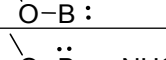
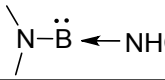
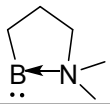
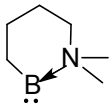
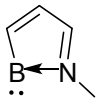
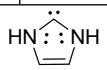
Electronic structure of mono(Lewis base)-stabilized borylenes

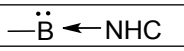
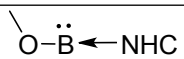
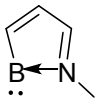
Table S1. Singlet-triplet gap by different model chemistries.

Short name	Molecular structure[1]	ΔE_{ST} [2]		
		B3LYP [3]	MP2[4]	CCSD(T)[5]
bh		110	97	127
bh-nhc		-34	-41	-35
bch3		158	156	167
bch3-nhc		-19	-23	-19
bnh2		191	179	198
bnh2-nhc		38	46	N/A
bph		129	225	157
bome		277	270	289
bome-nhc		5	7	13
bnme2		190	179	198
bnme2-nhc		48	57	N/A
r5nme2		64	51	64
r6nme2		40	31	N/A
r5nme		-22	N/A	-19
r6nme		53	107	72

Notes: 1. NHC = 

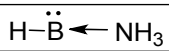
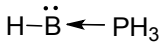
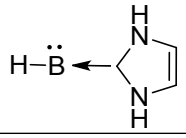
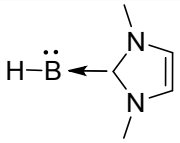
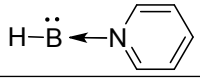
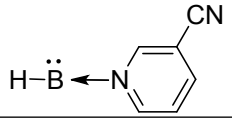
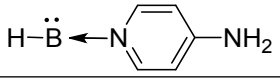
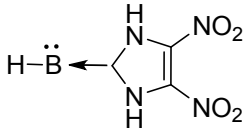
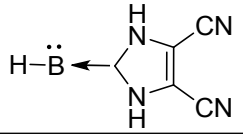
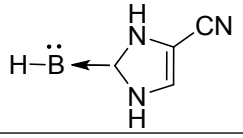
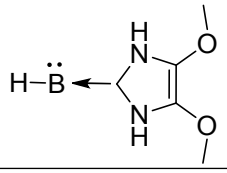
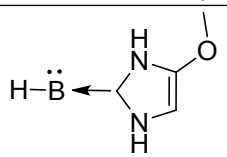
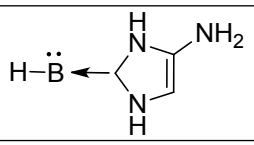
2. ΔE_{ST}(kJ/mol) = E_T - E_s. If $\Delta E_{ST} < 0$, triplet is more stable, and vice versa.
3. Structure optimized with (U)B3LYP/6-311+g(d, p), and energy is ZPE-corrected.
4. Structure optimized with (U)MP2/cc-pVTZ, and energy is ZPE-corrected.
5. (U)CCSD(T)/cc-pVTZ//(U)B3LYP/6-311+g(d, p).

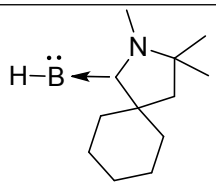
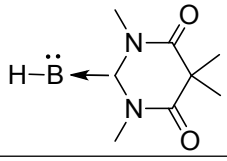
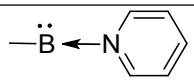
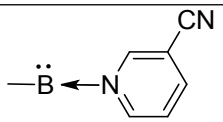
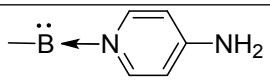
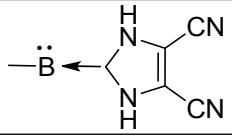
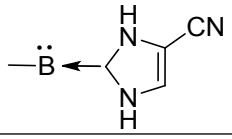
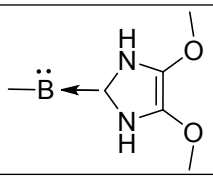
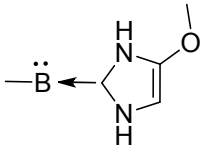
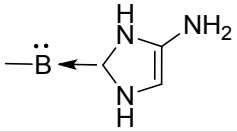
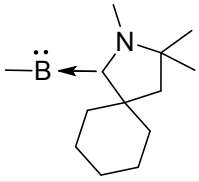
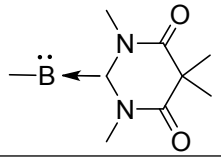
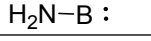
Table S2. T1 diagnostic calculations on selected borylenes.

