



Supporting Information

for

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

Tapasi Manna, Arin Guchait and Anup Kumar Misra

Beilstein J. Org. Chem. **2020**, *16*, 106–110. doi:10.3762/bjoc.16.12

Experimental and analytical data and copies of NMR spectra

Index

Subject	Page No.
Detailed experimental methods for the synthesis of compounds 1, 8–15	S2–S9
1D and 2D NMR spectra of compounds 1, 8–15	S10–S27

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(SO₄)₂ in 2N H₂SO₄) 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 CDCl₃ 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. ¹H NMR, ¹³C NMR, ¹³C 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 HClO₄/SiO₂ catalyst: HClO₄ (3.6 g, 25 mmol, as a 70% aq solution) was added to a suspension of SiO₂ (230–400 mesh, 47.5 g) in Et₂O (140 mL). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to furnish HClO₄/SiO₂ (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- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-O-benzylidene-2-deoxy- α -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 CH₂Cl₂ (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 HClO₄/SiO₂ (40 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH₂Cl₂ (50 mL). The organic layer was successively washed with 5% aq. Na₂S₂O₃ (50 mL), H₂O (50 mL), dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-EtOAc (4:1) as eluant to give pure compound **8** (2.6 g, 79%). Colorless oil; $[\alpha]_D$ –7 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 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_A), 5.46 (s, 1 H, PhCH), 5.45 (t, *J* = 8.5 Hz, 1 H, H-2_B), 4.96 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.72 (d, *J* = 8.0 Hz, 1 H, H-1_B), 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_A, 2 PhCH), 4.29 (dd, *J* = 9.0 Hz,

3.0 Hz, 1 H, H-3_A), 4.14 (d, *J* = 12.5 Hz, 1 H, H-6_{aA}), 3.91 (br s, 1 H, H-4_B), 3.89 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-2_A), 3.82 (d, *J* = 12.5 Hz, 1 H, H-6_{bA}), 3.74 (s, 3 H, OCH₃), 3.68 (br s, 1 H, H-5_B), 3.65-3.64 (m, 2 H, H-6_{abB}), 3.60-3.58 (m, 1 H, H-5_A), 3.55 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3_B), 2.02 (s, 3 H, COCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 169.3 (COCH₃), 155.2-114.6 (Ar-C), 102.4 (C-1_B), 100.3 (PhCH), 98.4 (C-1_A), 80.7 (C-3_B), 75.5 (C-4_A), 74.4 (C-3_A), 74.3 (PhCH₂), 73.9 (C-4_B), 73.5 (PhCH₂), 72.7 (C-5_A), 72.2 (PhCH₂), 71.1 (C-2_B), 69.2 (C-6_B), 68.9 (C-6_A), 63.8 (C-5_B), 58.7 (C-2_A), 55.5 (OCH₃), 20.9 (COCH₃); HRMS [M+Na]⁺: Calcd. 896.3371; found, 896.3380.

***p*-Methoxyphenyl (3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (9):** A solution of compound **8** (2 g, 2.29 mmol) in 0.1 M CH₃ONa in CH₃OH (25 mL) was allowed to stir at room temperature for 2 h and neutralized with Dowex 50W X8 (H⁺) 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, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 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_A), 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_B), 4.41-4.39 (m, 3 H, H-4_A, 2 PhCH), 4.32 (dd, *J* = 10.5 Hz, 3.0 Hz, 1 H, H-3_A), 4.16 (d, *J* = 12.5 Hz, 1 H, H-6_{aA}), 4.06 (t, *J* = 9.5 Hz, 1 H, H-2_B), 4.00 (dd, *J* = 10.5 Hz, 3.0 Hz, 1 H, H-2_A), 3.86-3.82 (m, 2 H, H-5_B, H-6_{bA}), 3.74 (s, 3 H, OCH₃), 3.69 (br s, 1 H, H-4_B), 3.63-3.62 (m, 2 H, H-6_{abB}), 3.55-3.54 (m, 1 H, H-5_A), 3.49 (dd, *J* = 9.5 Hz, 2.5 Hz, 1 H, H-3_B); ¹³C NMR (125 MHz, CDCl₃): δ 155.3-114.6 (Ar-C), 105.2 (C-1_B), 100.6 (PhCH), 98.2 (C-1_A), 81.7 (C-3_B), 75.8 (C-4_A), 75.4 (C-3_A), 74.5 (PhCH₂), 74.0 (C-4_B), 73.9 (C-5_A), 73.5 (PhCH₂), 73.1 (PhCH₂), 71.6 (C-2_B), 69.3 (C-6_B), 68.9 (C-6_A), 63.7 (C-5_B), 58.9 (C-2_A), 53.2 (OCH₃); HRMS [M+Na]⁺: Calcd. 854.3265; found, 854.3272.

Ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-3,4-di-*O*-benzyl-1-thio- β -L-fucopyranoside (10): A solution of compound **4** (1.5 g, 3.86 mmol) and compound **5** (2.4 g, 4.52 mmol) in CH₂Cl₂ (20 mL) was cooled to -10 °C. To the cooled reaction mixture was added HClO₄/SiO₂ (50 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was diluted with satd. aq. NaHCO₃ (50 mL) and extracted with CH₂Cl₂ (50 mL). The

organic layer was washed with H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (6:1) as eluant to give pure compound **10** (2.2 g, 76%); Colorless oil; $[\alpha]_D + 28$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.32-7.20 (m, 20 H, Ar-H), 5.52-5.51 (m, 1 H, H-2_D), 5.26 (d, J = 1.5 Hz, 1 H, H-1_D), 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_C), 4.12-4.06 (m, 1 H, H-5_D), 4.00 (t, J = 9.5 Hz, 1 H, H-2_C), 3.89 (dd, J = 9.5 Hz, 3.5 Hz, 1 H, H-3_D), 3.58 (d, J = 2.0 Hz, 1 H, H-4_C), 3.47-3.46 (m, 1 H, H-5_C), 3.40 (dd, J = 9.5 Hz, 3.0 Hz, 1 H, H-3_C), 3.38 (t, J = 9.5 Hz, 1 H, H-4_D), 2.79-2.62 (m, 2 H, SCH_2CH_3), 2.13 (s, 3 H, COCH_3), 1.29 (t, J = 4.5 Hz, 3 H, SCH_2CH_3), 1.20 (d, J = 6.5 Hz, 3 H, CCH_3), 1.09 (d, J = 6.0 Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, CDCl_3): δ 169.8 (COCH_3), 138.8-127.4 (Ar-C), 98.4 (C-1_D), 84.8 (C-1_C), 83.4 (C-3_C), 80.1 (C-4_D), 77.9 (C-3_D), 76.0 (C-4_C), 75.2 (PhCH₂), 74.5 (2 C, C-5_C, PhCH₂), 73.8 (C-2_C), 72.6 (PhCH₂), 71.4 (PhCH₂), 68.5 (C-2_D), 68.2 (C-5_D), 24.1 (SCH_2CH_3), 21.1 (COCH_3), 17.7 (CCH_3), 17.3 (CCH_3), 14.9 (SCH_2CH_3); HRMS $[\text{M}+\text{Na}]^+$: Calcd. 779.3230; found, 779.3238.

***p*-Methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -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_2Cl_2 (10 mL) was added MS 4 \AA (1 g) and the reaction mixture was cooled to -40 $^{\circ}\text{C}$ under argon. To the cooled reaction mixture was added NIS (130 mg, 0.58 mmol) followed by $\text{HClO}_4/\text{SiO}_2$ (10 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH_2Cl_2 (20 mL). The organic layer was successively washed with 5% aq. $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL), H_2O (20 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 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_2Cl_2 (5 mL) was cooled to -10 $^{\circ}\text{C}$ under argon. To the cooled reaction mixture was added $\text{HClO}_4/\text{SiO}_2$ (10 mg) and it was allowed to stir at same temperature for 1 h. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The organic layer was successively washed with 5% aq. $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to

give pure compound **11** (700 mg, 76%). Colorless oil; $[\alpha]_D - 17$ (*c* 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.46-6.81 (m, 44 H, Ar-H), 5.72 (d, $J = 3.5$ Hz, 1 H, H-1_A), 5.58 (d, $J = 3.5$ Hz, 1 H, H-1_C), 5.51 (s, 1 H, PhCH), 5.44-5.43 (m, 1 H, H-2_D), 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_B), 4.73 (d, $J = 11.5$ Hz, 1 H, PhCH), 4.71 (br s, 1 H, H-1_D), 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_A, H-4_A, 3 PhCH), 4.30 (dd, $J = 9.0$ Hz, 3.0 Hz, 1 H, H-3_C), 4.26 (t, $J = 8.0$ Hz, 1 H, H-2_B), 4.18-4.16 (m, 2 H, H-5_B, H-6_{aA}), 4.15-4.12 (m, 1 H, H-5_D), 3.99 (br s, 1 H, H-4_C), 3.97 (dd, $J = 8.0$ Hz, 3.0 Hz, 1 H, H-3_D), 3.92-3.89 (m, 2 H, H-3_B, H-6_{bA}), 3.77 (s, 3 H, OCH_3), 3.77-3.72 (m, 3 H, H-2_C, H-5_A, H-5_C), 3.65-3.62 (m, 2 H, H-6_{abB}), 3.60 (dd, $J = 9.0$ Hz, 3.0 Hz, 1 H, H-2_A), 3.48 (br s, 1 H, H-4_B), 3.26 (t, $J = 8.0$ Hz, 1 H, H-4_D), 1.84 (s, 3 H, COCH_3), 1.16 (d, $J = 6.0$ Hz, 3 H, CCH_3), 0.91 (d, $J = 6.0$ Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, CDCl_3): δ 170.0 (COCH_3), 155.4-114.7 (Ar-C), 103.3 (C-1_B), 100.6 (PhCH), 99.0 (C-1_C), 95.0 (C-1_A), 94.1 (C-1_D), 84.3 (C-3_C), 80.0 (C-4_D), 78.3 (C-4_B), 78.1 (C-3_D), 77.6 (C-4_A), 76.1 (C-5_C), 74.9, 74.8, 74.2 (3 C, 3 PhCH₂), 73.5 (C-3_B), 73.4 (PhCH₂), 73.1 (C-5_A), 72.9, 71.6 (2 C, 2 PhCH₂), 71.3 (C-5_B), 70.7 (C-4_C), 70.5 (PhCH₂), 70.3 (C-2_B), 69.0 (C-6_A), 68.9 (C-2_D), 68.8 (C-6_B), 67.3 (C-5_D), 66.2 (C-3_A), 63.9 (C-2_C), 58.7 (C-2_A), 55.5 (OCH_3), 20.9 (COCH_3), 17.6 (CCH_3), 16.2 (CCH_3); HRMS $[\text{M}+\text{Na}]^+$: Calcd. 1548.6407; found, 1548.6400.

p-Methoxyphenyl (3,4-di-O-acetyl-2-O-(*p*-methoxybenzyl))- α -L-fucopyranosyl-(1 \rightarrow 2)-(3,4,6-tri-O-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-O-benzylidene-2-deoxy- α -D-galactopyranoside (12): To a solution of compound **9** (1.2 g, 1.44 mmol) and compound **6** (625 mg, 1.51 mmol) in CH_2Cl_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 CH_2Cl_2 (50 mL). The organic layer was successively washed with 5% aq. $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over 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, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.47-6.63 (m, 28 H, Ar-H), 5.67 (d, $J = 3.0$ Hz, 1 H, H-1_A), 5.60 (d, $J = 3.5$ Hz,

1 H, H-1_C), 5.50 (s, 1 H, PhCH), 5.44 (dd, *J* = 10.5 Hz, 3.0 Hz, 1 H, H-3_C), 5.12 (br s, 1 H, H-4_C), 4.85 (d, *J* = 11.5 Hz, 1 H, PhCH), 4.79 (d, *J* = 7.5 Hz, 1 H, H-1_B), 4.73-4.70 (m, 2 H, H-5_A, 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_A, H-5_B, PhCH), 4.28 (d, *J* = 12.0 Hz, 1 H, PhCH), 4.22-4.16 (m, 2 H, H-2_B, H-6_{aA}), 4.06-4.05 (m, 2 H, H-6_{abB}), 3.92-3.90 (m, 2 H, H-4_B, H-6_{bA}), 3.81 (s, 3 H, OCH₃), 3.80-3.76 (m, 2 H, H-2_A, H-3_A), 3.72 (s, 3 H, OCH₃), 3.72-3.71 (m, 2 H, H-2_C, H-5_C), 3.65-3.63 (m, 1 H, H-3_B), 2.03 (s, 3 H, COCH₃), 1.93 (s, 3 H, COCH₃), 0.70 (d, *J* = 6.0 Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 170.0, 169.6 (2 C, 2 COCH₃), 155.3-113.4 (Ar-C), 103.3 (C-1_B), 100.8 (PhCH), 99.0 (C-1_A), 97.1 (C-1_C), 84.1 (C-2_C), 76.1 (C-4_A), 74.4 (PhCH₂), 73.6 (2C, C-3_B, C-5_B), 73.5 (PhCH₂), 72.5 (C-4_C), 72.4 (C-2_B), 72.3 (C-4_B), 72.0 (C-5_C), 71.6, 71.5 (2 C, 2 PhCH₂), 70.0 (C-3_C), 68.8 (C-6_A), 66.8 (C-6_B), 64.3 (C-5_A), 63.8 (C-3_A), 58.2 (C-2_A), 55.4 (OCH₃), 55.0 (OCH₃), 23.0, 22.7 (2 C, 2 COCH₃), 15.2 (CCH₃); HRMS [M+Na]⁺: Calcd. 1204.4631; found, 1204.4640.

