Supplementary Materials: Orbital Energy-Based Reaction Analysis of S_N2 Reactions

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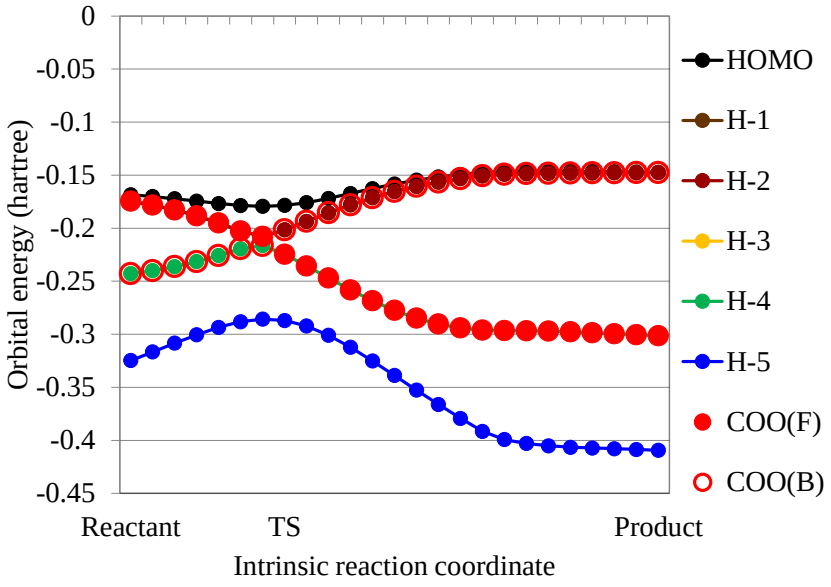
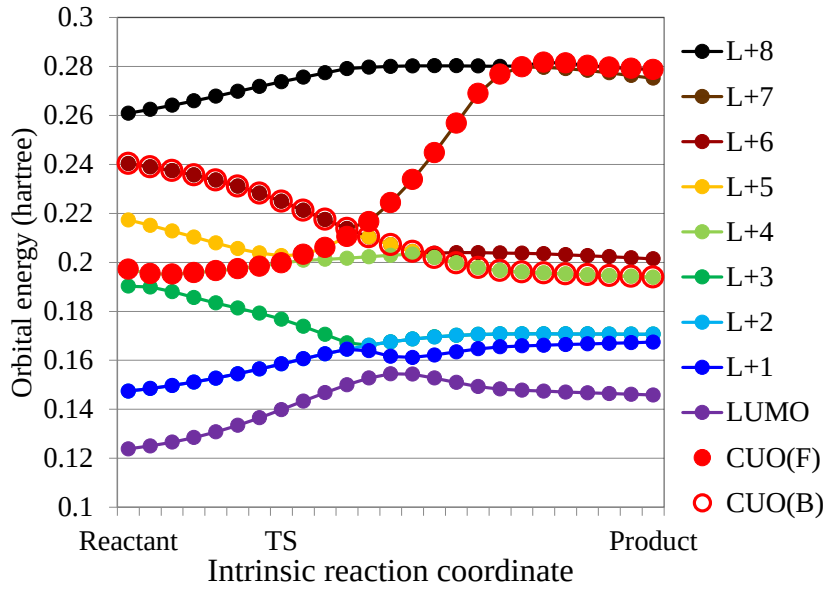
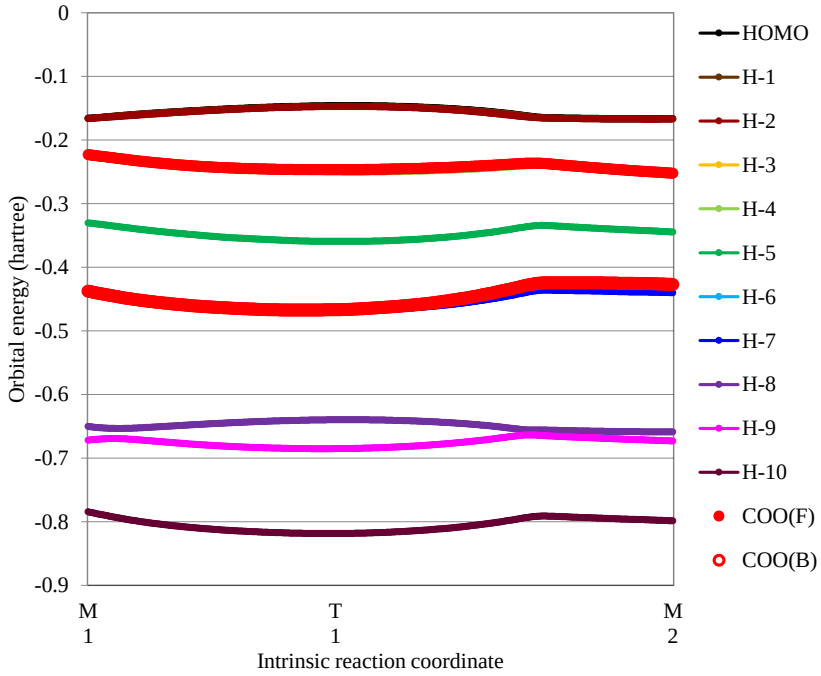


