Supporting Information: Deconvoluting the Reactivity of Two Intermediates Formed From Modified Pyrimidines**.**

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General Methods. All solvents were distilled before use. *tert*-Butylthiol was distilled over CaO. Dichloromethane, benzene, triethylamine and DMF were distilled from CaH_2. All photolyses were conducted in Pyrex tubes using a Rayonet photoreactor (RPR-100) equipped with 16 lamps with a maximum output at 350 nm. Anaerobic photolyses were carried out in sealed Pyrex tubes using standard freeze-pump-thaw cycles (three times). The oligonucleotide used here was the same as previously reported.[1] Radiolabeling was conducted using standard protocols,[2] which was followed

by hybridization with 1.5 eq. of complementary oligonucleotide in 10 mM potassium phosphate (pH 7.2) and 100 mM NaCl at 65 °C for 15 min and cooled to room temperature. Quantification of radiolabel oligonucleotides was carried out using a Molecular Dynamics phosphorimager equipped with ImageQuant Version TL software. LC samples were analyzed using an Agilent 1290 Infinity, with a RP-18 column (VARIAN, Microsorb-MV 100-5 C18 250 × 4.6 mm).

Photoreaction of oligonucleotides. Photoreactions of duplex DNA (20 nM) were carried out in 100 mM sodium phosphate (pH 7.2) buffer. The stock solution of MeO-NH_2•HCl (2 M) was titrated with 5 M NaOH solution to adjust the pH to ~ 7.0. It was then added to the photolysis mixture as appropriate for the desired concentration. HO-TEMPO (**13**) was dissolved in H_2O without adjusting the pH. After 1.5 h photolysis, an aliquot was mixed in 1:1 ratio with 90% formamide loading buffer and subjected to 20% denaturing PAGE analysis.

Photoreaction of monomers 4 and 5. Monomers **4** or **5** was dissolved in CH_3CN/H_2O (1:1) in stock solution (20 mM) and diluted with H_2O in reactions. Photoreaction solutions typically contained 50 μM of **4** or **5** and 100 mM phosphate buffer (pH 7.2), together with 10 μM of the internal standard 5-methyl-uridine (MeU). Photolyses were carried out for 1.5 h. Methoxyamine and HO-TEMPO solutions were prepared and added as described above. *t*-Butylthiol was dissolved in CH_3CN (1 M) and diluted by H_2O in the photolysis reaction as appropriate for the desired concentration. The general gradient employed to analyze the photolysate was 0-12.5 min, 3-11.5% B in A; 12.5-15 min, 11.5-50% B in A; 15-20 min, 50-80% B in A; at a flow rate 1.0 mL/min. [A: H2O; B: CH_3CN]. The photoreactions containing **13** were analyzed using a different gradient: 0-1, 3% B in A; 1-13.5 min, 3-11.5% B in A; 13.5-16 min, 11.5-15% B in A; 16-25 min, 15-35% B in A, 25-28 min, 35-80% B in A; at a flow rate 1.0 mL/min. [A: H2O; B: CH_3CN].

Determination of response factors. Response factors for compounds at 260 nm were calculated versus 5-methyluridine (MeU) as an internal standard. The following formula was used to calculate response factors ([X]/[IS])=Rf(A(X)/A(IS)), where [X] is the concentration of the compound of interest and [IS] is the concentration of the internal standard. A(X) and A(IS) are the areas under the peaks corresponding to the compound of interest and the internal standard, respectively (SI Table 1).

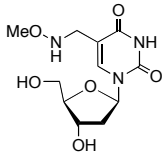
Supporting Information Table 1. Response factors and retention time using MeU as internal standard.

Compound	Response Factor	Retention time (min)
Thymidine	0.83	7.59
4	0.882	16.98
5	1.036	16.94
7	0.942	5.08
8	0.942[a]	5.75
11	1.293	16.79
14	0.779	20.72
15	0.844	7.04

[a.] The response factor for **8** was assumed to be the same as **7**.

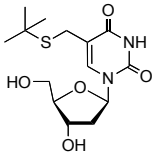
Digestion of photolyzed duplex 17. The hybridized **17** (2 nmol) with the complementary strand (2.5 nmol) was photolyzed at 350 nm in the presence of 300 mM methoxyamine or 200 mM **13** for 4 h. The stock solutions of 3 M methoxyamine and 2 M **13** were prepared as described above. The photolyzed duplex was precipitated twice from 0.3 M NaOAc (pH 5.2) followed by washing with 70% cold ethanol. The pallet was then suspended in 17.5 μL 1 × Antarctic phosphatase buffer (50 mM Bis-Tris-Propane HCl, 1 mM $MgCl_2$, 0.1 mM $ZnCl_2$, pH 6.0 at 25 ^oC), to which was added 1 μL of nuclease P1 (1 unit/μL), 1 μL phosphodiesterase II (bovine spleen, 10 unit/μL) and 0.5 μL DNase II (10 unit/μL). After the mixture was incubated at 37 ^oC for 2 h, 3 μL of 10 × NEB buffer 3 (1 M NaCl, 500 mM Tris-HCl, 100 mM $MgCl_2$, 1 mg/mL BSA, pH 7.9 at 25 ^oC) with 2.4 μL 500 mM $MgCl_2$, 1 μL phosphodiesterase I (snake venom, 0.105 unit/μL), 1 μL shrimp alkaline phosphatase (1 unit/μL) and

2.6 μL H_2O were added. The resulting solution was incubated at 37 ^oC for 2 h followed by filtration through 0.22 μm. Half of the filtrate (~ 15 μL) was directly subject to LC analysis. The remaining solution (~ 15 μL) was mixed with 200 pmol of **15** or 250 pmol of **14** before LC analysis.

