Supplementary Material

Facile synthesis of tetrasaccharide fragments of bioactive Asterosaponins novaeguinosides I and II from starfish *Culcita novaeguineae*

Geeta Karki[ab] and Pintu Kumar Mandal[ab*]

[a]Medicinal and Process Chemistry Division, CSIR-Central Drug Research Institute, BS-10/1, Sector 10, Jankipuram extension, Sitapur Road, P.O. Box 173, Lucknow, 226031, India.
[b]Academy of Scientific and Innovative Research, New Delhi 110001, India
* Corresponding author; Email: *pintuchem06@gmail.com*

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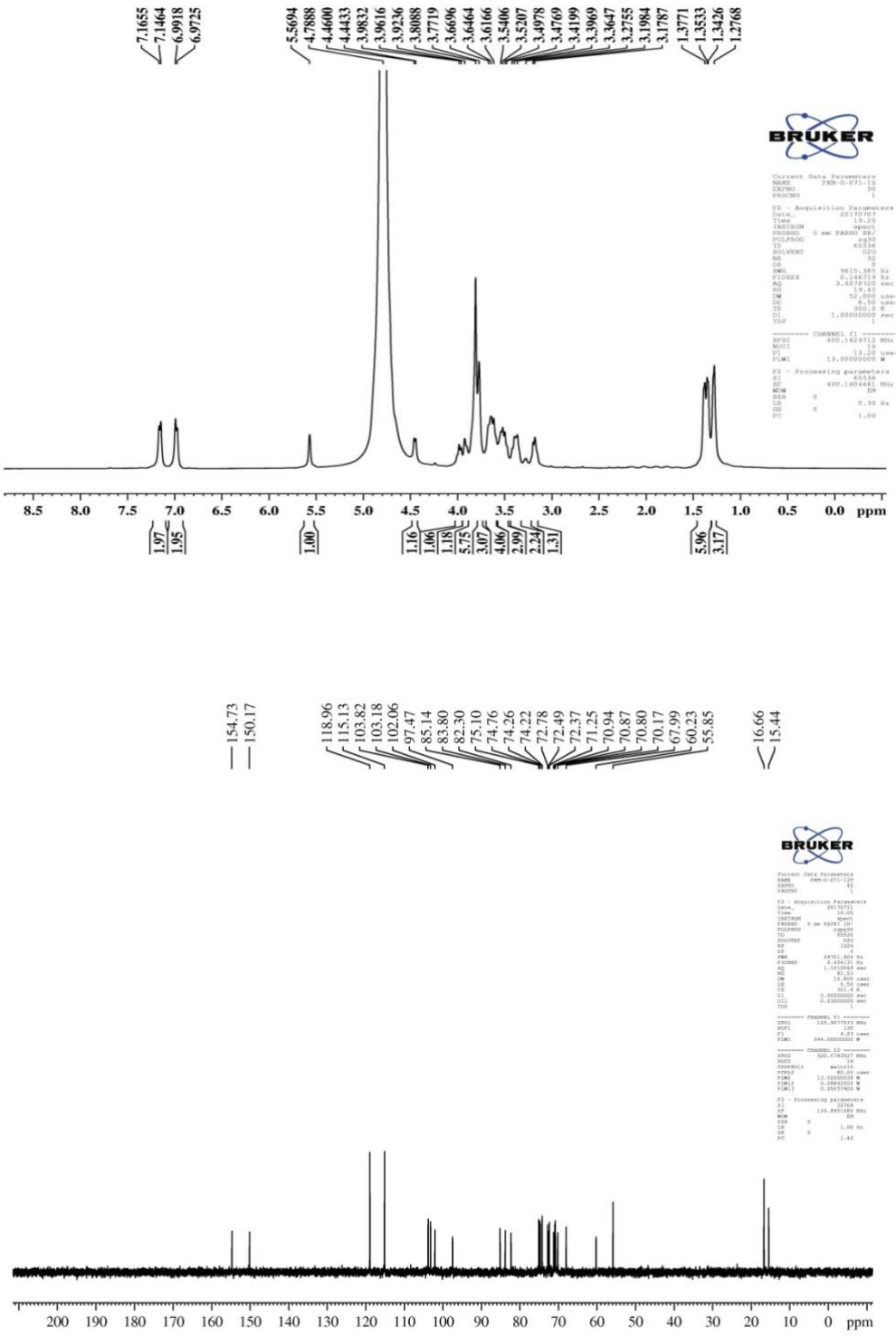
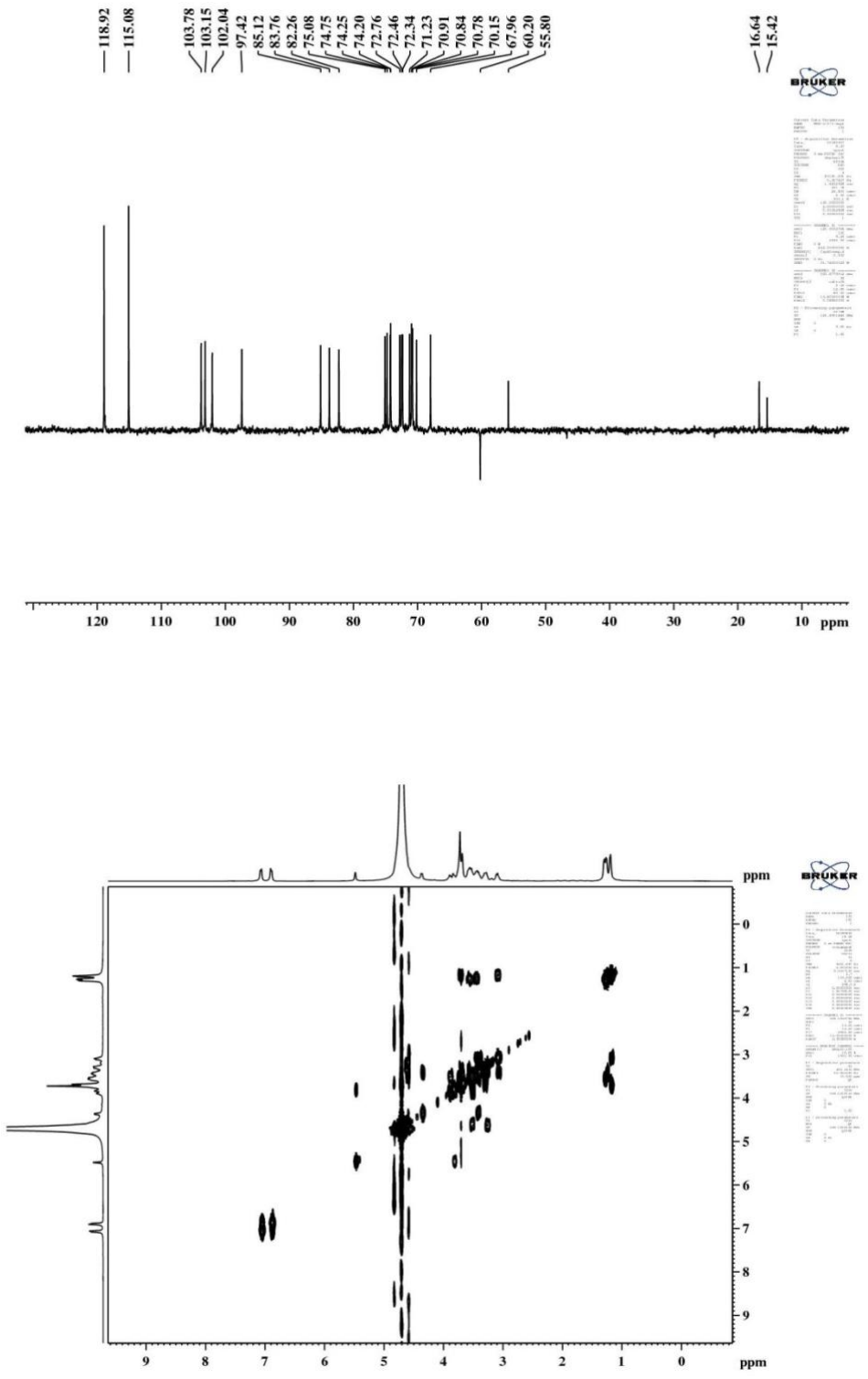
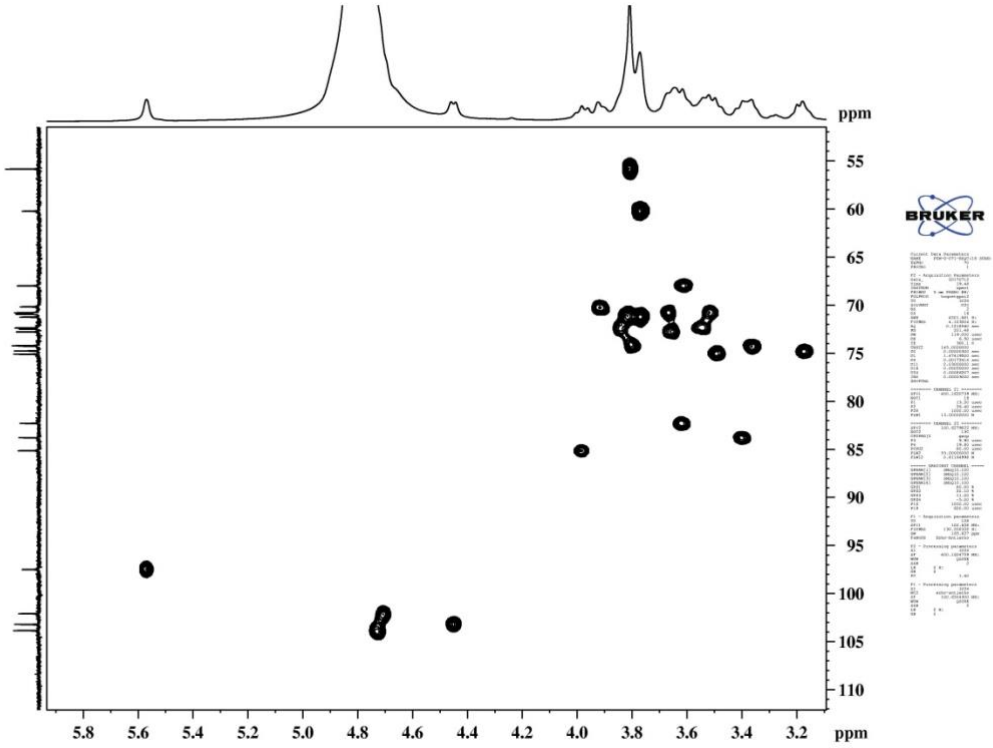
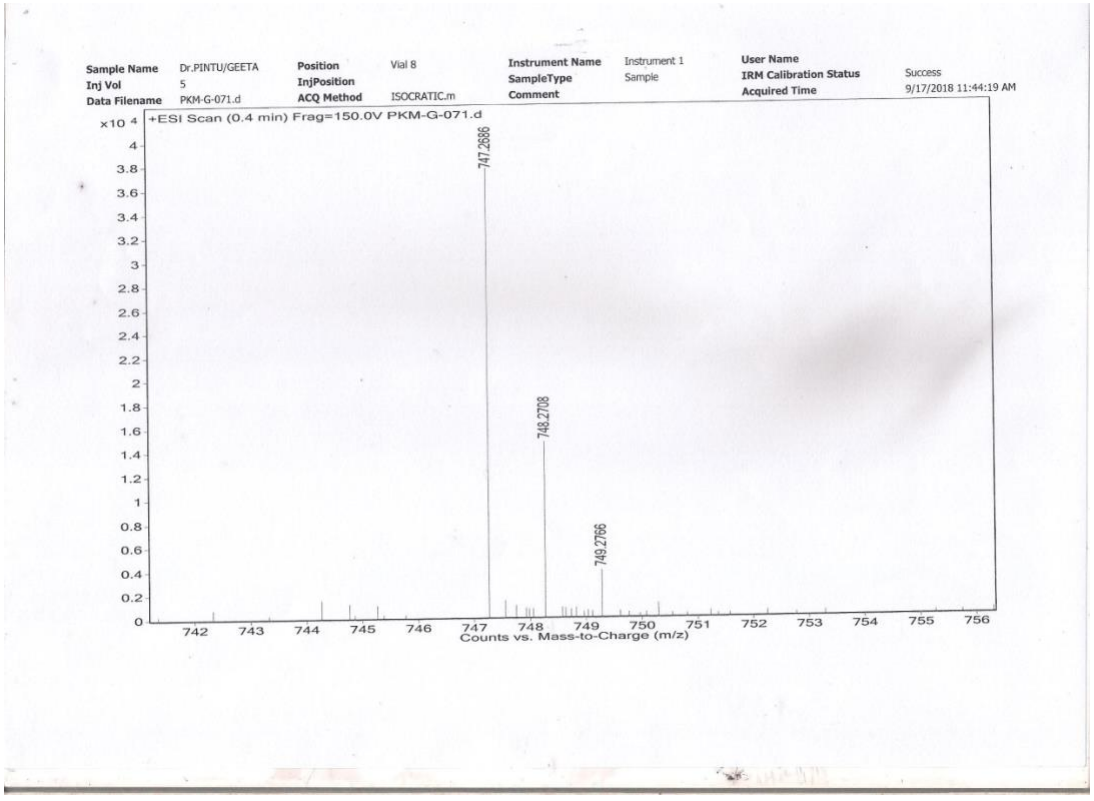


