Supporting Information

Double-Boron Heterocyclic Carbenes: Computational Study of Diels-Alder Reactions

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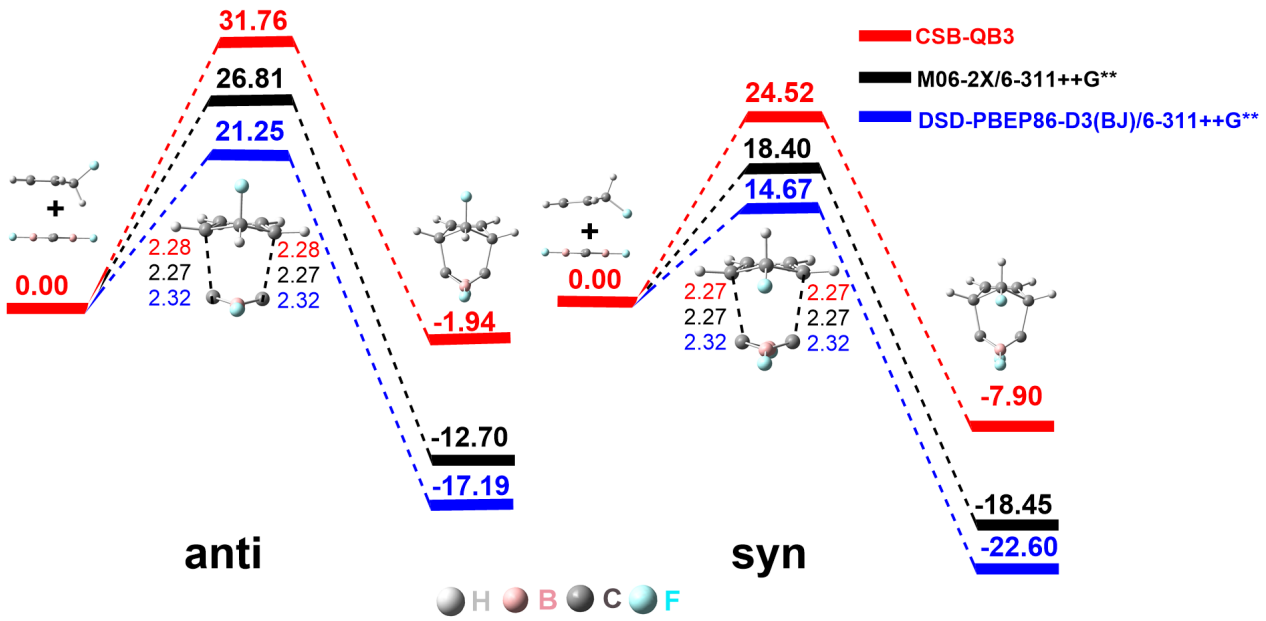

Fig S1 The energy barriers for the Diels-Alder reactions of **A8** and **B10** calculated using the M06-2X(in black), CBS-QB3(in red), and DSD-PBEP86-D3(BJ)(in blue) functionals

