



UNIVERSITAT DE  
BARCELONA

**P-Stereogenic ligands  
with the *tert*-butylmethylphosphine fragment.  
Coordination chemistry and catalysis  
of their organometallic complexes**

Guillem Vázquez Bigas

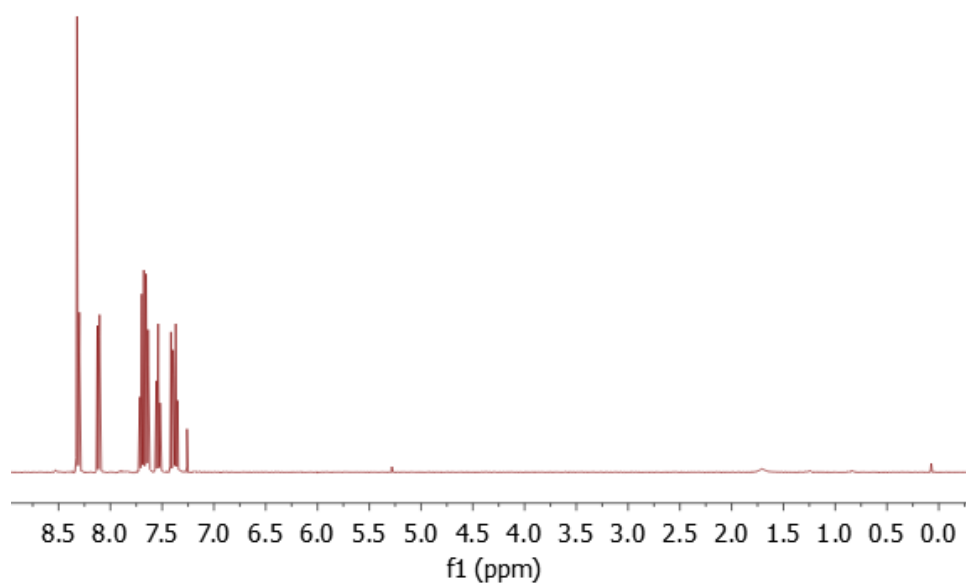
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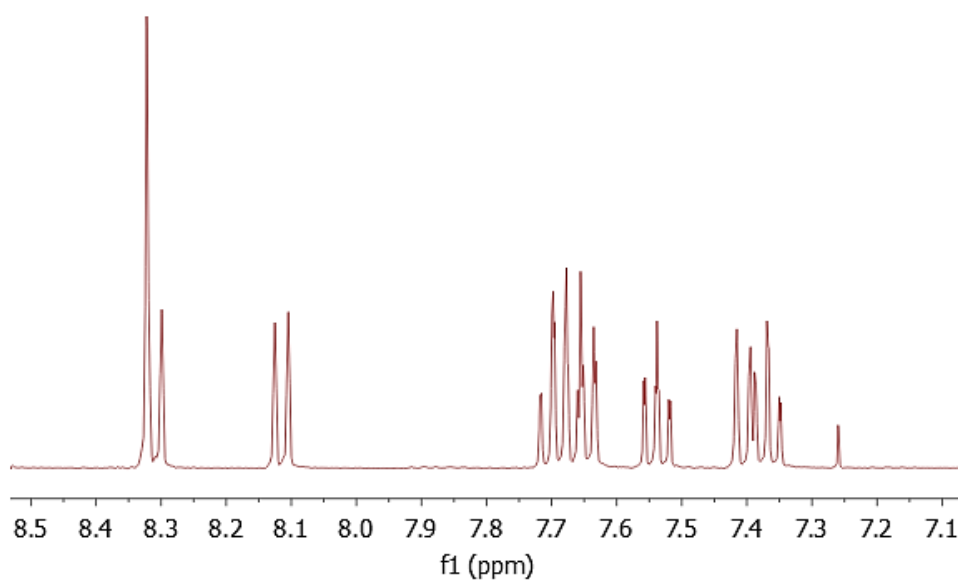
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## Chapter 2: Synthesis of emissive chelating peptides

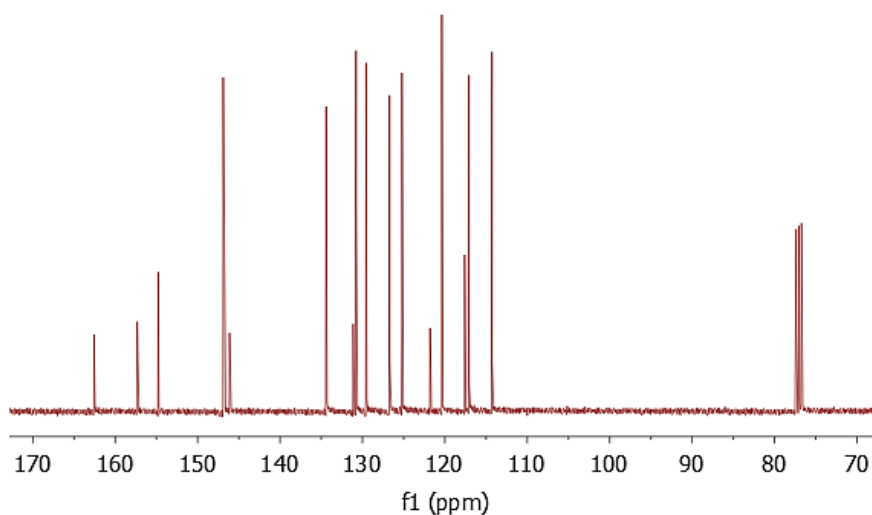
### *3-(1H-Benzotriazol-1-ylcarbonyl)-2H-chromen-2-one*



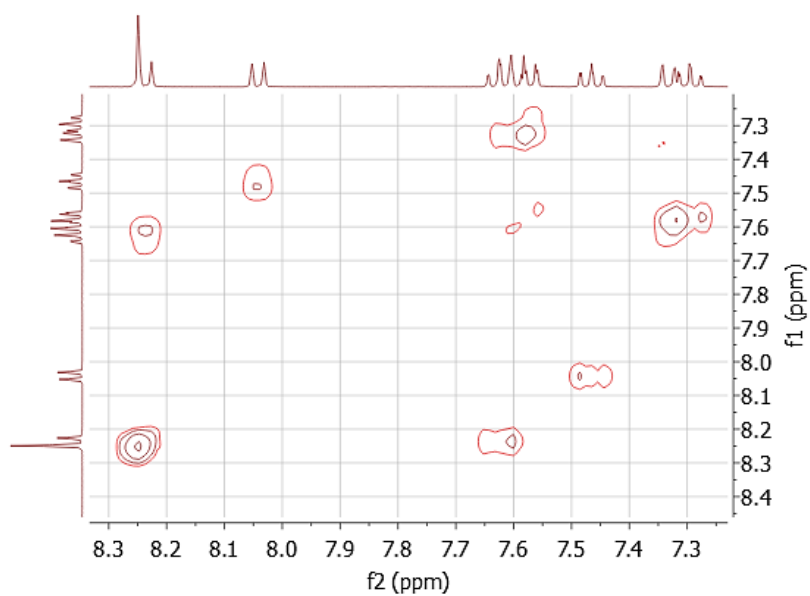
**Figure S2.1:** <sup>1</sup>H NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in CDCl<sub>3</sub>.



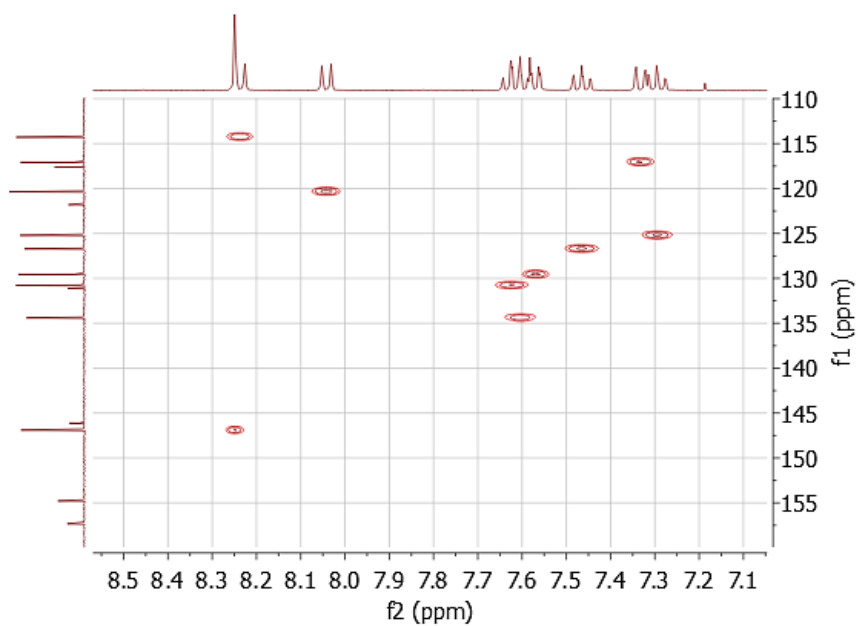
**Figure S2.2:** <sup>1</sup>H NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in CDCl<sub>3</sub> (magnified).



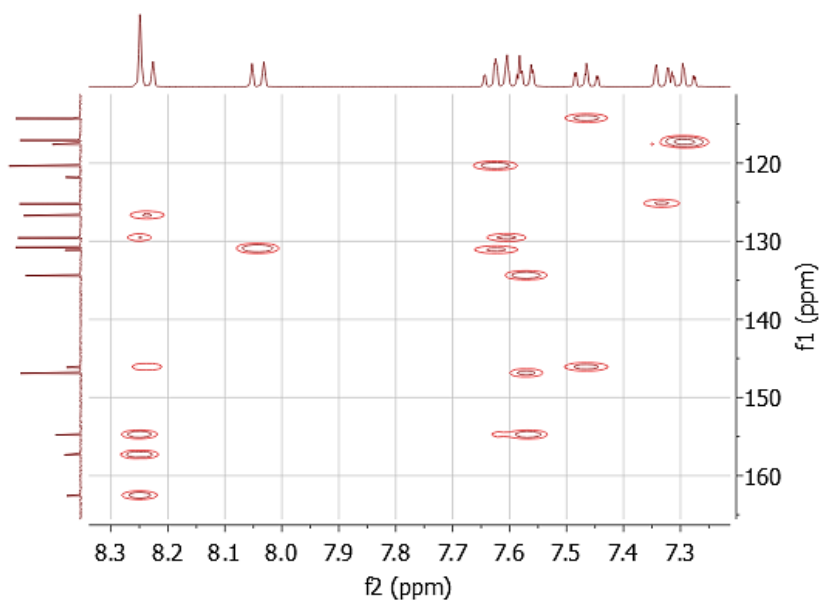
**Figure S2.3:**  $^{13}\text{C}$  NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in  $\text{CDCl}_3$ .



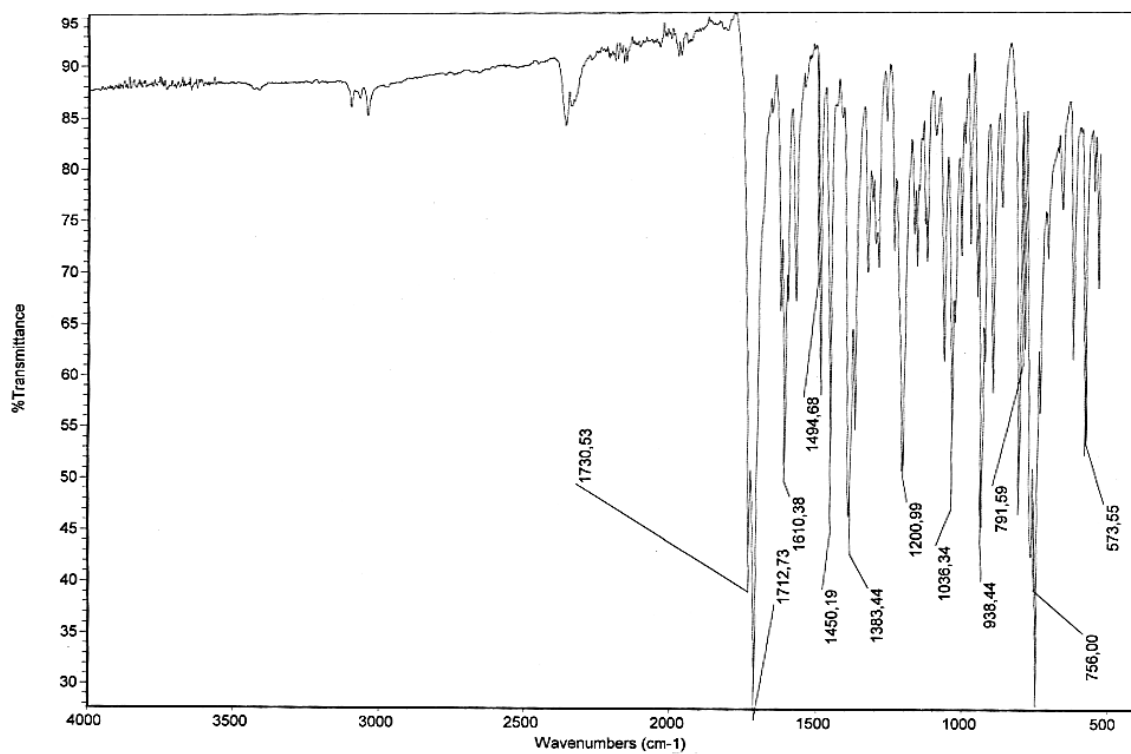
**Figure S2.4:** COSY NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in  $\text{CDCl}_3$ .



**Figure S2.5:** HSQC NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in CDCl<sub>3</sub>.

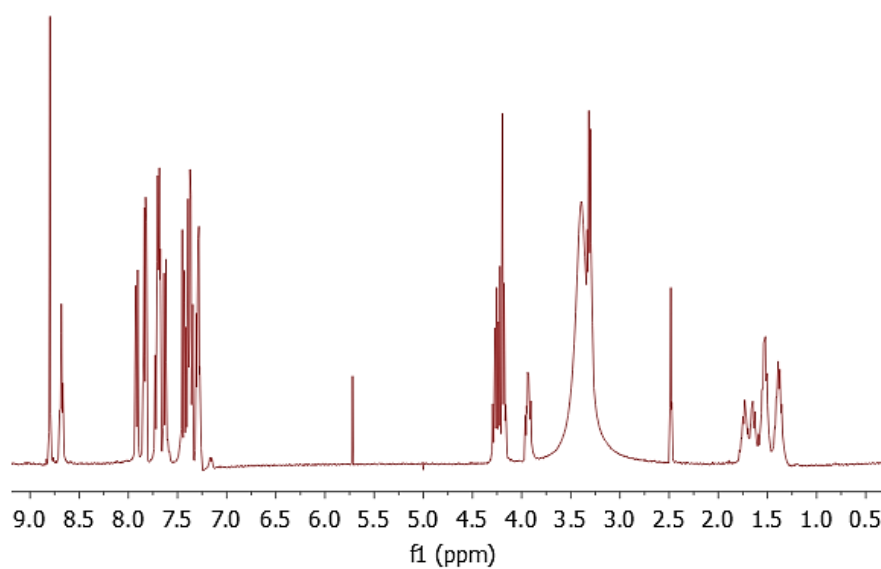


**Figure S2.6:** HMBC NMR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one in CDCl<sub>3</sub>.

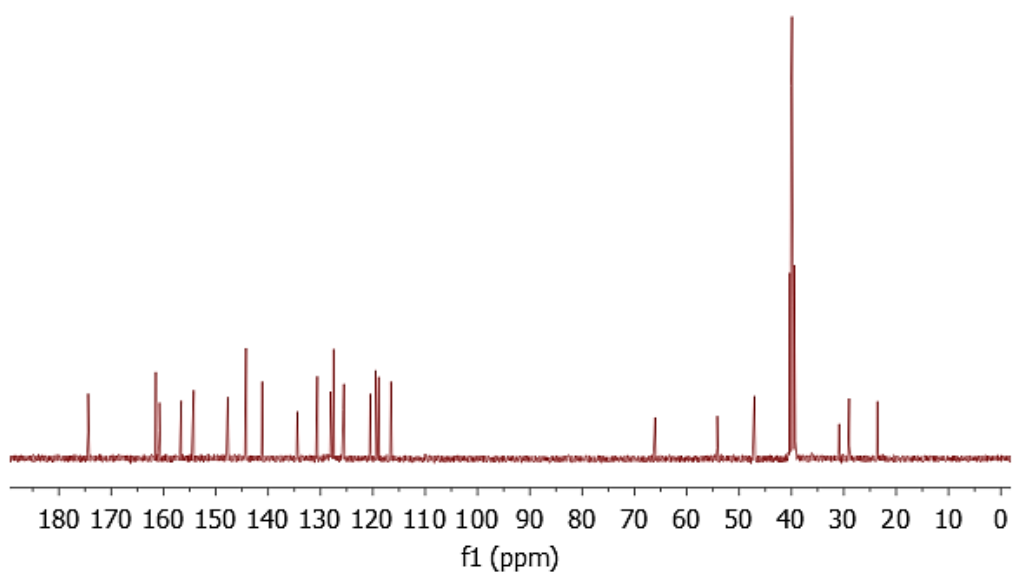


**Figure S2.7:** IR spectrum of 3-(1*H*-Benzotriazol-1-ylcarbonyl)-2*H*-chromen-2-one.

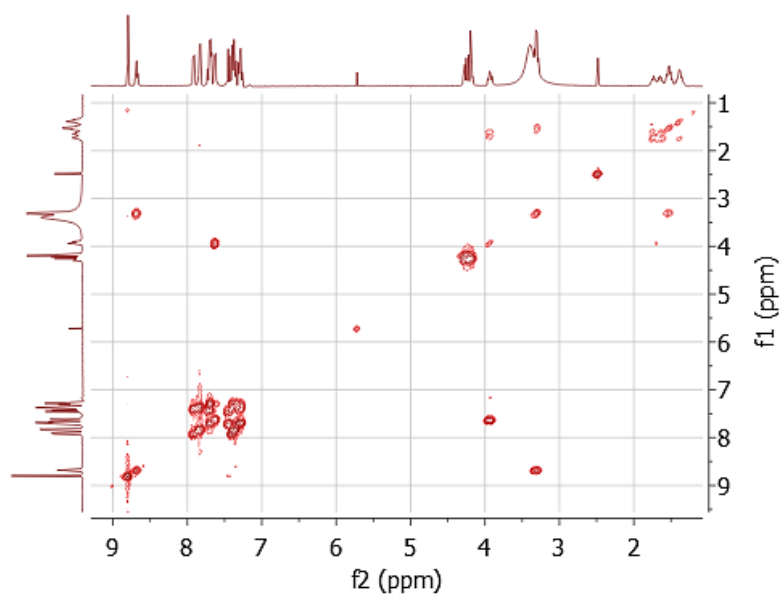
***Fmoc-Lys(Coum)-OH***



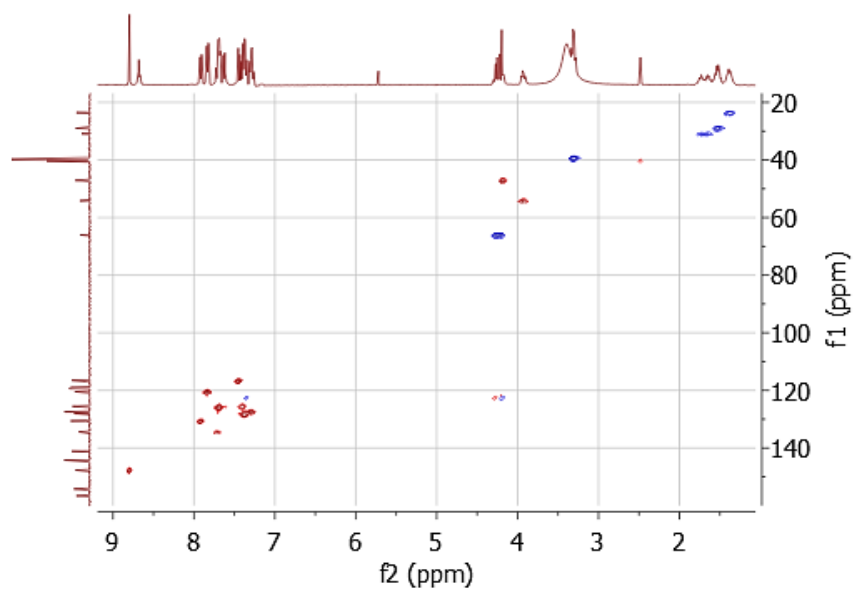
**Figure S2.8:** <sup>1</sup>H NMR spectrum of *Fmoc-Lys(Coum)-OH* in DMSO-*d*<sub>6</sub>.



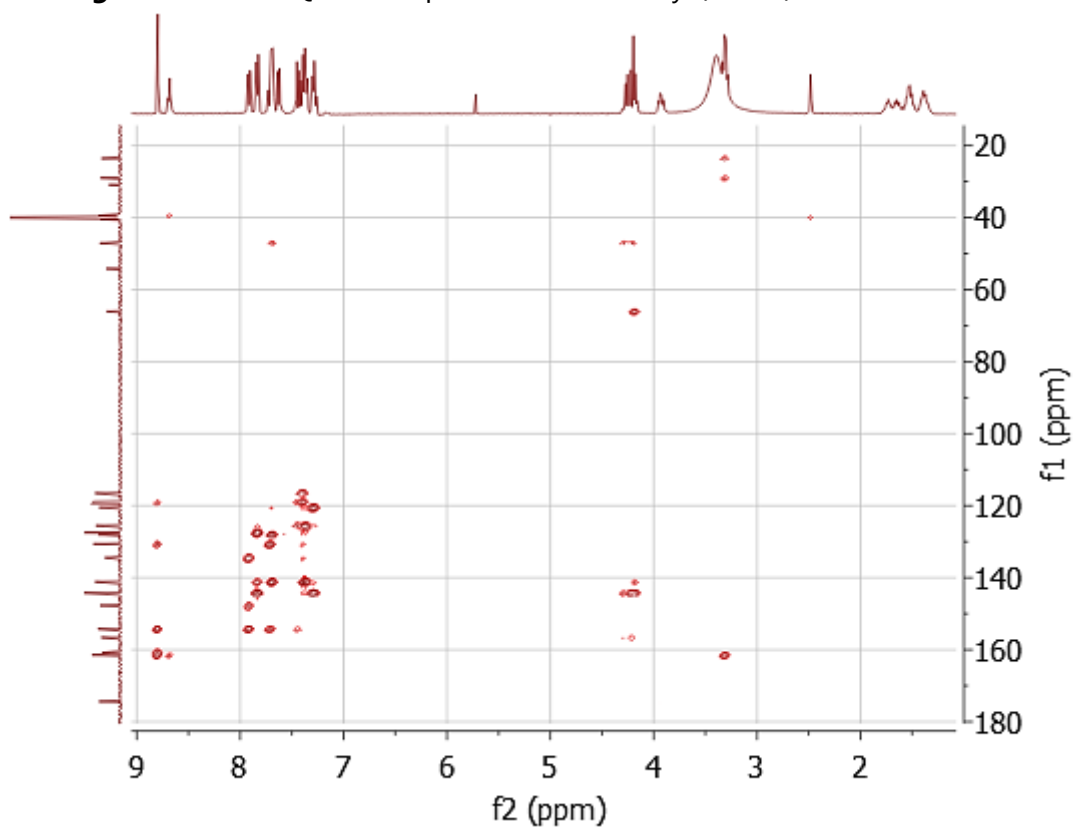
**Figure S2.9:**  $^{13}\text{C}$  NMR spectrum of Fmoc-Lys(Coum)-OH in DMSO- $\text{d}_6$ .



