



## Supporting Information

for

### **Convenient synthesis of the pentasaccharide repeating unit corresponding to the cell wall O-antigen of *Escherichia albertii* O4**

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### **Experimental and analytical data and copies of NMR spectra**

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## Experimental

**General methods:** All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% Ce(SO<sub>4</sub>)<sub>2</sub> in 2N H<sub>2</sub>SO<sub>4</sub>) 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<sub>3</sub> as solvent and TMS as internal reference unless stated otherwise. Chemical shift value is expressed in  $\delta$  ppm. The complete assignment of proton and carbon spectra was carried out by using a standard set of NMR experiments, e.g. <sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>13</sup>C DEPT 135, 2D COSY and 2D HSQC etc. HRMS were recorded on a Bruker mass spectrometer. Optical rotations were recorded in a Jasco P-2000 spectrometer. Commercially available grades of organic solvents of adequate purity are used in all reactions.

**Preparation of HClO<sub>4</sub>/SiO<sub>2</sub> catalyst:** HClO<sub>4</sub> (3.6 g, 25 mmol, as a 70% aq solution) was added to a suspension of SiO<sub>2</sub> (230–400 mesh, 47.5 g) in Et<sub>2</sub>O (140 mL). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to furnish HClO<sub>4</sub>/SiO<sub>2</sub> (0.5 mmol/g) as a free flowing powder. **Caution!:** Although no explosions were reported under these conditions, special care should be taken for large-scale preparation.

***p*-Methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (8):** To a solution of compound **2** (1.5 g, 3.76 mmol) and compound **3** (2.1 g, 3.91 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added MS 4 Å (2 g) and the reaction mixture was cooled to –45 °C under argon. To the cooled reaction mixture was added NIS (900 mg, 4.0 mmol) followed by HClO<sub>4</sub>/SiO<sub>2</sub> (40 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic layer was successively washed with 5% aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (50 mL), H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (4:1) as eluant to give pure compound **8** (2.6 g, 79%). Colorless oil; [ $\alpha$ ]<sub>D</sub> –7 (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.30-7.21 (m, 20 H, Ar-H), 7.00 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.79 (d, *J* = 9.0 Hz, 2 H, Ar-H), 5.52 (d, *J* = 2.5 Hz, 1 H, H-1<sub>A</sub>), 5.46 (s, 1 H, PhCH), 5.45 (t, *J* = 8.5 Hz, 1 H, H-2<sub>B</sub>), 4.96 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.72 (d, *J* = 8.0 Hz, 1 H, H-1<sub>B</sub>), 4.67 (d, *J* = 12.0 Hz, 1 H, PhCH), 4.58-4.52 (m, 2 H, 2 PhCH), 4.40-4.39 (m, 3 H, H-4<sub>A</sub>, 2 PhCH), 4.29 (dd, *J* = 9.0 Hz,

3.0 Hz, 1 H, H-3<sub>A</sub>), 4.14 (d,  $J = 12.5$  Hz, 1 H, H-6<sub>aA</sub>), 3.91 (br s, 1 H, H-4<sub>B</sub>), 3.89 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-2<sub>A</sub>), 3.82 (d,  $J = 12.5$  Hz, 1 H, H-6<sub>bA</sub>), 3.74 (s, 3 H, OCH<sub>3</sub>), 3.68 (br s, 1 H, H-5<sub>B</sub>), 3.65-3.64 (m, 2 H, H-6<sub>abB</sub>), 3.60-3.58 (m, 1 H, H-5<sub>A</sub>), 3.55 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-3<sub>B</sub>), 2.02 (s, 3 H, COCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.3 (COCH<sub>3</sub>), 155.2-114.6 (Ar-C), 102.4 (C-1<sub>B</sub>), 100.3 (PhCH), 98.4 (C-1<sub>A</sub>), 80.7 (C-3<sub>B</sub>), 75.5 (C-4<sub>A</sub>), 74.4 (C-3<sub>A</sub>), 74.3 (PhCH<sub>2</sub>), 73.9 (C-4<sub>B</sub>), 73.5 (PhCH<sub>2</sub>), 72.7 (C-5<sub>A</sub>), 72.2 (PhCH<sub>2</sub>), 71.1 (C-2<sub>B</sub>), 69.2 (C-6<sub>B</sub>), 68.9 (C-6<sub>A</sub>), 63.8 (C-5<sub>B</sub>), 58.7 (C-2<sub>A</sub>), 55.5 (OCH<sub>3</sub>), 20.9 (COCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 896.3371; found, 896.3380.

***p*-Methoxyphenyl (3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (9):** A solution of compound **8** (2 g, 2.29 mmol) in 0.1 M CH<sub>3</sub>ONa in CH<sub>3</sub>OH (25 mL) was allowed to stir at room temperature for 2 h and neutralized with Dowex 50W X8 (H<sup>+</sup>) resin. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give pure compound **9** (1.8 g, 95%). Colorless oil;  $[\alpha]_D -7$  ( $c$  1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.27-7.22 (m, 20 H, Ar-H), 7.02 (d,  $J = 9.0$  Hz, 2 H, Ar-H), 6.80 (d,  $J = 9.0$  Hz, 2 H, Ar-H), 5.54 (d,  $J = 2.5$  Hz, 1 H, H-1<sub>A</sub>), 5.44 (s, 1 H, PhCH), 4.94 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.85 (d,  $J = 12.0$  Hz, 1 H, PhCH), 4.74 (d,  $J = 12.0$  Hz, 1 H, PhCH), 4.59 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.54 (d,  $J = 7.5$  Hz, 1 H, H-1<sub>B</sub>), 4.41-4.39 (m, 3 H, H-4<sub>A</sub>, 2 PhCH), 4.32 (dd,  $J = 10.5$  Hz, 3.0 Hz, 1 H, H-3<sub>A</sub>), 4.16 (d,  $J = 12.5$  Hz, 1 H, H-6<sub>aA</sub>), 4.06 (t,  $J = 9.5$  Hz, 1 H, H-2<sub>B</sub>), 4.00 (dd,  $J = 10.5$  Hz, 3.0 Hz, 1 H, H-2<sub>A</sub>), 3.86-3.82 (m, 2 H, H-5<sub>B</sub>, H-6<sub>bA</sub>), 3.74 (s, 3 H, OCH<sub>3</sub>), 3.69 (br s, 1 H, H-4<sub>B</sub>), 3.63-3.62 (m, 2 H, H-6<sub>abB</sub>), 3.55-3.54 (m, 1 H, H-5<sub>A</sub>), 3.49 (dd,  $J = 9.5$  Hz, 2.5 Hz, 1 H, H-3<sub>B</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  155.3-114.6 (Ar-C), 105.2 (C-1<sub>B</sub>), 100.6 (PhCH), 98.2 (C-1<sub>A</sub>), 81.7 (C-3<sub>B</sub>), 75.8 (C-4<sub>A</sub>), 75.4 (C-3<sub>A</sub>), 74.5 (PhCH<sub>2</sub>), 74.0 (C-4<sub>B</sub>), 73.9 (C-5<sub>A</sub>), 73.5 (PhCH<sub>2</sub>), 73.1 (PhCH<sub>2</sub>), 71.6 (C-2<sub>B</sub>), 69.3 (C-6<sub>B</sub>), 68.9 (C-6<sub>A</sub>), 63.7 (C-5<sub>B</sub>), 58.9 (C-2<sub>A</sub>), 53.2 (OCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 854.3265; found, 854.3272.

**Ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl-1-thio- $\beta$ -L-fucopyranoside (10):** A solution of compound **4** (1.5 g, 3.86 mmol) and compound **5** (2.4 g, 4.52 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was cooled to  $-10$  °C. To the cooled reaction mixture was added HClO<sub>4</sub>/SiO<sub>2</sub> (50 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was diluted with satd. aq. NaHCO<sub>3</sub> (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The

organic layer was washed with H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (6:1) as eluant to give pure compound **10** (2.2 g, 76%); Colorless oil; [ $\alpha$ ]<sub>D</sub> + 28 (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.32-7.20 (m, 20 H, Ar-H), 5.52-5.51 (m, 1 H, H-2<sub>D</sub>), 5.26 (d, *J* = 1.5 Hz, 1 H, H-1<sub>D</sub>), 4.91-4.87 (m, 2 H, 2 PhCH), 4.71 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.62-4.54 (m, 4 H, 4 PhCH), 4.49 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.23 (d, *J* = 9.5 Hz, 1 H, H-1<sub>C</sub>), 4.12-4.06 (m, 1 H, H-5<sub>D</sub>), 4.00 (t, *J* = 9.5 Hz, 1 H, H-2<sub>C</sub>), 3.89 (dd, *J* = 9.5 Hz, 3.5 Hz, 1 H, H-3<sub>D</sub>), 3.58 (d, *J* = 2.0 Hz, 1 H, H-4<sub>C</sub>), 3.47-3.46 (m, 1 H, H-5<sub>C</sub>), 3.40 (dd, *J* = 9.5 Hz, 3.0 Hz, 1 H, H-3<sub>C</sub>), 3.38 (t, *J* = 9.5 Hz, 1 H, H-4<sub>D</sub>), 2.79-2.62 (m, 2 H, SCH<sub>2</sub>CH<sub>3</sub>), 2.13 (s, 3 H, COCH<sub>3</sub>), 1.29 (t, *J* = 4.5 Hz, 3 H, SCH<sub>2</sub>CH<sub>3</sub>), 1.20 (d, *J* = 6.5 Hz, 3 H, CCH<sub>3</sub>), 1.09 (d, *J* = 6.0 Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  169.8 (COCH<sub>3</sub>), 138.8-127.4 (Ar-C), 98.4 (C-1<sub>D</sub>), 84.8 (C-1<sub>C</sub>), 83.4 (C-3<sub>C</sub>), 80.1 (C-4<sub>D</sub>), 77.9 (C-3<sub>D</sub>), 76.0 (C-4<sub>C</sub>), 75.2 (PhCH<sub>2</sub>), 74.5 (2 C, C-5<sub>C</sub>, PhCH<sub>2</sub>), 73.8 (C-2<sub>C</sub>), 72.6 (PhCH<sub>2</sub>), 71.4 (PhCH<sub>2</sub>), 68.5 (C-2<sub>D</sub>), 68.2 (C-5<sub>D</sub>), 24.1 (SCH<sub>2</sub>CH<sub>3</sub>), 21.1 (COCH<sub>3</sub>), 17.7 (CCH<sub>3</sub>), 17.3 (CCH<sub>3</sub>), 14.9 (SCH<sub>2</sub>CH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 779.3230; found, 779.3238.

***p*-Methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**11**)**: To a solution of compound **9** (0.4 g, 0.48 mmol) and compound **10** (0.4 g, 0.53 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added MS 4Å (1 g) and the reaction mixture was cooled to -40 °C under argon. To the cooled reaction mixture was added NIS (130 mg, 0.58 mmol) followed by HClO<sub>4</sub>/SiO<sub>2</sub> (10 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The organic layer was successively washed with 5% aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (20 mL), H<sub>2</sub>O (20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (4:1) as eluant to give pure compound **11** (160 mg, 22%).

**Following sequential strategy**: A solution of compound **13** (700 mg, 0.60 mmol) and compound **5** (380 mg, 0.72 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was cooled to -10 °C under argon. To the cooled reaction mixture was added HClO<sub>4</sub>/SiO<sub>2</sub> (10 mg) and it was allowed to stir at same temperature for 1 h. The reaction mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic layer was successively washed with 5% aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (50 mL), H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (4:1) as eluant to

