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Supporting Information

Expedient Synthesis of the Pentasaccharide Repeating Unit of the Polysaccharide O-Antigen of *Escherichia coli* O11

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Supporting Information

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Experimental Section

General methods: All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming 5% H_2SO_4 in EtOH sprayed plates in hot plate. Silica gel 230-400 mesh was used for column chromatography. NMR spectra were recorded on Bruker Avance 500 MHz using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in δ ppm. The complete assignment of proton and carbon spectra was carried out by using a standard set of NMR experiments, e.g. ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT 135, 2D COSY and 2D HSQC etc. MALDI-MS were recorded on a Bruker Daltonics mass spectrometer. Optical rotations were recorded in a Jasco P-2000 polarimeter. Elemental analysis was carried out on Carlo Erba analyzer. Commercially available grades of organic solvents of adequate purity are used in all reactions. $HClO_4$-SiO_2 was prepared using the experimental condition reported by Chakraborti *et al.*[1]

2-(*N*-Benzyloxycarbonyl)aminoethyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-galactopyranoside (3): To a solution of compound **2** (3 g, 8.03 mmol) in anhydrous CH_3CN (25 mL) were added 2-(*N*-benzyloxycarbonyl)amino ethanol (3.2 g, 16.39 mmol) and $BF_3 \cdot OEt_2$ (2 mL, 16.20 mmol) at 0 °C and the reaction mixture was allowed to stir at room temperature for 36 h under argon. The reaction mixture was poured into water and extracted with CH_2Cl_2 (100 mL). The organic layer was successively washed with satd. aq. $NaHCO_3$ (200 mL) and H_2O (100 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 (20% EtOAc/hexane) to give the pure compound **3** (2.8 g, 69%) as yellow oil. $[\alpha]_D^{25}$ + 12.2 (*c* 1.0, $CHCl_3$); IR (neat): 3356, 3033, 2930, 1755, 1458, 1389, 1232, 1110, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.33-7.28 (m, 5 H, Ar-H), 5.30-5.27 (m, 2 H, H-4, N*H*), 5.08 (br s, 2 H, PhC*H*$_2$, Cbz), 4.71 (dd, *J* = 10.5, 3.0 Hz, 1 H, H-3), 4.30 (d, *J* = 8.0 Hz, 1 H, H-1), 4.10-4.07 (m, 2 H, H-6$_{ab}$), 3.97-3.92 (m, 1 H, OC*H*), 3.82-3.75 (m, 2 H, H-5, OC*H*), 3.63 (dd, *J* = 8.0 Hz each, 1 H, H-2), 3.50-3.38 (m, 2 H, NC*H*$_2$), 2.14, 2.02, 2.00 (3 s, 9 H, 3COC*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.1, 169.8, 169.6 (3 *C*OCH$_3$), 156.3 (*C*O, Cbz), 136.4-128.0 (Ar-C), 102.6 (C-1), 70.9 (C-3), 70.8 (C-4), 69.9 (C-6), 66.7 (O*C*H$_2$), 66.2 (C-5), 61.2 (Ph*C*H$_2$, Cbz), 60.7 (C-2), 41.0 (N*C*H$_2$), 20.6 (2 C), 20.5 (3 CO*C*H$_3$); ESI-MS: 531.1 $[M+Na]^+$; Anal. Calcd. for $C_{22}H_{28}N_4O_{10}$ (508.48): C, 51.97; H, 5.55%; found: C, 51.80; H, 5.76%.

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[1] A. K. Chakraborti, R. Gulhane, *Chem. Commun.* **2003**, 1896-1897.

2-(*N*-Benzyloxycarbonyl)aminoethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (4): A solution of compound **3** (2 g, 3.93 mmol) in 0.1 M CH_3ONa in CH_3OH (40 mL) was allowed to stir at room temperature for 3 h. The reaction mixture was neutralized with Dowex 50W-X8 (H^+) resin, filtered and concentrated under reduced pressure. To a solution of the de-*O*-acetylated product in anhydrous CH_3CN (20 mL) were added MS 3Å (2 g), $PhCH(OCH_3)_2$ (1.2 mL, 8.0 mmol) and *p*-TsOH (200 mg) and the reaction mixture was allowed to stir at room temperature for 8 h. The reaction mixture was filtered and washed with $CHCl_3$ (100 mL). The combined filtrate was concentrated under reduced pressure to give the crude product, which was purified over SiO_2 (50% EtOAc/hexane) to give pure compound **4** (1.4 g, 76%) as white solid. m.p. 82-83 °C [EtOH]; $[\alpha]_D^{25}$ + 11 (*c* 1.0, $CHCl_3$); IR (KBr): 3327, 3068, 2940, 2890, 2104, 1689, 1545, 1369, 1273, 1151, 1083, 1001, 902, 822, 732, 695, 650, 536 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.60-7.37 (m, 10 H, Ar-H), 5.65 (s, 1 H, PhC*H*), 5.50-5.42 (m, 1 H, N*H*), 5.21 (br s, 2 H, PhCH_2, Cbz), 4.41 (d, *J* = 12.5 Hz, 1 H, H-6_a), 4.36 (d, *J* = 8.0 Hz, 1 H, H-1), 4.26 (d, *J* = 3.0 Hz, 1 H, H-4), 4.14 (d, *J* = 12.5 Hz, 1 H, H-6_b), 4.12-4.06 (m, 1 H, OC*H*), 3.89-3.82 (m, 1 H, OC*H*), 3.71 (t, *J* = 8.0 Hz each, 1 H, H-2), 3.68-3.53 (m, 3 H, H-3, NCH_2), 3.52-3.50 (m, 1 H, H-5); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.0 (*C*O, Cbz), 136.5-126.3 (Ar-C), 102.4 (Ph*C*H), 101.4 (C-1), 74.5 (C-3), 71.4 (C-4), 69.6 (C-6), 68.8 (O*C*H_2), 66.7 [2 C, C-5, Ph*C*H_2 (Cbz)], 64.0 (C-2), 41.0 (N*C*H_2); ESI-MS: 493.1 $[M+Na]^+$; Anal. Calcd. for $C_{23}H_{26}N_4O_7$ (470.48): C, 58.72; H, 5.57%; found: C, 58.55; H, 5.76%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (6): To a solution of compound **4** (1.2 g, 2.55 mmol) and compound **5** (1.2 g, 2.79 mmol) in anhydrous CH_2Cl_2 (10 mL) was added MS 4Å (2 g) and it was cooled to − 15 °C under argon. To the cold reaction mixture were added NIS (660 mg, 2.93 mmol) and $HClO_4$-SiO_2 (25 mg) and it was allowed to stir at same temperature for 25 min. The reaction mixture was filtered and washed with CH_2Cl_2 (100 mL). The combined filtrate was successively washed with 5% $Na_2S_2O_3$ (100 mL), satd. aq. $NaHCO_3$ (100 mL) and water (100 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 (20% EtOAc/hexane) to furnish pure compound **6** (1.5 g, 70%) as colorless oil. $[\alpha]_D^{25}$ + 1.1 (*c* 1.0, $CHCl_3$); IR (neat): 3448, 3018, 2928, 2401, 2117, 1876, 1718, 1517, 1454, 1365, 1216, 1083, 1051, 911, 822, 755, 668 cm^{-1}; ^1H NMR ($CDCl_3$, 500

