Supplementary Material

Metal-Mediated Base Pairing within the Simplified Nucleic Acid GNA

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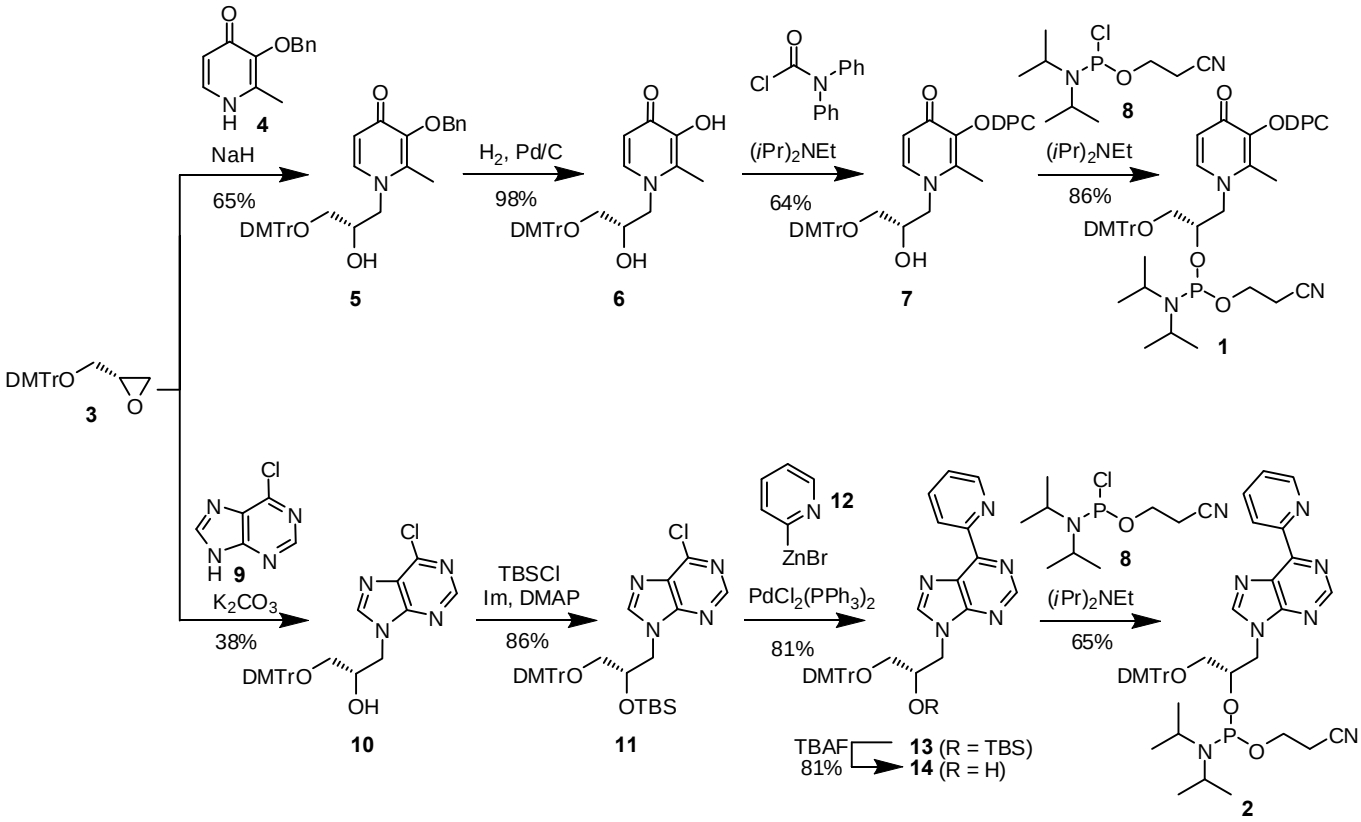
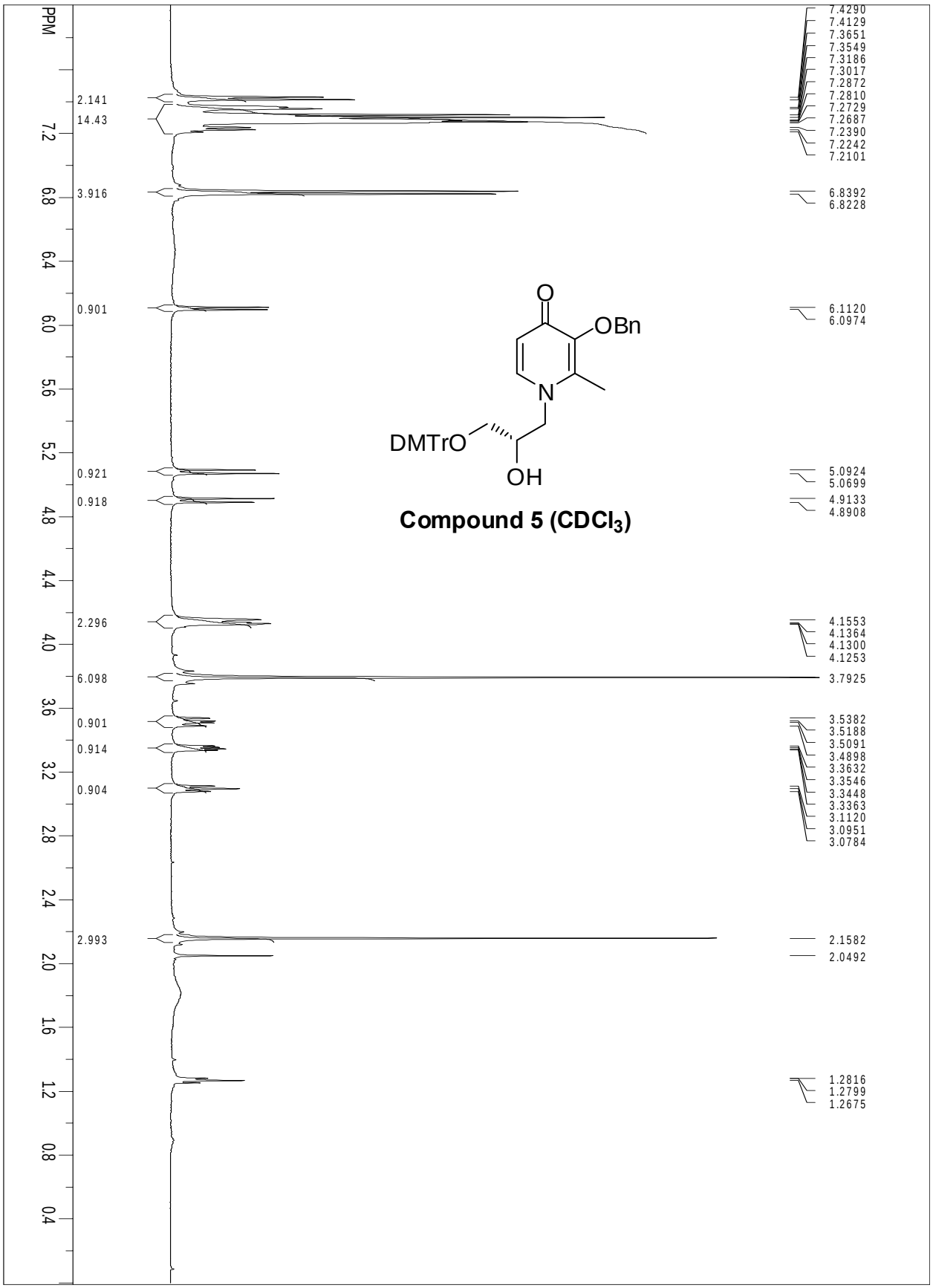
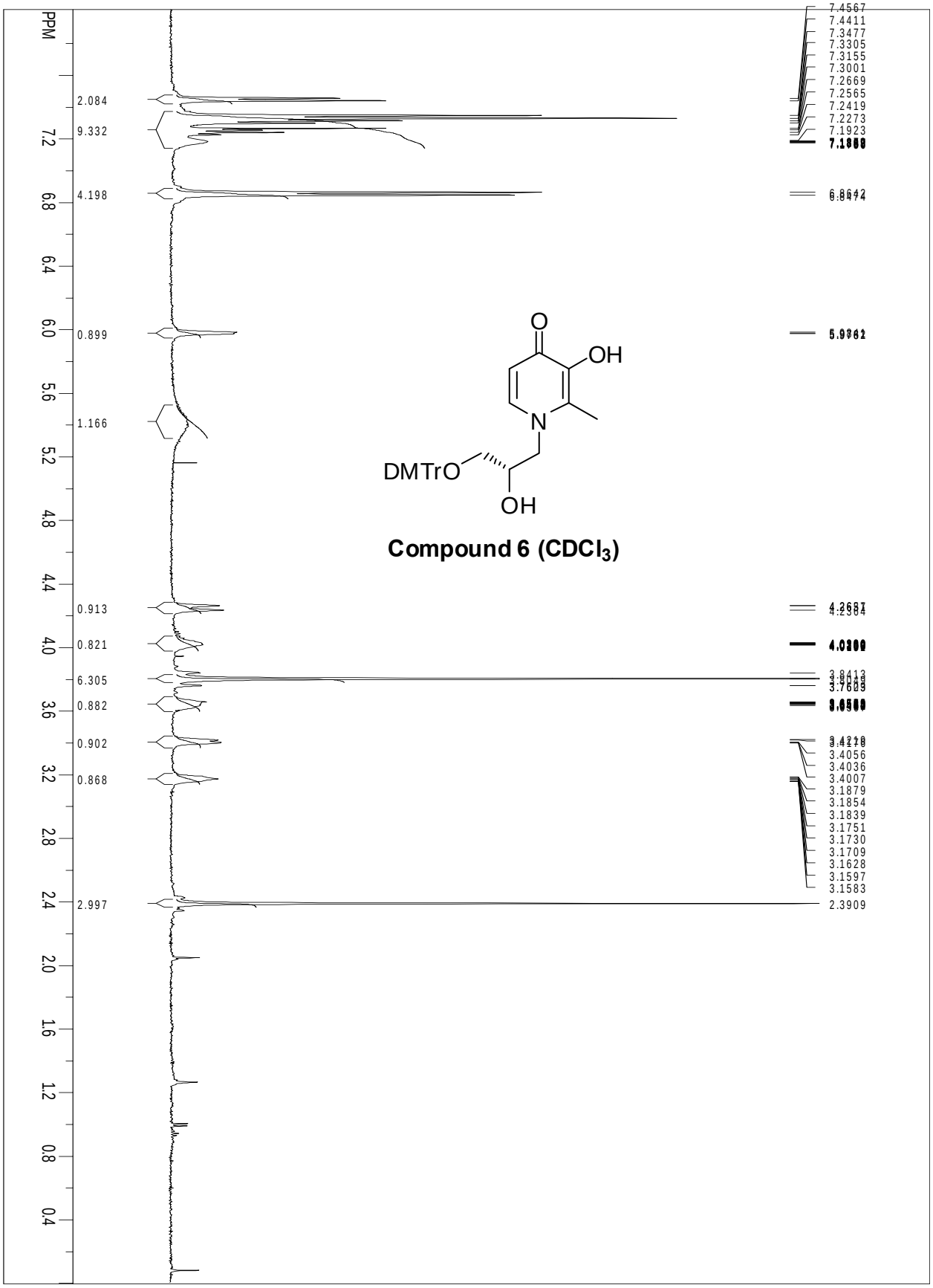
Content:

1.) Proton NMR data of compounds

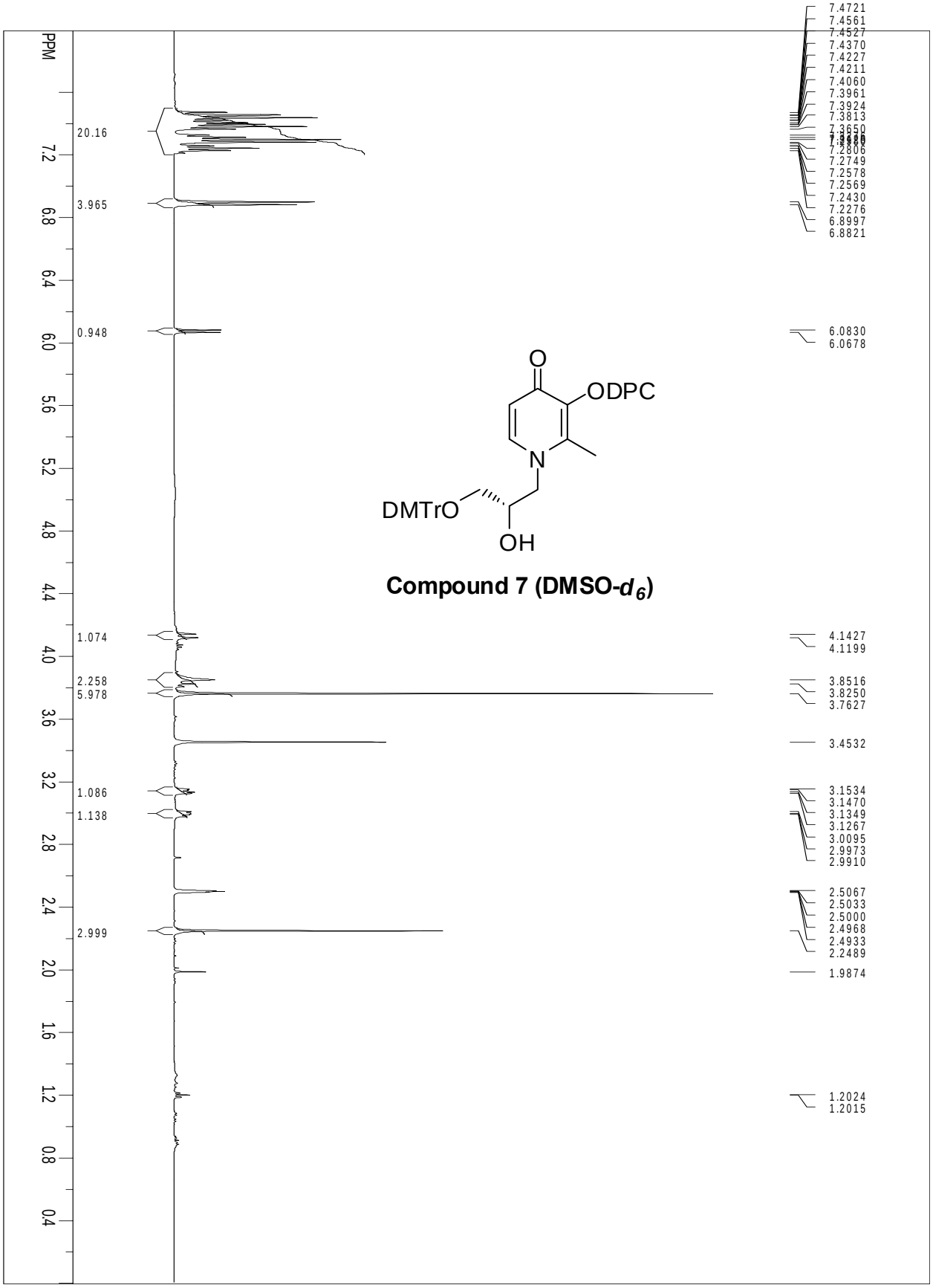




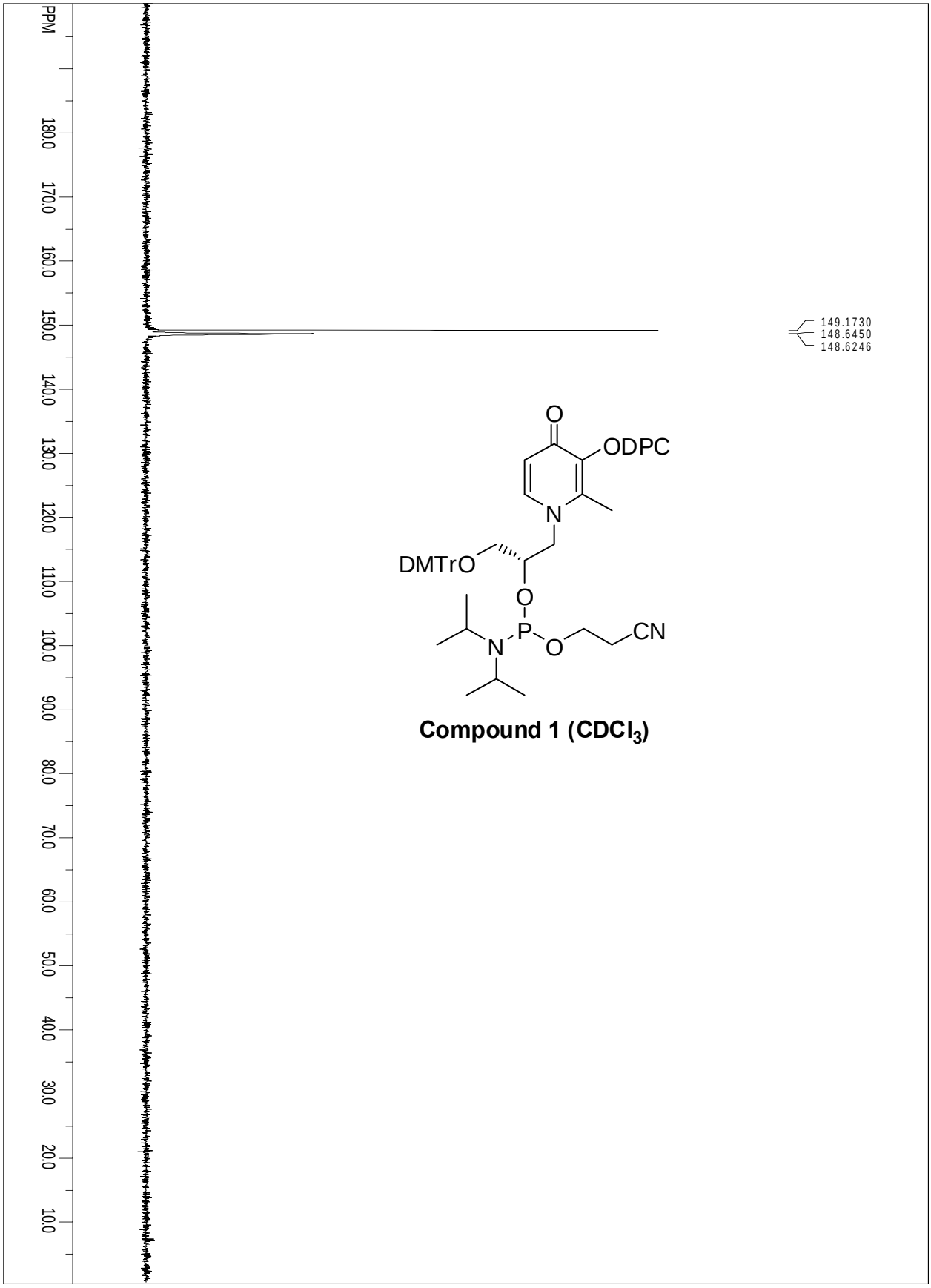
Compound 5 ($CDCl_3$)



