Supporting Information

Promotive effect of platinum moiety on the DNA cleavage activity of copper-based artificial nucleases

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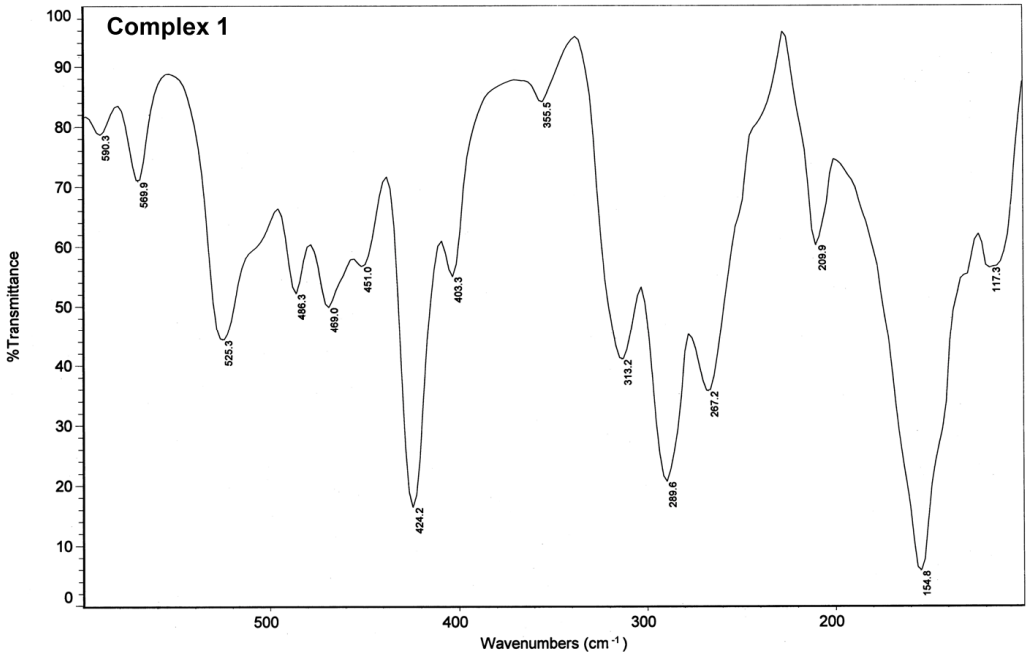
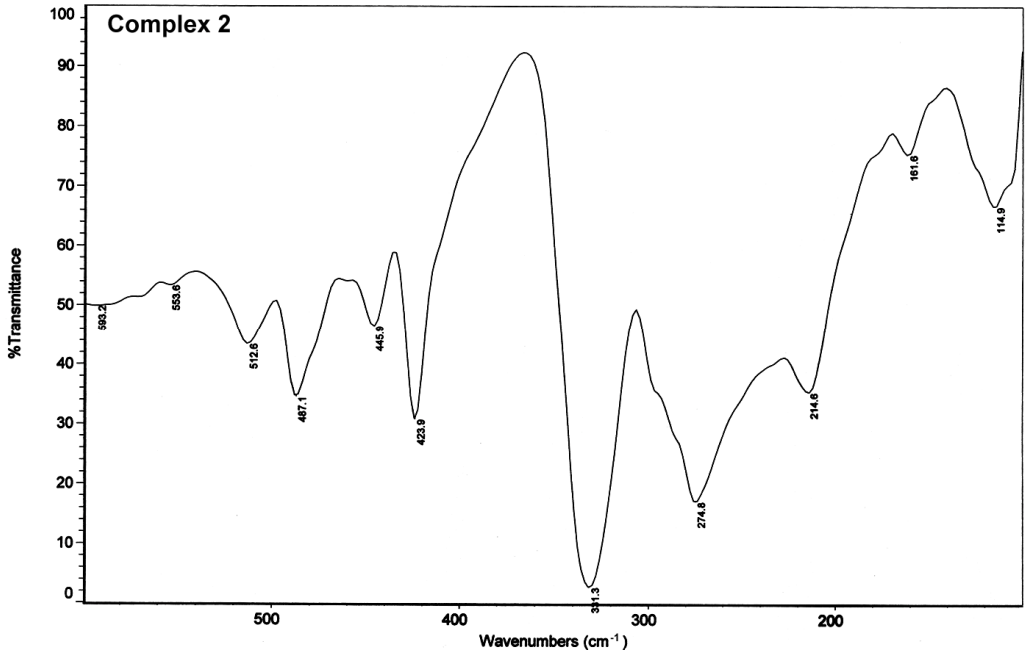




