Supporting Information For

The Effects of Deuteration of ^{13}C-enriched Phospholactate On the Efficiency of Parahydrogen-Induced Polarization By Magnetic Field Cycling

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1. Characterization of potassium 1-^{13}C-phosphoenolpyruvate

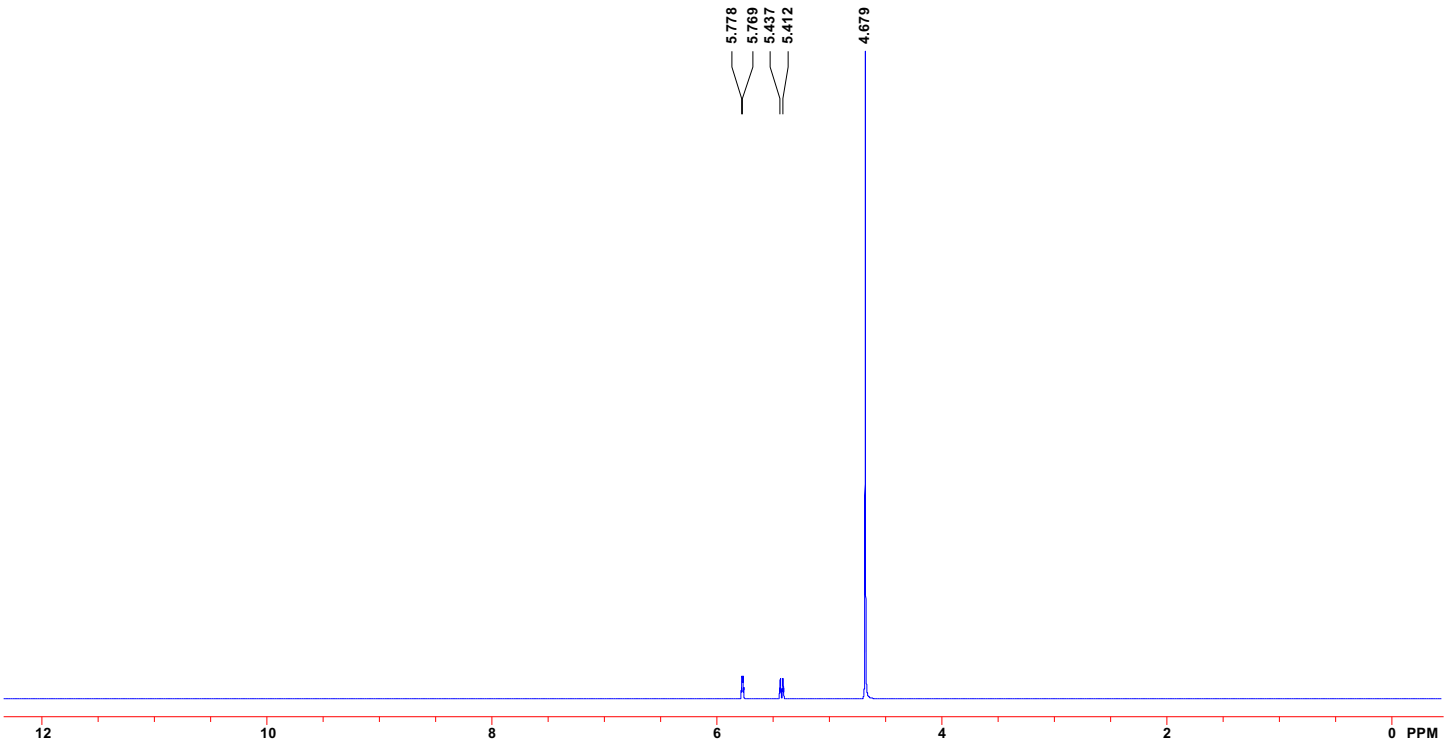


Figure S1. ^{1}H NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate in D_2O. Note two NMR multiplets at ~5.8 ppm and ~5.4 ppm corresponding to two protons of 1-^{13}C-phosphoenolpyruvate. The resonance at 4.7 ppm is the residual proton signal of D_2O.

