Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Electronic Supplementary Information

Stereoselective Synthesis of Light-Activatable Perfluorophenylazide-Conjugated Carbohydrates for Glycoarray Fabrication and Evaluation of Structural Effects on Protein Binding by SPR Imaging

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^{1}H-NMR and ^{13}C-NMR spectra of compound 14

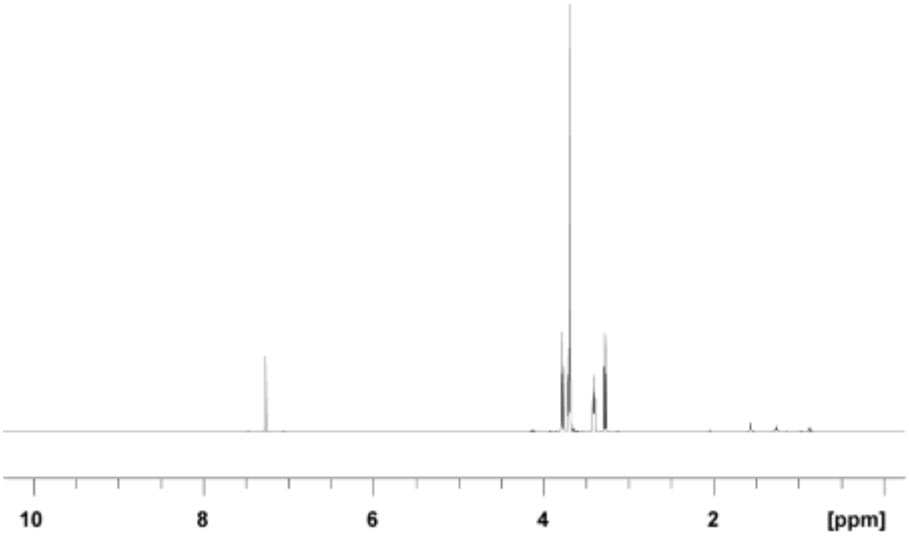


Figure S1. ^{1}H-NMR spectrum of compound **14** in $CDCl_3$ (500 MHz)

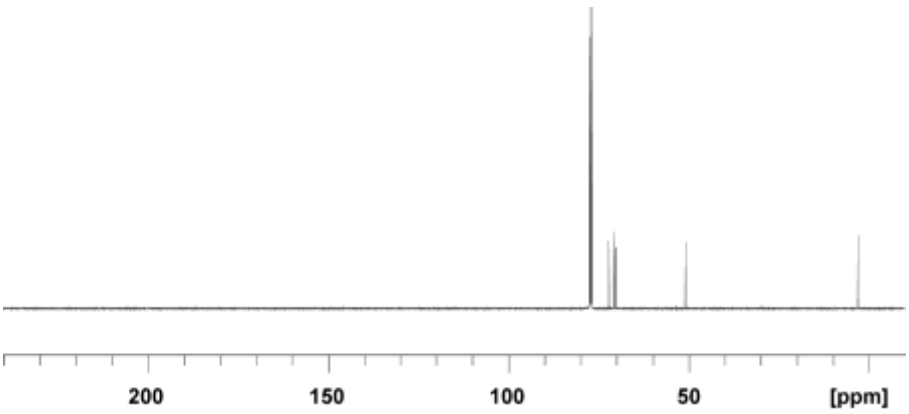


Figure S2. ^{13}C-NMR spectrum of compound **14** in $CDCl_3$ (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 18

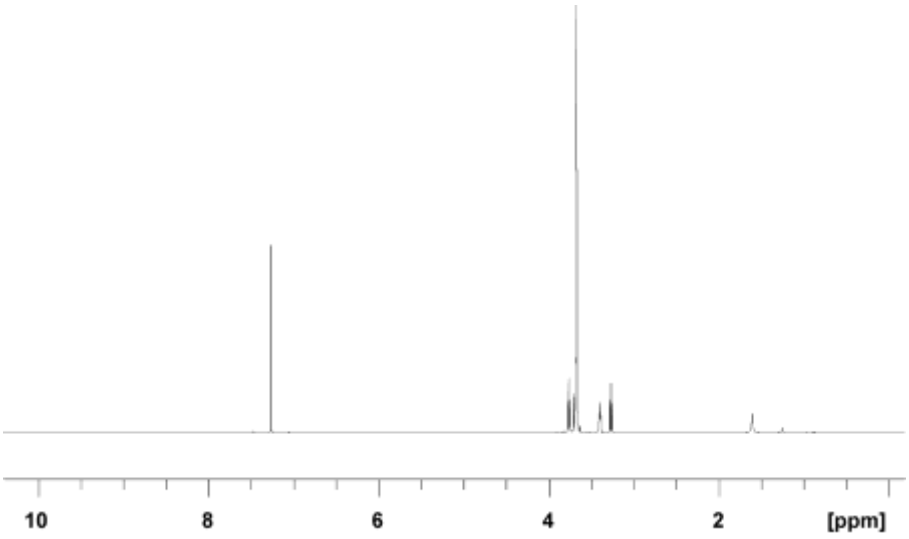


Figure S3. ^{1}H-NMR spectrum of compound **18** in $CDCl_3$ (500 MHz)

