# SUPPLEMENTARY MATERIALS

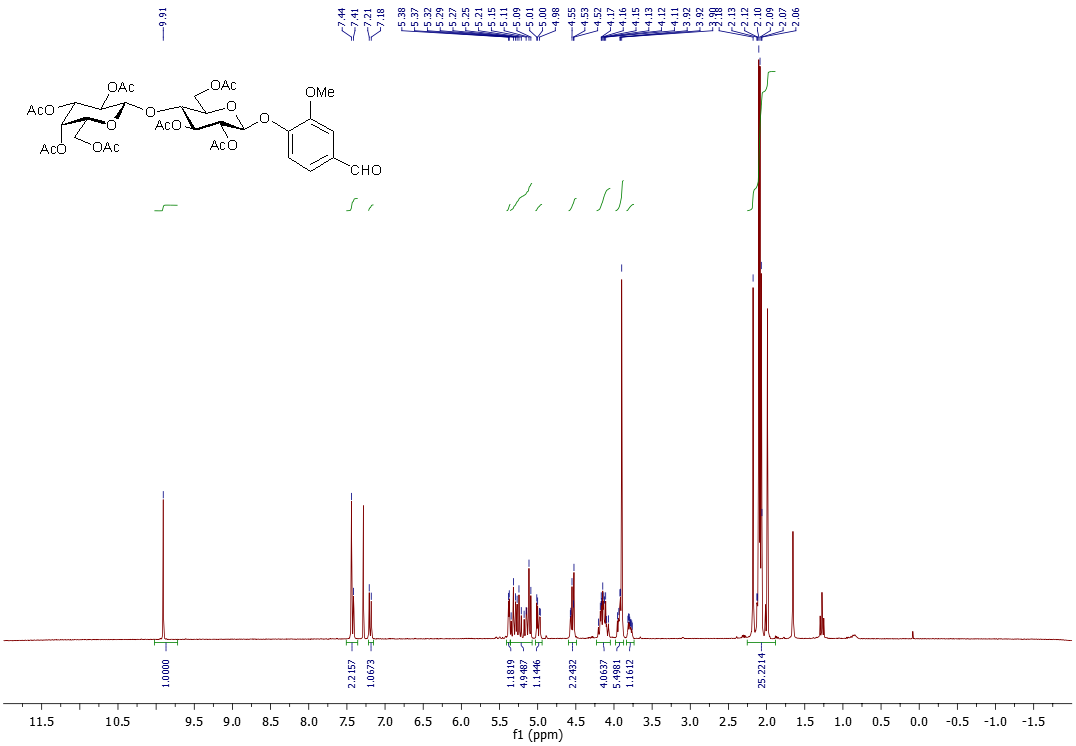
# Synthesis of Galectins Inhibitors by Regioselective 3'-O-Sulfation of Vanillin Lactosides Obtained Under Phase Transfer Catalysis

**Karima Belkhadem[1], Yihong Cao[1] and René Roy[1,2,*]**

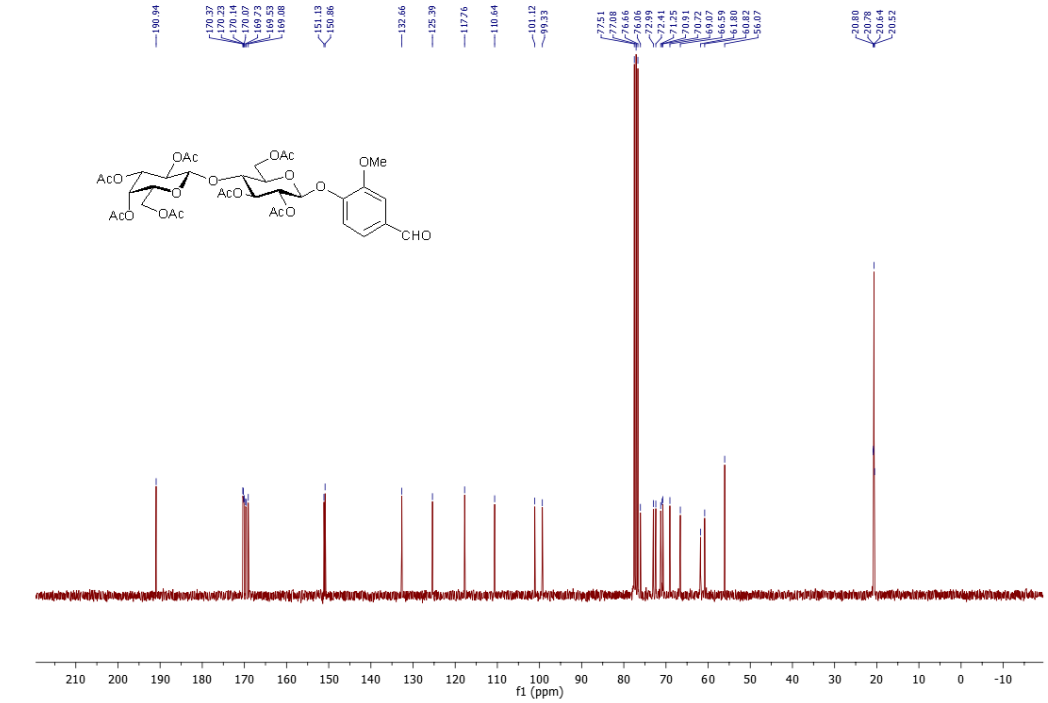
[1] Department of Chemistry, University of Québec a Montréal, P.O. Box 8888, Succ. Centre-Ville, Montréal, Québec H3C 3P8, Canada, E-mail : roy.rene@uqam.ca

[2] INRS-Institut Armand-Frappier, Université du Québec, 531 boul. des Prairies, Laval, Québec, H7V 1B7, Canada

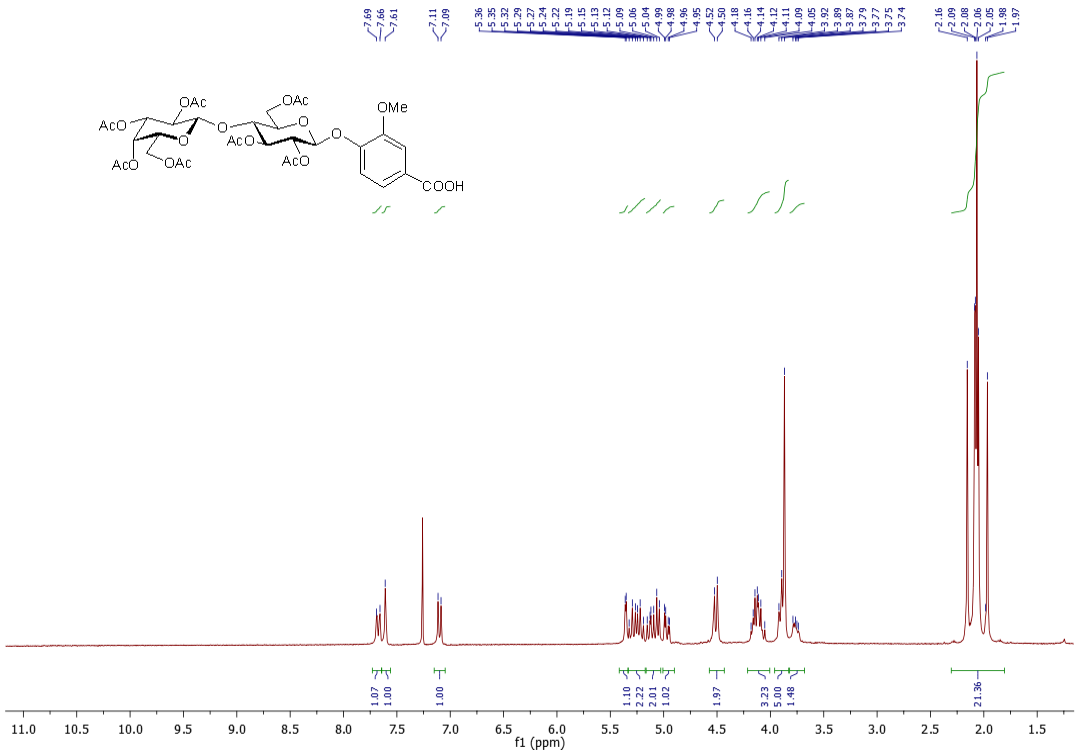
* Correspondence: roy.rene@uqam.ca; Tel.: +1 514-987-3000, ext. 2546



