Supplementary Table S2 ^{1}H and ^{13}C NMR chemical shifts (δ, ppm) of *S. flexneri* O-polysaccharides

Residue	Monosaccharide					
	C1	C2	C3	C4	C5	C6
	H1	*H2*	*H3 (3a,3b)*	*H4*	*H5*	*H6 (6a,6b)*
Sf301, 301ΔoacB_pSQZ4 (2a)						
→2)-α-L-Rha*p*3Ac^{III}-(1→	102.8	78.2	74.1	71.6	70.8	18.3
	5.15	*4.26*	*5.09*	*3.50*	*3.82*	*1.32*
→2)-α-L-Rha*p*4Ac^{III}-(1→	102.8	79.3	69.7	75.8	68.6	18.2
	5.10	*4.23*	*4.10*	*4.80*	*3.92*	*1.18*
→2)-α-L-Rha*p*^{II}-(1→	102.8	81.0	71.2	73.6	70.7	18.0
	5.06	*4.09*	*3.88*	*3.49*	*3.81*	*1.30*
→3,4)-α-L-Rha*p*^{I}-(1→	102.2	72.2	80.5	76.1	70.5	19.3
	4.88	*3.94*	*3.94*	*3.79*	*4.16*	*1.34*
→3)-β-D-Glc*p*NAc6Ac-(1→	103.7	57.0	82.5	71.2	74.6	64.8
	4.54	*3.85*	*3.66*	*3.42*	*3.63*	*4.21, 4.33*
α-D-Glc*p*-(1→	98.9	72.7	74.1	71.2	73.2	62.1
	5.20	*3.54*	*3.73*	*3.42*	*3.97*	*3.80, 3.89*
301Δoac3B_pSQZ4 (2a)						
→2)-α-L-Rha*p*^{III}-(1→	102.8	80.1	71.2	73.8	70.8	18.3
	5.13	*4.15*	*3.88*	*3.33*	*3.76*	*1.29*
→2)-α-L-Rha*p*^{II}-(1→	103.1	80.7	71.2	73.6	70.8	18.0
	5.02	*4.10*	*3.88*	*3.48*	*3.80*	*1.29*
→3,4)-α-L-Rha*p*^{I}-(1→	102.4	72.2	80.7	76.1	70.5	19.3
	4.84	*3.94*	*3.92*	*3.79*	*4.16*	*1.34*
→3)-β-D-Glc*p*NAc6Ac-(1→	103.7	57.0	82.5	71.2	74.6	64.8
	4.54	*3.85*	*3.66*	*3.42*	*3.63*	*4.21, 4.33*
α-D-Glc*p*-(1→	98.9	72.7	74.1	71.2	73.2	62.1
	5.20	*3.54*	*3.73*	*3.42*	*3.97*	*3.80, 3.89*

