

Supporting information to:

Synthesis of Azide-Modified Chondroitin Sulfate Precursors: Substrates for 'Click'- Conjugation with Fluorescent Labels and Oligonucleotides

Satish Jadhav,^{*a,b} Vijay Gulumkar,^a Prasannakumar Deshpande,^c Eleanor T. Coffey,^c Harri Lönnberg,^a and Pasi Virta^{*a}

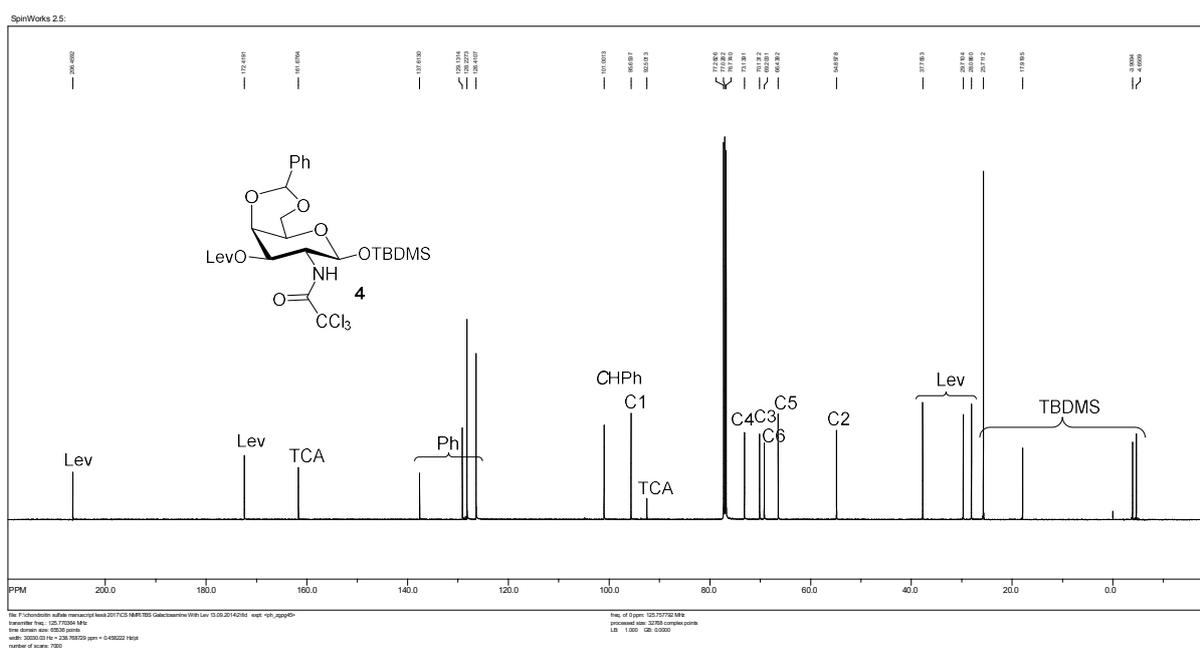
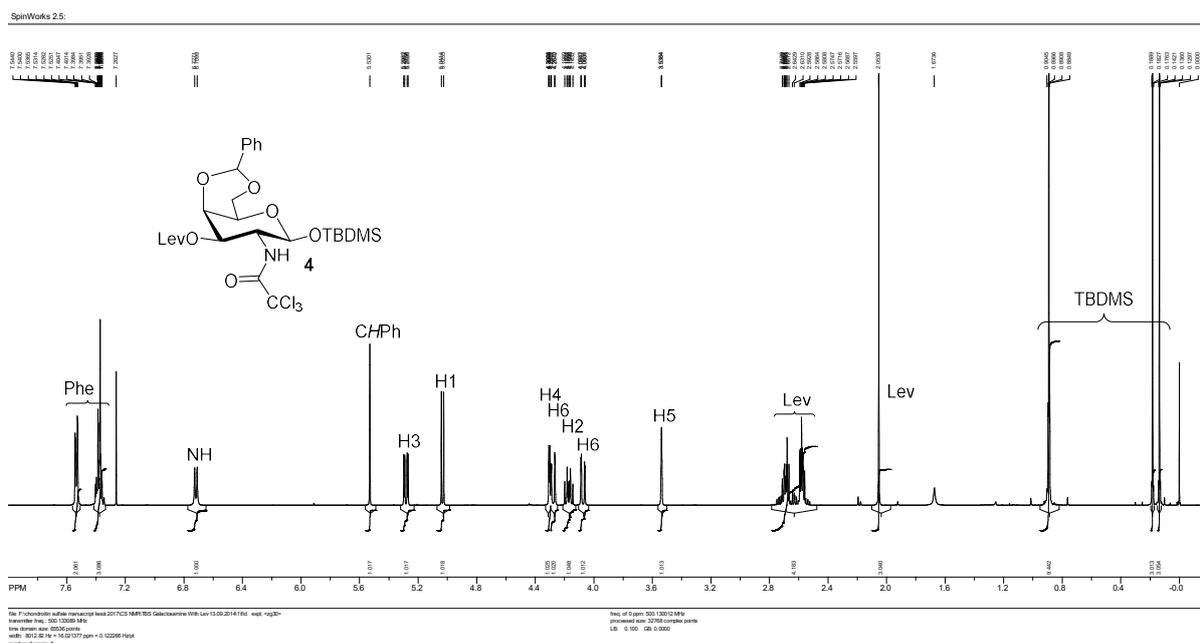
a) Department of Chemistry, University of Turku, Vatselankatu 2, FI-20014 Turku, Finland

b) Department of Cellular and Molecular Medicine, School of Medicine, University of California, San Diego, La Jolla, CA 92093, USA

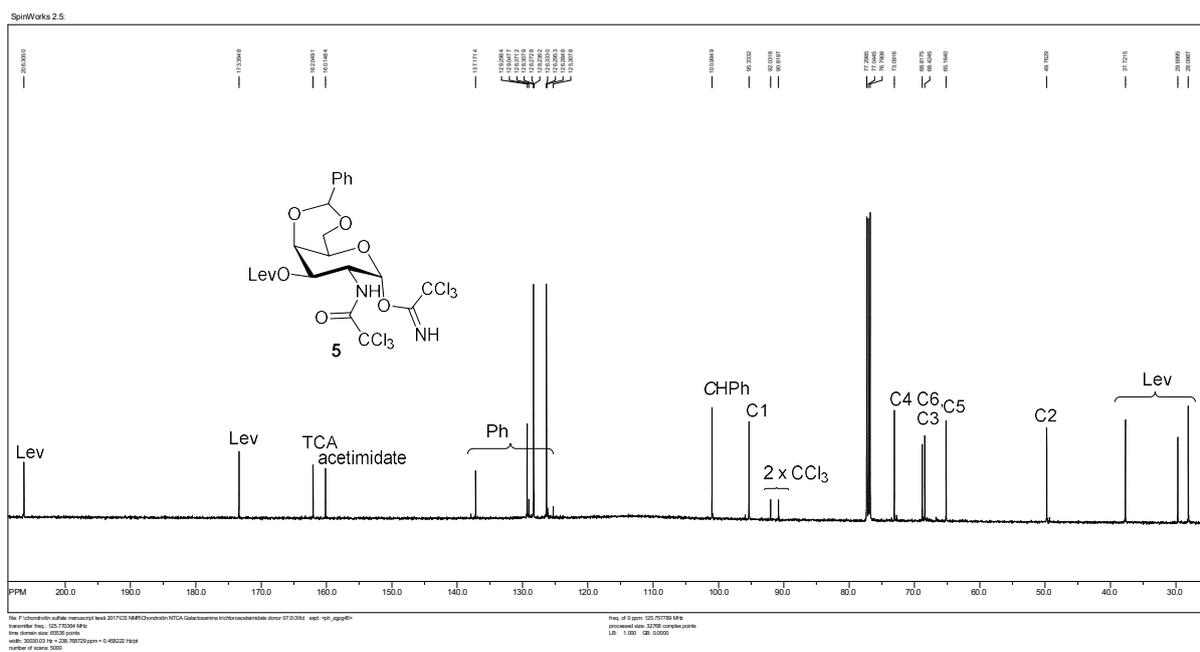
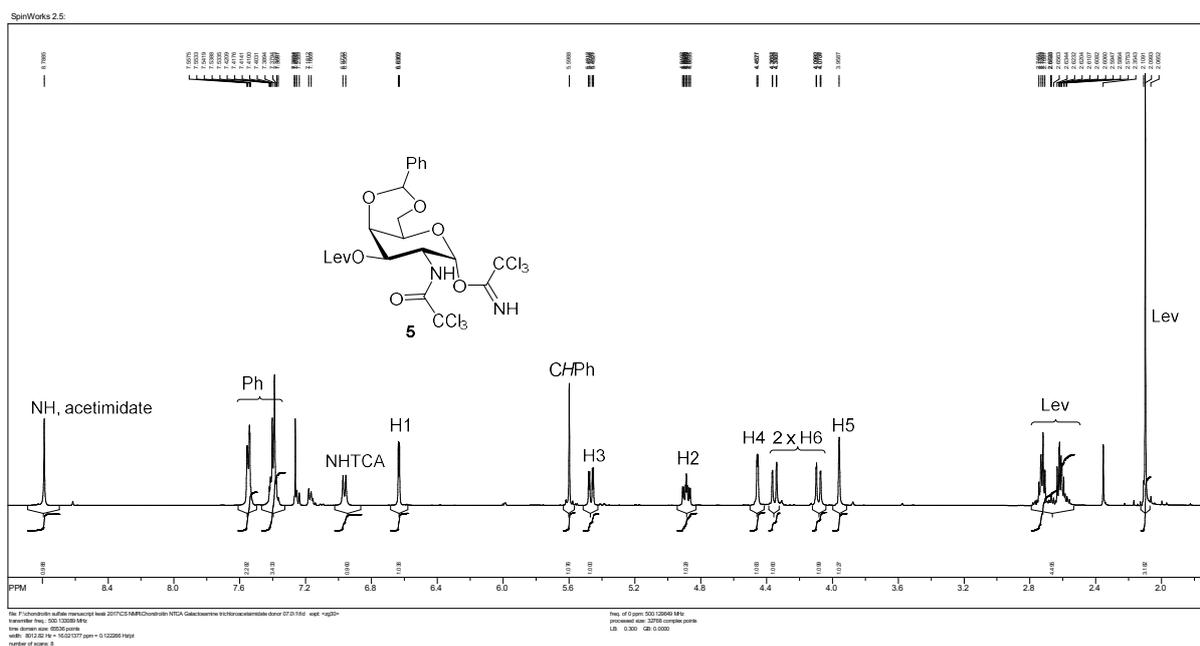
c) Turku Centre for Biotechnology, University of Turku, Åbo Akademi University, Tykistökatu 6, FI-20520 Turku, Finland

