Supporting Information

for

Synthesis and properties of oligonucleotides modified with an N-methylguanidine-bridged nucleic acid (GuNA[Me]) bearing adenine, guanine, or 5-methylcytosine nucleobases

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$^1$H, $^{13}$C, and $^{32}$P NMR spectra for all new compounds, HPLC charts and MALDI–TOF mass data for all new oligonucleotides, UV melting curves of the duplexes formed between GuNA[Me]-modified oligonucleotides and ssDNAs (or ssRNAs), and CD spectra of ON4/ssRNA and ON4/ssDNA
Table of contents

1. $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra of new compounds

2. Characterisation of oligonucleotides

3. UV melting experiments

4. CD spectral analysis
1. $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra of new compounds

Figure S1: Compound 2a ($^1$H NMR, CDCl$_3$, 300 MHz)
Figure S2: Compound 2a (13C NMR, CDCl₃, 76 MHz)
Figure S3: Compound 2b (H NMR, CDCl₃, 300 MHz)
Figure S4: Compound 2b (13C NMR, CDCl₃, 76 MHz)
Figure S5: Compound 2c (¹H NMR, CDCl₃, 300 MHz)
Figure S6: Compound 2c (\(^{13}\)C NMR, CDCl\(_3\), 76 MHz)
Figure S7: Compound 3a (31P NMR, CDCl₃, 122 MHz)
Figure S8: Compound 3b (31P NMR, CDCl3, 122 MHz)
Figure S9: Compound 3c (31P NMR, CDCl3, 122 MHz)
2. Characterisation of oligonucleotides

**ON1** 5'-d(GCG TTA TTT GCT)-3’

**ON2** 5'-d(GCG TTG TTT GCT)-3’

**ON3** 5'-d(GCG TTmC TTT GCT)-3’

*Figure S10:* HPLC charts of all new oligonucleotides. HPLC conditions: Reversed-phase HPLC (Waters XBridge™ C18 column) with a linear gradient of acetonitrile (5 to 10% over 5 min, then 10 to 15% over 20 min, then 15 to 15%, over 5 min) in 0.1 M triethylammonium acetate buffer (pH 7.0). A, G, and mC indicate GuNA[Me] modifications.
ON1 5'-d(GCGGTTTCTT)-3' (A)
ON2 5'-(GCG TTG TTT GCT)-3' (B)
Figure S11: MALDI-TOF-MS charts of all new oligonucleotides. **ON1** 5’-d(GCG TTA TTT GCT)-3’ (A), **ON2** 5’-(GCG TTG TTT GCT)-3’ (B), **ON3** 5’-d(GCG TTmC TTT GCT)-3’ (C); A, G, and mC indicate GuNA[Me] modifications.
3. UV melting experiments

**Figure S12:** Normalized UV melting curves for the duplexes formed between ON1/ON6 and the complementally DNA or RNA strands. The sequences are 5’-d(GCG TT\_ TTT GCT)-3’ and 5’-r(d(AGC AAA YAA CGC))-3’, respectively.

**Figure S13:** Normalized UV melting curves for the duplexes formed between ON2/ON7 and the complementally DNA or RNA strands. The sequences are 5’-d(GCG TT\_ TTT GCT)-3’ and 5’-r(d(AGC AAA CAA CGC))-3’, respectively. Y indicates U for RNA, and T for DNA.
Figure S14: Normalized UV melting curves for the duplexes formed between ON3/ON8 and the complementally DNA or RNA strands. The sequences are 5′-d(GCG TT\textsuperscript{m}CTTT GCT)-3′ and 5′-r(d(AGC AAA GAA CGC)-3′, respectively.
4. CD spectral analysis

Figure S15: CD spectra of the ON5/ssRNA, ON4/ssRNA, ON5/ssDNA and ON4/ssDNA duplexes. Conditions: 10 mM sodium phosphate buffer (pH 7.2), 100 mM NaCl, 4 µM each oligonucleotide. Sequences of the complementary ssRNA and ssDNA are 5’-r(AGC AAA AAA CGC)-3’ and 5’-d(AGC AAA AAA CGC)-3’, respectively.