Supplementary Figure 1A. Peptide sequencing using MS/MS analysis of tryptic peptide from modified peptide at GAPDH 247C to dehydroalanine, sulfinic acid and sulfonic acid.
Supplementary Figure 1B. Quantitative analyses of various modifications at redox-active sites (152 and 156C) in peptide 146\textsuperscript{IISNASCTTNCLAPLAK}\textsuperscript{162} (1718.8695 Da) in GAPDH were performed measuring the integrated area of extracted MS chromatogram of precursor ions.
Supplementary Figure 2. Peptide sequencing using MS/MS analysis of thiosulfonate of NDPK A as a further modified intra-disulfide linked “GDFCIQVGR” and “ANCER”. The annotation marked by ‘C^\Delta’ represents dehydroalanine (DHA, -34 Da)
Supplementary Figure 3A. Peptide sequencing using MS/MS analysis of tryptic peptide from modified peptide at NDPK A 109C to dehydroalanine (-34 Da), cyano (+25 Da) and sulfur dioxide (+64 Da).
Supplementary Figure 3B. Quantitative analysis of various modifications on redox active site at NDPK A 109C (106GDFC1QVGR114, 993.4701 Da) were performed using MS chromatogram of precursor ions.
Experimental procedure for 3

To a stirred solution of 2 (210 mg, 0.393 mmol) in anhydrous CH$_2$Cl$_2$ (5 mL) was added mCPBA (264 mg, 77% max, 1.18 mmol) at 0°C. After stirring for 5 h at room temperature, the solvent was evaporated off. The residue was purified by flash column chromatography on silica gel (EtOAc/Hexane=1:2 to 1:1) to yield 86.6 mg (0.152 mmol, 39%) of 3.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.31 (br, 10H), 5.99 (d, 1H, $J$ = 7.5 Hz), 5.89 (d, 1H, $J$ = 7.3 Hz), 5.10-5.08 (m, 4H), 4.75-4.69 (m, 1H), 4.65-4.61 (m, 1H), 3.97 (d, 2H, $J$ = 5.0 Hz), 3.74 (s, 3H), 3.73 (s, 3H), 3.65 (dd, 1H, $J$ = 14.8 Hz, $J$ = 4.7 Hz), 3.46 (dd, 1H, $J$ = 14.3 Hz, $J$ = 6.1 Hz).

Supplementary Figure 4. Synthetic schemes of model compounds 2 and 3.
Supplementary Figure 5. To confirm which chemical labeling path has priority in scheme 2, we examined the modifications of NDPK A treated without and with H₂O₂ and then N-ethylmaleimide (C and D), or treated with NEM first and then with H₂O₂ (E). (A) Separation of each sample on 12 % SDS-PAGE under non-reducing condition. (B) Quantative analysis of chemical modifications of each sample were summarized.
Supplementary Figure 5. (C), (D) and (E) MS chromatogram of precursor ions corresponding to each modification in sample C, D, and E in Supplementary Figure 4A were extracted (0.1 Da window) and integrated.
Supplementary Figure 6. Peptide sequencing using MS/MS analysis of tryptic peptide from modified peptide at PRX6 47C to Cys47 + 87 Da (O + AA) and + 103 Da (O₂ + AA).
Supplementary Figure 7. Identification of Cys-SO₂-SH (m/z 701.78) in recombinant PRX6 using in solution digestion-MS/MS analysis without SDS-PAGE separation. Human PRX6 was observed from AB frontier (Cat.No. LF-P0004. Korea). Their oxidation was obtained by incubation at 37°C for 0.5 h in mild condition.