Supporting Information.

(2-picolyl)diethylborane dimer (1)

Output report of DFT calculation:

```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 4 (out of 168) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .10
Mechanics Wall Time: .45
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build 10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 160
Number of basis functions: 424
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -940.626796 0.029102 0.077856
2 -940.649522 0.020645 0.089849
3 -940.664342 0.010743 0.097891
4 -940.669859 0.006605 0.096225
5 -940.671424 0.007409 0.099683
6 -940.672450 0.004519 0.072160
7 -940.671231 0.007184 0.042964
8 -940.672815 0.001729 0.053431
9 -940.671708 0.006210 0.038806
10 -940.672878 0.001381 0.050595
11 -940.672177 0.005308 0.040578
12 -940.672931 0.000457 0.015865
13 -940.672854 0.002287 0.011634
14 -940.672944 0.000194 0.010165
15 -940.672948 0.000154 0.034407
16 -940.672954 0.000282 0.002973
17 -940.672956 0.000214 0.008391
18 -940.672958 0.000091 0.002727
19 -940.672959 0.000063 0.003436
20 -940.672959 0.000033 0.001251
Reason for exit: Successful completion
Quantum Calculation CPU Time : 2:38:58.09
Quantum Calculation Wall Time: 3:02:30.71
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 3.84
Properties Wall Time: 4.07
molecule M0001 terminated normally
End- molecule "M0001" Fri Apr 1 20:01:42 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
```

Atom	X	Y	Z
1 H H1	2.7980822	0.8979340	-1.7063889
2 C C1	1.8190135	1.3423212	-1.6245001
3 C C4	-0.6436380	2.4224970	-1.3364033
4 N N1	1.1196617	1.0263811	-0.5048910
5 C C6	1.3501434	2.1762195	-2.6207199
6 C C5	0.0815380	2.7380540	-2.4707326
7 C C3	-0.1336570	1.5558832	-0.3480952
8 H H6	1.9732503	2.3802024	-3.4847454
9 H H5	-0.3266652	3.4100641	-3.2206547
10 H H4	-1.6316289	2.8400533	-1.1775451
11 B B1	1.8968128	0.0860579	0.6641825
12 H H17	1.4628962	-1.8608233	1.6699389
13 C C14	0.8290281	-1.1022503	1.1994469
14 H H21	-0.4008666	1.0915993	1.7100233
15 C C15	-0.9951212	1.2004046	0.8077943
16 H H23	-1.6664207	2.0457870	0.9875109
17 B B2	-2.0191754	-0.1122937	0.5525715
18 H H33	0.1728521	-0.7235737	1.9784368
19 H H2	1.6030419	-3.2115237	-0.2088648
20 C C7	0.6411031	-2.8560824	-0.5603507
21 C C8	-1.7627877	-1.9001472	-1.3518664
22 C C9	0.0599986	-1.7647160	0.1158528
23 C C10	0.0172267	-3.4599476	-1.6364485
24 C C11	-1.2195028	-2.9618695	-2.0490516
25 N N2	-1.1652423	-1.3039868	-0.2898905
26 H H7	0.4802552	-4.3020262	-2.1436736
27 H H8	-1.7616157	-3.3854773	-2.8875064
28 H H10	-2.7215017	-1.4969116	-1.6367942
29 C C2	3.2252265	-0.6019402	-0.0243252
30 H H3	3.9382805	0.1735035	-0.3442701
31 H H9	2.9724913	-1.1565459	-0.9438119
32 C C12	4.0196209	-1.5467786	0.8973217
33 H H11	4.3002113	-1.0516592	1.8341545
34 H H12	4.9461929	-1.8937275	0.4219177
35 H H13	3.4488849	-2.4433319	1.1706662
36 C C13	2.2989808	1.0760751	1.9104449
37 H H14	1.4112236	1.4877072	2.4123991
38 H H16	2.7804406	0.4511622	2.6792063
39 C C16	3.2424668	2.2455466	1.5794339
40 H H15	3.4728422	2.8517365	2.4655845
41 H H18	2.8040665	2.9227263	0.8340972
42 H H19	4.1988225	1.8947467	1.1730221
43 C C17	-2.4982348	-0.8415038	1.9522464
44 H H22	-1.7837156	-1.6191773	2.2599174
45 H H24	-3.4308536	-1.3918357	1.7447976
46 C C18	-2.7344023	0.0659289	3.1740139
47 H H20	-1.8125251	0.5731580	3.4849255
48 H H25	-3.0907154	-0.5073464	4.0401850
49 H H26	-3.4766642	0.8468820	2.9756021
50 C C19	-3.2946555	0.3516735	-0.3768439
51 H H28	-3.9613213	-0.5074100	-0.5570062
52 H H29	-2.9686825	0.6814265	-1.3788047
53 C C20	-4.1982379	1.4552538	0.2061566
54 H H27	-3.6557376	2.3885158	0.4054799
55 H H30	-4.6549864	1.1433740	1.1514371

```
56 H H31 -5.0184773 1.7065384 -0.4794274
Point Group = C1 Order = 1 Nsymop = 1
Reason for exit: Successful completion
Properties CPU Time : 3.77
Properties Wall Time: 4.27
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:35:30 2012
```

(2-picolyl)borabicyclononane dimer (2)

Output report of DFT calculation:

```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 3 (out of 216) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .17
Mechanics Wall Time: .35
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build 10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 208
Number of basis functions: 560
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -1250.276293 0.023134 0.066956
2 -1250.298293 0.018079 0.067323
3 -1250.312946 0.010069 0.075956
4 -1250.319487 0.003624 0.083805
5 -1250.320778 0.004556 0.108206
6 -1250.321504 0.003640 0.137545
7 -1250.321846 0.002053 0.065618
8 -1250.321603 0.003033 0.023488
9 -1250.322010 0.001329 0.019873
10 -1250.321974 0.001354 0.016472
11 -1250.322043 0.000657 0.024778
12 -1250.322049 0.000825 0.015465
13 -1250.322065 0.000235 0.004949
14 -1250.322060 0.000679 0.004891
15 -1250.322069 0.000081 0.003913
16 -1250.322068 0.000235 0.002747
17 -1250.322069 0.000022 0.001266
18 -1250.322069 0.000012 0.001056
Reason for exit: Successful completion
Quantum Calculation CPU Time : 4:45:52.16
Quantum Calculation Wall Time: 5:23:06.65
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 7.28
Properties Wall Time: 7.52
molecule M0001 terminated normally
End- molecule "M0001" Thu Apr 7 22:05:27 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
--------- ------------- ------------- -------------
1 H H1 -1.3058376 -1.2109178 3.1191152
2 C C1 -0.4059541 -1.4727700 2.5732034
3 C C4 1.8031400 -2.0397198 1.1181054
```

```
4 C C2 0.0713453 -0.5480372 1.6217070
5 C C6 0.2237984 -2.6853721 2.7834474
6 C C5 1.3456201 -2.9903863 2.0090474
7 N N2 1.2315149 -0.8209470 0.9459645
8 H H6 -0.1585033 -3.3890106 3.5179013
9 H H5 1.8632180 -3.9398475 2.0913368
10 H H4 2.6566175 -2.2451517 0.4937242
11 H H7 -2.7920336 -2.1640634 -0.4036889
12 C C7 -1.9018047 -2.0458647 -1.0009243
13 C C8 0.3542314 -1.6711787 -2.4468210
14 C C9 -1.4726694 -3.0707003 -1.8208082
15 N N1 -1.2722857 -0.8484401 -0.8863255
16 C C11 -0.0975199 -0.6646107 -1.5686674
17 C C12 -0.3219465 -2.8681054 -2.5870947
18 H H8 -2.0373515 -3.9956631 -1.8617472
19 H H11 0.0405457 -3.6337081 -3.2676159
20 H H12 1.2685445 -1.4809220 -2.9987221
21 H H13 -1.2687576 0.9452757 2.2077102
22 C C13 -0.7650380 0.6290060 1.2917232
23 H H14 -0.1605011 1.4660519 0.9606665
24 B B2 -1.9584126 0.3253556 0.1219298
25 B B1 1.9505114 0.2627891 -0.1270845
26 H H25 0.1898129 1.3885400 -1.0760145
27 C C16 0.7751040 0.5092629 -1.3285415
28 H H26 1.2950499 0.7369750 -2.2622270
29 C C18 -3.3894443 -0.1896221 0.7586655
30 H H3 -3.2949791 -1.1358329 1.3185852
31 C C17 -2.3555658 1.7109921 -0.6763358
32 H H16 -1.5007441 2.1818688 -1.1777732
33 C C19 -4.5173047 -0.3743739 -0.3232245
34 H H17 -5.4298654 0.1306392 0.0225356
35 H H18 -4.8049545 -1.4325660 -0.4078484
36 C C20 -3.4695692 1.5162354 -1.7575684
37 H H15 -4.2261433 2.3070759 -1.6477929
38 H H20 -3.0452797 1.6606642 -2.7602057
39 C C21 -4.1712328 0.1449523 -1.7336081
40 H H23 -3.5254575 -0.5837644 -2.2369080
41 H H24 -5.0870321 0.1887228 -2.3391982
42 C C22 -2.8240080 2.7405510 0.3908026
43 H H9 -3.0740058 3.6932773 -0.1006435
44 H H10 -1.9946389 2.9682829 1.0737892
45 C C23 -3.8777943 0.8597008 1.7966254
46 H H27 -3.1885658 0.8990715 2.6505190
47 H H28 -4.8417711 0.5352922 2.2174069
48 C C24 -4.0413815 2.2697530 1.2042996
49 H H19 -4.2550430 2.9868305 2.0088607
50 H H30 -4.9287677 2.2835135 0.5565719
51 C C26 2.3554670 1.6834873 0.5891102
52 H H29 1.4973862 2.2069810 1.0317253
53 C C25 3.3962310 -0.3112091 -0.6835386
54 H H31 3.3199351 -1.3074937 -1.1578233
55 C C27 2.8789384 2.6498220 -0.5098824
56 H H2 3.2115710 3.5930891 -0.0497989
57 H H33 2.0256372 2.9221076 -1.1457380
58 C C28 3.8980904 0.6308529 -1.8118333
59 H H35 3.2269201 0.5444180 -2.6765927
60 H H36 4.8785650 0.2850073 -2.1737943
```

```
61 C C29 4.0171442 2.1203559 -1.4150777
62 H H22 4.0592607 2.7302025 -2.3283078
63 H H37 4.9805303 2.2812881 -0.9213407
64 C C30 3.3504579 1.4679770 1.7529529
65 H H21 3.5774572 2.4264056 2.2452587
66 H H40 2.8567413 0.8508883 2.5191416
67 C C31 4.6719182 0.7954934 1.3435955
68 H H39 5.3148790 1.5318659 0.8516702
69 H H42 5.2219945 0.4865495 2.2435616
70 C C32 4.4834327 -0.4358614 0.4306887
71 H H43 5.4506693 -0.6858294 -0.0328828
72 H H44 4.2563036 -1.2877693 1.0842154
Point Group = C1 Order = 1 Nsymop = 1
Reason for exit: Successful completion
Properties CPU Time : 7.12
Properties Wall Time: 7.34
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:42:00 2012
```

(2-picolyl)diphenylborane dimer (3)

Output report of DFT calculation:

```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 8 (out of 216) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .16
Mechanics Wall Time: .27
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build 10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 224
Number of basis functions: 664
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -1550.320910 0.027132 0.070842
2 -1550.348324 0.018871 0.083755
3 -1550.366103 0.012338 0.083429
4 -1550.374923 0.005624 0.081243
5 -1550.377175 0.004877 0.096910
6 -1550.378322 0.002984 0.074539
7 -1550.378469 0.003230 0.051603
8 -1550.378878 0.002470 0.029875
9 -1550.378881 0.002564 0.022453
10 -1550.379031 0.001806 0.026273
11 -1550.379073 0.001466 0.020445
12 -1550.379116 0.001309 0.027690
13 -1550.379159 0.000921 0.027986
14 -1550.379179 0.000965 0.038899
15 -1550.379215 0.000483 0.014485
16 -1550.379229 0.000389 0.020381
17 -1550.379241 0.000549 0.012364
18 -1550.379245 0.000510 0.008427
19 -1550.379246 0.000314 0.002672
20 -1550.379246 0.000165 0.001493
Reason for exit: Successful completion
Quantum Calculation CPU Time : 6:30:01.55
Quantum Calculation Wall Time: 86:11:20.16
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 11.35
Properties Wall Time: 11.69
molecule M0001 terminated normally
End- molecule "M0001" Tue Apr 5 10:13:17 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
--------- ------------ ------------ -------------
1 H H1 -3.1197982 1.7026499 -1.5586223
```

