Electronic Supplementary Information

Important Role of Mo-Mo Quintuple Bond in Catalytic Synthesis of Benzene from Alkyne. A Theoretical Study

Yue Chen and Shigeyoshi Sakaki*

Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishihiraki-cho 34-4, Sakyo-ku,

Kyoto 606-8103, Japan

Fragment MO (FMO) Analysis S2

Figure S1. The DFT-optimized geometries of **1** and **1^{m}**. S3

Figure S2. The occupation numbers of natural orbitals of **1^{m}**. S4

Figure S3. Electron population changes of fragment's orbitals. S5

Figure S4. The DFT-optimized geometries of intermediates and transition states. S7

Figure S5. The π and π* orbitals of **3** and disilabenzene. S8

Fragment MO (FMO) Analysis

In general, the MO of complex AB can be represented by a linear combination of MOs of fragments A and B,[1-3] as eq. (1),

$$\varphi_i^{AB} = \sum_m C_{im}^A \varphi_m^A + \sum_n C_{in}^B \varphi_n^B \qquad (1)$$

where φ_i^{AB} represents the ith MO of the complex AB and φ_m^A and φ_n^B are the mth and the nth MOs of fragments A and B, respectively. C_{im}^A and C_{in}^B are expansion coefficients of φ_m^A and φ_n^B, respectively, and the electron populations of φ_m^A and φ_n^B can be obtained from these coefficients.

