Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

The Biolabile 2ô-*O*-Pivaloyloxymethyl Modification in an RNA helix: an NMR Solution Structure

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(1.) Characterization of the PivOM containing strand

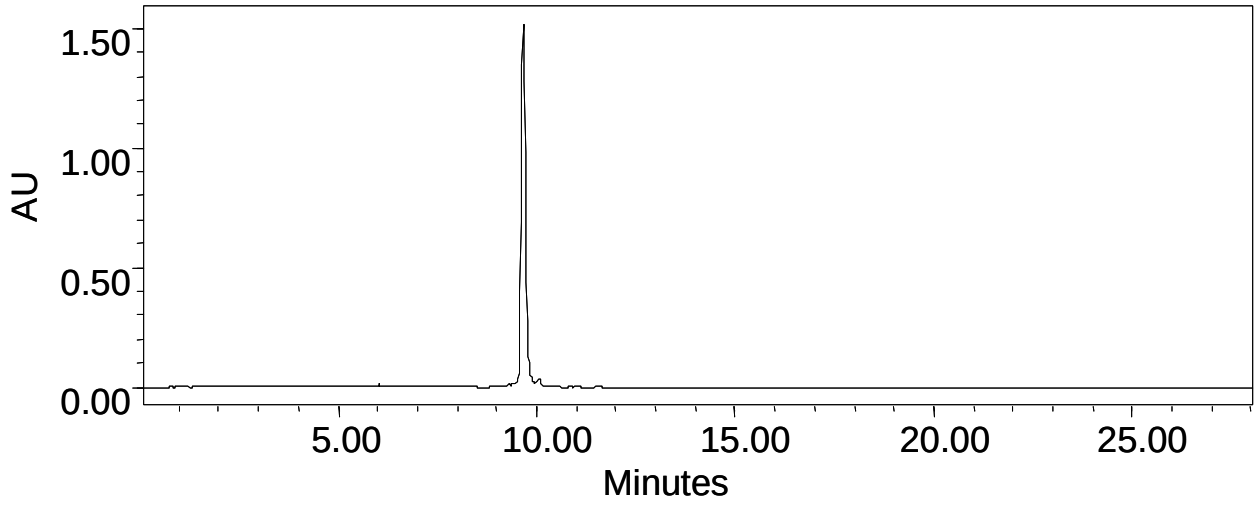

Figure S1. HPLC chromatogram of the pure modified 9-mer 5'-rCGCU$_{Piv}$ACGCdT-3' after Na ions exchange (column Nucleosil C18 150 x 4.6 mm; flow rate 1 ml/min; 0 to 24 % of acetonitrile in TEEAc 0.05M pH7 buffer; UV detection at 260 nm).