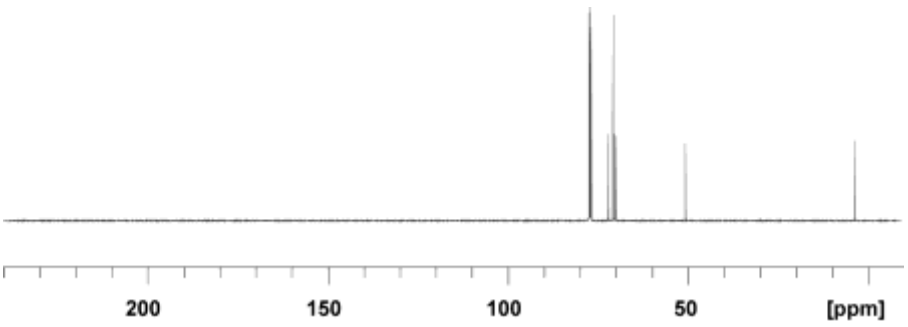


Figure S4. ^{13}C-NMR spectrum of compound **18** in $CDCl_3$ (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 21

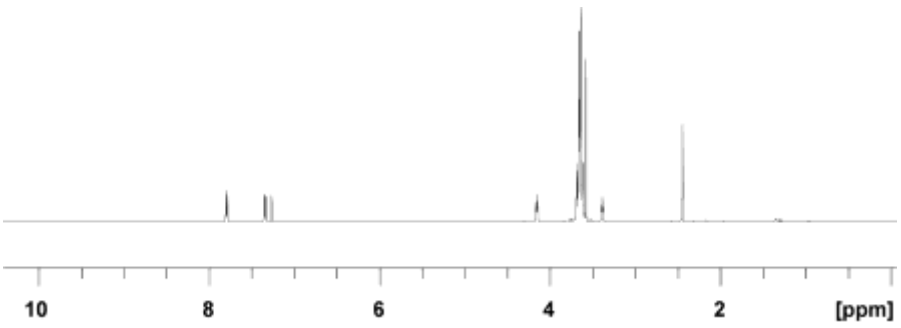


Figure S5. ^{1}H-NMR spectrum of compound **21** in $CDCl_3$ (500 MHz)

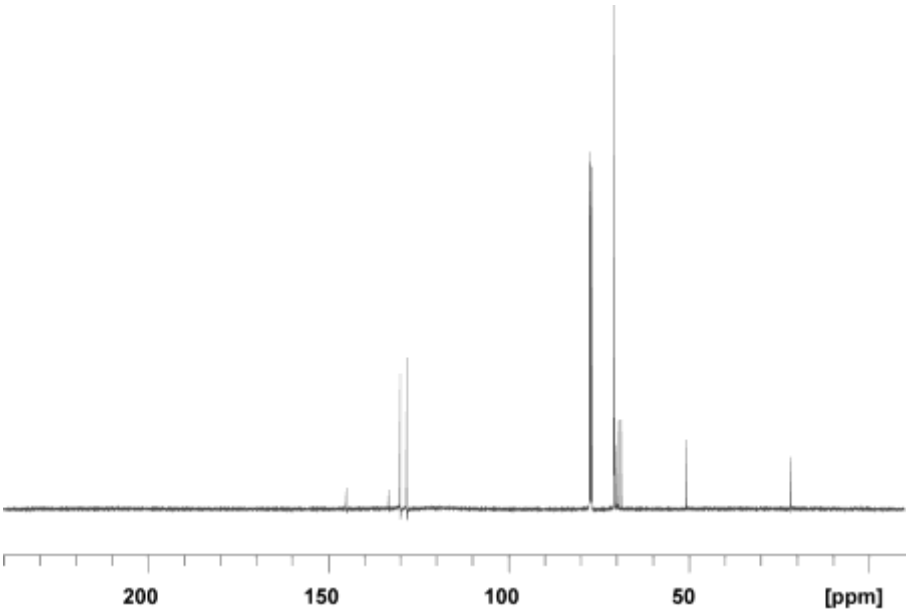


Figure S6. ^{13}C-NMR spectrum of compound **21** in $CDCl_3$ (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 22

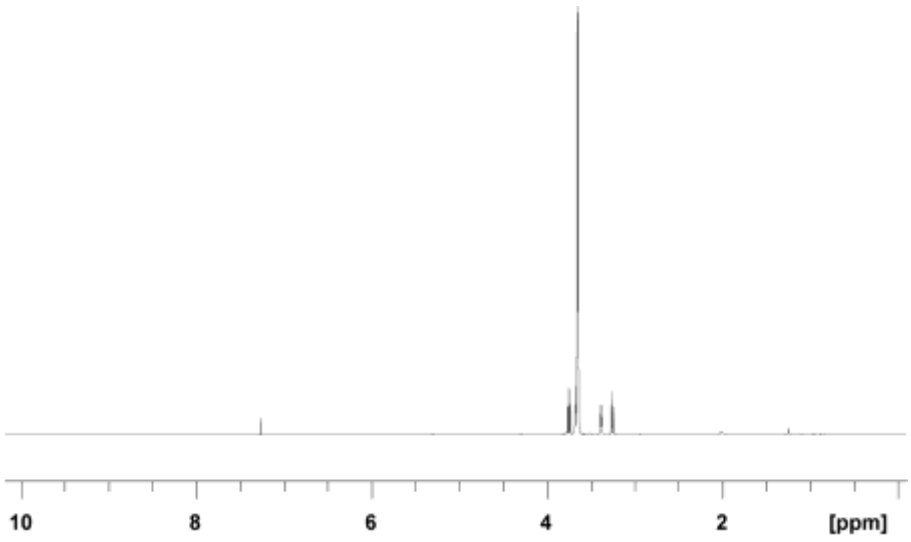


Figure S7. ^{1}H-NMR spectrum of compound **22** in $CDCl_3$ (500 MHz)

