

Supporting Information for

**“Characterization of DNA-Protein Cross-Links Induced by Oxanine, a Cellular Damage
Derived from Nitric Oxide and Nitrous Acid”**

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Figure S6. Molecular mechanics calculation of thioester and amide analogues.

The literature data of dOxo-glycine [14]. ^1H NMR (500 MHz, DMSO- d_6 at 27 $^\circ\text{C}$): δ 8.21 (s, 1H, NHCONH₂), 7.83 (s, 1H, H-2), 7.72 (dd, 1H, CONHCH₂), 6.34 (s, 2H, NH₂), 5.81 (dd, 1H, H-1'), 4.27 (m, 1H, H-3'), 3.77 (ddd, 1H, H-4'), 3.64 (d, 1H, CH₂), 3.52 (ABX, 2H, H-5',5''). 2.29 (m, 2H, H-2',2''). ^{13}C NMR (125 MHz, DMSO- d_6 at 27 $^\circ\text{C}$): δ 171.5 (COO⁻), 162.1 (CONHCH₂), 156.6 (NHCONH₂), 131.6 (C-5), 130.4 (C-2), 123.9 (C-4), 87.6 (C-4'), 84.2 (C-1'), 70.5 (C-3'), 61.5 (C-5'), 41.9 (CH₂), 30.9 (C-2'). UV: λ_{max} 235 nm (pH 7). APCI LC/MS (negative): m/z 342 (M⁻), 226 (M_{base fragment}⁻ + H).

Figure S1. ^1H - ^1H COSY NMR spectrum of Oxa-S-GSH.

