

Supporting Information

***De Novo* Glycan Sequencing by Electronic Excitation Dissociation and Fixed-Charge Derivatization**

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Figure S-1. Zoomed-in regions of the EED MS/MS spectra of Me-PRAGS-labeled (a) laminarihexaose, (b) maltohexaose, and (c) isomaltohexaose, illustrating the extent of hydrogen transfer products in reducing-end glycosidic fragments. Each panel shows a comparison of spectra obtained at three different electron energies: 12 eV, 16 eV, and 20 eV (from bottom to top). " indicates double hydrogen losses; ‡ indicates double hydrogen gains.

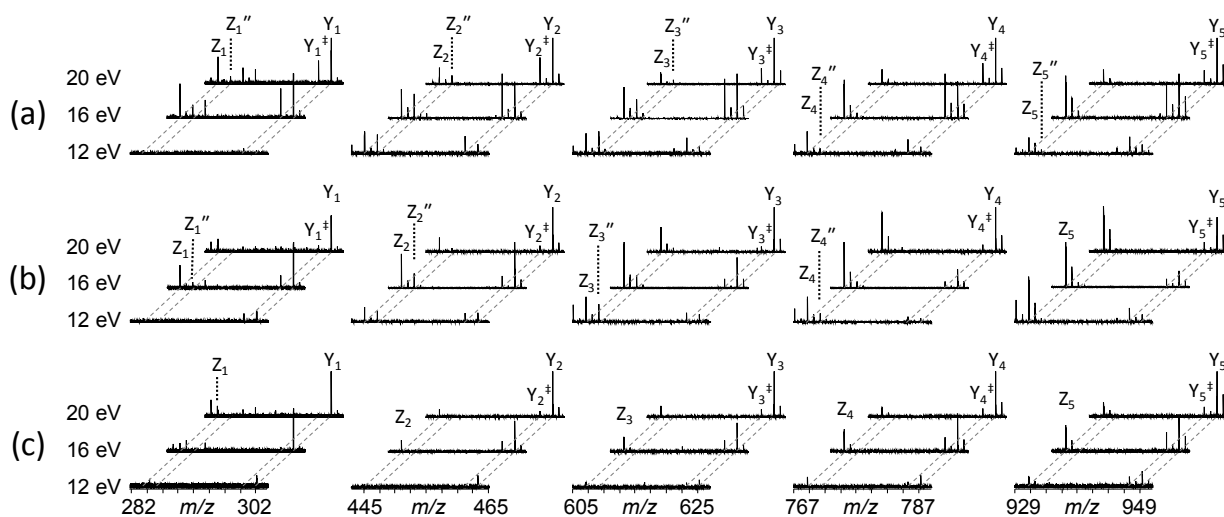


Figure S-2. EED (16 eV) MS/MS spectra of Me-PRAGS-labeled (a) LNFP I, (b) LNFP II, (c) LNFP III, (d) LNFP V, and (e) LNFP VI. Fragments formed by EED at 16 eV but not at 12 eV are highlighted.

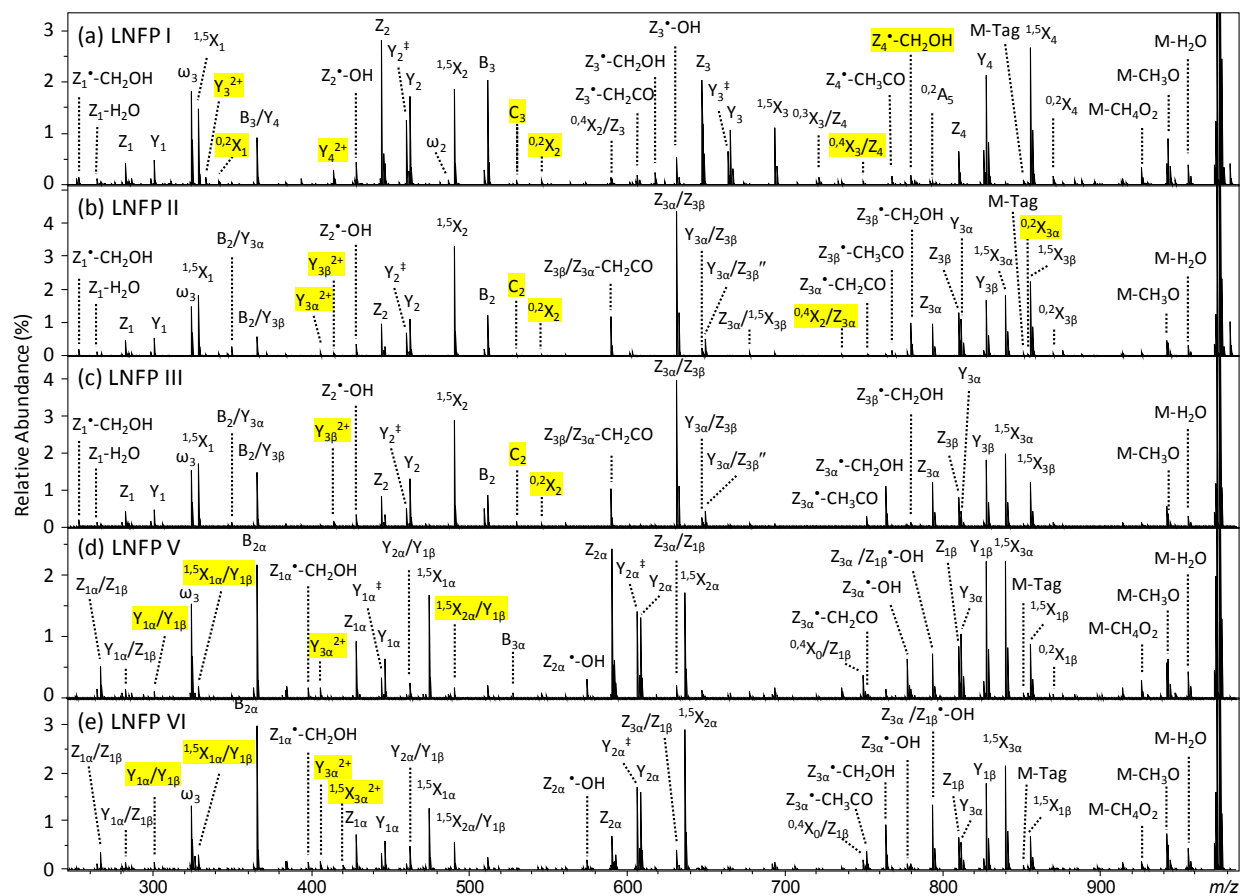


Figure S-3. Zoomed-in regions of the EED MS/MS spectra of Me-PRAGS-labeled (a) LNFP I (12 eV), (b) LNFP I (16 eV), and (c) LNFP V (16 eV), showing potential interference in topology analysis posed by secondary fragment ions.

