Supporting Information

A STUDY FOR THE ACCESS TO A SEMI-SYNTHETIC REGIOISOMER OF NATURAL FUCOSYLATED CHONDROITIN SULFATE WITH FUCOSYL BRANCHES ON *N*-ACETYL-GALACTOSAMINE UNITS

GIULIA VESSELLA,[1] SERENA TRABONI,[1] ANNA V.A. PIROZZI,[2] ANTONIO LAEZZA,[3]

ALFONSO IADONISI,[1] CHIARA SCHIRALDI,[2] EMILIANO BEDINI,[1]

[1]Department of Chemical Sciences, University of Naples Federico II,
Complesso Universitario Monte S.Angelo, via Cintia 4, I-80126 Napoli, Italy
[2] Department of Experimental Medicine, Section of Biotechnology,
University of Campania "Luigi Vanvitelli", via de Crecchio 7, I-80138 Napoli, Italy
[3] Department of Sciences, University of Basilicata, viale dell'Ateneo Lucano 10, I-85100 Potenza, Italy

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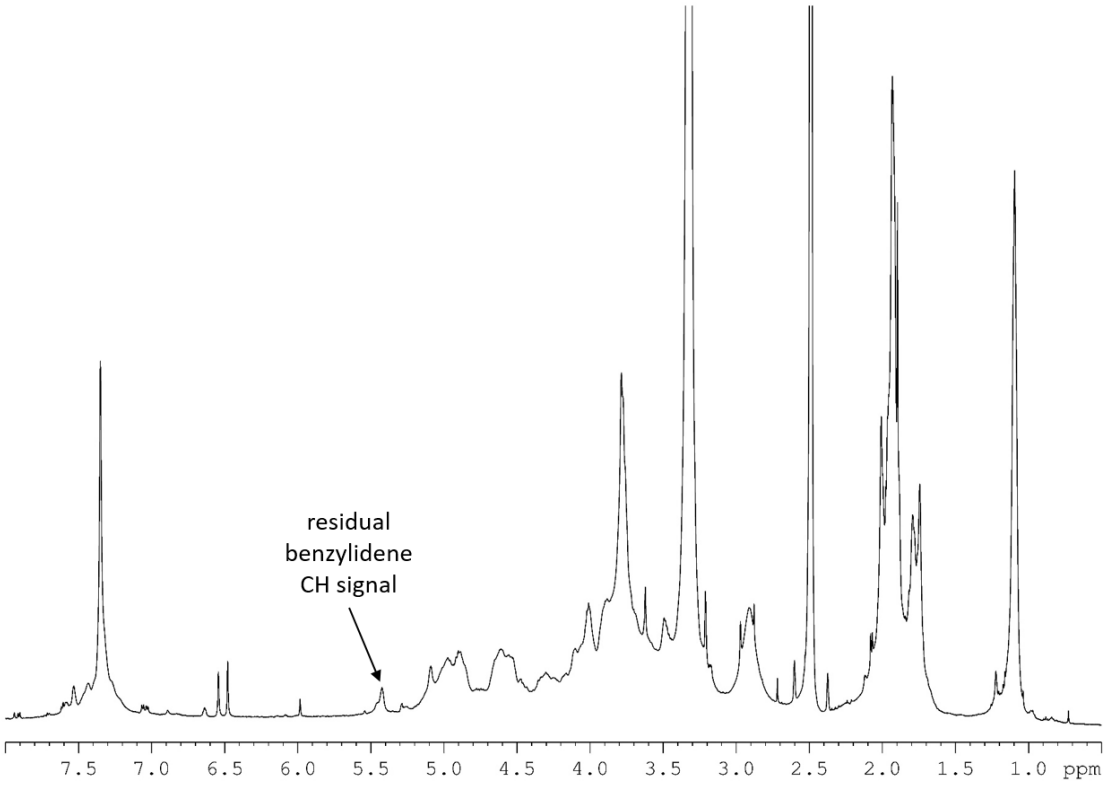

