Supp. Fig. 1. Total ion current chromatogram of peptides from native GAPDH digested with trypsin. Purified rabbit muscle GAPDH was digested with trypsin and ESI-LC-MS was performed with a LCQ ion trap mass spectrometer (LCQ Deca, Thermo Finnigan, San Jose, CA).

Supp. Fig. 2. A) MALDI-TOF analysis of the tryptic digest of OA-NO_2-treated GAPDH peptide #23 (m/z 2214.10), shows the concomitant existence of both the non-modified (m/z 2214.10) and OA-NO_2-modified peptide #23 (m/z 2541.53). **B) PSD MALDI-TOF analysis of modified peptide #23** ($[M+H]^+$ 2541.53) gives a principal product ion of m/z 437.7, corresponding to the immonium ion of the histidine-OA-NO_2 adduct.

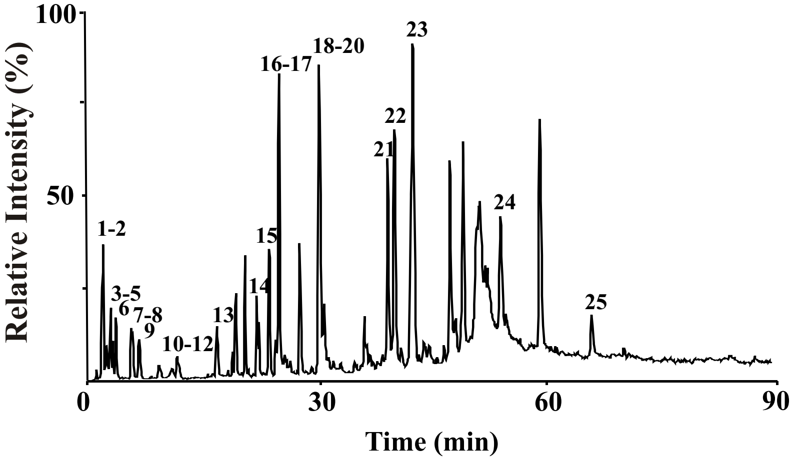
Supp. Fig. 3. MS/MS spectrum of the doubly-charged ion at m/z 462.06 corresponding to OA-NO_2-adducted peptide #2. Inset: Amino acid sequence indicating major C- and N- terminal fragment ion detected by full-scan MS/MS (LTQ, Thermo Electron, San Jose, CA). **Table. List of MS/MS fragment ions m/z from peptide #2. Ions that are detected are highlighted in color.**

Supp. Fig. 4. MS/MS spectrum of triply-charged ion at m/z 478.02 corresponding to OA-NO_2-adducted peptide #21, labeling doubly-charged ions (LTQ, Thermo Electron, San Jose, CA). Inset: Amino acid sequence indicating major C- and N- terminal fragment ion detected by full-scan MS/MS. **Table. List of MS/MS fragment ions m/z from the OA-NO_2-modified peptide #21. Ions that are detected are highlighted in color.**

Supp. Fig. 5. MS/MS spectrum of the triply-charged ion at m/z 687.89 corresponding to OA-NO_2-adducted peptide #19, labeling doubly-charged ions (LTQ, Thermo Electron, San Jose, CA). Inset: Amino acid sequence indicating the major C- and N- terminal fragment ions detected by full-scan MS/MS. **Table. List of MS/MS fragment ions m/z from the OA-NO_2-modified peptide #19. Ions that are detected are highlighted in color.**

