Supporting Information for:
"Oxygen Insertion into Boroles as a Route to 1,2-Oxaborines"

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EXPERIMENTAL SECTION

General Considerations. All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glove box. Solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents and stored over molecular sieves. N-methylmorpholine N-oxide was purchased from Sigma-Aldrich Chemicals and used as received. Boroles **8** and **8Ph** were prepared via the literature procedures.[1] Dry oxygen gas was purchased from Airgas and used as received. $CDCl_3$ for NMR spectroscopy was purchased from Cambridge Isotope Laboratories and dried by stirring for 3 days over CaH_2, distilled, and stored over 4 Å molecular sieves. Multinuclear NMR spectra were recorded on Bruker 400 or 600 MHz spectrometers. FT-IR spectra were recorded on a Bruker Alpha ATR FT-IR spectrometer on solid samples. High Resolution mass spectra (HRMS) were obtained at the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using +ESI. Elemental analyses (C and H) were performed by Atlantic Microlab, Inc. (Norcross, GA). Melting points were measured with a Thomas Hoover Uni-melt capilliary melting point apparatus and are uncorrected. UV-vis spectra were recorded using a Thermo Scientific Evolution 201 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Horiba Jobin-Yvon Fluoromax 4 spectrofluorometer, with excitation at the absorbance λ_{max}. Solutions were prepared in an Ar filled glovebox and measured in screw capped quartz cuvettes for both UV-vis and fluorescence. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K_α radiation (λ = 0.71073 Å). Crystals were selected under paratone oil, mounted on micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL and figures were produced using OLEX2.[2,3]

Reaction of **8** with O_2: A $CDCl_3$ solution of **8** was prepared in a quartz NMR tube equipped with a septum. Oxygen gas was bubbled directly into the solution via a long needle and using a 22 gauge needle attached to a bubbler to prevent back-flow. An immediate color change from blue to orange occurred.^{1}H and ^{11}B{^{1}H} NMR spectra were acquired revealing a complex mixture.

General synthesis of **9** and **9Ph** (Quantities and characterization details follow): At room temperature, a dichloromethane solution of N-methylmorpholine N-oxide was added dropwise to a dichloromethane solution of borole. The solution color changed from dark blue to yellow within 1 min. The solution was allowed to stir for 1 h, and the solvent removed *in vacuo*. The residue was recrystallized by vapor diffusion of *n*-pentane into chloroform giving **9** and **9Ph** as off-white crystalline material.

Quantities and characterization details for **9**: N-methylmorpholine N-oxide (78.0 mg, 0.664 mmol) in 1 mL dichloromethane; **8** (295.0 mg, 0.664 mmol) in 1 mL dichloromethane; Yield: 204.0 mg, 66%; m.p 159-160˚C. Crystals for an X-ray diffraction study were grown by vapor diffusion of a *n*-pentane into chloroform solution. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 6.0 Hz, 2H), 7.42 (dd, *J* = 9.6, 6.0 Hz, 2H), 7.34 (t, *J* = 6.0 Hz, 1H), 7.26-7.21 (m, 5H), 7.14-7.06 (m, 3H), 7.04-7.01 (m, 3H), 6.99-6.97 (m, 2H), 6.94-6.89 (m, 5H), 6.74 (dd, *J* = 12.0, 6.0 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 158.97, 153.82, 142.31, 139.40, 139.04, 138.06, 136.83, 136.67, 135.14, 132.04, 130.08, 130.00, 129.95, 129.71, 128.36, 127.85, 127.81, 127.68, 127.58, 126.90, 126.47, 125.96, 125.46, 123.87; ^{11}B{^{1}H} NMR (193 MHz, $CDCl_3$): δ 38.4 (br); FT-IR (cm^{-1}(ranked intensity)): 1586(15), 1561(7), 1487(10), 1459(14), 1438(3), 1345(9), 1291(5), 1072(13), 1025(6), 754(2), 720(11), 692(1), 636(4), 587(8), 544(12); High-resolution mass spectrometry (HRMS) electrospray ionization (ESI): calcd. for $C_{34}H_{25}BO$ $[M+Na]^+$: 483.1897; found 483.1885; Elemental Analysis: calculated for $C_{34}H_{25}BO$: C, 88.70; H, 5.47. Found: C, 88.20; H, 5.57; UV-Vis (CH_2Cl_2) λ_{max} (333 nm): ε = 12,000 $Lmol^{-1}$ cm^{-1}; (305 nm): ε = 7500 $Lmol^{-1}$ cm^{-1}; (282 nm): ε = 5600 $Lmol^{-1}$ cm^{-1}; Fluorescence (CH_2Cl_2) λ_{em} 388 nm; Stokes shift (CH_2Cl_2) 55 nm (4,300 cm^{-1}).

Quantities and characterization details for **9Ph**: N-methylmorpholine N-oxide (26.0 mg, 0.225 mmol) in 1 mL dichloromethane; **8Ph** (117.0 mg, 0.225 mmol; 1 mL) in 1 mL dichloromethane; Yield: 68.0 mg, 56%; m.p 191-192˚C**.** Crystals of X for an X-ray diffraction study were grown by vapor diffusion of *n*-pentane into chloroform solution. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 6.0 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 2H), 7.48 (d, *J* = 12.0 Hz, 2H), 7.43-7.40 (m, 4H), 7.33 (t, *J* = 12.0 Hz, 1H), 7.24-7.22 (m, 3H), 7.14-7.12 (m, 2H), 7.09-7.07 (m, 1H), 7.03-7.00 (m, 5H), 6.94-6.89 (m, 5H), 6.75 (m, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 158.97, 153.90, 142.44, 142.35, 141.20, 139.39, 139.17, 138.06, 136.70, 135.66, 132.05, 130.09, 129.96, 129.73, 128.83, 128.39, 127.87, 127.82, 127.75, 127.48, 127.25, 126.91, 126.48, 126.28, 125.98, 125.52, 123.91; $^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$): δ 38.8 (br); FT-IR (cm^{-1}(ranked intensity)): 1584(9), 1486(12), 1497(15), 1439(5), 1297(3), 1070(11), 1026(14), 836(4), 752(2), 712(7), 692(1), 639(10), 589(8), 554(13), 532(6); High-resolution mass spectrometry (HRMS) electrospray ionization (ESI): calcd. for $C_{40}H_{29}BO$ $[M+Na]^+$: 559.2211; found 559.2196; Elemental Analysis: calculated for $C_{40}H_{29}BO$: C, 89.55; H, 5.45. Found: C, 88.52; H, 5.48; UV-Vis (CH_2Cl_2) λ_{max} (333 nm): ε = 11,000 $Lmol^{-1}$ cm^{-1}; (295 nm): ε = 17,000 $Lmol^{-1}$ cm^{-1}; Fluorescence (CH_2Cl_2) λ_{em} 387 nm; Stokes shift (CH_2Cl_2) 54 nm (4,200 cm^{-1}).

Figure S-1: Crude ^{1}H NMR spectrum of the reaction of **8** with O_2.

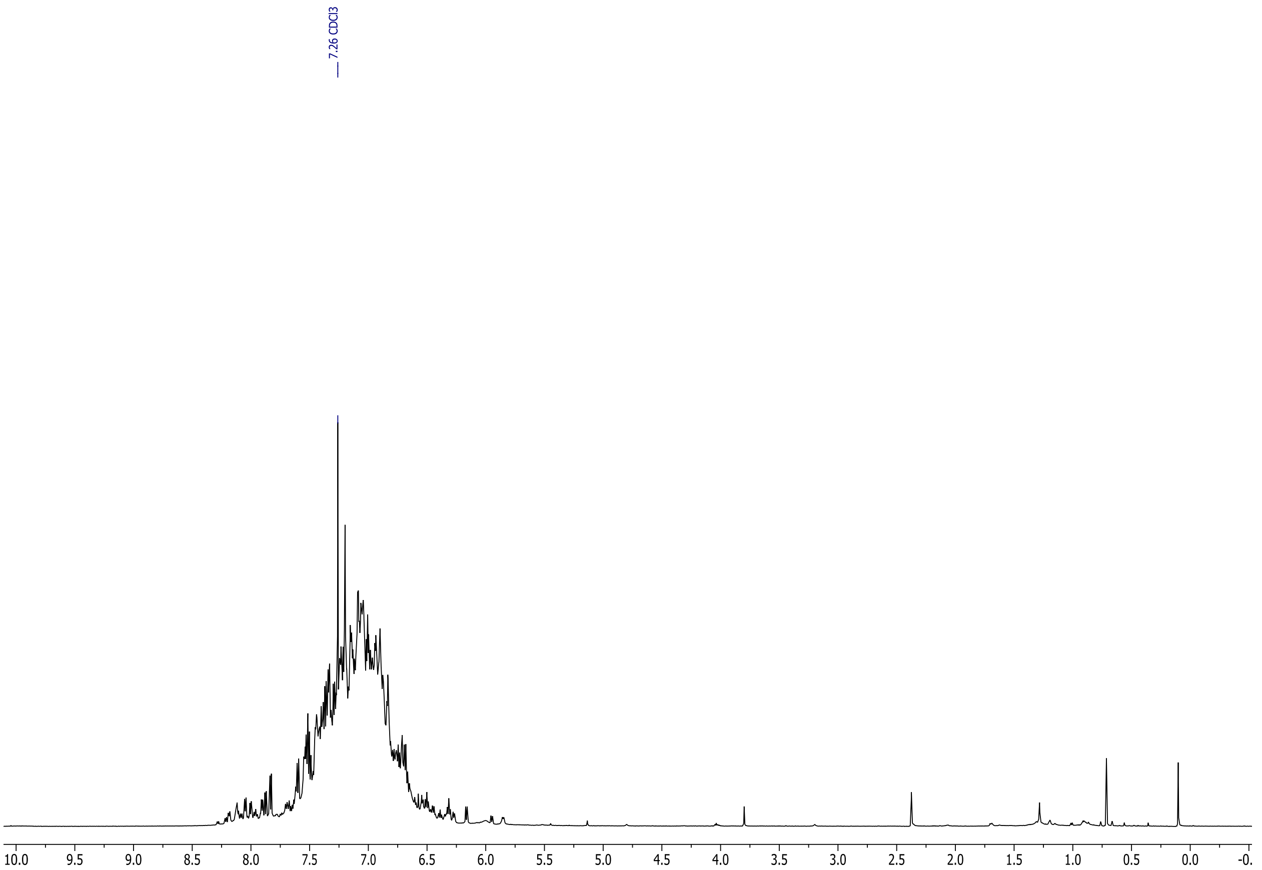


Figure S-2: Crude $^{11}B\{^{1}H\}$ NMR spectrum of the reaction of **8** with O_2.

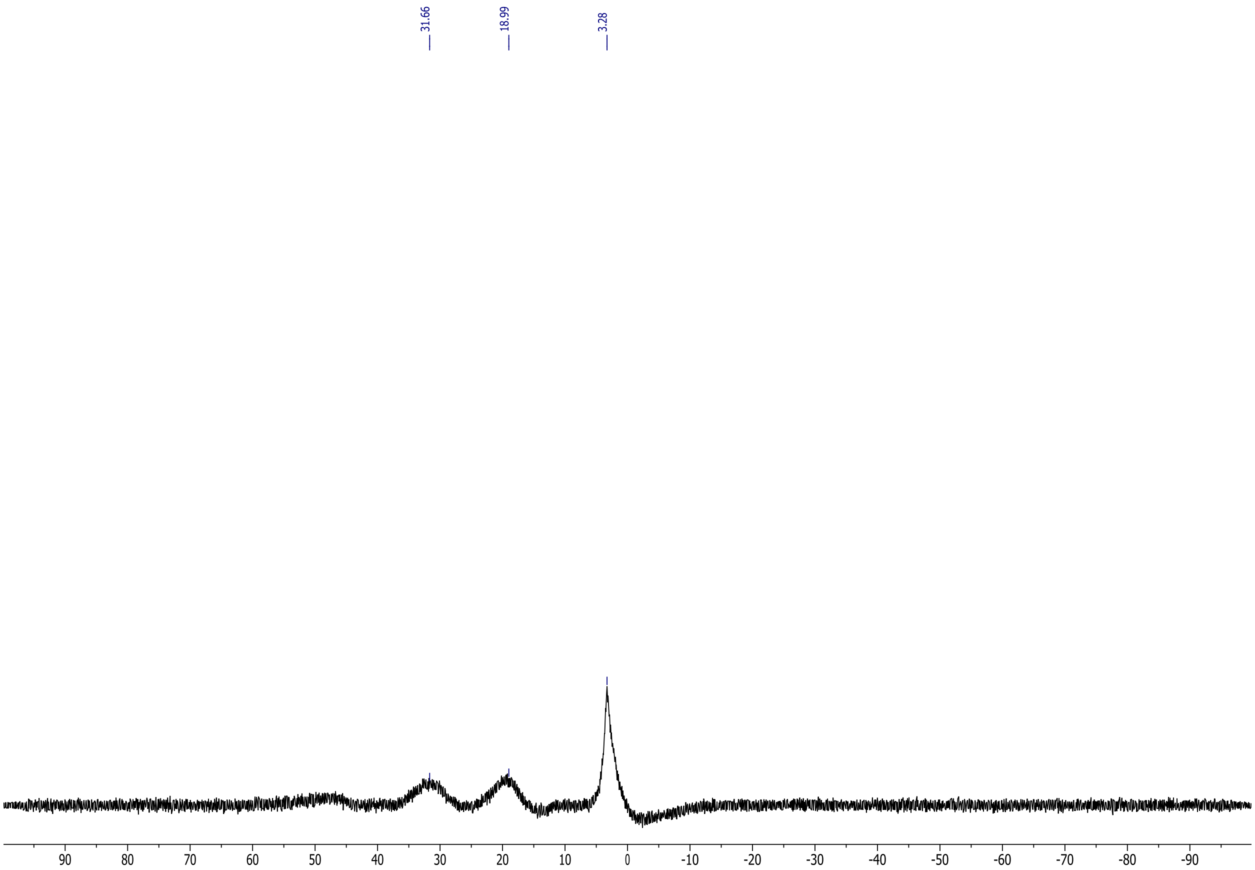


Figure S-3: Crude ^{1}H NMR spectrum of the reaction of **8** with N-methylmorpholine-N-oxide after 30 min (• grease).