Figure S1: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **8-i**

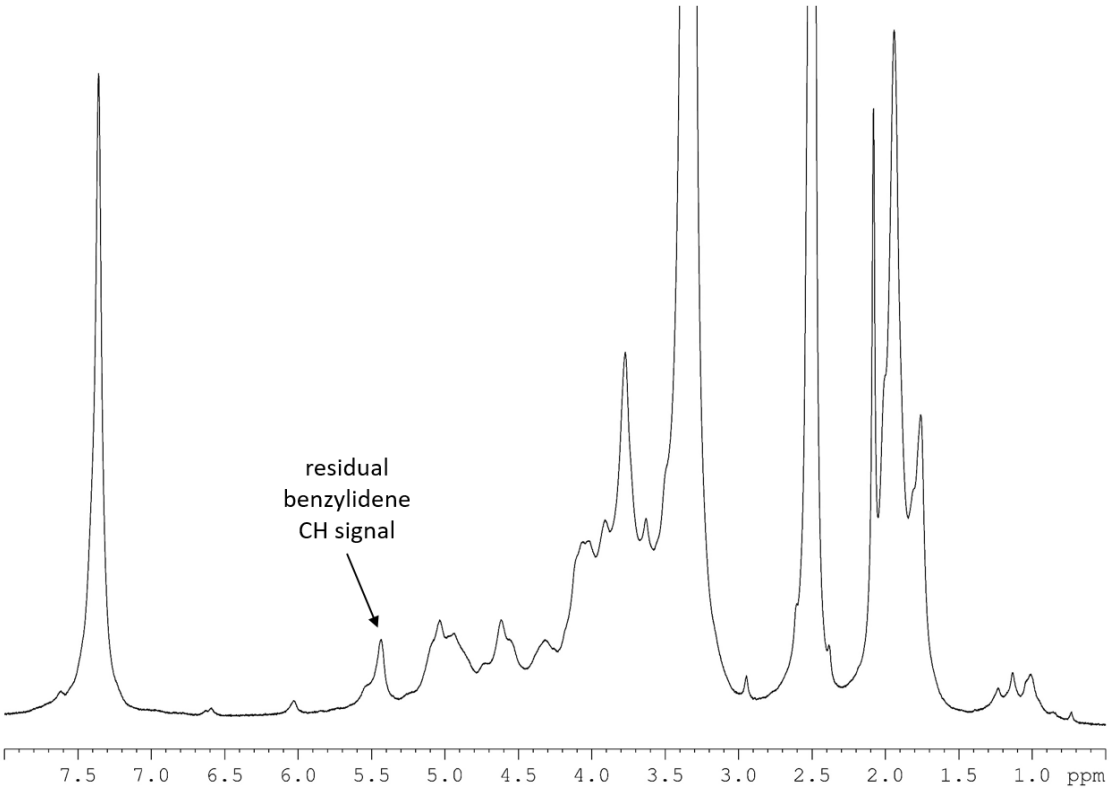

Figure S2: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **8-ii**

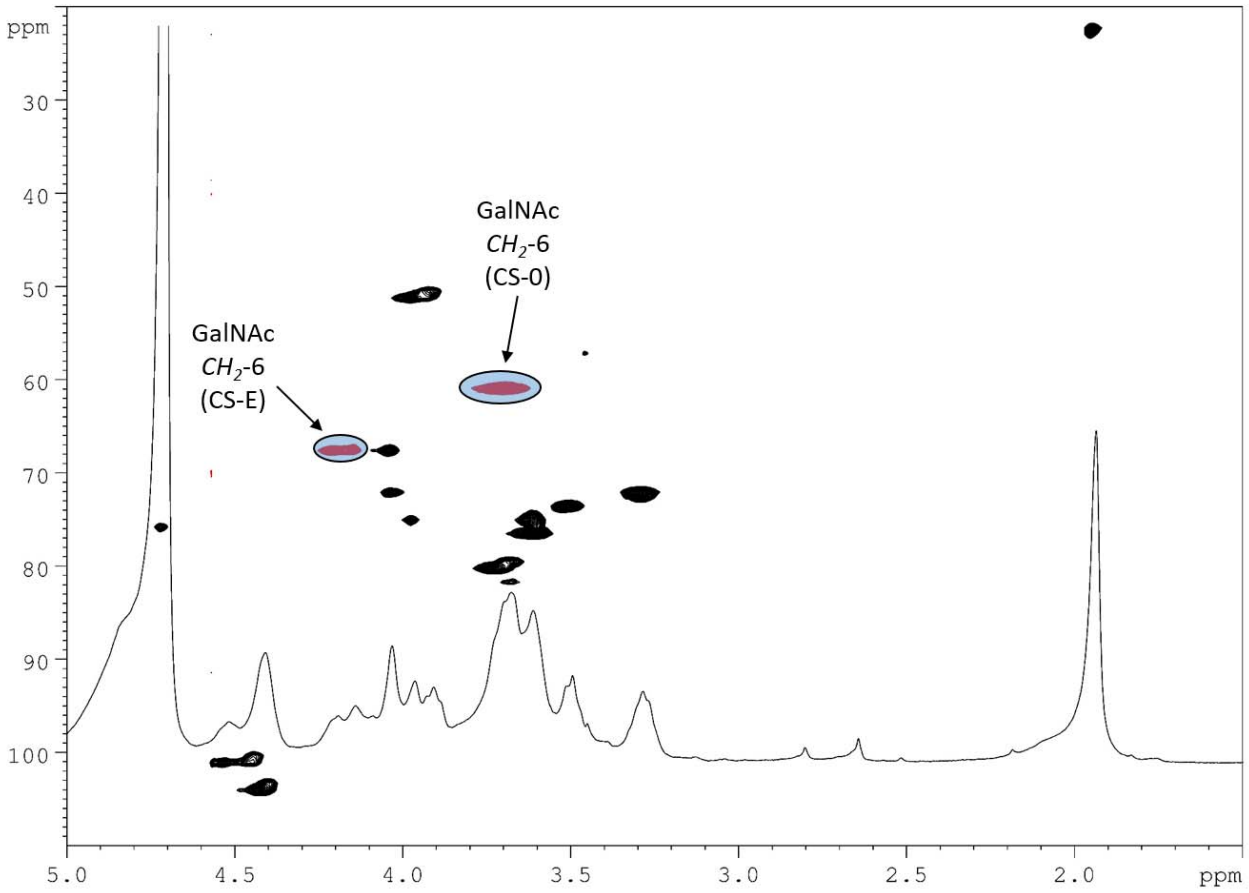

Figure S3: ^{1}H and DEPT-HSQC NMR spectra (400 MHz, D_2O, 298K) of **CS-i**
(densities enclosed in the highlighted areas were integrated for CS-0/CS-E ratio estimation)

