Highly Efficient One-Pot Assemble of Peptides by Double Chemoselective Coupling

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Supporting Information

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*1. NMR spectra of compounds **1a–n***

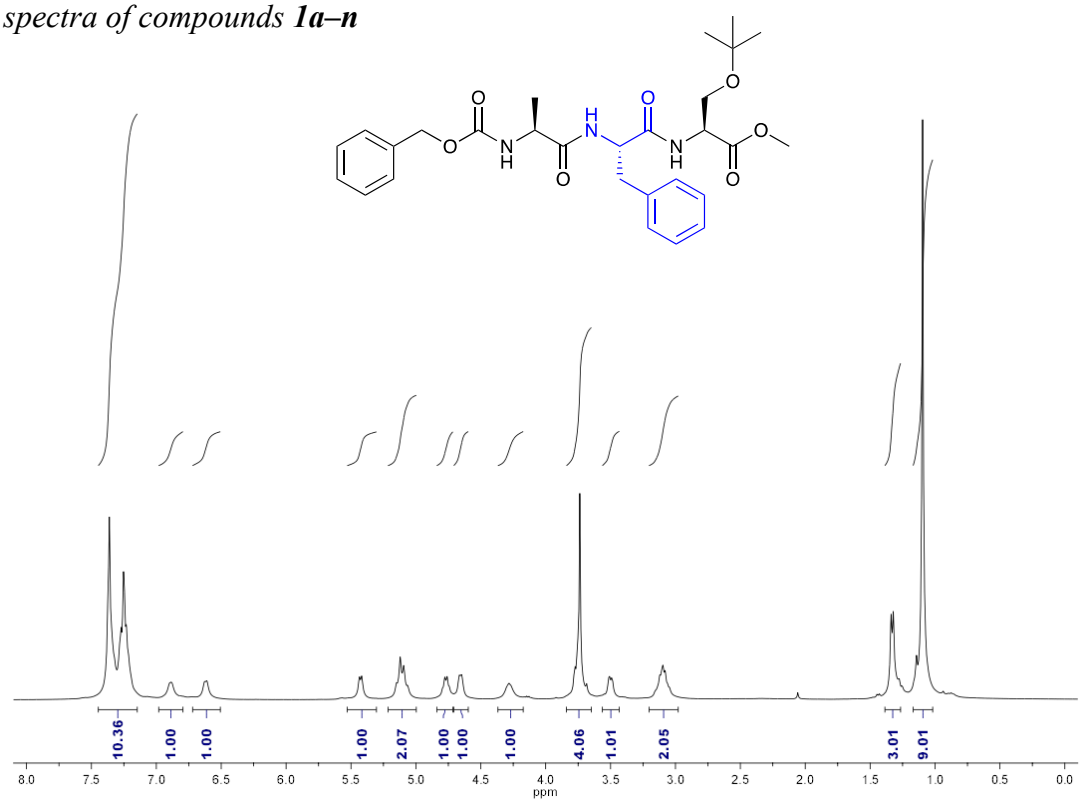

Fig. S1. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1a**.

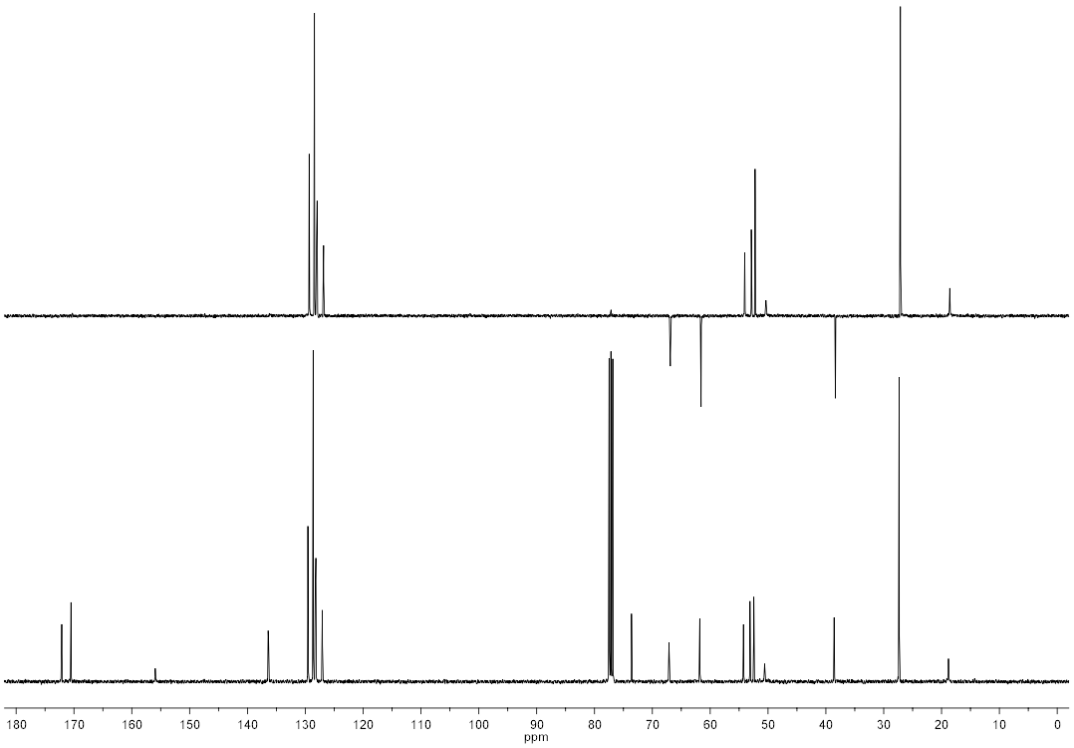

Fig. S2. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1a**.

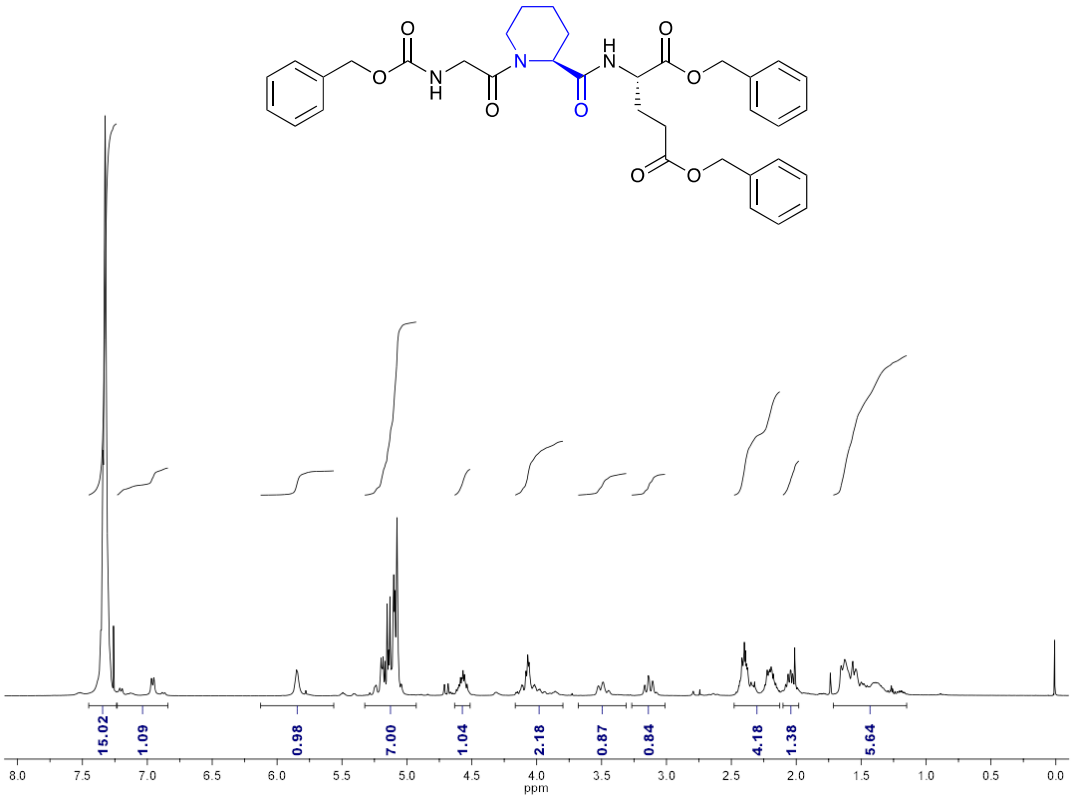

Fig. S3. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1b**.

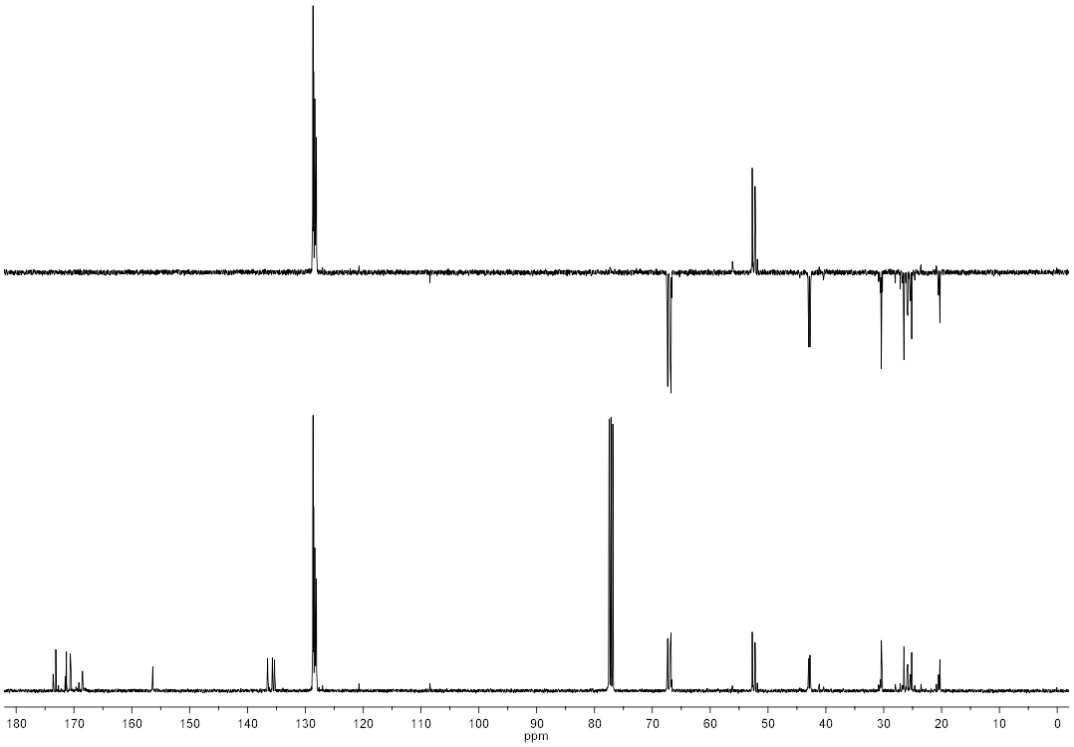

Fig. S4. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1b**.

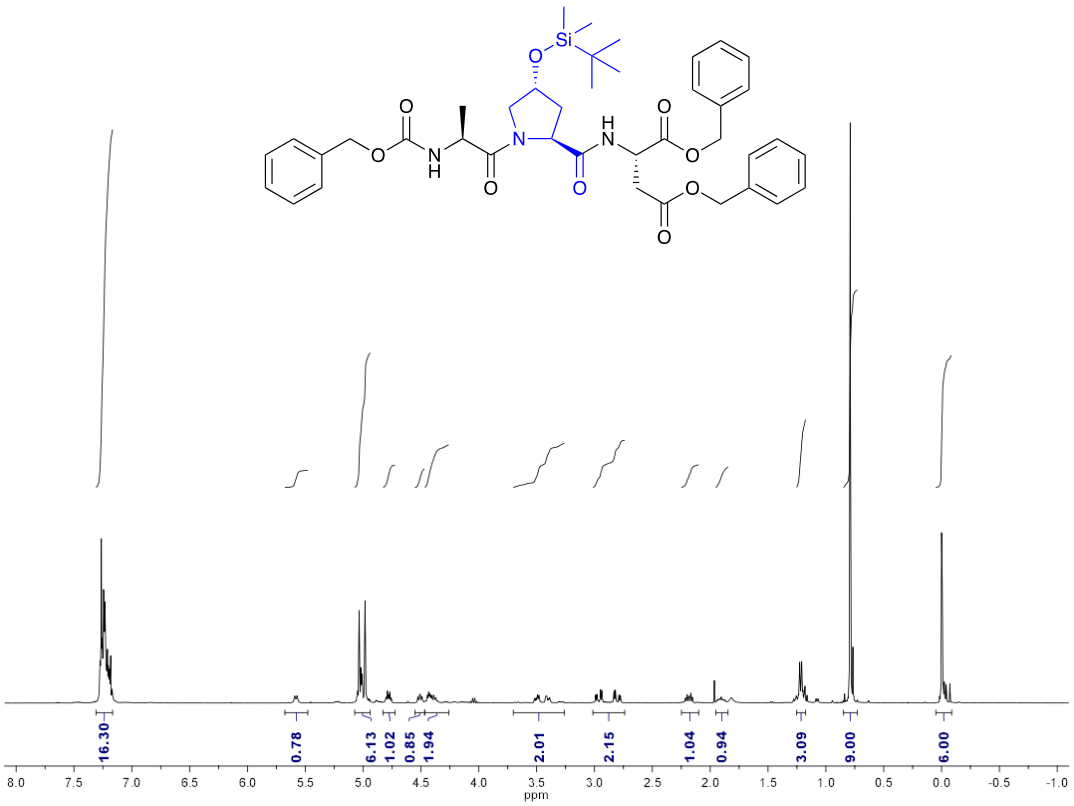

Fig. S5. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1c**.

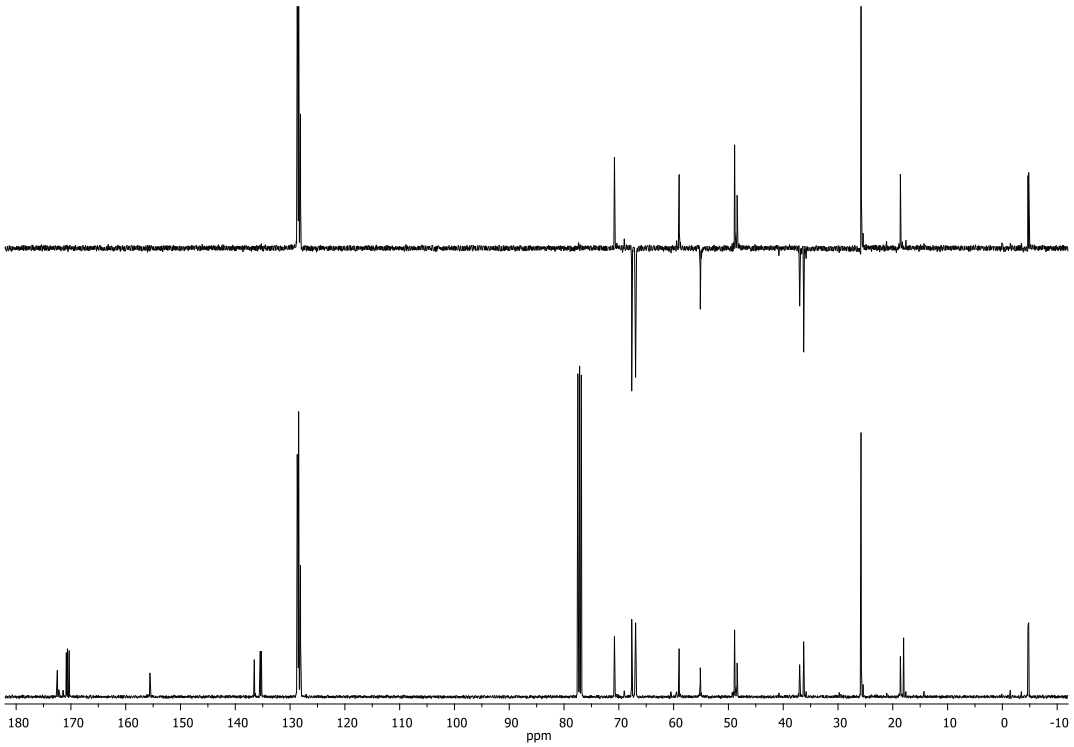

Fig. S6. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1c**.

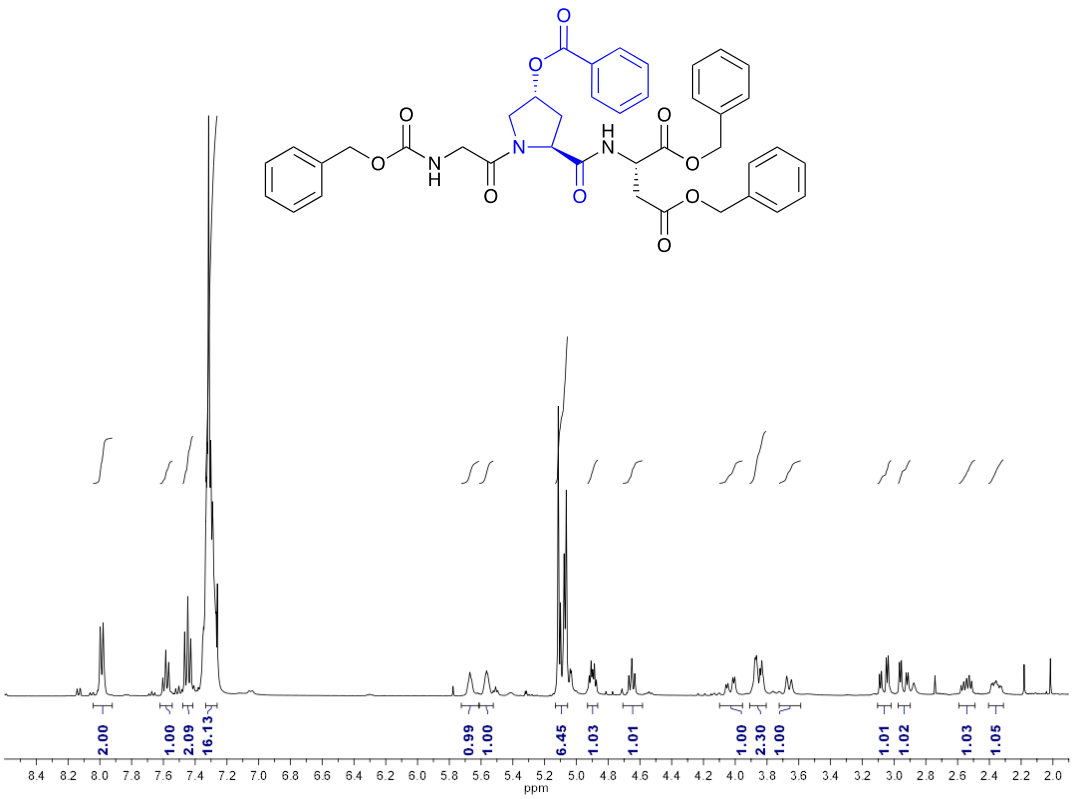

Fig. S7. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1d**.

