

Supporting Information for

## Buffer catalyzed cleavage of uridylyl-3',5'-uridine in aqueous DMSO: comparison to its activated analog, 2-hydroxypropyl 4-nitrophenyl phosphate

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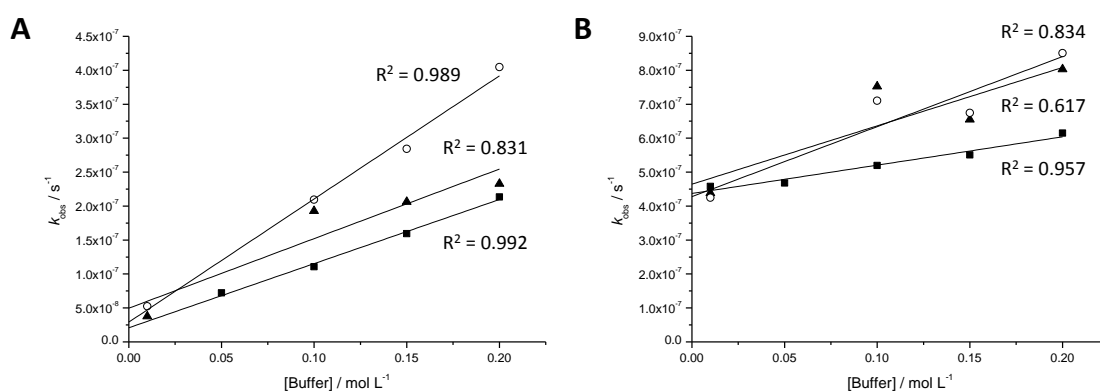
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**Table S1** Observed rate constants for the cleavage and isomerization of UpU in morpholine buffers containing 80% (v/v) of DMSO;  $T = 90\text{ }^{\circ}\text{C}$ ,  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

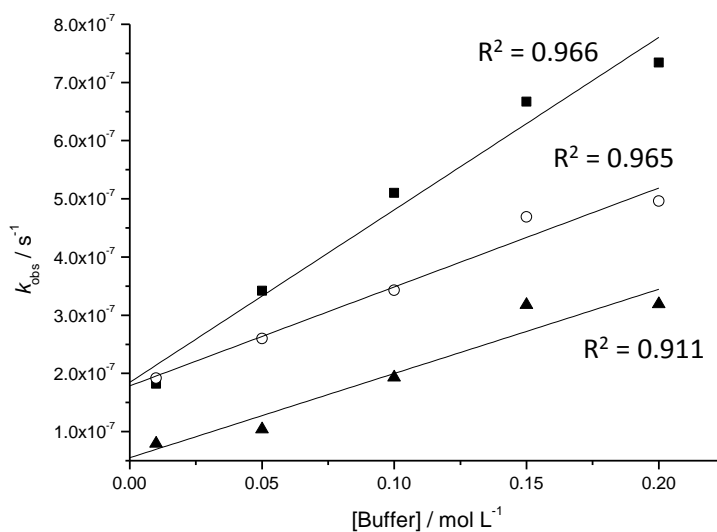
$[\text{BH}^+]:[\text{B}]$	[Buffer] / mol L <sup>-1</sup>	$k_{\text{obs}}^{\text{clv}} / 10^{-7}\text{ s}^{-1}$	$k_{\text{obs}}^{\text{iso}} / 10^{-7}\text{ s}^{-1}$
3:1	0.01	0.377	4.38
	0.10	1.93	7.53
	0.15	2.06	6.55
	0.20	2.33	8.03
1:1	0.01	0.523	4.25
	0.10	2.09	7.10
	0.15	2.84	6.75
	0.20	4.05	8.50
1:3	0.01	0.796	4.58
	0.05	0.722	4.68
	0.10	1.11	5.20
	0.15	1.59	5.51
	0.20	2.13	6.15



**Figure S1** Rate constants for the cleavage (A,  $k_{\text{obs}}^{\text{clv}}$ ) and isomerization (B,  $k_{\text{obs}}^{\text{iso}}$ ) of UpU in morpholine buffers as a function of total buffer concentration at  $[\text{BH}^+]:[\text{B}] = 3:1$  ( $\blacktriangle$ ),  $1:1$  ( $\circ$ ) and  $1:3$  ( $\blacksquare$ );  $T = 90\text{ }^{\circ}\text{C}$ ;  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

**Table S2** Observed rate constants for the cleavage and isomerization of UpU in 4-hydroxypiperidine buffers containing 80% (v/v) of DMSO;  $T = 90\text{ }^{\circ}\text{C}$ ,  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

