Electronic Supplementary Material (ESI) for RSC Advances

Double-headed nucleotides in DNA-zipper structures; base-base interactions and UV-induced cross-coupling in the minor groove

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MALDI-data for oligonucleotides

Table S1. MALDI-MS of synthesized oligonucleotides containing monomer $\mathbf{T^A}$, $\mathbf{T^C}$, $\mathbf{T^{mp}}$.

Sequence	MW calculated	MW found
5′-GCG AAT^AATG CG	3528.4	3528.3
5′-GCG AAT AT^AG CG	3528.4	3527.4
5′-CGC ATA TT^AC GC	3439.3	3435.4
5′-CGC ATA T^ATC GC	3439.3	3441.5
5′-CGC AT^AA T^ATC GC	3586.4	3586.4
5′-GCG AAT^A AT^AG CG	3675.5	3675.2
5′-GCG AAT^C ATG CG	3504.3	3499.9
5′-GCG AAT AT^CG CG	3504.3	3509.1
5′-CGC ATA TT^CC GC	3504.3	3503.0
5′-CGC ATA T^CTC GC	3413.6	3418.1
5′-CGC AT^CA T^CTC GC	3413.6	3415.9
5′-GCG AAT^C AT^CG CG	3536.7	3538.9
5′-GCG AAT^{mp} ATG CG	3491.7	3490.9
5′-GCG AAT AT^{mp}G CG	3402.7	3401.5
5′-CGC ATA TT^{mp}C GC	3402.7	3402.9
5′-CGC ATA T^{mp}TC GC	3514.8	3515.7
5′-CGC AT^{mp}A T^{mp}TC GC	3491.7	3592.4
5′-GCG AAT^{mp} AT^{mp}G CG	3605.5	3604.7

Exact T_m-values

Table S2. Thermal stability data of modified DNA duplexes (corresponding to Table 1).

					ΔT_m /°C[a] [$\Delta\Delta T_m$]/°C[b]		
Entry	**Zipper**	**ON**	**Duplex**	**X=**	**T^C**	**T^A**	**T^{mp}**
0		T1 T2	5′-d(CGC ATA TTC GC) 3′-d(GCG TAT AAG CG)		46.2	46.2	46.2
1		T1 X1	5′-d(CGC ATA TTC GC) 3′-d(GCG **X**AT AAG CG)		42.0 −4.2	39.3 −5.9	45.2 −1.0
2		T1 X2	5′-d(CGC ATA TTC GC) 3′-d(GCG TA**X** AAG CG)		40.6 −5.6	39.3 −5.9	45.7 −0.5
3		T1 X3	5′-d(CGC ATA TTC GC) 3′-d(GCG **X**A**X** AAG CG)		35.8 −10.4	30.7 −14.5	44.7 −1.5
4		X4 T2	5′-d(CGC ATA T**X**C GC) 3′-d(GCG TAT AAG CG)		43.0 −3.2	39.2 −6.0	44.7 −1.5
5		X5 T2	5′-d(CGC ATA **X**TC GC) 3′-d(GCG TAT AAG CG)		41.2 −5.0	39.6 −5.6	44.2 −2.0
6		X6 T2	5′-d(CGC A**X**A **X**TC GC) 3′-d(GCG TAT AAG CG)		35.2 −11.0	30.2 −15.0	43.0 −3.2
7	(−1)	X5 X2	5′-d(CGC ATA **X**TC GC) 3′-d(GCG TA**X** AAG CG)		36.8 −9.4 [+1.2]	33.1 −12.1 [−0.6]	43.2 −3.0 [−0.5]
8	(−2)	X4 X2	5′-d(CGC ATA T**X**C GC) 3′-d(GCG TA**X** AAG CG)		37.7 −8.5 [+0.3]	35.7 −9.5 [+2.4]	44.3 −1.9 [+0.1]
9	(−3)	X5 X1	5′-d(CGC ATA **X**TC GC) 3′-d(GCG **X**AT AAG CG)		38.9 −7.3 [+1.9]	37.3 −7.9 [+3.6]	42.2 −4.0 [-1.0]
10	(−4)	X4 X1	5′-d(CGC ATA T**X**C GC) 3′-d(GCG **X**AT AAG CG)		37.8 −8.4 [−1.0]	30.6 −14.6 [−2.7]	43.1 −3.1 [−0.6]
11	(−2)/(−4)	X4 X3	5′-d(CGC ATA T**X**C GC) 3′-d(GCG **X**A**X**AAG CG)		32.0 −14.2 [−0.6]	25.1 −20.1 [+0.4]	43.0 −3.2 [−0.2]
12	(−1)/(−3)	X5 X3	5′-d(CGC ATA **X**TC GC) 3′-d(GCG **X**A**X** AAG CG)		34.2 −12.0 [+3.4]	29.3 −15.9 [+4.2]	42.1 −4.1 [−0.6]
13	(−3)/(−1)	X6 X1	5′-d(CGC A**X**A **X**TC GC) 3′-d(GCG **X**AT AAG CG)		31.9 −14.3 [+0.9]	29.3 −15.9 [+5.0]	41.1 −5.1 [-0.9]
14	(−1)/(+1)	X6 X2	5′-d(CGC A**X**A **X**TC GC) 3′-d(GCG TA**X** AAG CG)		27.6 −18.6 [−2.0]	26.2 −19.0 [+1.9]	43.2 −3.1 [+0.6]
15	(−1)/(−3)/ (+1)/(−1)	X6 X3	5′-d(CGC A**X**A **X**TC GC) 3′-d(GCG **X**A**X** AAG CG)		27.7 −18.5 [+2.9]	23.0 −22.2 [+7.3]	40.7 −5.5 [−0.8]

[a] Differences in melting temperatures as compared to the unmodified duplex. $\Delta T_m = T_{m(\mathbf{x}:\mathbf{y})} - T_{m(T1:T2)}$. Melting temperatures were obtained from the maxima of the first derivatives of the melting curves (A_{260} *vs.* temperature) recorded in a medium salt buffer (Na_2HPO_4 (2.5 mM), NaH_2PO_4 (5 mM), NaCl (100 mM), EDTA (0.1 mM), pH 7.0) using 1.0 µM concentrations of each strand.. [b] Differences in melting temperatures as compared to singly modified duplexes; $\Delta\Delta T_m = \Delta T_{m(\mathbf{x}:\mathbf{y})} - (\Delta T_{m(\mathbf{x}:T2)} + \Delta T_{m(T1:\mathbf{y})})$.

