

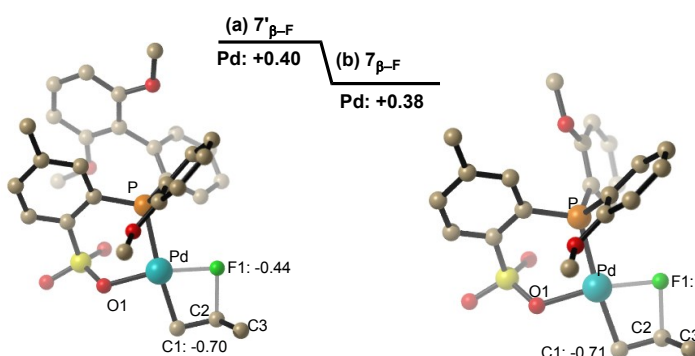
## Supporting Information

# Origin of Different Chain-end Microstructures in Ethylene/Vinyl Halides Copolymerization by Phosphine-Sulfonate Palladium Complexes

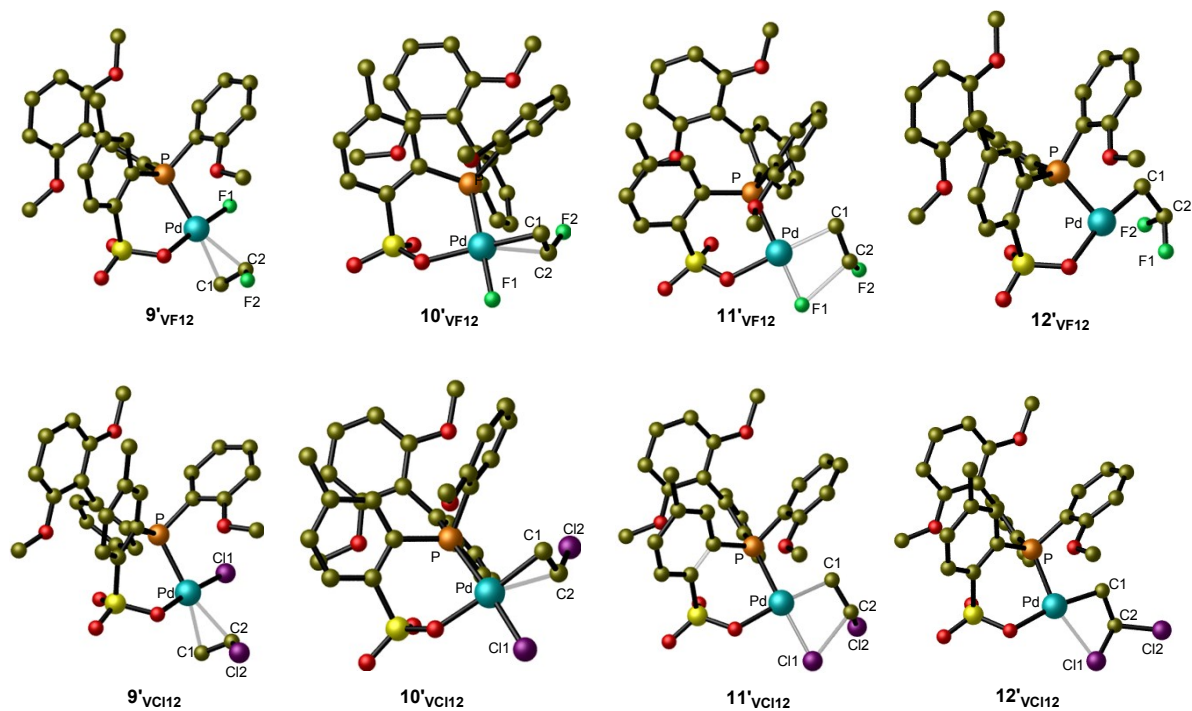
Andleeb Mehmood,<sup>δa</sup> Xiaowei Xu,<sup>δa</sup> Xiaohui Kang,<sup>\*b</sup> and Yi Luo<sup>\*a</sup>