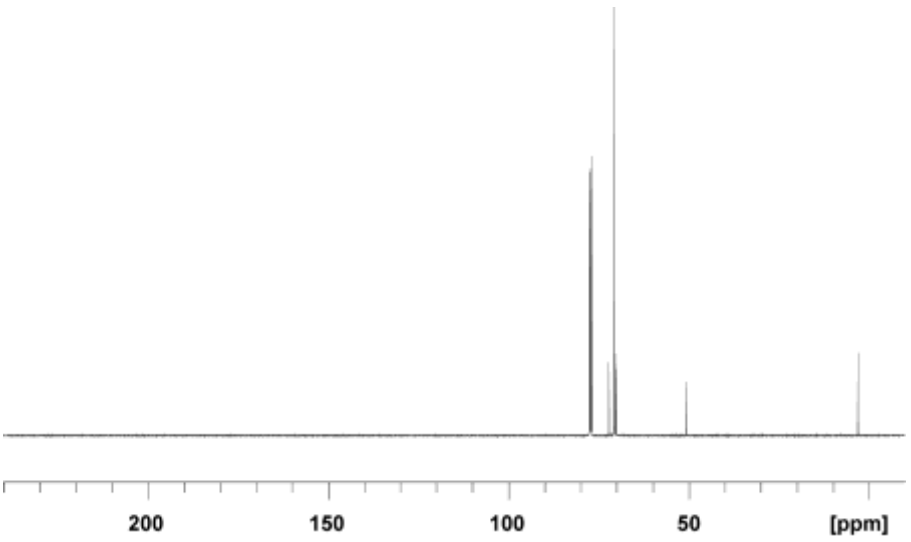


Figure S8. ^{13}C-NMR spectrum of compound **22** in $CDCl_3$ (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 24

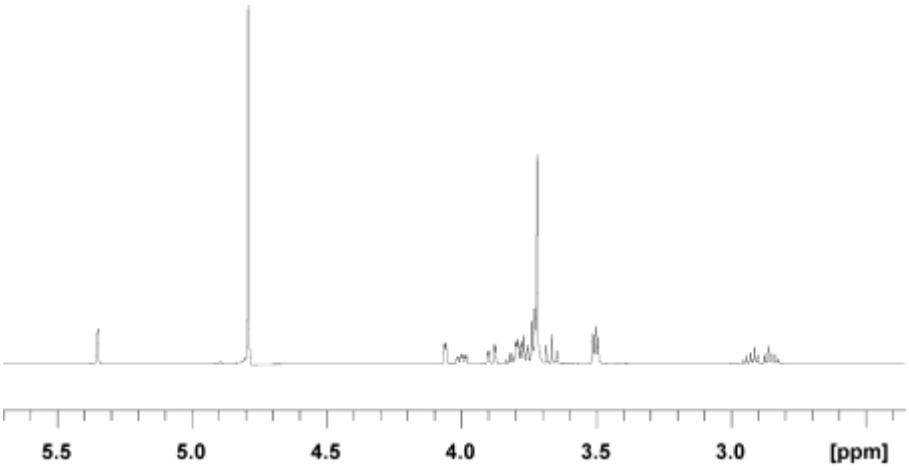


Figure S9. ^{1}H-NMR spectrum of compound **24** in D_2O (500 MHz)

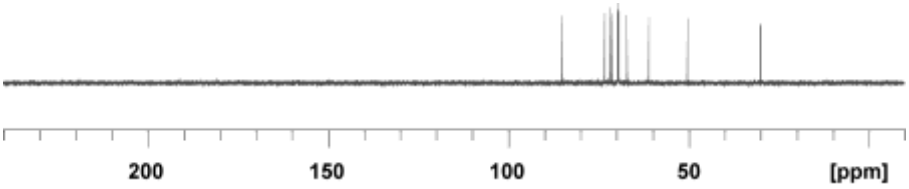


Figure S10. ^{13}C-NMR spectrum of compound **24** in D_2O (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 25

