Electronic Supplementary Material (ESI) for ChemComm.

Isolable diboryl radicals acting as highly efficient reaction intermediates under mild conditions

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Content

Experimental part

General considerations: All operations were performed on a dry argon Schlenk line or in the nitrogen-filled glovebox. Solvents were dried following the published procedures and degassed prior to use. Dimesitylborane fluoride (Mes_2BF)[S1] and **2**[S2] was synthesized according to the reported procedures and the other chemicals were purchased from commercial vendors. X-ray single crystal diffraction analyses were performed on Bruker D8 Venture detectors at low temperatures. The structures were solved by direct method and all refined on F^2 with the SHELX-2014 or SHELX-2018 programs. CCDC 1913373-1913377 contain the supplementary crystallographic data for this paper, these data are provided free of charge by The Cambridge Crystallographic Data Center. The positions of the H atoms were placed in calculated positions using an appropriate riding model. The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra were collected on a Bruker Ultra Shield 500 MHz spectrometer using C_6D_6 as solvent. FT-IR spectra were recorded on a VECTOR22 FT-IR spectrometer in the 400-4000 cm^{-1} region (KBr pellet). UV/Vis absorption spectra were measured on a Lambda 750 spectrometer. Elemental analyses were performed on an Elementar Vario EL III instrument at Shanghai Institute of Organic Chemistry, the Chinese Academy of Science. EPR spectra were obtained using a Bruker EMX-10/12 X-band variable-temperature apparatus and were simulated with the software of WINEPR SimFonia.

Synthesis of 1: Under an argon atmosphere, the solution of 4-bromo-pyridine (1.90 g, 12 mmol) in dry ether (150 mL) was treated with *n*-BuLi (2.5 M in *n*-hexane, 5.1 mL, 12.8 mmol) at –78 °C. After 2 hours stirring at –78 °C, dimesitylfluoroborane (3.49 g, 13.0 mmol) dissolved in dry ether (20 mL) was added dropwise forming an orange solution, which was allowed to warm up to room temperature and stirred for 12 h. After removal of all the volatiles under vacuum, the yellow solid was purified by silica gel column chromatography (hexane/EtOAc, 40:1). The concentrated *n*-hexane solution of the obtained raw material was stored at –20 °C for 1 day to afford pale yellow X-ray-quality crystals of **1**. Yield: 1.00 g, 26%. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 8.64 (d, $J_{H,H}$ = 5.6 Hz, 2H, Ar-*H*), 7.12 (d, $J_{H,H}$ = 5.6 Hz, 2H, Ar-*H*), 6.74 (s, 4H, Ar-*H*), 2.17 (s, 6H, C*H*$_3$), 1.99 (s, 12H, C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6, ppm): δ 153.04, 150.53, 141.54, 141.08,

139.82, 128.99, 128.60, 23.64, 21.31; ^{11}B NMR (160 MHz, C_6D_6, ppm): δ 75.99. UV-vis (*n*-hexane): ε (327 nm) = 3.26 × 10^4 L·mol^{-1}·cm^{-1}. FT-IR (KBr pellet, cm^{-1}): 2917 (s), 1603 (s), 1546 (m), 1413 (s), 1312 (m), 1238 (s), 1163 (m), 1029 (m), 849 (s), 805 (s), 727 (w), 668 (m), 638 (m), 572 (w), 517 (w). Elemental analysis (%) Calcd for $C_{23}H_{26}BN$: C 84.41; H 8.01; N 4.28; Found: C 84.50, H 7.92, N 4.28.

Synthesis of 3: Under an argon atmosphere, compound **1** (65.1 mg, 0.2 mmol) and B_2mpd_2 (28.2 mg, 0.1 mmol) were placed in a Schlenk flask. *n*-Hexane (15 mL) were added into the flask forming a brown solution, which was stirred at room temperature for 24 h. The mixture was filtered, concentrated and stored at 5 ^{o}C overnight to afford brown X-ray-quality crystals of **3**. Yield: 37 mg, 40%. UV-vis (n-hexane): ε(279 nm) = 6.07 × 10^4 L·mol^{-1}·cm^{-1}, ε(305 nm) = 4.69 × 10^4 L·mol^{-1}·cm^{-1}, ε(333 nm) = 4.54 × 10^4 L·mol^{-1}·cm^{-1}, ε(412 nm) = 3.83 × 10^4 L·mol^{-1}·cm^{-1}, ε(487 nm) = 4.85 × 10^4 L·mol^{-1}·cm^{-1}. FT-IR (KBr pellet, cm^{-1}): 2979 (s), 2930 (s), 1642 (w), 1607 (w), 1365 (s), 1326 (s), 1195 (s), 1152 (s), 1004 (w), 845 (w), 767 (m), 659 (w), 528 (m).

Synthesis of 4: Under an atmosphere of argon, compound **2** (71.1 mg, 0.2 mmol) and B_2mpd_2 (28.2 mg, 0.1mmol) were placed in a Schlenk flask. *n*-Hexane (15 mL) was added into the flask forming a blue solution, which was stirred at room temperature for 48 h. The mixture was filtered and stored at room temperature overnight to afford blue X-ray-quality crystals of **4**. Yield: 56 mg, 56%. UV-vis(*n*-hexane): ε(270 nm) = 5.53 × 10^4 L·mol^{-1}·cm^{-1}, ε(292 nm) = 5.67 × 10^4 L·mol^{-1}·cm^{-1}, ε(347 nm) = 4.02 × 10^4 L·mol^{-1}·cm^{-1}, ε(409 nm) = 1.90 × 10^4 L·mol^{-1}·cm^{-1}, ε(590 nm) = 3.92 × 10^4 L·mol^{-1}·cm^{-1}. FT-IR (KBr pellet, cm^{-1}): 2970 (s), 2920 (s), 1659 (w), 1603 (m), 1407 (s), 1335 (s), 1197 (w), 1029 (m), 989 (m), 954 (m), 884 (w), 826 (m), 768 (w), 702 (w), 662 (w), 508 (w). Elemental analysis (%) Calcd for $C_{32}H_{44}B_2NO_2$: C 77.44; H 8.94; N 2.82; Found: C 77.70, H 9.48, N 2.94.

Reactivity of 3 or 4 with *p*-benzoquinone: Under an atmosphere of argon, compound **1** (65.1 mg, 0.2mmol) or **2** (71.1 mg, 0.2 mmol) and B_2mpd_2 (28.2 mg, 0.1 mmol) were placed in a Schlenk flask. *n*-Hexane (15 mL) was added into the flask forming a brown or blue solution, which was stirred at room temperature for 48 h. To the brown or blue solution *p*-benzoquinone (10.8 mg, 0.1 mmol) was added in an argon-filled glovebox, the

mixture was stirred for another 12 hours. After removal of all the volatiles, toluene (10 mL) was added into the flask. The resultant pale yellow solution was filtered and stored at –40 °C overnight to afford pale yellow X-ray-quality crystals of **5**. Yield: 21 mg, 54%. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.19 (s, 4H, Ar-*H*), 1.32 (s, 4H, CH_2), 1.09 (s, 24H, CH_3); ^{13}C NMR (125 MHz, C_6D_6): δ 149.76, 120.88, 72.25, 48.53, 31.53; ^{11}B NMR (160 MHz, C_6D_6): δ 18.12. FT-IR (KBr pellet, cm^{-1}): 2981 (s), 2938 (w), 1513 (m), 1397 (s), 1327 (s), 1244 (m), 1186 (s), 1098 (w), 1037 (w), 837 (m), 770 (m), 660 (m), 501 (w). Elemental analysis (%) Calcd for $C_{50}H_{60}B_2N_2$: C 61.58; H 8.27; Found: C 61.65, H 8.08.