Supp. Table 1: GAPDH Tryptic Peptides Identified by LC-MS

Peak/ Pept. #	**RT (min)**	**Sequence Position**	**Sequence**	**Molecular Mass (MI, Da.)**	**z**	**Theoretical m/z**	**Measured m/z**	**Control**	**OA-NO$_2$ Treated**
1	2.05	258-260	VVK	344.25	1	345.25	345.2	X	X
2	**2.06**	**105-110**	**AGAH^{108}LK**	**595.35**	**1**	**596.35**	**596.3**	**X**	↓
3	2.5	184-191	TVDGPSGK	759.38	1	760.38	760.4	X	X
4	2.62	53-58	FHGTVK	687.38	1	688.38	688.1	X	X
5	2.85	14-17	LVTR	487.32	1	488.32	488.9	X	X
6	3.17	18-24	AAFNSGK	693.35	1	694.35	694.7	X	X
7	5.14	78-83	DPANIK	656.36	1	657.36	657.3	X	X
8	5.3	252-256	YDDIK	652.31	1	653.31	653.2	X	X
9	6.11	137-142	YDNSLK	738.36	1	739.36	739.3	X	X
10	8.41	261-268	QASEGPLK	828.44	1	829.44	829.3	X	X
11	10.7	59-63	AENGK	517.26	1	518.26	518.5	X	X
12	10.76	192-194	LWR	473.28	1	474.28	474.2	X	X
13	15.52	64-69	LVINGK	642.41	1	643.41	643.4	X	X
14	20.46	3-10	VGVNGFGR	804.43	1	805.43	805.5	X	X
15	21.91	217-224	VIPELNGK	868.51	1	869.51	869.4	X	X
16	23.11	225-231	LTGMAFR	794.42	1	795.42	795.5	X	X
17	23.19	198-212	GAAQNIIPASTGAAK	1368.74	1	1369.74	1369.7	X	X
18	**27.86**	**321-331**	**VVDLMVH^{327}MASK**	**1228.64**	**1**	**1229.64**	**1229.5**	**X**	↓
19	**28.02**	**143-159**	**IVSNASC^{149}TTNC^{153}LAPLAK**	**1704.86**	**1**	**1705.86**	**1703.8**	**X**	↓↓↓
20	28.1	70-77	AITIFQER	976.54	1	977.54	977.5	X	X
21	**36.36**	**232-245**	**VPTPNVSVVDLTC^{244}R**	**1498.79**	**1**	**1499.79**	**1499.7**	**X**	↓↓↓
22	37.23	307-320	LISWYDNEFGYSNR	1762.8	1	1763.8	1763.7	X	X
23	**39.39**	**116-136**	**VIISAPSADAPMFVMGVNH^{134}EK**	**2212.11**	**2**	**1107.05**	**1107.1**	**X**	↓
24	50	160-183	VI**H**^{162}D**H**^{164}FGIVEGLMTTV**H**^{176}AITATQK	2617.38	2	1309.69	1309.7	X	X
25	61.26	25-52	VDVVAINDPFIDL**H**^{38}YMVYMFQYDST**H**^{50}GK	3316.57	3	1106.52	1106.5	X	X



Supp. Fig. 1
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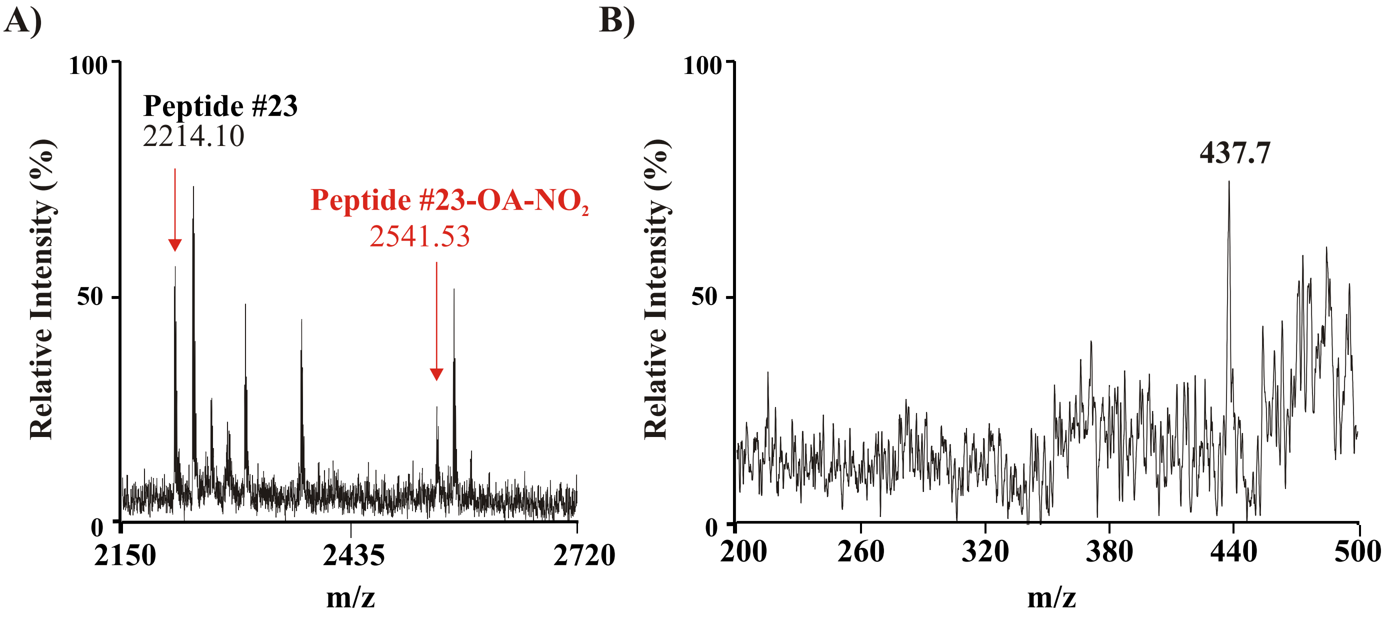

