Effects of Sodium Cationization vs. Protonation on the Conformations and N-Glycosidic

Bond Stabilities of Sodium Cationized Uridine and 2′-Deoxyuridine:

Solution Conformation of [Urd+Na]+ is Preserved Upon ESI

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Table S1. Mass List of Protonated and Sodium Cationized Urd and dUrd

m/z	Symbol	[Urd+H]+	[dUrd+H]+	[Urd+Na]+	[dUrd+Na]+
267.0	•	–	–	[Urd+Na]+	–
251.0	•	–	–	–	[dUrd+Na]+
245.0	•	[Urd+H]+	–	–	–
229.0	•	–	[dUrd+H]+	–	–
227.0	•	[Urd–W+H]+	–	–	–
211.0	•	–	[dUrd–W+H]+	–	–
203.0	•	[Urd–K+H]+	–	–	–
193.0	•	–	[dUrd–2W+H]+	–	–
185.0	•	[Urd–K–W+H]+	–	–	–
155.0	•	–	–	[Urd–Ura+Na]+	–
139.0	•	–	–	–	[dUrd–Ura+Na]+
135.0	•	–	–	[Ura+Na]+	[Ura+Na]+
131.0	•	–	[Ura+W+H]+	–	–
117.0	•	–	[dUrd–Ura+H]+	–	–
113.0	•	[Ura+H]+	[Ura+H]+	–	–
99.0	•	–	[dUrd–Ura–W+H]+	–	–
81.0	•	–	[dUrd–Ura–2W+H]+	–	–

Table S2. Relative Gibbs Free Energies of the B3LYP/6-311+G(d,p) Optimized Structures of the T1(O2O4'O5') and B1(O2O2') Conformers of [Urd+Na]$^+$ and Their Water Adducts ([Urd+Na]$^+$•nW, n=1, 2) Calculated Using Different Computational Approaches. $^{\alpha}$

	B3LYP		MP2(full)	
[Urd+Na]$^+$	6-311+G(2d,2p)	def2-TZVPPD	6-311+G(2d,2p)	def2-TZVPPD
T1(O2O4'O5')	**0.0**	**0.0**	**0.0**	**0.0**
B1(O2O2')	6.1	4.5	9.5	9.6
T1(O2O4'O5')•W	1.6	3.1	**0.0**	**0.0**
B1(O2O2')•W	**0.0**	**0.0**	4.1	4.1
T1(O2O4'O5')•2W	3.9	13.4	1.2	0.0
B1(O2O2')•2W	**0.0**	**0.0**	**0.0**	**0.0**

$^{\alpha}$All values are given in kJ/mol.

Table S3. Relative Gibbs Free Energies of the B3LYP/6-311+G(d,p) Optimized Structures of the T1, T2, T3 and T4(O2O4'O5') Conformers of [dUrd+Na]$^+$ Calculated Using Different Computational Approaches. $^{\alpha}$

	B3LYP		MP2(full)	
[dUrd+Na]$^+$	6-311+G(2d,2p)	def2-TZVPPD	6-311+G(2d,2p)	def2-TZVPPD
T1(O2O4'O5')	**0.0**	**0.0**	**0.0**	**0.0**
T2(O2O4'O5')	3.5	3.3	2.9	3.7
T3(O2O4'O5')	5.5	5.0	1.5	1.9
T4(O2O4'O5')	7.5	7.2	6.1	4.9

$^{\alpha}$All values are given in kJ/mol.

Figure Captions

Figure S1. Designations for nucleobase orientation and pseudorotation phase angle (P) of nucleosides. The pseudorotation phase angle, P, is calculated using eq (S1). E and T forms alternate every 18º.

$$\tan P = \frac{(v_4+v_1)-(v_3+v_0)}{2 \times v_2 \times (\sin 36° + \sin 72°)} \tag{S1}$$

The angles, v_0, v_1, v_2, v_3 and v_4, represent the $\angle$C4'O4'C1'C2', $\angle$O4'C1'C2'C3', $\angle$C1'C2'C3'C4', $\angle$C2'C3'C4'O4' and $\angle$C3'C4'O4'C1', respectively. In the upper section of the diagram, $v_2 > 0$, whereas in the lower section of the diagram, $v_2 < 0$. The combination of P and v_2 are used to identify the sugar puckering. If $v_2 > 0$, $P = P$; if $v_2 < 0$ $P \rightarrow P+180º$.

Figure S2. The mass spectra of MS^3 experiments of [dUrd–W+H]$^+$, [dUrd–2W+H]$^+$, [dUrd–Ura+H]$^+$ and [Urd–K+H]$^+$.

Figure S3. Stable low-energy conformers of [Urd+Na]$^+$. The Na$^+$ binding modes, orientations of uracil, sugar puckering, and the relative 298 K Gibbs free energies at the B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) level of theory are also listed for each structure.

Figure S4. Stable low-energy conformers of [dUrd+Na]$^+$. The Na$^+$ binding modes, orientations of uracil, sugar puckering, and the relative 298 K Gibbs free energies at the B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) level of theory are also listed for each structure.

Figure S5. Comparison of the experimental IRMPD action spectrum of [Urd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for *syn* oriented O2 binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

**Figure S6.** Comparison of the experimental IRMPD action spectrum of [Urd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for *anti* oriented O2 binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S7. Comparison of the experimental IRMPD action spectrum of [Urd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for O4 binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S8. Comparison of the experimental IRMPD action spectrum of [Urd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for sugar binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S9. Comparison of the experimental IRMPD action spectrum of [Urd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for tautomeric conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S10. Comparison of the experimental IRMPD action spectrum of [dUrd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for T(O2O4'O5') conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S11. Comparison of the experimental IRMPD action spectrum of [dUrd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for bidentate and monodentate O2 binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S12. Comparison of the experimental IRMPD action spectrum of [dUrd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for O4 binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S13. Comparison of the experimental IRMPD action spectrum of [dUrd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for sugar binding conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.

Figure S14. Comparison of the experimental IRMPD action spectrum of [dUrd+Na]$^+$ with the B3LYP/6-311+G(d,p) optimized structures and calculated linear IR spectra for tautomeric conformers with spectral misalignments shaded in red. The B3LYP/6-311+G(2d,2p) relative Gibbs free energies at 298 K is also shown.
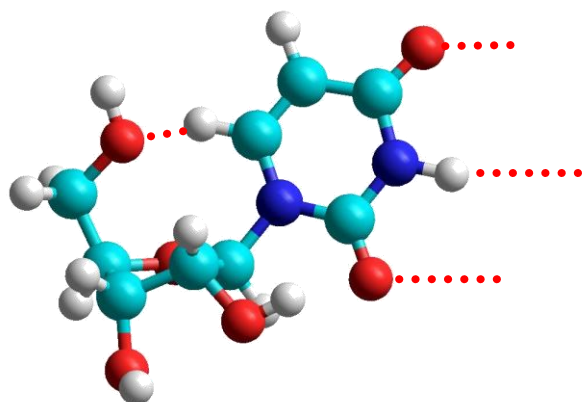
Figure S1.

