

Supporting Information

Allylboration of Ketones Catalyzed by BINOL Derivatives: Which Species Are Involved Depending on Substrate Reactivity?

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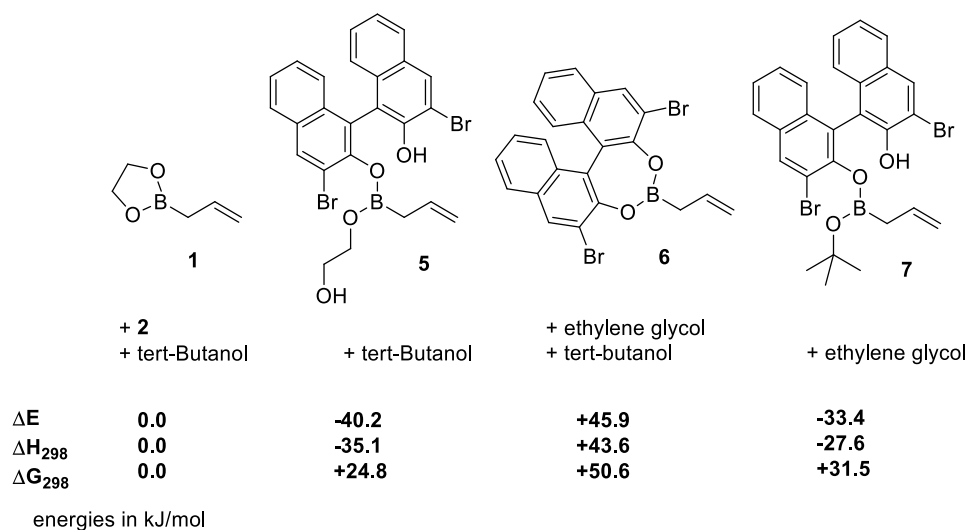
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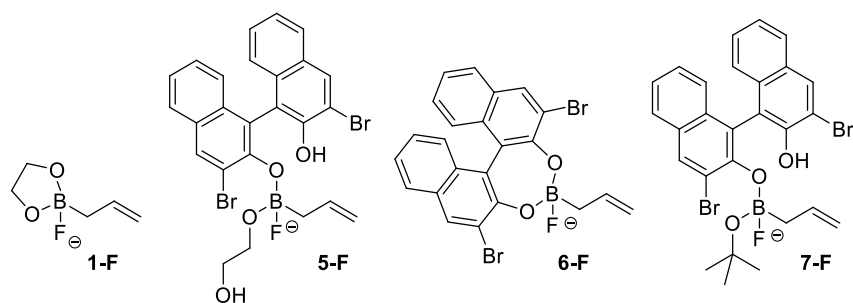
1. Table S1 : Relative energy of the effective catalysts compared to the starting materials



	E	ZPE	H^o₂₉₈	G^o₂₉₈	Number of imaginary frequencies
tert-Butanol	-233.63769655	-233.501385	-233.49375	-233.530342	0
1	-371.273867663	-371.131979	-371.122749	-371.166364	0
2	-6068.07031873	-6067.805321	-6067.784741	-6067.855792	0
Ethylene glycol	-230.237907721	-230.151505	-230.145552	-230.178696	0
5	-6439.35949934	-6438.950963	-6438.920841	-6439.012698	0
6	-6209.08879633	-6208.769326	-6208.74532	-6208.824171	0
7	-6442.75670254	-6442.298145	-6442.266208	-6442.361786	0

Table S1. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H^o₂₉₈) and Gibbs free energy at 248K (G^o₂₉₈), in Hartree.

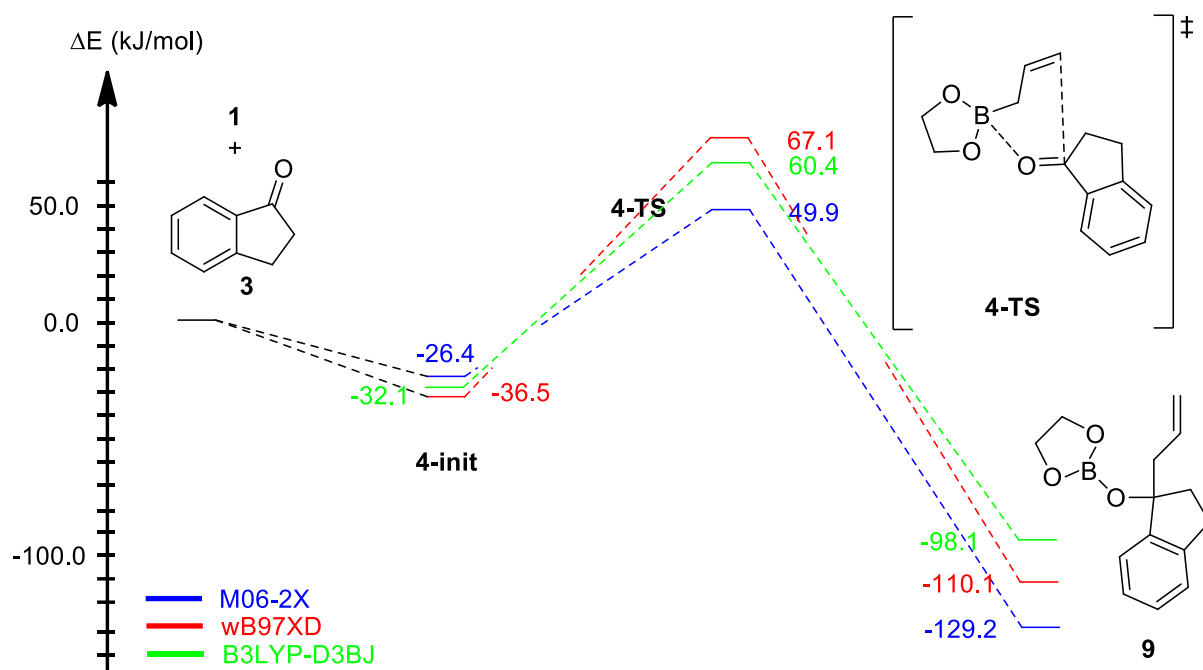
2. Table S2 : Relative energy of the catalysts complexed with a fluoride ion



