SUPPLEMENTAL MATERIALS

Site-specific proteomic analysis of lipoxidation adducts in cardiac mitochondria reveals chemical diversity of 2-alkenal adduction

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- Figure S1-77: Mass spectral data for the peptides identified with 2-alkenal adductions.
- Figure S78: Proposed structures of ARP-specific ions observed in the MS/MS spectra reported.
- Figure S79: Biological network and pathway analysis of the carbonylated proteins identified in this study.

AT5F1_RAT: ATP synthase B chain





Figure S1. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the $[M+2H]^{2+}$ ion of the ARP labeled, acrolein modified peptide C*IGDLK; monoisotopic m/z_{calc} 509.25; accuracy $\Delta(m/z) = 0.00$ Da

AT5F1_RAT: ATP synthase B chain



Figure S2. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*IGDLK; monoisotopic m/z_{calc} 1017.49; accuracy Δ (m/z) = -0.04 Da

ATP5H_RAT: ATP synthase D chain





Figure S3. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the $[M+2H]^{2+}$ ion of the ARP labeled, acrolein modified peptide NC*AQFVTGSQAR; monoisotopic m/z_{calc} 825.88; accuracy $\Delta(m/z) = -0.01$ Da

ATP5H_RAT: ATP synthase D chain





Figure S4. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide NC*AQFVTGSQAR; monoisotopic m/z_{calc} 1650.75; accuracy Δ (m/z) = 0.00 Da





Figure S5. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the $[M+2H]^{2+}$ ion of the ARP labeled, acrolein modified peptide GC*SMGEYFR; monoisotopic m/z_{calc} 709.79; accuracy $\Delta(m/z) = -0.02$ Da





Figure S6. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide GC*SMGEYFR; monoisotopic m/z_{calc} 1418.57; accuracy Δ (m/z) = 0.01 Da





Figure S7. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the $[M+2H]^{2+}$ ion of the ARP labeled, acrolein modified peptide SGC*SMGEYFR; monoisotopic m/z_{calc} 753.30; accuracy $\Delta(m/z) = -0.03$ Da





Figure S8. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide SGC*SMGEYFR; monoisotopic m/z_{calc} 1505.60; accuracy Δ (m/z) = 0.01 Da





Figure S9. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the $[M+2H]^{2+}$ ion of the ARP labeled, acrolein modified peptide YSGC*SMGEYFR; monoisotopic m/z_{calc} 834.83; accuracy $\Delta(m/z) = -0.02$ Da

Y-S-G-C* $\overline{\mathbf{S}}$ - $\overline{\mathbf{M}}$ -**G-E** $\overline{\mathbf{Y}}$ -**F**- $\overline{\mathbf{R}}$



Figure S10. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide YSGC*SMGEYFR; monoisotopic m/z_{calc} 1668.66; accuracy Δ (m/z) = -0.01 Da





Figure S11. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide LAPYSGC*SMGEYFR; monoisotopic m/z_{calc} 975.42; accuracy Δ (m/z) = -0.04 Da

ATPB_RAT: ATP synthase subunit beta





Figure S12. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, crotonaldehyde modified peptide H*GGYSVFAGVGER; monoisotopic m/z_{calc} 859.91; accuracy Δ (m/z) = -0.04 Da

ATPB_RAT: ATP synthase subunit beta



Figure S13. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, crotonaldehyde modified peptide H*GGYSVFAGVGER; monoisotopic m/z_{calc} 1718.81; accuracy Δ (m/z) = -0.01 Da





Figure S14. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide GLC*GAIHSSVAK; monoisotopic m/z_{calc} 756.38; accuracy Δ (m/z) = 0.02 Da



Figure S15. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide GLC*GAIHSSVAK; monoisotopic m/z_{calc} 1511.75; accuracy Δ (m/z) = 0.07 Da



A.



Figure S16. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide H*SDQFLVSFK; monoisotopic m/z_{calc} 788.88; accuracy Δ (m/z) = -0.02 Da



Figure S17. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide H*SDQFLVSFK; monoisotopic m/z_{calc} 1576.76; accuracy Δ (m/z) = -0.04 Da



Α.



