Binding of an Organo-osmium (II) Anticancer Complex to Guanine and Cytosine on DNA Revealed by Electron-based Dissociations in High Resolution Top-Down FT-ICR Mass Spectrometry

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Supporting Information

Tables S1-S5

Figure S1

Figure S2

Table S1. Fragment assignments for Figure 2A: CAD MS/MS of the [**DNA12**-7H]$^{7-}$ species. Highlighted species (red) were used for internal calibration.

Assignment	Observed m/z	Exact mass/ m/z	Mass error/ppm
[w3]3-	307.04607	307.046068	0.01
[w2]2-	316.54956	316.549554	0.02
[w1]1-	330.06062	330.060346	0.83
[w4]3-	411.39860	411.398603	-0.01
[w7]5-	430.66642	430.666187	0.54
[w6]4-	460.32002	460.320152	-0.29
[w3]2-	461.07251	461.072740	-0.50
[w8]5-	493.27759	493.277708	-0.24
[w5]3-	512.74725	512.747282	-0.06
[DNA12-7H]7-	519.22994	519.230058	-0.23
[w7]4-	538.58456	538.584553	0.01
[a2]1-	536.12963	536.130584	-1.78
[a4]2-	584.11046	584.110931	-0.81
[a8]4-	600.10311	600.103648	-0.90
[w6]3-	614.09573	614.095961	-0.38
[w4]2-	617.60162	617.601542	0.13
[w10]5-	619.89740	619.897419	-0.03
[w8]4-	616.84874	616.848954	-0.35
[a9-BH]4-	644.60404	644.604562	-0.81
[w2]1-	634.10696	634.106383	0.91
[y11]5-	666.51578	666.515674	0.16
[w9]4-	692.86094	692.860463	0.69
[a7]3-	699.12472	699.125277	-0.80
[w7]3-	718.44837	718.448496	-0.17
[a5]2-	740.63912	740.639733	-0.83
[a10-BH]4-	722.86938	722.868963	0.58
[w5]2-	769.62440	769.624561	-0.21
[w10]4-	775.12451	775.123593	1.18
[a8]3-	800.47396	800.473956	0.005
[a6-B]2-	829.64287	829.641559	1.58
[a3]1-	865.18203	865.183104	-1.24
[a6]2-	897.16734	897.168536	-1.33
[w6]2-	921.64754	921.647579	-0.04
[w3]1-	923.15106	923.152755	-1.84
[d3]1-	963.15877	963.158902	-0.14
[a7-B]2-	986.16924	986.170361	-1.14
[a7]2-	1049.19067	1049.191554	-0.84
[w7]2-	1078.17740	1078.176382	0.94
[a8-B]2-	1138.19271	1138.193380	-0.59
[a4]1-	1169.22763	1169.229141	-1.29
[w4]1-	1236.21034	1236.210360	-0.02