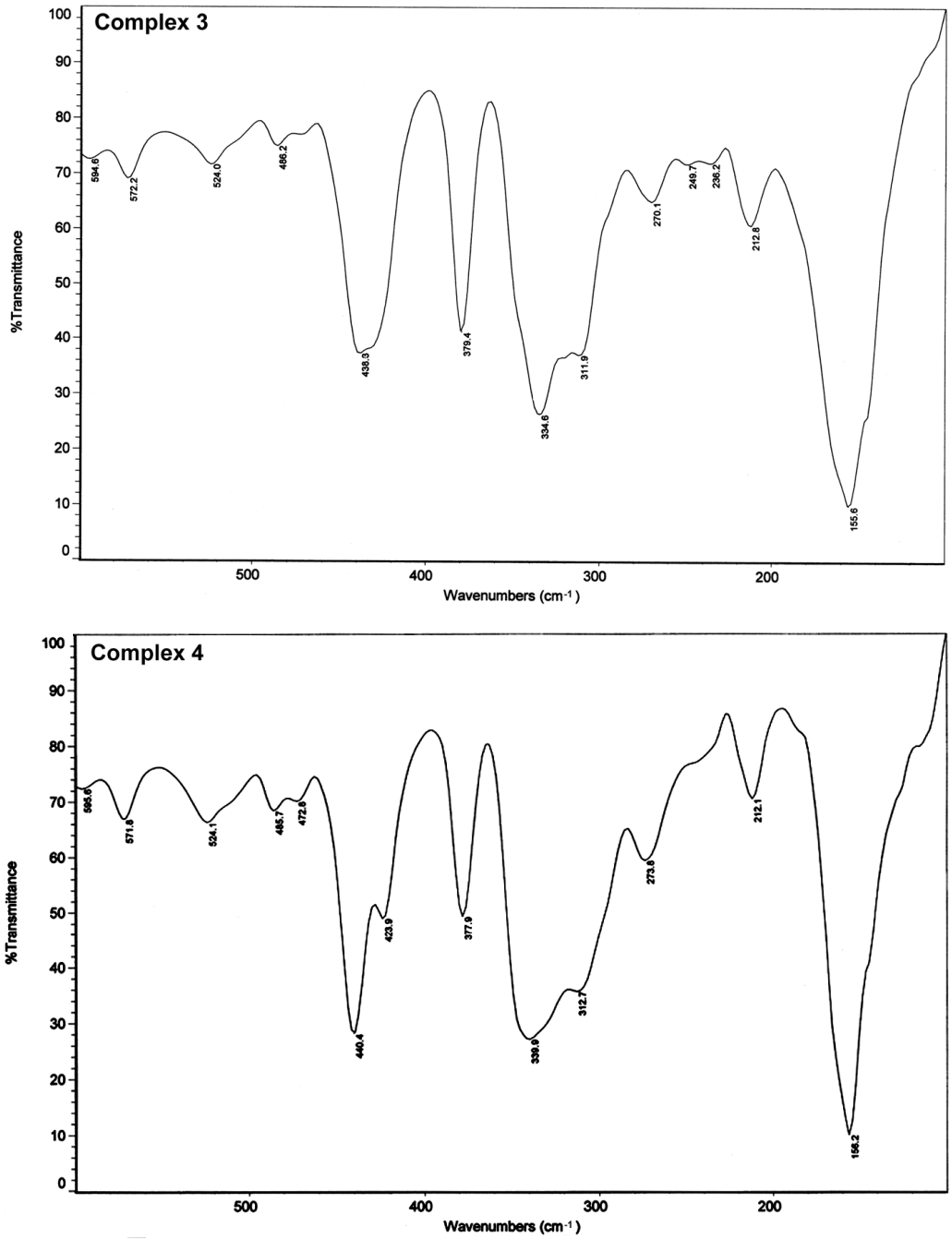


Figure S1. Far IR spectra of complexes **1**, **2**, **3**, and **4** in the range of 100–600 cm^{-1} showing the vibration of Cu–Cl (267.2–274.8 cm^{-1}), Pt–Cl (311.9–339.9 cm^{-1}), and Pt–S (438.3–440.4 cm^{-1}) bonds.