	E	ZPE	H[°]₂₉₈	G[°]₂₉₈	Number of imaginary frequencies
1-F	-471.2537938	-471.111593	-471.101454	-471.146582	0
5-F	-6539.359119	-6538.948547	-6538.918104	-6539.008647	0
6-F	-6309.108724	-6308.787434	-6308.762574	-6308.841972	0
7-F	-6542.748893	-6542.289954	-6542.257486	-6542.35295	0
Fluoride ion	-99.92621436	-99.926214	-99.923854	-99.940373	0

Table S2. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 248K (G[°]₂₉₈), in Hartree.

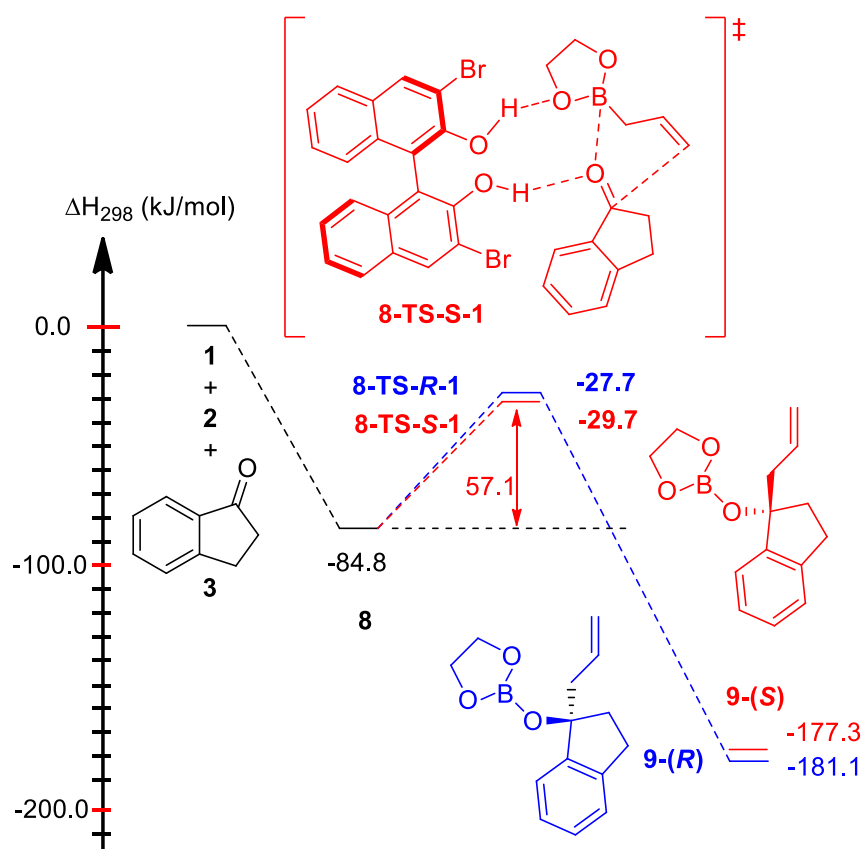
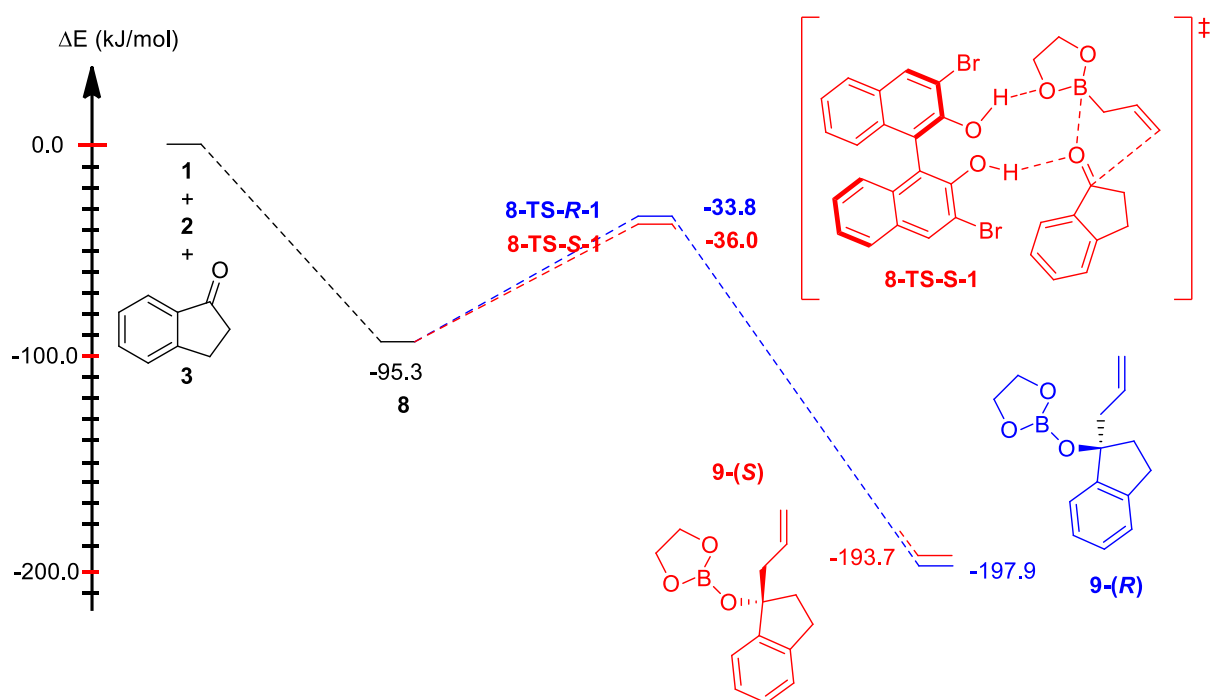
3. Table S3: Energy profile in absence of 2