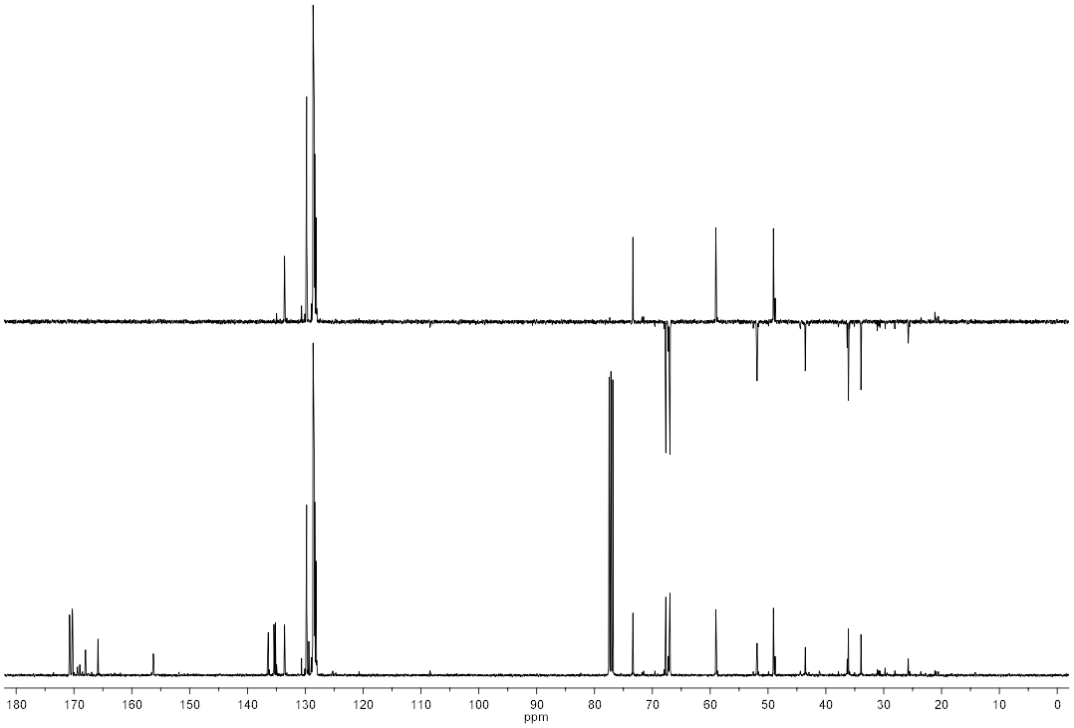

Fig. S8. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1d**.

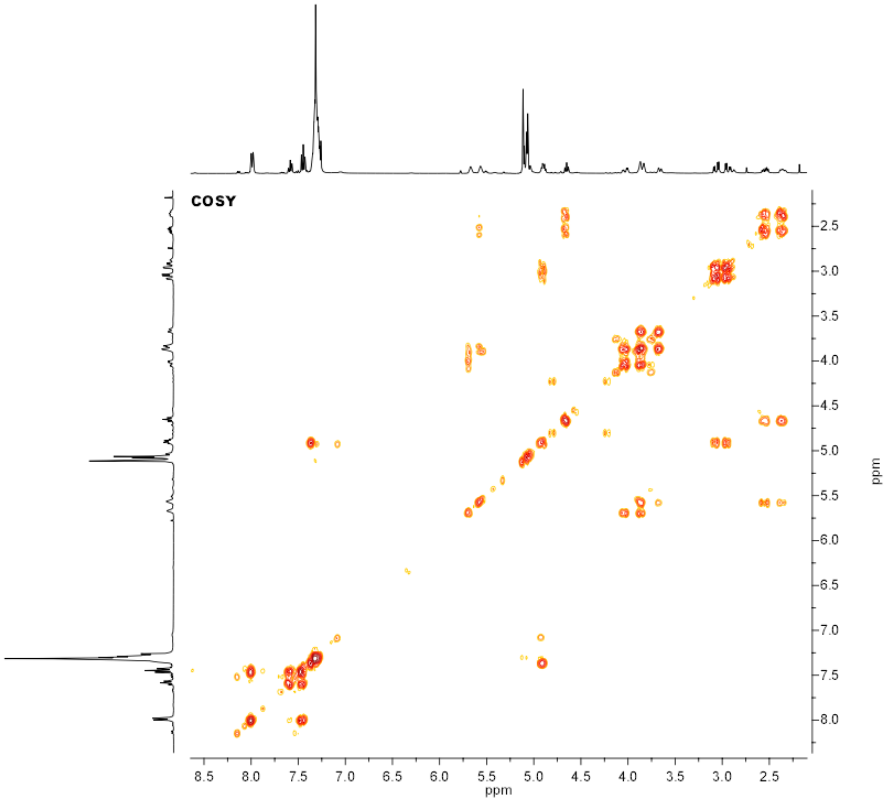

Fig. S9. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$) of compound **1d**.

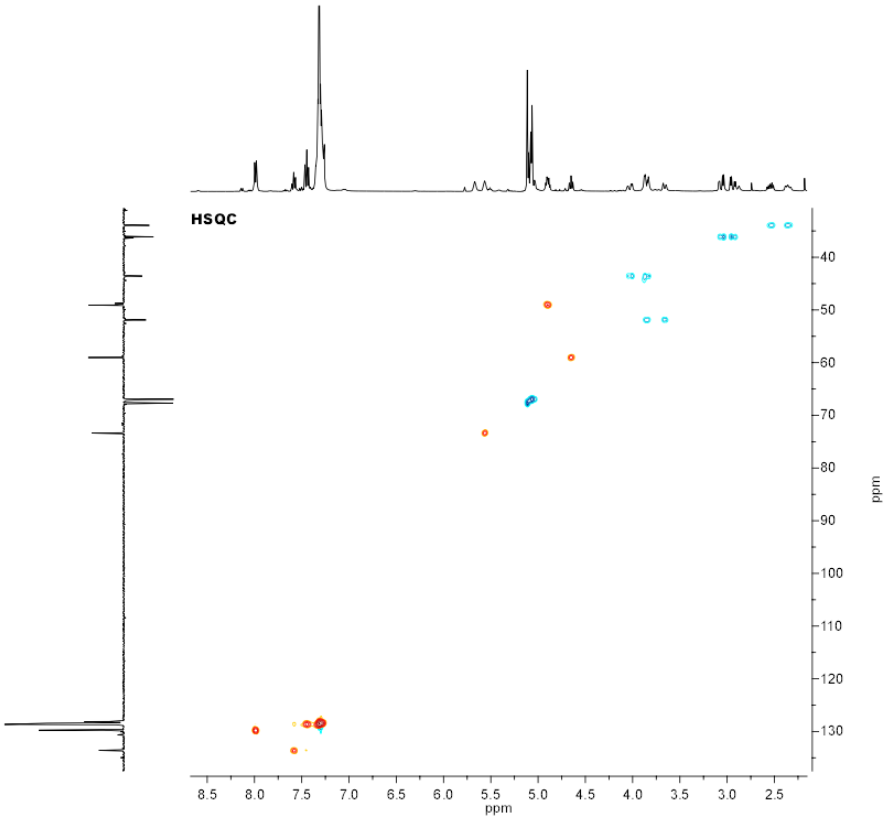

Fig. S10. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$) of compound **1d**.

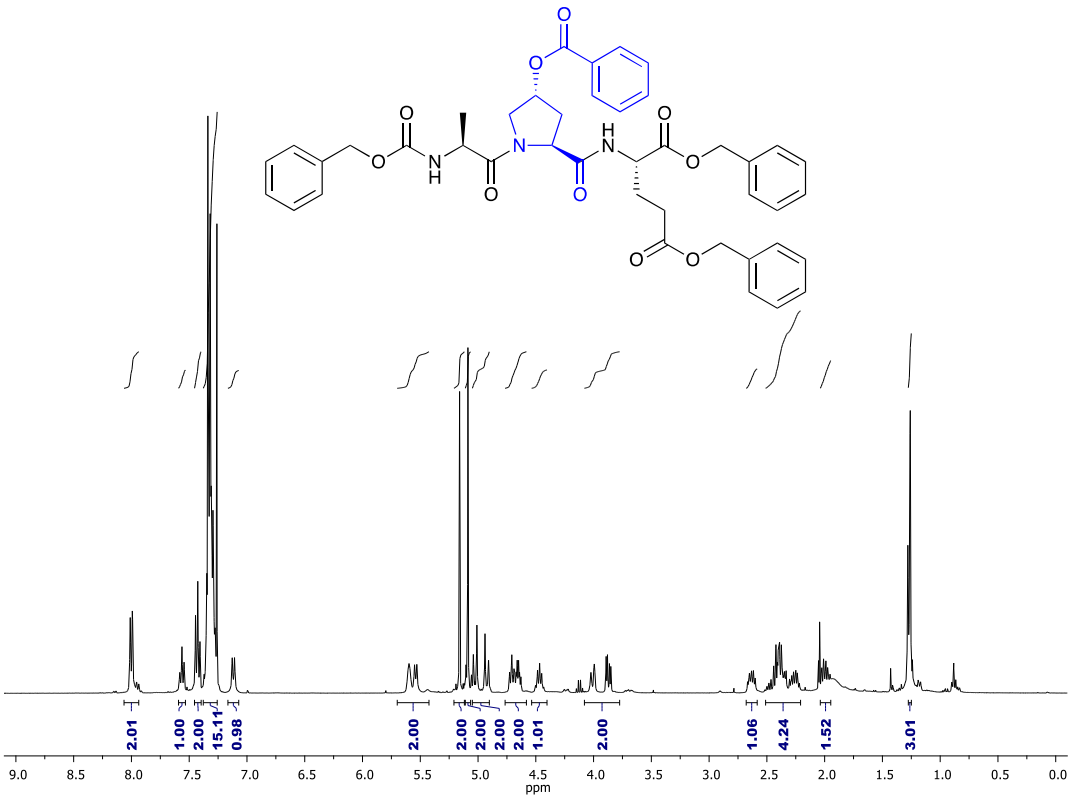

Fig. S11. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1e**.

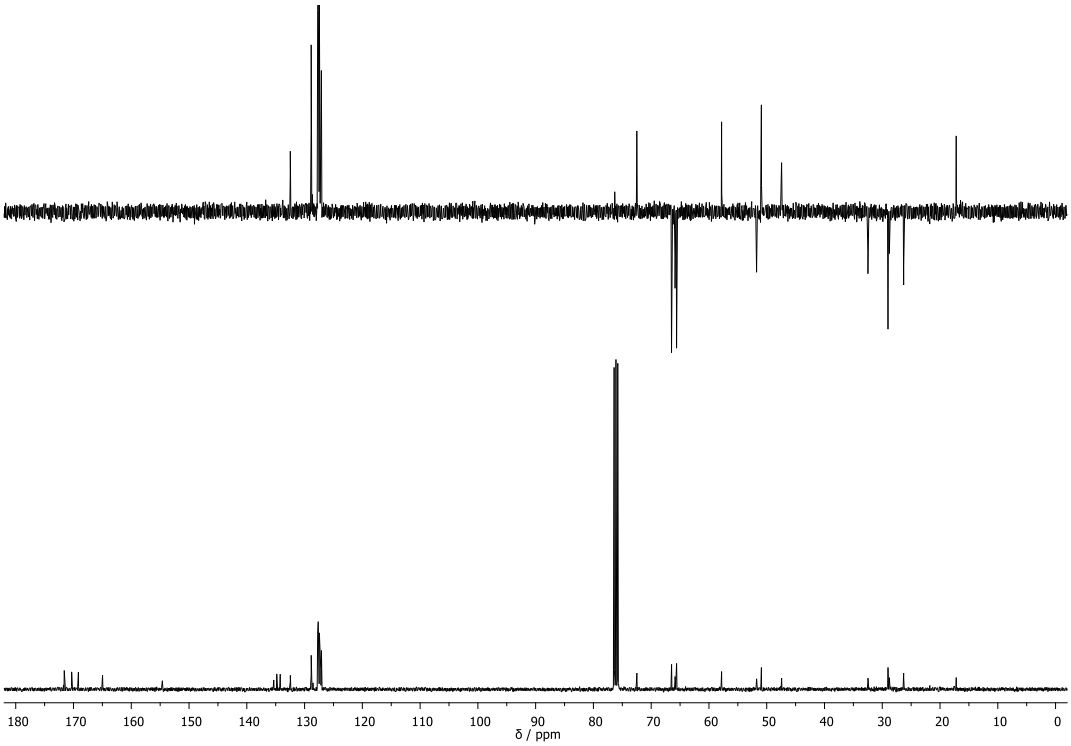

Fig. S12. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1e**.

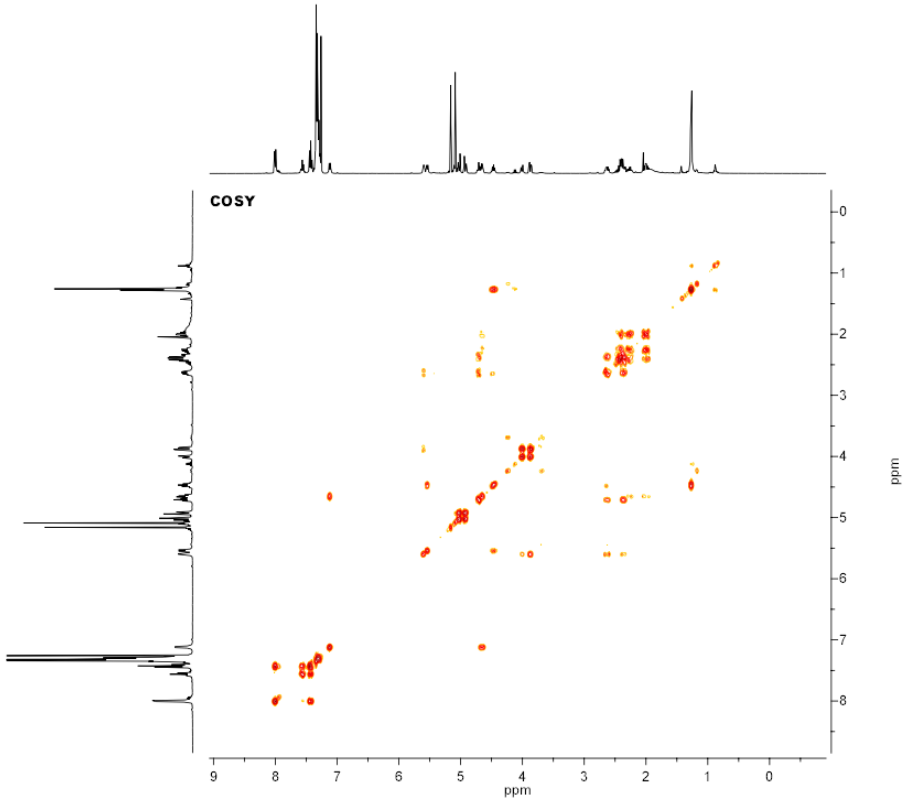

Fig. S13. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$) of compound **1e**.

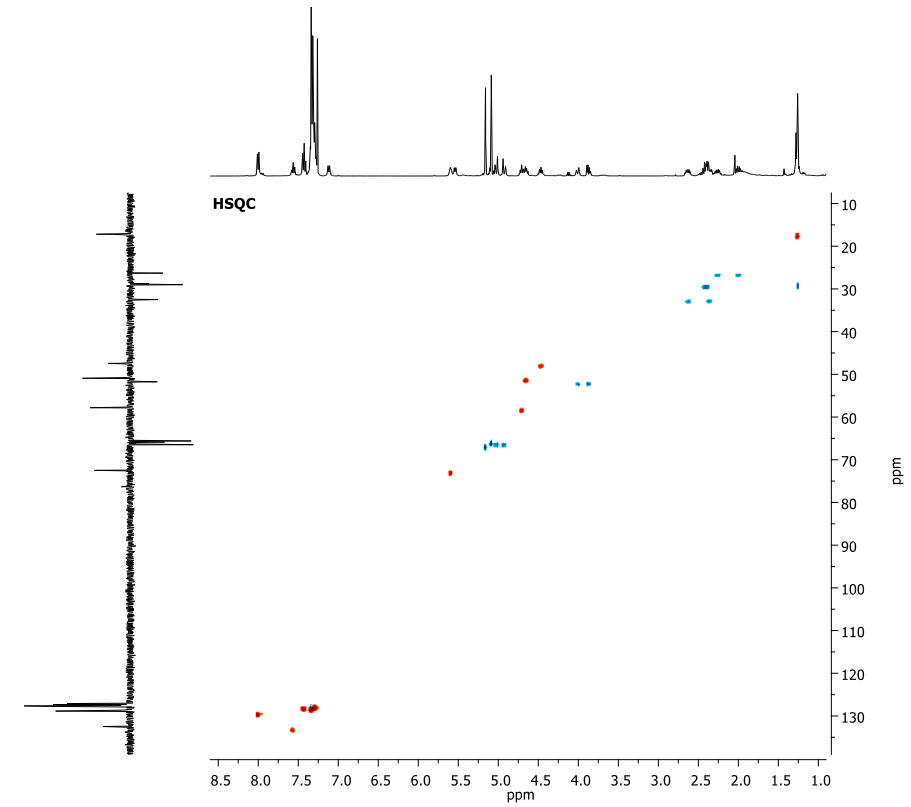

Fig. S14. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$) of compound **1e**.

