

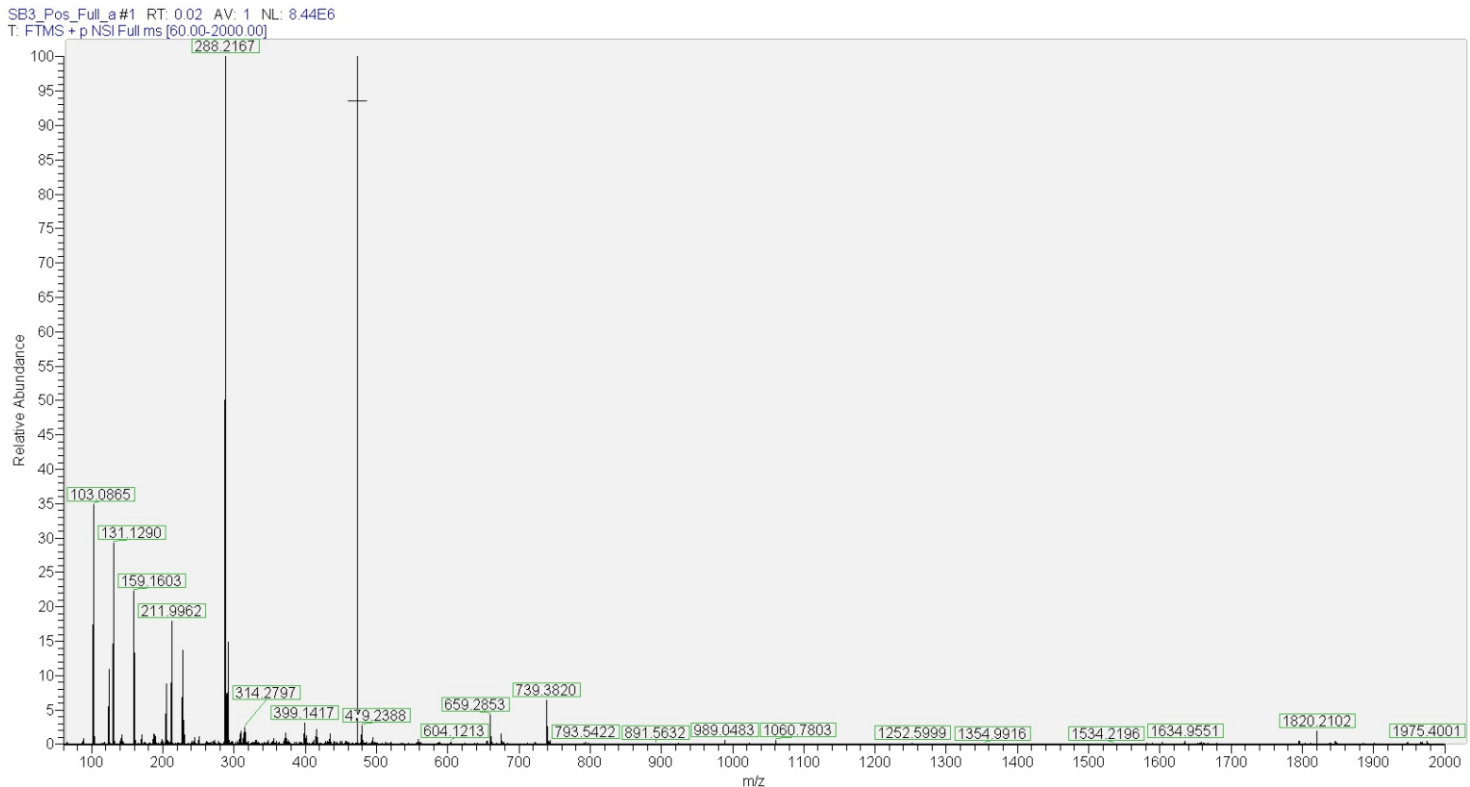


Fig. S1. 60-200 Da MS/MS spectrum of the gluey silk secretion of the orb web spider *Argiope keyserlingi* (Araneidae).