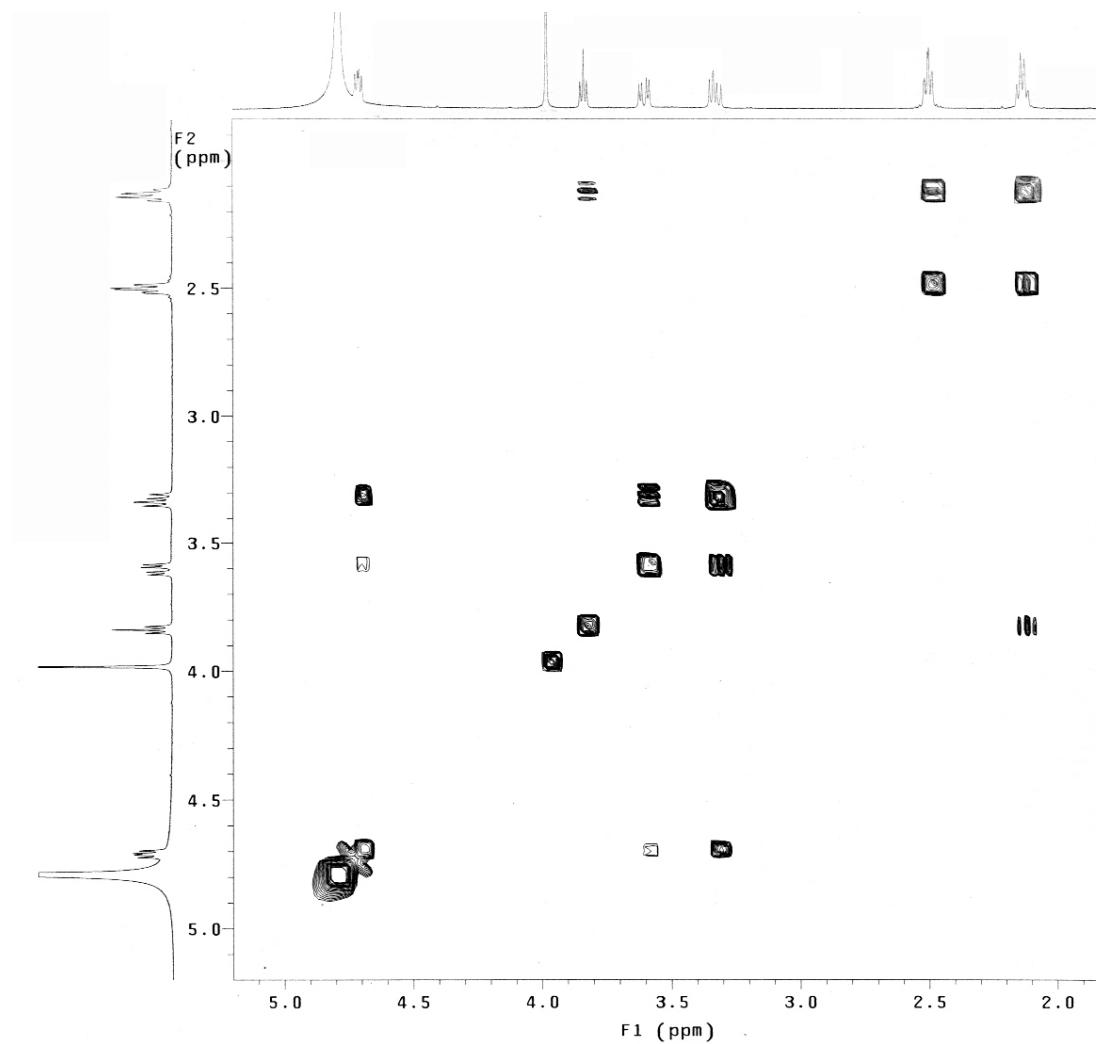
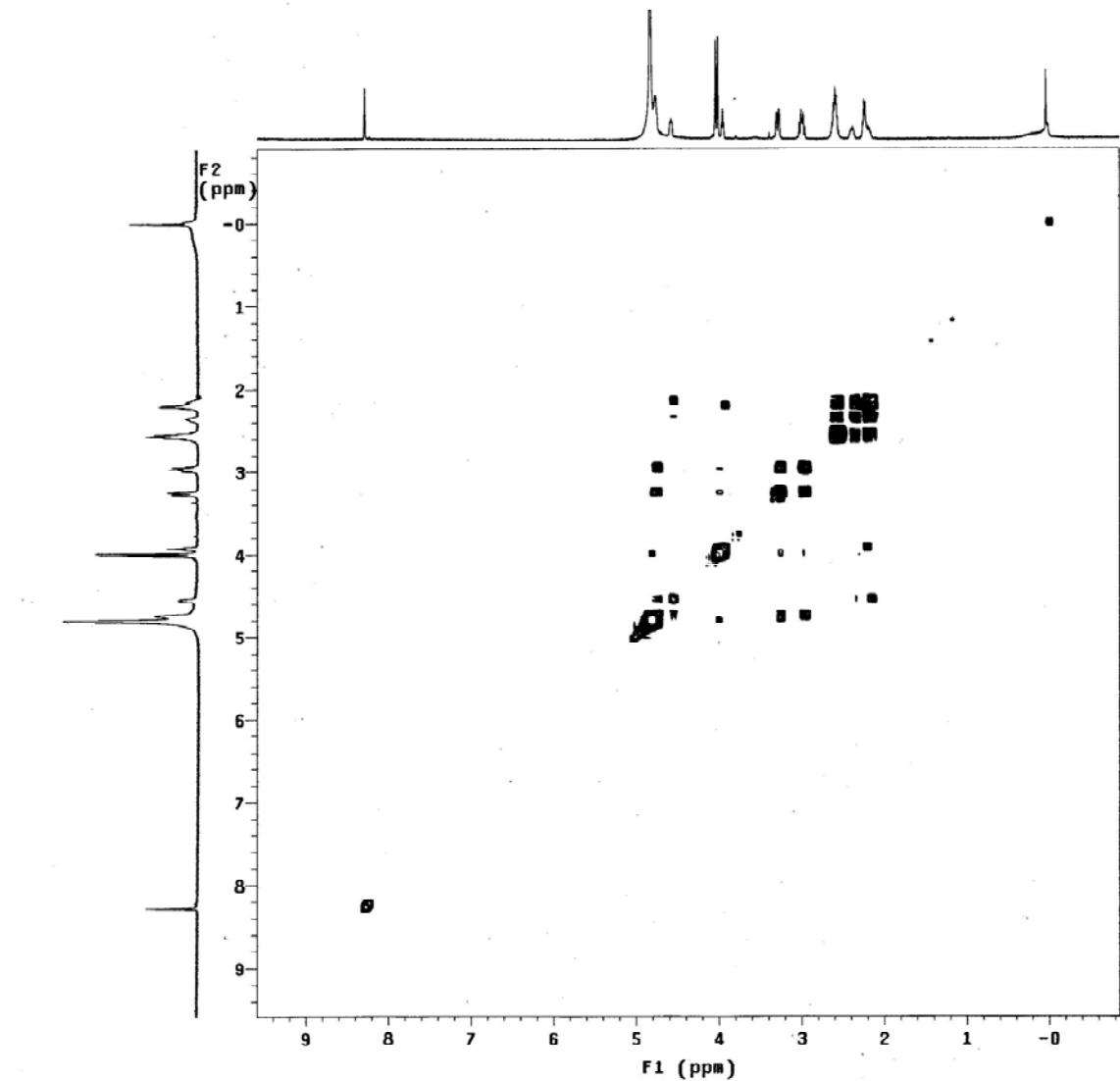


Figure S2. (a) ^1H - ^1H COSY and (b) ^1H - ^{13}C HMQC NMR spectra of Oxa-*N*-GSSG.

