Supporting Information

for

Chemoenzymatic synthesis of mono- and di-fluorinated Thomsen-Friedenreich (T) antigens and their sialylated derivatives

Jun Yan,^a Xi Chen,^b Fengshan Wang,^{*a,c} and Hongzhi Cao^{*a,d}

^a National Glycoengineering Research Center, School of Pharmaceutical Science, Shandong University, Jinan 250012, China.

^b Department of Chemistry, University of California, One Shields Avenue, Davis, California 95616, USA.

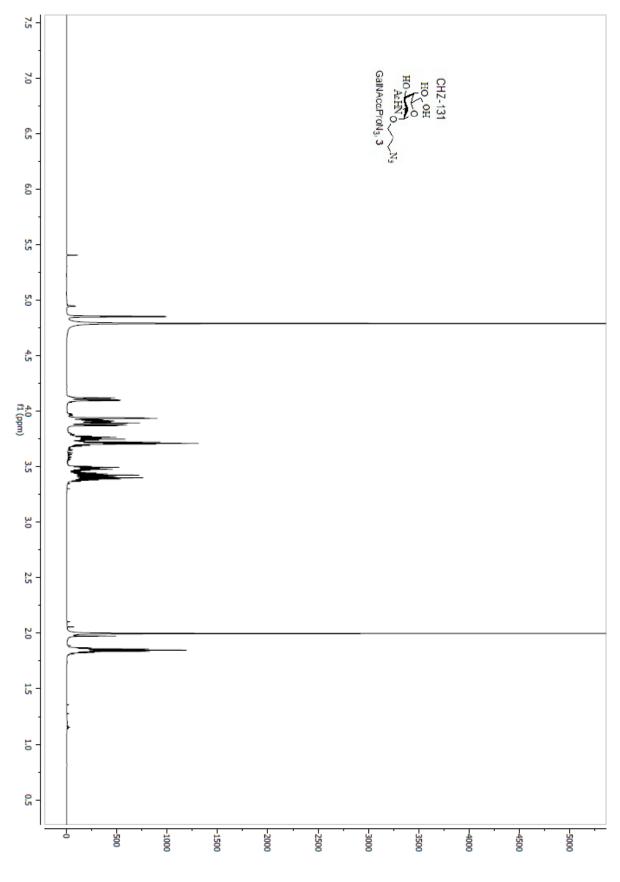
^c Key Laboratory of Chemical Biology (Ministry of Education), Shandong University, Jinan 250012, China

^d State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

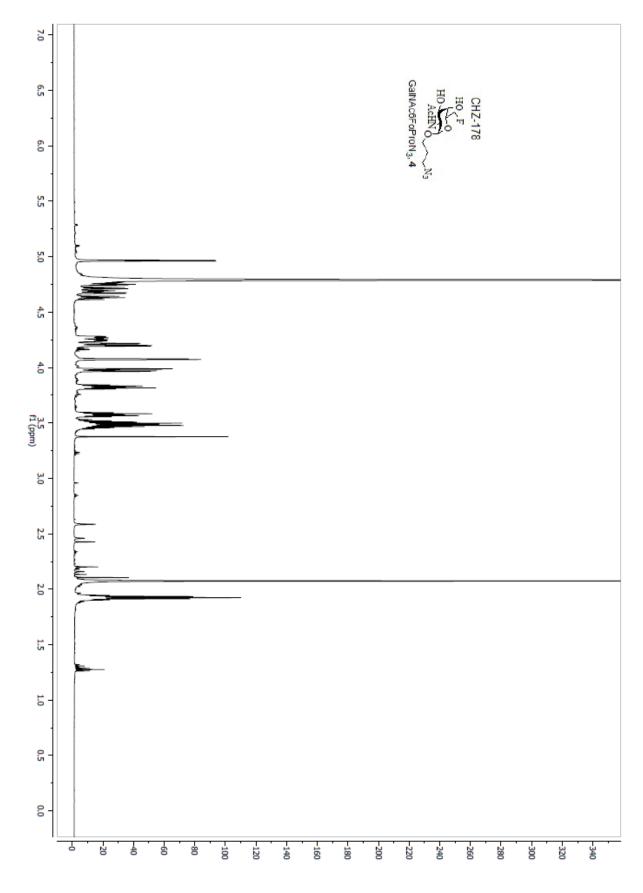
^{*}To whom correspondence should be addressed: Tel: +86-531-8838-2235; Fax: +86-531-8836-3002; E-mail: hzcao@sdu.edu.cn; fswang@sdu.edu.cn

Table of Contents

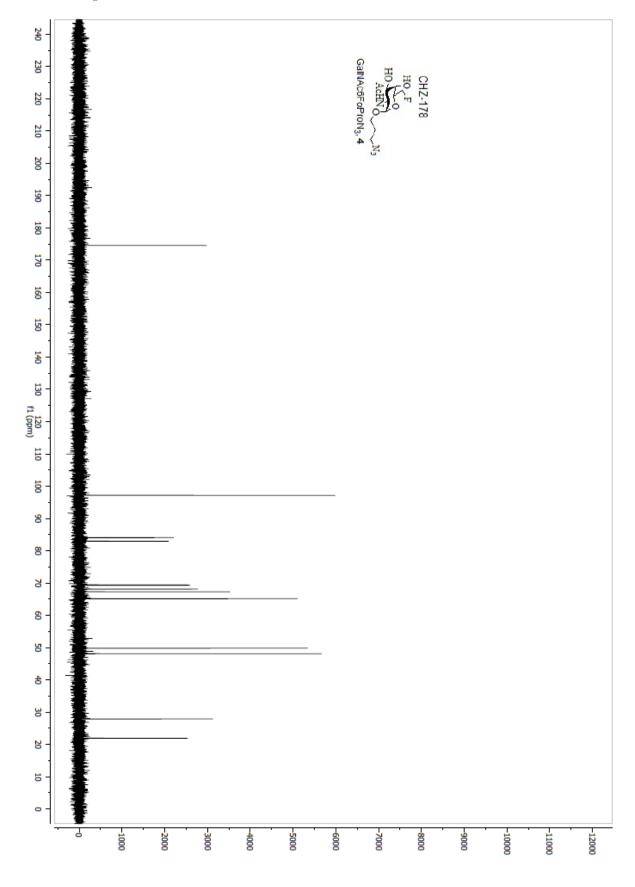
¹ H NMR spectrum for compound 3	S2
¹ H and ¹³ C NMR spectra for compound 4	S3–S4
¹ H and ¹³ C NMR spectra for compound 5	S5–S6
¹ H NMR spectrum for compound 6	
¹ H NMR spectrum for compound 7	S8
¹ H and ¹³ C NMR spectra for compound 8	
¹ H and ¹³ C NMR spectra for compound 9	
¹ H and ¹³ C NMR spectra for compound 10	
¹ H and ¹³ C NMR spectra for compound 11	S15–S16
¹ H NMR spectrum for compound 12	
¹ H NMR spectrum for compound 13	
¹ H and ¹³ C NMR spectra for compound 14	
¹ H and ¹³ C NMR spectra for compound 15	
¹ H and ¹³ C NMR spectra for compound 16	
¹ H and ¹³ C NMR spectra for compound 17	
¹ H NMR spectrum for compound 18	
¹ H and ¹³ C NMR spectra for compound 19	
HPLC conditions and chromatograms of ST-antigens (12-17)	