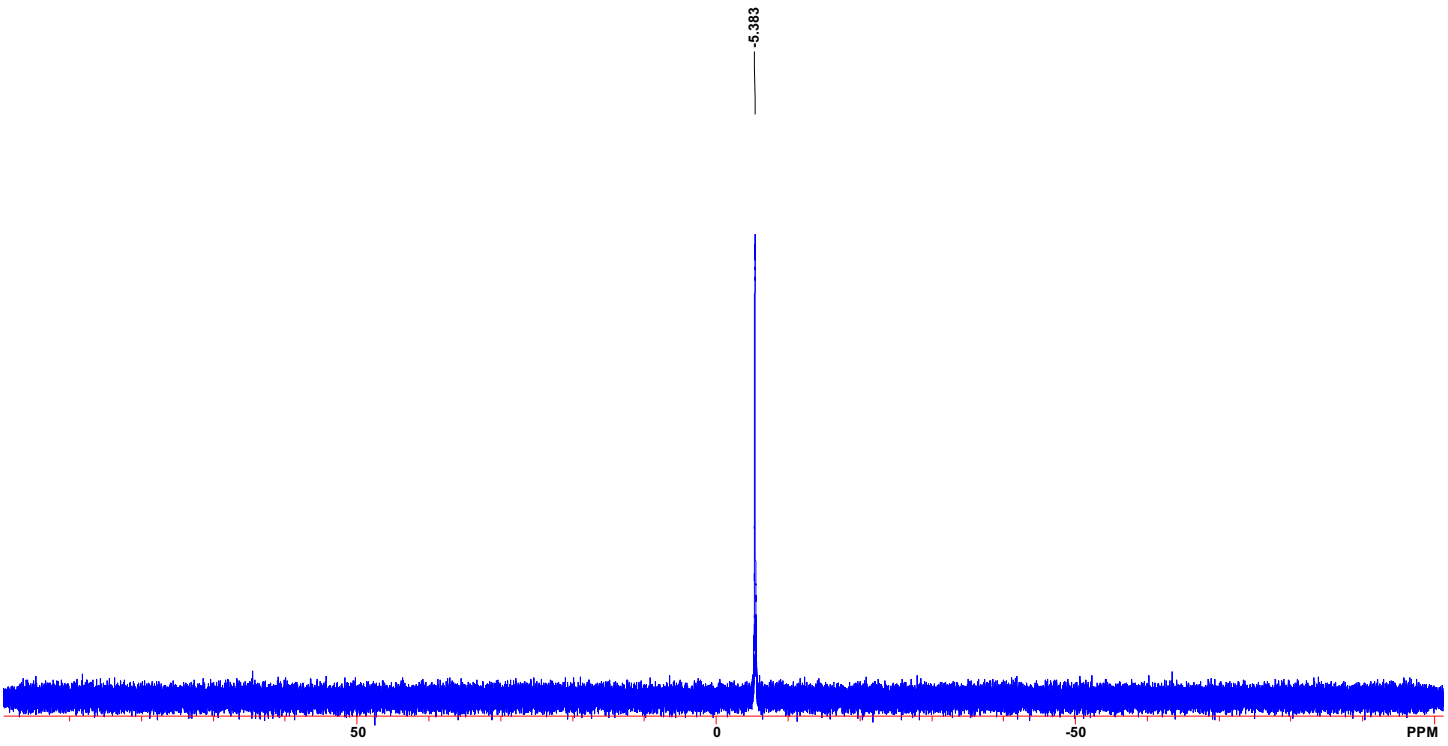


Figure S2. ^{31}P NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate in D_2O.

