Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Stereoselective synthesis of highly *O*-functionalized enantiopure 2,3,4-trisubstituted tetrahydrofurans by tandem debenzylative cyclization of glycal derived 2,3-epoxy alcohols

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General Consideration:

All the solvents used for the reactions and purification were commercially available and used after distillation. All the products were characterized by ^{1}H, ^{13}C, Two-Dimensional Heteronuclear Single Quantum Coherence (HSQC), Heteronuclear Multiple Bond Correlation Spectroscopy (HMBC), ESI-MS and EI-HRMS (C, H, O). Analytical TLC was performed using 2.5 x 5 cm plates coated with a 0.25 mm thickness of silica gel (60F-254), and visualization was accomplished with cerric sulphate and subsequent charring over hot plate.

Column chromatography was performed using silica gel (100-200 and 230-400 mesh).The NMR spectra were recorded at 298K using a 300 MHz and 400 MHz FT-NMR spectrometer equipped with a 5 mm multinuclear inverse probehead with z-shielded gradient. Experiments were recorded in $CDCl_3$ at 25°C. Chemical shifts are given on the δ scale and are referenced to the TMS at 0.00 ppm for proton and 0.00 ppm for carbon. In the 1D measurement (^{1}H, and ^{13}C) 32K data points were used for the FID. The pulse programs of the following 2D experiments were taken from the Bruker software library and the parameters were as follows.

300/75 MHz gradient HSQC spectra: relaxation delay d1 = 2s; evolution delay d2 = 3.44 ms; 90° pulse, 6.85 µs for 1H, 10µs for 13C hard pulses at –3.0 dB and 60µs for 13C GARP decoupling with gradient ratio GPZ1:GPZ2:GPZ3 = 50:30:40.1; 1024 data points in t2; spectral width 9.0 ppm in F2 and 160ppm in F1; number of scans 32; 256 experiments in t1; linear prediction to 512; zero filling up to 1K and apodization with sine-bell in both dimensions prior to double Fourier transformation.

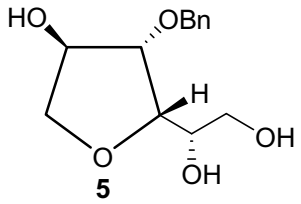
300/75 MHz gradient HMBC spectra: relaxation delay d1 = 2s; delay of the low-pass *J*-filter d2 = 3.44 ms; delay for evolution of long-range coupling d6 = 71 ms with gradient ratio same as HSQC; 2048 data points in t_2; spectral width 11.0 ppm in F2 and 240 ppm in F1; number of scans 52; 256 experiments in t_1; linear prediction to 512; zero filling up to 2K and apodization with 90° shifted square sine-bell in F1 dimension and sine-bell in F2 dimension prior to double Fourier transformation.

Representative procedure for synthesis of 2,3,4-trisubstituted tetrahydrofuran.

To a solution of epoxy alcohol **4** (0.5 g, 1.45 mmol) in absolute alcohol (10 mL), catalytic amount of phenyl hydrazine hydrochloride (14.46 mg, 0.10 mmol) was added and the mixture was stirred at reflux temperature for 2 h. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and neutralized with excess of saturated K_2CO_3 solution. The organic layer was evaporated under reduced pressure and aqueous layer was extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered and evaporated to yield the crude product which was purified by silica gel column chromatography to afford the pure tetrahydrofuran derivative **5** as white shiny solid**.**

Spectral data:

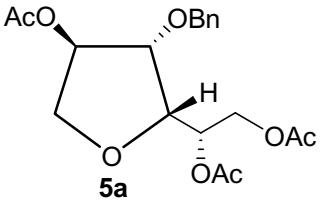
(*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (5)



5

5. 82% yield, mp 76-78 °C, $[\alpha]^{20}_D$ 53.12 (*c* 0.064, $CHCl_3$), column chromatography, 3/97 MeOH/$CHCl_3$ v/v, R_f 0.27 (1:9 MeOH/$CHCl_3$), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.41 (brs, 3H, 3×OH), 3.67-3.81 (m, 3H, H-1 and H-6a), 3.92 (brm, 1H, H-2), 4.02-4.06 (m, 3H, H-3, H-4, H-6b), 4.28 (brd, *J*= 2.4 Hz, 1H, H-5), 4.55 (d, *J*= 11.6 Hz, 1H, C*H*$_2$Ph), 4.63 (d, *J*= 12 Hz, 1H, C*H*$_2$Ph); 7.26-7.30 (m, 5H, Ar*H*) ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 64.1 (C-1), 69.3 (C-2), 72.3 (*C*H$_2$Ph), 73.8 (C-6), 74.4 (C-5), 79.6 (C-3), 84.1 (C-4), 127.6 (Ar*C*), 127.7 (Ar*C*), 128.4 (Ar*C*), 138.0 (qC); IR (KBr, cm^{-1}) 3393 (O-H str), 3018 (=C-H str), 2933, 2882 (C-H str), 1655, 1497, 1456 (C=C str), 1216, 1086 (C-O str); mass (ESI-MS) *m*/*z* 277 [M$^+$+Na]; EI-HRMS: (M + H) calcd for $C_{13}H_{18}O_5$ + H 255.1241, found 255.1232.

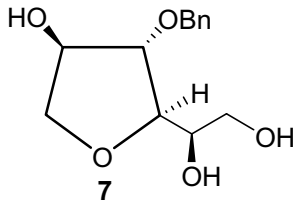
(*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol (5a)



5a

5a. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.86, 2.06, 2.10(3×COC*H*$_3$), 3.85 (d, *J*= 10.5 Hz, 1H, H-6a), 3.95 (d, *J*= 3.3 Hz, 1H, H-4), 4.12 (dd (o), *J*= 3.6 Hz, *J*= 8.7 Hz, 1H, H-3), 4.19 (m(o), 1H, H-1a), 4.25 (dd(o), *J*= 4.2 Hz, *J*= 10.2 Hz, 1H, H-6b), 4.52 (d, *J*= 12.0 Hz, 1H, C*H*$_2$Ph), 4.63-4.73 (m, 2H, H-1b, C*H*$_2$Ph), 5.28 (brm, 2H, H-2, H-5), 7.31 (brs, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 20.9, 21.0 (3×*C*H$_3$), 63.0 (C-1), 68.7 (C-2), 71.5 (C-6), 71.7 (*C*H$_2$Ph), 76.0 (C-5), 78.0 (C-3), 80.1 (C-4), 128.0 (Ar*C*), 128.4 (Ar*C*), 128.5 (Ar*C*), 136.9 (qC), 169.5, 170.3, 170.7 (3×*C*OCH$_3$); IR (film, cm^{-1}) 3031 (=C-H str), 2939, 2886 (C-H str), 1744 (C=O str), 1656, 1496, 1452 (C=C str), 1372 (C-H def of CH_3), 1230, 1053 (C-O str); mass ESI-MS: *m*/*z* 403 [M^{+}+Na].

(*2R, 3R, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (7)

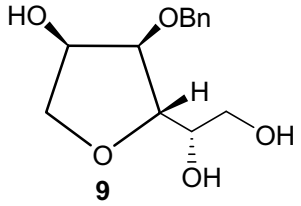


7

7. 78% yield, mp 80-82 °C, [α]$^{20}_{D}$ 35.48 (*c* 0.062, $CHCl_3$), column chromatography, 4/96 MeOH/$CHCl_3$ v/v, R_f 0.21 (1:9 MeOH/$CHCl_3$), ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.44 (dd, *J*= 12.0 Hz, *J*= 8.0 Hz, 1H), 3.66 (m, 1H), 3.84-3.89 (brm, 7H), 3.98 (d, 1H), 4.20 (brs, 1H), 4.53 (d, *J*= 12.0 Hz, 1H, C*H*$_2$Ph), 4.58 (d, *J*= 12.0 Hz, 1H, C*H*$_2$Ph), 7.26-7.38 (brs, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.8, 71.8, 71.9, 74.0, 74.7, 84.8, 85.2, 127.7 (ArC), 127.9 (ArC), 128.5 (ArC), 137.6 (qC); IR (KBr, cm^{-1}) 3391 (O-H str), 3030 (=C-H str), 2931 (C-H str), 1592, 1496, 1457 (C=C str), 1100, 1064 (C-O str);mass (ESI-MS)

m/z 277 (M^++Na); EI-HRMS: (M + H) calcd for $C_{13}H_{18}O_5$ + H 255.1243, found 255.1232.

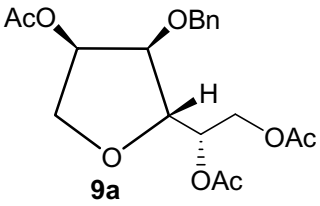
(*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (9)



9

9. 76% yield, mp 58-60 °C, $[\alpha]^{20}_D$ -22.72 (*c* 0.044, $CHCl_3$), column chromatography, 4/96 MeOH/$CHCl_3$ v/v, R_f 0.22 (1:9 MeOH/$CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.61-3.70 (m, 2H, H-1), 3.80-3.82 (m, 2H, H-2, H-6a), 3.89 (t, *J*= 5.6 Hz, 1H, H-3), 3.98 (dd, *J*= 9.6 Hz, *J*= 4.4 Hz, 1H, H-6b), 4.07 (t, *J*= 5.6 Hz, 1H, H-4), 4.20 (brm, 1H, H-5), 4.59 (d, *J*= 11.6 Hz, 1H, C*H*$_2$Ph), 4.66 (d, *J*= 11.2 Hz, 1H, C*H*$_2$Ph), 7.36 (brs, 5 H, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 63.3 (C-1), 69.8 (C-5), 71.8 (C-2), 72.7 (*C*H$_2$Ph), 73.3 (C-6), 79.3 (C-4), 80.8 (C-3), 127.9 (Ar*C*), 128.2 (Ar*C*), 128.4 (Ar*C*), 128.6 (Ar*C*), 136.8 (q*C*); IR (KBr, cm^{-1}) 3407 (O-H str), 3028 (=C-H str), 2926 (C-H str), 1638, 1543, 1457 (C=C str), 1117, 1065 (C-O str); mass (ESI-MS) *m/z* 277 (M^++Na); EI-HRMS: calcd for (M^+) $C_{13}H_{18}O_5$ 254.1154, found 254.1154.

(*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl--D-glucitol (9a)

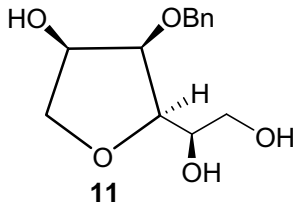


9a

9a. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.00, 2.04, 2.11 (3×-COC*H*$_3$), 3.91 (dd, *J*= 2.1 Hz and *J*= 10.8 Hz, 1H, H-6a), 4.00 (m, 1H, H-3), 4.07-4.16 (m, 3H, H-1a, H-4, H-6b), 4.34 (dd, *J*= 3.3 Hz, and *J*= 12.3 Hz, 1H, H-1b), 4.43 (d, *J*= 11.1 Hz, C*H*$_2$Ph), 4.60 (d, *J*= 11.1 Hz, 1H, C*H*$_2$Ph), 5.25 (ddd, *J*= 7.8 Hz, *J*= 6.3 Hz, *J*= 3.0 Hz, 1H, H-2), 5.36-5.39 (m, 1H, H-

5), 7.30-7.34 (brs, 5H, Ar*H*);^{13}C NMR ($CDCl_3$, 75 MHz) δ 20.8, 20.9 (3×-*C*H_3), 62.7 (C-1), 71.1 (C-6), 71.2 (C-5 and C-2), 73.1 (*C*H_2Ph), 77.9 (C-3), 79.7 (C-4), 128.1 (Ar*C*), 128.5 (Ar*C*), 137.0 (q*C*), 170.2, 170.4, 170.6 (3×-*C*OCH_3); IR (film, cm^{-1}) 3032 (=C-H str), 2943 (C-H str), 1743 (C=O str), 1655, 1564, 1457 (C=C str), 1371 (C-H def of CH_3), 1234, 1048 (C-O str); mass ESI-MS: *m*/*z* 403 [M^++Na].

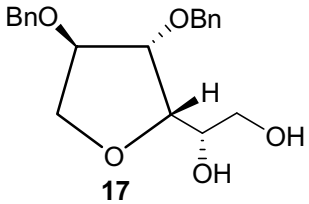
(*2R, 3R, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (11)



11

11. 83% yield, mp 86-88 °C, $[\alpha]^{20}_D$ -20.58 (*c* 0.068, $CHCl_3$), column chromatography, 2/98 MeOH/$CHCl_3$ v/v, R_f 0.25 (1:9 MeOH/$CHCl_3$), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.28 (brs, 3H, O*H*), 3.69-3.89 (m, 5H), 3.97-4.03 (qt, 1H), 4.24 (t, *J*= 5.7 Hz, 1H), 4.30 (dd, *J*= 4.5 Hz, *J*= 7.8 Hz 1H), 4.68 (d, *J*= 11.4 Hz, 1H, C*H*$_2$Ph), 4.75 (d, *J*= 11.4 Hz, 1H, C*H*$_2$Ph), 7.37 (brs, 5H, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.0, 70.3, 70.8, 73.0, 73.9, 79.0, 79.9, 127.8 (Ar*C*), 128.5 (Ar*C*), 128.8 (Ar*C*), 136.8 (q*C*); IR (KBr, cm^{-1}) 3394 (O-H str), 3035 (=C-H str), 2926 (C-H str), 1606, 1439 (C=C str), 1156, 1051 (C-O str);mass (ESI-MS) *m/z* 277 (M^++Na); EI-HRMS: (M + H) calcd for $C_{13}H_{18}O_5$ + H 255.1237, found 255.1232.

(*2S, 3S, 4S, 5R*) 3,6-Anhydro-4,5-di-*O*-benzyl-D-galactitol (17)

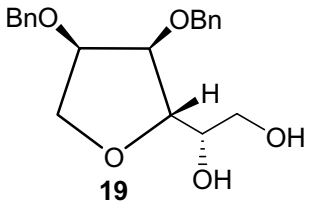


17

17. 68% yield, Oil, $[\alpha]^{20}_D$ 30.76 (*c* 0.052, $CHCl_3$), column chromatography, 1/99 MeOH/$CHCl_3$ v/v, R_f 0.25 (1:49 MeOH/$CHCl_3$), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.67-3.71 (m, 1H), 3.81-3.86 (m, 2H), 3.99 (brd, *J*= 2.7 Hz, 2H), 4.12-4.18 (m, 3H), 4.68-4.50

(m, 4H, 2×C*H*$_2$Ph), 7.27-7.35 (m, 10H, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 64.6, 69.7, 71.4, 71.6, 72.1, 80.4, 81.6, 82.2, 127.7 (Ar*C*), 127.9 (Ar*C*), 128.0 (Ar*C*), 128.2 (Ar*C*), 128.5 (Ar*C*), 128.7 (Ar*C*), 137.4 (q*C*), 137.5 (q*C*); IR (film, cm^{-1}) 3405 (O-H str), 3063, 3029 (=C-H str), 2931, 2874 (C-H str), 1658, 1495, 1455 (C=C str), 1086 (C-O str); mass (ESI-MS) *m/z* 367 (M^++Na); EI-HRMS: (M + H) calcd for $C_{20}H_{24}O_5$ + H 345.1709, found 345.1702.

(*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (19)



19

19. 60% yield, Oil, $[\alpha]^{20}_D$ -54.16 (*c* 0.024, $CHCl_3$), column chromatography, 1/99 MeOH/$CHCl_3$ v/v, R_f 0.32 (1:49 MeOH/$CHCl_3$), ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.70-3.68 (brd, *J*= 4.8 Hz, 2H), 3.89 (brs, 1H), 3.96-4.01 (m, 2H), 4.06 (m, 3H), 4.48-4.59 (m, 2H, C*H*$_2$Ph), 4.63-4.67 (m, 2H, C*H*$_2$Ph), 7.27-7.36 (m, 10H, Ar*H*); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 63.3, 70.6, 71.6, 71.8, 72.1, 76.1, 77.7, 81.0, 127.7 (Ar*C*), 127.9 (Ar*C*), 128.0 (Ar*C*), 128.2 (Ar*C*), 128.5 (Ar*C*), 137.1 (q*C*), 137.6 (q*C*); IR (film, cm^{-1}) 3433 (O-H str), 2930, 2828 (C-H str), 1620, 1595, 1460 (C=C str), 1072 (C-O str); mass (ESI-MS) *m/z* 367 (M^++Na); EI-HRMS: (M + H) calcd for $C_{20}H_{24}O_5$ + H 345.1700, found 345.1702.

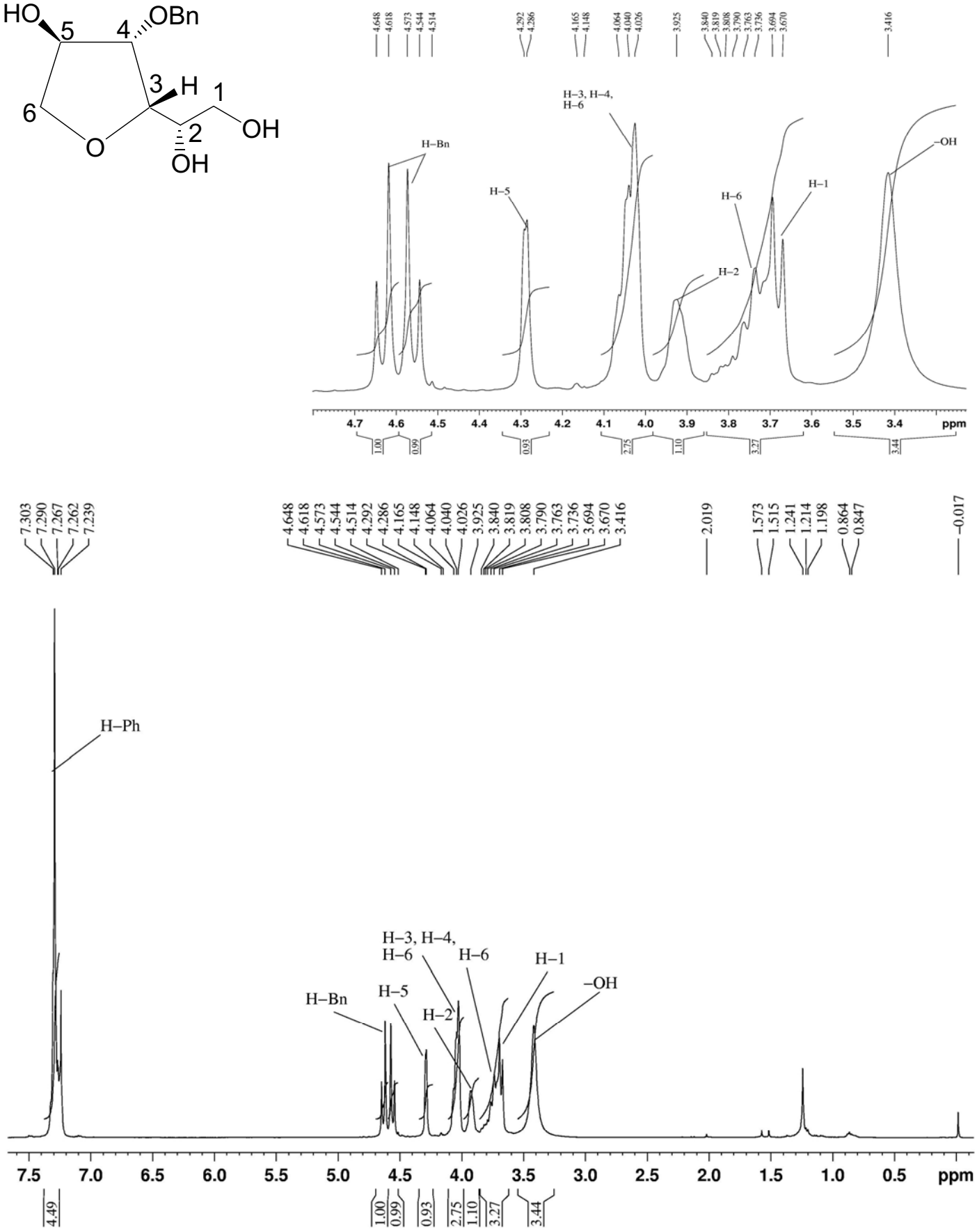


Fig. S-1: [1]H NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

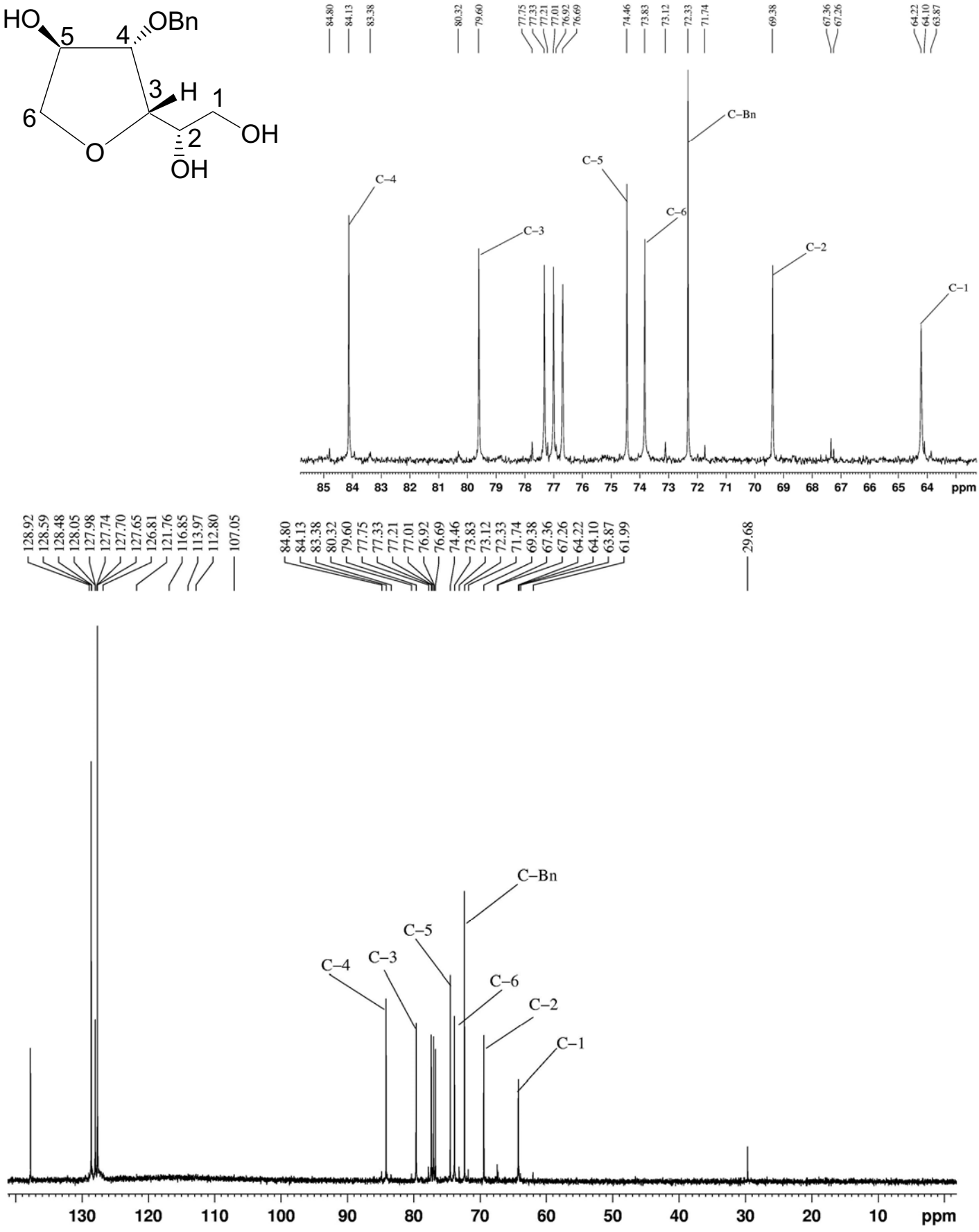
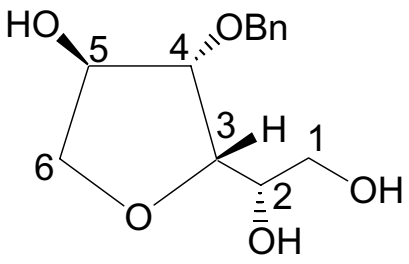