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

To a solution of compound **12** (1.1 g, 0.93 mmol) in THF (25 mL) were added benzyl bromide (550 μ 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 H₂O (100 mL) and extracted with CH₂Cl₂ (100 mL). The organic layer was washed with H₂O (50 mL), dried (Na₂SO₄) and concentrated. To a solution of the crude product in CH₂Cl₂ (50 mL) was added DDQ (500 mg, 2.20 mmol) in H₂O (10 mL) and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with satd. NaHCO₃ (50 mL) and extracted with CH₂Cl₂ (50 mL). The organic layer was washed with H₂O (50 mL), dried (Na₂SO₄) and concentrated. The crude product was purified over SiO₂ using hexane-EtOAc (5:1) as eluant to give pure compound **13** (775 mg, 72%). Colorless oil; $[\alpha]_D$ + 42 (*c* 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.45-6.80 (m, 34 H, Ar-H), 5.58 (d, *J* = 3.0 Hz, 1 H, H-1_A), 5.50 (s, 1 H, PhCH), 5.35 (d, *J* = 4.0 Hz, 1 H, H-1_C), 4.89-4.85 (m, 2 H, H-5_A, PhCH), 4.67 (d, *J* = 11.0 Hz, 1 H, PhCH), 4.61 (d, *J* = 7.5 Hz, 1 H, H-1_B), 4.57-4.51 (m, 3 H, 3 PhCH), 4.44-4.38 (m, 6 H, H-4_A, 5 PhCH), 4.33 (dd, *J* = 11.0 Hz, 3.5 Hz, H-3_C), 4.24 (t, *J* = 8.0 Hz, 1 H, H-2_B), 4.18 (d, *J* = 12.0 Hz, 1 H, H-6_{aA}), 3.94-3.93 (m, 2 H, H-4_B, H-4_C), 3.92-3.91 (m, 2 H, H-5_B, H-6_{bA}), 3.76 (s, 3

H, OCH₃), 3.76-3.74 (m, 2 H, H-3_A, H-5_C), 3.72 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-2_A), 3.65-3.64 (m, 2 H, H-2_C, H-6_{aB}), 3.63-3.57 (m, 2 H, H-3_B, H-6_{bB}), 0.95 (d, *J* = 6.0 Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 155.5-114.7 (Ar-C), 103.1 (C-1_B), 100.9 (PhCH), 98.7 (C-1_A), 95.5 (C-1_C), 83.3 (C-3_B), 81.9 (C-5_B), 80.0 (C-5_A), 76.0 (C-4_A), 74.6 (2 C, 2 PhCH₂), 73.8 (C-4_B), 73.5 (2 C, 2 PhCH₂), 73.4 (C-4_C), 72.4 (C-3_C), 72.3 (C-2_B), 72.7 (PhCH₂), 68.8 (C-6_A), 68.7 (C-6_B), 65.6 (C-2_C), 63.9 (C-3_A), 62.8 (C-5_C), 58.9 (C-2_A), 55.5 (OCH₃), 14.9 (CCH₃); HRMS [M+Na]⁺: Calcd. 1180.4783; found, 1180.4790.

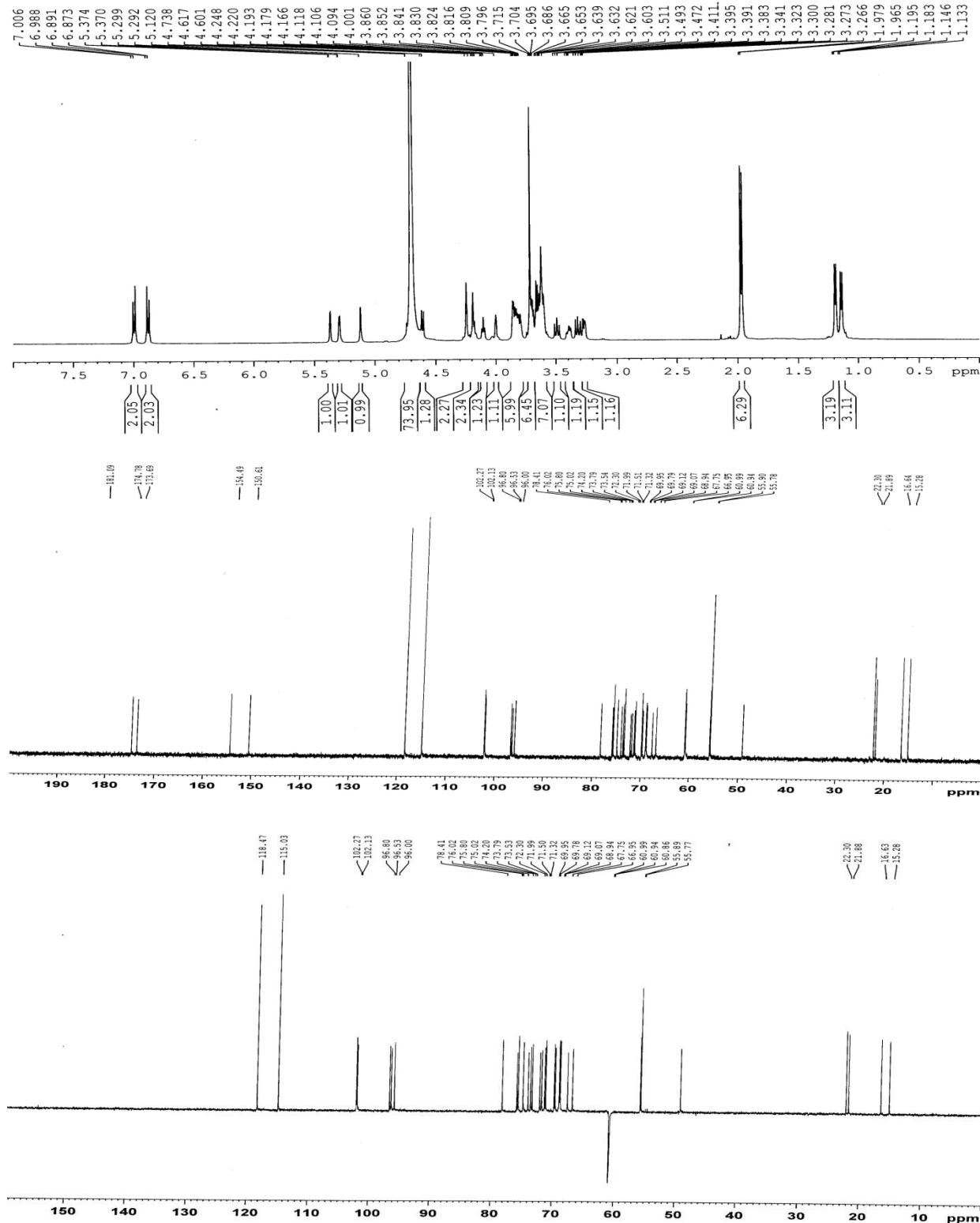
***p*-Methoxyphenyl (3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (14):** A solution of compound **11** (700 mg, 0.46 mmol) in 0.1 M CH₃ONa in CH₃OH (25 mL) was allowed to stir at room temperature for 2 h and neutralized with Dowex 50W X8 (H⁺) resin. The reaction mixture was filtered and the filtrate was concentrated under reduced pressure to give pure compound **14** (640 mg, 94%). Colorless oil; $[\alpha]_D$ -97 (c 1.0, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ 7.47-6.80 (m, 44 H, Ar-H), 5.64 (d, *J* = 3.5 Hz, 1 H, H-1_A), 5.59 (d, *J* = 3.0 Hz, 1 H, H-1_C), 5.51 (s, 1 H, PhCH), 4.82 (br s, 1 H, H-1_D), 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_B), 4.59-4.58 (m, 3 H, 3 PhCH), 4.51-4.39 (m, 7 H, H-4_A, 6 PhCH), 4.35 (dd, *J* = 9.0 Hz, 3.0 Hz, 1 H, H-3_A), 4.23 (t, *J* = 9.0 Hz, 1 H, H-2_B), 4.17 (d, *J* = 12.5 Hz, 1 H, H-6_{aA}), 3.96-3.94 (m, 2 H, H-3_D, H-5_A), 3.90 (d, *J* = 10.0 Hz, 1 H, H-6_{bA}), 3.87 (br s, 1 H, H-4_C), 3.83 (br s, 1 H, H-4_B), 3.82 (s, 3 H, OCH₃), 3.82-3.71 (m, 4 H, H-2_A, H-2_D, H-3_B, H-5_B), 3.70-3.62 (m, 3 H, H-2_C, H-5_D, H-6_{aB}), 3.58-3.57 (m, 2 H, H-3_C, H-6_{bB}), 3.50-3.49 (m, 1 H, H-5_C), 3.41 (t, *J* = 8.0 Hz, 1 H, H-4_D), 0.96 (d, *J* = 6.0 Hz, 3 H, CCH₃), 0.89 (d, *J* = 6.0 Hz, 3 H, CCH₃); ¹³C NMR (125 MHz, CDCl₃): δ 155.3-114.7 (Ar-C), 103.4 (C-1_B), 100.7 (PhCH), 99.2 (C-1_D), 99.0 (C-1_C), 96.6 (C-1_A), 84.6 (C-3_C), 79.7 (2 C, C-3_B, C-4_D), 78.4 (C-4_B), 76.0 (C-4_A), 75.3, 74.3 (2 C, 2 PhCH₂), 73.6 (C-2_B), 73.4 (PhCH₂), 73.2 (C-2_C), 72.2 (C-5_D), 72.1, 71.9 (3 C, 3 PhCH₂), 71.8 (C-3_A), 71.7 (C-3_D), 69.0 (C-6_A), 68.9 (2 C, C-4_C, C-5_A), 68.8 (C-6_B), 68.4 (C-5_B), 65.3 (C-5_C), 65.1 (PhCH₂), 63.9 (C-2_D), 58.8 (C-2_A), 55.5 (OCH₃), 15.6 (CCH₃), 14.1 (CCH₃); HRMS [M+Na]⁺: Calcd. 1506.6301; found, 1506.6310.

