Supporting Information

Protein Modification by Adenine Propenal[†]

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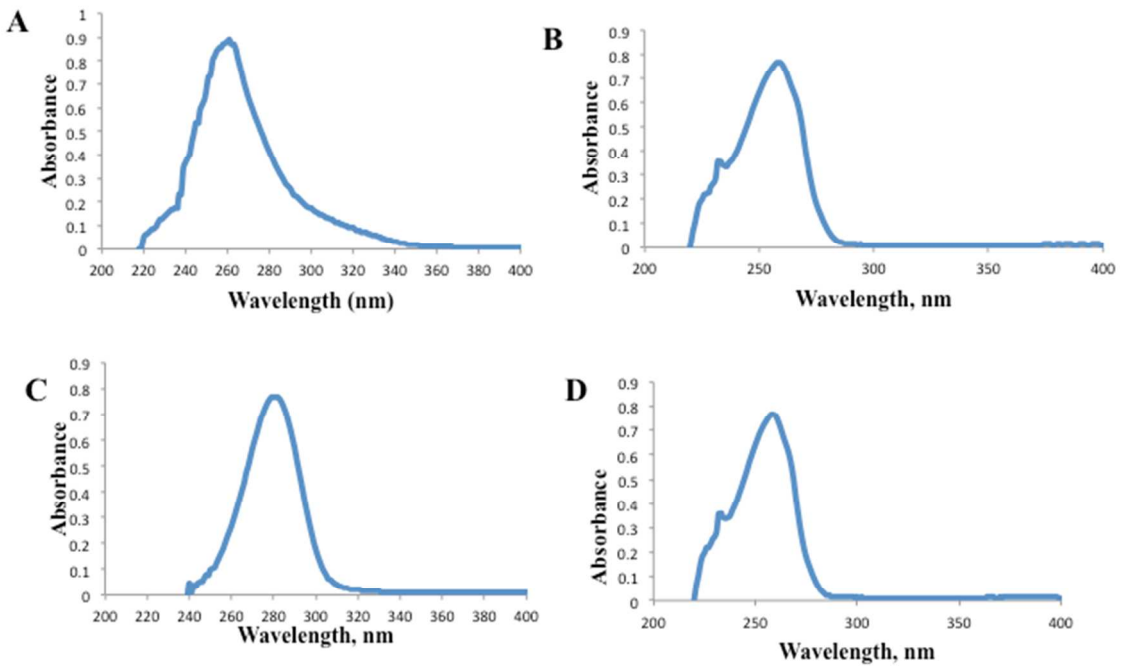

Figure S1. UV/vis spectra of the adenine propenal reactant and its reaction products with N-α-acetyllysine. Spectra are provided for (A) 27 μM adenine propenal, (B) 46 μM adenine, (C) 23 μM N^{ε}-oxopropenyl-N-α-acetyllysine, and (D) 8.5 μM of the lysine-lysine cross-link.

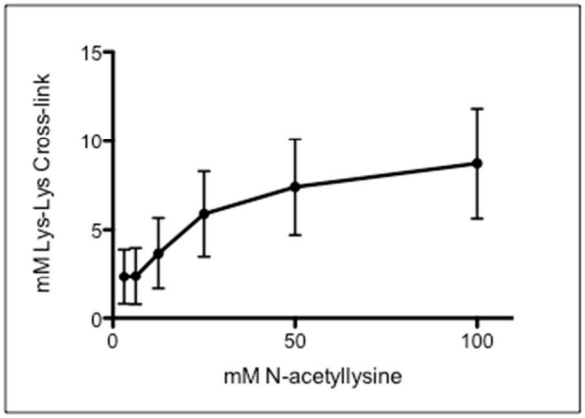

Figure S2. Spectrometric quantification of **4** formation. The indicated amounts of N-α-acetyllysine (NAL) were incubated with a fixed amount of adenine propenal (10 mM), and reactions were incubated for 6 h. Following incubation, reactions were diluted 1:1000, and the absorbance at 300 nm was obtained. The concentration of **4** was calculated from the molar extinction coefficient of the purified compound. Assuming a **4**:**3** product ratio of 10:1, and complete consumption of adenine propenal at >10 mM NAL concentrations, the contribution of the presence of other compounds in the reaction mixture to the absorbance at 300 nm is estimated to be less than 3%.