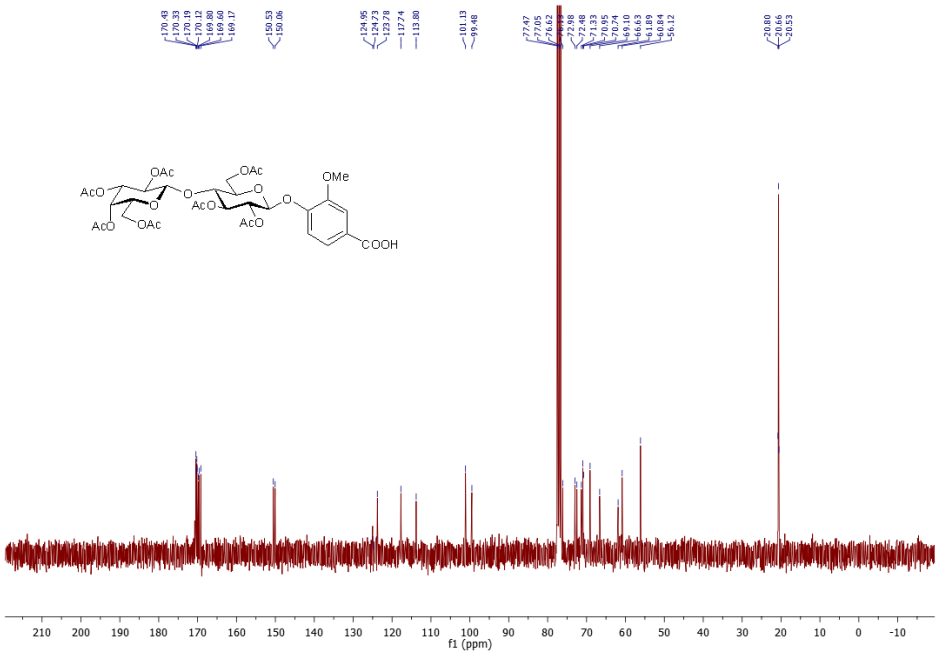

$^{1}$H NMR spectrum (300 MHz, CDCl3) of compound **5**



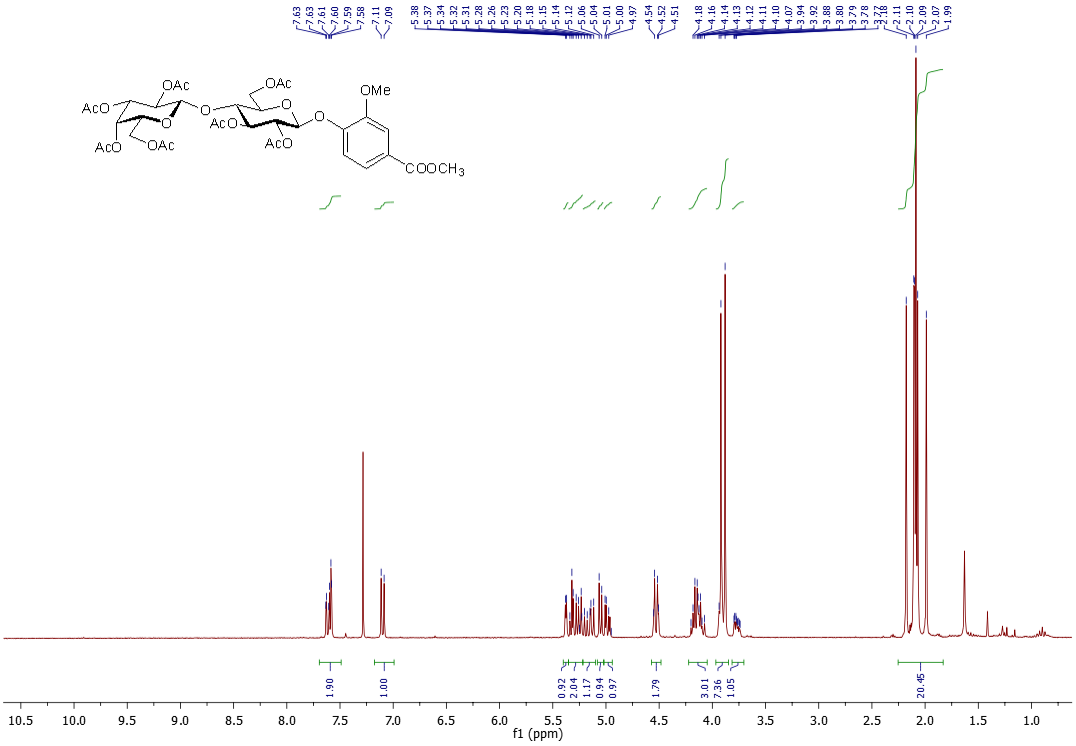

$^{13}$C NMR spectrum (75 MHz, CDCL3) of compound **5**



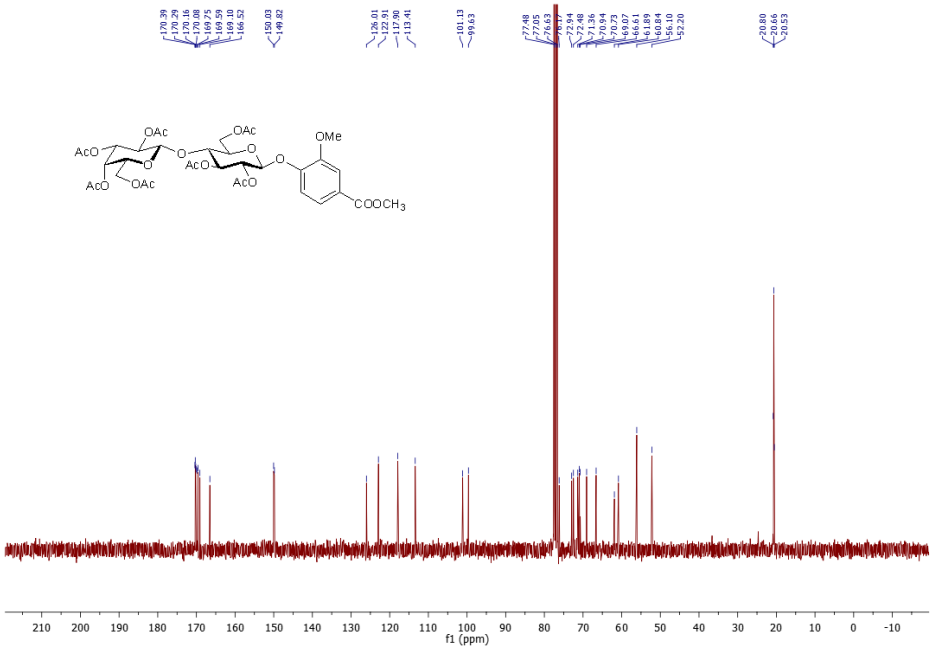

$^{1}$H NMR spectrum (300 MHz, CDCl3) of compound **6**



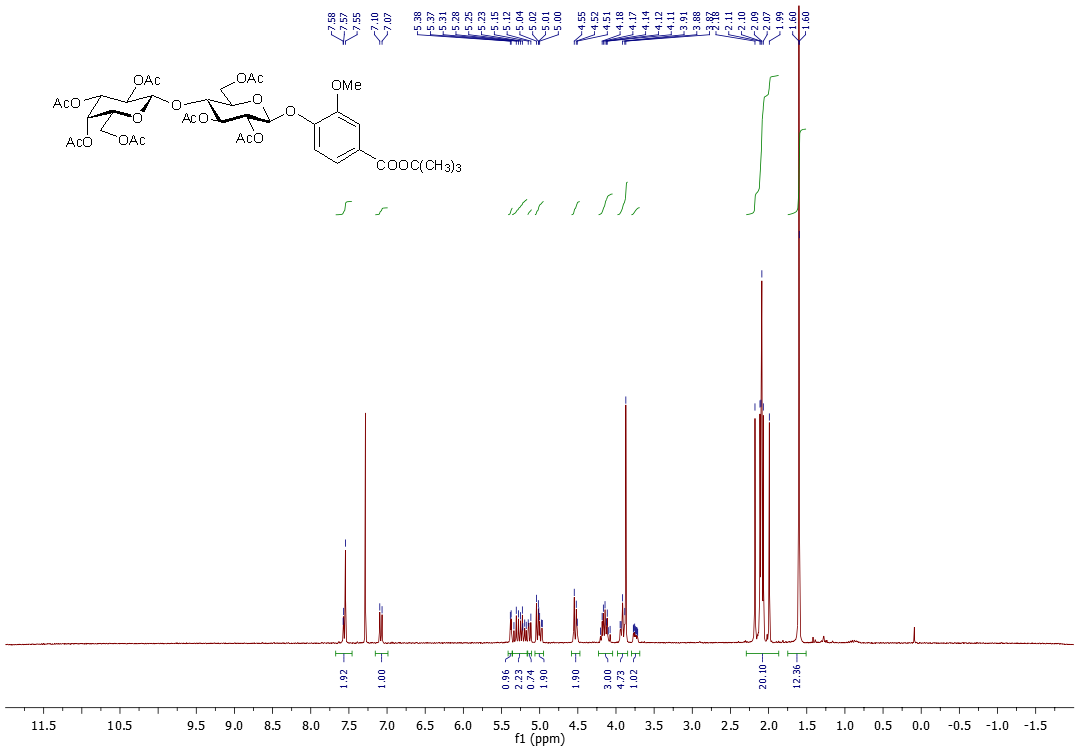

$^{13}$C NMR spectrum (75 MHz, CDCL3) of compound **6.**



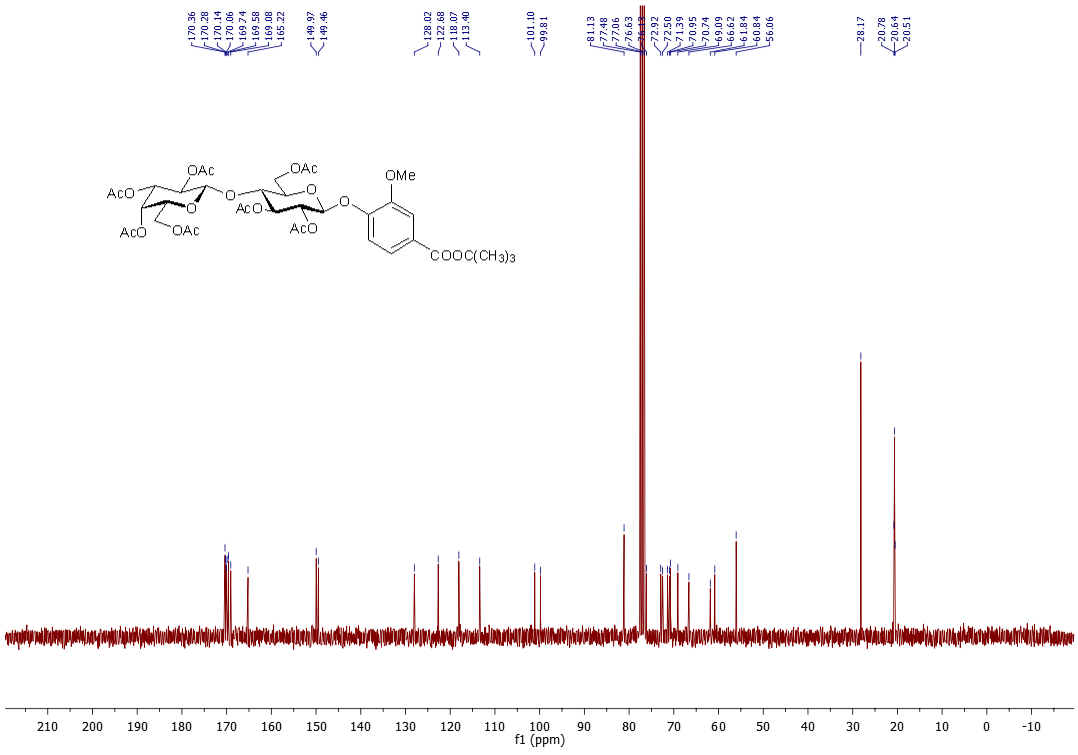

$^{1}$H NMR spectrum (300 MHz, CDCl3) of compound **7**



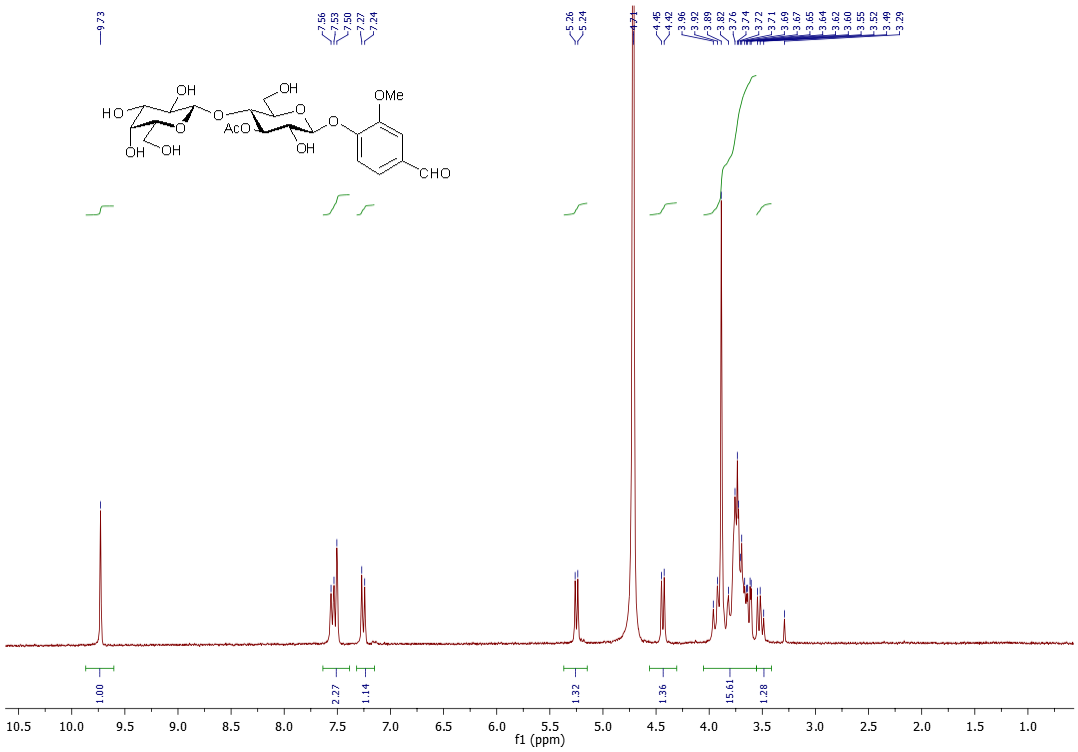

$^{13}$C NMR spectrum (75 MHz, CDCL3) of compound **7**.



