Labelling of Endogenous Target Protein via N-S Acyl Transfer-Mediated Activation of N-Sulfanylethylanilide

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**Fig. S1.** Mass spectral analysis of the labelling site of hCA1 using SEAL 4. (a) The primary sequence of hCA1. (b) Crystal structure of hCA1 complexed with 3-Actoxymercuri-4-aminobenzenesulfonamide (PDB ID: 1CZM). The amino acid (Lys 137) modified by 4 is highlighted by a colored stick model. (c) nanoLC-MS/MS analysis of the fragment labelled at Lys137.
S2. (a) HPLC analysis of the SEAL 6 (○, 10 μM) with butylamine (1 M) in 50 mM HEPES buffer (pH 7.2) at 37 ºC for 5 min > (left), 24 h (middle) or 48 h (right) of incubation. × denotes oxidated SEAL 6. However, the aminolysis product S1 and S2 was not detected. (b) Chemical structures of S1, S2. (c) HPLC analysis of the SEAL 6 (△, 10 μM) with L-Cys methyl ester (1 mM) in 50 mM HEPES buffer (pH 7.2) at 37 ºC for 5 min > (left), 24 h (middle) or 48 h (right) of incubation.
$^1$H NMR spectrum of Fmoc-L-Lys(4-sulfamoyl-benzoyl)-OH

$^{13}$C NMR spectrum of Fmoc-L-Lys(4-sulfamoyl-benzoyl)-OH