

Supplementary Materials:

Enzymatic synthesis of tri-deuterated sialosides

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Table S1. NMR signals and correlations of X-Gal-Neu5Ac and tri-deuterated X-Gal-Neu5Ac (**9a**).

Position	Non-deuterated X-Gal-Neu5Ac				Deuterated X-Gal-Neu5Ac			
	¹ H	¹³ C	COSY	HMBC	¹ H	¹³ C	COSY	HMBC
I2	7.19 (s)	113.41	-	I7a,I3,I3a	7.19 (s)	113.47	-	I7a,I3,I3a
I3	-	138.51	-	-	-	138.43	-	-
I3a	-	119.56	-	-	-	119.57	-	-
I4	-	125.54	-	-	-	125.51	-	-
I5	-	113.95	-	-	-	114.09	-	-
I6	7.27 (d)	127.09	I7	I7a,I4	7.27 (d)	127.09	I7	I7a,I4
I7	7.12 (d)	112.61	I6	I5,I3a	7.12 (d)	112.61	I6	I5,I3a
I7a	-	135.06	-	-	-	135.08	-	-
G1	4.79 (d)	105.68	G2	I3,G5	4.79 (d)	105.64	G2	I3
G2	3.89 (m)	70.88	G1,G3	G1,G3	3.92 (m)	70.84	G1,G3	G1
G3	3.51 (dd)	69.60	G2	G4	3.54 (d)	62.26	G2	G4
G4	3.62 (m)	74.98	-	G3,G2	3.67 (m)	74.93	-	-
G5	3.62 (m)	77.07	G6	G6	3.67 (m)	76.63	G6	G6
G6	3.81 (m)	62.92	G5	G5	3.83 (m)	61.26	G5	G5
	3.74 (m)				3.77 (dd)			
S1	-	175.51	-	-	-	175.57	-	-
S2	-	101.26	-	-	-	101.57	-	-
S3	2.88 (dd)	42.23	S4	S5,S4,S2	-	28.20	-	-
	1.78 (t)							
S4	3.74 (m)	70.15	S3	-	3.83 (m)	69.81	-	-
S5	3.74 (m)	54.05	-	S4	-	54.61	-	-
S'5	-	175.18	-	-	-	175.57	-	-
S''5	2.01 (s)	22.70	-	S'5	2.02 (s)	22.78	-	S'5
S6	4.14 (dd)	77.87	S7	S7,S2	4.14 (dd)	77.81	S7	S7,S2
S7	3.89 (m)	73.04	S6	S8	3.92 (m)	73.08	S6	-
S8	4.00 (d)	69.14	-	S7	4.06 (d)	67.56	-	-
S9	3.81 (m)	64.54	-	-	3.83 (m)	62.91	-	-
	3.62 (m)				3.67 (m)			

Table S2. NMR signals and correlations of X-Gal-Neu5Gc and tri-deuterated X-Gal-Neu5Gc (**9b**).

Position	Non-deuterated X-Gal-Neu5Gc				Deuterated X-Gal-Neu5Gc			
	¹ H	¹³ C	COSY	HMBC	¹ H	¹³ C	COSY	HMBC
I2	7.19 (s)	113.45	-	I7a,I3,I3a	7.19 (s)	113.41	-	I7a,I3,I3a
I3	-	138.49	-	-	-	138.56	-	-
I3a	-	119.59	-	-	-	119.59	-	-
I4	-	125.55	-	-	-	125.59	-	-
I5	-	114.02	-	-	-	113.91	-	-
I6	7.27 (d)	127.09	I7	I7a,I4	7.27 (d)	127.09	I7	I7a,I4
I7	7.12 (d)	112.61	I6	I5,I3a	7.12 (d)	112.61	I6	I5,I3a
I7a	-	135.08	-	-	-	135.08	-	-
G1	4.79 (d)	105.69	G2	I3	4.79 (s)	105.71	G2	I3
G2	3.90 (m)	70.86	G1,G3	G1	3.89 (m)	70.87	G1,G3	G1
G3	3.52 (d)	69.34	G2	G4,G2	3.50 (dd)	70.17	G2	G4
G4	3.75 (m)	74.71	-	-	3.70 (s)	74.67	-	G5,G3
G5	3.63 (m)	76.86	G6	G6	3.64 (dd)	77.10	G6	G6
G6	3.83 (m)	64.42	G5	-	3.82 (m)	62.95	G5	G5
	3.75 (m)				3.73 (dd)			
S1	-	177.24	-	-	-	180.39	-	-
S2	-	101.49	-	-	-	101.19	-	-
S3	2.87 (dd)	41.96	S4	S5,S4,S2	-	24.23	-	-
	1.82 (t)							
S4	3.90 (m)	70.11	S3	-	3.82 (m)	69.24	S5	S5
S5	3.83 (m)	53.81	S6	-	-	49.95	-	S4
S'5	-	175.64	-	-	-	177.31	-	-
S''5	4.06 (s)	62.70	-	S'5	4.06 (s)	62.69	-	
S6	4.15 (dd)	77.85	S5,S7	S2	4.15 (dd)	77.90	S7	S2
S7	3.90 (m)	73.15	S6	S6	3.89 (m)	73.11	S6	S6
S8	4.04 (d)	69.34	-	S7,S6	4.04 (d)	69.14	-	-
S9	3.83 (m)	62.93	-	S8	3.82 (m)	64.63	-	-
	3.63 (m)				3.61 (dd)			

