Supporting Information

Theoretical study on regioselectivity of functionalized Vinyl Monomers insertion catalyzed by α-diimine Pd(II) complex

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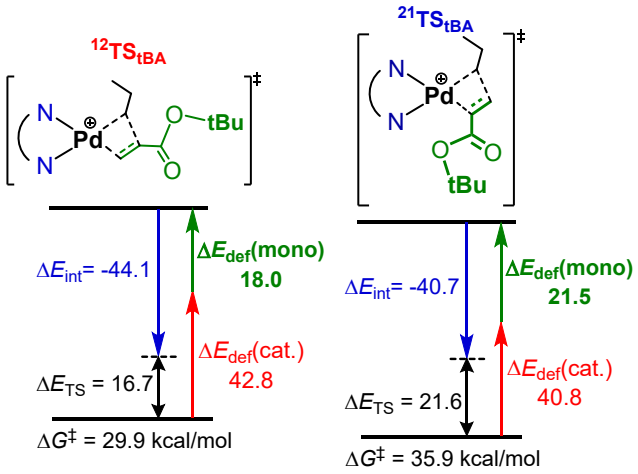

Figure S1. Distortion-interaction analysis of ᵗBA monomer insertion transition state catalyzed by the DBB-Ipty Pd(II) complex. Energies are given in kcal/mol.

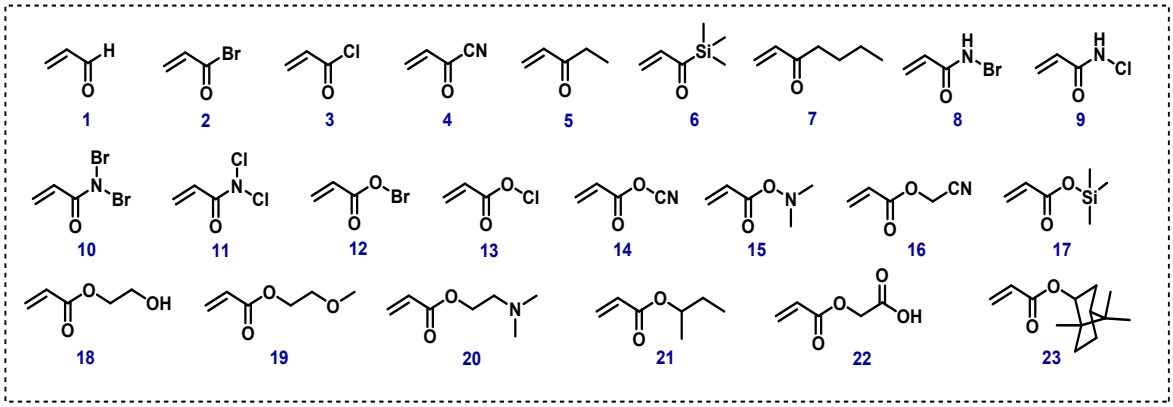

Figure S2. Structures of 23 PVMs used for modeling.