Supp. Fig 2
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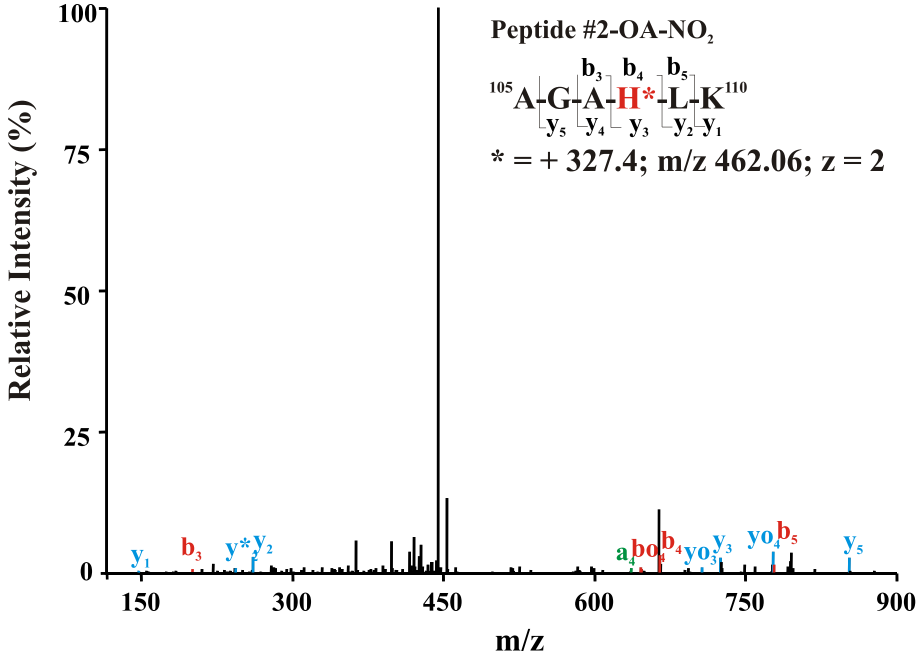

Table. *MS-MS data of OA-NO$_2$-modified peptide #2*

	AA	a	b	y	
1	A	44.05	72.04	-	6
2	G	101.07	129.07	852.71	5
3	A	172.11	200.10	795.69	4
4	H*	636.57	664.56	724.66	3
5	L	749.65	777.65	260.20	2
6	K	-	-	147.11	1

