

Supporting Information

Significant Effect of Spin Flip on the Oxygen Atom Transfer  
Reaction from (Oxo)manganese(V) Corroles to Thioanisole:  
Insight from Density Functional Calculations

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**Table S1.** Thermodynamic values (kcal/mol) for **1-MnO** in the singlet (S), triplet (T), and quintet states (Q) by using different density functionals.

| Method/Basis set              | Spin states | $\Delta E^a$ | $\Delta H^a$ | $\Delta G^a$ |
|-------------------------------|-------------|--------------|--------------|--------------|
| B3LYP/6-31G(d)<br>and LANL2DZ | S           | 0            | 0            | 0            |
|                               | T           | 3.61         | 3.9          | 2.7          |
|                               | Q           | 5.2          | 5.5          | 3.6          |
| OPBE/6-31G(d)                 | S           | 0            | 0            | 0            |
|                               | T           | 13.1         | 13.4         | 11.8         |
|                               | Q           | 24.9         | 25.3         | 23.2         |
| OPBE/6-311+G(d,p)             | S           | 0            | 0            | 0            |
|                               | T           | 13.4         | 13.7         | 12.2         |
| OPBE(D)/ 6-31G(d)             | S           | 0            | 0            | 0            |
|                               | T           | 13.1         | 13.4         | 11.8         |
|                               | Q           | 24.9         | 25.3         | 23.2         |
| OPBE(D)/<br>6-311+G(d,p)      | S           | 0            | 0            | 0            |
|                               | T           | 13.4         | 13.7         | 12.2         |
| OLYP/6-31G(d)                 | S           | 0            | 0            | 0            |
|                               | T           | 12.7         | 13.0         | 11.6         |

|                              |   |      |      |      |
|------------------------------|---|------|------|------|
| OLYP(D)/ 6-31G(d)            | S | 0    | 0    | 0    |
|                              | T | 12.7 | 13.0 | 11.6 |
| M06/6-31G(d)<br>and LANL2DZ  | S | 0    | 0    | 0    |
|                              | T | 9.1  | 9.5  | 7.8  |
| B97D/6-31G(d)                | S | 0    | 0    | 0    |
|                              | T | 11.6 | 11.9 | 10.3 |
| B97D/6-31G(d)<br>and LANL2DZ | S | 0    | 0    | 0    |
|                              | T | 11.6 | 11.9 | 10.5 |
| O3LYP/6-31G(d)               | S | 0    | 0    | 0    |
|                              | T | 9.7  | 9.9  | 8.7  |
| PBE/6-31G(d)                 | S | 0    | 0    | 0    |
|                              | T | 14.1 | 14.4 | 13.1 |

<sup>a</sup> Units in kcal/mol and  $T= 298.15$  K.  $\Delta E$ ,  $\Delta H$  and  $\Delta G$  are relative energies, enthalpies and free energies, respectively. Zero-point energies are included.

**Table S2.** Thermodynamic values (kcal/mol) for the oxygen atom transfer reactions of Model 1 in the singlet state by B3LYP and M06.

| Species                 | $\Delta E^a$ |      | $\Delta H^a$ |      | $\Delta G^a$ |      |
|-------------------------|--------------|------|--------------|------|--------------|------|
|                         | B3LYP        | M06  | B3LYP        | M06  | B3LYP        | M06  |
| <sup>1</sup> [1-MnO-S]  | 0.0          | 0.0  | 0.0          | 0.0  | 0.0          | 0.0  |
| <sup>1</sup> [1-Mn-O-S] | 25.1         | 32.1 | 24.9         | 31.7 | 27.7         | 33.5 |
| <sup>1</sup> [1-Mn-OS]  | 21.1         | 31.0 | 21.0         | 30.8 | 23.1         | 31.5 |

<sup>a</sup> Units in kcal/mol and  $T= 298.15$  K.  $\Delta E$ ,  $\Delta H$  and  $\Delta G$  are relative energies, enthalpies and free energies, respectively. Zero-point energies are included.

**Table S3.** Selected Bond Lengths(Å), Mulliken Atomic Charges and Spin  
Densities of **3-MnO** in Singlet (S) and Triplet States (T)

| State | Bond Length |                   |                   |                   |                   | Charges and Spin Densities (Italic) |                     |                       |                       |                       |                       |
|-------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------------------------|---------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|       | Mn-O        | Mn-N <sub>1</sub> | Mn-N <sub>2</sub> | Mn-N <sub>3</sub> | Mn-N <sub>4</sub> | O                                   | Mn                  | N <sub>1</sub>        | N <sub>2</sub>        | N <sub>3</sub>        | N <sub>4</sub>        |
| S     | 1.536       | 1.901             | 1.902             | 1.930             | 1.929             | -0.31                               | 0.89                | -0.62                 | -0.65                 | -0.65                 | -0.62                 |
| T     | 1.632       | 1.932             | 1.913             | 1.948             | 1.915             | -0.36<br><i>-0.37</i>               | 1.02<br><i>2.56</i> | -0.63<br><i>-0.02</i> | -0.70<br><i>-0.07</i> | -0.68<br><i>-0.03</i> | -0.65<br><i>-0.06</i> |

**Table S4.** Selected Bond Lengths(Å), Mulliken Atomic Charges and Spin  
Densities of **4-MnO** in Singlet (S) and Triplet States (T)

| State | Bond Length |                   |                   |                   |                   | Charges and Spin Densities (Italic) |                     |                       |                      |                      |                      |
|-------|-------------|-------------------|-------------------|-------------------|-------------------|-------------------------------------|---------------------|-----------------------|----------------------|----------------------|----------------------|
|       | Mn-O        | Mn-N <sub>1</sub> | Mn-N <sub>2</sub> | Mn-N <sub>3</sub> | Mn-N <sub>4</sub> | O                                   | Mn                  | N <sub>1</sub>        | N <sub>2</sub>       | N <sub>3</sub>       | N <sub>4</sub>       |
| S     | 1.536       | 1.899             | 1.913             | 1.923             | 1.933             | -0.31                               | 0.89                | -0.62                 | -0.65                | -0.65                | -0.64                |
| T     | 1.574       | 1.907             | 1.975             | 1.930             | 1.975             | -0.38<br><i>0.20</i>                | 0.82<br><i>0.83</i> | -0.63<br><i>-0.03</i> | -0.62<br><i>0.07</i> | -0.65<br><i>0.04</i> | -0.59<br><i>0.09</i> |

**Table S5.** Selected Bond Lengths(Å), Mulliken Atomic Charges and Spin Densities of Reaction Species Model 2 in Singlet (S) and Triplet States (T)

| Param                               |       | S        |       |         | T              |                |                |
|-------------------------------------|-------|----------|-------|---------|----------------|----------------|----------------|
|                                     |       | reactant | TS    | product | reactant       | TS             | product        |
| Bond Length                         | O-S   | 3.742    | 1.853 | 1.592   | 2.582          | 1.867          | 1.575          |
|                                     | O-Mn  | 1.538    | 1.706 | 1.900   | 1.677          | 1.763          | 1.952          |
|                                     | Mn-N1 | 1.900    | 1.964 | 2.005   | 1.922          | 1.922          | 1.943          |
|                                     | Mn-N2 | 1.904    | 1.888 | 1.885   | 1.927          | 1.923          | 1.903          |
|                                     | Mn-N3 | 1.930    | 1.940 | 1.919   | 1.928          | 1.932          | 1.936          |
|                                     | Mn-N4 | 1.931    | 1.917 | 1.916   | 1.944          | 1.931          | 1.924          |
| Charges and Spin Densities (Italic) | Mn    | 0.85     | 0.81  | 0.76    | 1.04<br>2.83   | 0.96<br>2.49   | 0.84<br>2.13   |
|                                     | O     | -0.29    | -0.58 | -0.67   | -0.44<br>-0.43 | -0.61<br>-0.04 | -0.68<br>-0.01 |
|                                     | S     | 0.13     | 0.64  | 0.89    | 0.27<br>-0.18  | 0.58<br>-0.29  | 0.89<br>0.00   |
|                                     |       |          |       |         |                |                |                |

**Table S6.** Selected Bond Lengths(Å), Mulliken Atomic Charges of Reaction Species Model 3 in Singlet (S) and Triplet States (T).