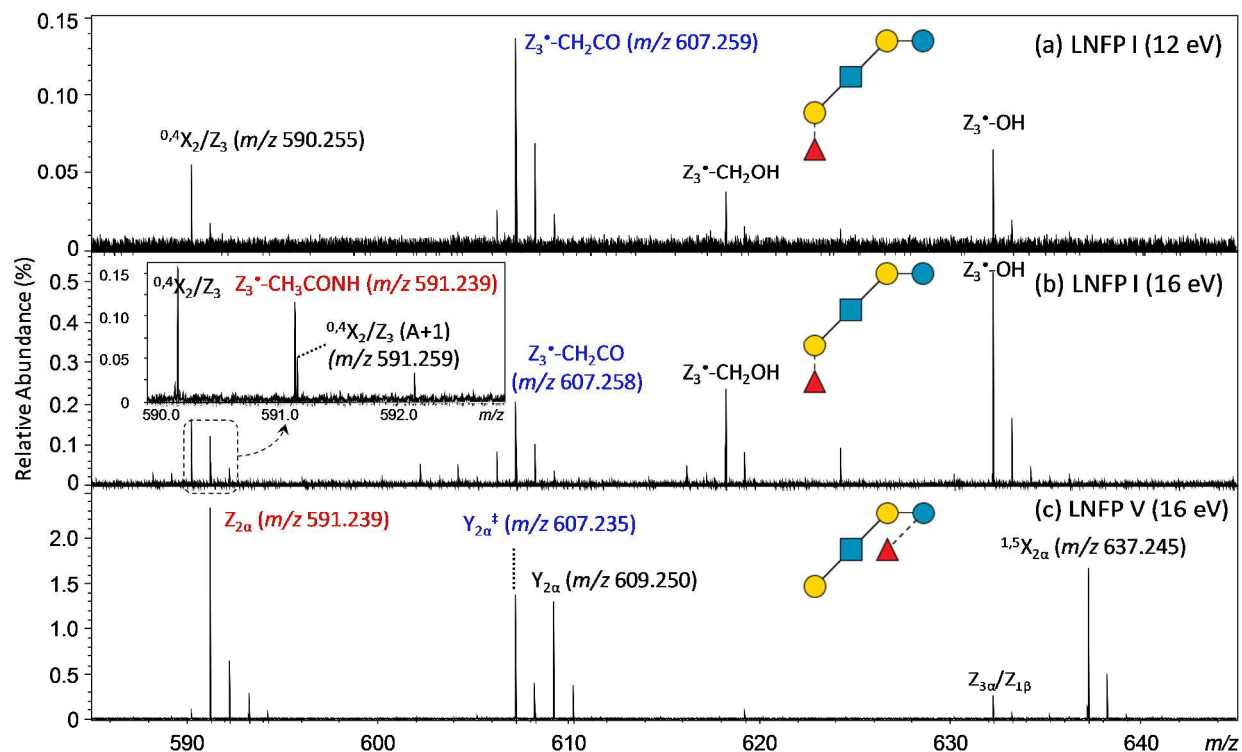
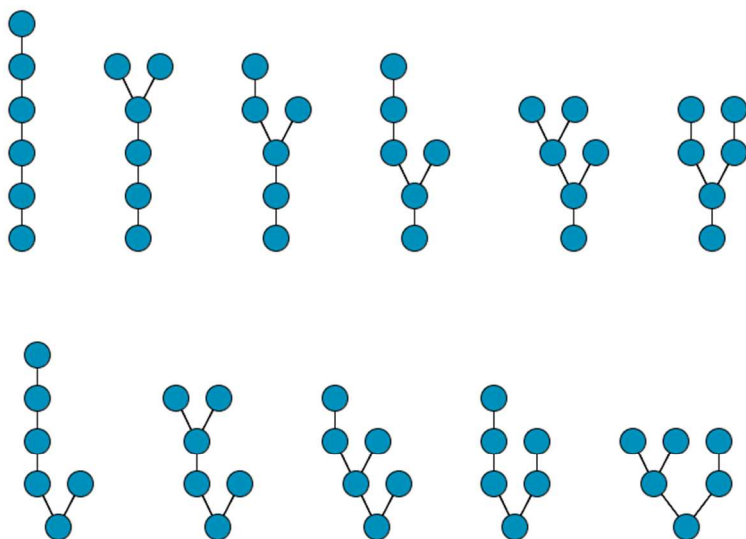
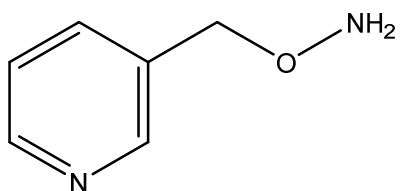


Figure S-4. Candidate topologies reconstructed by GlycoDeNovo based on the 16 eV EED spectra of Me-PRAGS-labeled linear hexaose glycans.