2	C	C1	-2.1197868	1.6341422	-1.9599082
3	C	C4	0.4030637	1.3500829	-2.8918196
4	N	N1	-1.3047574	0.7463124	-1.3335952
5	C	C6	-1.7289890	2.4138145	-3.0303222
6	C	C5	-0.4204667	2.2834369	-3.4963178
7	C	C3	-0.0388069	0.5513451	-1.8204379
8	H	H6	-2.4376308	3.1019561	-3.4777700
9	H	H5	-0.0571070	2.8827711	-4.3263793
10	H	H4	1.4154038	1.2077274	-3.2469332
11	B	B1	-1.9463663	-0.1381515	-0.0750926
12	H	H17	-1.4477436	-0.4267693	2.0874549
13	C	C14	-0.8360478	-0.2399252	1.1990620
14	B	B2	1.9152107	-0.0783197	-0.0289387
15	H	H2	0.2376239	-1.3467335	-0.9361177
16	C	C15	0.8507333	-0.5053612	-1.2572496
17	H	H3	1.4573070	-0.8831391	-2.0865310
18	H	H18	-0.1949255	-1.1088765	1.0714391
19	H	H7	-1.3984661	1.7563029	2.8875470
20	C	C7	-0.4698081	1.9479612	2.3635636
21	C	C8	1.8471687	2.3287224	1.0058162
22	C	C9	-0.0079647	0.9625725	1.4701192
23	C	C10	0.2212748	3.1320084	2.5547872
24	C	C11	1.3978519	3.3400072	1.8329761
25	N	N2	1.1962553	1.1502943	0.8413004
26	H	H9	-0.1503300	3.8817424	3.2478992
27	H	H10	1.9738804	4.2548094	1.9195880
28	H	H12	2.7726910	2.4284657	0.4574472
29	H	H8	-1.7636252	-2.7030236	1.1381581
30	C	C2	-2.1381962	-2.7841308	0.1207153
31	C	C12	-3.0978049	-3.0787791	-2.4665696
32	C	C13	-2.4720221	-4.0532278	-0.3585329
33	C	C16	-2.2714443	-1.6247297	-0.6672852
34	C	C17	-2.7644245	-1.8164019	-1.9725144
35	C	C18	-2.9515905	-4.2077333	-1.6590696
36	H	H11	-2.3508920	-4.9216270	0.2850489
37	H	H14	-2.8942830	-0.9591696	-2.6307883
38	H	H15	-3.2075707	-5.1938032	-2.0388581
39	H	H16	-3.4707630	-3.1804944	-3.4835014
40	H	H19	-4.4453197	3.6095656	1.7192913
41	C	C19	-4.4623443	2.5549905	1.4513947
42	C	C20	-4.4720119	-0.1276101	0.7364811
43	C	C21	-5.6055341	1.7899244	1.6891533
44	C	C22	-3.3382728	1.9690022	0.8660860
45	C	C23	-3.2969443	0.6076782	0.4903758
46	C	C24	-5.6030571	0.4436624	1.3267921
47	H	H20	-6.4846533	2.2389241	2.1449551
48	H	H21	-2.4704790	2.6008559	0.6878659
49	H	H23	-6.4866561	-0.1674777	1.4975368
50	H	H24	-4.5029833	-1.1782843	0.4639728
51	H	H13	2.1820878	-0.2378676	2.8519089
52	C	C25	2.3228620	-1.2085951	2.3795530
53	C	C26	2.6748353	-3.7215816	1.2551700
54	C	C27	2.1744317	-1.3338353	0.9859365
55	C	C28	2.6357286	-2.2992258	3.1949547
56	C	C29	2.8133649	-3.5645069	2.6354323
57	C	C30	2.3622407	-2.6235095	0.4529828
58	H	H25	2.7377209	-2.1591146	4.2690403

```
59 H H26 3.0547443 -4.4169953 3.2655390
60 H H27 2.2697914 -2.7742962 -0.6202892
61 H H28 2.8096111 -4.7011788 0.8019279
62 C C31 3.3974524 0.3931151 -0.5703677
63 C C32 6.0568737 1.0534440 -1.3983266
64 C C33 3.7747992 0.4421100 -1.9235913
65 C C34 4.4342905 0.6634143 0.3523676
66 C C35 5.7288857 0.9971741 -0.0414868
67 C C36 5.0720000 0.7631595 -2.3386775
68 H H30 3.0551722 0.1902819 -2.6964420
69 H H31 4.2250787 0.5910632 1.4175715
70 H H32 6.4878761 1.1962458 0.7118756
71 H H33 5.3082730 0.7801975 -3.4003902
72 H H34 7.0667224 1.3043457 -1.7131225
Point Group = C1 Order = 1 Nsymop = 1
Reason for exit: Successful completion
Properties CPU Time : 11.11
Properties Wall Time: 11.38
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:43:45 2012
```

9-(2-picolyl)-9-borafluorene dimer (4)

Output report of DFT calculation:

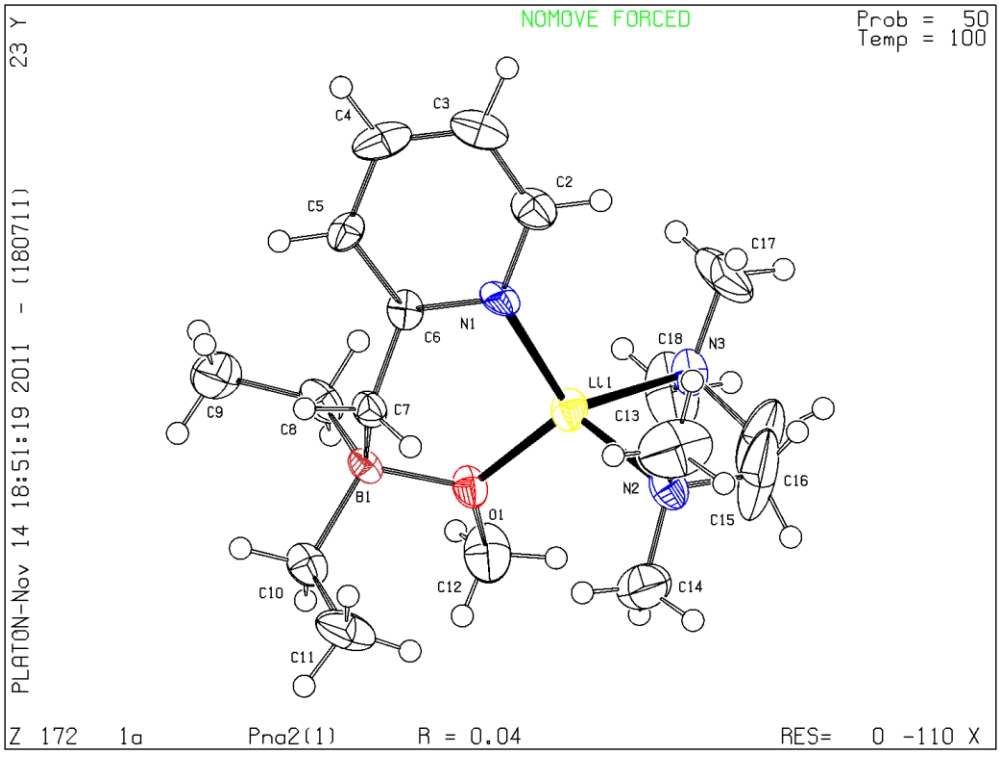
```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 4 (out of 204) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .16
Mechanics Wall Time: .32
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build 10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 216
Number of basis functions: 656
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -1547.951691 0.079560 0.120504
2 -1547.979705 0.045111 0.104902
3 -1547.996987 0.021824 0.108152
4 -1548.004160 0.009928 0.114036
5 -1548.004700 0.008146 0.063103
6 -1548.005972 0.004362 0.028929
7 -1548.005979 0.004872 0.016465
8 -1548.006173 0.001212 0.011367
9 -1548.006191 0.001129 0.022210
10 -1548.006214 0.000940 0.018571
11 -1548.006224 0.000859 0.037417
12 -1548.006268 0.000977 0.124876
13 -1548.006336 0.001703 0.023872
14 -1548.006409 0.001187 0.070167
15 -1548.006485 0.000811 0.016544
16 -1548.006501 0.000422 0.023196
17 -1548.006514 0.000404 0.007575
18 -1548.006516 0.000382 0.002994
19 -1548.006518 0.000151 0.001156
Reason for exit: Successful completion
Quantum Calculation CPU Time : 5:46:12.20
Quantum Calculation Wall Time: 25:28:48.70
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 10.88
Properties Wall Time: 11.17
molecule M0001 terminated normally
End- molecule "M0001" Thu Apr 7 11:01:55 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry enabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
--------- ------------- ------------- -------------
1 H H1 -1.4748441 3.2963112 0.8408085
2 C C1 -0.4909715 2.9141119 1.0854475
```

```
3 C C4 1.9594040 1.8885471 1.6195121
4 C C31 -0.0345093 1.7830155 0.3825868
5 C C6 0.2832066 3.5259620 2.0557354
6 C C5 1.5477239 2.9995648 2.3267086
7 N N3 1.2006532 1.2748894 0.6736895
8 H H6 -0.0842683 4.4016224 2.5833105
9 H H5 2.2092633 3.4372342 3.0660860
10 H H4 2.9289122 1.4419703 1.7880005
11 H H7 -2.9289122 -1.4419703 1.7880005
12 C C7 -1.9594040 -1.8885471 1.6195121
13 C C8 0.4909715 -2.9141119 1.0854475
14 C C9 -1.5477239 -2.9995648 2.3267086
15 N N1 -1.2006532 -1.2748894 0.6736895
16 C C39 0.0345093 -1.7830155 0.3825868
17 C C12 -0.2832066 -3.5259620 2.0557354
18 H H8 -2.2092633 -3.4372342 3.0660860
19 H H11 0.0842683 -4.4016224 2.5833105
20 H H12 1.4748441 -3.2963112 0.8408085
21 B B2 -1.9392970 -0.0525140 -0.1555820
22 B B1 1.9392970 0.0525140 -0.1555820
23 H H2 4.5134491 -2.2508282 3.3652093
24 C C2 4.4710111 -1.7510534 2.4000990
25 H H3 2.3715113 -1.3206215 2.5611364
26 C C11 3.2573654 -1.2252920 1.9348950
27 C C13 5.5829321 -0.9776529 0.3928933
28 C C16 3.1808366 -0.5759261 0.6985348
29 C C17 5.6274386 -1.6320389 1.6264039
30 C C18 4.3718010 -0.4479525 -0.0613107
31 H H9 6.5672944 -2.0431611 1.9871612
32 H H10 6.0997236 0.3652831 -2.1970197
33 H H14 6.4893742 -0.8799565 -0.2005557
34 C C21 2.7595090 0.6625425 -1.4243638
35 C C22 2.3648616 1.3967055 -2.5445375
36 C C23 4.1241197 0.2983928 -1.3119471
37 C C24 3.2938044 1.7626795 -3.5272702
38 H H20 1.3278407 1.7026409 -2.6703193
39 H H21 2.9707168 2.3389308 -4.3911088
40 C C25 4.6335964 1.3886677 -3.4020994
41 H H23 5.3512497 1.6719499 -4.1683551
42 C C26 5.0547393 0.6525247 -2.2924283
43 H H15 -4.5134491 2.2508282 3.3652093
44 C C19 -4.4710111 1.7510534 2.4000990
45 H H19 -6.5672944 2.0431611 1.9871612
46 C C20 -5.6274386 1.6320389 1.6264039
47 C C27 -3.1808366 0.5759261 0.6985348
48 C C28 -5.5829321 0.9776529 0.3928933
49 C C29 -3.2573654 1.2252920 1.9348950
50 C C30 -4.3718010 0.4479525 -0.0613107
51 H H25 -2.3715113 1.3206215 2.5611364
52 C C33 -5.0547393 -0.6525247 -2.2924283
53 C C34 -4.6335964 -1.3886677 -3.4020994
54 C C35 -4.1241197 -0.2983928 -1.3119471
55 C C36 -3.2938044 -1.7626795 -3.5272702
56 H H31 -5.3512497 -1.6719499 -4.1683551
57 H H32 -2.9707168 -2.3389308 -4.3911088
58 C C37 -2.3648616 -1.3967055 -2.5445375
59 H H33 -1.3278407 -1.7026409 -2.6703193
```

```
60 C C38 -2.7595090 -0.6625425 -1.4243638
61 H H35 -6.0997236 -0.3652831 -2.1970197
62 H H36 -6.4893742 0.8799565 -0.2005557
63 C C15 0.9100013 -1.1665528 -0.6524792
64 H H16 0.3257673 -0.8754207 -1.5218528
65 H H22 1.5965099 -1.9440254 -1.0040287
66 H H13 -0.3257673 0.8754207 -1.5218528
67 C C3 -0.9100013 1.1665528 -0.6524792
68 H H18 -1.5965099 1.9440254 -1.0040287
Point Group = CN Order = 2 Nsymop = 2
Reason for exit: Successful completion
Properties CPU Time : 10.67
Properties Wall Time: 10.94
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:45:06 2012
```

(2-picolyl)diethylborane LiOMe-TMEDA (1a)

1.0 g (10.7 mmol) of 2-picoline and 1.25 g (10.8 mmol) of TMEDA were mixed in a flask and 4.3 mL of 2.5 M n-BuLi solution in hexane was added via syringe. The solution was cooled to -78°C, upon which brownish red crystals formed. To 10 mL THF, 2.7 mL of 4 M solution of diethylmethoxyborane in THF was added. The diethylmethoxyborane solution was added to the reaction via cannula, and the solution was allowed to warm to room temperature overnight. The solvent was removed in vacuo, and the product was dissolved in pentane. Crystals of **1a** were obtained by cooling the solution to -78°C. The supernatant was removed by cannula and the product was washed with pentane. The product was dried in vacuo. Yield: 2.16 g (64%). Mp: 68-70°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.78-0.92 (4 H, m, CH_2CH$_3$), 1.26 (6 H, t, 7.6, CH$_2$CH_3), 1.71 (4 H, s, TMEDA CH_2), 1.84 (12 H, s, TMEDA CH_3), 2.22 (2 H, s, CH_2), 3.38 (3 H, s, OCH_3), 6.51 (1 H, dt, J 6.0 and 1.5, *H*3), 7.02-7.15 (2 H, m, *H*4 and *H*5), 7.81 (1 H, td, J 5.4 and 1.0, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 11.5 (CH$_2$*C*H$_3$), 15.6 (br, *C*H$_2$CH$_3$), 38.9 (*C*7), 45.9 (TMEDA *C*H$_3$), 50.3 (O*C*H$_3$), 56.8 (TMEDA *C*H$_2$), 116.8 (*C*3), 124.8 (*C*4), 136.2 (*C*5), 146.3 (*C*2). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.87. HRMS (ESI) m/z calcd for $C_{17}H_{35}BLiN_3O$ (**1a**$^+$): 315.30332, found: 315.35429.