^{1}H and ^{13}C NMR spectra of *p*-Methoxyphenyl (6-deoxy-β-D-galactopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)- α-D-glucopyranoside (**1**) (D_2O).

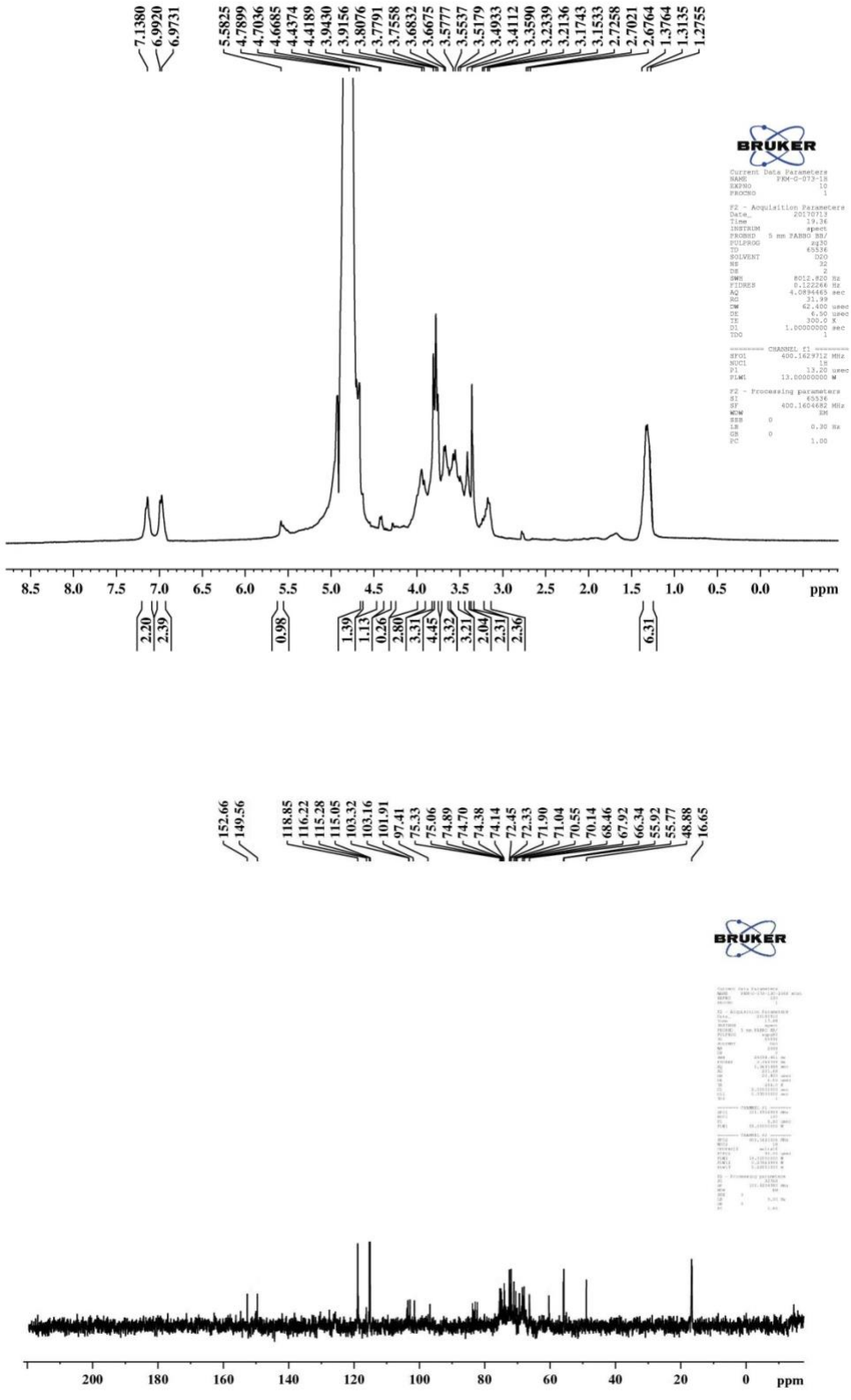


^{13}C DEPT 135 NMR and 2D COSY spectra of *p*-Methoxyphenyl (6-deoxy-β-D-galactopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)- α-D-glucopyranoside (**1**) (D_2O).