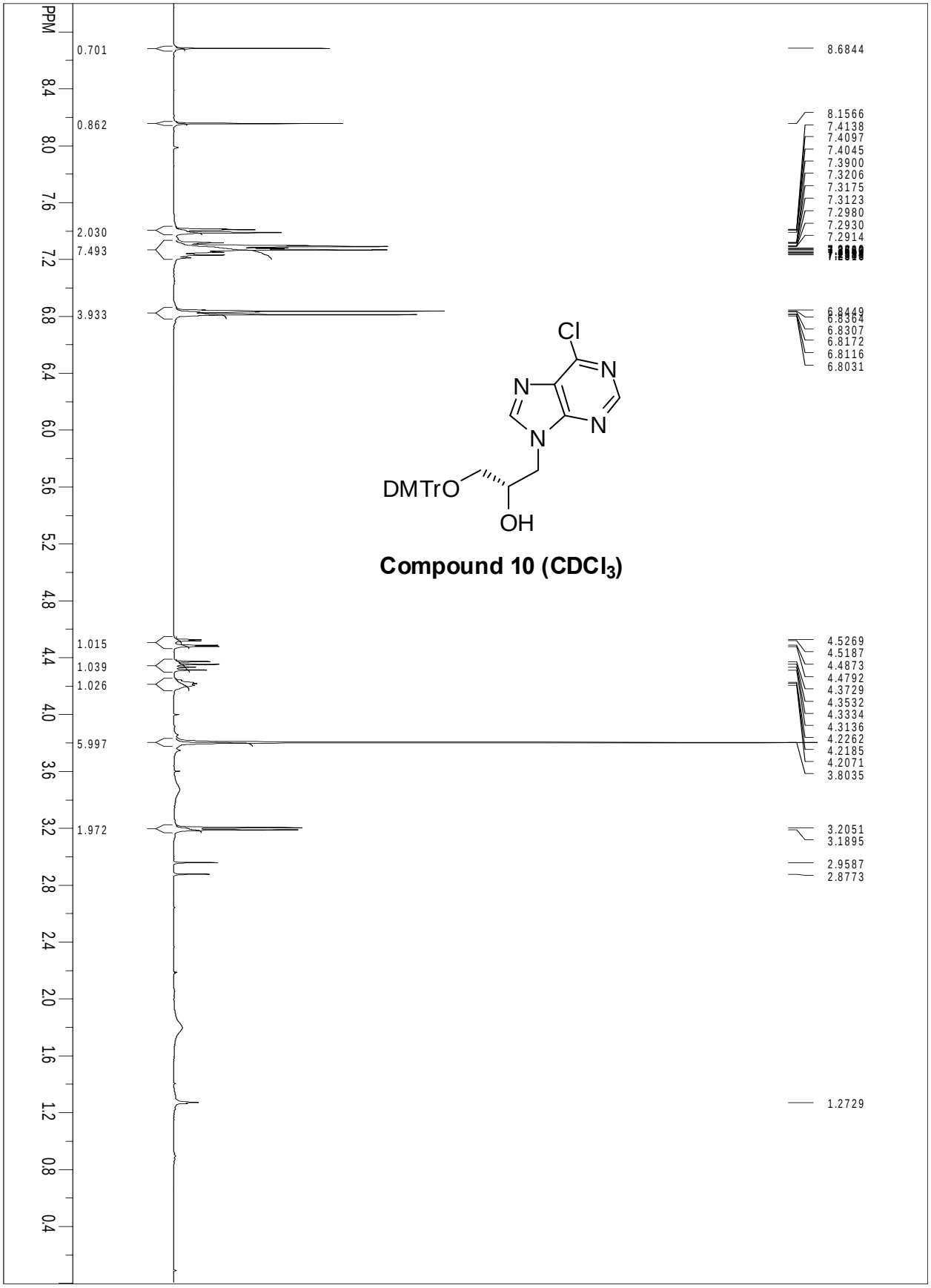
Compound 6 ($CDCl_3$)



