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SUPPLEMENTAL INFORMATION

Figure 1. Mass Spectra of Control Reactions

(A). Negative-ion electrospray ionization mass spectra of PEP. A solution containing 10 mM ammonium acetate buffer was rapidly mixed with PEP (1000 μ M) for approximately 28 milliseconds before quenching into the electrospray mass spectrometer. Arrows denote peaks for PEP, PEP dimers and buffer and ion adducts. The mass spectra represent an average of 6 scans collected after an individual pulse of solution.

(B). Negative-ion electrospray ionization mass spectra of Enz-S3P. A solution containing enzyme (250 μ M) and S3P (500 μ M) was rapidly mixed with 10 mM ammonium acetate buffer for approximately 28 milliseconds before quenching into the electrospray mass spectrometer. Arrows denote peaks for S3P and buffer and ion adducts. The mass spectra represent an average of 30 scans collected after an individual pulse of solution.

(C). Negative-ion electrospray ionization mass spectra of the EPSP synthase reaction at longer times. A solution containing enzyme (250 μ M) and S3P (500 μ M) was rapidly mixed with PEP (1000 μ M) for approximately 2 seconds before quenching into the electrospray mass spectrometer. Arrows denote peaks for PEP, EPSP, and buffer and ion adducts. Note that at longer times no S3P (*m*/*z* 253) or tetrahedral intermediate (*m*/*z* 421) are observed. The mass spectra represent an average of 11 scans collected after an individual pulse of solution.

