Supplementary Table 1. Variation in amide HN chemical shifts with pH for selected oligosaccharides.

Chemical shifts of high- and low-field components of each couplet are given, with their mean in bold
These data were fit to generate the pK_a values shown in Table 1.

A. Titration of HA_3^{NN}

pH	**6.03**	**5.48**	**4.94**	**4.56**	**4.15**	**3.79**	**3.35**	**2.84**	**2.46**	**2.06**	**1.77**	**1.43**
βHN	8.278	8.279	8.278	8.278	8.278	8.277	8.274	8.268	8.265	8.261	8.261	8.263
	8.265	8.265	8.265	8.264	8.265	8.263	8.261	8.255	8.251	8.248	8.247	8.250
ppm	**8.272**	**8.272**	**8.272**	**8.271**	**8.272**	**8.270**	**8.268**	**8.262**	**8.258**	**8.255**	**8.254**	**8.257**
αHN	8.194	8.195	8.194	8.194	8.194	8.193	8.191	8.187	8.184	8.182	8.182	8.184
	8.182	8.182	8.181	8.181	8.181	8.180	8.179	8.174	8.172	8.169	8.169	8.171
ppm	**8.188**	**8.189**	**8.188**	**8.188**	**8.188**	**8.187**	**8.185**	**8.181**	**8.178**	**8.176**	**8.176**	**8.178**
ωHN	7.955	7.956	7.957	7.958	7.963	7.970	7.989	8.026	8.050	8.076	8.087	8.095
	7.942	7.943	7.943	7.945	7.949	7.957	7.976	8.013	8.037	8.063	8.074	8.082
ppm	**7.949**	**7.950**	**7.950**	**7.952**	**7.956**	**7.964**	**7.983**	**8.020**	**8.044**	**8.070**	**8.081**	**8.089**

B. Titration of Δ4,5-HA_4

pH	**6.03**	**4.98**	**4.46**	**4.08**	**3.78**	**3.43**	**3.04**	**2.64**	**2.19**	**1.82**	**1.43**
βHN	8.279	8.279	8.278	8.277	8.276	8.273	8.27	8.265	8.261	8.262	8.262
	8.265	8.265	8.265	8.264	8.262	8.26	8.256	8.252	8.248	8.248	8.248
	8.272	**8.272**	**8.2715**	**8.2705**	**8.269**	**8.2665**	**8.263**	**8.2585**	**8.2545**	**8.255**	**8.255**
αHN	8.199	8.199	8.198	8.197	8.195	8.193	8.19	8.186	8.183	8.182	8.182
	8.186	8.186	8.185	8.184	8.182	8.18	8.177	8.173	8.17	8.169	8.169
ppm	**8.1925**	**8.1925**	**8.1915**	**8.1905**	**8.1885**	**8.1865**	**8.1835**	**8.1795**	**8.1765**	**8.1755**	**8.1755**
ωHN	8.147	8.148	8.151	8.156	8.164	8.179	8.199	8.227	8.252	8.266	8.272
	8.134	8.135	8.138	8.143	8.15	8.166	8.186	8.213	8.239	8.252	8.259
ppm	**8.1405**	**8.1415**	**8.1445**	**8.1495**	**8.157**	**8.1725**	**8.1925**	**8.22**	**8.2455**	**8.259**	**8.2655**
vinyllic ^{1}H	**5.849**	**5.854**	**5.867**	**5.89**	**5.922**	**5.98**	**6.049**	**6.125**	**6.183**	**6.212**	**6.224**