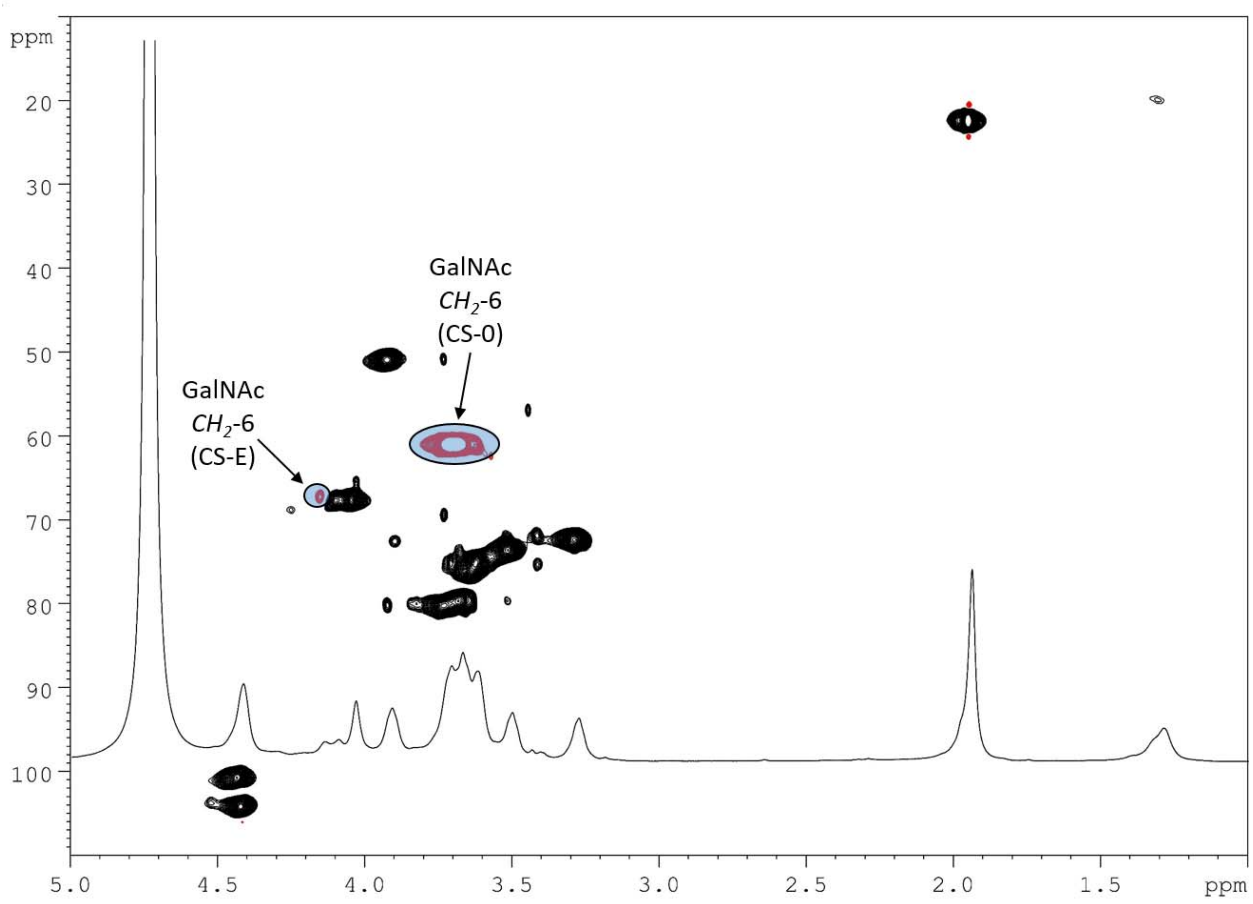

Figure S4: ^{1}H and DEPT-HSQC NMR spectra (400 MHz, D_2O, 298K) of **CS-ii**
(densities enclosed in the highlighted areas were integrated for CS-0/CS-E ratio estimation)

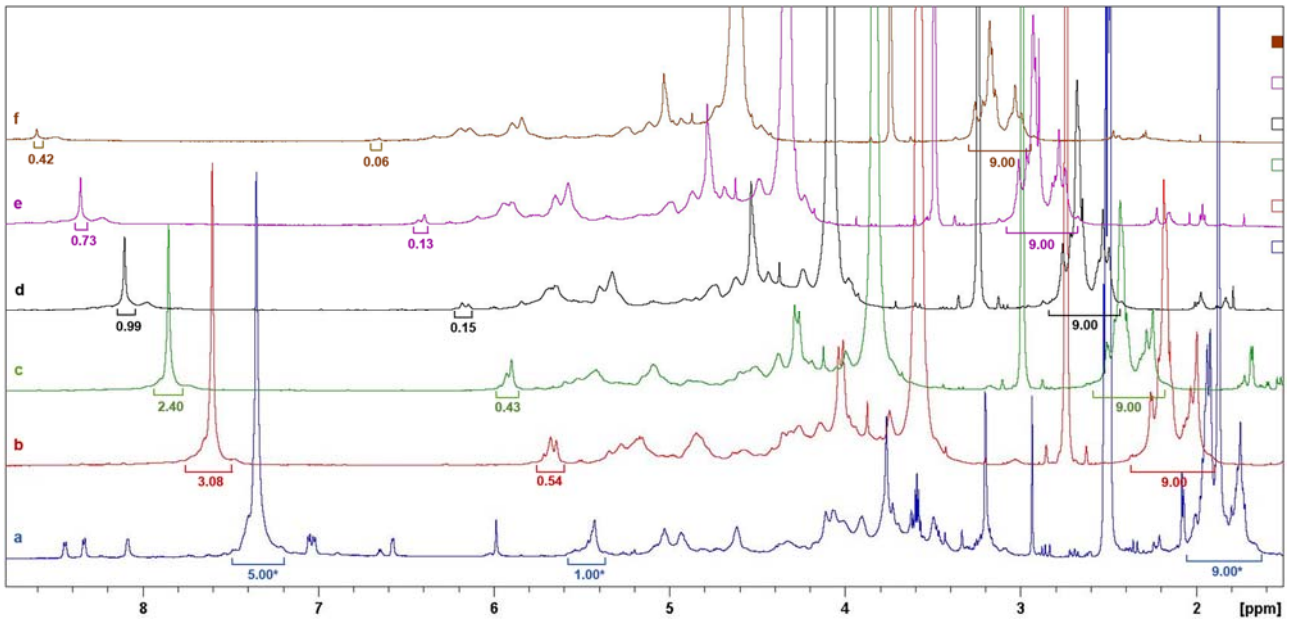

Figure S5: Stacked (with a $\Delta\delta$ = 0.25 ppm shift) ^{1}H-NMR spectra (600 MHz, DMSO-d_6, 298 K) of aliquots taken at different times (a: 0, b:3, c:6, d:24, e:42, f:66 hours) from hydrolysis reaction **2→5** with 90% aq. AcOH. Integration values are relative to signals, from left to right, of benzylidene ring protons at δ_H 7.5-7.2, of benzylidene methine proton at 5.45-5.35 ppm, and of *O*- and *N*-acetyl methyl protons at δ_H 2.0-1.7 ppm (integration of *O*- and *N*-acetyl signal for t=0 hours spectrum was taken from literature[S1] due to superimposition with other peaks)