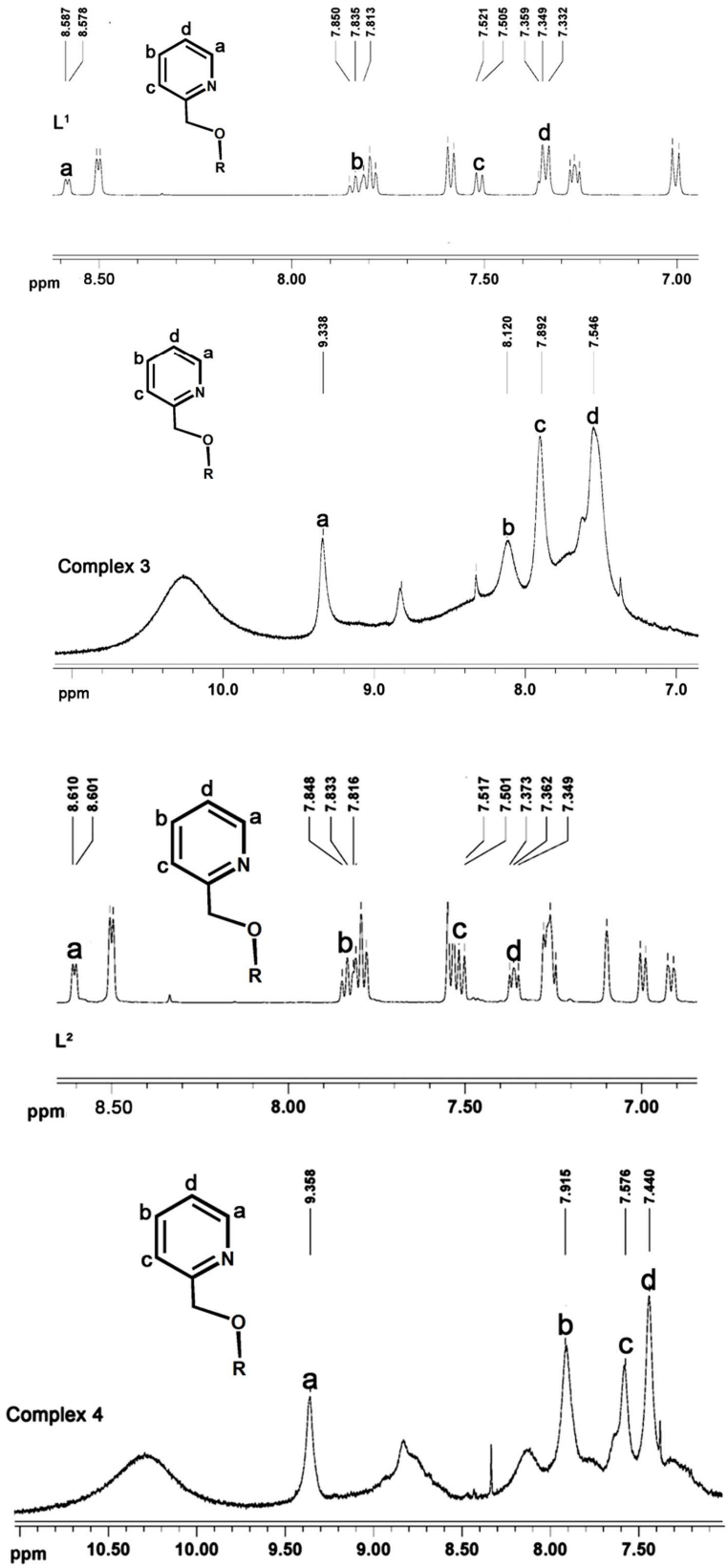


Figure S2. ^{1}H NMR spectra (DMSO-d_6) of L^1, complex **3**, L^2, and complex **4** showing the changes of the picolin proton signals after the formation of the complexes. The unassigned large peaks can be assigned to proton signals of the pyridyls coordinated directly to the paramagnetic Cu^{2+}.

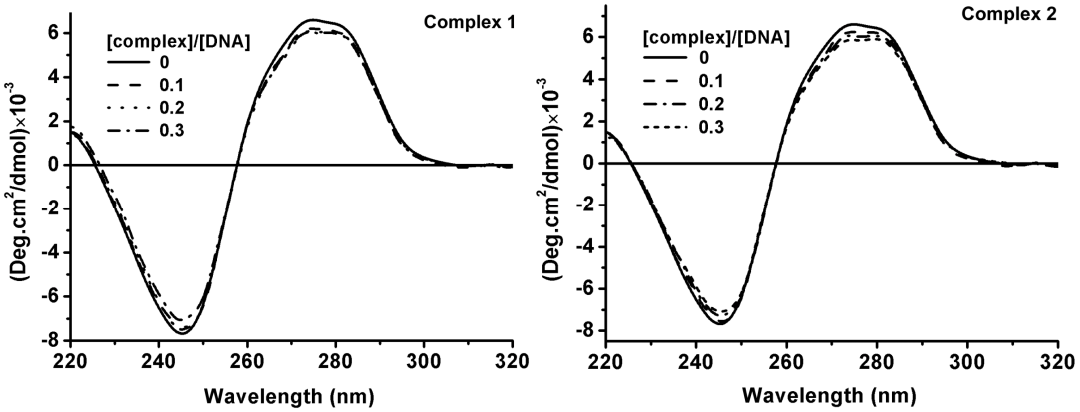
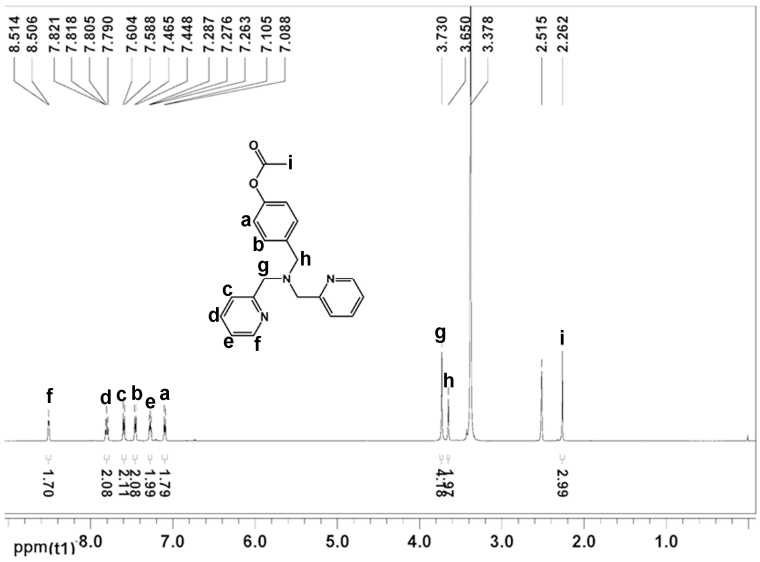