Reactivity of 3 or 4 with 4-benzoyloxy-2,2,6,6-tetramethyl-1-piperidinyloxy: Under an atmosphere of argon, compound **1** (130.1 mg, 0.4 mmol) or **2** (142.1 mg, 0.4 mmol) and B_2mpd_2 (56.4 mg, 0.2 mmol) were placed in a Schlenk flask. *n*-Hexane (15 mL) was added into the flask forming a brown or blue solution, which was stirred at room temperature for 48 h. To the brown or blue solution 4-(benzoyloxy)-2,2,6,6-tetramethyl-1-piperidinyloxy (110.5 mg, 0.4 mmol) was added in an argon-filled glovebox, the mixture was stirred for another 12 hours. The resultant yellow solution was filtered and stored at –40 °C to afford colorless X-ray-quality crystals of **6**. Yield: 27 mg, 16%. ^{1}H NMR (500 MHz, C_6D_6): δ 8.15 (d, $J_{H,H}$ = 6.7 Hz, 2H, Ar-*H*), 7.13 (t, $J_{H,H}$ = 7.1 Hz, 1H, Ar-*H*), 7.07 (t, $J_{H,H}$ = 7.1 Hz, 2H, Ar-*H*), 5.43 (m, 1H, C*H*), 1.96 (d, $J_{H,H}$ = 9.3 Hz, 2H, CH_2), 1.84 (d, $J_{H,H}$ = 10.7 Hz, 2H, CH_2), 1.39 (s, 2H, CH_2), 1.30 (s, 6H, CH_3), 1.26 (s, 6H, CH_3), 1.19 (s, 6H, CH_3), 1.17 (s, 6H, CH_3); ^{13}C NMR (125 MHz, C_6D_6): δ 165.75, 132.75, 131.54, 129.92, 128.52, 71.61, 67.58, 59.65, 48.87, 44.15, 32.60, 31.76, 20.51; ^{11}B NMR (160 MHz, C_6D_6): δ 20.30. FT-IR (KBr pellet, cm^{-1}): 2979 (s), 1716 (s), 1392 (s),1337 (s), 1278 (s), 1197 (s), 1116 (s), 1001 (w), 770 (w), 717 (m), 662 (w). Elemental analysis (%) Calcd for $C_{23}H_{36}BNO_5$: C 66.19, H 8.69, N 3.36; Found: C 65.96, H 8.67, N 3.55.

Reactivity of 3 or 4 with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO): The reaction was carried out in the same manner as that of 4-benzoyloxy-TEMPO. The reaction proceeded similarly, however no crystalline products were formed.

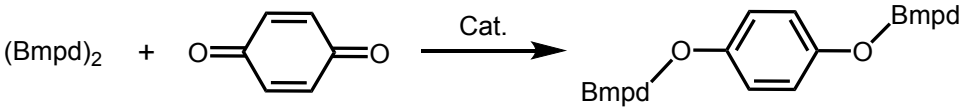
Catalytic reactions of B_2mpd_2 and *p*-benzoquinone: Under an atmosphere of argon, *p*-benzoquinone (54.0 mg, 0.5 mmol, 1 equiv), B_2mpd_2 (141.0 mg, 0.5 mmol, 1 equiv), compound **1** (32.7 mg, 0.1 mmol, 0.2 equiv) or **2** (35.5 mg, 0.1 mmol, 0.2 equiv) and

hexane (20 mL) were placed in a Schlenk flask. The mixture was stirred at room temperature for 12 h. All the volatiles were removed in vacuum, and 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) was added as internal standard for ^{1}H NMR analysis to determine the yield. Yield: 99% for catalyst **1**, and 82% for catalyst **2**. 4-cyanopyridine was also used as a catalyst under the same reaction conditions, but the yield is only 14%.

Table S1. Crystal Data and Structure Refinement.

	1	**3**	**4**	**5**	**6**
Formula	$C_{23}H_{26}BN$	$C_{30}H_{40}B_2NO_2$	$C_{32}H_{44}B_2NO_2$	$C_{10}H_{16}BO_3$	$C_{23}H_{36}BNO_5$
Formula weight	327.26	468.25	496.30	195.04	417.34
Temp. (K)	193(2)	173(2)	153(2)	153(2)	193(2)
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	*P*-1	*P*-1	*P*ccn	$P2_1/c$	*P*bca
a (Å)	8.4562(7)	9.3885(5)	7.3012(19)	6.0306(5)	10.0847(14)
b (Å)	11.3431(9)	10.4150(5)	14.676(4)	11.4395(9)	15.143(3)
c (Å)	11.8941(10)	14.9188(7)	28.022(7)	15.2784(14)	31.376(8)
α(°)	108.839(3)	105.469(2)	90	90	90
β(°)	109.210(3)	96.649(2)	90	99.144(3)	90
γ(°)	101.912(3)	90.638(2)	90	90	90
V [Å^3]	955.21(14)	1395.13(12)	3002.6(14)	1040.62(15)	4791.4(16)
Z	2	2	4	4	8
ρ_{calcd}(g·cm^{-3})	1.138	1.115	1.098	1.245	1.157
μ(mm^{-1})	0.307	0.328	0.066	0.088	0.407
F(000)	352	506	1076	420	1808
Collected data	12455	50543	19848	9178	43613
Unique data	3465 [*R*(int) = 0.0522]	4747 [*R*(int) = 0.0946]	2658 [*R*(int) = 0.0901]	2421 [*R*(int) = 0.0525]	4199 [*R*(int) = 0.1014]
GOF on F^2	1.050	1.009	1.035	1.027	1.121
Final *R* indexes [I > 2σ(I)]	R_1= 0.0508 ωR_2=0.1459	R_1=0.0866 ωR_2=0.1510	R_1=0.0632 ωR_2=0.1538	R_1=0.0495 ωR_2=0.1133	R_1=0.0772 ωR_2=0.1450
R indexes (all data)	R_1= 0.0628 ωR_2=0.1567	R_1=0.1111 ωR_2=0.1639	R_1=0.0967 ωR_2=0.1761	R_1=0.0686 ωR_2=0.1219	R_1=0.1210 ωR_2=0.1680
Completeness	0.986	0.962	0.999	0.998	0.996

Table S2. Optimization of the catalyst loadings.