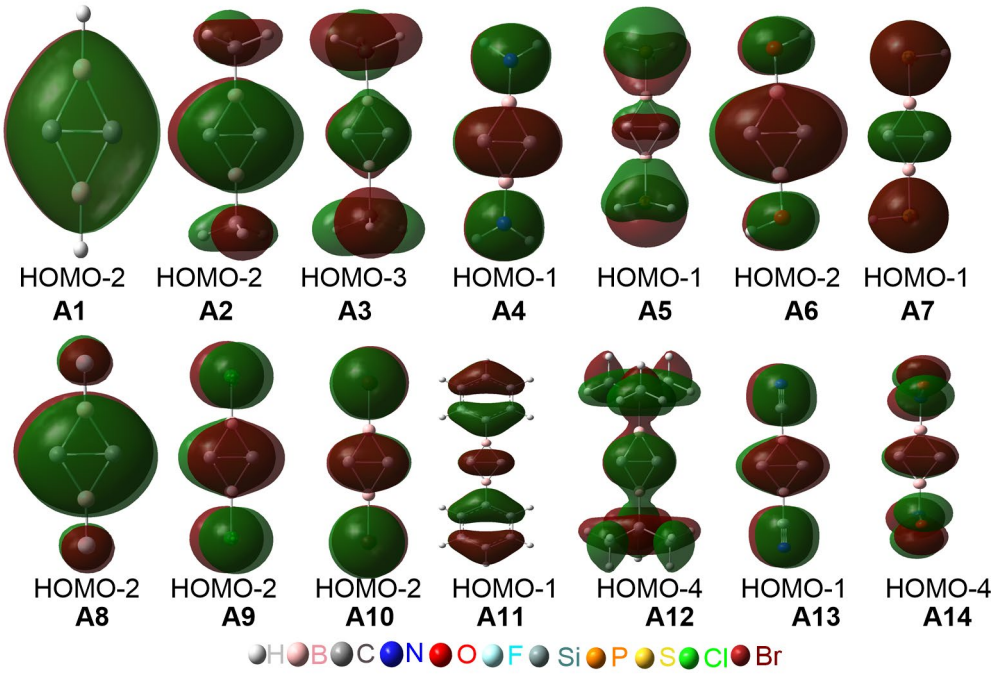

Fig S2. Occupied π orbitals of **Ai** (i=1-14).