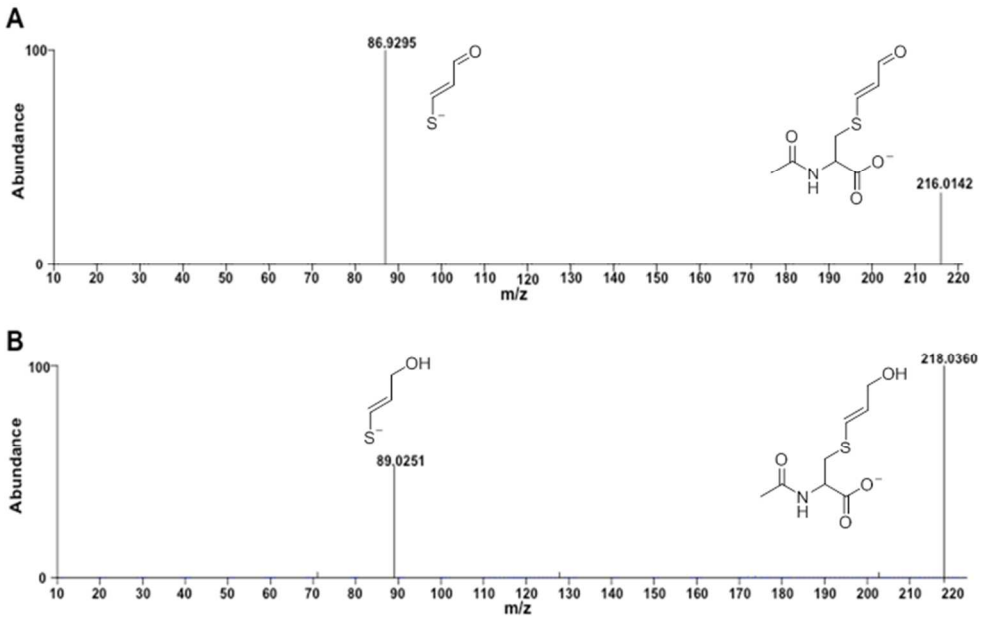

Figure S3. Adenine propenal reacts with N-α-acetylcysteine. A molar excess of NAC was incubated with adenine propenal as described in Experimental Procedures. Following incubation, mass spectrometric analysis in negative ion mode was performed on reaction mixtures treated without (A) or with (B) 50 mM $NaBH_4$.

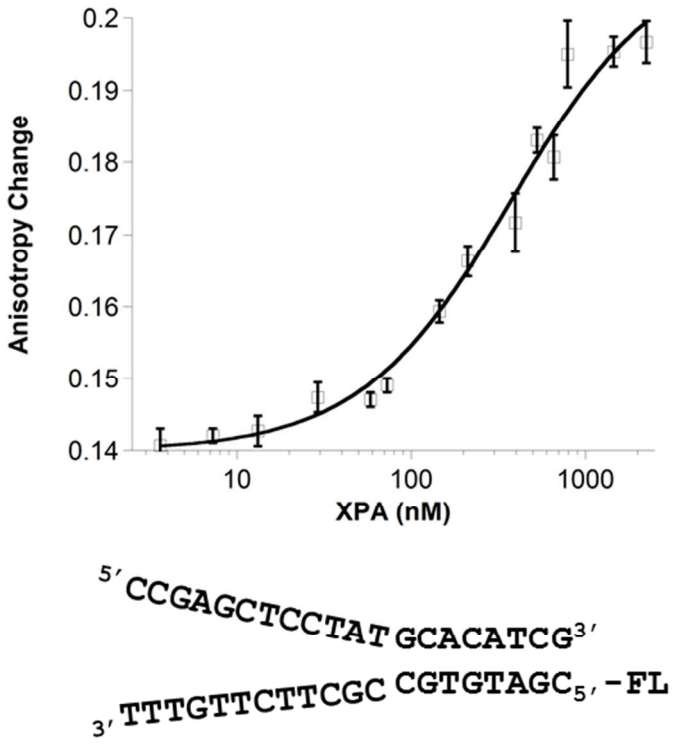

Figure S4. Human XPA binding to an ssDNA-dsDNA junction substrate. The change in fluorescence anisotropy for the indicated fluorescein-labeled DNA substrate (50 nM) versus added XPA protein is shown. Each data point represents the mean ± SD of three titrations.