 1H NMR spectrum for GalNAcaProN_3, 3

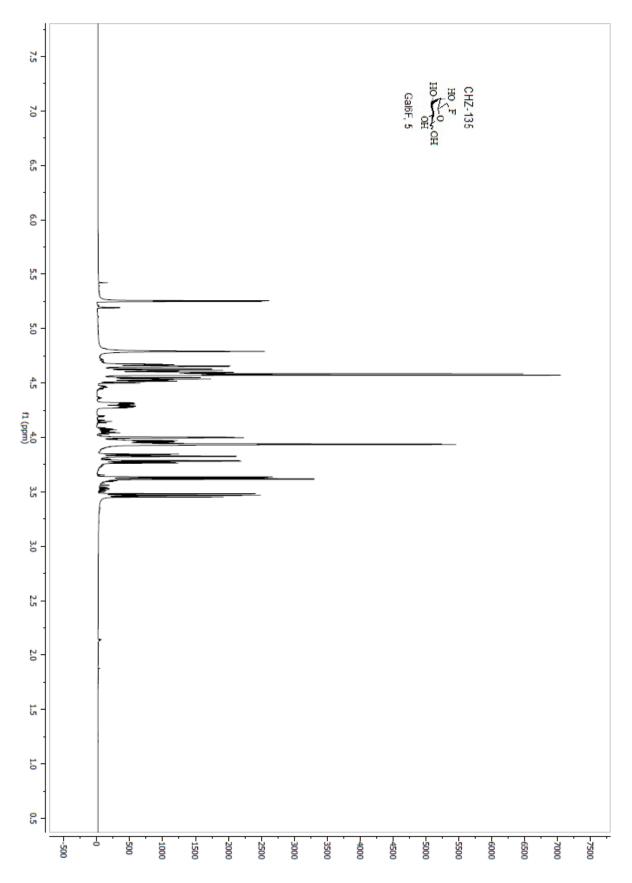


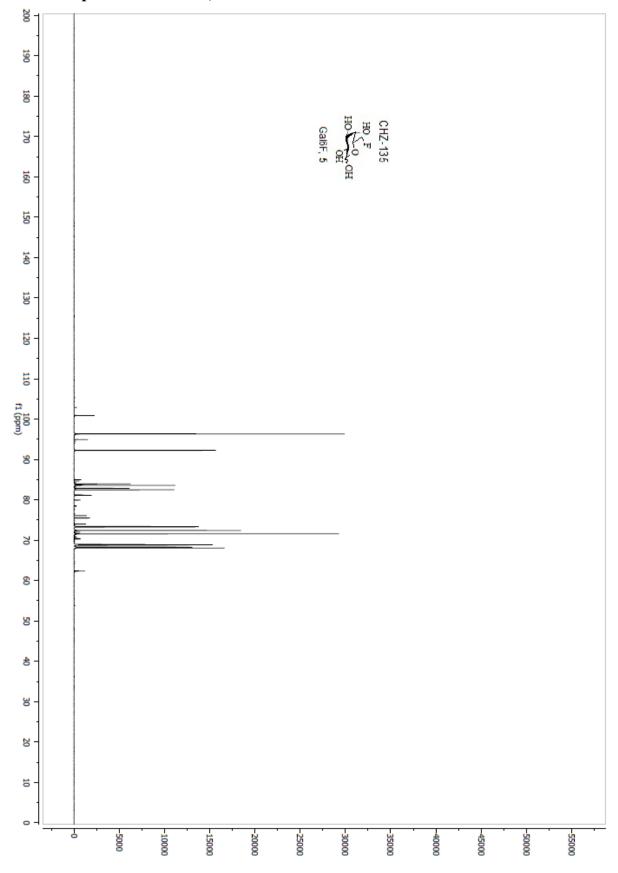
 1H NMR spectrum for GalNAc6F\alphaProN_3, 4

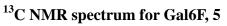


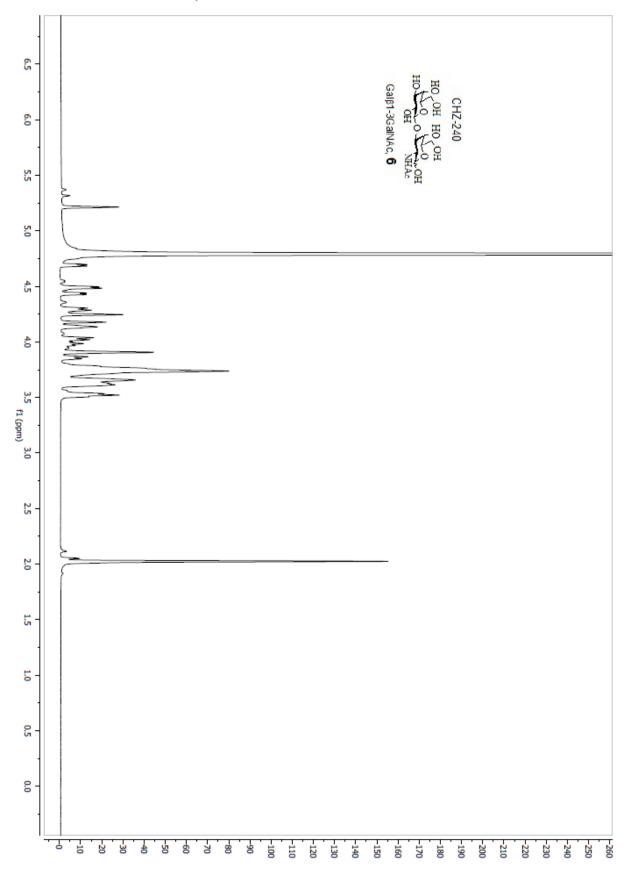
 ^{13}C NMR spectrum for GalNAc6FaProN_3, 4

