Electronic Supplementary Information (ESI)

Microwave-assisted synthesis of glycopolymers by ring-opening metathesis polymerization (ROMP) in an emulsion system

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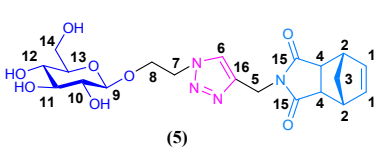
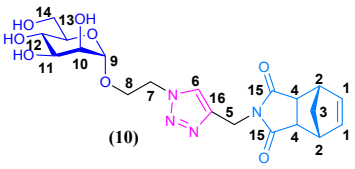
1. NMR data for glycomonomers.

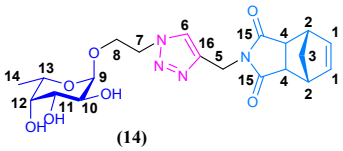
Table S1. ^{1}H and ^{13}C NMR data for glycomonomers (**5**, **10**, **14**).



(5)



(10)



(14)

Atom	5					10					14				
	δ_H	n_H	m.	*J*[Hz]	δ_C	δ_H	n_H	m.	*J*[Hz]	δ_C	δ_H	n_H	m.	*J*[Hz]	δ_C
1	6.32	2	s		137.59 137.58	6.25	2	s		137.90	6.33	2	s		137.61 137.55
2	3.19	2	s		45.06	3.21	2	s		45.25	3.19	2	d	10.3	45.07 45.06
3	1.44 1.23	1 1	d d	9.8 9.8	42.20	1.43 1.23	1 1	d d	8.8 9.2	42.86	1.45 1.28	1 1	d d	9.8 9.8	42.21
4	2.76	2	d	0.8	47.66	2.72	2	s		47.91	2.77	2	s		47.68 47.67
5	4.73	2	s		32.92	4.71	2	s		33.50	4.73	2	t	4.1	32.95
6	8.04	1	s		124.59	7.79	1	s		124.23	8.02	1	s		124.40
7	4.61	2	t	5.1	50.22	4.54	2	t	17.8	50.00	4.61	2	m		49.85
8	4.20 3.98	1 1	m dt	 11.0, 5.0	67.60	4.01 3.82	1 1	s d	 10.9	66.49	4.01 3.79	1 1	ddd dt	11.7, 7.7, 4.3 10.7, 4.0	65.66
9	4.28	1	d	7.8	103.17	4.76	1	s		99.86	4.73	1	t	4.1	98.95
10	3.16	1	dd	9.0, 7.9	73.55	3.82	1	d	10.9	70.44	3.71	1	dd	10.0, 3.7	68.38
11	3.31	1	dt	3.1, 1.6	76.52	3.66	1	d	8.5	71.28	3.61	1	m		70.10
12	3.27	1	m		76.67[b]	3.07	1	d	8.1	72.76	3.59	1	m		71.94
13	3.27	1	m		70.14[b]	3.76	1	d	9.4	65.49	3.29	1	d	6.6	66.28
14	3.87 3.66	1 1	d dd	11.0 11.9, 5.3	61.31	3.76 3.66	1 1	d d	9.4 8.5	61.06	1.08	3	d	6.6	15.16
15					177.86					177.86					177.814
										177.83					177.805
16					141.85					141.91					142.01

[b] might be interchanged

2. The features of polymerization for glycopmonomer 5 with H-G 2nd as catalyst.

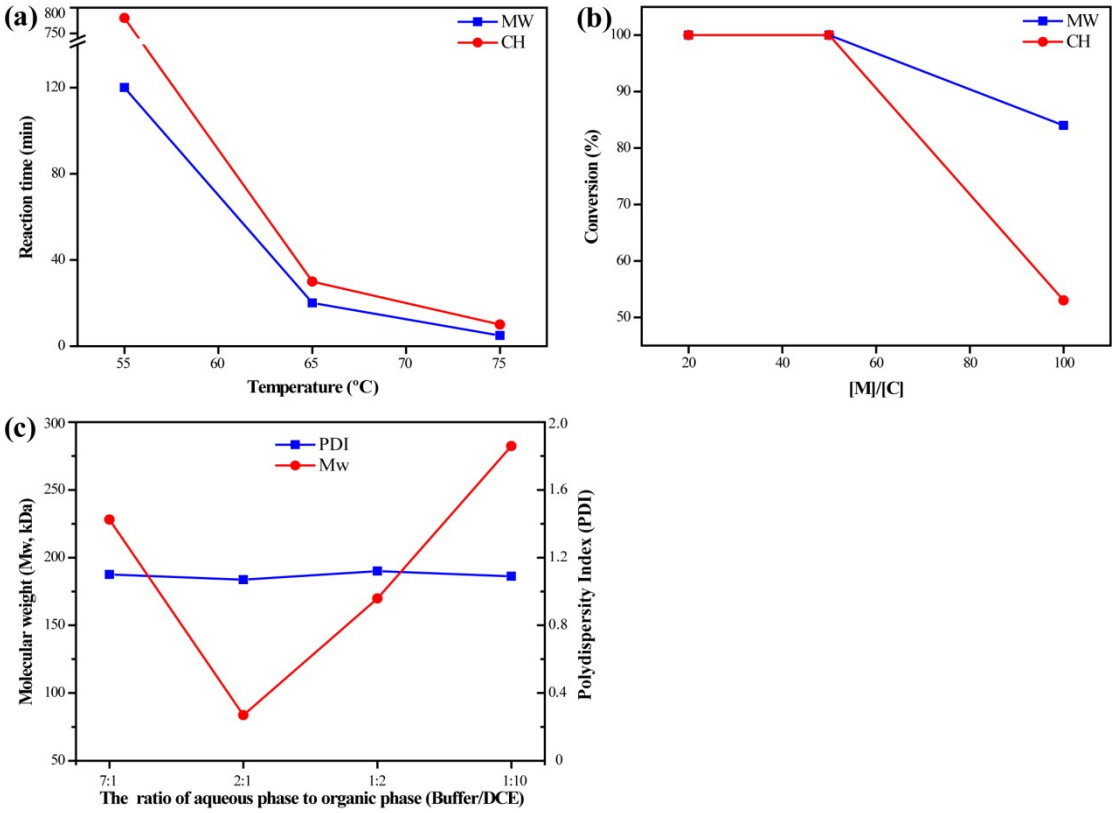


Figure S1. (a) Reaction time of polymerization for [M]/[C] is 20 with H-G 2nd as catalyst under various reaction temperature (table 1, entries 6-11). (b) Monomer conversion of polymerization for various [M]/[C] ratio with H-G 2nd as catalyst under the reaction temperature 75 °C (table 1, entries 10, 11, 14-17). The black plot represents standard microwave heating, the red plot represents conventionally heating. (c) Different molecular weight (red) and polydispersity index (PDI, blue) polymerization with H-G 2nd as catalyst under different ratio of aqueous phase to organic phase.

3. The specific refractive index increment (d*n*/d*c*) determination.

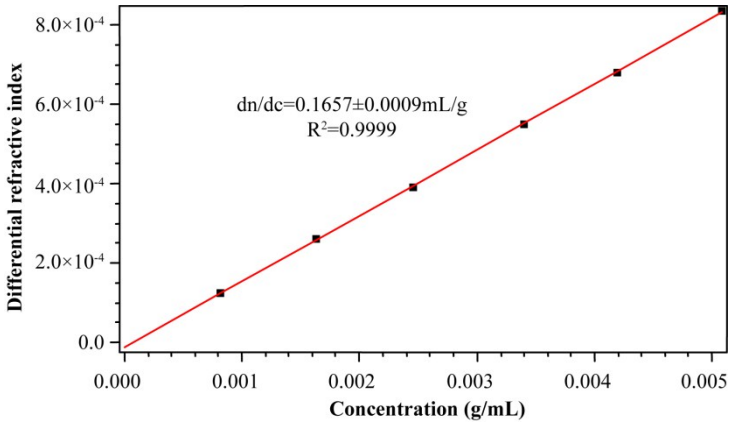
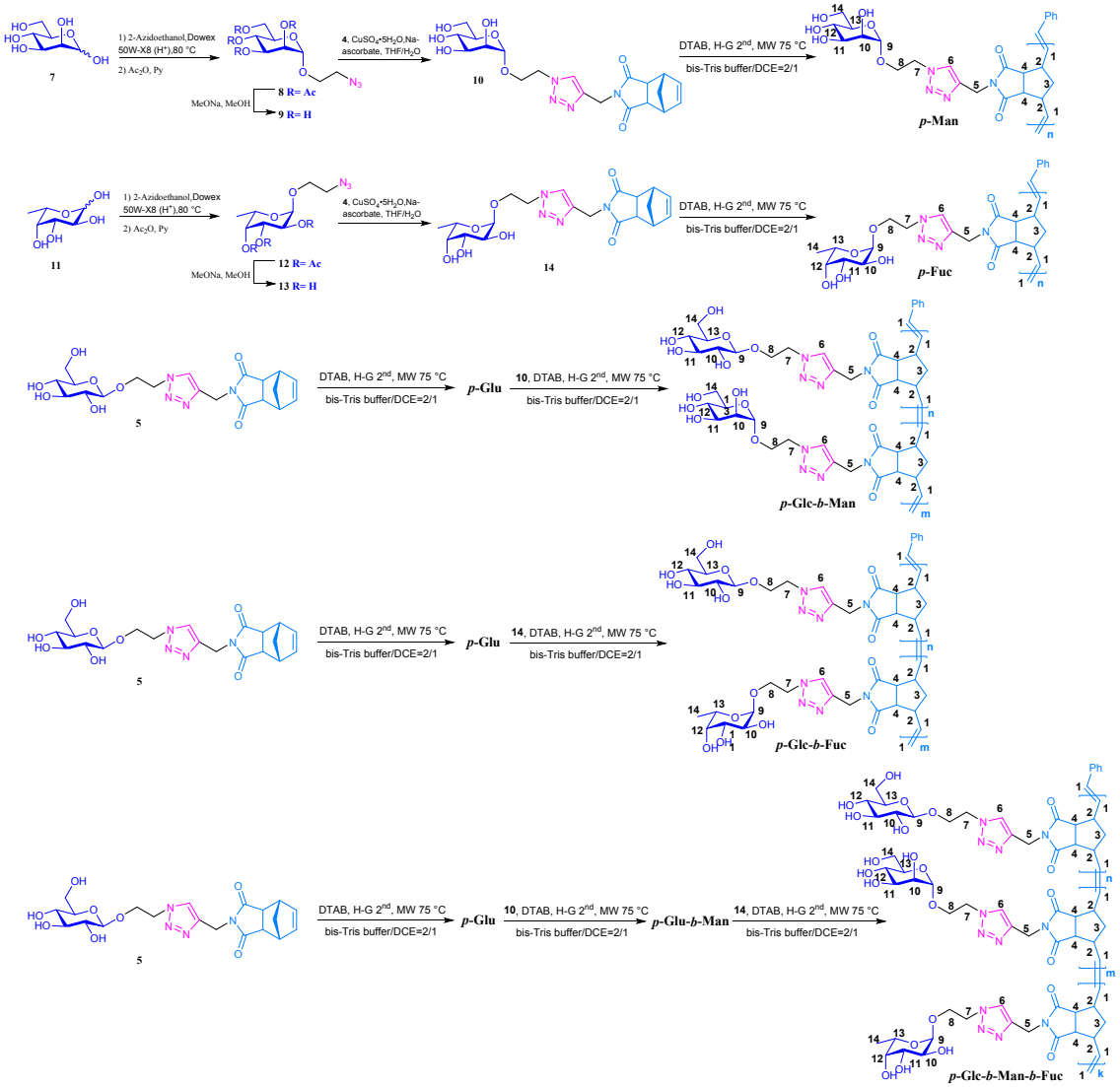


Figure S2. The standard curve for the specific refractive index increment (d*n*/d*c*) determination.

4. Synthetic routes of homoglycopolymers and mult-block glycopolymers.



Scheme S1. Synthetic details of homoglycopolymers (*p*-Glu, *p*-Man, *p*-Fuc) and multi-block glycopolymers (*p*-Glu-*b*-Man, *p*- Glu-*b*-Fuc, *p*-Glu-*b*-Man-*b*-Fuc). The labels of atoms correspond with the labels of signals in figure 4.

5. NMR spectra.

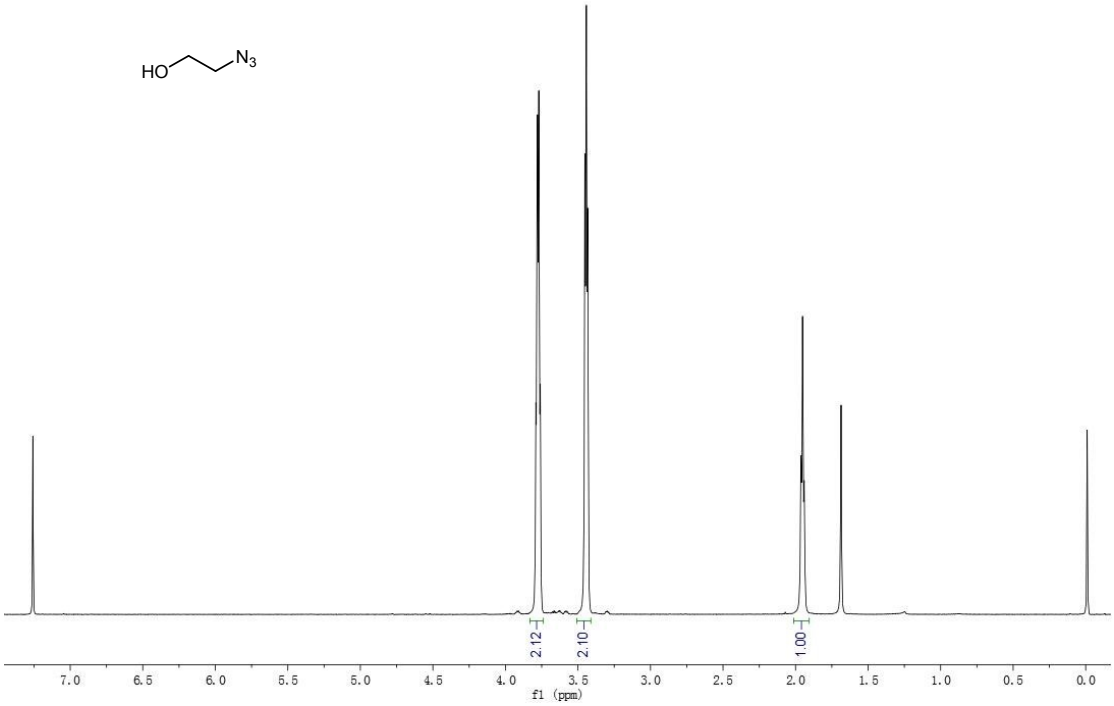


Figure S3. ^{1}H NMR spectrum of 2-Azidoethanol.

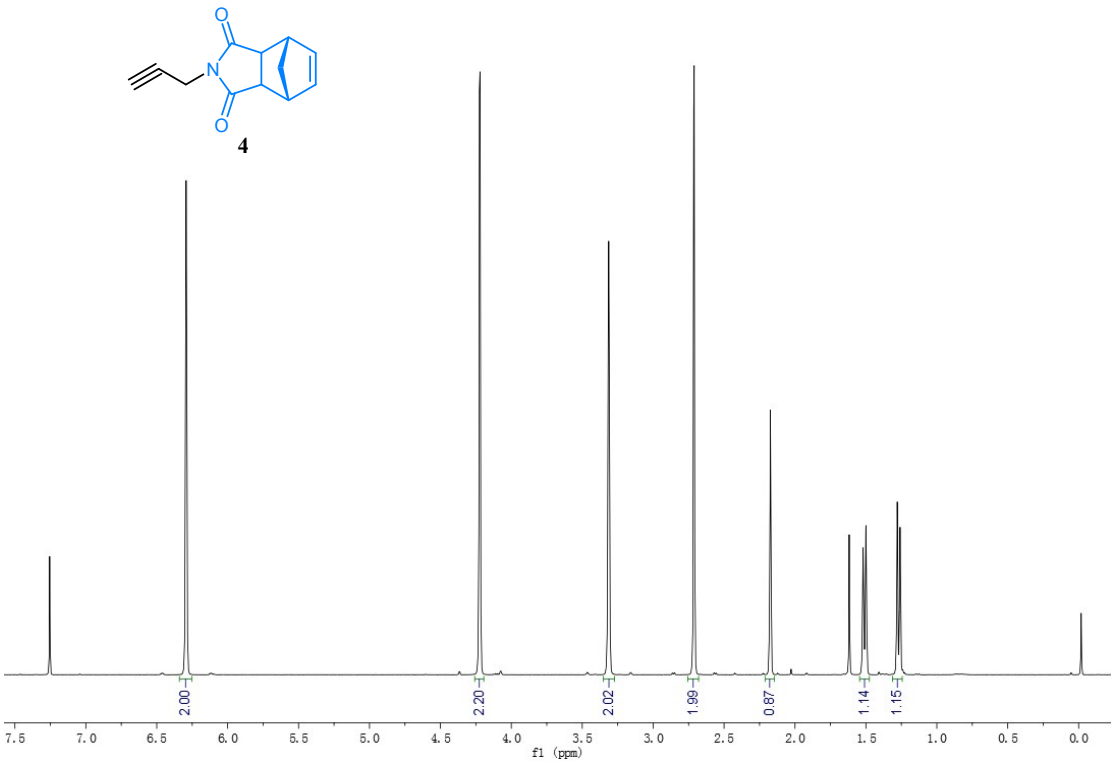


Figure S4. ^{1}H NMR spectrum of compound **4**.

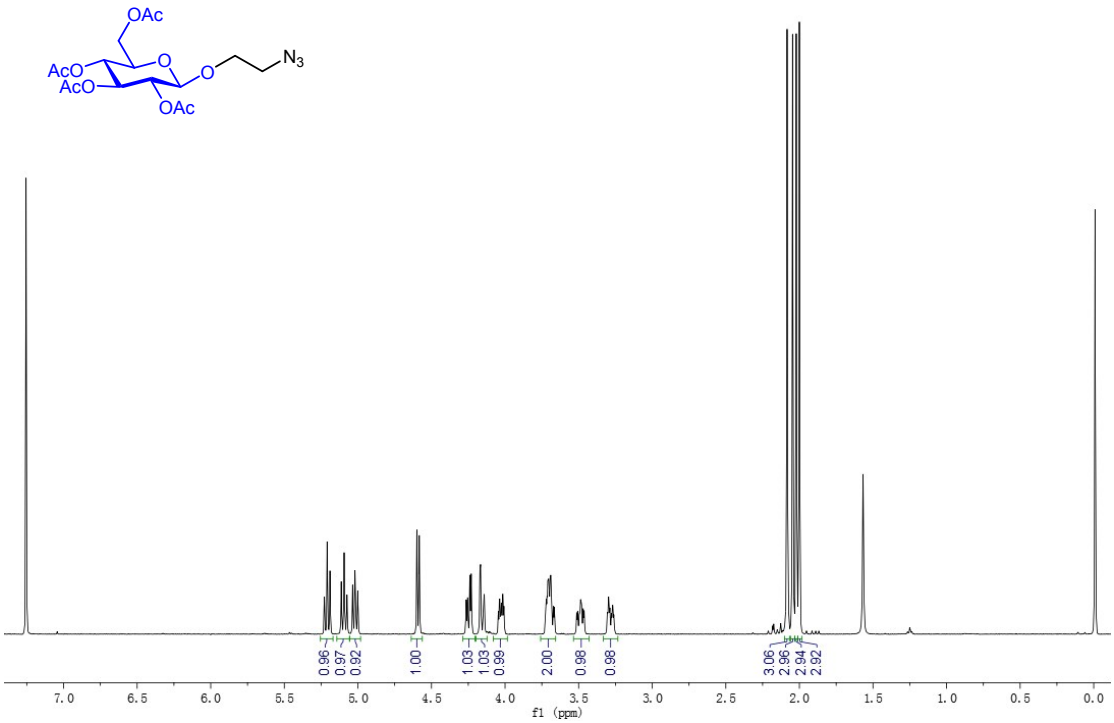


Figure S5-1. [1]H NMR spectrum of 1-azidoethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.

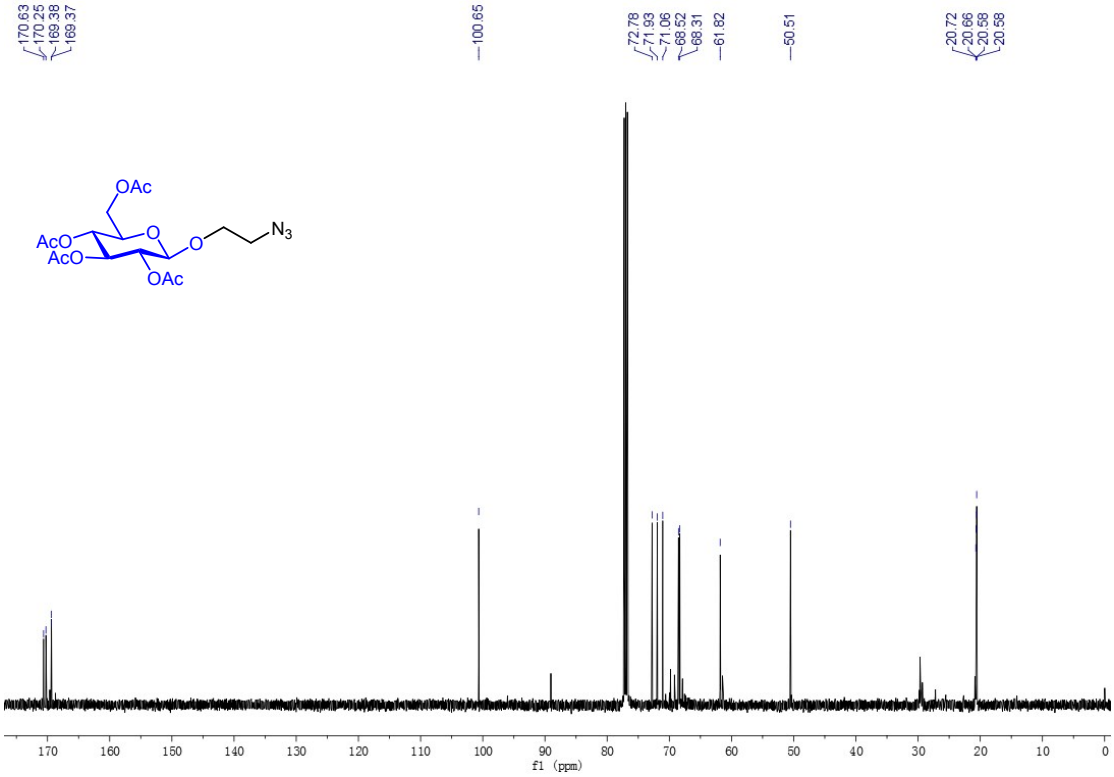


Figure S5-2. [13]C NMR spectrum of 1-azidoethyl-2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside.

