

Supplementary Information

Photoinduced changes in hydrogen bonding patterns of 8-thiopurine nucleobase analogues in a DNA strand

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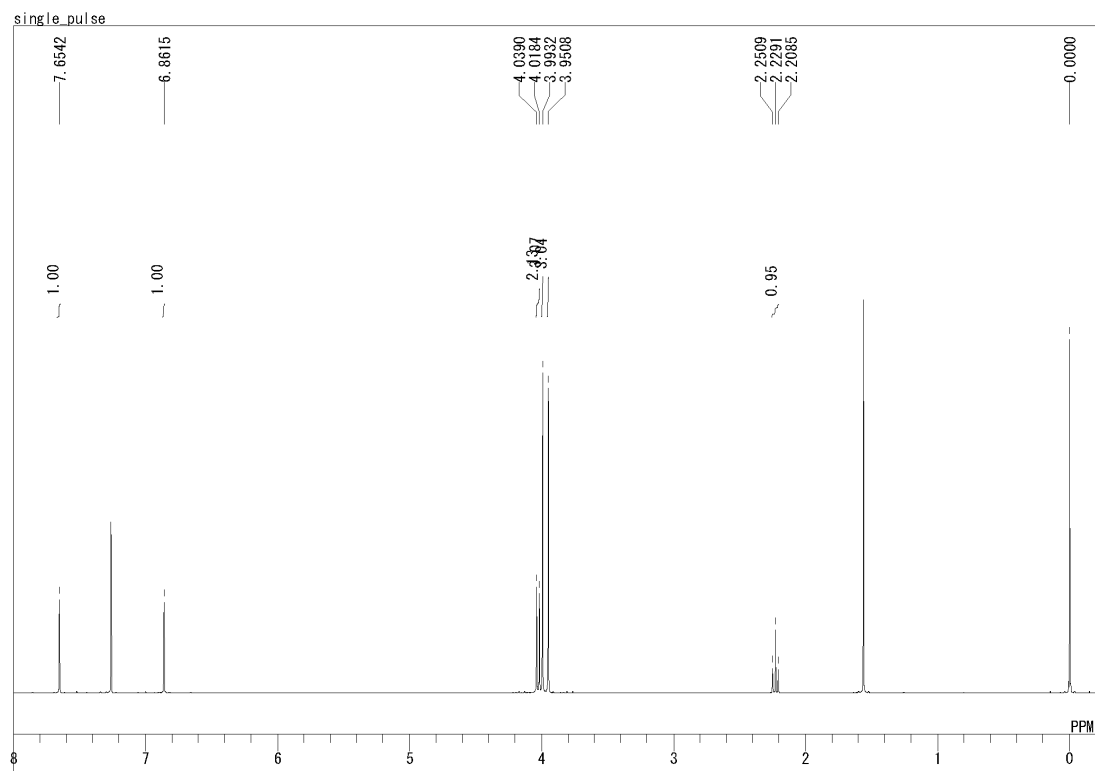
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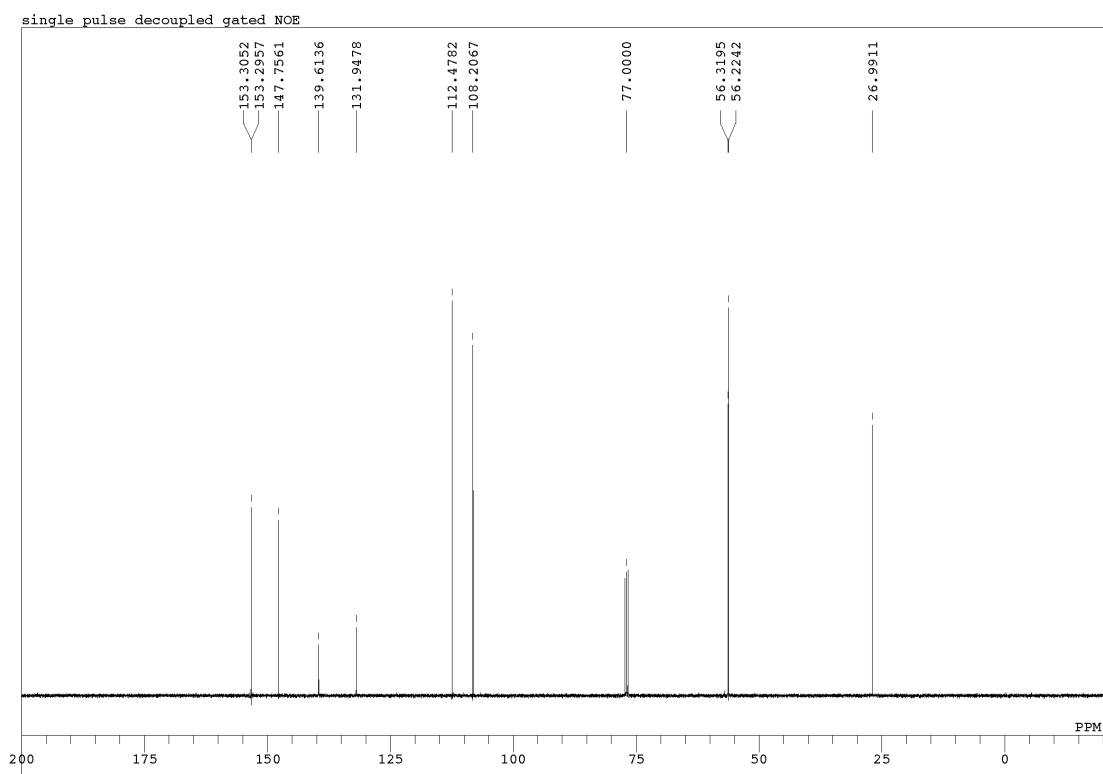
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1. ^1H , ^{13}C and ^{31}P spectra of new compounds

