Supporting information

Structure and mechanism of *Pseudomonas aeruginosa* PA0254/HudA, a prFMN-dependent pyrrole-2-carboxylic acid decarboxylase linked to virulence

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DFT Supporting Information:

Table S1. HF energy (hartrees) computed for the $Int1^{closed}$ adducts of P2C, F2C, T2C, Im2C and Im4C with prFMN in implicit water.

	$Int1^{open}$	$Int1^{closed}$		$Int1^{open}$–$Int1^{closed}$ (kJ/mol)
P2C	-1580.872256	-1580.875149		+7.6
F2C	-1600.725775	-1600.738391		+33.1
T2C	-1923.710723	-1923.721422		+28.1
Im2C	-1596.912481	-1596.897529		-39.3*
Im2C-H^+	-1597.369815	Not stable		-
Im4C	-1596.921557	-1596.93624		+38.5

* note that only Im2C has a more stable $Int1^{open}$ adduct relative to $Int1^{closed}$.

Table S2. Natural charges computed for the substrate moiety of the Int1^{open} and Int1^{closed} adducts of P2C, F2C, T2C, Im2C and Im4C with prFMN in implicit water.

	Int1^{open}	Int1^{closed}	Int1^{open} – Int1^{closed}
P2C	-0.36	-0.90	+0.53
F2C	-0.56	-0.91	+0.36
T2C	-0.62	-0.93	+0.31
Im2C	-0.49	-1.13	+0.65
Im2C-H$^+$	-0.10*	Not stable	-
Im4C	-0.50	-0.91	+0.41

* note that Im2C-H$^+$ has a neutral charge, whereas all other substrates/inhibitors have a charge of -1.

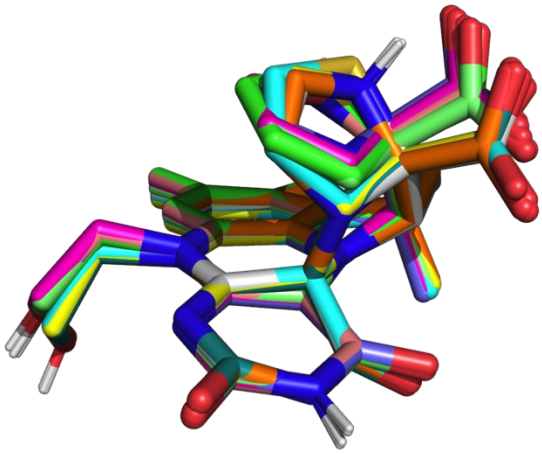
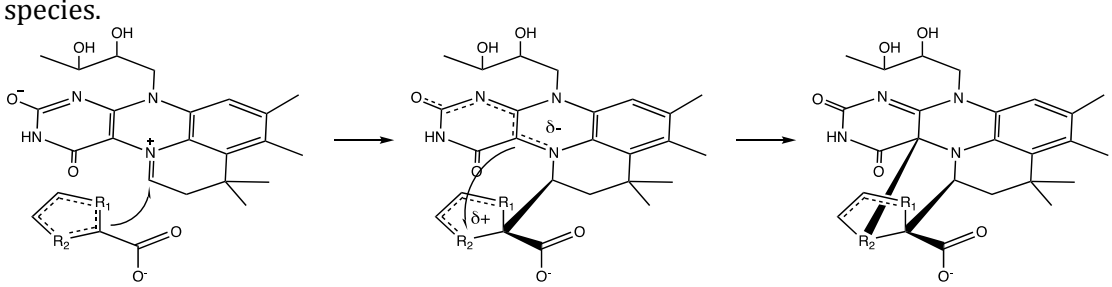


Figure S1. Alignment of the Int1^{open} and Int1^{closed} prFMN- P2C, F2C, T2C, Im2C and Im4C species.



Scheme S1. The DFT models used in this study, showing a 2-step mechanism for the formation of Int 1. In all cases except for protonated Im2C, there is partial electron transfer from the substrate to the prFMN to form the ring-open adduct. The ring closed adduct is formed by electron transfer back from the prFMN to the substrate moiety of the adduct.