

Supplementary data

Palladium(II) diamine complex induces reduction of glutathione disulfide

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Experimental

[Pd(1*R*,2*R*-dach)Cl₂] was synthesised following adapted published procedures (D. S. Gill in “Platinum coordination complexes in cancer chemotherapy: Proceedings of the 4th International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy”, Vermont, 1983. Ed. M.P.Hacker, E.B.Double and I.H.Krakoff, Martinus Nijhoff Publishing, Boston, p268). K₂PdCl₄ (Johnson Matthey Chemicals, 0.50 g, 1.5 mmol) and 1*R*,2*R*-dach (Sigma Aldrich, 0.17 g, 1.5 mmol) were reacted in the dark for 3 hours at 328 K in a 0.5 mM NaOH solution. The resulting dark yellow solid was filtered off, washed with cold water and dried over silica. Yield: 0.39 g, 71%. Found: C, 23.99; H, 4.24; N, 9.55. Calc.: C, 24.72; H, 4.84; N, 9.61.

Table S1 ¹H NMR chemical shifts (ppm) for GSSG and product **3** in 90% H₂O/ 10% D₂O, pH 7, 298 K. For proton labels, see Figure S1.

Residue	Proton	δ ¹ H /ppm		
		GSSG	{Pd(1 <i>R</i> ,2 <i>R</i> -dach)} ²⁺ *	3
Gly	NH	8.26	-	- ^a
	H(α)	3.75 ^c	-	-
Cys	NH	8.57	-	8.43
	H(α)	- ^b	-	5.38
	H(β)	2.95, 3.29	-	3.53, 3.73
γ-Glu	NH	- ^a	-	- ^a
	H(α)	3.75	-	3.65
	H(β)	2.13 ^c	-	2.09, 2.22
	H(γ)	2.52 ^c	-	2.55 ^c
{Pd(1 <i>R</i> ,2 <i>R</i> -dach)}-NH	A	-	4.93	4.89
	B	-	4.27	4.37
	C	-	4.69	4.48
	D	-	5.20	4.93
{Pd(1 <i>R</i> ,2 <i>R</i> -dach)}-CH	a	-	1.11	1.10
	b	-	1.26	1.22
	c	-	1.64	1.60
	d	-	2.02	1.98
	e/f	-	2.48	2.45 ^c

^a not observed ; ^b under residual water peak ; ^c although non-equivalent protons, peaks overlap