give pure compound **11** (700 mg, 76%). Colorless oil;  $[\alpha]_D - 17$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46-6.81 (m, 44 H, Ar-H), 5.72 (d,  $J = 3.5$  Hz, 1 H, H-1<sub>A</sub>), 5.58 (d,  $J = 3.5$  Hz, 1 H, H-1<sub>C</sub>), 5.51 (s, 1 H, PhCH), 5.44-5.43 (m, 1 H, H-2<sub>D</sub>), 4.83 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.82 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.80 (d,  $J = 7.5$  Hz, 1 H, H-1<sub>B</sub>), 4.73 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.71 (br s, 1 H, H-1<sub>D</sub>), 4.69 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.66 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.63 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.56 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.54 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.53 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.50 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.48 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.45-4.36 (m, 5 H, H-3<sub>A</sub>, H-4<sub>A</sub>, 3 PhCH), 4.30 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-3<sub>C</sub>), 4.26 (t,  $J = 8.0$  Hz, 1 H, H-2<sub>B</sub>), 4.18-4.16 (m, 2 H, H-5<sub>B</sub>, H-6<sub>aA</sub>), 4.15-4.12 (m, 1 H, H-5<sub>D</sub>), 3.99 (br s, 1 H, H-4<sub>C</sub>), 3.97 (dd,  $J = 8.0$  Hz, 3.0 Hz, 1 H, H-3<sub>D</sub>), 3.92-3.89 (m, 2 H, H-3<sub>B</sub>, H-6<sub>bA</sub>), 3.77 (s, 3 H,  $\text{OCH}_3$ ), 3.77-3.72 (m, 3 H, H-2<sub>C</sub>, H-5<sub>A</sub>, H-5<sub>C</sub>), 3.65-3.62 (m, 2 H, H-6<sub>abB</sub>), 3.60 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-2<sub>A</sub>), 3.48 (br s, 1 H, H-4<sub>B</sub>), 3.26 (t,  $J = 8.0$  Hz, 1 H, H-4<sub>D</sub>), 1.84 (s, 3 H,  $\text{COCH}_3$ ), 1.16 (d,  $J = 6.0$  Hz, 3 H,  $\text{CCH}_3$ ), 0.91 (d,  $J = 6.0$  Hz, 3 H,  $\text{CCH}_3$ );  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  170.0 ( $\text{COCH}_3$ ), 155.4-114.7 (Ar-C), 103.3 (C-1<sub>B</sub>), 100.6 (PhCH), 99.0 (C-1<sub>C</sub>), 95.0 (C-1<sub>A</sub>), 94.1 (C-1<sub>D</sub>), 84.3 (C-3<sub>C</sub>), 80.0 (C-4<sub>D</sub>), 78.3 (C-4<sub>B</sub>), 78.1 (C-3<sub>D</sub>), 77.6 (C-4<sub>A</sub>), 76.1 (C-5<sub>C</sub>), 74.9, 74.8, 74.2 (3 C, 3 PhCH<sub>2</sub>), 73.5 (C-3<sub>B</sub>), 73.4 (PhCH<sub>2</sub>), 73.1 (C-5<sub>A</sub>), 72.9, 71.6 (2 C, 2 PhCH<sub>2</sub>), 71.3 (C-5<sub>B</sub>), 70.7 (C-4<sub>C</sub>), 70.5 (PhCH<sub>2</sub>), 70.3 (C-2<sub>B</sub>), 69.0 (C-6<sub>A</sub>), 68.9 (C-2<sub>D</sub>), 68.8 (C-6<sub>B</sub>), 67.3 (C-5<sub>D</sub>), 66.2 (C-3<sub>A</sub>), 63.9 (C-2<sub>C</sub>), 58.7 (C-2<sub>A</sub>), 55.5 ( $\text{OCH}_3$ ), 20.9 ( $\text{COCH}_3$ ), 17.6 ( $\text{CCH}_3$ ), 16.2 ( $\text{CCH}_3$ ); HRMS  $[\text{M}+\text{Na}]^+$ : Calcd. 1548.6407; found, 1548.6400.

***p*-Methoxyphenyl (3,4-di-*O*-acetyl-2-*O*-(*p*-methoxybenzyl))- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**12**):** To a solution of compound **9** (1.2 g, 1.44 mmol) and compound **6** (625 mg, 1.51 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added MS 4 Å (1 g) and the reaction mixture was cooled to  $-45$  °C under argon. To the cooled reaction mixture was added NIS (350 mg, 1.56 mmol) followed by  $\text{HClO}_4/\text{SiO}_2$  (20 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with  $\text{CH}_2\text{Cl}_2$  (50 mL). The organic layer was successively washed with 5% aq.  $\text{Na}_2\text{S}_2\text{O}_3$  (50 mL),  $\text{H}_2\text{O}$  (50 mL), dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The crude product was purified over  $\text{SiO}_2$  using hexane-EtOAc (4:1) as eluant to give pure compound **12** (1.26 g, 74%). Colorless oil;  $[\alpha]_D + 10$  ( $c$  1.0,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47-6.63 (m, 28 H, Ar-H), 5.67 (d,  $J = 3.0$  Hz, 1 H, H-1<sub>A</sub>), 5.60 (d,  $J = 3.5$  Hz,

1 H, H-1<sub>C</sub>), 5.50 (s, 1 H, PhCH), 5.44 (dd,  $J = 10.5$  Hz, 3.0 Hz, 1 H, H-3<sub>C</sub>), 5.12 (br s, 1 H, H-4<sub>C</sub>), 4.85 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.79 (d,  $J = 7.5$  Hz, 1 H, H-1<sub>B</sub>), 4.73-4.70 (m, 2 H, H-5<sub>A</sub>, PhCH), 4.60 (d,  $J = 12.0$  Hz, 1 H, PhCH), 4.52 (d,  $J = 11.5$  Hz, 1 H, PhCH), 4.43 (br s, 2 H, PhCH), 4.41-4.34 (m, 3 H, H-4<sub>A</sub>, H-5<sub>B</sub>, PhCH), 4.28 (d,  $J = 12.0$  Hz, 1 H, PhCH), 4.22-4.16 (m, 2 H, H-2<sub>B</sub>, H-6<sub>aA</sub>), 4.06-4.05 (m, 2 H, H-6<sub>abB</sub>), 3.92-3.90 (m, 2 H, H-4<sub>B</sub>, H-6<sub>bA</sub>), 3.81 (s, 3 H, OCH<sub>3</sub>), 3.80-3.76 (m, 2 H, H-2<sub>A</sub>, H-3<sub>A</sub>), 3.72 (s, 3 H, OCH<sub>3</sub>), 3.72-3.71 (m, 2 H, H-2<sub>C</sub>, H-5<sub>C</sub>), 3.65-3.63 (m, 1 H, H-3<sub>B</sub>), 2.03 (s, 3 H, COCH<sub>3</sub>), 1.93 (s, 3 H, COCH<sub>3</sub>), 0.70 (d,  $J = 6.0$  Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  170.0, 169.6 (2 C, 2 COCH<sub>3</sub>), 155.3-113.4 (Ar-C), 103.3 (C-1<sub>B</sub>), 100.8 (PhCH), 99.0 (C-1<sub>A</sub>), 97.1 (C-1<sub>C</sub>), 84.1 (C-2<sub>C</sub>), 76.1 (C-4<sub>A</sub>), 74.4 (PhCH<sub>2</sub>), 73.6 (2C, C-3<sub>B</sub>, C-5<sub>B</sub>), 73.5 (PhCH<sub>2</sub>), 72.5 (C-4<sub>C</sub>), 72.4 (C-2<sub>B</sub>), 72.3 (C-4<sub>B</sub>), 72.0 (C-5<sub>C</sub>), 71.6, 71.5 (2 C, 2 PhCH<sub>2</sub>), 70.0 (C-3<sub>C</sub>), 68.8 (C-6<sub>A</sub>), 66.8 (C-6<sub>B</sub>), 64.3 (C-5<sub>A</sub>), 63.8 (C-3<sub>A</sub>), 58.2 (C-2<sub>A</sub>), 55.4 (OCH<sub>3</sub>), 55.0 (OCH<sub>3</sub>), 23.0, 22.7 (2 C, 2 COCH<sub>3</sub>), 15.2 (CCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 1204.4631; found, 1204.4640.

***p*-Methoxyphenyl (3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (13):**

To a solution of compound **12** (1.1 g, 0.93 mmol) in THF (25 mL) were added benzyl bromide (550  $\mu$ L, 4.63 mmol), powdered NaOH (750 mg, 18.75 mmol) and TBAB (50 mg) and the reaction mixture was vigorously stirred at room temperature for 6 h. The reaction mixture was diluted with H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The organic layer was washed with H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. To a solution of the crude product in CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added DDQ (500 mg, 2.20 mmol) in H<sub>2</sub>O (10 mL) and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with satd. NaHCO<sub>3</sub> (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic layer was washed with H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (5:1) as eluant to give pure compound **13** (775 mg, 72%). Colorless oil;  $[\alpha]_D + 42$  ( $c$  1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.45-6.80 (m, 34 H, Ar-H), 5.58 (d,  $J = 3.0$  Hz, 1 H, H-1<sub>A</sub>), 5.50 (s, 1 H, PhCH), 5.35 (d,  $J = 4.0$  Hz, 1 H, H-1<sub>C</sub>), 4.89-4.85 (m, 2 H, H-5<sub>A</sub>, PhCH), 4.67 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.61 (d,  $J = 7.5$  Hz, 1 H, H-1<sub>B</sub>), 4.57-4.51 (m, 3 H, 3 PhCH), 4.44-4.38 (m, 6 H, H-4<sub>A</sub>, 5 PhCH), 4.33 (dd,  $J = 11.0$  Hz, 3.5 Hz, H-3<sub>C</sub>), 4.24 (t,  $J = 8.0$  Hz, 1 H, H-2<sub>B</sub>), 4.18 (d,  $J = 12.0$  Hz, 1 H, H-6<sub>aA</sub>), 3.94-3.93 (m, 2 H, H-4<sub>B</sub>, H-4<sub>C</sub>), 3.92-3.91 (m, 2 H, H-5<sub>B</sub>, H-6<sub>bA</sub>), 3.76 (s, 3

H, OCH<sub>3</sub>), 3.76-3.74 (m, 2 H, H-3<sub>A</sub>, H-5<sub>C</sub>), 3.72 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-2<sub>A</sub>), 3.65-3.64 (m, 2 H, H-2<sub>C</sub>, H-6<sub>aB</sub>), 3.63-3.57 (m, 2 H, H-3<sub>B</sub>, H-6<sub>bB</sub>), 0.95 (d,  $J = 6.0$  Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 155.5-114.7 (Ar-C), 103.1 (C-1<sub>B</sub>), 100.9 (PhCH), 98.7 (C-1<sub>A</sub>), 95.5 (C-1<sub>C</sub>), 83.3 (C-3<sub>B</sub>), 81.9 (C-5<sub>B</sub>), 80.0 (C-5<sub>A</sub>), 76.0 (C-4<sub>A</sub>), 74.6 (2 C, 2 PhCH<sub>2</sub>), 73.8 (C-4<sub>B</sub>), 73.5 (2 C, 2 PhCH<sub>2</sub>), 73.4 (C-4<sub>C</sub>), 72.4 (C-3<sub>C</sub>), 72.3 (C-2<sub>B</sub>), 72.7 (PhCH<sub>2</sub>), 68.8 (C-6<sub>A</sub>), 68.7 (C-6<sub>B</sub>), 65.6 (C-2<sub>C</sub>), 63.9 (C-3<sub>A</sub>), 62.8 (C-5<sub>C</sub>), 58.9 (C-2<sub>A</sub>), 55.5 (OCH<sub>3</sub>), 14.9 (CCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 1180.4783; found, 1180.4790.

***p*-Methoxyphenyl (3,4-di-*O*-benzyl-α-*L*-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-*L*-fucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-β-*D*-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-*D*-galactopyranoside (14)**: A solution of compound **11** (700 mg, 0.46 mmol) in 0.1 M CH<sub>3</sub>ONa in CH<sub>3</sub>OH (25 mL) was allowed to stir at room temperature for 2 h and neutralized with Dowex 50W X8 (H<sup>+</sup>) resin. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give pure compound **14** (640 mg, 94%). Colorless oil; [α]<sub>D</sub> -97 (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.47-6.80 (m, 44 H, Ar-H), 5.64 (d,  $J = 3.5$  Hz, 1 H, H-1<sub>A</sub>), 5.59 (d,  $J = 3.0$  Hz, 1 H, H-1<sub>C</sub>), 5.51 (s, 1 H, PhCH), 4.82 (br s, 1 H, H-1<sub>D</sub>), 4.81 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.80 (d,  $J = 11.0$  Hz, 1 H, PhCH), 4.69 (d,  $J = 7.5$  Hz, 1 H, H-1<sub>B</sub>), 4.59-4.58 (m, 3 H, 3 PhCH), 4.51-4.39 (m, 7 H, H-4<sub>A</sub>, 6 PhCH), 4.35 (dd,  $J = 9.0$  Hz, 3.0 Hz, 1 H, H-3<sub>A</sub>), 4.23 (t,  $J = 9.0$  Hz, 1 H, H-2<sub>B</sub>), 4.17 (d,  $J = 12.5$  Hz, 1 H, H-6<sub>aA</sub>), 3.96-3.94 (m, 2 H, H-3<sub>D</sub>, H-5<sub>A</sub>), 3.90 (d,  $J = 10.0$  Hz, 1 H, H-6<sub>bA</sub>), 3.87 (br s, 1 H, H-4<sub>C</sub>), 3.83 (br s, 1 H, H-4<sub>B</sub>), 3.82 (s, 3 H, OCH<sub>3</sub>), 3.82-3.71 (m, 4 H, H-2<sub>A</sub>, H-2<sub>D</sub>, H-3<sub>B</sub>, H-5<sub>B</sub>), 3.70-3.62 (m, 3 H, H-2<sub>C</sub>, H-5<sub>D</sub>, H-6<sub>aB</sub>), 3.58-3.57 (m, 2 H, H-3<sub>C</sub>, H-6<sub>bB</sub>), 3.50-3.49 (m, 1 H, H-5<sub>C</sub>), 3.41 (t,  $J = 8.0$  Hz, 1 H, H-4<sub>D</sub>), 0.96 (d,  $J = 6.0$  Hz, 3 H, CCH<sub>3</sub>), 0.89 (d,  $J = 6.0$  Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 155.3-114.7 (Ar-C), 103.4 (C-1<sub>B</sub>), 100.7 (PhCH), 99.2 (C-1<sub>D</sub>), 99.0 (C-1<sub>C</sub>), 96.6 (C-1<sub>A</sub>), 84.6 (C-3<sub>C</sub>), 79.7 (2 C, C-3<sub>B</sub>, C-4<sub>D</sub>), 78.4 (C-4<sub>B</sub>), 76.0 (C-4<sub>A</sub>), 75.3, 74.3 (2 C, 2 PhCH<sub>2</sub>), 73.6 (C-2<sub>B</sub>), 73.4 (PhCH<sub>2</sub>), 73.2 (C-2<sub>C</sub>), 72.2 (C-5<sub>D</sub>), 72.1, 71.9 (3 C, 3 PhCH<sub>2</sub>), 71.8 (C-3<sub>A</sub>), 71.7 (C-3<sub>D</sub>), 69.0 (C-6<sub>A</sub>), 68.9 (2 C, C-4<sub>C</sub>, C-5<sub>A</sub>), 68.8 (C-6<sub>B</sub>), 68.4 (C-5<sub>B</sub>), 65.3 (C-5<sub>C</sub>), 65.1 (PhCH<sub>2</sub>), 63.9 (C-2<sub>D</sub>), 58.8 (C-2<sub>A</sub>), 55.5 (OCH<sub>3</sub>), 15.6 (CCH<sub>3</sub>), 14.1 (CCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 1506.6301; found, 1506.6310.