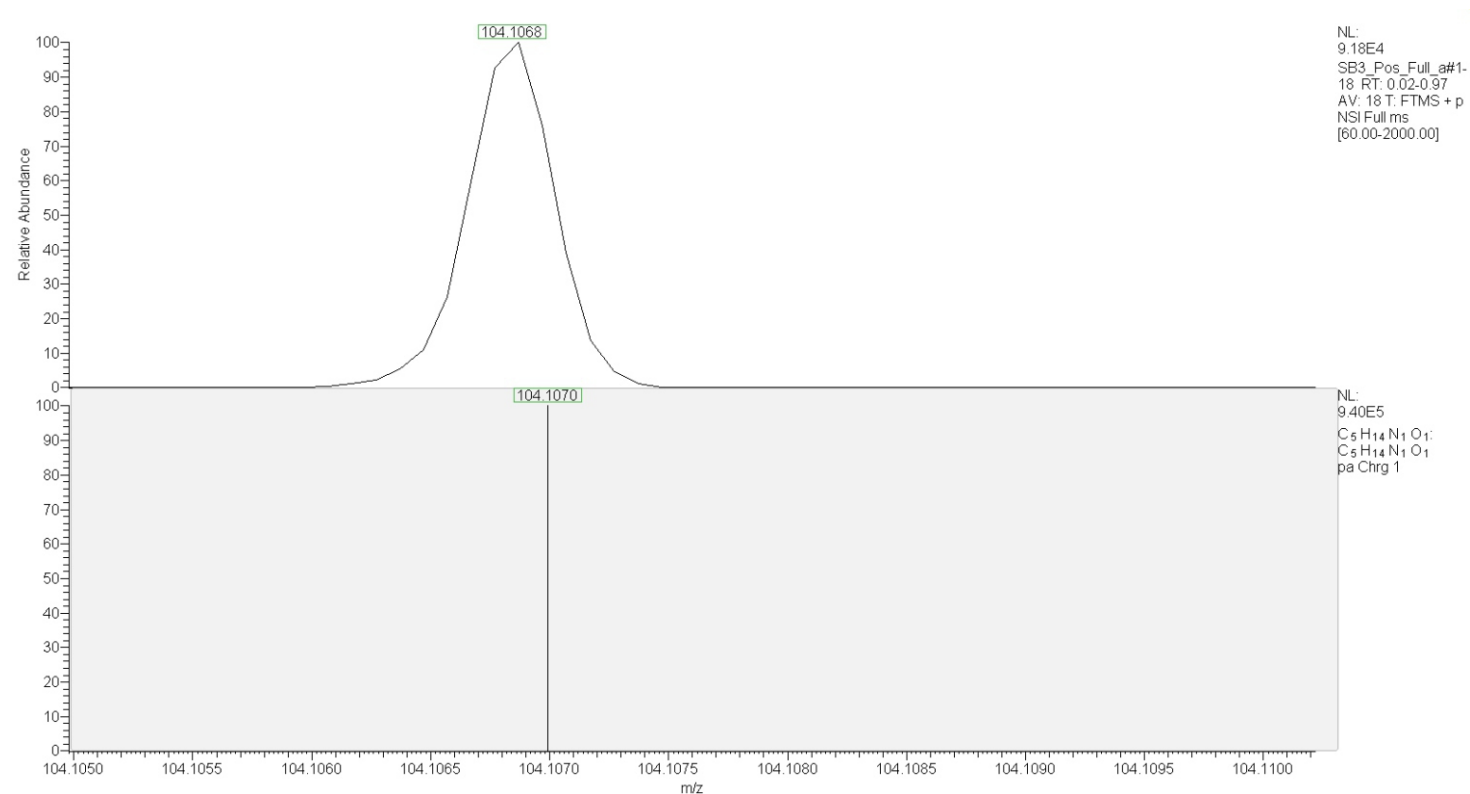


Fig. S2. Zoomed in MS/MS spectrum of the gluey silk secretion of the orb web spider *Argiope keyserlingi* (Araneidae), confirming the presence of choline.

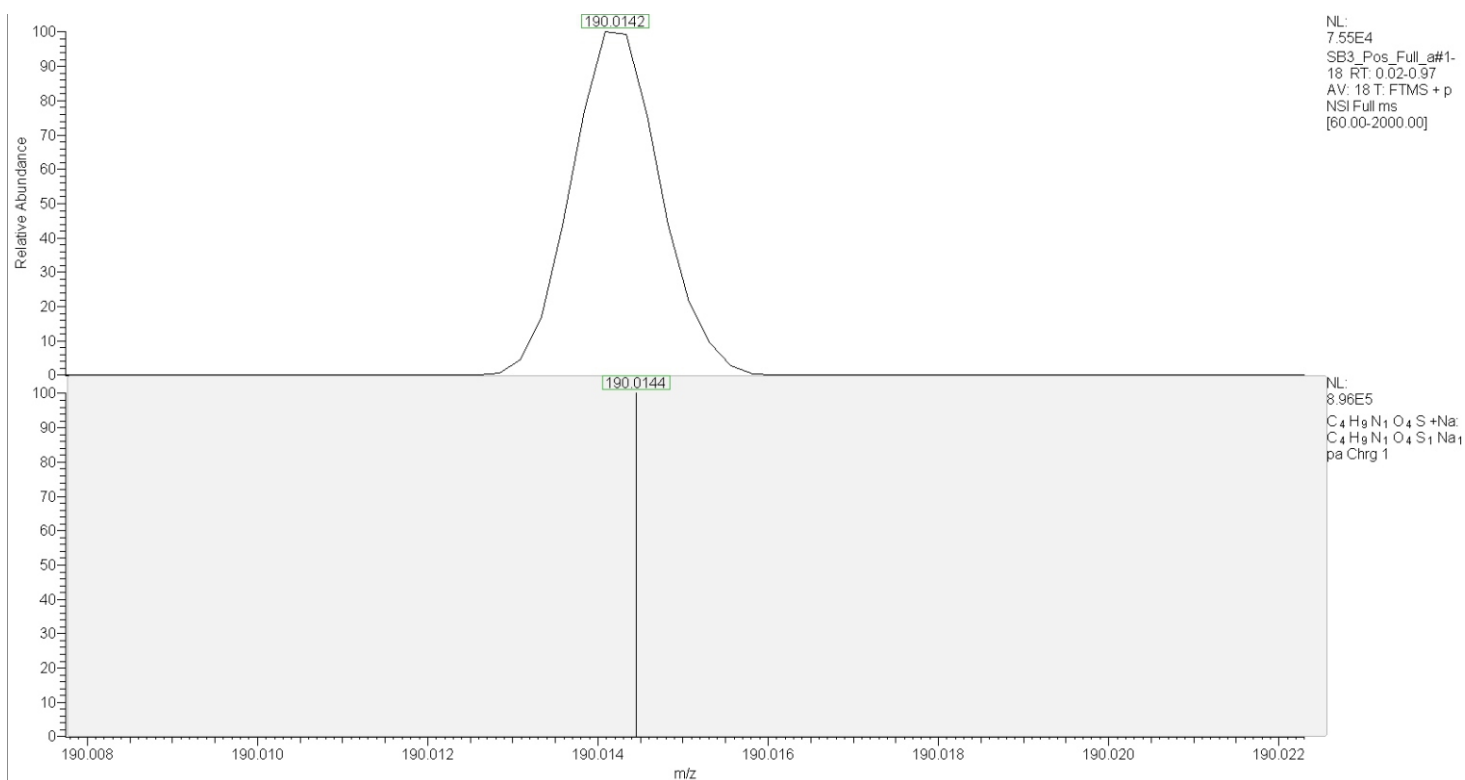


Fig. S3. Zoomed in MS/MS spectrum of the gluey silk secretion of the orb web spider *Argiope keyserlingi* (Araneidae), confirming the presence of N-acetyltaurine.