		E	ZPE	H [°] ₂₉₈	G [°] ₂₉₈	Number of imaginary frequencies
M06-2X	Indanone	-422.95098102	-422.804707	-422.796123	-422.837609	0
	1	-371.2738677	-371.131979	-371.122749	-371.166364	
	4-init	-794.23489850	-793.945327	-793.926931	-793.992858	0
	4-TS	-794.20584978	-793.91556	-793.899701	-793.957292	1
	9	-794.27406682	-793.980705	-793.963962	-794.024346	0
B3LYP-D3BJ	Indanone	-423.1689255	-423.024005	-423.015437	-423.056729	0
	1	-371.4604771	-371.320187	-371.3109	-371.354933	
	4-init	-794.6416285	-794.355116	-794.336395	-794.403506	0
	4-TS	-794.6064039	-794.31878	-794.302864	-794.360327	1
	9	-794.6667743	-794.376586	-794.359543	-794.420944	0
WB97XD	Indanone	-422.9859291	-422.8396	-422.831073	-422.872372	0
	1	-371.3082332	-371.166647	-371.157402	-371.201223	
	4-init	-794.3080634	-794.018503	-794.000186	-794.065509	0
	4-TS	-794.2686154	-793.978316	-793.962569	-794.019823	1
	9	-794.3360807	-794.042701	-794.025972	-794.086501	0

Table S3. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 298K (G[°]₂₉₈), in Hartree. Values with the three DFT methods studied.

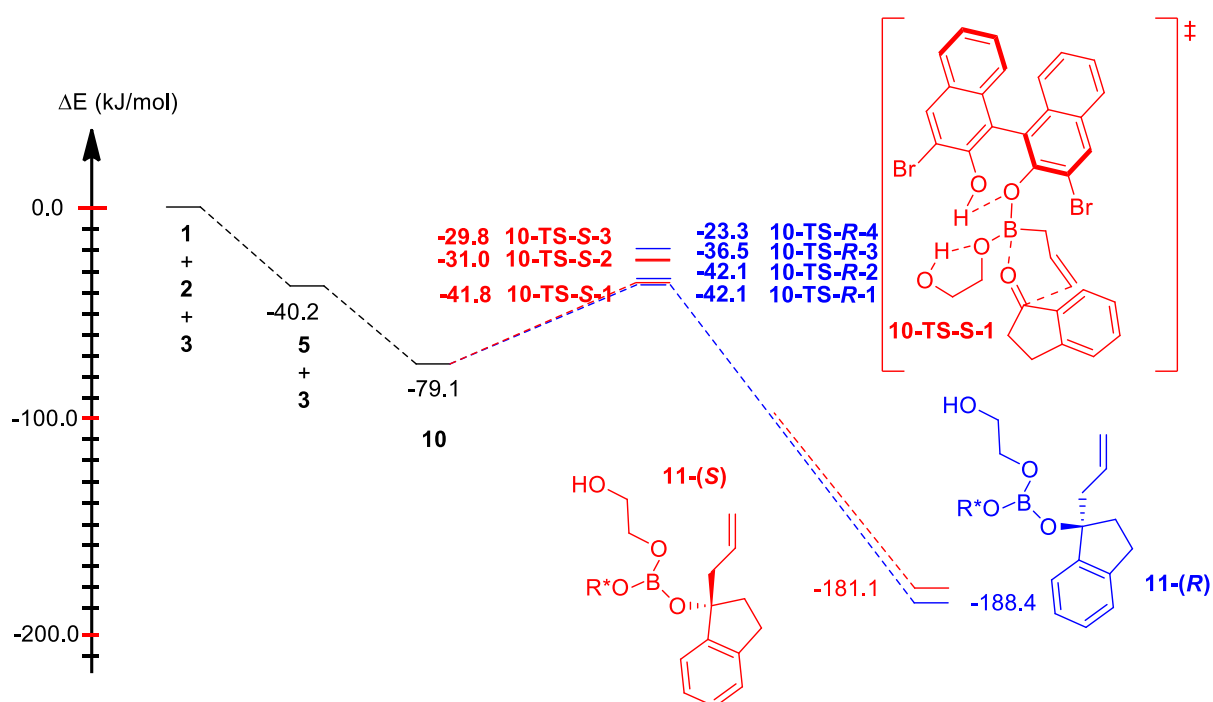
4. Table S4 : Energy profile via pathway C

