

## Supporting Information

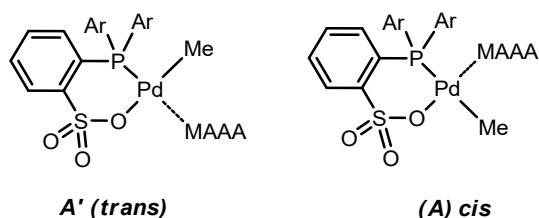
### Computational study of copolymerization mechanism of ethylene with methyl 2-acetamidoacrylate catalyzed by phosphine-sulfonate palladium complexes

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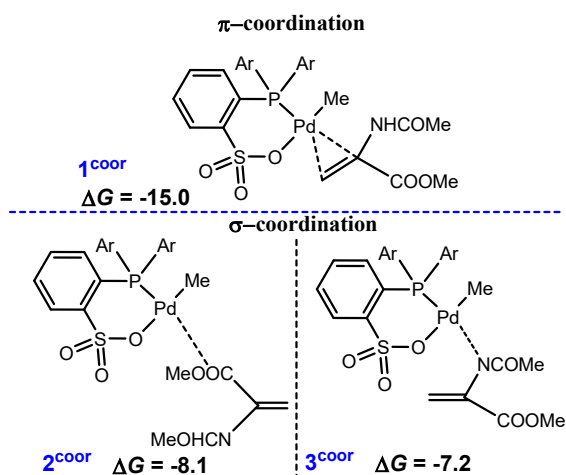
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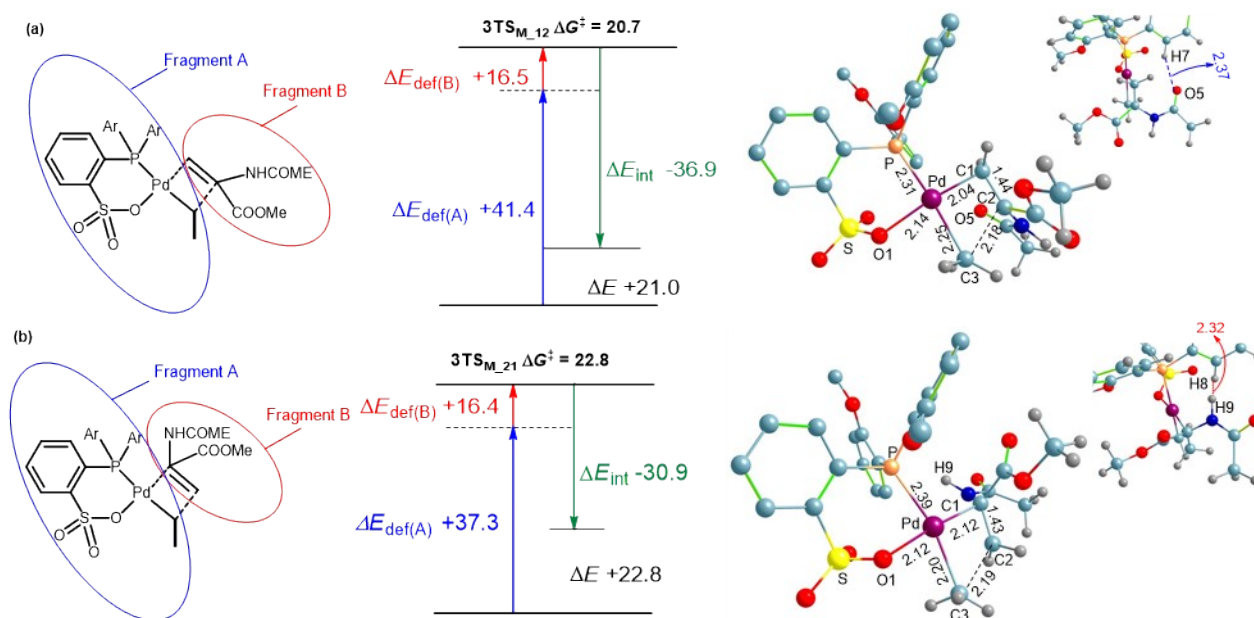
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**Fig. S1.** Two coordinated manners (*Trans* (**A'**) and *cis* (**A**), Ar = 2-MeOC<sub>6</sub>H<sub>4</sub>) of the MAAA corresponding to P-atom of phosphine-sulfonate based Pd complexes.