Fig. S-2: ^{13}C NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**



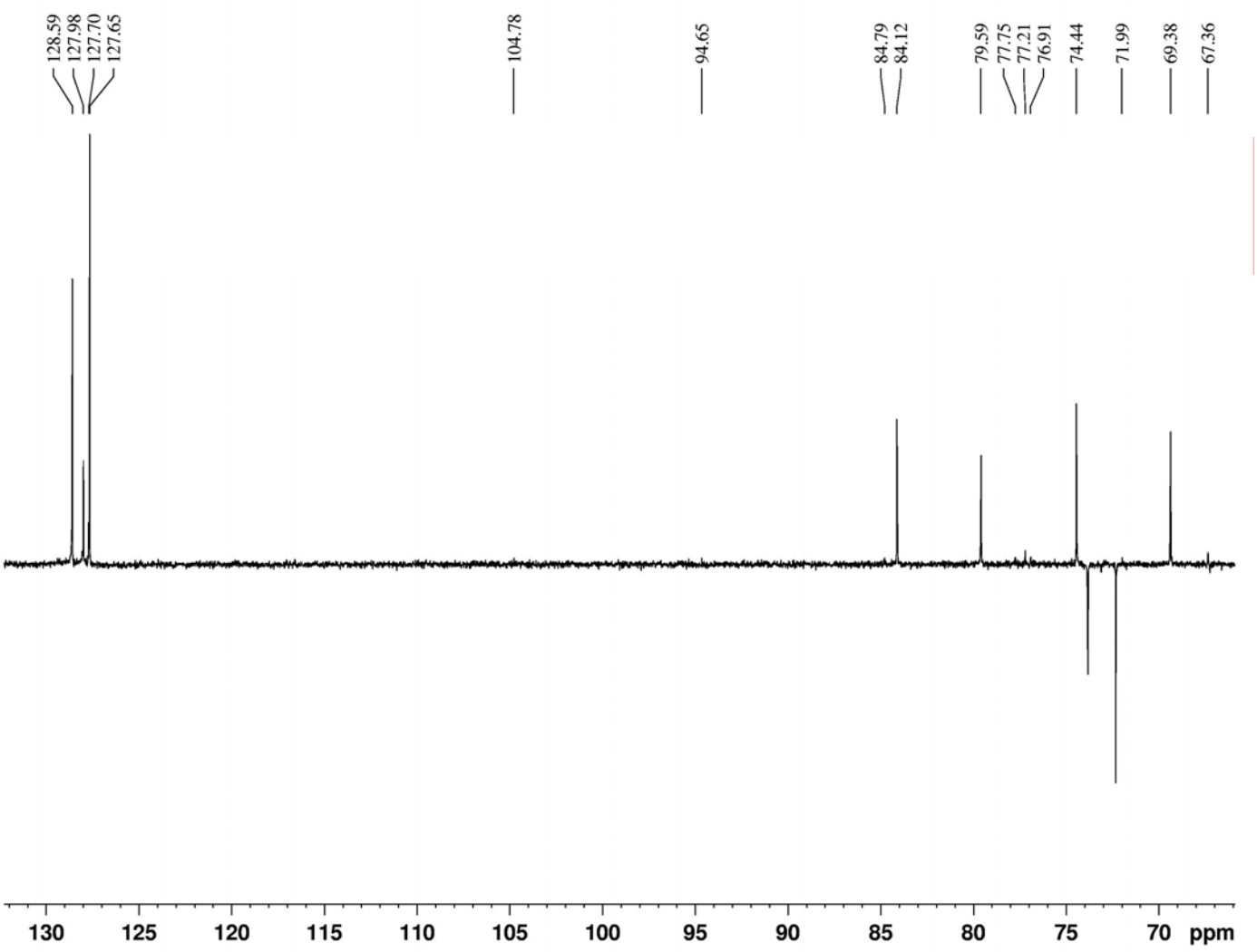
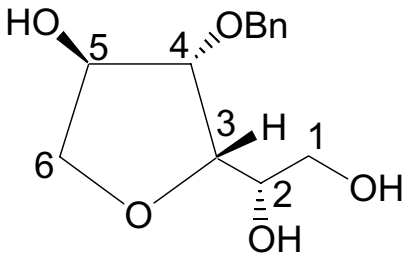


Fig. S-3: DEPT-135 NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**



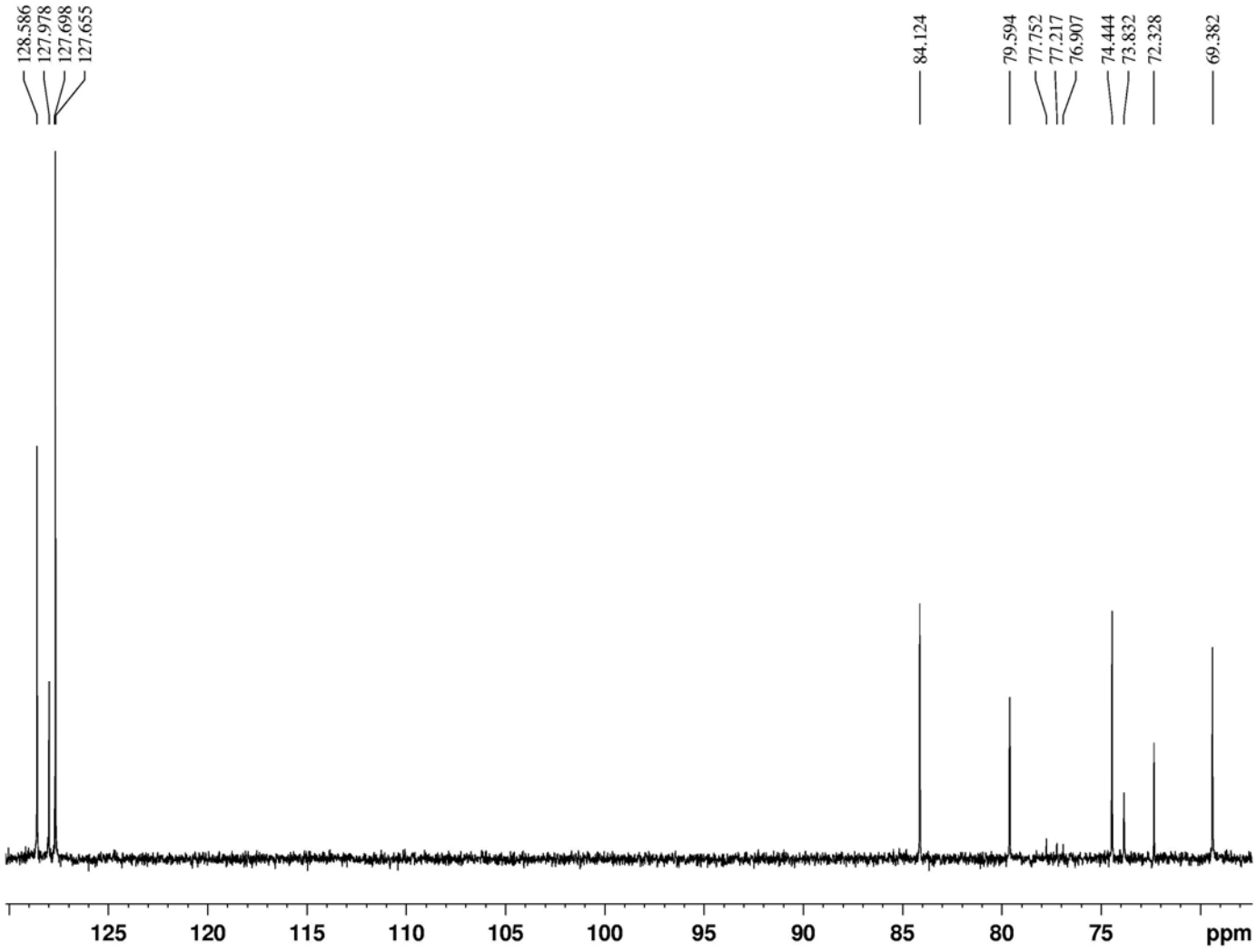


Fig. S-4: DEPT-90 NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

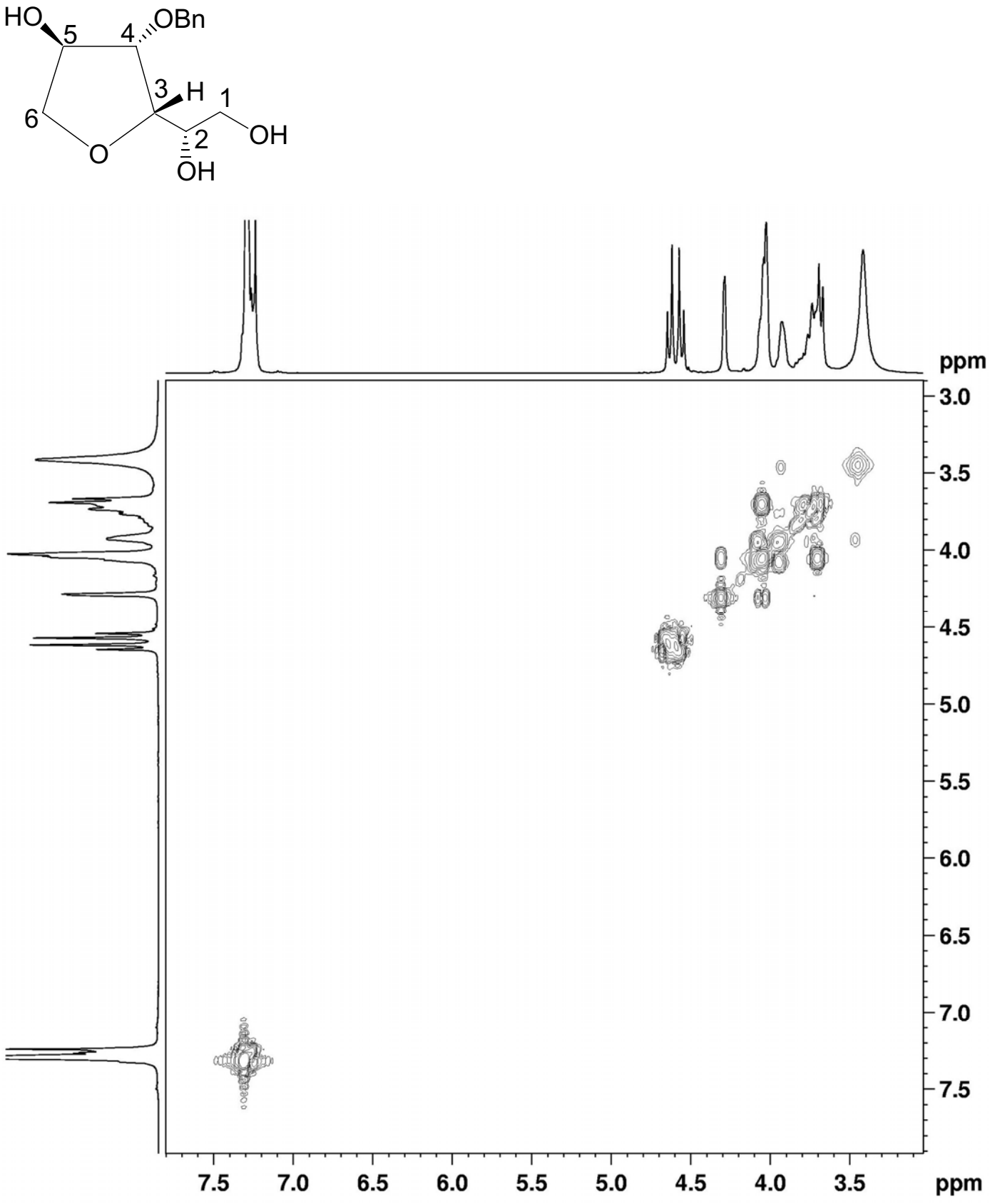


Fig. S-5: 2D COSY Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

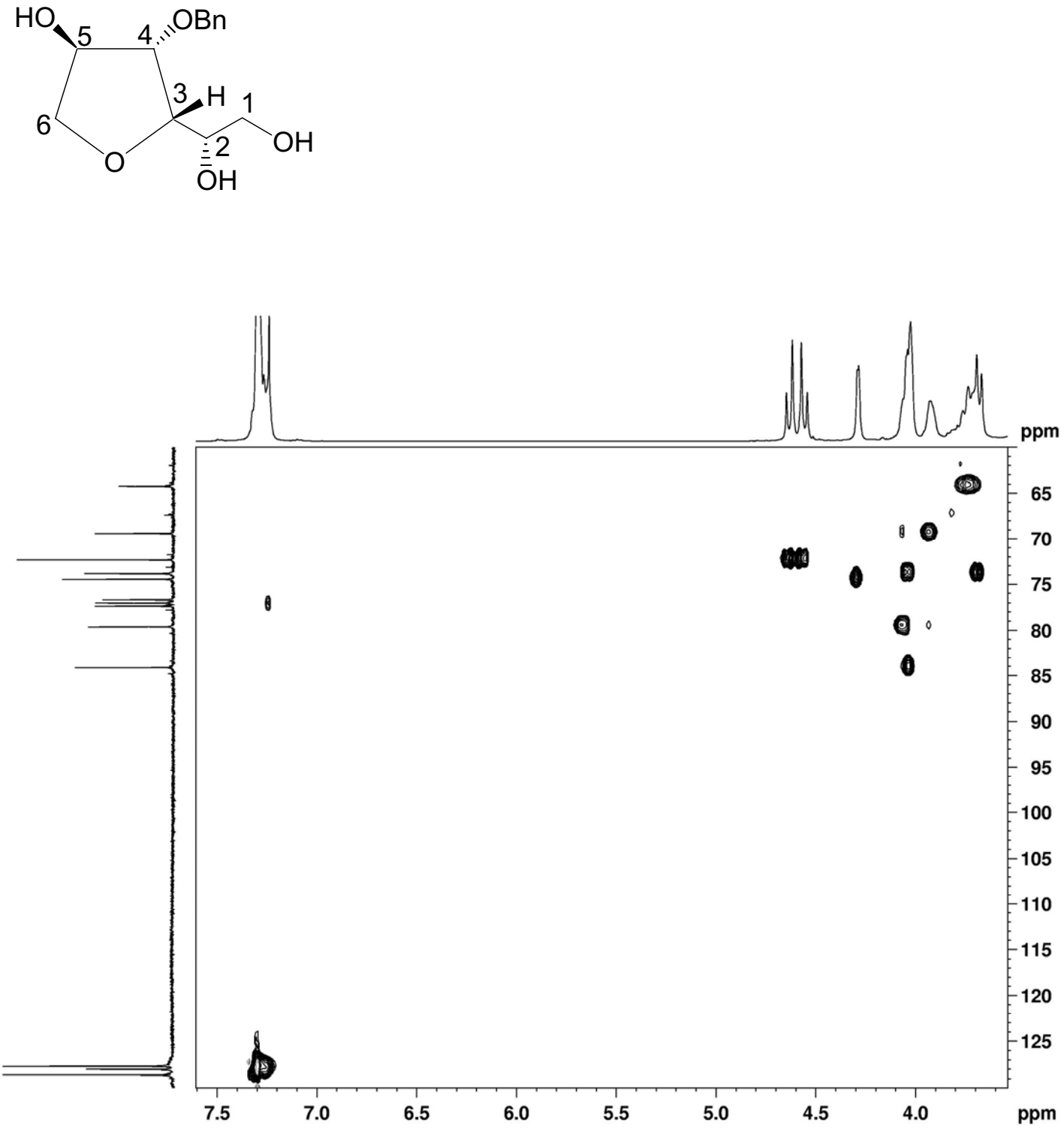


Fig. S-6: 2D HSQC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

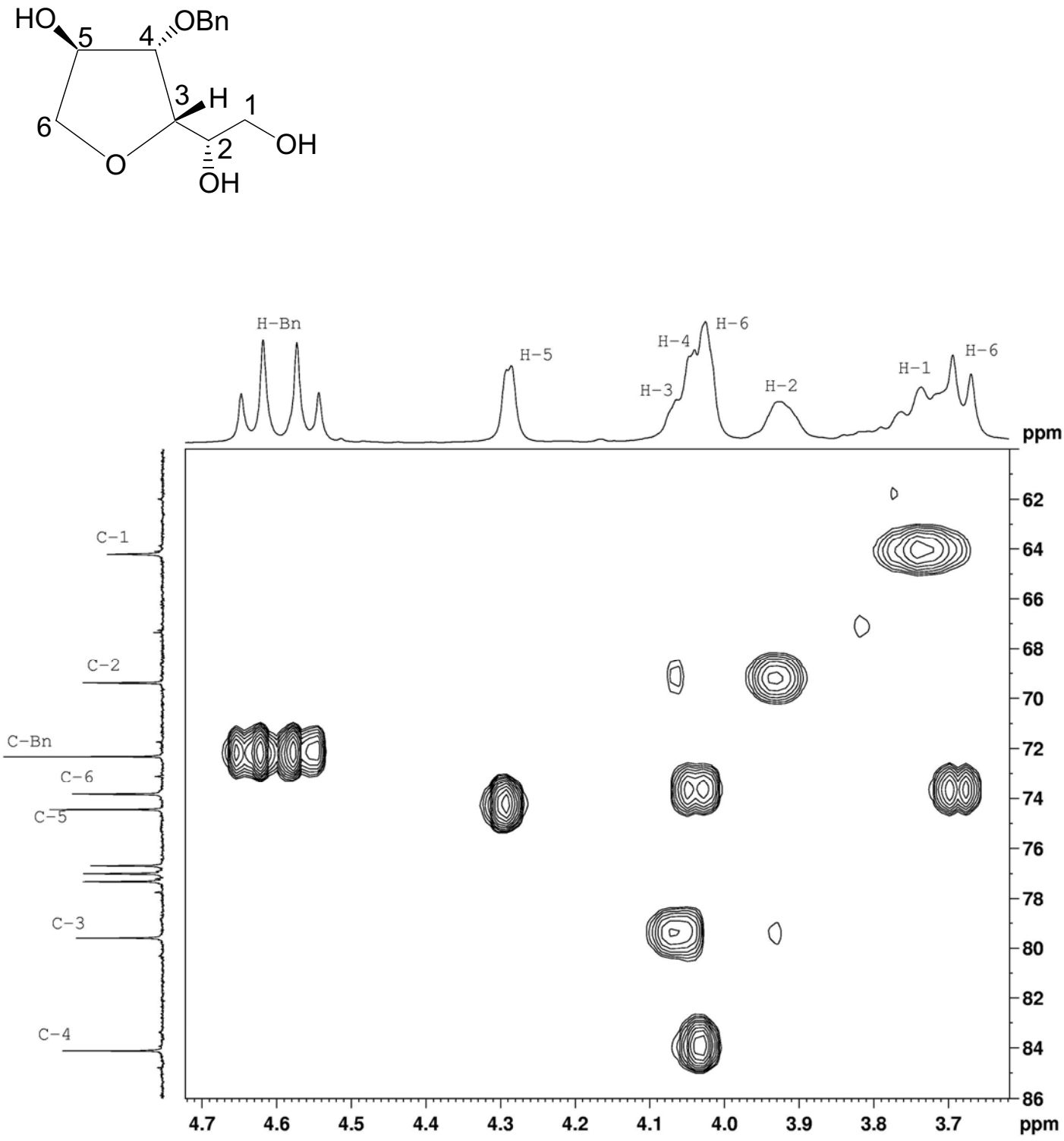
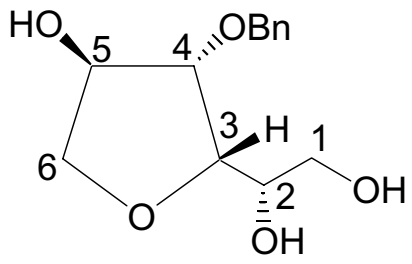


Fig. S-7: Expanded region of 2D HSQC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**