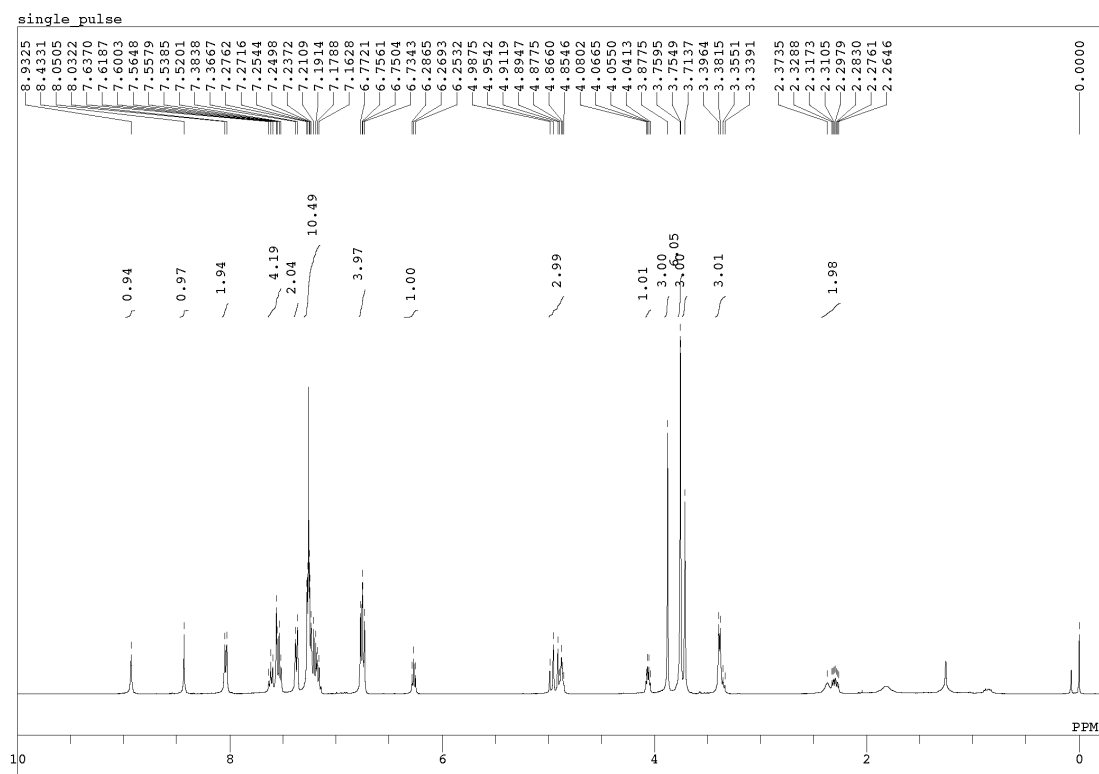
1-1. ^1H spectrum of compound 2



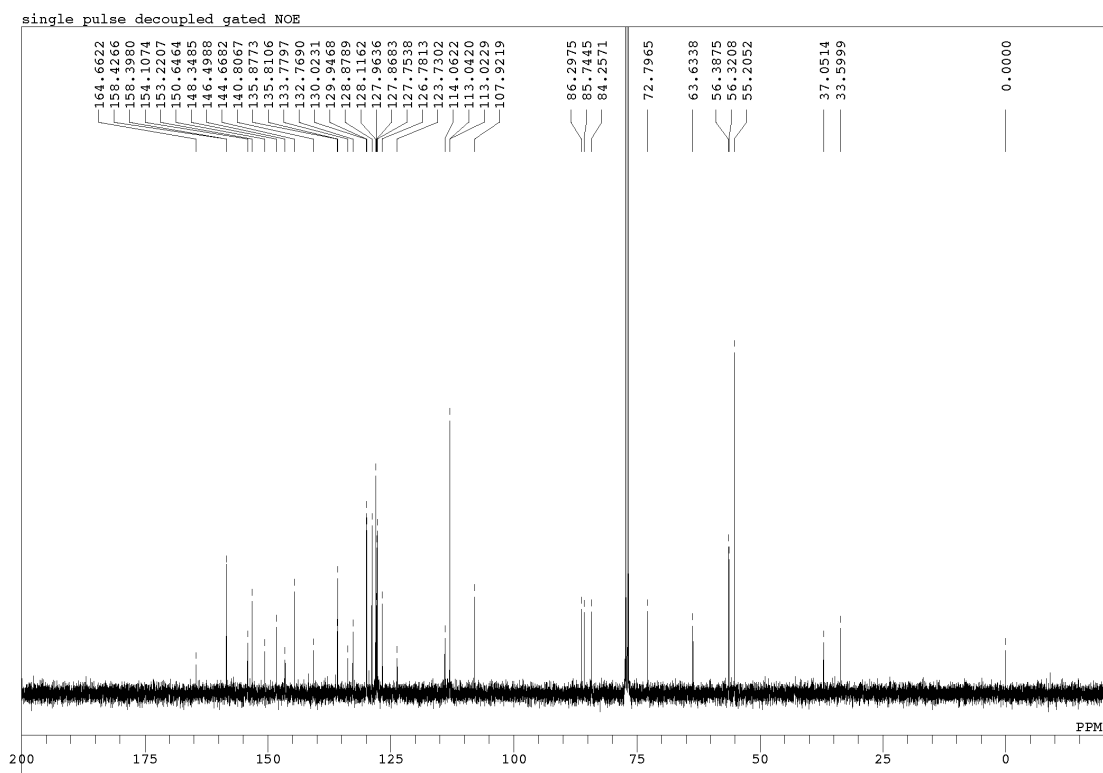
1-2. ^{13}C spectrum of compound 2



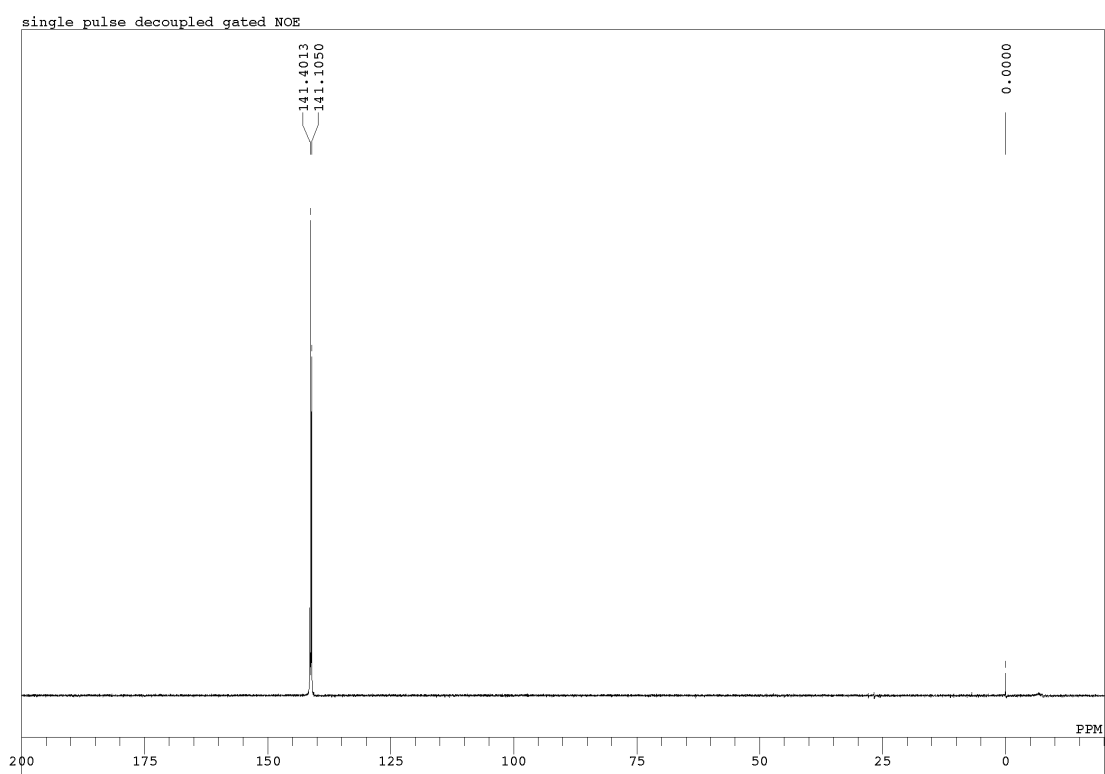
1-3. ^1H spectrum of compound 4



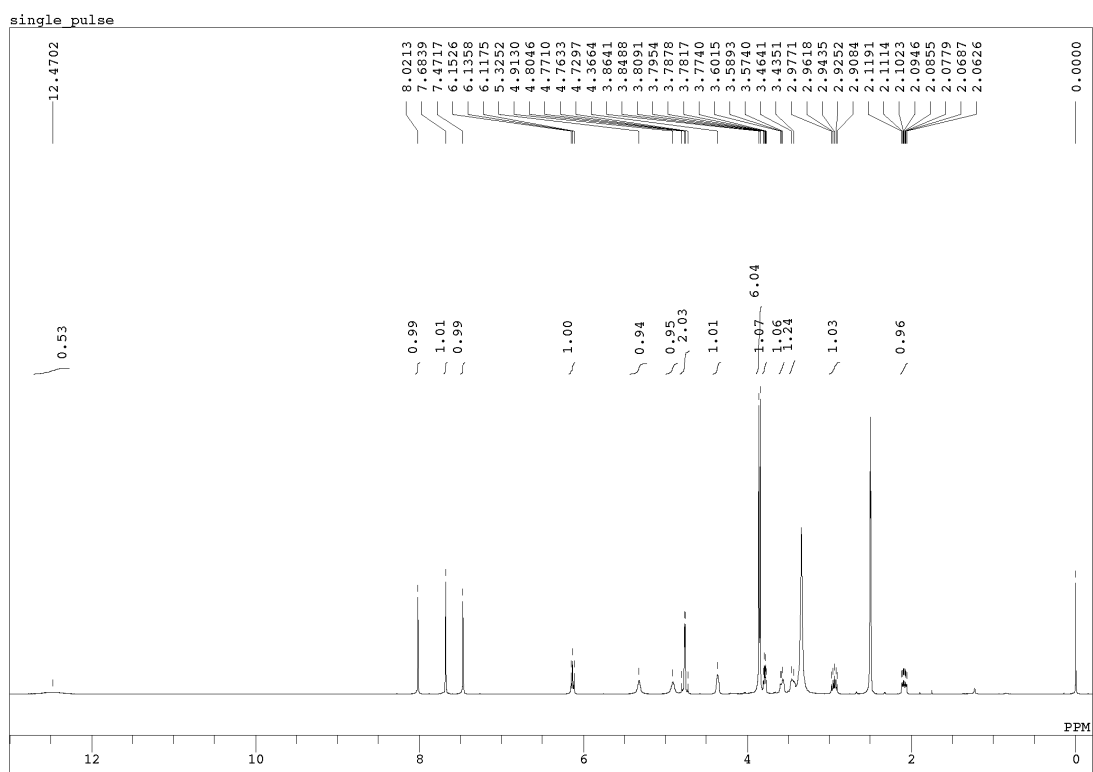
1-4. ^{13}C spectrum of compound 4



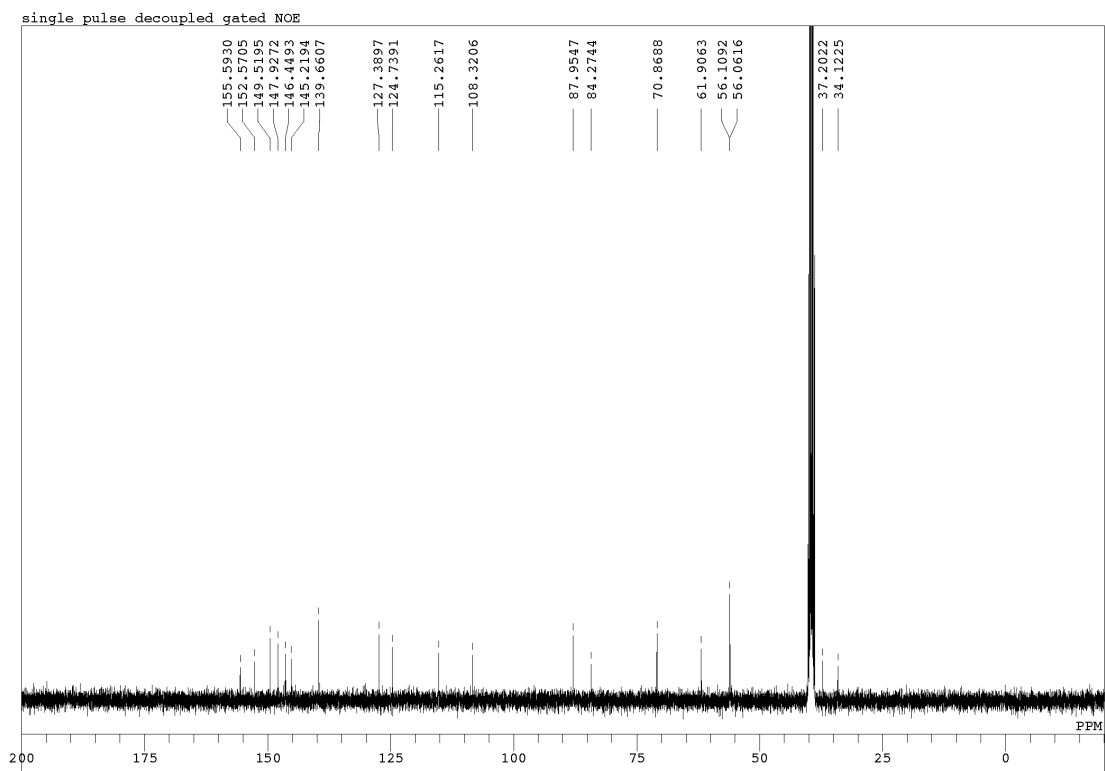
1-5. ^{31}P spectrum of compound 5



