## Supporting Information for

## Mechanistic Studies on CymD: A Tryptophan Reverse

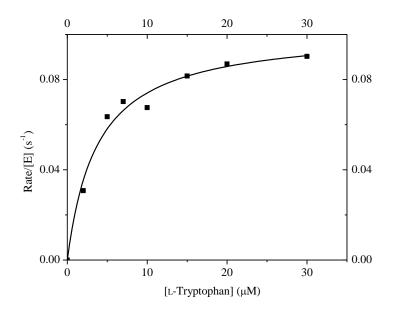
## N-Prenyltransferase

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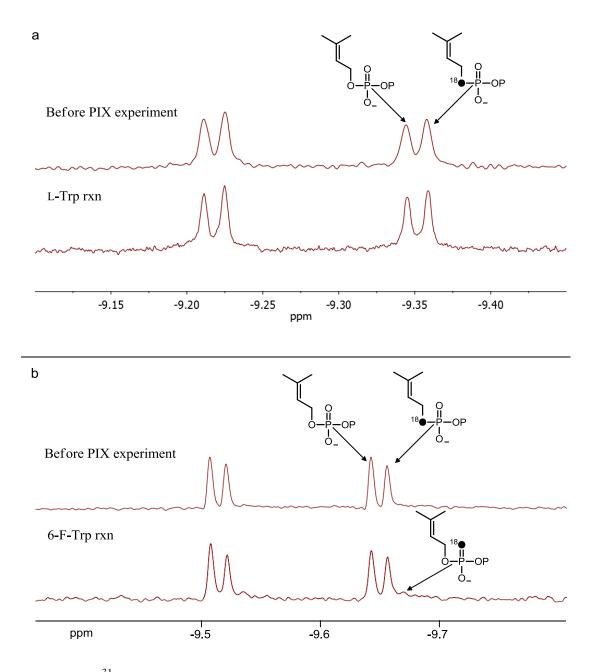
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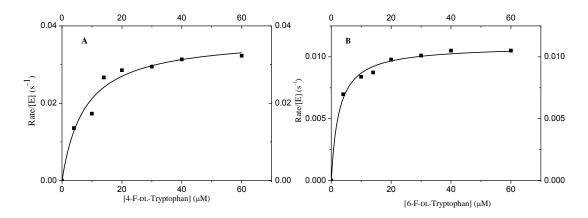
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**Figure S1**. Enzyme kinetics plot of rate/[E] versus [S] for the prenyltransferase CymD with L-tryptophan (variable) and 20  $\mu$ M DMAPP.



**Figure S2**. <sup>31</sup>P NMR spectra showing the  $\alpha$ -phosphorus signals of the DMAPP mixture in the PIX reactions catalyzed by CymD. (a. PIX experiment with L-Trp. b. PIX experiment with 6-F-Trp.)



**Figure S3.** Enzyme kinetics plots of rate/[E] versus [S] for the prenyltransferase CymD with fluorinated tryptophans (variable) and 20  $\mu$ M DMAPP. (A. 4-F-DL-tryptophan; B. 6-F-DL-tryptophan)

Conc. <sup>a</sup>	10 µM	20 µM
Rate/[E]		
$V_{DMAPP}/[E] (s^{-1})$	0.031	0.031
$V_{E-F-DMAPP}/[E] (s^{-1})$	2.5*10 <sup>-4</sup>	3.2*10 <sup>-4</sup>
k <sub>rel</sub>	0.008	0.010

Table S1. Kinetic rates measured for DMAPP and *E*-F-DMAPP.

a. In both cases [L-tryptophan] =  $100 \ \mu M$