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Supporting Information

Contiguous Metal-Mediated Base Pairs Comprising Two Ag^{I} Ions

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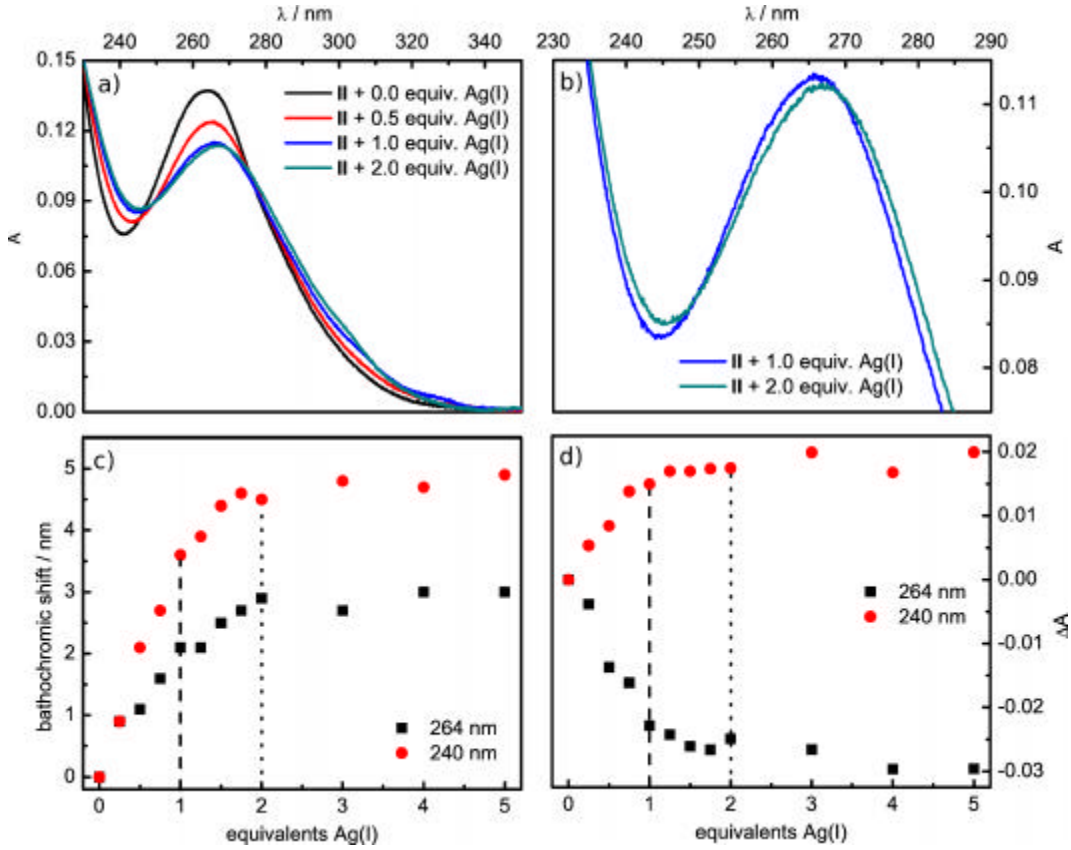

Figure S1. a) UV spectra of **II** in the presence of various amounts of $AgNO_3$; b) enlarged cutout of the UV spectra of **II** in the presence of one and two equivalents of $AgNO_3$; c) bathochromic shifts of the absorption minimum (originally at 240 nm) and maximum (originally at 264 nm) of **II**; d) changes of absorption at 240 and 264 nm, respectively, upon the addition of $AgNO_3$. In Figures S1c and S1d, one and two equivalents of Ag^+ per base pair are marked by broken and dotted lines, respectively. Conditions: 1 µM oligonucleotide, 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8).

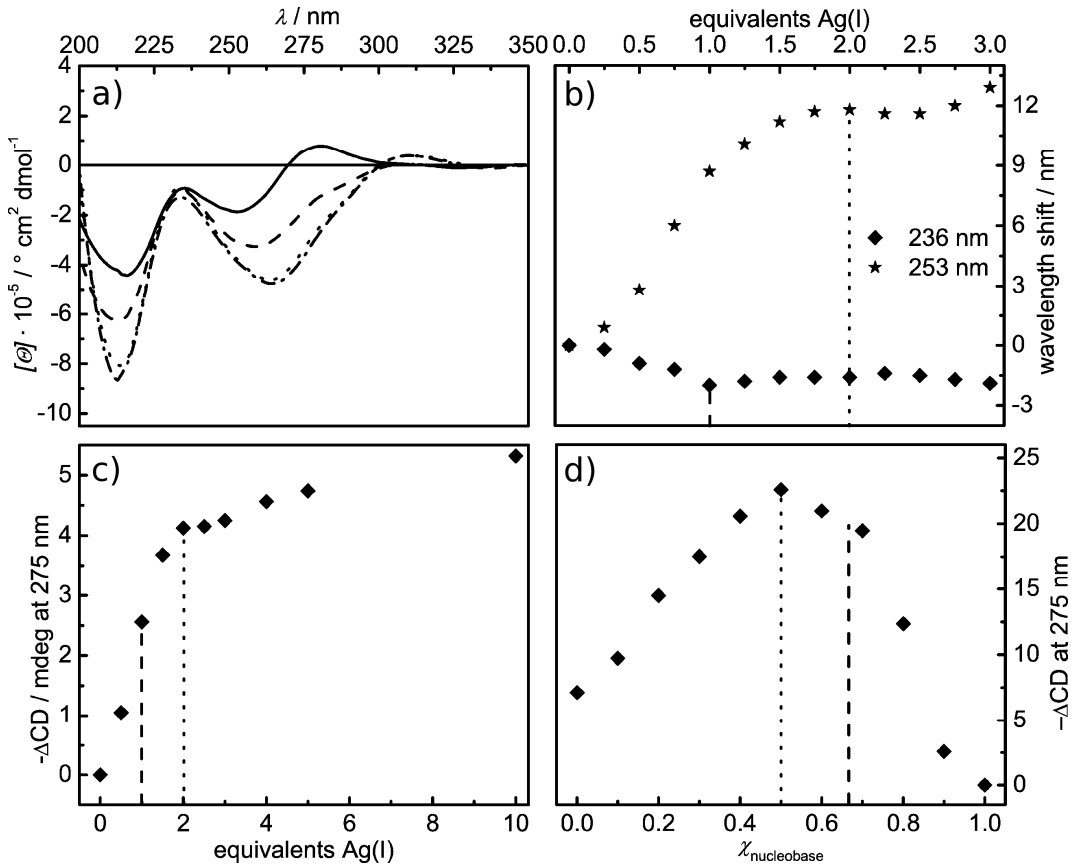

Figure S2. a) CD spectra of **II** in the presence of various amounts of $AgNO_3$ (0 equiv.: —; 1 equiv.: – – –; 2 equiv.: · · ·; 3 equiv.: – · – ·); b) wavelength shifts of the minimum (253 nm) and maximum (236 nm) upon the addition of Ag^+; c) change of the CD at 275 nm upon the addition of Ag^+; d) Job plot based on the CD signal at 275 nm. It is interesting to note that this Job plot has two points of discontinuity, corresponding to the incorporation of one and two Ag^+ ions per base pair. In good agreement with all other experiments, this shows that in oligonucleotide sequence **II** the singly and doubly metalated base pairs are of similar stability, hence that the second Ag^+ ion is weakly bound. In Figures 2b–d, one and two equivalents of Ag^+ per base pair are marked by broken and dotted lines, respectively. Conditions: 1 μM oligonucleotide (Job plot: 0.83 – 8.3 μM), 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8).