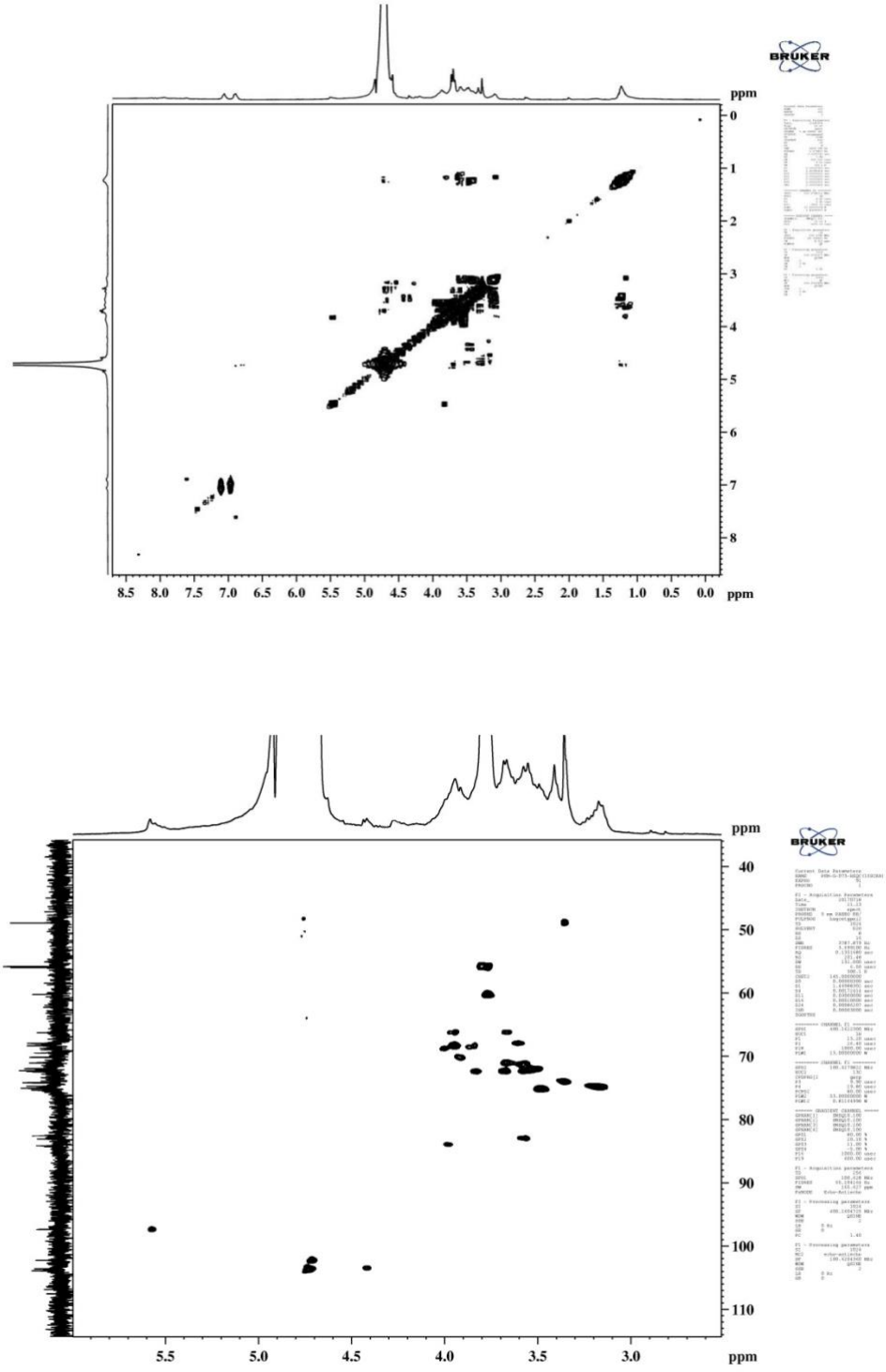




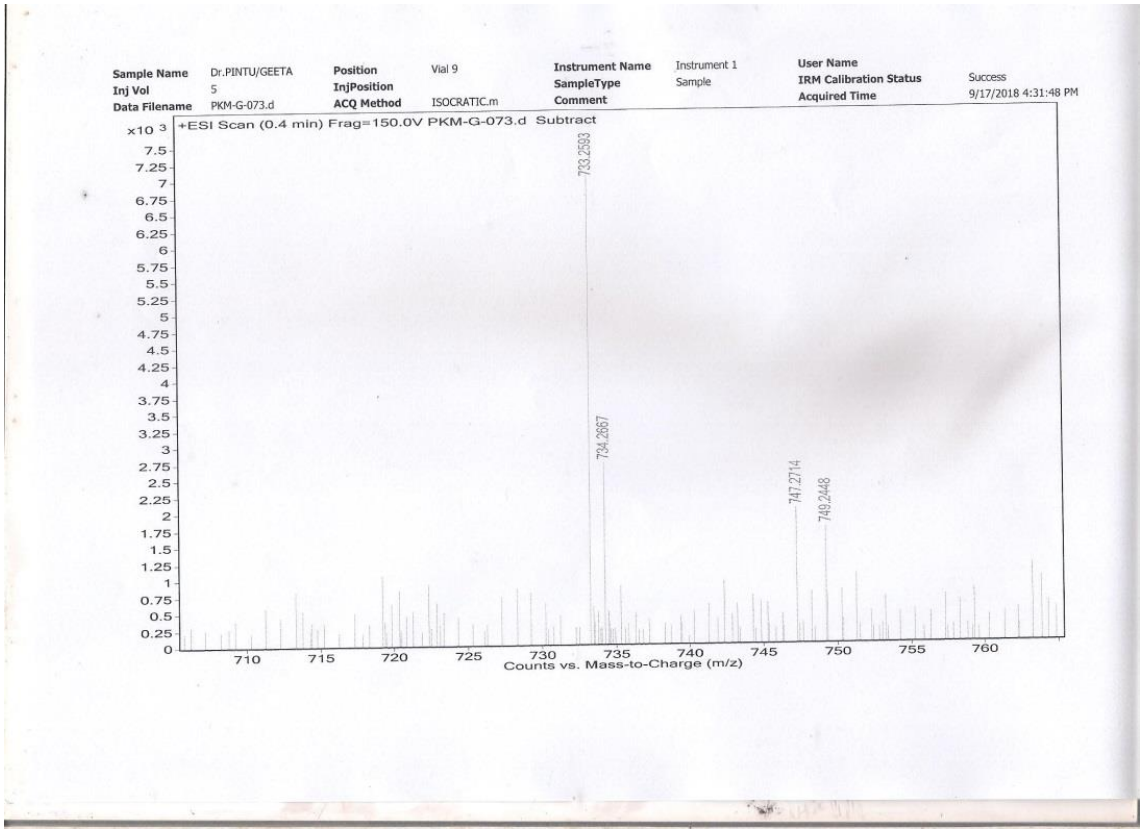
2D HSQC (selected region) and HRMS of *p*-Methoxyphenyl (6-deoxy-β-D-galactopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)- α-D-glucopyranoside (**1**) (D_2O).



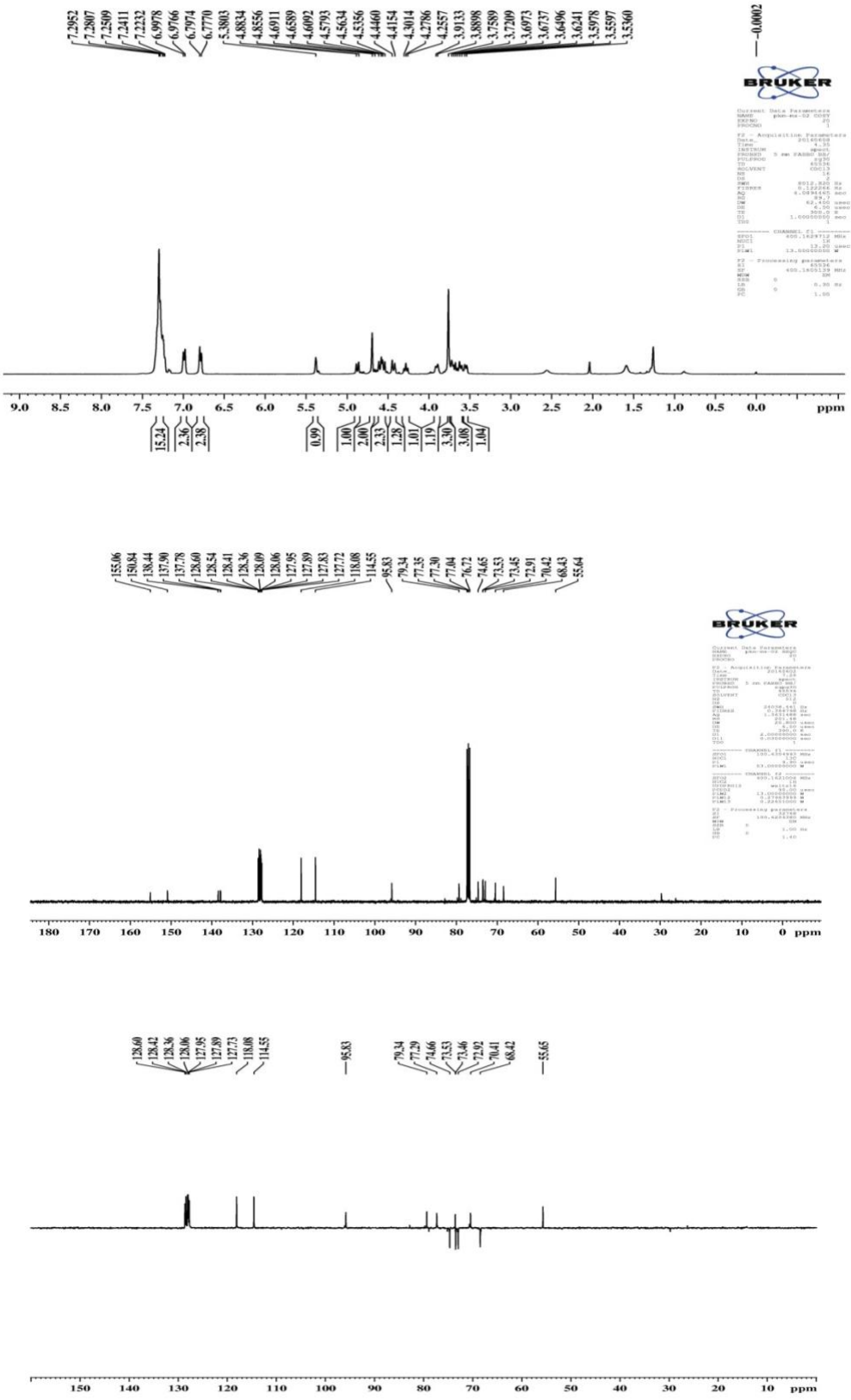
^{1}H and ^{13}C NMR spectra of *p*-Methoxyphenyl (β-L-arabinopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)- α-D-glucopyranoside (**2**) (D_2O).



