SUPPORTING INFORMATION

Carbon Tetrachloride-Free Allylic Halogenation-Mediated Glycosylations of Allyl Glycosides

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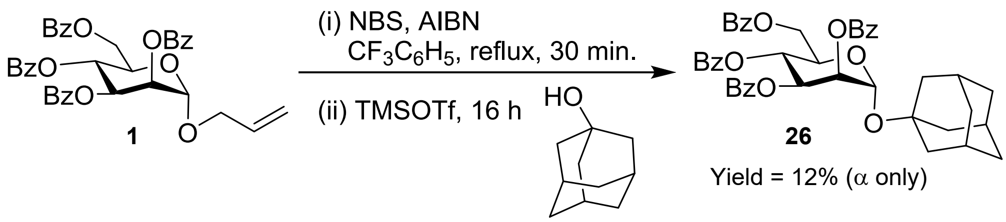
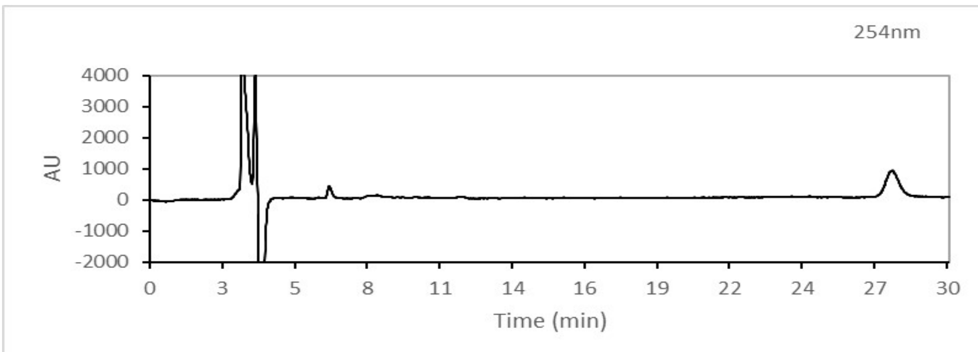
HPLC Traces of the Glycosylations

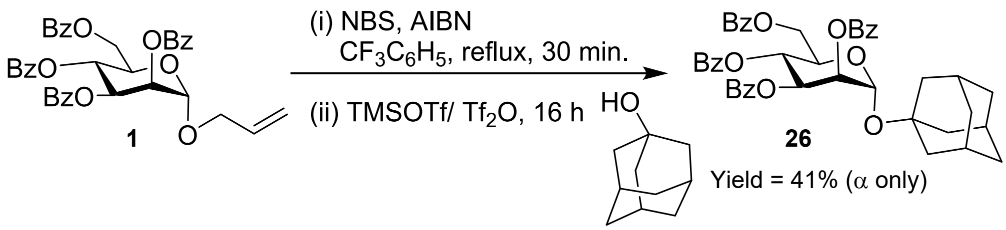


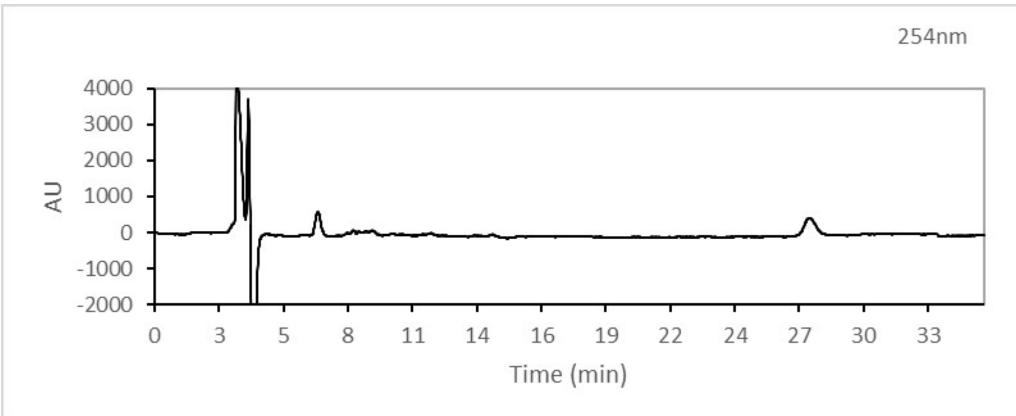


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.731	4063	12.432
2	27.861	28618	87.568
Total		32681	100.000

Figure S1. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **26** (RT 6.731) using TMSOTf as promotor. RT 27.861 refers to lactol.

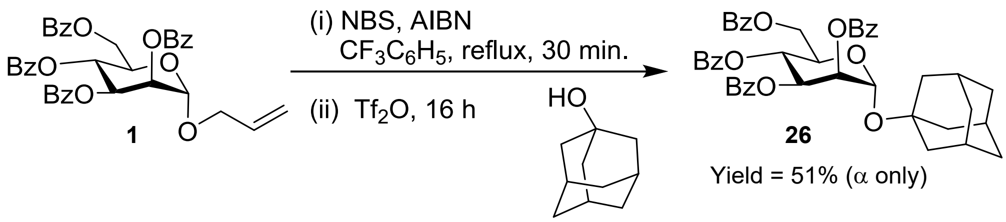


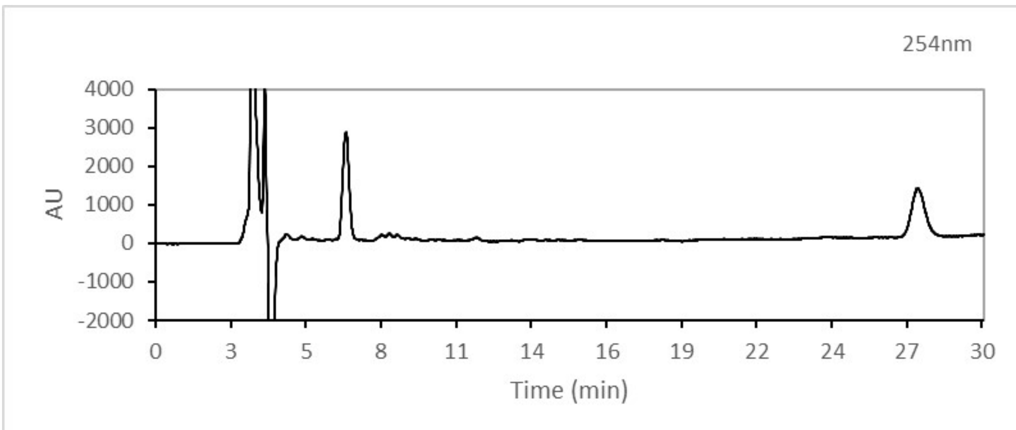


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.901	11113	40.668
2	27.637	16213	59.332
Total		27326	100.000

Figure S2. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **26** (RT 6.901) using TMSOTf + Tf_2O as promotor. RT 27.637 refers to lactol.

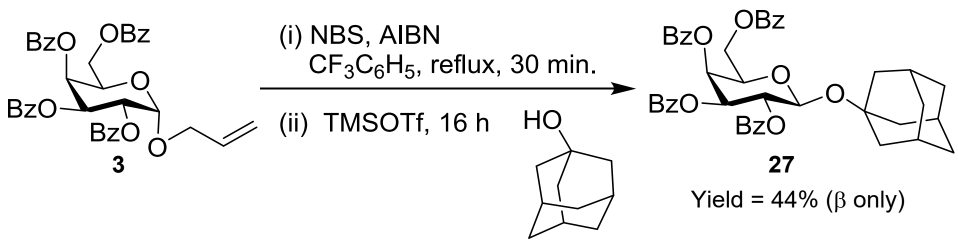


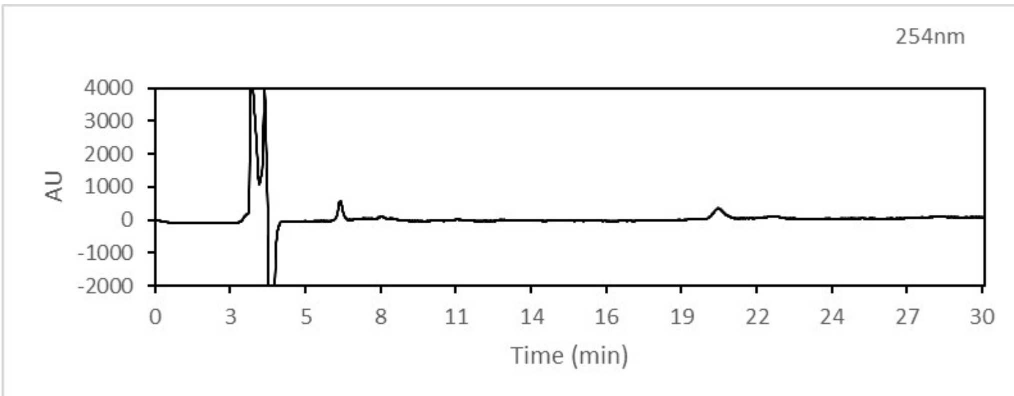


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.891	44889	51.016
2	27.605	43101	48.984
Total		87990	100.000

Figure S3. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **26** (RT 6.891) using Tf_2O as promotor. RT 27.605 refers to lactol.

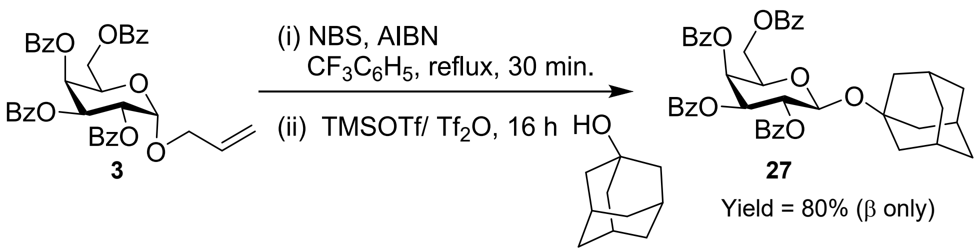


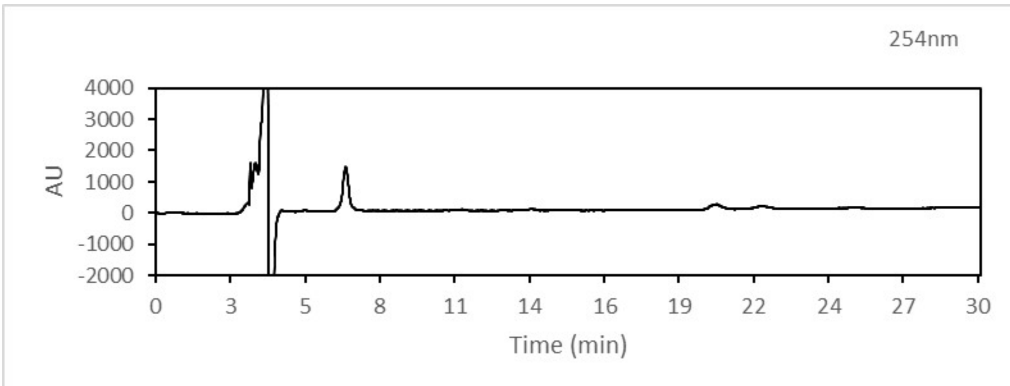


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.788	7201	44.213
2	20.373	9086	57.787
Total		16287	100.000

Figure S4. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **27** (RT 6.788) using TMSOTf as promotor. RT 20.373 refers to lactol.

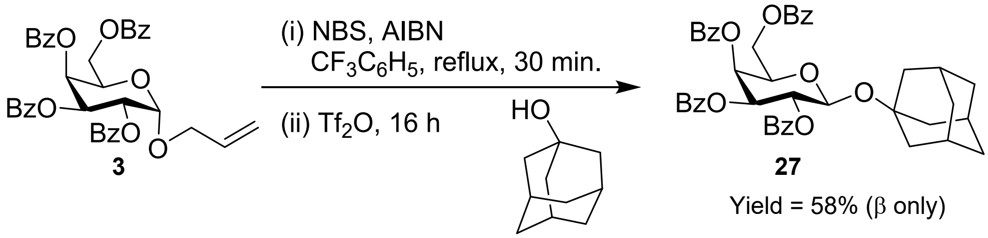


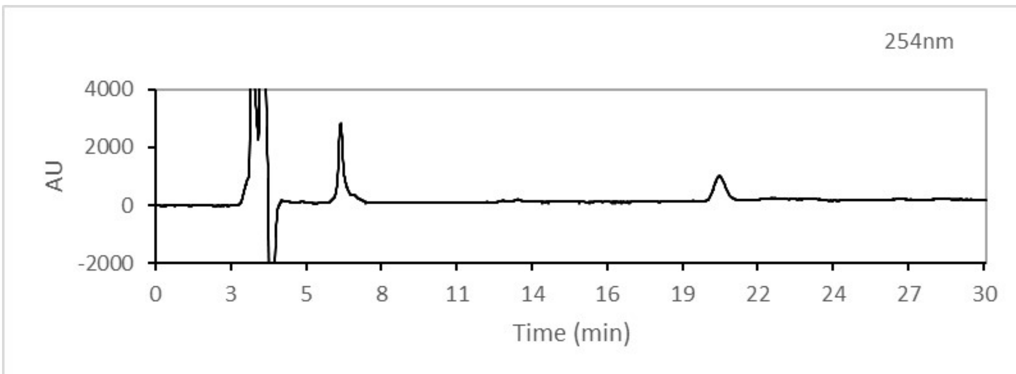


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.912	18920	79.811
2	20.427	4786	20.189
Total		23706	100.000

Figure S5. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **27** (RT 6.912) using TMSOTf + Tf_2O as promotor. RT 20.427 refers to lactol.

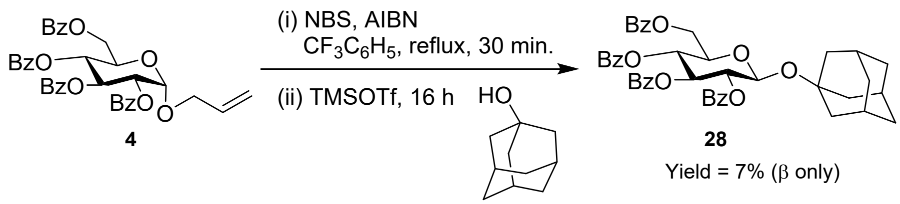


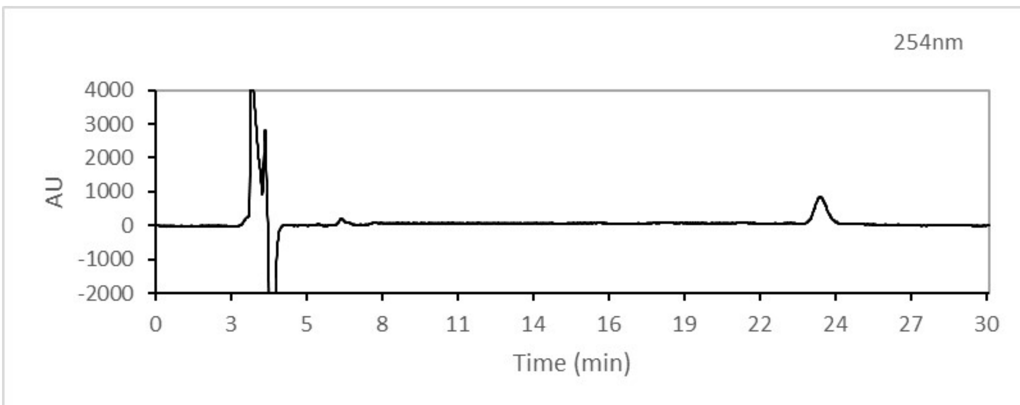


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.688	32539	58.595
2	20.352	22993	41.405
Total		55532	100.000

Figure S6. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **27** (RT 6.688) using Tf_2O as promotor. RT 20.352 refers to lactol.

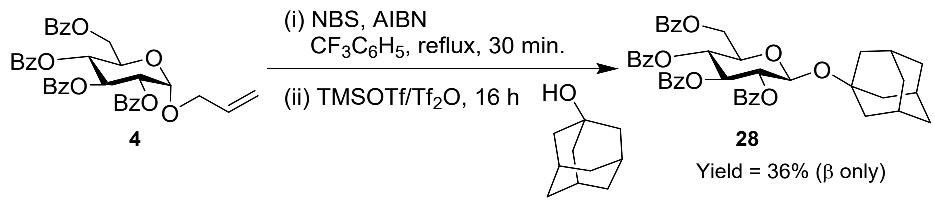




PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.051	3891	7.742
2	23.360	46367	92.258
Total		50258	100.000

Figure S7. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **28** (RT 7.051) using TMSOTf as promotor. RT 23.360 refers to lactol.



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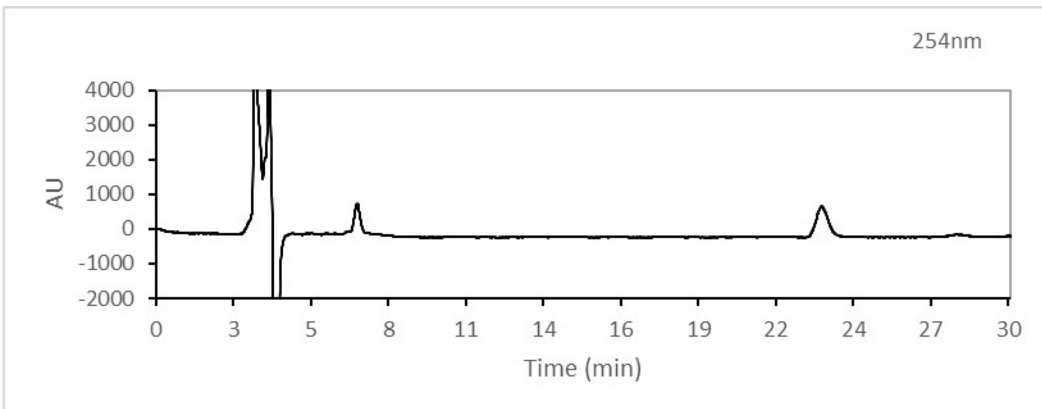
28

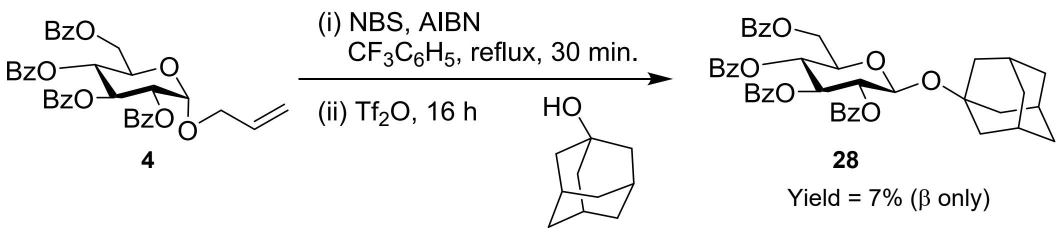
Yield = 36% (β only)

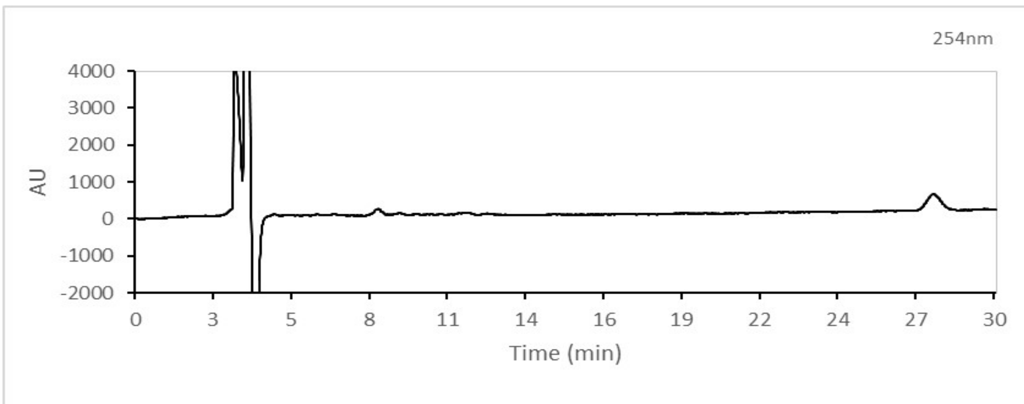


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.051	11760	36.018
2	23.360	20890	63.982
Total		32650	100.000

Figure S8. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **28** (RT 7.051) using TMSOTf + Tf_2O as promotor. RT 23.360 refers to lactol.

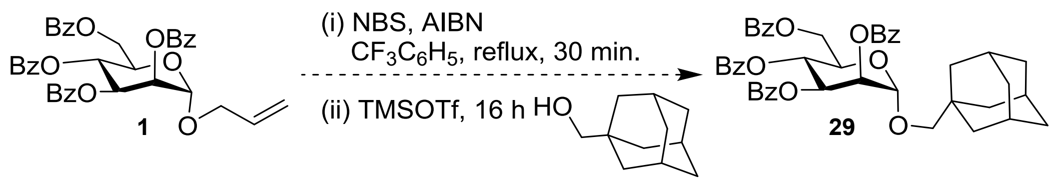


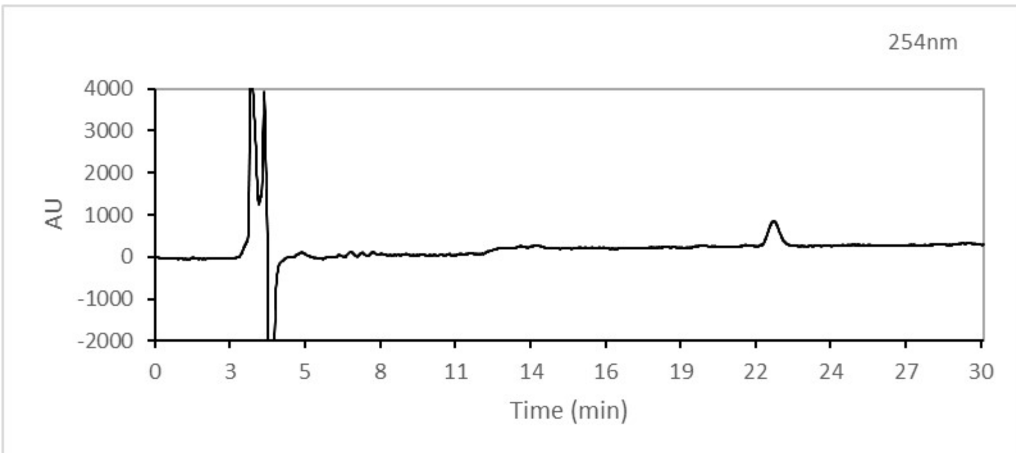


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.083	1796	7.559
2	22.411	21963	92.441
Total		23759	100.000

Figure S9. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **28** (RT 7.083) using Tf_2O as promotor. RT 22.411 refers to lactol.

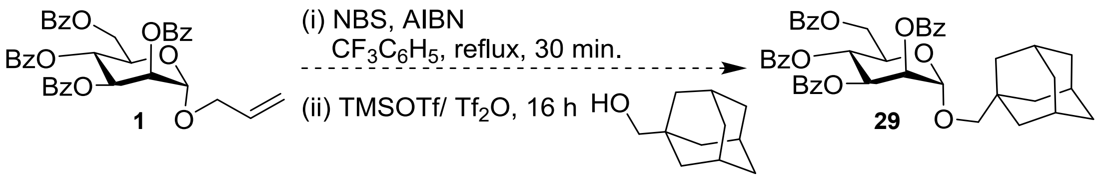


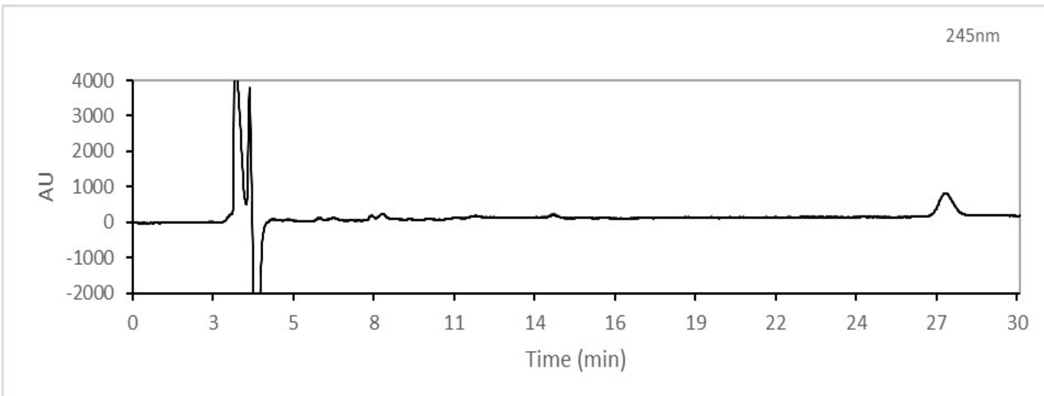


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.818	15135	100.000
Total		15135	100.000

Figure S10. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **29** using TMSOTf as promotor. RT 27.818 refers to lactol.

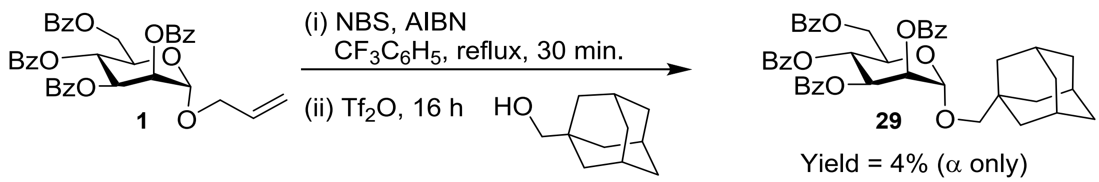


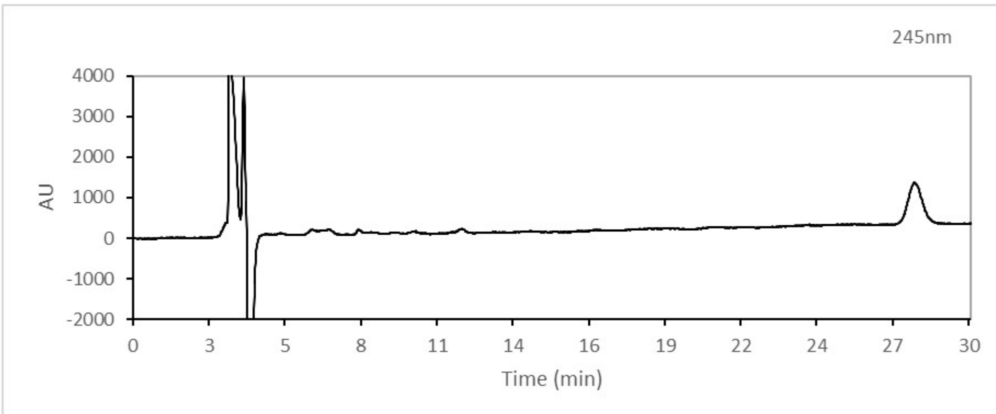


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	27.818	15135	100.000
Total		15135	100.000

Figure S11. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **29** using TMSOTf + Tf_2O as promotor. RT 27.818 refers to lactol.

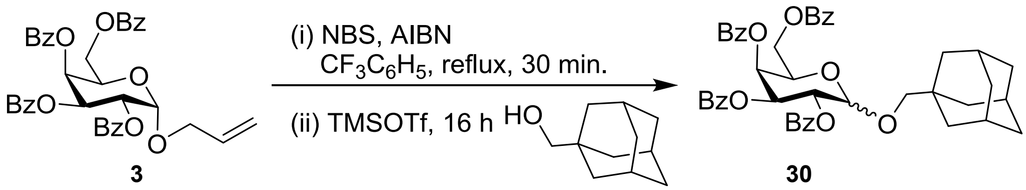




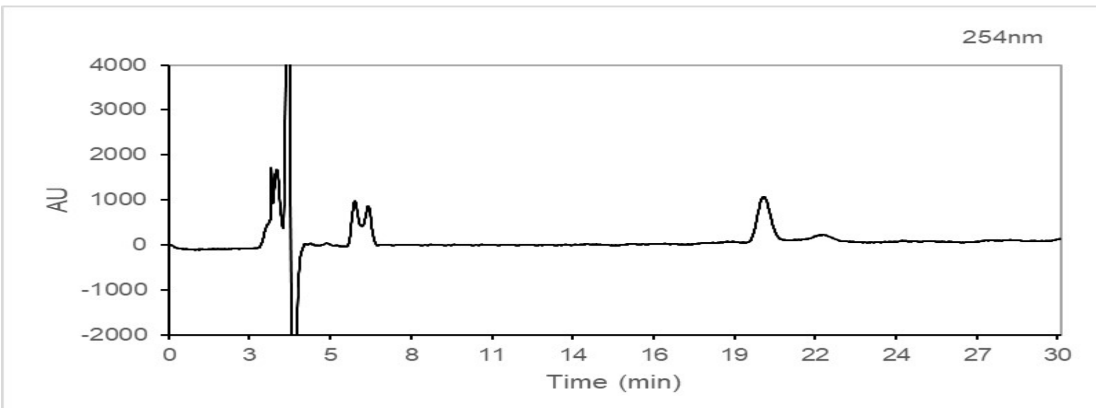
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.773	856	3.734
2	27.477	22064	96.266
Total		22920	100.000

Figure S12. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **29** (RT 6.773) using Tf_2O as promotor. RT 27.477 refers to lactol.



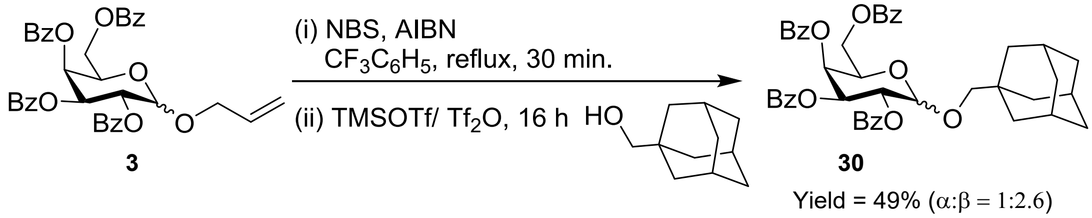
Yield = 37% (α:β = 1:1.1)

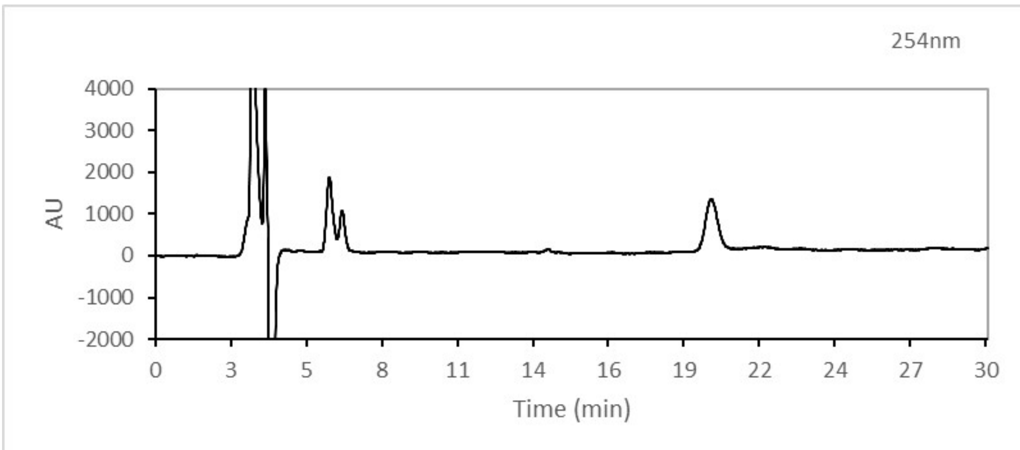


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.251	7023	19.233
2	6.720	6384	17.483
3	20.032	23108	63.284
Total		36515	100.000

Figure S13. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **30** (RT 6.251 & 6.720) using TMSOTf as promotor. RT 20.032 refers to lactol.

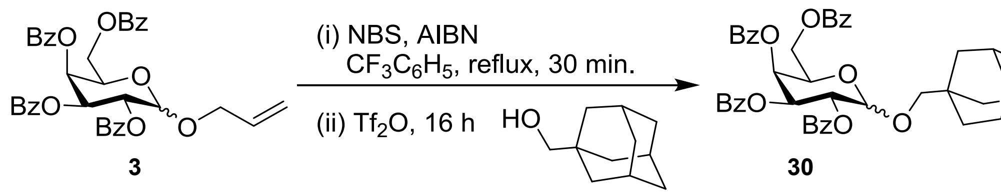


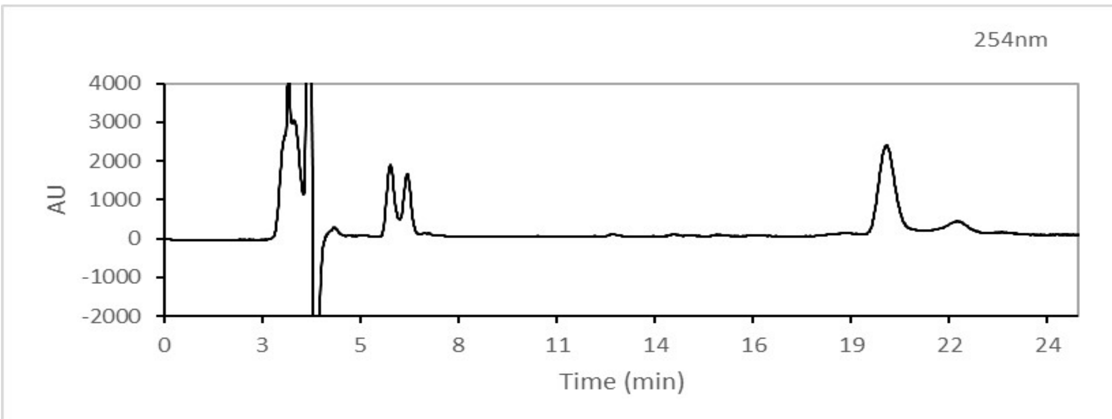


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.261	24347	35.238
2	6.720	9343	13.522
3	20.011	35404	51.240
Total		69094	100.000

Figure S14. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **30** (RT 6.261 & 6.720) using TMSOTf + Tf_2O as promotor. RT 20.011 refers to lactol.