Catalyst	Cat.[mol%]	Yield [%]
1	20	99
1	15	92
1	10	53
1	5	25
2	20	82
2	15	45
2	10	37
2	5	12
4-cyanopyridine	20	14
4-cyanopyridine	15	12
4-cyanopyridine	10	9
4-cyanopyridine	5	5

Reaction conditions: benzoquinone (0.5 mmol, 1 equiv), B_2mpd_2 (0.5 mmol, 1 equiv), catalyst loading relative to benzoquinone, solvent (hexane, 20 ml), room temperature for 12 h. The yields were determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

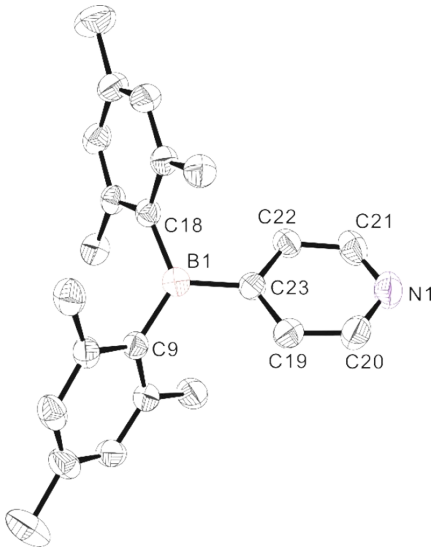


Fig. S1 Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1–C9 1.571(2), B1–C18 1.570(2), B1–C23 1.581(2), N1–C21 1.323(3), C21–C22 1.385(2), C22–C23 1.392(2), C19–C23 1.395(2), C19–C20 1.381(2), N1–C20 1.335(2); C9-B1-C18 125.66(16), C9-B1-C23 119.30(14), C18-B1-C23 115.02(13).

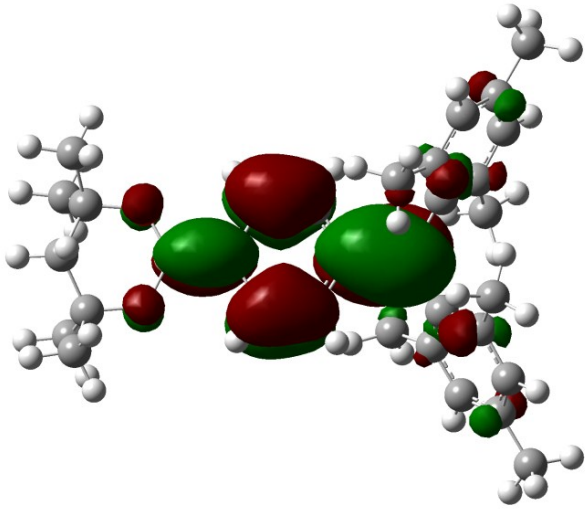


Fig. S2 SOMO of **3** (Isovalue = 0.02)**.**

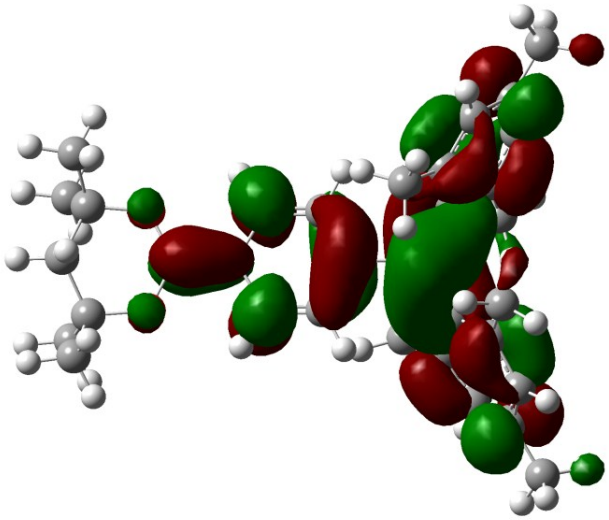


Fig. S3 LUMO of **3** (Isovalue = 0.02).

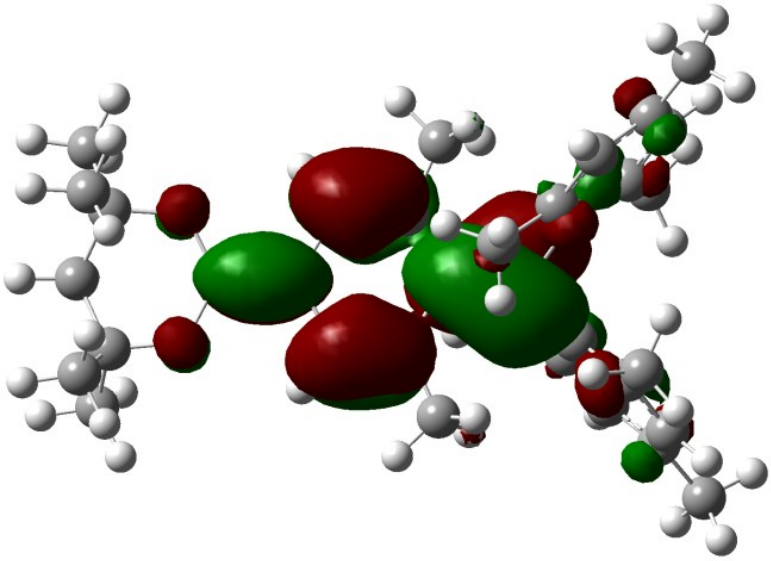


Fig. S4 SOMO of **4** (Isovalue = 0.02).

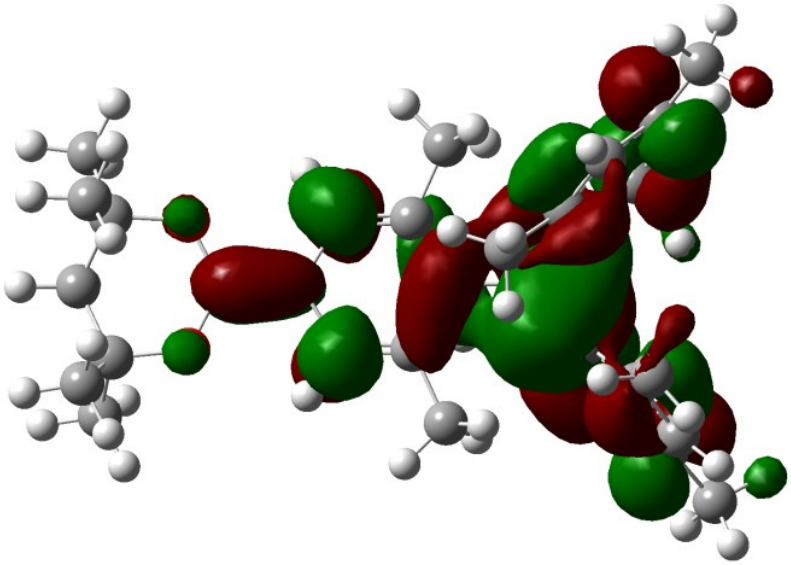


Fig. S5 LUMO of **4** (Isovalue = 0.02).