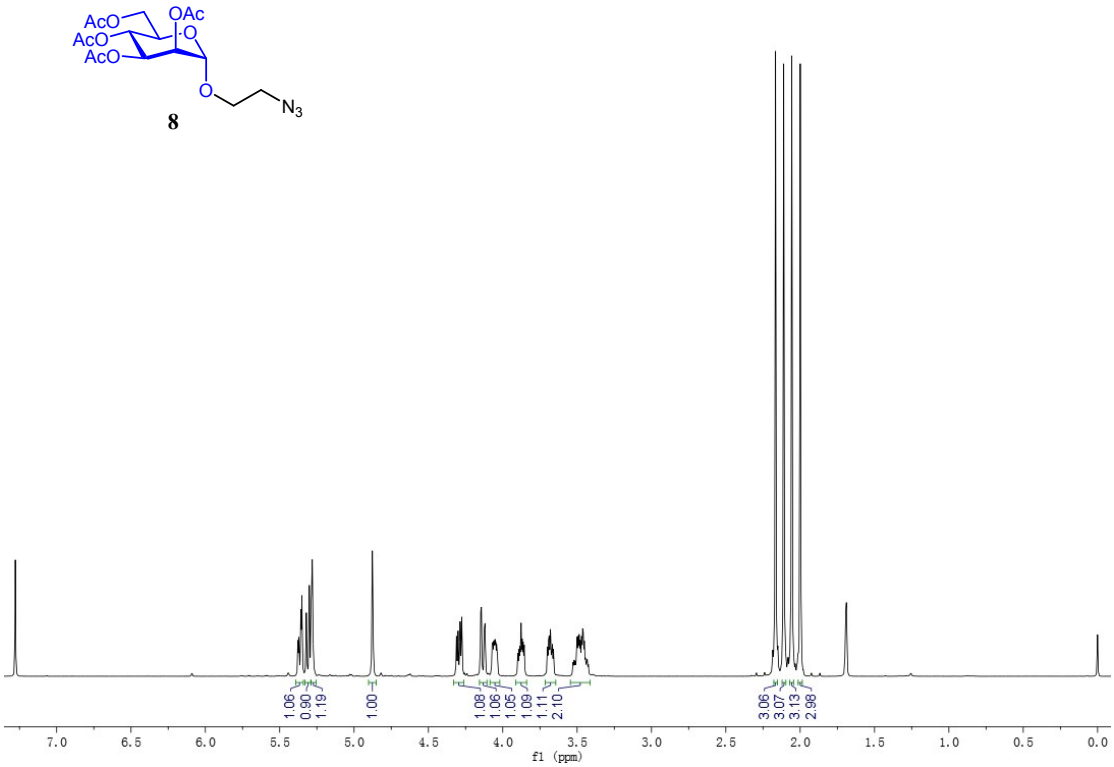


Figure S6-1. [1]H NMR spectrum of compound **8**.

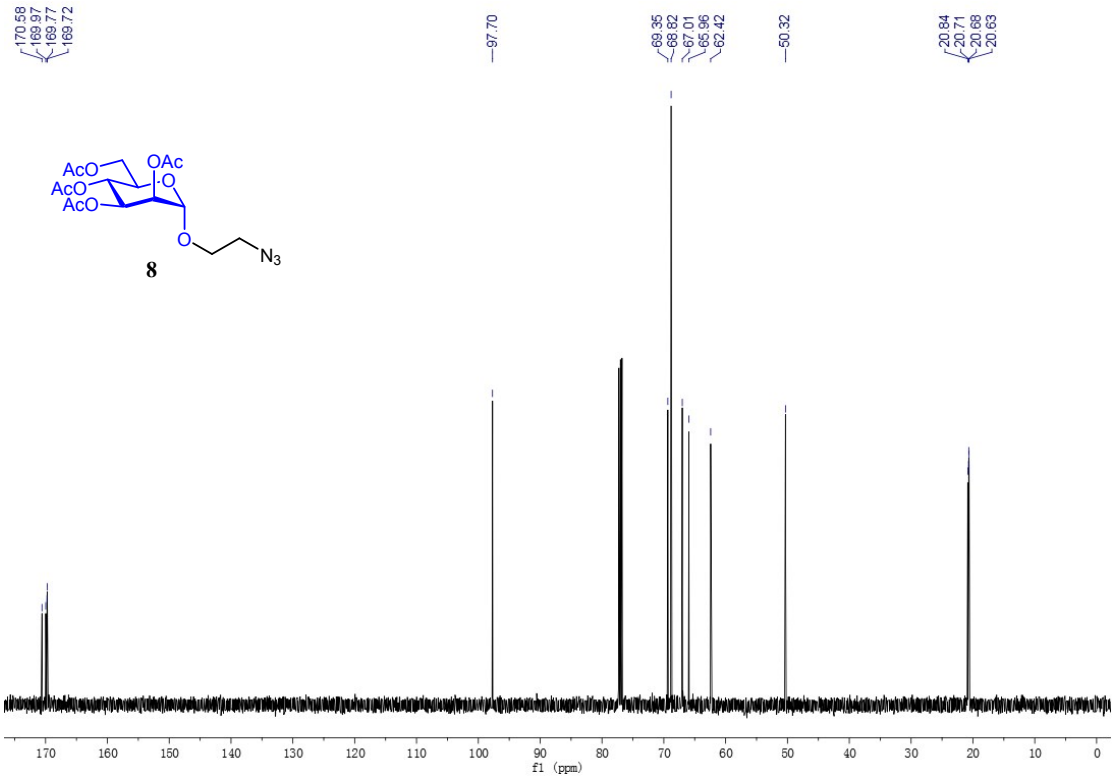


Figure S6-2. [13]C NMR spectrum of compound **8**.

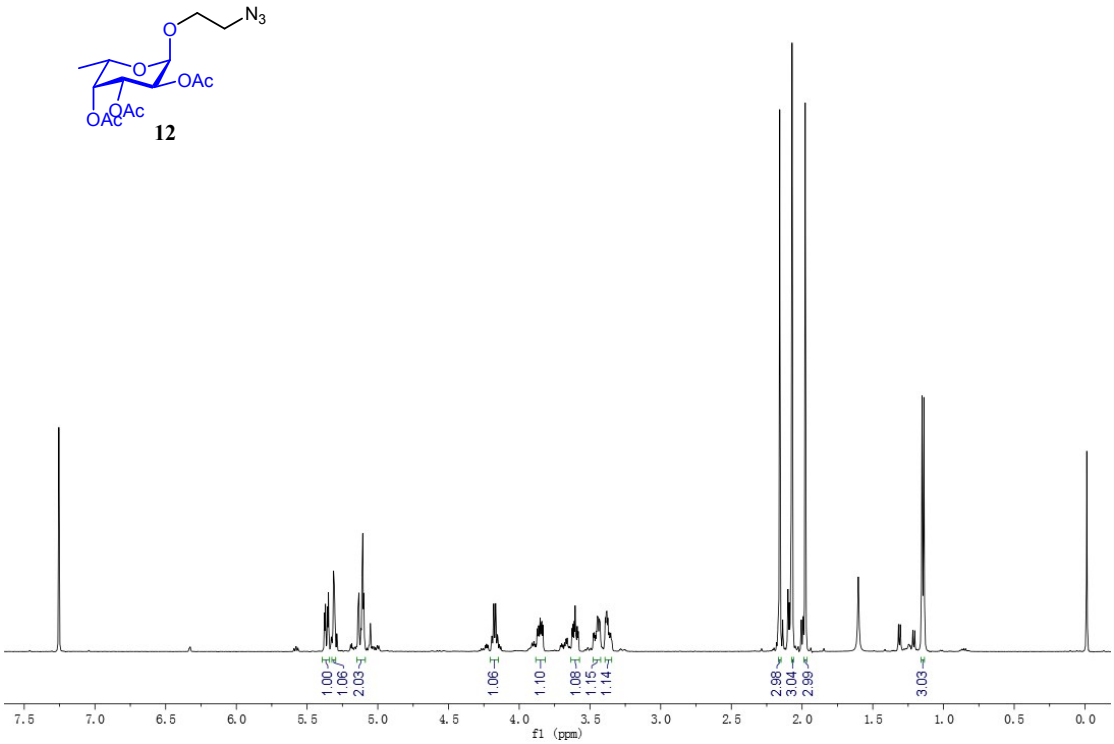


Figure S7-1. ^{1}H NMR spectrum of compound **12**.

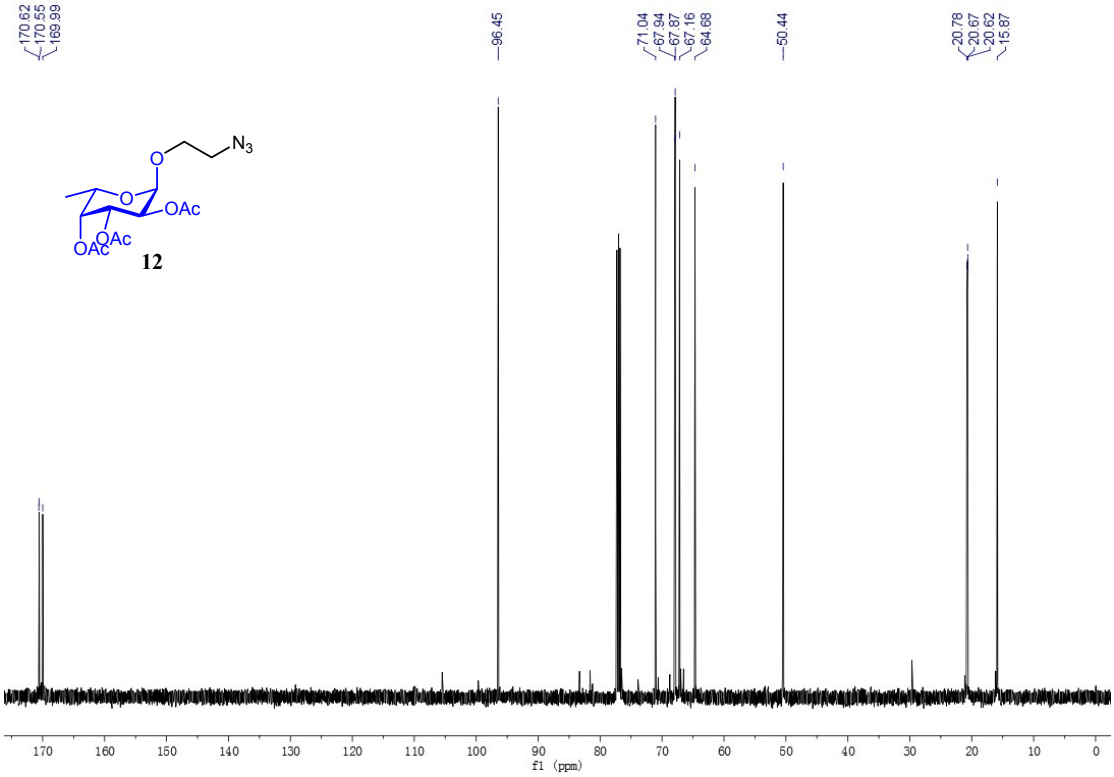


Figure S7-2. ^{13}C NMR spectrum of compound **12**.

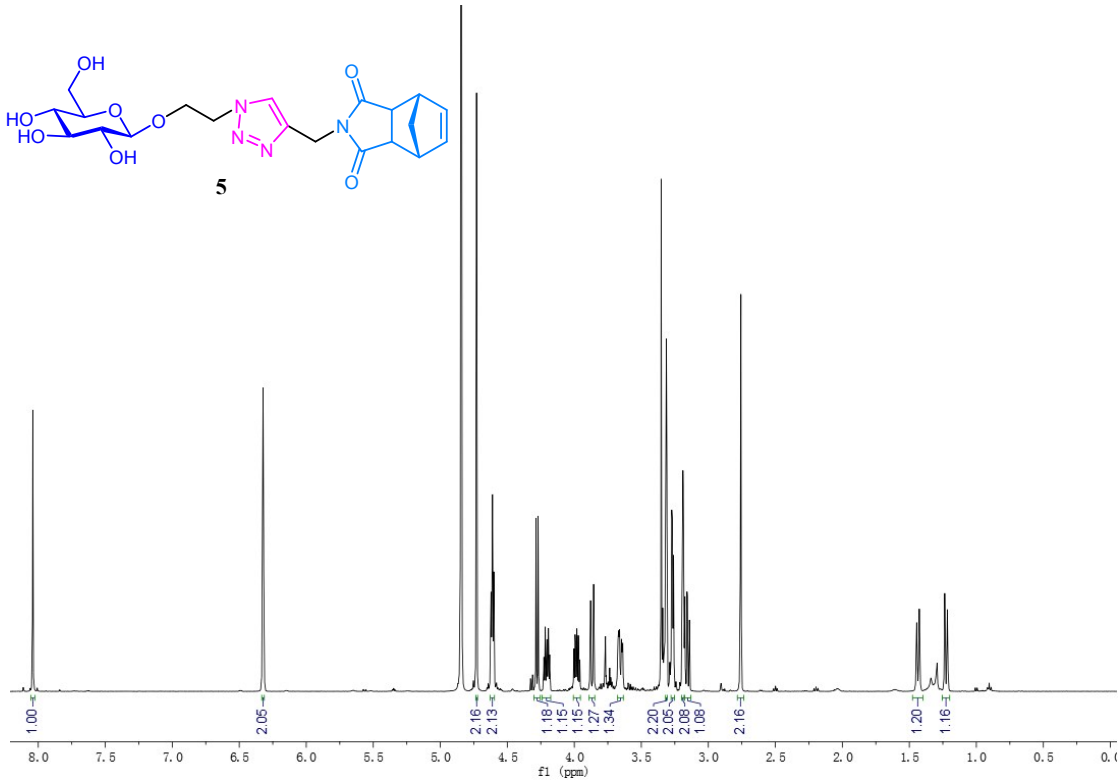


Figure S8-1. ^{1}H NMR spectrum of monomer **5**.

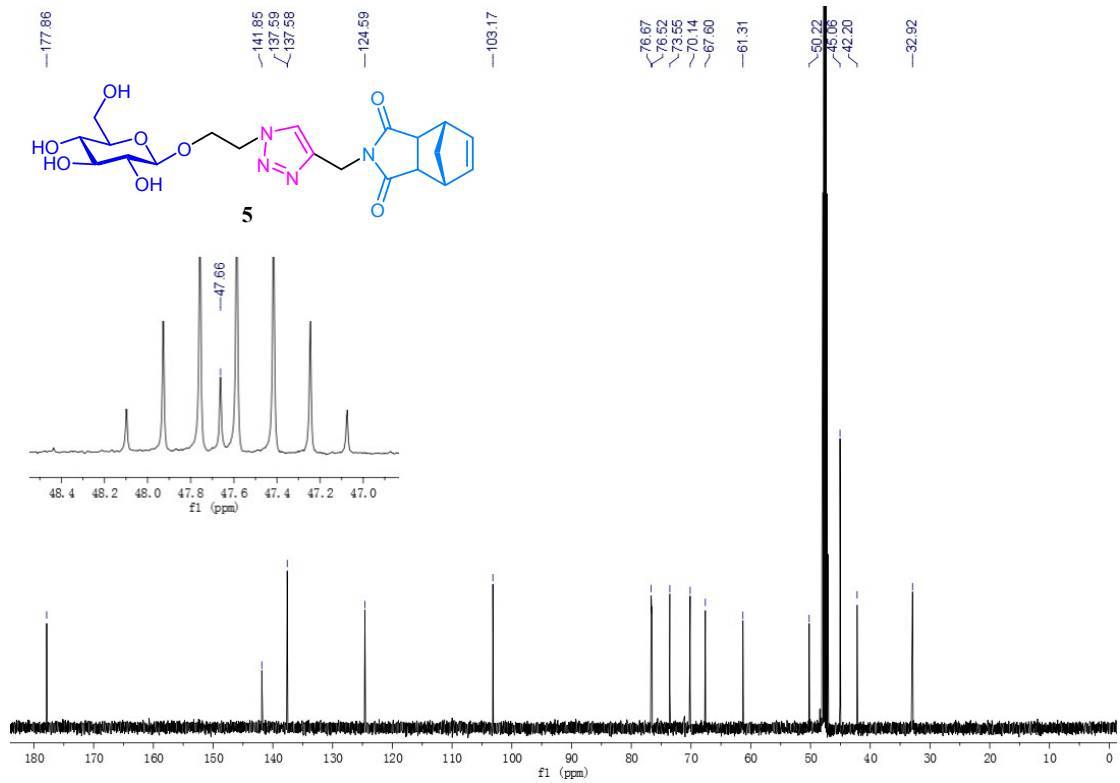


Figure S8-2. ^{13}C NMR spectrum of monomer **5**.

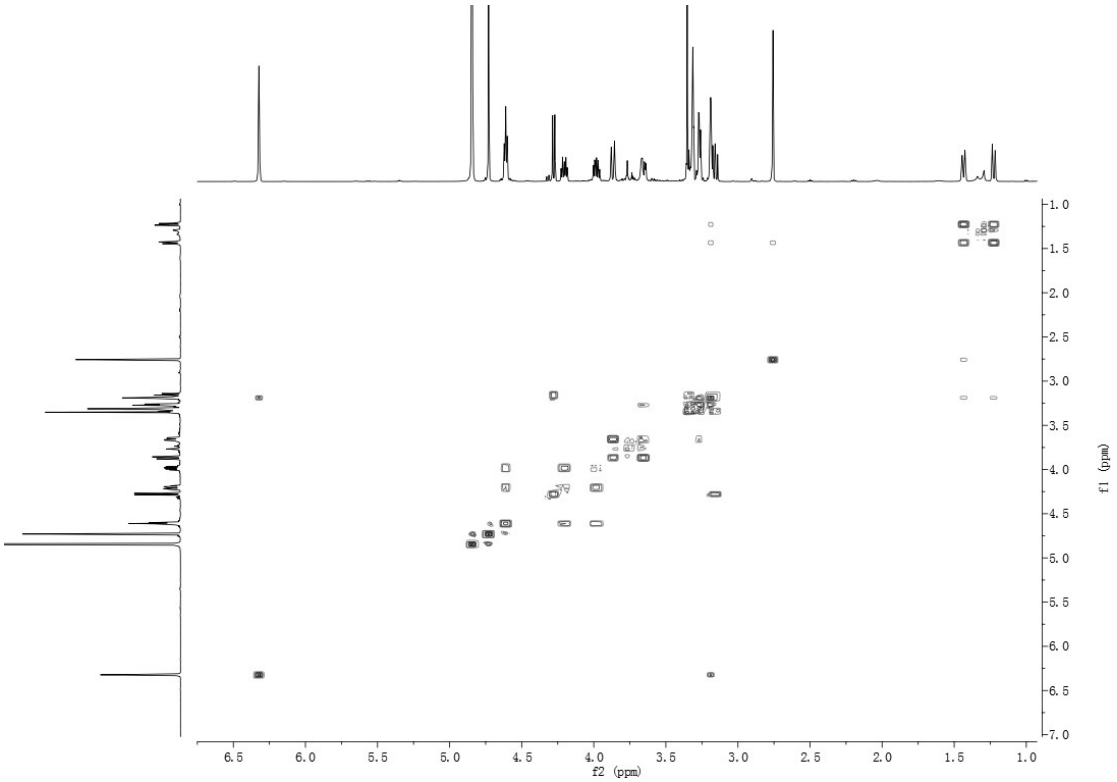


Figure S8-3. COSY spectrum of monomer **5**.

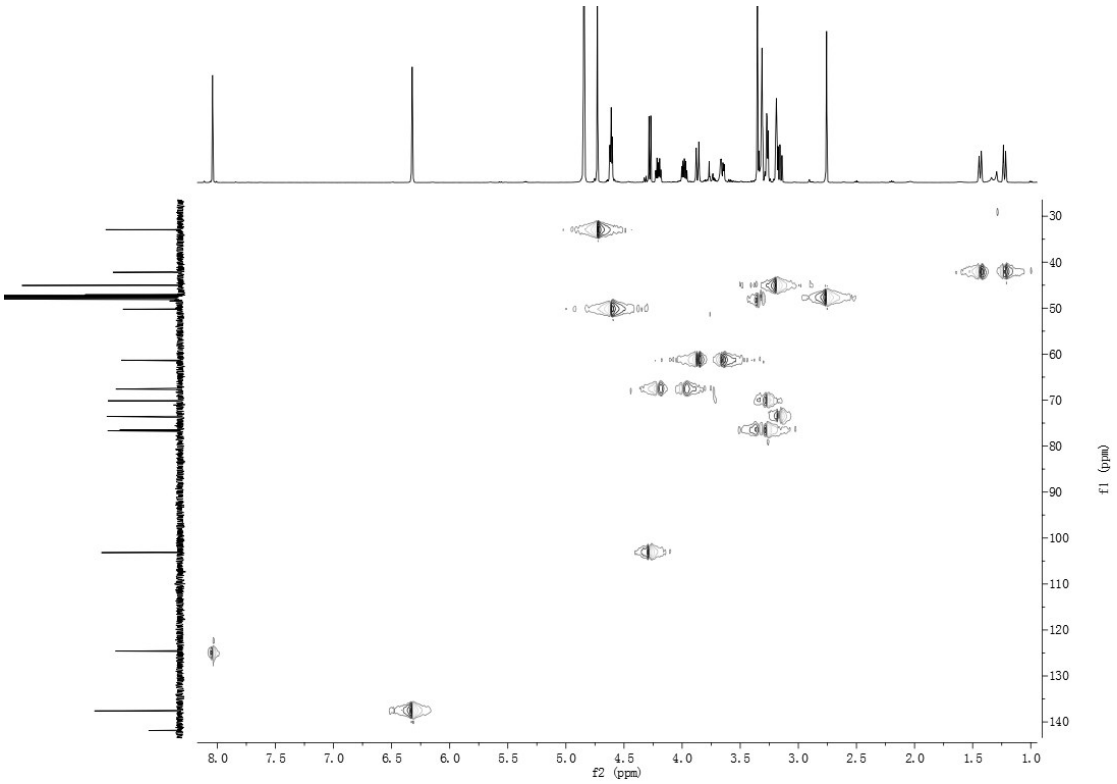


Figure S8-4. HSQC spectrum of monomer **5**.

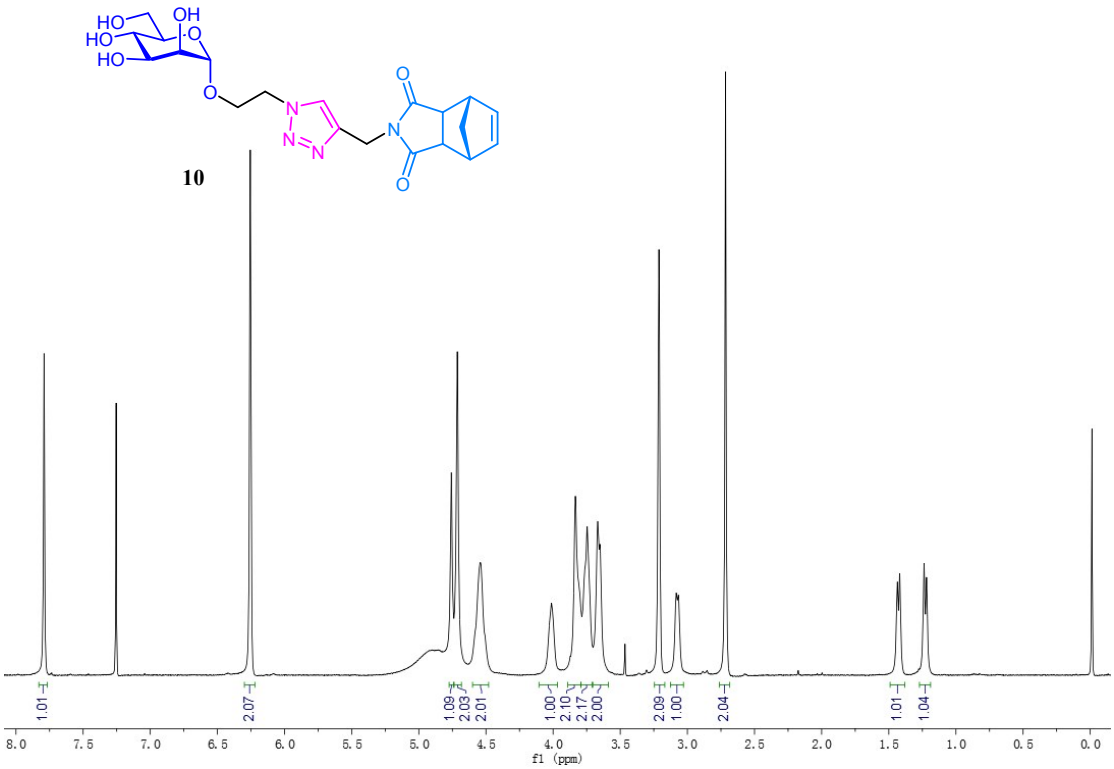


Figure S9-1. [1]H NMR spectrum of monomer **10**.

