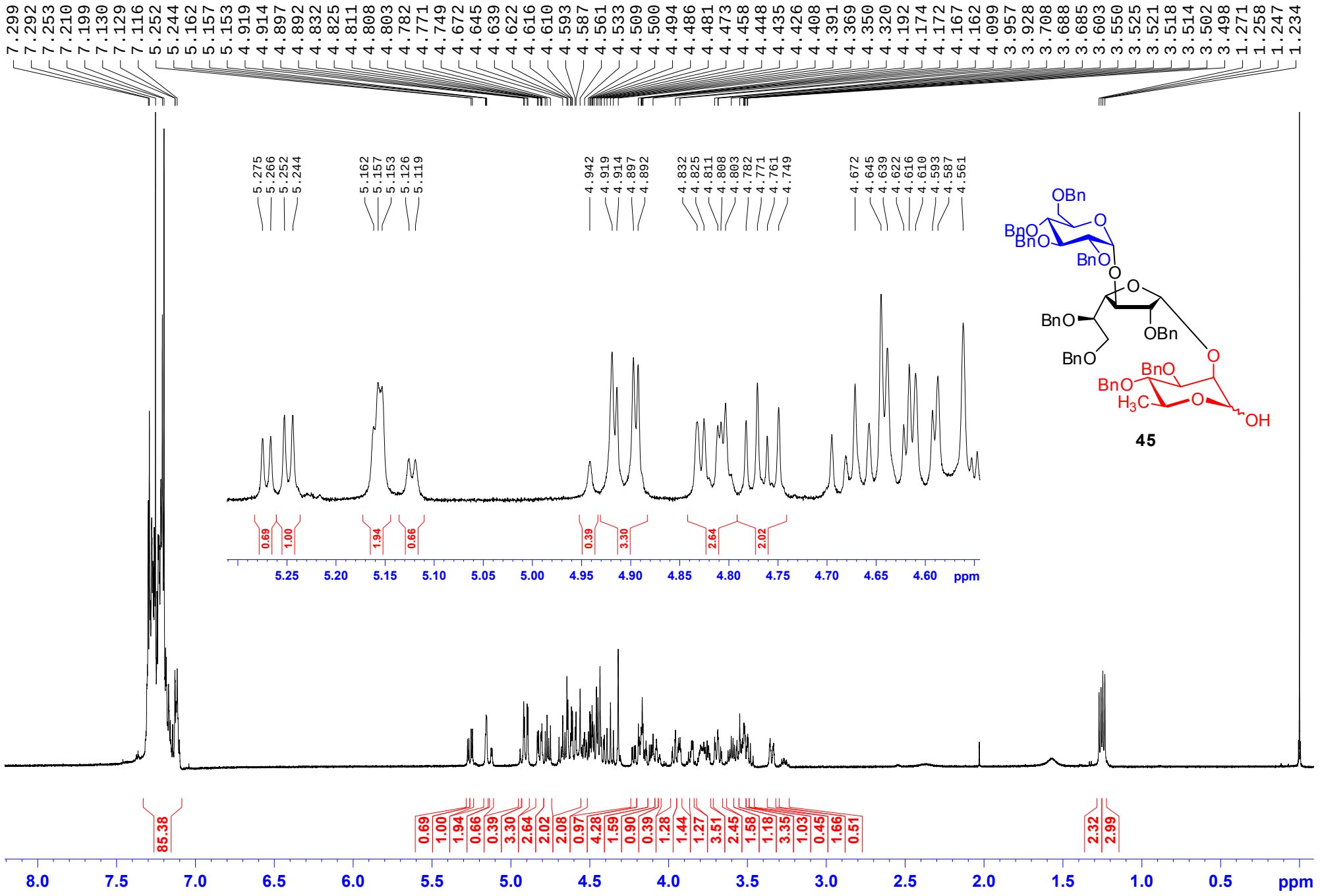
^{13}C NMR spectrum of compound **4** ($CDCl_3$; 125.8 MHz).