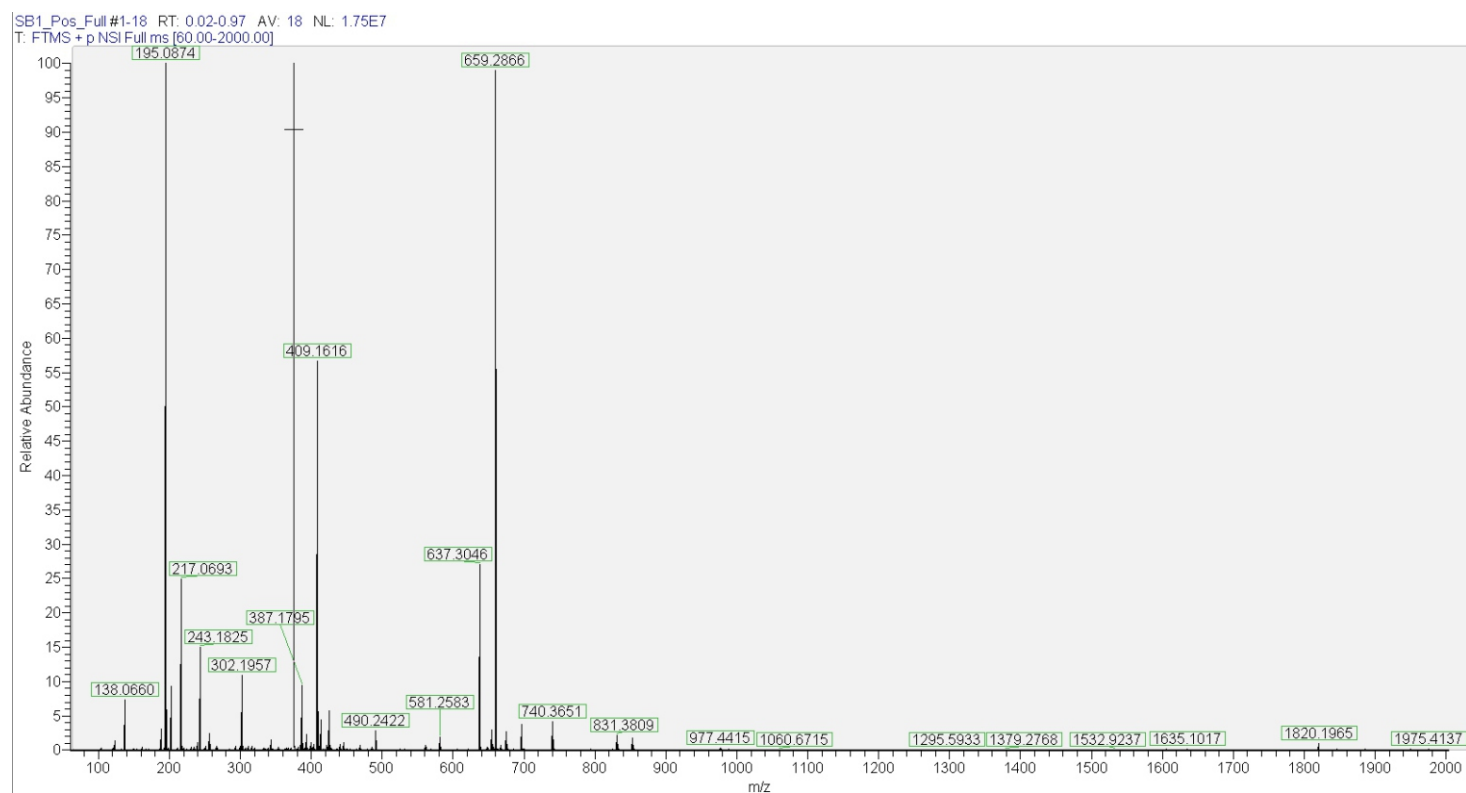


Fig. S4. 60-200 Da MS/MS spectrum of the gluey silk secretion of the cob web spider *Latrodectus hasselti* (Theridiidae).

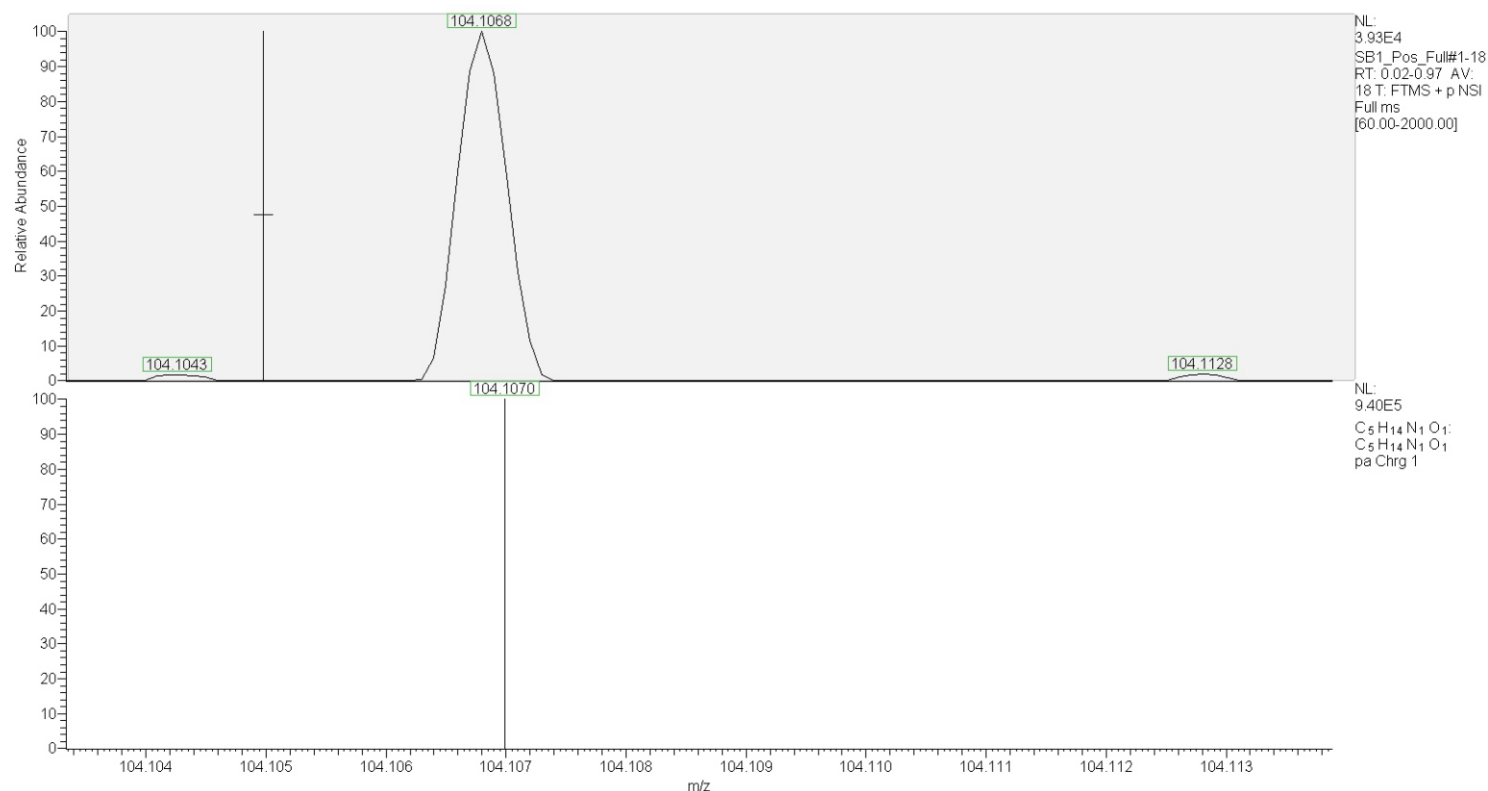


Fig. S5. Zoomed in MS/MS spectrum of the gluey silk secretion of the cob web spider *Latrodectus hasselti* (Theridiidae), confirming the presence of choline.

