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SUPPLEMENTARY INFORMATION

Intramolecular crankshaft-type rearrangement in a photoisomerised glycoconjugate.

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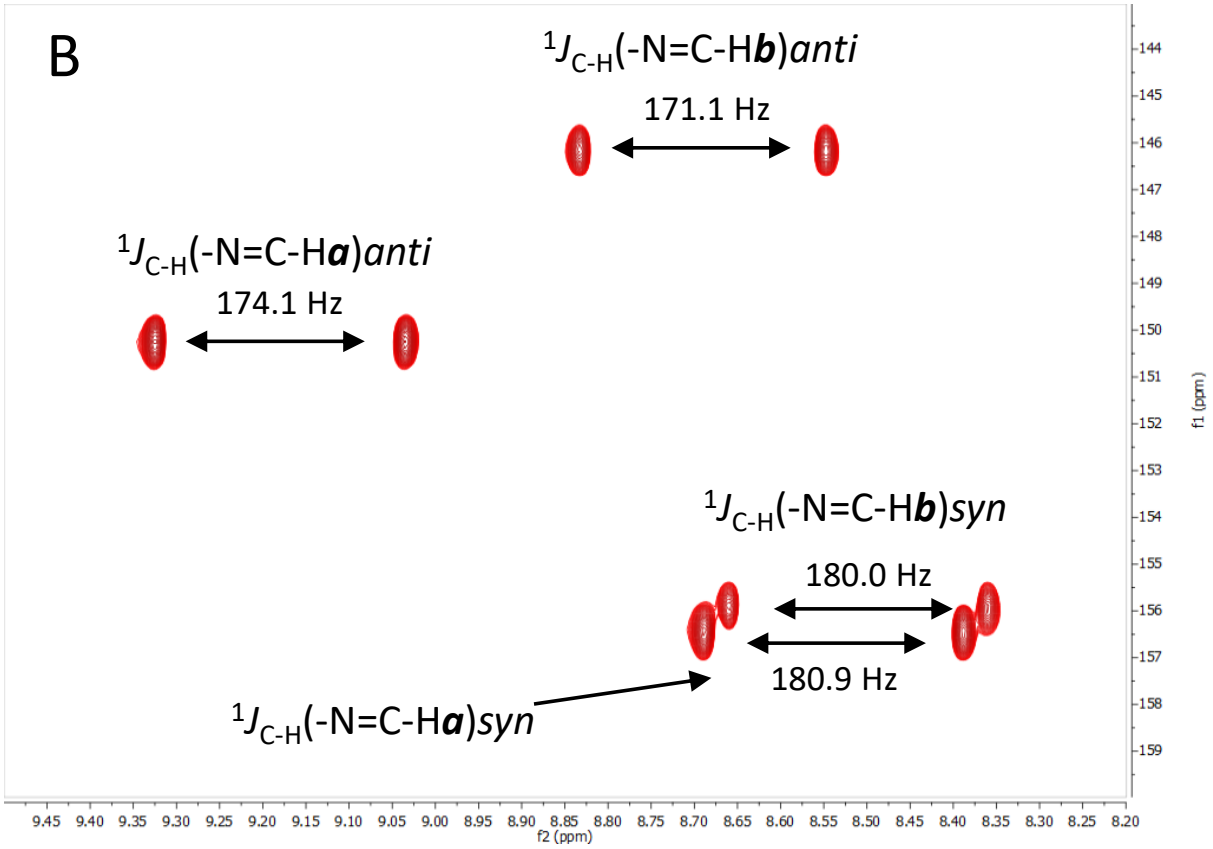