Table S3. Mixed (−3) zipper motifs (corresponding to Table 2).

5´- CGC ATA **Y**TC GC
3´- GCG **X**AT AAG CG

	ΔT_m /°C[a] [$\Delta\Delta T_m$]/°C[b]					
X\Y	T	**T^{T}**	**T^{C}**	**T^{A}**	**T^{mp}**	**T^{Ph}**
T	46.2	ref	41.2 −5.0	39.6 −5.6	44.2 −2.0	ref
T^{T}	ref	ref	41.7 −4.5 [+5.8]	38.3 −6.9 [+4.3]	39.1 −7.0 [+0.2]	ref
T^{C}	42.0 −4.2	40.3 −5.9 [+3.7]	38.9 −7.3 [+1.9]	34.9 −10.3 [−0.2]	40.2 −5.9 [+0.2]	42.7 −3.5 [+5.2]
T^{A}	39.3 −5.9	37.6 −7.6 [+3.7]	35.2 −10.0 [+0.6]	37.3 −7.9 [+3.6]	37.0 −9.1 [−1.2]	38.7 −6.5 [+3.9]
T^{mp}	45.2 −1.0	40.1 −6.1 [+0.3]	40.3 −5.8 [−1.7]	38.1 −8.1 [−1.2]	42.2 −4.0 [−1.0]	40.5 −5.6 [−0.2]
T^{Ph}	ref	ref	43.8 −2.4[+5.8]	41.2 −4.0 [+4.8]	40.7 −5.4 [−0.3]	ref

[a,b] See Table S2. "ref" corresponds to data taken from ref. 8.

HPLC chromatograms of T-T dimer

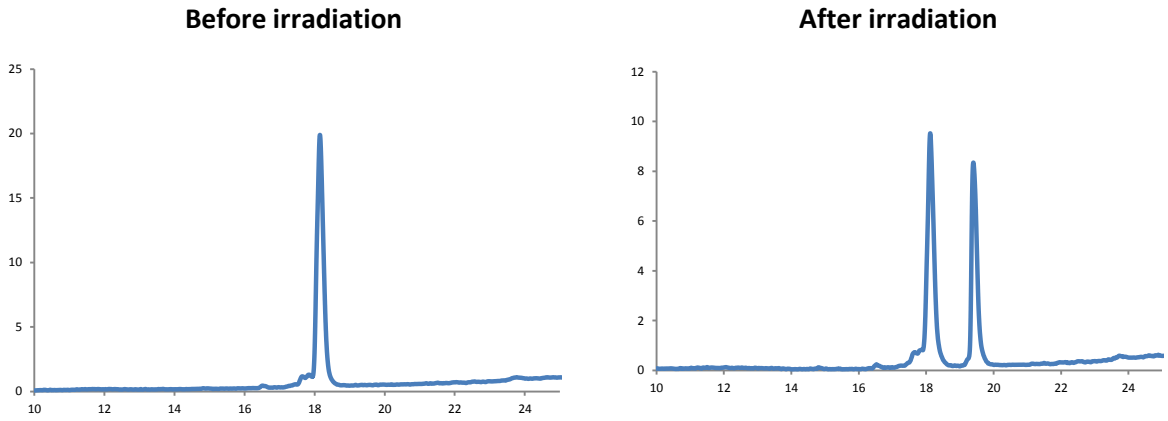
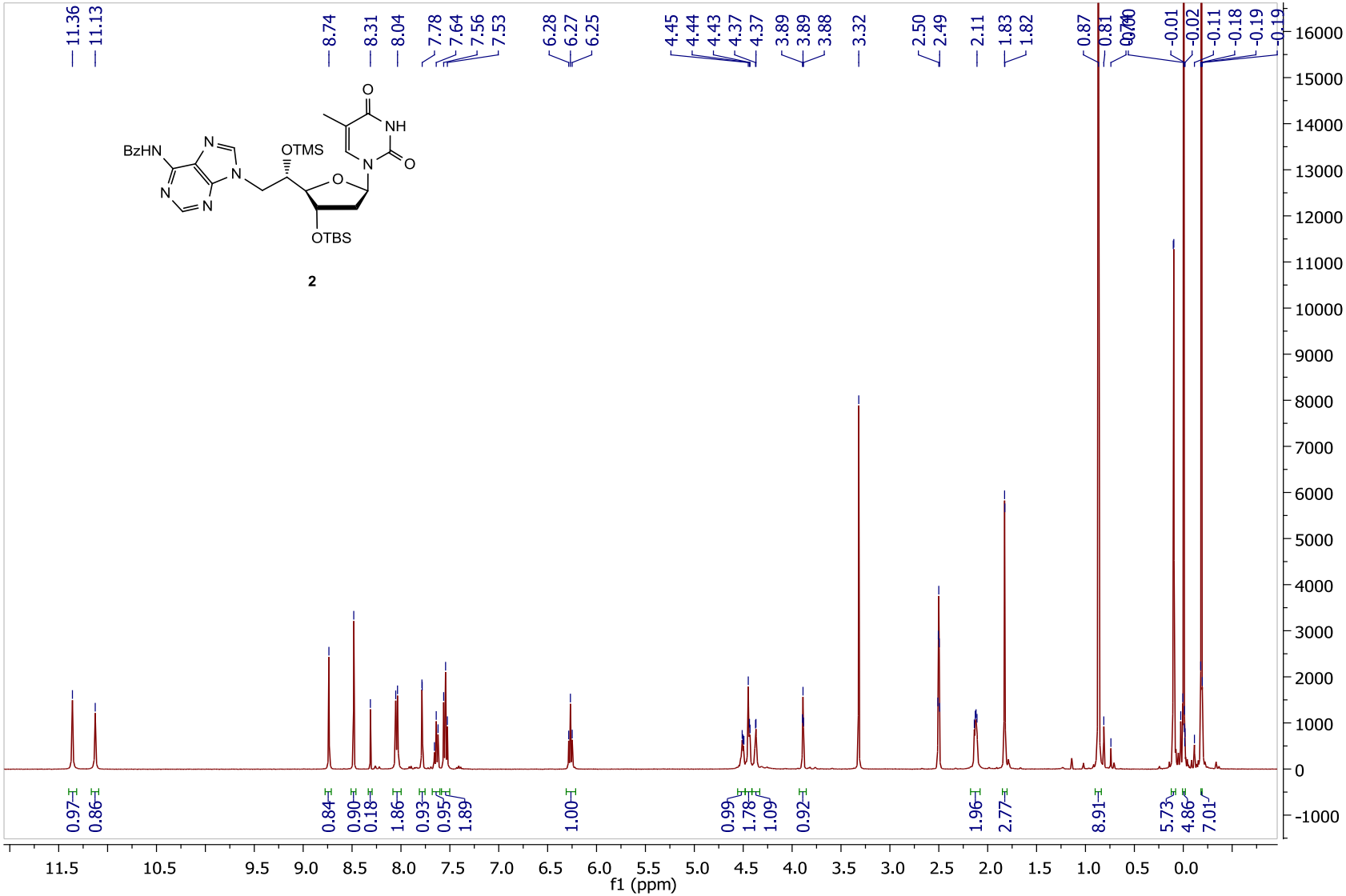