¹H NMR spectrum for Gal6F, 5

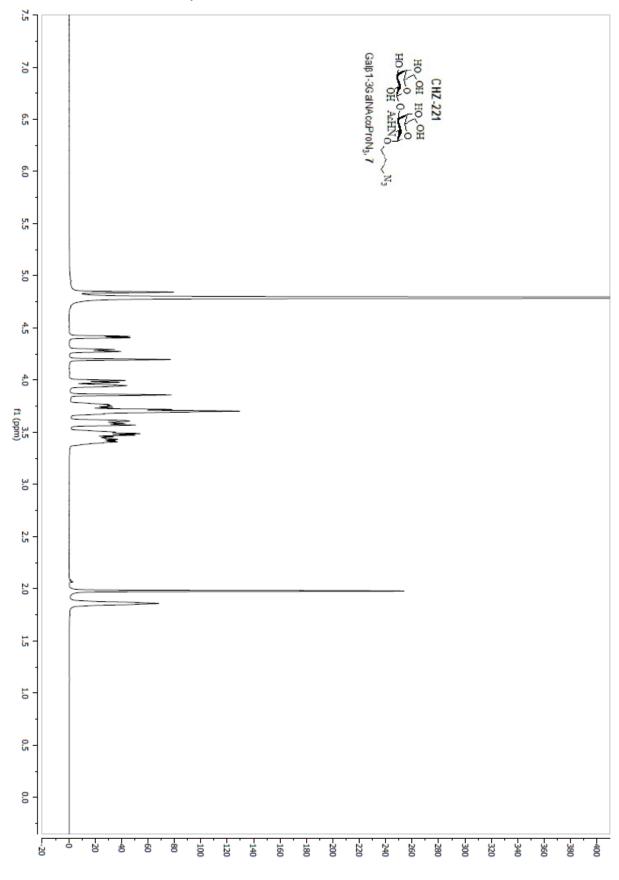




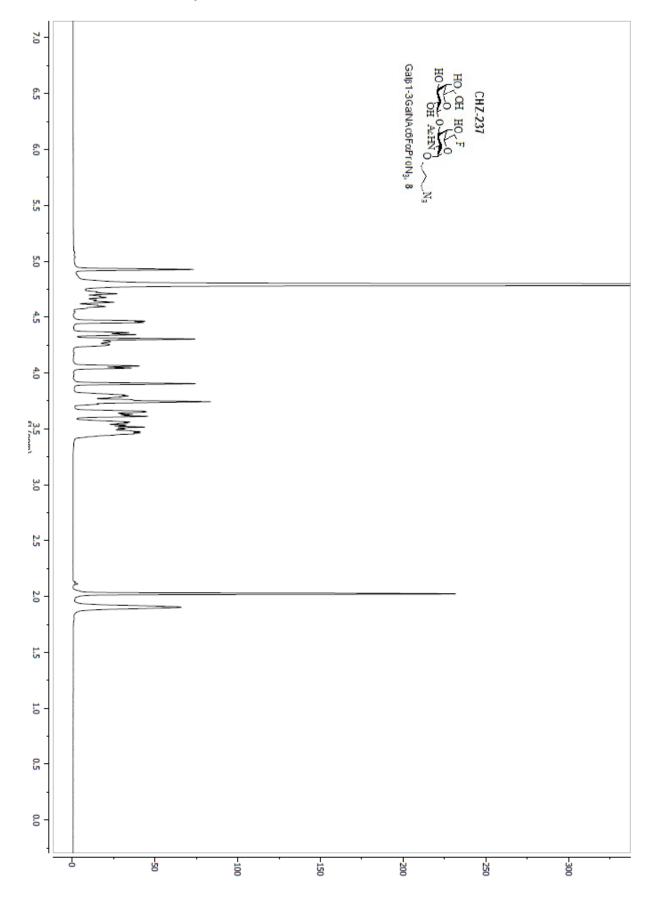




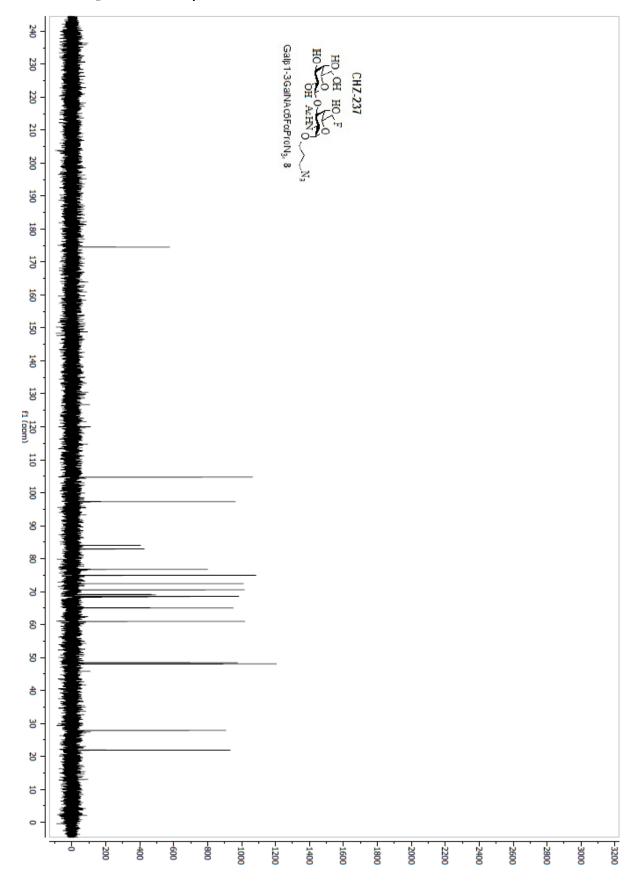
¹H NMR spectrum for Galβ1–3GalNAc, 6

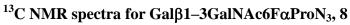


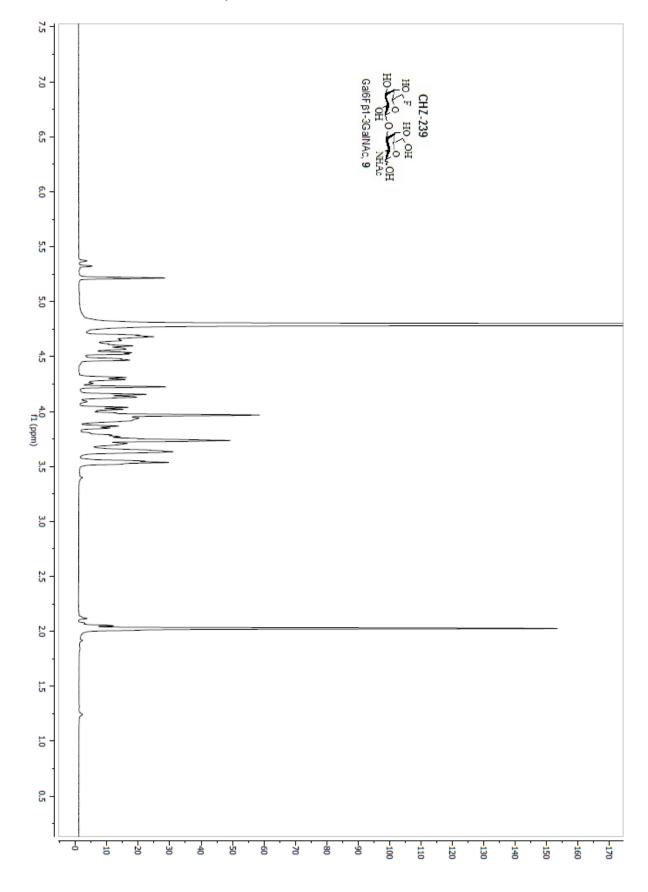