(**a**)

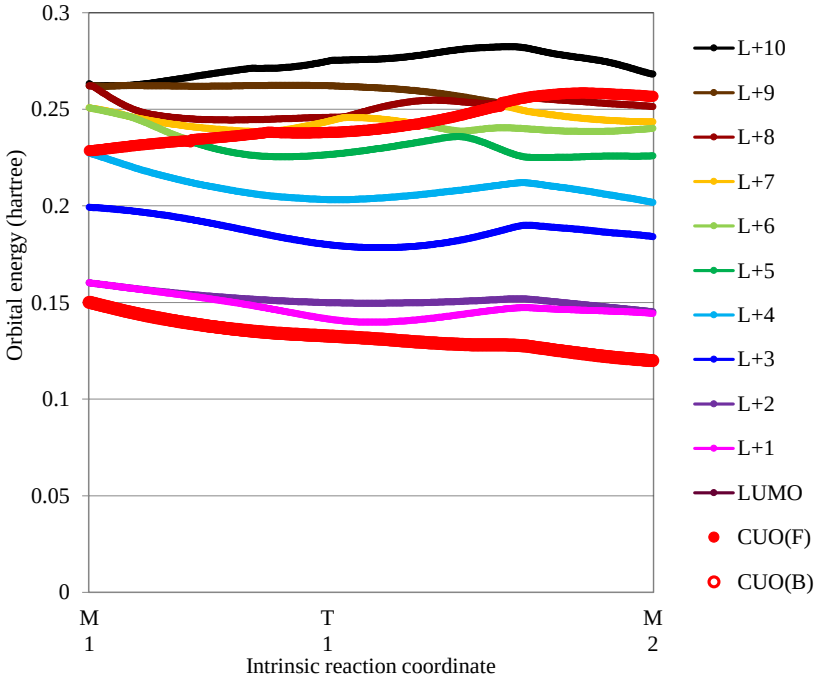


(**b**)

Figure S1. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction by LC-BOP/Def2-TZVPD calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction by LC-BOP/Def2-TZVPD calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.