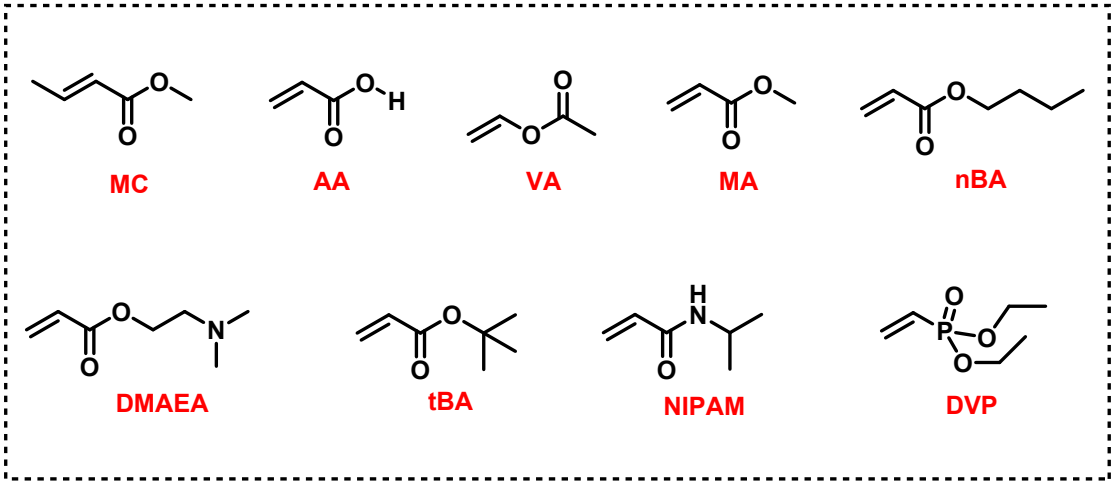

Figure S3. Structures of 9 PVMs for external verification.

Table S1. 23 PVMs descriptor data and $\Delta\Delta G^{\ddagger}$ (kcal/mol) used for modeling.

NO.	$\%V_{bur}$	*E*(HOMO)	*E*(LUMO)	NMR_{C1}	NMR_{C2}	NBO_{C1}	NBO_{C2}	$\Delta\Delta G^{\ddagger}$
1	37.7	-0.262	-0.074	47.121	44.064	-0.255	-0.317	-0.196
2	51.3	-0.289	-0.095	38.226	42.223	-0.214	-0.342	2.738
3	49.7	-0.306	-0.089	38.497	43.610	-0.224	-0.336	2.209
4	49.0	-0.305	-0.116	39.019	43.775	-0.218	-0.305	1.519
5	52.6	-0.253	-0.060	49.343	44.186	-0.266	-0.310	5.128
6	61.7	-0.228	-0.071	54.905	43.953	-0.265	-0.309	8.661
7	52.7	-0.252	-0.060	49.418	44.032	-0.266	-0.309	5.395
8	51.2	-0.269	-0.102	41.787	54.037	-0.251	-0.321	3.181
9	50.7	-0.268	-0.069	42.025	54.988	-0.252	-0.324	2.666
10	60.3	-0.283	-0.138	33.956	52.881	-0.218	-0.345	5.533
11	58.9	-0.286	-0.104	32.703	53.839	-0.217	-0.347	4.857
12	51.8	-0.298	-0.134	40.526	54.956	-0.256	-0.313	5.040
13	51.1	-0.302	-0.102	39.560	54.926	-0.249	-0.321	4.054
14	50.6	-0.317	-0.093	31.940	55.066	-0.216	-0.339	1.844
15	54.0	-0.244	-0.052	45.056	49.626	-0.273	-0.314	5.834
16	51.2	-0.299	-0.066	40.742	50.676	-0.254	-0.318	3.788
17	57.3	-0.278	-0.054	43.692	46.935	-0.271	-0.311	8.750
18	51.2	-0.278	-0.053	44.306	44.306	-0.271	-0.313	5.720
19	51.2	-0.263	-0.053	44.255	48.721	-0.270	-0.313	4.256
20	51.2	-0.220	-0.052	44.693	48.369	-0.272	-0.312	3.242
21	54.2	-0.278	-0.050	45.025	47.543	-0.275	-0.309	3.254
22	51.2	-0.287	-0.058	42.953	49.194	-0.264	-0.314	6.806
23	54.6	-0.276	-0.051	45.163	47.908	-0.274	-0.308	7.070

Table S2. 9 PVMs descriptor data and $\Delta\Delta G^{\ddagger}$ (kcal/mol) used for external verification.