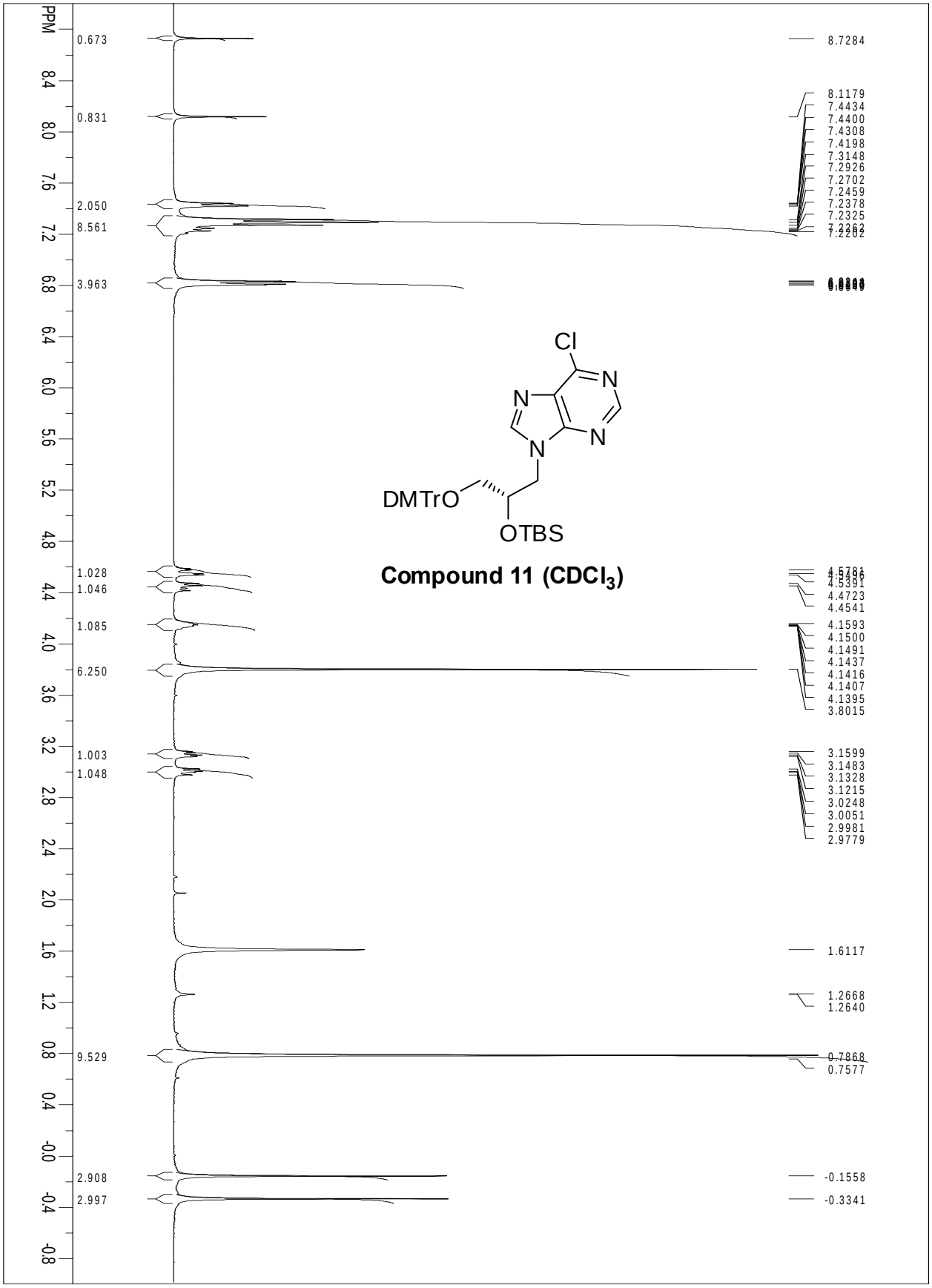
Compound 7 (DMSO-d_6)



Compound 1 ($CDCl_3$)



Compound 10 ($CDCl_3$)