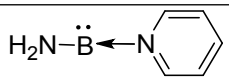
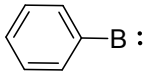
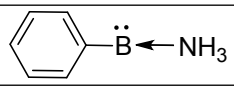
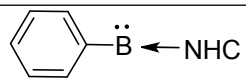
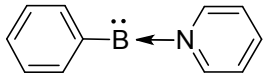
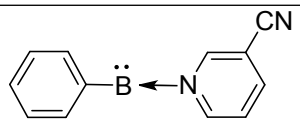
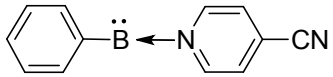
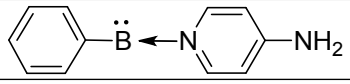
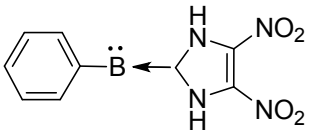
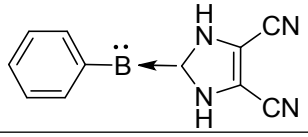
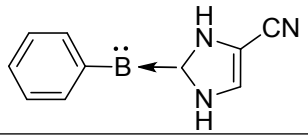
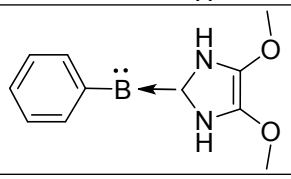
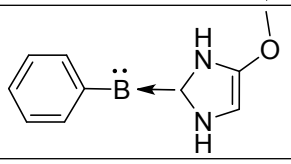
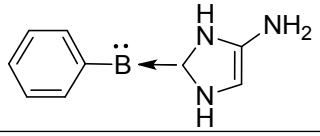
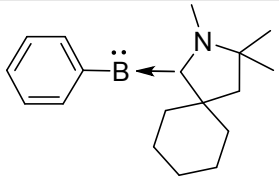
Short name	Molecular structure[1]	ΔE_{ST} [1]	
		T1 diagnostic	CCSD(T)[2]
bh		0.01719156	127
bh-nhc		0.01586108	-35
bch3-nhc		0.01521242	-19
bome-nhc		0.01582444	13
r5nme		0.02589239	-19

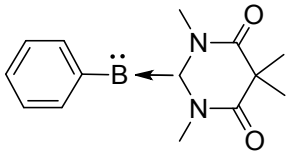
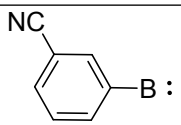
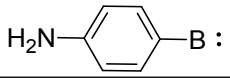
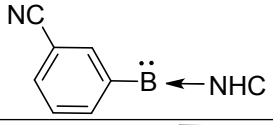
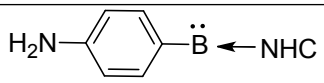
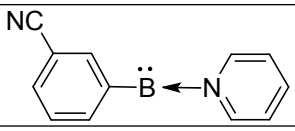
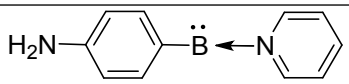
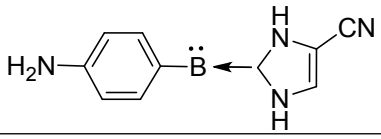
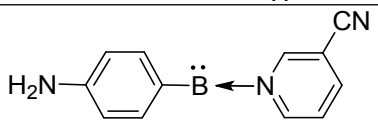
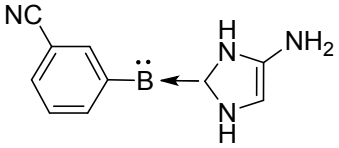
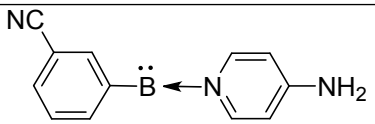
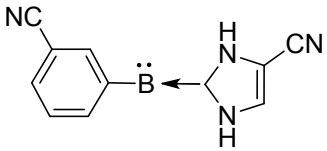
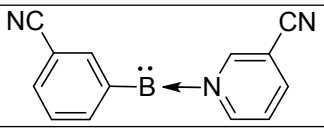
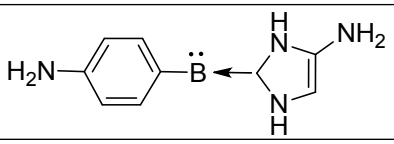
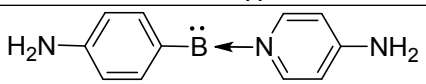
Notes: 1. ΔE_{ST}(kJ/mol) = E_T - E_s. If ΔE_{ST} < 0, triplet is more stable, and vice versa.
2. (U)CCSD(T)/cc-pVTZ//(U)B3LYP/6-311+g(d, p).
3. The empirical good T1 threshold is < 0.02. Reference: *Int. J. Quantum Chem., Quant. Chem. Symp.*, **S23** (1989) 199-207