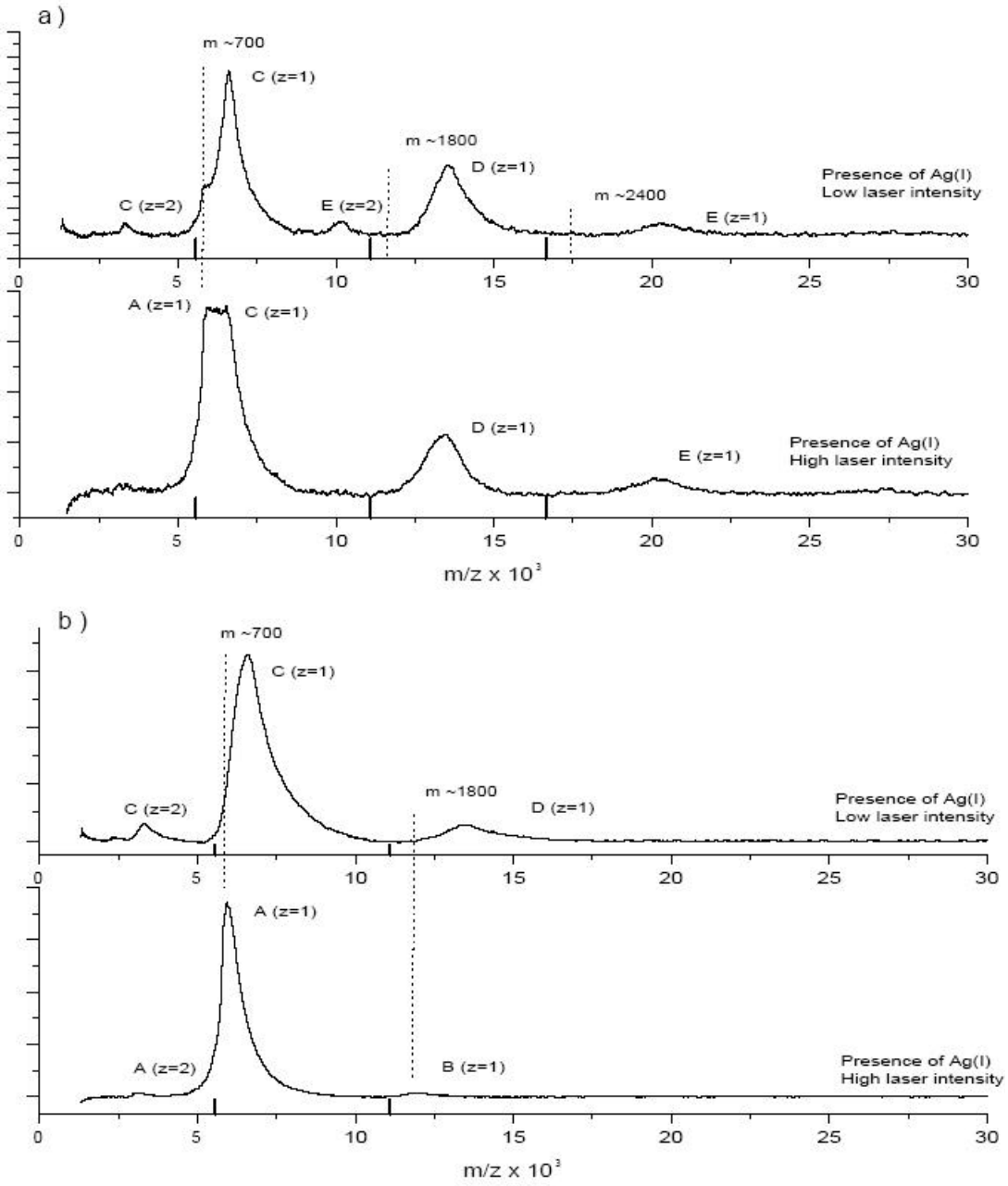

Figure S3. LILBID mass spectra of a) **I** and b) **II** recorded with low (upper panel) and higher laser intensity (i.e. under harsher conditions, lower panel). Black bars indicate the mass of the single strand and the resulting masses of hypothetical dimeric and trimeric aggregates, respectively. Dotted lines represent the peak maxima of the non-metalated species used to determine the metal-induced mass shift. Peak assignment: **A**, non-metalated single strand; **B**, non-metalated duplex or two non-metalated single strands; **C**, single strand with 6 – 7 Ag^+; **D**, duplex with ~17 Ag^+; **E**, aggregate of unknown structure comprising three single strands and 22 Ag^+.

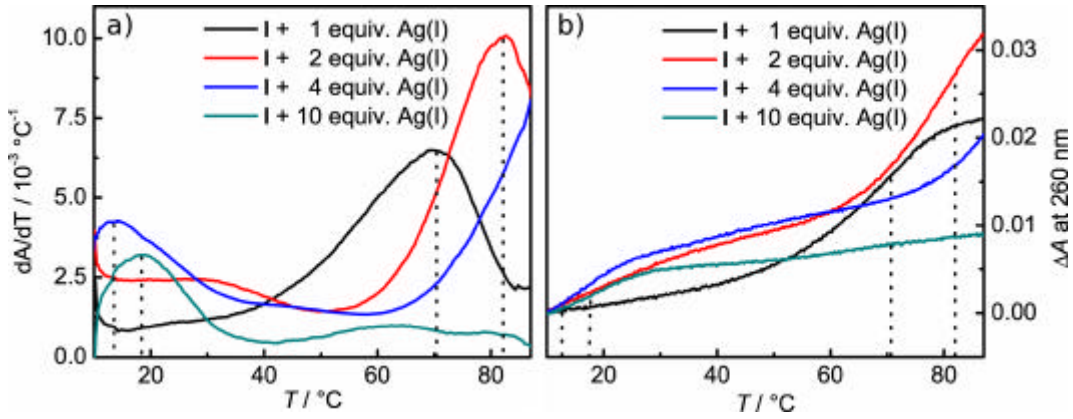

Figure S4. a) First derivatives of the UV melting curves of oligonucleotide **I** as shown in (b) in the presence of different equivalents of $AgNO_3$. The respective melting temperatures are indicated by dotted lines. The plots show two facts: 1) The duplex melting temperature increases significantly with increasing amounts of Ag^+. 2) In the presence of a large excess of Ag^+, a new melting transition emerges at a low temperature. This transition might be attributed to a higher-order aggregate, in agreement with peak **E** in the mass spectrum of **I** (Figures 4 and S3). Conditions: 1 μM oligonucleotide, 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8).