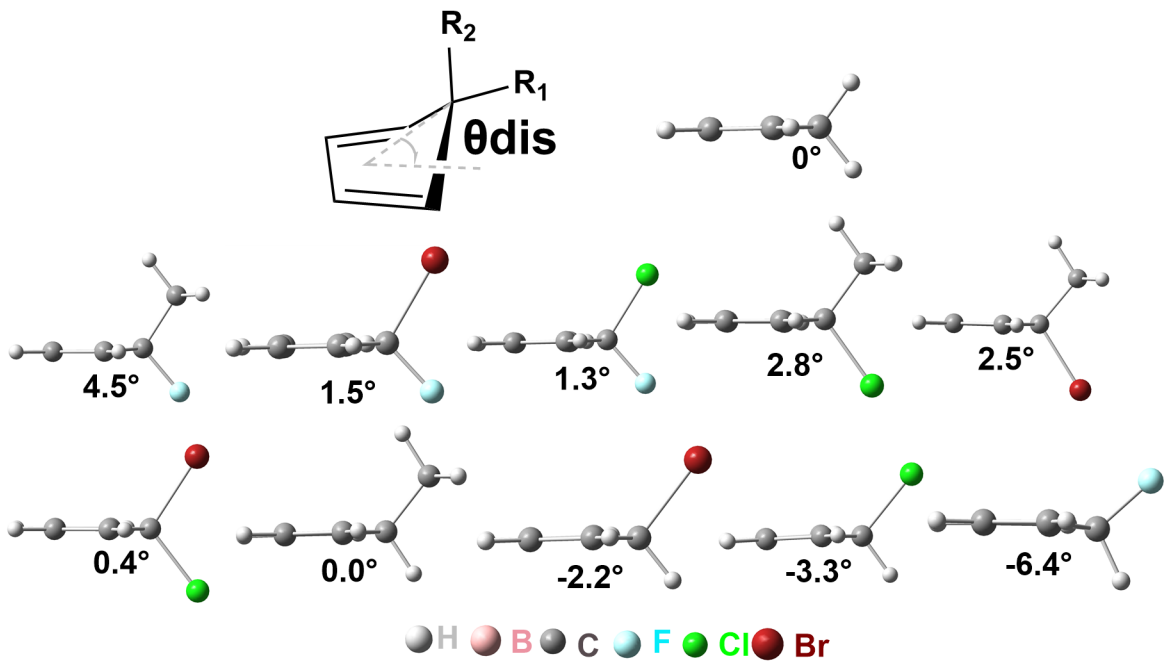

Fig S3 The distortion angle of 5-substituted cyclopentadienes' plane

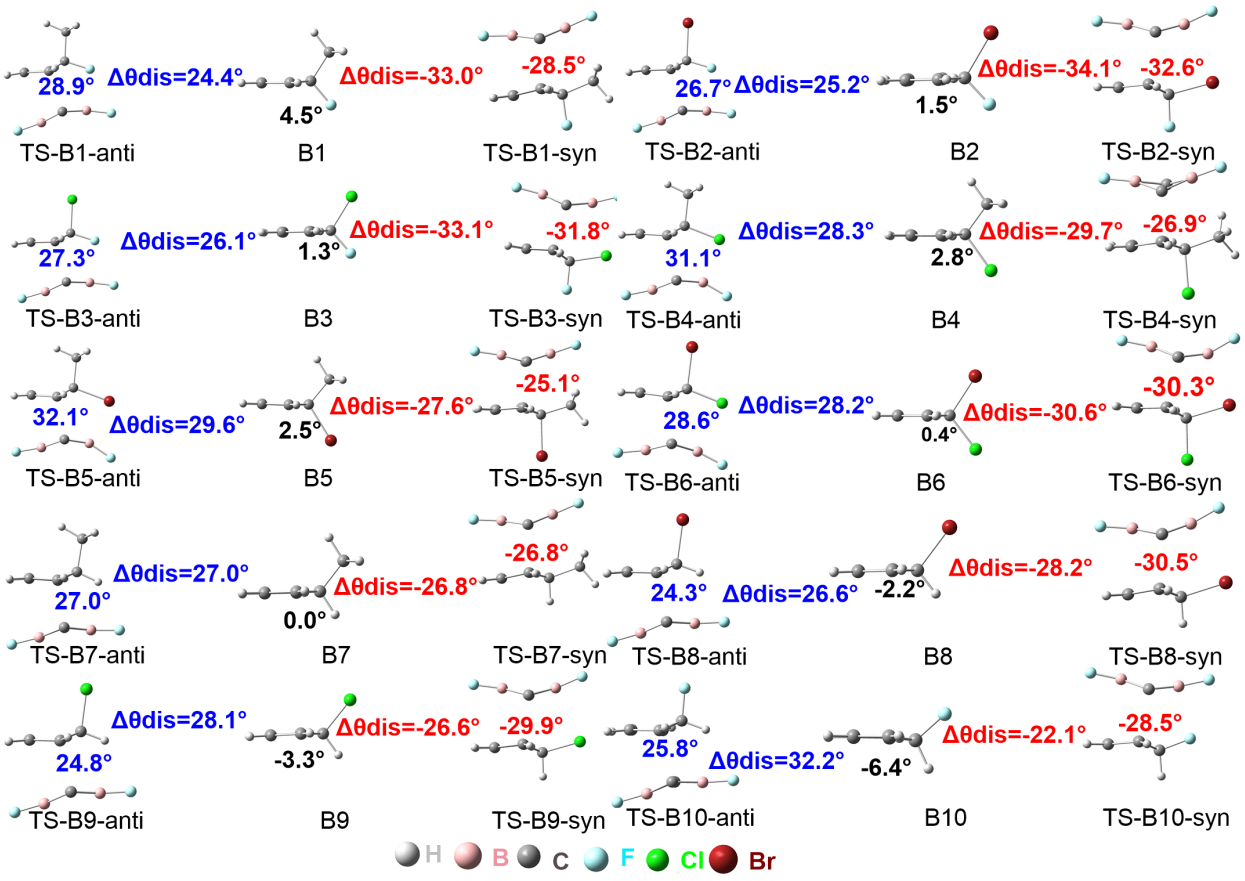

Fig S4 The distortion angles of the transition-state of Diels-Alder reactions of **Bi** (i=1-10).