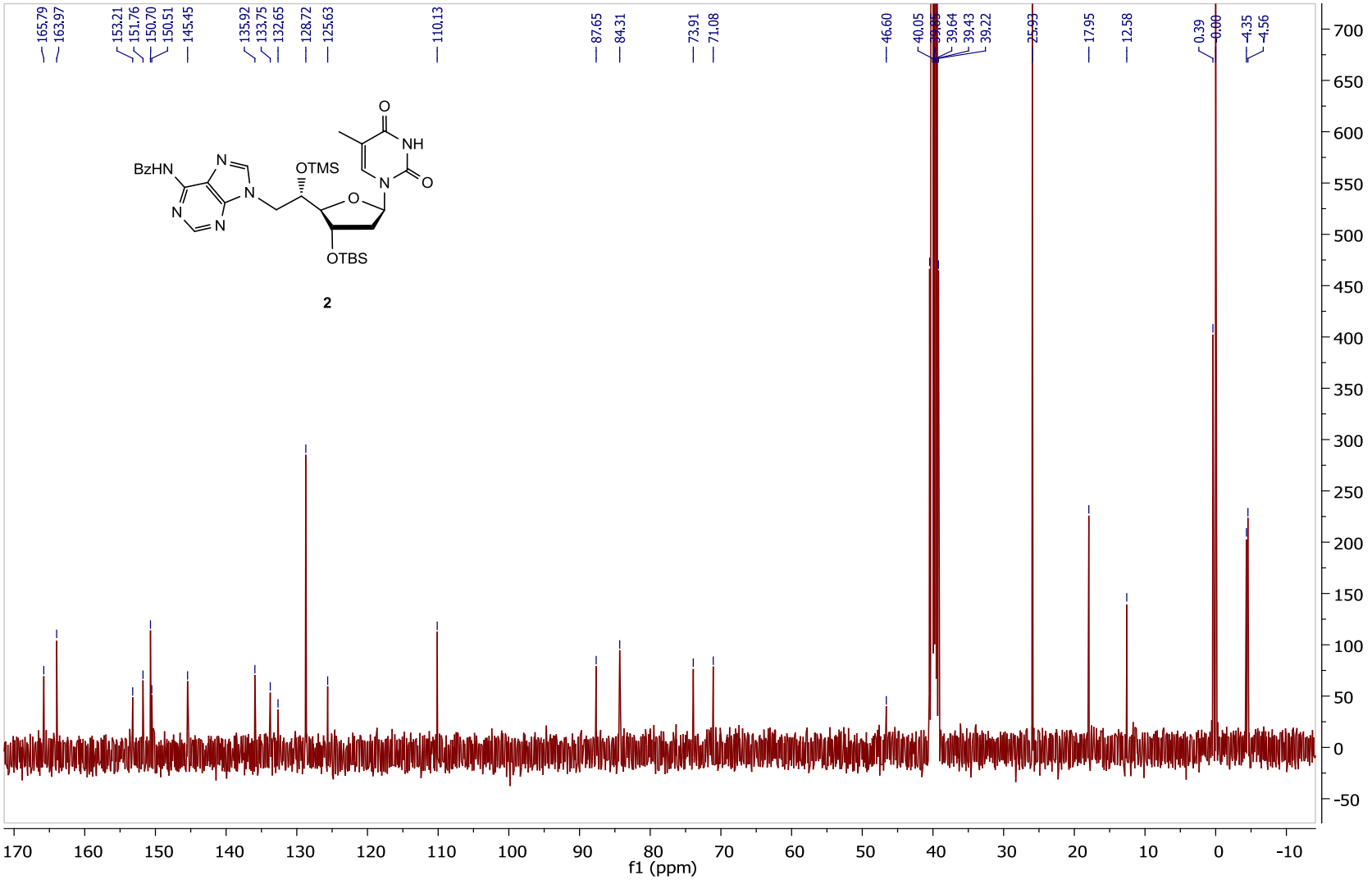
Figure S1. IC-HPLC profiles (60°C) of the (−3) $\mathbf{T^T/T^T}$ zipper duplex before (left) and after (right) irradiation (254 nm, 15 min.).