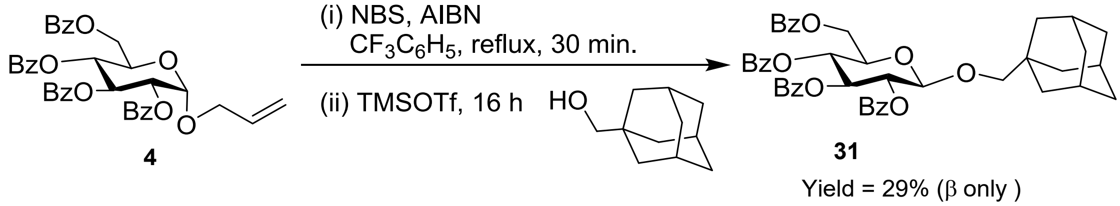


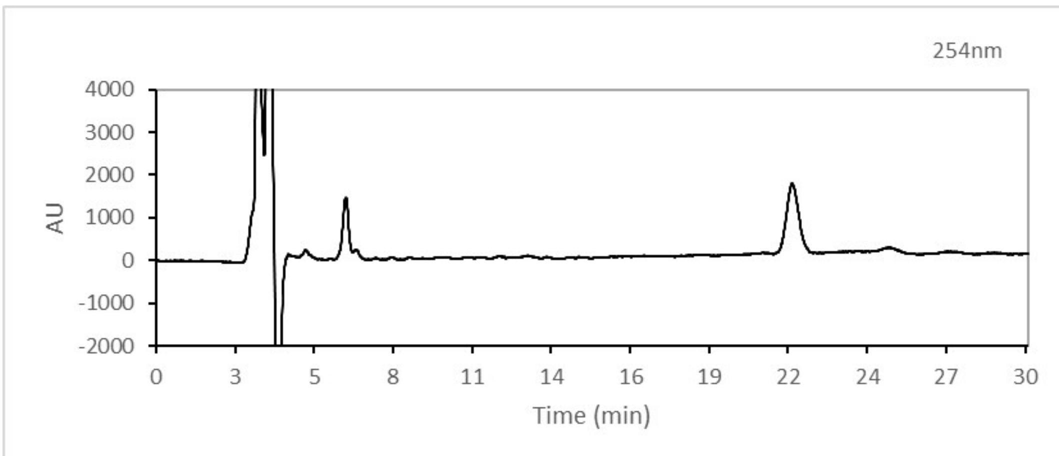


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.251	16143	19.417
2	6.741	14676	17.652
3	20.000	52321	62.931
Total		83140	100.000

Figure S15. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **30** (RT 6.251 & 6.741) using Tf_2O as promotor. RT 20.000 refers to lactol.

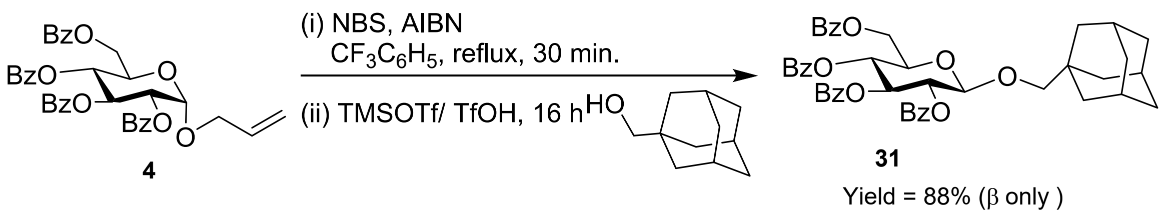


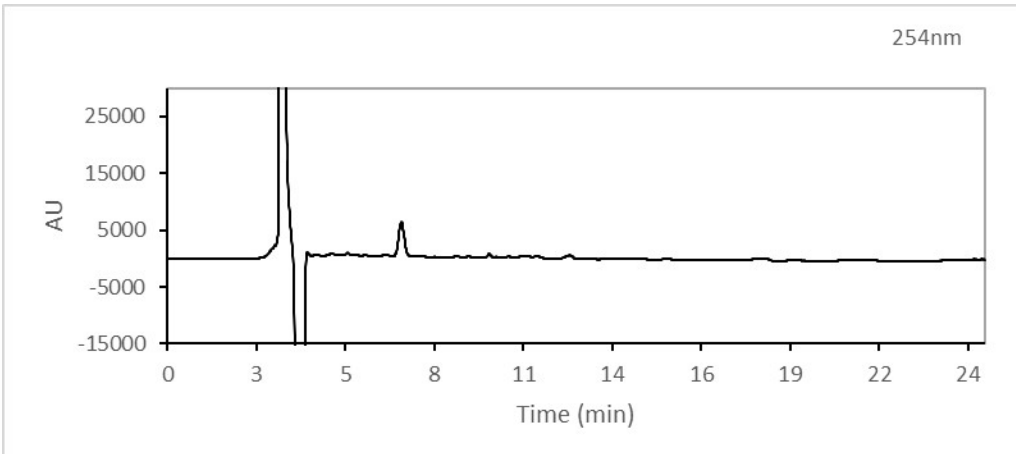


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.099	18923	29.077
2	21.041	46157	70.923
Total		65080	100.000

Figure S16. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **31**(RT 7.099) using TMSOTf as promotor. RT 20.041 refers to lactol.

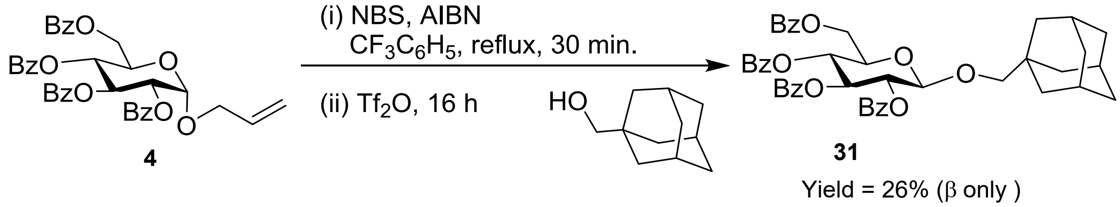


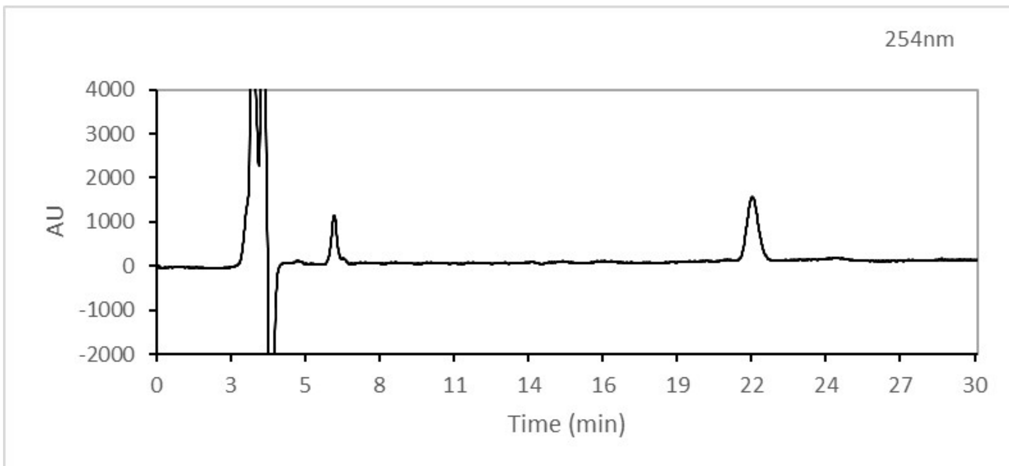


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.147	31660	88.003
2	21.088	4316	11.997
Total		35976	100.000

Figure S17. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **31** (RT 7.147) using TMSOTf + Tf_2O as promotor. RT 21.088 refers to lactol.

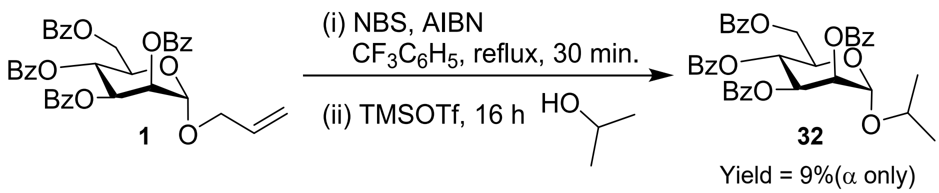


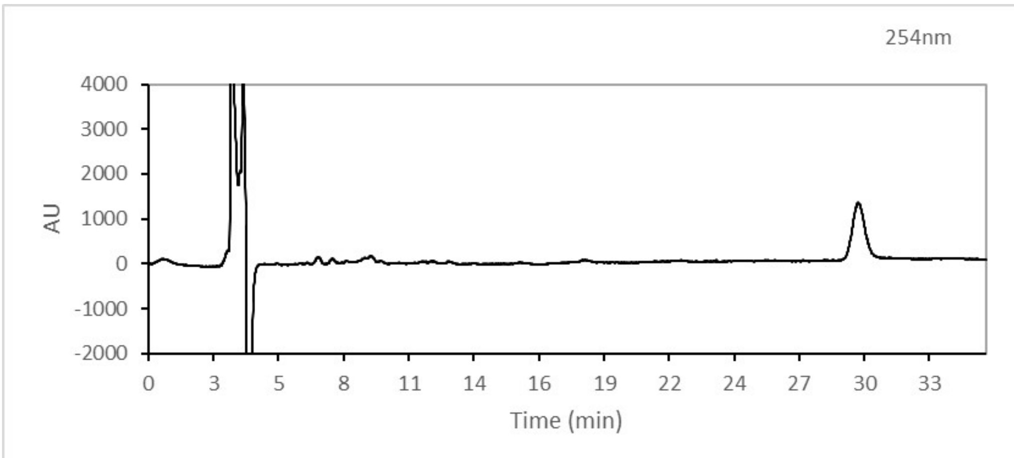


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.987	11367	26.573
2	20.928	31409	73.427
Total		42776	100.000

Figure S18. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **31** (RT 6.987) using Tf_2O as promotor. RT 20.928 refers to lactol.

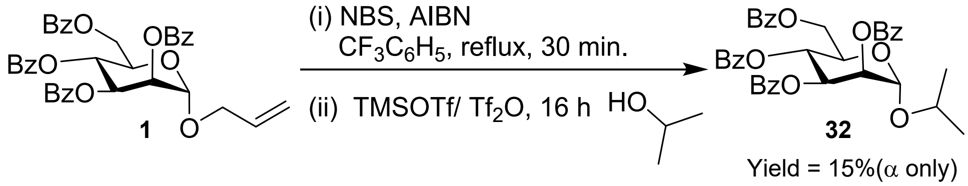


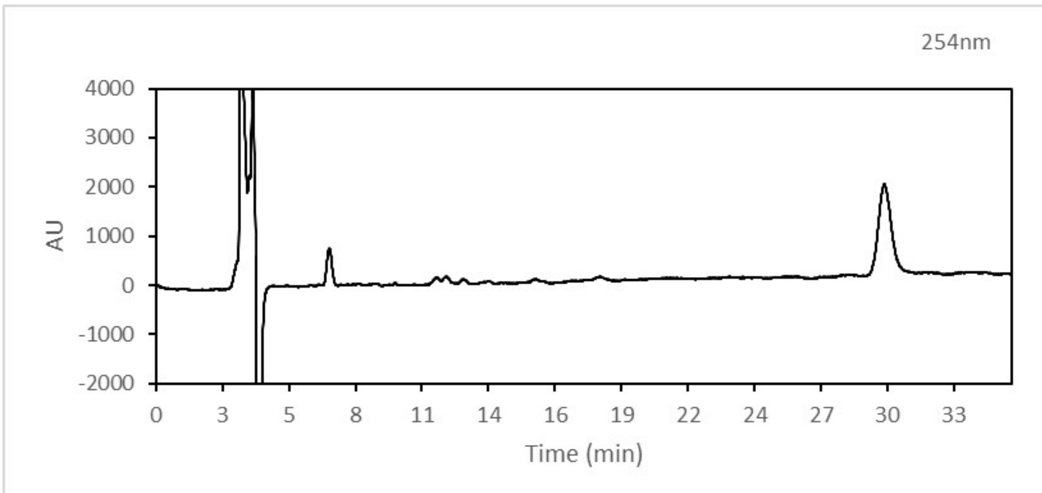


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.061	2440	9.312
2	29.663	23762	90.688
Total		26202	100.000

Figure S19. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **32** (RT 7.061) using TMSOTf as promotor. RT 29.663 refers to lactol.

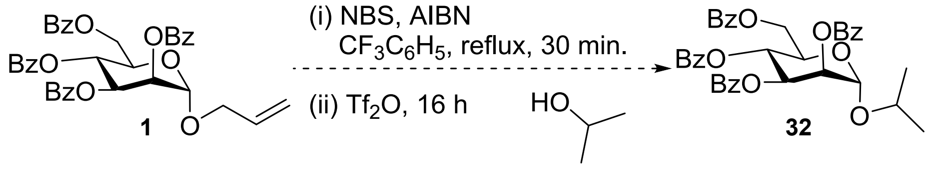


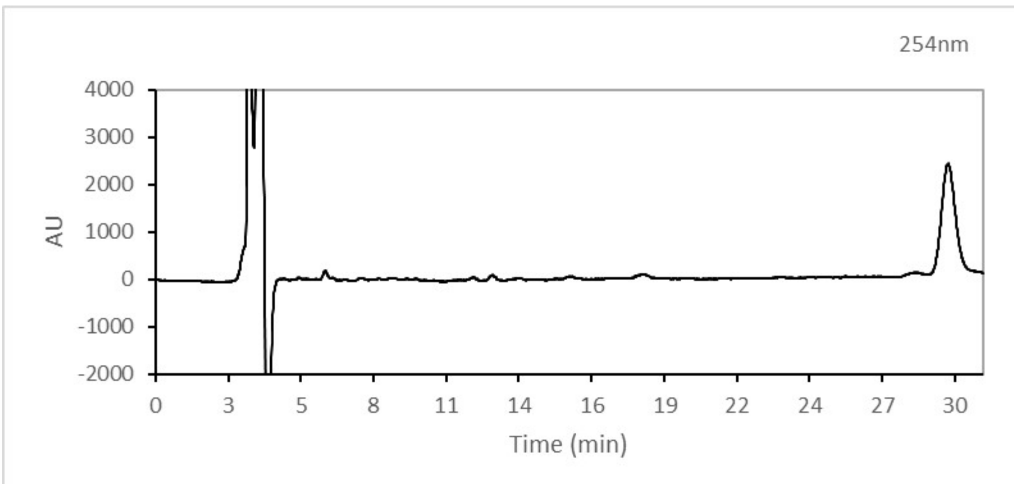


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.093	10818	14.988
2	29.803	61362	85.012
Total		72180	100.000

Figure S20. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **32** (RT 7.093) using TMSOTf + Tf_2O as promotor. RT 29.803 refers to lactol.

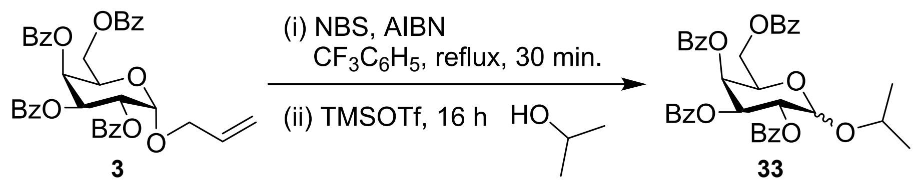




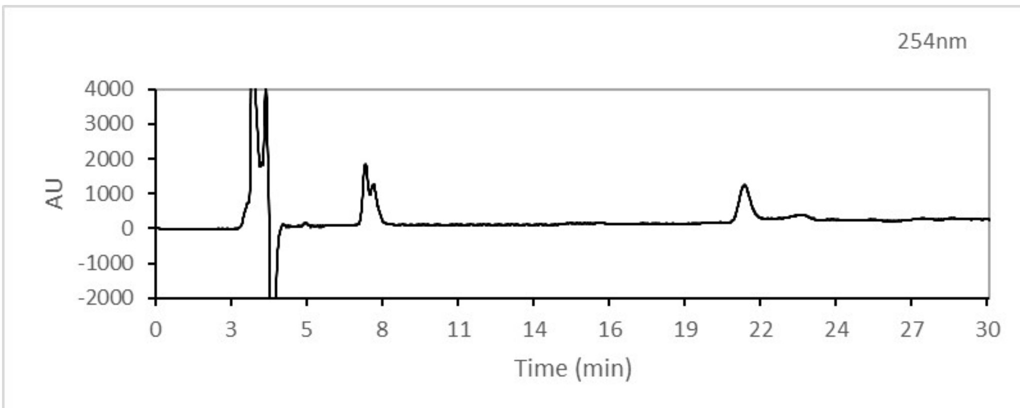
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	29.675	22483	100.000
Total		22483	100.000

Figure S21. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **32** using Tf_2O as promotor. RT 29.675 refers to lactol.



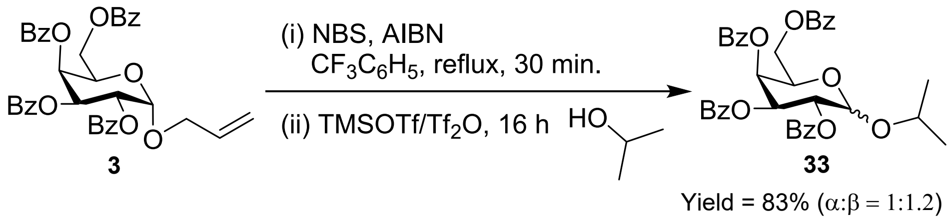
Yield = 56% (α:β = 1:1.3)

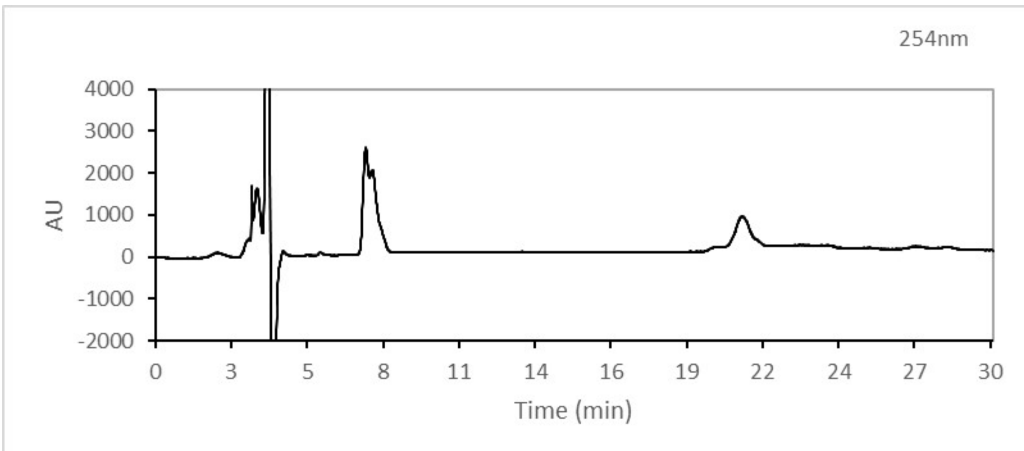


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.552	24825	31.454
2	7.829	19282	24.431
3	21.184	34818	44.115
Total		78925	100.000

Figure S22. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.552 & 7.829) using TMSOTf as promotor. RT 21.184 refers to lactol.

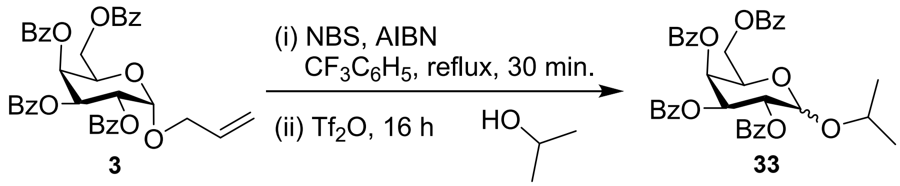




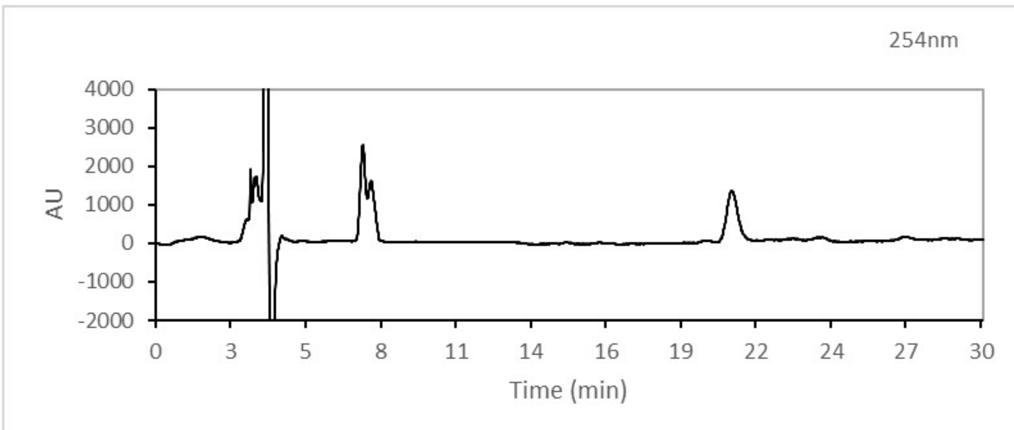
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.531	26766	40.785
2	7.776	27213	41.466
3	21.035	11648	17.749
Total		65627	100.000

Figure S23. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.531 & 7.776) using TMSOTf + Tf_2O as promotor. RT 21.035 refers to lactol.



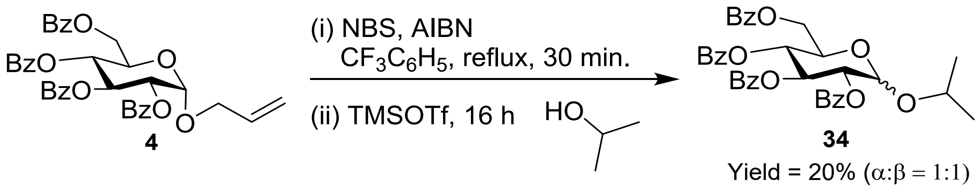
Yield = 64% (α:β = 1:1.4)

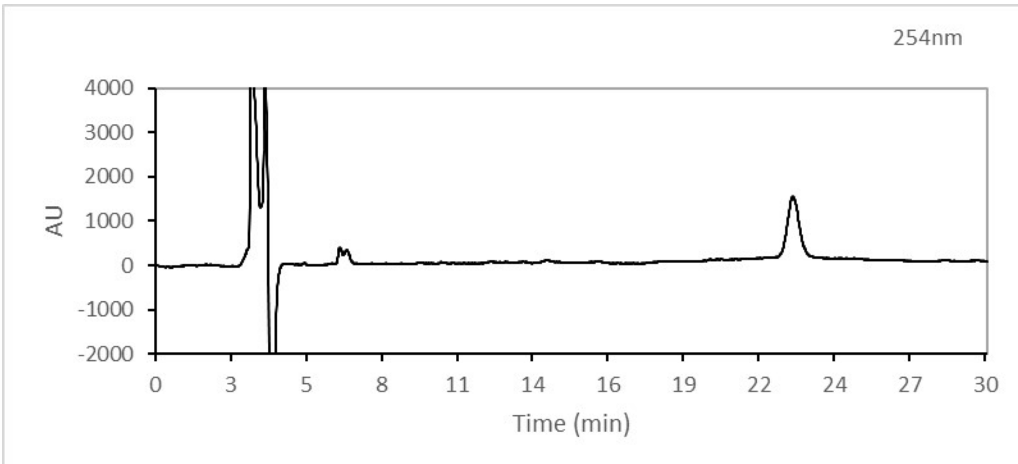


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.509	27049	34.782
2	7.819	22280	28.649
3	20.875	28439	36.569
Total		77768	100.000

Figure S24. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.509 & 7.819) using Tf_2O as promotor. RT 20.875 refers to lactol.

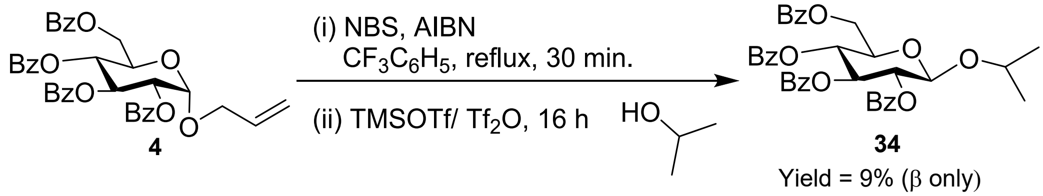


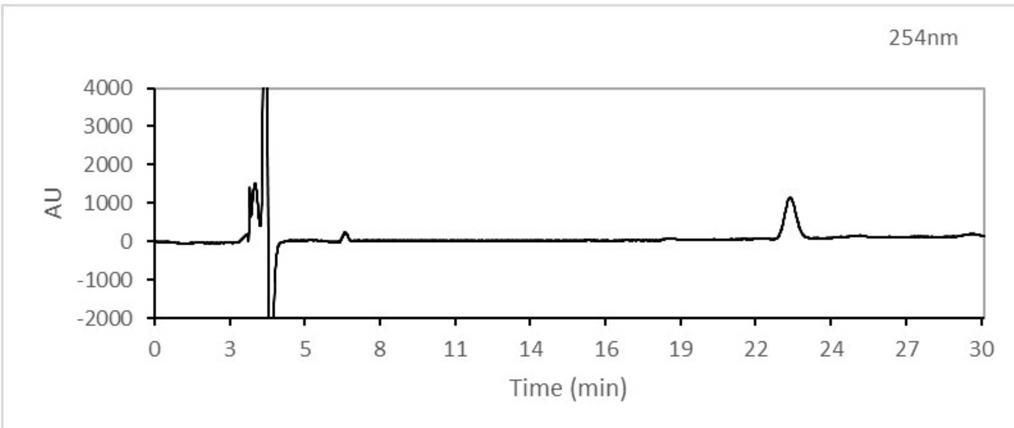


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.645	4889	10.268
2	6.891	4908	10.308
3	22.997	37817	79.424
Total		47614	100.000

Figure 25. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **34** (RT 6.645 & 6.891) using TMSOTf as promotor. RT 22.997 refers to lactol.

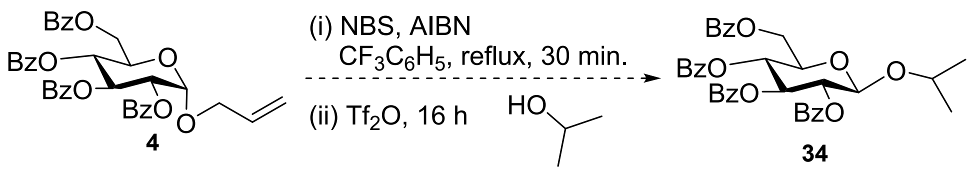


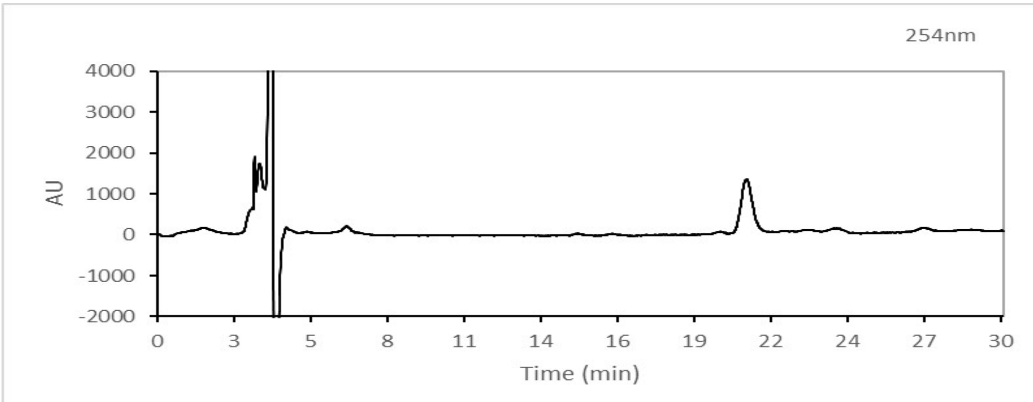


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	6.912	2692	9.607
2	23.008	25328	90.393
Total		28020	100.000

Figure S26. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **34** (RT 6.912) using TMSOTf + Tf_2O as promotor. RT 23.008 refers to lactol.

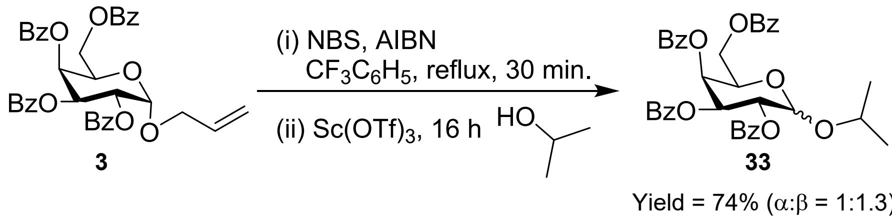


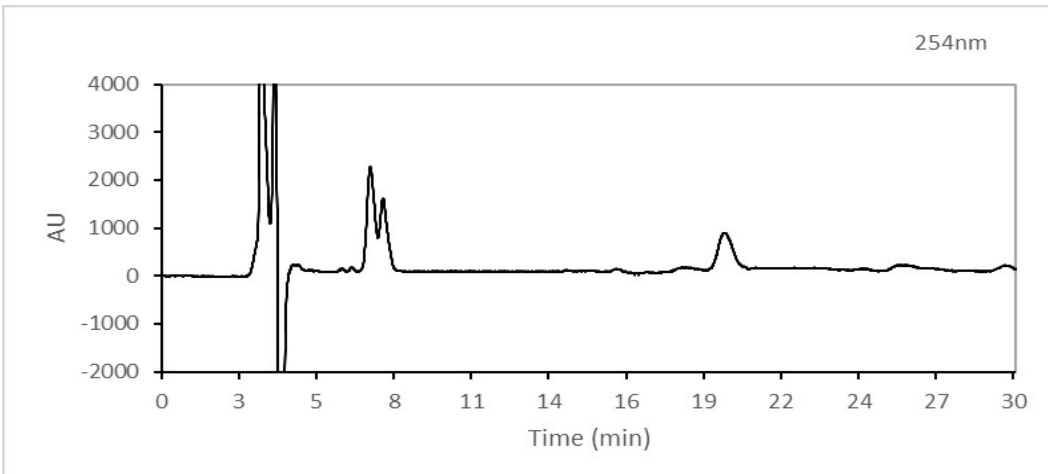


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	23.019	35184	100.000
Total		35184	100.000

Figure S27. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **34** using Tf_2O as promotor. RT 23.019 refers to lactol.

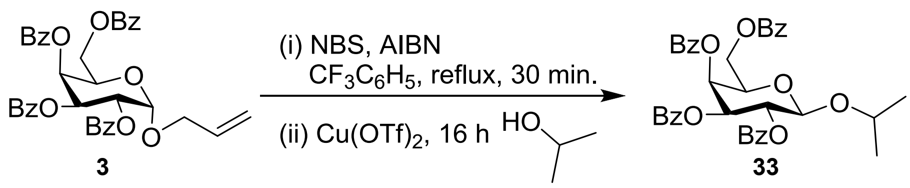


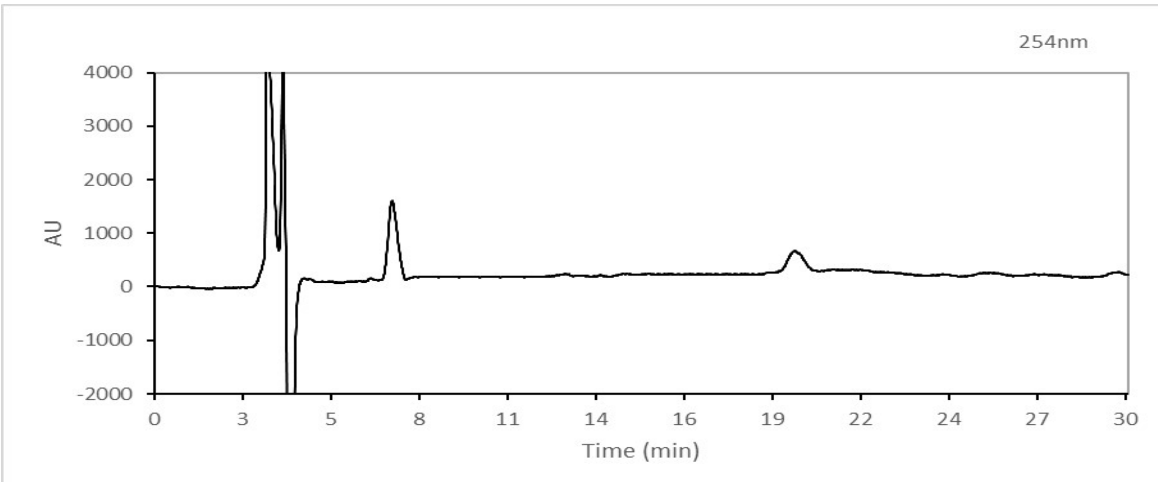


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.328	56210	45.196
2	7.787	35225	28.323
3	19.744	32934	26.481
Total		124369	100.000

Figure S28. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.328 & 7.787) using $Sc(OTf)_3$ as promotor. RT 19.744 refers to lactol.