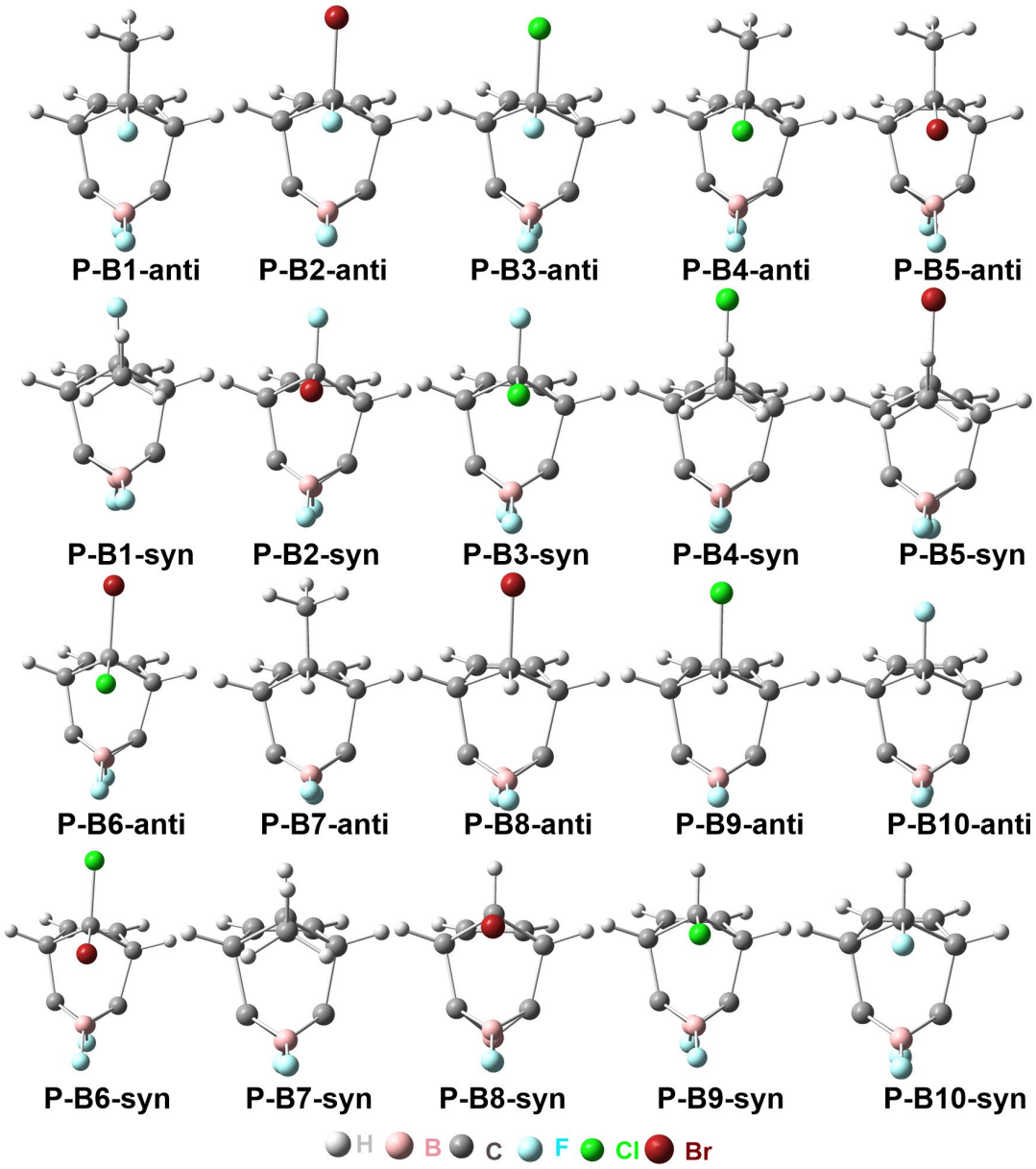

Fig S5 Optimized products of the Diels-Alder reactions of $C_2B_2F_2$ with **Bi** (i=1-10)

