

## SUPPORTING INFORMATION

### Synthesis of $\beta$ -C-glycopyranosyl aldehydes and 2,6-anhydro-heptitols

Vinod Khatri, Amit Kumar, Balram Singh, Shashwat Malhotra and Ashok K. Prasad\*

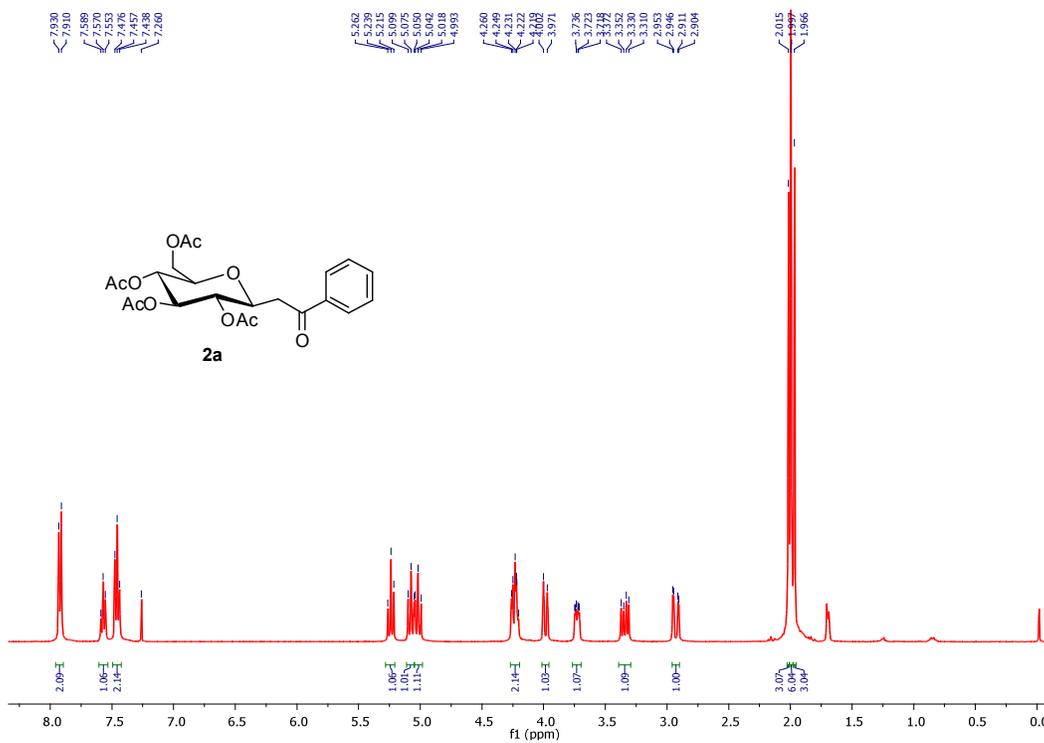
Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi 110007, India

#### \*Corresponding Author

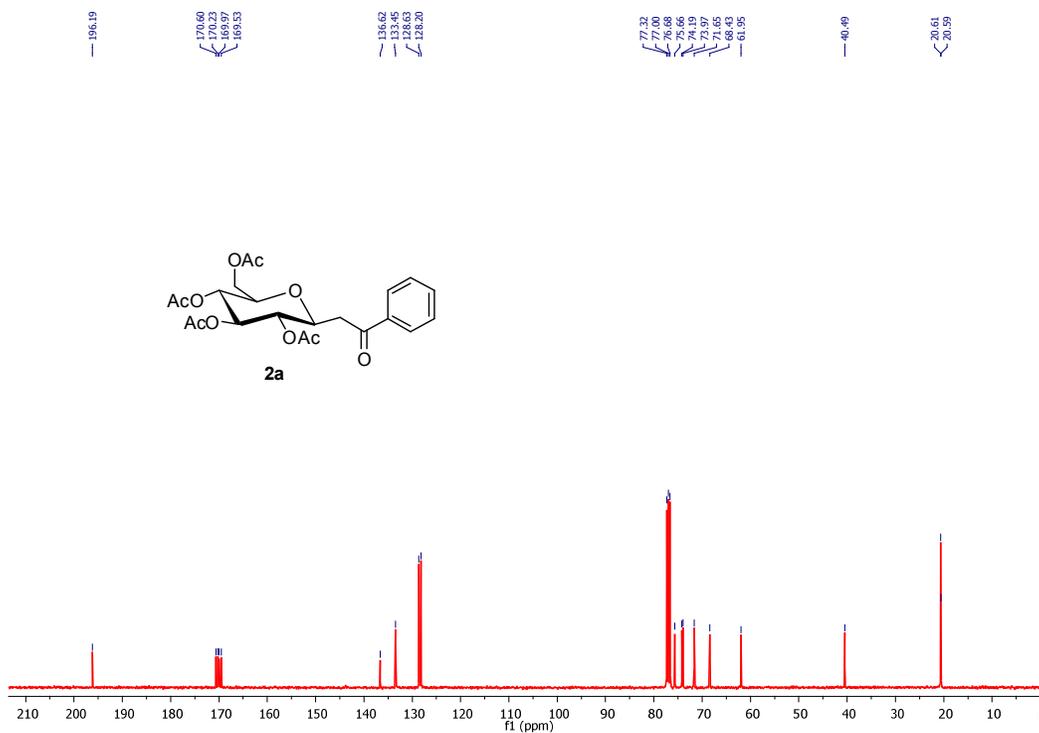
**Ashok K. Prasad:** Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi 110007, India; Phone: 00-91-11-27662486; E-mail: [ashokenzyme@gmail.com](mailto:ashokenzyme@gmail.com).

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**Figure S1.** <sup>1</sup>H NMR spectrum of compound **2a** (400 MHz, CDCl<sub>3</sub>)



**Figure S2.** <sup>13</sup>C NMR spectrum of compound **2a** (100.6 MHz, CDCl<sub>3</sub>)

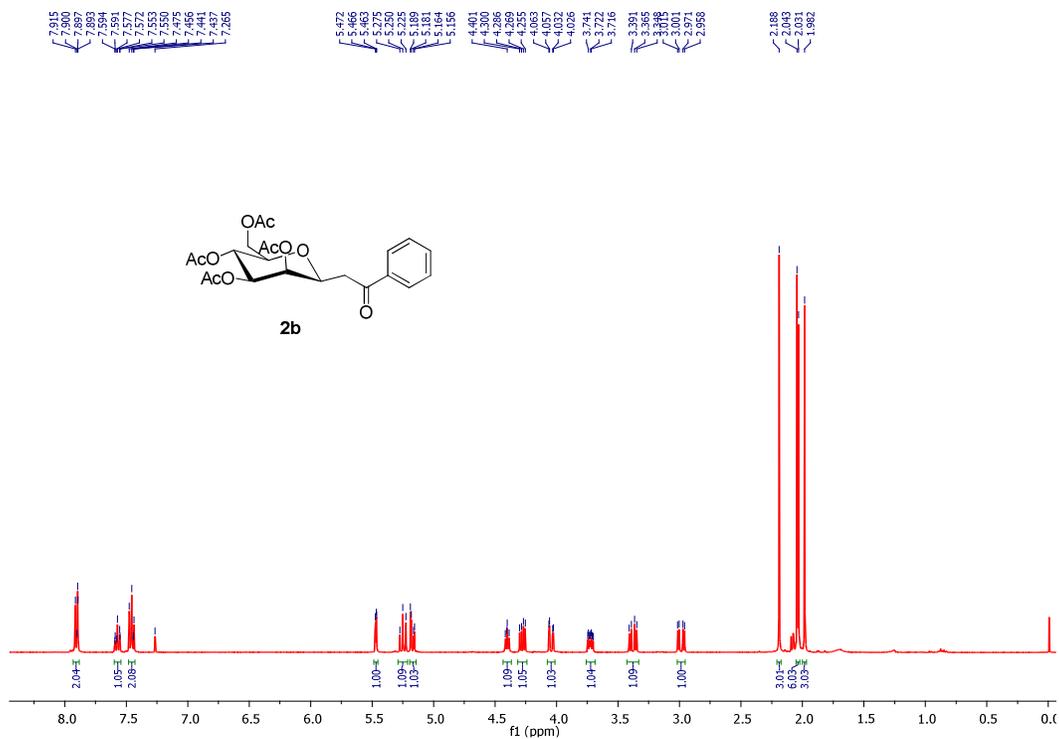


Figure S3. <sup>1</sup>H NMR spectrum of compound **2b** (400 MHz, CDCl<sub>3</sub>)

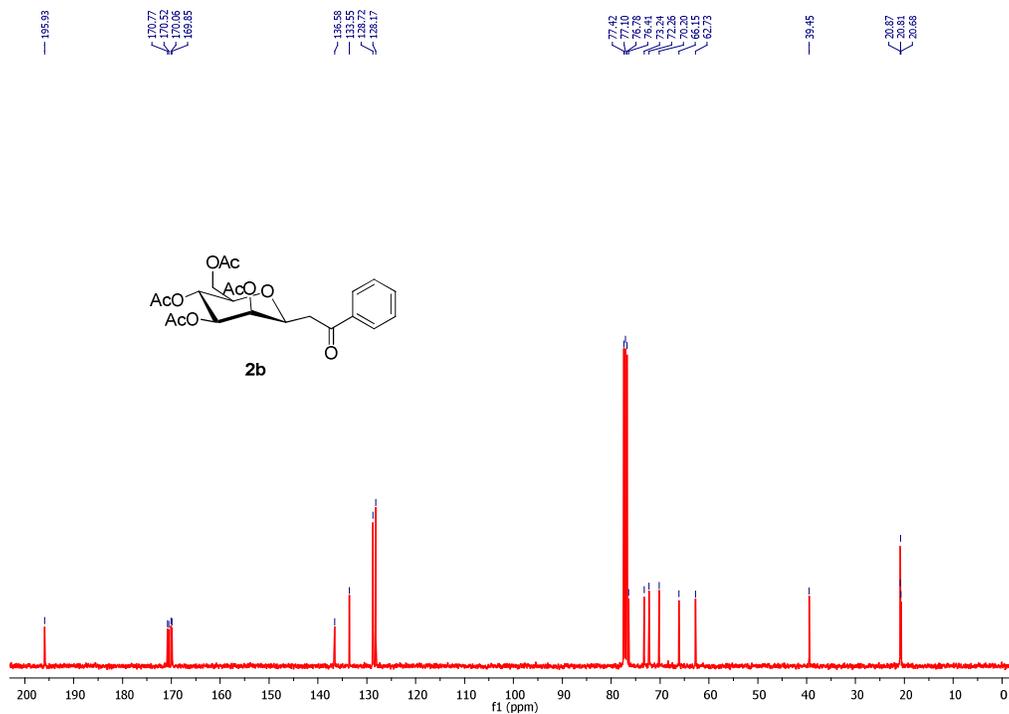


Figure S4. <sup>13</sup>C NMR spectrum of compound **2b** (100.6 MHz, CDCl<sub>3</sub>)

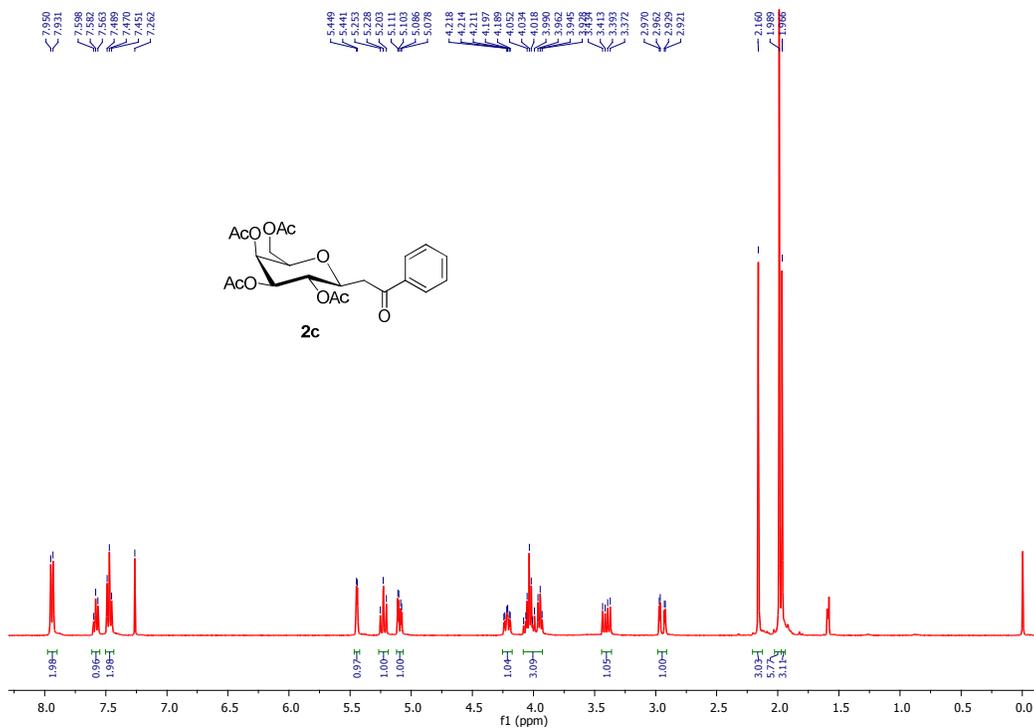


Figure S5. <sup>1</sup>H NMR spectrum of compound **2c** (400 MHz, CDCl<sub>3</sub>)