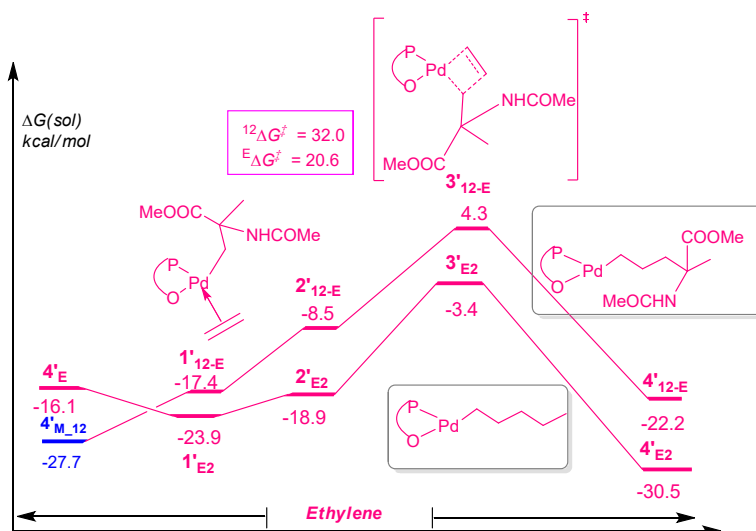
**Fig. S2.** Two coordination sites for polar monomers with phosphine-sulfonate based Pd complexes.



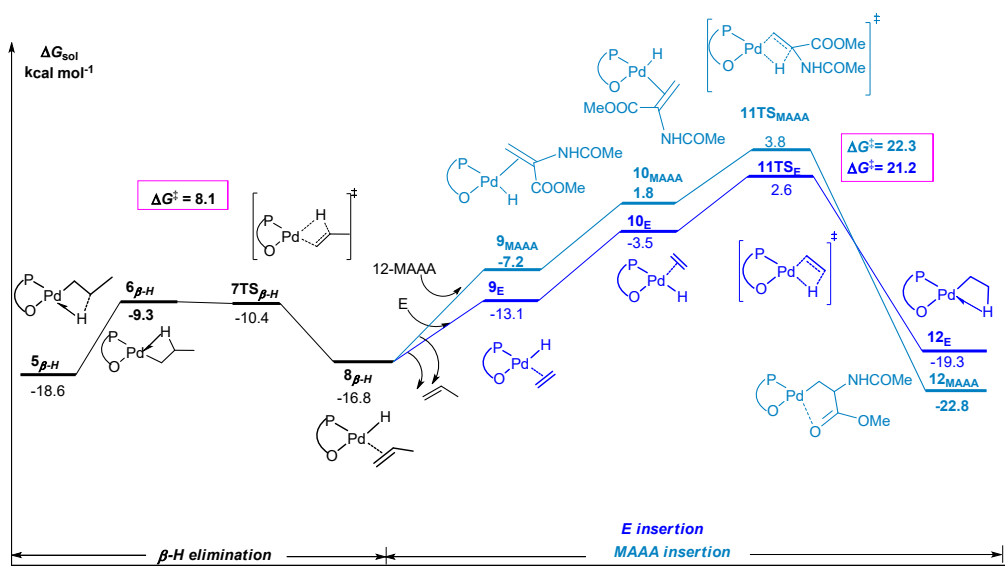
**Fig. S3.** Detailed distortion/interaction analysis of the transition state: (a)  $3\text{TS}_{\text{M}_12\text{M}}$  and (b)  $3\text{TS}_{\text{AM}_21\text{M}}$ . Energy in  $\text{kcal mol}^{-1}$  and distances in Å. Hydrogen atoms of the catalyst's ligand have been omitted for clarity.