1. Baba, H.; Suzuki, S.; Takemura, T., *J. Chem. Phys.* 1969, **50**, 2078-2086.

2. Fujimoto, H.; Kato, S.; Yamabe, S.; Fukui, K., *J. Chem. Phys.* 1974, **60**, 572-578.

3. Dapprich, S.; Frenking, G., *J. Phys. Chem.* 1995, **99**, 9352-9362.

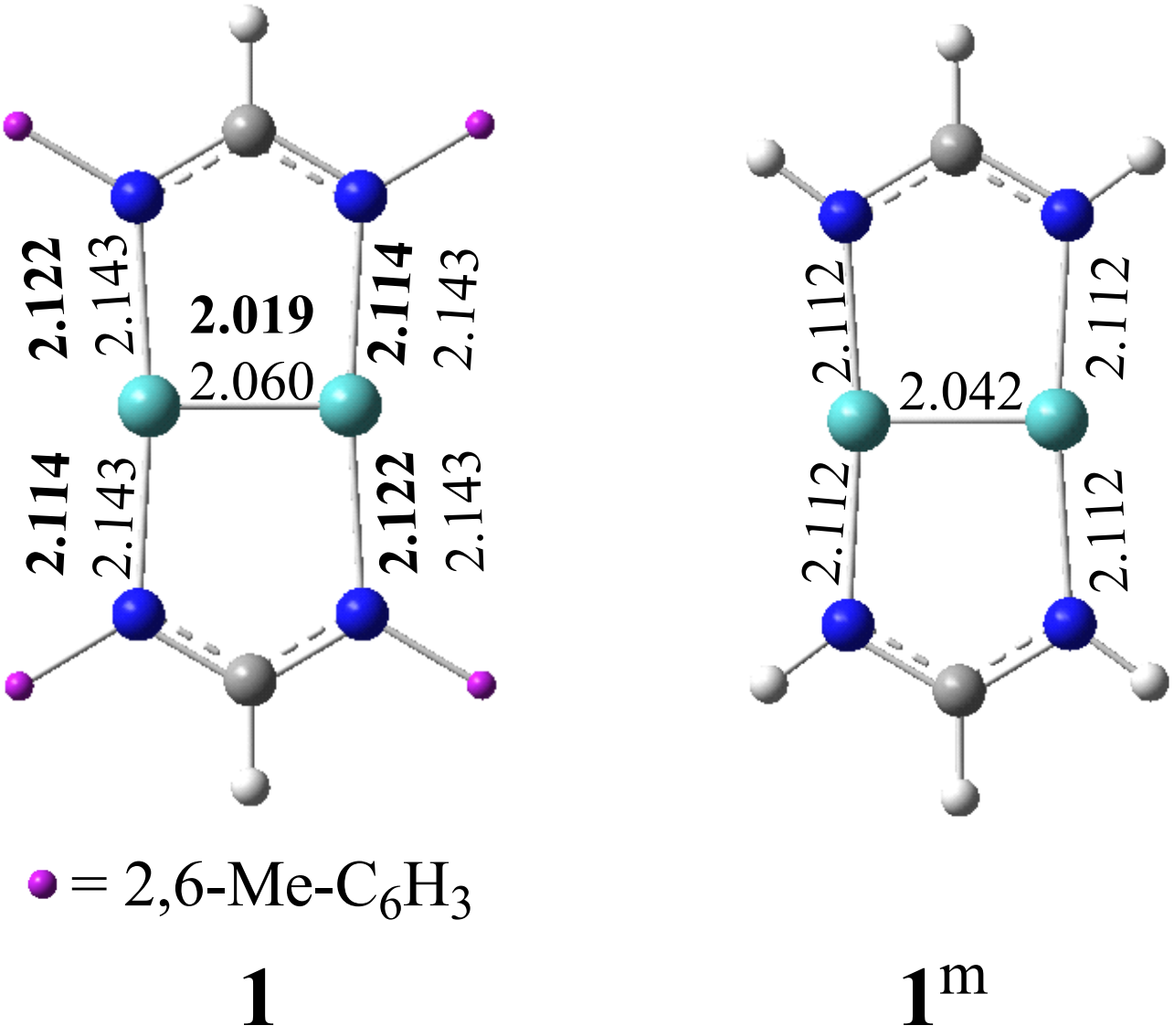


Figure S1. The DFT-optimized geometries of **1** and **1**^{m}.

Unit of bond length is Å; the bold text is experimental value.

