Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## The Role of Attractive Dispersion Interaction in Promoting The Catalytic Activity of Asymmetric Hydrogenation

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CONTENTS

# 1. DFT Computation

## 1.1 Computational methods

Computations were performed using the Gaussian 09 (revision D.01) suite of quantum chemical programs. The level of theories that the references in the manuscript are shown below. The methods for dealing with the dispersion interaction were processed by Grimme, and we selected the Grimme-D2 version to match the $\omega$-b97xd functional.

**Table S1. The level of theories that the references in the manuscript.**

| Ref. | Basis set | | Functional | Method for dispersion interaction | Implicit solvent model |
|---|---|---|---|---|---|
| | Light atoms | Heavy atoms | | | |
| [9] for Figure 1 | 6-31g(d,p)[a] | SDD | $\omega$-b97xd | Grimme-D2 | $SMD_{TFE}$ |
| [10] for Figure 2 | 6-31g(d,p)[a] | SDD | $\omega$-b97xd | Grimme-D2 | $SMD_{DCM}$ |
| [11] for Figure 3 | 6-31g(d,p) | 6-31g(d,p) | $\omega$-b97xd | Grimme-D2 | $SMD_{TFE}$ |
| [14] for Figure 4 | 6-31g(d,p) | 6-31g(d,p) | $\omega$-b97xd | Grimme-D2 | $SMD_{TFE}$ |
| [15] for Figure 5 | 6-31g(d,p) | 6-31g(d,p) | $\omega$-b97xd | Grimme-D2 | $SMD_{TFE}$ |

[a]: Extra basis was used for P atom: P 0/D 1 1.0/0.55 0.100D+01.

IGM analysis was performing using Multiwfn and energy decomposition analysis was performing using Psi4.

Given the complexities of metal complexes, the hydrogenation pathway of all configurations and conformations of metal catalyst were considered, which also conclude other potential hydrogenation mechanisms. For more details about the other configurations and conformations of metal catalyst, please see the relative supporting information of cited references. For the coordinates of the mentioned structure, please see the relative supporting information of cited references as well.

## 1.2 Visual analysis of secondary interactions.

In this section, a series of visual analysis of secondary interactions according to IGM[1] (Independent Gradient Model) analysis by using Multiwfn[2] were exhibited. All isovalue surfaces were set as 0.01. And diagrams of all figures in this section was shown in Figure S1. Besides, it is worth noting that the interactions in the manuscript were selected according to IGM analysis or AIM analysis.

IGM methods are greatly inspired by the RDG[3] approach (or known as NCI analysis), but the underlying idea is different. Like RDG, IGM is focused on the weak interaction region and its characteristics. However, the information given will be clearly divided into two sets of data, intersegment and intramolecular, so that the intramolecular interaction will not be interfered by the intramolecular interaction.