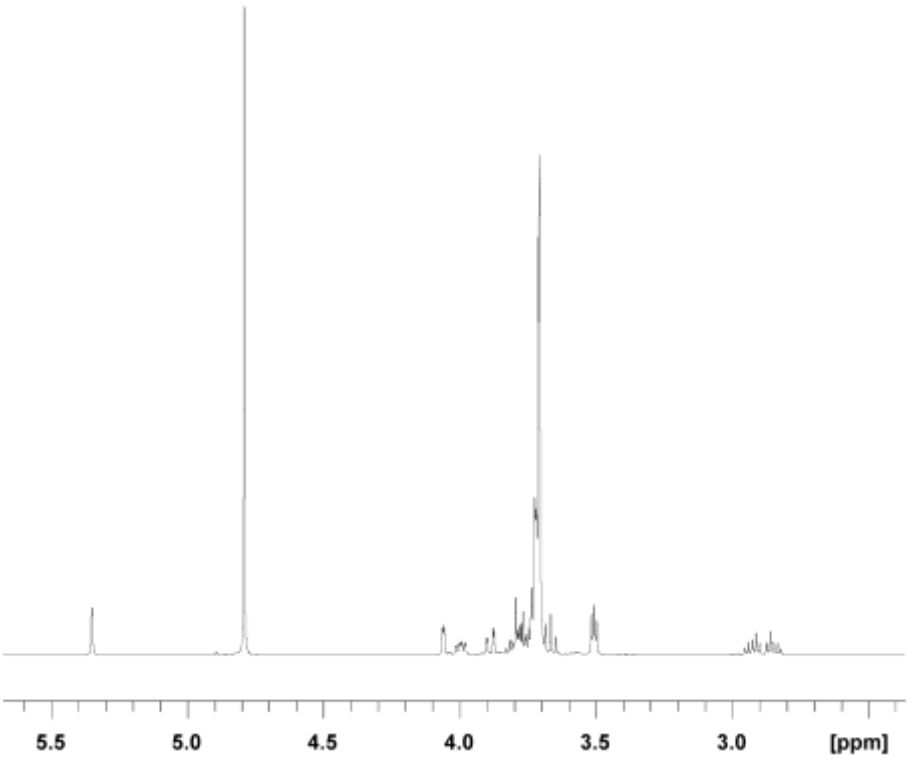


Figure S11. ^{1}H-NMR spectrum of compound **25** in D_2O (500 MHz)

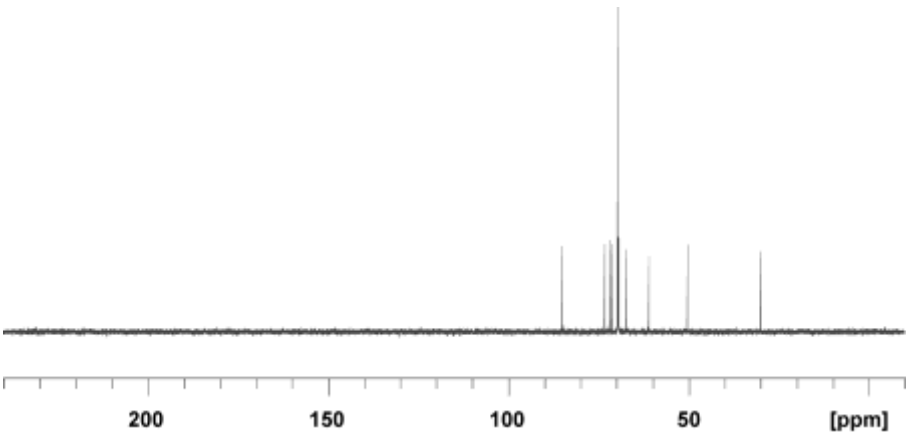


Figure S12. ^{13}C-NMR spectrum of compound **25** in D_2O (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 26

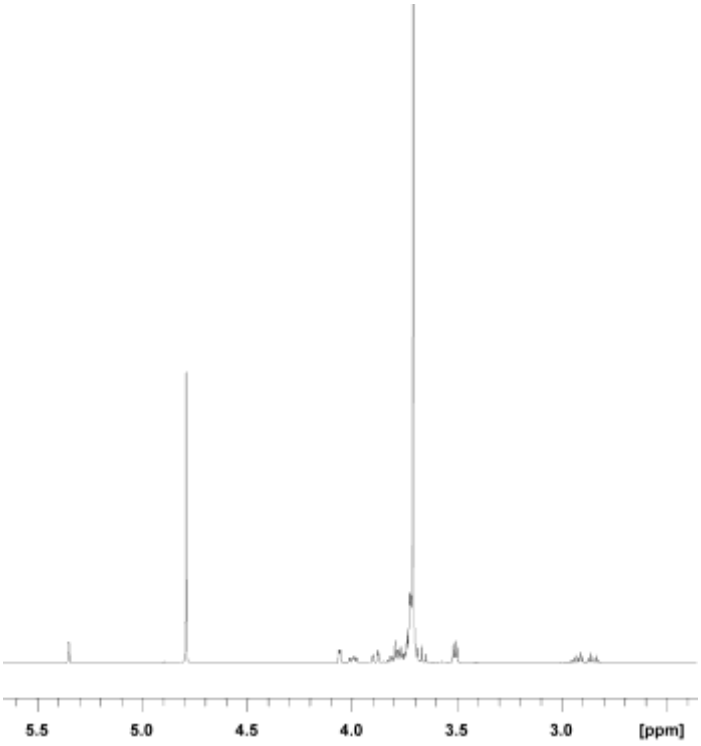


Figure S13. ^{1}H-NMR spectrum of compound **26** in D_2O (500 MHz)