(a)



(b)

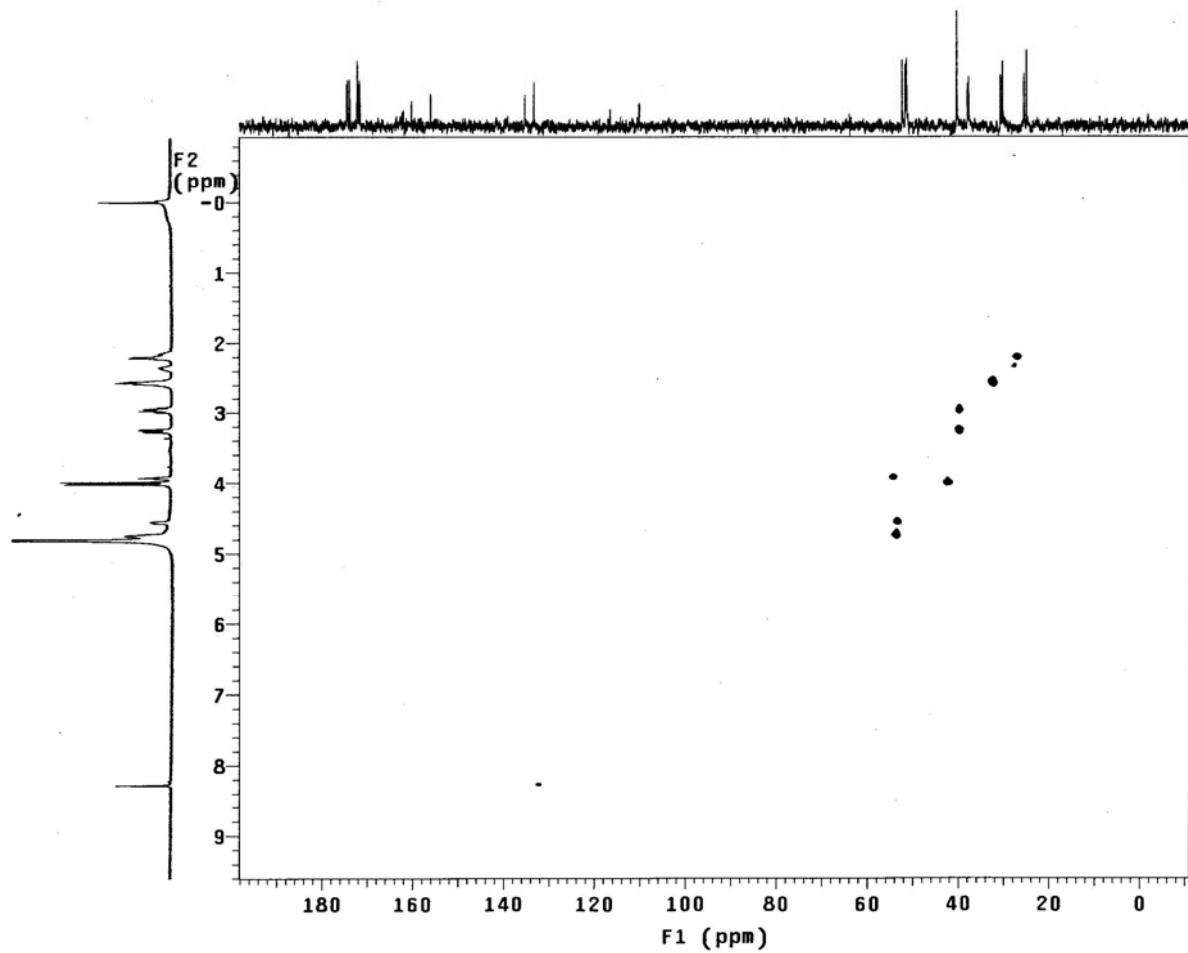
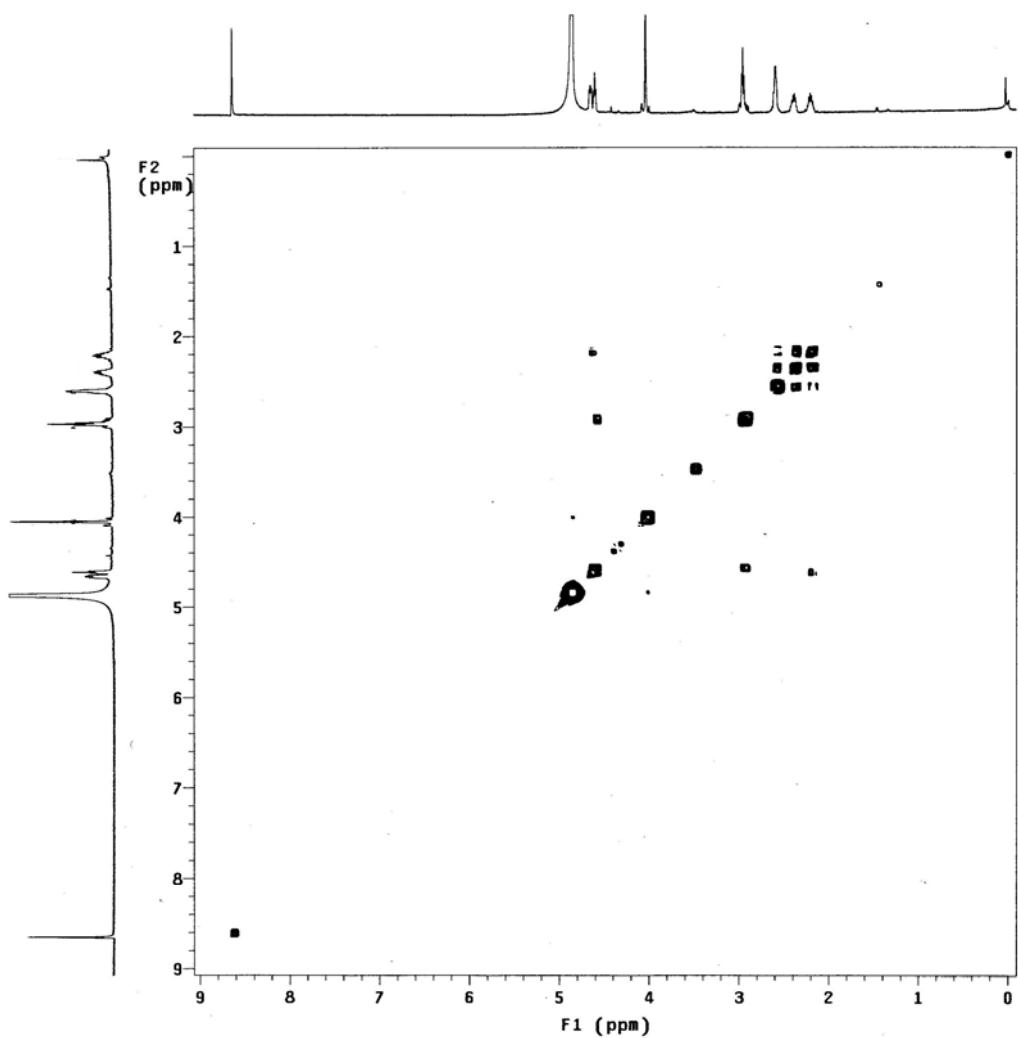