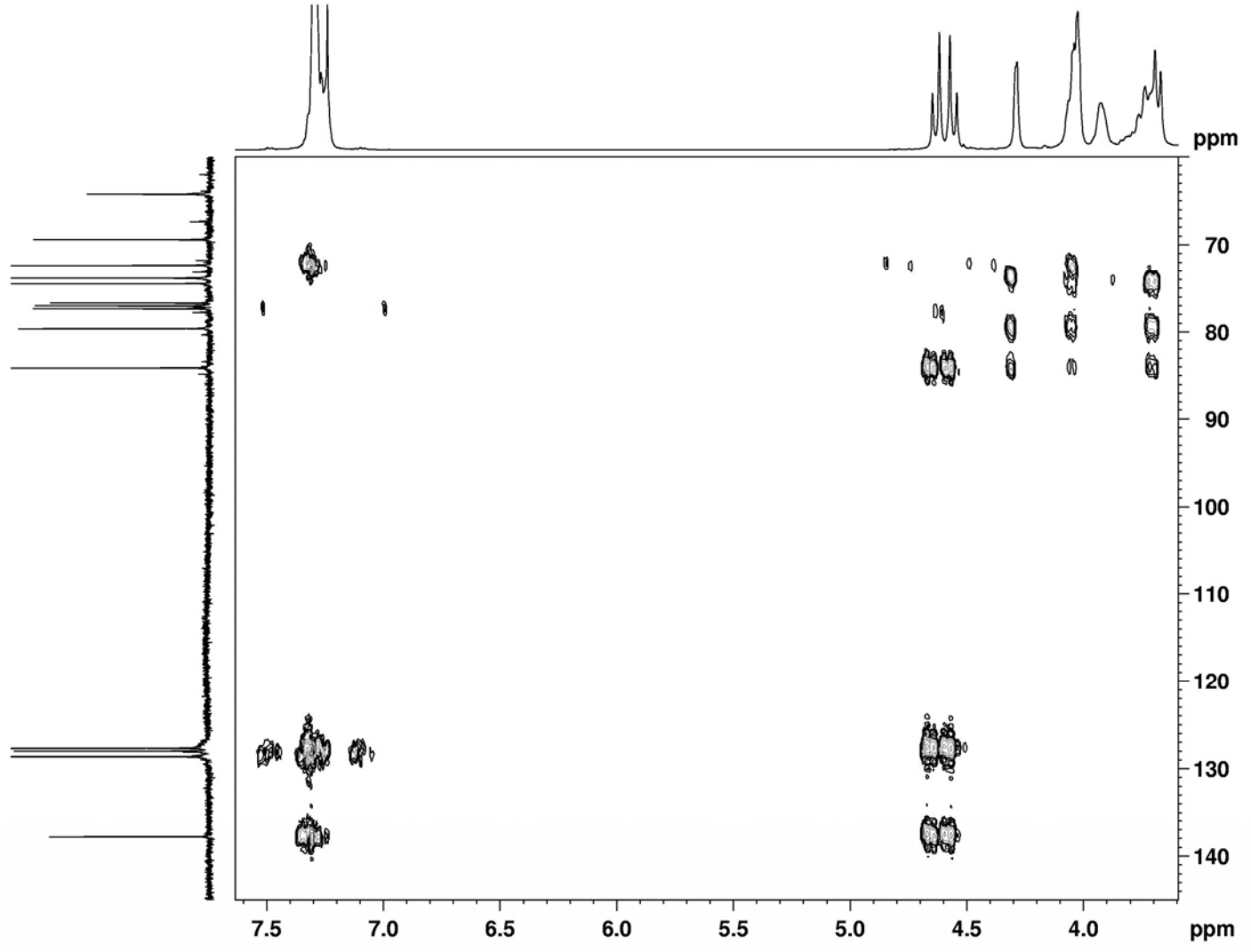


Fig. S-8: 2D HMBC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

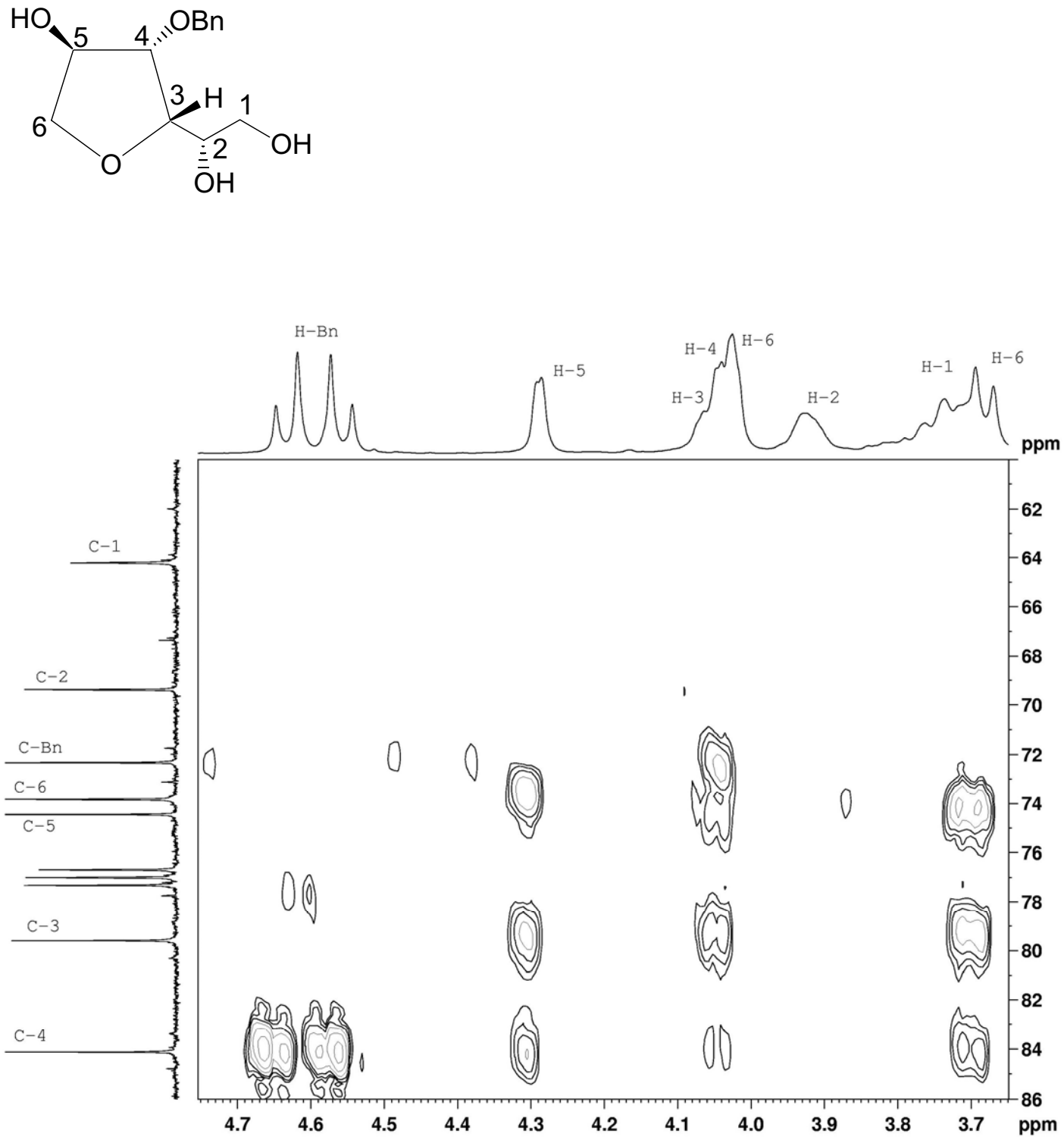


Fig. S-9: Expanded region of 2D HSQC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(5)**

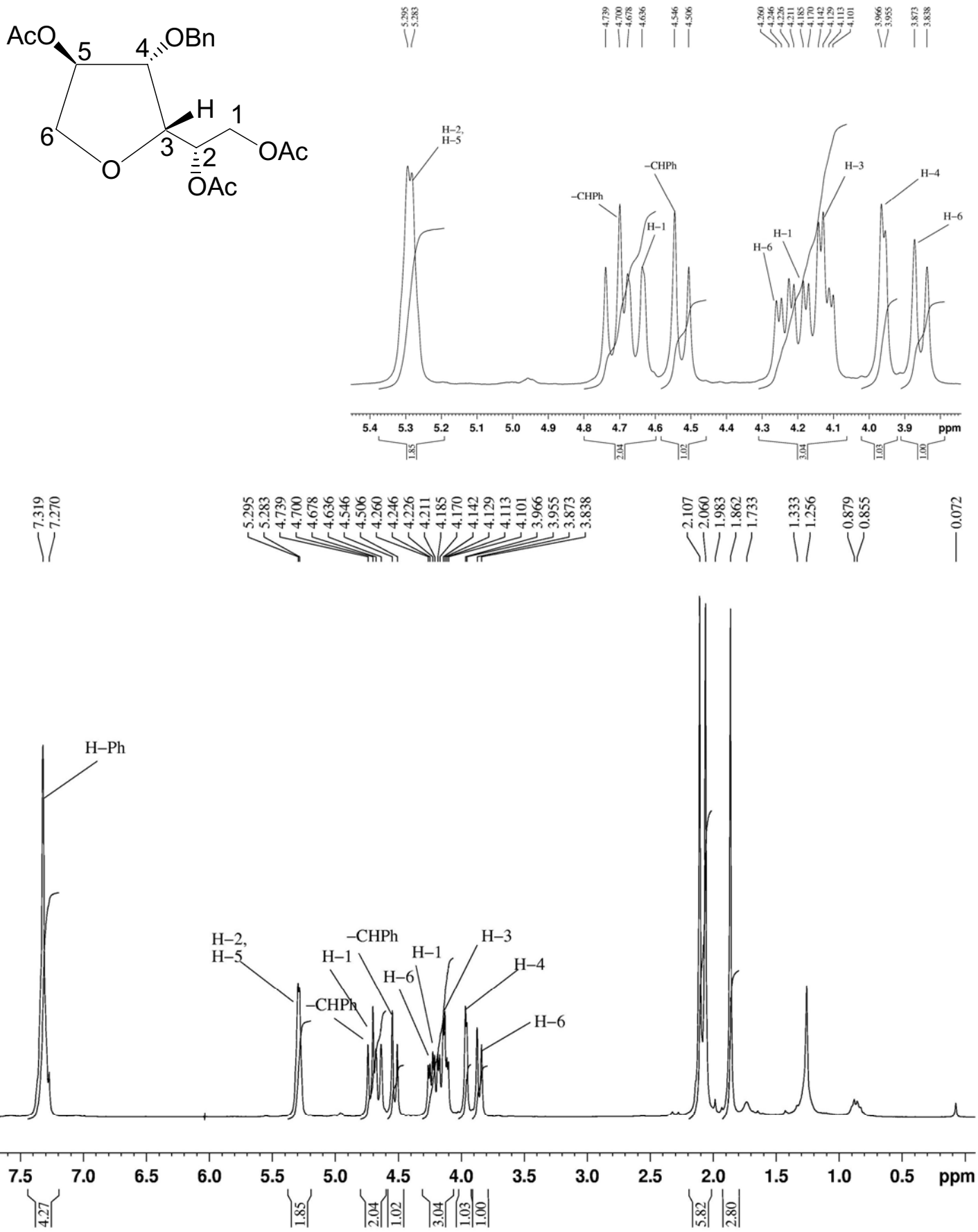


Fig. S-10: [1]H NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**

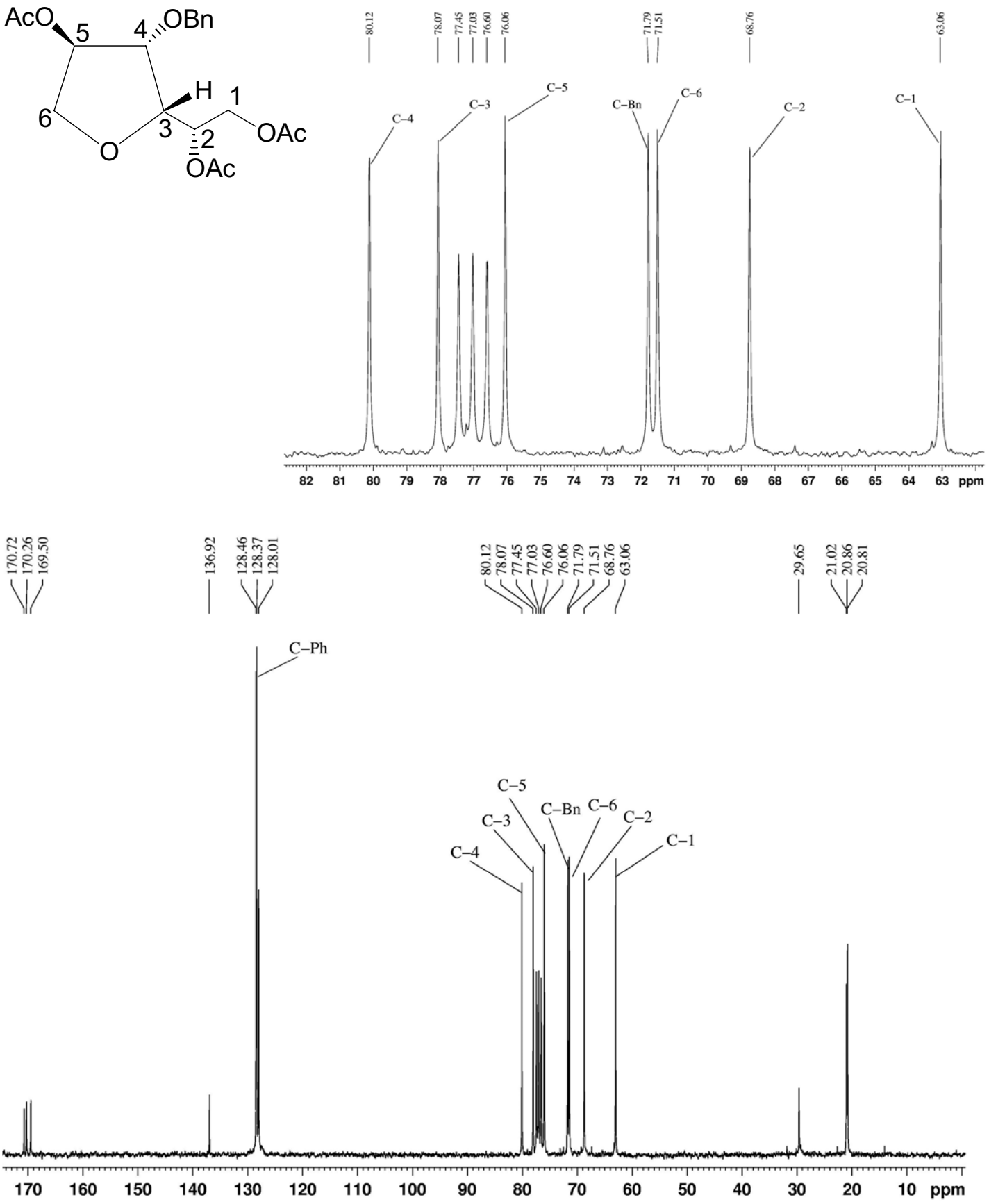


Fig. S-11: ^{13}C NMR Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**

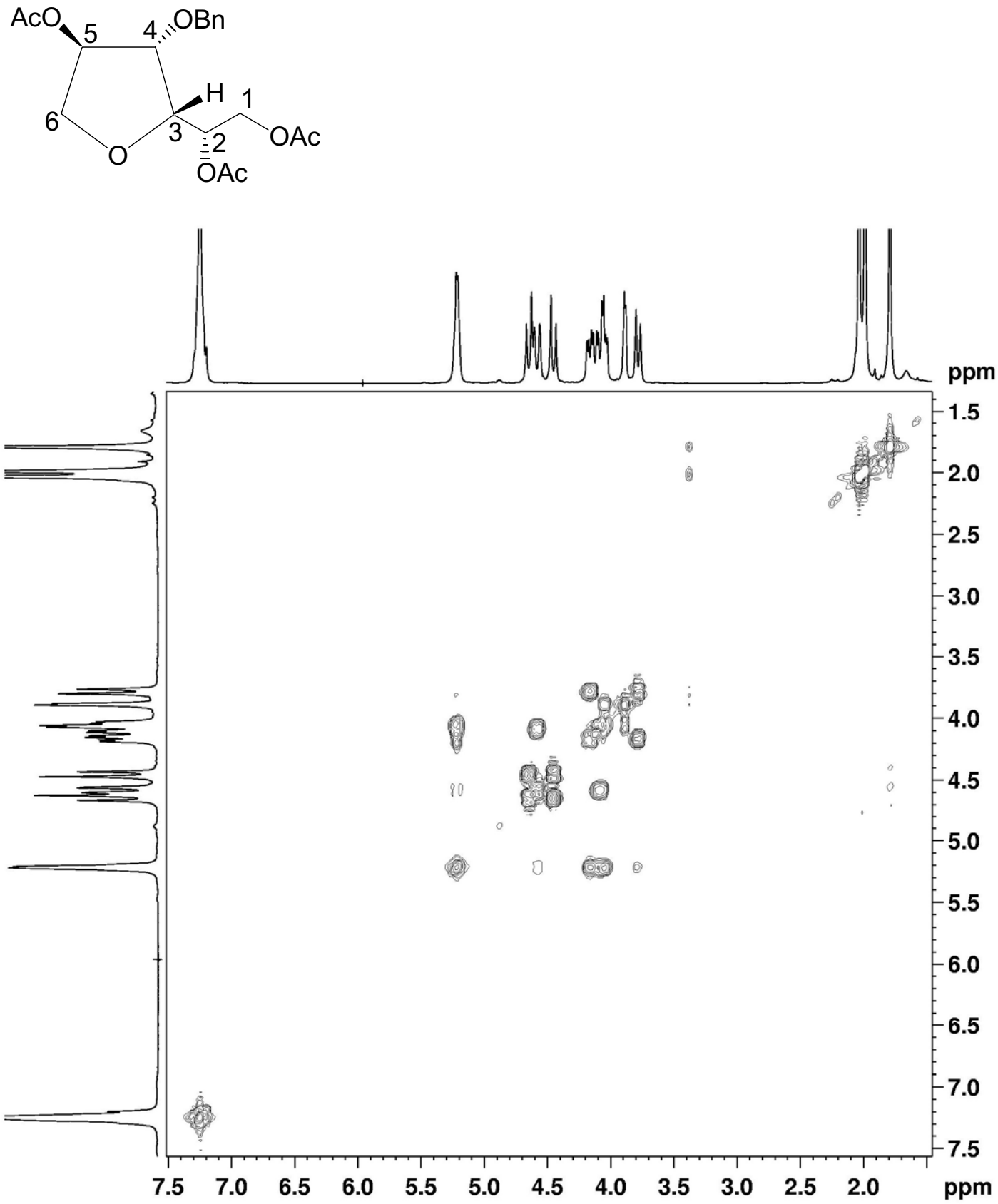


Fig. S-12: 2D COSY Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**

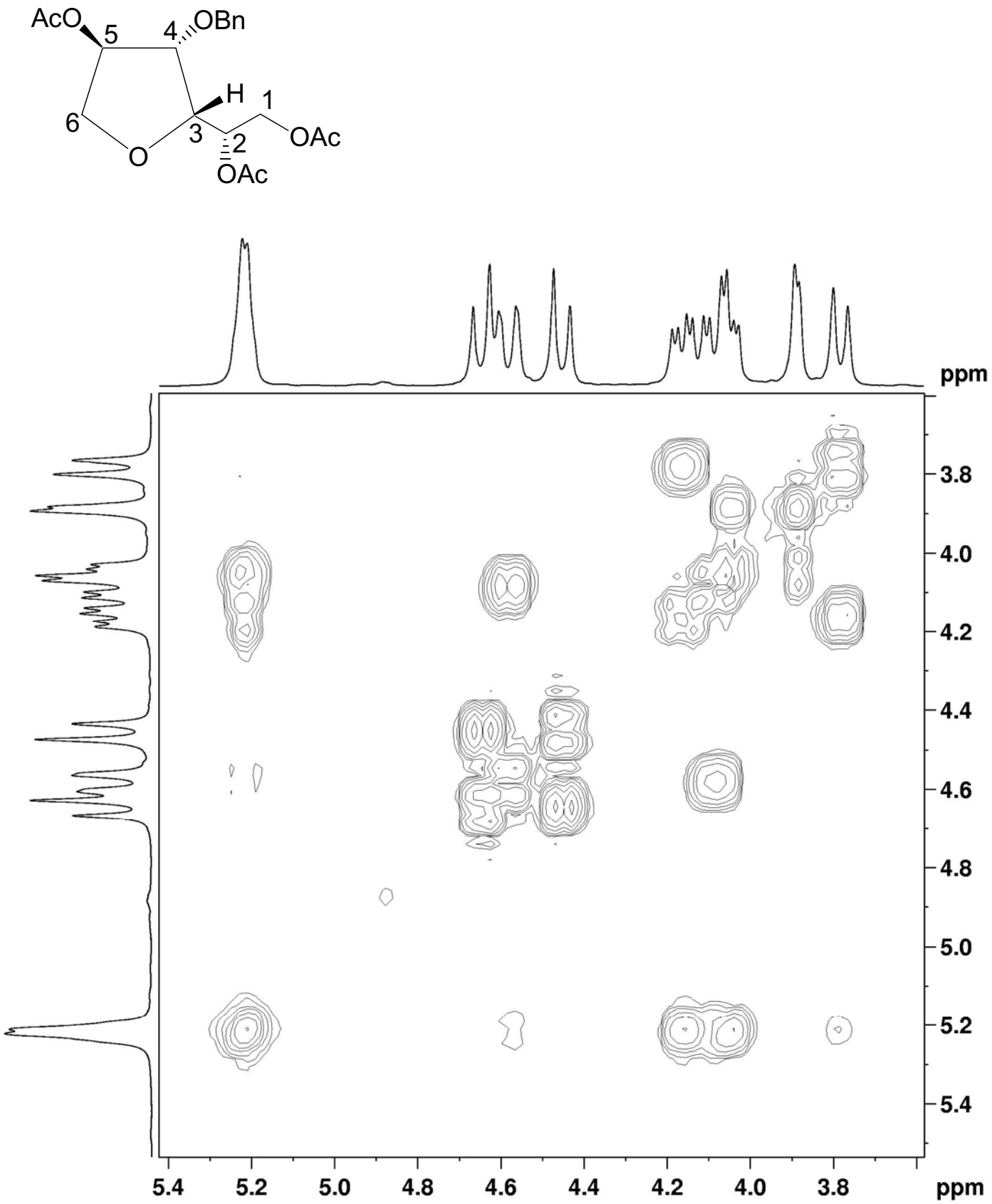
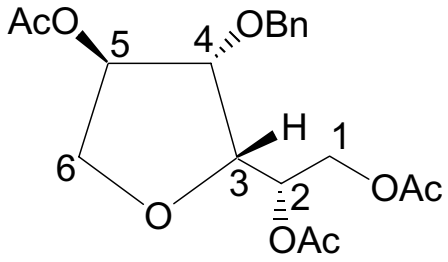