Supp. Fig 3 & Table
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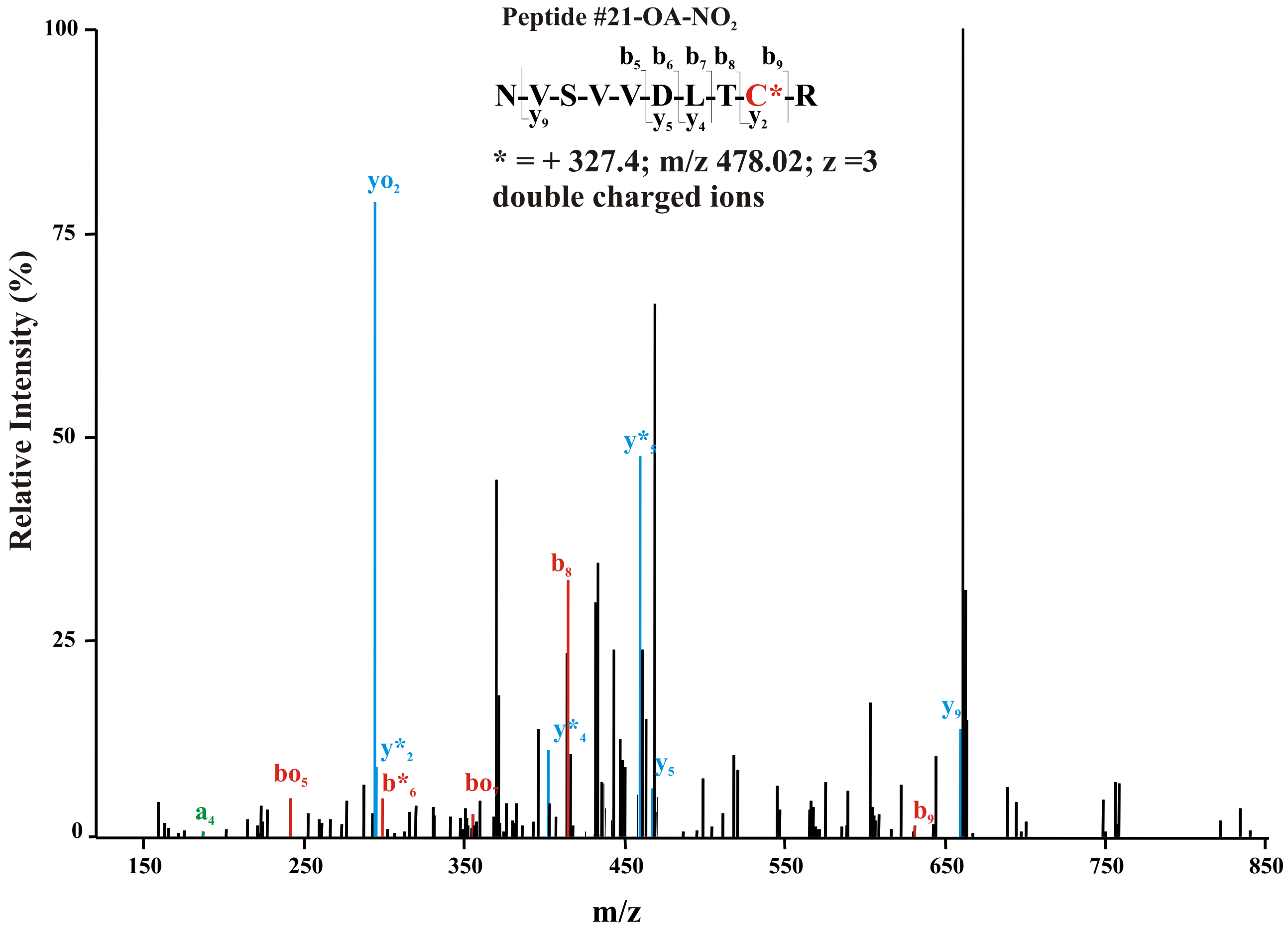

Table. ***MS-MS data of OA-NO$_2$-modified peptide #21***

	AA	a	b	b*	y	y*	
1	N	44.03	58.03	49.52	-	-	10
2	V	93.57	107.56	99.05	659.97	651.45	9
3	S	137.08	151.08	142.57	610.43	601.92	8
4	V	186.62	200.61	192.10	566.92	558.40	7
5	V	236.15	250.15	241.63	517.38	508.87	6
6	D	293.66	307.66	299.15	467.85	459.33	5
7	L	350.21	364.20	355.69	410.33	401.82	4
8	T	400.73	414.73	406.21	353.79	345.28	3
9	C*	615.93	629.93	621.42	303.27	294.75	2
10	R	-	-	-	88.06	79.55	1