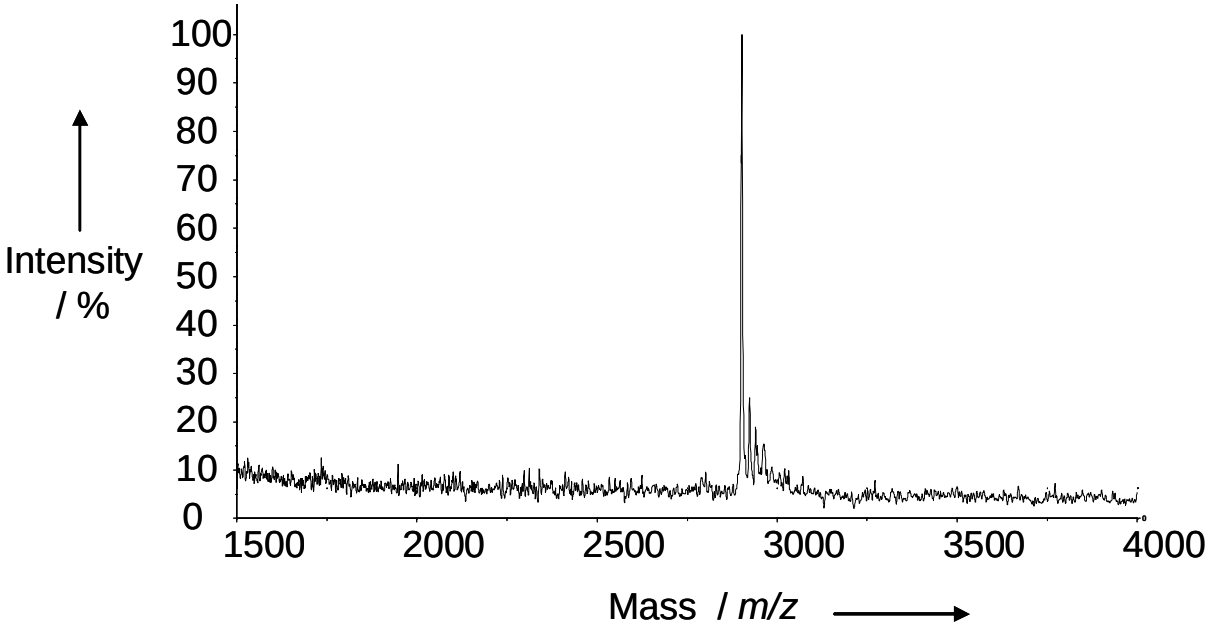

Figure S2. MALDI-TOF spectrum of the pure modified 9-mer 5'-r(CGCU$_{Piv}$ACGC)dT-3' after Na ions exchange (matrix: THAP).

(2.) Hybridization of the natural and modified duplexes

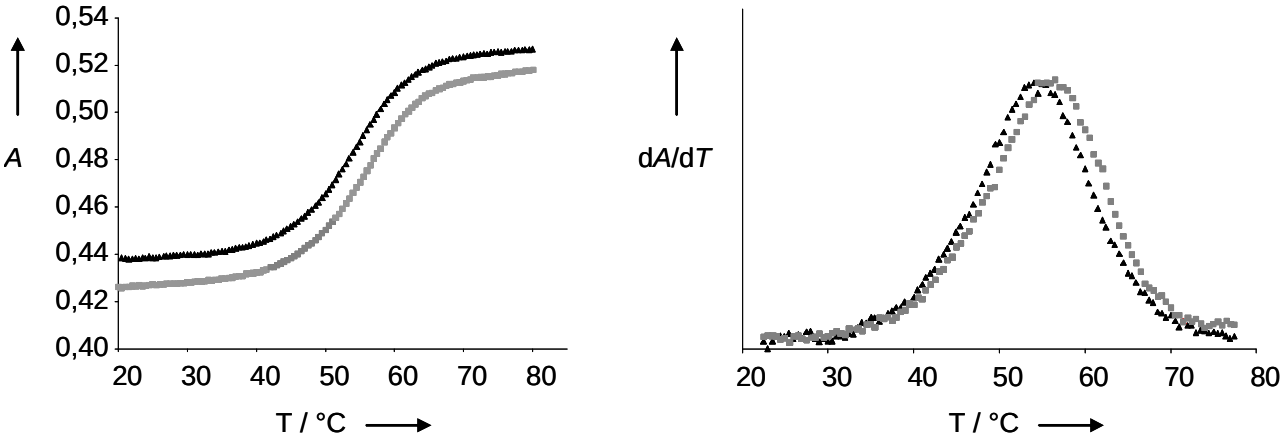

Figure S3. Melting curves (left) and their derivatives (right) for both modified (z) and natural (y) duplexes (hybridization).