C. Titration of unlabelled HA_4

pH	**6.06**	**5.60**	**5.21**	**4.85**	**4.51**	**4.14**	**3.78**	**3.48**	**3.08**	**2.73**	**2.41**	**2.10**	**1.76**	**1.40**
βHN	8.279	8.279	8.279	8.279	8.278	8.278	8.275	8.274	*8.270*	8.265	8.262	8.260	8.260	8.261
	8.265	8.266	8.266	8.265	8.265	8.264	8.261	8.260	8.256	*8.251*	8.249	8.247	8.246	8.248
ppm	**8.272**	**8.273**	**8.273**	**8.272**	**8.272**	**8.271**	**8.268**	**8.267**	**8.263**	**8.258**	**8.256**	**8.254**	**8.253**	**8.255**
αHN	8.198	8.199	8.199	8.198	8.199	8.198	8.195	8.193	8.189	8.185	8.182	8.181	8.180	8.181
	8.185	8.186	8.186	8.185	8.186	8.185	8.182	8.180	8.176	8.172	8.170	8.168	8.168	8.168
ppm	**8.192**	**8.193**	**8.193**	**8.192**	**8.193**	**8.192**	**8.189**	**8.187**	**8.183**	**8.179**	**8.176**	**8.175**	**8.174**	**8.175**
ωHN	8.063	8.064	8.064	8.064	8.067	8.071	8.078	8.088	8.106	8.124	8.143	8.157	8.168	8.175
	8.049	8.050	8.050	8.051	8.053	8.058	8.064	8.074	8.093	8.111	8.129	8.144	8.154	8.161
ppm	**8.056**	**8.057**	**8.057**	**8.058**	**8.060**	**8.065**	**8.071**	**8.081**	**8.100**	**8.118**	**8.136**	**8.151**	**8.161**	**8.168**

D. Titration of ^{15}N-HA_4

pH	**6.11**	**5.05**	**4.42**	**4.06**	**3.66**	**3.26**	**2.97**	**2.65**	**2.32**	**1.92**	**1.67**	**1.4**
βHN	8.274	8.273	8.272	8.272	8.269	8.266	8.263	8.260	8.256	8.254	8.253	8.252
	8.261	8.260	8.259	8.259	8.256	8.253	8.250	8.247	8.243	8.241	8.240	8.239
ppm	**8.268**	**8.267**	**8.266**	**8.266**	**8.263**	**8.260**	**8.257**	**8.254**	**8.250**	**8.248**	**8.247**	**8.246**
^{15}N ppm	**122.078**	**122.074**	**122.064**	**122.048**	**122.017**	**121.958**	**121.891**	**121.840**	**121.786**	**121.754**	**121.752**	**121.765**
αHN	8.194	8.193	8.192	8.192	8.189	8.186	8.183	8.180	8.176	8.174	8.174	8.172
	8.181	8.180	8.179	8.179	8.176	8.173	8.170	8.167	8.164	8.162	8.161	8.159
ppm	**8.188**	**8.187**	**8.186**	**8.186**	**8.183**	**8.180**	**8.177**	**8.174**	**8.170**	**8.168**	**8.168**	**8.166**
^{15}N ppm	**122.945**	**122.941**	**122.934**	**122.922**	**122.899**	**122.858**	**122.815**	**122.781**	**122.749**	**122.730**	**122.728**	**122.738**
ω^{α}HN	8.059	8.059	8.062	8.067	8.076	8.093	8.114	8.130	8.146	8.159	8.164	8.166
	8.046	8.046	8.049	8.054	8.062	8.080	8.100	8.117	8.133	8.146	8.151	8.152
ppm	**8.053**	**8.053**	**8.056**	**8.061**	**8.069**	**8.087**	**8.107**	**8.124**	**8.140**	**8.153**	**8.158**	**8.159**
^{15}N ppm	**122.145**	**122.136**	**122.112**	**122.072**	**122.001**	**121.867**	**121.718**	**121.604**	**121.486**	**121.403**	**121.379**	**121.377**
ω^{β}HN	8.059	8.059	8.062	8.066	8.073	8.088	8.108	8.125	8.142	8.157	8.163	8.164
	8.046	8.046	8.049	8.053	8.059	8.075	8.095	8.112	8.129	8.144	8.149	8.152
ppm	**8.053**	**8.053**	**8.056**	**8.060**	**8.066**	**8.082**	**8.102**	**8.119**	**8.136**	**8.151**	**8.156**	**8.158**
^{15}N ppm	**122.145**	**122.136**	**122.112**	**122.08**	**122.013**	**121.885**	**121.742**	**121.63**	**121.511**	**121.422**	**121.397**	**121.393**