anti orientation
∠C2N1C1′O4′ = 90° to 270°
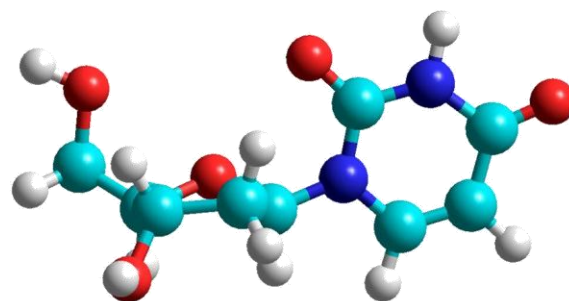
syn orientation
∠C2N1C1′O4′ = −90° to 90°
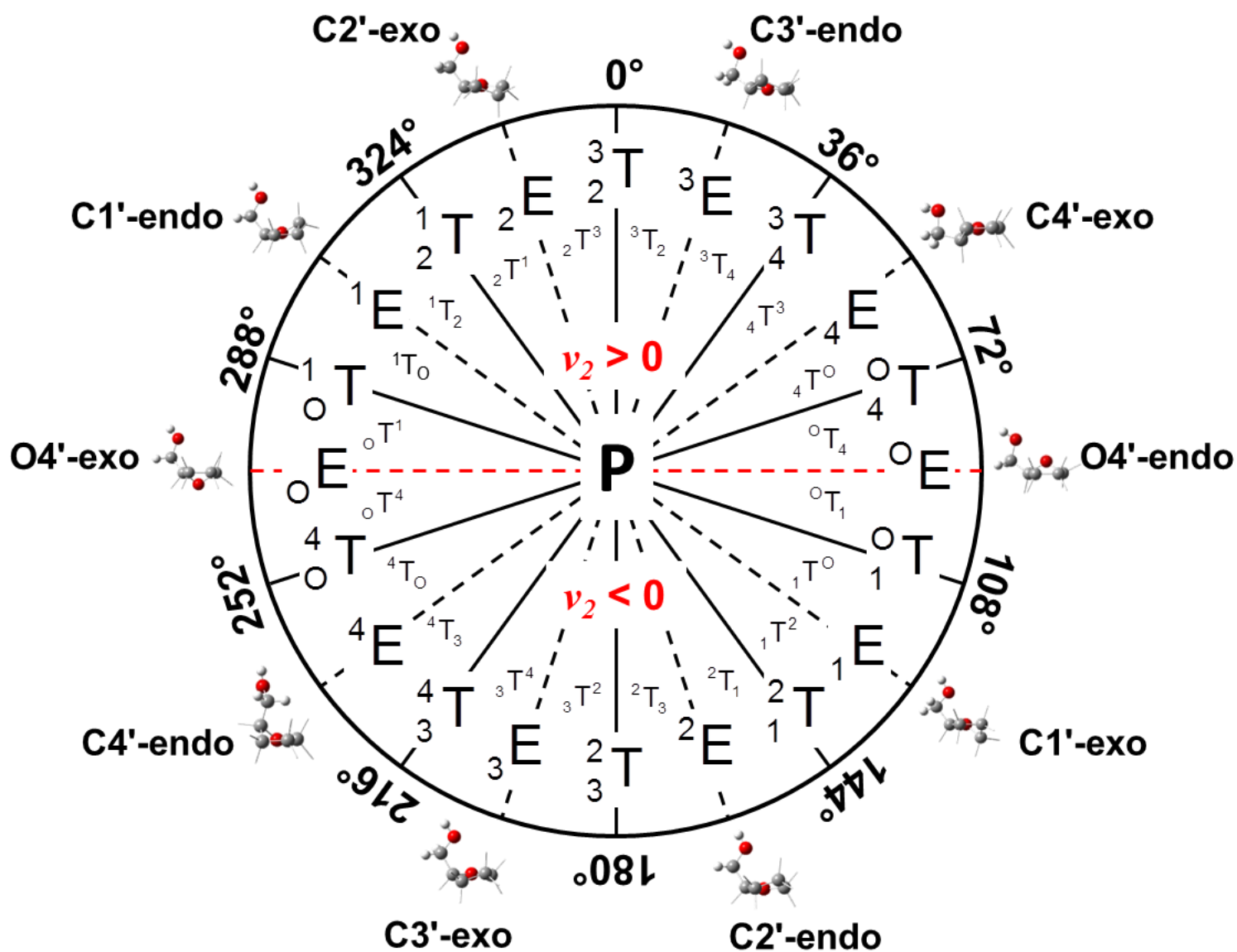
Figure S2.
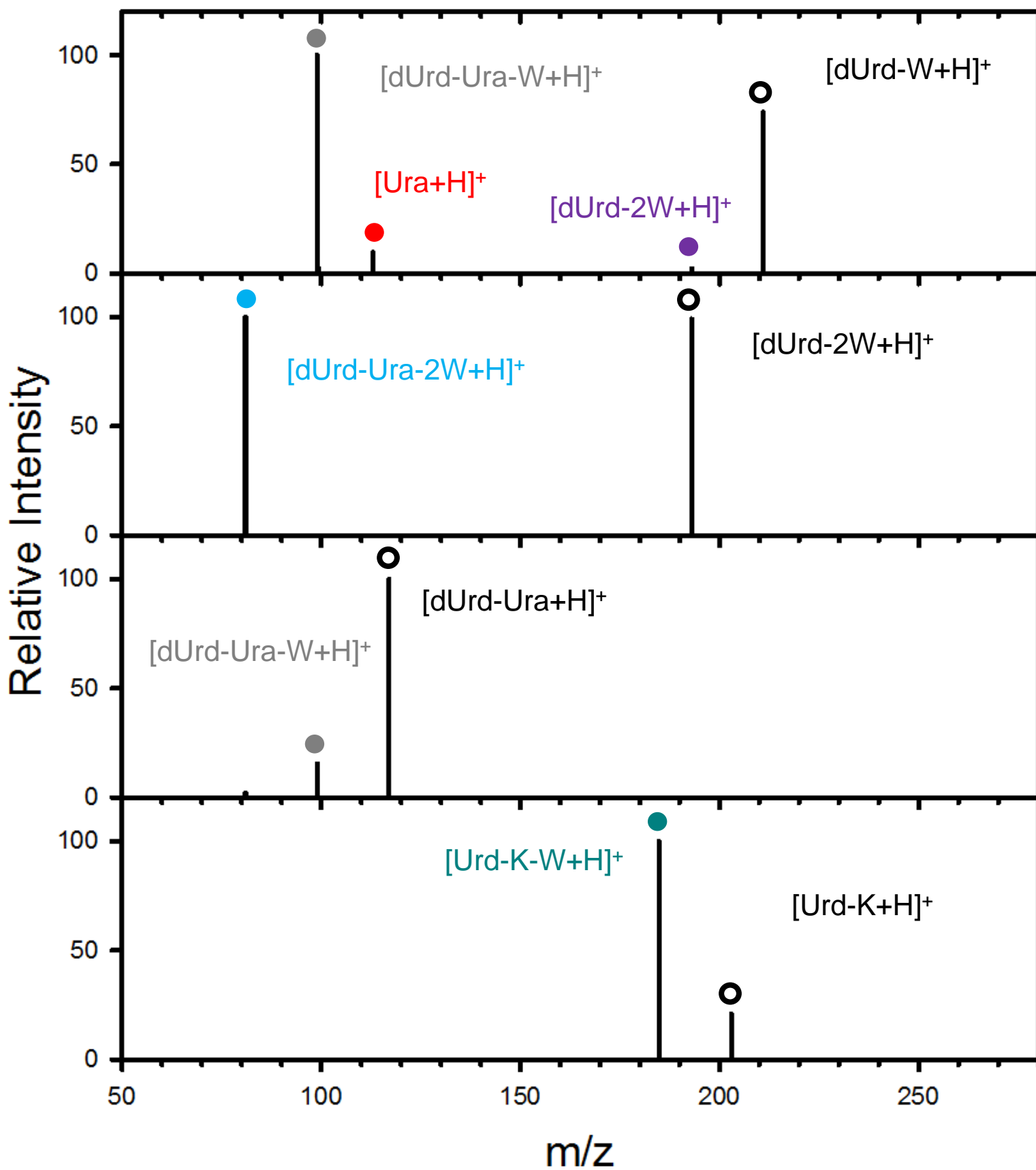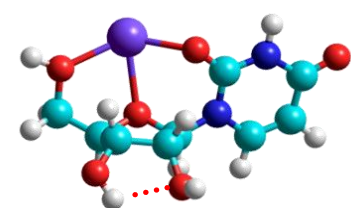
T1(O2O4'O5')
syn, O4'-endo ($^{O}T_4$)
0.0 kJ/mol
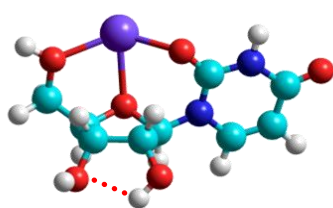
T2(O2O4'O5')
syn, O4'-endo ($^{O}T_1$)
1.4 kJ/mol
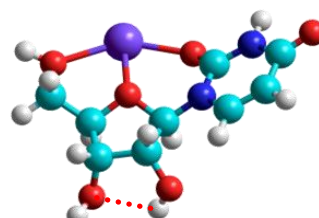
T3(O2O4'O5')
syn, O4'-endo ($^{O}T_1$)
2.8 kJ/mol
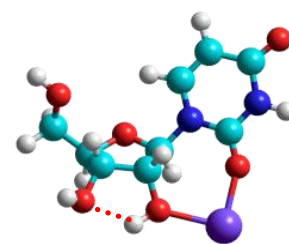
B1(O2O2')
anti, C4'-exo ($_4T^O$)
6.1 kJ/mol
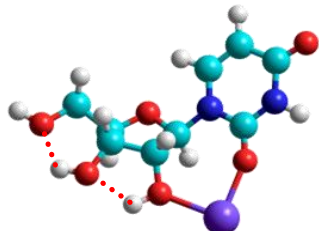
B2(O2O2')
anti, C4'-exo ($_4T^O$)
7.1 kJ/mol
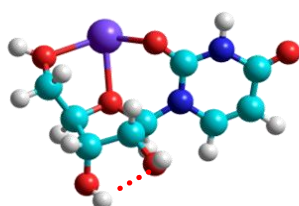
T4(O2O4'O5')
syn, C2'-endo ($^2T_1$)
8.0 kJ/mol
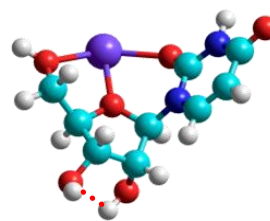
T5(O2O4'O5')
syn, C3'-endo ($^3T_2$)
8.5 kJ/mol
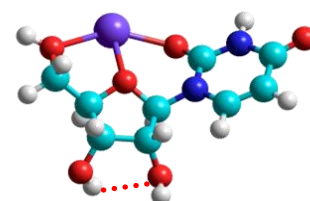
T6(O2O4'O5')
syn, O4'-endo ($^{O}T_4$)
9.1 kJ/mol

B3(O2O2')
anti, C3'-exo ($_3T^4$)
9.2 kJ/mol
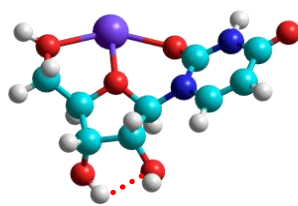
T7(O2O4'O5')
syn, C1'-exo ($_1T^O$)
10.2 kJ/mol
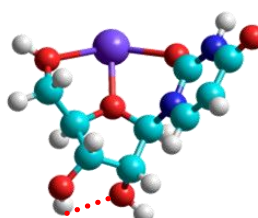
T8(O2O4'O5')
syn, C2'-exo ($_2T^3$)
11.7 kJ/mol
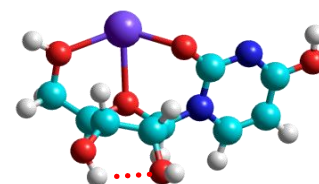
T1(O2O4'O5')t4
syn, O4'-endo ($^{O}T_4$)
16.6 kJ/mol
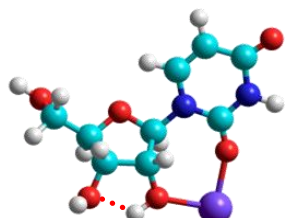
B4(O2O2')
anti, C4'-exo ($_4T^O$)
17.7 kJ/mol
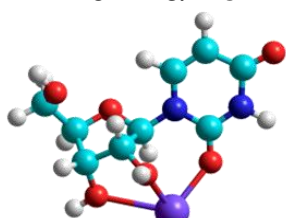
T1(O2O2'O3')
anti, C2'-endo ($^2T_1$)
18.2 kJ/mol
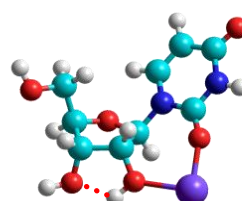
B5(O2O2')
anti, C4'-endo ($^4T_3$)
18.5 kJ/mol
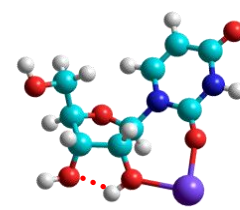
B6(O2O2')
anti, C4'-endo ($^4T_3$)
18.6 kJ/mol
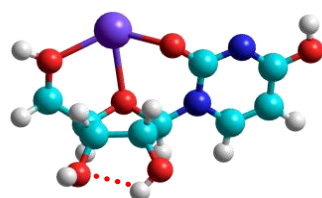
T2(O2O4'O5')t4
syn, O4'-endo ($^{O}T_1$)
19.0 kJ/mol
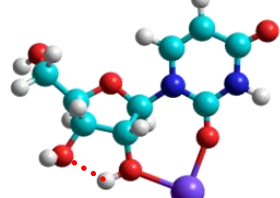
B7(O2O2')
anti, C4'-exo ($_4T^O$)
20.5 kJ/mol
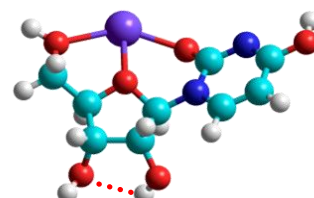
T3(O2O4'O5')t4
syn, O4'-endo ($^{O}T_1$)
21.8 kJ/mol
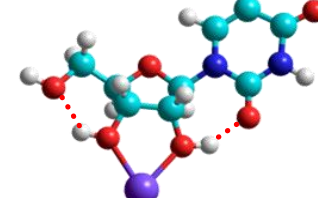
B1(O2'O3')
anti, O4'-endo ($^{O}T_4$)
22.9 kJ/mol

[Urd+Na]$^+$

Figure S3.
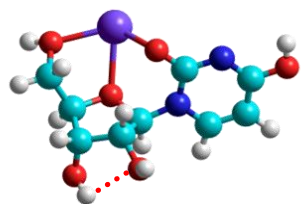
T4(O2O4'O5')t4
syn, C2'-endo ($^2T_1$)
25.9 kJ/mol
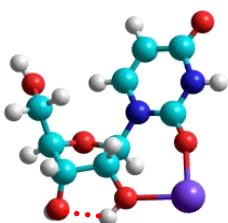
B8(O2O2')
anti, C4'-endo ($^4T_3$)
26.7 kJ/mol
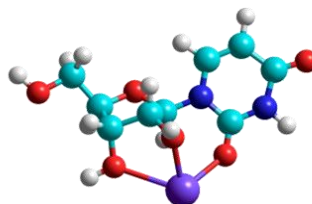
T2(O2O2'O3')
anti, C1'-exo ($_1T^2$)
26.9 kJ/mol
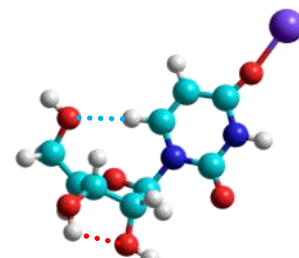
M1(O4)
anti, C3'-endo ($^3T_2$)
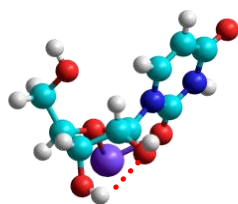27.4 kJ/mol
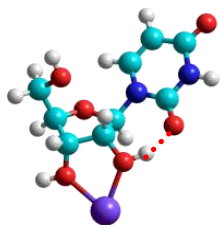
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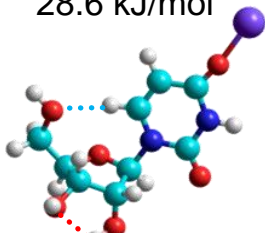28.5 kJ/mol
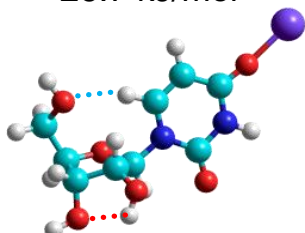
M2(O4)
anti, C2'-endo ($^2T_3$)
28.6 kJ/mol
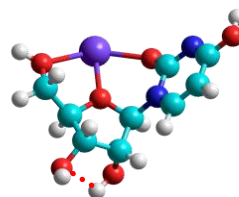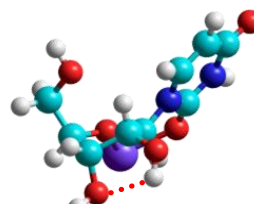
T5(O2O4'O5')t4
syn, C3'-endo ($^3T_2$)
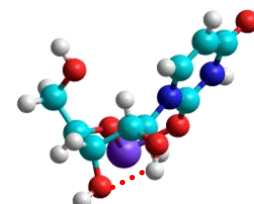29.0 kJ/mol
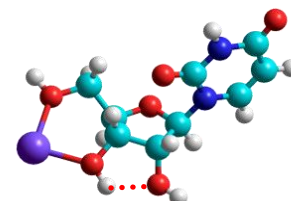
B1(O3'O5')
syn, C3'-endo ($^3T_4$)
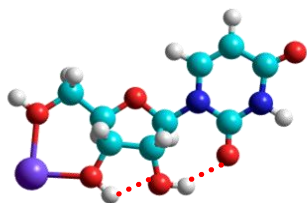29.4 kJ/mol

