Supplementary Information to:

Functionalisation of Diene-Modified Hairpin Mimics *via* the *Diels-Alder* Reaction

Rolf Tona and Robert Häner*

Department of Chemistry and Biochemistry, University of Bern

Freiestrasse 3, CH-3012 Bern, Switzerland

(phone: +41 31 631 4382; e-mail: robert.haener@ioc.unibe.ch)

Figure 1 suppl.: Thermal denaturation curves of oligomers **2** and **4a-f**. Conditions: 2.5µM oligomers, 100mM NaCl, 10mM Tris.HCl buffer, pH 7.5.

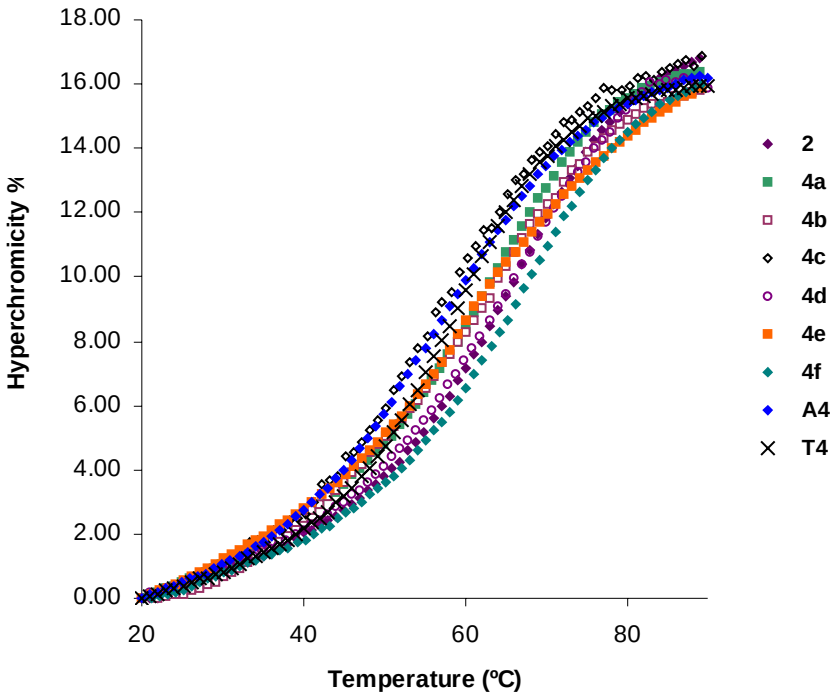


Figure 2 suppl.: Concentration dependence of *Tm's* of hairpin mimics **2** and **4c.** Conditions: 0.5-5µM oligomers; 100mM NaCl; 10mM Tris.HCl, pH 7.5.

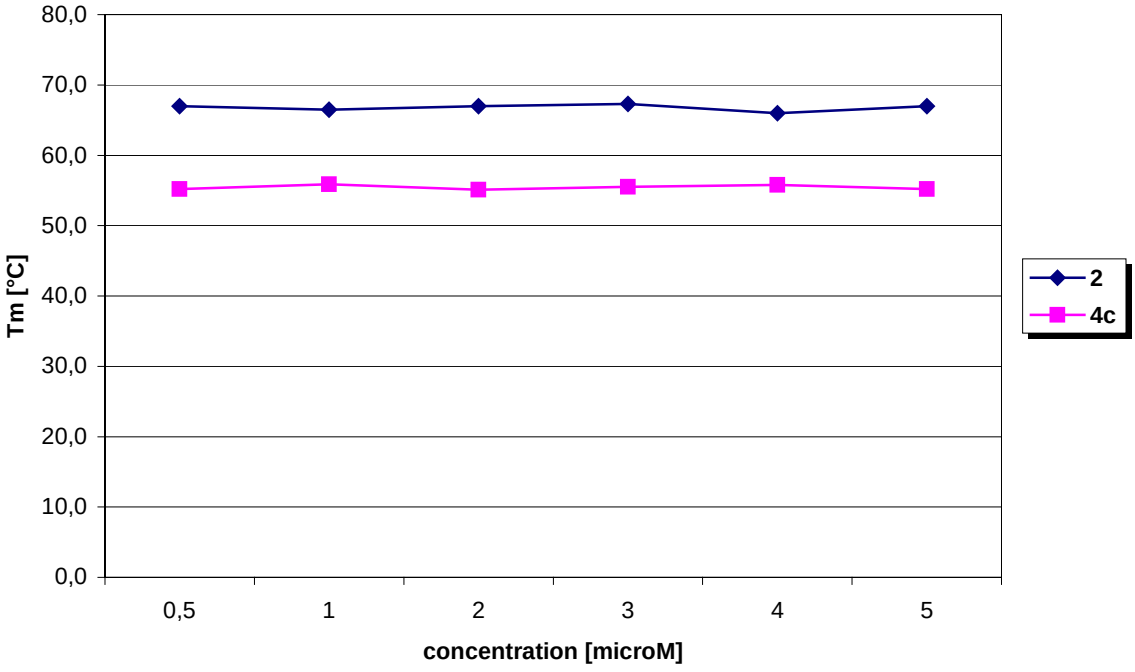


Figure 3 suppl.: Circular dichroism curves of hairpin mimics **2** and **4a-f,** as well as **T4** and **A4.** Conditions: 2.5µM oligomers; 100mM NaCl; 10mM Tris.HCl, pH 7.5.