Figure S3. (a) ^1H - ^1H COSY and (b) ^1H - ^{13}C HMQC NMR spectra of Oxa-*N*-GSH.

(a)



(b)

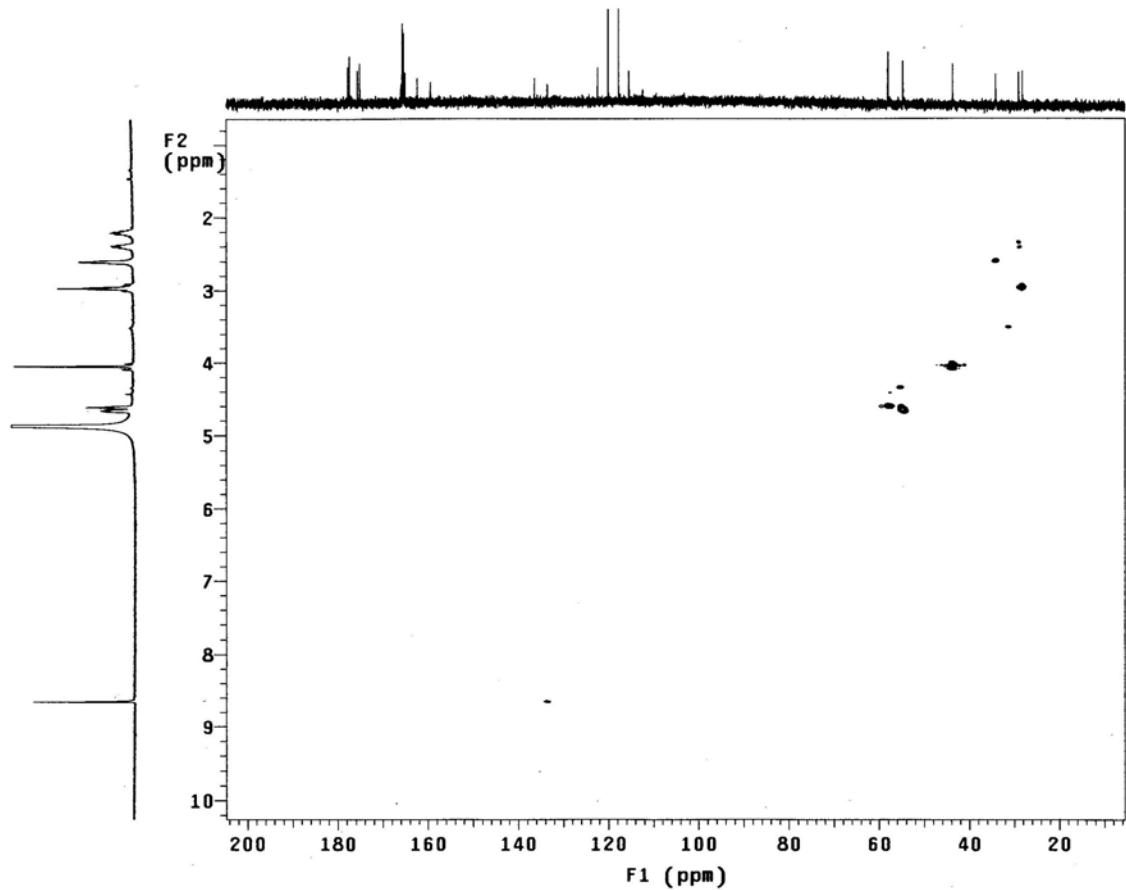


Figure S4. Collision-induced dissociation mass spectra of (a) Oxa-S-GSH, (b) Oxa-N-GSH and (c) GSH.

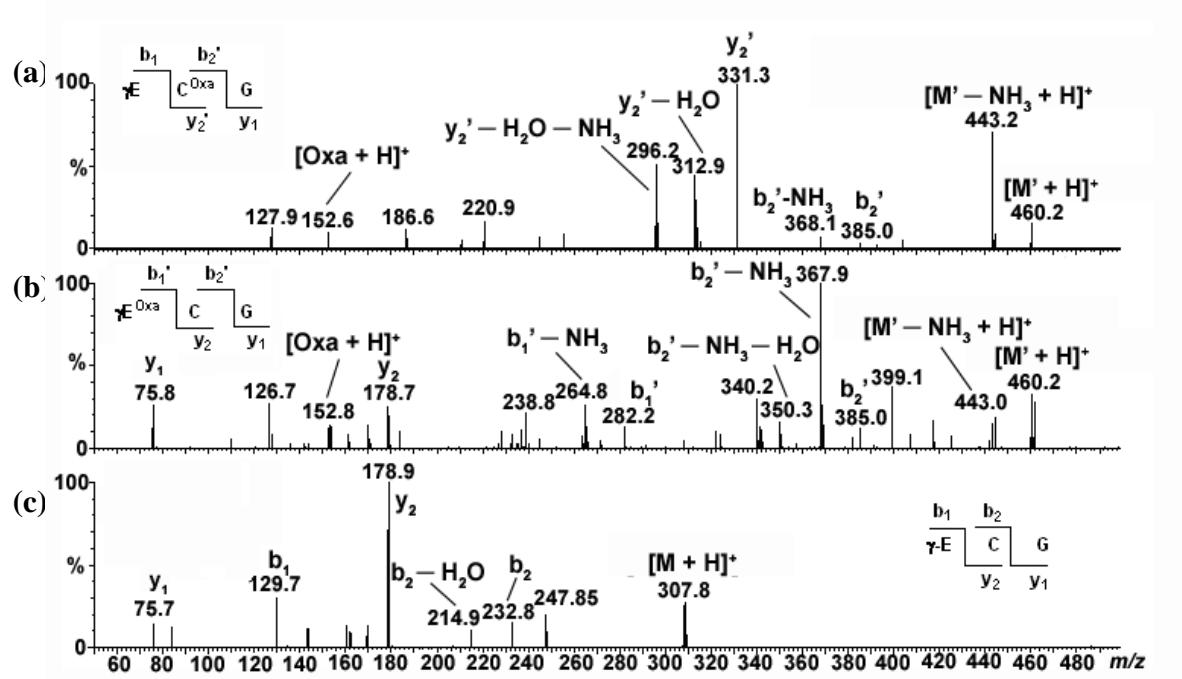


Figure S5. Collision-induced dissociation mass spectra of (a) Oxa-N-GSSG and (b) GSSG.