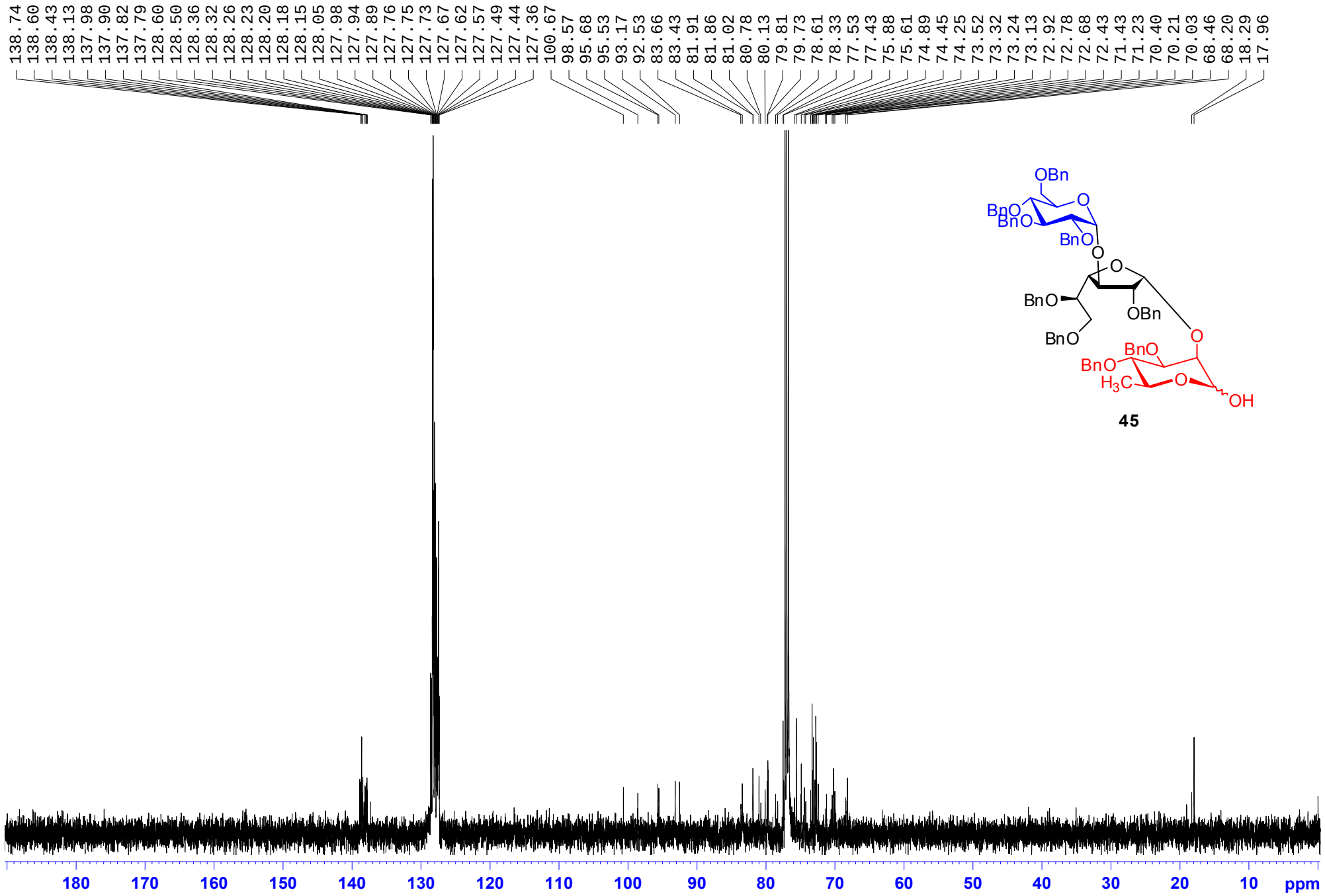
^{1}H NMR spectrum of compound **44** ($CDCl_3$; 500 MHz)