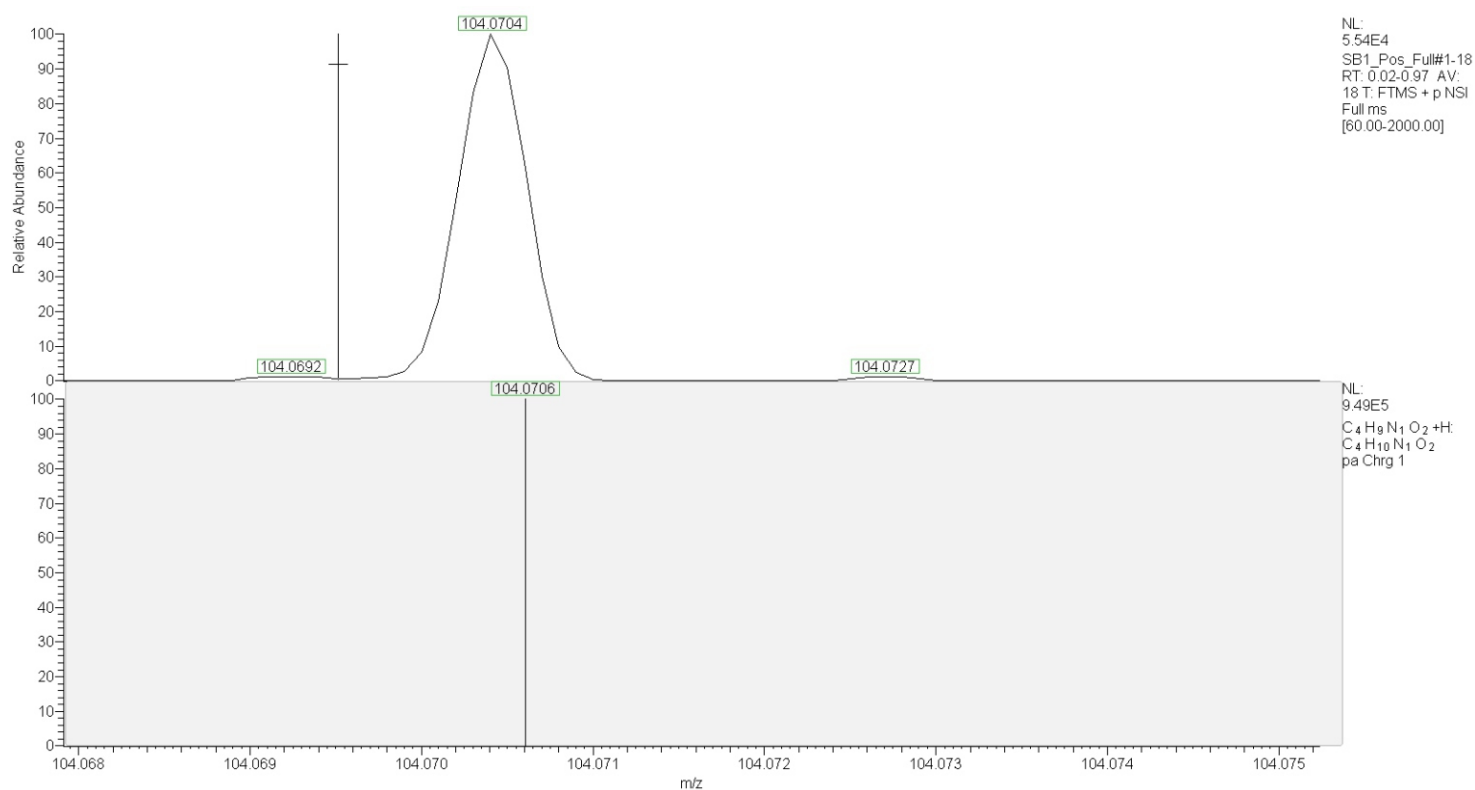


Fig. S6. Zoomed in MS/MS spectrum of the gluey silk secretion of the cob web spider *Latrodectus hasselti* (Theridiidae), confirming the presence of GABA.