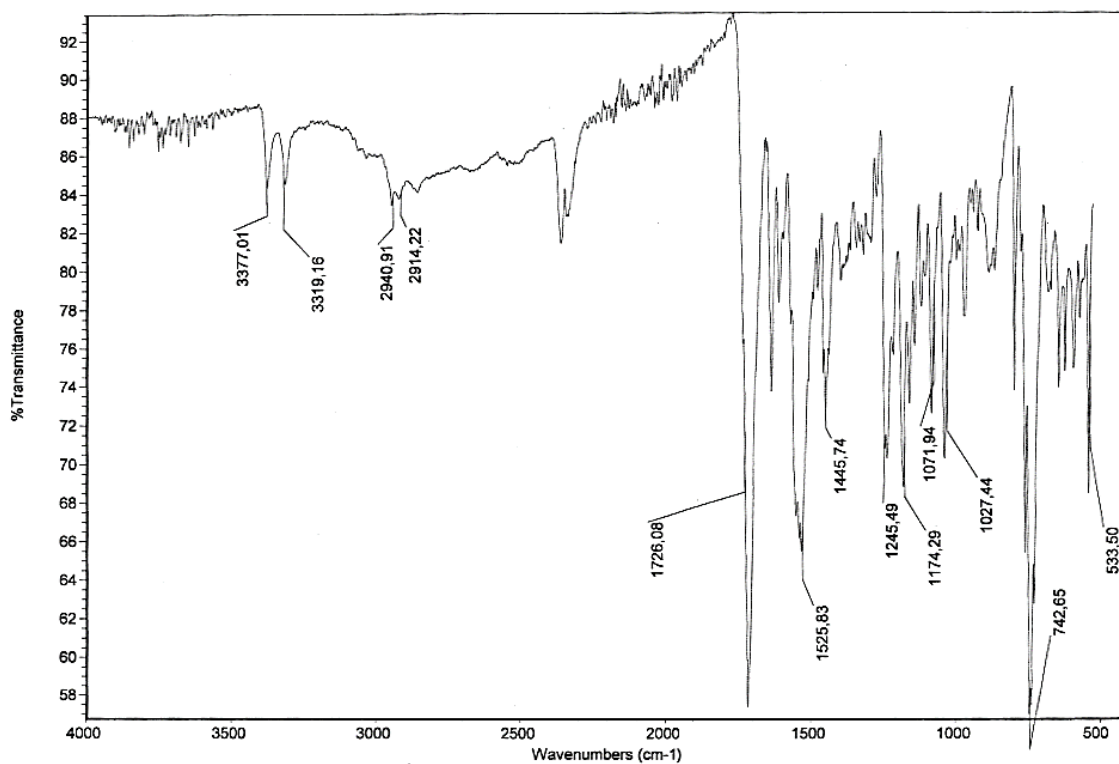
**Figure S2.10:** COSY NMR spectrum of Fmoc-Lys(Coum)-OH in DMSO- $\text{d}_6$ .



**Figure S2.11:** HSQC NMR spectrum of Fmoc-Lys(Coum)-OH in DMSO-d<sub>6</sub>.

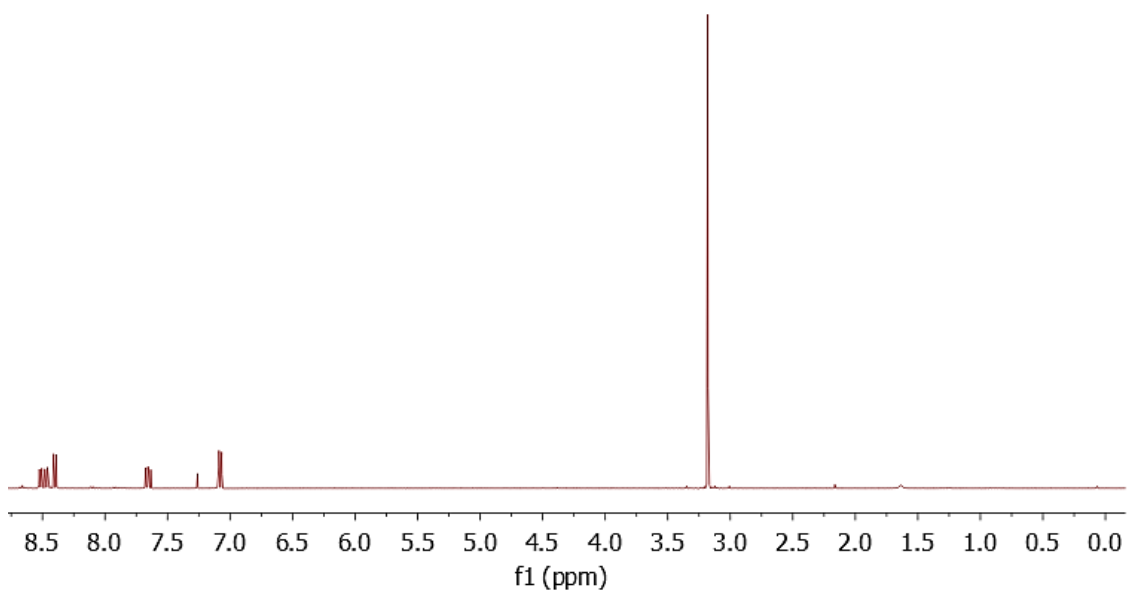


**Figure S2.12:** HMBC NMR spectrum of Fmoc-Lys(Coum)-OH in DMSO-d<sub>6</sub>.



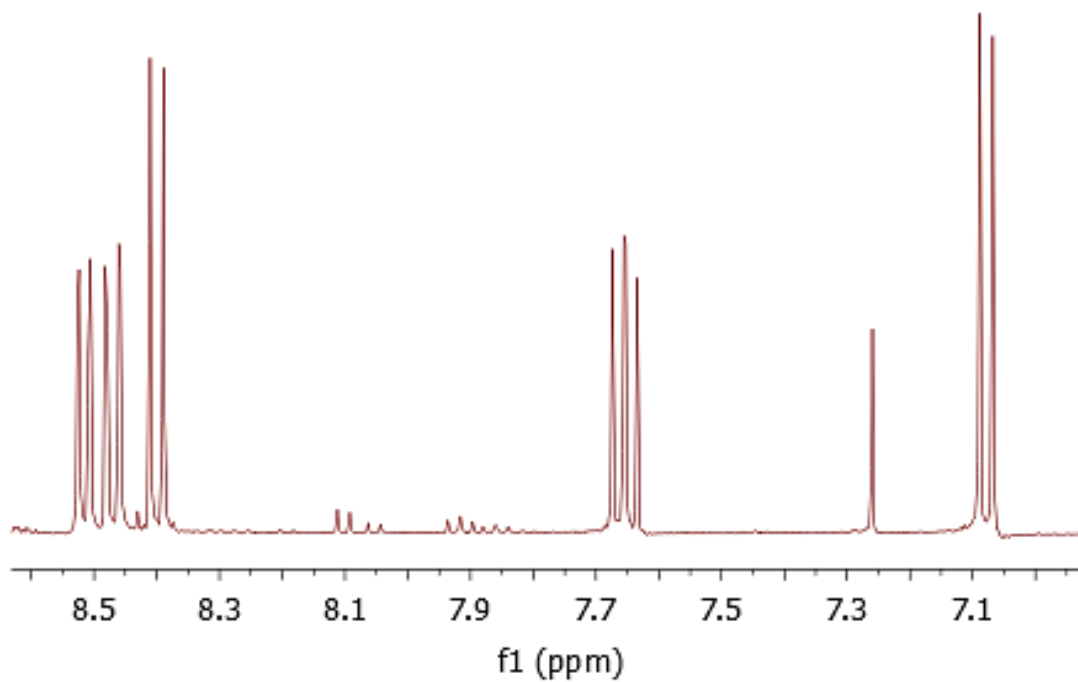
**Figure S2.13:** IR spectrum of Fmoc-Lys(Coum)-OH.

***4-N,N-dimethylamino-1,8-naphthalic anhydride***

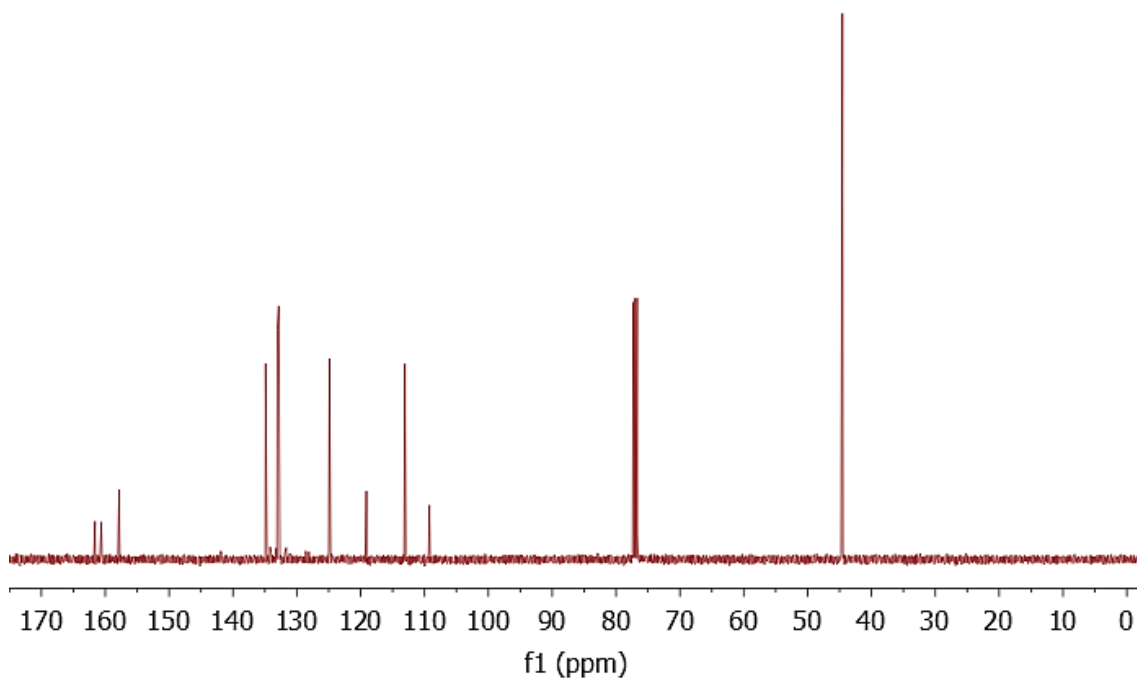


**Figure S2.14:** <sup>1</sup>H NMR spectrum of 4-N,N-dimethylamino-1,8-naphthalic anhydride in CDCl<sub>3</sub>.

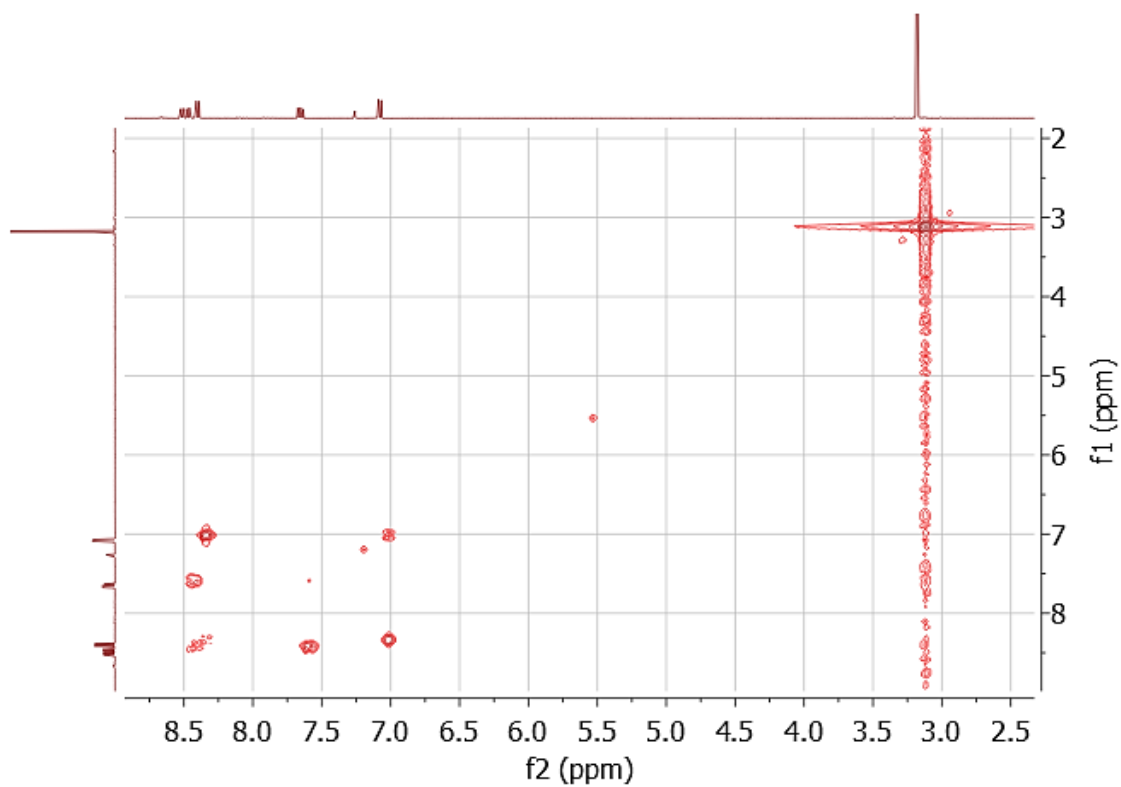




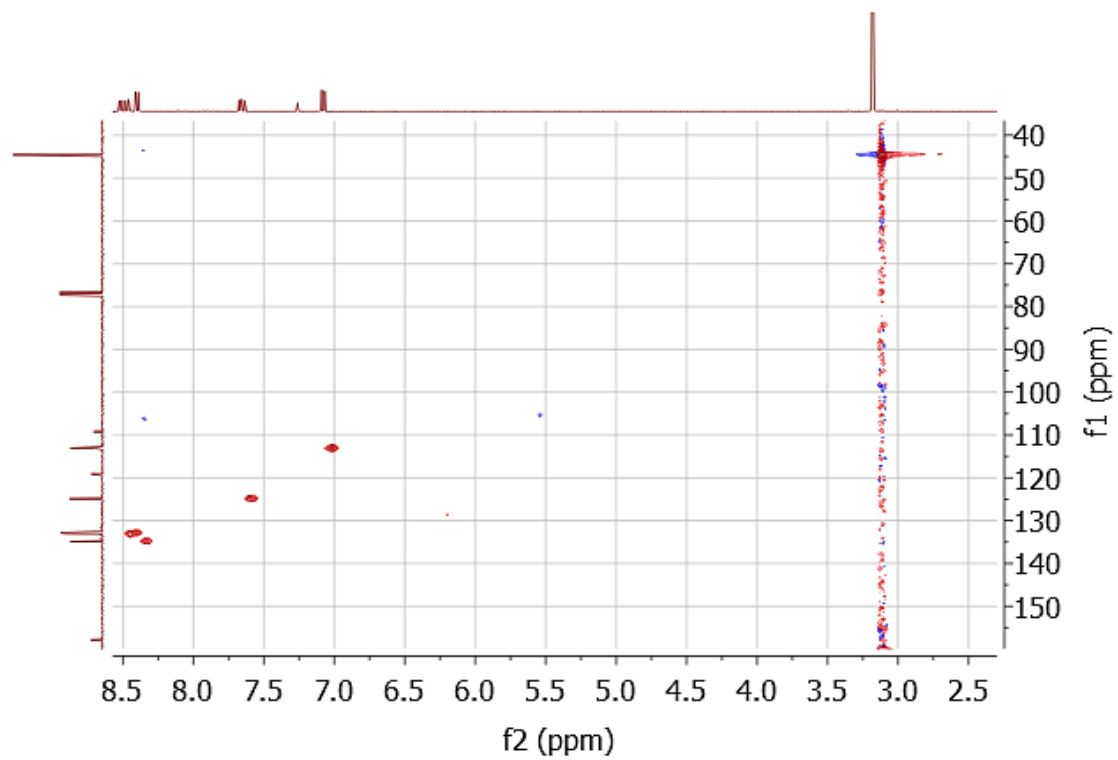
**Figure S2.15:** <sup>1</sup>H NMR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride in CDCl<sub>3</sub> (magnified).



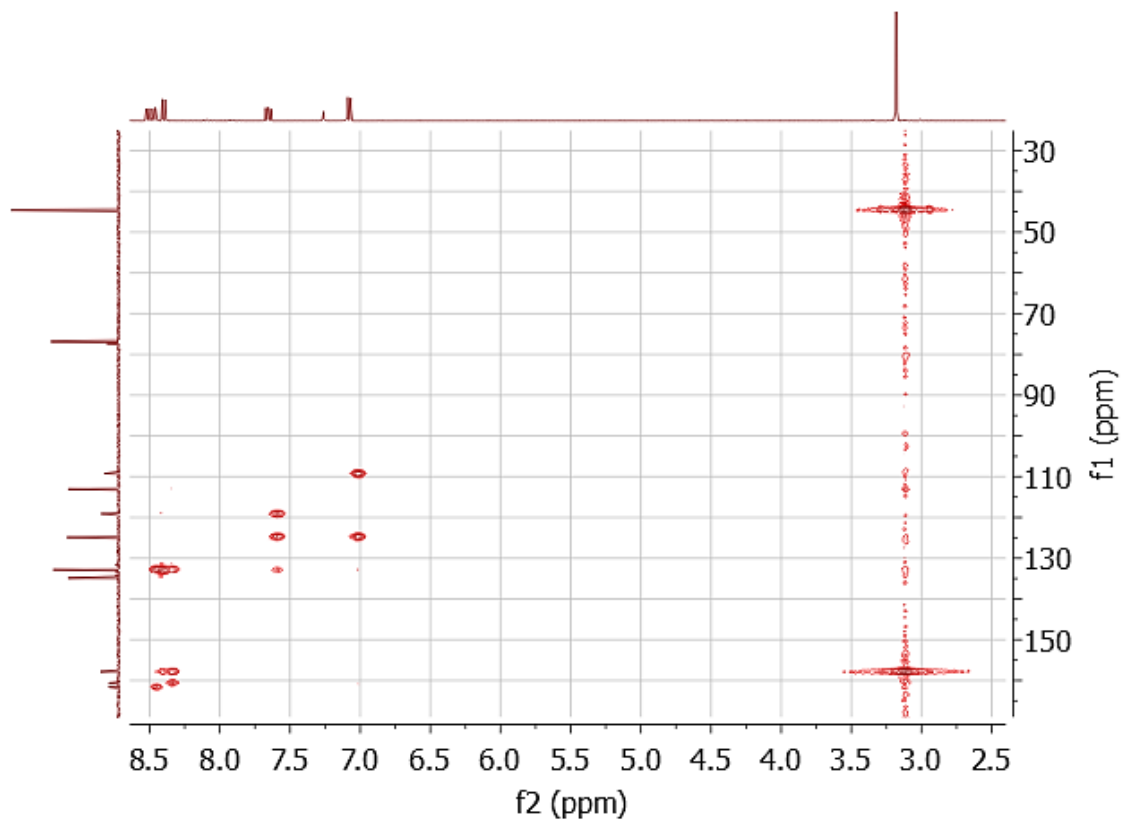
**Figure S2.16:** <sup>13</sup>C NMR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride in CDCl<sub>3</sub>.



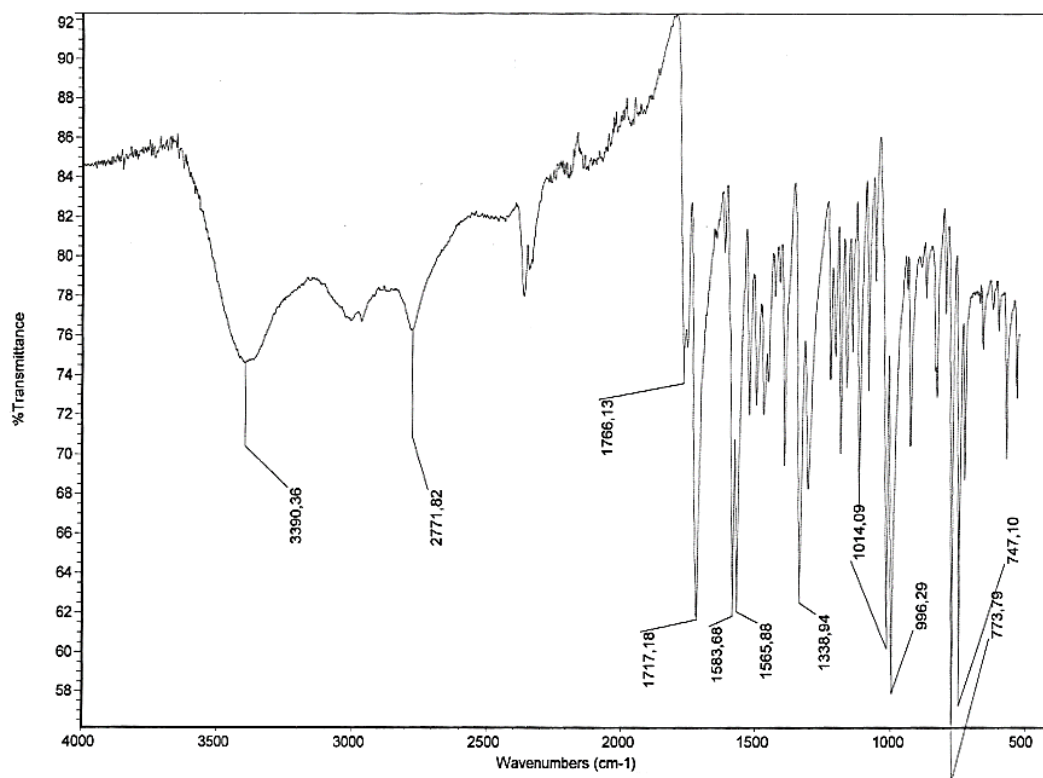
**Figure S2.17:** COSY NMR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride in  $\text{CDCl}_3$ .