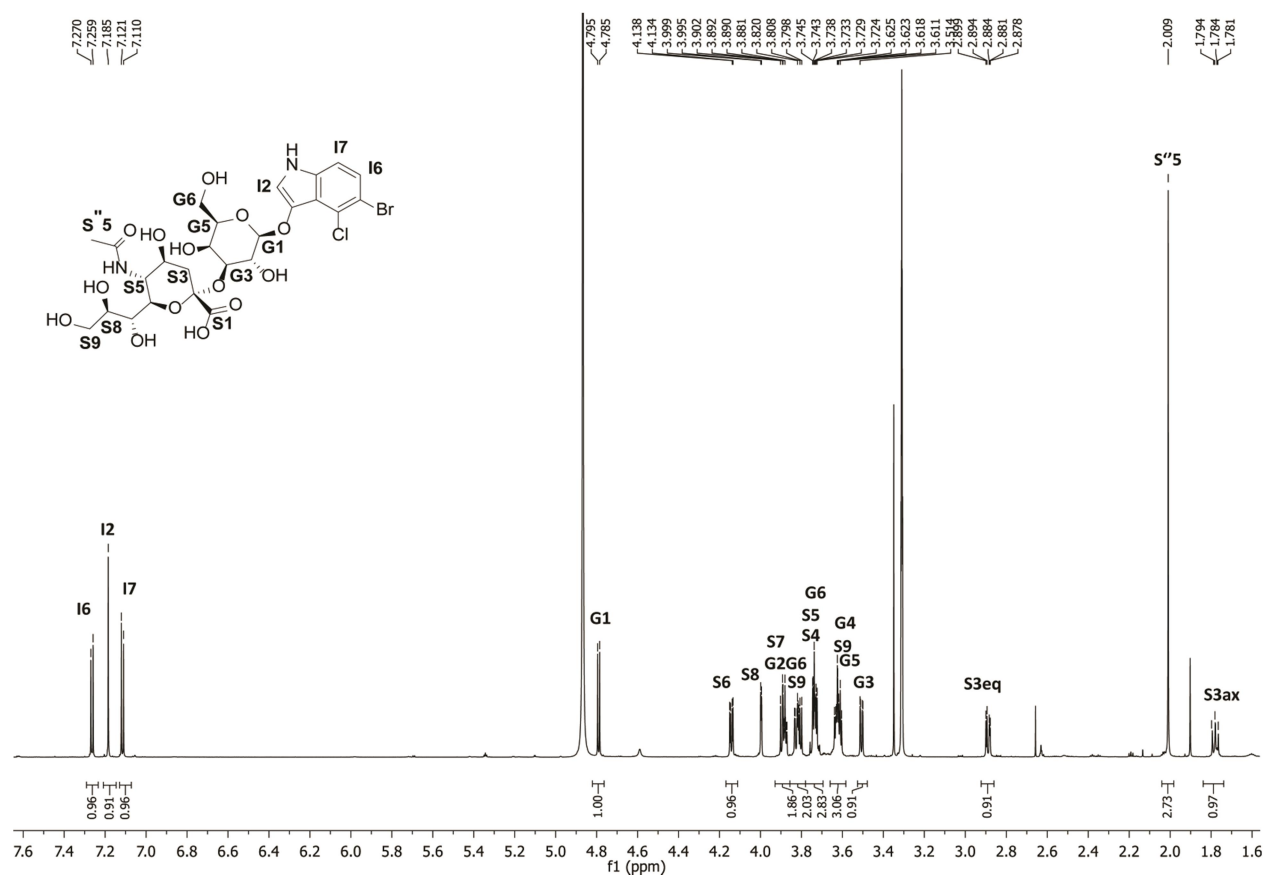


Figure S1. ^1H NMR spectrum of X-Gal-Neu5Ac. The spectrum was collected in a Bruker Avance AV400 using the deuterated methanol residual signal as internal standard.

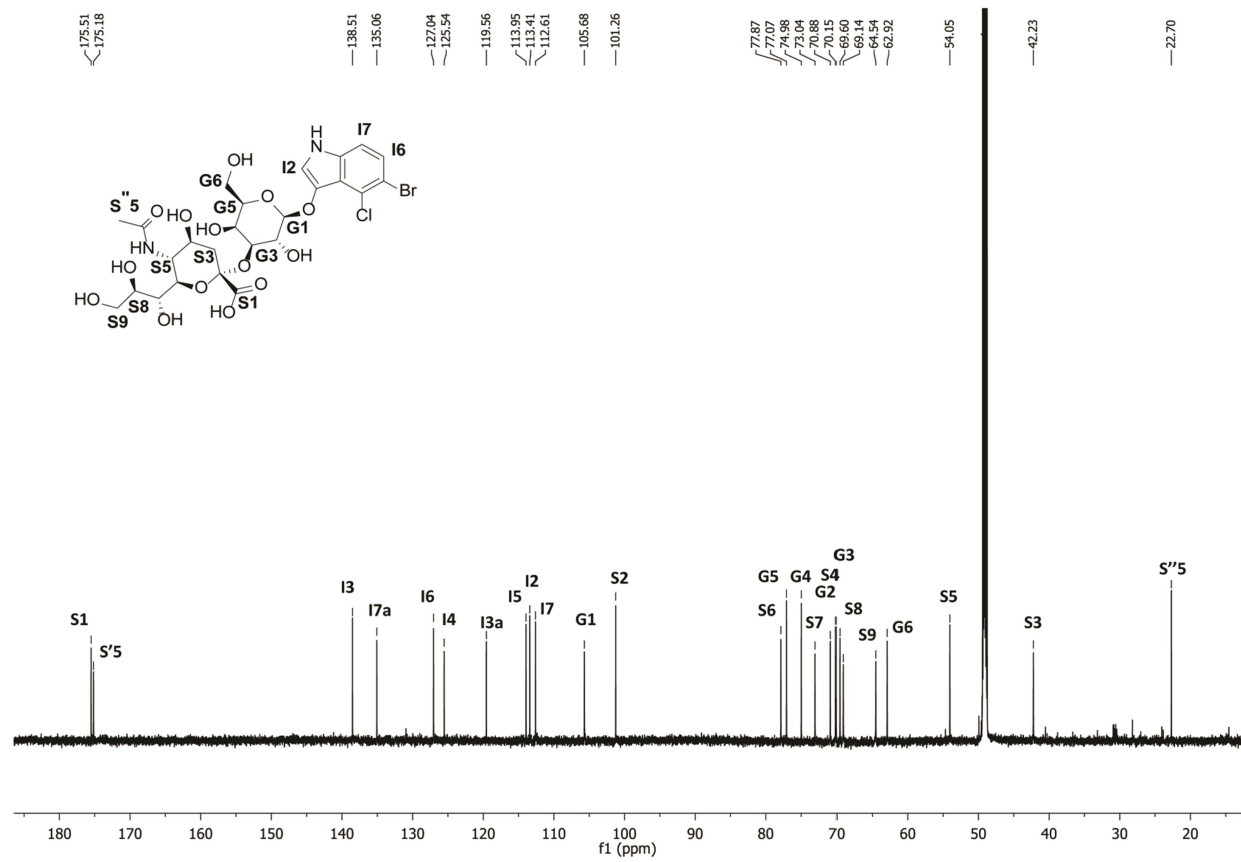


Figure S2. ¹³C NMR spectrum of X-Gal-Neu5Ac. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