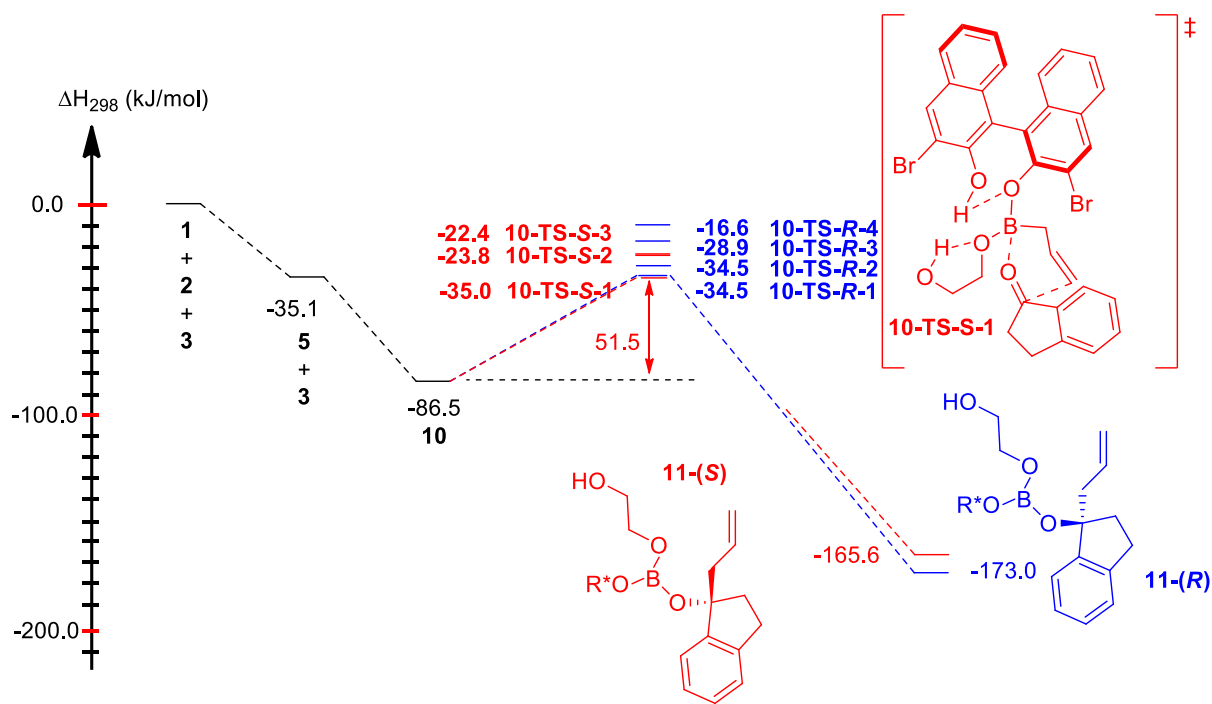


	E	ZPE	H [°] ₂₉₈	G [°] ₂₉₈	Number of imaginary frequencies
8	-6862.33145431	-6861.774962	-6861.735908	-6861.849231	0
8-TS-R-1	-6862.30803701	-6861.750831	-6861.714175	-6861.818808	1
8-TS-S-1	-6862.30889732	-6861.751702	-6861.71491	-6861.821147	1
9-R	-6862.37053871	-6861.810209	-6861.772577	-6861.879914	0
9-S	-6862.36896114	-6861.809018	-6861.771133	-6861.880169	0

Table S4. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 298K (G[°]₂₉₈), in Hartree.