Fig. S-13: Expanded region of 2D COSY Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**



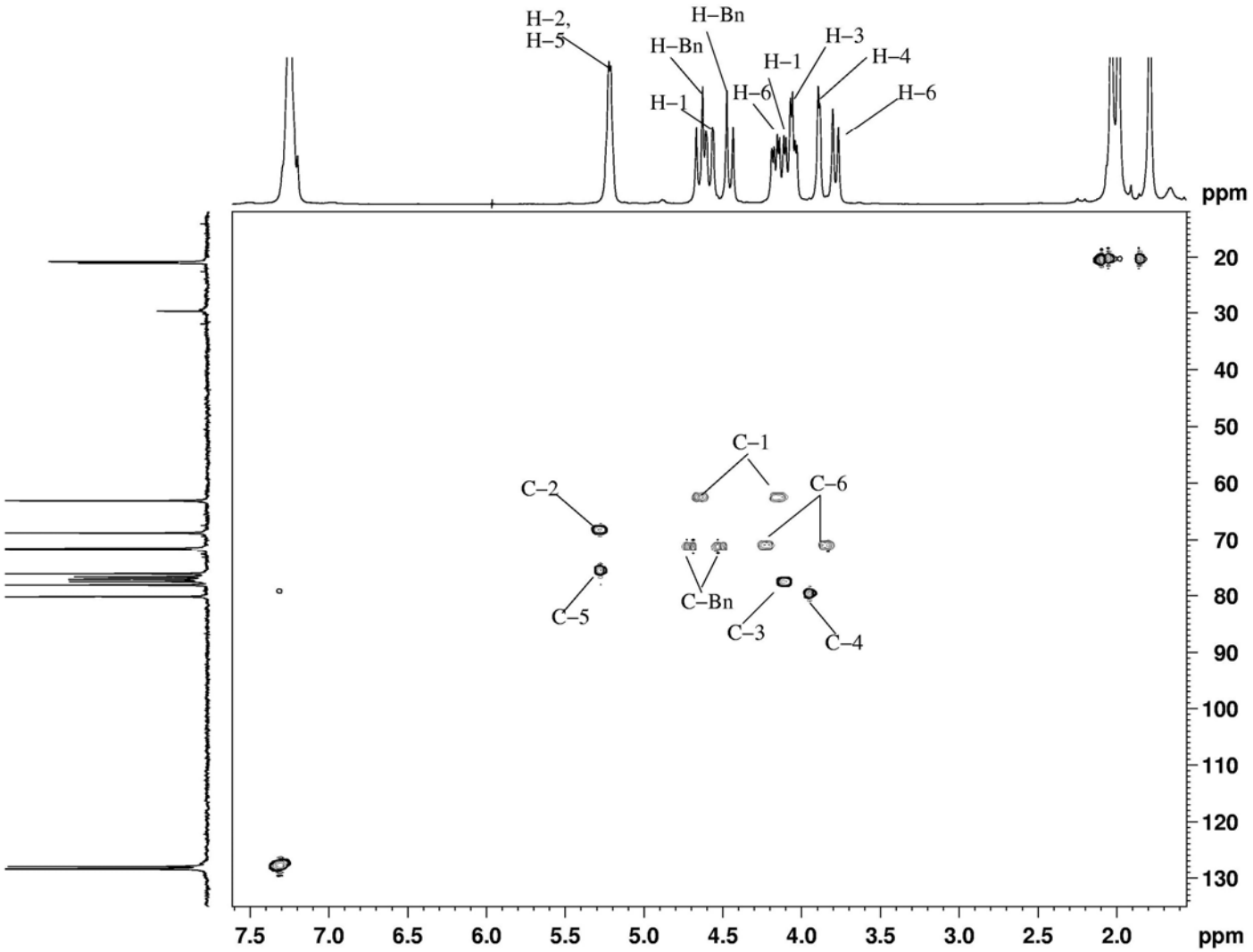
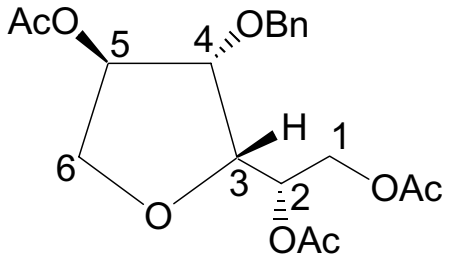


Fig. S-14: 2D HSQC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**



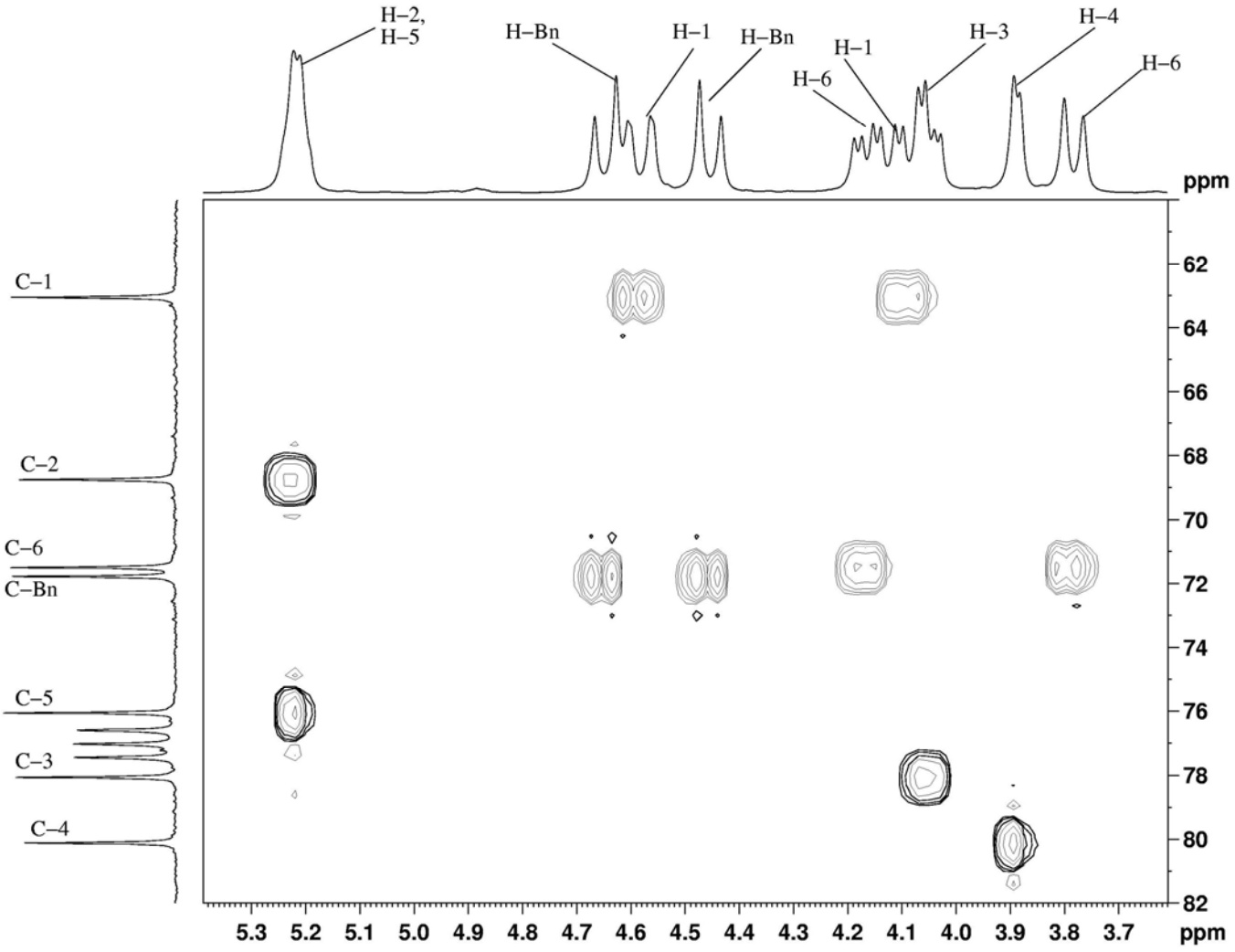


Fig. S-15: Expanded region of 2D HSQC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**

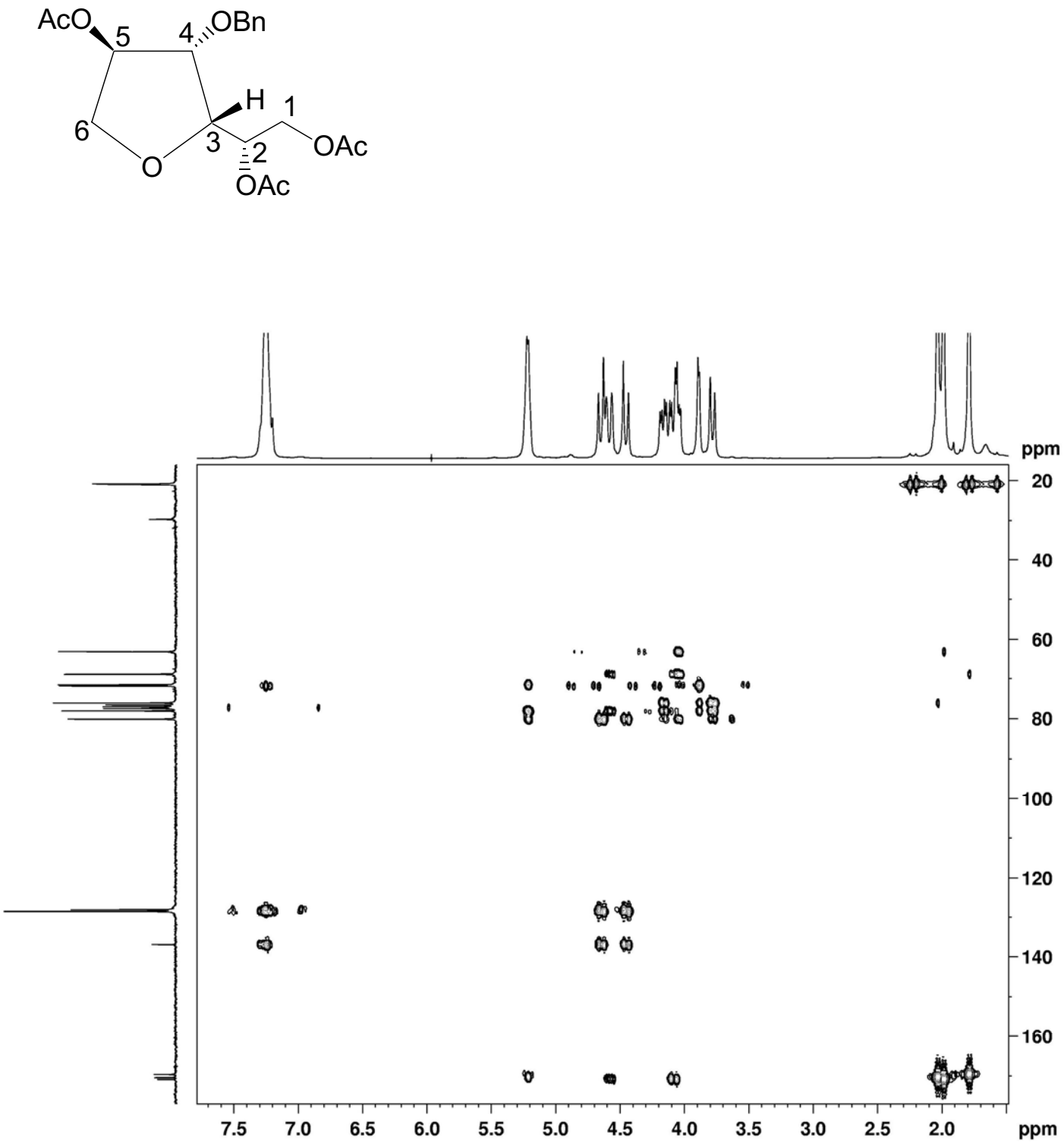
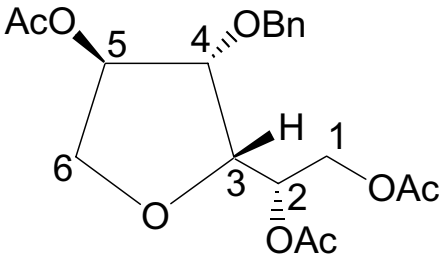


Fig. S-16: 2D HMBC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**



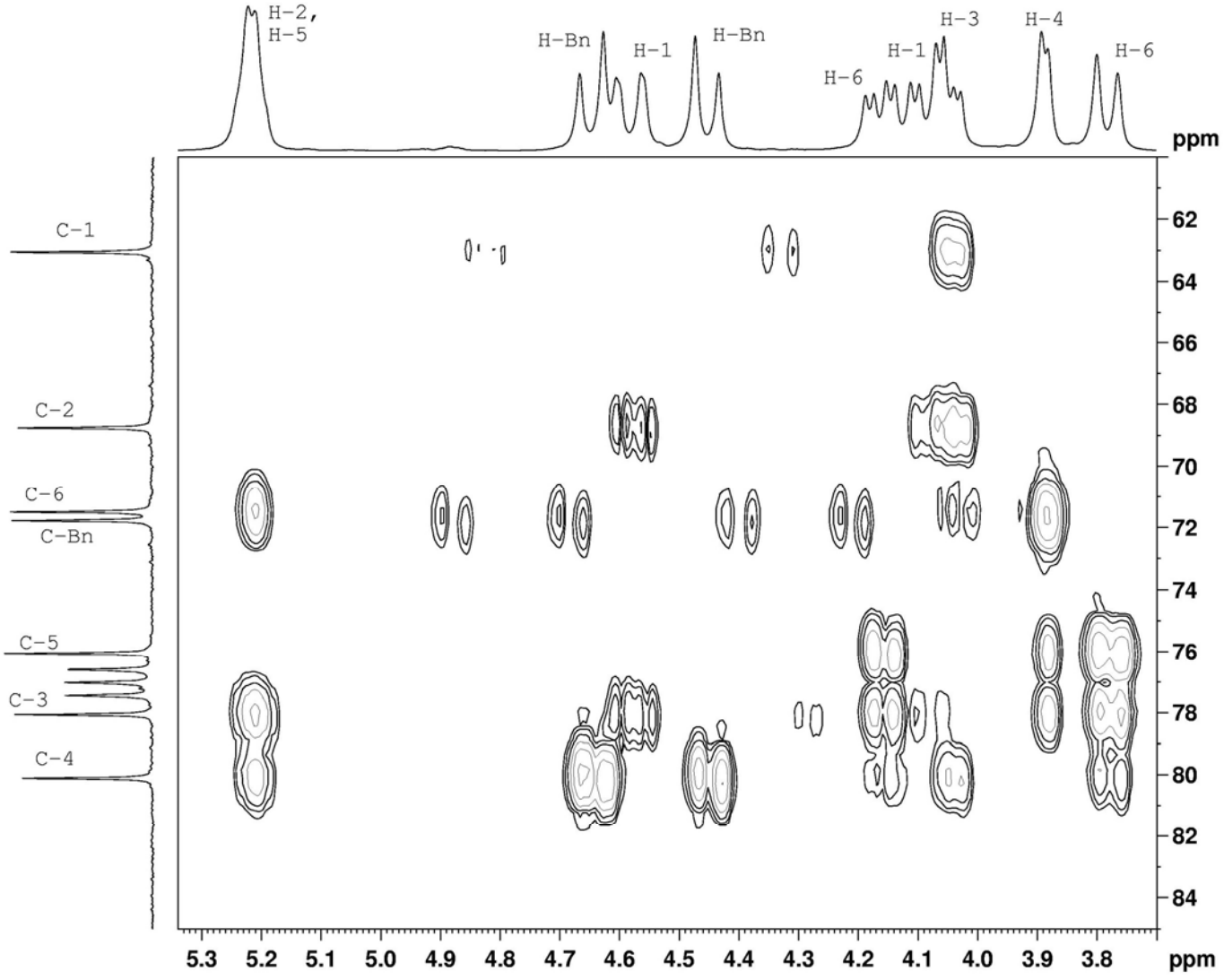


Fig. S-17: Expanded region of 2D HMBC Spectrum of (*2S, 3S, 4S, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-galactitol **(5a)**

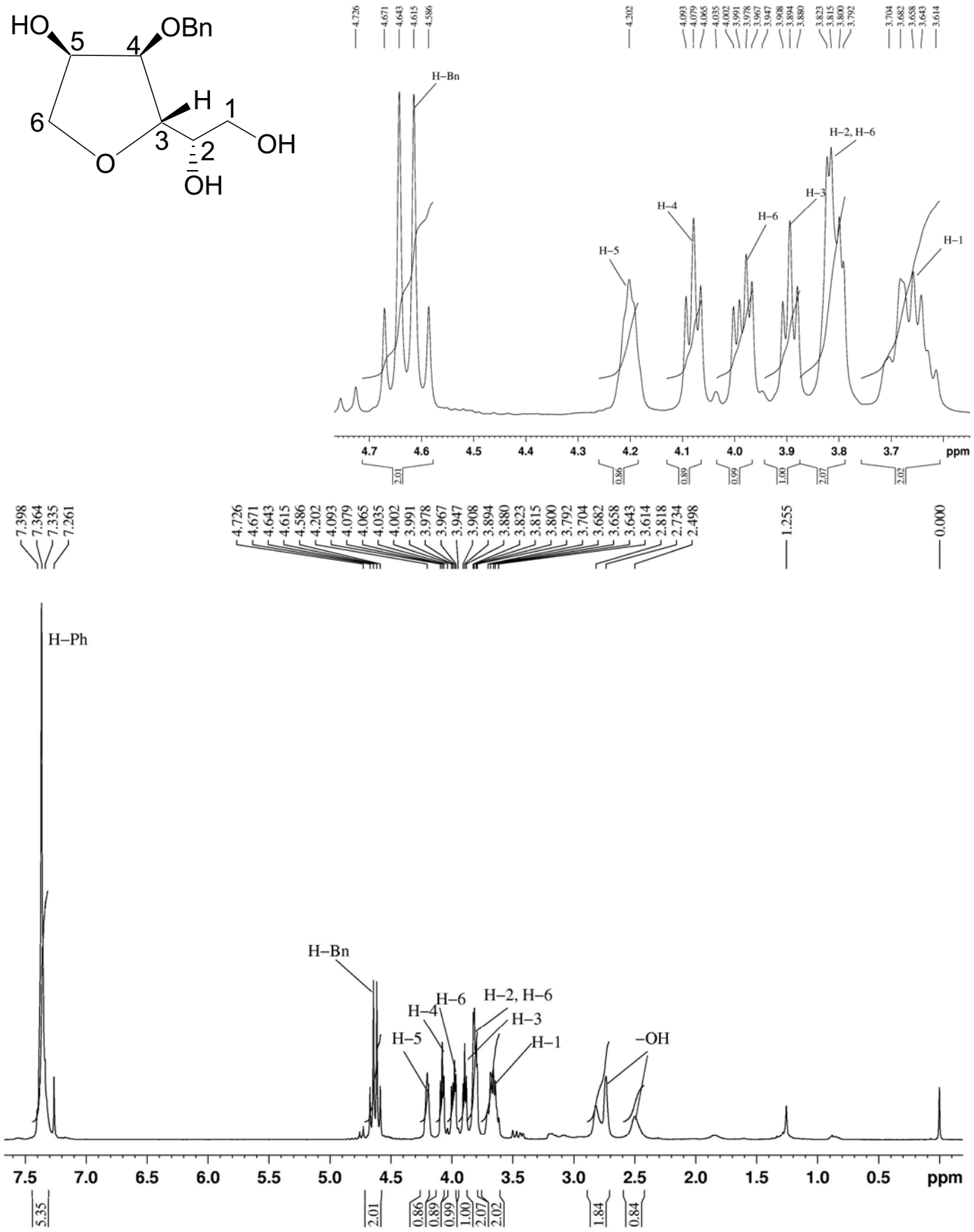


Fig. S-18: [1]H NMR Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)