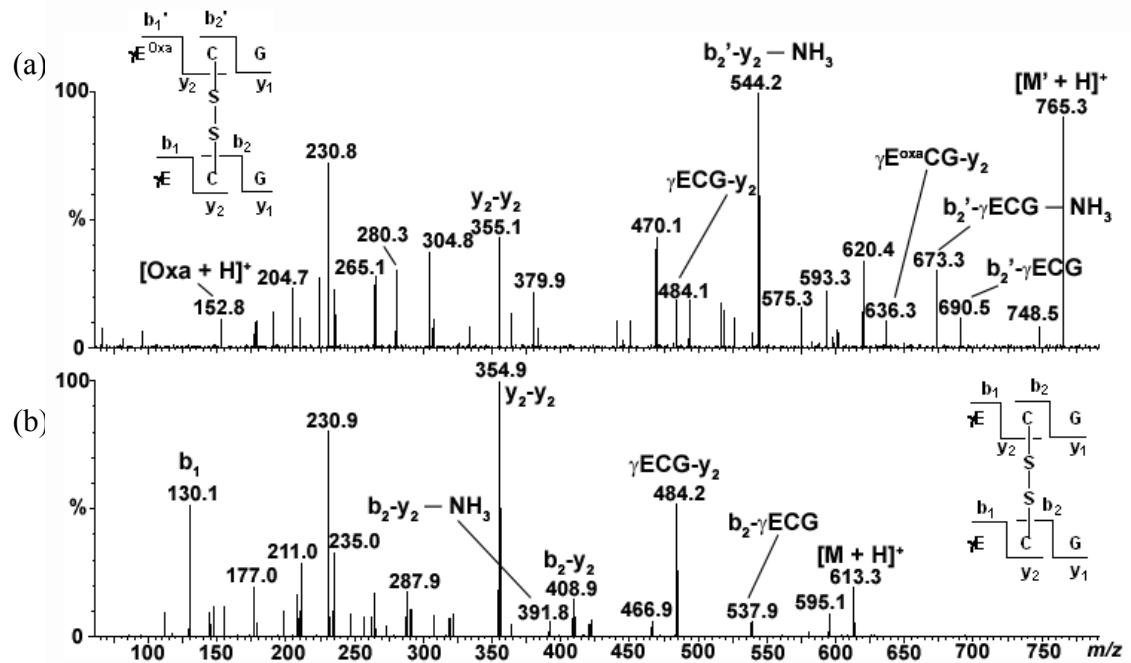
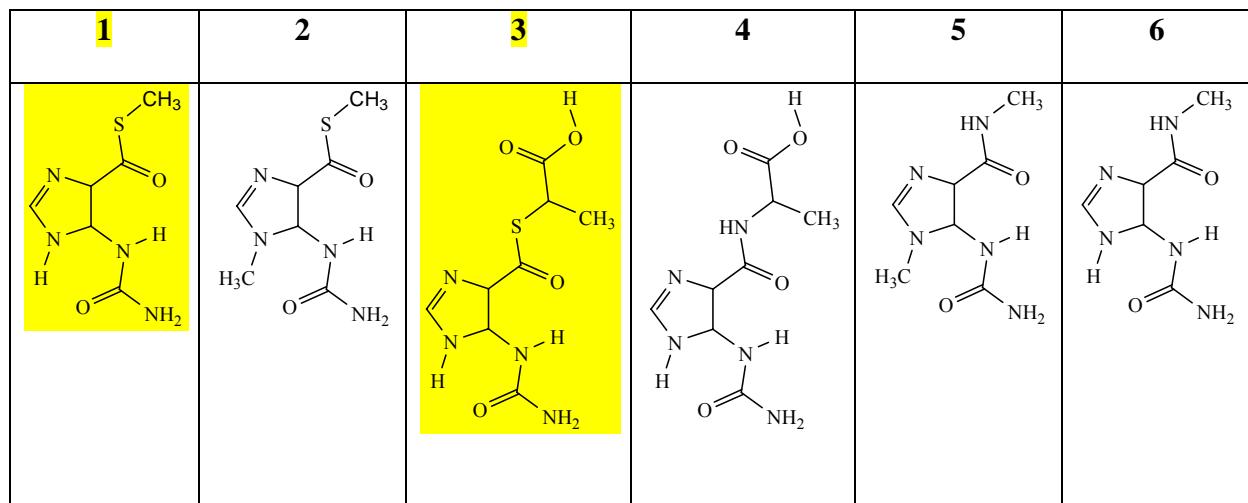


Figure S6. Molecular mechanics calculation of thioester and amide analogues.