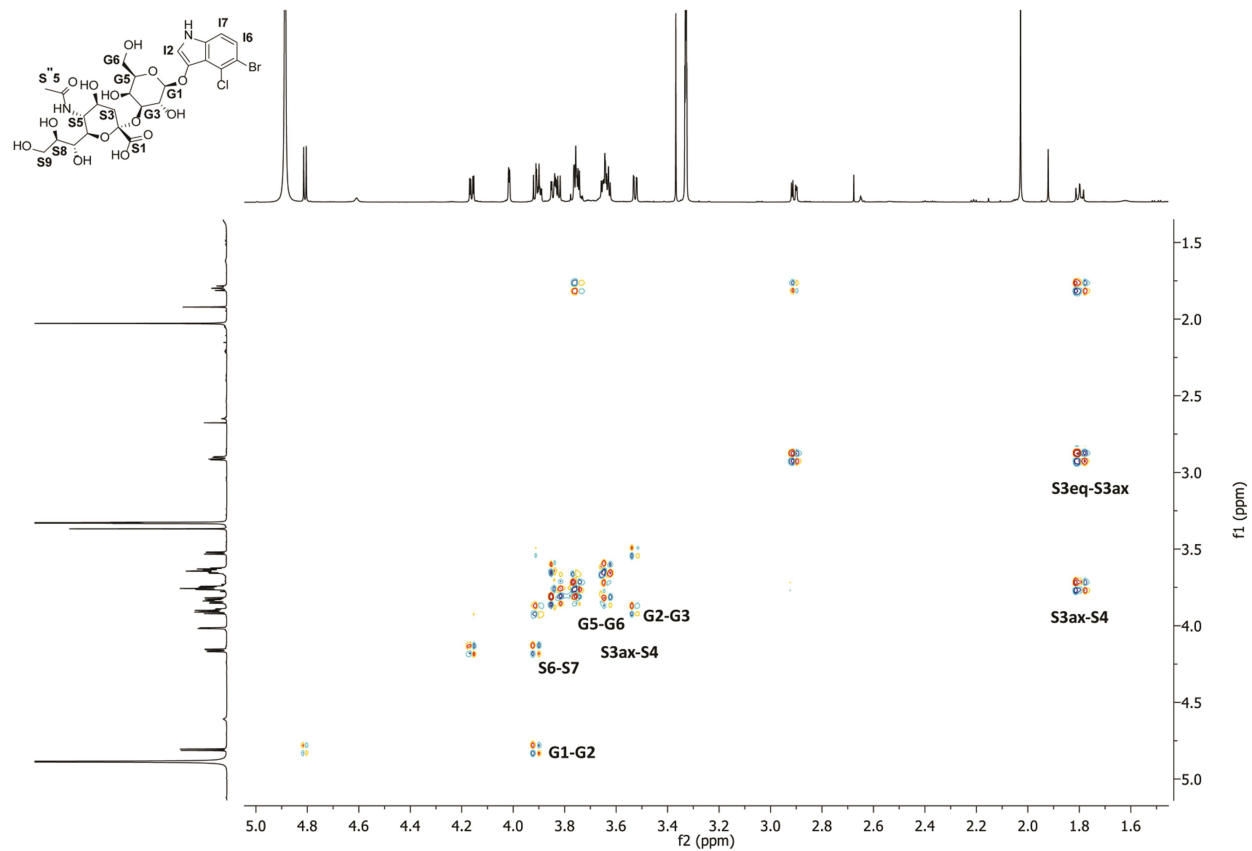


Figure S3. COSY NMR spectrum of X-Gal-Neu5Ac. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

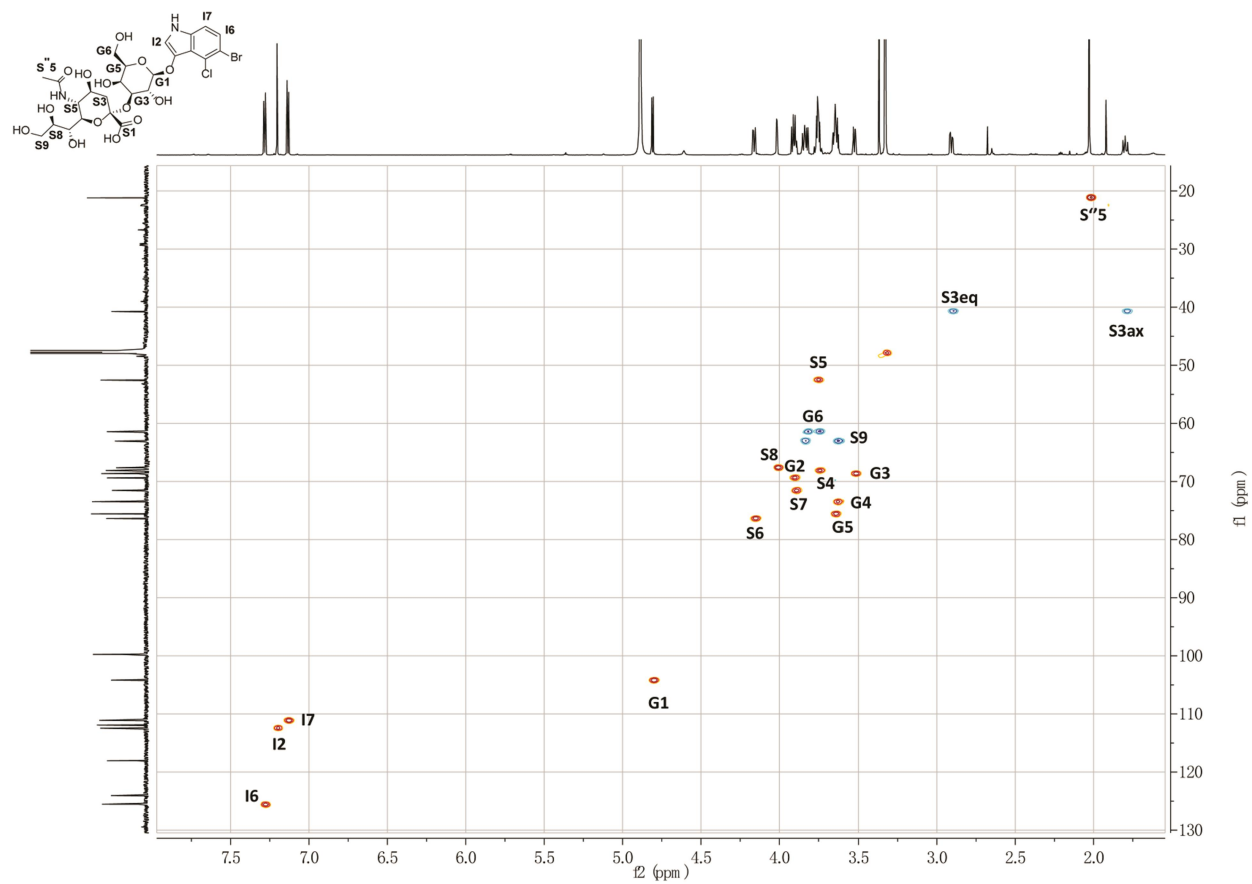


Figure S4. HSQC NMR spectrum of X-Gal-Neu5Ac. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

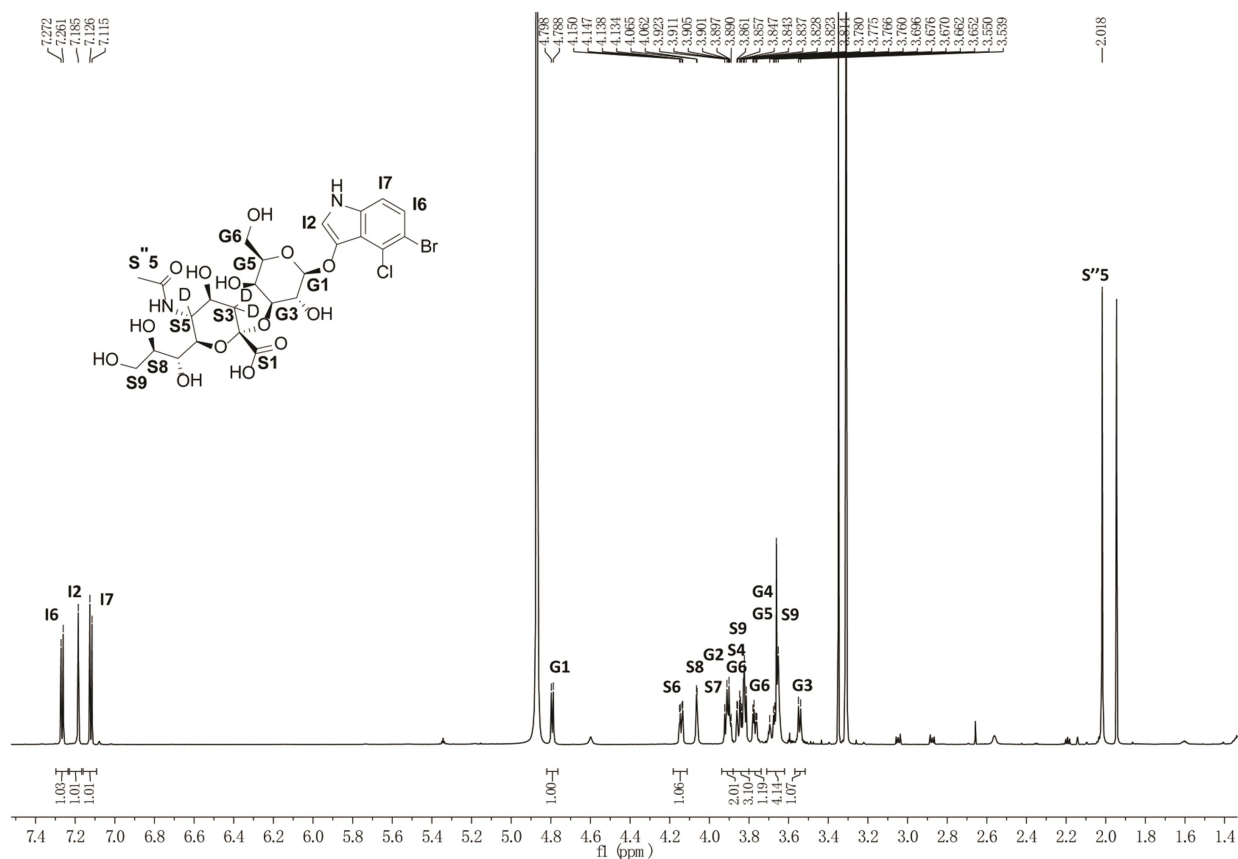


Figure S5. ¹H NMR spectrum of tri-deuterated X-Gal-Neu5Ac (9a). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