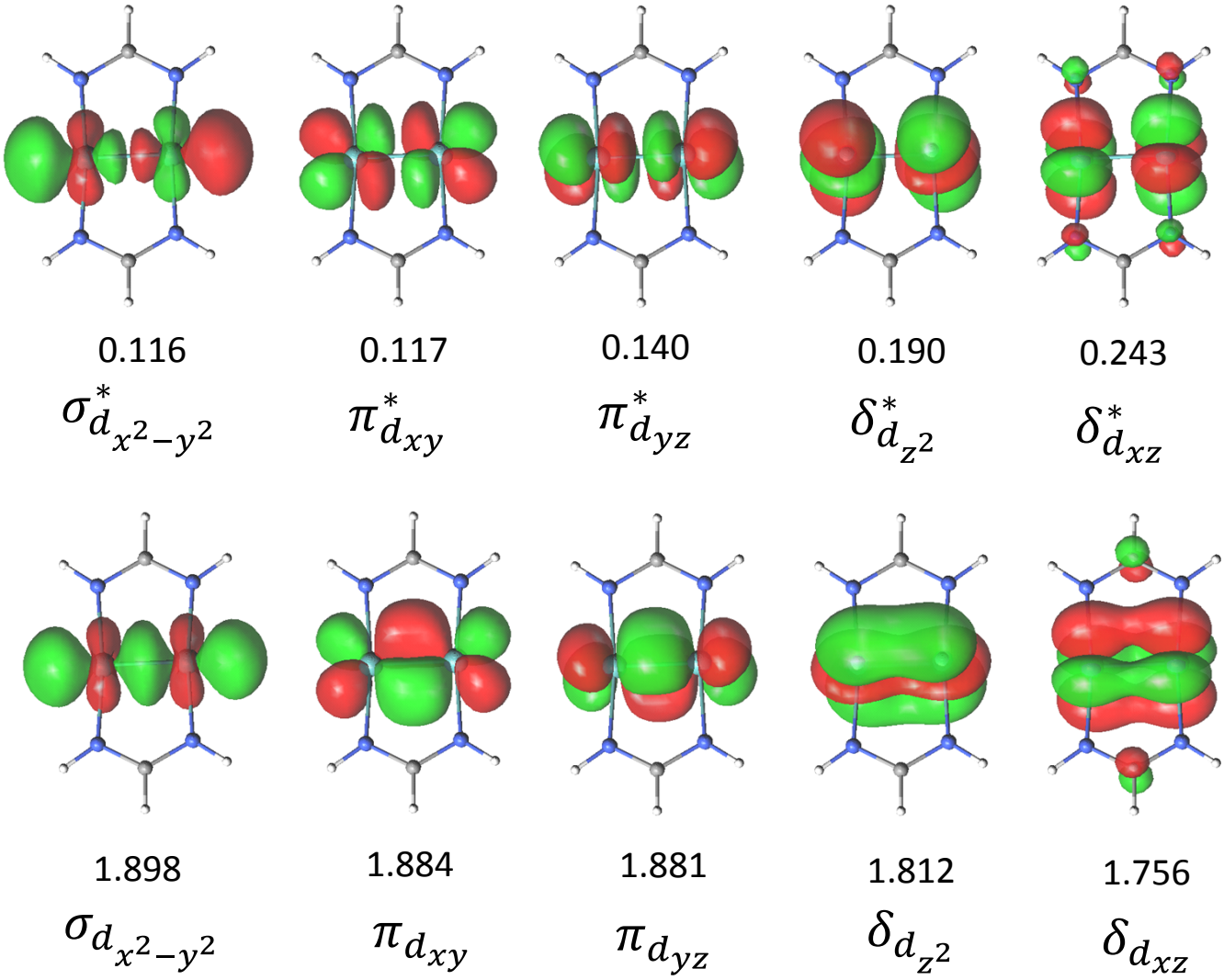


Figure S2. The occupation numbers of natural orbitals of **1**$^{\mathbf{m}}$.