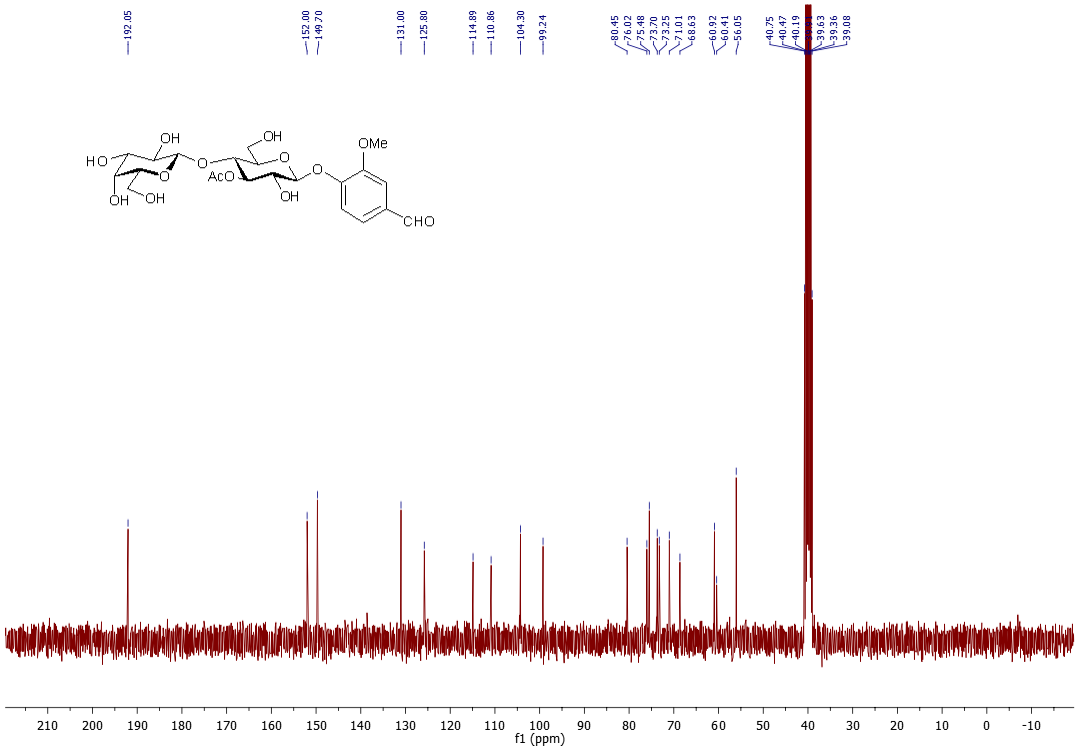

$^{1}$H NMR spectrum (300 MHz, CDCl3) of compound **8**



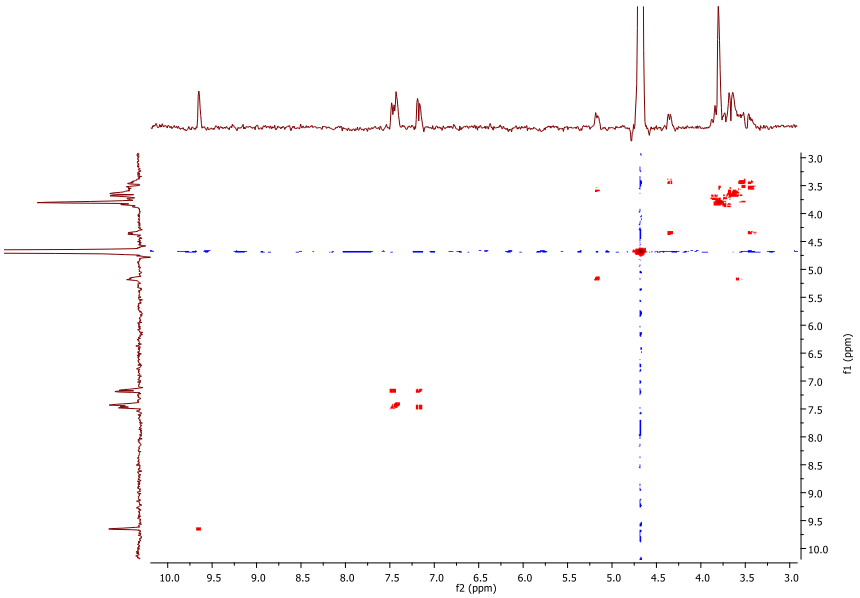

$^{13}$C NMR spectrum (75 MHz, CDCL3) of compound **8**



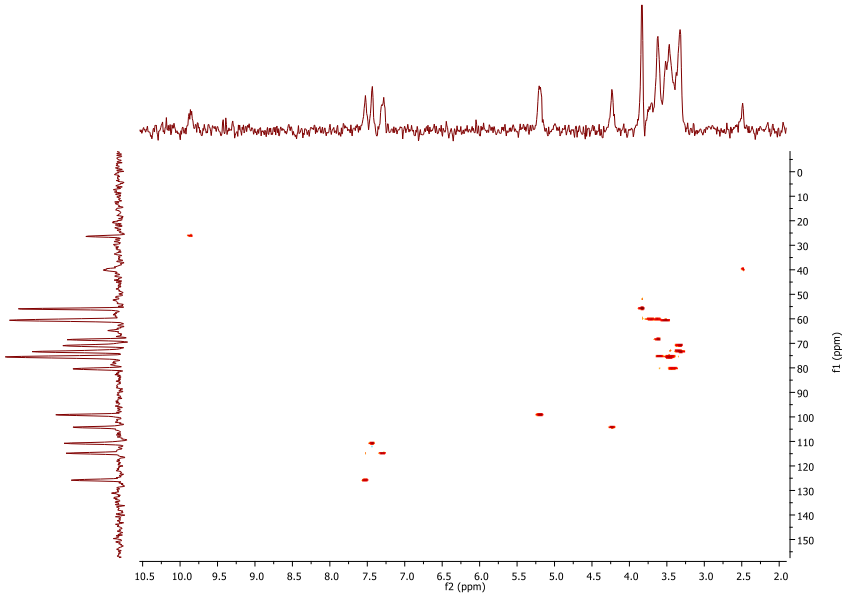

1H NMR spectrum (300 MHz, D2O) of compound **9**.



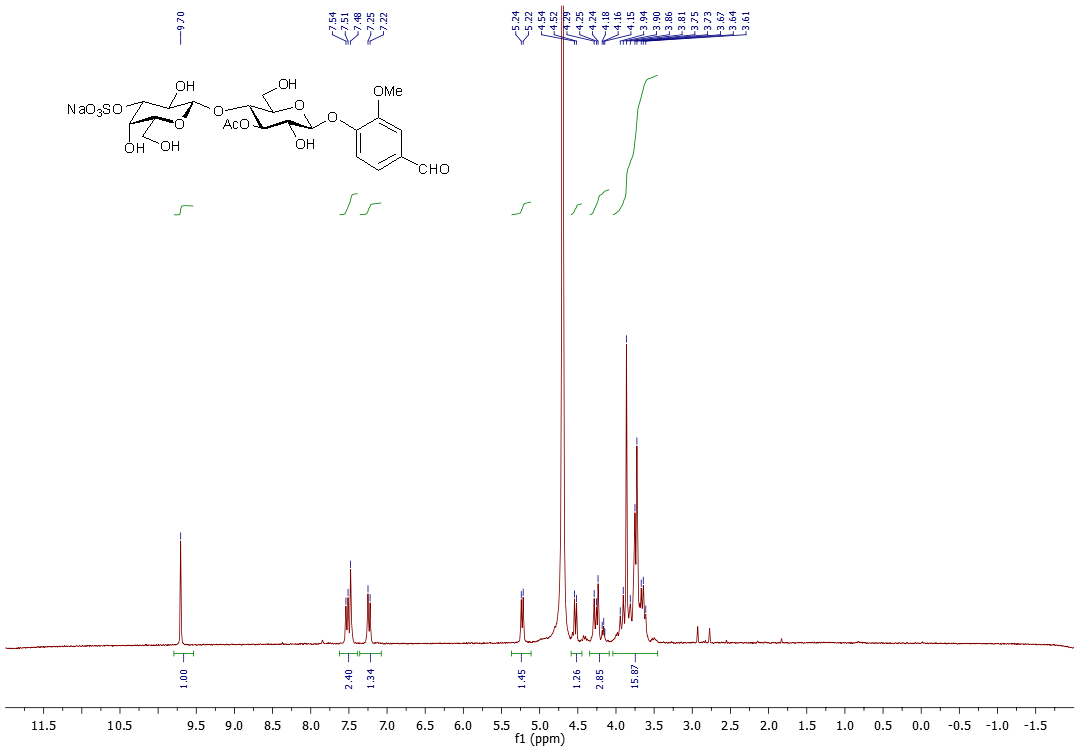

$^{13}$C NMR spectrum (75MHz, DMSO-d6) of compound **9**.



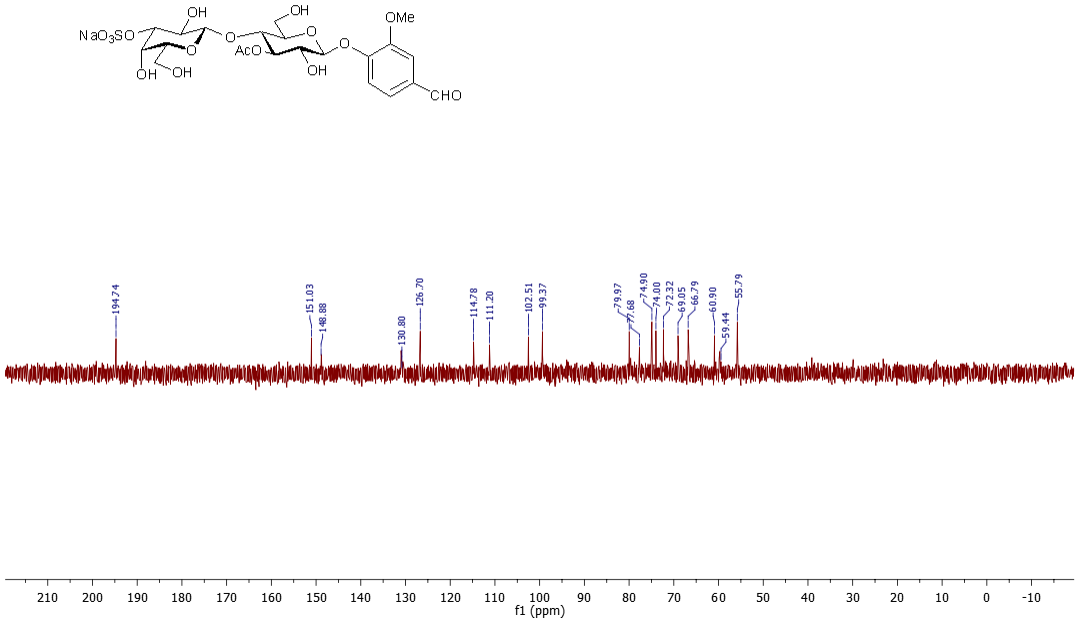

COSY NMR spectrum (300 MHz, D2O) of compound **9**.



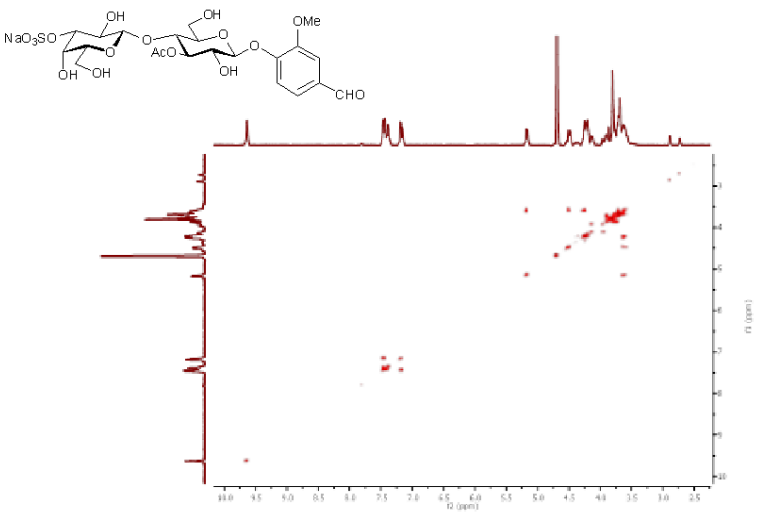

HSQC NMR spectrum (75 MHz, DMSO-d6) of compound **9**.



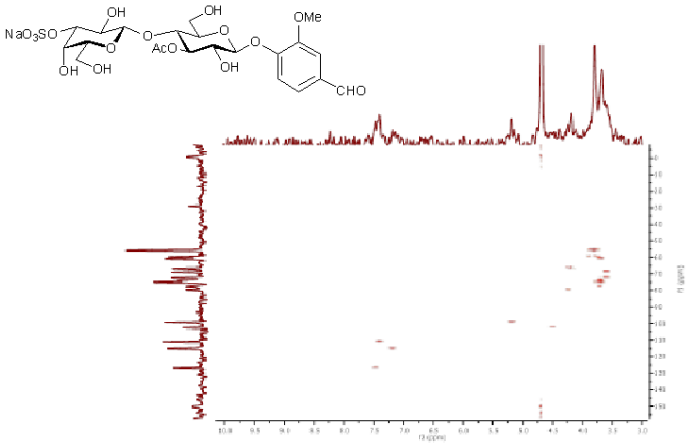

1H NMR spectrum (300 MHz, $D_2O$) of compound **10**.



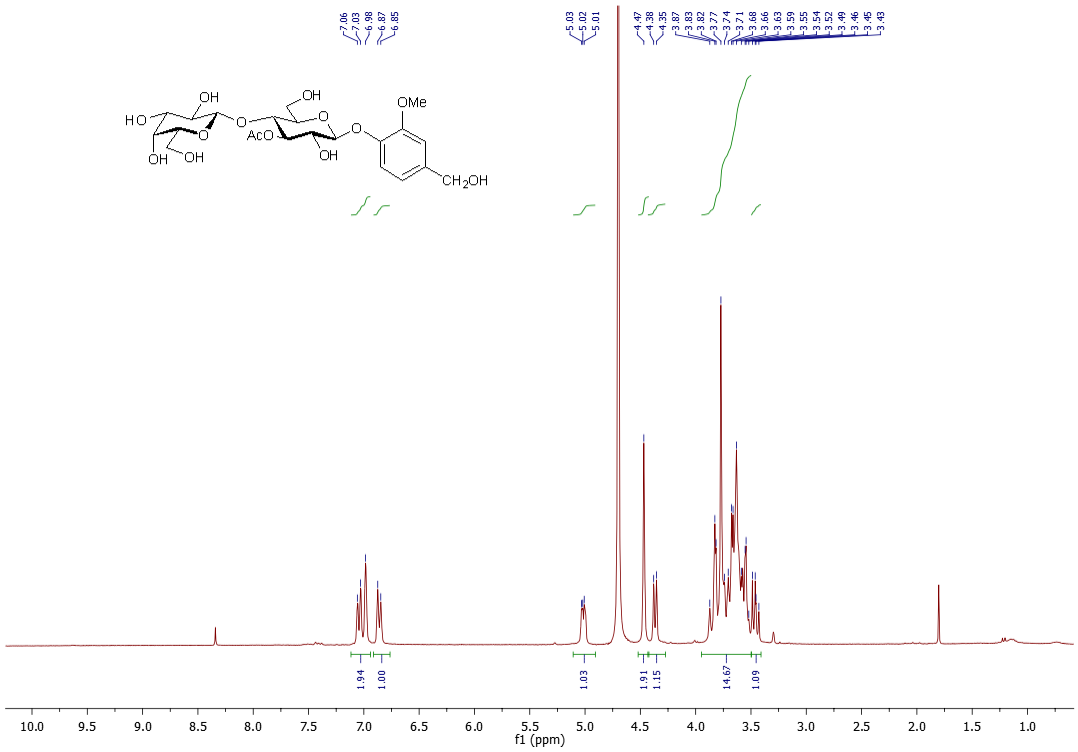

$^{13}C$ NMR spectrum (75MHz, $D_2O$) of compound **10**.



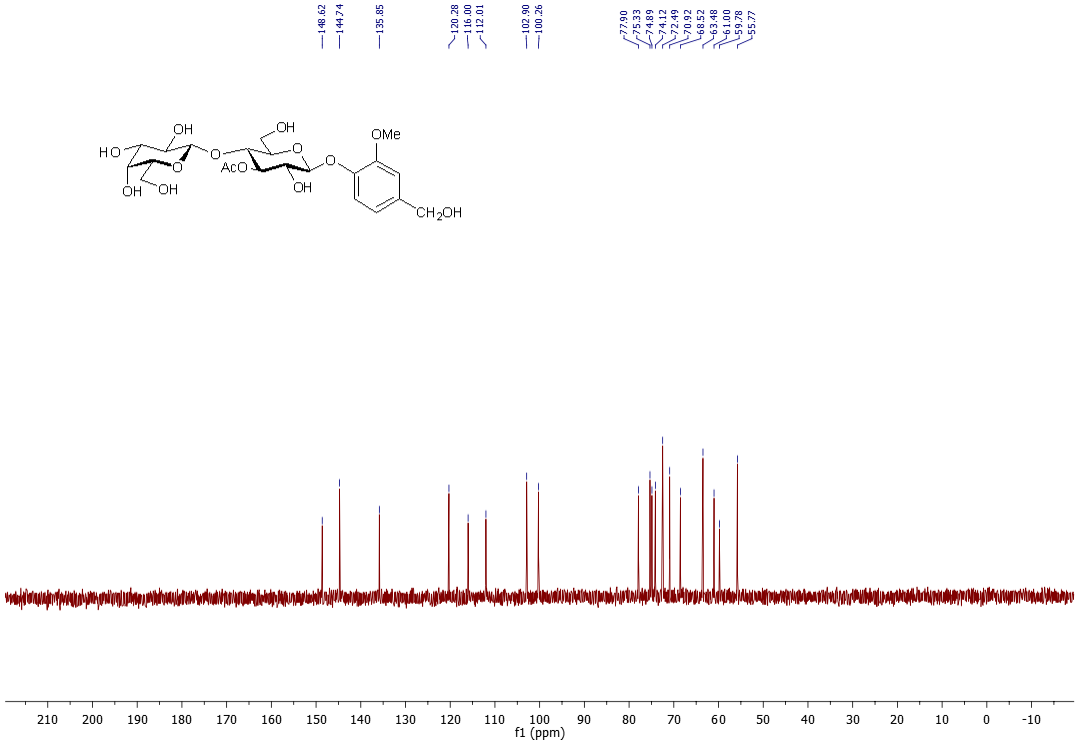

COSY NMR spectrum (300 MHz, $D_2O$) of compound **10**.