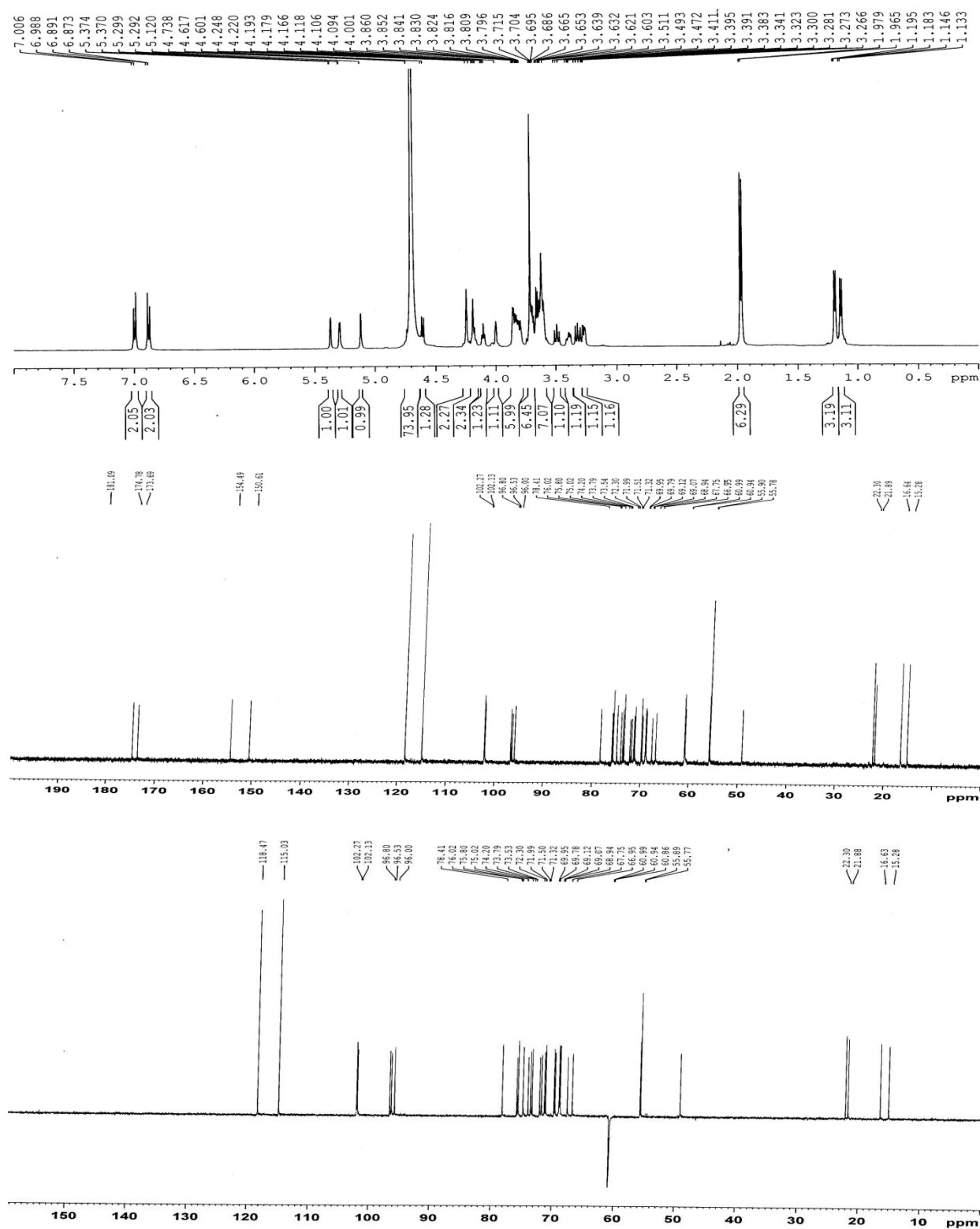
***p*-Methoxyphenyl (2-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-*D*-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-*L*-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-**



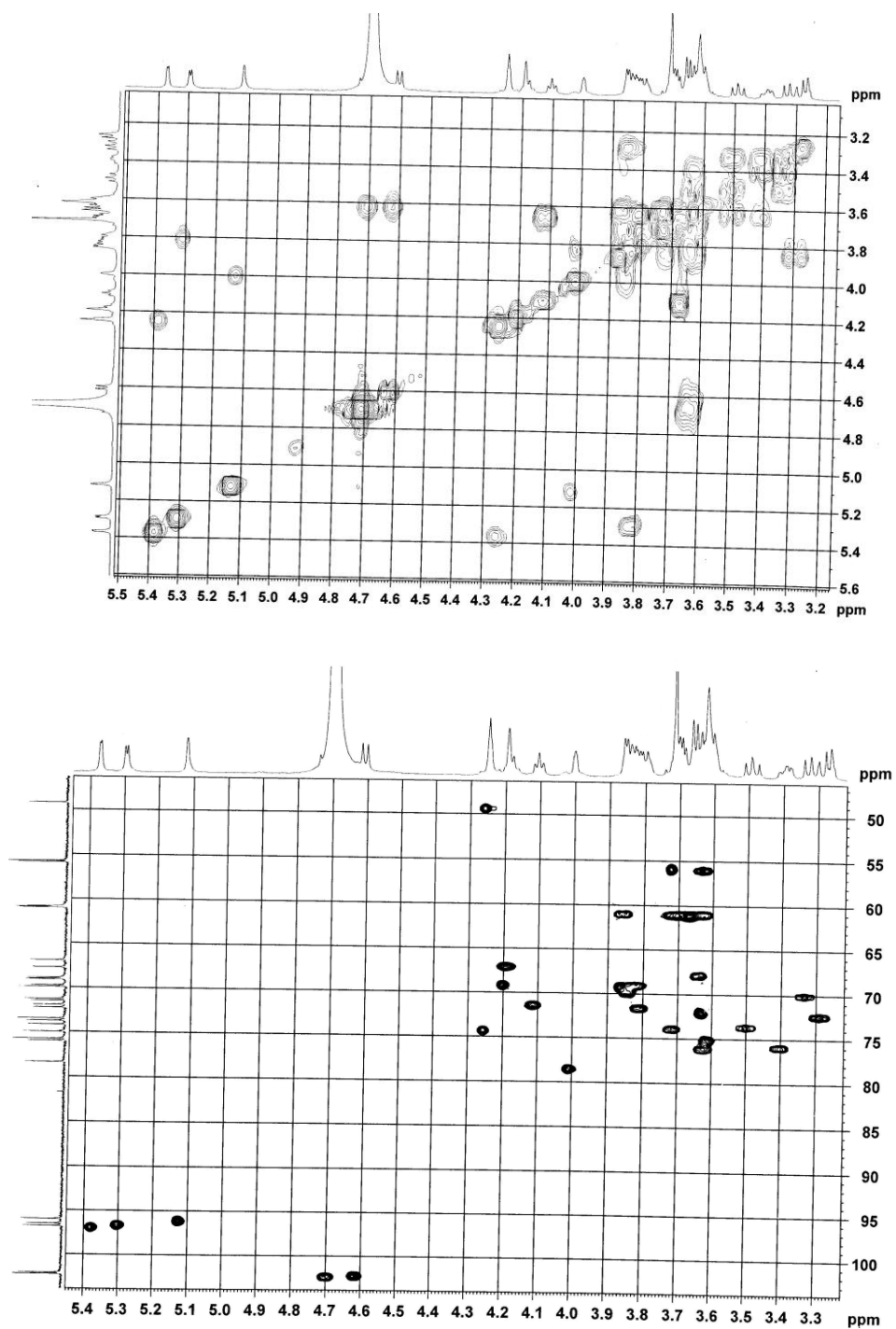
**L-fucopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (15):** To a solution of compound **14** (600 mg, 0.40 mmol) and compound **7** (230 mg, 0.47 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added MS 4 Å (0.5 g) and the reaction mixture was cooled to –15 °C under argon. To the cooled reaction mixture was added NIS (120 mg, 0.53 mmol) followed by HClO<sub>4</sub>-SiO<sub>2</sub> (10 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The organic layer was successively washed with 5% aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (50 mL), H<sub>2</sub>O (50 mL), dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated. The crude product was purified over SiO<sub>2</sub> using hexane-EtOAc (4:1) as eluant to give pure compound **15** (535 mg, 70%). Colorless oil; [α]<sub>D</sub> – 50 (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.57-6.82 (m, 53 H, Ar-H), 6.05 (t, *J* = 8.5 Hz, 1 H, H-3<sub>E</sub>), 5.64 (d, *J* = 3.5 Hz, 1 H, H-1<sub>A</sub>), 5.54 (d, *J* = 3.0 Hz, 1 H, H-1<sub>C</sub>), 5.50 (d, *J* = 8.5 Hz, 1 H, H-1<sub>E</sub>), 5.48 (s, 1 H, PhCH), 5.41 (s, 1 H, PhCH), 4.98 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.96 (br s, 1 H, H-1<sub>D</sub>), 4.76 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.71 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.69 (d, *J* = 8.0 Hz, 1 H, H-1<sub>B</sub>), 4.63 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.57 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.51 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.44-4.41 (m, 3 H, 3 PhCH), 4.38-4.27 (m, 7 H, H-2<sub>E</sub>, H-4<sub>A</sub>, 5 PhCH), 4.17-4.11 (m, 4 H, H-2<sub>B</sub>, H-3<sub>A</sub>, H-4<sub>E</sub>, H-6<sub>AA</sub>), 4.01 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3<sub>C</sub>), 4.00 (br s, 1 H, H-4<sub>C</sub>), 3.90 (d, *J* = 8.0 Hz, 1 H, H-6<sub>BA</sub>), 3.84-3.79 (m, 3 H, H-2<sub>D</sub>, H-3<sub>D</sub>, H-4<sub>B</sub>), 3.77 (s, 3 H, OCH<sub>3</sub>), 3.77-3.74 (m, 2 H, H-2<sub>C</sub>, H-3<sub>B</sub>), 3.67-3.63 (m, 5 H, H-5<sub>A</sub>, H-5<sub>B</sub>, H-5<sub>D</sub>, H-5<sub>E</sub>, H-6<sub>AB</sub>), 3.61-3.59 (m, 5 H, H-2<sub>A</sub>, H-2<sub>C</sub>, H-6<sub>BB</sub>, H-6<sub>abE</sub>), 3.36-3.32 (m, 1 H, H-5<sub>C</sub>), 2.86 (t, *J* = 8.0 Hz, 1 H, H-4<sub>D</sub>), 1.92 (s, 3 H, COCH<sub>3</sub>), 1.02 (d, *J* = 6.0 Hz, 3 H, CCH<sub>3</sub>), 0.84 (d, *J* = 6.0 Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 169.6 (COCH<sub>3</sub>), 155.3-114.7 (Ar-C), 103.4 (C-1<sub>B</sub>), 101.6, 100.4 (2 C, 2 PhCH), 100.1 (C-1<sub>E</sub>), 99.0 (C-1<sub>C</sub>), 94.9 (C-1<sub>D</sub>), 94.7 (C-1<sub>A</sub>), 84.1 (C-5<sub>E</sub>), 80.9 (C-4<sub>D</sub>), 79.4 (C-5<sub>D</sub>), 78.7 (C-3<sub>D</sub>), 78.0 (2C, C-3<sub>B</sub>, C-3<sub>C</sub>), 77.8 (C-5<sub>B</sub>), 75.9 (C-5<sub>A</sub>), 74.7, 74.5, 74.3 (3 C, 3 PhCH<sub>2</sub>), 73.6 (C-4<sub>B</sub>), 73.4, 73.1 (2 C, 2 PhCH<sub>2</sub>), 72.9 (C-2<sub>D</sub>), 72.5 (C-4<sub>C</sub>), 72.4, 71.9 (2 C, 2 PhCH<sub>2</sub>), 71.1 (C-3<sub>A</sub>), 70.4 (C-4<sub>E</sub>), 69.2 (C-3<sub>E</sub>), 68.8 (2 C, C-6<sub>A</sub>, C-6<sub>B</sub>), 68.7 (C-6<sub>E</sub>), 68.0 (C-4<sub>A</sub>), 66.2 (C-2<sub>B</sub>), 65.6 (C-5<sub>C</sub>), 63.8 (C-2<sub>C</sub>), 58.7 (C-2<sub>A</sub>), 55.5 (OCH<sub>3</sub>), 55.3 (C-2<sub>E</sub>), 20.6 (COCH<sub>3</sub>), 17.6 (CCH<sub>3</sub>), 16.2 (CCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 1927.7463; found, 1927.7470.