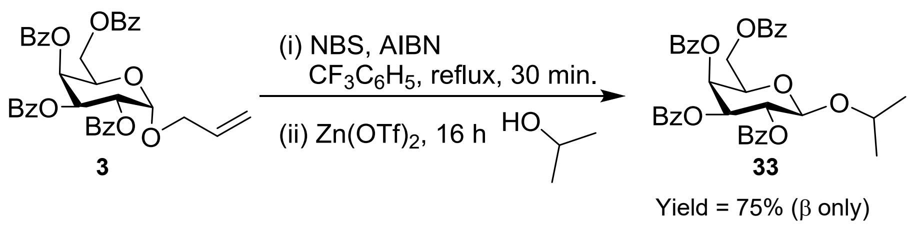


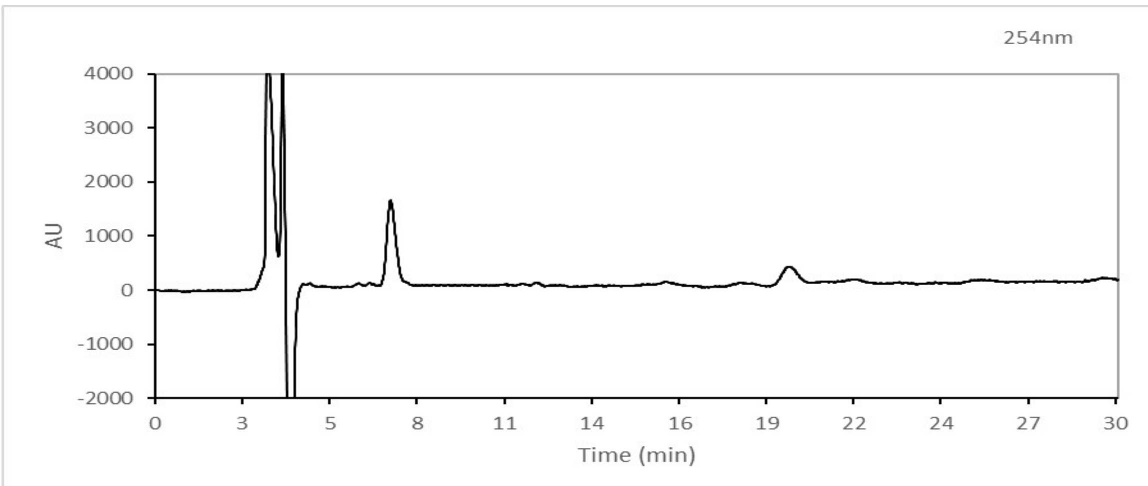


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.317	40914	70.597
2	19.744	17040	29.403
Total		57954	

Figure S29. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.317) using $Cu(OTf)_2$ as promotor. RT 19.744 refers to lactol.

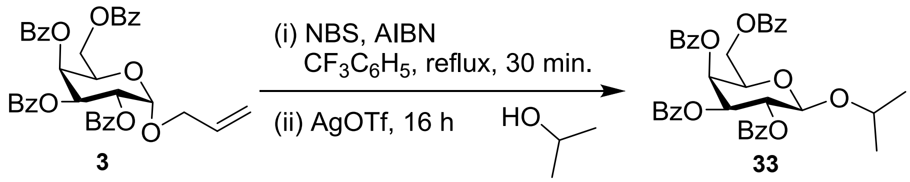


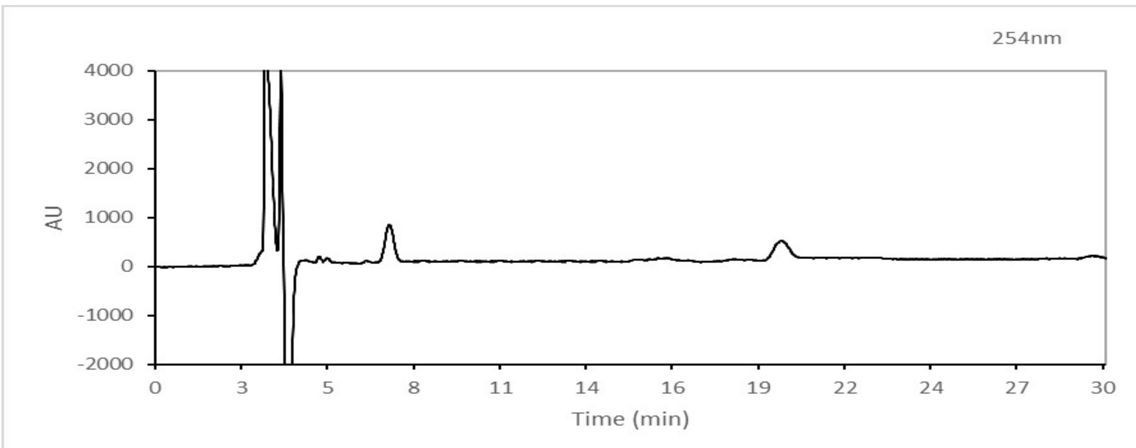


PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.339	42215	74.852
2	19.723	14183	25.148
Total		56398	100.000

Figure S30. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.339) using $Zn(OTf)_2$ as promotor. RT 19.723 refers to lactol.





PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%
1	7.371	22256	52.458
2	19.755	20170	47.542
Total		42426	100.000

Figure S31. HPLC trace of the one-pot glycosylation reaction mixture, corresponding to the synthesis of **33** (RT 7.371) using AgOTf as promotor. RT 19.755 refers to lactol.

[1]H and [13]C NMR Spectra of New Compounds

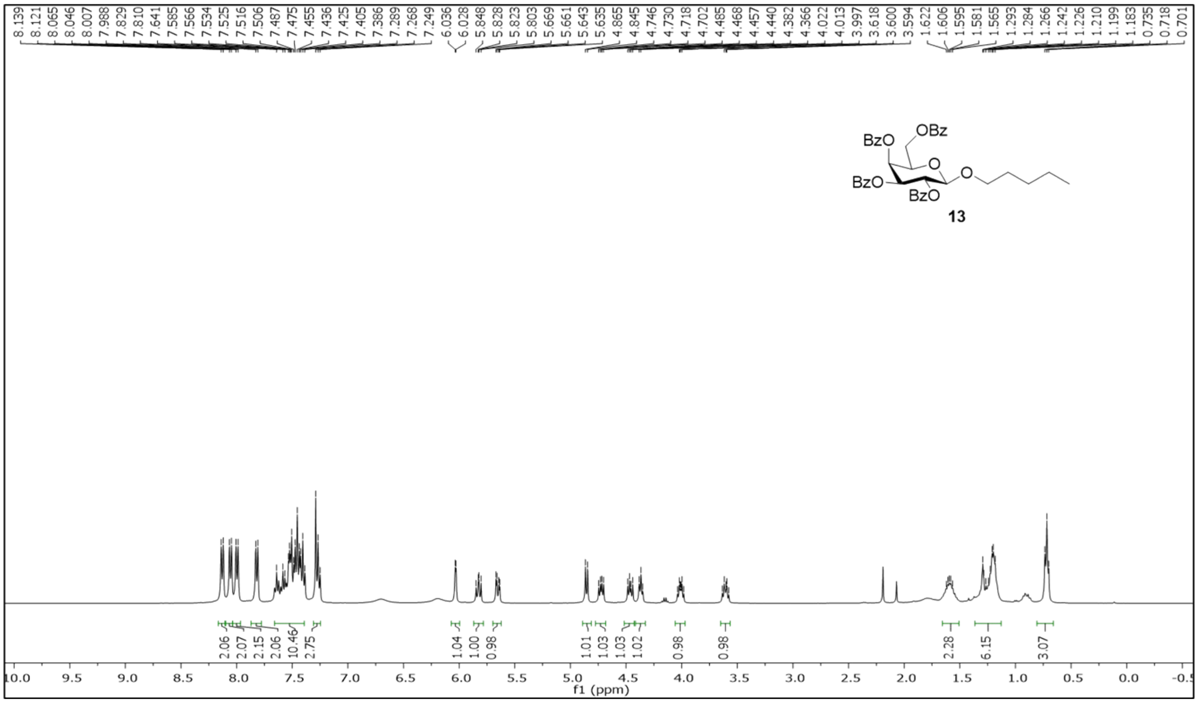


Figure S32. ^{1}H NMR spectrum of **13** (400 MHz, $CDCl_3$).

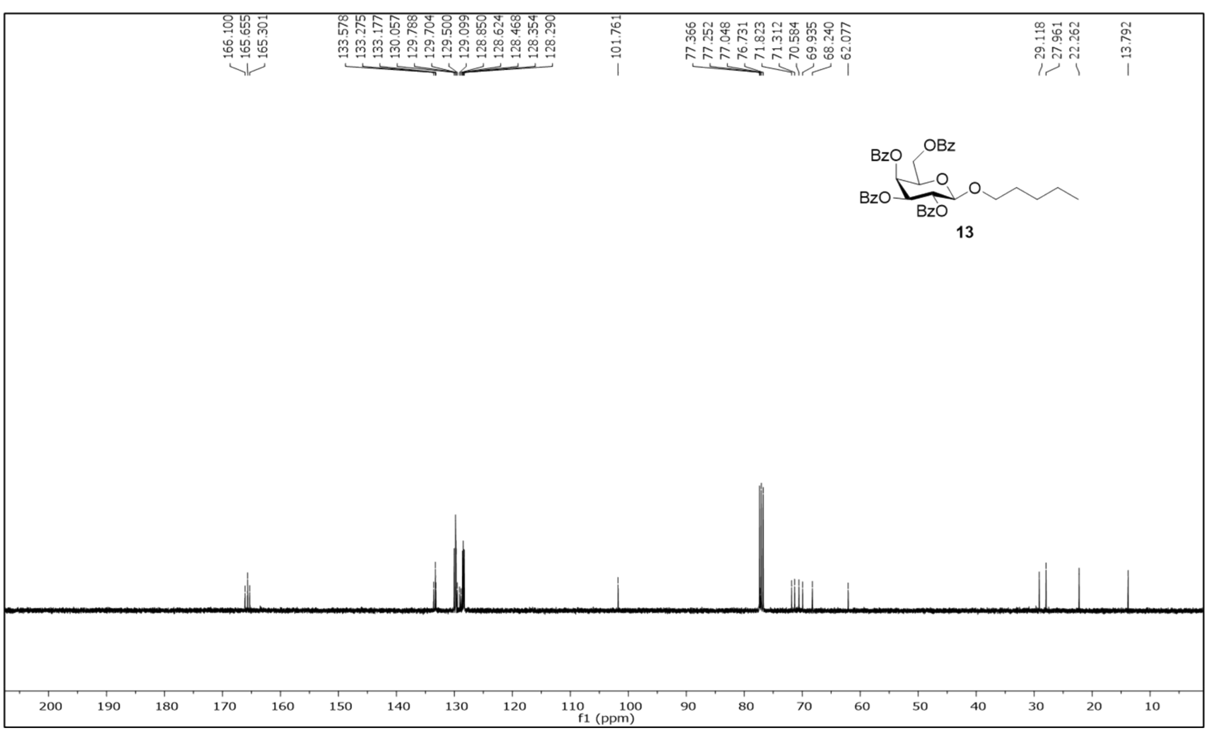


Figure S33. ^{13}C NMR spectrum of **13** (100 MHz, $CDCl_3$).

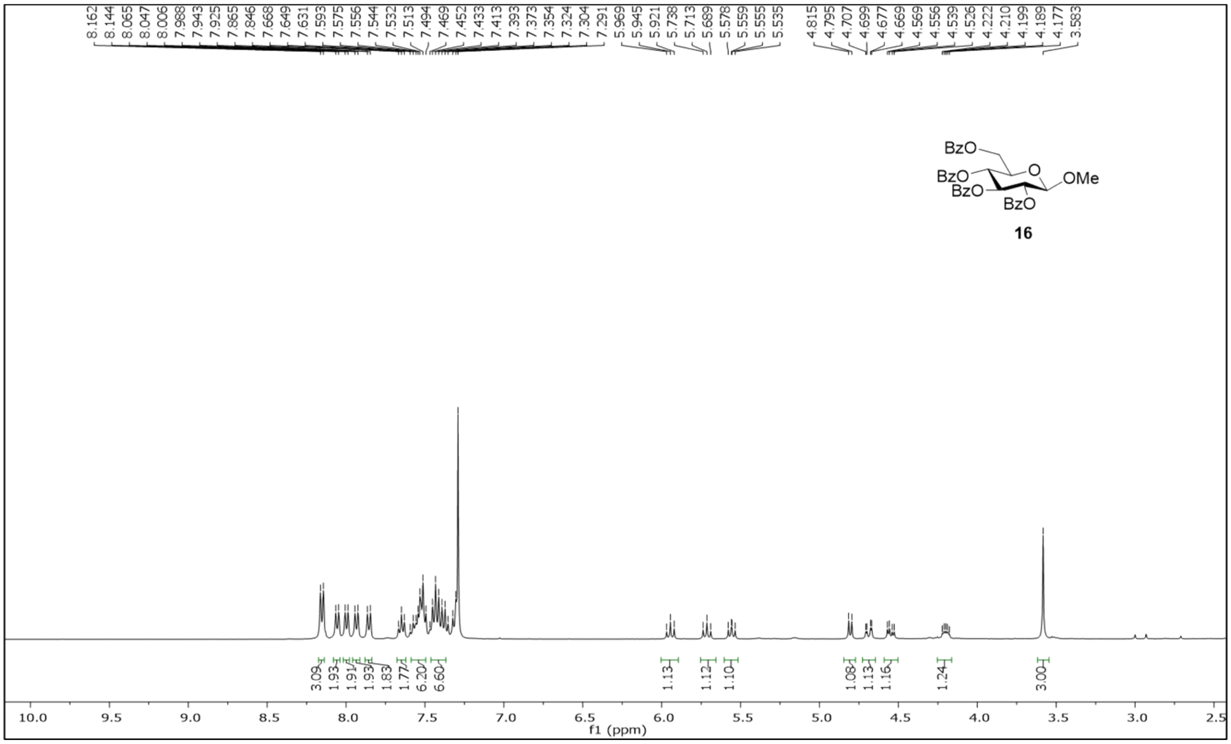


Figure S34. ^{1}H NMR spectrum of **16** (400 MHz, $CDCl_3$).

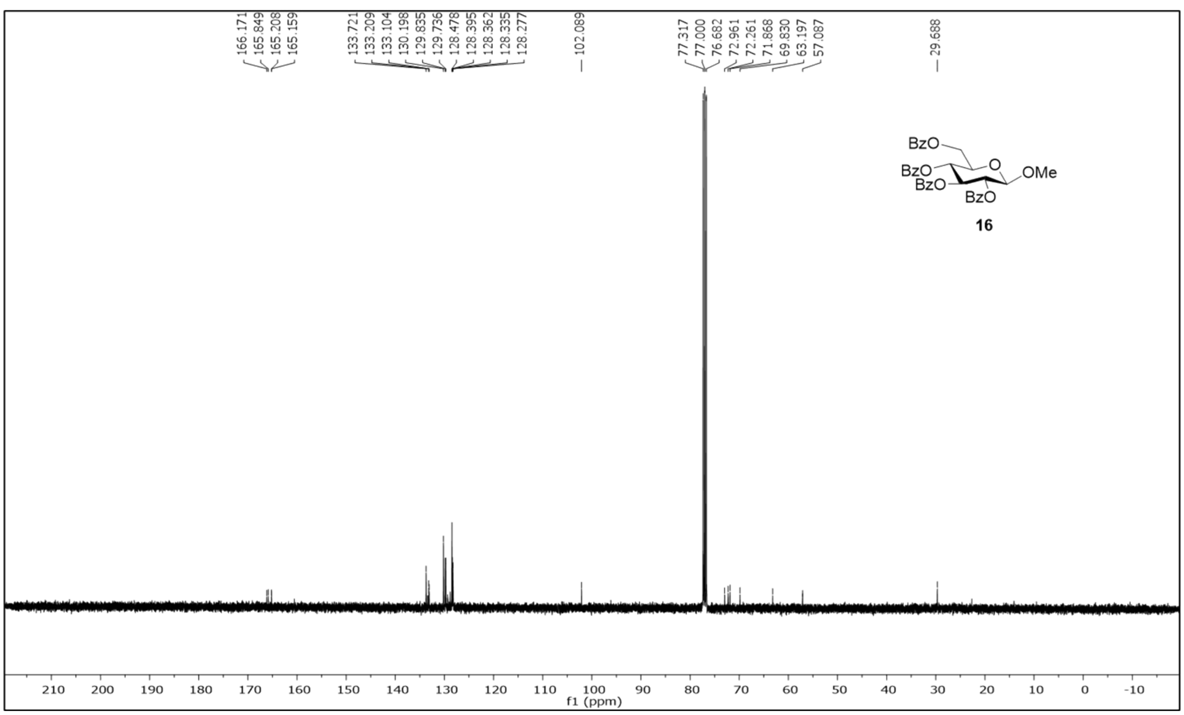


Figure S35. ^{13}C NMR spectrum of **16** (100 MHz, $CDCl_3$).

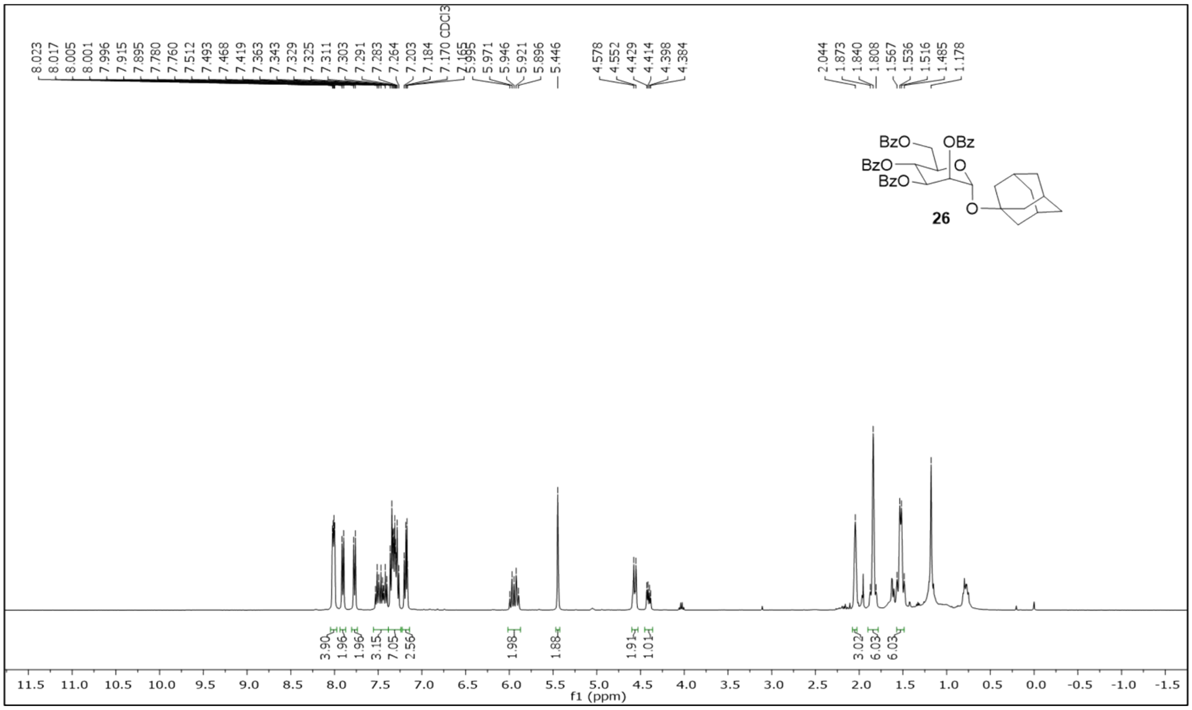


Figure S36. ^{1}H NMR spectrum of **26** (400 MHz, $CDCl_3$).

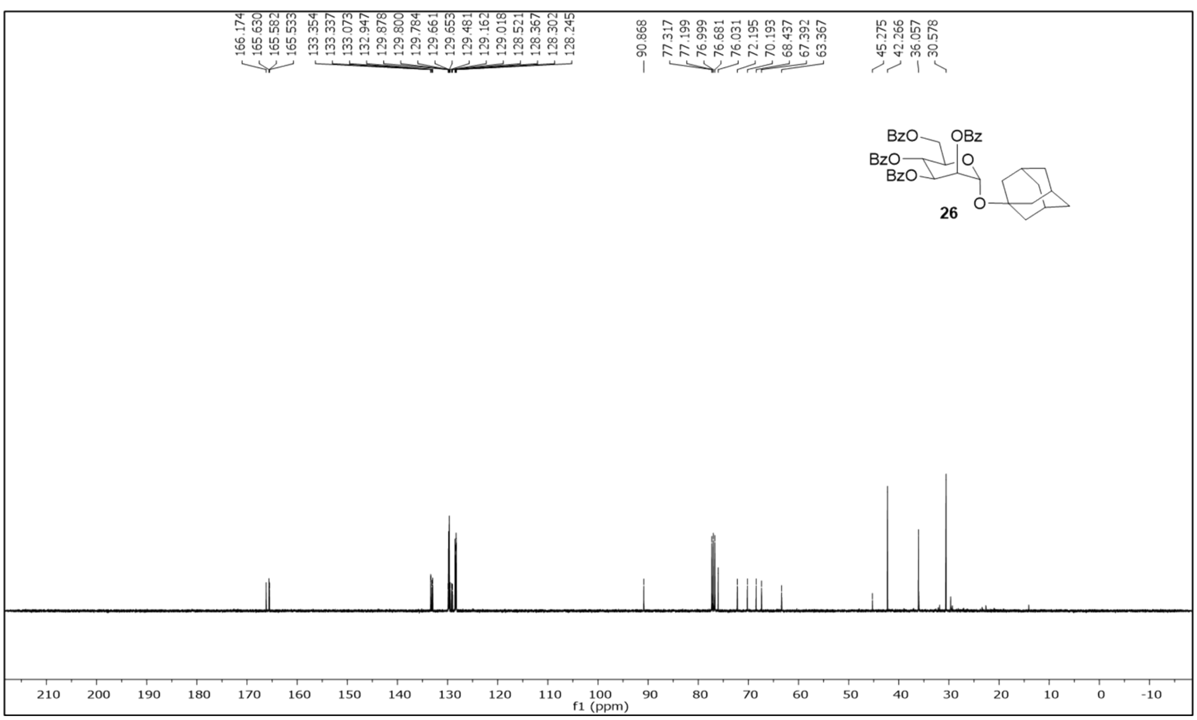


Figure S37. ^{13}C NMR spectrum of **26** (100 MHz, $CDCl_3$).

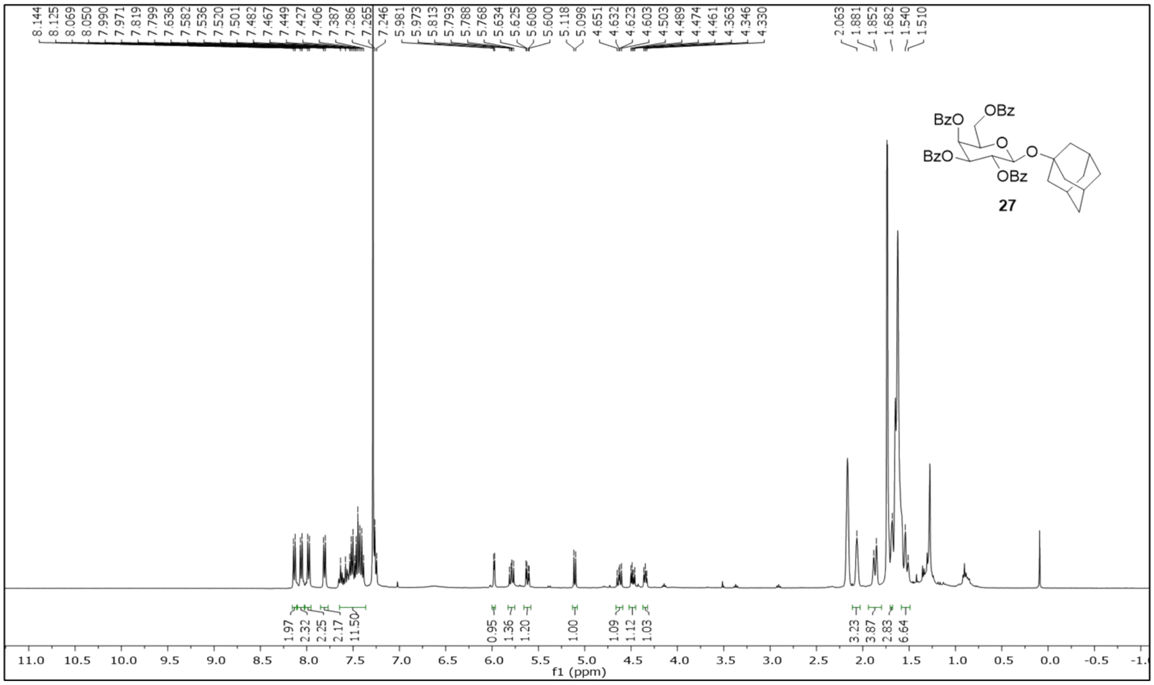


Figure S38. ^{1}H NMR spectrum of **27** (400 MHz, $CDCl_3$).

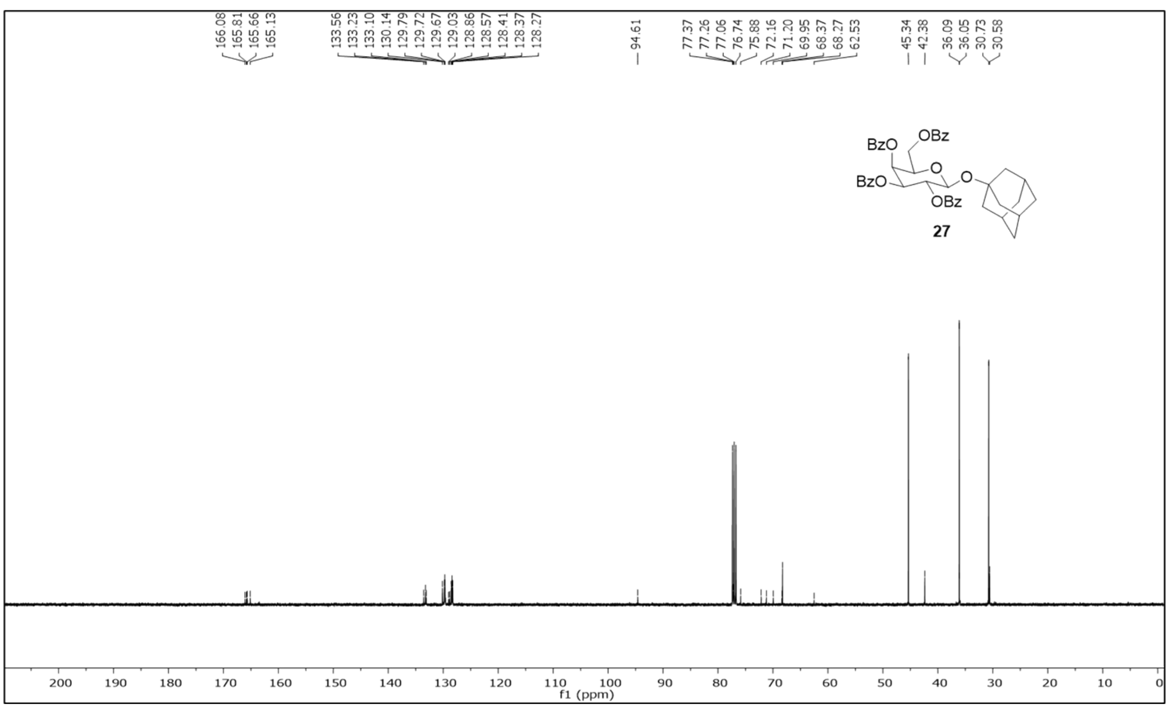


Figure S39. ^{13}C NMR spectrum of **27** (100 MHz, $CDCl_3$).

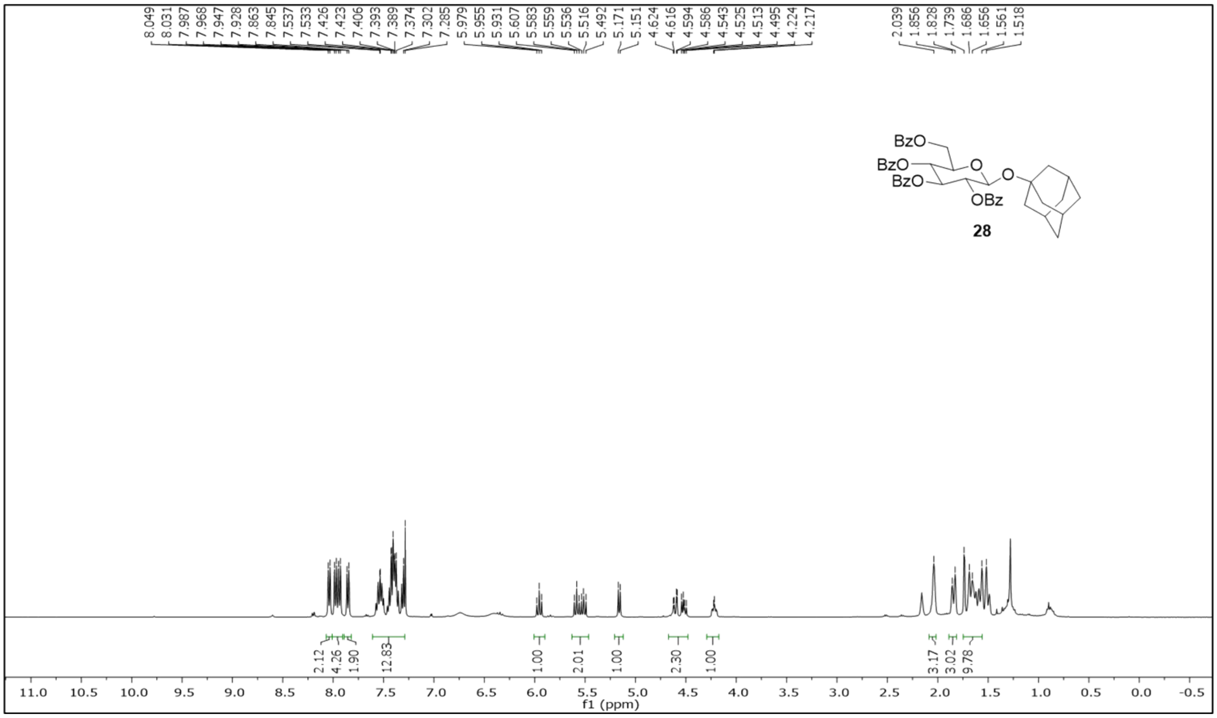


Figure S40. ^{1}H NMR spectrum of **28** (400 MHz, $CDCl_3$).

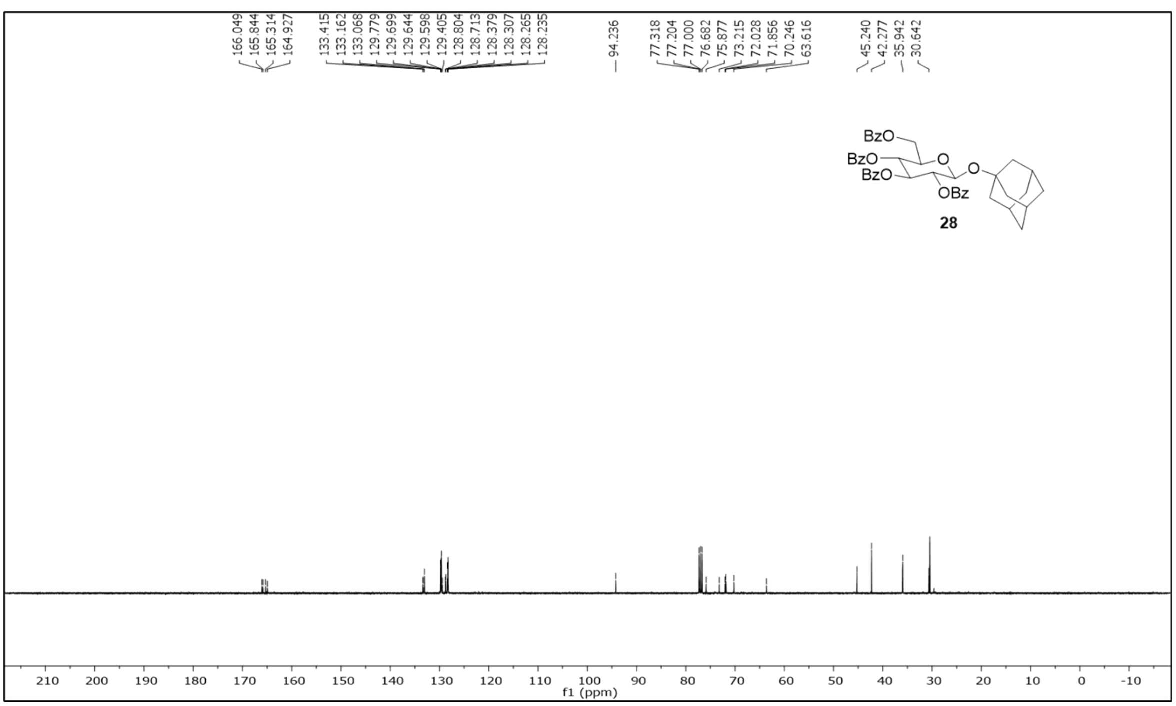


Figure S41. ^{13}C NMR spectrum of **28** (100 MHz, $CDCl_3$).

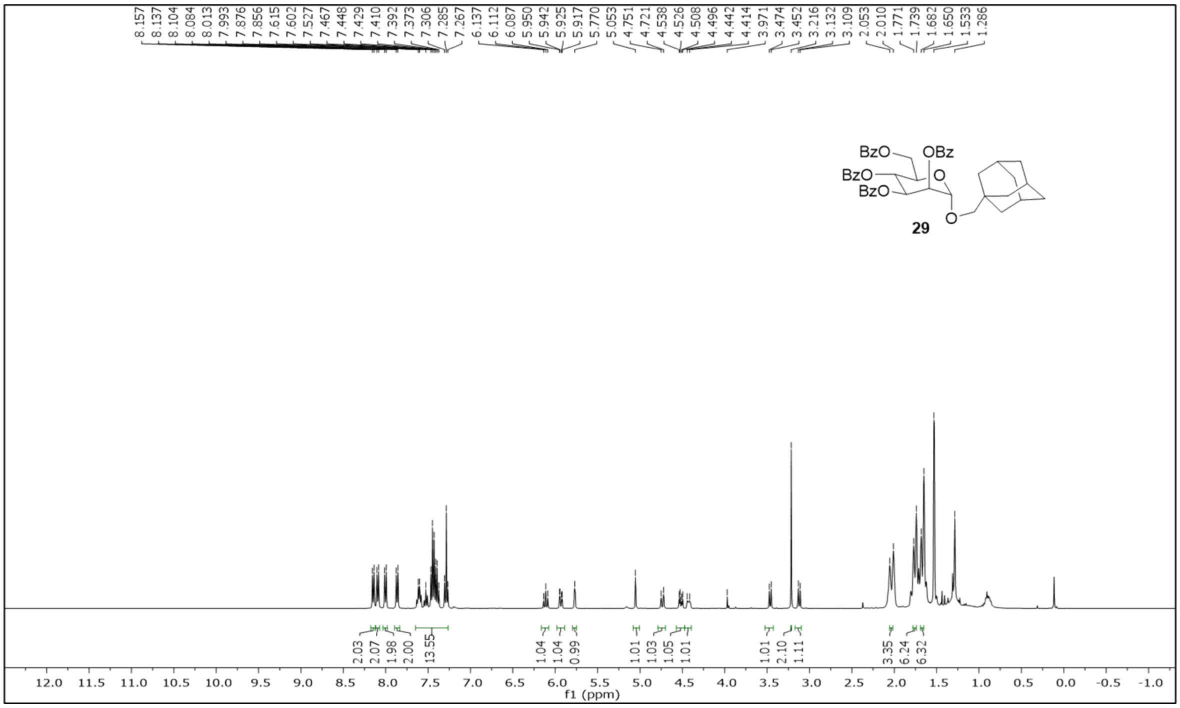


Figure S42. ^{1}H NMR spectrum of **29** (400 MHz, $CDCl_3$).

