**Supporting Information**

**Table S11.** The main geometric parameters of the optimized structures of dGpdG, dGAsdG, and mono-hydrated dGAsdG. Angle in degree (°) and distance in Å.

<table>
<thead>
<tr>
<th></th>
<th>dGpdG</th>
<th>dGAsdG</th>
<th>dGAsdG</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi(\tau_1, \tau_2)^a$</td>
<td>8.8</td>
<td>9.1</td>
<td>9.5</td>
</tr>
<tr>
<td>$R(O_1, O_2)$</td>
<td>3.208</td>
<td>3.19</td>
<td>3.209</td>
</tr>
<tr>
<td>X—O3'</td>
<td>1.588 (1.58)$^c$</td>
<td>1.736 (1.73)$^d$</td>
<td>1.774</td>
</tr>
<tr>
<td>X—O5'</td>
<td>1.582 (1.58)$^c$</td>
<td>1.730 (1.73)$^d$</td>
<td>1.788</td>
</tr>
<tr>
<td>X—OH</td>
<td>1.597</td>
<td>1.745</td>
<td>1.646 $^b$</td>
</tr>
<tr>
<td>X═O</td>
<td>1.469 (1.47)$^c$</td>
<td>1.621</td>
<td>1.652 $^b$</td>
</tr>
</tbody>
</table>

$^a$ $\tau_1$: vector of base G1, defined by the N1, N3, and C5 atoms of G; $\tau_2$: vector of base G2, defined by the N1, N3, and C5 atoms of G2. $\phi(\tau_1, \tau_2)$: angle between $\tau_1$ and $\tau_2$. (see Figure 1). $O_1$: center of base G1, defined as the geometric center of the N1, N3, and C5 atoms of G1; $O_2$: center of base G2, defined as the geometric center of the N1, N3, and C5 atoms of G2. $R(O_1, O_2)$: distance between $O_1$ and $O_2$. X = P for dGpdG; X = As for dGAsdG.

$^b$ As—O bond lengths in mono-hydrated dGAsdG.

$^c$ Experiment, 7BNA, Ref. 2.

$^d$ Experiment, GFAJ1, Refs. 1, 2.
Table SI2. The relative energies along the reaction pathways of hydrolysis of Me₂AsO₄⁻ and Me₂PO₄⁻ (in Kcal/mol).a

<table>
<thead>
<tr>
<th></th>
<th>Me₂AsO₄</th>
<th>Me₂PO₄⁻</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔE(PCM)</td>
<td>ΔE(PCM)</td>
<td>ΔE(PCM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>0.00, 0.00</td>
<td>0.00</td>
<td>0.00, 0.00</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>TS01</td>
<td>19.83, 21.61</td>
<td>21.32</td>
<td>35.49, 37.23</td>
<td>37.26</td>
<td></td>
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<tr>
<td>Im1</td>
<td>6.97, 9.62</td>
<td>8.06</td>
<td>30.54, 32.79</td>
<td>31.45</td>
<td></td>
</tr>
<tr>
<td>TS12</td>
<td>15.89, 18.12</td>
<td>14.99</td>
<td>41.52, 43.44</td>
<td>40.68</td>
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<tr>
<td>Im2</td>
<td>6.66, 9.32</td>
<td>7.85</td>
<td>30.17, 32.59</td>
<td>31.35</td>
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<tr>
<td>TS23</td>
<td>22.64, 24.36</td>
<td>23.32</td>
<td>34.64, 36.49</td>
<td>38.01</td>
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<td>P</td>
<td>2.01, 1.47</td>
<td>1.60</td>
<td>2.72, 2.24</td>
<td>2.30</td>
<td></td>
</tr>
</tbody>
</table>

aΔE(PCM): relative energy in aqueous solution. Values in plain are calculated at the M06-2X/6-31+G(d,p) level of theory, in bold are with the M06-2X/6-311++G(3df,2pd)/M06-2X/6-31+G(d,p) approach.
**Figure S1.** The superimposition of the optimized structures of dGpdG (black) and dGAsdG (red).