51251 (2b)						
→2,3)-α-L-Rha*p*^{III}-(1→	102.8	75.7	75.1	72.3	70.7	18.4
	5.12	*4.43*	*3.95*	*3.36*	*3.79*	*1.30*
→2)-α-L-Rha*p*^{II}-(1→	102.7	80.9	71.2	73.6	70.7	18.1
	5.05	*4.11*	*3.88*	*3.49*	*3.79*	*1.31*
→3,4)-α-L-Rha*p*^{I}-(1→	102.4	72.2	80.5	76.1	70.4	19.3
	4.83	*3.92*	*3.92*	*3.79*	*4.15*	*1.34*
→3)-β-D-Glc*p*NAc-(1→	103.0	56.8	83.0	69.8	77.4	62.2
	4.80	*3.86*	*3.49*	*3.54*	*3.48*	*3.76, 3.91*
α-D-Glc*p*^{I}-(1→	98.7	72.7	74.1	71.2	73.2	61.8
	5.19	*3.55*	*3.72*	*3.43*	*3.96*	*3.78, 3.83*
α-D-Glc*p*^{II}-(1→	95.9	72.8	74.6	71.0	72.8	62.1
	5.18	*3.72*	*3.83*	*3.50*	*4.04*	*3.79, 3.87*
51251_pSQZ4 (2a)						
→2)-α-L-Rha*p*3Ac^{III}-(1→	102.7	78.2	74.0	71.6	70.8	18.2
	5.16	*4.25*	*5.07*	*3.50*	*3.85*	*1.31*
→2)-α-L-Rha*p*4Ac^{III}-(1→	102.*7*	79.1	69.5	75.6	68.7	18.2
	5.14	*4.23*	*4.10*	*4.79*	*3.91*	*1.17*
→2)-α-L-Rha*p*^{II}-(1→	102.7	80.9	71.1	73.4	70.7	18.0
	5.05	*4.12*	*3.88*	*3.53*	*3.80*	*1.29*
→3,4)-α-L-Rha*p*^{I}-(1→	102.2	72.2	80.5	76.0	70.5	19.2
	4.87	*3.93*	*3.93*	*3.80*	*4.16*	*1.34*
→3)-β-D-Glc*p*NAc-(1→	103.8	56.9	82.4	69.4	76.9	62.1
	4.52	*3.84*	*3.65*	*3.56*	*3.38*	*3.78, 3.88*
α-D-Glc*p*-(1→	98.8	72.6	74.0	71.2	73.2	62.1
	5.19	*3.54*	*3.72*	*3.42*	*3.97*	*3.78, 3.88*

51580 (X)						
→2,3)-α-L-Rha*p*^{III}-(1→	102.2	75.6	74.9	72.1	70.7	18.0
	5.10	*4.43*	*3.94*	*3.35*	*3.72*	*1.24*
→2)-α-L-Rha*p*^{II}-(1→	101.9	79.6	71.1	73.2	70.3	17.8
	5.19	*4.07*	*3.92*	*3.48*	*3.74*	*1.31*
→3)-α-L-Rha*p*^{I}-(1→	102.2	71.8	78.4	72.9	70.2	17.6
	4.85	*3.84*	*3.78*	*3.53*	*4.02*	*1.23*
→3)-β-D-Glc*p*NAc-(1→	102.5	56.7	82.8	69.5	77.3	62.0
	4.82	*3.85*	*3.49*	*3.51*	*3.43*	*3.74, 3.90*
α-D-Glc*p*-(1→	95.7	72.6	74.4	70.7	72.7	61.5
	5.18	*3.72*	*3.83*	*3.49*	*4.04*	*3.78, 3.82*
51580_pSQZ4 (Y)						
→2)-α-L-Rha*p*3Ac^{III}-(1→	102.5	78.3	74.0	71.4	70.7	18.1
	5.16	*4.25*	*5.06*	*3.50*	*3.79*	*1.27*
→2)-α-L-Rha*p*4Ac^{III}-(1→	102.8	79.2	69.6	75.6	68.6	18.1
	5.13	*4.23*	*4.10*	*4.78*	*3.85*	*1.13*
→2)-α-L-Rha*p*^{II}-(1→	102.2	79.9	71.4	73.5	70.6	18.1
	5.18	*4.07*	*3.92*	*3.53*	*3.76*	*1.31*
→3)-α-L-Rha*p*^{I}-(1→	102.6	72.0	78.6	73.1	70.5	17.8
	4.89	*3.85*	*3.80*	*3.55*	*4.01*	*1.23*
→3)-β-D-Glc*p*NAc-(1→	103.6	57.1	82.6	69.5	77.1	62/0
	4.54	*3.85*	*3.65*	*3.55*	*3.40*	*3.73, 3.93*

Only major chemical shifts are given for GlcNAc6Ac and non-O-acetylated monosaccharide residues, whose signals are split owing to non-stoichiometric O-acetylation on Rha^{III}.
Additional signals for NAc are at δ_C 175.3-176.0 (CO) and 23.7-23.8 (CH_3), δ_H 2.05-2.11 (CH_3); for OAc at δ_C 175.1-175.3 (CO) and 21.7-22.1 (CH_3), δ_H 2.13-2.21.