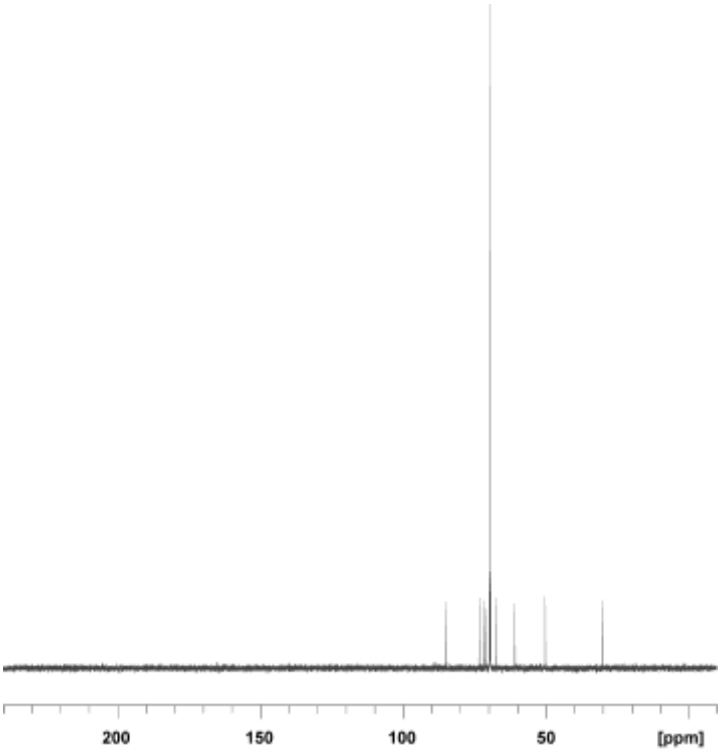


Figure S14. ^{13}C-NMR spectrum of compound **26** in D_2O (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 2

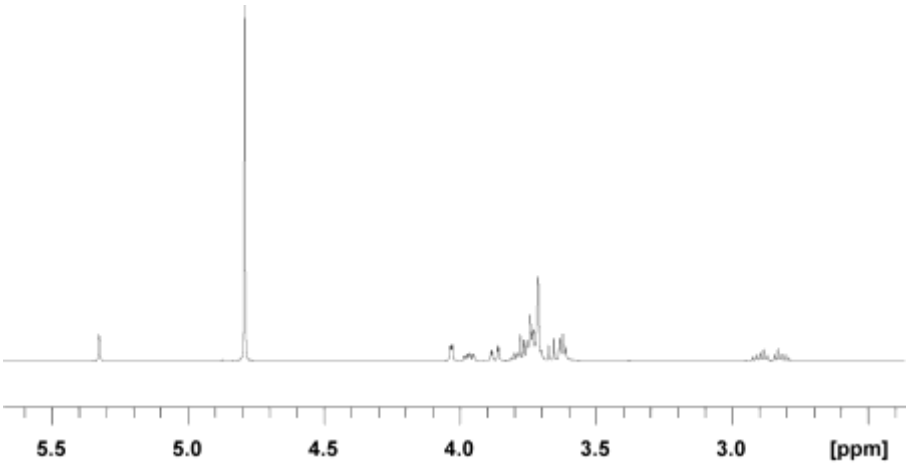


Figure S15. ^{1}H-NMR spectrum of compound **2** in D_2O (500 MHz)

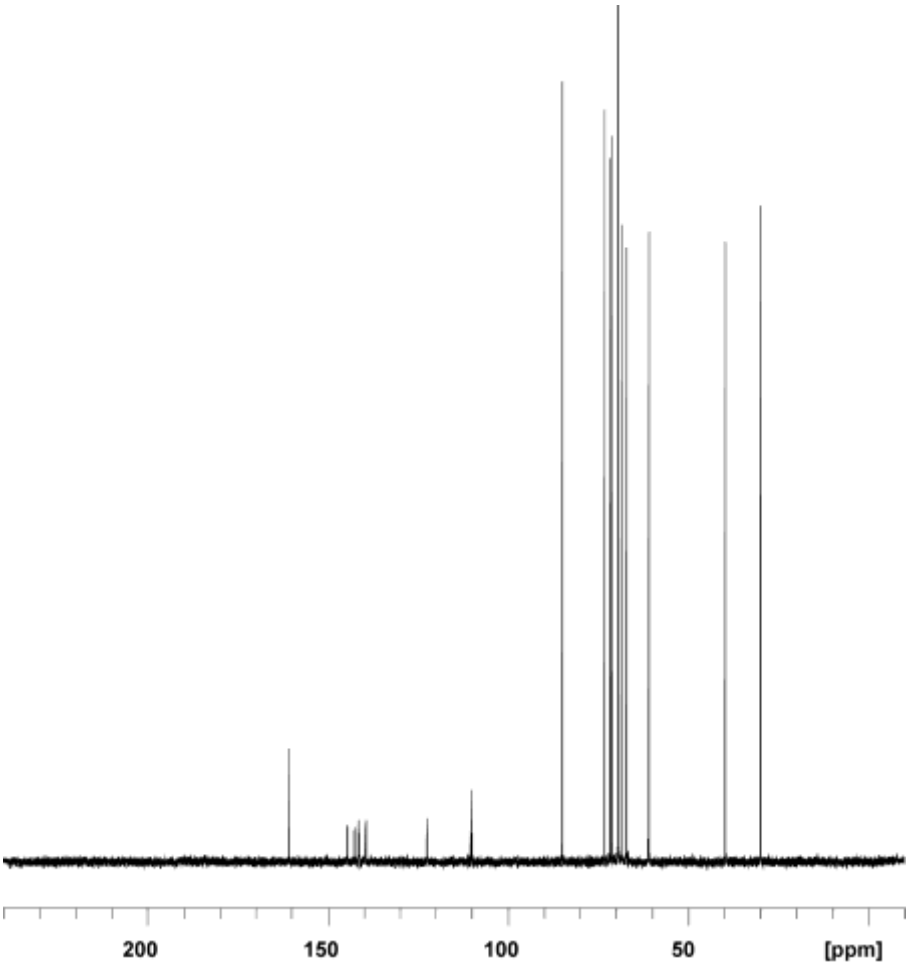


Figure S16. ^{13}C-NMR spectrum of compound **2** in D_2O (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 3