* complex hydrolyses in water

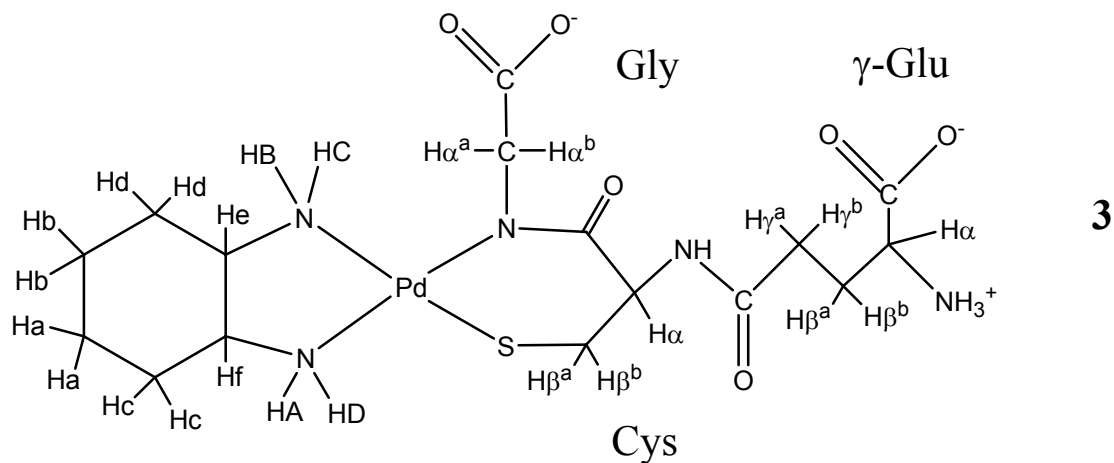


Fig. S1 Structure of **3** and numbering scheme

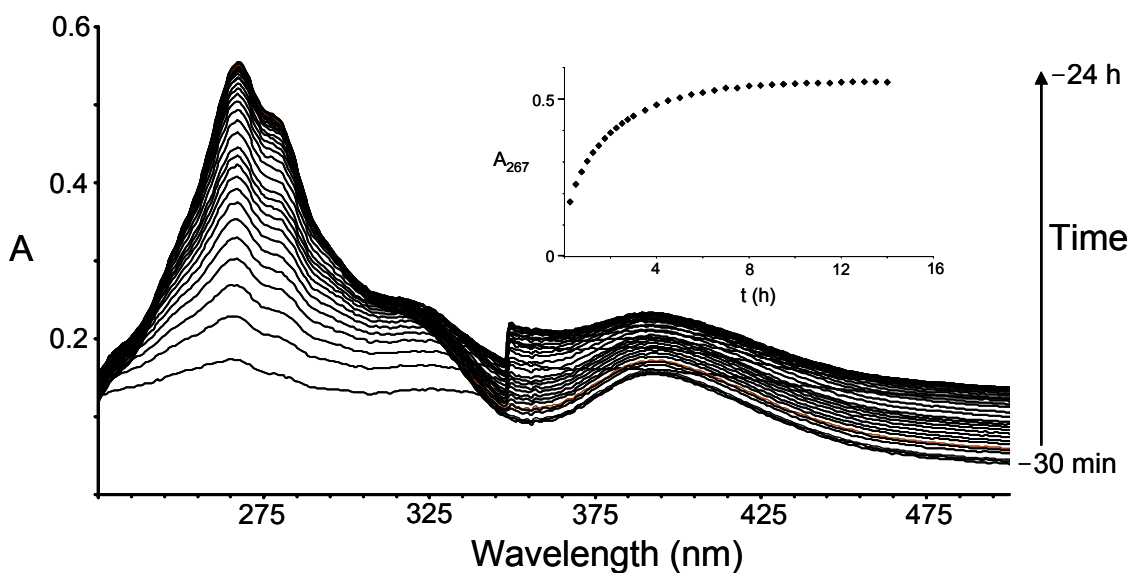


Figure S2 Uv-vis spectra recorded during the reaction of $[\text{Pd}(1R,2R\text{-dach})\text{Cl}_2]$ (0.1 mM) with GSH (0.2 mM) at pH 7, 310 K. Spectra were recorded every 30 min. The inset shows the variation in A_{267} with time.

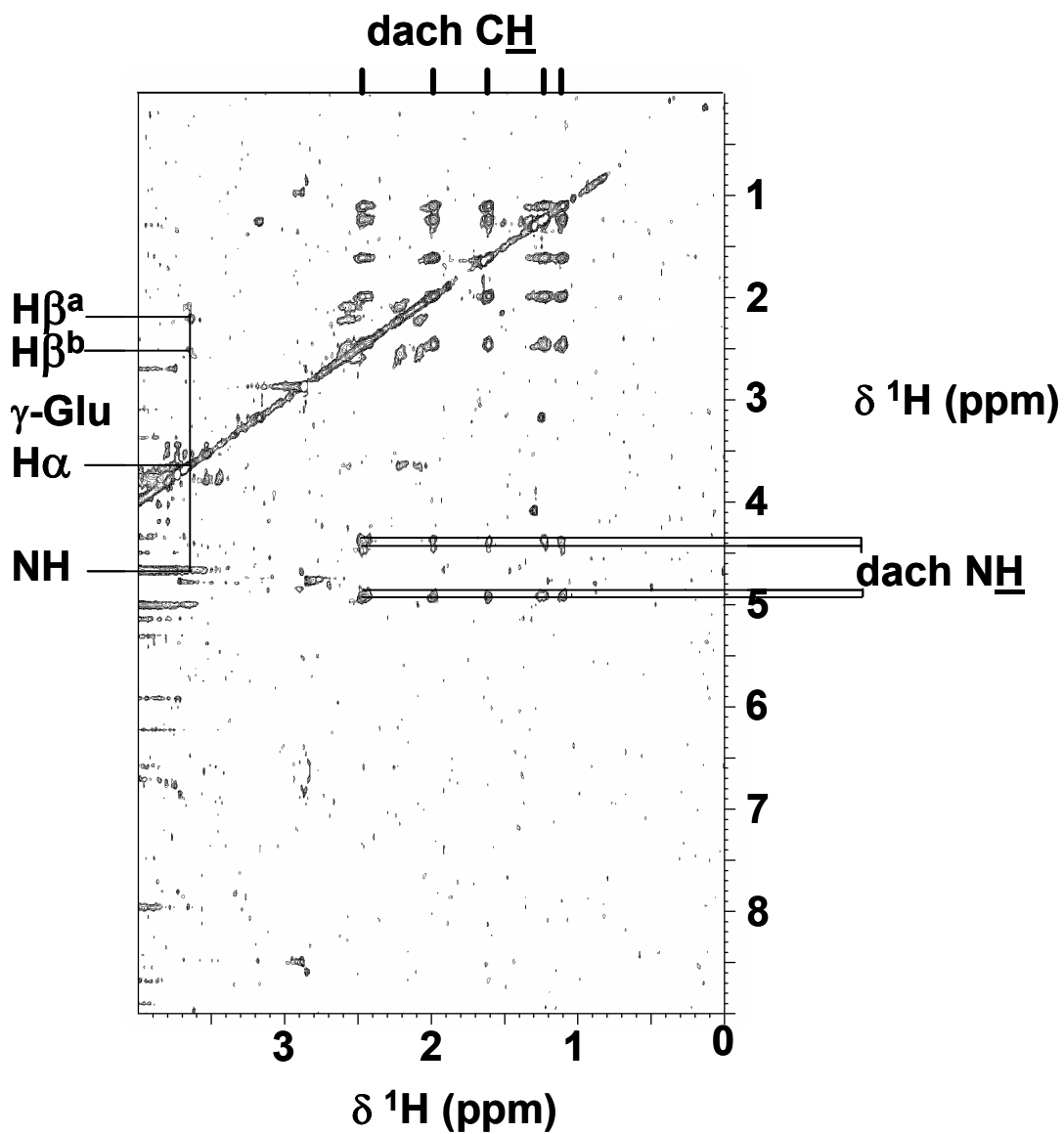


Figure S3 800 MHz 2D TOCSY ¹H NMR spectrum of **3** in H₂O/D₂O (90:10), 298 K.

For proton labelling, see Figure S1.