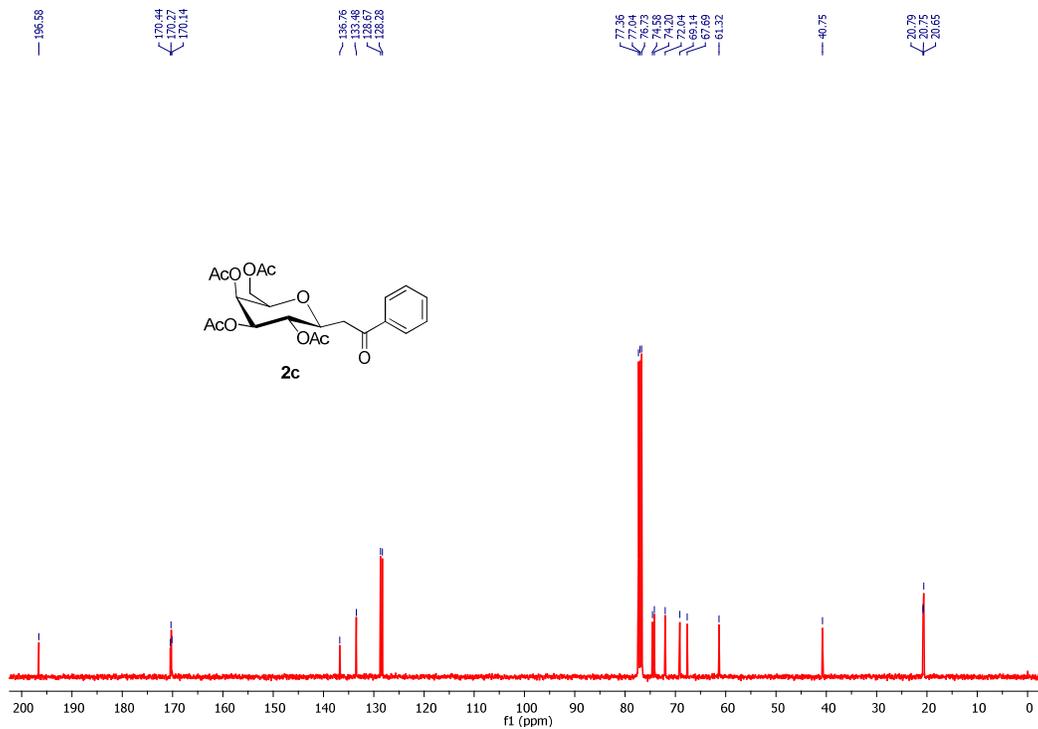
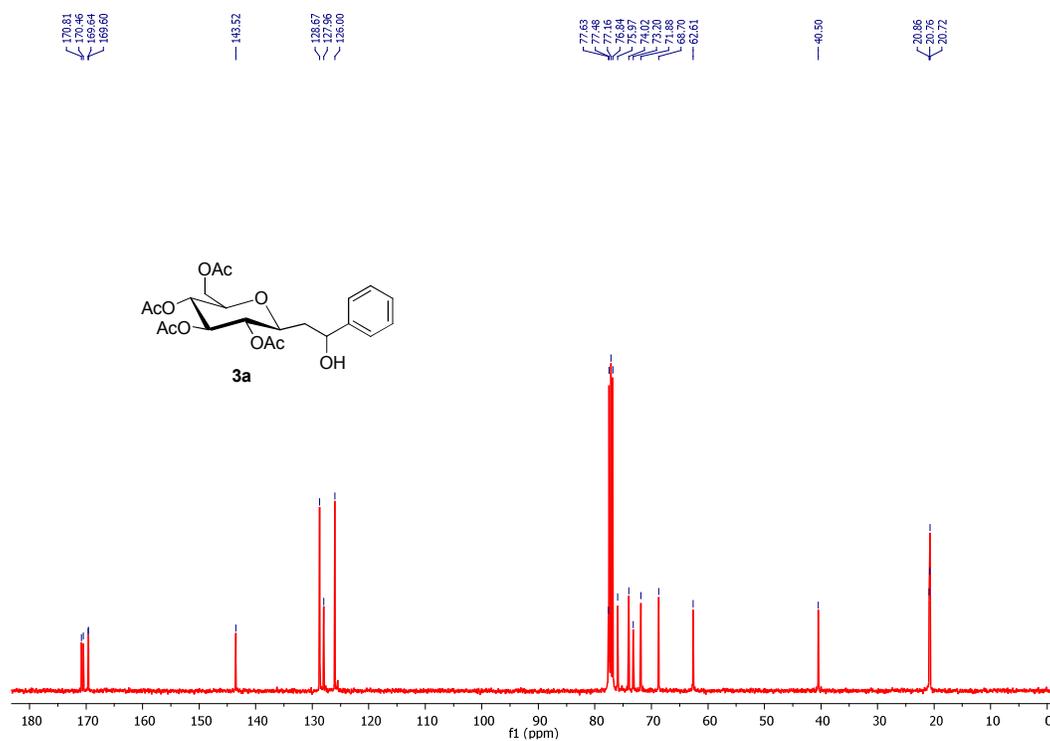
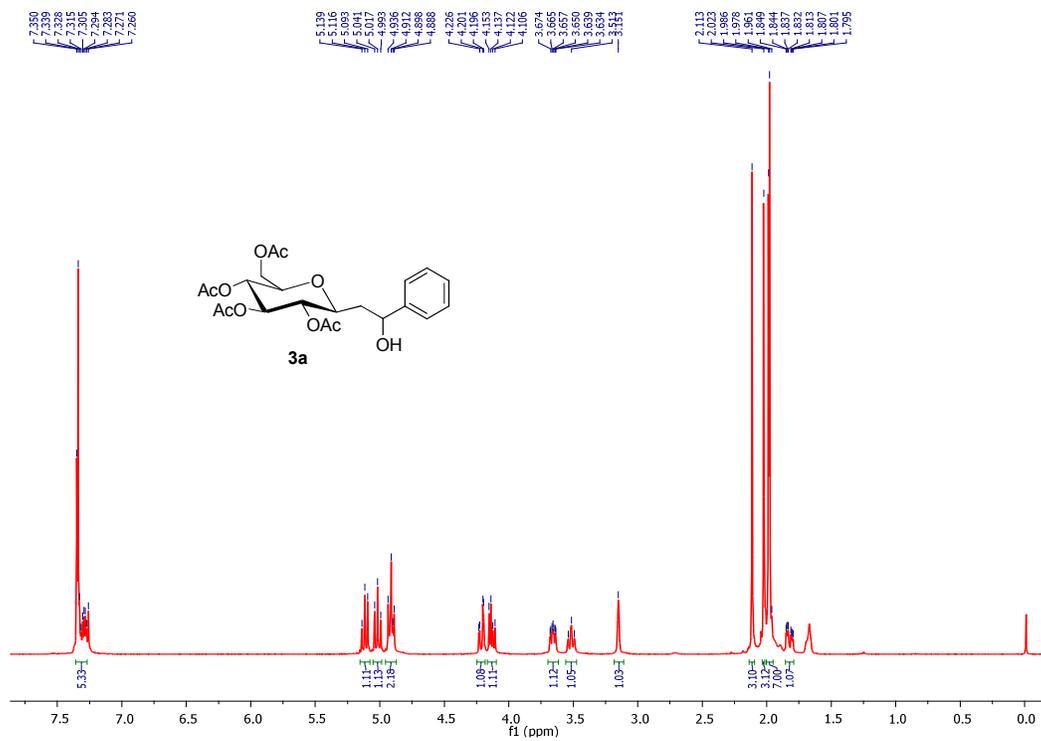
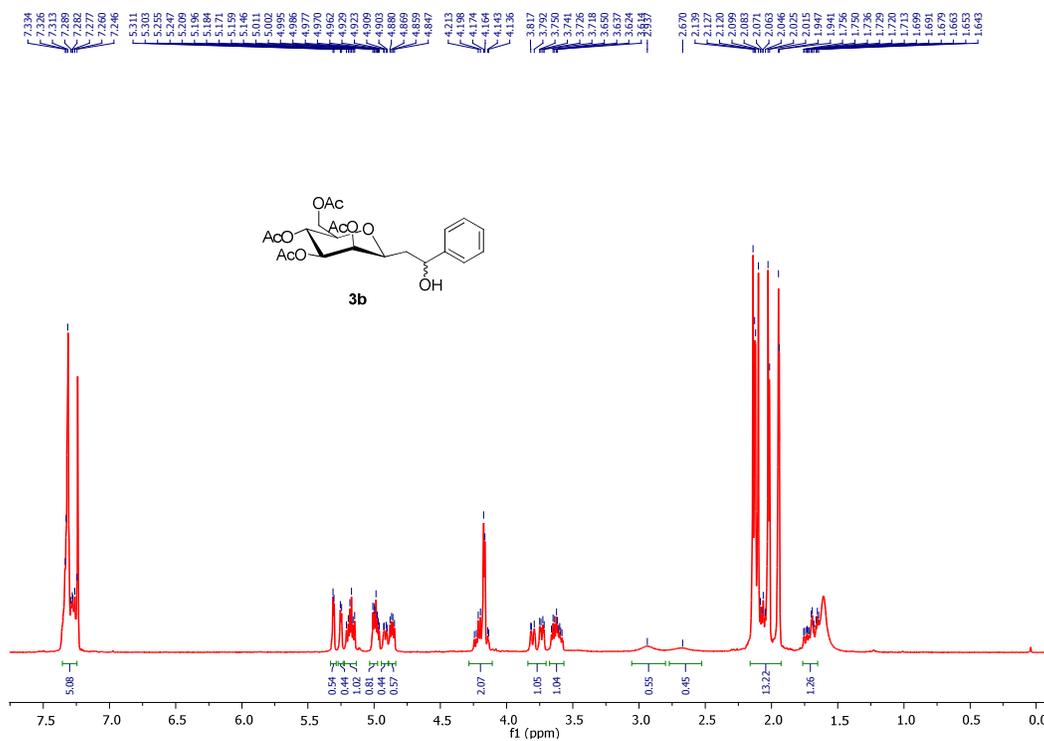
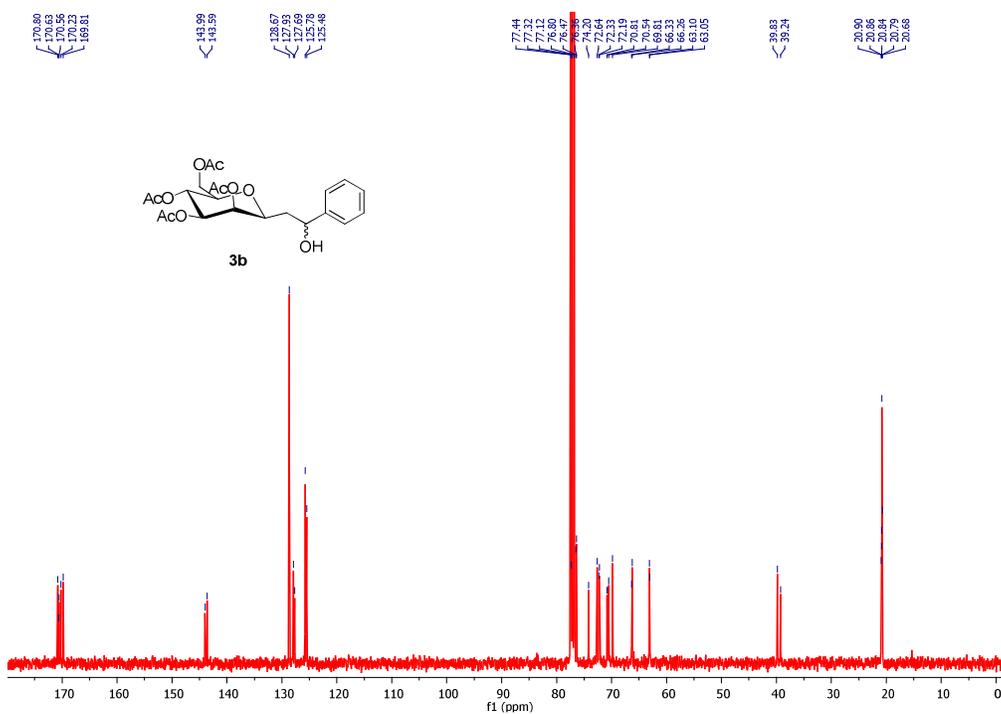


Figure S6. <sup>13</sup>C NMR spectrum of compound **2c** (100.6 MHz, CDCl<sub>3</sub>)

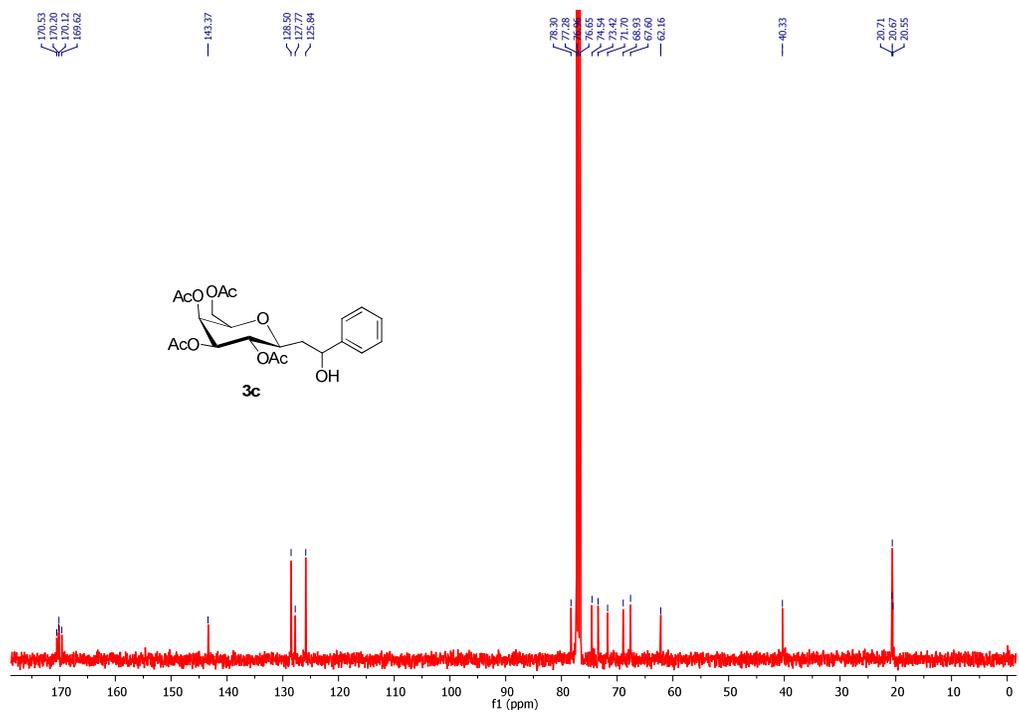
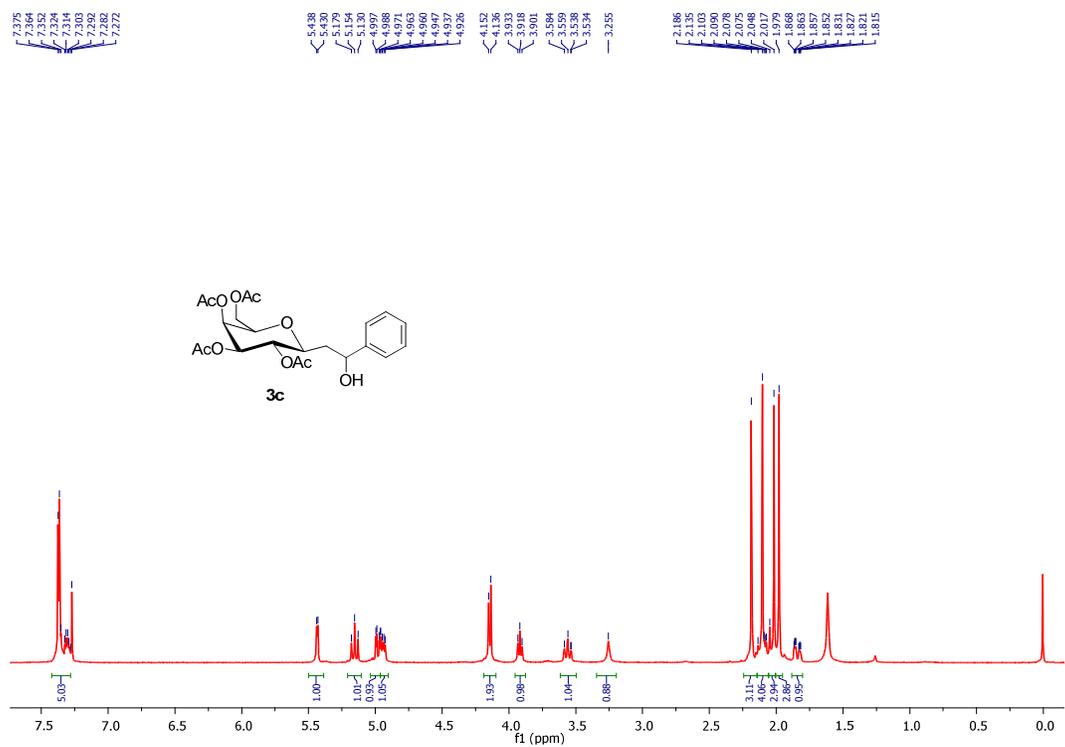




**Figure S9.** <sup>1</sup>H NMR spectrum of compound **3b** (400 MHz, CDCl<sub>3</sub>)



**Figure S10.** <sup>13</sup>C NMR spectrum of compound **3b** (100.6 MHz, CDCl<sub>3</sub>)



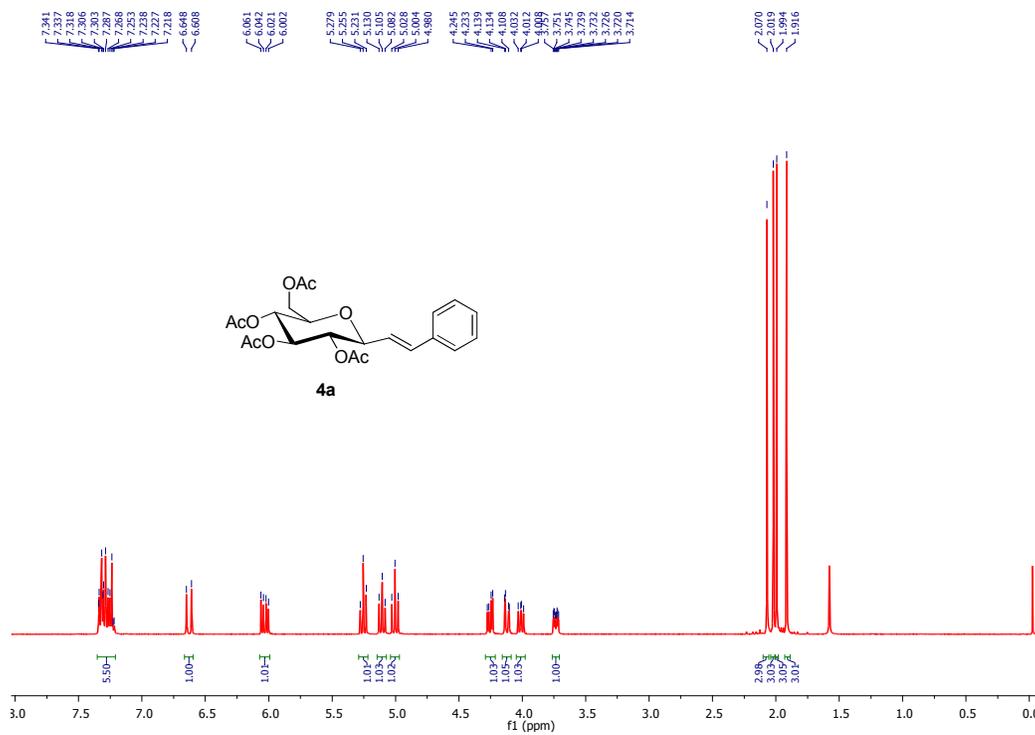


Figure S13.  $^1\text{H}$  NMR spectrum of compound **4a** (400 MHz,  $\text{CDCl}_3$ )