Model compounds of thioesters and amides as analogs of Oxa-S-GSH and Oxa-N-GSH was calculated as the following. The results showed that the characteristic UV absorption maxima for these thioesters are at higher wavelength than the amide analogs, which is consistent with our findings.



Compound 1	λ (nm)	E (eV)	f	Assignment
S ₁	290.3	4.27	0.4498	HOMO → LUMO (+83%)
S ₂	286.8	4.32	0.0003	HOMO-2 → LUMO (+91%)
				HOMO-3 → LUMO (+9%)
S ₃	259.4	4.78	0.0015	HOMO-1 → LUMO (+83%)

Compound 2				
S ₁	294.4	4.21	0.2592	HOMO → LUMO (+59%)
				HOMO-2 → LUMO (27%)
S ₂	287.5	4.31	0.1369	HOMO-2 → LUMO (+60%)

HOMO → LUMO (+24%)

S₃ 261.4 4.74 0.0020 HOMO-1 → LUMO (+80%)

Compound 3

S₁ 294.8 4.21 0.4729 HOMO → LUMO (+80%)

S₂ 280.2 4.43 0.0002 HOMO-2 → LUMO (+88%)

S₃ 267.7 4.63 0.0301 HOMO→ LUMO+1(+35%)

HOMO-1 → LUMO (31%)

HOMO-1→LUMO+1(17%)

Compound 4

S₁ 269.1 4.61 0.0461 HOMO → LUMO (+94%)

HOMO → LUMO+1 (+6%)

S₂ 259.5 4.78 0.4173 HOMO → LUMO+1 (+91%)

S₃ 249.7 4.96 0.0007 HOMO → LUMO+2 (+83%)

Compound 5

S₁ 257.2 4.82 0.3310 HOMO → LUMO (+83%)

S₂ 246.6 5.03 0.0024 HOMO → LUMO+1 (+96%)

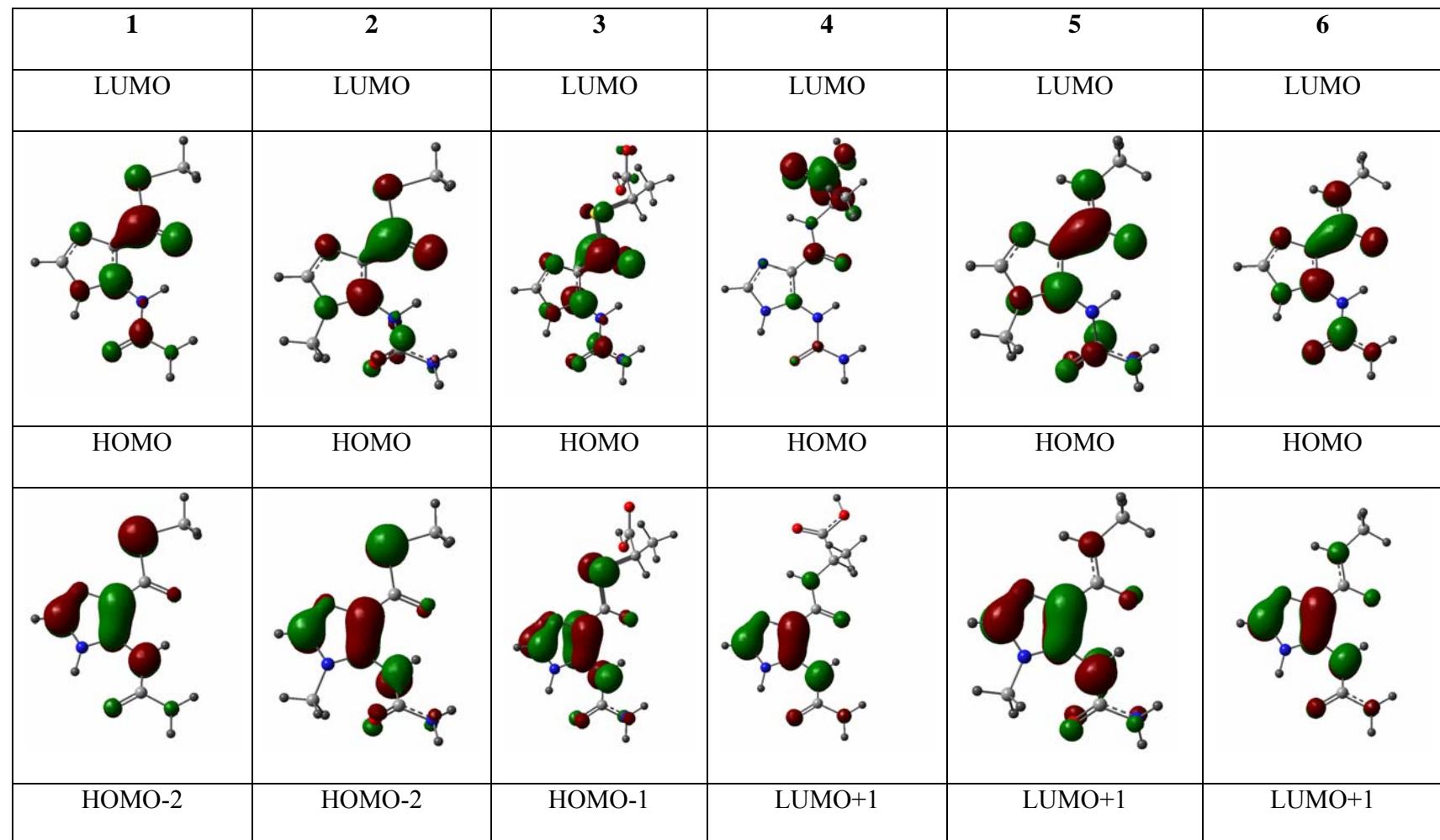
S₃ 243.5 5.09 0.0138 HOMO-2 → LUMO (+86%)