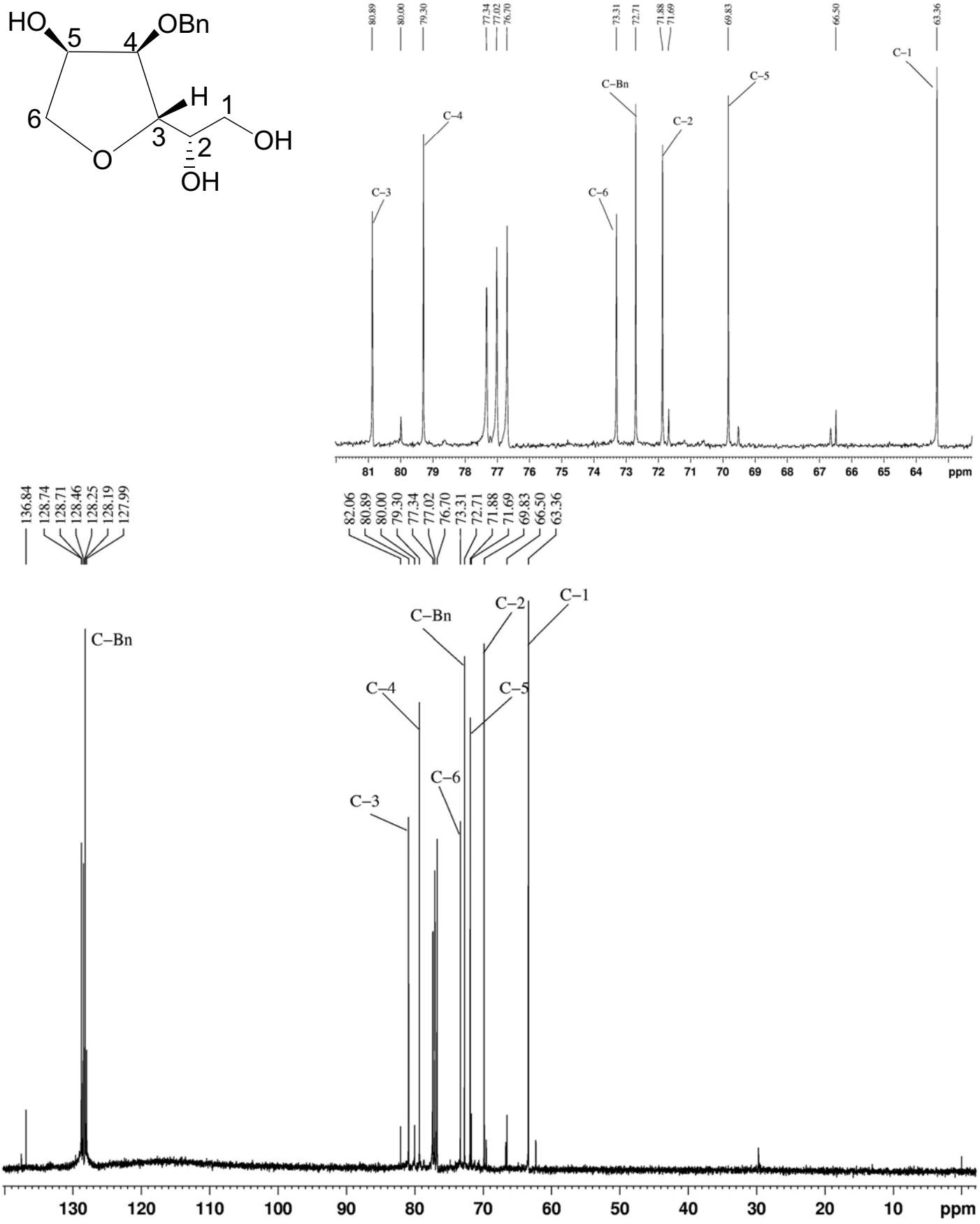
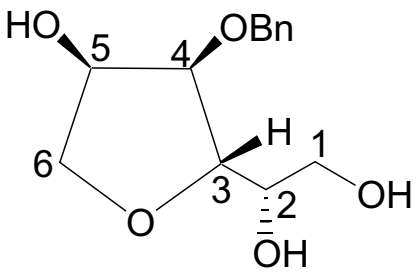


Fig. S-19: ^{13}C NMR Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)



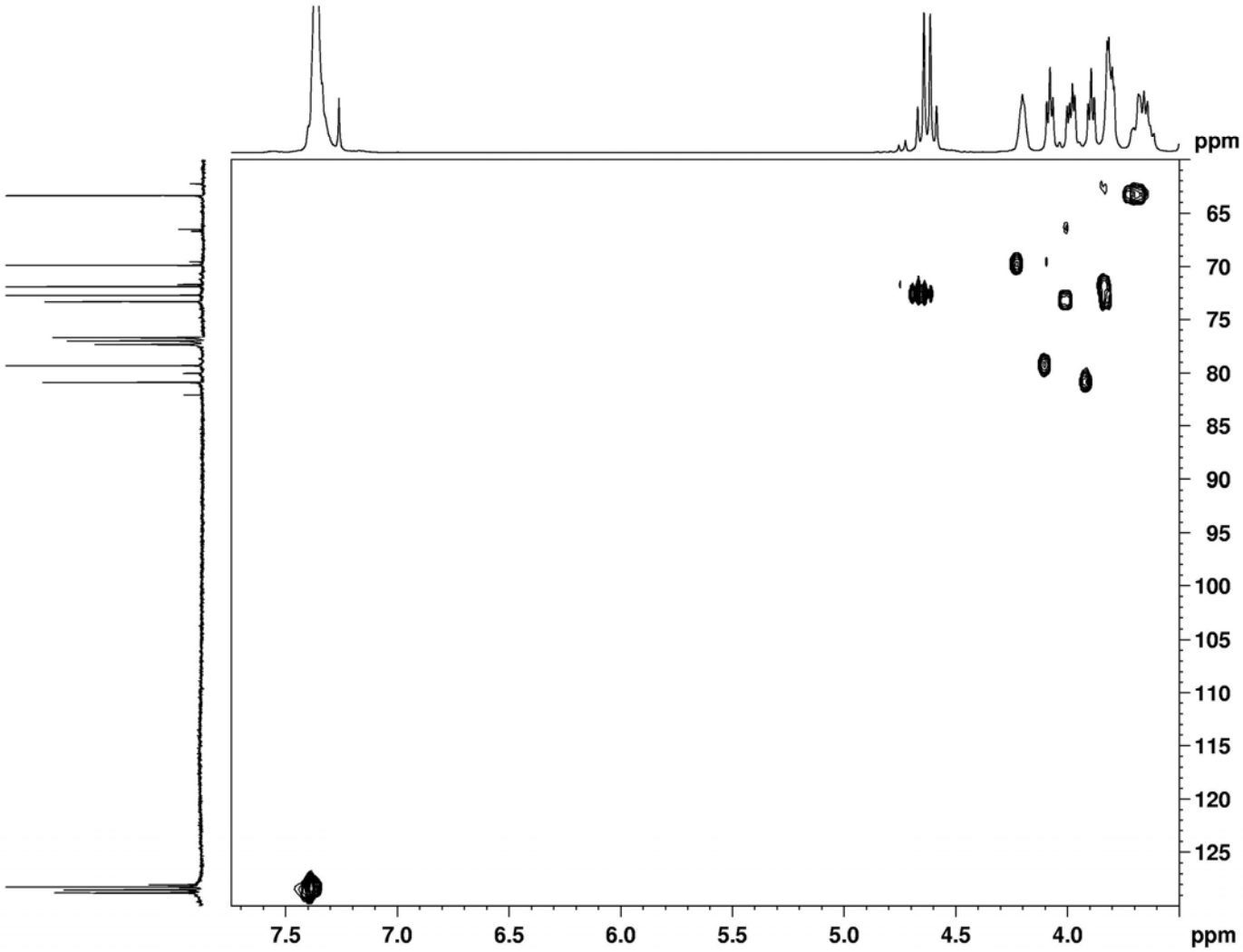
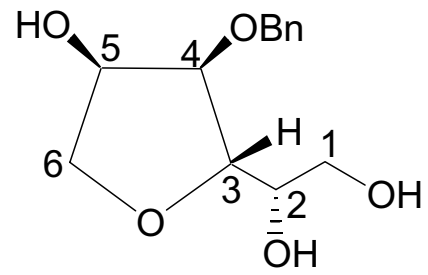


Fig. S-20: 2D HSQC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)



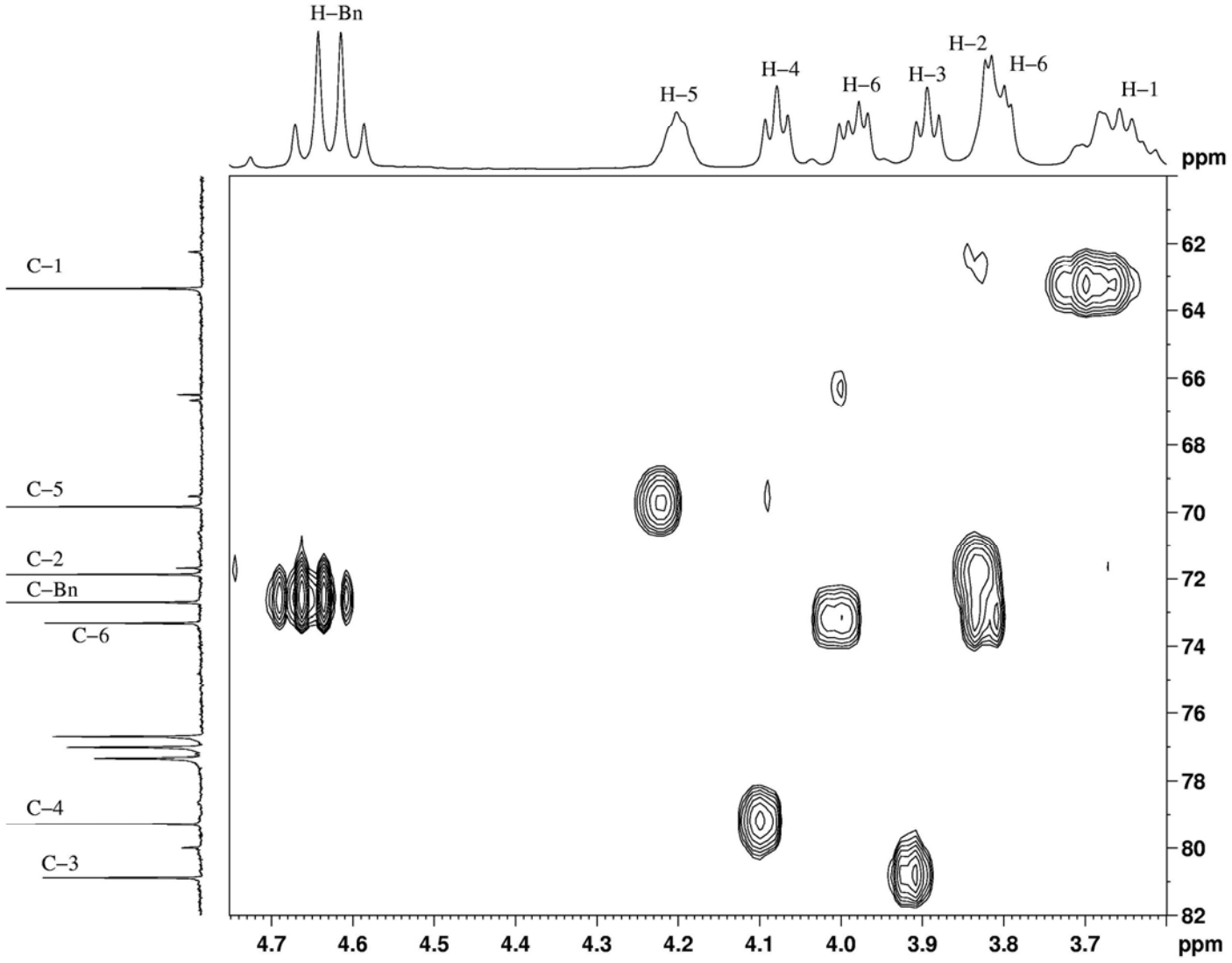


Fig. S-21: Expanded region of 2D HSQC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)

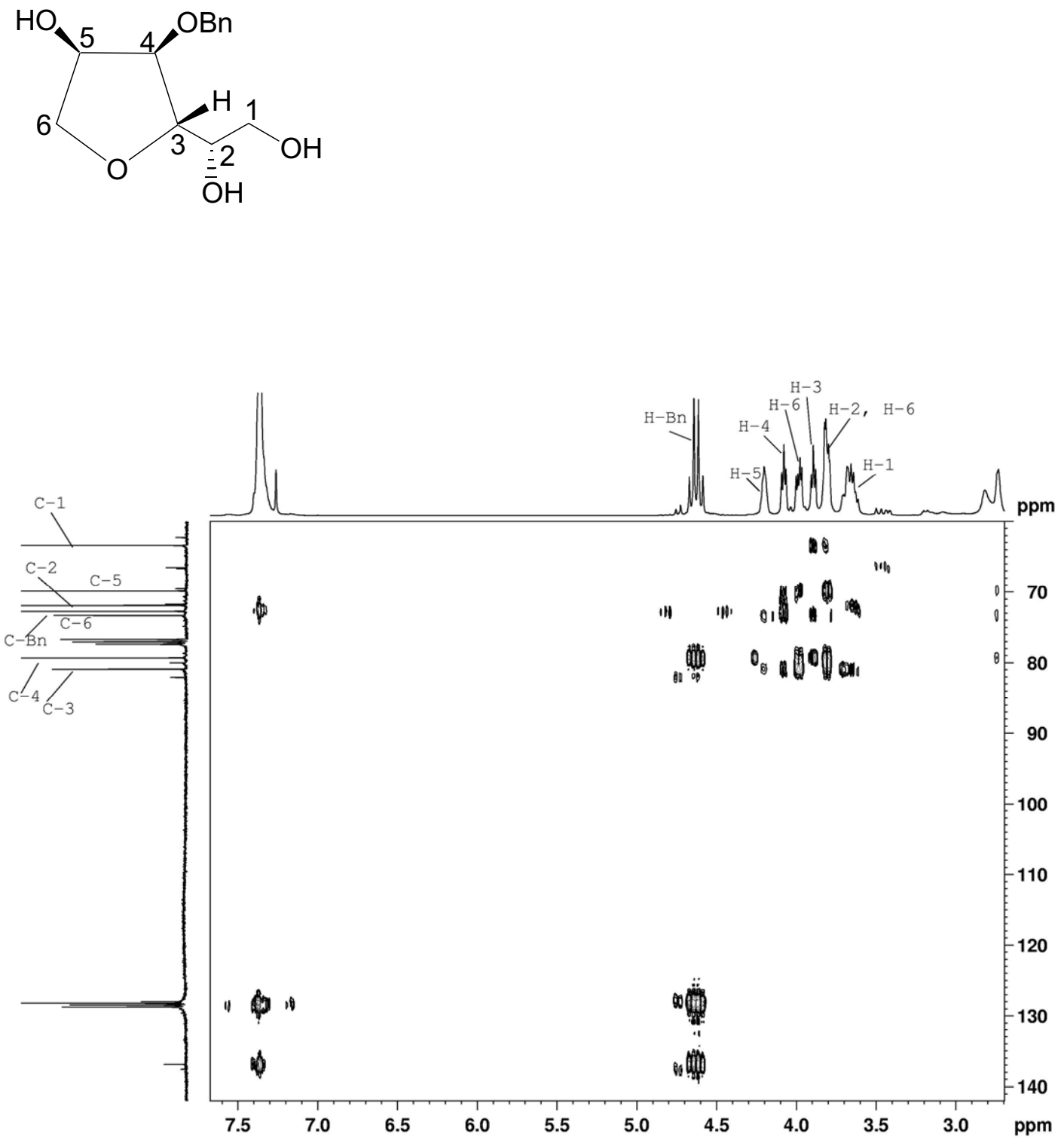
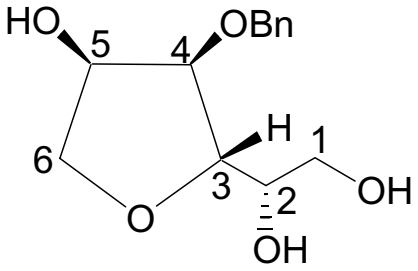


Fig. S-22: 2D HMBC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)



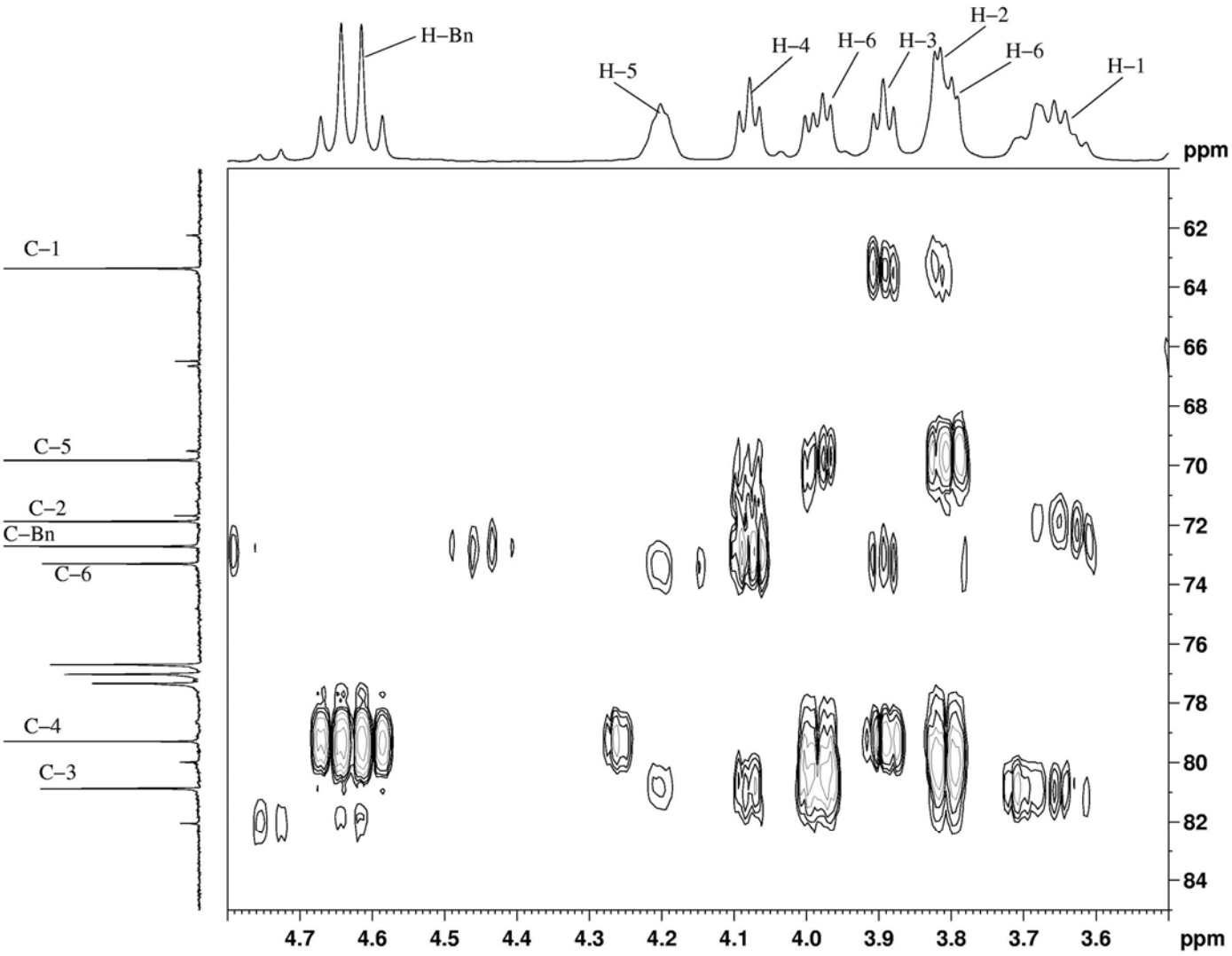


Fig. S-23: Expanded region of 2D HMBC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**9**)

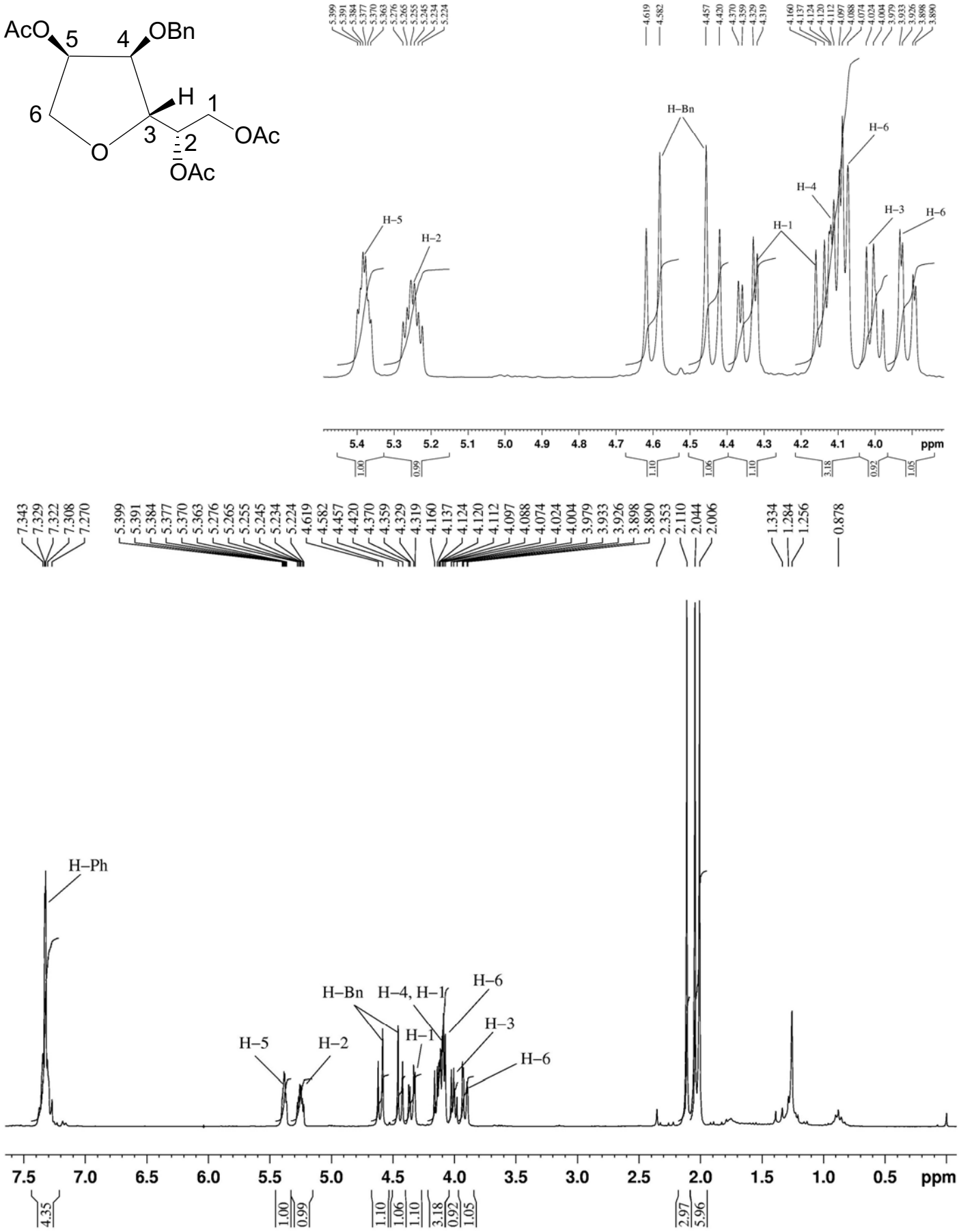


Fig. S-24: ^{1}H NMR Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl -D-glucitol (**9a**)

