

Figure S1. Endoglycosidase F3 reveals core fucosylated N-glycans. A) Endo F3 cleaves N-glycans between GlcNAc residues on the chitobiose core only in the presence of a core fucose residue and is unable to cleave terminally fucosylated isomers. B) Terminally fucosylated isomers were detected minimally (Hex4dHex1HexNAc3 m/z 1444.5071, Hex4dHex1HexNAc4 m/z 1647.5865, Hex6dHex1HexNAc5 m/z 2174.7715) or not at all (Hex4dHex1HexNAc5SO₄1 m/z 1952.6125). C) Endo F3 cleavage products from core fucosylated isomers with a distinct -349.1373 mass shift were observed in much greater abundance for the four representative structures shown (Hex4HexNAc2 m/z 1095.3698, Hex4HexNAc3 m/z 1298.4492, Hex4HexNAc4SO₄1 m/z 1603.4752, Hex6HexNAc4 m/z 1825.6342) as well as for most structures with at least one fucose residue in this report.



Figure S2. Sialic Acid Stabilization of TMA cores. A-L) Representative $\alpha 2,3$ -sialylated N-glycan structures enriched in tumor tissue cores as compared to patient matched normal tissue cores. Log₂ FC between patient matched tumor and normal cores, where positive values represent enrichment in tumor tissue.



Figure S3. N-glycan colocalization with CA19-9. A) Representative whole tissue block sections from which TMA cores were derived were IHC stained for CA19-9 expression. B) A color-based k-means clustering algorithm was applied to high-resolution staining images to generate unbiased staining classifications, the most intense of which (outlined in red) were co-registered with original scans in Fleximaging and used to draw regions of interest around stained tissue. C) SCiLS lab software was used to identify and create images of N-glycans colocalized to areas of CA19-9 staining. Shown are

three representative N-glycans (Hex5dHex2HexNAc4 m/z 1955.6975, Hex6dHex2HexNAc5 m/z 2320.8294, Hex6dHex3HexNAc5 m/z 2466.8873). D, E) Segmentation analysis across eight nodes of 72 N-glycan structures showing differential associations of glycans between CA19-9-staining and non-CA19-9-staining tissue.

TB#	Race	Sex	Age	Vital Status	Recurrence	Type of Recurrence	Days between Surgery and Recurrence	Days between Surgery and Date of last contact/Death	Histological Type	Histological Grade	Staging
2204	WHITE	м	75	Unknown	Unknown	N/A	N/A	272	Adenocarcinoma	moderately differentiated	T3NOMX
2278	WHITE	м	76	Unknown	Unknown	N/A	N/A	211	cholangiocarcinoma	moderately differentiated	T3N1MX
2279	WHITE	F	61	Unknown	YES	distant recurrence - GAST	2233	2486	Adenocarcinoma	well differentiated	T3NOMX
2381	WHITE	м	73	Unknown	YES	Distant recurrence - CNS	2499	2587	Mucinous Adenocarcinoma	Not Reported	
2417	WHITE	м	80	Unknown	Unknown	N/A	N/A	23	Adenocarcinoma	poorly differentiated	T3N1MX
2454	WHITE	F	69	Unknown	Unknown	N/A	N/A	Unknown	Adenocarcinoma	moderately differentiated	T3NOMX
2487	BLACK	м	73	Unknown	Unknown	N/A	N/A	106	Adenocarcinoma	well differentiated	T3N1MX
2464	BLACK	F	61	Unknown	YES	metasticized to liver and omentum	N/A	Unknown	Adenocarcinoma	poorly differentiated	T4N1Mx
1751	WHITE	м	65	Unknown	Unknown	N/A	N/A	101	Adenocarcinoma	well differentiated	T3N1MX
1800	BLACK	F	67	Unknown	Unknown	N/A	N/A	204	Adenocarcinoma	poorly differentiated	T3N1MX
1691	WHITE	м	69	Unknown	Unknown	N/A	N/A	92	Adenocarcinoma	Not Reported	T3N1MX
1848	WHITE	м	71	Unknown	NO	Never disease free	N/A	314	Adenocarcinoma	poorly differentiated	T3N1MX
1911	WHITE	м	83	Unknown	NO	Disease free	N/A	118	Adenocarcinoma	moderately differentiated	T3N1MX
1747	WHITE	F	63	Unknown	NO	Possible recurrence	N/A	138	Adenocarcinoma	poorly differentiated	T3N1MX
1673	WHITE	м	78	Unknown	NO	Disease free	N/A	440	Adenocarcinoma	moderately differentiated	T3N1
1685	BLACK	м	66	Unknown	NO	Never disease free	N/A	173	Adenocarcinoma	poorly differentiated	T3N1MX
1987	WHITE	F	58	Unknown	NO	Disease free	N/A	404	Adenocarcinoma	moderately differentiated	T3N1MX
2055	WHITE	м	69	Unknown	Unknown	N/A	N/A	808	Adenocarcinoma	poorly differentiated	T3NXMX
1955	BLACK	F	51	Unknown	Unknown	N/A	N/A	392	Adenocarcinoma	moderately differentiated	T3N1MX
1958	WHITE	м	42	Unknown	Unknown	N/A	N/A	429	Adenocarcinoma	poorly differentiated	T3N1MX
1982	WHITE	F	66	Unknown	Unknown	N/A	N/A	336	Adenocarcinoma	moderately differentiated	T2N1MX
2572	WHITE	F	87	Unknown	NO	Disease free	N/A	1387	Adenocarcinoma	moderately differentiated	T1NOMX
2091	WHITE	F	54	Unknown	YES	Local Recurrence	406	547	Adenocarcinoma	Not Reported	T2NOMX
2495	WHITE	м	56	Dead	NO	Never disease free	N/A	76	Adenocarcinoma	Not Reported	T3N1MX
2807	BLACK	F	62	Unknown	NO	Never disease free	N/A	126	Adenocarcinoma	poorly differentiated	T3NOMX
2815	WHITE	F	76	Unknown	Unknown	N/A	N/A	Unknown	Ductal adenocarcinoma	moderately differentiated	T3NOMX
2893	BLACK	F	68	Unknown	YES	Local recurrence	613	613	Adenocarcinoma	moderately differentiated	T3N1MX
2916	WHITE	F	37	Unknown	YES	Distant recurrence	165	236	Adenocarcinoma	moderately differentiated	T3N1MX
2790	WHITE	M	78	Unknown	NO	Never disease free	N/A	32	Adenocarcinoma	moderately differentiated	T2N1bMX
2695	WHITE	м	70	Unknown	NO	Never disease free	N/A	185	Adenocarcinoma	Not Reported	T2NOMX
3721	WHITE	F	66	Unknown	NO	Never diease free	N/A	50	Ductal adenocarcinoma	poorly differentiated	T3N0MX
3627	BLACK	F	84	Unknown	Unknown	N/A	N/A	Unknown	Adenocarcinoma	moderately differentiated	T2N1MX
3508	WHITE	м	49	Unknown	NO	Never disease free	N/A	221	Adenocarcinoma	moderately differentiated	T3N1MX
3727	WHITE	м	74	Unknown	YES	Distant recurrence	140	140	Adenosquamous carcinoma	moderately differentiated	T3NOMX
3499	WHITE	F	66	Unknown	NO	Disease free	N/A	125	Ductal adenocarcinoma	Not Reported	T1NOMX
3463	WHITE	F	64	Unknown	NO	Disease free	N/A	215	Ductal adenocarcinoma	moderately differentiated	T3N1MX
3832	WHITE	м	68	Unknown	YES	Distant recurrence - LUNG	332	353	Adenocarcinoma	moderately differentiated	T3N1MX
3978	WHITE	м	63	Unknown	NO	Disease free	N/A	25	Adenocarcinoma	Not Reported	T2N1bMX
3922	BLACK	м	72	Unknown	NO	Disease free	N/A	94	Ductal adenocarcinoma	moderately differentiated	T1NOMX
3986	WHITE	F	70	Unknown	NO	Disease free	N/A	27	Adenocarcinoma	poorly differentiated	T3N1MX
3406	WHITE	F	74	Unknown	NO	Disease free	N/A	62	Ductal adenocarcinoma	moderately differentiated	T3N1MX
4038	WHITE	м	71	Unknown	YES	Distant recurrence - LUNG	525	318	Adenocarcinoma	moderately differentiated	T3N1MX
3859	WHITE	F	50	Dead	YES	Distant recurrence - HEPT	196	202	Ductal adenocarcinoma	moderately differentiated	T3N1MX
3915	WHITE	F	53	Dead	YES	Distant recurrence - LUNG	1182	1213	Ductal adenocarcinoma	moderately differentiated	T2N0MX
3891	WHITE	F	62	Unknown	Unknown	N/A	N/A	1148	Ductal adenocarcinoma	moderately differentiated	T3N1bM
3886	WHITE	M	62	Unknown	YES	Distant recurrence - HEPT	337	604	Adenocarcinoma	moderately differentiated	T3N1bMX
4072	WHITE	F	71	Unknown	NO	Disease Free	N/A	27	Ductal adenocarcinoma	moderately differentiated	T3N0MX
4524	WHITE	F	60	Unknown	NO	Disease Free	N/A	130	Ductal adenocarcinoma	moderately differentiated	T3N1MX
4071	BLACK	M	64	Unknown	NO	Disease Free	N/A	43	Ductal adenocarcinoma	moderately differentiated	T1N1bMX
4365	WHITE	F	78	Unknown	NO	Disease Free	N/A	90	Adenocarcinoma	moderately differentiated	T1N0MX
4180	WHITE	м	87	Unknown	NO	Disease Free	N/A	69	Adenocarcinoma	poorly differentiated	T3N1bMX
4374	BLACK	M	51	Unknown	YES	Distant recurrence - HEPT	735	736	Ductal adenocarcinoma	moderately differentiated	T3N1MX
4257	ASIAN	м	39	Dead	NO	Never disease free	N/A	9	Ductal adenocarcinoma	moderately differentiated	T3N1MX
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 Table S1. Clinical information for patient samples used for TMA cores and for whole tissue analysis.