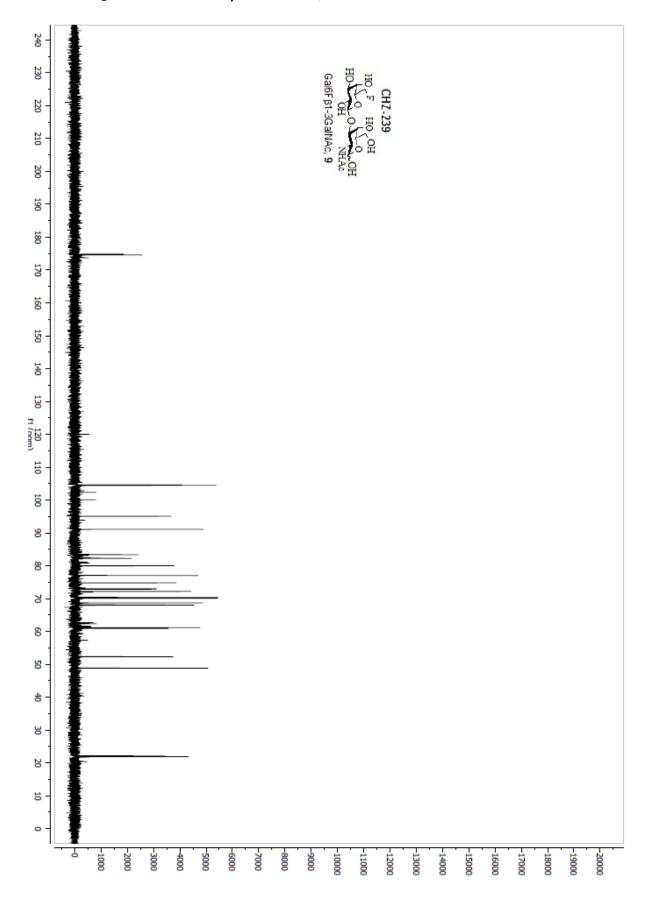




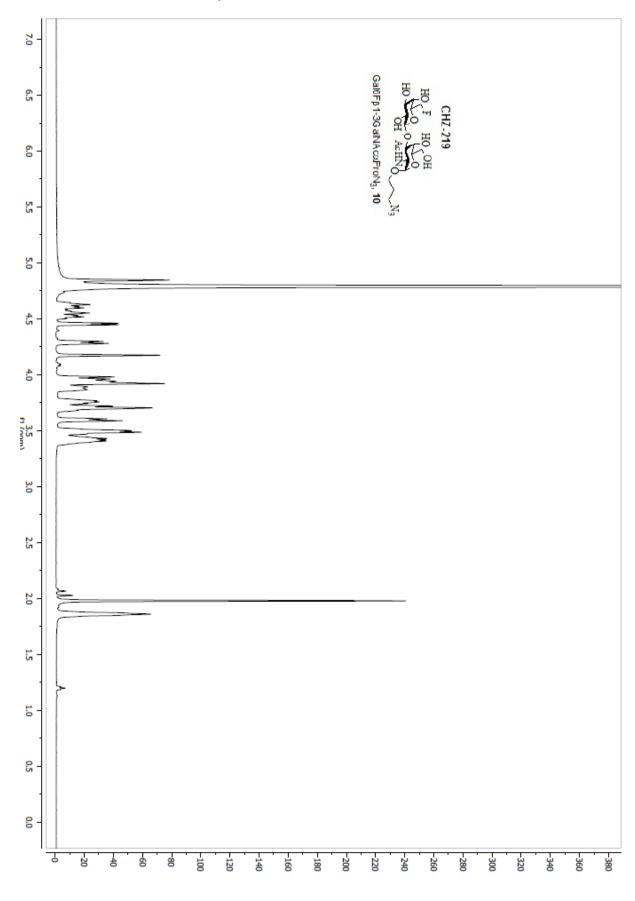




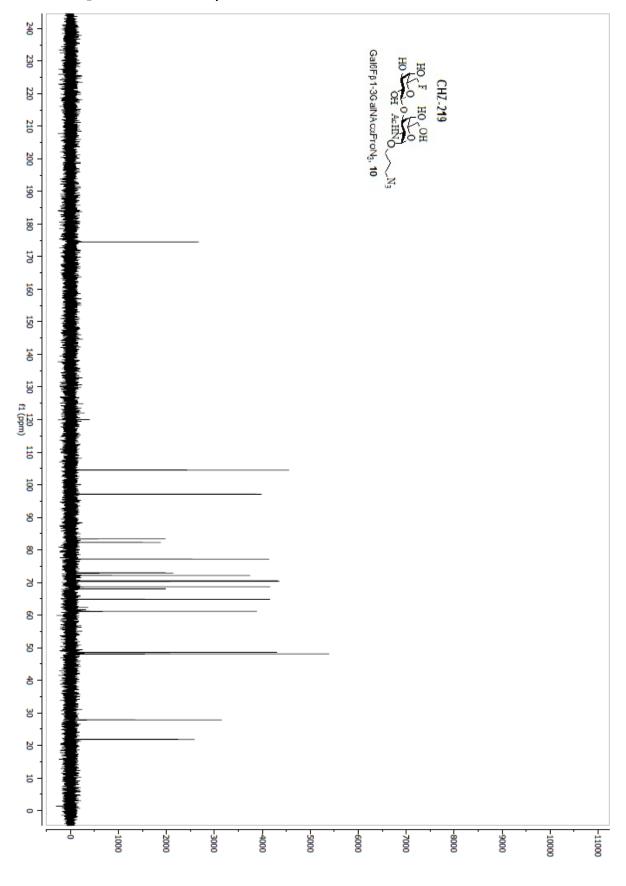
¹H NMR spectrum for Gal6Fβ1–3GalNAc, 9



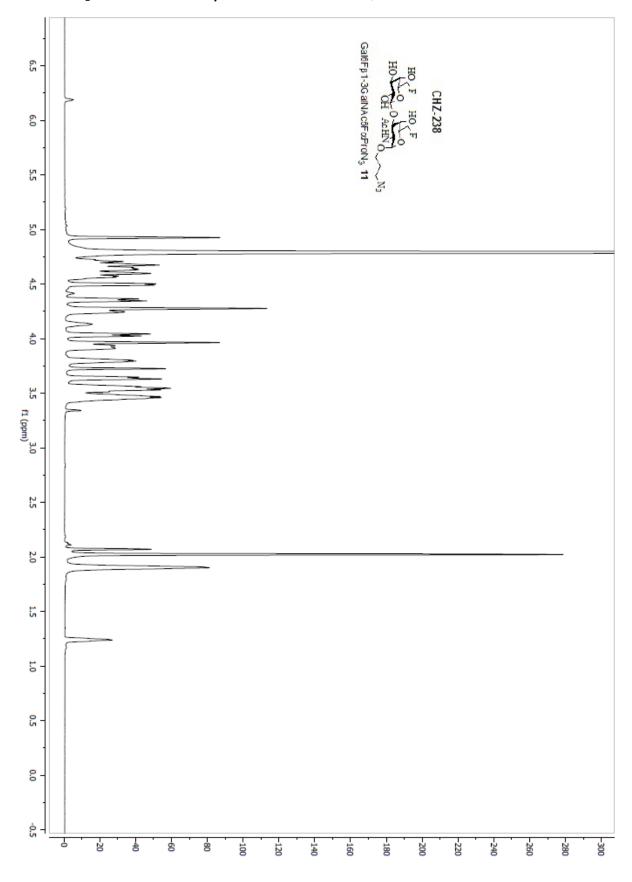
^{13}C NMR spectrum for Gal6F β 1–3GalNAc, 9