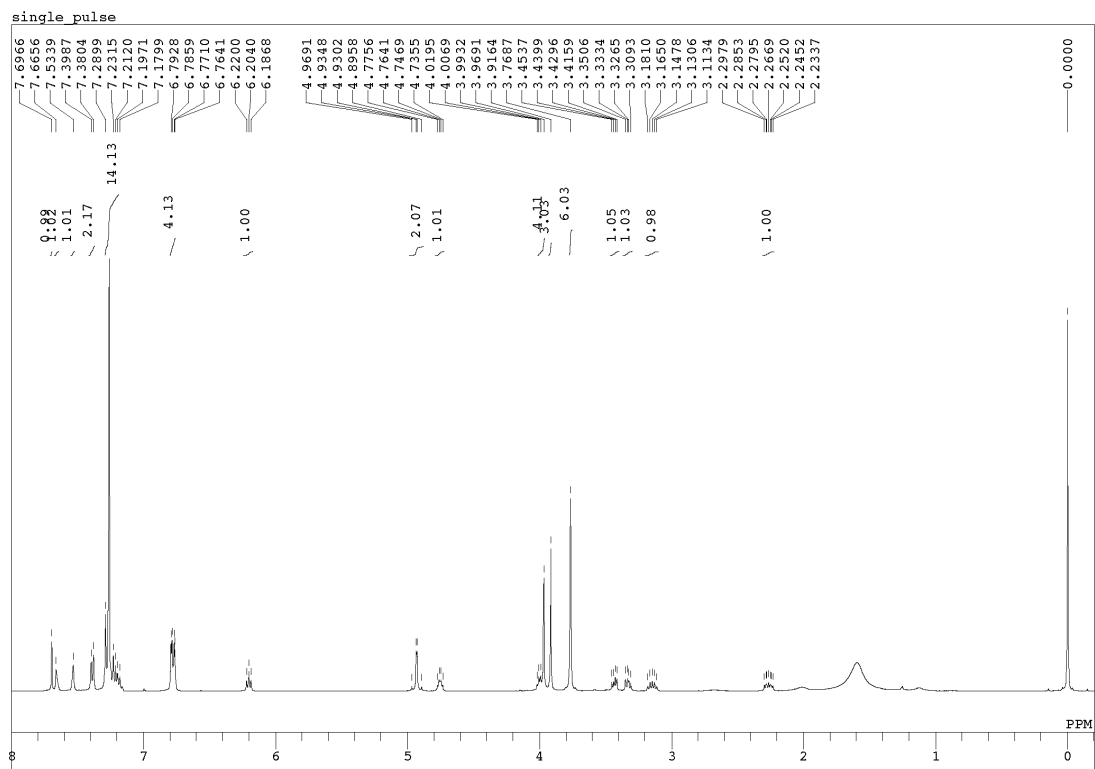
1-6. ¹H spectrum of compound 7



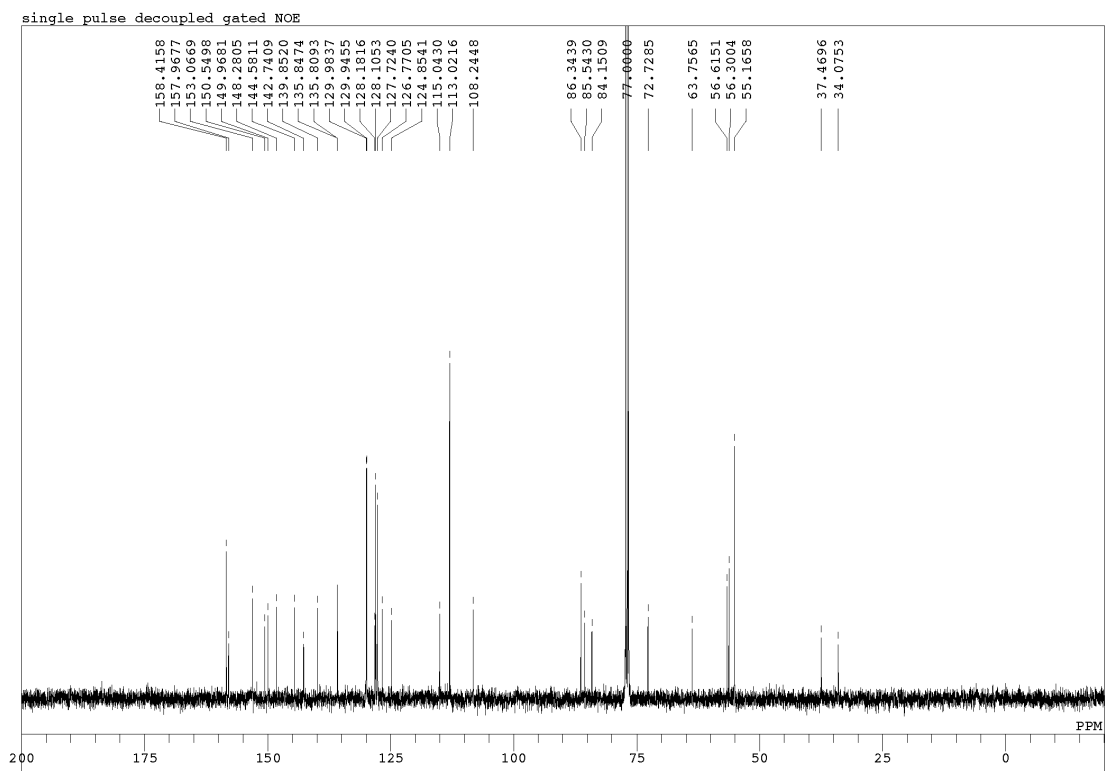
1-7. ^{13}C spectrum of compound 7



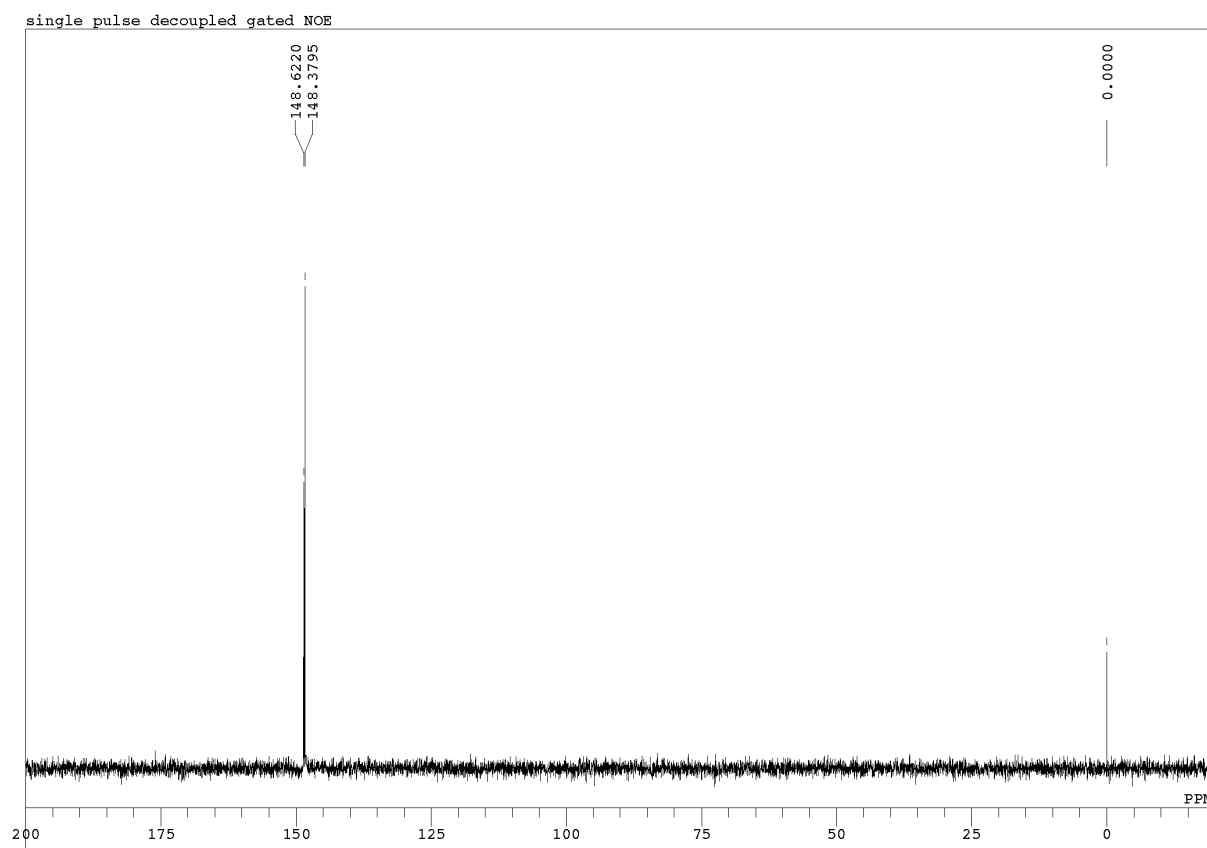
1-8. ^{13}C spectrum of compound 8



1-9. ^{13}C spectrum of compound 8



1-10. ^{31}P spectrum of compound 9



2. HPLC and MALDI-TOF MS analysis of SA^{NV}- and SH^N-modified ODNs