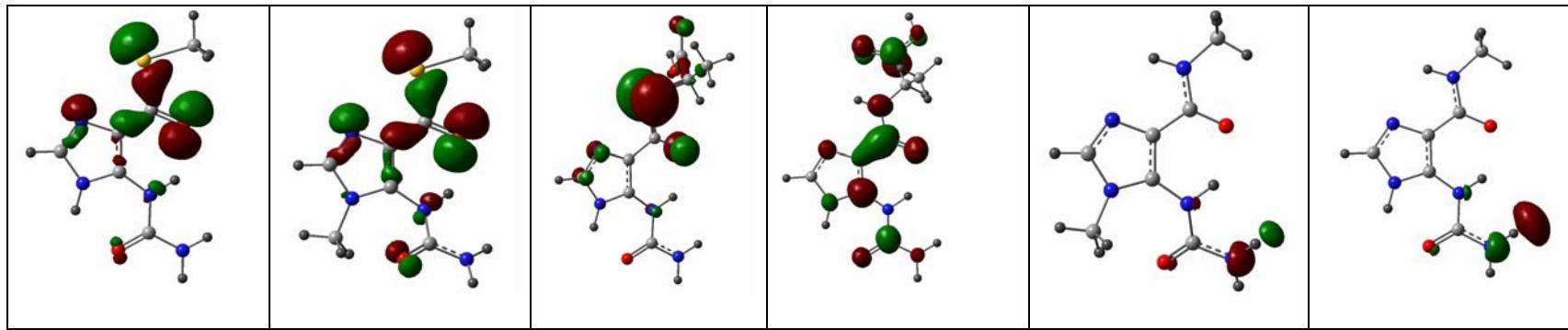
Compound 6

S₁ 255.4 4.86 0.4333 HOMO → LUMO (+85%)

S₂ 250.4 4.95 0.0001 HOMO → LUMO+1 (+97%)

S₃ 242.7 5.11 0.0001 HOMO-2 → LUMO (+91%)





Methodology

The compounds **1-6** have been truncated to afford DFT calculations. Calculations on the electronic ground states were carried out using B3LYP density functional theory with a double- ζ quality basis set,¹ i.e., 6-31++G. A time-dependent DFT (TDDFT) calculation using the B3LYP functional was then performed on the basis of the optimized geometry to analyze the excited state energetics and the associated frontier orbitals. Typically, the lowest 3 singlet roots of the nonhermitian eigen value equations were obtained to determine the vertical excitation energies. Oscillator strengths were also deduced from the dipole transition matrix elements. The ground-state B3LYP and excited-state TDDFT calculations were carried out using Gaussian 03.²

References

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