**Figure S2.18:** HSQC NMR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride in  $\text{CDCl}_3$ .

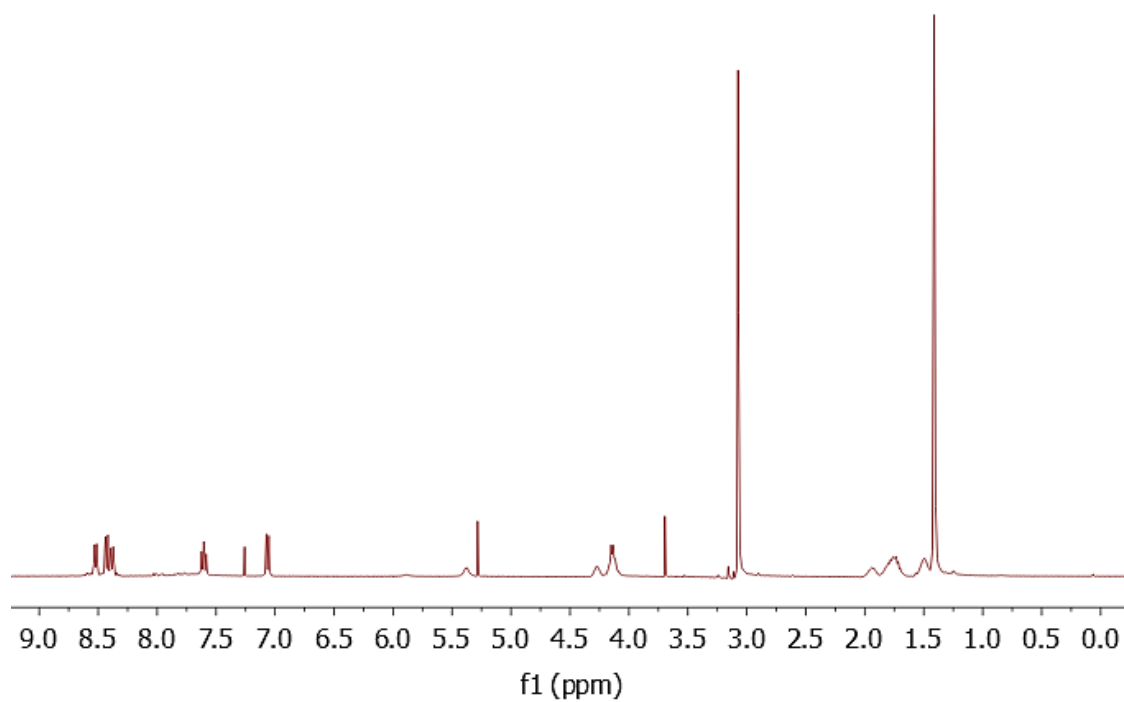


**Figure S2.19:** HMBC NMR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride in  $\text{CDCl}_3$ .

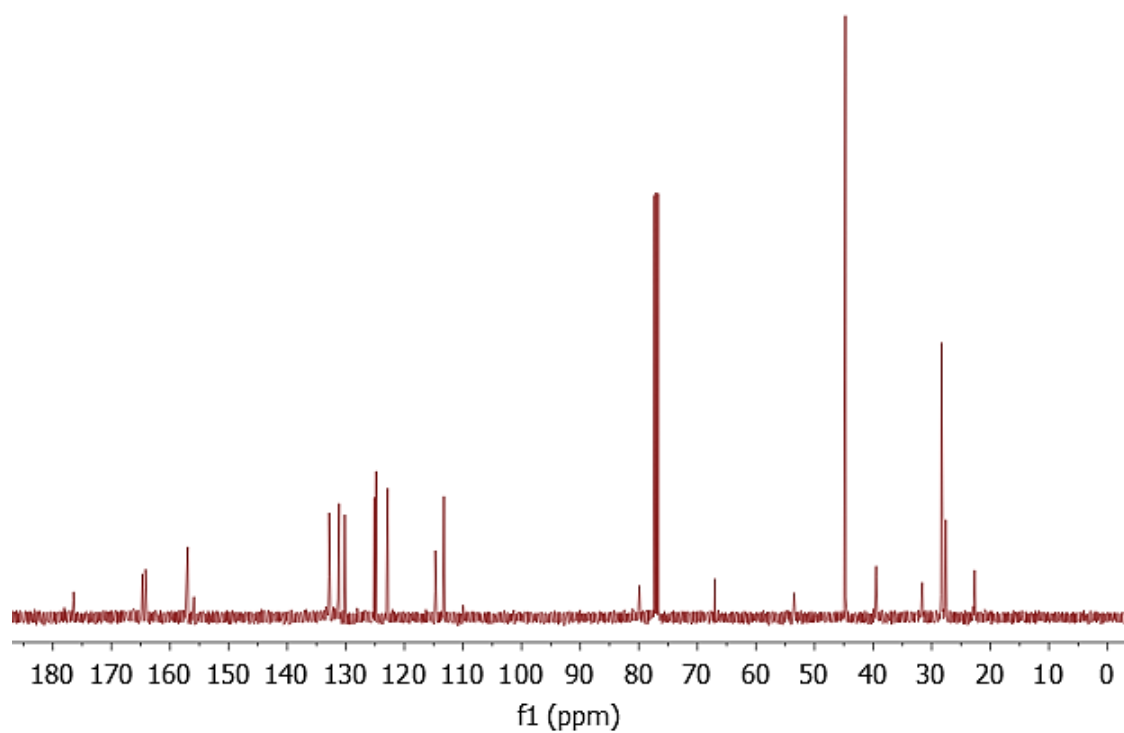


**Figure S2.20:** IR spectrum of 4-*N,N*-dimethylamino-1,8-naphthalic anhydride.

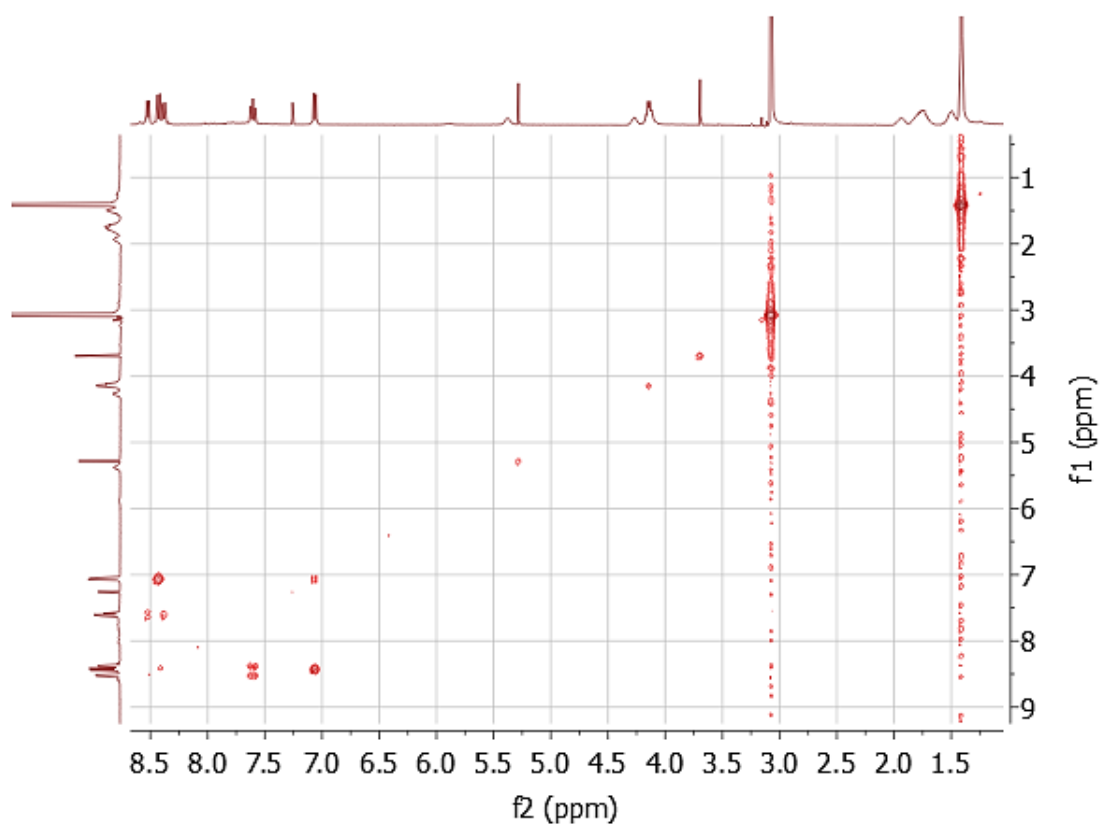
***Boc-Lys(4DMN)-OH***



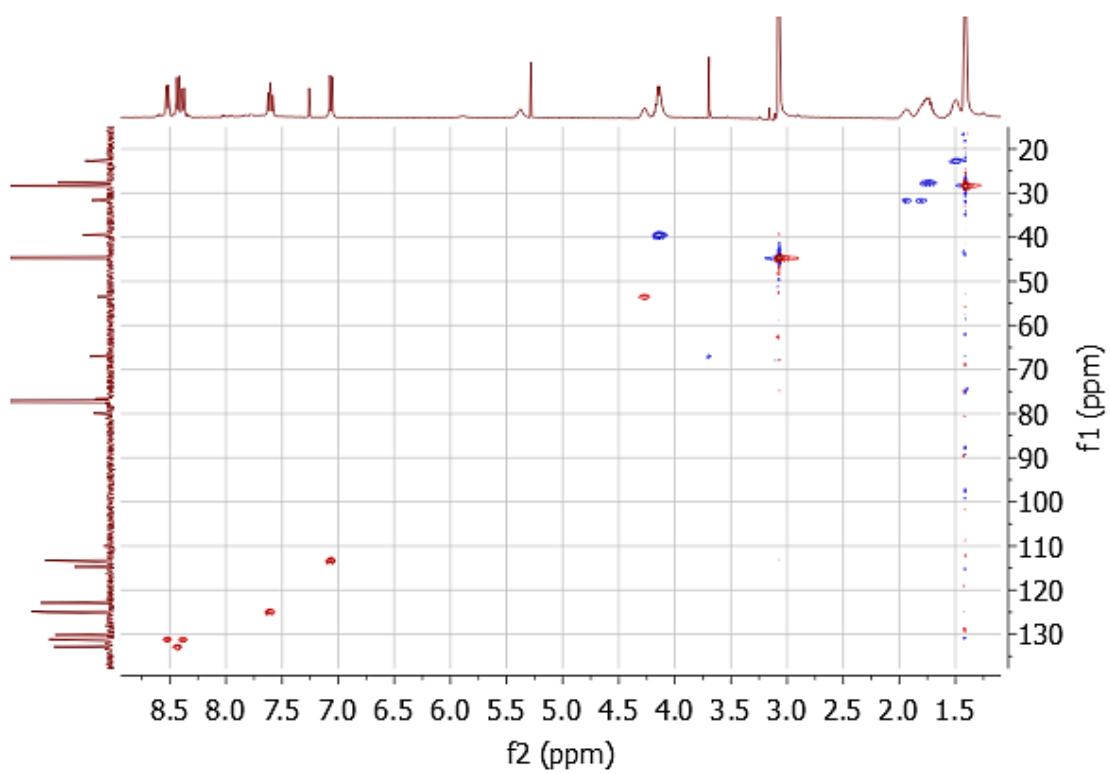
**Figure S2.21:**  $^1\text{H}$  NMR spectrum of Boc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .



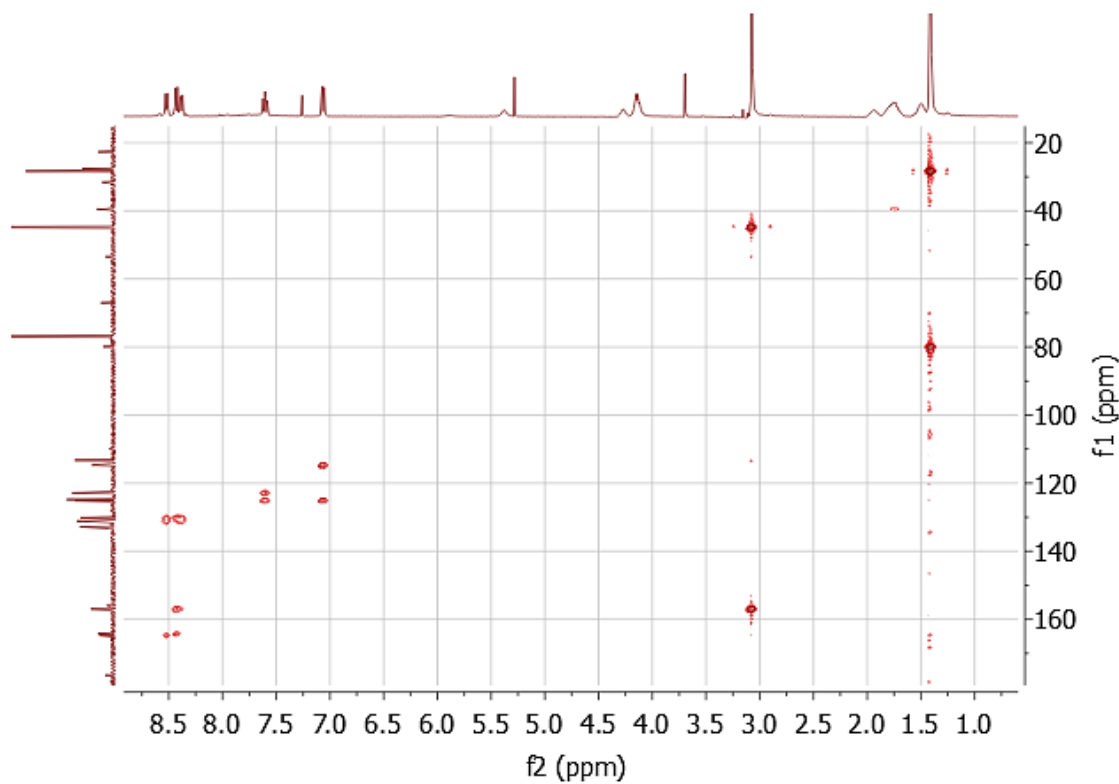
**Figure S2.22:**  $^{13}\text{C}$  NMR spectrum of Boc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .



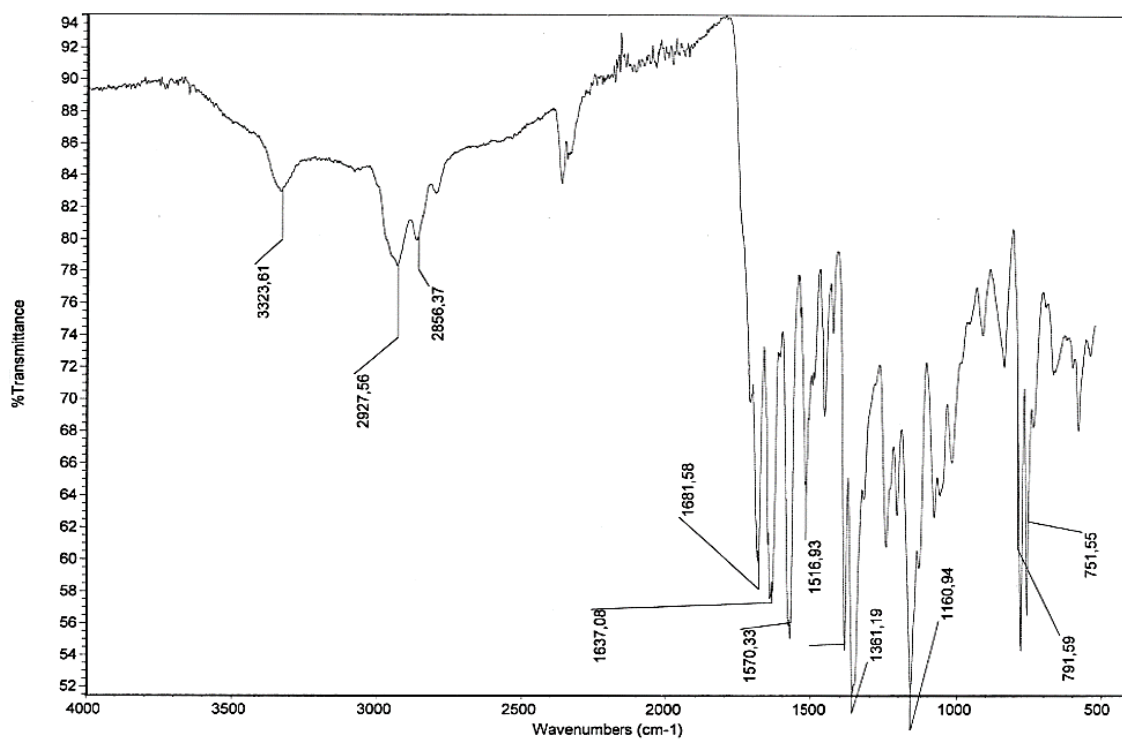
**Figure S2.23:** COSY NMR spectrum of Boc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .



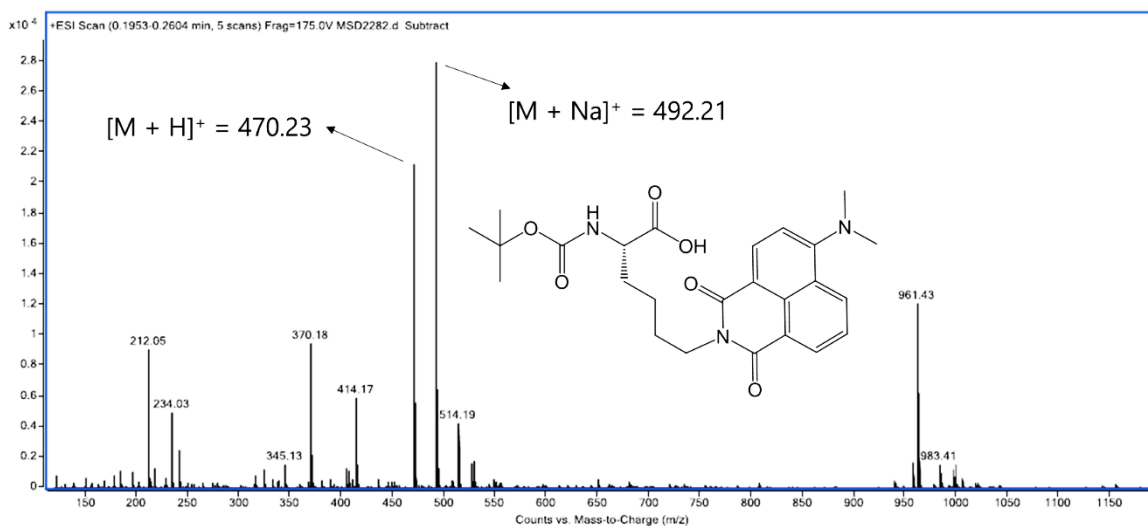
**Figure S2.24:** HSQC NMR spectrum of Boc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .



**Figure S2.25:** HMBC NMR spectrum of Boc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .

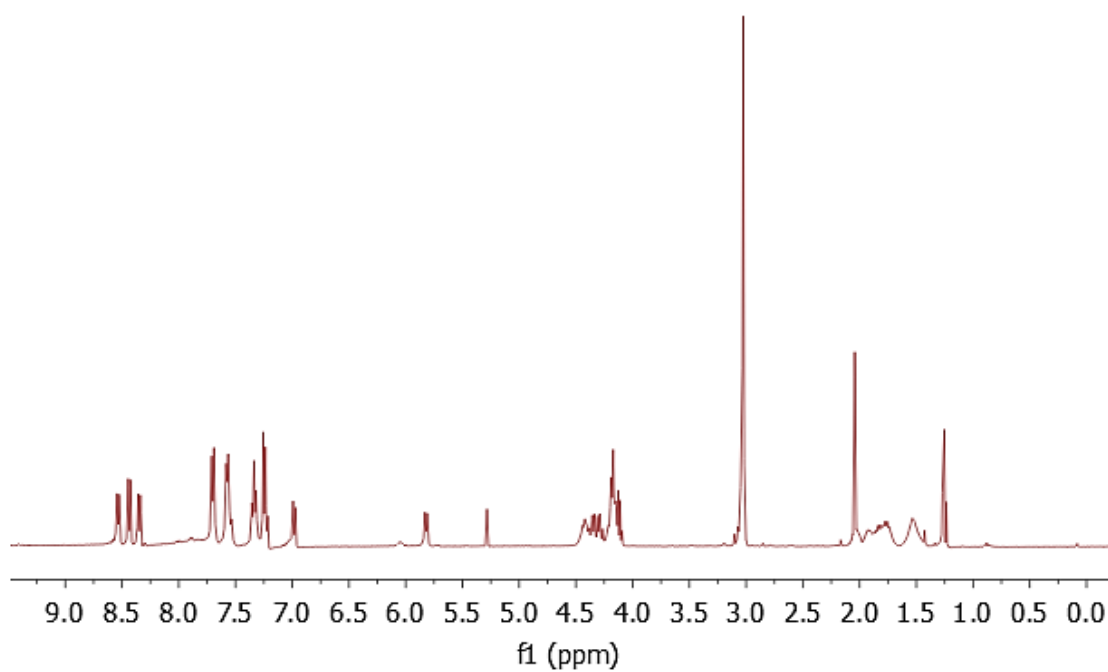


**Figure S2.26:** IR spectrum of Boc-Lys(4DMN)-OH.

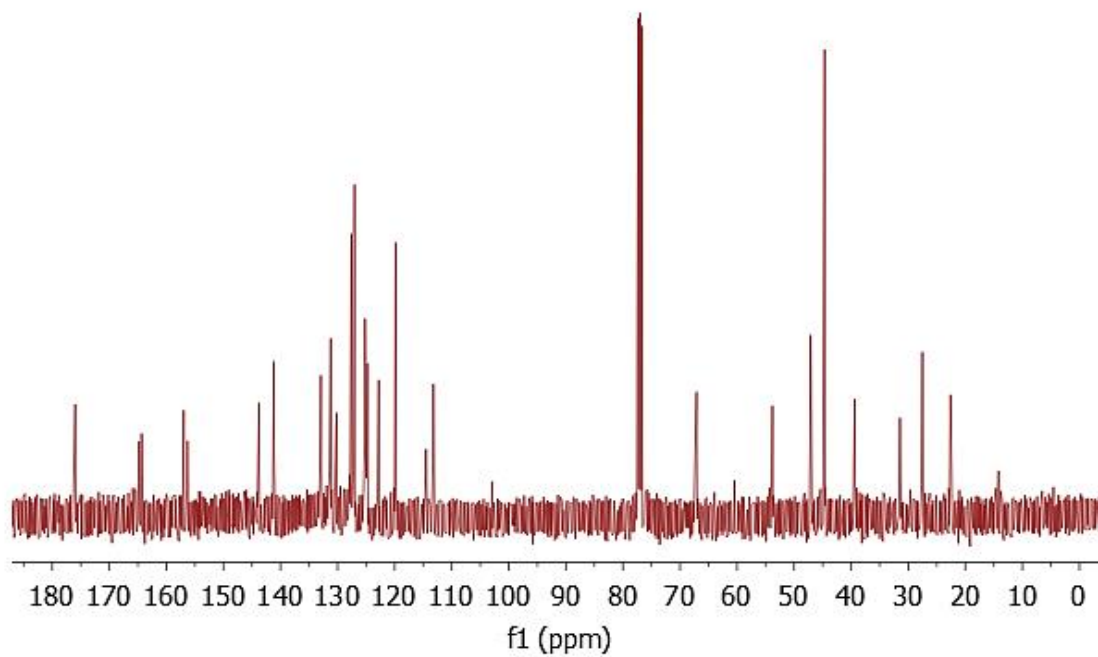


**Figure S2.27:** ESI mass spectrum of Boc-Lys(4DMN)-OH.

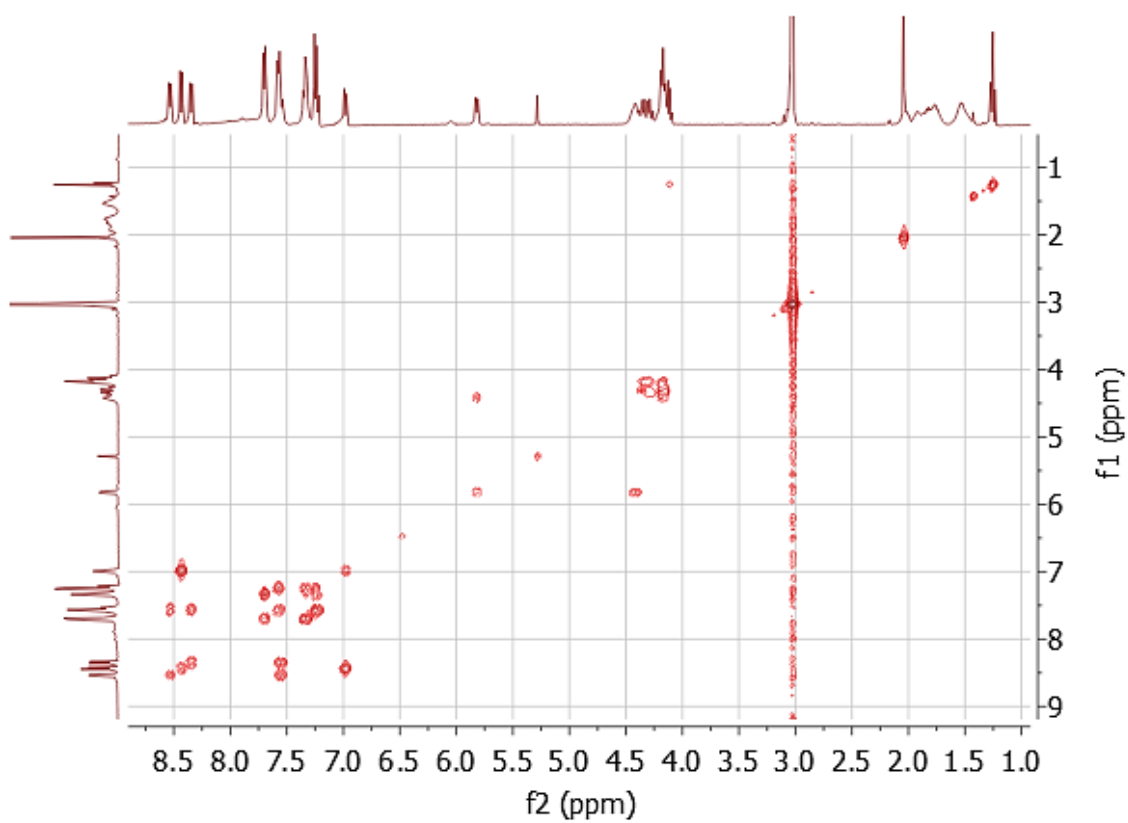
***Fmoc-Lys(4DMN)-OH***



**Figure S2.28:** <sup>1</sup>H NMR spectrum of Fmoc-Lys(4DMN)-OH in CDCl<sub>3</sub>.

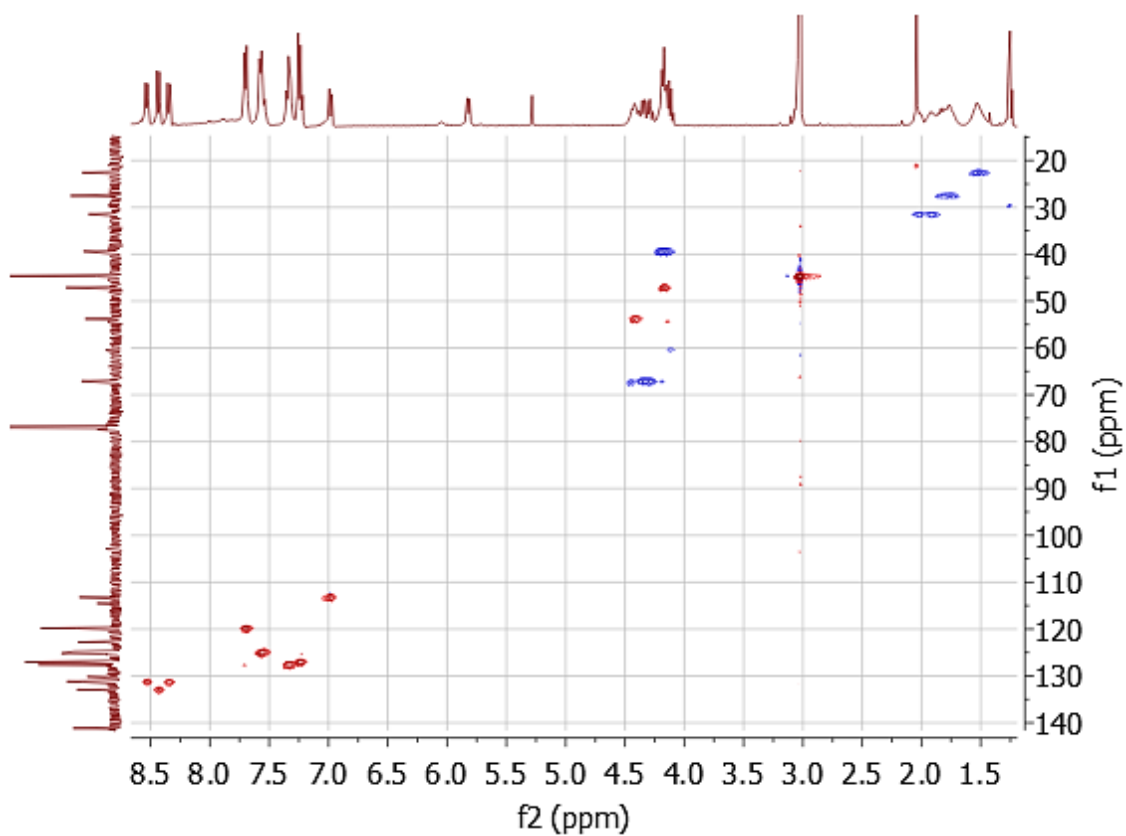


**Figure S2.29:**  $^{13}\text{C}$  NMR spectrum of Fmoc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .

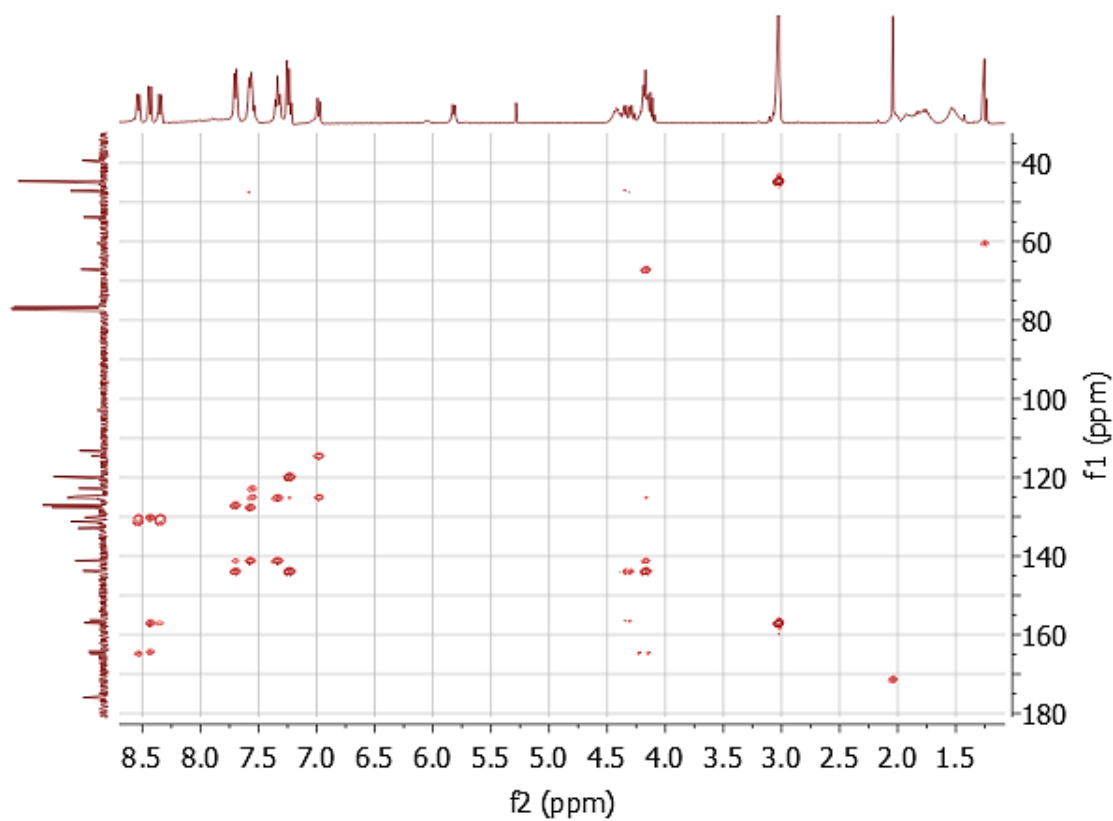


**Figure S2.30:** COSY NMR spectrum of Fmoc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .

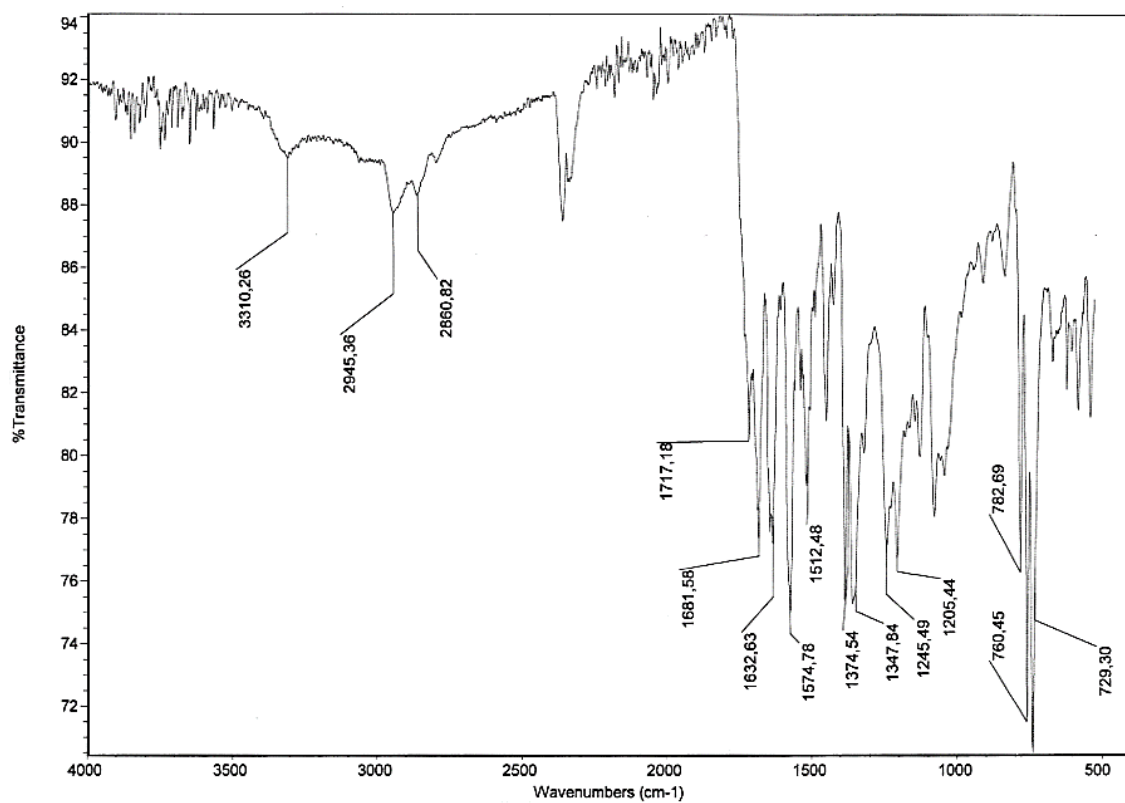




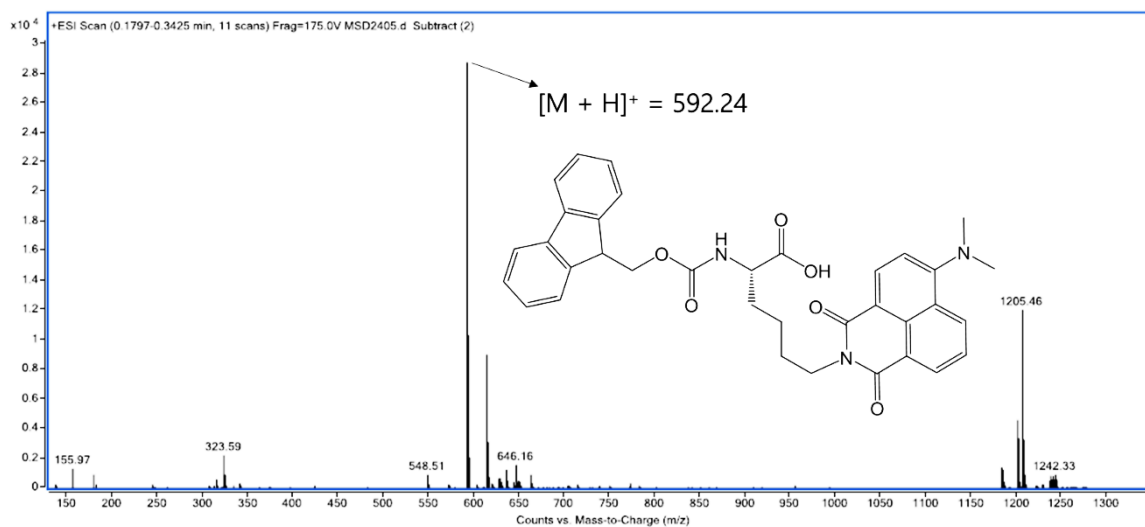
**Figure S2.31:** HSQC NMR spectrum of Fmoc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .



**Figure S2.32:** HMBC NMR spectrum of Fmoc-Lys(4DMN)-OH in  $\text{CDCl}_3$ .

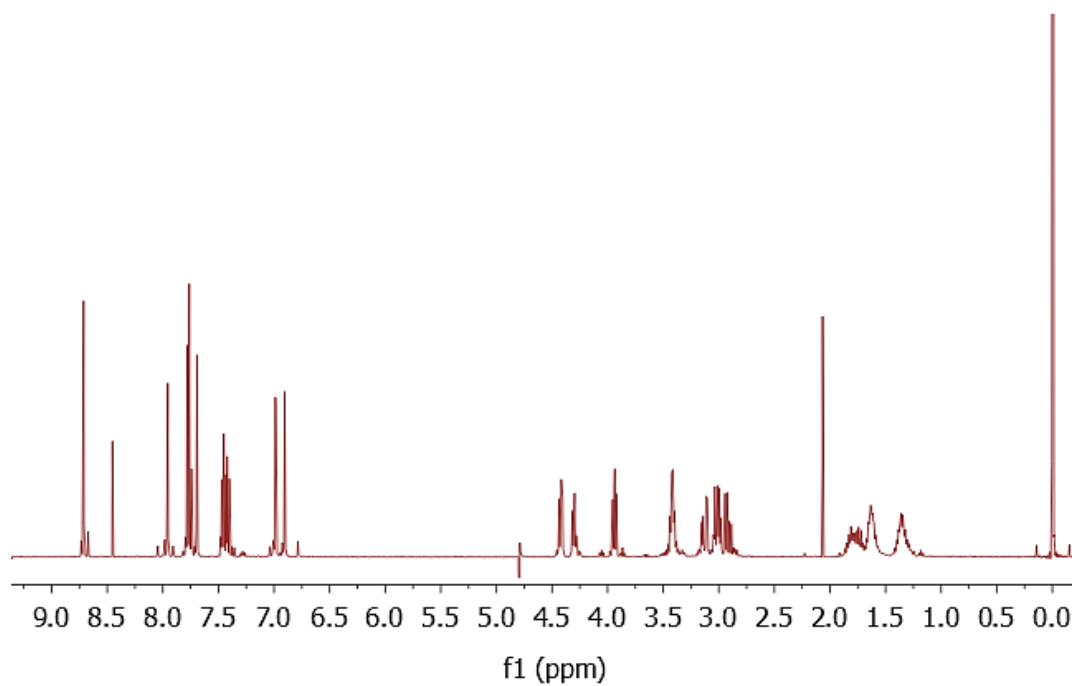


**Figure S2.33:** IR spectrum of Fmoc-Lys(4DMN)-OH.

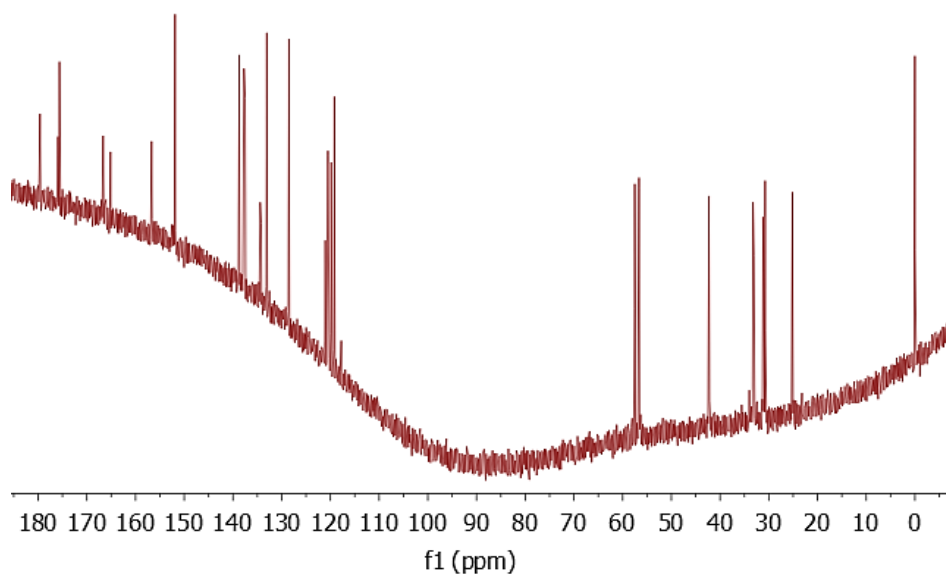


**Figure S2.34:** ESI mass spectrum of Fmoc-Lys(4DMN)-OH.

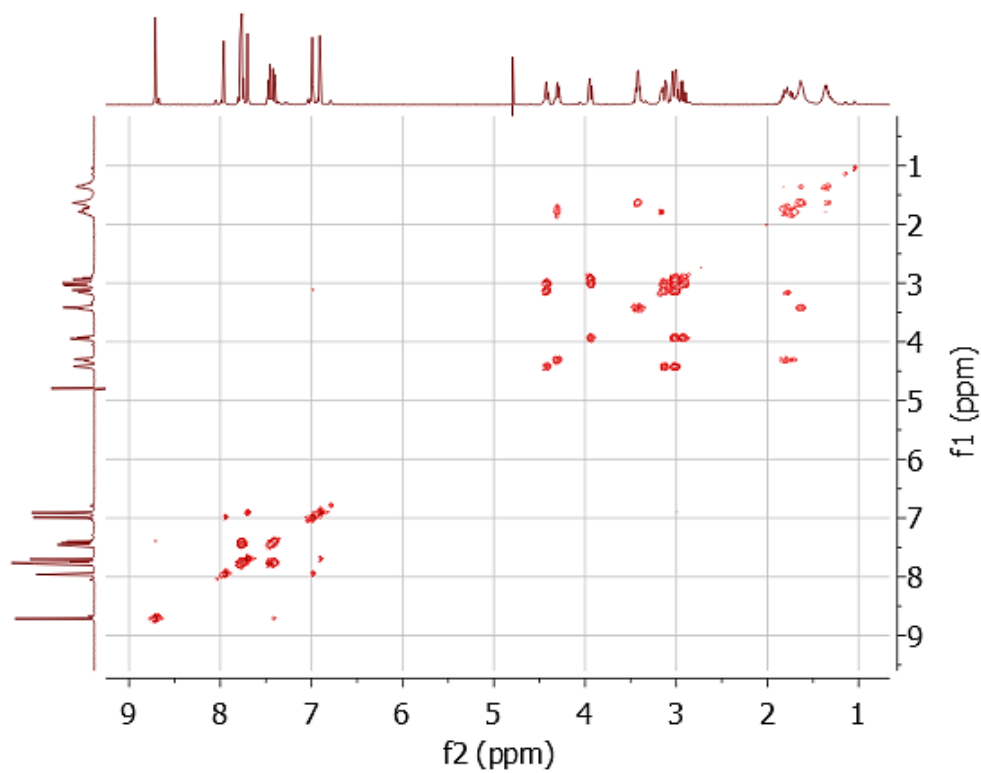
***H-His-Lys(Coum)-His-OH (HK<sup>c</sup>H)***



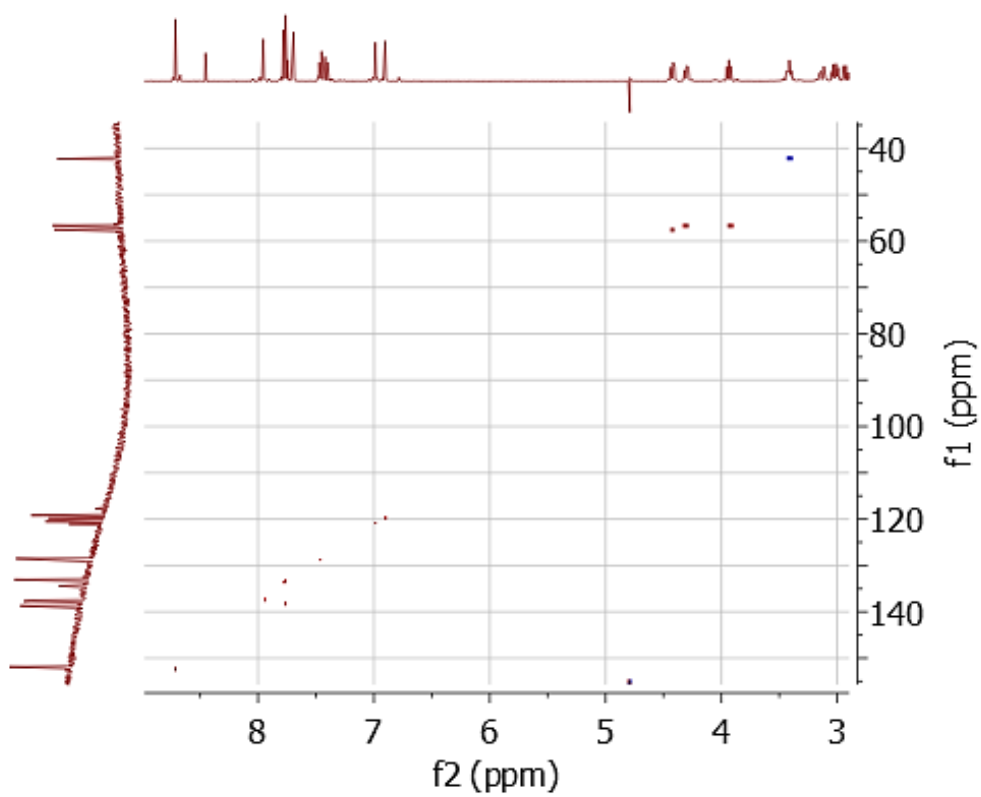
**Figure S2.35:** <sup>1</sup>H NMR spectrum of H-His-Lys(Coum)-His-OH (HK<sup>c</sup>H) in D<sub>2</sub>O (pH 7.4).



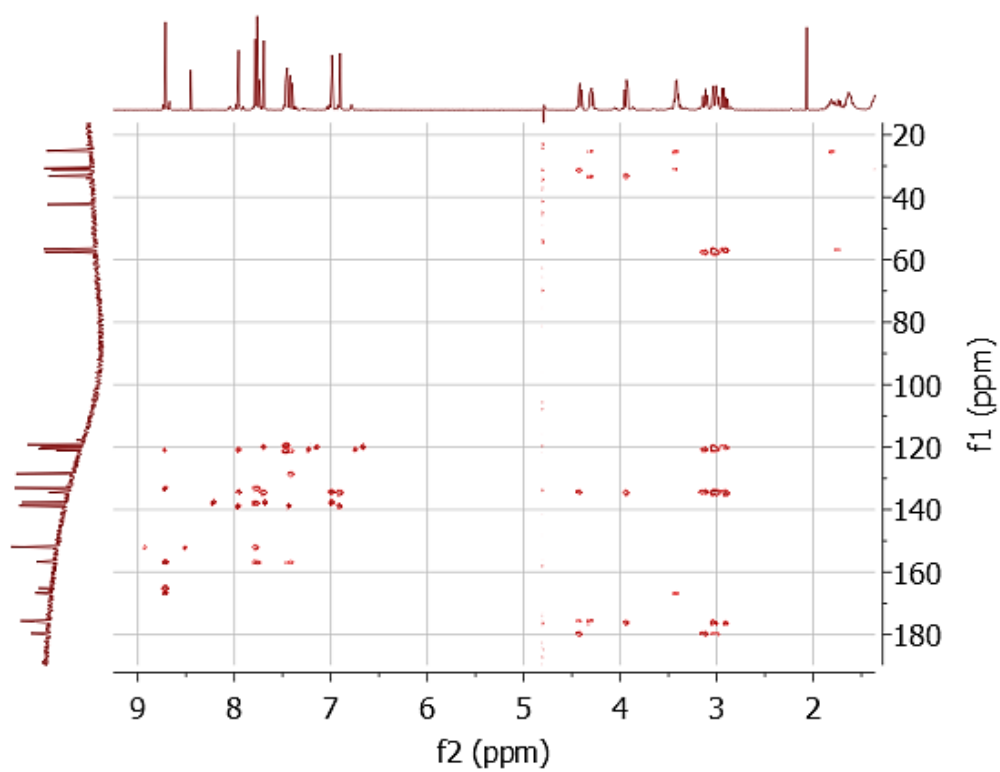
**Figure S2.36:** <sup>13</sup>C NMR spectrum of H-His-Lys(Coum)-His-OH (HK<sup>c</sup>H) in D<sub>2</sub>O (pH 7.4).



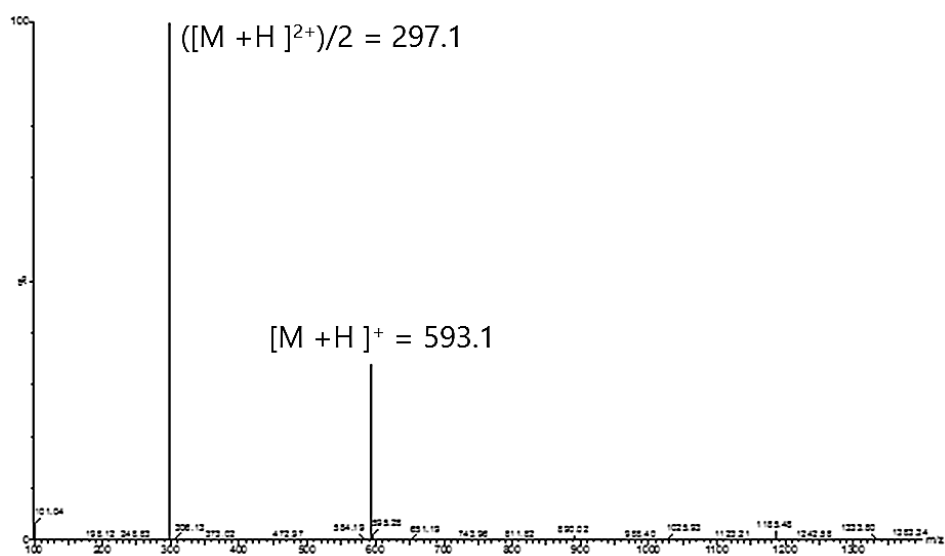
**Figure S2.37:** COSY NMR spectrum of H-His-Lys(Coum)-His-OH (HK<sup>C</sup>H) in D<sub>2</sub>O (pH 7.4).