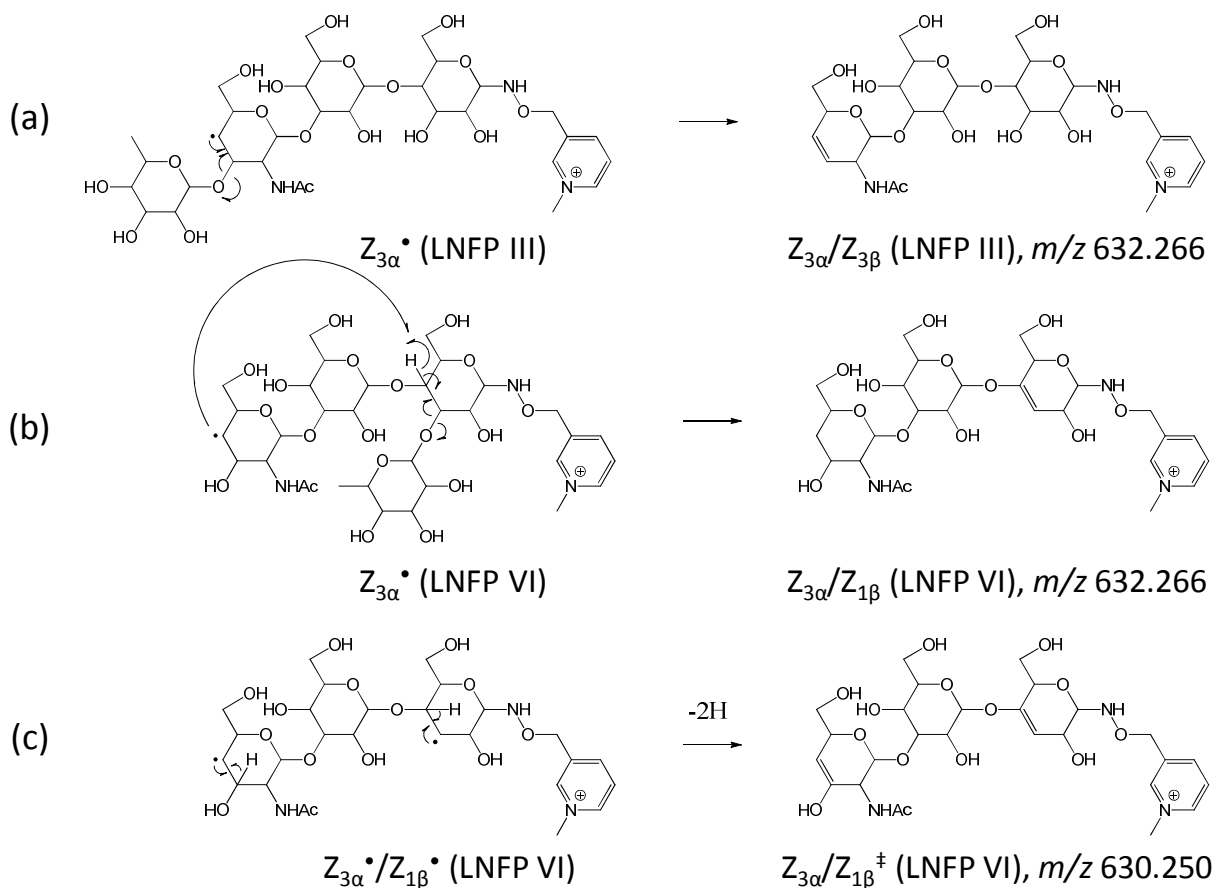


Scheme S-1. Chemical structure of the PRAGS reagent

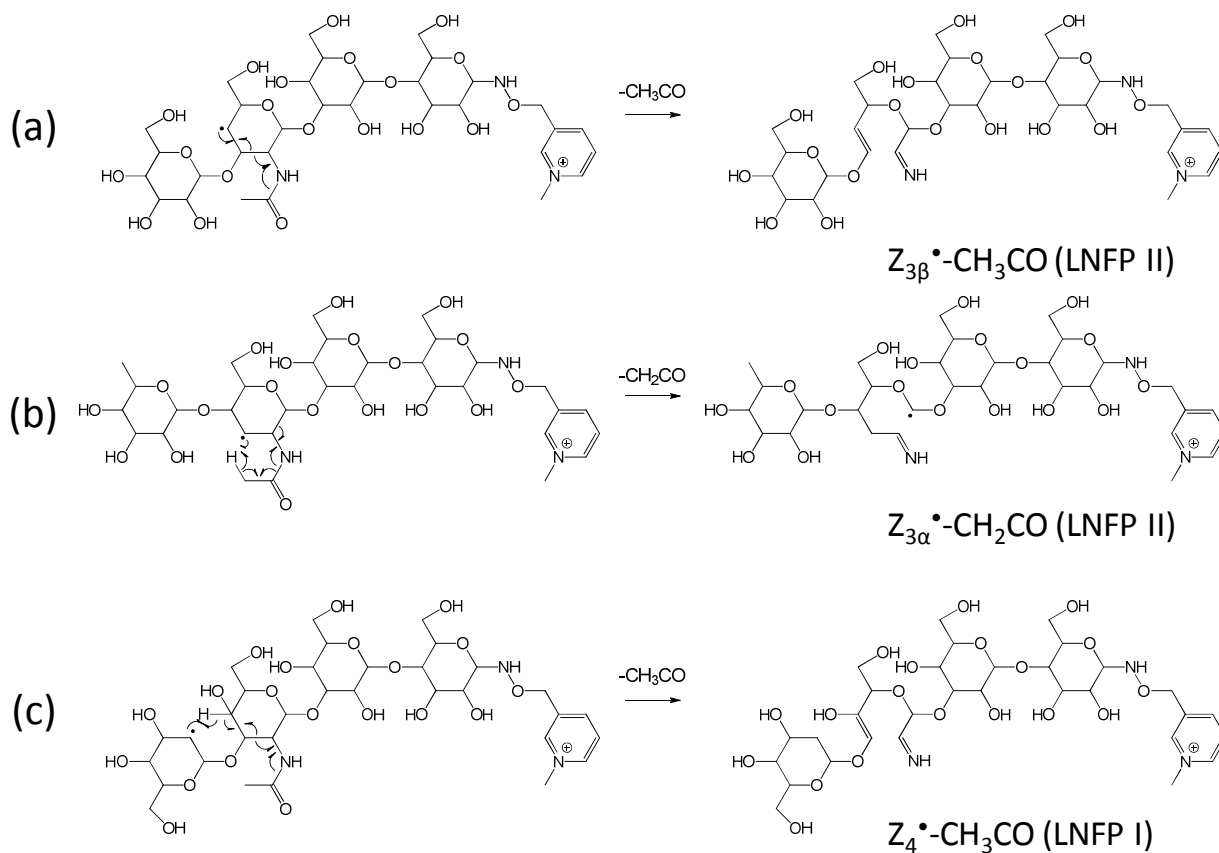


O-(pyridin-3-ylmethyl)hydroxylamine

Scheme S-2. Proposed mechanisms for formation of internal fragments: (a) $Z_{3\alpha}/Z_{3\beta}$ of LNFP III via direct β -elimination, (b) $Z_{3\alpha}/Z_{1\beta}$ of LNFP VI via radical migration, and (c) $Z_{3\alpha}/Z_{1\beta}$ of LNFP VI via consecutive EED processes.



Scheme S-3. Proposed mechanisms for formation of linkage-specific secondary fragments at a GlcNAc residue: (a) $Z_{3\beta}^{\bullet}$ -CH₃CO (LNFP II), (b) $Z_{3\alpha}^{\bullet}$ -CH₃CO (LNFP II), and (c) Z_4^{\bullet} -CH₃CO (LNFP I).



Scheme S-4. Proposed mechanism for formation of Z_3^{\bullet} -CH₃CONH (LNFP I).