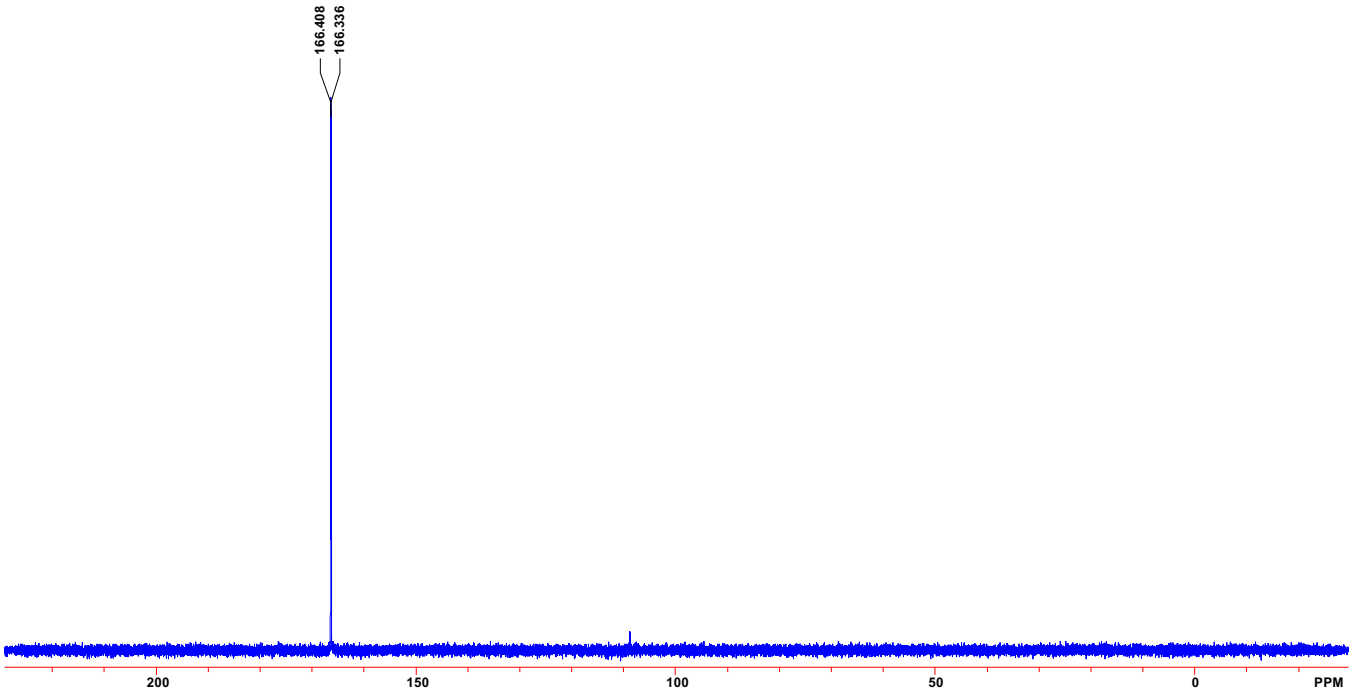


Figure S3. ^{13}C NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate in D_2O.