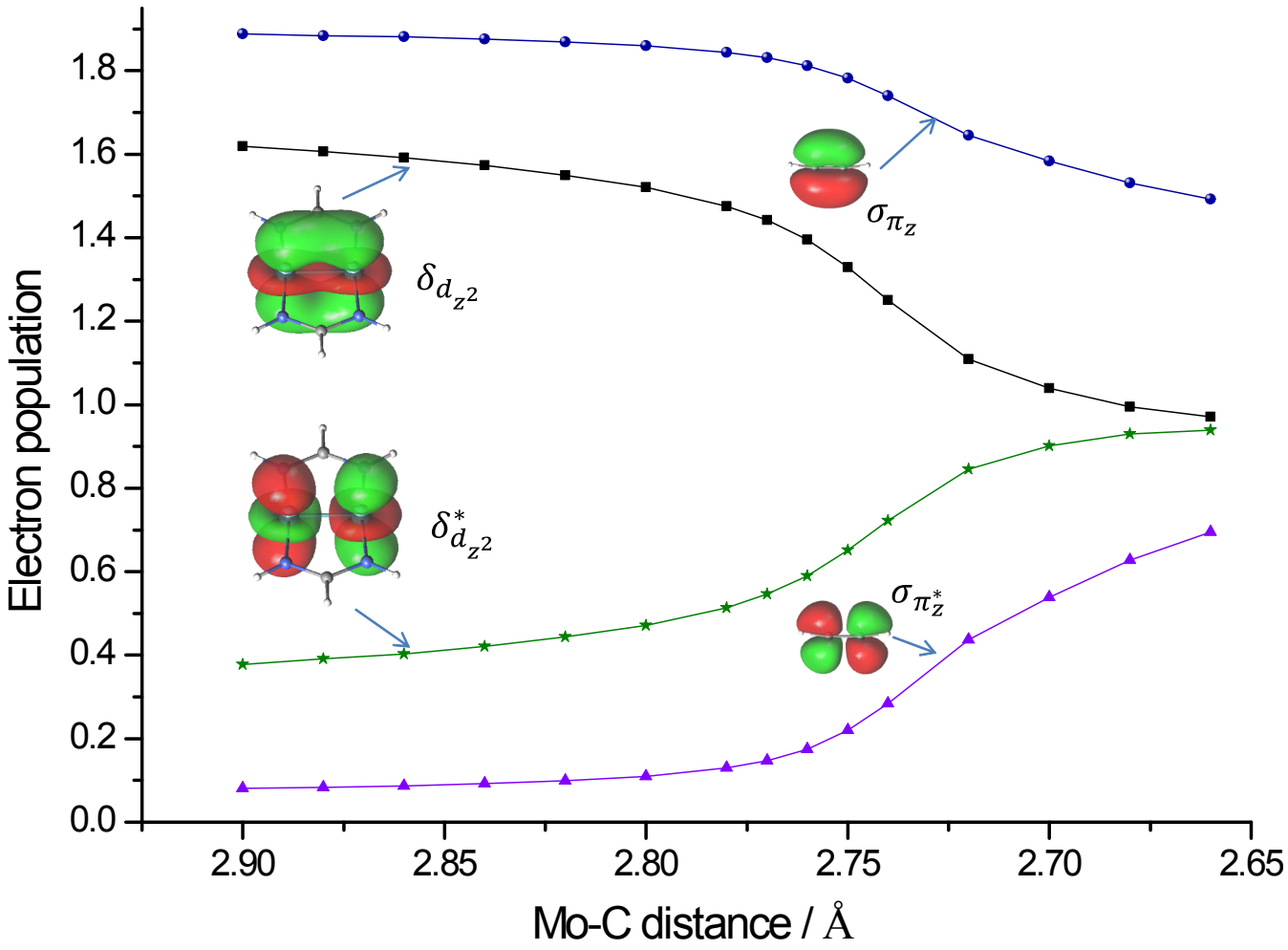
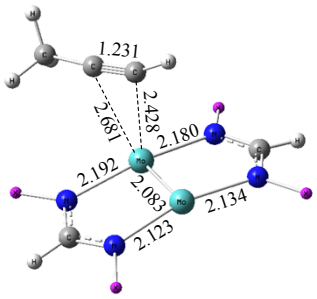
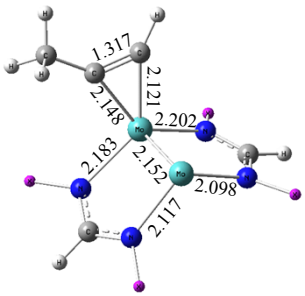


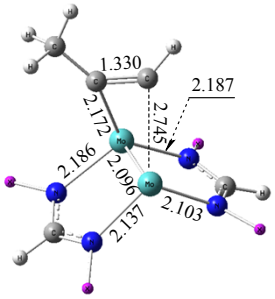
Figure S3. Electron population changes of fragment's orbitals.