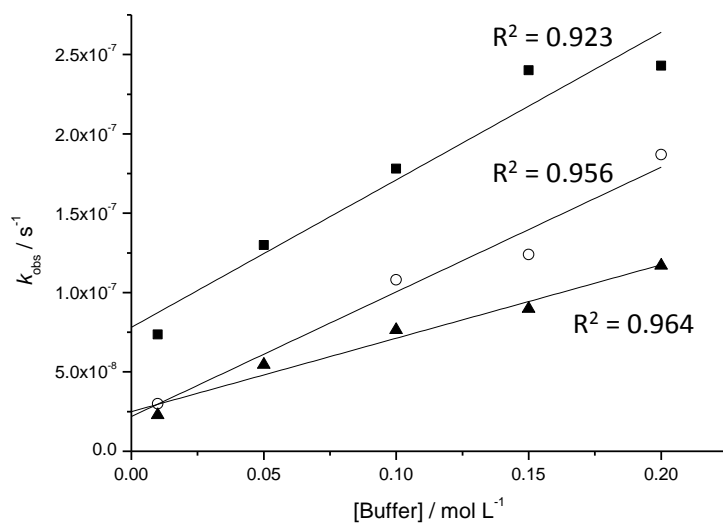
$[\text{BH}^+]:[\text{B}]$	[Buffer] / $\text{mol L}^{-1}$	$k_{\text{obs}}^{\text{clv}} / 10^{-7}\text{ s}^{-1}$	$k_{\text{obs}}^{\text{iso}} / 10^{-7}\text{ s}^{-1}$
3:1	0.01	0.796	4.42
	0.05	1.04	4.64
	0.10	1.93	5.44
	0.15	3.18	5.46
	0.20	3.19	6.18
1:1	0.01	1.92	4.34
	0.05	2.60	4.44
	0.10	3.43	4.14
	0.15	4.69	4.56
	0.20	4.96	4.76
1:3	0.01	1.82	3.74
	0.05	3.42	3.76
	0.10	5.10	3.94
	0.15	6.67	4.54
	0.20	7.34	4.28



**Figure S2** Observed first-order rate constants for the cleavage of UpU ( $k_{\text{obs}}^{\text{clv}}$ ) in 4-hydroxypiperidine buffers as a function of total buffer concentration at  $[\text{BH}^+]:[\text{B}] = 3:1$  ( $\blacktriangle$ ),  $1:1$  ( $\circ$ ) and  $1:3$  ( $\blacksquare$ );  $T = 90\text{ }^{\circ}\text{C}$ ;  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

**Table S3** Observed rate constants for the cleavage and isomerization of UpU in piperidine buffers containing 80% (v/v) of DMSO;  $T = 90\text{ }^{\circ}\text{C}$ ,  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

$[\text{BH}^+]:[\text{B}]$	[Buffer] / $\text{mol L}^{-1}$	$k_{\text{obs}}^{\text{clv}} / 10^{-7}\text{ s}^{-1}$	$k_{\text{obs}}^{\text{iso}} / 10^{-7}\text{ s}^{-1}$
3:1	0.01	0.229	4.38
	0.05	0.546	4.42
	0.10	0.765	4.38
	0.15	0.898	4.96
	0.20	1.17	4.82
1:1	0.01	0.299	4.02
	0.10	1.08	4.16
	0.15	1.24	4.54
	0.20	1.87	5.00
1:3	0.01	0.735	4.08
	0.05	1.30	3.96
	0.10	1.78	4.48
	0.15	2.40	4.58
	0.20	2.43	4.82



**Figure S3** Observed first-order rate constants for the cleavage of UpU ( $k_{\text{obs}}^{\text{clv}}$ ) in piperidine buffers as a function of total buffer concentration at  $[\text{BH}^+]:[\text{B}] = 3:1$  ( $\blacktriangle$ ),  $1:1$  ( $\circ$ ) and  $1:3$  ( $\blacksquare$ );  $T = 90\text{ }^{\circ}\text{C}$ ;  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

**Table S4** Observed rate constants for the cleavage of UpU in 1,3,5-trimethylphenol buffers containing 80% (v/v) of DMSO;  $T = 90\text{ }^{\circ}\text{C}$ ,  $I(\text{NaClO}_4) = 0.2\text{ mol L}^{-1}$ .

$[\text{BH}^+]:[\text{B}]$	[Buffer] / mol L <sup>-1</sup>	$k_{\text{obs}}^{\text{clv}} / 10^{-4}\text{ s}^{-1}$
3:1	0.01	2.31
	0.03	9.21
	0.05	8.81
	0.07	9.61
	0.10	11.5
1:1	0.01	16.4
	0.015	15.0
	0.025	24.0
	0.05	27.0
	0.075	28.1
1:3	0.10	30.8
	0.01	21.8
	0.02	41.0
	0.03	48.4
	0.04	68.6
	0.05	61.1