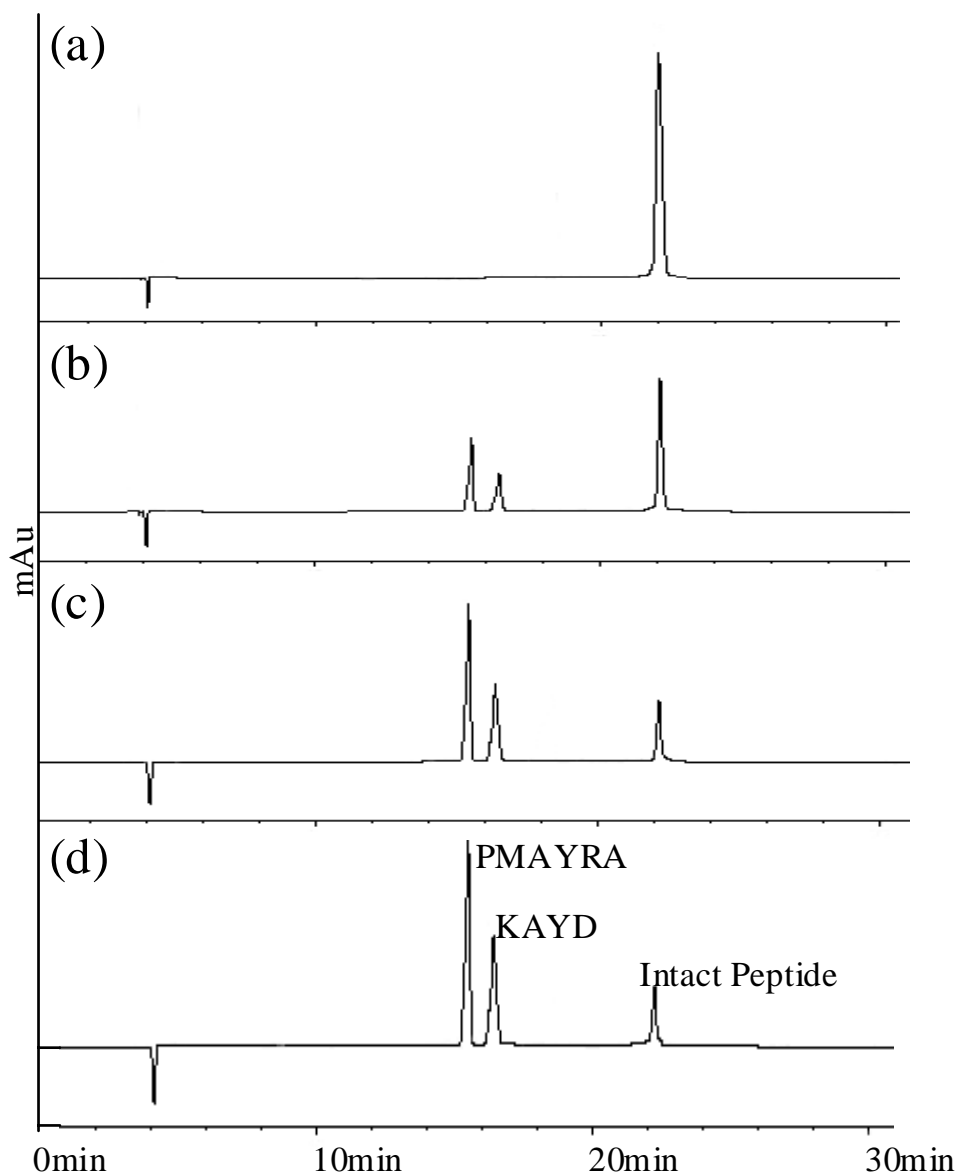
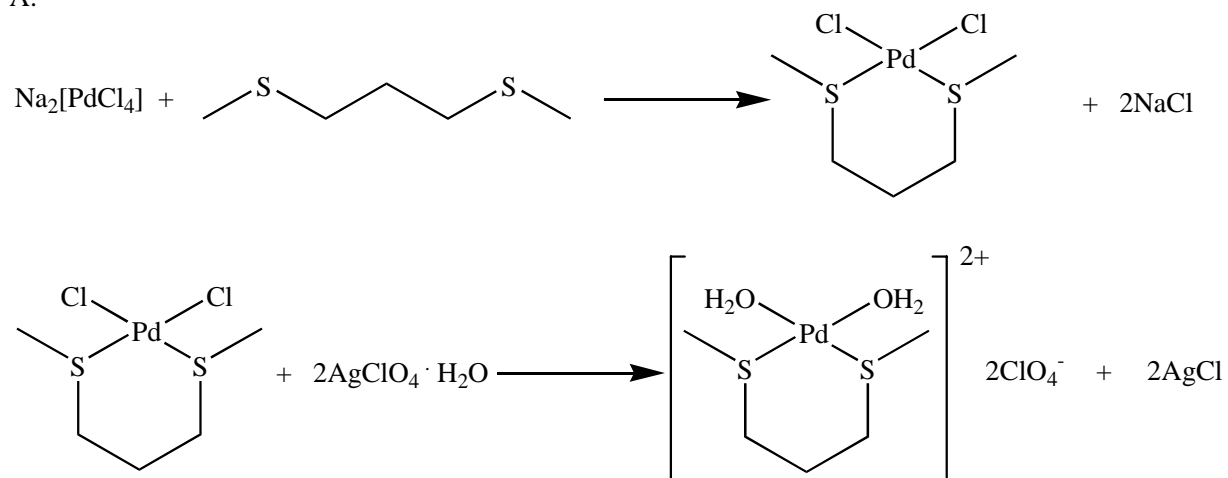