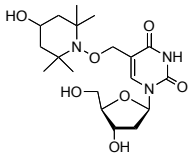


Synthesis of 5-(*N*-methoxymethylamine)-2'-deoxyuridine (15). To a solution of 3', 5'-*O*-diacetyl-2'-deoxyuridine (150 mg, 0.46 mmol) in distilled benzene (5 mL) was added *N*-bromosuccinimide (106 mg, 0.6 mmol) and azobisisobutyronitrile (AIBN, 8 mg, 0.06 mmol). The mixture was heated to reflux for 3 h, during which time the color changed from colorless to orange. The solution was cooled down and the solvent was removed to give the crude allylic bromide (**12**), which was used without purification. To a solution of MeO-NH_2•HCl (76.8 mg, 0.92 mmol) in DMF (2.5 mL), was added triethylamine (TEA, 130 μL, 0.92 mmol) via syringe. White precipitate crushed out upon the addition of TEA. The mixture was stirred at 25 °C for 1 h. A solution of **12** in DMF (2.5 mL) was then added. After stirring overnight, the mixture was poured into a beaker containing 30 mL of water and extracted with methylene chloride. The organic phases were combined, washed with water, and brine. Evaporation of the solvent gave the crude product, which was purified by flash chromatography (CH_2Cl_2:MeOH, 50:1) to give a pale yellow foam (45 mg, 26% for two steps): ^{1}H-NMR ($CDCl_3$) δ 9.13 (br, 1H), 7.49 (s, 1H), 6.29 (dd, 1H, *J* = 7.2, 4.8 Hz), 5.18-5.15 (m, 1H,), 4.39-4.17 (m, 3H), 3.81-3.64 (m, 2H), 3.47 (s, 3H), 2.44 (ddd, 1H, *J* = 11.9, 4.1, 1.4 Hz), 2.15 (ddd, 1H, *J* = 11.9, 7.5, 3.2 Hz), 2.08 (s, 3H), 2.05 (s, 3H). 3', 5'-*O*-Diacetyl-5-(*N*-methoxymethylamine)-2'-deoxyuridine (45 mg, 0.12 mmol) was dissolved in methanol (3 mL), to which was added a concentrated solution of ammonia in methanol (1 mL, 7 M). The resulting yellow solution was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by flash column chromatography (CH_2Cl_2:MeOH, 10:1) to give **15** as a colorless solid (28 mg, 81%): ^{1}H-NMR (MeOH-d_4) δ 8.05 (s, 1H), 6.32 (t, 1H, *J* = 11.2 Hz), 4.45-4.41 (m, 1H), 3.95 (q, 1H, *J*

= 3.6 Hz), 3.85-3.73 (m, 4H), 3.53 (s, 3H), 2.36-2.20 (m, 2H); ^{13}C-NMR (MeOH-d_4) δ 164.2, 150.7, 139.4, 109.7, 87.5, 85.1, 70.7, 61.4, 59.8, 39.9; IR (neat) 3394, 2940, 2345, 1734, 1691, 1679, 1469, 1276 cm^{-1}; HRMS *m/z* (M+H$^+$) calc. 288.1190, found 288.1187.



Synthesis of 5-(*t*-butylthiomethyl)-2'-deoxyuridine (11). The allylic bromide (**12**, 214mg, 0.46 mmol) was obtained by the same procedure as described above. To a suspension of NaH (44 mg, 60% in oil, 1.84 mmol) in DMF (2.5 mL) was added *t*-butylthiol (104 mL, 0.92 mmol) via syringe. After stirring the mixture at room temperature for 1 h, a solution of the allylic bromide in DMF (2.5 mL) was added. The resulting solution was stirred at room temperature overnight. The reaction was quenched by pouring into 30 mL water and extracted with methylene chloride. The organic phases were separated, washed with water, and brine. Evaporation of the solvent gave the crude product, which was purified by flash chromatography (hexane:ethyl acetate, 1:1) to give a yellow solid (80 mg, 42%):^{1}H-NMR ($CDCl_3$) δ 9.71-9.56 (m, 1H), 7.57 (s, 1H), 6.30 (t, 1H, *J* = 8.0 Hz), 5.21 (dd, 1H, *J* = 6.4, 1.6 Hz), 4.37-4.25 (m, 2H), 4.24-4.21 (m, 1H), 3.53-3.41 (m, 2H), 2.47 -2.41 (m, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 1.30 (s, 9H). Similarly, the purified 3', 5'-*O*-diacetyl-5-*t*-butylthiomethyl-2'-deoxyuridine (80 mg, 0.19 mmol) was deprotected by a concentrated solution of ammonia in methanol (1 mL, 7 M). The solvent was evaporated after overnight stirring and the residue was purified by flash column chromatography (CH_2Cl_2:MeOH, 20:1) to give **11** as a white foam (63 mg, 100%): ^{1}H-NMR (MeOH-d_4) δ 8.05 (s, 1H), 6.31 (t, 1H, *J* = 6.6 Hz), 4.45-4.42 (m, 1H), 3.96 (dd, 1H, *J* = 7.0, 3.4 Hz), 3.82 (dd, 1H, *J* = 11.8, 3.4 Hz), 3.77 (dd, 1H, *J* = 11.8, 3.8 Hz), 3.56-3.48 (m, 2H), 2.34-2.21 (m, 2H), 1.36 (s, 9H); ^{13}C-NMR (MeOH-d_4) δ 163.6, 150.6, 138.4, 112.1, 87.5, 85.1, 70.8, 61.5, 42.3, 39.9, 29.8, 23.6, 20.7; IR (neat) 3369, 2926, 2346, 1734, 1666, 1469, 1277 cm^{-1}; HRMS m/z (M+H$^+$) calc. 331.1322, found 331.1316.



Synthesis of 14. Monomer **4** (50 mg, 0.13 mmol) was mixed with **13** (216.8 mg, 1.3 mmol) in 3 mL CH_3CN/H_2O (1:1) in a Pyrex tube. Argon was bubbled through the solution for 0.5 h. The photolysis was carried out for 3 h under argon. The solvent was evaporated *in vacuo* to yield the crude product, which was subjected to flash column chromatography (CH_2Cl_2:MeOH, 10:1) to give **14** as a white foam (5 mg, 9%): ^{1}H-NMR (MeOH-d_4) δ 8.07 (s, 1H), 6.3 (t, 1H, *J* = 6.6 Hz), 4.53 (d, 1H, *J* = 11.0 Hz), 4.48 (d, 1H, *J* = 11.0 Hz), 4.42-4.39 (m, 1H), 3.95-3.82 (m, 2H), 3.77 (dd, 1H, *J* = 11.8, 3.4 Hz), 3.72 (dd, 1H, *J* = 11.8, 3.4 Hz), 2.35-2.18 (m, 2H), 1.80-1.73 (m, 2H), 1.48-1.41 (m, 2H), 1.29 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H), 1.16 (s, 3H); ^{13}C-NMR (MeOH-d_4) δ 150.8, 139.6, 128.0, 110.6, 87.6, 85.2, 71.0, 70.6, 62.0, 61.5, 60.0, 40.1, 32.3, 29.0, 20.1; IR (neat) 3369, 2926,1678, 1470, 1275, 1050 cm^{-1}; HRMS m/z ($M+H^+$) calc. 414.2235, found 414.2244.

[1] Hong, I. S.; Ding, H.; Greenberg, M. M. *J. Am. Chem. Soc.* **2006**, *128*, 485-491

[2] Maniatis, T.; Fritsch, E. F.; Sambrook, J. *Molecular Cloning*; Cold Spring Harbor Laboratory, Cold Spring Harbor, NY., **1982**.