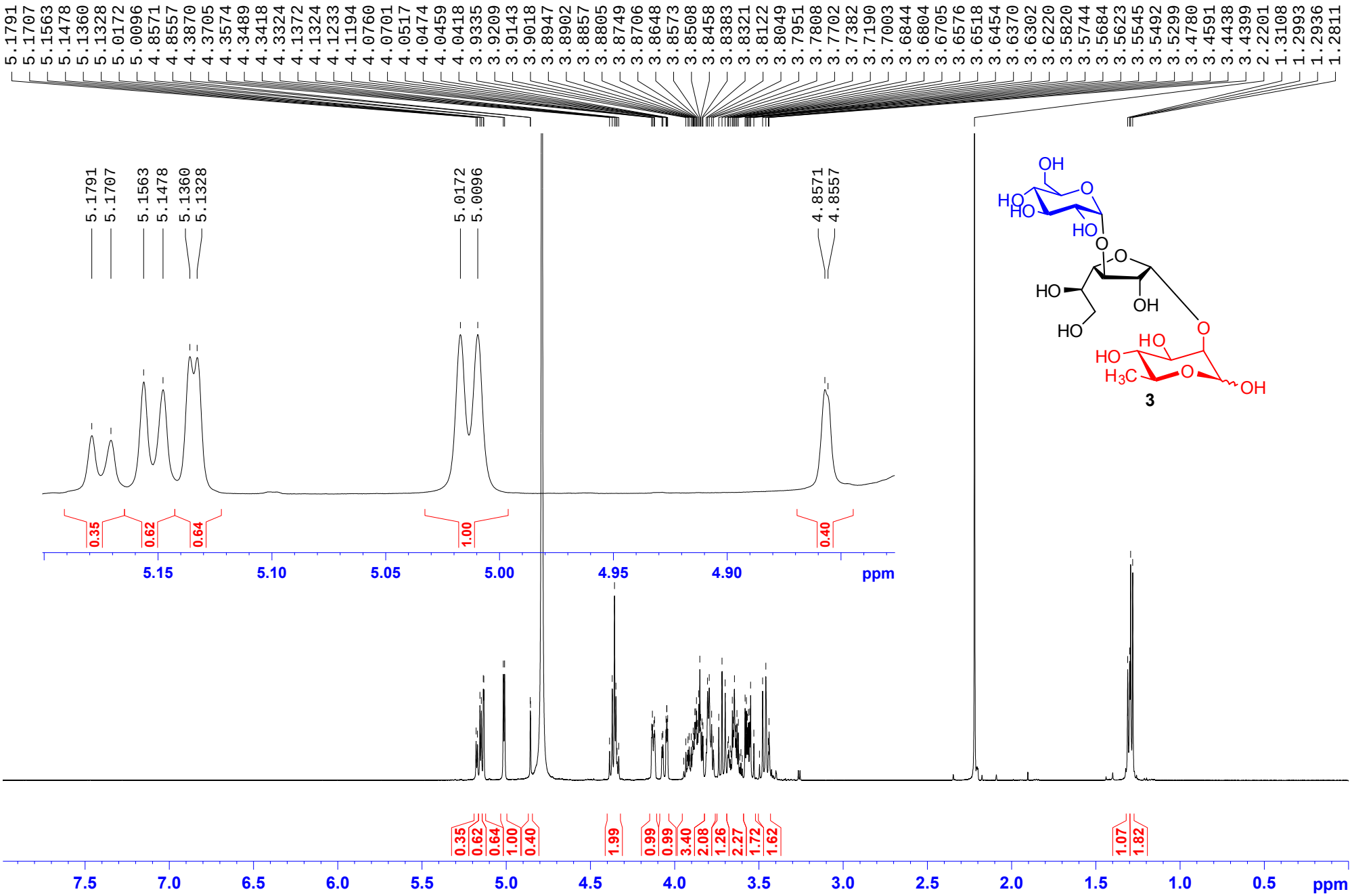
^{13}C NMR spectrum of compound **44** ($CDCl_3$; 125.8 MHz).