## Supporting Information

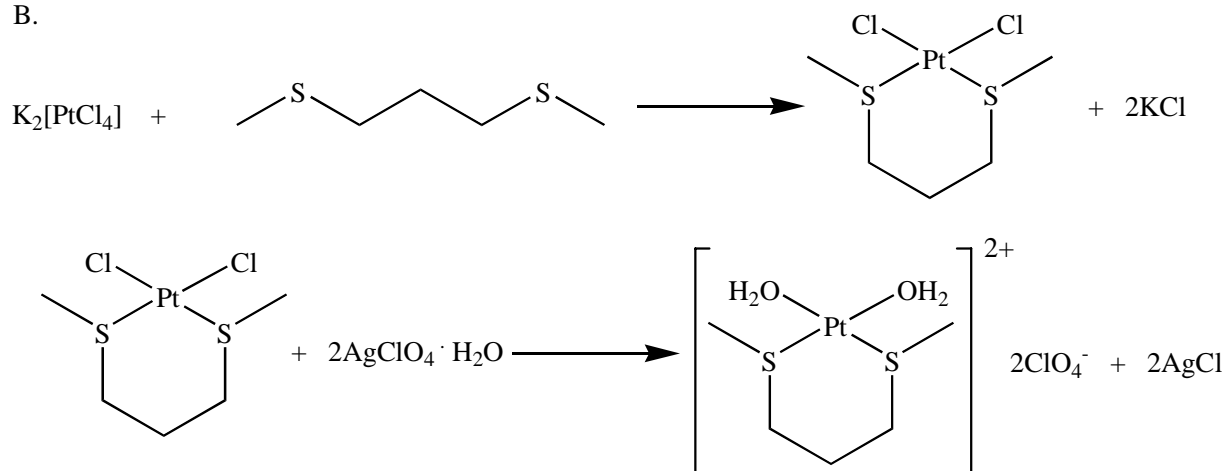
**Figure S1.** Typical HPLC chromatograms of cleavage reaction mixtures. Separation of the cleaved fragments was achieved by use of a C18 analytical column. Cleavage of Pro-Met peptide promoted by *cis*-[Pd(CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> at pH 2.0 at 60°C for (a) 0 , (b) 5, (c) 15, and (d) 24hrs.