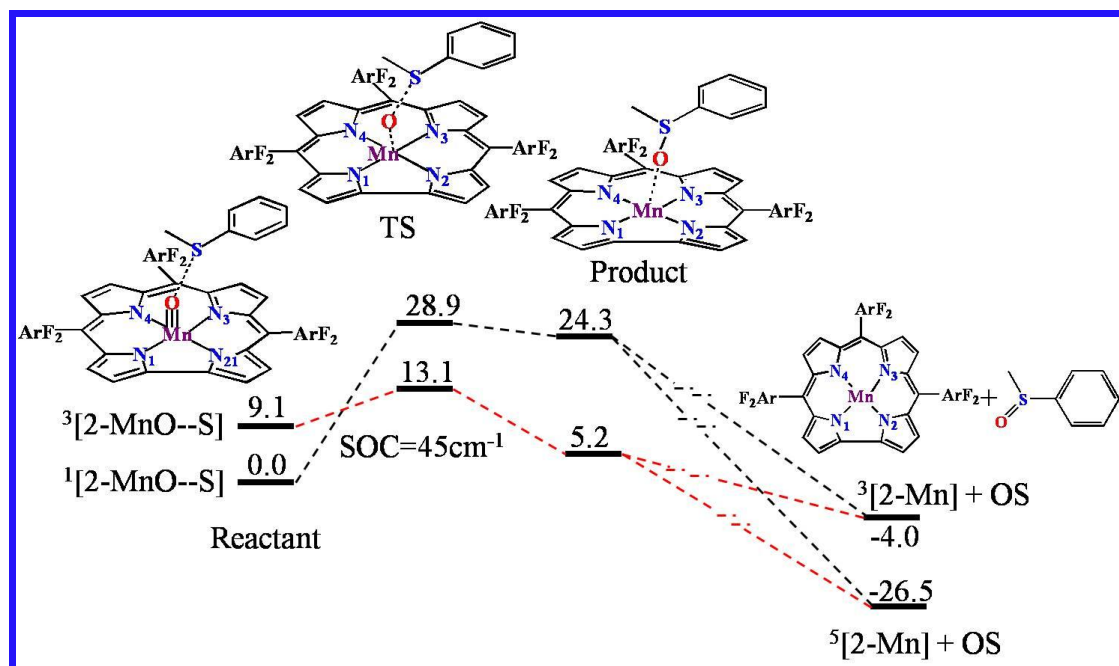
| Param                               | Singlet state |       |         | Triplet state |       |         |       |
|-------------------------------------|---------------|-------|---------|---------------|-------|---------|-------|
|                                     | reactant      | TS    | product | reactant      | TS    | product |       |
| Bond Length                         | O-S           | 3.433 | 1.861   | 1.595         | 2.473 | 1.867   | 1.575 |
|                                     | O-Mn          | 1.535 | 1.701   | 1.895         | 1.681 | 1.763   | 1.947 |
|                                     | Mn-N1         | 1.901 | 1.964   | 2.004         | 1.921 | 1.922   | 1.944 |
|                                     | Mn-N2         | 1.901 | 1.888   | 1.884         | 1.926 | 1.923   | 1.900 |
|                                     | Mn-N3         | 1.931 | 1.940   | 1.921         | 1.931 | 1.932   | 1.935 |
|                                     | Mn-N4         | 1.930 | 1.917   | 1.917         | 1.943 | 1.931   | 1.922 |
| Charges and Spin Densities (Italic) | Mn            | 0.87  | 0.81    | 0.77          | 1.04  | 1.05    | 0.86  |
|                                     |               |       |         |               | 2.83  | 2.48    | 0.80  |
|                                     | O             | -0.39 | -0.58   | -0.68         | -0.44 | -0.44   | -0.68 |
|                                     |               |       |         |               | -0.38 | -0.05   | -0.68 |
| S                                   | 0.22          | 0.65  | 0.88    | 0.27          | 0.28  | 0.89    |       |
|                                     |               |       |         | -0.25         | -0.32 | 0.88    |       |

**Table S7.** Selected Bond Lengths(Å), Mulliken Atomic Charges and Spin Densities of Reaction Species Model 4 in Singlet (S) and Triplet States (T).

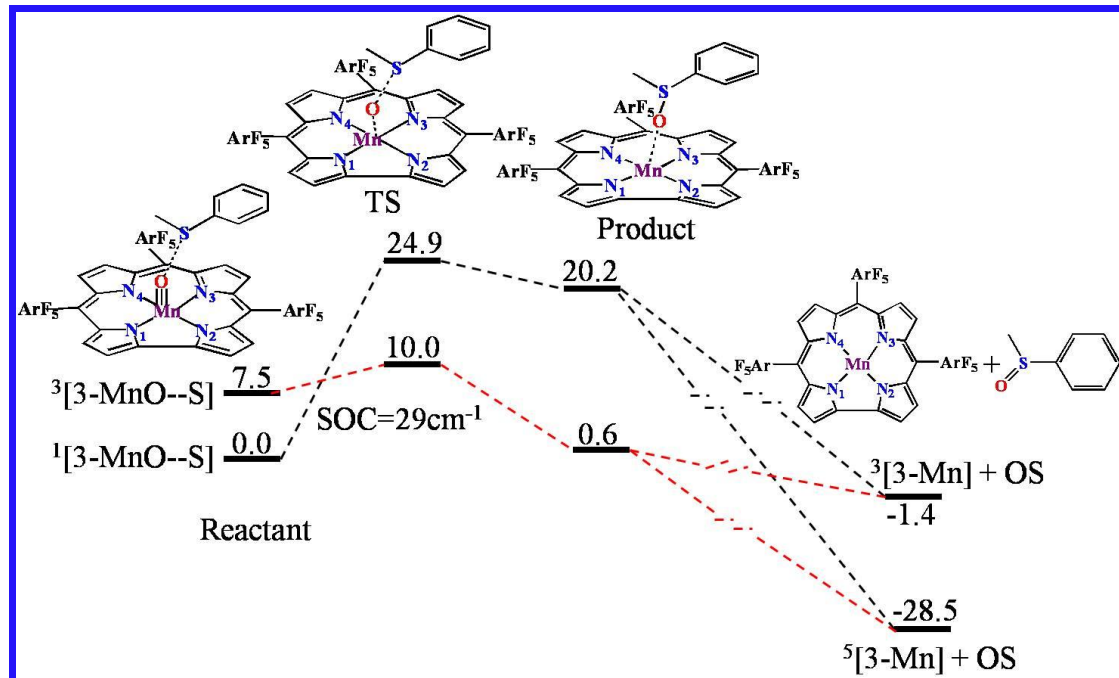
| Param                               |                   | S        |       |         | T                     |                       |                      |
|-------------------------------------|-------------------|----------|-------|---------|-----------------------|-----------------------|----------------------|
|                                     |                   | reactant | TS    | product | reactant              | TS                    | product              |
| Bond Length                         | O-S               | 3.559    | 1.870 | 1.597   | 2.433                 | 1.905                 | 1.577                |
|                                     | O-Mn              | 1.536    | 1.696 | 1.889   | 1.679                 | 1.748                 | 1.929                |
|                                     | Mn-N <sub>1</sub> | 1.899    | 1.961 | 2.000   | 1.917                 | 1.919                 | 1.923                |
|                                     | Mn-N <sub>2</sub> | 1.913    | 1.902 | 1.899   | 1.941                 | 1.939                 | 1.929                |
|                                     | Mn-N <sub>3</sub> | 1.924    | 1.934 | 1.913   | 1.927                 | 1.929                 | 1.920                |
|                                     | Mn-N <sub>4</sub> | 1.933    | 1.920 | 1.917   | 1.939                 | 1.929                 | 1.941                |
| Charges and Spin Densities (Italic) | Mn                | 0.89     | 0.82  | 0.78    | 1.06<br><i>2.81</i>   | 0.86<br><i>2.47</i>   | 0.82<br><i>2.08</i>  |
|                                     | O                 | -0.31    | -0.58 | -0.68   | -0.44<br><i>-0.31</i> | -0.62<br><i>-0.03</i> | -0.70<br><i>0.00</i> |
|                                     | S                 | 0.14     | 0.65  | 0.89    | 0.29<br><i>-0.28</i>  | 0.72<br><i>-0.32</i>  | 0.89<br><i>0.01</i>  |
|                                     |                   |          |       |         |                       |                       |                      |