Composition	Theoretical Mass	Observed Mass	Mass Error	Composition	Theoretical Mass	Observed Mass	Mass Error	Composition	Theoretical Mass	Observed Mass	Mass Error
Hex3dHex1HexNAc2 + Na	1079.3749	1079.3735	1.2961	Hex5HexNAc5(2,6)NeuAc1 + Na	2184.8035	2184.8077	1.9224	Hex6dHex4HexNAc5(2,3)NeuAc1 + Na	2903.0566	2903.0591	0.8612
Hex3HexNAc3 + Na	1136.3964	1136.3971	0.6169	Hex5dHex1HexNAc6 + Na	2215.7980	2215.7952	1.2637	Hex8dHex1HexNAc7 + Na	2906.0393	2906.0507	3.9229
Hex5HexNAc2 + Na	1257.4226	1257.4224	0.1583	Hex6HexNAc6 + Na	2232.7964	2232.7902	2.7589	Hex7dHex4HexNAc6 + Na	2979.0808	2979.0835	0.9063
Hex3dHex1HexNAc3 + Na	1282.4543	1282.4522	1.6367	Hex3dHex2HexNAc6 + Na + 2S	2242.6469	2242.6535	2.9430	Hex6dHex1HexNAc6(2,3)NeuAc1(2,6)NeuAc1 + Na	2986.1050	2986.1060	0.3349
Hex4HexNAc3 + Na	1298.4492	1298.4495	0.2318	Hex5HexNAc4(2,3)NeuAc2 + Na	2243.8042	2243.8000	1.8718	Hex6dHex2HexNAc7(2,3)NeuAc1 + Na	3017.0996	3017.1001	0.1657
Hex6HexNAc2 + Na	1419.4754	1419.4769	1.0574	Hex5dHex2HexNAc4(2,3)NeuAc1 + Na	2245.8086	2245.8094	0.3562	Hex7dHex3HexNAc7 + Na	3036.1023	3036.1050	0.8893
Hex4dHex1HexNAc3 + Na	1444.5071	1444.5063	0.5531	Hex5HexNAc4(2,3)NeuAc1(2,6)NeuAc1 + Na	2271.8355	2271.8445	3.9616	Hex6dHex2HexNAc7(2,6)NeuAc1 + Na	3045.1309	3045.1407	3.2183
Hex5HexNAc3 + Na	1460.5020	1460.5026	0.4115	Hex4dHex2HexNAc5(2,3)NeuAc1 + Na	2286.8352	2286.8368	0.6997	Hex6dHex3HexNAc5(2,3)NeuAc2 + Na	3047.1101	3047.0993	3.5443
Hex3dHex1HexNAc4 + Na	1485.5337	1485.5338	0.0680	Hex5dHex1HexNAc5(2,3)NeuAc1 + Na	2302.8301	2302.8257	1.9107	Hex8HexNAc7(2,3)NeuAc1 + Na	3049.0894	3049.0859	1.1479
Hex4HexNAc4 + Na	1501.5286	1501.5282	0.2657	Hex5dHex3HexNAc5 + Na	2304.8345	2304.8318	1.1710	Hex8dHex1HexNac8 + Na	3109.1187	3109.1186	0.0322
Hex3HexNAc5 + Na	1542.5552	1542.5536	1.0366	Hex6HexNAc5(2,3)NeuAc1 + Na	2318.8250	2318.8205	1.9406	Hex7dHex1HexNAc6(2,3)NeuAc2 + Na	3120.1265	3120.1198	2.1473
Hex7HexNAc2 + Na	1581.5282	1581.5320	2.4034	Hex6dHex2HexNAc5 + Na	2320.8294	2320.8242	2.2401	Hex7dHex3HexNAc6(2,3)NeuAc1 + Na	3122.1309	3122.1277	1.0249
Hex4HexNAc3(2,3)NeuAc1 + Na	1588.5606	1588.5557	3.0846	Hex5dHex1HexNAc5(2,6)NeuAc1 + Na	2330.8614	2330.8532	3.5180	Hex9HexNAc8 + Na	3124.1353	3124.1252	3.2329
Hex5dHex1HexNAc3 + Na	1606.5599	1606.5528	4.4188	Hex6HexNAc5(2,6)NeuAc1 + Na	2346.8563	2346.8634	3.0253	Hex6HexNAc6(2,3)NeuAc2(2,6)NeuAc1 + Na	3130.1585	3130.1478	3.4184
Hex4dHex1HexNAc4 + Na	1647.5865	1647.5862	0.1815	Hex6dHex1HexNAc6 + Na	2377.8509	2377.8482	1.1351	Hex6dHex2HexNAc6(2,3)NeuAc1(2,6)NeuAc1 + Na	3132.1629	3132.1748	3.7993
Hex5HexNAc4 + Na	1663.5814	1663.5831	1.0225	Hex5HexNAc6(2,6)NeuAc1 + Na	2387.8828	2387.8879	2.1358	Hex7dHex2HexNAc7(2,3)NeuAc1 + Na	3179.1524	3179.1513	0.3460
Hex3dHex1HexNAc5 + Na	1688.6131	1688.6128	0.1771	Hex5dHex1HexNAc4(2,3)NeuAc2 + Na	2389.8621	2389.8575	1.9248	Hex8dHex3HexNAc7 + Na	3198.1551	3198.1541	0.3127
Hex4HexNAc5 + Na	1704.6080	1704.6083	0.1766	Hex5dHex3HexNAc4(2,3)NeuAc1 + Na	2391.8665	2391.8600	2.7175	Hex8dHex2HexNAc8 + Na	3255.1766	3255.1788	0.6758
Hex4dHex1HexNAc3(2,3)NeuAc1 + Na	1734.6158	1734.6101	3.2860	Hex7HexNAc6 + Na	2393.8458	2393.8466	0.3346	Hex7HexNAc6(2,3)NeuAc3 + Na	3264.1800	3264.1855	1.6850
Hex8HexNAc2 + Na	1743.5810	1743.5814	0.2300	Hex5dHex1HexNAc4(2,3)NeuAc1(2,6)NeuAc1 + Na	2417.8934	2417.8946	0.4963	Hex7dHex2HexNAc6(2,3)NeuAc2 + Na	3266.1844	3266.1844	0.0000
Hex5HexNAc3(2,3)NeuAc1 + Na	1750.6134	1750.6177	2.4563	Hex5dHex3HexNAc4(2.6)NeuAc1 + Na	2419.8978	2419.9008	1.2397	Hex7dHex4HexNAc6(2,3)NeuAc1 + Na	3268.1888	3268.1996	3.3046
Hex4HexNAc4(2.3)NeuAc1 + Na	1791.6489	1791.6489	0.0000	Hex5dHex2HexNAc5(2.3)NeuAc1 + Na	2448.8880	2448.8986	4.3285	Hex9dHex1HexNAc8 + Na	3270.1681	3270.1758	2.3549
Hex5dHex1HexNAc4 + Na	1809.6393	1809.6394	0.0558	Hex6dHex1HexNAc5(2.3)NeuAc1 + Na	2464.8829	2464.8741	3.5701	Hex7dHex1HexNAc7(2.3)NeuAc2 + Na	3323.2059	3323.2070	0.3310
Hex4dHex1HexNAc5 + Na	1850.6659	1850.6646	0.7019	Hex6dHex3HexNAc5 + Na	2466.8873	2466.8915	1.7030	Hex7dHex3HexNAc7(2,3)NeuAc1 + Na	3325.2103	3325.2053	1.5037
Hex5HexNAc5 + Na	1866.6608	1866.6627	1.0184	Hex5HexNAc5(2,3)NeuAc1(2,6)NeuAc1 + Na	2474.9149	2474.9121	1.1314	Hex7dHex5HexNAc7 + Na	3328.2181	3328.2107	2.2234
Hex3dHex1HexNAc6 + Na	1891.6925	1891.6903	1.1625	Hex5dHex3HexNAc6 + Na	2507.9139	2507.9015	4.9443	Hex6dHex1HexNAc6(2,6)NeuAc3 + Na	3332.2790	3332.2829	1.1704
Hex9HexNAc2 + Na	1905.6338	1905.6345	0.3679	Hex6dHex2HexNAc6 + Na	2523,9088	2523.9113	0.9909	Hex7dHex1HexNAc6(2,3)NeuAc3 + Na	3410.2379	3410.2364	0.4399
Hex5dHex1HexNAc4 + 2Na + S	1911.5859	1911.5781	4.0636	Hex7dHex1HexNAc6 + Na	2539.9037	2539.9033	0.1571	Hex7dHex2HexNAc7(2.3)NeuAc2 + Na	3469.2638	3469.2783	4.1796
Hex6HexNAc3(2.3)NeuAc1 + Na	1912.6662	1912.6619	2.2482	Hex6dHex1HexNAc7 + Na	2581.9336	2581.9336	0.0155	Hex8dHex1HexNAc7(2.3)NeuAc2 + Na	3485.2587	3485.2551	1.0329
Hex4dHex1HexNAc4(2.3)NeuAc1 + Na	1937.6979	1937.6928	2.6320	Hex5dHex1HexNAc5(2.3)NeuAc2 + Na	2592.9415	2592.9445	1.1570	Hex8dHex3HexNAc7(2.3)NeuAc1 + Na	3487.2631	3487.2583	1.3764
Hex4dHex1HexNAc5 + Na + S	1952.6125	1952.6059	3.3801	Hex5dHex3HexNAc5(2.3)NeuAc1 + Na	2594.9459	2594,9536	2.9673	Hex8dHex2HexNAc8(2.3)NeuAc1 + Na	3544.2846	3544.2935	2.5111
Hex5HexNAc4(2.3)NeuAc1 + Na	1953.6928	1953.6928	0.0000	Hex7HexNAc7 + Na	2596.9252	2596.9269	0.6550	Hex7dHex2HexNAc6(2.3)NeuAc3 + Na	3556.3210	3556.3148	1.7434
Hex5dHex2HexNAc4 + Na	1955.6972	1955.6959	0.6642	Hex6HexNAc5(2.3)NeuAc2 + Na	2608.9364	2608.9475	4.2546	Hex7dHex4HexNAc6(2.3)NeuAc2 + Na	3558.3002	3558.3117	3.2319
Hex3dHex1HexNAc6 + Na + S	1993.6390	1993.6337	2.6585	Hex6dHex2HexNAc5(2.3)NeuAc1 + Na	2610.9408	2610.9421	0.4979	Hex9dHex1HexNAc8(2.3)NeuAc1 + Na	3560.2795	3560.2885	2.5279
Hex4HexNAc5(2.3)NeuAc1 + Na	1994,7193	1994,7098	4.7626	Hex6dHex4HexNAc5 + 1Na	2613.9486	2613.9419	2.5632	Hex9dHex1HexNAc8(2.6)NeuAc1 + Na	3588.3108	3588.3089	0.5295
Hex4dHex2HexNAc5 + Na	1996,7238	1996.7235	0.1502	Hex6dHex1HexNAc6(2.3)NeuAc1 + Na	2667.9623	2667.9623	0.0000	Hex8dHex4HexNAc7(2.3)NeuAc1 + Na	3633.3210	3633.3287	2.1193
Hex5dHex1HexNAc5 + Na	2012.7187	2012.7180	0.3473	Hex6dHex3HexNAc6 + Na	2669.9667	2669.9796	4.8319	Hex10dHex1HexNAc9 + Na	3636.3037	3636.2973	1.7600
Hex4HexNAc5(2.6)NeuAc1 + Na	2022.7506	2022 7546	1.9775	Hex7dHex2HexNAc6 + Na	2685.9616	2685 9595	0.7815	Hex7dHex4HexNAc8(2.3)NeuAc1 + Na	3674 3476	3674 3471	0.1361
Hex6HexNAc5 + Na	2028.7136	2028.7158	1.0849	Hex7dHex1HexNAc7 + Na	2742.9831	2742.9857	0.9482	Hex7dHex3HexNAc6(2.3)NeuAc3 + Na	3702.3789	3702.3866	2.0797
Hex5dHex2HexNAc4 + 2Na + S	2057.6438	2057.6533	4.6325	Hex6dHex1HexNAc5(2.3)NeuAc2 + Na	2754.9943	2754,9948	0.1815	Hex9HexNAc8(2.3)NeuAc2 + Na	3704.3330	3704.3417	2.3486
Hex6dHex1HexNAc3(2.3)NeuAc1 + Na	2058.7242	2058.7323	3.9345	Hex6dHex3HexNAc5(2.3)NeuAc1 + Na	2756.9987	2756.9994	0.2539	Hex9dHex4HexNAc8 + Na	3709.3452	3709.3412	1.0784
Hex4dHex2HexNAc4(2,3)NeuAc1 + Na	2083,7558	2083.7473	4.0792	Hex6dHex2HexNAc6(2.3)NeuAc1 + Na	2814.0202	2814.0335	4.7263	Hex9dHex2HexNAc8(2.6)NeuAc1 + Na	3734.3687	3734.3618	1.8477
Hex3dHex1HexNAc6 + Na + 25	2095.5856	2095.5805	2.4337	Hex7dHex1HexNAc6(2.3)NeuAc1 + Na	2830.0151	2830.0192	1.4488	Hex10HexNAc9(2,3)NeuAc1 + Na	3779.3888	3779.3858	0.7938
Hex5dHex1HexNAc4(2.3)NeuAc1 + Na	2099 7507	2099 7501	0.2857	Hex7dHex3HexNAc6 + Na	2832.0195	2832.0124	2.5067	Hex8dHex4HexNAc8(23)NeuAc1 + Na	3836.4004	3836.4063	1.5379
Hex5dHex3HexNAc4 + Na	2101.7551	2101.7545	0.2850	Hex6HexNAc6(2.3)NeuAc1(2.6)NeuAc1 + Na	2840.0471	2840.0494	0.8098	Hex9dHex1HexNAc8(2,3)NeuAc2 + Na	3850.3909	3850.3930	0.5454
Hey5dHey1HeyNAr4(2.6)NeuAr1 + Na	2127 7820	2127 7791	1 3629	Hey6dHey2HeyNAr6(26)NeuAr1 + Na	2842.0515	2842.0592	2 7093	Her9dHer3HerNAc8(2,3)NeuAc1 + Na	3852 3953	3852.4069	3.0111
Hex3dHex2HexNAc6 + Na + S	2139.6969	2139.6970	0.0467	Hex7dHex1HexNAc6(2.6)NeuAc1 + Na	2858.0464	2858.0526	2.1693	Hex9dHex5HexNAc8 + Na	3855.4031	3855.3881	3.8906
Hex4dHex1HexNAc5(2.3)NeuAc1 + Na	2140.7773	2140.7724	2.2889	Hex6dHex3HexNAc7+Na	2873.0461	2873.0321	4.5245	Hex9dHex3HexNAc8(2.6)NeuAc1 + No	3880.4266	3880.4128	3.5563
HerSHerNAc5(2.3)NeuAc1 + Na	2156 7722	2156 7735	0.6028	Hex7dHex2HexNAc7 + Na	2890.0444	2890.0463	0.6574	Hey8dHey5HeyNAc8/23NeuAc1 + Na	3982.4583	3982.4489	2.3604
Hey5dHey2HeyNAr5 + Na	2158 7766	2158 7746	0.9260	Hey6dHey1HeyNAc7(2.6)NeuAc1 + Na	2899.0729	2899.0729	0.3449		5502.4503	3302.4403	1.5004
Hey6dHey1HeyNAr5 + Na	2174 7715	2174 7747	1 4719	Hey6dHey2HeyNΔr5/23\NeuΔr2 + No	2901.0523	2901.0474	1.6546				
THE ADDITION AT THE ADDITION AND ADDITION ADDITICON ADDITION ADDITION ADDITION ADDITICON ADDITICON ADDITICON AD	£1/4.//15	61/7.//4/	1.4/19	nexouriexcreationCo(2,5)NeuAc2 + Na	2301.0322	2502.0474	4.0340		-		·

Table S2. Composition and mass accuracy of 151 N-glycan structures obtained via MALDI-IMS analysis. All detected structures are monoisotopic, underivatized and singly-sodiated unless otherwise indicated. Sialic acid derivatization by amidation amidation (AA) reaction yields a mass difference of +290.1114 for 2,3 linked sialic acid residues and +318.1427 for 2,6 linked sialic acid residues. Mass error calculation: ((ABS(Theoretical m/z – Observed m/z)/Theoretical m/z)*1,000,000).

m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure	m/z	Structure
1079.3745*		1905.6338		2215.7980*		2539.9037*	*	2979.0808*	**	3485.2587	r-<
1136.3964		1911.5859*	s	2232.7964		2581.9336		2986.1050		3487.2631	
1257.4226	***	1912.6662		2242.6469*	\$ x2	2592.9415	••	3017.0996		3544.2846	
1282.4543*		1937.6979		2243.8042		2594.9459		3036.1023*		3556.3210	
1298.4492		1952.6125*	s and the second	2245.8086		2596.9252		3045.1309		3558.3002	
1419.4754		1953.6928		2271.8355		2608.9364		3047.1101		3560.2795	
1444.5071*		1955.6972*	₩ ₩ ₩	2286.8352		2610.9408		3049.0894		3588.3108	
1460.5020		1993.6390*	s	2302.8301		2613.9486	H	3109.1187*		3633.3210	.
1485.5337*		1994.7193		2304.8345*		2667.9623		3120.1265		3636.3037	
1501.5286		1996.7238*		2318.8250		2669.9667*		3122.1309		3674.3476	r (
1542.5552		2012.7187*		2320.8294*		2685.9616*		3124.1353*	T I	3702.3789	
1581.5282		2022.7506		2330.8614		2742.9831*		3130.1585		3704.3330	••• \$
1588.5606		2028.7136		2346.8563		2754.9943		3132.1629		3709.3452	
1606.5599*		2057.6438	→ → → → → → → → → →	2377.8509*		2756.9987		3179.1524		3734.3687	
1647.5865*		2058.7242		2387.8828	•••	2814.0202		3198.1551*	 =	3779.3888	• <
1663.5814		2083.7558		2389.8621	T =<	2830.0151		3255.1766*		3836.4004	r
1688.6131*		2095.5856*	\$ 12	2391.8665		2832.0195*		3264.1800		3850.3909	
1704.6080		2099.7507		2393.8458	•••	2840.0471		3266.1844		3852.3953	
1734.6158	*** *	2101.7551*	T=<	2417.8934		2842.0515		3268.1888	r	3855.4031	
1743.5810		2127.7820		2419.8978		2858.0464		3270.1681*		3880.4266	
1750.6134		2139.6969*		2448.8880		2873.0461*		3323.2059		3982.4583	r4
1791.6489		2140.7773		2464.8829		2890.0444*		3325.2103		0 0	ialactose (Hex)
1809.6393*		2156.7722		2466.8873*		2899.0729		3328.2181*	-		Aannose (Hex) I-acetylglucosamine (HexNAc)
1850.6659*		2158.7766*		2474.9149		2901.0522		3332.2790			I-acetylgalactosamine (HexNAc)
1866.6608		2174.7715*		2507.9139*		2903.0566		3410.2379		▲ ⊧	ucose (dHex)
1891.6925*		2184.8035		2523.9088*		2906.0393*		3469.2638		2 2	,5-Sialic Acid (2,3NeuAc) ,6-Sialic Acid (2,6NeuAc)

Table S3. Summary table of N-glycan structures cumulatively detected across all analyzed tissues. A key to the monosaccharide unit symbols is provided in the bottom right. N-glycan structures denoted with a * indicates that the presence of a core fucose reside has been confirmed via analysis

using Endo F3. It is important to note that the representative structures provided do not encompass all possible isomeric conformations for these N-glycans, but are the most likely based on previous reporting, orthogonal analyses and the available biosynthetic pathways.

	Both CA19.9 and sTRA		CA	19.9	sT	RA	Neither CA19-9 nor sTRA		
Centroid [m/z]	Fold Change	Intensity	Fold Change	Intensity	Fold Change	Intensity	Fold Change	Intensity	
1079.3749	0.5580	1030.2615	0.5620	1013,5629	0.7529	799.8649	0.0691	681.6336	
1136 3964	0.6459	676 5595	0.3493	637,1259	0.7473	578 7372	0.7534	556 2163	
1257 4226	0.1402	2654 0624	-0.0147	2351 0033	0.3208	2490 4892	0.0796	2039 8801	
1282 4543	0.3096	2313 2134	0.3698	2365 8460	0.6335	2372 4875	0.3087	1953 0532	
1298 4492	0.2279	3618 3780	0.0596	3606 5293	0.4242	3475 8308	0.5033	3542 7250	
1230.4452	-0.0708	1/135 2276	0.0330	/350 8/60	-0.0115	/282 0775	-0.0462	1038 3505	
1413.4734	0.0708	6781 2728	0.2031	7//0 2053	0.6529	7254 8175	0.0402	6307 8605	
1444.5071	0.2024	1261 6067	0.2551	1421.0725	0.0323	1162 6526	0.4100	1079 5600	
1400.5020	0.2207	4406 0126	0.2437	1421.0725	0.0495	4141 5009	0.5052	2047 4255	
1465.5557	0.5597	2504.0746	0.1030	4925.0555	0.7490	4141.5006	0.5575	2222 8205	
1501.5280	0.4488	3504.0746	0.1823	3252.7713	0.5855	3217.3858	0.0130	3322.8205	
1542.5552	0.6699	031.8115	0.0037	4/9.50/8	0.5234	704.8998	0.2051	4/2.34//	
1581.5282	0.2772	3565.8188	0.2526	3591.4847	0.3927	2961.3900	0.1304	2688.9080	
1606.5599	0.36/1	940.9854	0.4849	1080.3293	0.9305	1025.6925	0.6006	931.9258	
1647.5865	0.2576	10790.2408	0.2137	11085.4327	0.4937	11279.3008	0.3803	11031.1855	
1663.5814	0.2230	47111.1360	0.0303	48719.1733	0.4207	45885.2833	0.5582	48841.2200	
1688.6131	0.0528	2952.7942	-0.2663	2889.9897	0.5822	3677.0442	0.0743	2442.0707	
1704.6080	0.9186	2452.2669	0.3307	2116.1872	1.1304	1949.8679	0.8319	1476.5198	
1743.5810	-0.0583	8841.7870	0.0148	8836.4647	-0.0550	7861.5800	-0.1055	7811.1225	
1791.6489	0.4449	3437.4208	0.5246	4130.0147	1.1472	2999.8529	0.5074	2359.7695	
1809.6393	0.2343	126072.3760	0.3589	145564.3267	0.7564	141867.2083	0.5121	119715.5000	
1850.6659	0.4498	13157.5664	0.1981	13928.0233	0.8493	14265.8200	0.5151	11948.0795	
1866.6608	0.6915	5408.9500	0.3092	4009.2933	0.8292	4745.9275	0.6856	5016.9438	
1891.6925	0.0593	771.5054	0.2295	1007.8143	-0.1452	546.2488	-0.7741	468.9750	
1905.6338	-0.3614	4891.3512	-0.1989	5941.8553	-0.0484	4008.0575	-0.1055	4541.7310	
1911.5859	0.0774	9652.6898	-0.2242	10247.3253	0.2193	9037.3833	0.6677	11668.2585	
1955.6972	-0.2590	7289.5402	-0.0843	7869.6207	-0.0750	6896.1758	-0.3268	6893.2070	
1996.7238	0.8381	4608.1824	0.6761	3736.5147	0.5950	3428.9295	-0.2268	2940.5792	
2012.7187	0.4143	43498.1460	0.3009	45450.9400	0.9035	51220.2250	0.4612	38769.4650	
2028.7136	0.4012	9839.5872	0.2221	10008.1940	0.7816	9078.7983	0.8338	9383.0765	
2057.6438	0.0535	18426.9780	0.1073	21937.0833	0.4448	20046.7167	0.5167	21521.1305	
2101.7551	-0.0692	7501.7748	0.0102	8503.1773	0.6562	7969.7775	0.2302	7388.0085	
2158.7766	0.4011	11363.7478	0.3342	9282.0100	-0.0345	7989.2683	-0.5551	7531.1735	
2174.7715	0.2815	53484.7100	0.4252	57246.1800	0.7232	64477.1917	0.5321	59652.0200	
2215.7980	0.9590	4382.5464	0.5851	4778.4880	1.2673	3955.2642	0.4642	3491.0819	
2232.7964	0.9598	4320.7963	0.8038	3384.2840	1.4892	2737.8392	0.8888	2981.5574	
2304.8345	0.8943	6529,6180	0.9264	6704.9727	0.5532	3284,2436	-0.2947	3249.5261	
2320.8294	-0.1965	6459,7967	-0.1060	6053,7300	0.1800	5034,5917	-0.4141	5075,9610	
2377.8509	0.4545	16636.5238	0.2718	14331,7167	0.9078	18517,2333	0.2226	17797.5590	
2393.8458	0.5722	4319,5450	0.4443	4369.4367	1.2084	3761,7533	1,2048	3747,1576	
2466 8873	-0.2042	8261 3122	-0 1177	8194 9387	0.2008	8662 9767	-0 3248	8401 9900	
2507 9139	0.6044	2482 9564	0.8787	2573 6232	-0.4874	1244 8233	-0.7505	1571 1613	
2523 9088	0.6238	8240 1160	0.4511	6913 1740	0.5957	5074 2350	-0.5965	4028 8324	
2529.9037	0.0230	3/950 5//0	0.730	3/169 / 800	0.5337	47457 7000	0.3586	46961 3775	
2581 9336	0.9281	3156 8733	0.4690	3384 8950	0.8477	2477 0816	0.2002	3008 1229	
2613 9/96	-0 5574	1040 7924	-0.16/3	1097 / 900	-1.0460	1052 5307	-1.6169	1427 1412	
2650 0667	1,2122	3157 0727	0.1045	3087 5575	0.5325	865 8590	-0.6520	927 7//0	
2005.5007	0.2670	6207 2249	0.3/13	5072 2425	0.0170	5614 4559	0.0000	5776 5140	
2083.3010	-0.3070	11120 2204	-0.2400	10064 4012	1.0265	0672 5075	-0.0945	5770.3140	
2742.9651	0.9924	7215 9054	0.0045	10004.4915	1.9205	7255 2022	0.5077	7729 5217	
2832.0195	-0.3598	7215.8054	-0.3907	0204.5100	-0.0894	/300.2933	-0.6649	1702.0054	
2890.0444	1.1449	5095.1726	0.4796	4355.5224	1.0930	1939.7393	-0.6336	1/92.3854	
2906.0393	0.3592	13588.1608	0.5779	16/25.3580	1.1644	16365.6783	1.0149	14296.7880	
29/9.0808	-0.7050	2110.1836	-0.8280	3538.4809	-0.7391	1756.5904	-1.4827	2281.3808	
3036.1023	0.9367	12185.8834	0.6211	/251.7120	0.2973	6190.2181	-0.7168	54/3.1566	
3109.1187	0.7600	3619.1301	0.8687	3715.9760	0.6550	3580.1689	0.4216	3847.6254	
3124.1102	-0.0703	1367.6939	-0.2554	1744.9258	-0.2194	1498.8243	-0.9417	1624.6381	
3198.1551	-0.5800	4070.1716	-0.4382	4077.9780	-0.6499	5322.4083	-0.9959	4366.8126	
3255.1766	0.4646	4019.1874	0.3279	3363.3185	0.2530	2510.7031	-0.5447	2158.0608	
3270.1681	0.3299	2498.8385	0.7281	3600.9105	1.3078	3232.0292	0.7372	2983.1392	
3328.2181	0.9078	6558.7212	1.1305	6332.3680	-0.0396	3531.0183	-0.1763	3367.1860	
3636.3037	0.0741	7494.0596	0.4479	8220.9520	0.4143	10278.0333	0.2161	10434.0220	
3709.3452	-0.6620	2239.3698	-0.7074	2430.1141	-0.7433	3195.2648	-1.0279	2632.6308	
3855,4031	-0.4590	2145,1399	-0.5476	1865,9784	-0.7010	3220,6986	-0.9423	3064,2660	

Table S4. Log₂FC and AUP intensity data for biomarker-classified TMA core groupings. Log₂FC of area under the peak (AUP) measurements for 62 N-glycan masses between individual patient normal and tumor cores were calculated then averaged for the 4 biomarker-designations. Positive values represent enrichment in tumor tissue. Shown too are the average tumor AUP intensities for each N-glycan in each category.

	Both CA19.9 and sTRA		CA	19.9	sT	RA	Neither CA19.9 nor sTRA		
Centroid [m/z]	Fold Change	Intensity	Fold Change	Intensity	Fold Change	Intensity	Fold Change	Intensity	
1588.5557	0.7300	878.9225	0.2582	698.8101	0.6013	914.8836	1.0571	900.6399	
2099.7507	0.4085	46658.9906	0.6431	45193.2667	0.7600	67360.1333	0.9116	51497.8833	
2391.8665	0.4367	34321.2866	0.8654	37454.7827	0.9439	53369.4667	0.9800	36108.7595	
2389.8621	0.4071	33339.7756	0.8272	38784.7980	0.9122	49766.4667	0.9518	34549.3119	
3045.1309	0.6408	13394.7468	0.6678	12234.5000	0.9185	20410.6367	0.7377	13590.6520	
3047.1101	0.6488	12995.0706	0.6338	11794.2727	0.9016	19478.3375	0.8882	13156.2914	
2245.8086	0.6080	11617.8172	0.0660	8465.1040	0.4763	12004.9650	0.9556	11237.0686	
2754.9943	0.5707	11507.1192	0.7844	11127.6347	0.8623	16962.4208	0.8884	12515.7129	
2243.8042	0.5690	11289.2776	0.0248	8271.0900	0.5687	12303.3358	1.0540	11417.7861	
2756.9987	0.6774	10354.7216	0.6550	8177.2100	0.8206	14632.9867	0.7978	10887.5210	
1953.6928	0.5610	5341.5294	0.1919	4483.8242	0.2918	5800.5642	1.0531	5745.1135	
3122.1309	0.5321	5251.0380	0.3164	3755.3627	0.4770	6739.2292	0.5712	5701.2346	
3120.1265	0.2387	4072.2387	0.2652	3178.2790	0.5609	5881.9900	0.6059	4716.3866	
2302.8301	1.4655	3847.4997	0.9116	3172.0937	1.3803	4229.3554	1.1299	2820.8969	
2464.8829	0.9450	3460.7556	1.1502	3142.9455	1.3584	5208.6625	1.3483	3688.6793	
1937.6979	0.8157	2947.7337	0.7730	2664.7448	0.9204	3516.7792	0.8982	2645.7965	
2330.8614	1.1615	2824.5832	0.3524	2297.8135	0.5762	2525.8255	1.3915	2862.6964	
2899.0729	0.5971	2181.1156	-0.4711	1199.2390	0.6073	2430.2258	1.0099	2032.7094	
2901.0522	0.7902	2170.4498	-0.2949	1141.1947	0.4682	2071.1514	0.7954	1771.5648	
2814.0202	1.3854	1855,9642	0.7914	1118,1365	-0.0829	401,2256	0.2334	549.3123	
3179 1524	1 3878	1669.0263	0.4102	1522 2567	0 1445	357 5152	0.0920	512 8538	
1734 6158	0.8024	1607 1447	1 0297	1632 8729	1 1968	2150 3284	1 1124	1489 2360	
3049 0894	0.5562	1284 9651	0.3277	1123 7731	1 1540	2015 6976	0.9335	1379.2139	
2592 9415	1 2570	1263 7442	0.7126	1020 7995	1 1694	1692 1517	0.3048	835 1244	
2184 8025	0.9619	1045 4470	1 35/2	1027 8779	1 3159	11/15 7501	1.4707	1051 8201	
1701 6490	0.9770	1043 3444	0.4214	775 6200	0.8272	997 3272	1.0619	842 1190	
2225 2102	1 1212	1009 9397	0.4214	1170 1020	-0.1210	256 0020	0.4174	432.0052	
2504 0450	1.1212	053.4420	1.0905	656 9922	1 2411	250.9930	0.41/4	430.9953	
2354.9459	0.2052	953.4439	0.1211	720.6502	-0.0221	715 1000	0.3377	931 5400	
3200.1844	0.3052	952.2453	0.1311	720.6593	-0.0221	715.1896	0.3677	531.5409 E44.4500	
2140.7773	1.5996	898.3702	0.9094	820.8087	1.6031	1022.2772	1.1/31	544.4596	
2417.8934	0.7703	885.0449	0.5632	781.6632	0.8685	1023.3772	0.8630	778.8700	
2667.9623	1.1839	881.8418	0.6622	906.5518	0.9665	597.8705	0.5209	557.4260	
3588.3108	-0.1586	870.4476	-0.0132	771.8786	-0.2820	557.7137	-0.1153	561.1179	
3633.3210	0.0963	846.9732	0.1725	731.8269	0.2039	761.6313	0.0689	719.0854	
3556.3210	0.0232	801.2463	-0.0855	655.2075	-0.0248	673.1899	-0.0190	668.3081	
3702.3789	0.0218	801.0947	-0.1589	584.6486	0.2690	1368.1991	0.1782	749.8388	
3734.3687	0.3393	780.6715	0.2635	402.7431	0.1676	307.3056	0.3022	358.2584	
3852.3953	0.2559	763.1563	0.6593	675.2545	1.1005	1101.8338	0.3252	928.5617	
3880.4266	0.1475	737.3105	0.1582	250.2074	0.3917	243.8357	-0.0014	289.7402	
2474.9149	0.8946	686.1145	0.9829	656.6366	1.1113	800.4861	0.9617	629.4493	