B1(O2O4')
syn, C3'-exo ($_3T^2$)
30.9 kJ/mol

M3(O4)
anti, C3'-endo ($^3T_2$)
31.9 kJ/mol

B2(O2O4')
syn, C3'-exo ($_3T^2$)
32.8 kJ/mol

B3(O2O4')
syn, C3'-exo ($_3T^2$)
32.9 kJ/mol

B2(O3'O5')
anti, O4'-endo ($^OT_4$)
33.5 kJ/mol
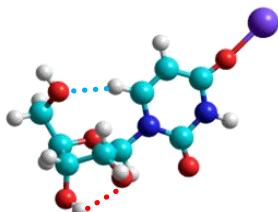
M4(O4)
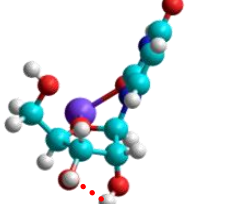*anti*, C2'-endo ($^2T_3$)
34.3 kJ/mol
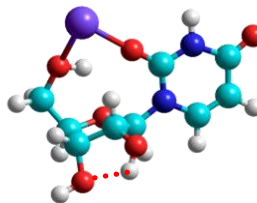
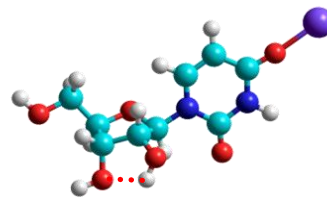B1(O2O5')
syn, C2'-endo ($^2T_1$)
34.5 kJ/mol
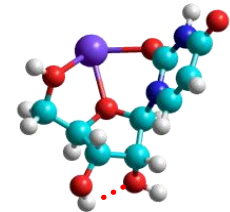
T9(O2O4'O5')
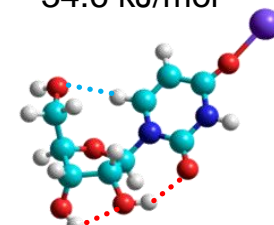*syn*, C3'-endo ($^3T_2$)
34.6 kJ/mol
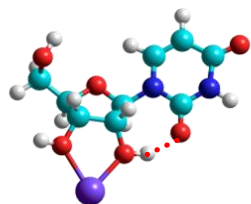
B3(O2'O3')
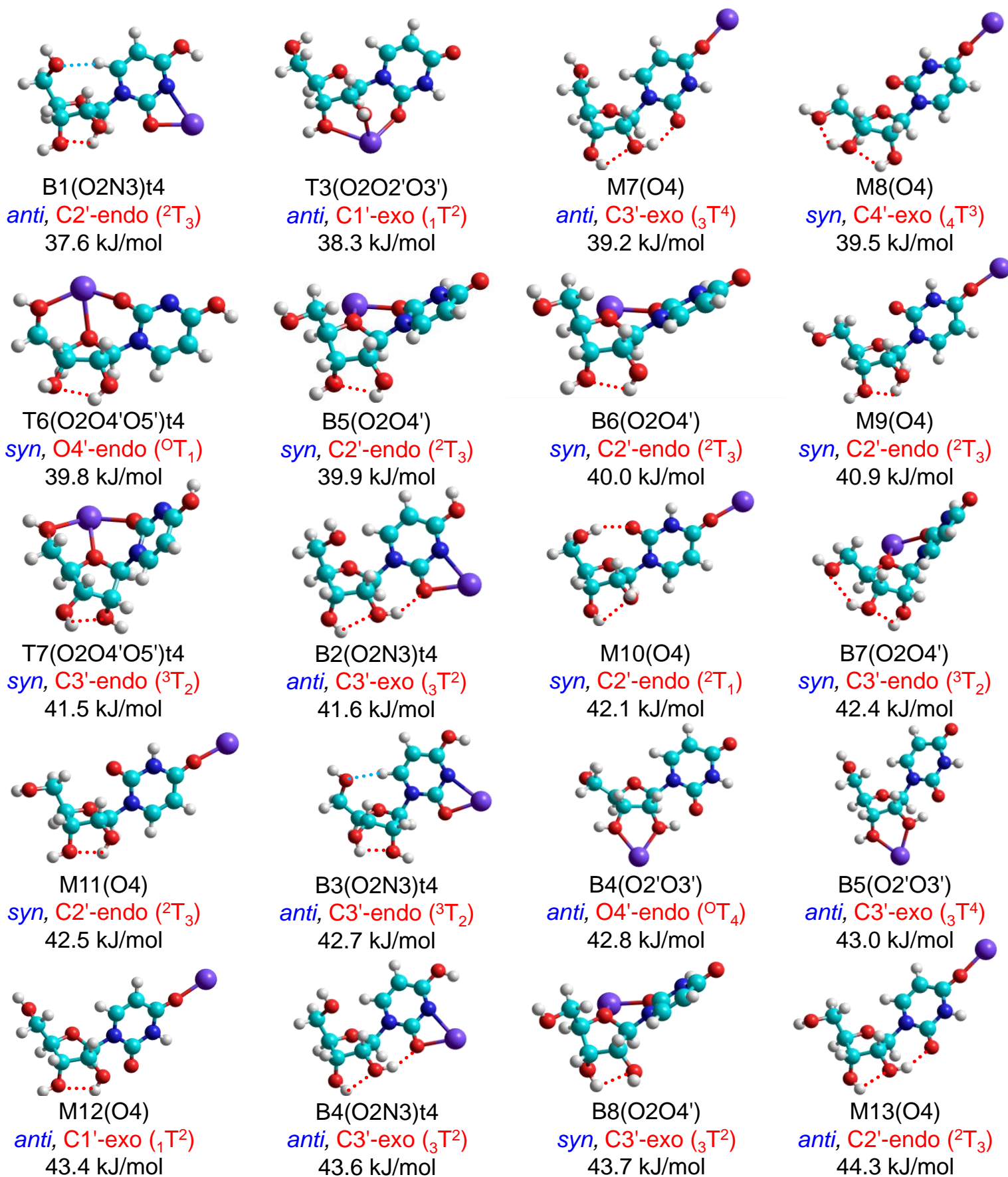*anti*, O4'-endo ($^OT_4$)
34.7 kJ/mol

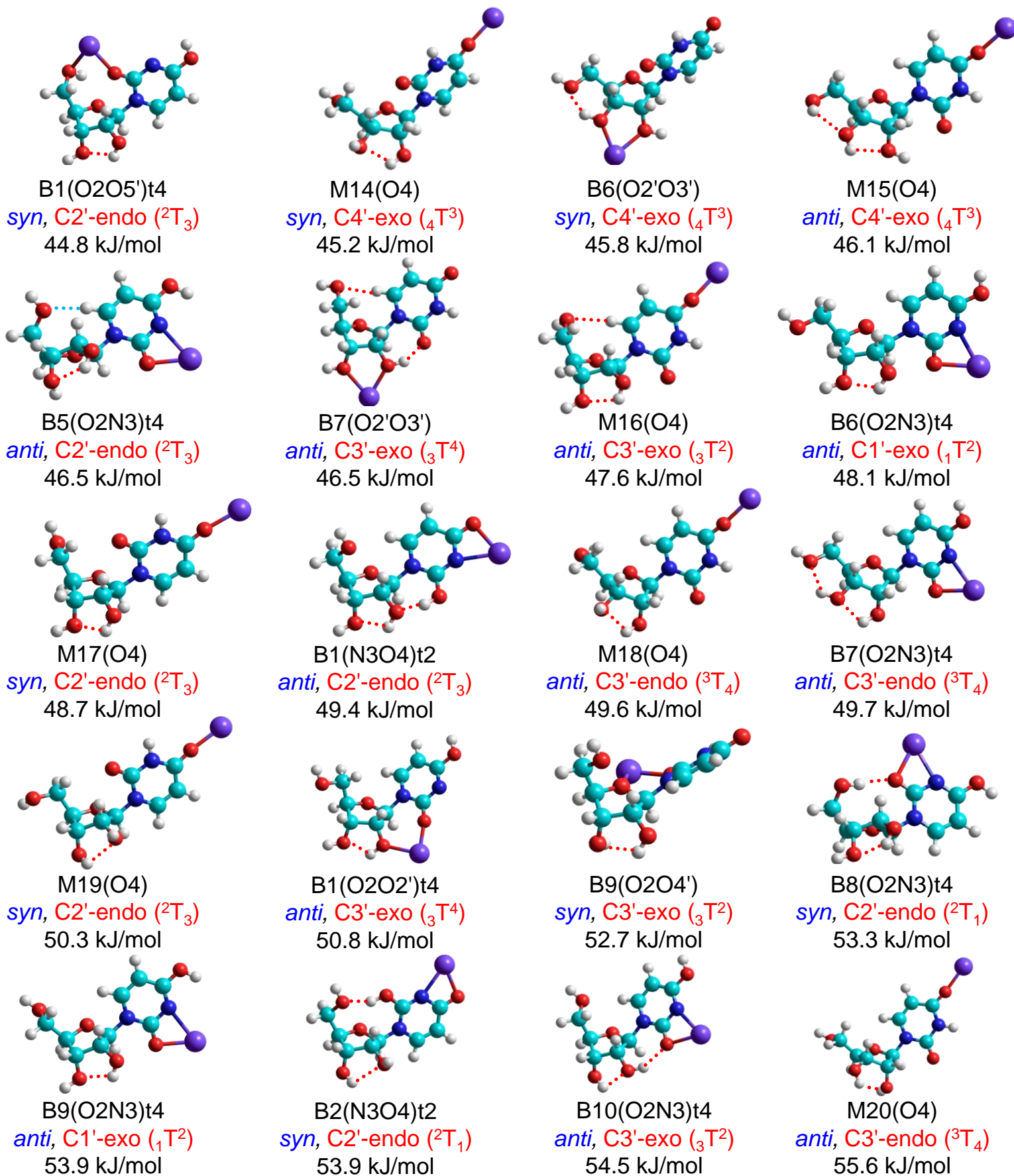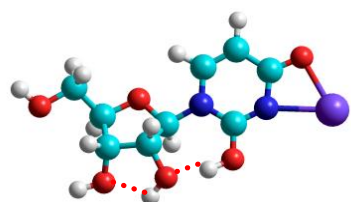B4(O2O4')
syn, C2'-exo ($_2T^3$)
35.1 kJ/mol

M5(O4)
anti, C1'-exo ($_1T^2$)
36.8 kJ/mol

M6(O4)
anti, C3'-exo ($_3T^4$)
37.5 kJ/mol

[Urd+Na]$^+$

Figure S3.