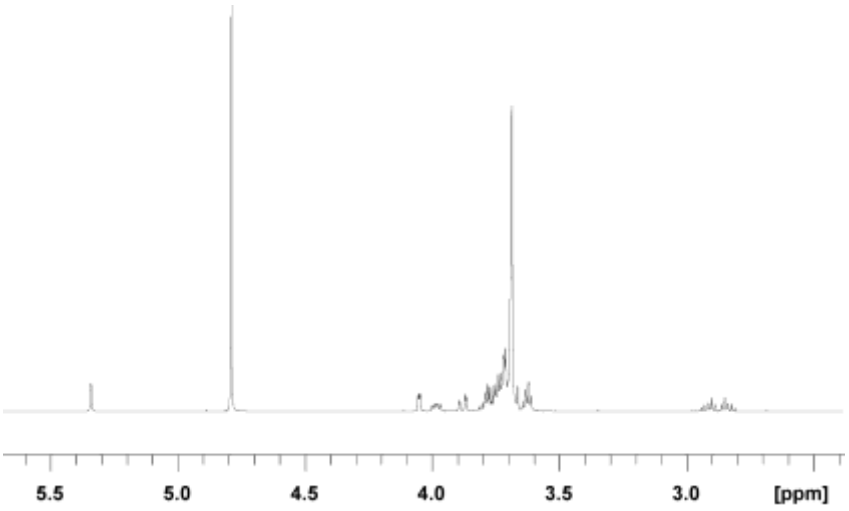


Figure S17. ^{1}H-NMR spectrum of compound **3** in D_2O (500 MHz)

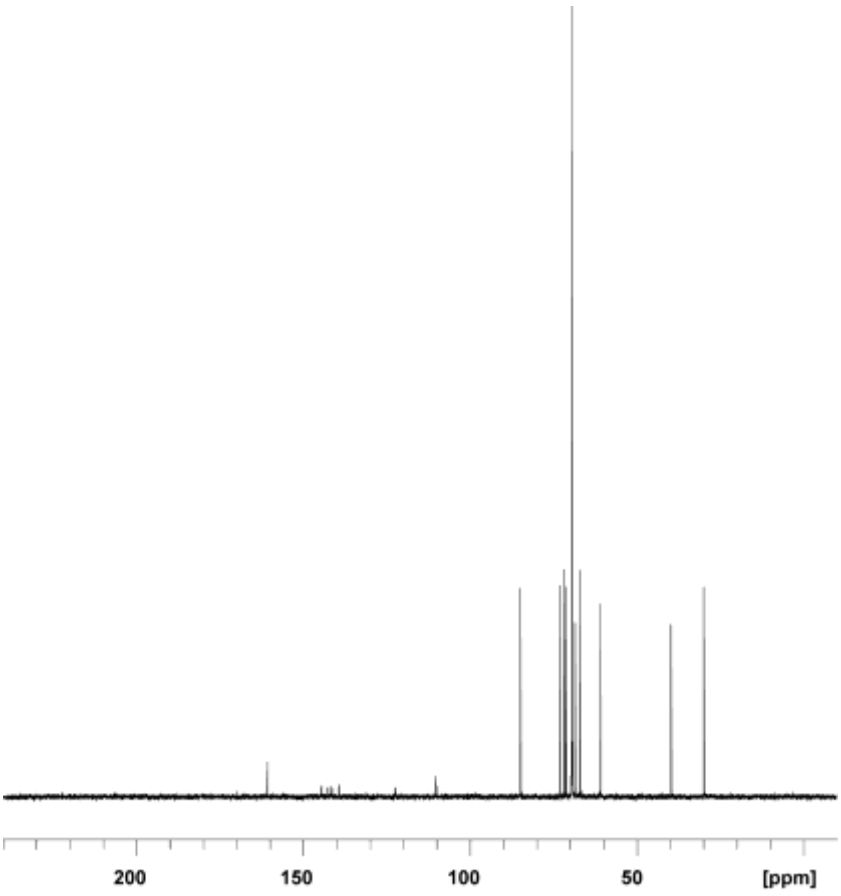


Figure S18. ^{13}C-NMR spectrum of compound **3** in D_2O (125 MHz)

^{1}H-NMR and ^{13}C-NMR spectra of compound 4

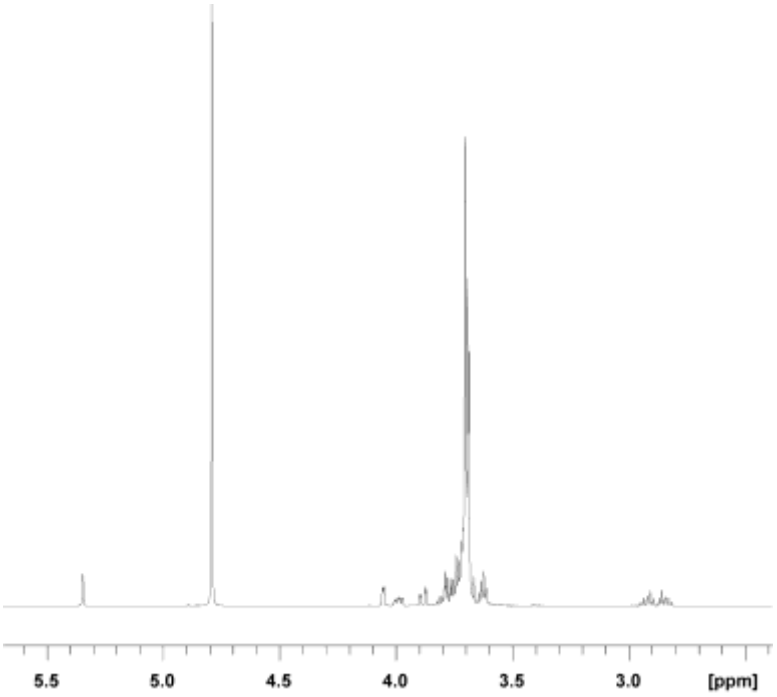


Figure S19. ^{1}H-NMR spectrum of compound **4** in D_2O (500 MHz)