2-1. ODN 10

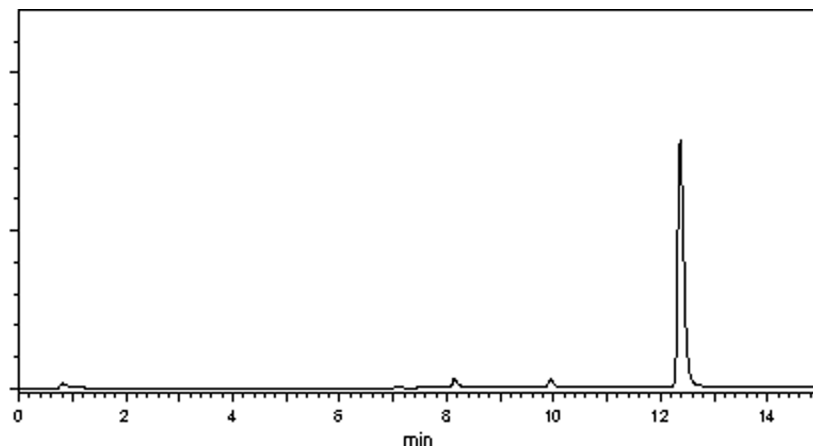
RP-HPLC

Column: Waters XBridge™ OST C18 2.5 μm , 4.6 x 50 mm

Gradient: 6-15% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

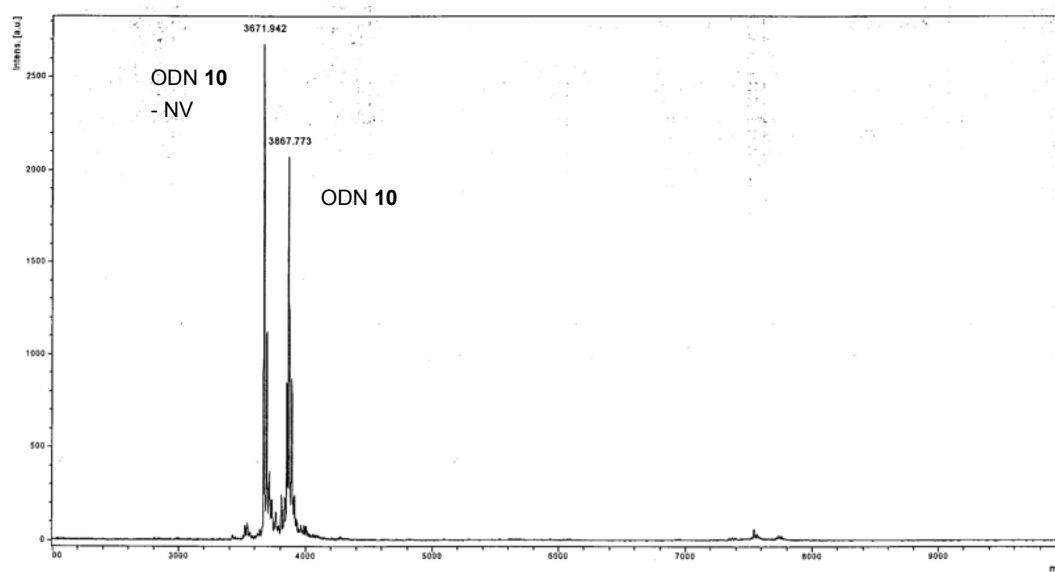
Flow rate: 1.0 mL/min

Column temperature: 50 °C



MALDI-TOF MS

Calcd. 3868.6 [M-H]⁻



2-2. ODN 11