MHz): δ 7.50-7.25 (m, 20 H, Ar-H), 5.48 (s, 1 H, PhC*H*), 5.43-5.38 (m, 1 H, N*H*), 5.24 (dd, *J* = 10.5, 3.0 Hz, 1 H, H-3$_B$), 5.10 [br s, 2 H, PhCH_2 (Cbz)], 5.05 (d, *J* = 3.5 Hz, 1 H, H-1$_B$), 4.72, 4.67, 4.63, 4.52 (4 d, *J* = 12.0 Hz each, 4 H, 4 PhC*H*), 4.28 (d, *J* = 9.0 Hz, 1 H, H-1$_A$), 4.26 (d, *J* = 12.0 Hz, 1 H, H-6$_{aA}$), 4.22-4.19 (m, 2 H, H-4$_A$, H-5$_B$), 4.03-3.95 (m, 3 H, H-2$_B$, H-6$_{bA}$, OC*H*), 3.87 (t, *J* = 9.0 Hz each, 1 H, H-2$_A$), 3.76-3.74 (m, 1 H, H-4$_B$), 3.73-3.70 (m, 1 H, OC*H*), 3.54-3.39 (m, 2 H, NCH_2), 3.37-3.33 (m, 2 H, H-3$_A$, H-5$_A$), 1.97 (s, 3 H, COCH_3), 1.04 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170.5 (*C*OCH$_3$), 156.5 (*C*O, Cbz), 138.4-126.1 (Ar-C), 102.7 (C-1$_A$), 101.1 (Ph*C*H), 100.3 (C-1$_B$), 80.1 (C-3$_A$), 78.1 (C-4$_B$), 75.6 (Ph*C*H$_2$), 74.8 (C-4$_A$), 73.4 (C-3$_B$), 72.8 (C-2$_B$), 72.4 (Ph*C*H$_2$), 69.5 (O*C*H$_2$), 69.0 (C-6$_A$), 66.7 (C-5$_B$), 66.6 [Ph*C*H$_2$ (Cbz)], 66.5 (C-5$_A$), 61.7 (C-2$_A$), 41.0 (N*C*H$_2$), 21.0 (CO*C*H$_3$), 16.5 (C*C*H$_3$); MALDI-MS: 861.2 [M+Na]$^+$; Anal. Calcd. for $C_{45}H_{50}N_4O_{12}$ (838.90): C, 64.43; H, 6.01%; found: C, 64.25; H, 6.22%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (7): A solution of compound **6** (1.4 g, 1.67 mmol) in 0.1 M CH_3ONa in CH_3OH (20 mL) was allowed to stir at room temperature for 1 h. The reaction mixture was neutralized with Dowex 50W X8 (H$^+$) resin, filtered and concentrated under reduced pressure. The crude mass was passed through a short pad of SiO_2 (75% EtOAc/hexane) to give pure compound **7** (1.2 g, 90%) as white solid. m.p. 95-96 °C [EtOH]; $[\alpha]_D^{25}$ + 1.6 (*c* 1.0, $CHCl_3$); IR (KBr): 3456, 3062, 2905, 2110, 1815, 1716, 1517, 1453, 1363, 1247, 1137, 1099, 1058, 975, 819, 750, 700, 621, 592, 492 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45-7.25 (m, 20 H, Ar-H), 5.56 (s, 1 H, PhC*H*), 5.53-5.48 (m, 1 H, N*H*), 5.21 [br s, 2 H, PhCH_2 (Cbz)], 5.17 (d, *J* = 3.5 Hz, 1 H, H-1$_B$), 5.02 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.90 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.72, 4.70 (2 d, *J* = 12.0 Hz each, 2 H, 2 PhC*H*), 4.40 (d, *J* = 8.5 Hz, 1 H, H-1$_A$), 4.37 (d, *J* = 12.5 Hz, 1 H, H-6$_{aA}$), 4.29 (d, *J* = 3.0 Hz, 1 H, H-4$_A$), 4.23-4.19 (m, 2 H, H-3$_B$, H-5$_B$), 4.10 (d, *J* = 12.5 Hz, 1 H, H-6$_{bA}$), 4.09-4.06 (m, 1 H, OC*H*), 3.95 (t, *J* = 8.5 Hz each, 1 H, H-2$_A$), 3.94 (dd, *J* = 10.5, 4.0 Hz, 1 H, H-2$_B$), 3.87-3.82 (m, 1 H, OC*H*), 3.70-3.68 (m, 1 H, H-4$_B$), 3.65-3.50 (m, 2 H, NCH_2), 3.44-3.42 (m, 1 H, H-5$_A$), 3.40 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3$_A$), 1.19 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.4 (*C*O, Cbz), 138.5-126.1 (Ar-C), 102.8 (C-1$_A$), 101.0 (Ph*C*H), 99.8 (C-1$_B$), 80.0 (C-3$_A$), 78.7 (C-4$_B$), 76.6 (C-4$_A$), 75.3 (Ph*C*H$_2$), 74.9 (C-2$_B$), 72.0 (Ph*C*H$_2$), 70.4 (C-3$_B$), 69.5 (C-6$_A$), 68.9 (O*C*H$_2$), 67.1 (C-5$_B$), 66.6 [Ph*C*H$_2$ (Cbz)], 66.5 (C-5$_A$), 61.7 (C-2$_A$), 41.0 (N*C*H$_2$), 16.9 (C*C*H$_3$); MALDI-MS: 819.2 [M+Na]$^+$; Anal. Calcd. for $C_{43}H_{48}N_4O_{11}$ (796.86): C, 64.81; H, 6.07%; found: C, 64.67; H, 6.25%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (9): A solution of compound **7** (1 g, 1.25 mmol), compound **8** (0.8 g, 1.30 mmol) and MS 4Å (2 g) in anhydrous CH_2Cl_2 (10 mL) was cooled to – 15 °C under argon. NIS (350 mg, 1.55 mmol) and $HClO_4$-SiO_2 (15 mg) were added to the cold reaction mixture and it was allowed to stir at same temperature for 25 min. The reaction mixture was filtered and washed with CH_2Cl_2 (100 mL). The combined filtrate was successively washed with 5% $Na_2S_2O_3$ (100 mL), satd. aq. $NaHCO_3$ (100 mL) and water (100 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 (20% EtOAc/hexane) to furnish pure compound **9** (1.2 g, 71%) as colorless oil. $[\alpha]_D^{25}$ – 0.5 (*c* 1.0, $CHCl_3$); IR (neat): 3433, 3064, 2925, 2115, 1729, 1585, 1453, 1366, 1261, 1178, 1095, 1053, 1026, 821, 739, 711 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.20-7.20 (m, 35 H, Ar-H), 6.09 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3_C), 6.02-6.00 (m, 1 H, H-2_C), 5.92 (t, *J* = 10.0 Hz each, 1 H, H-4_C), 5.71 (br s, 1 H, H-1_C), 5.59 (s, 1 H, PhC*H*), 5.52-5.46 (m, 1 H, N*H*), 5.25 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 5.21 [br s, 2 H, PhCH_2 (Cbz)], 5.10 (d, *J* = 3.5 Hz, 1 H, H-1_B), 4.97 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.84 (br s, 2 H, 2 PhC*H*), 4.53-4.44 (m, 2 H, H-5_C, H-6_{aC}), 4.42 (d, *J* = 8.5 Hz, 1 H, H-1_A), 4.41-4.35 (m, 3 H, H-3_B, H-6_{aA}, H-6_{bC}), 4.28 (d, *J* = 3.5 Hz, 1 H, H-4_A), 4.25-4.21 (m, 2 H, H-2_B, H-5_B), 4.13 (d, *J* = 12.0 Hz, 1 H, H-6_{bA}), 4.12-4.07 (m, 1 H, OC*H*), 3.97 (t, *J* = 8.5 Hz each, 1 H, H-2_A), 3.90 (d, *J* = 15.0 Hz, 1 H, -C*H*Cl), 3.86-3.83 (m, 1 H, OC*H*), 3.78 (d, *J* = 15.0 Hz, 1 H, -C*H*Cl), 3.76-3.75 (m, 1 H, H-4_B), 3.65-3.50 (m, 2 H, NCH_2), 3.46-3.44 (m, 1 H, H-5_A), 3.40 (dd, *J* = 10.5, 3.0 Hz, 1 H, H-3_A), 1.24 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.7 ($COCH_2Cl$), 165.4, 165.3, 164.9 (3 Ph*C*O), 156.4 (*C*O, Cbz), 137.9-126.2 (Ar-C), 102.7 (C-1_A), 101.1 (Ph*C*H), 100.1 (C-1_B), 99.1 (C-1_C), 80.3 (C-3_A), 79.2 (C-4_B), 76.5 (C-4_A), 75.9 (C-2_B), 75.3 (PhCH_2), 74.8 (C-3_B), 72.6 (PhCH_2), 69.9 (C-3_C), 69.6 (C-2_C), 69.5 (C-6_A), 69.0 (C-5_C), 68.9 (C-6_C), 67.4 (C-4_C), 67.3 (C-5_B), 66.6 (OCH_2), 66.4 (C-5_A), 64.6 [PhCH_2 (Cbz)], 61.5 (C-2_A), 41.0 (NCH_2), 40.3 (OCH_2Cl), 16.9 (CCH_3); MALDI-MS: 1369.3 $[M+Na]^+$; Anal. Calcd. for $C_{72}H_{71}ClN_4O_{20}$ (1347.80): C, 64.16; H, 5.31%; found: C, 64.00; H, 5.50%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (10): To a solution of compound **9** (1.1 g, 0.82 mmol) in CH_2Cl_2-

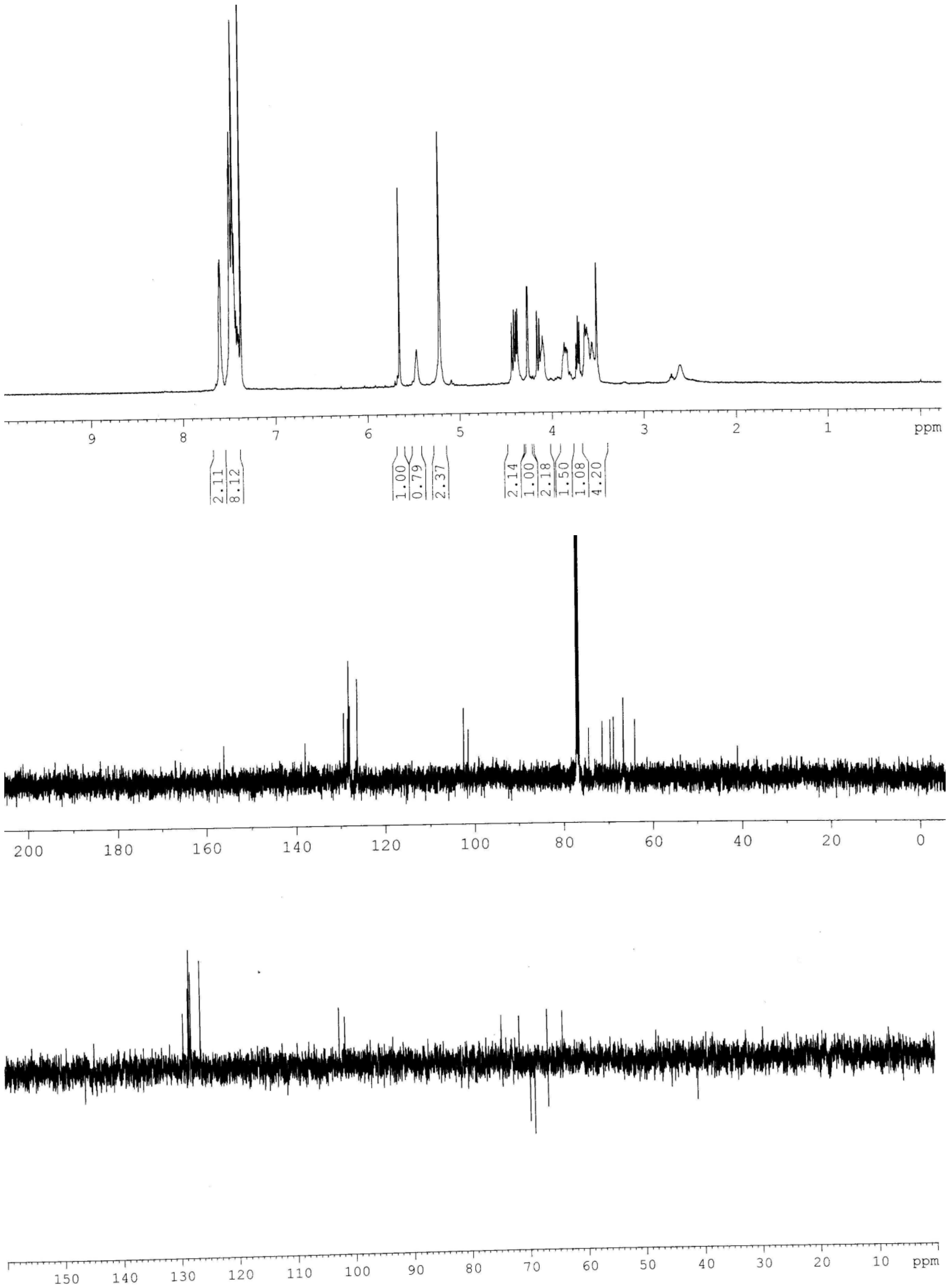
CH_3OH (15 mL, 1:4 v/v) was added thiourea (125 mg, 1.64 mmol) and the reaction mixture was allowed to stir at 50 °C for 24 h. The reaction mixture was cooled and evaporated to dryness. The crude product was purified over SiO_2 (15% EtOAc/hexane) to give pure compound **10** (730 mg, 70%) as colorless oil. $[\alpha]_D^{25}$ − 0.8 (*c* 1.0, $CHCl_3$); IR (neat): 3437, 3064, 2926, 2115, 1963, 1603, 1520, 1497, 1453, 1367, 1262, 1095, 907, 821, 739, 711, 594 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.18-7.30 (m, 35 H, Ar-H), 6.16 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3_C), 6.02-6.00 (m, 1 H, H-2_C), 5.88 (t, *J* = 10.0 Hz each, 1 H, H-4_C), 5.76 (br s, 1 H, H-1_C), 5.57 (s, 1 H, PhC*H*), 5.52-5.47 (m, 1 H, N*H*), 5.28 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 5.21 [br s, 2 H, PhCH_2 (Cbz)], 5.10 (d, *J* = 3.5 Hz, 1 H, H-1_B), 4.97 (d, *J* = 11.5 Hz, 1 H, PhC*H*), 4.84 (br s, 2 H, 2 PhC*H*), 4.43 (dd, *J* = 12.0, 2.0 Hz, 1 H, H-6_{aA}), 4.41 (br s, 1 H, H-4_A), 4.38 (d, *J* = 8.5 Hz, 1 H, H-1_A), 4.28-4.20 (m, 4 H, H-2_B, H-3_B, H-5_B, H-5_C), 4.11 (d, *J* = 12.0 Hz, 1 H, H-6_{bA}), 4.09-4.05 (m, 1 H, OC*H*), 3.95 (t, *J* = 8.5 Hz each, 1 H, H-2_A), 3.88-3.72 (m, 3 H, H-6_{abC}, OC*H*), 3.78-3.78 (m, 1 H, H-4_B), 3.64-3.48 (m, 2 H, NCH_2), 3.44-3.43 (m, 1 H, H-5_A), 3.38 (dd, *J* = 10.0, 3.5 H, 1 H, H-3_A), 1.24 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.8, 165.4, 164.9 (3 Ph*C*O), 156.3 (*C*O, Cbz), 138.3-126.1 (Ar-C), 102.7 (C-1_A), 101.1 (Ph*C*H), 99.9 (C-1_B), 98.8 (C-1_C), 80.1 (C-3_A), 79.1 (C-4_B), 76.8 (C-4_A), 75.3 (PhCH_2), 75.2 (C-2_B), 74.8 (C-3_B), 72.6 (PhCH_2), 71.9 (C-2_C), 70.1 (C-3_C), 69.6 (C-5_C), 69.5 (OCH_2), 68.9 (C-6_A), 67.5 (C-5_B), 67.4 (C-4_C), 66.6 [PhCH_2 (Cbz)], 66.4 (C-5_A), 61.7 (C-6_C), 61.6 (C-2_A), 41.0 (NCH_2), 16.9 (CCH_3); MALDI-MS: 1293.3 $[M+Na]^+$; Anal. Calcd. for $C_{70}H_{70}N_4O_{19}$ (1271.32): C, 66.13; H, 5.55%; found: C, 65.94; H, 5.73%.