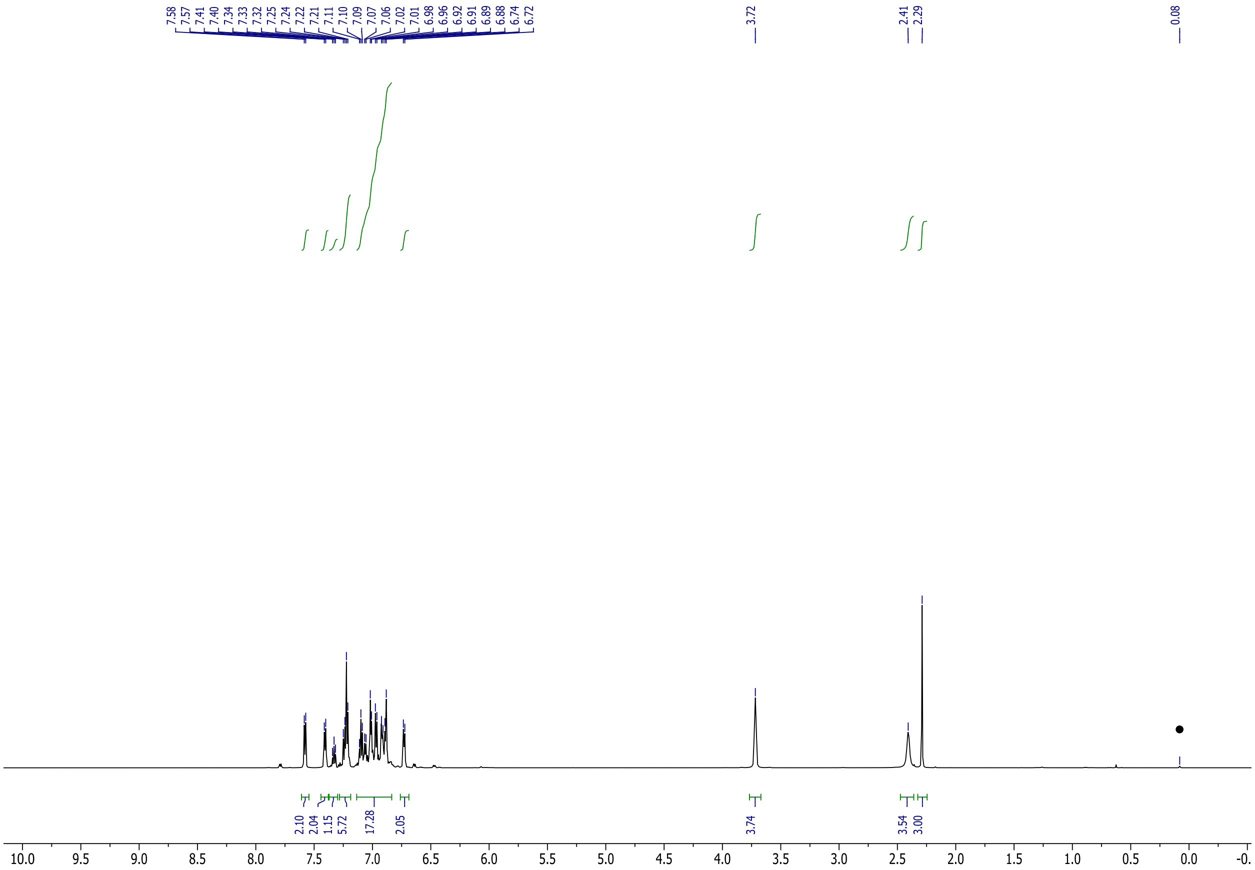


Figure S-4: Expansion of the crude ^{1}H NMR spectrum of the reaction of **8** with N-methylmorpholine-N-oxide after 30 min.

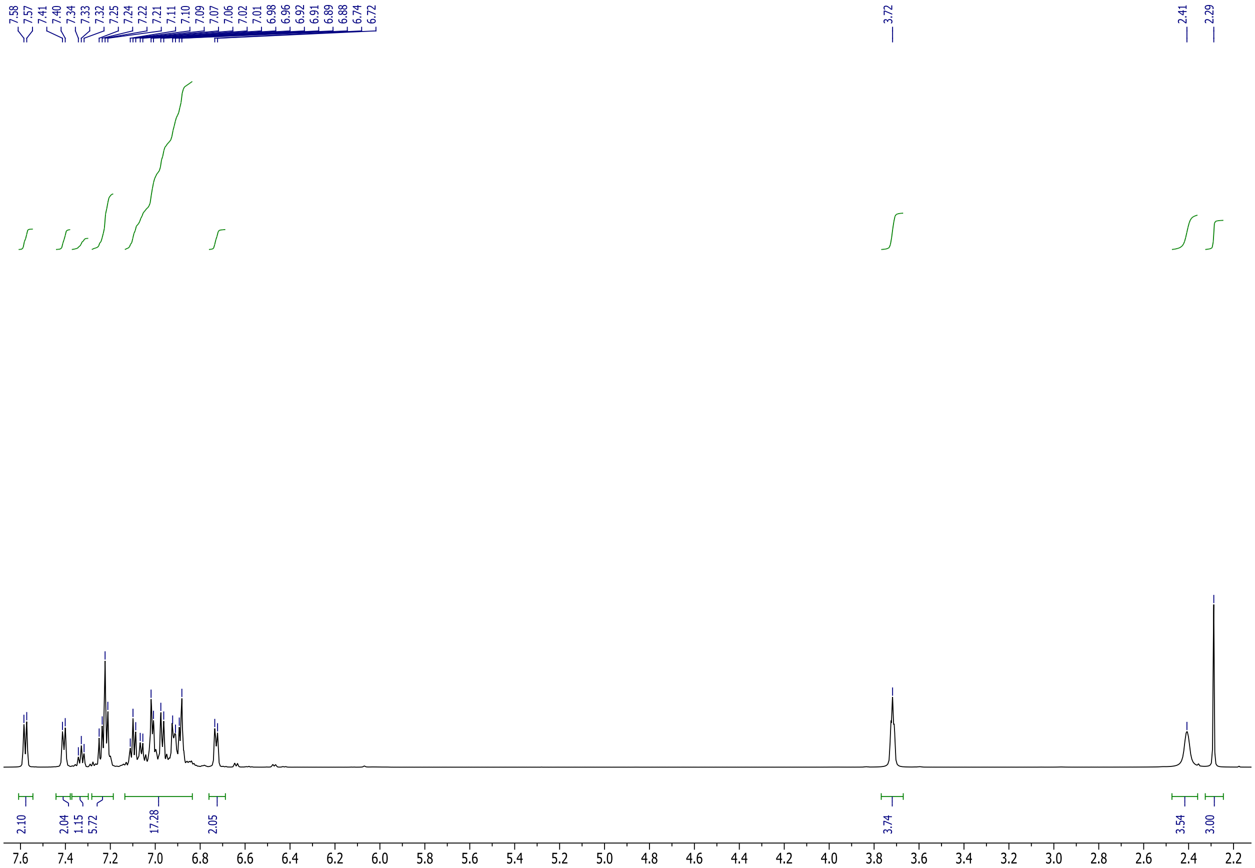


Figure S-5: ^{1}H NMR spectrum of **9** in $CDCl_3$ (* *n*-pentane).

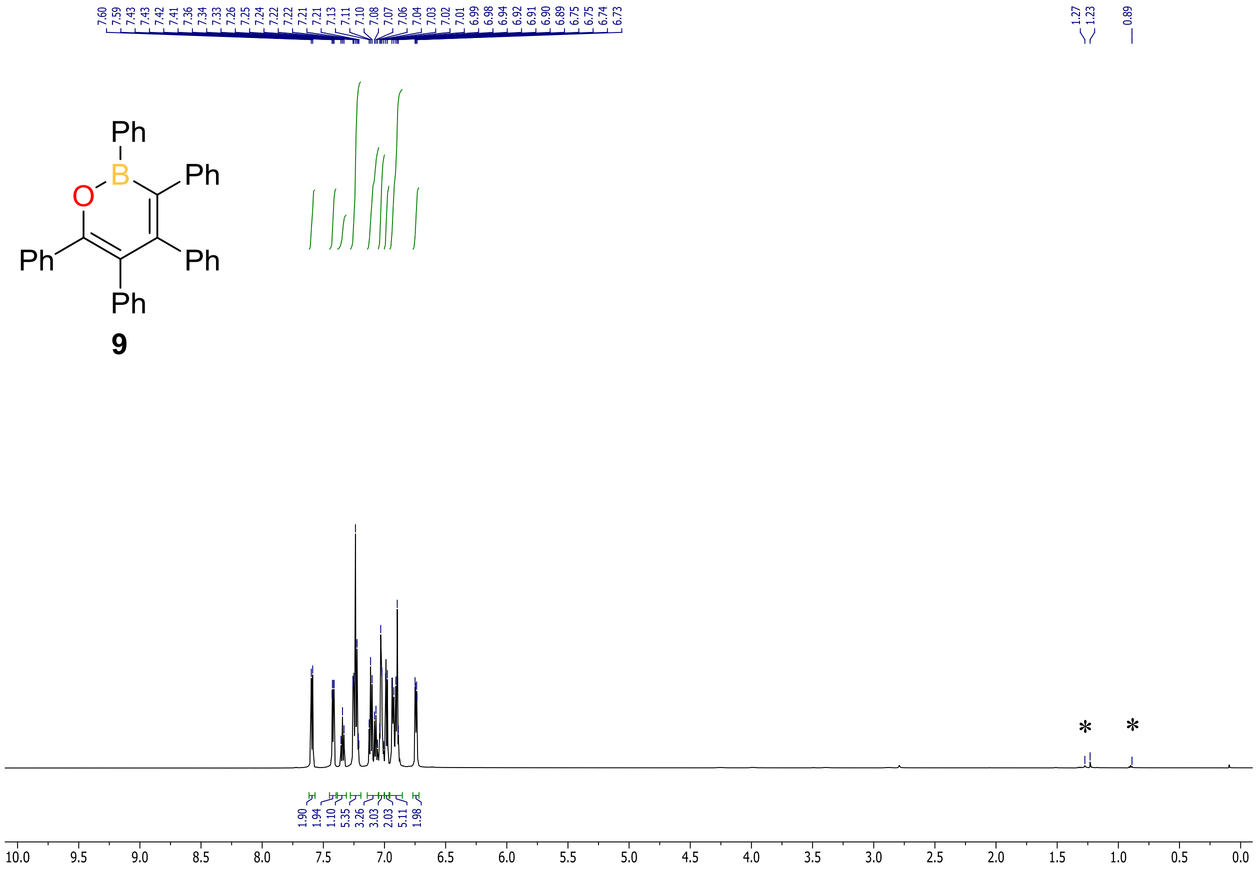
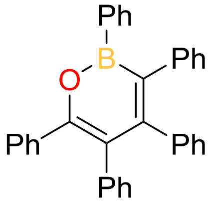


Figure S-6: Expansion of ^{1}H NMR spectrum of **9** in $CDCl_3$.



9

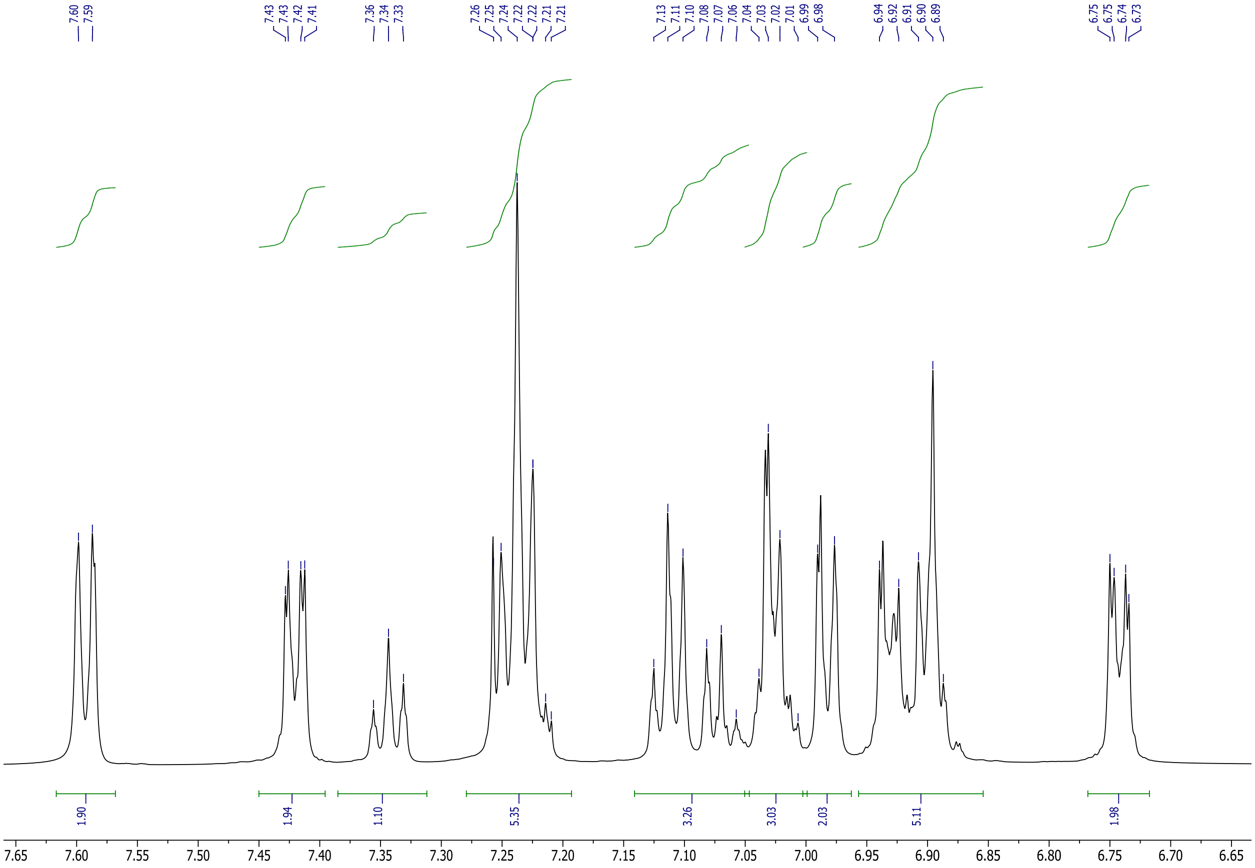


Figure S-7: $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$.