Figure S3. Circular dichroism (CD) spectra of CT-DNA (0.1 mM) in the presence of complex **1** and **2**, respectively, at different [complex]/[DNA] molar ratios.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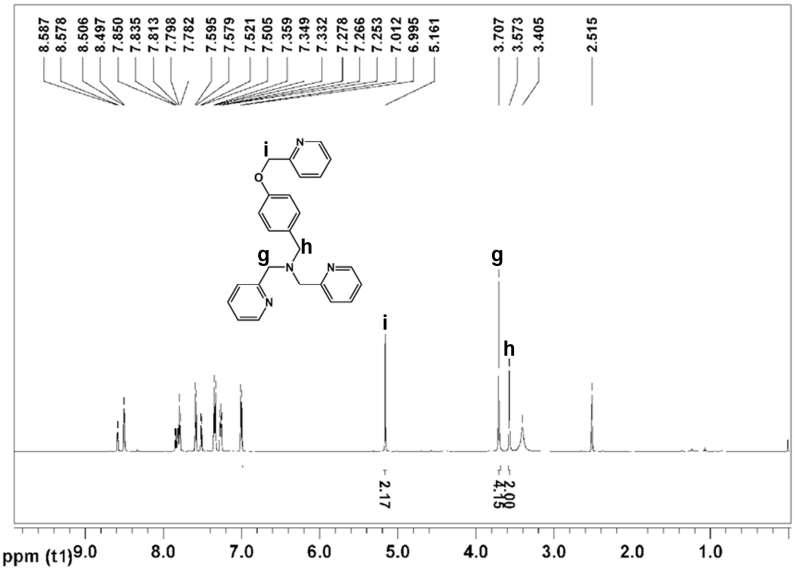
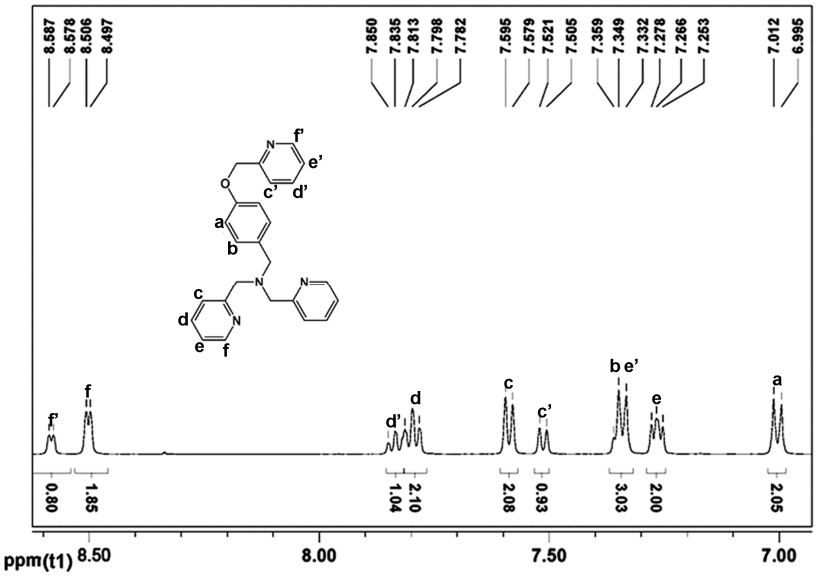
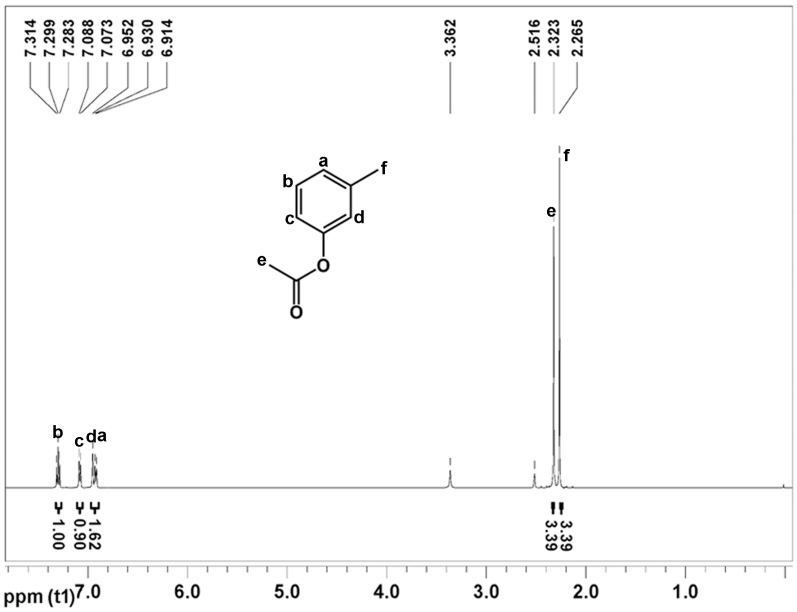
8.506
7.821
7.818
7.805
7.790
7.604
7.588
7.465
7.448
7.287
7.276
7.263
7.105
7.088
3.730
3.650
3.378
2.515
2.262
ppm(t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


8.587
8.578
8.506
8.497
7.850
7.835
7.813
7.798
7.782
7.595
7.579
7.521
7.505
7.359
7.349
7.332
7.278
7.266
7.253
7.012
6.995
5.161
3.707
3.573
3.405
2.515
ppm (t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


8.587
8.578
8.506
8.497
7.850
7.835
7.813
7.798
7.782
7.595
7.579
7.521
7.505
7.359
7.349
7.332
7.278
7.266
7.253
7.012
6.995
ppm(t1)
8.50
8.00
7.50
7.00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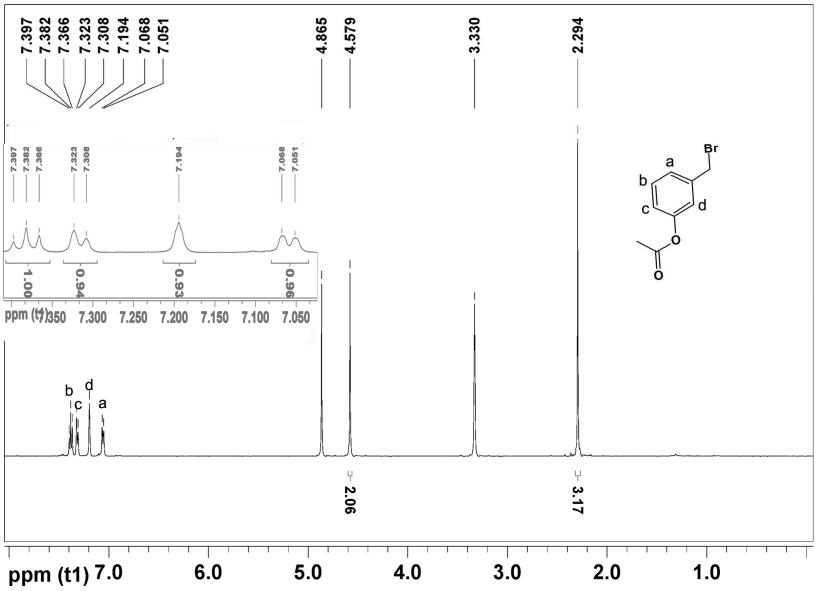
7.299
7.283
7.088
7.073
6.952
6.930
6.914
3.362
2.516
2.323
2.265
a
b
c
d
e
f
O
O
b
c
d
a
1.00
0.90
1.62
3.39
3.39
ppm (t1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0