***p*-Tolyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside (13)**: A solution of compound **11** (0.6 g, 1.25 mmol), compound **12** (0.5 g, 1.25 mmol) and MS 4Å (1 g) in anhydrous CH_2Cl_2-Et_2O (10 mL, 1:4 v/v) was cooled to − 10 °C under argon. NIS (290 mg, 1.29 mmol) and $HClO_4$-SiO_2 (10 mg) were added to the cold reaction mixture and it was allowed to stir at same temperature for 30 min. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The combined filtrate was successively washed with 5% $Na_2S_2O_3$ (50 mL), satd. aq. $NaHCO_3$ (50 mL) and water (50 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 (15% EtOAc/hexane) to furnish pure compound **13** (690 mg, 68%) as colorless syrup; $[\alpha]_D^{25}$ − 0.2 (*c* 1.0, $CHCl_3$); IR (neat): 3356, 3031, 2924, 2117, 1713, 1605, 1494, 1454, 1404, 1359, 1282, 1172, 1136, 1092, 1049, 1001, 809, 731, 696, 589, 500 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.53-6.97

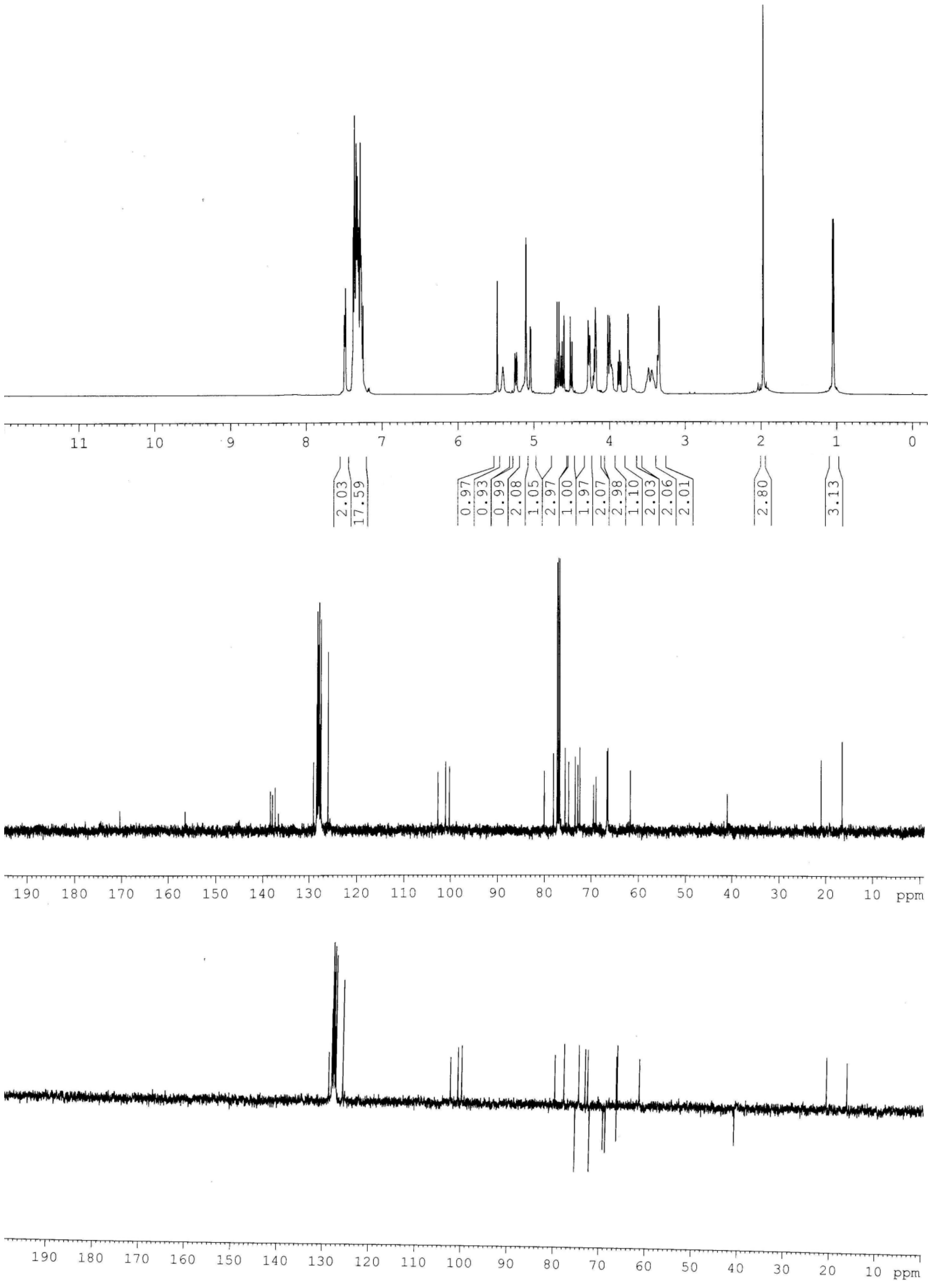
(m, 24 H, Ar-H), 5.35 (s, 1 H, PhC*H*), 4.91 (d, *J* = 3.5 Hz, 1 H, H-1_E), 4.86 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.74 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.67 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.61 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.58 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.50 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.31 (d, *J* = 9.5 Hz, 1 H, H-1_D), 4.28 (d, *J* = 12.0 Hz, 1 H, H-6_{aD}), 4.15 (d, *J* = 2.5 Hz, 1 H, H-4_D), 3.94-3.89 (m, 3 H, H-2_E, H-4_E, H-6_{bD}), 3.80 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3_E), 3.64 (t, *J* = 9.5 Hz each, 1 H, H-2_D), 3.44-3.42 (m, 1 H, H-5_E), 3.36-3.35 (m, 1 H, H-5_D), 3.34 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-3_D), 2.27 (s, 3 H, CH_3), 0.91 (d, *J* = 6.5 Hz, 3 H, CCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.1-126.3 (Ar-C), 101.1 (Ph*C*H), 100.8 (C-1_E), 85.4 (C-1_D), 82.6 (C-3_D), 78.9 (C-3_E), 77.7 (C-5_E), 76.4 (C-2_E), 74.8 (Ph*C*H_2), 74.7 (C-4_D), 73.3 (Ph*C*H_2), 72.9 (Ph*C*H_2), 69.7 (C-5_D), 69.4 (C-6_D), 67.1 (C-4_E), 59.6 (C-2_D), 21.3 (*C*H_3), 16.8 (C*C*H_3); MALDI-MS: 838.3 $[M+Na]^+$; Anal. Calcd. for $C_{47}H_{49}N_3O_8S$ (815.97): C, 69.18; H, 6.05%; found: C, 69.00; H, 6.25%.

2-(*N*-Benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-(2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (14): A solution of compound **10** (700 mg, 0.55 mmol), compound **13** (500 mg, 0.61 mmol) and MS 4Å (1 g) in anhydrous CH_2Cl_2-Et_2O (15 mL, 1:4 v/v) was cooled to − 10 °C under argon. NIS (150 mg, 0.67 mmol) and $HClO_4$-SiO_2 (10 mg) were added to the cold reaction mixture and it was allowed to stir at same temperature for 30 min. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The combined filtrate was successively washed with 5% $Na_2S_2O_3$ (50 mL), satd. aq. $NaHCO_3$ (50 mL) and water (50 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purified over SiO_2 (15% EtOAc/hexane) to furnish pure compound **14** (750 mg, 70%) as white solid; m.p. 125-126 °C [EtOH]; $[\alpha]_D^{25}$ + 4 (*c* 1.0, $CHCl_3$); IR (KBr): 3360, 3068, 2921, 2114, 1921, 1728, 1607, 1530, 1453, 1260, 1172, 1095, 1001, 910, 815, 751, 697, 560 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05-7.19 (m, 55 H, Ar-H), 6.08 (t, *J* = 10.0 Hz each, 1 H, H-4_C), 5.93 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-3_C), 5.91-5.89 (m, 1 H, H-2_C), 5.64 (br s, 1 H, H-1_C), 5.46 (s, 1 H, PhC*H*), 5.38-5.34 (m, 1 H, N*H*), 5.33 (s, 1 H, PhC*H*), 5.14 (d, *J* = 3.5 H, 1 H, H-1_D), 5.12 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 5.08 [br s, 2 H, PhCH_2 (Cbz)], 5.05 (d, *J* = 3.5 Hz, 1 H, H-1_B), 5.01 (d, *J* = 3.5 Hz, 1 H, H-1_E), 4.97 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.88, 4.85 (2 d, *J* = 12.0 Hz each, 2 H, 2 PhC*H*), 4.76-4.65 (m, 5 H, 5 PhC*H*), 4.58 (d, *J* = 12.0 Hz, 1 H, PhC*H*), 4.38-4.35 (m, 1 H, H-5$_C$), 4.32 (dd, *J* = 12.0, 2.5 Hz, 1 H, H-6$_{aA}$), 4.25 (d, *J* = 8.5 Hz, 1 H, H-1$_A$), 4.24-4.20 (m, 2 H, H-5$_B$, H-6$_{aD}$), 4.19-4.06 (m, 5 H, H-2$_B$, H-3$_B$, H-4$_A$, H-6$_{bA}$, H-6$_{bD}$), 4.02-3.96 (m, 3 H, H-2$_E$, H-4$_D$, H-5$_E$), 3.95-3.83 (m, 5 H, H-2$_A$, H-2$_D$, H-3$_E$, 2 OC*H*), 3.72-3.66 (m, 2 H, H-3$_D$, H-6$_{aC}$), 3.64 (br s, 1 H, H-4$_B$), 3.55 (br s, 1 H, H-4$_E$), 3.52 (d, *J* = 12.0 Hz, 1 H, H-6$_{bC}$), 3.48-3.32 (m, 2 H, NCH_2), 3.31-3.27 (m, 3 H, H-3$_A$, H-5$_A$, H-5$_D$), 1.11, 1.02 (2 d, *J* = 6.5 Hz each, 6 H, 2 CCH_3); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 165.8, 165.4, 165.1 (3 *C*OPh), 156.4 (*C*O, Cbz), 138.9-126.0 (Ar-C), 102.8 (C-1$_A$), 101.0 (Ph*C*H), 100.8 (Ph*C*H), 100.6 (C-1$_D$), 99.6 (C-1$_C$), 99.4 (C-1$_E$), 98.9 (C-1$_B$), 79.8 (C-3$_A$), 79.6 (C-3$_D$), 79.2 (C-4$_B$), 78.1 (C-3$_E$), 76.6 (C-4$_A$), 76.5 (C-5$_E$), 75.9 (C-2$_E$), 75.7 (C-2$_B$), 75.6 (C-3$_B$), 75.3 (PhCH_2), 74.8 (C-4$_D$), 74.7 (PhCH_2), 73.4 (PhCH_2), 72.6 (2 C, 2 PhCH_2), 70.3 (C-5$_C$), 70.2 (C-2$_C$), 69.9 (C-3$_C$), 69.5 (C-6$_D$), 68.9 (C-6$_A$), 68.8 (2 C, C-6$_C$, OCH_2), 67.4 (C-5$_D$), 67.1 (C-5$_B$), 67.0 (C-4$_C$), 66.5 [PhCH_2 (Cbz)], 66.4 (C-4$_E$), 62.7 (C-5$_A$), 61.4 (C-2$_D$), 58.4 (C-2$_A$), 41.0 (NCH_2), 16.9, 16.8 (2 CCH_3); MALDI-MS: 1984.6 [M+Na]$^+$; Anal. Calcd. for $C_{110}H_{111}N_7O_{27}$ (1963.09): C, 67.30; H, 5.70%; found: C, 67.13; H, 5.92%.