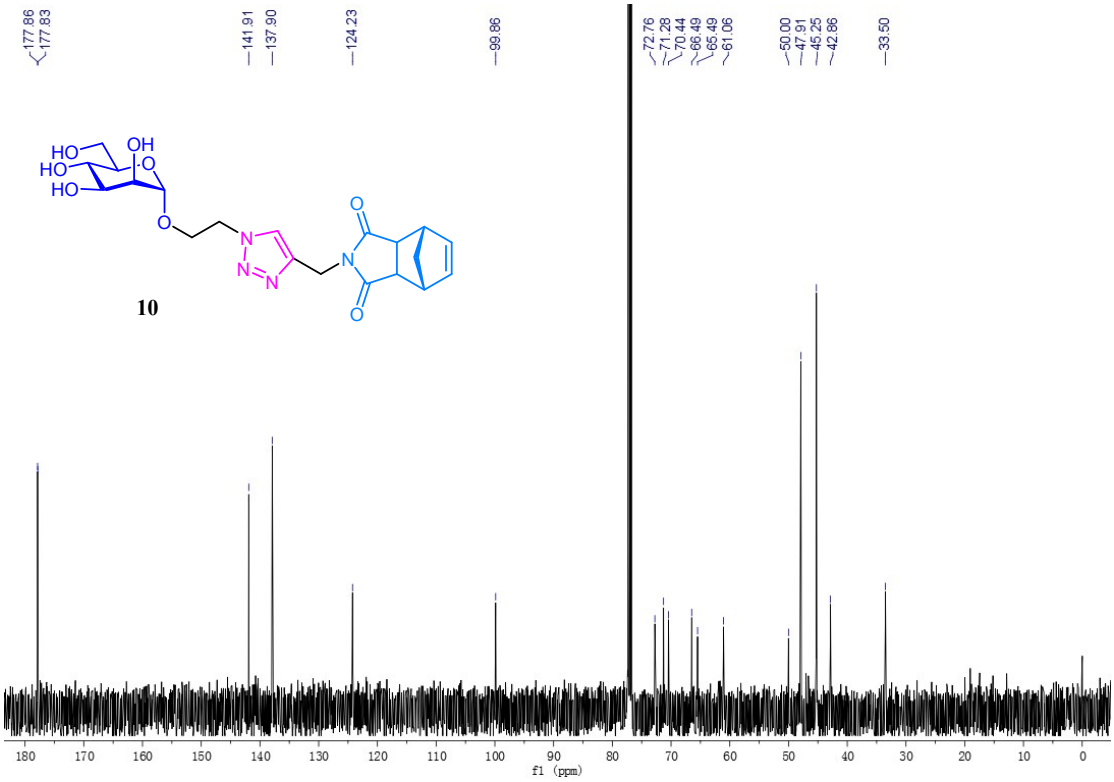


Figure S9-2. [13]C NMR spectrum of monomer **10**.

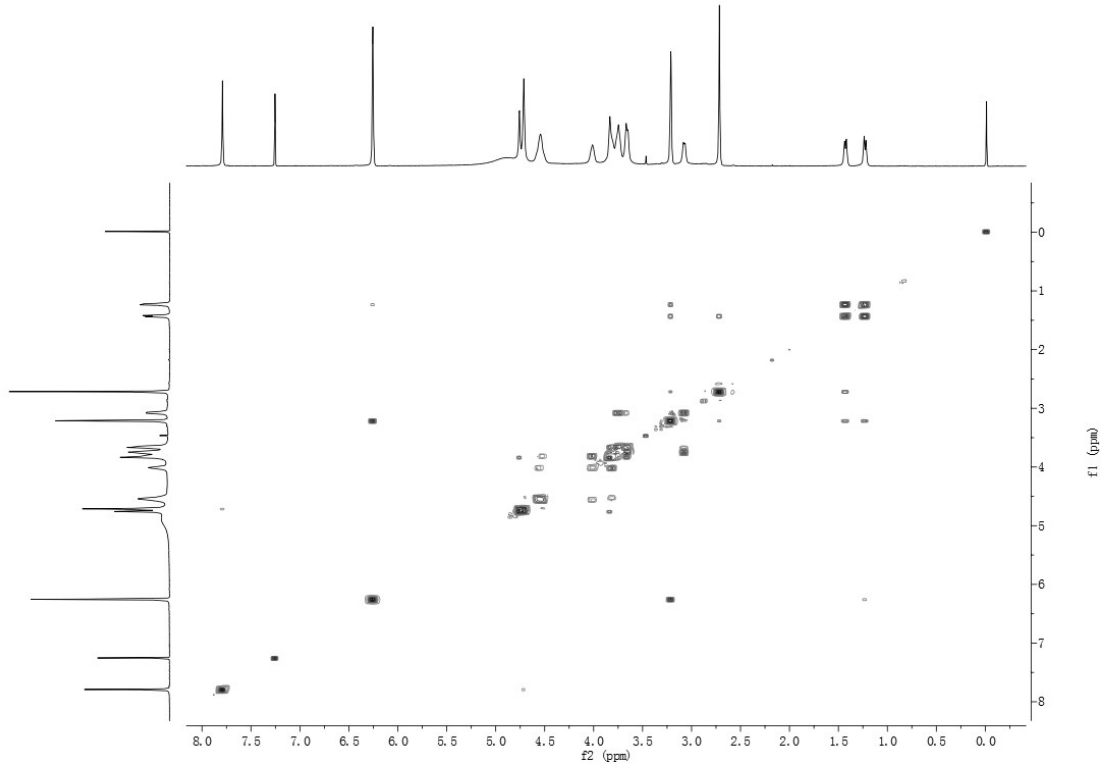


Figure S9-3. COSY spectrum of monomer **10**.

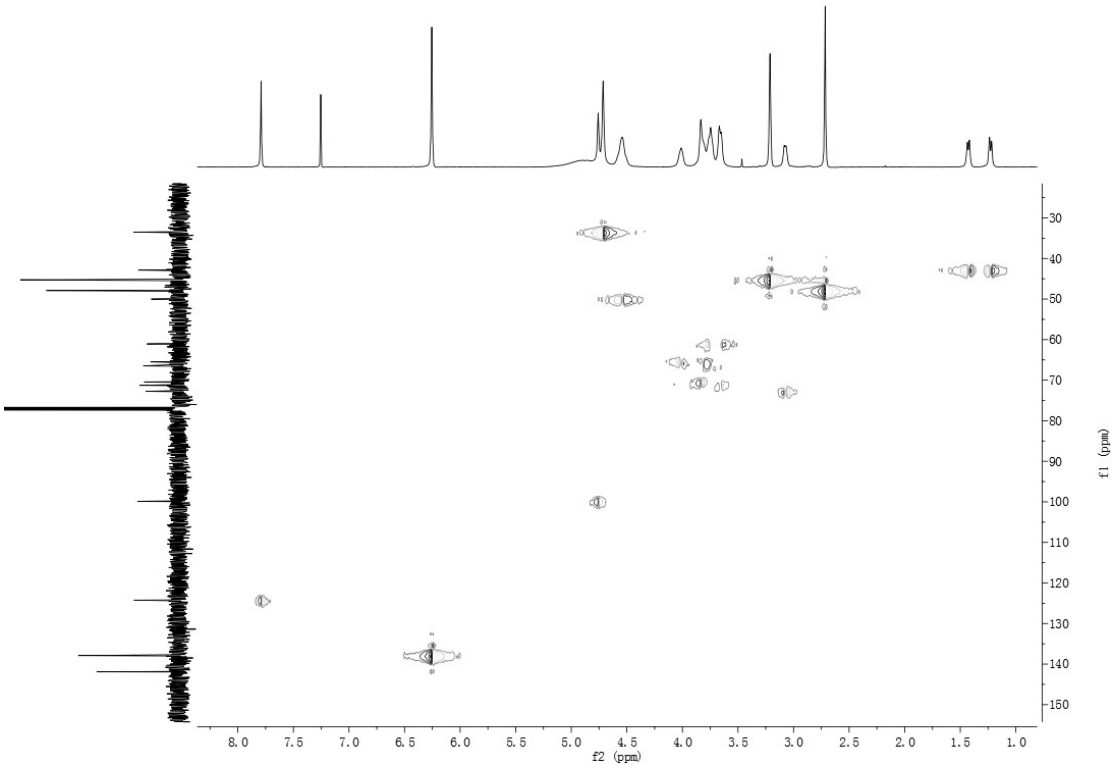


Figure S9-4. HSQC spectrum of monomer **10**.

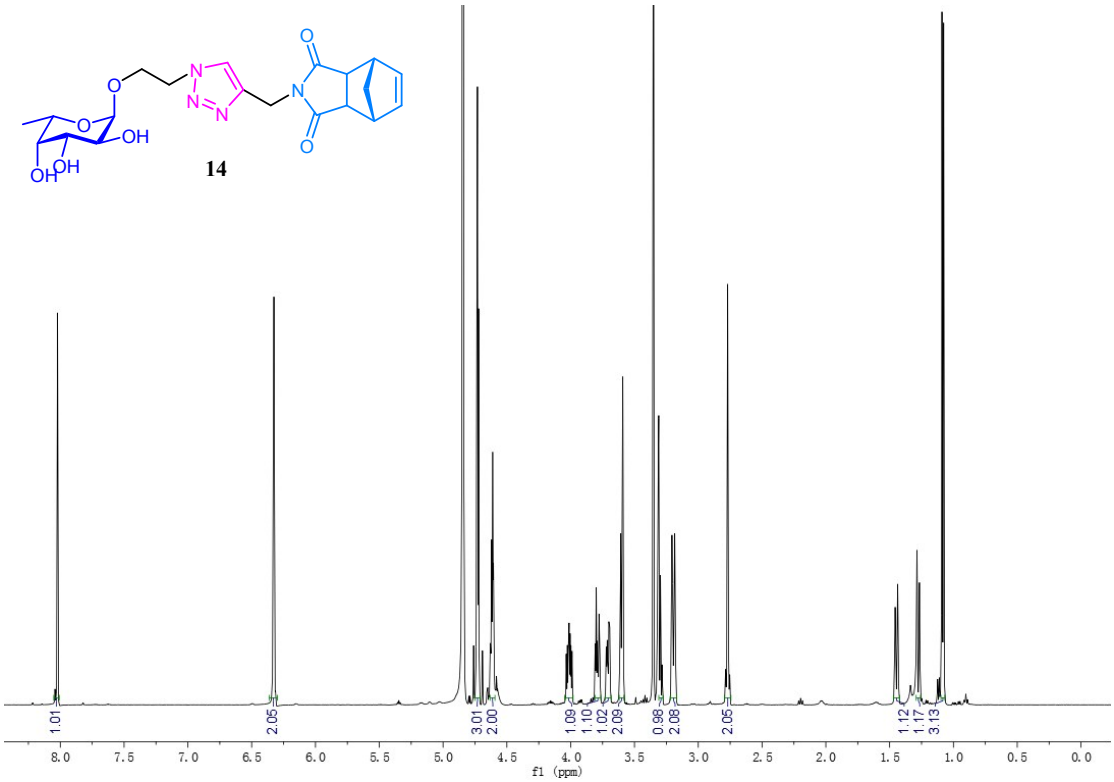


Figure S10-1. [1]H NMR spectrum of monomer **14**.

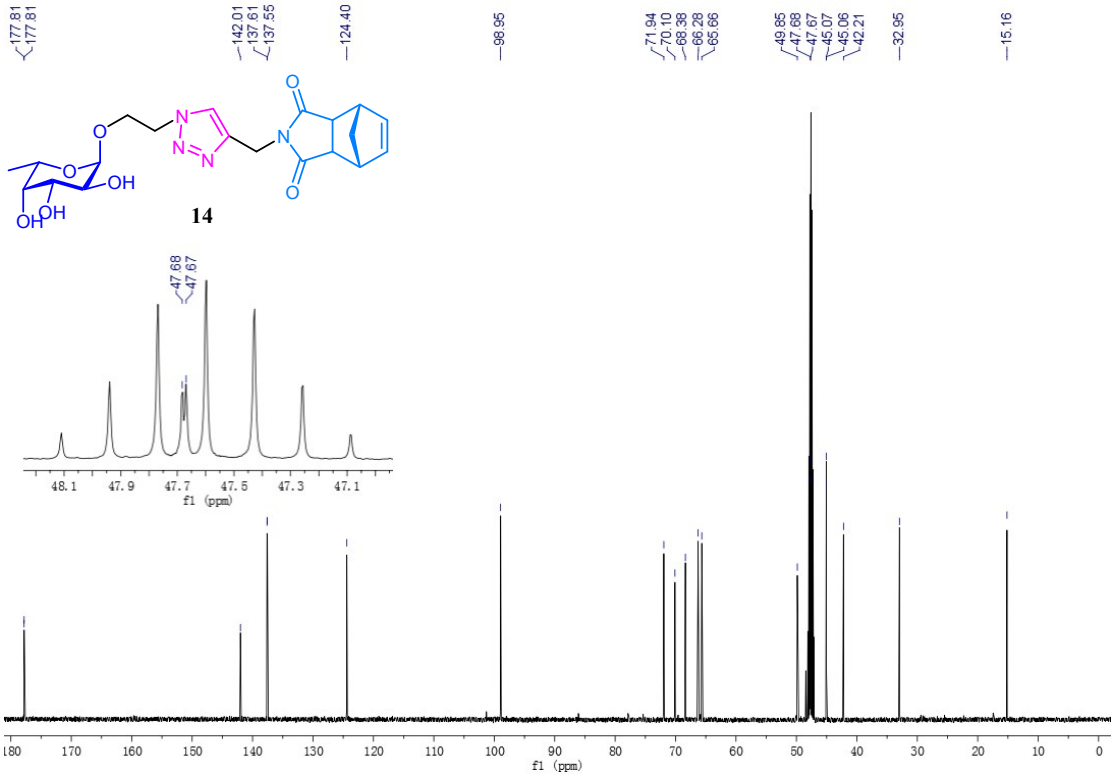


Figure S10-2. [13]C NMR spectrum of monomer **14**.

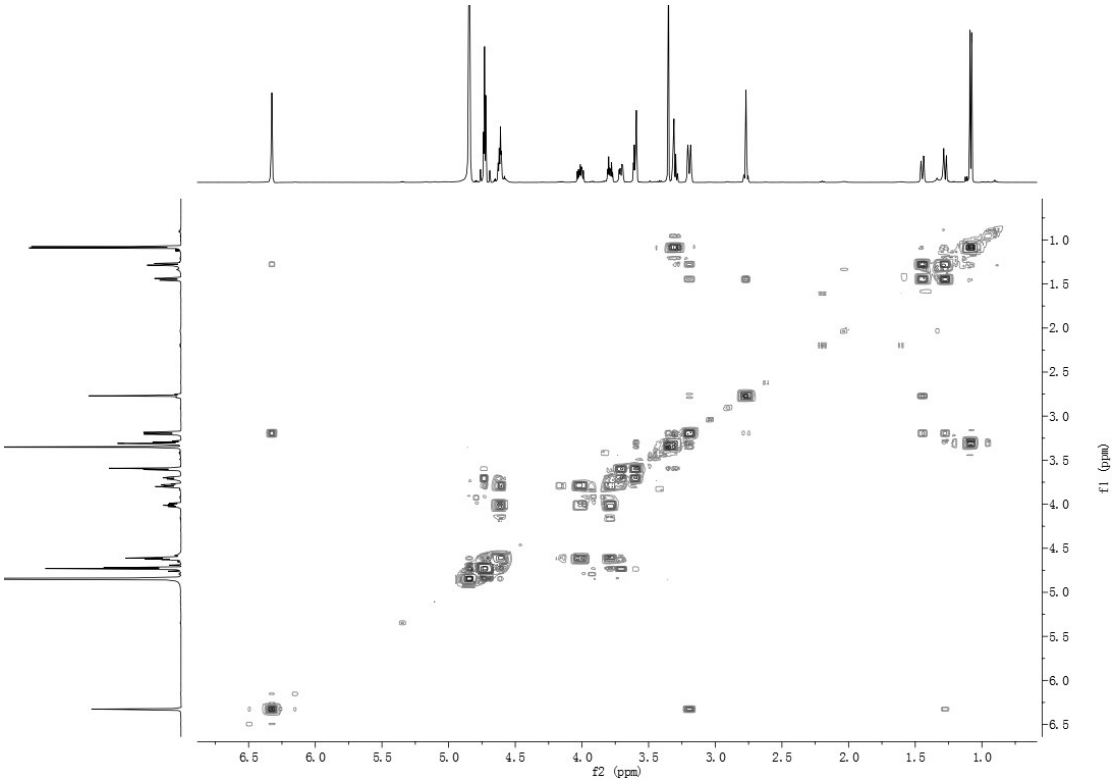


Figure S10-3. COSY spectrum of monomer **14**.

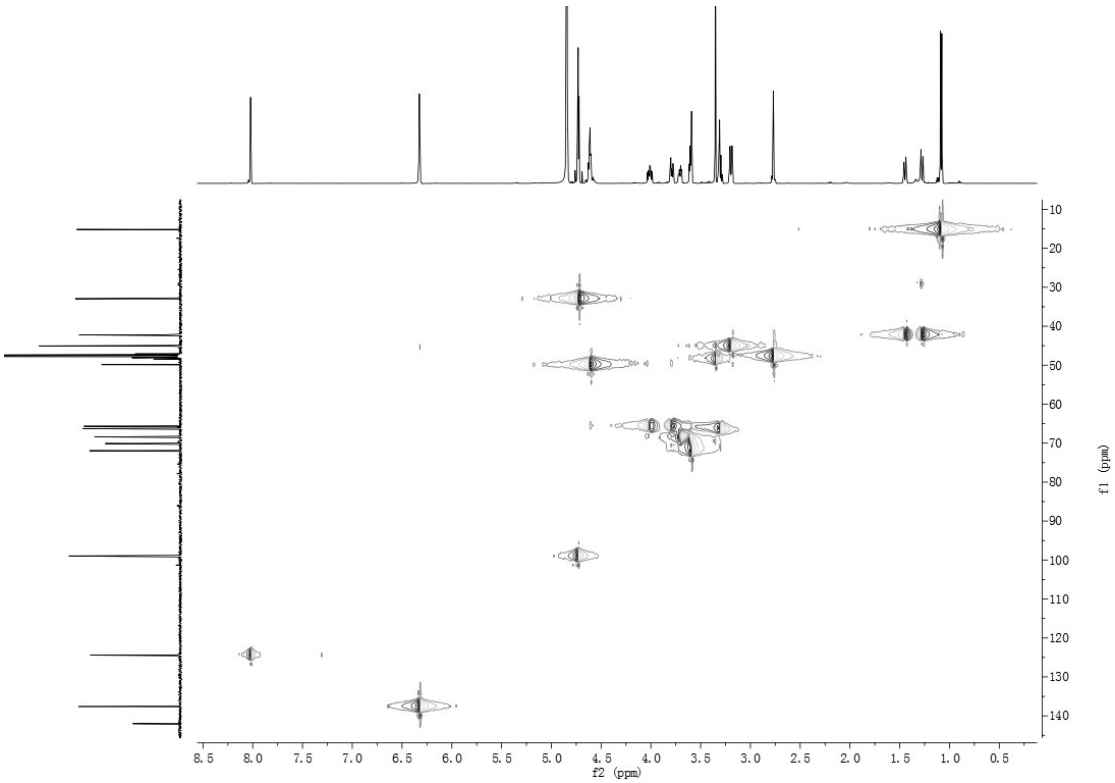


Figure S10-4. HSQC spectrum of monomer **14**.

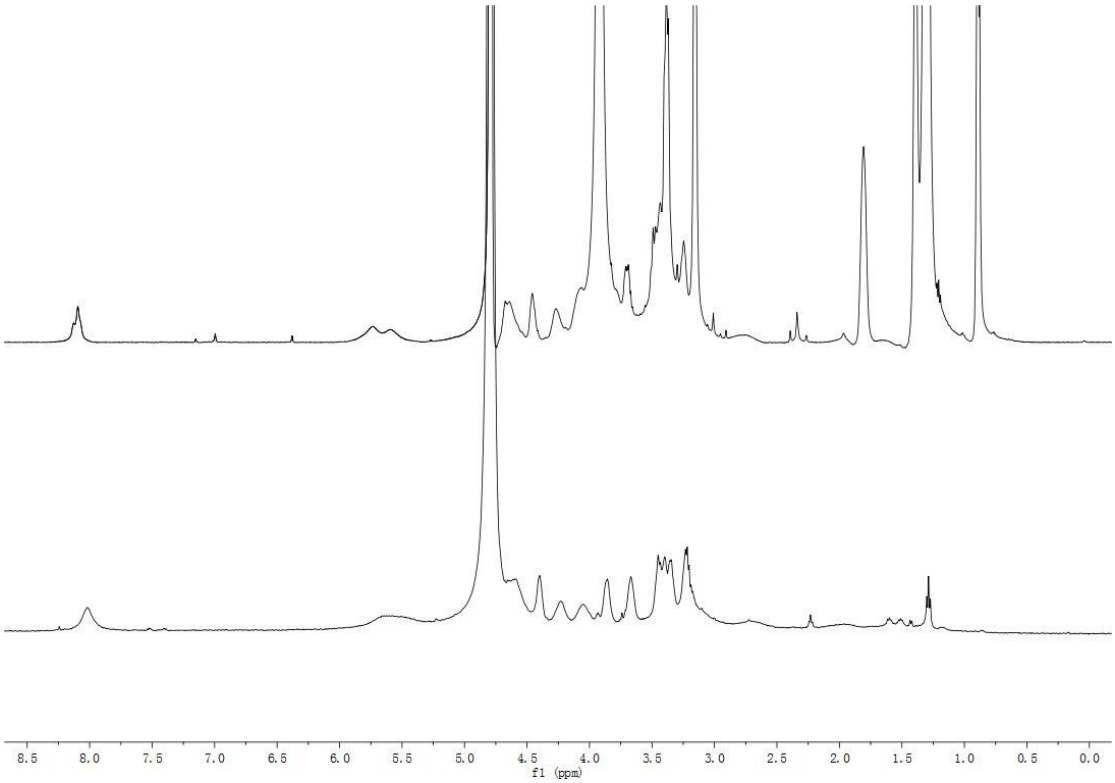


Figure S11. ^{1}H NMR spectrum of crude *p*-Glu (upper) and purified *p*-Glu (blow). The results showed that the degree of purity of glycopolymers had no influence on conversion assay based on the ^{1}H NMR integrations shifting from monomer olefin signals (6.36 ppm) to polymer olefin signals (5.3~5.9 ppm). Therefore, the crude glycopolymers in table 1 and table 2 were used for the conversion assay based on ^{1}H NMR apectrum.

