

Table S1. Mass spectrometry data from the 1 h reaction of wild-type *PttXET16-34* with XXXGXXXG. Corresponding HPAEC-PAD data is shown in Figure 4A. Calculated exact mass and m/z values are shown. Values highlighted in bold red text were observed, with errors of less than 35 ppm.

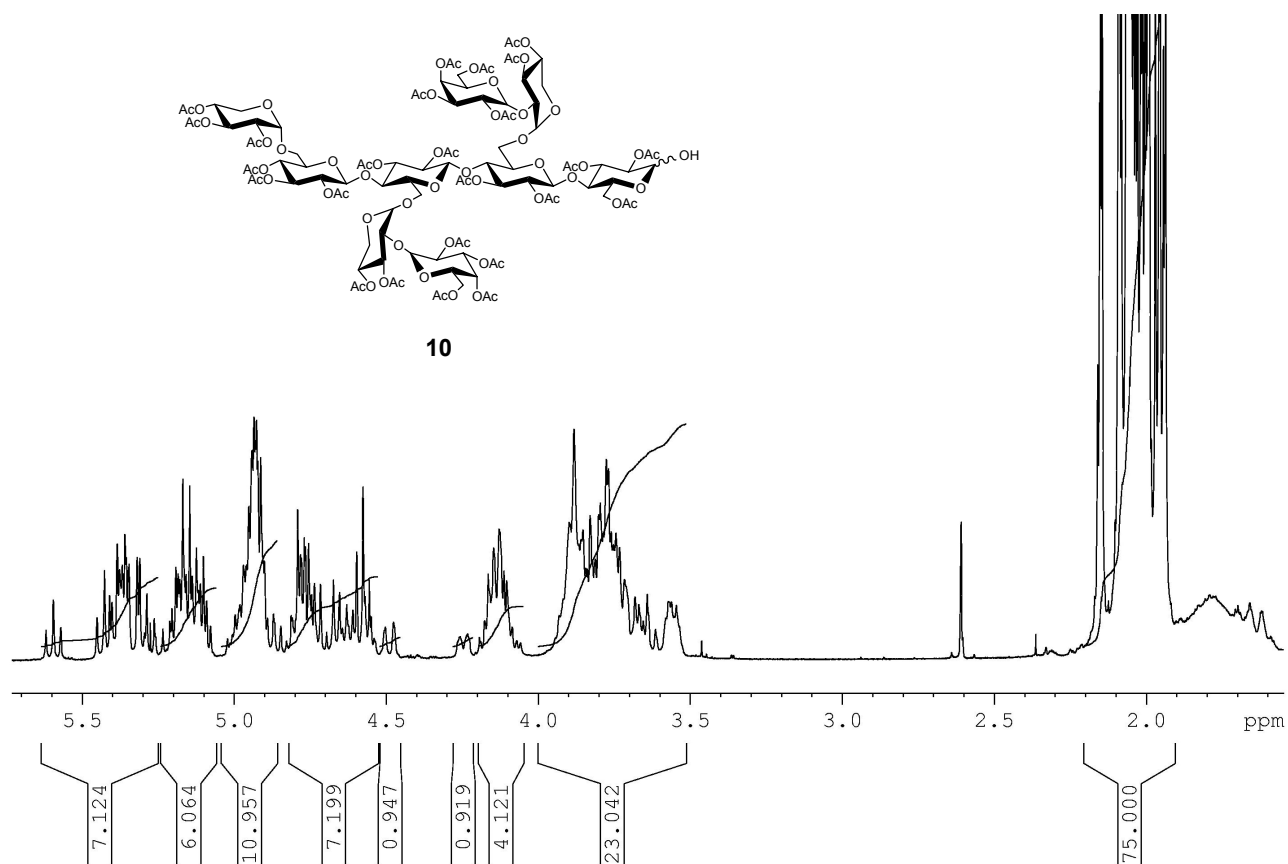
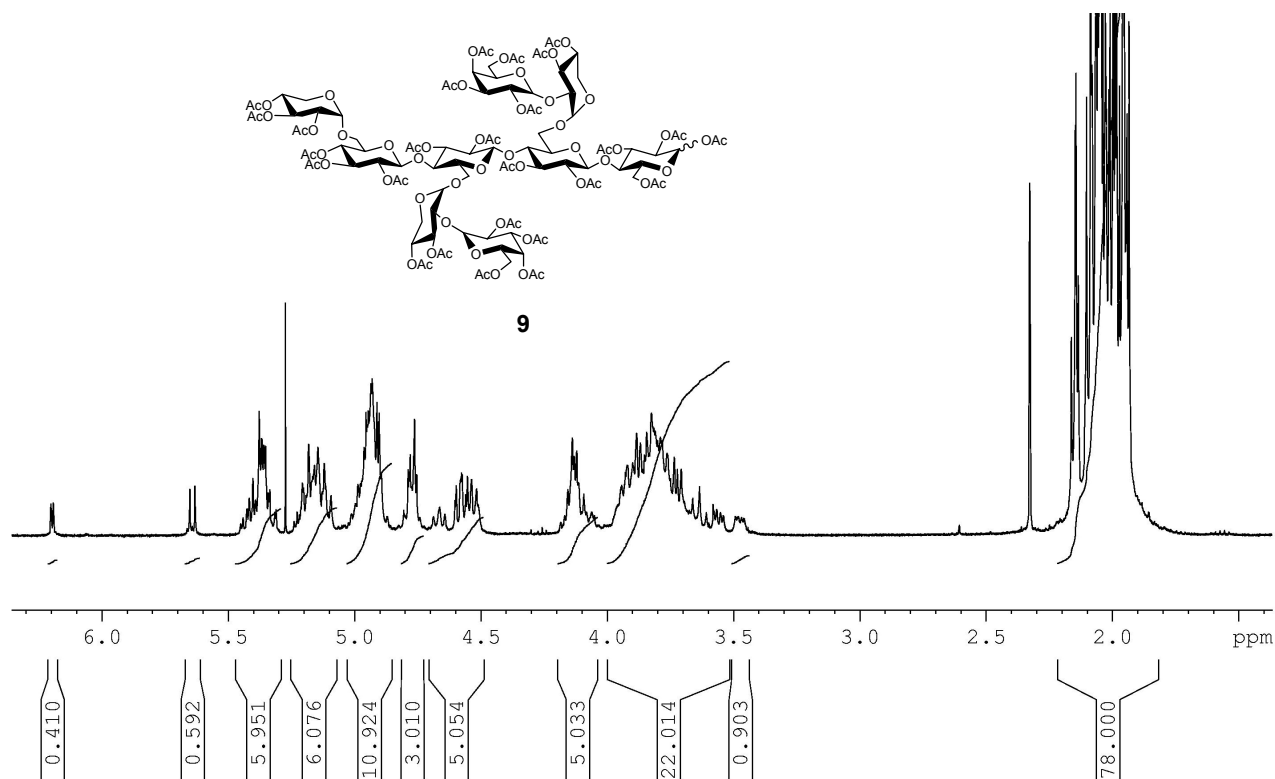
	Exact mass	m/z				
	M_r	$[M+Na]^+$	$[M+2Na]^{2+}$	$[M+3Na]^{3+}$	$[M+4Na]^{4+}$	$[M+5Na]^{5+}$
(XXXG)	1062.3486	1085.3384	554.1641	377.1060	288.5770	235.4595
(XXXG) ₂	2106.6820	2129.6718	1076.3308	725.2171	549.6603	444.3262
(XXXG) ₃	3151.0154	3174.0052	1598.4975	1073.3283	810.7437	653.1929
(XXXG) ₄	4195.3488	4218.3386	2120.6642	1421.4394	1071.8270	862.0596
(XXXG) ₅	5239.6822	5262.6720	2642.8309	1769.5505	1332.9104	1070.9262
(XXXG) ₆	6284.0156	6307.0054	3164.9976	2117.6617	1593.9937	1279.7929
(XXXG) ₇	7328.3490	7351.3388	3687.1643	2465.7728	1855.0771	1488.6596