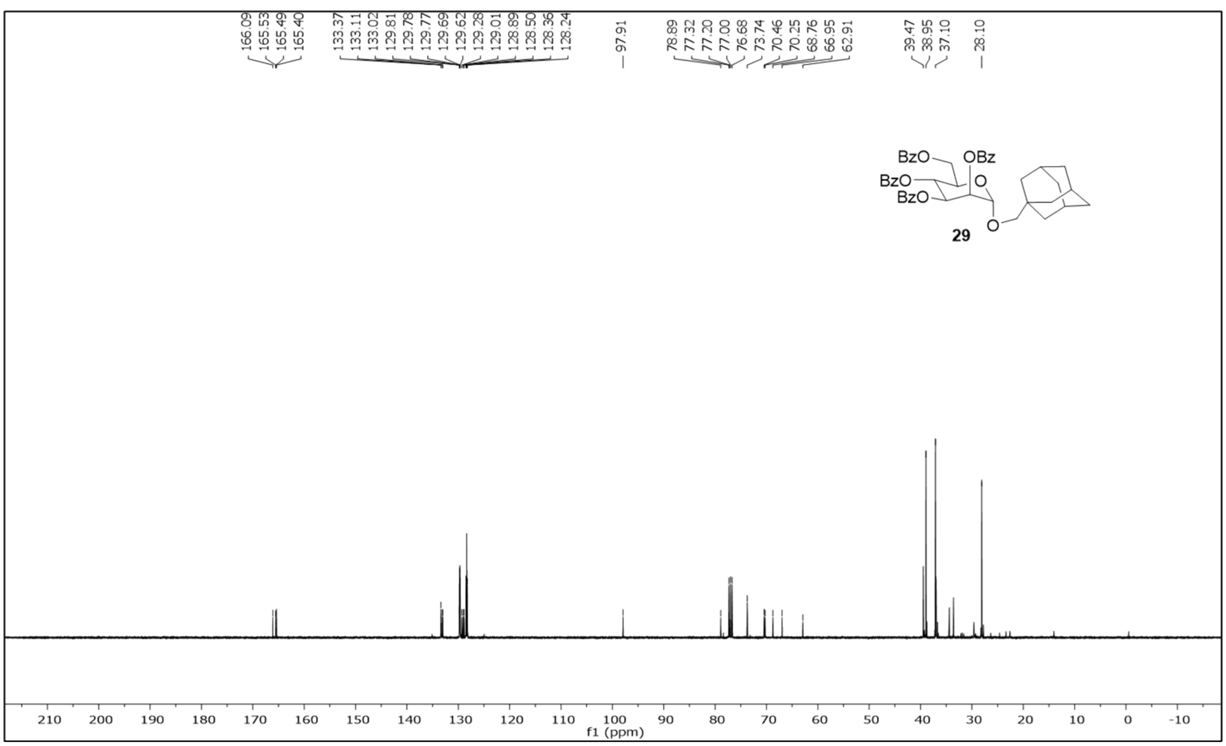


Figure S43. ^{13}C NMR spectrum of **29** (100 MHz, $CDCl_3$).

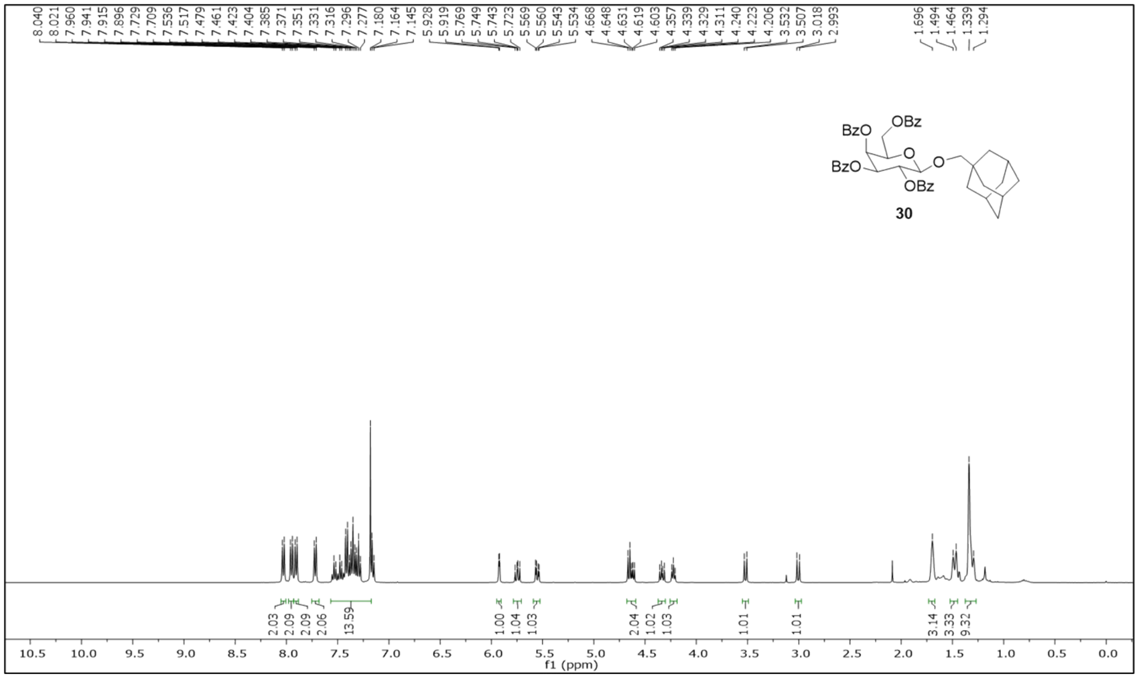


Figure S44. ^{1}H NMR spectrum of **30** (400 MHz, $CDCl_3$).

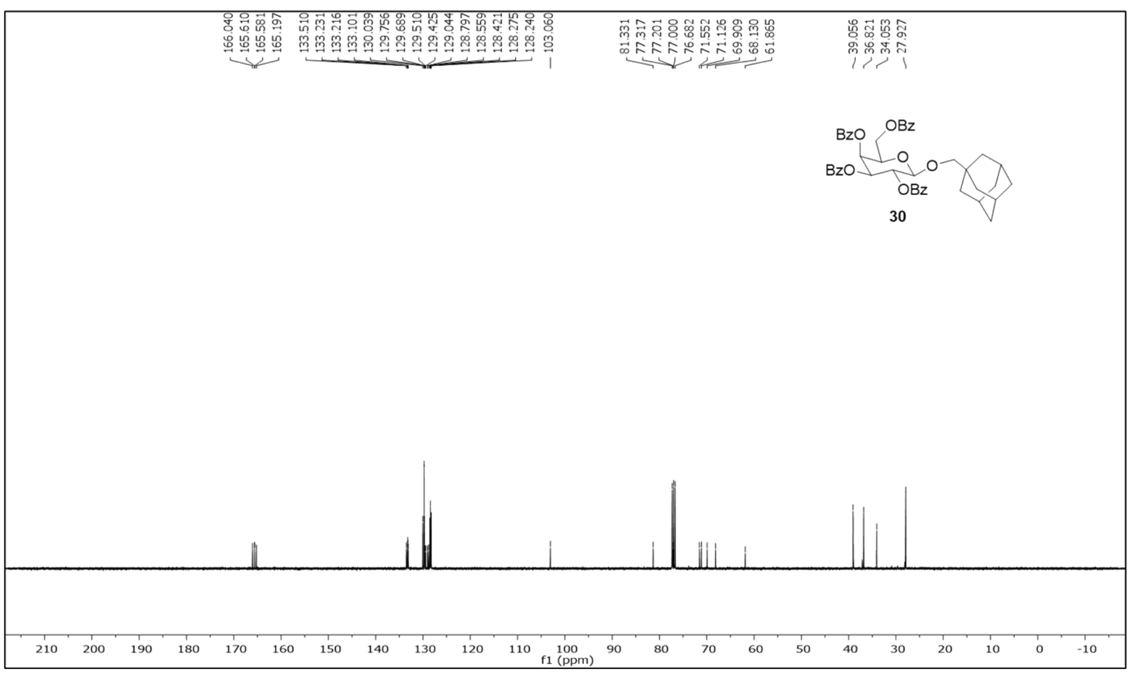


Figure S45. ^{13}C NMR spectrum of **30** (100 MHz, $CDCl_3$).

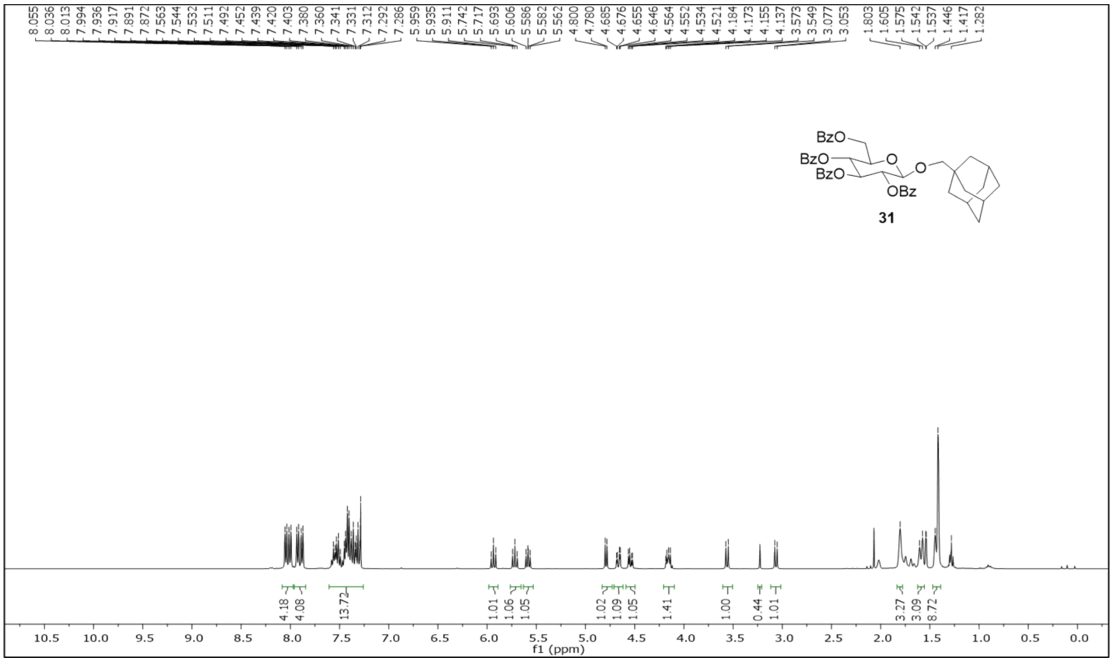


Figure S46. ^{1}H NMR spectrum of **31** (400 MHz, $CDCl_3$).

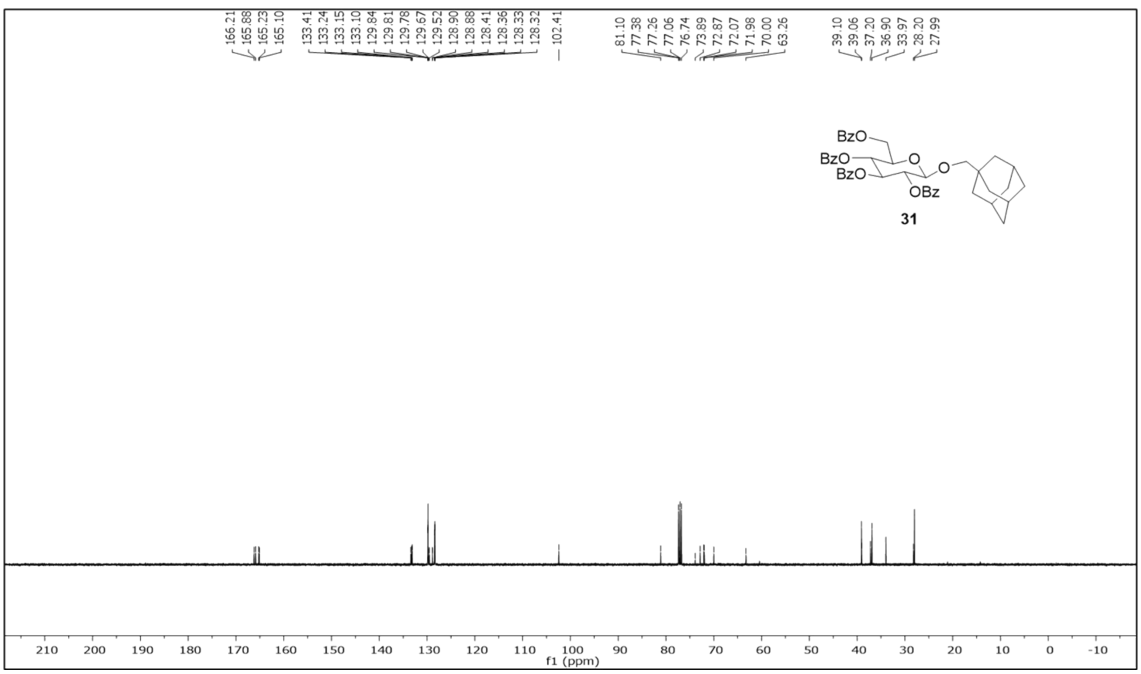


Figure S47. ^{13}C NMR spectrum of **31** (100 MHz, $CDCl_3$).

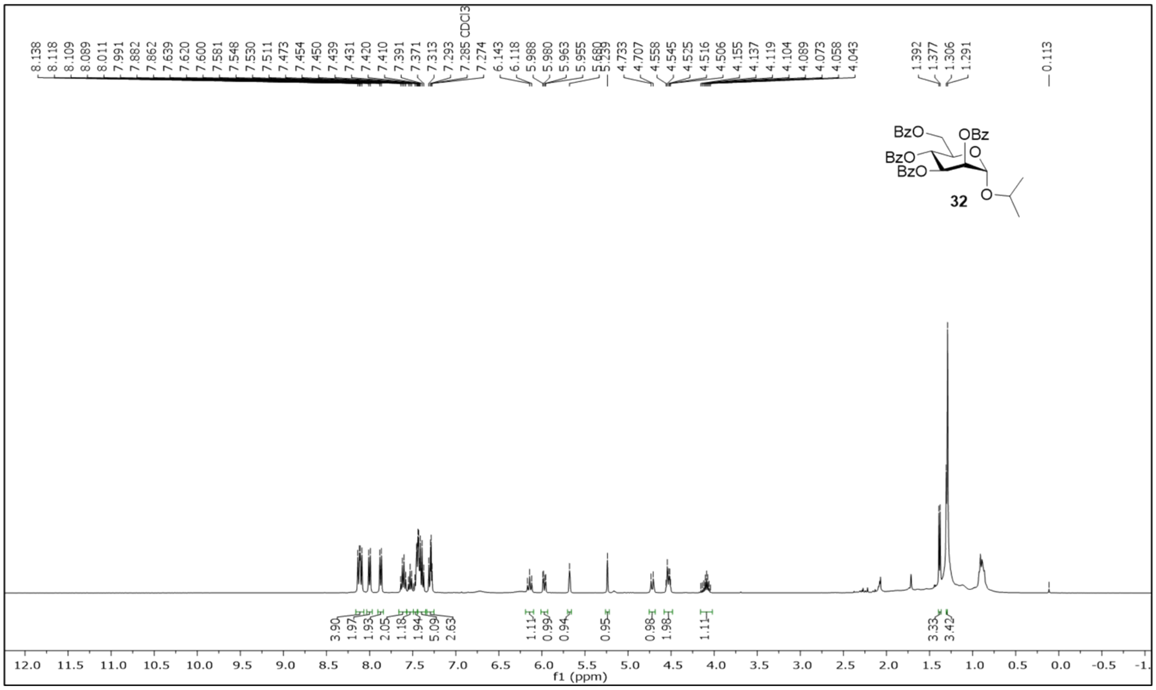


Figure S48. ^{1}H NMR spectrum of **32** (400 MHz, $CDCl_3$).

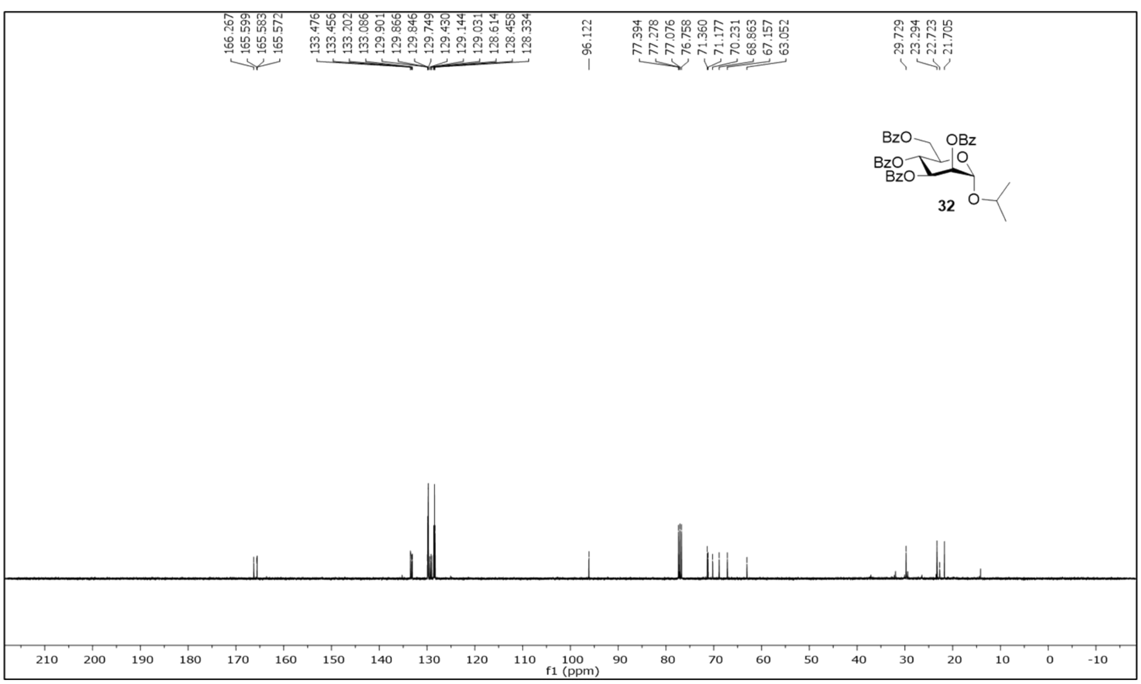


Figure S49. ^{13}C NMR spectrum of **32** (100 MHz, $CDCl_3$).

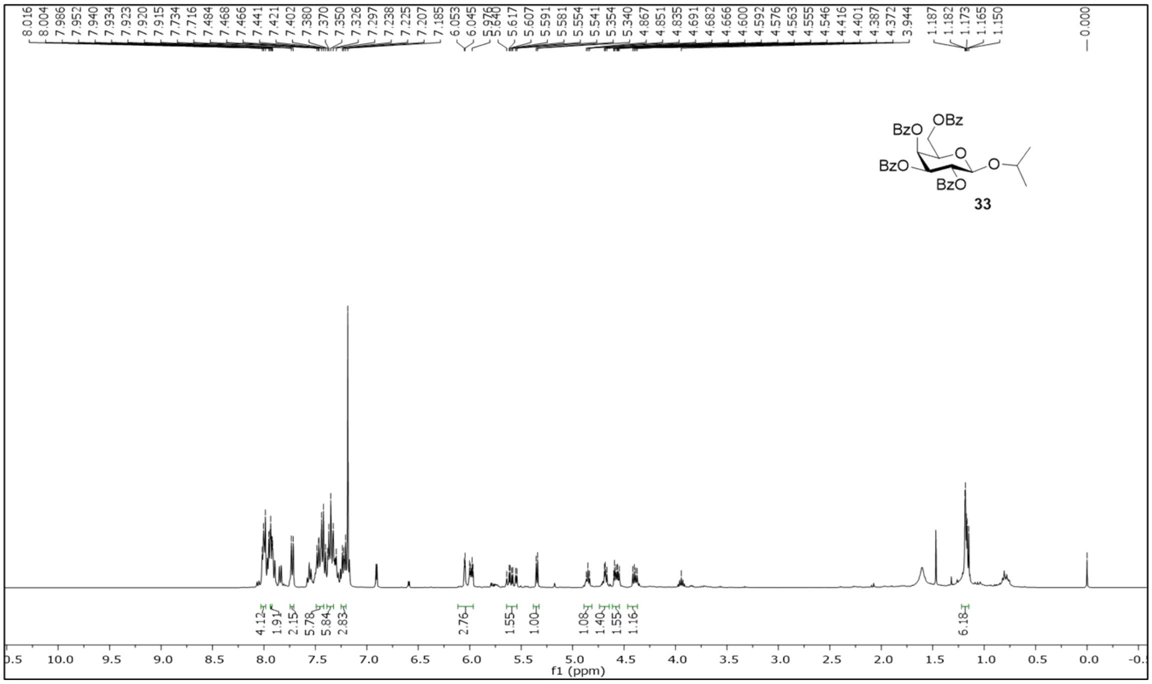


Figure S50. ^{1}H NMR spectrum of **33** (400 MHz, $CDCl_3$).

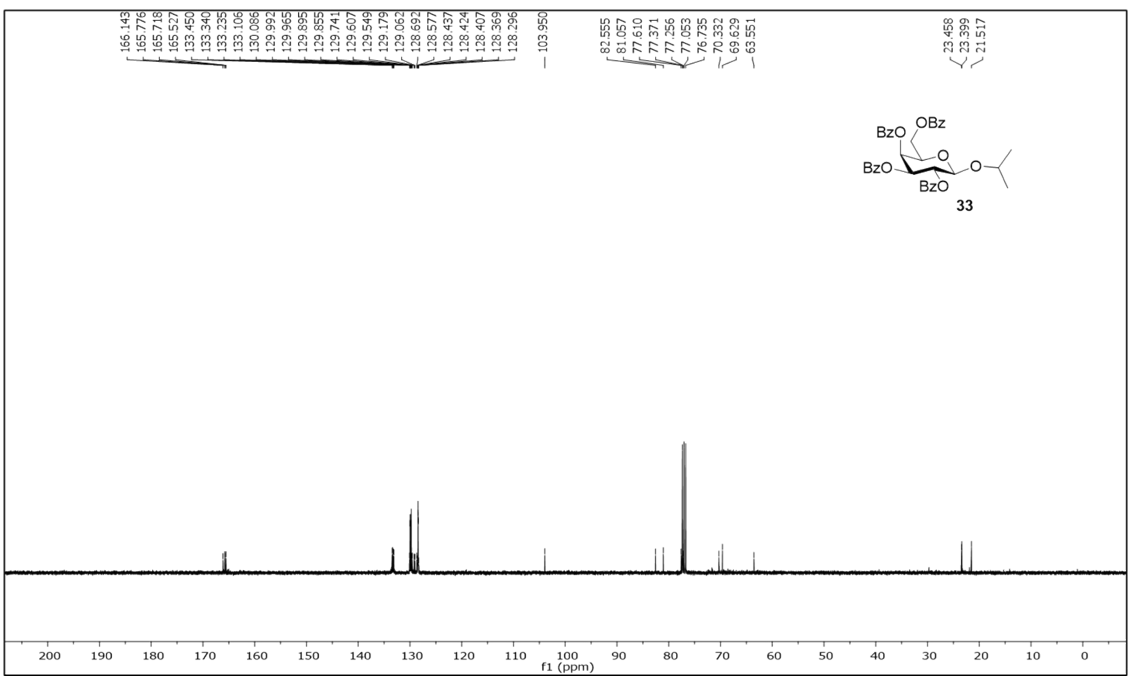


Figure S51. ^{13}C NMR spectrum of **33** (100 MHz, $CDCl_3$).

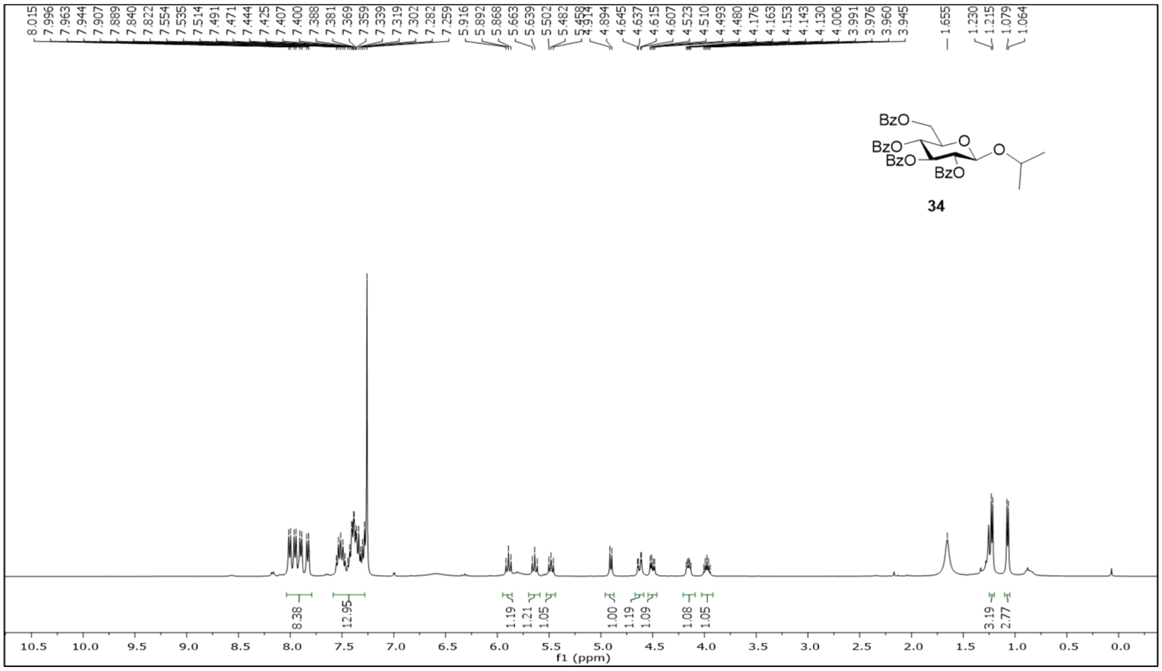


Figure S52. ^{1}H NMR spectrum of **34** (400 MHz, $CDCl_3$).

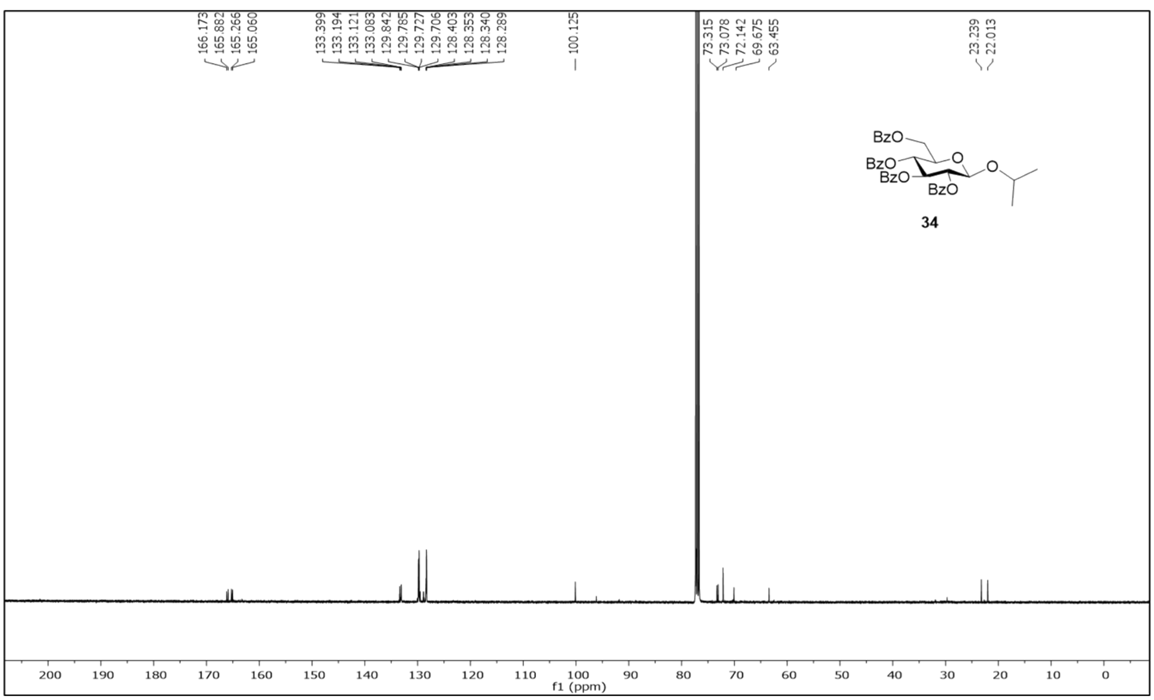


Figure S53. ^{13}C NMR spectrum of **34** (100 MHz, $CDCl_3$).

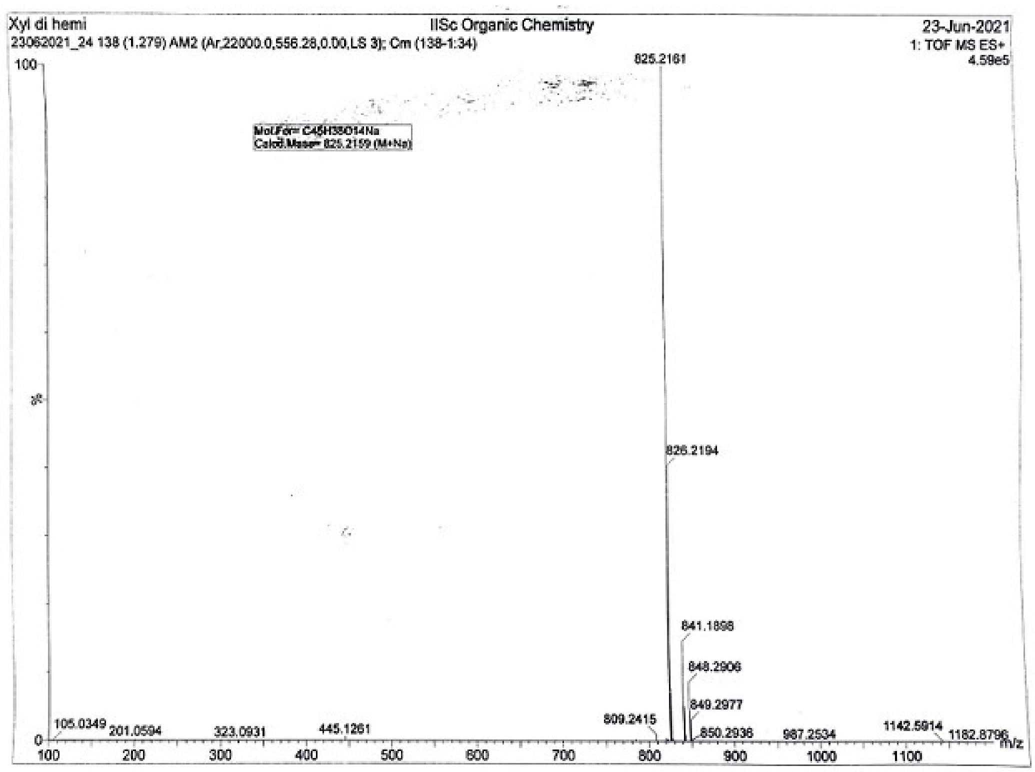


Figure S54. ESI-Mass spectrum of **38**.

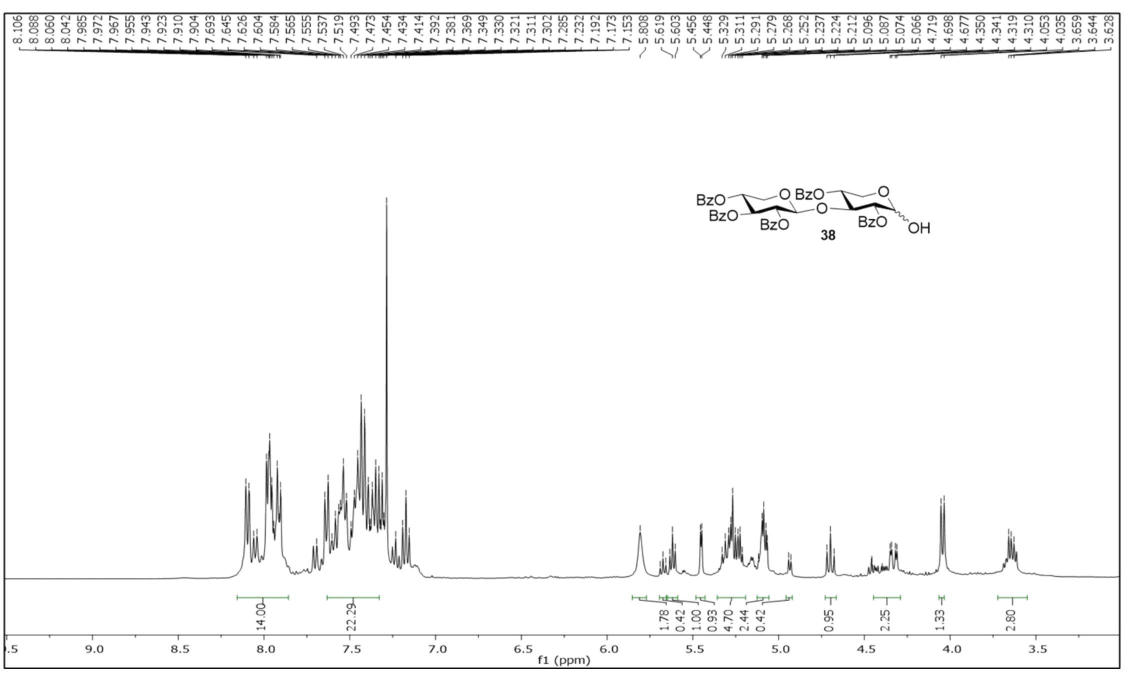


Figure S55. [1]H NMR spectrum of **38** (400 MHz, $CDCl_3$).