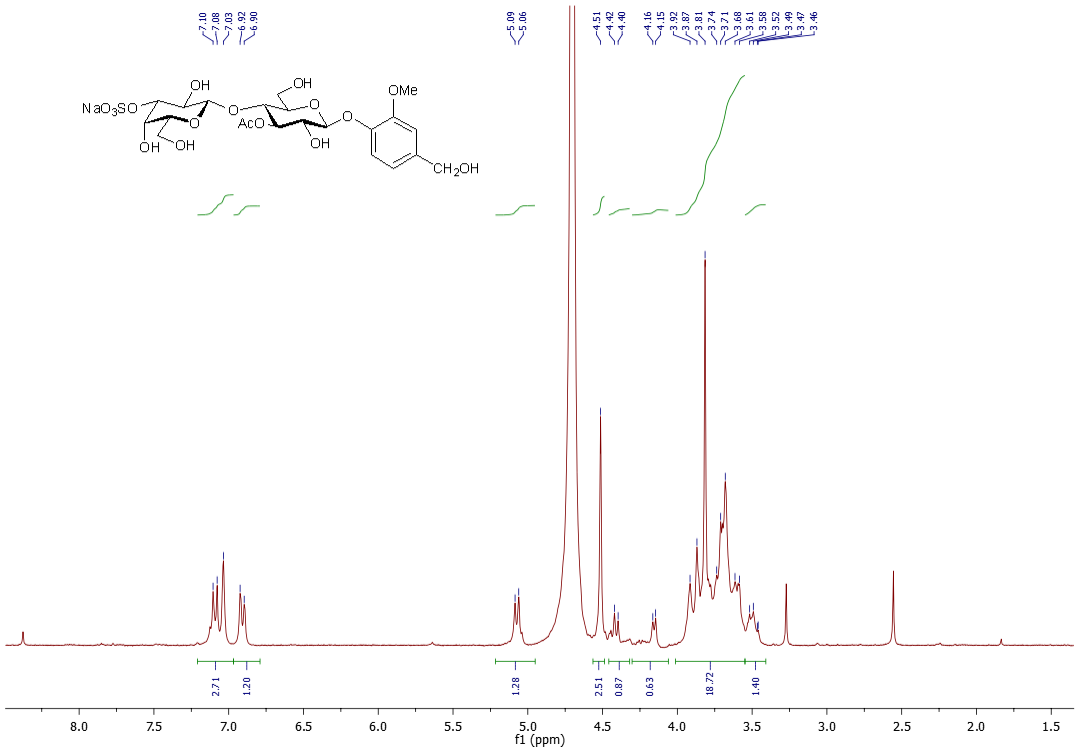

HSQC NMR spectrum (75 MHz, $D_2O$) of compound **10**.



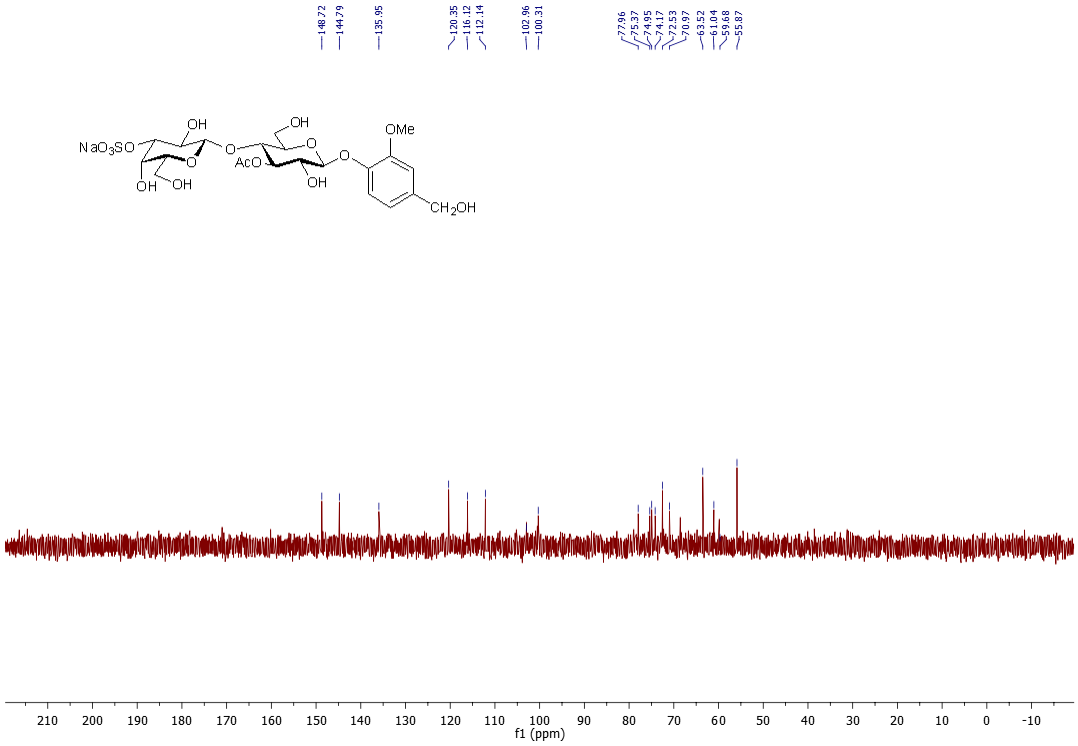

$^{1}$H NMR spectrum (300 MHz, $D_2O$) of compound **11**.



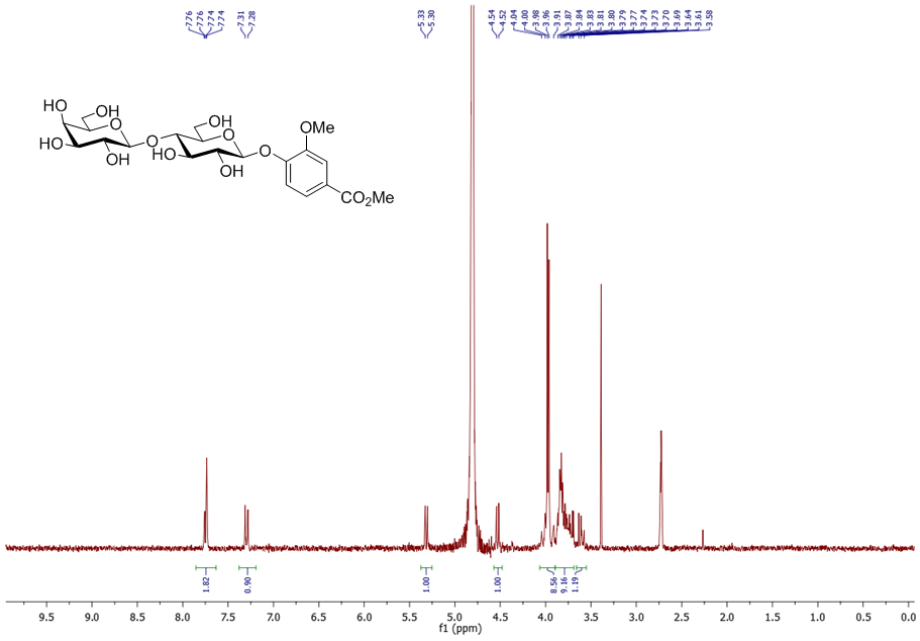

$^{13}$C NMR spectrum (75 MHz, $D_2O$) of compound **11**.



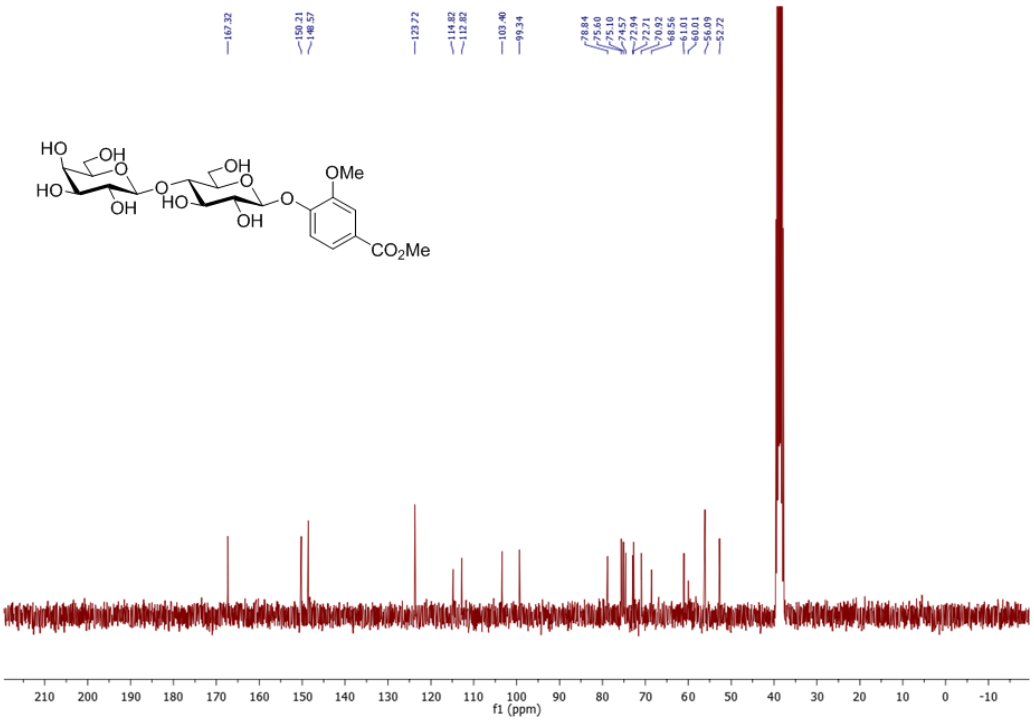

$^{1}$H NMR spectrum (300 MHz, $D_2O$) of compound **12**.



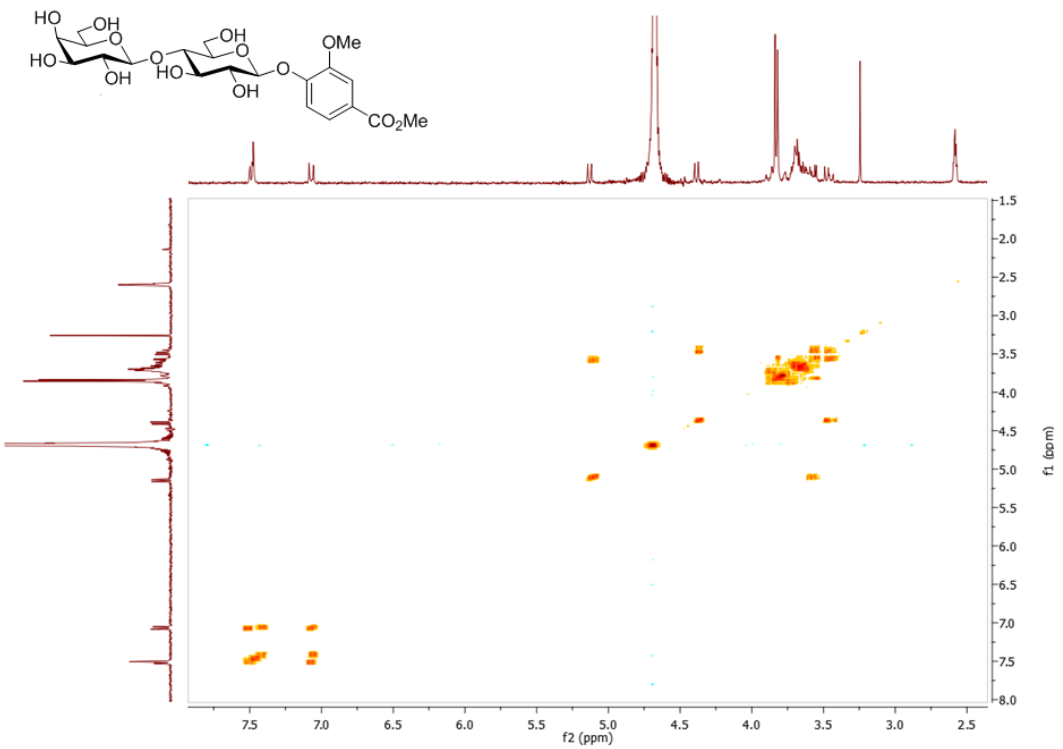

$^{13}$C NMR spectrum (75 MHz, $D_2O$) of compound **12**.