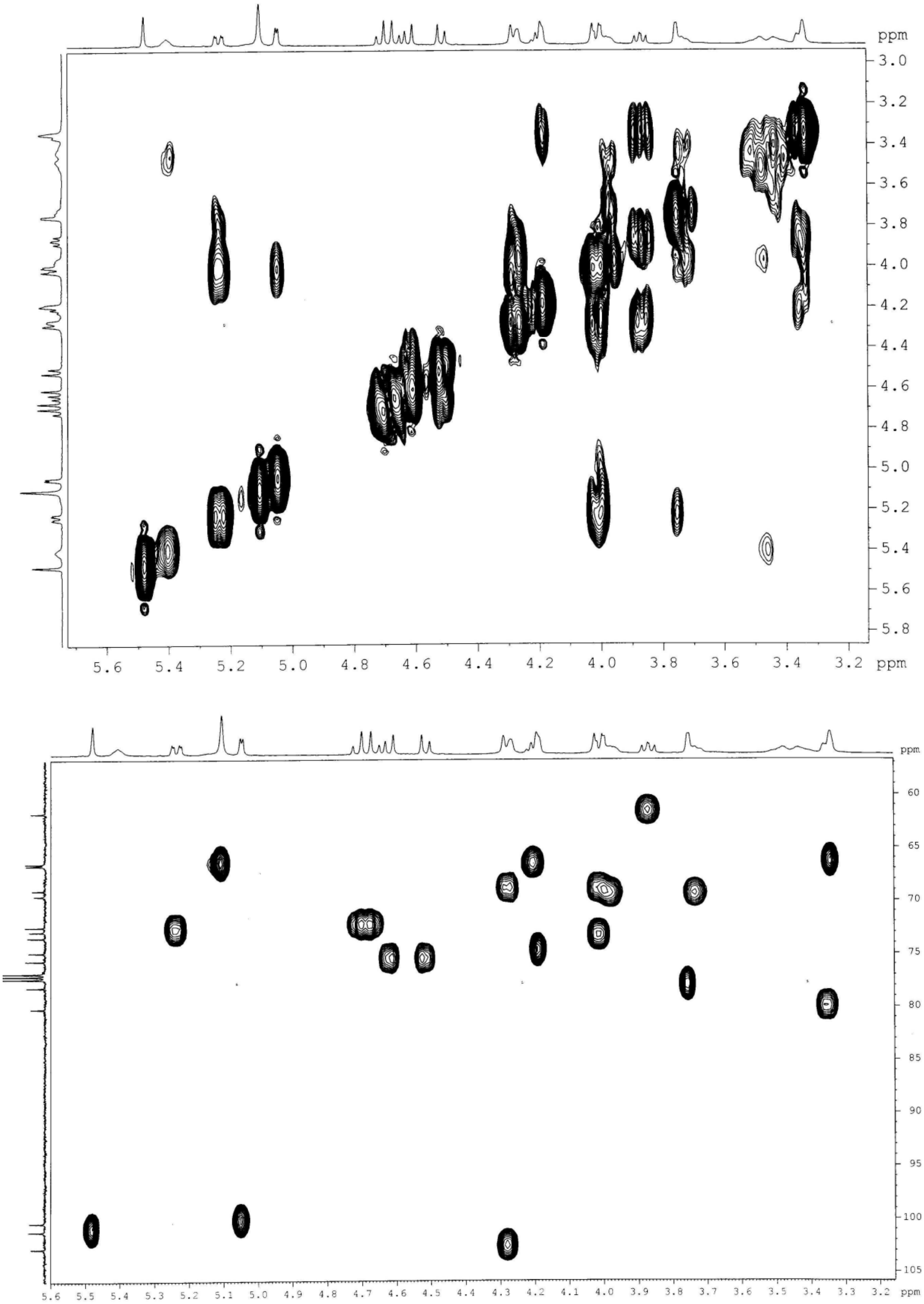
2-Aminoethyl *O*-(α-L-fucopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→3)-(α-L-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside (1): To a solution of compound **14** (700 mg, 0.36 mmol) in pyridine (2 mL) was added CH_3COSH (0.5 mL, 7.09 mmol) and the reaction mixture was allowed to stir at room temperature for 48 h. The solvents were evaporated under reduced pressure and crude product was passed through a short pad of SiO_2 (EtOAc) to give the *N*-acetylated product. A solution of the product in 0.1 M CH_3ONa in CH_3OH (10 mL) was allowed to stir at room temperature for 6 h. The reaction mixture was neutralized with Dowex 50W X8 (H$^+$) resin, filtered and concentrated under reduced pressure to give the de-*O*-benzoylated product. To a solution of the product in CH_3OH (5 mL) were added $Pd(OH)_2$-C (20%; 150 mg) and Et_3SiH (2.5 mL, 15.65 mmol) and the reaction mixture was allowed to stir at room temperature for 18 h. The reaction mixture was filtered through a Celite® bed and the filtering bed was washed with CH_3OH-H_2O (15 mL, 2:1). The combined filtrate was concentrated and passed through a Sephadex® LH-20 column (30% H_2O/CH_3OH) to furnish pure compound **1** (180 mg, over all 54%) as white amorphous solid. $[\alpha]_D^{25}$ + 1 (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 500 MHz): δ 5.10 (br s, 1 H, H-1$_C$), 5.04 (d, *J* = 3.0 Hz, 1 H, H-1$_B$), 5.03 (d, *J* = 3.0 Hz, 1 H, H-1$_E$), 4.92 (d, *J* = 3.5 Hz, 1 H, H-1$_D$), 4.59 (d, *J* = 8.5 Hz, 1 H, H-1$_A$), 4.39 (dd, *J* = 10.5, 3.5 Hz, 1 H, H-2$_D$), 4.25-4.18 (m, 1 H, OC*H*), 4.17-4.12 (m, 3 H, H-4$_A$, H-5$_B$, H-6$_{aC}$), 4.11-4.09 (m, 2 H, H-2$_{A}$, H-2$_{C}$), 4.08-4.03 (m, 2 H, H-4$_{B}$, H-5$_{D}$), 4.01-3.93 (m, 5 H, H-3$_{B}$, H-4$_{D}$, H-4$_{E}$, H-5$_{A}$, OC*H*), 3.92-3.88 (m, 5 H, H-3$_{C}$, H-3$_{E}$, H-4$_{C}$, H-5$_{C}$, H-5$_{E}$), 3.86-3.74 (m, 7 H, H-2$_{B}$, H-3$_{A}$, H-3$_{D}$, H-6$_{abA}$, H-6$_{abD}$), 3.70 (dd, *J* = 10.5, 4.0 Hz, 1 H, H-2$_{E}$), 3.62 (d, *J* = 10.5 Hz, 1 H, H-6$_{bC}$), 3.39-3.34 (m, 2 H, NCH_2), 2.04 (s, 6 H, 2 COCH_3), 1.23-1.18 (m, 6 H, 2 CCH_3); ^{13}C NMR (D_2O, 125 MHz): δ 175.2, 174.9 (2 *C*OCH$_3$), 102.6 (C-1$_{C}$), 101.2 (C-1$_{B}$), 101.0 (C-1$_{E}$), 100.9 (C-1$_{A}$), 97.2 (C-1$_{D}$), 78.4 (C-3$_{A}$), 77.6 (C-3$_{B}$), 76.0 (C-5$_{A}$), 75.0 (C-3$_{D}$), 71.7 (C-2$_{B}$), 71.6 (C-3$_{C}$), 71.5 (C-2$_{C}$), 71.0 (C-5$_{C}$), 70.6 (C-4$_{B}$), 70.0 (C-4$_{D}$), 69.4 (C-4$_{E}$), 68.7 (C-3$_{E}$), 68.2 (C-4$_{C}$), 67.9 (C-2$_{E}$), 67.2 (C-5$_{D}$), 67.0 (2 C, C-5$_{B}$, C-5$_{E}$), 66.0 (C-4$_{A}$), 65.2 (C-6$_{C}$), 63.2 (O*C*H$_2$), 61.0 (C-6$_{A}$), 60.9 (C-6$_{D}$), 56.8 (C-2$_{D}$), 48.9 (C-2$_{A}$), 42.7 (N*C*H$_2$), 22.2, 22.0 (2 CO*C*H$_3$), 15.3, 15.2 (2 C*C*H$_3$); MALDI-MS: 944.3 [M+Na]$^{+}$; Anal. Calcd. for $C_{36}H_{63}N_3O_{24}$ (921.89): C, 46.90; H, 6.89%; found: C, 46.73; H, 7.10%.



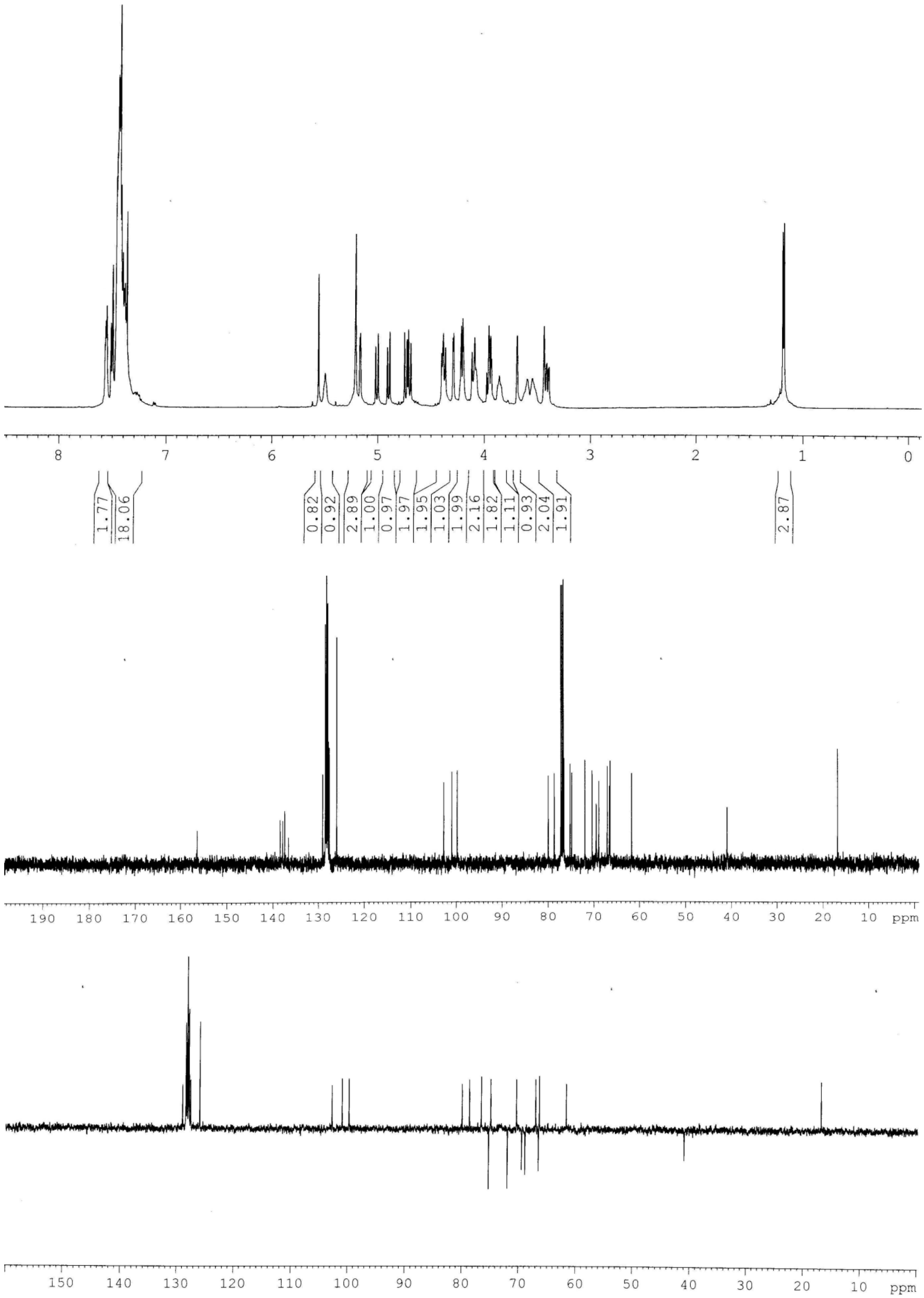
^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**4**) ($CDCl_3$).



