Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Mechanistic study to reveal steric and electronic aspects involved in the formation of microstructures during Pd catalyzed olefin/divinyl formal copolymerization: Reactivity to catalyst choice

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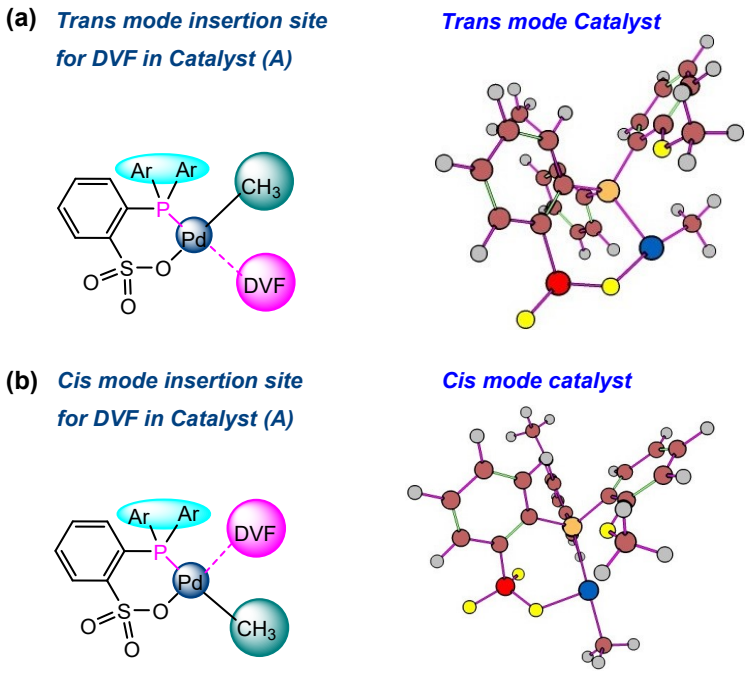

Fig S1. Two coordination manners (trans and cis, Ar = 2-$MeOC_6H_4$) of the Ethylene and DVF correspond to the P-atom of phosphine-sulfonate-based Pd complexes.

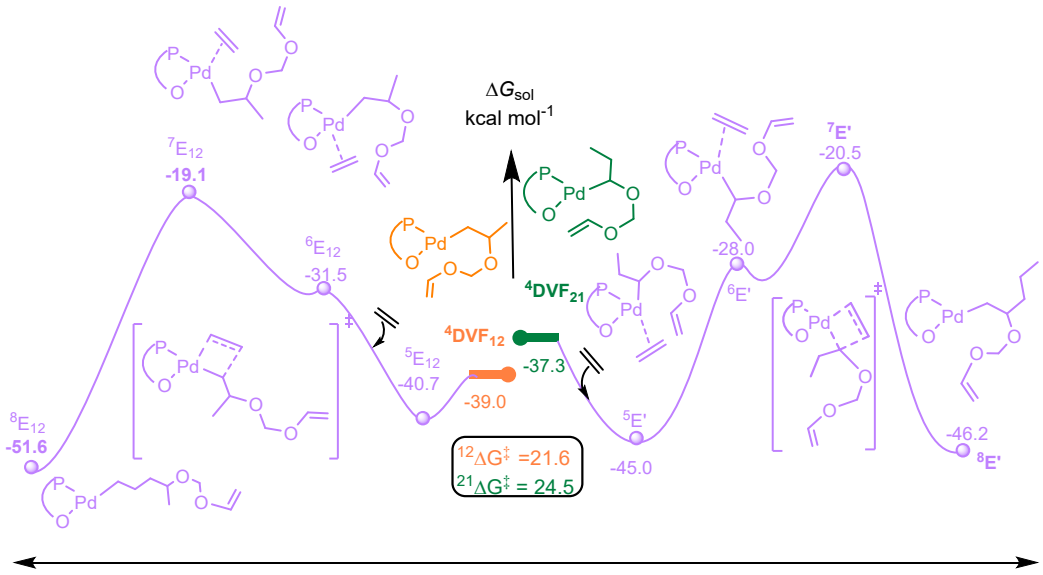

Fig S2. Energy profiles for chain propagation with E after 1,2/2,1-insertion of DVF in the 1,2/2,1-DVF pre-insertion chains.