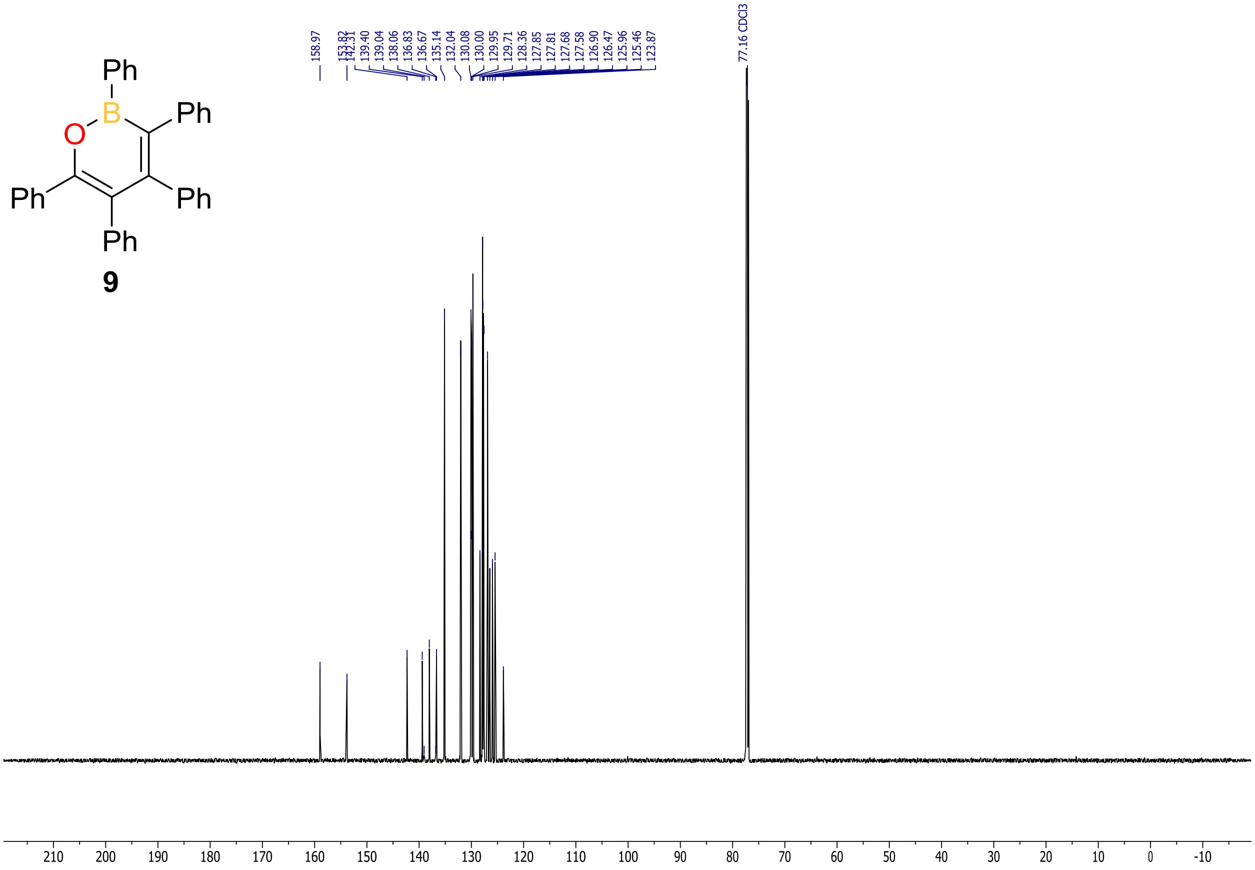

9

Figure S-8: Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$.

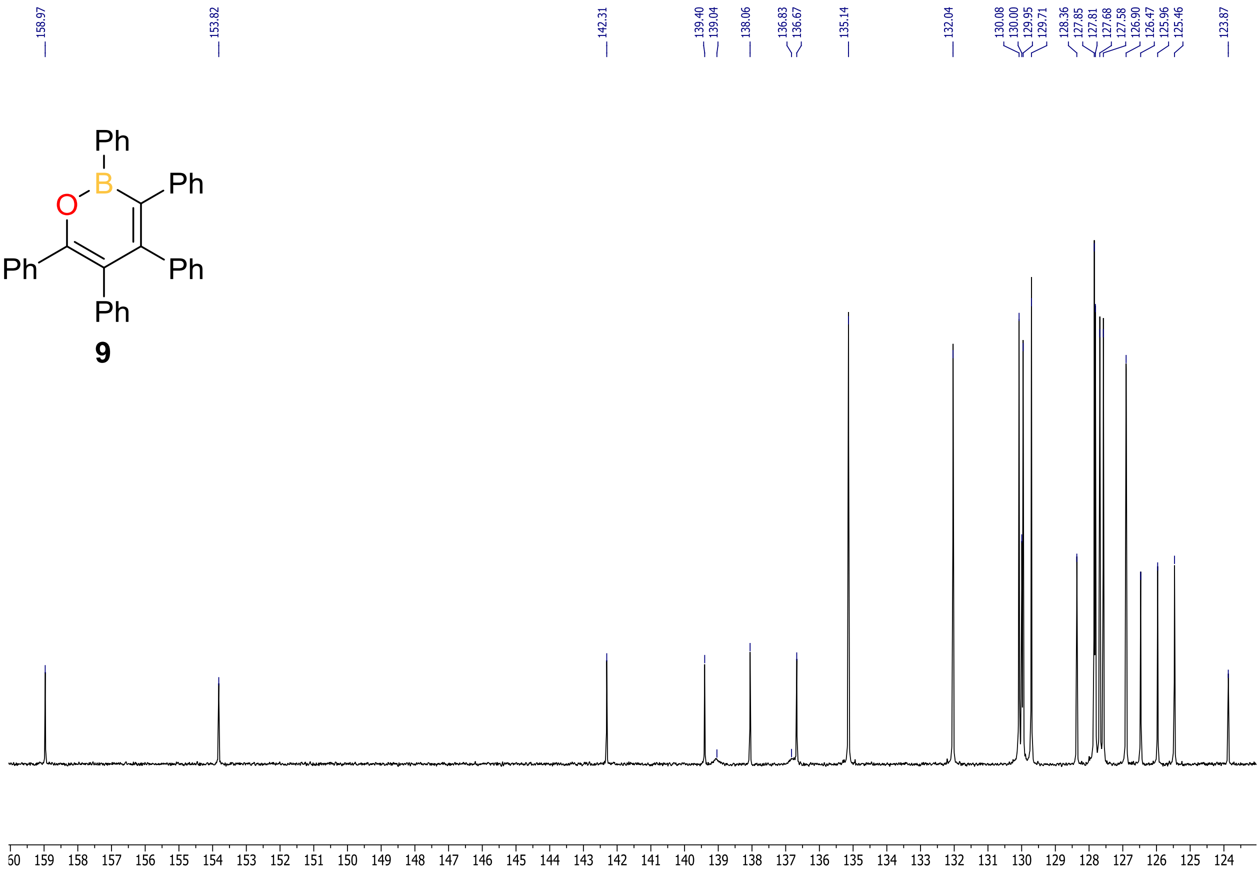


Figure S-9: $^{11}B\{^{1}H\}$ NMR spectrum of **9** in $CDCl_3$.

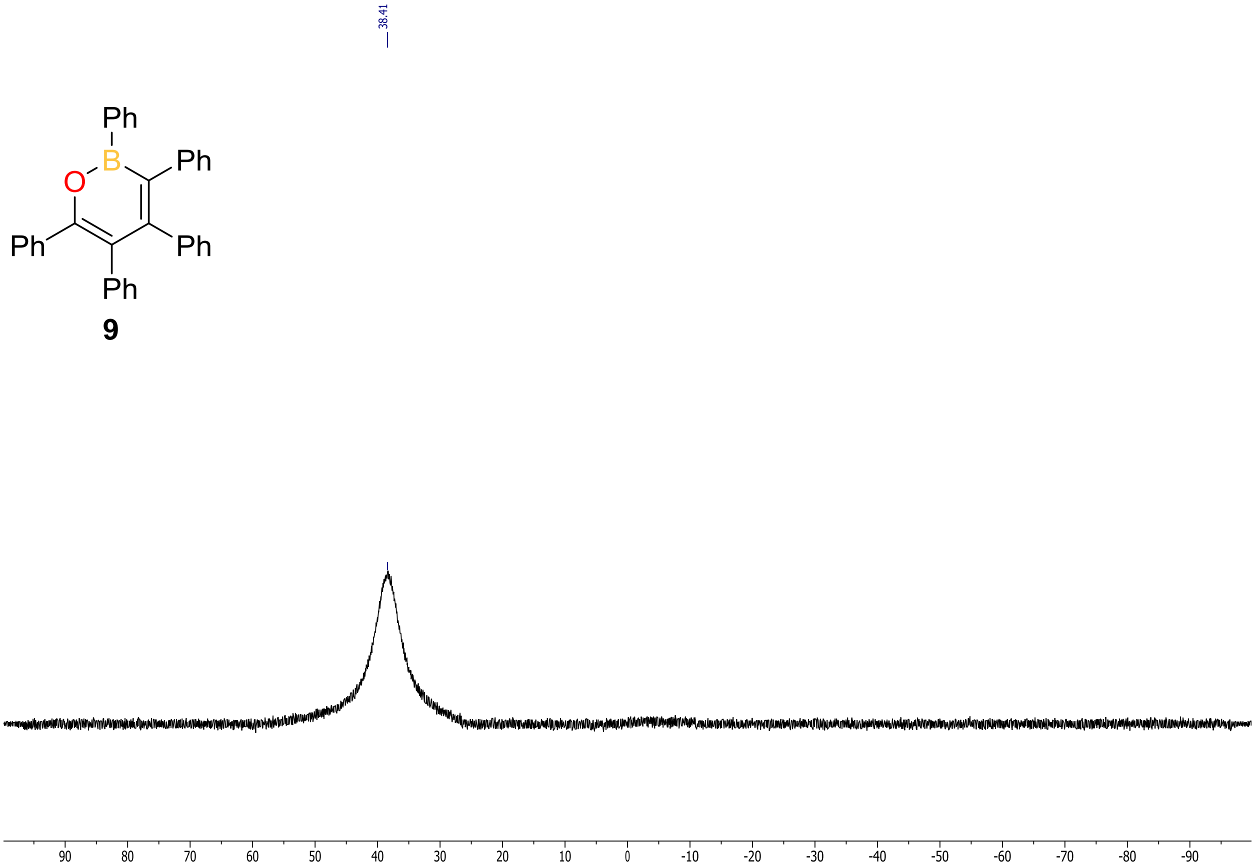


Figure S-10: FT-IR spectrum of **9**.

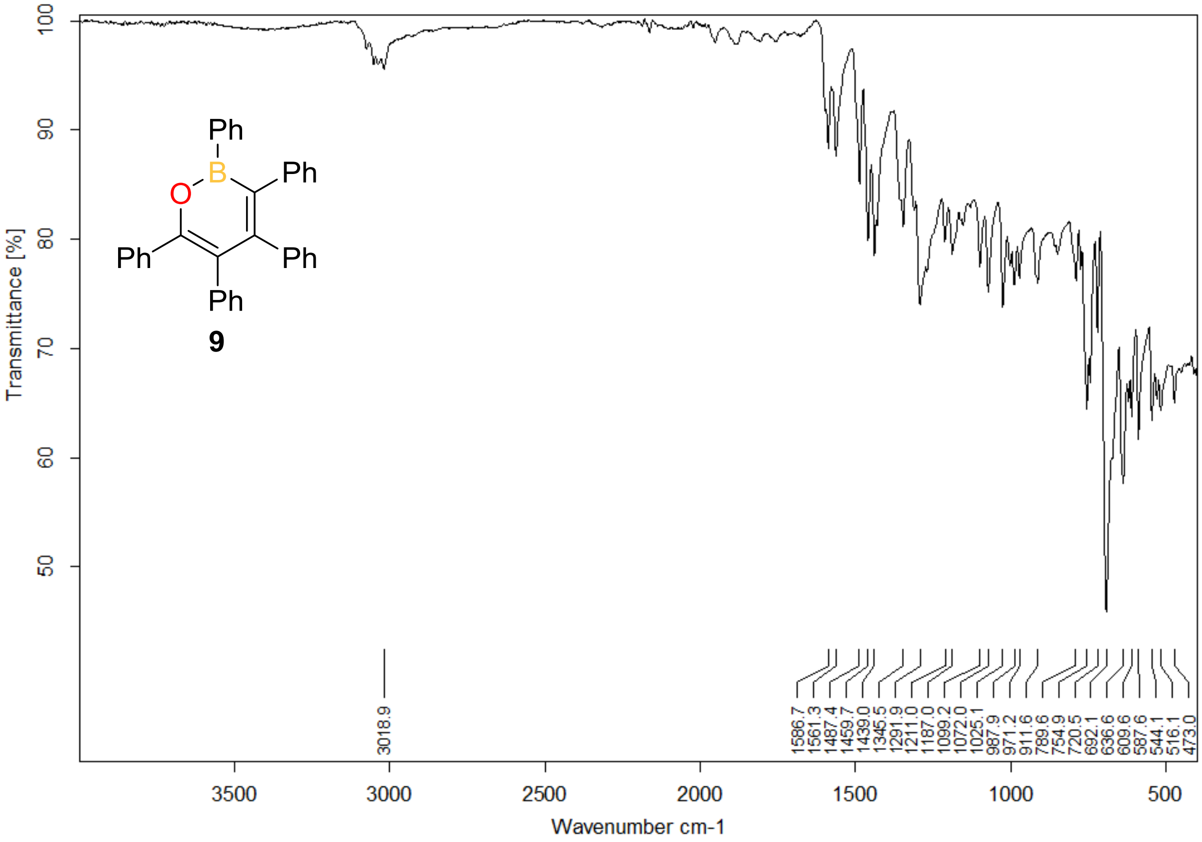


Figure S-11: ^{1}H NMR spectrum of **9Ph** in CDCl$_3$ (* *n*-pentane, • grease).