B1(O2N3)t4
anti, C2'-endo ($^2T_3$)
37.6 kJ/mol

T3(O2O2'O3')
anti, C1'-exo ($_1T^2$)
38.3 kJ/mol

M7(O4)
anti, C3'-exo ($_3T^4$)
39.2 kJ/mol

M8(O4)
syn, C4'-exo ($_4T^3$)
39.5 kJ/mol

T6(O2O4'O5')t4
syn, O4'-endo ($^OT_1$)
39.8 kJ/mol

B5(O2O4')
syn, C2'-endo ($^2T_3$)
39.9 kJ/mol

B6(O2O4')
syn, C2'-endo ($^2T_3$)
40.0 kJ/mol

M9(O4)
syn, C2'-endo ($^2T_3$)
40.9 kJ/mol

T7(O2O4'O5')t4
syn, C3'-endo ($^3T_2$)
41.5 kJ/mol

B2(O2N3)t4
anti, C3'-exo ($_3T^2$)
41.6 kJ/mol

M10(O4)
syn, C2'-endo ($^2T_1$)
42.1 kJ/mol

B7(O2O4')
syn, C3'-endo ($^3T_2$)
42.4 kJ/mol

M11(O4)
syn, C2'-endo ($^2T_3$)
42.5 kJ/mol

B3(O2N3)t4
anti, C3'-endo ($^3T_2$)
42.7 kJ/mol

B4(O2'O3')
anti, O4'-endo ($^OT_4$)
42.8 kJ/mol

B5(O2'O3')
anti, C3'-exo ($_3T^4$)
43.0 kJ/mol

M12(O4)
anti, C1'-exo ($_1T^2$)
43.4 kJ/mol

B4(O2N3)t4
anti, C3'-exo ($_3T^2$)
43.6 kJ/mol

B8(O2O4')
syn, C3'-exo ($_3T^2$)
43.7 kJ/mol

M13(O4)
anti, C2'-endo ($^2T_3$)
44.3 kJ/mol

[Urd+Na]$^+$

B1(O2O5')t4
syn, C2'-endo ($^2T_3$)
44.8 kJ/mol

M14(O4)
syn, C4'-exo ($_4T^3$)
45.2 kJ/mol

B6(O2'O3')
syn, C4'-exo ($_4T^3$)
45.8 kJ/mol

M15(O4)
anti, C4'-exo ($_4T^3$)
46.1 kJ/mol

B5(O2N3)t4
anti, C2'-endo ($^2T_3$)
46.5 kJ/mol

B7(O2'O3')
anti, C3'-exo ($_3T^4$)
46.5 kJ/mol

M16(O4)
anti, C3'-exo ($_3T^2$)
47.6 kJ/mol

B6(O2N3)t4
anti, C1'-exo ($_1T^2$)
48.1 kJ/mol

M17(O4)
syn, C2'-endo ($^2T_3$)
48.7 kJ/mol

B1(N3O4)t2
anti, C2'-endo ($^2T_3$)
49.4 kJ/mol

M18(O4)
anti, C3'-endo ($^3T_4$)
49.6 kJ/mol

B7(O2N3)t4
anti, C3'-endo ($^3T_4$)
49.7 kJ/mol

M19(O4)
syn, C2'-endo ($^2T_3$)
50.3 kJ/mol

B1(O2O2')t4
anti, C3'-exo ($_3T^4$)
50.8 kJ/mol

B9(O2O4')
syn, C3'-exo ($_3T^2$)
52.7 kJ/mol

B8(O2N3)t4
syn, C2'-endo ($^2T_1$)
53.3 kJ/mol

B9(O2N3)t4
anti, C1'-exo ($_1T^2$)
53.9 kJ/mol

B2(N3O4)t2
syn, C2'-endo ($^2T_1$)
53.9 kJ/mol

B10(O2N3)t4
anti, C3'-exo ($_3T^2$)
54.5 kJ/mol

M20(O4)
anti, C3'-endo ($^3T_4$)
55.6 kJ/mol

[Urd+Na]$^+$

B3(N3O4)t2
anti, C1'-exo ($_1T^2$)
56.3 kJ/mol
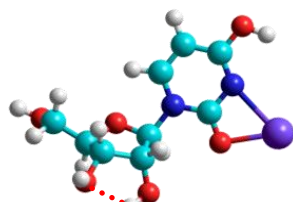
B11(O2N3)t4
anti, C4'-exo ($_4T^3$)
56.3 kJ/mol
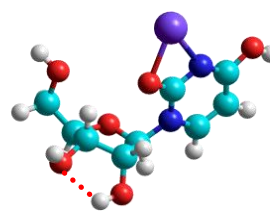
B12(O2N3)t4
syn, C4'-exo ($_4T^3$)
56.5 kJ/mol
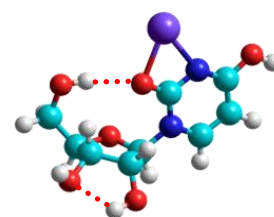
B13(O2N3)t4
syn, C4'-exo ($_4T^O$)
56.6 kJ/mol
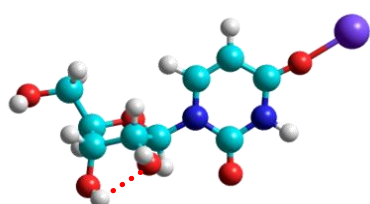
M21(O4)
anti, C2'-endo ($^2T_1$)
56.8 kJ/mol
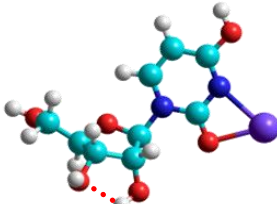
B14(O2N3)t4
anti, C4'-exo ($_4T^3$)
56.9 kJ/mol
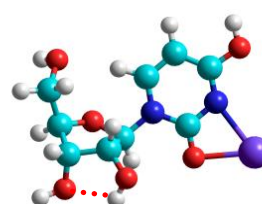
B15(O2N3)t4
anti, C3'-exo ($_3T^2$)
58.0 kJ/mol
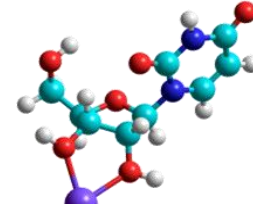
B8(O2'O3')
syn, C4'-exo ($_4T^3$)
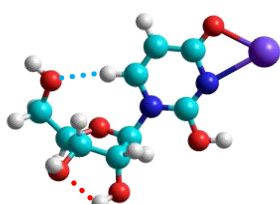59.0 kJ/mol
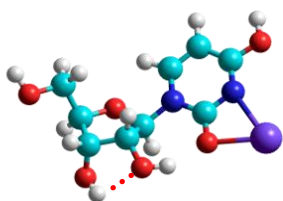
B16(O2N3)t4
anti, C2'-endo ($^2T_3$)
59.2 kJ/mol
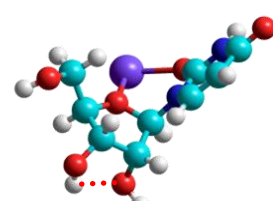
B10(O2O4')
syn, C2'-exo ($_2T^1$)
61.2 kJ/mol
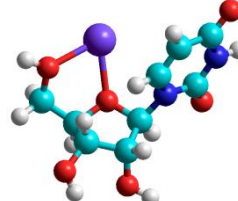
B1(O4'O5')
anti, C4'-exo ($_4T^3$)
62.1 kJ/mol
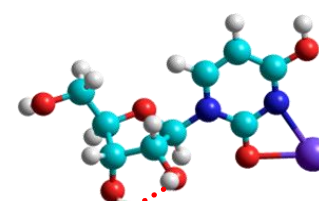
B17(O2N3)t4
anti, C2'-endo ($^2T_1$)
62.3 kJ/mol

B4(N3O4)t2
anti, C3'-endo ($^3T_4$)
63.1 kJ/mol
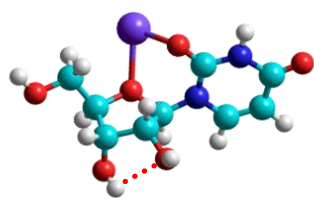
B11(O2O4')
syn, C1'-exo ($_1T^2$)
64.3 kJ/mol
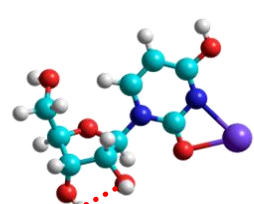
B18(O2N3)t4
anti, C3'-exo ($_3T^2$)
64.6 kJ/mol
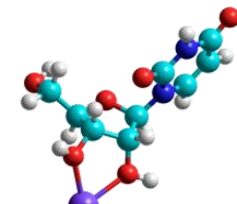
B9(O2'O3')
syn, C4'-exo ($_4T^3$)
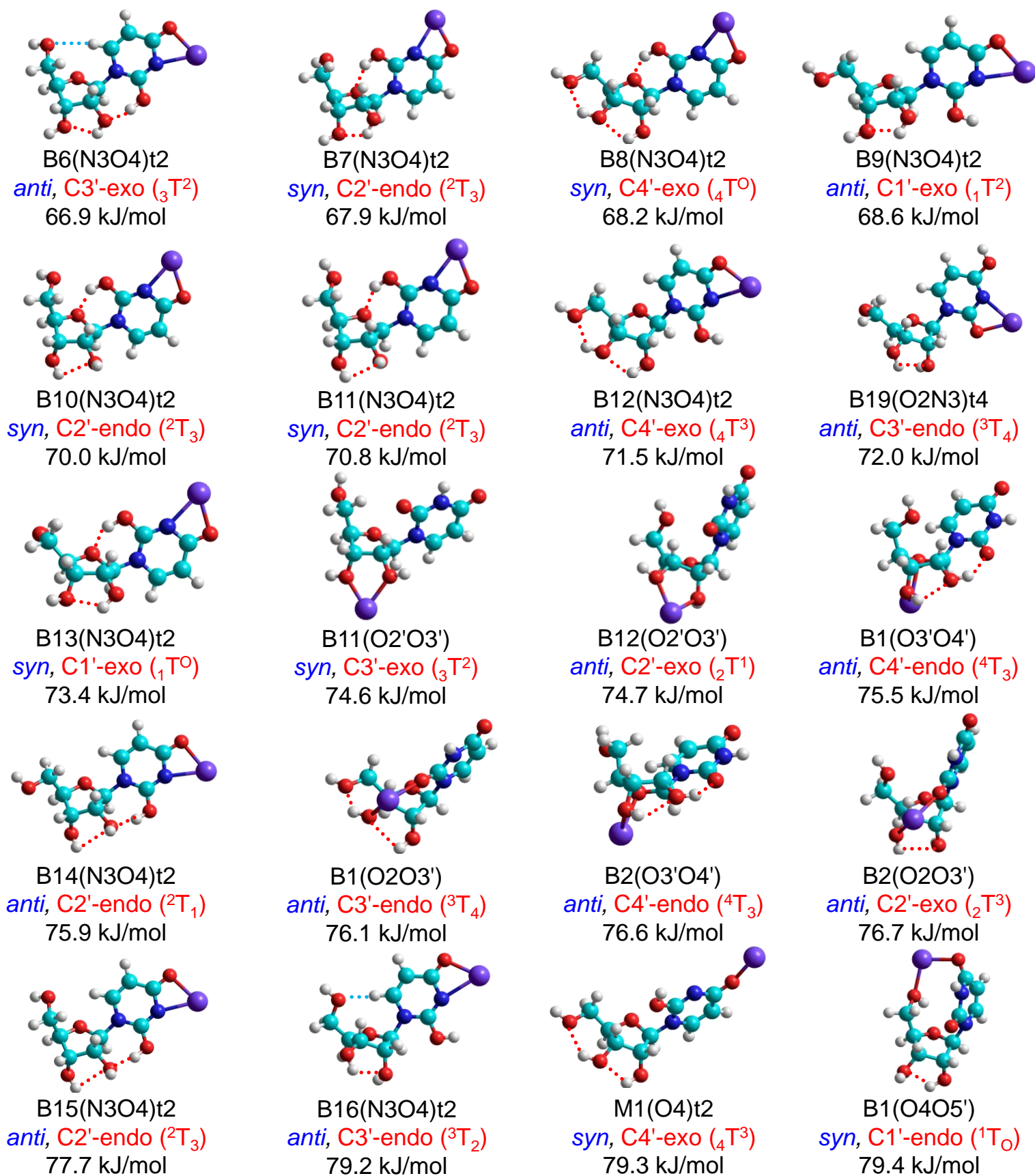64.7 kJ/mol