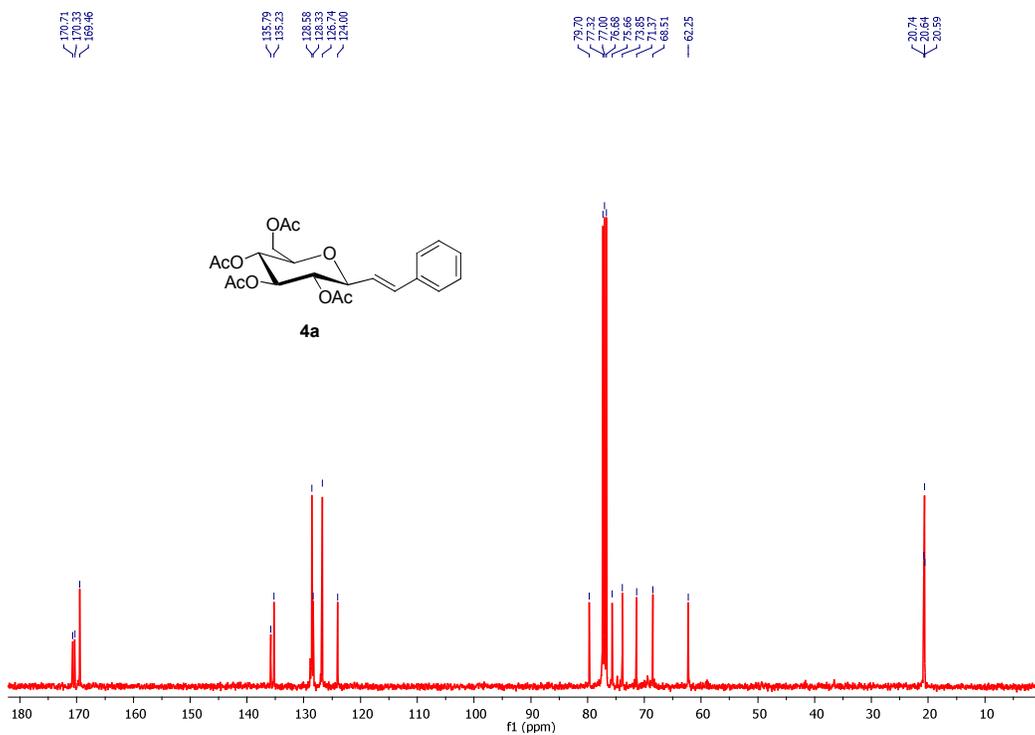
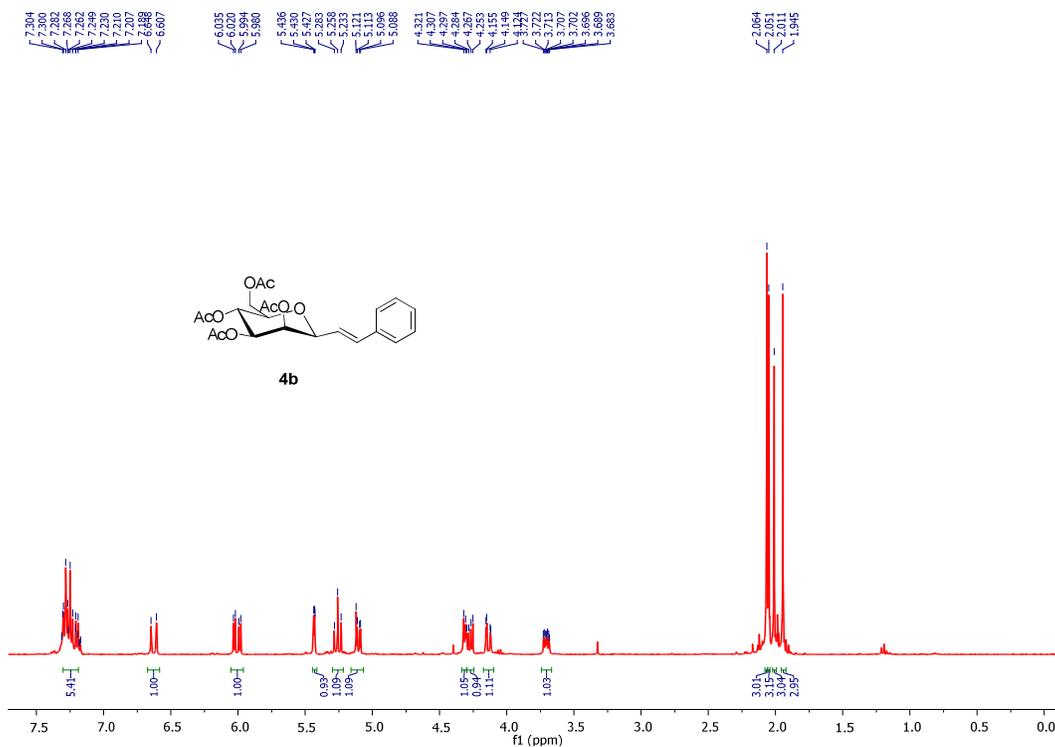
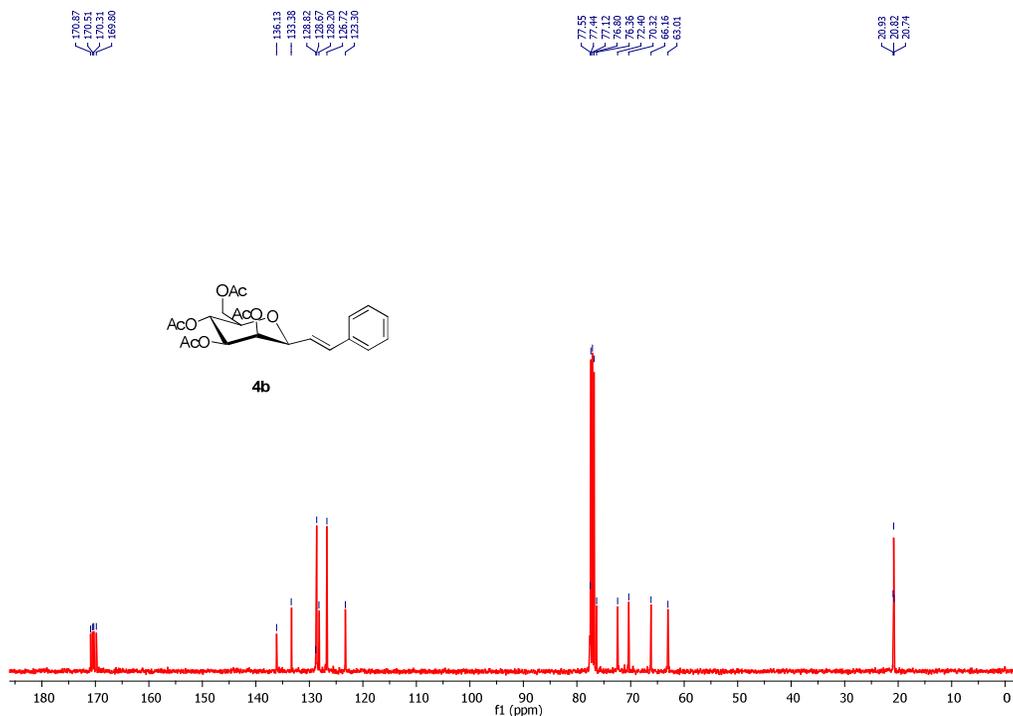


Figure S14.  $^{13}\text{C}$  NMR spectrum of compound **4a** (100.6 MHz,  $\text{CDCl}_3$ )



**Figure S15.**  $^1\text{H}$  NMR spectrum of compound **4b** (400 MHz,  $\text{CDCl}_3$ )



**Figure S16.**  $^{13}\text{C}$  NMR spectrum of compound **4b** (100.6 MHz,  $\text{CDCl}_3$ )

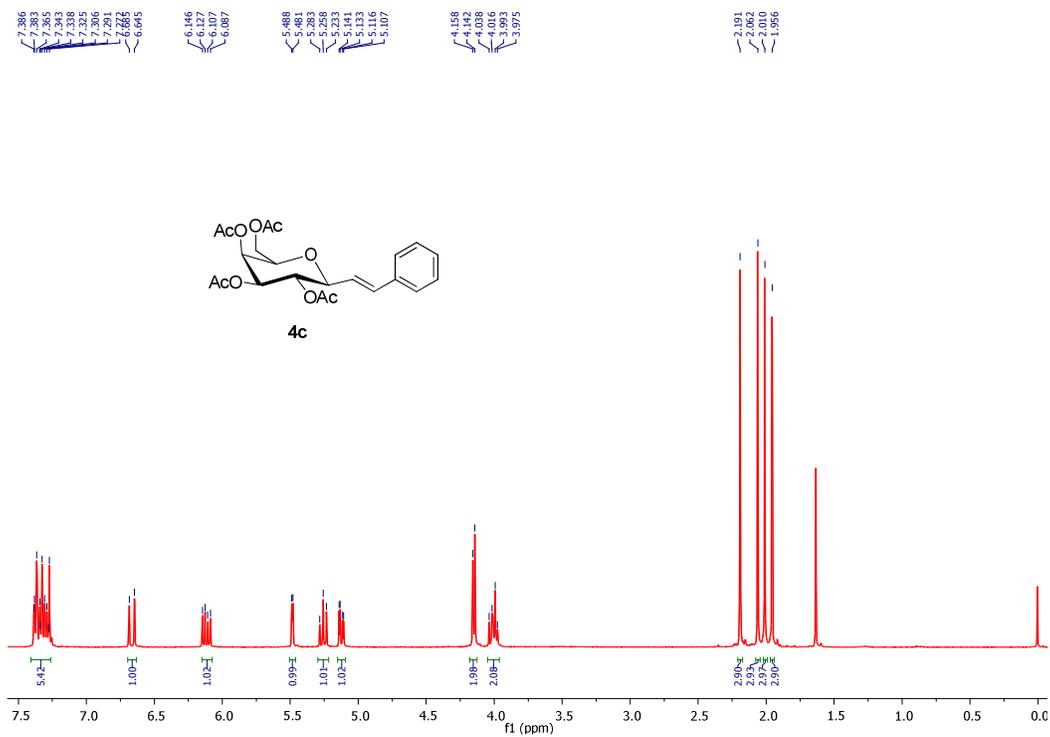


Figure S17. <sup>1</sup>H NMR spectrum of compound **4c** (400 MHz, CDCl<sub>3</sub>)

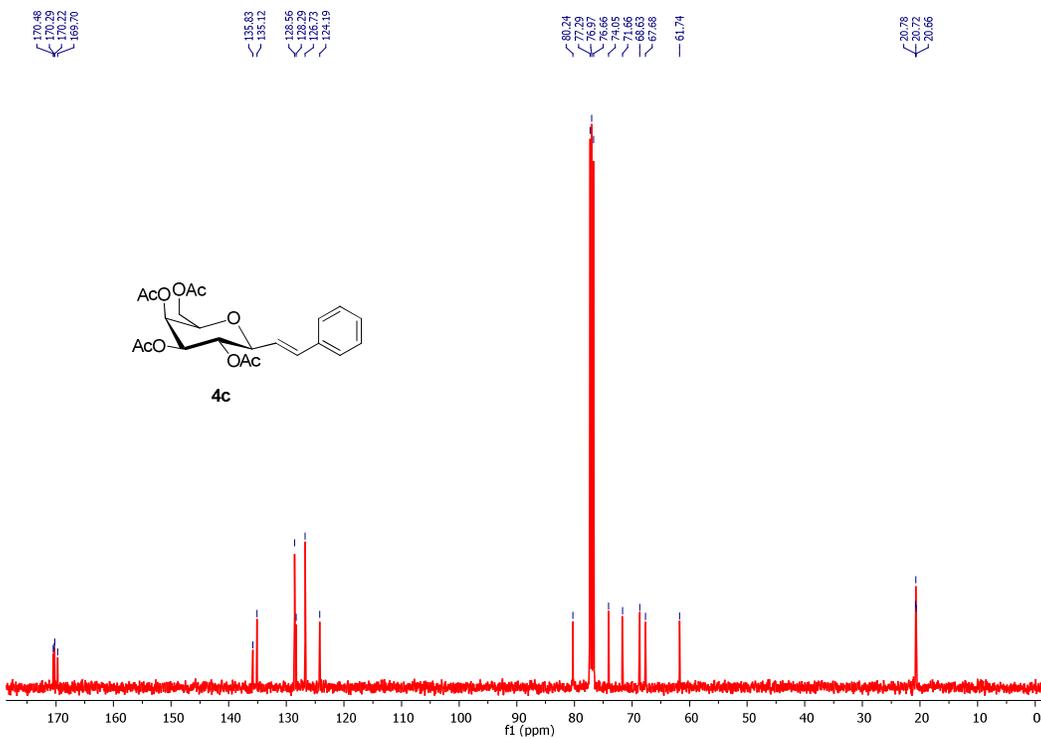


Figure S18. <sup>13</sup>C NMR spectrum of compound **4c** (100.6 MHz, CDCl<sub>3</sub>)

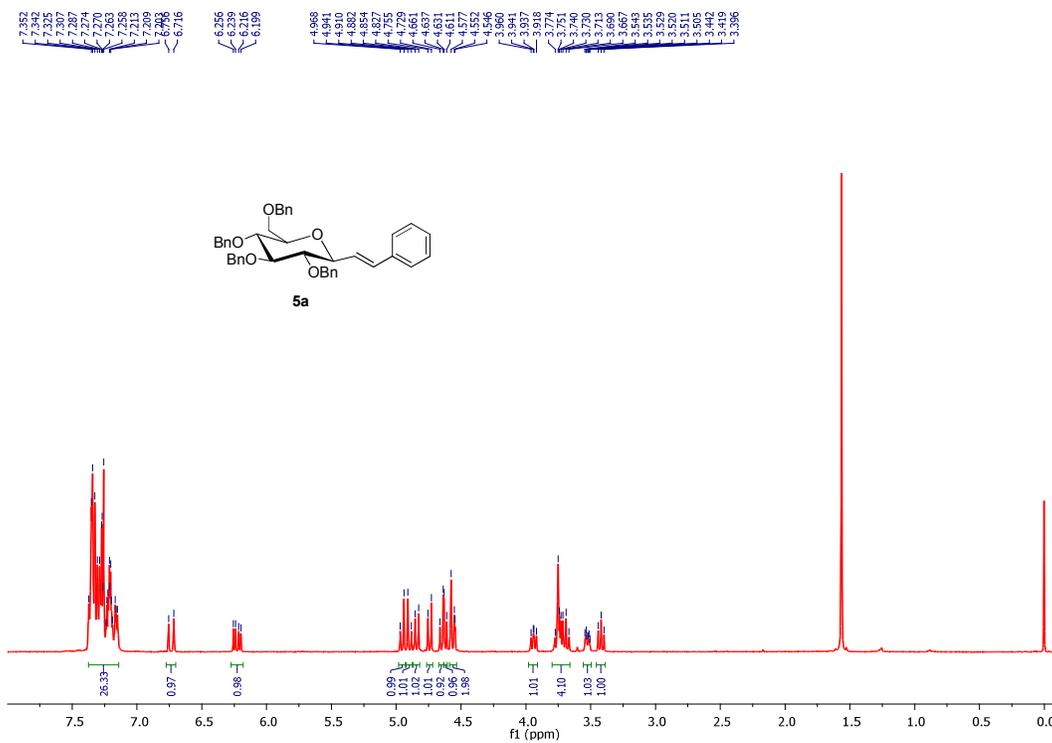


Figure S19. <sup>1</sup>H NMR spectrum of compound **5a** (400 MHz, CDCl<sub>3</sub>)