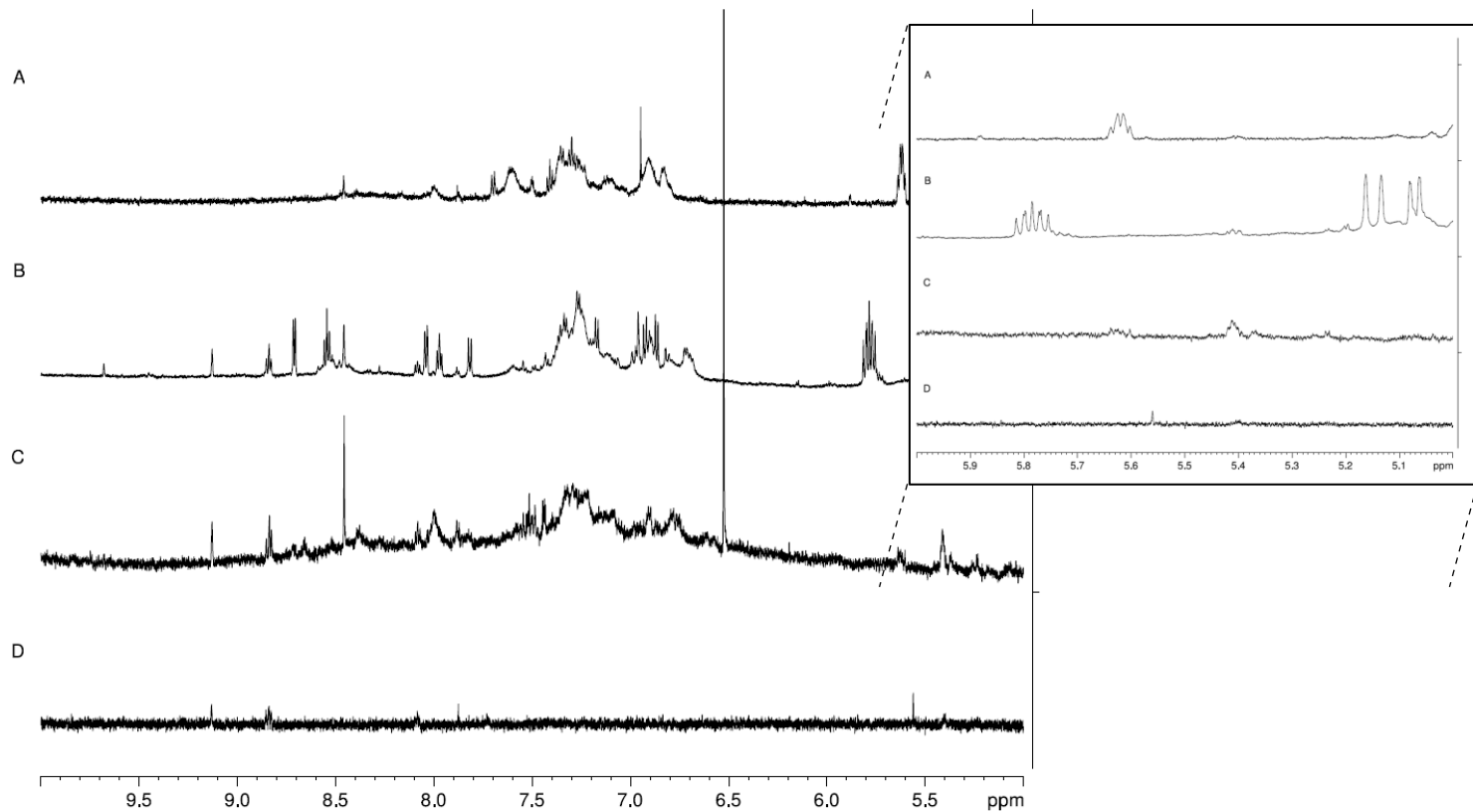


Fig. S7. ^1H NMR spectra of *Argiope keyserlingi* (A), *Latrodectus hasselti* (B), *Steatoda grossa* (C), and *Pholcus phalangioides* (D) glues across the 5 to 10 ppm spectral range. The 5 to 6 ppm spectral range is enhanced as an inset.

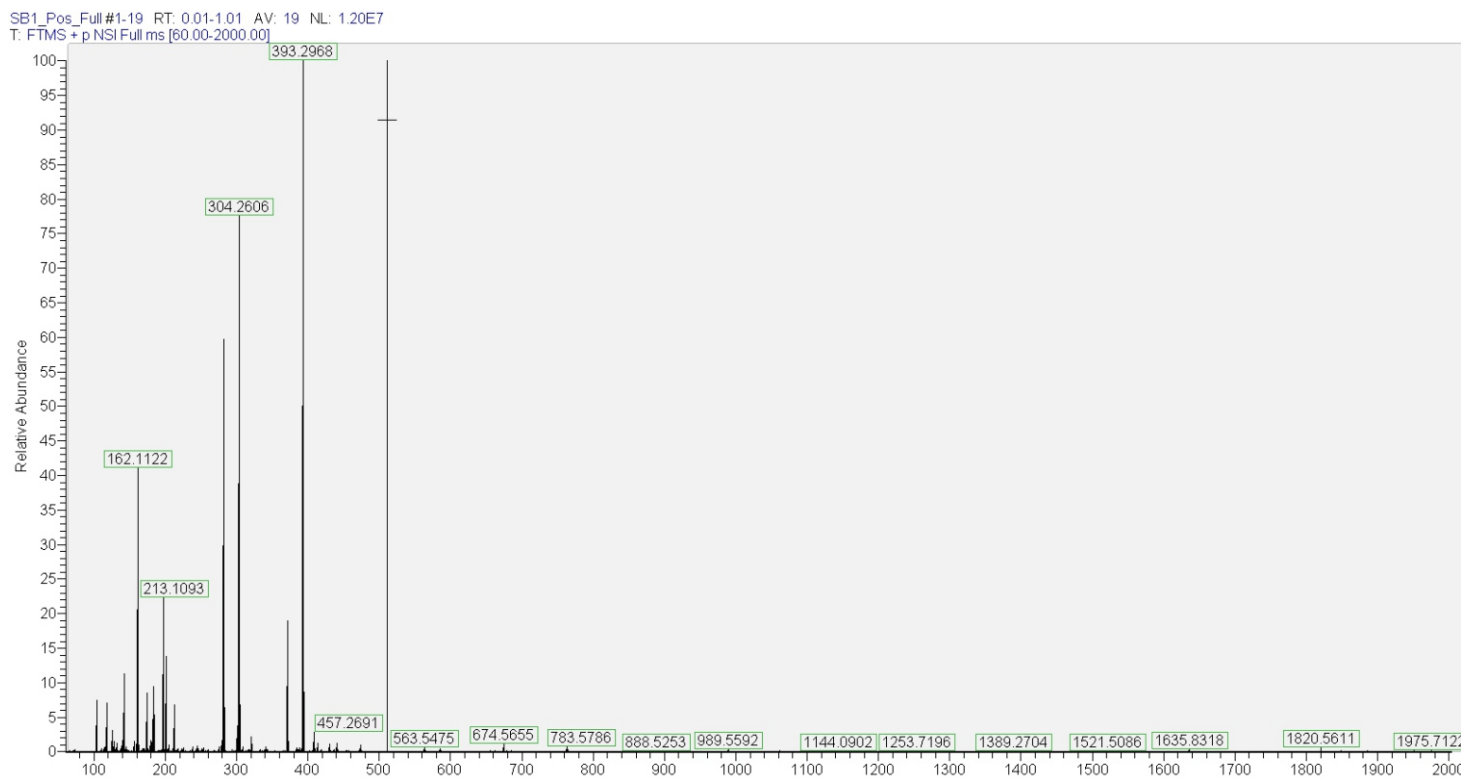


Fig. S8. 60-200 Da MS/MS spectrum of the gluey silk secretion of the cob web spider *Steatoda grossa* (Theridiidae).