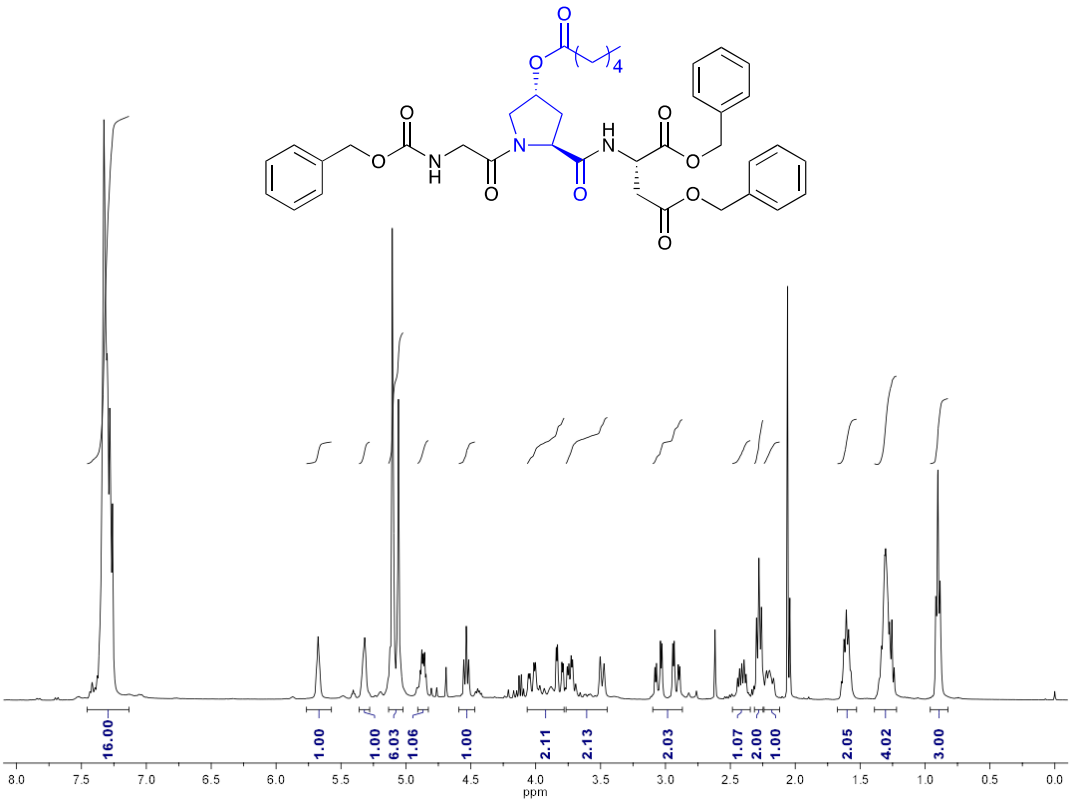

Fig. S15. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1f**.

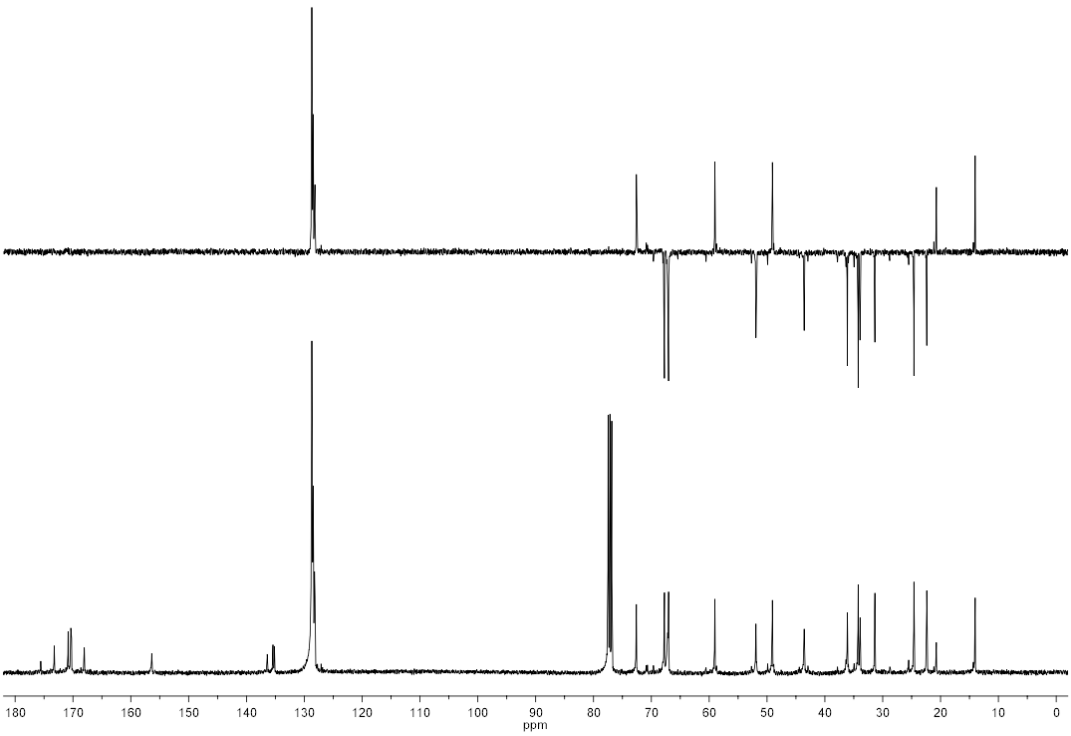

Fig. S16. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1f**.

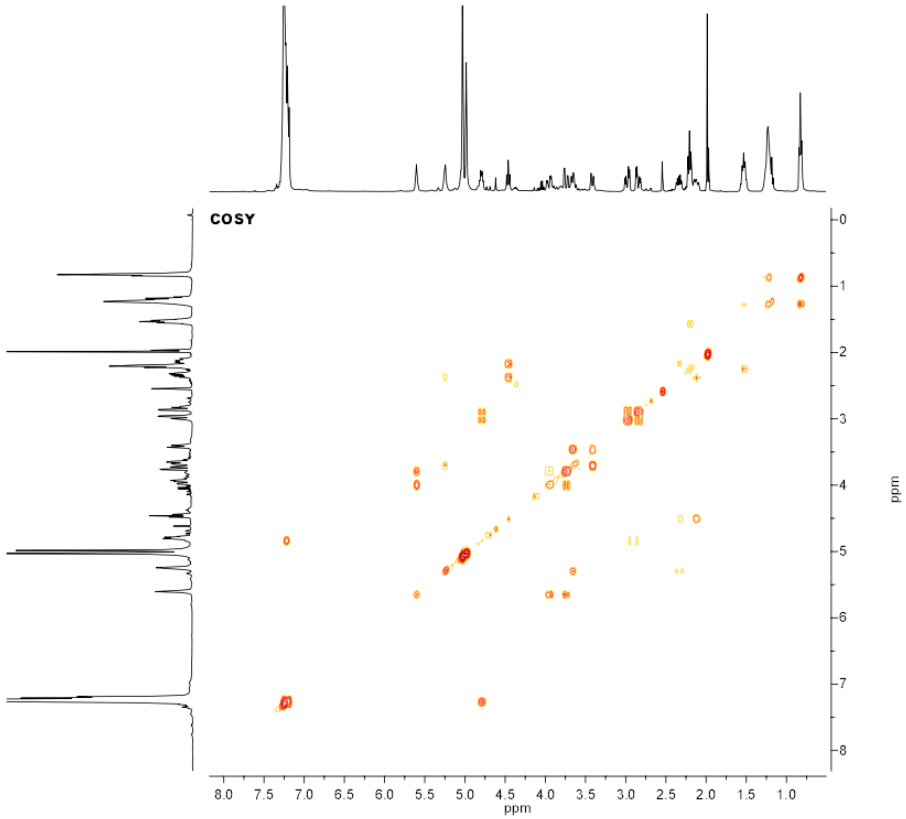

Fig. S17. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$) of compound **1f**.

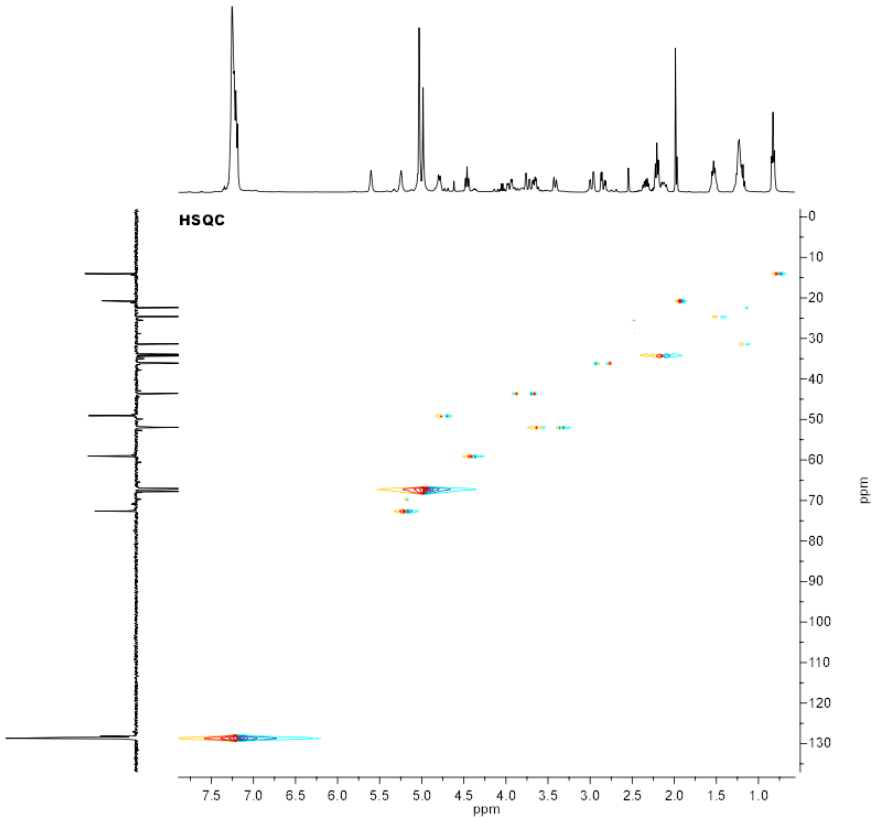

Fig. S18. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$) of compound **1f**.

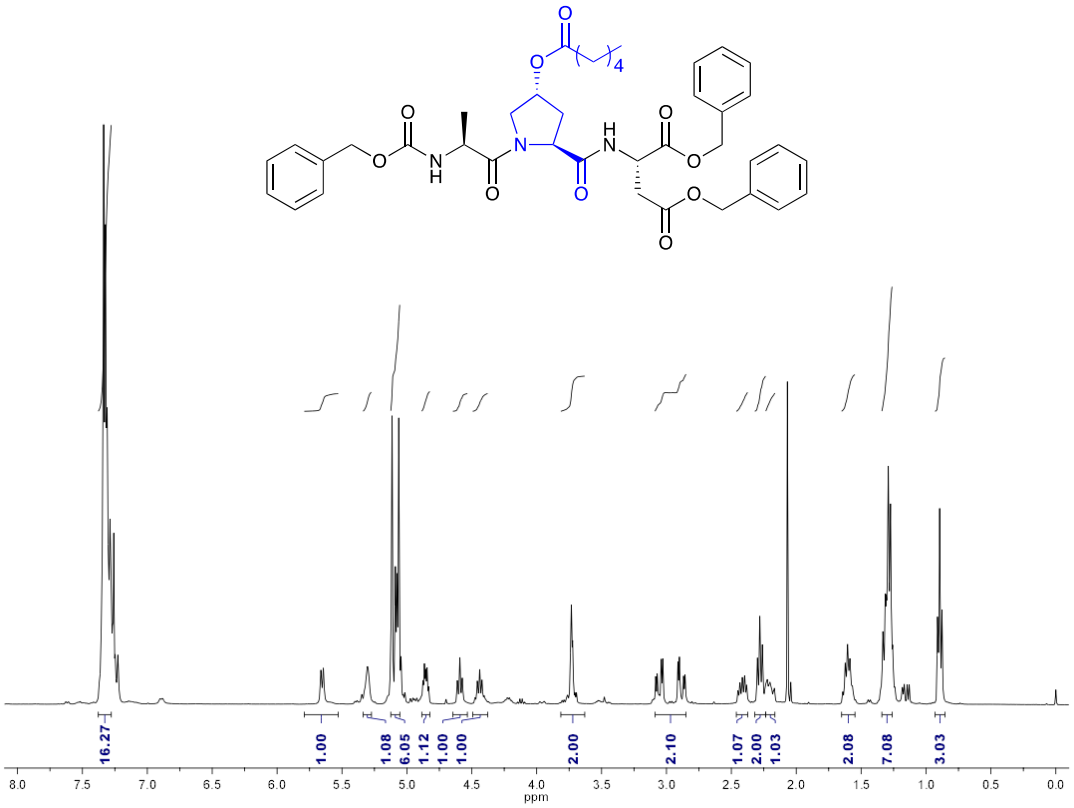

Fig. S19. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1g**.

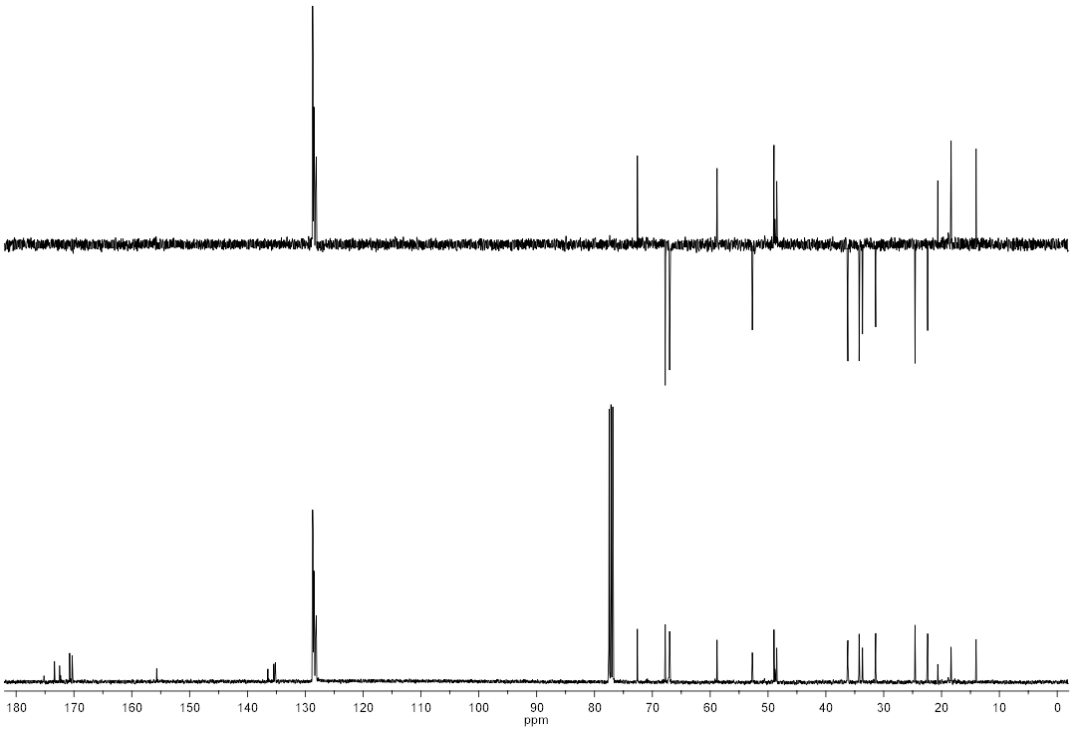

Fig. S20. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1g**.

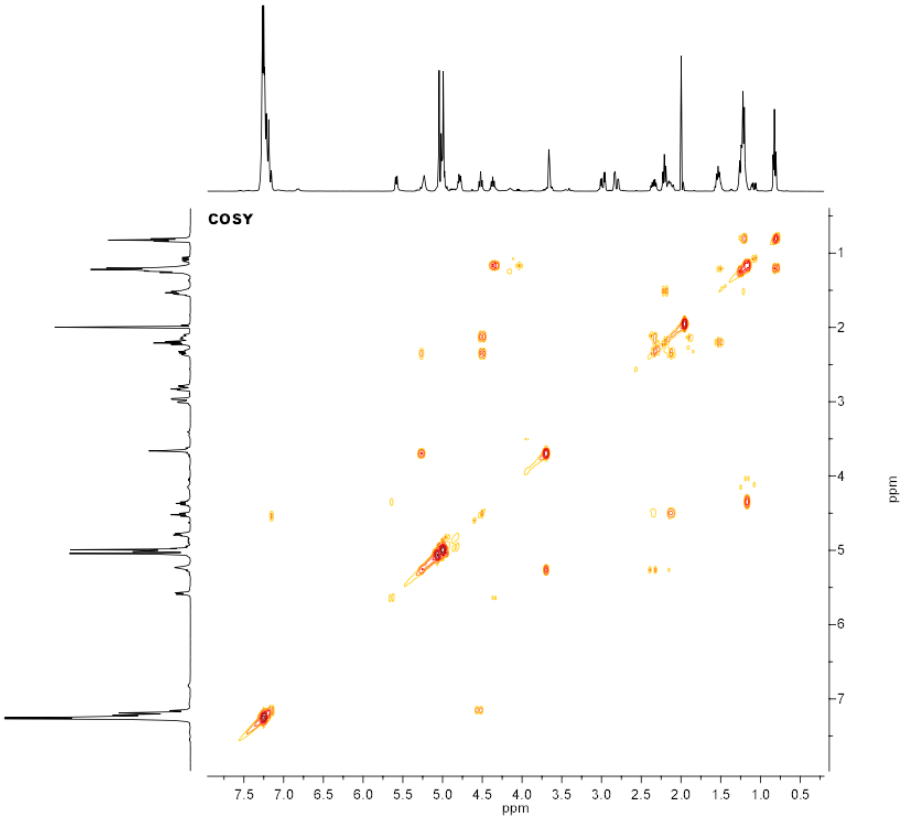

Fig. S21. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$, 400 MHz) of compound **1g**.