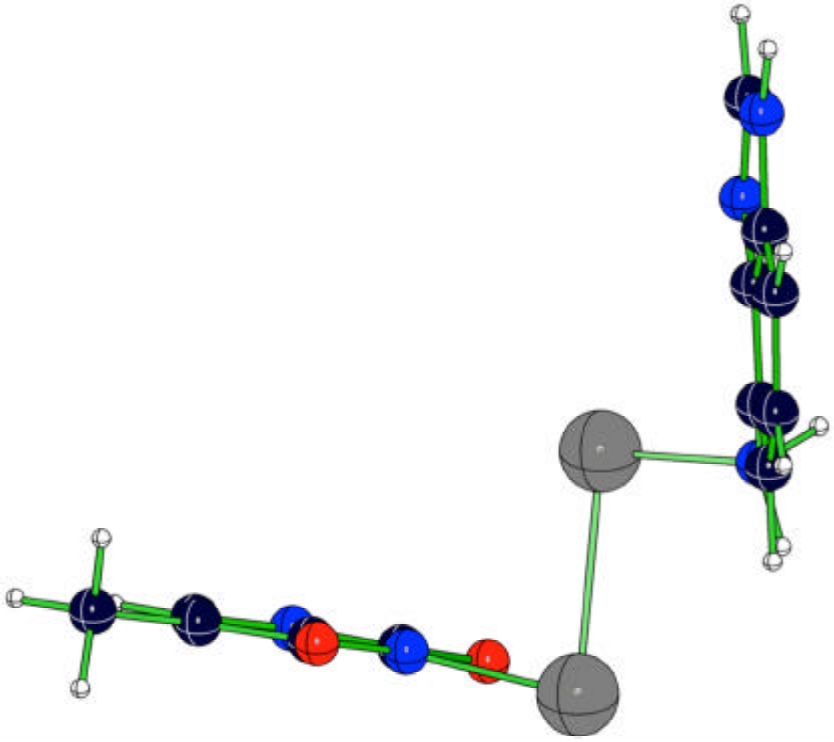

Figure S5. Base pair **bp3***.

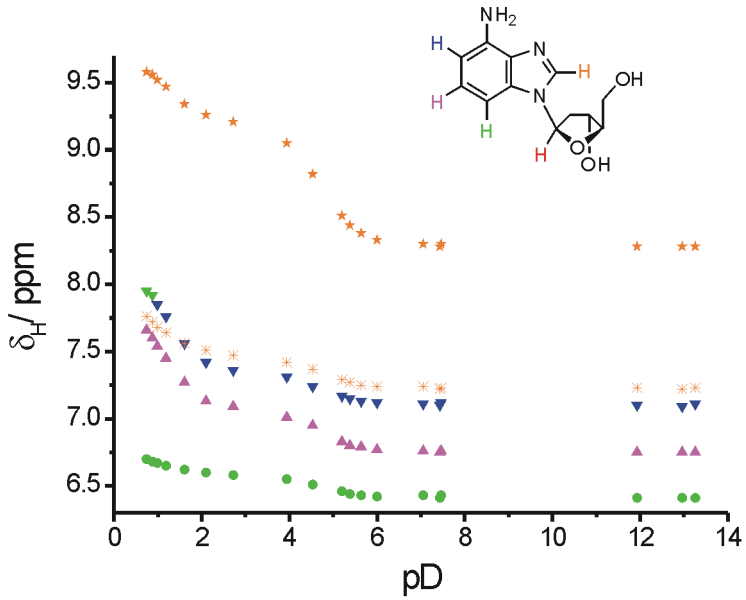

Figure S6. Plot of the chemical shifts of the aromatic protons and H1' of 1,3-dideaza-2'-deoxy-adenosine **5** at different pD values. The pD values were obtained by adding 0.4 to the pH meter reading.[1] The pK_a values in H_2O (4.12 ± 0.03 and 0.8 ± 0.2, see publication) were calculated from the pK_a* values in D_2O as obtained of the above figure according to pK_a* = 1.015 pK_a + 0.45.[2]

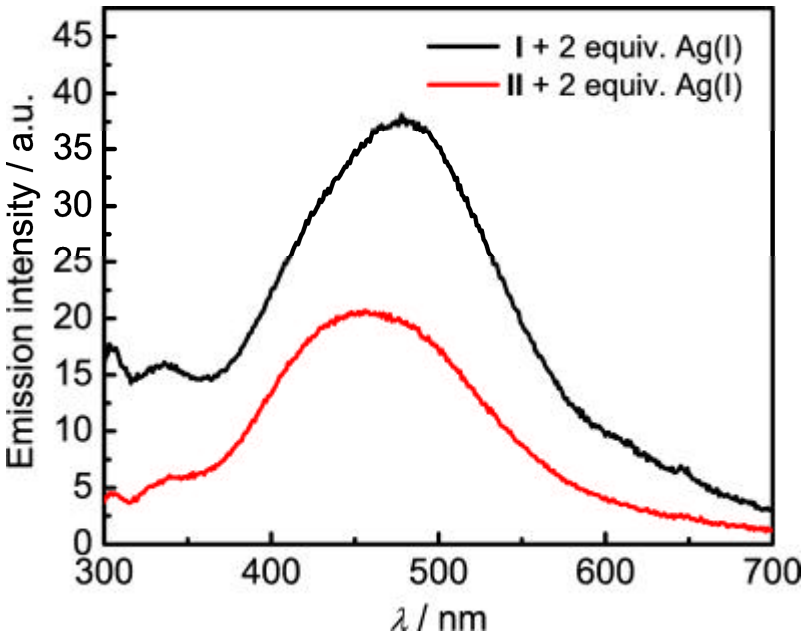

Figure S7. Fluorescence spectra of oligonucleotides **I** and **II**, respectively, in the presence of 2 equiv. of Ag^+ upon irradiation at 270 nm. Oligonucleotide **I** shows a maximum emission at 475 nm (fluorescence life times: t_1 = 1.03(1) ns (48.95%); t_2 = 5.49(5) ns (51.05%)). Oligonucleotide **II** shows a maximum emission at 454 nm (fluorescence life times: t_1 = 1.37(3) ns (48.45%); t_2 = 5.65(5) ns (51.55%)). Conditions: 10 μM oligonucleotide, 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8).