**p-Methoxyphenyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-(α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (1):** To a solution of compound **15** (500 mg, 0.26

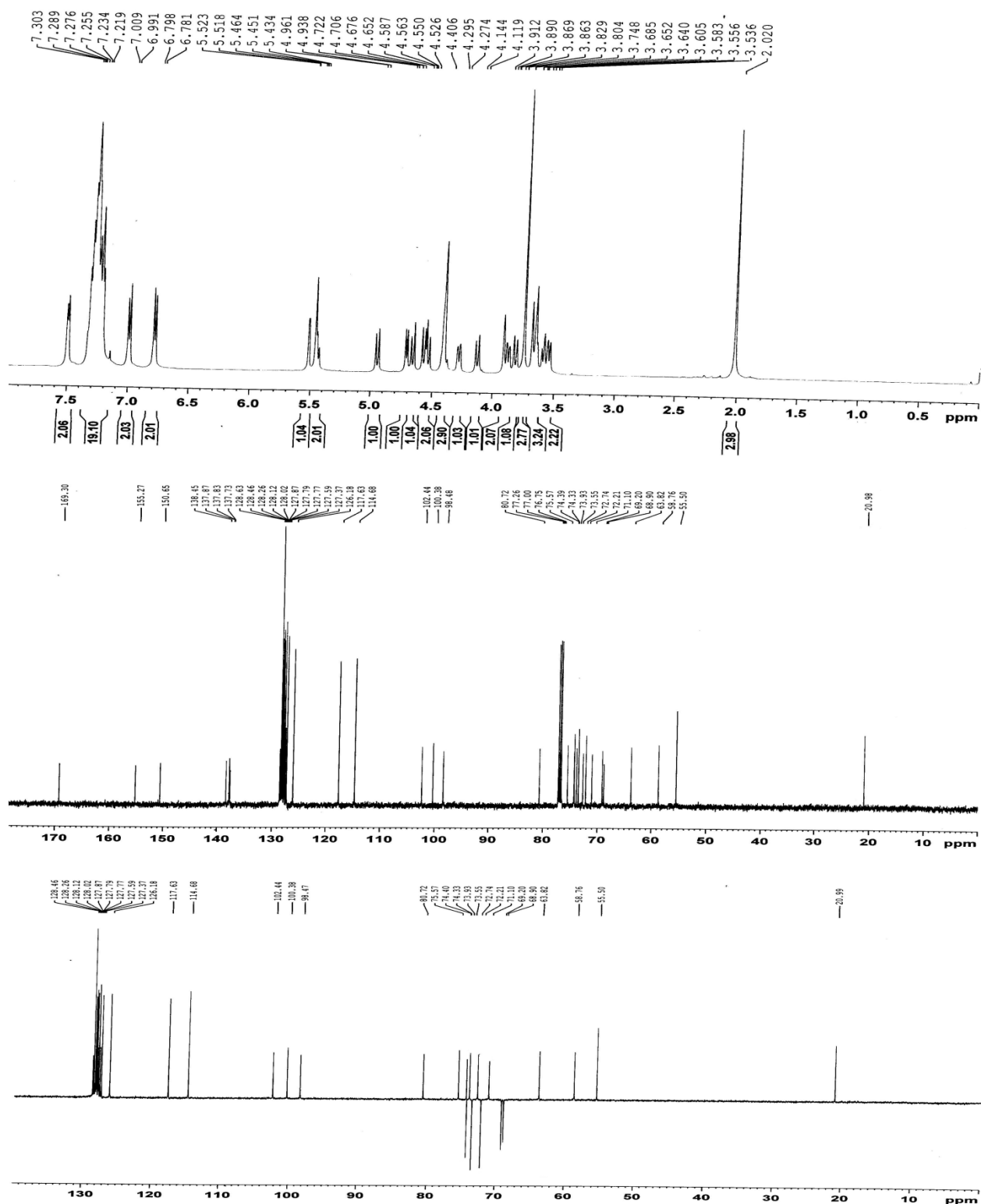
mmol) in pyridine (5 mL) was added CH<sub>3</sub>COSH (0.5 mL, 7.1 mmol) and it was allowed to stir at room temperature for 16 h. The solvents were removed under reduced pressure and co-evaporated with toluene (3 × 10 mL). To a solution of the crude product in EtOH (15 mL) was added NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O (0.2 mL) and the reaction mixture was allowed to stir at 80 °C for 12 h. The solvents were removed under reduced pressure and a solution of the crude product in CH<sub>3</sub>OH (5 mL) was treated with acetic anhydride (1 mL) at room temperature for 30 min. The solvents were removed under reduced pressure and co-evaporated with toluene (3 × 10 mL). To a solution of the crude product in CH<sub>3</sub>OH (10 mL) was added 20% Pd(OH)<sub>2</sub>/C (100 mg) and the reaction mixture was allowed to stir at room temperature under a positive pressure of hydrogen for 24 h. The reaction mixture was filtered through a Celite bed and concentrated. The hydrogenolized product was passed through a Sephadex LH-20 column using CH<sub>3</sub>OH-H<sub>2</sub>O (5:1) as eluant to give pure compound **1** (125 mg, 49%). White powder; [α]<sub>D</sub> (*c* 1.0, H<sub>2</sub>O); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.00 (d, *J* = 9.0 Hz, 2 H, Ar-H), 6.89 (d, *J* = 9.0 Hz, 1 H, Ar-H), 5.37 (d, *J* = 2.0 Hz, 1 H, H-1<sub>A</sub>), 5.29 (d, *J* = 3.5 Hz, 1 H, H-1<sub>C</sub>), 5.12 (br s, 1 H, H-1<sub>D</sub>), 4.73 (d, *J* = 7.5 Hz, 1 H, H-1<sub>E</sub>), 4.61 (d, *J* = 8.0 Hz, 1 H, H-1<sub>B</sub>), 4.26-4.22 (m, 2 H, H-2<sub>A</sub>, H-5<sub>C</sub>), 4.19-4.17 (m, 2 H, H-3<sub>A</sub>, H-4<sub>A</sub>), 4.11-4.09 (m, 1 H, H-5<sub>A</sub>), 4.01-3.98 (m, 1 H, H-2<sub>D</sub>), 3.86-3.79 (m, 6 H, H-2<sub>C</sub>, H-3<sub>B</sub>, H-3<sub>D</sub>, H-4<sub>C</sub>, H-5<sub>D</sub>, H-6<sub>aA</sub>), 3.71 (s, 3 H, OCH<sub>3</sub>), 3.71-3.68 (m, 3 H, H-3<sub>C</sub>, H-4<sub>B</sub>, H-5<sub>B</sub>), 3.66-3.60 (m, 7 H, H-2<sub>B</sub>, H-2<sub>E</sub>, H-6<sub>bA</sub>, H-6<sub>abB</sub>, H-6<sub>abE</sub>), 3.49 (t, *J* = 9.0 Hz, 1 H, H-3<sub>E</sub>), 3.41-3.39 (m, 1 H, H-5<sub>E</sub>), 3.32 (t, *J* = 9.0 Hz, 1 H, H-4<sub>E</sub>), 3.27 (t, *J* = 9.0 Hz, 1 H, H-4<sub>D</sub>), 1.97 (s, 3 H, NHCOCH<sub>3</sub>), 1.96 (s, 3 H, NHCOCH<sub>3</sub>), 1.19 (d, *J* = 6.0 Hz, 3 H, CCH<sub>3</sub>), 1.14 (d, *J* = 6.0 Hz, 3 H, CCH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 174.7, 173.6 (2 C, 2 NHCOCH<sub>3</sub>), 154.4-114.0 (Ar-C), 102.2 (C-1<sub>E</sub>), 102.1 (C-1<sub>B</sub>), 96.8 (C-1<sub>A</sub>), 96.5 (C-1<sub>C</sub>), 96.0 (C-1<sub>D</sub>), 78.4 (C-2<sub>D</sub>), 76.0 (C-5<sub>E</sub>), 75.8 (C-2<sub>B</sub>), 75.0 (C-3<sub>B</sub>), 74.2 (C-3<sub>E</sub>), 73.7 (C-5<sub>C</sub>), 73.5 (C-5<sub>B</sub>), 72.3 (C-5<sub>A</sub>), 71.9 (C-2<sub>C</sub>), 71.5 (C-4<sub>C</sub>), 71.3 (C-4<sub>B</sub>), 69.9 (C-4<sub>E</sub>), 69.7 (C-3<sub>D</sub>), 69.1 (C-5<sub>D</sub>), 69.0 (C-3<sub>A</sub>), 68.9 (C-4<sub>D</sub>), 67.7 (C-3<sub>C</sub>), 66.9 (C-4<sub>A</sub>), 61.0 (C-6<sub>E</sub>), 60.9 (C-6<sub>B</sub>), 60.8 (C-6<sub>A</sub>), 55.8 (C-2<sub>E</sub>), 55.7 (OCH<sub>3</sub>), 49.5 (C-2<sub>A</sub>), 22.3 (NHCOCH<sub>3</sub>), 21.8 (NHCOCH<sub>3</sub>), 16.6 (CCH<sub>3</sub>), 15.2 (CCH<sub>3</sub>); HRMS [M+Na]<sup>+</sup>: Calcd. 1007.3696; found, 1007.3704.



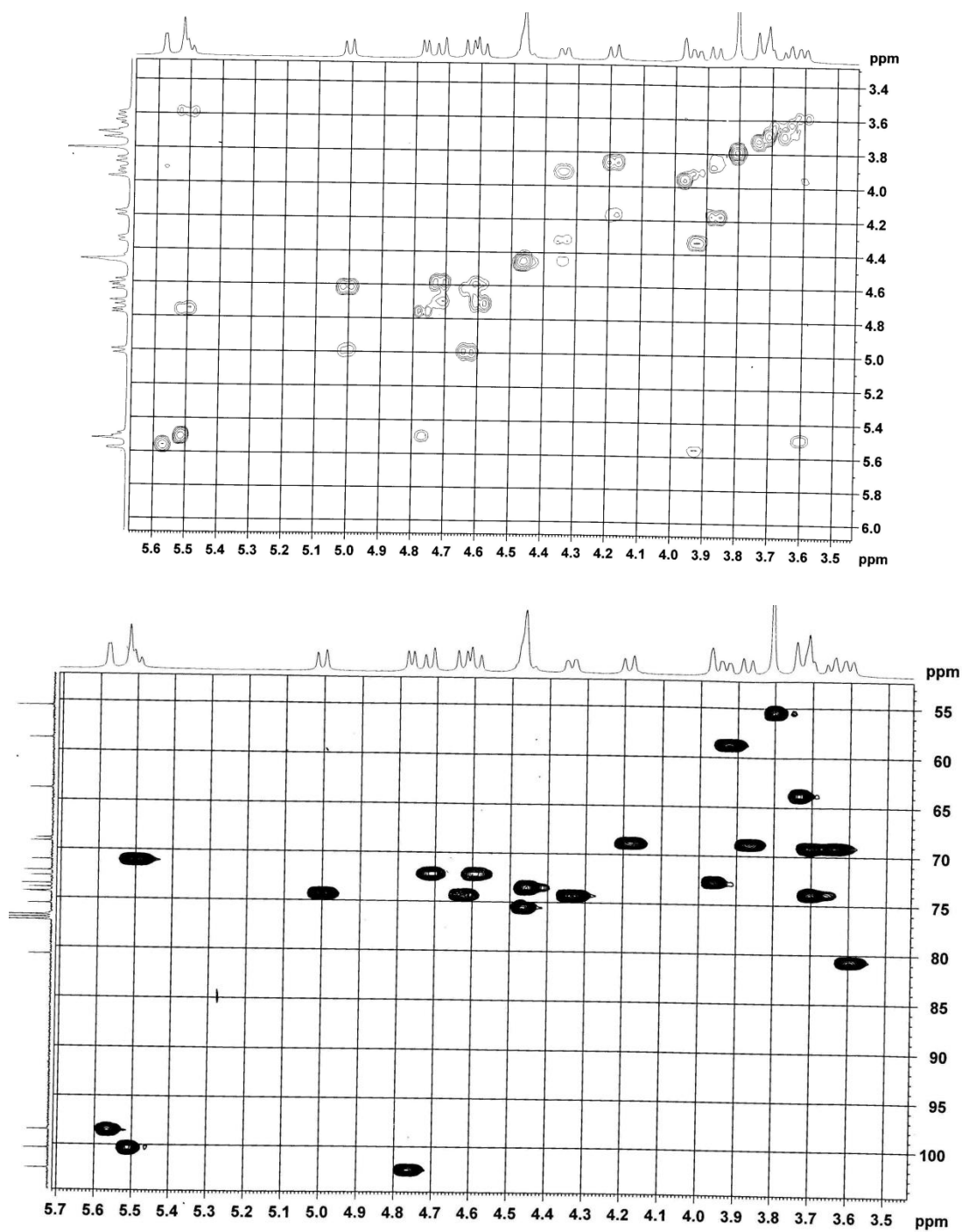
<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-(α-L-rhamnopyranosyl)-(1→2)-(α-L-fucopyranosyl)-(1→2)-(β-D-galactopyranosyl)-(1→3)-2-acetamido-2-deoxy-α-D-galactopyranoside (**1**) (D<sub>2</sub>O).