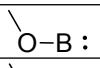
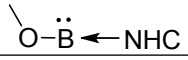
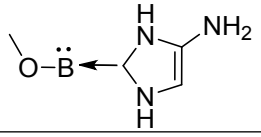
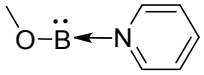
Table S3. Singlet-triplet gap of all studied borylenes by (U)B3LYP/6-311+g(d, p). The energy is ZPE-Corrected. $\Delta E_{ST} < 0$, triplet is more stable and is highlighted in red.

No.	Short name	Molecular structure[1]	ΔE_{ST} (B3LYP)
1	bh		110
2	bh-nh3		25
3	bh-ph3		-15
4	bh-nhc		-34
5	bh-nhc(Me)$_2$		-24
6	bh-py		-50
7	bh-pyCN		-52
8	bh-py(NH$_2$)		-49
9	bh-nhc(NO$_2$)$_2$		-257
10	bh-nhc(CN)$_2$		-19
11	bh-nhcCN		-27
12	bh-nhc(OMe)$_2$		-30
13	bh-nhcOMe		-33
14	bh-nhc(NH$_2$)		-34

15	bh-CAAC		64
16	bh-DAC		63
17	bch3		158
18	bch3-nh3		63
19	bch3-nhc		-19
20	bch3-py		-36
21	bch3-pyCN		-39
22	bch3-py(NH_2)		-38
23	bch3-nhc($CN)_2$		1
24	bch3-nhcCN		-10
25	bch3-nhc($OMe)_2$		2
26	bch3-nhcOMe		-11
27	bch3-nhc(NH_2)		-14
28	bch3-CAAC		89
28	bch3-DAC		87
30	bnh2		191

31	bnh2-nh3		137
32	bnh2-nhc		38
33	bnh2-py		0
34	bph		129
35	bph-nh3		20
36	bph-nhc		-24
37	bph-py		-34
38	bph-pyCN		-33
39	bph-pyCN4		-28
40	bph-py(NH_2)		-35
41	bph-nhc(NO_2)$_2$		-240
42	bph-nhc(CN)$_2$		2
43	bph-nhcCN		-10
44	bph-nhc(OMe)$_2$		-10
45	bph-nhcOMe		-20
46	bph-nhc(NH_2)		-27
47	bph-CAAC		64

48	bph-DAC		81
49	bphCN		120
50	bph(NH_2)		142
51	bphCN-nhc		-29
52	bph(NH_2)-nhc		-10
53	bphCN-py		-38
54	bph(NH_2)-py		-22
55	bph(NH_2)-nhcCN		7
56	bph(NH_2)-pyCN		-20
57	bphCN-nhc(NH_2)		-29
58	bphCN-py(NH_2)		-34
59	bphCN-nhcCN		-20
60	bphCN-pyCN		-37
61	bph(NH_2)-nhc(NH_2)		-12
62	bph(NH_2)-py(NH_2)		-28