E. Titration of ^{15}N-HA$_6$

pH	6.11	4.98	4.41	4.00	3.60	3.30	2.96	2.57	2.21	1.84	1.42
βHN	8.275	8.275	8.274	8.272	8.269	8.266	8.262	8.257	8.254	8.254	8.255
	8.262	8.262	8.261	8.259	8.256	8.253	8.248	8.244	8.242	8.241	8.242
ppm	**8.269**	**8.269**	**8.268**	**8.266**	**8.263**	**8.260**	**8.255**	**8.251**	**8.248**	**8.248**	**8.249**
^{15}N ppm	**122.093**	**122.093**	**122.074**	**122.046**	**121.994**	**121.951**	**121.887**	**121.820**	**121.772**	**121.750**	**121.762**
αHN	8.196	8.196	8.195	8.193	8.190	8.187	8.182	8.178	8.176	8.175	8.175
	8.184	8.184	8.183	8.180	8.177	8.174	8.170	8.165	8.163	8.162	8.162
ppm	**8.190**	**8.190**	**8.189**	**8.187**	**8.184**	**8.181**	**8.176**	**8.172**	**8.170**	**8.169**	**8.169**
^{15}N ppm	**122.956**	**122.950**	**122.941**	**122.920**	**122.884**	**122.855**	**122.811**	**122.769**	**122.741**	**122.728**	**122.740**
ωHN	8.048	8.050	8.055	8.063	8.078	8.090	8.108	8.127	8.145	8.159	8.167
	8.035	8.037	8.042	8.050	8.066	8.078	8.095	8.114	8.132	8.145	8.155
ppm	**8.042**	**8.044**	**8.049**	**8.057**	**8.072**	**8.084**	**8.102**	**8.121**	**8.139**	**8.152**	**8.161**
^{15}N ppm	**122.109**	**122.095**	**122.066**	**122.009**	**121.908**	**121.824**	**121.699**	**121.569**	**121.470**	**121.406**	**121.384**
γ^{α}HN	8.057	8.058	8.062	8.068	8.080	8.092	8.109	8.128	8.144	8.155	8.162
	8.044	8.045	8.048	8.054	8.067	8.078	8.096	8.115	8.131	8.143	8.149
ppm	**8.051**	**8.052**	**8.055**	**8.061**	**8.074**	**8.085**	**8.103**	**8.122**	**8.138**	**8.149**	**8.156**
^{15}N ppm	**122.000**	**121.989**	**121.966**	**121.919**	**121.830**	**121.754**	**121.637**	**121.510**	**121.405**	**121.339**	**121.317**
γ^{β}HN	8.057	8.058	8.062	8.065	8.076	8.086	8.103	8.124	8.141	8.153	8.162
	8.044	8.045	8.048	8.051	8.063	8.073	8.090	8.110	8.127	8.140	8.148
ppm	**8.051**	**8.052**	**8.055**	**8.058**	**8.070**	**8.080**	**8.097**	**8.117**	**8.134**	**8.147**	**8.155**
^{15}N ppm	**122.000**	**121.989**	**121.966**	**121.928**	**121.844**	**121.773**	**121.661**	**121.535**	**121.429**	**121.357**	**121.332**

F. Titration of GlcNAc

pH	6.10	5.99	4.98	3.99	3.07	2.29	1.41
βHN	8.180	8.180	8.180	8.180	8.180	8.181	8.184
	8.167	8.167	8.167	8.167	8.167	8.168	8.172
ppm	**8.174**	**8.174**	**8.174**	**8.174**	**8.174**	**8.175**	**8.178**
αHN	8.079	8.079	8.079	8.079	8.079	8.080	8.082
	8.067	8.067	8.067	8.067	8.067	8.068	8.071
ppm	**8.073**	**8.073**	**8.073**	**8.073**	**8.073**	**8.074**	**8.077**

Supplementary Table 2. Temperature coefficients of amide HN chemical shifts in selected oligosaccharides.