Output report of DFT calculation:

```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 4 (out of 174) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .11
Mechanics Wall Time: .58
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build
10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 162
Number of basis functions: 415
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -940.795782 0.039829 0.074126
2 -940.827084 0.020996 0.080160
3 -940.841819 0.011059 0.105537
4 -940.848388 0.006623 0.078754
5 -940.851498 0.004622 0.104662
6 -940.853516 0.004122 0.077931
7 -940.854995 0.003584 0.087572
8 -940.855999 0.003781 0.082549
9 -940.857184 0.003968 0.071547
10 -940.857878 0.002284 0.071175
11 -940.858288 0.001769 0.110430
12 -940.858523 0.001567 0.119820
13 -940.858680 0.002100 0.084623
14 -940.858772 0.001600 0.060520
15 -940.858849 0.000658 0.111365
16 -940.858932 0.000893 0.155331
17 -940.859034 0.001436 0.156897
18 -940.859092 0.001395 0.039883
19 -940.859177 0.001011 0.100706
20 -940.859255 0.000658 0.067401
21 -940.859293 0.000581 0.126126
22 -940.859340 0.000648 0.202411
23 -940.859406 0.000607 0.122544
24 -940.859421 0.000793 0.080034
25 -940.859454 0.000500 0.012484
26 -940.859475 0.000342 0.027062
27 -940.859482 0.000285 0.018280
28 -940.859492 0.000512 0.032030
29 -940.859506 0.000796 0.097793
30 -940.859533 0.000789 0.024158
```

```
31 -940.859545 0.000579 0.033818
32 -940.859559 0.000265 0.013219
33 -940.859568 0.000290 0.016978
34 -940.859576 0.000257 0.021191
35 -940.859583 0.000145 0.014384
36 -940.859589 0.000179 0.018089
37 -940.859598 0.000272 0.029127
38 -940.859610 0.000474 0.046257
39 -940.859627 0.000447 0.052829
40 -940.859644 0.000422 0.015988
41 -940.859657 0.000325 0.032085
42 -940.859669 0.000648 0.021866
43 -940.859675 0.000475 0.015472
44 -940.859680 0.000231 0.013742
45 -940.859682 0.000093 0.004363
46 -940.859682 0.000091 0.004651
Reason for exit: Successful completion
Quantum Calculation CPU Time : 5:43:17.05
Quantum Calculation Wall Time: 6:44:11.73
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 3.84
Properties Wall Time: 4.31
molecule M0001 terminated normally
End- molecule "M0001" Thu Jun 9 23:45:10 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
--------- ------------- ------------- -------------
1 C C1 1.2604676 -1.6833634 0.4134571
2 C C4 0.2634590 -4.0104618 -0.7326062
3 N N1 -0.0177615 -1.7135900 -0.0459215
4 C C6 2.0777554 -2.8278983 0.3020033
5 C C5 1.5837698 -3.9892985 -0.2713062
6 C C3 -0.4827254 -2.8483020 -0.5951016
7 H H6 3.0966442 -2.7815238 0.6738188
8 H H5 2.2128270 -4.8722447 -0.3545507
9 H H3 -1.5135263 -2.8205801 -0.9417575
10 H H4 -0.1726462 -4.8962578 -1.1833120
11 B B1 2.1186443 0.8672891 -0.0300786
12 C C7 3.1584555 0.4667405 -1.2386138
13 H H1 3.6285913 1.3811974 -1.6392568
14 H H11 4.0020328 -0.0925197 -0.8003077
15 C C8 2.6192370 -0.3454761 -2.4308752
16 H H10 1.8023191 0.1806566 -2.9436250
17 H H12 2.2185438 -1.3167090 -2.1181982
18 H H13 3.3945765 -0.5460251 -3.1845645
19 C C9 2.7184245 2.0799293 0.9096488
20 H H9 2.7763121 3.0100766 0.3211866
21 H H15 2.0131662 2.3052032 1.7302438
22 C C10 4.1118812 1.8453218 1.5192691
```

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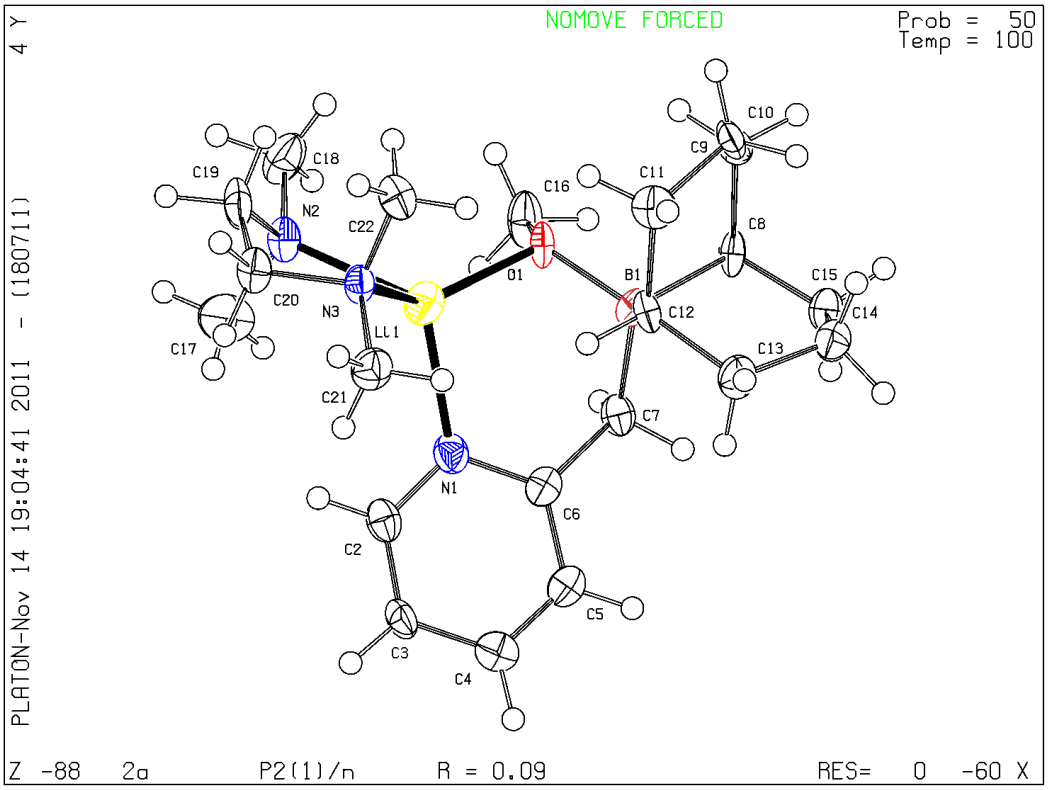
23 H H14 4.8653614 1.6865913 0.7374346
24 H H16 4.1332822 0.9581210 2.1669165
25 H H17 4.4534255 2.6927870 2.1308104
26 Li Li1 -0.7414296 0.2459934 -0.1515702
27 C C11 0.7515604 2.4411237 -1.4384590
28 H H8 0.9748431 3.3624636 -0.8811064
29 H H21 -0.2312286 2.5628356 -1.9104857
30 H H22 1.4978722 2.3487774 -2.2397958
31 N N2 -1.9218460 0.7664012 1.6670442
32 N N3 -2.7842695 0.4336329 -1.1861972
33 C C12 -3.7052317 0.3533514 -0.0361785
34 H H29 -4.7245802 0.6754018 -0.3192187
35 H H30 -3.7781943 -0.6996334 0.2545360
36 C C14 -3.2396336 1.1839947 1.1612523
37 H H31 -4.0114399 1.1320975 1.9509609
38 H H32 -3.1665966 2.2371721 0.8718034
39 C C13 -1.3164897 1.8352288 2.4758637
40 H H18 -0.3232477 1.5234701 2.8075020
41 H H24 -1.9254926 2.0786062 3.3644463
42 H H26 -1.1985320 2.7380151 1.8703594
43 C C15 -2.0130372 -0.4660204 2.4626829
44 H H23 -1.0108146 -0.7647384 2.7797300
45 H H27 -2.4226071 -1.2812270 1.8615888
46 H H28 -2.6455684 -0.3337434 3.3587643
47 C C16 -2.8685461 1.7428729 -1.8495590
48 H H25 -2.2110421 1.7452086 -2.7225781
49 H H33 -2.5377123 2.5406882 -1.1811891
50 H H34 -3.8969265 1.9665453 -2.1859452
51 C C17 -3.0988829 -0.6135476 -2.1672992
52 H H20 -2.3486780 -0.6071129 -2.9635621
53 H H35 -4.0954875 -0.4736779 -2.6224911
54 H H36 -3.0806356 -1.5940772 -1.6849533
55 H H2 1.0138533 -0.0381626 1.7216622
56 C C2 1.7588835 -0.4154780 1.0044733
57 H H7 2.6651572 -0.6267180 1.5825535
58 O O1 0.7369544 1.3068295 -0.6018146
Point Group = C1 Order = 1 Nsymop = 1
Reason for exit: Successful completion
Properties CPU Time : 3.73
Properties Wall Time: 3.90
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:46:42 2012
```

(2-picolyl)borabicyclononane LiOMe-TMEDA (2a)

1.0 g (10.8 mmol) of 2-picoline and 1.25 g (10.8 mmol) of TMEDA was mixed and 4.3 mL of 2.5 M n-BuLi solution in hexane was added via syringe. The solution was cooled to -78°C after 1 hour upon which brownish red crystals formed. To this solution, 7.5 g (10.5 mmol) of 1.0 M BBNOMe solution in hexane was added via cannula and warmed to room temperature overnight. Colorless crystals formed in the solution. The supernatant was removed using a cannula and the solid was washed with pentane (2 x 15 mL). The solid was dried under vacuum. The product can also be recrystallized from toluene. Yield: 2.46 g (62%). Mp: 95-97°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.85 (2 H, br s, BBN CH_x), 1.72 (4 H, s, TMEDA CH_2), 1.79 (12 H, s, TMEDA CH_3), 2.02-2.44 (12 H, br m, BBN CH_x), 2.40 (2 H, s, CH_2), 3.29 (3 H, s, OCH_3), 6.50 (1 H, dt, J 6.1 and 1.6, *H*3), 7.04 (1 H, td, J 7.0 and 2.0, *H*4), 7.12 (1 H, d, J 6.8, *H*5), 7.70 (1 H, br d, J 3.8, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 26.1 (BBN*C*H), 26.5 (BBN*C*H), 32.7 (BBNCH_2), 33.7 (BBNCH_2 and *C*7), 45.8 (TMEDACH_3), 48.6 (OCH_3), 56.9 (TMEDACH_2), 116.9 (*C*3), 125.9 (*C*4), 135.8 (*C*5), 146.6 (*C*2). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.11. HRMS (ESI) m/z calcd for $C_{21}H_{39}BLiN_3O$ (**2a**$^+$): 367.33462, found: 367.36938.



Output report of DFT calculation:

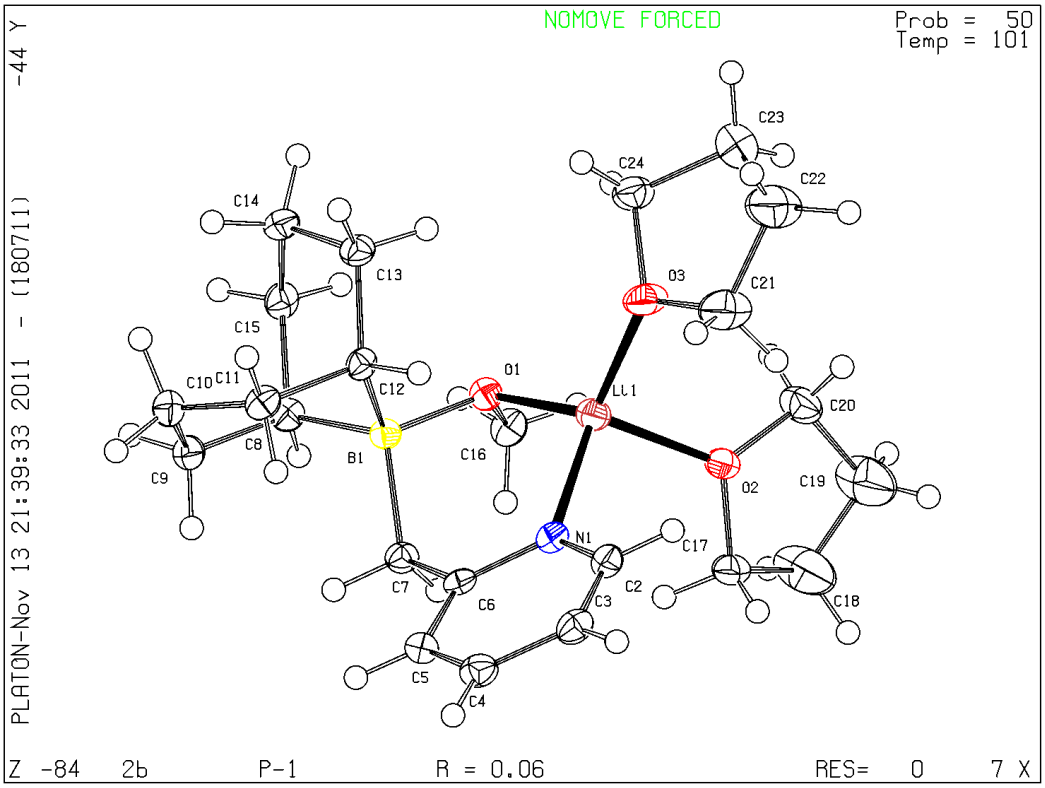
```
MacSPARTAN '10 MECHANICS PROGRAM: x86/Darwin 10.0.1
Frequency Calculation
Adjusted 3 (out of 198) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .13
Mechanics Wall Time: .25
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build
10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 186
Number of basis functions: 483
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
1 -1095.631609 0.042592 0.058719
2 -1095.661860 0.020372 0.074613
3 -1095.675209 0.010941 0.081483
4 -1095.681109 0.006189 0.109511
5 -1095.683385 0.003376 0.100712
6 -1095.684692 0.003119 0.098121
7 -1095.685777 0.002904 0.093078
8 -1095.686584 0.002427 0.101057
9 -1095.687282 0.001889 0.118965
10 -1095.687511 0.002152 0.055514
11 -1095.687723 0.001519 0.055119
12 -1095.687885 0.000617 0.014376
13 -1095.687934 0.000548 0.021890
14 -1095.687984 0.000662 0.025452
15 -1095.688029 0.000793 0.038476
16 -1095.688078 0.000772 0.040234
17 -1095.688115 0.000630 0.032672
18 -1095.688148 0.000578 0.027540
19 -1095.688177 0.000463 0.019482
20 -1095.688195 0.000513 0.029547
21 -1095.688210 0.000326 0.021501
22 -1095.688220 0.000286 0.012751
23 -1095.688229 0.000200 0.010774
24 -1095.688232 0.000186 0.007799
25 -1095.688234 0.000134 0.007245
26 -1095.688237 0.000140 0.005680
27 -1095.688238 0.000095 0.005741
28 -1095.688240 0.000098 0.003496
29 -1095.688239 0.000042 0.002393
Reason for exit: Successful completion
```