7.397
7.382
7.366
7.323
7.308
7.194
7.068
7.051
4.865
4.579
3.330
2.294
1.00
0.94
0.93
0.96
ppm (t1)
7.350
7.300
7.250
7.200
7.150
7.100
7.050
Br
a
b
c
d
O
O
b
c
d
a
2.09
3.17
ppm (t1)
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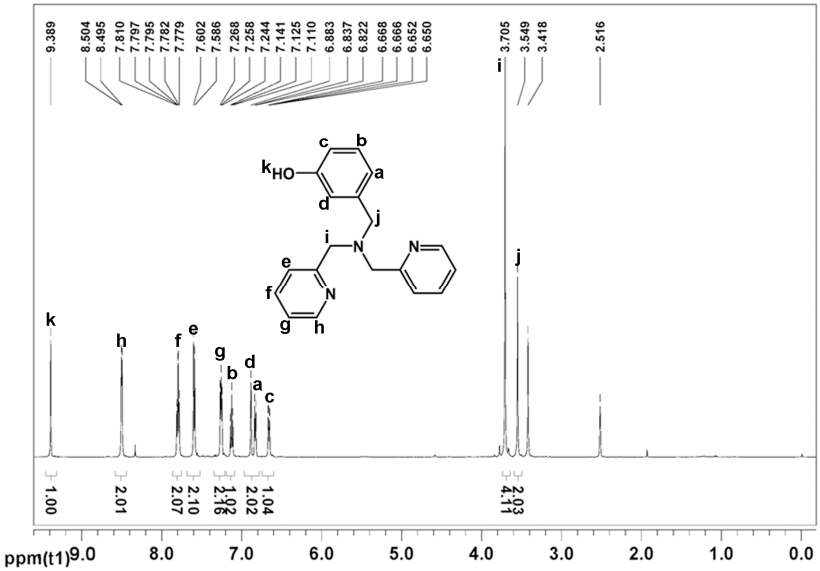
6.0
5.0
4.0
3.0
2.0
1.0