PPM
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
-0.0
-0.4
-0.8
0.673
0.831
2.050
8.561
3.963
1.028
1.046
1.085
6.250
1.003
1.048
9.529
2.908
2.997
8.7284
8.1179
7.4434
7.4400
7.4308
7.4198
7.3148
7.2926
7.2702
7.2459
7.2378
7.2325
7.2262
7.2202
4.5781
4.5396
4.5391
4.4723
4.4541
4.1593
4.1500
4.1491
4.1437
4.1416
4.1407
4.1395
3.8015
3.1599
3.1483
3.1328
3.1215
3.0248
3.0051
2.9981
2.9779
1.6117
1.2668
1.2640
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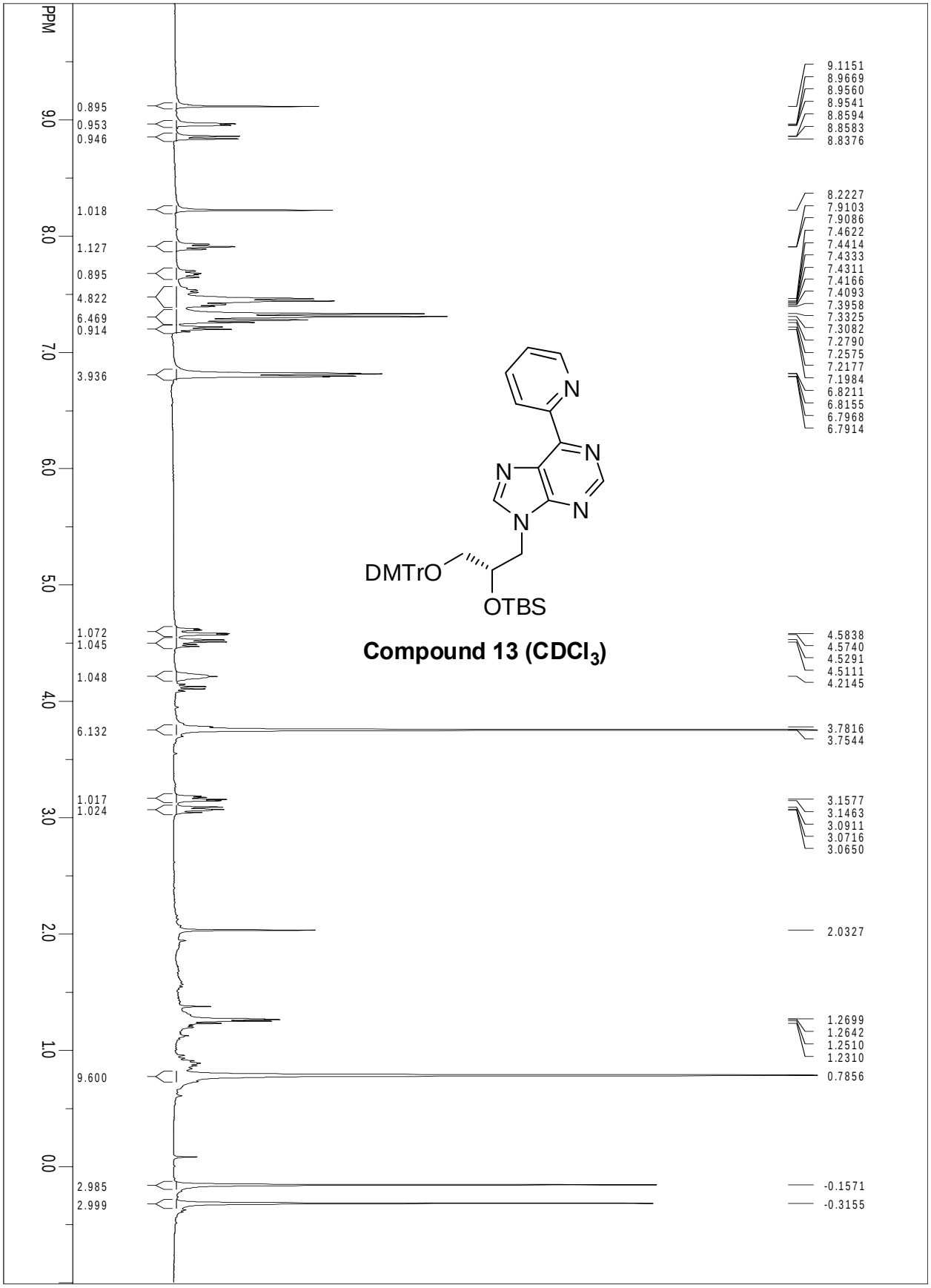
Cl
N
N
N
N
DMTrO
OTBS
Compound 11 (CDCl3)