```
Quantum Calculation CPU Time : 5:24:12.74
Quantum Calculation Wall Time: 6:17:42.54
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 5.39
Properties Wall Time: 5.64
molecule M0001 terminated normally
End- molecule "M0001" Fri Jun 10 06:03:04 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
--------- ------------- ------------- -------------
1 N N1 0.9187466 -1.6685712 -0.0665135
2 C C4 0.2108681 -4.3662446 0.0389469
3 C C2 -0.1858216 -2.0944254 -0.7339592
4 C C6 1.6486424 -2.5617304 0.6235177
5 C C5 1.3488292 -3.9134950 0.7135599
6 C C3 -0.5492585 -3.4575930 -0.6814504
7 H H6 2.5251071 -2.1650943 1.1334933
8 H H5 1.9796545 -4.5825316 1.2901125
9 H H3 -1.4331015 -3.7826224 -1.2213381
10 H H4 -0.0726437 -5.4152745 0.0735174
11 Li Li1 1.1749708 0.3918294 -0.0574755
12 N N3 3.1391322 0.6940794 -1.2269479
13 N N2 2.2483981 1.4126142 1.5618252
14 C C1 4.0525438 0.9083116 -0.0877751
15 H H10 4.2128583 -0.0609175 0.3969091
16 H H15 5.0442437 1.2568654 -0.4302381
17 C C7 3.4914790 1.9004030 0.9332624
18 H H9 4.2643240 2.1220123 1.6899717
19 H H16 3.2648862 2.8475338 0.4349143
20 C C8 3.4972752 -0.5349157 -1.9506959
21 H H1 3.4317006 -1.3946040 -1.2810021
22 H H18 4.5161591 -0.4853122 -2.3738960
23 H H19 2.7897420 -0.6928003 -2.7697175
24 C C9 3.1878221 1.8268600 -2.1623558
25 H H11 4.1982770 1.9623211 -2.5876841
26 H H20 2.8958003 2.7552041 -1.6665976
27 H H21 2.4863630 1.6532765 -2.9823420
28 C C10 1.4285597 2.5330952 2.0495559
29 H H13 1.9617786 3.1363712 2.8048464
30 H H22 0.5106819 2.1426169 2.4938548
31 H H23 1.1453671 3.1756369 1.2121541
32 C C11 2.5361139 0.4941767 2.6725417
33 H H12 3.1645185 -0.3321634 2.3297584
34 H H24 1.6002675 0.0751336 3.0531441
35 H H25 3.0587013 1.0027181 3.5020213
36 C C13 -1.0016914 -1.0929286 -1.4757707
37 H H2 -1.7901664 -1.6280458 -2.0158382
38 H H27 -0.3709624 -0.6317480 -2.2522631
39 B B1 -1.6178694 0.1990834 -0.5489334
```