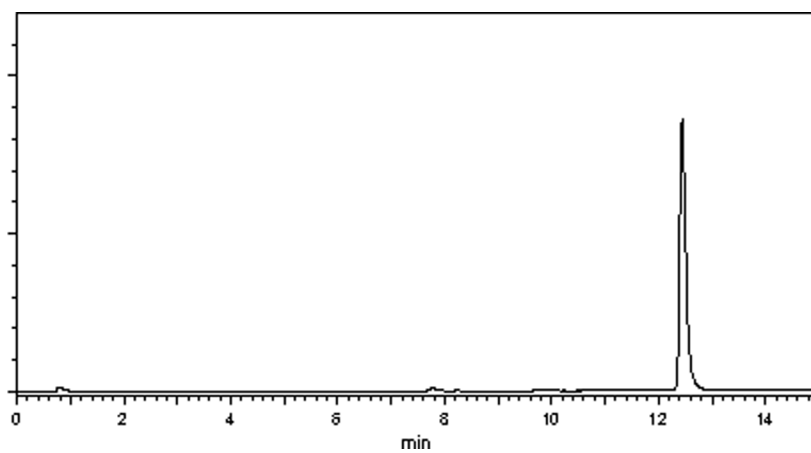
RP-HPLC

Column: Waters XBridge™ OST C18 2.5 µm, 4.6 x 50 mm

Gradient: 6-15% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

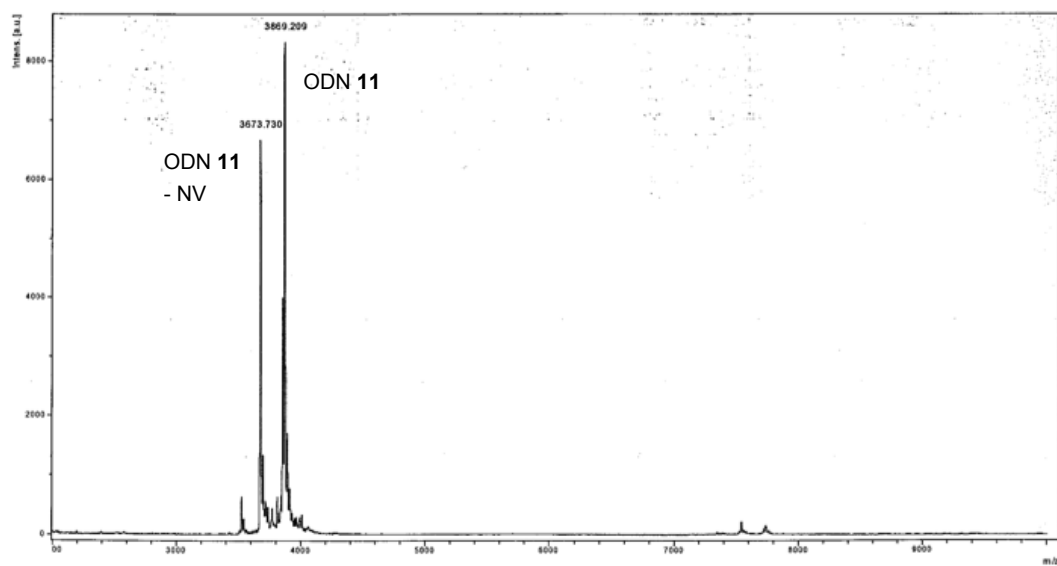
Flow rate: 1.0 mL/min

Column temperature: 50 °C



MALDI-TOF MS

Calcd. 3869.6 [M-H]⁻



2-3. ODN 16

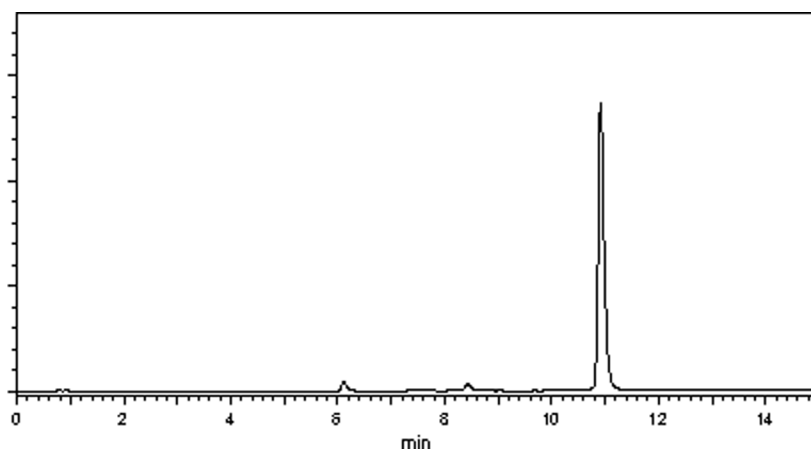
RP-HPLC