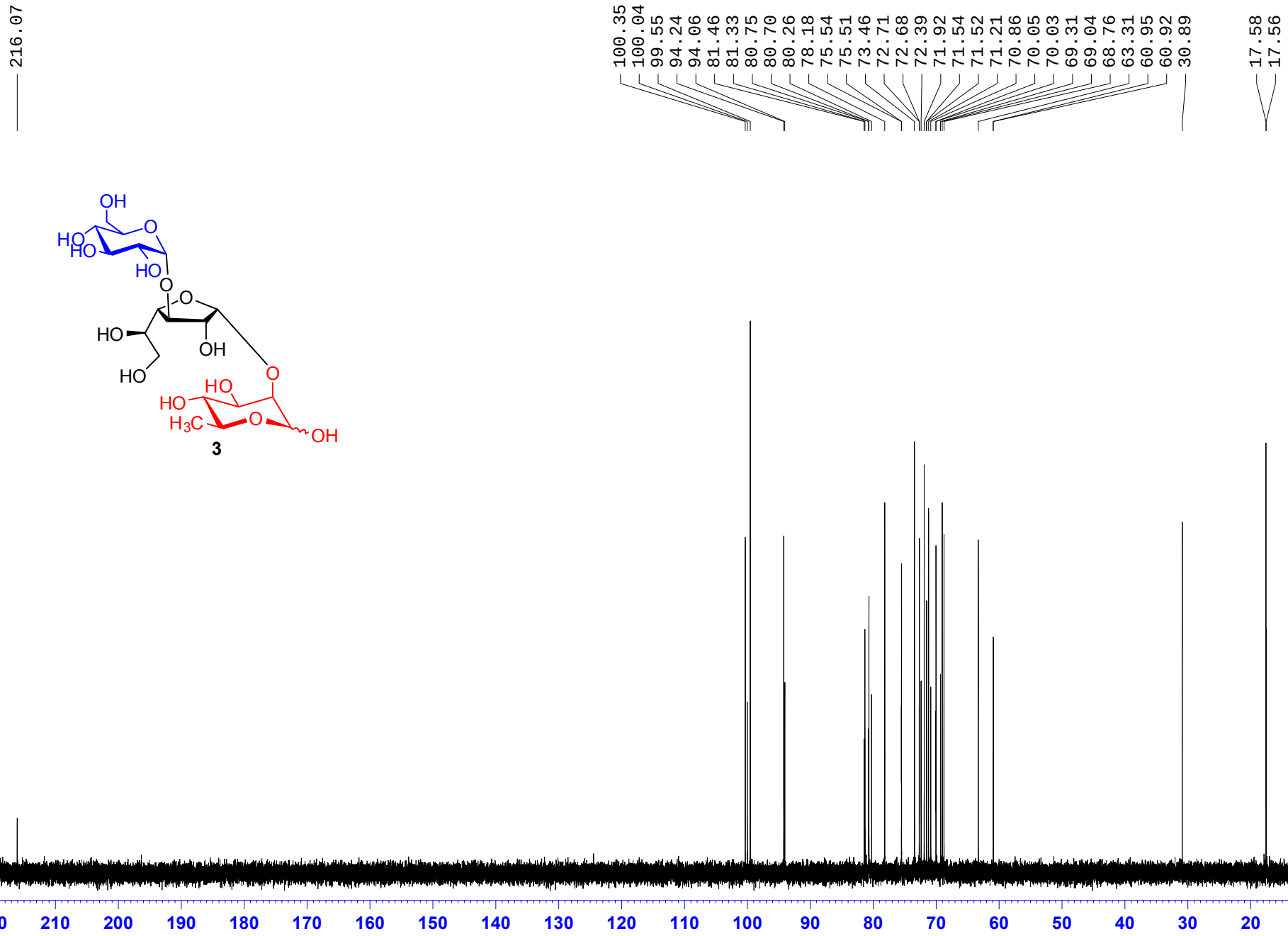
^{1}H NMR spectrum of compound **45** ($CDCl_3$; 500 MHz)



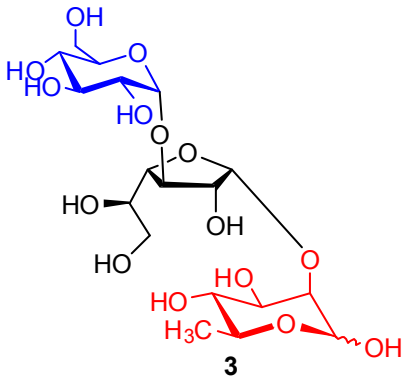
^{13}C NMR spectrum of compound **45** ($CDCl_3$; 125.8 MHz).