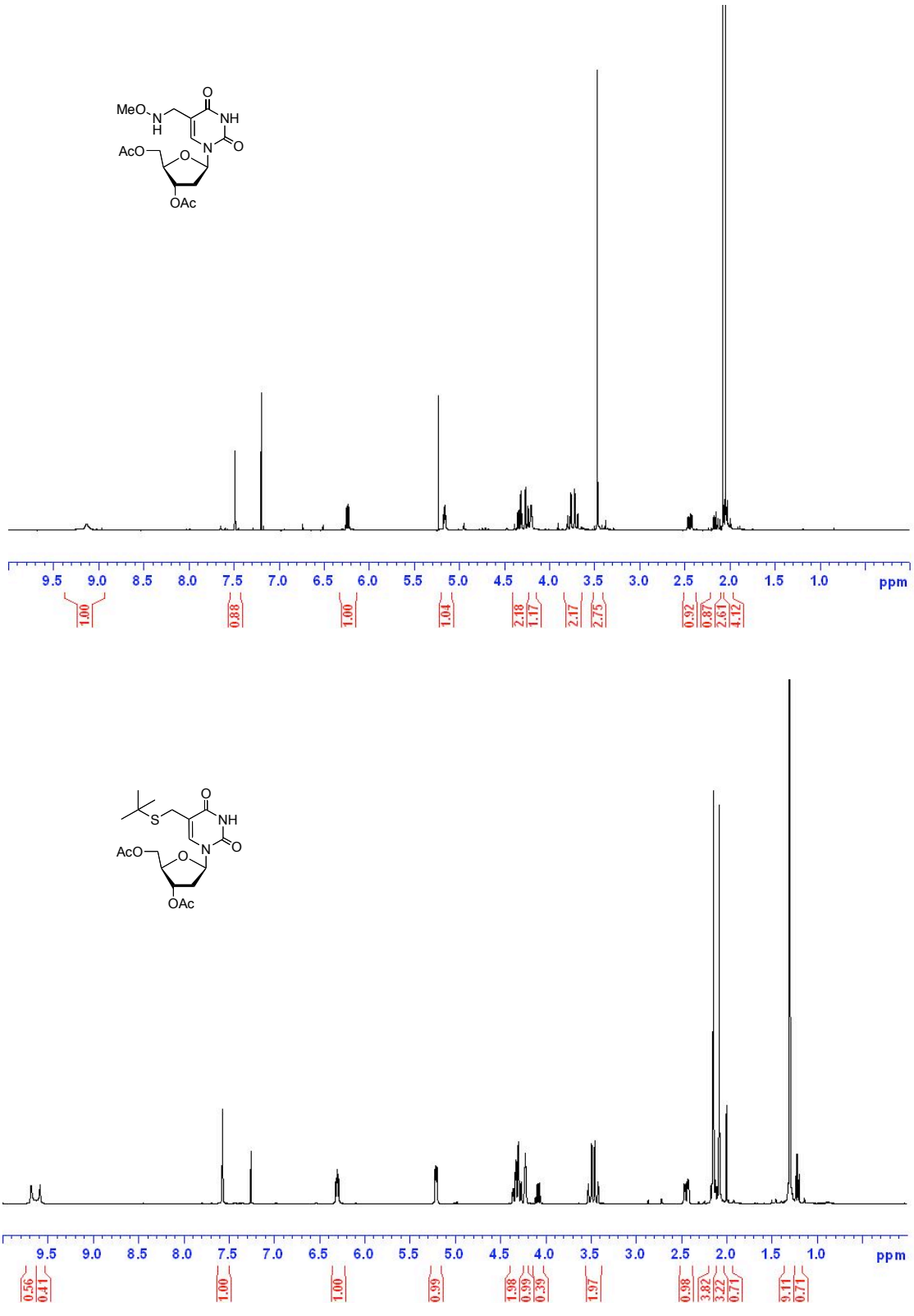


Figure S1. ^{1}H NMR spectra of 3', 5'-*O*-diacetyl-5-(*N*-methoxymethylamine)-2'-deoxyuridine and 3', 5'-*O*-diacetyl-5-(*t*-butylthiomethyl)-2'-deoxyuridine.

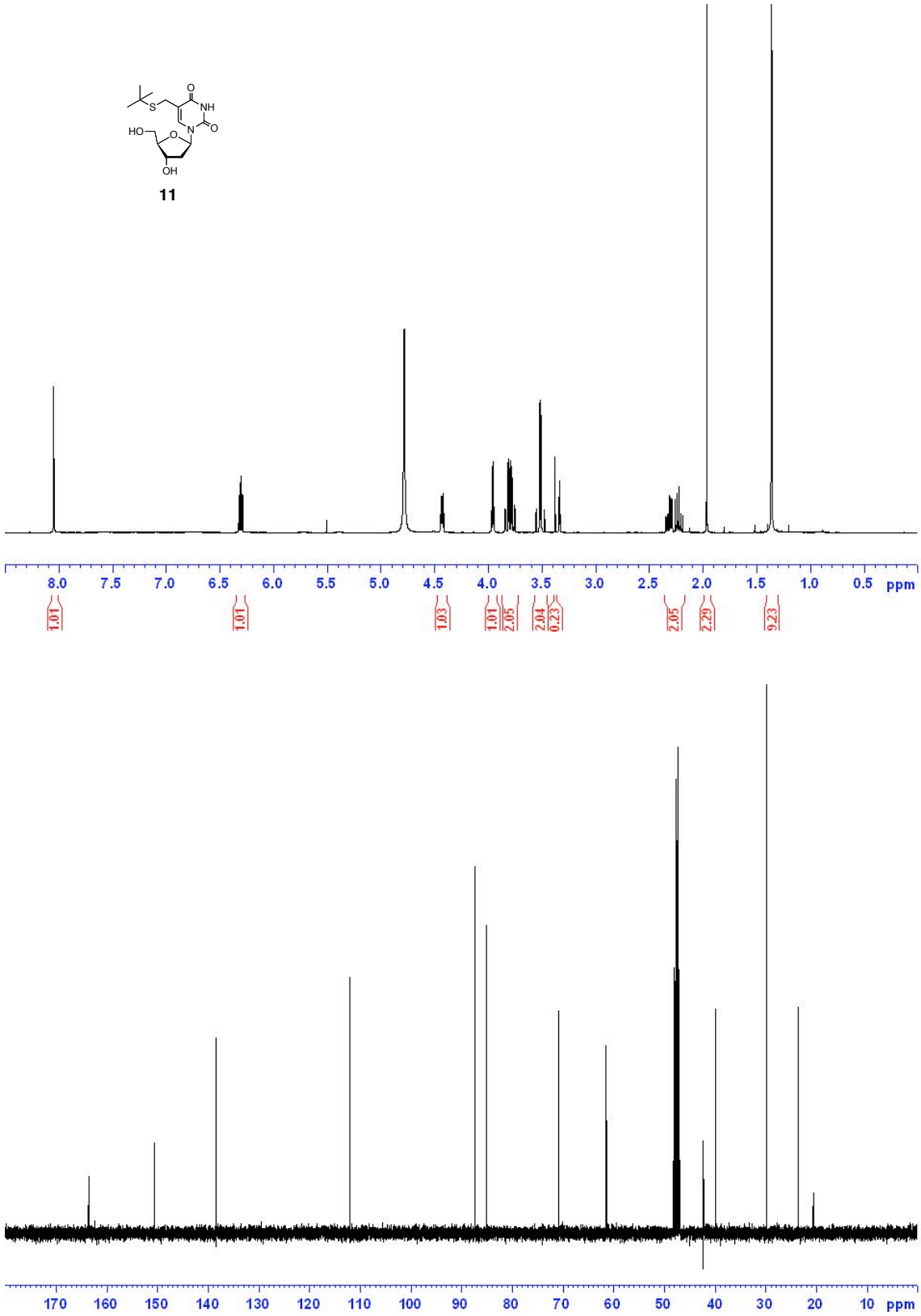


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of **11**.