[DNA12-7H]$^{7-}$ CAD 8V

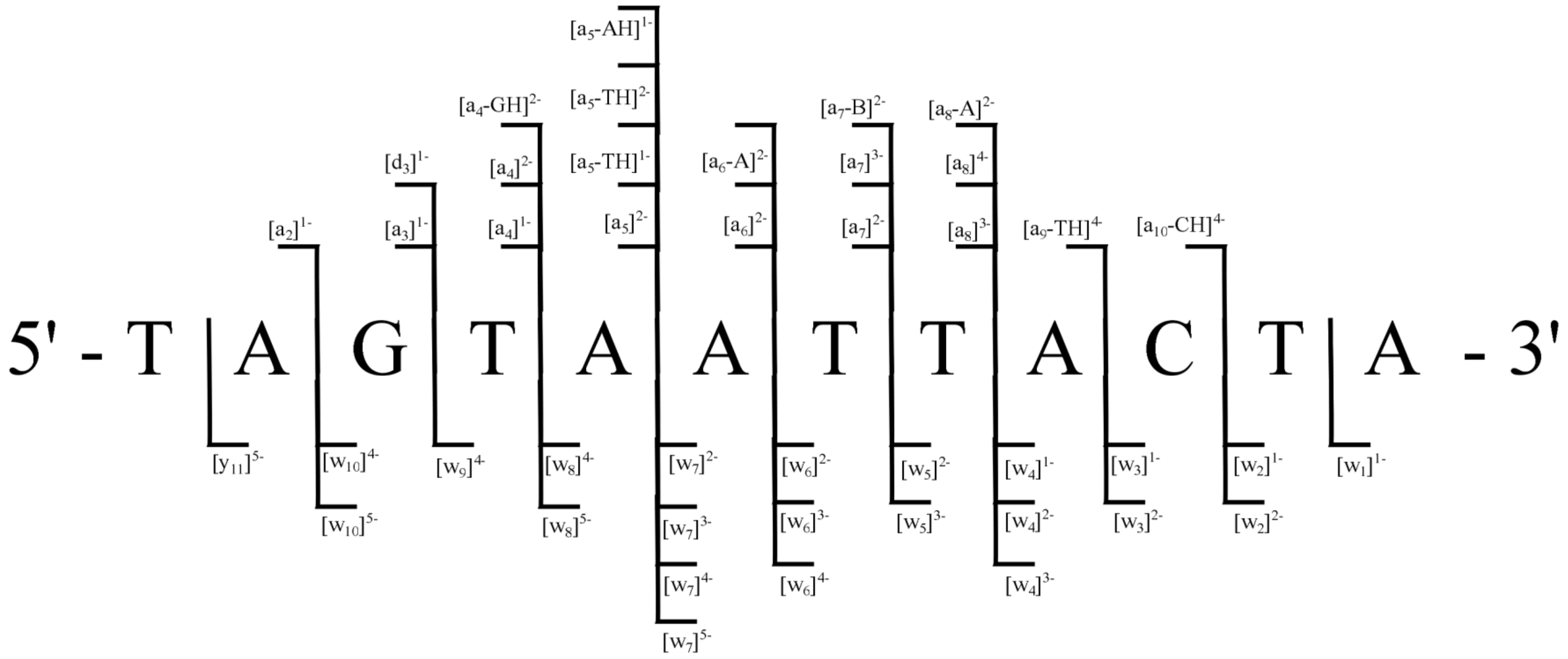


Table S2. Fragment assignments for Figure 2B: CAD MS/MS of the [**DNA12**+**Os1**-8H]$^{6-}$ species. Highlighted species (red) were used for internal calibration. Note: the highest intensity isotope was used for fragments containing the osmium modification.

Assignment	Observed m/z	Exact mass/ m/z	Mass error/ppm
[w2]2-	316.54955	316.549554	-0.01
[w1]1-	330.06062	330.060346	0.83
[w4]3-	411.39854	411.398603	-0.15
[w6]4-	460.32003	460.320152	-0.26
[w3]2-	461.07265	461.072740	-0.19
[w7-BH]4-	504.82084	504.821065	-0.45
[w5]3-	512.74730	512.747282	0.04
[w7]4-	538.58431	538.584553	-0.45
[w6]3-	614.09598	614.095961	0.03
[w4]2-	617.60194	617.601542	0.64
[w2]1-	634.10680	634.106383	0.66
[w11]5-	682.50854	682.508940	-0.59
[w9]4-	692.86044	692.860463	-0.03
[w7]3-	718.44849	718.448496	-0.01
[a9-BH+Os1]4-	745.62715	745.627830	-0.91
[w11+Os1]5-	763.12695	763.126400	0.72
[w5]2-	769.62518	769.624561	0.80
[w10]4-	775.12384	775.123593	0.32
[a5-BH+Os1]2-	875.15856	875.158910	-0.40
[w6]2-	921.64732	921.647579	-0.28
[w3]1-	923.15207	923.152755	-0.74
[a9-BH+Os1]3-	994.50451	994.506200	-1.70
[a6-BH+Os1]2-	1031.68664	1031.687800	-1.12
[a5-BH+Os1]1-	1749.32253	1749.322510	0.01