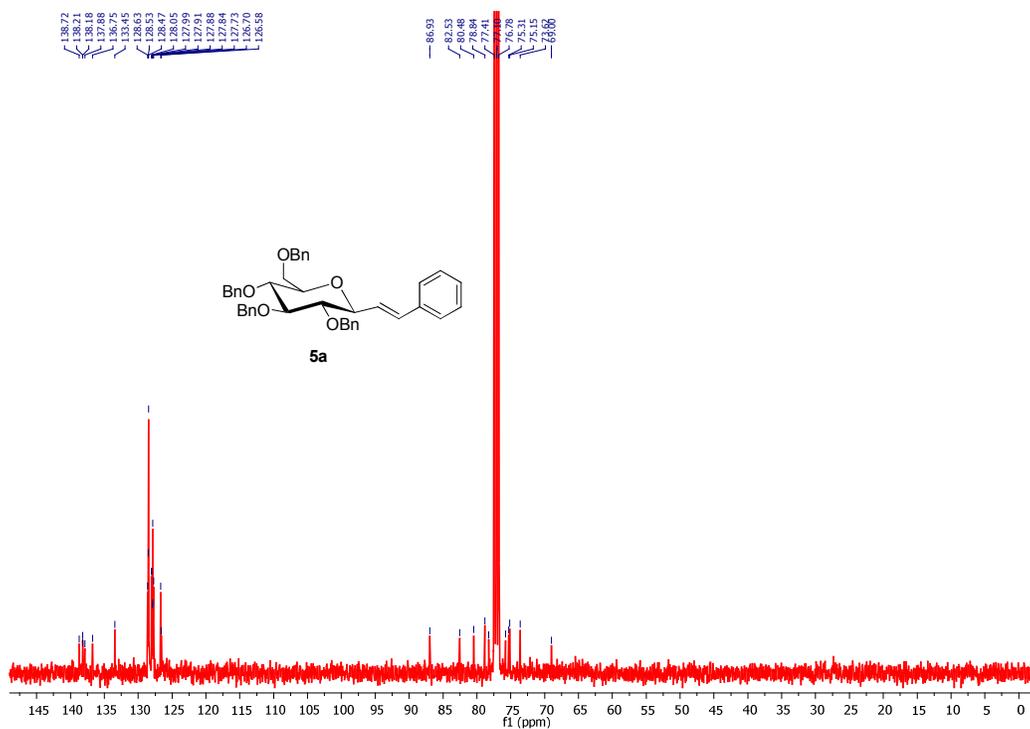
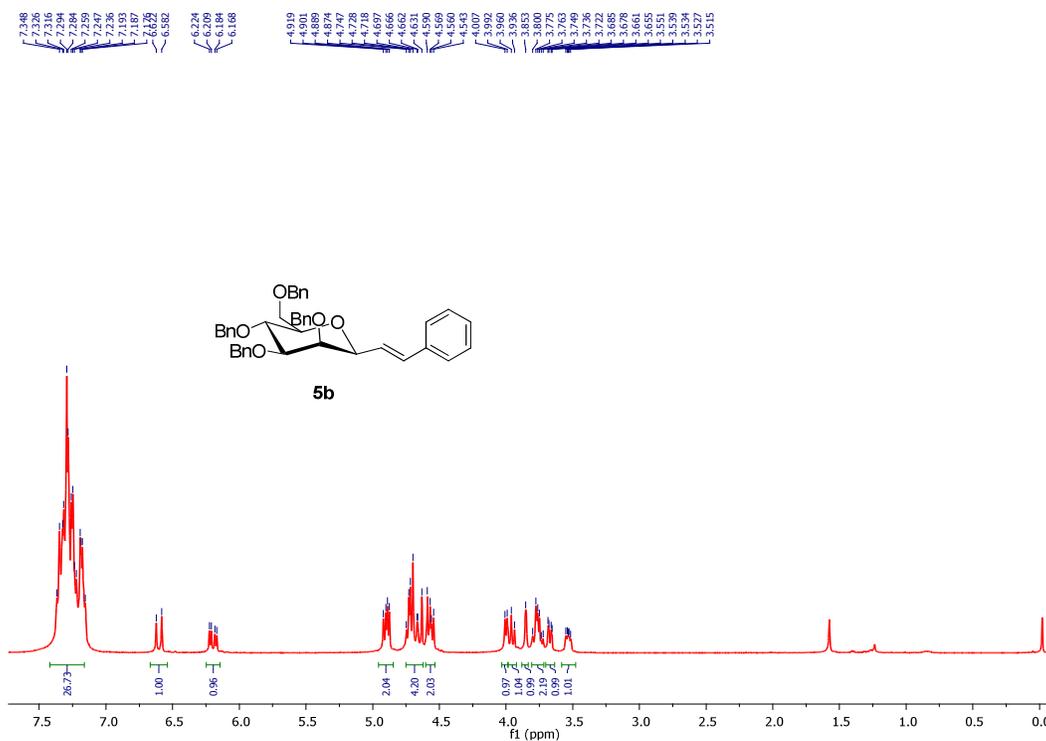
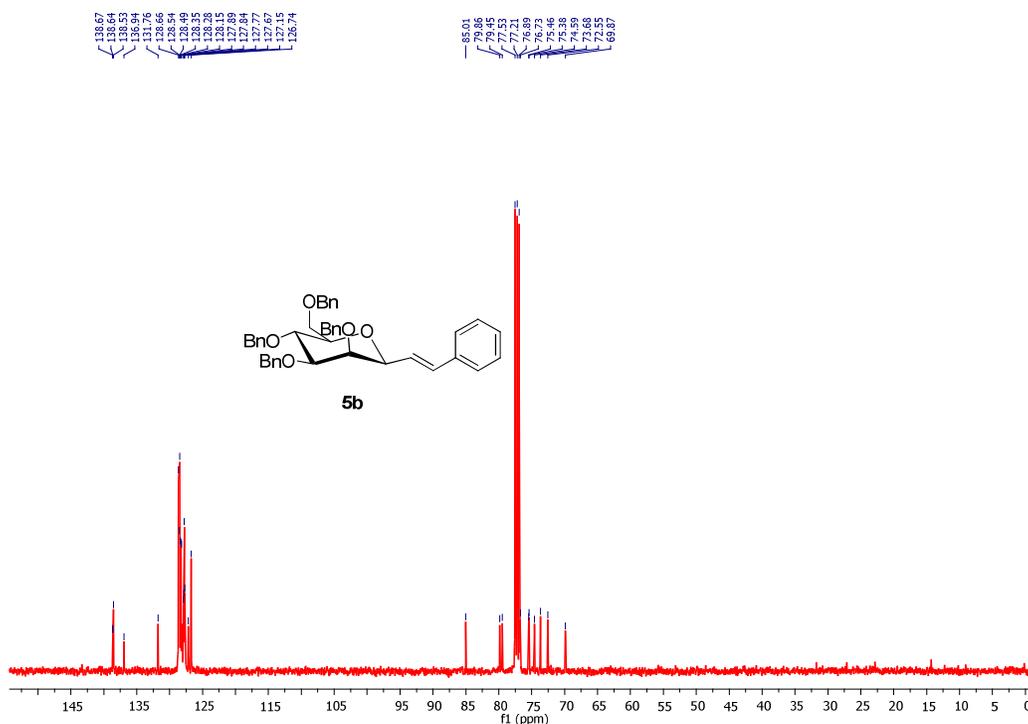


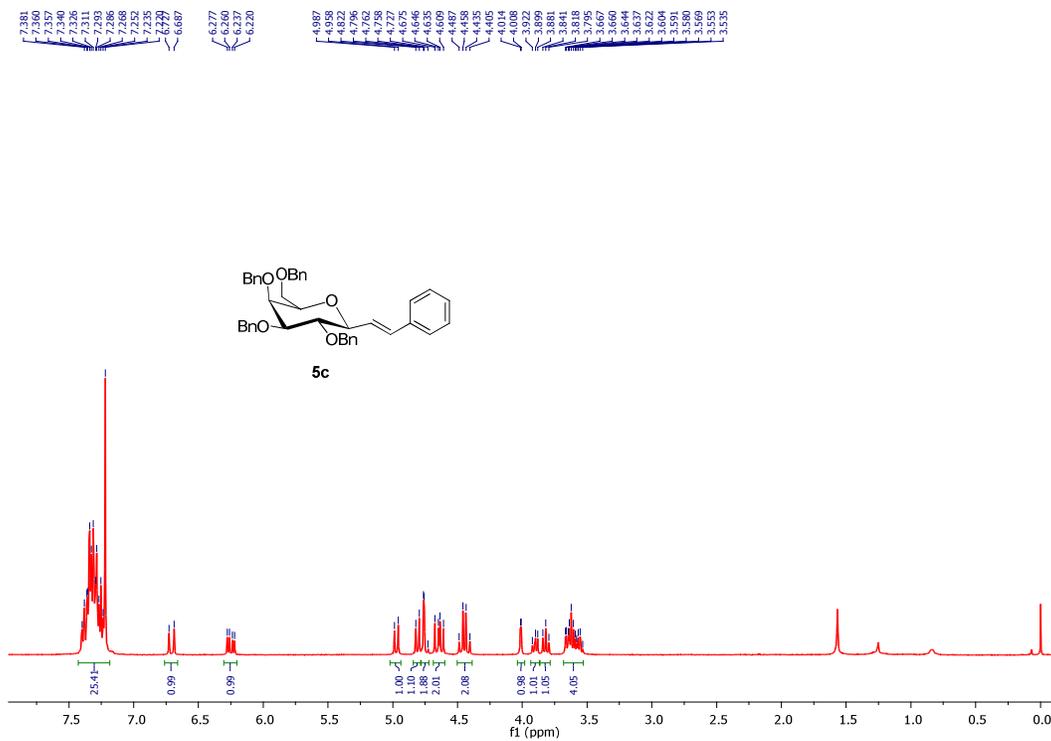
Figure S20. <sup>13</sup>C NMR spectrum of compound **5a** (100.6 MHz, CDCl<sub>3</sub>)



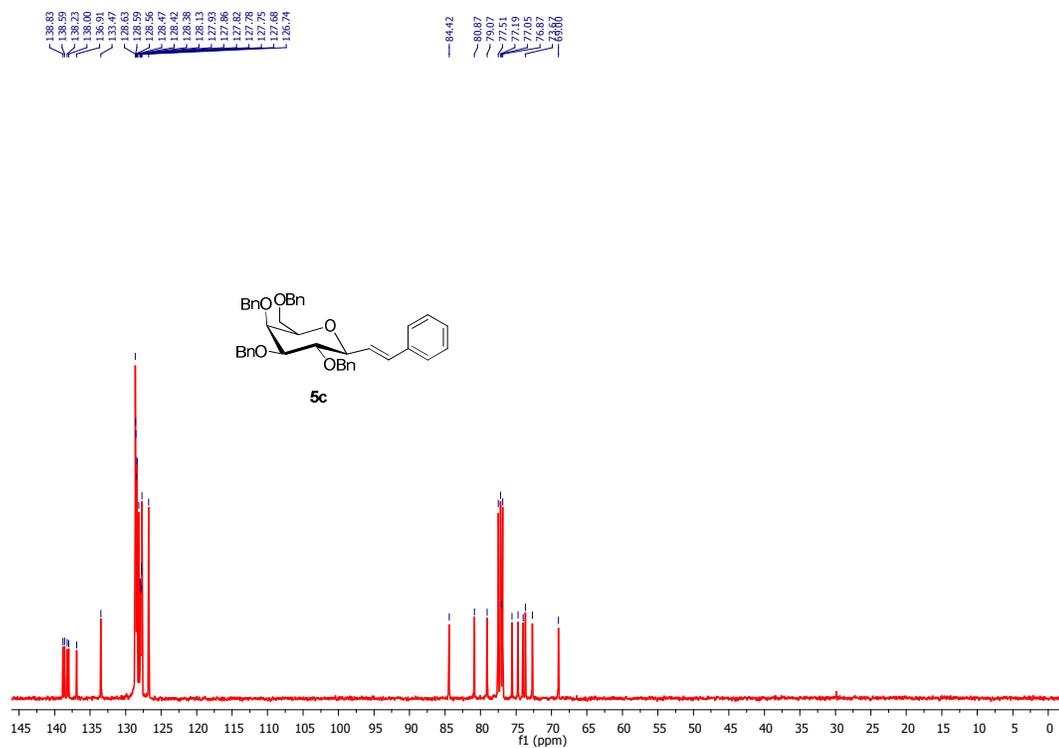
**Figure S21.** <sup>1</sup>H NMR spectrum of compound **5b** (400 MHz, CDCl<sub>3</sub>)



**Figure S22.** <sup>13</sup>C NMR spectrum of compound **5b** (100.6 MHz, CDCl<sub>3</sub>)



**Figure S23.**  $^1\text{H}$  NMR spectrum of compound **5c** (400 MHz,  $\text{CDCl}_3$ )



**Figure S24.**  $^{13}\text{C}$  NMR spectrum of compound **5c** (100.6 MHz,  $\text{CDCl}_3$ )

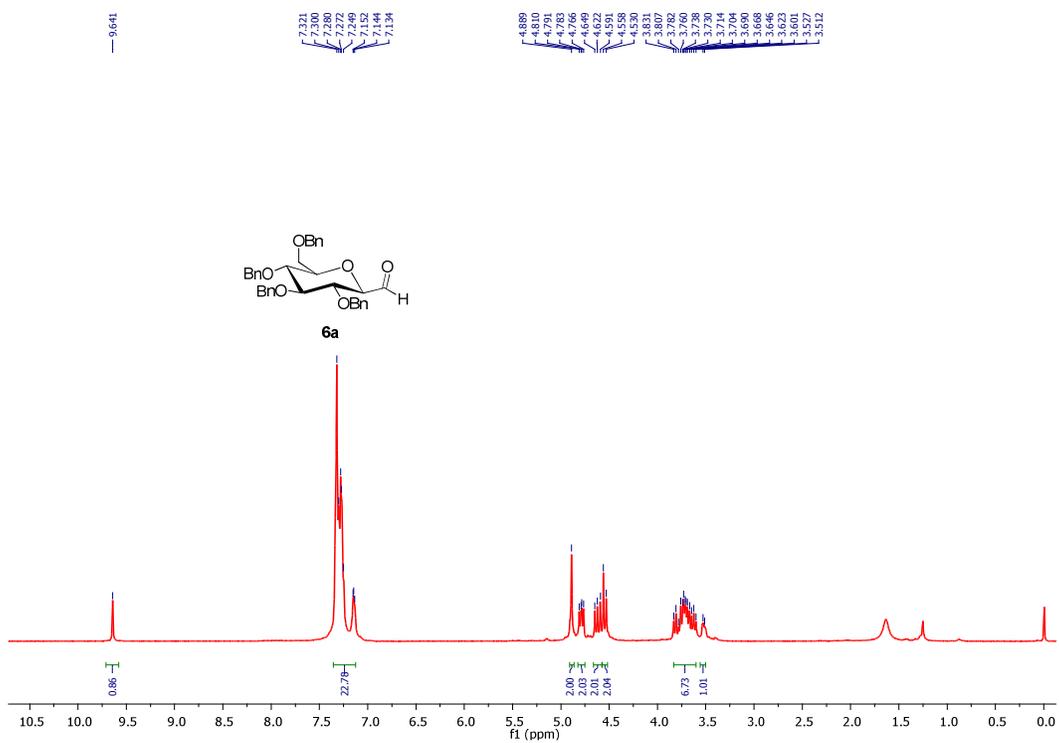


Figure S25. <sup>1</sup>H NMR spectrum of compound **6a** (400 MHz, CDCl<sub>3</sub>)