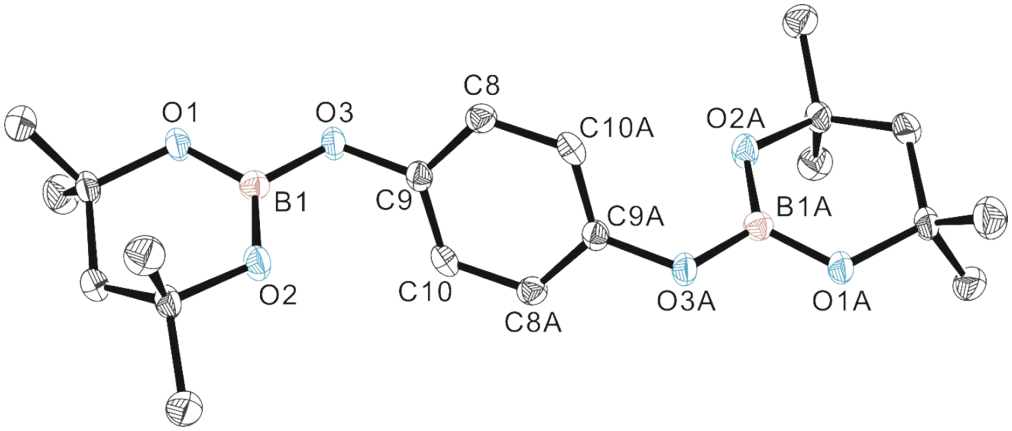


Fig. S6 Molecular structure of **5**.

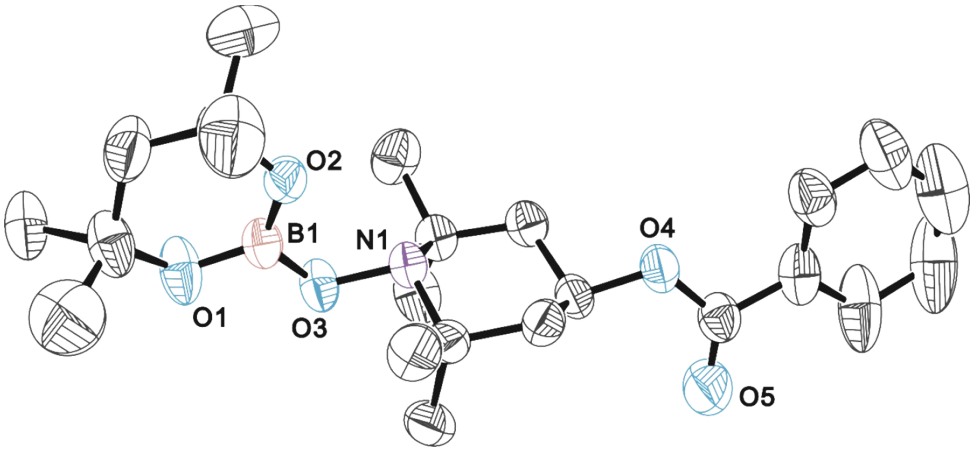


Fig. S7 Molecular structure of **6**.

Selected NMR spectra of compounds 1, 5 and 6

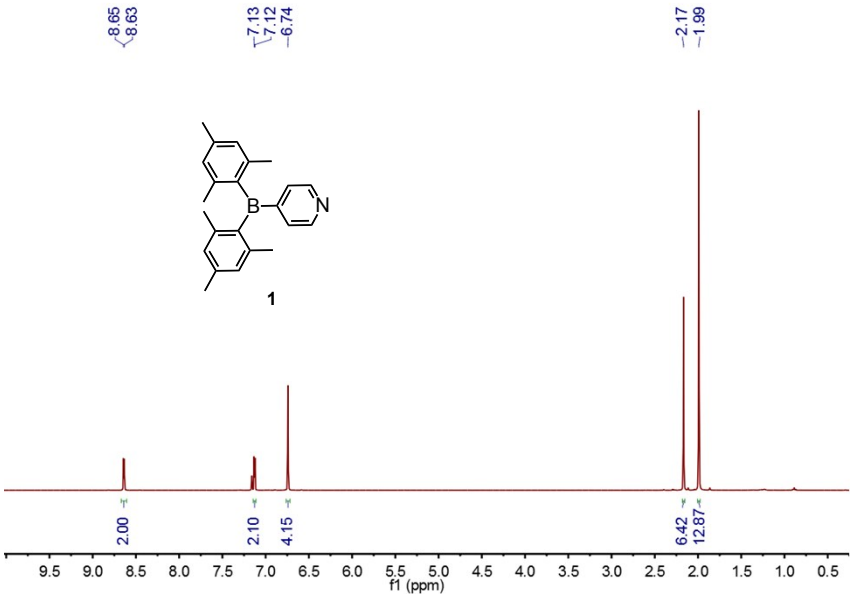


Fig. S8 ^{1}H NMR spectrum of **1** in C_6D_6.

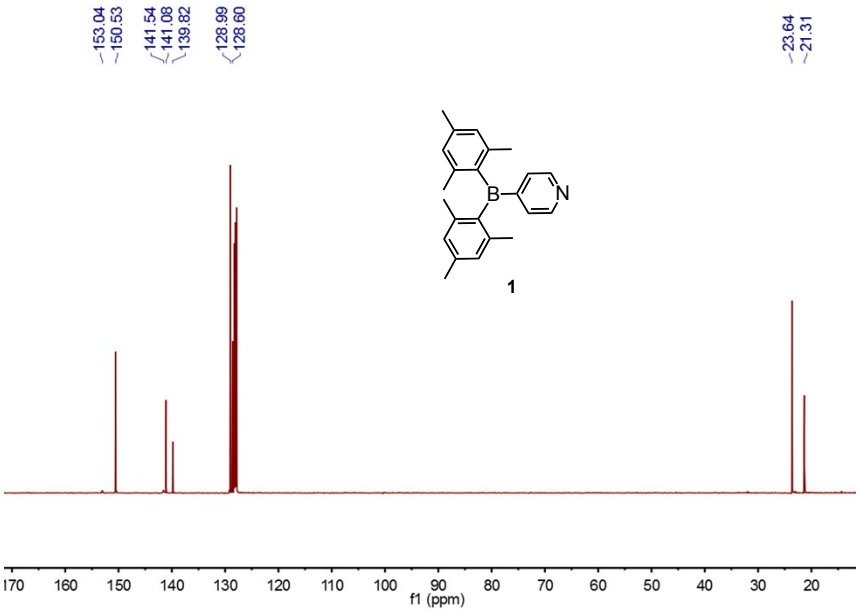


Fig. S9 ^{13}C NMR spectrum of **1** in C_6D_6.

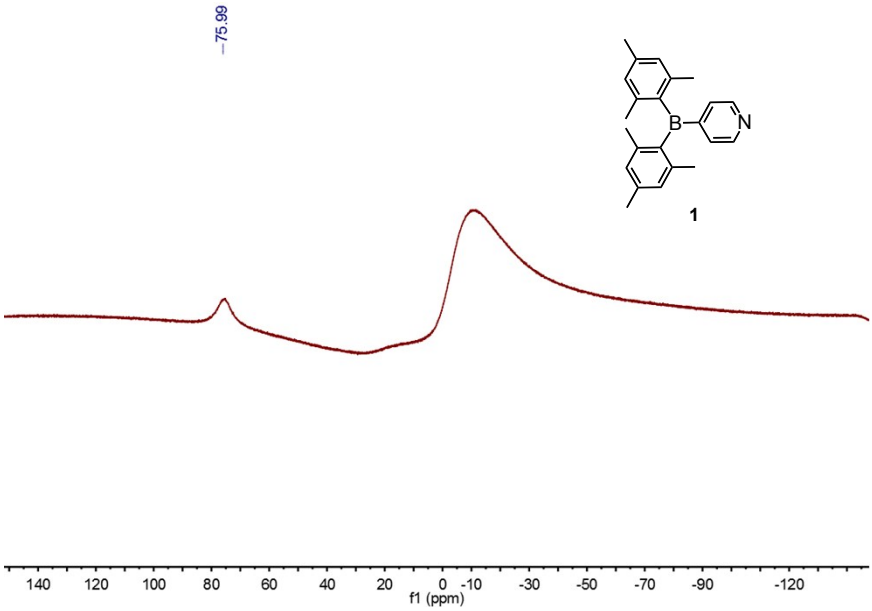


Fig. S10 ^{11}B NMR spectrum of **1** in C_6D_6.