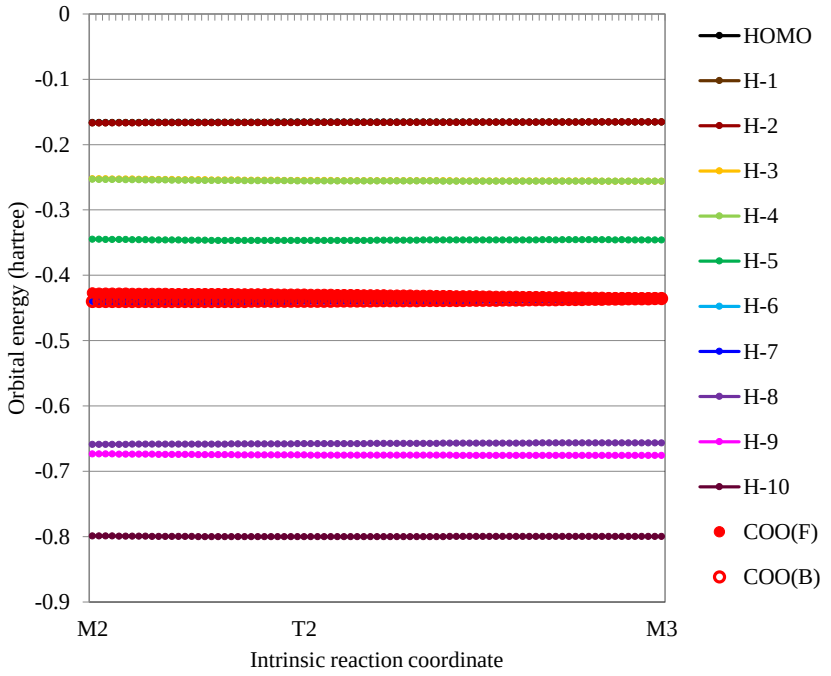


(**a**)

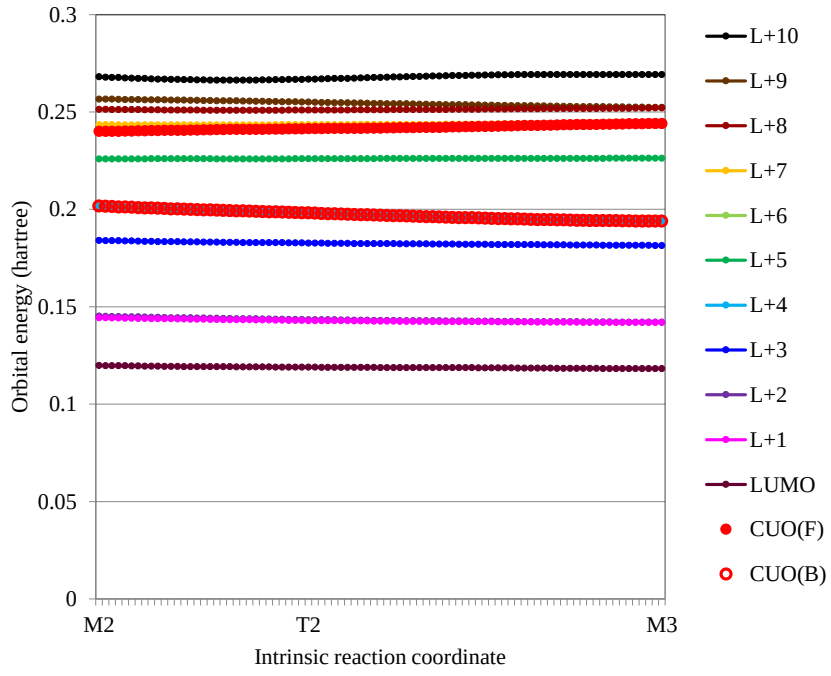


(**b**)

Figure S2. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the first step (Min1 to Min2 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the first step (Min1 to Min2 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.