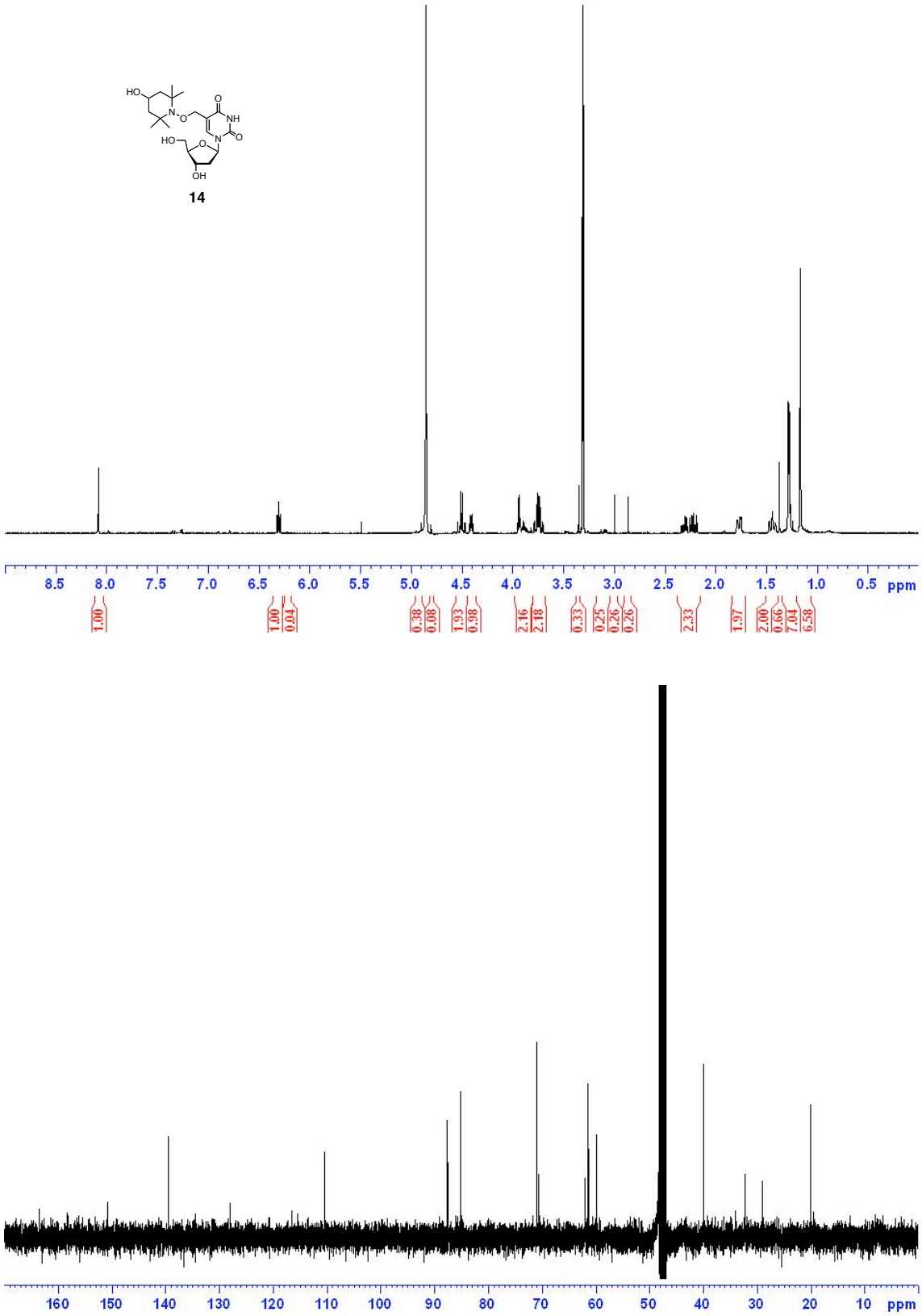


Figure S3. ^{1}H NMR and ^{13}C NMR spectra of **14**.