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

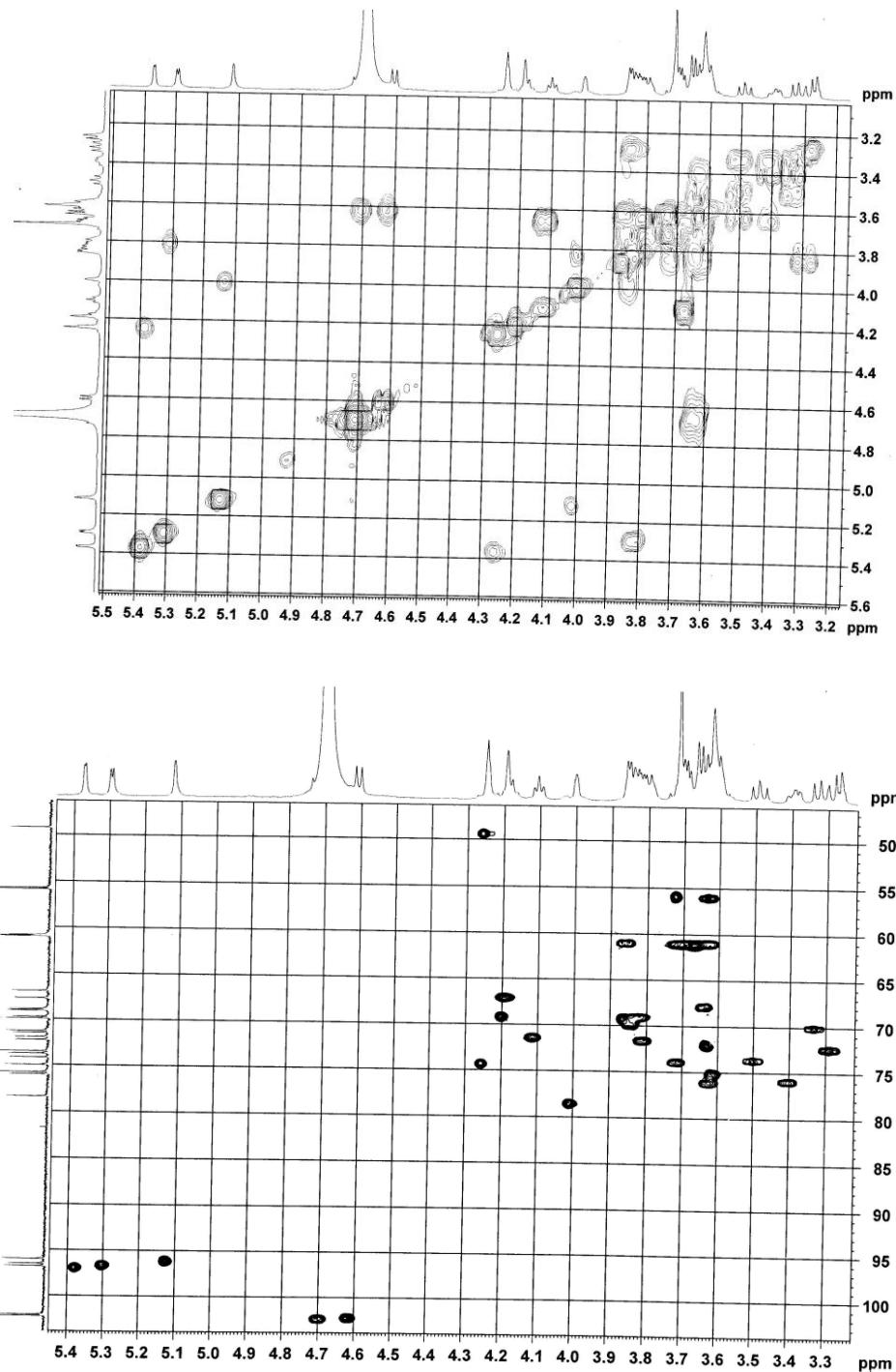
L-fucopyranosyl)-(1→2)-(3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1→3)-2-azido-4,6-O-benzylidene-2-deoxy-α-D-galactopyranoside (15): To a solution of compound **14** (600 mg, 0.40 mmol) and compound **7** (230 mg, 0.47 mmol) in CH_2Cl_2 (5 mL) was added MS 4 Å (0.5 g) and the reaction mixture was cooled to -15 °C under argon. To the cooled reaction mixture was added NIS (120 mg, 0.53 mmol) followed by $\text{HClO}_4\text{-SiO}_2$ (10 mg) and it was allowed to stir at the same temperature for 1 h. The reaction mixture was filtered and washed with CH_2Cl_2 (50 mL). The organic layer was successively washed with 5% aq. $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane-EtOAc (4:1) as eluant to give pure compound **15** (535 mg, 70%). Colorless oil; $[\alpha]_D - 50$ (c 1.0, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ 7.57-6.82 (m, 53 H, Ar-H), 6.05 (t, $J = 8.5$ Hz, 1 H, H-3_E), 5.64 (d, $J = 3.5$ Hz, 1 H, H-1_A), 5.54 (d, $J = 3.0$ Hz, 1 H, H-1_C), 5.50 (d, $J = 8.5$ Hz, 1 H, H-1_E), 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_D), 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_B), 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_E, H-4_A, 5 PhCH), 4.17-4.11 (m, 4 H, H-2_B, H-3_A, H-4_E, H-6_{aA}), 4.01 (dd, $J = 9.0$ Hz, 3.0 Hz, 1 H, H-3_C), 4.00 (br s, 1 H, H-4_C), 3.90 (d, $J = 8.0$ Hz, 1 H, H-6_{bA}), 3.84-3.79 (m, 3 H, H-2_D, H-3_D, H-4_B), 3.77 (s, 3 H, OCH_3), 3.77-3.74 (m, 2 H, H-2_C, H-3_B), 3.67-3.63 (m, 5 H, H-5_A, H-5_B, H-5_D, H-5_E, H-6_{aB}), 3.61-3.59 (m, 5 H, H-2_A, H-2_C, H-6_{bB}, H-6_{abE}), 3.36-3.32 (m, 1 H, H-5_C), 2.86 (t, $J = 8.0$ Hz, 1 H, H-4_D), 1.92 (s, 3 H, COCH_3), 1.02 (d, $J = 6.0$ Hz, 3 H, CCH_3), 0.84 (d, $J = 6.0$ Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, CDCl_3): δ 169.6 (COCH_3), 155.3-114.7 (Ar-C), 103.4 (C-1_B), 101.6, 100.4 (2 C, 2 PhCH), 100.1 (C-1_E), 99.0 (C-1_C), 94.9 (C-1_D), 94.7 (C-1_A), 84.1 (C-5_E), 80.9 (C-4_D), 79.4 (C-5_D), 78.7 (C-3_D), 78.0 (2 C, C-3_B, C-3_C), 77.8 (C-5_B), 75.9 (C-5_A), 74.7, 74.5, 74.3 (3 C, 3 PhCH₂), 73.6 (C-4_B), 73.4, 73.1 (2 C, 2 PhCH₂), 72.9 (C-2_D), 72.5 (C-4_C), 72.4, 71.9 (2 C, 2 PhCH₂), 71.1 (C-3_A), 70.4 (C-4_E), 69.2 (C-3_E), 68.8 (2 C, C-6_A, C-6_B), 68.7 (C-6_E), 68.0 (C-4_A), 66.2 (C-2_B), 65.6 (C-5_C), 63.8 (C-2_C), 58.7 (C-2_A), 55.5 (OCH_3), 55.3 (C-2_E), 20.6 (COCH_3), 17.6 (CCH_3), 16.2 (CCH_3); HRMS $[\text{M}+\text{Na}]^+$: 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

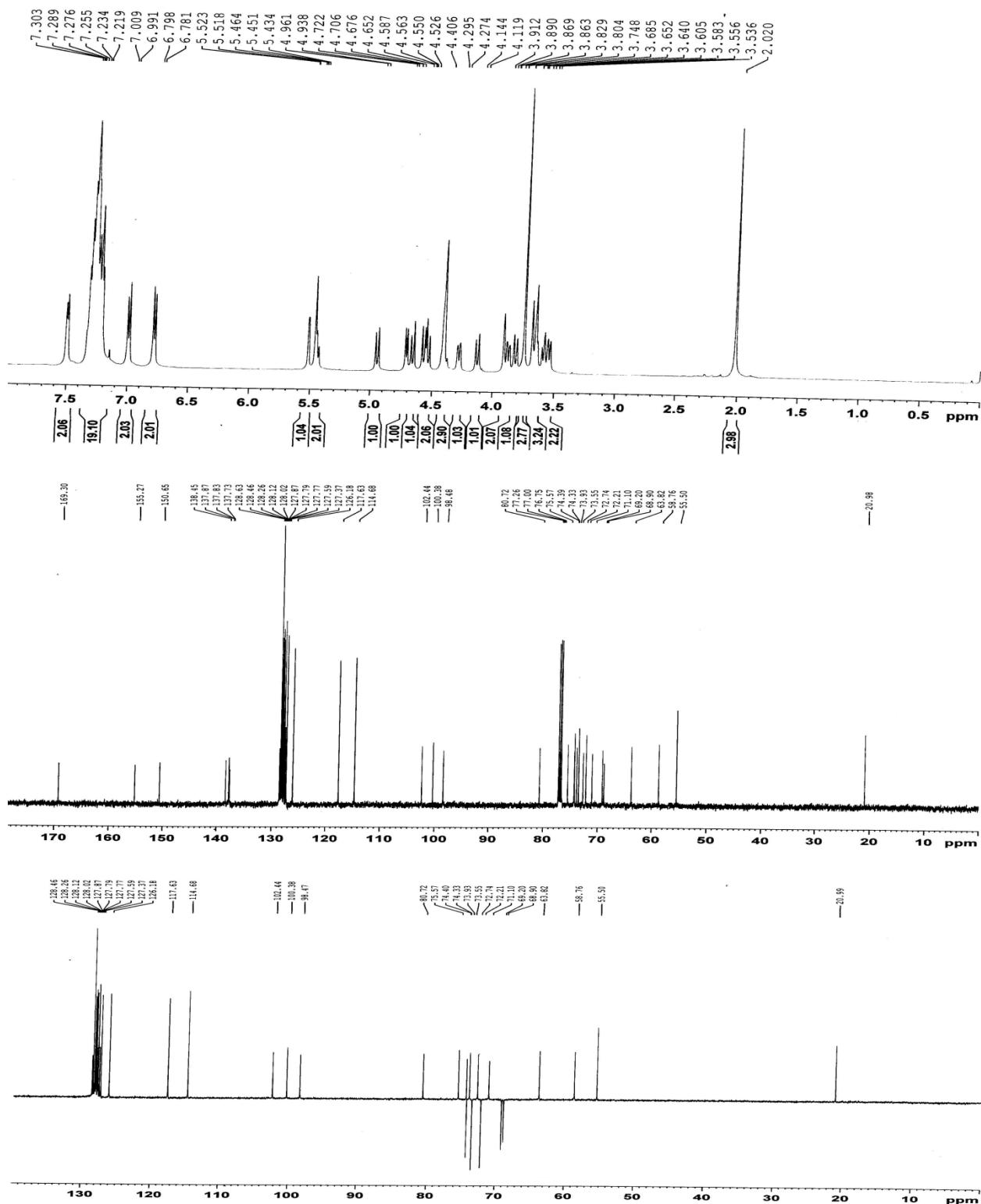
mmol) in pyridine (5 mL) was added CH_3COSH (0.5 mL, 7.1 mmol) and it was allowed to stir at room temperature for 16 h. The solvents were removed under reduced pressure and co-evaporated with toluene (3×10 mL). To a solution of the crude product in EtOH (15 mL) was added $\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}$ (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_3OH (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_3OH (10 mL) was added 20% $\text{Pd}(\text{OH})_2/\text{C}$ (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 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (5:1) as eluant to give pure compound **1** (125 mg, 49%). White powder; $[\alpha]_D$ (*c* 1.0, H_2O); ^1H NMR (500 MHz, CDCl_3): 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_A), 5.29 (d, *J* = 3.5 Hz, 1 H, H-1_C), 5.12 (br s, 1 H, H-1_D), 4.73 (d, *J* = 7.5 Hz, 1 H, H-1_E), 4.61 (d, *J* = 8.0 Hz, 1 H, H-1_B), 4.26-4.22 (m, 2 H, H-2_A, H-5_C), 4.19-4.17 (m, 2 H, H-3_A, H-4_A), 4.11-4.09 (m, 1 H, H-5_A), 4.01-3.98 (m, 1 H, H-2_D), 3.86-3.79 (m, 6 H, H-2_C, H-3_B, H-3_D, H-4_C, H-5_D, H-6_{aA}), 3.71 (s, 3 H, OCH_3), 3.71-3.68 (m, 3 H, H-3_C, H-4_B, H-5_B), 3.66-3.60 (m, 7 H, H-2_B, H-2_E, H-6_{bA}, H-6_{abB}, H-6_{abE}), 3.49 (t, *J* = 9.0 Hz, 1 H, H-3_E), 3.41-3.39 (m, 1 H, H-5_E), 3.32 (t, *J* = 9.0 Hz, 1 H, H-4_E), 3.27 (t, *J* = 9.0 Hz, 1 H, H-4_D), 1.97 (s, 3 H, NHCOCH_3), 1.96 (s, 3 H, NHCOCH_3), 1.19 (d, *J* = 6.0 Hz, 3 H, CCH_3), 1.14 (d, *J* = 6.0 Hz, 3 H, CCH_3); ^{13}C NMR (125 MHz, CDCl_3): δ 174.7, 173.6 (2 C, 2 NHCOCH_3), 154.4-114.0 (Ar-C), 102.2 (C-1_E), 102.1 (C-1_B), 96.8 (C-1_A), 96.5 (C-1_C), 96.0 (C-1_D), 78.4 (C-2_D), 76.0 (C-5_E), 75.8 (C-2_B), 75.0 (C-3_B), 74.2 (C-3_E), 73.7 (C-5_C), 73.5 (C-5_B), 72.3 (C-5_A), 71.9 (C-2_C), 71.5 (C-4_C), 71.3 (C-4_B), 69.9 (C-4_E), 69.7 (C-3_D), 69.1 (C-5_D), 69.0 (C-3_A), 68.9 (C-4_D), 67.7 (C-3_C), 66.9 (C-4_A), 61.0 (C-6_E), 60.9 (C-6_B), 60.8 (C-6_A), 55.8 (C-2_E), 55.7 (OCH_3), 49.5 (C-2_A), 22.3 (NHCOCH_3), 21.8 (NHCOCH_3), 16.6 (CCH_3), 15.2 (CCH_3); HRMS $[\text{M}+\text{Na}]^+$: Calcd. 1007.3696; found, 1007.3704.