**Table S8.** The S-square expectation values of reaction systems

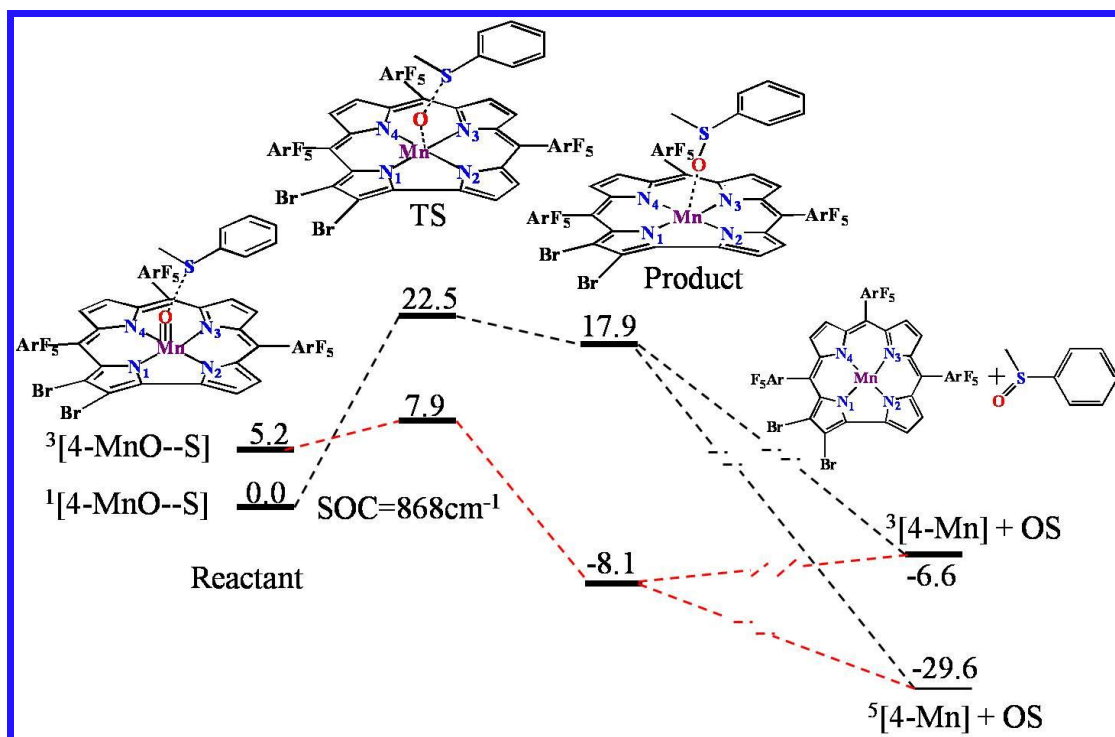
| species    | S-square<br>expectation values | The relative errors of S-square<br>expectation values (%) |
|------------|--------------------------------|-----------------------------------------------------------|
| 1-MnO--S   | 2.19                           | 9.5                                                       |
| 1-Mn--O--S | 2.05                           | 2.5                                                       |
| 1-Mn--OS   | 2.00                           | 0.0                                                       |
| 2-MnO--S   | 2.15                           | 7.5                                                       |
| 2-Mn--O--S | 2.04                           | 2.0                                                       |
| 2-Mn--OS   | 2.00                           | 0.0                                                       |
| 3-MnO--S   | 2.15                           | 7.5                                                       |
| 3-Mn--O--S | 2.03                           | 1.5                                                       |
| 3-Mn--OS   | 2.00                           | 0.0                                                       |
| 4-MnO--S   | 2.13                           | 6.5                                                       |
| 4-Mn--O--S | 2.03                           | 1.5                                                       |
| 4-Mn--OS   | 2.00                           | 0.0                                                       |



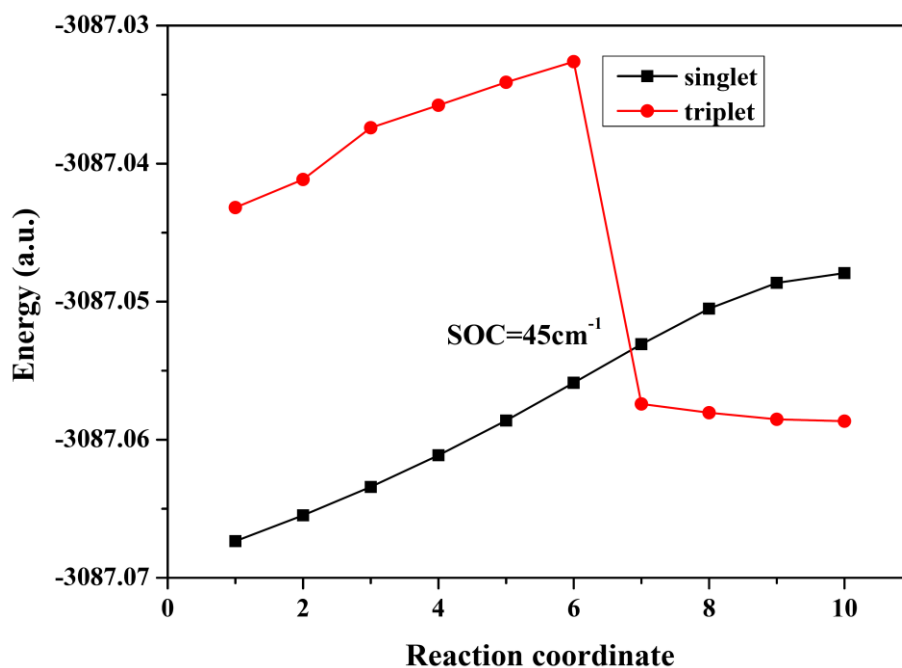
**Figure S1.** Predicted relative Gibbs free energy profiles (kcal/mol) for the OAT reaction of **2-MnO** with thioanisole.



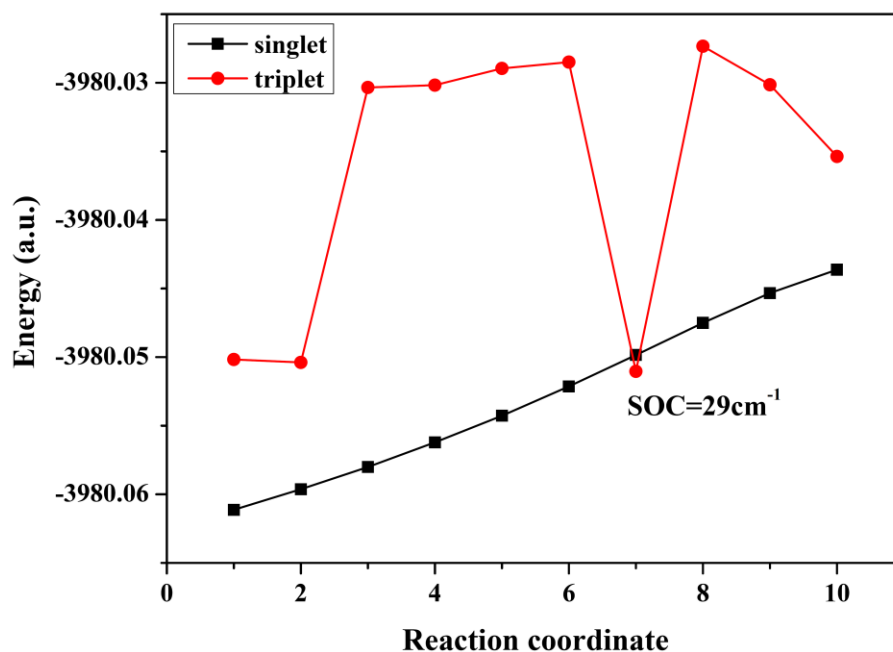
**Figure S2.** Predicted relative Gibbs free energy profiles (kcal/mol) for the OAT reaction of **3-MnO** with thioanisole.



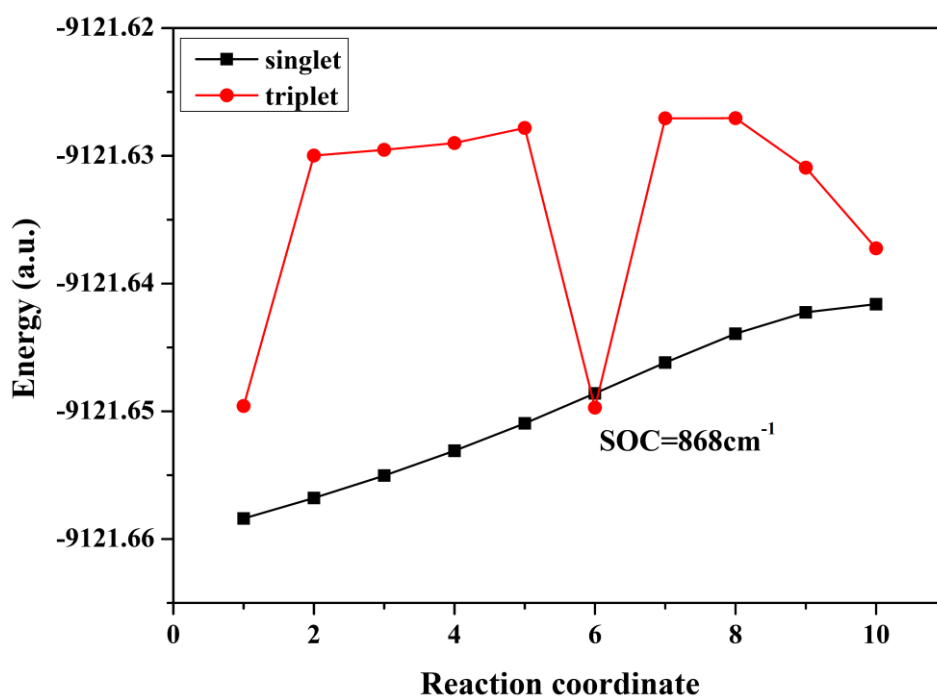
**Figure S3.** Predicted relative Gibbs free energy profiles (kcal/mol) for the OAT reaction of 4-MnO with thioanisole.