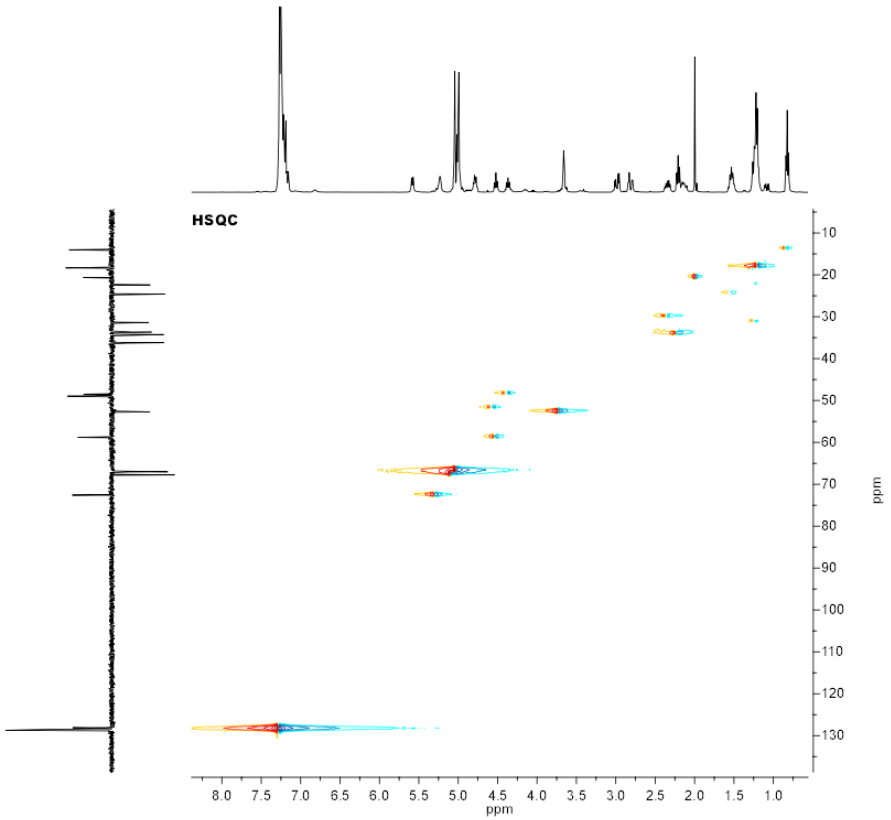

Fig. S22. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$, 400 MHz) of compound **1g**.

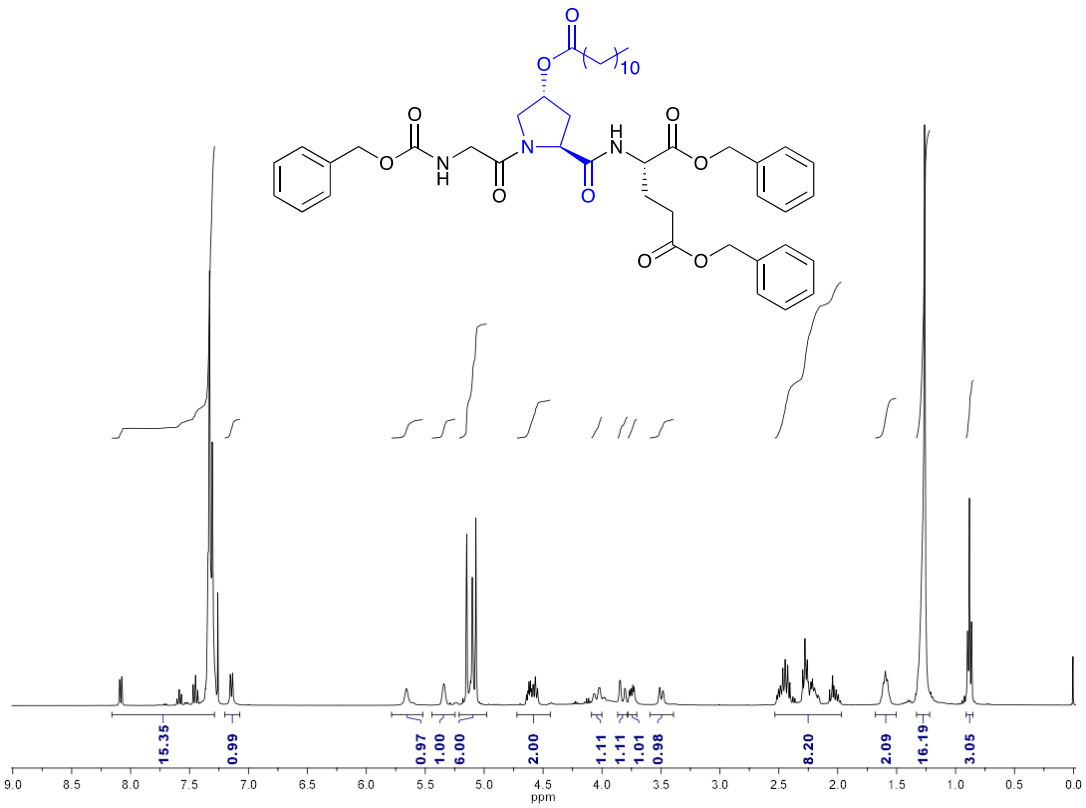

Fig. S23. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1h**.

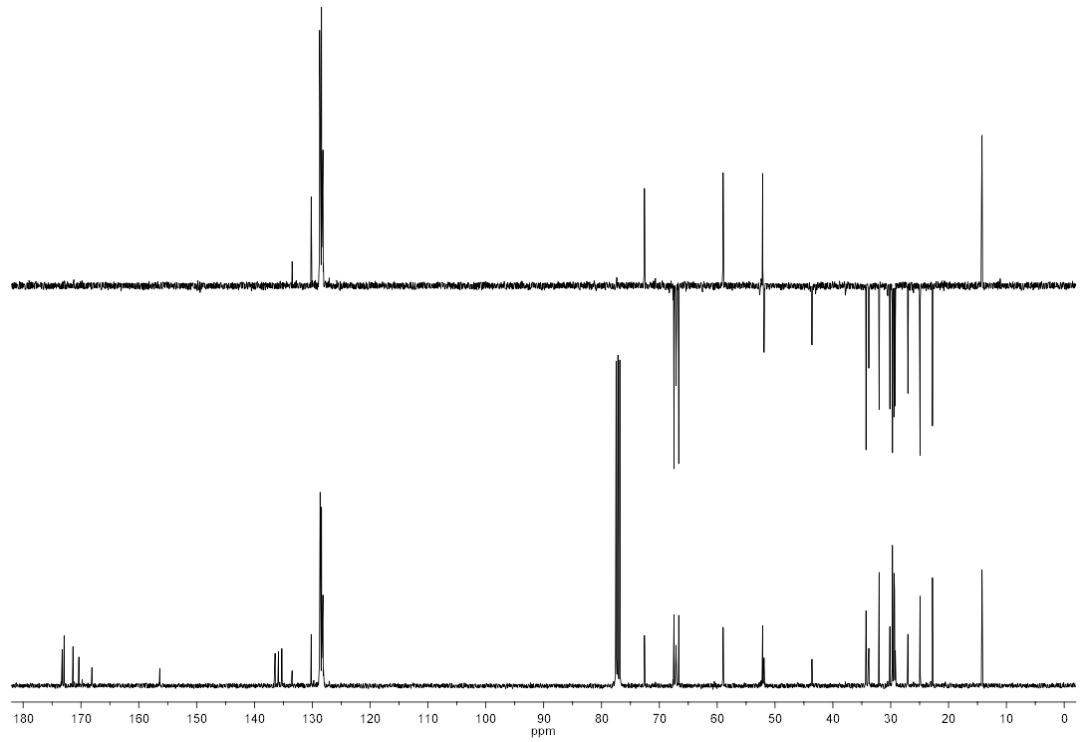

Fig. S24. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1h**.

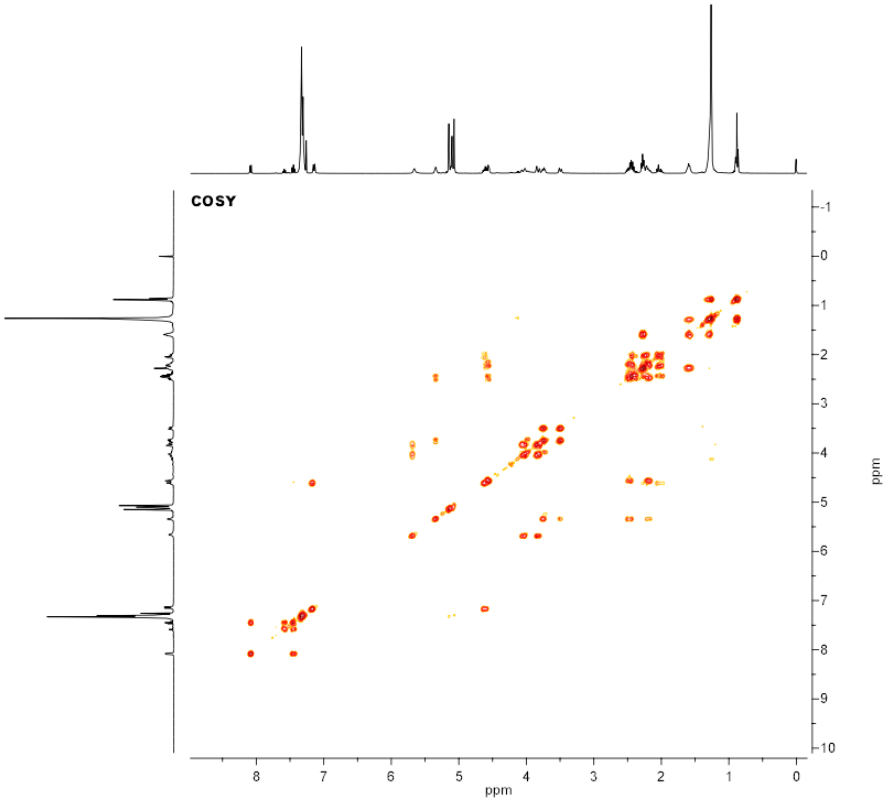

Fig. S25. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$, 400 MHz) of compound **1h**.

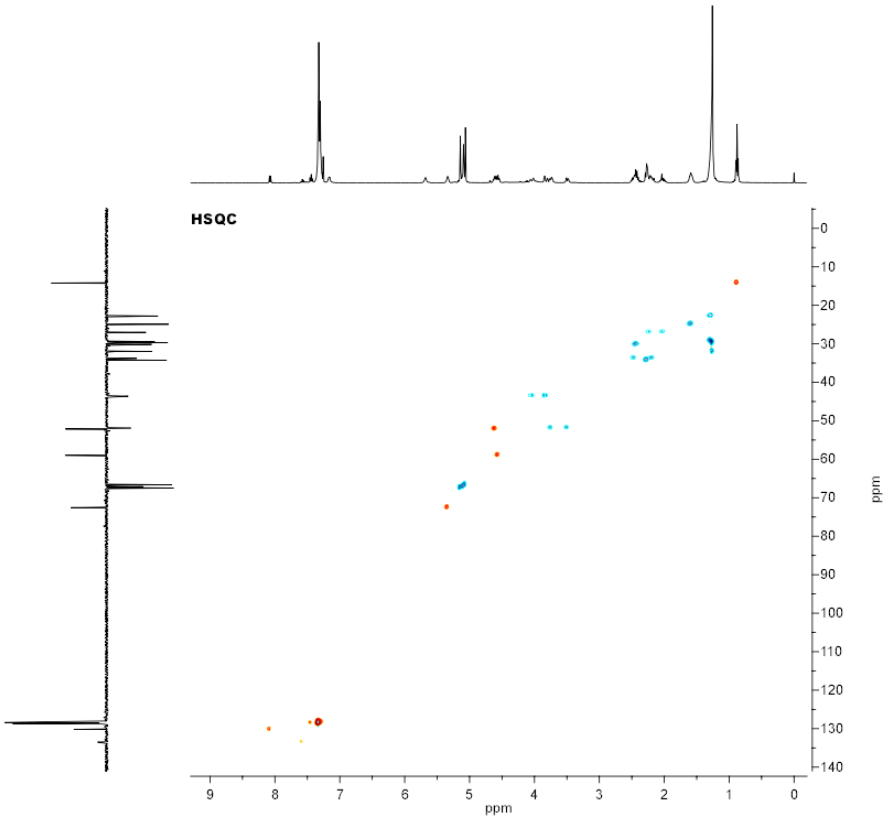

Fig. S26. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$, 400 MHz) of compound **1h**.

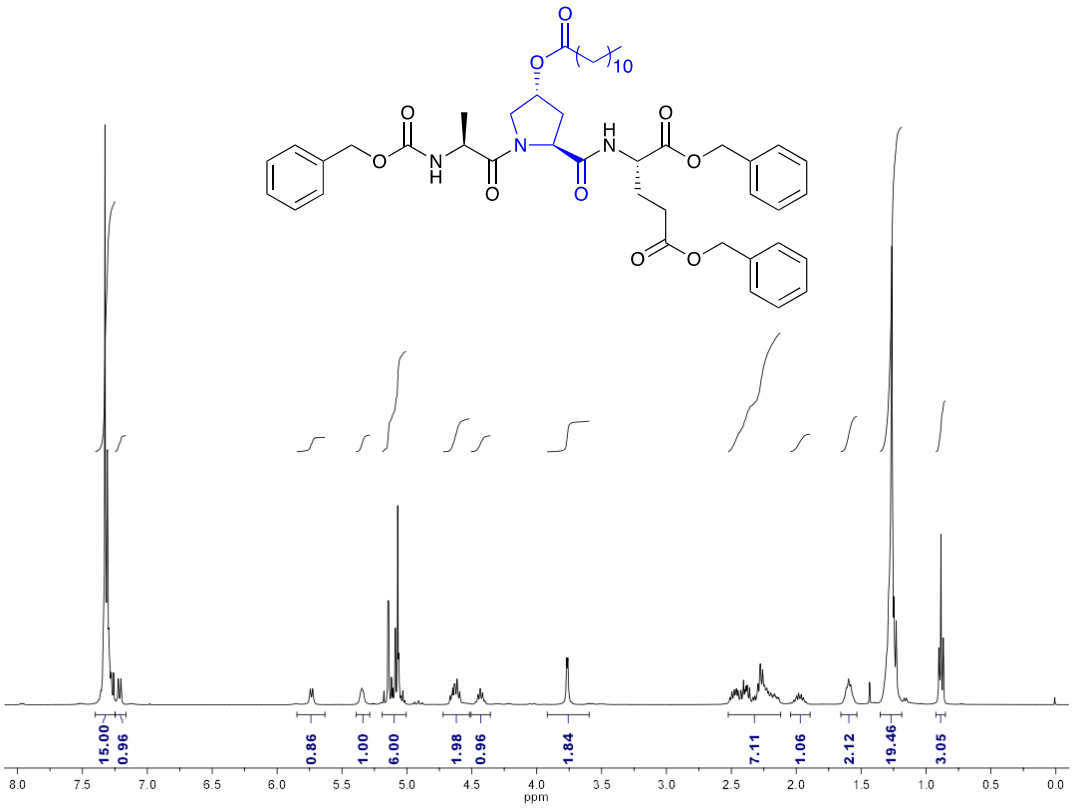

Fig. S27. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1i**.

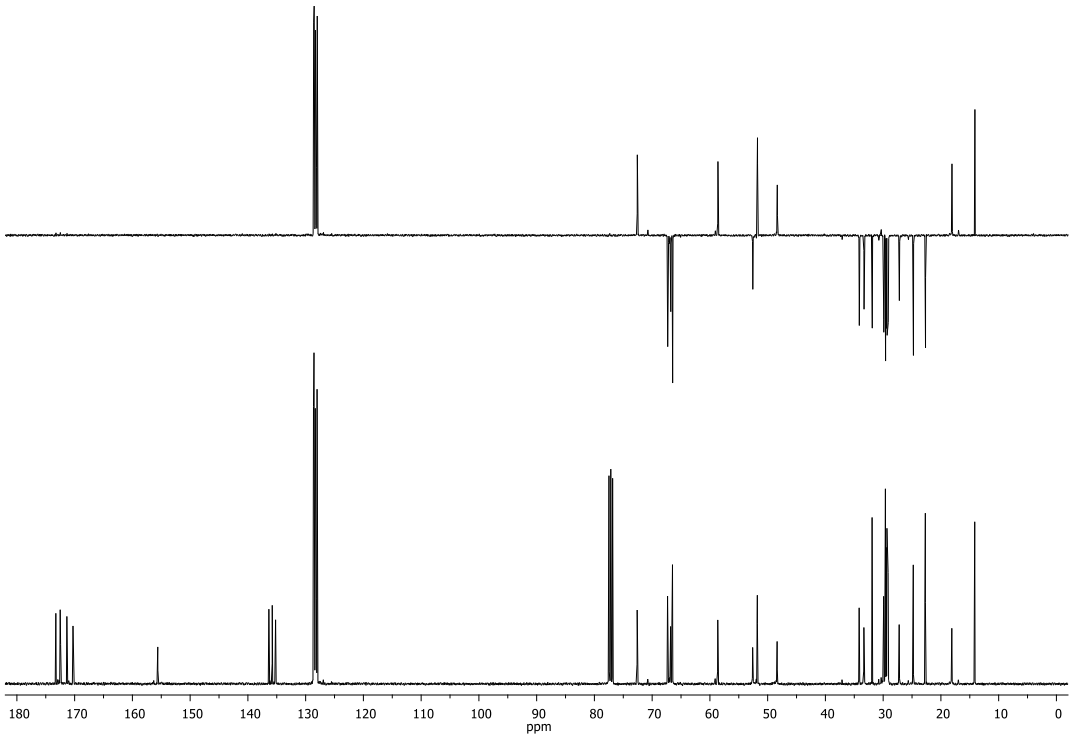

Fig. S28. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1i**.

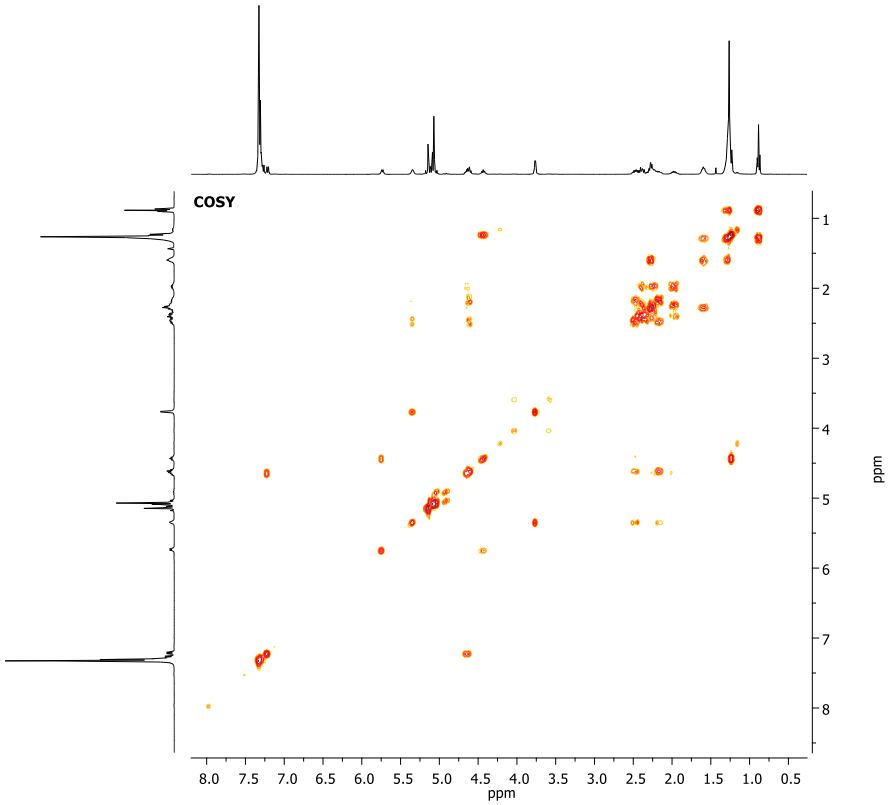

Fig. S29. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$, 400 MHz) of compound **1i**.