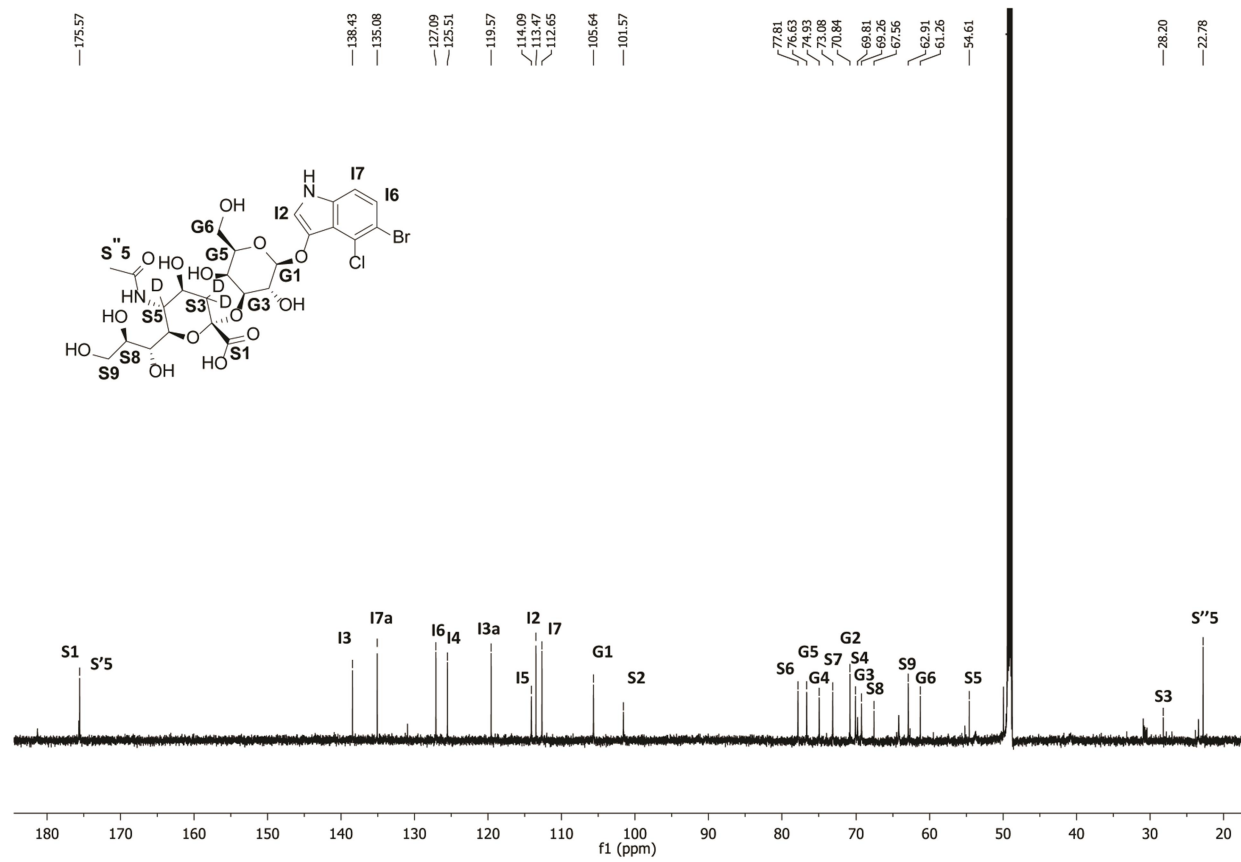


Figure S6. ^{13}C NMR spectrum of tri-deuterated X-Gal-Neu5Ac (9a). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

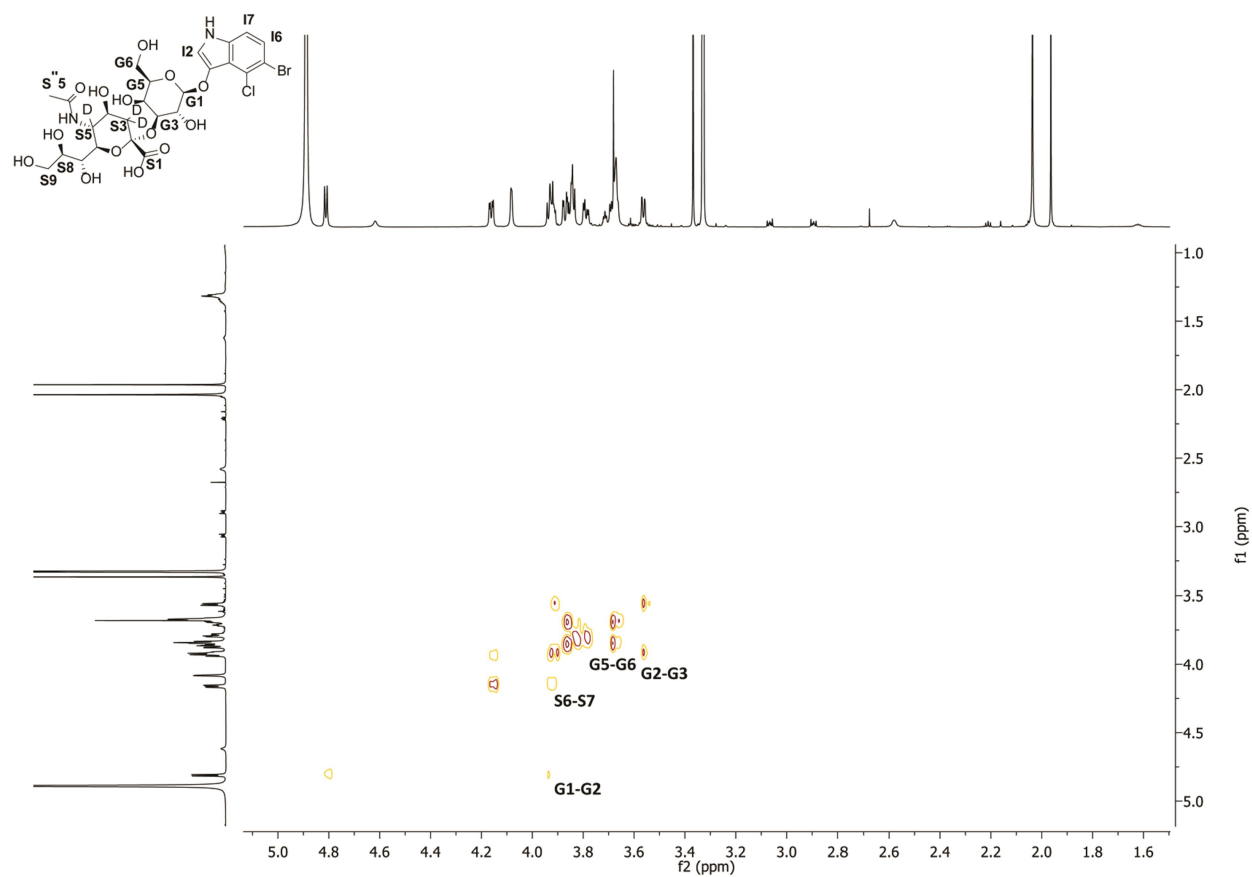


Figure S7. COSY NMR spectrum of tri-deuterated X-Gal-Neu5Ac (**9a**). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