2. Characterization of potassium 1-^{13}C-phosphoenolpyruvate-d_2

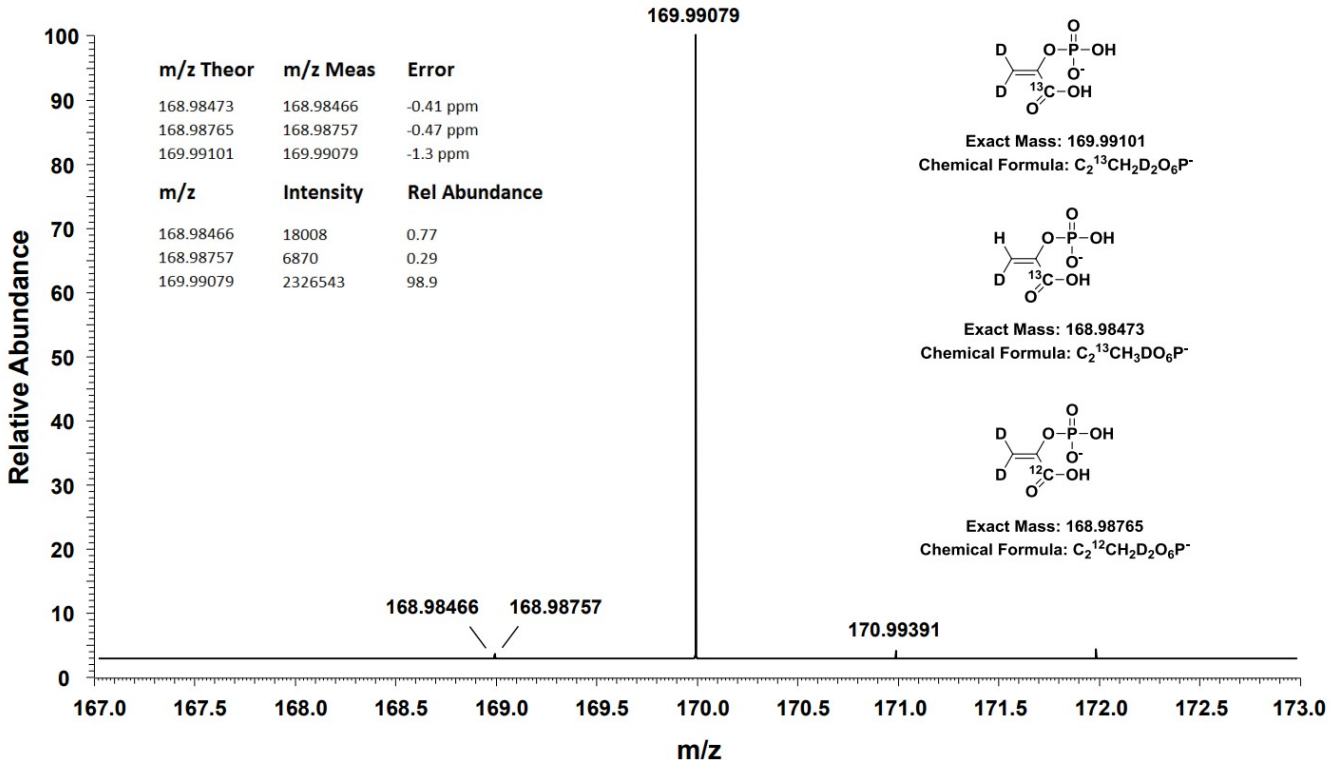


Figure S4. HR-MS negative ion spectrum of 1-^{13}C-phosphoenolpyruvate-d_2. High resolution mass spectrometry was performed by direct liquid infusion using an Orbitrap mass spectrometer (Thermo-Finnigan, San Jose, CA) equipped an Ion-Max source housing and a standard electrospray (ESI) ionization probe in negative ion mode at a resolving power of 60,000 (at m/z 400). Calculated for $^{12}C_2{}^{13}C_1H_2D_2O_6P^-$ (M-H-): 169.99101; found 169.99079 (-1.3 ppm).