Column: Waters XBridge™ OST C18 2.5 µm, 4.6 x 50 mm

Gradient: 8-24% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

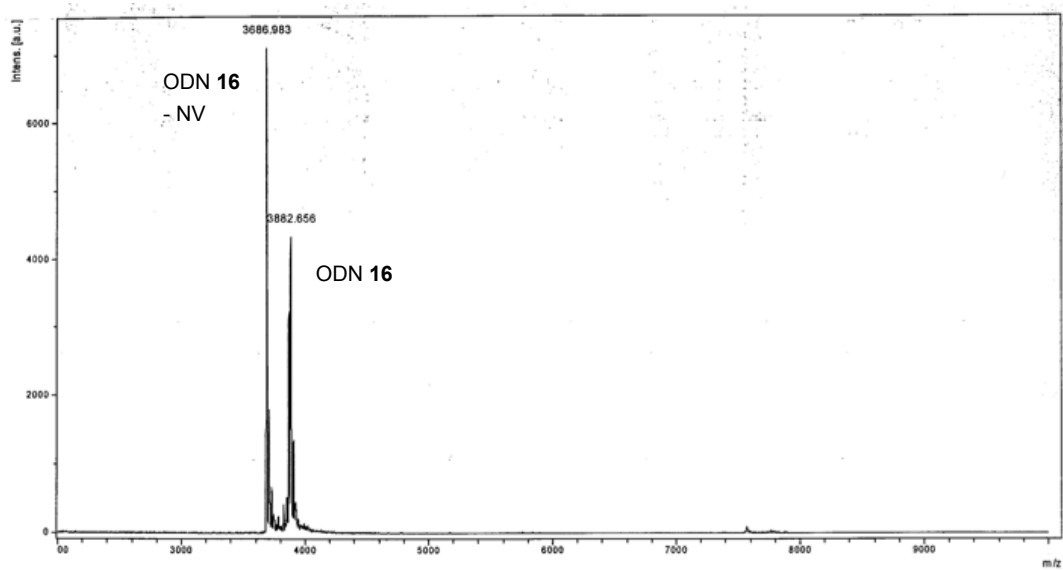
Flow rate: 1.0 mL/min

Column temperature: 50 °C



MALDI-TOF MS

Calcd. 3882.7 [M-H]⁻



2-4. ODN 17

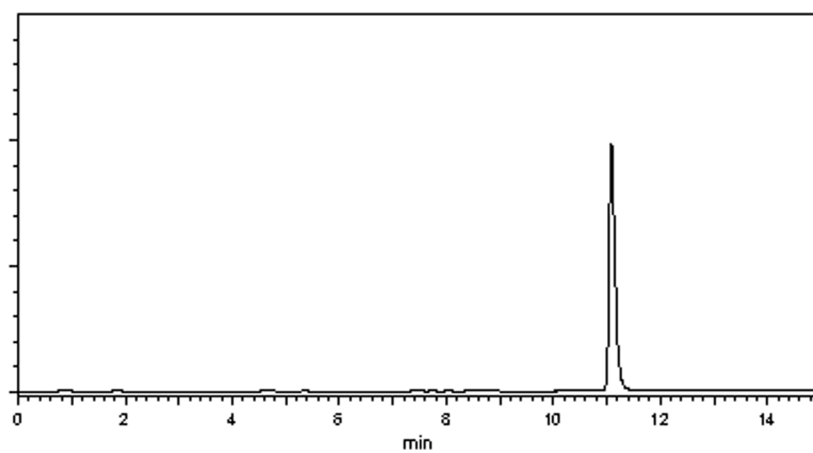
RP-HPLC

Column: Waters XBridge™ OST C18 2.5 μm , 4.6 x 50 mm