Figure S18. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide GEVPC*TVTTAFPLDEAVLSELK; monoisotopic m/z_{calc} 896.78; accuracy Δ (m/z) = 0.06 Da



Figure S19. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide GEVPC*TVTTAFPLDEAVLSELK; monoisotopic m/z_{calc} 2688.33; accuracy Δ (m/z) = 0.12 Da

CX6B1_MOUSE, Cytochrome c oxidase subunit VIb isoform





Figure S20. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide GGDVSVC*EWYR; monoisotopic m/z_{calc} 820.35; accuracy Δ (m/z) = -0.02 Da



Figure S21. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide QIEGHTIC*ALGDGAAWPVQGLIR; monoisotopic m/z_{calc} 925.47; accuracy Δ (m/z) = -0.03 Da



Figure S22. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide NALISHLDGTTPVC*EDIGR; monoisotopic m/z_{calc} 794.05; accuracy Δ (m/z) = -0.01 Da



Figure S23. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide NALISHLDGTTPVC*EDIGR; monoisotopic m/z_{calc} 2380.14; accuracy Δ (m/z) = -0.01 Da



Figure S24. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide YFYDQC*PAVAGYGPIEQLSDYNR; monoisotopic m/z_{calc} 3038.34; accuracy Δ (m/z) = -0.07 Da



Figure S25. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide NALANPLYC*PDYR; monoisotopic m/z_{calc} 939.93; accuracy Δ (m/z) = -0.04 Da

QCR2_RAT: Ubiquinol-cytochrome-c reductase complex core protein 2







Figure S26. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide NALANPLYC*PDYR; monoisotopic m/ z_{calc} 1878.86; accuracy Δ (m/z) = 0.00 Da



Figure S27. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, HNE modified peptide NALANPLYC*PDYR; monoisotopic m/z_{calc} 1978.95; accuracy Δ (m/z) = 0.04 Da

QCR2_RAT: Ubiquinol-cytochrome-c reductase complex core protein 2







Figure S28. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide NPLYC*PDYR; monoisotopic m/z_{calc} 755.33; accuracy Δ (m/z) = 0.04 Da

DHSA_RAT: Succinate dehydrogenase [ubiquinone] flavoprotein subunit







Figure S29. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide GH*SLLHTLYGR; monoisotopic m/z_{calc} 541.61; accuracy Δ (m/z) = 0.00 Da

DHSA_RAT: Succinate dehydrogenase [ubiquinone] flavoprotein subunit





Figure S30. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide GH*SLLHTLYGR; monoisotopic m/z_{calc} 1622.82; accuracy Δ (m/z) = -0.01 Da







Figure S31. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide AVEEQYSC*EYGSGR; monoisotopic m/z_{calc} 1946.80; accuracy Δ (m/z) = 0.01 Da





Figure S32. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide GADIMYTGTVDC*WR; monoisotopic m/z_{calc} 978.92; accuracy Δ (m/z) = 0.03 Da



Figure S33. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide GADIMYTGTVDC*WR; monoisotopic m/z_{calc} 1956.84; accuracy Δ (m/z) = 0.01 Da



Figure S34. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide TGTVDC*WR; monoisotopic m/z_{calc} 653.79; accuracy Δ (m/z) = 0.00 Da





Figure S35. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide EFNGLGDC*LTK; monoisotopic m/z_{calc} 783.36; accuracy Δ (m/z) = -0.02 Da


Figure S36. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide YFAGNLASGGAAGATSLC*; monoisotopic m/z_{calc} 1000.45; accuracy Δ (m/z) = -0.01 Da





Figure S37. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, HNE modified peptide VSFAK*DFLAGGVAAAISK; monoisotopic m/z_{calc} 741.07; accuracy Δ (m/z) = -0.02 Da

ADT1_RAT: ADP/ATP translocase 1 C*-F-V-Y-P-L-D-F-A-R

У₈

 $y_7 y_6 y_5$

 y_3

y₁



Figure S38. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide C*FVYPLDFAR; monoisotopic m/z_{calc} 800.38; accuracy Δ (m/z) = -0.03 Da

ADT1_RAT: ADP/ATP translocase 1



Figure S39. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*FVYPLDFAR; monoisotopic m/z_{calc} 1599.74; accuracy Δ (m/z) = 0.05 Da

ADT1_RAT: ADP/ATP translocase 1



Figure S40. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide DIMYTGTVDC*WR; monoisotopic m/z_{calc} 1828.78; accuracy Δ (m/z) = -0.07 Da

ADT1_RAT: ADP/ATP translocase 1

 $\textbf{K-G-A-D-I-M-Y}^{y_9} - \textbf{T-Y-F}^{y_7} - \textbf{T-V-D-Y}^{y_4} - \textbf{V}^{y_3} - \textbf{W-R}^{y_1}$



Figure S41. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide KGADIMYTGTVDC*WR; monoisotopic m/z_{calc} 2084.94; accuracy Δ (m/z) = 0.04 Da