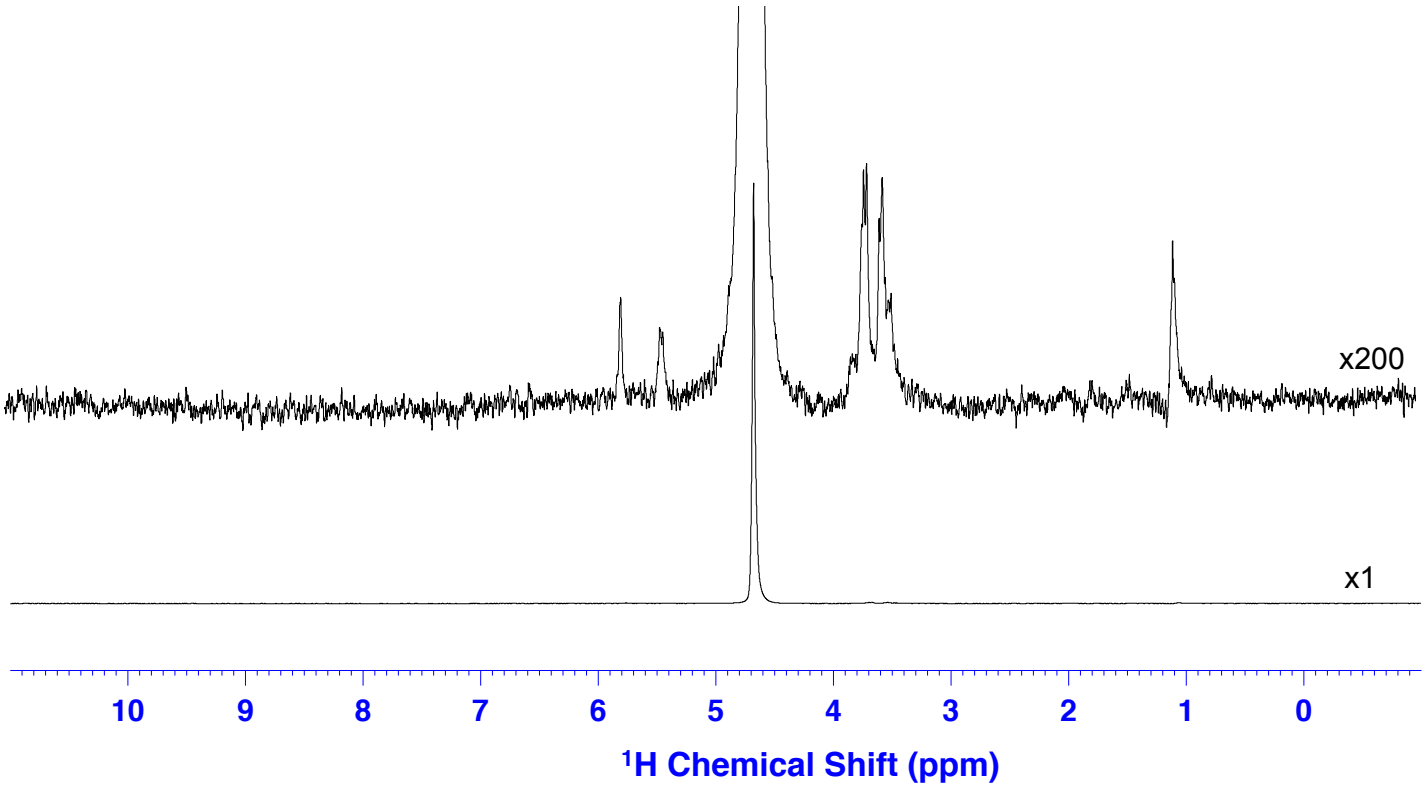


Figure S5. ^{1}H NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate-d_2 in D_2O. Note two NMR multiplets at ~5.8 ppm and ~5.4 ppm (corresponding to two protons of 1-^{13}C-phosphoenolpyruvate) have significantly reduced intensity compared to those seen in Figure S1. The resonance at 4.7 ppm is the residual proton signal of D_2O.

