Phosphorane intermediate vs. leaving group stabilization by intramolecular hydrogen bonding in the cleavage of trinucleoside monophosphates: implications to catalysis by the large ribozymes

Tuomas Lönnberg and Maarit Laine

Supplementary information

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number of scans: 16

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Hz/cm: 255.657  ppm/cm: 0.51118
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SpinWorks 3: 5’-O-Methyl-2’-azido-2’-deoxyuridine

![NMR spectrum of 5’-O-Methyl-2’-azido-2’-deoxyuridine](image)

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- Time domain size: 65536 points
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- Number of scans: 16

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- Processed size: 32768 complex points
- LB: 0.000, GF: 0.00000
- Hz/cm: 111.091, ppm/cm: 0.22212
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width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16
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**SpinWorks 3: 5'-O-Methyl-2'-azido-2'-deoxyuridine**

![SpinWorks 3: 5'-O-Methyl-2'-azido-2'-deoxyuridine](image)

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SpinWorks 3: 5'-O-Methyl-2'-amino-2'-deoxyuridine

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time domain size: 65536 points
width: 10330.58 Hz = 20.6557 ppm = 0.157632 Hz/pt
number of scans: 16
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SpinWorks 3: 5’-O-Methyl-2’-amino-2’-deoxyuridine

file: E:\Maarit\spektrit\amino\113\fid  exp: <zpgg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 30030.03 Hz  = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 1528

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 0.000  GF: 0.0000
Hz/cm: 1000.247  ppm/cm: 7.95296

11
**Fig. S1** HPLC chromatogram of 11 [Hypersil-Keystone Aquasil C18 column (4 × 150 mm, 5 μm); flow rate = 1 mL min⁻¹; 60 mM acetate buffer (pH = 4.3) and a linear gradient of 3→50% MeCN during 60 min, then 50% MeCN for 20 min].
Fig. S2 UV spectrum of 11.
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SpinWorks 3: 5'-O-Methyl-2'-trifluoroacetamido-2'-deoxyuridine

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number of scans: 16

freq. of 0 ppm: 500.130000 MHz
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number of scans: 16

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number of scans: 16

freq. of 0 ppm: 500.130000 MHz
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SpinWorks 3: 5′-O-Methyl-2′-trifluoroacetamido-2′-deoxyuridine

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processed size: 32768 complex points
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width: 30030.03 Hz = 238.7687 ppm = 0.458222 Hz/pt
number of scans: 1196
Fig. S3 HPLC chromatogram of 7 [Hypersil-Keystone Aquasil C18 column (4 × 150 mm, 5 μm); flow rate = 1 mL min⁻¹; 60 mM acetate buffer (pH = 4.3) and a linear gradient of 3→50% MeCN during 60 min, then 50% MeCN for 20 min].
Fig. S4 UV spectrum of 7.
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SpinWorks 3:

$N^\text{\textregistered}$-Benzoyl-2'$,3'$-O-methyleneadenosin-5'-yl 5'-O-methyl-3'$-O-(4,4'$-dimethoxytrityl)uridin-2'$-yl 5'$-O-methyl-2'$-trifluoroacetamido-2'$-deoxyuridin-3'$-yl phosphate

file: ...\t\\trit¥\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textregistered\textreg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registered

transmitter freq.: 500.130000 MHz
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time domain size: 65536 points
data: 0.000000 ppm/cm: 0.13449

number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
Hz/cm: 67.262 ppm/cm: 0.13449
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SpinWorks 3:

$N^\alpha$-Benzoyl-2',3'-O-methyleneadenosin-5'-yl 5'-O-methyl-3'-O-(4,4'-dimethoxytrityl)uridin-2'-yl 5'-O-methyl-2'-trifluoroacetamido-2'-deoxyuridin-3'-yl phosphate

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processed size: 32768 complex points
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Hz/cm: 44.301  ppm/cm: 0.08858