**Figure S2.38:** HSQC NMR spectrum of H-His-Lys(Coum)-His-OH (HK<sup>C</sup>H) in D<sub>2</sub>O (pH 7.4).

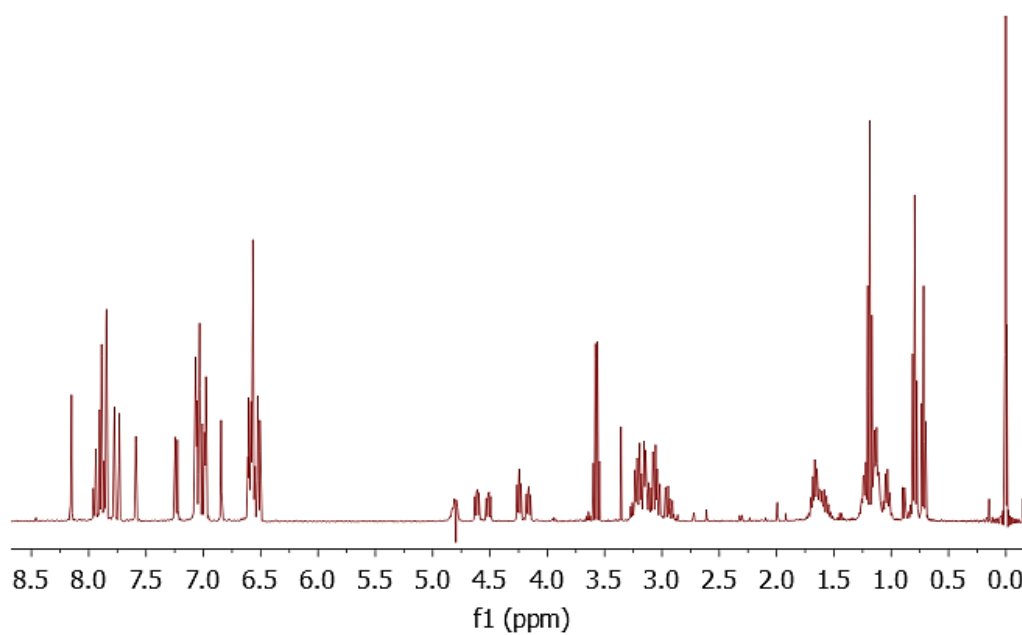


**Figure S2.39:** HMBC NMR spectrum of H-His-Lys(Coum)-His-OH (HK<sup>C</sup>H) in D<sub>2</sub>O (pH 7.4).

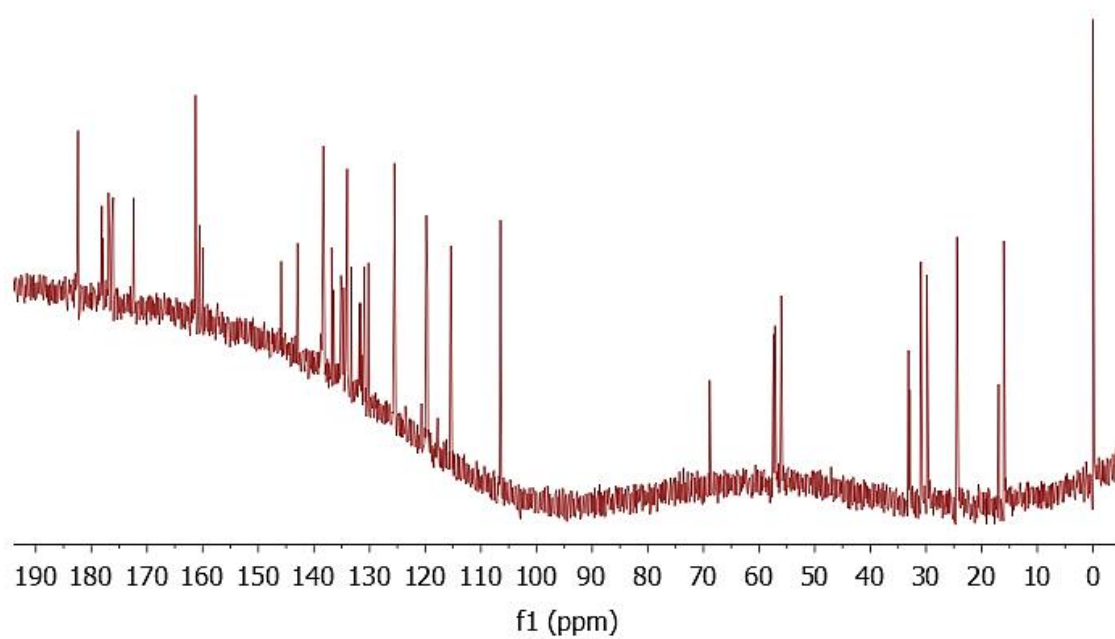


**Figure S2.40:** ESI mass spectrum of H-His-Lys(Coum)-His-OH (HK<sup>C</sup>H).

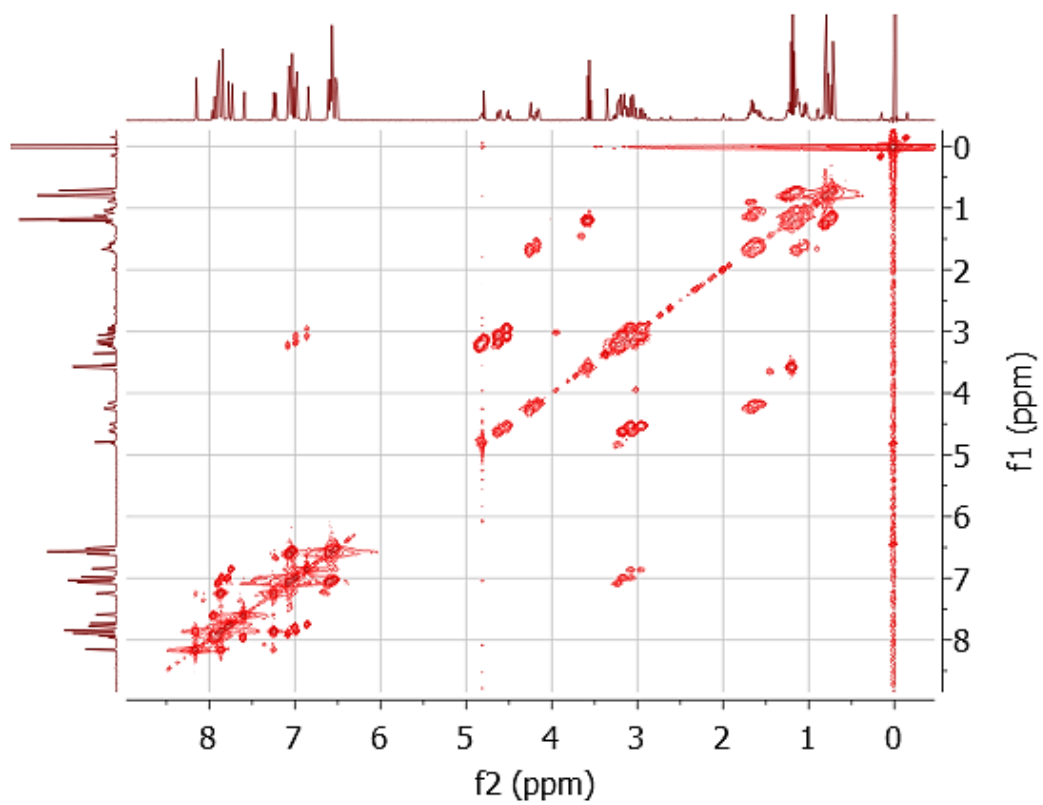
***Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH)***



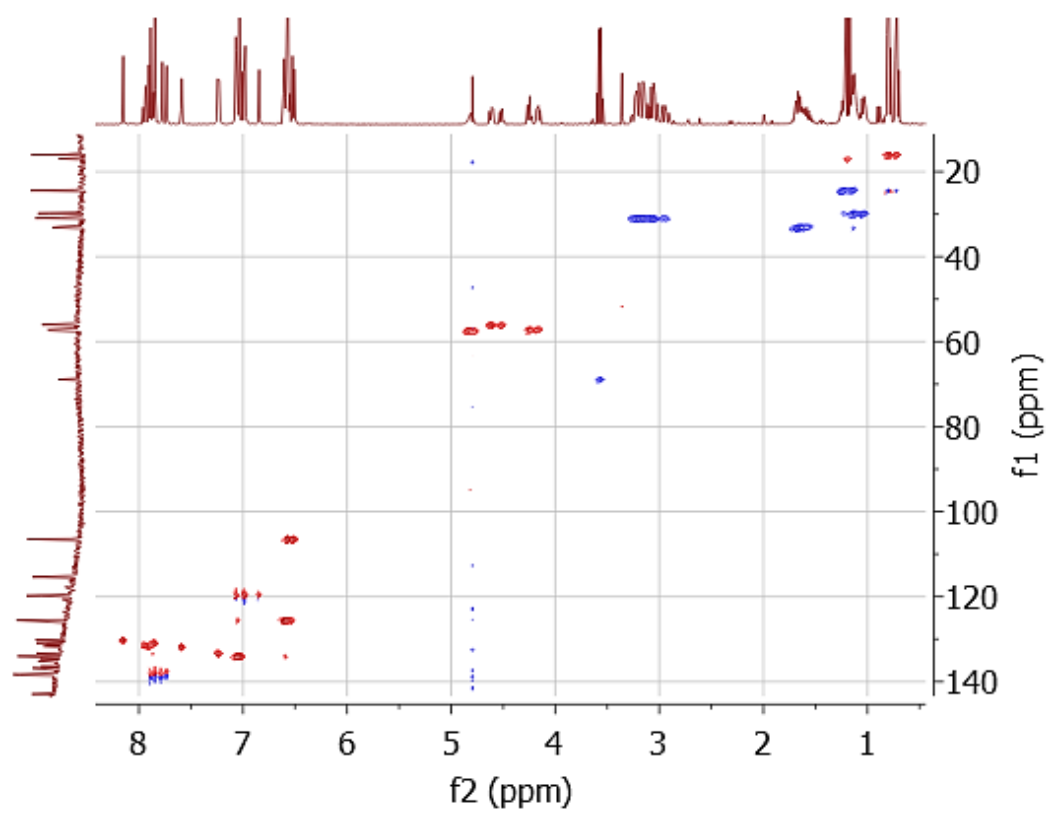
**Figure S2.41:** <sup>1</sup>H NMR spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH) in D<sub>2</sub>O (pH 7.4).



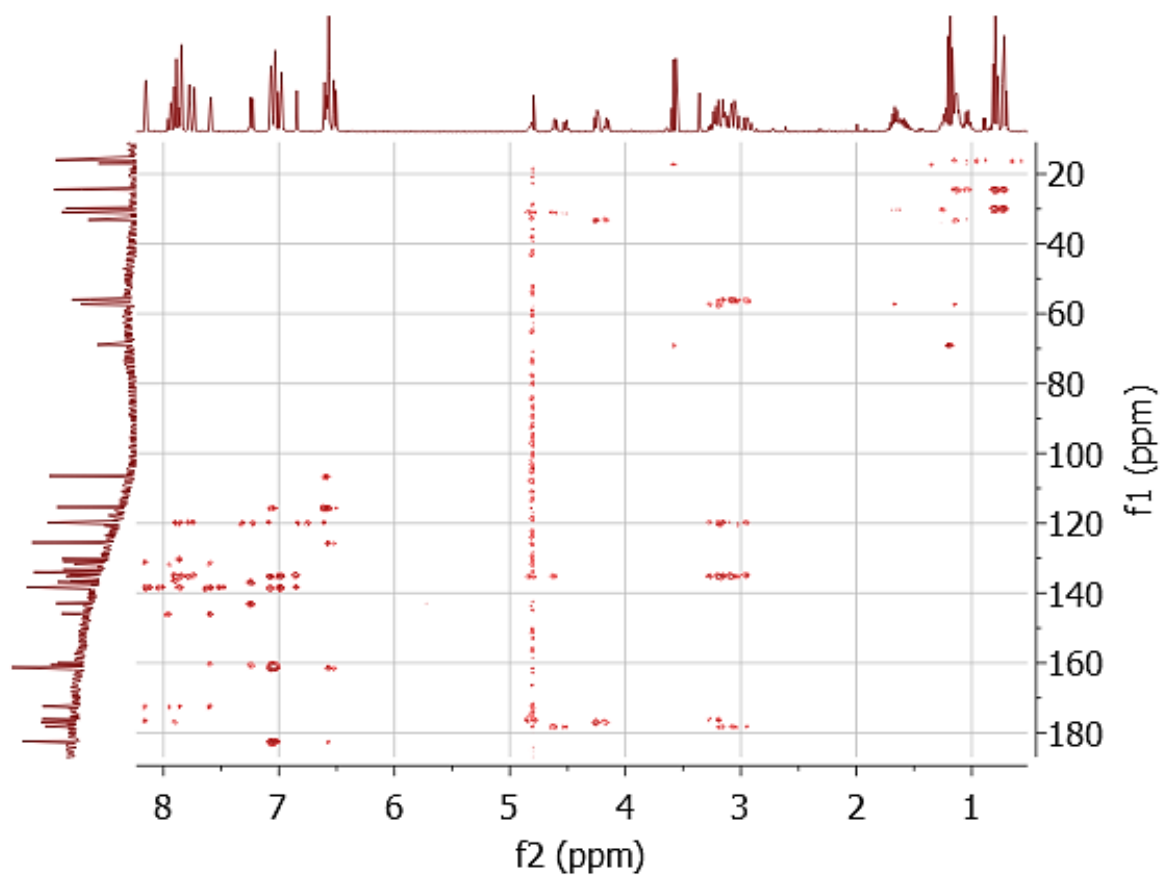
**Figure S2.42:** <sup>13</sup>C NMR spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH) in D<sub>2</sub>O (pH 7.4).



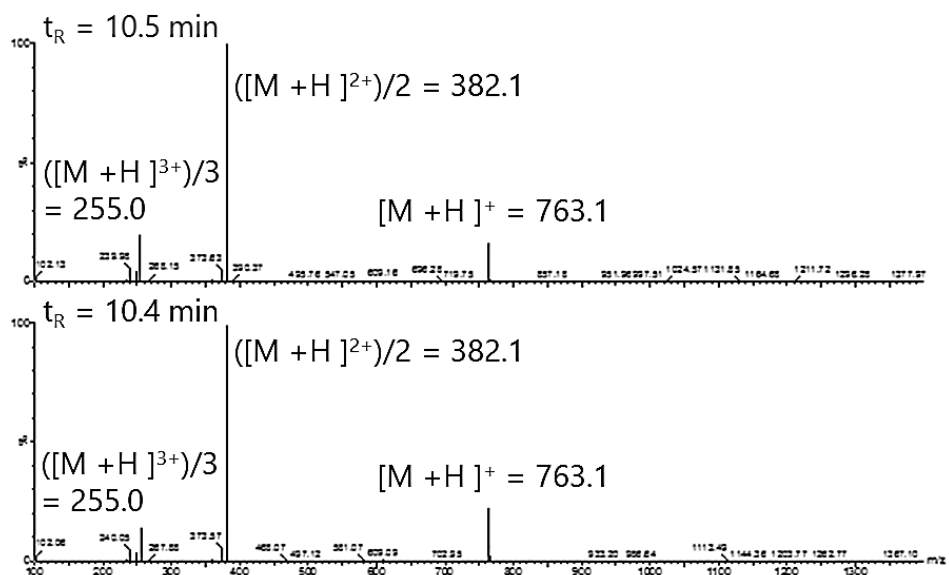
**Figure S2.43:** COSY NMR spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH) in D<sub>2</sub>O (pH 7.4).



**Figure S2.44:** HSQC NMR spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH) in D<sub>2</sub>O (pH 7.4).



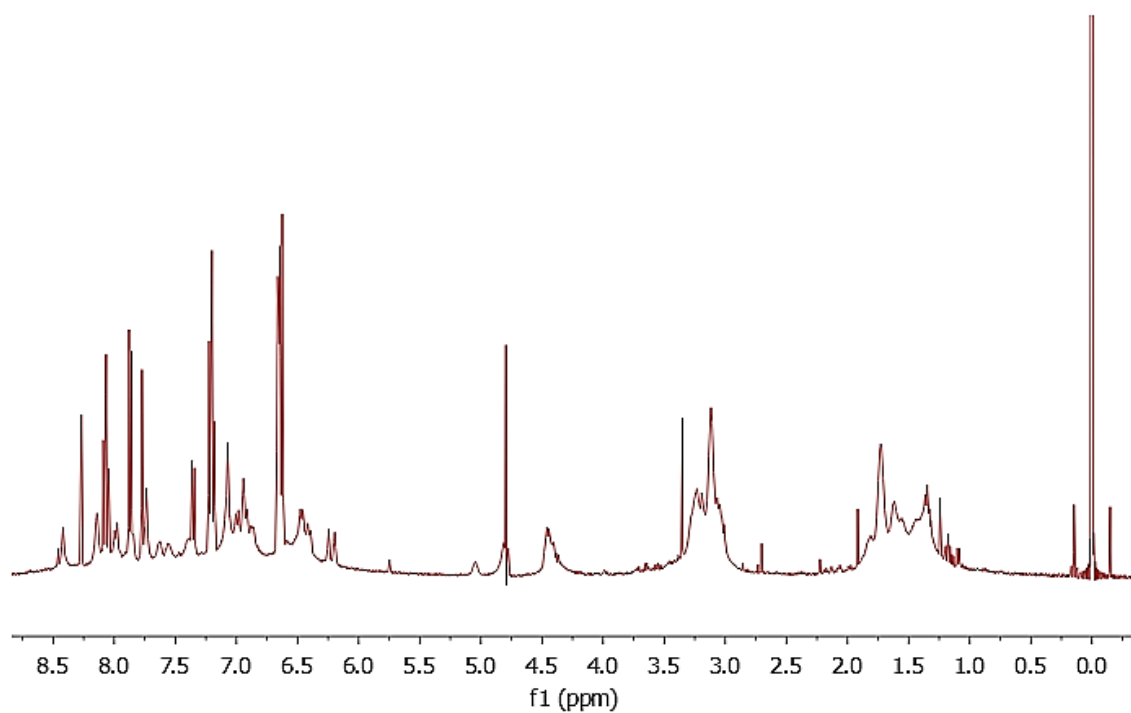
**Figure S2.45:** HMBC NMR spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH) in D<sub>2</sub>O (pH 7.4).



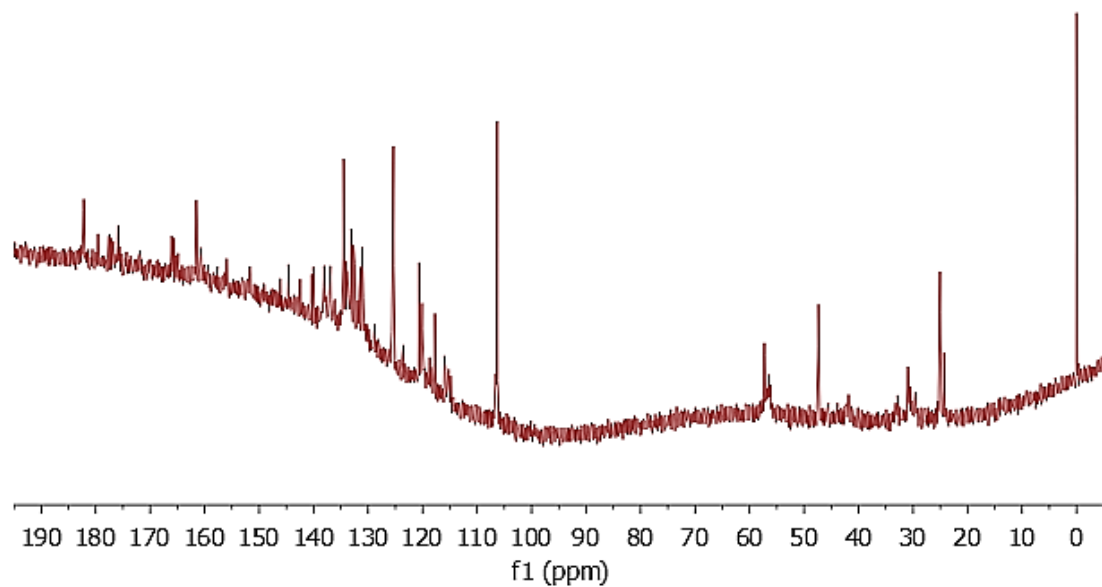
**Figure S2.46:** ESI mass spectrum of Fluo-His-Nle-His-NH<sub>2</sub> (FluoHJH).



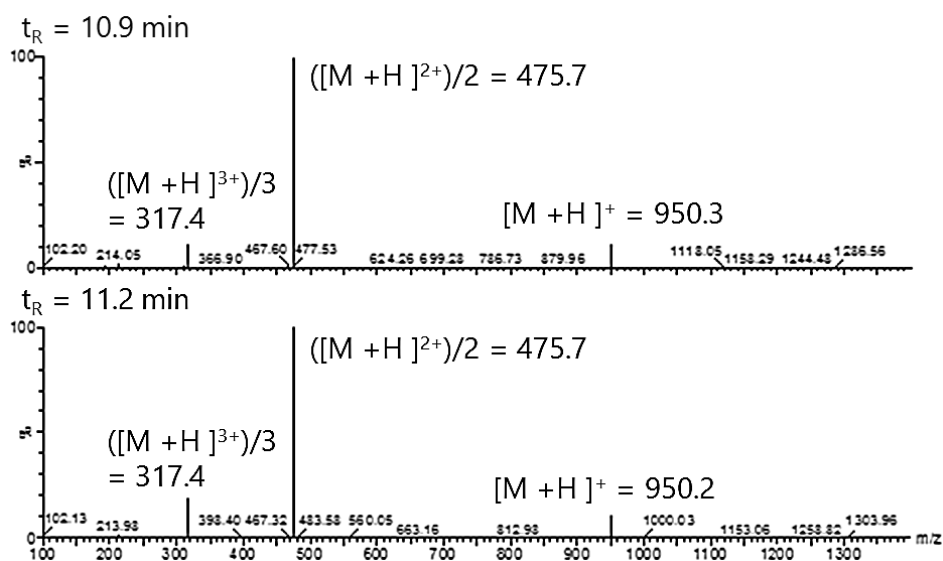
***Fluo-His-Lys(Coum)-His-NH<sub>2</sub> (FluoHK<sup>c</sup>H)***



**Figure S2.47:** <sup>1</sup>H NMR spectrum of Fluo-His-Lys(Coum)-His-NH<sub>2</sub> (FluoHK<sup>c</sup>H) in D<sub>2</sub>O (pH 7.4).

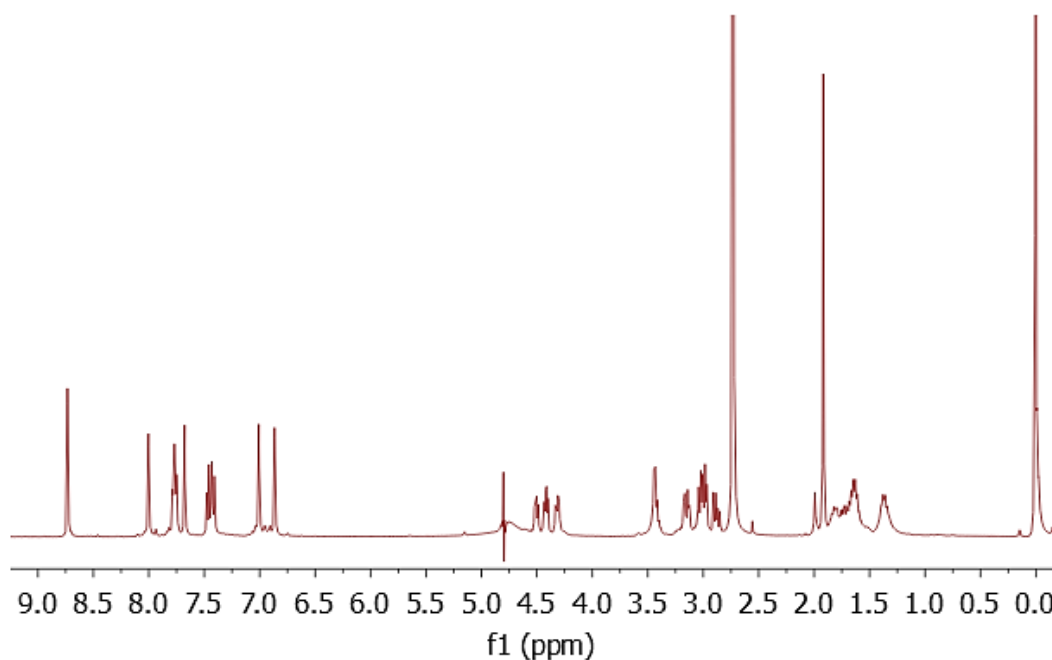


**Figure S2.48:** <sup>13</sup>C NMR spectrum of Fluo-His-Lys(Coum)-His-NH<sub>2</sub> (FluoHK<sup>c</sup>H) in D<sub>2</sub>O (pH 7.4).