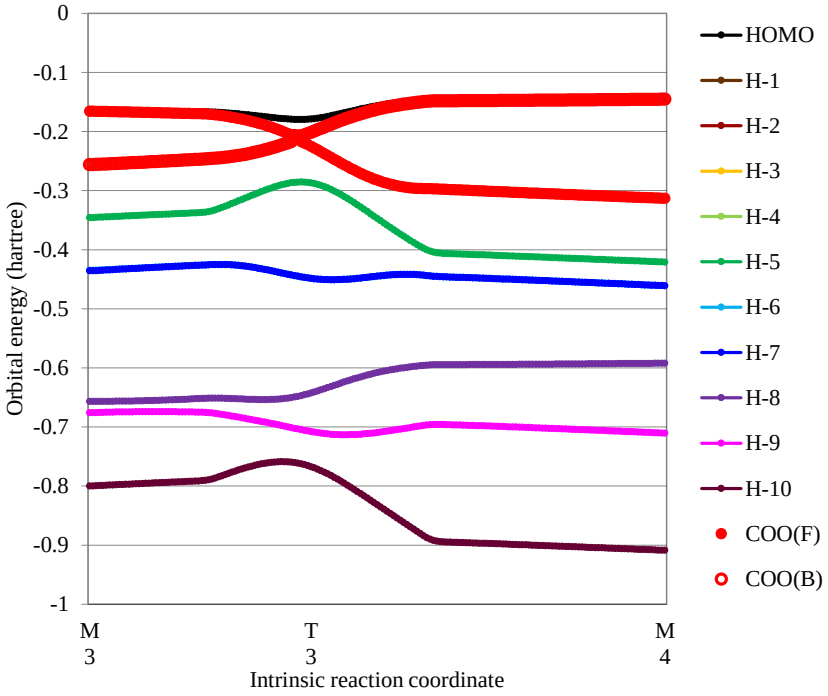


(**a**)

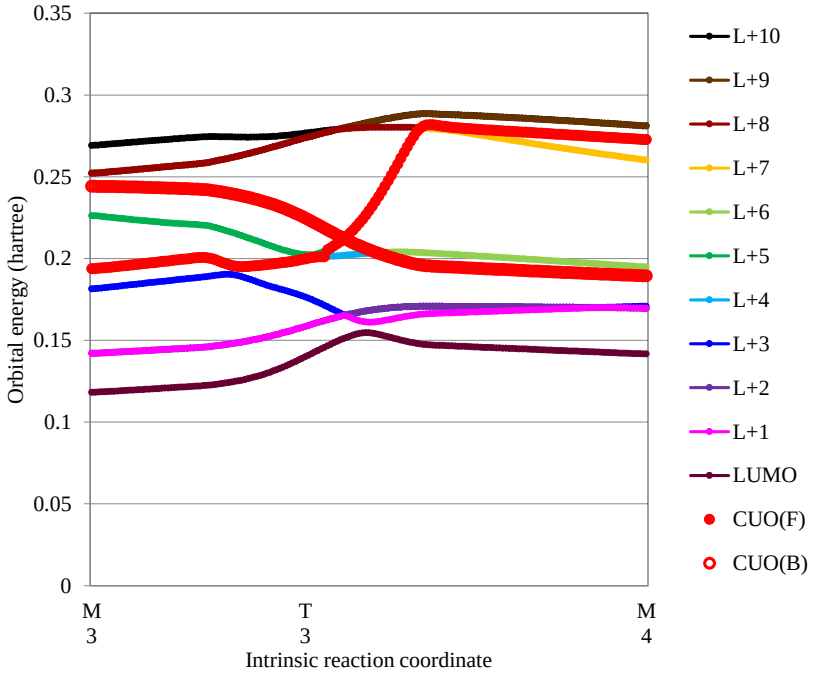


(**b**)

Figure S3. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the second step (Min2 to Min3 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the second step (Min2 to Min3 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.



(**a**)



(**b**)

Figure S4. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the third step (Min3 to Min4 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the third step (Min3 to Min4 of Figure 3) of the $Cl^- + CH_3I \rightarrow CH_3Cl + I^-$ reaction, which was determined by the artificial force induced reaction method in the GRRM program, by LC-BOP+LRD/Def2-TZVPD calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.