**Figure S4.** Calculation of the crossing point and the SOC constant for Model 2.



**Figure S5.** Calculation of the crossing point and the SOC constant for Model 3.



**Figure S6.** Calculation of the crossing point and the SOC constant for Model 4.

**Table S9.** Optimized cartesian coordinates (Å) of [1-M--O--S] (TS) in singlet state by using B3LYP method.

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 0. 71690300  | 2. 59827700  | 1. 12145200  |
| C  | 0. 21266500  | 3. 47503100  | 2. 12830500  |
| H  | 0. 31544500  | 4. 55261600  | 2. 14935200  |
| C  | -0. 37377300 | 2. 67267900  | 3. 09659600  |
| H  | -0. 82793400 | 2. 99988200  | 4. 02400500  |
| C  | -0. 21714500 | 1. 30864400  | 2. 67853100  |
| C  | -0. 45066500 | 0. 08786400  | 3. 32475000  |
| C  | 0. 01368500  | -1. 13382400 | 2. 83721300  |
| C  | -0. 15604000 | -2. 40582400 | 3. 47707300  |
| H  | -0. 67762000 | -2. 55436800 | 4. 41492200  |
| C  | 0. 45683600  | -3. 35340000 | 2. 70082700  |
| H  | 0. 51895700  | -4. 41977500 | 2. 87984300  |
| C  | 1. 01329600  | -2. 68725300 | 1. 55889900  |
| C  | 1. 69021800  | -3. 30237700 | 0. 50460600  |
| C  | 2. 21051800  | -2. 64055900 | -0. 60544000 |
| C  | 3. 04824200  | -3. 18612500 | -1. 64305600 |
| H  | 3. 34552600  | -4. 22488200 | -1. 71860900 |
| C  | 3. 41729600  | -2. 14659900 | -2. 45255900 |
| H  | 4. 07552100  | -2. 17818400 | -3. 31248600 |
| C  | 2. 81744700  | -0. 94829900 | -1. 92194200 |
| C  | 3. 04726600  | 0. 35799200  | -2. 34503700 |
| C  | 2. 59143300  | 1. 48815400  | -1. 65208400 |
| C  | 2. 75799700  | 2. 87920100  | -1. 91961100 |
| H  | 3. 30232200  | 3. 29096100  | -2. 76084500 |
| C  | 2. 09617000  | 3. 59402800  | -0. 92416500 |
| H  | 2. 03892300  | 4. 67068700  | -0. 82466300 |
| C  | 1. 52371500  | 2. 64231700  | -0. 04398200 |
| N  | 0. 39468000  | 1. 31100700  | 1. 45753600  |
| N  | 0. 74669000  | -1. 32654700 | 1. 65747100  |
| N  | 2. 04278800  | -1. 29033600 | -0. 81988300 |
| N  | 1. 84260900  | 1. 37342600  | -0. 49714800 |
| H  | -0. 96375200 | 0. 08257700  | 4. 28215300  |
| H  | 3. 66665900  | 0. 50765400  | -3. 22472900 |
| H  | 1. 85184600  | -4. 37384000 | 0. 57863600  |
| Mn | 0. 88405500  | -0. 09955000 | 0. 19591200  |
| O  | -0. 62749100 | -0. 10506700 | -0. 62106200 |
| C  | -4. 26606500 | -1. 52038000 | -2. 44034600 |
| C  | -3. 17980600 | -0. 74187400 | -2. 04542500 |
| C  | -3. 32109000 | 0. 11337900  | -0. 94497100 |
| C  | -4. 52221900 | 0. 17606600  | -0. 22899200 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -5.60162900 | -0.60957900 | -0.63557300 |
| C | -5.47534500 | -1.45262300 | -1.74118300 |
| H | -4.16520400 | -2.18867500 | -3.29062800 |
| H | -2.22856700 | -0.81657000 | -2.56076900 |
| H | -4.60978800 | 0.83102300  | 0.63305500  |
| H | -6.53734900 | -0.56344000 | -0.08624600 |
| H | -6.31659000 | -2.06407600 | -2.05493400 |
| S | -1.96882000 | 1.12090700  | -0.36130700 |
| C | -1.56865200 | 2.13259800  | -1.81804100 |
| H | -2.40164500 | 2.81027200  | -2.02177700 |
| H | -0.66704100 | 2.69592700  | -1.56484500 |
| H | -1.37495500 | 1.47905600  | -2.67071400 |

**Table S10.** Optimized cartesian coordinates (Å) of [1-Mn--O--S] (TS) in triplet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 0.39101700  | -1.23192300 | 2.38329600  |
| C | 1.39417500  | -1.14319000 | 3.39278500  |
| H | 1.77084900  | -1.96322500 | 3.99090800  |
| C | 1.76263400  | 0.19376000  | 3.48503600  |
| H | 2.48717000  | 0.62015500  | 4.16807900  |
| C | 0.98502700  | 0.93154000  | 2.53163000  |
| C | 0.89821300  | 2.29852800  | 2.23238500  |
| C | -0.00872900 | 2.84631600  | 1.31672800  |
| C | -0.20885300 | 4.23936900  | 1.01663600  |
| H | 0.34468800  | 5.05231100  | 1.47058900  |
| C | -1.21833600 | 4.33119100  | 0.09355100  |
| H | -1.63534700 | 5.23005900  | -0.34325300 |
| C | -1.66143200 | 2.99394400  | -0.19858300 |
| C | -2.68166200 | 2.60403200  | -1.07376000 |
| C | -3.12274700 | 1.29498200  | -1.29942300 |
| C | -4.19505800 | 0.86512900  | -2.15675800 |
| H | -4.81467600 | 1.52560600  | -2.75054900 |
| C | -4.28095300 | -0.49988900 | -2.05889300 |
| H | -4.98751700 | -1.15278100 | -2.55690800 |
| C | -3.26796000 | -0.94199900 | -1.13739000 |
| C | -3.02010000 | -2.25515000 | -0.71630100 |
| C | -2.06006300 | -2.60575900 | 0.24518100  |
| C | -1.72956200 | -3.84805600 | 0.88184000  |
| H | -2.19943900 | -4.80237800 | 0.67752600  |
| C | -0.73341100 | -3.59622800 | 1.81717400  |
| H | -0.27578400 | -4.31382900 | 2.48614000  |
| C | -0.44610300 | -2.20172000 | 1.75883200  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| N  | 0.17604400  | 0.02884200  | 1.88887800  |
| N  | -0.91346500 | 2.11486800  | 0.55989300  |
| N  | -2.58205200 | 0.17944700  | -0.69018700 |
| N  | -1.25490400 | -1.64272900 | 0.80227400  |
| H  | 1.54549800  | 2.98819600  | 2.76617600  |
| H  | -3.64548800 | -3.03890000 | -1.13403700 |
| H  | -3.19505500 | 3.39492500  | -1.61282700 |
| Mn | -0.94276200 | 0.19763100  | 0.33451100  |
| O  | 0.27649600  | -0.03947200 | -0.92608400 |
| C  | 4.53802600  | 0.52888700  | -2.80969500 |
| C  | 3.32934800  | -0.13354200 | -2.60112200 |
| C  | 3.02128000  | -0.61677100 | -1.32034100 |
| C  | 3.91114800  | -0.41128700 | -0.25122400 |
| C  | 5.11000500  | 0.26013300  | -0.47394500 |
| C  | 5.42984000  | 0.72690900  | -1.75259700 |
| H  | 4.77958400  | 0.89807600  | -3.80249100 |
| H  | 2.63920200  | -0.26666500 | -3.42696900 |
| H  | 3.65653500  | -0.76982600 | 0.74252700  |
| H  | 5.79724800  | 0.41686600  | 0.35247600  |
| H  | 6.36829000  | 1.24635700  | -1.92350100 |
| S  | 1.51122200  | -1.43584900 | -0.91107300 |
| C  | 0.90777300  | -2.09585600 | -2.48611900 |
| H  | 1.64801800  | -2.76843500 | -2.92655400 |
| H  | -0.00548000 | -2.64118700 | -2.23876800 |
| H  | 0.65877700  | -1.26981700 | -3.15505200 |