63	bome		277
64	bome-nhc		5
65	bome-nhc(NH_2)		4
66	bome-py		-16
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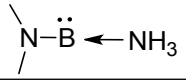
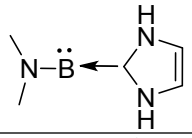
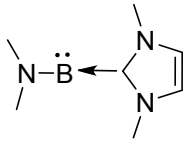
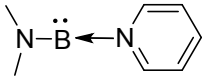
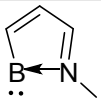
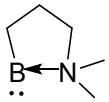
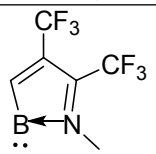
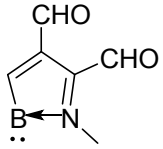
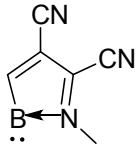
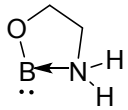
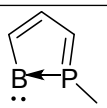
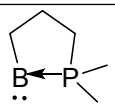
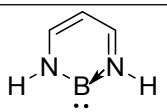
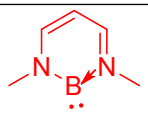
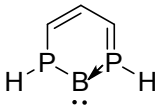
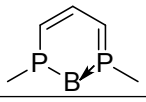
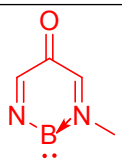
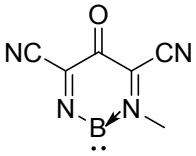
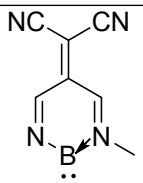
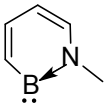
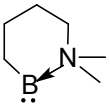
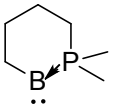
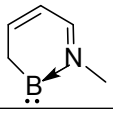
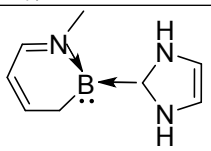
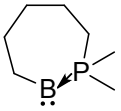
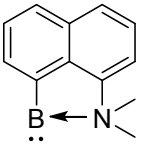
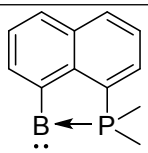
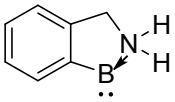
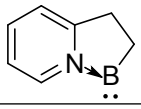
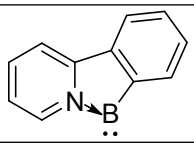
68	bnme2-nh3		130
69	bnme2-nhc		48
70	bnme2-nhc($Me)_2$		72
71	bnme2-py		16
72	r5nme		-22
73	r5nme2		64
74	r5nme(cf3)2		-6
75	r5nme(cho)2		14
76	r5nme(cn)2		-9
77	r5on		191
78	r5pme		48
79	r5pme2		-11

80	r6		-24
81	r6me2		-8
82	r6p		1
83	r6pme2		23
84	r6o		-15
85	r6ocn		15
86	r6cn2		-35
87	r6nme		53
88	r6nme2		40
89	r6pme2s		-34
90	r6nmeh2		-34
91	r6nmeh2-nhc		19
92	r7pme2s		-14
93	2rn		-1

94	2rp		-37
95	2rphn		28
96	2rpy		-43
97	2rpyph		-60

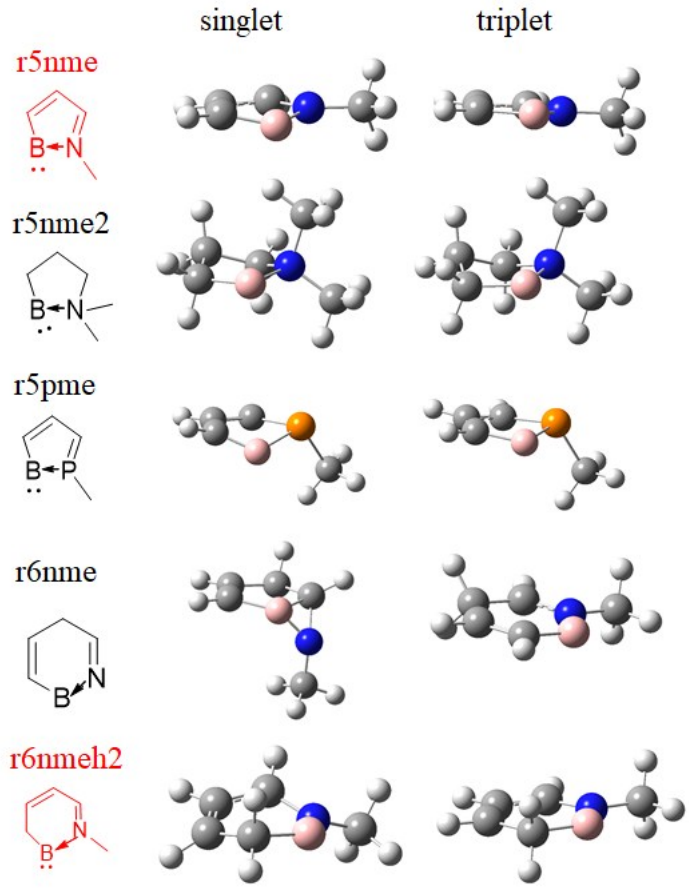


Figure S1. Geometry of selected cyclic borylenes. Red colored structures have triplet ground state.