Table S2. Mass spectrometry data from the 24 h reaction of *PttXET16-34* E95A with XXXGαF and XXXG. Corresponding HPAEC-PAD data is shown in Figure 4C. Calculated exact mass and m/z values are shown. Values highlighted in bold red text were observed, with errors of less than 21 ppm.

	Exact mass	m/z				
	M_r	$[M+Na]^+$	$[M+2Na]^{2+}$	$[M+3Na]^{3+}$	$[M+4Na]^{4+}$	$[M+5Na]^{5+}$
(XXXG)	1062.3486	1085.3384	554.1641	377.1060	288.5770	235.4595
(XXXG) ₂	2106.6820	2129.6718	1076.3308	725.2171	549.6603	444.3262
(XXXG) ₃	3151.0154	3174.0052	1598.4975	1073.3283	810.7437	653.1929
(XXXG) ₄	4195.3488	4218.3386	2120.6642	1421.4394	1071.8270	862.0596
(XXXG) ₅	5239.6822	5262.6720	2642.8309	1769.5505	1332.9104	1070.9262
(XXXG) ₆	6284.0156	6307.0054	3164.9976	2117.6617	1593.9937	1279.7929
(XXXG) ₇	7328.3490	7351.3388	3687.1643	2465.7728	1855.0771	1488.6596

Table S3. Mass spectrometry data from the 36 h reaction of *PttXET16-34* E95A with XLLGαF and XLLG. Corresponding HPAEC-PAD data is shown in Figure 5B. Calculated exact mass and m/z values are shown. Values highlighted in bold red text were observed, with errors of less than 29 ppm.