Contents

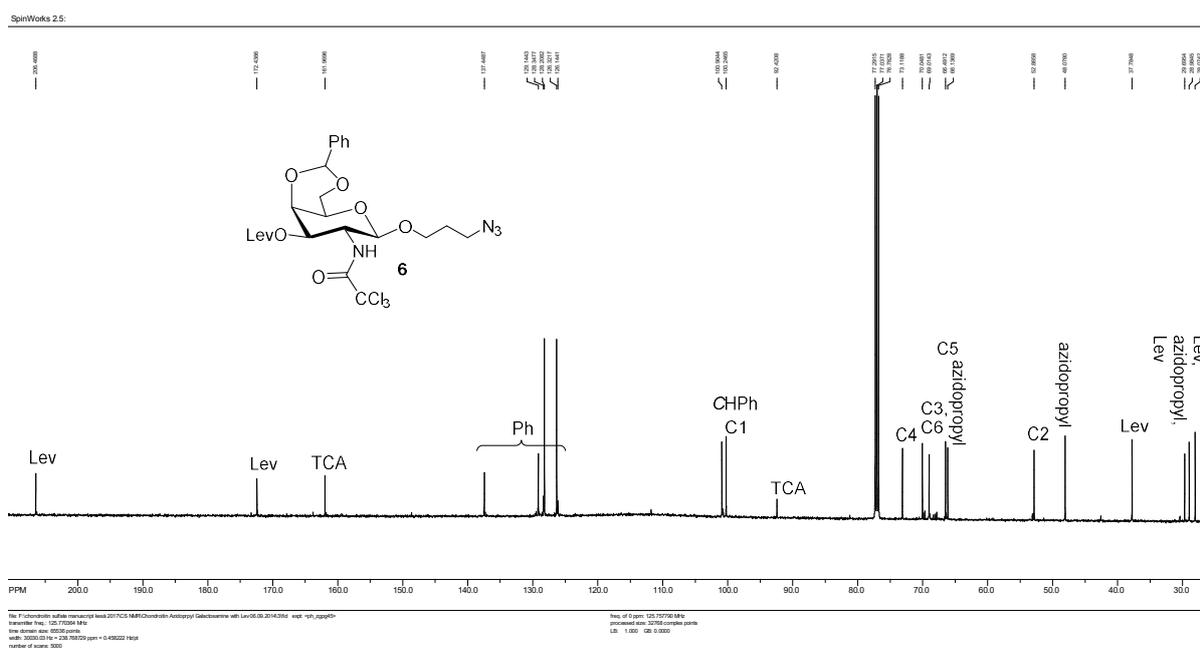
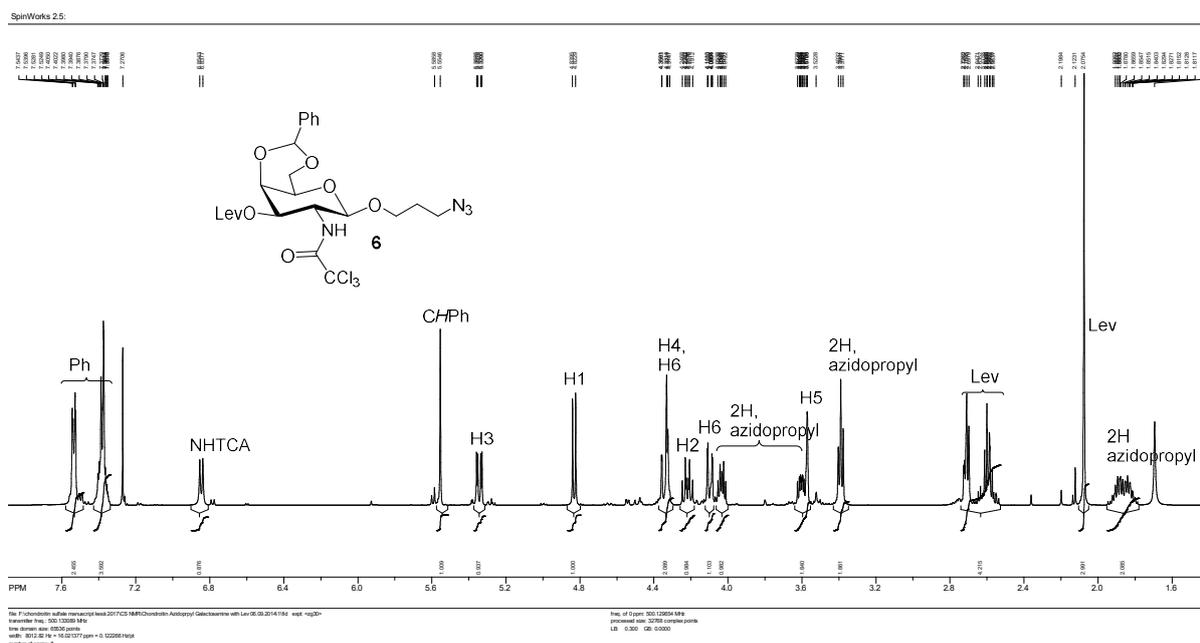
Figures S1. ¹ H and ¹³ C NMR spectrum of 2	S2
Figures S2. ¹ H and ¹³ C NMR spectrum of 3	S3
Figures S3. ¹ H and ¹³ C NMR spectrum of 4	S4
Figures S4. ¹ H and ¹³ C NMR spectrum of 5	S5
Figures S5. ¹ H and ¹³ C NMR spectrum of 6	S6
Figures S6. ¹ H and ¹³ C NMR spectrum of 7	S7
Figures S7. ¹ H NMR spectra of 9	S8
Figures S8. ¹³ C NMR spectra of 9	S9
Figures S9. ¹ H NMR spectra of 10	S10
Figures S10. ¹³ C NMR spectra of 10	S11
Figures S11. ¹ H NMR spectra of 11	S12
Figures S12. ¹³ C NMR spectra of 11 .	S13
Figures S13. ¹ H NMR and HSQC spectrum of 12 .	S14
Figures S14. ¹³ C NMR spectra of 12 .	S16
Figures S16. HSQC spectra of 13	S17
Figures S17. ¹³ C NMR spectra of 13	S18
Figures S18. ¹ H and ¹³ C NMR spectrum of 15	S19
Figures S19. ¹³ C NMR spectra of 15	S20
Figures S20. HSQC and COSY spectrum of 15	S21
Figure S21. HSQC spectrum of 15	S22
Figures S22. ¹ H NMR and COSY spectrum of 16	S23
Figures S23. ¹³ C NMR and HSQC spectrum of 16	S24
Figure S24. HSQC spectrum of 16	S25
Figures S25. ¹ H NMR and ¹³ C NMR spectrum of 18	S26
Figures S25. ¹ H and ¹³ C NMR spectrum of 18	S27
Figures S26. HSQC spectra of 18	S28
Figures S28. ¹³ C NMR and HSQC spectrum of 21	S29
Figure S29. HSQC spectrum of 21	S30
Figures S30. ¹ H NMR spectra of 23	S31
Figures S31. ¹³ C NMR and HSQC spectrum of 23	S32
Figure S32. HSQC spectrum of 23	S33
Figure S33. MS (ESI-TOF) spectrum of 24	S34
Figure S34. MS (ESI-TOF) spectrum of 25	S34
Figure S35. MS (ESI-TOF) spectrum of 26	S35
Figure S36. MS (ESI-TOF) spectrum of 29	S35
Figure S37. MS (ESI-TOF) spectrum of 30	S36
Figure S38. MS (ESI-TOF) spectra of 32-33	S37



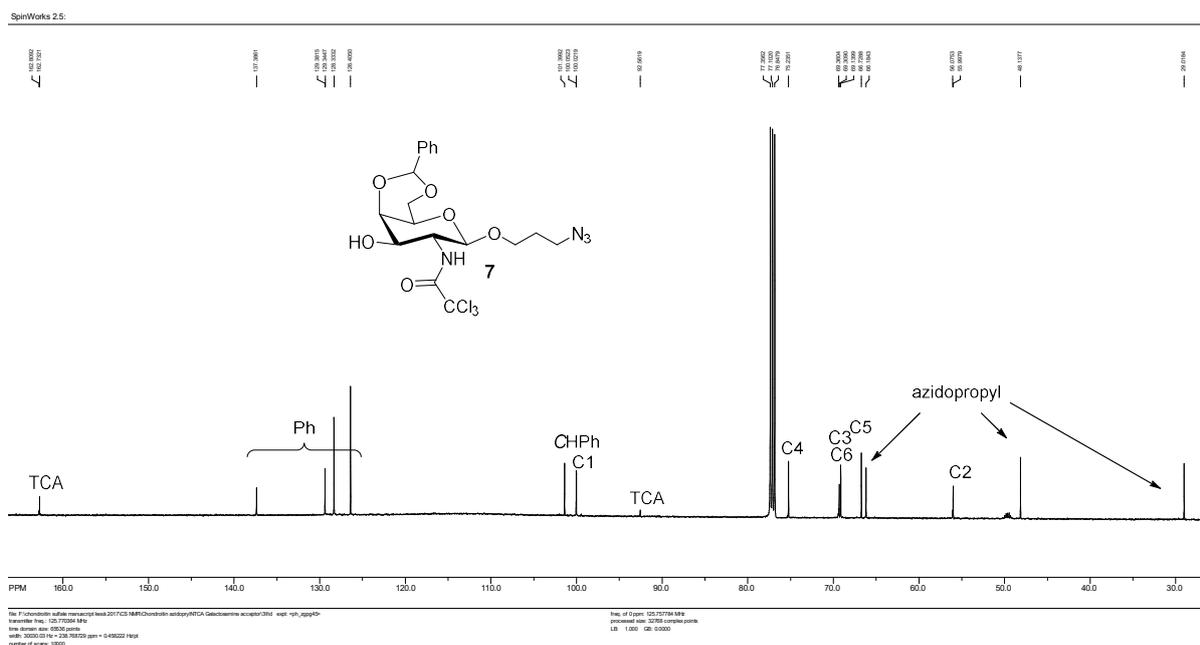
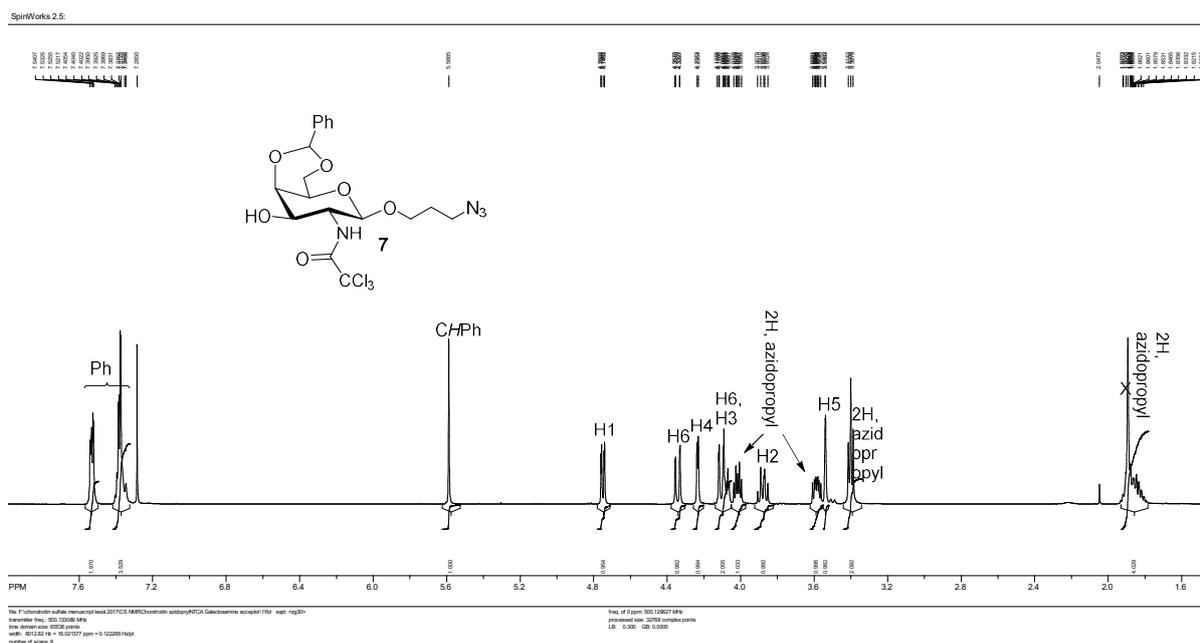
Figures S3. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **4**.



