**Supplementary Material for 'Tuning the activity of glutathione peroxidase mimics through Se···N,O interactions: A DFT study incorporating solvent-assisted proton exchange (SAPE)'**

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**Table S1**. DFT(mPW1PW91)/BSI bond distances (Å) and NBO donor-acceptor energies (kcal/mol) of selenenyl halides RSe-X (X = Cl, Br, I)

| | Cl | | | Br | | | I | | |
|---|---|---|---|---|---|---|---|---|---|
| | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ |
| **4a-X** | 2.306 | 2.321 | 41.8 | 2.331 | 2.478 | 40.2 | 2.345 | 2.703 | 40.2 |
| **4b-X** | 2.310 | 2.316 | 45.2 | --- | --- | --- | --- | --- | --- |
| **5-X** | 2.070 | 2.281 | 55.8 | --- | --- | --- | --- | --- | --- |
| **6-X** | 2.179 | 2.336 | 64.2 | 2.214 | 2.489 | 59.2 | 2.233 | 2.715 | 57.2 |
| **7-X** | 2.125 | 2.364 | 78.7 | 2.147 | 2.524 | 76.3 | 2.150 | 2.759 | 77.3 |
| **8a-X** | 2.387 | 2.305 | 40.5 | --- | --- | --- | --- | --- | --- |
| **8b-X** | 2.380 | 2.318 | 35.8 | --- | --- | --- | --- | --- | --- |
| **9-X** | 2.314 | 2.314 | 41.0 | 2.335 | 2.472 | 39.9 | 2.344 | 2.699 | 40.3 |
| **10a-X** | 2.207 | 2.285 | 49.7 | 2.238 | 2.440 | 40.0 | 2.258 | 2.662 | 39.1 |
| **11a-X** | 2.484 | 2.230 | 16.8 | 2.542 | 2.383 | 14.6 | 2.587 | 2.597 | 12.9 |
| **11b-X** | 2.445 | 2.237 | 16.9 | 2.494 | 2.390 | 14.9 | 2.519 | 2.605 | 13.9 |
| **12-X** | 2.540 | 2.239 | 15.1 | --- | --- | --- | --- | --- | --- |
| **13-X** | 2.201 | 2.282 | 43.1 | 2.250 | 2.434 | 39.1 | 2.289 | 2.653 | 36.1 |
| **14a-X** | 2.287 | 2.232 | 32.0 | 2.330 | 2.386 | 29.1 | 2.367 | 2.604 | 26.9 |

**Table S2**. DFT(mPW1PW91)/BSI bond distances (Å) and NBO donor-acceptor energies (kcal/mol) of selenenic acids RSe-OH, selenenyl nitrosyls RSe-NO and selenenyl azides RSe-$N_3$.

| | OH | | | NO | | | $N_3$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ |
| **4a-X** | 2.430 | 1.868 | 20.0 | 2.764 | 2.012 | 7.7 | 2.367 | 1.988 | 25.2 |
| **4b-X** | 2.433 | 1.865 | 22.2 | --- | --- | --- | --- | --- | --- |
| **6-X** | 2.387 | 1.860 | 24.0 | 2.700 | 1.997 | 8.7 | 2.304 | 1.979 | 21.6 |
| **7-X** | 2.289 | 1.877 | 33.8 | --- | --- | --- | --- | --- | --- |
| **8-X** | 2.539 | 1.861 | 18.4 | --- | --- | --- | --- | --- | --- |
| **9-X** | 2.423 | 1.864 | 20.3 | --- | --- | --- | --- | --- | --- |
| **10a-X** | 2.328 | 1.851 | 19.9 | 2.728 | 2.004 | 4.3 | | | |
| **11a-X** | 2.557 | 1.833 | 10.4 | --- | --- | --- | --- | --- | --- |
| **11b-X** | 2.537 | 1.835 | 9.2 | --- | --- | --- | --- | --- | --- |
| **13-X** | 2.350 | 1.847 | 19.0 | --- | --- | --- | --- | --- | --- |
| **14a-X** | 2.383 | 1.826 | 17.4 | --- | --- | --- | --- | --- | --- |

**Table S3**. DFT(mPW1PW91)/BSI bond distances (Å) and NBO donor-acceptor energies (kcal/mol) of selenenyl sulfides RSe-SMe and hetero diselenides RSe-SeMe

| | SMe | | | SeMe | | |
|---|---|---|---|---|---|---|
| | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ |
| **4a-X** | 2.591 | 2.250 | 12.3 | 2.624 | 2.376 | 11.3 |
| **4b-X** | 2.609 | 2.246 | 13.3 | 2.642 | 2.372 | 12.2 |
| **4d-X** | 2.611 | 2.250 | 11.8 | --- | --- | --- |
| **4e-X** | 2.739 | 2.240 | 8.11 | --- | --- | --- |
| **6-X** | 2.619 | 2.232 | 10.9 | 2.549 | 2.358 | 16.8 |
| **7-X** | 2.476 | 2.257 | 19.2 | 2.502 | 2.384 | 17.8 |
| **8-X** | 2.759 | 2.238 | 9.6 | 2.790 | 2.365 | 9.1 |
| **9-X** | 2.527 | 2.253 | 15.5 | 2.544 | 2.382 | 15.0 |
| **10a-X** | 2.495 | 2.230 | 15.3 | 2.537 | 2.356 | 10.1 |
| **11a-X** | 2.790 | 2.210 | 5.0 | 2.837 | 2.336 | 4.2 |
| **11b-X** | 2.745 | 2.212 | 4.5 | 2.796 | 2.338 | 3.7 |
| **13-X** | 2.599 | 2.224 | 9.2 | 2.632 | 2.351 | 8.4 |
| **14a-X** | 2.544 | 2.216 | 140 | --- | --- | --- |

**Table S4**. DFT(mPW1PW91)/BSI bond distances (Å) and NBO donor-acceptor energies (kcal/mol) of selenenyl cyanides RSe-CN and methyl selenides RSe-Me

| | CN | | | Me | | |
|---|---|---|---|---|---|---|
| | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ | d(Se-N,O) | d(Se-X) | $\Delta E_{d\rightarrow a}$ |
| **4a-X** | 2.552 | 1.891 | 9.4 | 2.794 | 1.975 | 5.0 |
| **5-X** | --- | --- | --- | 2.485 | 1.798 | 8.3 |
| **6-X** | 2.630 | 1.869 | 9.7 | 2.803 | 1.963 | 4.6 |
| **7-X** | 2.429 | 1.903 | 8.8 | 2.627 | 1.975 | 9.4 |
| **9-X** | 2.489 | 1.896 | 9.3 | --- | --- | --- |
| **11a-X** | 2.715 | 1.856 | 5.1 | --- | --- | --- |
| **11b-X** | 2.653 | 1.859 | 4.8 | 2.920 | 1.964 | 1.9 |
| **13-X** | 2.519 | 1.873 | 8.9 | 2.703 | 1.964 | 4.9 |