	Exact mass	m/z				
	M_r	$[M+Na]^+$	$[M+2Na]^{2+}$	$[M+3Na]^{3+}$	$[M+4Na]^{4+}$	$[M+5Na]^{5+}$
(XLLG)	1386.4543	1409.4441	716.2170	485.1412	369.6034	300.2807
(XLLG) ₂	2754.8934	2777.8832	1400.4365	941.2876	711.7132	573.9685
(XLLG) ₃	4123.3325	4146.3223	2084.6561	1397.4340	1053.8229	847.6563
(XLLG) ₄	5491.7716	5514.7614	2768.8756	1853.5803	1395.9327	1121.3441
(XLLG) ₅	6860.2107	6883.2005	3453.0952	2309.7267	1738.0425	1395.0319
(XLLG) ₆	8228.6498	8251.6396	4137.3147	2765.8731	2080.1523	1668.7198
(XLLG) ₇	9597.0889	9620.0787	4821.5343	3222.0194	2422.2620	1942.4076



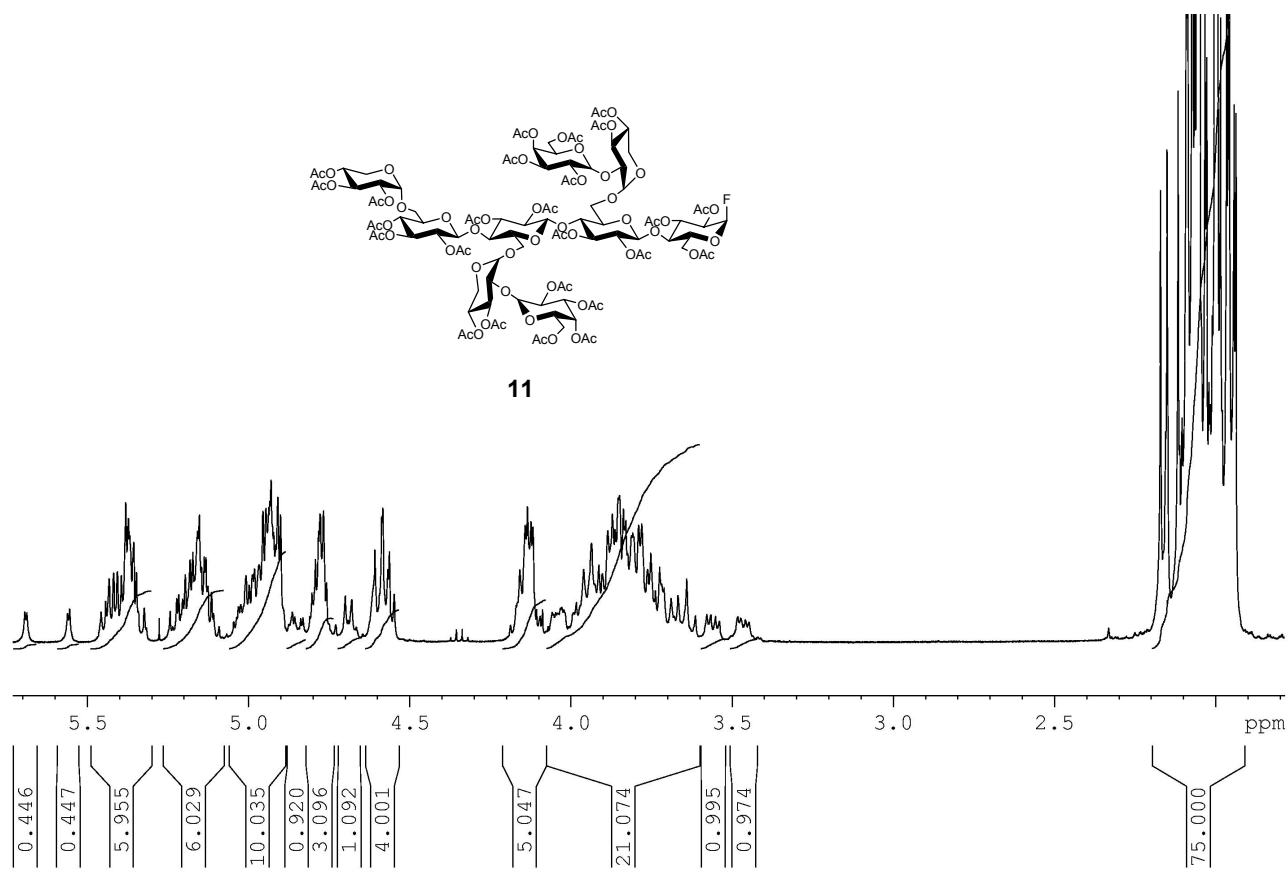


Figure S1. ^1H NMR spectra of xyloglucan oligosaccharide derivatives **9-11** (CDCl_3 , 400 MHz)