Supp. Fig 4 & Table
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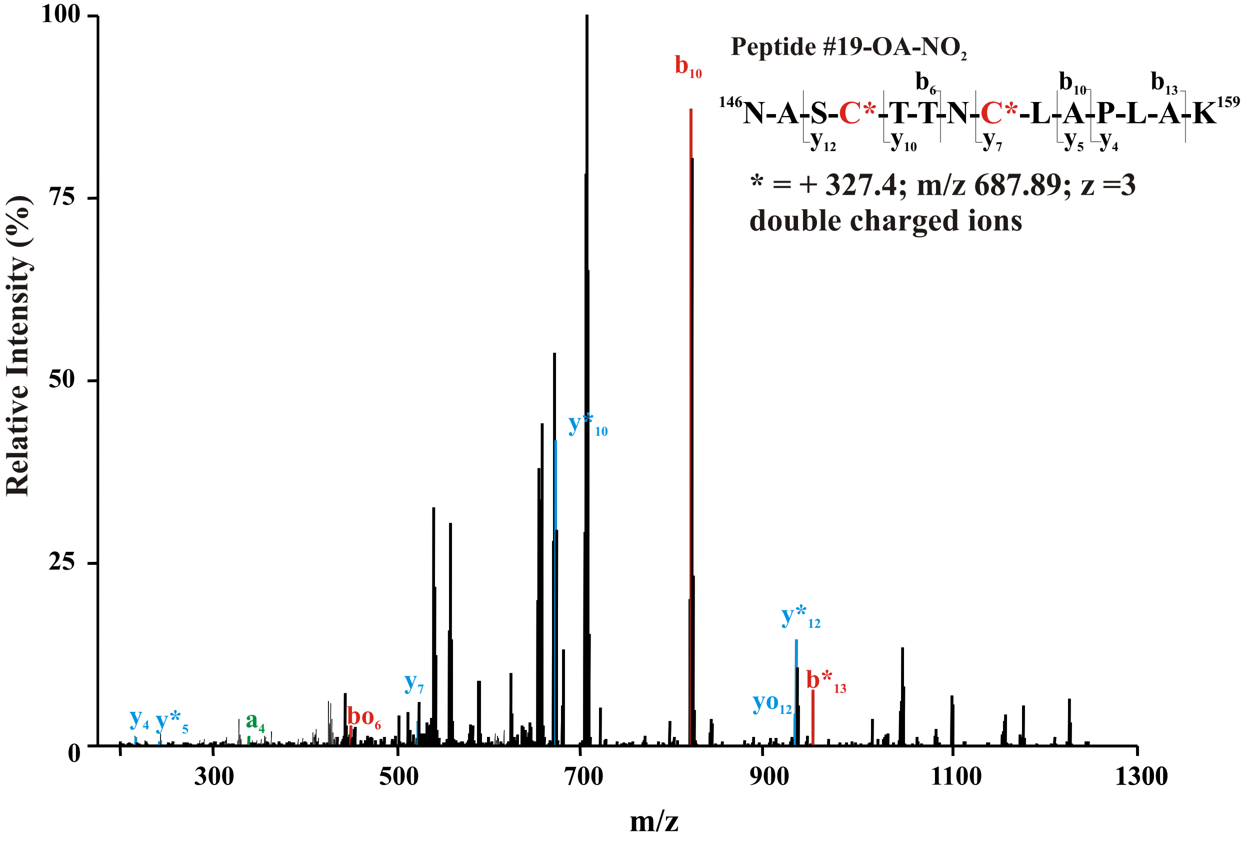

Table. *MS-MS data of OA-NO$_2$-modified peptide #19*

	AA	a	b	b*	y	y*	
1	N	44.03	58.03	49.52	-	-	14
2	A	79.55	93.55	85.03	974.22	965.71	13
3	S	123.07	137.06	128.55	938.70	930.19	12
4	C*	338.27	352.27	343.75	895.19	886.67	11
5	T	388.79	402.79	394.28	679.98	671.47	10
6	T	439.32	453.32	444.80	629.46	620.94	9
7	N	496.34	510.34	501.33	578.93	570.42	8
8	C*	711.54	725.54	716.54	521.91	513.40	7
9	L	768.09	782.08	773.08	306.71	298.19	6
10	A	803.60	817.60	808.60	250.17	241.65	5
11	P	852.13	866.13	857.12	214.65	206.13	4
12	L	908.67	922.67	913.67	166.12	157.61	3
13	A	944.19	958.19	949.18	109.58	101.07	2
14	K	-			74.06	65.55	1

Supp. Fig 5 & Table
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