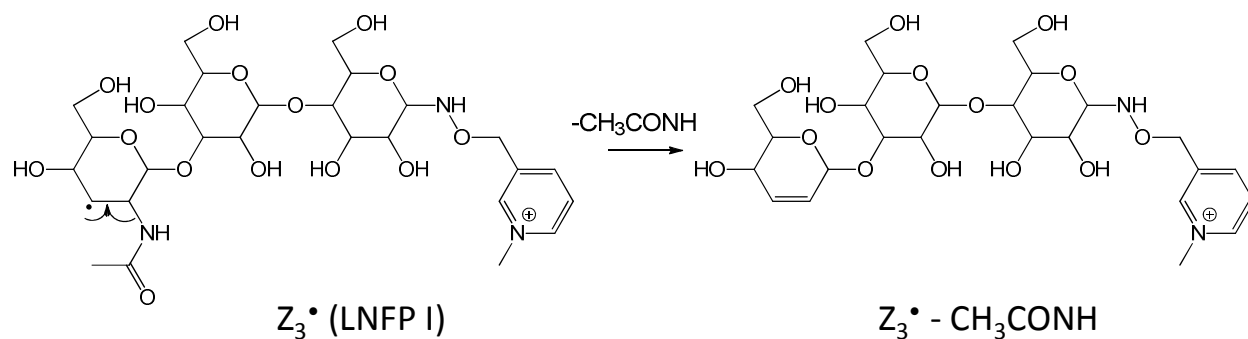


Table S-1. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled laminarihexaose.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.1334	1+	Z ₁ [•] -OH	267.1334	0.00
283.1282	1+	Z ₁	283.1288	2.12
299.1232	1+	Y ₁ [†]	299.1233	0.33
301.1389	1+	Y ₁	301.1389	0.00
325.1124	1+	B ₂	325.1129	1.54
329.1338	1+	^{1,5} X ₁	329.1338	0.00
370.4741		ω ₃		
415.1704	1+	Z ₂ [•] -CH ₂ OH	415.1706	0.48
429.1862	1+	Z ₂ [•] -OH	429.1862	0.00
445.1811	1+	Z ₂	445.1811	0.00
447.1968	1+	Z ₂ ^{''}	447.1967	-0.22
461.1761	1+	Y ₂ [†]	461.1761	0.00
463.1916	1+	Y ₂	463.1917	0.22
487.1651	1+	B ₃	487.1657	1.23
491.1866	1+	^{1,5} X ₂	491.1866	0.00
505.2022	1+	^{0,2} X ₂	505.2023	0.20
577.2237	1+	Z ₃ [•] -CH ₂ OH	577.2234	-0.52
591.2387	1+	Z ₃ [•] -OH	591.239	0.51
607.2345	1+	Z ₃	607.2339	-0.99
609.2497	1+	Z ₃ ^{''}	609.2495	-0.33
623.2287	1+	Y ₃ [†]	623.2289	0.32
625.2446	1+	Y ₃	625.2445	-0.16
649.2183	1+	B ₄	649.2186	0.46
653.2394	1+	^{1,5} X ₃	653.2394	0.00
667.2549	1+	^{0,2} X ₃	667.2551	0.30
739.276	1+	Z ₄ [•] -CH ₂ OH	739.2763	0.41
753.2921	1+	Z ₄ [•] -OH	753.2919	-0.27
769.2866	1+	Z ₄	769.2868	0.26
785.2825	1+	Y ₄ [†]	785.2817	-1.02
787.2972	1+	Y ₄	787.2973	0.13
811.2704	1+	B ₅	811.2714	1.23
815.2923	1+	^{1,5} X ₄	815.2922	-0.12
829.3077	1+	^{0,2} X ₄	829.3079	0.24
901.33	1+	Z ₅ [•] -CH ₂ OH	901.3291	-1.00
915.3447	1+	Z ₅ [•] -OH	915.3447	0.00
931.3411	1+	Z ₅	931.3396	-1.61
947.3355	1+	Y ₅ [†]	947.3346	-0.95
949.3501	1+	Y ₅	949.3502	0.11
977.3453	1+	^{1,5} X ₅	977.3451	-0.20
988.3352	1+	M-Tag	988.3357	0.51
991.3607	1+	^{0,2} X ₅	991.3607	0.00
1049.3672	1+	M-C ₂ H ₆ O ₂	1049.3669	-0.29
1063.3816	1+	M-CH ₄ O ₂	1063.3825	0.85
1080.3847	1+	M-CH ₃ O	1080.3852	0.46
1093.3923	1+	M-H ₂ O	1093.393	0.64
1111.4035	1+	Precursor	1111.4035	0.00

Table S-2. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled maltohexaose.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.1332	1+	Z ₁ [•] -CH ₂ OH	267.1334	0.75
283.1283	1+	Z ₁	283.1288	1.77
301.1388	1+	Y ₁	301.1389	0.33
325.1124	1+	B ₂	325.1129	1.54
329.1338	1+	^{1,5} X ₁	329.1338	0.00
370.4749		ω ₃		
415.1706	1+	Z ₂ [•] -CH ₂ OH	415.1706	0.00
429.1861	1+	Z ₂ [•] -OH	429.1862	0.23
445.1811	1+	Z ₂	445.1811	0.00
463.1916	1+	Y ₂	463.1917	0.22
487.1652	1+	B ₃	487.1657	1.03
491.1865	1+	^{1,5} X ₂	491.1866	0.20
505.2022	1+	^{0,2} X ₂	505.2023	0.20
577.2235	1+	Z ₃ [•] -CH ₂ OH	577.2234	-0.17
591.2391	1+	Z ₃ [•] -OH	591.239	-0.17
607.2345	1+	Z ₃	607.2339	-0.99
625.2444	1+	Y ₃	625.2445	0.16
649.2181	1+	B ₄	649.2186	0.77
653.2395	1+	^{1,5} X ₃	653.2394	-0.15
667.2552	1+	^{0,2} X ₃	667.2551	-0.15
739.2761	1+	Z ₄ [•] -CH ₂ OH	739.2763	0.27
753.2919	1+	Z ₄ [•] -OH	753.2919	0.00
769.2865	1+	Z ₄	769.2868	0.39
787.2973	1+	Y ₄	787.2973	0.00
811.2704	1+	B ₅	811.2714	1.23
815.2924	1+	^{1,5} X ₄	815.2922	-0.25
829.3078	1+	^{0,2} X ₄	829.3079	0.12
901.3292	1+	Z ₅ [•] -CH ₂ OH	901.3291	-0.11
915.3434	1+	Z ₅ [•] -OH	915.3447	1.42
931.3396	1+	Z ₅	931.3396	0.00
949.3502	1+	Y ₅	949.3502	0.00
977.3452	1+	^{1,5} X ₅	977.3451	-0.10
988.3351	1+	M-Tag	988.3357	0.61
991.3611	1+	^{0,2} X ₅	991.3607	-0.40
1051.382	1+	M-C ₂ H ₄ O ₂	1051.3825	0.48
1063.3834	1+	M-CH ₄ O ₂	1063.3825	-0.85
1080.3861	1+	M-CH ₃ O	1080.3852	-0.83
1093.3929	1+	M-H ₂ O	1093.393	0.09
1111.403	1+	Precursor	1111.4035	0.45