Gradient: 8-24% MeCN (over 15 min) in triethylammonium acetate buffer (pH 7.0, 0.1 M)

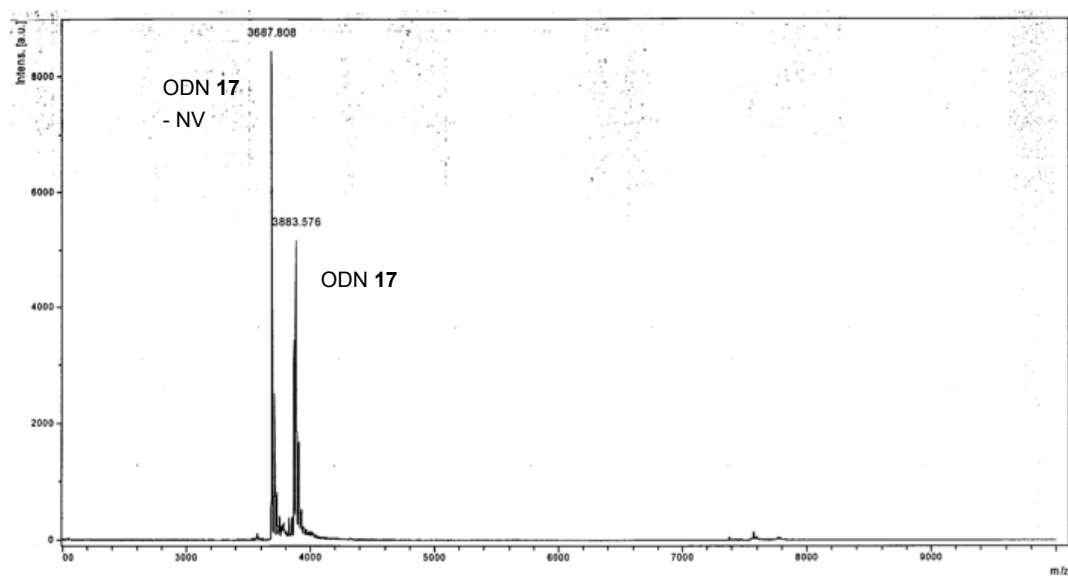
Flow rate: 1.0 mL/min

Column temperature: 50 °C



MALDI-TOF MS

Calcd. 3883.7 [M-H]⁻



3. Photoreaction of SA^{NV}- and SH^{NV}-modified ODNs

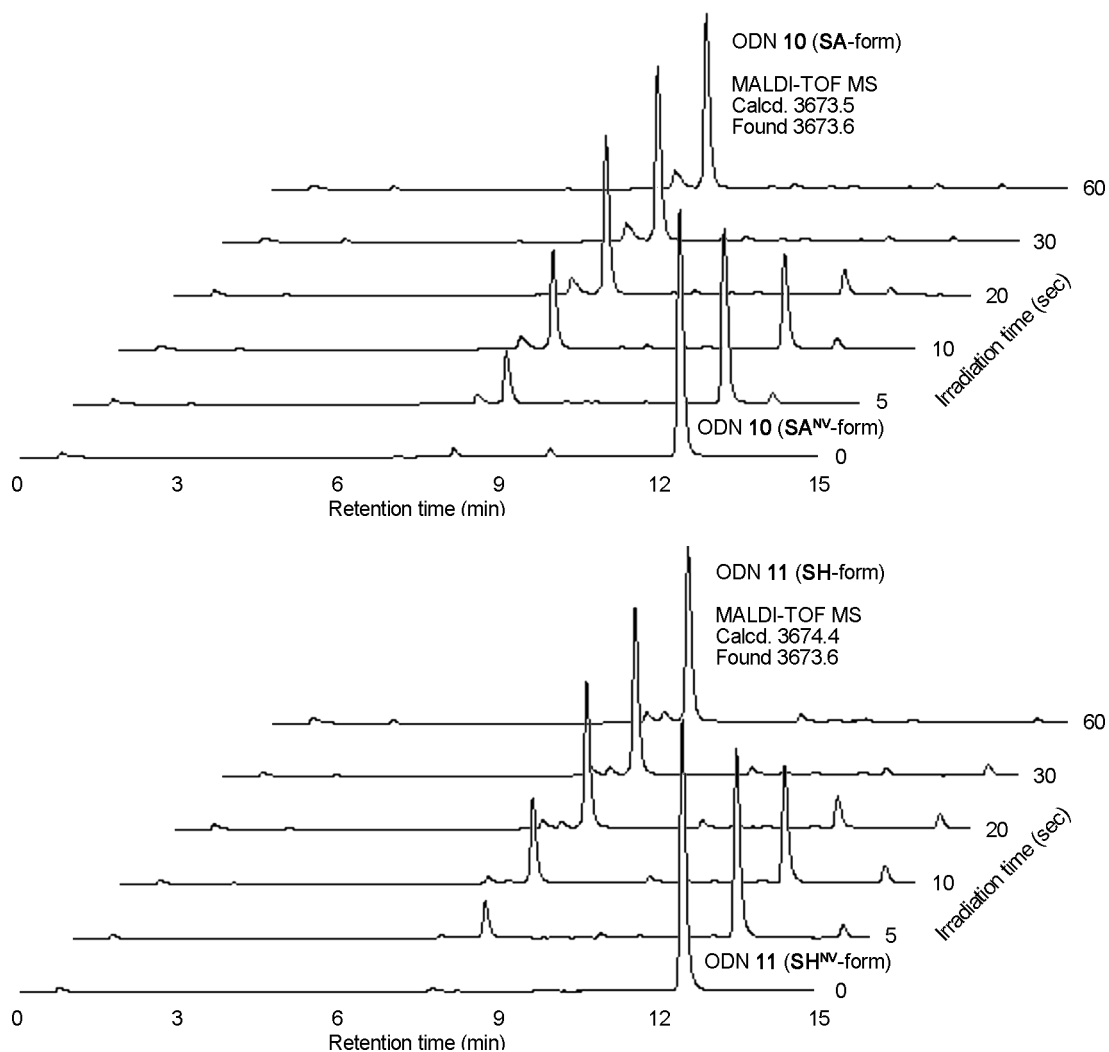


Fig. S1. HPLC analysis of the photoreaction of ODNs (a) **10** and (b) **11**.