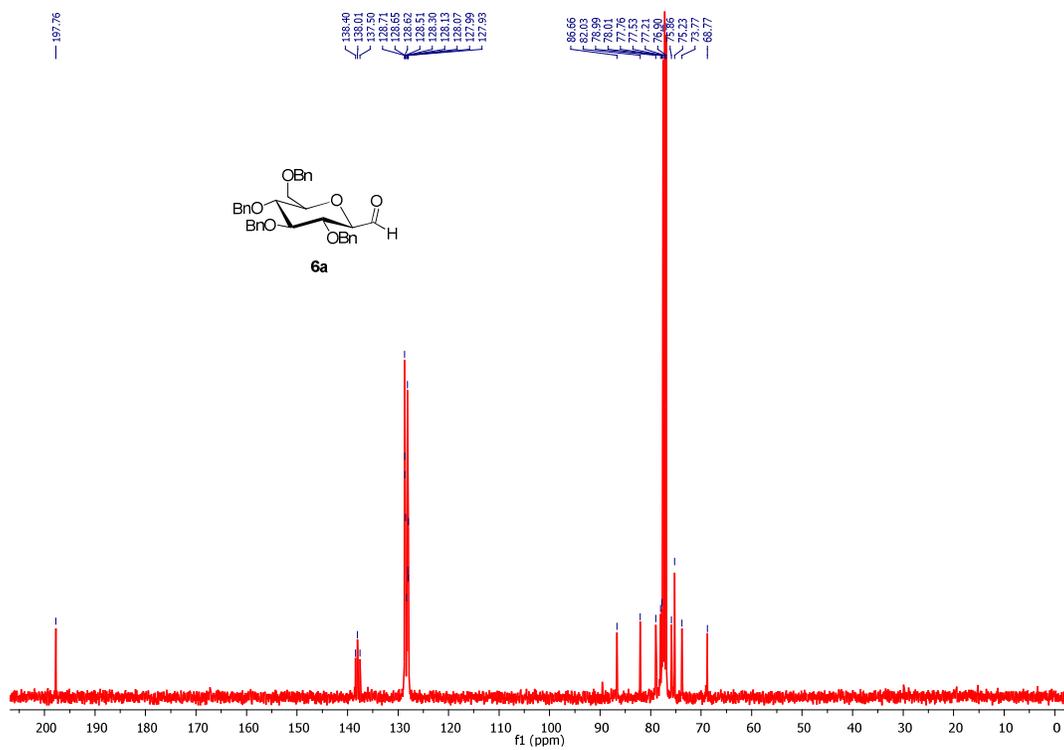


Figure S26. <sup>13</sup>C NMR spectrum of compound **6a** (100.6 MHz, CDCl<sub>3</sub>)

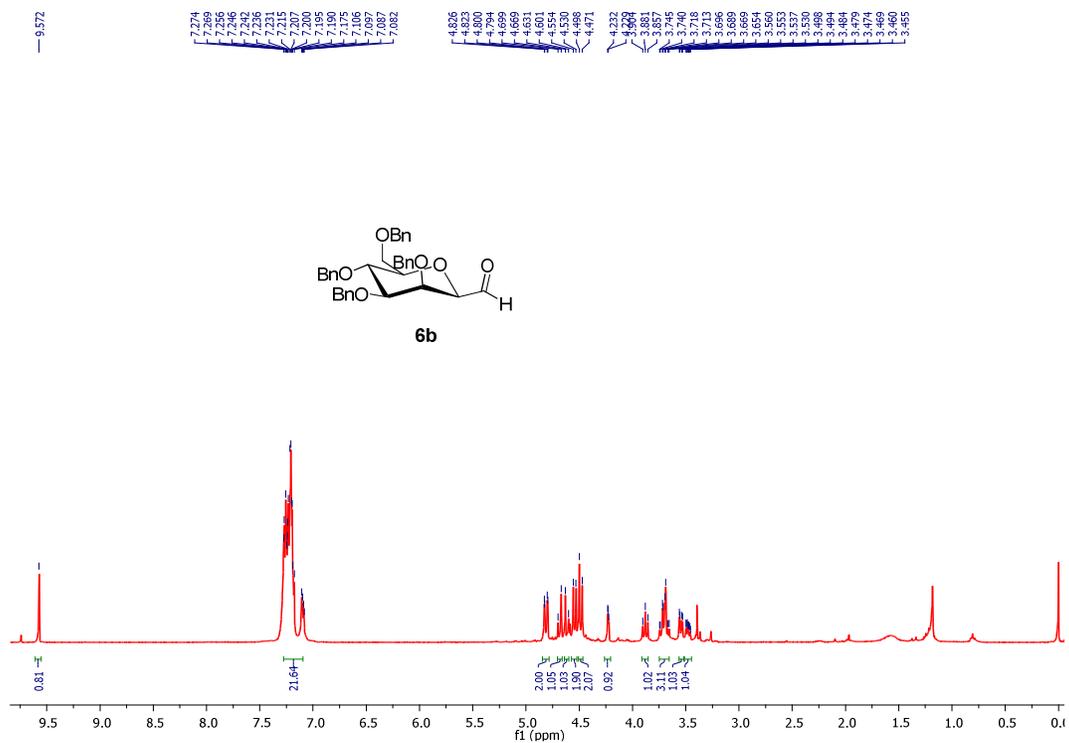


Figure S27. <sup>1</sup>H NMR spectrum of compound **6b** (400 MHz, CDCl<sub>3</sub>)

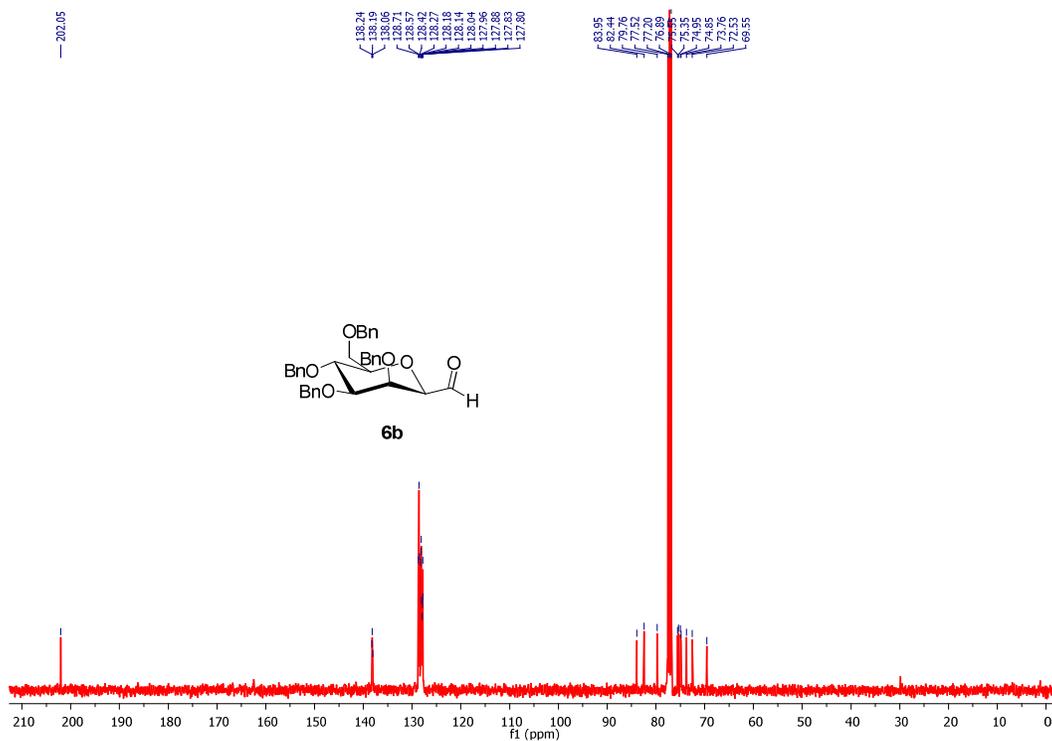


Figure S28. <sup>13</sup>C NMR spectrum of compound **6b** (100.6 MHz, CDCl<sub>3</sub>)

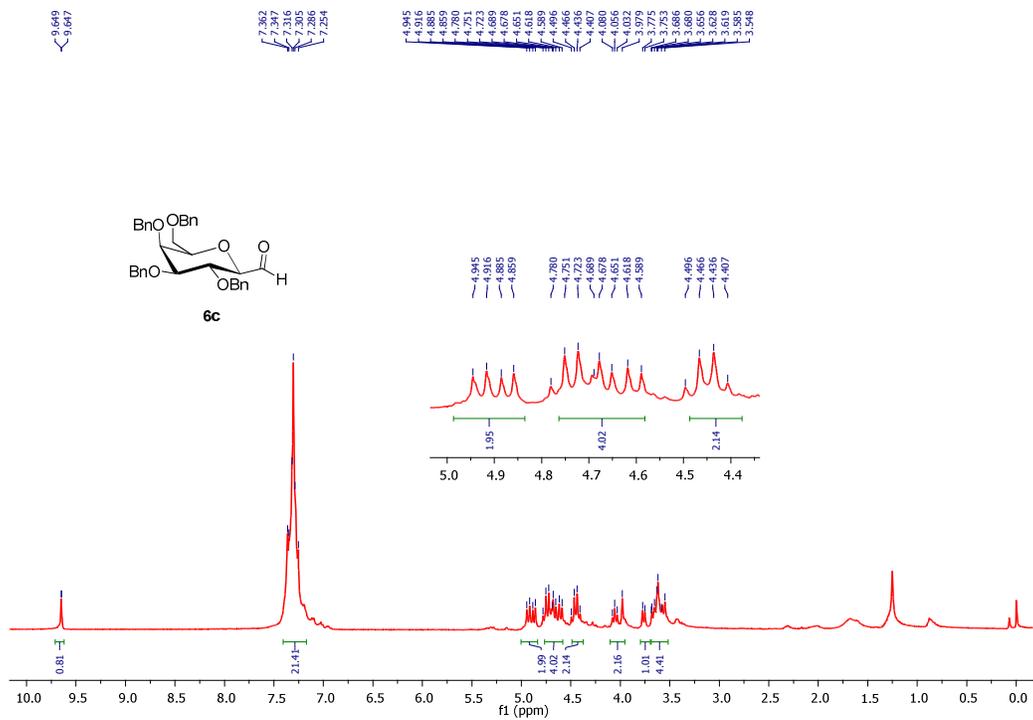


Figure S29.  $^1\text{H}$  NMR spectrum of compound **6c** (400 MHz,  $\text{CDCl}_3$ )

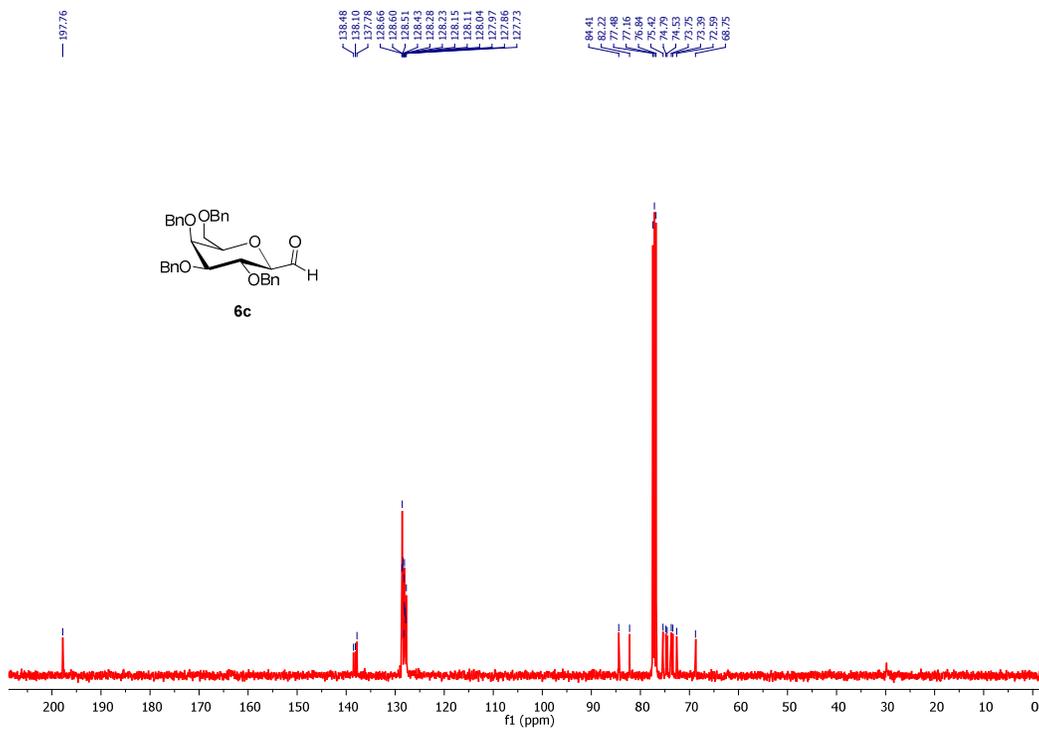


Figure S30.  $^{13}\text{C}$  NMR spectrum of compound **6c** (100.6 MHz,  $\text{CDCl}_3$ )

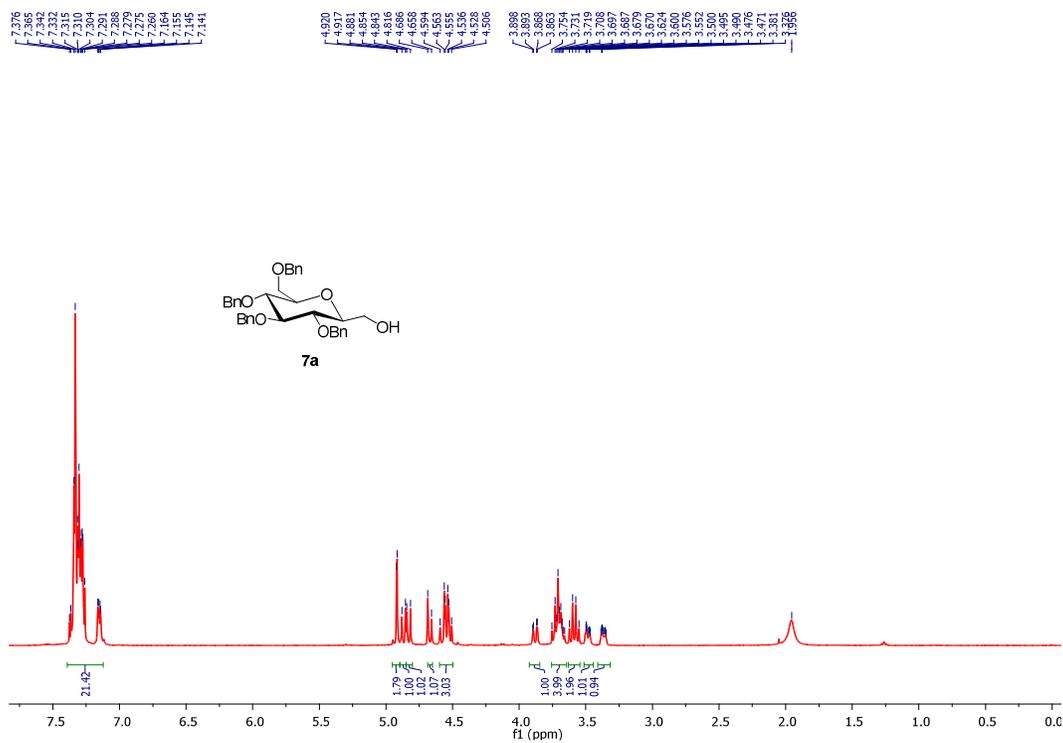


Figure S31. <sup>1</sup>H NMR spectrum of compound 7a (400 MHz, CDCl<sub>3</sub>)

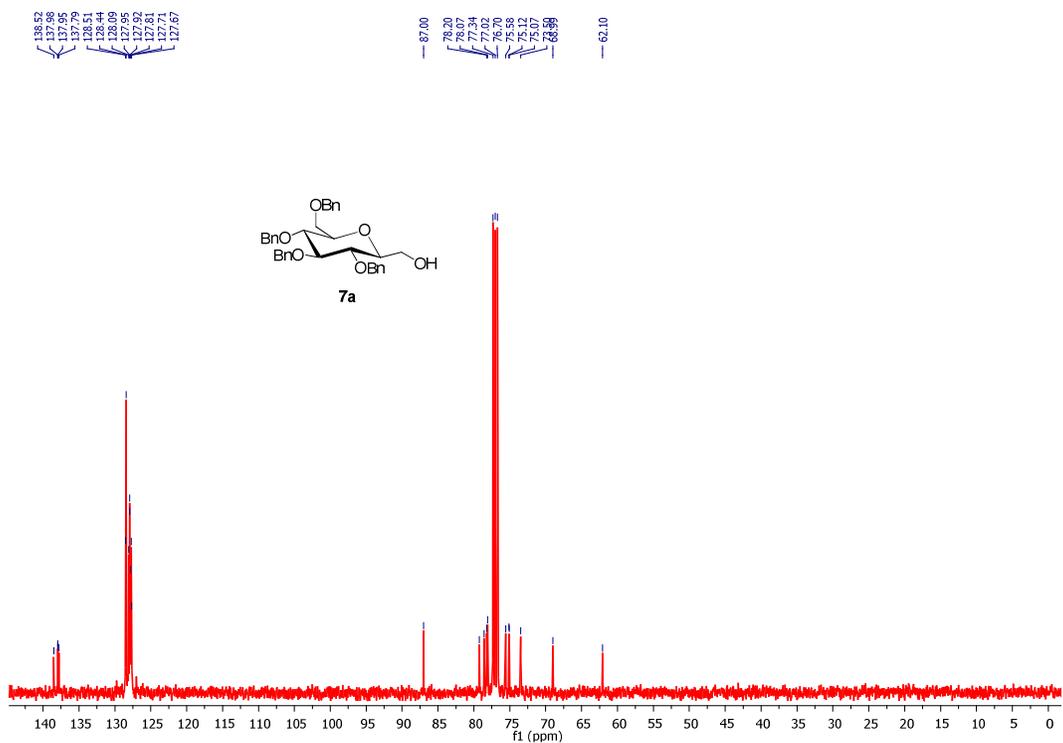


Figure S32. <sup>13</sup>C NMR spectrum of compound 7a (100.6 MHz, CDCl<sub>3</sub>)