$[DNA12+Os1-8H]^{6-}$ CAD 10V:

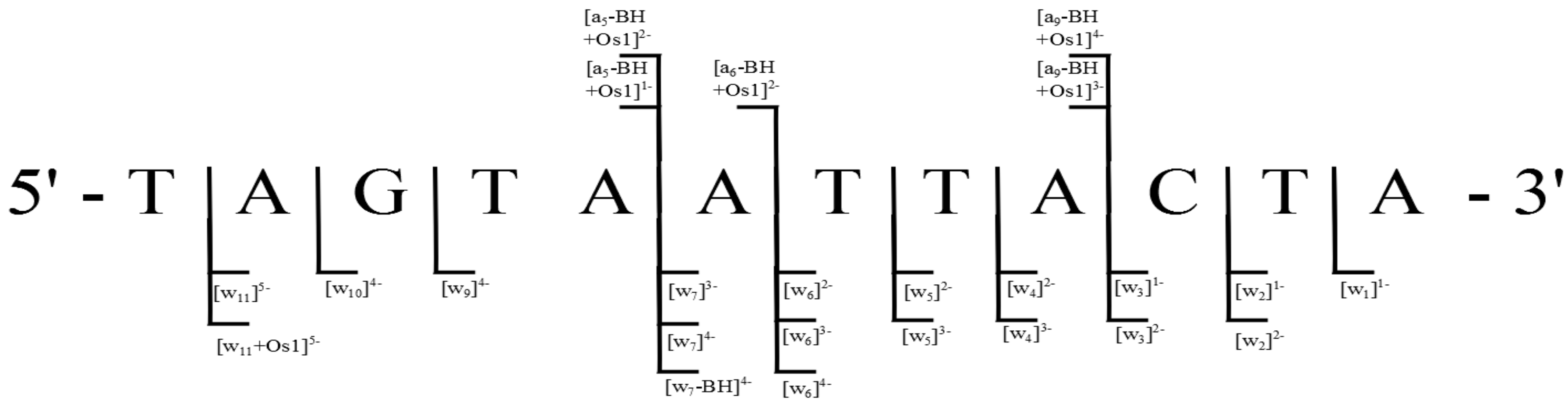


Table S3. Fragment assignments for Figure 3A: EDD MS/MS of the [**DNA12**-7H]$^{7-}$ species. Highlighted species (red) were used for internal calibration.

Assignment	Observed m/z	Exact mass/ m/z	Mass error/ppm
[d2+H]2-	316.54955	316.549555	-0.02
[d1+H]1-	321.04900	321.048777	0.69
[w1]1-	330.06060	330.060346	0.77
[w6]4-	460.31995	460.320152	-0.44
[w3]2-	461.07274	461.072740	0.00
[w5]3-	512.74716	512.747282	-0.24
[w7]4-	538.58460	538.584553	0.09
[w9]5-	554.08685	554.086915	-0.12
[w6]3-	614.09572	614.095961	-0.39
[w4]2-	617.60167	617.601542	0.21
[w10]5-	619.89676	619.897419	-1.06
[d8+H]4-	624.59780	624.597600	0.32
[d6+H]3-	630.43500	630.435200	-0.32
[d4+H]2-	633.09880	633.098834	-0.05
[d2+H]1-	634.10650	634.106382	0.19
[w11]5-	682.50894	682.508940	0.00
[w9]4-	692.86046	692.860463	0.00
[d9+H]4-	702.86181	702.862001	-0.27
[w7]3-	718.44892	718.448496	0.59
[d7+H]3-	731.78376	731.783879	-0.16
[w5]2-	769.62471	769.624561	0.19
[d10+H]4-	775.12384	775.123594	0.32
[d11+H]4-	851.13487	851.135103	-0.27
[w6]2-	921.64801	921.647579	0.47
[w3]1-	923.15276	923.152755	0.01

$[\mathrm{DNA12\text{-}7H}]^{7-}$ EDD:

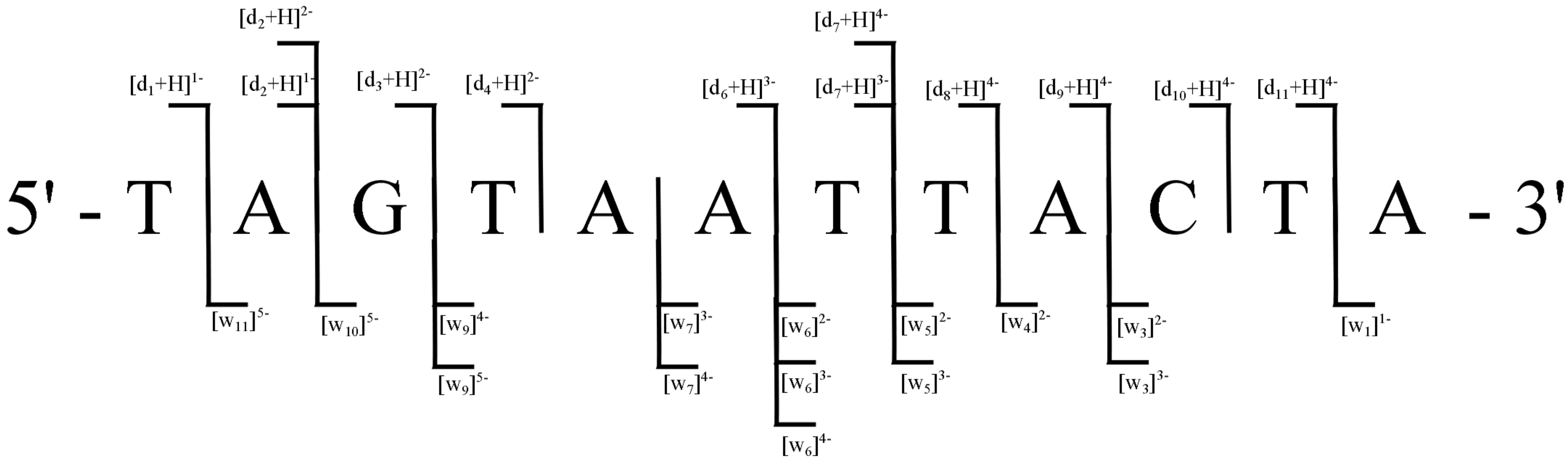


Table S4. Fragment assignments for Figure 3A: EDD MS/MS of the [**DNA12**+**Os1**-9H]$^{7-}$ species. Highlighted species (red) were used for internal calibration. Note: the highest intensity isotope was used for fragments containing the osmium modification.

Assignment	Observed m/z	Exact mass/ m/z	Mass error/ppm
[d2+H]2-	316.54955	316.549555	-0.02
[d1+H]1-	321.04908	321.048777	0.94
[w1]1-	330.06057	330.060346	0.68
[w6]4-	460.32029	460.320152	0.30
[w3]2-	461.07274	461.072740	0.00
[w6]3-	614.09596	614.095961	0.00
[w4]2-	617.60160	617.601542	0.09
[d6+H]3-	630.43488	630.435200	-0.51
[d4+H]2-	633.09931	633.098834	0.75
[w2]1-	634.10669	634.106383	0.48
[w9]4-	692.86083	692.860463	0.53
[d9+2H]4-	703.11513	703.113821	1.86
[w7]3-	718.44839	718.448496	-0.15
[d7+H]3-	731.78402	731.7838793	0.19
[w5]2-	769.62436	769.624561	-0.26
[d5+H]2-	789.62774	789.627636	0.13
[z10+Os1]4-	851.65110	851.651640	-0.63
[d10+Os1+H]4-	876.14725	876.147330	-0.09
[w6]2-	921.64677	921.647579	-0.88
[w3]1-	923.15289	923.152755	0.15
[d11+Os1+H]4- HP	952.40935	952.409350	0.00

$[DNA12+Os1-9H]^{7-}$ EDD:

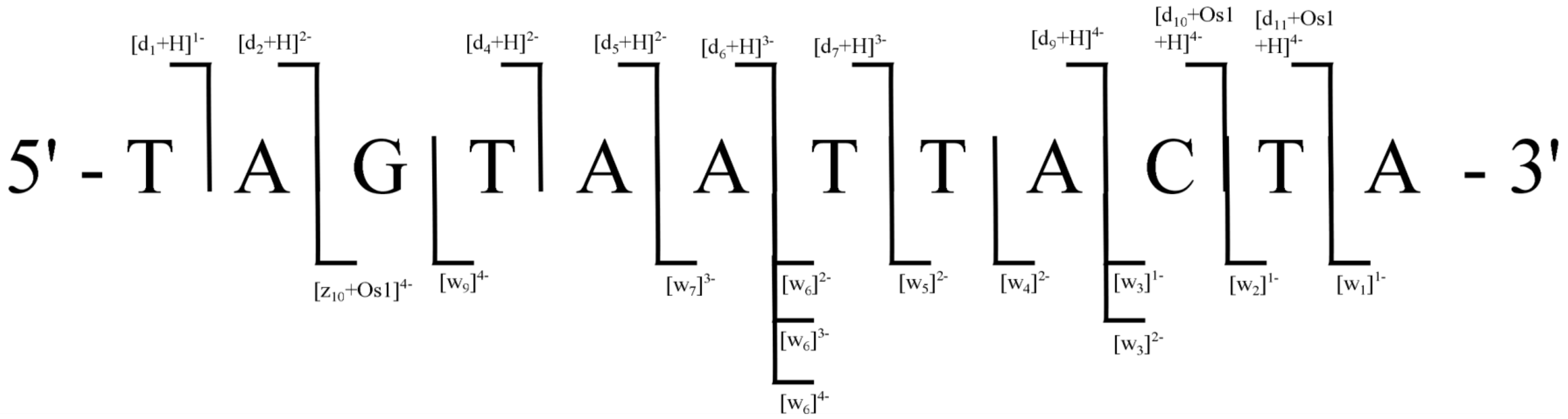
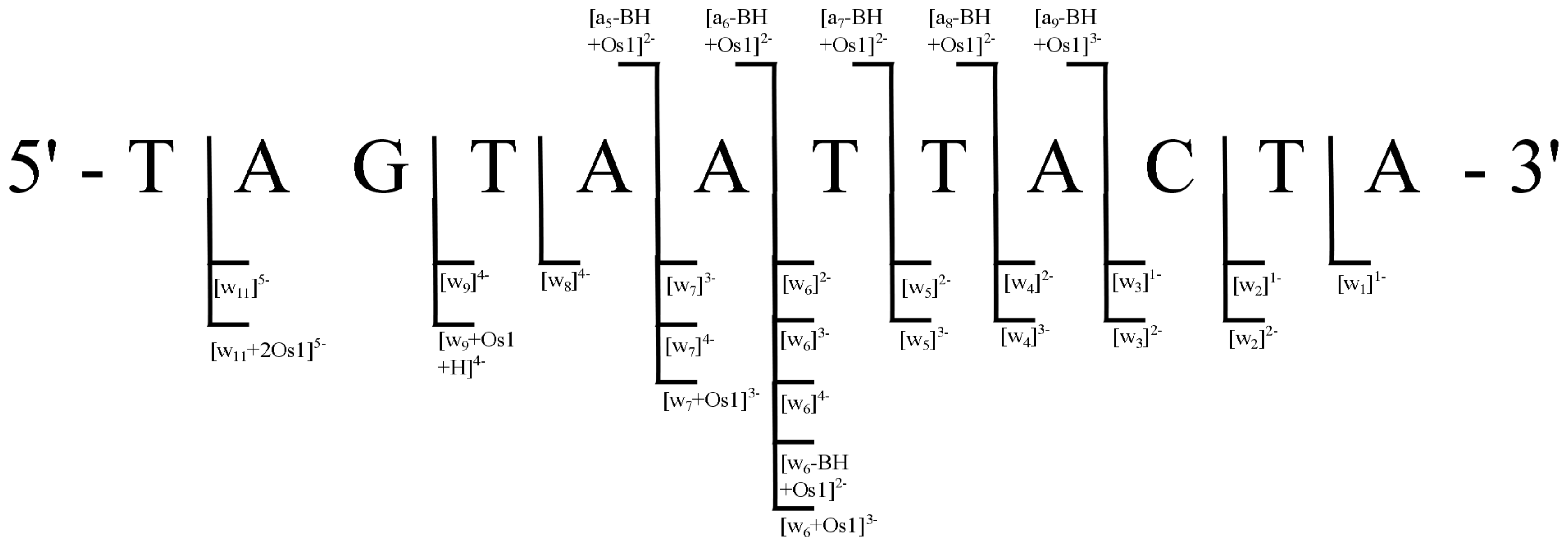