These data were fit to generate the temperature coefficients values shown in Table 4.

A. Chemical shifts (ppm) and temperature coefficients at pH 6.0

	T/K	H_2O	βHN	αHN					βNH	αNH
GlcNAc	9.98	4.922	8.289	8.205					123.219	124.015
	24.41	4.760	8.172	8.072					122.947	123.705
	35.04	4.649	8.091	7.980					122.742	123.480
	Δδ/ΔT	**-10.9**	**-7.8**	**-9.0**					**-19.0**	**-21.4**

	T/K	H_2O	βHN	αHN	ωHN
HA_3^{NN}	9.98	4.923	8.384	8.322	8.055
	24.41	4.761	8.272	8.189	7.949
	35.04	4.650	8.192	8.095	7.877
	Δδ/ΔT	**-10.9**	**-7.7**	**-9.1**	**-7.1**

	T/K	H_2O	βHN	αHN	ωHN
HA_4	9.98	4.921	8.383	8.324	8.159
	24.41	4.759	8.271	8.188	8.055
	35.04	4.648	8.191	8.097	7.984
	Δδ/ΔT	**-10.9**	**-7.7**	**-9.1**	**-7.0**

	T/K	H_2O	βHN	αHN	ωHN
HA_4 + NaCl	9.98	4.908	8.378	8.313	8.150
	24.41	4.754	8.271	8.184	8.050
	35.04	4.645	8.192	8.091	7.979
	Δδ/ΔT	**-10.5**	**-7.4**	**-8.9**	**-6.8**

	T/K	H_2O	βHN	αHN	ωHN	vinyllic
Δ4,5-HA_4	9.98	4.920	8.383	8.325	8.242	5.851
	24.41	4.764	8.272	8.193	8.141	5.847
	35.04	4.651	8.192	8.099	8.069	5.846
	Δδ/ΔT	**-10.7**	**-7.6**	**-9.0**	**-6.9**	**-0.2**

	T/K	H_2O	βHN	αHN	ωHN	γHN	βNH	αNH	ωNH
HA_6^{NN}	9.98	4.923	8.383	8.327	8.044	8.153	122.309	123.231	122.374
	24.41	4.766	8.273	8.193	7.941	8.051	122.089	122.943	122.134
	35.04	4.650	8.191	8.098	7.869	7.978	121.926	122.746	121.975
	Δδ/ΔT	**-10.9**	**-7.7**	**-9.1**	**-7.0**	**-7.0**	**-15.3**	**-19.4**	**-16.0**

	T/K	H_2O	γ'HN	γβHN	ωHN	γ'NH	γβNH	ωNH
HA_6^{AA}	9.98	4.918	8.138	8.141	8.139	122.164	122.195	122.326
	24.41	4.750	8.045	8.045	8.045	121.947	121.973	122.105
	35.04	4.652	7.976	7.972	7.974	121.789	121.812	121.946
	Δδ/ΔT	**-10.7**	**-6.5**	**-6.7**	**-6.6**	**-15.0**	**-15.3**	**-15.2**

	T/K	H_2O	βHN	αHN	ωHN	γHN	βNH	αNH	ωNH	γNH
HA_6	9.98	4.920	8.382	8.325	8.147	8.153	122.315	123.233	122.338	122.220
	24.41	4.756	8.271	8.189	8.042	8.052	122.098	122.947	122.097	121.996
	35.04	4.647	8.192	8.099	7.974	7.981	121.935	122.752	121.940	121.835
	Δδ/ΔT	**-10.9**	**-7.6**	**-9.0**	**-6.9**	**-6.9**	**-15.2**	**-19.2**	**-15.9**	**-15.4**