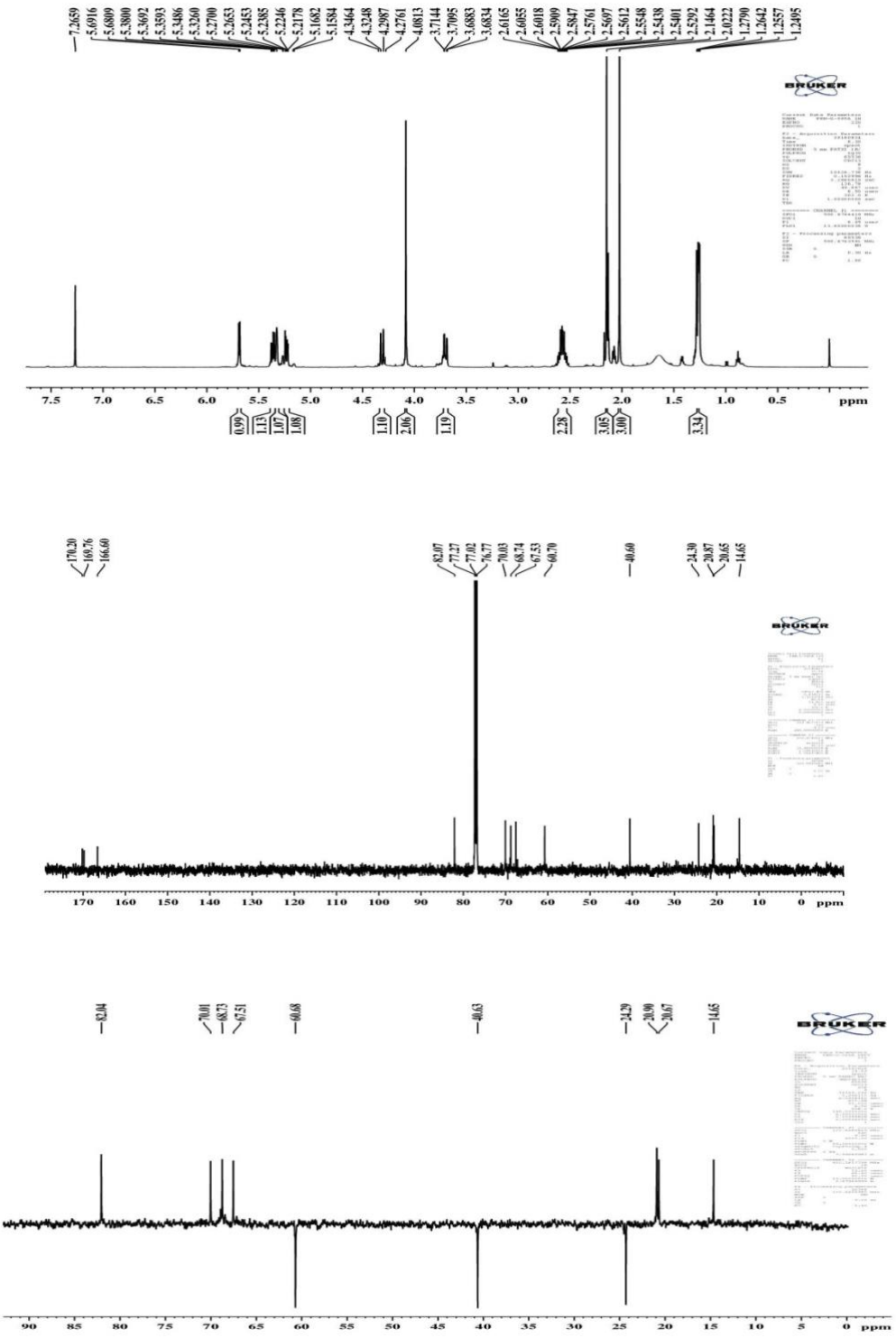
2D COSY and 2D HSQC (selected region) of *p*-Methoxyphenyl (β-L-arabinopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)- α-D-glucopyranoside (**2**) (D_2O).



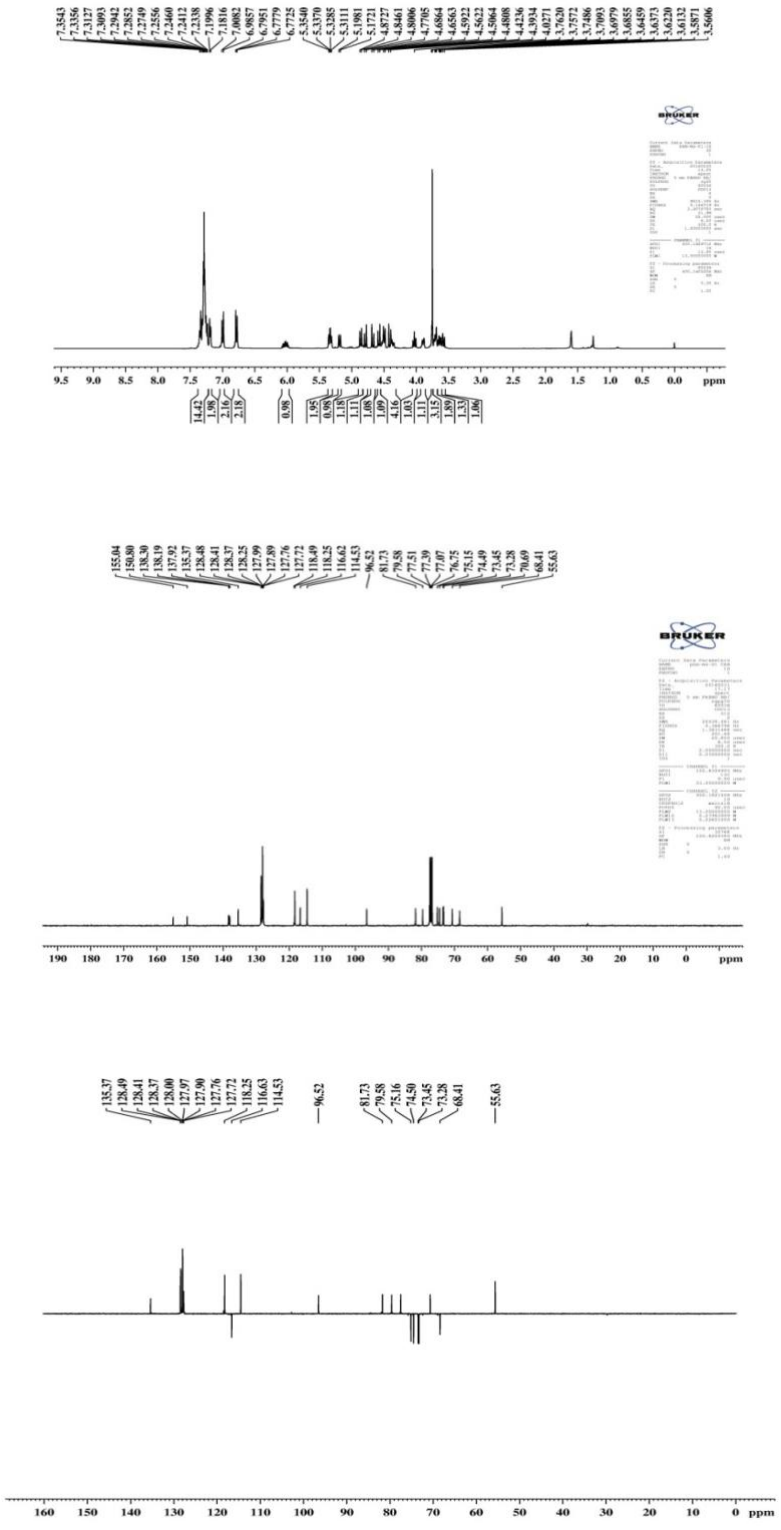
HRMS of *p*-Methoxyphenyl (β-L-arabinopyranosyl)-(1→4)-(6-deoxy-β-D glucopyranosyl)-(1→2)-(6-deoxy-β-D-glucopyranosyl)-(1→3)-α-D-glucopyranoside (**2**) (D_2O).



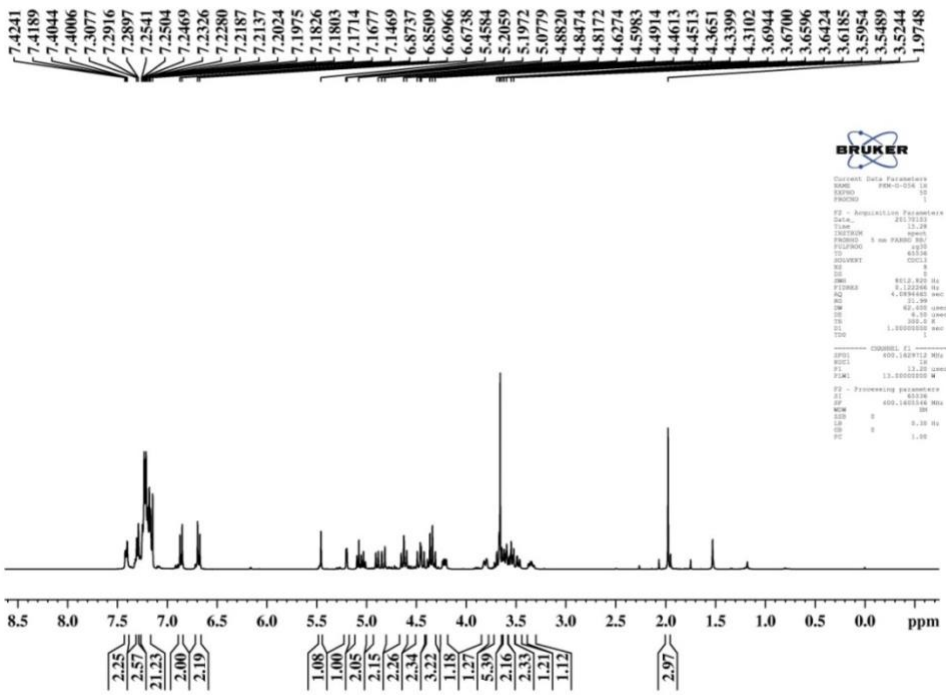
^{1}H, ^{13}C and DEPT 135 NMR spectra of *p*-Methoxyphenyl-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**3**) ($CDCl_3$).

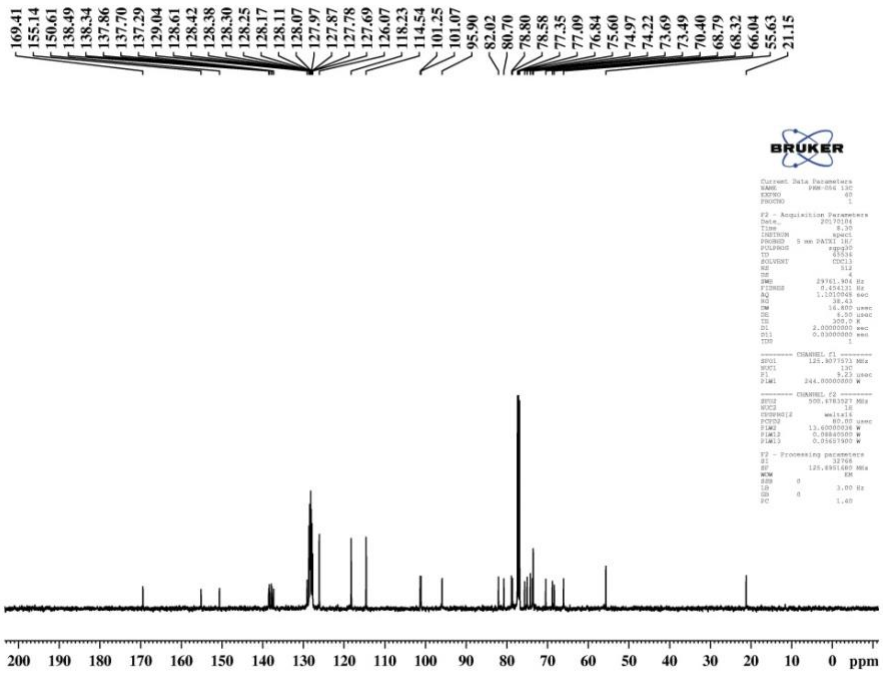


^{1}H, ^{13}C and DEPT 135 NMR spectra of ethyl-3,4-di-*O*-acetyl-2-*O*-chloroacetyl 1-thio-β-L-arabinopyranoside (7) ($CDCl_3$).