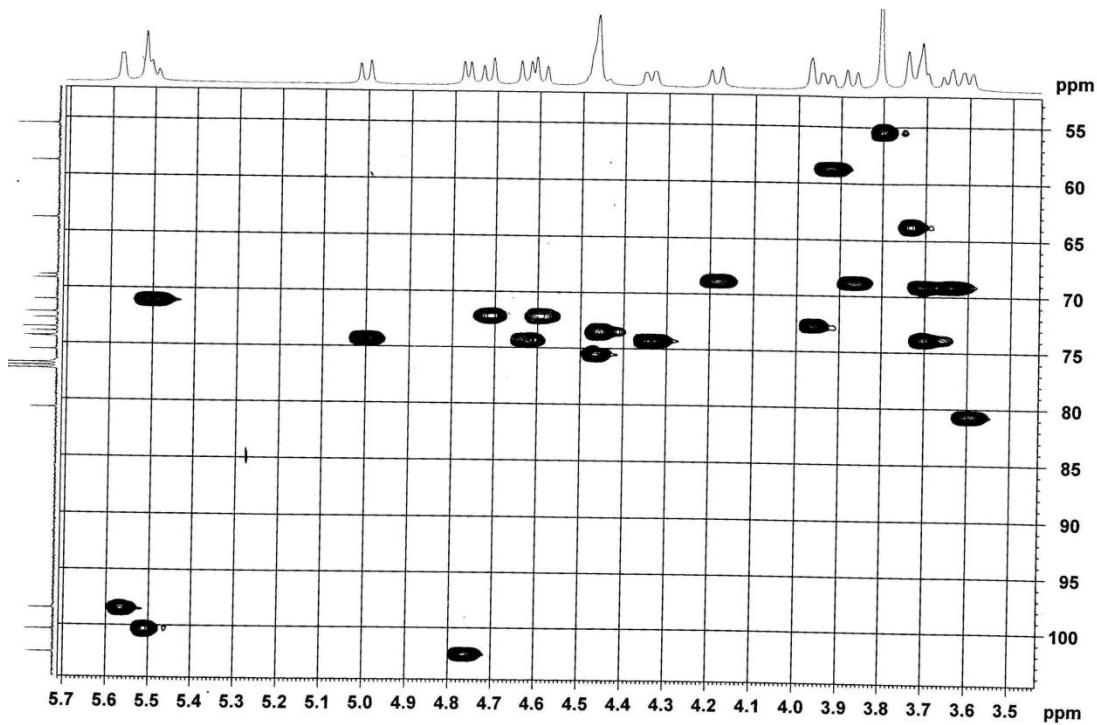
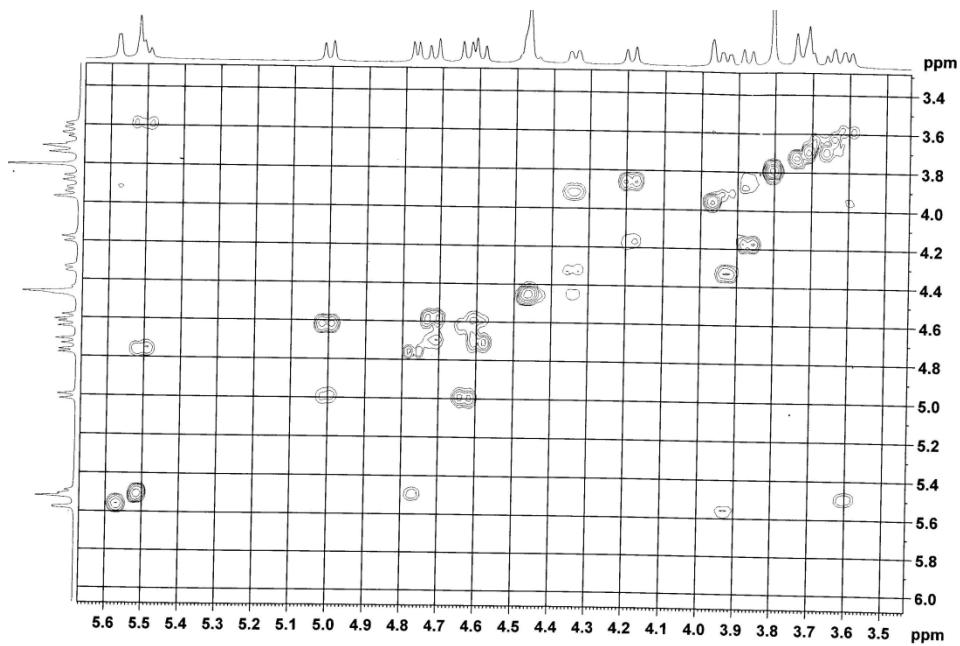
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-acetamido-2-deoxy- β -D-glucopyranosyl)-(1 \rightarrow 2)-(α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(α -L-fucopyranosyl)-(1 \rightarrow 2)-(β -D-galactopyranosyl)-(1 \rightarrow 3)-2-acetamido-2-deoxy- α -D-galactopyranoside (**1**) (D_2O).



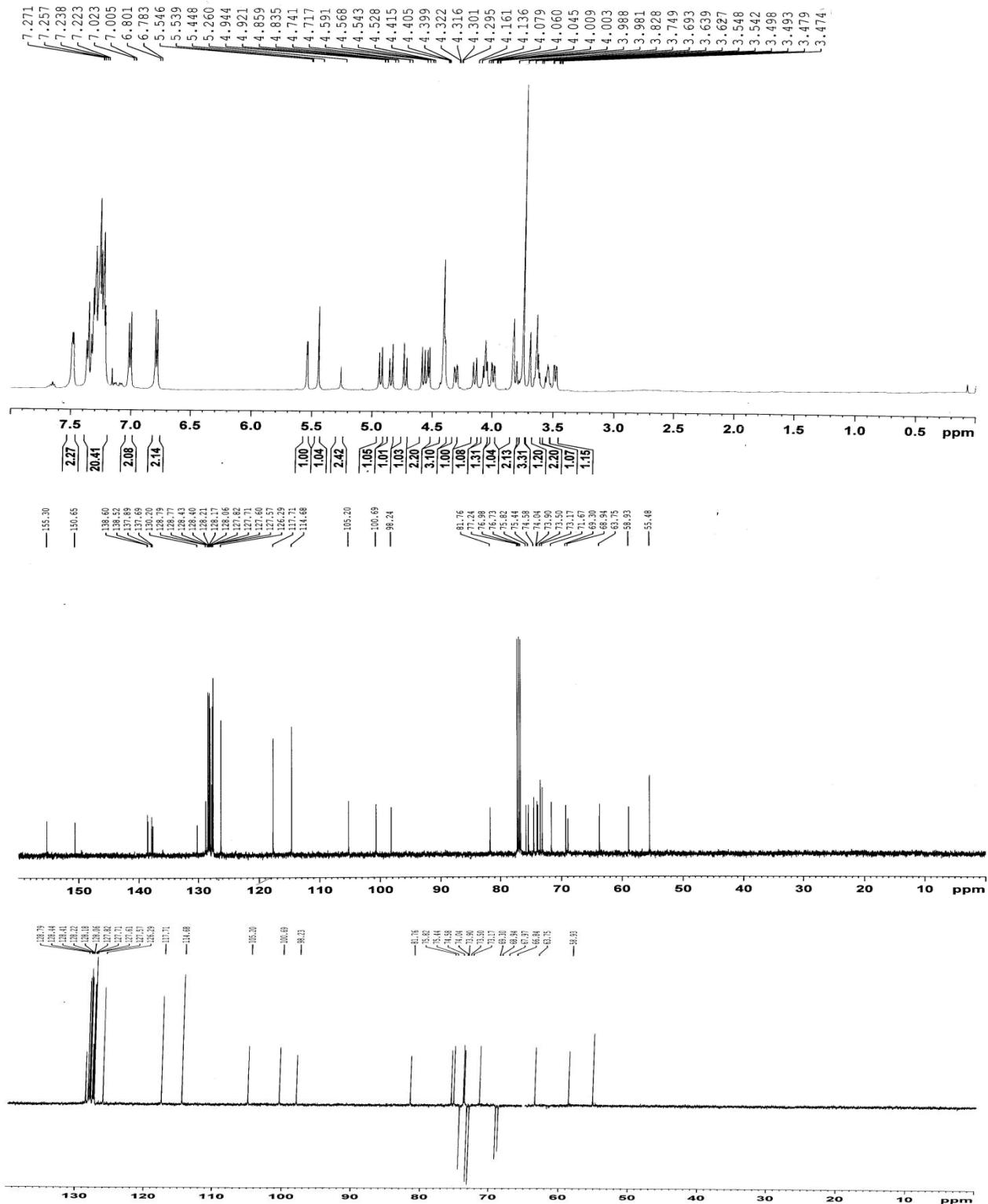
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-acetamido-2-deoxy- β -D-glucopyranosyl)-(1 \rightarrow 2)-(α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(α -L-fucopyranosyl)-(1 \rightarrow 2)-(β -D-galactopyranosyl)-(1 \rightarrow 3)-2-acetamido-2-deoxy- α -D-galactopyranoside (**1**) (D_2O) (Selected region).



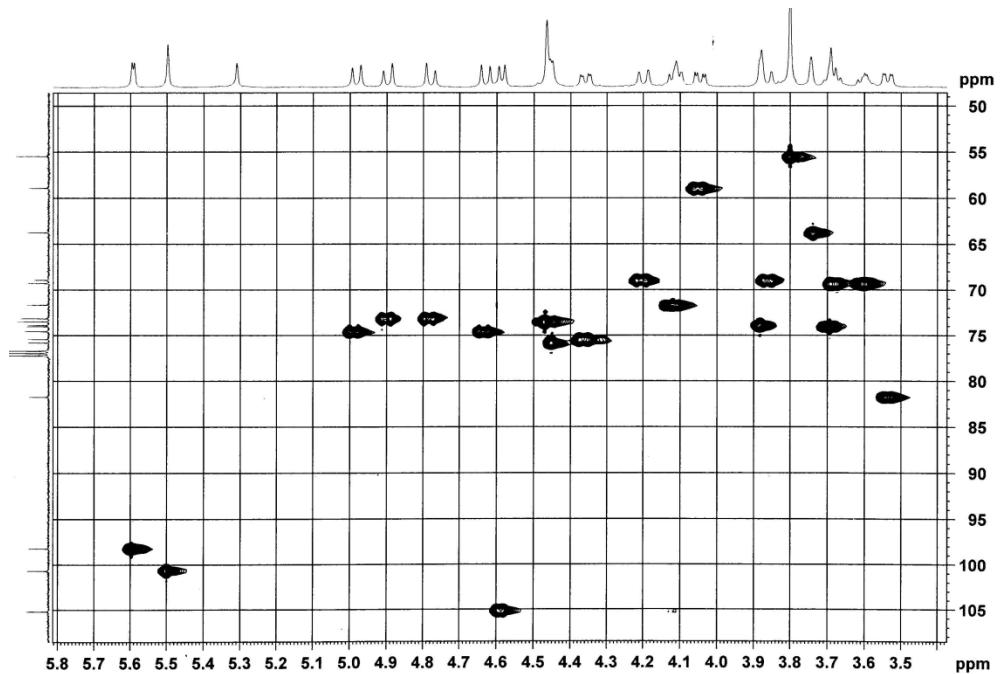
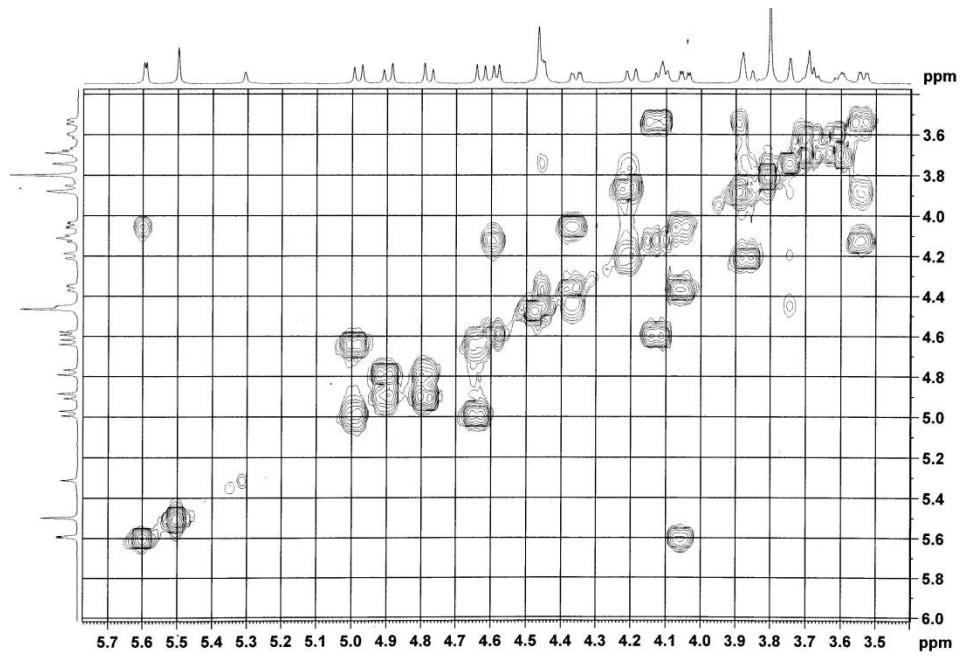
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (CDCl₃). (8)