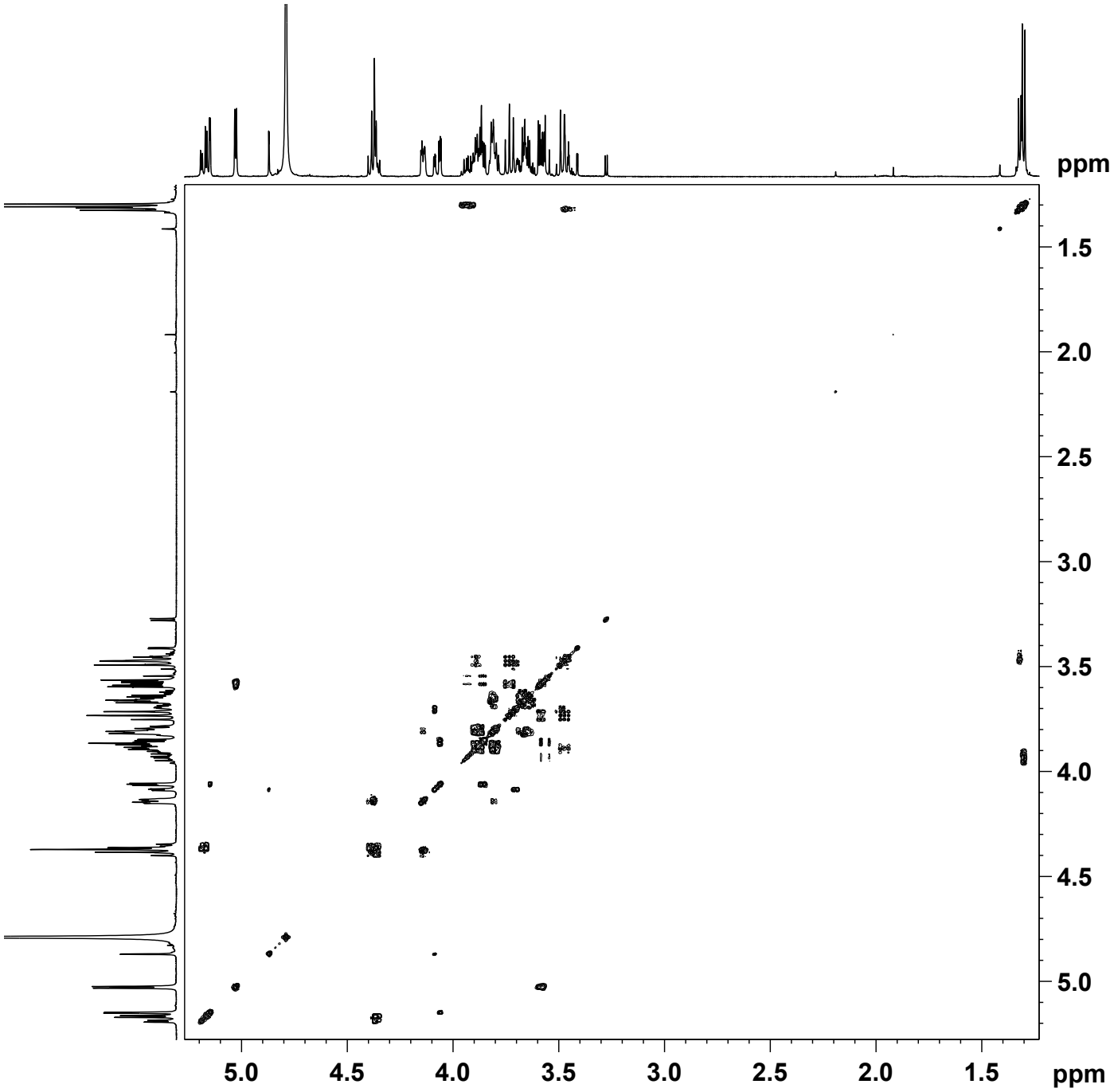
^{1}H NMR spectrum of compound **3** (D_2O; 500 MHz)



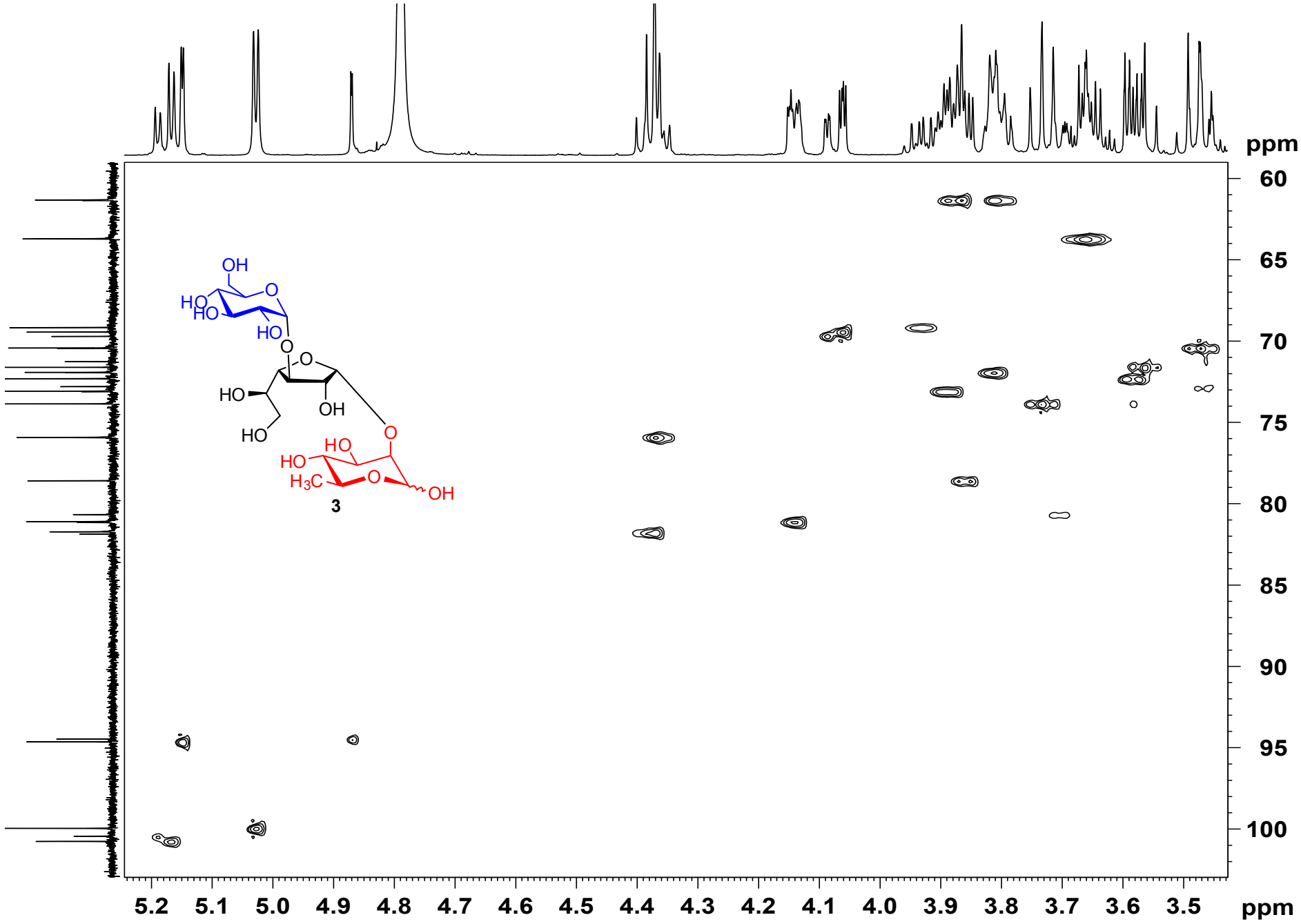
^{13}C NMR spectrum of compound **3** (D_2O; 125.8 MHz).



3



COSY spectrum of compound **3** (D_2O; 500 MHz)



HSQC spectrum of compound **3** (D_2O; 500 MHz)