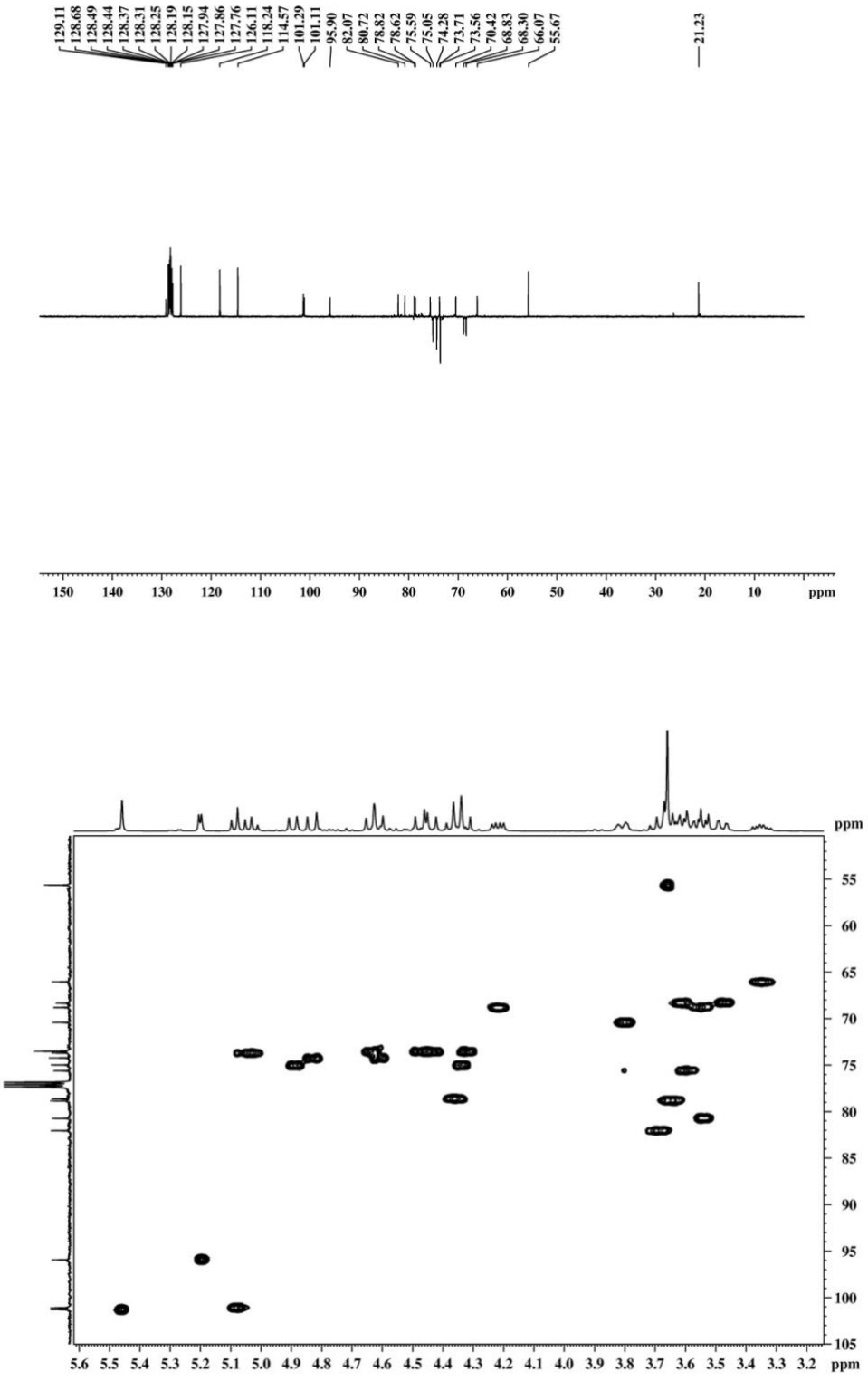


^{1}H, ^{13}C and DEPT 135 NMR spectra of *p*-Methoxyphenyl-2,4,6-tri-*O*-benzyl-3-*O*-allyl-α-D-glucopyranoside (**12**) ($CDCl_3$).