5. Table S5 : Energy profile via pathway A

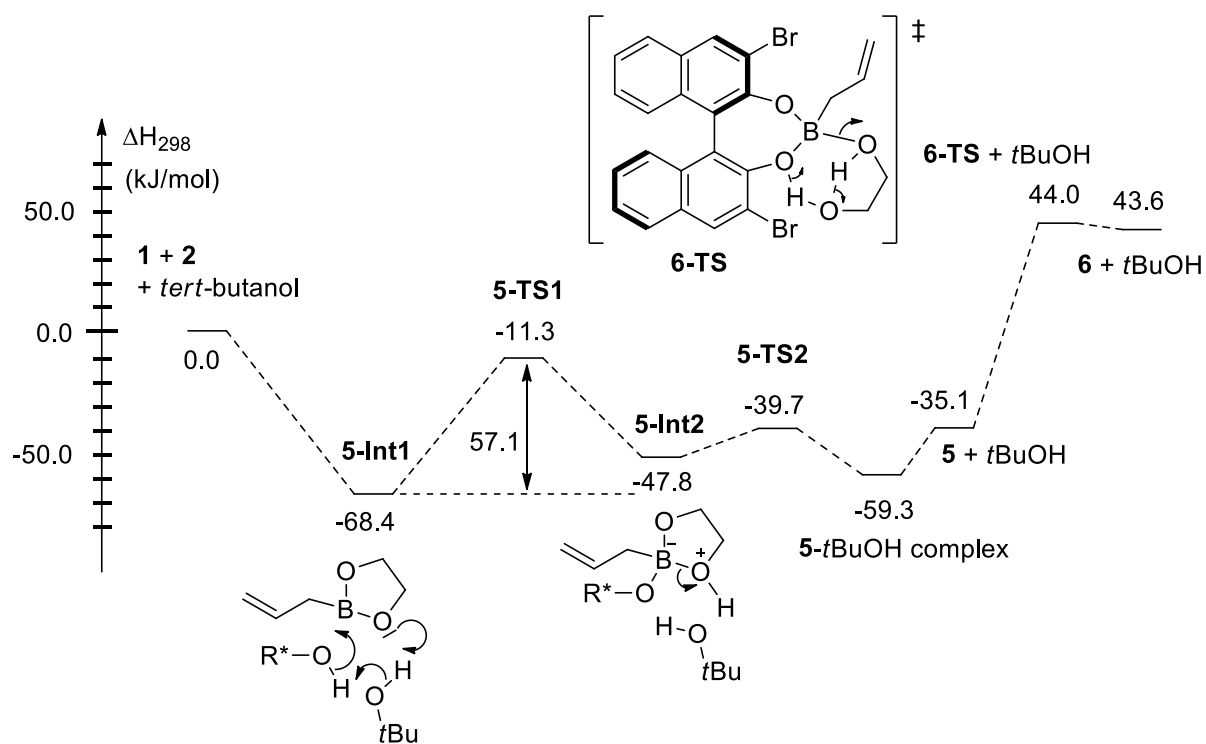
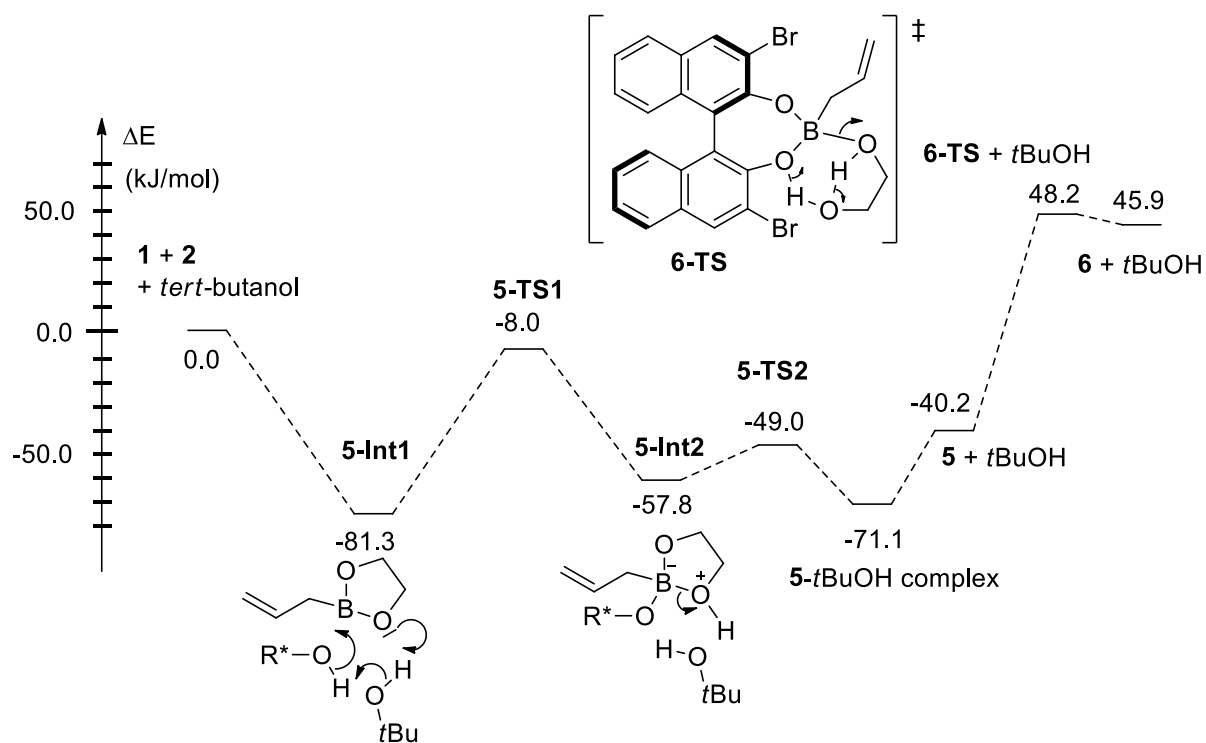