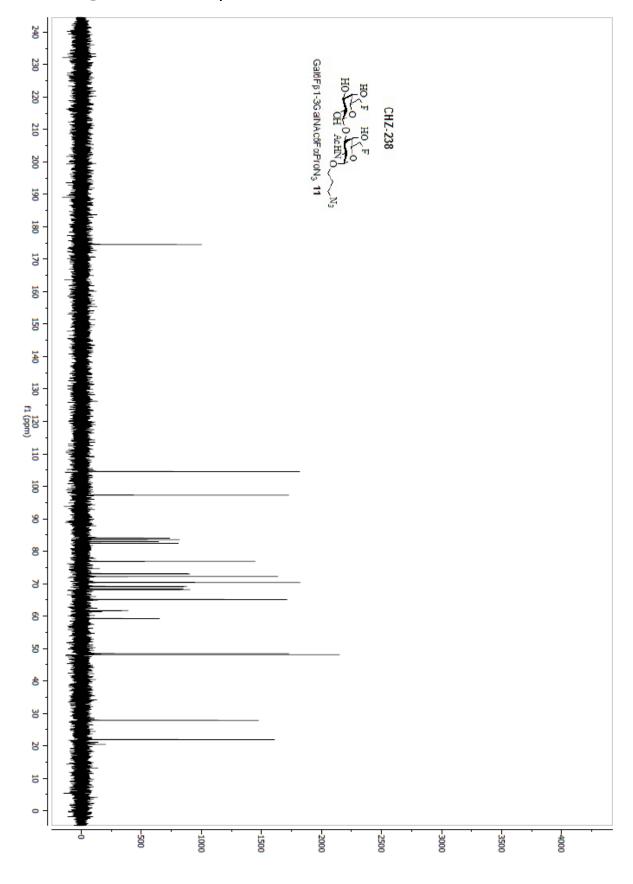
 1H NMR spectrum for Gal6F β 1–3GalNAcaProN_3, 10



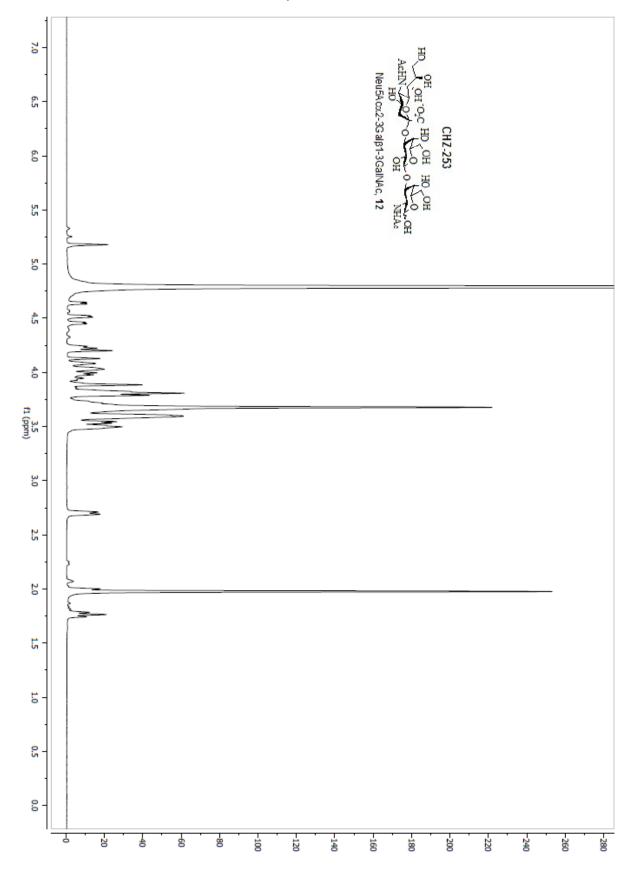




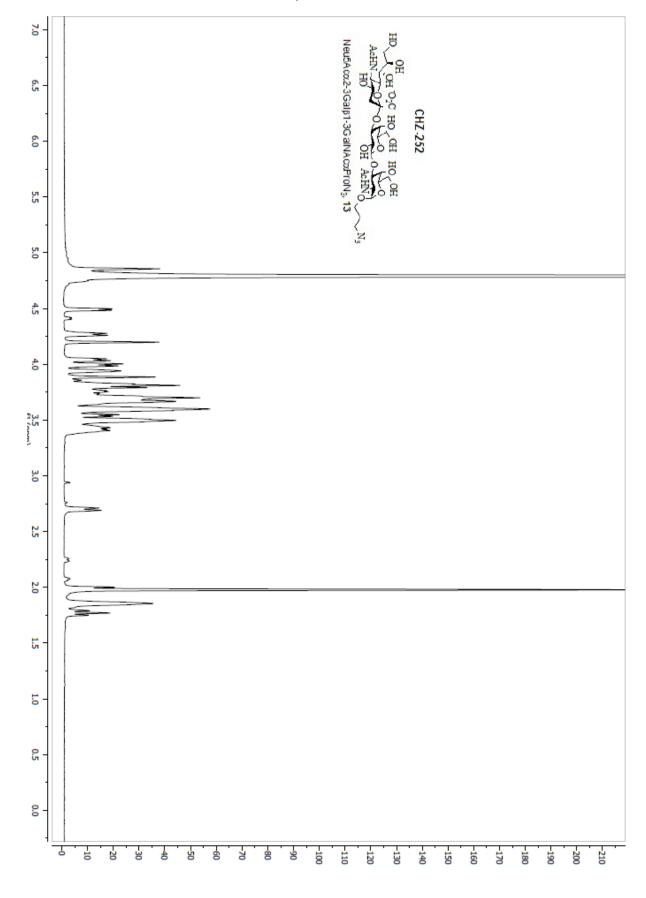
 ^{1}H NMR spectrum for Gal6F β 1–3GalNAc6F α ProN_3, 11