**Table S11.** Optimized cartesian coordinates (Å) of [2-Mn--O--S] (TS) in singlet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.95505900 | -2.52810200 | -1.41012500 |
| C | -2.12380000 | -3.16702500 | -1.91397600 |
| H | -2.16557700 | -4.13335400 | -2.40002200 |
| C | -3.17460100 | -2.28337300 | -1.71723900 |
| H | -4.20449600 | -2.41866300 | -2.02102600 |
| C | -2.63257100 | -1.10608900 | -1.10120200 |
| C | -3.19615500 | 0.15559600  | -0.83627700 |
| C | -2.39843500 | 1.25987100  | -0.48903400 |
| C | -2.88719800 | 2.56824300  | -0.16730200 |
| H | -3.93039500 | 2.85192000  | -0.15291900 |
| C | -1.81266400 | 3.36508600  | 0.11222700  |
| H | -1.82799500 | 4.40573400  | 0.40419100  |
| C | -0.62841500 | 2.56676400  | -0.02046300 |

|    |             |             |             |
|----|-------------|-------------|-------------|
| C  | 0.68236400  | 3.01172800  | 0.22229700  |
| C  | 1.82094100  | 2.19580400  | 0.13705700  |
| C  | 3.19638200  | 2.61649000  | 0.19040300  |
| H  | 3.53330900  | 3.63215000  | 0.34560000  |
| C  | 3.96658800  | 1.51244500  | -0.04712300 |
| H  | 5.04458900  | 1.46945600  | -0.12379400 |
| C  | 3.07900000  | 0.39904900  | -0.25338400 |
| C  | 3.44043300  | -0.89527500 | -0.65570900 |
| C  | 2.48200800  | -1.85245900 | -1.03585400 |
| C  | 2.64485400  | -3.20184500 | -1.47252500 |
| H  | 3.59260700  | -3.71321800 | -1.57538400 |
| C  | 1.38462900  | -3.73020000 | -1.72117000 |
| H  | 1.15384700  | -4.72979600 | -2.06645200 |
| C  | 0.44652600  | -2.71280900 | -1.42748700 |
| N  | -1.30251700 | -1.31699700 | -0.87806700 |
| N  | -0.99695300 | 1.27822000  | -0.39683100 |
| N  | 1.77161400  | 0.83925600  | -0.09498100 |
| N  | 1.12730400  | -1.57772400 | -1.02766900 |
| C  | -4.67179800 | 0.30127100  | -0.94117700 |
| C  | -5.54461000 | -0.42152400 | -0.11594100 |
| C  | -6.92926700 | -0.34304600 | -0.19937900 |
| C  | -7.49347500 | 0.50057500  | -1.15711600 |
| C  | -6.67703500 | 1.24460500  | -2.00878000 |
| C  | -5.29654700 | 1.12755700  | -1.88662700 |
| C  | 0.88564800  | 4.45048300  | 0.56064600  |
| C  | 1.31492000  | 4.86310600  | 1.82854300  |
| C  | 1.52804900  | 6.19405300  | 2.17112700  |
| C  | 1.30207600  | 7.17723200  | 1.20731300  |
| C  | 0.87229000  | 6.82594400  | -0.07261600 |
| C  | 0.67741600  | 5.48030600  | -0.36619000 |
| C  | 4.88294800  | -1.25574000 | -0.72398400 |
| C  | 5.53027300  | -1.55245500 | -1.93127500 |
| C  | 6.87557800  | -1.89549500 | -2.01457500 |
| C  | 7.62888800  | -1.94671400 | -0.84161800 |
| C  | 7.03815200  | -1.66006800 | 0.38936400  |
| C  | 5.68884700  | -1.32547500 | 0.42053100  |
| F  | -5.01558500 | -1.23210200 | 0.83365000  |
| F  | -4.52272900 | 1.83966400  | -2.72586900 |
| F  | 4.81794900  | -1.49386500 | -3.07257700 |
| F  | 5.12675700  | -1.06280300 | 1.61734400  |
| Mn | 0.15399400  | -0.23163700 | -0.13103500 |
| F  | 1.52715000  | 3.92167700  | 2.77020000  |
| F  | 0.27031900  | 5.15174300  | -1.60679700 |
| O  | -0.12745300 | -0.66408100 | 1.49471400  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -2.56153300 | -5.26047400 | 1.57439000  |
| C | -2.64285200 | -3.86894400 | 1.62849800  |
| C | -1.54509800 | -3.14313900 | 2.11109300  |
| C | -0.36268900 | -3.78701800 | 2.49970900  |
| C | -0.29841100 | -5.17713600 | 2.43716100  |
| C | -1.39699600 | -5.91387700 | 1.98262900  |
| H | -3.40939000 | -5.83195600 | 1.20824500  |
| H | -3.53584200 | -3.34852600 | 1.29793200  |
| H | 0.49918000  | -3.21072500 | 2.82005000  |
| H | 0.61437400  | -5.68532500 | 2.73418500  |
| H | -1.33941100 | -6.99772900 | 1.93729000  |
| S | -1.70963300 | -1.37337300 | 2.14751100  |
| C | -1.22723600 | -0.96371900 | 3.85031100  |
| H | -0.20643300 | -1.30119300 | 4.03905700  |
| H | -1.27148800 | 0.12461700  | 3.92866700  |
| H | -1.93213800 | -1.42502800 | 4.54599200  |
| H | -7.53739800 | -0.92900200 | 0.48112200  |
| H | -8.57330900 | 0.57794700  | -1.23962900 |
| H | -7.08598600 | 1.90232800  | -2.76794400 |
| H | 0.69353600  | 7.56747900  | -0.84357600 |
| H | 1.46205900  | 8.22235800  | 1.45484300  |
| H | 1.85874800  | 6.43718400  | 3.17502200  |
| H | 7.30839300  | -2.10623500 | -2.98640700 |
| H | 8.68128000  | -2.21034100 | -0.88703100 |
| H | 7.59673800  | -1.69587600 | 1.31831800  |

**Table S12.** Optimized cartesian coordinates (Å) of [2-Mn--O--S] (TS) in triplet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.74934000 | -2.75852000 | -1.65824500 |
| C | -1.90269000 | -3.47650400 | -2.08580900 |
| H | -1.91744400 | -4.48831600 | -2.47021600 |
| C | -2.98867200 | -2.62359500 | -1.94873300 |
| H | -4.01722200 | -2.83865100 | -2.20655600 |
| C | -2.50152800 | -1.37458700 | -1.43529400 |
| C | -3.14375400 | -0.14776900 | -1.17283600 |
| C | -2.44699600 | 1.01071500  | -0.76595600 |
| C | -3.00959800 | 2.30400600  | -0.48984800 |
| H | -4.05884200 | 2.55326800  | -0.56841100 |
| C | -1.98710000 | 3.14489400  | -0.13688600 |
| H | -2.06194200 | 4.19463900  | 0.11083500  |
| C | -0.76544400 | 2.38801200  | -0.17938500 |
| C | 0.53900800  | 2.85141100  | 0.09266200  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| C  | 1. 71816500  | 2. 08867500  | -0. 03576100 |
| C  | 3. 06917700  | 2. 53181500  | 0. 18452800  |
| H  | 3. 35894400  | 3. 53239900  | 0. 47322700  |
| C  | 3. 89744200  | 1. 46743500  | -0. 04914700 |
| H  | 4. 97748300  | 1. 45937600  | 0. 00251200  |
| C  | 3. 08094000  | 0. 33985100  | -0. 40987500 |
| C  | 3. 52738700  | -0. 95955100 | -0. 73123600 |
| C  | 2. 65073400  | -1. 99365600 | -1. 11398500 |
| C  | 2. 88261200  | -3. 34541300 | -1. 53362800 |
| H  | 3. 85062100  | -3. 82055700 | -1. 61855800 |
| C  | 1. 65197700  | -3. 91465000 | -1. 82830000 |
| H  | 1. 47162300  | -4. 92052300 | -2. 18525400 |
| C  | 0. 66289400  | -2. 92025800 | -1. 58693000 |
| N  | -1. 14882900 | -1. 50959100 | -1. 26502500 |
| N  | -1. 07254400 | 1. 09787700  | -0. 56874800 |
| N  | 1. 75778400  | 0. 75837700  | -0. 40608500 |
| N  | 1. 29844500  | -1. 78110700 | -1. 16540900 |
| C  | -4. 61953700 | -0. 07259600 | -1. 35953900 |
| C  | -5. 51463200 | -0. 76327800 | -0. 53385000 |
| C  | -6. 89450600 | -0. 73306600 | -0. 69654400 |
| C  | -7. 42669000 | 0. 02802200  | -1. 73775400 |
| C  | -6. 58537400 | 0. 74028900  | -2. 59260500 |
| C  | -5. 21137200 | 0. 67338400  | -2. 38834200 |
| C  | 0. 67614800  | 4. 26802400  | 0. 54240600  |
| C  | 0. 23621800  | 4. 69751700  | 1. 79993200  |
| C  | 0. 34334400  | 6. 00864600  | 2. 24828600  |
| C  | 0. 92406400  | 6. 95618400  | 1. 40445400  |
| C  | 1. 38236000  | 6. 58811000  | 0. 13943700  |
| C  | 1. 24701800  | 5. 26318000  | -0. 26184500 |
| C  | 4. 98766700  | -1. 24925200 | -0. 67840900 |
| C  | 5. 73395800  | -1. 54377800 | -1. 82717400 |
| C  | 7. 09457800  | -1. 83090800 | -1. 80351400 |
| C  | 7. 75947400  | -1. 82593000 | -0. 57727200 |
| C  | 7. 06750100  | -1. 53926300 | 0. 59981300  |
| C  | 5. 70707600  | -1. 26186800 | 0. 52384400  |
| F  | -5. 01565700 | -1. 49290700 | 0. 49142200  |
| F  | -4. 40882000 | 1. 35732300  | -3. 22450000 |
| F  | 5. 10449000  | -1. 54217700 | -3. 01789100 |
| F  | 5. 04691400  | -0. 99548900 | 1. 66845300  |
| Mn | 0. 18724900  | -0. 36381700 | -0. 49254200 |
| F  | -0. 32615400 | 3. 78919000  | 2. 63239400  |
| F  | 1. 68639100  | 4. 91983900  | -1. 48679100 |
| O  | 0. 07217400  | -0. 77109600 | 1. 21875500  |
| C  | -2. 80748700 | -4. 36239900 | 3. 01236200  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -2.68660500 | -3.06777800 | 2.51232400  |
| C | -1.61584400 | -2.26232000 | 2.93473100  |
| C | -0.66173700 | -2.75990800 | 3.83517900  |
| C | -0.80199000 | -4.05413300 | 4.33196700  |
| C | -1.87194600 | -4.85656000 | 3.92541400  |
| H | -3.63671100 | -4.98493800 | 2.68885500  |
| H | -3.41040900 | -2.68021400 | 1.80254000  |
| H | 0.18517900  | -2.15417100 | 4.13750300  |
| H | -0.06660100 | -4.44014000 | 5.03231300  |
| H | -1.97234600 | -5.86547800 | 4.31528200  |
| S | -1.51237300 | -0.65738700 | 2.19970300  |
| C | -0.72865300 | 0.37317000  | 3.46844900  |
| H | 0.28849800  | 0.01819800  | 3.64484100  |
| H | -0.68637400 | 1.38243600  | 3.05405600  |
| H | -1.32614100 | 0.35878300  | 4.38335900  |
| H | -7.52325200 | -1.29190100 | -0.01209800 |
| H | -8.50198400 | 0.06645700  | -1.88298100 |
| H | -6.96975200 | 1.33604400  | -3.41324100 |
| H | -0.01927500 | 6.26420100  | 3.23789000  |
| H | 1.01915400  | 7.98616700  | 1.73454400  |
| H | 1.83322300  | 7.30345900  | -0.53963300 |
| H | 7.55626300  | -1.53306900 | 1.56794600  |
| H | 8.82202200  | -2.04624800 | -0.53861700 |
| H | 7.60666100  | -2.04454900 | -2.73532400 |