Table S1 Computed energies for copolymerization and homo-polymerization steps. All coordination complexes (**C¹**, **C²**, **C³**, and **C⁴**) and transition states (**TS¹** and **TS²**) of DVF homo-polymers.

Monomer	E/1,2/2,1 **C¹**	E/1,2/2,1 **C²**	E/1,2/2, **TS¹**	E/1,2/2, **P¹**	E/1,2/2,1 **ΔG¹‡**	E/1,2/2, **C³**	E/1,2/2, **C⁴**	E/1,2/2, **TS²**	E/1,2/2,1 **P²**	E/1,2/2,1 **ΔG²‡**
	2nd insertion in $^4DVF_{12}$					**2nd insertion in $^4DVF_{21}$**				
1,2-DVF	-54.4	-42.4	-32.2	-54.2	**22.2**	-55.7	-49.9	-32.6	-65.9	**23.1**
2,1-DVF	-61.9	-49.2	-30.4	-66.5	**31.5**	-59.5	-46.0	-26.4	-40.5	**33.1**

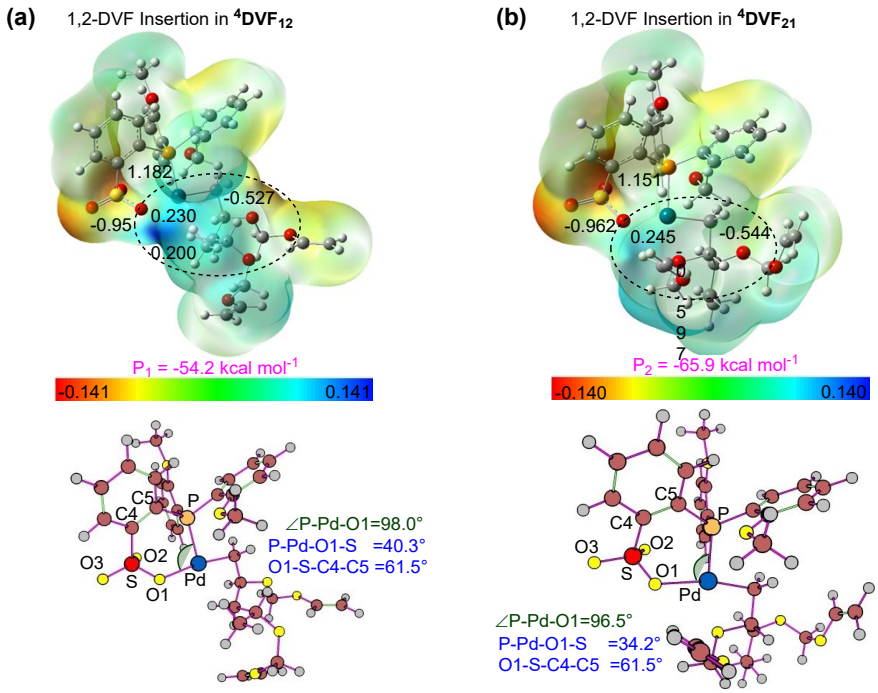

Fig S3. Molecular electrostatic potential (MEP) formed by mapping of total density over the electrostatic potential of products **(a)** 1,2-DVF Insertion in **^{4}DVF$_{12}$**, **(b)** 1,2-DVF Insertion in **^{4}DVF$_{21}$** geometric parameter analysis. Energies in kcal mol^{-1}, and angles in degree (˚). NBO charges are also mentioned on important atoms.