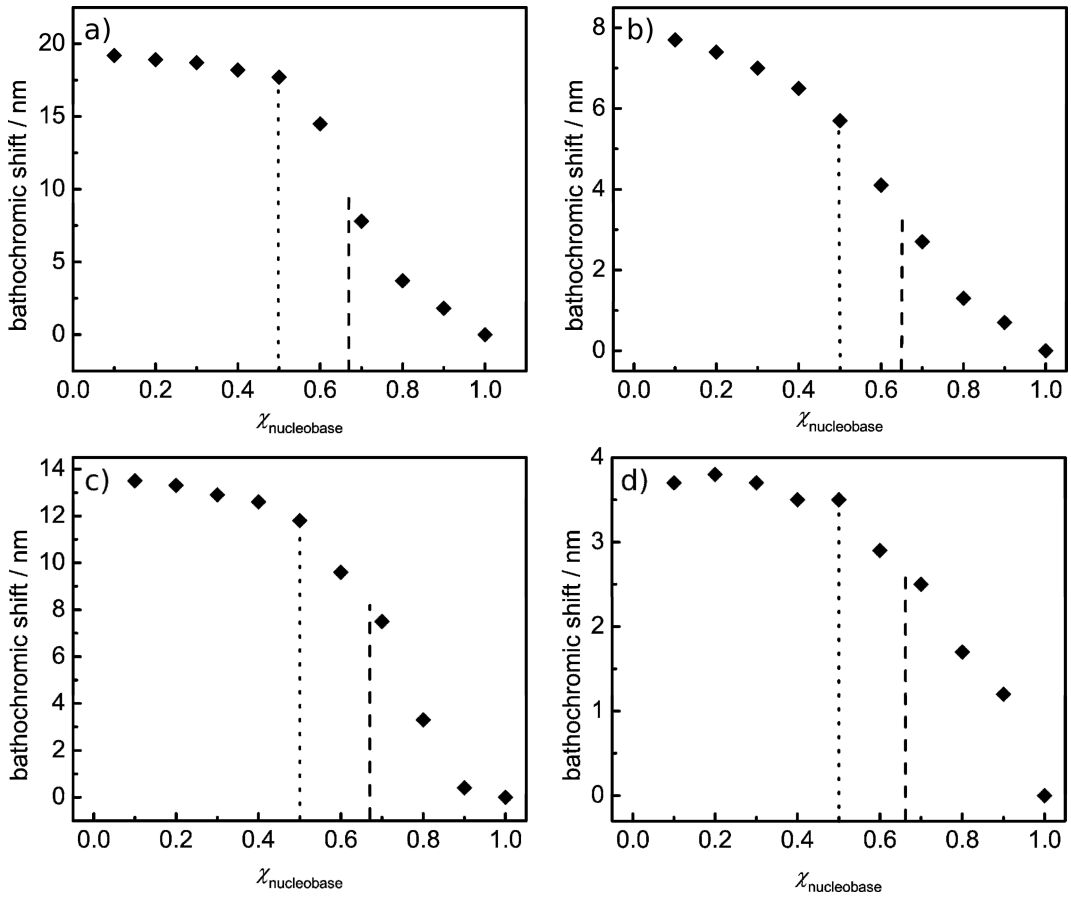

Figure S8. Job plots based on the bathochromic shift of a minimum or maximum in the respective spectrum upon the addition of Ag^+. One and two equivalents of Ag^+ per base pair are marked by broken and dotted lines, respectively. In all four Job plots, a distinct change of slope is observed at $c_{nucleobase} = 0.5$, indicating a 1:1 stoichiometry between nucleobases and Ag^+ ions, thereby proving the binding of two Ag^+ ions per base pair. a) Based on the CD spectrum of oligonucleotide **I**, minimum originally at 252 nm; b) based on the UV spectrum of oligonucleotide **I**, maximum originally at 264 nm; c) based on the CD spectrum of oligonucleotide **II**, minimum originally at 253 nm; d) based on the UV spectrum of oligonucleotide **II**, maximum originally at 262 nm. Conditions: 0.83 – 8.3 μM oligonucleotide, 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8).

Table S1. Cartesian coordinates (in a.u.) of stationary points optimized at ZORA-BLYP-D/TZ2P.

bp1 (gas phase)

N	-2.548527	-0.333874	0.038000
C	-3.236007	-1.532885	0.017286
N	-4.627469	-1.376473	-0.046485
C	-5.256701	-0.144743	-0.093481
C	-4.564195	1.022725	-0.081563
C	-3.096880	0.954586	-0.015790
O	-2.358667	1.950789	-0.006202
O	-2.703214	-2.642390	0.050137
C	-5.218169	2.379447	-0.132856
H	-1.490762	-0.410940	0.084060
H	-5.162388	-2.236733	-0.062110
H	-6.341623	-0.177732	-0.141231
H	-4.943176	2.971202	0.750611
H	-6.310352	2.286909	-0.178262
H	-4.867418	2.941390	-1.008920
C	2.977233	1.748590	0.058673
C	4.033095	0.823310	-0.058725
C	3.820526	-0.559081	-0.109250
C	2.479350	-0.962740	-0.038836
C	1.401451	-0.054950	0.075039
C	1.628175	1.342920	0.133201
N	1.870067	-2.218117	-0.066027
C	0.510318	-2.028536	0.024618
N	0.194358	-0.751436	0.110854
N	0.586969	2.229145	0.296190
H	5.050512	1.203182	-0.111657
H	2.339809	-3.110391	-0.140886
H	-0.211640	-2.835694	0.019651
H	-0.380215	1.935806	0.147065
H	0.775391	3.206599	0.117372
H	4.640827	-1.265452	-0.199552
H	3.201890	2.813115	0.100204

bp1 (COSMO)

N	-2.573900	-0.348300	0.105100
C	-3.287100	-1.530700	0.090100
N	-4.654200	-1.363000	-0.054400
C	-5.257400	-0.131000	-0.184600
C	-4.546400	1.030100	-0.176600
C	-3.100100	0.940200	-0.021100
O	-2.329900	1.926800	0.004600
O	-2.753800	-2.647700	0.196500
C	-5.188300	2.386800	-0.322200
H	-1.527600	-0.440500	0.192200
H	-5.218500	-2.206400	-0.067100
H	-6.335900	-0.154700	-0.293700
H	-4.968600	3.015800	0.551200
H	-6.274700	2.288800	-0.426000
H	-4.792100	2.910500	-1.203000

C	2.966400	1.763800	0.081700
C	4.020900	0.858600	-0.174300
C	3.813500	-0.521100	-0.288300
C	2.485100	-0.948900	-0.132500
C	1.411600	-0.061500	0.124800
C	1.634500	1.332100	0.242200
N	1.892500	-2.206000	-0.182400
C	0.551700	-2.046100	0.033400
N	0.216200	-0.778500	0.224800
N	0.594100	2.201200	0.557100
H	5.027100	1.254100	-0.288400
H	2.363200	-3.087400	-0.349900
H	-0.144700	-2.873600	0.037600
H	-0.356200	1.904800	0.317900
H	0.770900	3.177900	0.341500
H	4.625400	-1.214700	-0.485500
H	3.179400	2.828100	0.161000

bp2 (gas phase)