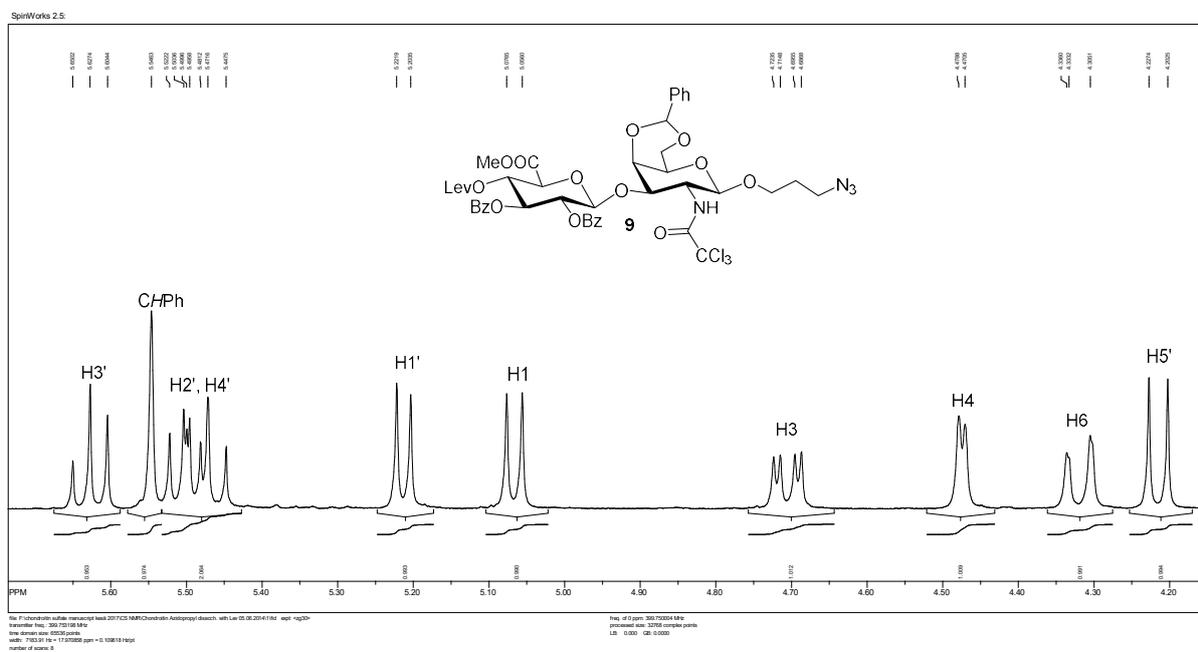
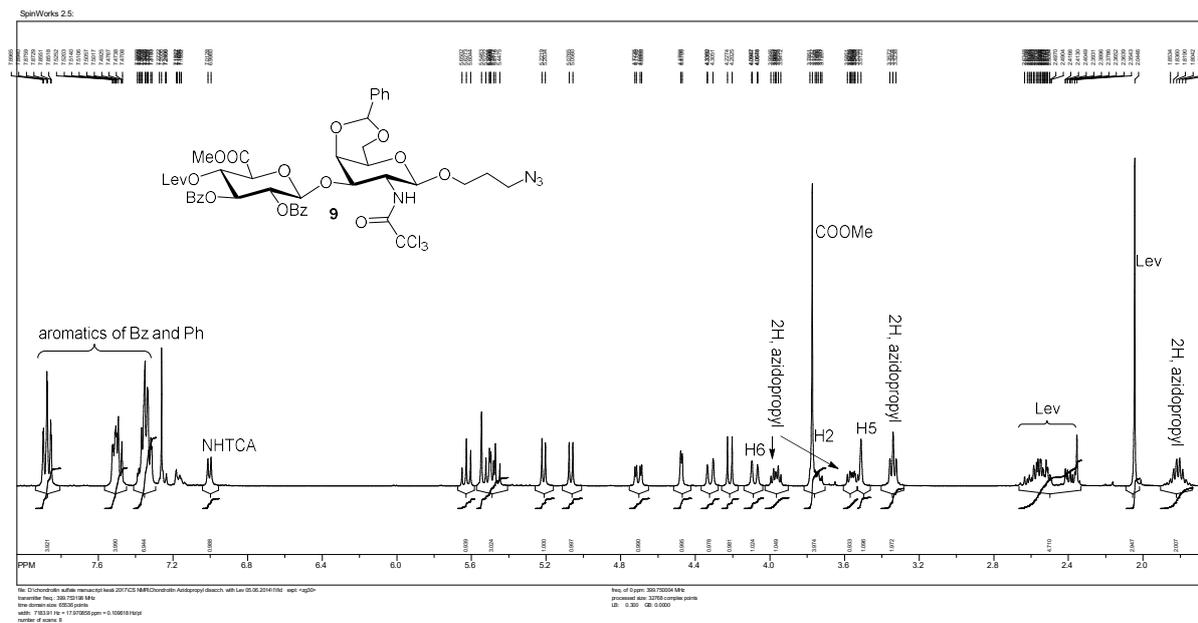
Figures S4. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **5**.



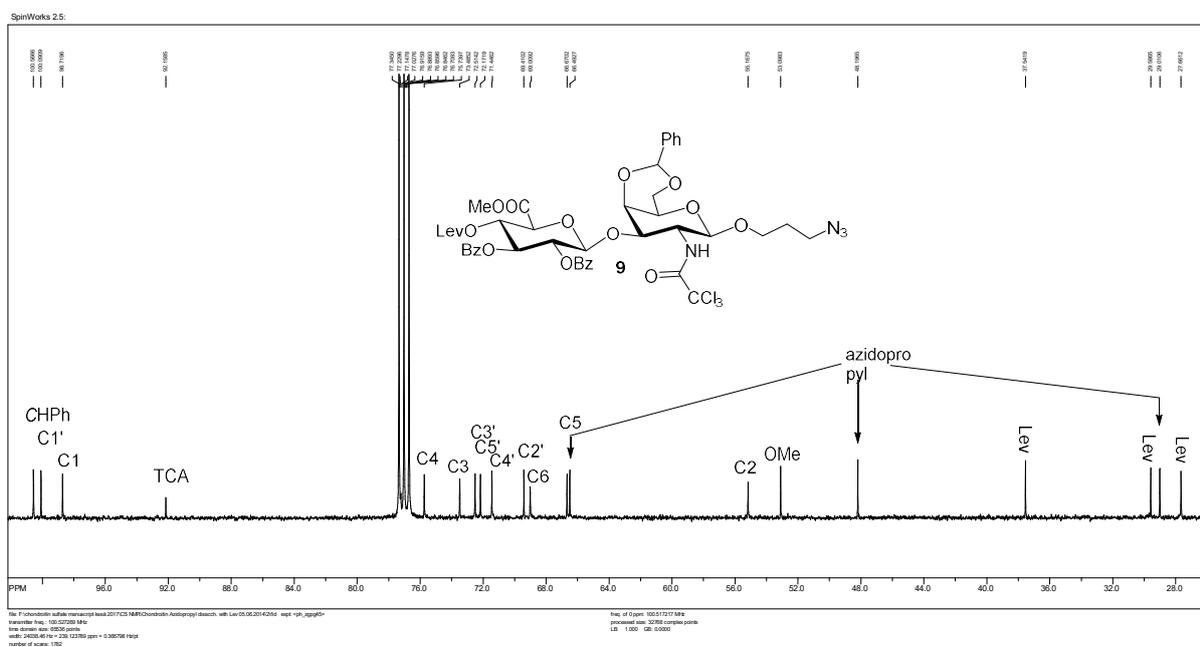
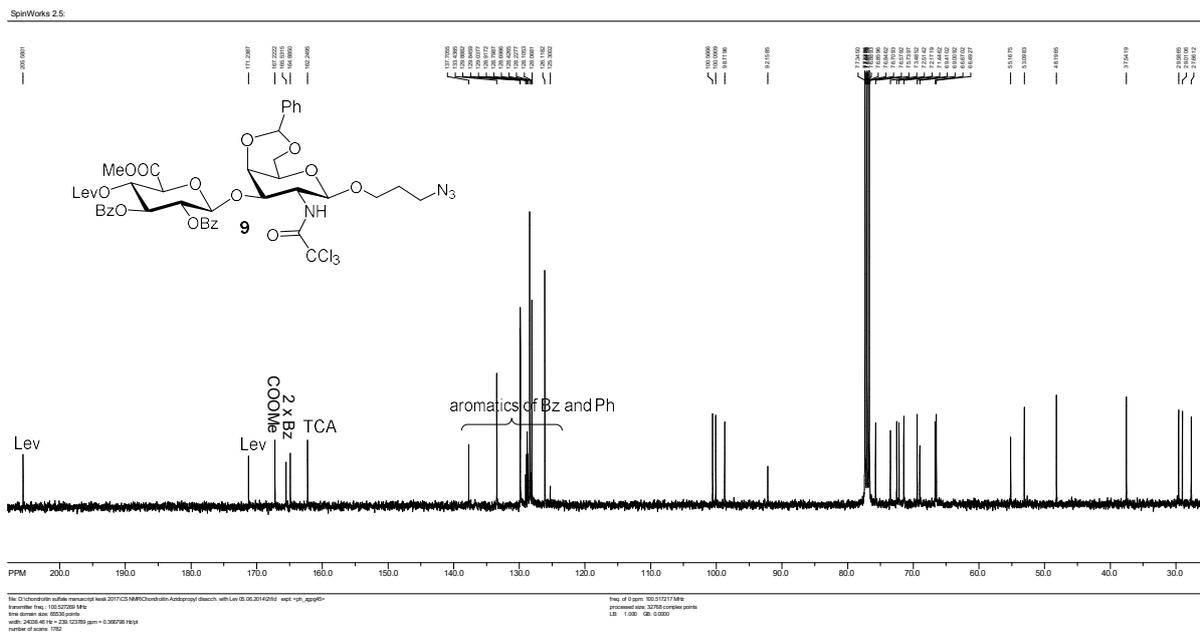
Figures S5. ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃) spectrum of **6**.



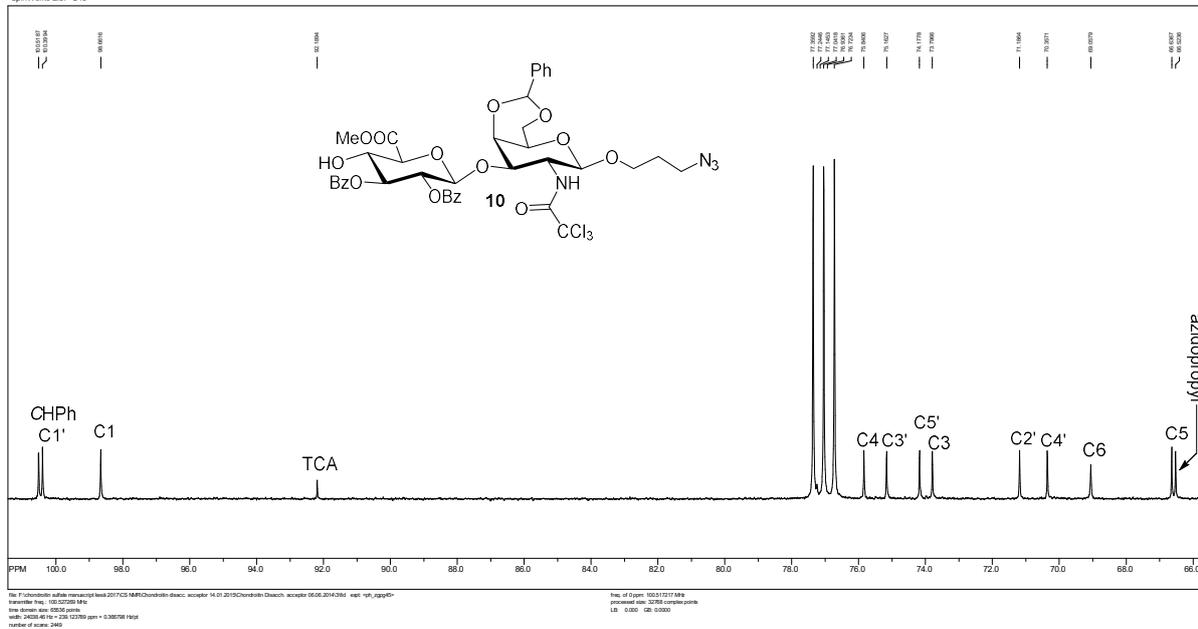
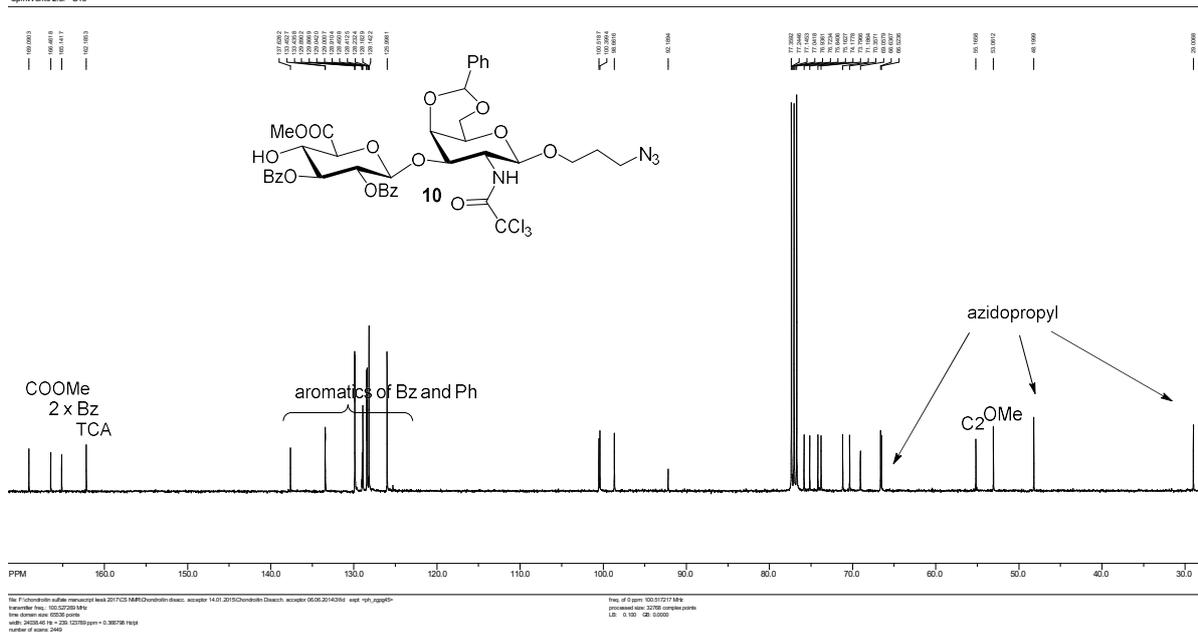
Figures S6. ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) spectrum of **7**.