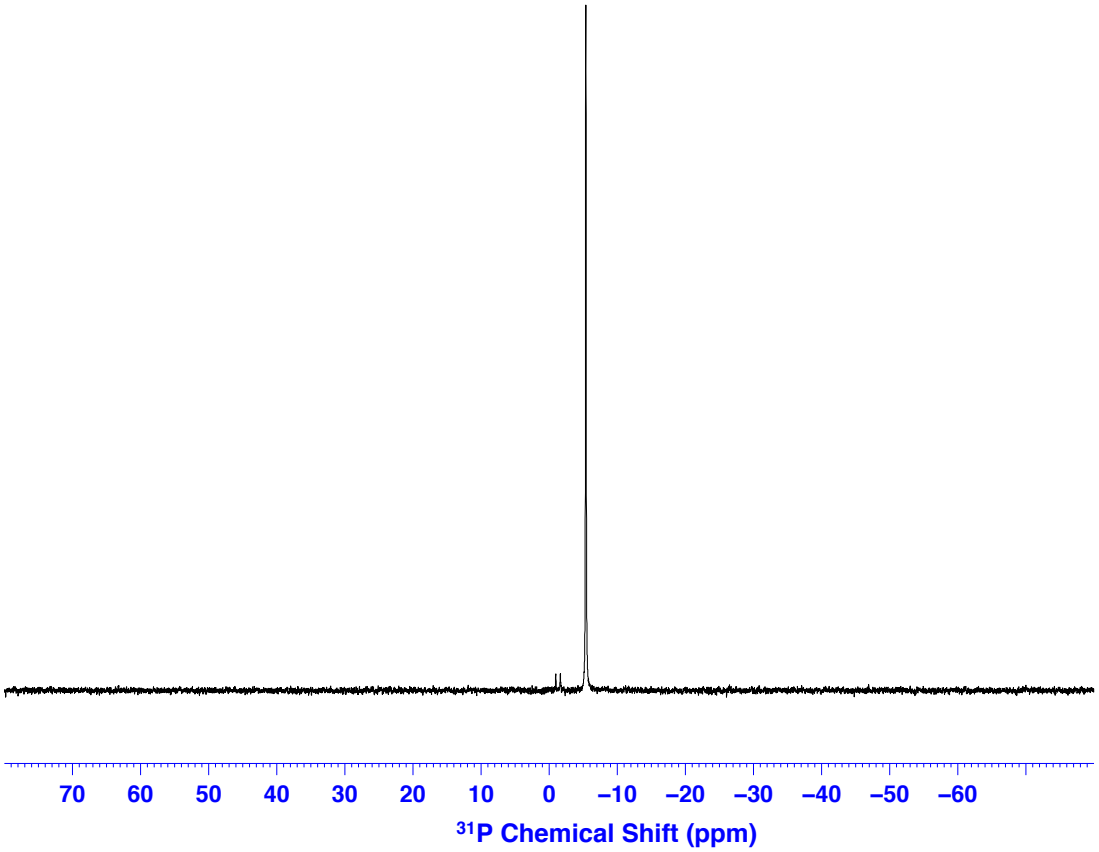


Figure S6. ^{31}P NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate-d_2 in D_2O.