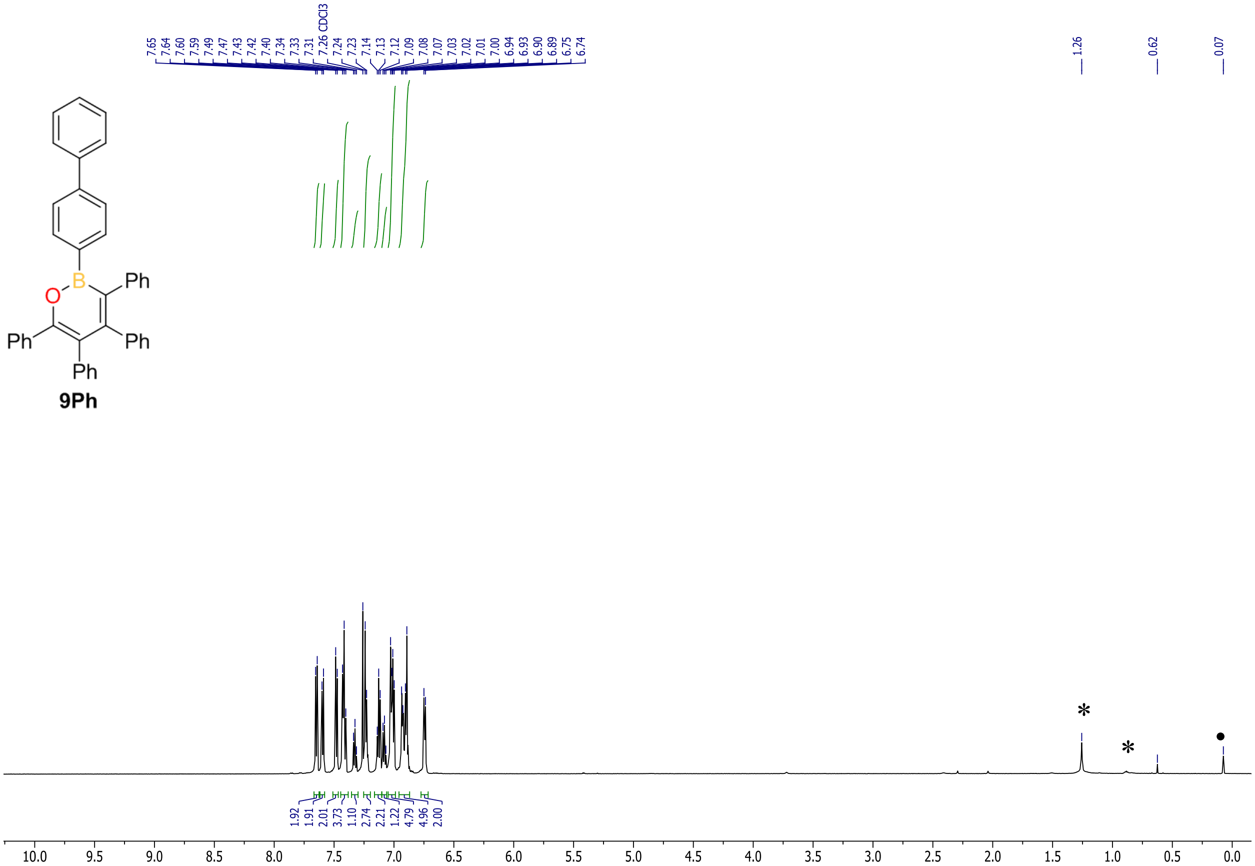


Figure S-12: Expansion of ^{1}H NMR spectrum of **9Ph** in CDCl$_3$.

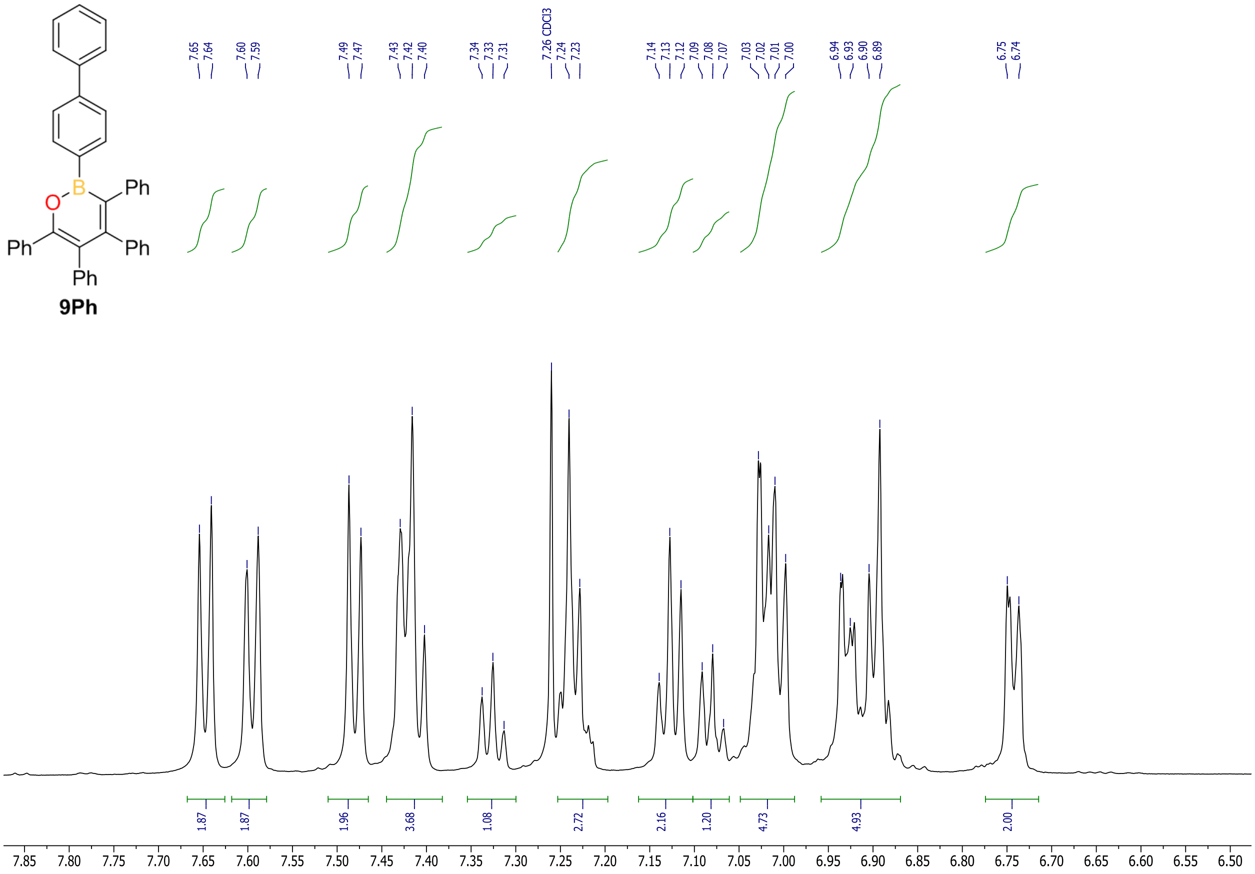


Figure S-13: $^{13}C\{^1H\}$ NMR spectrum of **9Ph** in $CDCl_3$ (**n*-pentane).

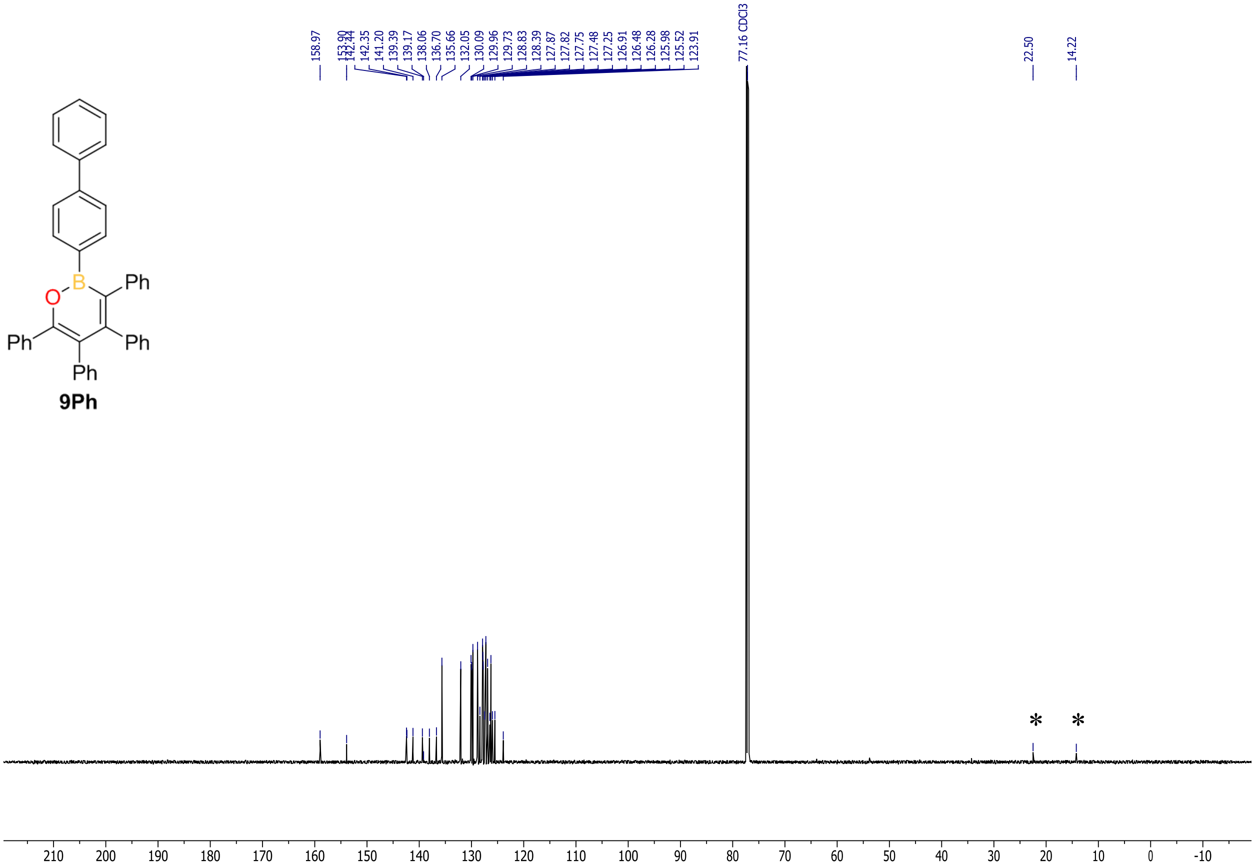


Figure S-14: Expansion of $^{13}C\{^{1}H\}$ NMR spectrum of **9Ph** in $CDCl_3$.

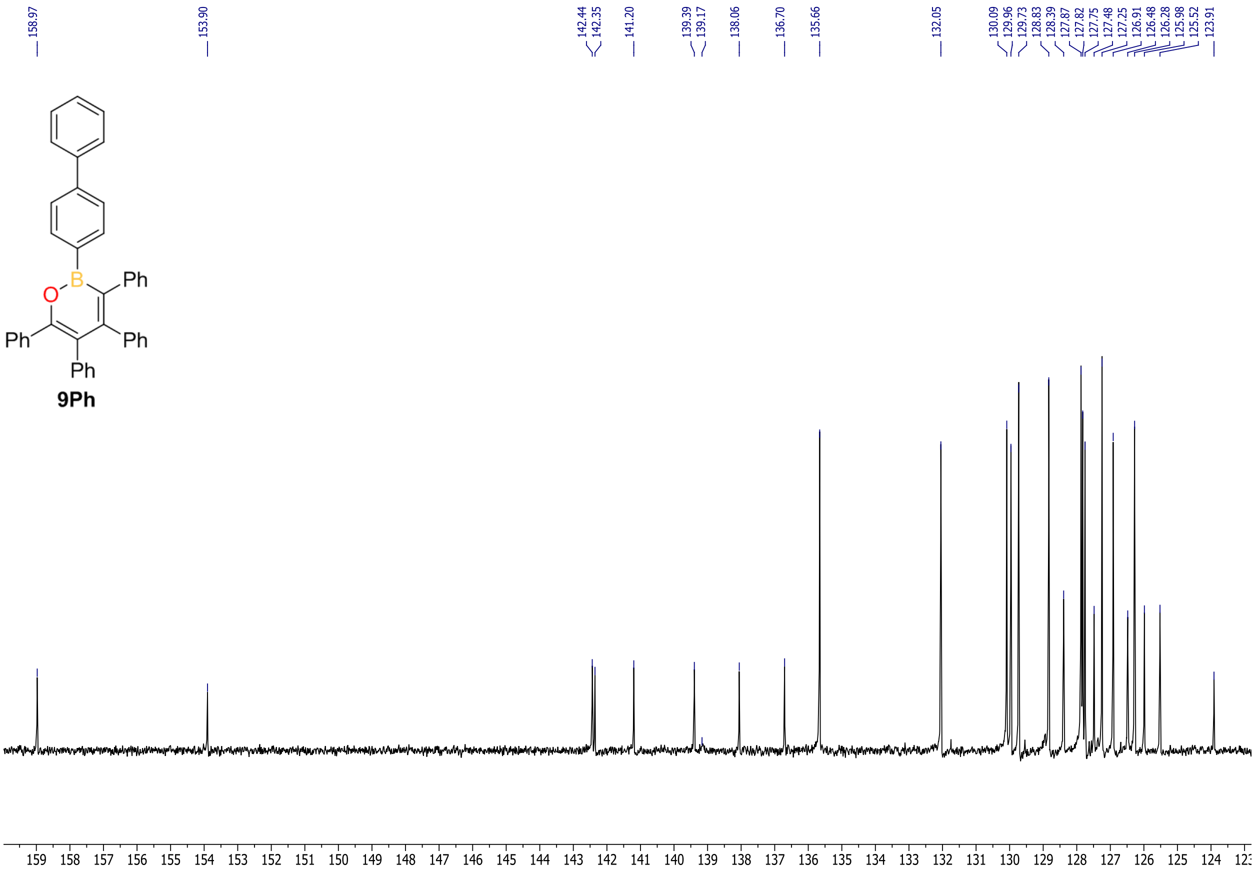


Figure S-15: ^{11}B{^{1}H} NMR spectrum of **9Ph** in $CDCl_3$.