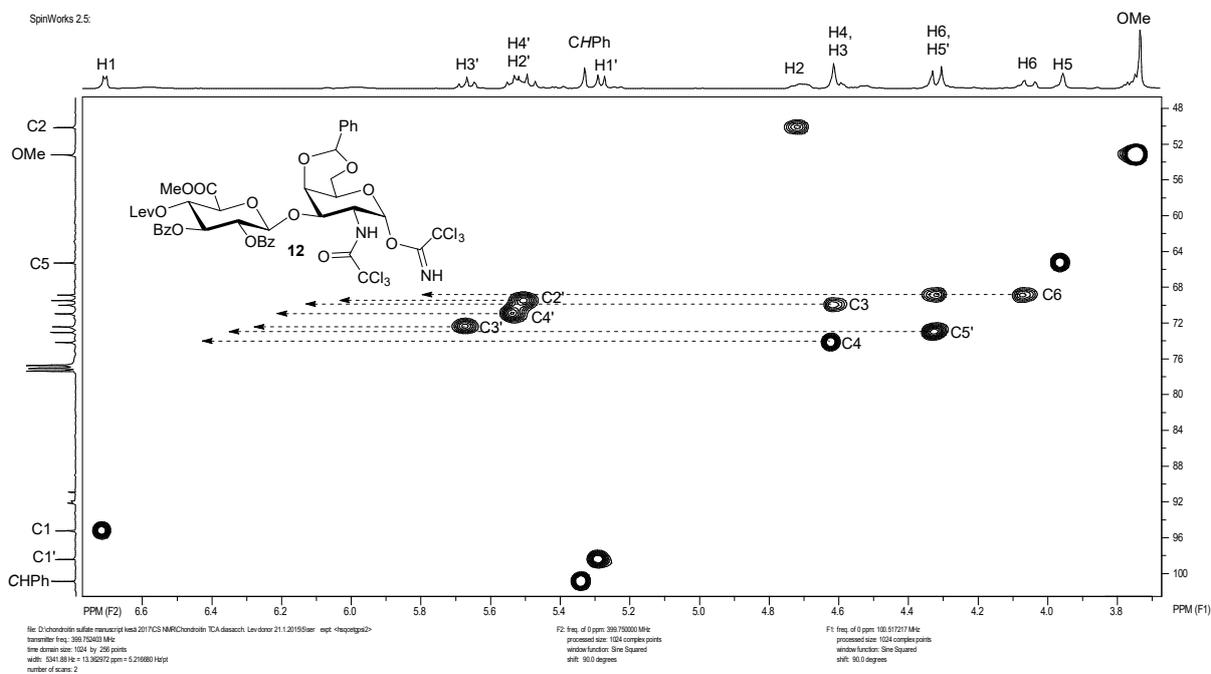
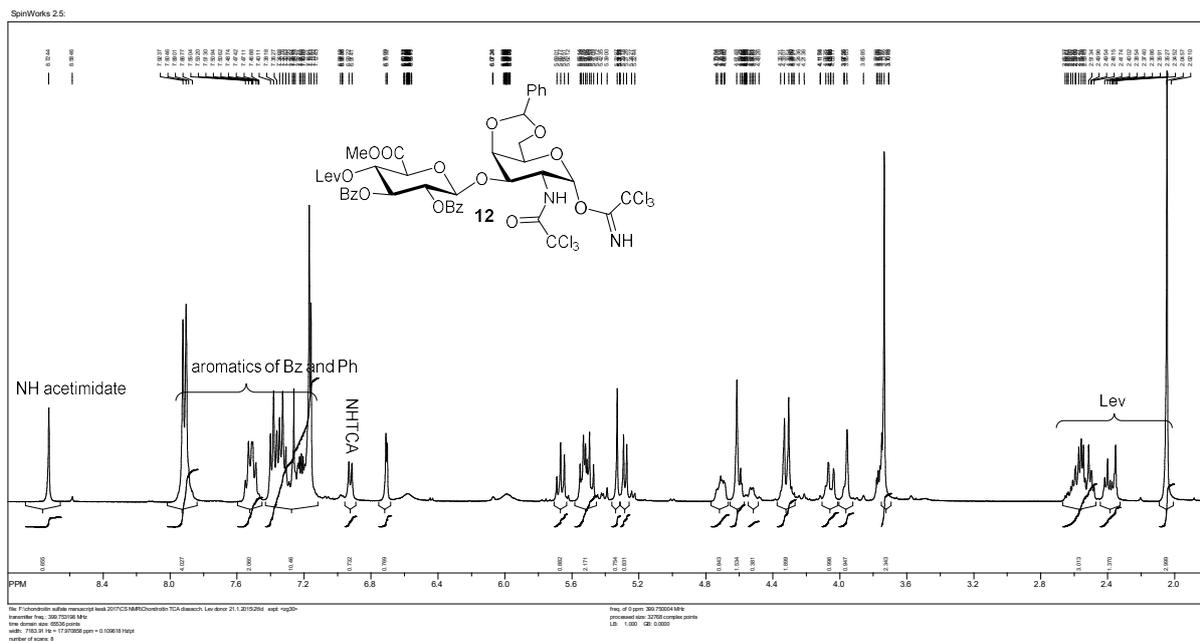
Figures S7. ¹H NMR (400 MHz, CDCl₃) spectra of **9**.



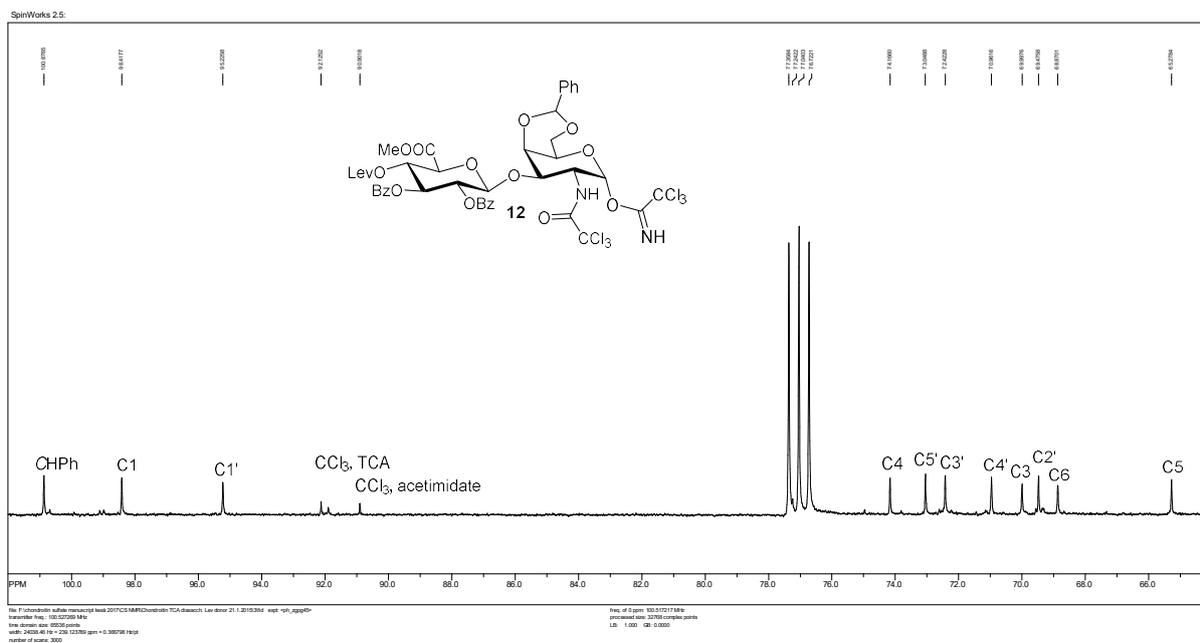
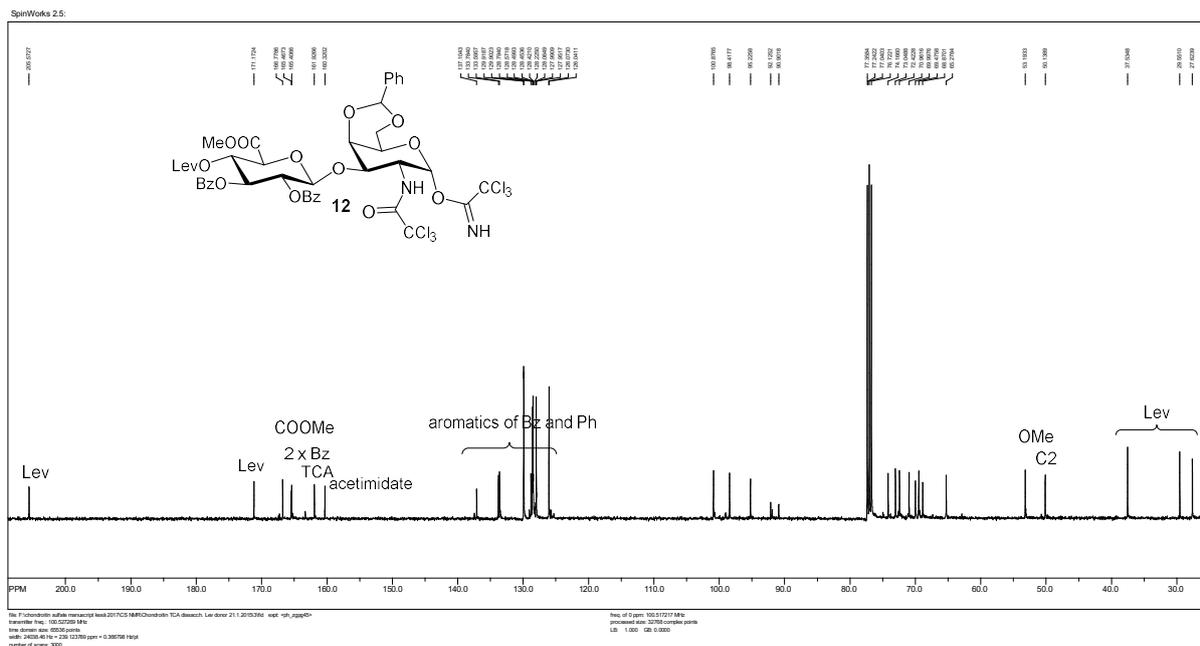
Figures S8. ¹³C NMR (100 MHz, CDCl₃) spectra of 9.