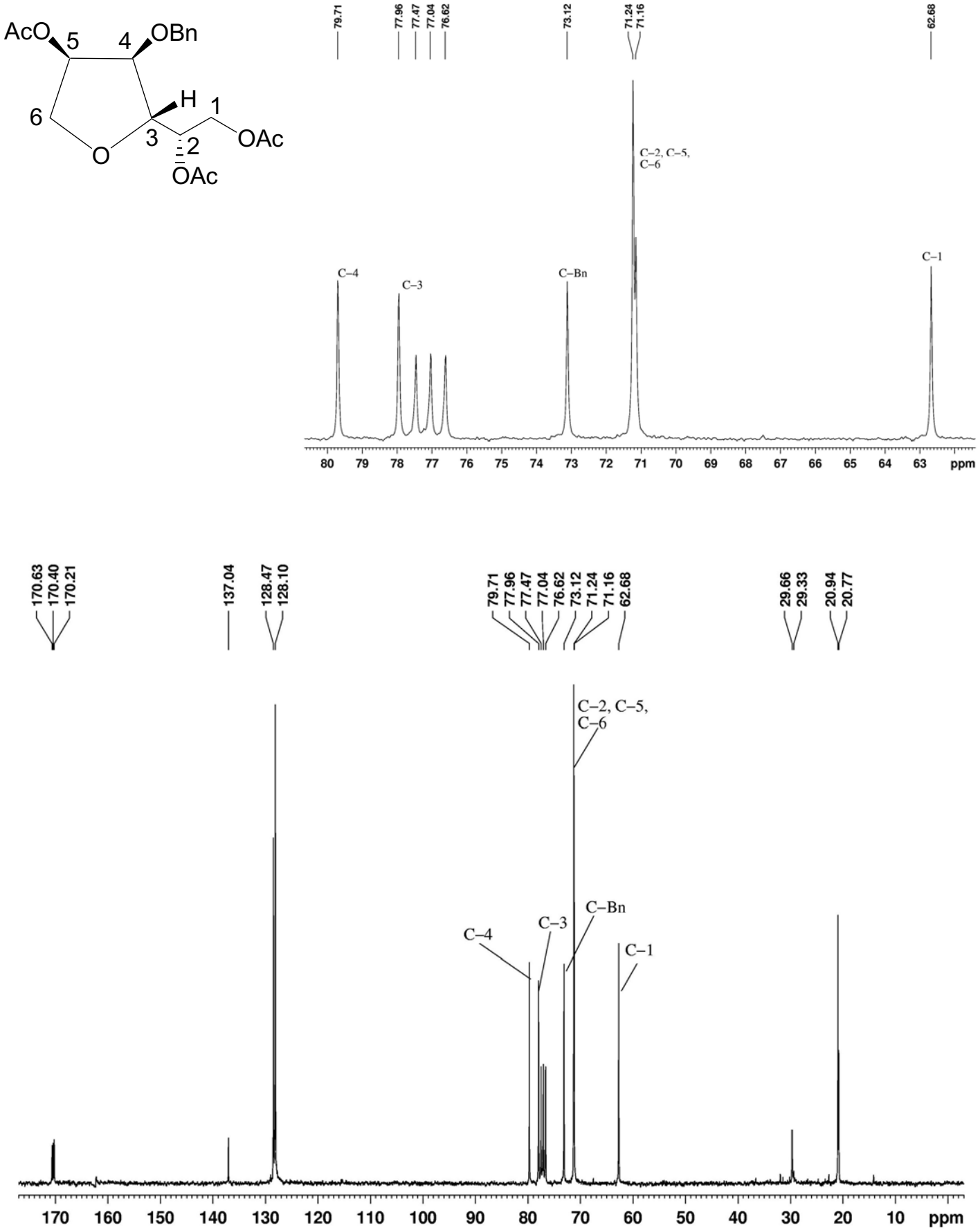


Fig. S-25: ^{13}C NMR Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl -D-glucitol (**9a**)

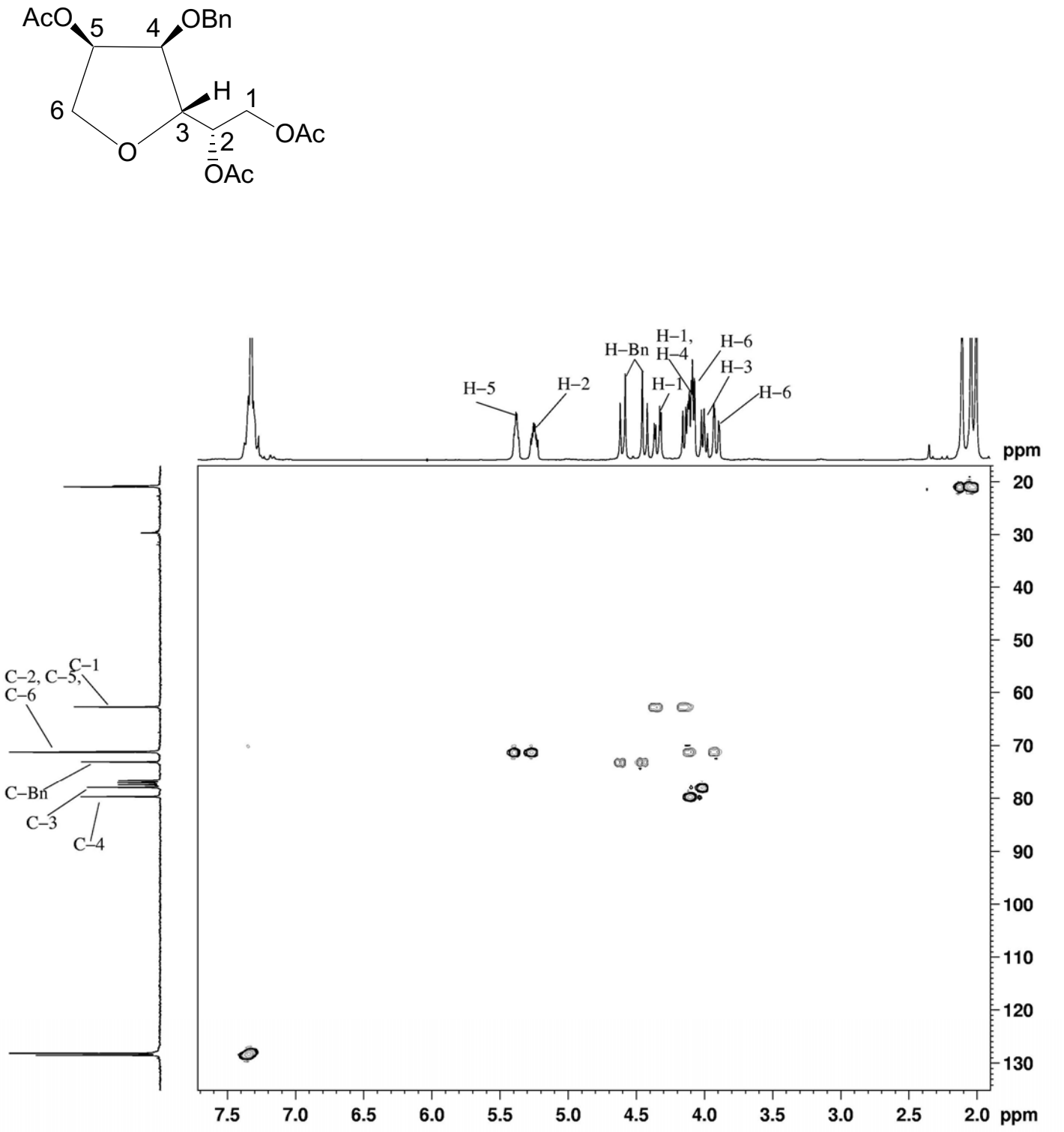
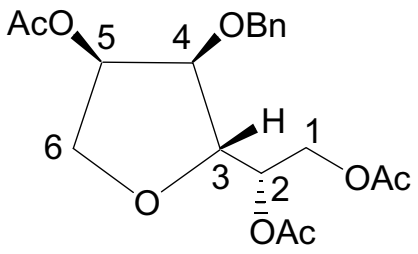


Fig. S-26: 2D HSQC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl -D-glucitol (**9a**)



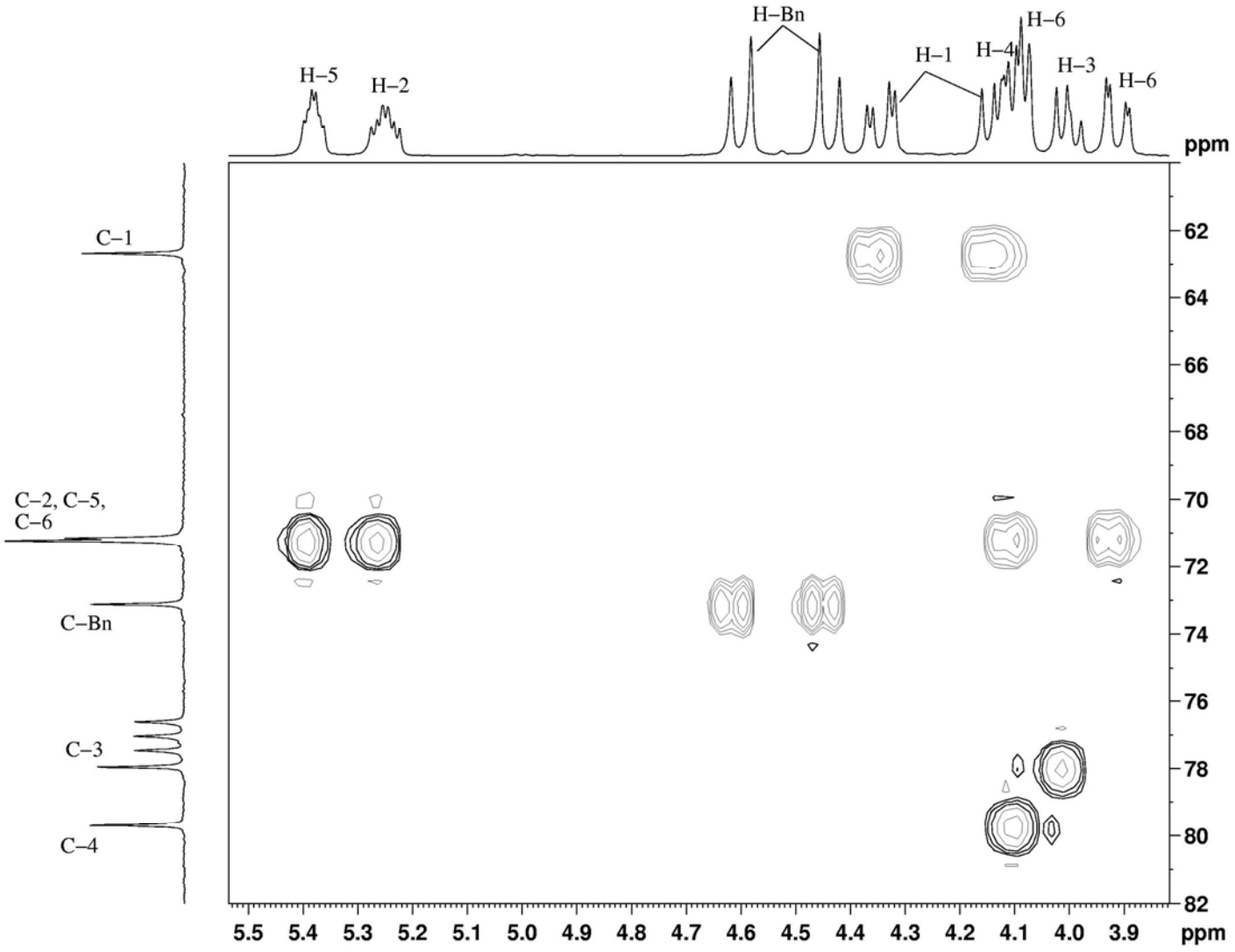
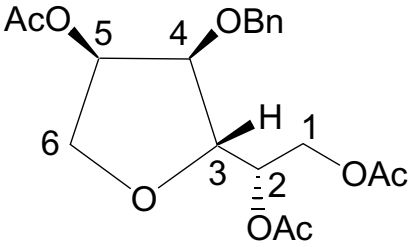


Fig. S-27: Expanded region of 2D HSQC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-glucitol (**9a**)



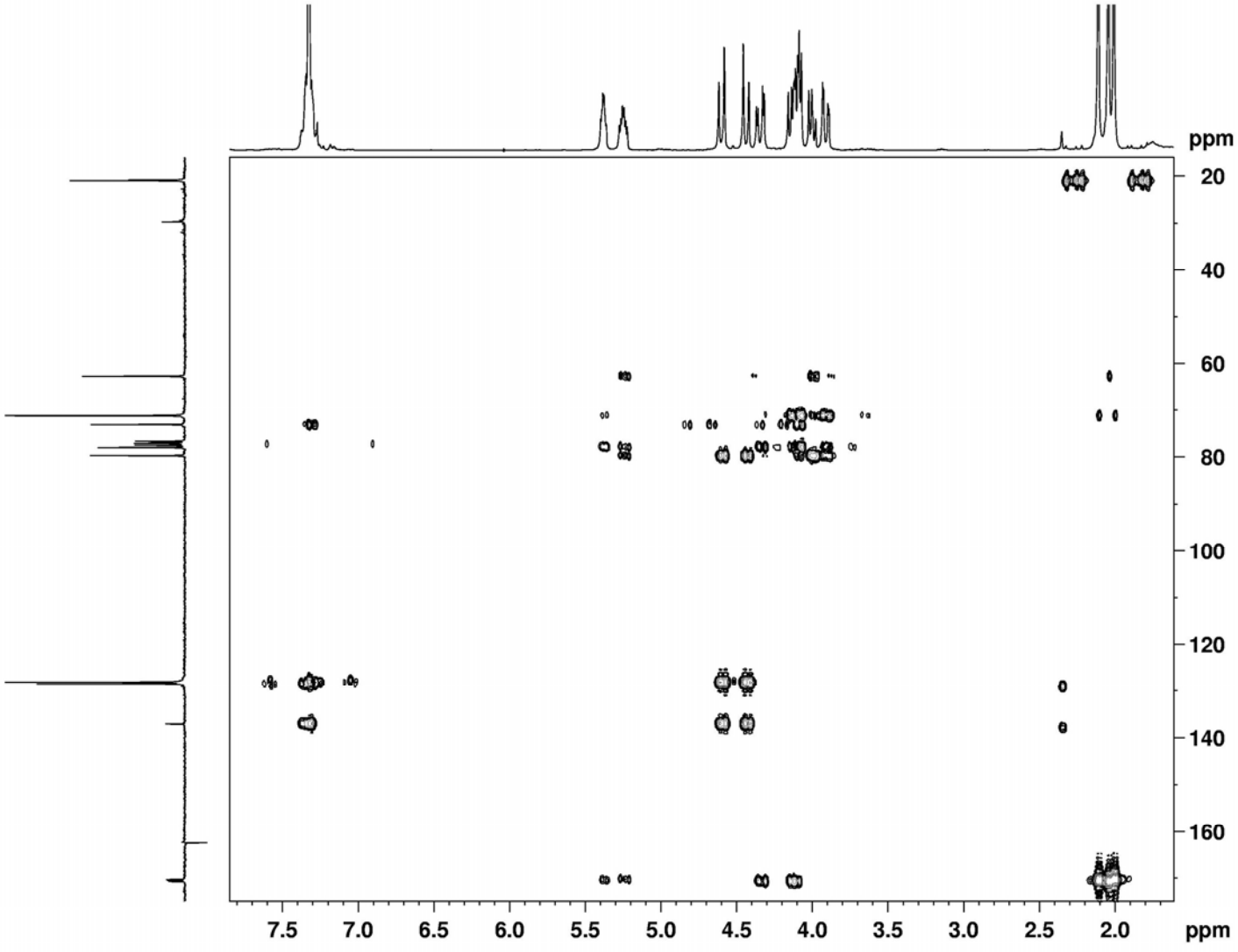


Fig. S-28: 2D HMBC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl -D-glucitol (**9a**)

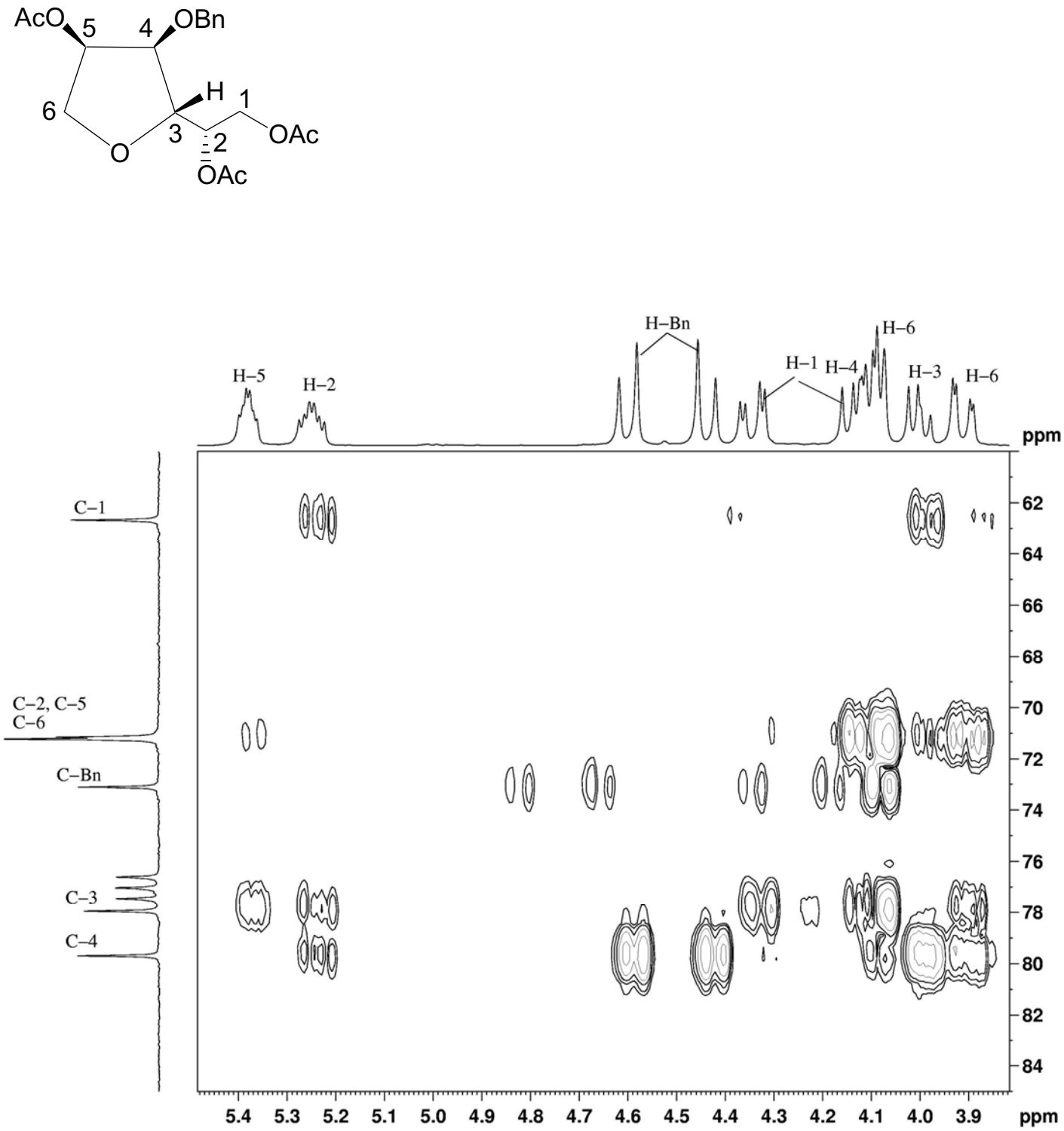


Fig. S-29: Expanded region of 2D HMBC Spectrum of (*2S, 3S, 4R, 5R*) 3,6-Anhydro-1,2,5-tri-*O*-acetyl-4-*O*-benzyl-D-glucitol (**9a**)