	E	ZPE	H [°] ₂₉₈	G [°] ₂₉₈	Number of imaginary frequencies
10	-6862.332026	-6861.775432	-6861.736545	-6861.84747	0
10-TS-S-1	-6862.311106	-6861.753702	-6861.716944	-6861.821563	1
10-TS-S-2	-6862.306959	-6861.748958	-6861.712655	-6861.815271	1
10-TS-S-3	-6862.306501	-6861.748311	-6861.712132	-6861.815011	1
10-TS-R-1	-6862.311219	-6861.753088	-6861.716766	-6861.820296	1
10-TS-R-2	-6862.311219	-6861.753086	-6861.716765	-6861.820291	1
10-TS-R-3	-6862.309068	-6861.751429	-6861.714617	-6861.820582	1
10-TS-R-4	-6862.304049	-6861.746713	-6861.709935	-6861.81501	1
11-(S)	-6862.364139	-6861.804315	-6861.766699	-6861.873533	0
11-(R)	-6862.366939	-6861.807597	-6861.769521	-6861.879433	0

Table S5. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 298K (G[°]₂₉₈), in Hartree.

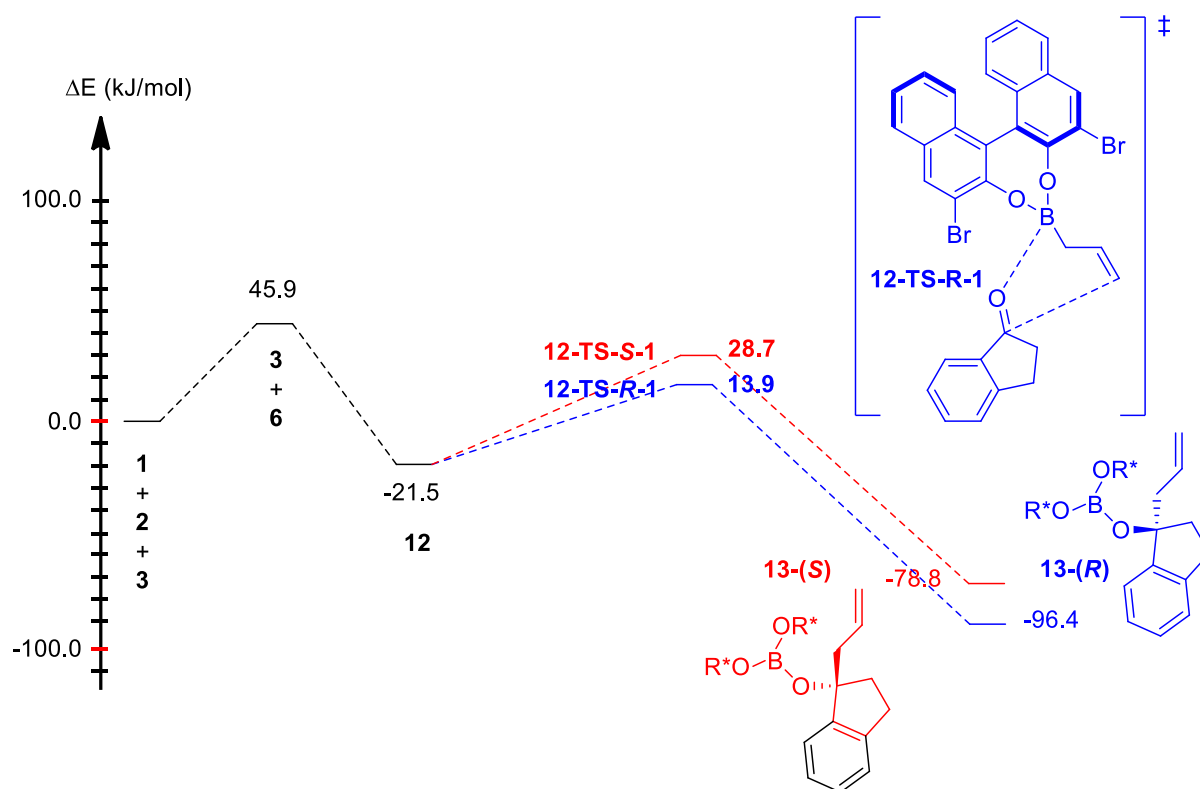
6. Table S6: Pathway to 6

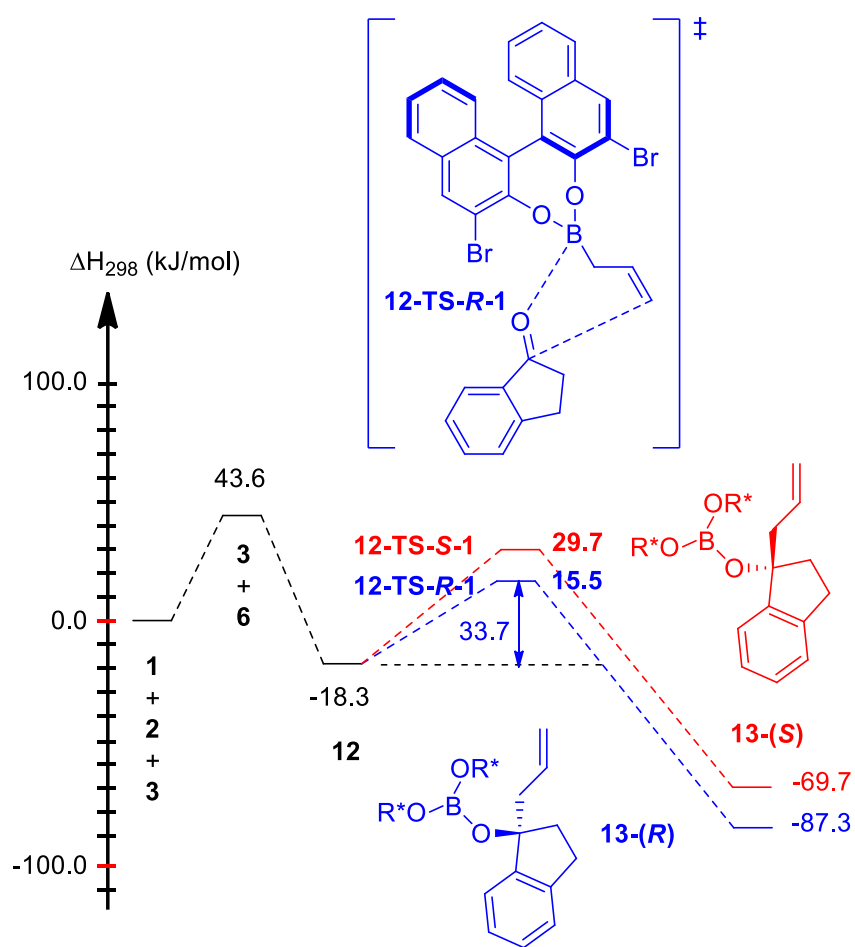