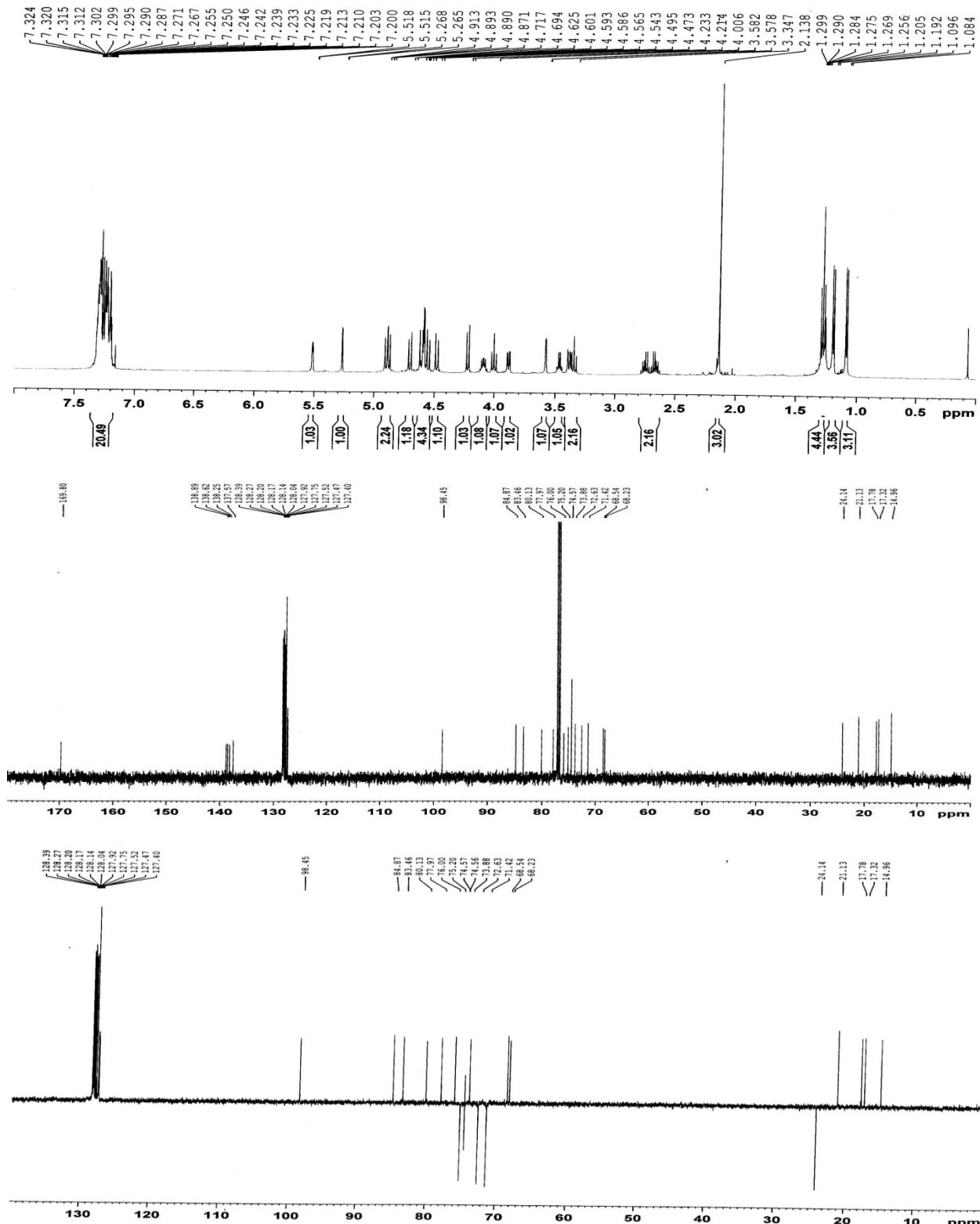
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (8) (CDCl_3).



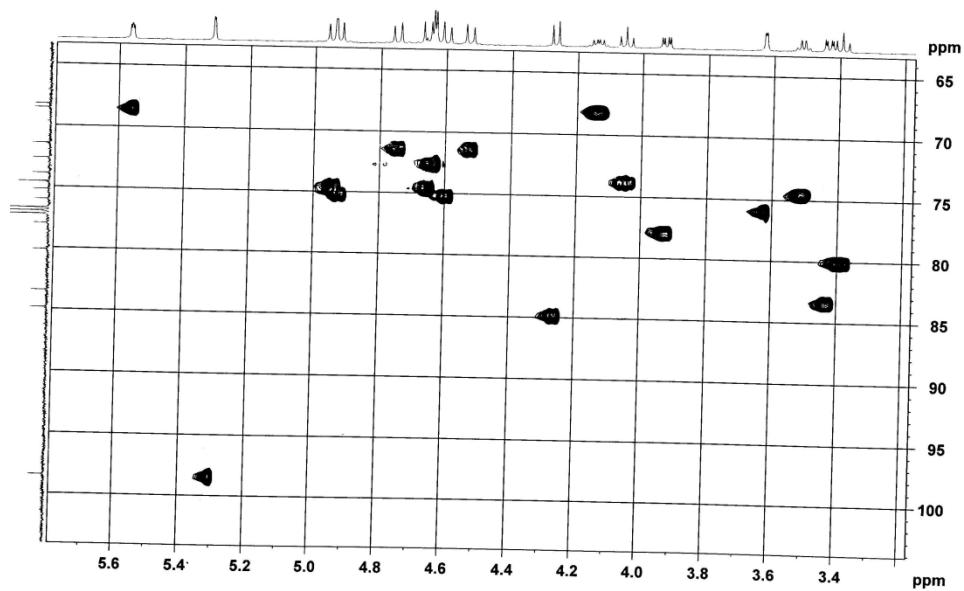
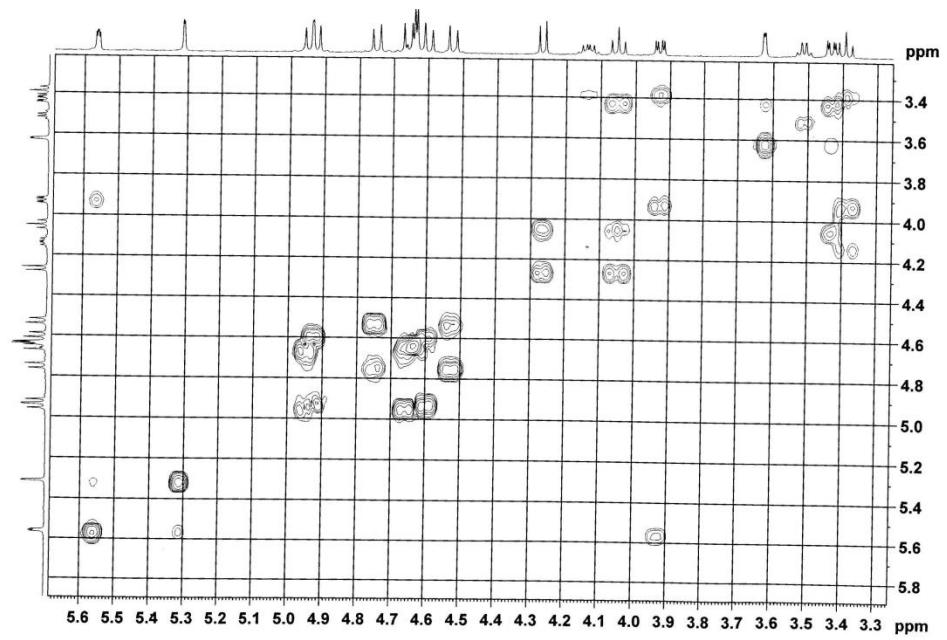
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (CDCl₃). (9)



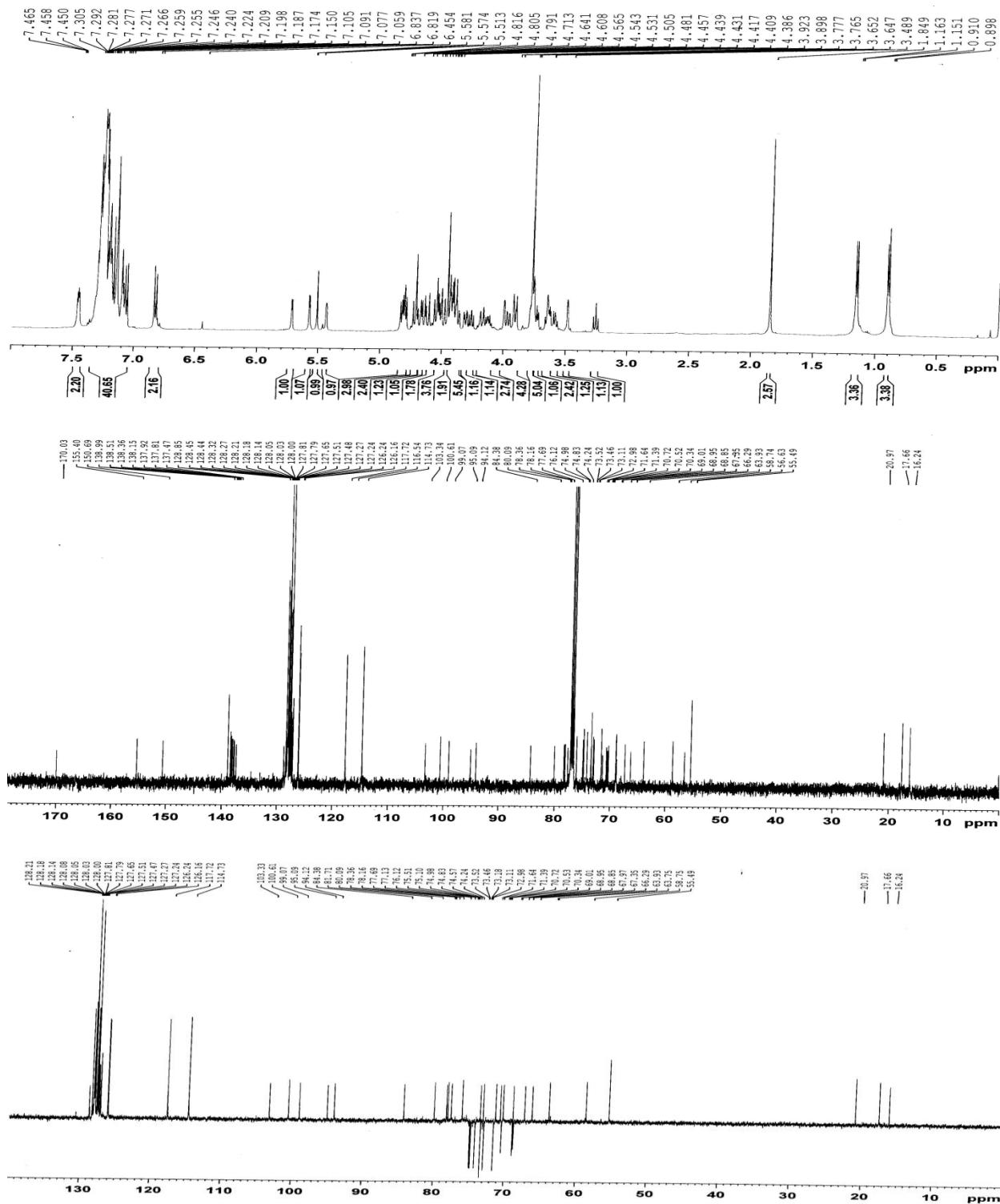
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (9) (CDCl_3) (selected region).