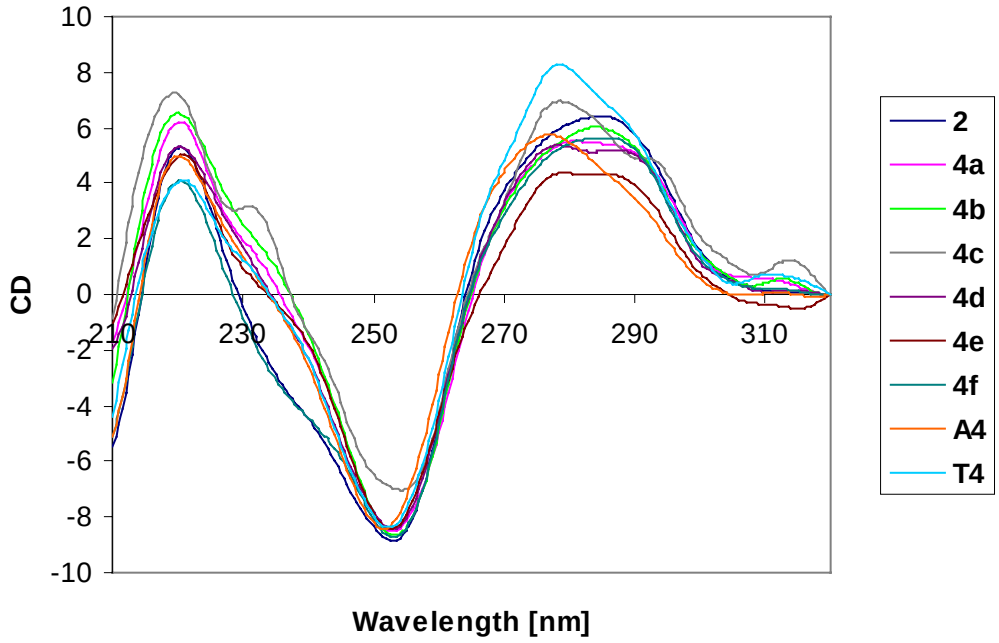
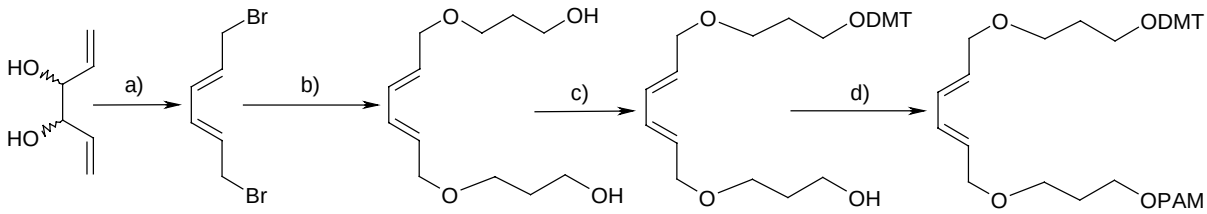


Figure 4 suppl.: Synthesis of phosphoramidite **1**.



1

a) PBr_3, rt (81%) b) $NaOCH_2CH_2CH_2OH$, THF, 50°C (43%) c) 4,4'-dimethoxytrityl chloride, pyridine, rt (46%) d) bis(*N*,*N*-di-*iso*-propylamino)-2-cyanoethylphosphoramidite, di-*iso*-propylammonium tetrazolide, CH_2Cl_2, rt (98%).

Oligonucleotide Synthesis

Building block **1** was incorporated into oligonucleotides *via* standard automated oligonucleotide synthesis using I_2/pyridine/water in the oxidation step. Coupling yield(s) with **1** were somewhat lower than with standard phosphoramidite building blocks but always >80%. No products arising from oxidation of the diene-moiety were observed by MS.

Figure 5 suppl.: Representative *reverse-phase* HPLC trace of a crude bioconjugate (**4f**); eluents: A: 200 mM triethylammonium actate, B: acetonitrile, 260 nm). Bioconjugate **4f** was eluted at 56 minutes (15% B), followed by some unidentified by-products (100% B).