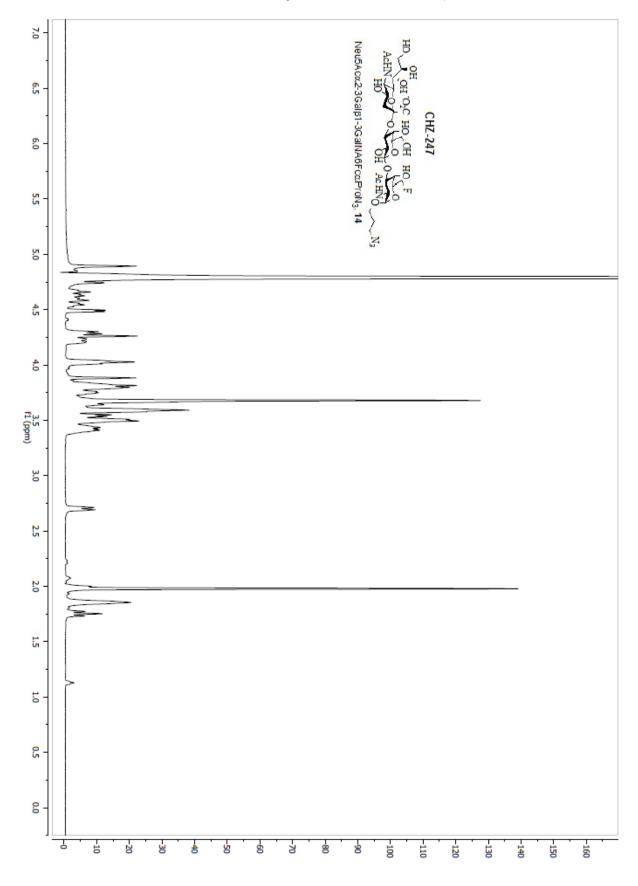
 ^{13}C NMR spectrum for Gal6Fβ1–3GalNAc6FαProN_3, 11



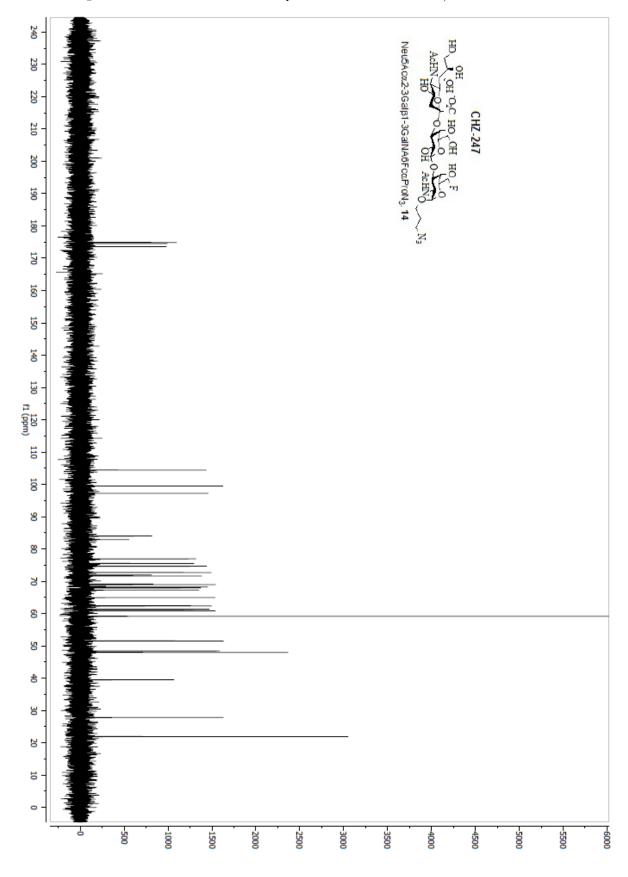




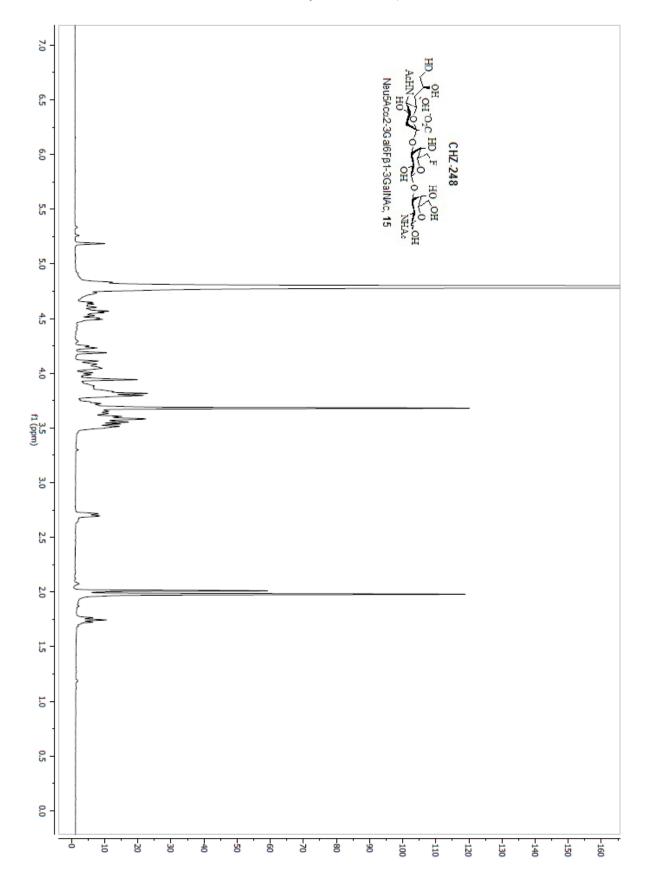
¹H NMR spectrum for Neu5Acα2–3Galβ1–3GalNAcαProN₃, 13