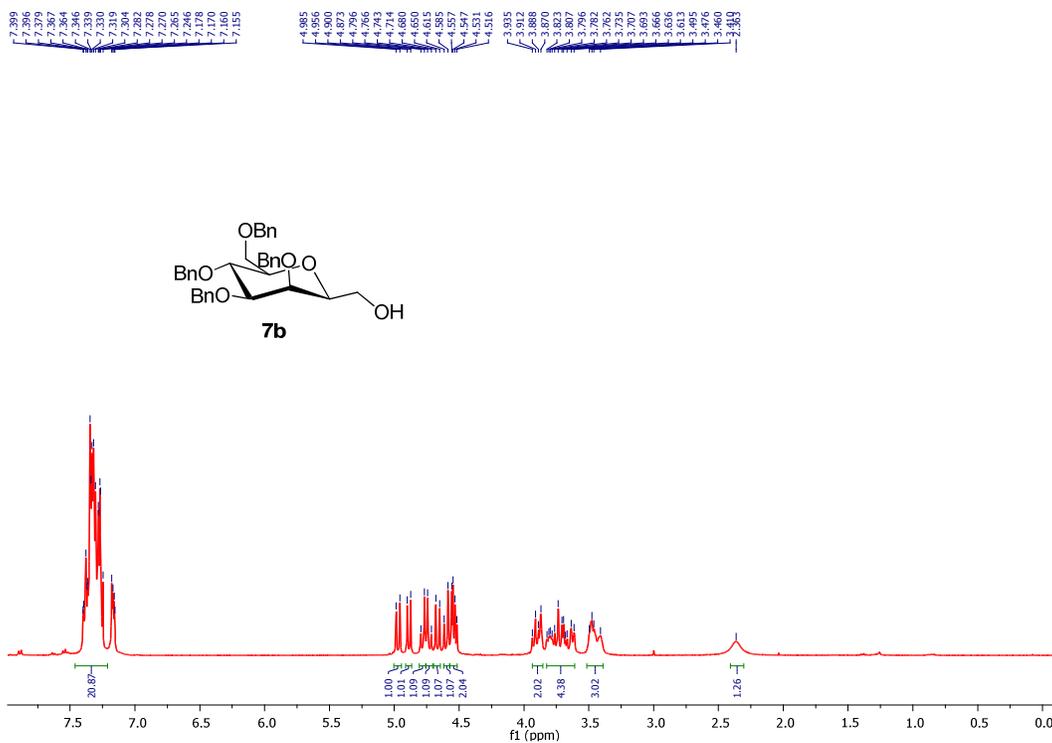


Figure S33.  $^1\text{H}$  NMR spectrum of compound **7b** (400 MHz,  $\text{CDCl}_3$ )

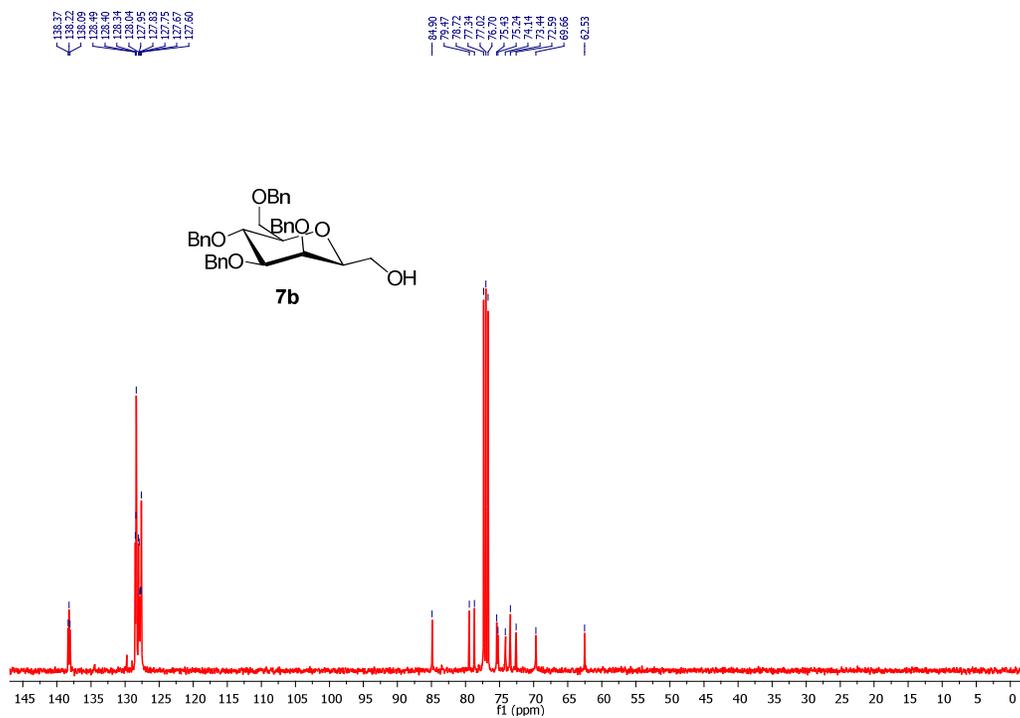


Figure S34.  $^{13}\text{C}$  NMR spectrum of compound **7b** (100.6 MHz,  $\text{CDCl}_3$ )

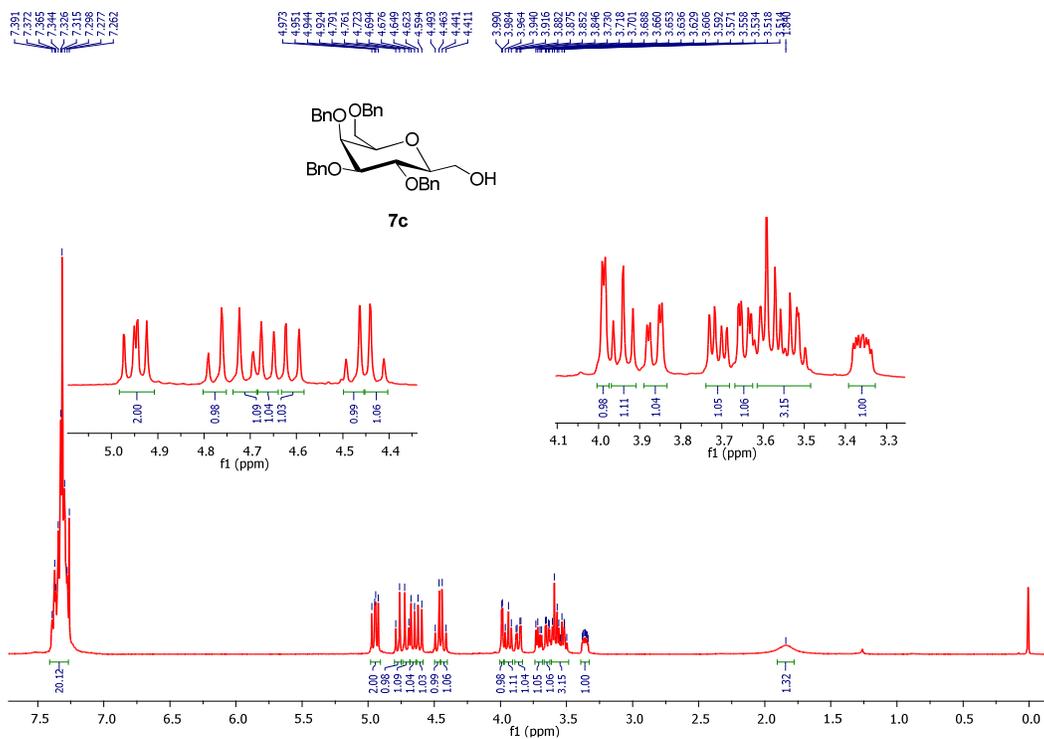


Figure S35. <sup>1</sup>H NMR spectrum of compound **7c** (400 MHz, CDCl<sub>3</sub>)

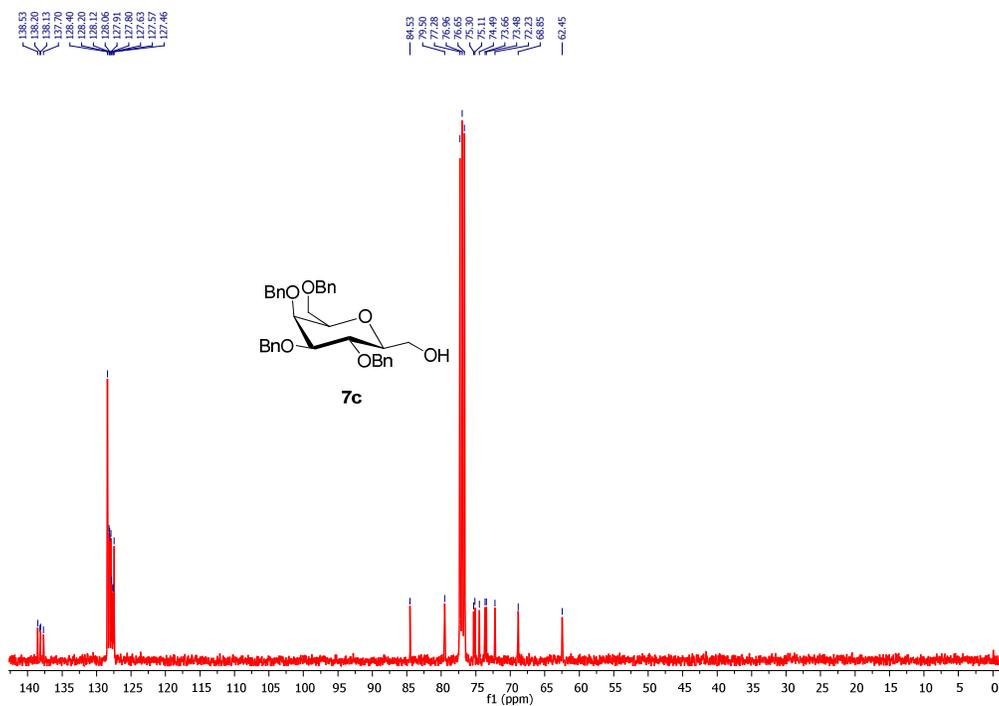


Figure S36. <sup>13</sup>C NMR spectrum of compound **7c** (100.6 MHz, CDCl<sub>3</sub>)

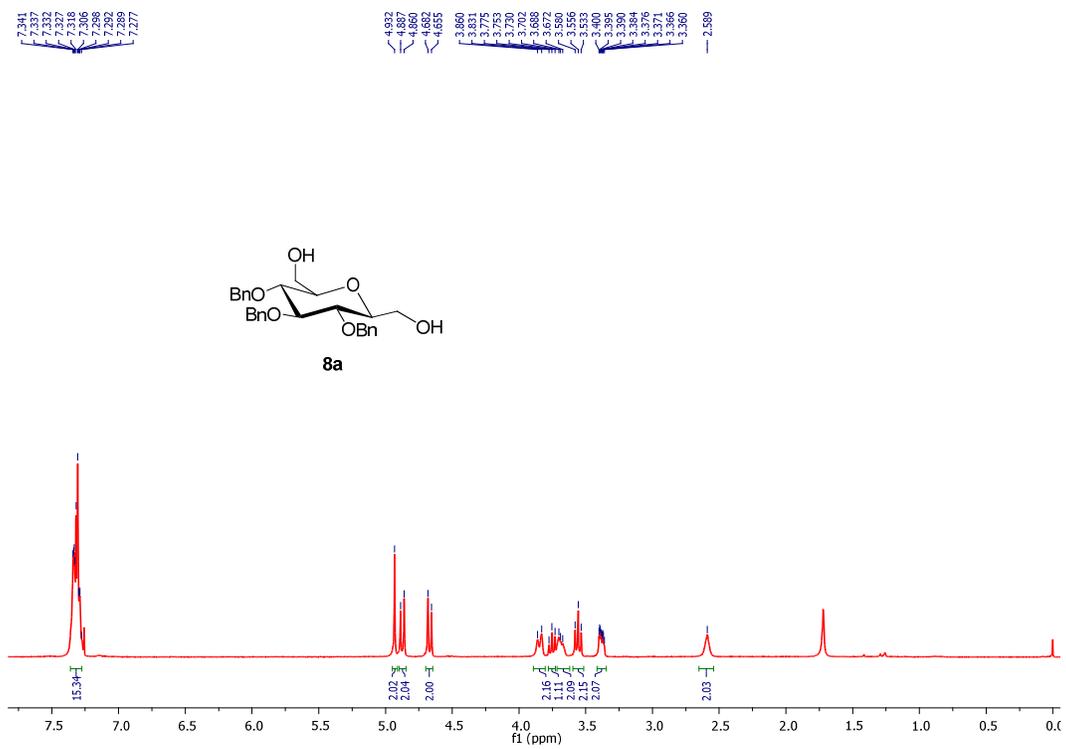


Figure S37.  $^1\text{H}$  NMR spectrum of compound **8a** (400 MHz,  $\text{CDCl}_3$ )

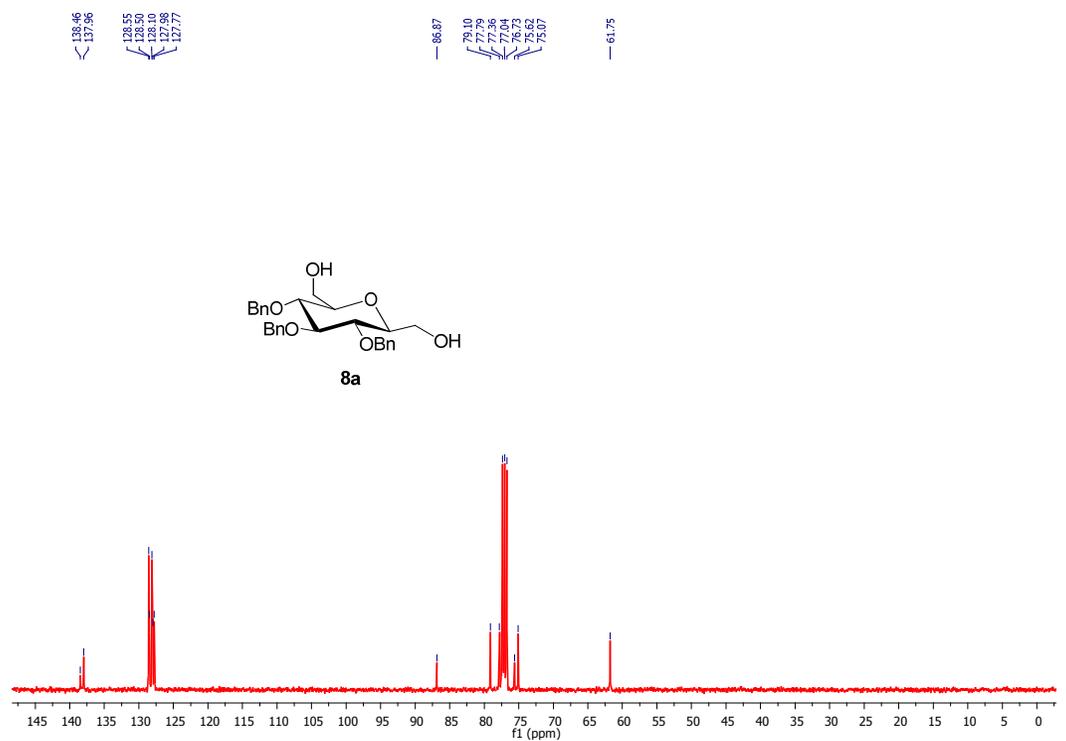


Figure S38.  $^{13}\text{C}$  NMR spectrum of compound **8a** (100.6 MHz,  $\text{CDCl}_3$ )