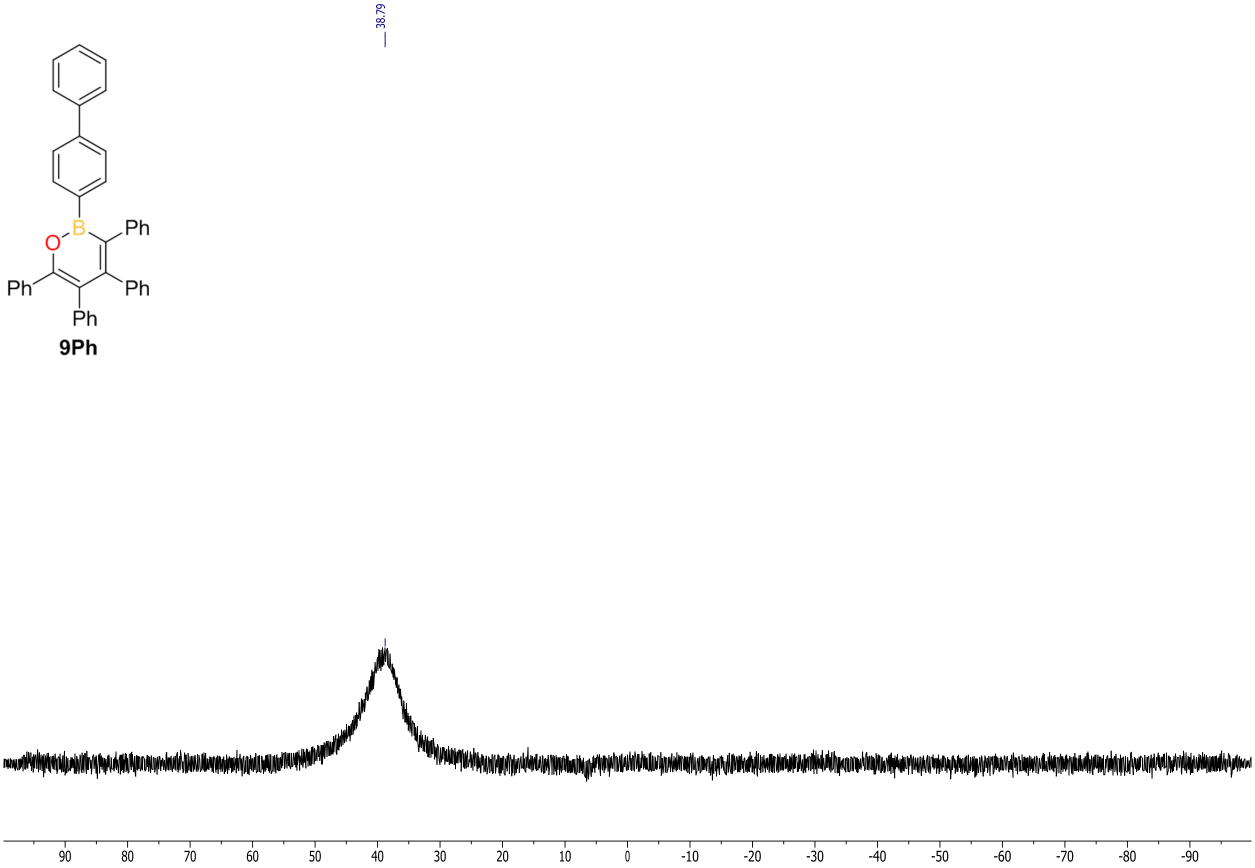
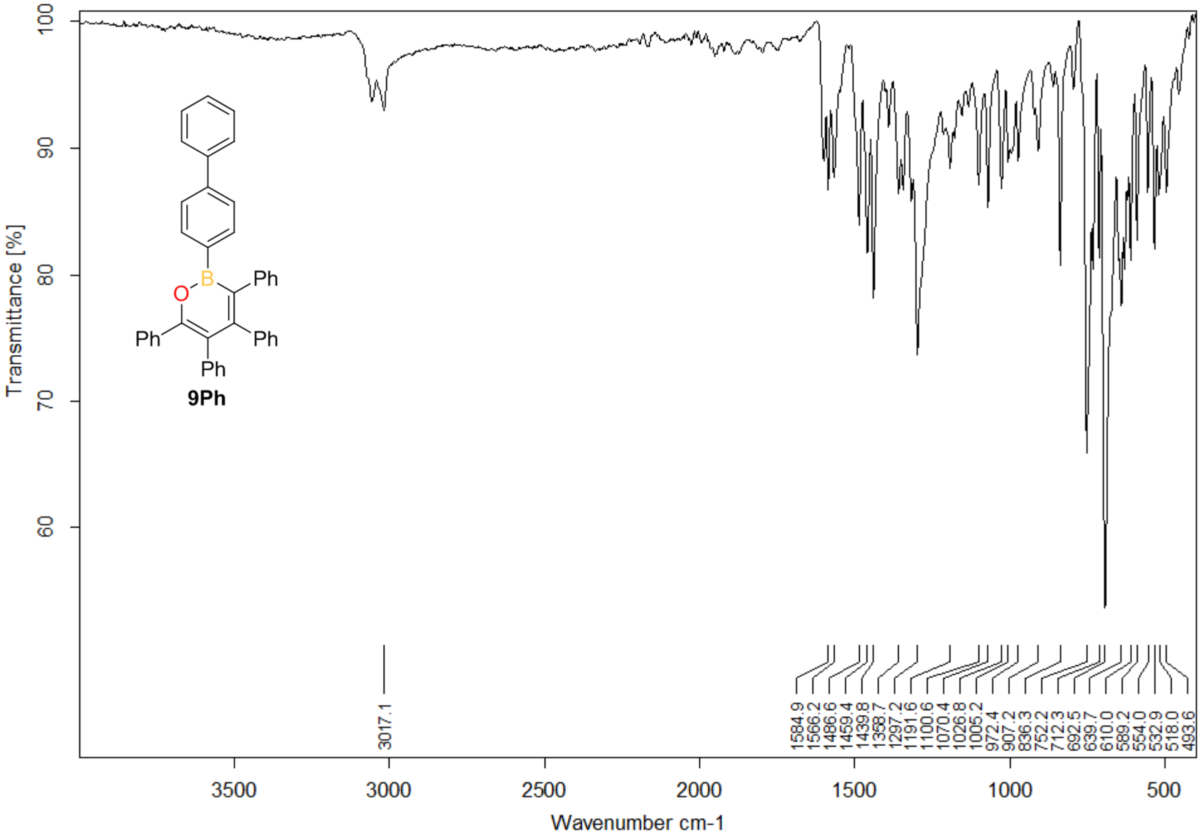
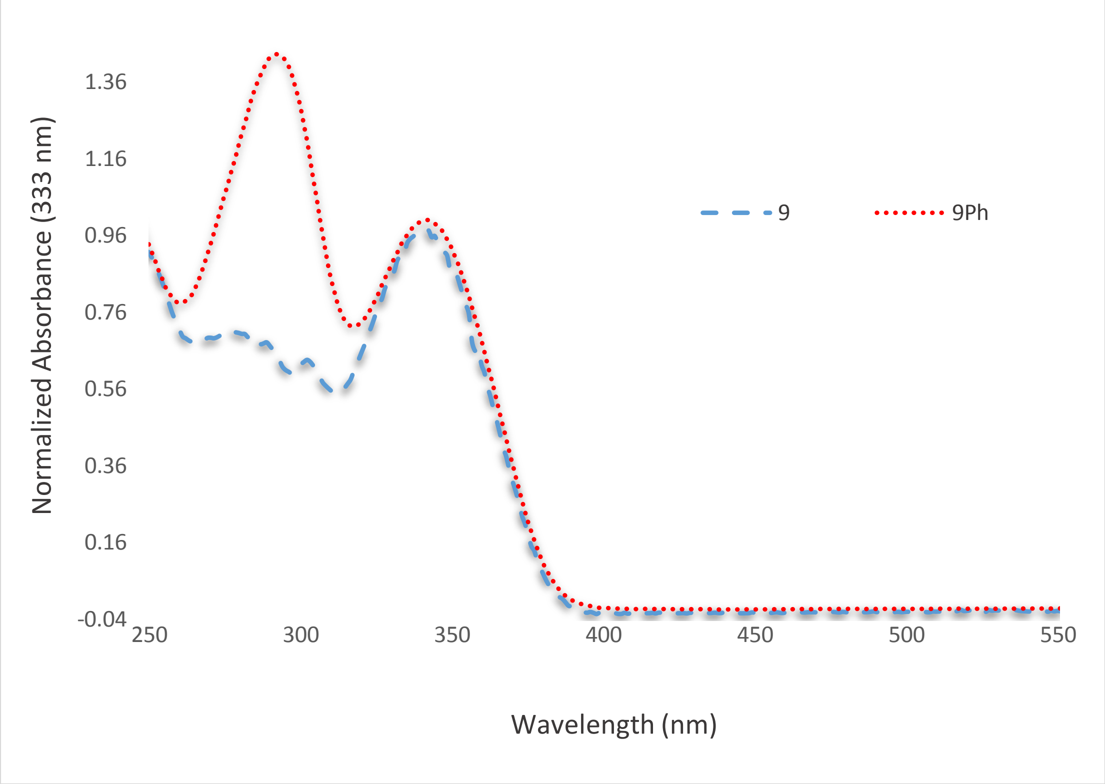


Figure S-16: FT-IR spectrum of **9Ph**.



UV-Vis and Fluorescence Studies

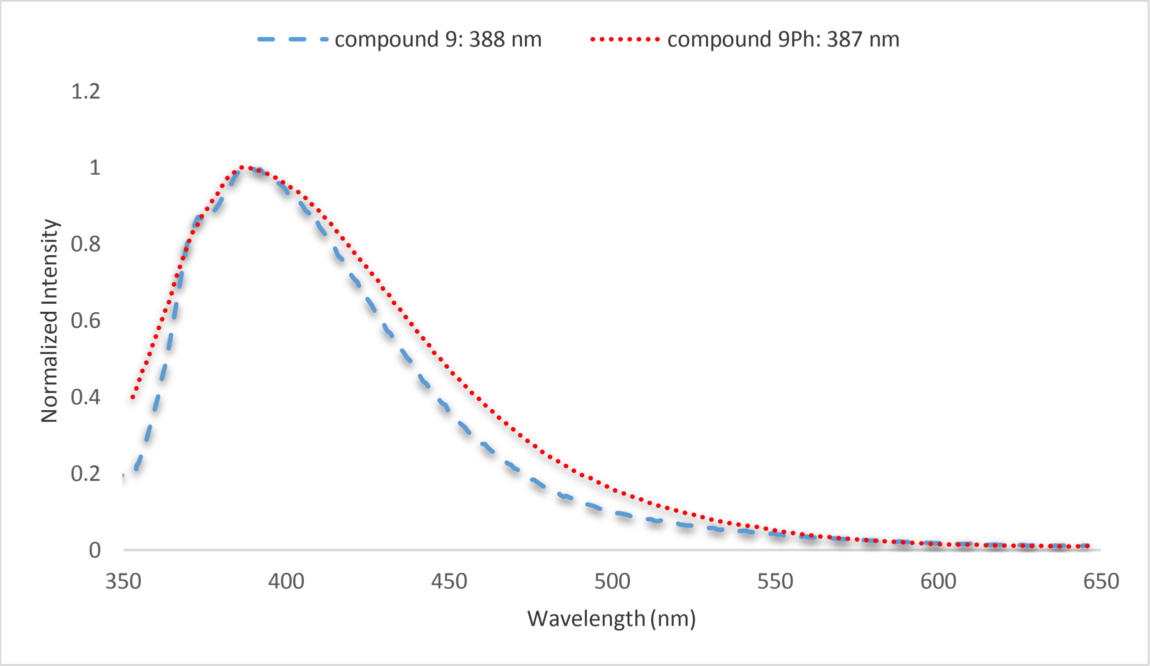
Figure S17: Normalized absorption spectrum of **9** and **9Ph** in CH_2Cl_2 (normalized at the 333 nm peak).



9 (333 nm): ε = 12,000 $\mathrm{Lmol^{-1}\ cm^{-1}}$; (305 nm): ε = 7500 $\mathrm{Lmol^{-1}\ cm^{-1}}$; (282 nm): ε = 5600 $\mathrm{Lmol^{-1}\ cm^{-1}}$

9Ph (333 nm): ε = 11,000 $\mathrm{Lmol^{-1}\ cm^{-1}}$; (295 nm): ε = 17,000 $\mathrm{Lmol^{-1}\ cm^{-1}}$

Figure S18: Normalized emission spectra of **9** and **9Ph** in CH_2Cl_2 (both compounds excited at 333 nm). Concentrations of samples **9**: 6.66 × 10^{-7} M; **9Ph**: 6.58 × 10^{-7} M.