	T/K	H_2O	βHN	αHN	ωHN	γHN	ψHN	βNH	αNH	ωNH	γNH	ψNH
HA_8	9.98	4.919	8.382	8.324	8.144	8.154	8.143	122.316	123.238	122.335	122.224	122.185
	24.41	4.765	8.271	8.191	8.042	8.052	8.042	122.101	122.953	122.097	121.996	121.954
	35.04	4.648	8.192	8.099	7.973	7.983	7.973	121.939	122.754	121.937	121.839	121.797
	Δδ/ΔT	**-10.8**	**-7.6**	**-9.0**	**-6.8**	**-6.8**	**-6.8**	**-15.0**	**-19.3**	**-15.9**	**-15.4**	**-15.5**

	T/K	H_2O	βHN	αHN	ωHN	γHN	ψHN	δHN	βNH	αNH	ωNH	γNH	ψNH	δNH
HA_{10}	9.98	4.920	8.382	8.326	8.143	8.155	8.145	8.140	122.323	123.246	122.340	122.231	122.190	122.180
	24.41	4.767	8.271	8.191	8.042	8.053	8.043	8.038	122.098	122.951	122.093	121.993	121.952	121.943
	35.04	4.650	8.192	8.099	7.971	7.983	7.973	7.968	121.940	122.758	121.937	121.841	121.797	121.789
	Δδ/ΔT	**-10.7**	**-7.6**	**-9.1**	**-6.9**	**-6.9**	**-6.9**	**-6.9**	**-15.3**	**-19.5**	**-16.1**	**-15.6**	**-15.7**	**-15.7**

	T/K	H_2O	βHN	αHN	ωHN
HA_{40}	9.98	4.922	8.382	8.325	8.141
	24.41	4.760	8.272	8.193	8.041
	35.04				
	Δδ/ΔT	**-11.2**	**-7.6**	**-9.1**	**-6.9**

	T/K	H_2O	βHN	αHN	ωHN
HA_{40} + NaCl	9.98				
	24.41	4.747	8.269	8.180	8.035
	35.04	4.637	8.191	8.087	7.964
	Δδ/ΔT	**-10.3**	**-7.3**	**-8.7**	**-6.7**

A (cont). Chemical shifts (ppm) and temperature coefficients at pH 6.0

	T/K	H_2O	βHN	αHN	ωHN
$HA_{0.5\text{-}1.5M}$	9.98	4.916	-	-	8.139
	24.41	4.761	-	-	8.042
	35.04	4.650	-	-	7.970
	Δδ/ΔT	**-10.6**			**-6.7**

	T/K	H_2O	βHN	αHN	ωHN
$HA_{0.5\text{-}1.5M}$	9.98	4.908	-	-	8.138
+ NaCl	24.41	4.757	-	-	8.035
	35.04	4.645	-	-	7.965
	Δδ/ΔT	**-10.5**			**-6.9**

B. Chemical shifts (ppm) and temperature coefficients at pH 1.4

	T/K	H_2O	βHN	αHN			βHN	αHN
GlcNAc	9.98	4.948	8.293	8.207			123.307	124.072
	24.41	4.792	8.181	8.078			123.047	123.772
	35.04	4.680	8.100	7.987			122.846	123.550
	Δδ/ΔT	**-10.7**	**-7.7**	**-8.8**			**-18.4**	**-20.8**

	T/K	H_2O	βHN	αHN	ωHN
HA_3^{NN}	9.98	4.939	8.368	8.311	8.214
	24.41	4.773	8.257	8.178	8.089
	35.04	4.671	8.176	8.083	7.998
	Δδ/ΔT	**-10.7**	**-7.7**	**-9.1**	**-8.6**

	T/K	H_2O	βHN	αHN	ωHN		βHN	αHN	ωHN
HA_4	9.98	4.929	8.360	8.301	8.281		122.007	123.035	121.724
	24.41	4.772	8.250	8.170	8.163		121.769	122.742	121.381
	35.04	4.666	8.169	8.075	8.077		121.585	122.530	121.131
	Δδ/ΔT	**-10.5**	**-7.6**	**-9.0**	**-8.1**		**-16.8**	**-20.2**	**-23.7**