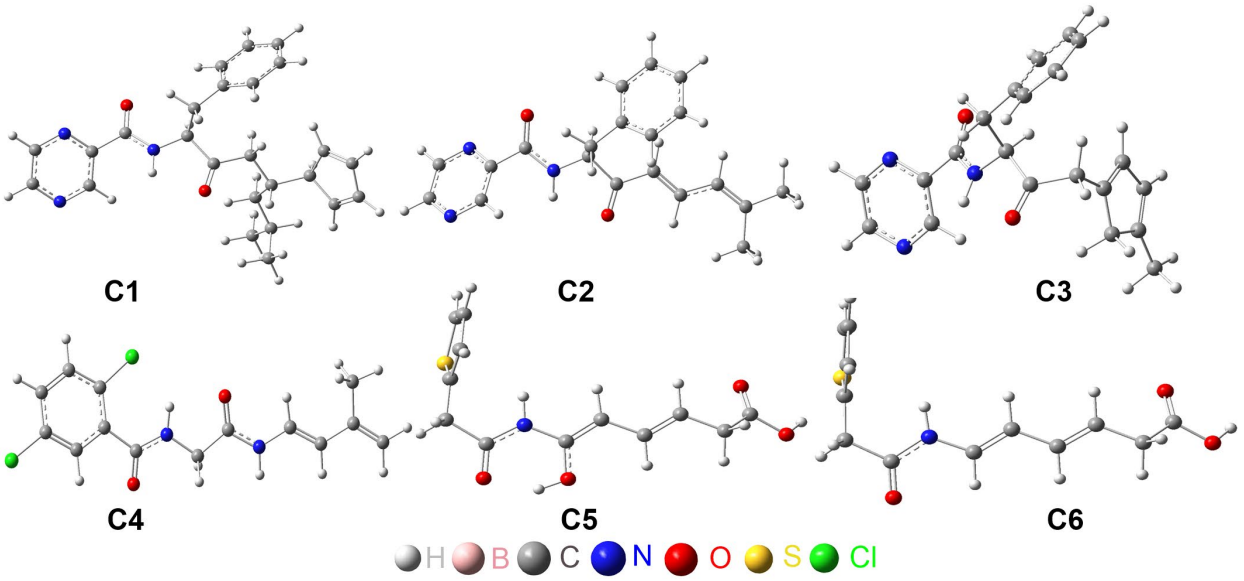

Fig S6 Optimized geometries of **Ci** (i=1-6).