**Table S13.** Optimized cartesian coordinates (Å) of [3-Mn--O--S] (TS) in singlet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.80627900 | -2.96943000 | -1.20046300 |
| C | -1.92245200 | -3.73279200 | -1.64958700 |
| H | -1.88708100 | -4.72313700 | -2.08471200 |
| C | -3.04189400 | -2.93385500 | -1.47967700 |
| H | -4.05951800 | -3.17418000 | -1.75874900 |
| C | -2.59457300 | -1.68279100 | -0.93418600 |
| C | -3.25994500 | -0.46119700 | -0.72536800 |
| C | -2.55851000 | 0.72682700  | -0.45258000 |
| C | -3.15482700 | 2.00315200  | -0.19026500 |
| H | -4.21784600 | 2.19884800  | -0.16695200 |
| C | -2.14937300 | 2.90408900  | 0.02245100  |
| H | -2.25386400 | 3.95358700  | 0.25899500  |
| C | -0.90300800 | 2.20456000  | -0.09362900 |
| C | 0.36917100  | 2.77099200  | 0.09505200  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| C | 1. 57391600  | 2. 05454400  | 0. 03027500  |
| C | 2. 90782100  | 2. 59457000  | 0. 02945000  |
| H | 3. 16081400  | 3. 64190300  | 0. 11955600  |
| C | 3. 76669500  | 1. 54911000  | -0. 16410600 |
| H | 4. 84261800  | 1. 59747000  | -0. 26271300 |
| C | 2. 97514600  | 0. 35427800  | -0. 28846400 |
| C | 3. 43833700  | -0. 92595400 | -0. 62766000 |
| C | 2. 56263000  | -1. 98255300 | -0. 93447200 |
| C | 2. 83494200  | -3. 33401200 | -1. 30867500 |
| H | 3. 82065200  | -3. 76839000 | -1. 40871800 |
| C | 1. 62214900  | -3. 98055100 | -1. 50253900 |
| H | 1. 47348200  | -5. 01201500 | -1. 79448500 |
| C | 0. 60429700  | -3. 03395100 | -1. 23641700 |
| N | -1. 24950300 | -1. 76644900 | -0. 72437700 |
| N | -1. 16355000 | 0. 87045000  | -0. 39182200 |
| N | 1. 63817500  | 0. 68808000  | -0. 12525000 |
| N | 1. 19041900  | -1. 82582000 | -0. 90693900 |
| C | -4. 74368000 | -0. 45058400 | -0. 80792000 |
| C | -5. 51808600 | -1. 21987800 | 0. 07080900  |
| C | -6. 90731900 | -1. 26282000 | -0. 00011300 |
| C | -7. 56803700 | -0. 51739800 | -0. 97360300 |
| C | -6. 83210000 | 0. 26013600  | -1. 86445900 |
| C | -5. 44152200 | 0. 28074500  | -1. 77840100 |
| C | 0. 45214400  | 4. 23825300  | 0. 35096100  |
| C | 0. 86710400  | 4. 73848000  | 1. 59073600  |
| C | 0. 96542800  | 6. 10455200  | 1. 84430800  |
| C | 0. 63847100  | 7. 01461100  | 0. 84201800  |
| C | 0. 21931000  | 6. 55169400  | -0. 40296300 |
| C | 0. 13515500  | 5. 18043200  | -0. 63491800 |
| C | 4. 90517900  | -1. 16403200 | -0. 70906500 |
| C | 5. 53873400  | -1. 47225700 | -1. 91956900 |
| C | 6. 91011300  | -1. 70458900 | -1. 99914900 |
| C | 7. 69036400  | -1. 62500200 | -0. 84833400 |
| C | 7. 09313000  | -1. 31742800 | 0. 37163300  |
| C | 5. 71940900  | -1. 09540300 | 0. 42842100  |
| F | -4. 92680700 | -1. 93833200 | 1. 04538600  |
| F | -7. 61011300 | -2. 00449700 | 0. 86536800  |
| F | -8. 90105400 | -0. 54756900 | -1. 05088600 |
| F | -7. 46366200 | 0. 96925300  | -2. 80634100 |
| F | -4. 77429000 | 1. 02392100  | -2. 66942600 |
| F | 4. 82811200  | -1. 54232100 | -3. 05275000 |
| F | 7. 48307100  | -1. 99293300 | -3. 17371000 |
| F | 9. 00672700  | -1. 84359500 | -0. 91404100 |
| F | 7. 83936400  | -1. 24851000 | 1. 48096700  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| F  | 5.18149400  | -0.81856200 | 1.62488200  |
| Mn | 0.11775100  | -0.51985200 | -0.06692500 |
| F  | 1.17803600  | 3.89468500  | 2.58541000  |
| F  | 1.36146000  | 6.54731900  | 3.04416400  |
| F  | 0.72547000  | 8.32740900  | 1.07460400  |
| F  | -0.08988400 | 7.42504400  | -1.36868300 |
| F  | -0.26074900 | 4.77514300  | -1.84832200 |
| O  | -0.09242400 | -0.88054800 | 1.58171200  |
| C  | -2.03875400 | -5.68868000 | 1.96592100  |
| C  | -2.25654400 | -4.31110200 | 1.94527200  |
| C  | -1.23664900 | -3.45553300 | 2.38483600  |
| C  | 0.00179400  | -3.95791700 | 2.80659600  |
| C  | 0.20263900  | -5.33629900 | 2.81855400  |
| C  | -0.81646200 | -6.20090700 | 2.40583200  |
| H  | -2.82595700 | -6.35975200 | 1.63542000  |
| H  | -3.19748700 | -3.90098300 | 1.59296400  |
| H  | 0.80101500  | -3.28454700 | 3.09854300  |
| H  | 1.15905100  | -5.73570600 | 3.14294400  |
| H  | -0.65258500 | -7.27460400 | 2.41979600  |
| S  | -1.58041600 | -1.71310800 | 2.32821300  |
| C  | -1.10119800 | -1.15203000 | 3.98781200  |
| H  | -0.03960200 | -1.34516800 | 4.15289400  |
| H  | -1.28413700 | -0.07578100 | 4.01438400  |
| H  | -1.71782900 | -1.66153800 | 4.73181700  |