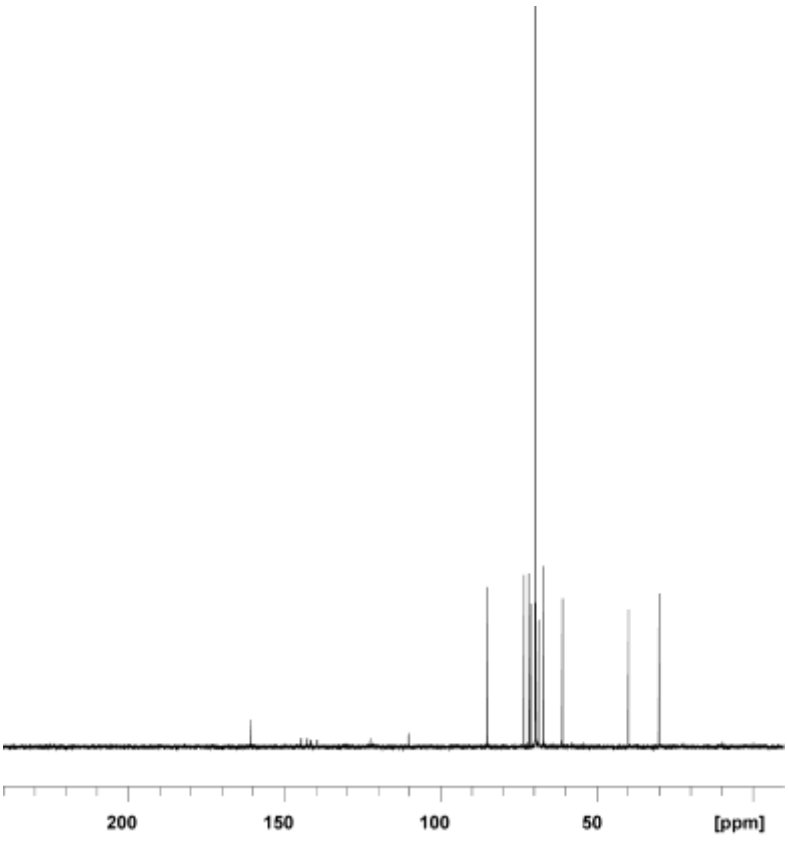
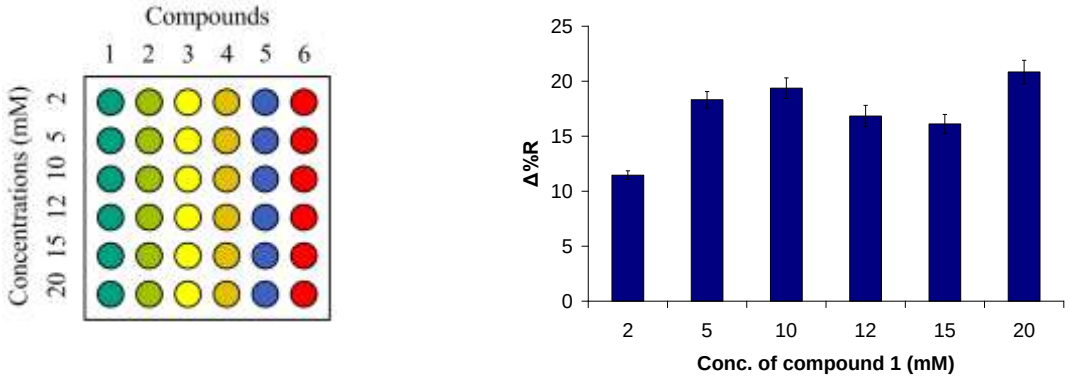


Figure S20. ^{13}C-NMR spectrum of compound **4** in D_2O (125 MHz)

SPR imaging

Printing concentration: A 6 × 6 array pattern of the PFPA-carbohydrate conjugates was created with six different concentrations of each compound (Figure S21). Printing solutions of 2-20 mM were employed, and the resulting sensor was treated by an interrogating solution of 10 μM of Con A. The sequence of steps followed during SPR measurements were as follows: 1) PBS with 0.1% tween 20, 2) 0.2% BSA in PBS with 0.1% tween 20, 3) PBS with 0.1% tween 20, 4) Con A in PBS with 0.1 % tween 20, 5) PBS with 0.1% tween 20, 6) 8 M urea in water, 7) PBS with 0.1% tween 20. Regeneration of the surface was achieved by treating the surfaces with 8 M urea to remove bound Con A. Repetitive regeneration provided consistent results, demonstrating the robustness of the sensor surfaces.

a) b)



c)