<sup>a</sup>State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

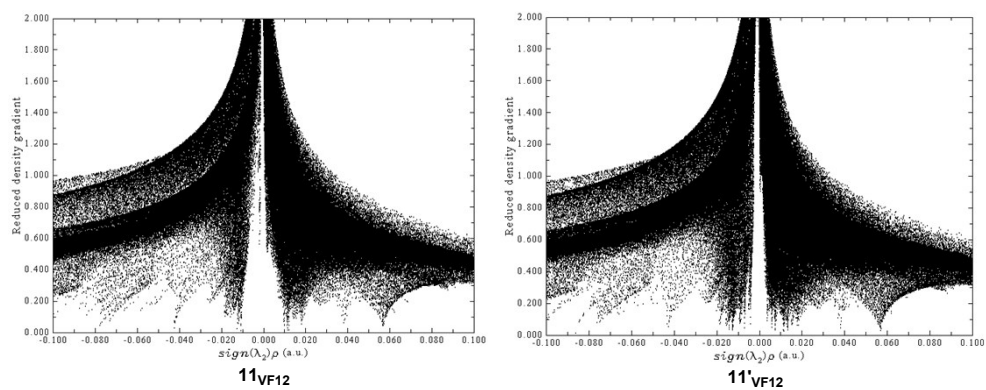
<sup>b</sup>College of Pharmacy, Dalian Medical University, Dalian, Liaoning 116044, China



**Fig. S1.** Optimized structural descriptors for NBO analysis of important TS ( $7_{\beta-F}$  and  $7'_{\beta-F}$ ) and coordination complexes ( $5_{\beta-F}$  and  $5'_{\beta-F}$ ) catalyzed by **A'** and by **A**. All the hydrogen atoms are omitted for clarity.

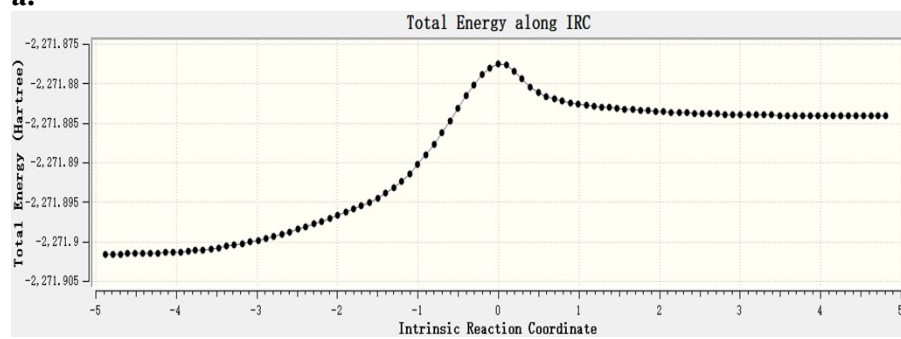


**Fig. S2.** Optimized structures for coordination complexes  $9'_{VF12}$ ,  $9'_{VC12}$ ,  $10'_{VF12}$ , and  $10'_{VC12}$  after  $\beta$ -X elimination along with TSs  $11'_{VF12}$  and  $11'_{VC12}$  to the products  $12'_{VF12}$  and  $12'_{VC12}$ .



**Fig. S3.** The RDG vs  $\text{sign}(\lambda_2)\rho$  plot of  $11_{VF12}$  and  $11'_{VF12}$ .

a.



b.

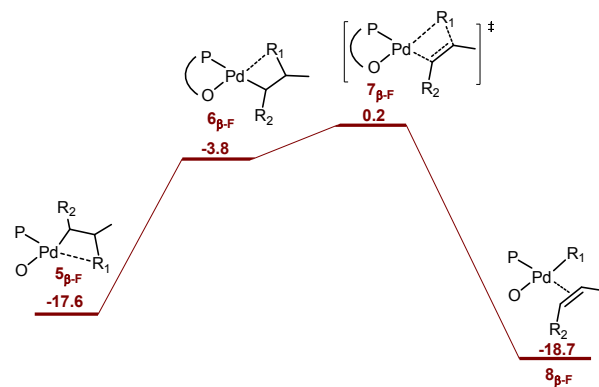


Fig. S4. (a) IRC plot and (b) the energy profile of ( $5_{\beta-F} \rightarrow 6_{\beta-F} \rightarrow 7_{\beta-F} \rightarrow 8_{\beta-F}$ ) process in gas phase.