(3.) NMR data

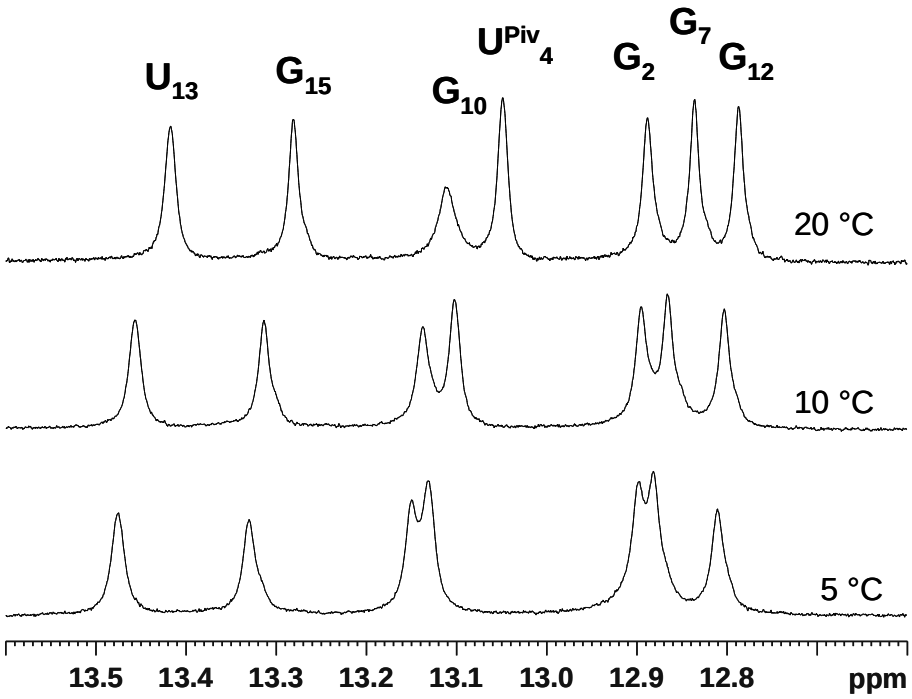

Figure S4. Imino protons region of the 1D ^{1}H spectra in H_2O/D_2O of the duplex r(CGCU*ACGC)dT/r(GCGUAGCG)dT at several temperatures.

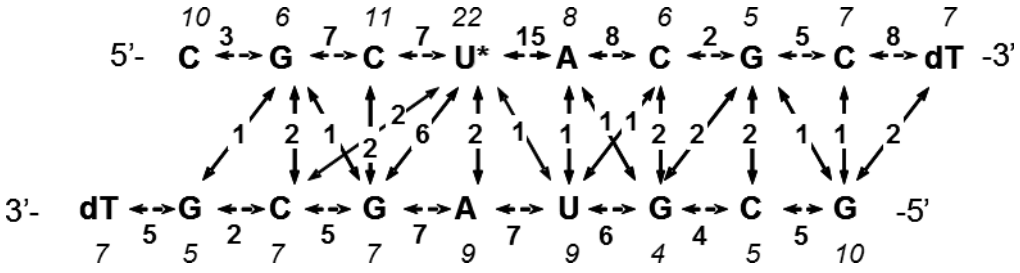

Figure S5. Distribution of the distance restraints extracted from the NOE. The numbers of inter- and intra-residue cross peaks are given in bold and italic characters respectively.

(4.) Structure analysis

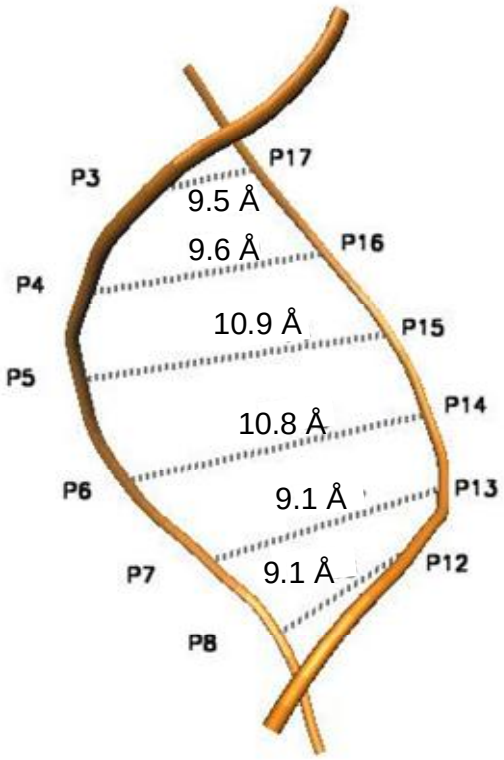

Figure S6. Minor groove width. The given values are the result of the smallest distances between two P atoms of each strand minus 5.8 Å (twice the Van der Waals radius of the phosphate group).