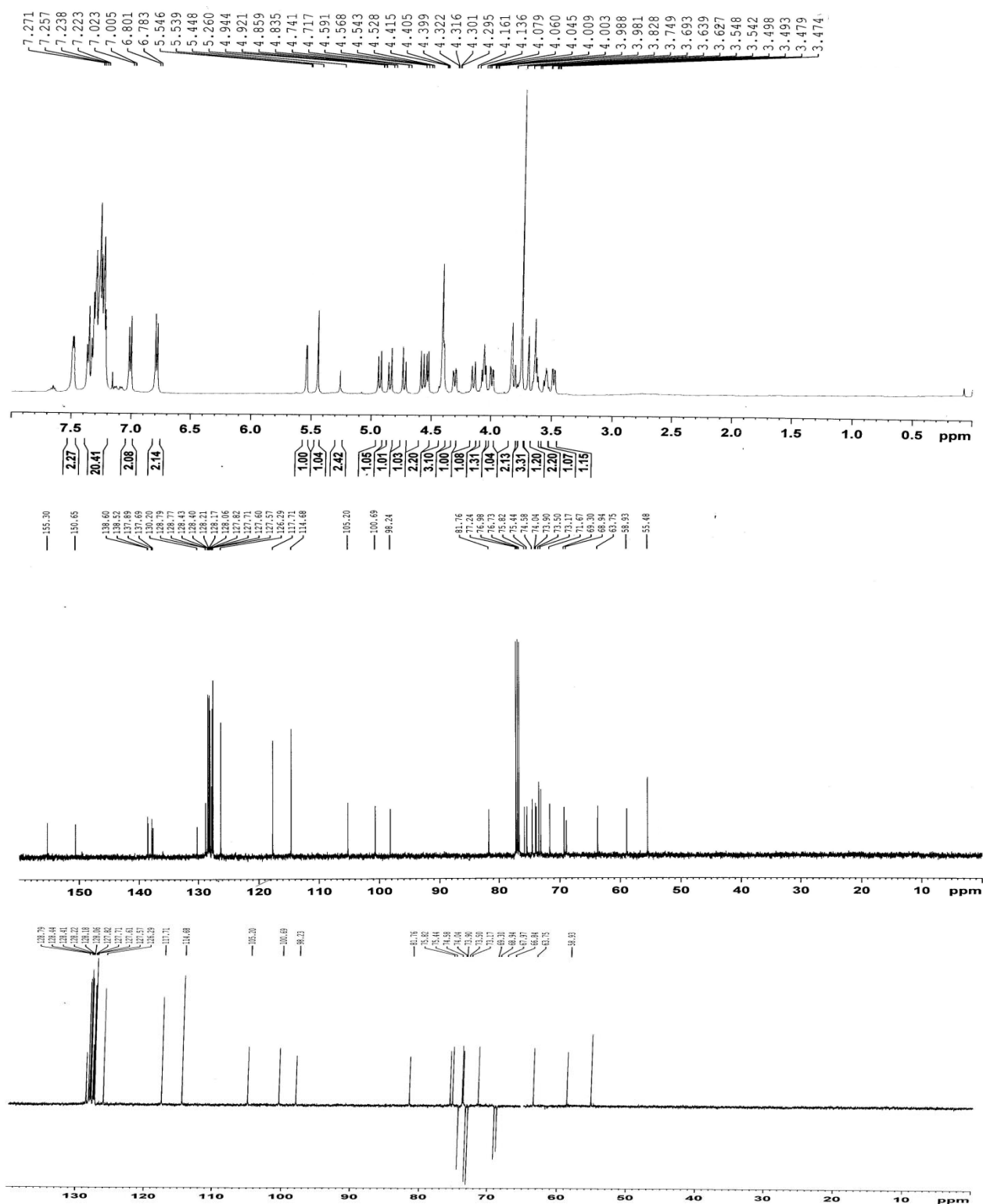
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-acetamido-2-deoxy- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 2)-( $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-( $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-( $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-acetamido-2-deoxy- $\alpha$ -D-galactopyranoside (**1**) (D<sub>2</sub>O) (Selected region).



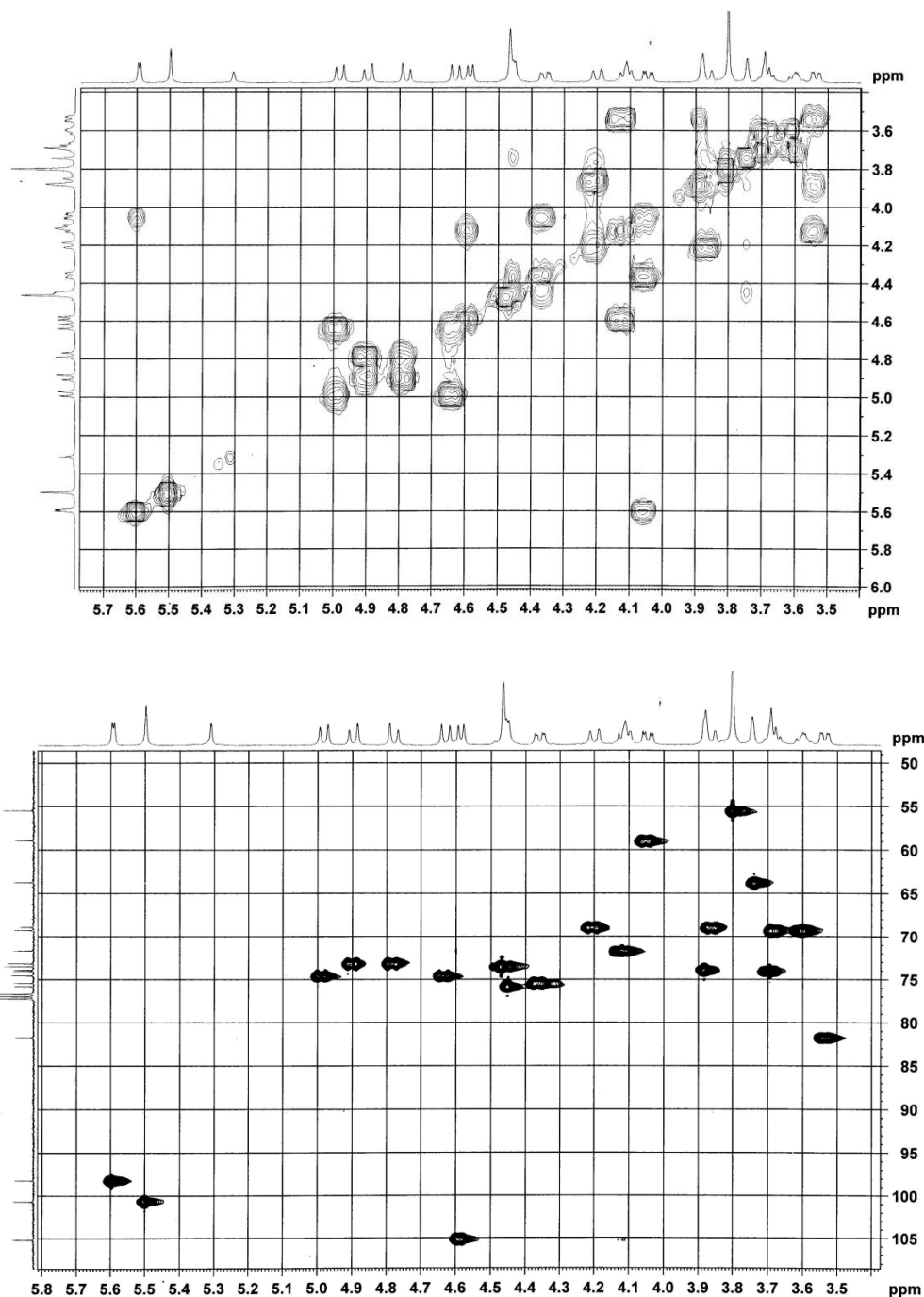
<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (8) (CDCl<sub>3</sub>).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**8**) (CDCl<sub>3</sub>).

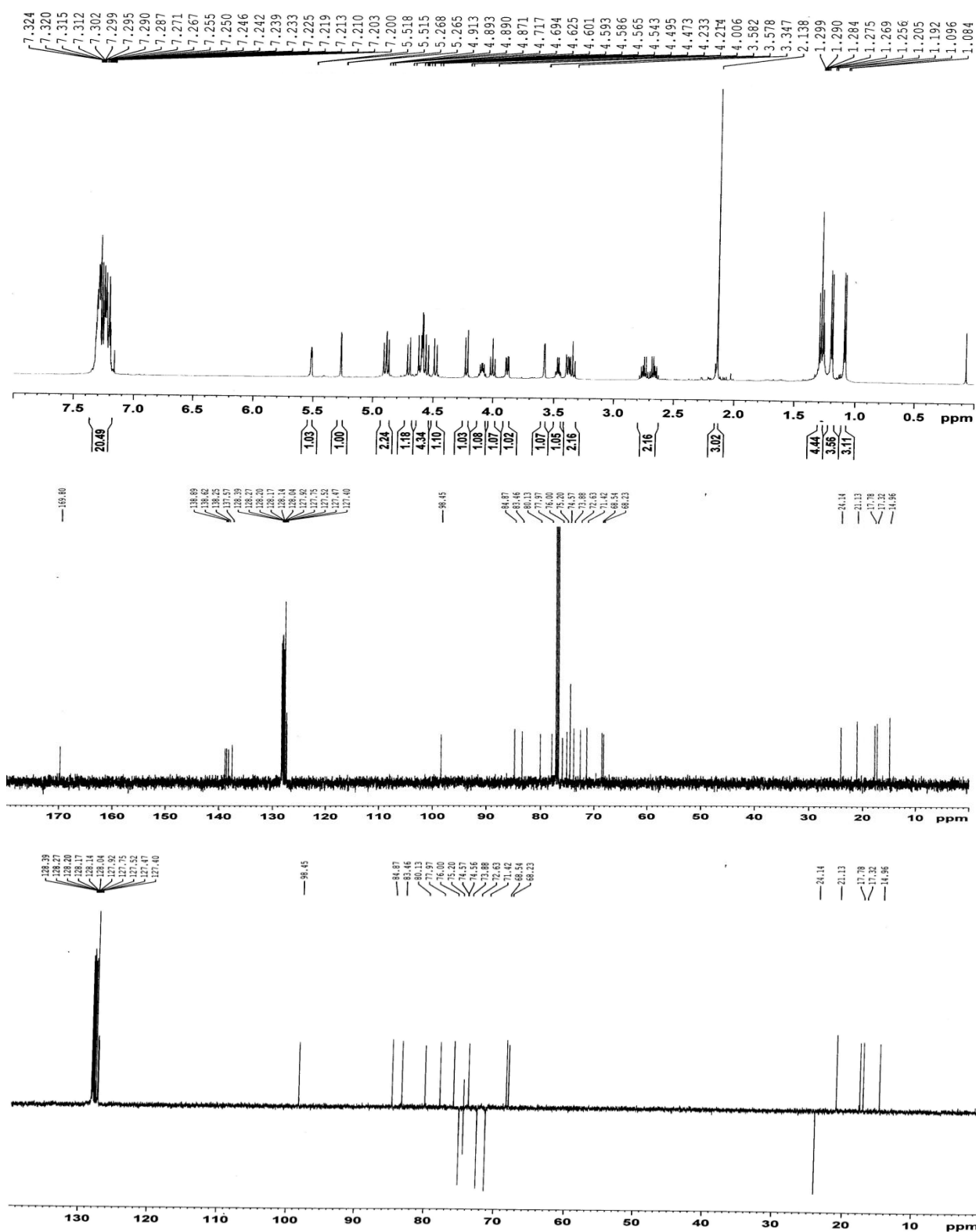


<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (**9**) (CDCl<sub>3</sub>).