	E	ZPE	H[°]₂₉₈	G[°]₂₉₈	Number of imaginary frequencies
5-Int1	-6673.012854	-6672.465599	-6672.427284	-6672.540073	0
5-TS1	-6672.984917	-6672.441735	-6672.40554	-6672.509101	1
5-Int2	-6673.003896	-6672.456505	-6672.419466	-6672.526386	0
5-TS2	-6673.000537	-6672.453366	-6672.416378	-6672.522436	1
7-<i>t</i>BuOH	-6673.008955	-6672.461818	-6672.423818	-6672.532889	0
6-TS	-6439.325824	-6438.918833	-6438.890735	-6438.977858	1

Table S6. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 298K (G[°]₂₉₈), in Hartree.

7. Table S7 : Energy profile via pathway B





	E	ZPE	H [°] ₂₉₈	G [°] ₂₉₈	Number of imaginary frequencies
12	-6632.065441	-6631.597224	-6631.565016	-6631.661517	0
12-TS-S-1	-6632.046299	-6631.577413	-6631.546733	-6631.638465	1
12-TS-R-1	-6632.05195	-6631.582844	-6631.552176	-6631.644269	1
13-(S)	-6632.087274	-6631.616292	-6631.584613	-6631.680172	0
13-(R)	-6632.093977	-6631.623074	-6631.591322	-6631.68726	0