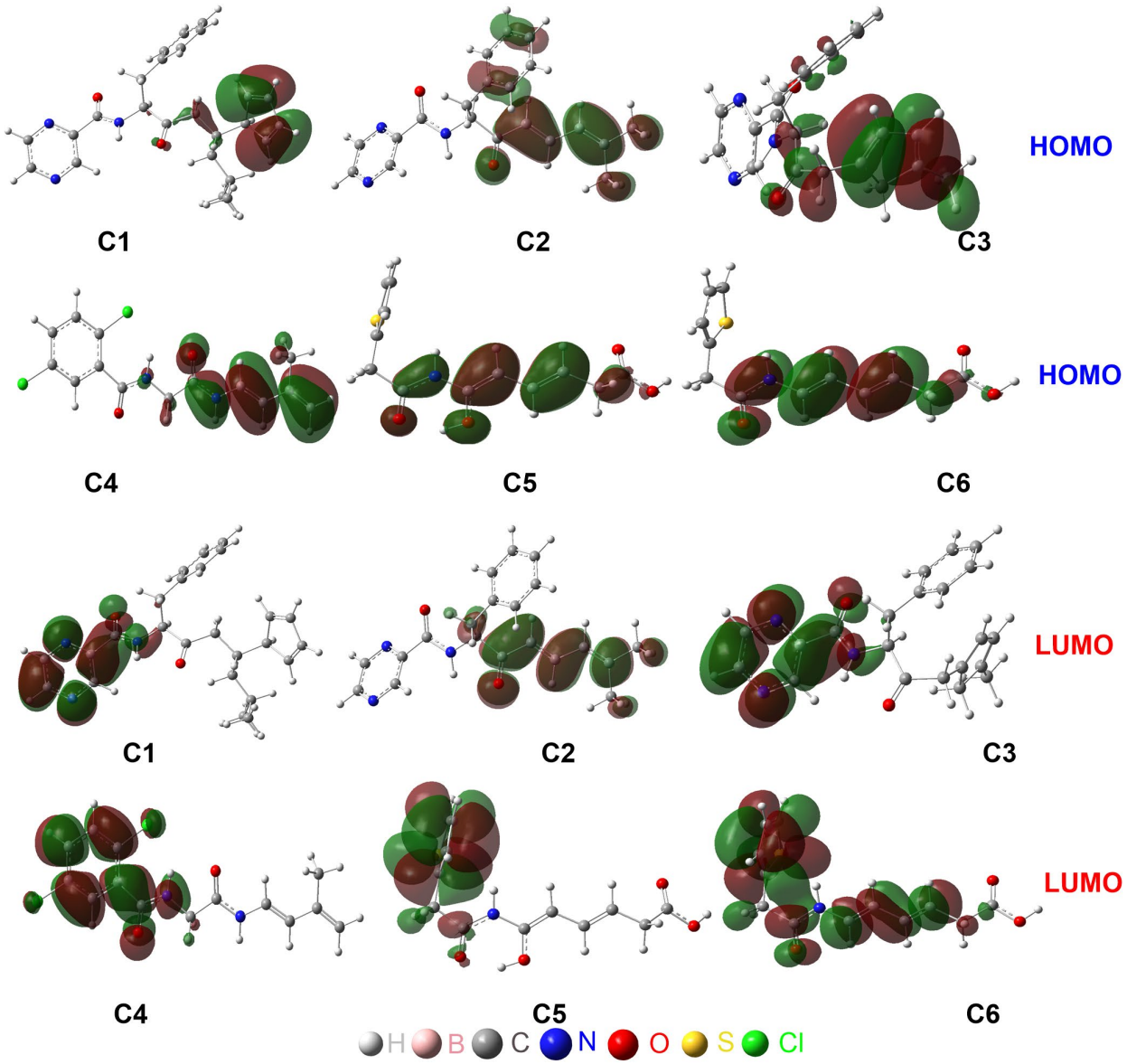

Fig S7 HOMO and LUMO of **Ci** (i=1-6).