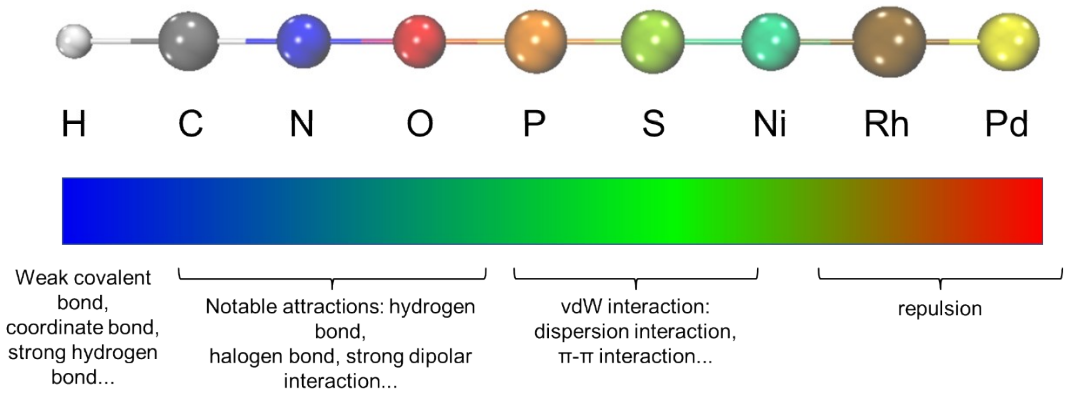


**Figure S1 Diagram of all figures in this section.**

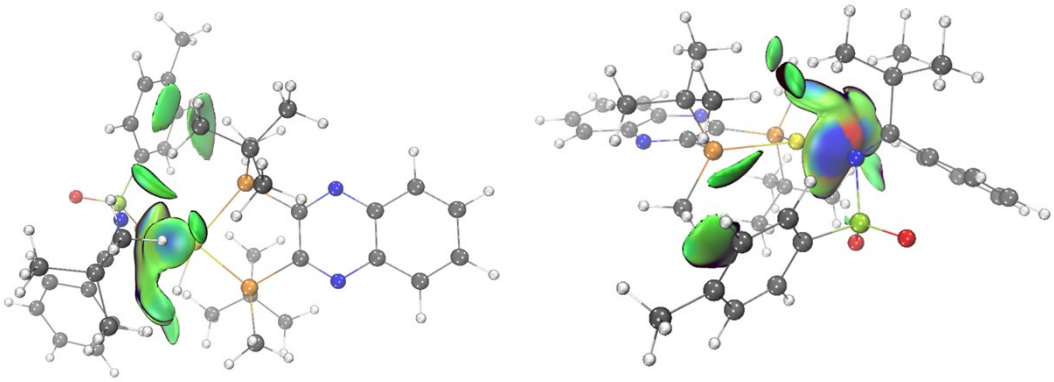

**Figure S2 Two side of views of TS(*S*) in Figure 2.**

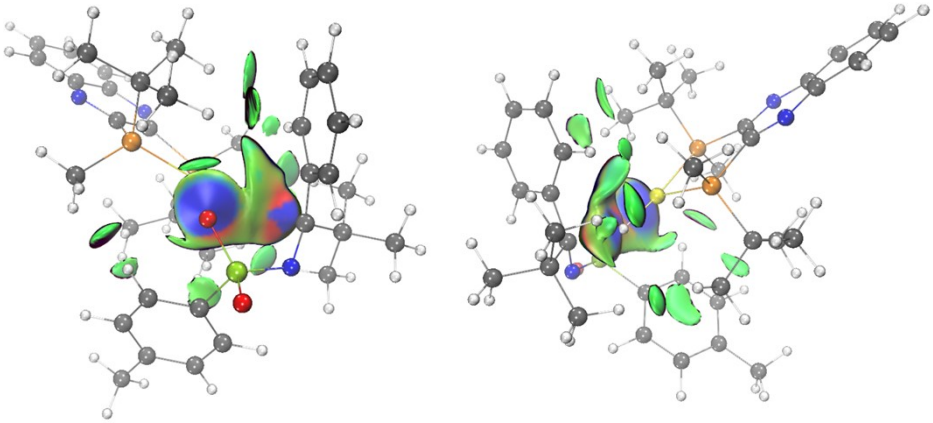

**Figure S3 Two side of views of TS(*R*) in Figure 2.**

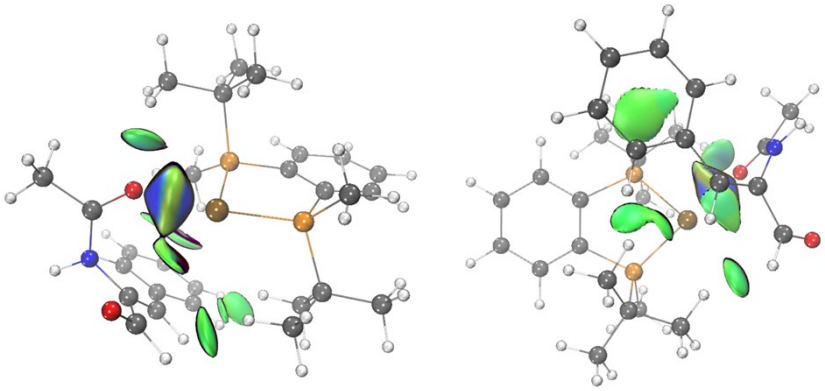

**Figure S4 Two side of views of 18 in Figure 3.**

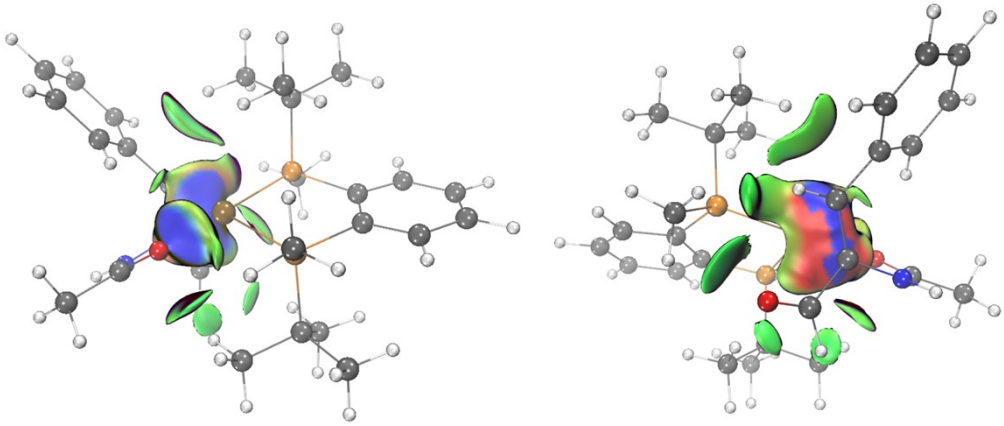