	T/K	H_2O	βHN	αHN	ωHN
HA_4 + NaCl	9.98	4.920	8.363	8.301	8.282
	24.41				
	35.04	4.659	8.177	8.081	8.081
	Δδ/ΔT	**-10.4**	**-7.4**	**-8.8**	**-8.0**

	T/K	H_2O	βHN	αHN	ωHN	vinyllic
Δ4,5-HA4	9.98	4.935	8.367	8.308	8.383	6.232
	24.41	4.771	8.255	8.178	8.266	6.224
	35.04	4.670	*8.180*	8.082	8.181	6.219
	Δδ/ΔT	**-10.6**	**-7.5**	**-9.0**	**-8.1**	**-5.2**

	T/K	H_2O	γ'HN	γβHN	ωHN		γ'HN	γβHN	ωHN
HA_6^{AA}	9.98	4.925	8.278	8.282	8.285		121.588	121.657	121.776
	24.41	4.764	8.155	8.157	8.162		121.243	121.311	121.427
	35.04	4.658	8.071	8.073	8.078		121.000	121.068	121.182
	Δδ/ΔT	**-10.7**	**-8.3**	**-8.4**	**-8.3**		**-23.5**	**-23.5**	**-23.7**

	T/K	H_2O	βHN	αHN	ωHN	γHN	βHN	αHN	ωHN	γHN
HA_6	9.98	4.928	8.360	8.301	8.279	8.276	122.002	123.033	121.727	121.650
	24.41	4.763	8.248	8.170	8.162	8.156	121.765	122.741	121.384	121.319
	35.04	4.663	8.169	8.075	8.075	8.070	121.584	122.531	121.139	121.076
	Δδ/ΔT	**-10.6**	**-7.6**	**-9.0**	**-8.1**	**-8.2**	**-16.7**	**-20.0**	**-23.5**	**-22.9**

	T/K	H_2O	βHN	αHN	ωHN	γHN/ψHN	βHN	αHN	ωHN	γHN/ψHN
HA_8	9.98	4.928	8.361	8.302	8.280	8.275	122.000	123.034	121.727	121.657
	24.41	4.770	8.249	8.169	8.161	8.155	121.763	122.741	121.386	121.327
	35.04	4.661	8.168	8.075	8.074	8.068	121.579	122.529	121.136	121.082
	Δδ/ΔT	**-10.7**	**-7.7**	**-9.1**	**-8.2**	**-8.3**	**-16.8**	**-20.2**	**-23.6**	**-22.9**

B (cont). Chemical shifts (ppm) and temperature coefficients at pH 1.4

	T/K	H_2O	βHN	αHN	ωHN
HA_{40}	9.98				
	24.41	4.777	8.254	8.181	8.159
	35.04	4.666	8.175	8.086	8.073
	Δδ/ΔT	**-10.4**	**-7.4**	**-8.9**	**-8.1**
	T/K	H_2O	βHN	αHN	ωHN
HA_{40} + NaCl	9.98				
	24.41	4.764	8.253	-	8.153
	35.04	4.654	8.175	-	8.068
	Δδ/ΔT	**-10.3**	**-7.3**		**-8.0**
	T/K	H_2O	βHN	αHN	ωHN
$HA_{0.5\text{-}1.5M}$	9.98		-	-	
	24.41	4.778	-	-	8.157
	35.04	4.667	-	-	8.071
	Δδ/ΔT	**-10.4**			**-8.1**
	T/K	H_2O	βHN	αHN	ωHN
$HA_{0.5\text{-}1.5M}$	9.98	4.915	-	-	8.266
+ NaCl	24.41	4.761	-	-	8.150
	35.04	4.652	-	-	8.067
	Δδ/ΔT	**-10.5**			**-7.9**