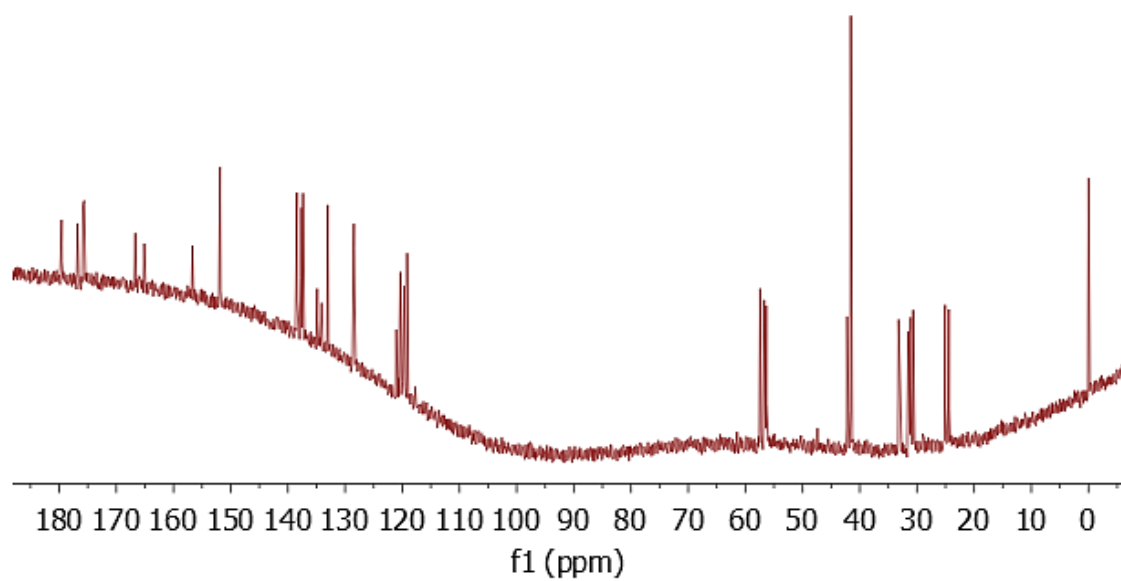


**Figure S2.49:** ESI mass spectrum of Fluo-His-Lys(Coum)-His-NH<sub>2</sub> (FluoHK<sup>c</sup>H).

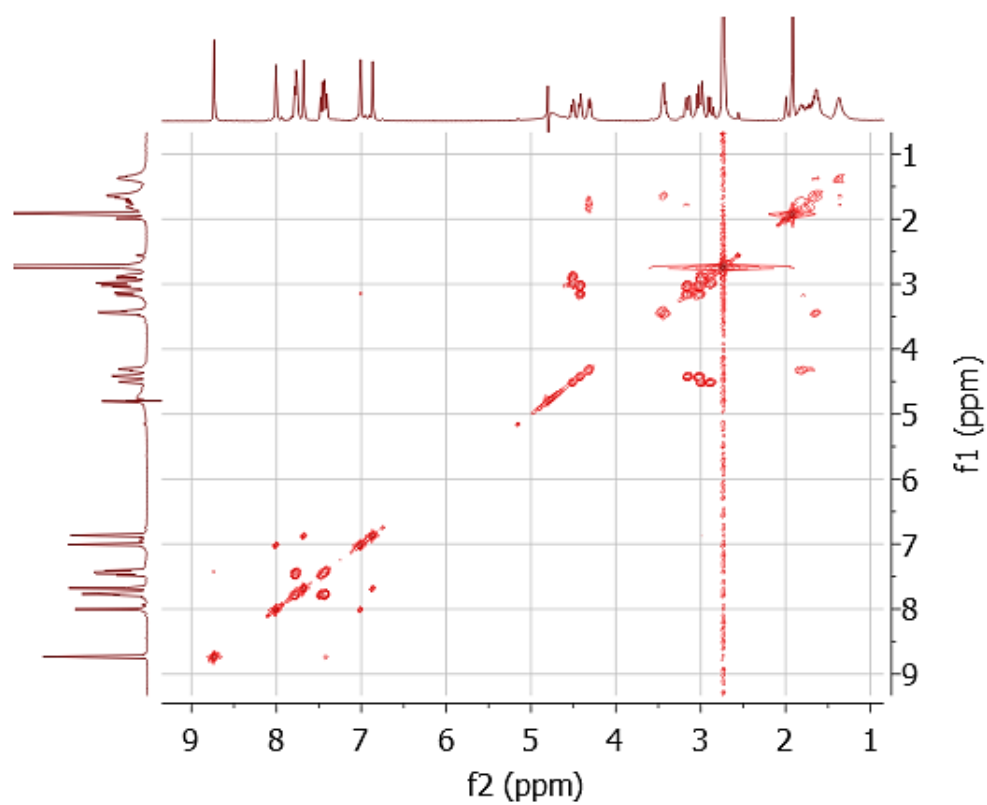
***Ac-His-Lys(Coum)-His-OH (AcHK<sup>c</sup>H)***



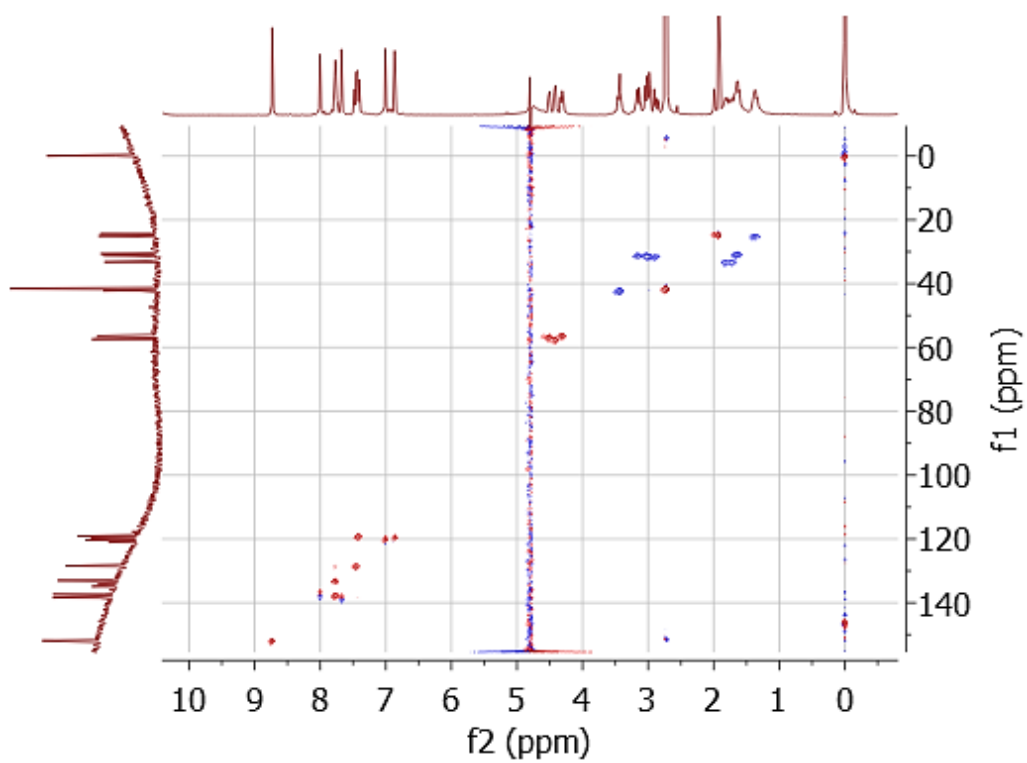
**Figure S2.50:** <sup>1</sup>H NMR spectrum of Ac-His-Lys(Coum)-His-OH (AcHK<sup>c</sup>H) in D<sub>2</sub>O (pH 7.4).



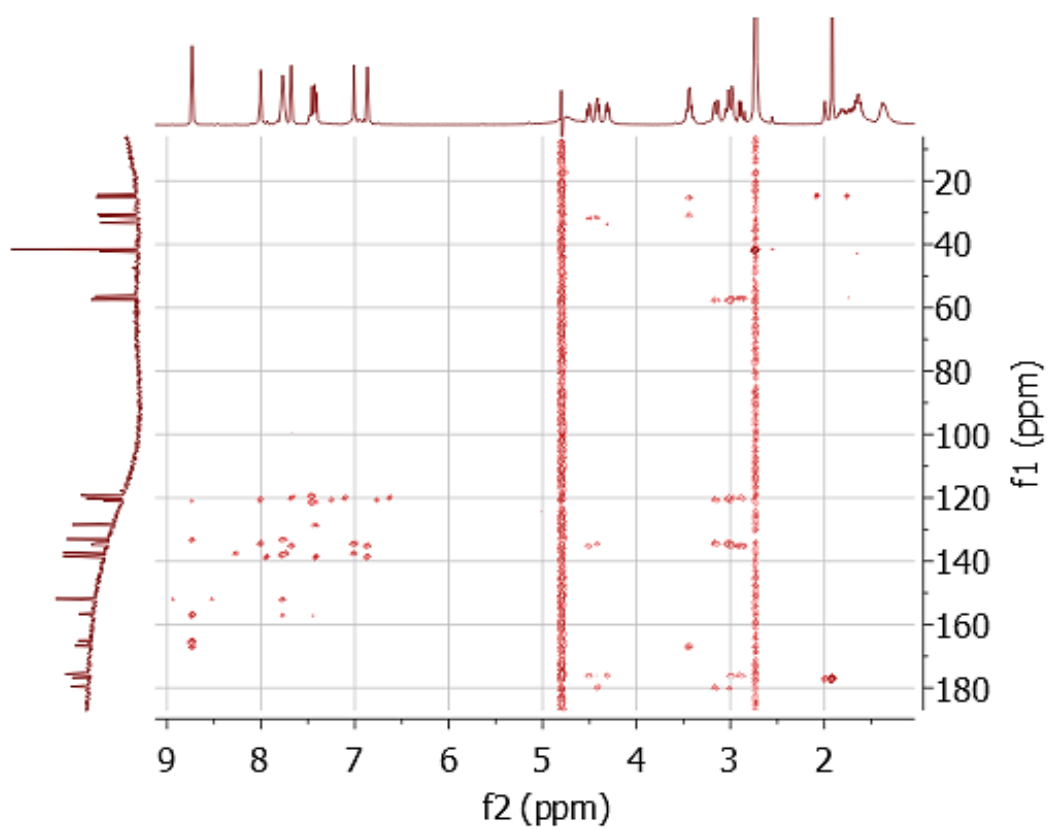
**Figure S2.51:**  $^{13}\text{C}$  NMR spectrum of Ac-His-Lys(Coum)-His-OH ( $\text{AcHK}^{\text{C}^{\text{H}}}$ ) in  $\text{D}_2\text{O}$  (pH 7.4).



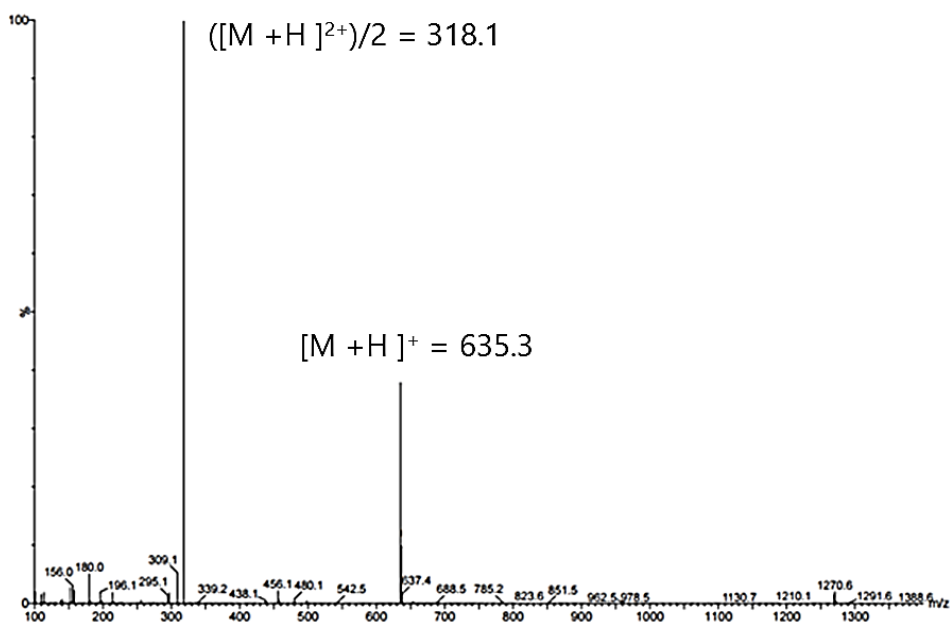
**Figure S2.52:** COSY NMR spectrum of Ac-His-Lys(Coum)-His-OH ( $\text{AcHK}^{\text{C}^{\text{H}}}$ ) in  $\text{D}_2\text{O}$  (pH 7.4).



**Figure S2.53:** HSQC NMR spectrum of Ac-His-Lys(Coum)-His-OH (AcHK<sup>H</sup>) in D<sub>2</sub>O (pH 7.4).

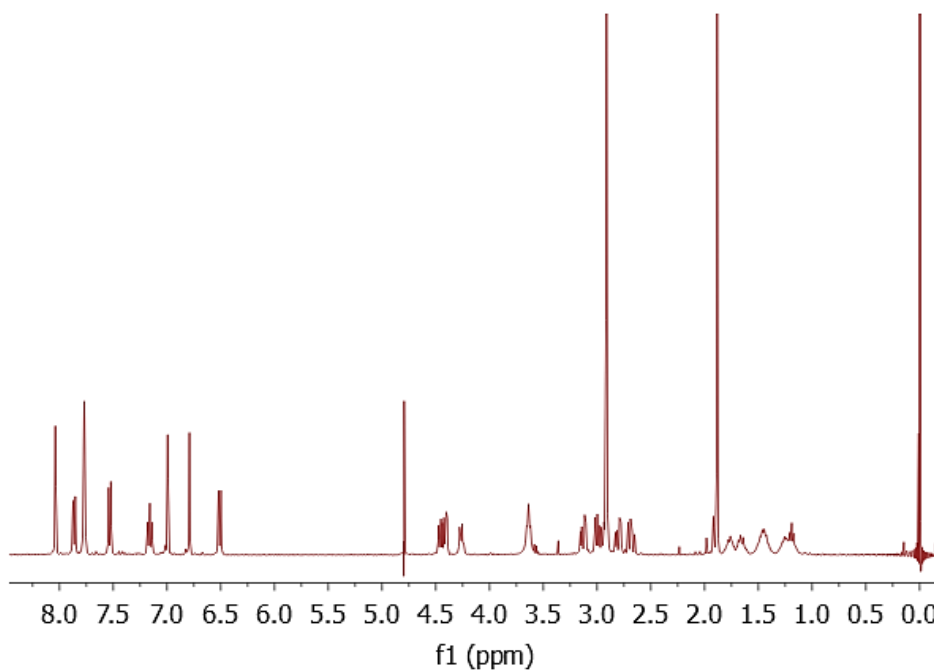


**Figure S2.54:** HMBC NMR spectrum of Ac-His-Lys(Coum)-His-OH (AcHK<sup>H</sup>) in D<sub>2</sub>O (pH 7.4).

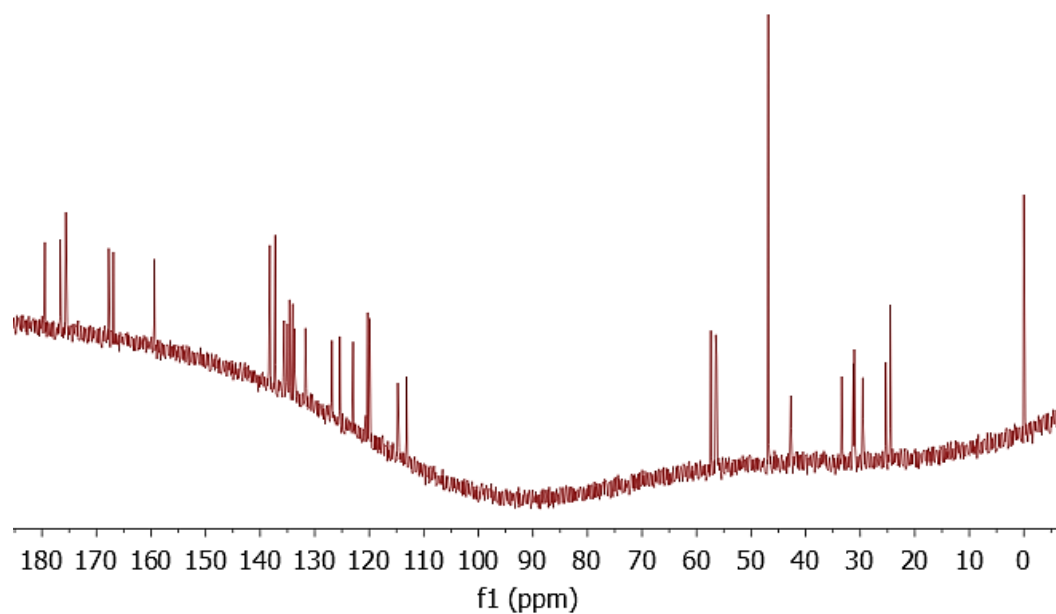


**Figure S2.55:** ESI mass spectrum of Ac-His-Lys(Coum)-His-OH (AcHK<sup>c</sup>H).

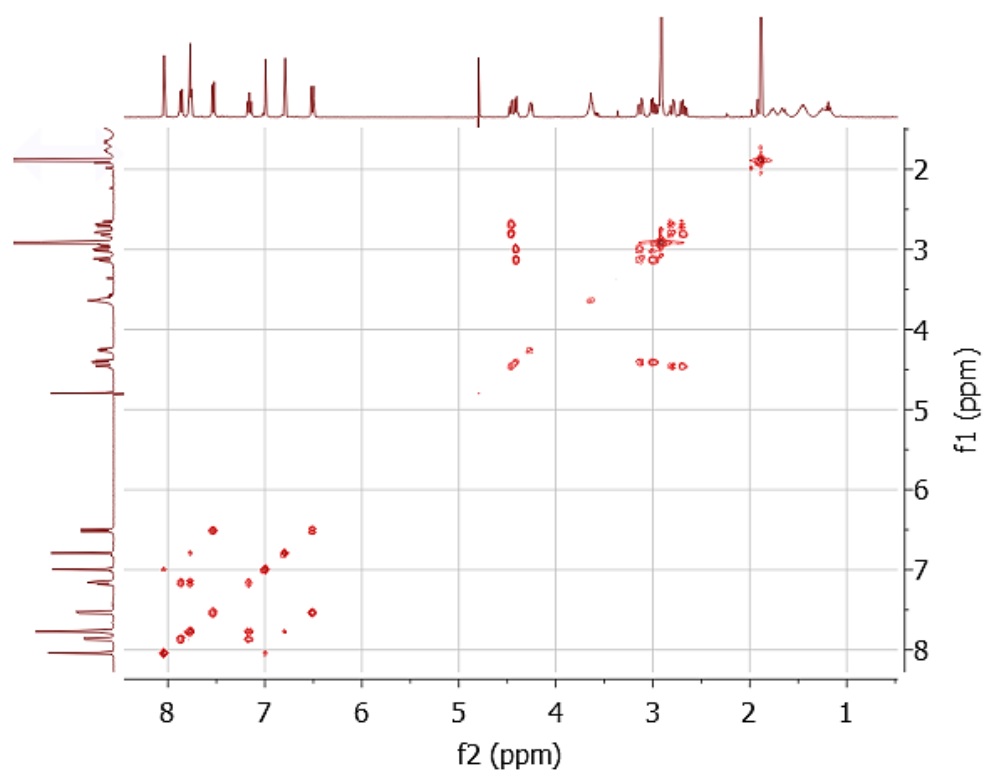
***Ac-His-Lys(4DMN)-His-OH (AcHK<sup>d</sup>H)***



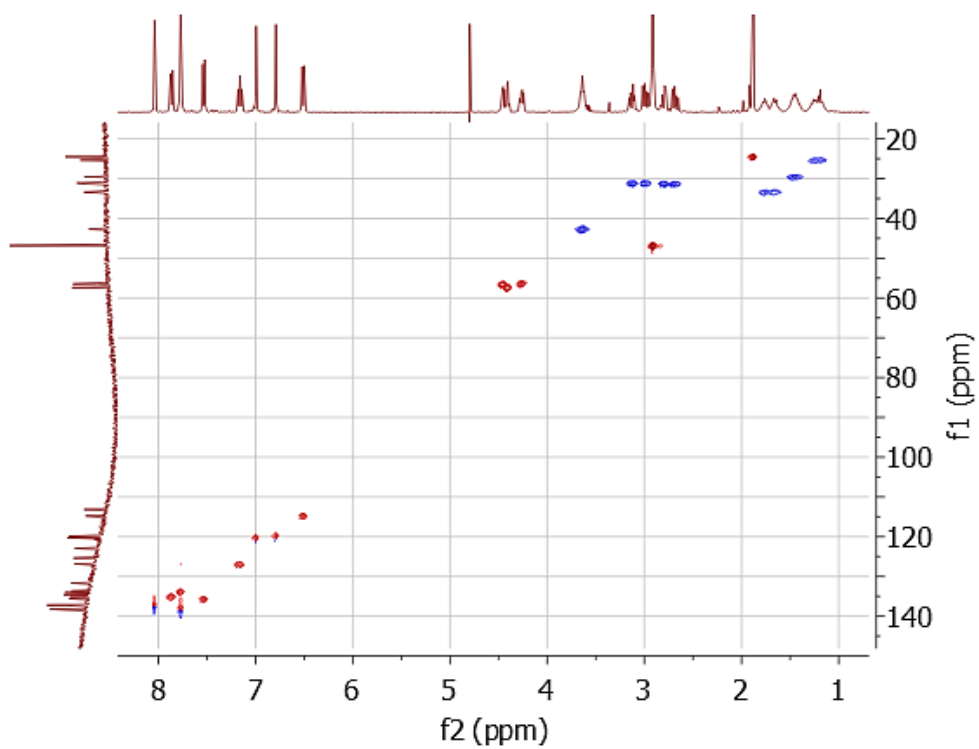
**Figure S2.56:** <sup>1</sup>H NMR spectrum of Ac-His-Lys(4DMN)-His-OH (AcHK<sup>d</sup>H) in D<sub>2</sub>O (pH 7.4).



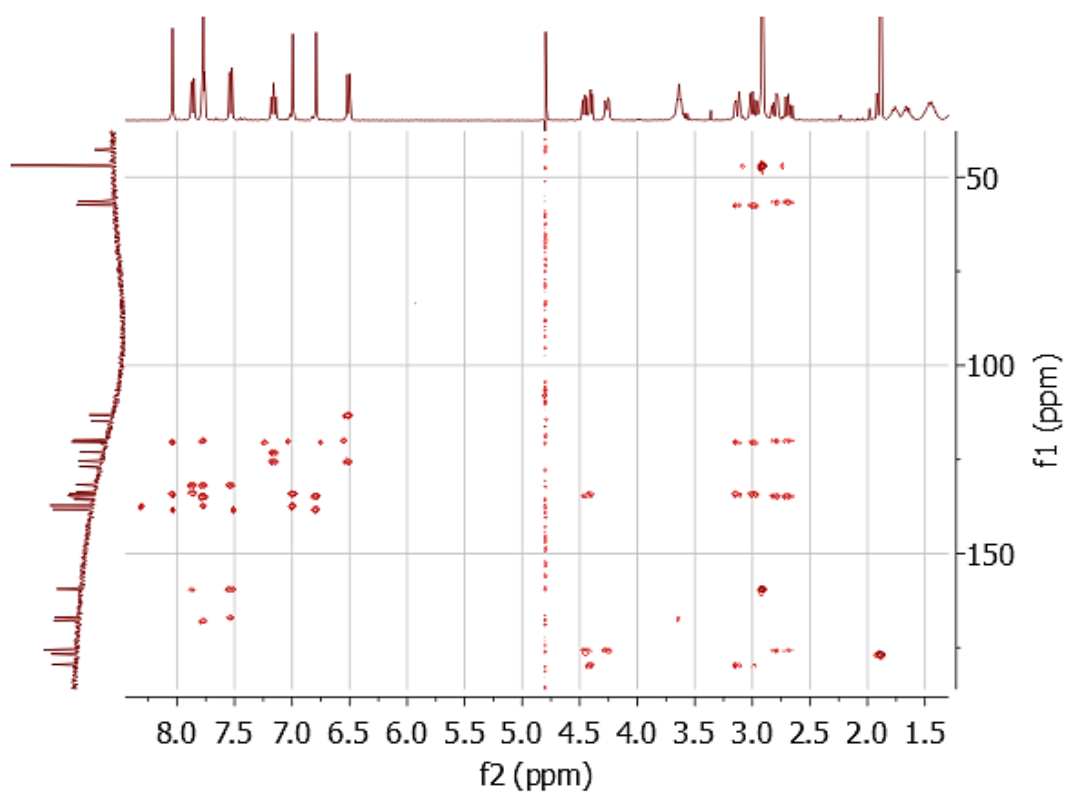
**Figure S2.57:**  $^{13}\text{C}$  NMR spectrum of Ac-His-Lys(4DMN)-His-OH (ACHK<sup>d</sup>H) in D<sub>2</sub>O (pH 7.4).