B5(N3O4)t2
syn, C1'-exo ($_1T^2$)
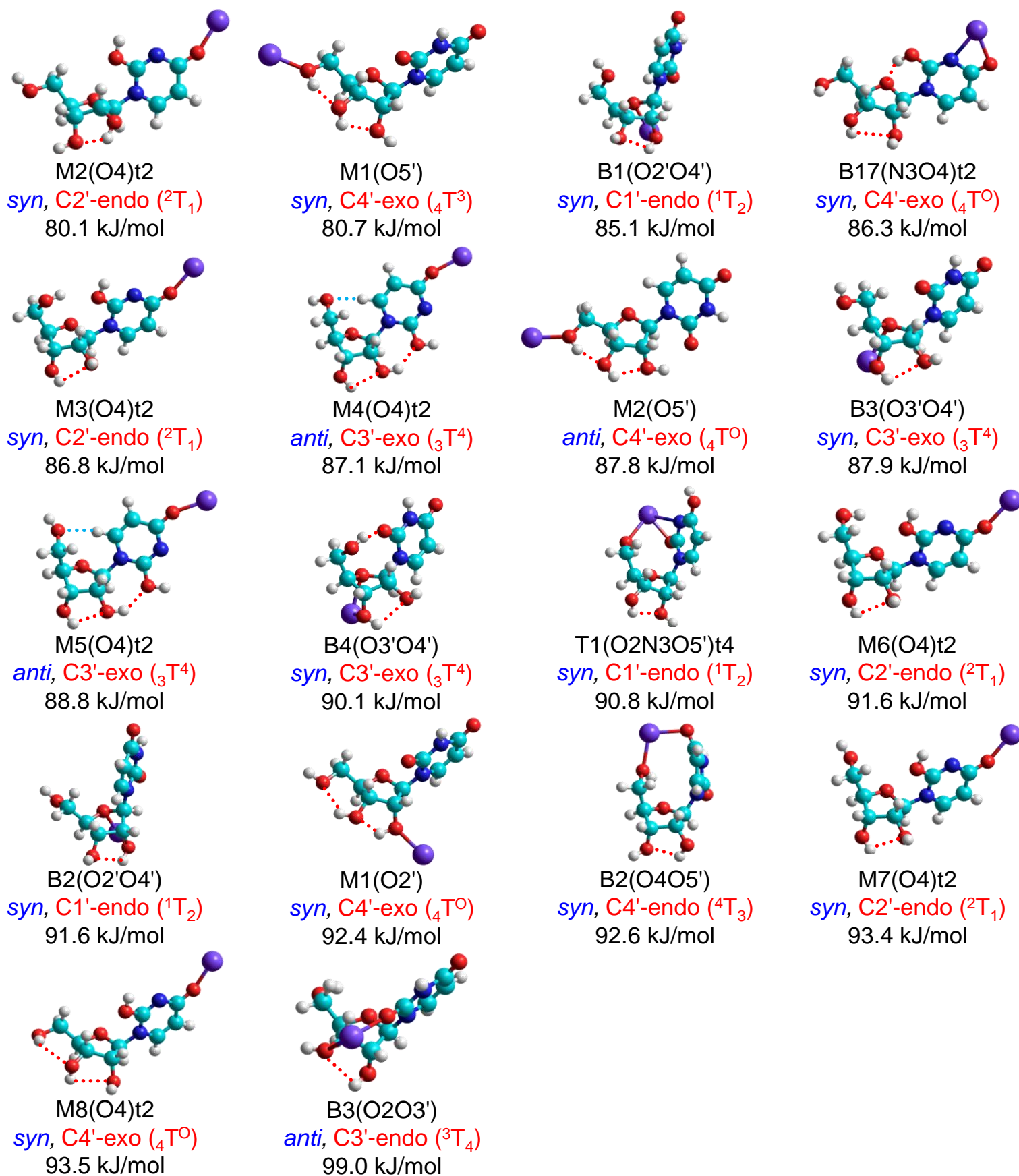64.9 kJ/mol

B12(O2O4')
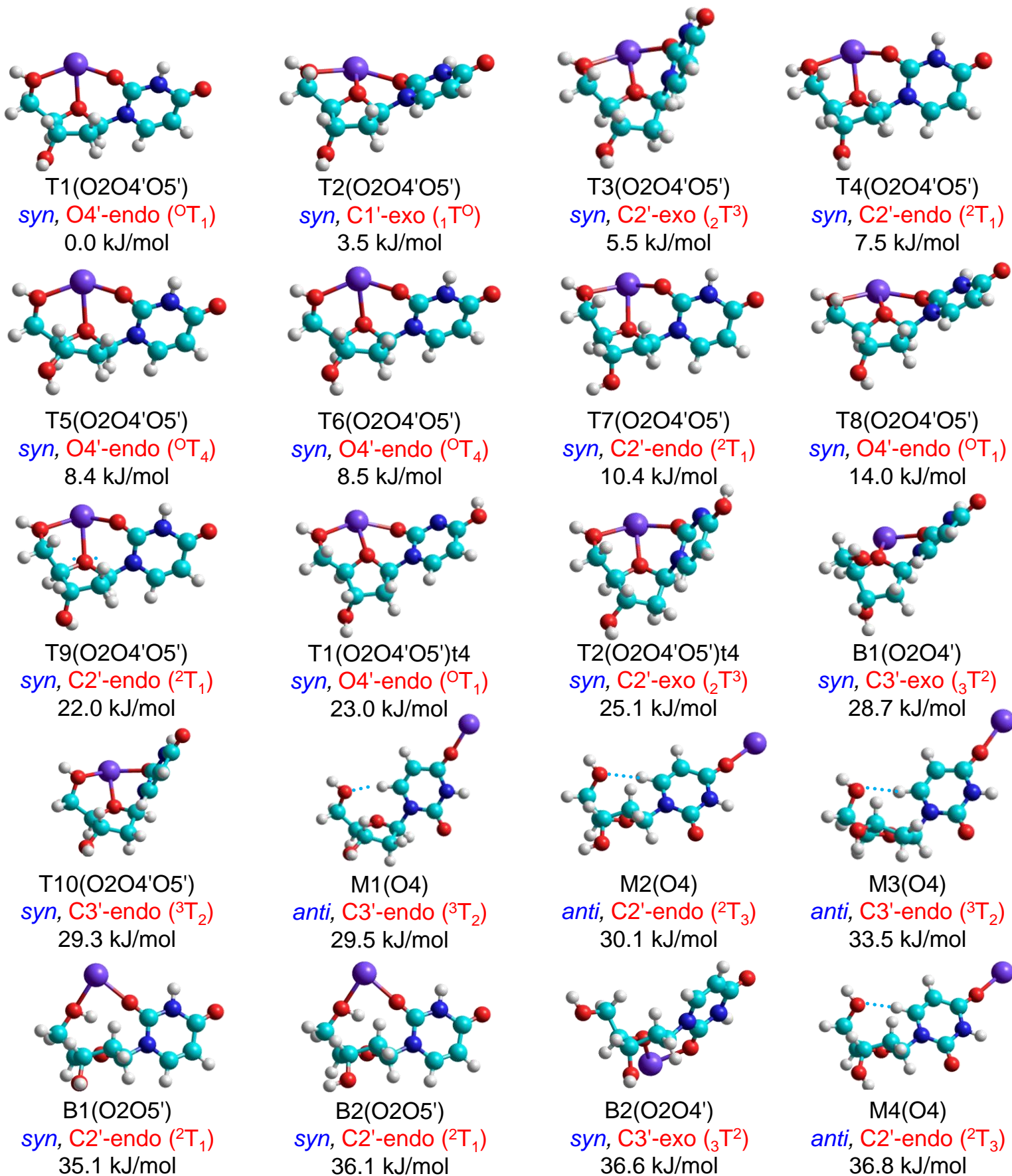*syn,* C2'-endo ($^2T_3$)
65.6 kJ/mol

B10(O2'O3')
syn, C4'-exo ($_4T^3$)
65.8 kJ/mol
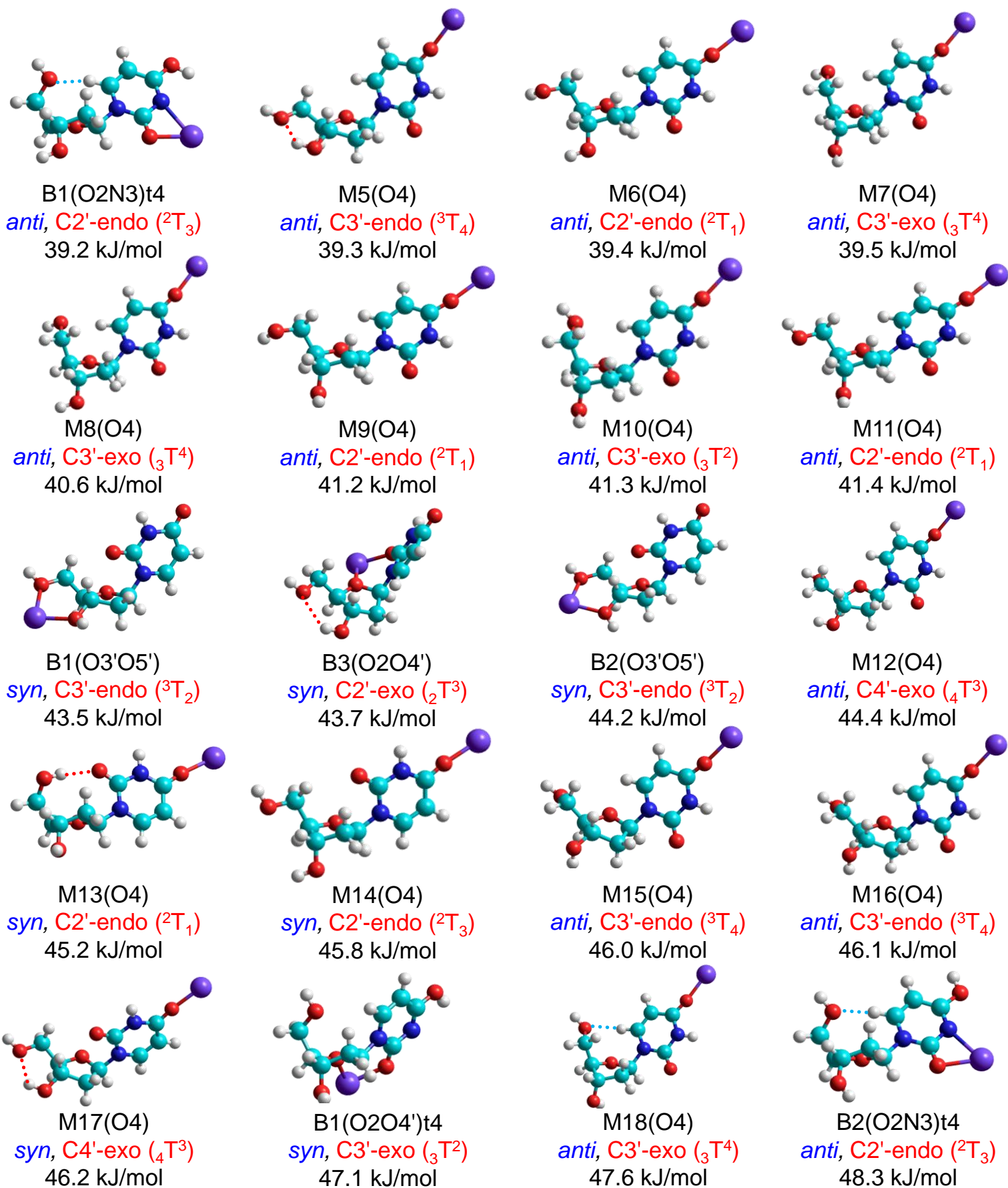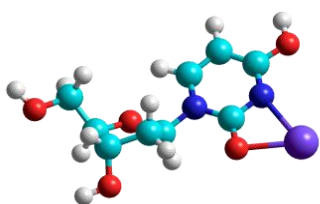
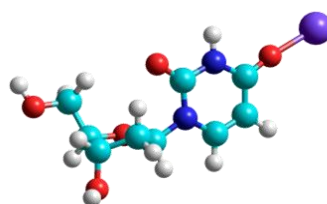B14(O2N3)
syn, C2'-endo ($^2T_3$)
66.1 kJ/mol