ADT2_RAT: ADP/ATP translocase 2





Figure S42. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide TGTLDC*WR; monoisotopic m/z_{calc} 660.79; accuracy Δ (m/z) = 0.00 Da

VDAC1_RAT: Voltage-dependent anionselective channel protein 1



Figure S43. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide YQVDPDAC*FSAK; monoisotopic m/z_{calc} 856.87; accuracy Δ (m/z) = 0.00 Da



Figure S44. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide YQVDPDAC*FSAK; monoisotopic m/z_{calc} 1712.74; accuracy Δ (m/z) = 0.03 Da



Figure S45. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide VC*NYGLIFTQK; monoisotopic m/z_{calc} 827.91; accuracy Δ (m/z) = -0.01 Da

ACON_RAT: Aconitate hydratase





Figure S46. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide VGLIGSC*TNSSYEDMGR; monoisotopic m/z_{calc} 1079.47; accuracy Δ (m/z) = 0.01 Da

ACON_RAT:Aconitate hydratase ^y₉ ^y₈ ^y₇ ^y₆ ^y₅ ^y₄ ^y₃ ^y₂ ^y₁ **V-G-L-I-G-S-C*-T-N-S-S-Y-E-D-M-G-R**



Figure S47. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide VGLIGSC*TNSSYEDMGR; monoisotopic m/z_{calc} 2157.94; accuracy Δ (m/z) = -0.05 Da





Figure S48. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide VAVPSTIHC*DHLIEAQLGGEK; monoisotopic m/z_{calc} 862.77; accuracy Δ (m/z) = 0.00 Da

IDHP_RAT: Isocitrate dehydrogenase [NADP]



Figure S49. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*ATITPDEAR; monoisotopic m/z_{calc} 1445.65; accuracy Δ (m/z) = 0.00 Da

IDHP_RAT: Isocitrate dehydrogenase [NADP]



Figure S50. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide DLAGC*IHGLSNVK; monoisotopic m/z_{calc} 848.42; accuracy Δ (m/z) = 0.00 Da

MDHM_RAT: Malate dehydrogenase y_{12} y_{11} y_{10} y_{9} y_{8} y_{7} y_{6} y_{4} y_{3} y_{2} E-T-E-C*-T-Y-F-S-T-P-L-L-L-G-K





Figure S51. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide ETEC*TYFSTPLLLGK; monoisotopic m/z_{calc} 1036.00; accuracy Δ (m/z) = -0.01 Da



Figure S52. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide ETEC*TYFSTPLLLGK; monoisotopic m/z_{calc} 2070.99; accuracy Δ (m/z) = -0.05 Da



Figure S53. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, HHE modified peptide ETEC*TYFSTPLLLGK; monoisotopic m/z_{calc} 2129.03; accuracy Δ (m/z) = -0.05 Da



Figure S54. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide TEC*TYFSTPLLLGK; monoisotopic m/z_{calc} 971.48; accuracy Δ (m/z) = 0.02 Da



Figure S55. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide TEC*TYFSTPLLLGK; monoisotopic m/z_{calc} 1941.94; accuracy Δ (m/z) = -0.04 Da

MDHM_RAT: Malate dehydrogenase E-G-V-I-E-C*-S-F-V-Q-S-K

 $y_9 y_8 y_7$



Figure S56. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide EGVIEC*SFVQSK; monoisotopic m/z_{calc} 847.90; accuracy Δ (m/z) = 0.00 Da

G-Y-L-G-P+E+Q+L-P+D-C*-L-K



Figure S57. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide GYLGPEQLPDC*LK; monoisotopic m/z_{calc} 901.43; accuracy Δ (m/z) = 0.00 Da





Figure S58. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide TIIPLISQC*TPK; monoisotopic m/z_{calc} 841.95; accuracy Δ (m/z) = 0.01 Da



Figure S59. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide GC*DVVVIPAGVPR; monoisotopic m/z_{calc} 825.93; accuracy Δ (m/z) = 0.00 Da



Figure S60. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide VDGMDILC*VR; monoisotopic m/z_{calc} 1489.70; accuracy Δ (m/z) = -0.06 Da

ODPA_RAT: Pyruvate dehydrogenase E1 component alpha subunit





Figure S61. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, crotonaldehyde modified peptide H*GFTFTR; monoisotopic m/z_{calc} 624.80; accuracy Δ (m/z) = -0.02 Da