**Figure S5 Two side of views of 25 in Figure 3.**

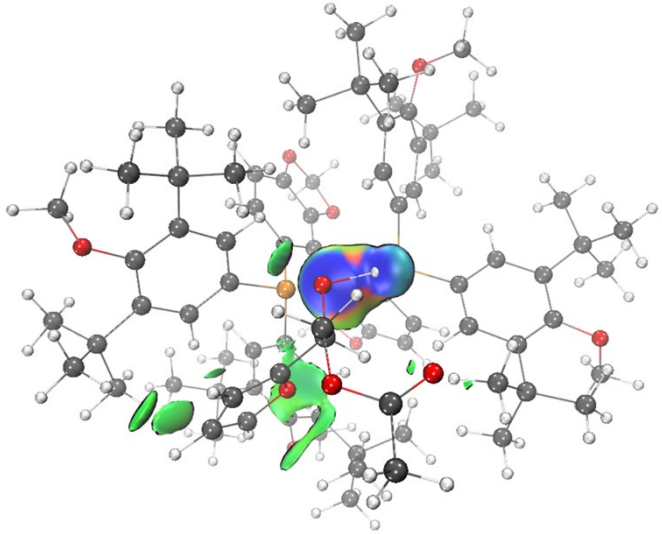

**Figure S6 TS-2a in Figure 4.**

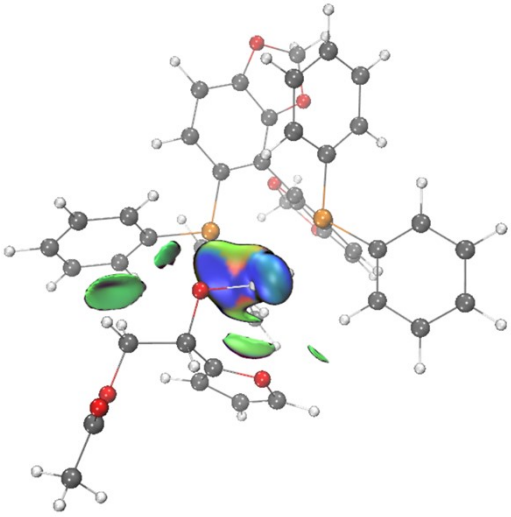

**Figure S7 TS-2b in Figure 4.**

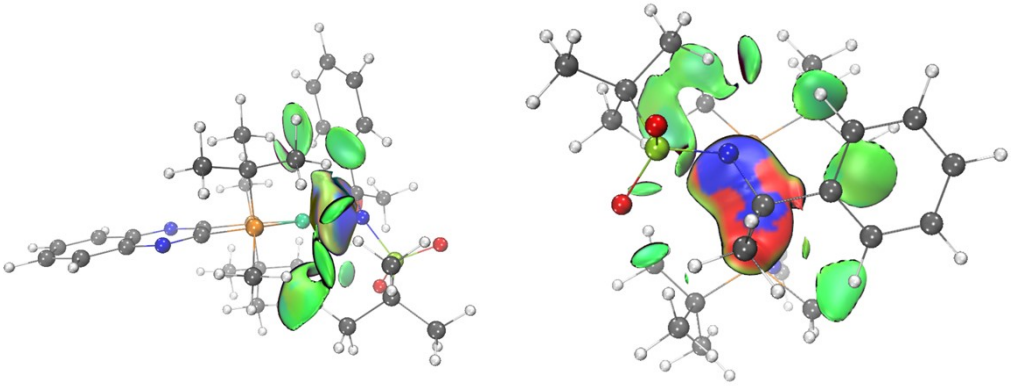

**Figure S8 Two side of views of TS(*R*) in Figure 5.**

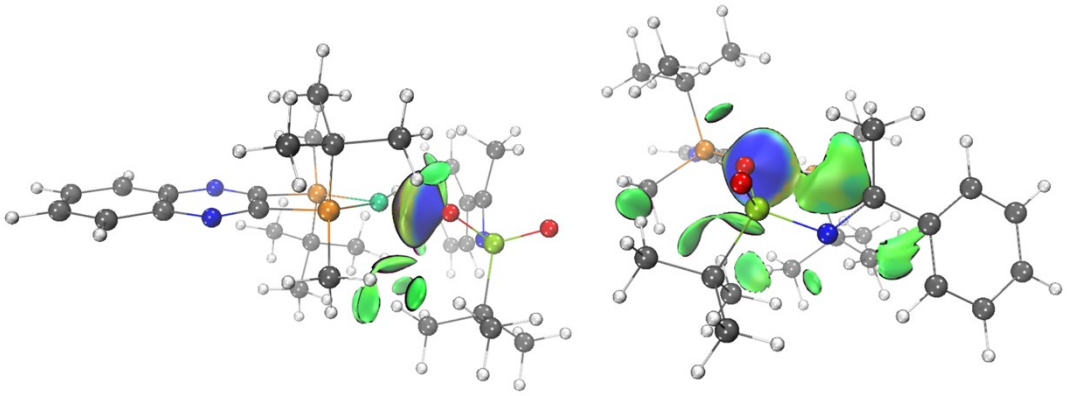

**Figure S9 Two side of views of TS(*S*) in Figure 5.**

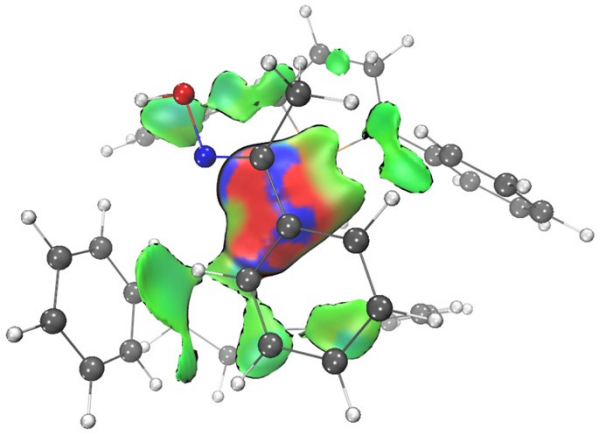

Figure S10 TS(*S*) in Figure 6.