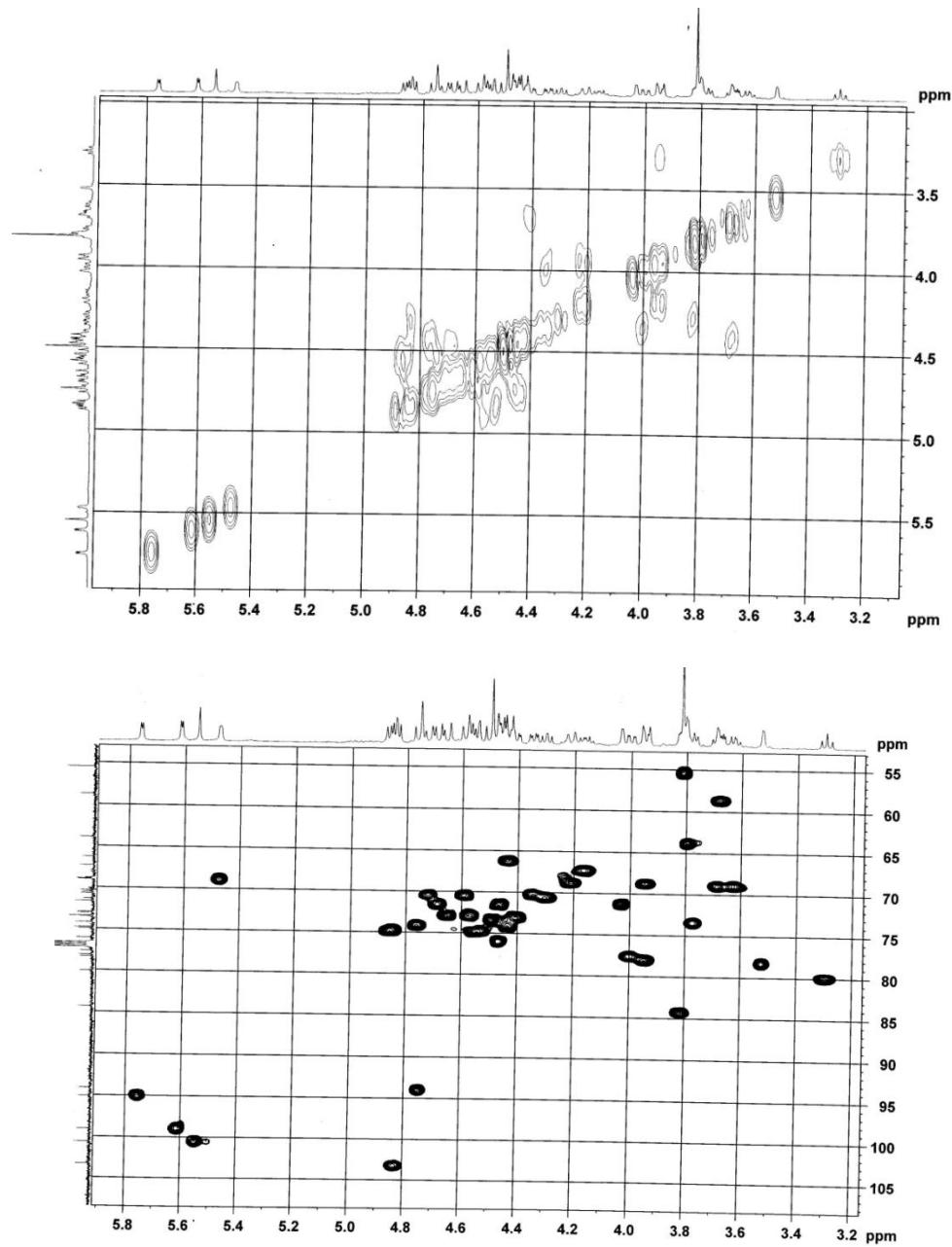
¹H, ¹³C and DEPT 135 NMR spectra of ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-3,4-di-*O*-benzyl-1-thio- β -L-fucopyranoside (**10**) (CDCl₃).



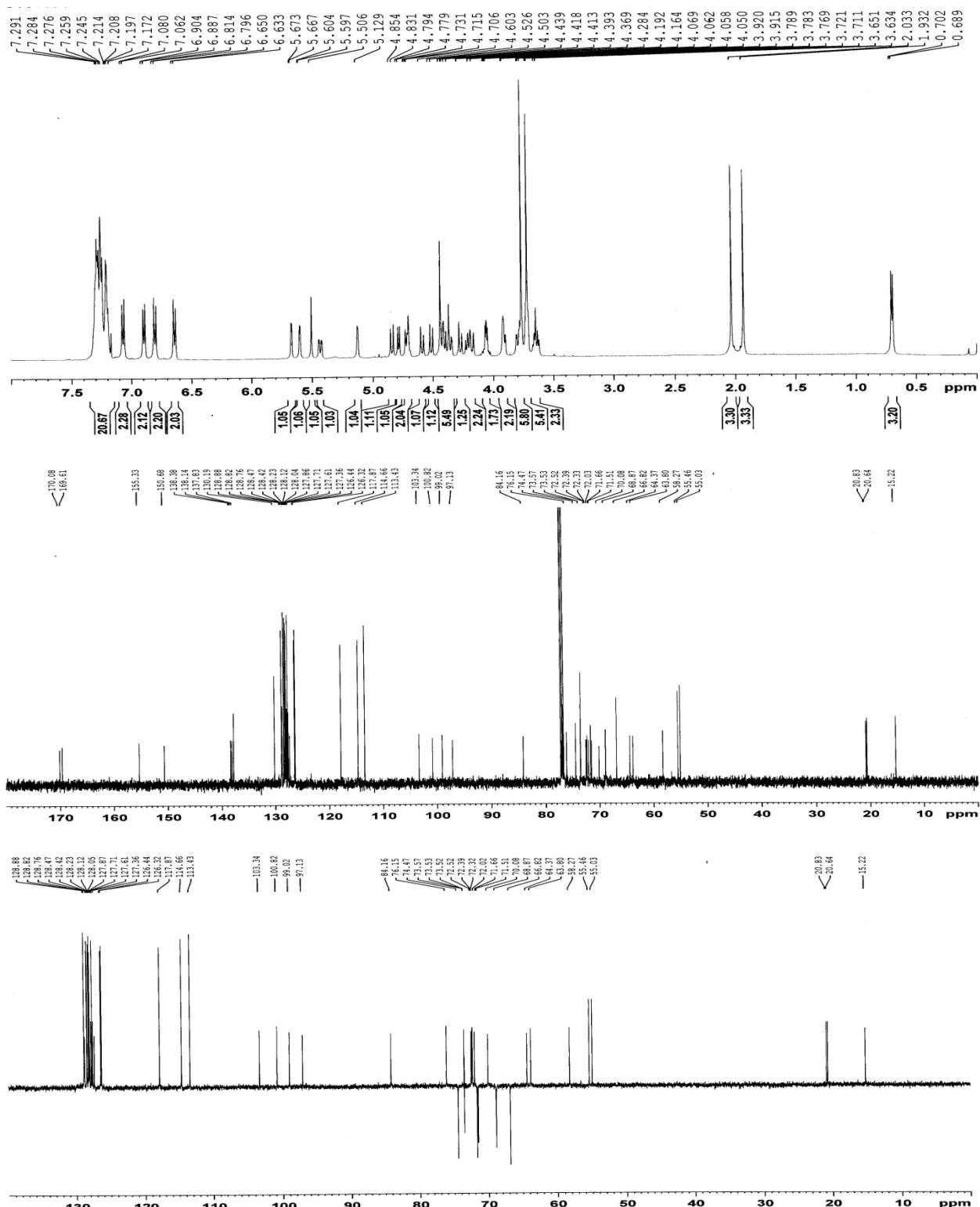
2D COSY and HSQC NMR spectra of ethyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-3,4-di-*O*-benzyl-1-thio- β -L-fucopyranoside (**10**) (CDCl_3) (Selected region).



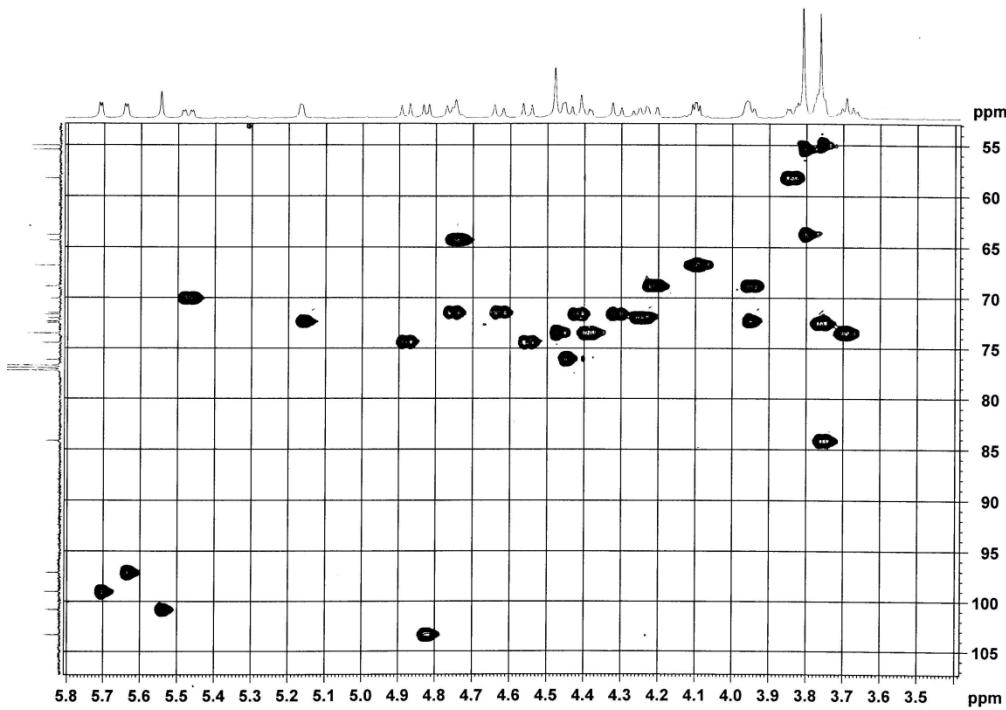
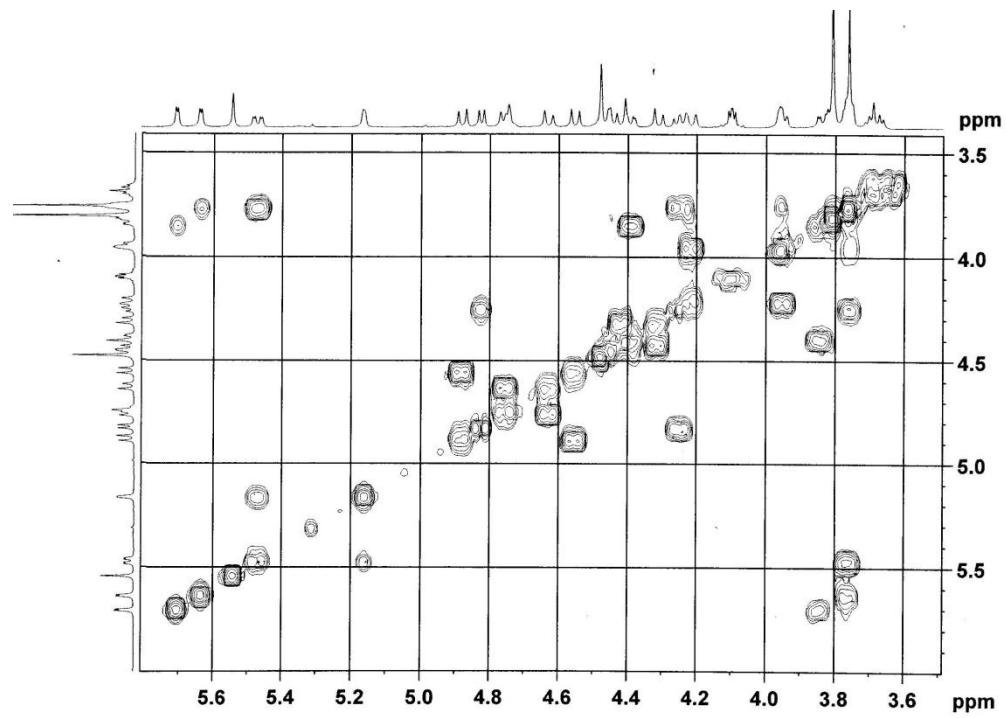
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (11) (CDCl_3).