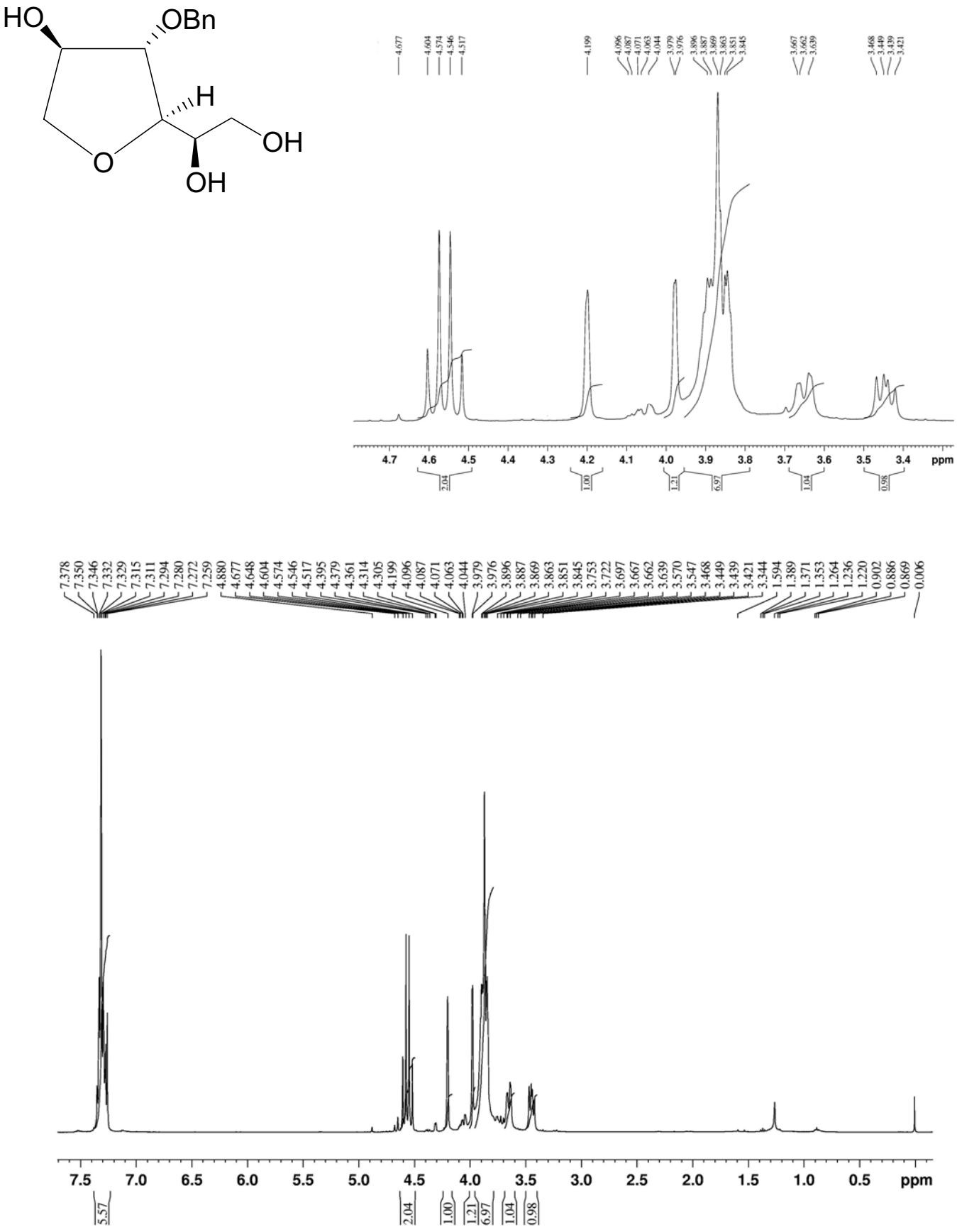


Fig. S-30: ^{1}H NMR Spectrum of (*2R, 3R, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**7**)

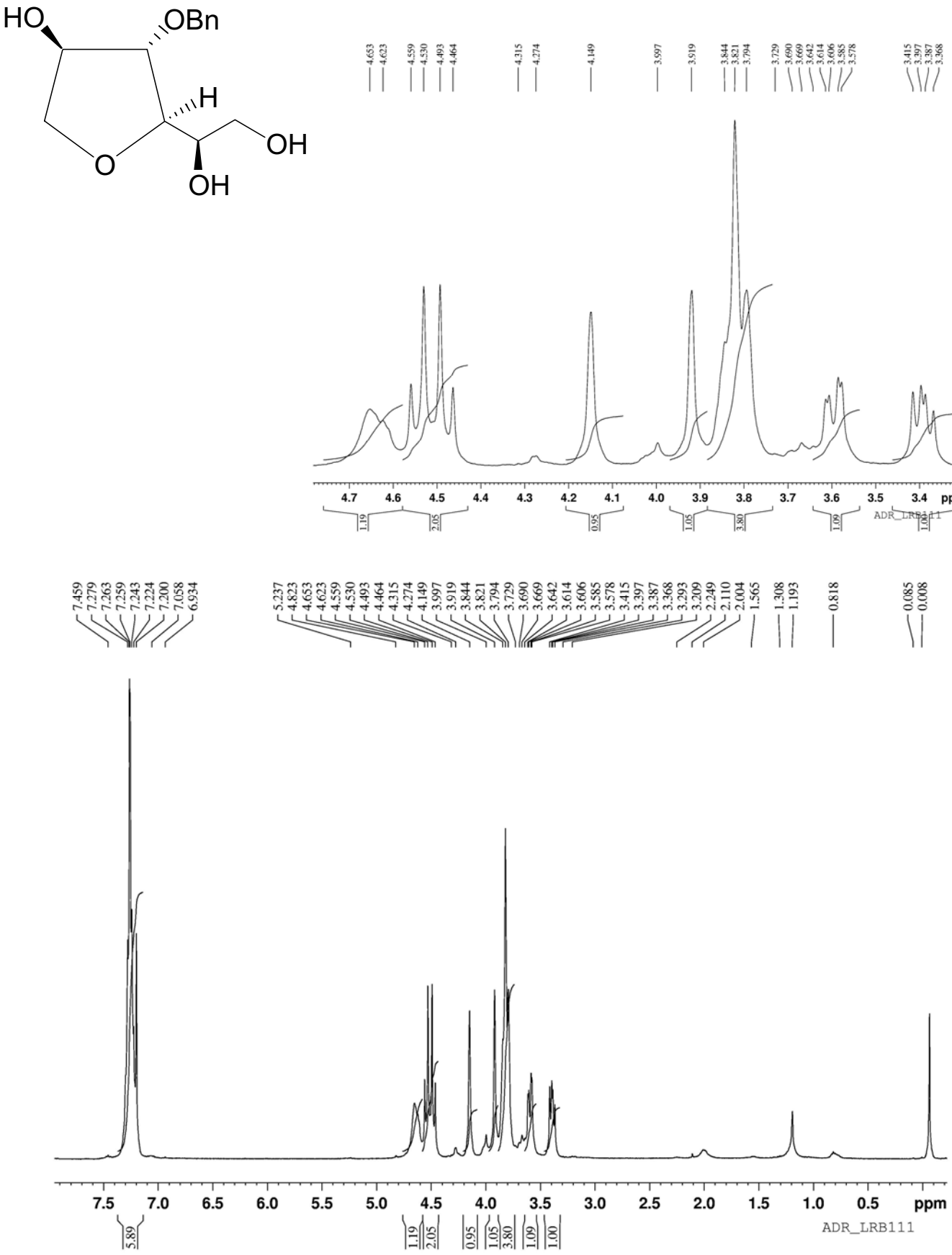


Fig. S-31: ^{1}H NMR Spectrum (D_2O Shake) of (*2R, 3R, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**7**)

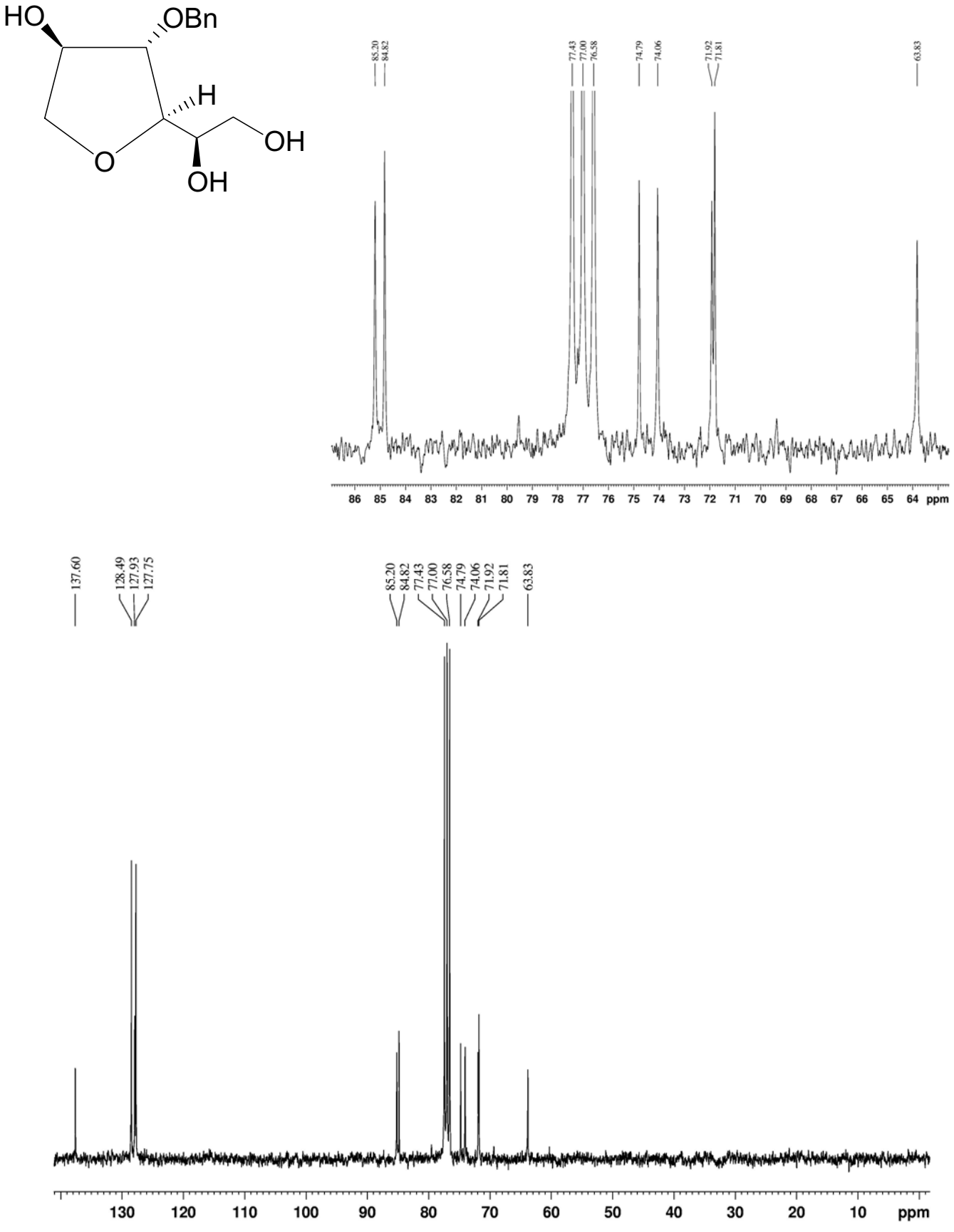


Fig. S-32: ^{13}C NMR Spectrum of (*2R, 3R, 4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**7**)

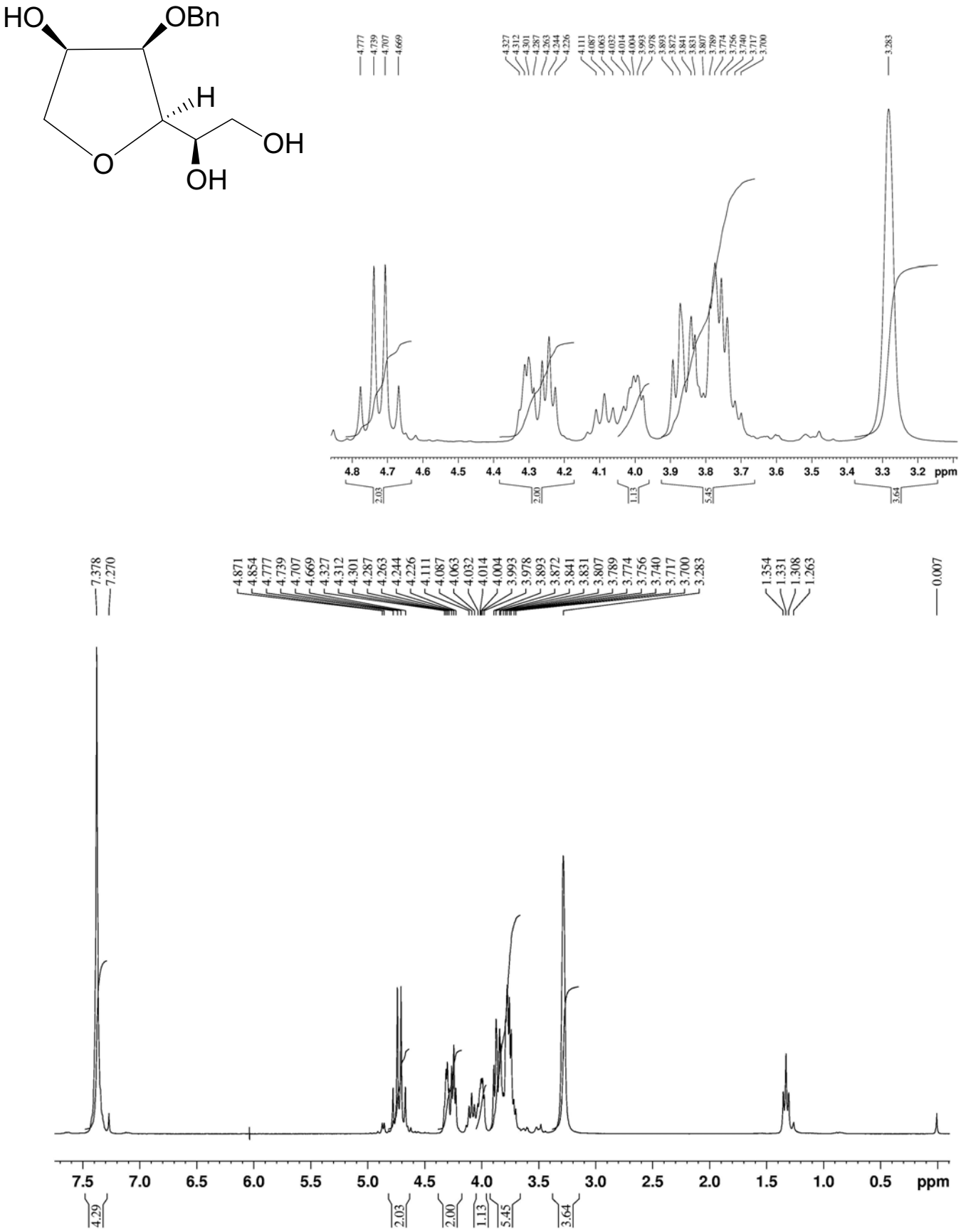


Fig. S-33: ^{1}H NMR Spectrum of (*2R, 3R, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**11**)

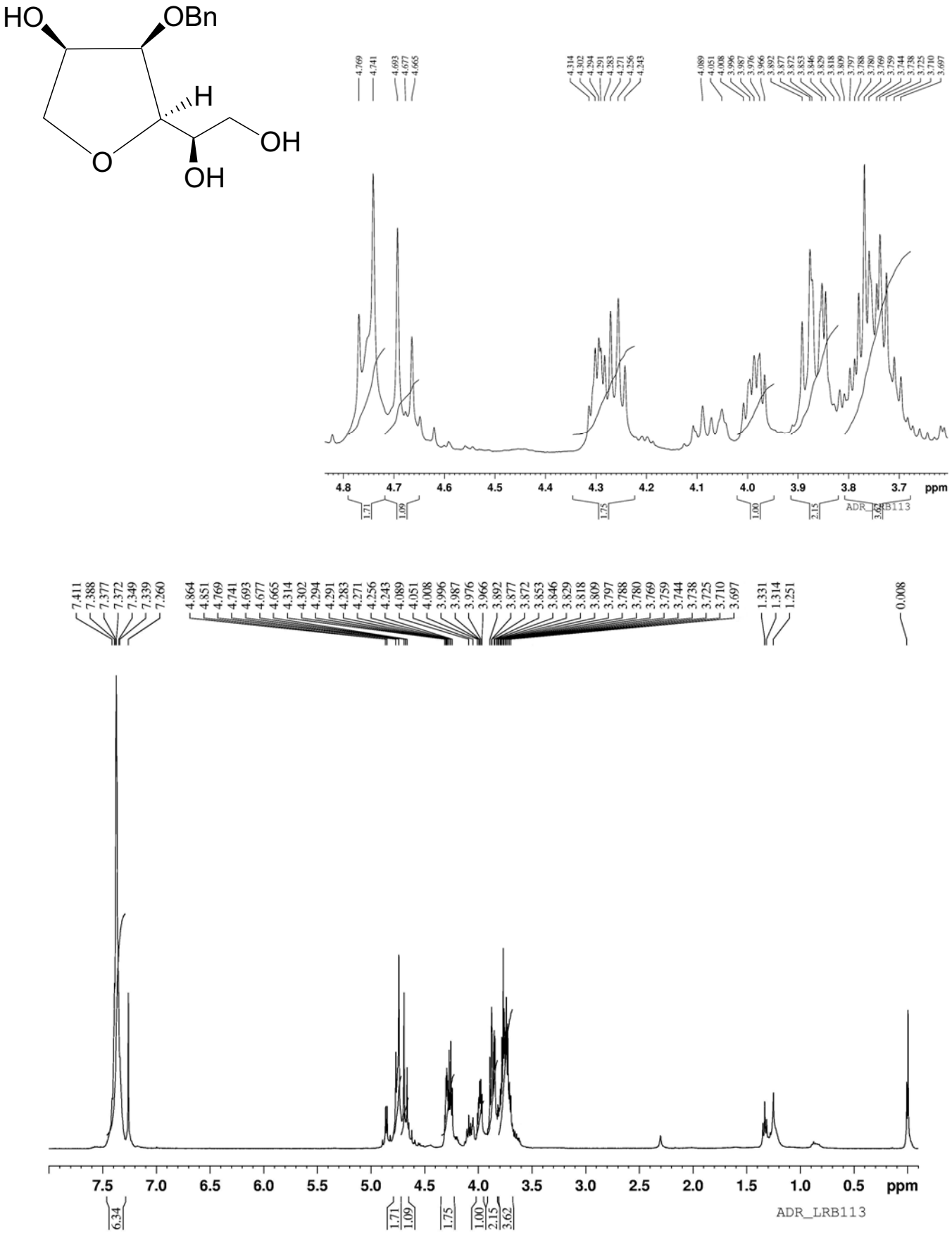


Fig. S-34: ^{1}H NMR Spectrum (D_2O Shake)of (*2R, 3R, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**11**)

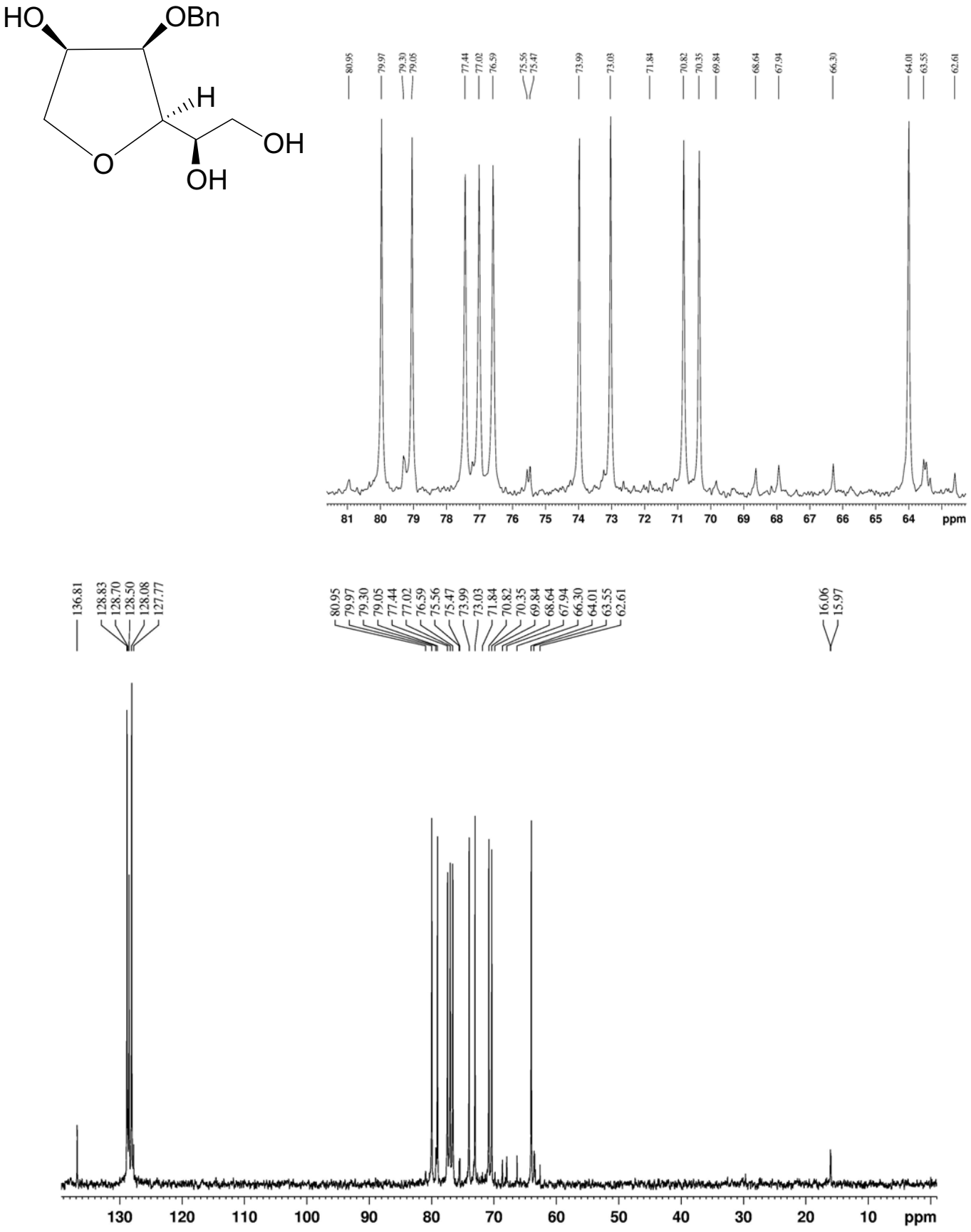


Fig. S-35: ^{13}C NMR Spectrum of (*2R, 3R, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol (**11**)