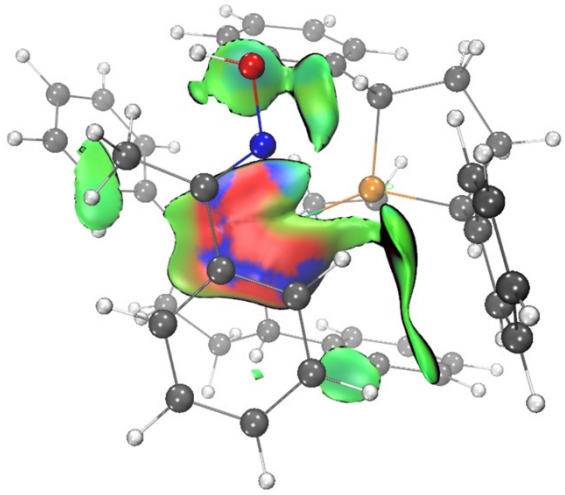

Figure S11 TS(*R*) in Figure 6.

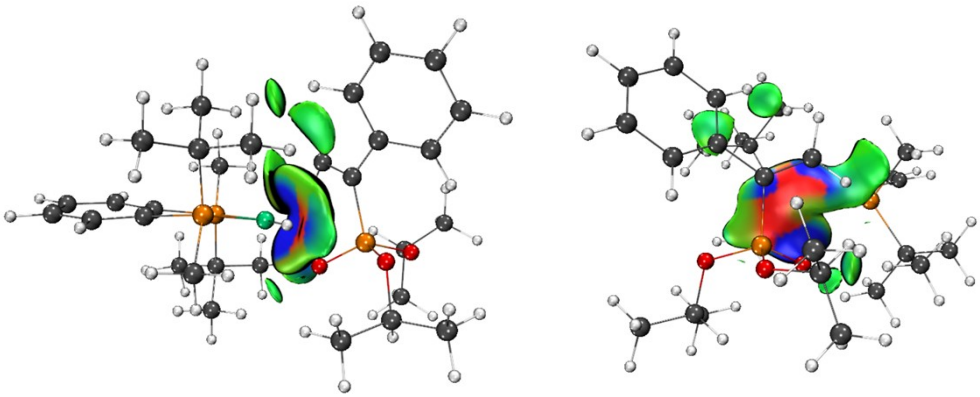

Figure S12 Two side of views of TS(*R*) in Figure 7.

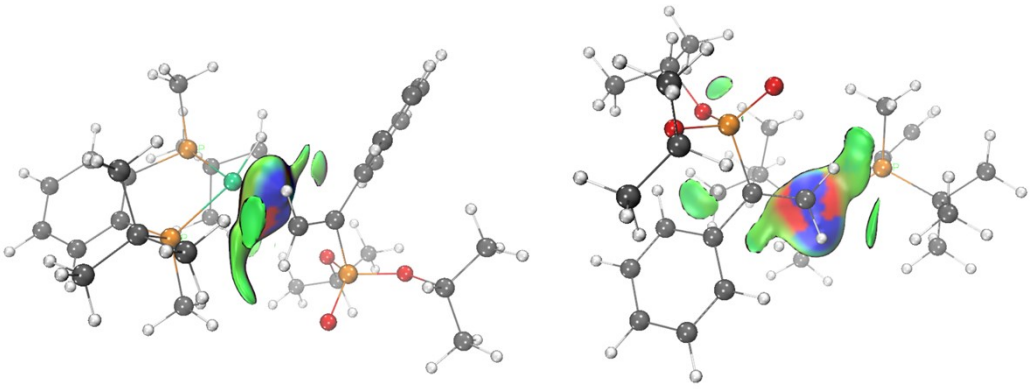

**Figure S13 Two side of views of TS(*S*) in Figure 7.**

## 1.3 Energy decomposition analysis (EDA).

In this section, a series of energy decomposition analysis were exhibited. The EDA was aimed at the interaction between substrate and metal complex. The total interaction energy, marked as $E_{total}$, was divided into six parts: the electrostatic interaction ($E_{ele}$), the exchange repulsion interaction ($E_{ex}$), the induction interaction ($E_{ind}$), the dispersion interaction ($E_{disp}$), the distortion of substrate ($E_{dist(sub)}$), and the distortion of metal complex ($E_{dist(cat)}$). In general, the total interaction energies $E_{total}$ were always negative and the relative level of energies were corresponded to the free energies in the manuscript. $E_{ele}$ (always positive) represented the coordination interaction in these computations, $E_{ind}$ (always negative) represented interaction between dipole and induced dipole like C-H…O or C-H…π, and $E_{disp}$ (always negative) represented interaction between interaction between instantaneous dipoles like C-H…H-C. $E_{dist(sub)}$ and $E_{dist(cat)}$ represented distortion of substrate and the distortion of metal complex respectively, which were always positive.