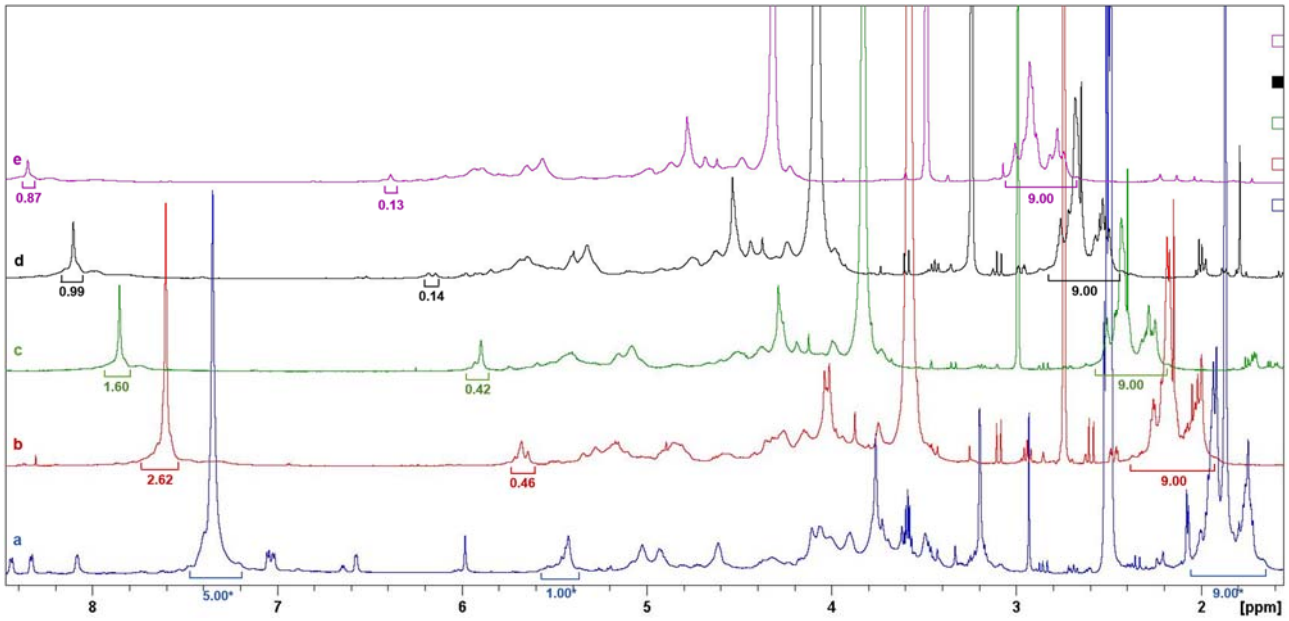

Figure S6: Stacked (with a $\Delta\delta$ = 0.25 ppm shift) ^{1}H-NMR spectra (600 MHz, DMSO-d_6, 298 K) of aliquots taken at different times (a: 0, b:5, c:25, d:49, e:73 hours) from hydrolysis reaction **2→5** with DTT and CSA. Integration values are relative to signals, from left to right, of benzylidene ring protons at δ_H 7.5-7.2, of benzylidene methine proton at 5.45-5.35 ppm, and of *O*- and *N*-acetyl methyl protons at δ_H 2.0-1.7 ppm (*integration of signals for t=0 hours spectrum was imposed from literature[S1] due to superimposition with other peaks)