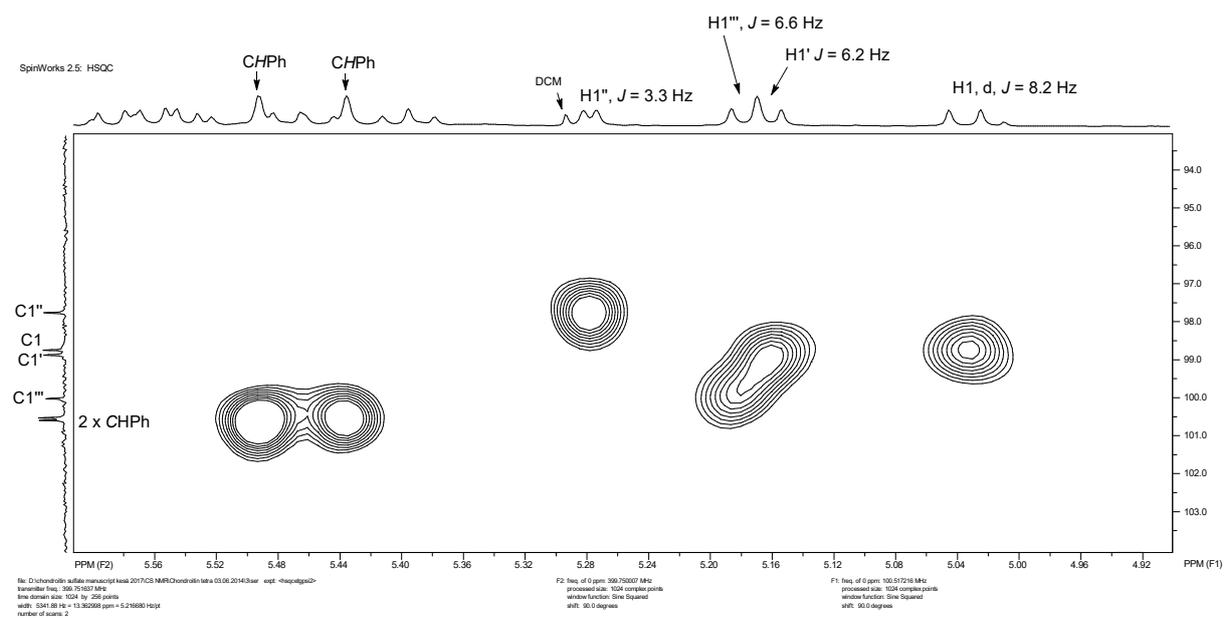
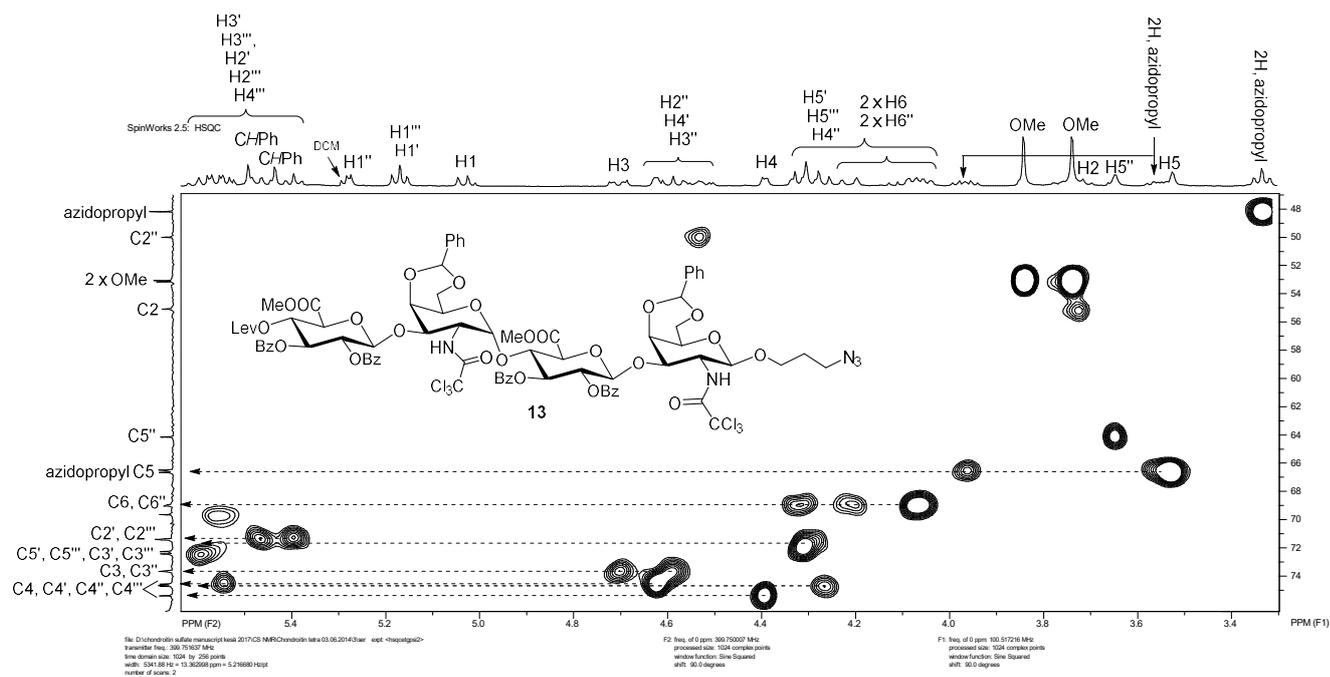
Figures S10. ¹³C NMR (100 MHz, CDCl₃) spectra of **10**.



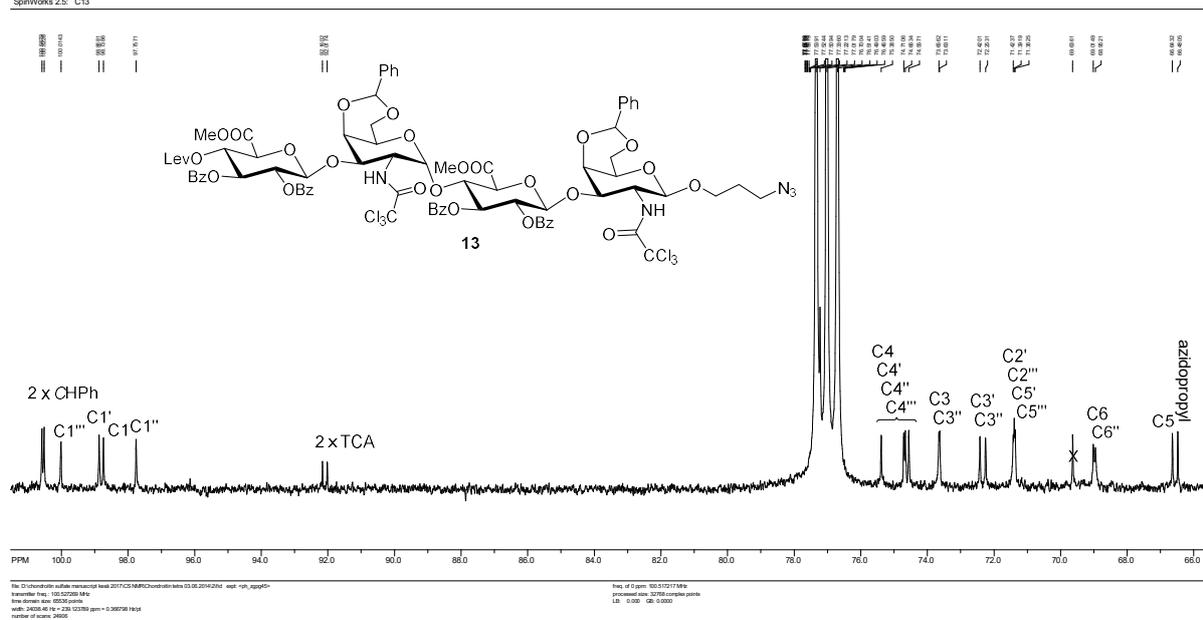
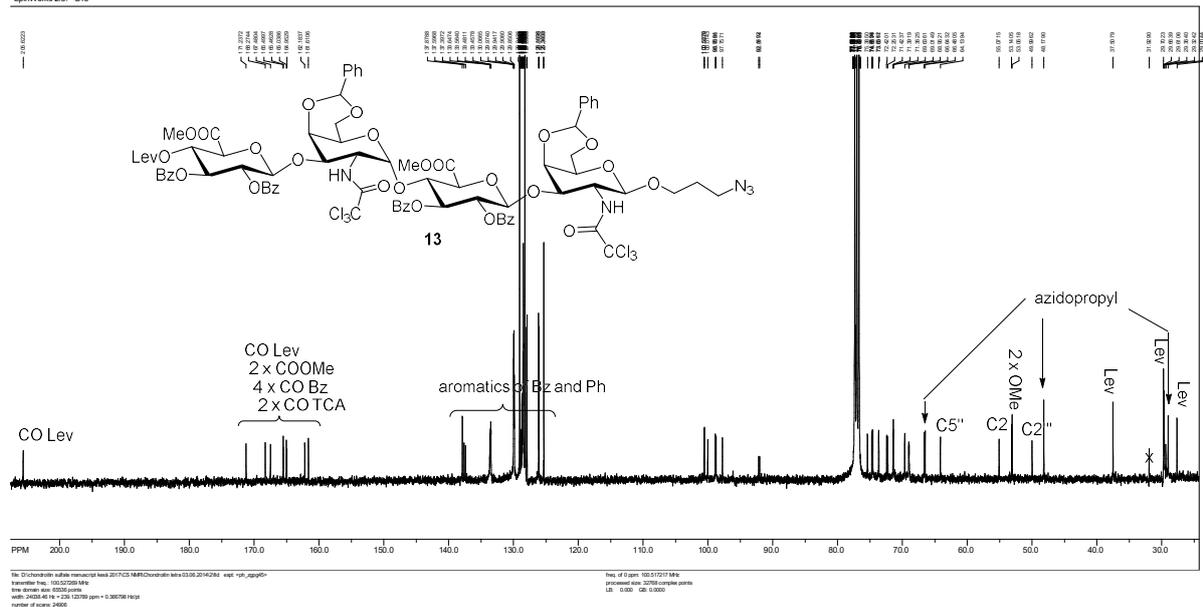
Figures S13. ¹H NMR (400 MHz, CDCl₃) and HSQC spectrum of **12**.