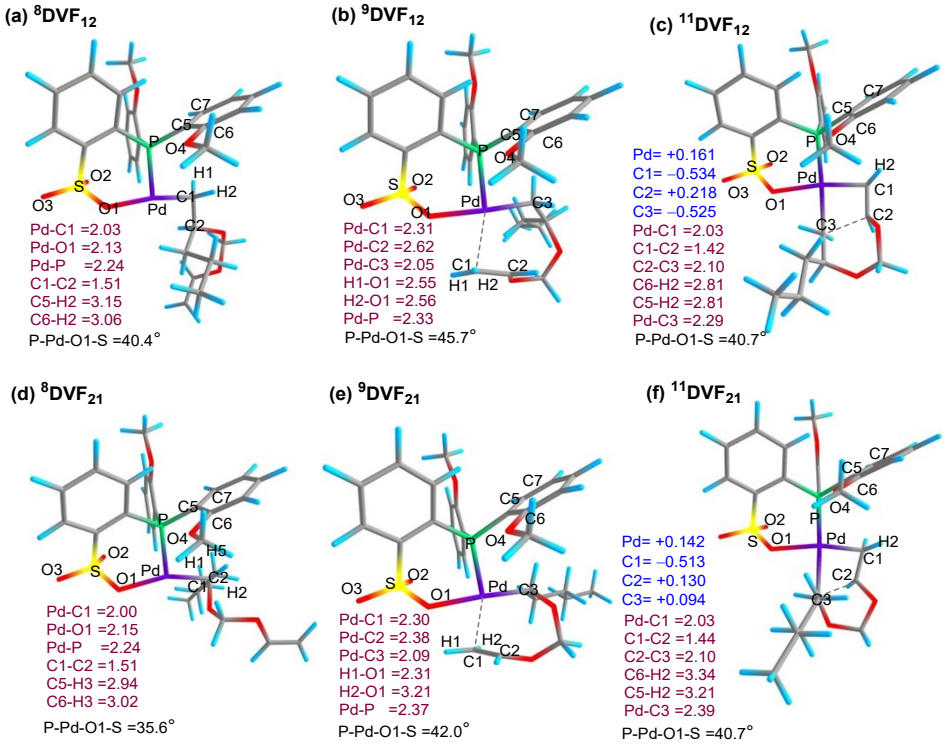

Fig S4. Geometrical analysis of **(a) ^{8}DVF$_{12}$**, **(b) ^{9}DVF$_{12}$**, **(c) ^{11}DVF$_{12}$**, **(d) ^{8}DVF$_{21}$**, **(e) ^{9}DVF$_{21}$**, and **(f) ^{11}DVF$_{21}$**. Bond distances in Å and dihedral angles in degree (˚). Hydrogen atoms of the catalyst's ligand have been omitted for clarity.

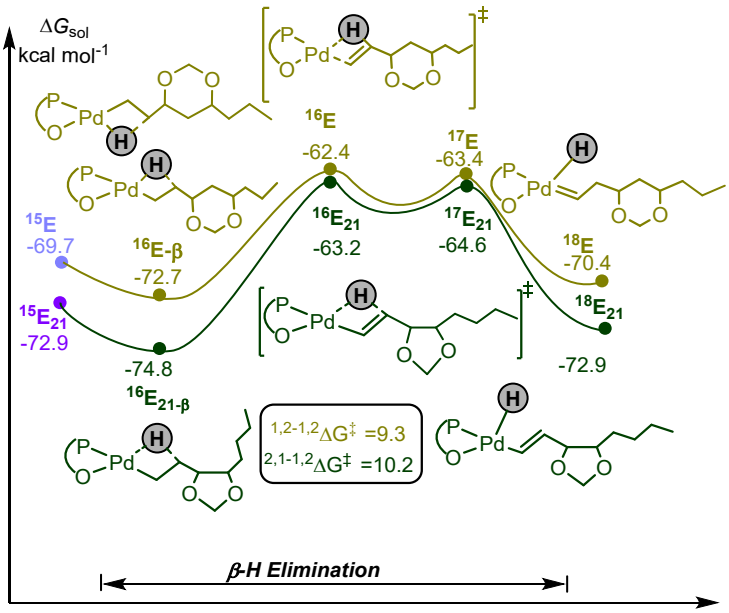

Fig S5. Energy profiles for the β-hydride elimination after cyclization.