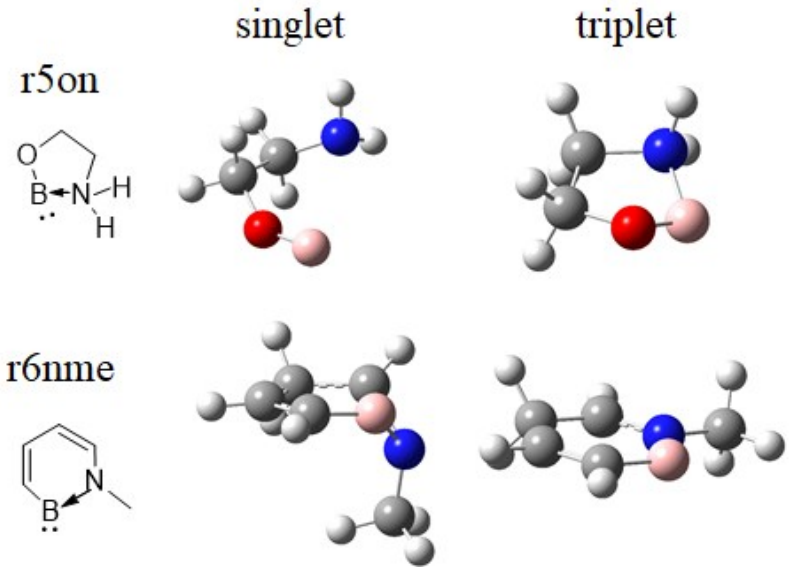


Figure S2. Geometry of most distorted cyclic borylenes.

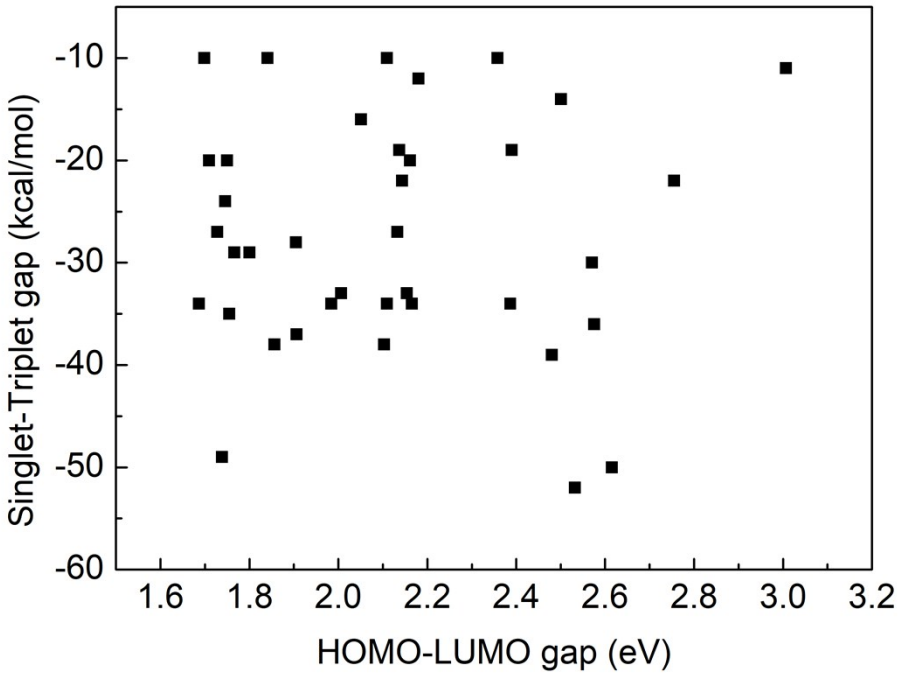


Figure S3. HOMO-LUMO gap versus singlet-triplet gap of borylenes with the triplet states as the ground states.