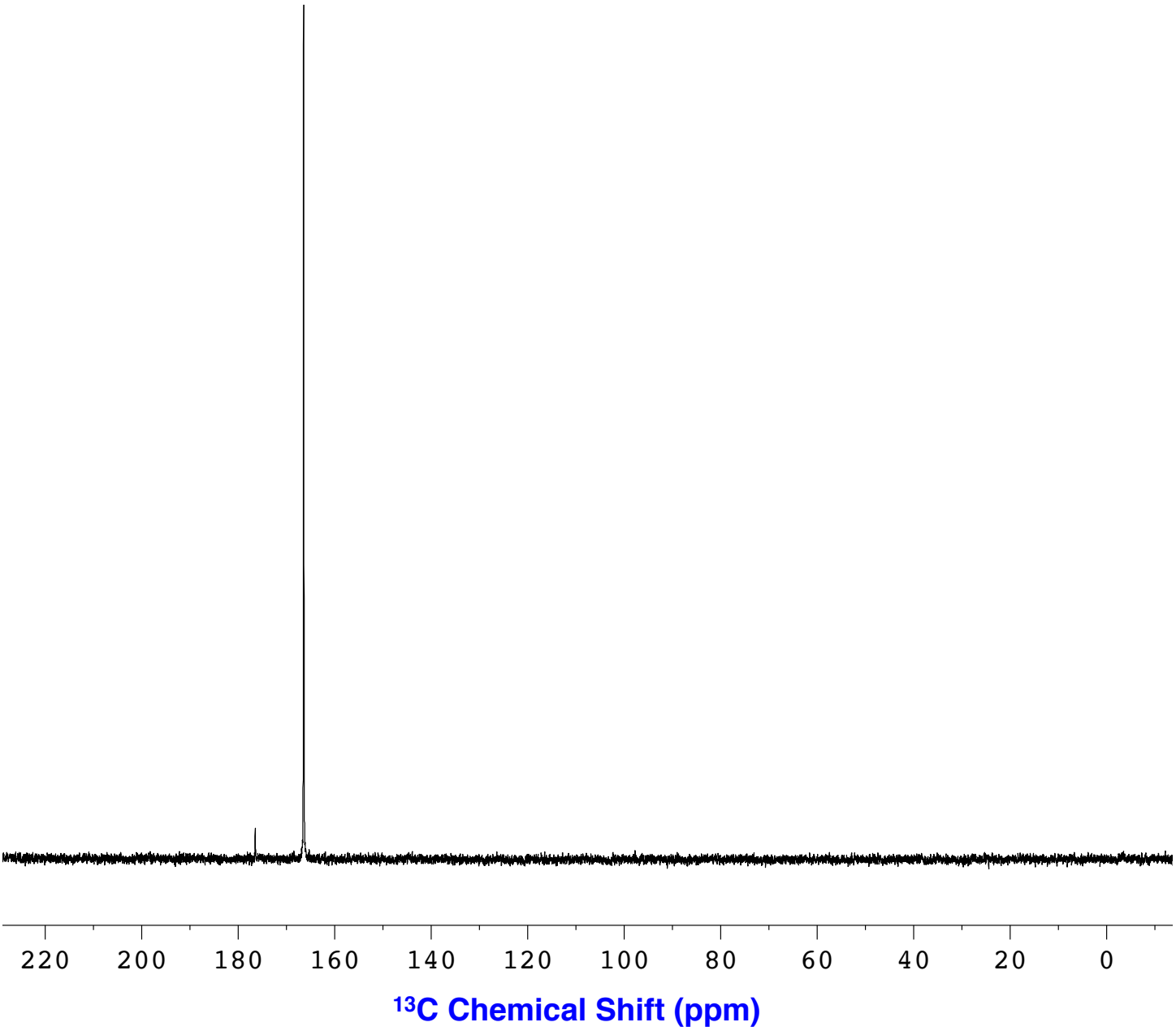


Figure S7. ^{13}C NMR spectrum of potassium 1-^{13}C-phosphoenolpyruvate-d_2 in D_2O.

3. Additional data

Table S1. Signal enhancements and ^{1}H polarizations obtained in PASADENA and ALTADENA experiments with phosphoenolpyruvate and phosphoenolpyruvate-d_2 after 5 s of p-H_2 bubbling.

HP molecule	Protocol	p-H_2 fraction, %	ε_{1H}	P_{1H}, %	
				experimental	at 85% p-H_2
Phospholactate	PASADENA	85	240	0.71	0.71
	ALTADENA	66	17	0.05	0.07
Phospholactate-d_2	PASADENA	69	640	1.86	2.53
	ALTADENA	70	220	0.64	0.87

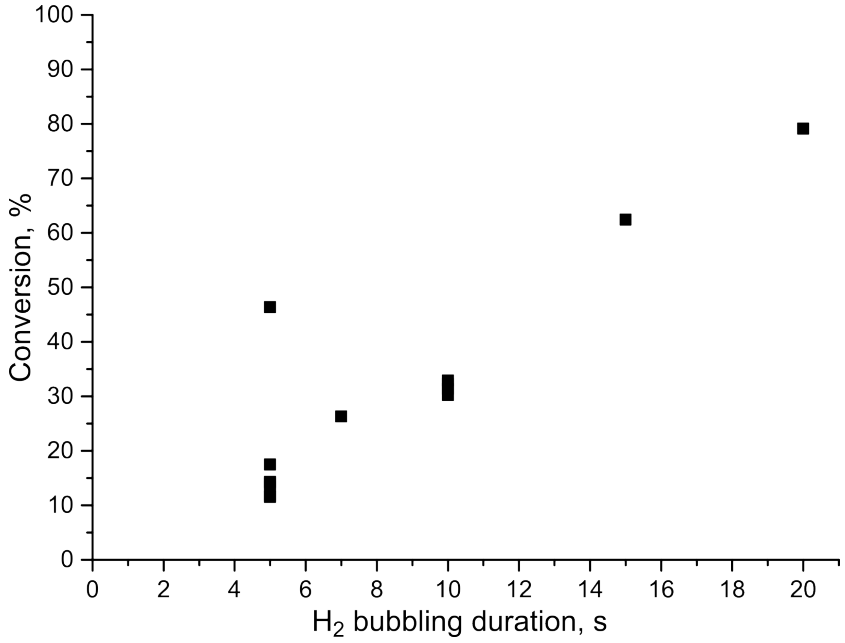
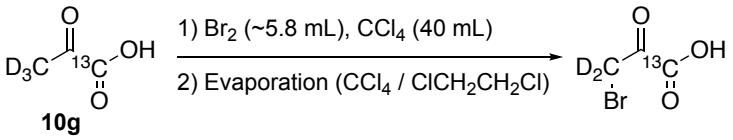


