(1). Unless stated elsewhere, all structures were obtained from M06-2X-D3/6-31G(d,p) in gas phase. For alpha-Cl\_4-CH3\_triplet-insertion-TS and alpha-F\_4-CH3\_triplet-insertion-TS, the additional keyword "nosymm" is required to ensure only one imaginary frequency of the transition state.

(2). For coordinates of optimized structures in .xyz files, the format is shown below:

*electronic energy*

*enthalpy*

*Gibbs free energy*

*number of atoms*

*charge multiplicity*

*Cartesian coordinates*