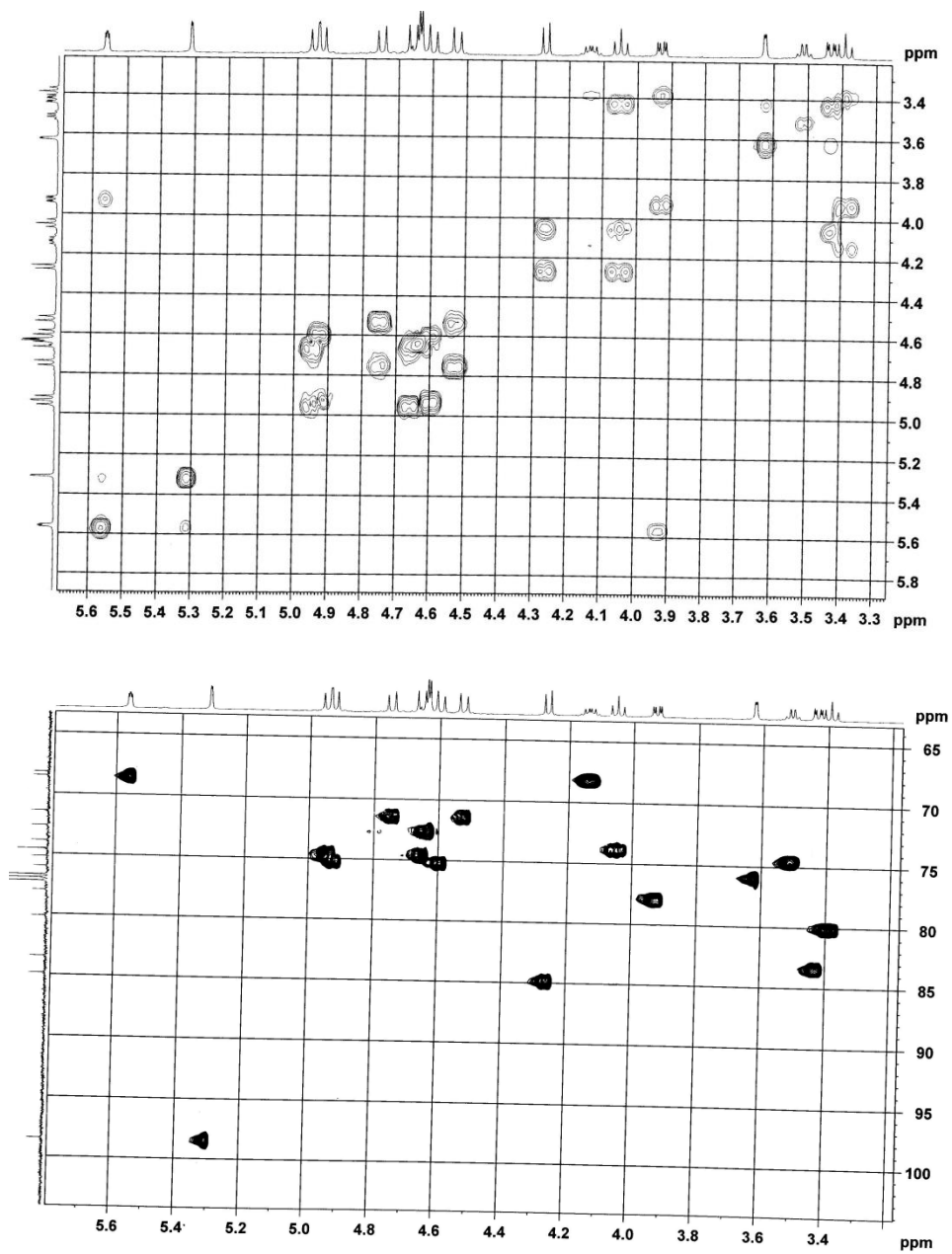


2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**9**) (CDCl<sub>3</sub>) (selected region).

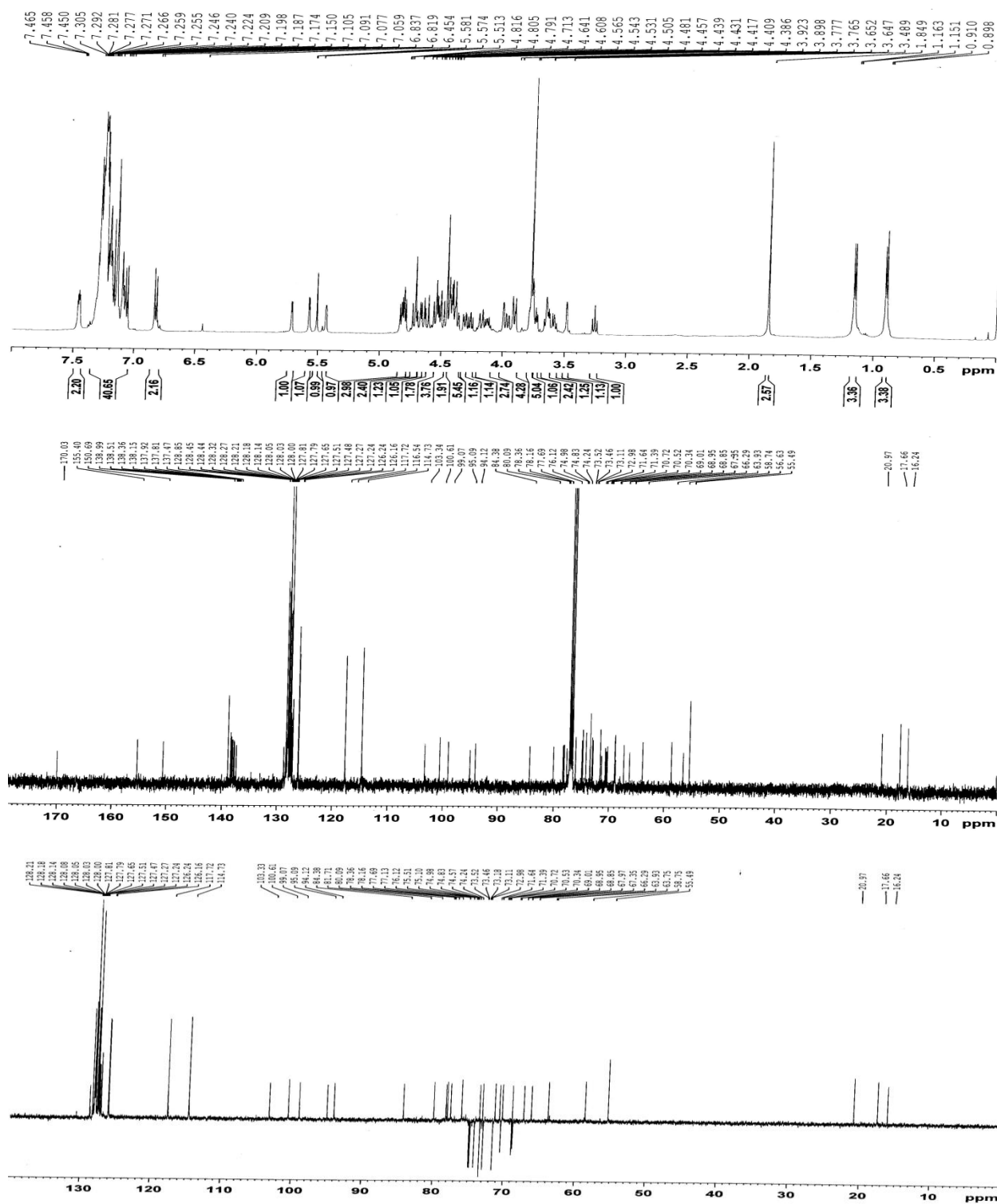




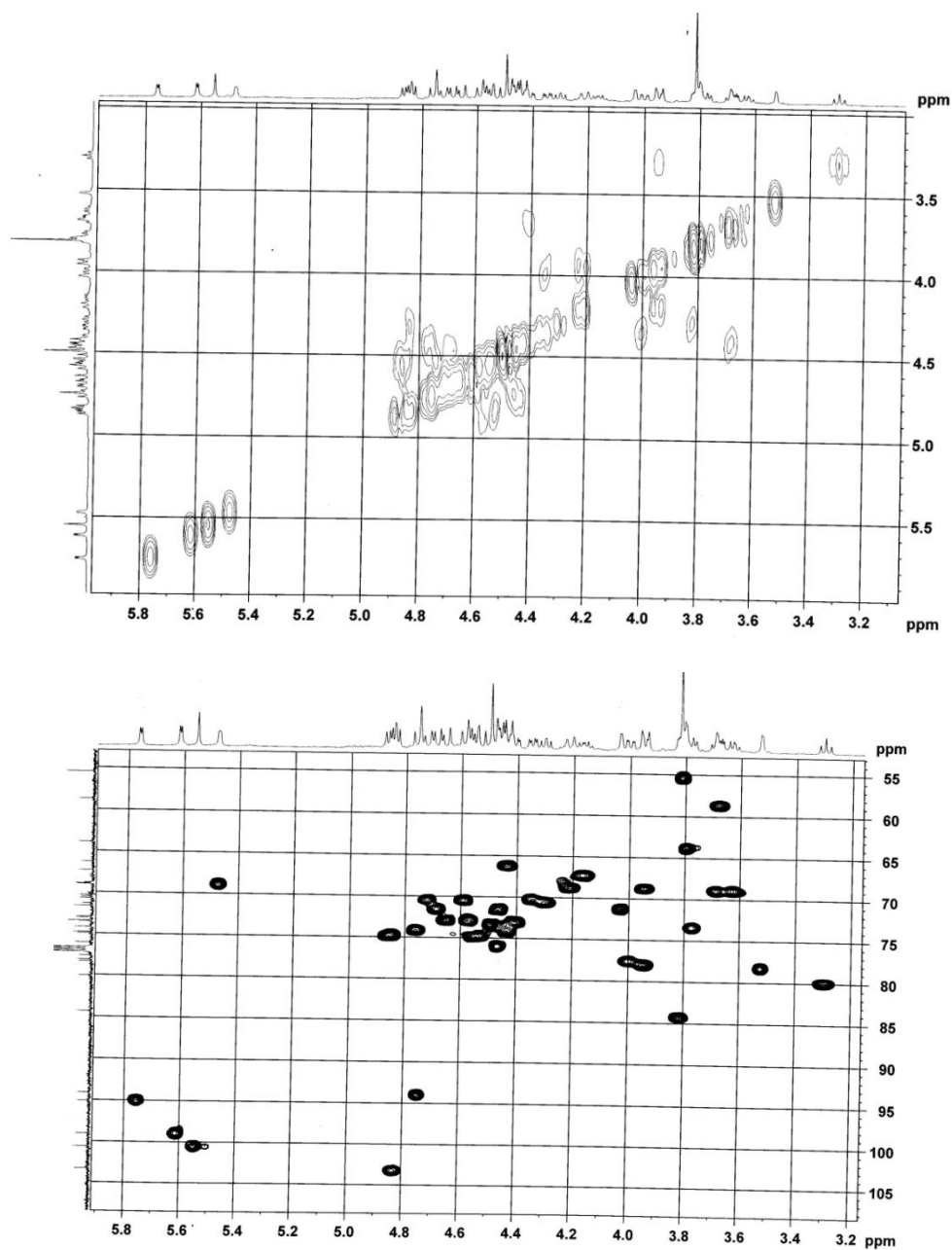
<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl-1-thio- $\beta$ -L-fucopyranoside (**10**) (CDCl<sub>3</sub>).