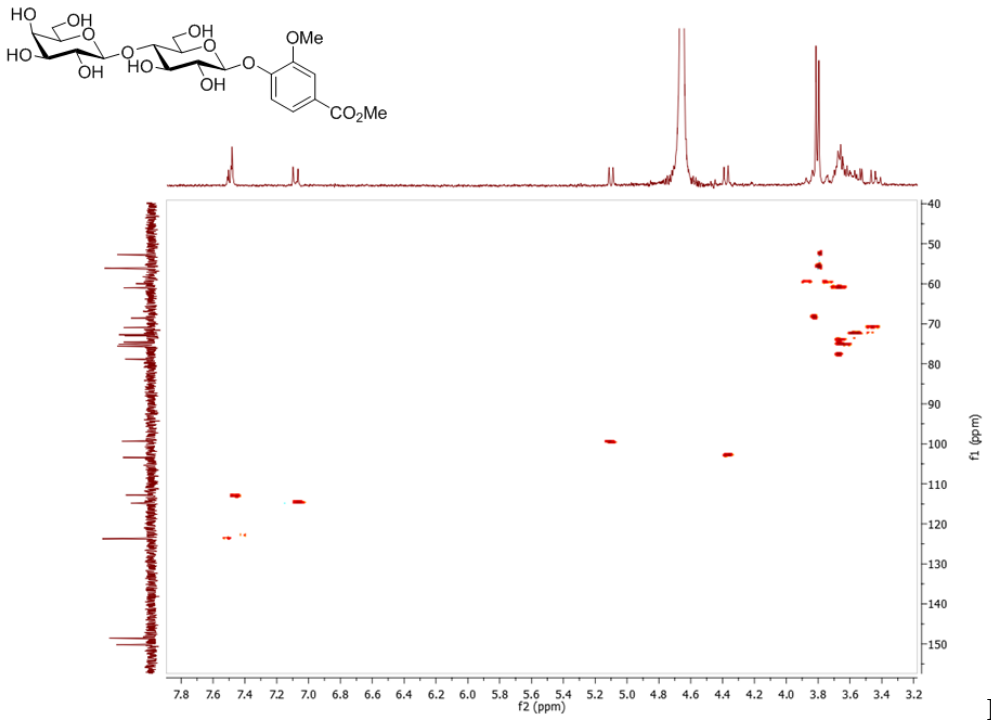

$^{1}$H NMR spectrum (300 MHz, $D_2O$+DMSO-$d_6$) of compound **13**



$^{13}$C NMR spectrum (75 MHz, $D_2O$+DMSO-$d_6$) of compound **13**

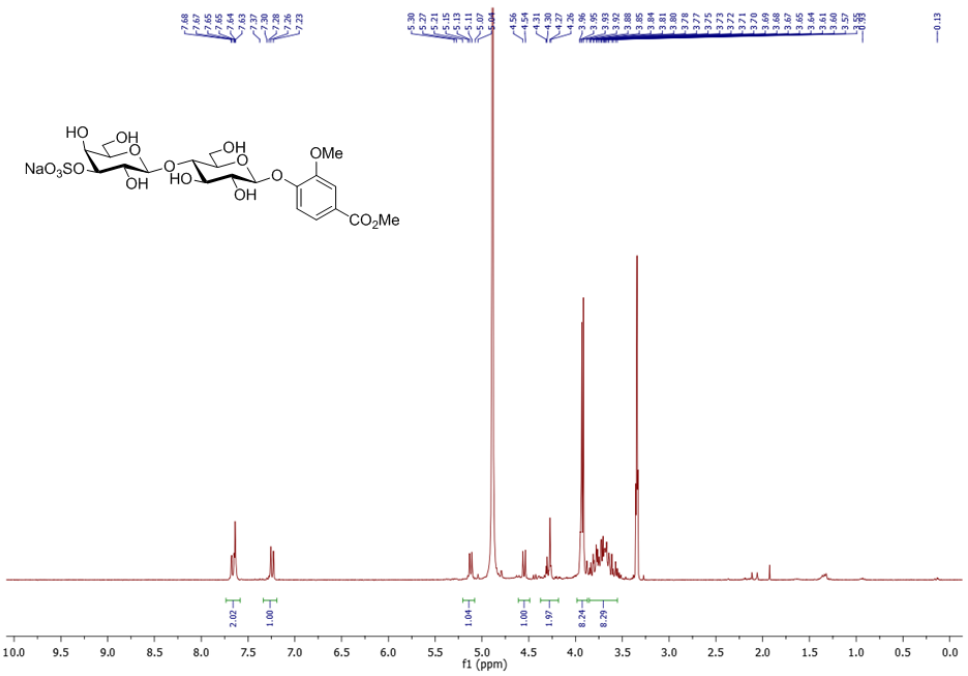



COSY NMR spectrum ($D_2O$+DMSO-$d_6$) of compound **13**

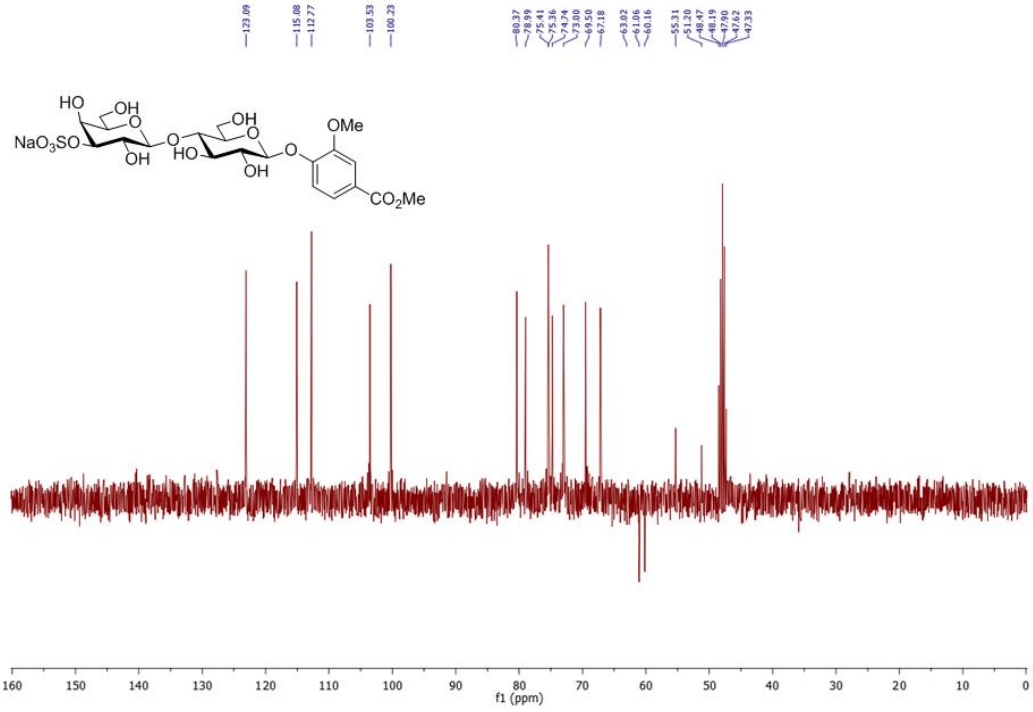



HSQC

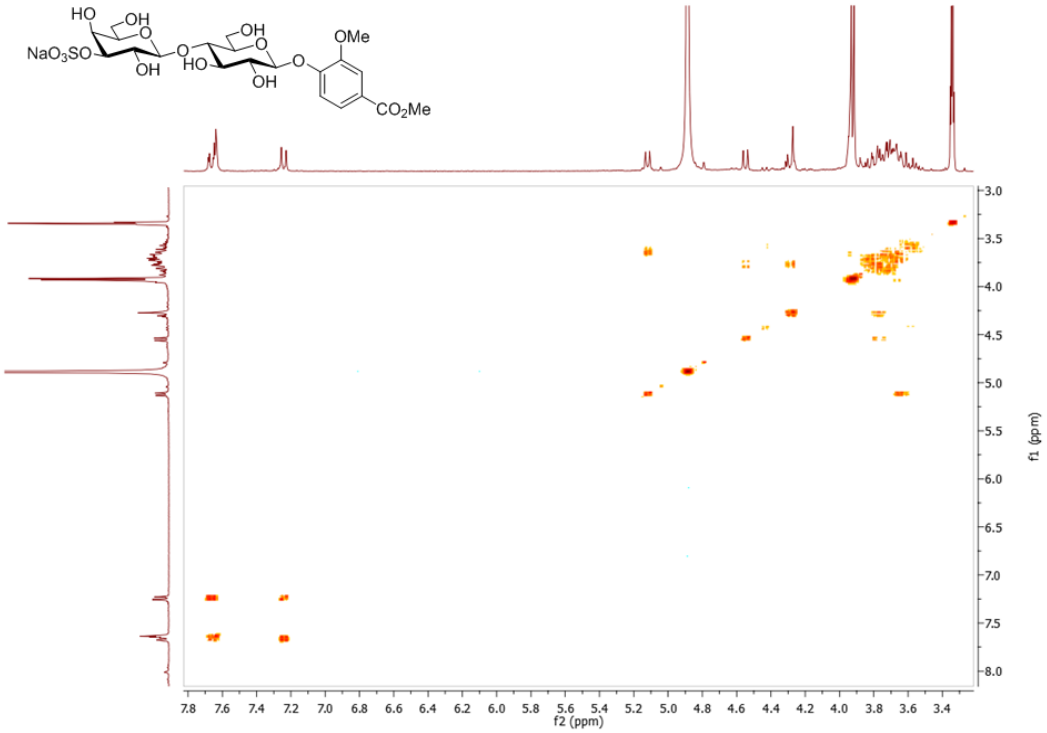
HSQC NMR spectrum ($D_2O$+DMSO-$d_6$) of compound **13**



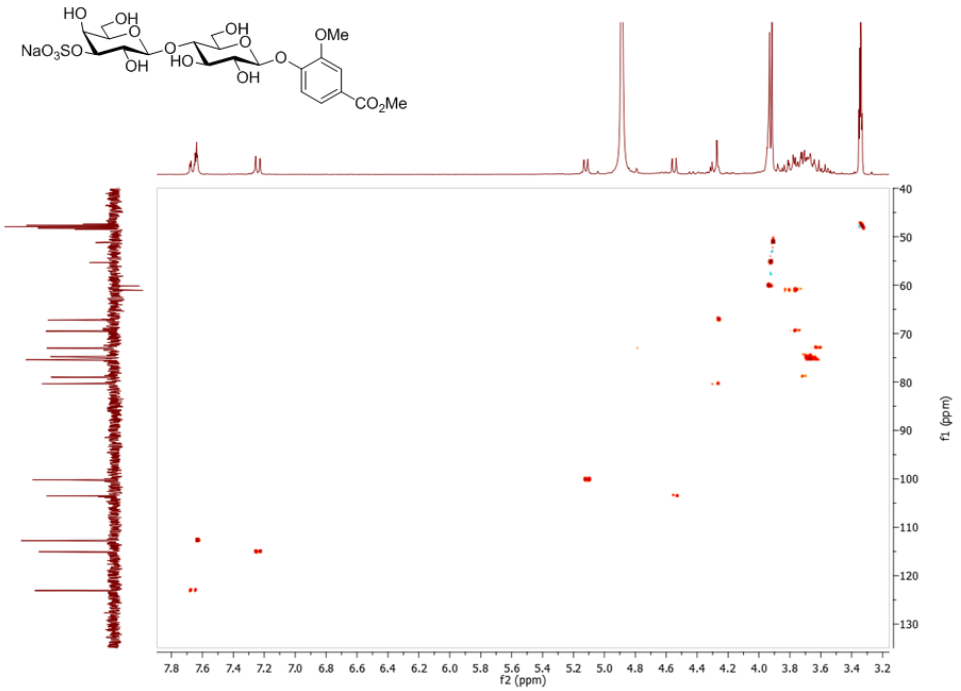

$^{1}$H NMR spectrum (300 MHz, MeOD) of compound **14**



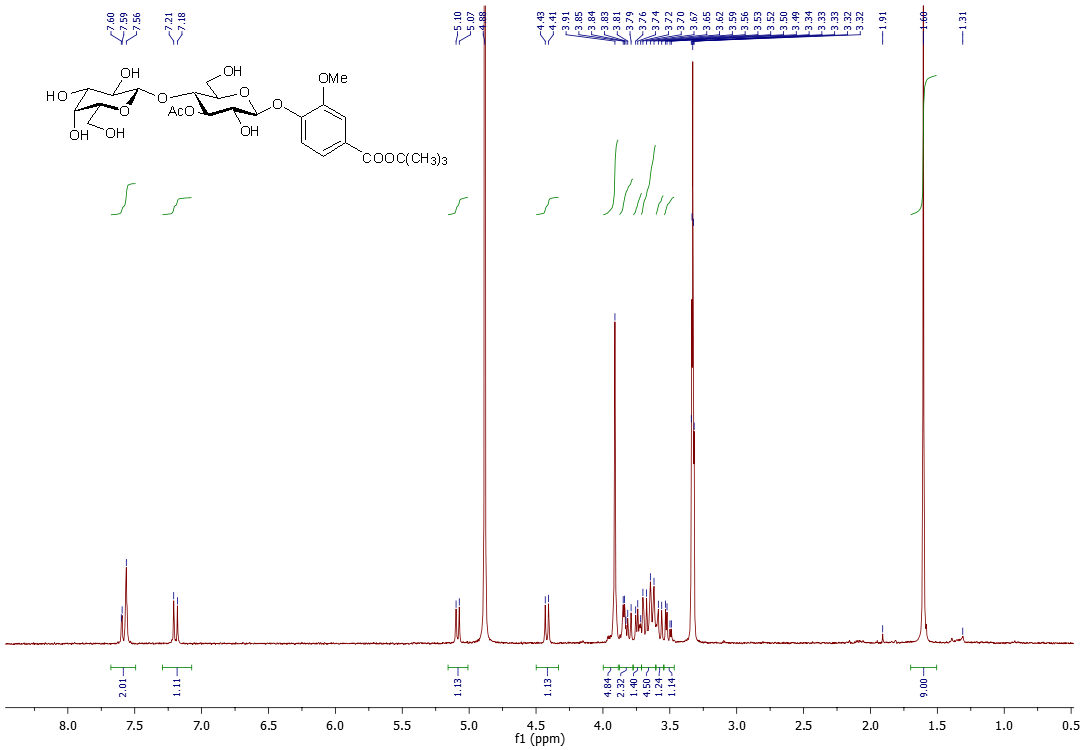
$^{13}$C Dept135 NMR spectrum (75 MHz, MeOD) of compound **14**