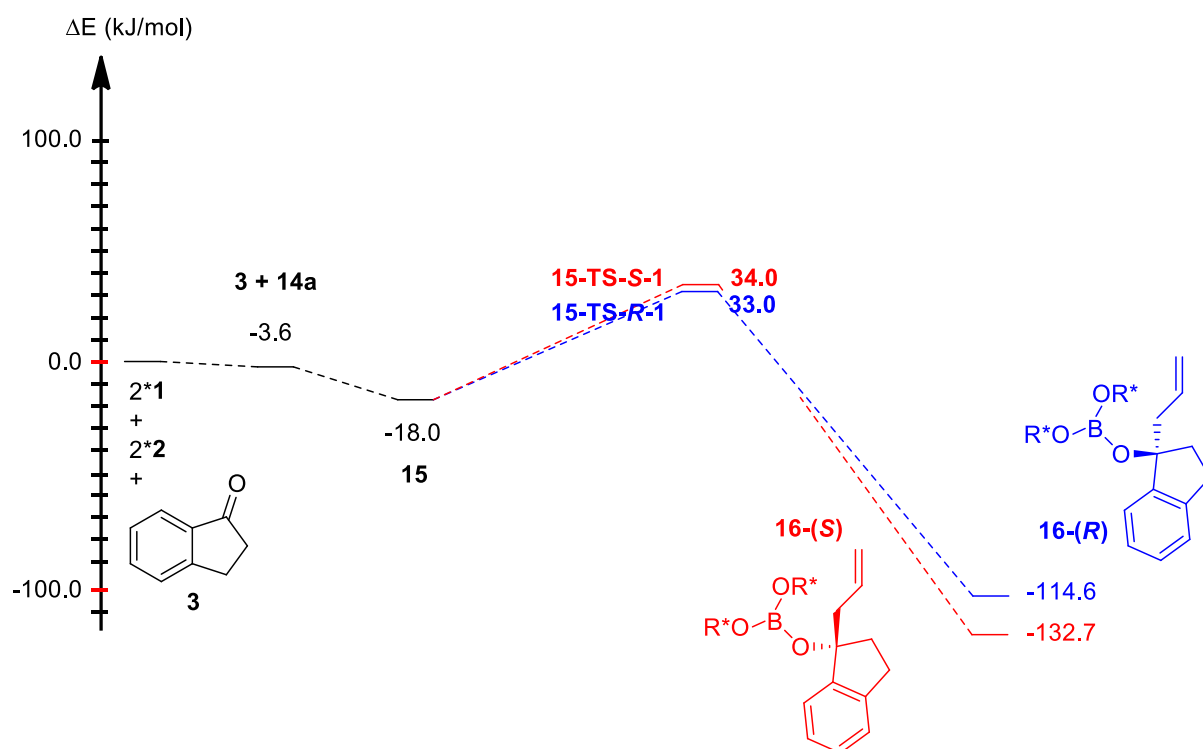
Table S7. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H[°]₂₉₈) and Gibbs free energy at 298K (G[°]₂₉₈), in Hartree.

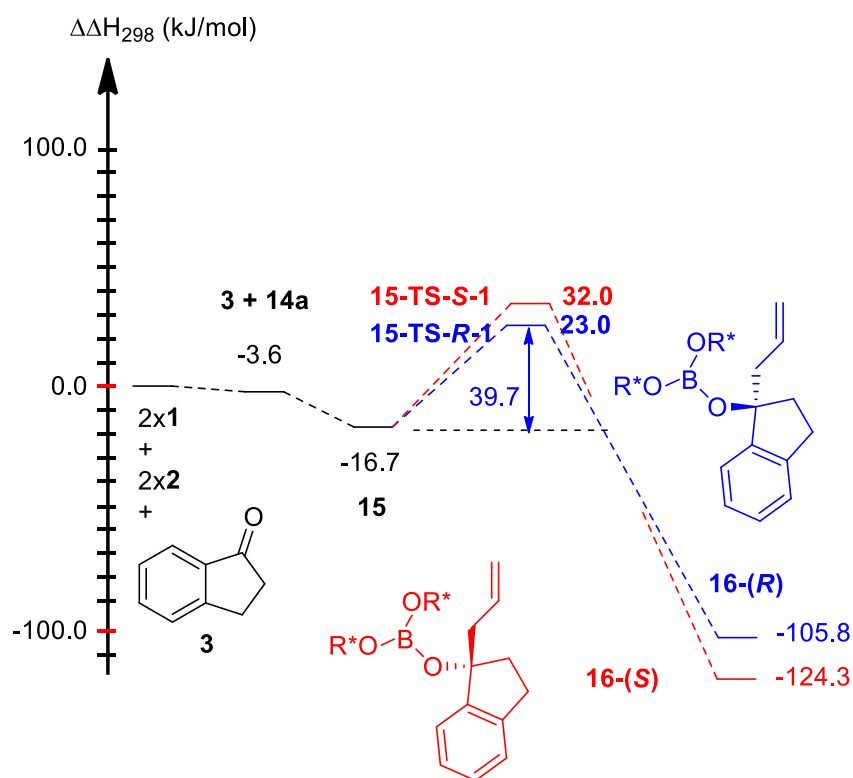
8. Table S8 : Dimers 14a and 14b

	E	ZPE	H° ₂₉₈	G° ₂₉₈	Number of imaginary frequencies
14a	-12418.21461	-12417.57386	-12417.52526	-12417.65875	0
14b	-12418.20835	-12417.56662	-12417.51844	-12417.64987	0

Table S8. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H°₂₉₈) and Gibbs free energy at 298K (G°₂₉₈), in Hartree.

9. Table S9 : Energy profile via pathway D





	E	ZPE	H°₂₉₈	G°₂₉₈	Number of imaginary frequencies
15	-12841.17038	-12840.38243	-12840.32634	-12840.47179	0
15-TS-S-1	-12841.1506	-12840.36285	-12840.30783	-12840.4513	1
15-TS-R-1	-12841.15099	-12840.36516	-12840.31123	-12840.44992	1
16-(S)	-12841.2141	-12840.42299	-12840.36735	-12840.51277	0
16-(R)	-12841.20718	-12840.41556	-12840.36029	-12840.50342	0

Table S9. Electronic energy (E), zero-point energy (ZPE), enthalpy at 298K (H°₂₉₈) and Gibbs free energy at 298K (G°₂₉₈), in Hartree.