¹H NMR spectrum for Neu5Acα2–3Galβ1–3GalNAc6FαProN₃, 14

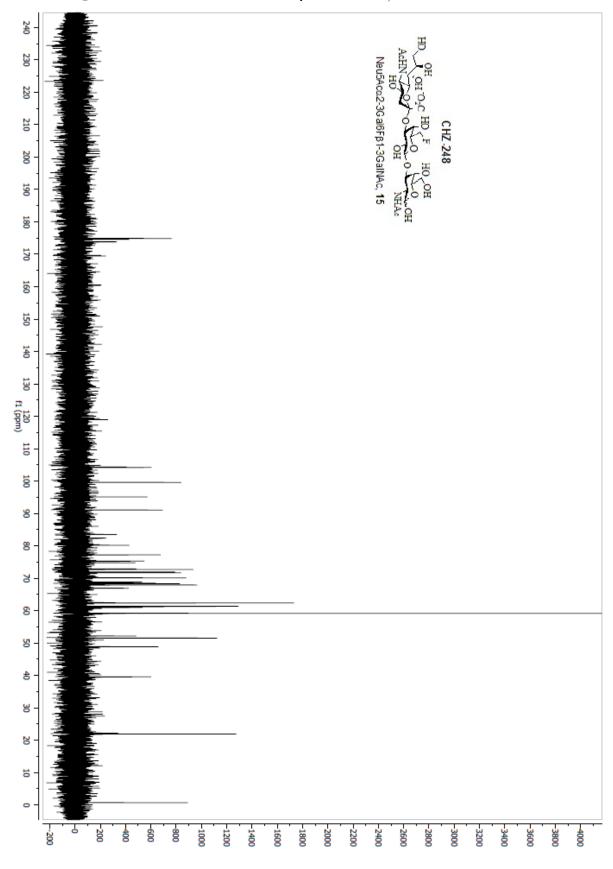


 ^{13}C NMR spectrum for Neu5Aca2–3Gal\beta1–3GalNAc6FaProN_3, 14

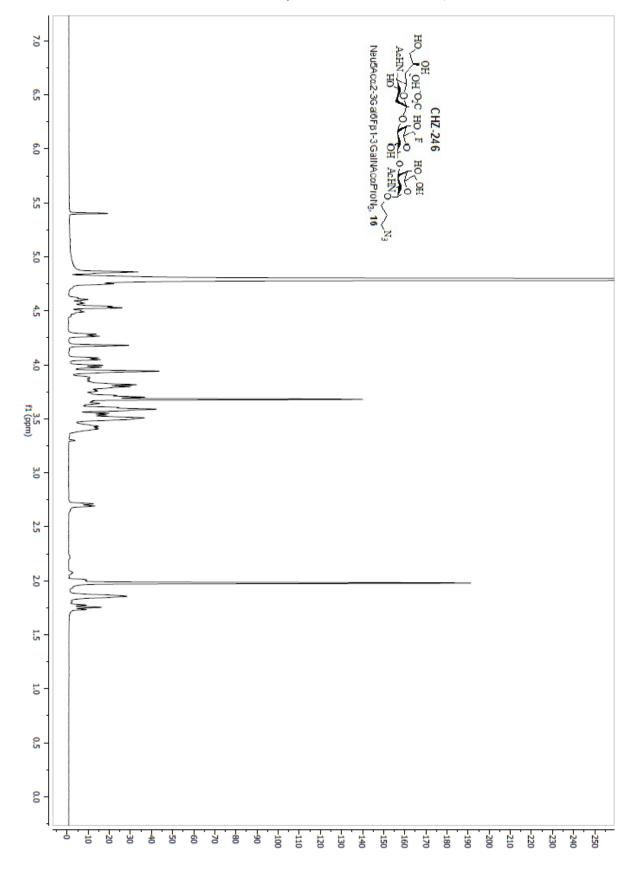


¹H NMR spectrum for Neu5Acα2–3Gal6Fβ1–3GalNAc, 15

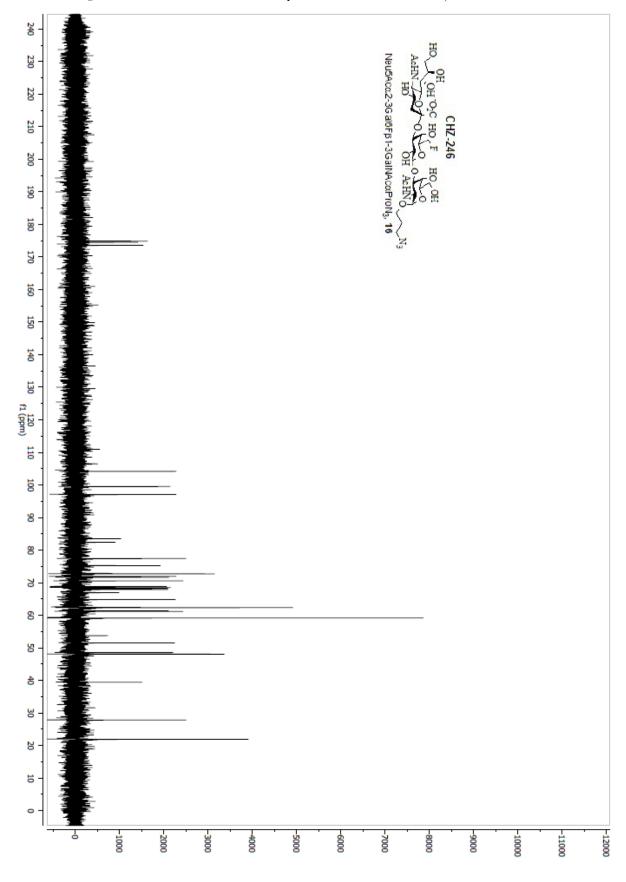
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is © The Royal Society of Chemistry 2012



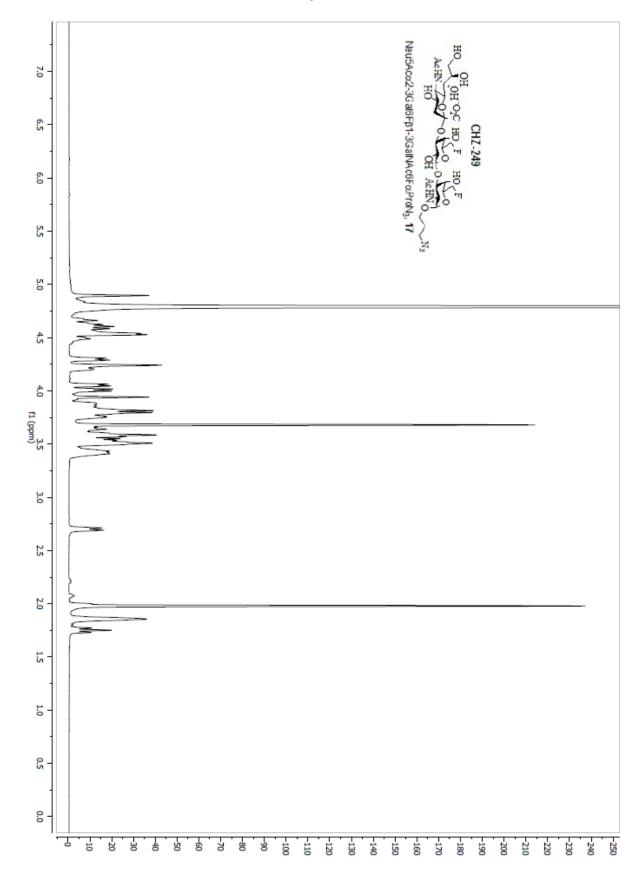
 ^{13}C NMR spectrum for Neu5Aca2–3Gal6Fβ1–3GalNAc, 15