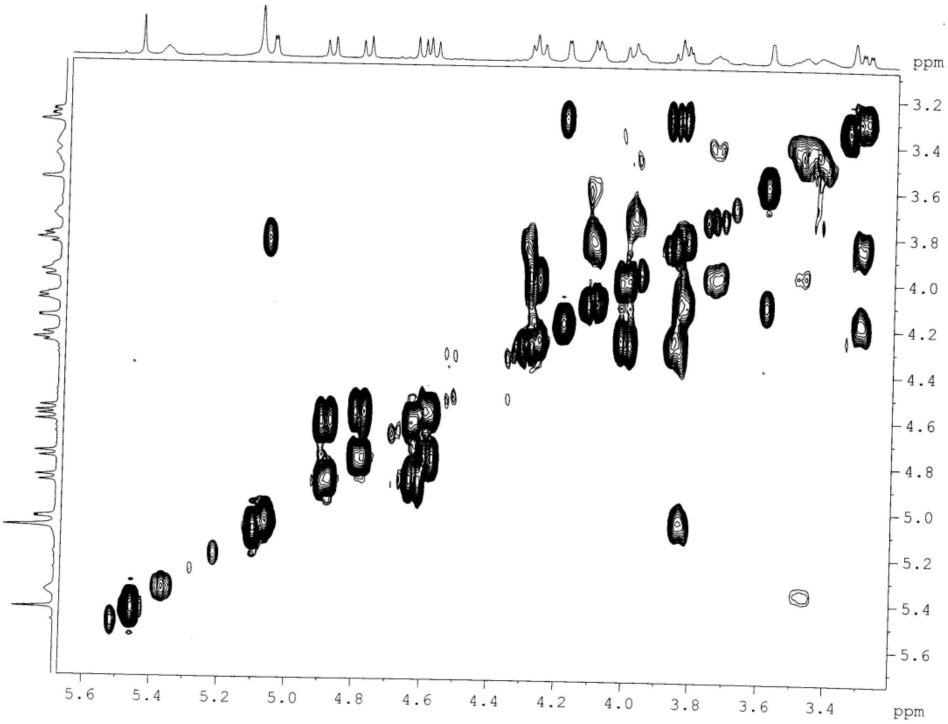
^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**6**) ($CDCl_3$).

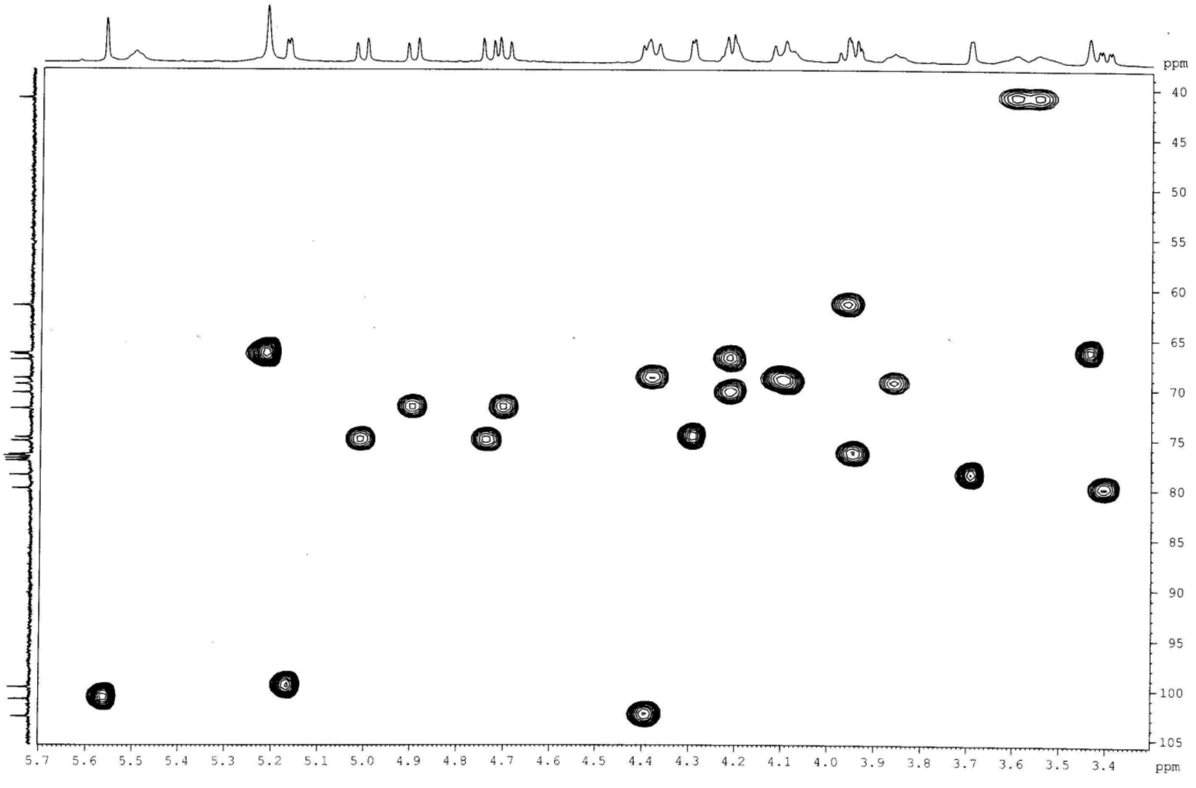


2D COSY and HSQC spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**6**) ($CDCl_3$) (selected regions).

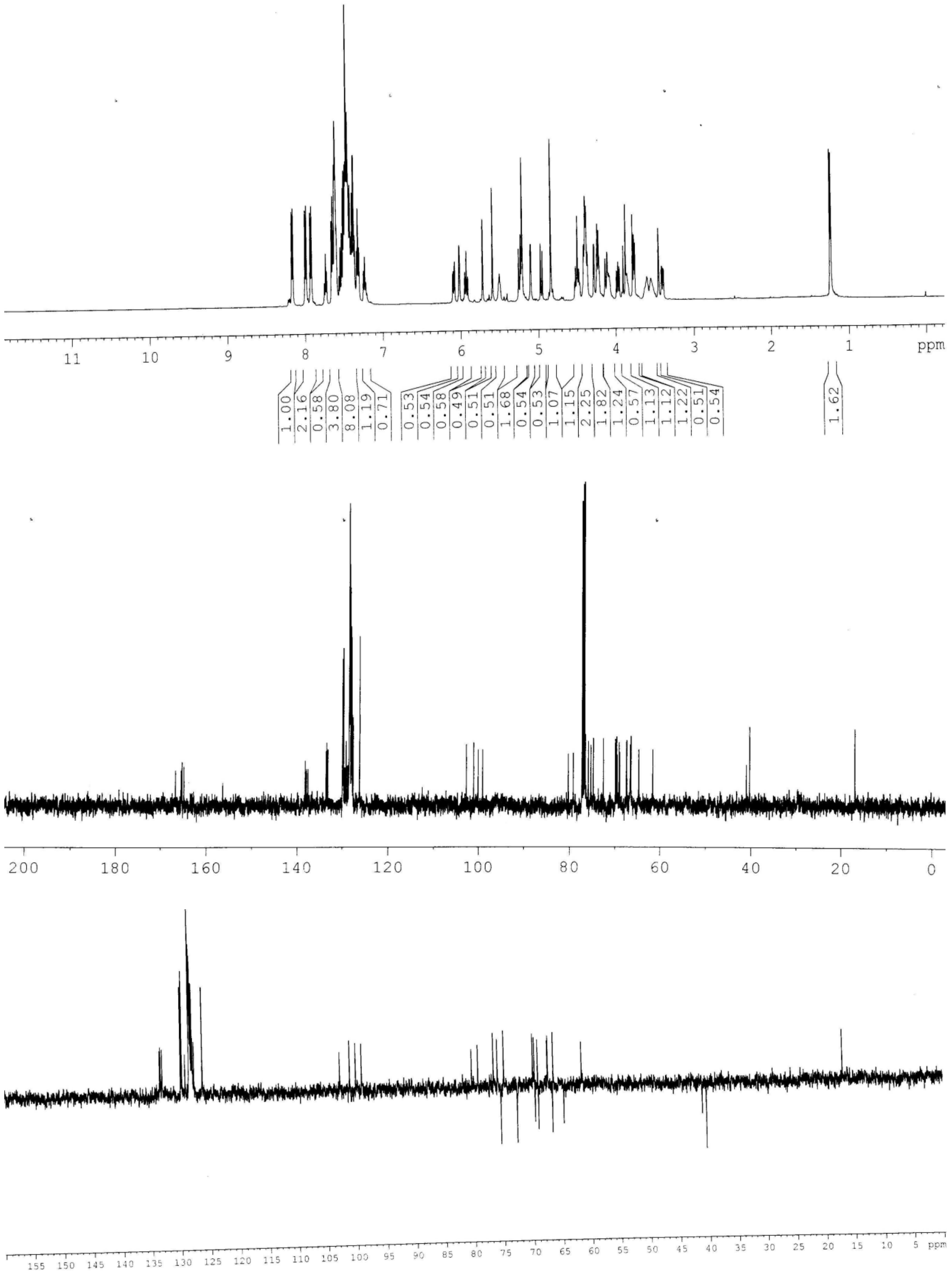


^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**7**) ($CDCl_3$).