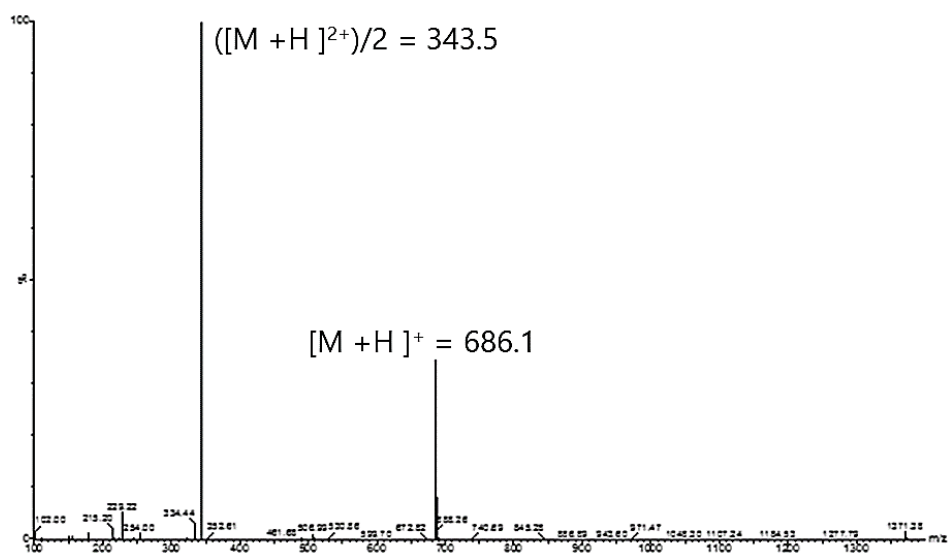
**Figure S2.58:** COSY NMR spectrum of Ac-His-Lys(4DMN)-His-OH (ACHK<sup>d</sup>H) in D<sub>2</sub>O (pH 7.4).



**Figure S2.59:** HSQC NMR spectrum of Ac-His-Lys(4DMN)-His-OH (AChK<sup>d</sup>H) in D<sub>2</sub>O (pH 7.4).

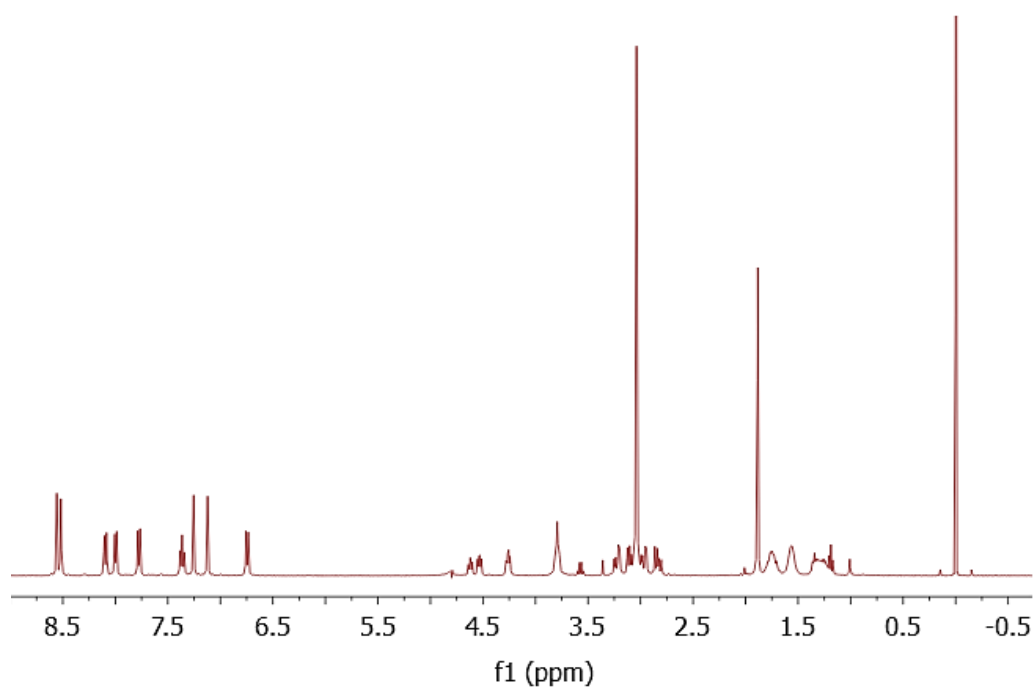


**Figure S2.60:** HMBC NMR spectrum of Ac-His-Lys(4DMN)-His-OH (AChK<sup>d</sup>H) in D<sub>2</sub>O (pH 7.4).



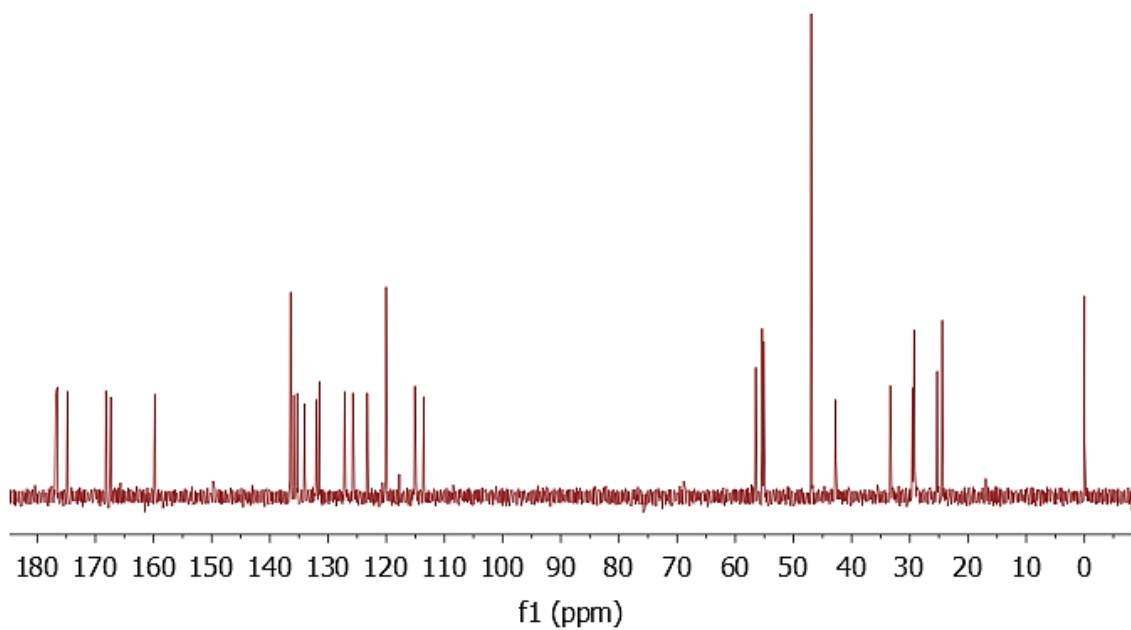
**Figure S2.61:** ESI mass spectrum of Ac-His-Lys(4DMN)-His-OH (AcHK<sup>d</sup>H).

***Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (AcHK<sup>d</sup>H-NH<sub>2</sub>)***

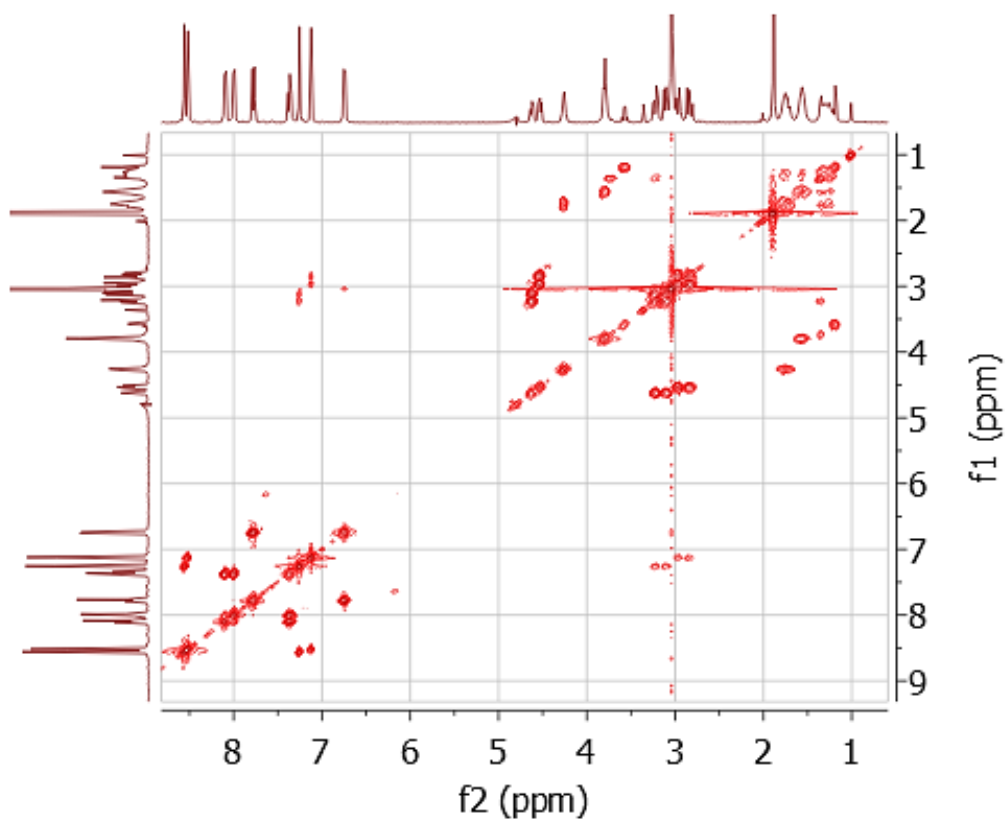


**Figure S2.62:** <sup>1</sup>H NMR spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (AcHK<sup>d</sup>H-NH<sub>2</sub>) in D<sub>2</sub>O (pH 4.5).

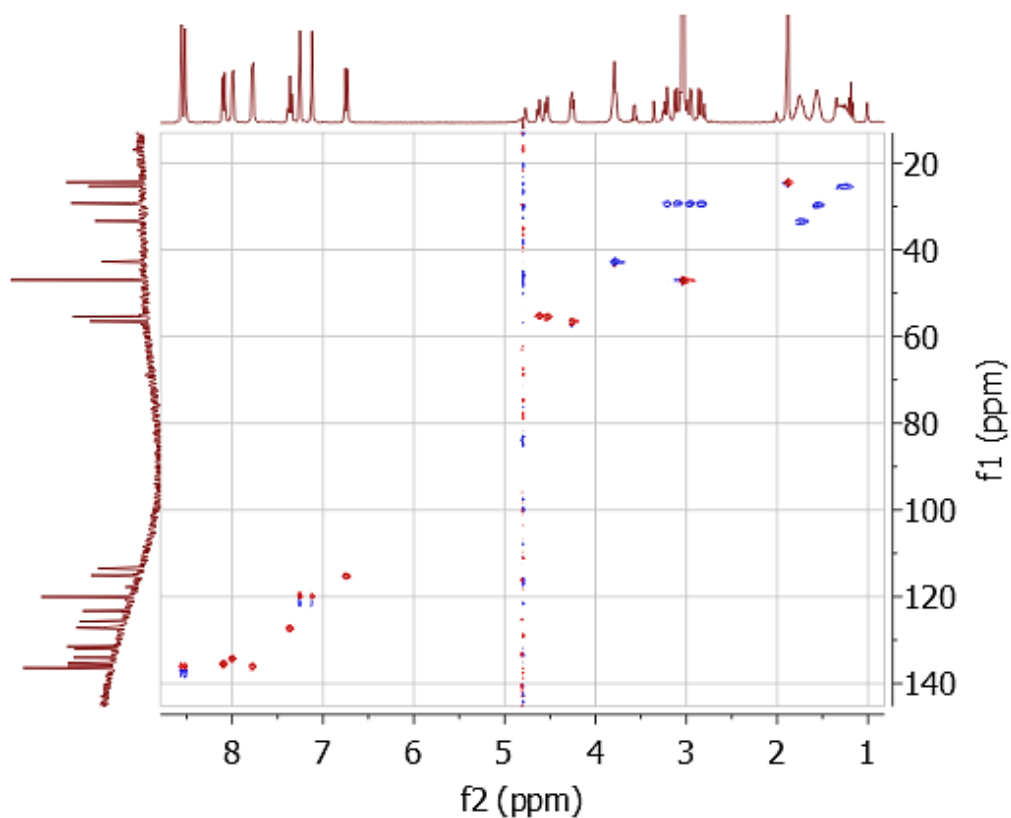




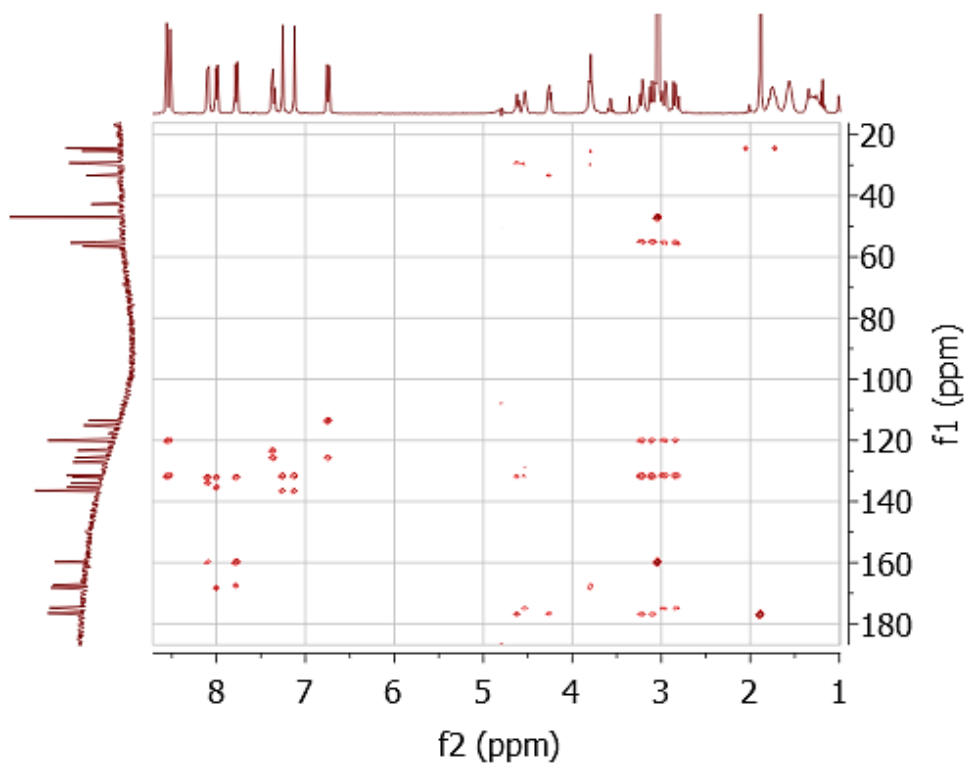
**Figure S2.63:**  $^{13}\text{C}$  NMR spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (ACHK<sup>d</sup>H-NH<sub>2</sub>) in D<sub>2</sub>O (pH 4.5).



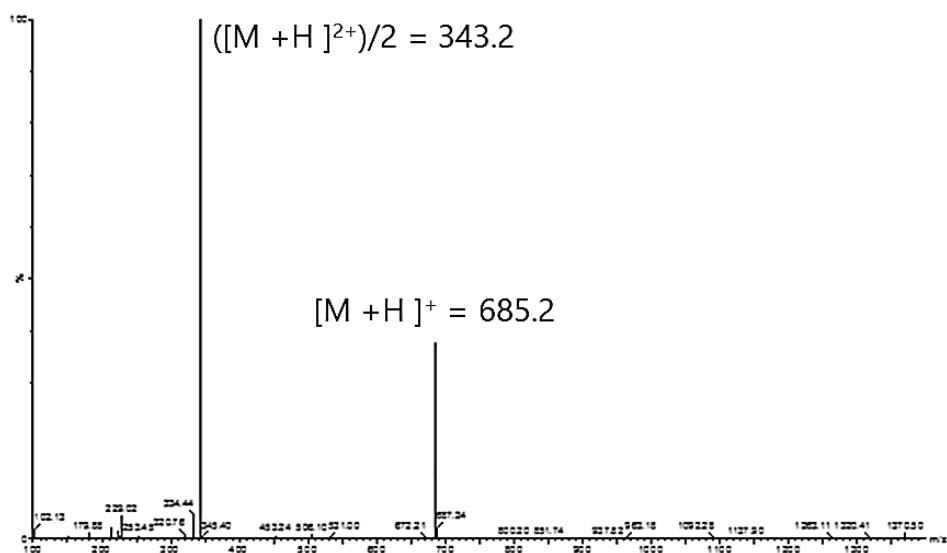
**Figure S2.64:** COSY NMR spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (ACHK<sup>d</sup>H-NH<sub>2</sub>) in D<sub>2</sub>O (pH 4.5).



**Figure S2.65:** HSQC NMR spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (A<sub>2</sub>CHK<sup>d</sup>H-NH<sub>2</sub>) in D<sub>2</sub>O (pH 4.5).

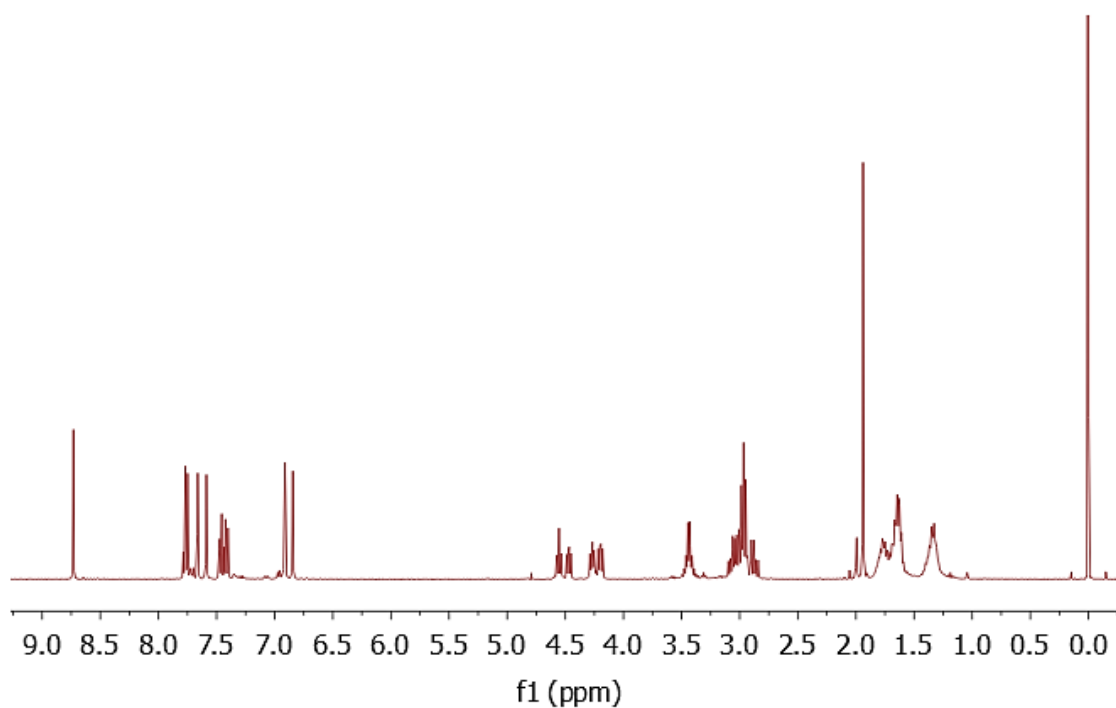


**Figure S2.66:** HMBC NMR spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (A<sub>2</sub>CHK<sup>d</sup>H-NH<sub>2</sub>) in D<sub>2</sub>O (pH 4.5).

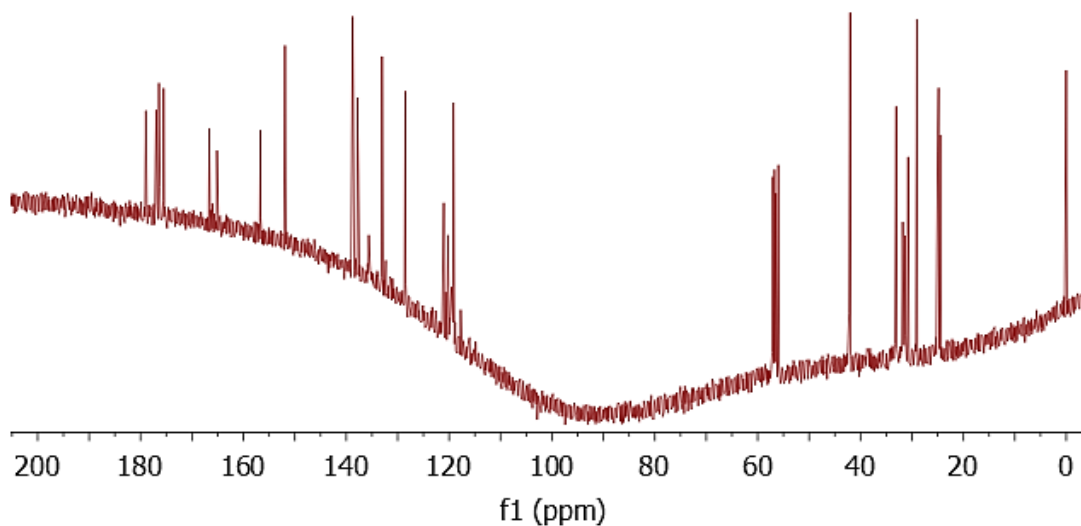


**Figure S2.67:** ESI mass spectrum of Ac-His-Lys(4DMN)-His-NH<sub>2</sub> (AcHK<sup>d</sup>H-NH<sub>2</sub>).

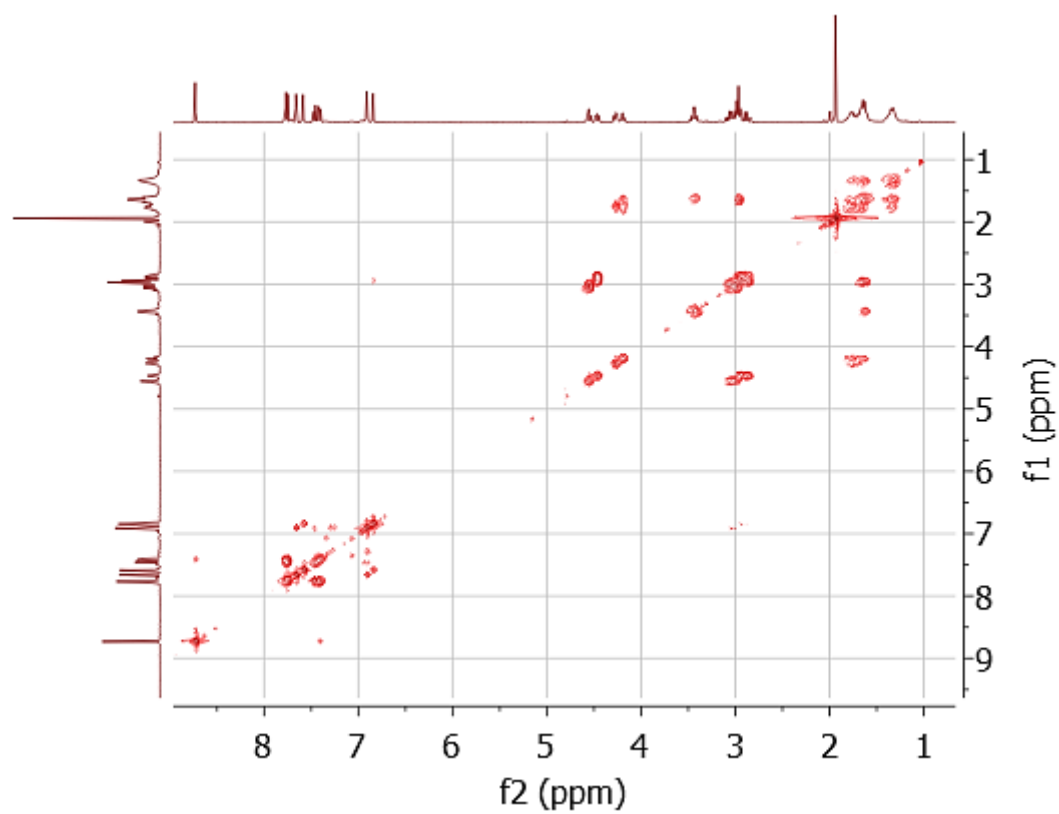
***Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (AcHK<sup>c</sup>HK)***



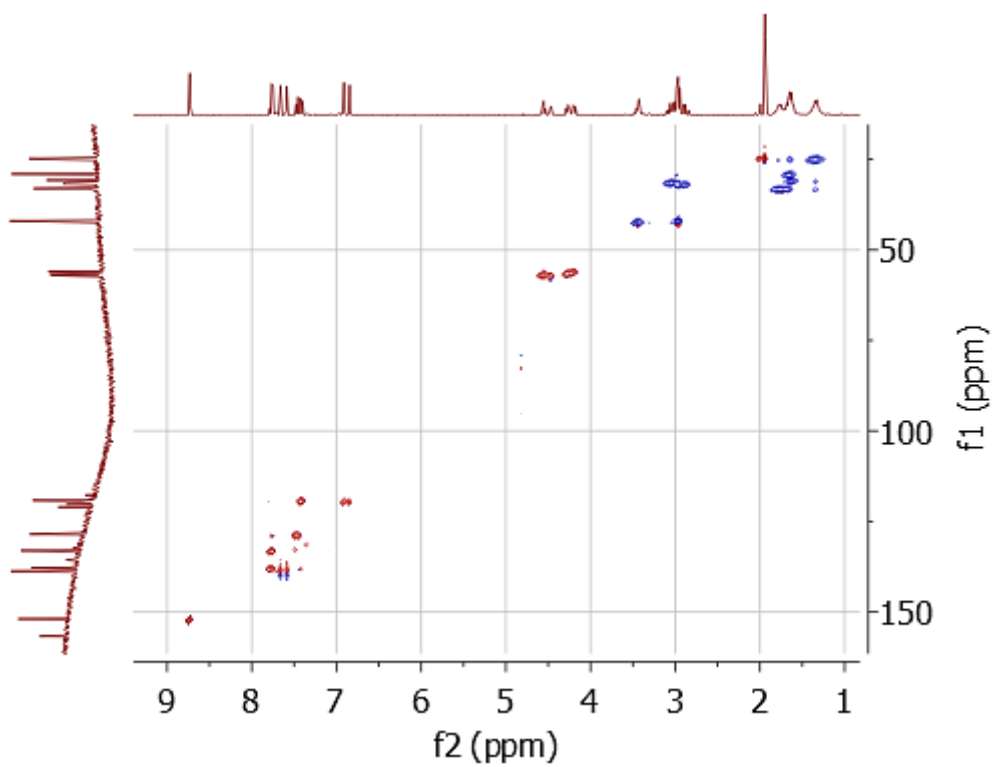
**Figure S2.68:** <sup>1</sup>H NMR spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (AcHK<sup>c</sup>HK) in D<sub>2</sub>O (pH 7.4).