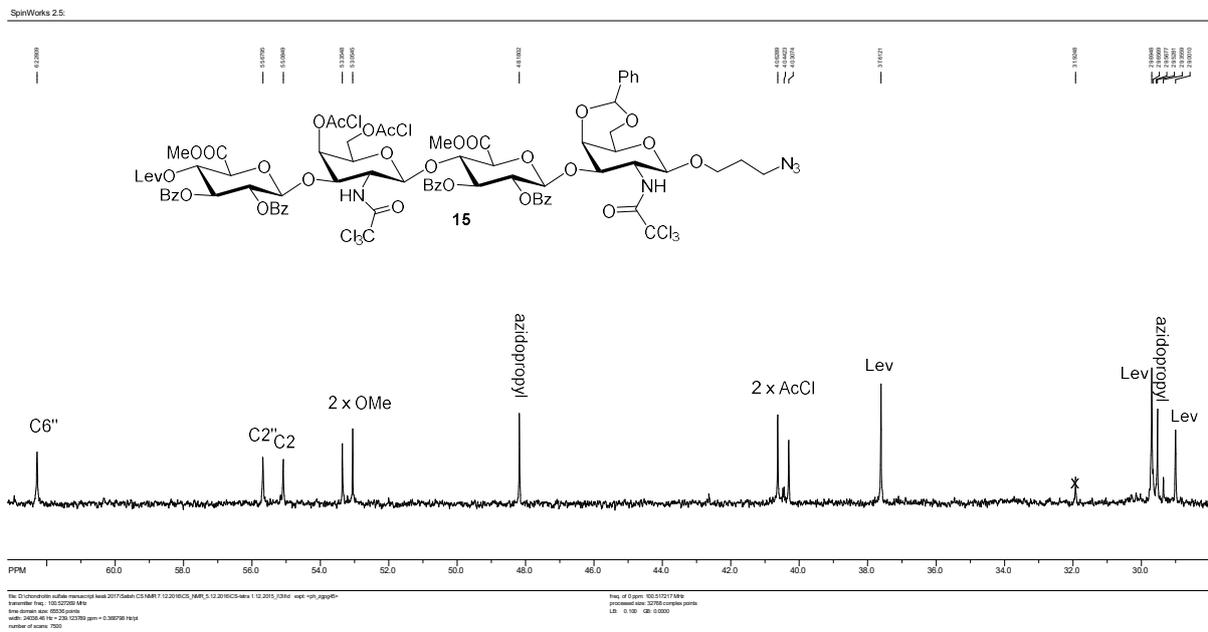
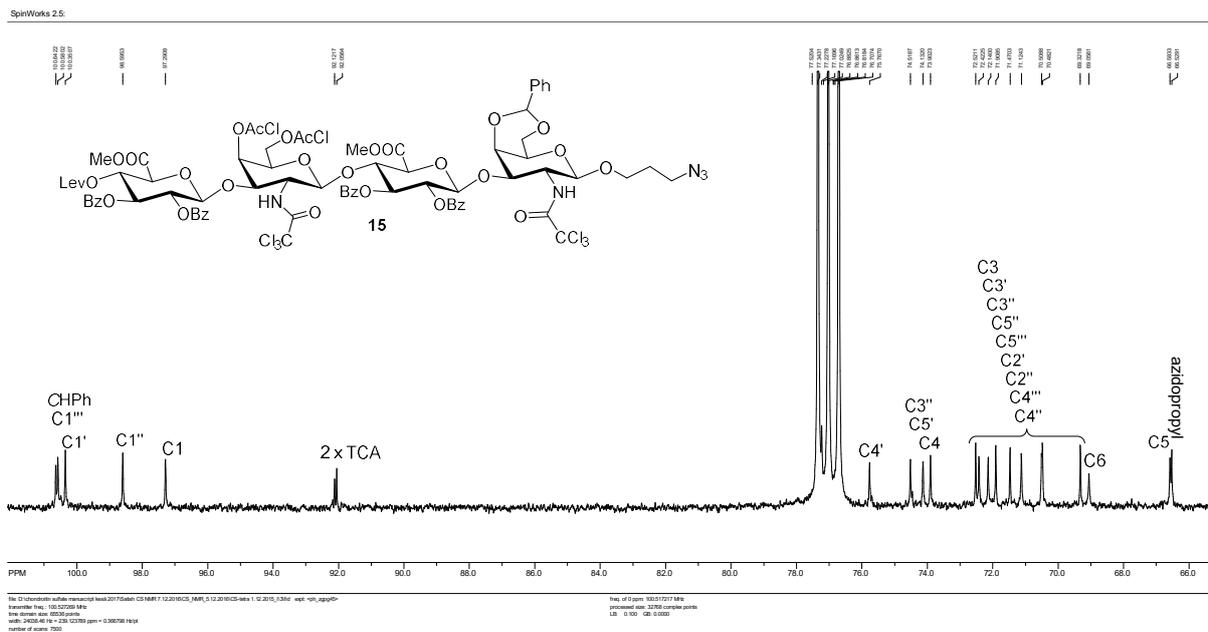
Figures S14. ^{13}C NMR (100 MHz, CDCl_3) spectra of **12**.



Figures S16. HSQC spectra of **13**.



Figures S17. ¹³C NMR (100 MHz, CDCl₃) spectra of 13.



Figures S19. ¹³C NMR (100 MHz, CDCl₃) spectra of **15**.

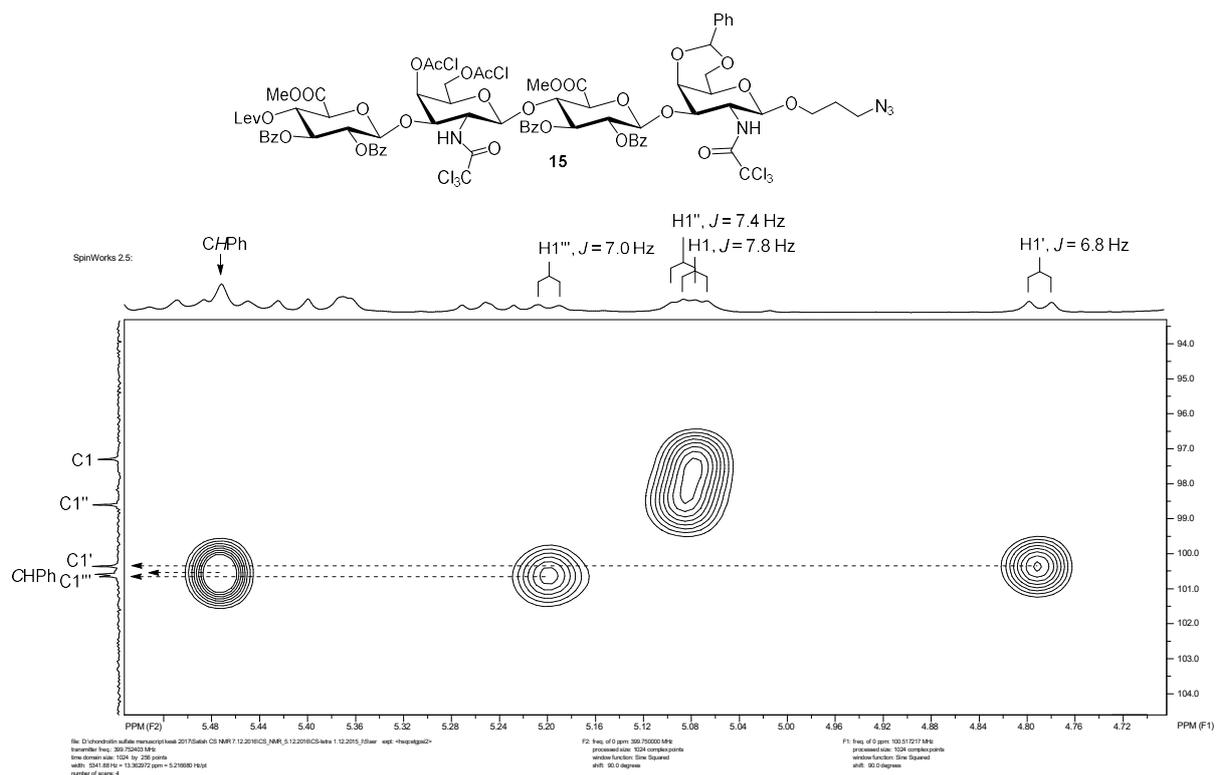
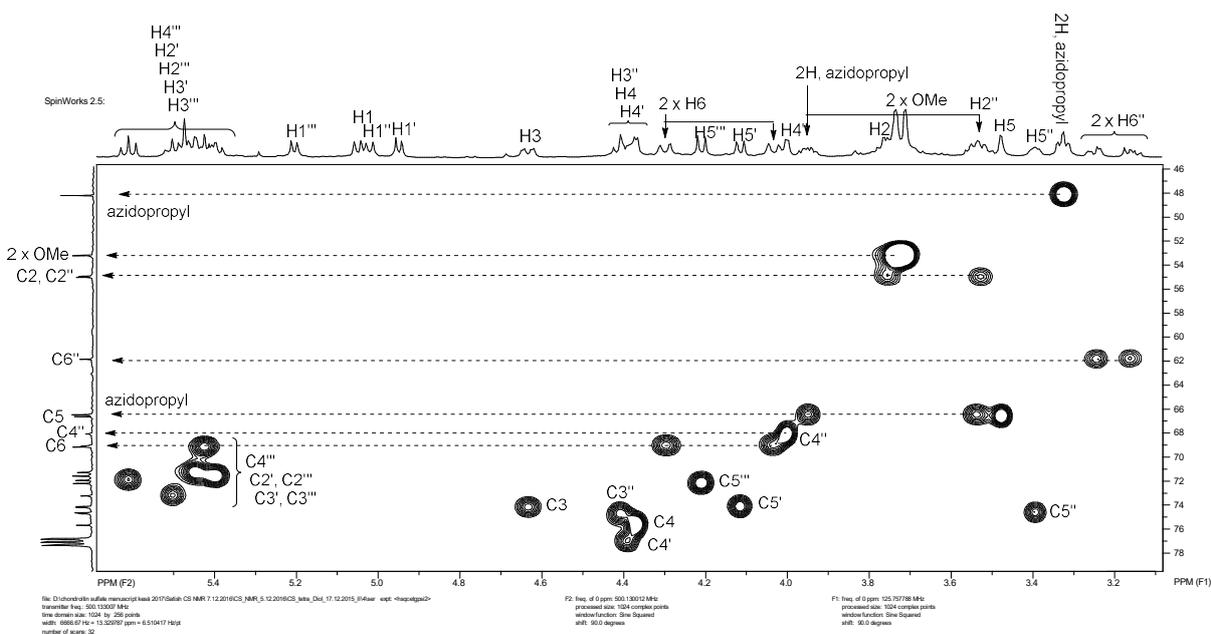
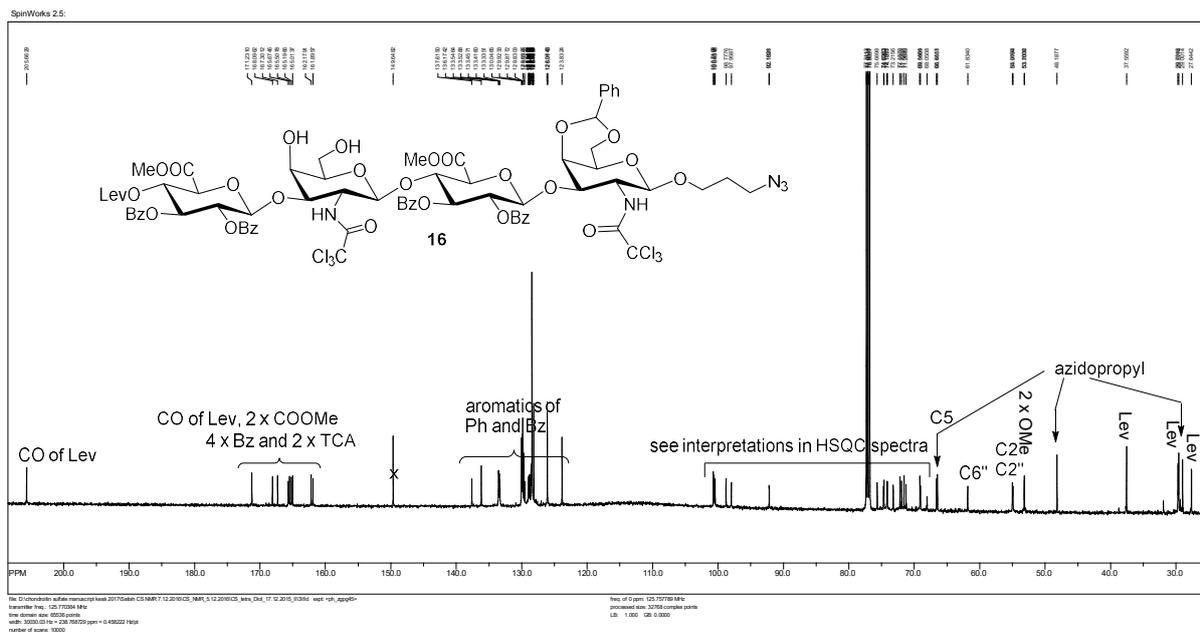


Figure S21. HSQC spectrum of **15**.



Figures S23. ¹³C NMR (125MHz, CDCl₃) and HSQC spectrum of **16**.