N	-3.231325	-0.374974	-0.018411
C	-4.232855	-1.320714	-0.078820
N	-5.546663	-0.808292	-0.063004
C	-5.833310	0.538838	0.010019
C	-4.848389	1.470676	0.071421
C	-3.454868	0.997808	0.056845
O	-2.489157	1.795352	0.110226
O	-4.039661	-2.540160	-0.142888
C	-5.112274	2.952596	0.152658
Ag	-1.215135	-0.961477	-0.028803
H	-6.285321	-1.499865	-0.107425
H	-6.888755	0.798878	0.014925
H	-4.663669	3.374456	1.062537
H	-6.190285	3.159940	0.154314
H	-4.647332	3.473734	-0.695465
C	2.838798	2.072466	-0.034285
C	4.112868	1.492919	0.068976
C	4.299483	0.109176	0.149579
C	3.124858	-0.650251	0.120263
C	1.825264	-0.096991	0.017543
C	1.644232	1.313466	-0.067814
N	2.924156	-2.029625	0.175469
C	1.582090	-2.270525	0.108615
N	0.889269	-1.145308	0.013413
N	0.429219	1.927070	-0.216681
H	4.980182	2.147528	0.088270
H	3.645297	-2.734587	0.250190
H	1.156288	-3.262995	0.133118
H	-0.481841	1.494130	-0.048838
H	0.413020	2.937196	-0.163930
H	5.283640	-0.342589	0.229834
H	2.751532	3.155726	-0.095240

bp2 (COSMO)

N	-3.261000	-0.356200	-0.025900

C	-4.238300	-1.312300	-0.138600
N	-5.557100	-0.864700	-0.114800
C	-5.896300	0.462000	0.015900
C	-4.943200	1.425600	0.130000
C	-3.542400	1.002300	0.108300
O	-2.593800	1.829000	0.207300
O	-3.993500	-2.537000	-0.258300
C	-5.275300	2.889700	0.278000
Ag	-1.205300	-0.904200	-0.036500
H	-6.282800	-1.568700	-0.197900
H	-6.959700	0.676500	0.020500
H	-4.864800	3.289000	1.216100
H	-6.361100	3.041900	0.272800
H	-4.829800	3.474900	-0.538400
C	2.943300	2.029600	-0.115100
C	4.201400	1.417200	0.059900
C	4.339000	0.034200	0.211200
C	3.144700	-0.698500	0.179400
C	1.868600	-0.108800	0.005500
C	1.740500	1.295000	-0.154300
N	2.899800	-2.061800	0.294100
C	1.562600	-2.266400	0.194700
N	0.899200	-1.125400	0.020500
N	0.524200	1.923800	-0.410900
H	5.087400	2.046100	0.079600
H	3.593900	-2.787800	0.425900
H	1.111500	-3.245000	0.253700
H	-0.332200	1.498800	-0.055600
H	0.534100	2.929500	-0.266100
H	5.303300	-0.445500	0.346400
H	2.884700	3.110100	-0.229700

bp3 (gas phase)

N	-3.181343	-0.174559	0.032628
C	-3.996117	-1.296963	0.170941
N	-5.355064	-1.092377	-0.079891
C	-5.870510	0.116309	-0.481671
C	-5.077362	1.211795	-0.640887
C	-3.658914	1.047289	-0.352899
O	-2.891922	2.073502	-0.473896
O	-3.553309	-2.403593	0.489958
C	-5.606210	2.553442	-1.084230
Ag	-1.137543	-0.744941	0.324446
H	-6.941070	0.140784	-0.660937
H	-5.396624	3.321641	-0.328621
H	-6.688259	2.504967	-1.252480
H	-5.115703	2.874345	-2.012502
H	-5.952152	-1.906249	0.026411
C	3.311120	1.781927	0.006115
C	4.359199	1.100111	-0.649589
C	4.281736	-0.264301	-0.920765
C	3.097165	-0.905246	-0.543125
C	2.013349	-0.237065	0.077199

C	2.143068	1.128563	0.392181
N	2.680677	-2.229085	-0.657192
C	1.423482	-2.324057	-0.152104
N	0.973191	-1.153031	0.297165
N	1.104537	1.834481	1.125512
H	5.251622	1.652391	-0.926172
H	0.860438	-3.246916	-0.138994
Ag	-0.873381	2.106872	0.157467
H	5.098206	-0.798572	-1.397880
H	3.425228	2.839530	0.236108
H	0.863780	1.301964	1.967608
H	1.469688	2.736735	1.439719
H	3.217679	-2.997527	-1.042888

bp3* (gas phase)
[deformation w.r.t. **bp3**: 90° rotation of thymine around N3-Ag axis + 180° rotation of 1,3-dideazaadenine around Ag-N6 axis]

N	-1.83172	-2.59834	0.66380
C	-2.65858	-2.41114	-0.44256
N	-4.02441	-2.31134	-0.16678
C	-4.54533	-2.43200	1.09897
C	-3.74584	-2.63760	2.18205
C	-2.31135	-2.71057	1.93933
O	-1.53268	-2.88160	2.94950
O	-2.22105	-2.34099	-1.59414
C	-4.28137	-2.77909	3.58541
H	-5.62522	-2.35229	1.17837
H	-3.86030	-2.00569	4.24080
H	-5.37425	-2.69492	3.59142
H	-3.99684	-3.75015	4.01129
H	-4.62871	-2.16832	-0.96962
Ag	0.18746	-2.86275	0.00000
Ag	0.00000	0.00000	0.00000
C	3.70392	-0.31380	1.95474
C	4.43581	0.18252	3.05533
C	4.41595	1.53436	3.39197
C	3.60346	2.35739	2.60513
C	2.82595	1.87887	1.52235
C	2.91135	0.51927	1.16854
N	3.34495	3.72488	2.65181
C	2.45630	4.02315	1.66895
N	2.10716	2.94722	0.96441
N	2.21889	0.00000	0.00000
H	5.04285	-0.50588	3.63458
H	2.07342	5.02027	1.50163
H	5.00118	1.92509	4.21932
H	3.77615	-1.36920	1.69911
H	2.43703	0.58753	-0.81110
H	2.57070	-0.93721	-0.20972
H	3.74970	4.39183	3.29911

bp4 (gas phase)