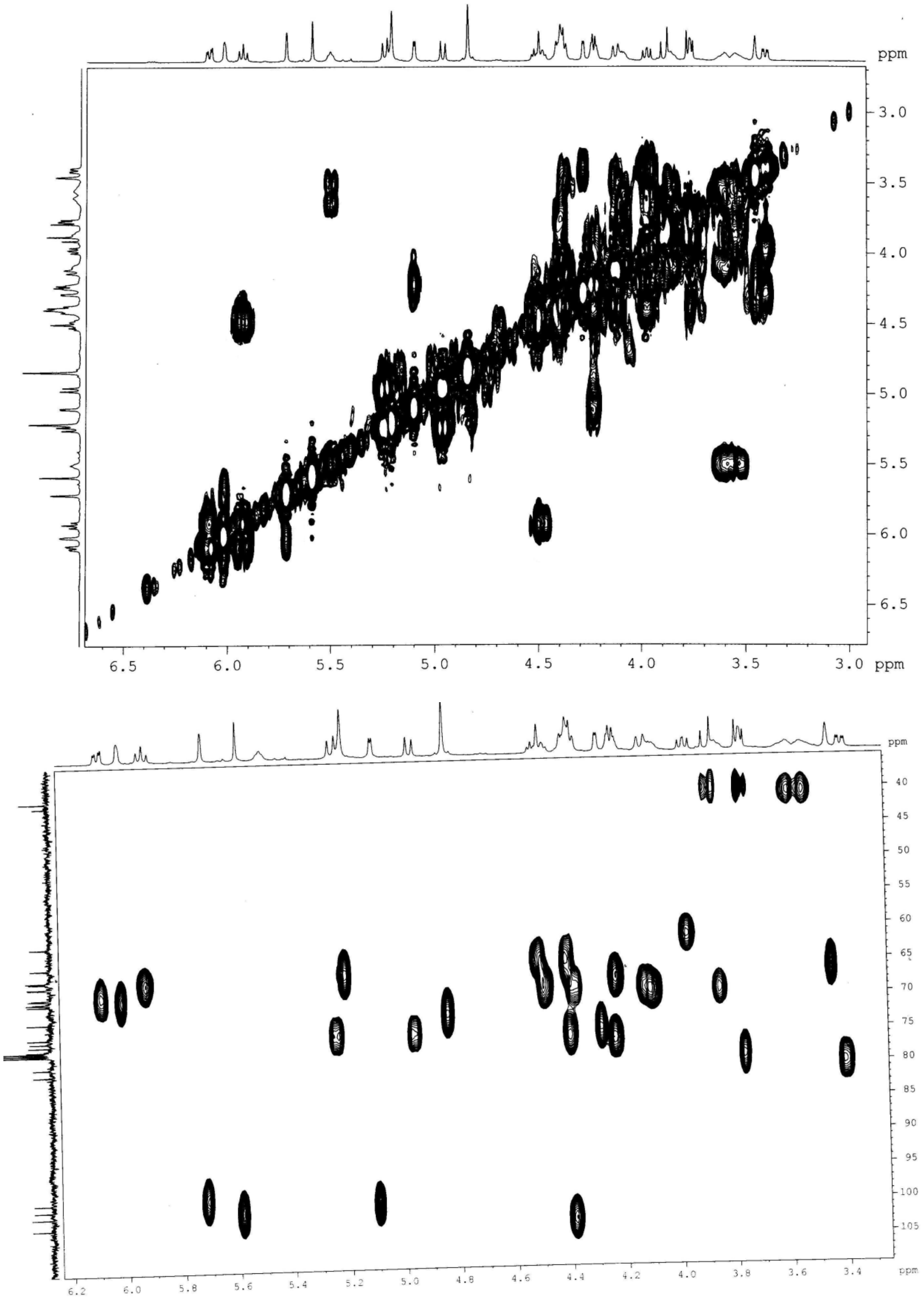




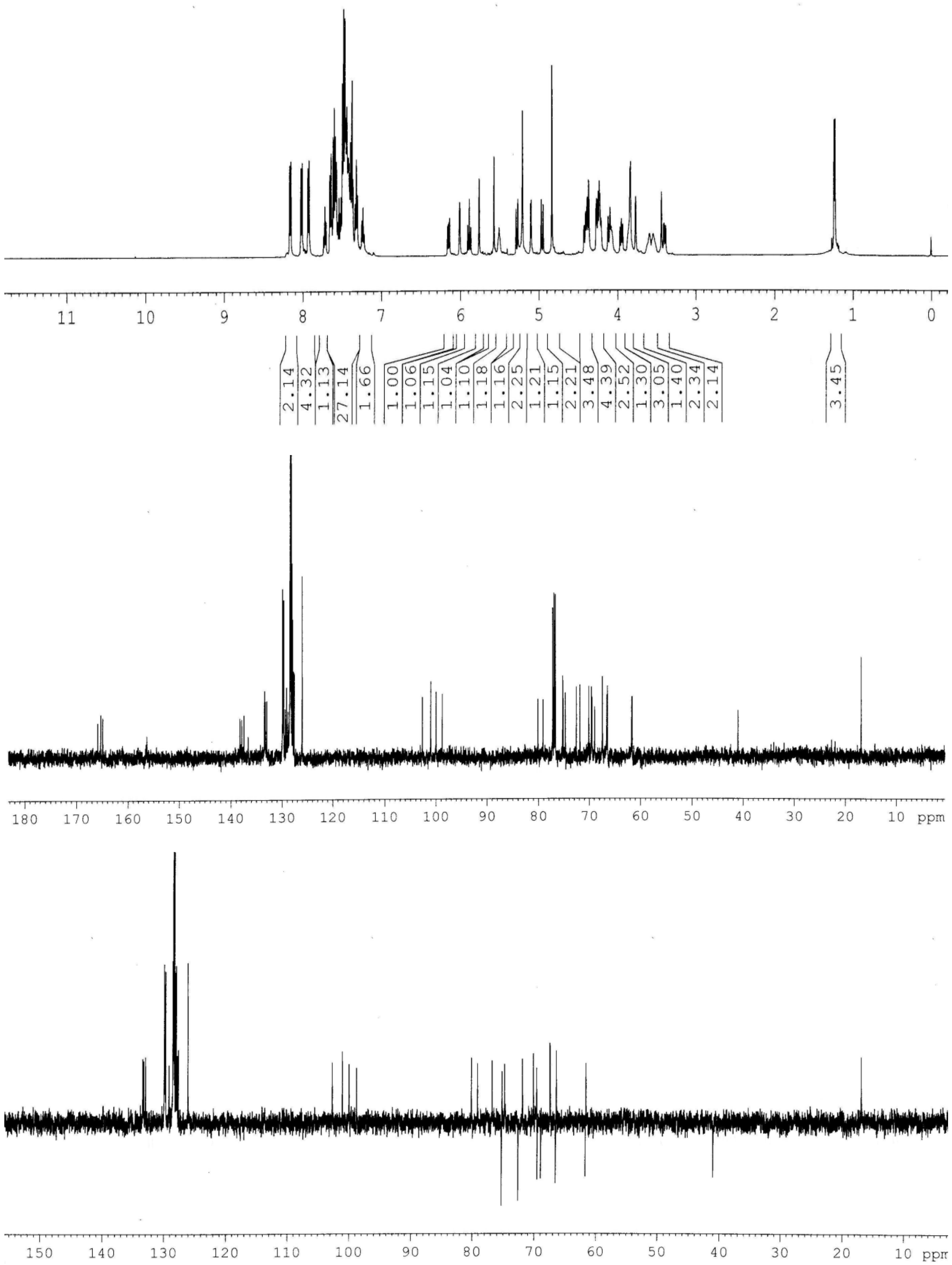
2D COSY and HSQC spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (7) ($CDCl_3$) (selected regions).



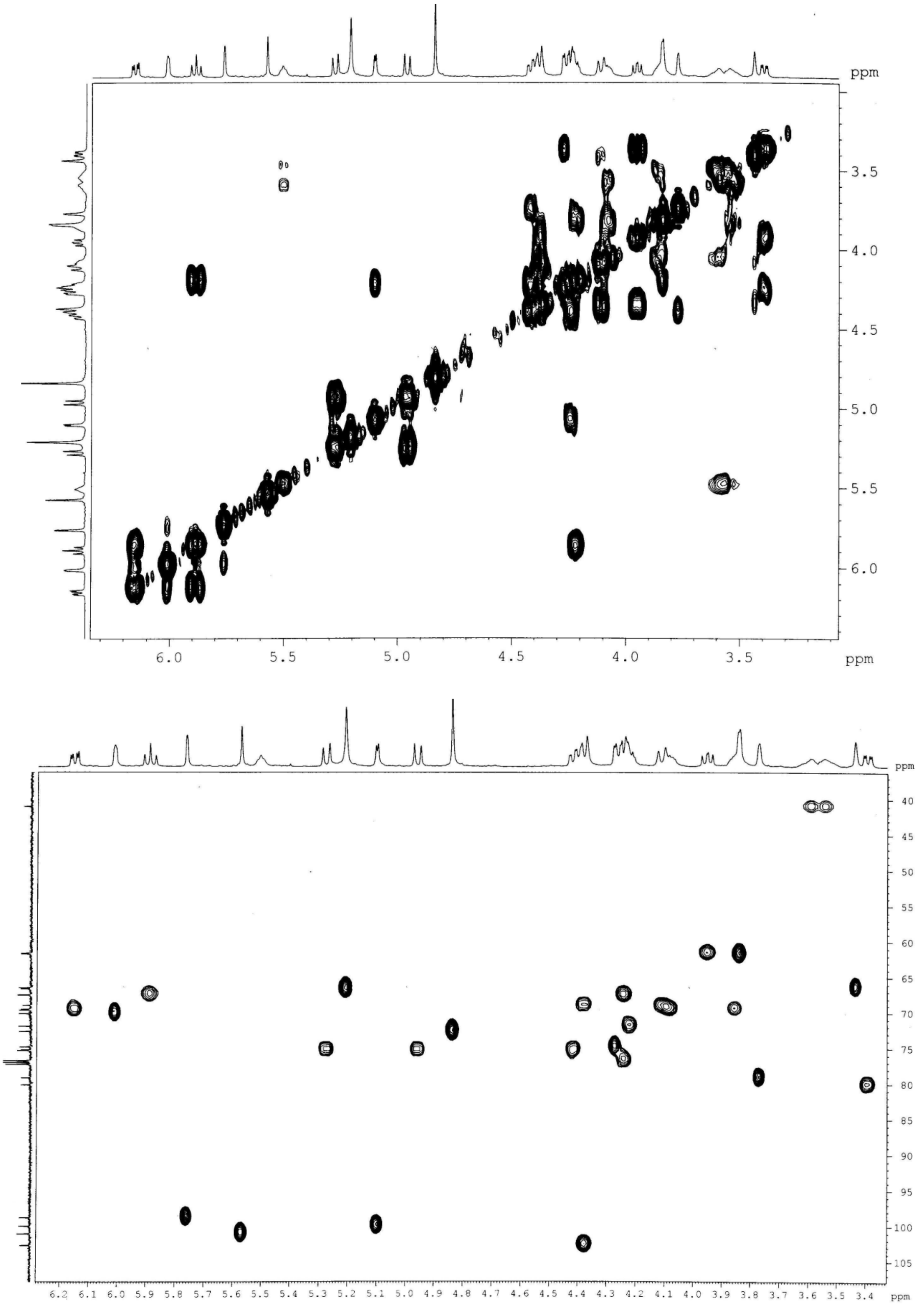
^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**9**) ($CDCl_3$).