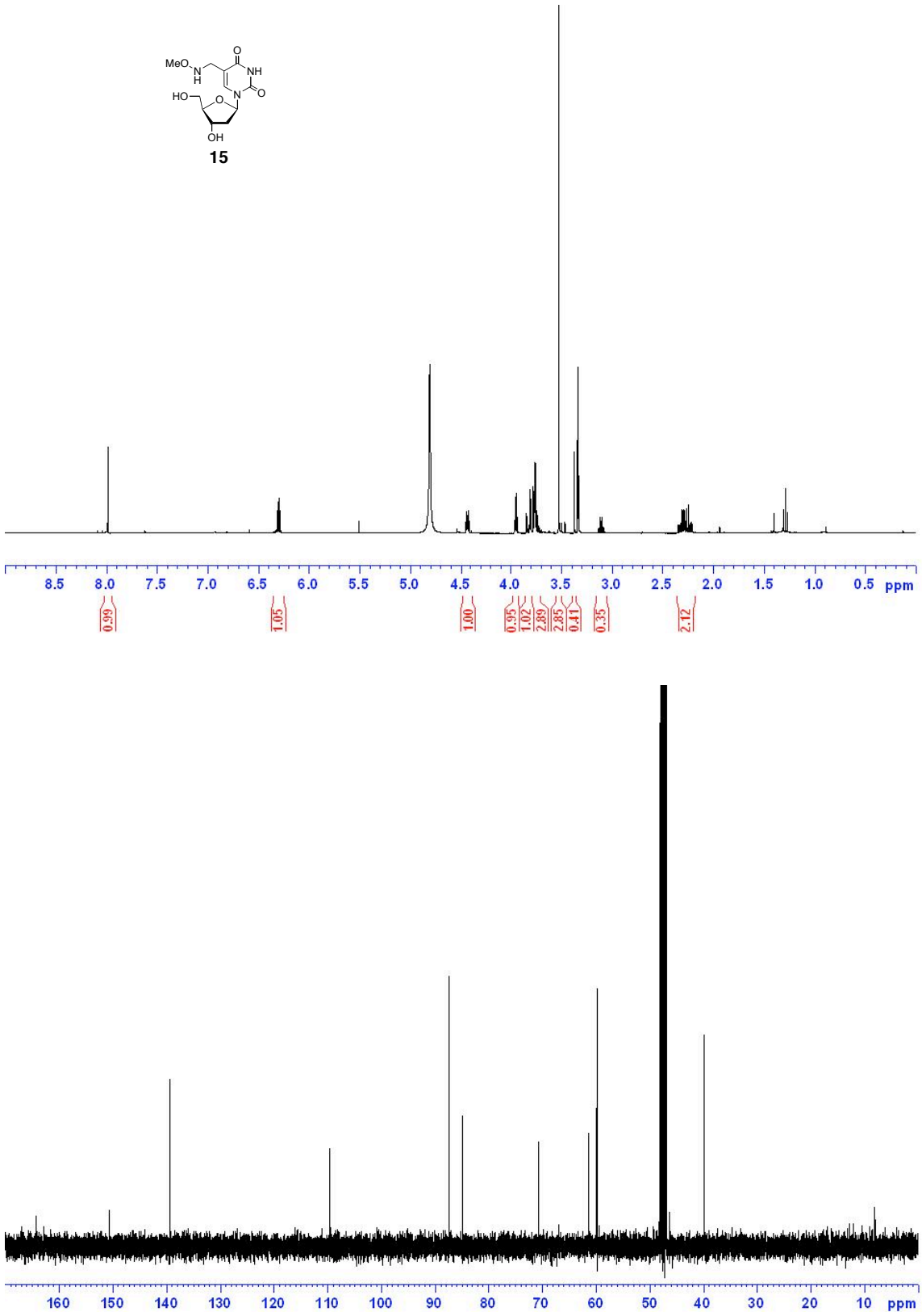


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of **15**.

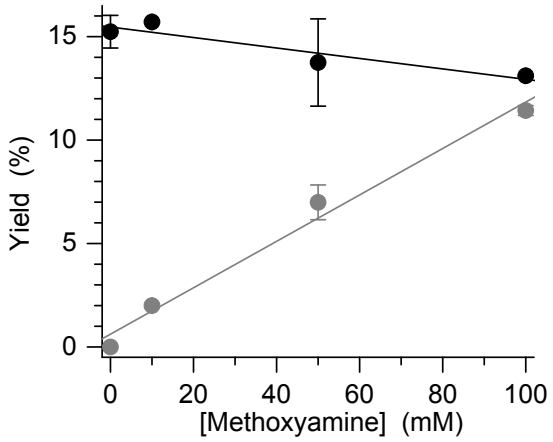


Figure S5. Effect of methoxyamine on product distribution from **5** under anaerobic conditions.

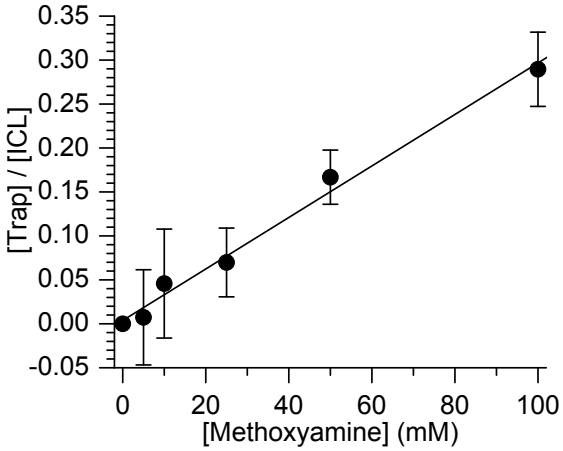


Figure S6. Effect of methoxyamine on interstrand cross-link formation from **5** (**17**) under anaerobic conditions.

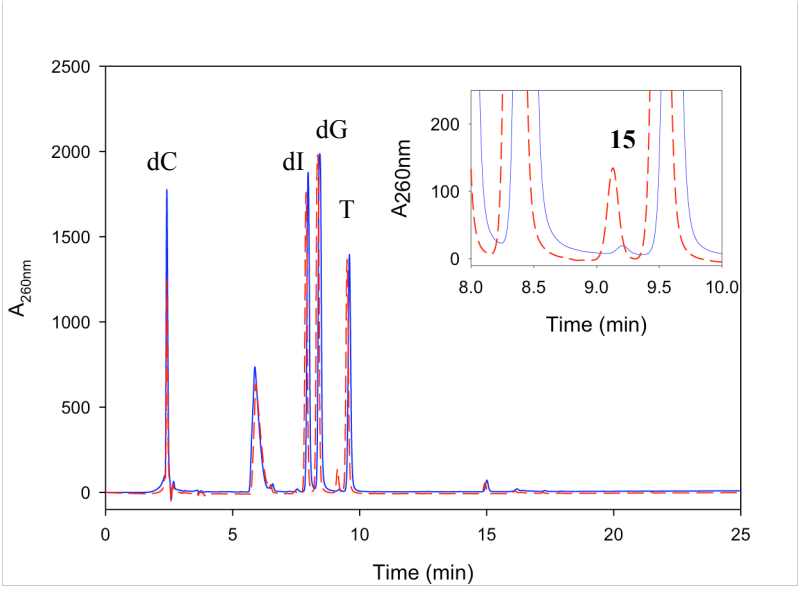


Figure S7. Chomatograms of digested duplex **17** photolyzed in the presence of methoxyamine (blue line represents the digested duplex, the red dashed line is the coinjection with 200 pmol of **15**).

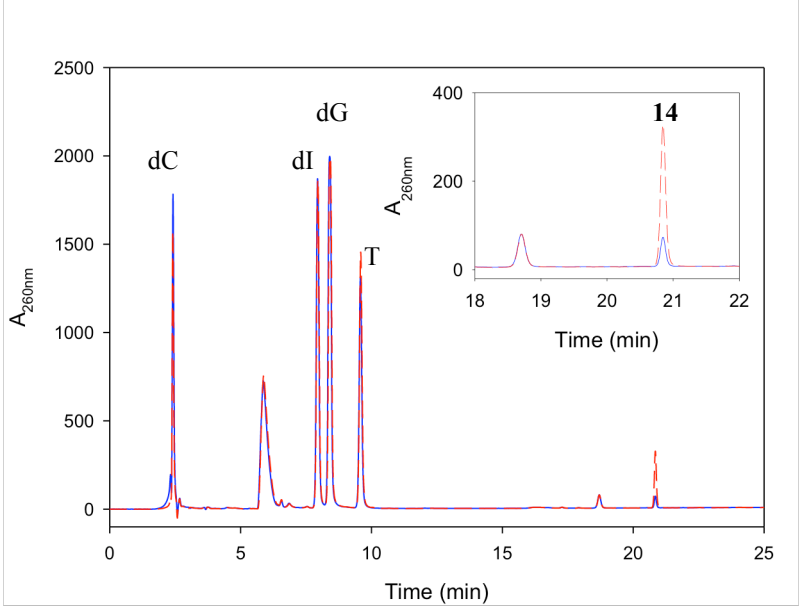


Figure S8. Chomatograms of digested duplex **17** photolyzed in the presence of HO-TEMPO (**13**). (blue line represents the digested duplex, the red dashed line is the coinjection with 250 pmol of **14**).