Table S4. T_m measurements before and after UV irradiation (254 nm).

Sequence	T_m(before)	T_m (after)	ΔT_m[a]
5′-d(CGC ATA TTC GC) 3′-d(GCG TAT AAG CG)	45.8	45.5	−0.3
5′-d(CGC ATA **T^T**TC GC) 3′-d(GCG **T^T**AT AAG CG)	42.1	39.5	−2.6

[a] Melting temperatures (T_m values/ °C) was obtained from the maxima of the first derivatives of the melting curves (A_{260} *vs.* temperature) recorded in a medium salt buffer (Na_2HPO_4 (7.5 mM), NaCl (100 mM), EDTA (0.1 mM), pH 7.0) using 1.0 µM concentrations of each strand. $\Delta T_m = T_{m(after)} - T_{m(before)}$.





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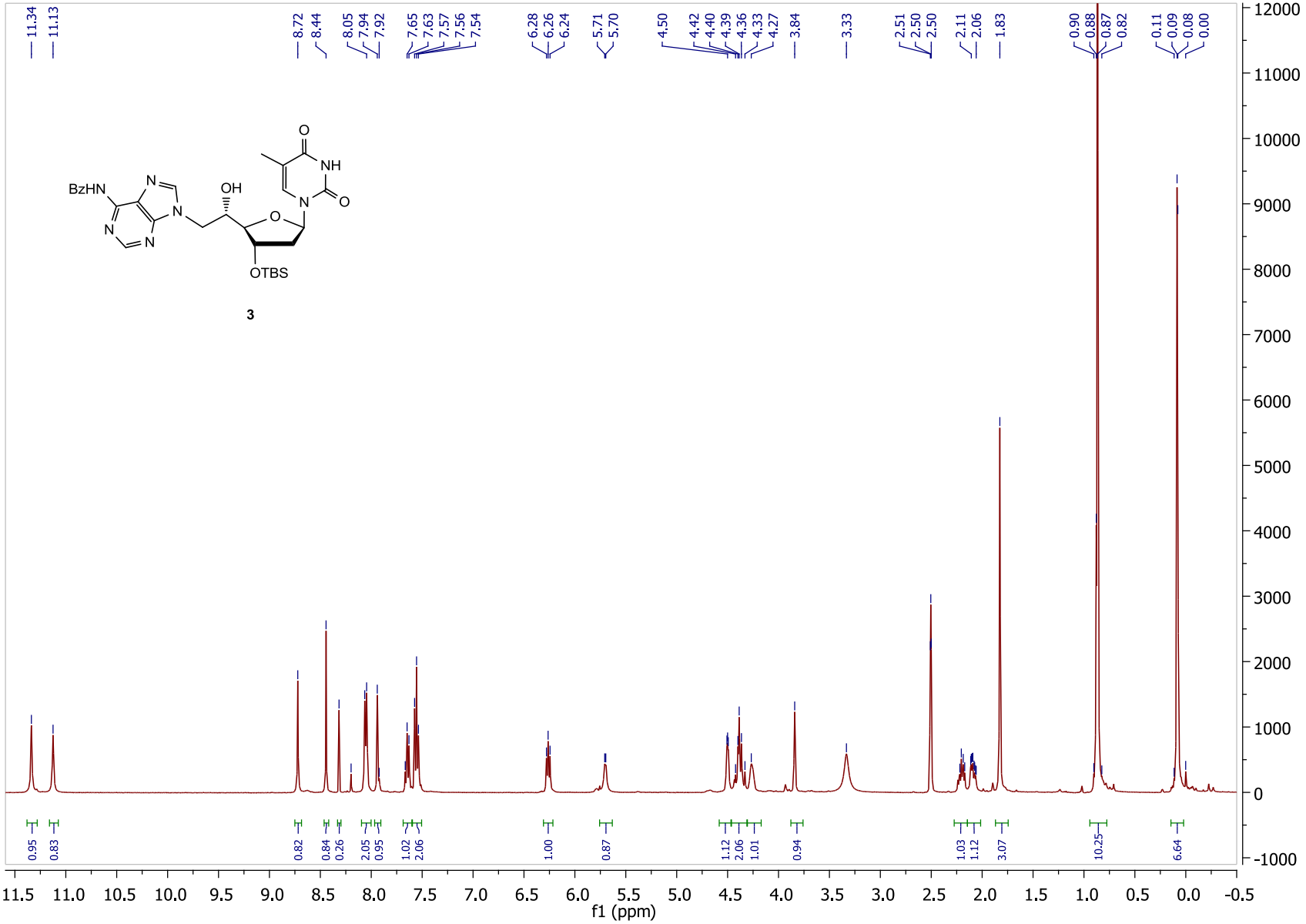