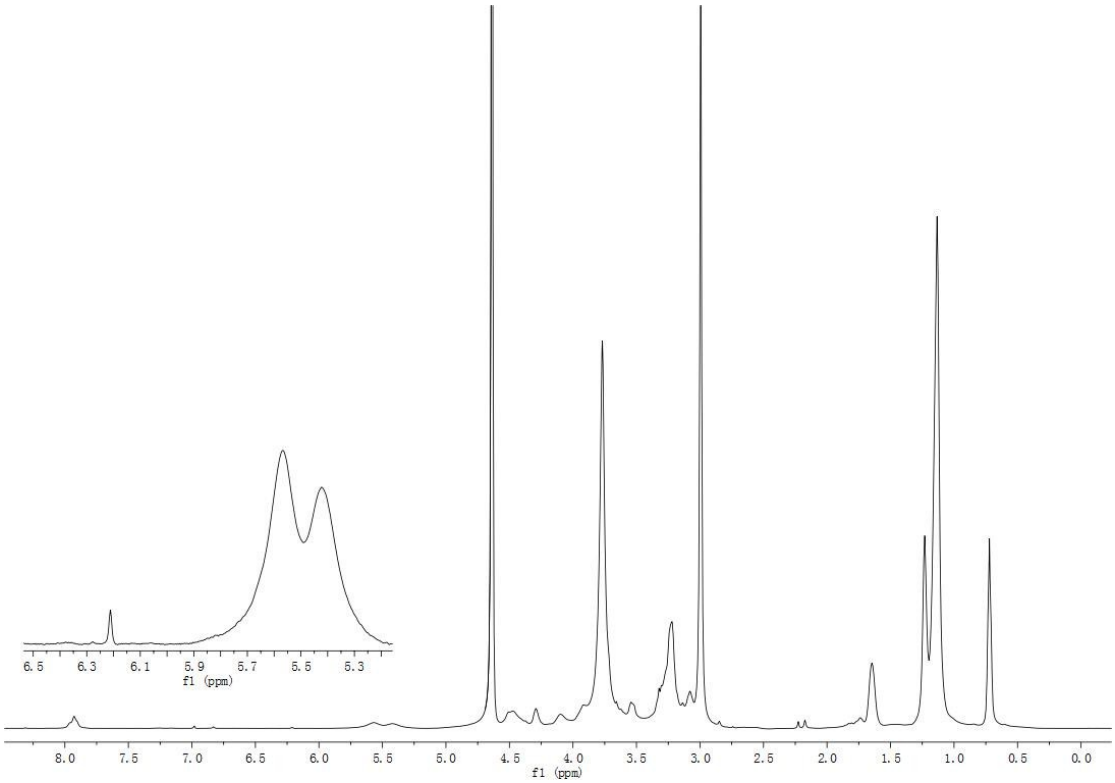


Figure S12-1. ^{1}H NMR spectrum of *p*-Glu in table 1, entry 1.

Figure S12-2. ^{1}H NMR spectrum of *p*-Glu in table 1, entry 2.

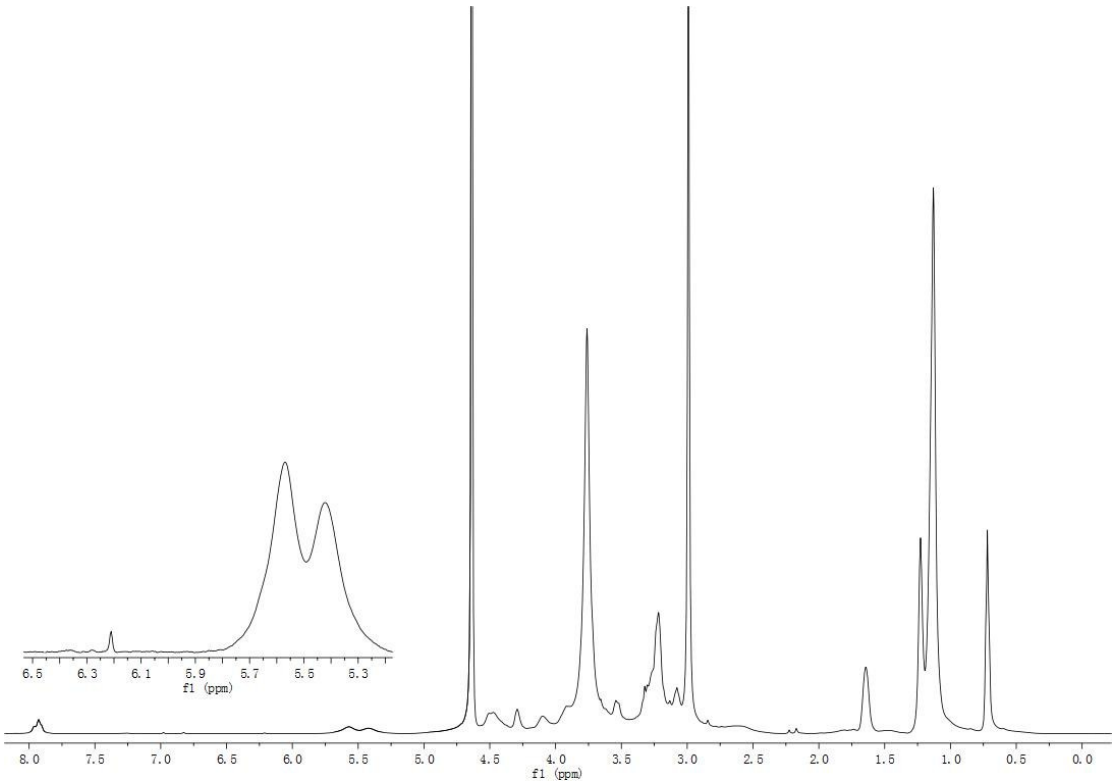


Figure S12-3. ^{1}H NMR spectrum of *p*-Glu in table 1, entry 3.

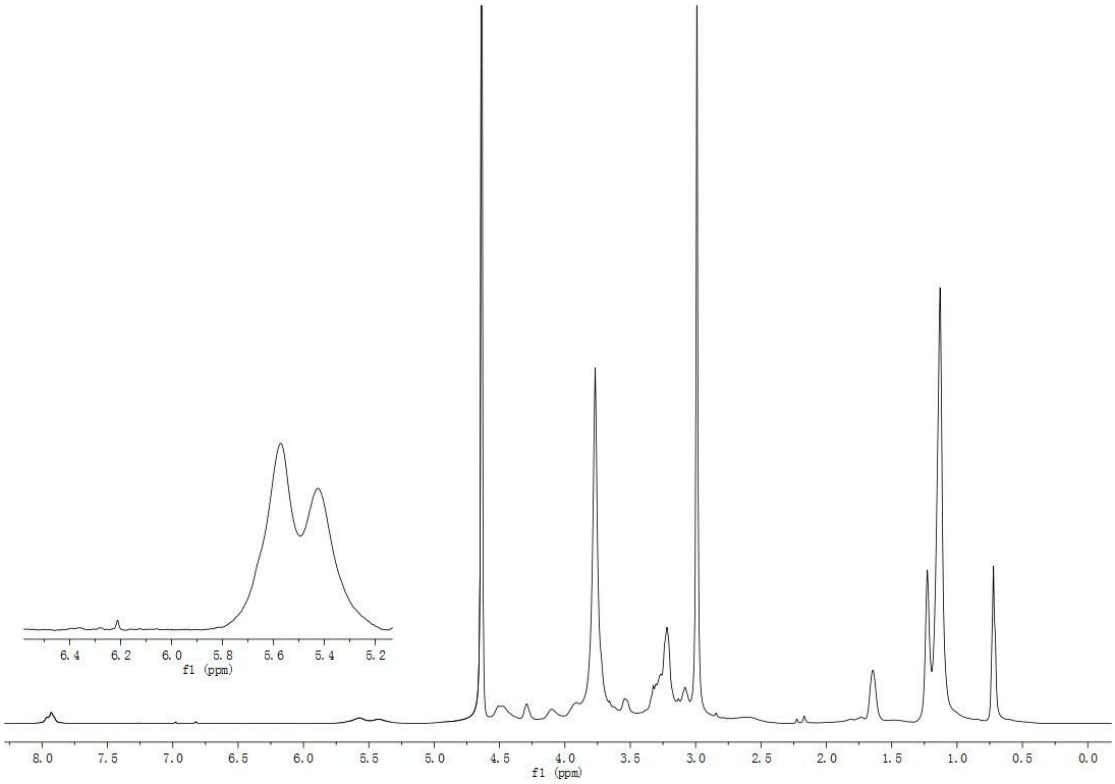


Figure S12-4. [1]H NMR spectrum of *p*-Glu in table 1, entry 4.

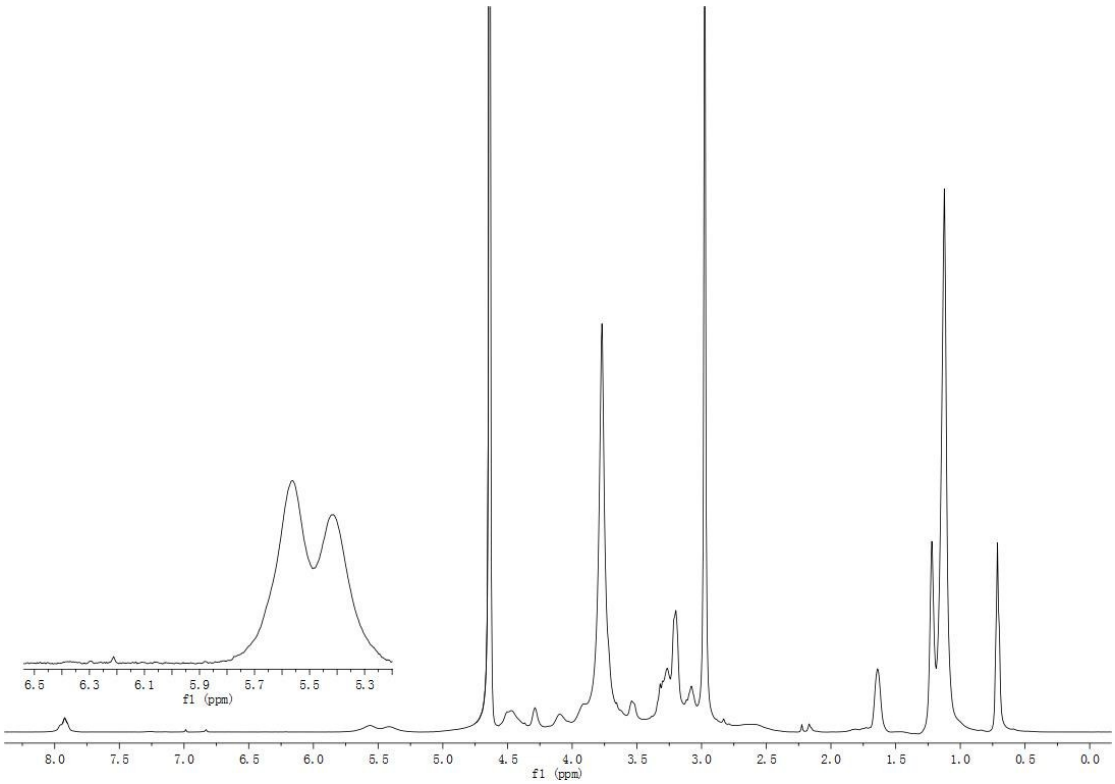


Figure S12-5. [1]H NMR spectrum of *p*-Glu in table 1, entry 5.

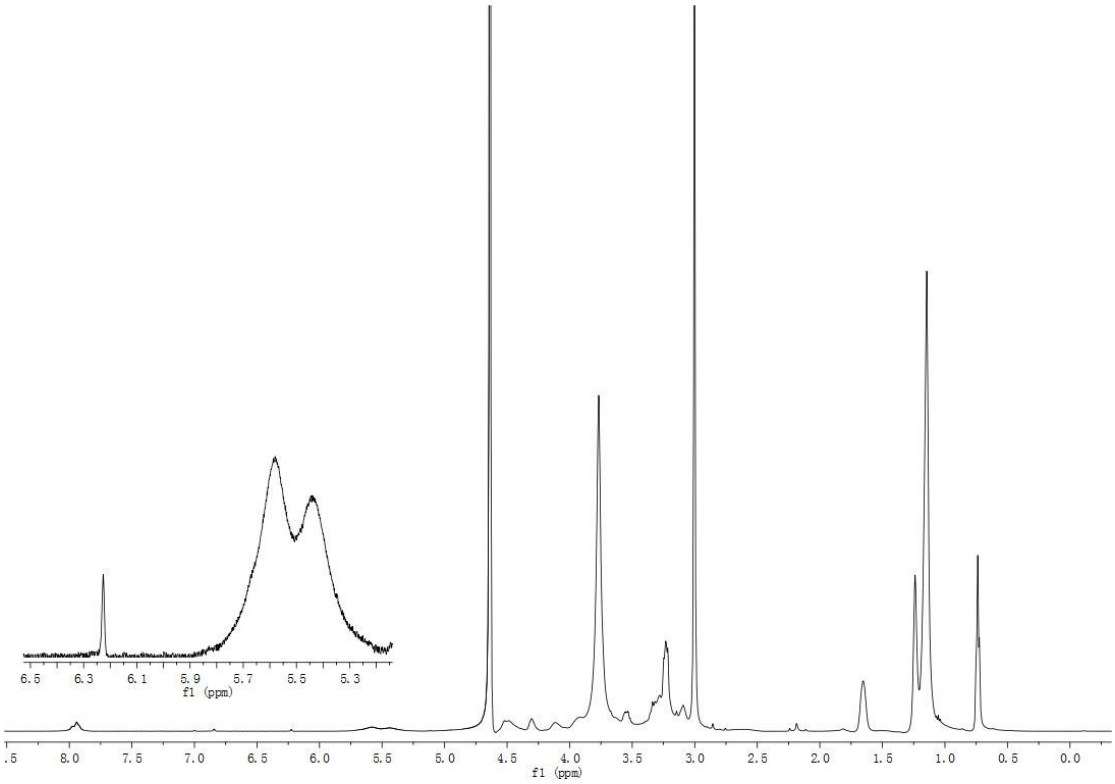


Figure S12-6. [1]H NMR spectrum of *p*-Glu in table 1, entry 6.

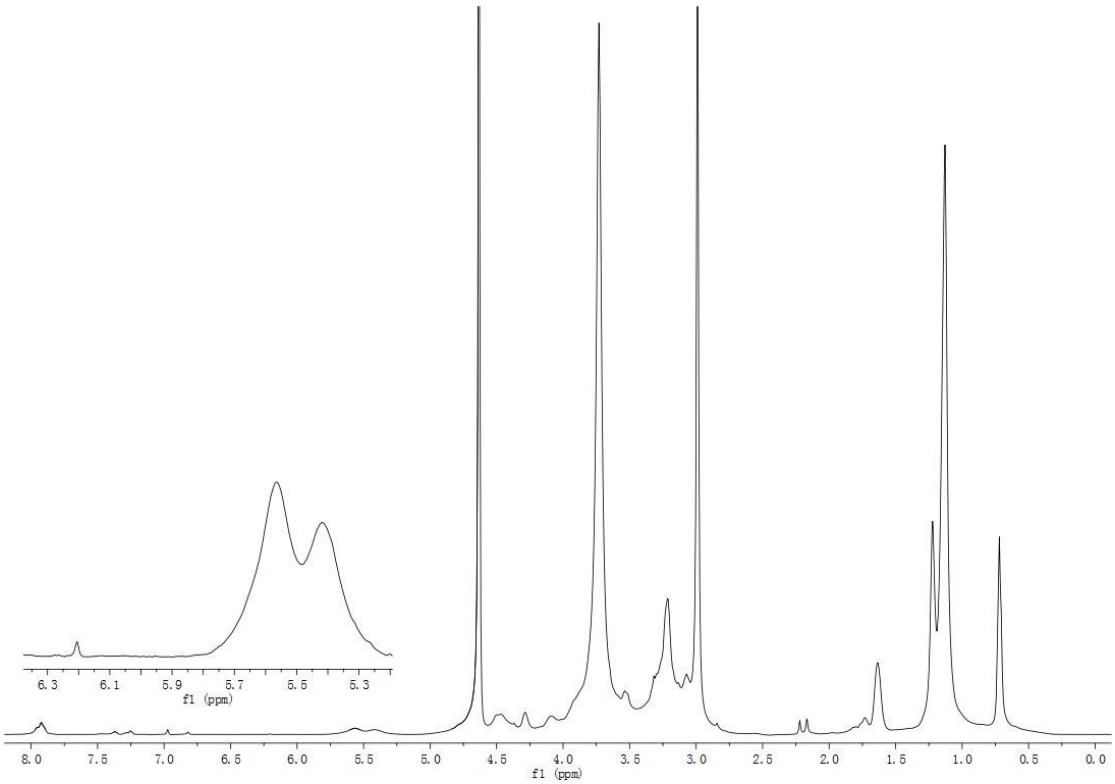


Figure S12-7. [1]H NMR spectrum of *p*-Glu in table 1, entry 7.

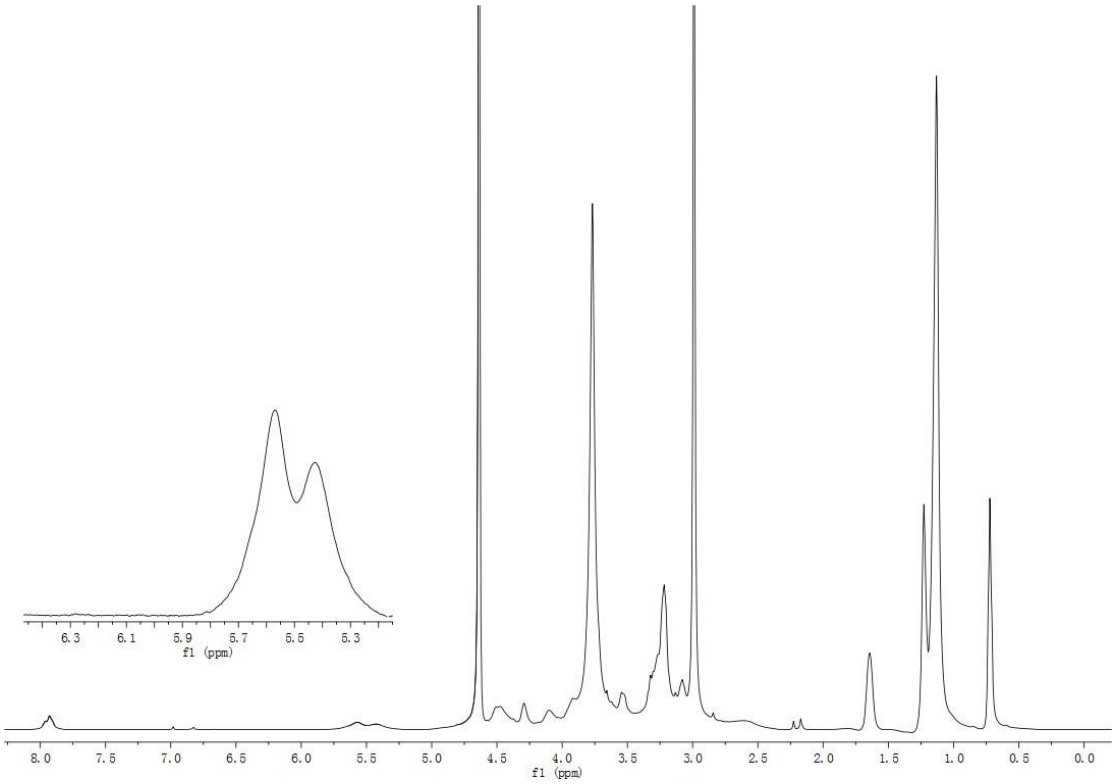


Figure S12-8. [1]H NMR spectrum of *p*-Glu in table 1, entry 8.

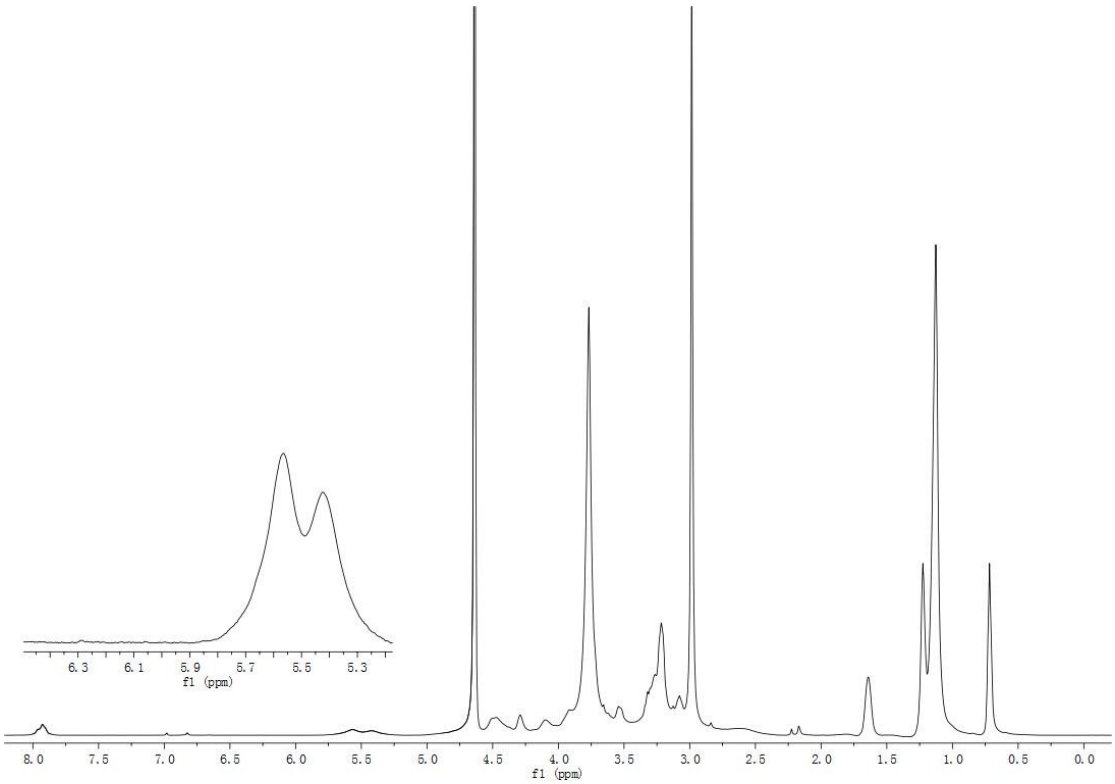


Figure S12-9. [1]H NMR spectrum of *p*-Glu in table 1, entry 9.