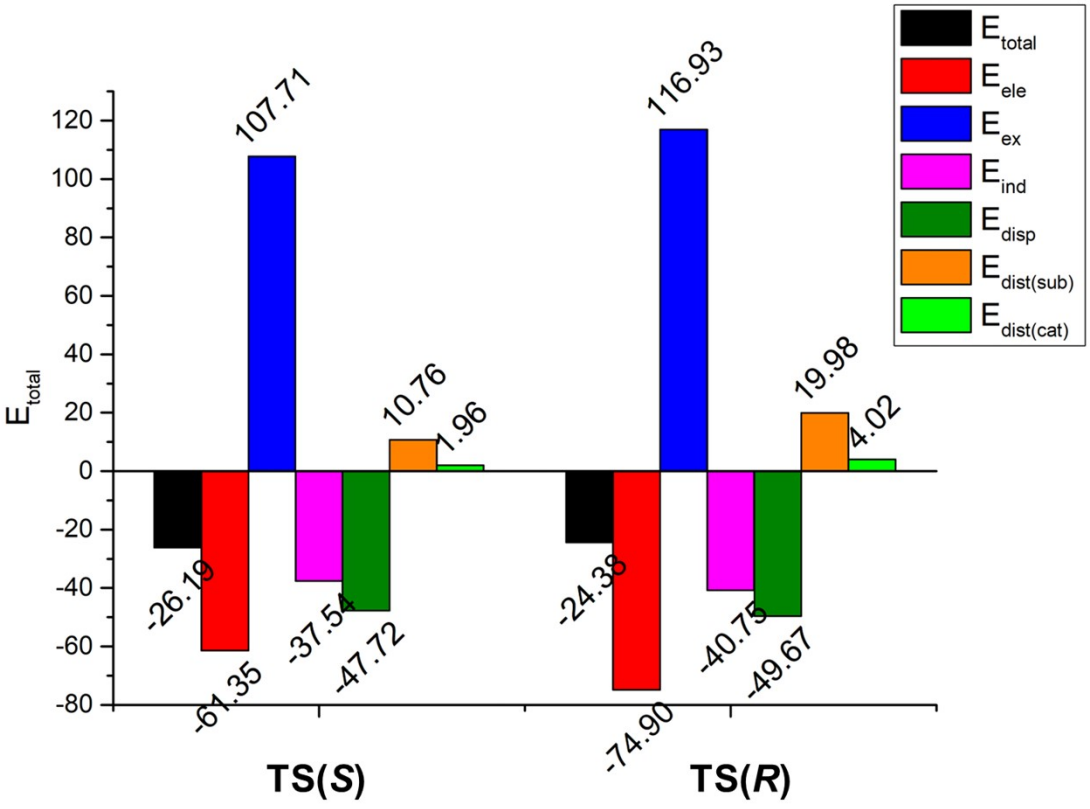


**Figure S14 EDA of TS(*S*) and TS(*R*) in Figure 2.**

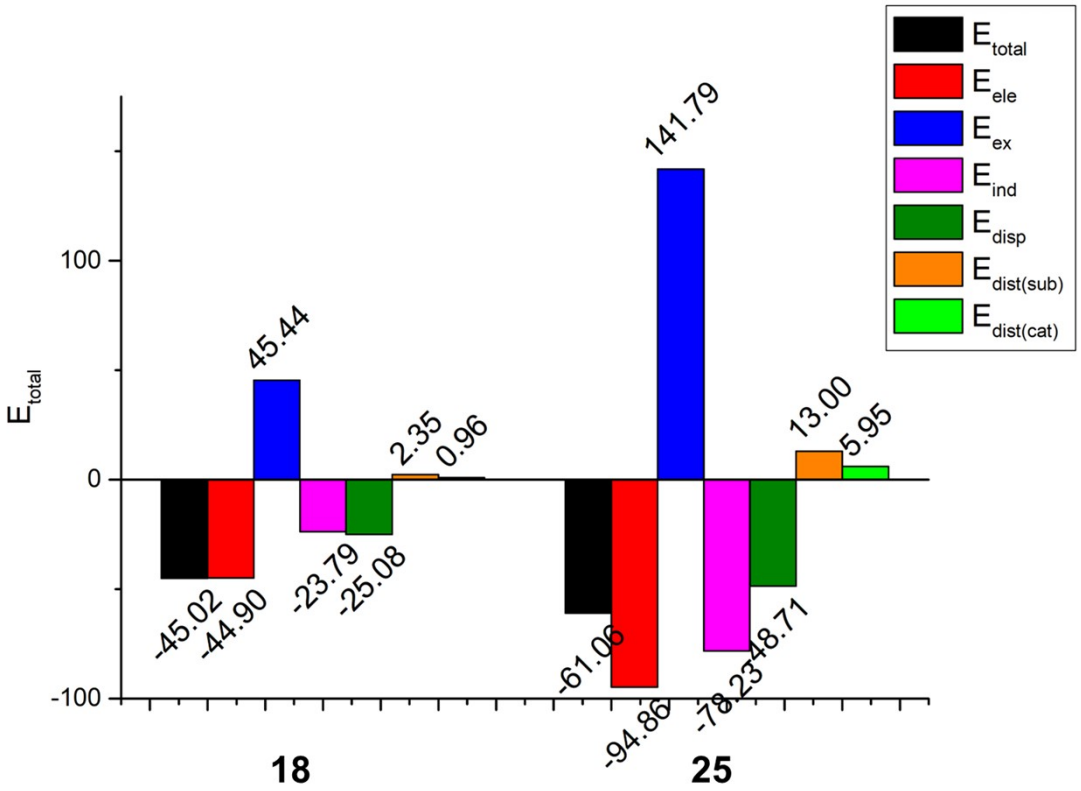


**Figure S15 EDA of 18 and 25 in Figure 3.**

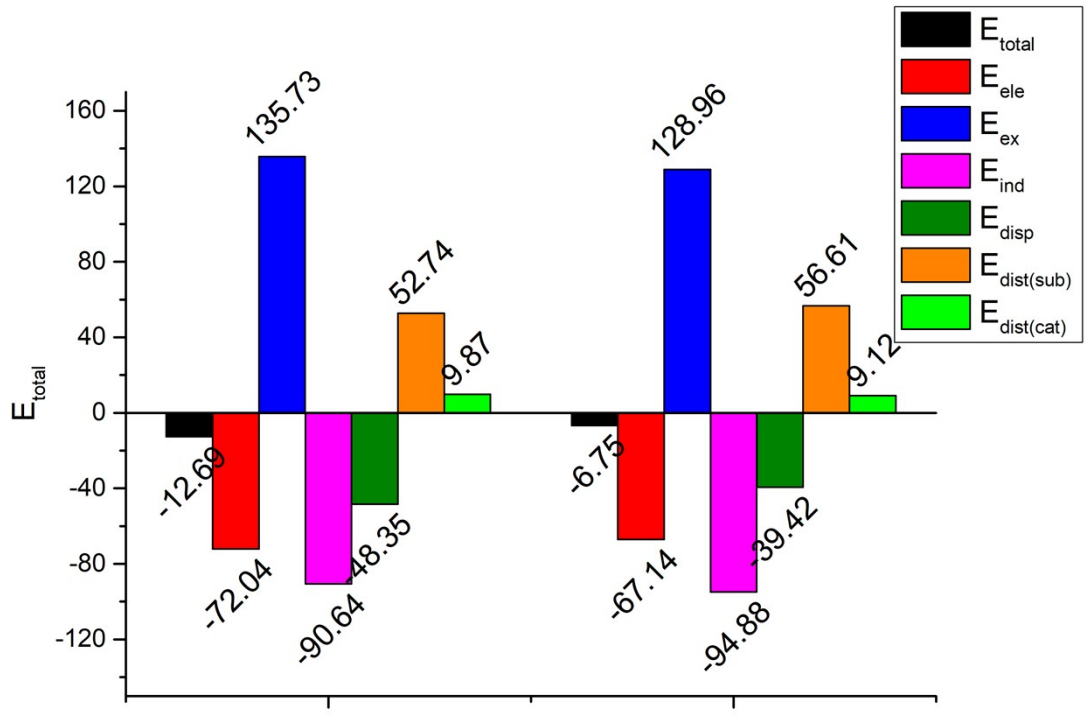


**Figure S16 EDA of TS-2a and TS-2b in Figure 4.**

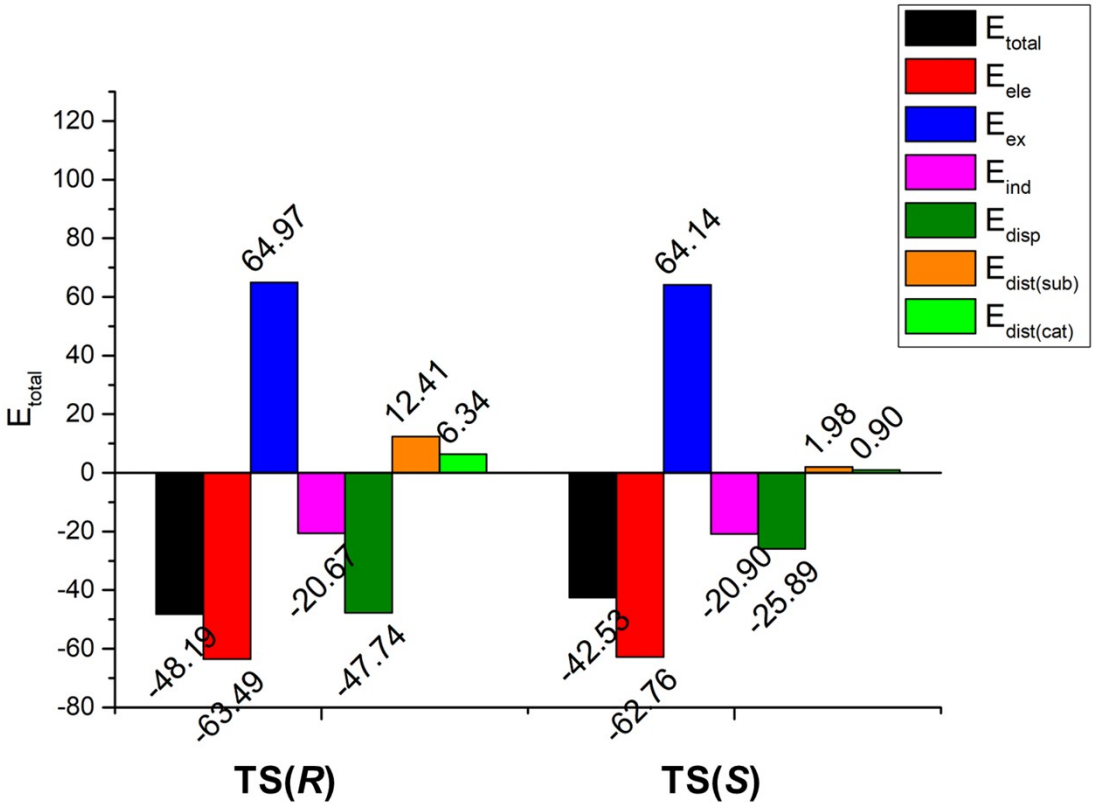


**Figure S17 EDA of TS(*R*) and TS(*S*) in Figure 5.**

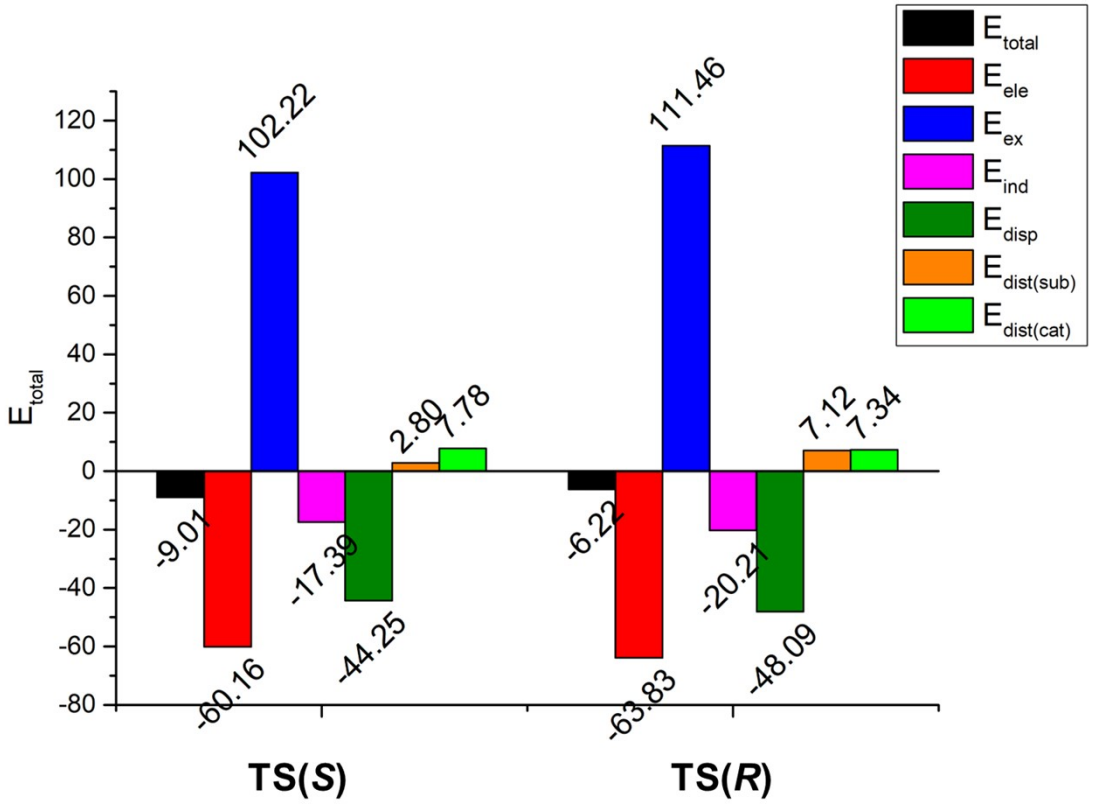


**Figure S18 EDA of TS(*S*) and TS(*R*) in Figure 6.**

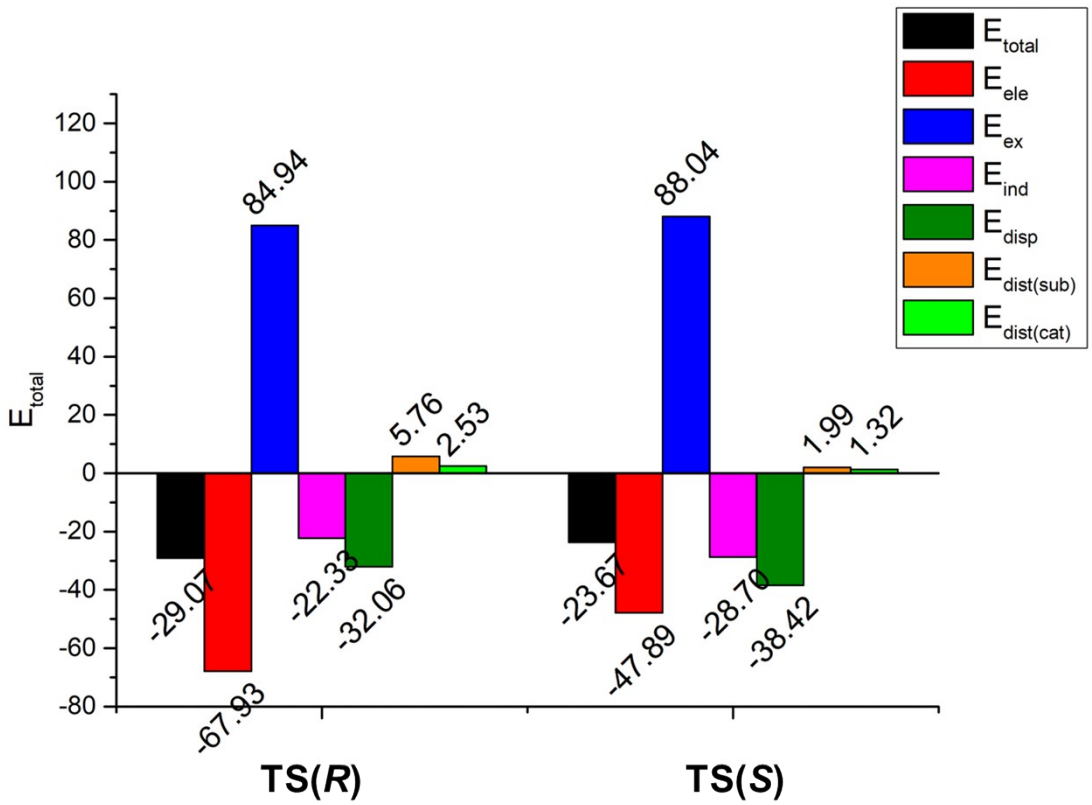


**Figure S19 EDA of TS(*R*) and TS(*S*) in Figure 7.**

**Table S2 The percentage of contribution from each item in EDA.[a]**

| | $E_{Ele}$ | $E_{Ex}$ | $E_{Ind}$ | $E_{Disp}$ | $E_{Dist(Sub)}$ | $E_{Dist(Cat)}$ |