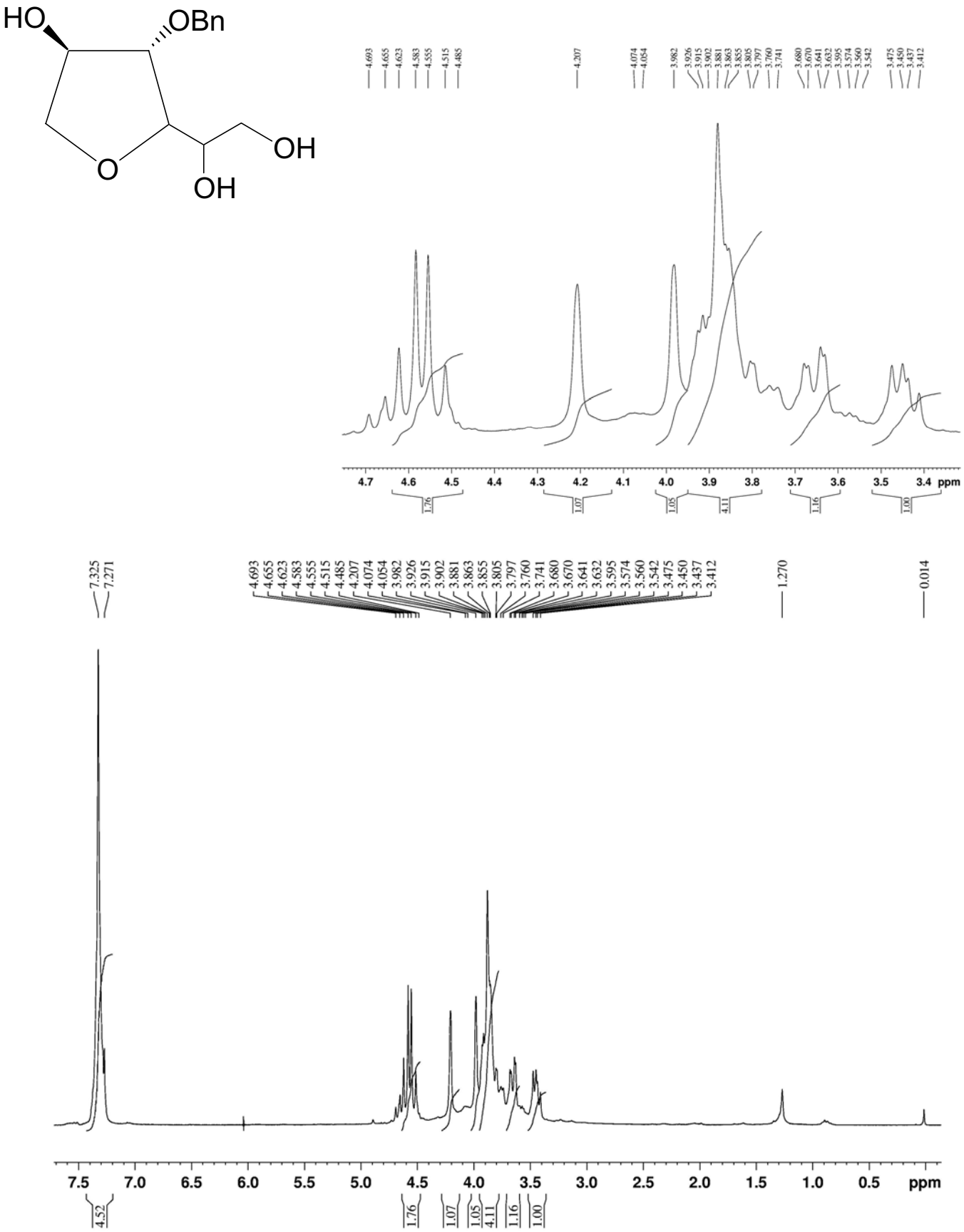


Fig. S-36: [1]H NMR Spectrum (*4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(13)**

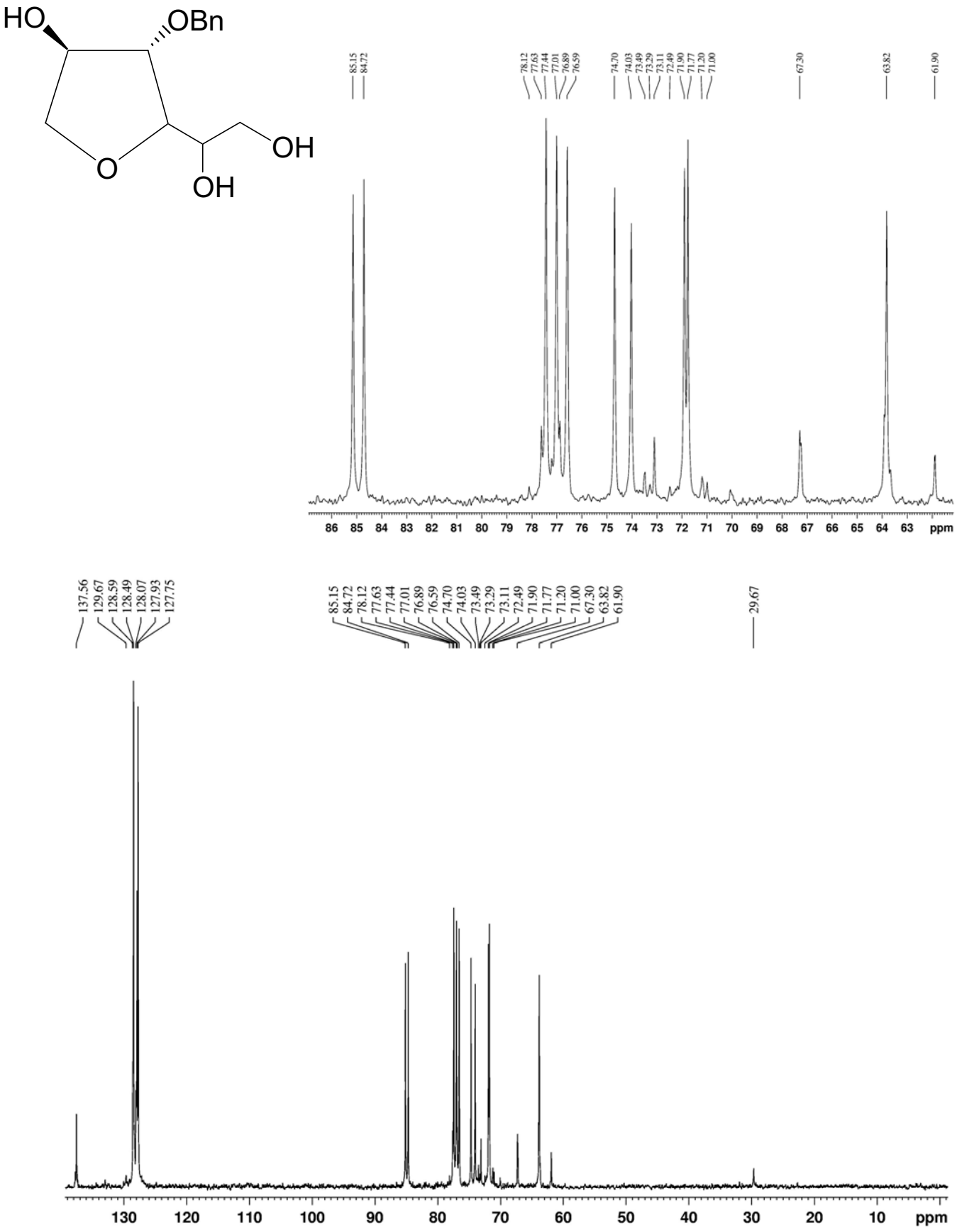


Fig. S-37: ^{13}C NMR Spectrum (*4S, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-galactitol **(13)**

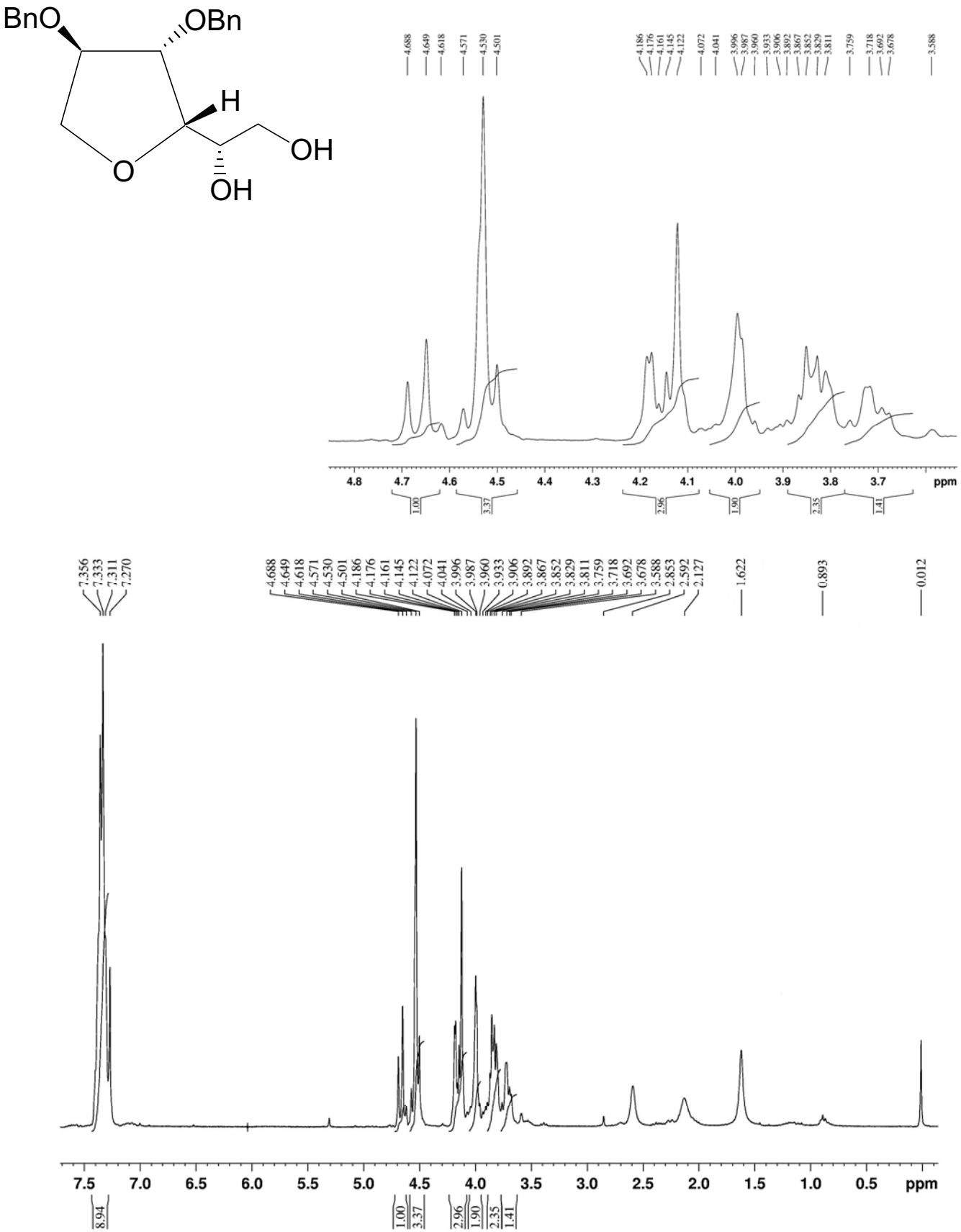


Fig. S-38: ^{1}H NMR Spectrum (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4,5-di-*O*-benzyl-D-galactitol (**17**)

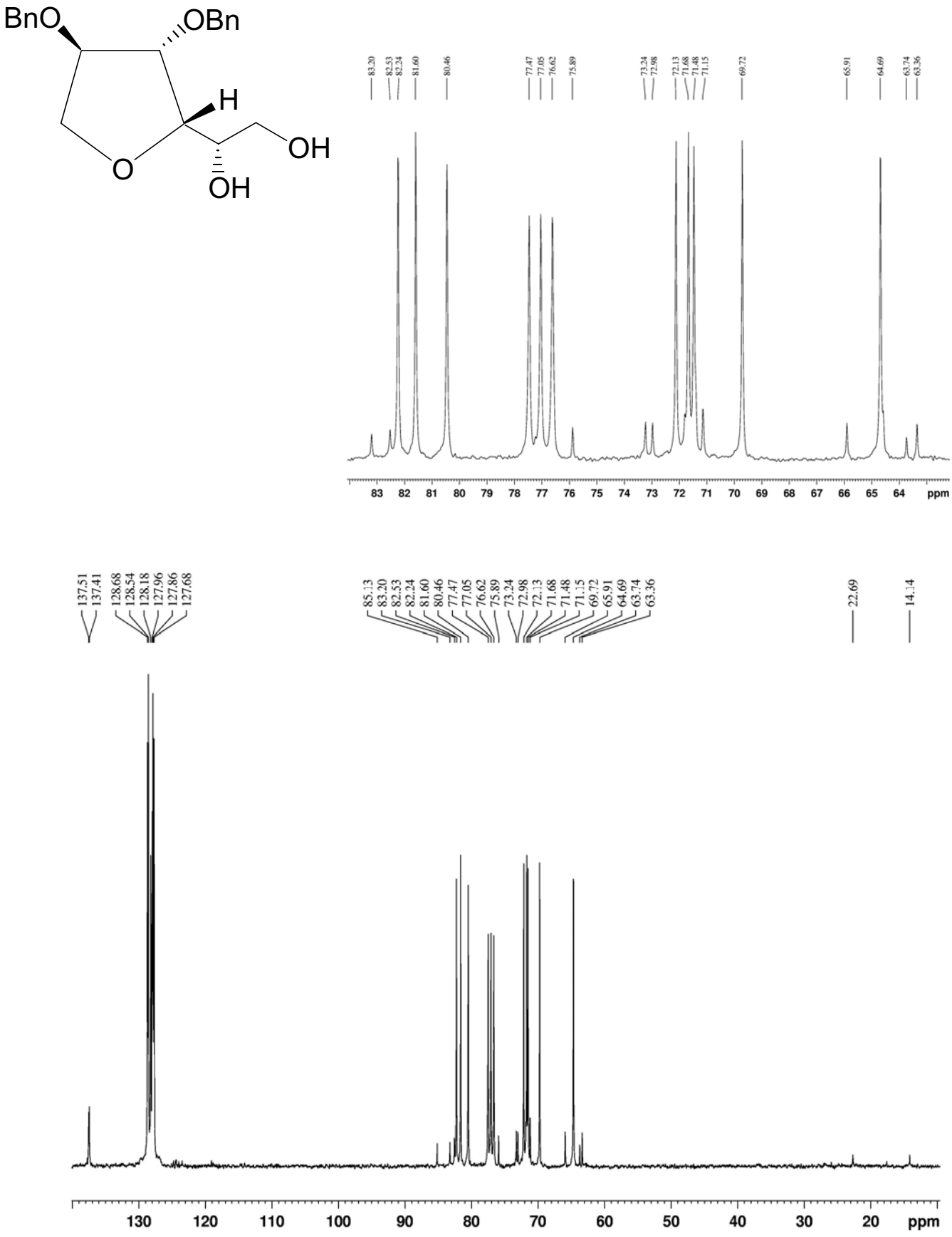


Fig. S-39: ^{13}C NMR Spectrum (*2S, 3S, 4S, 5R*) 3,6-Anhydro-4,5-di-*O*-benzyl-D-galactitol (**17**)

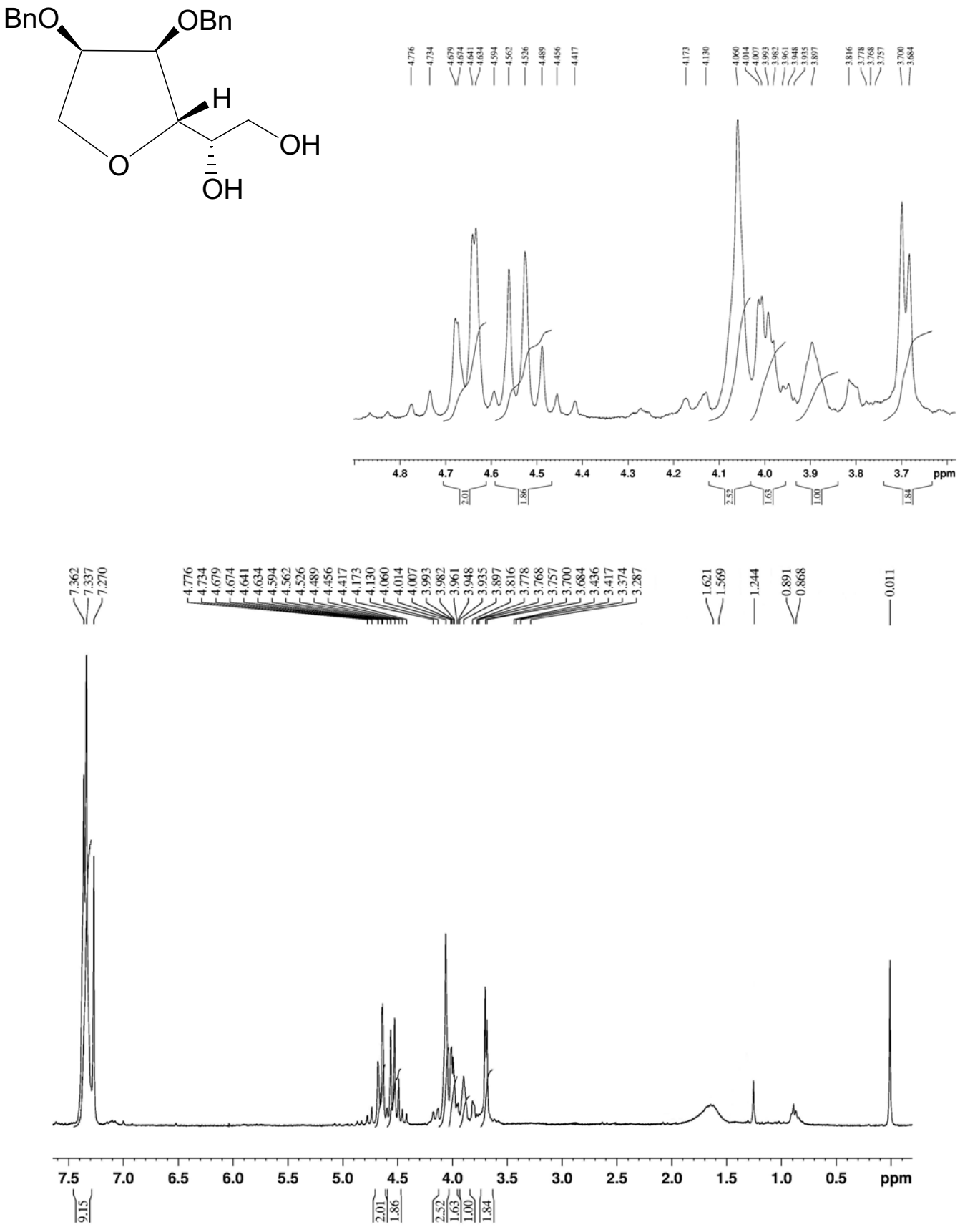


Fig. S-40: [1]H NMR Spectrum (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**19**)

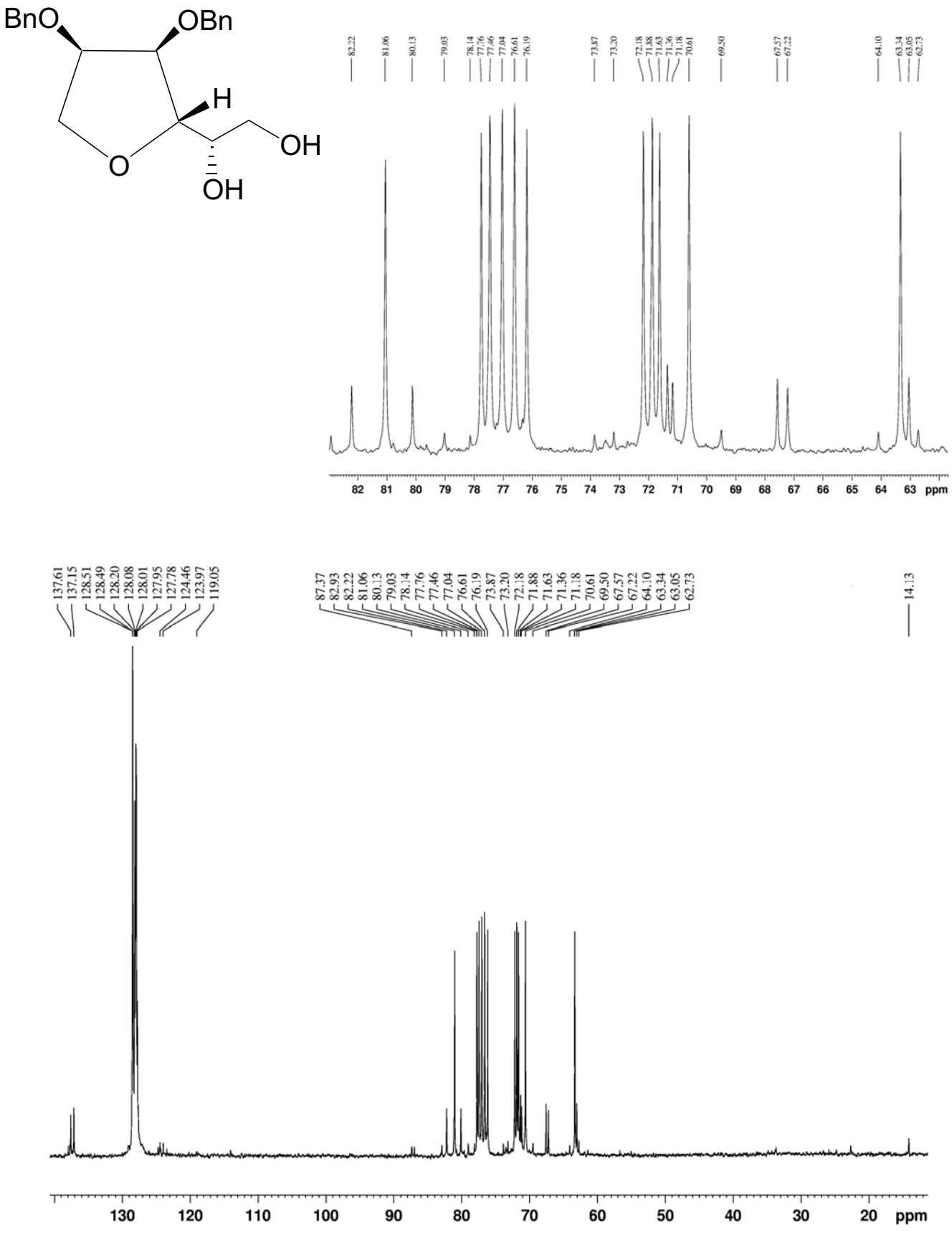


Fig. S-41: ^{13}C NMR Spectrum (*2S, 3S, 4R, 5R*) 3,6-Anhydro-4-*O*-benzyl-D-glucitol (**19**)