Mono.	$\%V_{bur}$	$E_{(HOMO)}$	$E_{(LUMO)}$	NMR_{C1}	NMR_{C2}	NBO_{C1}	NBO_{C2}	$\Delta\Delta G^{\ddagger}$
MC	50.7	-0.270	-0.045	27.934	53.556	-0.072	-0.335	-0.018
AA	43.4	-0.286	-0.057	41.851	50.976	-0.262	-0.326	-0.294
VA	46.2	-0.257	-0.018	85.354	34.944	-0.439	0.131	3.437
MA	50.6	-0.281	-0.052	44.797	48.676	-0.272	-0.313	1.519
nBA	51.1	-0.279	-0.279	44.992	48.140	-0.274	-0.311	5.72
DMAEA	52.9	-0.215	-0.061	49.229	43.923	-0.264	-0.309	6.024
tBA	57.6	-0.271	-0.049	45.854	46.303	-0.278	-0.305	6.012
NIPAM	52.1	-0.201	0.031	101.647	36.787	-0.516	0.026	7.794
DVP	65.6	-0.279	-0.027	46.009	47.273	-0.296	-0.581	9.197

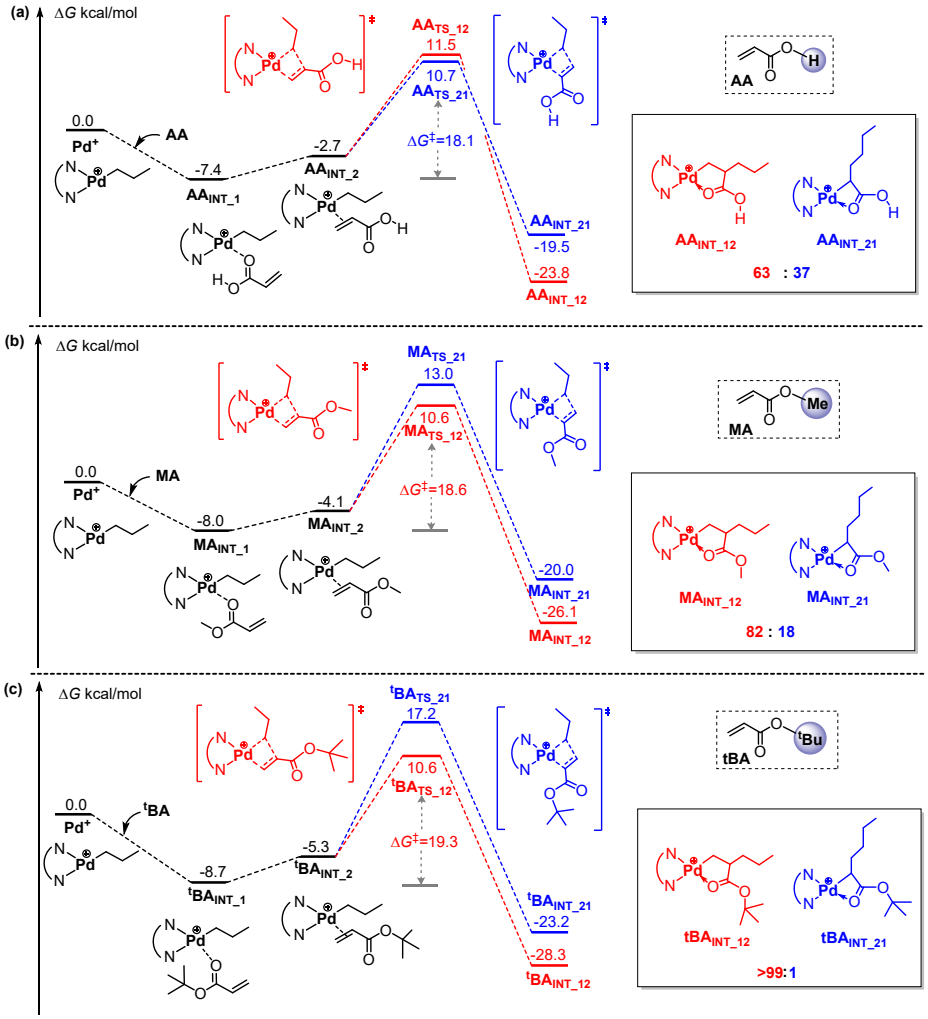

Figure S4. Calculated energy profiles for AA(a), MA(b), and tBA(c) insertion into the DBB-Ipty Pd(II) complex (B3LYP-D3).