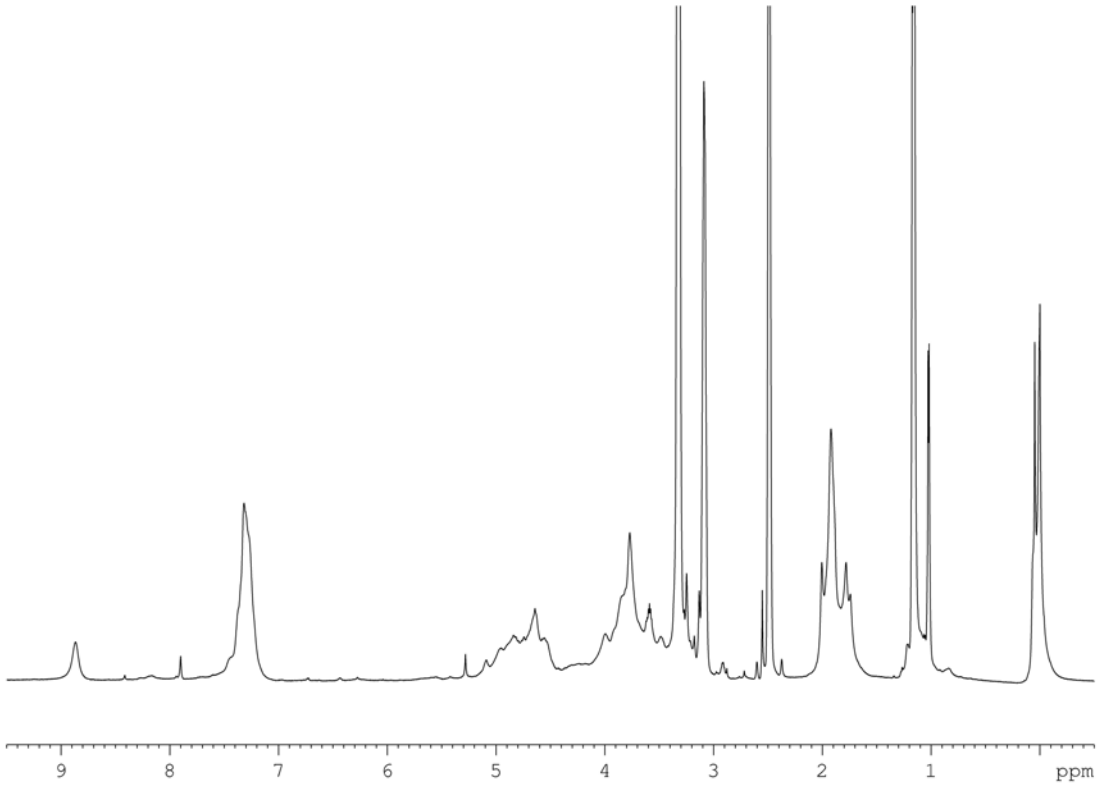

Figure S7: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **12-i**

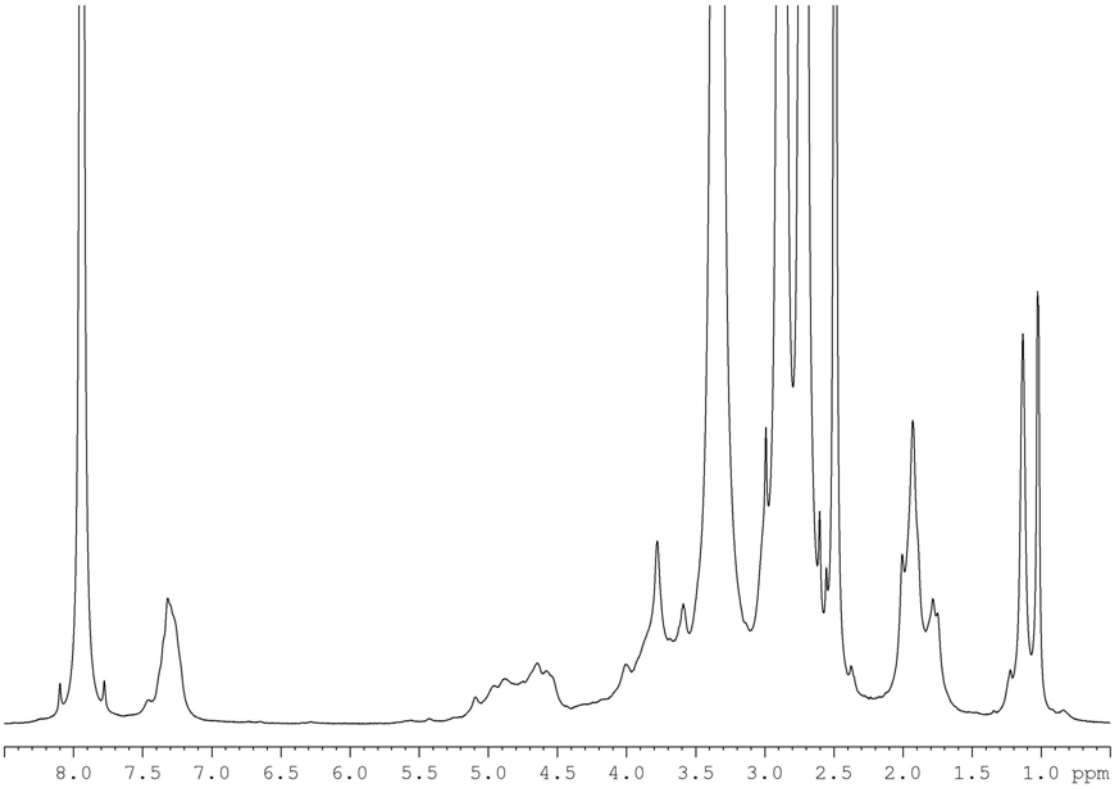

Figure S8: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **12-ii**

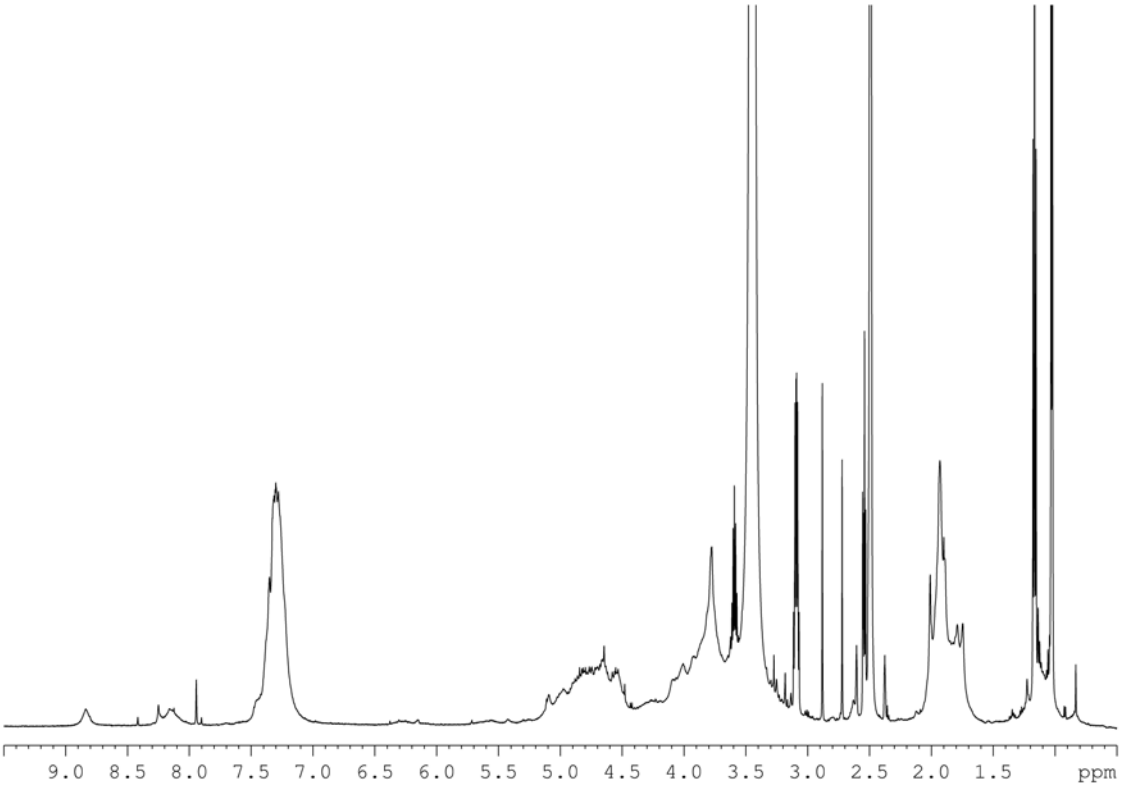

Figure S9: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **12-iii**

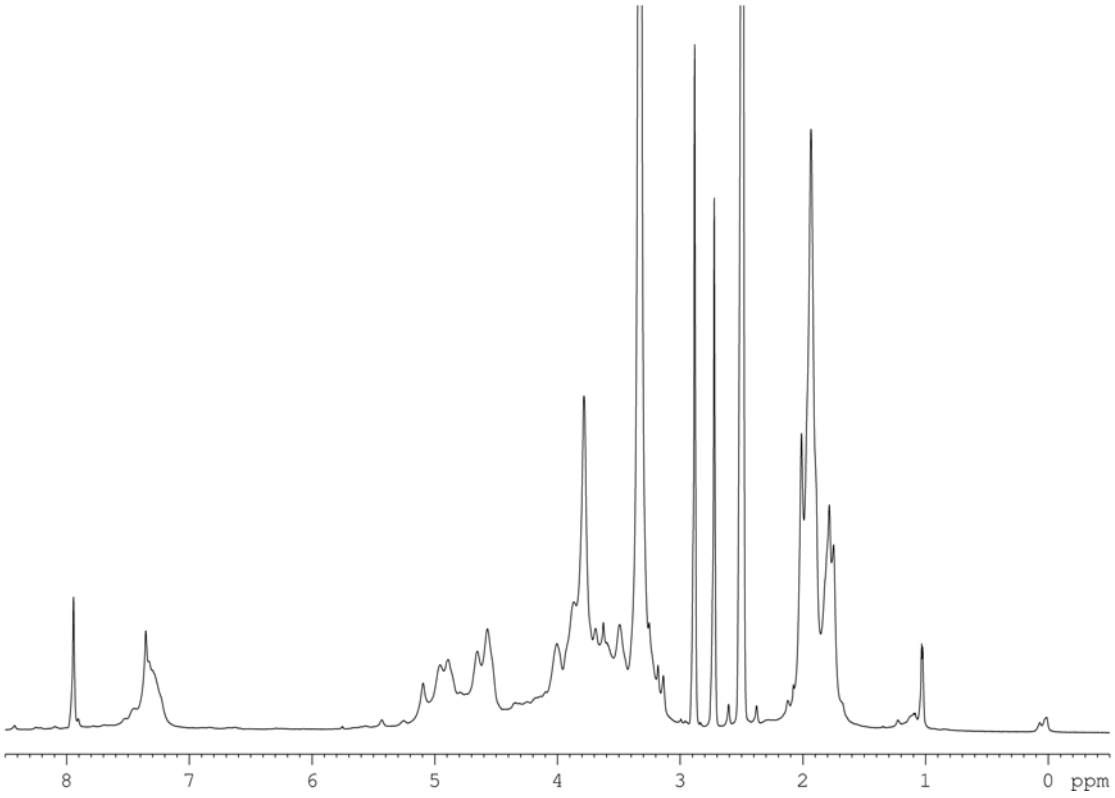