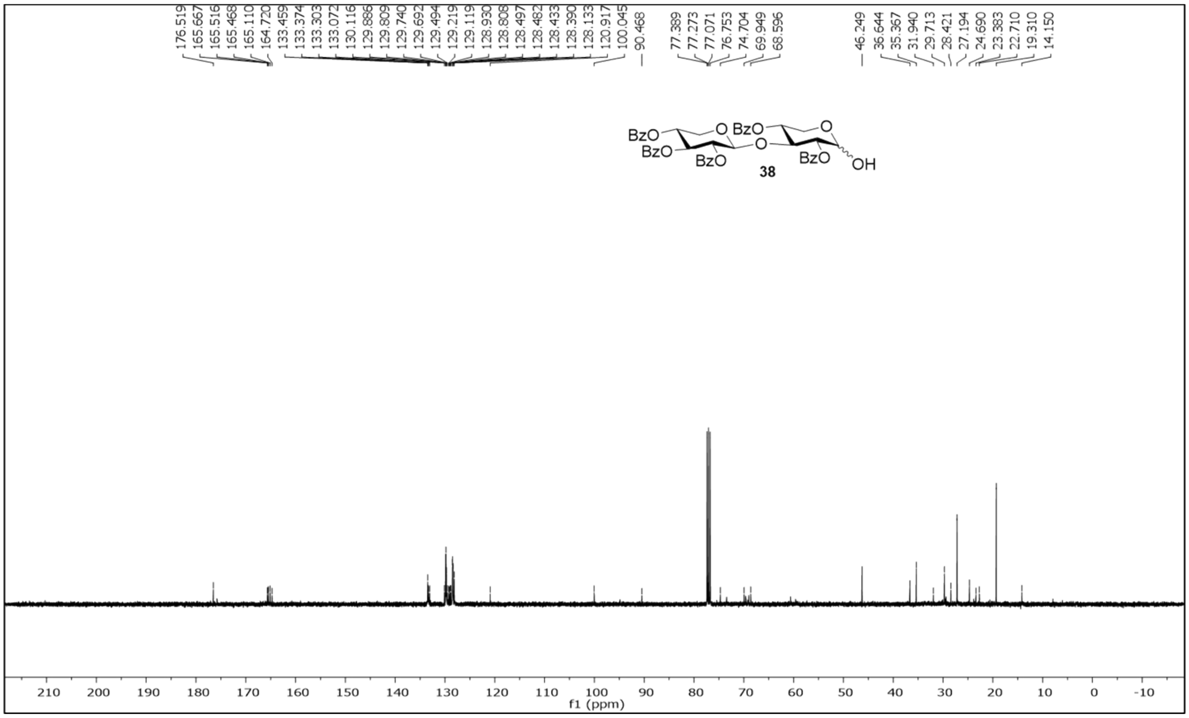


Figure S56. ^{13}C NMR spectrum of **38** (100 MHz, $CDCl_3$).

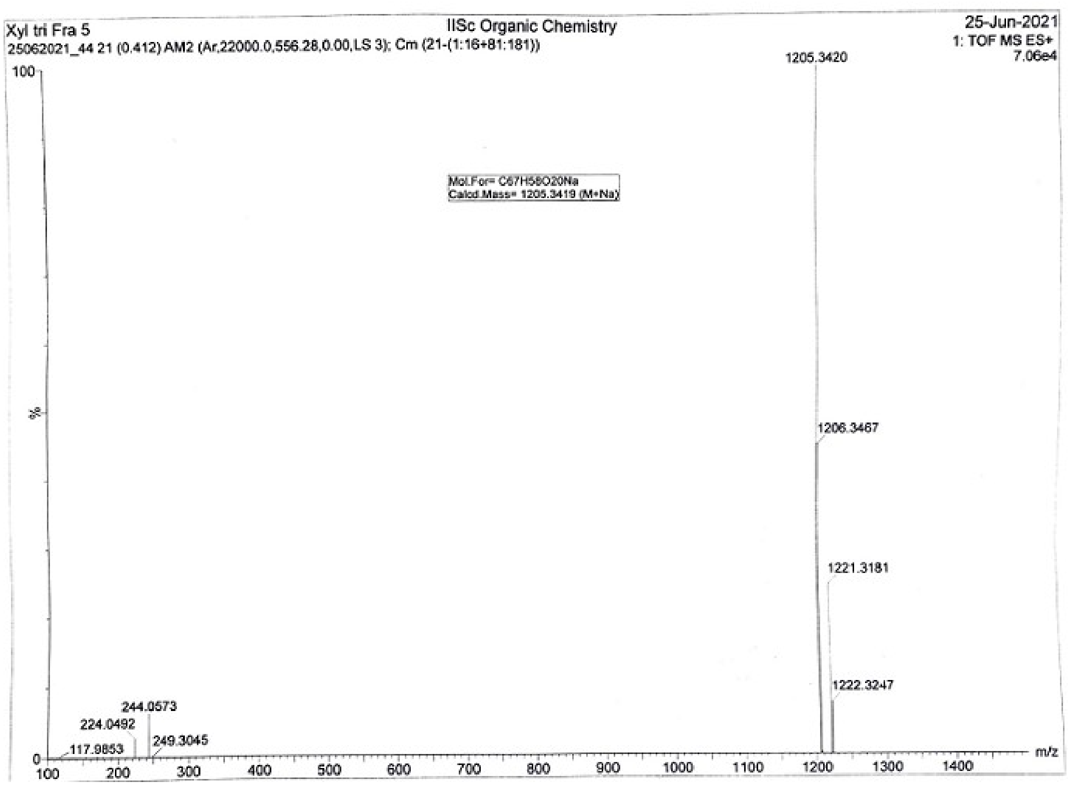


Figure S57. ESI-Mass spectrum of **39**.

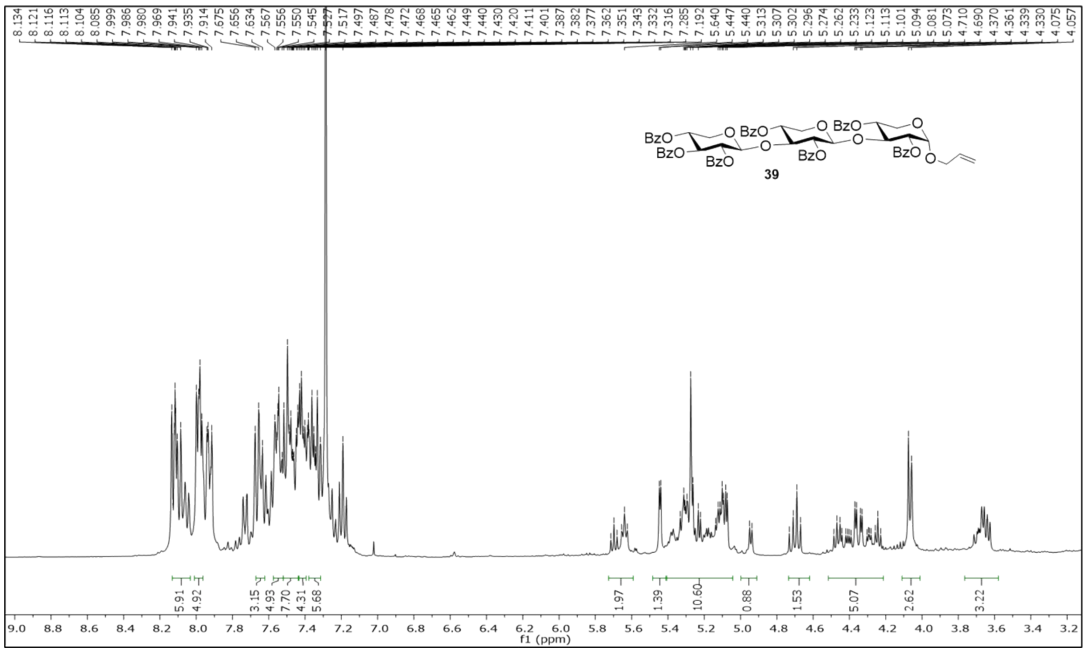


Figure S58. ^{1}H NMR spectrum of the inseparable mixture of **38** and **39** (400 MHz, $CDCl_3$), in ~60:40 ratio, on the basis of the integrations.

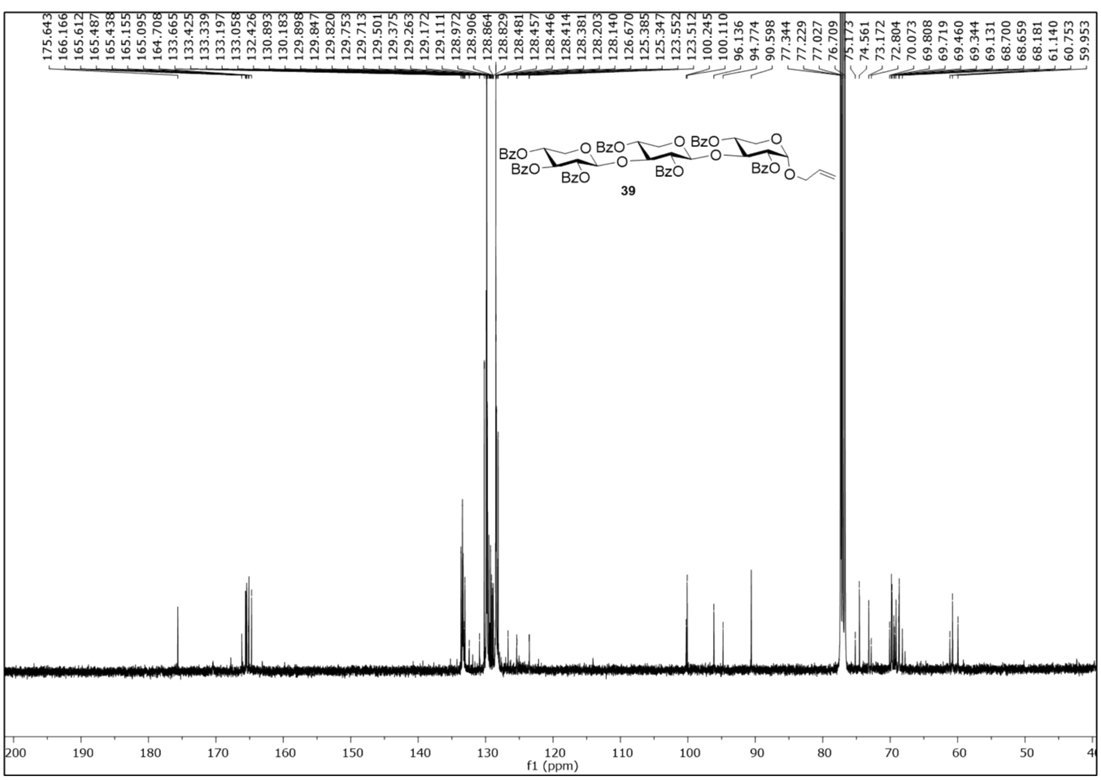


Figure S59. ^{13}C NMR spectrum of the inseparable mixture of **38** and **39** (100 MHz, $CDCl_3$).

[1]H and [13]C NMR Spectra of Known Compounds

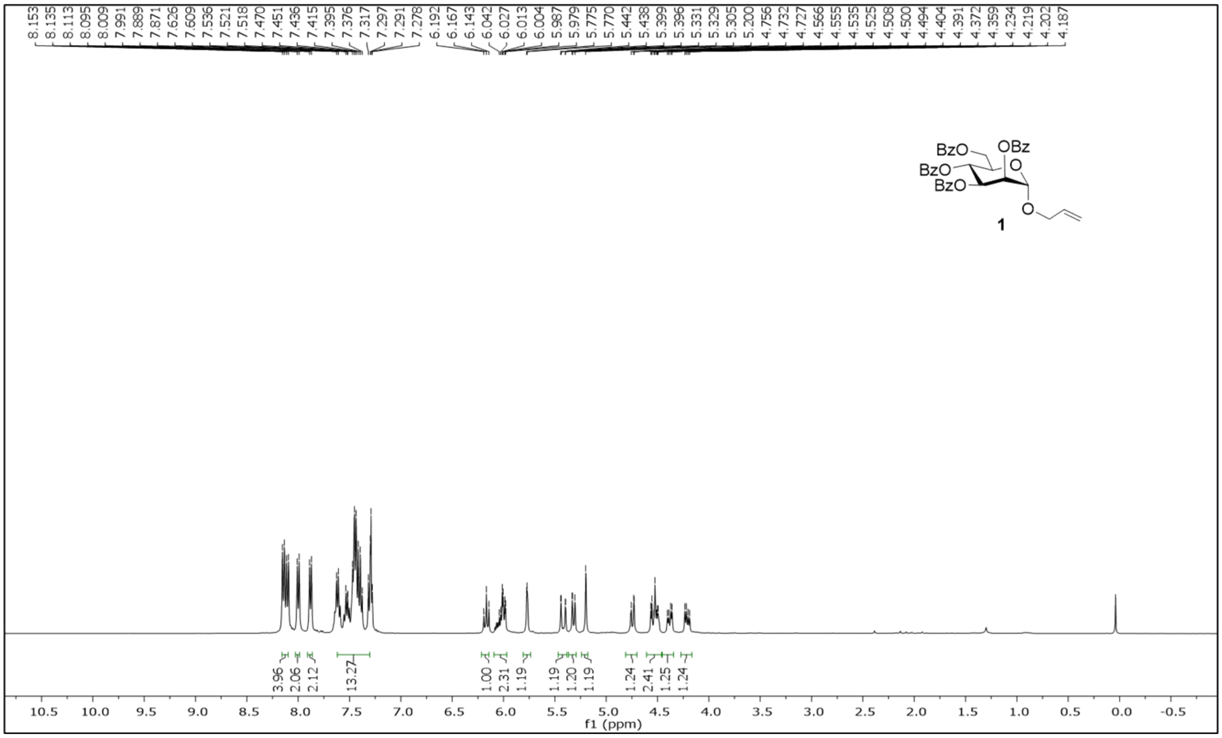


Figure S60. ^{1}H NMR spectrum of **1** (400 MHz, $CDCl_3$).

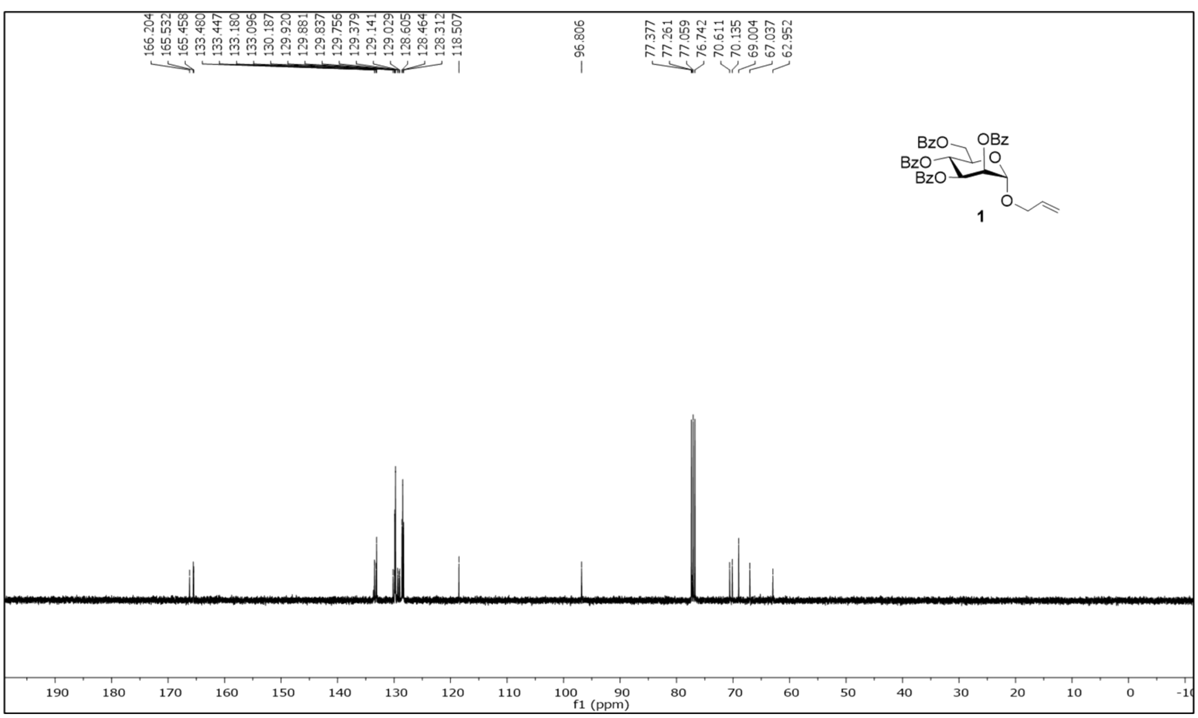


Figure S61. ^{13}C NMR spectrum of **1** (100 MHz, $CDCl_3$).

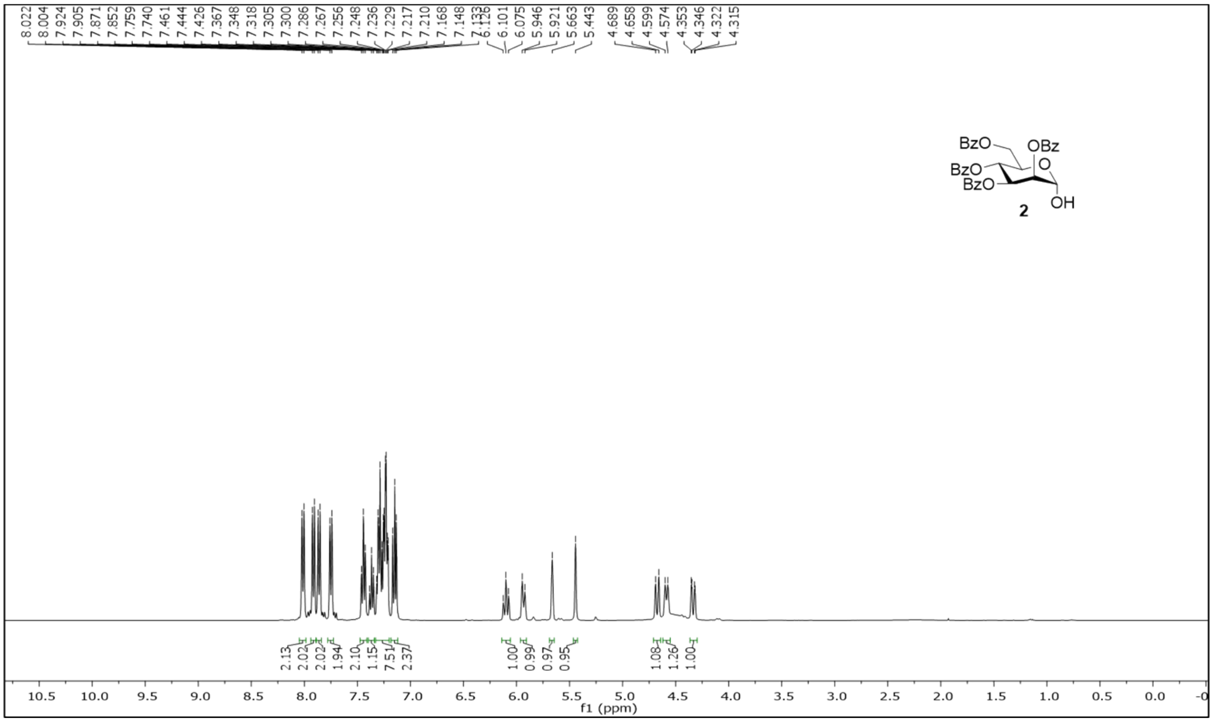


Figure S62. ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

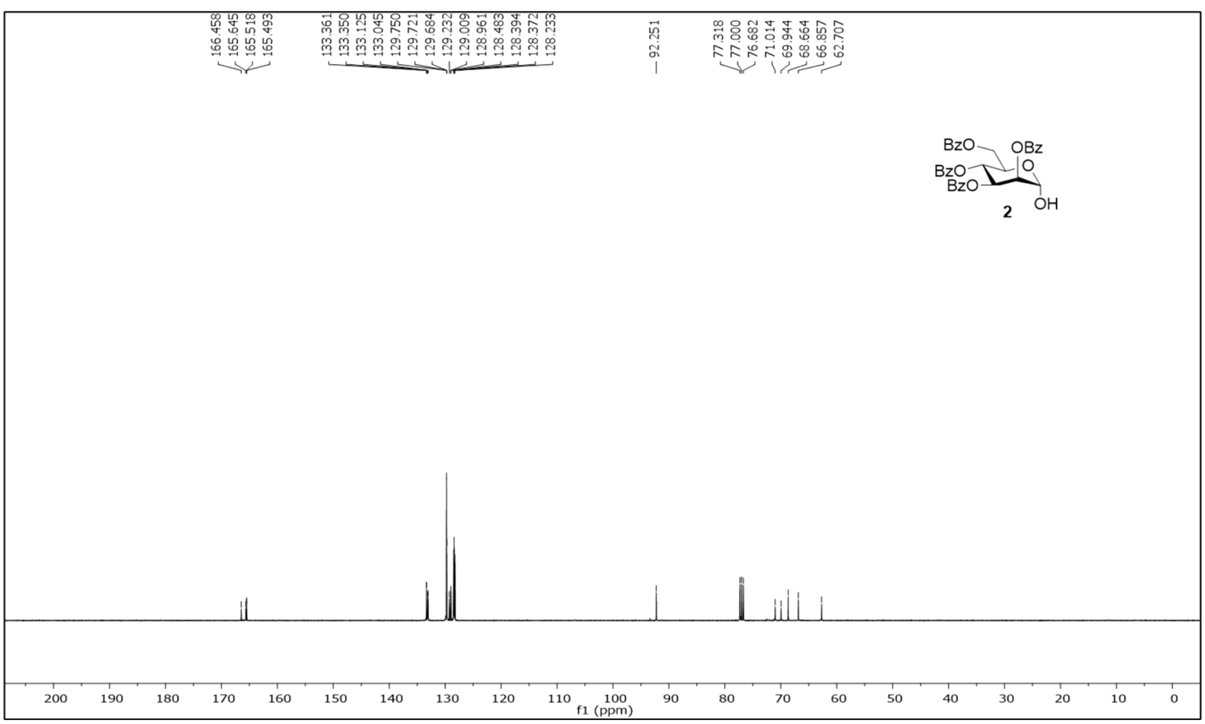


Figure S63. ^{13}C NMR spectrum of **2** (100 MHz, $CDCl_3$).

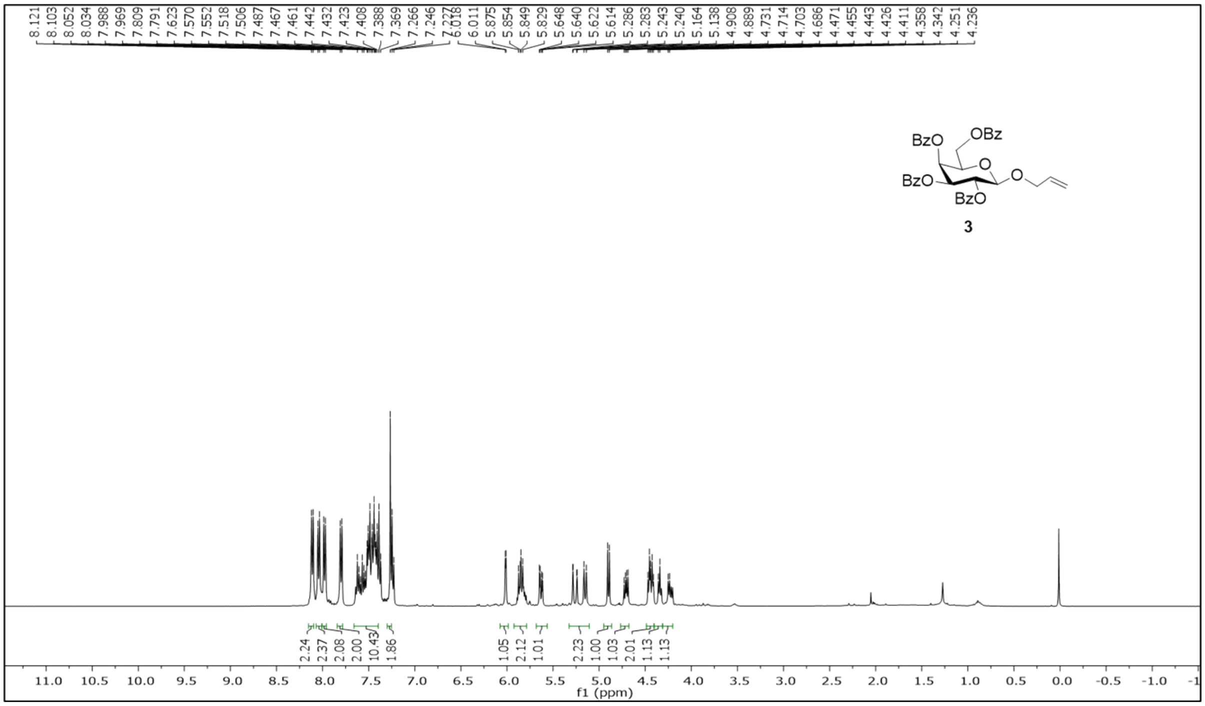


Figure S64. ^{1}H NMR spectrum of **3** (400 MHz, $CDCl_3$).

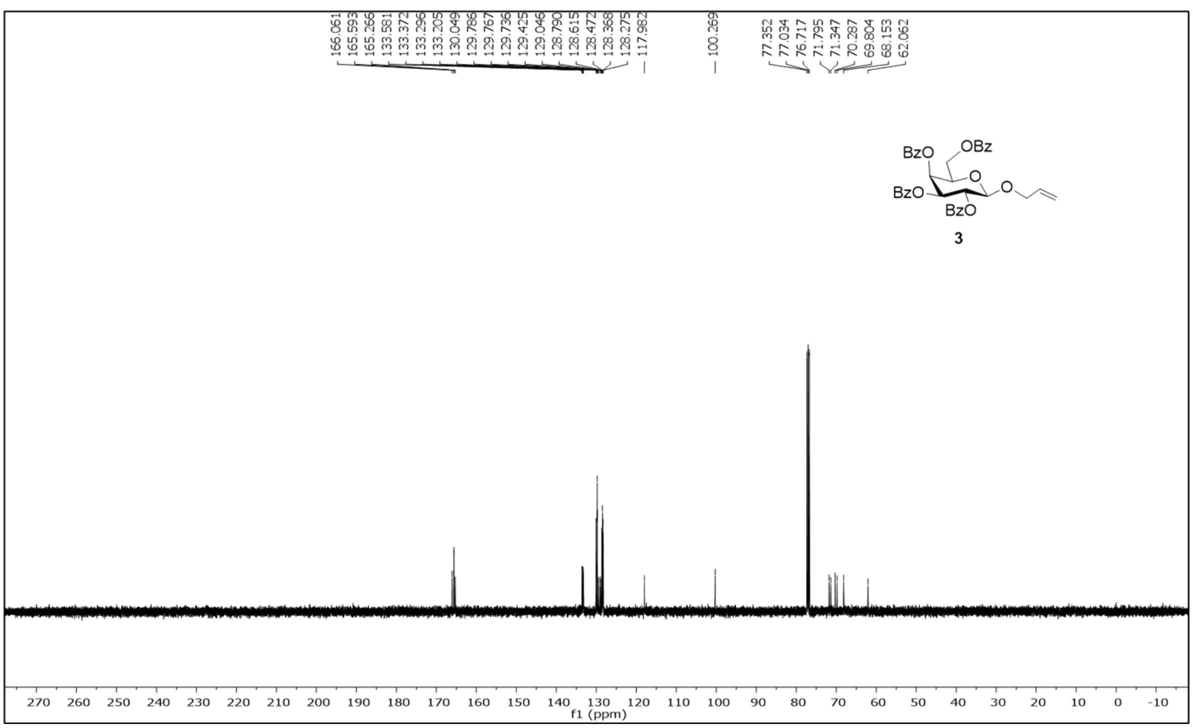


Figure S65. ^{13}C NMR spectrum of **3** (100 MHz, $CDCl_3$).

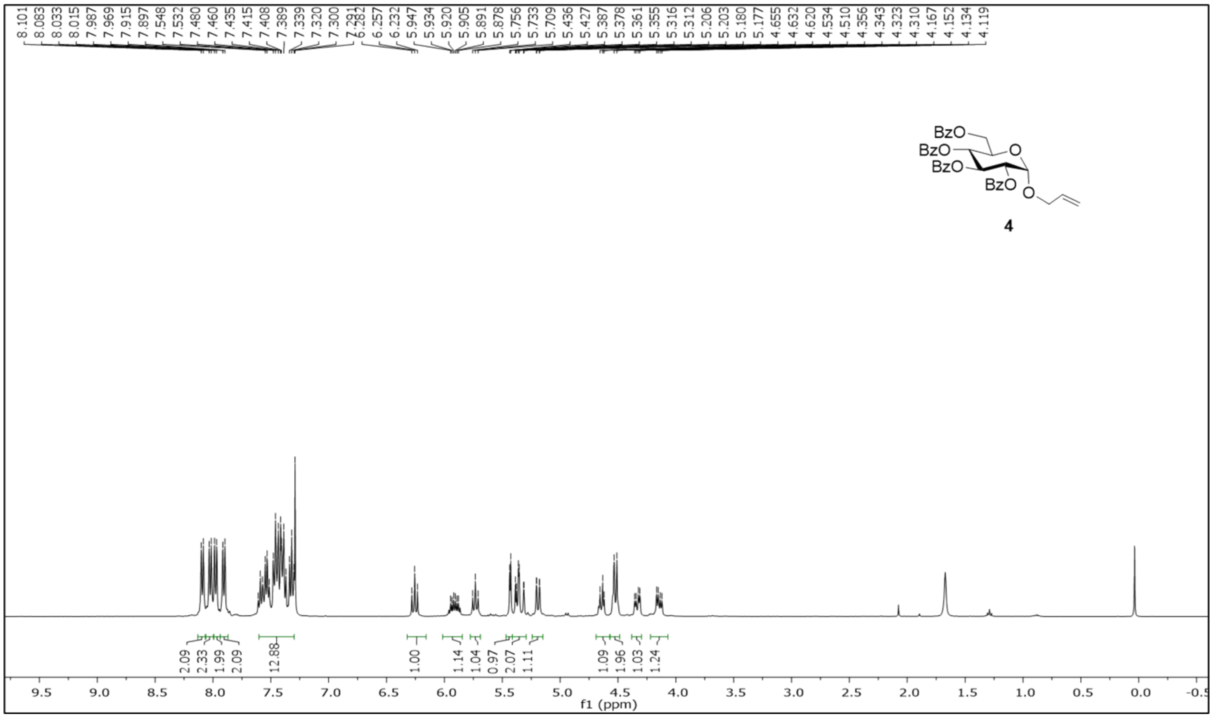


Figure S66. ^{1}H NMR spectrum of **4** (400 MHz, $CDCl_3$).

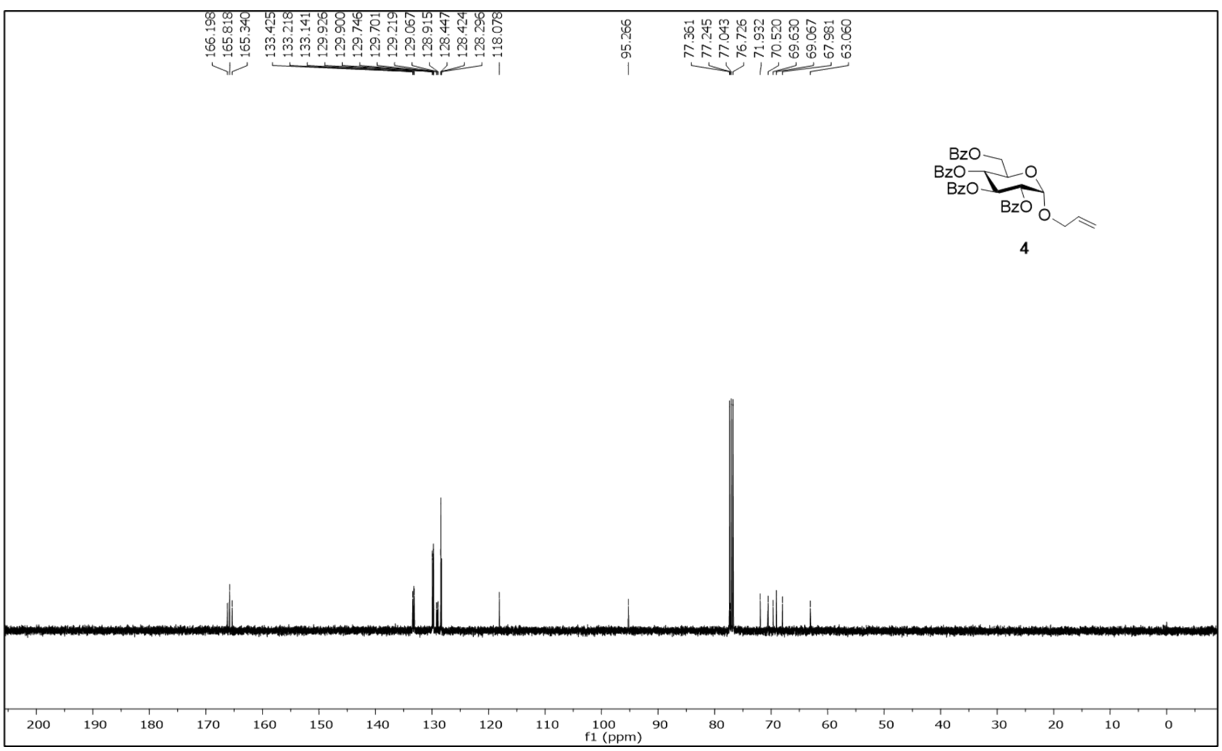


Figure S67. ^{13}C NMR spectrum of **4** (100 MHz, $CDCl_3$).