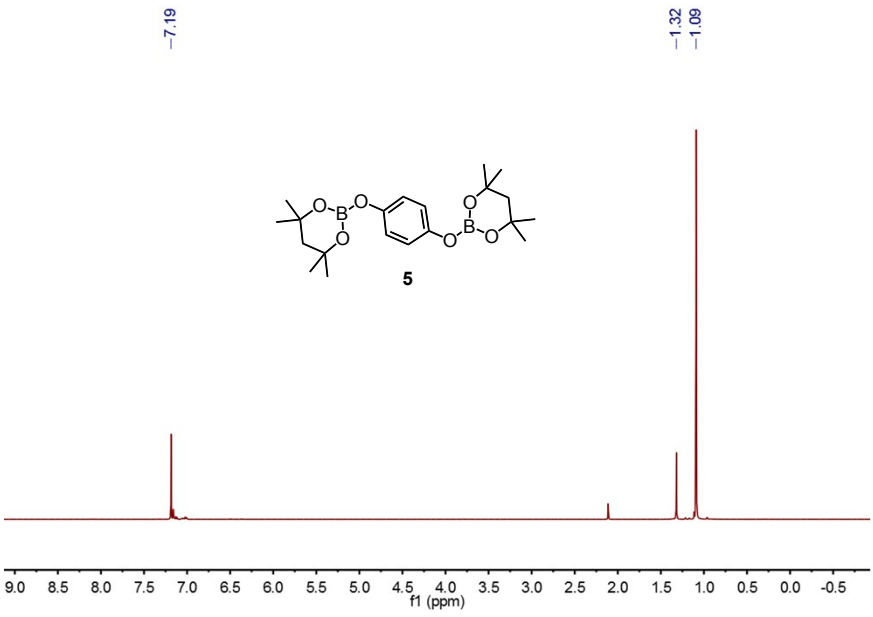


Fig. S11 ^{1}H NMR spectrum of **5** in C_6D_6.

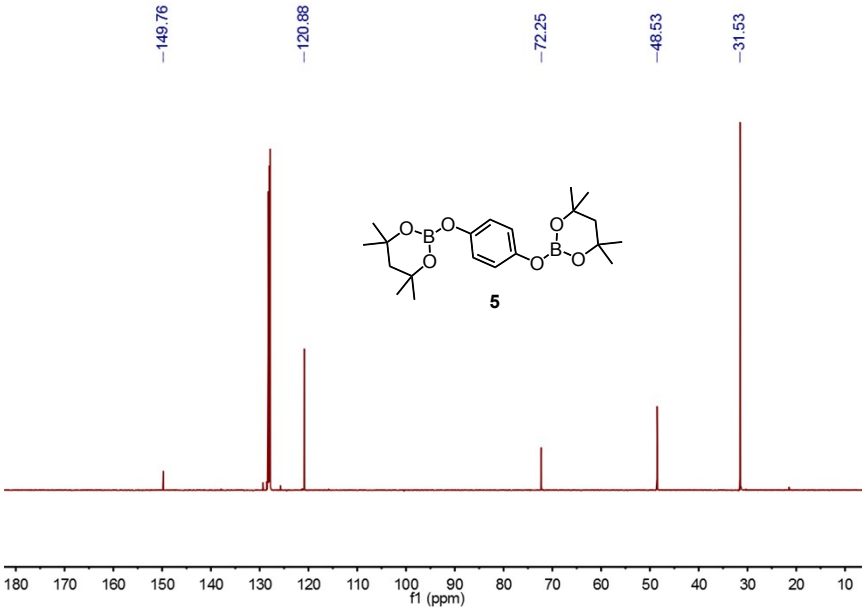


Fig. S12 ^{13}C NMR spectrum of **5** in C_6D_6.

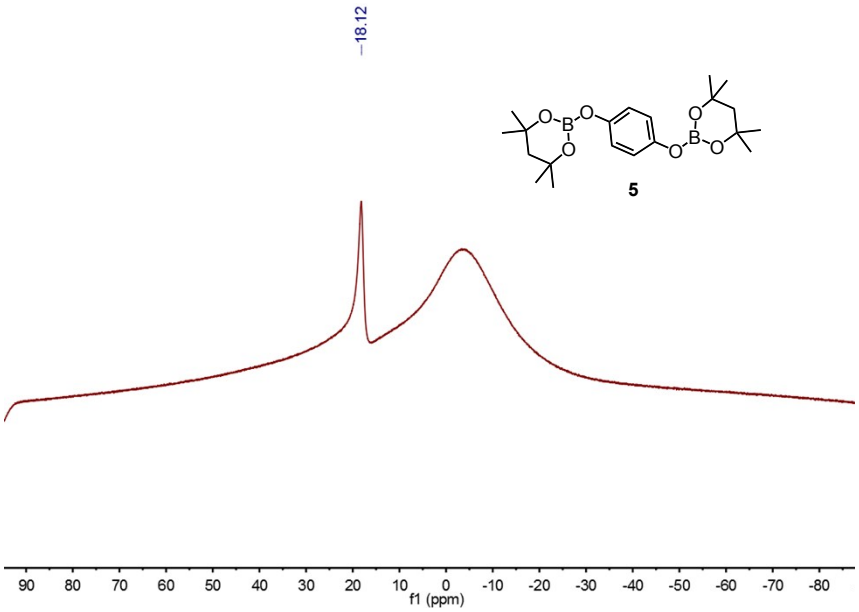


Fig. S13 ^{11}B NMR spectrum of **5** in C_6D_6.

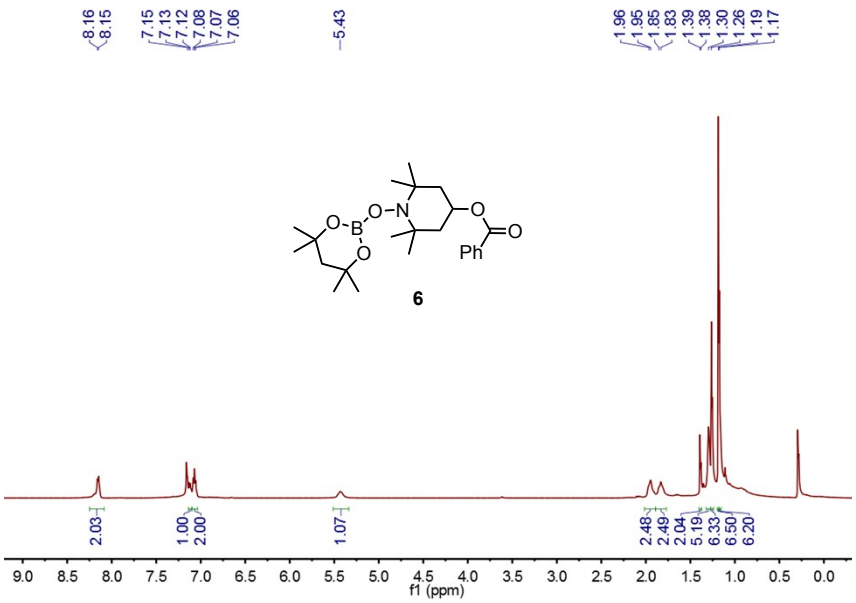


Fig. S14 ^{1}H NMR spectrum of **6** in C_6D_6.