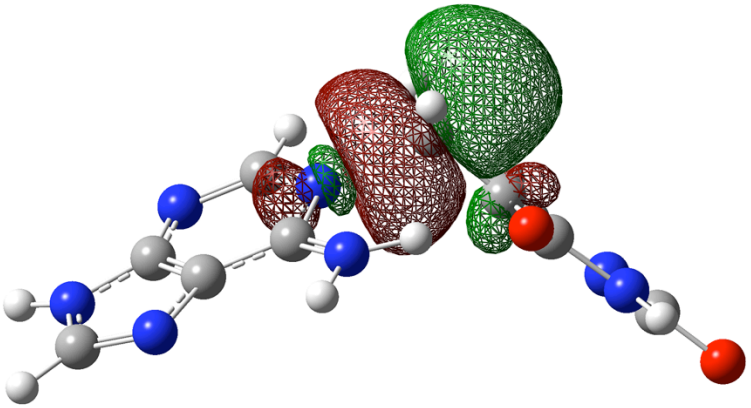


Figure S9. BHandHLYP/6-311G (d,p) generated depiction of the LP_N → SOMO interaction in **21**.

Table S2. Effect of HO-TEMPO (**13**) on interstrand cross-link (ICLs) yields from **17** under anaerobic conditions.

[HO-TEMPO] (mM)	ICL (%)
0	23.2 ± 0.1
1	22.8 ± 0.1
5	23.1 ± 0.5
10	22.8 ± 0.3
20	22.0 ± 0.9
100	22.1 ± 0.7

Table S3. Effect of HO-TEMPO (**13**) on interstrand cross-link (ICLs) yields from **17** under aerobic conditions.

[HO-TEMPO] (mM)	ICL (%)
0	22.9 ± 1.5
0.5	23.2 ± 0.6
5	23.3 ± 0.2
50	23.9 ± 0.1

Table S4. Calculated energy barriers ($\Delta E^{\ddagger}$) for the reaction of ademine (17) with the uridinylmethyl radical (**18**) (Scheme 5), and (imaginary) frequency (ν) for the transition state vector in **21**.

Method	$\Delta E_1^{\ddagger}$	$\Delta E_1^{\ddagger}$ + ZPE	υ
ROHF/6-31G(d)	210.7	217.0	1846i
ROHF/6-311G(d,p)	213.5	219.5	1858i
BHandHLYP/6-311G(d,p)	94.9	103.2	460i
BHandHLYP/cc-pVDZ	90.3	97.1	452i
BHandHLYP/aug-cc-pVDZ	99.9	114.2	392i
BHandHLYP/6-311G(2d,p)	96.5	103.7	464i
BHandHLYP/6-311++G(2d,p)	100.4	108.2	468i
M06-2X/6-311G(d,p)	58.8	64.9	455i
ROMP2/6-311G(d,p)//BHandHLYP/6-311G(d,p)	65.2		
ROMP2/cc-pVDZ//BHandHLYP/cc-pVDZ	64.7		
ROMP2/6-311G(2d,p)//BHandHLYP/6-311G(2d,p)	57.9		
ROMP2/6-311++G(2d,p)//BHandHLYP/6-311++G(2d,p)	58.1		
ROMP2/6-311G(d,p)//M06-2X/6-311G(d,p)	65.3		

Gaussian Archive Entries for optimized geometries for 21.

ROHF/6-31G(d)

1\1\GINC-MERRI044\FTS\ROHF\6-31G(d)\C10H10N7O2(2)\SHORVAT\17-Apr-2013\
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ROHF/6-311G(d,p)

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,-0.549233803\N,-3.948219639,0.9757196848,0.2055848224\H,-4.5515037958
,1.7644782693,0.1227629554\O,-2.3053060159,2.3473162853,0.8519005514\\
Version=AM64L-G09RevC.01\State=2-A\HF=-915.5446845\RMSD=3.943e-09\RMSF
=1.146e-05\Dipole=1.2675493,-1.7617657,-0.4190002\Quadrupole=-12.24744
25,8.2293744,4.0180682,-2.4153309,-4.0515167,0.5579053\PG=C01 [X(C10H1
0N7O2)]\\@

BHandHLYP/6-311G(d,p)

1\1\GINC-MERRI060\FTS\UBHandHLYP\6-311G(d,p)\C10H10N7O2(2)\SHORVAT\27-
Mar-2013\0\\#BHandHLYP/6-311G** 6D INT(grid=ultrafine) OPT=(TS,readfc,
noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman geom=checkpoint guess
=check\\thymine/adenine radical ts\\0,2\C,1.8274824604,-1.5374069691,-
4.5044220189\H,2.1639533154,-1.709423479,-5.507809202\N,1.1112264634,-
0.5339091378,-4.1190011624\C,0.9353621882,-0.7407900828,-2.7754104272\
C,0.2249692943,0.0007273605,-1.8142801884\N,-0.4280012944,1.106151795,
-2.1094379064\H,-1.0999244082,1.5609335576,-1.4747188076\H,-0.43463755
56,1.3689467045,-3.0745344778\C,0.9259602006,-1.6355661949,-0.28968381
83\H,0.8902970291,-1.9436295825,0.741765151\N,1.5830536891,-2.38977996
08,-1.1218869105\C,1.5631627486,-1.895342389,-2.3623031333\N,2.1350215
75,-2.4010575844,-3.4864733408\H,2.6695508428,-3.2434483937,-3.5447517

442\N,0.2737308277,-0.4946573619,-0.5604438882\C,-0.6110118015,0.30582
01167,0.7834629163\H,-0.057210165,-0.1841422786,1.5698582113\H,-0.2799
785326,1.3136336133,0.603023389\C,-2.0066451996,0.1159442105,0.7800593
136\C,-2.6350468084,-1.040377663,1.3382594909\C,-2.8018227875,1.100888
2139,0.1404519713\H,-2.1406356691,-1.6589365412,2.0662252784\C,-4.8452
754035,-0.1056880645,0.8493701738\N,-4.0356953699,-1.0423497378,1.4015
716057\H,-4.5200044241,-1.8260180199,1.7865095943\O,-6.0479125364,-0.1
639952542,0.8618358216\N,-4.1707691397,0.9417875963,0.2481931796\H,-4.
7439903387,1.639809494,-0.1822680201\O,-2.3766774086,2.0709528517,-0.4
961045444\\Version=AM64L-G09RevC.01\State=2-A\HF=-920.4854706\S2=0.759
89\S2-1=0.\S2A=0.750051\RMSD=9.181e-09\RMSF=7.237e-06\Dipole=3.2739991
,-1.6250425,-1.2770185\Quadrupole=-11.4623297,1.2420596,10.2202701,-3.
6937055,-2.452673,3.015119\PG=C01 [X(C10H10N7O2)]\\@