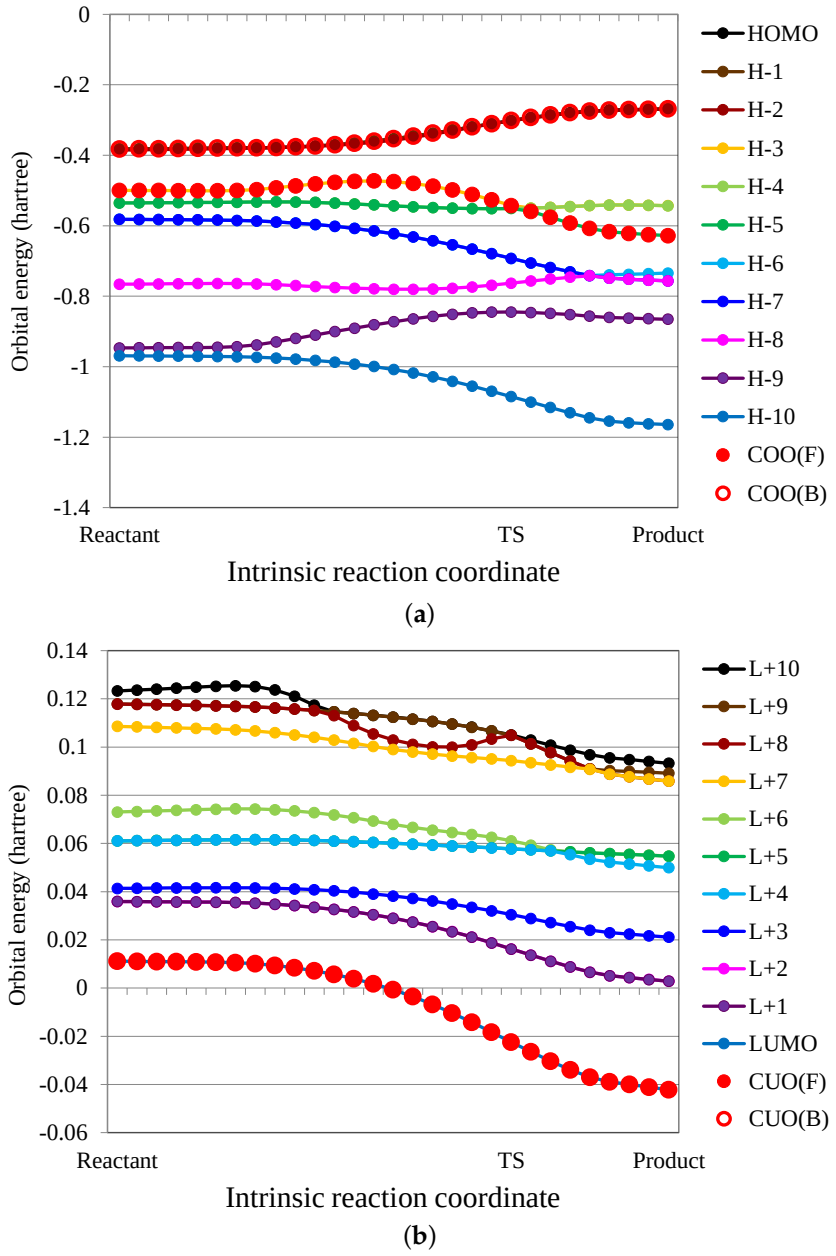


Figure S5. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the NH_3 + CH_3Cl → $NH_3CH_3^+$ + Cl^- reaction in gas phase by LC-BOP/aug-cc-pVTZ calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the $NH_3 + CH_3Cl \rightarrow NH_3CH_3^+ + Cl^-$ reaction in gas phase by LC-BOP/aug-cc-pVTZ calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.