PPM
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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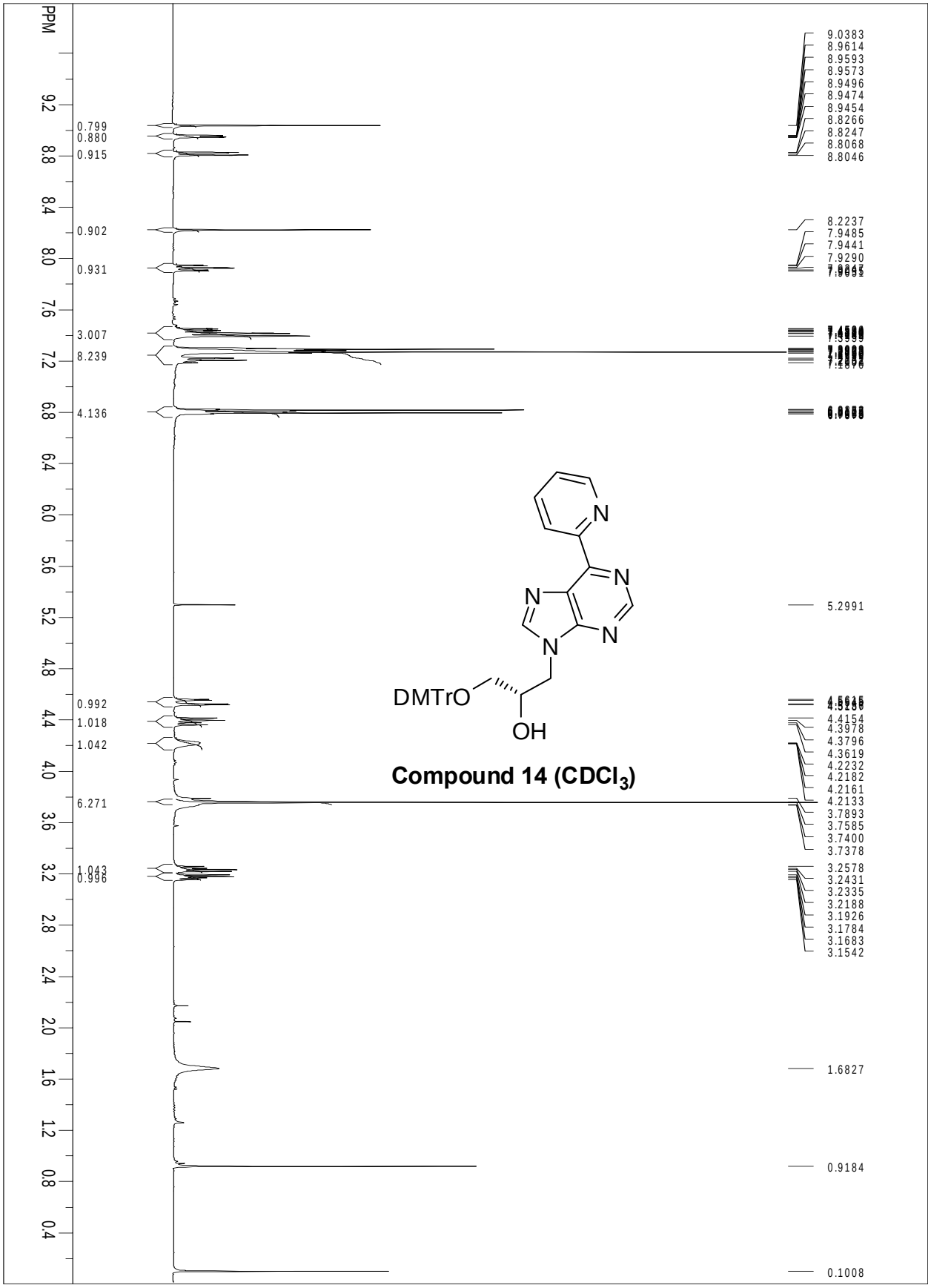
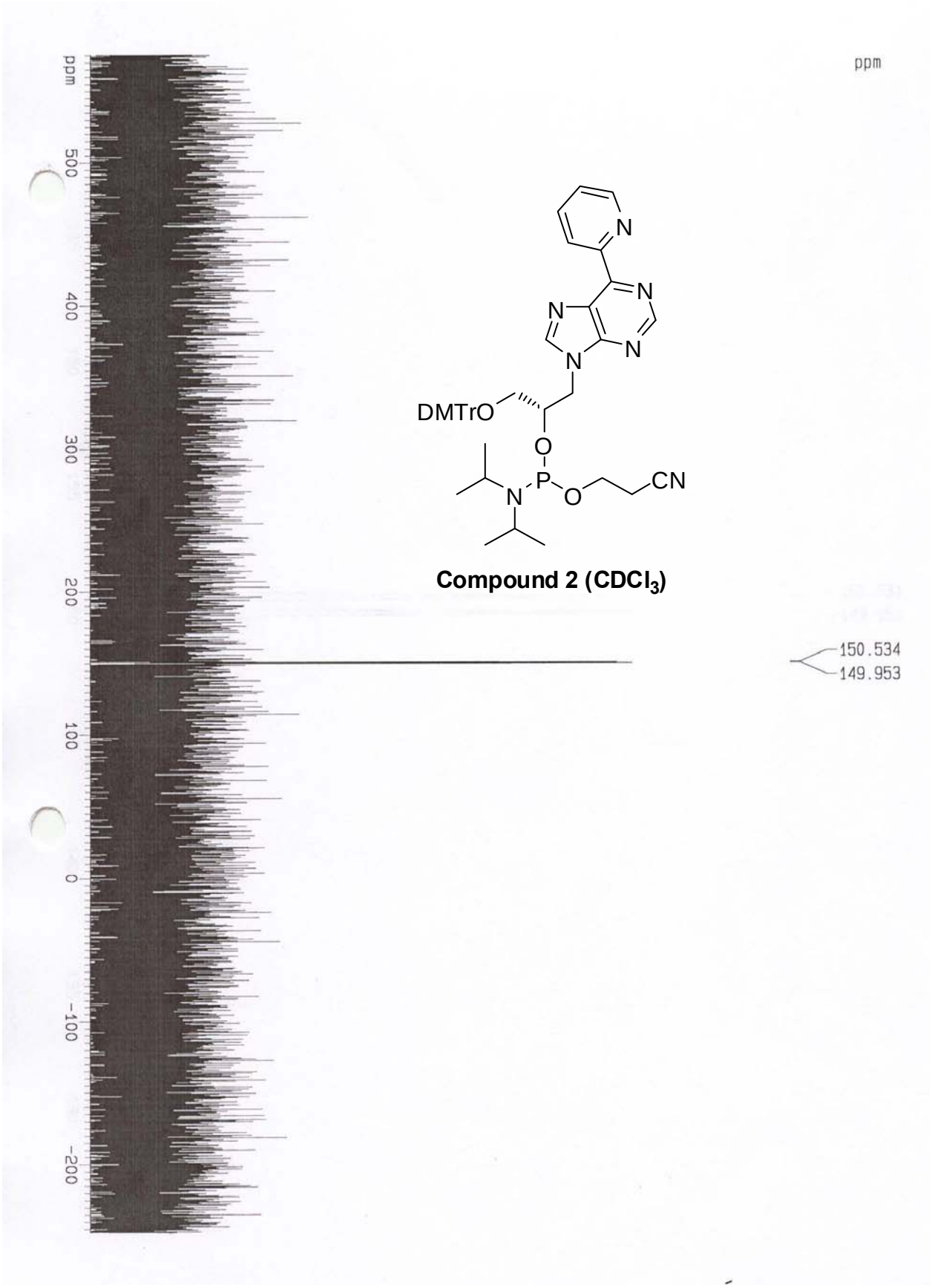
0.953
0.946
1.018
1.127
0.895
4.822
6.469
0.914
3.936
1.072
1.045
1.048
6.132
1.017
1.024
9.600
2.985
2.999
9.1151
8.9669
8.9560
8.9541
8.8594
8.8583
8.8376
8.2227
7.9103
7.9086
7.4622
7.4414
7.4333
7.4311
7.4166
7.4093
7.3958
7.3325
7.3082
7.2790
7.2575
7.2177
7.1984
6.8211
6.8155
6.7968
6.7914
4.5838
4.5740
4.5291
4.5111
4.2145
3.7816
3.7544
3.1577
3.1463
3.0911
3.0716
3.0650
2.0327
1.2699
1.2642
1.2510
1.2310
0.7856
-0.1571
-0.3155
N
N
N
N
N
DMTrO
OTBS
Compound 13 (CDCl3)