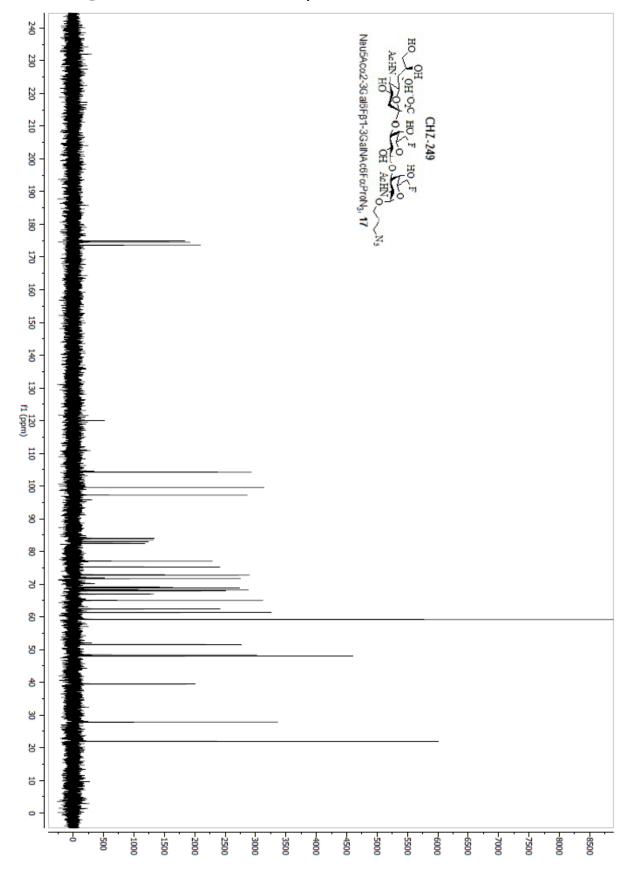
¹H NMR spectrum for Neu5Aca2–3Galβ1–3GalNAc6FαProN₃, 16



 ^{13}C NMR spectrum for Neu5Aca2–3Gal\beta1–3GalNAc6FaProN_3, 16

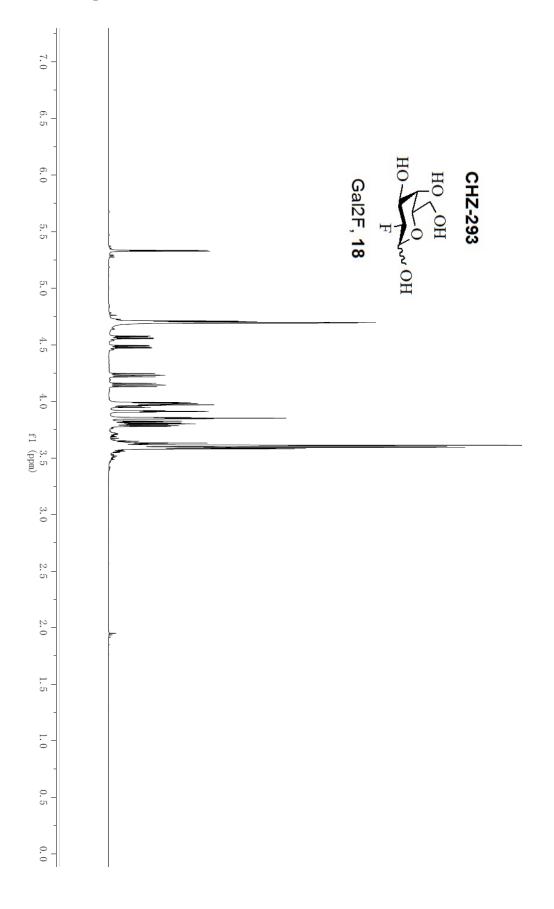


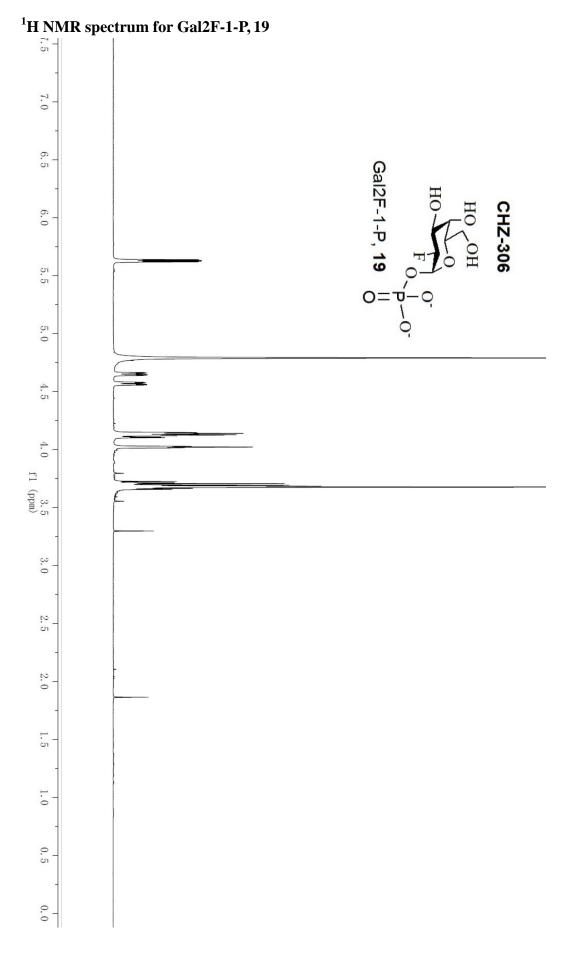
¹H NMR spectrum for Neu5Acα2–3Gal6Fβ1–3GalNAc6FαProN₃, 17



 ^{13}C NMR spectrum for Neu5Aca2–3Gal6F β 1–3GalNAc6F α ProN_3, 17

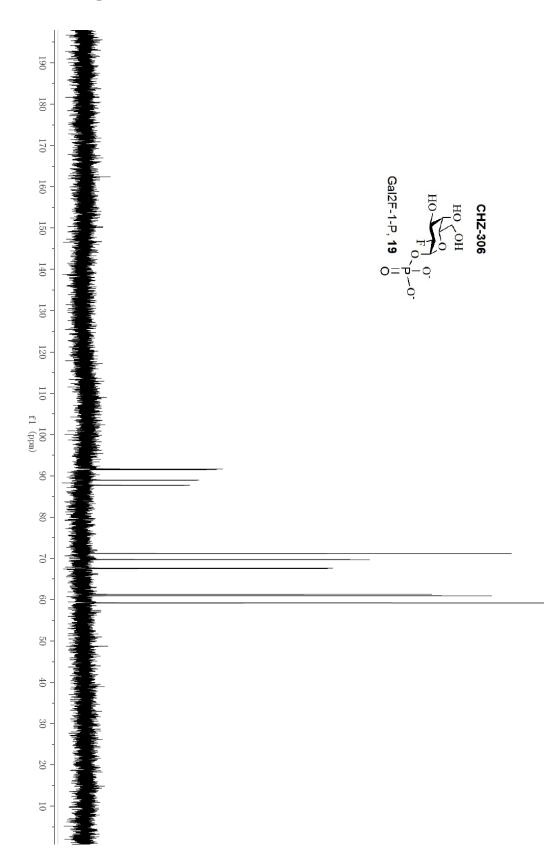
¹H NMR spectrum for Gal2F, 18





Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is C The Royal Society of Chemistry 2012

¹³C NMR spectrum for Gal2F-1-P, 19



HPLC conditions and chromatograms of ST-antigens (12–17)

HPLC Conditions:

HPLC instrument: Waters 2695 Separation Module Column: GE Healthcare SuperdexTM Peptide 10/300 GL Eluent: 0.1 M NH₄HCO₃ Flow rate: 0.5 mL/min Injection volume: 10 μ L Run time: 50 min

HPLC chromatograms:

