Supplementary materials

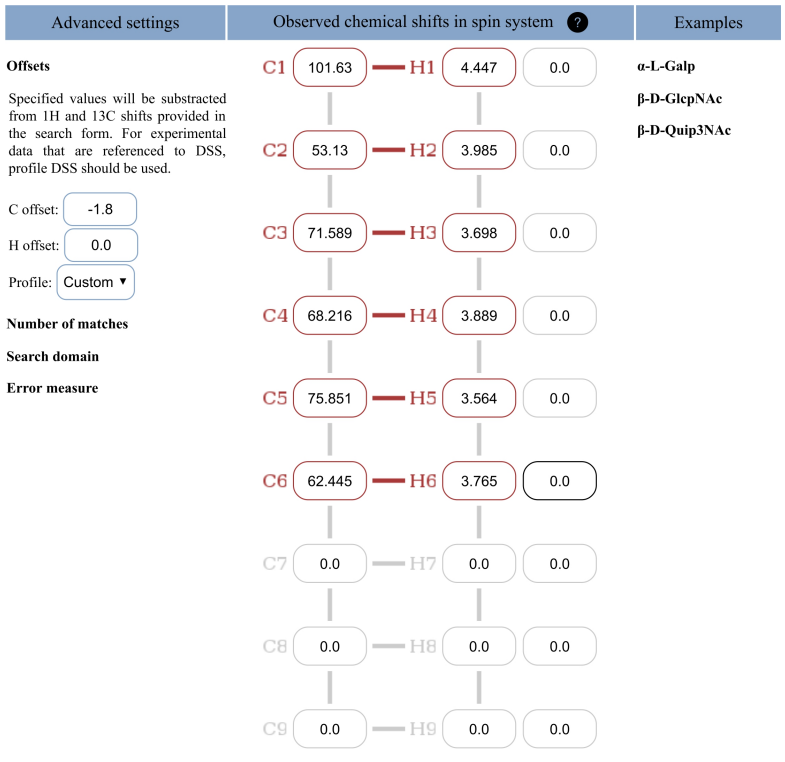

Fig. S1. Typical search, using six C-H correlations that are found in a ^{13}C-HSQC, illustrated by a search with six C-H chemical shift pairs of GalNAc of LDNF trisaccharide. For the case of an CH_2 group a second ^{1}H chemical shift could be added next to the first one. However in this particular case only one of the two H6 chemical shifts is used and the second field is empty. Additional search options can be selected on the left, for example offsets and the number of matches

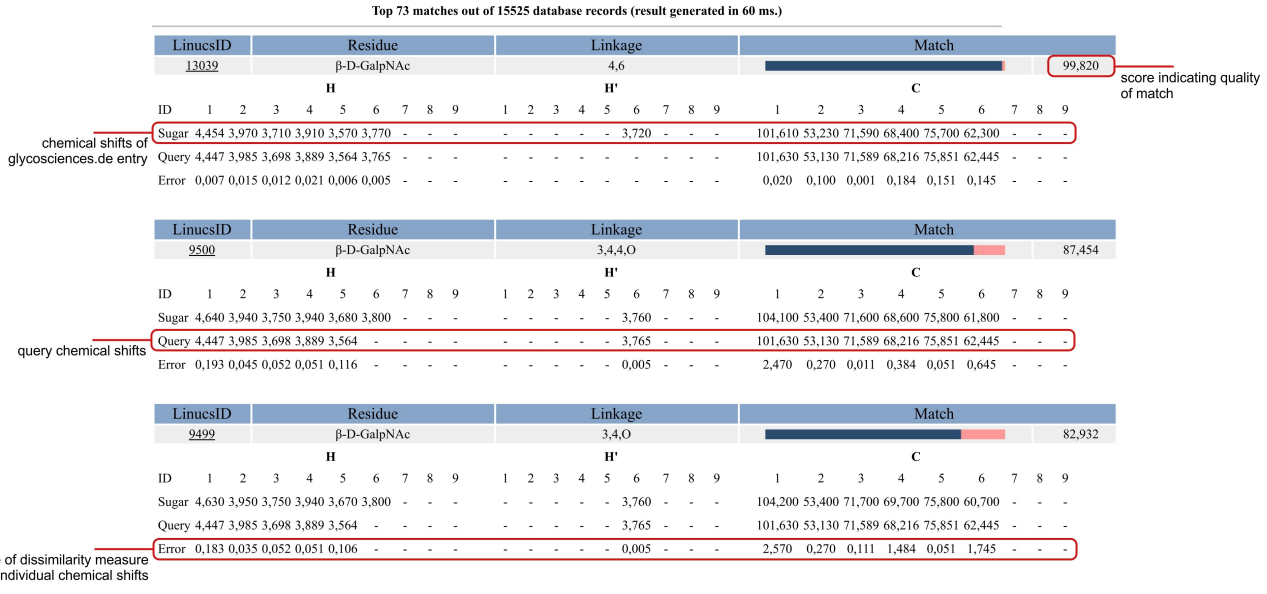

Fig. S2. Typical results illustrated by a search with six C-H chemical shift pairs of GalNAc of LDNF trisaccharide. Highlighted is the score on the top right, and the different output lines with a description on the left.

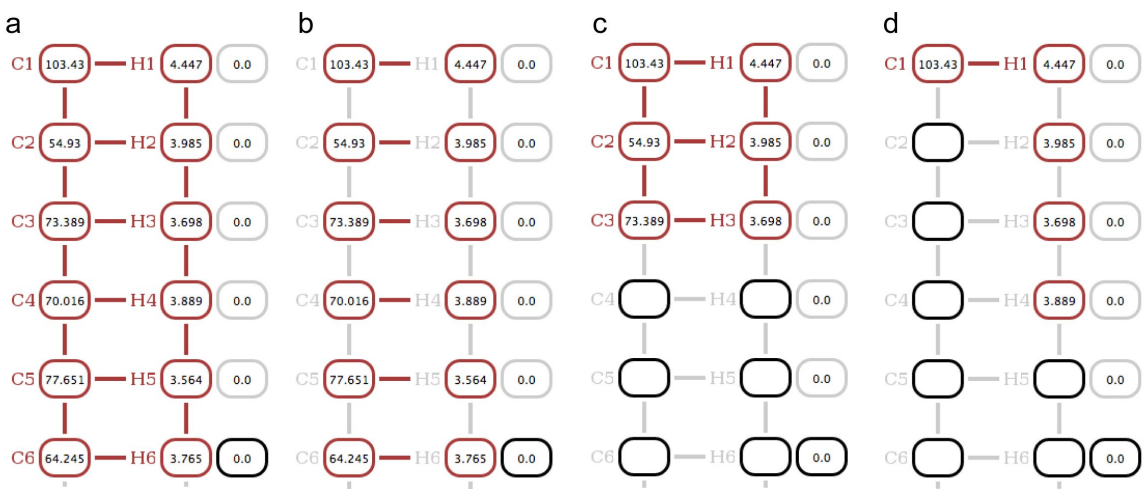

Fig. S3. Tested search patterns illustrated with the chemical shifts of GalNAc of the LDNF trisaccharide. a) Completely assigned spin system with chemical shifts for carbons C1 to C6 and the associated protons H1 to H6. H6 can be any of the two methylen protons (H61 and H62 or H6 and H6′). b) Six unassigned C-H chemical shift pairs. c) Partially assigned spin system with chemical shifts for carbons C1 to C3 and the associated protons H1 to H3. d) C1-H1 chemical shift pair together with proton resonances correlating with H1 in a 2D TOCSY.

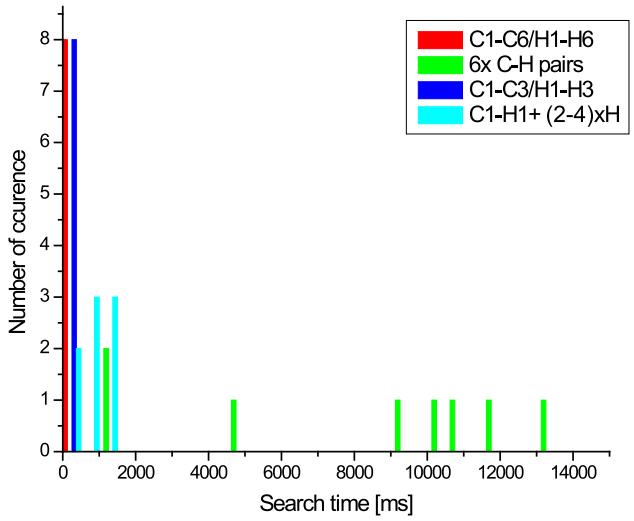

Fig. S4. Search times of the different strategies illustrated with the 32 test searches of Figure 3.

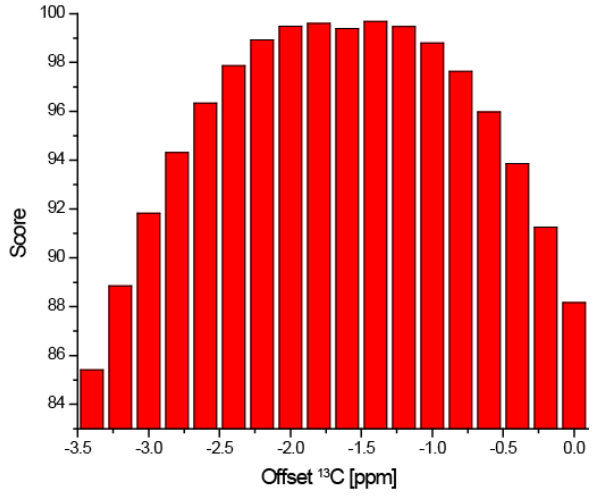

Fig. S5. Offset dependency of the ^{13}C chemical shifts illustrated with a search of the chemical shifts of Fuc within Bv9 (C1 to C6 and H1 to H6). An offset of -1.8 ppm means, that 1.8 ppm needs to be subtracted from the experimental values in order to fit to the database.

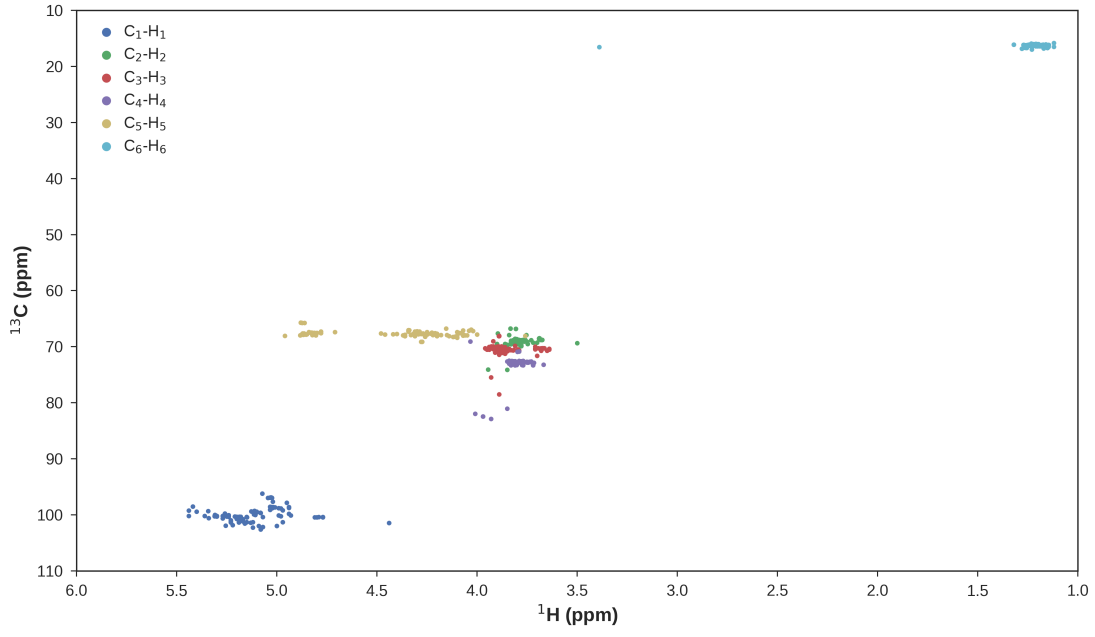

Fig. S6. Visualization of C-H chemical shift pairs of α-L Fuc pyranoses in the glycosciences.de database.

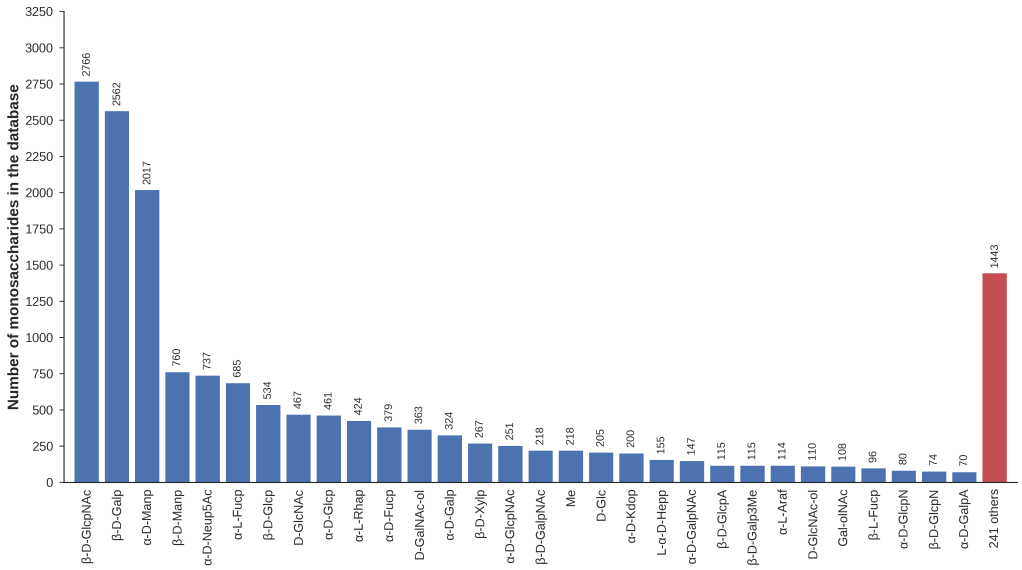

Fig. S7. Most frequent types of monosaccharides in the glycosciences.de database

Top 134 matches out of 16465 database records (result generated in 683 ms.)

LinucsID	Residue	Linkage	Match
2690	α-D-Neup5Ac	3,4,6,3	99,973

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,800	3,700	3,846	3,642	3,600	3,900	3,860	-	-	2,769	-	-	-	-	-	3,650	-	100,710	40,670	69,190	52,580	73,780	69,030	72,630	63,500
Query	-	-	1,800	3,700	3,840	3,640	3,610	-	-	-	-	2,780	-	-	-	-	-	-	-	-	40,700	-	-	-	-	-	-
Error	-	-	0,000	0,000	0,006	0,002	0,010	-	-	-	-	0,011	-	-	-	-	-	-	-	-	0,030	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
26396	α-D-NeupAc	4, 6, 4, 3	99,896

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,800	3,690	3,850	3,640	3,590	3,890	3,870	-	-	2,780	-	-	-	-	-	3,640	174,700	100,660	40,490	69,200	52,540	73,730	68,960	72,590	63,440
Query	-	-	1,800	3,700	3,840	3,640	3,610	-	-	-	-	2,780	-	-	-	-	-	-	-	-	40,700	-	-	-	-	-	-
Error	-	-	0,000	0,010	0,010	0,000	0,020	-	-	-	-	0,000	-	-	-	-	-	-	-	-	0,210	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
527	α-D-Neup5Ac	3,3,3,4	99,839

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,783	3,702	3,834	3,665	3,590	3,875	3,660	-	-	2,760	-	-	-	-	-	3,820	174,630	100,470	40,610	69,160	52,510	73,620	68,890	72,640	63,310
Query	-	-	1,800	3,700	3,840	-	3,610	-	3,640	-	-	2,780	-	-	-	-	-	-	-	-	40,700	-	-	-	-	-	-
Error	-	-	0,017	0,002	0,006	-	0,020	-	0,020	-	-	0,020	-	-	-	-	-	-	-	-	0,090	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
2838	α-D-Neup5Ac	3,3,4	99,838

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,801	3,680	3,850	3,630	3,590	3,880	3,640	-	-	2,762	-	-	-	-	-	3,870	174,600	100,200	40,500	69,200	52,500	73,700	68,900	72,600	63,400
Query	-	-	1,800	3,700	3,840	3,610	-	-	3,640	-	-	2,780	-	-	-	-	-	-	-	-	40,700	-	-	-	-	-	-
Error	-	-	0,001	0,020	0,010	0,020	-	-	0,000	-	-	0,018	-	-	-	-	-	-	-	-	0,200	-	-	-	-	-	-

Fig. S8. Top 4 results for the first sialic acid spin system observed in a commercial human serum albumin sample.

Top 128 matches out of 16465 database records (result generated in 1224 ms.)

LinucsID	Residue	Linkage	Match
2836	α-D-Neup5Ac	6,4,6,4	99,736

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,712	3,660	3,790	3,710	3,560	3,890	-	-	-	2,669	-	-	-	-	-	-	174,100	-	40,900	69,000	52,700	73,400	69,200	72,500	63,500
Query	-	-	1,710	3,670	3,790	3,690	3,590	3,870	-	-	-	2,690	-	-	-	-	-	-	-	-	41,100	-	-	-	-	-	-
Error	-	-	0,002	0,010	0,000	0,020	0,030	0,020	-	-	-	0,021	-	-	-	-	-	-	-	-	0,200	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
529	α-D-Neup5Ac	6,4,3,4	99,732

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,713	3,666	3,810	3,670	3,560	3,870	3,670	-	-	2,668	-	-	-	-	3,860		174,260	100,940	40,880	68,980	52,710	73,230	69,210	72,510	63,480
Query	-	-	1,710	-	3,790	3,670	3,590	3,870	3,690	-	-	2,690	-	-	-	-	-	-	-	-	41,100	-	-	-	-	-	-
Error	-	-	0,003	-	0,020	0,000	0,030	0,000	0,020	-	-	0,022	-	-	-	-	-	-	-	-	0,220	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
2839	α-D-Neup5Ac	6,4,6,4	99,691

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,712	3,650	3,790	3,700	3,550	3,880	3,640	-	-	2,668	-	-	-	-	3,880		174,100	-	40,900	69,100	52,700	73,400	69,300	72,600	63,500
Query	-	-	1,710	3,670	3,790	3,690	3,590	3,870	-	-	-	2,690	-	-	-	-	-	-	-	-	41,100	-	-	-	-	-	-
Error	-	-	0,002	0,020	0,000	0,010	0,040	0,010	-	-	-	0,022	-	-	-	-	-	-	-	-	0,200	-	-	-	-	-	-

LinucsID	Residue	Linkage	Match
1166	α-D-Neup5Ac	6,3,4	99,536

	H									H'									C								
ID	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
Sugar	-	-	1,685	3,680	3,816	3,680	3,590	3,880	3,750	-	-	2,741	-	-	-	-	3,820		174,200	101,010	40,890	69,080	52,700	73,300	69,080	72,500	63,420
Query	-	-	1,710	3,670	3,790	3,690	3,590	3,870	-	-	-	2,690	-	-	-	-	-	-	-	-	41,100	-	-	-	-	-	-
Error	-	-	0,025	0,010	0,026	0,010	0,000	0,010	-	-	-	0,051	-	-	-	-	-	-	-	-	0,210	-	-	-	-	-	-

Fig. S9. Top 4 results for the second sialic acid spin system observed in a commercial human serum albumin sample.