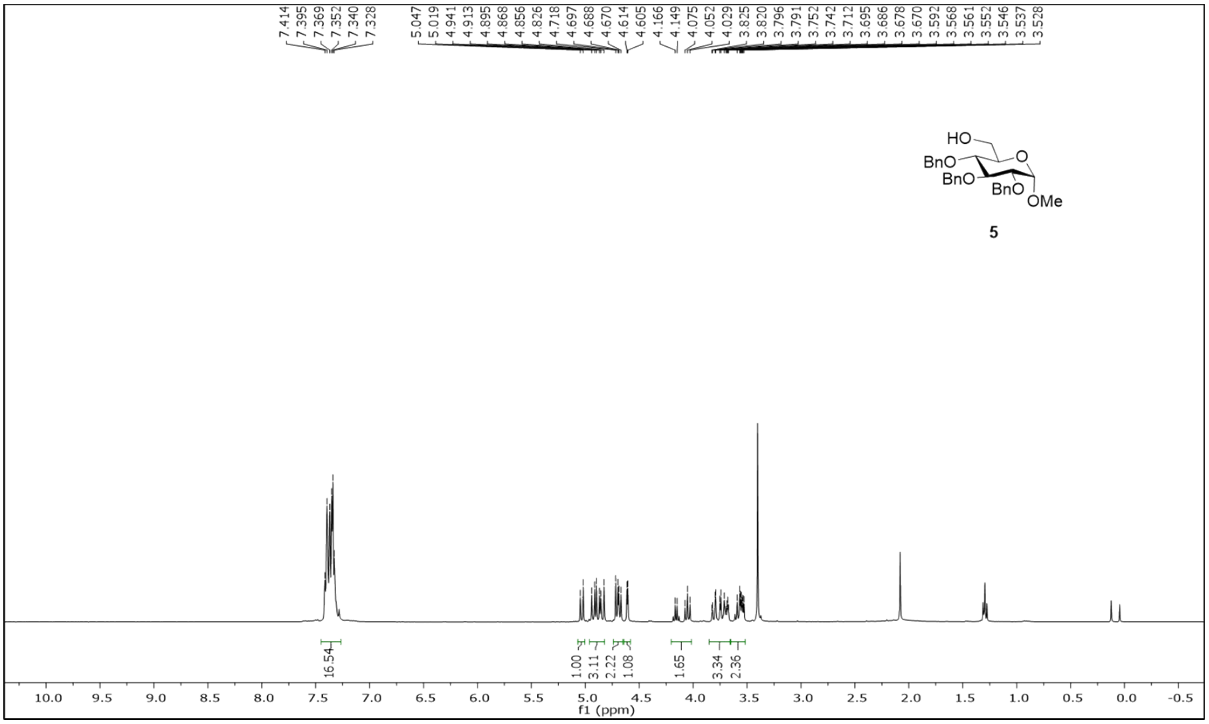


Figure S68. ^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$).

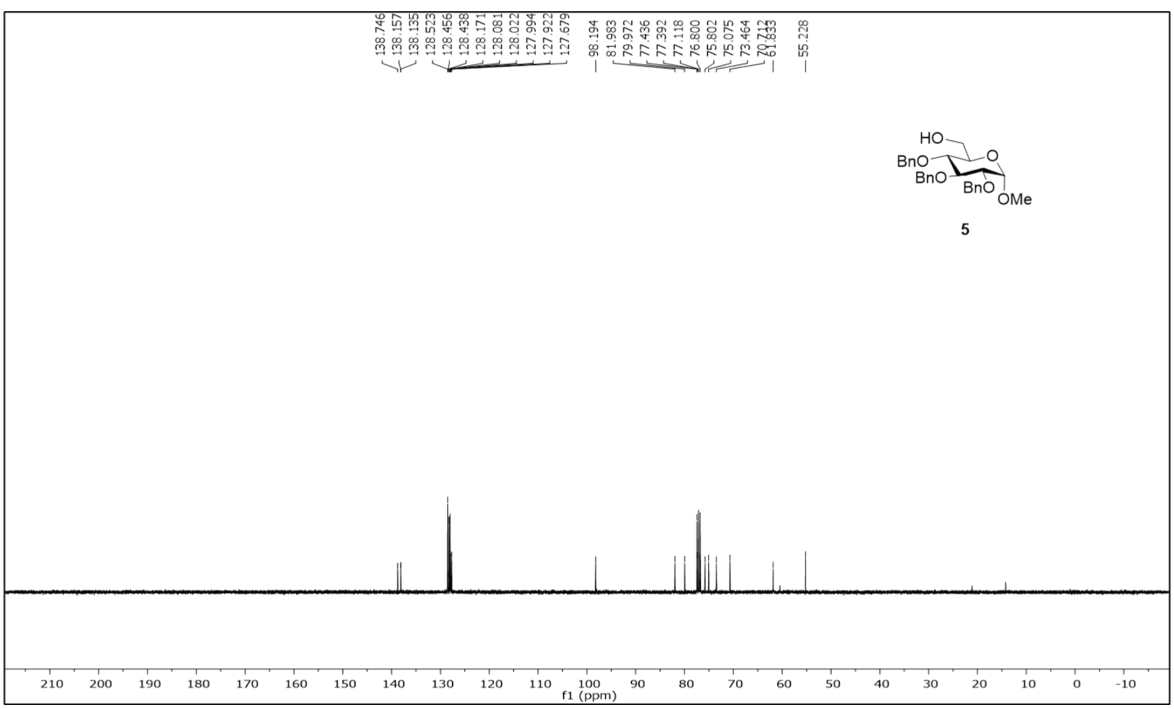


Figure S69. ^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$).

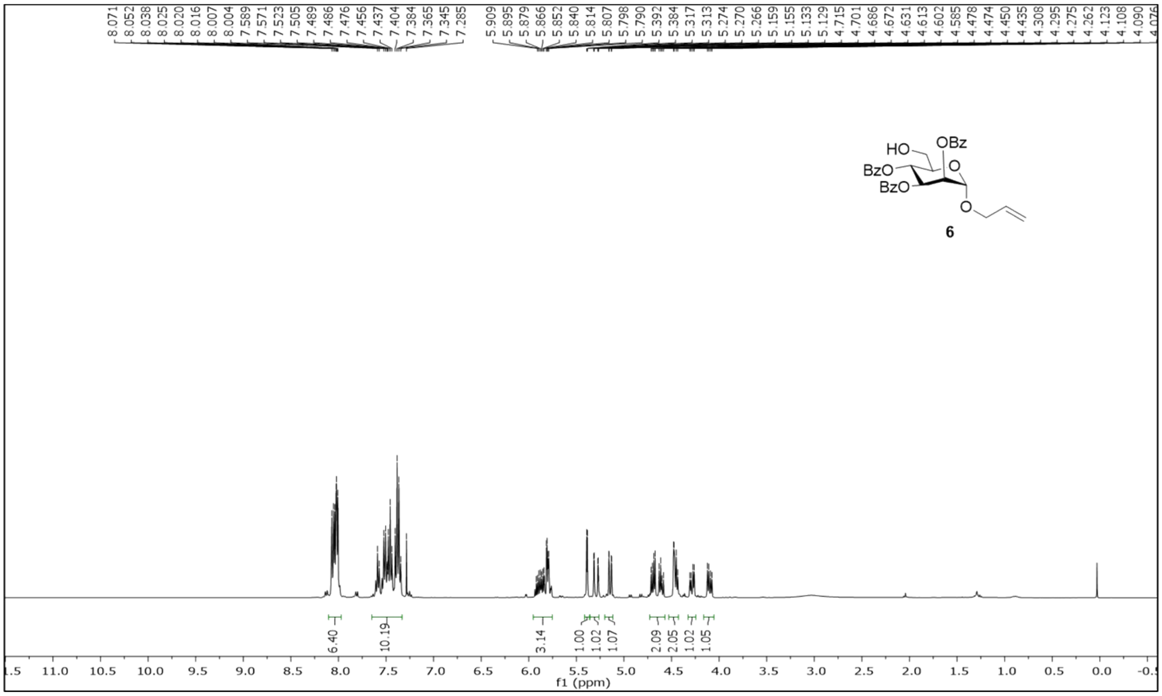


Figure S70. ^{1}H NMR spectrum of **6** (400 MHz, $CDCl_3$).

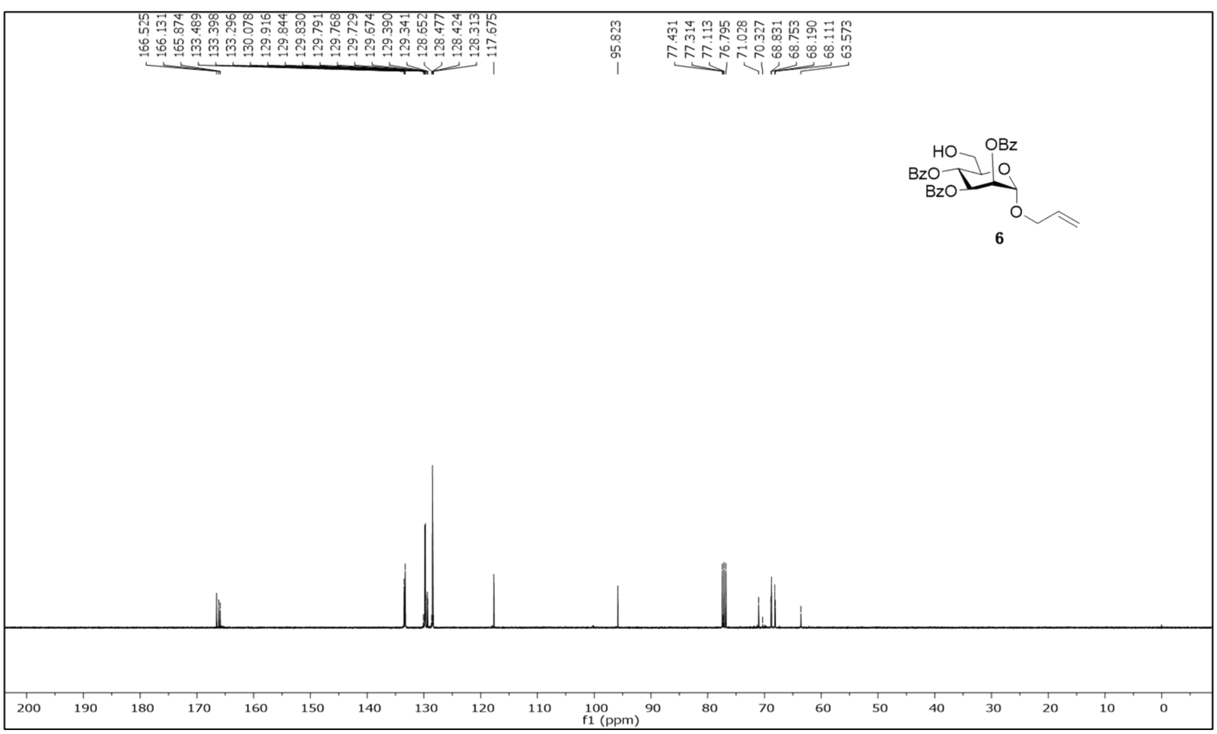


Figure S71. ^{13}C NMR spectrum of **6** (100 MHz, $CDCl_3$).

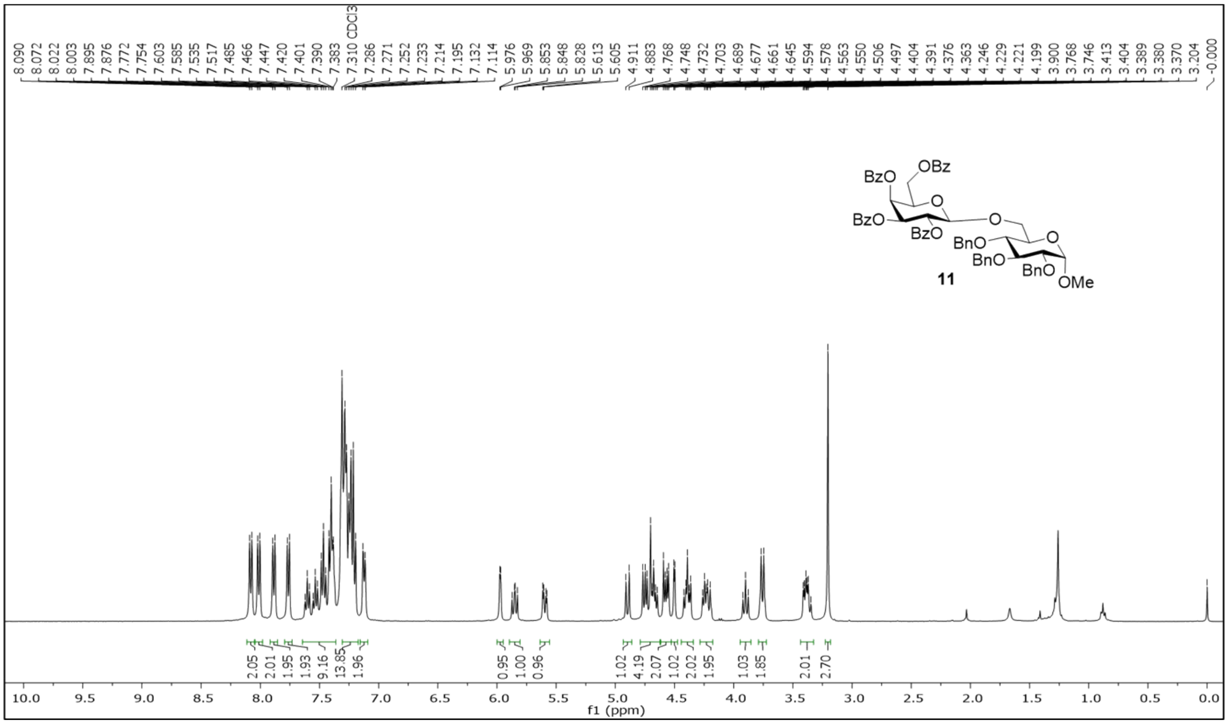


Figure S72. ^{1}H NMR spectrum of **11** (400 MHz, $CDCl_3$).

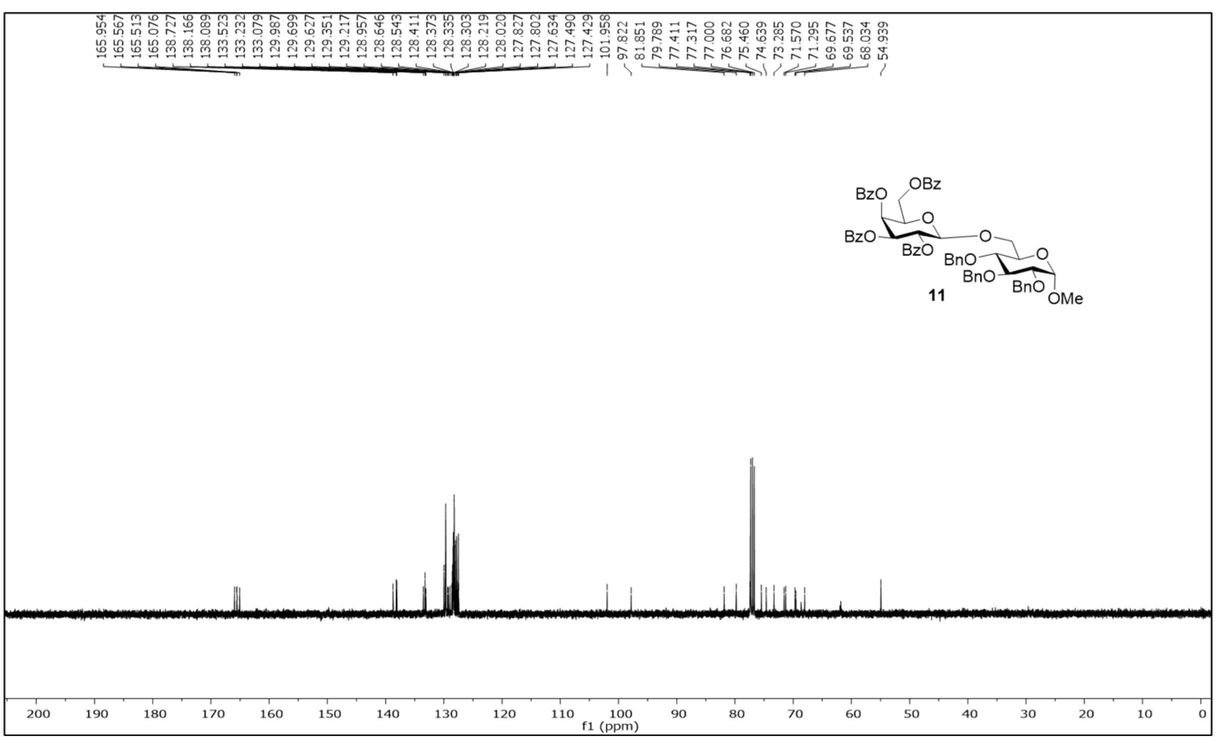


Figure S73. ^{13}C NMR spectrum of **11** (100 MHz, $CDCl_3$).

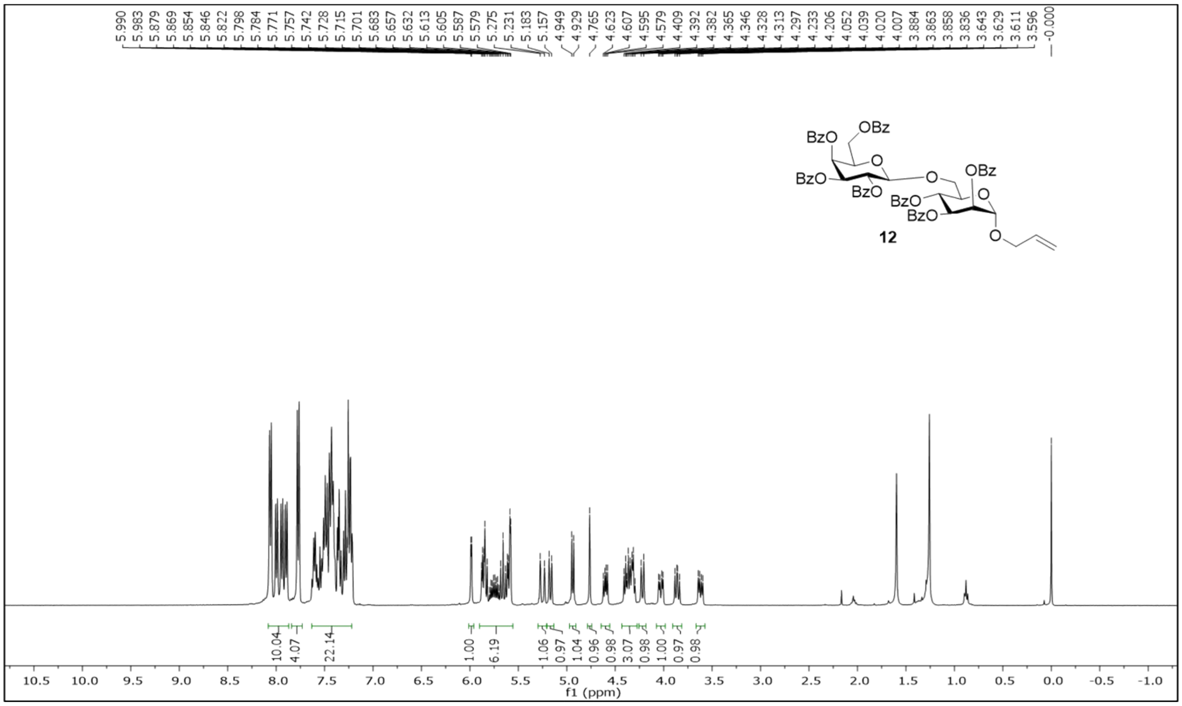


Figure S74. [1]H NMR spectrum of **12** (400 MHz, $CDCl_3$).

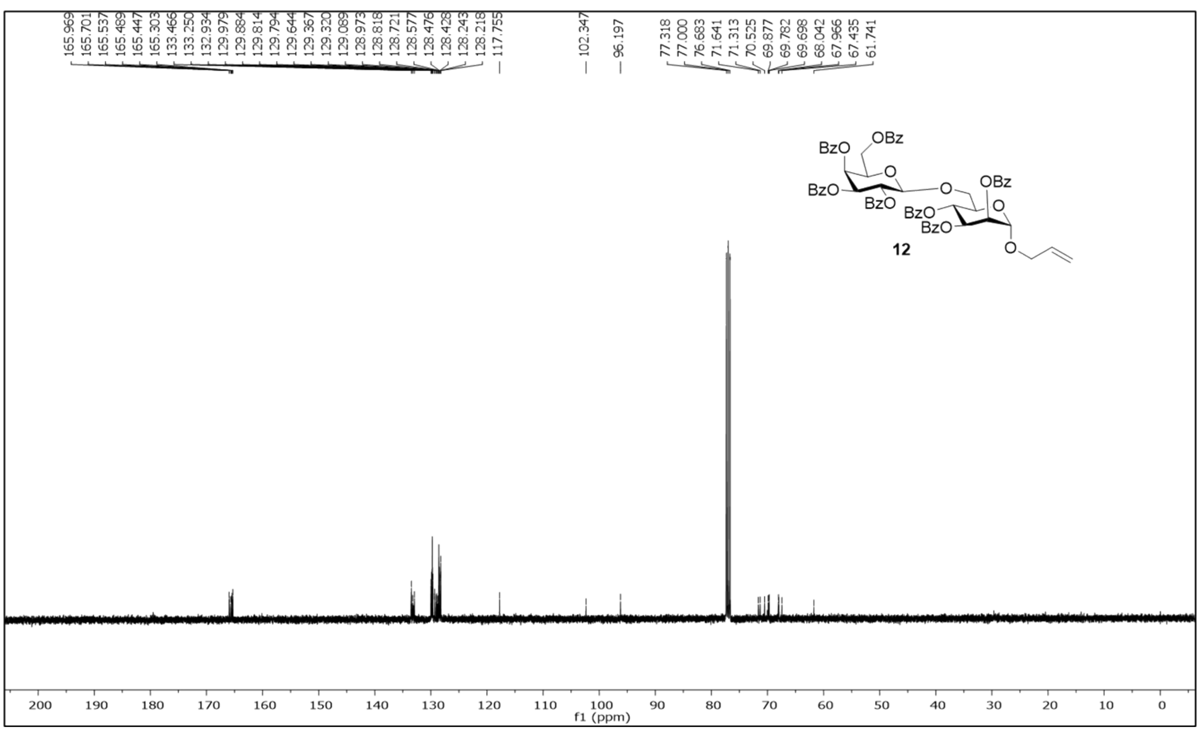


Figure S75. [13]C NMR spectrum of **12** (100 MHz, $CDCl_3$).

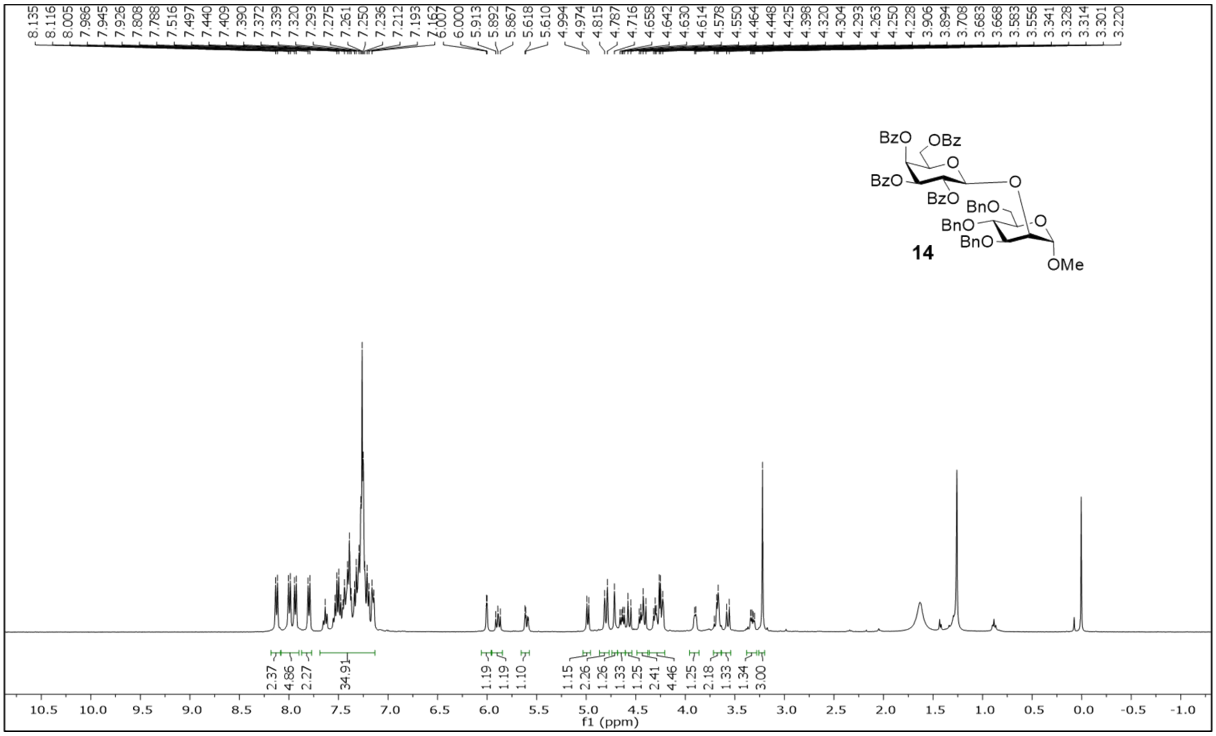


Figure S76. ^{1}H NMR spectrum of **14** (400 MHz, $CDCl_3$).

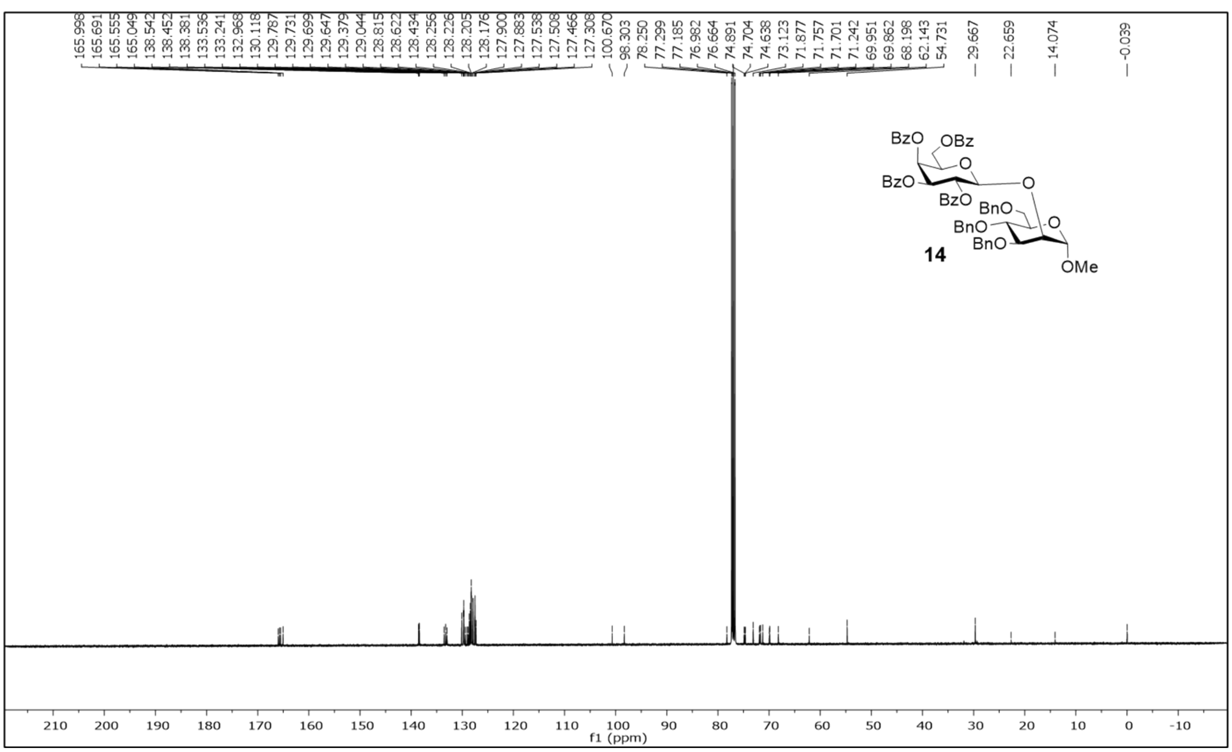


Figure S77. ^{13}C NMR spectrum of **14** (100 MHz, $CDCl_3$).

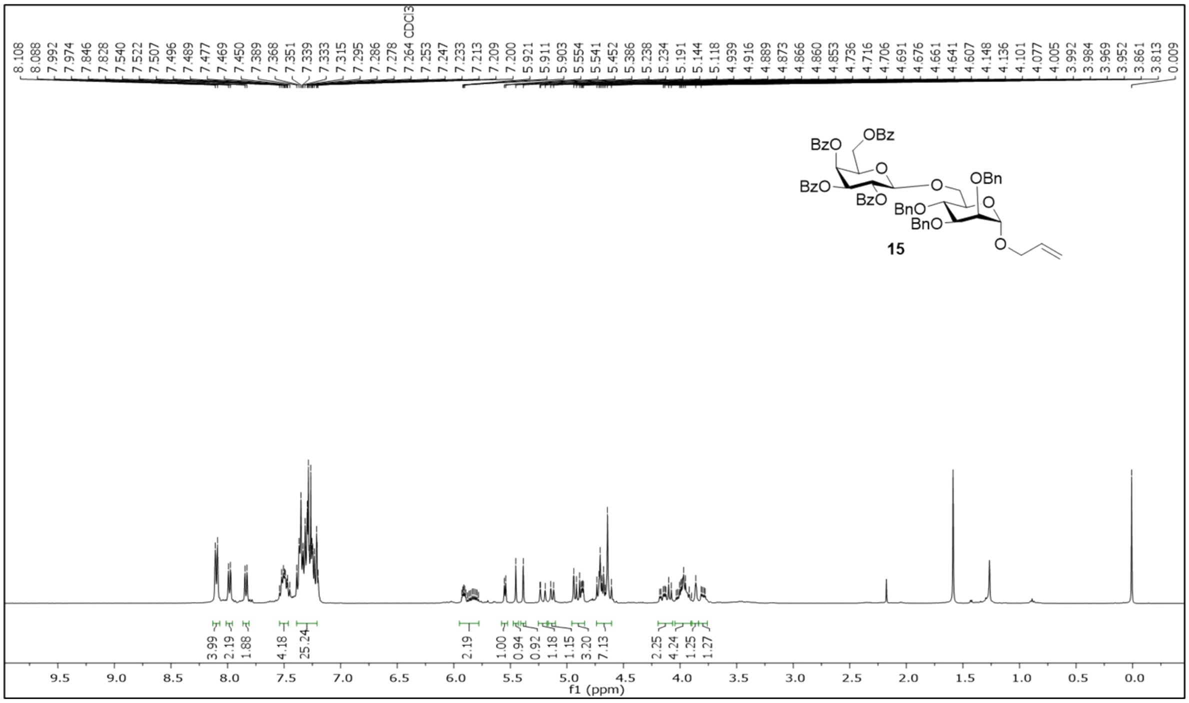


Figure S78. [1]H NMR spectrum of **15** (400 MHz, $CDCl_3$).

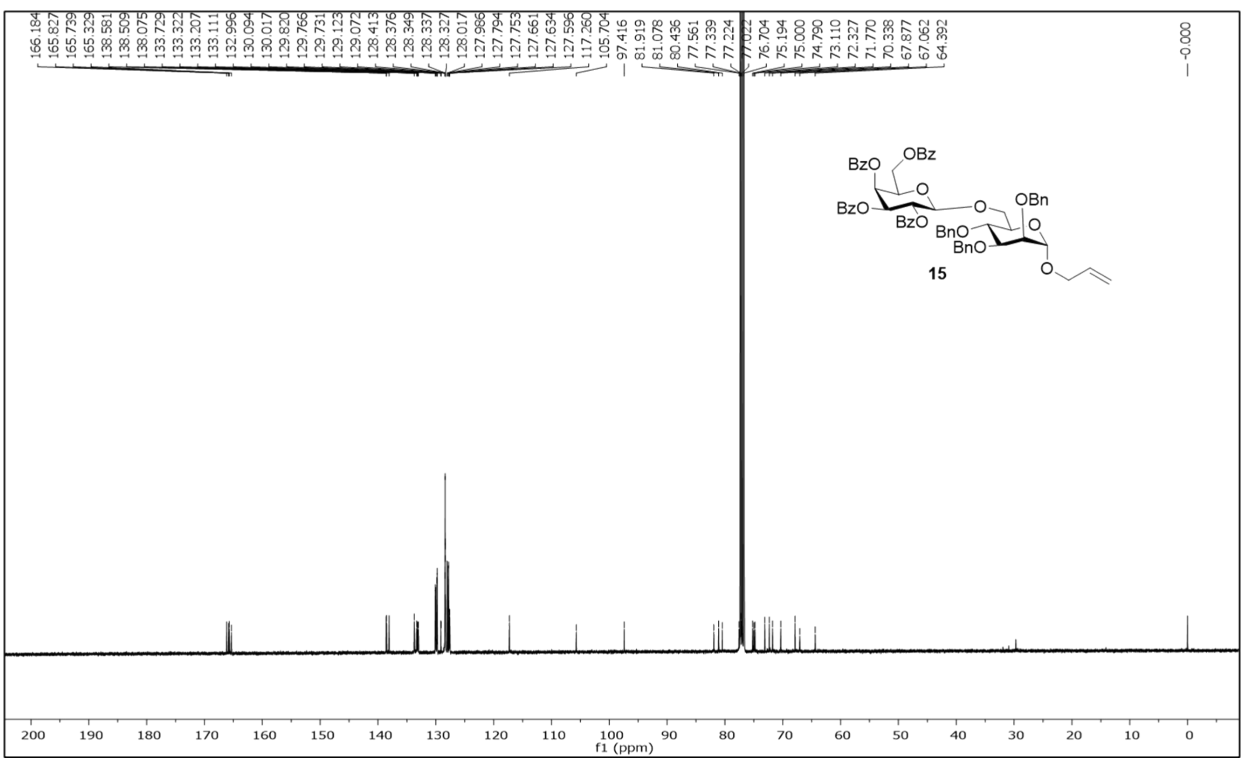


Figure S79. [13]C NMR spectrum of **15** (100 MHz, $CDCl_3$).

