Supporting Information

Tuning the hybridization properties of modified oligonucleotides: from flexible to conformationally constrained phosphonate internucleotide linkages.

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NMR Spectra
Figure S1  $^1$H NMR spectrum (600 MHz) of compound 23a in d$_6$DMSO at 47 °C.

Figure S2  $^{13}$C NMR spectrum (150.9 MHz) of compound 23a in d$_6$DMSO at 47 °C.
Figure S3  
\(^{1}\text{H} \) NMR spectrum (600 MHz) of compound 24a in d\(_{6}\)DMSO at 47 °C.

Figure S4  
\(^{13}\text{C} \) NMR spectrum (150.9 MHz) of compound 24a in d\(_{6}\)DMSO at 47 °C.
**Figure S5** $^1$H NMR spectrum (500 MHz) of compound 23b in d$_6$DMSO at 50 °C.

**Figure S6** $^{13}$C NMR spectrum (150.9 MHz) of compound 23b in d$_6$DMSO.
Figure S7  $^1$H NMR spectrum (500 MHz) of compound 24b in d$_6$DMSO at 50 °C.

Figure S8  $^{13}$C NMR spectrum (150.9 MHz) of compound 24b in d$_6$DMSO.
Figure S9  $^1$H NMR spectrum (600 MHz) of compound 27a in d$_6$DMSO.

Figure S10  $^{13}$C NMR spectrum (150.9 MHz) of compound 27a in d$_6$DMSO.
Figure S11  $^1$H NMR spectrum (600 MHz) of compound 27b in d$_6$DMSO.

Figure S12  $^{13}$C NMR spectrum (150.9 MHz) of compound 27b in d$_6$DMSO.
Figure S13  $^1$H NMR spectrum (500 MHz) of compound 33a in d$_6$DMSO.

Figure S14  $^{13}$C NMR spectrum (125.7 MHz) of compound 33a in d$_6$DMSO.
Figure S15  $^1$H NMR spectrum (600 MHz) of compound 33b in d$_6$DMSO.

Figure S16  $^{13}$C NMR spectrum (150.9 MHz) of compound 33b in d$_6$DMSO.
Figure S17 $^1$H NMR spectrum (600 MHz) of compound 33c in CDCl$_3$.

Figure S18 $^{13}$C NMR spectrum (150.9 MHz) of compound 33c in CDCl$_3$. 
Figure S19  \(^1\)H NMR spectrum (500 MHz) of compound 33d in d\textsubscript{6}DMSO.

Figure S20 \(^{13}\)C NMR spectrum (125.7 MHz) of compound 33d in d\textsubscript{6}DMSO.
Figure S21  $^1$H NMR spectrum (500 MHz) of compound 34a in d$_6$DMSO.

Figure S22  $^{13}$C NMR spectrum (125.7 MHz) of compound 34a in d$_6$DMSO.
Figure S23  $^1$H NMR spectrum (500 MHz) of compound 34c in CDCl$_3$.

Figure S24  $^{13}$C NMR spectrum (125.7 MHz) of compound 34c in CDCl$_3$. 

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