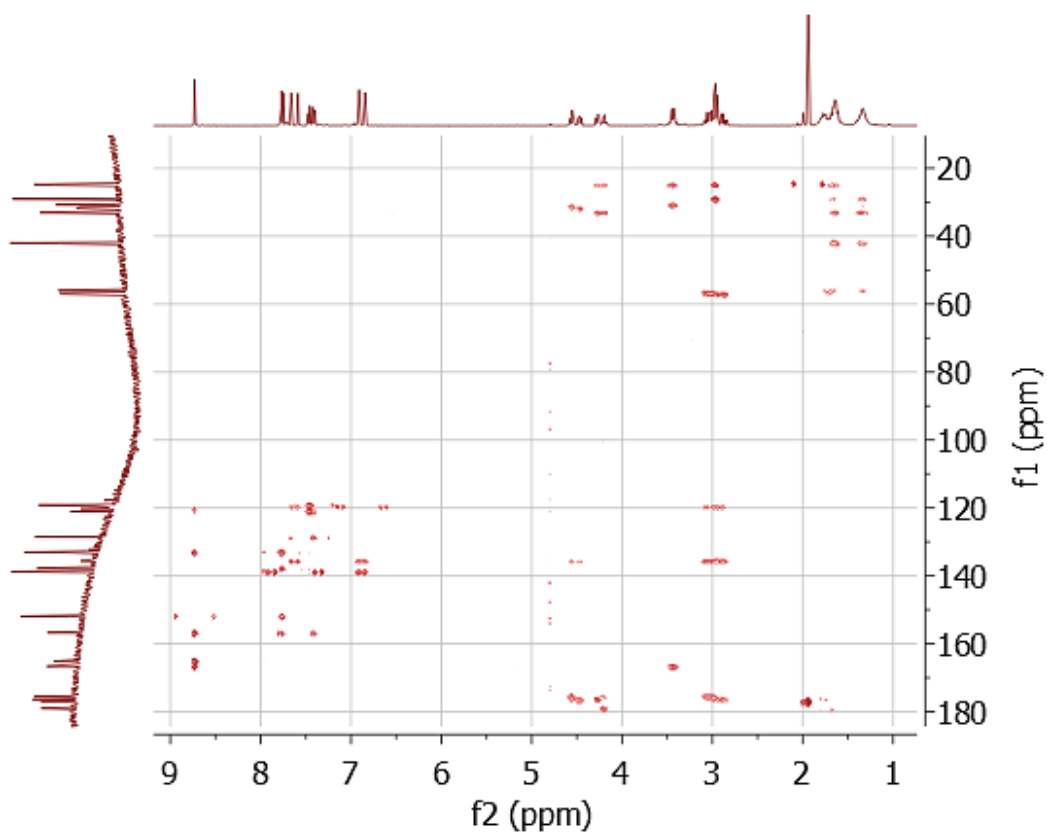
**Figure S2.69:**  $^{13}\text{C}$  NMR spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (AcHK<sup>c</sup>HK) in D<sub>2</sub>O (pH 7.4).



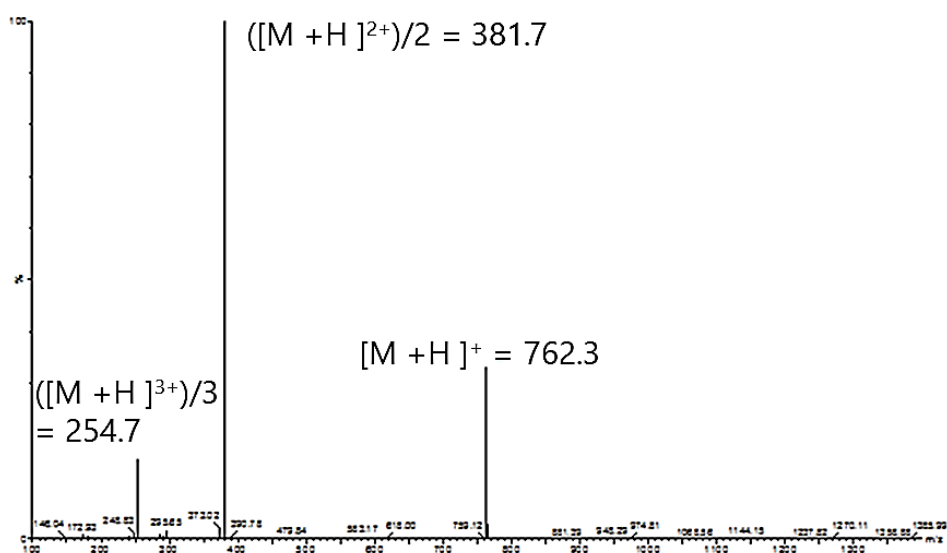
**Figure S2.70:** COSY NMR spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (AcHK<sup>c</sup>HK) in D<sub>2</sub>O (pH 7.4).



**Figure S2.71:** HSQC NMR spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (ACHK<sup>HK</sup>) in D<sub>2</sub>O (pH 7.4).

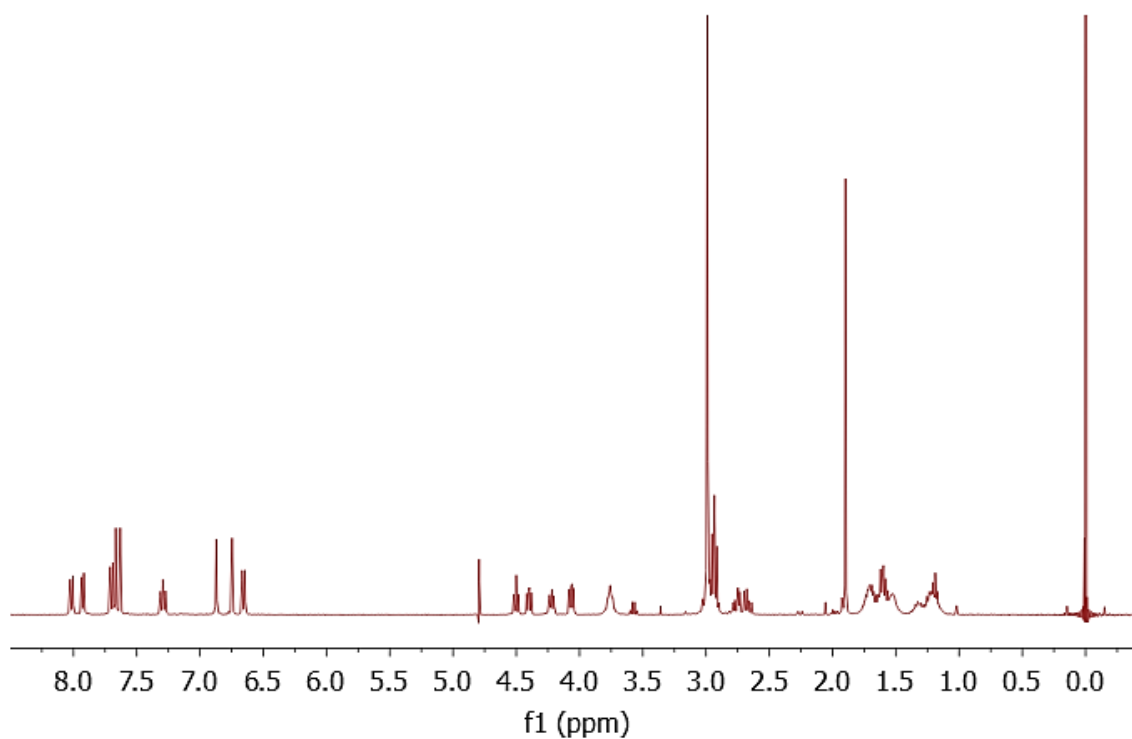


**Figure S2.72:** HMBC NMR spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (ACHK<sup>HK</sup>) in D<sub>2</sub>O (pH 7.4).

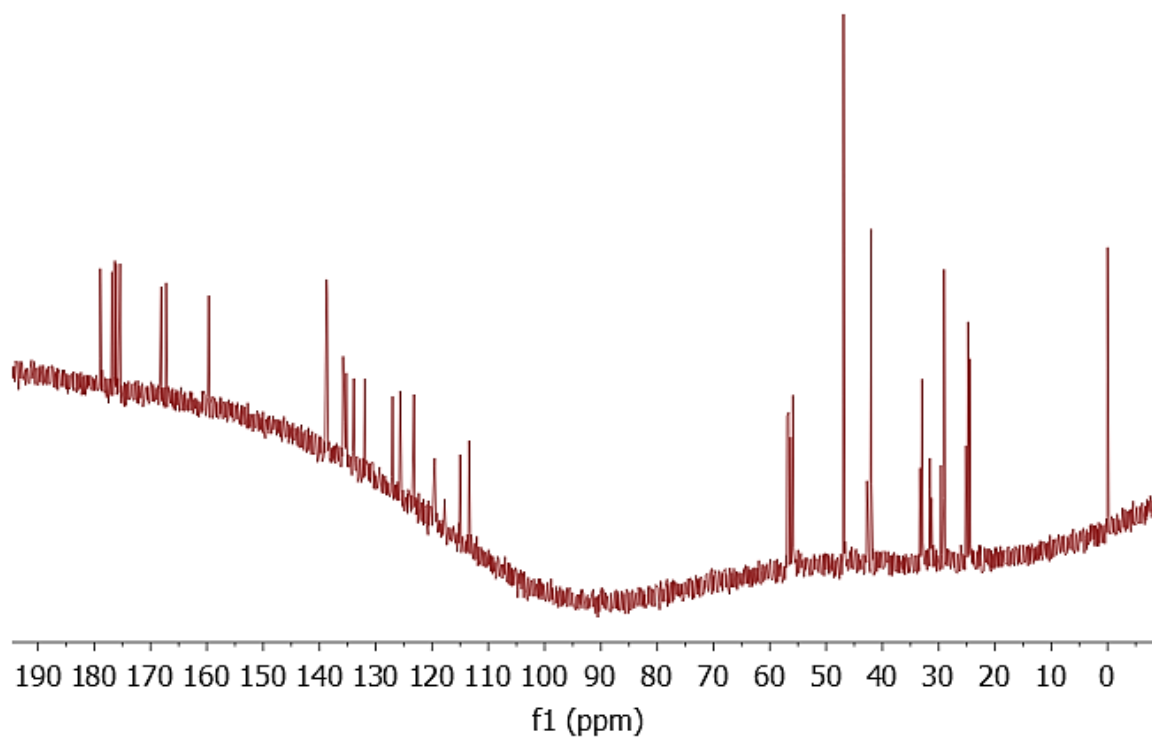


**Figure S2.73:** ESI mass spectrum of Ac-His-Lys(Coum)-His-Lys-NH<sub>2</sub> (AcHK<sup>c</sup>HK).

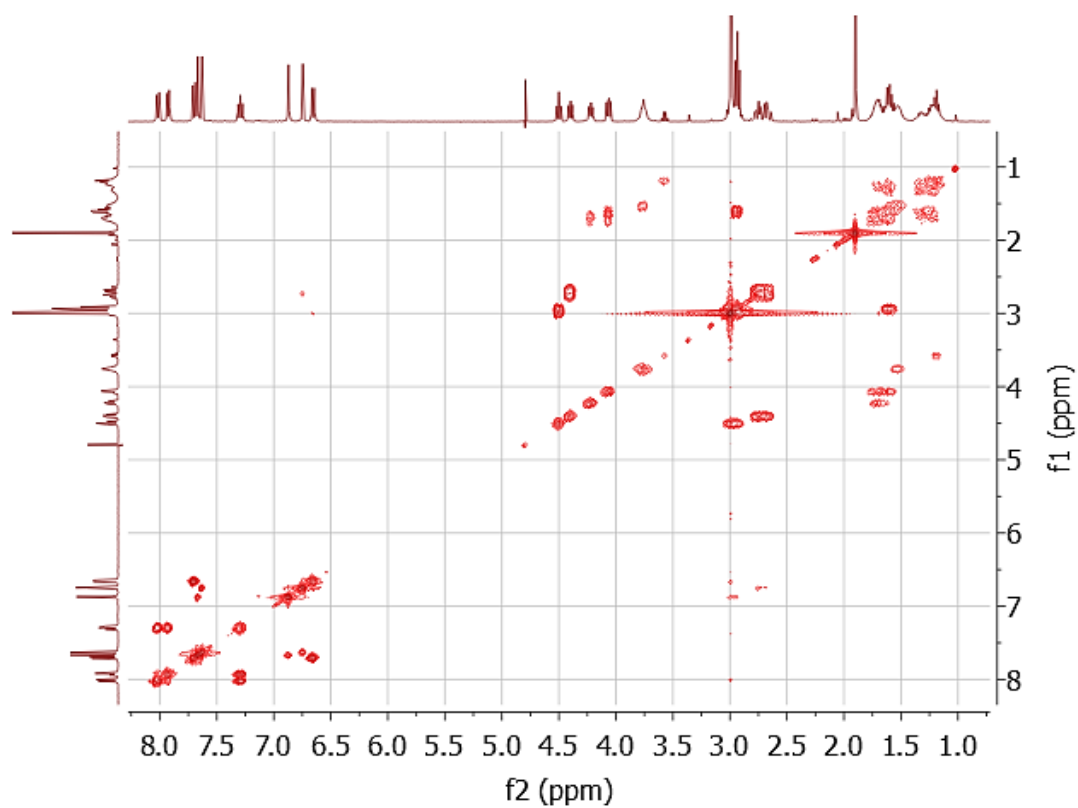
***Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (AcHK<sup>d</sup>HK)***



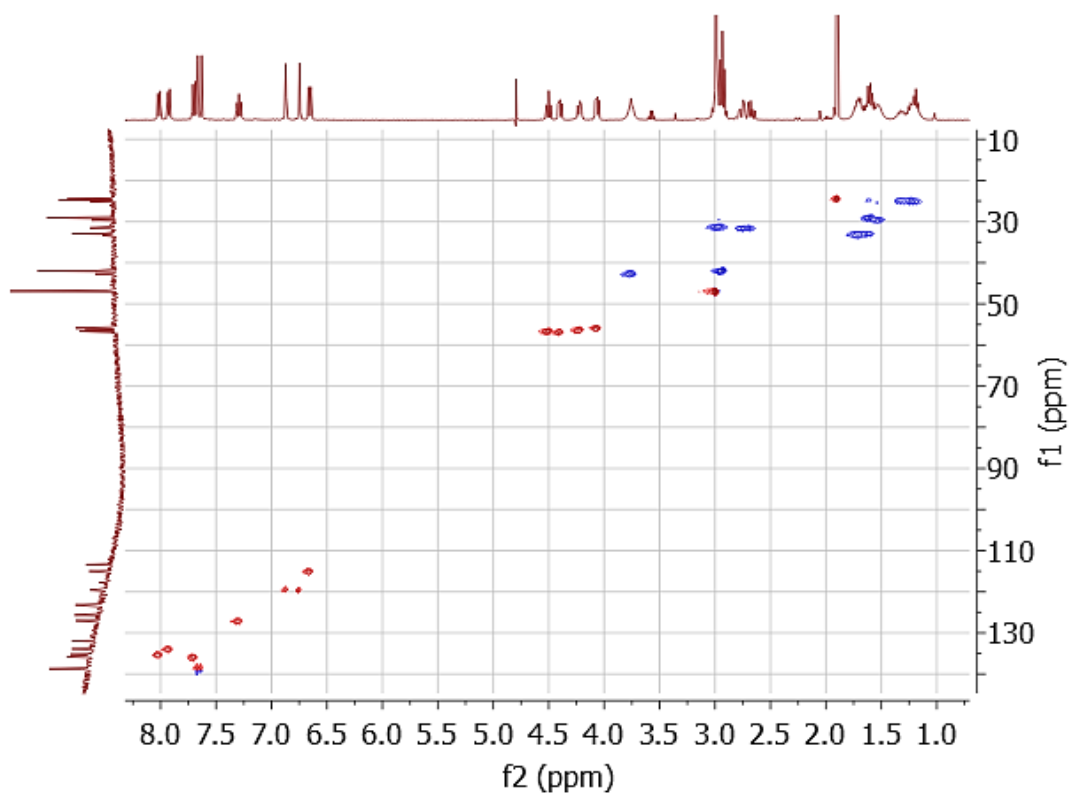
**Figure S2.74:** <sup>1</sup>H NMR spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (AcHK<sup>d</sup>HK) in D<sub>2</sub>O (pH 7.4).



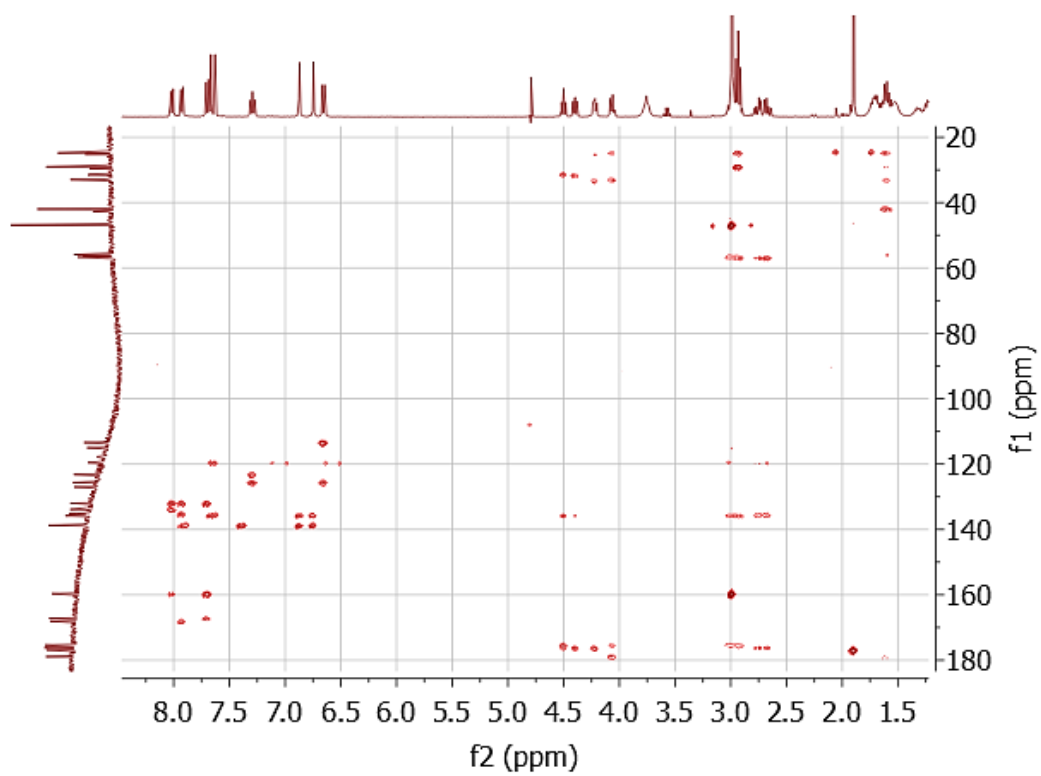
**Figure S2.75:**  $^{13}\text{C}$  NMR spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (ACHK<sup>d</sup>HK) in D<sub>2</sub>O (pH 7.4).



**Figure S2.76:** COSY NMR spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (ACHK<sup>d</sup>HK) in D<sub>2</sub>O (pH 7.4).

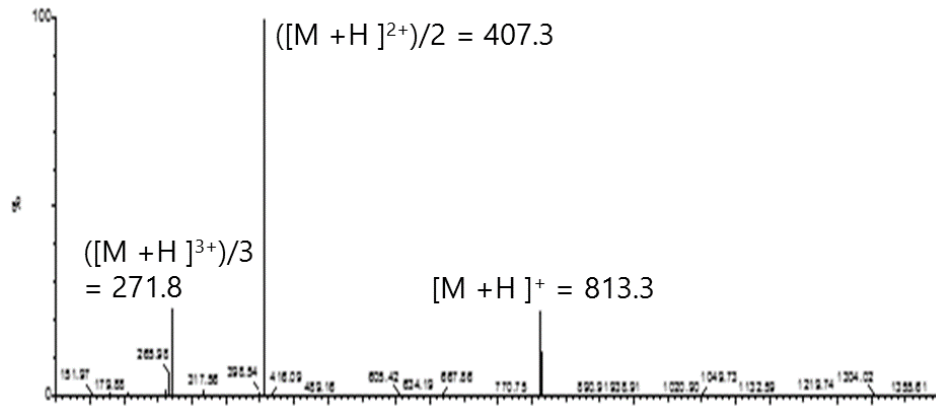


**Figure S2.77:** HSQC NMR spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (ACHK<sup>d</sup>HK) in D<sub>2</sub>O (pH 7.4).



**Figure S2.78:** HMBC NMR spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (ACHK<sup>d</sup>HK) in D<sub>2</sub>O (pH 7.4).





**Figure S2.79:** ESI mass spectrum of Ac-His-Lys(4DMN)-His-Lys-NH<sub>2</sub> (ACHK<sup>d</sup>HK).