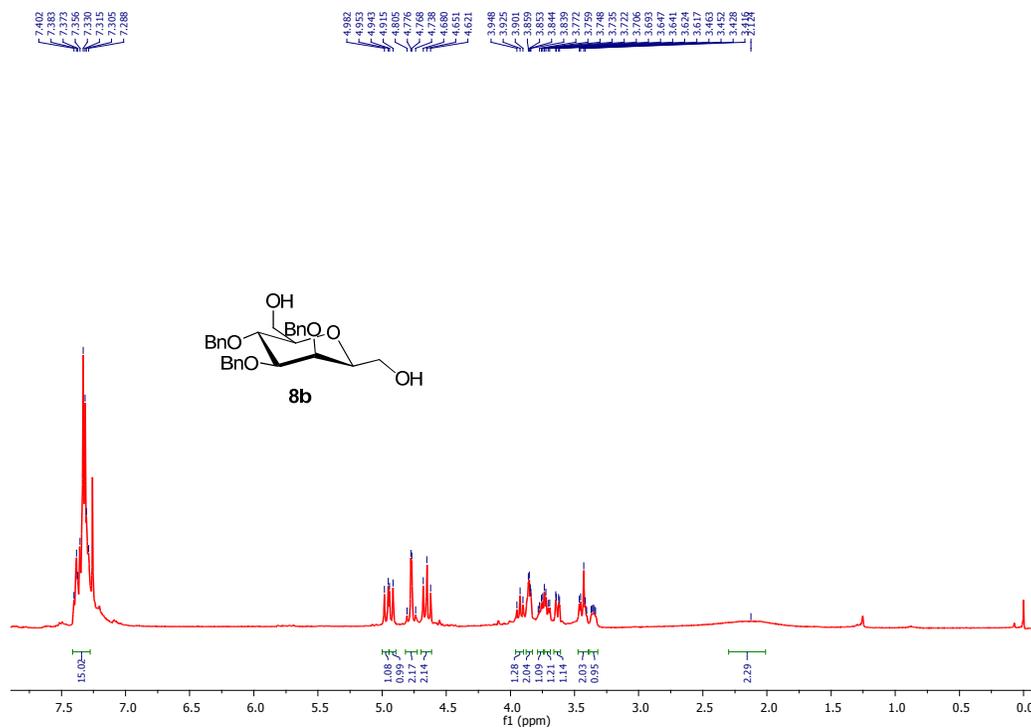
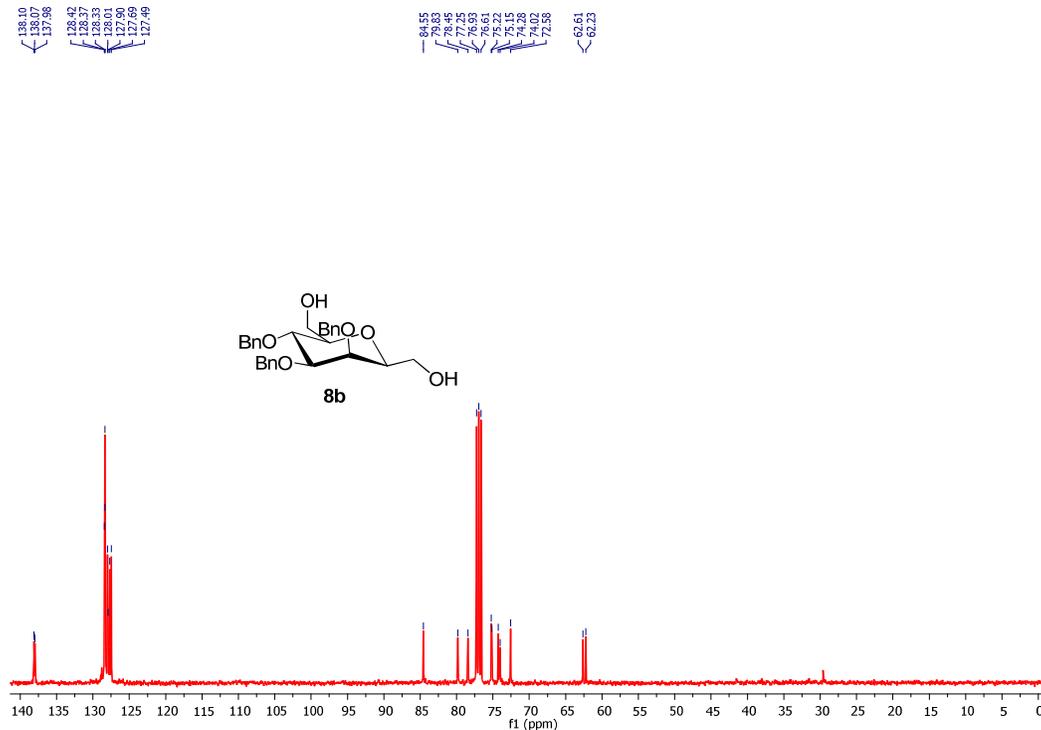


Figure S39. <sup>1</sup>H NMR spectrum of compound **8b** (400 MHz, CDCl<sub>3</sub>)



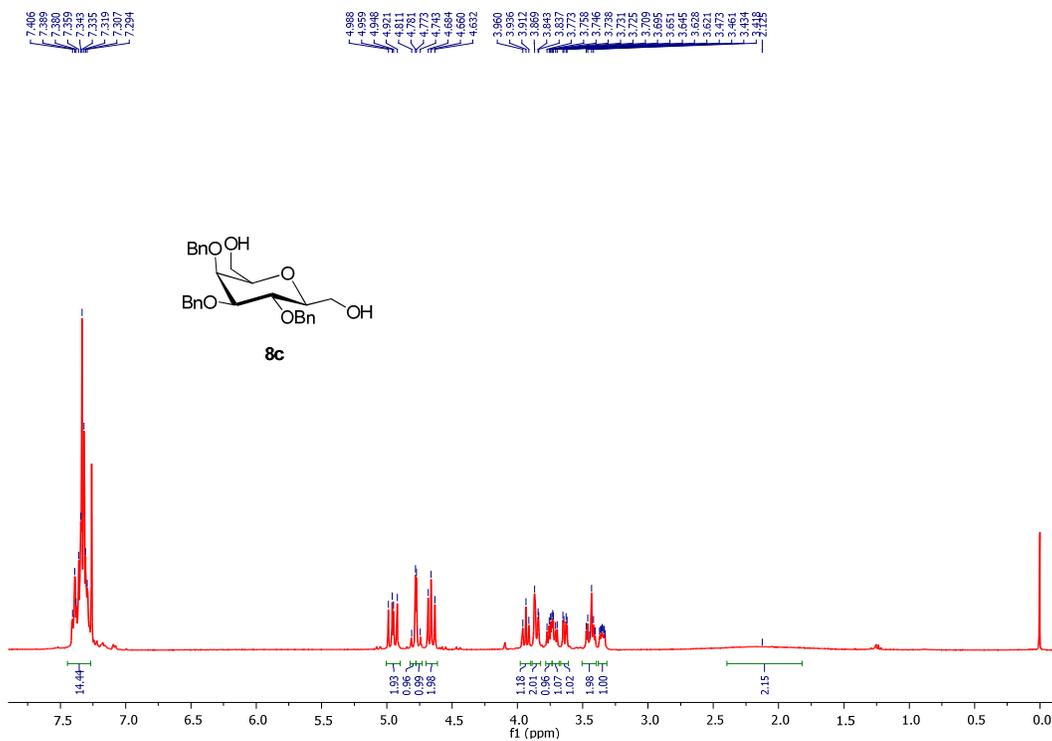


Figure S41. <sup>1</sup>H NMR spectrum of compound **8c** (400 MHz, CDCl<sub>3</sub>)

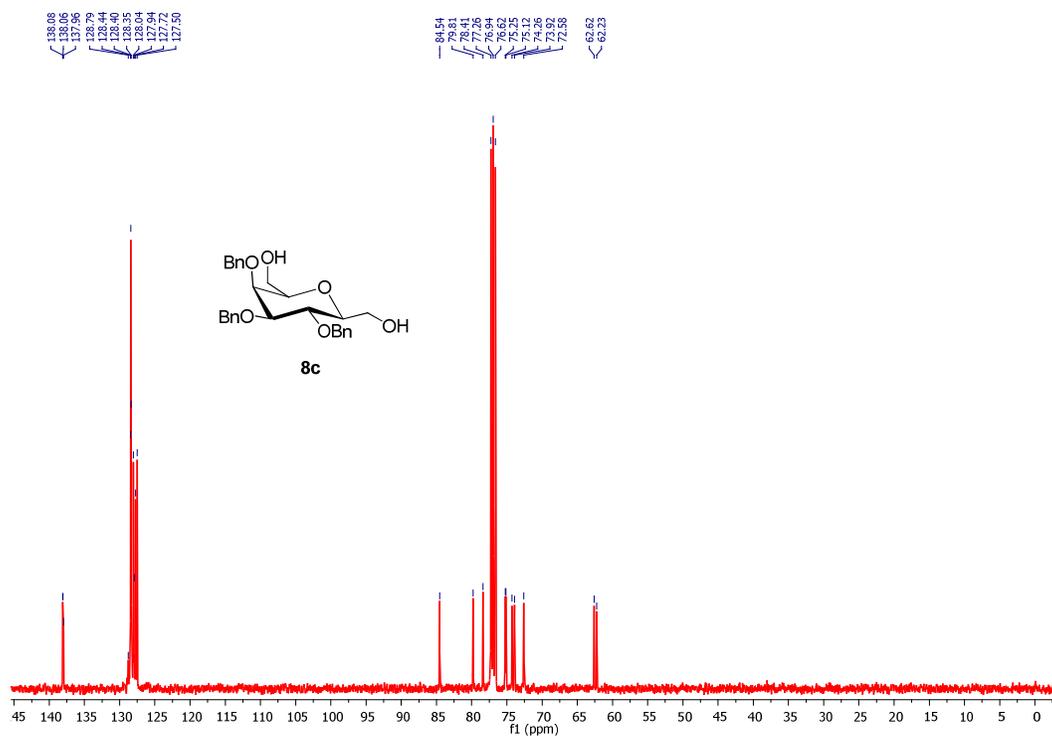


Figure S42. <sup>13</sup>C NMR spectrum of compound **8c** (100.6 MHz, CDCl<sub>3</sub>)

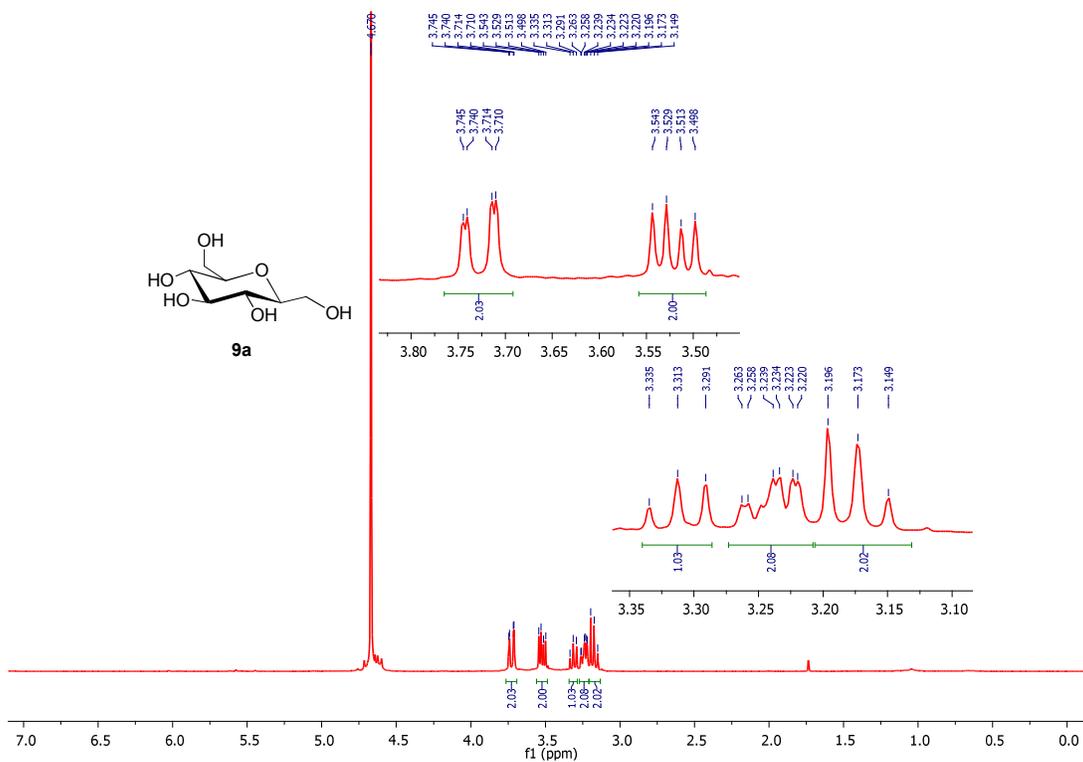


Figure S43. <sup>1</sup>H NMR spectrum of compound **9a** (400 MHz, CDCl<sub>3</sub>)

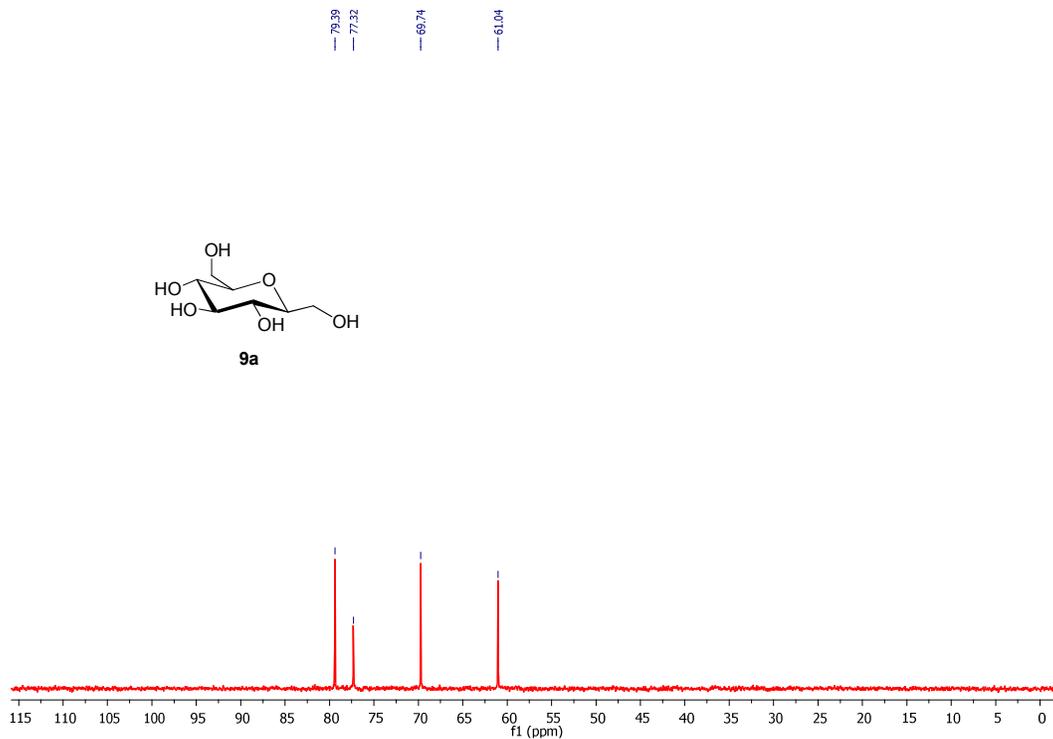
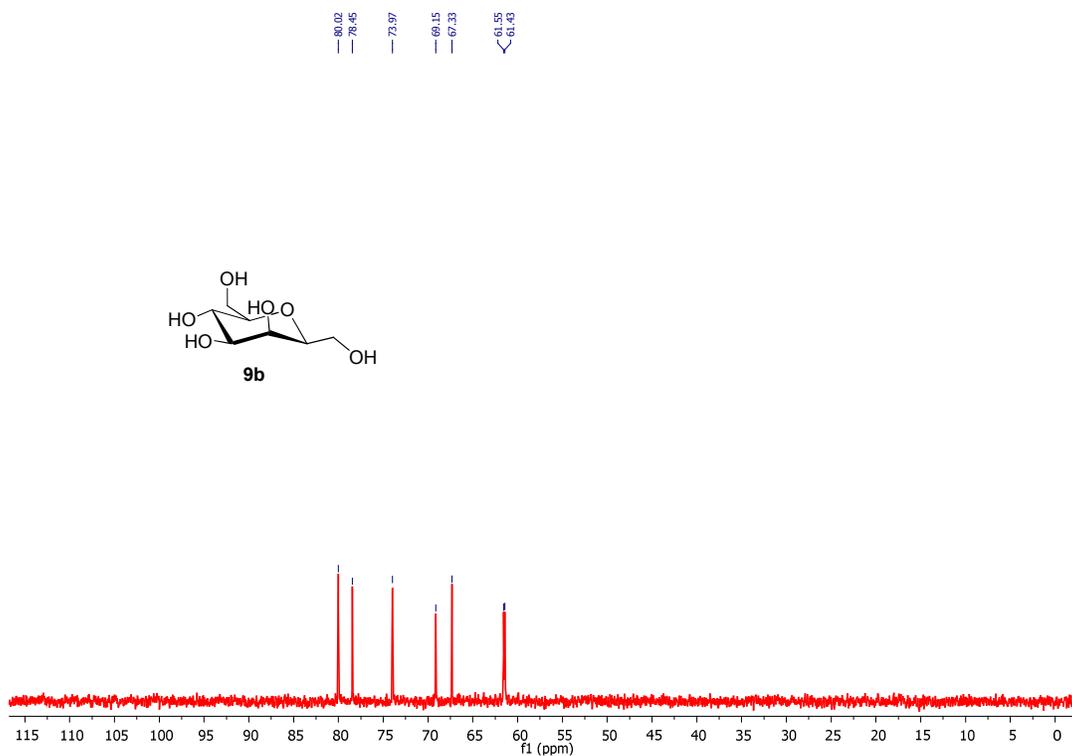
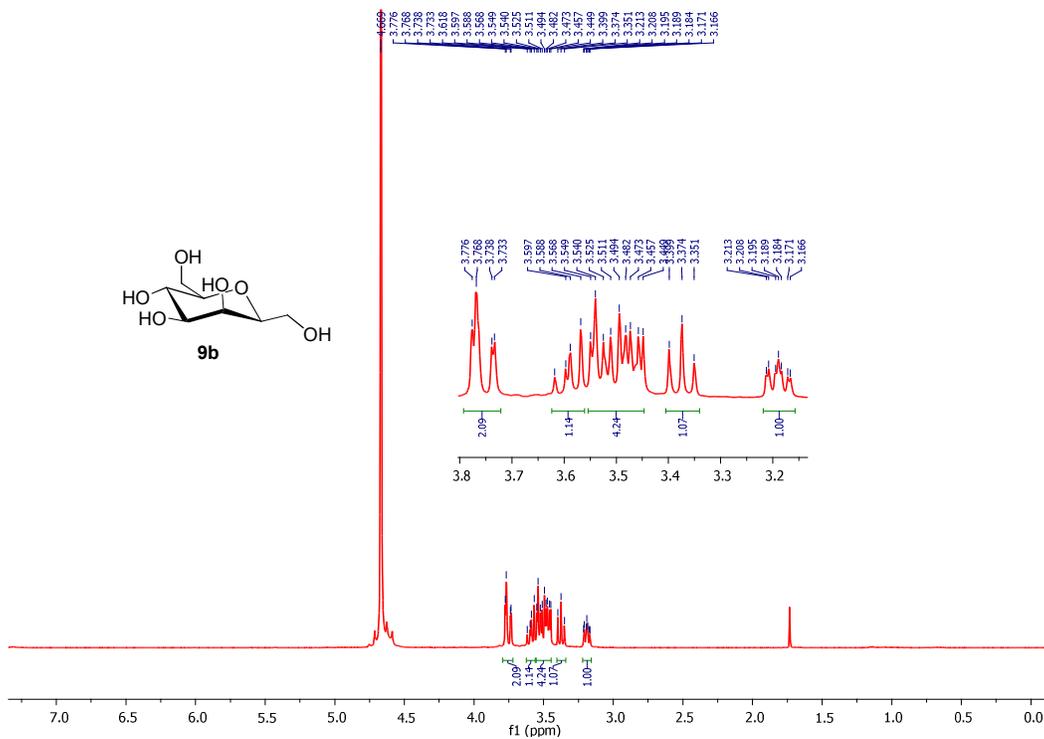