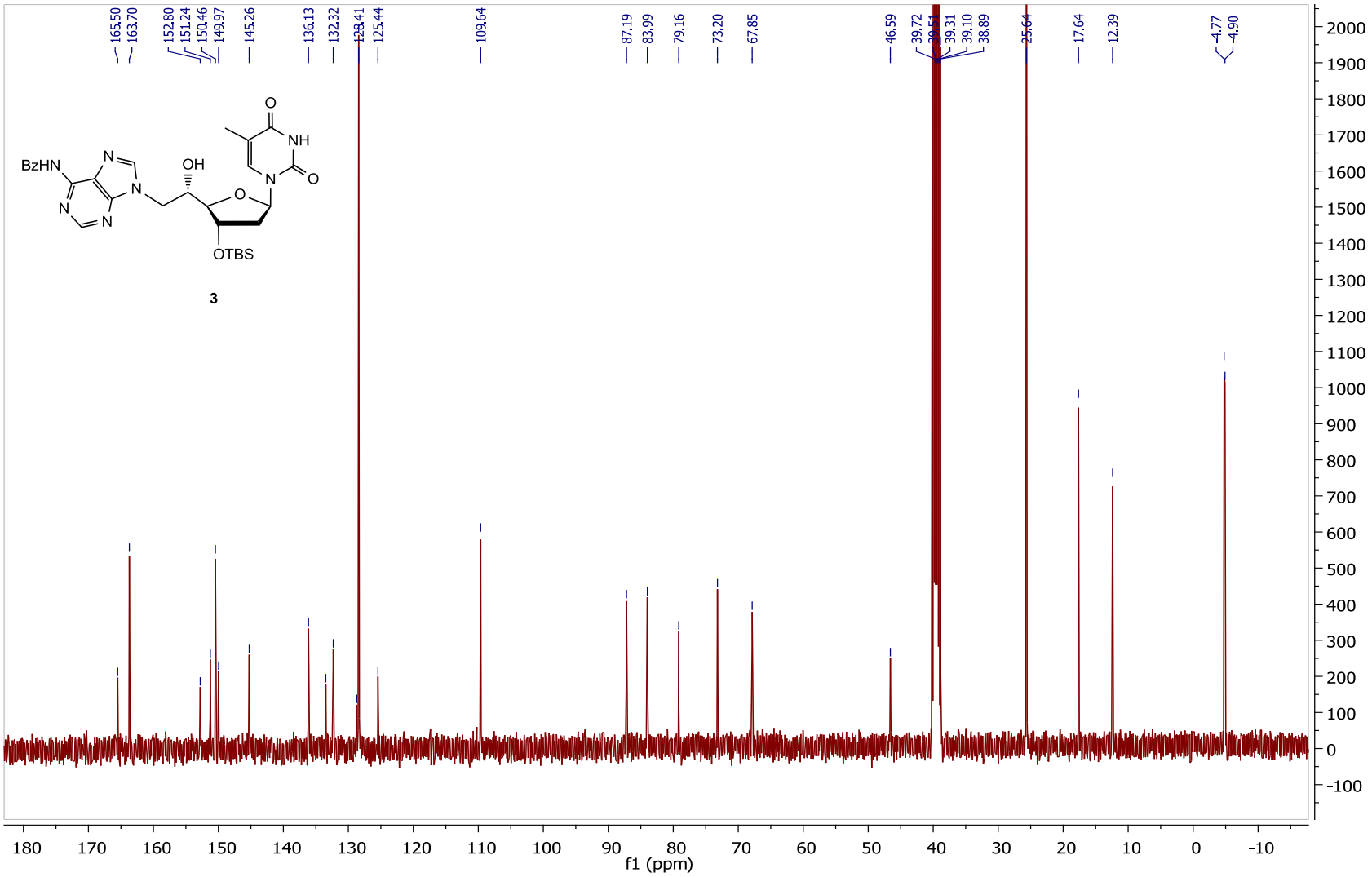

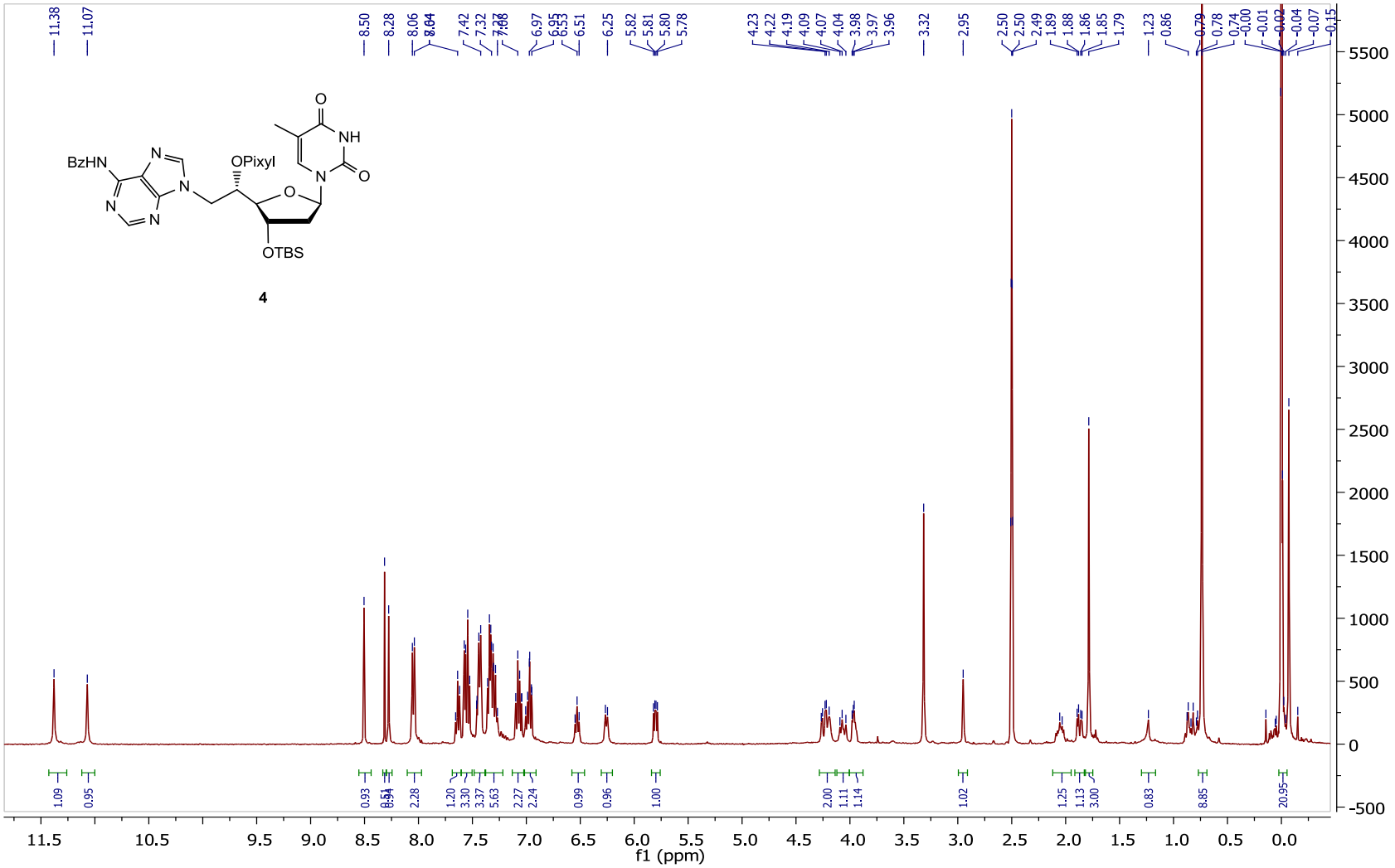