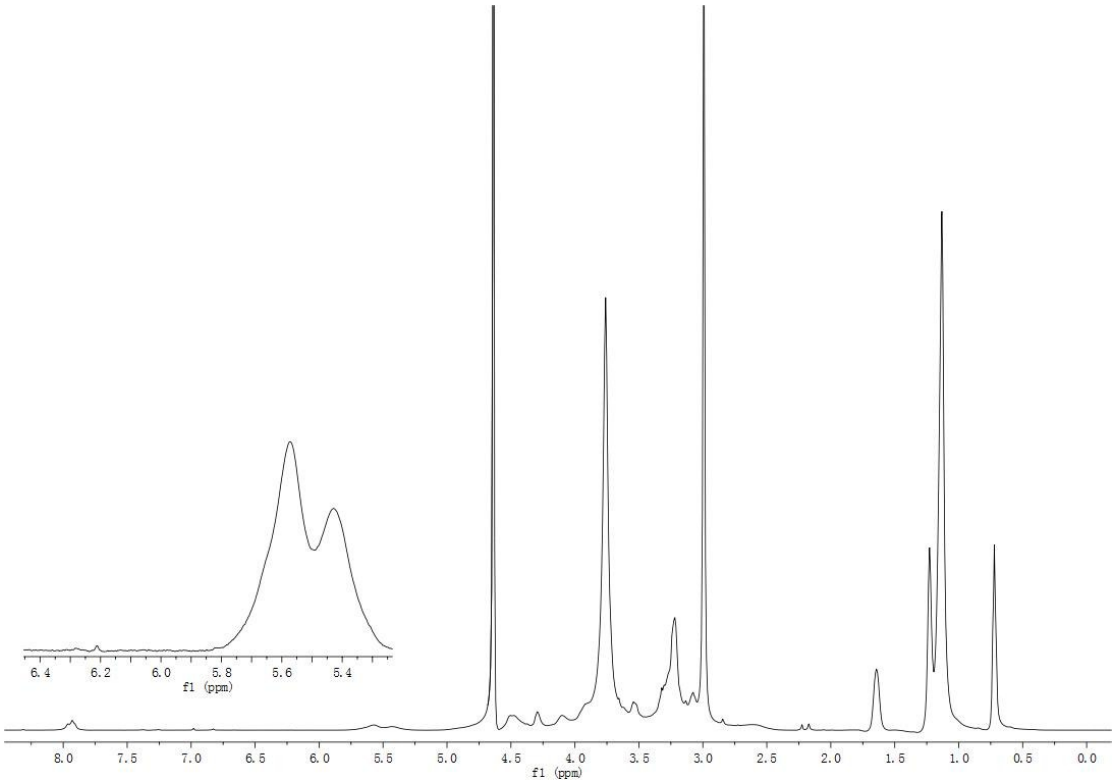


Figure S12-10. [1]H NMR spectrum of *p*-Glu in table 1, entry 10.

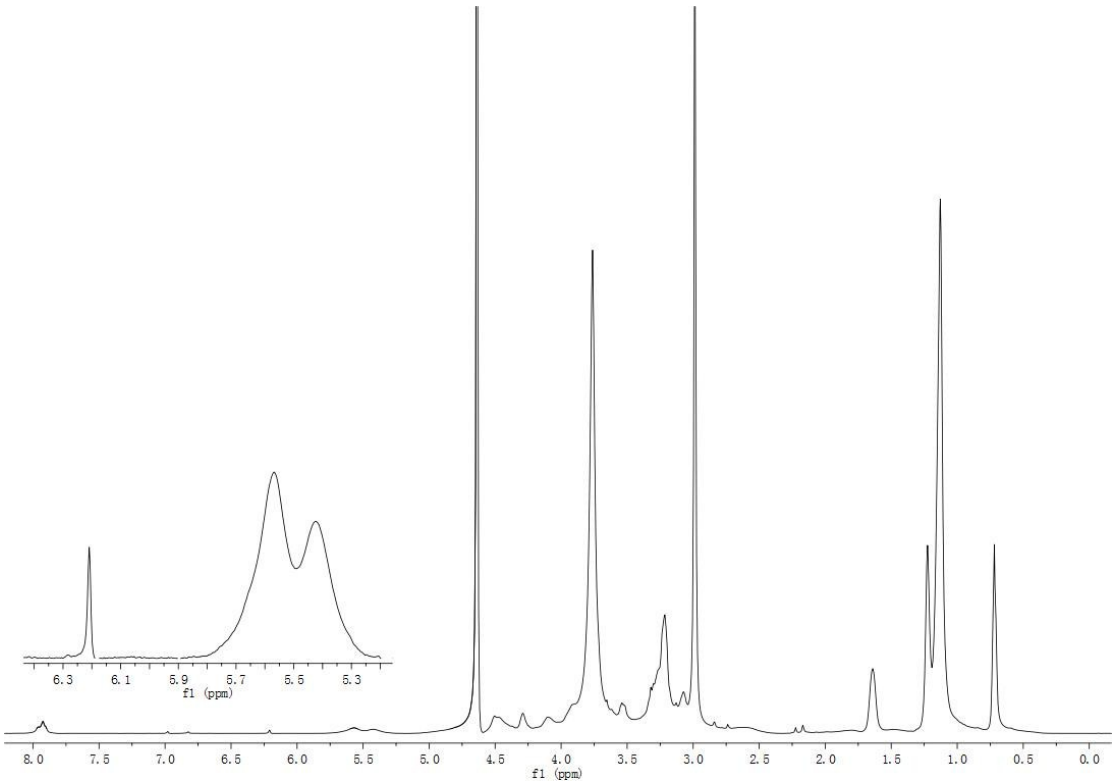


Figure S12-11. [1]H NMR spectrum of *p*-Glu in table 1, entry 11.

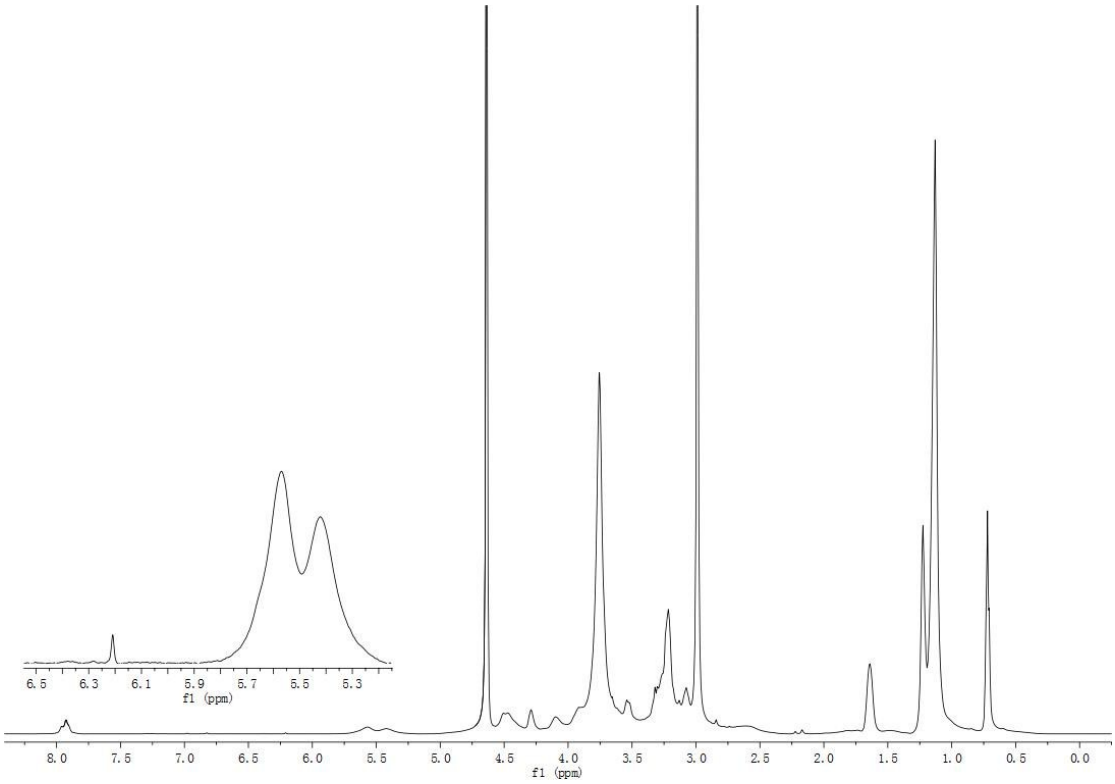


Figure S12-12. [1]H NMR spectrum of *p*-Glu in table 1, entry 12.

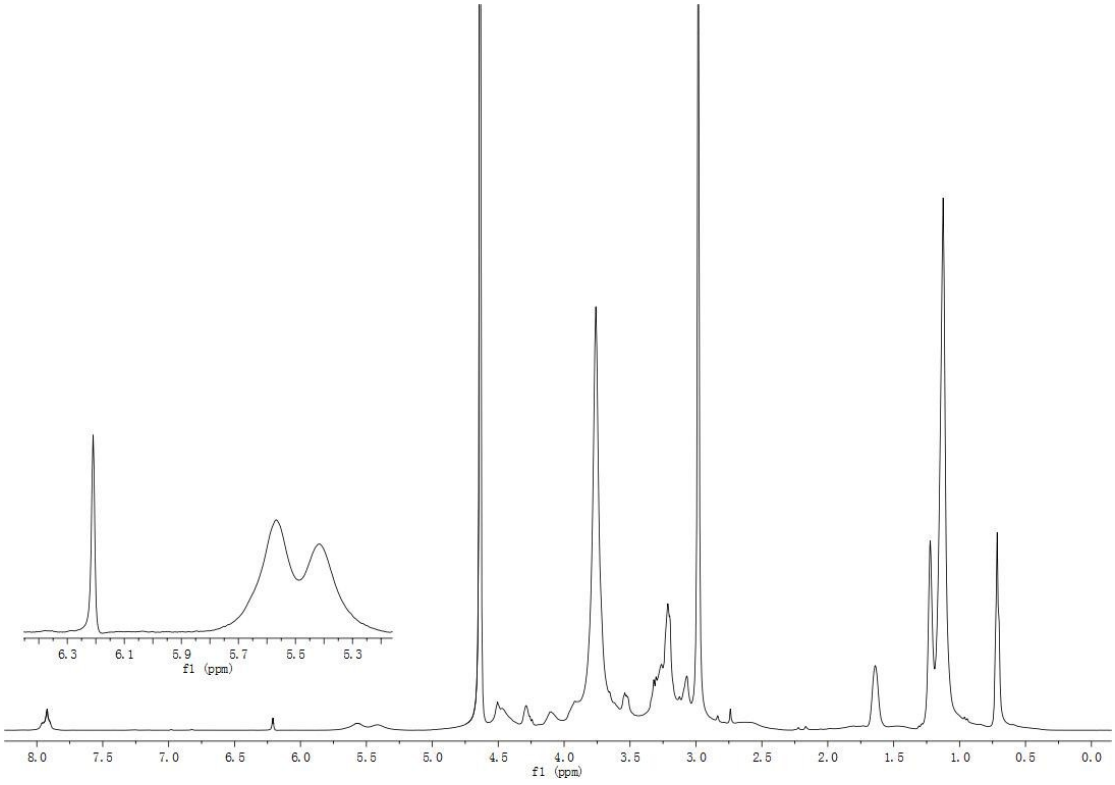


Figure S12-13. [1]H NMR spectrum of *p*-Glu in table 1, entry 13.

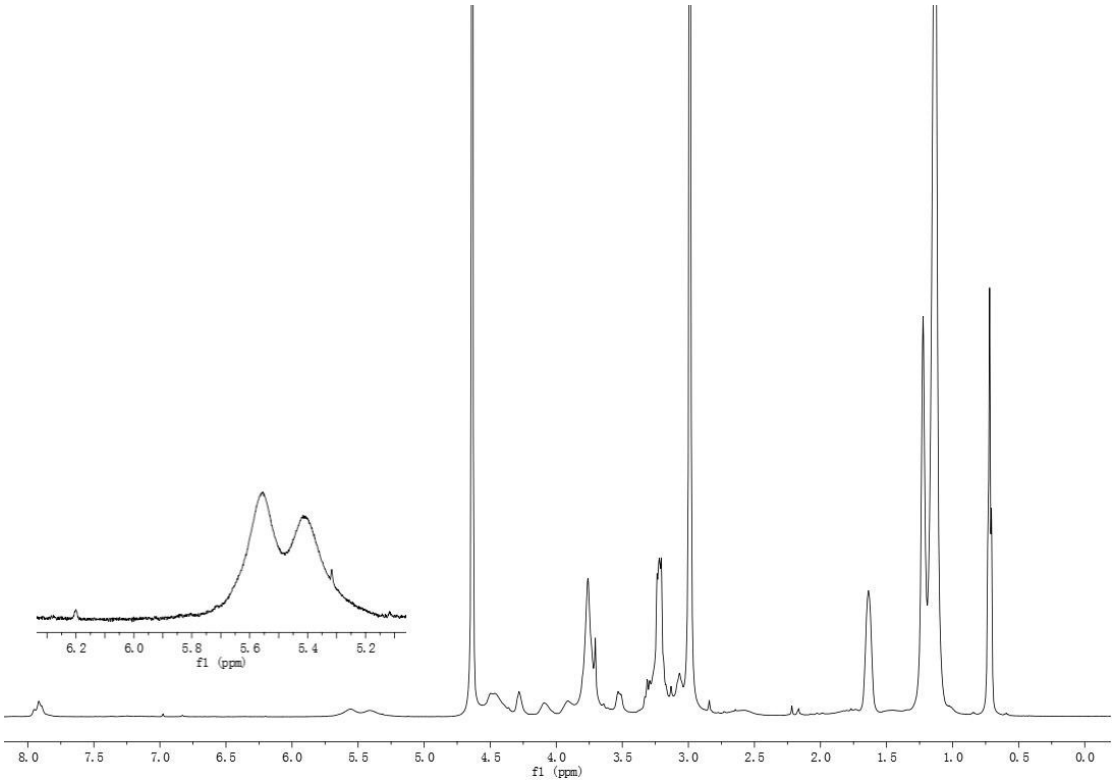


Figure S12-14. [1]H NMR spectrum of *p*-Glu in table 1, entry 14.

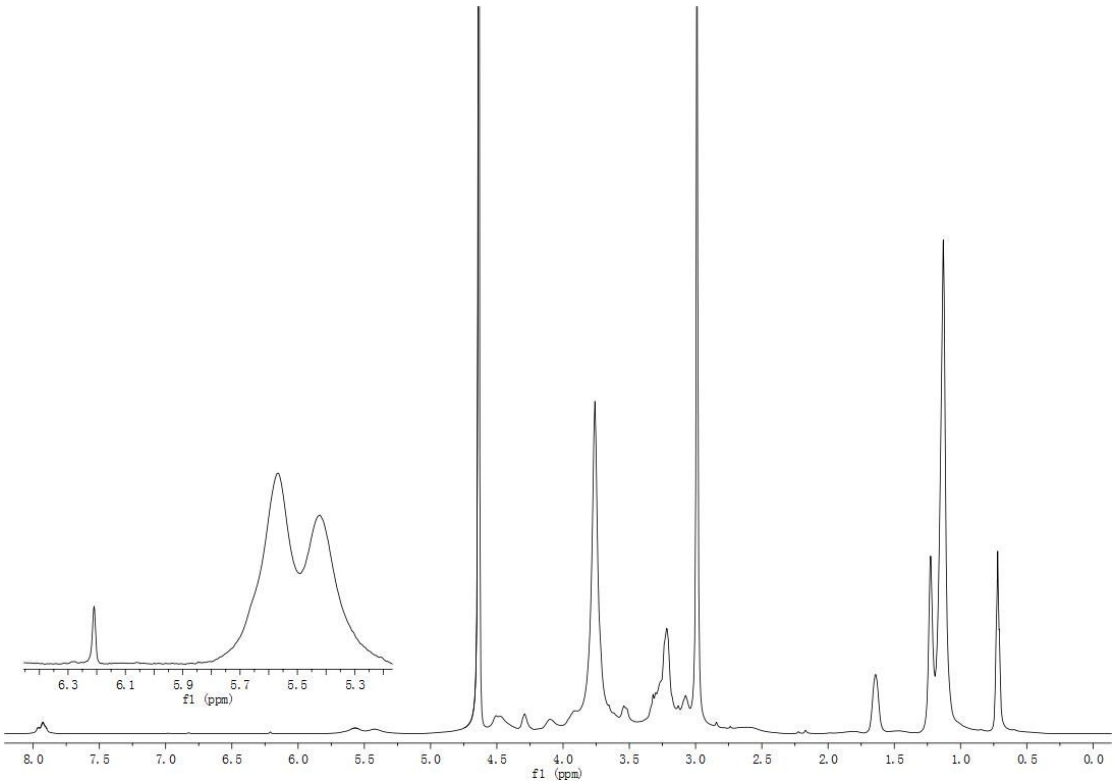


Figure S12-15. [1]H NMR spectrum of *p*-Glu in table 1, entry 15.

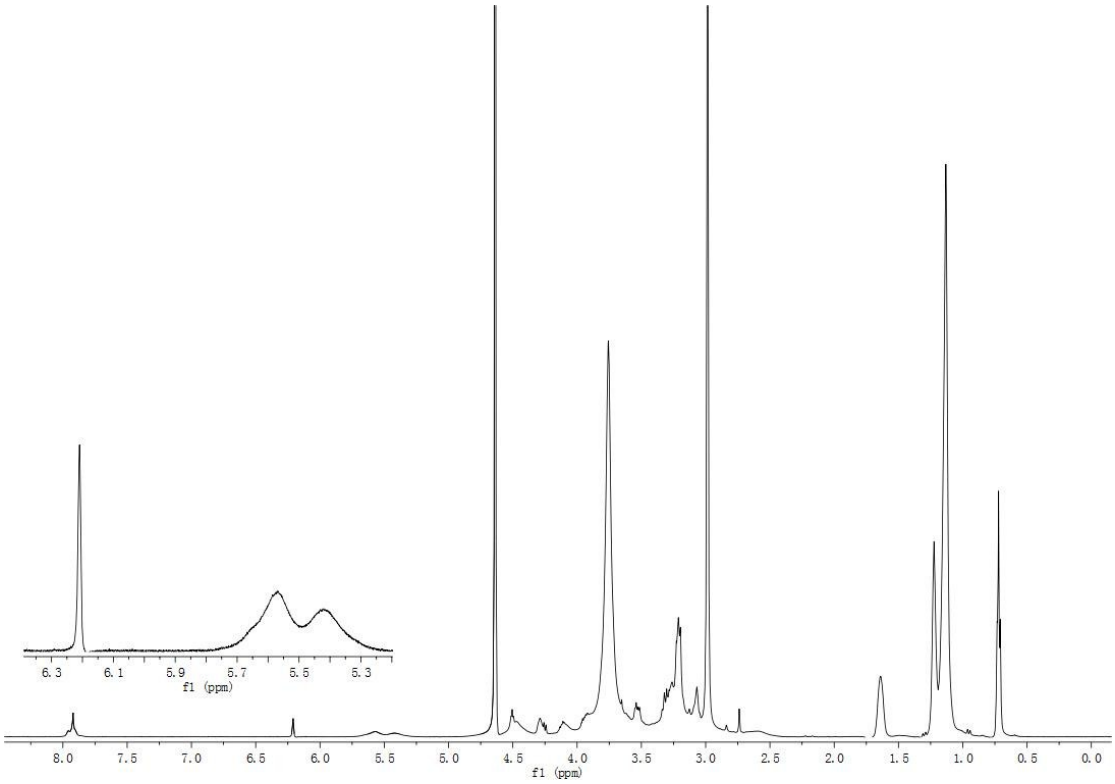


Figure S12-16. [1]H NMR spectrum of *p*-Glu in table 1, entry 16.

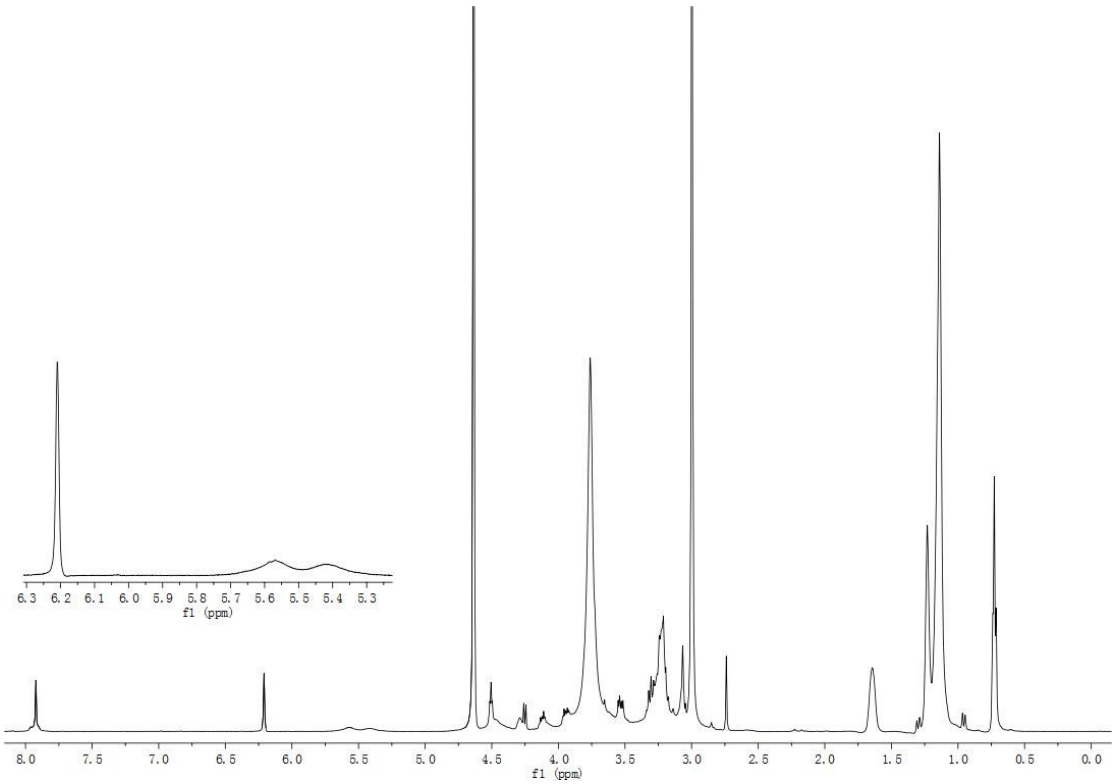


Figure S12-17. [1]H NMR spectrum of *p*-Glu in table 1, entry 17.

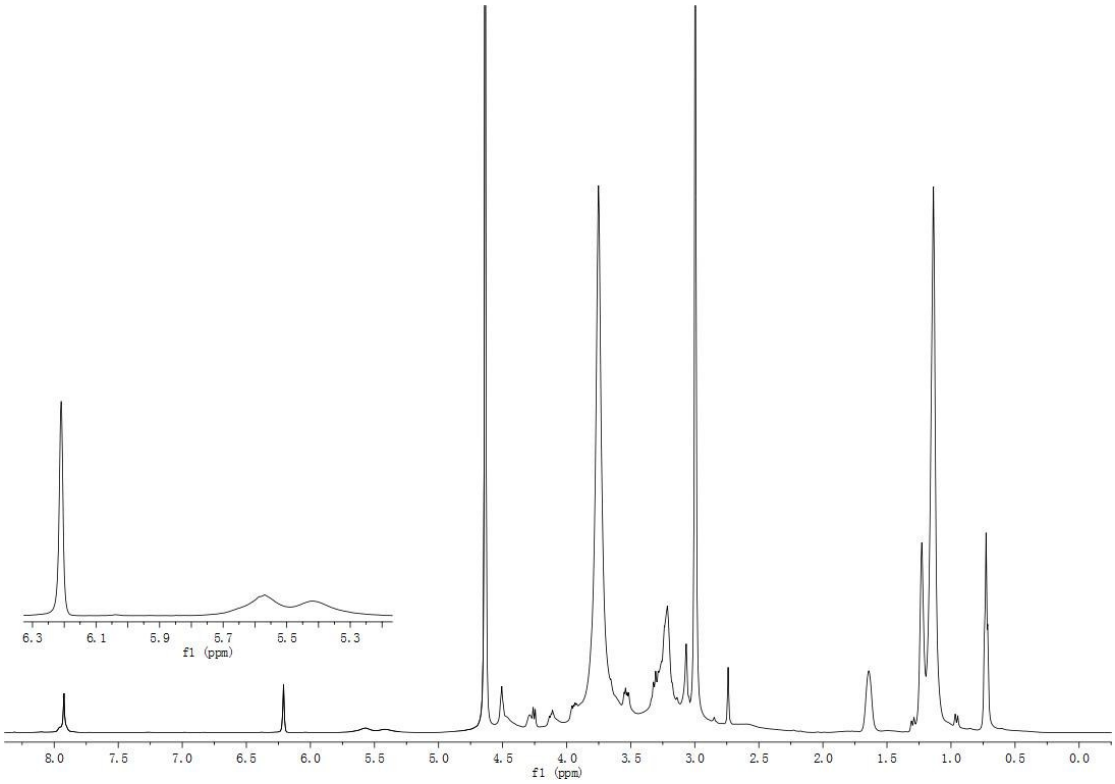


Figure S12-18. [1]H NMR spectrum of *p*-Glu in table 1, entry 18.