9.389
8.504
8.495
7.810
7.797
7.795
7.782
7.779
7.602
7.586
7.268
7.258
7.244
7.141
7.125
7.110
6.883
6.837
6.822
6.668
6.666
6.652
6.650
3.705
3.549
3.418
2.516
c
b
k
HO
a
d
j
i
N
N
e
f
N
g
h
k
h
f
e
g
b
d
a
c
i
j
1.00
2.01
2.07
2.10
1.02
2.02
1.04
4.11
2.03
ppm(t1)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
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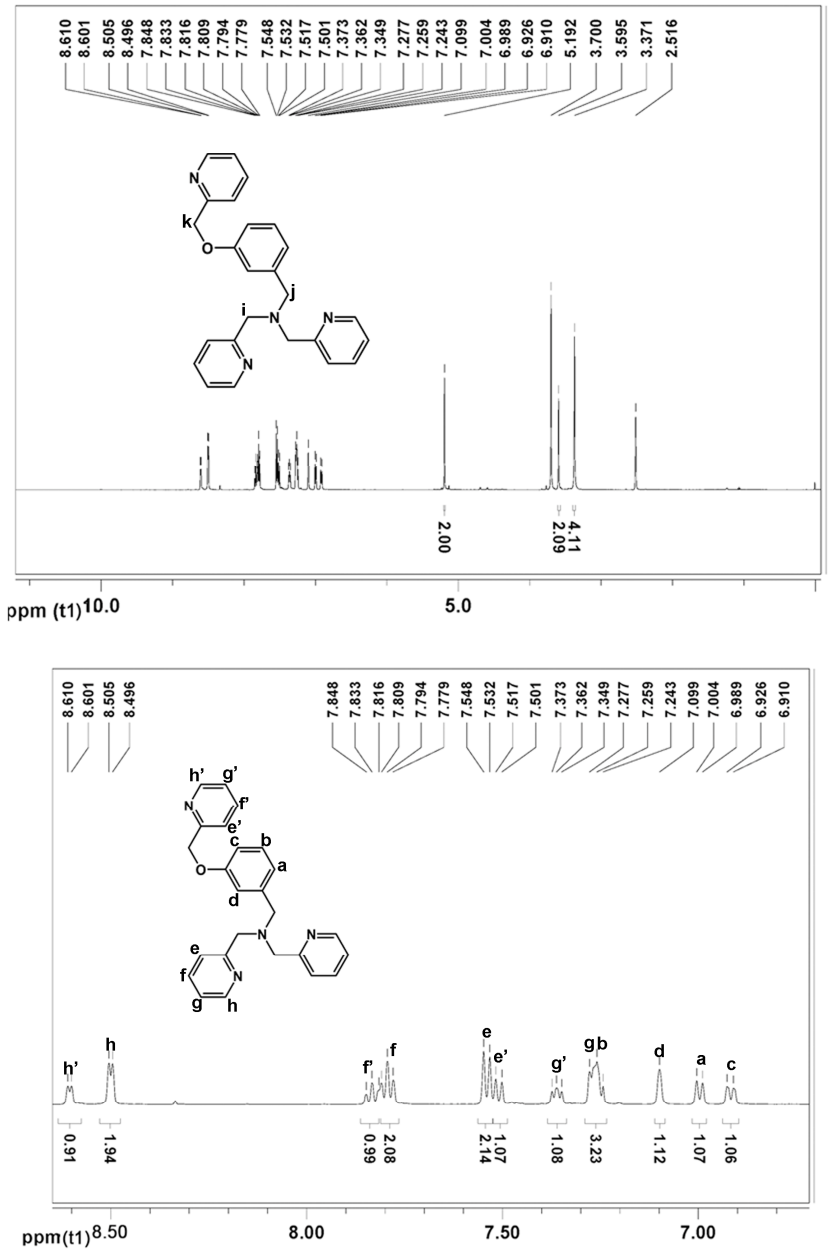
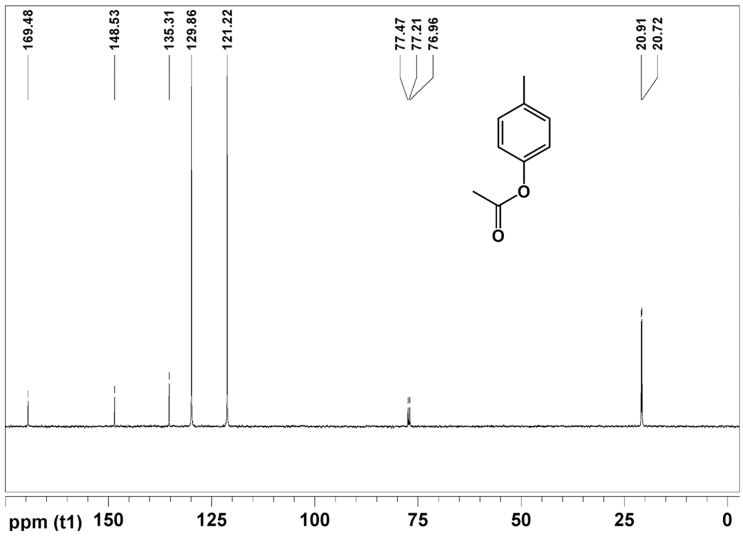
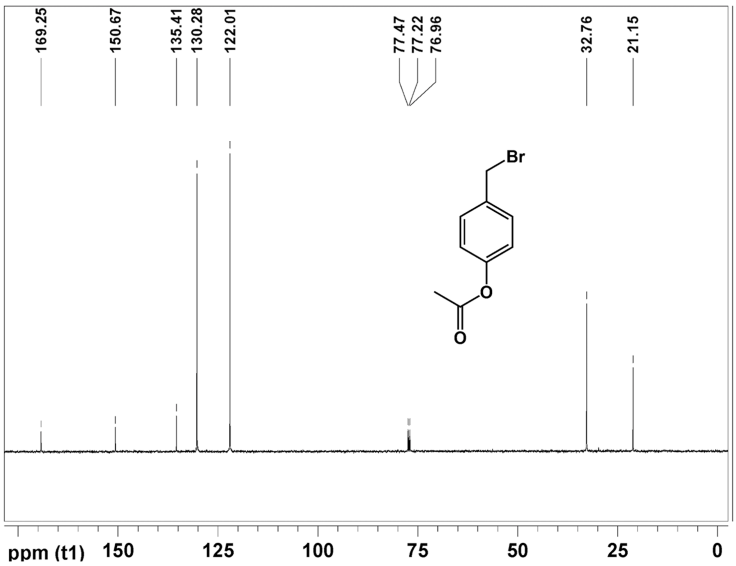
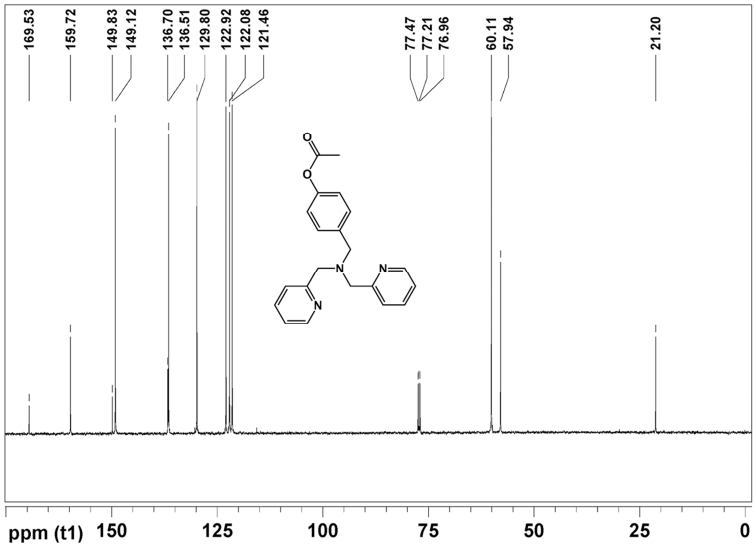
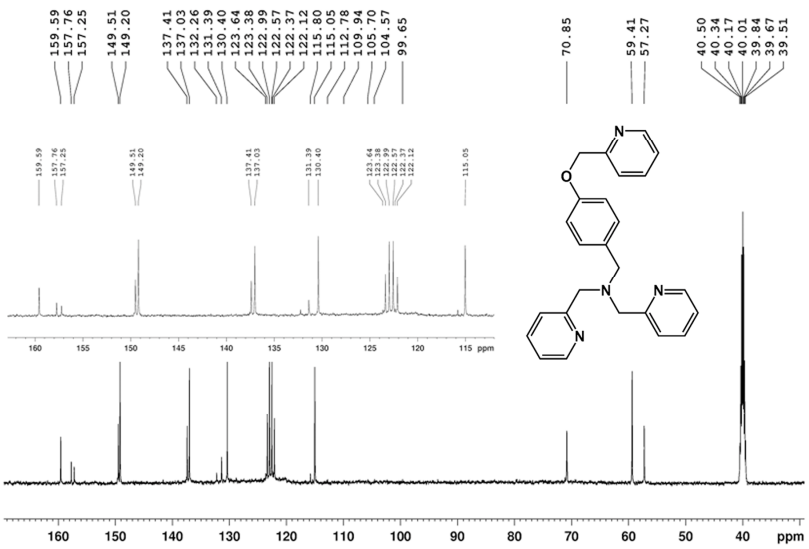


Figure S4. ^{1}H NMR spectra and corresponding proton signal assignments for different intermediates, L^{1} and L^{2}.