```
40 C C14 -3.0160991 0.7921977 -1.1709426
41 H H29 -2.9119460 1.1030902 -2.2257052
42 C C15 -1.9865737 -0.1846263 0.9999586
43 H H32 -1.1128908 -0.5923088 1.5432998
44 C C16 -4.0991417 -0.3172075 -1.1668190
45 H H33 -3.8128100 -1.0798954 -1.9041079
46 H H34 -5.0611147 0.0847606 -1.5247405
47 C C17 -3.4617376 2.0539243 -0.3821641
48 H H35 -4.4218008 2.4337330 -0.7700557
49 H H36 -2.7330961 2.8566263 -0.5620667
50 C C18 -2.4211369 1.0820741 1.7776274
51 H H31 -2.6887019 0.8320475 2.8184211
52 H H38 -1.5535669 1.7540667 1.8394577
53 C C19 -3.0569582 -1.3053331 1.0107759
54 H H28 -3.3517680 -1.5531481 2.0439613
55 H H39 -2.5961589 -2.2195062 0.6123984
56 C C20 -4.3386342 -1.0142777 0.1933288
57 H H40 -4.8746214 -1.9598431 0.0223767
58 H H42 -5.0225885 -0.4071220 0.7951802
59 C C21 -3.5862736 1.8689447 1.1448877
60 H H37 -4.5338956 1.3737208 1.3812544
61 H H44 -3.6544521 2.8584480 1.6217908
62 O O1 -0.4626828 1.2462684 -0.5233778
63 C C12 -0.3108850 2.0754918 -1.6526726
64 H H8 0.5098116 2.7836693 -1.4713309
65 H H41 -1.2136402 2.6605935 -1.8612274
66 H H43 -0.0697908 1.5075184 -2.5696318
Point Group = C1 Order = 1 Nsymop = 1
Reason for exit: Successful completion
Properties CPU Time : 5.26
Properties Wall Time: 5.46
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:48:24 2012
```

(2-picolyl)borabicyclononane LiOMe-(THF)$_2$ (2b)

2.0 g (21.5 mmol) of 2-picoline was dissolved in 30 mL of THF and cooled to -78°C. 14 mL of 1.6 M n-BuLi in hexane solution was added via syringe and kept cold for 30 min. 15 g (21 mmol) of 1.0 M BBNOMe solution in hexane was mixed with 20 mL of THF and added via cannula. Upon warming to room temperature overnight, colorless crystals formed in the flask. 100 mL of hexane was added and cooled to -78°C, which led to precipitation of additional crystals. The crystalline product was filtered through a frit and washed with hexane (2 x 15 mL). More crystals were collected by concentrating the filtrate solution. Yield: 6.6 g (78%). Mp: 68-70°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.94 (2 H, br s, BBN CH_x), 1.39-1.50 (4 H, m, THF CH_2), 2.07-2.44 (12 H, br m, BBN CH_x), 2.51 (2 H, s, CH_2), 3.46 (3 H, s, OCH_3), 3.50-3.63 (1 H, m, THF CH_2), 6.60 (1 H, dt, J 5.2 and 2.1, *H*3), 7.08-7.22 (2 H, m, *H*4 and *H*5), 8.04 (1 H, d, J 4.6, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 25.6 (BBN*C*H), 26.1 (THF), 32.3 (*C*7), 33.5 (BBN*C*H$_x$), 47.7 (O*C*H$_3$), 68.0 (THF), 117.7 (*C*3), 126.4 (*C*4), 136.4 (*C*5), 146.8 (*C*2). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.72. HRMS (ESI) m/z calcd for $C_{14}H_{23}BNO$ (**2b**-[CH_3O-Li(THF)$_2$]+H_3O^+): 232.187269, found: 232.18983.; calcd for $C_{14}H_{20}BNLi$ (1/2 **2**+Li^+): 220.184882, found: 220.17039.



Output report of DFT calculation:

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Frequency Calculation
Warning: global charge (+2.00) does not match input file (+0)!
Adjusted 4 (out of 204) low frequency modes
Reason for exit: Successful completion
Mechanics CPU Time : .16
Mechanics Wall Time: .50
MacSPARTAN '10 Quantum Mechanics Program: (x86/Darwin) build
10.0.1v4
Job type: Geometry optimization.
Method: RB3LYP
Basis set: 6-31G(D)
Number of shells: 194
Number of basis functions: 513
Multiplicity: 1
SCF model:
A restricted hybrid HF-DFT SCF calculation will be
performed using Pulay DIIS + Geometric Direct Minimization
Optimization:
Step Energy Max Grad. Max Dist.
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2 -1212.823912 0.023339 0.077296
3 -1212.837595 0.011469 0.107492
4 -1212.842706 0.004761 0.099468
5 -1212.844035 0.004015 0.117275
6 -1212.845613 0.004073 0.122932
7 -1212.847027 0.003175 0.118844
8 -1212.848155 0.003274 0.125295
9 -1212.849199 0.001459 0.141635
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11 -1212.850320 0.001363 0.133007
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15 -1212.851629 0.002004 0.130881
16 -1212.851967 0.001770 0.120002
17 -1212.852318 0.002515 0.113385
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26 -1212.853724 0.000911 0.027679
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34 -1212.853889 0.000144 0.005040
35 -1212.853893 0.000088 0.002664
36 -1212.853896 0.000079 0.001749
37 -1212.853895 0.000046 0.001345
38 -1212.853895 0.000037 0.001021
Reason for exit: Successful completion
Quantum Calculation CPU Time : 7:30:30.29
Quantum Calculation Wall Time: 74:08:38.80
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Reason for exit: Successful completion
Properties CPU Time : 6.66
Properties Wall Time: 7.01
molecule M0001 terminated normally
End- molecule "M0001" Sun Jul 10 18:52:42 2011
SPARTAN PROPERTIES PACKAGE: MAC/P4 build 10.0.1
Use of molecular symmetry disabled
Cartesian Coordinates (Angstroms)
Atom X Y Z
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1 C C1 1.6674331 -2.1679234 -1.4130066
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3 N N1 0.8481060 -1.6829570 -0.4644612
4 C C6 1.3679722 -3.2627322 -2.2122748
5 C C5 0.1325647 -3.8866015 -2.0110377
6 C C3 -0.3468057 -2.2891114 -0.2417584
7 H H6 2.0706123 -3.6096479 -2.9634116
8 H H5 -0.1562480 -4.7465989 -2.6104366
9 H H4 -1.6767208 -3.8754505 -0.8445514
10 B B1 -1.6995666 -0.1125648 0.6555662
11 Li Li1 1.1220032 0.1914337 0.3307302
12 O O1 -0.4886145 0.7088782 1.1918510
13 O O2 2.7471270 0.0319282 1.5448978
14 O O3 1.8598279 1.5149110 -0.9738277
15 C C2 2.7041390 -0.9940146 2.5685371
16 H H12 1.8809891 -1.6737992 2.3341218
17 H H13 2.5002489 -0.5095903 3.5308603
18 C C8 4.0790913 -1.6676936 2.5474610
19 H H2 4.3636219 -2.0635613 3.5266575
20 H H15 4.0892126 -2.4964010 1.8298574
21 C C9 4.9894923 -0.5281777 2.0615826
22 H H14 5.9276154 -0.8790154 1.6211465
23 H H16 5.2330869 0.1472048 2.8902282
24 C C10 4.0926428 0.1745284 1.0431387
25 H H18 4.1594425 -0.2998146 0.0547861
26 H H19 4.3032501 1.2414580 0.9294545
27 C C11 1.7872703 2.8891401 -0.5091962
28 H H9 2.6591748 3.0790503 0.1251833
29 H H20 0.8782567 2.9954512 0.0930857
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32 H H23 1.2146418 4.6942972 -1.6108738
33 C C13 1.0597003 2.8276076 -2.7831204
34 H H21 1.2733505 3.0892650 -3.8239203
35 H H24 -0.0248654 2.8435079 -2.6373162
36 C C14 1.6223748 1.4582215 -2.4016678
37 H H25 2.5774694 1.2567050 -2.9055981
38 H H26 0.9342816 0.6318380 -2.5962288
39 C C16 -3.0954972 0.2206508 1.4570786
40 H H1 -3.0356184 -0.0454017 2.5272263
41 C C17 -1.9906471 0.3580612 -0.8871494
42 H H28 -1.1138984 0.1953937 -1.5422116
43 C C18 -4.2527921 -0.6311515 0.8742542
44 H H17 -5.2077173 -0.3609852 1.3545809
45 H H30 -4.0794120 -1.6815591 1.1465567
46 C C19 -3.3990754 1.7406938 1.3996410
47 H H27 -4.3551581 1.9618830 1.9027416
48 H H33 -2.6309150 2.2749927 1.9754567
49 C C20 -3.1301349 -0.5081216 -1.4802908
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54 H H37 -1.3711815 2.4023619 -0.6203170
55 C C22 -4.4403229 -0.5425258 -0.6592423
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58 C C23 -3.4339185 2.3529005 -0.0177055
59 H H32 -4.3956835 2.1320744 -0.4913348