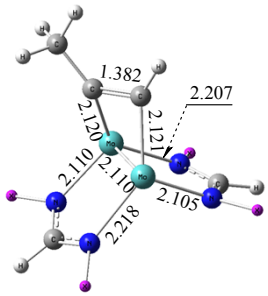
TS1



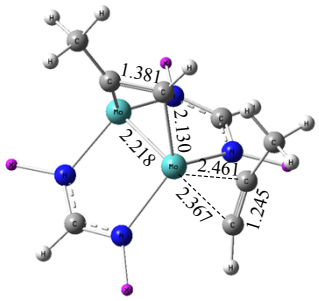
INT1



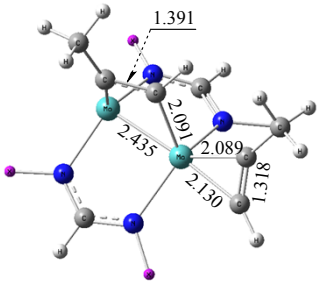
TS2



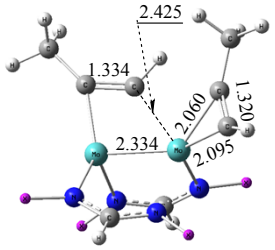
2



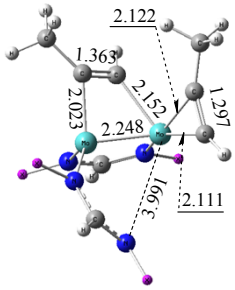
TS3a



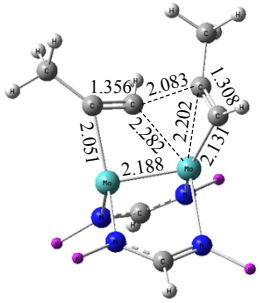
INT2



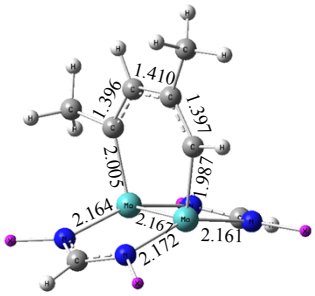
TS3b



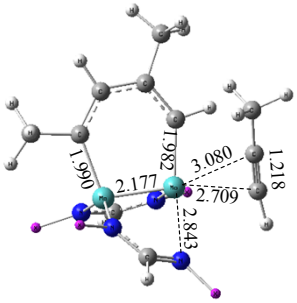
INT3



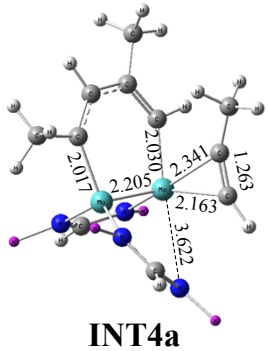
TS3c



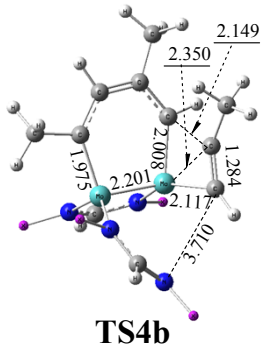
3