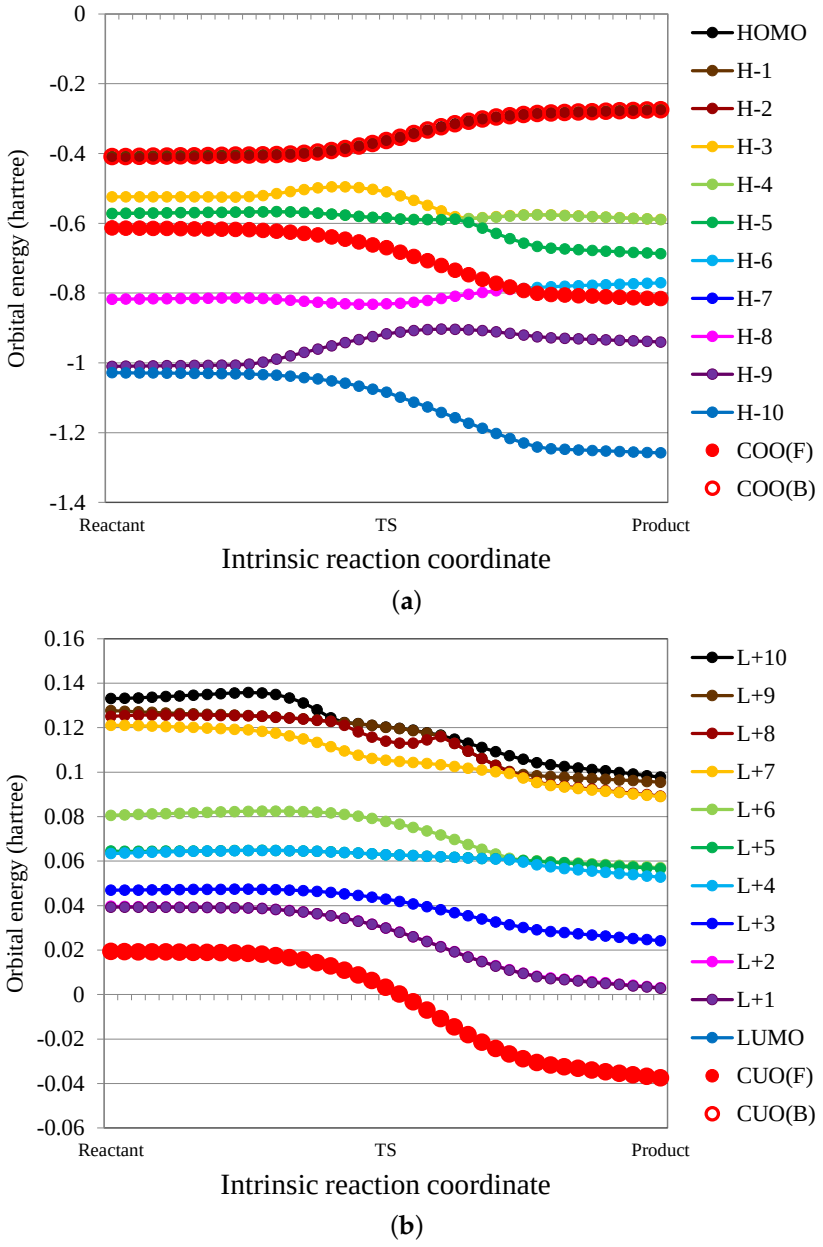
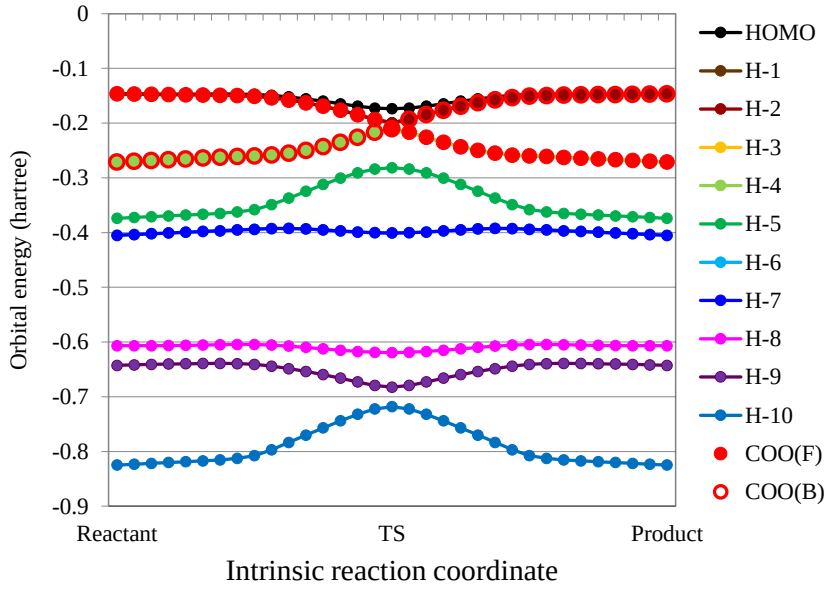