Figure S44. <sup>13</sup>C NMR spectrum of compound **9a** (100.6 MHz, CDCl<sub>3</sub>)



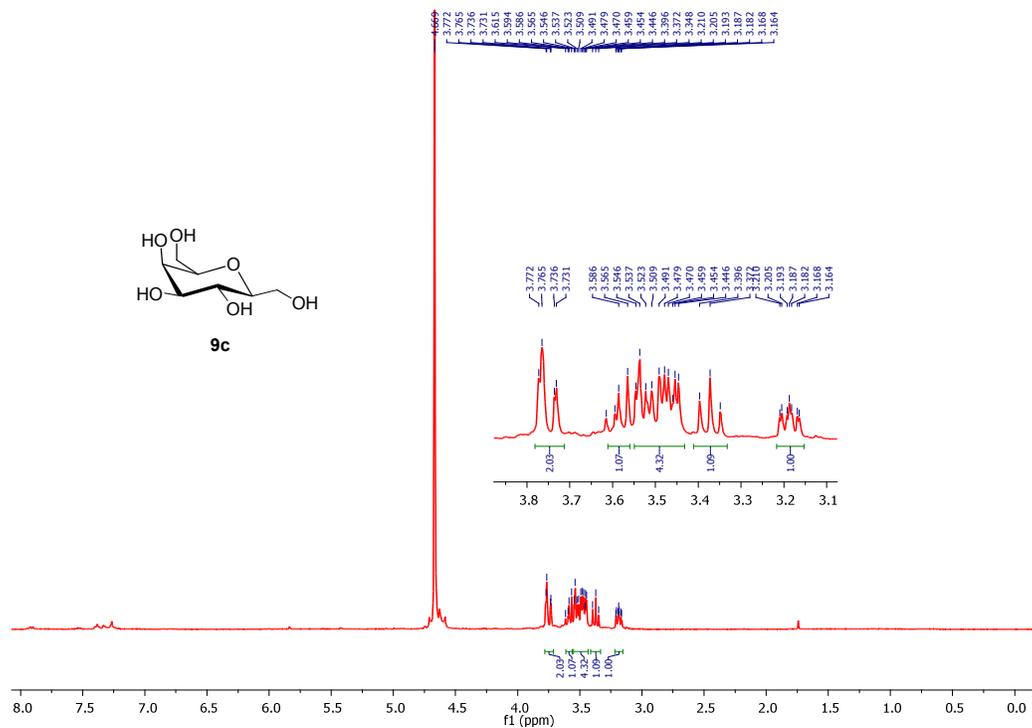


Figure S47. <sup>1</sup>H NMR spectrum of compound **9c** (400 MHz, CDCl<sub>3</sub>)

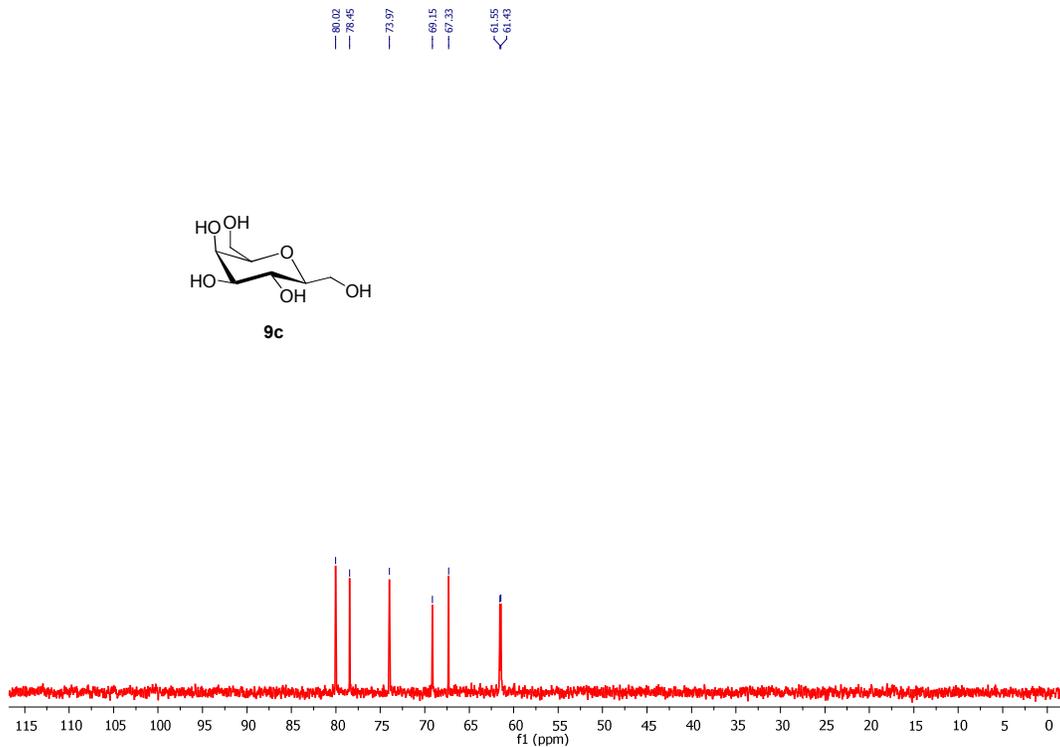
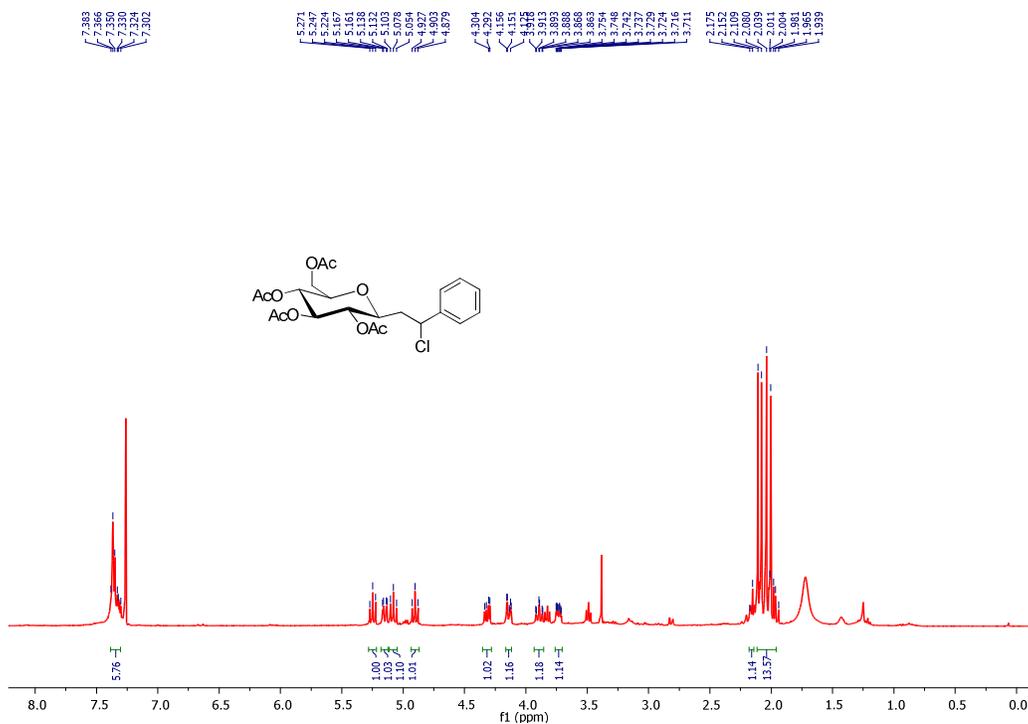
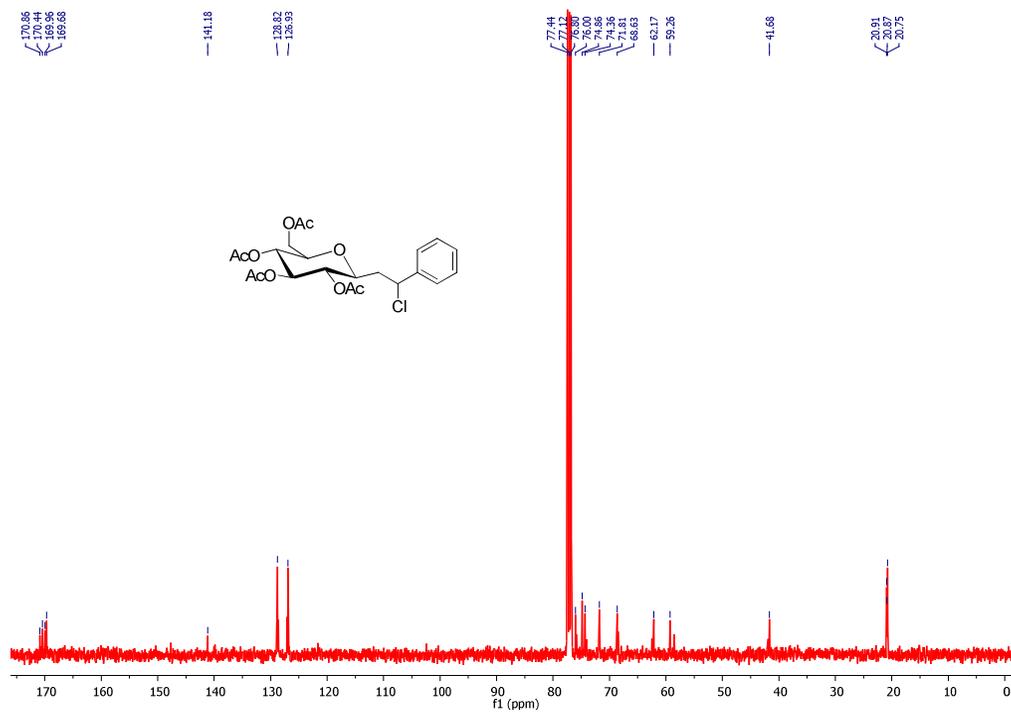


Figure S48. <sup>13</sup>C NMR spectrum of compound **9c** (100.6 MHz, CDCl<sub>3</sub>)

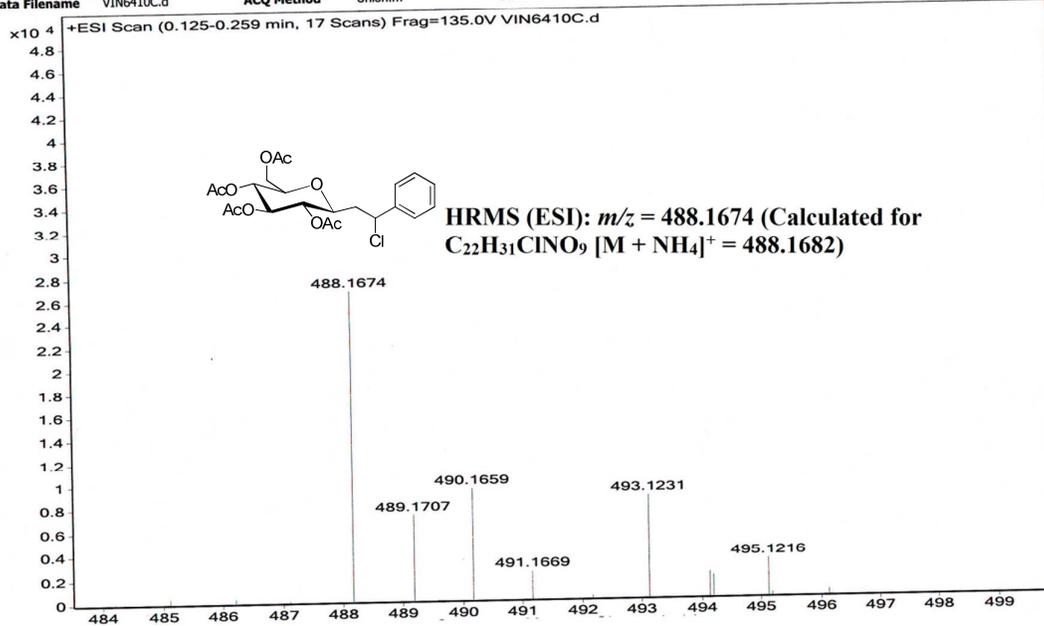


**Figure S49.** <sup>1</sup>H NMR spectrum of *1-chloro-1-phenyl-2-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)ethane* (400 MHz, CDCl<sub>3</sub>)



**Figure S50.** <sup>13</sup>C NMR spectrum of *1-chloro-1-phenyl-2-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)ethane* (100.6 MHz, CDCl<sub>3</sub>)

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Inj Vol	1	InjPosition		SampleType	Sample	IRM Calibration Status	Success
Data Filename	VIN6410C.d	ACQ Method	Union.m	Comment		Acquired Time	10-09-2014 15:16:58



**Figure 51.** HRMS (ESI) of *1-chloro-1-phenyl-2-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyl)ethane*