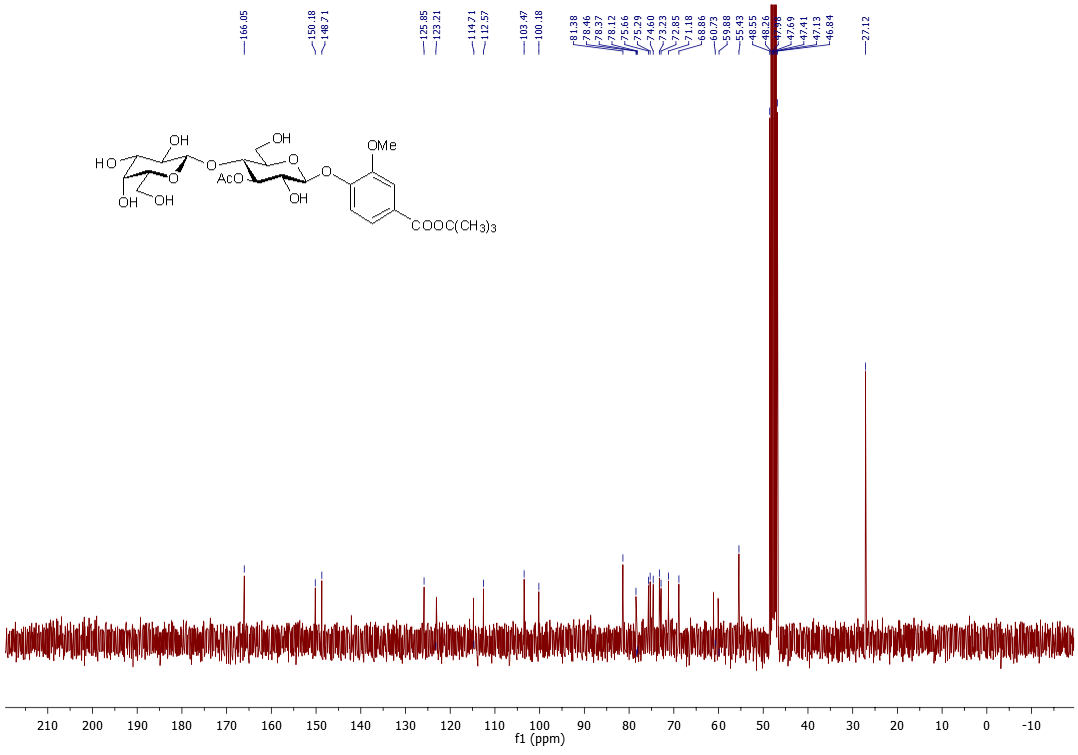

COSY NMR spectrum (MeOD) of compound **14**



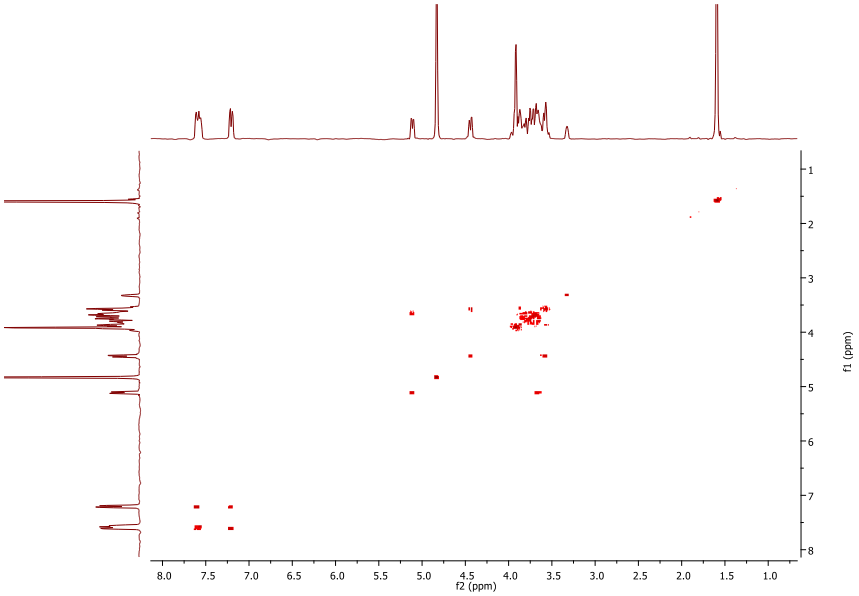

HSQC NMR spectrum (MeOD) of compound **14**



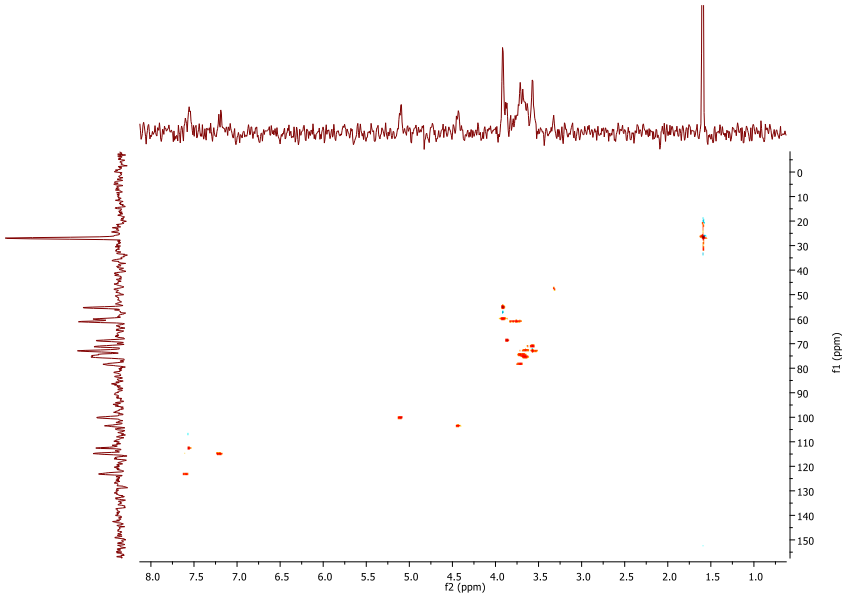

$^{1}$H NMR spectrum (300 MHz, $D_2O$) of compound **15**.



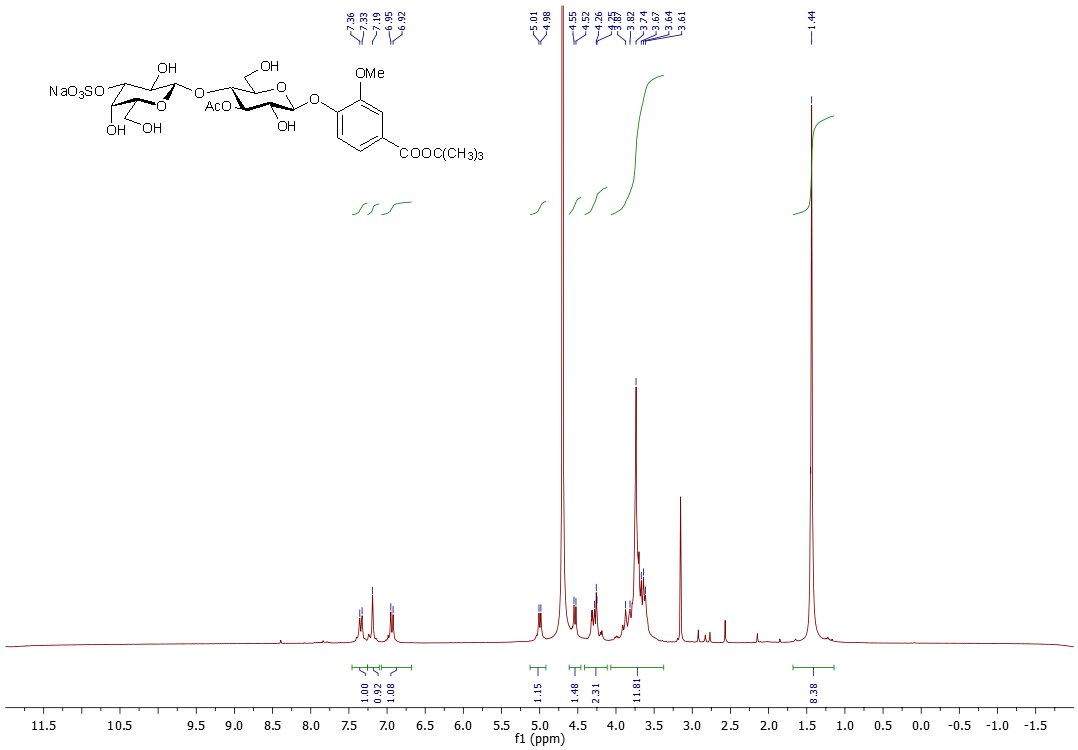

$^{13}$C NMR spectrum (75 MHz, $CD_3OD$-$d_4$) of compound **15**



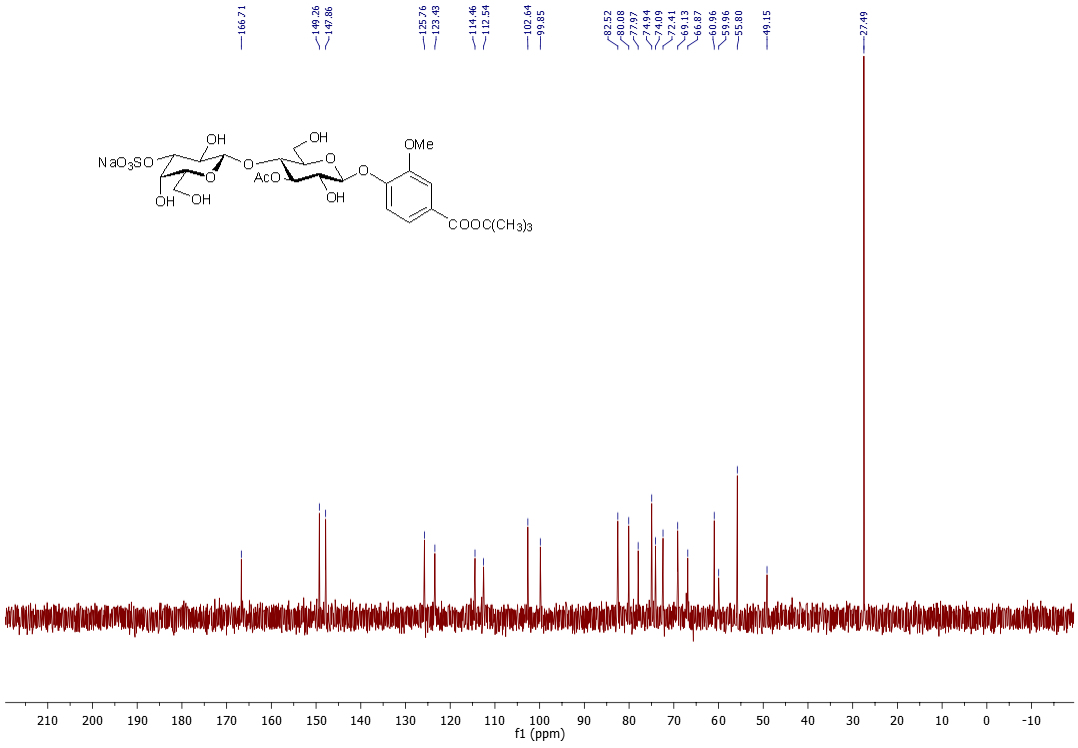

COSY NMR spectrum (300 MHz, $D_2O$) of compound **15**.



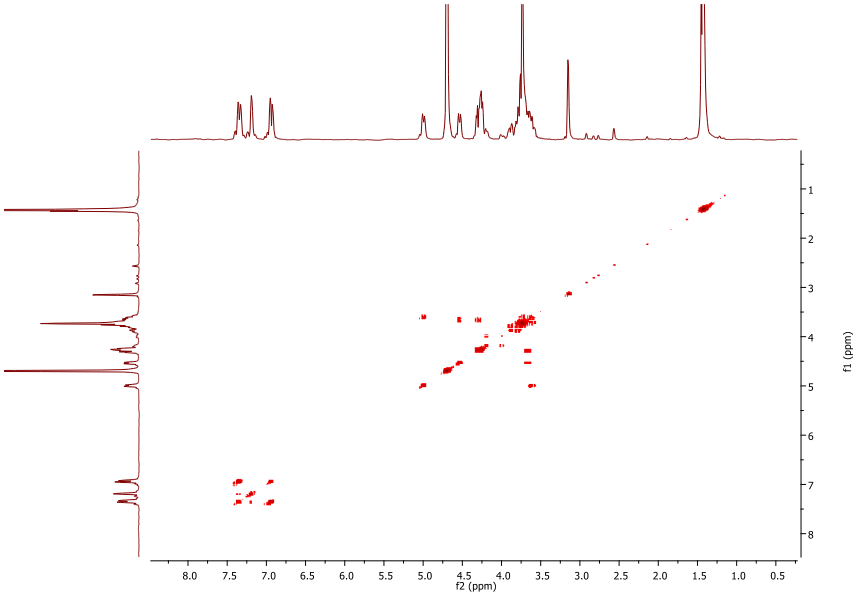

HSQC NMR spectrum (75 MHz, $D_2O$) of compound **15**.