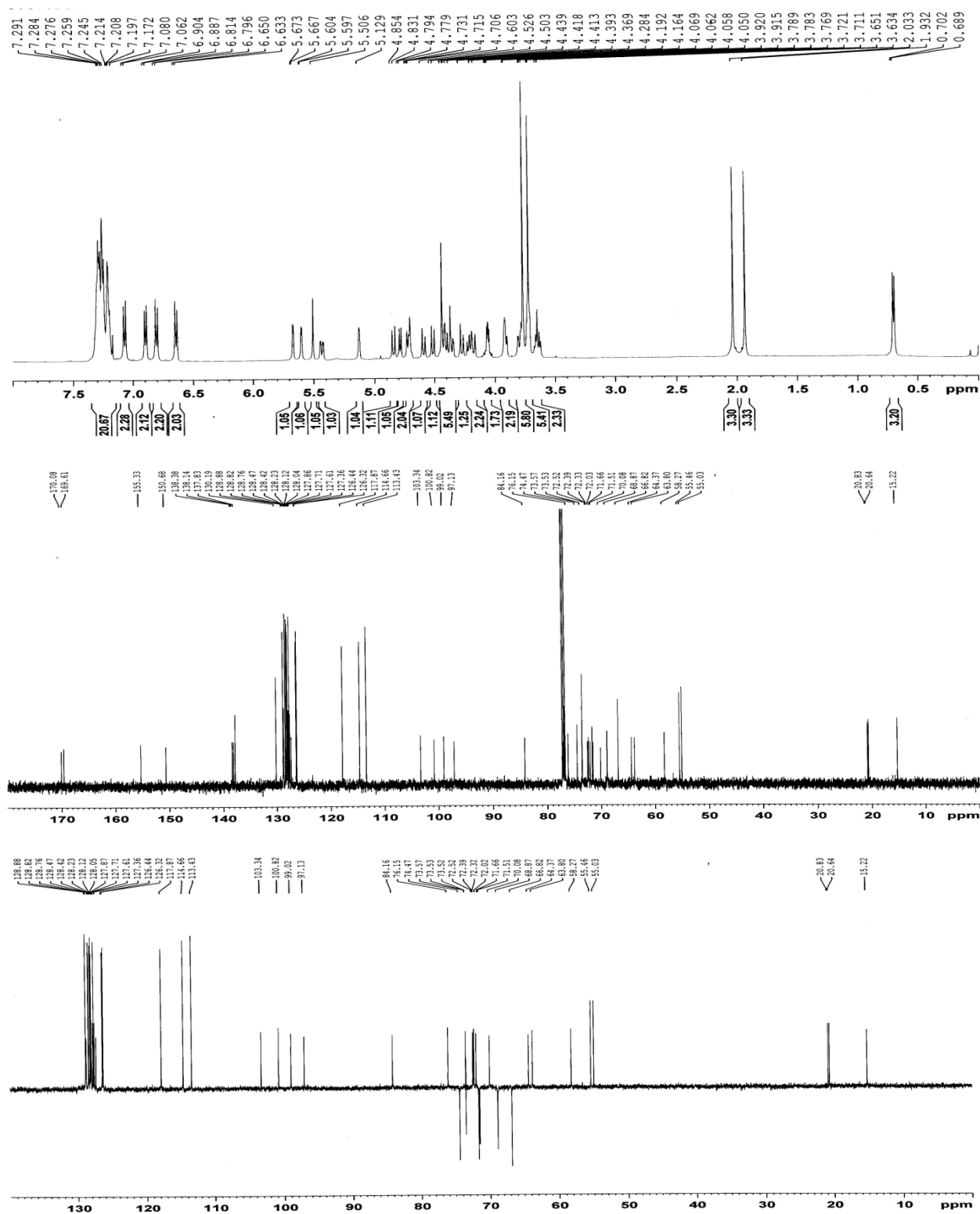
2D COSY and HSQC NMR spectra of ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-3,4-di-*O*-benzyl-1-thio- $\beta$ -L-fucopyranoside (**10**) (CDCl<sub>3</sub>) (Selected region).



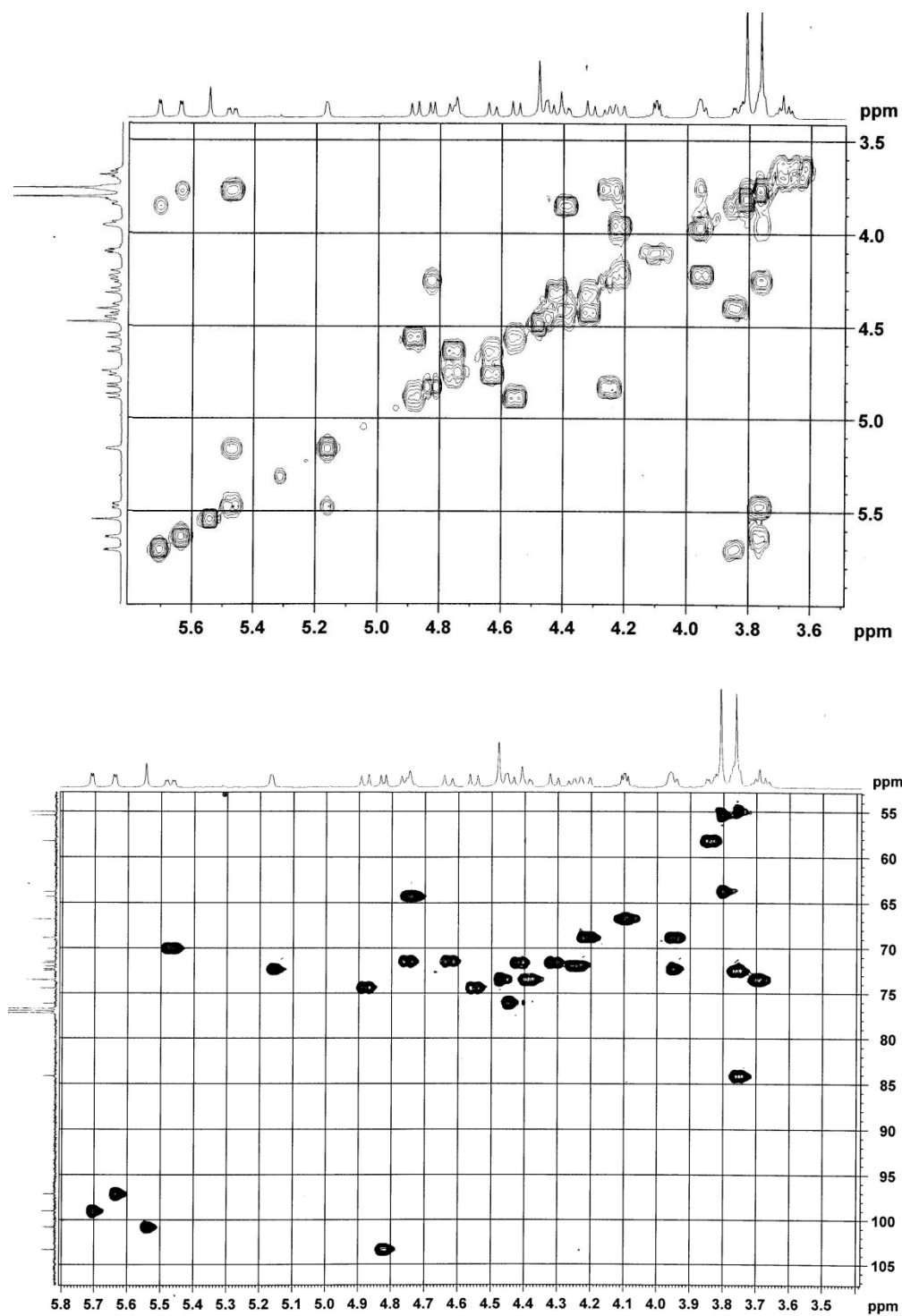
<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (11) (CDCl<sub>3</sub>).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (11) (CDCl<sub>3</sub>) (Selected region).

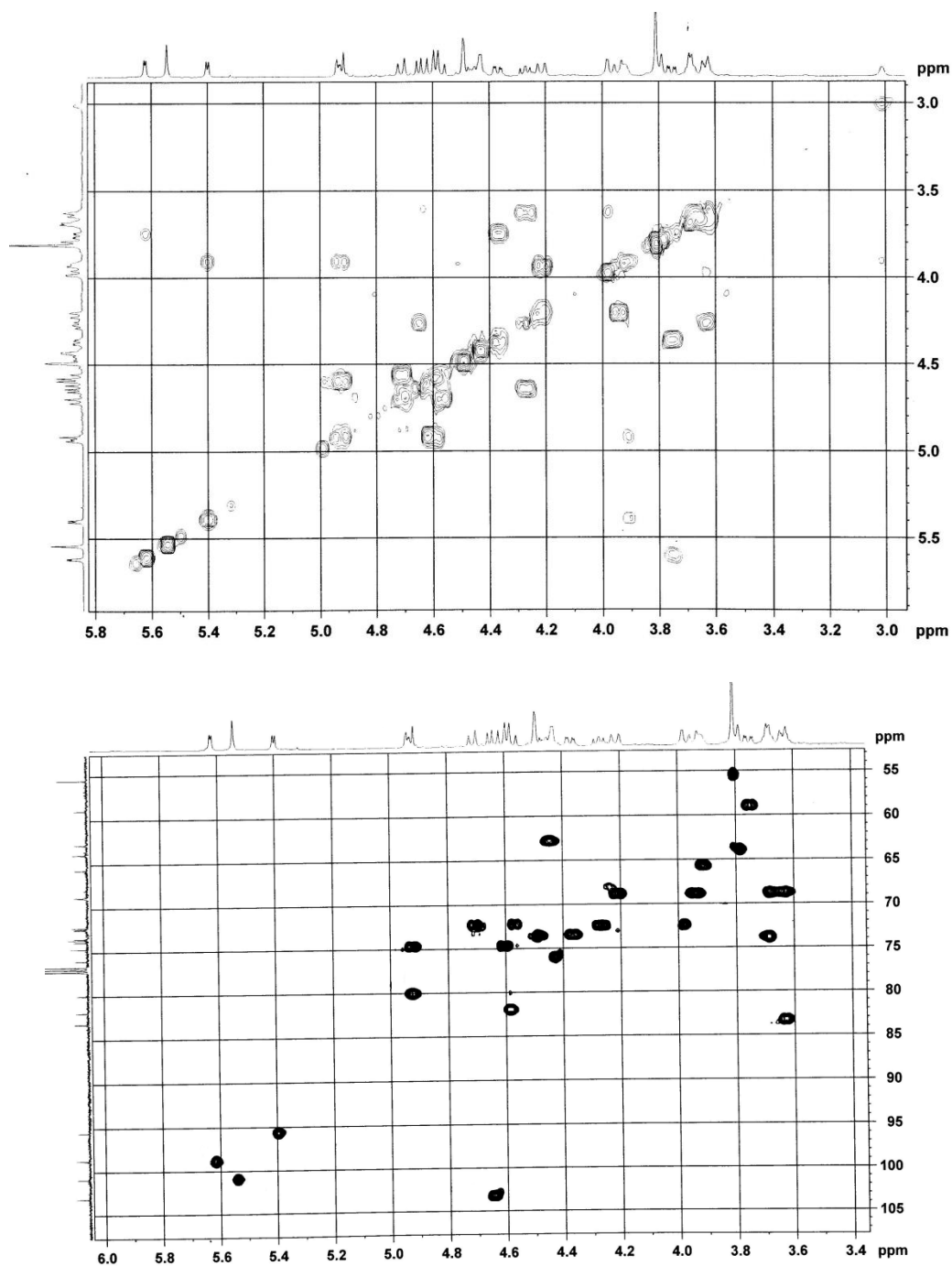


<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-acetyl-2-*O*-(*p*-methoxybenzyl))-α-*L*-fucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-β-*D*-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-*D*-galactopyranoside (**12**) (CDCl<sub>3</sub>).



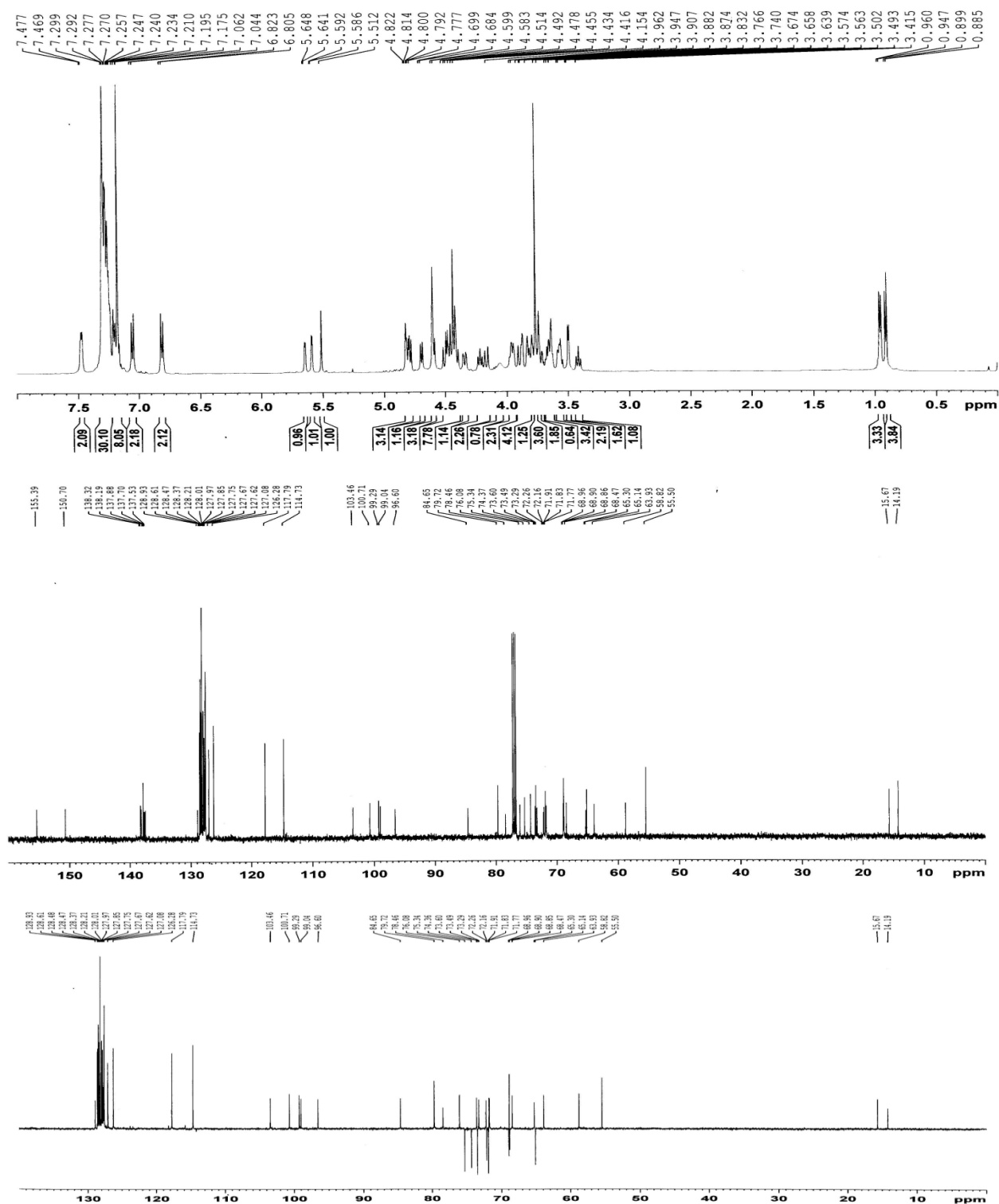
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-acetyl-2-*O*-(*p*-methoxybenzyl))- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**12**) (CDCl<sub>3</sub>) (selected region).