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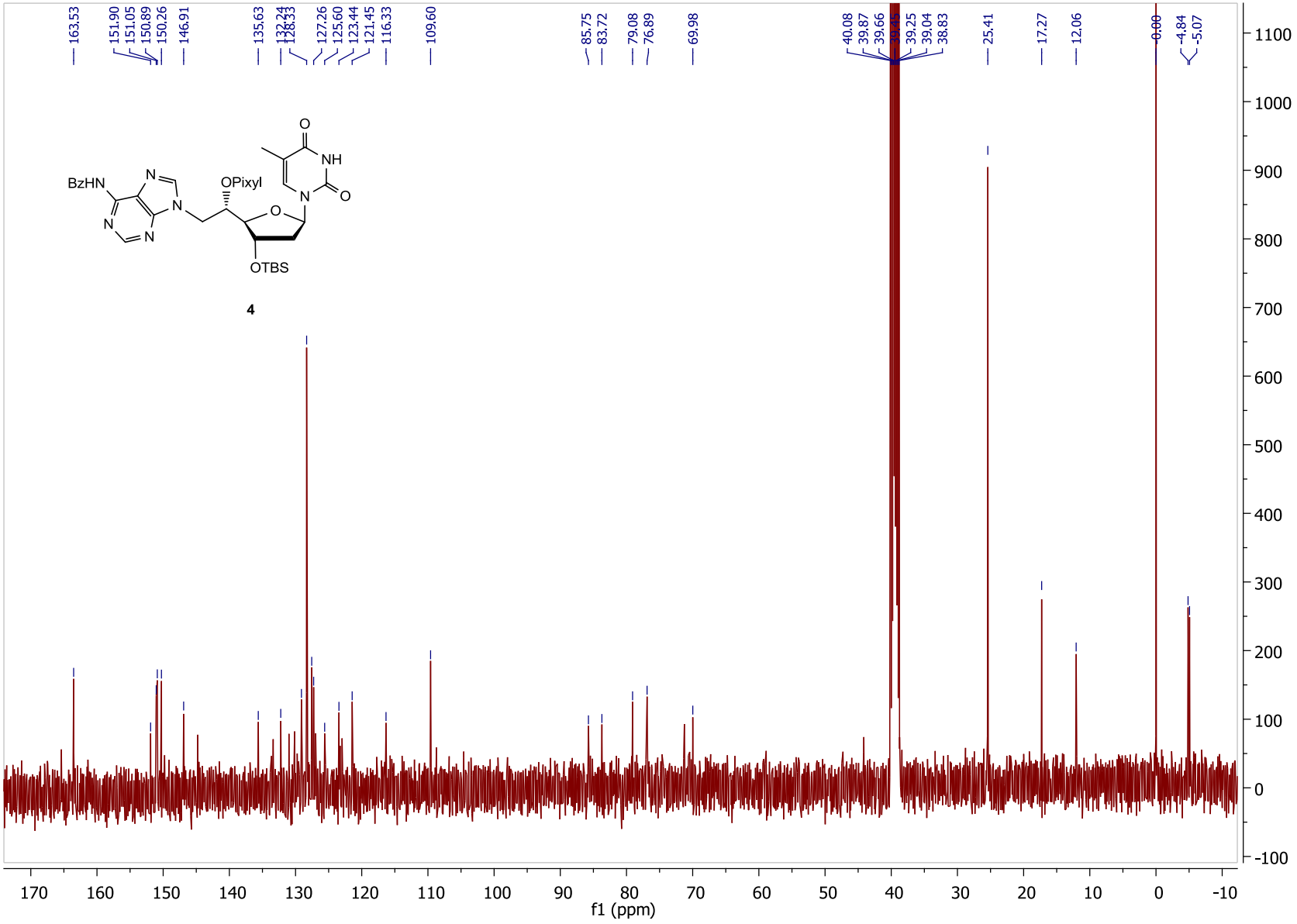