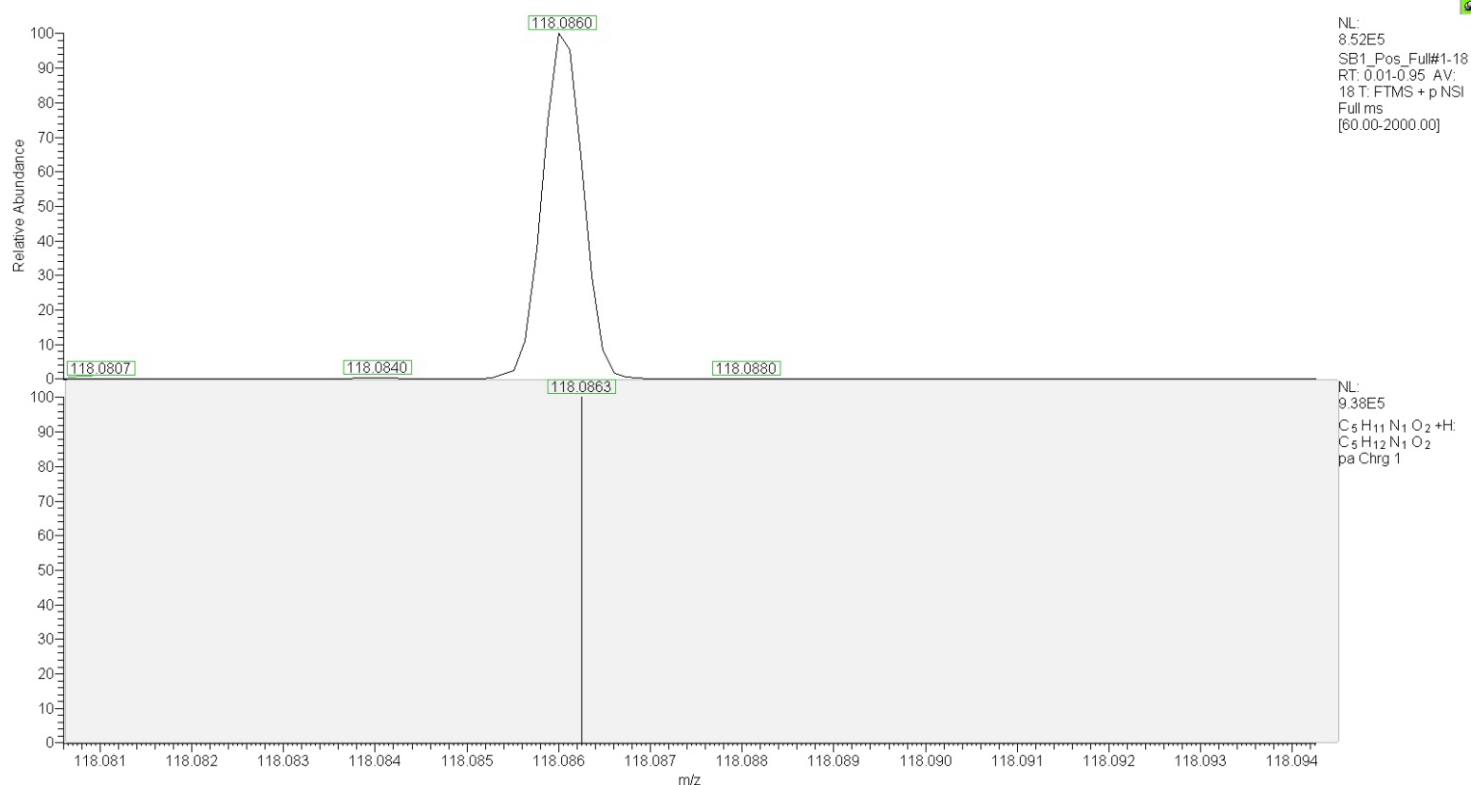


Fig. S9. Zoomed in MS/MS spectrum of the gluey silk secretion of the cob web spider *Steatoda grossa* (Theridiidae), confirming the presence of betaine.