|---|---|---|---|---|---|---|
| TS(*S*)-Figure 2 | 234% | -411% | 143% | 182% | -41% | -7% |
| TS(*R*)-Figure 2 | 307% | -480% | 167% | 204% | -82% | -16% |
| 18-Figure 3 | 100% | -101% | 53% | 56% | -5% | -2% |
| 25-Figure 3 | 155% | -232% | 128% | 80% | -21% | -10% |
| TS-2a-Figure 4 | 568% | -1070% | 714% | 381% | -416% | -78% |
| TS-2b-Figure 4 | 995% | -1911% | 1406% | 584% | -839% | -135% |
| TS(*R*)-Figure 5 | 132% | -135% | 43% | 99% | -26% | -13% |
| TS(*S*)-Figure 5 | 148% | -151% | 49% | 61% | -5% | -2% |
| TS(*S*)-Figure 6 | 668% | -1135% | 193% | 491% | -31% | -86% |
| TS(*R*)-Figure 6 | 1027% | -1793% | 325% | 774% | -115% | -118% |
| TS(*R*)-Figure 7 | 234% | -292% | 77% | 110% | -20% | -9% |
| TS(*S*)-Figure 7 | 202% | -372% | 121% | 162% | -8% | -6% |

[a]Note that the total combination energies are negative, so that the positive percentages in this chart refers to an item with negative energy. And the sum of all items in each row is 100%, which refers to $E_{tot}$.

**Table S3 The percentage of contribution from each item in EDA based on the difference of the activation energy between TSs or intermediates.[a]**

| | $E_{Ele}$ | $E_{Ex}$ | $E_{Ind}$ | $E_{Disp}$ | $E_{Dist(Sub)}$ | $E_{Dist(Cat)}$ |
|---|---|---|---|---|---|---|
| Figure 2 | -751% | 511% | -178% | -108% | 511% | 114% |
| Figure 3 | 311% | -601% | 339% | 147% | -66% | -31% |
| Figure 4 | -131% | 331% | -101% | -138% | 155% | -16% |
| Figure 5 | 13% | -15% | -4% | 386% | -184% | -96% |
| Figure 6 | -131% | 331% | -101% | -138% | 155% | -16% |
| Figure 7 | 371% | 57% | -118% | -118% | -70% | -23% |

[a]The relative energy was positive.

# 2. References.


[1] Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012,** *33*, 580-592.

[2] Lefebvre, C.; Rubez, G.; Khartabil, H.; Boisson, J.-C.; Contreras-García, J.; Hénon, E., Accurately extracting the signature of intermolecular interactions present in the NCI plot of the reduced density gradient versus electron density. *Phys. Chem. Chem. Phys.* **2017,** *19*, 17928-17936.

[3] Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W., Revealing Noncovalent Interactions. *J. Am. Chem. Soc.* **2010,** *132*, 6498-6506.