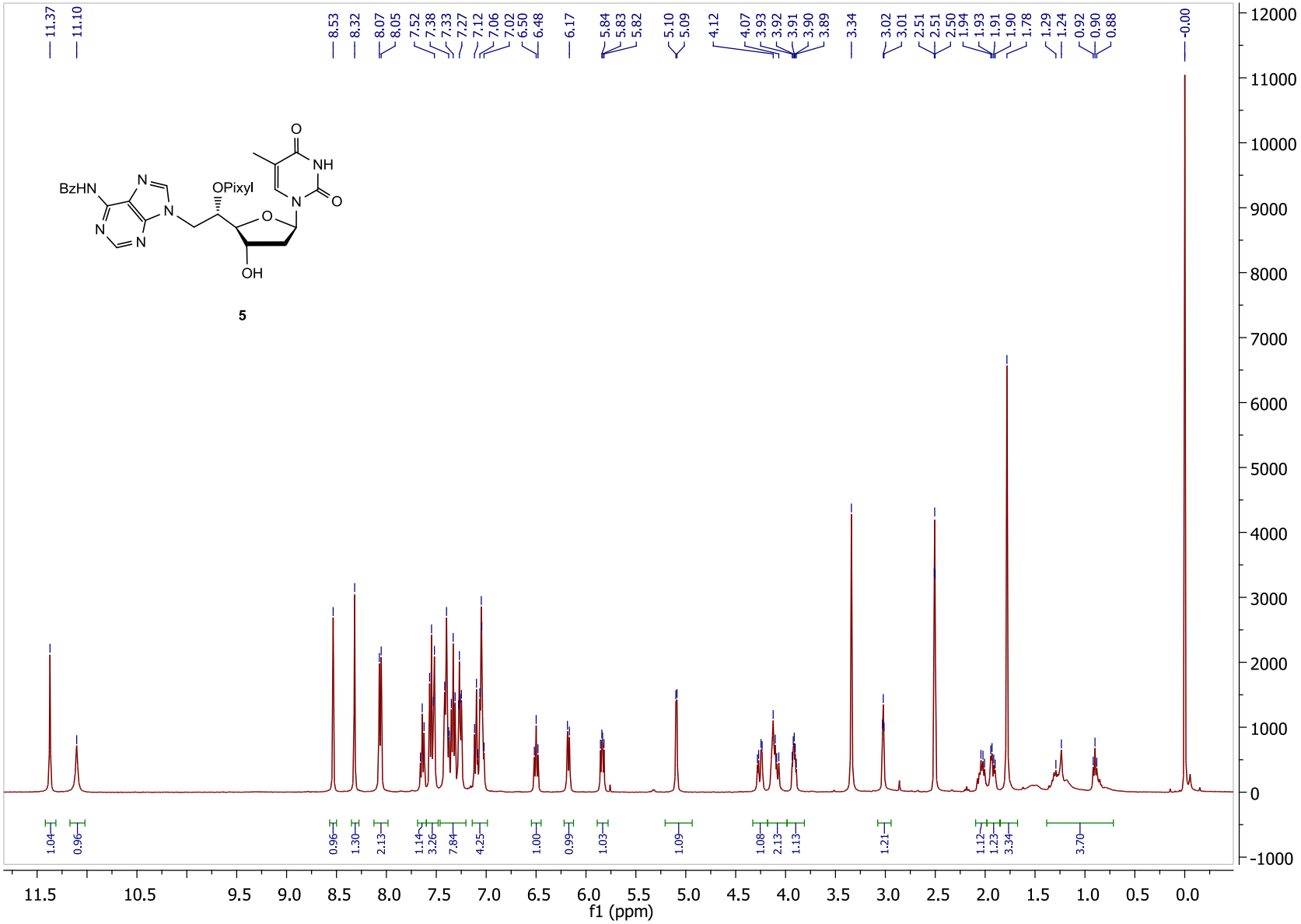

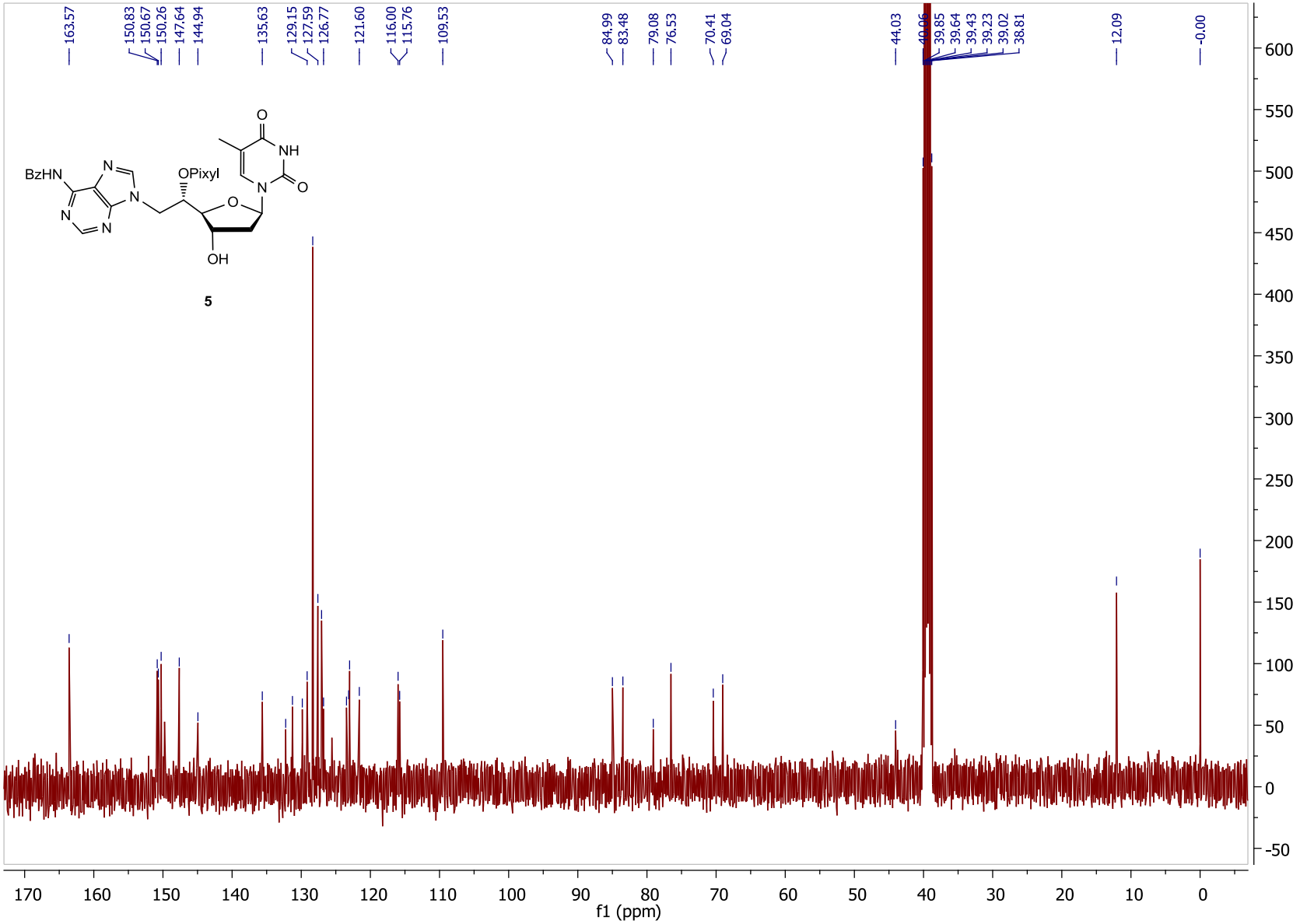