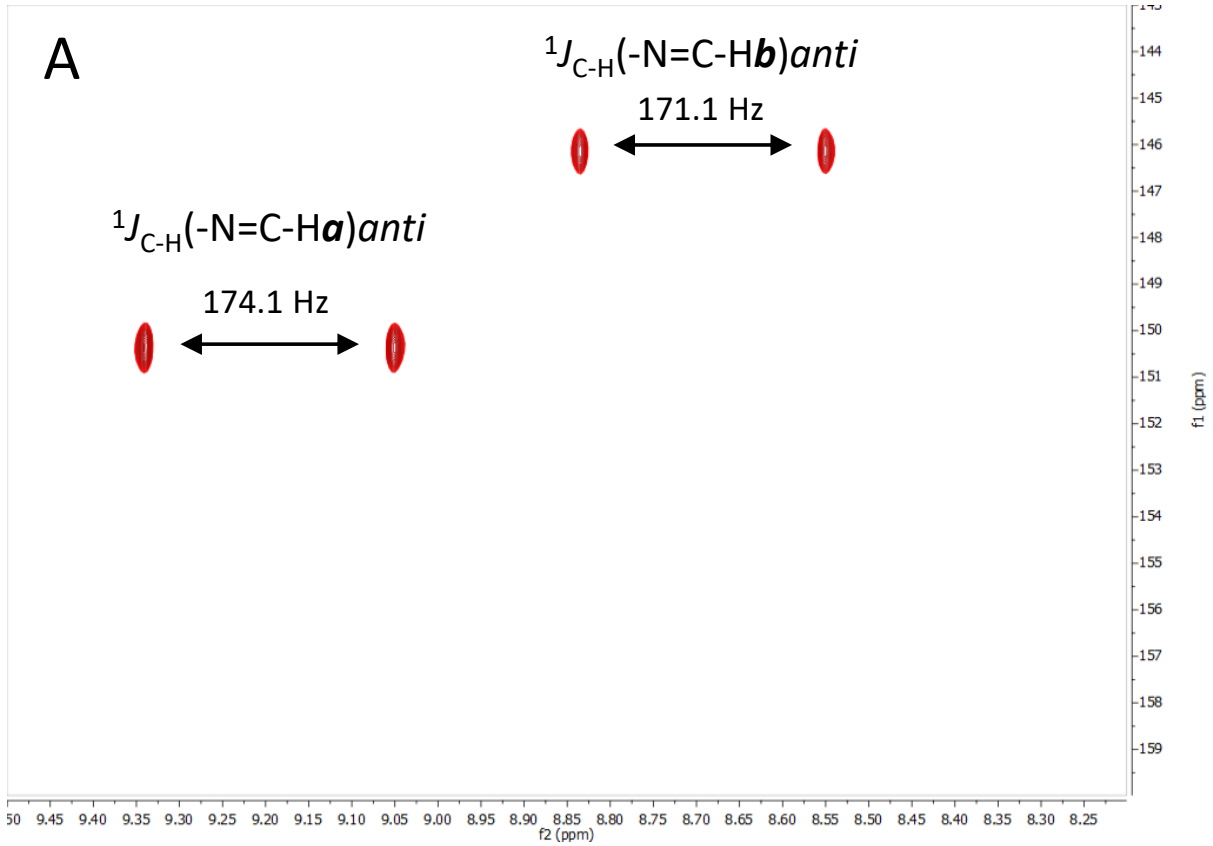

Fig. S1 Expansion of 2D NMR ^{1}H-^{13}C coupled HSQC spectrum showing the azomethine group signals originating from the two conformers (***a*** and ***b***) for *anti*- and *syn*-forms. (A): spectrum before irradiation (pure *anti*); (B): spectrum after irradiation (~1:1 mixture of *syn* and *anti*).