Table S-3. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled isomaltohexaose.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
283.1284	1+	Z ₁	283.1288	1.41
301.1388	1+	Y ₁	301.1389	0.33
325.1125	1+	B ₂	325.1129	1.23
329.1339	1+	^{1,5} X ₁	329.1338	-0.30
343.1492	1+	^{0,2} X ₁	343.1494	0.58
370.4744		ω ₃		
403.1706	1+	^{0,4} X ₁	403.1706	0.00
445.1811	1+	Z ₂	445.1811	0.00
463.1917	1+	Y ₂	463.1917	0.00
487.1661	1+	B ₃	487.1657	-0.82
491.1865	1+	^{1,5} X ₂	491.1866	0.20
505.2024	1+	^{0,2} X ₂	505.2023	-0.20
565.2229	1+	^{0,4} X ₂	565.2234	0.88
607.2344	1+	Z ₃	607.2339	-0.82
625.2443	1+	Y ₃	625.2445	0.32
649.2176	1+	B ₄	649.2186	1.54
653.2394	1+	^{1,5} X ₃	653.2394	0.00
667.2551	1+	^{0,2} X ₃	667.2551	0.00
727.2768	1+	^{0,4} X ₃	727.2762	-0.82
769.2865	1+	Z ₄	769.2868	0.39
787.2972	1+	Y ₄	787.2973	0.13
815.2924	1+	^{1,5} X ₄	815.2922	-0.25
829.3079	1+	^{0,2} X ₄	829.3079	0.00
889.3299	1+	^{0,4} X ₄	889.329	-1.01
931.3397	1+	Z ₅	931.3396	-0.11
949.3502	1+	Y ₅	949.3502	0.00
977.3452	1+	^{1,5} X ₅	977.3451	-0.10
988.3353	1+	M-Tag	988.3357	0.40
991.3611	1+	^{0,2} X ₅	991.3607	-0.40
1051.3819	1+	^{0,4} X ₅	1051.3819	0.00
1081.3931	1+	M-CH ₂ O	1081.393	-0.09
1093.3933	1+	M-H ₂ O	1093.393	-0.27
1111.4034	1+	Precursor	1111.4035	0.09

Table S-4. List of assigned EED (12 eV) fragments of the Me-PRAGS-labeled LNFP I.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1177	1+	Z ₁ [•] -CH ₂ OH	253.1183	2.37
283.1283	1+	Z ₁	283.1288	1.77
301.1389	1+	Y ₁	301.1394	1.66
324.7988		ω ₃		
329.1338	1+	^{1,5} X ₁	329.1343	1.52
366.1389	1+	B ₃ /Y ₄	366.1395	1.64
429.1862	1+	Z ₂ [•] -OH	429.1862	0.00
445.1811	1+	Z ₂	445.1816	1.12
447.1968	1+	Z ₂ ^{''}	447.1972	0.89
461.176	1+	Y ₂ [†]	461.1766	1.30
463.1916	1+	Y ₂	463.1922	1.30
487.191		ω ₂		
491.1866	1+	^{1,5} X ₂	491.1871	1.02
512.1969	1+	B ₃	512.1974	0.98
590.2549	1+	^{0,4} X ₂ /Z ₃	590.2556	1.19
607.2592	1+	Z ₃ [•] -CH ₂ CO	607.2583	-1.48
618.2503	1+	Z ₃ [•] -CH ₂ OH	618.2505	0.32
632.2656	1+	Z ₃ [•] -OH	632.2661	0.79
648.2612	1+	Z ₃	648.261	-0.31
664.2555	1+	Y ₃ [†]	664.256	0.75
666.2711	1+	Y ₃	666.2716	0.75
694.2661	1+	^{1,5} X ₃	694.2665	0.58
768.3027	1+	Z ₄ [•] -CH ₃ CO	768.3033	0.78
794.2922	1+	^{0,2} A ₅	794.2925	0.38
810.3143	1+	Z ₄	810.3138	-0.62
826.3083	1+	Y ₄ [†]	826.3088	0.61
828.324	1+	Y ₄	828.3244	0.48
851.3135	1+	M-Tag	851.3145	1.17
856.319	1+	^{1,5} X ₄	856.3193	0.35
870.3349	1+	^{0,2} X ₄	870.3349	0.00
926.3612	1+	M-CH ₄ O ₂	926.3613	0.11
943.3635	1+	M-CH ₃ O	943.364	0.53
956.3721	1+	M-H ₂ O	956.3718	-0.31
974.3819	1+	Precursor	974.3823	0.41

Table S-5. List of assigned EED (12 eV) fragments of the Me-PRAGS-labeled LNFP II.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1178	1+	Z ₁ [•] -CH ₂ OH	253.1183	1.98
283.1284	1+	Z ₁	283.1288	1.41
301.1389	1+	Y ₁	301.1394	1.66
324.7988		ω ₃		
329.1338	1+	^{1,5} X ₁	329.1343	1.52
350.144	1+	B ₂ /Y _{3α}	350.1446	1.71
366.1389	1+	B ₂ /Y _{3β}	366.1395	1.64
429.1863	1+	Z ₂ [•] -OH	429.1862	-0.23
445.1812	1+	Z ₂	445.1816	0.90
447.1968	1+	Z ₂ ''	447.1972	0.89
461.1761	1+	Y ₂ [‡]	461.1766	1.08
463.1917	1+	Y ₂	463.1922	1.08
487.1901		ω ₂		
491.1866	1+	^{1,5} X ₂	491.1871	1.02
512.1968	1+	B ₂	512.1974	1.17
590.2548	1+	Z _{3α} /Z _{3β} -CH ₂ CO	590.2556	1.36
632.2659	1+	Z _{3α} /Z _{3β}	632.2661	0.32
648.2609	1+	Y _{3α} /Z _{3β}	648.261	0.15
650.2761	1+	Y _{3α} /Z _{3β} ''	650.2766	0.77
678.2712	1+	Z _{3α} / ^{1,5} X _{3β}	678.2716	0.59
753.3166	1+	Z _{3α} [•] -CH ₂ CO	753.3162	-0.53
768.3026	1+	Z _{3β} [•] -CH ₃ CO	768.3033	0.91
780.3026	1+	Z _{3β} [•] -CH ₂ OH	780.3033	0.90
794.3186	1+	Z _{3α}	794.3189	0.38
810.3144	1+	Z _{3β}	810.3138	-0.74
812.3296	1+	Y _{3α}	812.3295	-0.12
828.324	1+	Y _{3β}	828.3244	0.48
840.3241	1+	^{1,5} X _{3α}	840.3244	0.36
851.3134	1+	M-Tag	851.3145	1.29
856.3189	1+	^{1,5} X _{3β}	856.3193	0.47
870.3347	1+	^{0,2} X _{3β}	870.3349	0.23
943.3637	1+	M-CH ₃ O	943.364	0.32
956.3711	1+	M-H ₂ O	956.3718	0.73
974.3817	1+	Precursor	974.3823	0.62