2083.7558	1.0305	683.1610	0.9682	688.7409	1.0032	819.3805	0.7386	580.6011	
3264.1800	0.1508	681.4168	0.1624	586.8056	-0.2936	466.6913	0.0243	587.8730	
3558.3002	0.0887	650.5435	0.3413	448.1070	-0.1998	377.3892	-0.2380	445.9021	
3017.0996	0.5944	628.9637	0.2463	897.2575	-0.1218	355.5194	0.2646	483.1616	
3268.1888	0.3009	619.2407	0.0105	370.1782	-0.2830	310.6225	-0.0844	513.8394	
3779.3888	0.0072	618.9588	-0.0012	491.1958	0.0765	590.6224	0.0306	592.2058	
2271.8355	0.6132	595.1615	0.0929	578.5817	0.3732	457.5226	1.5522	689.6138	
3544.2846	0.2542	594.1858	0.1111	567.3241	-0.4338	305.4741	-0.0415	332.0953	
2986.1050	0.2106	585.3374	-0.5972	292.6053	0.0032	404.1517	0.2094	431.8489	
2318.8250	0.6538	584.3362	0.3338	398.4857	0.5436	533.5258	0.9121	536.5304	
3982.4489	0.4478	580.6259	-0.2800	425.2241	0.1226	352.2969	-0.3154	303.5218	
3560.2795	0.3271	507.9753	0.1348	440.5444	0.1861	399.4267	0.0528	425.8965	
2903.0591	0.4282	501.0887	0.0034	292.1498	0.0105	344.4316	-0.0149	318.7844	
2830.0151	0.3095	497.6539	0.0635	333.8733	0.5711	682.2370	0.3720	670.9259	
3836.4004	0.4564	485.8277	-0.2249	372.0839	0.0272	213.7607	-0.0277	227.1791	
2858.0464	0.3286	471.1037	0.1159	399.8335	0.2109	351.9727	0.4582	408.8395	
3332.2790	-0.2879	467.4517	-0.1936	555.6265	-0.3919	420.6194	-0.2819	452.3097	
2156.7722	1.1207	463.3966	0.3849	198.9112	0.3225	211.8881	0.4691	176.1748	
3674.3476	-0.0949	461.6950	0.4208	617.0365	0.0559	382.7484	0.0033	377.7417	
3469.2638	0.3234	451.8388	0.2901	557,1624	0.1247	307.3554	-0.3367	235.0908	
2419.8978	0.7187	438,1490	1.0715	691,8955	0.8272	399,9938	0,6140	341,8993	
2840.0471	0.1858	435,9853	-0.1140	342,0754	-0.0157	372,8133	0.1023	411,9397	
3132 1629	0.5202	414 1247	-0.2280	291,2164	0.2698	349 5046	0.4708	379 7658	
2286 8352	1 2124	387 2843	0.7412	321 8799	0.6546	207 9919	0.0488	172 4521	
3850 3909	0.0671	381 4620	-0.2276	292 1214	0 3974	414 4407	0.4601	430 5678	
3485 2587	-0.0369	355 2222	0.3044	390 2540	0.6817	502 0180	0.2904	398 1496	
2387 2222	0.4619	353 2201	0.6471	476 2227	1 1562	356 9224	0.4027	255 9164	
3487 2621	0.4019	348 7502	-0.2127	280.0704	0.3020	414 5000	0.4037	425 8026	
2449 0000	1 2145	346.7392	1 2166	200.0704	0.5030	124.9090	0.3492	104 2220	
1012 5552	0.6200	340.3911	0.2907	203.4291	0.0341	266.0007	0.1/8/	271 2401	
2704 2220	0.8200	336.5000	0.2897	223.0775	0.0208	200.9027	0.3936	271.3491	
3704.3330	0.3689	334.1641	-0.0561	254.6241	0.0847	368.9007	0.1/81	370.4934	
3323.2059	0.3631	331.7865	0.3741	598.2298	-0.2183	262.0051	0.0551	305.2166	
2022.7506	0.5885	283.7597	0.5043	262.4727	0.7844	332.7603	0.7320	2/6.5223	
3410.2379	0.0387	278.9485	0.3709	243.1178	0.4703	363.7577	0.0509	260.5690	
3130.1585	0.2613	277.6546	0.3256	240.1254	0.1284	210.9380	0.0178	239.1858	
2610.9408	0.0568	217.1047	0.1058	147.2209	-0.4102	126.9894	-0.1188	148.4337	
2842.0515	0.0351	204.7200	-0.0433	159.2148	-0.1203	190.2229	0.0270	191.5226	
1994.7193	0.8127	197.2779	0.5334	157.6480	0.0055	119.7286	0.3797	115.8698	
2346.8563	0.3056	190.8673	0.5525	219.4622	0.5506	168.0192	0.5498	194.9802	
2058.7242	0.5841	187.8892	0.6469	125.5378	-0.2552	90.8619	0.3214	111.9037	
2608.9364	0.1552	186.2921	-0.1916	110.5371	0.1005	178.4843	0.2861	184.8986	
1750.6134	0.4084	172.3391	0.0769	142.8973	0.0794	146.7574	0.4893	159.4521	
2101 7551	0 2927	126 0026	0.7124	142 5501	0.0491	120 0102	0.6970	129 6026	