Computational details

Table S-1: Coordinates of the HSE06/6-311+G(d,p) geometry of **2** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.397343	-1.034286	0.006079
2	6	0	1.831846	1.366935	0.005033
3	6	0	0.478838	1.393573	0.004814
4	6	0	-0.250708	0.168294	0.005349
5	1	0	-0.187411	-1.948899	0.006505
6	1	0	2.453605	2.255443	0.004641
7	1	0	-0.028157	2.350431	0.004230
8	1	0	-1.337385	0.224128	0.005175
9	5	0	1.909040	-1.014922	0.006259
10	1	0	2.654896	-1.944609	0.006829
11	8	0	2.528709	0.233333	0.005703
12	0	0	1.117336	0.150963	0.005841
13	0	0	1.117336	0.150963	1.005841
14	0	0	1.117336	0.150963	-0.994159

Figure S19: Computed optimized structure of **2** displaying ghost atom positioning within the central ring.

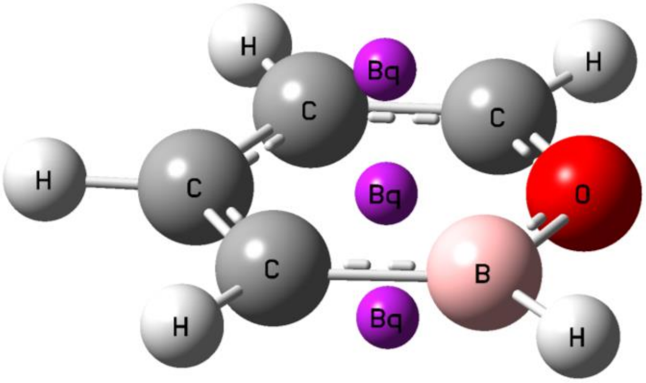


Table S-2: Coordinates of the HSE06/6-311+G(d,p) geometry of **6** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.313696	-0.847202	-0.000463
2	6	0	1.773142	0.392019	-0.001105
3	6	0	0.352766	0.539059	-0.001205
4	6	0	-0.467297	-0.550492	-0.000671
5	1	0	3.380991	-1.040332	-0.000355
6	1	0	2.428808	1.253684	-0.001530
7	1	0	-0.053200	1.548485	-0.001728
8	1	0	-1.540973	-0.387702	-0.000774
9	5	0	0.174720	-1.927553	0.000021
10	8	0	1.575983	-1.953950	0.000063
11	6	0	-0.529866	-3.315570	0.000705
12	6	0	0.210024	-4.507233	0.001273
13	6	0	-1.927638	-3.418374	0.000767
14	6	0	-0.416966	-5.745876	0.001873
15	1	0	1.294184	-4.453776	0.001239
16	6	0	-2.562650	-4.654051	0.001364
17	1	0	-2.532006	-2.516012	0.000338
18	6	0	-1.806697	-5.821572	0.001918
19	1	0	0.175413	-6.655351	0.002306
20	1	0	-3.646535	-4.708725	0.001398
21	1	0	-2.299313	-6.788681	0.002386
22	0	0	0.917534	-0.713656	-0.031292
23	0	0	0.917534	-0.713656	-1.031292
24	0	0	0.917534	-0.713656	0.968708

Figure S20: Computed optimized structure of **6** displaying ghost atom positioning within the central ring.

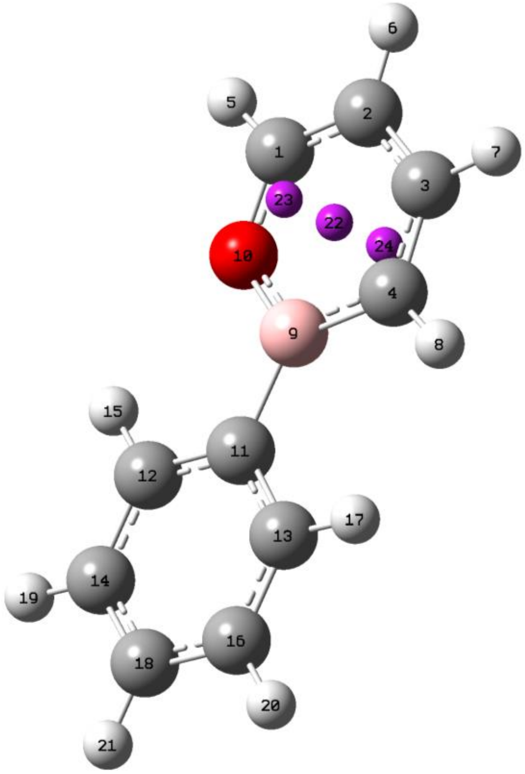


Table S-3: Coordinates of the HSE06/6-311+G(d,p) geometry of **hexaphenylbenzene** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.698849	-0.795613	0.001780
2	6	0	2.104734	-0.795723	-0.000351
3	6	0	2.807484	0.421975	0.000629
4	6	0	2.104920	1.639783	0.000926
5	6	0	0.699038	1.639888	-0.002570
6	6	0	-0.003713	0.422190	-0.000737
7	6	0	-0.047814	-2.086315	0.009502
8	6	0	0.041650	-2.970957	-1.066810
9	6	0	-0.851754	-2.435899	1.096095
10	6	0	-0.657810	-4.171108	-1.059506
11	1	0	0.667879	-2.715922	-1.915489
12	6	0	-1.545592	-3.639160	1.108859
13	1	0	-0.934432	-1.756280	1.937909
14	6	0	-1.452662	-4.510679	0.029534
15	1	0	-0.578355	-4.844742	-1.906515
16	1	0	-2.163567	-3.894607	1.963483
17	1	0	-1.996924	-5.449238	0.036838
18	6	0	2.851560	2.930505	0.007753
19	6	0	3.654474	3.281440	1.094673
20	6	0	2.763047	3.813846	-1.069705
21	6	0	4.348271	4.484730	1.106610
22	1	0	3.736391	2.602849	1.937389
23	6	0	3.462475	5.014021	-1.063222
24	1	0	2.137600	3.557761	-1.918645
25	6	0	4.256324	5.354927	0.026132
26	1	0	4.965447	4.741242	1.961492
27	1	0	3.383781	5.686623	-1.911122
28	1	0	4.800564	6.293504	0.032793
29	6	0	-1.495015	0.422301	-0.001466
30	6	0	-2.207304	-0.093633	-1.085596
31	6	0	-2.208292	0.938334	1.081964
32	6	0	-3.596430	-0.090555	-1.088863
33	1	0	-1.665934	-0.502598	-1.932413
34	6	0	-3.597422	0.935442	1.083874
35	1	0	-1.667695	1.347236	1.929303

36	6	0	-4.296752	0.422490	-0.002836
37	1	0	-4.133075	-0.493562	-1.941559
38	1	0	-4.134844	1.338525	1.936044
39	1	0	-5.381722	0.422561	-0.003365
40	6	0	2.851194	-2.086552	-0.006502
41	6	0	3.655091	-2.437537	-1.092678
42	6	0	2.761573	-2.969919	1.070842
43	6	0	4.348750	-3.640910	-1.104014
44	1	0	3.737884	-1.758919	-1.935287
45	6	0	3.460861	-4.170179	1.064967
46	1	0	2.135361	-2.713789	1.919204
47	6	0	4.255685	-4.511142	-0.023659
48	1	0	4.966700	-3.897461	-1.958326
49	1	0	3.381291	-4.842802	1.912768
50	1	0	4.799818	-5.449784	-0.029847
51	6	0	-0.047408	2.930712	-0.010983
52	6	0	0.041172	3.815289	1.065457
53	6	0	-0.850215	3.280503	-1.098348
54	6	0	-0.658059	5.015568	1.057531
55	1	0	0.666525	3.560097	1.914736
56	6	0	-1.543823	4.483890	-1.111727
57	1	0	-0.932194	2.600944	-1.940279
58	6	0	-1.451790	5.355336	-0.032265
59	1	0	-0.579309	5.689148	1.904649
60	1	0	-2.160914	4.739496	-1.966943
61	1	0	-1.995874	6.293994	-0.040053
62	6	0	4.298785	0.421856	0.001348
63	6	0	5.011007	-0.092939	1.086065
64	6	0	5.012135	0.936523	-1.082685
65	6	0	6.400133	-0.090071	1.089317
66	1	0	4.469583	-0.500856	1.933351
67	6	0	6.401263	0.933403	-1.084610
68	1	0	4.471594	1.344548	-1.930483
69	6	0	7.100526	0.421602	0.002687
70	1	0	6.936722	-0.492174	1.942474
71	1	0	6.938739	1.335413	-1.937253
72	1	0	8.185496	0.421502	0.003204
73	0	0	1.354410	0.443517	0.011111
74	0	0	1.354410	0.443517	1.000000
75	0	0	1.354410	0.443517	-1.000000

Figure S21: Computed optimized structure of **hexaphenyl-1,2-azaborine** displaying ghost atom positioning within the central ring.

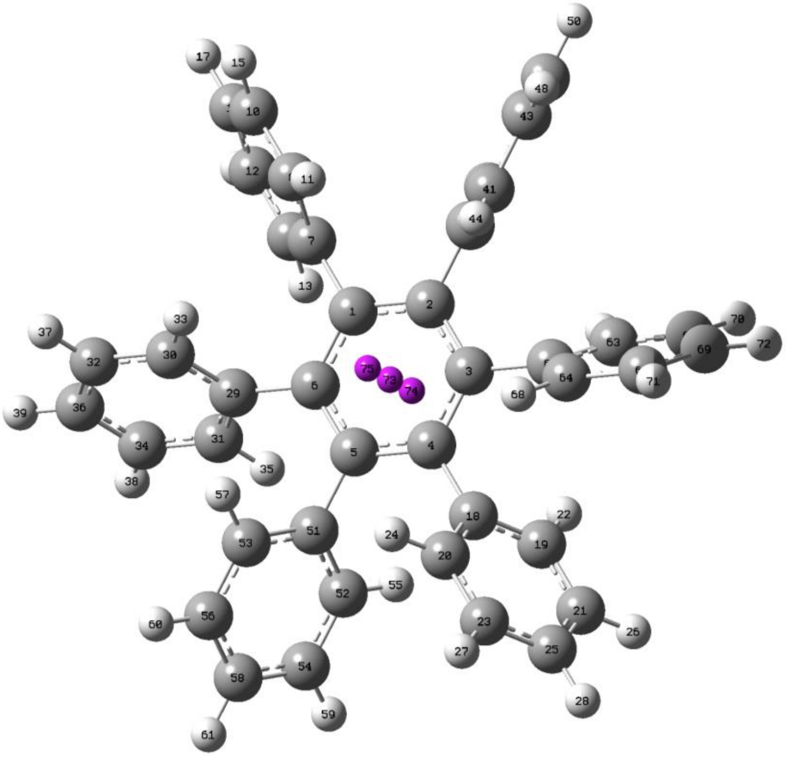


Table S-4: Coordinates of the HSE06/6-311+G(d,p) geometry of **hexaphenyl-1,2-azaborine** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.193775	0.298714	0.006791
2	6	0	1.503179	1.492731	0.009507
3	6	0	0.066211	1.515976	-0.002862
4	6	0	-0.665744	0.341593	-0.009056
5	6	0	-0.649893	-2.385902	-0.021382
6	6	0	-0.455982	-3.347615	-1.021488
7	6	0	-1.562645	-2.692781	0.997097
8	6	0	-1.138786	-4.558329	-1.007038
9	1	0	0.243346	-3.151263	-1.829174
10	6	0	-2.231706	-3.910581	1.031740
11	1	0	-1.760790	-1.960967	1.775182
12	6	0	-2.024515	-4.847276	0.025402
13	1	0	-0.974375	-5.280948	-1.800295
14	1	0	-2.925873	-4.123344	1.838668
15	1	0	-2.552985	-5.795096	0.042936
16	6	0	3.683782	0.278488	0.028168
17	6	0	4.409392	0.768141	-1.058234
18	6	0	4.377405	-0.208748	1.137458
19	6	0	5.798162	0.765327	-1.039887
20	1	0	3.878735	1.160463	-1.919204
21	6	0	5.765815	-0.206485	1.158680
22	1	0	3.825773	-0.588835	1.990752
23	6	0	6.480660	0.278026	0.068768
24	1	0	6.347961	1.149379	-1.892701
25	1	0	6.290761	-0.584465	2.029705
26	1	0	7.565428	0.278178	0.084996
27	6	0	-0.621092	2.840780	-0.019603
28	6	0	-1.416294	3.202707	-1.108298
29	6	0	-0.496742	3.734731	1.045302
30	6	0	-2.064733	4.430764	-1.136261
31	1	0	-1.529722	2.511220	-1.936730
32	6	0	-1.155546	4.957323	1.024816
33	1	0	0.121160	3.469506	1.896854
34	6	0	-1.938827	5.311702	-0.068112
35	1	0	-2.676043	4.696657	-1.992473

36	1	0	-1.052567	5.637426	1.864088
37	1	0	-2.449313	6.268916	-0.086372
38	6	0	2.294806	-2.121439	-0.050548
39	6	0	3.013641	-2.459273	-1.192150
40	6	0	2.288835	-2.976455	1.045198
41	6	0	3.736079	-3.645155	-1.230062
42	1	0	3.006716	-1.791236	-2.046289
43	6	0	3.008705	-4.163602	1.002262
44	1	0	1.709319	-2.711494	1.922647
45	6	0	3.736348	-4.499930	-0.133527
46	1	0	4.297404	-3.902369	-2.122007
47	1	0	2.996897	-4.828807	1.858998
48	1	0	4.298881	-5.426781	-0.165666
49	6	0	-2.151743	0.366500	0.017429
50	6	0	-2.851909	0.957589	1.074014
51	6	0	-2.889319	-0.239671	-1.003886
52	6	0	-4.240738	0.951474	1.103707
53	1	0	-2.298576	1.426539	1.881073
54	6	0	-4.278314	-0.236812	-0.982569
55	1	0	-2.363706	-0.719689	-1.823148
56	6	0	-4.960883	0.358306	0.072542
57	1	0	-4.762286	1.414183	1.935532
58	1	0	-4.829079	-0.707934	-1.790413
59	1	0	-6.045715	0.356256	0.093276
60	6	0	2.266697	2.774946	0.024603
61	6	0	3.039635	3.137574	1.129145
62	6	0	2.214327	3.647275	-1.064910
63	6	0	3.747134	4.333349	1.143413
64	1	0	3.087402	2.472373	1.985255
65	6	0	2.921810	4.842480	-1.054546
66	1	0	1.608934	3.386209	-1.926951
67	6	0	3.691610	5.190188	0.050200
68	1	0	4.342898	4.596023	2.011605
69	1	0	2.869444	5.505871	-1.911728
70	1	0	4.243376	6.124357	0.059304
71	5	0	0.075945	-0.987420	-0.020360
72	7	0	1.521867	-0.907318	-0.009053
73	0	0	0.699907	0.271937	-0.000661
74	0	0	0.699907	0.271937	-0.995809
75	0	0	0.699907	0.271937	0.991061

Figure S22: Computed optimized structure of **hexaphenyl-1,2-azaborine** displaying ghost atom positioning within the central ring.