169.48
148.53
135.31
129.86
121.22
77.47
77.21
76.96
20.91
20.72
O
O
ppm (t1) 150 125 100 75 50 25 0


169.25
150.67
135.41
130.28
122.01
77.47
77.22
76.96
32.76
21.15
Br
O
O
ppm (t1) 150 125 100 75 50 25 0


169.53
159.72
149.83
149.12
136.70
136.51
129.80
122.92
122.08
121.46
77.47
77.21
76.96
60.11
57.94
21.20
O
O
N
N
N
ppm (t1) 150 125 100 75 50 25 0


159.59
157.76
157.25
149.51
149.20
137.41
137.03
132.26
131.39
130.40
123.64
123.38
122.99
122.57
122.37
122.12
115.80
115.05
112.78
109.94
105.70
104.57
99.65
70.85
59.41
57.27
40.50
40.34
40.17
40.01
39.84
39.67
39.51
N
O
N
N
N
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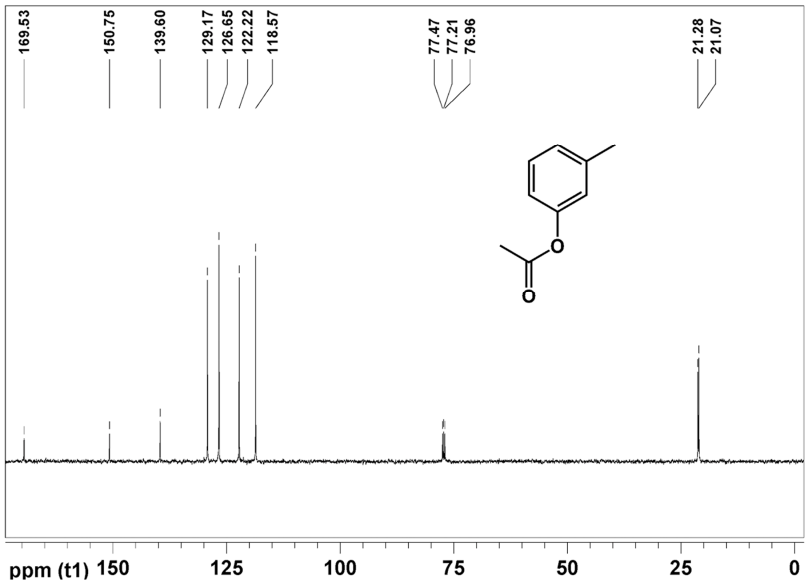
120
110
100
90
80
70
60
50
40
ppm


169.53
150.75
139.60
129.17
126.65
122.22
118.57
77.47
77.21
76.96
21.28
21.07
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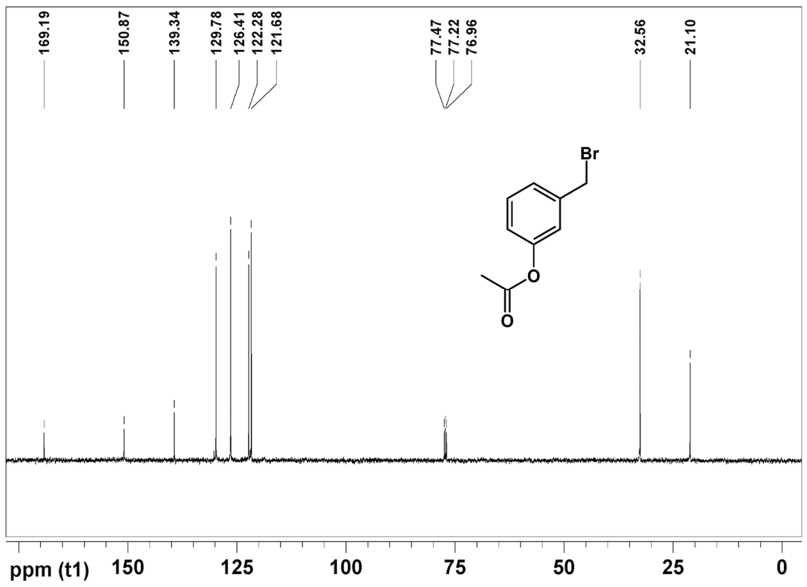
ppm (t1)
150
125
100
75
50
25
0


169.19
150.87
139.34
129.78
126.41
122.28
121.68
77.47
77.22
76.96
32.56
21.10
Br
O
O
ppm (t1)
150
125
100
75
50
25
0