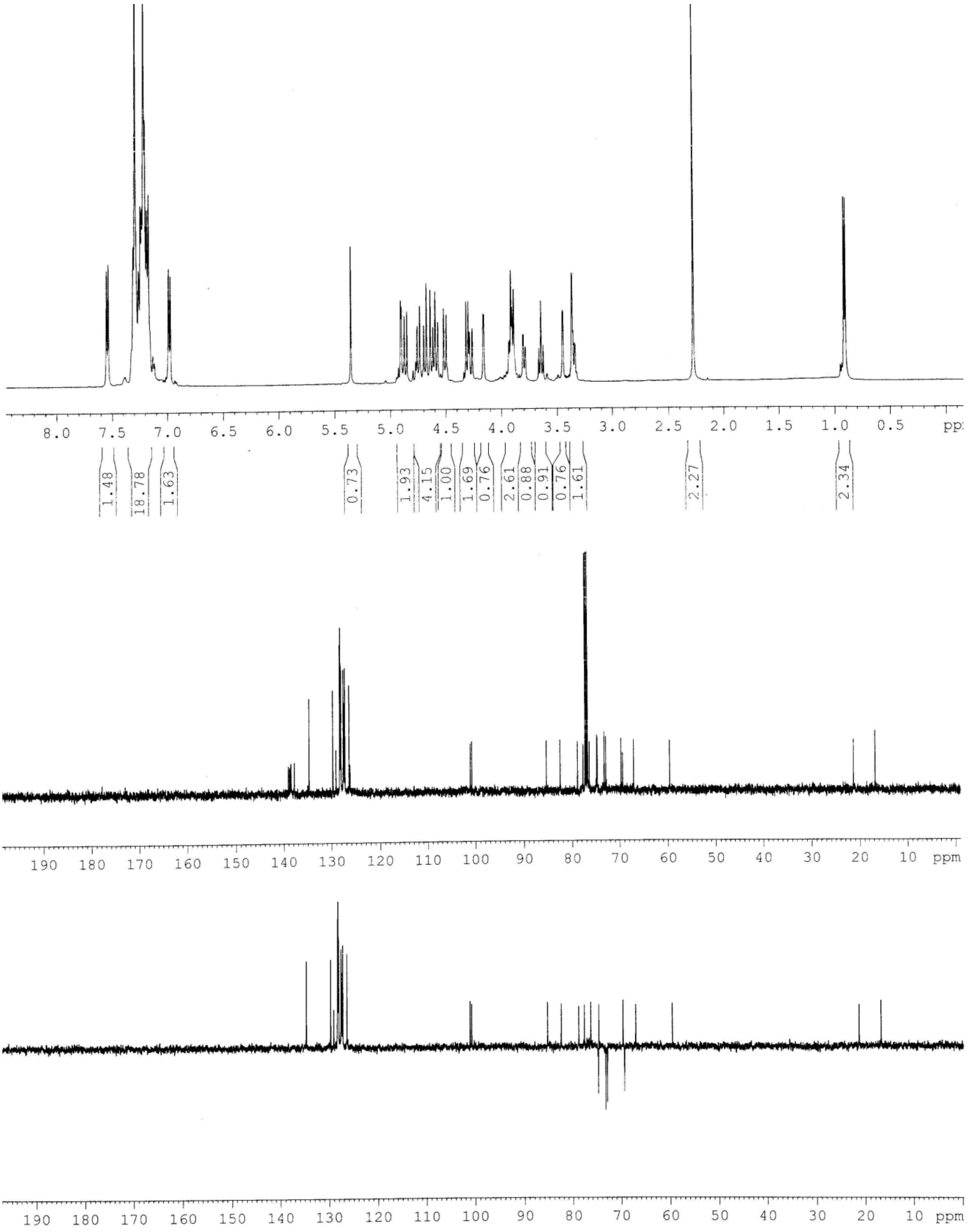
2D COSY and HSQC spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-6-*O*-chloroacetyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**9**) ($CDCl_3$) (selected regions).



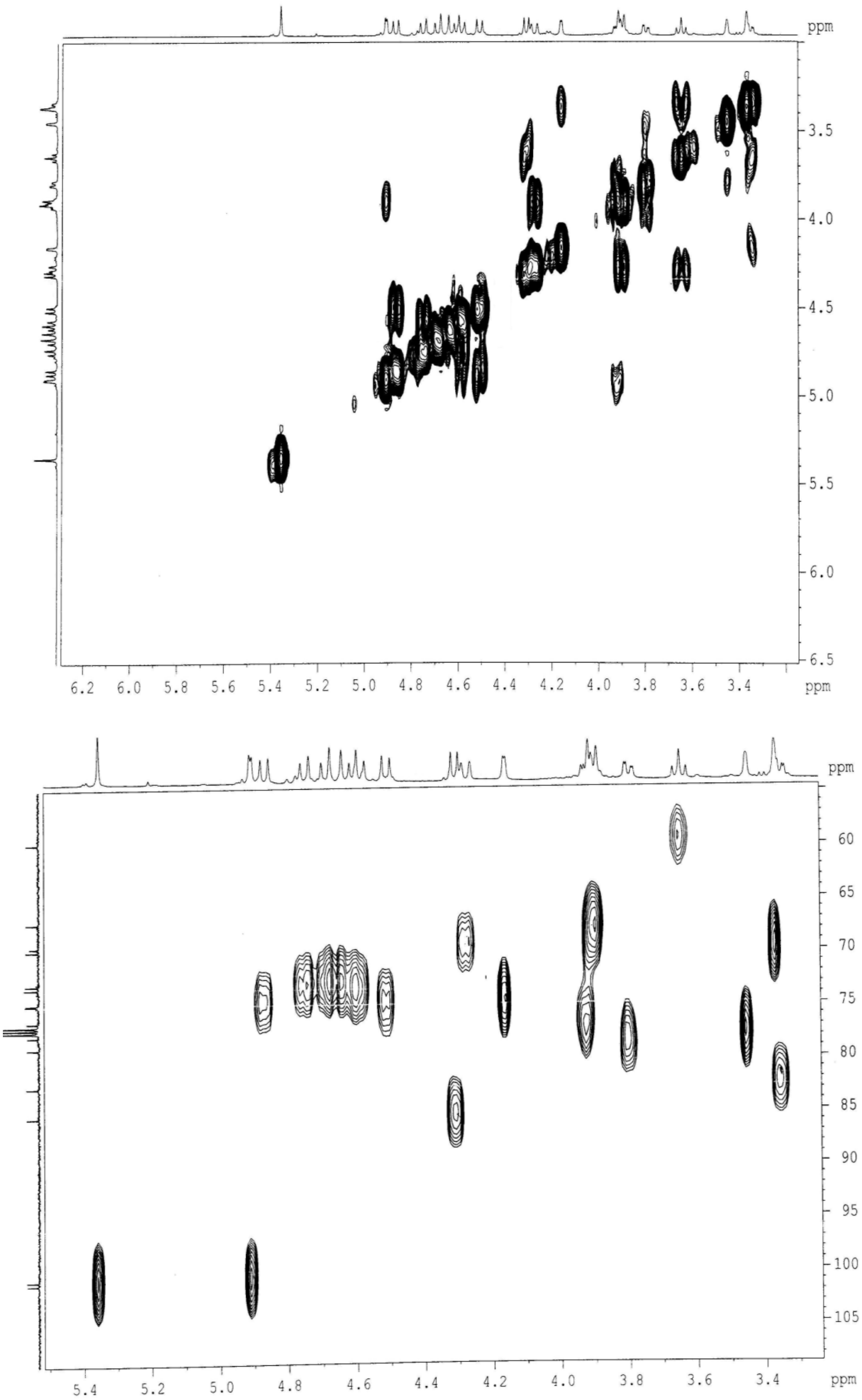
^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**10**) ($CDCl_3$).



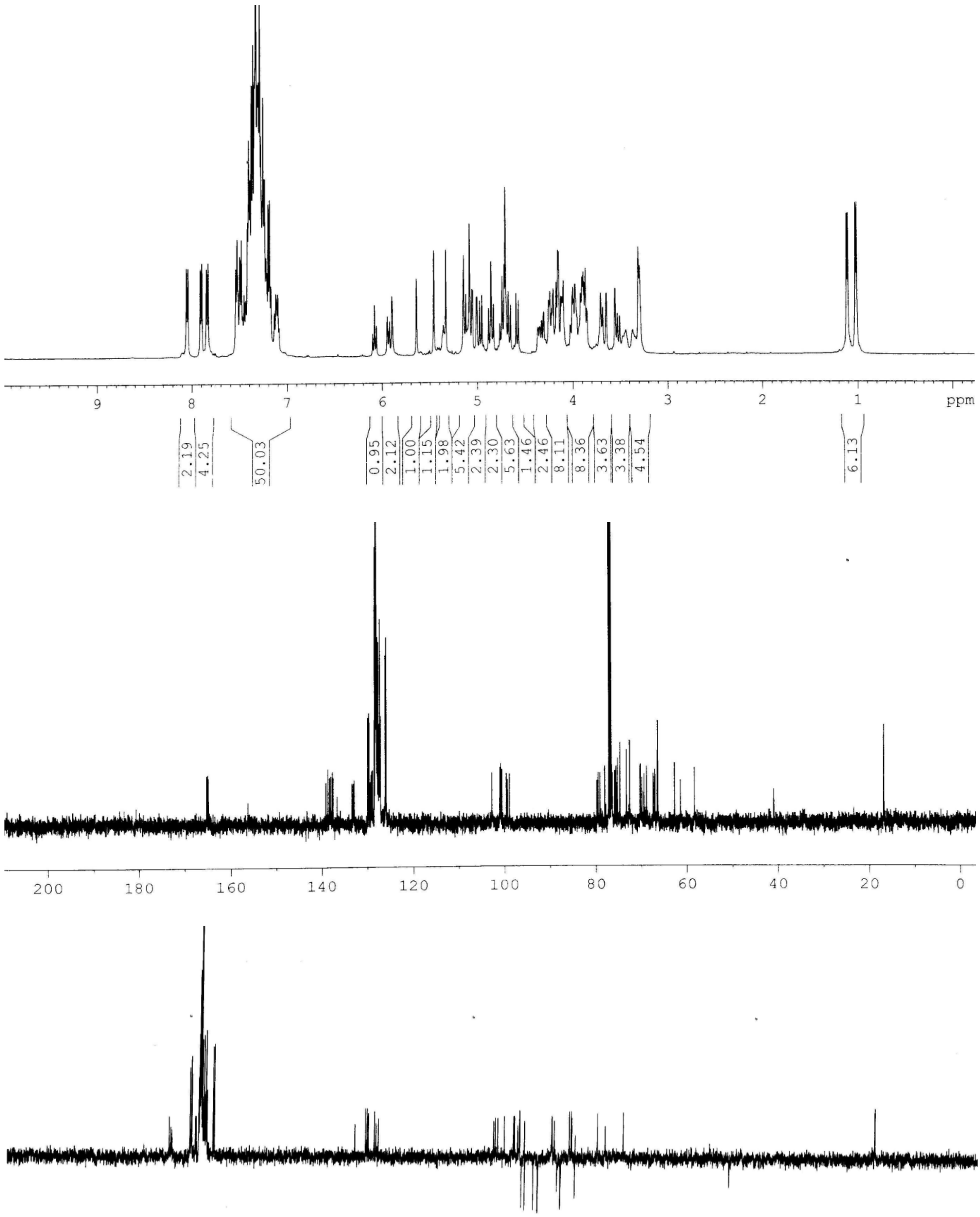
2D COSY and HSQC spectra of 2-(*N*-benzyloxycarbonyl)aminoethyl *O*-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**10**) ($CDCl_3$) (selected regions).