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61 H H42 2.6117529 -1.6383663 -1.5360788
62 C C7 -1.2398029 -1.7400985 0.8194295
63 H H3 -0.7126042 -1.8102601 1.7841597
64 H H7 -2.1077392 -2.4015661 0.9062797
65 H H8 -1.1602002 1.4025756 3.0420030
66 C C15 -0.3441027 0.8258324 2.5896755
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68 H H29 -0.3192208 -0.1547718 3.0954118
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Reason for exit: Successful completion
Properties CPU Time : 6.49
Properties Wall Time: 6.70
molecule M0001 terminated normally
End- molecule "M0001" Wed Mar 7 17:49:56 2012
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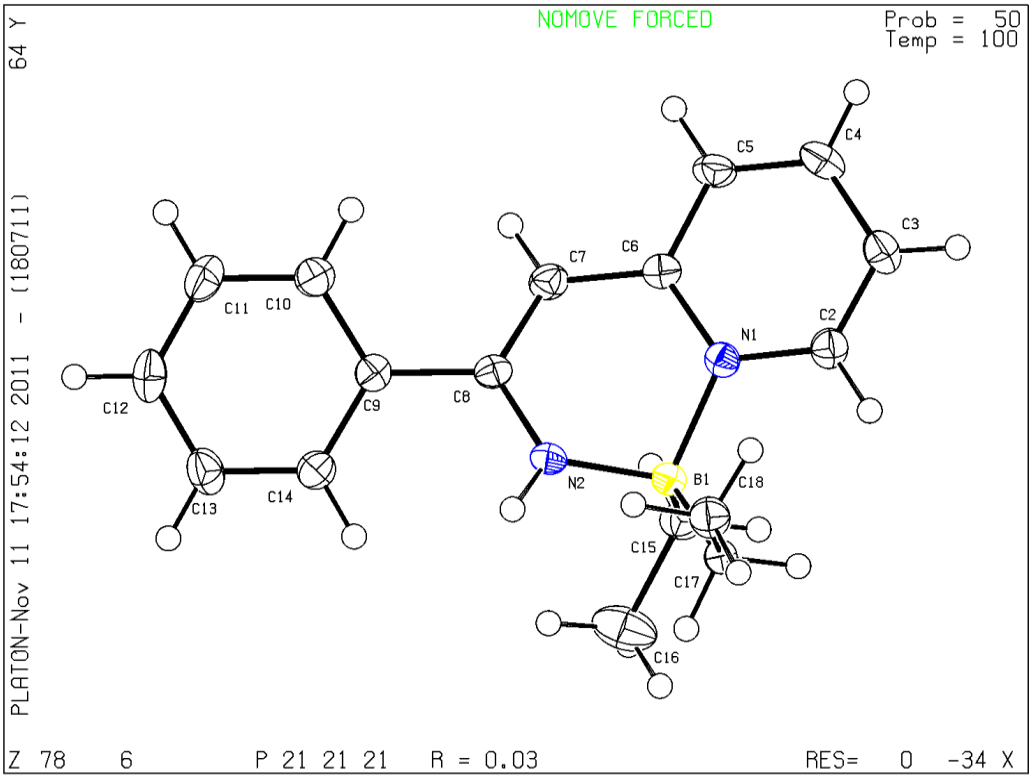
1 + Acetonitrile (5)

100 mg (0.3 mmol) of **1** was dissolved in 10 mL of toluene. 50 mg (1.22 mmol) of acetonitrile was added. The solution was heated at 70°C overnight. After cooling, solvent was removed in vacuo and orange oil was obtained. The pure product was extracted with pentane. Yield: 124 mg (99%). δ_H (200 MHz; C_6D_6; C_6H_6): 0.61-0.94 (4 H, m, C*H*$_2$CH$_3$), 1.08 (6 H, t, J 7.4, CH$_2$C*H*$_3$), 1.44 (3 H, s, C*H*$_3$), 3.85 (1 H, br s, N*H*), 4.42 (1 H, d, J 2.4, C*H*, *H*7), 5.94 (1 H, dt, J 6.8 and 1.2, *H*3), 6.15 (1 H, td, J 7.8 and 1.2, *H*5), 6.59 (1 H, dt, J 7.8 and 1.6, *H*4), 7.42 (1 H, dd, J 6.2 and 0.8, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.8 (CH$_2$*C*H$_3$), 17.0 (br, *C*H$_2$CH$_3$), 22.6 (*C*9), 87.3 (*C*7), 113.8 (*C*3), 119.9 (*C*5), 136.4 (*C*4), 140.6 (*C*2), 154.9 (*C*8), 158.7 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.37. HRMS (ESI) m/z calcd for $C_{12}H_{20}BN_2$ ([**5**+H]$^+$): 203.171953, found: 203.17327.

1 + Benzonitrile (6)

160 mg (0.5 mmol) of **1** and 102 mg (1.0 mmol) of benzonitrile were mixed with 10 mL of toluene. The flask was heated at 60°C for 3h, and the solution became intense orange. The solvent was removed in vacuo and the product was extracted with pentane. Evaporation of pentane gave orange-red crystalline product. Yield: 76 mg (29%). Mp: 72-74°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.70-1.03 (4 H, m, CH_2CH_3), 1.13 (6 H, t, J 7.4, CH_2CH_3), 4.38 (1 H, br s, N*H*), 5.02 (1 H, d, J 2.0, C*H*, *H*7), 6.01 (1 H, t, J 6.7, *H*3), 6.27 (1 H, dd, J 8.2 and 1.2, *H*5), 6.63 (1 H, td, J 7.6 and 1.8, *H*4), 7.02-7.13 (3 H, m, *H*-m and p), 7.33-7.39 (2 H, m, *H*-o), 7.50 (1 H, d, J 6.2, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.9 (CH_2CH_3), 17.1 (br, CH_2CH_3), 87.5 (*C*7), 115.0 (*C*3), 121.0 (*C*5), 126.4 (*C*-o), 128.8 (*C*-m), 129.7 (*C*-p), 136.6 (*C*4), 139.3 (*C*9), 140.7 (*C*2), 154.9 (*C*8), 158.9 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.52. HRMS (ESI) m/z calcd for $C_{17}H_{22}BN_2$ ([**6**+H]$^+$): 265.187603, found: 265.18981.

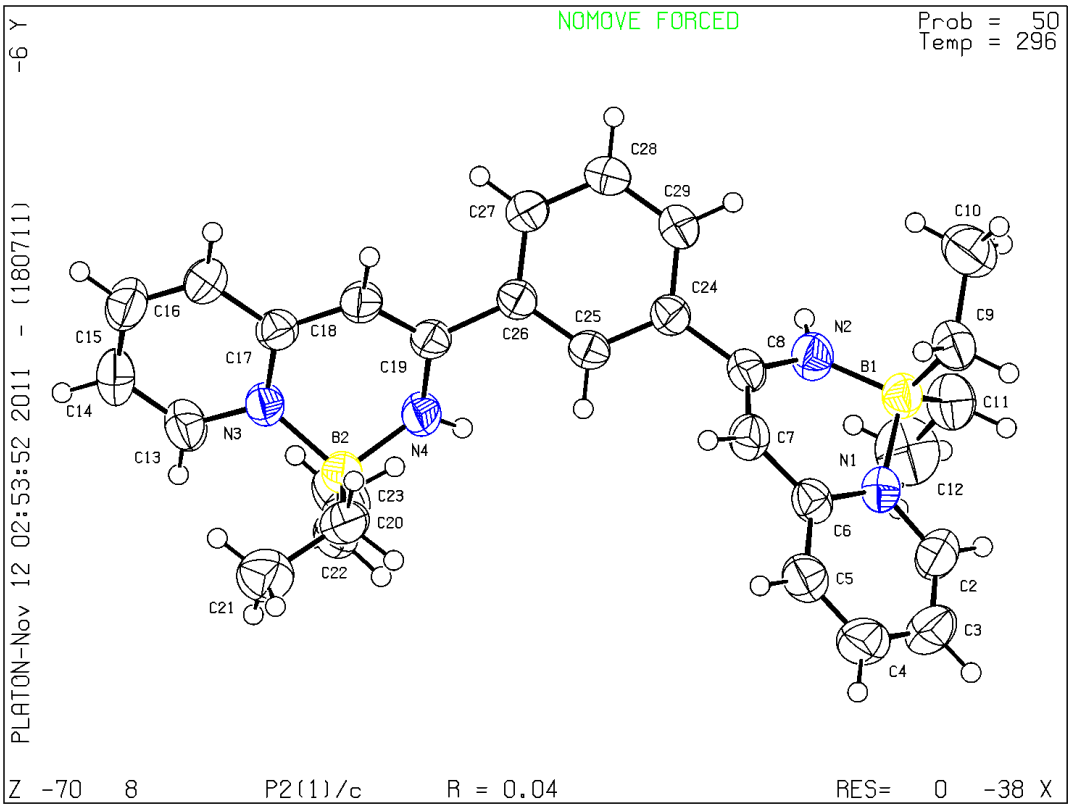


1 + 1,2-dicyanobenzene (7)

163 mg (0.5 mmol) of **1** and 63 mg (0.5 mmol) of 1,2-dicyanobenzene was dissolved in 10 mL of toluene. The flask was heated at 70°C for 4h. Solvent was removed in vacuo, yielding dark red thick oil. Yield: 235 mg (96%). δ_H (200 MHz; C_6D_6; C_6H_6): 0.67-0.94 (4 H, m, C*H*$_2$CH$_3$), 1.05 (6 H, t, J 7.4, CH$_2$C*H*$_3$), 4.21 (1 H, br s, N*H*), 4.87 (1 H, d, J 2.4, C*H*, *H*7), 5.93 (1 H, td, J 6.4 and 1.6, *H*3), 6.30 (1 H, dt, J 8.2 and 0.8, *H*5), 6.55 (1 H, td, J 7.8 and 1.6, *H*4), 7.04 (1 H, dd, J 5.7 and 3.3, *H*-m), 7.33 (1 H, dd, J 5.6 and 3.4, *H*-o), 7.53 (1 H, dt, J 6.2 and 0.8, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.9 (CH$_2$*C*H$_3$), 16.4 (br, *C*H$_2$CH$_3$), 89.7 (*C*7), 114.7 (*C*3), 120.8 (*C*5), 129.0 (*C*-o), 129.1 (*C*-m), 136.4 (*C*4), 138.4 (*C*9), 140.6 (*C*2), 154.4 (*C*8), 159.1 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 1.52. HRMS (ESI) m/z calcd for $C_{28}H_{37}B_2N_4$ ([**7**+H]$^+$): 451.320431, found: 451.31782.

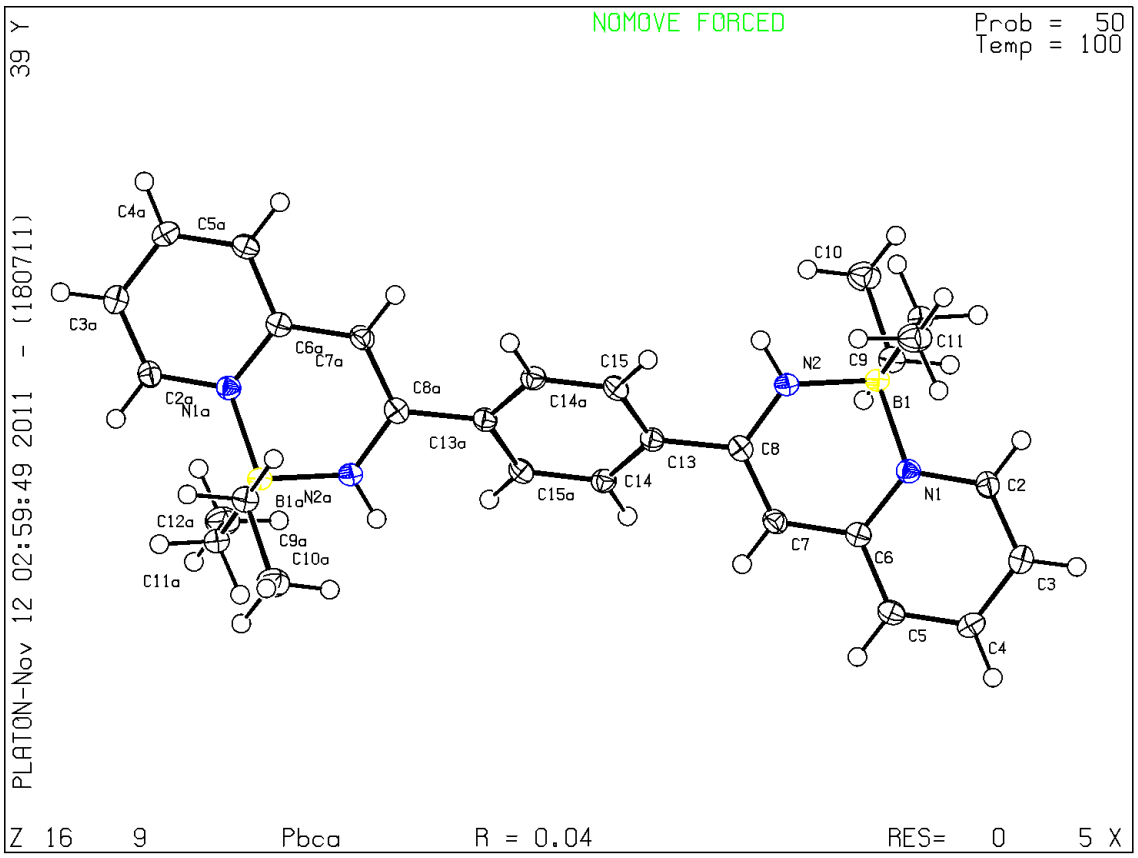
1 + 1,3-dicyanobenzene (8)

161 mg (0.5 mmol) of **1** and 64 mg (0.5 mmol) of 1,3-dicyanobenzene was weighed in a flask and dissolved in 10 mL of toluene. The solution was heated at 60°C overnight. Solvent was removed in vacuo after cooling and the product was recrystallized in CH_2Cl_2/hexane. Yield: 177 mg (79%). Mp: 124-126°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.76-1.09 (4 H, m, C*H*$_2$CH$_3$), 1.15 (6 H, t, J 7.4, CH$_2$C*H*$_3$), 4.38 (1 H, br s, N*H*), 5.05 (1 H, d, J 2.2, C*H*, *H*7), 6.00 (1 H, td, J 6.0 and 1.2, *H*3), 6.21 (1 H, dd, J 9.4 and 1.2, *H*5), 6.59 (1 H, td, J 7.8 and 1.6, *H*4), 7.04 (0.5 H, t, J 7.6, *H*-m), 7.38 (1 H, dd, J 7.8 and 2.0, *H*-o), 7.50 (1 H, d, J 6.2, *H*2), 7.88 (0.5 H, t, J 1.6, *H*-o). δ_C (50 MHz; C_6D_6; C_6H_6) 9.9 (CH$_2$*C*H$_3$), 16.6 (br, *C*H$_2$CH$_3$), 87.9 (*C*7), 115.3 (*C*3), 121.0 (*C*5), 124.6 (*C*-o1), 127.5 (*C*-o2), 129.4 (*C*-m), 136.7 (*C*4), 140.0 (*C*9), 140.7 (*C*2), 154.7 (*C*8), 158.4 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 0.61. HRMS (ESI) m/z calcd for $C_{28}H_{37}B_2N_4$ ($[M+H]^+$): 451.320431, found: 451.33108.



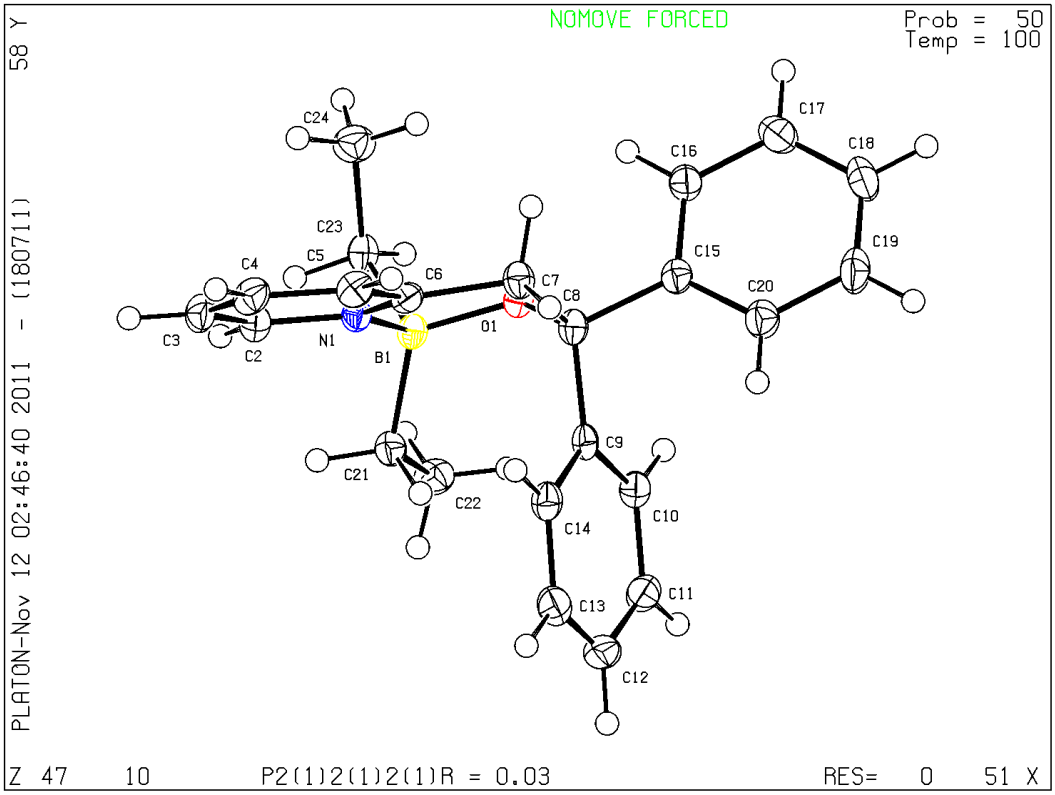
1 + 1,4-dicyanobenzene (9)

161 mg (0.5 mmol) of **1** and 64 mg (0.5 mmol) of 1,4-dicyanobenzene was weighed in a flask and dissolved in 10 mL of toluene. The solution was heated at 60°C overnight. Solvent was removed in vacuo after cooling and the product was recrystallized in CH_2Cl_2/hexane. Yield: 216 mg (96%). Mp: 179-181°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.81-1.10 (4 H, m, C*H*$_2$CH$_3$), 1.20 (6 H, t, J 7.4, CH$_2$C*H*$_3$), 4.41 (1 H, br s, N*H*), 5.09 (1 H, d, J 2.2, C*H*, *H*7), 6.02 (1 H, td, J 7.2 and 1.4, *H*3), 6.30 (1 H, dd, J 9.4 and 1.2, *H*5), 6.63 (1 H, td, J 7.8 and 1.6, *H*4), 7.53 (1 H, d, J 6.2, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.9 (CH$_2$*C*H$_3$), 16.6 (br, *C*H$_2$CH$_3$), 87.8 (*C*7), 115.3 (*C*3), 121.0 (*C*5), 126.6 (*C*10), 136.7 (*C*4), 140.3 (*C*9), 140.8 (*C*2), 154.8 (*C*8), 158.0 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 2.44. HRMS (ESI) m/z calcd for $C_{28}H_{37}B_2N_4$ ([**9**+H]$^+$): 451.320431, found: 451.32564.



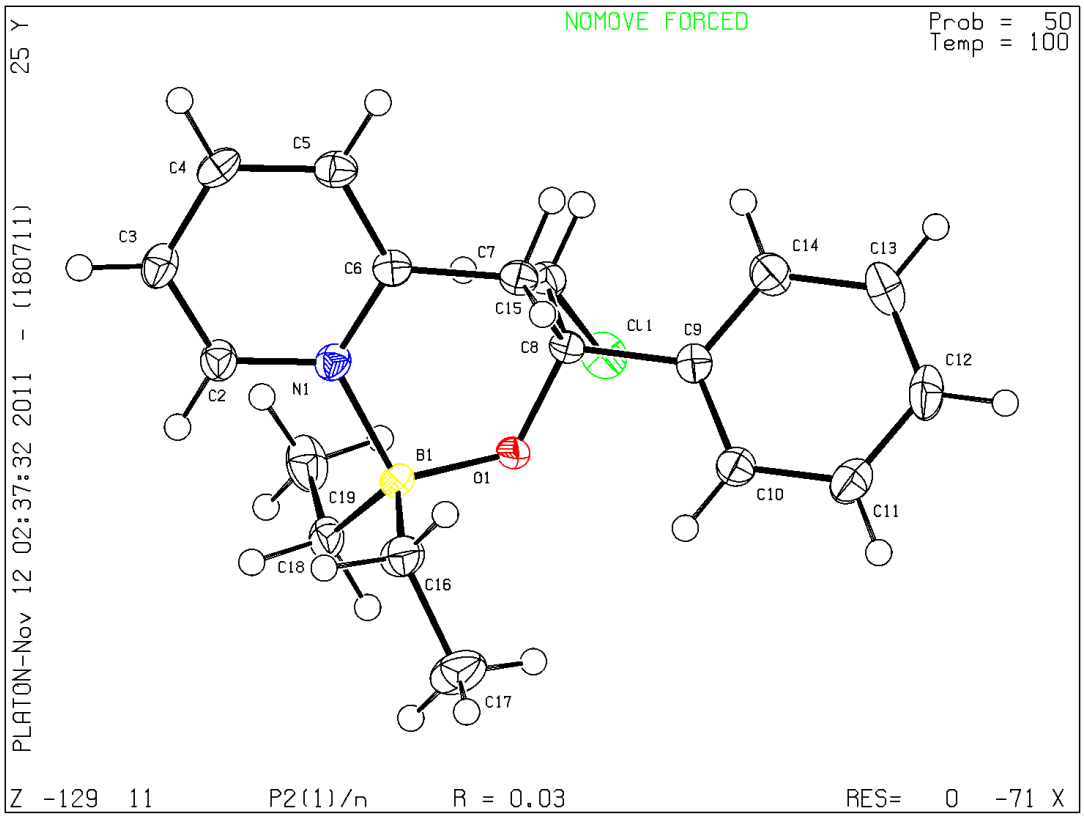
1 + Benzophenone (10)

161 mg (0.5 mmol) of **1** and 180 mg (1.0 mmol) of benzophenone was dissolved in 10 mL of toluene. The solution was heated at 60°C for 3h. Solvent was removed in vacuo after cooling, leaving light yellow sticky oil. Pentane was used to extract the product from the crude material. Crystals formed upon storage of the pentane solution in a 0°C freezer for a few days. Yield: 230 mg (76%). Mp: 152-154°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.95-1.15 (4 H, br m, C*H*$_2$CH$_3$), 1.36 (6 H, t, J 7.6, CH$_2$C*H*$_3$), 3.65 (2 H, s, C*H*$_2$), 6.31 (1 H, dt, J 6.7 and 1.4, *H*3), 6.50 (1 H, d, J 7.8, *H*5), 6.78 (1 H, dt, J 7.6 and 1.6, *H*4), 7.11-7.19 (2 H, m, *H*-p), 7.21-7.35 (4 H, m, *H*-m), 7.81-7.89 (4 H, m, *H*-o), 8.02 (1 H, dd, J 5.8 and 1.2, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 10.4 (CH$_2$*C*H$_3$), 16.1 (br, *C*H$_2$CH$_3$), 43.4 (*C*7), 76.4 (*C*8), 121.8 (*C*3), 125.9 (*C*5), 126.4 (*C*-p), 126.8 (*C*-o), 128.0 (*C*-m), 138.4 (*C*4), 143.2 (*C*2), 150.9 (*C*-ipso), 155.6 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 7.77. HRMS (ESI) m/z calcd for $C_{19}H_{18}NO$ (hydrolysis of **10** to the alcohol, protonated): 276.138839, found: 276.13540.