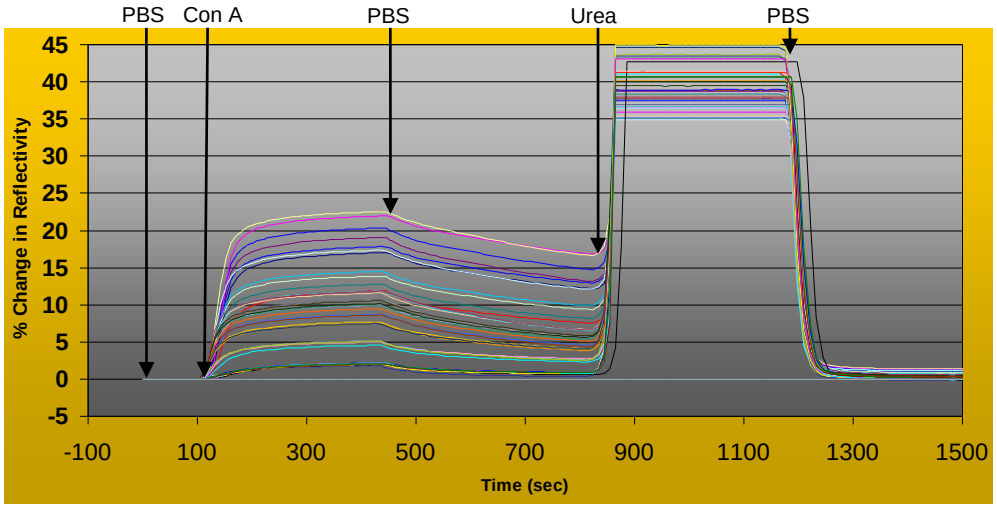


Figure S21. a) 6 × 6 array pattern of the PFPA-carbohydrate conjugates; b) SPRi responses of compound **1** toward Con A interrogation. Each data point was the average of two binding measurements; c) Corresponding SPRi binding curves.

Con A interrogation: A 6 × 6 array pattern of the PFPA-carbohydrate conjugates was created, with every horizontal column containing six different compounds while each vertical column 10 mM of a single compound (Figure S22). The resulting sensor was then treated by an interrogating solution of 10 μM of Con A. The sequence of steps followed during SPR measurements were as follows: 1) PBS with 0.1% tween 20, 2) 0.2% BSA in PBS with 0.1% tween 20, 3) PBS with 0.1% tween 20, 4) Con A in PBS with 0.1% tween 20, 5) PBS with 0.1% tween 20, 6) 8 M urea in water, 7) PBS with 0.1% tween 20.

a) b)

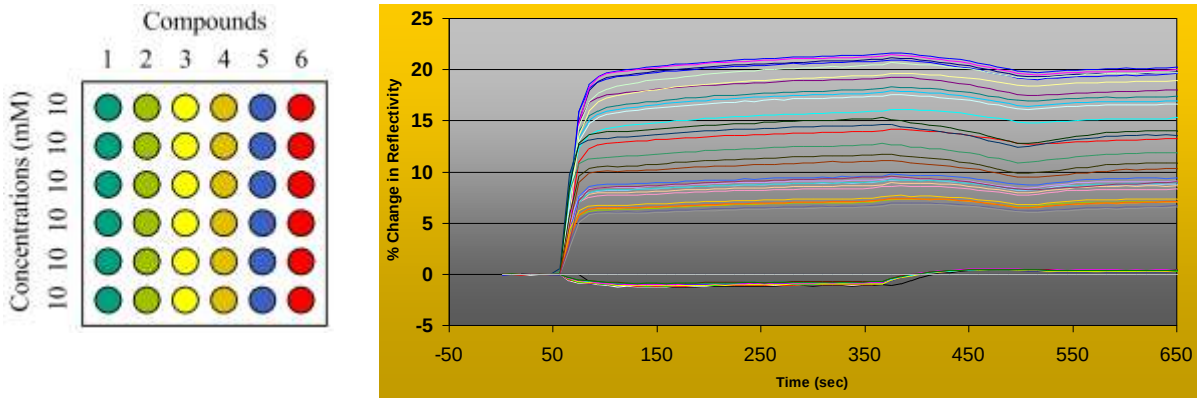


Figure S22. (a) 6 × 6 array pattern of the PFPA-carbohydrate conjugates, probe concentration fixed at 10 mM; (b) SPRi binding curves for 10 μM of Con A interrogation.

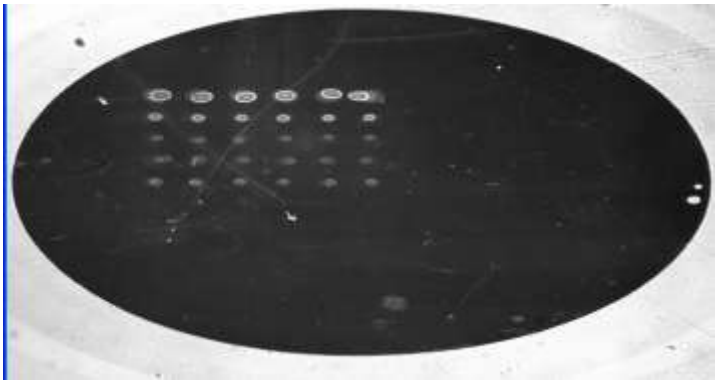


Figure S23. SPRi image of printed array for 10 μM of Con A interrogation. The array contained the six glycoconjugates **1-6**, printed in a 6 × 6 pattern.