Figure S8. Plot of phosphoenolpyruvate conversion to phospholactate vs. duration of H_2 bubbling.

Table S2. Signal enhancements and ^{13}C polarizations obtained in MFC experiments with phosphoenolpyruvate and phosphoenolpyruvate-d_2 after 5 s of p-H_2 bubbling.

HP molecule	Magnetic field, μT	p-H_2 fraction, %	ε_{13C}	P_{13C}, %	
				experimental	at 85% p-H_2
Phospholactate	0	71	2.4	0.002	0.002
	0.025	72	37	0.027	0.034
	0.05	72	85	0.062	0.078
	0.075	71	56	0.041	0.053
	0.1	81	31	0.022	0.024
Phospholactate-d_2	0	70	25	0.018	0.024
	0.025	69	62	0.045	0.062
	0.04	68	23	0.016	0.023
	0.05	69	104	0.076	0.10
	0.06	68	93	0.067	0.094
	0.075	69	7.2	0.005	0.007
	0.1	69	27	0.020	0.027



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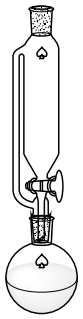
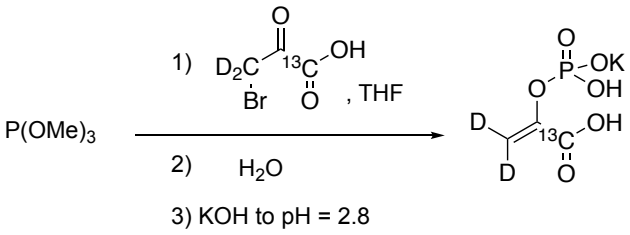


Figure S9. Experimental setup for the 1st step of 1-^{13}C-phosphoenolpyruvate-d_2 synthesis. Reagents, solvents and other preparations employed in this step were as follows: 1) Pyruvic acid-1-^{13}C-d_2 (MW= 91.08 g/mol, d = 1.25 g/mL, 10.0g, 0.110 mol); 2) Bromine, 470864 ALDRICH, ≥99.99% trace metals basis (MW = 159.8 g/mol, d= 3.12 g/mL, 0.110 mol, 5.6 mL). 3) Carbon tetrachloride, 289116 SIGMA-ALDRICH, anhydrous, ≥99.5% (~50mL). 4) 1,2-Dichloroethane, 284505 SIGMA-ALDRICH, anhydrous, 99.8% (~120 mL). 5) Ice bath should be prepared. 6) All glassware (250 mL round bottom flask, addition funnel, glass funnel and measuring cylinder) and magnetic stir bar were oven dried.



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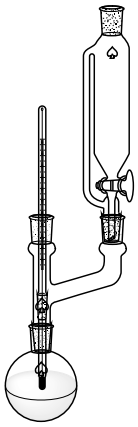

Figure S10. Experimental setup for the 2nd step of 1-^{13}C-phosphoenolpyruvate-d_2 synthesis. Reagents, solvents and other preparations employed in this step were as follows: 1) Trimethyl phosphite, 240907 Aldrich, ≥99% (MW= 124.08 g/mol, d = 1.05 g/mL, 1.1eq., 14.3mL, 0.110 mol). 2) Tetrahydrofuran anhydrous, contains 250 ppm BHT as inhibitor, ≥99.9%, 186562 Sigma-Aldrich, (~50mL). #) Ice bath should be prepared (for day #2). 4) All glassware (250 ml round bottom flask, addition funnel, glass funnel and measuring cylinder) and magnetic stir bar were oven dried.