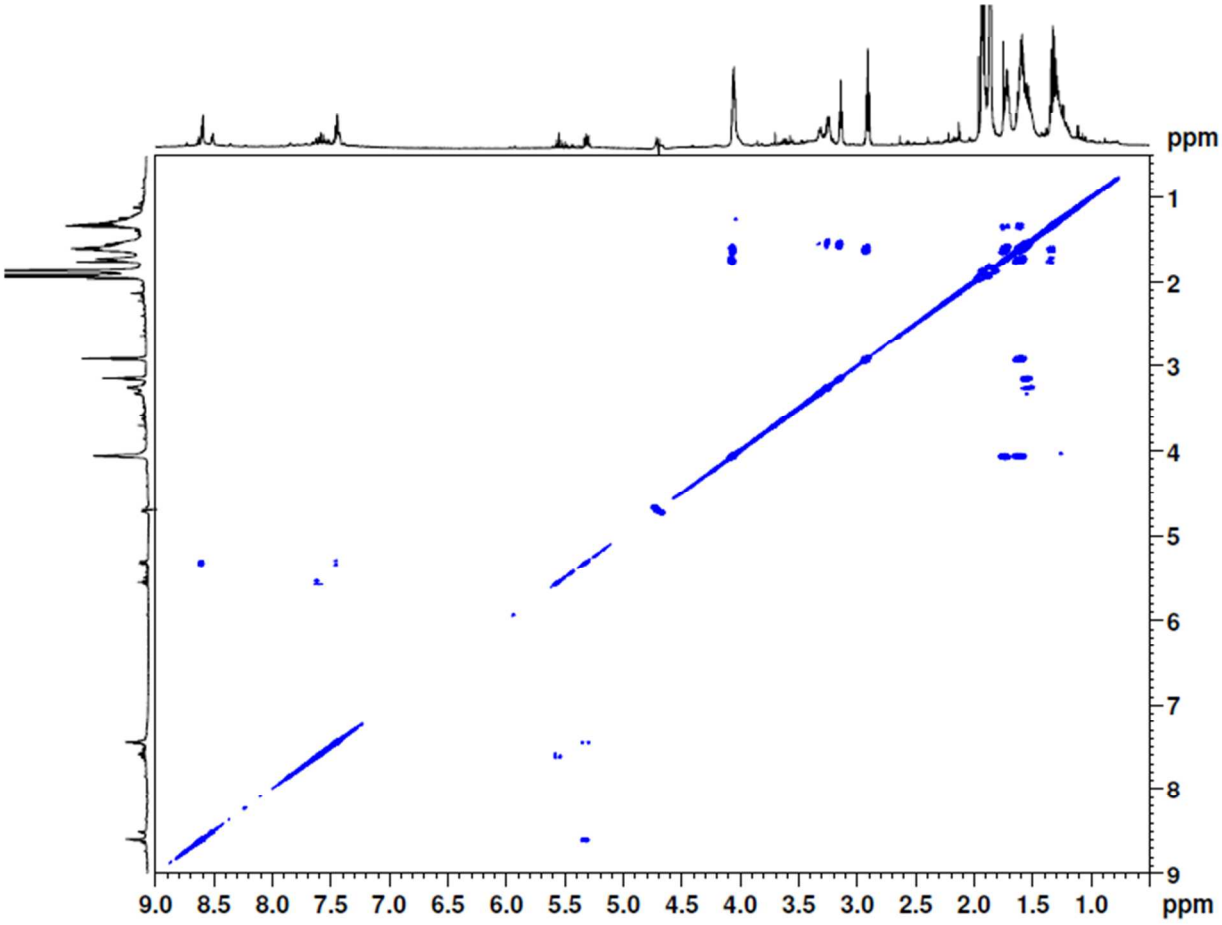

Figure S5. COSY spectrum of oxopropenyllysine **(3)**

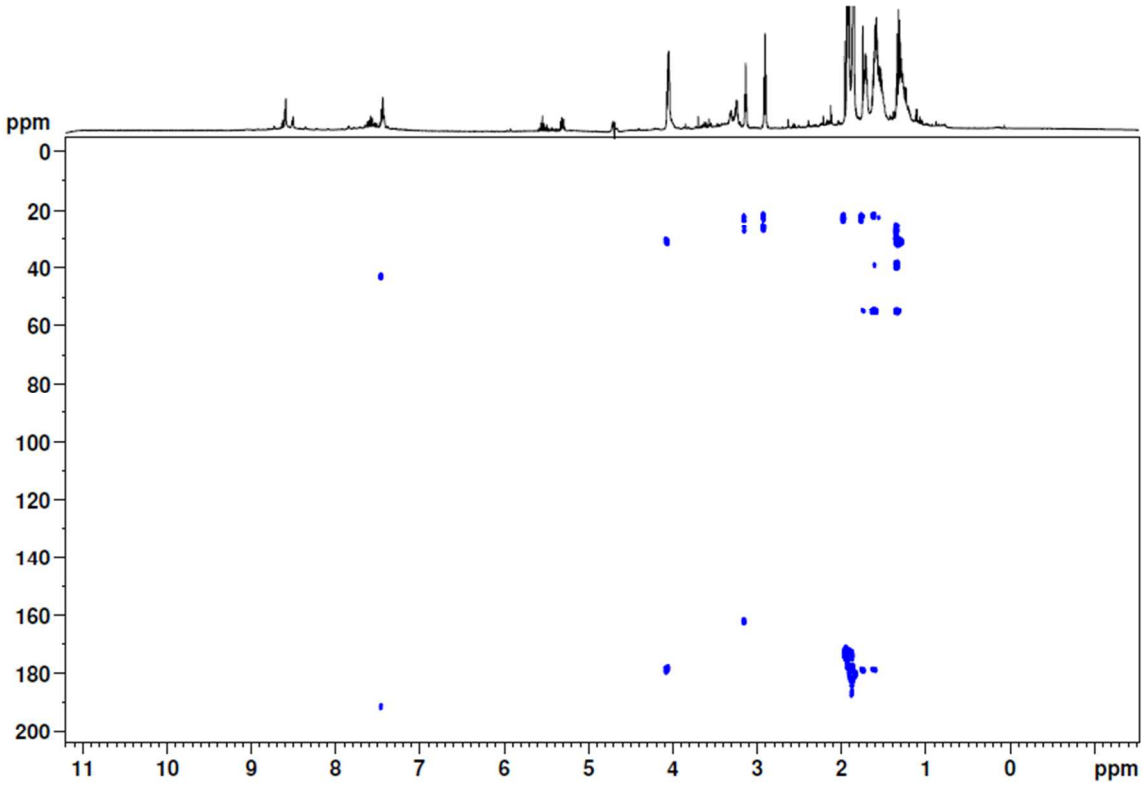

Figure S6. HMBC of oxopropenyllysine **(3)**