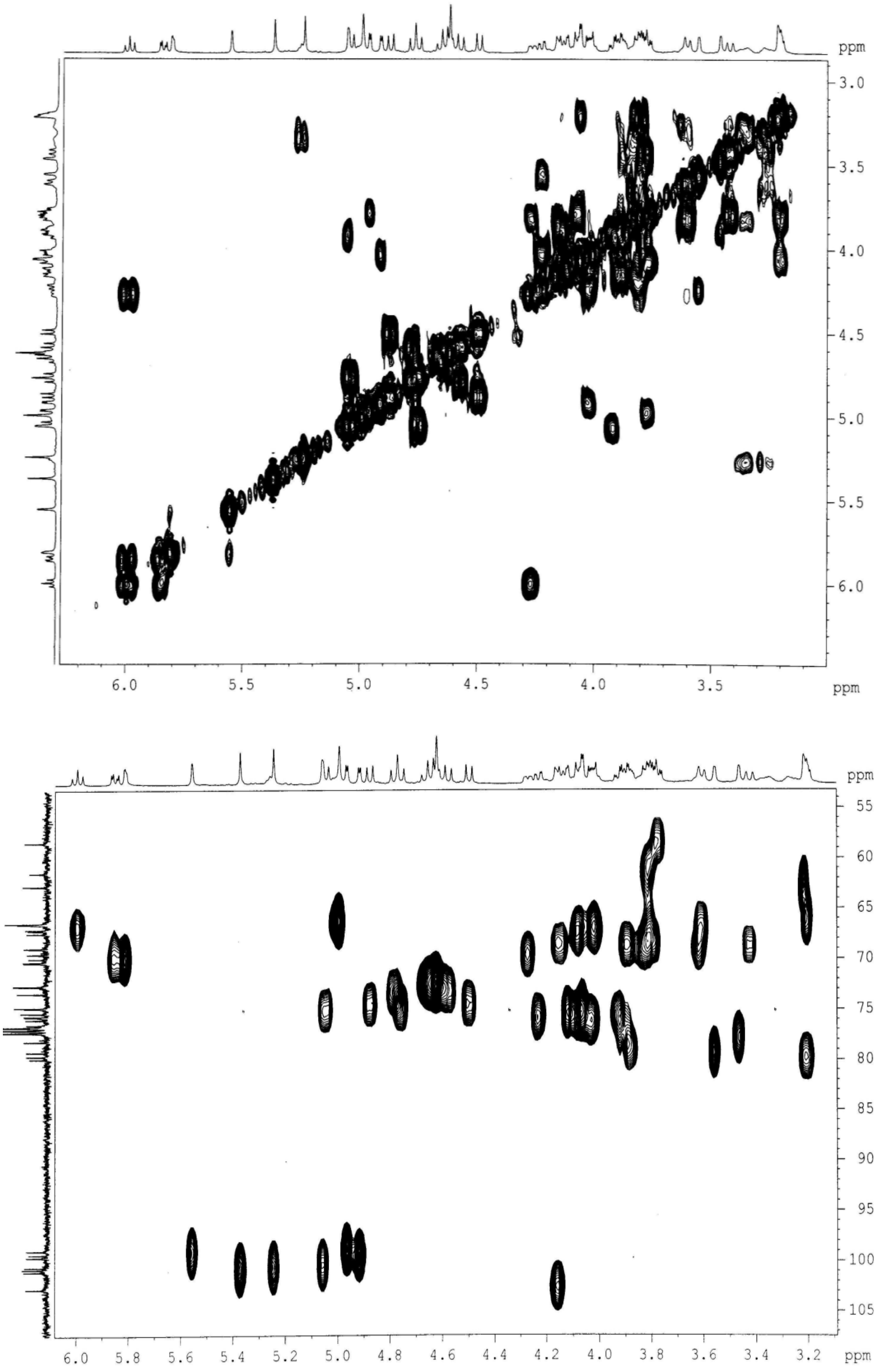
^{1}H, ^{13}C and DEPT 135 NMR spectra of *p*-tolyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside (**13**) (CDCl$_3$).



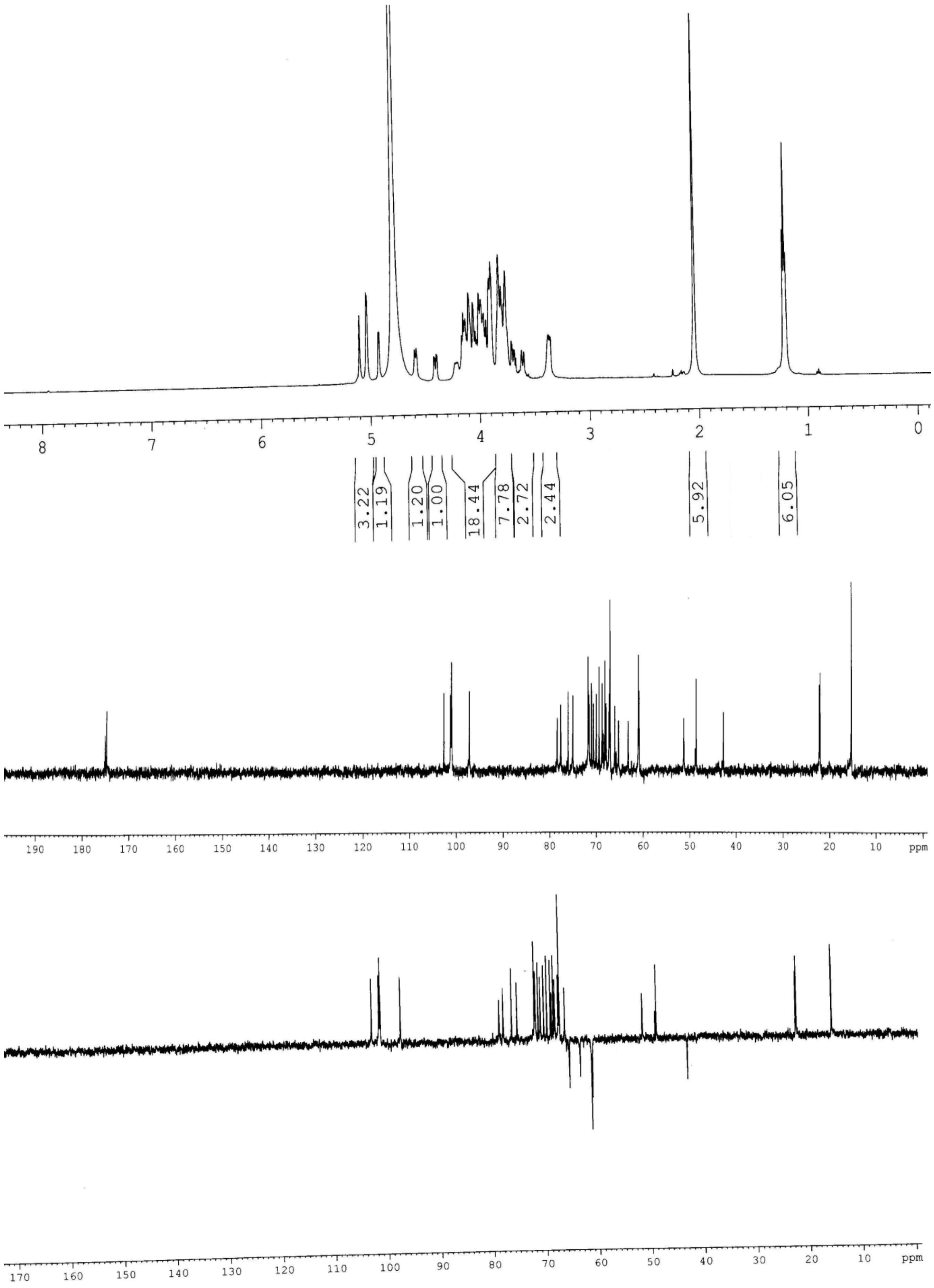
2D COSY and HSQC spectra of *p*-tolyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-galactopyranoside (**13**) ($CDCl_3$) (selected regions).



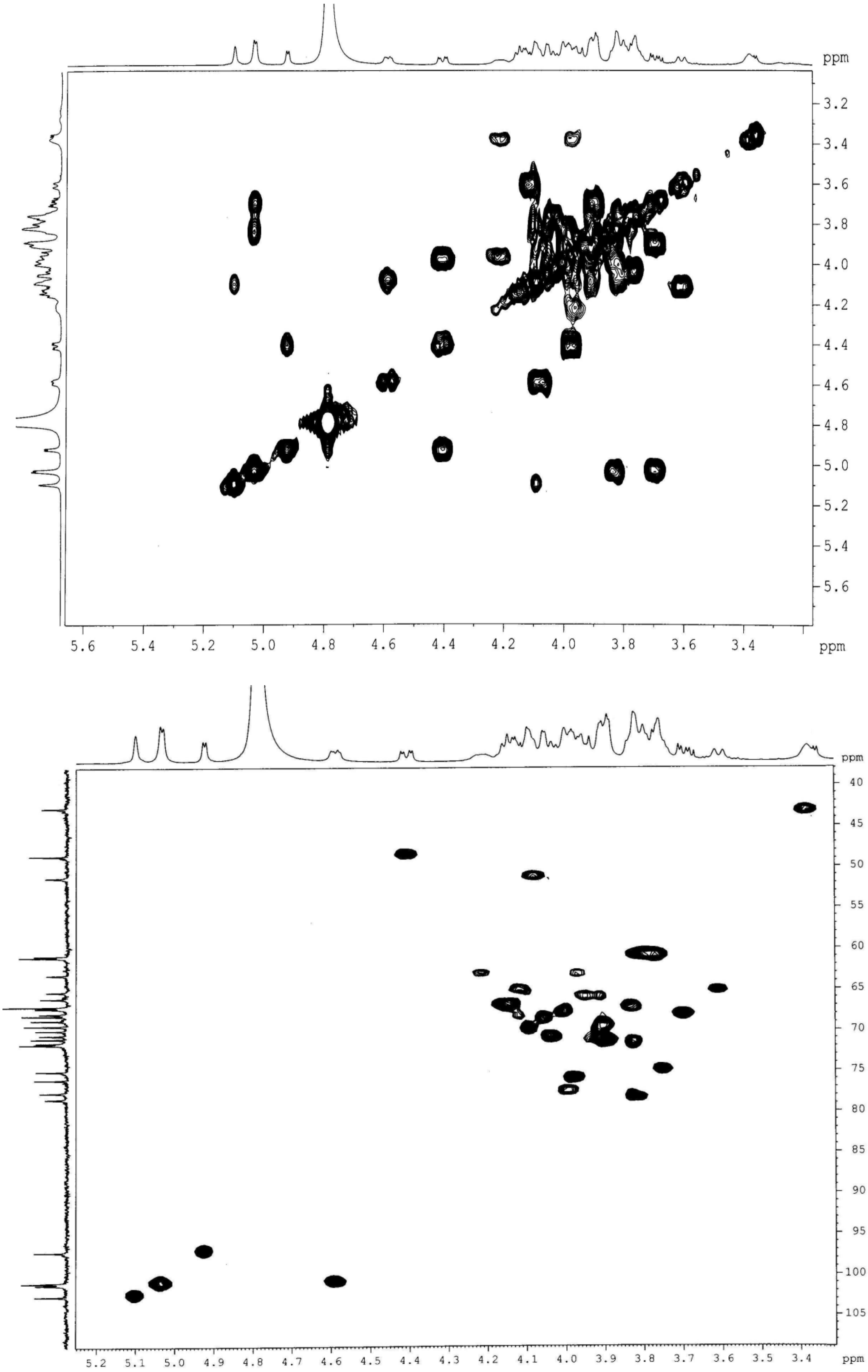
^{1}H, ^{13}C and 2D HSQC (selected region) NMR spectra of 2-(*N*-benzyloxycarbonyl) aminoethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-(2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**14**) ($CDCl_3$).



2D COSY and HSQC spectra of 2-(*N*-benzyloxycarbonyl) aminoethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-(2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranosyl)-(1→6)-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-(1→3)-(2,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**14**) ($CDCl_3$) (selected regions).



^{1}H, ^{13}C and DEPT 135 NMR spectra of 2-aminoethyl *O*-(α-L-fucopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→3)-(α-L-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside (**1**) (D$_2$O).



2D COSY and HSQC spectra of 2-aminoethyl *O*-(α-L-fucopyranosyl)-(1→3)-(2-acetamido-2-deoxy-α-D-galactopyranosyl)-(1→6)-(α-D-mannopyranosyl)-(1→3)-(α-L-fucopyranosyl)-(1→3)-2-acetamido-2-deoxy-β-D-galactopyranoside (**1**) (D_2O) (selected regions).