N	-3.247335	-0.263614	-0.011502

C	-4.047094	-1.398030	-0.032705
N	-5.434197	-1.167839	-0.041613
C	-5.990712	0.090204	-0.030338
C	-5.212370	1.203579	-0.009569
C	-3.762462	1.007704	0.000223
O	-3.013910	2.041946	0.019655
O	-3.603872	-2.549830	-0.043531
C	-5.773251	2.603380	0.003531
Ag	-1.147716	-0.680447	0.001174
H	-6.014530	-1.998616	-0.057115
H	-7.076102	0.132873	-0.039006
H	-5.432369	3.147625	0.894432
H	-6.870252	2.582258	-0.005969
H	-5.417542	3.170080	-0.867349
C	3.555338	1.710157	0.070821
C	4.668439	0.866379	0.069449
C	4.543993	-0.528967	0.050832
C	3.227122	-0.996269	0.034022
C	2.066812	-0.174667	0.034705
C	2.195552	1.259611	0.053841
N	2.751604	-2.307459	0.013610
C	1.391007	-2.269559	0.002805
N	0.940519	-1.020721	0.014719
N	1.175156	2.157521	0.056718
H	5.659833	1.312883	0.083322
H	3.318989	-3.144206	0.007821
H	0.770277	-3.153262	-0.013423
Ag	-0.881744	2.094515	0.038355
H	1.552781	3.103092	0.071787
H	5.399399	-1.197823	0.049508
H	3.714218	2.787756	0.085721

bp4 (COSMO)

N	-3.267600	-0.267200	0.004200
C	-4.081900	-1.381600	0.031900
N	-5.452100	-1.160500	-0.041700
C	-6.004200	0.091100	-0.144300
C	-5.220000	1.203200	-0.175900
C	-3.780500	1.004900	-0.094100
O	-3.015600	2.034500	-0.116200
O	-3.634100	-2.546700	0.118900
C	-5.786800	2.597000	-0.288000
Ag	-1.149300	-0.682400	0.071500
H	-6.050600	-1.979900	-0.020300
H	-7.086500	0.128300	-0.196700
H	-5.488800	3.209100	0.574200
H	-6.881200	2.561800	-0.338100
H	-5.405000	3.101400	-1.186100
C	3.567200	1.718200	0.079800
C	4.680400	0.878900	-0.075700
C	4.551900	-0.512100	-0.180700
C	3.234700	-0.989500	-0.120600
C	2.081400	-0.173800	0.034600

C	2.213200	1.254700	0.155200
N	2.761300	-2.294700	-0.184900
C	1.411400	-2.264600	-0.077100
N	0.953900	-1.021100	0.056700
N	1.186100	2.132200	0.357600
H	5.669800	1.328500	-0.117200
H	3.323100	-3.130700	-0.293100
H	0.798700	-3.152700	-0.103000
Ag	-0.874900	2.092200	0.082100
H	1.557600	3.080500	0.417600
H	5.400400	-1.178600	-0.299200
H	3.721700	2.794100	0.155300

thymine (gas phase)

N	-2.556120	-0.384314	-0.007471
C	-3.286762	-1.570286	-0.025581
N	-4.667674	-1.344634	-0.039560
C	-5.245871	-0.085154	-0.035643
C	-4.513626	1.056918	-0.017939
C	-3.045894	0.949699	-0.002268
O	-2.263413	1.896323	0.014225
O	-2.790783	-2.689459	-0.029113
C	-5.121410	2.435824	-0.013500
H	-1.544129	-0.490778	0.003218
H	-5.241154	-2.179660	-0.052944
H	-6.332104	-0.076523	-0.047865
H	-4.797514	2.994147	0.874813
H	-6.216715	2.380830	-0.025007
H	-4.779753	3.007740	-0.886404

thymine (COSMO)

N	-2.560980	-0.382247	-0.006074
C	-3.300404	-1.554604	-0.025675
N	-4.665330	-1.341079	-0.039434
C	-5.241714	-0.088484	-0.035257
C	-4.505340	1.056062	-0.016913
C	-3.052552	0.937538	-0.002185
O	-2.252470	1.890879	0.013467
O	-2.786597	-2.682297	-0.029924
C	-5.126456	2.429768	-0.014119
H	-1.548945	-0.493952	0.004148
H	-5.253853	-2.167569	-0.054330
H	-6.325678	-0.082622	-0.049396
H	-4.817729	2.992958	0.876974
H	-6.219493	2.356151	-0.027380
H	-4.797202	3.005448	-0.889763

thyminate (gas phase)

N	-2.477333	-0.387800	-0.006766
C	-3.242639	-1.502531	-0.024548
N	-4.679102	-1.328172	-0.039641
C	-5.274771	-0.087196	-0.036024
C	-4.515192	1.035981	-0.018098

C	-3.024858	0.878062	-0.002645
O	-2.313674	1.915896	0.013783
O	-2.841206	-2.689031	-0.029525
C	-5.107053	2.422525	-0.013304
H	-5.225586	-2.180543	-0.052596
H	-6.365745	-0.068000	-0.048205
H	-4.775379	2.984468	0.873083
H	-6.208738	2.384642	-0.025556
H	-4.756372	2.998724	-0.883081

thyminate (COSMO)

N	-2.495600	-0.387156	-0.006366
C	-3.277777	-1.496823	-0.024921
N	-4.671315	-1.329889	-0.039060
C	-5.263828	-0.088835	-0.035695
C	-4.509031	1.043081	-0.017954
C	-3.045948	0.878343	-0.002634
O	-2.283208	1.896807	0.013870
O	-2.818364	-2.677184	-0.029900
C	-5.120495	2.423235	-0.013935
H	-5.243887	-2.167489	-0.052608
H	-6.349141	-0.081069	-0.048162
H	-4.808542	2.988473	0.875896
H	-6.216127	2.362218	-0.026791
H	-4.788647	3.002234	-0.887548

silver(I) thyminate (gas phase)

N	-2.605504	-0.431484	-0.008210
C	-3.381512	-1.571060	-0.026494
N	-4.769535	-1.333835	-0.040610
C	-5.321823	-0.068081	-0.036649
C	-4.553320	1.049961	-0.018606
C	-3.086993	0.879839	-0.003051
O	-2.297189	1.841753	0.013941
O	-2.934466	-2.722390	-0.030742
C	-5.117418	2.447798	-0.013645
Ag	-0.479463	-0.581430	0.015120
H	-5.354695	-2.160683	-0.054163
H	-6.407863	-0.029539	-0.048899
H	-4.778344	2.996440	0.875454
H	-6.214712	2.426578	-0.026613
H	-4.757805	3.010976	-0.885410

silver(I) thyminate (COSMO)

N	-2.610558	-0.392473	-0.011169
C	-3.393428	-1.518021	-0.027909
N	-4.772231	-1.318203	-0.039528
C	-5.347706	-0.068858	-0.034739
C	-4.587625	1.058732	-0.018347
C	-3.130727	0.897685	-0.005872
O	-2.349717	1.887286	0.009847
O	-2.928898	-2.683649	-0.032634
C	-5.184362	2.444365	-0.012295

Ag	-0.448389	-0.609394	0.016247
H	-5.357219	-2.147016	-0.052499
H	-6.432291	-0.051764	-0.045211
H	-4.863557	3.003287	0.877833
H	-6.279617	2.392432	-0.022657
H	-4.847550	3.017983	-0.886986