**Table. S1.** Computed energies for ethylene (E) and polar monomer (MAAA) copolymerization catalyzed by  $\text{L}_2$  with substituent effect ( $\text{R} = \text{H}$  and  $\text{OMe}$ ) complex.  $^{\text{E-MAAA}}\text{C}_1$  and  $^{\text{E-MAAA}}\text{TS}_1$  are polar monomer MAAA coordination complexes and transition states, respectively.  $^{\text{E-MAAA-E}}\text{C}_2$  and  $^{\text{E-MAAA-E}}\text{TS}_1$  are coordination complexes and transition states of ethylene and MAAA copolymers, respectively.

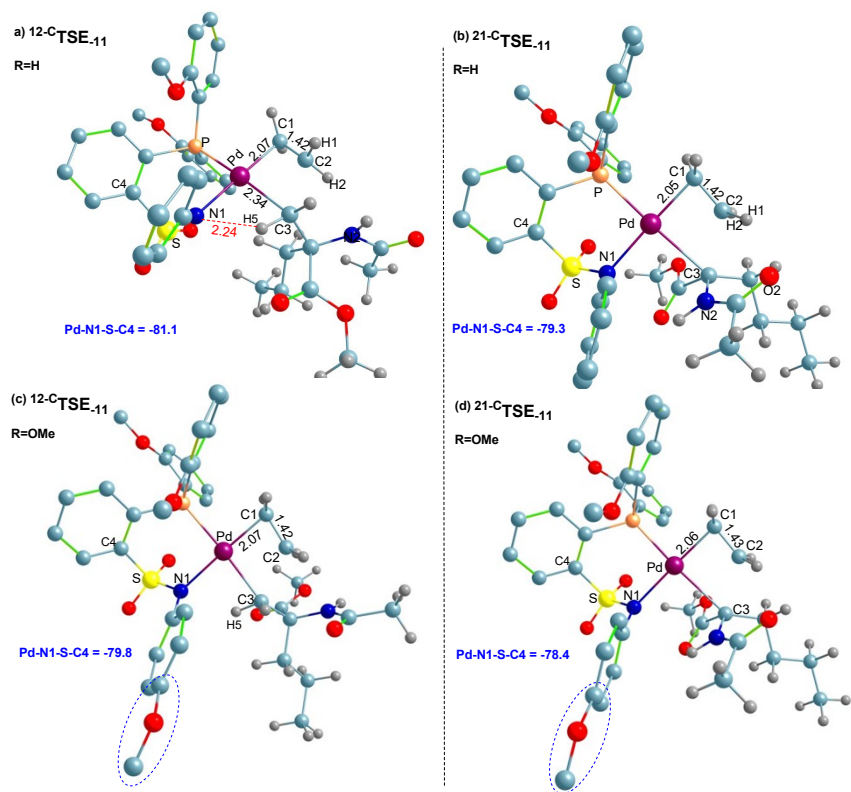
Catalyst $\text{L}_2$	Insertion	E-MAAA	E-MAAA	E-MAAA	E-MAAA-E	E-MAAA-E	E-MAAA-E
		$\text{C}_1$	$\text{TS}_1$	$\Delta\text{G}_1^\ddagger$	$\text{C}_2$	$\text{TS}_2$	$\Delta\text{G}_2^\ddagger$
$\text{L}_2$ ,	1,2	-21.5	2.0	23.5	-31.2	-8.0	23.2
<b>R= H</b>	2,1	-22.9	-2.7	20.1	-35.7	-14.1	21.6
$\text{L}_2$ ,	1,2	-27.9	-4.2	23.8	-41.4	-18.5	23.0
<b>R= OMe</b>	2,1	-22.2	-3.1	19.1	-42.1	-25.0	17.0



**Fig. S4.** Chain propagation via ethylene insertion in 1,2-MAAA enchainment and ethylene enchainment species by applying catalyst A.



**Fig. S5.** Energy profiles for  $\beta$ -H elimination and chain re-growth by using catalyst A.



**Fig. S6.** Geometrical analysis of transition states to compare the substituent effect (R= H and OMe) of catalyst C.