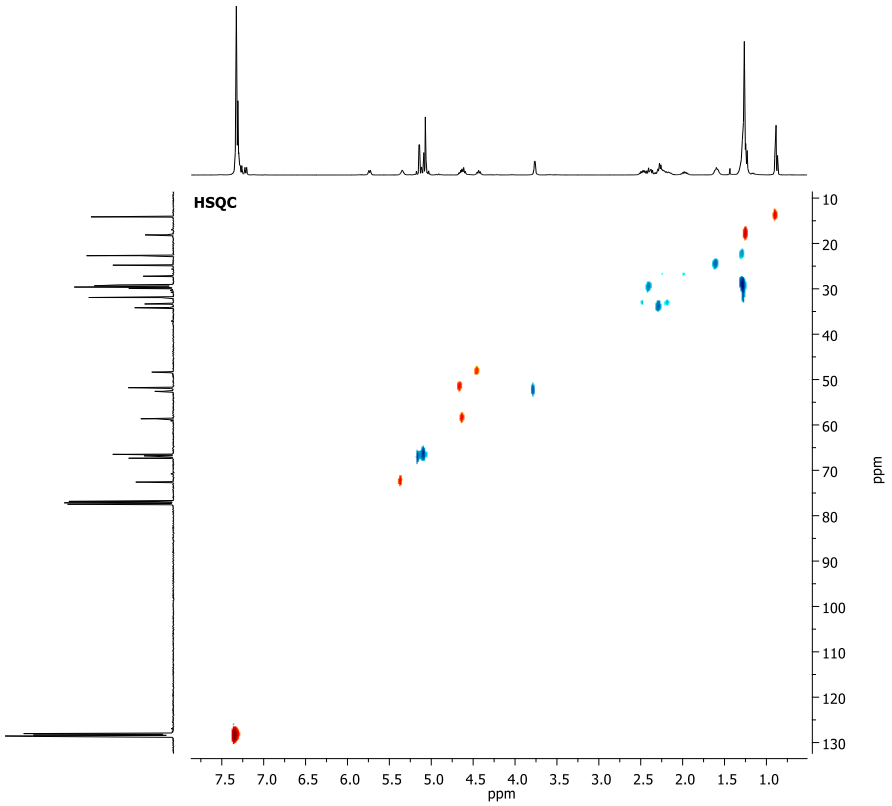

Fig. S30. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$, 400 MHz) of compound **1i**.

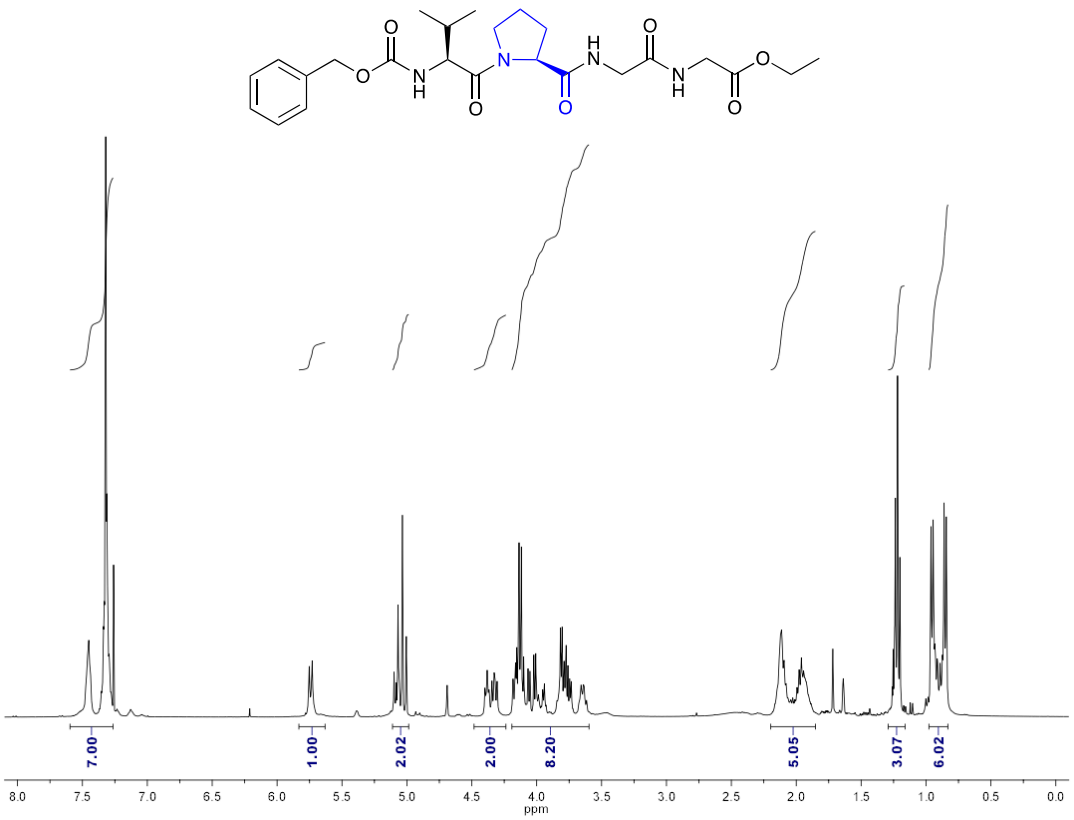

Fig. S31. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1j**.

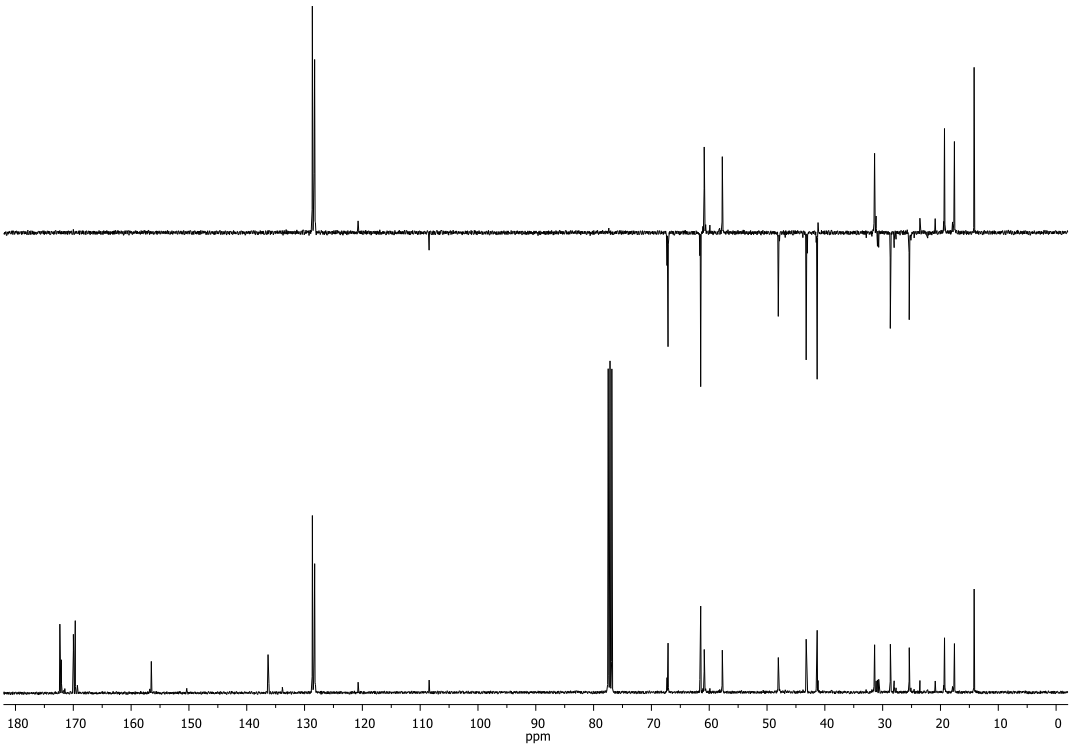

Fig. S32. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1j**.

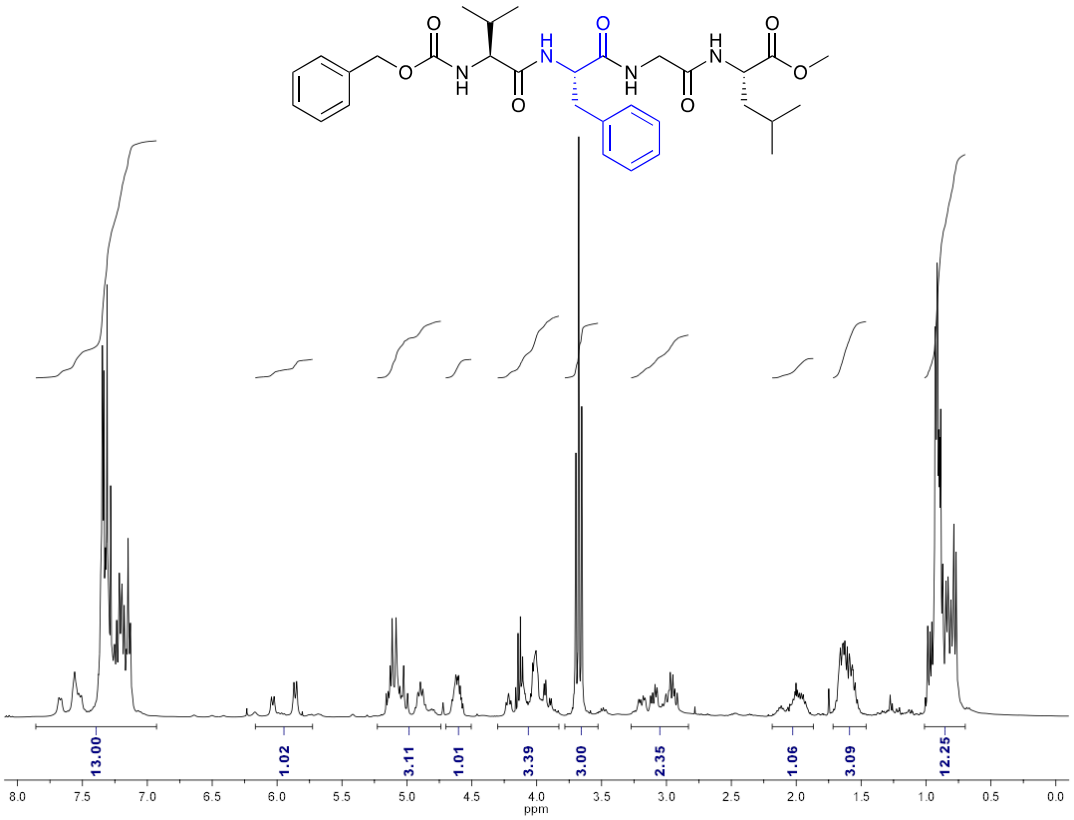

Fig. S33. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1k**.

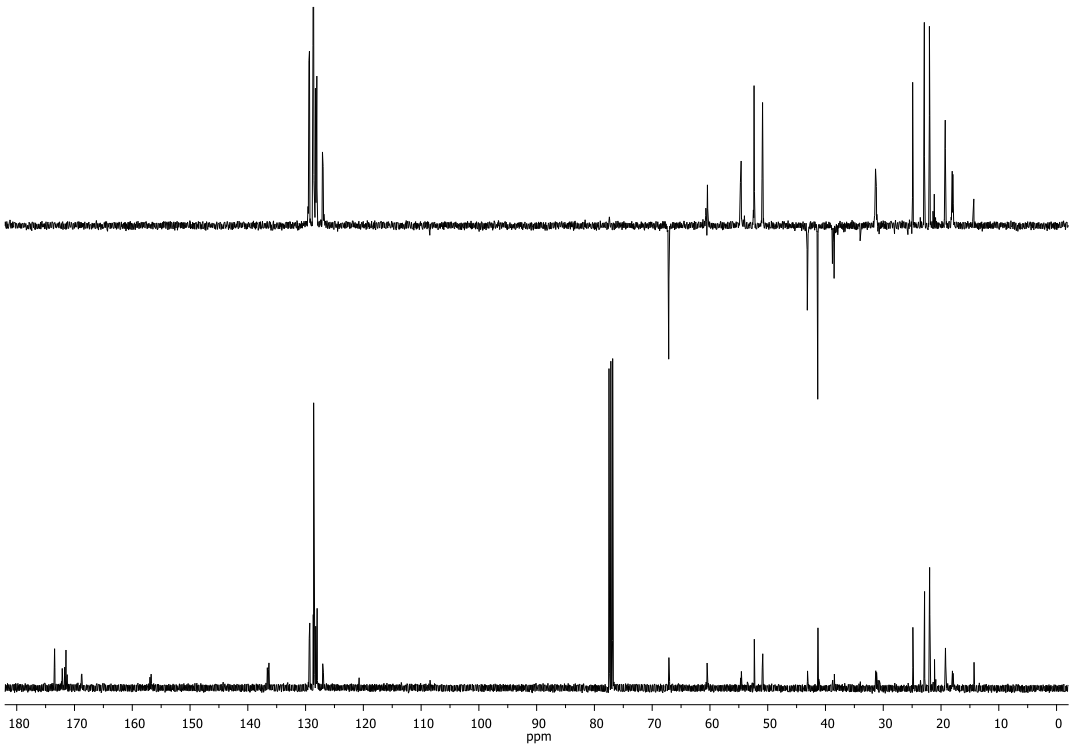

Fig. S34. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1k**.

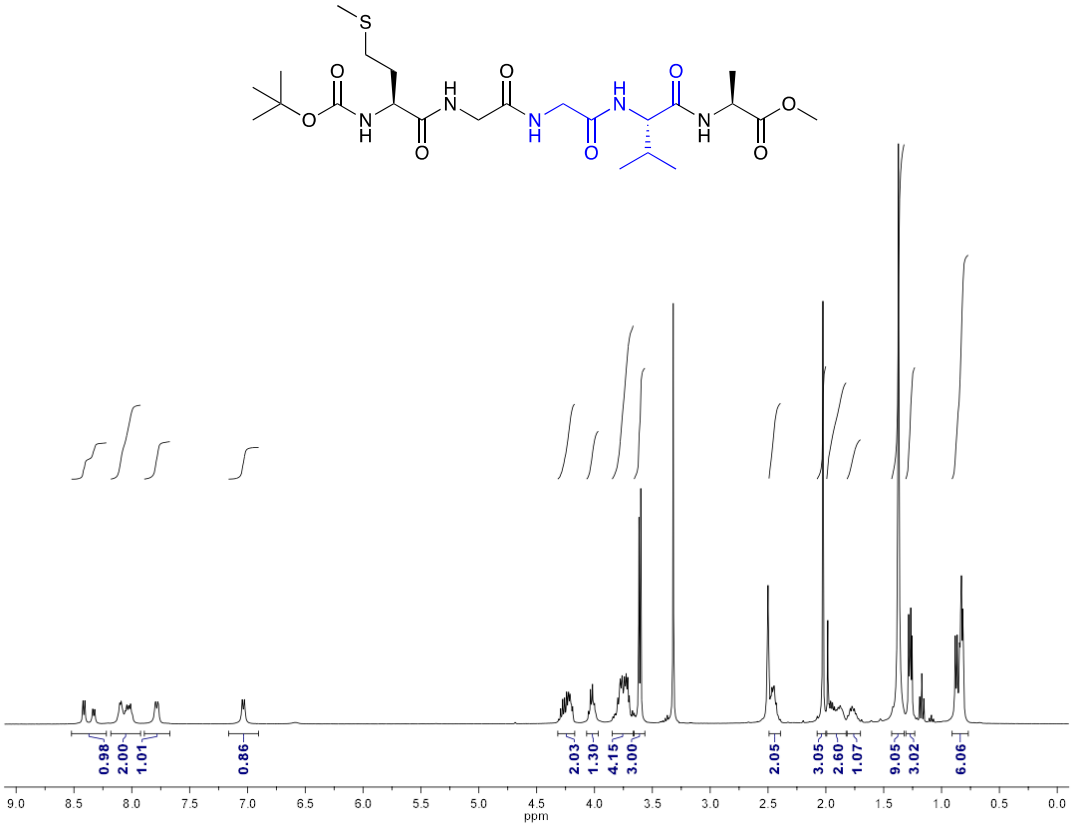

Fig. S35. ^{1}H-NMR spectrum (DMSO-d_6, 400 MHz) of compound **1l**.