1,3-dideazaadenine (gas phase)

C	2.909868	1.787509	0.050679
C	4.001675	0.892566	0.039008
C	3.833952	-0.495944	0.029937
C	2.505290	-0.947347	0.028746
C	1.393706	-0.072347	0.037134
C	1.582192	1.328396	0.053528
N	1.933242	-2.216648	0.002101
C	0.558662	-2.047911	-0.009754
N	0.193821	-0.784403	0.009397
N	0.476358	2.176218	0.118997
H	5.008383	1.302997	0.037269
H	2.427527	-3.098889	-0.013408
H	-0.111748	-2.898210	-0.033095
H	-0.401880	1.736911	-0.140930
H	0.604211	3.103636	-0.269575
H	4.682767	-1.174426	0.020200
H	3.097377	2.859733	0.065086

1,3-dideazaadenine (COSMO)

C	2.908447	1.787571	0.053062
C	4.001880	0.890830	0.044083
C	3.830140	-0.498116	0.028433
C	2.499263	-0.947255	0.022060
C	1.385990	-0.070367	0.033370
C	1.577628	1.331739	0.050444
N	1.935770	-2.216362	-0.001306
C	0.572163	-2.065866	-0.004462
N	0.189314	-0.797182	0.016271
N	0.480809	2.197904	0.120786
H	5.008841	1.300420	0.045947
H	2.434479	-3.098131	-0.016558
H	-0.088555	-2.922414	-0.021715
H	-0.385582	1.807240	-0.240648
H	0.655330	3.136066	-0.228632
H	4.672126	-1.184022	0.018481
H	3.092751	2.859981	0.062882

1,3-dideazaadenine silver(I) (gas phase)

C	2.602876	1.753227	0.149531
C	3.795170	0.990717	0.118029
C	3.784212	-0.403481	0.035597
C	2.526980	-1.015748	-0.014740
C	1.331482	-0.266339	0.015926
C	1.356358	1.133767	0.098811
N	2.101128	-2.342112	-0.097916

C	0.735364	-2.350677	-0.113886
N	0.234546	-1.125610	-0.047285
N	0.076975	1.851780	0.126613
H	4.747141	1.510645	0.159482
H	2.692119	-3.164991	-0.139538
H	0.158652	-3.263443	-0.174305
H	0.010120	2.500848	-0.659869
H	-0.008739	2.403574	0.982458
H	4.708132	-0.974422	0.012311
H	2.664041	2.837242	0.214221
Ag	-1.619325	0.145096	0.006372

1,3-dideazaadenine silver(I) (COSMO)

C	2.952700	1.786700	0.115500
C	4.030300	0.879300	0.223300
C	3.846600	-0.505700	0.169500
C	2.520800	-0.937500	0.022200
C	1.426100	-0.047200	-0.069600
C	1.625600	1.352000	-0.043400
N	1.955600	-2.205900	-0.050500
C	0.610200	-2.069400	-0.163900
N	0.243700	-0.788600	-0.181200
N	0.543000	2.239400	-0.113300
H	5.034700	1.277300	0.339400
H	2.452400	-3.088600	-0.022700
H	-0.062200	-2.911400	-0.225500
H	-0.193300	1.954500	-0.755500
H	0.815800	3.203700	-0.287800
H	4.674300	-1.204600	0.238700
H	3.146200	2.856900	0.143700
Ag	-1.782600	-0.073400	0.083800

Synthesis and characterization of 1,3-dideaza-2´-deoxyadenosine (5)

To a solution of 1,3-dideaza-6-nitropurine-*N9*-*b*-2´-deoxyribonucleoside **4** (1.690 g, 6.052 mmol) in methanol (200 mL), hydrazine hydrate (30 mL) and activated Raney nickel (5 g) were added. The resulting suspension was stirred for 16 hours at ambient temperature. The catalyst was filtered off, and the resulting colorless solution evaporated to dryness. The crude product was purified by column chromatography (SiO_2, $CHCl_3$ (4) : MeOH (1)) yielding **5** (R_f 0.4) as a colorless solid (1.111 g, 4.458 mmol, 74%). The spectroscopic data agree well with previously published data of **5** obtained via a different synthetic route.[3]

NMR: ^{1}H NMR (500 MHz, DMSO-d_6): δ / ppm = 8.22 (s, 1H, H8); 6.93 (dd, 1H, H2); 6.78 (d, 1H, H3); 6.39 (d, 1H, H1); 6.23 (dd, 1H, H1´); 5.34 (d, 1H, 3´-OH); 5.27 (s, 2H, NH_2); 4.95 (t, 1H, 5´-OH); 4.36 (m, 1H, H3´); 3.84 (m, 1H, H4´); 3.54 (m, 2H, H5´, H5´´); 2.56 (m, 1H, H2´); 2.26 (m, 1H, H2´´). ^{13}C NMR (126 MHz, DMSO-d_6): δ / ppm = 140.3 (C6); 138.9 (C8); 133.5 (C4); 132.2 (C5); 123.7 (C2); 104.7 (C1); 87.3 (C4´); 84.3 (C1´); 70.5 (C3´); 61.6 (C5´); 39.4 (C2´). **Elemental analysis:** calcd (%) for $C_{12}H_{15}N_3O_3$: C 57.8, H 6.1, N 16.9; found: C 57.6, H 6.7, N 16.8. **Mass spectrometry:** MALDI-TOF (pos., DHB): calcd for $C_{12}H_{16}N_3O_3$ $(MH)^+$: 250, found: 250.