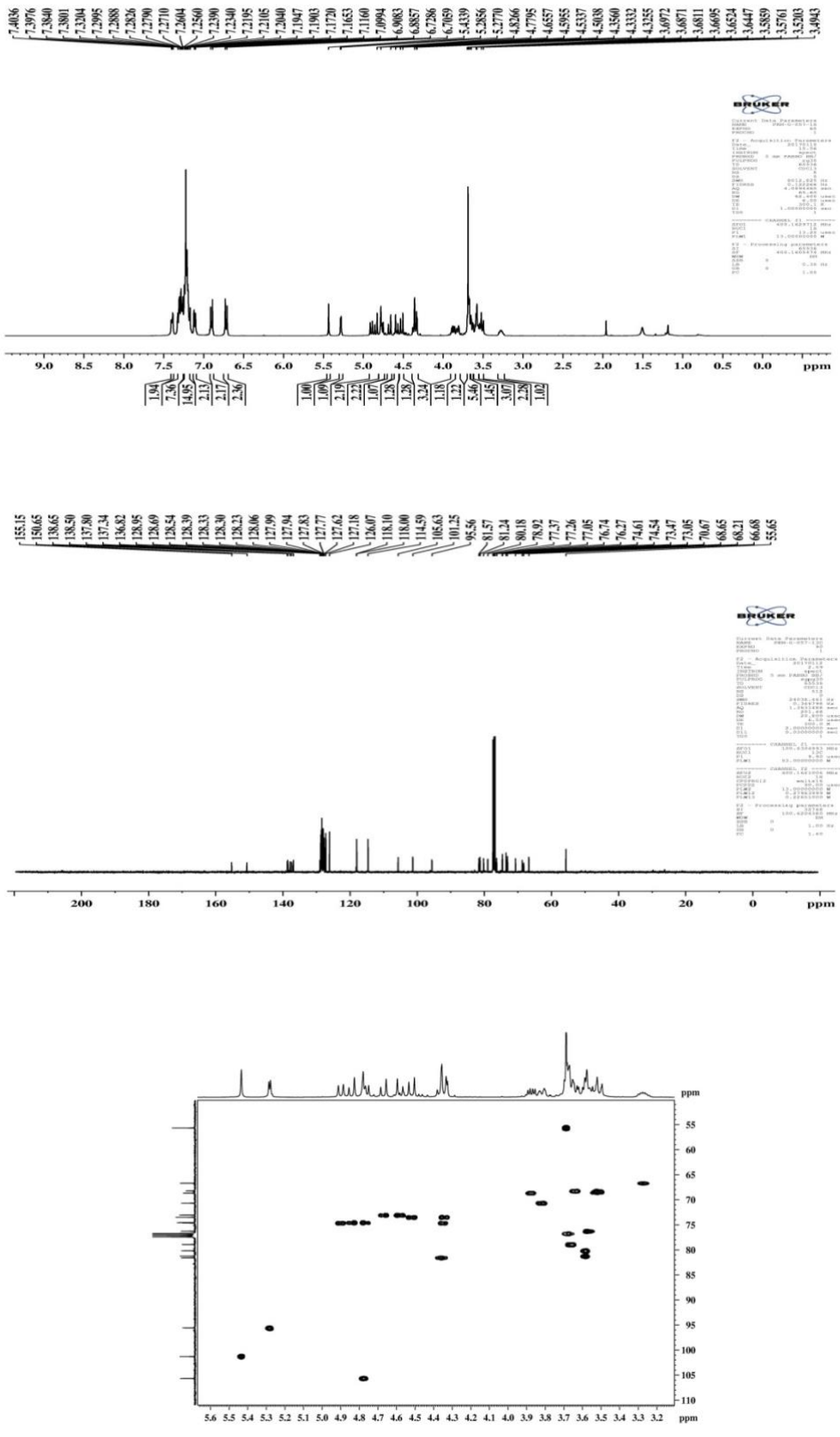




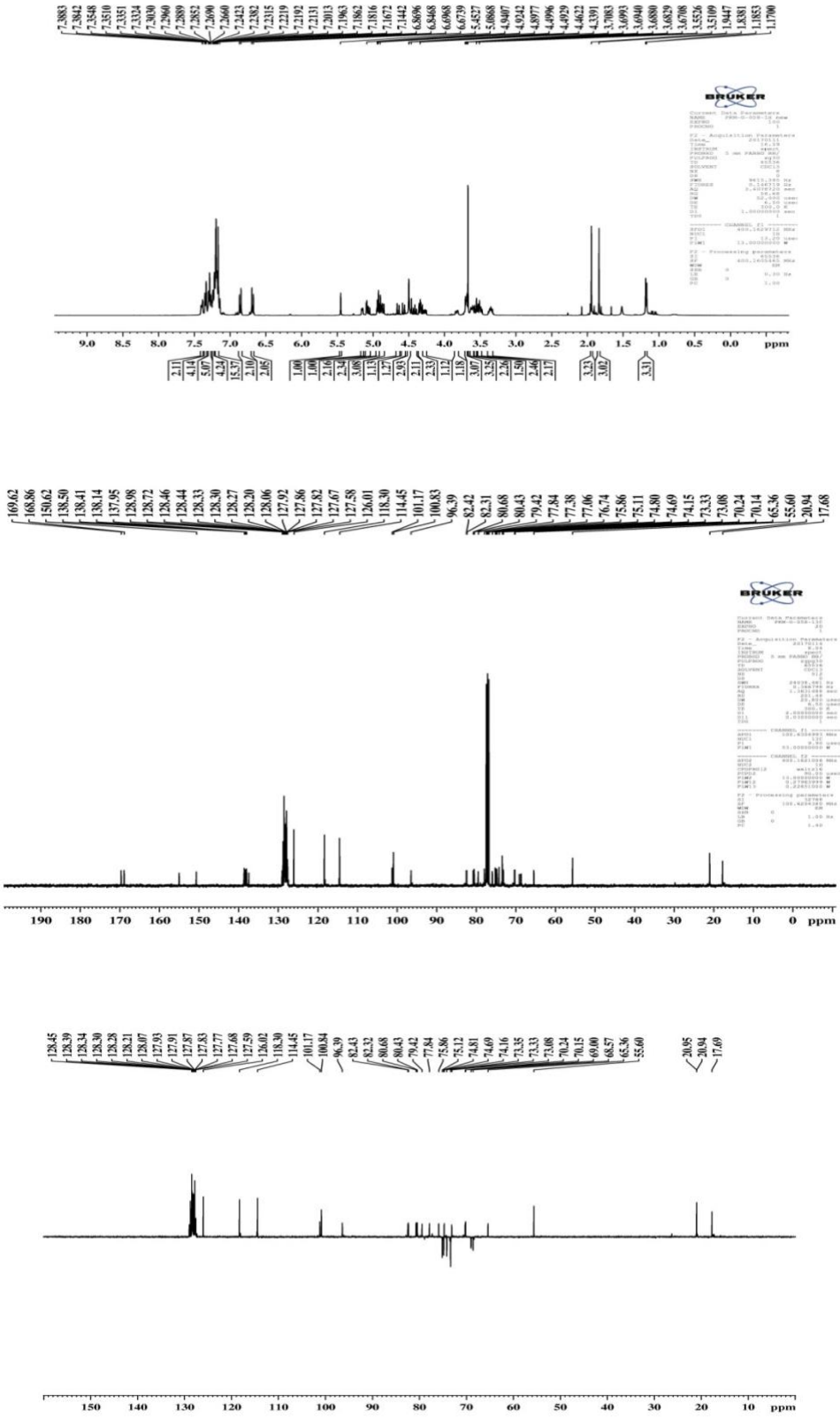
^{1}H and ^{13}C NMR spectra of *p*-Methoxyphenyl (2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β- D glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**14**) ($CDCl_3$).



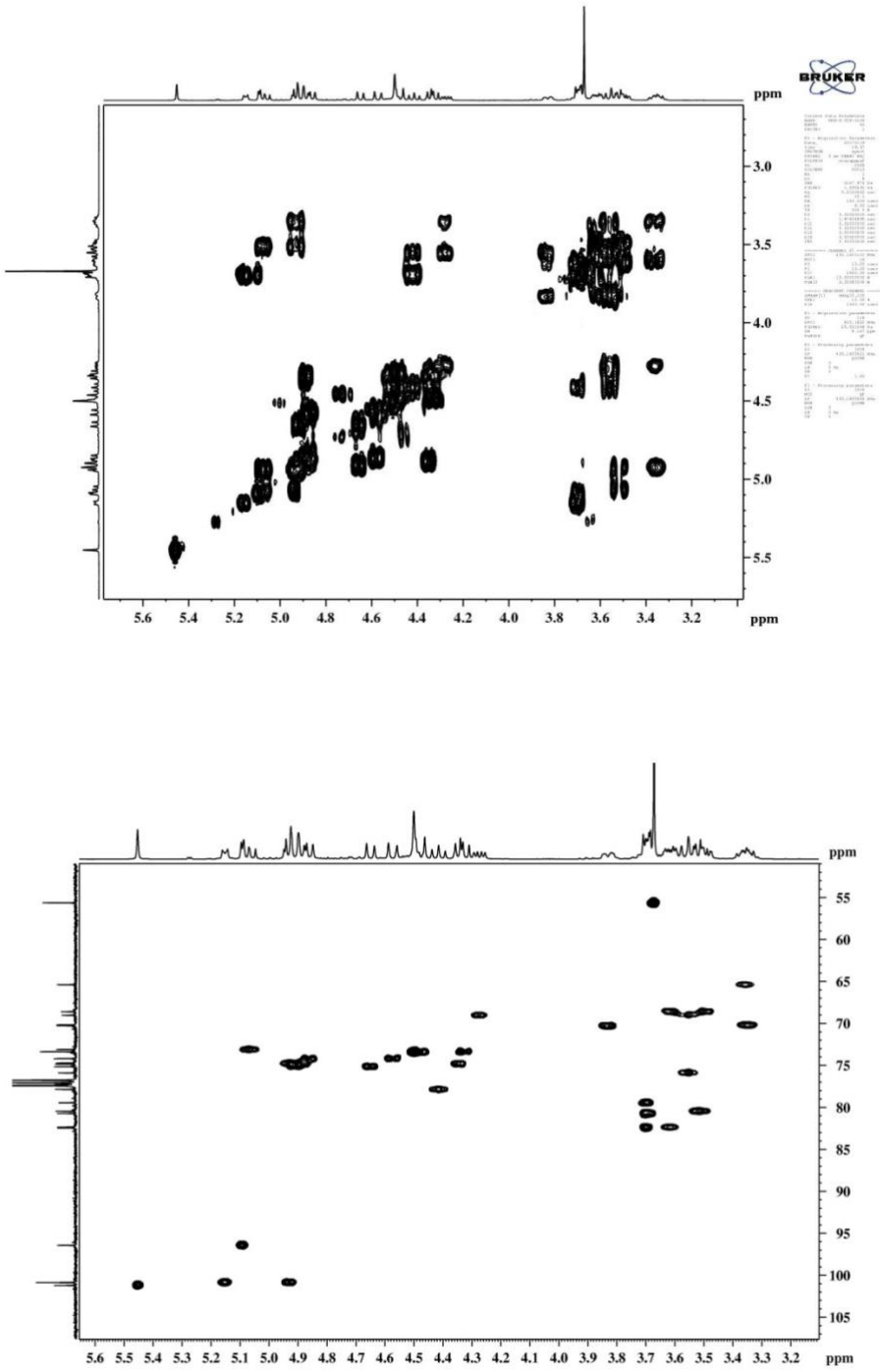
^{13}C DEPT 135 NMR and 2D HSQC (selected region) of *p*-Methoxyphenyl (2-*O*-acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β- D glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**14**) ($CDCl_3$).



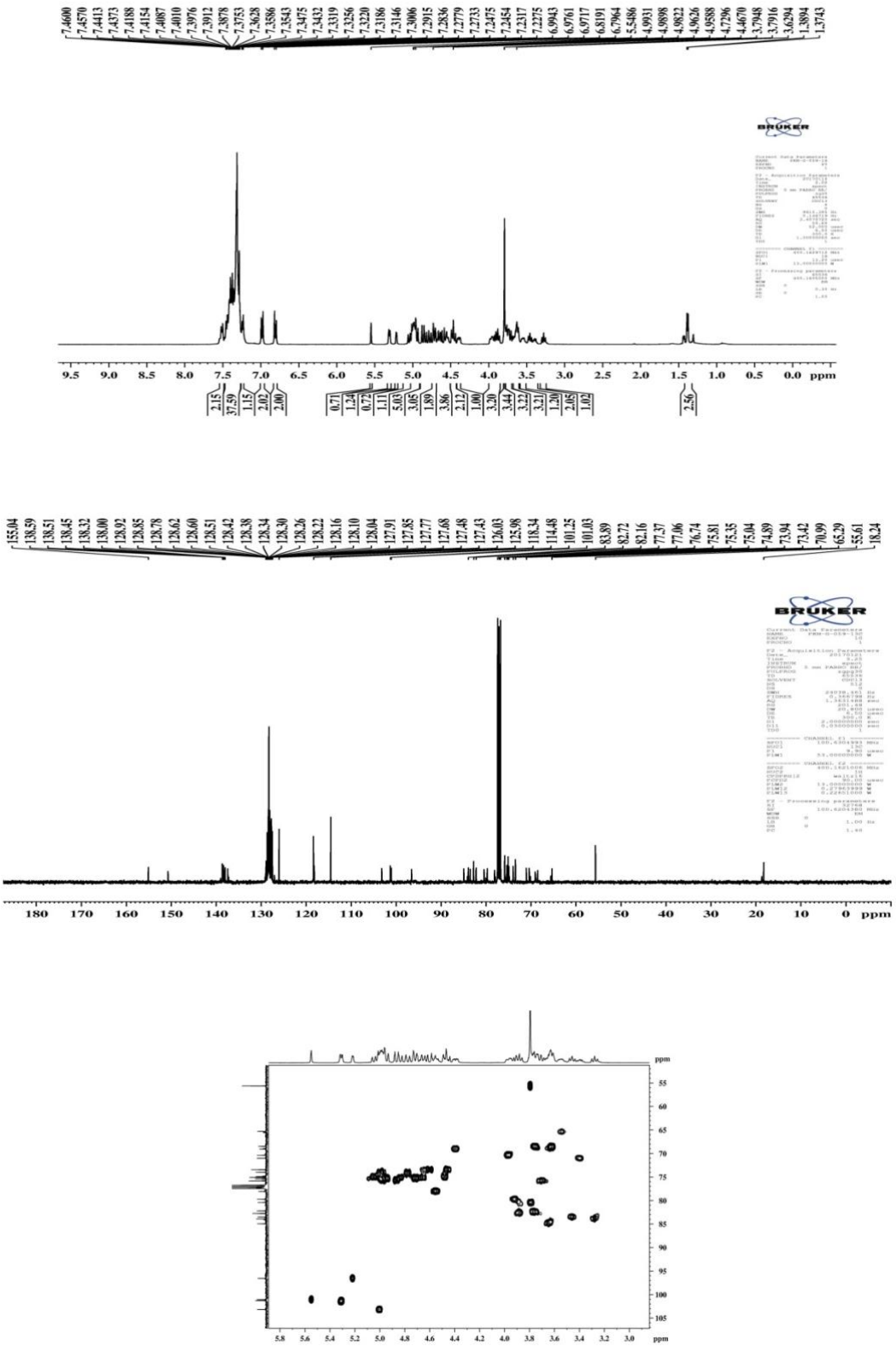
^{1}H, ^{13}C NMR and 2D HSQC (selected region) of *p*-Methoxyphenyl (3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**15**) ($CDCl_3$).