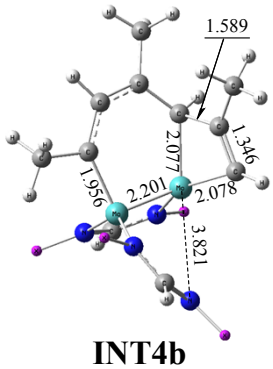
TS4a



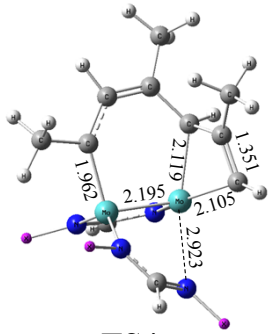
INT4a



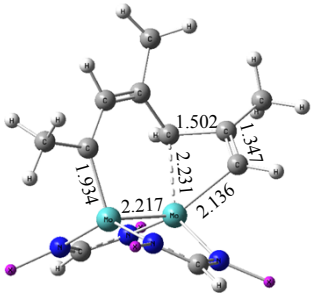
TS4b



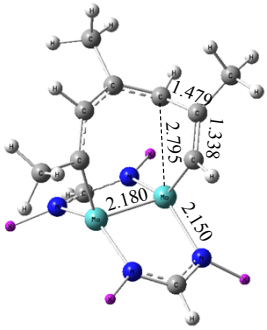
INT4b



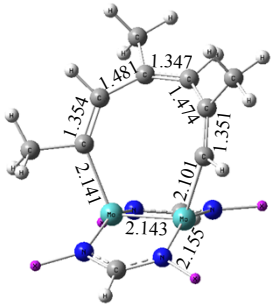
TS4c



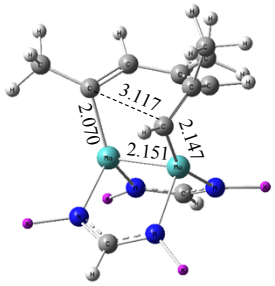
INT4c



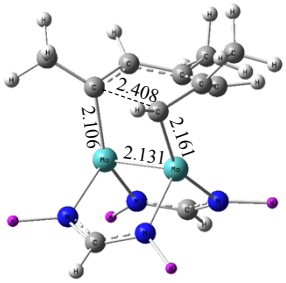
TS4d



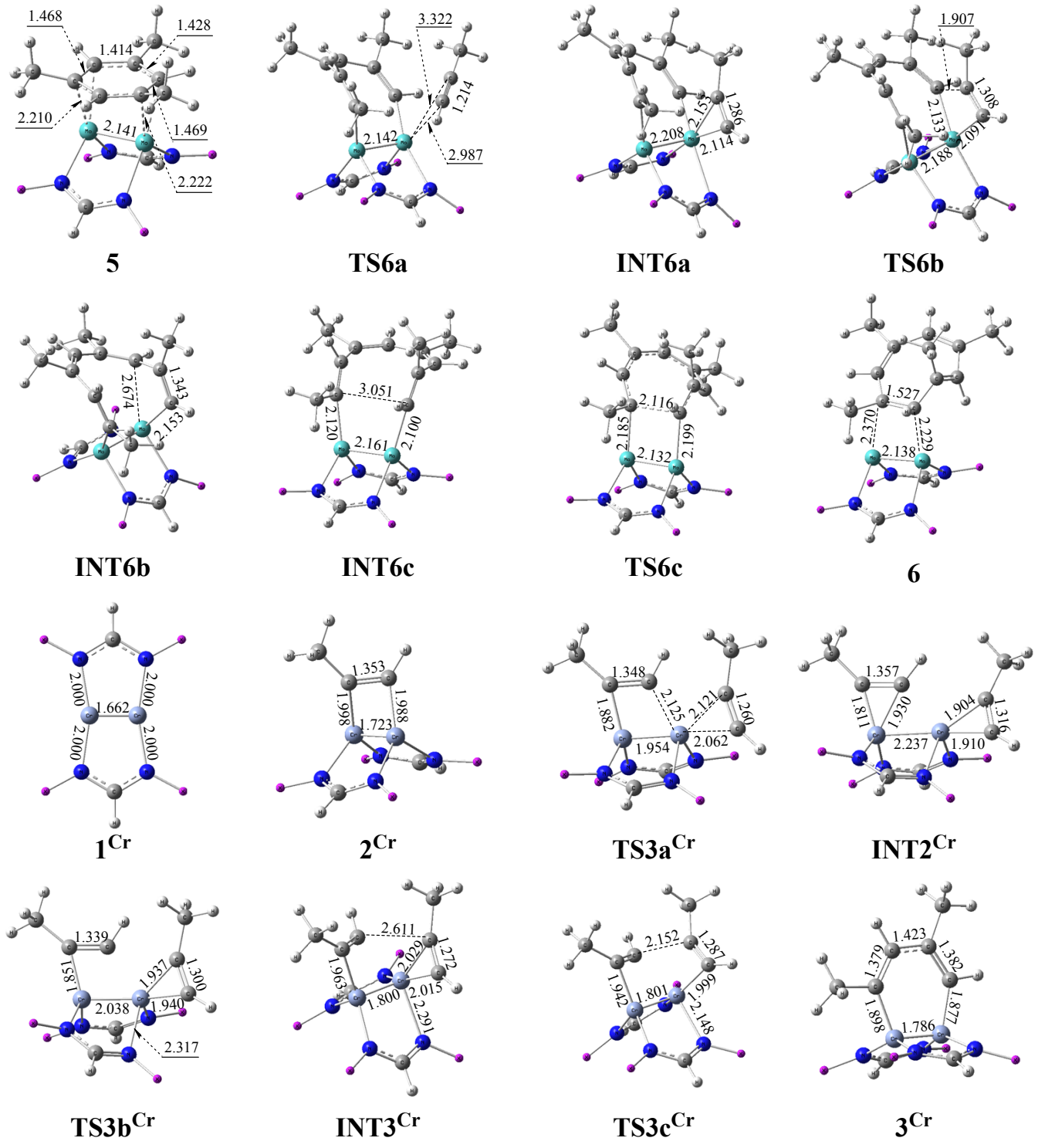
4



INT5



TS5a



● = 2,6-Me_2-C_6H_3

Figure S4. The DFT-optimized geometries of intermediates and transition states.