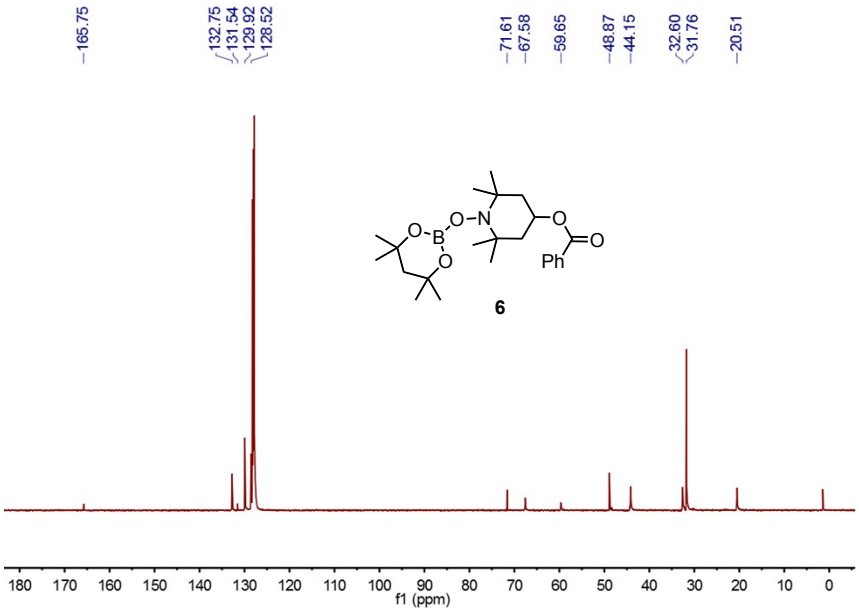


Fig. S15 ^{13}C NMR spectrum of **6** in C_6D_6.

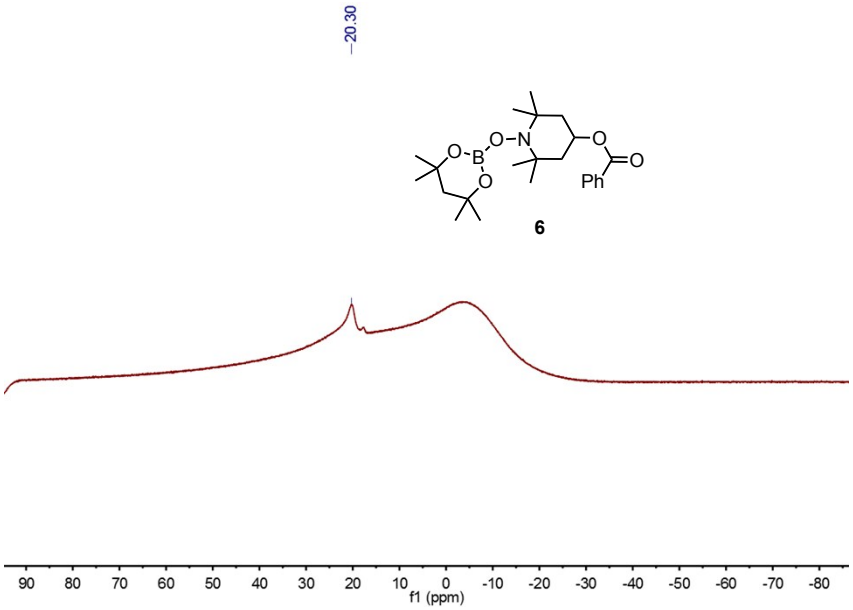


Fig. S16 ^{11}B NMR spectrum of **6** in C_6D_6.

Infra-red (IR) spectra of the new compounds

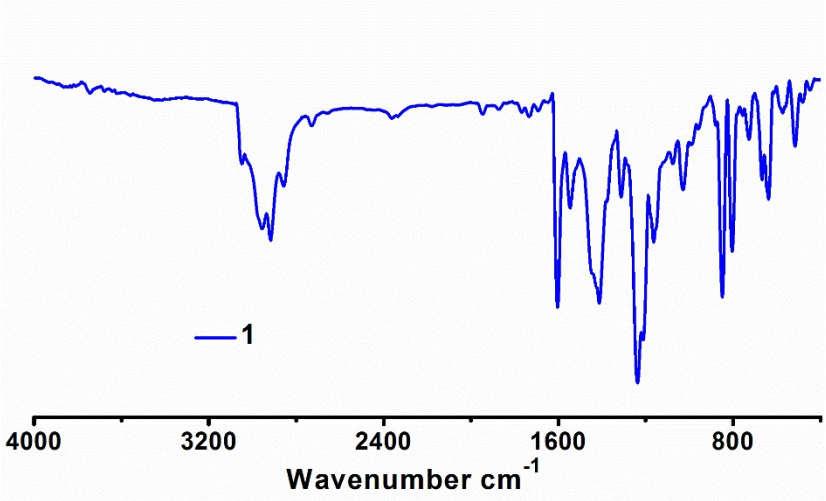


Fig. S17 IR spectrum of **1**.

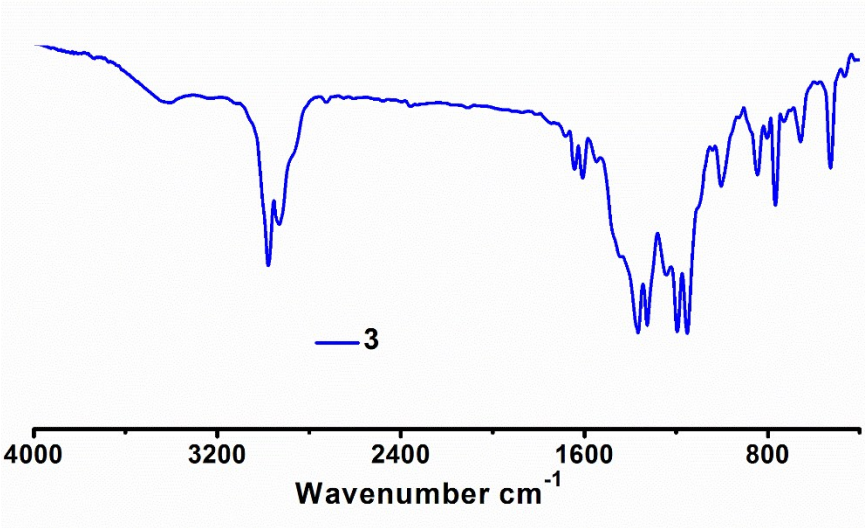


Fig. S18 IR spectrum of **3**.