Figure S10: ^{1}H-NMR spectrum (600 MHz, DMSO-d_6, 298 K) of **12-iv**

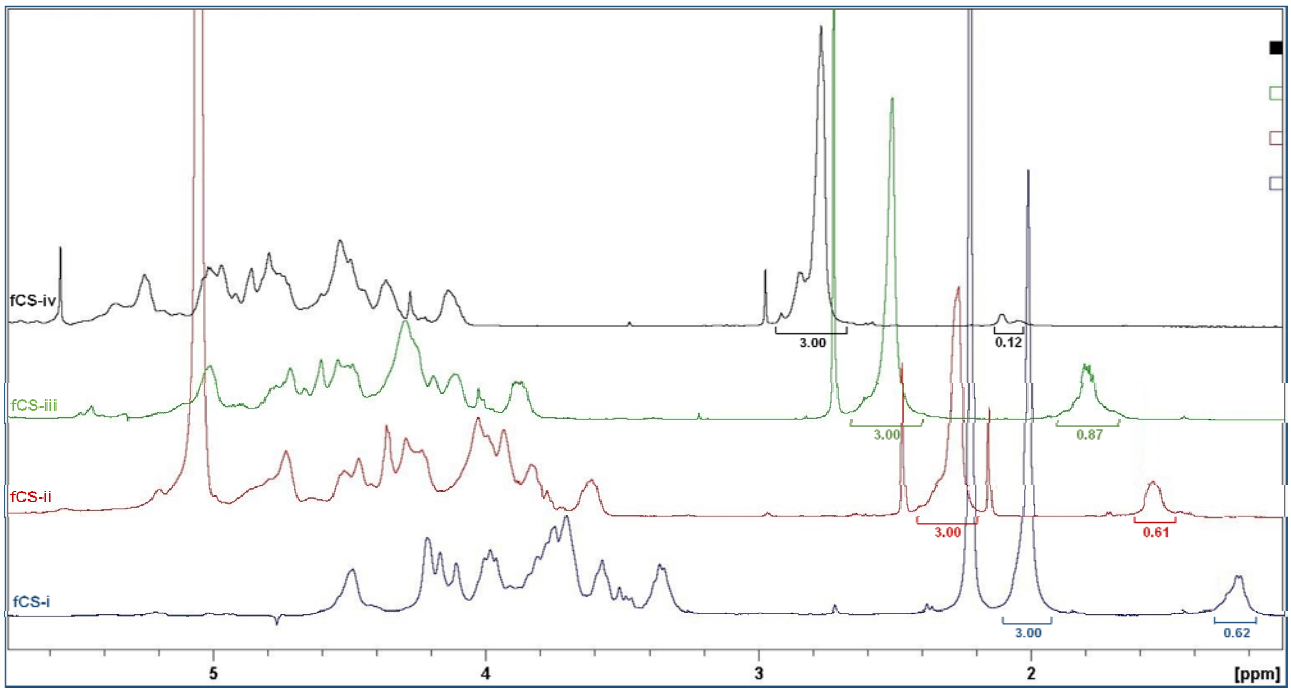

Figure S11: Stacked (with a $\Delta\delta$ = 0.25 ppm shift) ^{1}H-NMR spectra (600 MHz, D_2O, 298 K) of **fCS-i-iv**. Integration values are relative to signals, from left to right, of *N*-acetyl methyl protons at δ_H 2.10-1.95 ppm and of Fuc methyl protons at δ_H 1.35-1.20 ppm