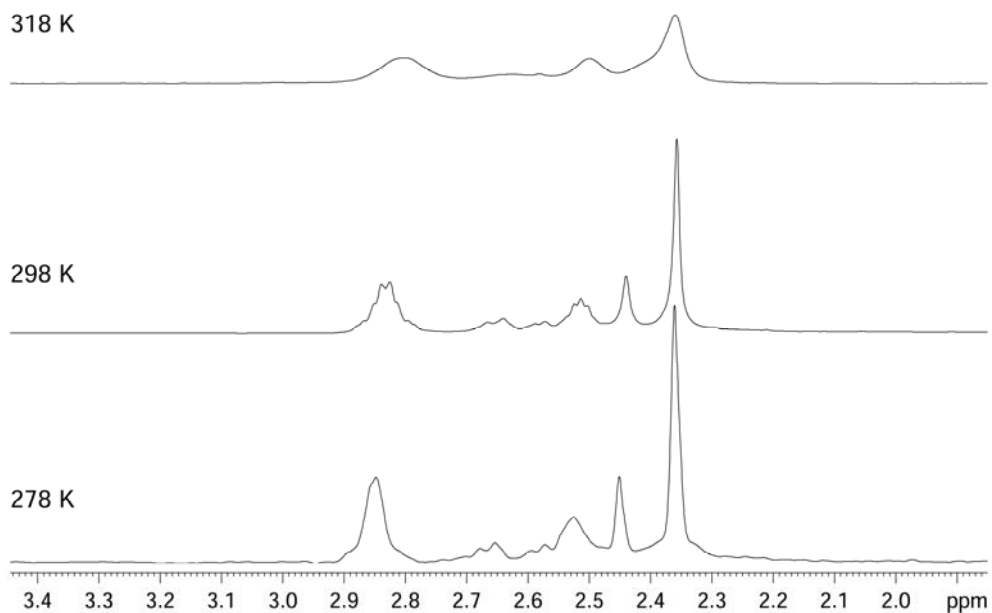
**Figure S2.** Reaction scheme for the preparation of *cis*- $[\text{Pd}(\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)(\text{H}_2\text{O})_2]^{2+}$  and *cis*- $[\text{Pt}(\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)(\text{H}_2\text{O})_2]^{2+}$ .  
A.



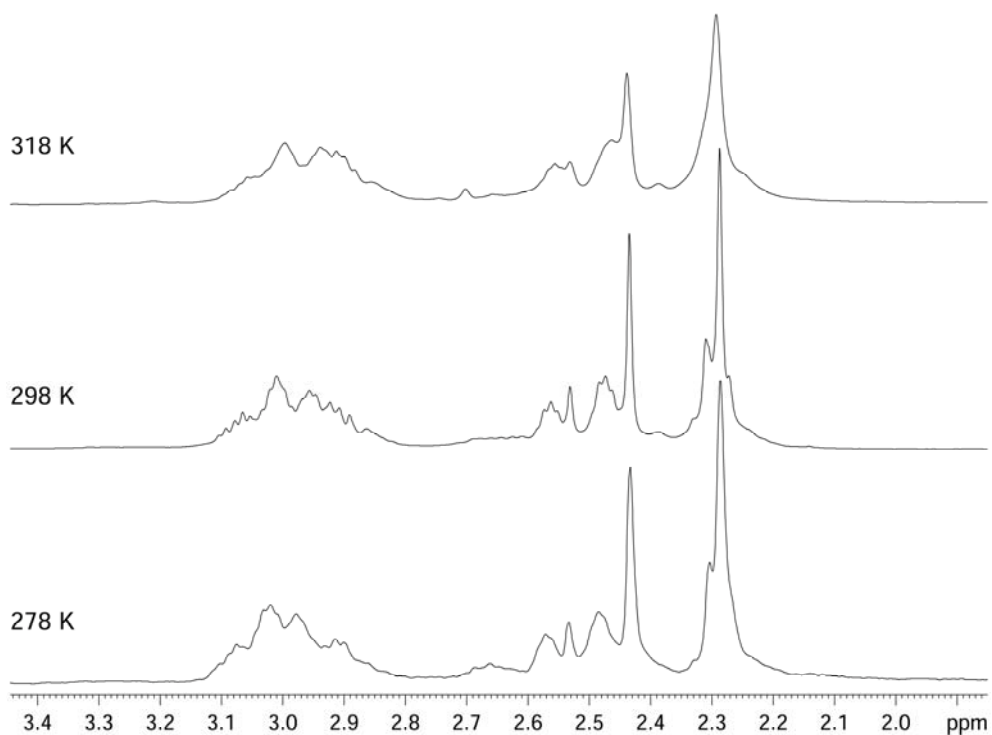
B.