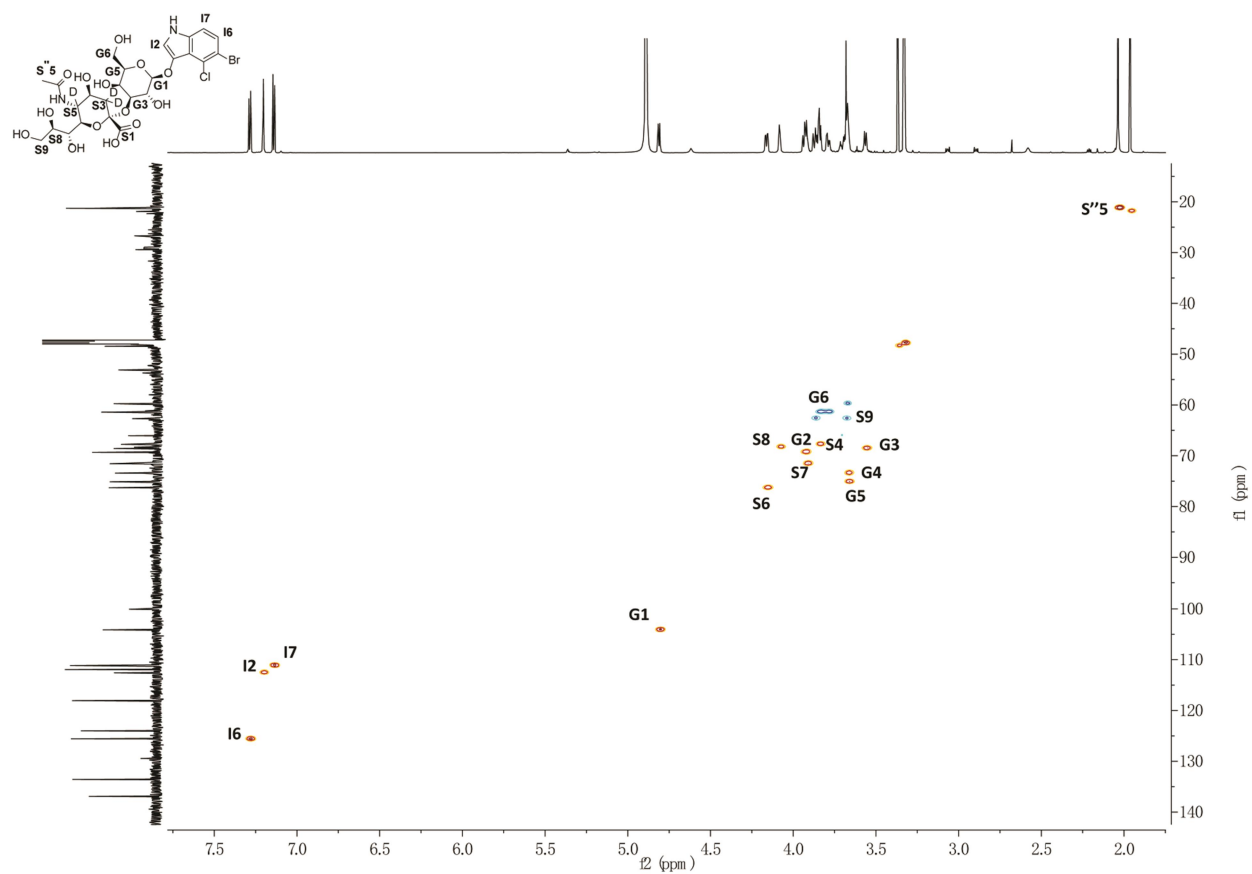


Figure S8. HSQC NMR spectrum of tri-deuterated X-Gal-Neu5Ac (**9a**). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

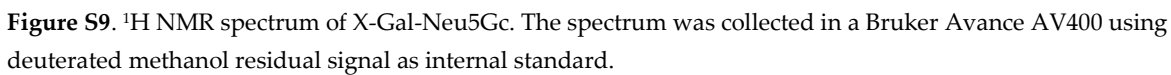


Figure S9. ^1H NMR spectrum of X-Gal-Neu5Gc. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

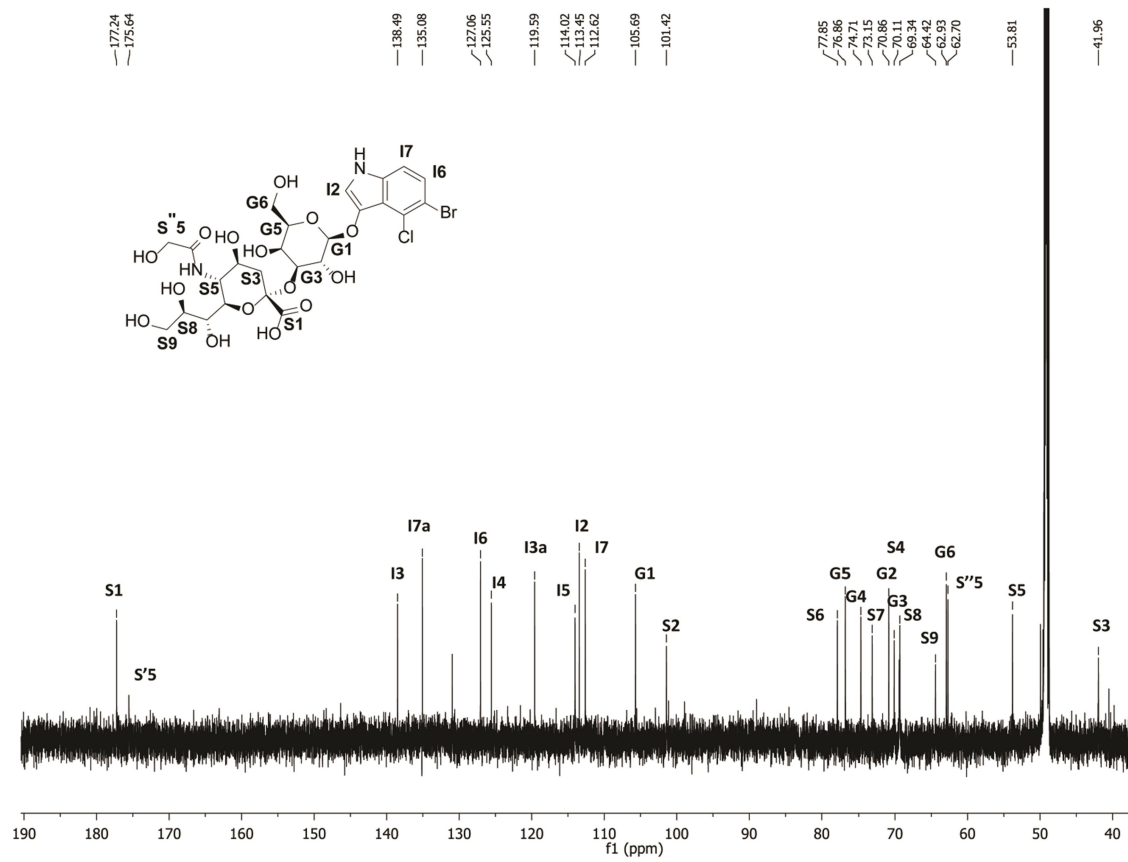


Figure S10. ^{13}C NMR spectrum of X-Gal-Neu5Gc. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