**Table S14.** Optimized cartesian coordinates (Å) of [3-Mn--O--S] (TS) in triplet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.75715300 | -3.05480500 | -1.24827700 |
| C | -1.88932900 | -3.84847200 | -1.58858500 |
| H | -1.86982400 | -4.88084700 | -1.91267100 |
| C | -3.00801500 | -3.03749600 | -1.46401100 |
| H | -4.03252300 | -3.31296300 | -1.67674000 |
| C | -2.56174400 | -1.73776100 | -1.04709400 |
| C | -3.24759800 | -0.52266000 | -0.84756700 |
| C | -2.59000700 | 0.69502500  | -0.57308500 |
| C | -3.20081500 | 1.97871900  | -0.35996600 |
| H | -4.26401100 | 2.17443700  | -0.38700500 |
| C | -2.20296400 | 2.89029800  | -0.13865000 |
| H | -2.31776100 | 3.95089900  | 0.03707900  |
| C | -0.94956500 | 2.18891500  | -0.20048500 |
| C | 0.34016900  | 2.73168300  | -0.03571000 |
| C | 1.54888700  | 2.01603000  | -0.14492700 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | 2.88514600  | 2.54294000  | -0.05787900 |
| H | 3.13963800  | 3.58122200  | 0.10251000  |
| C | 3.75246200  | 1.49894700  | -0.23107100 |
| H | 4.83239400  | 1.54860600  | -0.25046200 |
| C | 2.97476300  | 0.30380700  | -0.42207200 |
| C | 3.46315200  | -0.99859900 | -0.65634500 |
| C | 2.62008800  | -2.09641100 | -0.91809400 |
| C | 2.89726800  | -3.46770700 | -1.23384700 |
| H | 3.88121000  | -3.90934400 | -1.31614200 |
| C | 1.68494900  | -4.11236000 | -1.43031600 |
| H | 1.53869500  | -5.15132100 | -1.69570100 |
| C | 0.66082300  | -3.14565200 | -1.22937100 |
| N | -1.20123900 | -1.80341100 | -0.90902900 |
| N | -1.21206700 | 0.86071000  | -0.47823100 |
| N | 1.63536200  | 0.65727800  | -0.36907100 |
| N | 1.25808700  | -1.94549800 | -0.93396100 |
| C | -4.73339500 | -0.53743100 | -0.94020800 |
| C | -5.51368600 | -1.21432800 | 0.00438600  |
| C | -6.90255400 | -1.26564900 | -0.07545700 |
| C | -7.55292300 | -0.62162300 | -1.12539900 |
| C | -6.80910400 | 0.06494500  | -2.08225400 |
| C | -5.41957200 | 0.09664900  | -1.98336100 |
| C | 0.42933600  | 4.18954600  | 0.27580300  |
| C | 0.09471200  | 4.68229700  | 1.54167800  |
| C | 0.16790700  | 6.03789800  | 1.85253800  |
| C | 0.59068700  | 6.94251100  | 0.88127800  |
| C | 0.93346800  | 6.48540800  | -0.38900500 |
| C | 0.84705800  | 5.12470400  | -0.67701500 |
| C | 4.93536100  | -1.22150700 | -0.64438000 |
| C | 5.63128200  | -1.60638300 | -1.79699400 |
| C | 7.00575200  | -1.83361900 | -1.79104600 |
| C | 7.72582700  | -1.66988100 | -0.61038200 |
| C | 7.06558500  | -1.28472100 | 0.55384300  |
| C | 5.68965800  | -1.07137200 | 0.52597100  |
| F | -4.92877700 | -1.82925800 | 1.04929000  |
| F | -7.61392700 | -1.91761000 | 0.85226000  |
| F | -8.88484200 | -0.66066800 | -1.21248000 |
| F | -7.43172600 | 0.67838700  | -3.09446300 |
| F | -4.74014300 | 0.75460700  | -2.93061700 |
| F | 4.97899300  | -1.76079400 | -2.95681700 |
| F | 7.63846000  | -2.19838600 | -2.91224400 |
| F | 9.04457800  | -1.88190400 | -0.59416100 |
| F | 7.75368900  | -1.13339000 | 1.69199600  |
| F | 5.09015200  | -0.71810000 | 1.67187000  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| Mn | 0.11315000  | -0.53479700 | -0.31219800 |
| F  | -0.30991900 | 3.83951600  | 2.50458000  |
| F  | -0.15714100 | 6.47476200  | 3.07541800  |
| F  | 0.66723800  | 8.24488800  | 1.16780300  |
| F  | 1.33483500  | 7.35431400  | -1.32378500 |
| F  | 1.17851800  | 4.72213400  | -1.91054200 |
| O  | 0.04850600  | -0.82643100 | 1.41363300  |
| C  | -2.24092900 | -5.29773600 | 2.54433600  |
| C  | -2.38203100 | -3.92419700 | 2.34812100  |
| C  | -1.30136800 | -3.07746400 | 2.63599400  |
| C  | -0.07891200 | -3.59770400 | 3.08453900  |
| C  | 0.04384900  | -4.97154100 | 3.27941200  |
| C  | -1.03490100 | -5.82150700 | 3.01531000  |
| H  | -3.07655300 | -5.95743100 | 2.32932800  |
| H  | -3.31315200 | -3.51051700 | 1.97466500  |
| H  | 0.76840100  | -2.94143100 | 3.25192600  |
| H  | 0.98759800  | -5.38086000 | 3.62824800  |
| H  | -0.93135500 | -6.89181900 | 3.16915300  |
| S  | -1.52867600 | -1.34297900 | 2.33336300  |
| C  | -0.89670900 | -0.56027000 | 3.84437200  |
| H  | 0.16173000  | -0.79805600 | 3.96426100  |
| H  | -1.01072000 | 0.51630000  | 3.70095500  |
| H  | -1.48208000 | -0.89665900 | 4.70336100  |

**Table S15.** Optimized cartesian coordinates (Å) of **[4-Mn--O--S]** (TS) in singlet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.39062400 | -2.67443100 | -0.83731800 |
| C | -1.21241600 | -3.76330800 | -1.24574500 |
| H | -0.86424800 | -4.72684600 | -1.59094200 |
| C | -2.52133100 | -3.31677900 | -1.16453100 |
| H | -3.41247300 | -3.86498300 | -1.44075900 |
| C | -2.48123300 | -1.95368700 | -0.71449500 |
| C | -3.48192800 | -0.97107100 | -0.61181400 |
| C | -3.16917400 | 0.38570400  | -0.41821100 |
| C | -4.12213800 | 1.44612600  | -0.27313100 |
| H | -5.19608200 | 1.32220300  | -0.28838500 |
| C | -3.43240700 | 2.61544300  | -0.11475200 |
| H | -3.84726800 | 3.60270500  | 0.03240700  |
| C | -2.03267700 | 2.30472000  | -0.14695900 |
| C | -0.98886100 | 3.23142800  | 0.02274700  |
| C | 0.37123600  | 2.89131700  | 0.04560200  |
| C | 1.49391400  | 3.79321700  | 0.04597700  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| H  | 1. 43122100  | 4. 87248500  | 0. 06340500  |
| C  | 2. 62387000  | 3. 03114800  | -0. 03374900 |
| H  | 3. 64514200  | 3. 38092100  | -0. 09110200 |
| C  | 2. 21535400  | 1. 64999700  | -0. 09179100 |
| C  | 3. 05926700  | 0. 55158700  | -0. 30061800 |
| C  | 2. 56250000  | -0. 74547300 | -0. 53854400 |
| C  | 3. 20850400  | -2. 00050700 | -0. 78955200 |
| C  | 2. 22177800  | -2. 96616400 | -0. 96689200 |
| C  | 0. 97708100  | -2. 32958300 | -0. 81601900 |
| N  | -1. 17986800 | -1. 62136800 | -0. 47548800 |
| N  | -1. 87961700 | 0. 93589800  | -0. 33952900 |
| N  | 0. 83175200  | 1. 59472700  | -0. 00015800 |
| N  | 1. 19923200  | -0. 99065700 | -0. 56903200 |
| C  | -4. 90015600 | -1. 40375900 | -0. 71815800 |
| C  | -5. 44797000 | -2. 29982700 | 0. 20957000  |
| C  | -6. 76077200 | -2. 75354800 | 0. 12234100  |
| C  | -7. 57255900 | -2. 30921900 | -0. 91877100 |
| C  | -7. 06257400 | -1. 41805200 | -1. 85995400 |
| C  | -5. 74295000 | -0. 98294500 | -1. 75539300 |
| C  | -1. 34503800 | 4. 67350000  | 0. 16030200  |
| C  | -1. 14223900 | 5. 36194700  | 1. 36235700  |
| C  | -1. 45650800 | 6. 71127000  | 1. 50616100  |
| C  | -1. 99564700 | 7. 40971000  | 0. 42840700  |
| C  | -2. 21303600 | 6. 75518700  | -0. 78184700 |
| C  | -1. 88462700 | 5. 40663300  | -0. 90370600 |
| C  | 4. 52688200  | 0. 82249700  | -0. 31303200 |
| C  | 5. 21118500  | 1. 08940000  | -1. 50129400 |
| C  | 6. 57684400  | 1. 36003800  | -1. 51825300 |
| C  | 7. 28913700  | 1. 37004700  | -0. 32099800 |
| C  | 6. 63282300  | 1. 11523700  | 0. 88088100  |
| C  | 5. 26625400  | 0. 84950100  | 0. 87142100  |
| F  | -4. 70831800 | -2. 73918400 | 1. 24608400  |
| F  | -7. 24883200 | -3. 60276900 | 1. 03480200  |
| F  | -8. 83446300 | -2. 73509000 | -1. 01253700 |
| F  | -7. 83728000 | -0. 99729900 | -2. 86531000 |
| F  | -5. 28752200 | -0. 14358900 | -2. 69334200 |
| F  | 4. 55389300  | 1. 08084800  | -2. 66731000 |
| F  | 7. 20814800  | 1. 61053000  | -2. 67102700 |
| F  | 8. 59989400  | 1. 62868800  | -0. 32483500 |
| F  | 7. 31725000  | 1. 12793000  | 2. 03144400  |
| F  | 4. 66366900  | 0. 60087000  | 2. 04338300  |
| Mn | -0. 26520100 | 0. 00658700  | 0. 12182600  |
| F  | -0. 63666500 | 4. 72068500  | 2. 42613500  |
| F  | -1. 25352000 | 7. 33654200  | 2. 67209000  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| F  | -2.30417100 | 8.70299500  | 0.55552400  |
| F  | -2.72572400 | 7.42645700  | -1.81941100 |
| F  | -2.09800700 | 4.81498800  | -2.08609500 |
| O  | -0.42839000 | -0.28890100 | 1.78382700  |
| C  | -0.78263600 | -5.43792400 | 2.40641100  |
| C  | -1.43017500 | -4.20408200 | 2.34388900  |
| C  | -0.72298100 | -3.04822200 | 2.70270300  |
| C  | 0.62358100  | -3.10793500 | 3.08665500  |
| C  | 1.25540500  | -4.34800200 | 3.13799300  |
| C  | 0.55357500  | -5.51100200 | 2.80437500  |
| H  | -1.32320300 | -6.34024200 | 2.13689200  |
| H  | -2.46287600 | -4.13258600 | 2.01776300  |
| H  | 1.17425900  | -2.20124600 | 3.31464400  |
| H  | 2.30028000  | -4.40562000 | 3.42741400  |
| H  | 1.05459400  | -6.47362100 | 2.84474800  |
| S  | -1.59985500 | -1.50773600 | 2.58380300  |
| C  | -1.32076900 | -0.75134400 | 4.21151200  |
| H  | -0.25031300 | -0.62477200 | 4.38312400  |
| H  | -1.80609200 | 0.22669000  | 4.18625000  |
| H  | -1.77317700 | -1.38124200 | 4.98102800  |
| Br | 2.46949400  | -4.79330100 | -1.31935500 |
| Br | 5.04978700  | -2.38041100 | -0.85016400 |