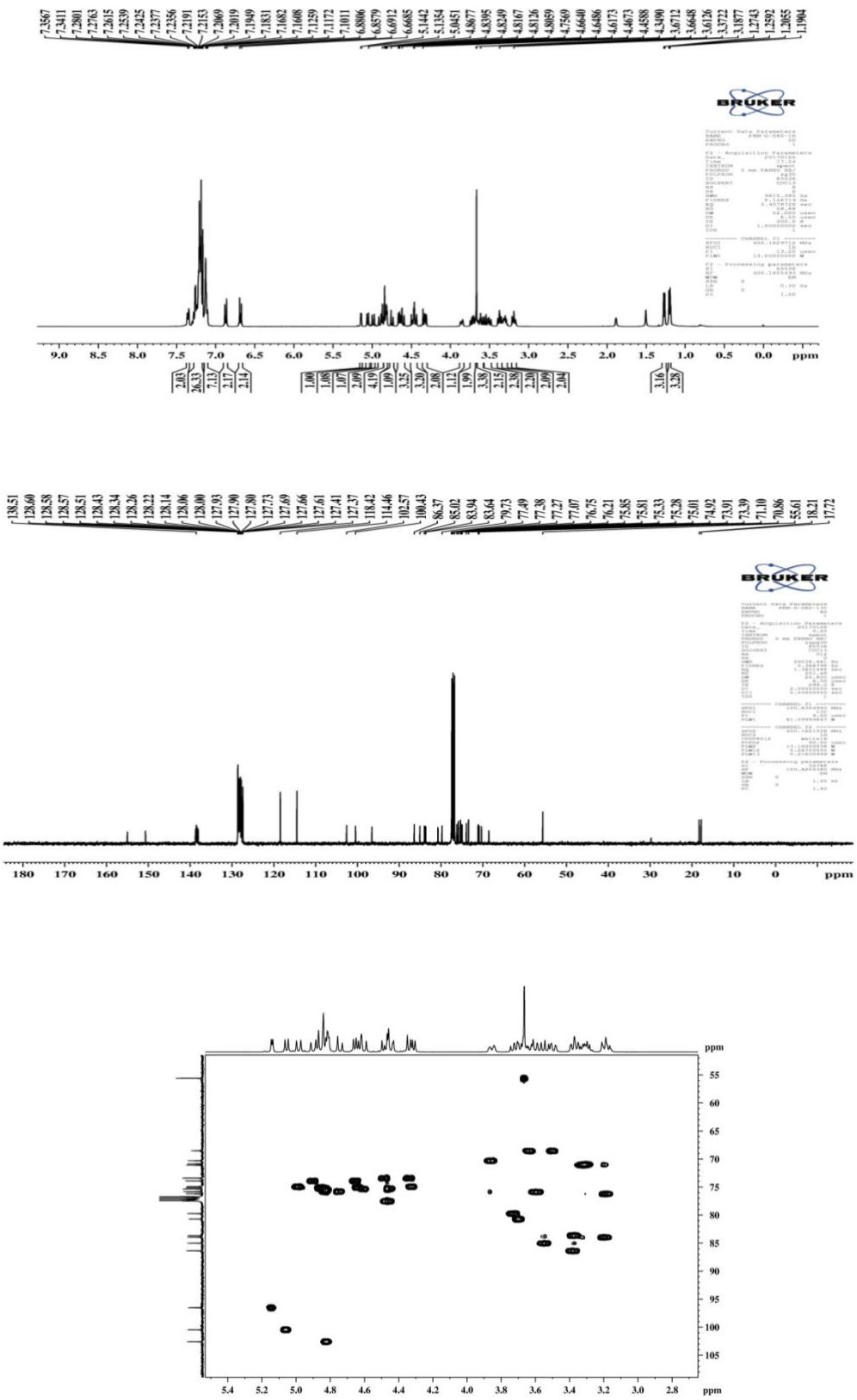
^{1}H, ^{13}C and DEPT 135 NMR spectra of *p*-Methoxyphenyl (2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**16**) ($CDCl_3$).



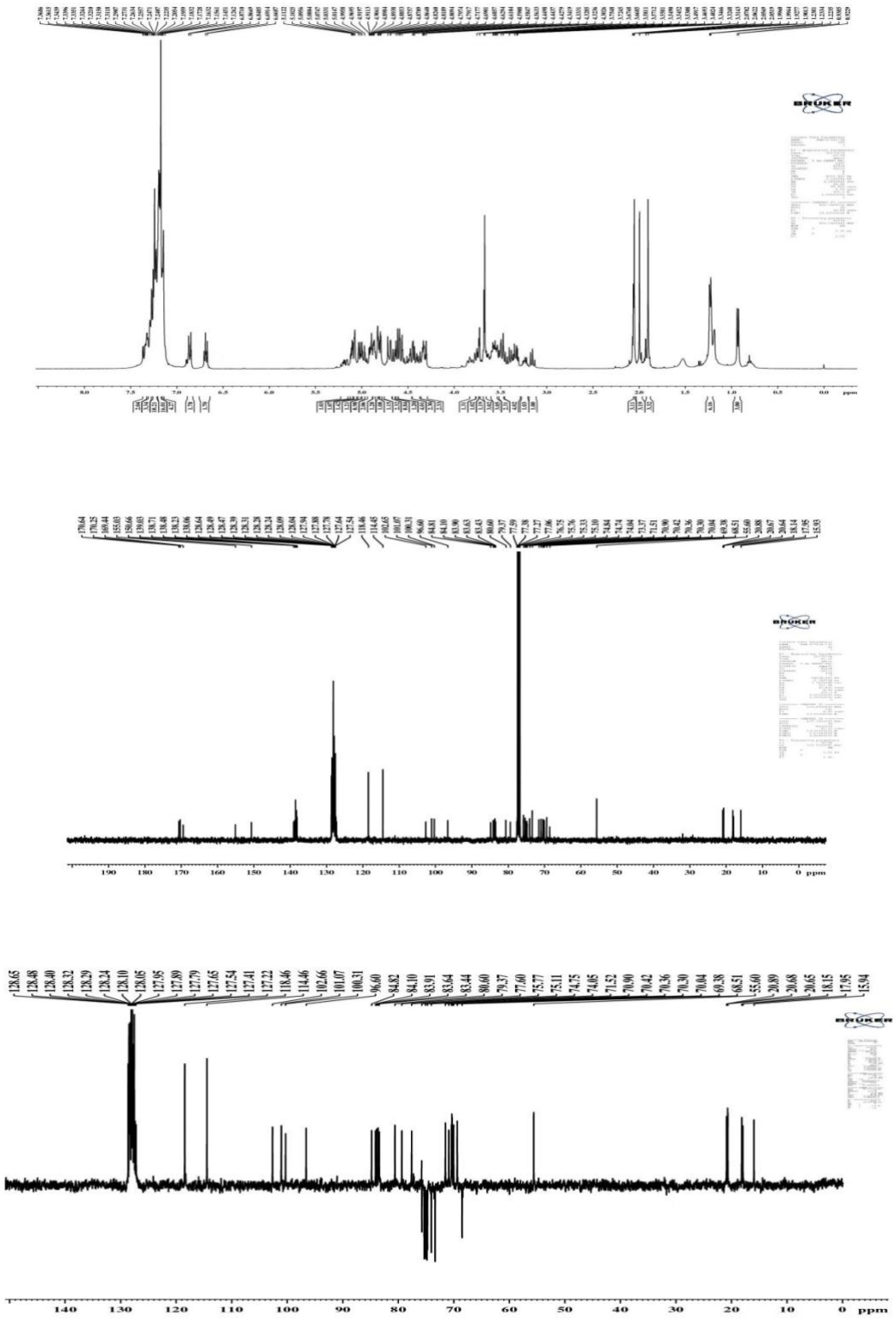
2D COSY and HSQC NMR spectra (selected regions) of *p*-Methoxyphenyl (2,4-di-*O*-acetyl-3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**16**) ($CDCl_3$).



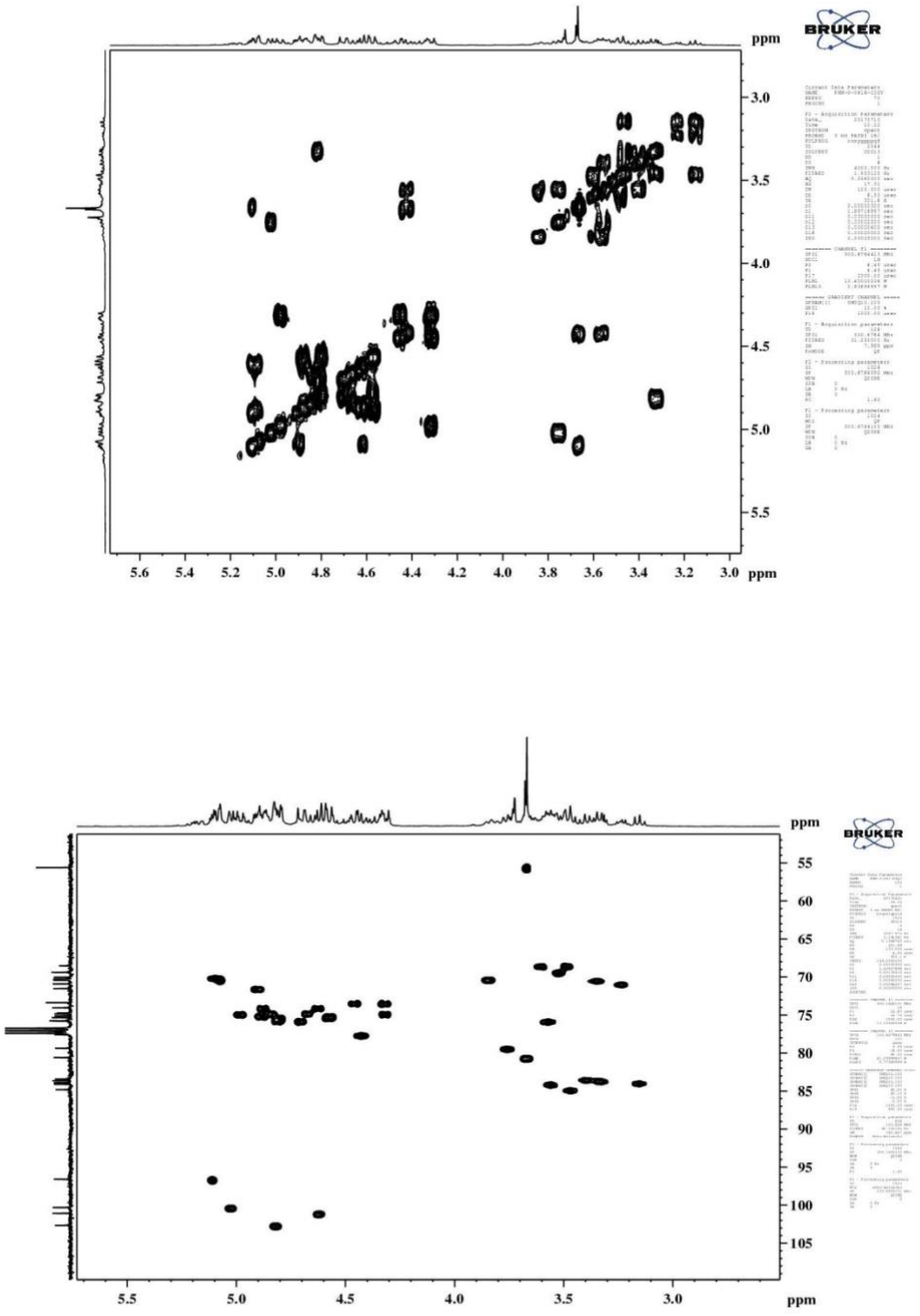
^{1}H, ^{13}C and and HSQC NMR spectra (selected regions) of *p*-Methoxyphenyl (2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-4,6-*O*-benzylidene-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**17**) ($CDCl_3$).



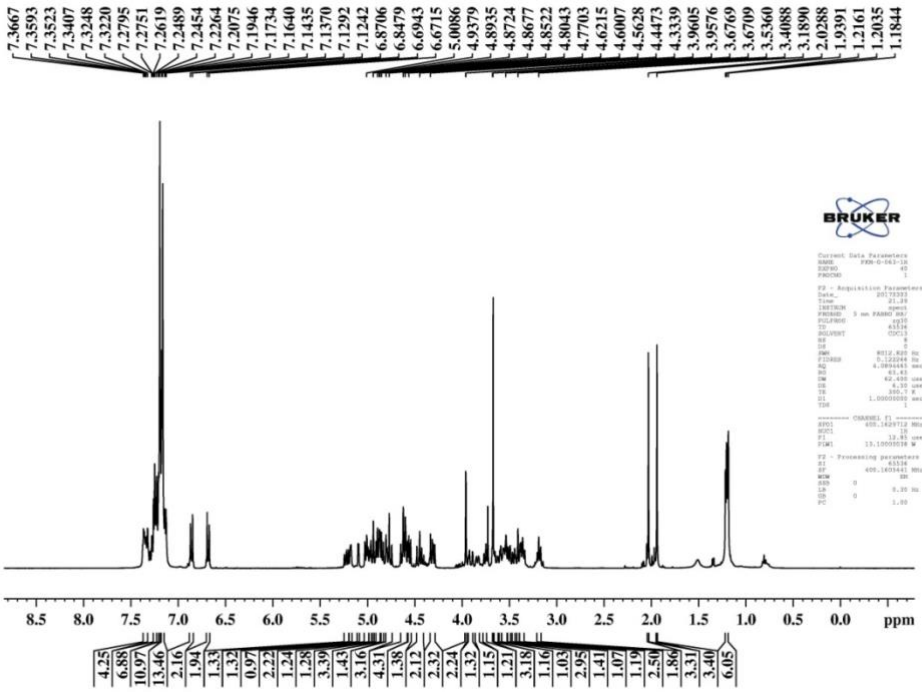
^{1}H, ^{13}C and and HSQC NMR spectra (selected regions) of *p*-Methoxyphenyl (2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**18**) ($CDCl_3$).

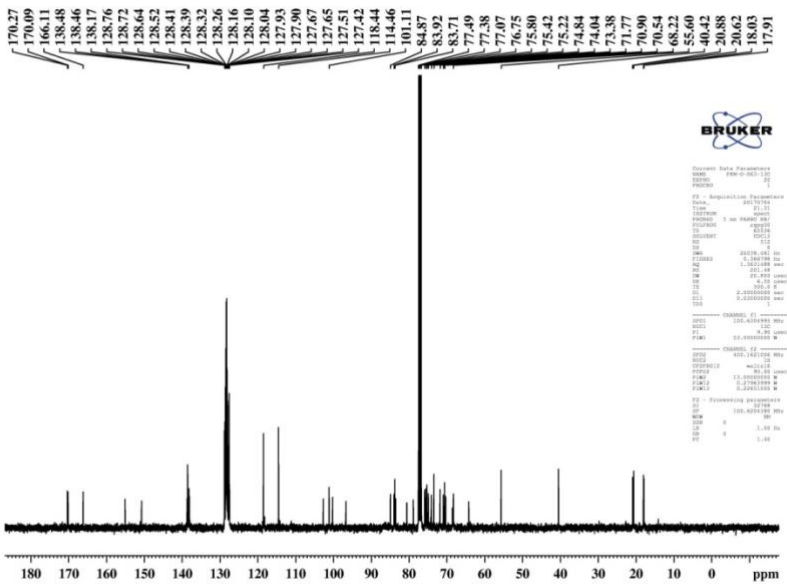


^{1}H, ^{13}C and DEPT 135 NMR spectra of *p*-Methoxyphenyl (2,3,4-tri-*O*-acetyl -6-deoxyβ-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**19**) ($CDCl_3$).

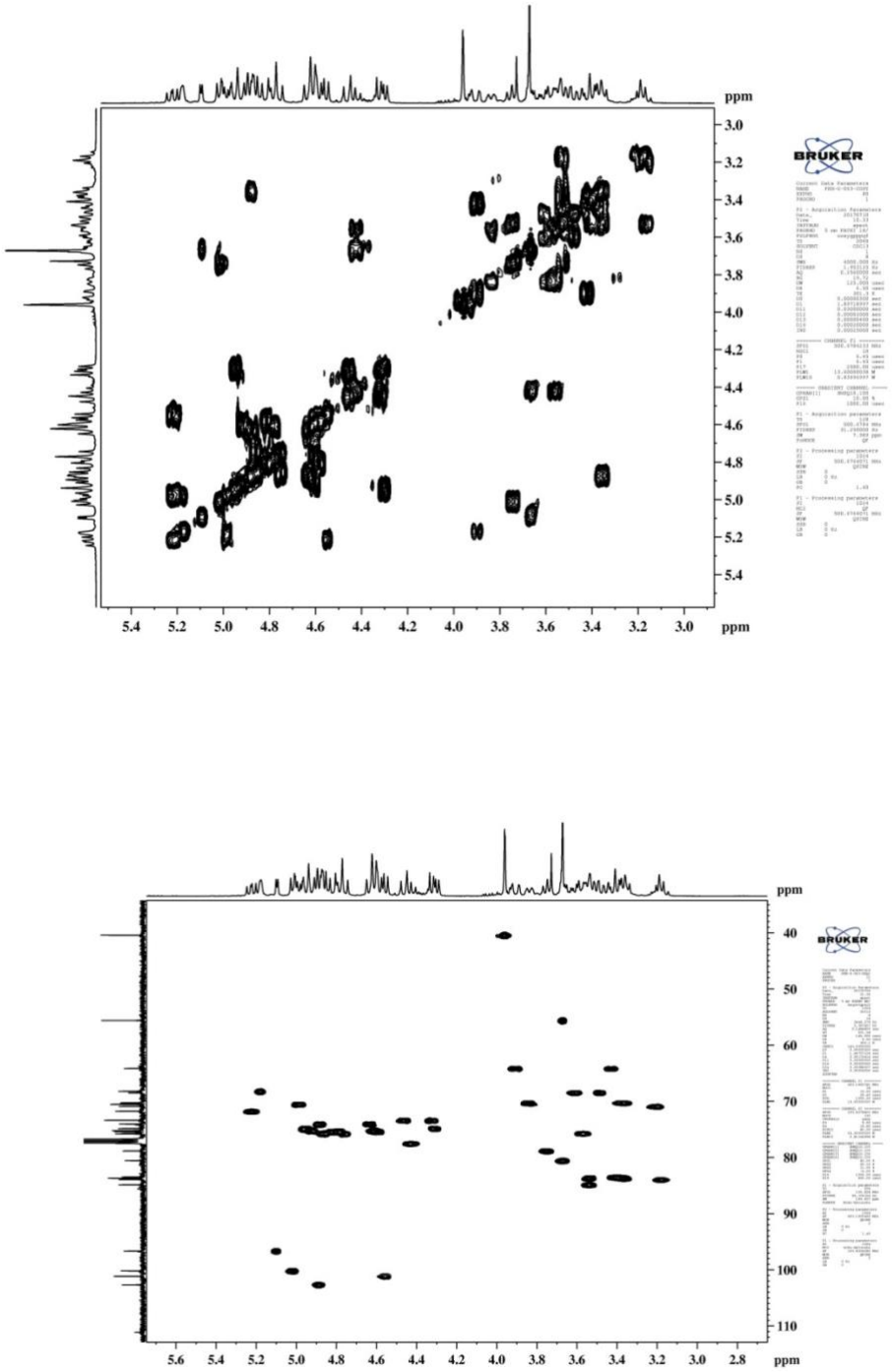


2D COSY and HSQC NMR spectra (selected regions) of *p*-Methoxyphenyl (2,3,4-tri-*O*-acetyl-6-deoxyβ-D-galactopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**19**) ($CDCl_3$).





^{1}H and ^{13}C NMR spectra of *p*-Methoxyphenyl (2-*O*-chloroacetyl-3,4-di-*O*-acetyl-β-L-arabinopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**20**) ($CDCl_3$).



2D COSY and HSQC NMR spectra (selected regions) of *p*-Methoxyphenyl (2-*O*-chloroacetyl-3,4-di-*O*-acetyl-β-L-arabinopyranosyl)-(1→4)-(2,3,4-tri-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→2)-(3-*O*-benzyl-6-deoxy-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**20**) ($CDCl_3$).