ODPB_RAT: Pyruvate dehydrogenase E1 component beta subunit



Figure S62. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide EGIEC*EVINLR; monoisotopic m/z_{calc} 822.40; accuracy Δ (m/z) = 0.00 Da

ETFD_RAT: Electron transfer flavoproteinubiquinone oxidoreductase



Figure S63. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+3H]³⁺ ion of the ARP labeled, acrolein modified peptide AAQIGAHTLSGAC*LDPAAFK; monoisotopic m/z_{calc} 771.05; accuracy Δ (m/z) = -0.02 Da



Figure S64. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide AAQIGAHTLSGAC*LDPAAFK; monoisotopic m/z_{calc} 2311.13; accuracy Δ (m/z) = 0.01 Da

MMSA_RAT: Methylmalonate-semialdehyde dehydrogenase



Figure S65. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide C*MALSTAVLVGEAK; monoisotopic m/z_{calc} 881.44; accuracy Δ (m/z) = -0.03 Da



Figure S66. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*MALSTAVLVGEAK; monoisotopic m/z_{calc} 1761.87; accuracy Δ (m/z) = 0.07 Da





Figure S67. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide EANSIVITPGYGLC*AAK; monoisotopic m/z_{calc} 1038.52; accuracy Δ (m/z) = -0.04 Da

NNTM_MOUSE: NAD(P) transhydrogenase



Figure S68. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide EANSIVITPGYGLC*AAK; monoisotopic m/z_{calc} 2076.03; accuracy Δ (m/z) = -0.01 Da

CH60_RAT: 60kDa heat shock protein



Figure S69. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*EFQDAYVLLSEK; monoisotopic m/z_{calc} 1913.88; accuracy Δ (m/z) = -0.07 Da

ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor





Figure S70. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 1158.05; accuracy Δ (m/z) = 0.02 Da

ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor





Figure S71. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, acrolein modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 2315.09; accuracy Δ (m/z) = 0.01 Da
ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor y₁₈ y₁₅ y₁₄ y₁₃ y₁₂ y₁₁ y₁₀ y₉ y₈ y₇ y₆ y₅ y₄ y₃ y₂ y₁



Figure S72. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, beta-hydroxyacrolein modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 2331.09; accuracy Δ (m/z) = 0.05 Da

ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor y₁₆ y₁₃ y₁₂ y₁₁ y₁₀ y₉ y₈ y₇ y₆ y₅ y₄ y₃ y₂ y₁ C*-I-G-A-I-A-M-T-E-P-G-A-G-S-D-L-Q-G-V-R



Figure S73. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, HHE modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 2373.14; accuracy Δ (m/z) = -0.11 Da

ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor

 $\begin{array}{c} y_{15} \\ y_{13} \\ y_{12} \\ y_{11} \\ y_{11$



Figure S74. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, ONE modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 2413.17; accuracy Δ (m/z) = -0.08 Da

ACADL_RAT: Long-chain specific acyl-CoA dehydrogenase, mitochondrial precursor y_{12} y_{11} y_{9} y_{8} y_{6} y_{5} y_{5} y_{3} y_{2} y_{1} C*-I-G-A-I-A-M-T-E-P-G-A-G-S-D-L-Q-G-V-R



Figure S75. (A) Full mass spectrum and (B) MS/MS spectrum acquired by MALDI-TOF/TOF of the [M+H]⁺ ion of the ARP labeled, HNE modified peptide C*IGAIAMTEPGAGSDLQGVR; monoisotopic m/z_{calc} 2415.18; accuracy Δ (m/z) = -0.10 Da

KCRB_RAT: Creatine kinase B-type





Figure S76. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide LGYILTC*PSNLGTGLR; monoisotopic m/z_{calc} 1024.03; accuracy Δ (m/z) = -0.01 Da

KCRB_RAT: Creatine kinase B-type





Figure S77. (A) Full mass spectrum and (B) MS/MS spectrum acquired by ESI-Q-TOF of the [M+2H]²⁺ ion of the ARP labeled, acrolein modified peptide ILTC*PSNLGTGLR; monoisotopic m/z_{calc} 857.44; accuracy Δ (m/z) = -0.01 Da

Observed ARP related neutral losses



Observed ARP related fragment ions





Figure S78. (A) Structure of ARP-HNE modified Cys, indicating the various neutral losses observed in CID MS/MS experiments. (B) Fragment ions generated by the ARP tag in CID MS/MS experiments



Figure S78. Biological network and pathway analysis from the carbonylated proteins generated with function data from the KEGG database. Carbonylated proteins are colored as yellow nodes and the functional pathways are displayed as colored nodes. White colored nodes represent pathways for which only one protein was identified.