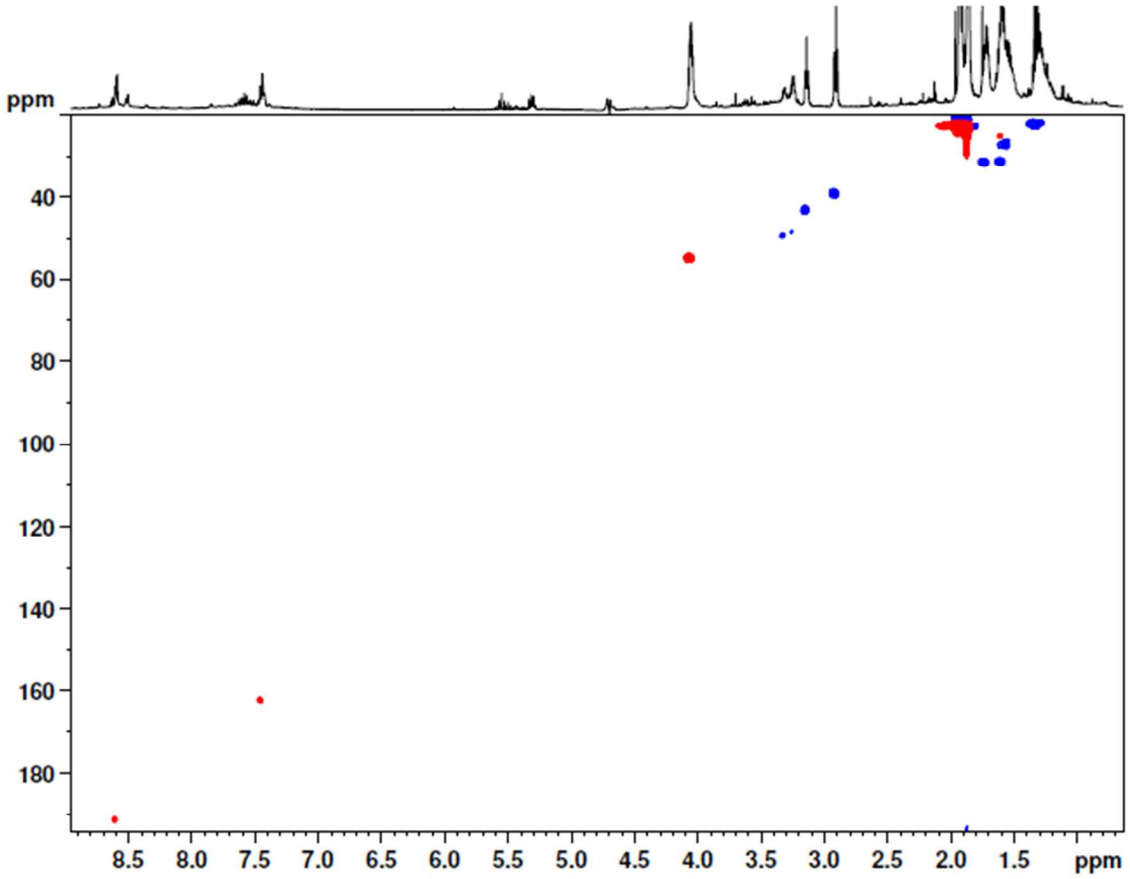

Figure S7. HSQC of oxopropenyllysine **(3)**

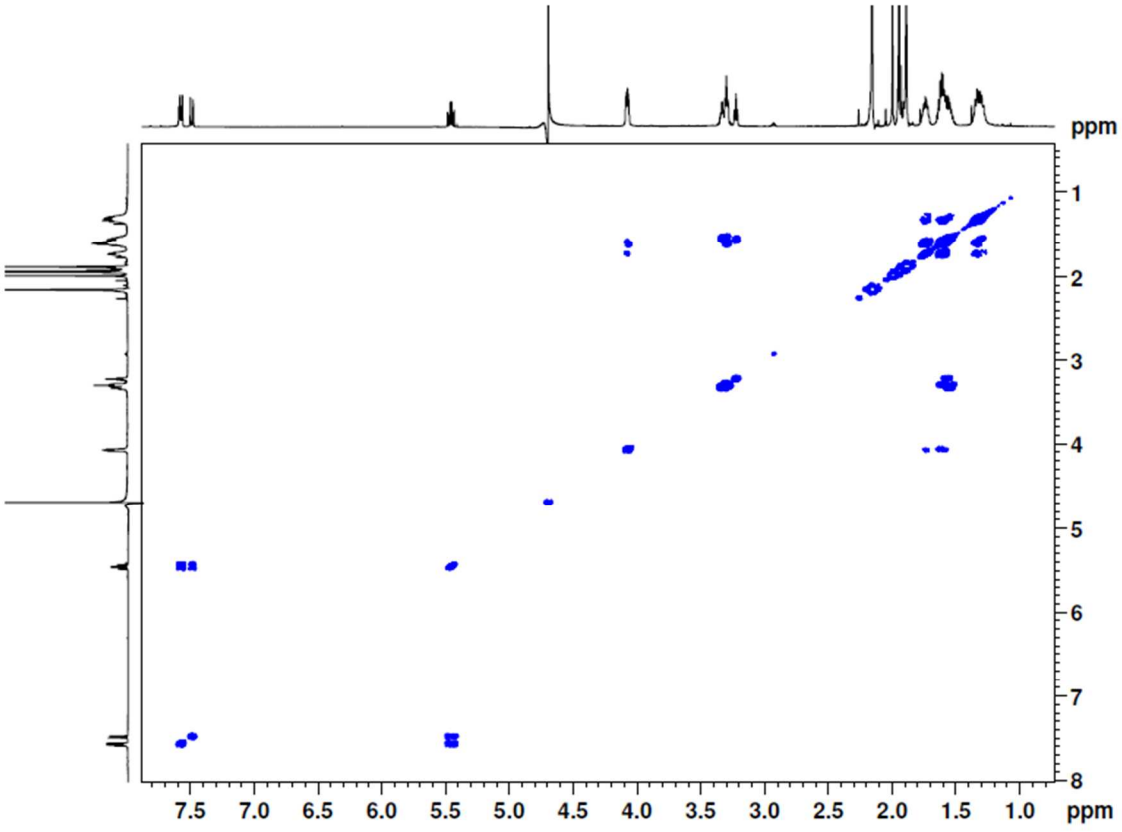

Figure S8. COSY of the lysine-lysine crosslink **(4)**

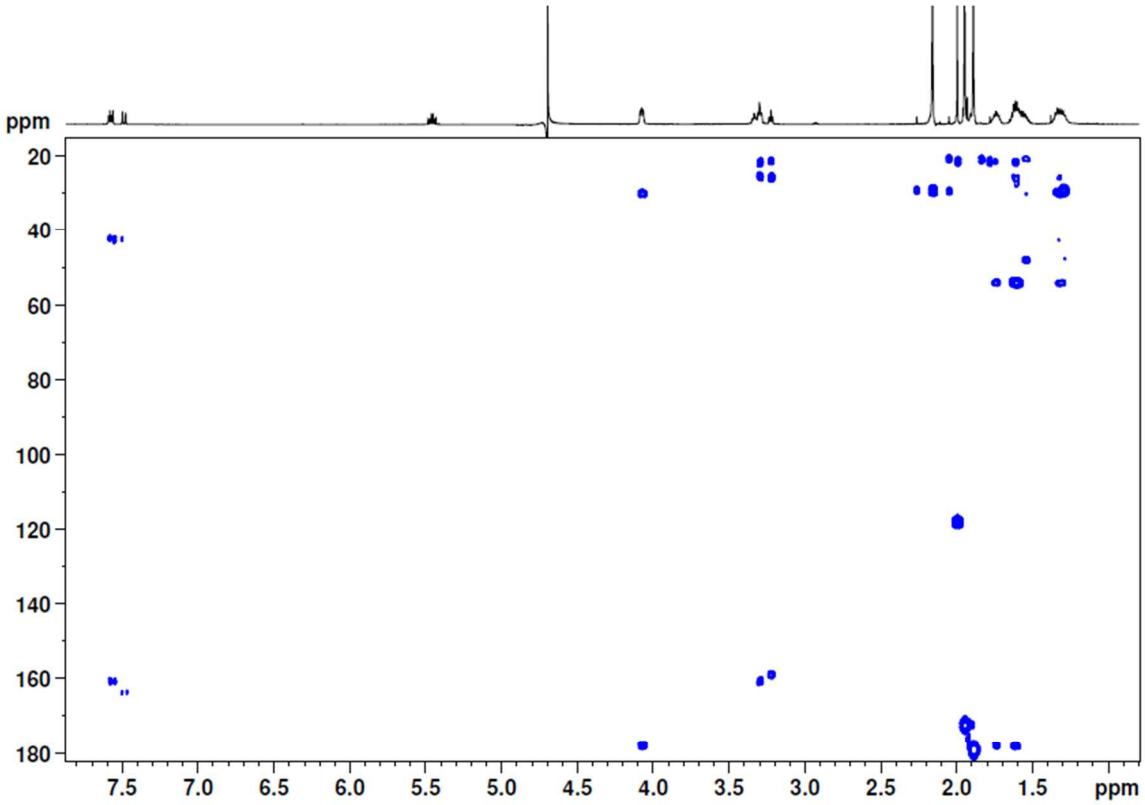

