Supplementary Information to:

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

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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.

![Circular dichroism curves](image)

Figure 4 suppl.: Synthesis of phosphoramidite 1.

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h HO    Br     OH
\H O
\OH
a) PBr₃, rt (81%) b) NaOCH₂CH₂CH₂OH, 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, CH₂Cl₂, rt (98%).
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**Oligonucleotide Synthesis**

Building block 1 was incorporated into oligonucleotides via standard automated oligonucleotide synthesis using I₂/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 acetate, B: acetonitrile, 260 nm). Bioconjugate 4f was eluted at 56 minutes (15% B), followed by some unidentified by-products (100% B).