

Supplementary Material

Electrophilic Allenes Participating in Polar Diels-Alder reactions. Study of the Reactivity and Site, Regio and Stereo Selectivity from a Molecular Electron Density Theory Perspective

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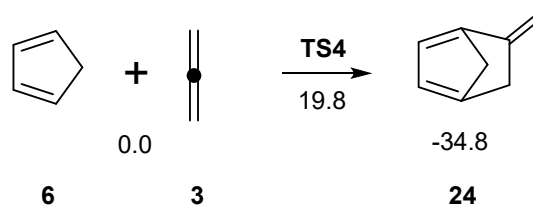
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Scheme S1. Diels-Alder reaction of simplest allene **3** with Cp **6**. Relative enthalpies in toluene are given in kcal·mol⁻¹.

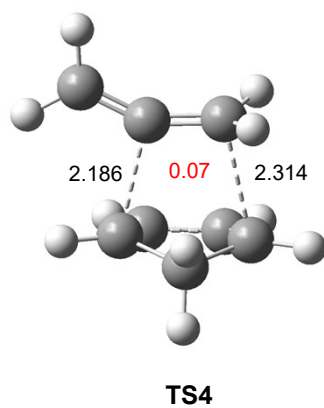


Figure S1. M06-2x/6-311G(d,p) Optimized geometry in toluene of **TS4** involved in the Diels-Alder reaction of the simplest allene **3** with Cp **6**. The GEDT value, in red, is given in average number of electrons, e.

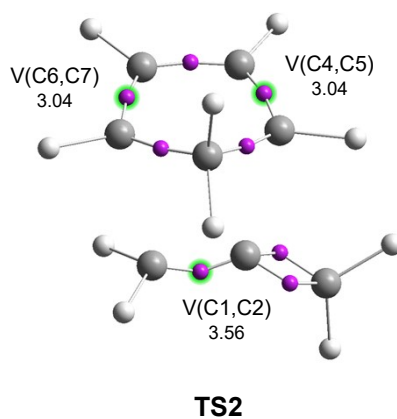


Figure S2. ELF basin attractor positions, along with the most relevant valence basin populations of **TS4** associated with the Diels-Alder reaction between the simplest allene **3** and Cp **6**. The electron populations are in average number of electrons e.

Table S1. Electrophilic P_k^+ and nucleophilic P_k^- and Parr functions of the reagents.

		Electrophilic Parr function	Nucleophilic Parr function
		P_k^+	P_k^-
5	C ₁	0.06	0.21
	C ₂	0.31	0.11
	C ₃	0.05	0.18
17	C ₁	0.09	0.31
	C ₂	0.60	0.11
	C ₃	0.13	0.23
6	C ₄	-0.09	-0.06
	C ₅	0.42	0.50
	C ₆	0.07	0.05
	C ₇	0.07	0.05
	C ₈	0.42	0.50
7	C ₄	-0.08	-0.06
	C ₅	0.51	0.25
	C ₆	0.11	-0.03
	C ₇	0.06	0.03
	C ₈	0.29	0.74
18	C ₄	0.43	0.48
	C ₅	0.03	-0.07
	C ₆	0.09	0.32
	C ₇	0.43	0.14

Table S2. M06-2x/6-311G(d,p) electronic energies, E in a.u., enthalpies, H in a.u., entropies S in cal·mol⁻¹·K⁻¹, Gibbs free energies, G in a.u., computed in toluene at 80 °C, of the stationary points associated with the Diels-Alder reactions of allene **3** and sulphonyl allenes **5** and **17** with the cyclic dienes **6** and **18**.

	E	H	S	G
17	-704.491020	-704.384321		-704.436447
6	-194.058193	-193.958299		-193.997655
TS1-n	-898.533921	-898.325502	10.7	-898.390227
TS1-x	-898.532958	-898.324586	11.3	-898.389757
TS-23	-898.527337	-898.319190	14.7	-898.386928
19	-898.615991	-898.403066	-37.9	-898.465595
20	-898.619281	-898.406145	-39.9	-898.467488
21	-898.618328	-898.405244	-39.3	-898.467785
5	-896.194118	-896.029454		-896.093142
TS2-n	-1090.237447	-1089.971153	10.4	-1090.047533
8	-1090.320955	-1090.049974	-39.0	-1090.122501
18	-308.566512	-308.430107		-308.478340
TS3-pn	-1013.052903	-1012.807969	4.1	-1012.880831
TS3-mn	-1013.046670	-1012.801701	8.0	-1012.873051
22	-1013.133870	-1012.884143	-43.7	-1012.953615
23	-1013.134119	-1012.884367	-43.9	-1012.952540
3	-116.62758	-116.566116		-116.601626
TS-4	-310.656007	-310.492846	19.8	-310.542441
24	-310.747872	-310.579929	-34.8	-310.626674