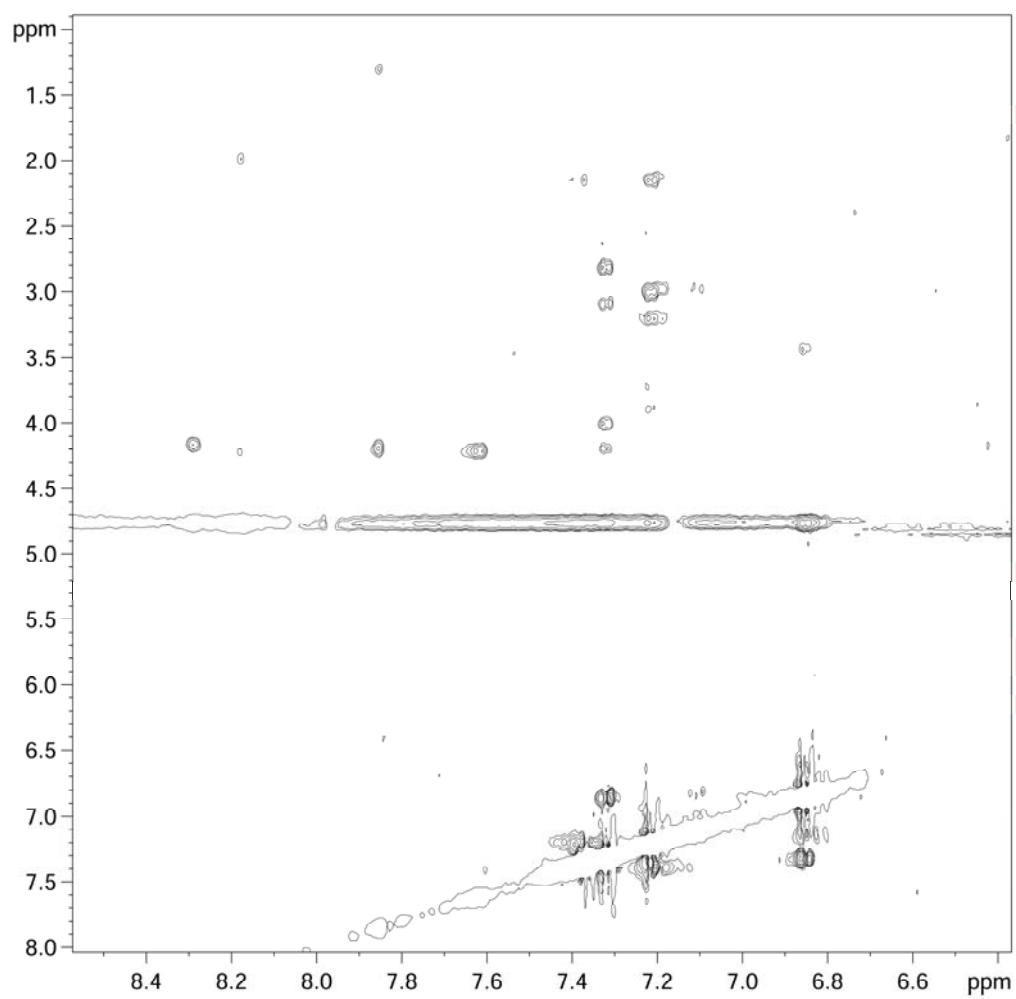
**Figure S3.**  $^1\text{H}$  NMR spectra of *cis*-[Pd(CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. The spectra were obtained at three different temperatures and indicate the presence of two configurational isomers interconverting at room temperature.



**Figure S4.**  $^1\text{H}$  NMR spectrum of *cis*-[Pt(CH<sub>3</sub>SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SCH<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. The spectra were obtained at three different temperatures and indicate the presence of two configurational isomers interconverting at room temperature.



**Figure S5.** ROESY  $^1\text{H}$  NMR spectrum of Met-Ala peptide used for the assignment of each residue in the peptide.



**Figure S6.**  $^1\text{H}$  NMR spectra of (a) the cleavage reaction mixture of Met-Ala peptide with *cis*- $[\text{Pd}(\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  after 24 hours of incubation at  $60^\circ\text{C}$ , (b) *cis*- $[\text{Pd}(\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3)(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ , and (c)  $\text{CH}_3\text{SCH}_2\text{CH}_2\text{CH}_2\text{SCH}_3$ . The spectra are aligned to indicate the absence of the free dithioether ligand in the cleavage reaction mixture.