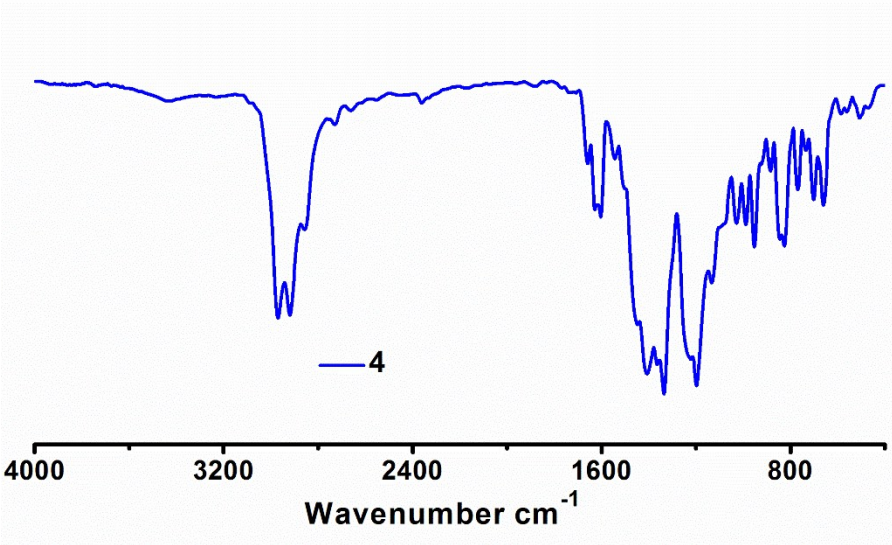


Fig. S19 IR spectrum of **4**.

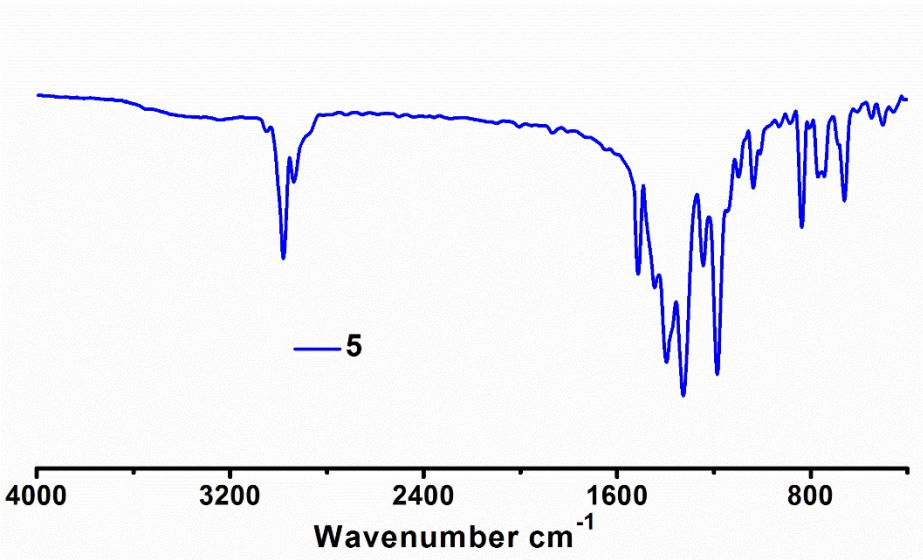


Fig. S20 IR spectrum of **5**.

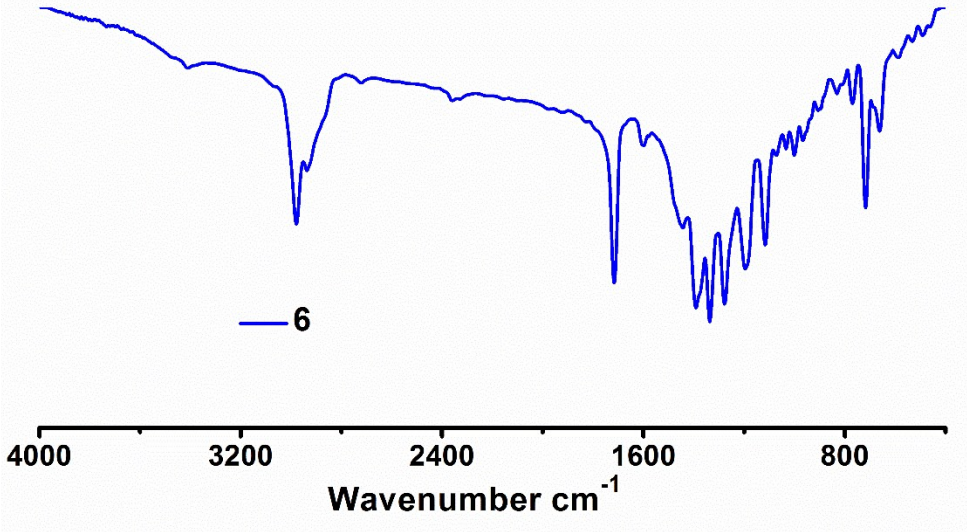


Fig. S21 IR spectrum of **6**.

Calculation details

All calculations were performed with the Gaussian 09 program suite.[S3] All the geometry optimizations were performed with the UB3LYP functional and 6-31G* basis set. Frequency calculations were carried out to confirm that all optimized geometries correspond to energy minima, and no imaginary frequency was found. The absolute energy and frequency values were shown as follows. The UV-Vis absorption spectra were calculated using the time-dependent DFT (TD-DFT) method and polarized continuum model (PCM) was adopted to consider solvent (n-hexane) effects.

Coordinates, absolute energy (E_a) and frequency values of the model molecules

3, E_a=-1422.36214 a.u., Frequency = 19.65 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates(Angstroms) X	Y	Z
1	8	0	4.418504	-1.146558	-0.40827
2	7	0	2.32895	0.00384	-0.027724
3	6	0	-2.864087	-1.395766	-0.032104
4	6	0	-0.549425	0.000568	-0.010589
5	6	0	-3.782737	-1.717653	-1.068946
6	6	0	0.238455	-1.147433	-0.363695
7	6	0	1.600598	-1.134655	-0.374452
8	1	0	2.199878	-1.99144	-0.65315
9	6	0	-2.662807	-2.370111	0.982744
10	6	0	-3.359805	-3.585214	0.950754
11	1	0	-3.196049	-4.305196	1.751684
12	6	0	-4.045595	-0.771346	-2.22233
13	1	0	-4.848146	-1.150809	-2.863685
14	1	0	-3.156024	-0.649958	-2.854018