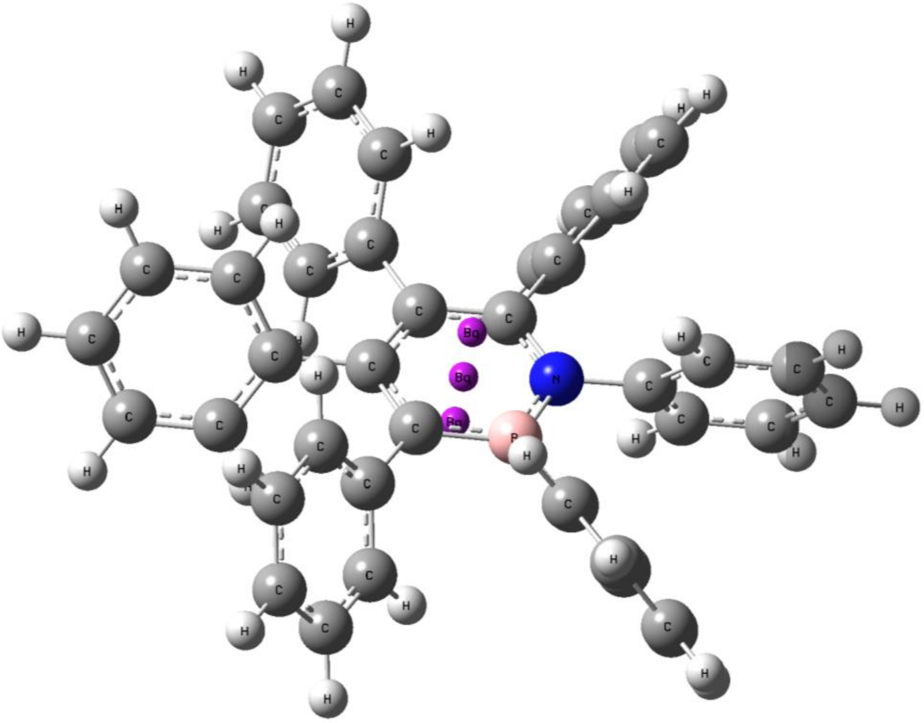


Table S-5: Coordinates of the HSE06/6-311+G(d,p) geometry of **9** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.408961	1.107799	-0.088849
2	6	0	0.748718	2.308586	-0.037103
3	6	0	-0.699999	2.321911	-0.012457
4	6	0	-1.433889	1.151674	-0.010585
5	5	0	-0.652785	-0.157407	0.025852
6	8	0	0.732174	-0.042656	-0.033386
7	6	0	-1.158090	-1.632271	0.134779
8	6	0	-0.335556	-2.678585	-0.312965
9	6	0	-2.392886	-1.977970	0.703242
10	6	0	-0.731197	-4.005804	-0.213990
11	1	0	0.630296	-2.440908	-0.748109
12	6	0	-2.786674	-3.305737	0.820308
13	1	0	-3.055521	-1.200183	1.067198
14	6	0	-1.960074	-4.322988	0.356270
15	1	0	-0.080748	-4.795070	-0.577573
16	1	0	-3.743277	-3.547043	1.272628
17	1	0	-2.271394	-5.359457	0.439784
18	6	0	-2.918348	1.169369	-0.010603
19	6	0	-3.646720	1.711121	1.052690
20	6	0	-3.623657	0.599822	-1.075170
21	6	0	-5.035928	1.688248	1.049116
22	1	0	-3.116343	2.150603	1.890931
23	6	0	-5.012859	0.586265	-1.085375
24	1	0	-3.072527	0.161126	-1.901314
25	6	0	-5.725234	1.129318	-0.021643
26	1	0	-5.582015	2.110910	1.886301
27	1	0	-5.540137	0.144346	-1.924660
28	1	0	-6.810056	1.114631	-0.025634
29	6	0	2.864303	0.881341	-0.191375
30	6	0	3.701273	1.688298	-0.968543
31	6	0	3.418479	-0.219316	0.473370
32	6	0	5.057891	1.410224	-1.061365
33	1	0	3.289224	2.530030	-1.511364
34	6	0	4.777541	-0.486068	0.388876
35	1	0	2.772448	-0.862587	1.059794
36	6	0	5.603298	0.328829	-0.377800
37	1	0	5.691353	2.041099	-1.675843

38	1	0	5.192284	-1.335614	0.921163
39	1	0	6.665250	0.118294	-0.448205
40	6	0	1.514127	3.584175	0.004012
41	6	0	2.348502	3.868209	1.086951
42	6	0	1.416284	4.520544	-1.028375
43	6	0	3.073634	5.052513	1.134700
44	1	0	2.431750	3.147959	1.894714
45	6	0	2.142632	5.703427	-0.983490
46	1	0	0.766673	4.318082	-1.873472
47	6	0	2.974226	5.973768	0.098306
48	1	0	3.717867	5.255210	1.983977
49	1	0	2.057264	6.417605	-1.795903
50	1	0	3.539843	6.898907	0.133829
51	6	0	-1.387271	3.645724	-0.002029
52	6	0	-2.193549	4.026792	-1.075656
53	6	0	-1.249134	4.518229	1.078724
54	6	0	-2.841337	5.255607	-1.072654
55	1	0	-2.314553	3.352373	-1.916841
56	6	0	-1.908585	5.740565	1.088849
57	1	0	-0.620805	4.236702	1.917376
58	6	0	-2.703456	6.115328	0.011147
59	1	0	-3.461132	5.538572	-1.917102
60	1	0	-1.796409	6.404533	1.939634
61	1	0	-3.213849	7.072686	0.016709
62	0	0	-0.028822	1.049494	0.008684
63	0	0	-0.028822	1.049494	-0.991316
64	0	0	-0.028822	1.049494	1.008684

Figure S23: Computed optimized structure of **9** displaying ghost atom positioning within the central ring.

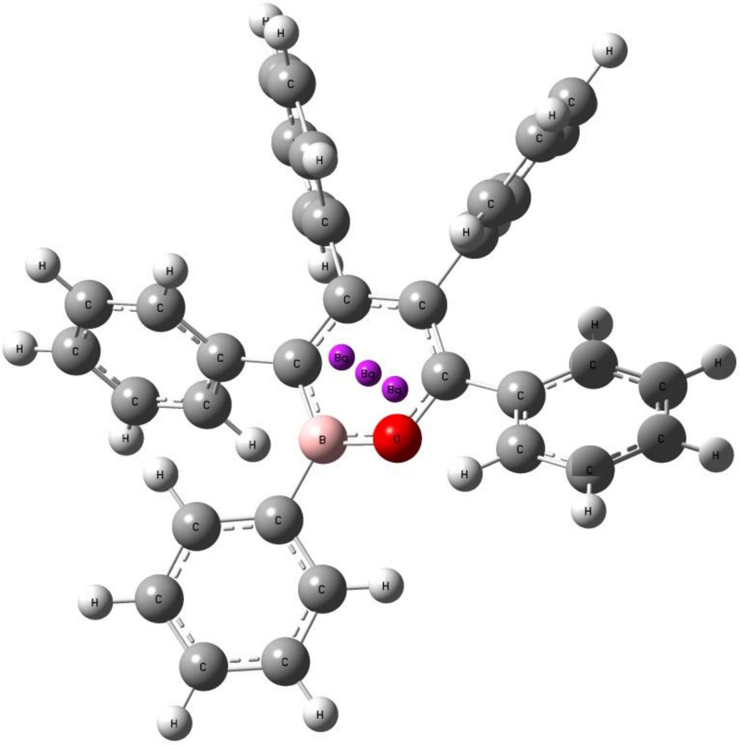


Table S-6: Coordinates of the HSE06/6-311+G(d,p) geometry of **9Ph** simulated in C1 symmetry.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.318282	-0.630638	-0.051679
2	6	0	1.296533	1.705251	-0.202112
3	6	0	-0.062846	1.826124	-0.069537
4	6	0	-0.879913	0.630928	-0.009529
5	5	0	1.203775	-0.711534	-0.099836
6	8	0	1.877575	0.502416	-0.189614
7	6	0	2.149685	-1.952631	-0.046274
8	6	0	1.786965	-3.172102	0.543539
9	6	0	3.450864	-1.858518	-0.564721
10	6	0	2.674494	-4.235870	0.613663
11	1	0	0.791555	-3.296784	0.955901
12	6	0	4.335090	-2.924464	-0.513380
13	1	0	3.774760	-0.923510	-1.011523
14	6	0	3.963828	-4.135641	0.081282
15	1	0	2.353716	-5.170464	1.062939
16	1	0	5.339183	-2.810268	-0.910091
17	6	0	4.905728	-5.271257	0.148221
18	6	0	4.959959	-6.092533	1.279736
19	6	0	5.768075	-5.554371	-0.916597
20	6	0	5.846039	-7.159601	1.344787
21	1	0	4.317121	-5.875129	2.126578
22	6	0	6.653984	-6.621826	-0.852562
23	1	0	5.724200	-4.945136	-1.813607
24	6	0	6.697173	-7.429383	0.278654
25	1	0	5.878257	-7.778117	2.235828
26	1	0	7.307360	-6.829350	-1.693729
27	1	0	7.389264	-8.263226	0.329046
28	6	0	-1.157956	-1.854318	-0.017899
29	6	0	-1.973869	-2.158040	1.076177
30	6	0	-1.114510	-2.759026	-1.083377
31	6	0	-2.724663	-3.326852	1.102305
32	1	0	-2.015430	-1.471581	1.915261
33	6	0	-1.872862	-3.922863	-1.063328
34	1	0	-0.474802	-2.545203	-1.934057
35	6	0	-2.680013	-4.212904	0.031288
36	1	0	-3.348439	-3.545122	1.963132
37	1	0	-1.827865	-4.608508	-1.903306

38	1	0	-3.268432	-5.124201	0.050676
39	6	0	-2.358847	0.798940	0.085413
40	6	0	-3.183642	0.351507	-0.947731
41	6	0	-2.944125	1.392180	1.205270
42	6	0	-4.562449	0.500828	-0.866967
43	1	0	-2.739035	-0.119972	-1.817888
44	6	0	-4.323638	1.527749	1.293108
45	1	0	-2.313976	1.749431	2.013149
46	6	0	-5.137153	1.086739	0.255123
47	1	0	-5.189467	0.151596	-1.680701
48	1	0	-4.763713	1.984505	2.173432
49	1	0	-6.214326	1.198099	0.321303
50	6	0	2.286041	2.789936	-0.356424
51	6	0	3.540547	2.645864	0.247933
52	6	0	2.038157	3.928879	-1.128737
53	6	0	4.508875	3.630275	0.109908
54	1	0	3.748040	1.754800	0.829464
55	6	0	3.013990	4.904683	-1.275876
56	1	0	1.082988	4.047283	-1.625233
57	6	0	4.248780	4.764482	-0.651537
58	1	0	5.471378	3.509002	0.595647
59	1	0	2.808861	5.777632	-1.886379
60	1	0	5.007221	5.532031	-0.764157
61	6	0	-0.688060	3.173370	0.027290
62	6	0	-0.393204	4.004379	1.110163
63	6	0	-1.576889	3.634729	-0.946910
64	6	0	-0.964534	5.266544	1.214653
65	1	0	0.295664	3.655809	1.873107
66	6	0	-2.146360	4.897535	-0.845505
67	1	0	-1.821265	2.998501	-1.791126
68	6	0	-1.842157	5.718163	0.235774
69	1	0	-0.722794	5.898371	2.063041
70	1	0	-2.831880	5.240931	-1.613275
71	1	0	-2.289079	6.703548	0.315412
72	0	0	0.489289	0.509824	-0.073490
73	0	0	0.489289	0.509824	-1.073490
74	0	0	0.489289	0.509824	0.926510

Figure S24: Computed optimized structure of **9Ph** displaying ghost atom positioning within the central ring.