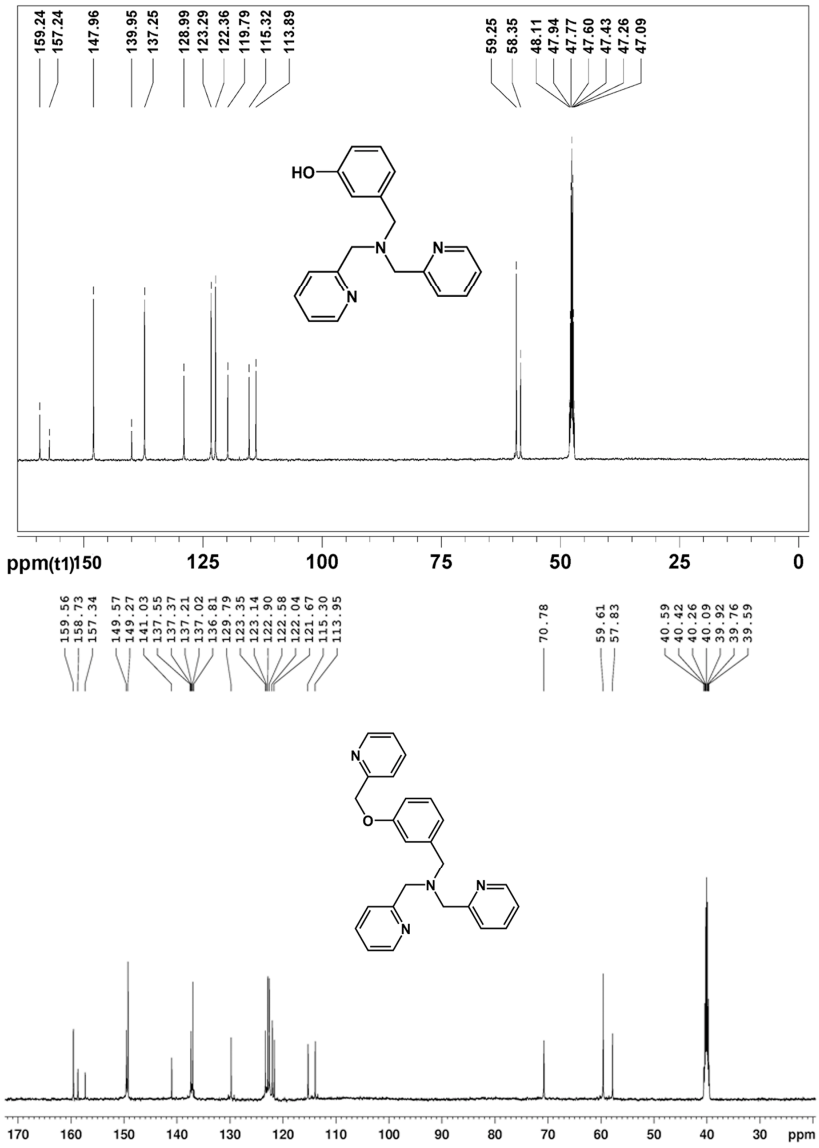


Figure S5. ^{13}C NMR spectra of different intermediates, L^1 and L^2.

Maxam-Gilbert Footprinting Experiments

5′-FAM (Carboxyfluorescein)-end-labeled 18mer- (3 μL, 20 μM; TaKaRa, Dalian) or 10mer-DNA (1 μL, 5 μM; Genescript, Nanjing) was incubated alone or with complex **3** or **4** respectively in 10 μL Tris buffer (0.05 M Tris, 0.1 M NaCl, pH 7.40) at 37 °C for 12 h. Formic acid (9 μL, 8.8%) was added to the solution and incubated at 37 °C for 7 min. Piperidine (150 μL, 1 M) was then added to the solution and the mixture was incubated at 90 °C for 30 min. Icy butanol (1.2 mL) was added to the mixture followed by shaking for 30 s at 4 °C and centrifuging to remove the supernatant. Sodium dodecyl sulfate (SDS, 150 μL, 1%) and butanol (1 ml) were added to the sample; after shaking for 30 s at 4 °C and centrifuging, butanol was removed. The isolated oligodeoxyribonucleotide was redissolved in 10 μL Tris buffer (0.05 M Tris, 0.1 M NaCl, pH 7.40) and separated by denaturing (7 M urea) polyacrylamide (20%) gel electrophoresis and visualized by autoradiography (Amersham Typhoon 9410).

Duplex **1**: 5′-CTCTGGTCTC-3′ ODN I -FAM
3′-GAGACCAGAG-5′ ODN II

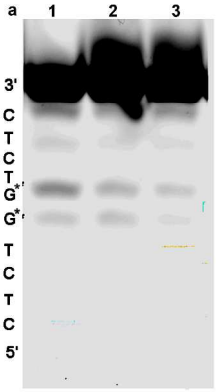


Figure S6. Polyacrylamide gel electrophoresis (PAGE) pattern of 5′-FAM-end-labeled duplex **1** (0.5 μM) without or with Cu-Pt complex. Lane 1, ODN I; Lane 2, ODN I + 1 μM complex **4**; Lane 3, ODN I + 1 μM complex **3**. The faded bands of G*G* in the presence of complex suggest that some GG has been platinated by the complex, which decreases the formic acid-catalyzed depurination and thus the subsequent cleavage by piperidine (V. Brabec, M. Leng, *Proc. Natl. Acad. Sci. USA* **1993**, 90, 5345-5349).

Duplex **2**: 5′-GAAGAAGTCACAAAATGT-3′ ODN III -FAM
3′-CTTCTTCAGTGTTTTACA-5′ ODN IV
Duplex **3**: 5′-ACATTTTGTGACTTCTTC-3′ ODN V -FAM
3′-TGTAAAACACTGAAGAAG-5′ ODN VI

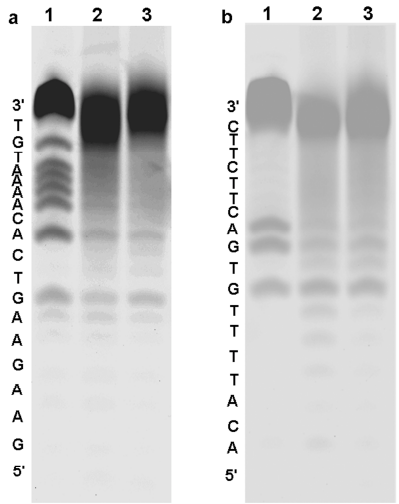


Figure S7. PAGE patterns of 5′-FAM-end-labeled duplex **2** or **3** (6 μM) without or with Cu-Pt complex. **a.** Lane 1, ODN III; Lane 2, ODN III + 12 μM complex **4**; Lane 3, ODN III + 12 μM complex **3**. **b.** Lane 1, ODN V; Lane 2, ODN V + 12 μM complex **4**; Lane 3, ODN V + 12 μM complex **3**. The faded bands of A and G in the presence of complex suggest that these nucleobases have been platinated by the complex.