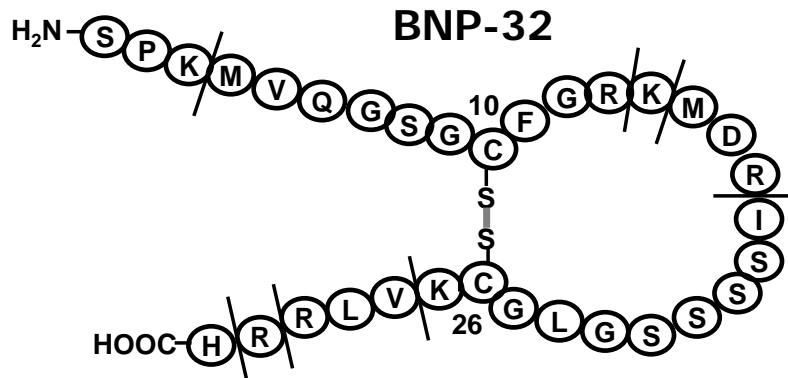


## Supporting Information Available

**Supplementary Figure S1. Disulfide bond and tryptic sites in Brain Natriuretic peptide-32.** Tryptic sites in BNP-32 are indicated by black lines. The disulfide bridge between Cys10 and Cys26 in BNP-32 forms a loop structure. Cleavage at any of the tryptic sites in this loop region (Arg13, Lys14 and Arg17) results in peptides with an inter-chain disulfide bond, and failure to cleave in the loop region results in peptides with an intra-chain disulfide bond.



**Supplementary Table S1. Inter- and intra-chain disulfide bonds identified in BNP-32.** Examples of disulfide-linked peptides identified from BNP-32. Grey lines indicate a disulfide bridge and black lines indicate an un-cleaved peptide sequence. Amino acid sequence derived from the sequence tags is underlined in each peptide.

Precursor Mass	Sequence Tag(s)	Peptide Mass	Modification mass	DiS species	MMA (ppm)
1975.9072	MVQ***** IS*****	1040.4531 937.4539	935.4529 1038.4408	<u>MVQGSGCFGR</u> <u>ISSSSGLGCK</u>	3.2
2344.1629	-VQG***** ISSSSGL*****	1040.4531 1305.7074	1303.6958 1038.4242	<u>MVQGSGCFGR</u> <u>ISSSSGLGCKVLR</u>	2.3
3186.6154	SPkm***** M*****SS	1352.6329 1835.9782	1833.9752 1350.6257	<u>SPKMQGSGCFGR</u> <u>MDRISSSGLGCKVLR</u>	2.3
3149.5533	mvQ***** ***RH	1168.5481 679.4241	1990.6086 2470.1242	<u>MVQGSGCF</u> <u>HRRLVKCG</u>	1.8
3461.7522	spKM*****R ***RRH	1882.8963 679.4241	1578.8300 2782.31	<u>SPKMQGSGCFRI</u> <u>HRRLVKCGLG</u>	3.9
3168.5792	spKmvQ--S*****	3170.5932	-2.0139	<u>SPKMQGSGCFGRK</u> <u>RLVKCGLGS</u>	0.2