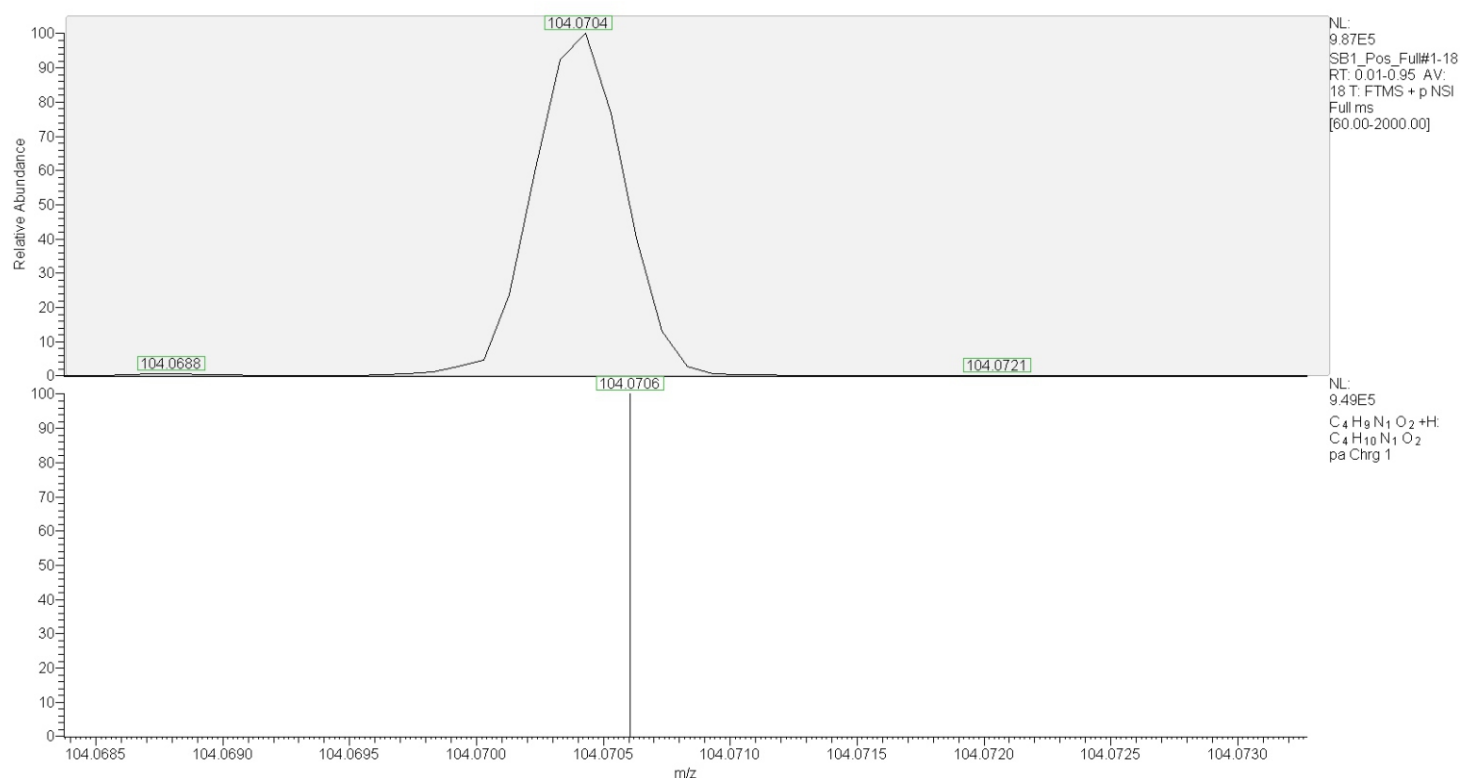


Fig. S10. Zoomed in MS/MS spectrum of the gluey silk secretion of the cob web spider *Steatoda grossa* (Theridiidae), confirming the presence of GABA.

SB2_Pos_Full#1-19 RT: 0.01-1.01 AV: 19 NL: 6.22E6
T: FTMS + p NSI Full ms [60.00-2000.00]

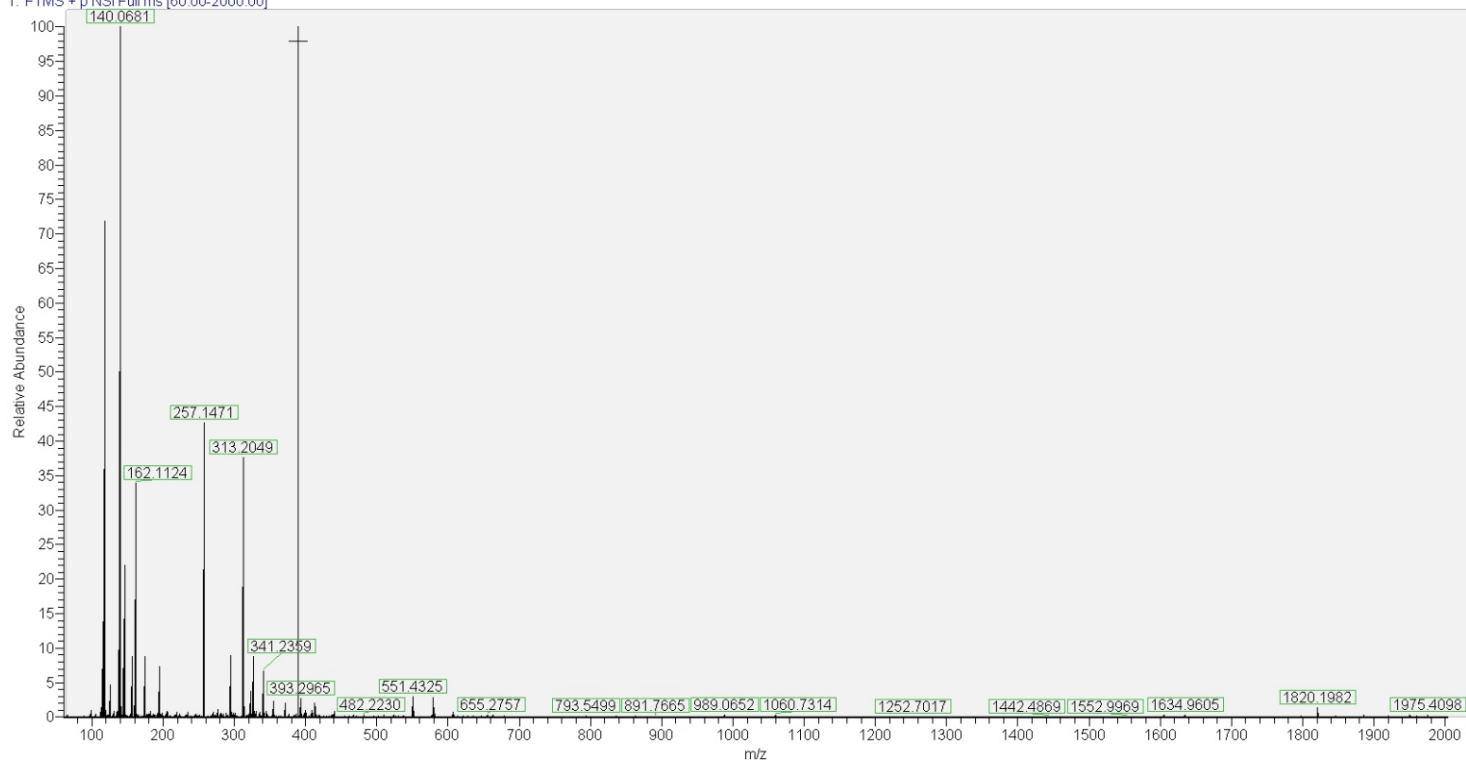


Fig. S11. 60-200 Da MS/MS spectrum of the gluey silk secretion of the daddy-longeg spider *Pholcus phalangioides* (Pholcidae).