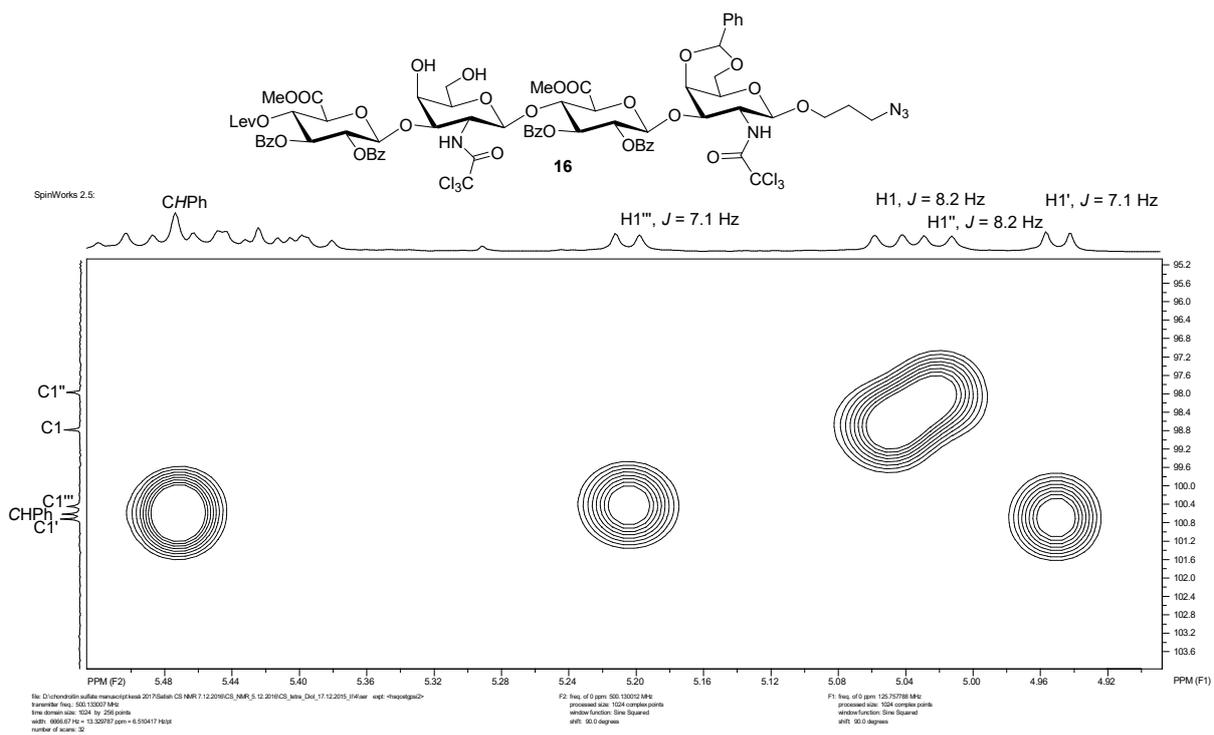
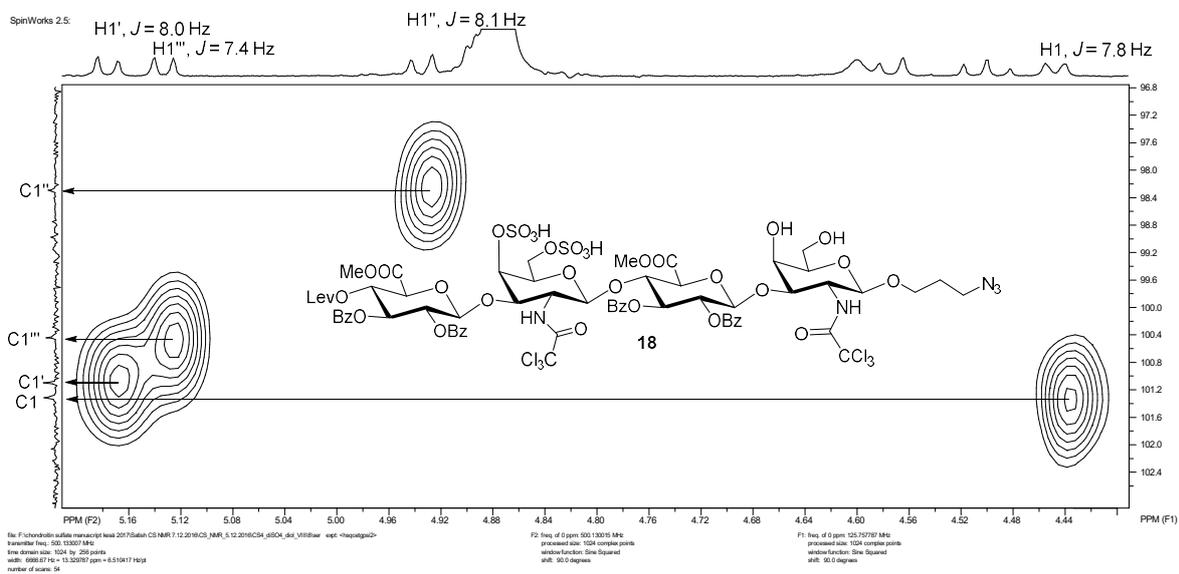
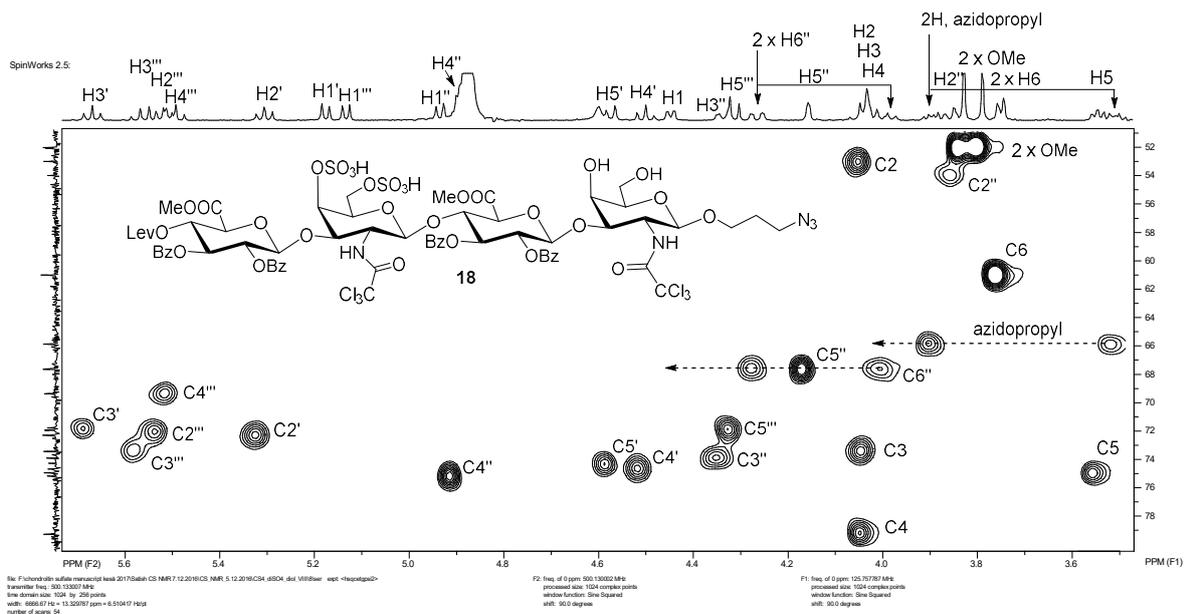
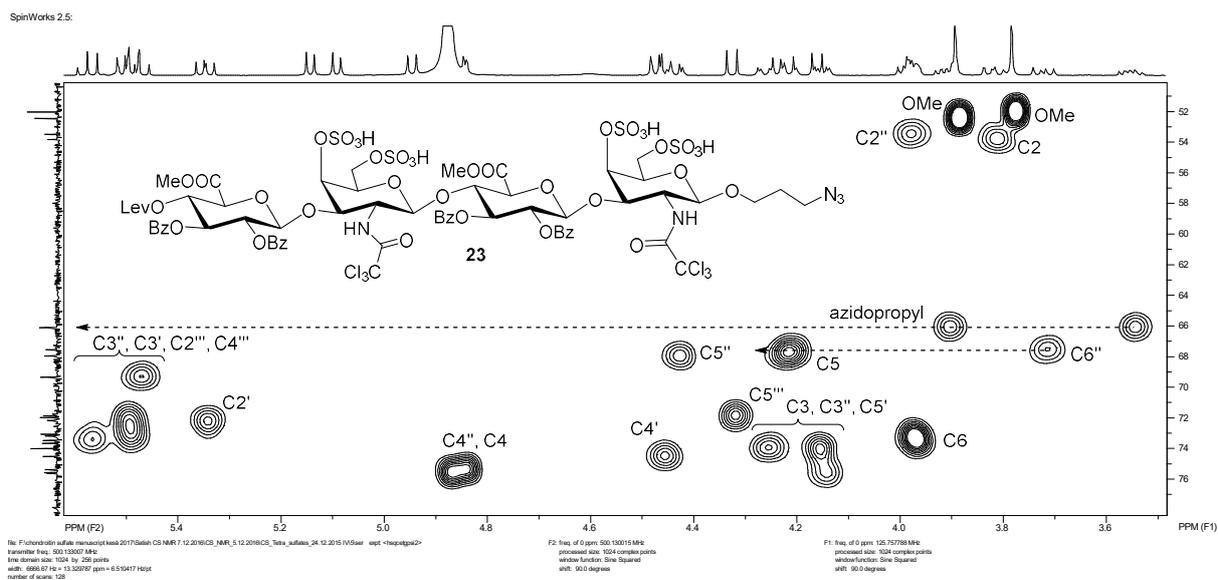
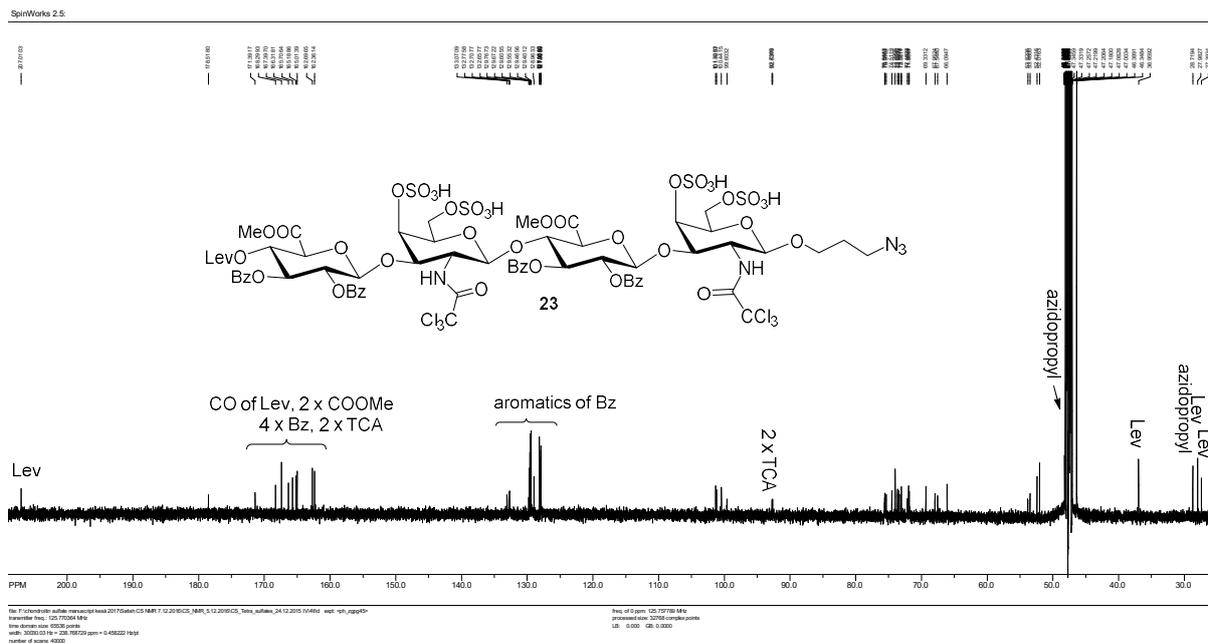


Figure S24. HSQC spectrum of **16**.