Table S-6. List of assigned EED (12 eV) fragments of the Me-PRAGS-labeled LNFP III.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1178	1+	Z ₁ [•] -CH ₂ OH	253.1183	1.98
283.1284	1+	Z ₁	283.1288	1.41
301.1388	1+	Y ₁	301.1394	1.99
324.7988		ω ₃		
329.1338	1+	^{1,5} X ₁	329.1343	1.52
350.144	1+	B ₂ /Y _{3α}	350.1446	1.71
366.139	1+	B ₂ /Y _{3β}	366.1395	1.37
429.1862	1+	Z ₂ [•] -OH	429.1862	0.00
445.1811	1+	Z ₂	445.1816	1.12
447.1968	1+	Z ₂ ''	447.1972	0.89
461.1758	1+	Y ₂ [‡]	461.1766	1.73
463.1917	1+	Y ₂	463.1922	1.08
487.1908		ω ₂		
491.1866	1+	^{1,5} X ₂	491.1871	1.02
512.1968	1+	B ₂	512.1974	1.17
590.2563	1+	Z _{3α} /Z _{3β} -CH ₂ CO	590.2556	-1.19
632.2658	1+	Z _{3α} /Z _{3β}	632.2661	0.47
648.2605	1+	Y _{3α} /Z _{3β}	648.261	0.77
650.2761	1+	Y _{3α} /Z _{3β} ''	650.2766	0.77
752.3079	1+	Z _{3α} [•] -CH ₃ CO	752.3084	0.66
764.3079	1+	Z _{3α} [•] -CH ₂ OH	764.3084	0.65
780.3031	1+	Z _{3β} [•] -CH ₂ OH	780.3033	0.26
794.318	1+	Z _{3α}	794.3189	1.13
810.3143	1+	Z _{3β}	810.3138	-0.62
812.3289	1+	Y _{3α}	812.3295	0.74
828.3242	1+	Y _{3β}	828.3244	0.24
840.3243	1+	^{1,5} X _{3α}	840.3244	0.12
851.3137	1+	M-Tag	851.3145	0.94
856.3183	1+	^{1,5} X _{3β}	856.3193	1.17
943.3631	1+	M-CH ₃ O	943.364	0.95
956.3717	1+	M-H ₂ O	956.3718	0.10
974.382	1+	Precursor	974.3823	0.31

Table S-7. List of assigned EED (12 eV) fragments of the Me-PRAGS-labeled LNFP V.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.134	1+	Z _{1α} /Z _{1β}	267.1339	-0.37
283.1291	1+	Y _{1α} /Z _{1β}	283.1288	-1.06
324.7995		ω ₃		
366.1395	1+	B _{2α}	366.1395	0.00
399.1759	1+	Z _{1α} [•] -CH ₂ OH	399.1762	0.75
429.1867	1+	Z _{1α}	429.1867	0.00
445.1815	1+	Y _{1α} [‡]	445.1817	0.45
447.1973	1+	Y _{1α}	447.1973	0.00
463.1924	1+	Y _{2α} /Y _{1β}	463.1922	-0.43
475.1922	1+	^{1,5} X _{1α}	475.1922	0.00
487.1911		ω ₂		
528.1922	1+	B _{3α}	528.1923	0.19
546.2027	1+	C _{3α}	546.2029	0.37
575.2444	1+	Z _{2α} [•] -OH	575.2446	0.35
591.2399	1+	Z _{2α}	591.2395	-0.68
593.2551	1+	Z _{2α} ^{''}	593.2555	0.67
607.2349	1+	Y _{2α} [‡]	607.2345	-0.66
609.2501	1+	Y _{2α}	609.2501	0.00
632.2659	1+	Z _{3α} /Z _{1β}	632.2661	0.32
637.2451	1+	^{1,5} X _{2α}	637.245	-0.16
750.2933	1+	^{0,4} X ₀ /Z _{1β}	750.2927	-0.80
753.3164	1+	Z _{3α} [•] -CH ₂ CO	753.3162	-0.27
778.3241	1+	Z _{3α} [•] -OH	778.3235	-0.77
794.3184	1+	Z _{3α} (Z _{1β} [•] -OH)	794.3189	0.63
810.3149	1+	Z _{1β}	810.3138	-1.36
812.329	1+	Y _{3α}	812.3295	0.62
828.3245	1+	Y _{1β}	828.3244	-0.12
840.3246	1+	^{1,5} X _{3α}	840.3244	-0.24
851.3137	1+	M-Tag	851.3145	0.94
856.3195	1+	^{1,5} X _{1β}	856.3193	-0.23
926.3613	1+	M-CH ₄ O ₂	926.3613	0.00
943.3645	1+	M-CH ₃ O	943.364	-0.53
956.3716	1+	M-H ₂ O	956.3718	0.21
974.3821	1+	Precursor	974.3823	0.21

Table S-8. List of assigned EED (12 eV) fragments of the Me-PRAGS-labeled LNFP VI.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.1339	1+	Z _{1α} /Z _{1β}	267.1339	0.00
283.1288	1+	Y _{1α} /Z _{1β}	283.1288	0.00
324.7993		ω ₃		
366.1394	1+	B _{2α}	366.1395	0.27
399.176	1+	Z _{1α} [•] -CH ₂ OH	399.1762	0.50
429.1867	1+	Z _{1α}	429.1867	0.00
445.1817	1+	Y _{1α} [‡]	445.1817	0.00
447.1973	1+	Y _{1α}	447.1973	0.00
463.1922	1+	Y _{2α} /Y _{1β}	463.1922	0.00
475.1922	1+	^{1,5} X _{1α}	475.1922	0.00
487.1909		ω ₂		
491.1871	1+	^{1,5} X _{2α} /Y _{1β}	491.1871	0.00
575.2443	1+	Z _{2α} [•] -OH	575.2446	0.52
591.2391	1+	Z _{2α}	591.2395	0.68
593.2552	1+	Z _{2α} ^{''}	593.2555	0.51
607.2345	1+	Y _{2α} [‡]	607.2345	0.00
609.2501	1+	Y _{2α}	609.2501	0.00
632.2659	1+	Z _{3α} /Z _{1β}	632.2661	0.32
637.2449	1+	^{1,5} X _{2α}	637.245	0.16
750.2929	1+	^{0,4} X ₀ /Z _{1β}	750.2927	-0.27
752.3079	1+	Z _{3α} [•] -CH ₃ CO	752.3084	0.66
764.3085	1+	Z _{3α} [•] -CH ₂ OH	764.3084	-0.13
778.3239	1+	Z _{3α} [•] -OH	778.3235	-0.51
794.3189	1+	Z _{3α} (Z _{1β} [•] -OH)	794.3189	0.00
810.314	1+	Z _{1β}	810.3138	-0.25
812.3305	1+	Y _{3α}	812.3295	-1.23
828.3245	1+	Y _{1β}	828.3244	-0.12
840.3245	1+	^{1,5} X _{3α}	840.3244	-0.12
851.3141	1+	M-Tag	851.3145	0.47
856.3194	1+	^{1,5} X _{1β}	856.3193	-0.12
926.3611	1+	M-CH ₄ O ₂	926.3613	0.22
943.3649	1+	M-CH ₃ O	943.364	-0.95
956.3717	1+	M-H ₂ O	956.3718	0.10
974.382	1+	Precursor	974.3823	0.31