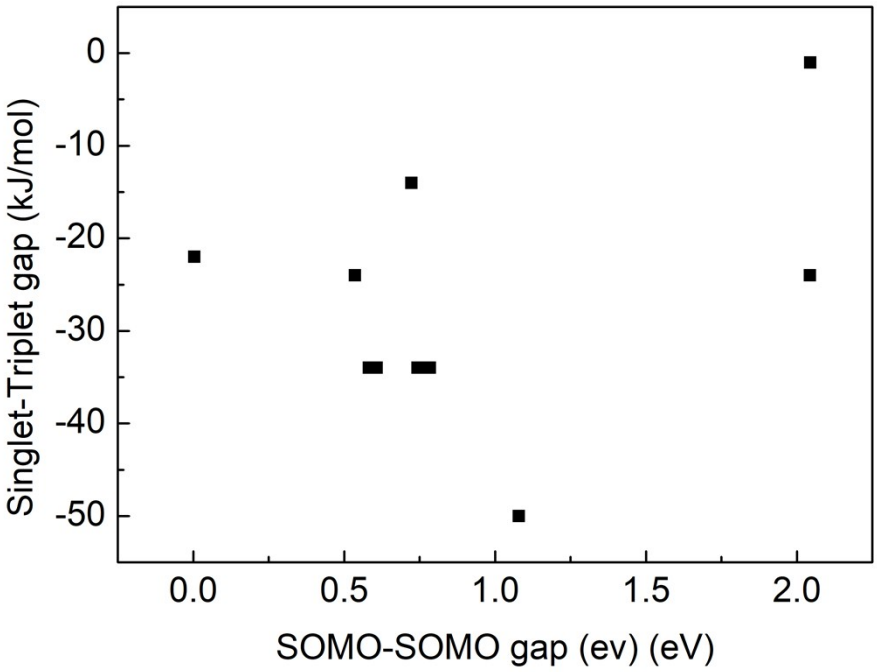


Figure S4. SOMO-SOMO gap versus singlet-triplet gap of borylenes with the triplet states as the ground states.

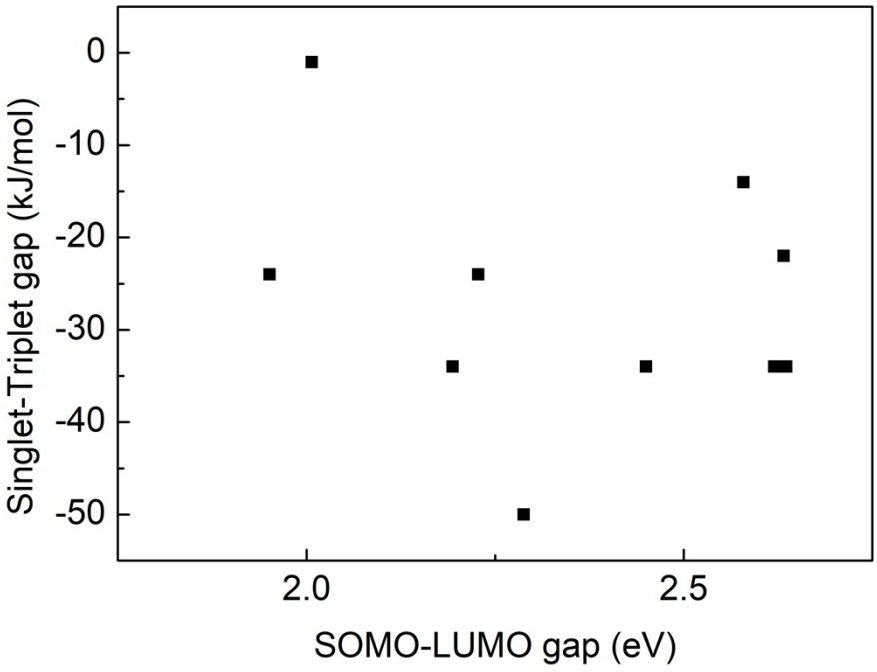


Figure S5. SOMO-LUMO gap versus singlet-triplet gap of borylenes with the triplet states as the ground states.