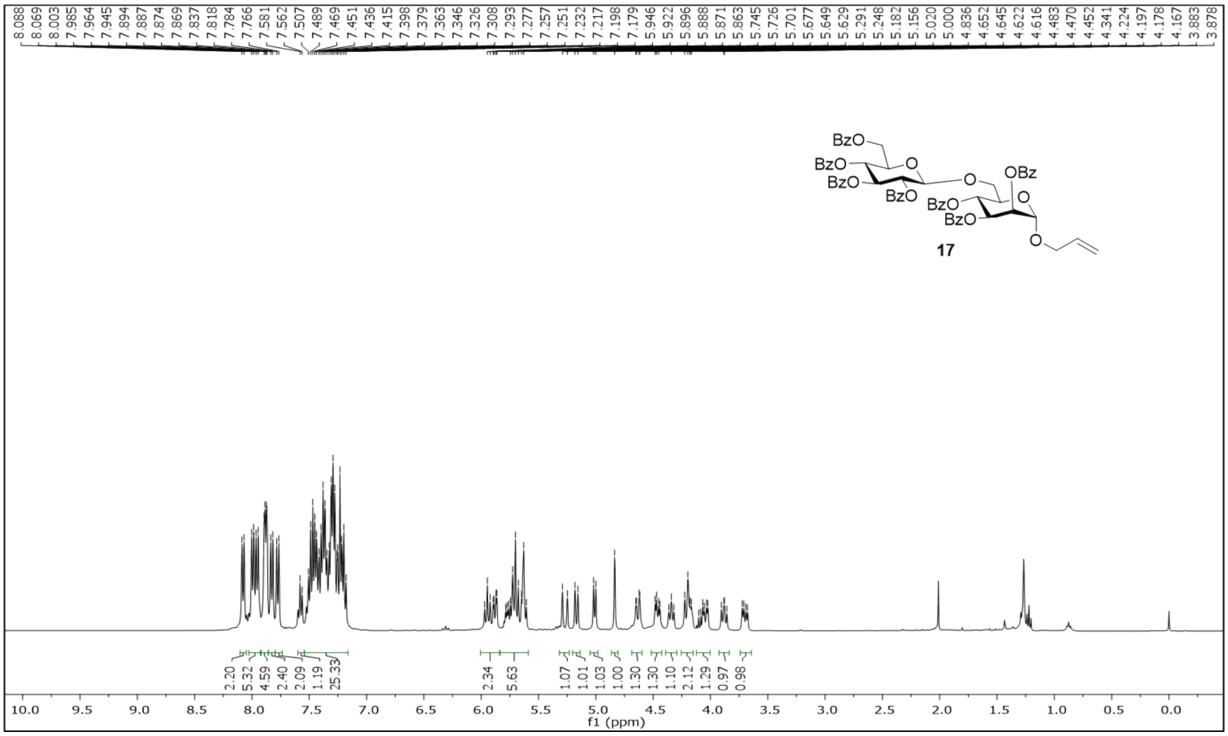


Figure S80. ^{1}H NMR spectrum of **17** (400 MHz, $CDCl_3$).

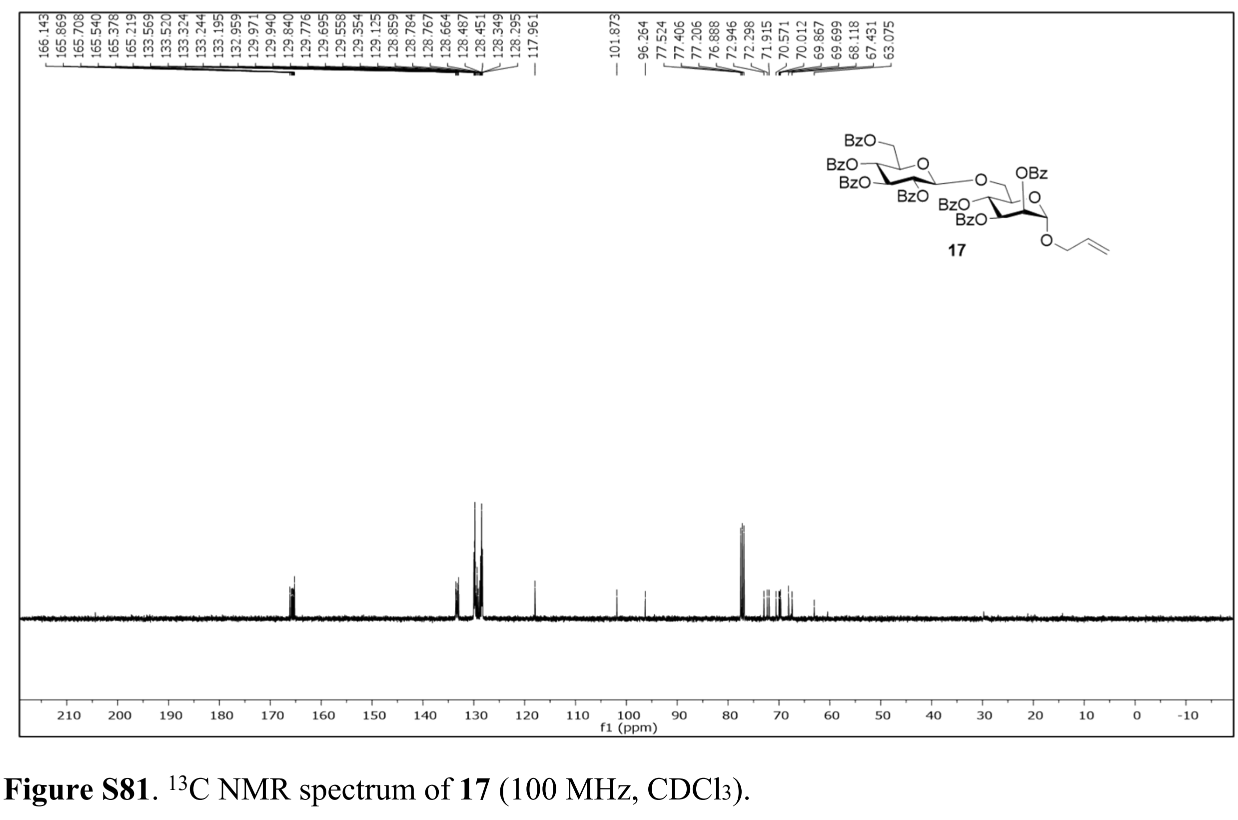


Figure S81. ^{13}C NMR spectrum of **17** (100 MHz, $CDCl_3$).

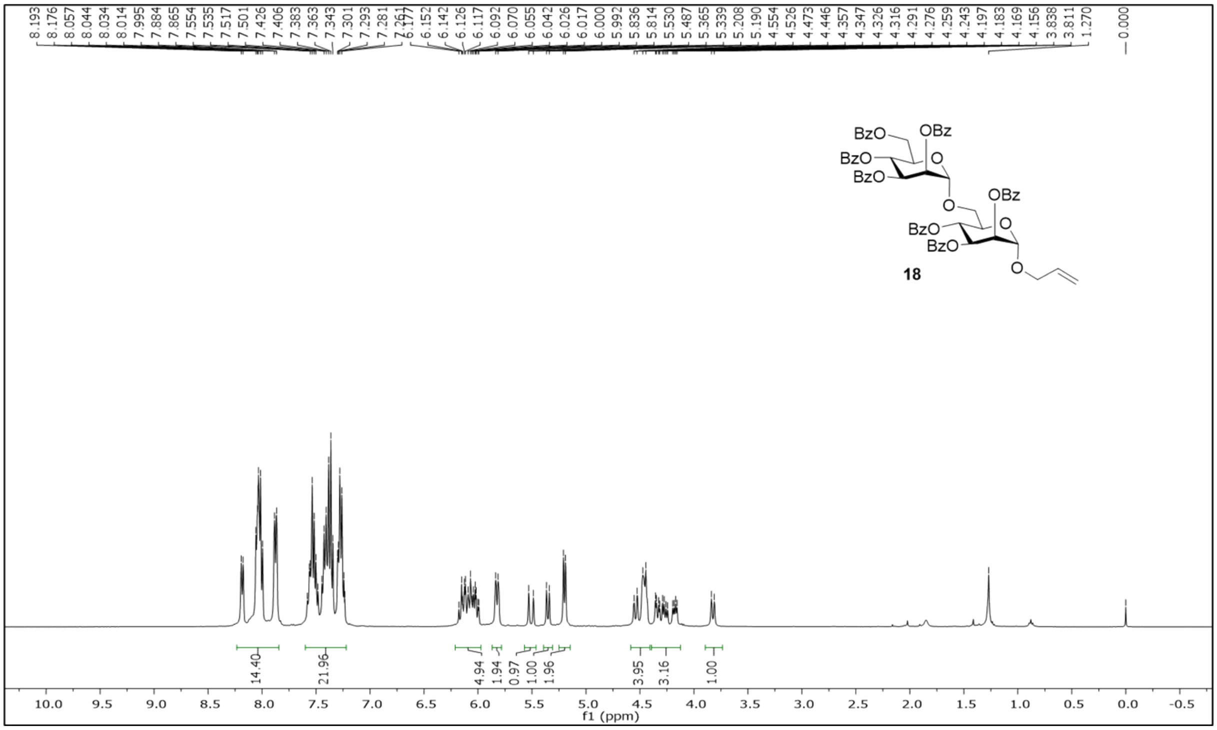


Figure S82. ^{1}H NMR spectrum of **18** (400 MHz, $CDCl_3$).

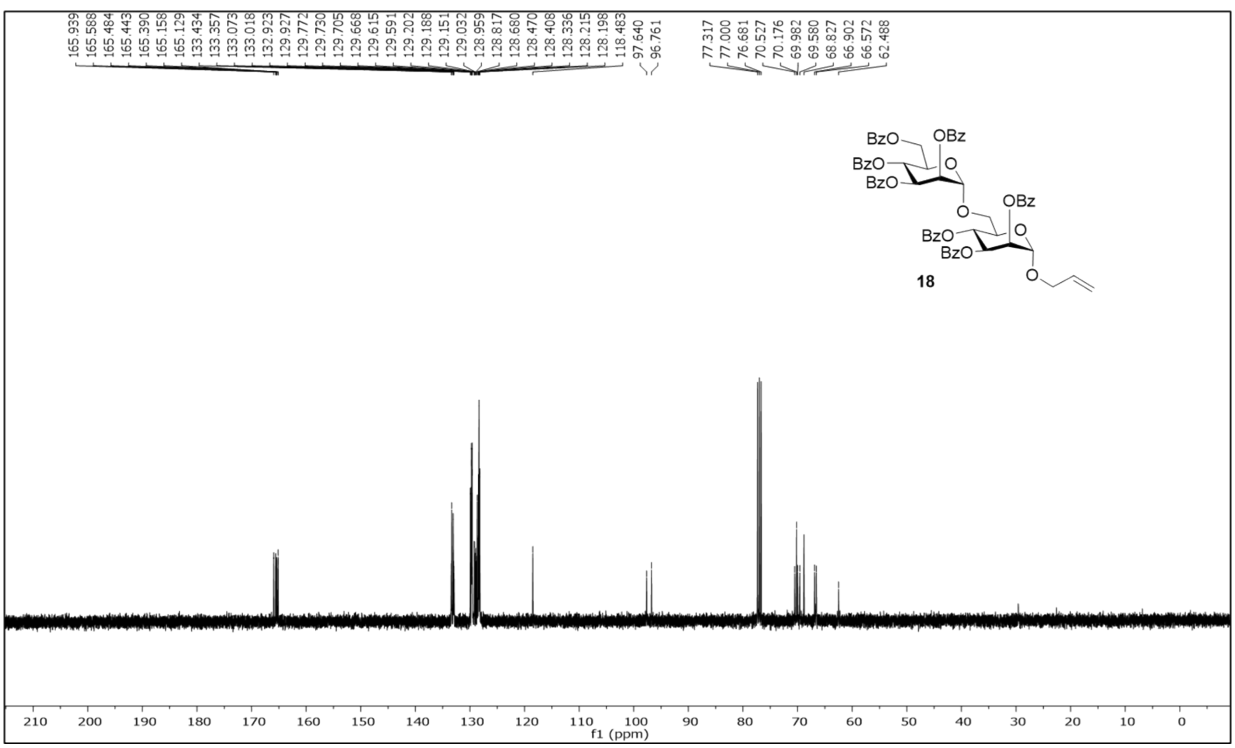


Figure S83. ^{13}C NMR spectrum of **18** (100 MHz, $CDCl_3$).

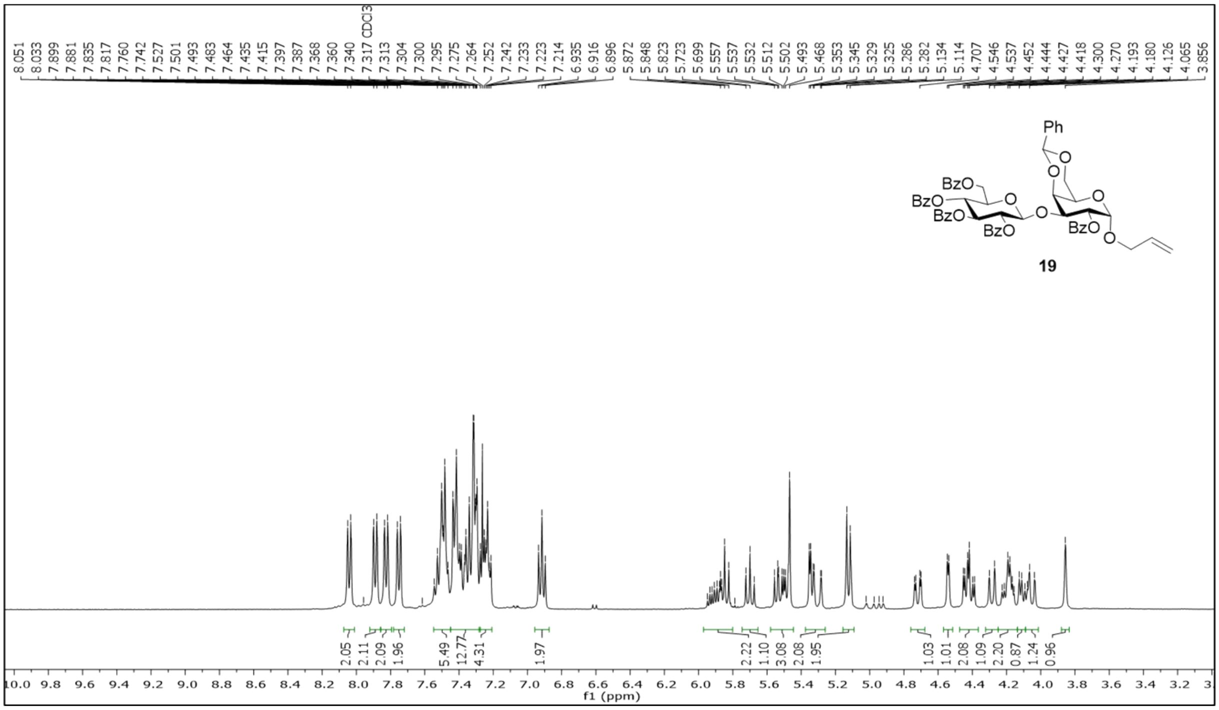


Figure S84. ^{1}H NMR spectrum of **19** (400 MHz, $CDCl_3$).

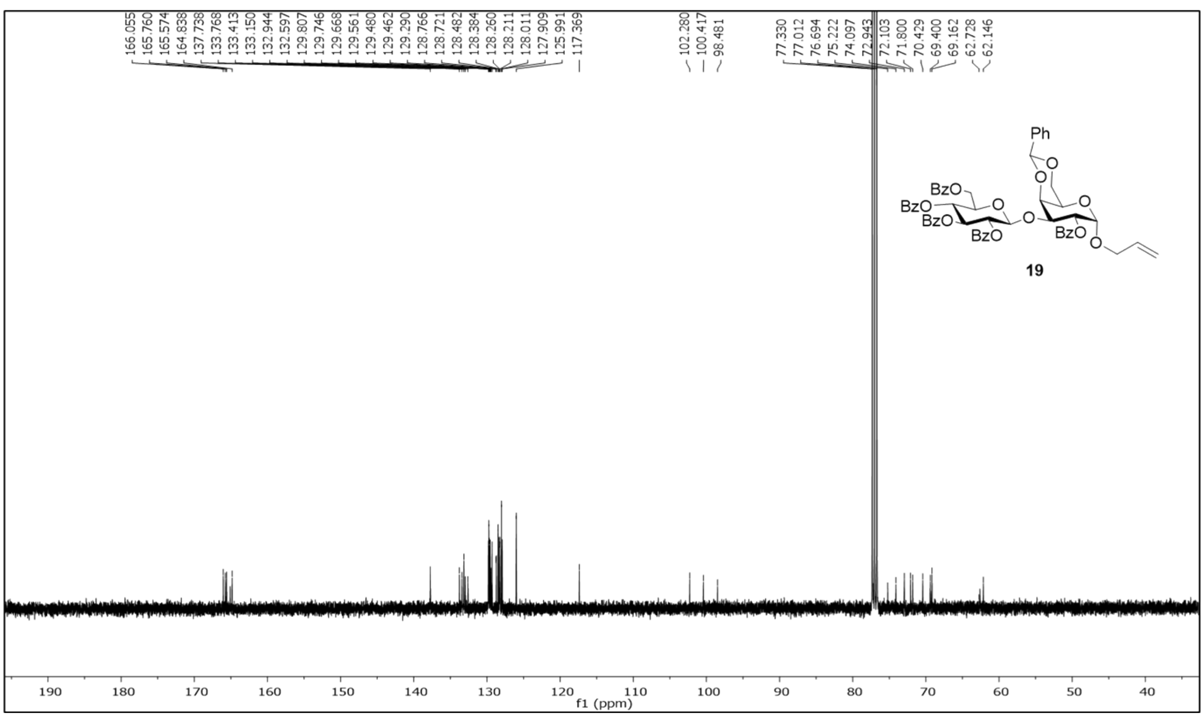


Figure S85. ^{13}C NMR spectrum of **19** (100 MHz, $CDCl_3$).

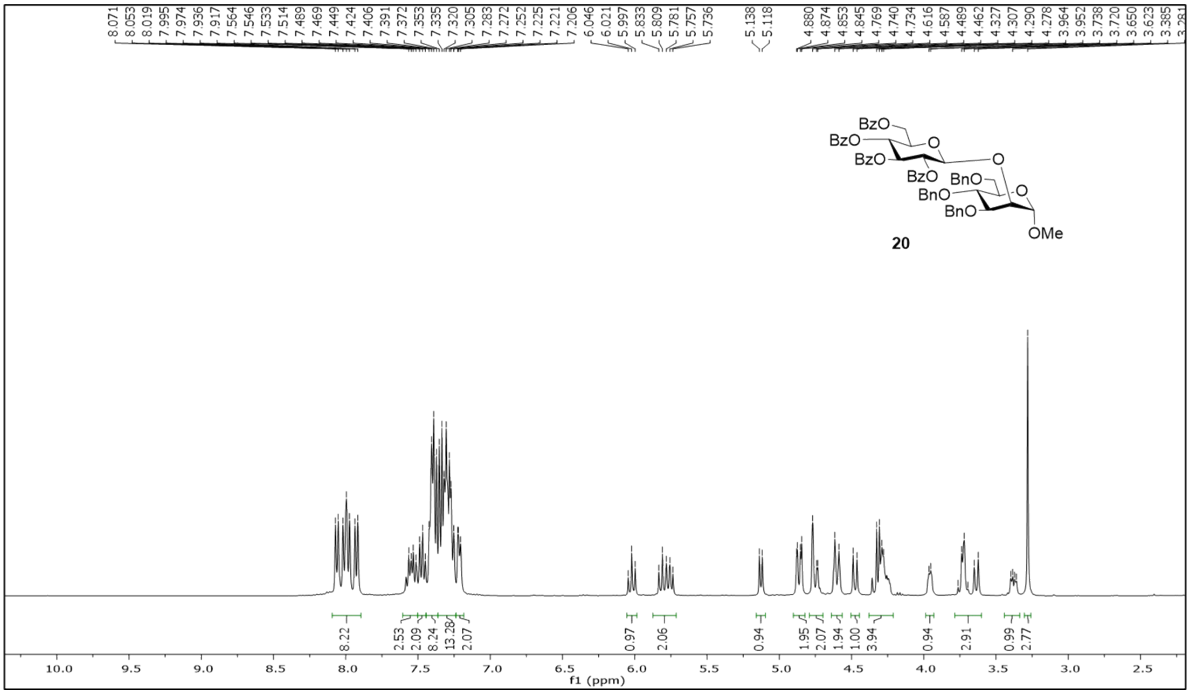


Figure S86. ^1H NMR spectrum of **20** (400 MHz, $CDCl_3$).

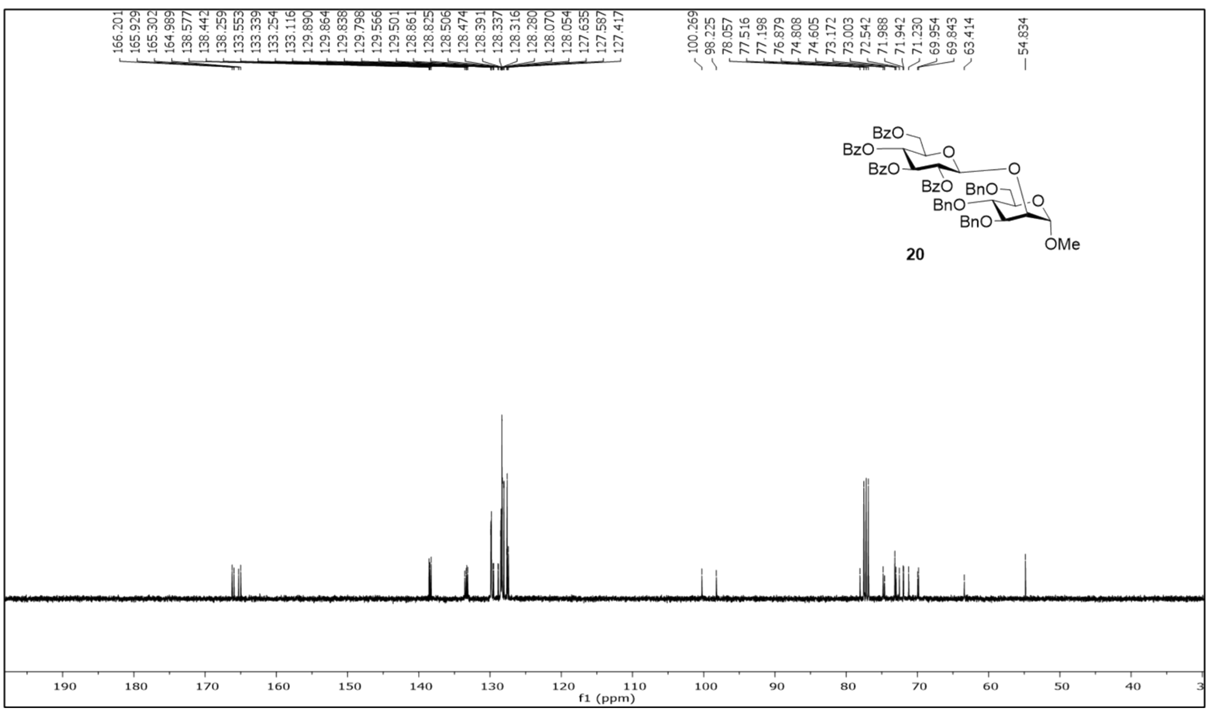


Figure S87. ^{13}C NMR spectrum of **20** (100 MHz, $CDCl_3$).

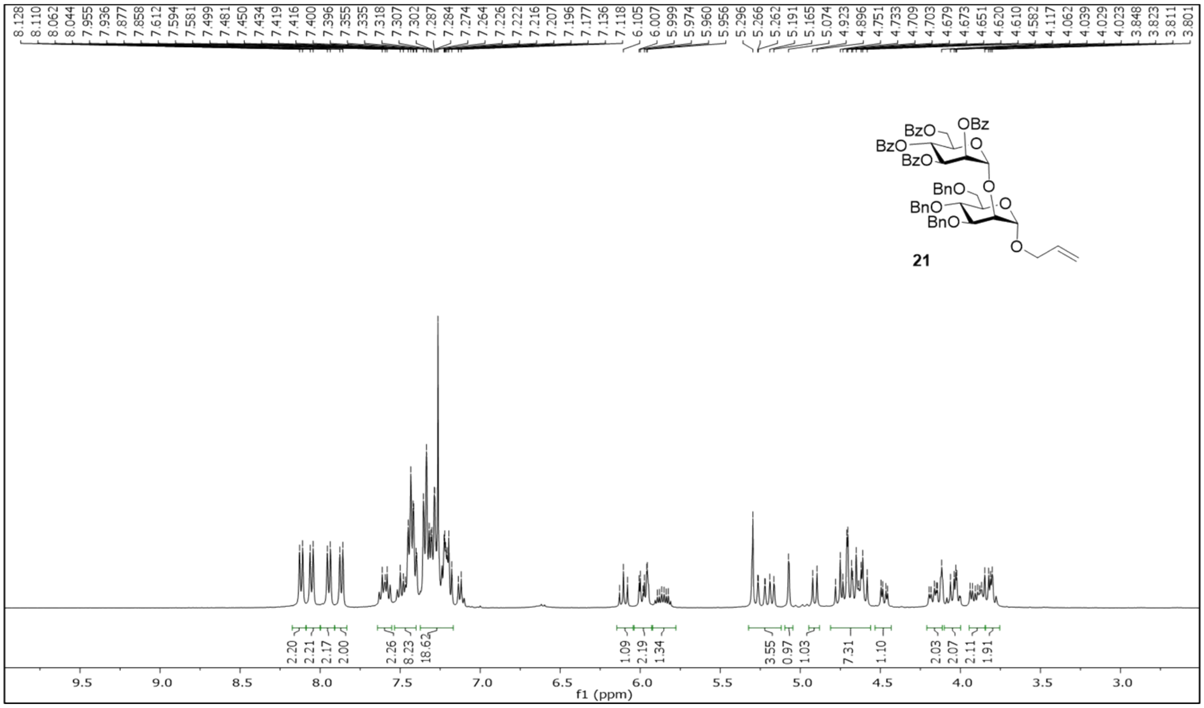


Figure S88. ^{1}H NMR spectrum of **21** (400 MHz, $CDCl_3$).

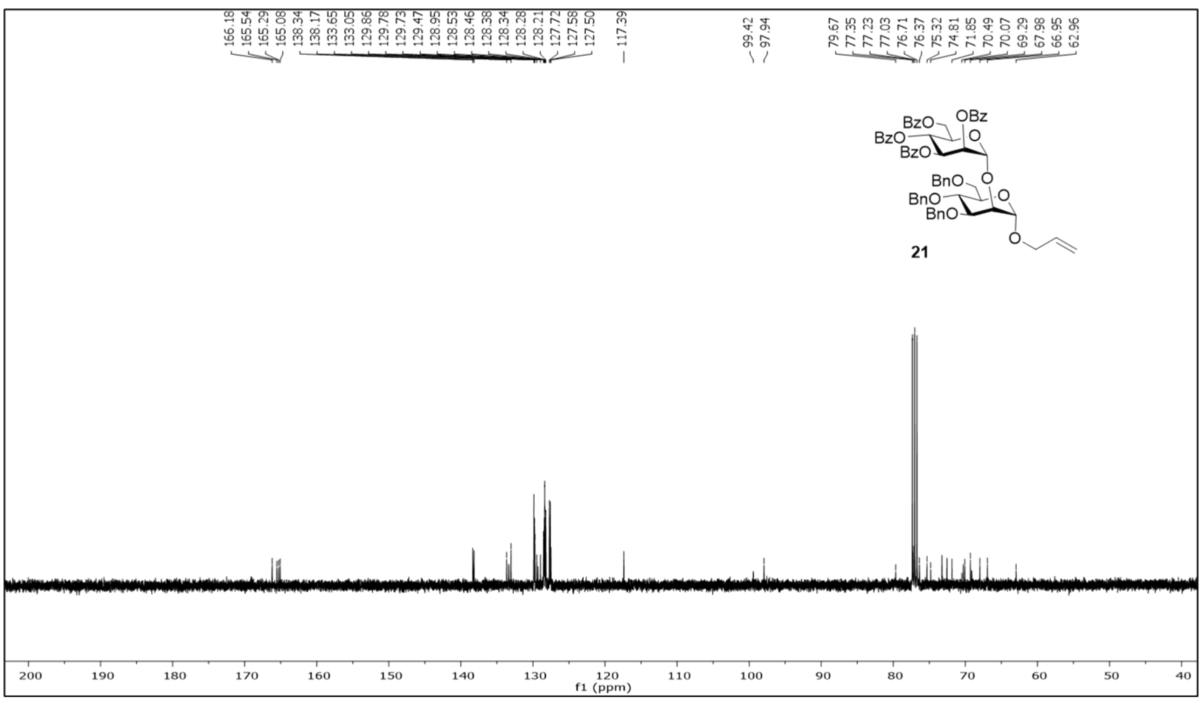


Figure S89. ^{13}C NMR spectrum of **21** (100 MHz, $CDCl_3$).

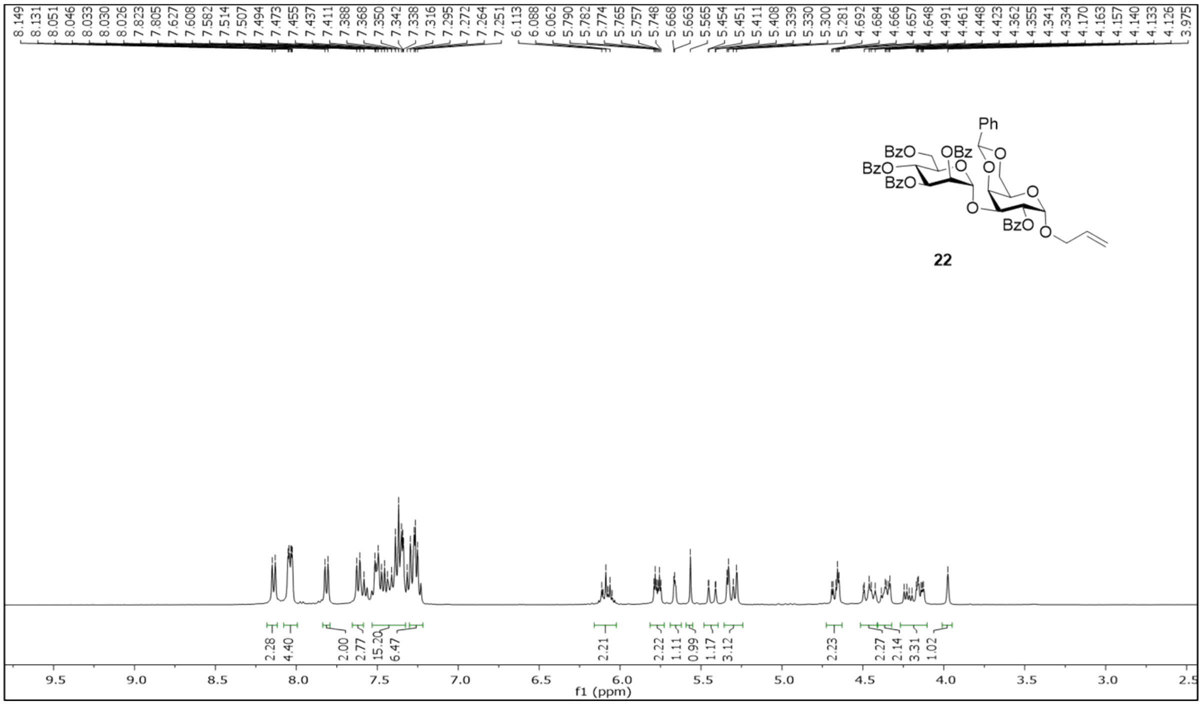


Figure S90. ^{1}H NMR spectrum of **22** (400 MHz, $CDCl_3$).

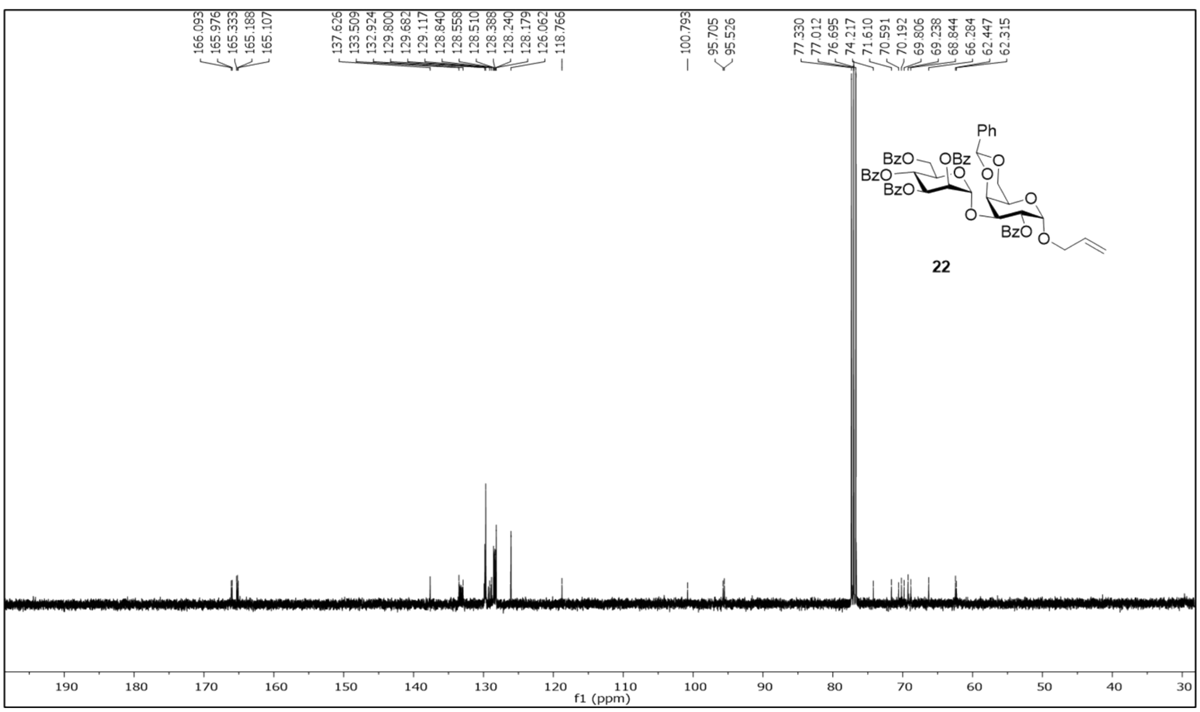


Figure S91. ^{13}C NMR spectrum of **22** (100 MHz, $CDCl_3$).

