Supplementary Information

Straightforward detection of the secondary ionization of the phosphate group and p*K* determinations by high-resolution solid-state ^{31}P NMR.

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T*ABLE* 1. Experimental ^{31}P values of the principal tensor elements δ_i and corresponding anisotropic parameters for L o-phosphoserine and AMP-5' at different pH

Compound	pH	δ_{iso} (ppm)	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	δ (ppm)	Ω (ppm)	η	κ
L o-phosphoserine	1.96	0.2	65.4	9.5	-74.3	-74.5	139.7	0.75	0.2
	5.61	2.9	73.4	13.0	-77.6	-80.5	151.0	0.75	0.2
		2.9	70.3	-17.3	-44.3	67.4	114.6	0.4	- 0.53
	11.96	8.4	84.1	-14.3	-44.5	75.7	128.6	0.4	-0.53
AMP-5'	3.92	1.6	69.3	11.2	-75.8	-77.4	152	0.75	0.19
	6.32	4.5	68.8	15.8	-71.1	-75.6	143	0.70	0.24
		4.5	68.6	-14.7	-40.4	64.1	109	0.4	-0.53
	8.48	7.4	79.9	-12.5	-45.1	72.5	125	0.45	-0.48

* estimated errors in δ_{11}, δ_{22}, δ_{33} are ± 1 ppm; anisotropy is calculated as $\delta=(\delta_{33}-\delta_{iso})$ and asymmetry as $\eta=(\delta_{22}-\delta_{11})/\delta$ when $|\delta_{11}-\delta_{iso}|\leq|\delta_{33}-\delta_{iso}|$ or as $\delta=(\delta_{11}-\delta_{iso})$ and $\eta=(\delta_{22}-\delta_{33})/\delta$ when $|\delta_{11}-\delta_{iso}|\geq|\delta_{33}-\delta_{iso}|$. Span is expressed as $\Omega=\delta_{11}-\delta_{33}$, skew as $\kappa=3(\delta_{22}-\delta_{iso})/\Omega$