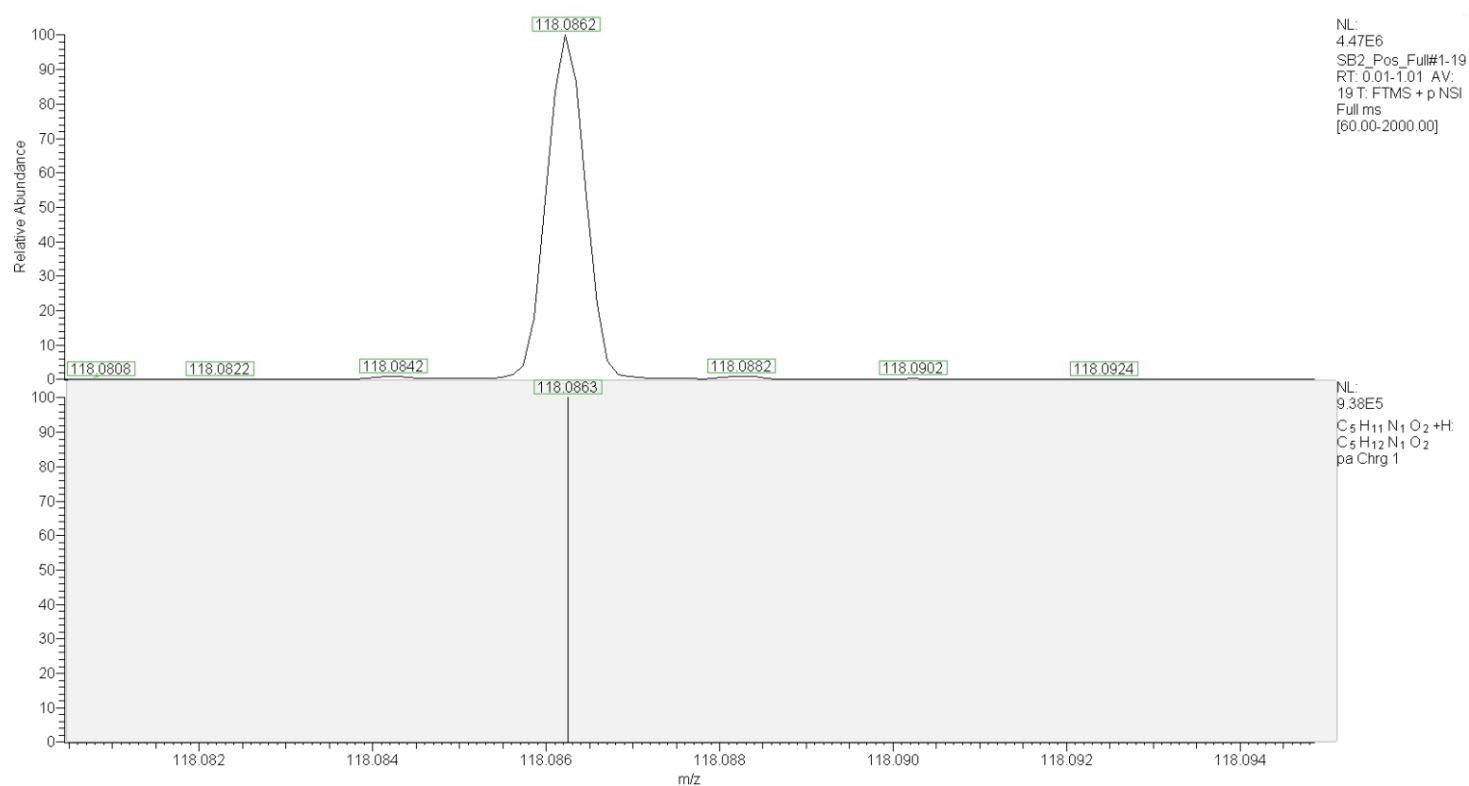


Fig. S12. Zoomed in MS/MS spectrum of the gluey silk secretion of the daddy-longeg spider *Pholcus phalangioides* (Pholcidae), confirming the presence of betaine.

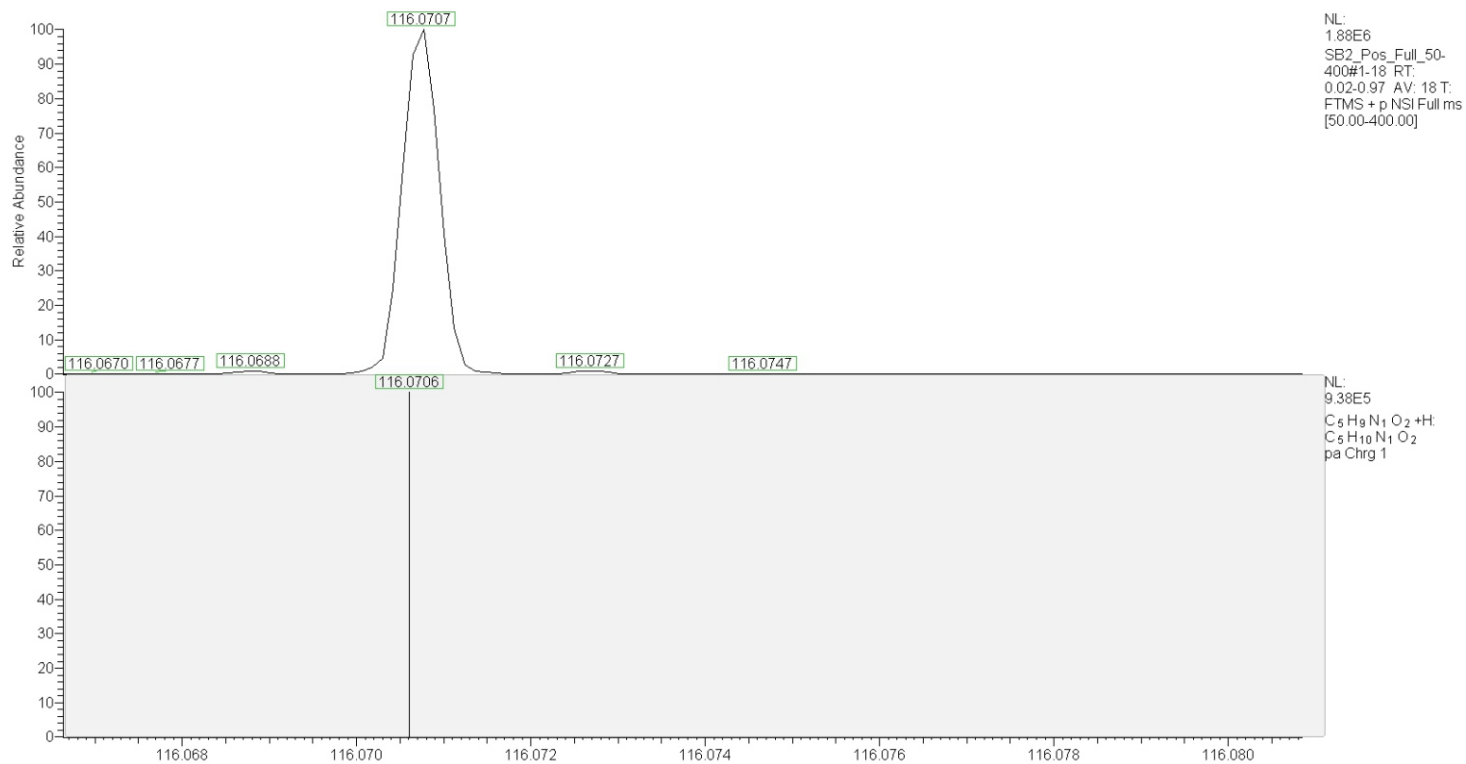


Fig. S13. Zoomed in MS/MS spectrum of the gluey silk secretion of the daddy-longeg spider *Pholcus phalangioides* (Pholcidae), confirming the presence of proline.