[Urd+Na]$^+$
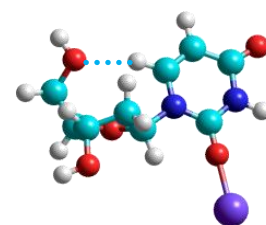
B6(N3O4)t2
anti, C3'-exo ($_3$T^2)
66.9 kJ/mol

B7(N3O4)t2
syn, C2'-endo (^{2}T$_3$)
67.9 kJ/mol

B8(N3O4)t2
syn, C4'-exo ($_4$T^O)
68.2 kJ/mol

B9(N3O4)t2
anti, C1'-exo ($_1$T^2)
68.6 kJ/mol

B10(N3O4)t2
syn, C2'-endo (^{2}T$_3$)
70.0 kJ/mol

B11(N3O4)t2
syn, C2'-endo (^{2}T$_3$)
70.8 kJ/mol

B12(N3O4)t2
anti, C4'-exo ($_4$T^3)
71.5 kJ/mol

B19(O2N3)t4
anti, C3'-endo (^{3}T$_4$)
72.0 kJ/mol

B13(N3O4)t2
syn, C1'-exo ($_1$T^O)
73.4 kJ/mol

B11(O2'O3')
syn, C3'-exo ($_3$T^2)
74.6 kJ/mol

B12(O2'O3')
anti, C2'-exo ($_2$T^1)
74.7 kJ/mol

B1(O3'O4')
anti, C4'-endo (^{4}T$_3$)
75.5 kJ/mol

B14(N3O4)t2
anti, C2'-endo (^{2}T$_1$)
75.9 kJ/mol

B1(O2O3')
anti, C3'-endo (^{3}T$_4$)
76.1 kJ/mol

B2(O3'O4')
anti, C4'-endo (^{4}T$_3$)
76.6 kJ/mol

B2(O2O3')
anti, C2'-exo ($_2$T^3)
76.7 kJ/mol

B15(N3O4)t2
anti, C2'-endo (^{2}T$_3$)
77.7 kJ/mol

B16(N3O4)t2
anti, C3'-endo (^{3}T$_2$)
79.2 kJ/mol

M1(O4)t2
syn, C4'-exo ($_4$T^3)
79.3 kJ/mol

B1(O4O5')
syn, C1'-endo (^{1}T$_O$)
79.4 kJ/mol

[Urd+Na]$^+$

Figure S3.

M2(O4)t2
syn, C2'-endo ($^{2}T_{1}$)
80.1 kJ/mol

M1(O5')
syn, C4'-exo ($_{4}T^{3}$)
80.7 kJ/mol

B1(O2'O4')
syn, C1'-endo ($^{1}T_{2}$)
85.1 kJ/mol

B17(N3O4)t2
syn, C4'-exo ($_{4}T^{O}$)
86.3 kJ/mol

M3(O4)t2
syn, C2'-endo ($^{2}T_{1}$)
86.8 kJ/mol

M4(O4)t2
anti, C3'-exo ($_{3}T^{4}$)
87.1 kJ/mol

M2(O5')
anti, C4'-exo ($_{4}T^{O}$)
87.8 kJ/mol

B3(O3'O4')
syn, C3'-exo ($_{3}T^{4}$)
87.9 kJ/mol

M5(O4)t2
anti, C3'-exo ($_{3}T^{4}$)
88.8 kJ/mol

B4(O3'O4')
syn, C3'-exo ($_{3}T^{4}$)
90.1 kJ/mol

T1(O2N3O5')t4
syn, C1'-endo ($^{1}T_{2}$)
90.8 kJ/mol

M6(O4)t2
syn, C2'-endo ($^{2}T_{1}$)
91.6 kJ/mol

B2(O2'O4')
syn, C1'-endo ($^{1}T_{2}$)
91.6 kJ/mol

M1(O2')
syn, C4'-exo ($_{4}T^{O}$)
92.4 kJ/mol

B2(O4O5')
syn, C4'-endo ($^{4}T_{3}$)
92.6 kJ/mol

M7(O4)t2
syn, C2'-endo ($^{2}T_{1}$)
93.4 kJ/mol

M8(O4)t2
syn, C4'-exo ($_{4}T^{O}$)
93.5 kJ/mol

B3(O2O3')
anti, C3'-endo ($^{3}T_{4}$)
99.0 kJ/mol

[Urd+Na]$^{+}$

T1(O2O4'O5')
syn, O4'-endo ($^OT_1$)
0.0 kJ/mol

T2(O2O4'O5')
syn, C1'-exo ($_1T^O$)
3.5 kJ/mol

T3(O2O4'O5')
syn, C2'-exo ($_2T^3$)
5.5 kJ/mol

T4(O2O4'O5')
syn, C2'-endo ($^2T_1$)
7.5 kJ/mol

T5(O2O4'O5')
syn, O4'-endo ($^OT_4$)
8.4 kJ/mol

T6(O2O4'O5')
syn, O4'-endo ($^OT_4$)
8.5 kJ/mol

T7(O2O4'O5')
syn, C2'-endo ($^2T_1$)
10.4 kJ/mol

T8(O2O4'O5')
syn, O4'-endo ($^OT_1$)
14.0 kJ/mol

T9(O2O4'O5')
syn, C2'-endo ($^2T_1$)
22.0 kJ/mol

T1(O2O4'O5')t4
syn, O4'-endo ($^OT_1$)
23.0 kJ/mol

T2(O2O4'O5')t4
syn, C2'-exo ($_2T^3$)
25.1 kJ/mol

B1(O2O4')
syn, C3'-exo ($_3T^2$)
28.7 kJ/mol

T10(O2O4'O5')
syn, C3'-endo ($^3T_2$)
29.3 kJ/mol

M1(O4)
anti, C3'-endo ($^3T_2$)
29.5 kJ/mol

M2(O4)
anti, C2'-endo ($^2T_3$)
30.1 kJ/mol

M3(O4)
anti, C3'-endo ($^3T_2$)
33.5 kJ/mol

B1(O2O5')
syn, C2'-endo ($^2T_1$)
35.1 kJ/mol

B2(O2O5')
syn, C2'-endo ($^2T_1$)
36.1 kJ/mol

B2(O2O4')
syn, C3'-exo ($_3T^2$)
36.6 kJ/mol

M4(O4)
anti, C2'-endo ($^2T_3$)
36.8 kJ/mol

[dUrd+Na]$^+$

Figure S4.

B1(O2N3)t4
anti, C2'-endo ($^2T_3$)
39.2 kJ/mol

M5(O4)
anti, C3'-endo ($^3T_4$)
39.3 kJ/mol

M6(O4)
anti, C2'-endo ($^2T_1$)
39.4 kJ/mol

M7(O4)
anti, C3'-exo ($_3T^4$)
39.5 kJ/mol

M8(O4)
anti, C3'-exo ($_3T^4$)
40.6 kJ/mol

M9(O4)
anti, C2'-endo ($^2T_1$)
41.2 kJ/mol

M10(O4)
anti, C3'-exo ($_3T^2$)
41.3 kJ/mol

M11(O4)
anti, C2'-endo ($^2T_1$)
41.4 kJ/mol

B1(O3'O5')
syn, C3'-endo ($^3T_2$)
43.5 kJ/mol

B3(O2O4')
syn, C2'-exo ($_2T^3$)
43.7 kJ/mol

B2(O3'O5')
syn, C3'-endo ($^3T_2$)
44.2 kJ/mol

M12(O4)
anti, C4'-exo ($_4T^3$)
44.4 kJ/mol

M13(O4)
syn, C2'-endo ($^2T_1$)
45.2 kJ/mol

M14(O4)
syn, C2'-endo ($^2T_3$)
45.8 kJ/mol

M15(O4)
anti, C3'-endo ($^3T_4$)
46.0 kJ/mol

M16(O4)
anti, C3'-endo ($^3T_4$)
46.1 kJ/mol

M17(O4)
syn, C4'-exo ($_4T^3$)
46.2 kJ/mol

B1(O2O4')t4
syn, C3'-exo ($_3T^2$)
47.1 kJ/mol

M18(O4)
anti, C3'-exo ($_3T^4$)
47.6 kJ/mol

B2(O2N3)t4
anti, C2'-endo ($^2T_3$)
48.3 kJ/mol

[dUrd+Na]$^+$

Figure S4.

B3(O2N3)t4
anti, C2'-endo (^{2}T$_1$)
48.5 kJ/mol

B4(O2N3)t4
anti, C2'-endo (^{2}T$_1$)
48.6 kJ/mol

M19(O4)
syn, C2'-endo (^{2}T$_3$)
48.9 kJ/mol

M1(O2)
anti, O4'-endo (^{O}T$_4$)
49.0 kJ/mol

M20(O4)
syn, C4'-exo ($_4$T^3)
49.5 kJ/mol

M2(O2)
anti, C2'-endo (^{2}T$_3$)
49.7 kJ/mol

B1(O2O3')
anti, C2'-endo (^{2}T$_1$)
49.9 kJ/mol
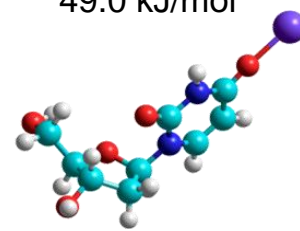
M21(O4)
syn, C4'-exo ($_4$T^3)
50.3 kJ/mol
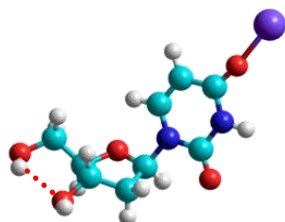
M22(O4)
anti, C3'-endo (^{3}T$_4$)
51.1 kJ/mol
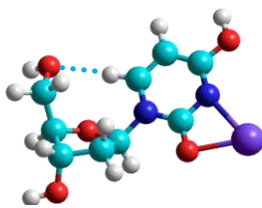
B5(O2N3)t4
anti, C3'-exo ($_3$T^4)
51.4 kJ/mol
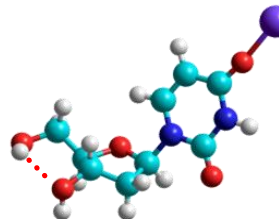
M23(O4)
anti, C3'-endo (^{3}T$_4$)
51.8 kJ/mol
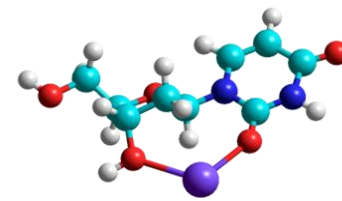
B2(O2O3')
anti, C1'-exo ($_1$T^2)
51.9 kJ/mol
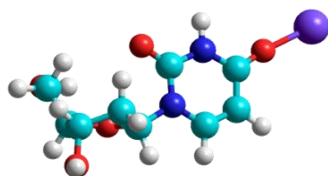
M24(O4)
syn, C2'-endo (^{2}T$_3$)
52.3 kJ/mol
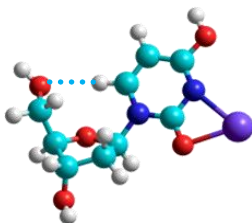
B6(O2N3)t4
anti, C3'-exo ($_3$T^2)
52.7 kJ/mol
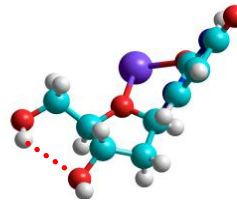
B4(O2O4')
syn, C3'-endo (^{3}T$_2$)
55.6 kJ/mol
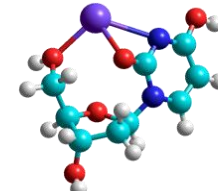
T1(O2N3O5')t4
syn, C3'-exo ($_3$T^2)
55.8 kJ/mol
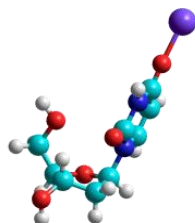
M25(O4)
anti, C2'-exo ($_2$T^1)
56.0 kJ/mol
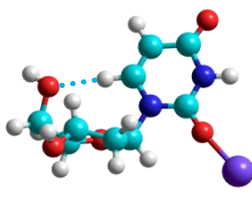
M3(O2)
anti, C3'-endo (^{3}T$_4$)
56.6 kJ/mol
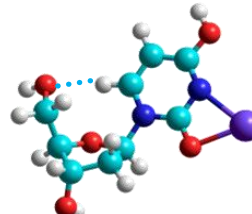
B7(O2N3)t4
anti, C3'-exo ($_3$T^4)
57.6 kJ/mol
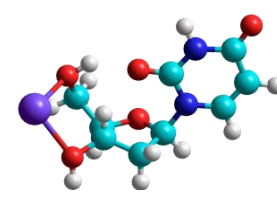
B2(O3'O5')
syn, C3'-endo (^{3}T$_2$)
57.8 kJ/mol