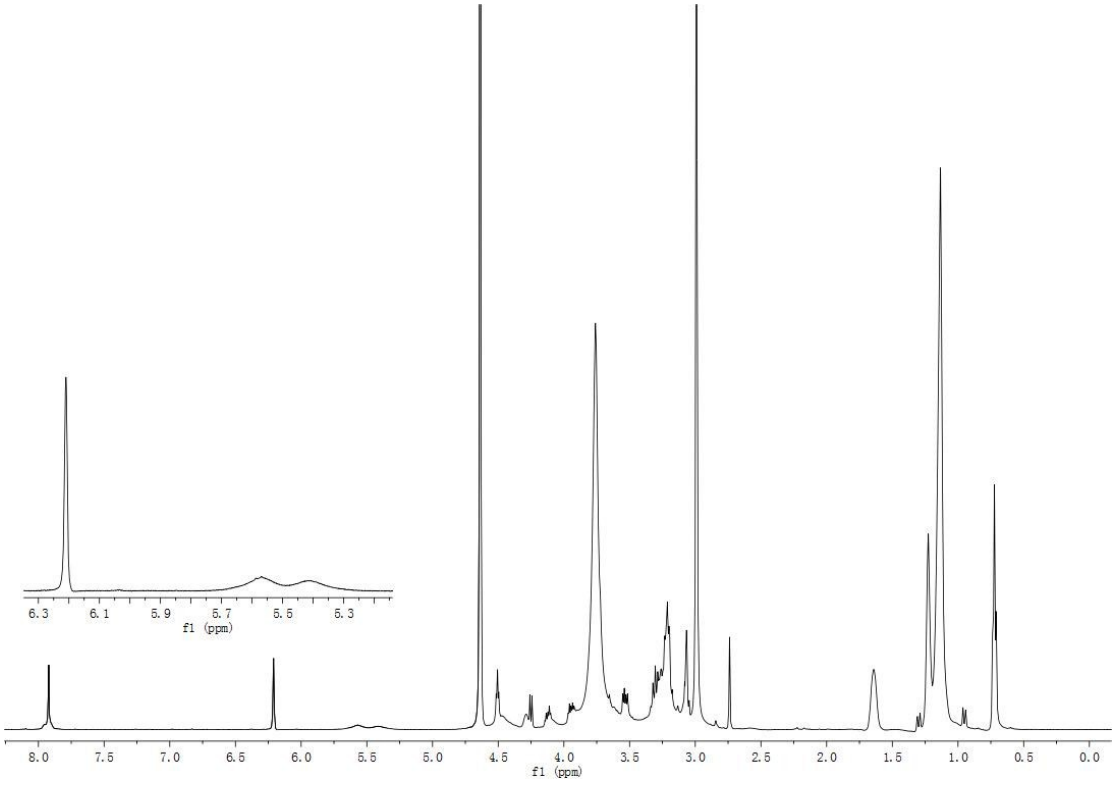


Figure S12-19. [1]H NMR spectrum of *p*-Glu in table 1, entry 19.

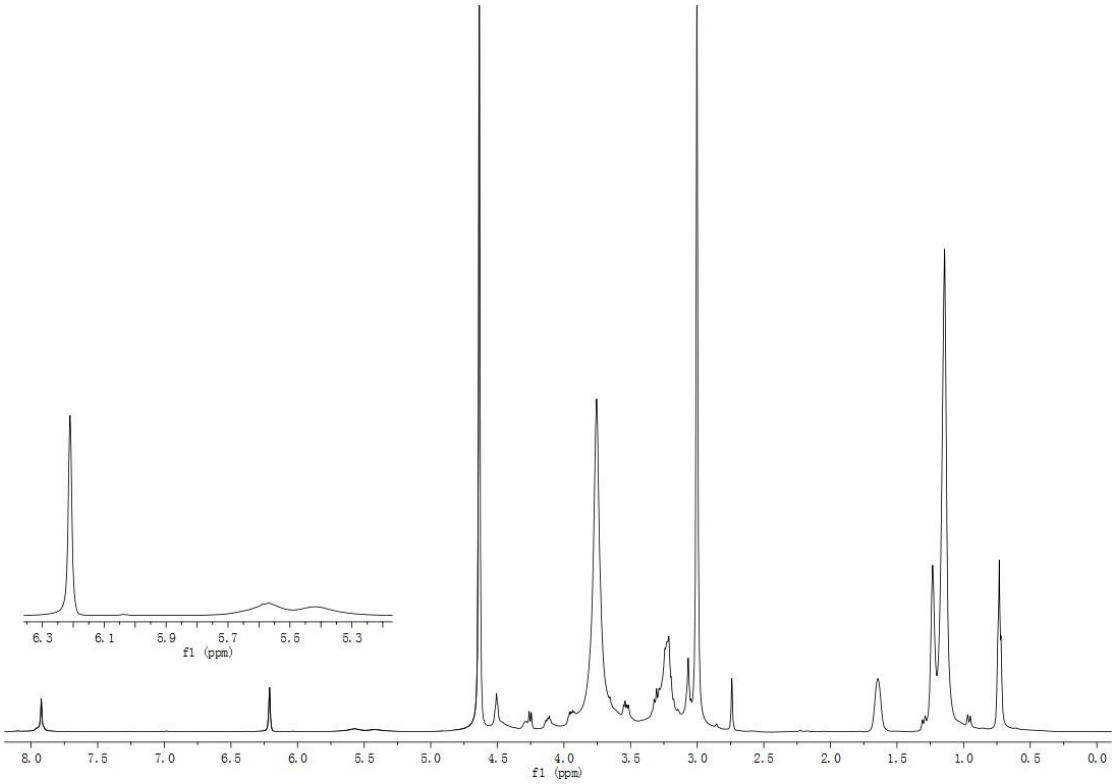


Figure S12-20. [1]H NMR spectrum of *p*-Glu in table 1, entry 20.

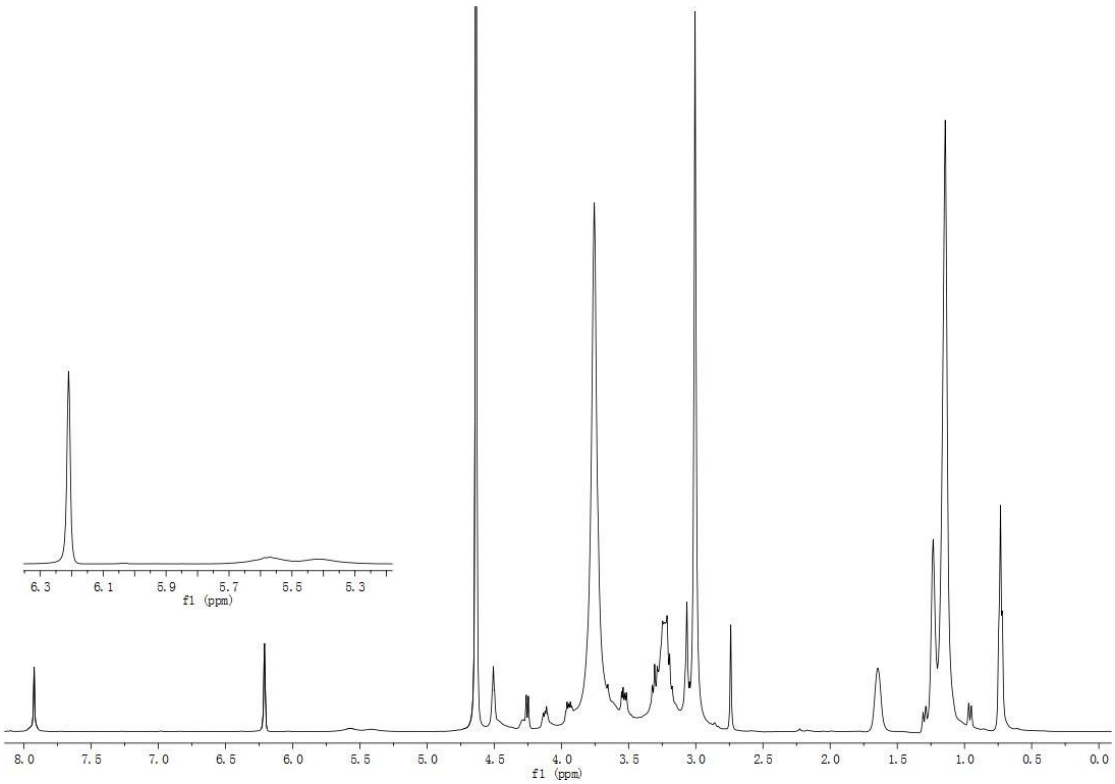


Figure S12-21. [1]H NMR spectrum of *p*-Glu in table 1, entry 21.

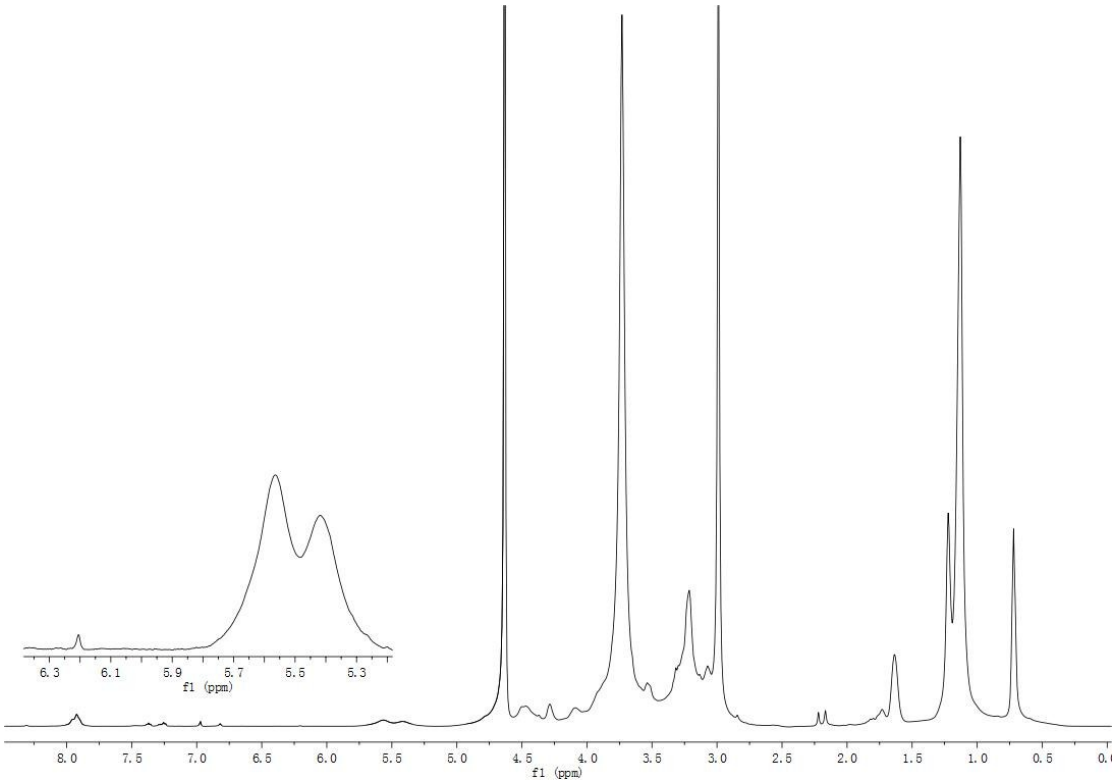


Figure S12-22. [1]H NMR spectrum of *p*-Glu in table 2, entry 1.

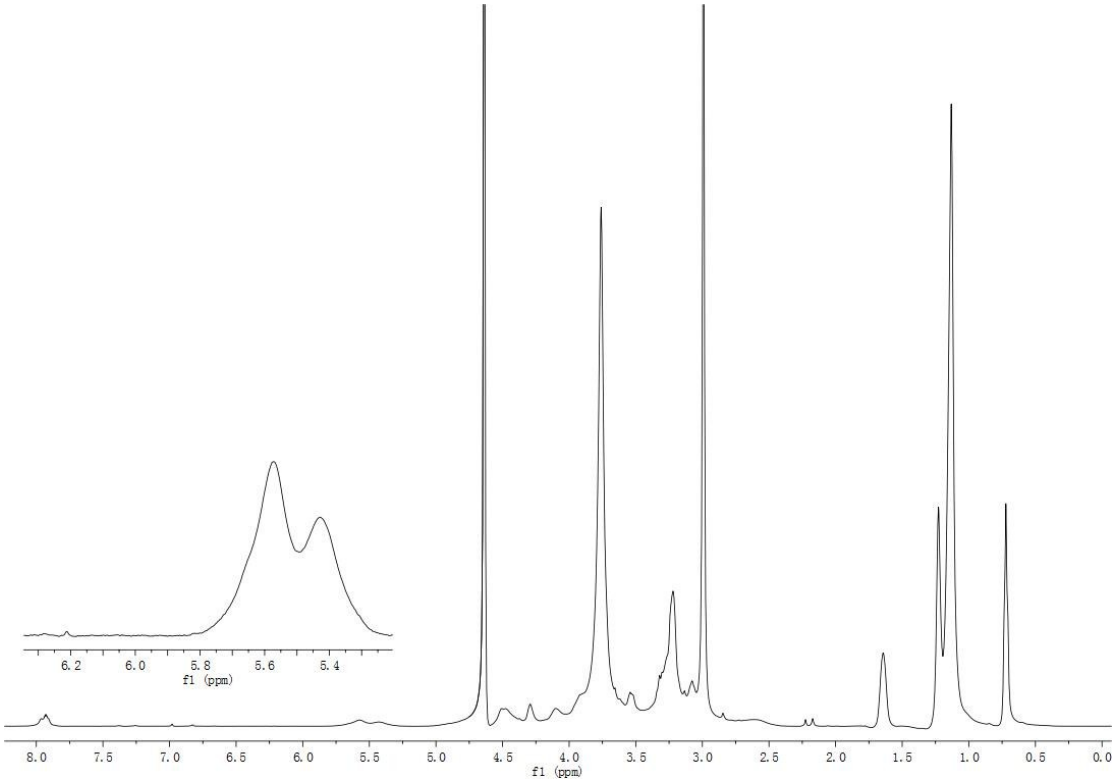


Figure S12-23. [1]H NMR spectrum of *p*-Glu in table 2, entry 2.

Figure S12-24. ^{1}H NMR spectrum of *p*-Glu in table 2, entry 3.

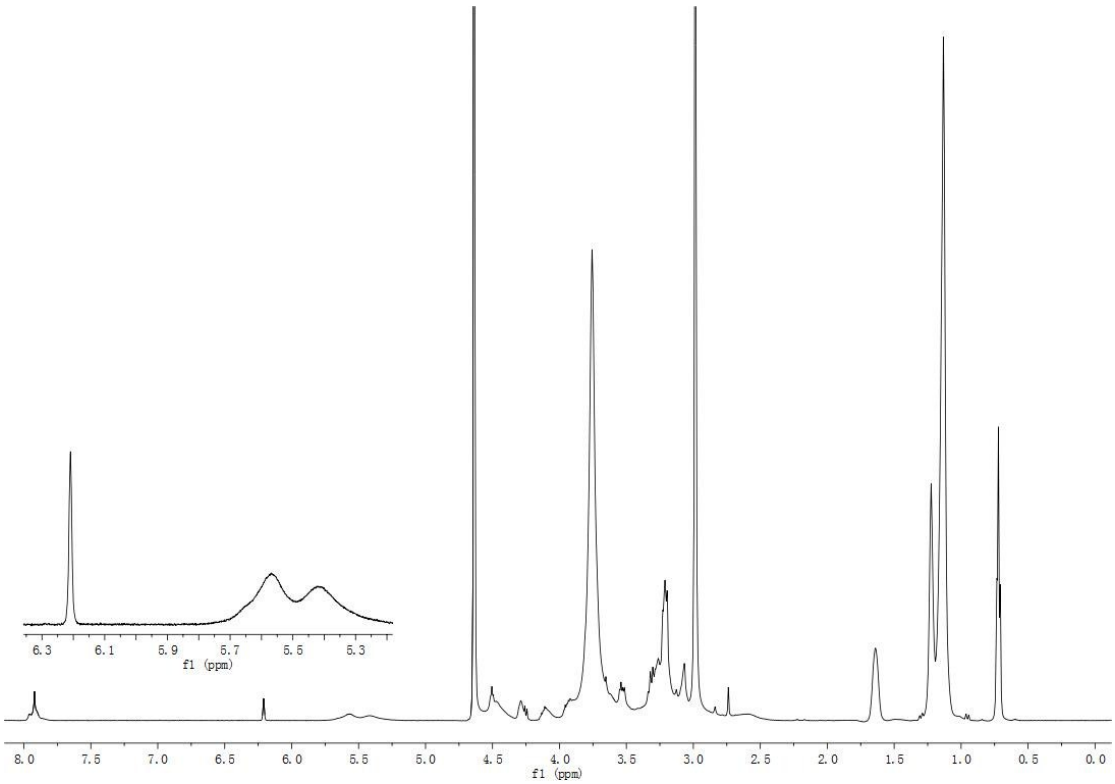


Figure S12-25. ^{1}H NMR spectrum of *p*-Glu in table 2, entry 4.

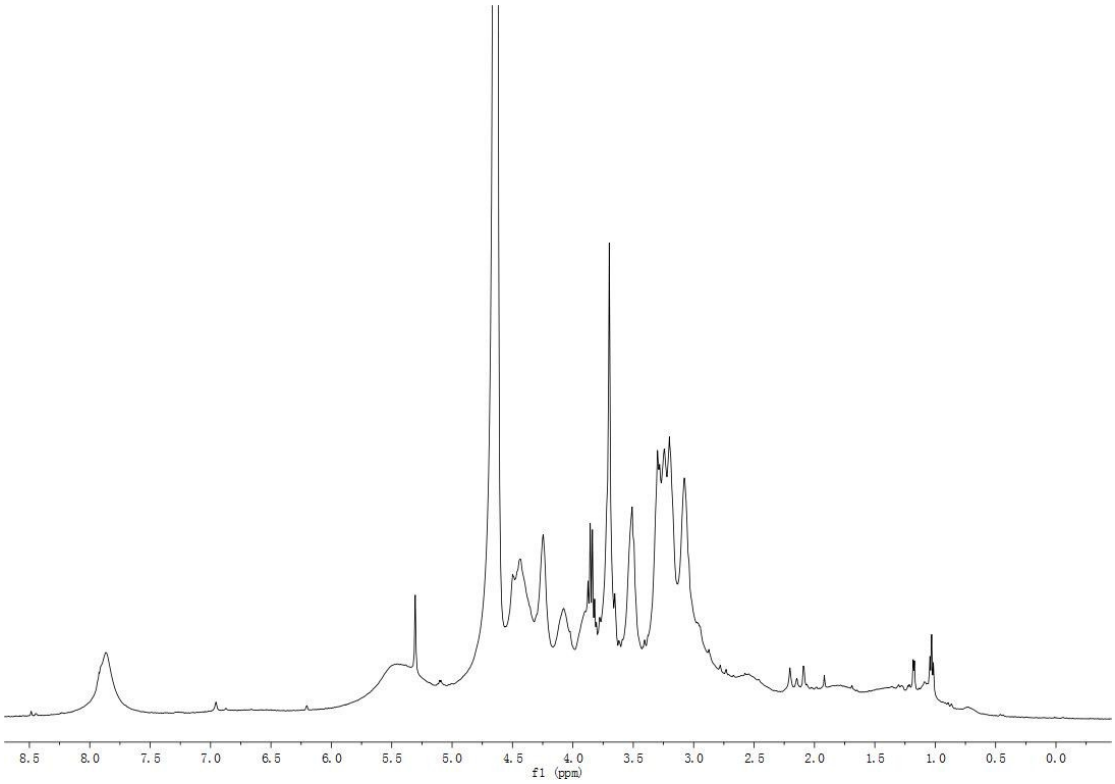


Figure S12-26. [1]H NMR spectrum of *p*-Glu in table 2, entry 5.

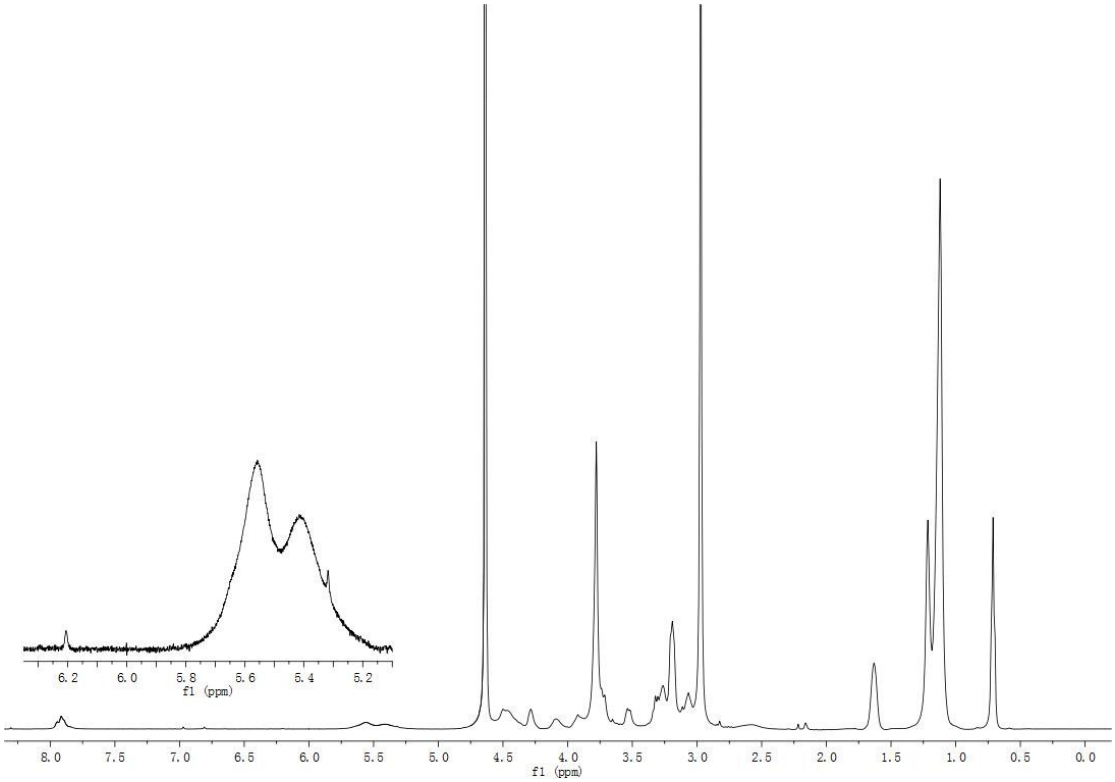


Figure S12-27. [1]H NMR spectrum of *p*-Glu in table 2, entry 6.