BHandHLYP/cc-pVDZ

1\1\GINC-MERRI016\FTS\UBHandHLYP\CC-pVDZ\C10H10N7O2(2)\SHORVAT\27-Mar-
2013\0\\#BHandHLYP/cc-pvdz 6D INT(grid=ultrafine) OPT=(TS,readfc,noeig
entest,maxcyc=200) IOP(2/17=4) Freq=noraman geom=checkpoint guess=chec
k\\thymine/adenine radical ts\\0,2\C,1.8377829474,-1.5334025243,-4.514
1936627\H,2.17735349,-1.7039197404,-5.5249818446\N,1.1081584036,-0.532
8751394,-4.1291983653\C,0.9375251215,-0.7434658315,-2.7832270295\C,0.2
201391493,-0.0077854019,-1.8172193372\N,-0.4450094693,1.0940679571,-2.
10797083\H,-1.1243255513,1.5463372575,-1.4667092748\H,-0.4546231386,1.
3541863168,-3.0786306992\C,0.9432988728,-1.6404986887,-0.2928479169\H,
0.9123088471,-1.9496738388,0.7464421276\N,1.6105659272,-2.3924221538,-
1.125783865\C,1.5805855311,-1.8942043173,-2.3687888316\N,2.1568800412,
-2.3942370154,-3.4954663706\H,2.7036341973,-3.233630324,-3.5567977158\
N,0.2758752912,-0.5047572637,-0.5610022498\C,-0.6129567716,0.295932222
1,0.7864345561\H,-0.0540422455,-0.2012941764,1.5748971641\H,-0.2784391
038,1.3089406441,0.5970780634\C,-2.0118045035,0.1103314536,0.785022503
\C,-2.650570682,-1.0408805055,1.3511595224\C,-2.8036042163,1.100907445
4,0.1417850314\H,-2.1575360213,-1.6612046884,2.0907242076\C,-4.8540619
678,-0.0893635394,0.8554657324\N,-4.0515890924,-1.0292645759,1.4168806

876\H,-4.5466496881,-1.8146113237,1.7968765956\O,-6.0612031241,-0.1436
398654,0.8610970553\N,-4.1731162704,0.9569190322,0.2559325727\H,-4.745
6087631,1.6547612598,-0.1862244756\O,-2.3704354189,2.0678241441,-0.503
696844\\Version=AM64L-G09RevC.01\State=2-A\HF=-920.3300653\S2=0.759955
\S2-1=0.\S2A=0.750052\RMSD=7.341e-09\RMSF=4.404e-07\Dipole=3.1589321,-
1.5637333,-1.2765861\Quadrupole=-10.8838889,1.3105088,9.5733802,-3.775
7633,-2.585439,2.922077\PG=C01 [X(C10H10N7O2)]\\@

BHandHLYP/aug-cc-pVDZ

1\1\GINC-MERRI022\FTS\ROBHandHLYP\Aug-CC-pVDZ\C10H10N7O2(2)\SHORVAT\06
-May-2013\0\\#BHandHLYP/aug-cc-pvdz scf=(conver=5) 6D INT(grid=ultrafi
ne) OPT=(TS,readfc,noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman ge
om=checkpoint guess=check\\thymine/adenine radical ts\\0,2\C,-4.614380
7282,-0.8400948877,-1.087070129\H,-5.4819553373,-1.2786302225,-1.55100
1428\N,-3.5757792429,-1.4954801861,-0.6713722714\C,-2.7452536356,-0.52
61804907,-0.1614314799\C,-1.4633715992,-0.6146323775,0.4164472863\N,-0
.822390966,-1.7621699774,0.5600918012\H,0.167123714,-1.8377291435,0.83
77814881\H,-1.2838872019,-2.5775750887,0.2050143847\C,-1.5932061869,1.
7138363798,0.6514529925\H,-1.0754175193,2.5938393723,1.0095015263\N,-2
.7684976223,1.8878031776,0.1081450882\C,-3.310755701,0.7279783706,-0.2
822693277\N,-4.5151819942,0.5120506064,-0.880998969\H,-5.1893273841,1.
2121323173,-1.1230437193\N,-0.9343160406,0.5577175258,0.8272495207\C,0
.7234878825,0.6277445651,1.6166603266\H,0.570192387,1.6177042575,2.028
9077995\H,0.5616505973,-0.1699731006,2.3273704906\C,1.8096211257,0.462
9931274,0.7383312389\C,2.3632953311,1.5408069228,-0.0235804784\C,2.328
4067017,-0.8503943161,0.5605620728\H,2.1973580015,2.5742691415,0.24269
15994\C,4.1011163824,0.0611724656,-0.9031885379\N,3.5401738426,1.28540
26174,-0.7385584279\H,3.9741711758,2.0117286331,-1.2729169641\O,5.0796
90297,-0.1445465967,-1.5880532611\N,3.4593794554,-0.9608550949,-0.2276
208492\H,3.8475282026,-1.8774030943,-0.3497511776\O,1.8485923882,-1.88
74362269,1.0426323998\\Version=AM64L-G09RevC.01\State=2-A\HF=-920.3890
672\RMSD=4.718e-06\RMSF=3.982e-06\Dipole=-3.6455986,1.1468182,0.167279
3\Quadrupole=-0.3252967,1.8975609,-1.5722642,3.5182508,11.6847914,1.53

63668\PG=C01 [X(C10H10N7O2)]\\@

BHandHLYP/6-311G(2d,p)