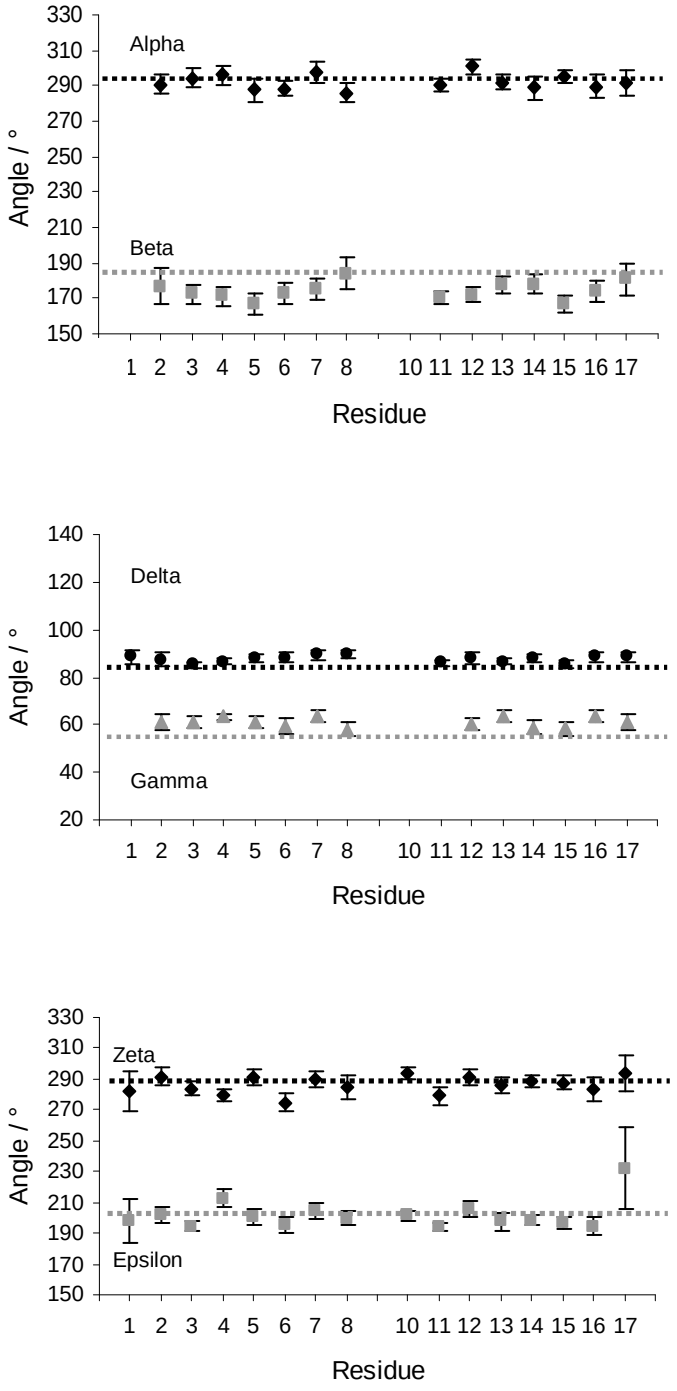

Figure S7. Averaged dihedral angles values for the backbone calculated with Curves+. The non significant angles (γ of C1 and G10 and all the angles for dT9 and dT18) were omitted for clarity. The dotted lines represent the angle values for the standard A-type helix.

Table S1. Backbone torsion angles and glycosidic angles for r(CGCU*ACGC)dT:r(GCGUAGCG)dT. [a]

Residue	α	β	γ	δ	ε	ζ	χ
C1	-	-	125 (94)	88 (3)	198 (14)	282 (13)	204 (13)
G2	291 (5)	177 (10)	61 (3)	87 (3)	202 (5)	292 (5)	193 (7)
C3	294 (5)	172 (5)	61 (2)	86 (1)	195 (3)	284 (5)	205 (5)
U*4	296 (5)	171 (5)	63 (1)	87 (1)	213 (6)	280 (4)	204 (3)
A5	288 (7)	167 (6)	61 (2)	88 (2)	200 (5)	291 (5)	205 (2)
C6	288 (4)	173 (6)	59 (3)	88 (2)	195 (5)	275 (6)	214 (3)
G7	298 (6)	175 (6)	64 (2)	89 (2)	205 (6)	289 (5)	192 (6)
C8	286 (6)	184 (9)	58 (3)	90 (2)	200 (4)	287 (8)	208 (5)
dT9	294 (4)	175 (5)	62 (2)	106 (2)	-	-	225 (3)
G10	-	-	257 (65)	86 (2)	202 (3)	294 (4)	201 (5)
C11	290 (4)	170 (4)	60 (2)	86 (2)	194 (3)	279 (6)	210 (4)
G12	301 (4)	172 (4)	64 (2)	88 (3)	206 (5)	291 (5)	191 (5)
U13	292 (5)	178 (4)	59 (2)	87 (1)	197 (5)	286 (5)	206 (5)
A14	289 (7)	178 (5)	58 (3)	88 (2)	198 (4)	289 (4)	205 (3)
G15	295 (4)	167 (5)	64 (3)	85 (2)	197 (4)	288 (4)	199 (3)
C16	289 (6)	174 (6)	61 (2)	89 (2)	194 (6)	284 (8)	214 (4)
G17	292 (7)	181 (9)	61 (3)	89 (2)	232 (27)	293 (12)	199 (12)
dT18	204 (76)	193 (10)	60 (3)	109 (4)	-	-	238 (8)
A-RNA [b]	292	178	54	82	207	289	202

[a] Mean values in degrees calculated with Curves+ for the 20 structures. The standard deviations are given under brackets
[b] Reference values for canonical RNA structure are from *Nucleic Acids in Chemistry and Biology* (Eds.:G. M. Blackburn, M.J. Gait, D. Loakes, D. M. Williams), Oxford University Press, **1996**, Chapter 2.