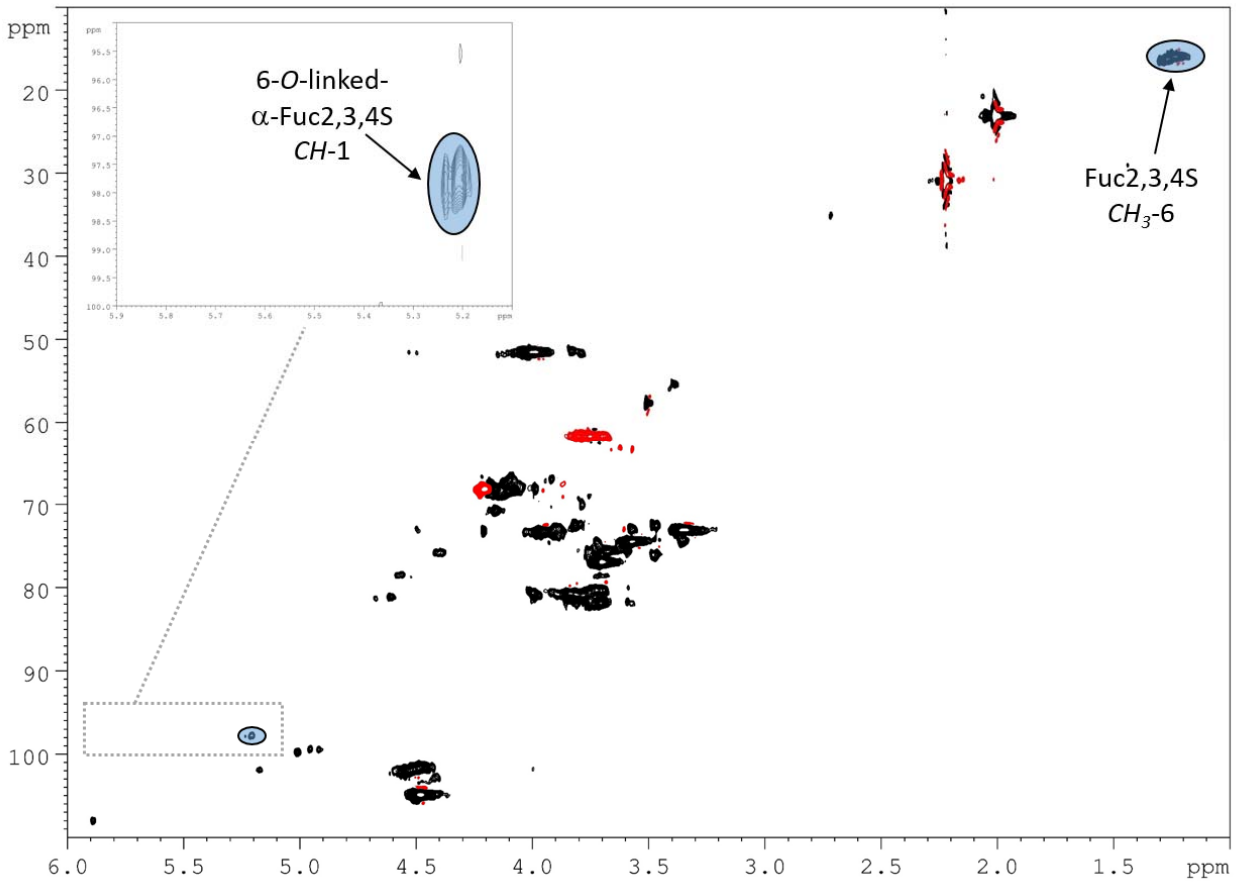

Figure S12: DEPT-HSQC NMR spectrum (600 MHz, D_2O, 298K) of **fCS-i**

(densities enclosed in the highlighted areas were integrated for α/β Fuc and GalNAc *O*-6/*O*-4 branching site ratio)