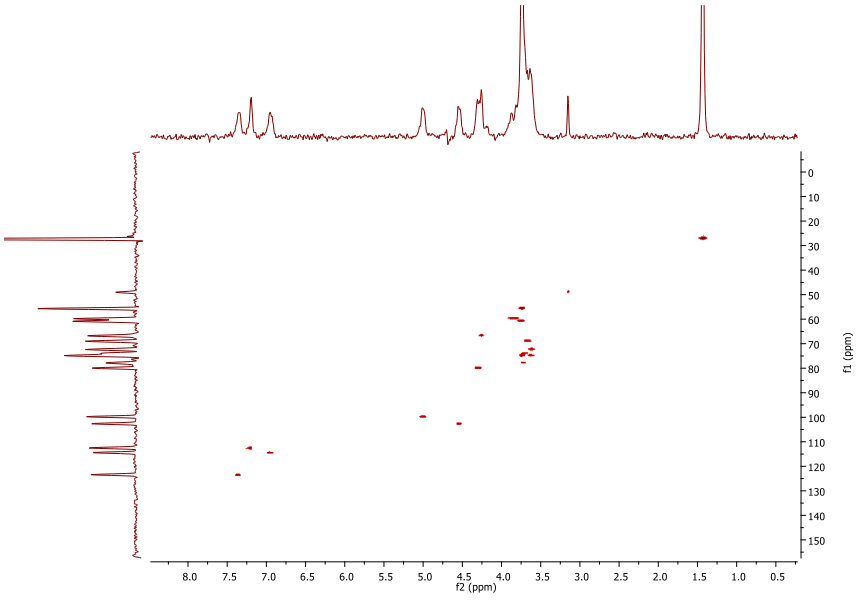

$^{1}$H NMR spectrum (300 MHz, $CD_3OD$-$d_4$) of compound **16**.



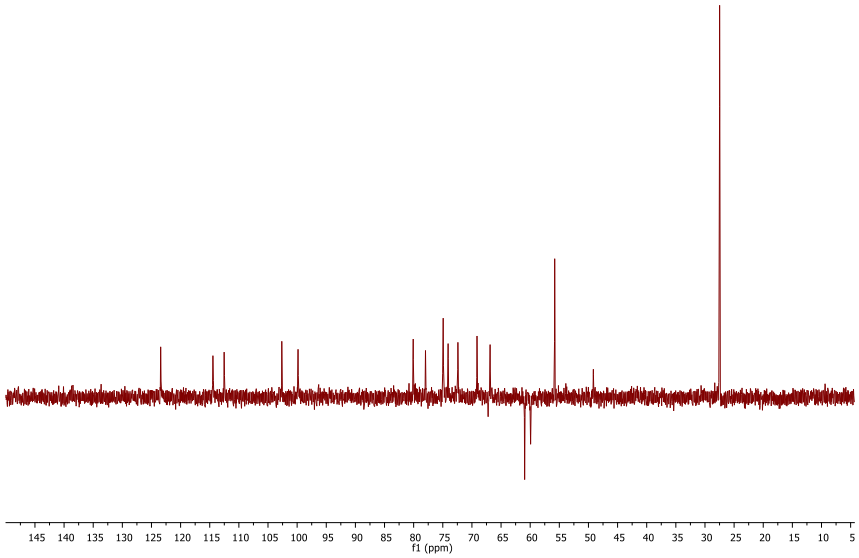

$^{13}$C NMR spectrum (75 MHz, $CD_3OD$-$d_4$) of compound **16**



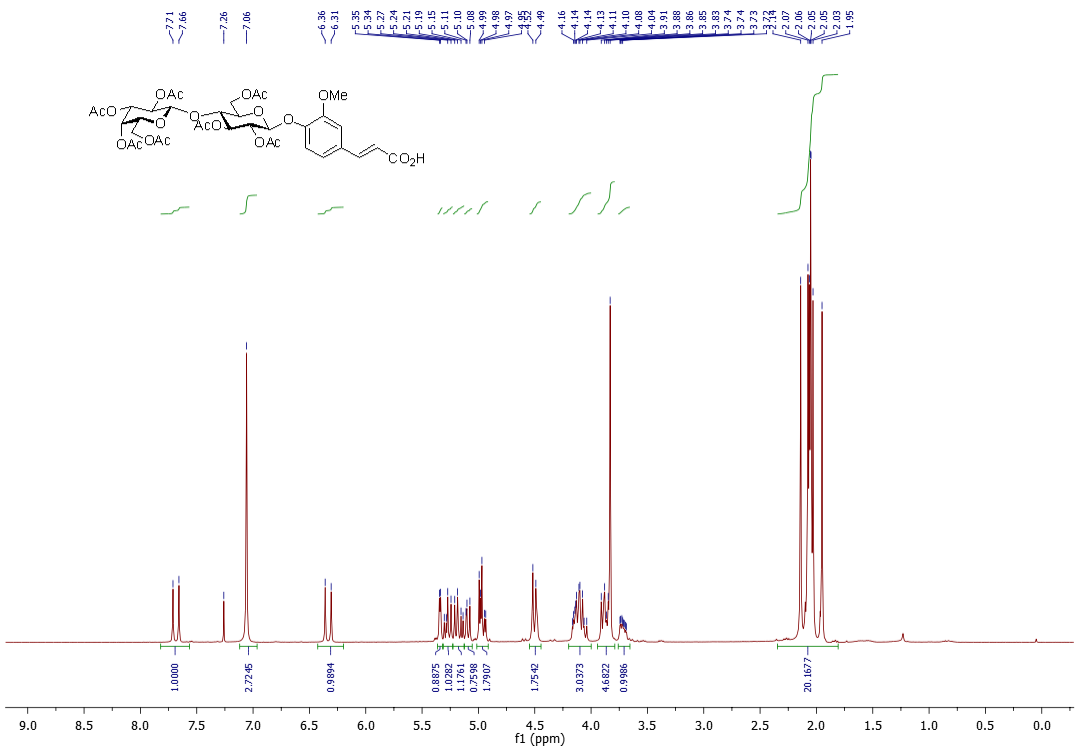

COSY NMR spectrum (300 MHz, $CD_3OD$-$d_4$) of compound **16**.



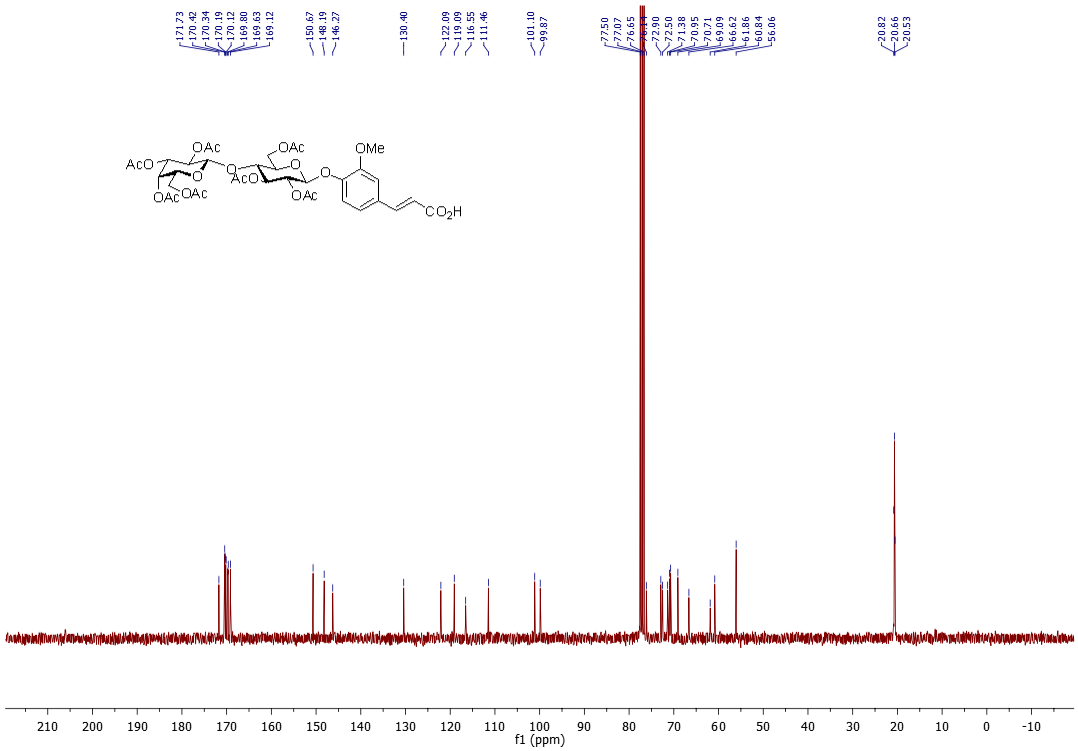

HSQC NMR spectrum (75 MHz, $CD_3OD$-$d_4$) of compound **16**.



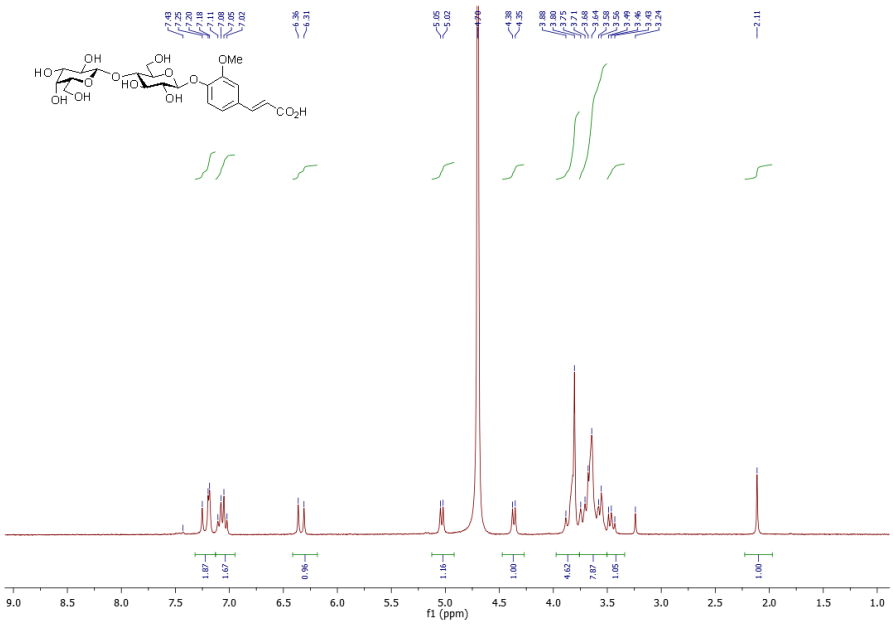

$^{13}$C Dept135 NMR spectrum (75 MHz, $CD_3OD$-$d_4$) of compound **16**.



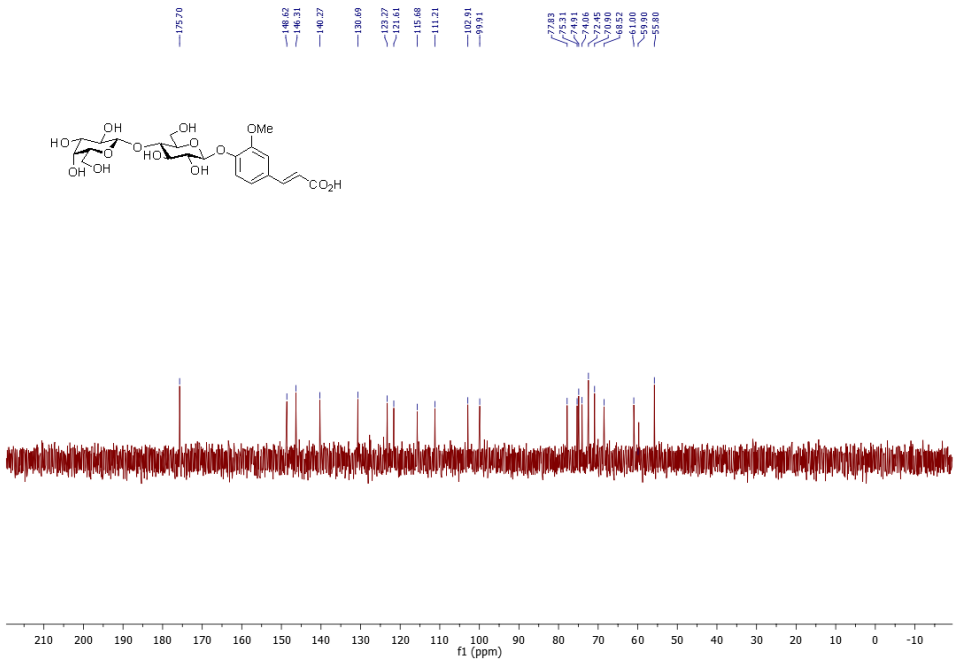

$^{1}$H NMR spectrum (300 MHz, $CDCl_3$) of compound **17**.