Table S-9. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled LNFP I.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1176	1+	Z ₁ [•] -CH ₂ OH	253.1183	2.77
265.1177	1+	Z ₁ [•] -H ₂ O	265.1183	2.26
283.1283	1+	Z ₁	283.1288	1.77
301.1389	1+	Y ₁	301.1394	1.66
324.7991		ω ₃		
329.1338	1+	^{1,5} X ₁	329.1343	1.52
333.6388	2+	Y ₃ ²⁺	333.6397	2.70
343.1494	1+	^{0,2} X ₁	343.1499	1.46
366.1389	1+	B ₃ /Y ₄	366.1395	1.64
414.6655	2+	Y ₄ ²⁺	414.6661	1.45
429.1863	1+	Z ₂ [•] -OH	429.1862	-0.23
445.1811	1+	Z ₂	445.1816	1.12
461.1761	1+	Y ₂ [‡]	461.1766	1.08
463.1917	1+	Y ₂	463.1922	1.08
487.1917		ω ₂		
491.1866	1+	^{1,5} X ₂	491.1871	1.02
512.1968	1+	B ₃	512.1974	1.17
530.2073	1+	C ₃	530.2079	1.13
546.229	1+	^{0,2} X ₂	546.2293	0.55
590.2551	1+	^{0,4} X ₂ /Z ₃	590.2556	0.85
607.2583	1+	Z ₃ [•] -CH ₂ CO	607.2583	0.00
618.2498	1+	Z ₃ [•] -CH ₂ OH	618.2505	1.13
632.2654	1+	Z ₃ [•] -OH	632.2661	1.11
648.2605	1+	Z ₃	648.261	0.77
664.2558	1+	Y ₃ [‡]	664.256	0.30
666.2711	1+	Y ₃	666.2716	0.75
694.2659	1+	^{1,5} X ₃	694.2665	0.86
720.2817	1+	^{0,3} X ₃ /Z ₄	720.2821	0.56
750.2925	1+	^{0,4} X ₃ /Z ₄	750.2927	0.27
768.3031	1+	Z ₄ [•] -CH ₃ CO	768.3033	0.26
780.3025	1+	Z ₄ [•] -CH ₂ OH	780.3033	1.03
794.292	1+	^{0,2} A ₅	794.2925	0.63
810.314	1+	Z ₄	810.3138	-0.25
828.324	1+	Y ₄	828.3244	0.48
851.3129	1+	M-Tag	851.3145	1.88
856.3189	1+	^{1,5} X ₄	856.3193	0.47
870.3346	1+	^{0,2} X ₄	870.3349	0.34
926.3604	1+	M-CH ₄ O ₂	926.3613	0.97
943.3632	1+	M-CH ₃ O	943.364	0.85
956.3712	1+	M-H ₂ O	956.3718	0.63
974.3817	1+	Precursor	974.3823	0.62

Table S-10. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled LNFP II.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1178	1+	Z ₁ [•] -CH ₂ OH	253.1183	1.98
265.1178	1+	Z ₁ [•] -H ₂ O	265.1183	1.89
283.1283	1+	Z ₁	283.1288	1.77
301.1389	1+	Y ₁	301.1394	1.66
324.7989		ω ₃		
329.1338	1+	^{1,5} X ₁	329.1343	1.52
350.144	1+	B ₂ /Y _{3α}	350.1446	1.71
366.1389	1+	B ₂ /Y _{3β}	366.1395	1.64
406.6677	2+	Y _{3α} ²⁺	406.6686	2.21
414.6653	2+	Y _{3β} ²⁺	414.6661	1.93
429.1861	1+	Z ₂ [•] -OH	429.1862	0.23
445.1811	1+	Z ₂	445.1816	1.12
461.1761	1+	Y ₂ [‡]	461.1766	1.08
463.1917	1+	Y ₂	463.1922	1.08
491.1865	1+	^{1,5} X ₂	491.1871	1.22
512.1967	1+	B ₂	512.1974	1.37
530.2074	1+	C ₂	530.2079	0.94
546.229	1+	^{0,2} X ₂	546.2293	0.55
590.2551	1+	Z _{3α} /Z _{3β} -CH ₂ CO	590.2556	0.85
632.2656	1+	Z _{3α} /Z _{3β}	632.2661	0.79
648.2604	1+	Y _{3α} /Z _{3β}	648.261	0.93
650.2762	1+	Y _{3α} /Z _{3β} ''	650.2766	0.62
678.271	1+	Z _{3α} / ^{1,5} X _{3β}	678.2716	0.88
736.3131	1+	^{0,4} X ₂ /Z _{3α}	736.3137	0.81
753.3158	1+	Z _{3α} [•] -CH ₂ CO	753.3162	0.53
768.3036	1+	Z _{3β} [•] -CH ₃ CO	768.3033	-0.39
780.3027	1+	Z _{3β} [•] -CH ₂ OH	780.3033	0.77
794.318	1+	Z _{3α}	794.3189	1.13
810.3143	1+	Z _{3β}	810.3138	-0.62
812.3289	1+	Y _{3α}	812.3295	0.74
828.324	1+	Y _{3β}	828.3244	0.48
840.324	1+	^{1,5} X _{3α}	840.3244	0.48
851.3131	1+	M-Tag	851.3145	1.64
854.3398	1+	^{0,2} X _{3α}	854.34	0.23
856.3189	1+	^{1,5} X _{3β}	856.3193	0.47
870.3347	1+	^{0,2} X _{3β}	870.3349	0.23
943.3631	1+	M-CH ₃ O	943.364	0.95
956.3713	1+	M-H ₂ O	956.3718	0.52
974.3818	1+	Precursor	974.3823	0.51