Table S5. Fragment assignments for Figure 4A: CAD MS/MS of the [**DNA12**+2**Os1**-10H]$^{6-}$ species. Highlighted species were used for internal calibration. Note: the highest intensity isotope was used for fragments containing the osmium modification.

Assignment	Observed m/z	Exact mass/ m/z	Mass error/ppm
[w2]2-	316.54955	316.549554	-0.01
[w1]1-	330.06062	330.060346	0.83
[w4]3-	411.39864	411.398603	0.09
[w6]4-	460.32015	460.320152	0.00
[w3]2-	461.07277	461.072740	0.07
[w5]3-	512.74745	512.747282	0.33
[w7]4-	538.58470	538.584553	0.27
[w6]3-	614.09589	614.095961	-0.12
[w8]4-	616.84921	616.848954	0.42
[w4]2-	617.60154	617.601542	0.00
[w2]1-	634.10670	634.106383	0.50
[w11]5-	682.50881	682.508940	-0.19
[w9]4-	692.86033	692.860463	-0.19
[w7]3-	718.44879	718.448496	0.41
[w6+Os1+H]3-	748.79373	748.794030	-0.40
[w5]2-	769.62505	769.624561	0.64
[w9+Os1+H]4-	793.63323	793.632200	1.30
[w11+2Os1-9H]5-	843.54589	843.544500	1.65
[w7+Os1+H]3-	853.14599	853.146620	-0.74
[a5-BH+Os1-4H]2-	875.15842	875.158910	-0.56
[w6]2-	921.64778	921.647579	0.22
[w3]1-	923.15296	923.152755	0.22
[a9-BH+Os1-5H]3-	994.50590	994.506200	-0.30
[a6-BH+Os1-4H]2-	1031.68728	1031.687800	-0.50
[w6+Os1+H]2-	1123.69411	1123.694680	-0.51
[a7-BH+Os1-4H]2-	1188.21684	1188.216690	0.13
[a8-BH+Os1-4H]2-	1340.23851	1340.239810	-0.97
[a5-BH+Os1-3H]1-	1749.32253	1749.322510	0.01

$[DNA12+2Os1-10H]^{6-}$ CAD 12V:



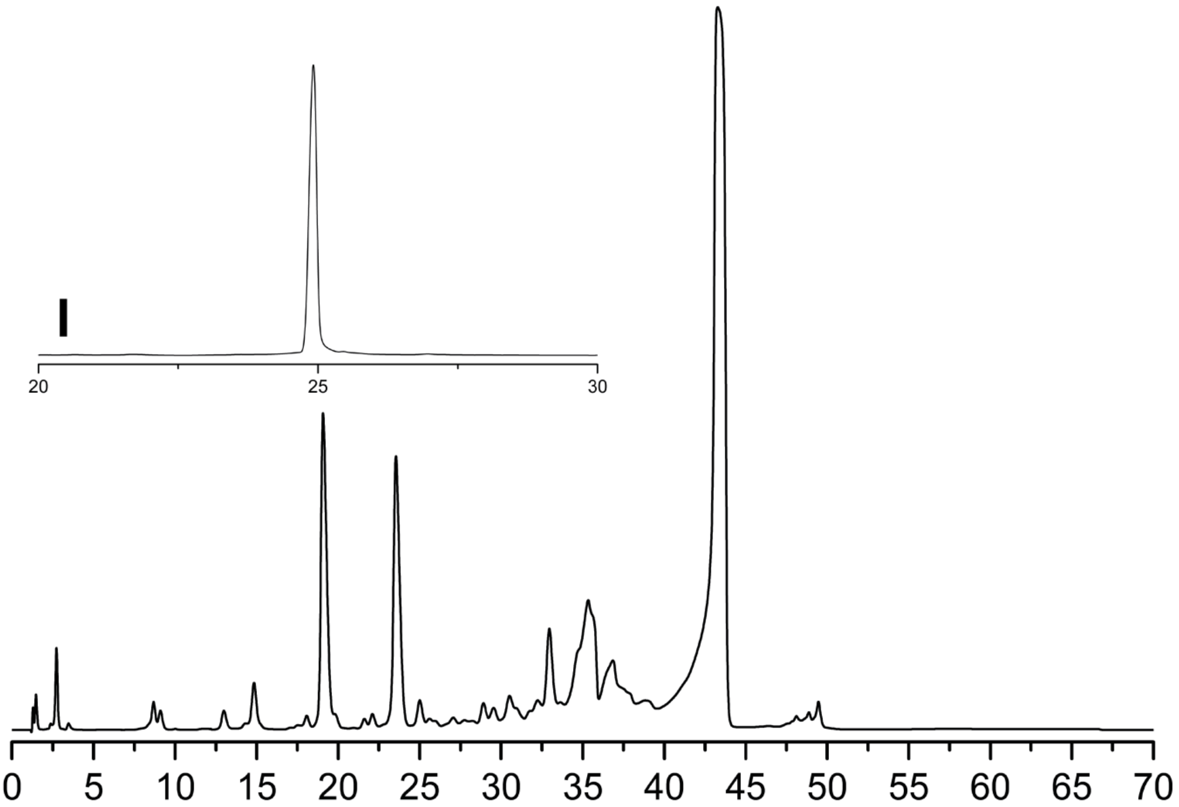


Figure S1. HPLC trace of the commercially-synthesised **DNA12** sample, showing multiple shorter oligonucleotides resulting from truncated synthesis and the DNA 12mer (highest peak) which was isolated and then re-analysed by HPLC; the resulting trace is inset, showing only one remaining product, the DNA 12mer (confirmed by UHR-FT-ICR MS, Figure 1A in main text).

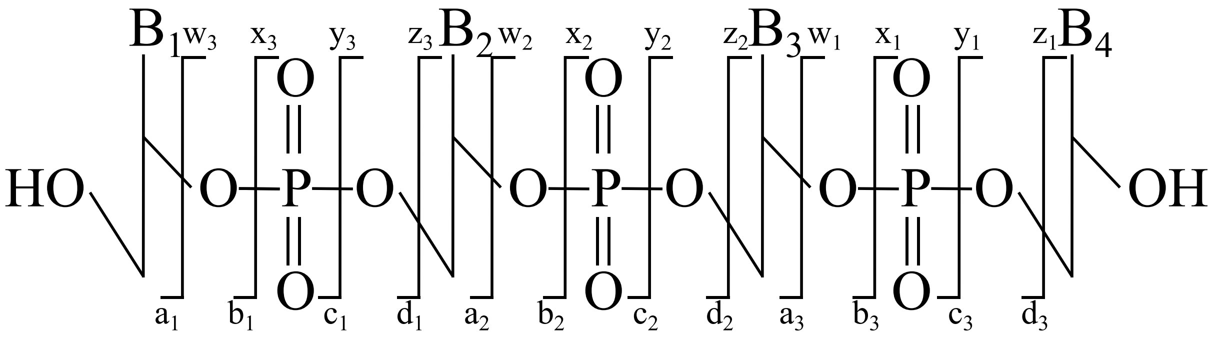


Figure S2. The nomenclature devised by McLuckey *et al.*[34] based on the McCloskey *et.al.* system[35] for assignment of oligonucleotide MS/MS fragments.