PPM
9.2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.799
0.880
0.915
0.902
0.931
3.007
8.239
4.136
0.992
1.018
1.042
6.271
1.043
0.996
9.0383
8.9614
8.9593
8.9573
8.9496
8.9474
8.9454
8.8266
8.8247
8.8068
8.8046
8.2237
7.9485
7.9441
7.9290
5.2991
4.4154
4.3978
4.3796
4.3619
4.2232
4.2182
4.2161
4.2133
3.7893
3.7585
3.7400
3.7378
3.2578
3.2431
3.2335
3.2188
3.1926
3.1784
3.1683
3.1542
1.6827
0.9184
0.1008
N
N
N
N
N
DMTrO
OH
Compound 14 (CDCl3)



Compound 2 ($CDCl_3$)

2.) GNA oligonucleotide synthesis and purification

GNA oligonucleotides were prepared on an ABI 394 DNA/RNA Synthesizer on a one micromole scale. GNA phosphoramidites (A, T, G, C, **1**, **2**) were used at a concentration of 100 mM with a standard protocol for 2-cyanoethyl phosphoramidites, except that the coupling was extended to 3 minutes (A, T, G, C), or 8 minutes (**1**, **2**). After the trityl-on synthesis, the resin was incubated with concentrated aqueous ammonia at 55-60 °C for 12 hours and then evaporated. The tritylated oligonucleotides were purified by C_{18}-reversed-phase HPLC (Varian Dynamax 250 × 10 mm, Microsorb 300–10, C_{18}) with aqueous triethylammonium acetate (50 mM TEAA) and acetonitrile as the eluent. The oligonucleotides were then detritylated with 80% acetic acid for 20 min and precipitated with *i*PrOH after the addition of 3 M sodium acetate. All oligonucleotides were finally purified at 55-60 °C using a Waters XTerra column (MS C18, 4.6 × 50 mm, 2.5 μm) with aqueous TEAA (50mM) and acetonitrile as the eluent. Purities were confirmed by HPLC as demonstrated with a representative trace in Figure S1. All identities were confirmed by MALDI-TOF MS (Table S1).

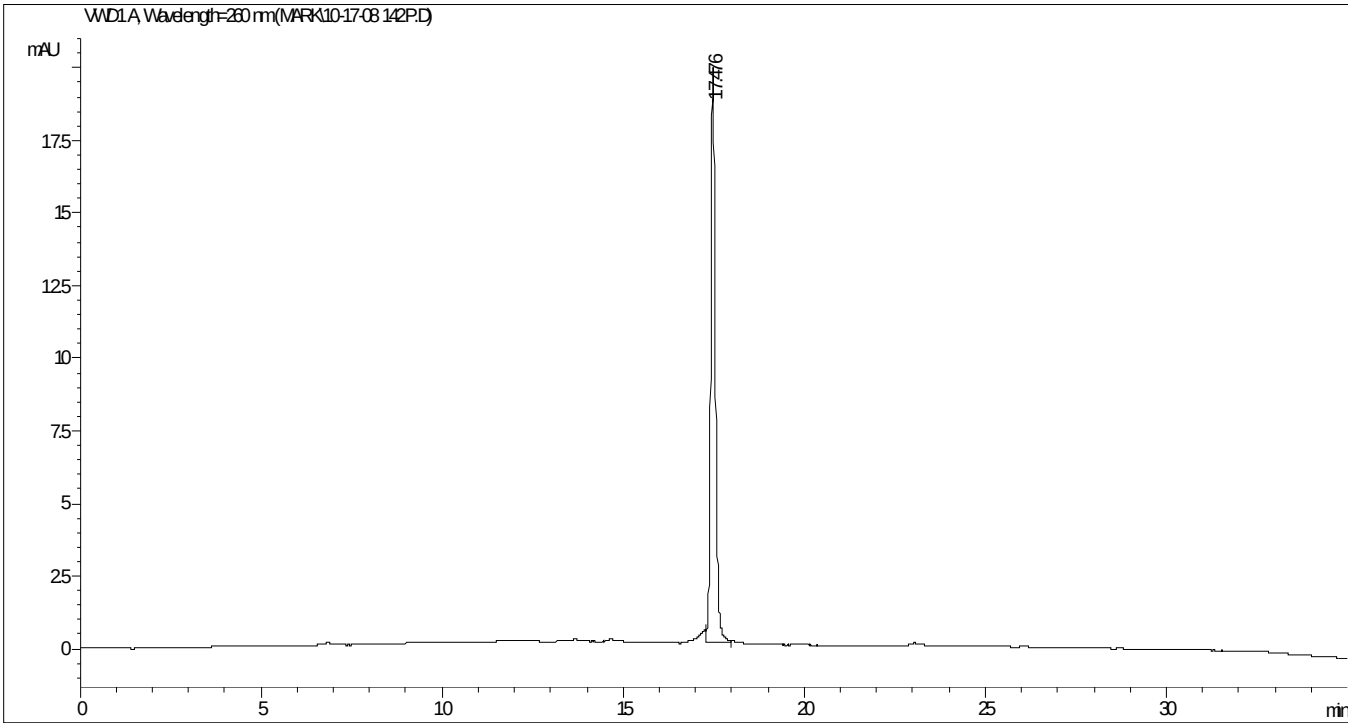


Figure S1. HPLC trace of the GNA sequence 3'-AAT ATT ATT ATT TTA-2'. The oligo was eluted with a linear gradient from 3-13% acetonitrile (97-87% TEAA) in 30 minutes. All GNA oligos were determined to be 98-100% pure by HPLC.

Table S1. Extinction coeffiecients and MALDI-TOF measured masses for all GNA oligonucleotides

Sequence (3'→2')	ε_{260}	Mass (calc)	Mass (measured)
AAT ATT ATT ATT TTA	153630	3924	3924
TAA AAT AAT AAT ATT	171720	3951	3952
AAT ATT AHT ATT TTA	150606	3923	3925
TAA AAT AHT AAT ATT	162666	3941	3943
AAT ATT APT ATT TTA	159660	3994	3997
TAA AAT APT AAT ATT	171720	4012	4015
TAA AAT ATT AAT ATT	165690	3942	3941