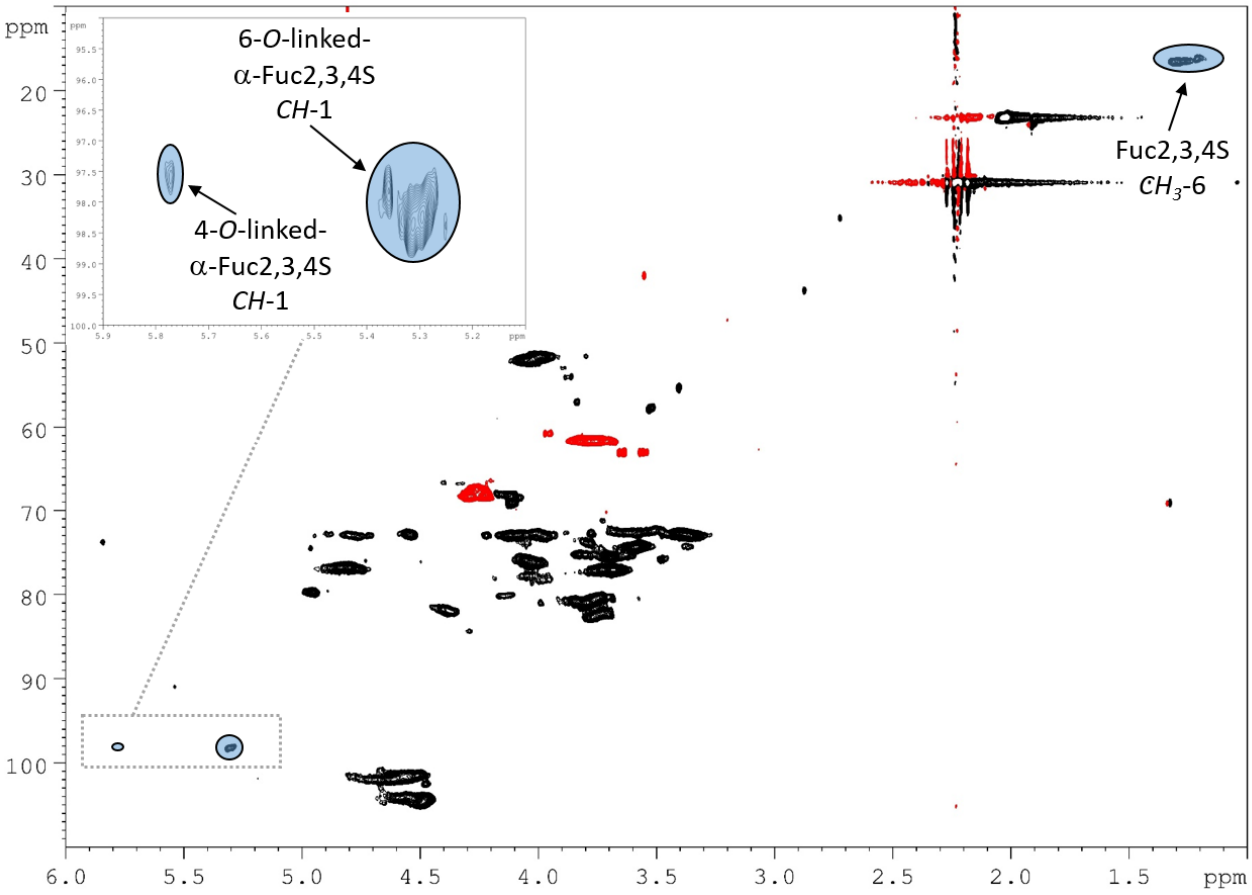

Figure S13: DEPT-HSQC NMR spectrum (600 MHz, D_2O, 298K) of **fCS-ii**

(densities enclosed in the highlighted areas were integrated for α/β Fuc and GalNAc *O*-6/*O*-4 branching site ratio)

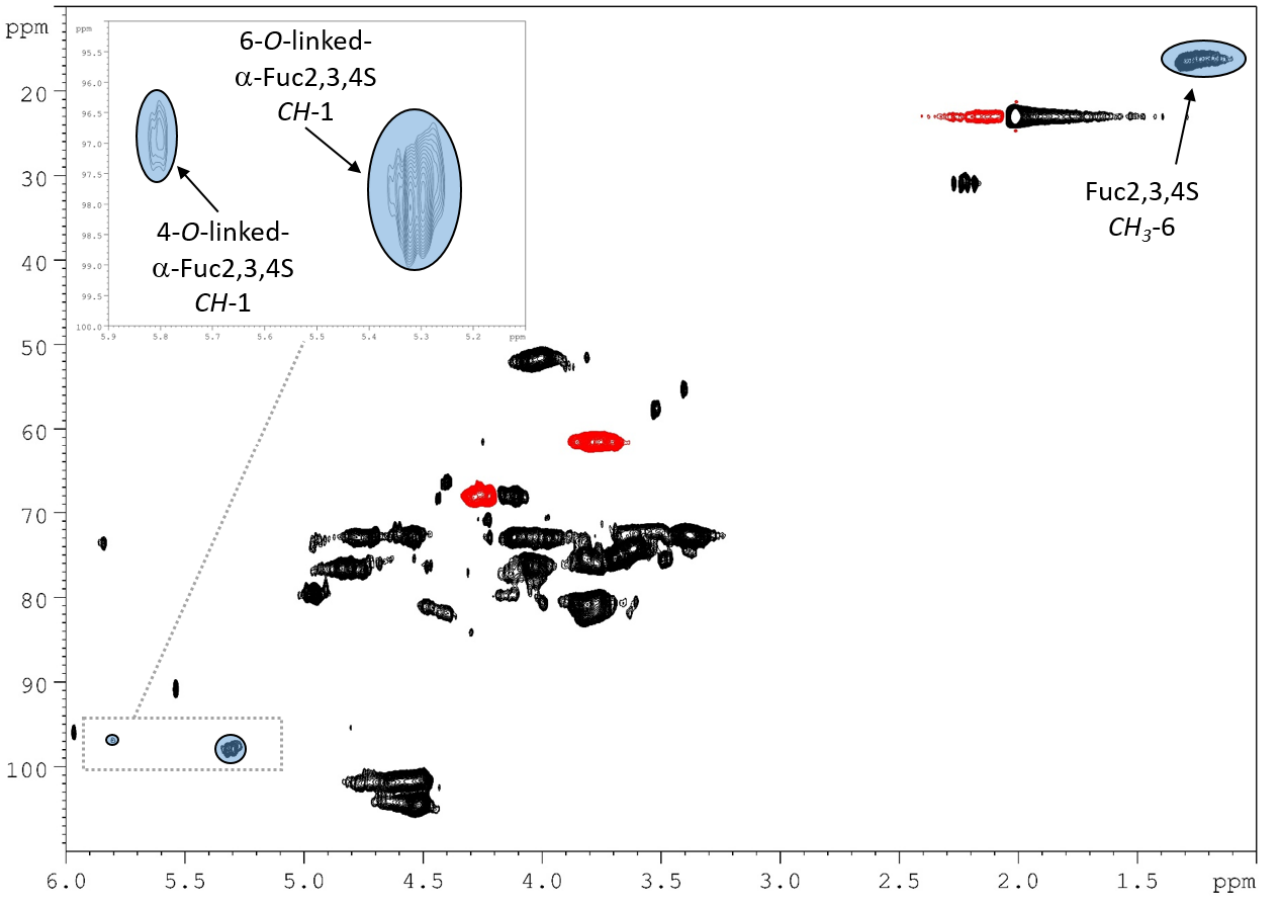

Figure S14: DEPT-HSQC NMR spectrum (600 MHz, D_2O, 298K) of **fCS-iii**

(densities enclosed in the highlighted areas were integrated for α/β Fuc and GalNAc *O*-6/*O*-4 branching site ratio)

References

S1. A. Laezza, A. Iadonisi, A. V. A. Pirozzi, P. Diana, M. De Rosa, C. Schiraldi, M. Parrilli, E. Bedini, *Chem. Eur. J.* **2016**, *22*, 18215–18226