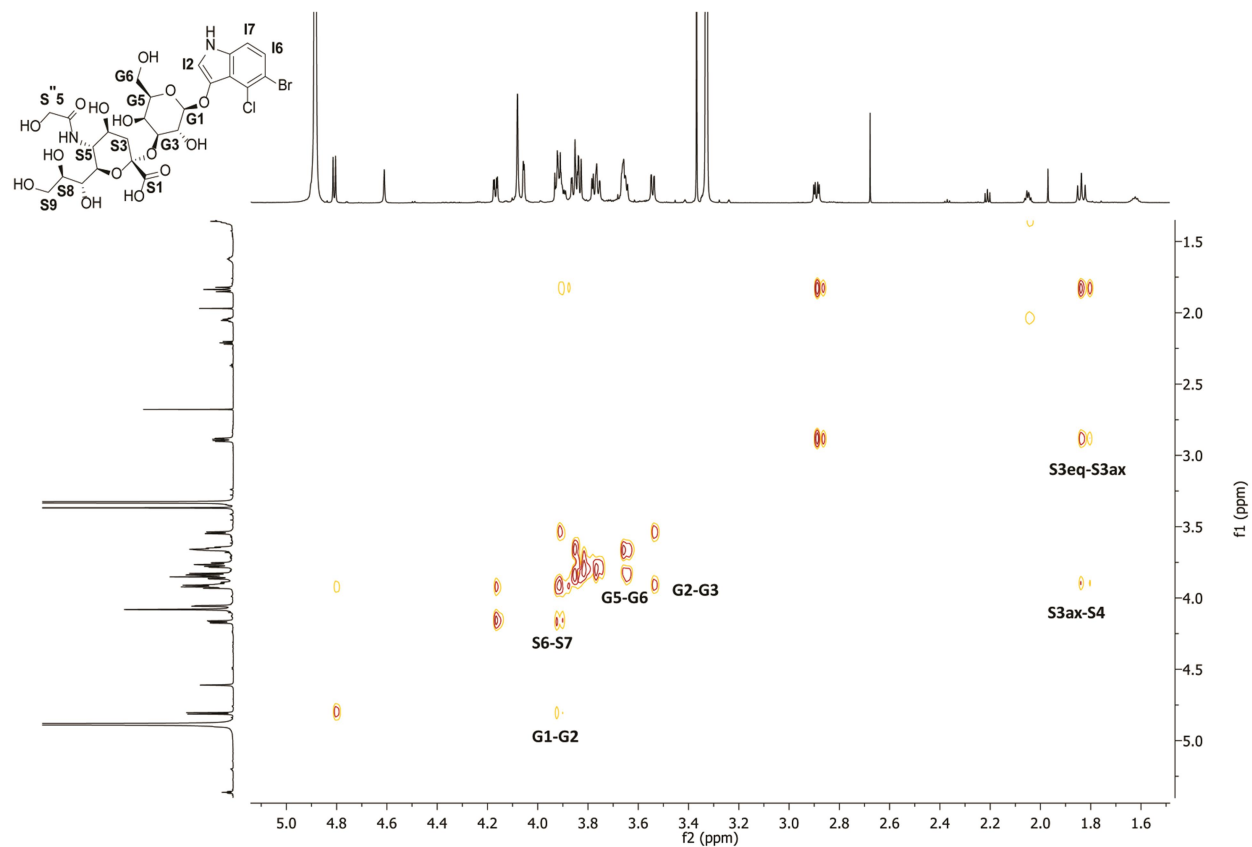


Figure S11. COSY NMR spectrum of X-Gal-Neu5Gc. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

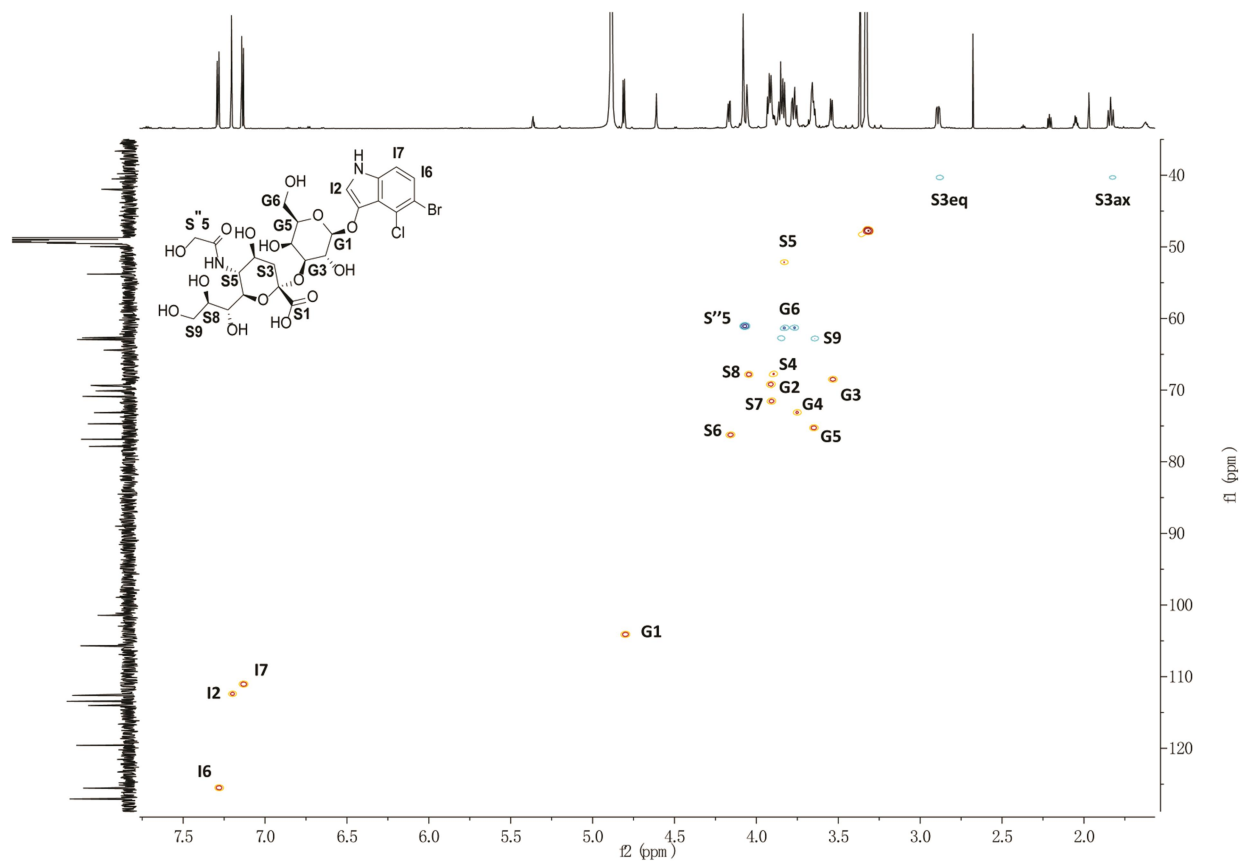


Figure S12. HSQC NMR spectrum of X-Gal-Neu5Gc. The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