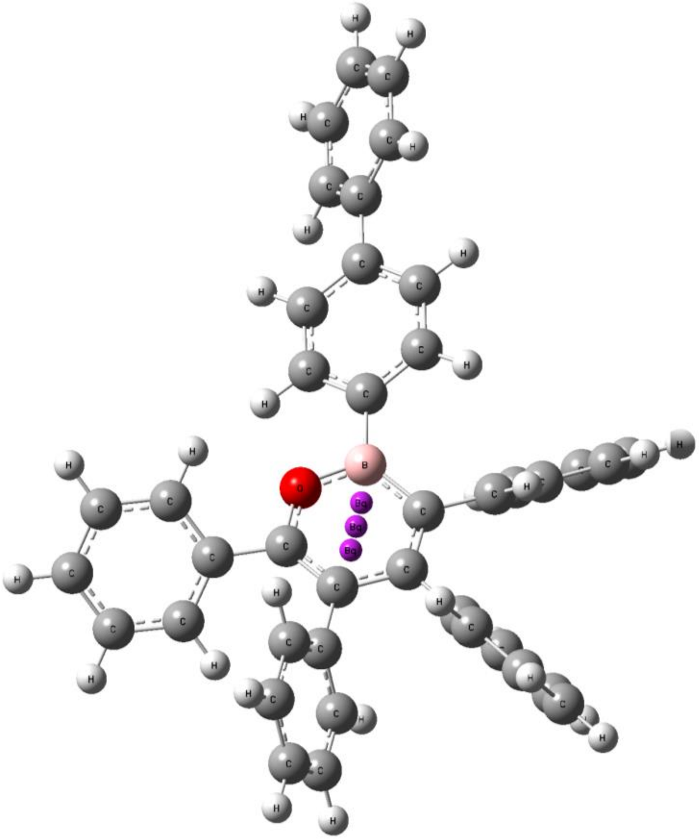
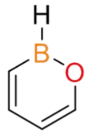
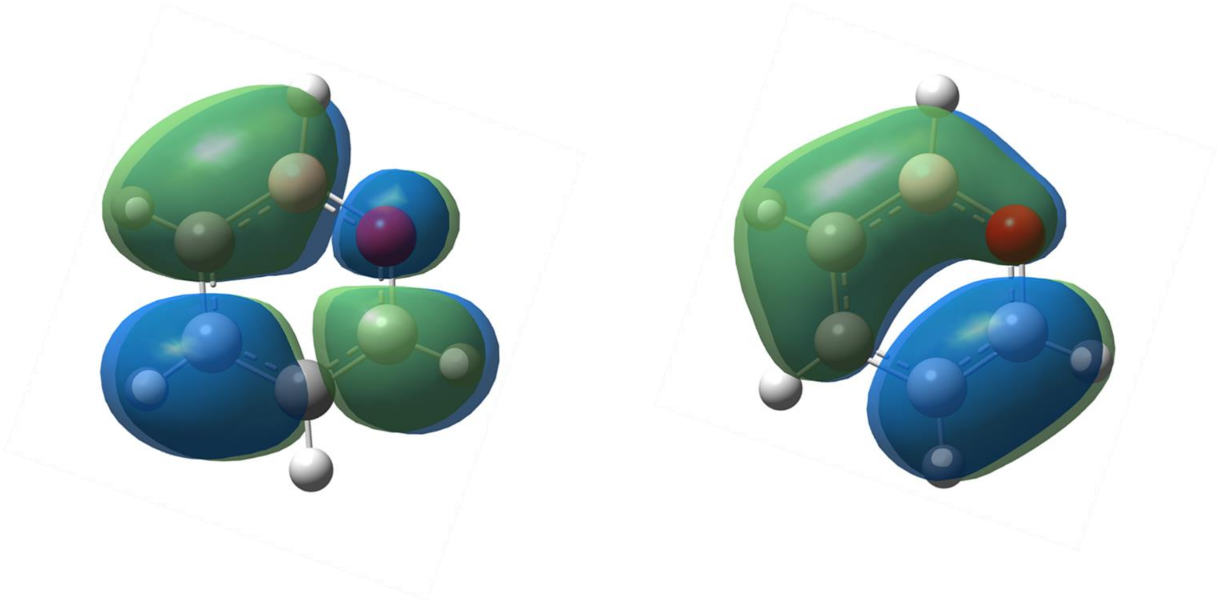


Figure S25: Frontier orbitals of **2** depicting contributions to the aromaticity at an isovalue of 0.02 a.u.

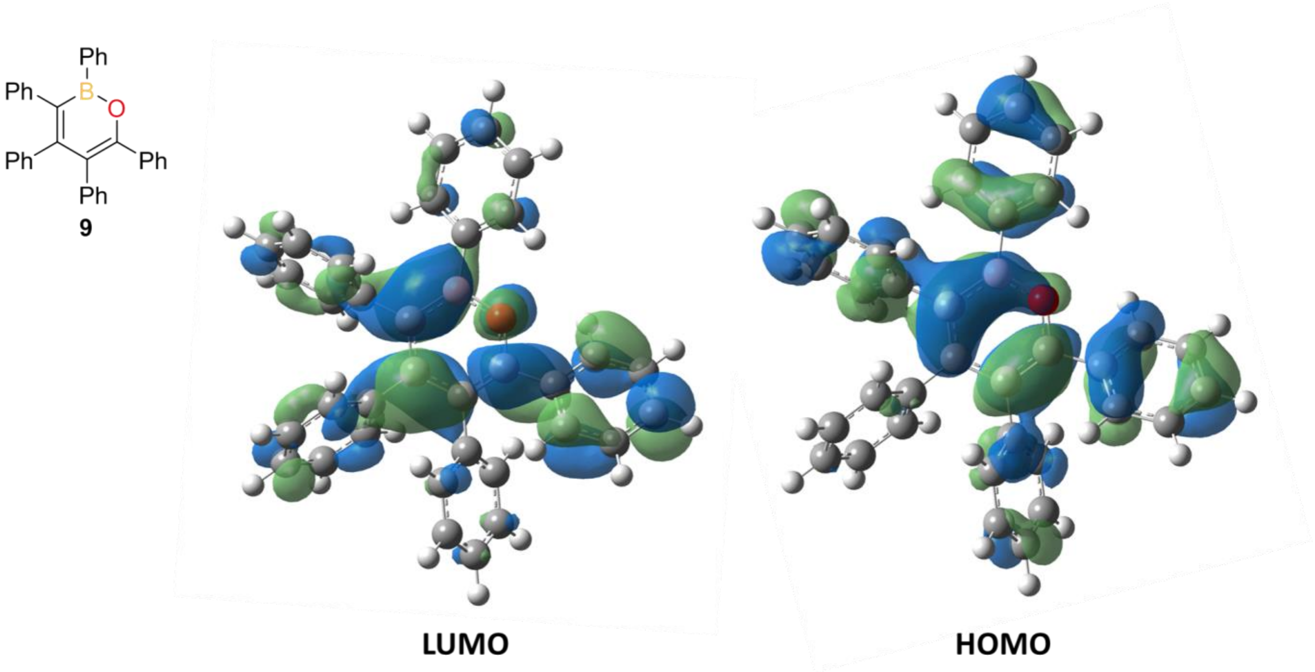


2



LUMO HOMO

Figure S26: Frontier orbitals of **9** depicting central ring contributions to the aromaticity at an isovalue of 0.02 a.u.

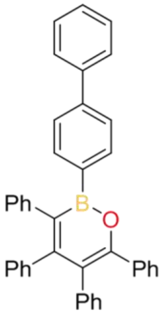


9

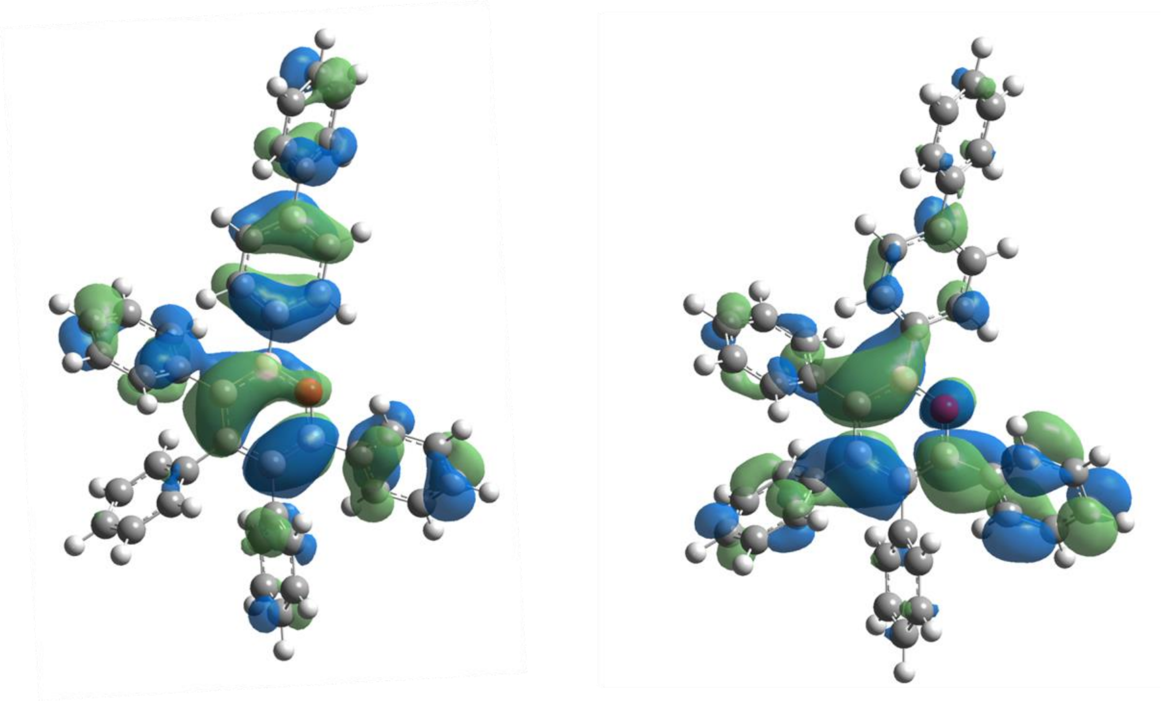
LUMO

HOMO

Figure S27: Frontier orbitals of **9Ph** depicting central ring contributions to the aromaticity at an isovalue of 0.02 a.u.



9Ph

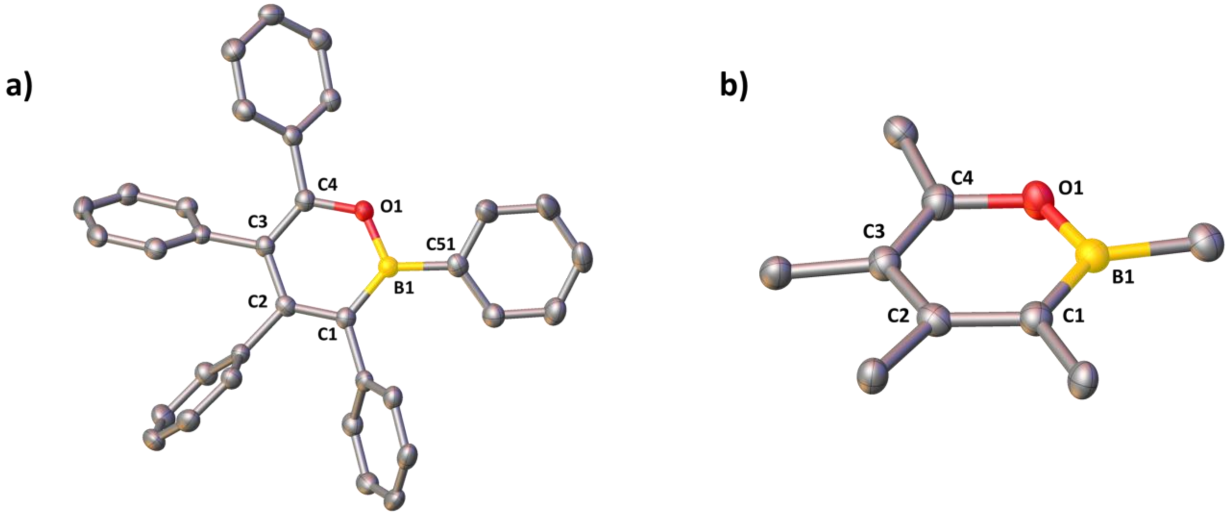


LUMO

HOMO

X-Ray Crystallography details: Crystals were selected under paratone oil, mounted on micromounts then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL.[2]

Figure S28. a) Solid-state structure of **9**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (˚): B(1)-O(1) 1.388(17), B(1)-C(1) 1.510(19), C(1)-C(2) 1.388(18), C(2)-C(3) 1.449(17), C(3)-C(4) 1.379(18), C(4)-O(1) 1.360(15), B(1)-C(51) 1.567(2), O(1)-B(1)-C(51) 112.40(11), O(1)-B(1)-C(1) 116.70(12), C(51)-B(1)-C(1) 130.88(12), C(4)-C(3)-C(2) 118.93(12), C(3)-C(2)-C(1) 121.56(11), C(2)-C(1)-B(1) 117.58(11); b) Simplified view along the BOC_4 plane of **9** (carbon atoms from aryl groups except *ipso* carbons have been removed).



Note: Similar boron heterocycles bearing phenyl groups on boron and carbon atoms within the ring have shown disorder. Therefore, the bond distances and bond angles are not discussed in detail. However, the structure confirms the identity of **9**.

Table S-7: Crystallographic data for **9** and **9Ph**.

	9	**9Ph**
CCDC	1457937	1457938
Empirical formula	$C_{34}H_{25}BO$	$C_{40}H_{29}BO$
FW (g/mol)	460.35	536.44
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a (Å)	9.7747(5)	10.5923(10)
b (Å)	11.2285(5)	11.7946(7)
c (Å)	12.0790(6)	12.5909(7)
α (deg)	86.439(2)	91.861(2)
β (deg)	70.815(1)	94.751(2)
γ (deg)	85.025(1)	113.478(2)
V (Å^3)	1246.59(11)	1434.13(14)
Z	2	2
D_c (mg m^{-3})	1.226	1.242
radiation, λ (Å)	0.71073	0.71073
temp (K)	150(2)	150(2)
$R1[I>2\sigma I]^a$	0.0470	0.0434
$wR2(F^2)^a$	0.1190	0.1281
GOF $(S)^a$	1.014	1.064

^{a} $R1(F[\mathrm{I} > 2(\mathrm{I})]) = \sum\|F_o| - |F_c\|/ \sum |F_o|$; $wR2(F^2$ [all data]$) = [w(F_o^2 - F_c^2)^2]^{1/2}$; S(all data) $= [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

References:

1. a) Eisch, J.J, Hota, N.H., and Kozima, S., *J. Am. Chem. Soc.*, 1969, **91**, 4575-4577. b) Barnard, J.H., Yruegas, S., Couchman, S.A., Wilson, D.J.D, Dutton, J.L., Martin, C.D. **2016**, DOI: 10.1021/acs.organomet.6b00123.

2. Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112.

3. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K, and Puschmann, H., *J. Appl. Crystallogr.*, 2009, **42**, 339-341.