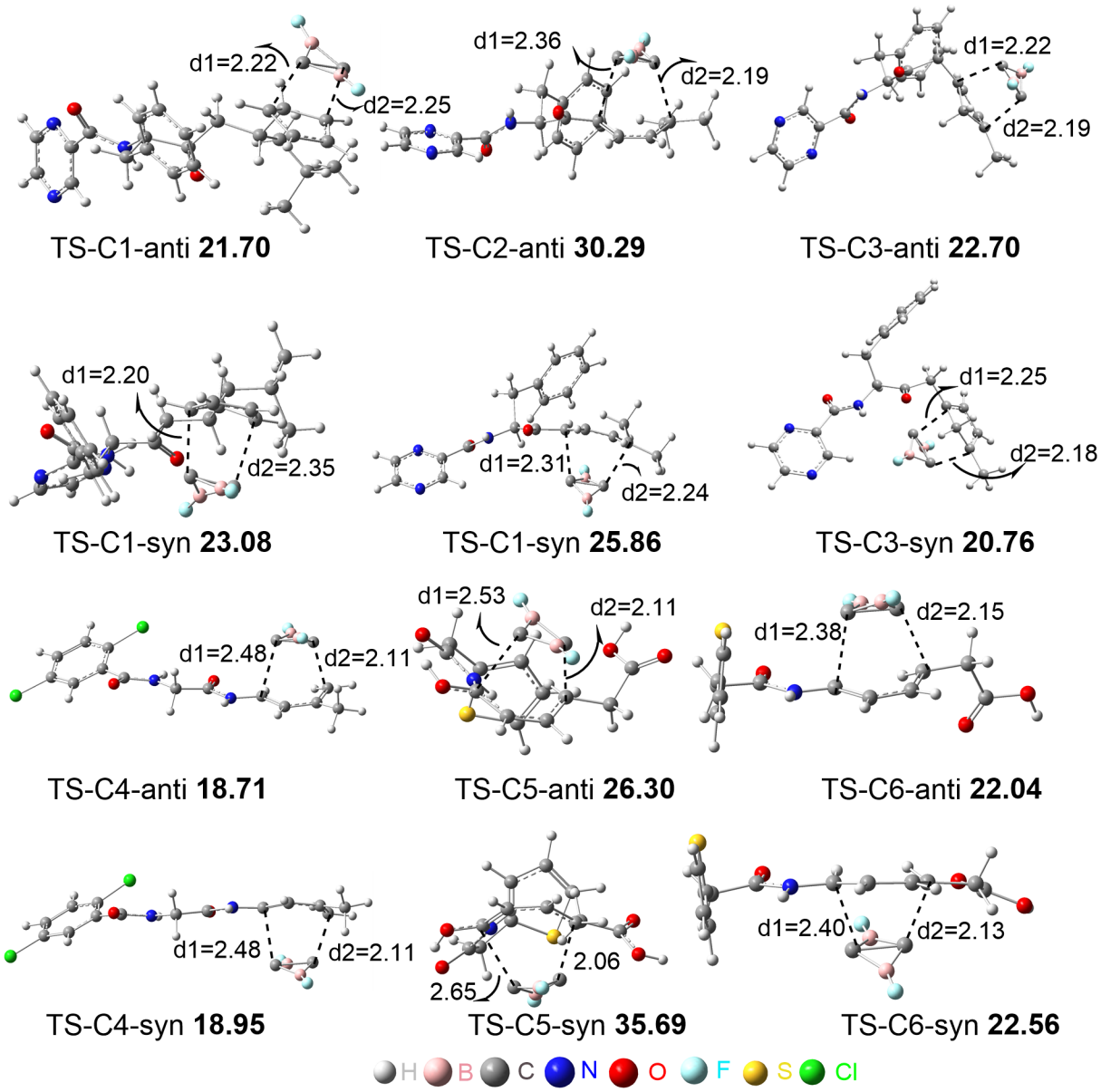

Fig S8. Bond lengths of transition states, energy barriers ΔG_{TS}, the energies and bond lengths are given in angstrom and kcal/mol, respectively.