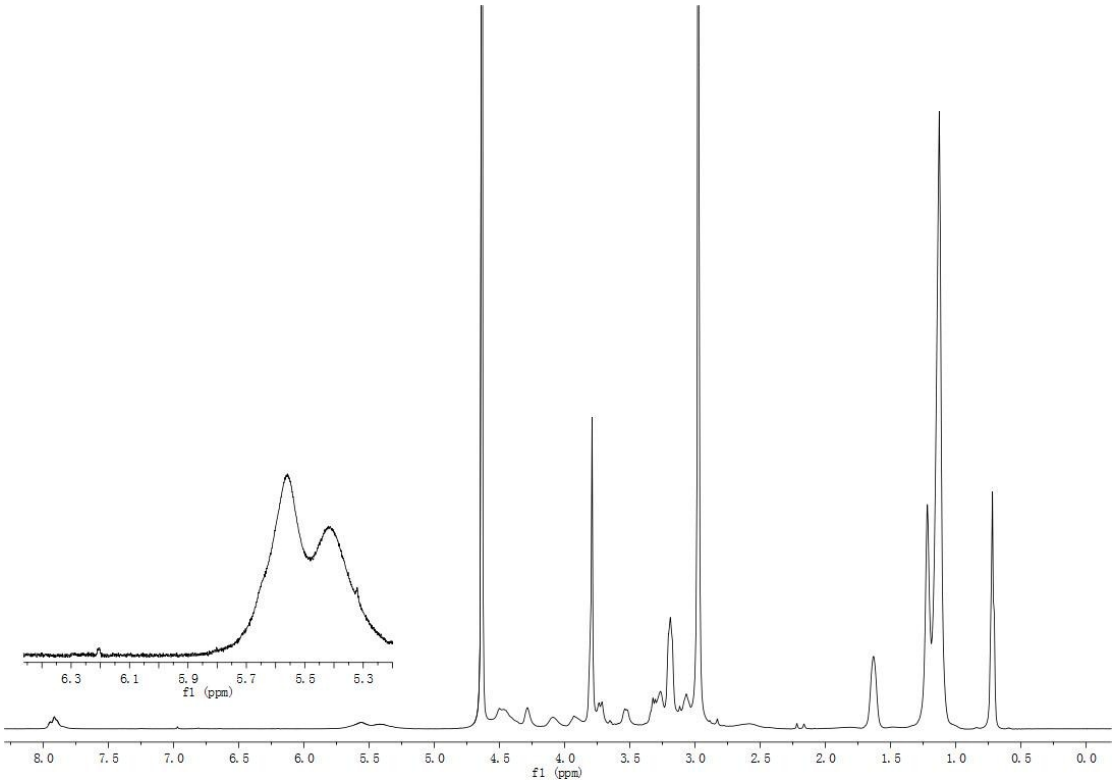


Figure S12-28. [1]H NMR spectrum of *p*-Glu in table 2, entry 7.

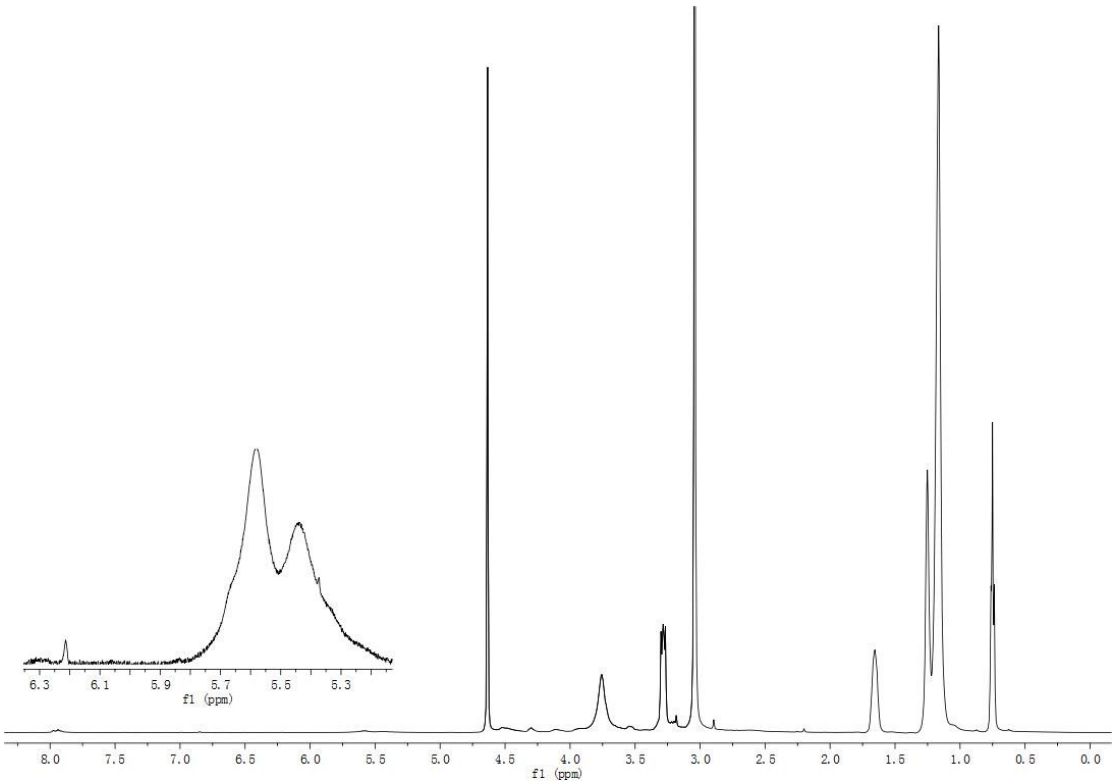


Figure S12-29. [1]H NMR spectrum of *p*-Glu in table 2, entry 8.