1\1\GINC-MERRI016\FTS\UBHandHLYP\6-311G(2d,p)\C10H10N7O2(2)\SHORVAT\27
-Mar-2013\0\\#BHandHLYP/6-311G(2d,p) 6D INT(grid=ultrafine) OPT=(TS,re
adfc,noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman geom=checkpoint
guess=check\\thymine/adenine radical ts\\0,2\C,1.8125691766,-1.5414570
259,-4.5015463878\H,2.144238502,-1.7150003205,-5.5058301785\N,1.089818
6441,-0.5445326989,-4.1175707502\C,0.924447906,-0.7459063646,-2.772353
3208\C,0.2155892175,-0.0093651388,-1.8106478692\N,-0.448680407,1.08830
51822,-2.1024103302\H,-1.1143735233,1.5417857239,-1.4598936035\H,-0.46
86879694,1.3458889571,-3.0681101388\C,0.9404712847,-1.6281182479,-0.28
68479387\H,0.9148802117,-1.9321472076,0.7457200186\N,1.5994440501,-2.3
776097424,-1.1188591325\C,1.5654981029,-1.8895032846,-2.3598834235\N,2
.1349832454,-2.3950489526,-3.4834308743\H,2.6775062098,-3.2312377136,-
3.5427765608\N,0.2758478536,-0.4983234323,-0.5579171988\C,-0.610112614
9,0.3041416674,0.7897671573\H,-0.0569126401,-0.1910724305,1.5719558438
\H,-0.2765772195,1.3097338327,0.6083070863\C,-2.0025013357,0.118927748
8,0.7841426814\C,-2.6340443789,-1.0363521516,1.3323517191\C,-2.7936108
816,1.1091759763,0.1524492146\H,-2.1436512041,-1.655273103,2.062326917
5\C,-4.8331973608,-0.1008897778,0.8327266326\N,-4.0318239857,-1.037733
1784,1.3892903647\H,-4.5205161611,-1.8323250763,1.7435640601\O,-6.0352
61324,-0.1674905786,0.82338968\N,-4.160183332,0.9575478679,0.257684102
\H,-4.7310921104,1.6509295682,-0.1815083495\O,-2.3655361641,2.08202672
01,-0.4770329145\\Version=AM64L-G09RevC.01\State=2-A\HF=-920.5115921\S
2=0.760249\S2-1=0.\S2A=0.750055\RMSD=5.799e-09\RMSF=5.116e-06\Dipole=3
.1979303,-1.5971908,-1.2658021\Quadrupole=-11.1780045,1.3238366,9.8541
678,-3.8467555,-2.5926875,2.9928387\PG=C01 [X(C10H10N7O2)]\\@

BHandHLYP/6-311++G(2d,p)

1\1\GINC-MERRI004\FTS\UBHandHLYP\6-311++G(2d,p)\C10H10N7O2(2)\SHORVAT\
28-Mar-2013\0\\#BHandHLYP/6-311++G(2d,p) 6D INT(grid=ultrafine) OPT=(T
S,readfc,noeigentest,maxcyc=200) IOP(2/17=4) Freq=noraman geom=checkpo

int guess=check\\thymine/adenine radical ts\\0,2\C,1.8434848665,-1.534
5172099,-4.5042442502\H,2.1858783765,-1.7028792097,-5.5057051202\N,1.1
172042578,-0.5387895747,-4.1225146905\C,0.9358719012,-0.7458418026,-2.
7798355569\C,0.2169483195,-0.0143835163,-1.8223773024\N,-0.4442687495,
1.0862786767,-2.1155652438\H,-1.1132889599,1.536623566,-1.4765581932\H
,-0.4527267745,1.3567281082,-3.0781381595\C,0.9236925744,-1.6396301572
,-0.297664356\H,0.8893905331,-1.9492945141,0.7327360407\N,1.5906985144
,-2.3853292119,-1.1278108193\C,1.5713806788,-1.8923195549,-2.366791630
8\N,2.1532624385,-2.3934196573,-3.4866000898\H,2.6960163839,-3.2299835
738,-3.544904917\N,0.2624367995,-0.5087218017,-0.5712030183\C,-0.61822
88849,0.3031184334,0.7873515841\H,-0.0630570196,-0.1968310299,1.564385
4767\H,-0.2767926788,1.3052019907,0.6023843717\C,-2.0113181947,0.12276
78281,0.789258102\C,-2.6420247663,-1.0285041311,1.3427435863\C,-2.8061
278588,1.1071961191,0.151786988\H,-2.1434024152,-1.6659359846,2.049287
1884\C,-4.8408729173,-0.0927172475,0.8587448997\N,-4.0376092736,-1.026
048084,1.4171602166\H,-4.5230563971,-1.8136771158,1.791965117\O,-6.045
8651659,-0.1538953309,0.8671247596\N,-4.1728015475,0.9531938711,0.2581
536127\H,-4.7471245721,1.646735757,-0.1777334237\O,-2.3791676769,2.073
9511763,-0.4883786656\\Version=AM64L-G09RevC.01\State=2-A\HF=-920.5306
898\S2=0.760939\S2-1=0.\S2A=0.750061\RMSD=3.554e-09\RMSF=1.265e-06\Dip
ole=3.3308523,-1.6428258,-1.2234538\Quadrupole=-11.9647418,1.3025467,1
0.662195,-3.53201,-2.4217263,3.0734337\PG=C01 [X(C10H10N7O2)]\\@

M06-2X/6-311G(d,p

1\1\GINC-MERRI017\FTS\UM062X\6-311G(d,p)\C10H10N7O2(2)\SHORVAT\27-Mar-
2013\0\\#M062X/6-311G** 6D INT(grid=ultrafine) OPT=(TS,readfc,noeigent
est,maxcyc=200) IOP(2/17=4) Freq=noraman geom=checkpoint guess=check\\
thymine/adenine radical ts\\0,2\C,1.6628227901,-1.6055992741,-4.492993
7522\H,1.9424224309,-1.8143588619,-5.5144401751\N,1.0032279913,-0.5559
049806,-4.0931613948\C,0.8914094411,-0.7317017911,-2.7338266054\C,0.24
9548684,0.0553292157,-1.750313126\N,-0.397088198,1.1748146461,-2.04144
30002\H,-1.0458867352,1.655214954,-1.3869973607\H,-0.4494412555,1.4071
23298,-3.0223863847\C,0.9724777346,-1.5806110094,-0.216047166\H,0.9752
439859,-1.8617696287,0.8327059905\N,1.5573538774,-2.3890122653,-1.0668

57851\C,1.4946666607,-1.9104659064,-2.3204877543\N,1.9880356965,-2.464
8773888,-3.4684732646\H,2.4881511012,-3.337956037,-3.5332866842\N,0.35
52365355,-0.4109468153,-0.4845969716\C,-0.5676480472,0.3935397512,0.84
91051227\H,-0.0166996546,-0.0924086834,1.6517925826\H,-0.2575027583,1.
4184136027,0.6748602128\C,-1.9582436953,0.1542308092,0.789875314\C,-2.
5623452479,-1.0429720567,1.2703077114\C,-2.7713861664,1.1437841738,0.1
491394204\H,-2.0560439226,-1.7252902013,1.9382686436\C,-4.8004251433,-
0.197378866,0.7070581117\N,-3.9628952456,-1.130817841,1.2440448924\H,-
4.4300052783,-1.9599868142,1.5746155654\O,-6.0051235245,-0.311603797,0
.6555299964\N,-4.1415100242,0.9222271269,0.197883652\H,-4.7333763415,1
.6187642332,-0.2320881995\O,-2.3564438991,2.159297226,-0.430731019\\Ve
rsion=AM64L-G09RevC.01\State=2-A\HF=-920.6773229\S2=0.758367\S2-1=0.\S
2A=0.750035\RMSD=5.933e-09\RMSF=1.920e-06\Dipole=2.9505803,-1.5874984,
-1.198524\Quadrupole=-11.8084857,1.8004086,10.0080771,-4.2504621,-2.83
12329,3.1277721\PG=C01 [X(C10H10N7O2)]\\@