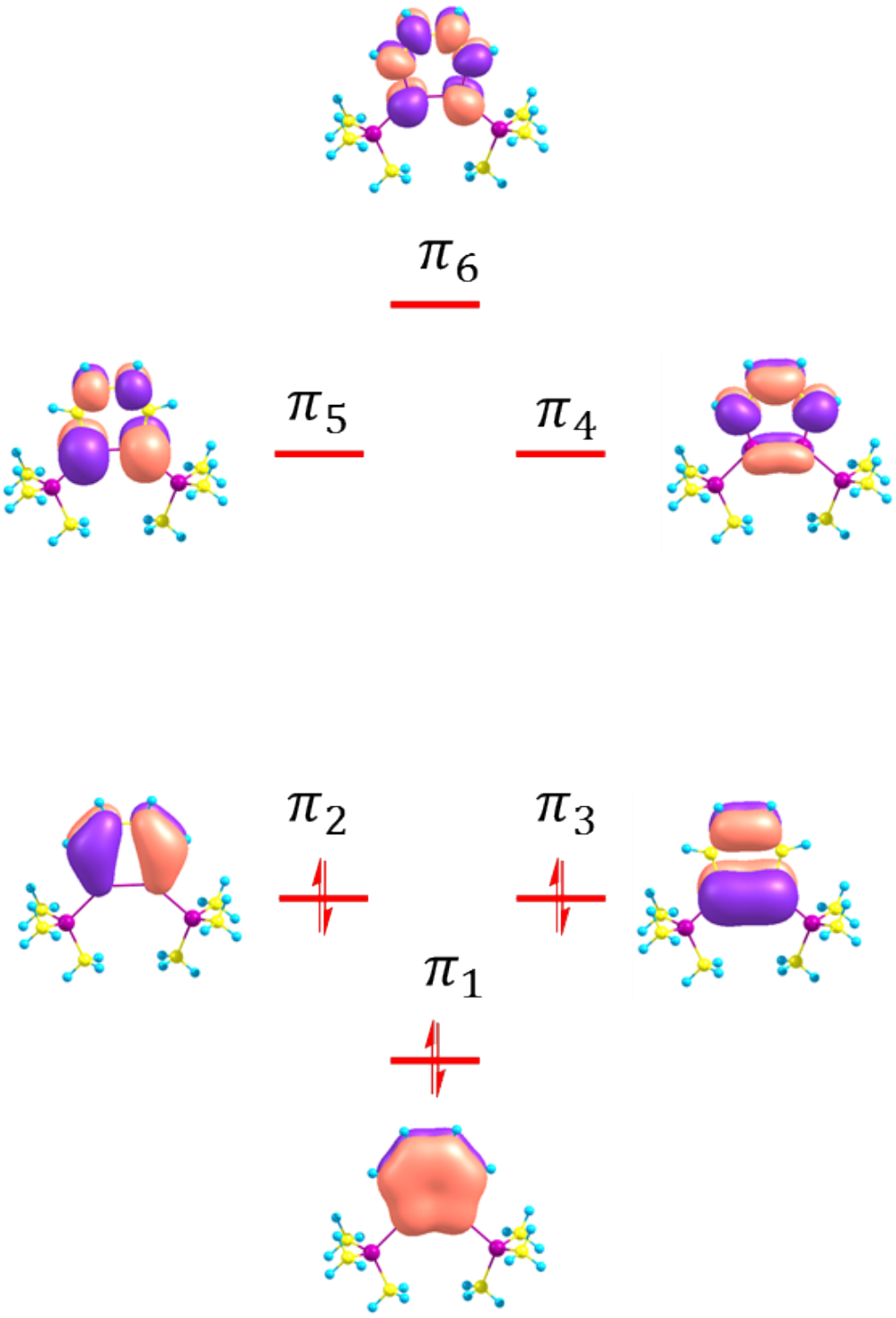


Figure S5. The π and π* orbitals of disilabenzene.