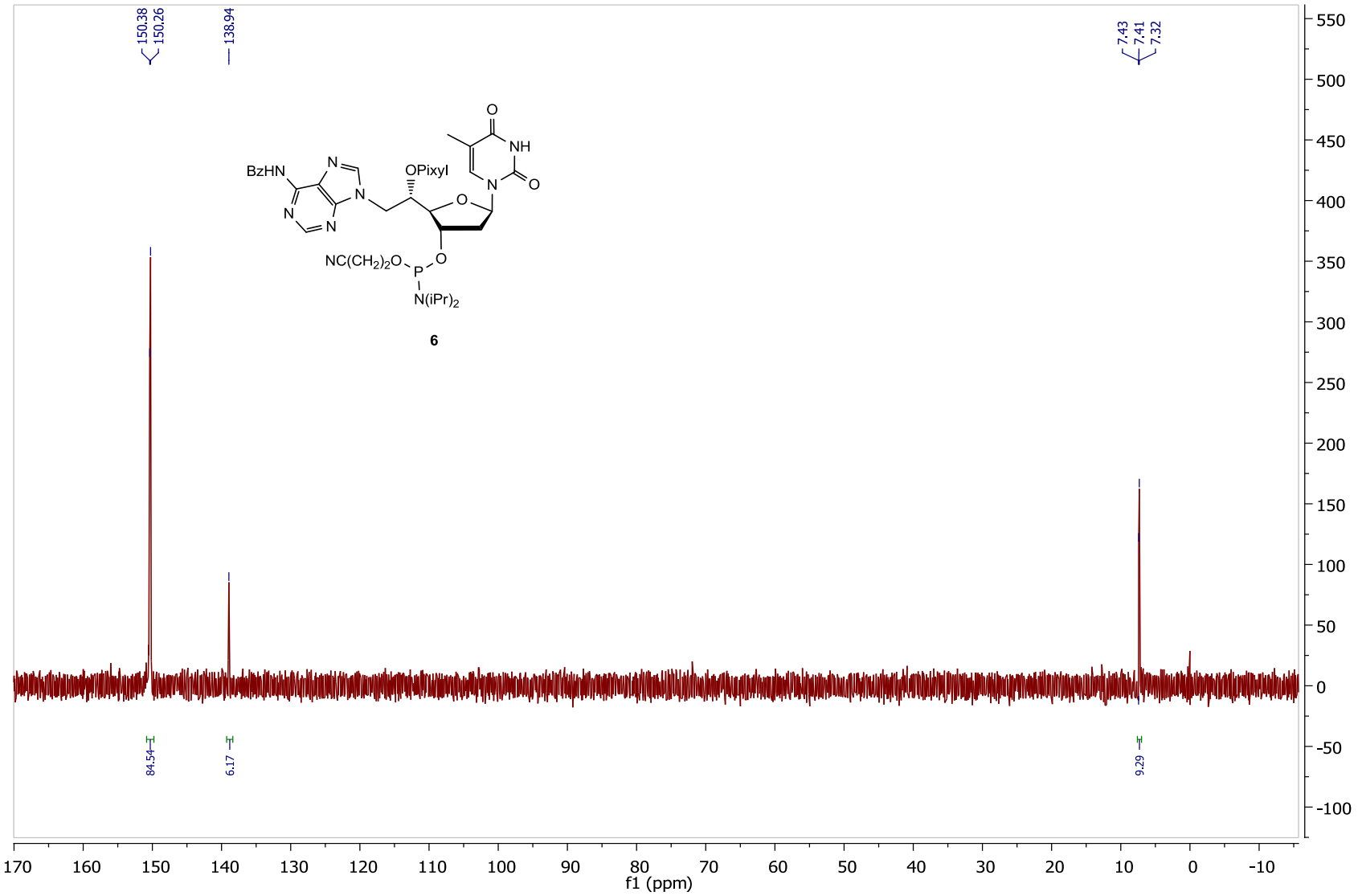

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