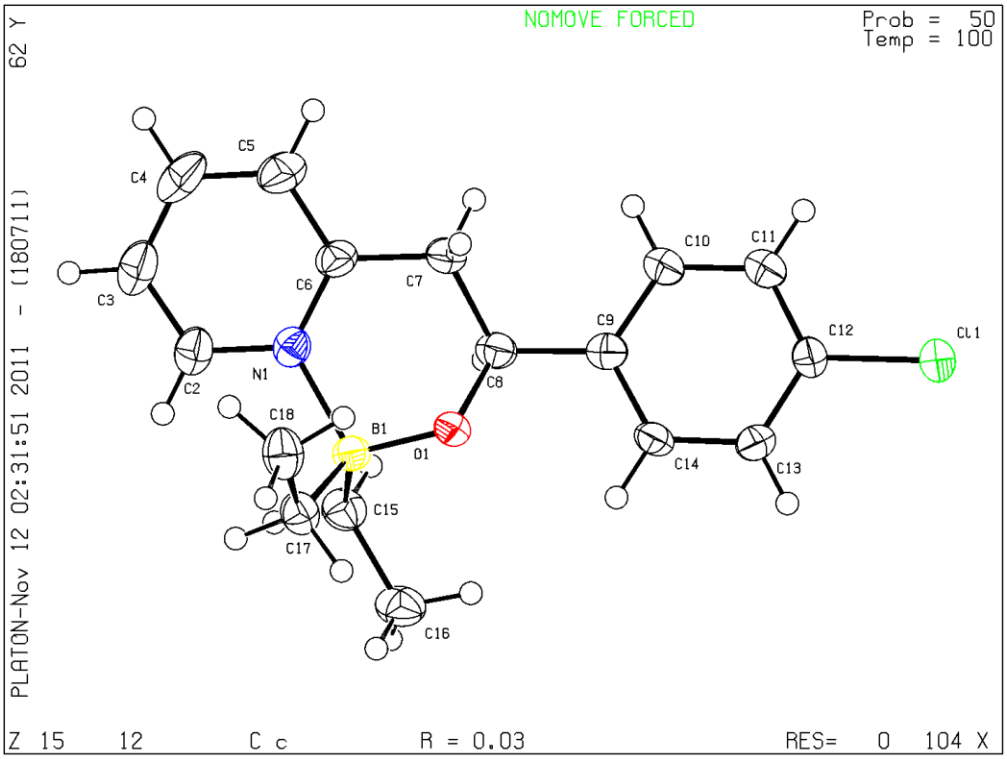
1 + 2-chloroacetophenone (11)

81 mg (0.25 mmol) of **1** and 90 mg (0.58 mmol) of 2-chloroacetophenone was dissolved in 10 mL of toluene. The solution was heated at 80°C overnight. The contents were cooled to room temperature. The solvent was removed in vacuo, and the nearly colorless oil was extracted with hexane. Crystals suitable for X-ray structure analysis formed while keeping the hexane solution in 0°C freezer. Yield: 75 mg (47%). Mp: 68-70°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.68 (2 H, br s, C*H*$_2$CH$_3$), 1.01 (5 H, br t, C*H*$_2$CH$_3$ and CH$_2$C*H*$_3$), 1.19 (3 H, br d, CH$_2$C*H*$_3$), 3.18 (1 H, d, J 15.6, C*H*$_2$), 3.40 (1 H, d, J 15.6, C*H*$_2$), 3.51 (2 H, s, C*H*$_2$Cl), 6.22 (1 H, dt, J 6.7 and 1.4, *H*3), 6.45 (1 H, qd, J 7.8 and 0.8, *H*5), 6.67 (1 H, dt, J 7.8 and 1.8, *H*4), 7.08 (1 H, tt, J 7.4 and 1.4, *H*-p), 7.23 (2 H, qt, J 7.4 and 1.4, *H*-m), 7.72 (2 H, td, J 8.2 and 1.6, *H*-o), 7.86 (1 H, dd, J 5.6 and 1.0, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.7 (br, CH$_2$*C*H$_3$), 10.3 (br, CH$_2$*C*H$_3$), 15.0 (br, *C*H$_2$CH$_3$), 38.8 (*C*7), 55.6 (*C*H$_2$Cl), 75.1 (*C*8), 121.7 (*C*3), 126.3 (*C*5), 126.5 (*C*-o), 127.2 (*C*-p), 128.1 (*C*-m), 138.6 (*C*4), 143.0 (*C*2), 147.6 (*C*-ipso), 155.3 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 7.32. Found: C,68.36; H,7.30; N,4.36. $C_{18}H_{23}BClNO$ requires C,68.49; H,7.34; N, 4.44.



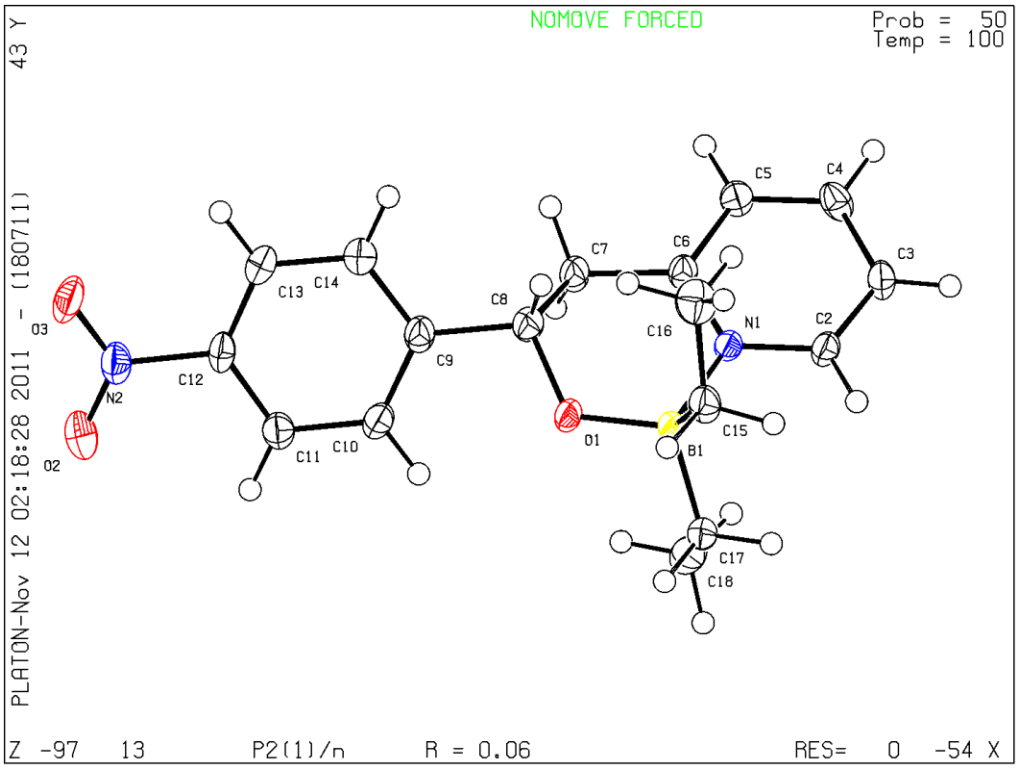
1 + 4-chlorobenzaldehyde (12)

81 mg (0.25 mmol) of **1** and 70 mg (0.50 mmol) of 4-chlorobenzaldehyde was dissolved in 20 mL of toluene. The solution was heated at 85°C overnight. The contents were cooled to room temperature. The solvent was removed in vacuo, and a light yellow oil was obtained. Pentane was used to extract the product from the crude material. Colorless crystals formed while keeping the pentane solution at 0°C. Yield: 136 mg (90%). Mp: 64-66°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.68-0.79 (4 H, br m, CH_2CH_3), 1.13 (6 H, br s, CH_2CH_3), 2.47 (1 H, dd, J 17.0 and 3.4, CH_2), 2.62 (1 H, dd, J 17.0 and 10.0, CH_2), 4.96 (1 H, dd, J 9.7 and 3.1, C*H*), 6.26 (1 H, dd, J 7.8 and 0.8, *H*5), 6.38 (1 H, dt, J 6.2 and 1.0, *H*3), 6.75 (1 H, dt, J 7.8 and 1.8, *H*4), 7.24 (2 H, dd, J 6.5 and 2.1, *H*-m), 7.37-7.43 (2 H, m, *H*-*o*), 7.91 (1 H, dd, J 6.0 and 1.2, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 10.1 (br, CH_2CH_3), 16.7 (br, CH_2CH_3), 40.9 (*C*7), 66.9 (*C*8), 122.2 (*C*3), 126.1 (*C*5), 127.7 (*C*-*o*), 128.5 (*C*-*m*), 132.6 (*C*-*p*), 138.0 (*C*4), 143.3 (*C*2), 145.0 (*C*-ipso), 156.9 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 8.38. HRMS (ESI) m/z calcd for $C_{17}H_{21}BNOCl$ ([**12**+H]$^+$): 302.148296, found: 302.14688.



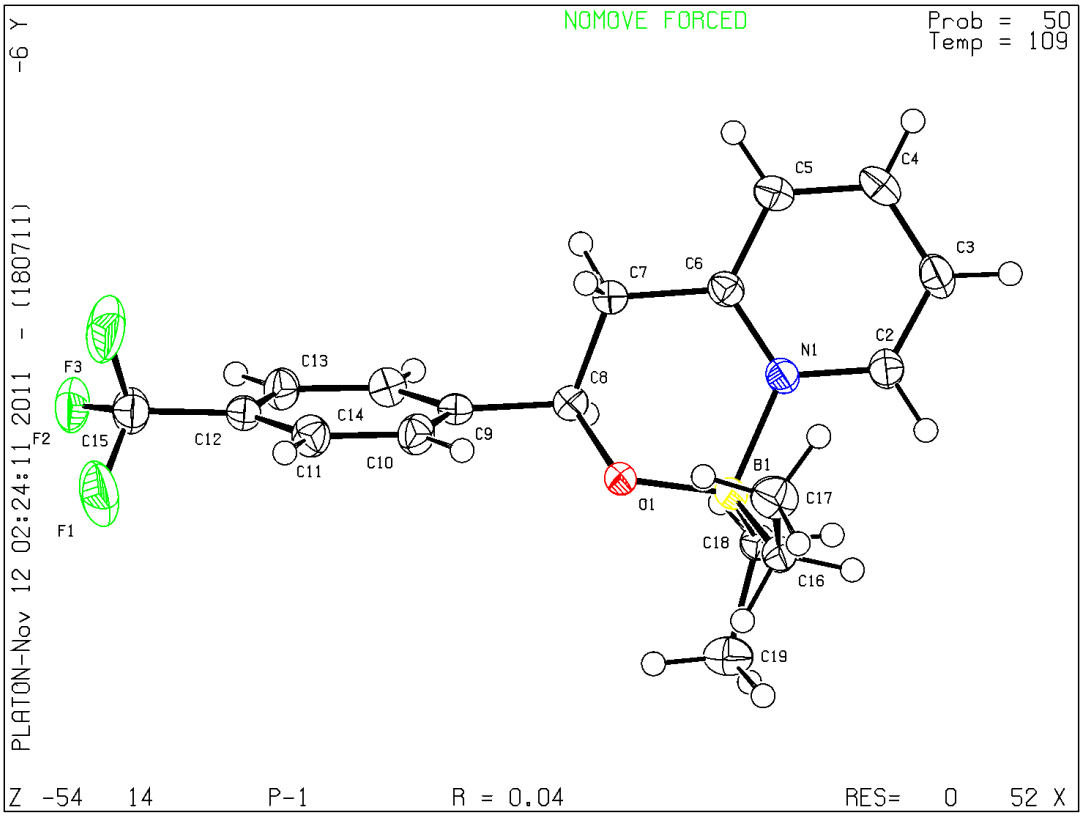
1 + 4-nitrobenzaldehyde (13)

83 mg (0.26 mmol) of **1** and 75 mg (0.50 mmol) of 4-nitrobenzaldehyde was dissolved in 10 mL of toluene. The solution was heated at 80°C for 1 hour. The contents were cooled to room temperature. The solvent was removed in vacuo, and thick yellow oil was obtained. From the oil, the product crystallized slowly in the glovebox. The crude crystalline product was recrystallized by slow evaporation of its toluene solution. Yield: 82 mg (51%). Mp: 108-110°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.68-0.88 (4 H, br m, C*H*$_2$CH$_3$), 1.14 (6 H, br s, CH$_2$C*H*$_3$), 2.38 (1 H, dd, J 11.3 and 5.5, C*H*$_2$), 2.51 (1 H, dd, J 16.7 and 9.3, C*H*$_2$), 4.93 (1 H, dd, J 9.4 and 4.0, C*H*), 6.26 (1 H, dd, J 7.8 and 0.8, *H*5), 6.36 (1 H, t, J 6.6, *H*3), 6.73 (1 H, dt, J 7.8 and 1.4, *H*4), 7.34-7.41 (2 H, m, *H*-m), 7.89 (1 H, dd, J 6.0 and 1.2, *H*2), 7.97-8.03 (2 H, m, *H*-o). δ_C (50 MHz; C_6D_6; C_6H_6) 10.1 (br, CH$_2$*C*H$_3$), 16.5 (br, *C*H$_2$CH$_3$), 40.3 (*C*7), 66.8 (*C*8), 122.4 (*C*3), 123.4 (*C*-*o*), 126.1 (*C*5), 126.6 (*C*-m), 129.8 (*C*-p), 138.1 (*C*4), 143.4 (*C*2), 153.2 (*C*-ipso), 156.3 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 8.39. Found: C,64.46; H, 6.65; N, 9.01. $C_{17}H_{21}BN_2O_3$ requires C,65.41; H,6.78; N,8.97.



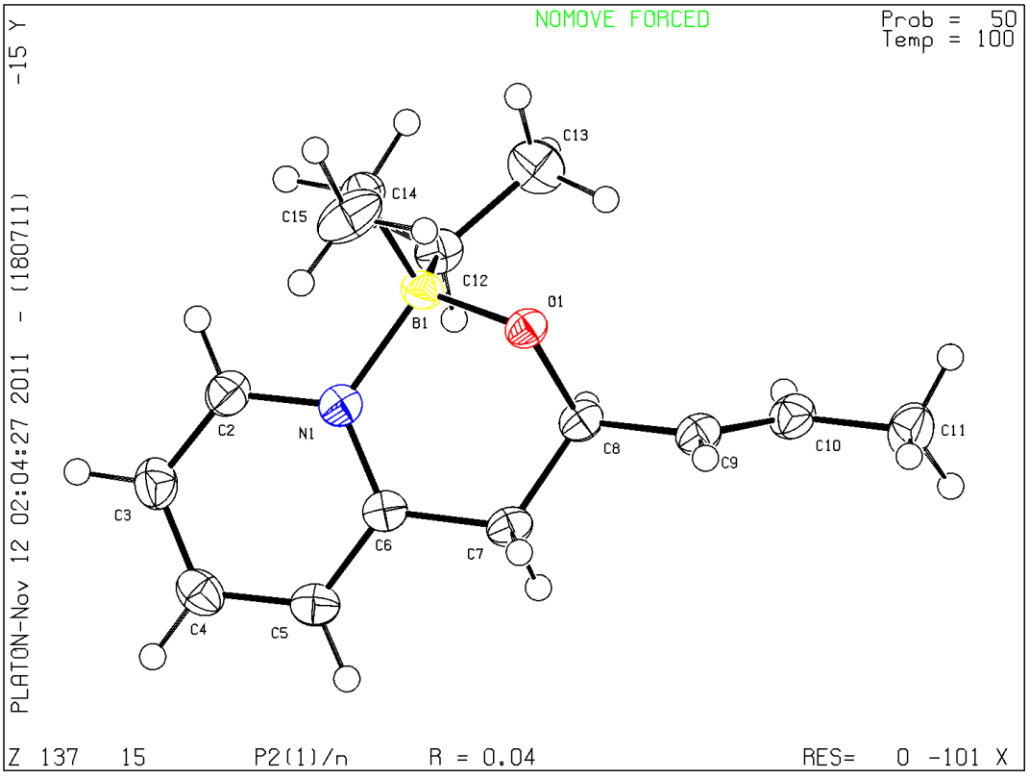
1 + *p*-trifluorotolualdehyde (14)

80 mg (0.25 mmol) of **1** and 80 mg (0.46 mmol) of *p*-triflurotolualdehyde was dissolved in 10 mL of toluene. The solution was heated at 80°C for 3 hours. The contents were cooled to room temperature. Polycrystalline product was obtained upon solvent removal in vacuo. Single crystals were obtained upon recrystallization from pentane at 0°C. Yield: 115 mg (69%). Mp: 80-82°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.70-0.87 (4 H, br m, C*H*$_2$CH$_3$), 1.16 (6 H, br s, CH$_2$C*H*$_3$), 2.44 (1 H, dd, J 16.8 and 3.6, C*H*$_2$), 2.58 (1 H, dd, J 16.8 and 10.2, C*H*$_2$), 4.99 (1 H, dd, J 9.8 and 3.0, C*H*), 6.21 (1 H, dd, J 7.8 and 0.8, *H*5), 6.33 (1 H, tt, J 7.2 and 0.8, *H*3), 6.69 (1 H, dt, J 7.6 and 1.6, *H*4), 7.50 (4 H, s, *H*-o and *H*-m), 7.90 (1 H, dd, J 6.0 and 1.0, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 9.9 (br, CH$_2$*C*H$_3$), 16.2 (br, *C*H$_2$CH$_3$), 40.6 (*C*7), 66.9 (*C*8), 122.2 (*C*3), 125.3 (q, J_{CF} 3.9, *C*-*m*), 126.1 (C5), 126.5 (*C*-o), 137.9 (*C*4), 143.4 (*C*2), 150.4 (*C*-ipso), 156.6 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 8.69. Found: C, 64.60, H, 6.23, N, 3.85. $C_{18}H_{21}BF_3NO$ requires C, 64.50; H, 6.32; N, 4.18.



1 + crotonaldehyde (15)

160 mg (0.5 mmol) of **1** was dissolved in 20 mL of toluene. 200mg (2.9 mmol) of crotonaldehyde was added and heated to 70°C for 3 hours. The contents were cooled to room temperature. The solvent was removed in vacuo, yielding yellow oil. The crude product was recrystallized from pentane at 0°C. Yield: 234 mg (100%). Mp: 54-56°C. δ_H (200 MHz; C_6D_6; C_6H_6): 0.66-0.88 (2 H, m, C*H*$_2$CH$_3$), 0.89-1.14 (2 H, m, C*H*$_2$CH$_3$), 1.19-1.27 (6 H, m, CH$_2$C*H*$_3$), 1.69 (3 H, td, J 6.2 and 1.2, CH3), 2.36 (1 H, dd, J 16.8 and 2.4, C*H*$_2$), 2.69 (1 H, dd, J 16.8 and 10.2, C*H*$_2$), 4.50-4.60 (1 H, m, *H*8), 5.73-5.84 (1 H, m, *H*9/10), 5.91-6.05 (1 H, m, *H*9/10), 6.19 (1 H, d, J 7.8, *H*5), 6.28 (1 H, t, J 7.0, *H*3), 6.64 (1 H, dt, J 7.8 and 1.6, *H*4), 7.89 (1 H, d, J 5.8, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 10.1 (CH$_2$*C*H$_3$), 17.0 (br, *C*H$_2$CH$_3$), 17.9 (*C*H3), 39.3 (*C*7), 66.0 (*C*8), 121.8 (*C*3), 124.2 (*C*9/10), 126.0 (*C*5), 135.7 (*C*9/10), 137.5 (*C*4), 143.3 (*C*2), 157.5 (*C*6). δ_B (64 MHz; C_6D_6; BF_3OEt_2) 9.18. Found: C, 72.09; H, 9.35; N, 6.42. $C_{14}H_{22}BNO$ requires C, 72.75; H, 9.59; N, 6.06 %.



1 + heptaldehyde (16)