Figure S9. HMBC of the lysine-lysine crosslink **(4)**

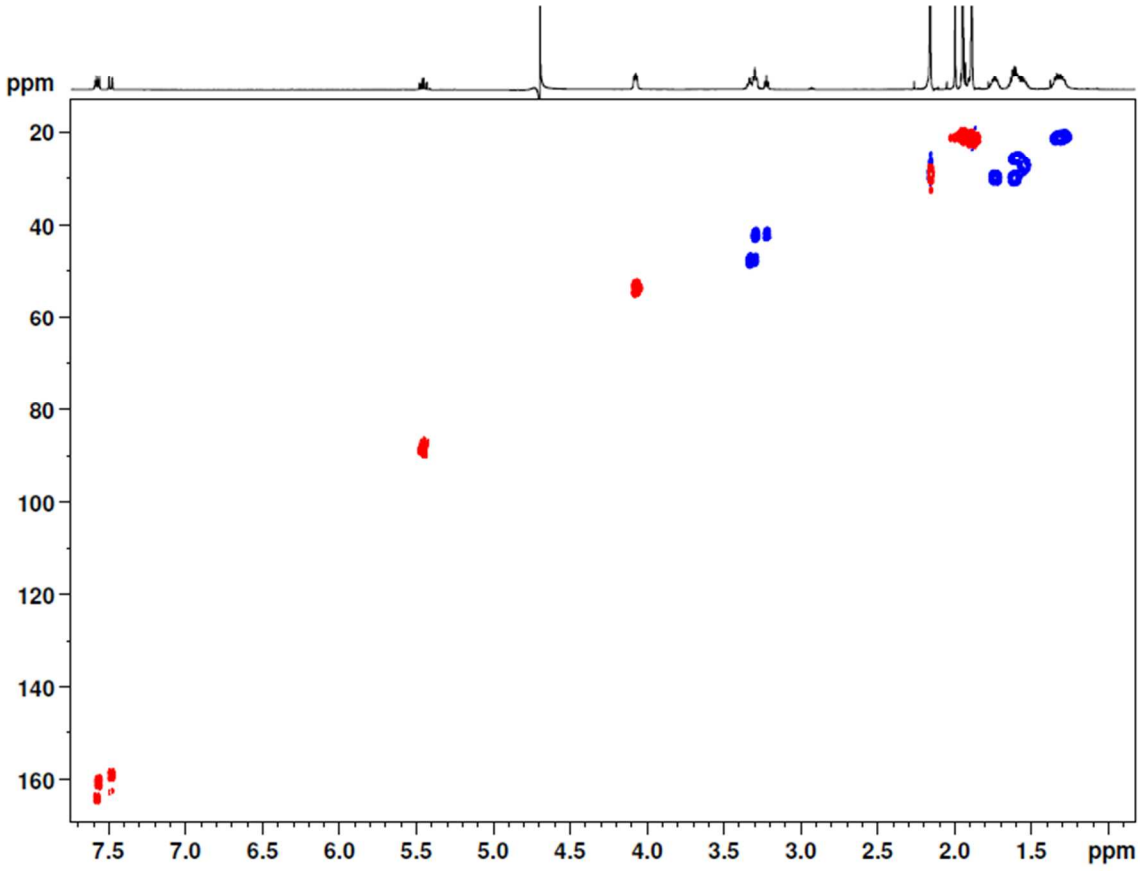

Figure S10. HSQC of the lysine-lysine crosslink **(4)**.

Table S1. Sequence Coverage of Human Serum Albumin Following LC-MS/MS Analysis.

Sample	Modified Lysines Identified	Sequence Coverage	Lysine Coverage
0 mM	0	90%	92%
1.5 mM	17	74%	70%
3.75 mM	19	71%	67%
7 mM	25	62%	60%

Purified HSA (15 μM) was incubated with increasing amounts of adenine propenal for 6 h at room temperature. Samples were then analyzed using LC/MS/MS, and sequence coverage was determined using Scaffold Data Viewer.