23
SpinWorks 3:

$N^\ominus$-Benzoyl-2',3'-O-methyleneadenosin-5'-yl 5'-O-methyl-3'-O-(4,4'-dimethoxytrityl)uridin-2'-yl 5'-O-methyl-2'-trifluoroacetamido-2'-deoxyuridin-3'-yl phosphate

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$N^\alpha$-Benzoyl-2'-3'-O-methyleneadenosin-5'-yl 5'-O-methyl-3'-O-(4,4'-dimethoxytrityl)uridin-2'-yl 5'-O-methyl-2'-trifluoroacetamido-2'-deoxyuridin-3'-yl phosphate

SpinWorks 3:

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live domain size: 65536 points
width: 80.645 Hz = 398.3536 ppm = 1.230548 Hz/pt
number of scans: 154

freq. of 0 ppm: 202.454310 MHz
processed size: 32768 complex points
LB: 0.000  GF: 0.0000
Hz/cm: 2185.381  ppm/cm: 10.79487
2',3'-O-Methyleneadenosin-5'-yl 5'-O-methyl-3'-O-(4,4'-dimethoxytrityl)uridin-2'-yl 5'-O-methyl-2'-trifluoroacetamido-2'-deoxyuridin-3'-yl phosphate
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SpinWorks 3:

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number of scans: 150

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Hz/cm: 41.113  ppm/cm: 0.08220
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**SpinWorks 3:**

![SpinWorks 3 diagram]

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hold: <zgpg30>
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time domain size: 65536 points
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number of scans: 200

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LB: 0.000  GF: 0.0000
Hz/cm: 2088.144  ppm/cm: 10.31457
Fig. S5 HPLC chromatogram of 4b [Hypersil-Keystone Aquasil C18 column (4 × 150 mm, 5 μm); flow rate = 1 mL min⁻¹; 60 mM acetate buffer (pH = 4.3) and a linear gradient of 3→50% MeCN during 60 min, then 50% MeCN for 20 min].
Fig. S6 UV spectrum of 4b.
**Table S1** Observed pseudo first-order rate constants and product distributions for the hydrolysis of 1a, b.

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<th>pH</th>
<th>[buffer] / mmol L(^{-1})</th>
<th>(k_{\text{obs}} / 10^{-4} \text{ s}^{-1})</th>
<th>(k_B / (k_A + k_B))</th>
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<td>39 ± 2</td>
<td>0.6 ± 0.1</td>
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<tr>
<td>0.39</td>
<td>-</td>
<td>11 ± 3</td>
<td>0.64 ± 0.07</td>
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<tr>
<td>1.00</td>
<td>-</td>
<td>5.6 ± 0.3</td>
<td>0.60 ± 0.06</td>
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<tr>
<td>1.37</td>
<td>-</td>
<td>2.8 ± 0.1</td>
<td>0.62 ± 0.03</td>
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<td>4.3 ± 0.4</td>
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<td>95.0</td>
<td>5.2 ± 0.1</td>
<td>0.60 ± 0.02</td>
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<td></td>
<td>190.0</td>
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<tr>
<td>3.37</td>
<td>47.5</td>
<td>6.2 ± 0.1</td>
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<td>95.0</td>
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<td>0.65 ± 0.02</td>
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<td>142.5</td>
<td>45 ± 1</td>
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</tr>
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<td>190.0</td>
<td>59 ± 2</td>
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<td>47.5</td>
<td>58 ± 2</td>
<td>0.74 ± 0.08</td>
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<td>6.27</td>
<td>47.5</td>
<td>138 ± 7</td>
<td>0.94 ± 0.02</td>
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</table>

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Fig. S7 HPLC chromatogram of a reaction solution of the hydrolysis of 1a and 1b [Hypersil-Keystone Aquasil C18 column (4 × 150 mm, 5 μm); flow rate = 1 mL min⁻¹; 60 mM formate buffer (pH = 3.0) and a linear gradient of 3→30% MeCN during 40 min].