Figures S26. HSQC spectra of **18**.



Figures S31. ¹³C NMR (500 MHz, CD₃OH) and HSQC spectrum of **23**.

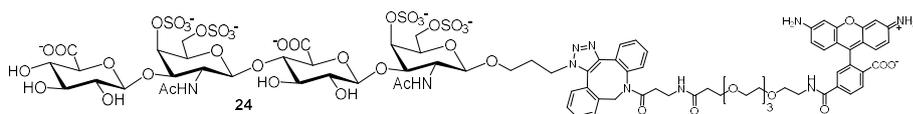
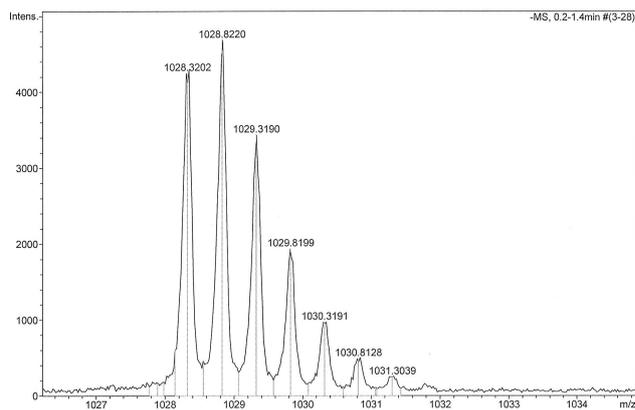


Figure S33. MS (ESI-TOF) spectrum of **24**. The observed monoisotopic mass: 1028.32 [(M-2H)/2]²⁻

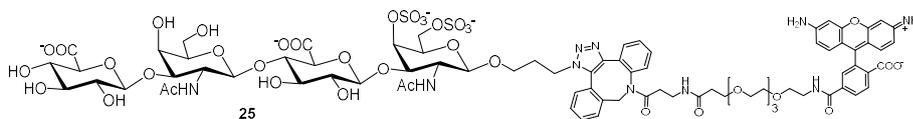
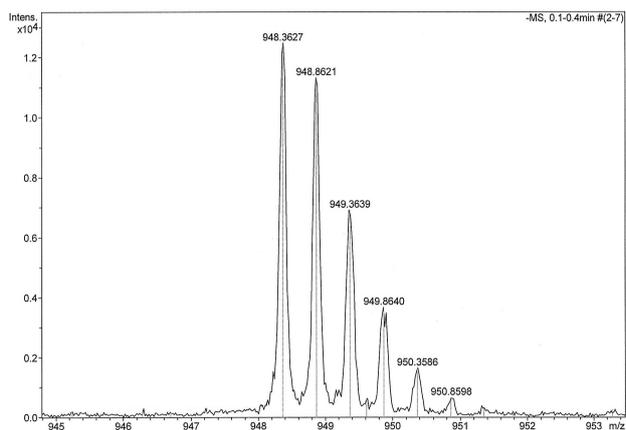


Figure S34. MS (ESI-TOF) spectrum of **25**. The observed monoisotopic mass: 948.36 [(M-2H)/2]²⁻

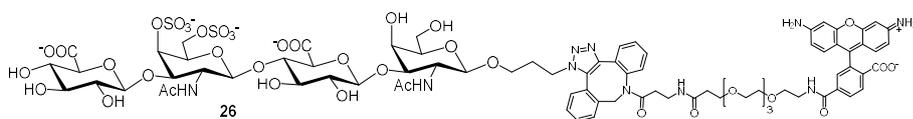
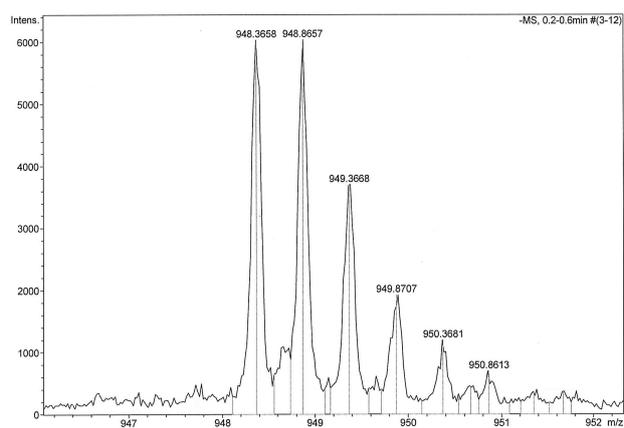


Figure S35. MS (ESI-TOF) spectrum of **26**. The observed monoisotopic mass: 948.37 $[(M-2H)/2]^{2-}$

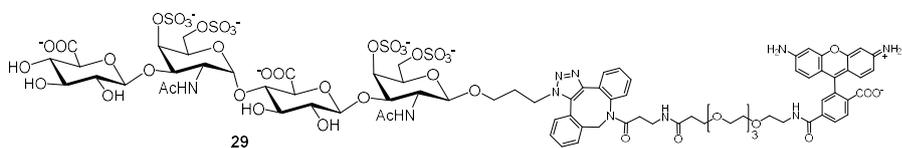
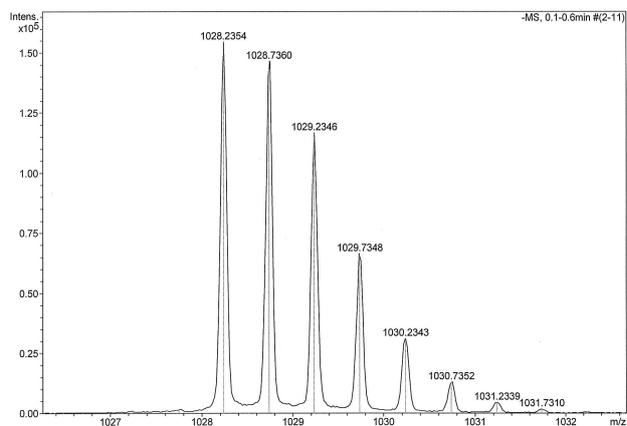


Figure S36. MS (ESI-TOF) spectrum of **29**. The observed monoisotopic mass: 1028.23 $[(M-2H)/2]^{2-}$

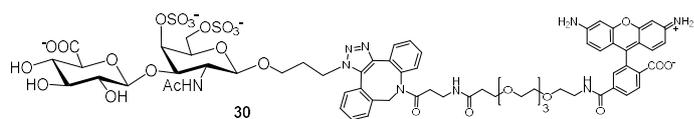
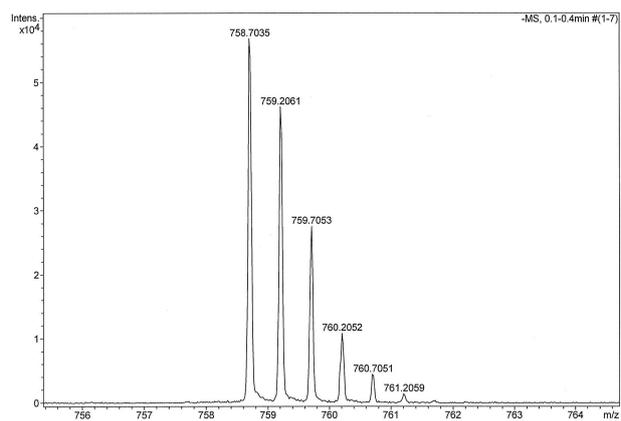


Figure S37. MS (ESI-TOF) spectrum of **30**. The observed monoisotopic mass: 758.70 [(M-2H)/2]²⁻

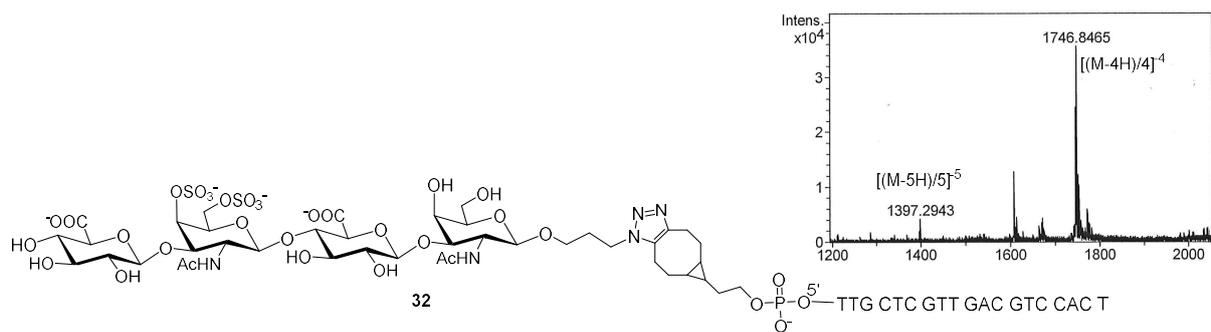


Figure S38. MS(ESI-TOF) spectrum of **32**

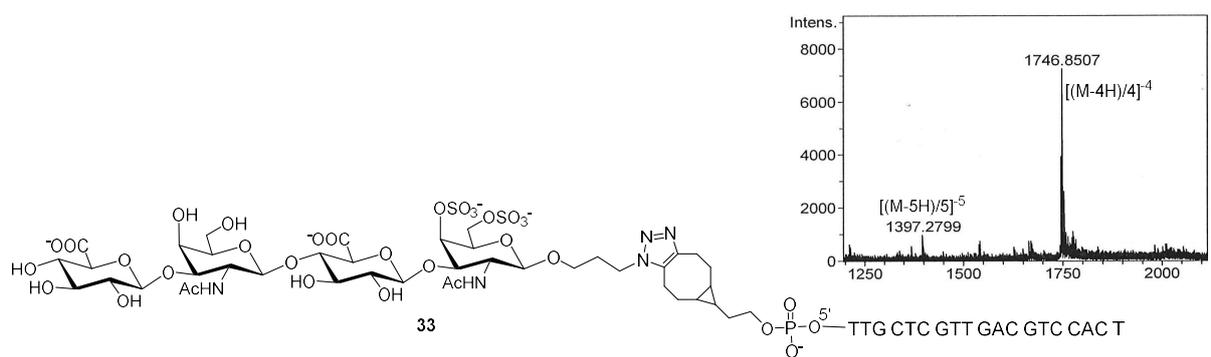


Figure S39. MS(ESI-TOF) spectrum of **33**

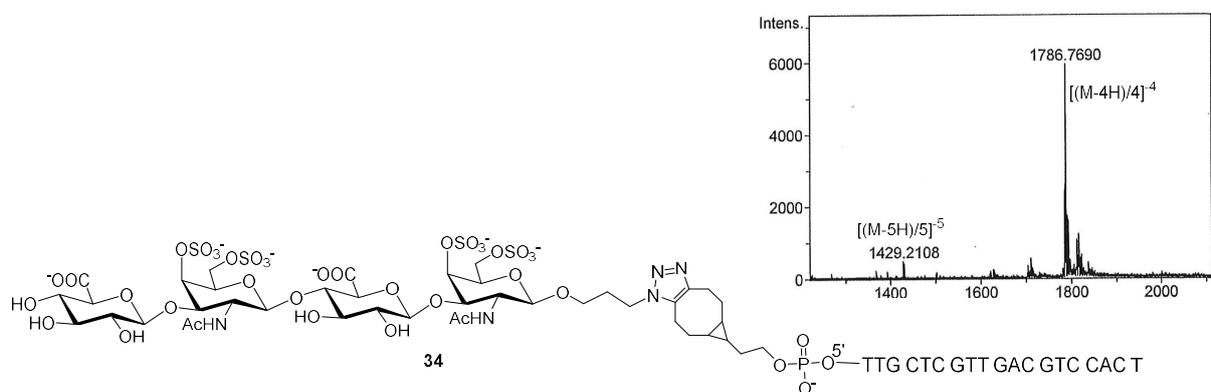


Figure S40. MS(ESI-TOF) spectrum of **34**