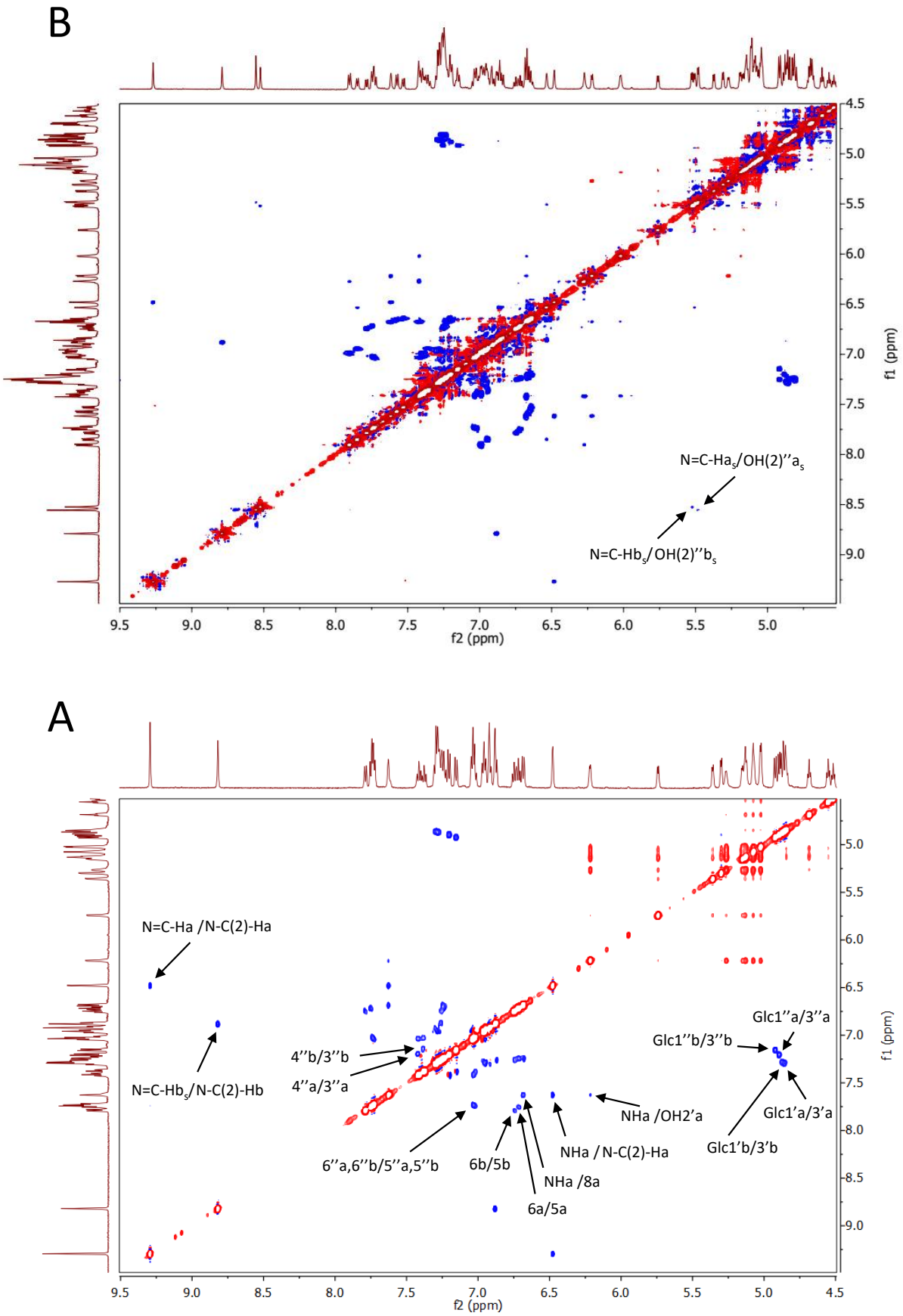

Fig. S2 2D NOESY spectrum (signals from aromatic protons) of **1** in DMSO at 25°C showing some of the most important dipolar interactions in the *anti*- and *syn*-forms. (A): spectrum before irradiation (pure *anti*); (B): spectrum after irradiation (~ 1:1 mixture of *syn* and *anti*).

Table S1 ^{1}H chemical shifts of **1** in DMSO at 25°C (referenced to TMS). The values are listed for the two different conformations ***a*** and ***b***.

	a	**b**		
=C–H	9.28	8.81		
–N–H	7.62	7.27		
2	6.48	6.88		
5	7.74	7.79		
6	6.75	6.72		
7	7.27	7.24		
8	6.68	6.87		
3'	7.29[a]	7.28[a]		
4'	7.28[a]	7.28[a]		
5'	6.96[a]	6.94[a]		
6'	6.92[a]	6.95[a]		
3''	7.20	7.15		
4''	7.41	7.38		
5''	7.03	7.03		
6''	7.75	7.73		
	Glc'a	**Glc 'b**	**Glc''a**	**Glc ''b**
1	4.86	4.87	4.89	4.92
2	3.49	3.52	3.25	3.26
3	3.39	3.81	3.26	3.30
4	3.25	3.20	3.22	3.16
5	3.38	3.38	3.21	3.22
6_a	3.82	3.78	3.71	3.66
6_b	3.26	3.54	3.51	3.43
$–OH_2$	6.23	5.80	5.32	5.40
$–OH_3$	5.26	5.14	5.08	5.15
$–OH_4$	5.13	5.07	5.03	5.03
$–OH_6$	4.69	4.86	4.56	4.52

[a] approximate values due to high-order spin system

Table S2. ^{1}H chemical shifts of –N=C(H) and –OH(2) protons in **1** at various temperatures (20°C – 65°C) in DMSO. The values are listed for the two different conformations ***a*** and ***b***. The temperature coefficients (*ppb/K*), computed from the chemical shift variations, are listed in the last column.

		(20°C)	**(25°C)**	**(35°C)**	**(45°C)**	**(55°C)**	**(65°C)**	**ppb/K**
anti-	–N=CH– (**a**)	9.216	9.220	9.227	9.230	9.234	9.235	0.42
	–N=CH– (**b**)	8.714	8.732	8.768	8.799	8.829	8.855	−3.13
	$-OH_2'$ (**a**)	6.257	6.227	6.163	6.099	6.035	*	−6.34
	$-OH_2'$ (**b**)	5.833	5.796	5.717	5.641	5.567	*	−7.60
	$-OH_2''$ (**a**)	5.360	5.323	5.247	5.171	5.098	*	−7.49
	$-OH_2''$ (**b**)	5.425	5.395	5.329	5.263	5.198	*	−6.49
syn-	–N=CH– (**a**)	8.546	8.546	8.545	8.544	8.543	8.539	−0.16
	–N=CH– (**b**)	8.519	8.517	8.510	8.504	8.500	8.493	−0.58
	$-OH_2'$ (**a**)	6.069	6.041	5.982	5.922	5.862	*	−5.91
	$-OH_2'$ (**b**)	5.572	5.542	5.470	5.416	5.345	*	−6.49
	$-OH_2''$ (**a**)	5.550	5.518	5.451	5.385	5.320	*	−6.57
	$-OH_2''$ (**b**)	5.590	5.557	5.488	5.421	5.353	*	−6.77

* not measured due to spectral overlap