## **Supporting information**

## New methylene-bridged hexopyranosyl nucleoside modified oligonucleotides (BHNA): synthesis and biochemical studies

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**Figure S1.** <sup>1</sup>H NMR spectrum of compound 1.



**Figure S2.** <sup>13</sup>C NMR spectrum of compound 1.



Figure S3. DEPT spectra of compound 1.



**Figure S4.** <sup>1</sup>H-<sup>13</sup>C HMQC spectra of compound 1. The part inside the red frame was expended in Figure s5.



**Figure S5.** Expension of  ${}^{1}$ H- ${}^{13}$ C HMQC spectra of compound 1.



Figure S6. COSY spectra of compound 1.



Figure S7. HMBC spectra of compound 1.

The part inside the red frame was expended in Figure S8.



**Figure S8.** Expension of HMBC spectrum of compound 1.



Figure S9. 1D nOe spectra of compound 1.

The model of product **5** shown on the right was obtained by *ab initio* geometry optimization.



Figure 10. 1D nOe spectra of rearrangement compound 1.

The model of product **5** shown on the right was obtained by ab initio geometry optimization.



**Figure S11.** <sup>1</sup>H NMR spectrum of compound 2.







**Figure S13.** <sup>1</sup>H NMR spectrum of compound 3.