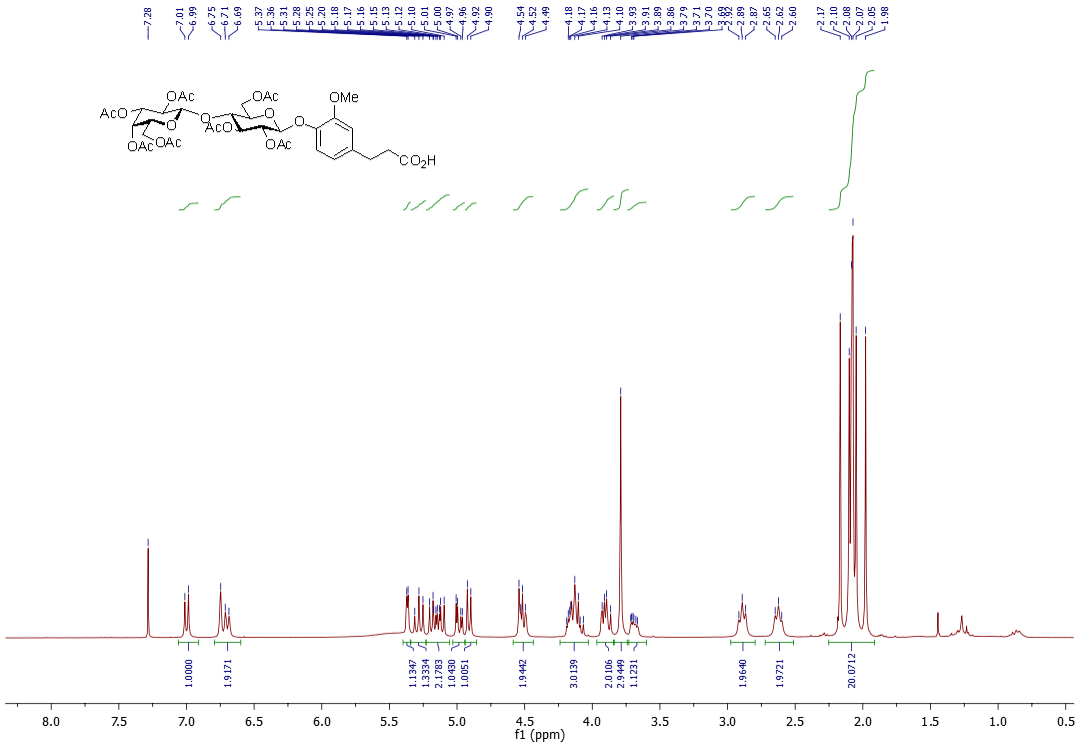

$^{13}$C NMR spectrum (75MHz, $CDCl_3$) of compound **17**.



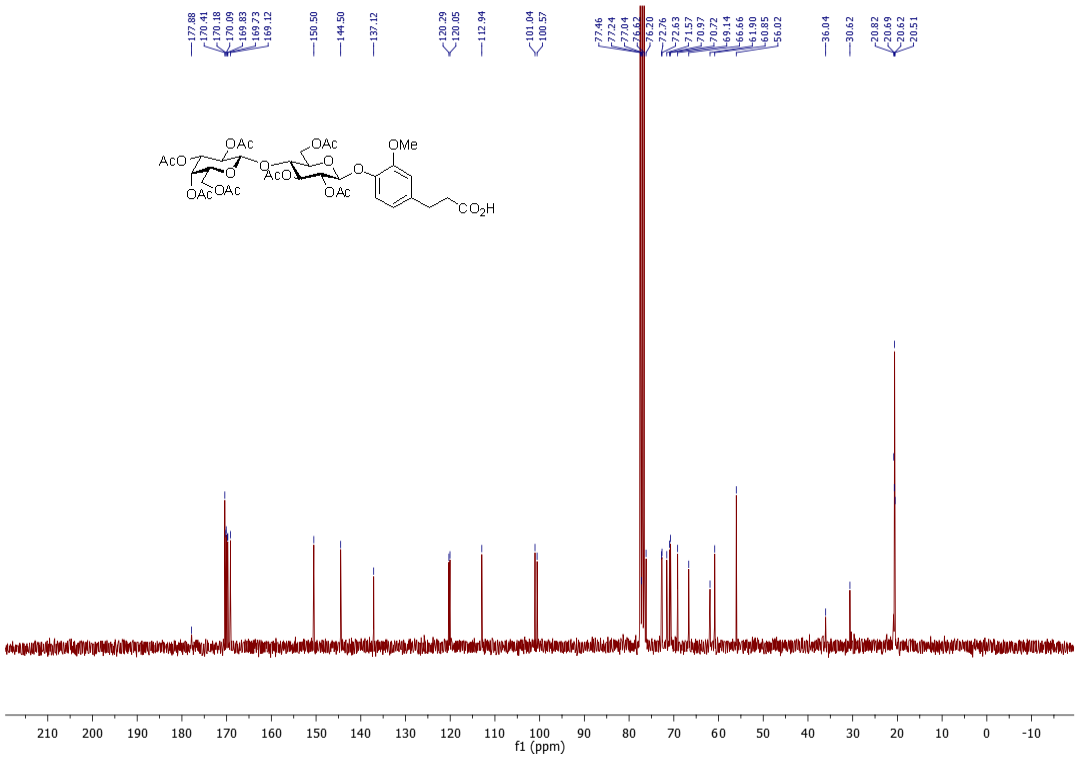

$^{1}$H NMR spectrum (300 MHz, $D_2O$) of compound **18**



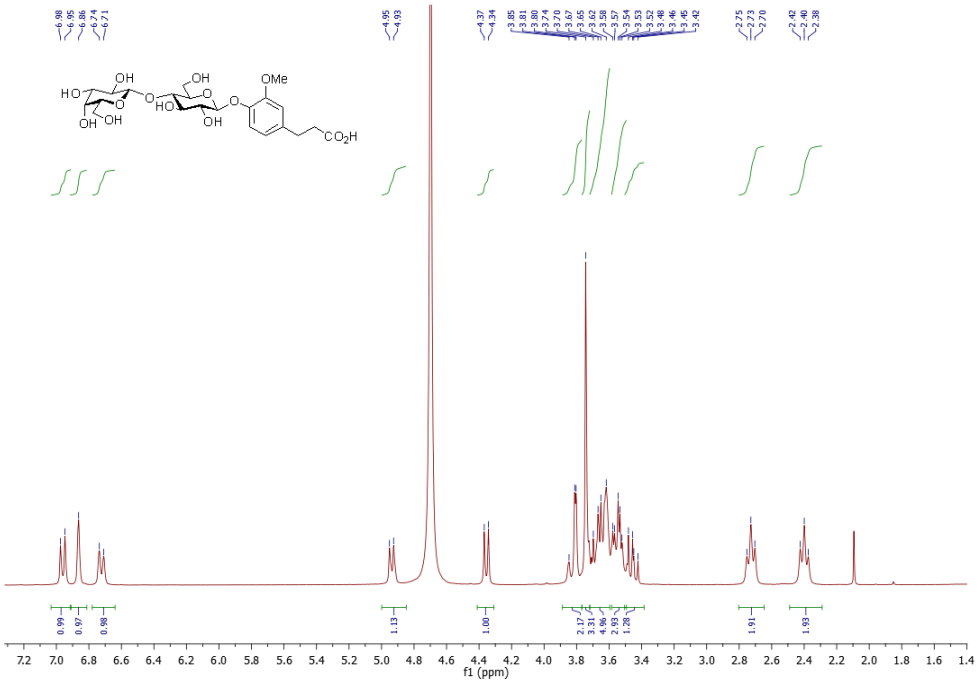

$^{13}$C NMR spectrum (75MHz, $D_2O$) of compound **18**.



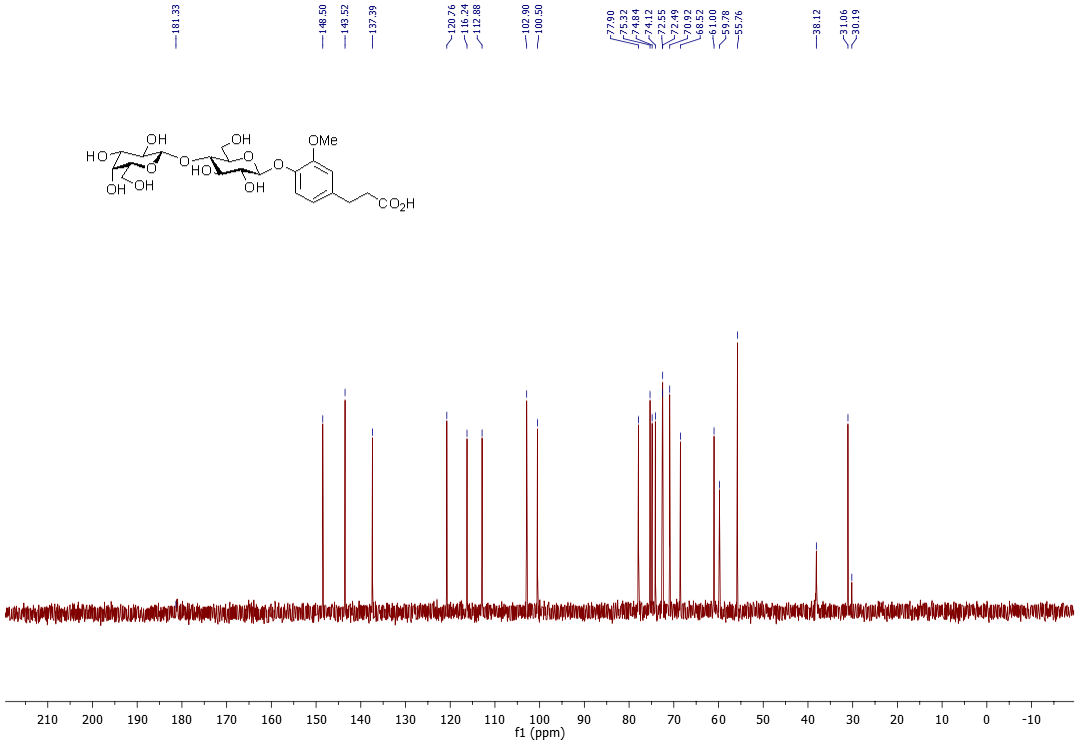

$^{1}$H NMR spectrum (300 MHz, $CDCl_3$) of compound **19**.



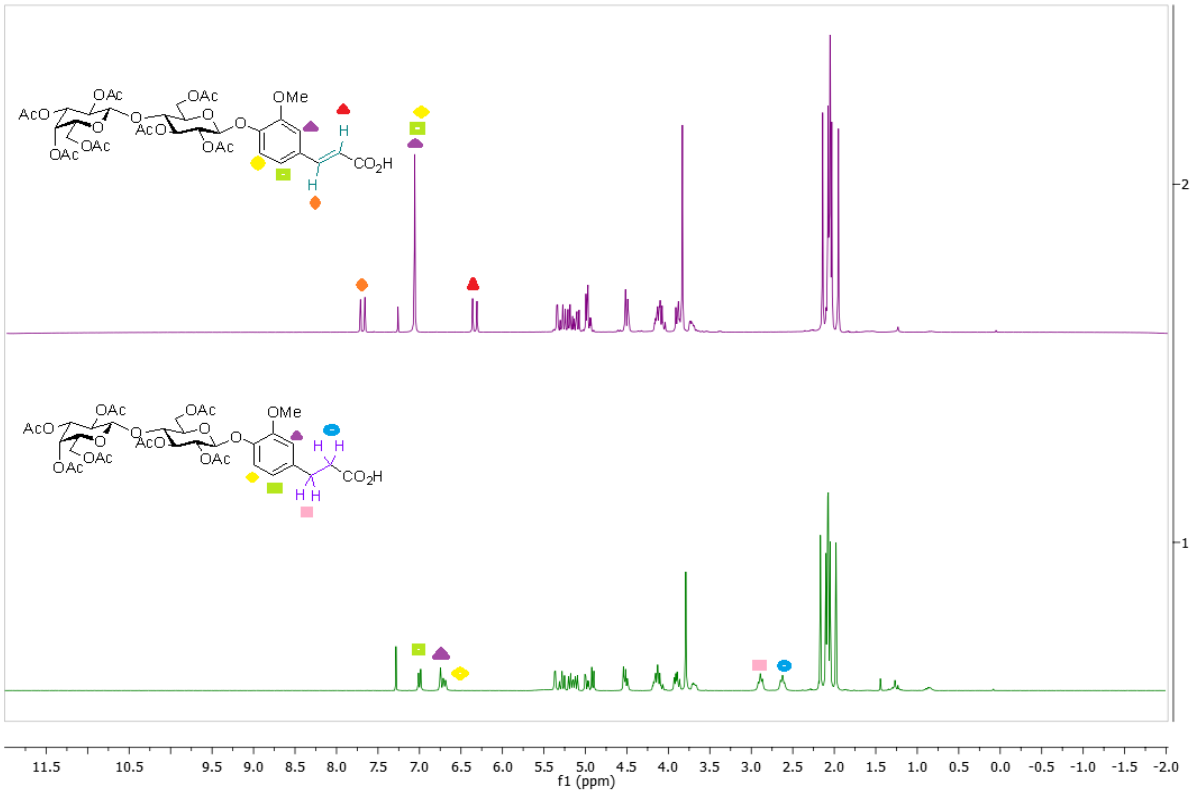

$^{13}C$ NMR spectrum (75 MHz, $CDCl_3$) of compound **19**.




$^{1}H$ NMR spectrum (300 MHz, $D_2O$) of compound **20**.




$^{13}$C NMR spectrum (75 MHz, $D_2O$) of compound **20**.




Comparison of $^{1}H$ NMR spectra ($CDCl_3$, 300 MHz) of **17** and **19** with the appearance/disappearance of protons of the α,β-unsaturation.