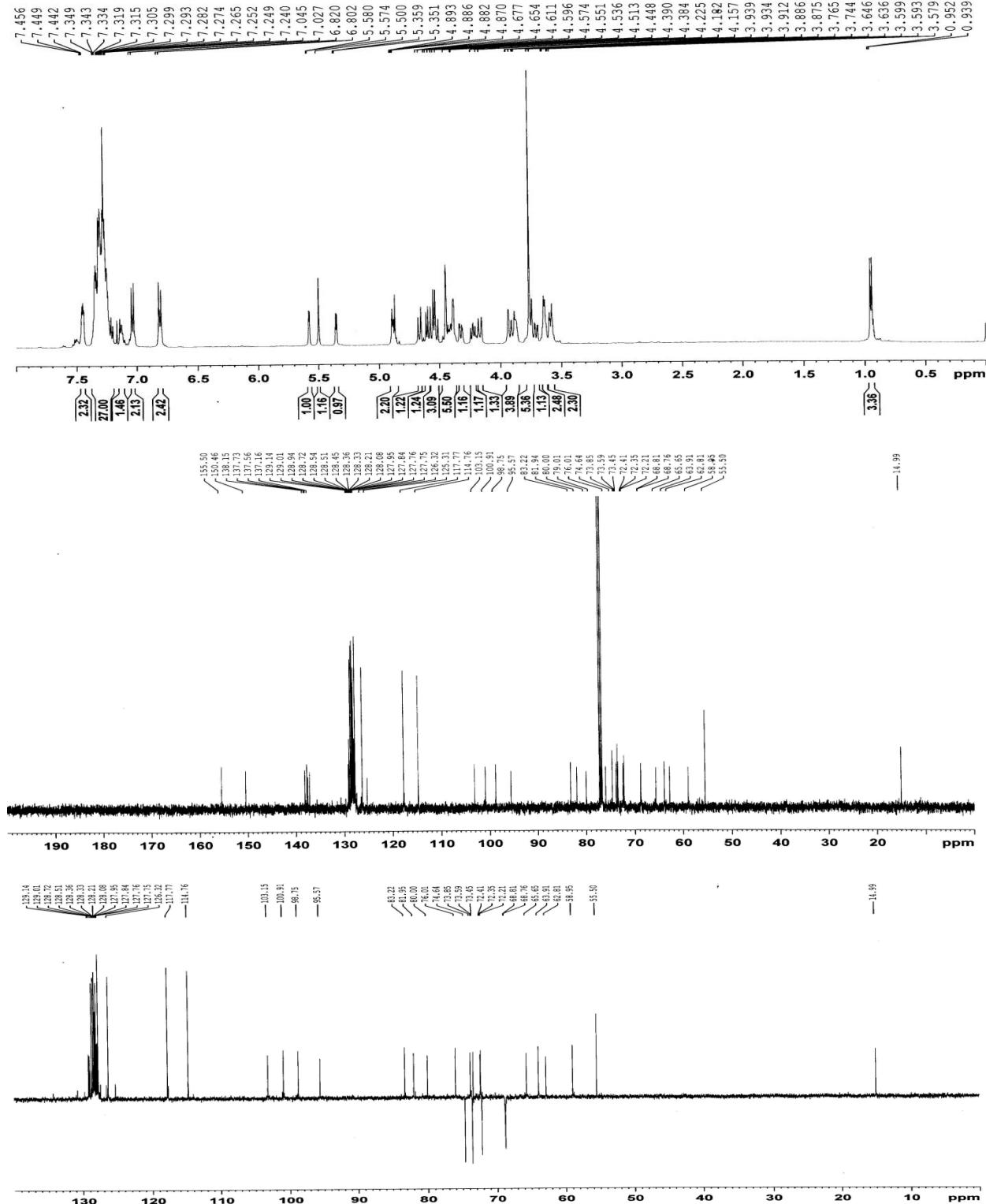
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (11) (CDCl_3) (Selected region).



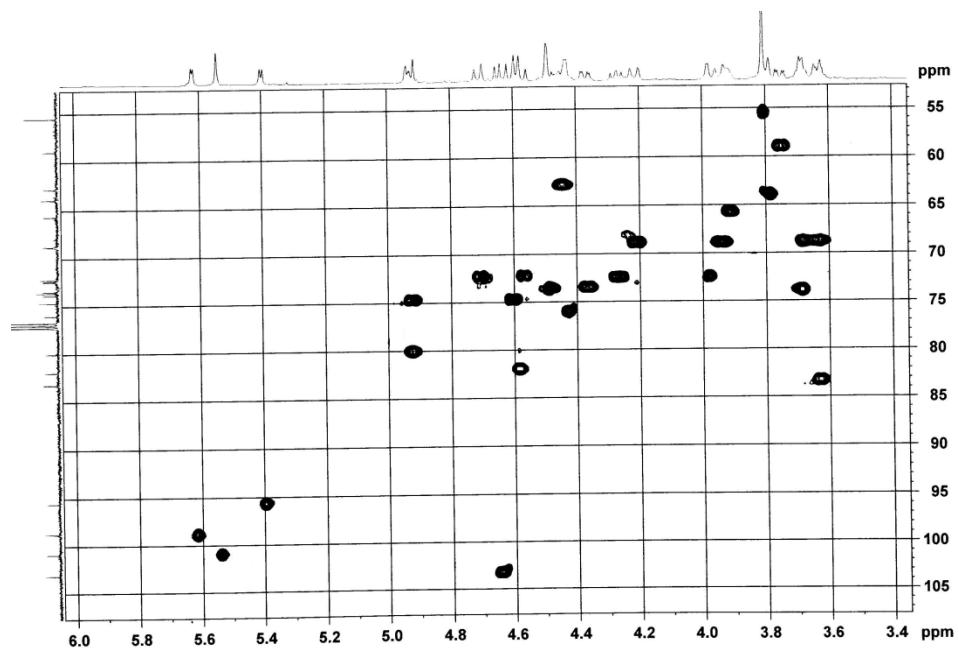
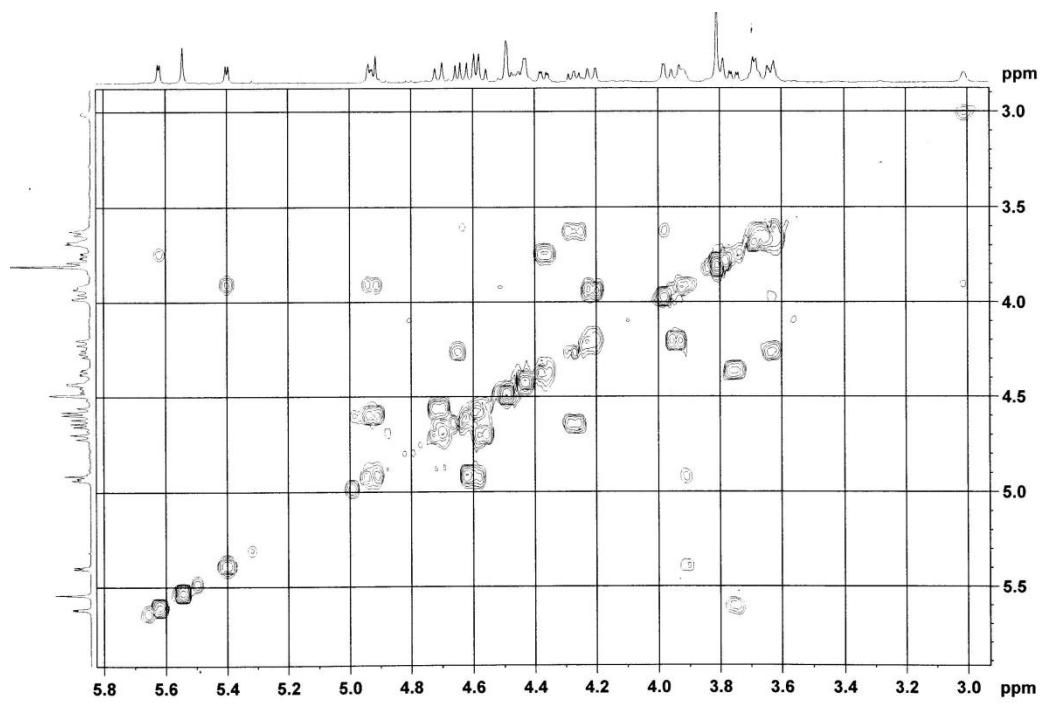
^1H , ^{13}C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-acetyl-2-*O*-(*p*-methoxybenzyl))- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**12**) (CDCl_3).



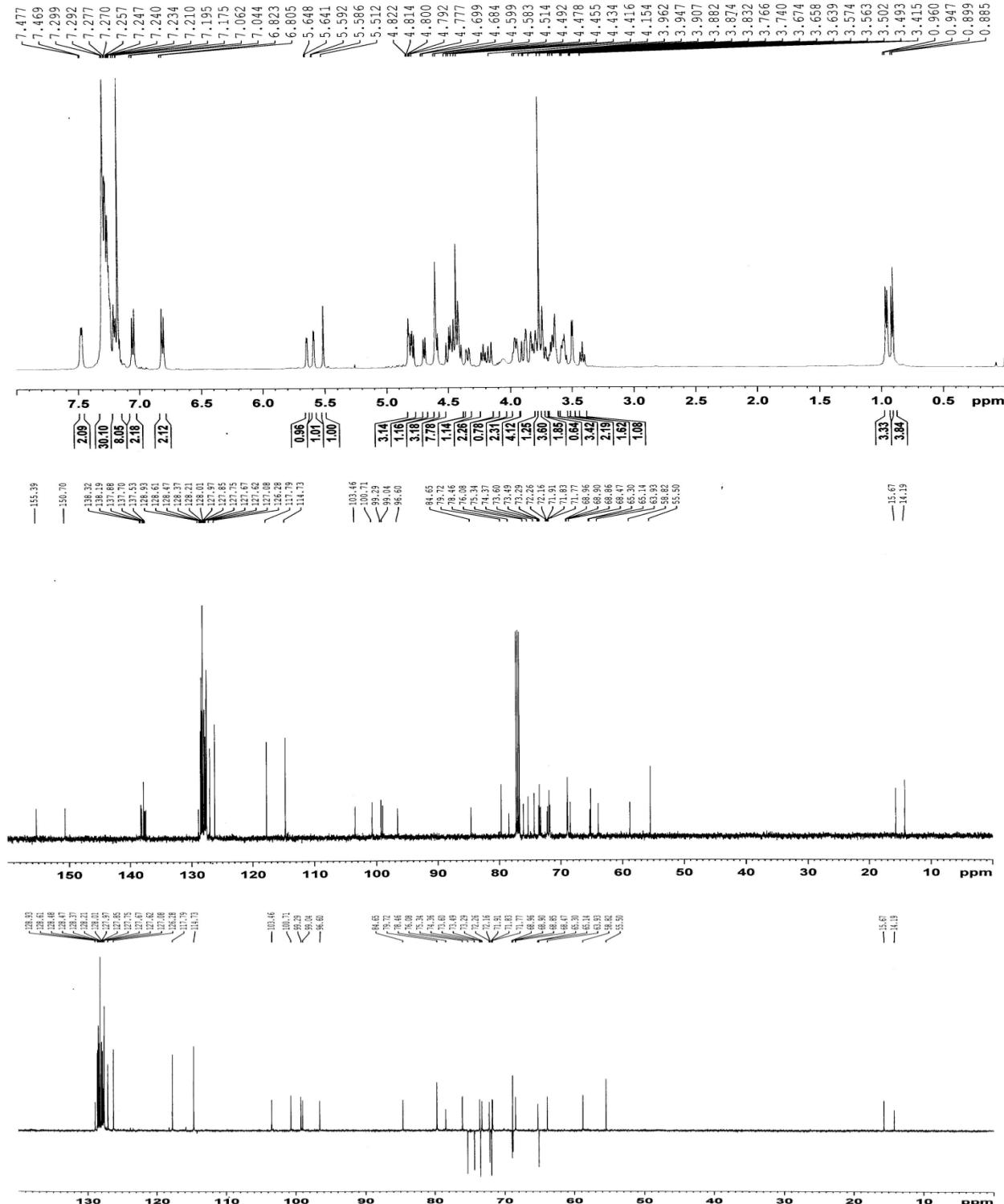
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-acetyl-2-*O*-(*p*-methoxybenzyl))- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**12**) (CDCl_3) (selected region).