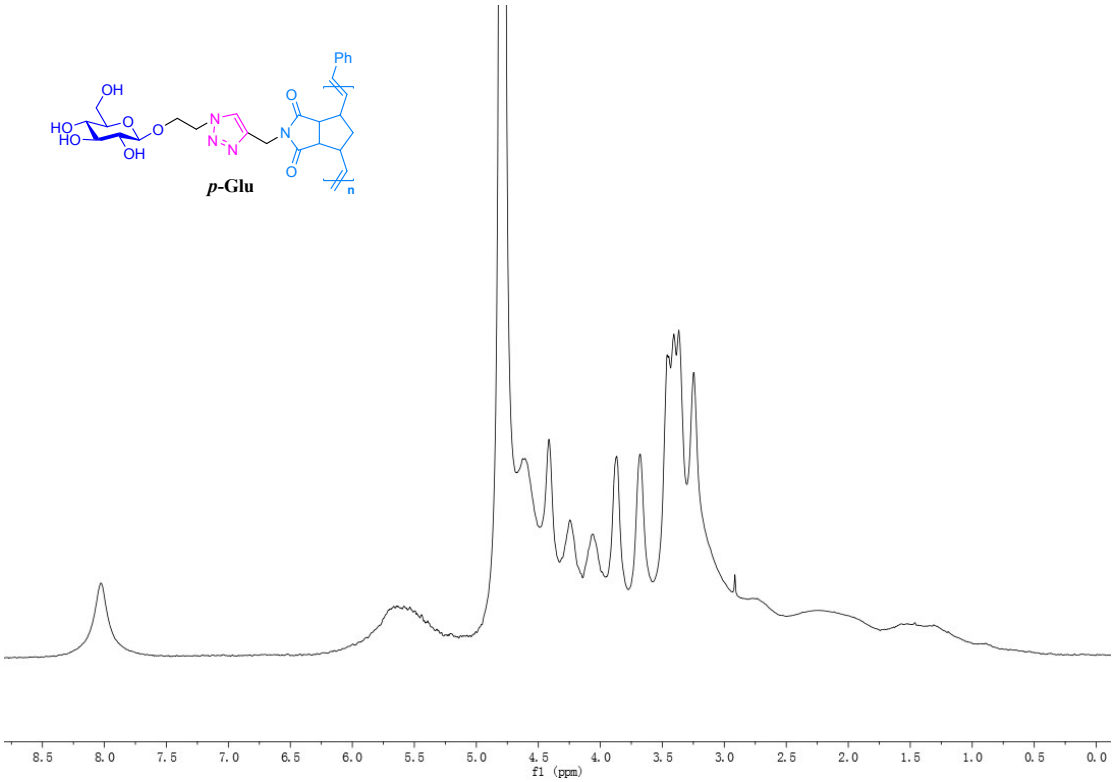


Figure S12-30. ^{1}H NMR spectrum of *p*-Glu

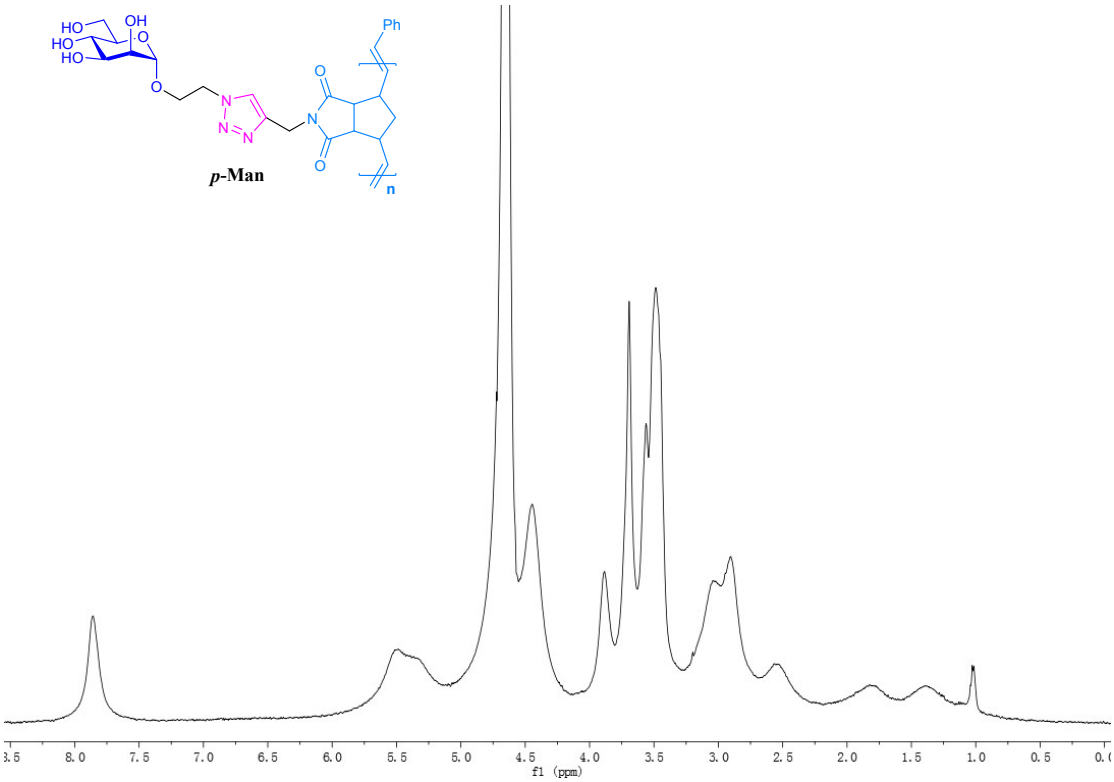


Figure S12-31. ^{1}H NMR spectrum of *p*-Man

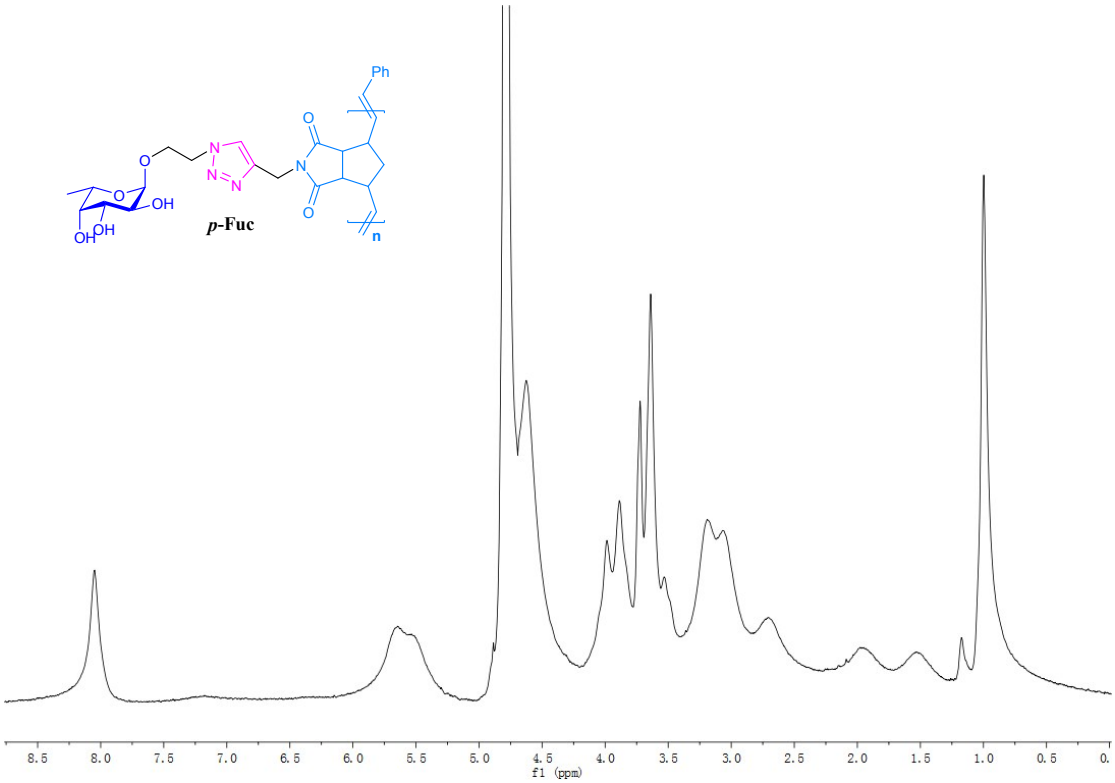


Figure S12-32. ^{1}H NMR spectrum of *p*-Fuc

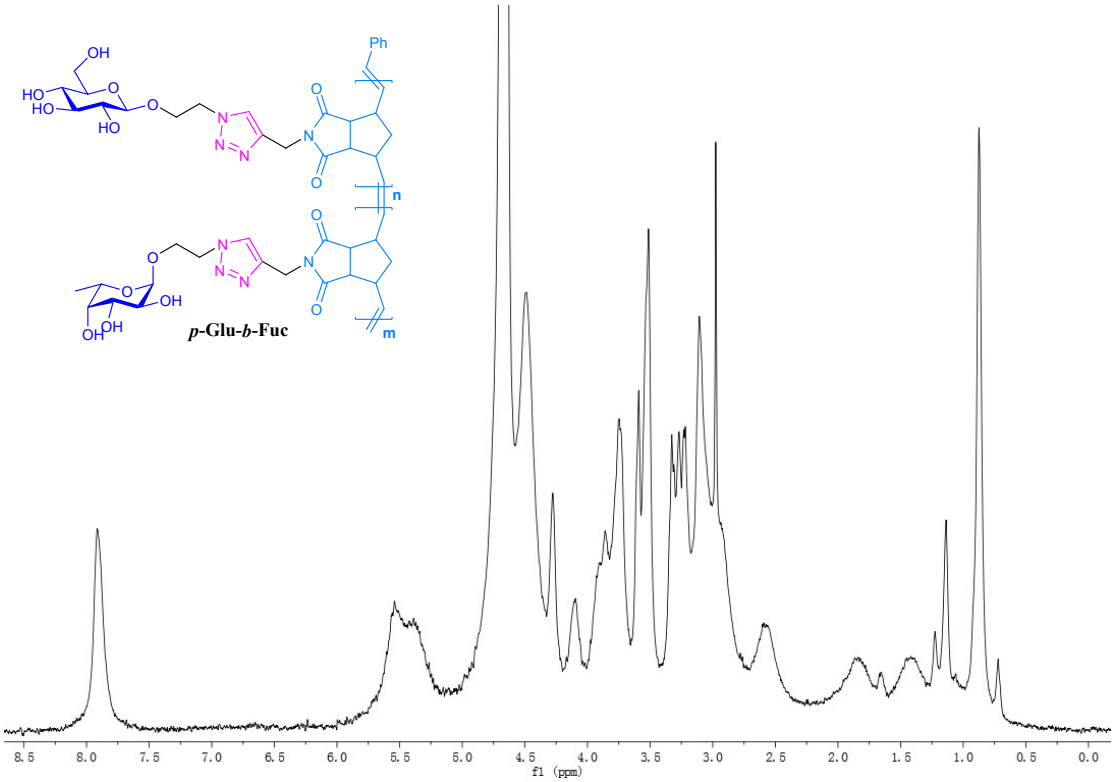


Figure S12-33. ^{1}H NMR spectrum of *p*-Glu-*b*-Fuc

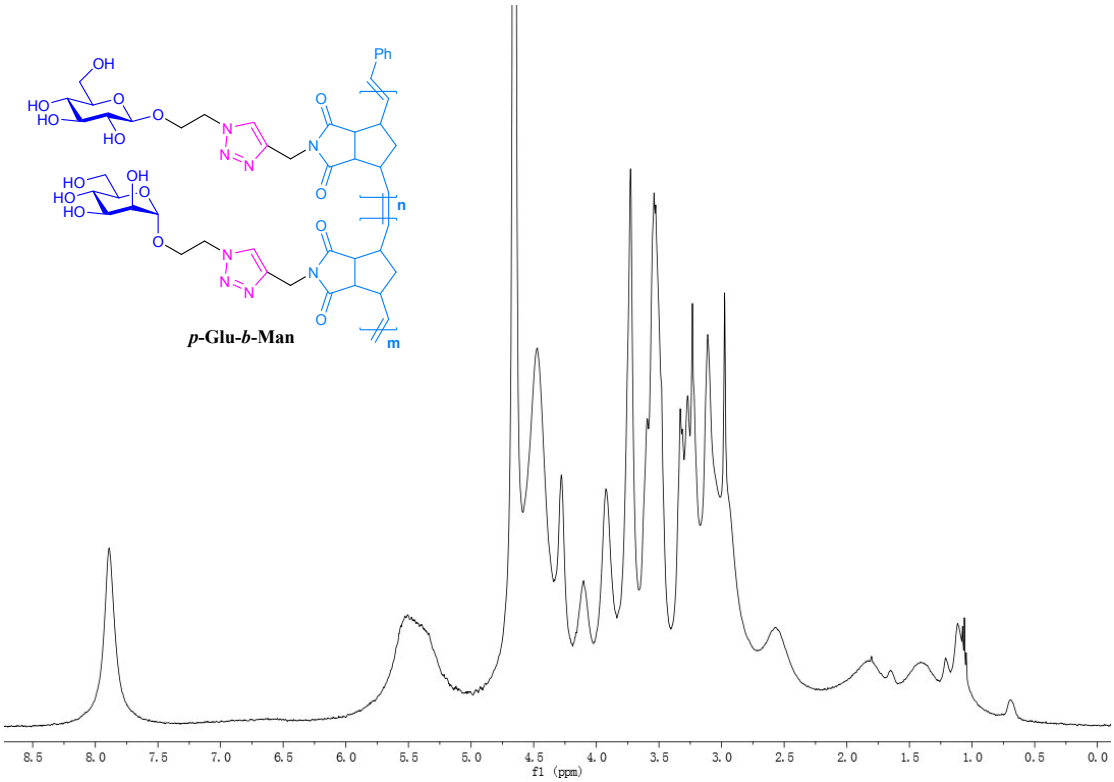


Figure S12-34. ^{1}H NMR spectrum of *p*-Glu-*b*-Man

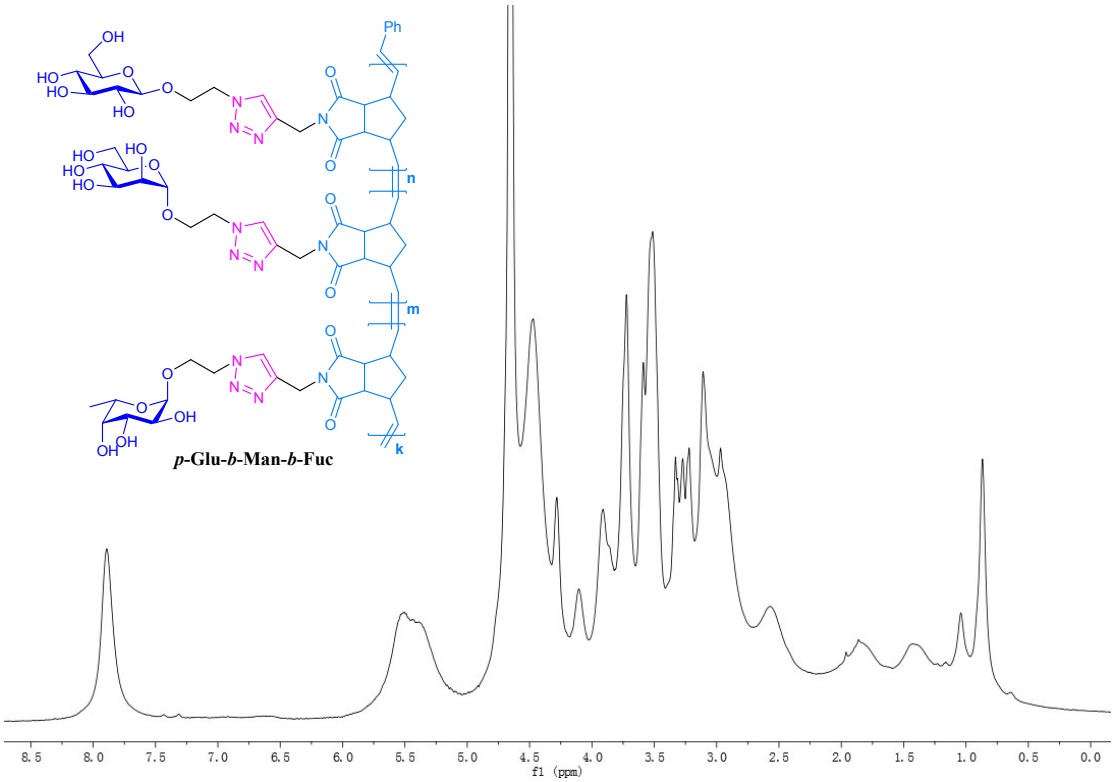


Figure S12-35. ^{1}H NMR spectrum of *p*-Glu-*b*-Man-*b*-Fuc

6. The size-exclusion chromatography (SEC) spectra.

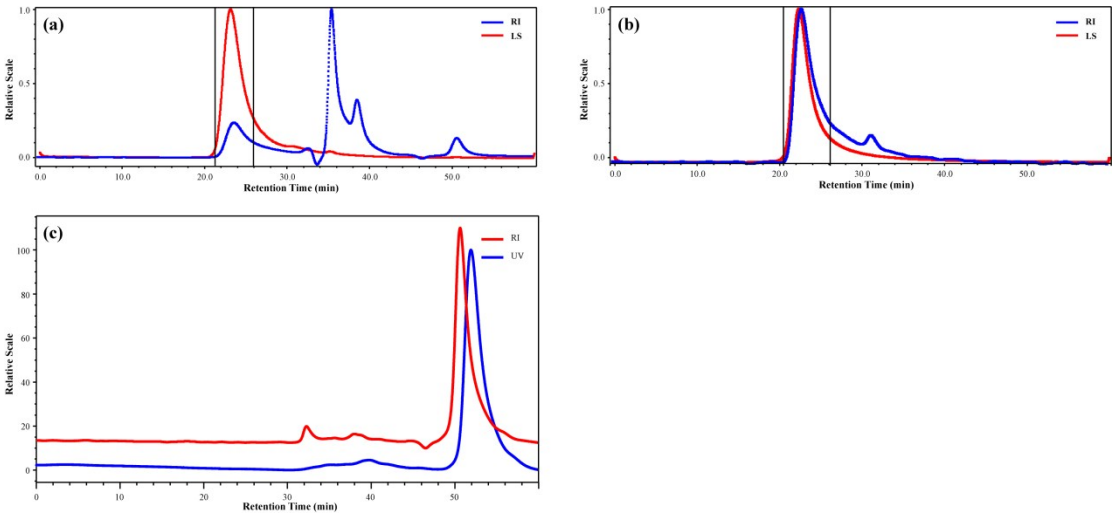
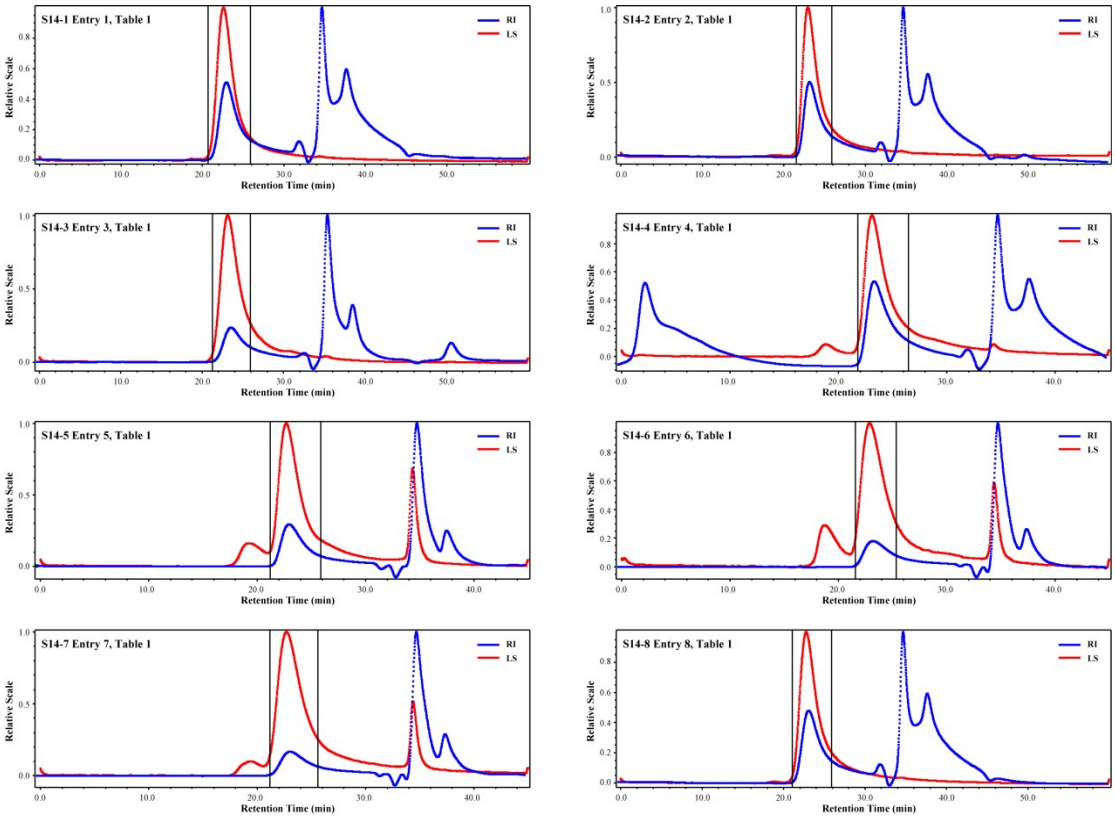
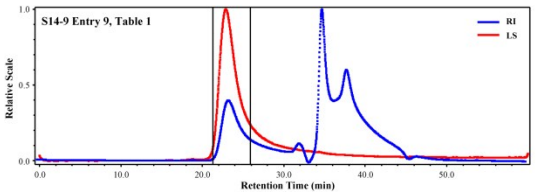
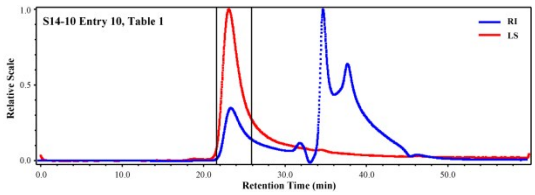


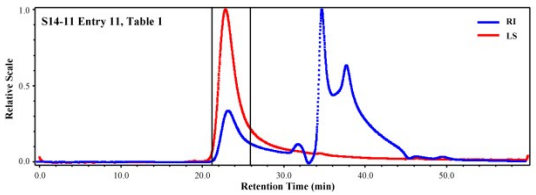
Figure S13. The size-exclusion chromatography (SEC) spectra of crude *p*-Glu (a), purified *p*-Glu (b), and glucose monomer (c). RI: refractive index singal, LS: light scattering singal, UV: ultraviolet singal.

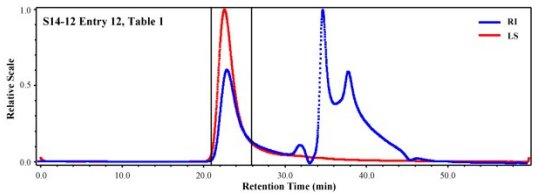
The results showed that the degree of purity of glycopolymers had no influence on SEC analysis, therefore crude glycopolymers in table 1and table 2 were used for SEC analysis. The monomer peak was eluted above 50 min which could be served as supplementary information of the conversion in SEC analysis.

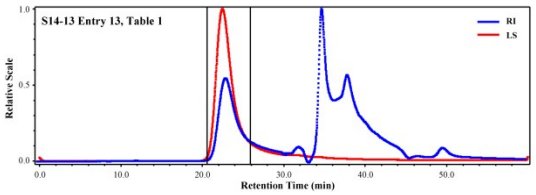


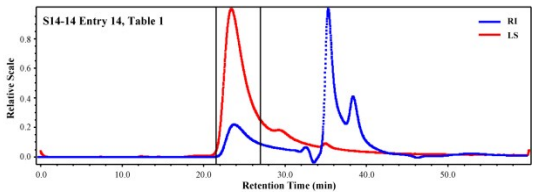

S14-9 Entry 9, Table 1
RI
LS
Relative Scale
Retention Time (min)

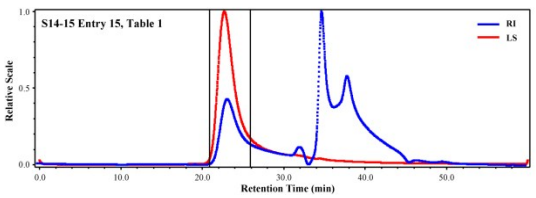

S14-10 Entry 10, Table 1
RI
LS
Relative Scale
Retention Time (min)

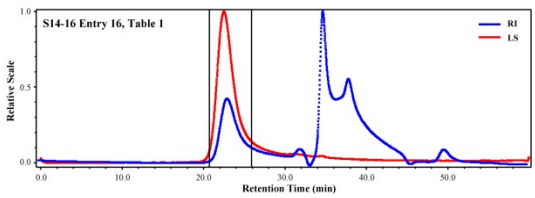

S14-11 Entry 11, Table 1
RI
LS
Relative Scale
Retention Time (min)

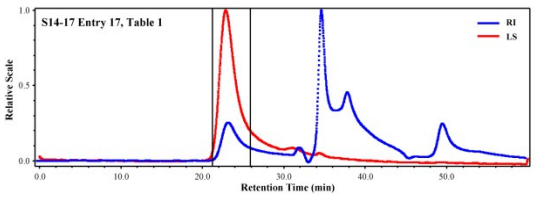

S14-12 Entry 12, Table 1
RI
LS
Relative Scale
Retention Time (min)

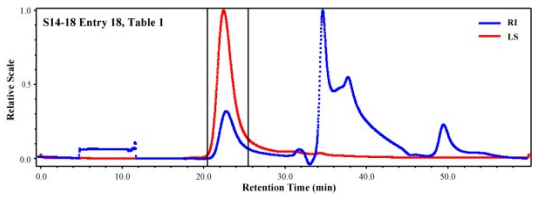

S14-13 Entry 13, Table 1
RI
LS
Relative Scale
Retention Time (min)

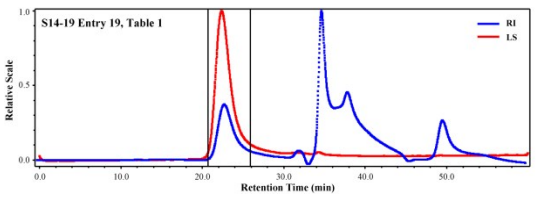

S14-14 Entry 14, Table 1
RI
LS
Relative Scale
Retention Time (min)

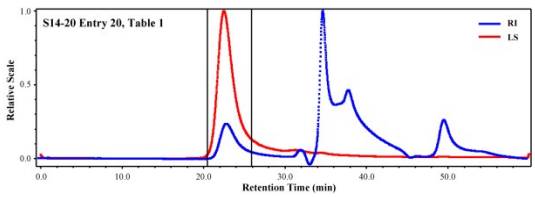

S14-15 Entry 15, Table 1
RI
LS
Relative Scale
Retention Time (min)

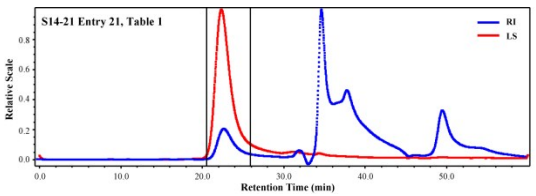

S14-16 Entry 16, Table 1
RI
LS
Relative Scale
Retention Time (min)

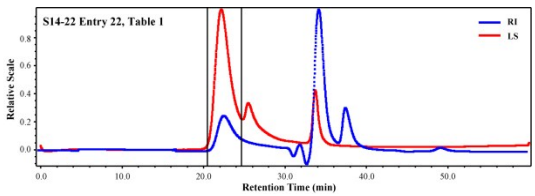

S14-17 Entry 17, Table 1
RI
LS
Relative Scale
Retention Time (min)

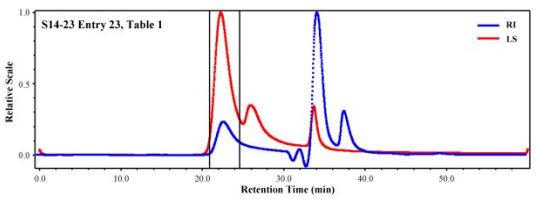

S14-18 Entry 18, Table 1
RI
LS
Relative Scale
Retention Time (min)

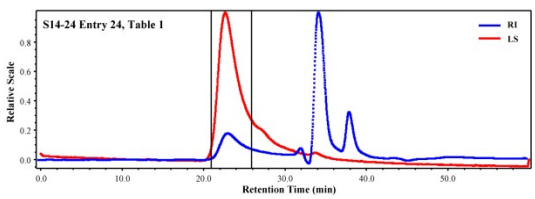

S14-19 Entry 19, Table 1
RI
LS
Relative Scale
Retention Time (min)


S14-20 Entry 20, Table 1
RI
LS
Relative Scale
Retention Time (min)


S14-21 Entry 21, Table 1
RI
LS
Relative Scale
Retention Time (min)


S14-22 Entry 22, Table 1
RI
LS
Relative Scale
Retention Time (min)


S14-23 Entry 23, Table 1
RI
LS
Relative Scale
Retention Time (min)


S14-24 Entry 24, Table 1
RI
LS
Relative Scale
Retention Time (min)

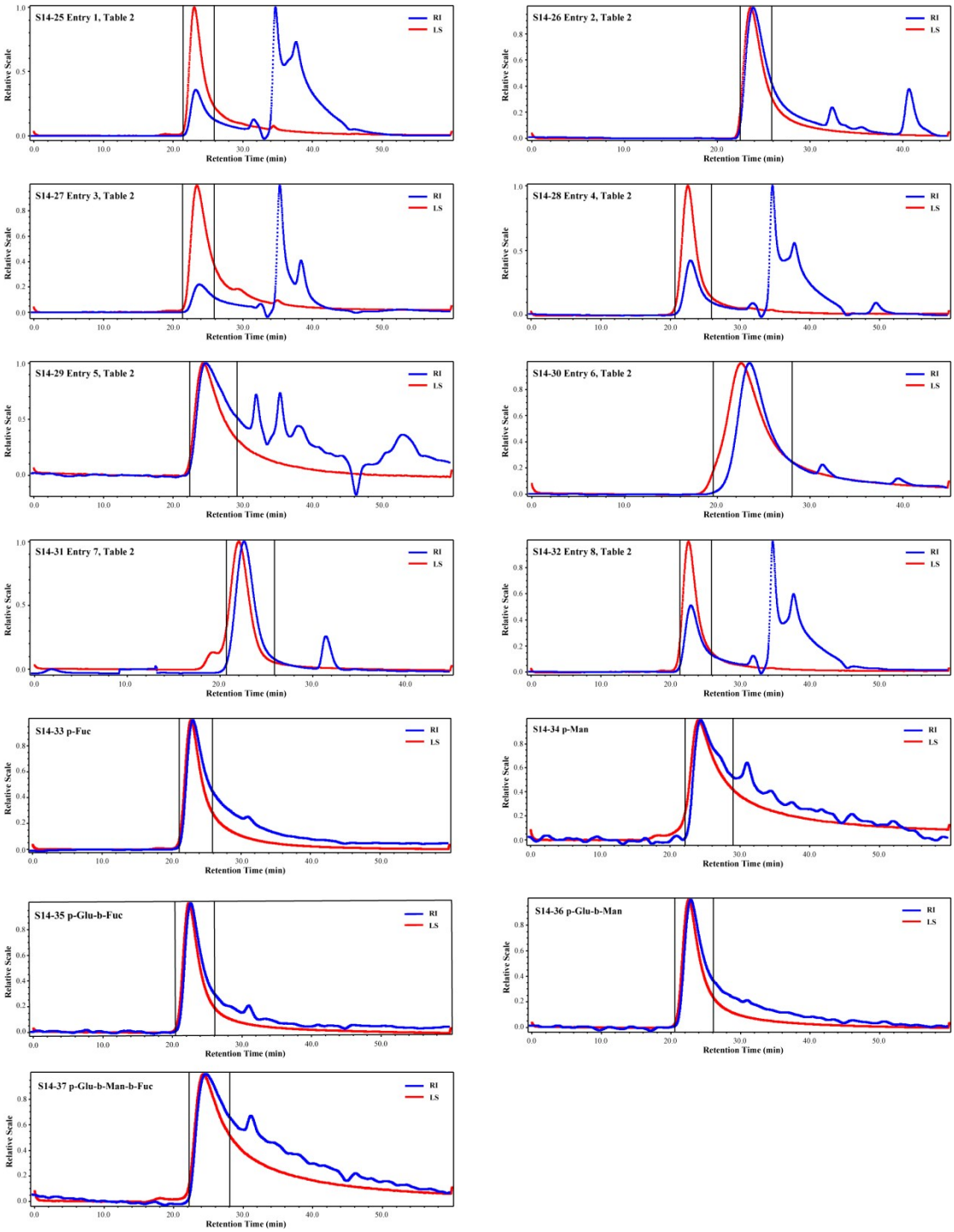


Figure S14. The size-exclusion chromatography (SEC) spectra of glycopolymers in this paper. RI: refractive index singal, LS: light scattering singal.

7. Surface Plasmon Resonance measurements.

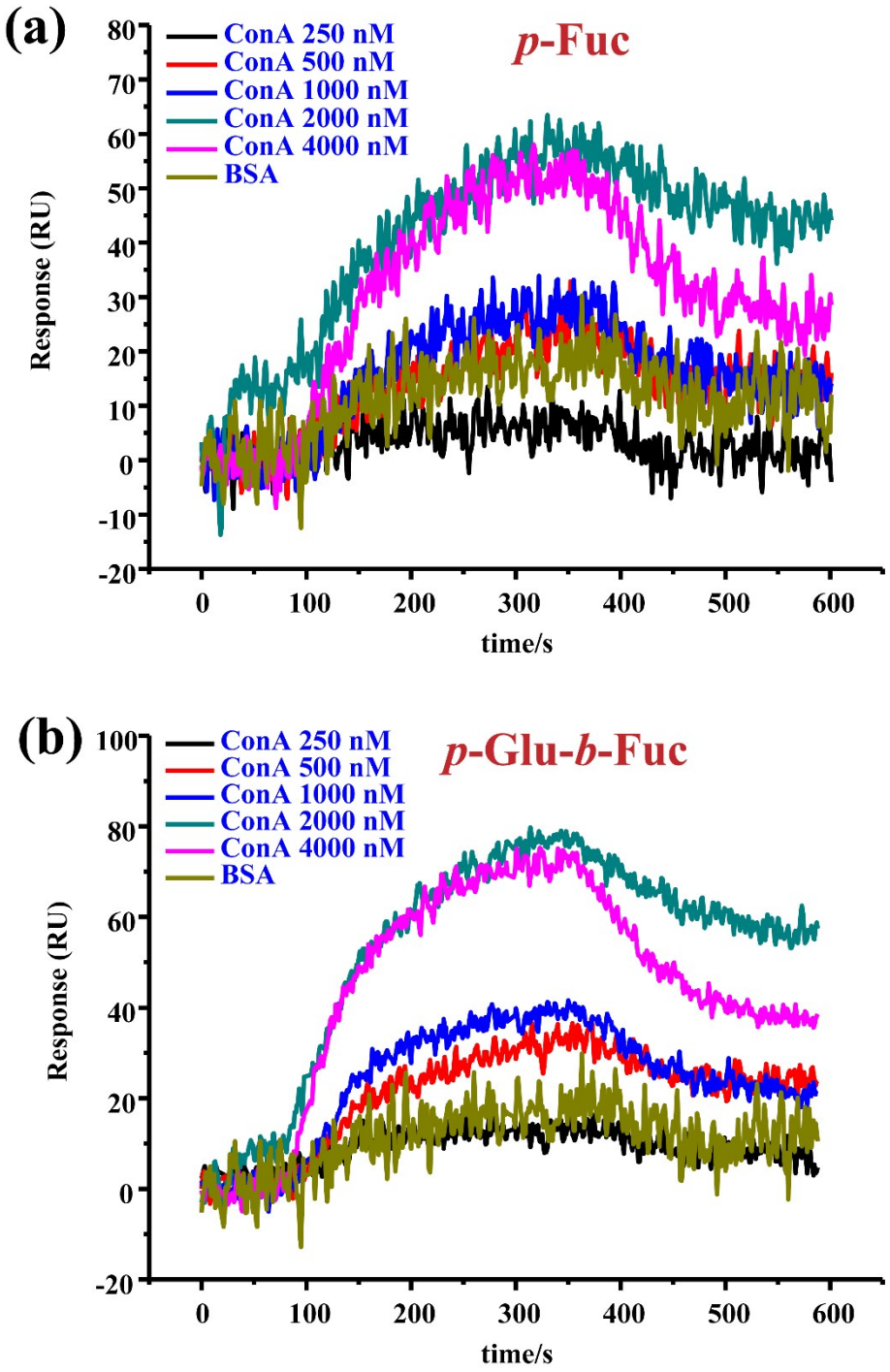


Figure S15. Surface plasmon resonance measurements for *p*-Fuc (a) and *p*-Glu-*b*-Fuc (b).

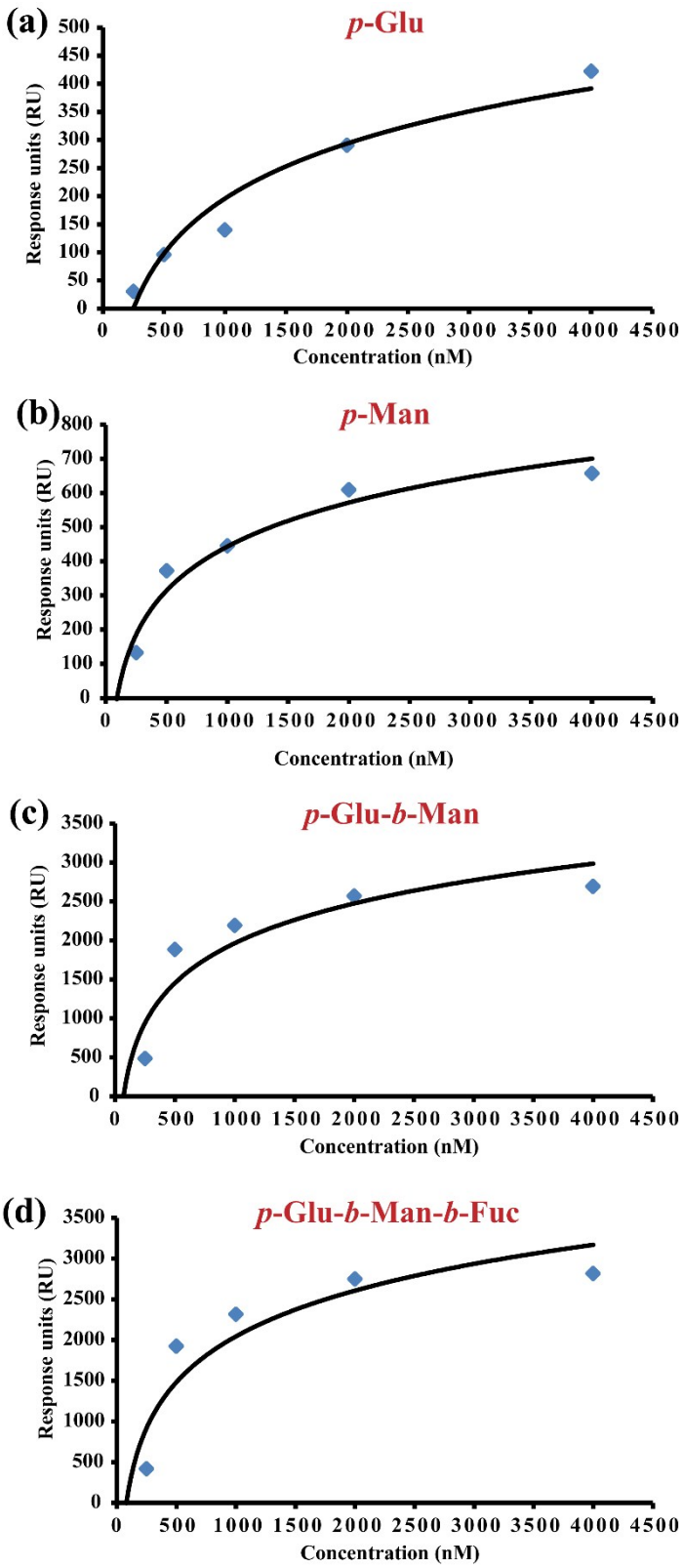


Figure S16. The equilibrium response as a function of concentration from *p*-Glu (a), *p*-Man (b), *p*-Glu-*b*-Man (c) and *p*- Glu-*b*-Man-*b*-Fuc (d) plotted using a steady state model.