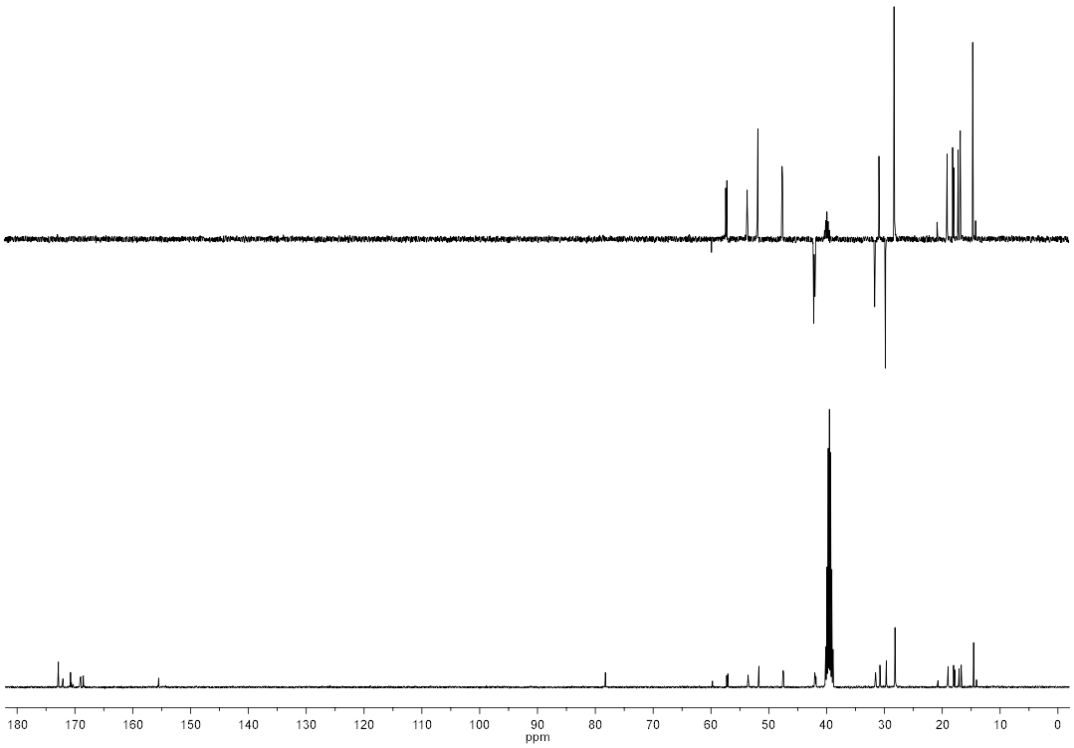

Fig. S36. DEPT (above) and ^{13}C-NMR (bottom) spectra (DMSO-d_6, 101 MHz) of compound **1l**.

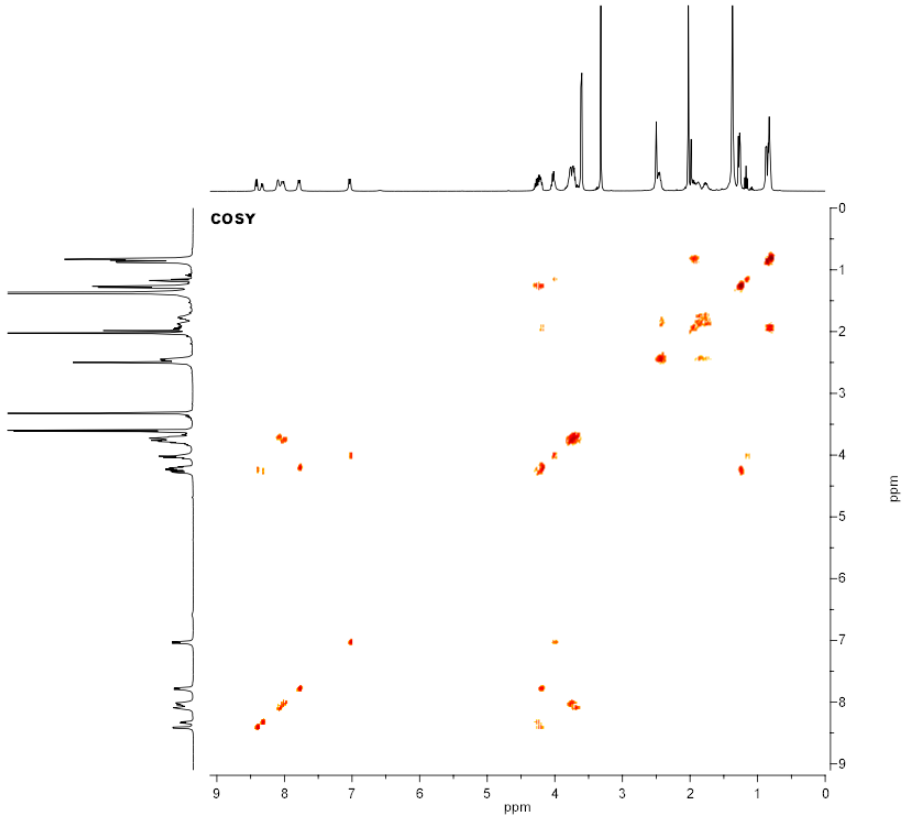

Fig. S37. ^{1}H-^{1}H-NMR (COSY) spectrum (DMSO-d_6) of compound **1l**.

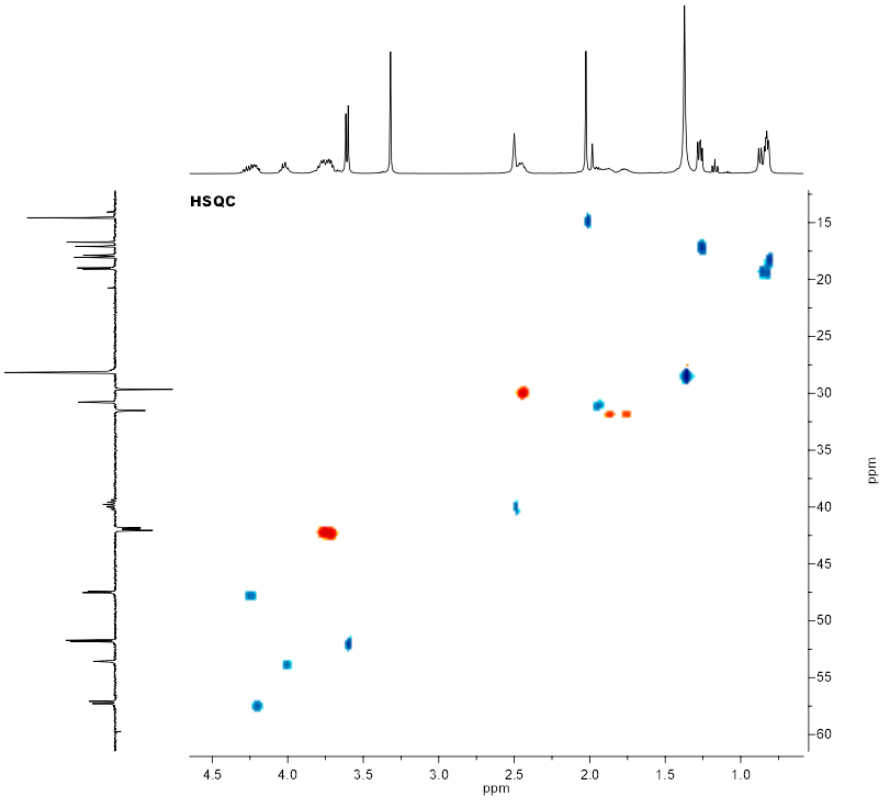

Fig. S38. ^{1}H-^{13}C-NMR (HSQC) spectrum (DMSO-d_6) of compound **1l**.

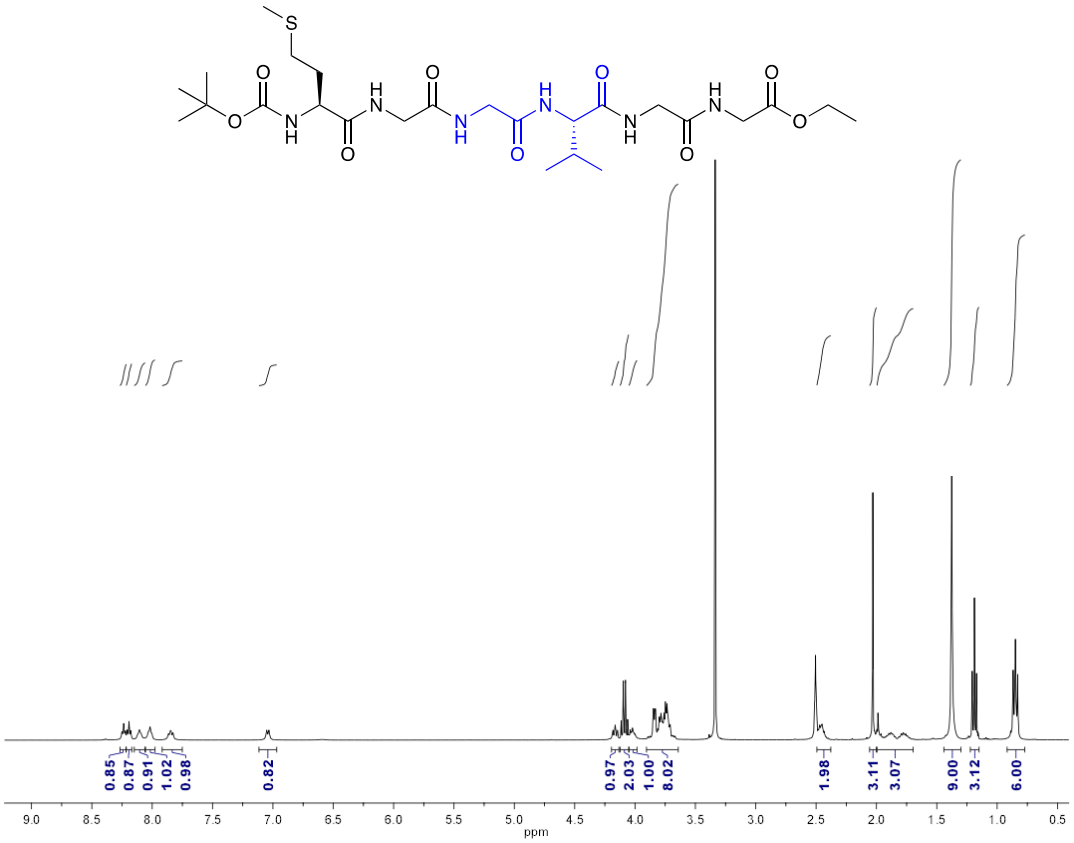

Fig. S39. ^{1}H-NMR spectrum (DMSO-d_6, 400 MHz) of compound **1m**.

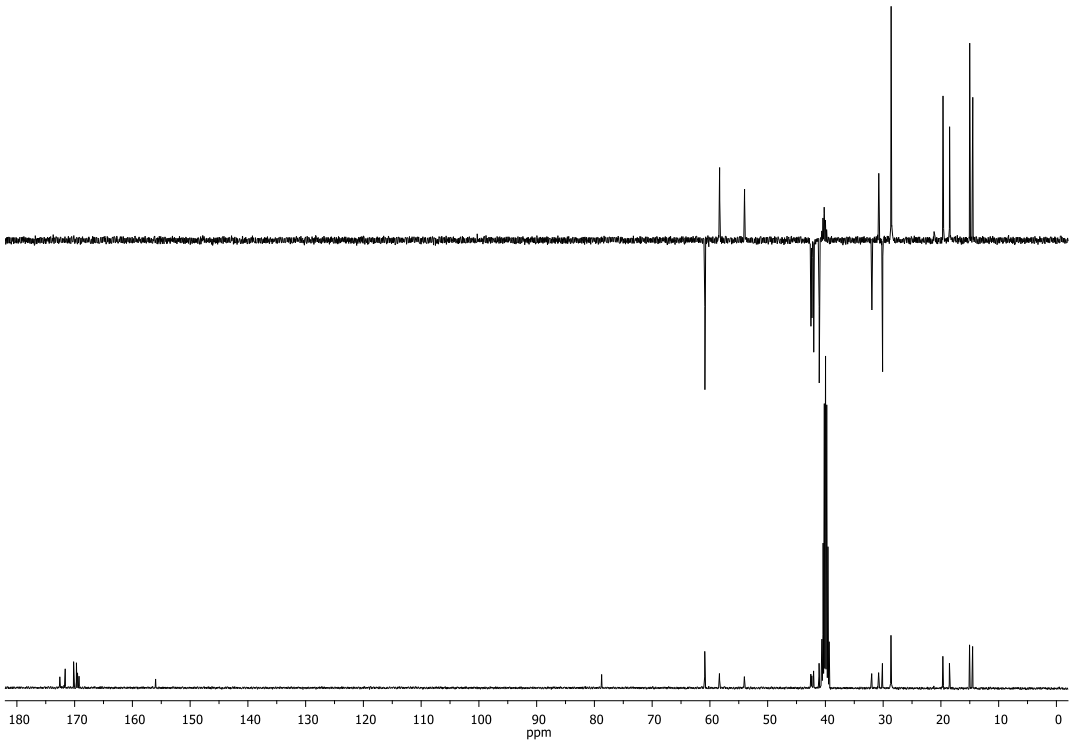

Fig. 40. DEPT (above) and ^{13}C-NMR (bottom) spectra (DMSO-d_6, 101 MHz) of compound **1m**.

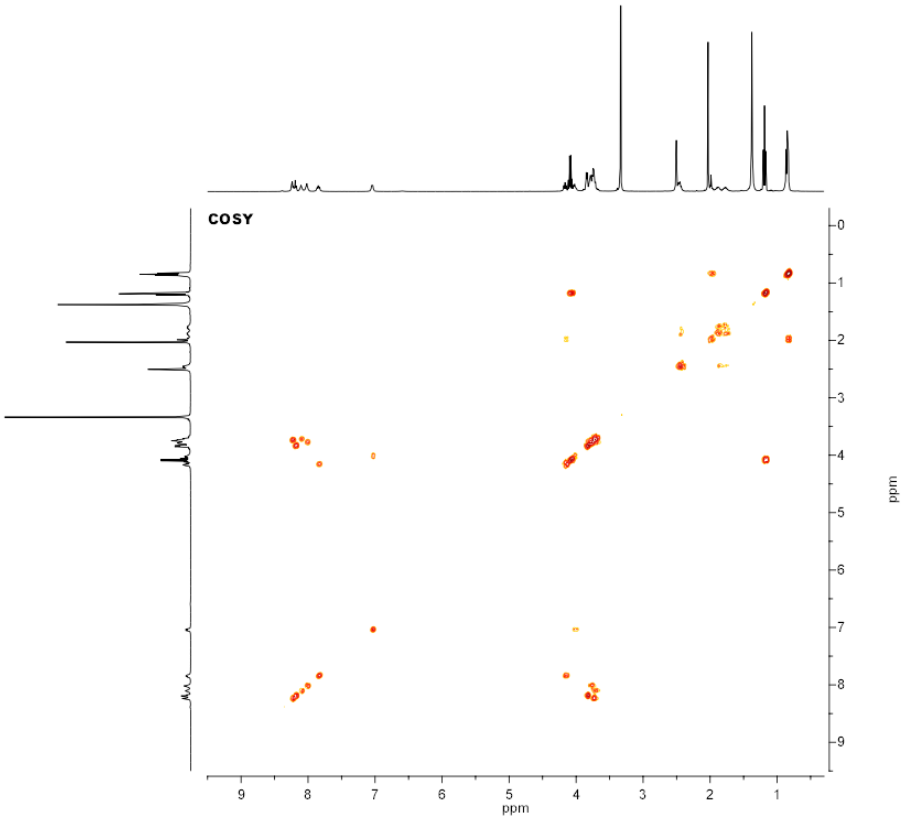

Fig. S41. ^{1}H-^{1}H-NMR (COSY) spectrum (DMSO-d_6) of compound **1m**.

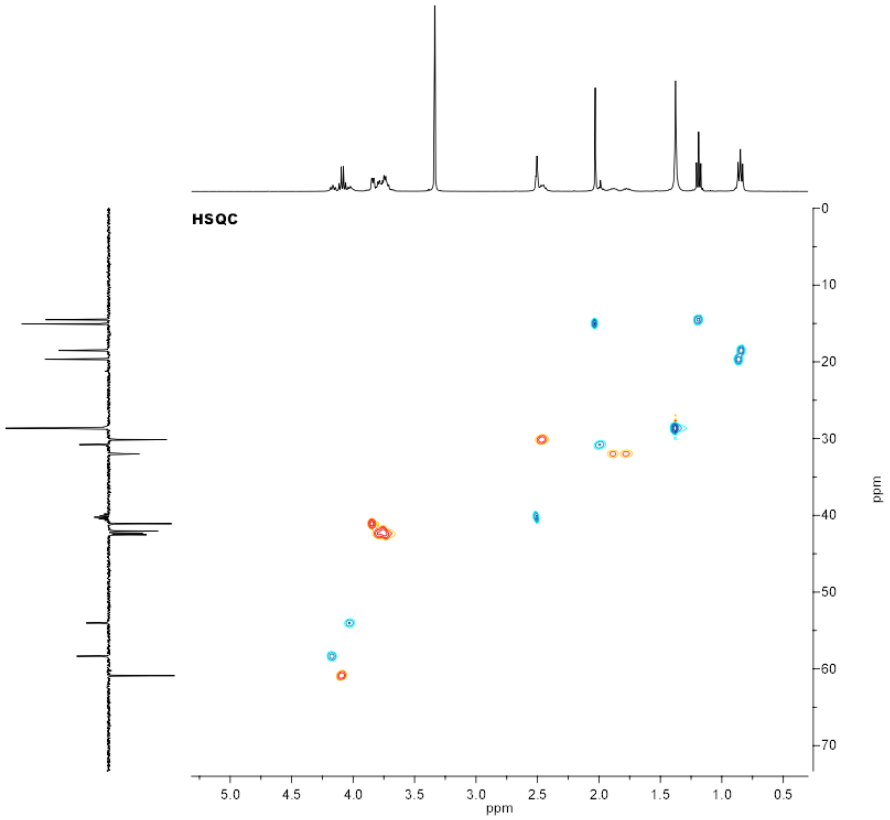

Fig. S42. ^{1}H-^{13}C-NMR (HSQC) spectrum (DMSO-d_6) of compound **1m**.