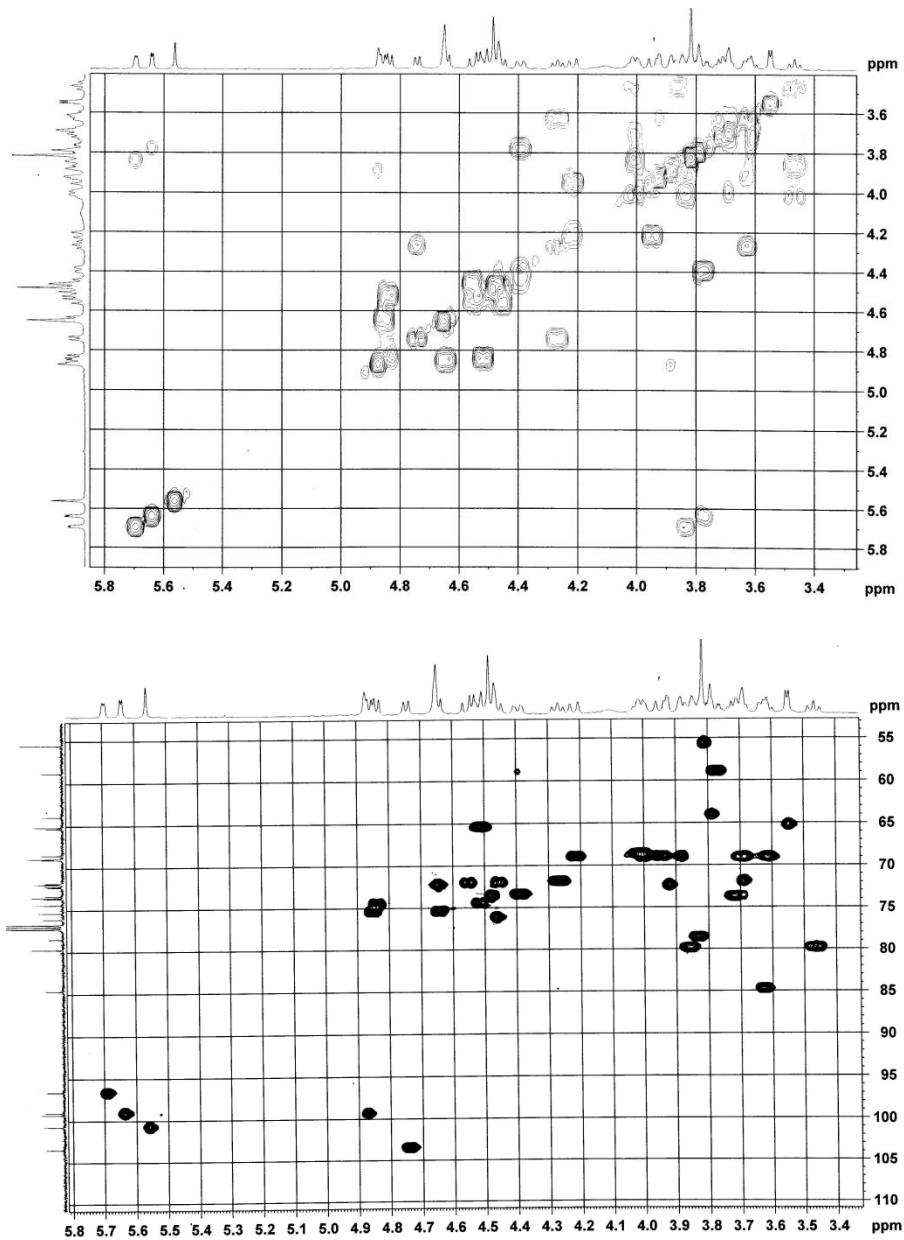
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**13**) (CDCl_3).



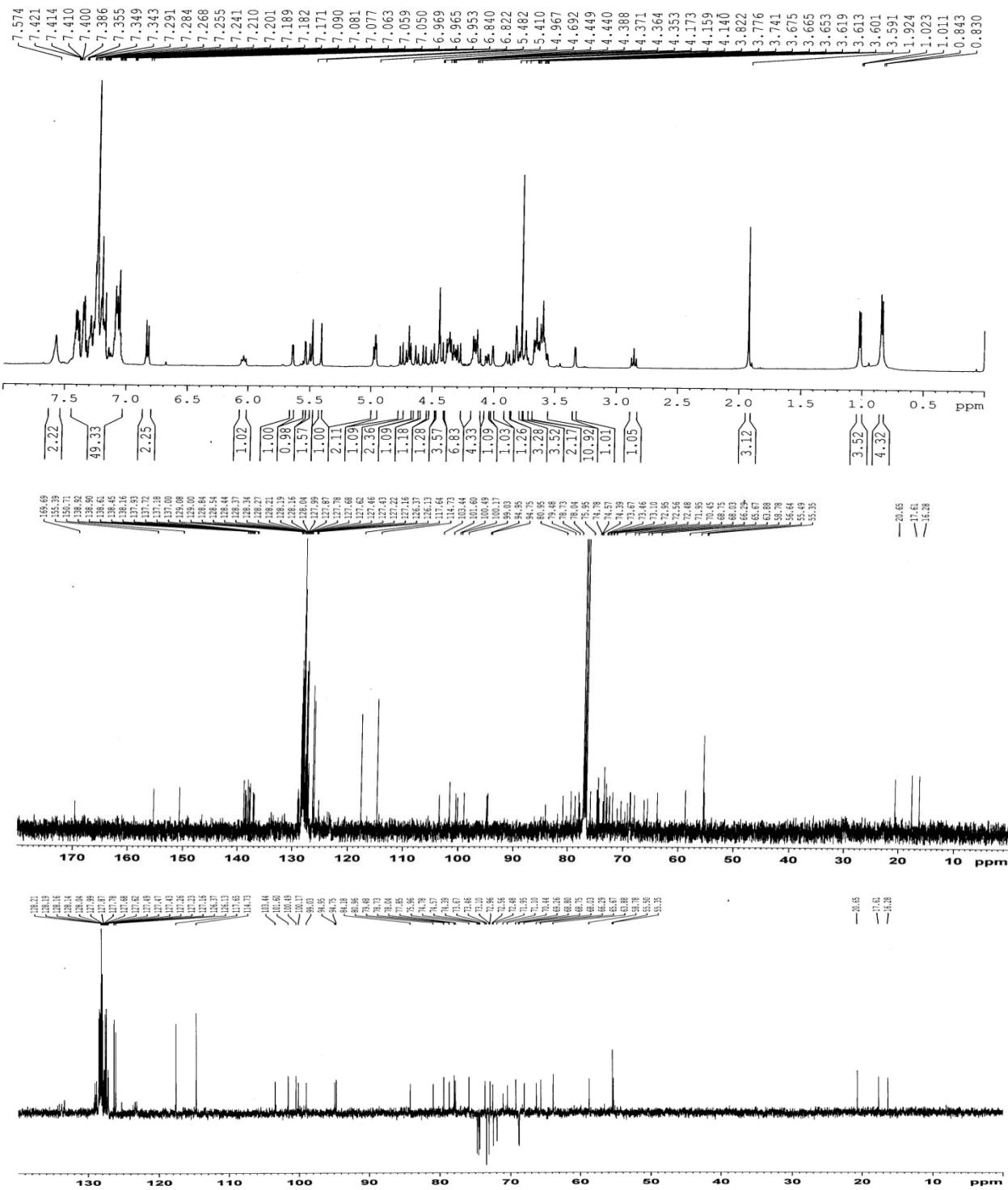
2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**13**) (CDCl_3) (Selected region).



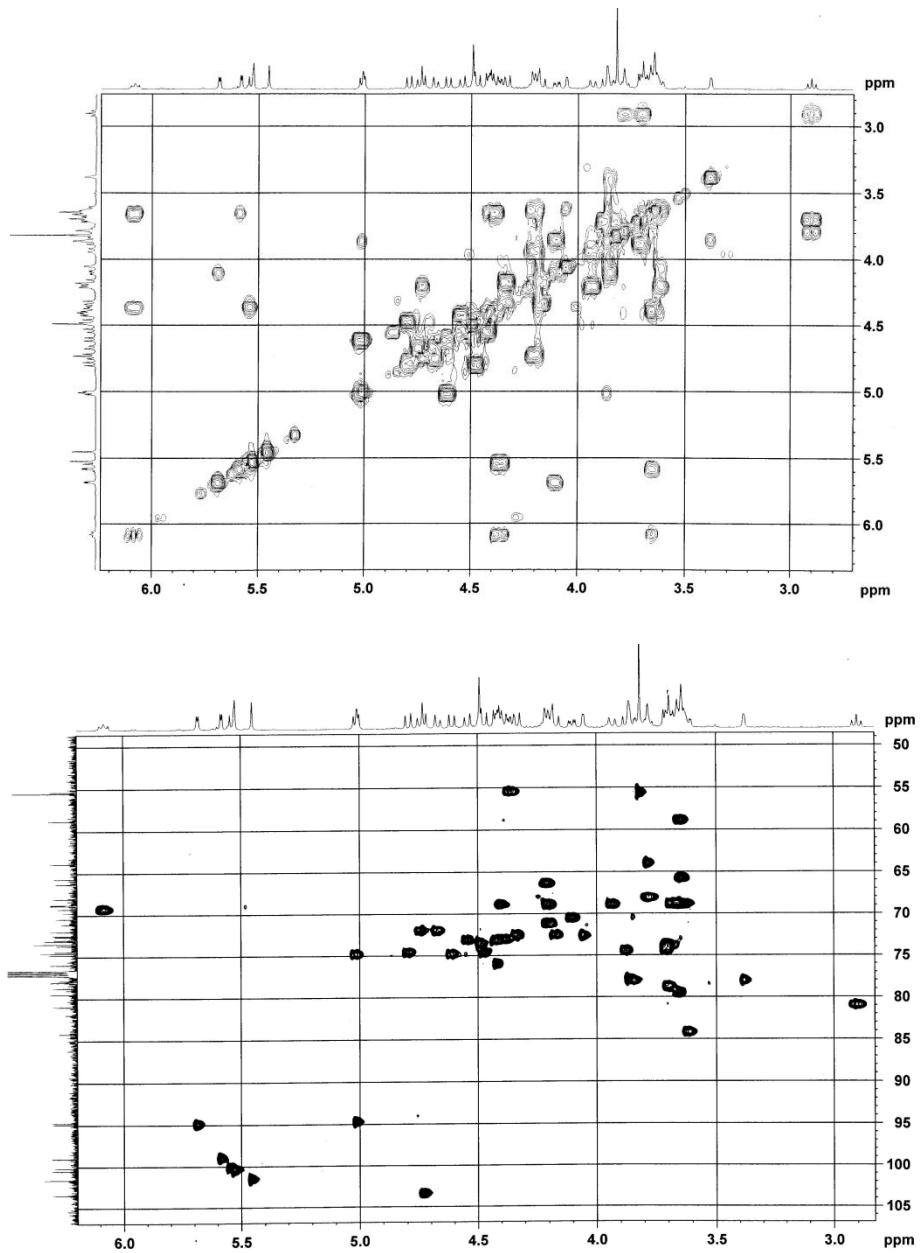
¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (14) (CDCl_3).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (14) (CDCl_3) (Selected region).



¹H, ¹³C and DEPT 135 NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**15**) (CDCl_3).



2D COSY and HSQC NMR spectra of *p*-methoxyphenyl (2-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-*N*-phthalimido- β -D-glucopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-rhamnopyranosyl)-(1 \rightarrow 2)-(3,4-di-*O*-benzyl- α -L-fucopyranosyl)-(1 \rightarrow 2)-(3,4,6-tri-*O*-benzyl- β -D-galactopyranosyl)-(1 \rightarrow 3)-2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-galactopyranoside (**15**) (CDCl_3) (selected region).