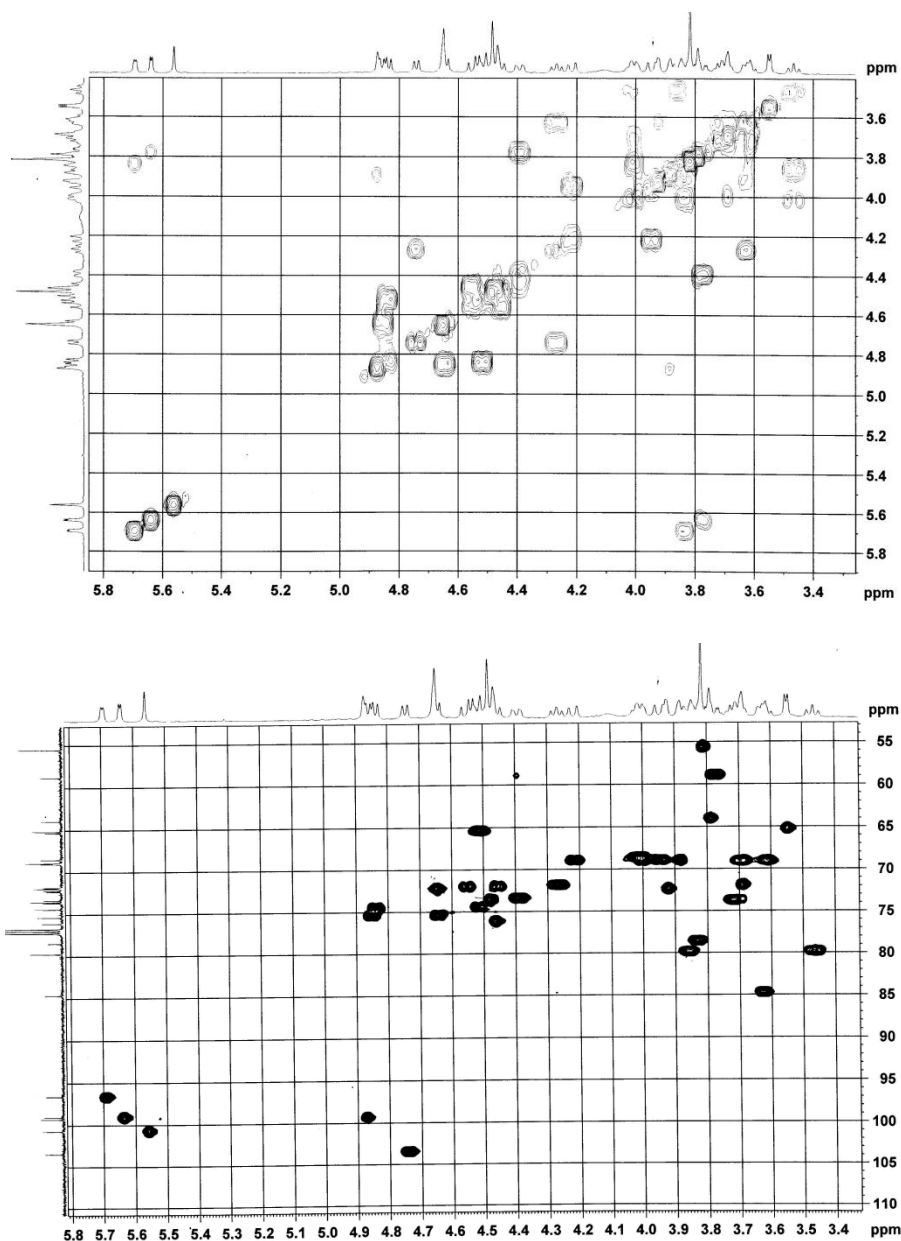


2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**13**) (CDCl<sub>3</sub>) (Selected region).

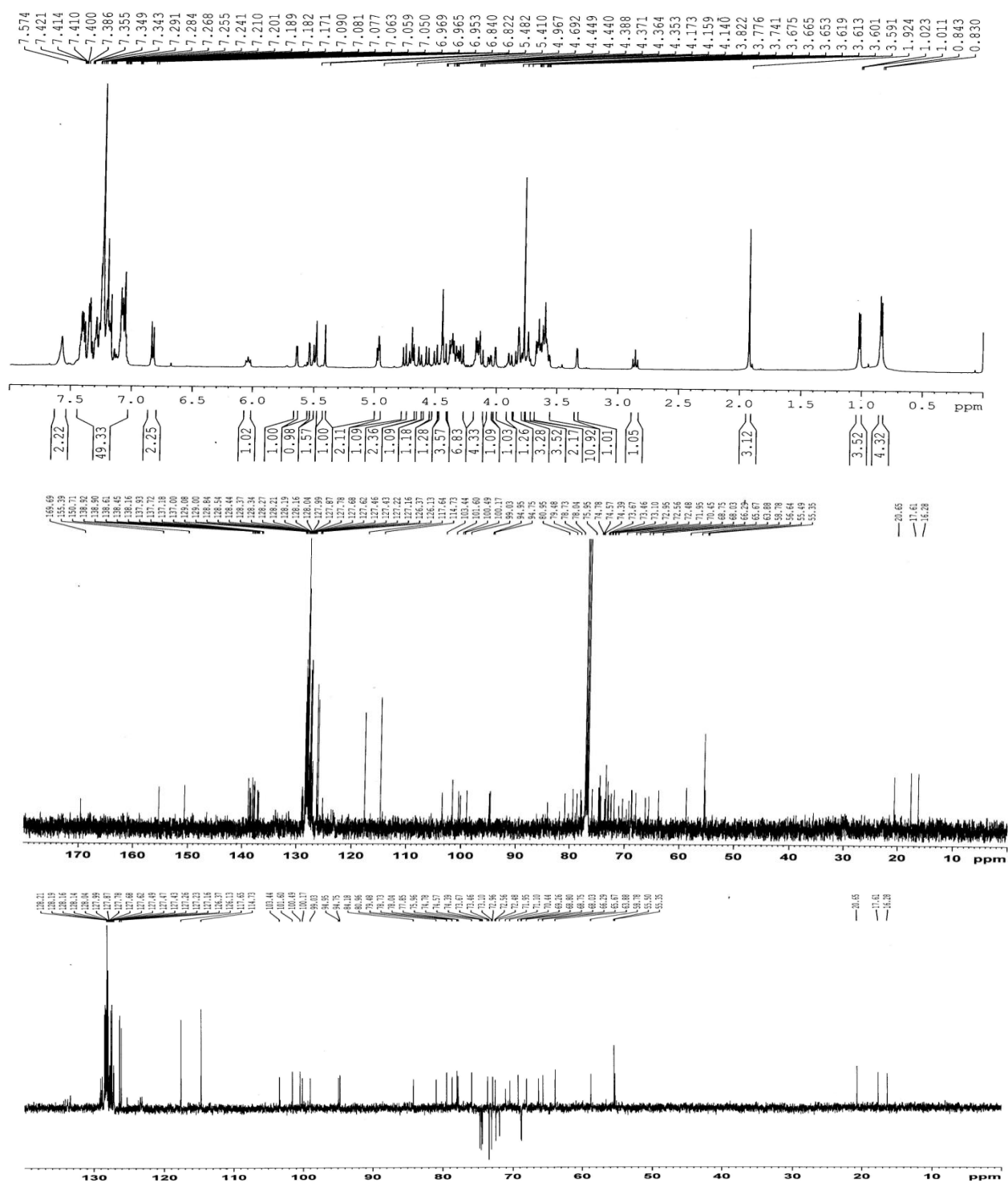




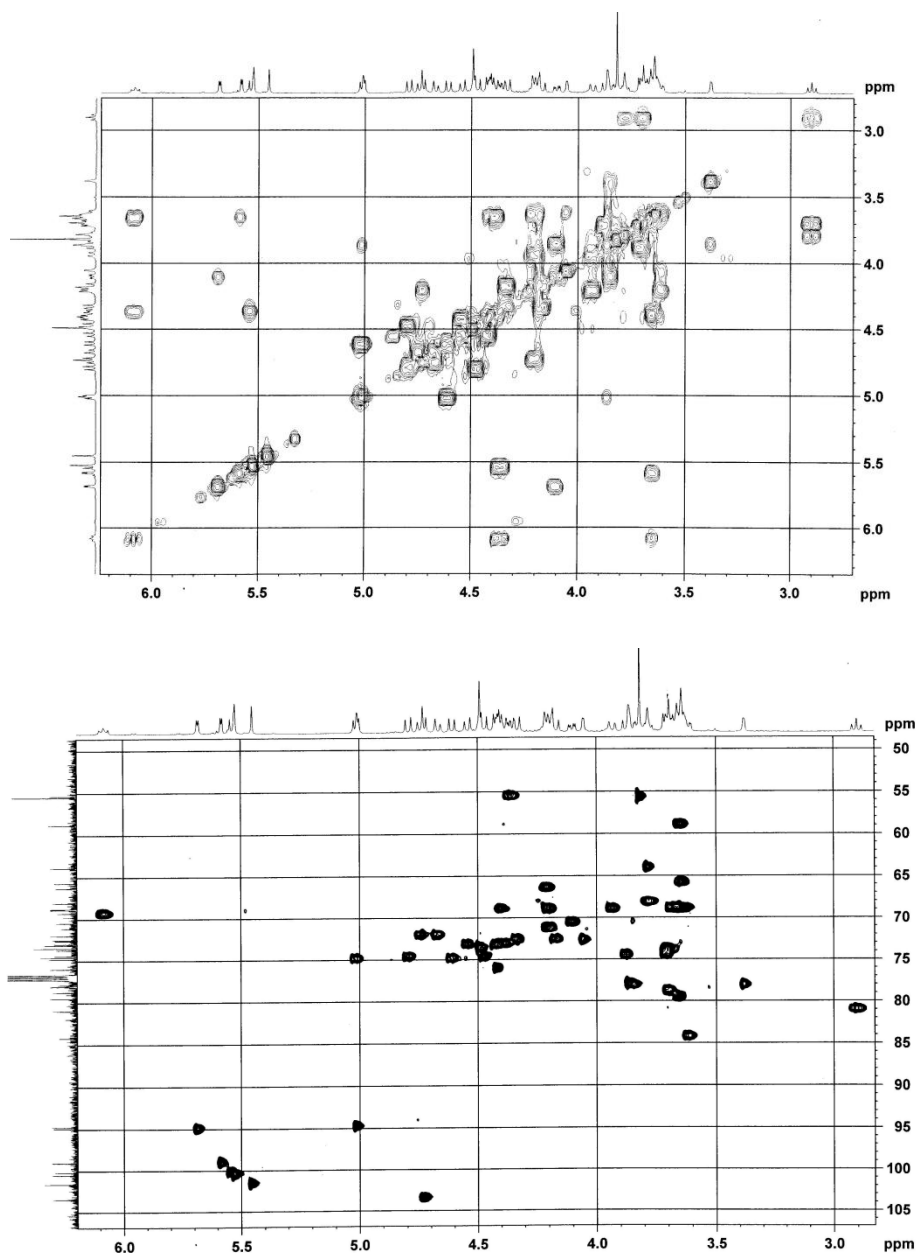
<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**14**) (CDCl<sub>3</sub>).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**14**) (CDCl<sub>3</sub>) (Selected region).



<sup>1</sup>H, <sup>13</sup>C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido-β-D-glucopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-(1→2)-(3,4-di-*O*-benzyl-α-L-fucopyranosyl)-(1→2)-(3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-galactopyranoside (**15**) (CDCl<sub>3</sub>).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido- $\beta$ -D-glucopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-rhamnopyranosyl)-(1 $\rightarrow$ 2)-(3,4-di-*O*-benzyl- $\alpha$ -L-fucopyranosyl)-(1 $\rightarrow$ 2)-(3,4,6-tri-*O*-benzyl- $\beta$ -D-galactopyranosyl)-(1 $\rightarrow$ 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- $\alpha$ -D-galactopyranoside (**15**) (CDCl<sub>3</sub>) (selected region).