[dUrd+Na]$^+$
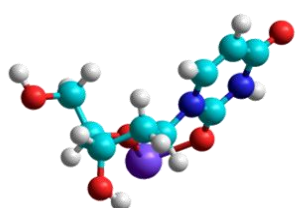
B5(O2O4')
syn, C3'-exo ($_3$T^2)
58.4 kJ/mol
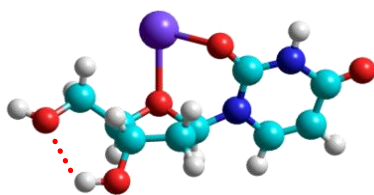
B6(O2O4')
syn, O4'-endo (^{O}T$_1$)
58.9 kJ/mol
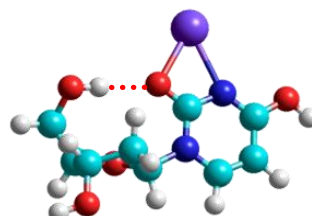
B8(O2N3)t4
syn, C2'-endo (^{2}T$_1$)
59.6 kJ/mol
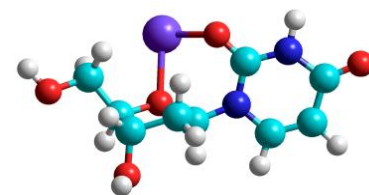
B7(O2O4')
syn, C1'-exo ($_1$T^2)
59.7 kJ/mol
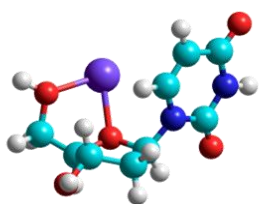
B1(O4'O5')
anti, C4'-exo ($_4$T^3)
60.6 kJ/mol
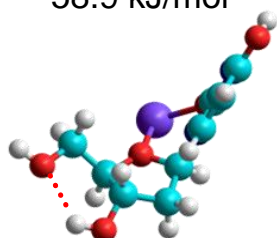
B2(O2O4')t4
syn, C2'-exo ($_2$T^3)
60.9 kJ/mol
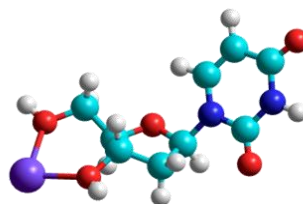
B3(O3'O5')
anti, C4'-exo ($_4$T^3)
62.4 kJ/mol
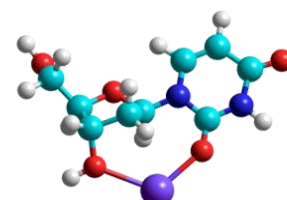
B3(O2O3')
anti, C1'-exo ($_1$T^2)
63.0 kJ/mol
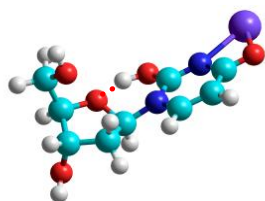
B1(N3O4)t2
syn, C2'-endo (^{2}T$_3$)
63.8 kJ/mol
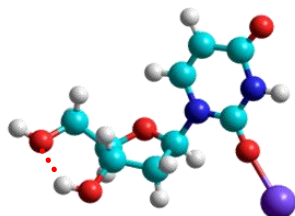
M4(O2)
anti, C3'-endo (^{3}T$_4$)
63.9 kJ/mol
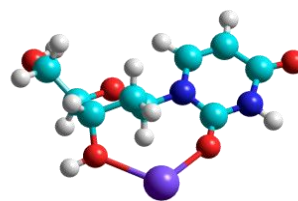
B4(O2O3')
anti, C1'-exo ($_1$T^2)
64.2 kJ/mol
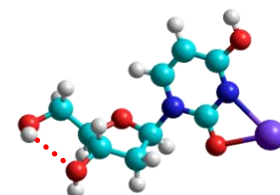
B9(O2N3)t4
anti, C3'-endo (^{3}T$_4$)
65.0 kJ/mol
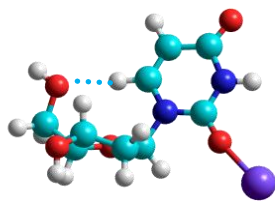
M5(O2)
anti, C3'-endo (^{3}T$_2$)
65.3 kJ/mol
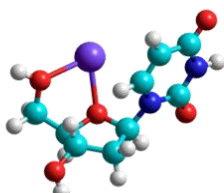
B2(O4'O5')
anti, C4'-exo ($_4$T^3)
66.1 kJ/mol
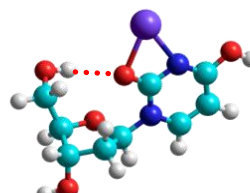
B10(O2N3)t4
syn, C2'-endo (^{2}T$_3$)
66.6 kJ/mol
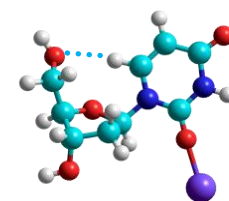
M6(O2)
anti, C3'-exo ($_3$T^2)
67.6 kJ/mol
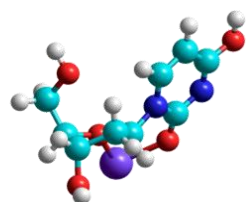
B3(O2O4')t4
syn, C3'-exo ($_3$T^2)
68.8 kJ/mol
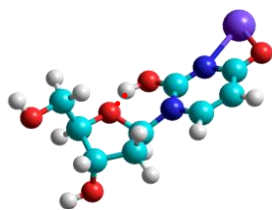
B2(N3O4)t2
syn, C2'-endo (^{2}T$_1$)
69.9 kJ/mol
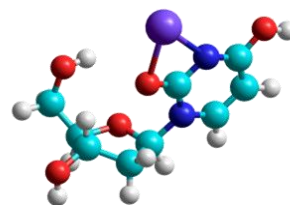
B11(O2N3)t4
syn, C4'-exo ($_4$T^3)
70.1 kJ/mol
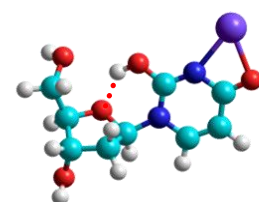
B3(N3O4)t2
syn, C2'-endo (^{2}E)
70.4 kJ/mol

[dUrd+Na]$^+$

Figure S4.
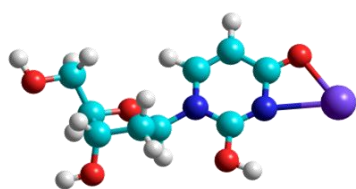
B4(N3O4)t2
anti, C2'-endo ($^2T_1$)
72.3 kJ/mol
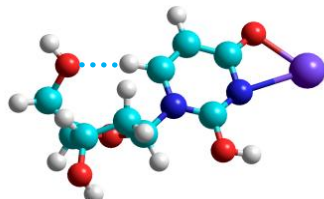
B5(N3O4)t2
anti, C2'-endo ($^2T_3$)
72.5 kJ/mol
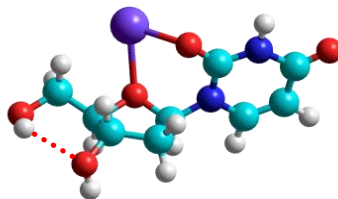
B8(O2O4')
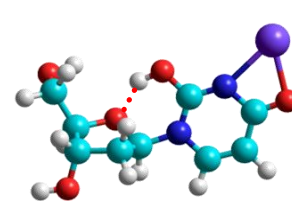*syn*, O4'-endo ($^OT_4$)
75.9 kJ/mol
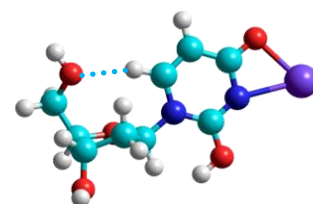
B6(N3O4)t2
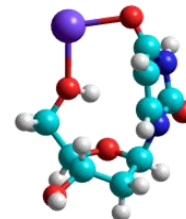*anti*, C2'-endo ($^2T_3$)
76.6 kJ/mol
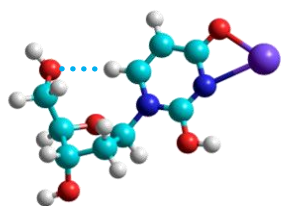
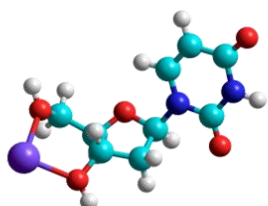B7(N3O4)t2
anti, C3'-exo ($_3T^2$)
77.5 kJ/mol
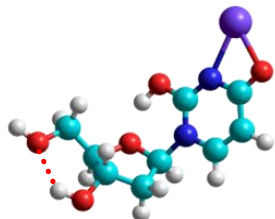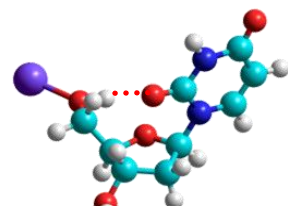
B8(N3O4)t2
syn, C3'-endo ($^3T_4$)
77.6 kJ/mol

B9(N3O4)t2
syn, C1'-exo ($_1T^2$)
78.9 kJ/mol
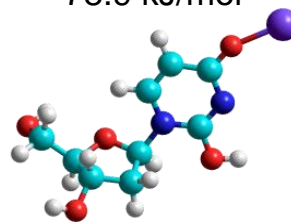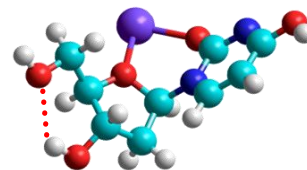
B1(O4O5')
syn, C2'-exo ($_2T^3$)
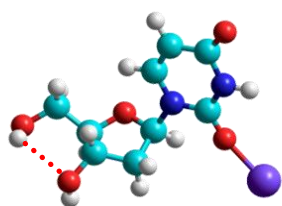79.0 kJ/mol

B4(O3'O5')
anti, C4'-exo ($_4T^3$)
80.9 kJ/mol

M1(O5')
syn, C3'-endo ($^3T_2$)
81.8 kJ/mol

M1(O4)t2
anti, C4'-exo ($_4T^3$)
82.2 kJ/mol

B4(O2O4')t4
syn, C2'-exo ($_2T^3$)
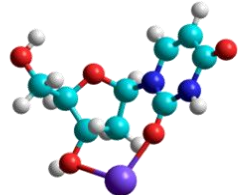82.7 kJ/mol

M7(O2)
anti, C3'-endo ($^3T_4$)
83.7 kJ/mol

B1(O2O3')t4
anti, C1'-exo ($_1T^2$)
85.1 kJ/mol
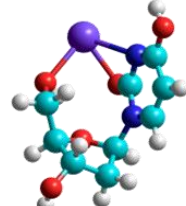
T2(O2N3O5')t4
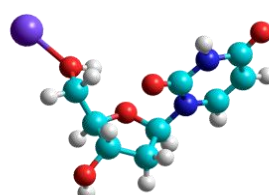*syn*, C1'-endo ($^1T_2$)
86.0 kJ/mol
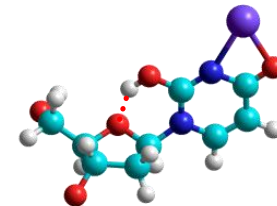
B10(N3O4)t2
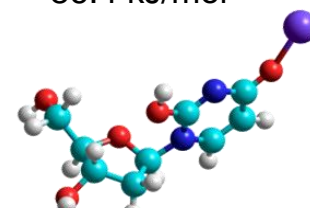*syn*, O4'-endo ($^OT_4$)
86.4 kJ/mol