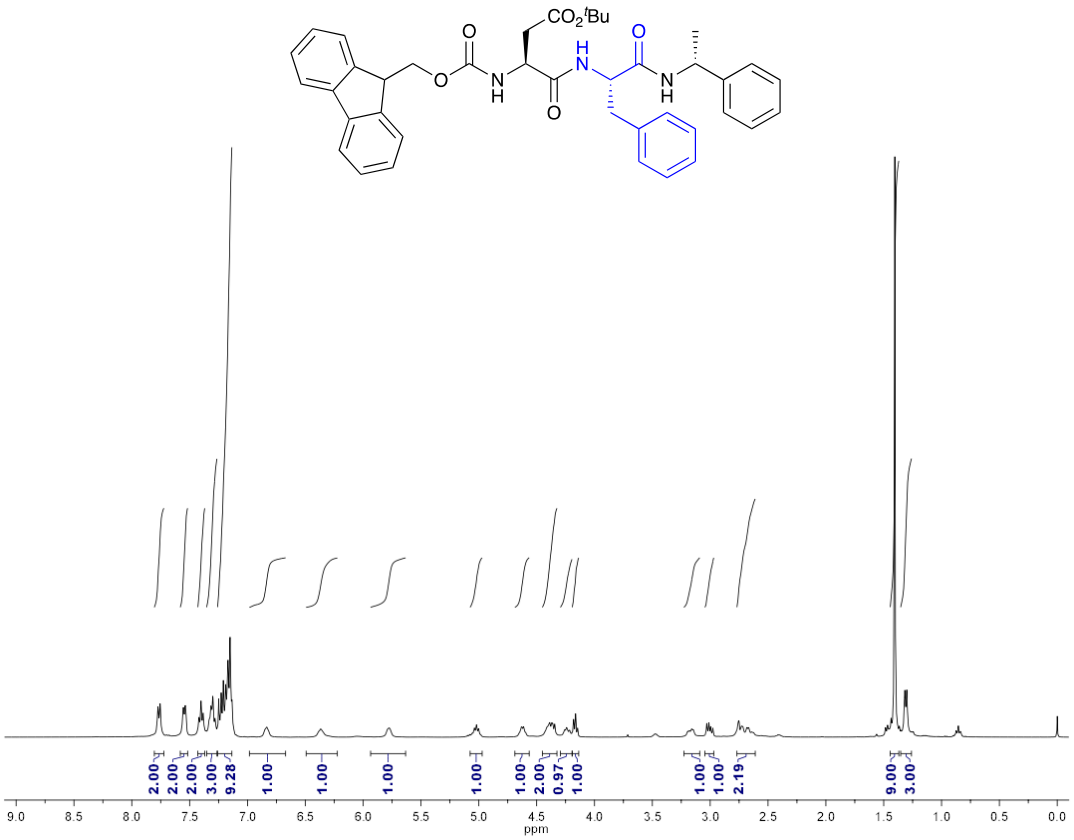

Fig. S43. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compound **1n**.

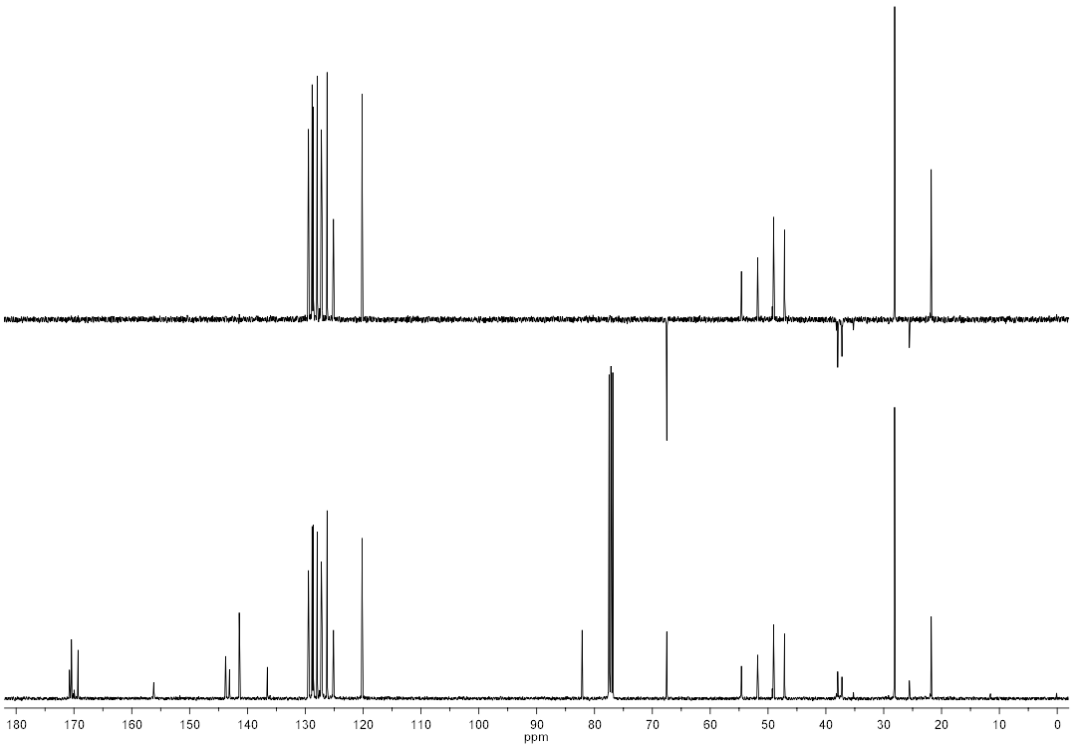

Fig. 44. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compound **1n**.

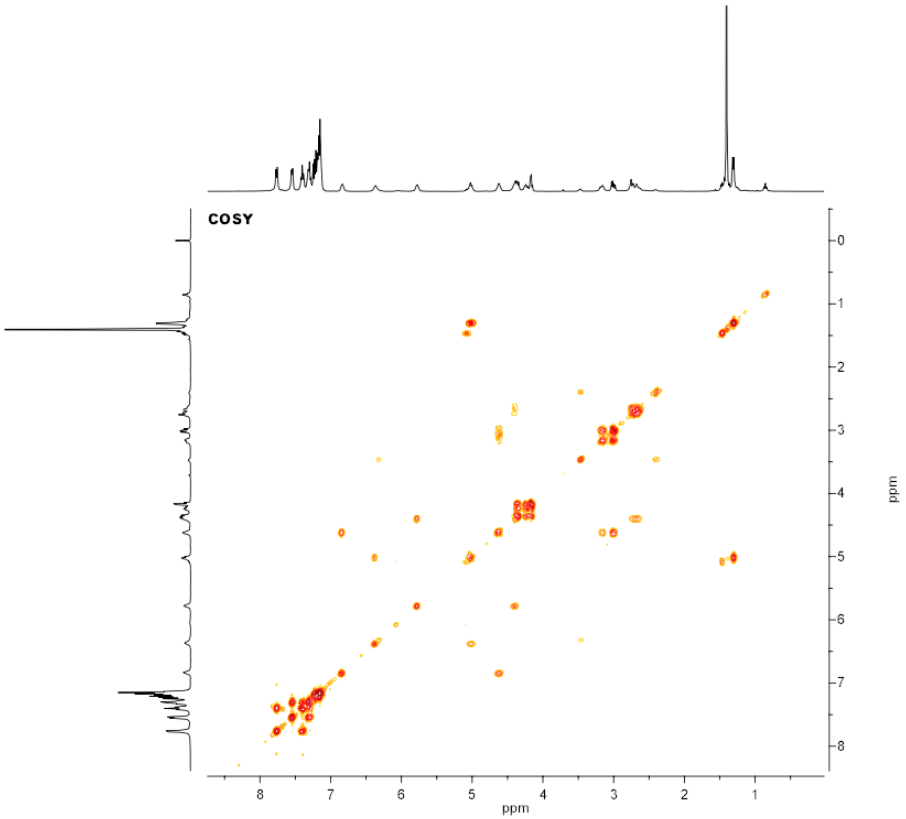

Fig. S45. ^{1}H-^{1}H-NMR (COSY) spectrum ($CDCl_3$) of compound **1n**.

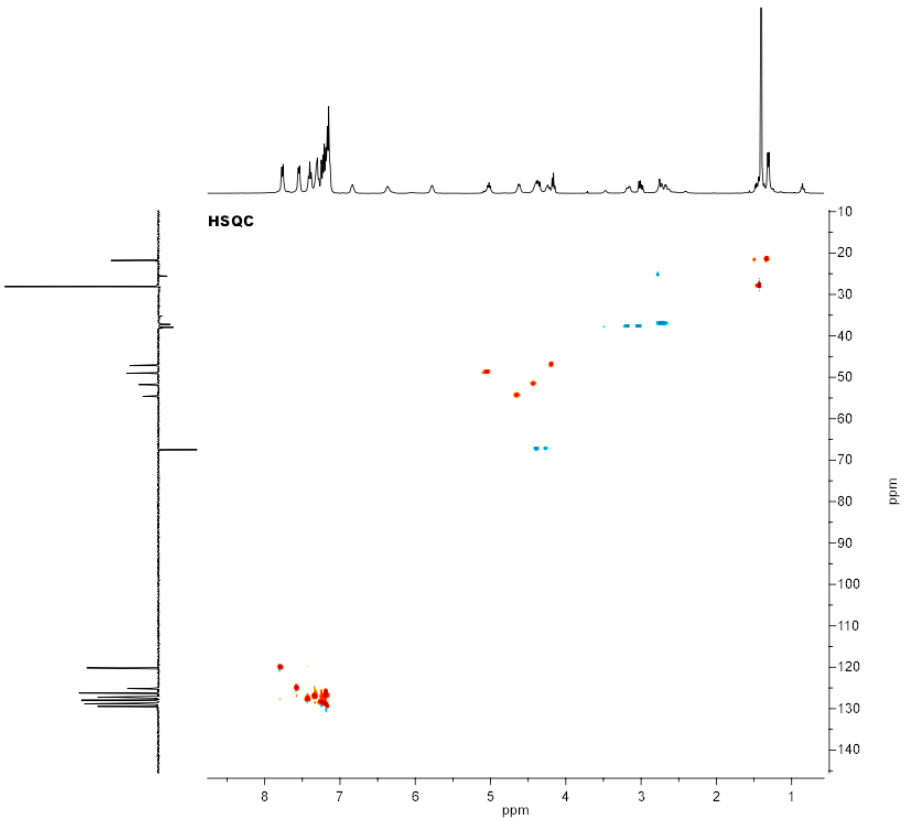

Fig. S46. ^{1}H-^{13}C-NMR (HSQC) spectrum ($CDCl_3$) of compound **1n**.

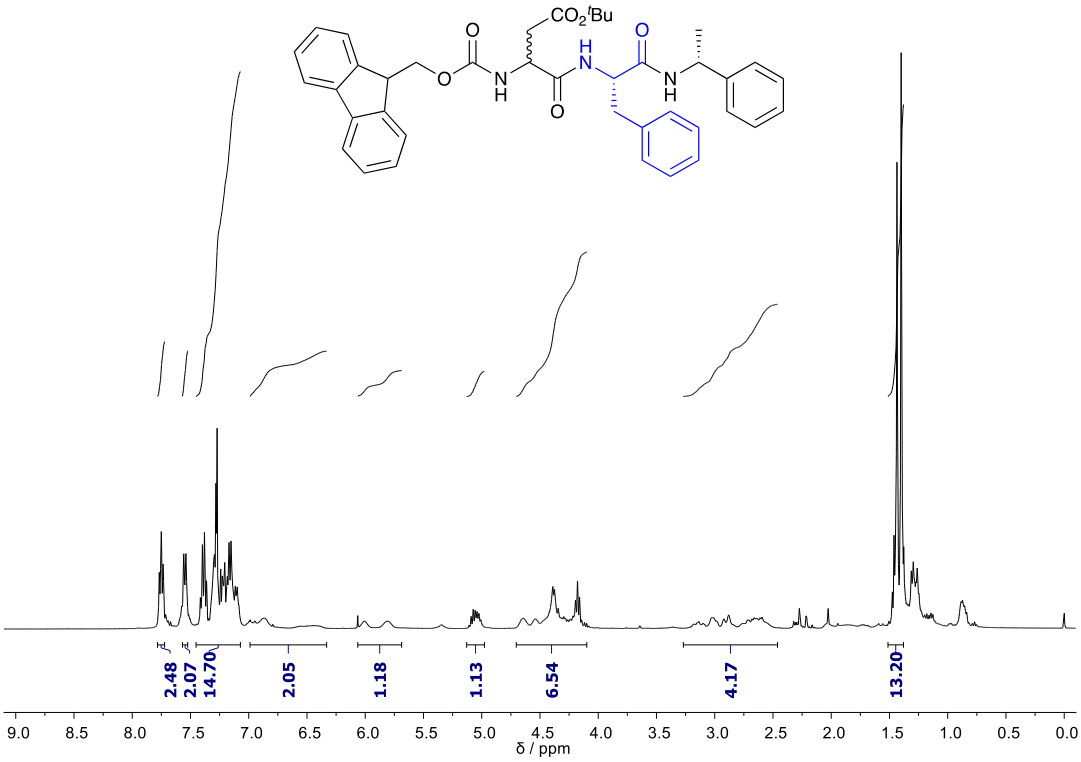

Fig. S47. ^{1}H-NMR spectrum ($CDCl_3$, 400 MHz) of compounds **1n/1n'**.

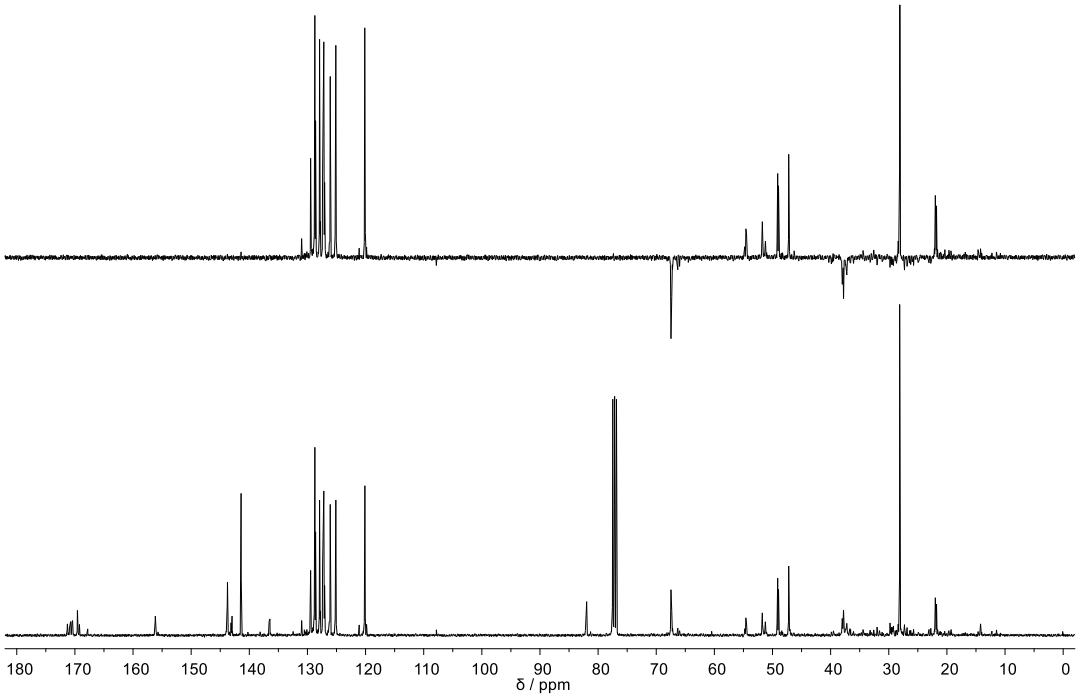

Fig. 48. DEPT (above) and ^{13}C-NMR (bottom) spectra ($CDCl_3$, 101 MHz) of compounds **1n/1n'**.

2. *[1]H-NMR experiment for the interaction between TBTU and HOSu performed in DMSO-d_6*

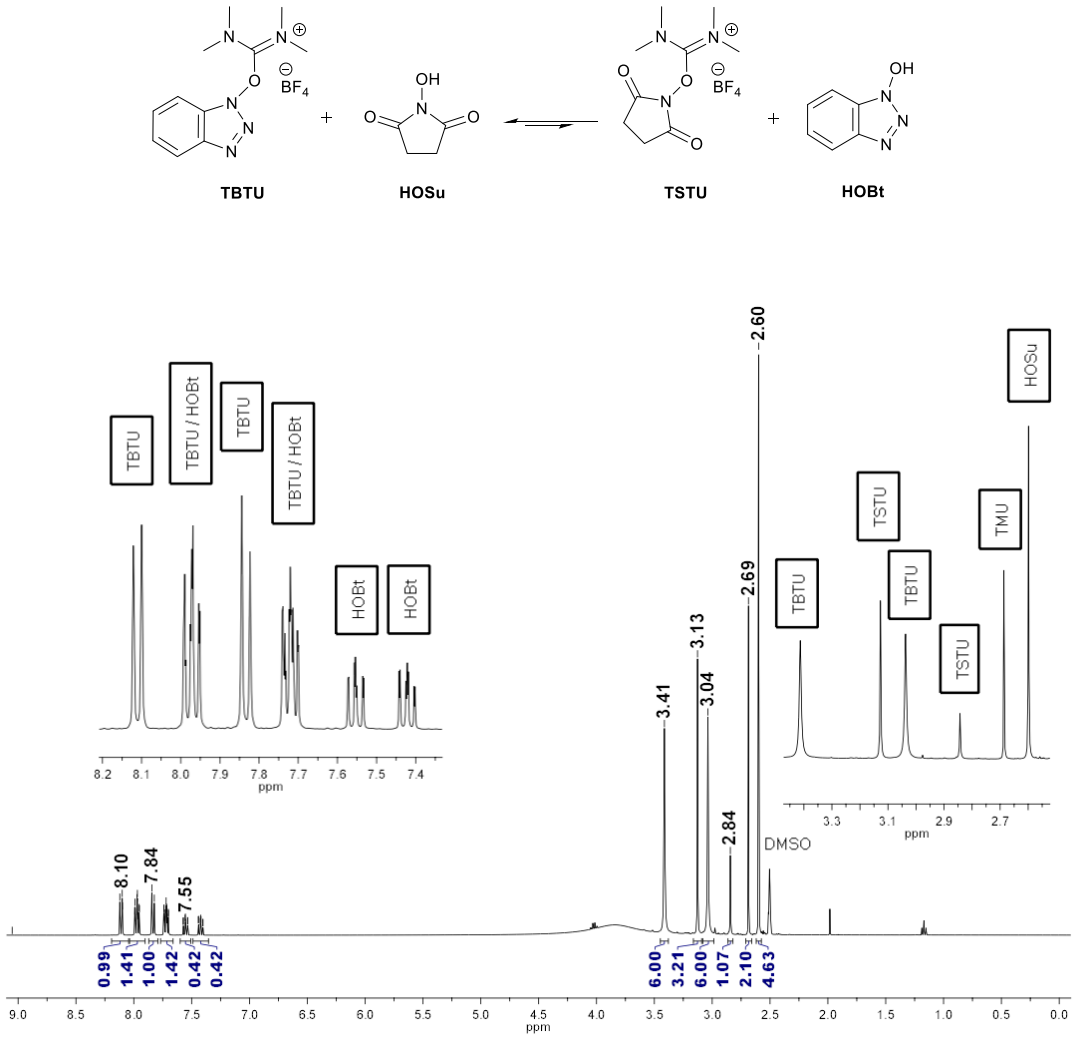

Fig. S49. [1]H-NMR spectrum (DMSO-d_6, 400 MHz) of the reaction between TBTU and HOSu.