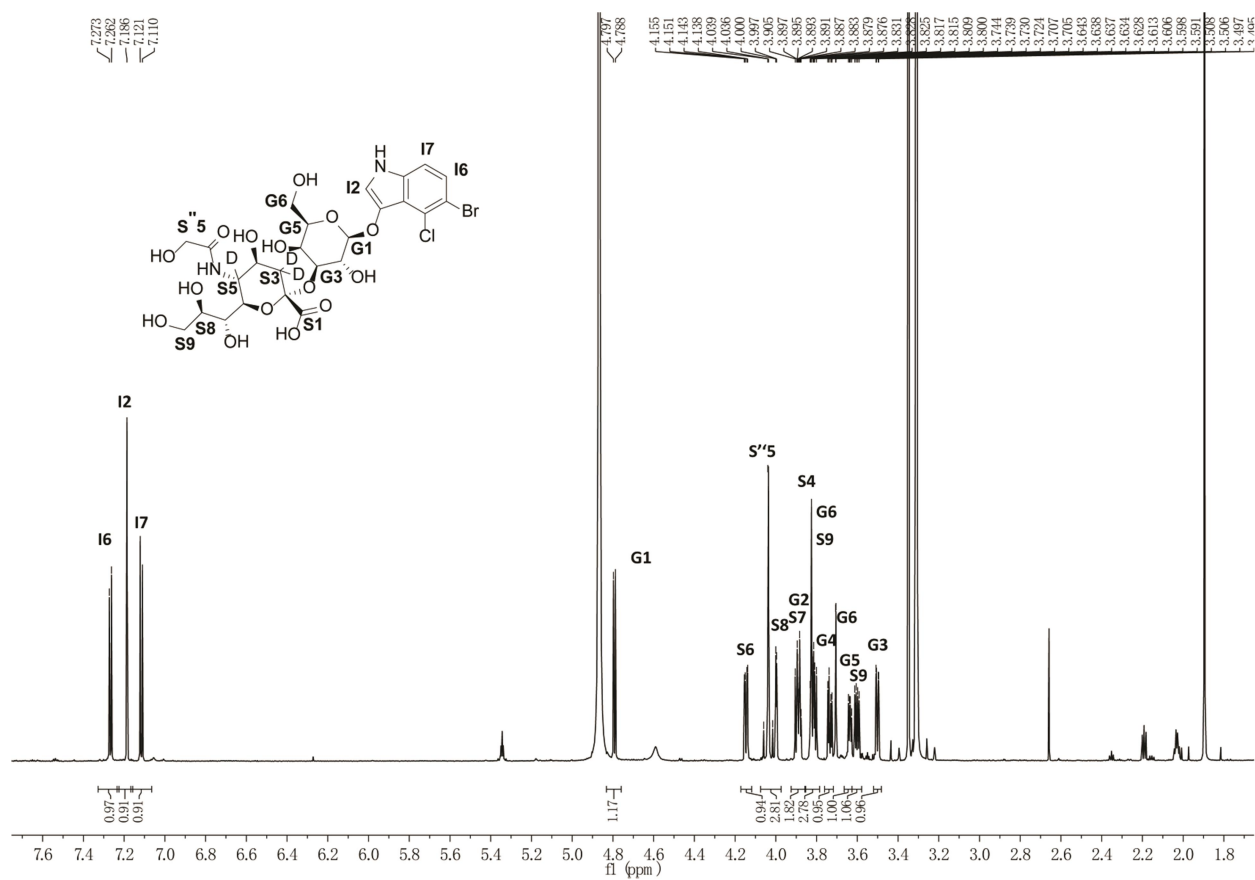


Figure S13. ¹H NMR spectrum of tri-deuterated X-Gal-Neu5Gc (9b). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

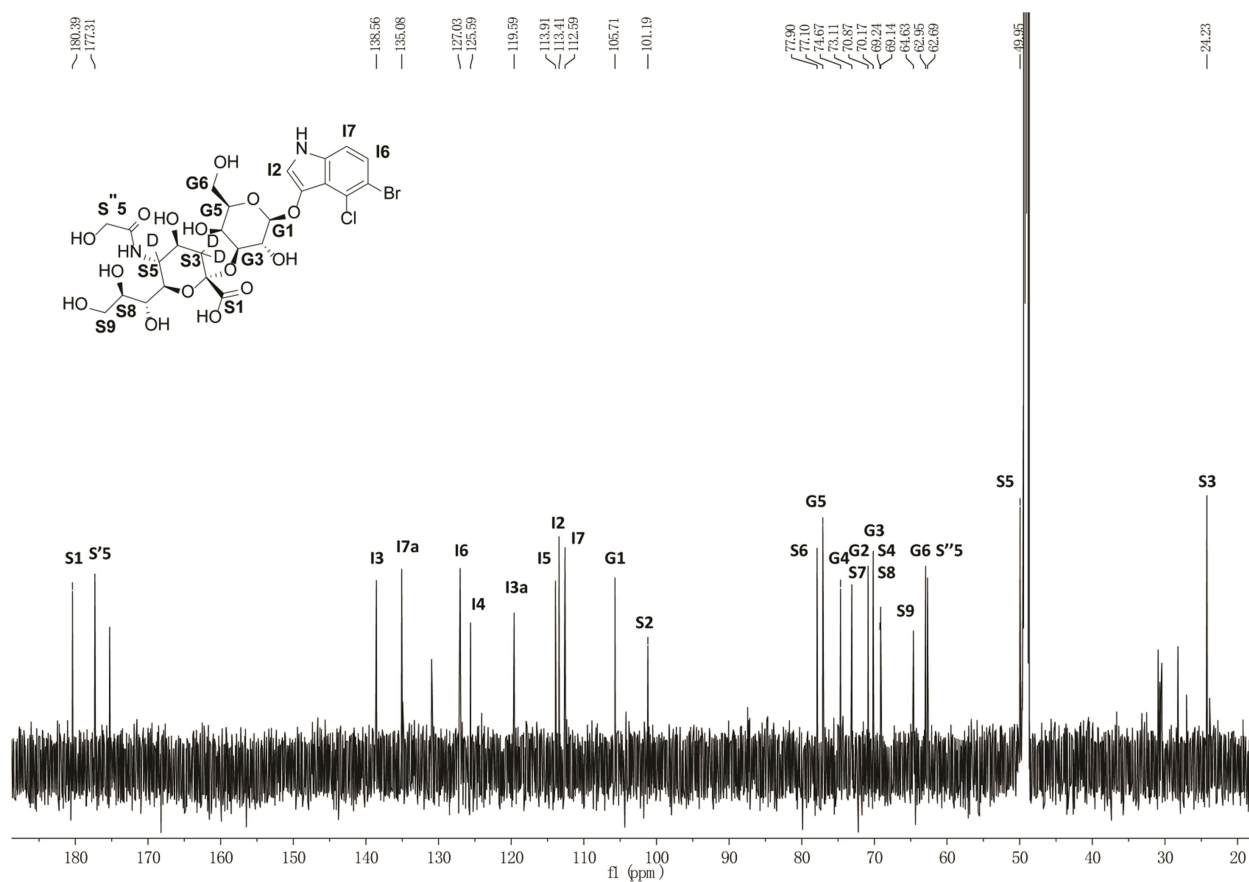


Figure S14. ^{13}C NMR spectrum of tri-deuterated X-Gal-Neu5Gc (**9b**). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