**Table S16.** Optimized cartesian coordinates (Å) of **[4-Mn--O--S]** (TS) in triplet state by using B3LYP method.

|   |             |             |             |
|---|-------------|-------------|-------------|
| C | -0.30437200 | -2.86394500 | -0.91611500 |
| C | -1.15801000 | -3.96856600 | -1.19399200 |
| H | -0.83657500 | -4.98264800 | -1.38765100 |
| C | -2.45654600 | -3.48303400 | -1.19834900 |
| H | -3.35579200 | -4.05022800 | -1.39773500 |
| C | -2.40022500 | -2.07565400 | -0.92233400 |
| C | -3.39870500 | -1.08443400 | -0.86538200 |
| C | -3.11193900 | 0.28535500  | -0.67763900 |
| C | -4.05447100 | 1.36942100  | -0.64318000 |
| H | -5.12501000 | 1.26798100  | -0.75383600 |
| C | -3.35452300 | 2.53422300  | -0.47308700 |
| H | -3.75884700 | 3.53594700  | -0.43277800 |
| C | -1.96055400 | 2.19518400  | -0.38676000 |
| C | -0.87173200 | 3.07866600  | -0.22933300 |
| C | 0.48644100  | 2.70511200  | -0.22991700 |
| C | 1.62591300  | 3.56912500  | -0.07250000 |
| H | 1.58656600  | 4.64246100  | 0.04887900  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| C  | 2.74623800  | 2.78573400  | -0.10393100 |
| H  | 3.77219100  | 3.11582100  | -0.02046000 |
| C  | 2.32902700  | 1.41920300  | -0.28246300 |
| C  | 3.17690100  | 0.29584000  | -0.35813400 |
| C  | 2.69455200  | -1.01748000 | -0.54239500 |
| C  | 3.32664500  | -2.29337000 | -0.75805700 |
| C  | 2.32236500  | -3.24025500 | -0.93016000 |
| C  | 1.08086100  | -2.56867600 | -0.82404900 |
| N  | -1.08005200 | -1.74865500 | -0.75318400 |
| N  | -1.84118200 | 0.82488200  | -0.51299600 |
| N  | 0.94393500  | 1.40903300  | -0.37043000 |
| N  | 1.34308200  | -1.24608100 | -0.59204800 |
| C  | -4.81679600 | -1.50627600 | -1.03505800 |
| C  | -5.45183100 | -2.32323000 | -0.09269100 |
| C  | -6.76987600 | -2.74623000 | -0.24011300 |
| C  | -7.49647100 | -2.34828300 | -1.35977200 |
| C  | -6.89738400 | -1.53467800 | -2.31868500 |
| C  | -5.57479200 | -1.12989500 | -2.15111500 |
| C  | -1.18948800 | 4.52673200  | -0.05869000 |
| C  | -1.80619300 | 5.00877100  | 1.10074600  |
| C  | -2.11548300 | 6.35456700  | 1.27709700  |
| C  | -1.79987600 | 7.26678300  | 0.27275400  |
| C  | -1.18267900 | 6.82378100  | -0.89480700 |
| C  | -0.89026400 | 5.47003200  | -1.04911500 |
| C  | 4.64214300  | 0.54758500  | -0.23016500 |
| C  | 5.40073600  | 1.02032400  | -1.30436100 |
| C  | 6.76799600  | 1.25985400  | -1.19000000 |
| C  | 7.40573800  | 1.02788100  | 0.02647600  |
| C  | 6.67458500  | 0.56402600  | 1.11776200  |
| C  | 5.30935300  | 0.33206000  | 0.97859600  |
| F  | -4.79051500 | -2.72345300 | 1.00828500  |
| F  | -7.34217500 | -3.52260800 | 0.68744700  |
| F  | -8.76205500 | -2.74437600 | -1.51233500 |
| F  | -7.59064900 | -1.15651300 | -3.39757800 |
| F  | -5.03190500 | -0.36042100 | -3.10273700 |
| F  | 4.81647300  | 1.24836500  | -2.48751800 |
| F  | 7.47068000  | 1.70911700  | -2.23615900 |
| F  | 8.71623900  | 1.25578600  | 0.14845300  |
| F  | 7.28711400  | 0.34773400  | 2.28802500  |
| F  | 4.63329200  | -0.11783800 | 2.04486900  |
| Mn | -0.19792400 | -0.13639000 | -0.20058200 |
| F  | -2.12257800 | 4.16362700  | 2.10018500  |
| F  | -2.70376500 | 6.77584200  | 2.40262900  |
| F  | -2.08787400 | 8.56077300  | 0.42954300  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| F  | -0.88371100 | 7.69716500  | -1.86184200 |
| F  | -0.30589600 | 5.08194800  | -2.18896200 |
| O  | -0.23752900 | -0.24296100 | 1.54378400  |
| C  | -2.29945900 | -3.88524500 | 4.30049300  |
| C  | -2.51282400 | -2.71349100 | 3.57523900  |
| C  | -1.51645800 | -1.72690400 | 3.55816400  |
| C  | -0.30489400 | -1.91564400 | 4.23826100  |
| C  | -0.10960800 | -3.08938100 | 4.96280900  |
| C  | -1.10417600 | -4.07184900 | 4.99835400  |
| H  | -3.06914600 | -4.65117100 | 4.31888700  |
| H  | -3.43612700 | -2.56516700 | 3.02482200  |
| H  | 0.48139700  | -1.17103700 | 4.18214400  |
| H  | 0.82653800  | -3.24209600 | 5.49199000  |
| H  | -0.94274700 | -4.98520900 | 5.56359400  |
| S  | -1.83660800 | -0.28397800 | 2.57847600  |
| C  | -1.27437500 | 1.09226700  | 3.61911100  |
| H  | -0.20161800 | 0.99763100  | 3.79661400  |
| H  | -1.47128100 | 2.00477300  | 3.05307000  |
| H  | -1.83571700 | 1.09647900  | 4.55664100  |
| Br | 2.53674200  | -5.07232500 | -1.27234600 |
| Br | 5.16276500  | -2.68204900 | -0.86756000 |