15	1	0	-4.330514	0.226578	-1.876486
16	6	0	-4.446148	-2.948216	-1.075499
17	1	0	-5.135068	-3.169099	-1.889714
18	6	0	-4.256291	-3.89919	-0.069911
19	6	0	-1.70947	-2.154085	2.144327
20	1	0	-1.984516	-2.79223	2.991498
21	1	0	-1.700926	-1.11782	2.492605
22	1	0	-0.675676	-2.400261	1.871643
23	5	0	-2.0872	-0.000772	-0.00209
24	6	0	-5.017614	-5.204292	-0.075084
25	1	0	-4.5299	-5.955251	0.555808
26	1	0	-5.102336	-5.6164	-1.087404
27	1	0	-6.040315	-5.073533	0.304397
28	5	0	3.79239	0.00607	-0.038278
29	6	0	5.861598	-1.253887	-0.40988
30	6	0	6.486449	0.155816	-0.534954
31	8	0	4.419402	1.162997	0.315193
32	6	0	-2.865875	1.393013	0.036112
33	6	0	-3.774013	1.713714	1.082521
34	6	0	0.24	1.150102	0.333827
35	6	0	1.602173	1.140424	0.328433
36	1	0	2.202774	1.998503	0.600127
37	6	0	-2.67664	2.367601	-0.980868
38	6	0	-3.374982	3.581715	-0.941579
39	1	0	-3.220621	4.301902	-1.744205
40	6	0	-4.022775	0.767419	2.239014
41	1	0	-4.820305	1.144785	2.887833
42	1	0	-3.126742	0.649485	2.862196
43	1	0	-4.307758	-0.231704	1.896761
44	6	0	-4.439189	2.943266	1.095924
45	1	0	-5.119797	3.163158	1.917378
46	6	0	-4.261212	3.894474	0.088361

47	6	0	-1.73515	2.153163	-2.152382
48	1	0	-2.02288	2.787479	-2.99822
49	1	0	-1.72487	1.115994	-2.497819
50	1	0	-0.699715	2.405588	-1.891767
51	6	0	-5.024379	5.198437	0.101378
52	1	0	-4.542562	5.951134	-0.531977
53	1	0	-5.102061	5.608778	1.114966
54	1	0	-6.049704	5.066773	-0.270642
55	6	0	5.861563	1.283562	0.320705
56	1	0	7.560857	0.095855	-0.326744
57	1	0	6.388715	0.455769	-1.585723
58	6	0	6.219215	-2.079795	-1.651407
59	1	0	7.303419	-2.219467	-1.725777
60	1	0	5.745952	-3.065383	-1.597495
61	1	0	5.869338	-1.580721	-2.560701
62	6	0	6.269992	-2.025869	0.852515
63	1	0	5.825894	-3.026118	0.828855
64	1	0	7.358876	-2.133975	0.906991
65	1	0	5.926632	-1.534394	1.765317
66	6	0	6.171951	2.641398	-0.321832
67	1	0	5.709546	3.44753	0.25658
68	1	0	7.253018	2.816321	-0.357053
69	1	0	5.779727	2.683054	-1.343006
70	6	0	6.317798	1.297821	1.785996
71	1	0	7.405375	1.41381	1.851126
72	1	0	5.850611	2.140169	2.306009
73	1	0	6.037517	0.384937	2.315329
74	1	0	-0.260105	2.068125	0.627777
75	1	0	-0.262986	-2.066726	-0.651365

4, E_a=-1500.9842 a.u., Frequency = 10.33 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates(Angstroms) X	Y	Z
1	6	0	-5.95647	1.164827	-0.63068
2	6	0	-6.58277	0.285491	0.478854
3	6	0	-5.95396	-1.10847	0.70636
4	1	0	-6.48745	0.832192	1.425145
5	6	0	-1.70027	0.978701	-0.64226
6	6	0	-1.69488	-0.96678	0.701677
7	6	0	-0.33308	1.016565	-0.66029
8	1	0	-2.30412	1.703962	-1.17179
9	6	0	-0.32767	-1.00756	0.704245
10	1	0	-2.29435	-1.69042	1.238433
11	6	0	0.459219	0.003111	0.016646
12	8	0	-4.5187	1.000862	-0.64506
13	8	0	-4.51337	-0.9817	0.741772
14	6	0	-6.20803	2.644542	-0.31201
15	1	0	-5.75287	3.279674	-1.07862
16	1	0	-7.28244	2.857438	-0.27841
17	1	0	-5.77095	2.908627	0.656351
18	6	0	-6.46899	0.855738	-2.04386
19	1	0	-7.55109	1.016991	-2.10397
20	1	0	-5.98195	1.522006	-2.76299
21	1	0	-6.25893	-0.17194	-2.3468
22	6	0	-6.3629	-1.63199	2.087764
23	1	0	-7.44848	-1.7684	2.146102
24	1	0	-5.8819	-2.59584	2.282605
25	1	0	-6.0571	-0.93169	2.871558
26	6	0	-6.30207	-2.15254	-0.36406
27	1	0	-5.87427	-3.12051	-0.08416

28	1	0	-7.38717	-2.27016	-0.45894
29	1	0	-5.89678	-1.88471	-1.34251
30	5	0	-3.88691	0.007841	0.04236
31	7	0	-2.42437	0.006614	0.033496
32	5	0	2.011729	-0.00066	0.004887
33	6	0	2.840856	1.364035	0.05717
34	6	0	3.854944	1.668711	-0.89062
35	6	0	2.615939	2.309148	1.095777
36	6	0	4.586785	2.857321	-0.79176
37	6	0	3.383931	3.476872	1.17348
38	6	0	4.377622	3.774603	0.239363
39	1	0	5.344471	3.072467	-1.54392
40	1	0	3.196669	4.17592	1.98754
41	6	0	2.832569	-1.36979	-0.06104
42	6	0	3.861488	-1.67971	0.869128
43	6	0	2.58474	-2.31397	-1.09525
44	6	0	4.585217	-2.8721	0.757954
45	6	0	3.345066	-3.48591	-1.18566
46	6	0	4.353179	-3.78865	-0.269
47	1	0	5.354899	-3.09102	1.496704
48	1	0	3.140235	-4.18427	-1.99604
49	6	0	4.167402	0.754475	-2.05921
50	1	0	3.267287	0.487459	-2.62529
51	1	0	4.860119	1.240006	-2.75494
52	1	0	4.622902	-0.18556	-1.7318
53	6	0	1.553102	2.10963	2.16121
54	1	0	1.680356	2.837006	2.970495
55	1	0	0.541251	2.236059	1.758819
56	1	0	1.587898	1.108962	2.604605
57	6	0	1.504882	-2.11007	-2.14269
58	1	0	0.499507	-2.23609	-1.72414
59	1	0	1.533793	-1.10843	-2.58419

60	1	0	1.617847	-2.83576	-2.95558
61	6	0	4.198617	-0.76739	2.03233
62	1	0	4.644508	0.17437	1.697006
63	1	0	3.310841	-0.50386	2.619324
64	1	0	4.907754	-1.25315	2.711127
65	6	0	5.178786	-5.04718	-0.39874
66	1	0	4.606167	-5.85739	-0.86388
67	1	0	6.067751	-4.88037	-1.02267
68	1	0	5.531468	-5.39835	0.577389
69	6	0	5.211719	5.028873	0.355303
70	1	0	4.646735	5.846098	0.817601
71	1	0	6.102935	4.861196	0.975779
72	1	0	5.561106	5.370633	-0.62528
73	6	0	0.285065	2.12482	-1.48653
74	1	0	0.834489	2.842629	-0.87183
75	1	0	1.000067	1.727142	-2.21526
76	1	0	-0.48846	2.670574	-2.03766
77	6	0	0.297738	-2.11564	1.525213
78	1	0	0.840363	-2.83458	0.905888
79	1	0	1.020419	-1.71755	2.24619
80	1	0	-0.47056	-2.65992	2.085032
81	1	0	-7.65664	0.174695	0.289569

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