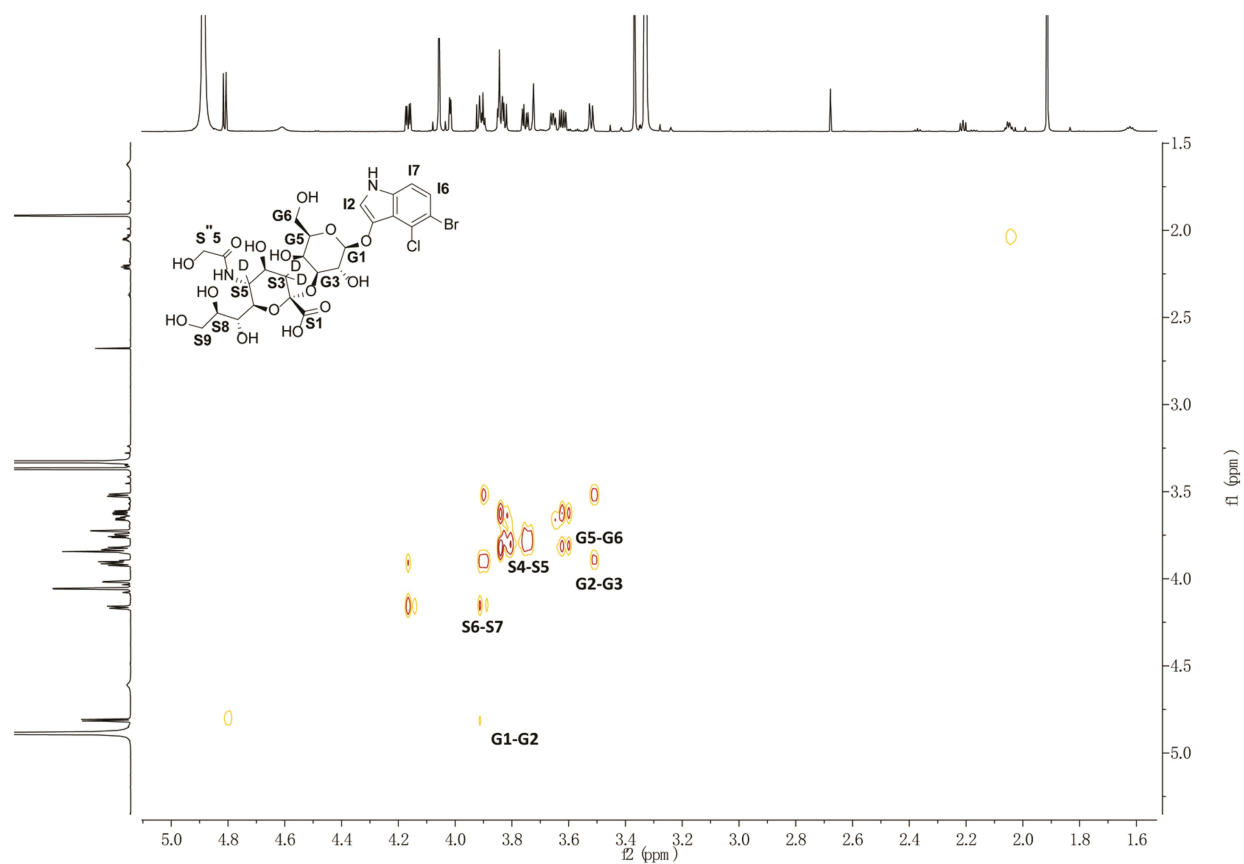


Figure S15. COSY NMR spectrum of tri-deuterated X-Gal-Neu5Gc (**9b**). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.

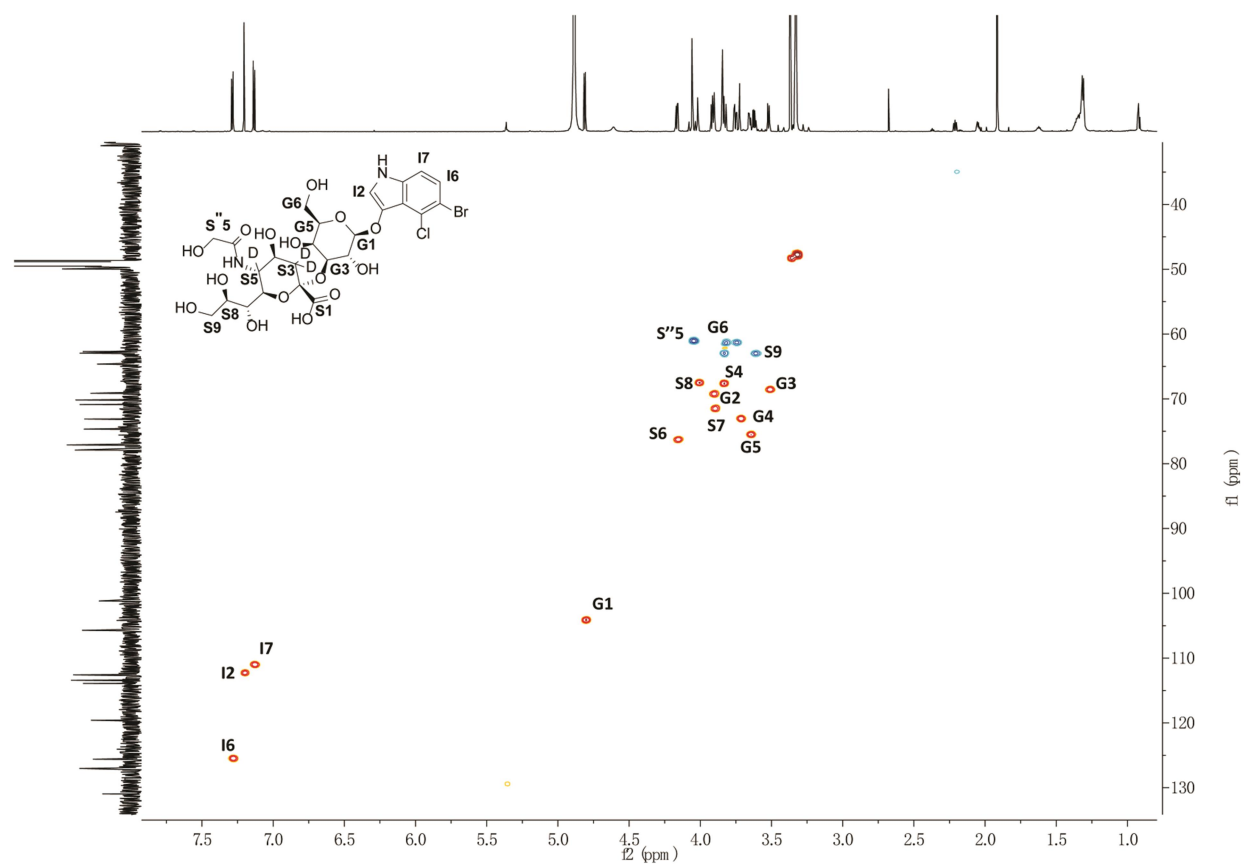


Figure S16. HSQC NMR spectrum of tri-deuterated X-Gal-Neu5Gc (**9b**). The spectrum was collected in a Bruker Avance AV400 using deuterated methanol residual signal as internal standard.