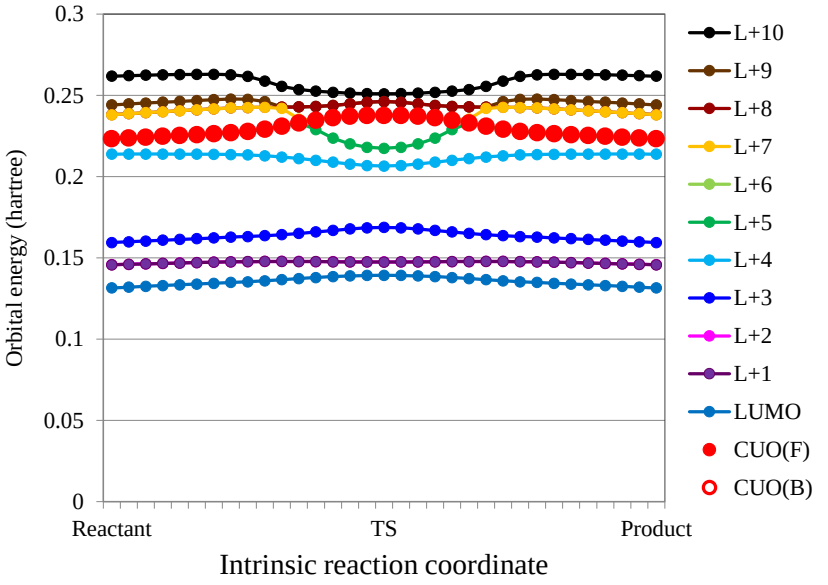