4. UV melting experiments

Table S1. T_m values of DNA duplexes ^a			
5' -d (GCGTT X TTTGCT) -3'			
3' -d (CGCAA Y AAACGA) -5'			
duplex	X:Y	T_m (°C)	T_m^b (°C)
12:16	A: SA ^{NV}	38	28
13:16	G: SA ^{NV}	43	32
14:16	C: SA ^{NV}	33	27
15:16	T: SA ^{NV}	40	38
12:17	A: SH ^{NV}	38	40
13:17	G: SH ^{NV}	42	32
14:17	C: SH ^{NV}	33	36
15:17	T: SH ^{NV}	31	31

^a Conditions: each ODN (4.0 μ M), NaCl (20 mM), sodium phosphate buffer (10 mM, pH 7.2). ^b T_m values of the duplexes after irradiation (365 nm) at 37 °C.

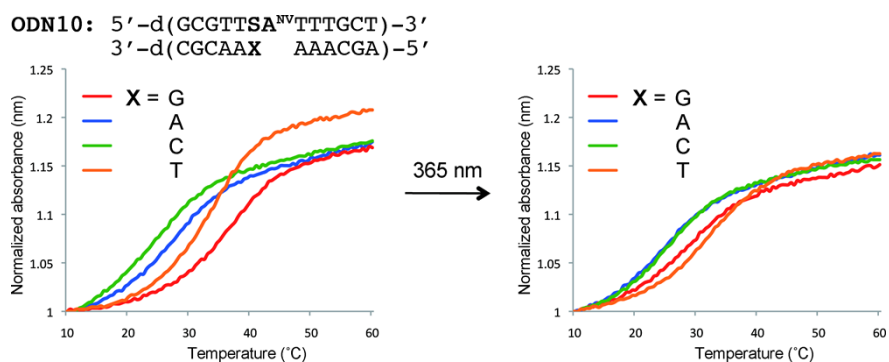


Fig. S2. Changes in UV melting curves for the duplexes with DNA targets triggered by light.

ODN16: 5'-d(AGCAAASA^{NV}AACGC)-3'
3'-d(TCGTTTX TTGCG)-5'

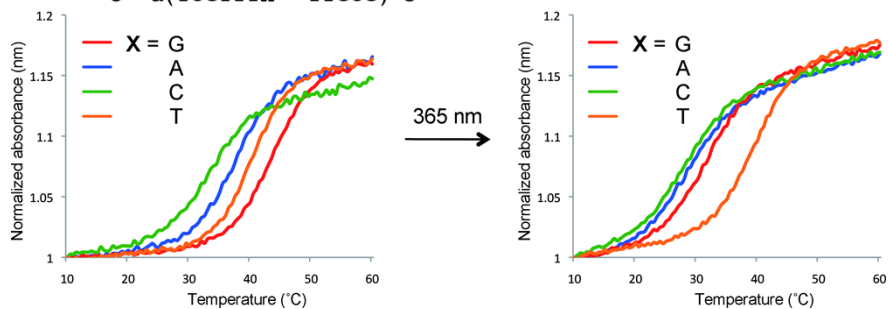


Fig. S3. Changes in UV melting curves for the duplexes with RNA targets triggered by light.

ODN17: 5'-d(AGCAAASH^{NV}AACGC)-3'
3'-d(TCGTTTX TTGCG)-5'

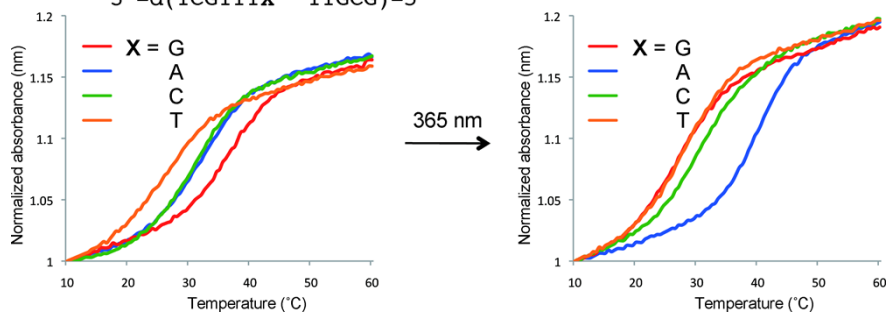


Fig. S4. Changes in UV melting curves for the duplexes **ODN3/*bad*** and **ODN3/*bcl*-xL** triggered by light.

5. 3D structures of base pairs

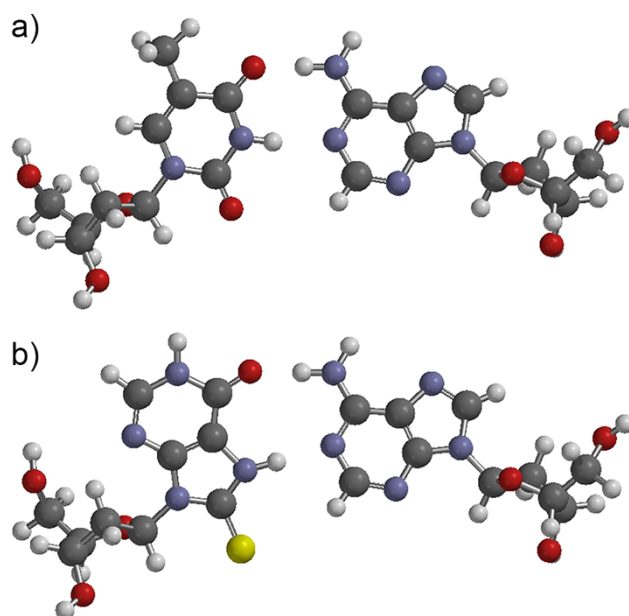


Fig. S5. 3D structures of (a) T:A base pair and (b) SH:A base pair.