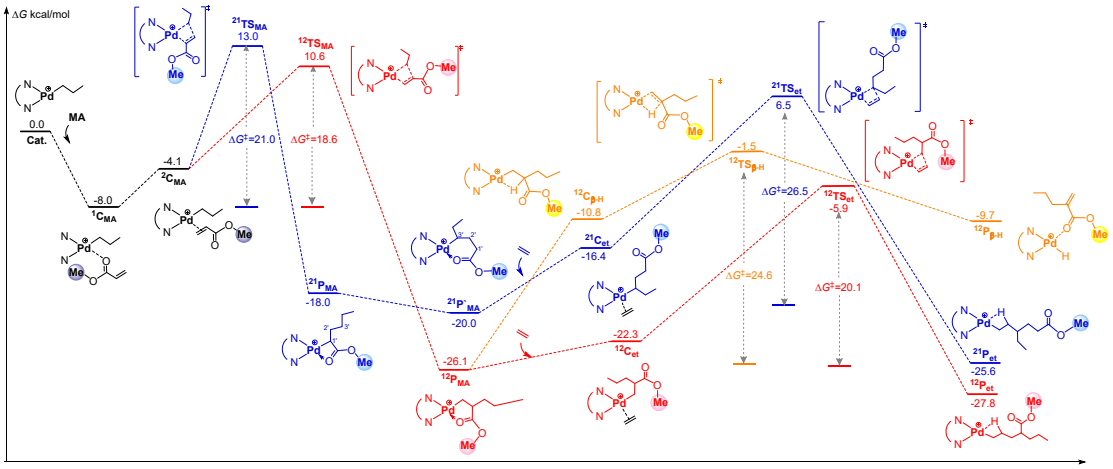

Figure S5. Energy profiles for ethylene insertion post-MA insertion and β-H elimination following MA insertion into the DBB-Ipty Pd(II) complex(B3LYP-D3).

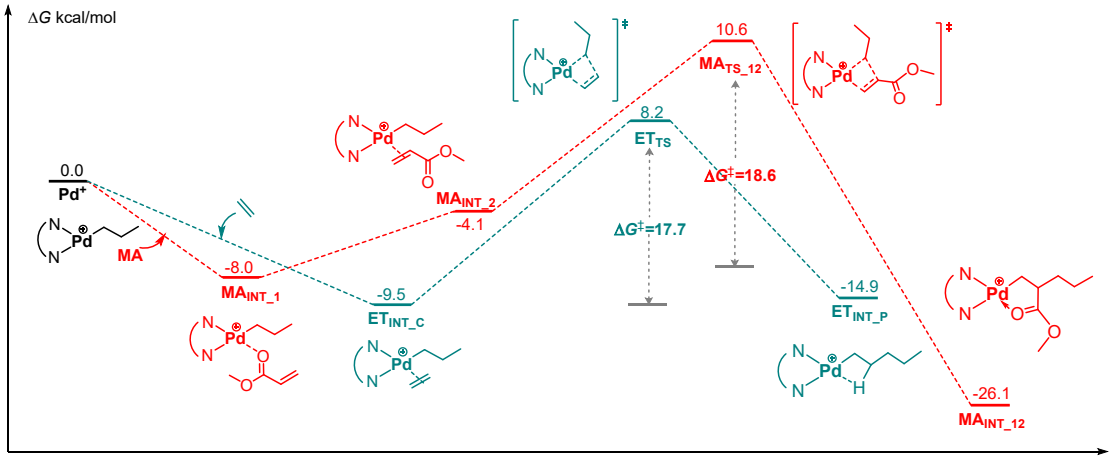

Figure S6. Calculated energy profiles for ethylene and MA insertion into the DBB-Ipty Pd(II) complex.