Table S-11. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled LNFP III.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
253.1177	1+	Z ₁ [•] -CH ₂ OH	253.1183	2.37
265.1177	1+	Z ₁ [•] -H ₂ O	265.1183	2.26
283.1283	1+	Z ₁	283.1288	1.77
301.1389	1+	Y ₁	301.1394	1.66
324.7988		ω ₃		
329.1337	1+	^{1,5} X ₁	329.1343	1.82
350.144	1+	B ₂ /Y _{3α}	350.1446	1.71
366.1389	1+	B ₂ /Y _{3β}	366.1395	1.64
414.6654	2+	Y _{3β} ²⁺	414.6661	1.69
429.1862	1+	Z ₂ [•] -OH	429.1862	0.00
445.1812	1+	Z ₂	445.1816	0.90
461.176	1+	Y ₂ [†]	461.1766	1.30
463.1916	1+	Y ₂	463.1922	1.30
491.1866	1+	^{1,5} X ₂	491.1871	1.02
512.1969	1+	B ₂	512.1974	0.98
530.2074	1+	C ₂	530.2079	0.94
546.2287	1+	^{0,2} X ₂	546.2293	1.10
590.2549	1+	Z _{3α} /Z _{3β} -CH ₂ CO	590.2556	1.19
632.2657	1+	Z _{3α} /Z _{3β}	632.2661	0.63
648.2601	1+	Y _{3α} /Z _{3β}	648.261	1.39
650.2761	1+	Y _{3α} /Z _{3β} ''	650.2766	0.77
752.3078	1+	Z _{3α} [•] -CH ₃ CO	752.3084	0.80
764.308	1+	Z _{3α} [•] -CH ₂ OH	764.3084	0.52
780.3033	1+	Z _{3β} [•] -CH ₂ OH	780.3033	0.00
794.3183	1+	Z _{3α}	794.3189	0.76
810.3142	1+	Z _{3β}	810.3138	-0.49
812.3291	1+	Y _{3α}	812.3295	0.49
828.324	1+	Y _{3β}	828.3244	0.48
840.324	1+	^{1,5} X _{3α}	840.3244	0.48
856.319	1+	^{1,5} X _{3β}	856.3193	0.35
943.364	1+	M-CH ₃ O	943.364	0.00
956.3715	1+	M-H ₂ O	956.3718	0.31
974.3819	1+	Precursor	974.3823	0.41

Table S-12. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled LNFP V.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.1342	1+	Z _{1α} /Z _{1β}	267.1339	-1.12
283.129	1+	Y _{1α} /Z _{1β}	283.1288	-0.71
301.1395	1+	Y _{1α} /Y _{1β}	301.1394	-0.33
324.7996		ω ₃		
329.1344	1+	^{1,5} X _{1α} /Y _{1β}	329.1343	-0.30
366.1395	1+	B _{2α}	366.1395	0.00
399.1762	1+	Z _{1α} [•] -CH ₂ OH	399.1762	0.00
406.6684	2+	Y _{3α} ²⁺	406.6686	0.49
429.1867	1+	Z _{1α}	429.1867	0.00
445.1817	1+	Y _{1α} [‡]	445.1817	0.00
447.1973	1+	Y _{1α}	447.1973	0.00
463.1926	1+	Y _{2α} /Y _{1β}	463.1922	-0.86
475.1922	1+	^{1,5} X _{1α}	475.1922	0.00
491.1871	1+	^{1,5} X _{2α} /Y _{1β}	491.1871	0.00
528.1923	1+	B _{3α}	528.1923	0.00
575.2446	1+	Z _{2α} [•] -OH	575.2446	0.00
591.2394	1+	Z _{2α}	591.2395	0.17
607.2349	1+	Y _{2α} [‡]	607.2345	-0.66
609.2501	1+	Y _{2α}	609.2501	0.00
632.266	1+	Z _{3α} /Z _{1β}	632.2661	0.16
637.245	1+	^{1,5} X _{2α}	637.245	0.00
750.2932	1+	^{0,4} X ₀ /Z _{1β}	750.2927	-0.67
753.3152	1+	Z _{3α} [•] -CH ₂ CO	753.3162	1.33
778.3238	1+	Z _{3α} [•] -OH	778.3235	-0.39
794.3193	1+	Z _{3α} (Z _{1β} [•] -OH)	794.3189	-0.50
810.3145	1+	Z _{1β}	810.3138	-0.86
812.3292	1+	Y _{3α}	812.3295	0.37
828.3242	1+	Y _{1β}	828.3244	0.24
840.3243	1+	^{1,5} X _{3α}	840.3244	0.12
851.3138	1+	M-Tag	851.3145	0.82
856.3191	1+	^{1,5} X _{1β}	856.3193	0.23
870.3354	1+	^{0,2} X _{1β}	870.3349	-0.57
926.3611	1+	M-CH ₄ O ₂	926.3613	0.22
943.3643	1+	M-CH ₃ O	943.364	-0.32
956.3715	1+	M-H ₂ O	956.3718	0.31
974.382	1+	Precursor	974.3823	0.31

Table S-13. List of assigned EED (16 eV) fragments of the Me-PRAGS-labeled LNFP VI.

<i>m/z (obsv'd.)</i>	<i>z</i>	<i>Assignment</i>	<i>m/z (calc'd.)</i>	<i>Δm/z (ppm)</i>
267.1339	1+	Z _{1α} /Z _{1β}	267.1339	0.00
283.1291	1+	Y _{1α} /Z _{1β}	283.1288	-1.06
301.1397	1+	Y _{1α} /Y _{1β}	301.1394	-1.00
324.7999		ω ₃		
329.1345	1+	^{1,5} X _{1α} /Y _{1β}	329.1343	-0.61
366.1395	1+	B _{2α}	366.1395	0.00
399.1762	1+	Z _{1α} [•] -CH ₂ OH	399.1762	0.00
406.6683	2+	Y _{3α} ²⁺	406.6686	0.74
420.6658	2+	^{1,5} X _{3α} ²⁺	420.6661	0.71
429.1867	1+	Z _{1α}	429.1867	0.00
445.1816	1+	Y _{1α} [‡]	445.1817	0.22
447.1973	1+	Y _{1α}	447.1973	0.00
463.1922	1+	Y _{2α} /Y _{1β}	463.1922	0.00
475.1922	1+	^{1,5} X _{1α}	475.1922	0.00
491.187	1+	^{1,5} X _{2α} /Y _{1β}	491.1871	0.20
575.2445	1+	Z _{2α} [•] -OH	575.2446	0.17
591.2399	1+	Z _{2α}	591.2395	-0.68
607.2348	1+	Y _{2α} [‡]	607.2345	-0.49
609.2498	1+	Y _{2α}	609.2501	0.49
632.2657	1+	Z _{3α} /Z _{1β}	632.2661	0.63
637.2449	1+	^{1,5} X _{2α}	637.245	0.16
750.2929	1+	^{0,4} X ₀ /Z _{1β}	750.2927	-0.27
752.3083	1+	Z _{3α} [•] -CH ₃ CO	752.3084	0.13
764.3083	1+	Z _{3α} [•] -CH ₂ OH	764.3084	0.13
778.3235	1+	Z _{3α} [•] -OH	778.3235	0.00
794.3189	1+	Z _{3α} (Z _{1β} [•] -OH)	794.3189	0.00
810.3144	1+	Z _{1β}	810.3138	-0.74
812.3295	1+	Y _{3α}	812.3295	0.00
828.3243	1+	Y _{1β}	828.3244	0.12
840.3243	1+	^{1,5} X _{3α}	840.3244	0.12
851.3137	1+	M-Tag	851.3145	0.94
856.3192	1+	^{1,5} X _{1β}	856.3193	0.12
926.362	1+	M-CH ₄ O ₂	926.3613	-0.76
943.3633	1+	M-CH ₃ O	943.364	0.74
956.3716	1+	M-H ₂ O	956.3718	0.21
974.3821	1+	Precursor	974.3823	0.21