Figure S6. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the NH_3 + CH_3Cl → $NH_3CH_3^+$ + Cl^- reaction in aqueous solution by LC-BOP/aug-cc-pVTZ calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes. The CPCM-SCRF method is used to evaluate the solvent effects; (**b**) Calculated unoccupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the NH_3 + CH_3Cl → $NH_3CH_3^+$ + Cl^- reaction in aqueous solution by LC-BOP/aug-cc-pVTZ calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes. The CPCM-SCRF method is used to evaluate the solvent effects.



(**a**)



(**b**)

Figure S7. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the $Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$ reaction in gas phase by LC-BOP/aug-cc-pVTZ calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the $Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$ reaction in gas phase by LC-BOP/aug-cc-pVTZ calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes.

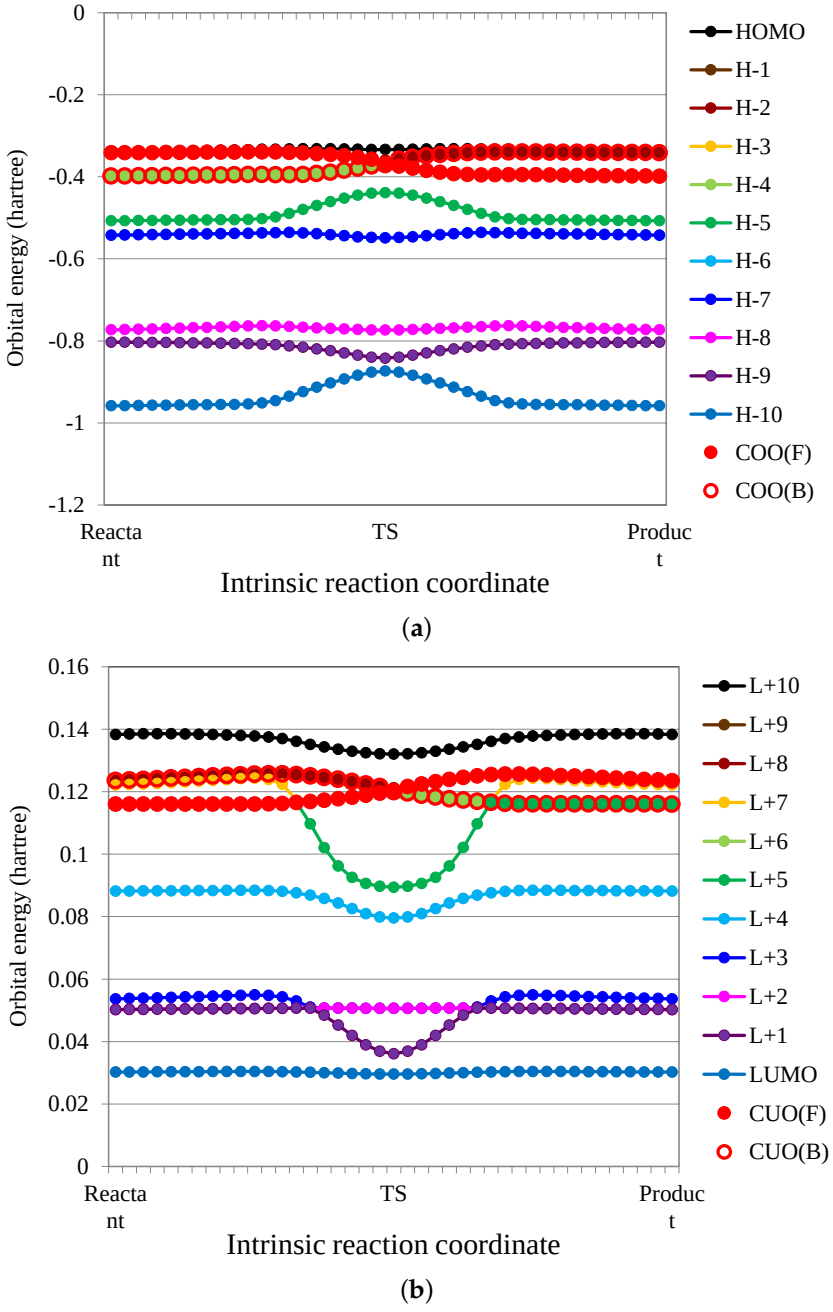


Figure S8. (**a**) Calculated occupied orbital energies and contributing occupied orbital energies on the intrinsic reaction coordinate of the $Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$ reaction in aqueous solution by LC-BOP/aug-cc-pVTZ calculations. "COO(F)" and "COO(R)" indicate the contributing occupied orbital energies for the forward and reverse processes. The CPCM-SCRF method is used to evaluate the solvent effects; (**b**) Calculated unoccupied orbital energies and contributing unoccupied orbital energies on the intrinsic reaction coordinate of the $Cl^-...CH_3Cl \rightarrow ClCH_3...Cl^-$ reaction in aqueous solution by LC-BOP/aug-cc-pVTZ calculations. "CUO(F)" and "CUO(R)" indicate the contributing unoccupied orbital energies for the forward and reverse processes. The CPCM-SCRF method is used to evaluate the solvent effects.