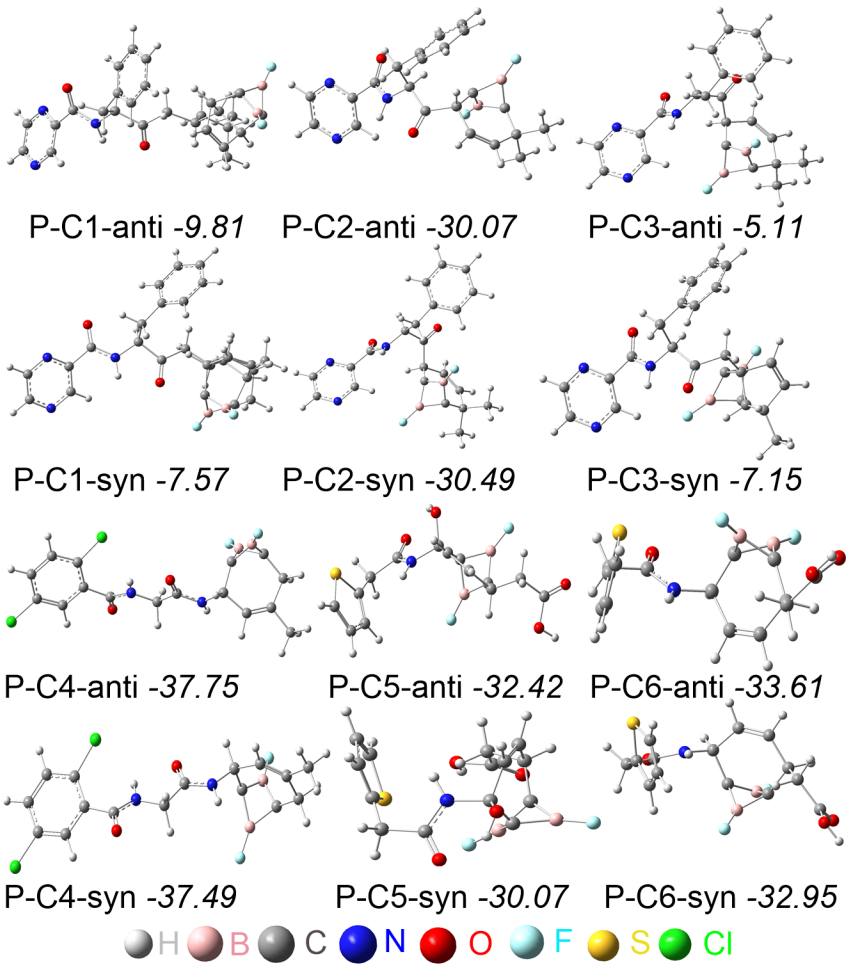

Fig S9 Optimized products and the reaction free energy ΔGre (in kcal/mol) of the Diels-Alder reactions of $C_2B_2F_2$ with **Ci** (i=1-6).

Table S1. Calculated bond energies of central C-C bonds (Eb, in kcal/mol), resonance energies (RE, in kcal/mol) and their relative values, as well as the weights of covalent (**1**) and two ionic (**2** and **3**) resonance structures of molecules **A1** ($C_2B_2H_2$) and **A8** ($C_2B_2F_2$)

Species	Eb	RE	RE%	1	2	3
A1	157.5	63.4	40	0.59	0.20	0.20
A8	155.0	66.3	43	0.58	0.21	0.21

Table S2. NICS(0) and NICS(1) values of **Ai** (i=1-14) calculated at M06-2X/6-311++G** level

Species	NICS(0)	NICS(1)	Species	NICS(0)	NICS(1)
A1	-14.10	-19.89	**A8**	-16.18	-17.91
A2	-15.21	-19.75	**A9**	-15.42	-18.25
A3	-12.81	-19.80	**A10**	-14.63	-18.03
A4	-23.90	-18.51	**A11**	-17.05	-18.54
A5	-16.92	-19.38	**A12**	-16.36	-19.62
A6	-19.34	-18.03	**A13**	-16.30	-19.66
A7	-20.30	-18.80	**A14**	-20.05	-18.20

Table S3. Bond length and Wiberg bond index of **P-Bi-anti** and **P-Bi-syn**.

Product	d(C1-C2)	WBI(C1-C2)	d(C1-C3)	WBI(C1-C3)
P-B1-anti	1.714	0.75	1.563	0.96
P-B1-syn	1.724	0.73	1.558	0.97
P-B2-anti	1.719	0.74	1.561	0.96
P-B2-syn	1.715	0.75	1.551	0.97
P-B3-anti	1.720	0.74	1.560	0.96
P-B3-syn	1.716	0.75	1.553	0.97
P-B4-anti	1.697	0.77	1.566	0.96
P-B4-syn	1.719	0.74	1.561	0.96
P-B5-anti	1.695	0.77	1.555	0.96
P-B5-syn	1.719	0.74	1.563	0.96
P-B6-anti	1.708	0.76	1.554	0.96
P-B6-syn	1.705	0.77	1.550	0.96
P-B7-anti	1.725	0.72	1.571	0.96
P-B7-syn	1.716	0.74	1.570	0.96
P-B8-anti	1.730	0.72	1.568	0.95
P-B8-syn	1.707	0.75	1.560	0.96
P-B9-anti	1.730	0.72	1.566	0.96
P-B9-syn	1.709	0.75	1.561	0.96
P-B10-anti	1.733	0.72	1.563	0.96
P-B10-syn	1.715	0.74	1.564	0.96