Table S5. Log₂FC and AUP intensity data for AA-stabilized TMA cores. Log₂FC of area under the peak (AUP) measurements for 84 AA-stabilized sialylated N-glycan masses between individual patient normal and tumor cores were calculated then averaged for the 4 biomarker-designations. Positive values represent enrichment in tumor tissue. Shown too are the average tumor AUP intensities for each sialylated N-glycan in each category.

Annotation of Reported N-glycan Structures by CID Fragmentation

timsTOF Flex MALDI-QTOF MS/MS Settings Notes on CID

Example MS/MS

Transfer

Funnel 1 RF: 425.0 Vpp **Funnel 2: RF:** 500.0 Vpp **Multipole RF**: 550.0 Vpp **Deflection Δ:** 70.0 V **MALDI Plate Offset:** 50.0 V

MS Settings

Scan Begin: 50 *m/z* Scan End: 2500 *m/z* Ion Polarity: Positive Scan Mode: MS/MS Laser Shots: 400 Laser Power: 36% Frequency: 10000 Hz

Pre-TOF Focus

Transfer Time: 72.0 μs **Pre-Pulse Storage:** 12.0 μs

Collision Cell

Collision Energy: 25.0 eV Collison RF: 1500.0 Vpp

Quadrupole

Ion Energy: 4.0 eV **Low Mass:** 150 *m/z*

CID Settings Isolation Width: 10.00 *m/z* **Collision Energy:** 150.00 eV

Supplemental Figure 4: Annotation of Reported N-glycan Structures by CID Fragmentation

CID fragmentation of 23 Nglycan base structures representing a mix of both core and terminally-fucosylated bi-, tri- and tetra-antennary configurations with and without bisecting GlcNAc residues. Where applicable EndoF3 was used to trim higher-mass corefucosylated N-glycans to improve CID performance

CID Legend

X,Y,Z ions B,C ions

Intermixed X,Y,Z/B,C ions Precursor ions













