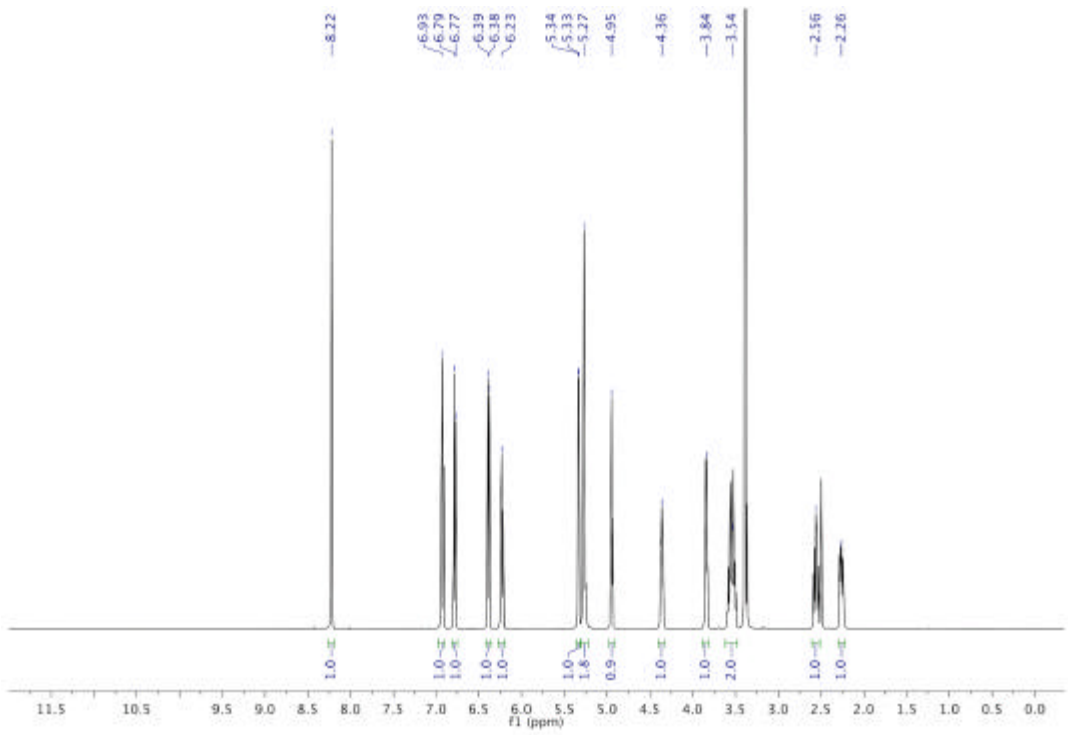

Figure: ^{1}H NMR spectrum of compound **5** (500 MHz, DMSO-d_6).

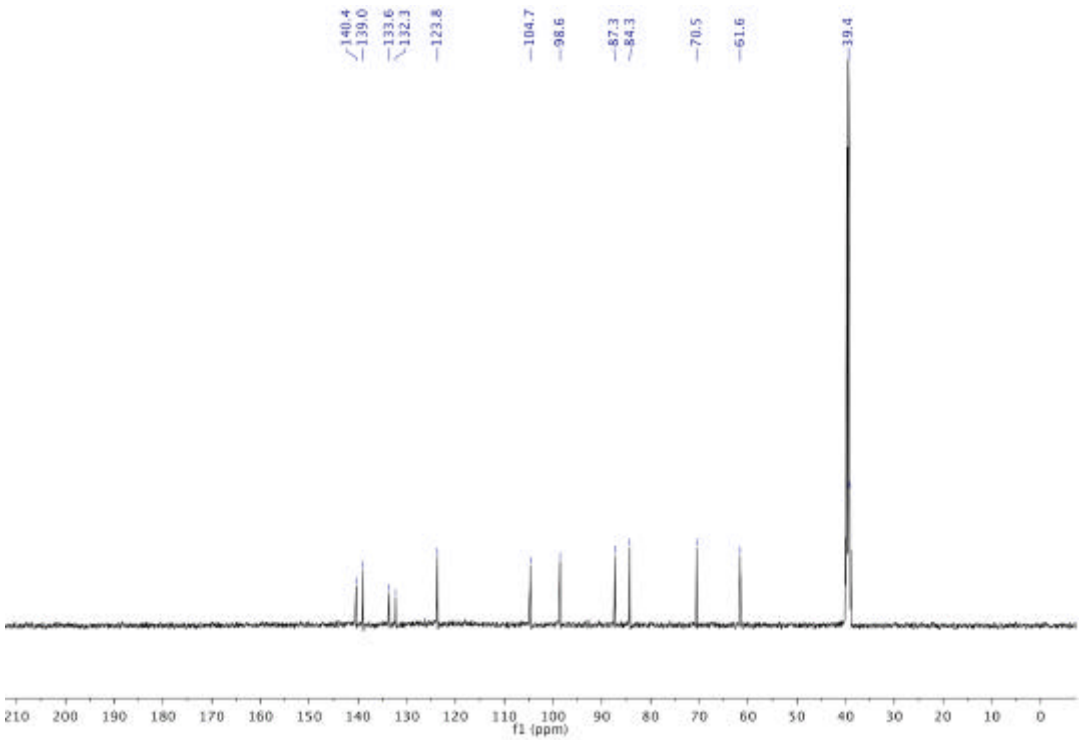

Figure: ^{13}C NMR spectrum of compound **5** (126 MHz, DMSO-d_6).

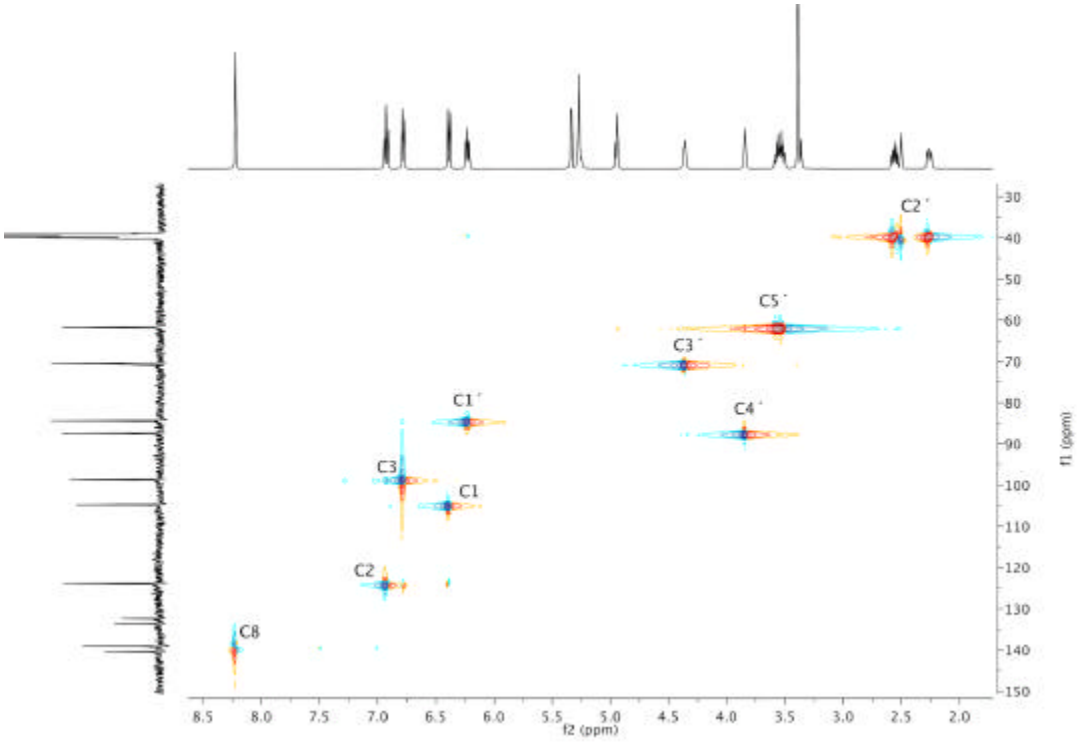

Figure: ^{1}H, ^{13}C HSQC NMR spectrum of compound **5** (DMSO-d_6), indicating that the C2' carbon signal is superimposed on the solvent signal.

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