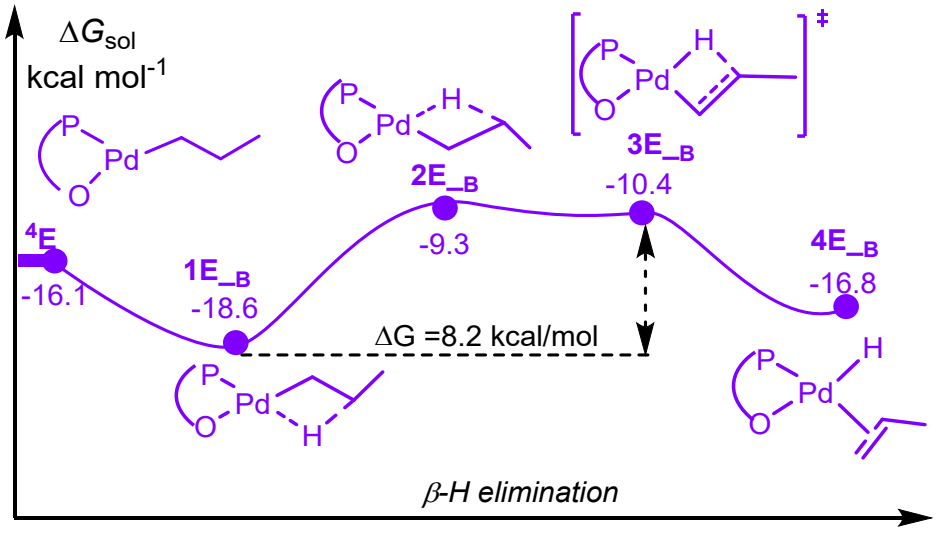

Fig S6. Energy profiles for the β-hydride elimination after ethylene insertion.

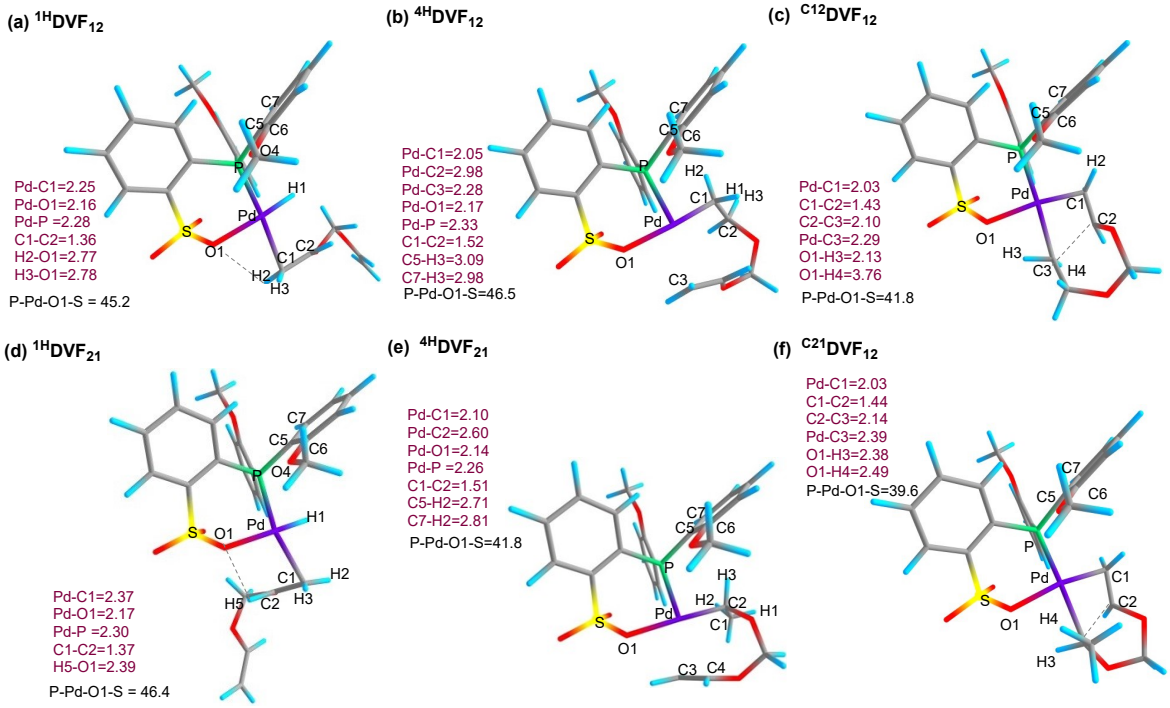

Fig S7. Geometrical analysis of **(a)** ^{1H}**DVF**$_{12}$, **(b)** ^{4H}**DVF**$_{12}$, **(c)** ^{C12}**DVF**$_{12}$, **(d)** ^{1H}**DVF**$_{21}$, (**e**) ^{4H}**DVF**$_{21}$, and **(f)** ^{C21}**DVF**$_{12}$. Bond distances in Å and dihedral angles in degree (˚). Hydrogen atoms of the catalyst's ligand have been omitted for clarity.