Table S2. Helical parameters for r(CGCU*ACGC)dT:r(GCGUAGCG)dT.

Base Pairs	Shear (Å)	Stretch (Å)	Stagger (Å)	Buckle (°)	Propeller twist (°)	Opening (°)
C1-G17	0.2 (0.4)	-0.6 (0.7)	-0.9 (1.4)	11 (22)	7 (11)	-2 (10)
G2-C16	-0.8 (0.5)	-0.5 (0.2)	-1.5 (0.6)	-21 (7)	4 (11)	-3 (7)
C3-G15	0.3 (0.4)	-0.3 (0.1)	-0.8 (0.5)	2 (8)	6 (9)	0 (4)
U*4-A14	0.0 (0.2)	-0.3 (0.0)	-0.2 (0.2)	3 (5)	-3 (6)	3 (3)
A5-U13	0.0 (0.3)	-0.5 (0.2)	-1.3 (0.5)	7 (7)	5 (11)	-1 (5)
C6-G12	1.1 (0.7)	-0.7 (0.3)	-2.2 (0.6)	26 (9)	1 (7)	1 (9)
G7-C11	-1.1 (0.5)	-0.6 (0.4)	-1.7 (0.6)	-21 (10)	5 (7)	1 (7)
C8-G10	0.7 (0.5)	-0.4 (0.1)	-0.7 (0.4)	2 (13)	14 (7)	-1 (6)

Base Steps	Shift (Å)	Slide (Å)	Rise (Å)	Tilt (°)	Roll (°)	Twist (°)
C1-G2	-0.2 (0.9)	-1.5 (0.5)	5.2 (1.1)	2 (10)	4 (10)	28 (5)
G2-C3	0.2 (0.5)	-1.2 (0.2)	3.2 (0.2)	-3 (3)	-9 (5)	34 (2)
C3-U*4	0.0 (0.3)	-1.5 (0.3)	3.9 (0.5)	-1 (3)	-4 (4)	26 (2)
U*4-A5	-0.2 (0.4)	-0.8 (0.2)	3.7 (0.3)	5 (3)	6 (7)	32 (2)
A5-C6	0.2 (0.5)	-1.2 (0.2)	3.1 (0.2)	4 (3)	0 (5)	33 (3)
C6-G7	-0.1 (0.7)	-1.7 (0.4)	6.1 (0.7)	-3 (3)	1 (3)	23 (4)
G7-C8	-0.6 (0.6)	-1.1 (0.3)	3.0 (0.4)	-5 (5)	0 (6)	36 (3)

Base Pairs	X-displacement (Å)	Y-displacement (Å)	Inclination (°)	Tip (°)	Axis Bend (°)
C1-G17	-2.4 (0.7)	0.3 (0.8)	-0.8 (11.2)	-0.8 (6.8)	-
C2-G16	-2.3 (0.6)	0.3 (0.6)	0.1 (5.9)	5.1 (5.1)	1.9 (1.3)
C3-G15	-1.8 (0.5)	0.4 (0.5)	-1.9 (4.8)	-3.4 (3.6)	1.5 (1.0)
U4-A14	-2.0 (0.6)	-0.1 (0.4)	-4.7 (5.3)	-5.8 (3.5)	1.4 (1.0)
A5-U13	-2.2 (0.6)	0.4 (0.4)	-0.7 (4.2)	2.0 (4.7)	1.3 (0.9)
C6-G12	-1.9 (0.6)	0.2 (0.6)	4.1 (4.3)	0.6 (4.1)	1.5 (1.0)
G7-C11	-2.2 (0.5)	-0.6 (0.7)	0.9 (5.4)	0.5 (3.1)	1.4 (0.9)
C8-G10	-2.7 (0.7)	0.4 (0.8)	-3.8 (6.1)	2.5 (5.9)	1.6 (0.9)

[a] Mean values calculated with Curves+ for the 20 structures. The standard deviations are given under brackets.