3. *HPLC chromatograms for pseudotripepeptide **1n** and diastereoisomeric mixture **1n/1n'***

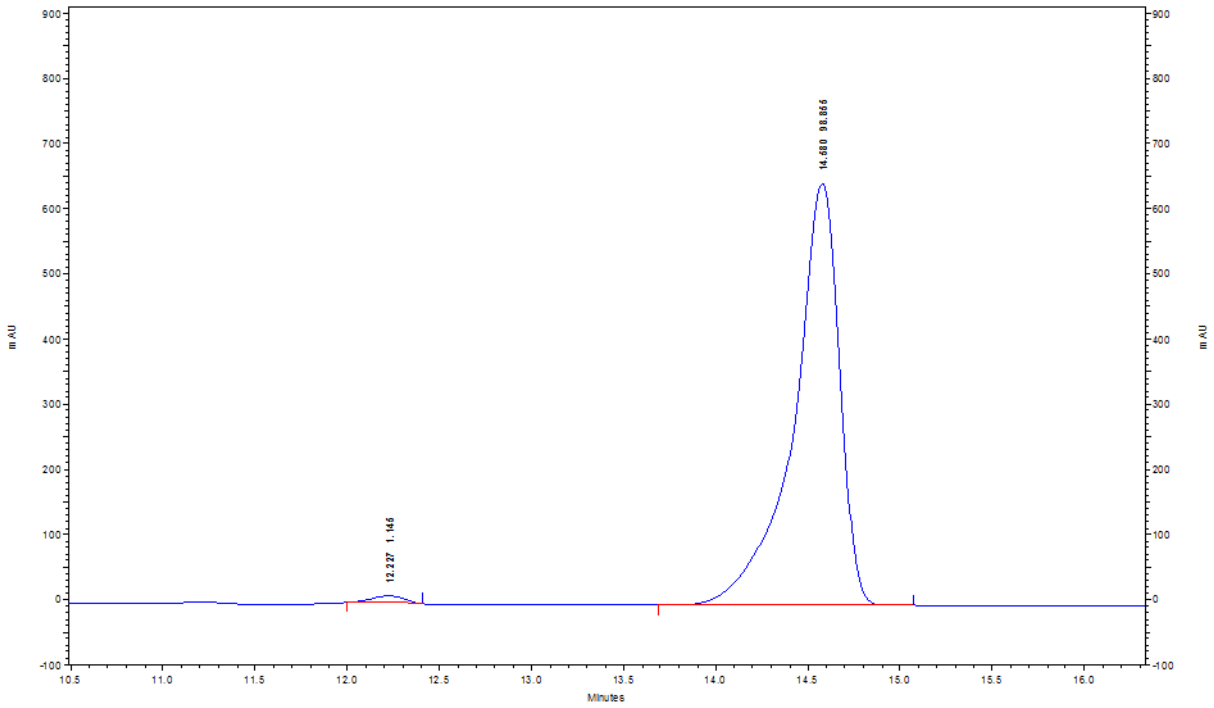

Fig. S50. HPLC chromatogram of pseudotripeptide **1n** (*dr*: 99%).

Eluent: 60-100% gradient of CH_3CN in water. t_R = 14.5 min for **1n** and t_R = 12.2 min for **1n'**.

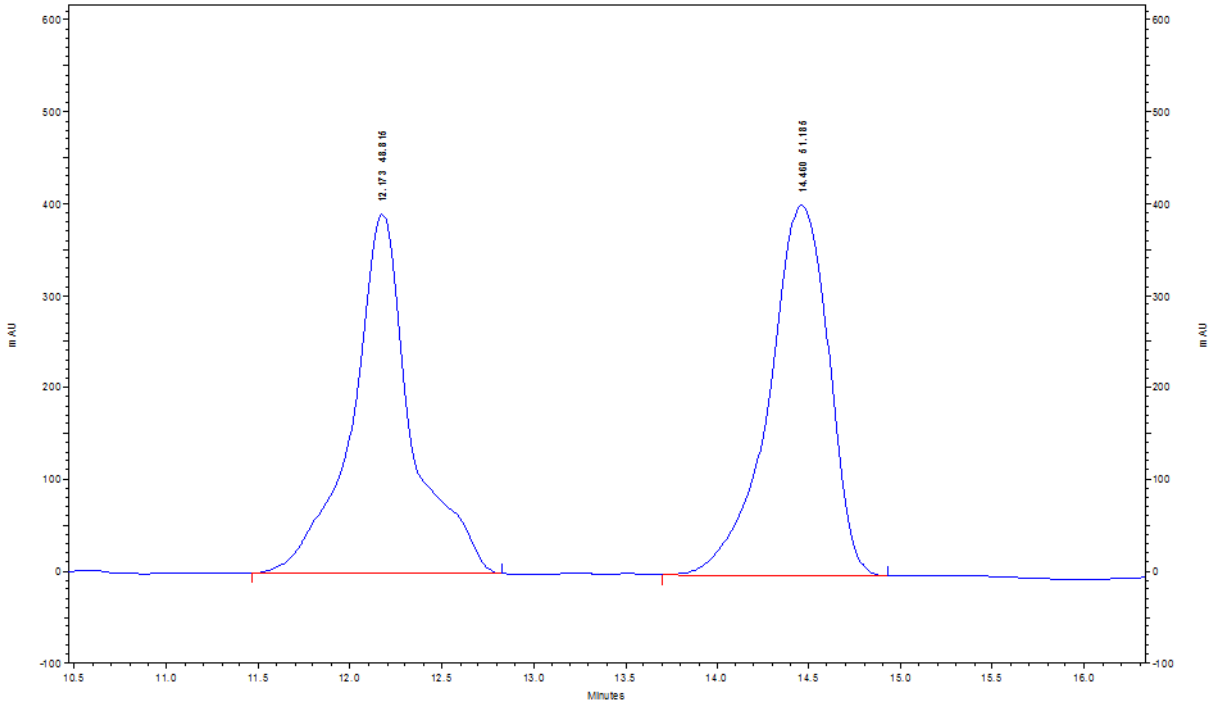

Fig. S51. HPLC chromatogram of diastereoisomeric mixture of **1n/1n'**.

Eluent: 60-100% gradient of CH_3CN in water. t_R = 14.5 min for **1n** and t_R = 12.2 min for **1n'**.

*4. [1]H-NMR experiments for hexapeptide **1m** in DMSO-d_6 at 26, 40, 60, 80 and 100ºC*

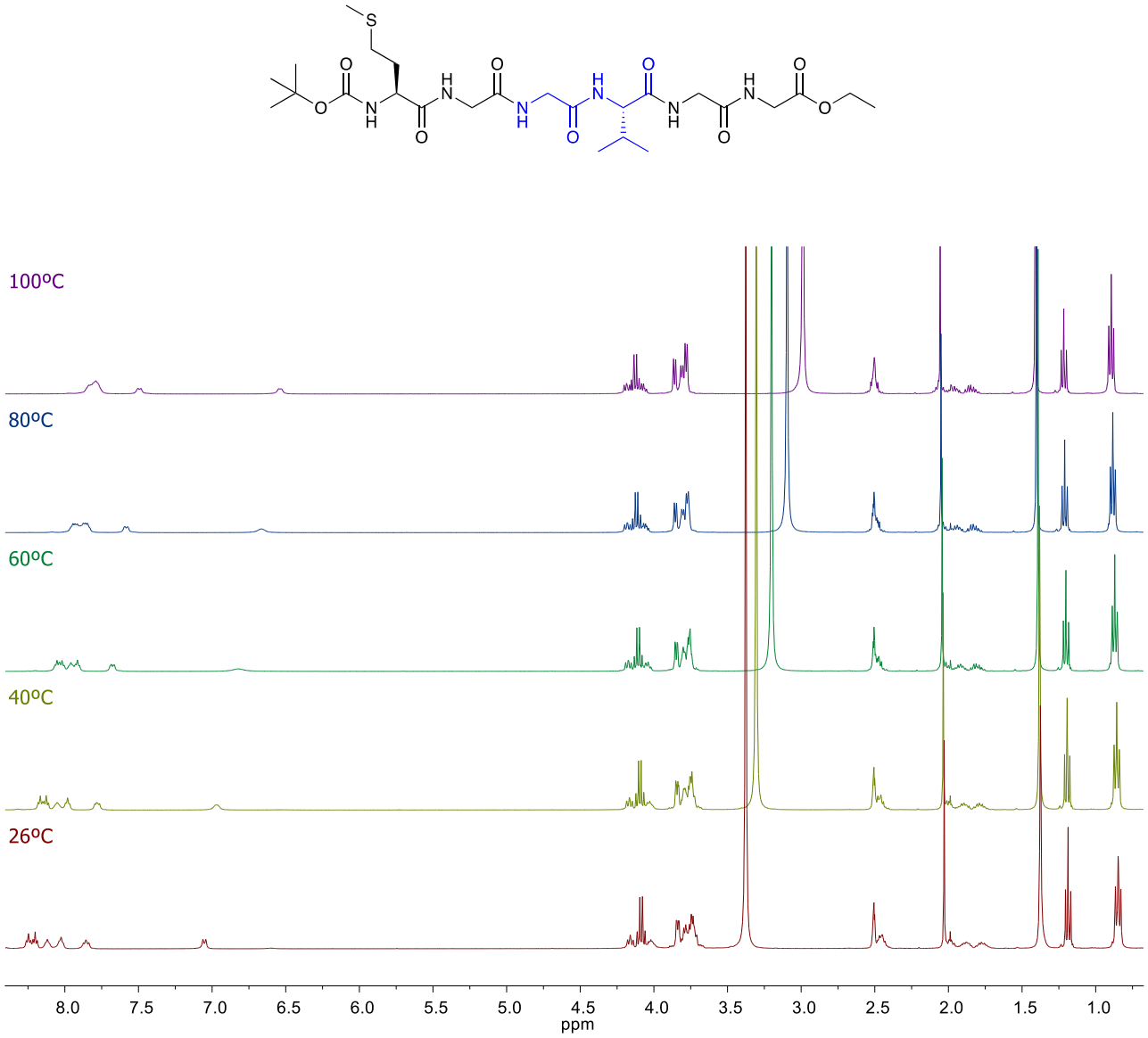

Fig. S52. [1]H-NMR spectra (DMSO-d_6, 400 MHz) of hexapeptide **1m** at 26, 40, 60, 80 and 100ºC.

5. *LC-ESI/MS for tripeptide **1b***

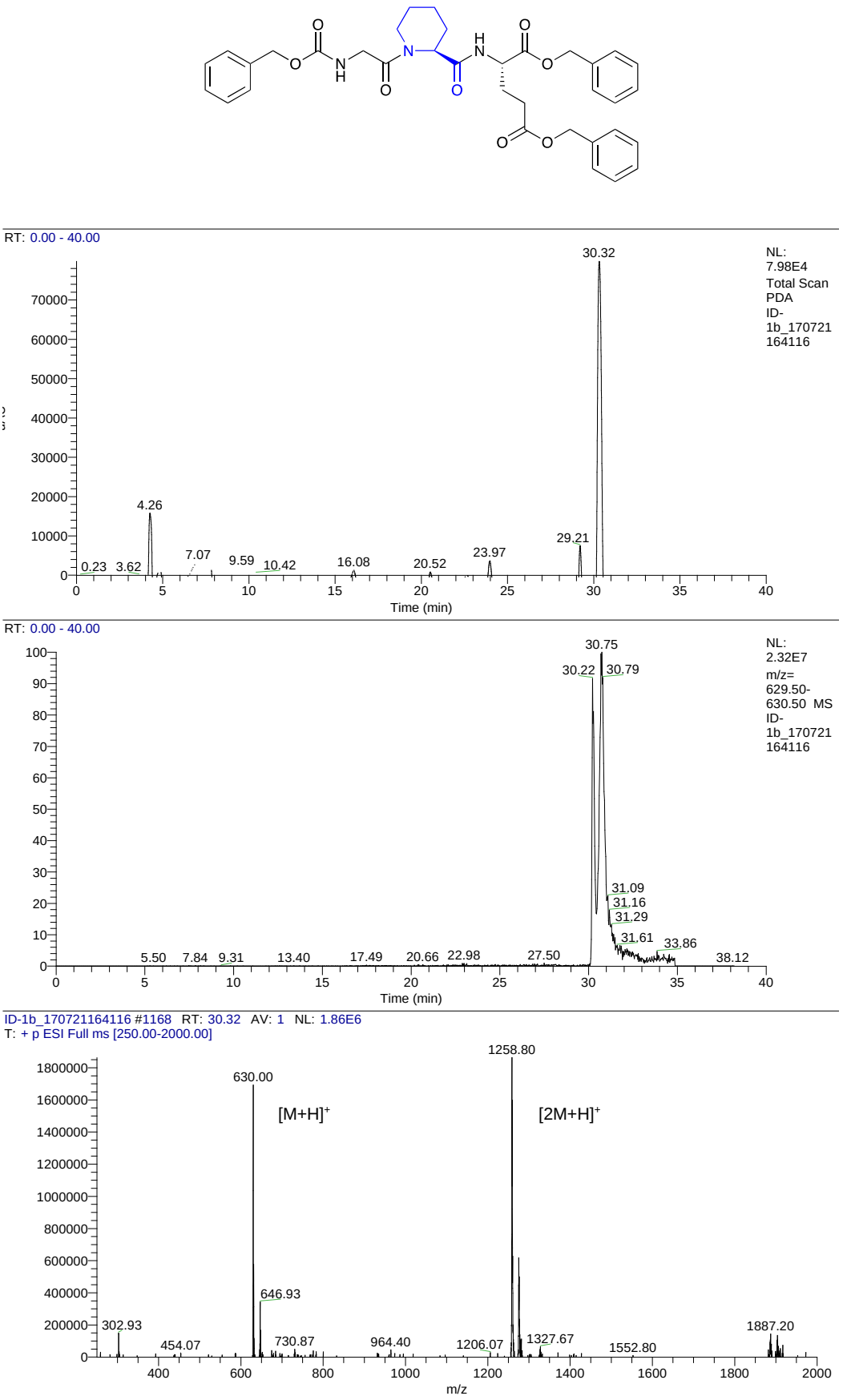

Fig. S53. LC-ESI/MS (Orbitrap, positive mode) for tripeptide **1b** (t_R =30.32 min).

6. *[1]H-NMR experiments for tripeptide **1b** in DMSO-d_6 at 26, 40, 60, 80, 100 and 115ºC*

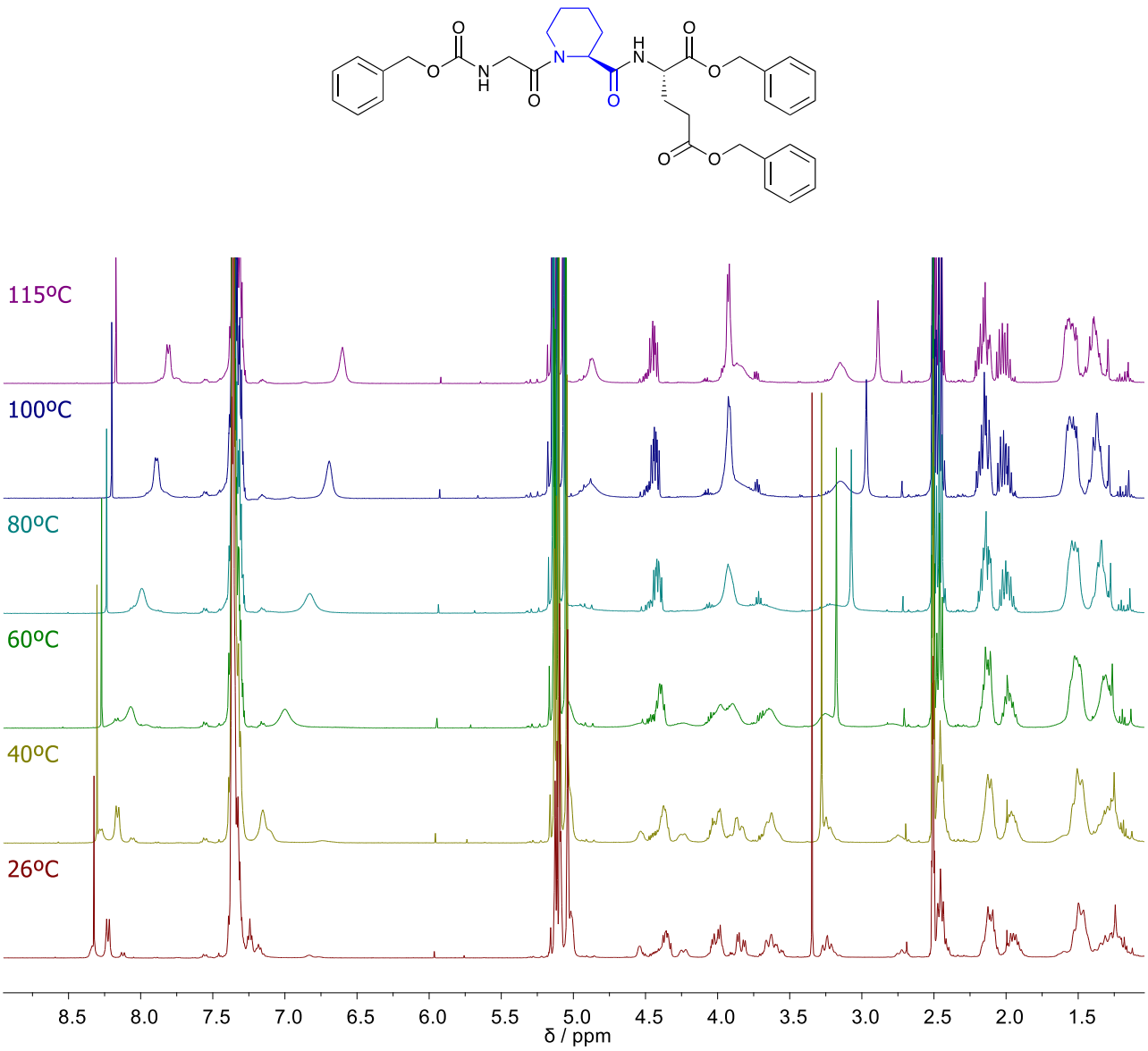

Fig. S54. [1]H-NMR spectra (DMSO-d_6, 400 MHz) of tripeptide **1b** at 26, 40, 60, 80, 100 and 115ºC.