B5(O2O3')
anti, C3'-endo ($^3T_2$)
88.1 kJ/mol

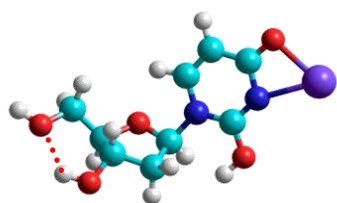M1(O3')
syn, C4'-exo ($_4T^3$)
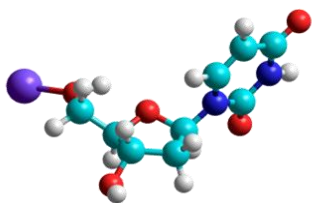88.3 kJ/mol

M2(O5')
syn, C3'-endo ($^3T_2$)
89.7 kJ/mol

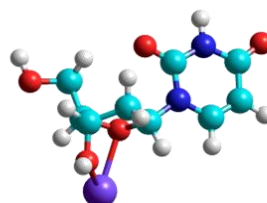M2(O4)t2
syn, C4'-exo ($_4T^O$)
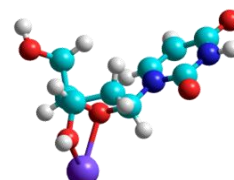91.3 kJ/mol

[dUrd+Na]$^+$

Figure S4.

B11(N3O4)t2
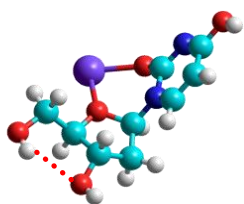*anti*, C3'-endo ($^3T_4$)
92.3 kJ/mol

M3(O5')
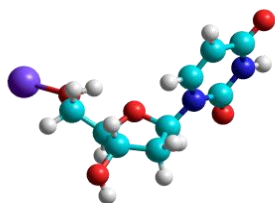*anti*, C4'-exo ($_4T^O$)
93.0 kJ/mol

B1(O3'O4')
syn, C3'-exo ($_3T^4$)
93.5 kJ/mol

B2(O3'O4')
anti, C4'-endo ($^4T_3$)
94.1 kJ/mol

B5(O2O4')t4
syn, C3'-endo ($^3T_2$)
95.2 kJ/mol
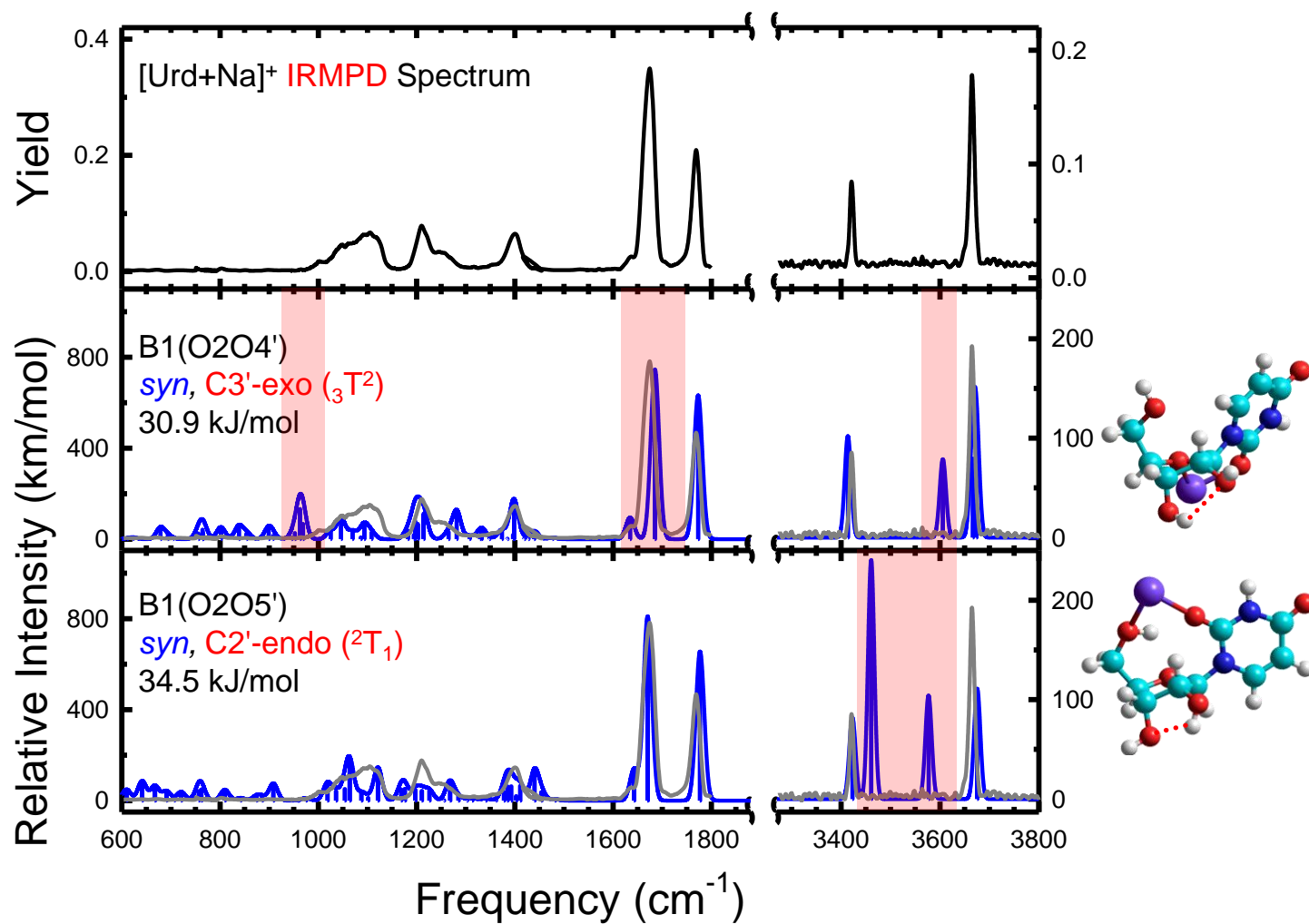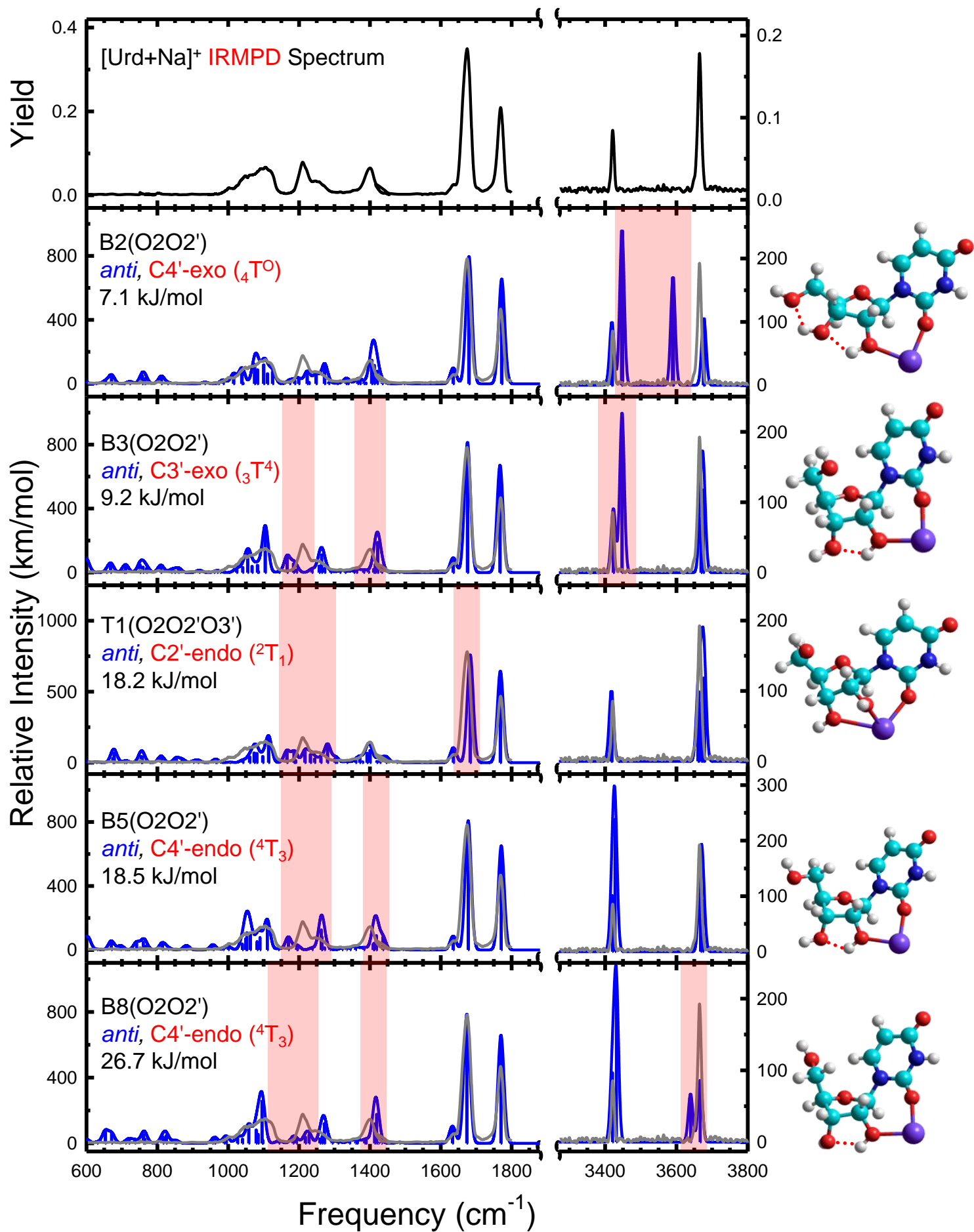
M4(O5')
anti, C4'-exo ($_4T^O$)
99.8 kJ/mol

[dUrd+Na]$^+$

[Urd+Na]⁺ IRMPD Spectrum

B2(O2O2')
anti, C4'-exo ($_4T^O$)
7.1 kJ/mol

B3(O2O2')
anti, C3'-exo ($_3T^4$)
9.2 kJ/mol

T1(O2O2'O3')
anti, C2'-endo ($^2T_1$)
18.2 kJ/mol

B5(O2O2')
anti, C4'-endo ($^4T_3$)
18.5 kJ/mol

B8(O2O2')
anti, C4'-endo ($^4T_3$)
26.7 kJ/mol

Frequency (cm⁻¹)

Relative Intensity (km/mol)

Yield

Figure S7.

Figure S10.

Figure S11.

[dUrd+Na]⁺ IRMPD Spectrum

B1(O2O4')
syn, C3'-exo ($_3T^2$)
28.7 kJ/mol

B1(O2O5')
syn, C2'-endo ($^2T_1$)
35.1 kJ/mol

M1(O2)
anti, O4'-endo ($^OT_4$)
49.0 kJ/mol

B1(O2O3')
anti, C2'-endo ($^2T_1$)
49.9 kJ/mol

Yield

Relative Intensity (km/mol)

Frequency (cm^{-1})

Yield (top panel)

[dUrd+Na]⁺ IRMPD Spectrum

Relative Intensity (km/mol)

M1(O4)
anti, C3'-endo ($^3T_2$)
29.5 kJ/mol

M13(O4)
syn, C2'-endo ($^2T_1$)
45.2 kJ/mol

B1(O4O5')
syn, C2'-exo ($_2T^3$)
79.0 kJ/mol

Frequency (cm⁻¹)

Figure S13.