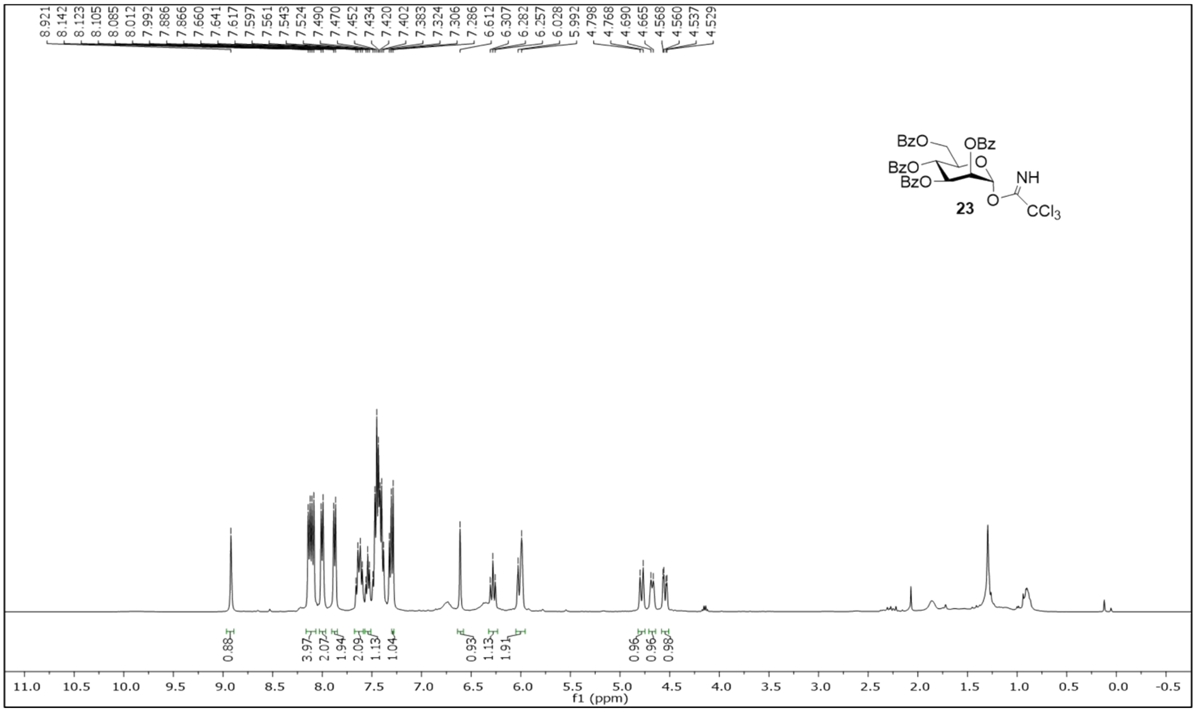


Figure S92. [1]H NMR spectrum of **23** (400 MHz, $CDCl_3$).

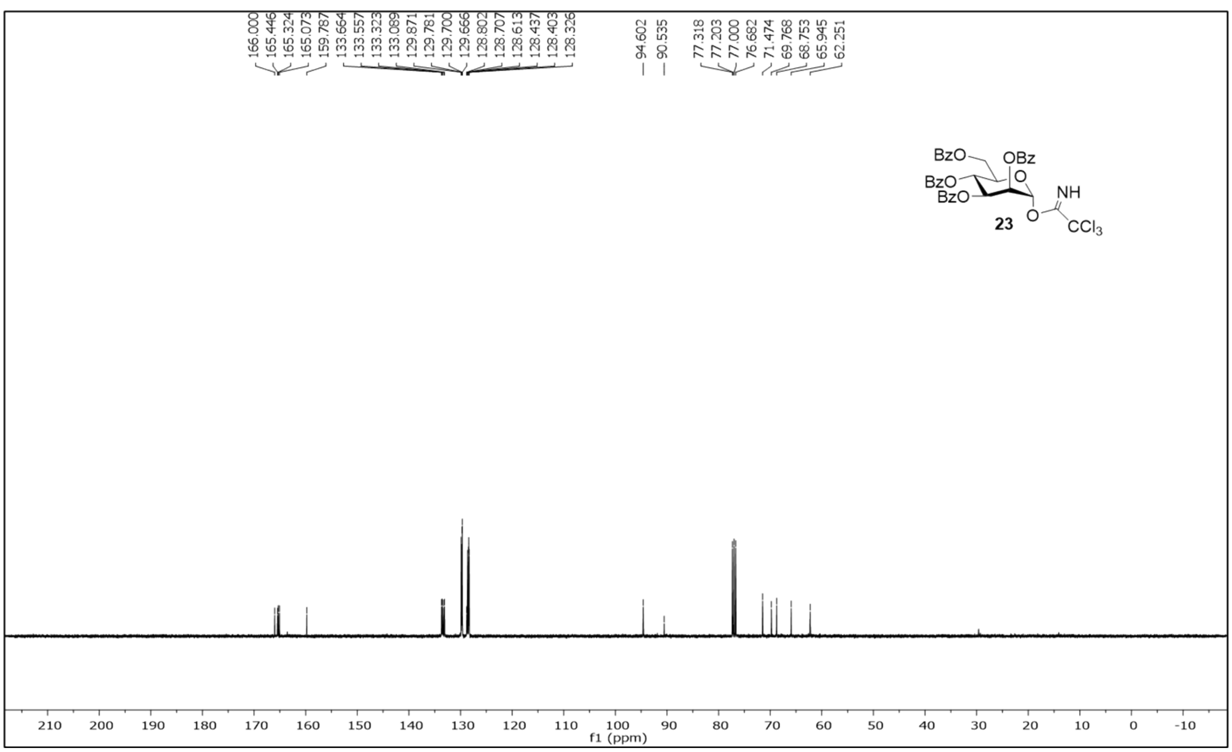


Figure S93. [13]C NMR spectrum of **23** (100 MHz, $CDCl_3$).

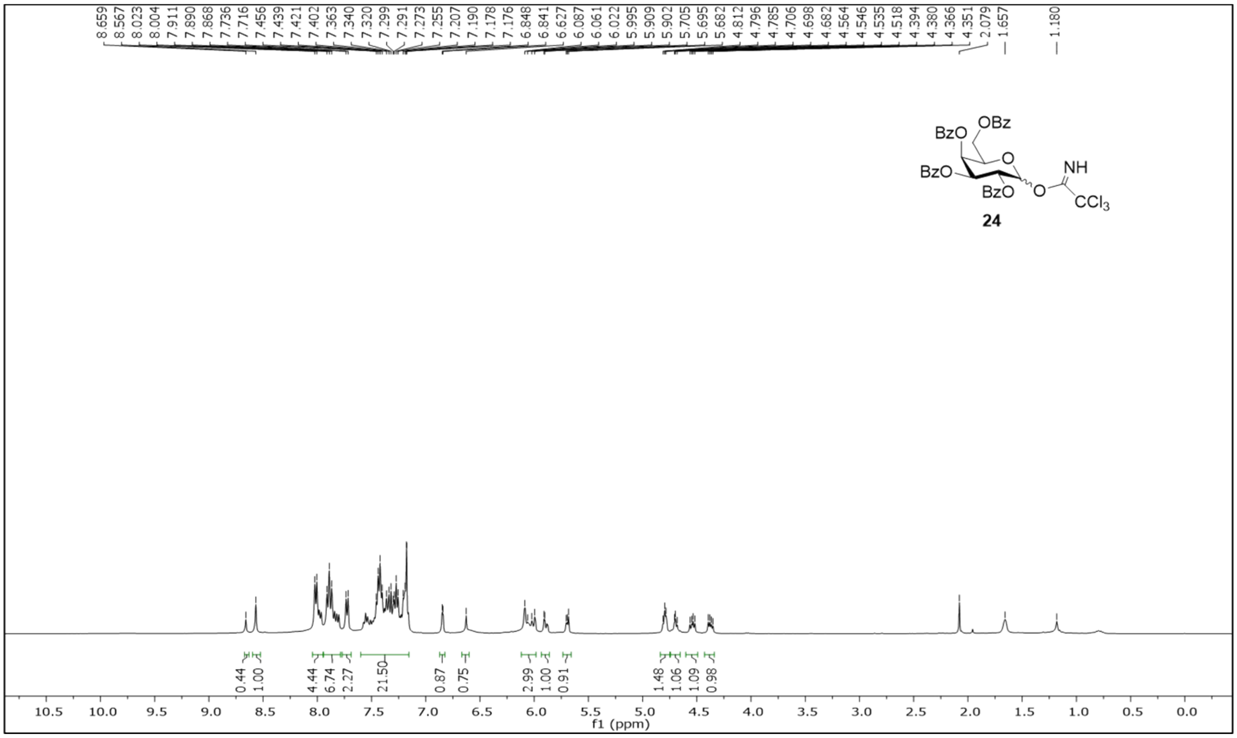


Figure S94. ^{1}H NMR spectrum of **24** (400 MHz, $CDCl_3$).

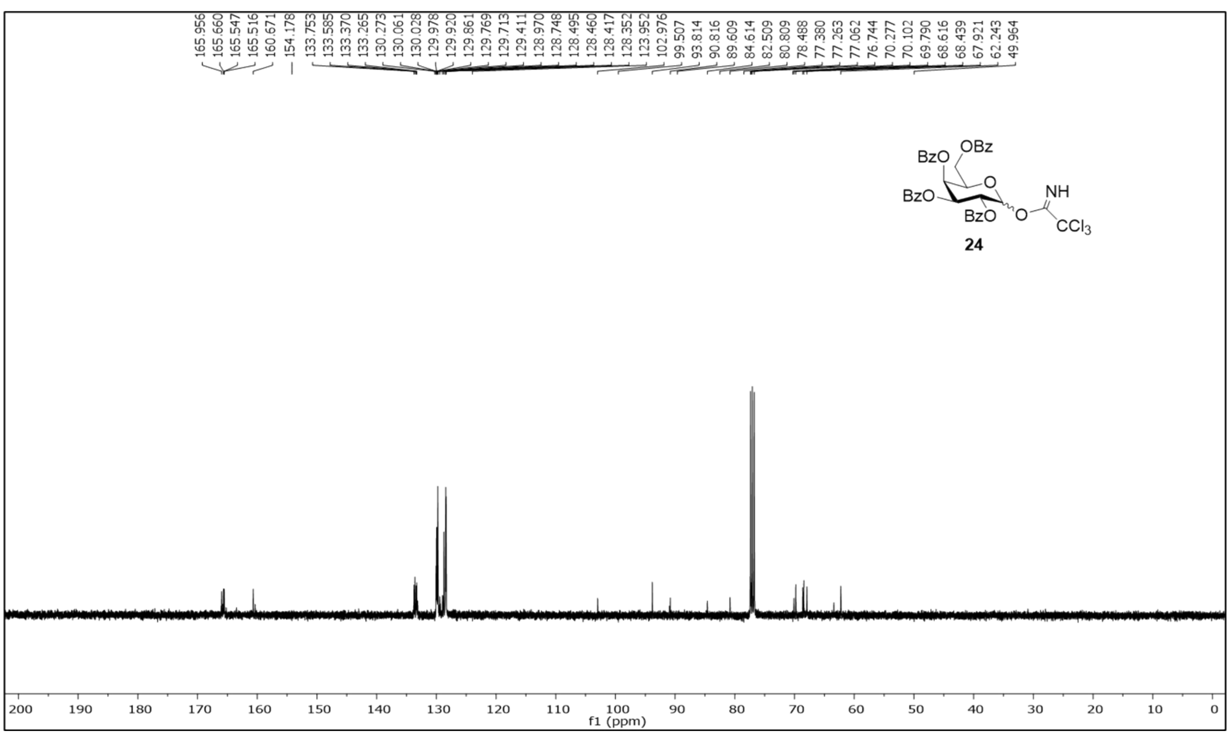


Figure S95. ^{13}C NMR spectrum of **24** (100 MHz, $CDCl_3$).

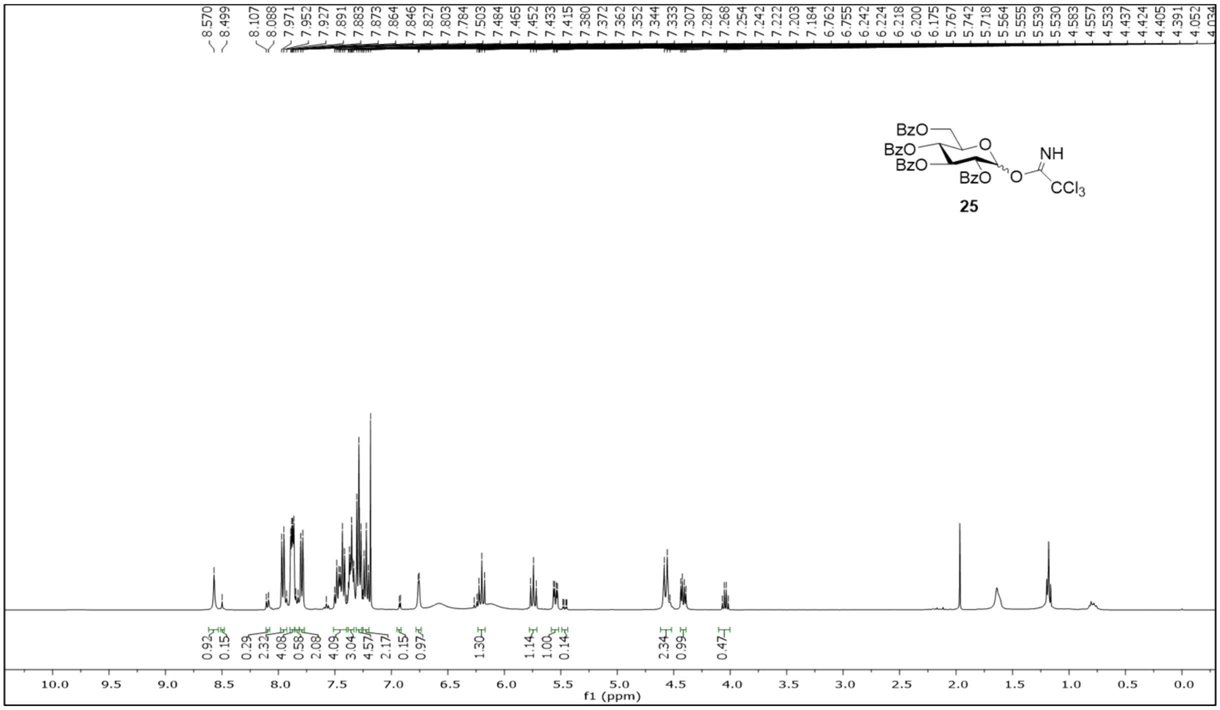


Figure S96. ^{1}H NMR spectrum of **25** (400 MHz, $CDCl_3$).

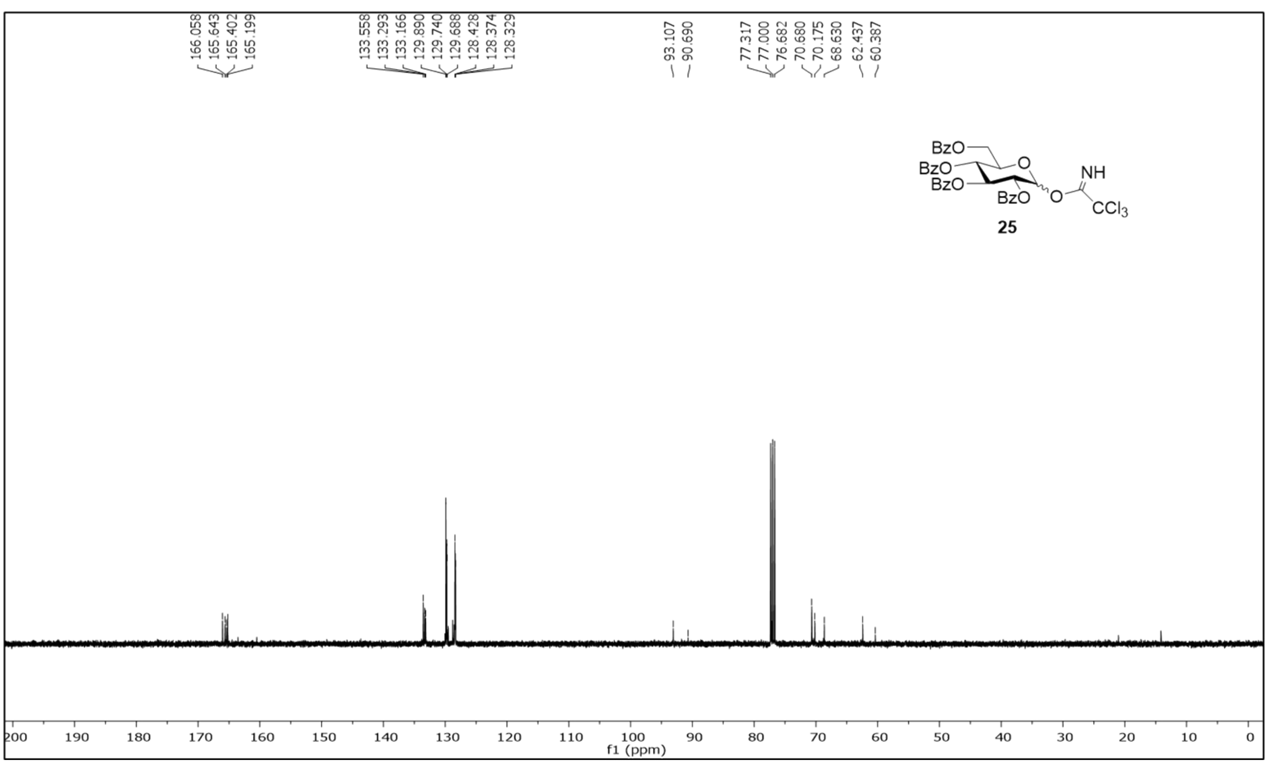


Figure S97. ^{13}C NMR spectrum of **25** (100 MHz, $CDCl_3$).

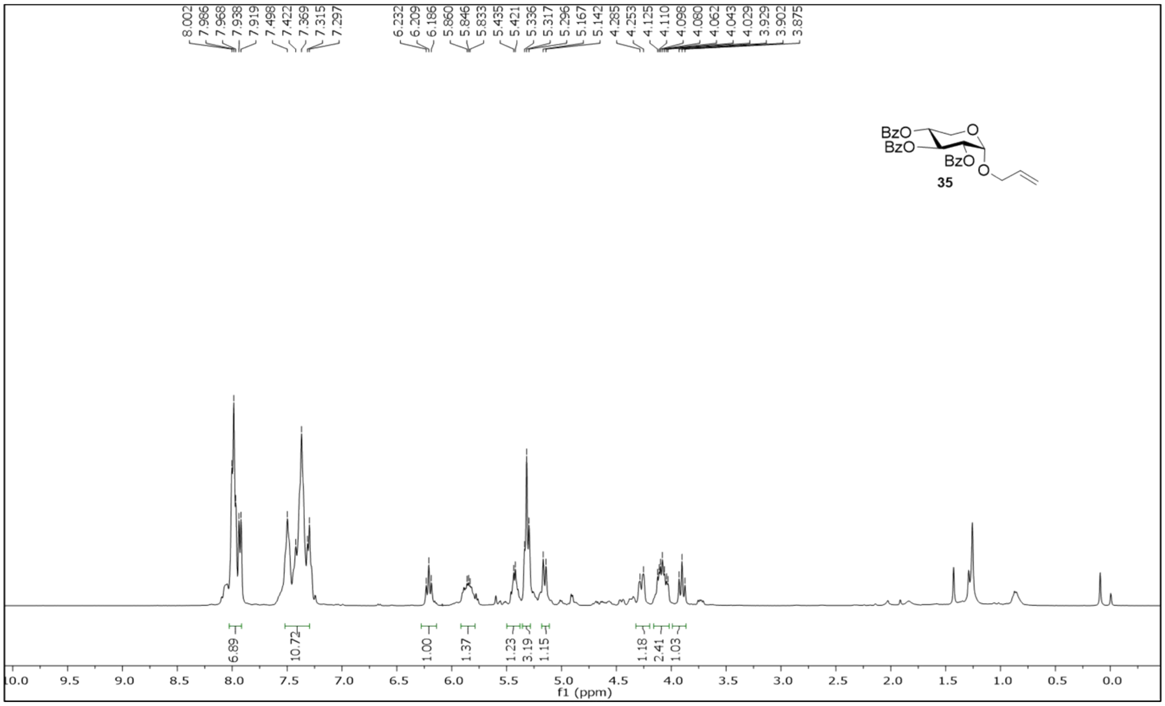


Figure S98. ^{1}H NMR spectrum of **35** (400 MHz, $CDCl_3$).

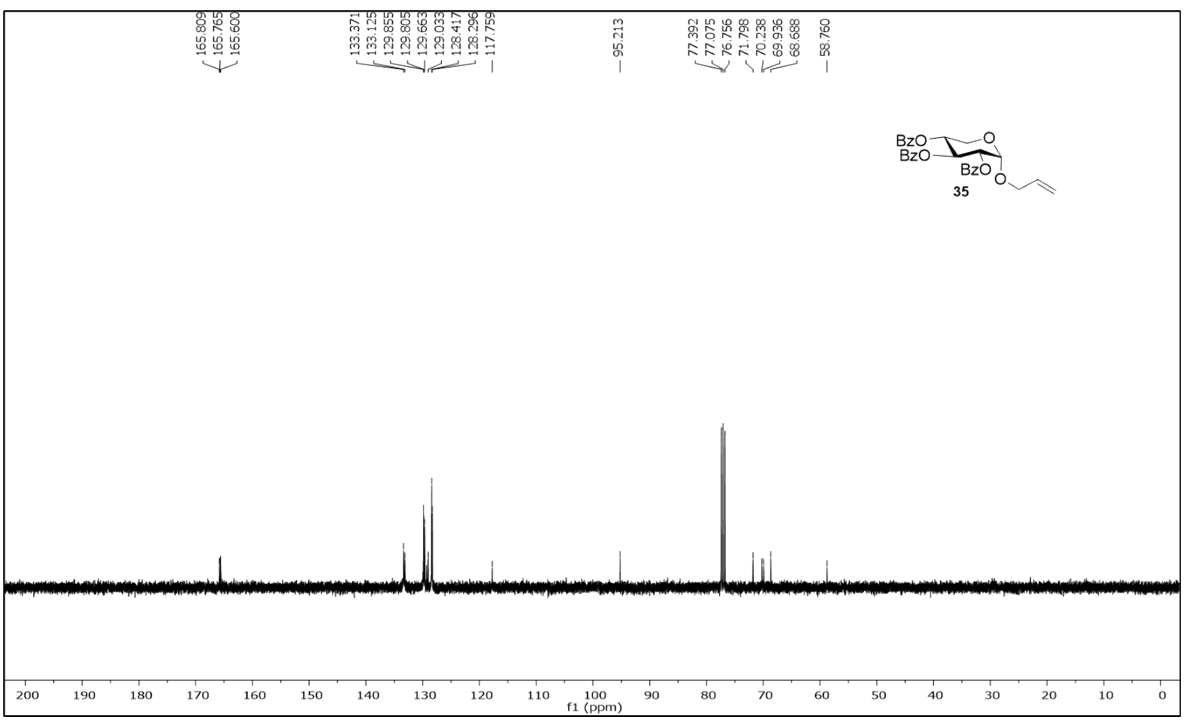


Figure S99. ^{13}C NMR spectrum of **35** (100 MHz, $CDCl_3$).

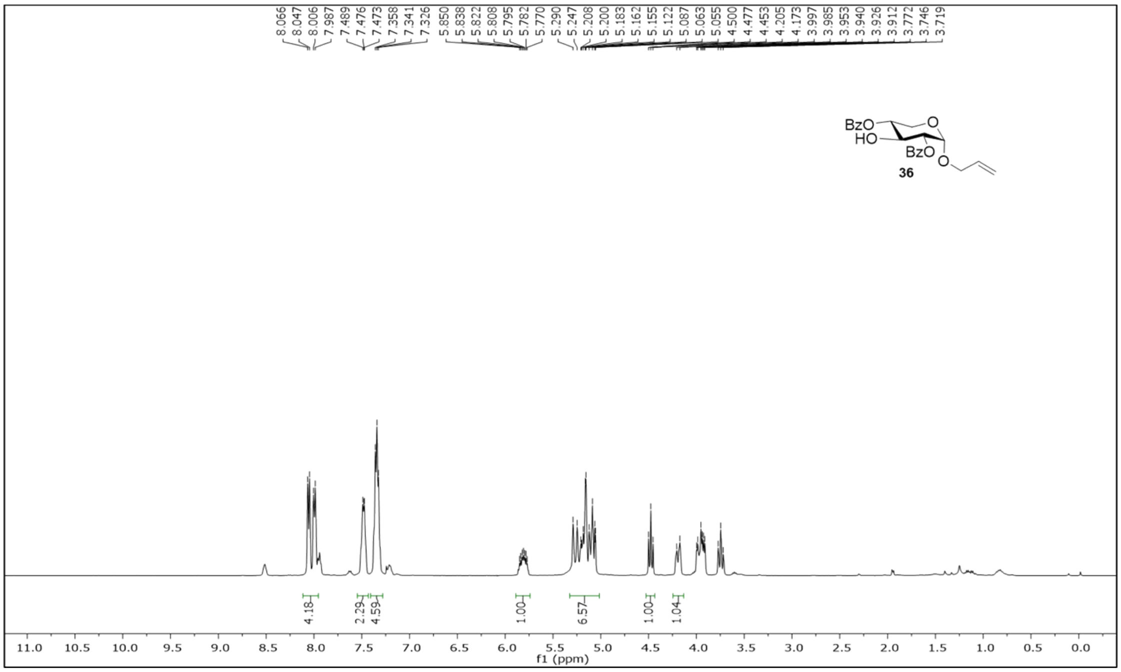


Figure S100. ^{1}H NMR spectrum of **36** (400 MHz, $CDCl_3$).

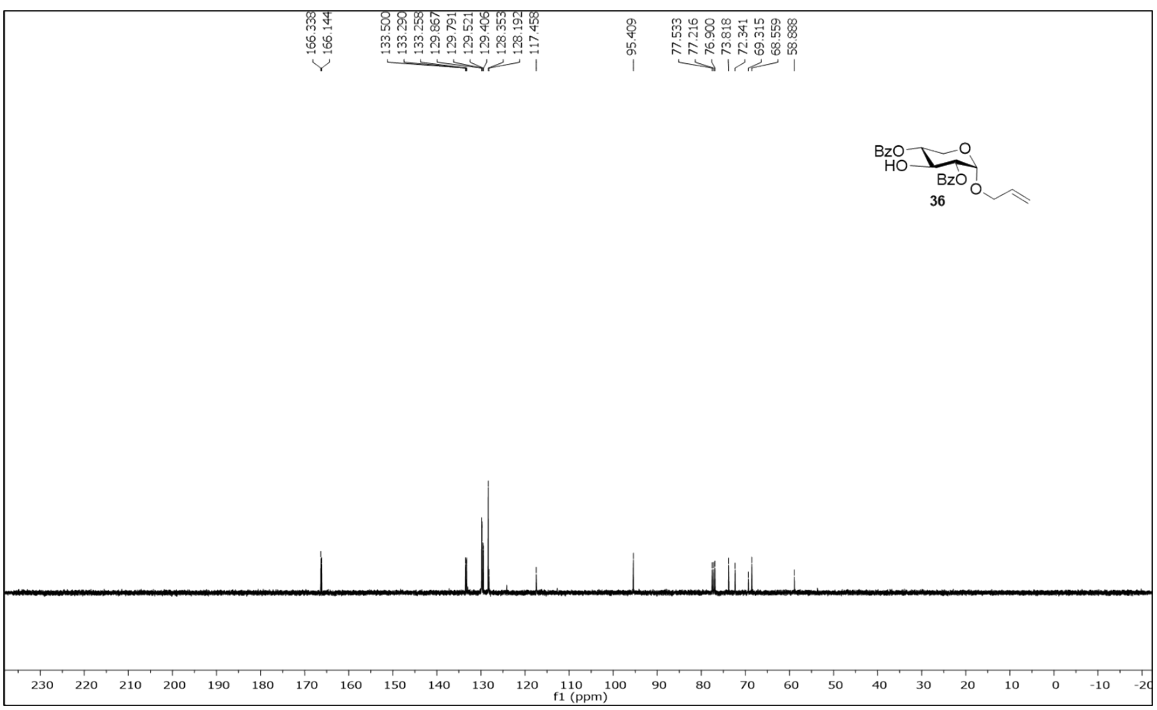


Figure S101. ^{13}C NMR spectrum of **36** (100 MHz, $CDCl_3$).

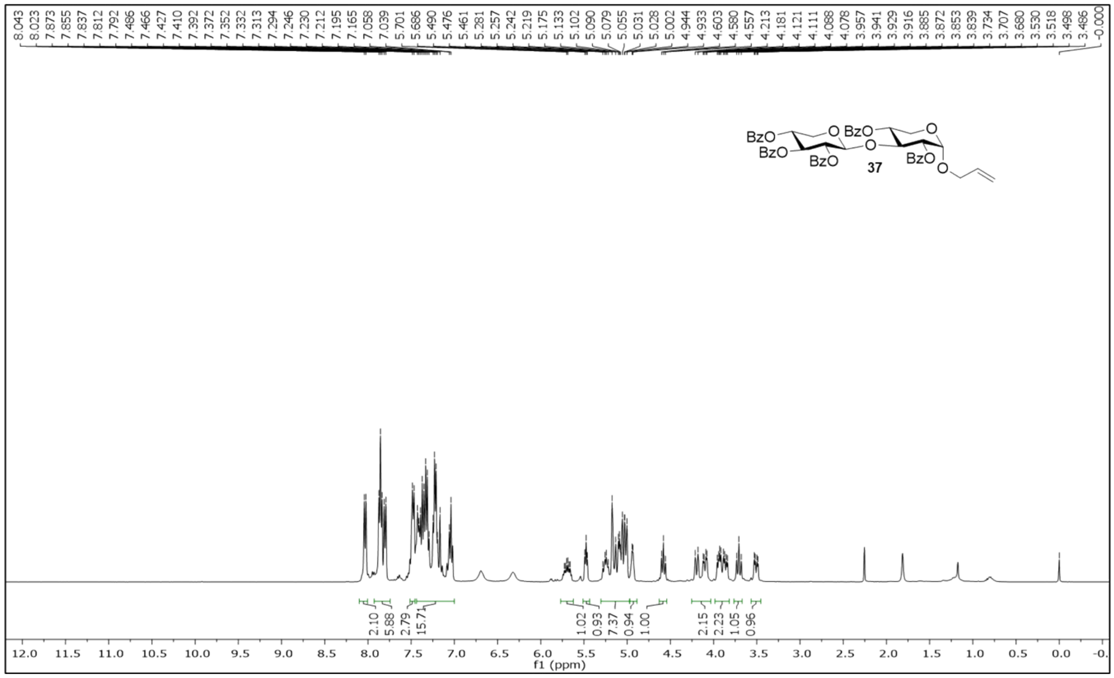


Figure S102. [1]H NMR spectrum of **37** (400 MHz, $CDCl_3$).

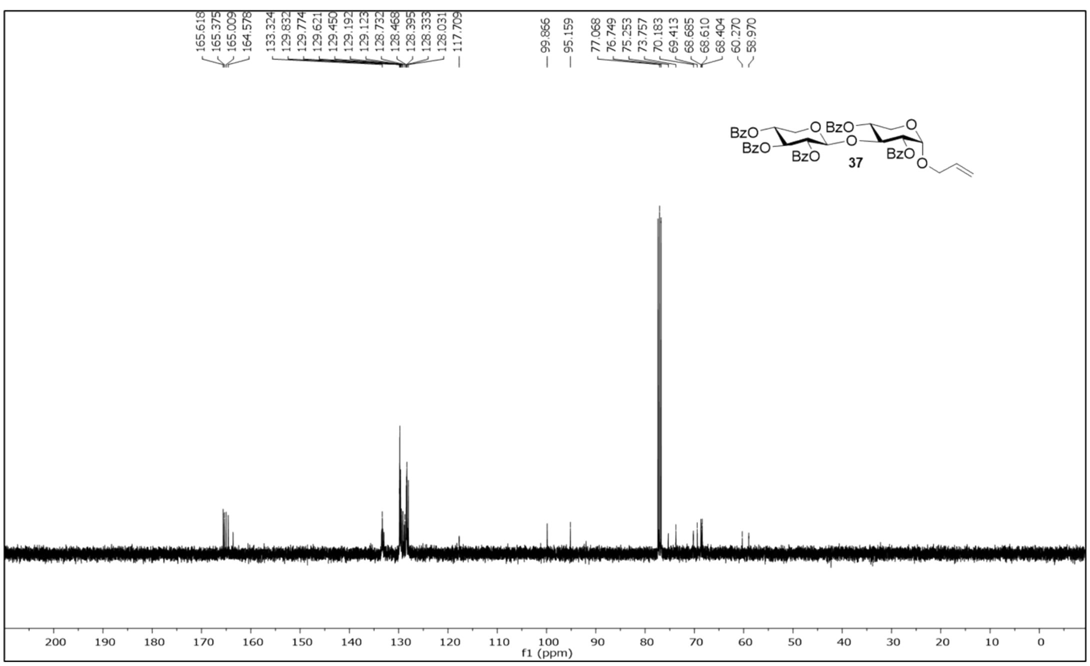


Figure S103. [13]C NMR spectrum of **37** (100 MHz, $CDCl_3$).