160 mg (0.5 mmol) of **1** was dissolved in 10 mL toluene. Heptaldehyde (114 mg, 1.0 mmol) was added, and the mixture was heated at 50°C for 2 hours. The contents were cooled to room temperature. The solvent was removed in vacuo, leaving pale yellow oil. Yield: 234 mg (85%). δ_H (200 MHz; C_6D_6; C_6H_6): 0.58-0.98 (10 H, br m, ethyl C*H*$_2$C*H*$_3$), 0.95-1.92 (13 H, br m, heptyl C*H*$_2$C*H*$_3$), 2.28 (1 H, dd, J 10.9 and 3.5, C*H*$_2$), 2.60 (1 H, dd, J 16.7 and 10.4, C*H*$_2$), 3.93-4.09 (1 H, m, *H*8), 6.23-6.33 (2 H, m, *H*3 and *H*5), 6.67 (1 H, t, J 8.0, *H*4), 7.89 (1 H, d, J 5.8, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 10.0 (*C*H$_3$), 14.3 (*C*H$_3$), 16.1 (br, *C*H$_2$CH$_3$), 23.1 (*C*H$_2$), 26.2 (*C*H$_2$), 30.1 (*C*H$_2$), 32.5 (*C*H$_2$), 38.6 (*C*H$_2$), 39.3 (*C*7), 65.1 (*C*8), 121.8 (*C*3), 126.0 (*C*5), 137.5 (*C*4), 143.4 (*C*2), 158.0 (*C*6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 9.33. HRMS (ESI) m/z calcd for $C_{13}H_{21}NO$ (hydrolysis of **16** to the alcohol; protonated): 208.170139, found: 208.16944.

1 + *N*,*N*-dimethylacetamide (17)

160 mg (0.5 mmol) of **1** and 180 mg (2.1 mmol) of *N*,*N*-dimethylacetamide was dissolved in 20 mL of hexane. The solution was heated at 60°C for 3 hours. The solution turned light yellow. The contents were cooled to room temperature. Yellow oil was obtained after solvent removal in vacuo. Yield: 77 mg (38%). δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 0.42-0.54 (4 H, m, C*H*$_2$CH$_3$), 0.67 (6 H, t, J 7.4, CH$_2$C*H*$_3$), 1.91 (3 H, s, C*H*$_3$), 5.18 (1 H, s, C*H*), 6.73 (1 H, dd, J 8.2 and 0.8, *H*5), 6.88 (1 H, td, J 6.6 and 1.4, *H*3), 7.49 (1 H, td, J 7.6 and 1.8, *H*4), 7.75 (1 H, dd, J 5.8 and 0.8, *H*2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 8.7 (CH$_2$*C*H$_3$), 13.9 (br, *C*H$_2$CH$_3$), 22.8 (*C*H$_3$), 93.6 (*C*7), 118.1 (*C*3), 119.9 (*C*5), 138.7 (*C*4), 140.5 (*C*2), 152.5 (*C*8), 169.9 (*C*6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 7.52. Found: C, 70.19; H, 8.63; N, 6.26. $C_{12}H_{18}BNO$ requires C, 70.97; H, 8.93; N, 6.90 %.

2b + Benzonitrile (18)

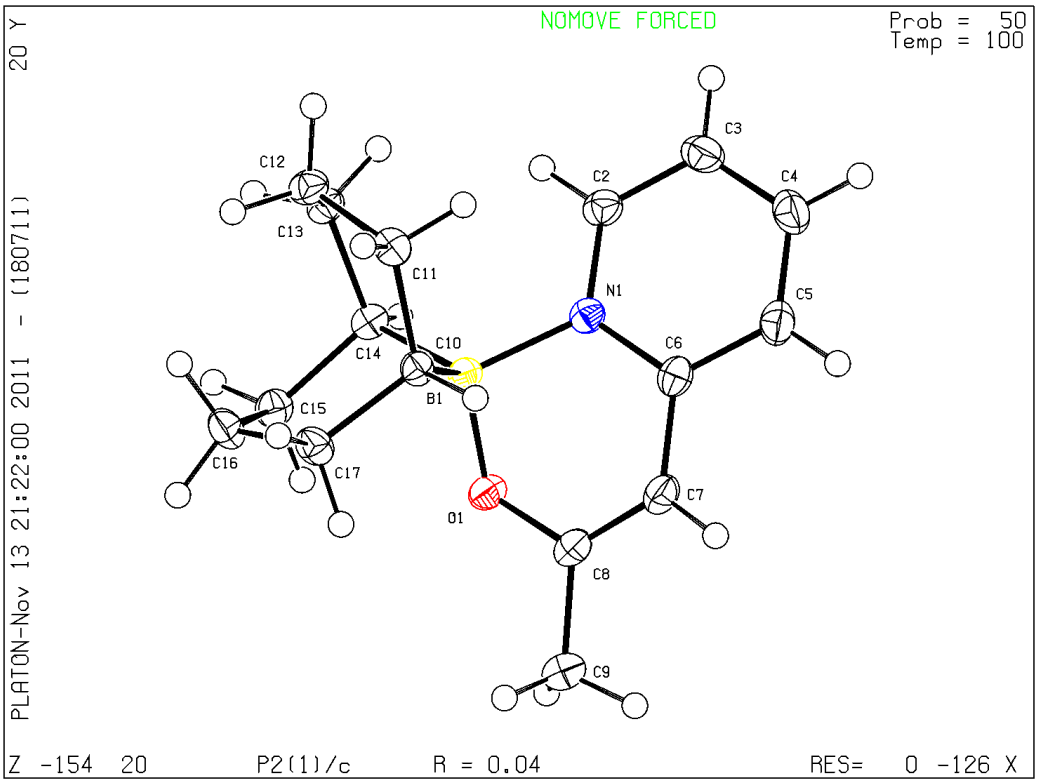
199 mg (0.5 mmol) of **2b** was mixed with 15 mL of toluene. 60 mg (0.58 mmol) of benzonitrile was added and heated at 50°C for 3 hours. The solution color became orange upon heating. After cooling, volatiles were removed in vacuo and the product was extracted with acetonitrile. The product was recovered after evaporation of the acetonitrile. Yield: 70 mg (44%). Mp: 118-120°C. δ_H (200 MHz; C_6D_6; C_6H_6): 1.59 (2 H, br s, BBN C*H*$_x$), 1.86-2.25 (12 H, m, BBN C*H*$_x$), 4.92 (1 H, br s, N*H*), 5.58 (1 H, d, J 1.6, C*H*, *H*7), 6.19 (1 H, dt, J 6.6 and 1.2, *H*3), 6.48 (1 H, td, J 8.6 and 0.8, *H*5), 6.74 (1 H, td, J 7.8 and 1.6, *H*4), 7.10-7.18 (3 H, m, *H*-m and p), 7.54-7.61 (2 H, m, *H*-o), 8.10 (1 H, dd, J 5.8 and 1.6, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 20.3 (br, BBN*C*H), 24.3 (BBN*C*H$_2$), 25.0 (BBN*C*H$_2$), 31.6 (BBN*C*H$_2$), 33.4 (BBN*C*H$_2$), 92.3 (*C*7), 115.1 (*C*3), 120.9 (*C*5), 127.2 (*C*-o), 128.9 (*C*-m), 130.0 (*C*-p), 135.4 (*C*4), 138.7 (*C*9), 141.3 (*C*2), 154.4 (*C*8), 156.5 (*C*6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 0.23. HRMS (ESI) m/z calcd for $C_{21}H_{26}BN_2$ ([**18**+H]$^+$): 317.218903, found: 317.22349.

2b + 4-chlorobenzaldehyde (19)

200 mg (0.5 mmol) of **2b** and 70 mg (0.5 mmol) of 4-chlorobenzaldehyde were dissolved in 5 mL of dichloromethane. The reaction was stirred at room temperature for 12 hours. The solvent was allowed to evaporate in the glovebox to give a powder. Yield: 143 mg (81%). Starting from **2**: 106 mg of **2** and 70 mg of 4-chlorobenzaldehyde was weighed in a flask and 10 mL of toluene was added. The solution was heated at 60°C overnight. The contents were cooled to room temperature, and the solvent was removed in vacuo after cooling. Yield: 150 mg (85%). Mp: 109-111°C. δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 0.91 (br s, BBNCH_x), 1.43 (br s, BBNCH_x), 1.65-1.86 (m, BBNCH_x), 3.13 (1 H, dd, J 16.0 and 8.6, CH_2), 3.43 (1 H, dd, J 16.0 and 4.6, CH_2), 5.29 (1 H, dd, J 8.8 and 4.8, C*H*), 7.19-7.35 (6 H, m, *H*5, *H*3 and *H*-o,m,p), 7.72 (1 H, dt, J 7.8 and 1.6, *H*4), 8.82 (1 H, d, J 5.4, *H*2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 23.7 (BBN*C*H_x), 32.4 (BBN*C*H_x), 32.8 (BBN*C*H_x), 41.2 (*C*7), 68.5 (*C*8), 121.8 (*C*3), 126.6 (*C*5), 126.9 (*C*-o), 128.2 (*C*-m), 138.4 (*C*4), 145.8 (*C*2), 157.2 (*C*6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 19.87. HRMS (ESI) m/z calcd for $C_{13}H_{12}ClNO$ (hydrolysis of **19** to the alcohol; protonated): 234.0686, found: 234.0705; calcd for $C_{21}H_{25}BNO^+$ (**19**-Cl^-): 318.202919, found: 318.09258.

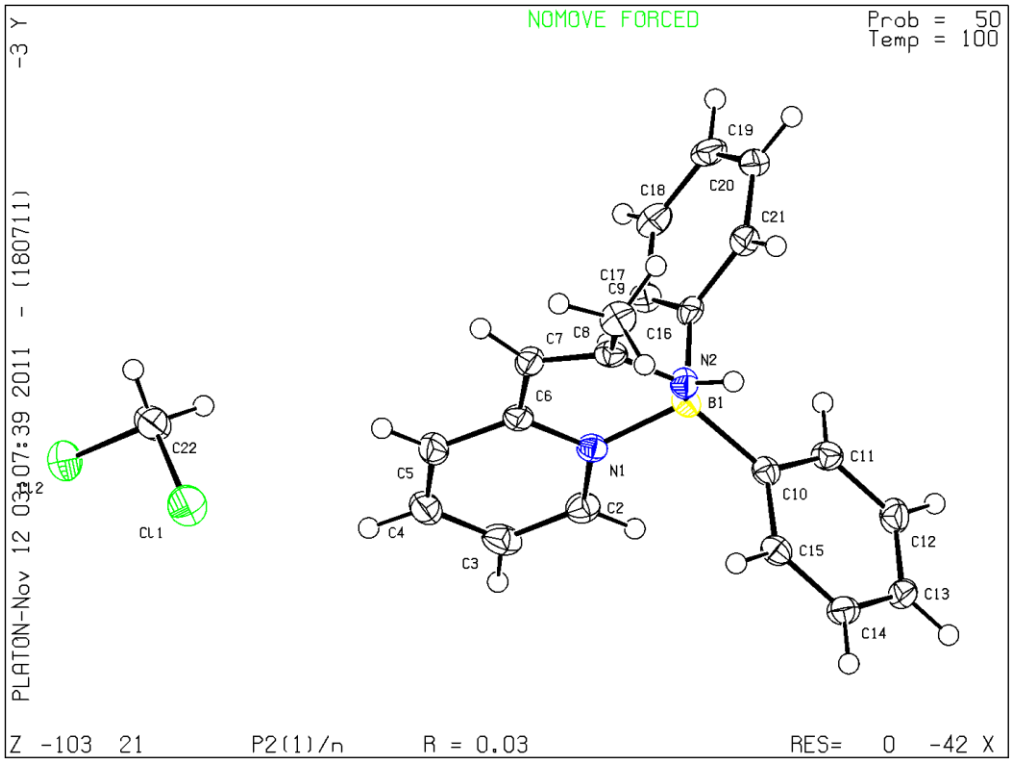
2 + *N*,*N*-dimethylacetamide (20)

218 mg (0.5 mmol) of **2** was dissolved in 20 mL of toluene. 90 mg (1.0 mmol) of *N*,*N*-dimethylacetamide was added and heated at 60°C for 2 h. The contents were cooled to room temperature, and the solvent was removed in vacuo after cooling. Pentane was used to extract the product from the crude material. Slow evaporation of the pentane solution in the glovebox yielded orange crystals. Yield: 241 mg (94%). Mp: 146-148°C. δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 1.09 (br s, BBNC*H*$_x$), 1.23 (br s, BBNC*H*$_x$), 1.48-1.99 (br m, BBNC*H*$_x$), 2.03 (3 H, s, CH3), 5.55 (1 H, s, C*H*), 6.86 (1 H, d, J 8.2 and 0.8, *H*5), 7.00 (1 H, dt, J 6.6 and 1.2, *H*3), 7.57 (1 H, dt, J 7.8 and 1.6, *H*4), 8.33 (1 H, d, J 6.2, *H*2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 22.6 (BBN*C*H$_x$), 24.1 (C9 and BBN*C*H$_x$), 31.6 (BBNCH$_x$), 32.7 (BBN*C*H$_x$), 97.9 (*C*7), 118.0 (*C*3), 120.1 (*C*5), 138.4 (*C*4), 141.8 (*C*2). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 6.59. HRMS (ESI) m/z calcd for $C_{16}H_{22}BNO$ (**20**$^+$): 255.179444, found: 255.20255.



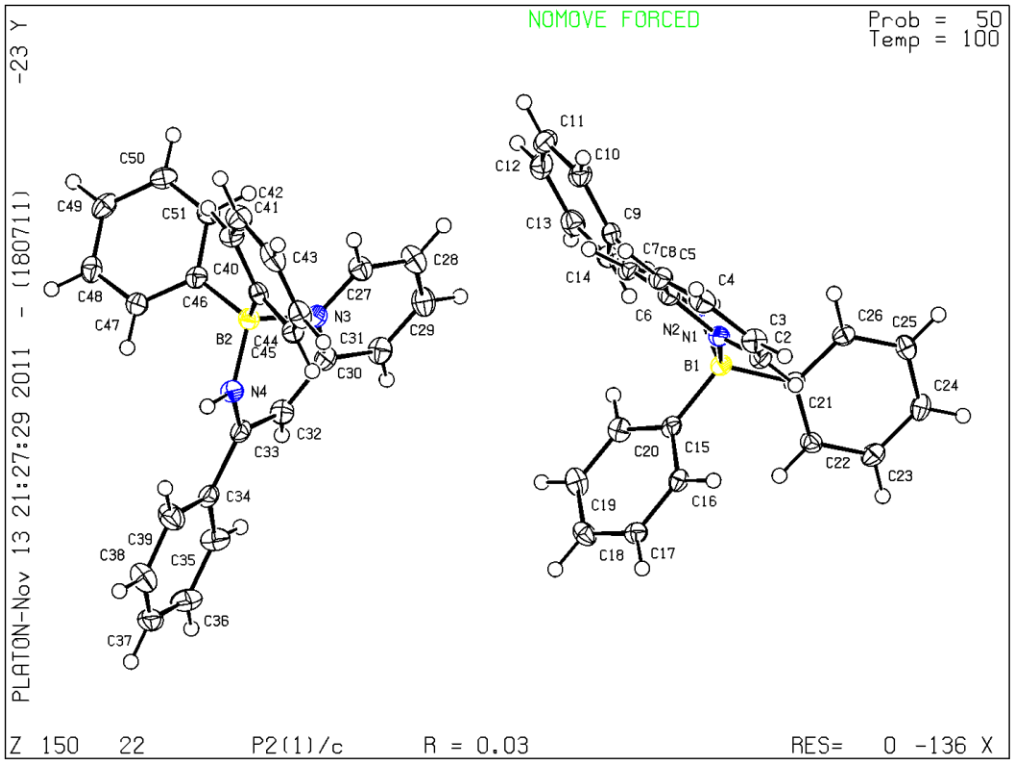
3 + acetonitrile (21)

A solution of 182 mg (0.35 mmol) of **3** in toluene (10 mL) was prepared. To this, 540 mg (13.2 mmol) of acetonitrile was added, and the contents were heated at 100°C overnight. The contents were cooled to room temperature, and the solvent was removed with vacuum leaving crude product. The product was recrystallized from dichloromethane. Yield: 204 mg (98%). Mp: 140-142°C. δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 1.97 (3 H, s, CH3), 4.83 (1 H, br s, N*H*), 4.88 (1 H, d, J 2.4, *H*7), 6.48 (1 H, dt, J 6.4 and 1.2, *H*3), 6.67 (1 H, dd, J 7.4 and 1.2, *H*5), 7.10-7.20 (10 H, m, Ph), 7.26 (1 H, dd, J 7.9 and 1.5, *H*4), 7.44 (1 H, d, J 6.8, *H*2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 22.5 (CH3), 90.1 (*C*7), 114.4 (*C*3), 120.3 (*C*5), 126.1 (Ph-p), 127.2 (Ph-m), 133.2 (Ph-o), 137.0 (*C*4), 142.0 (C2), 153.3(C8), 158.0 (C6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 0.65. HRMS (ESI) m/z calcd for $C_{20}H_{20}N_2B$ (**21**+H^+): 299.171953, found: 299.17157.



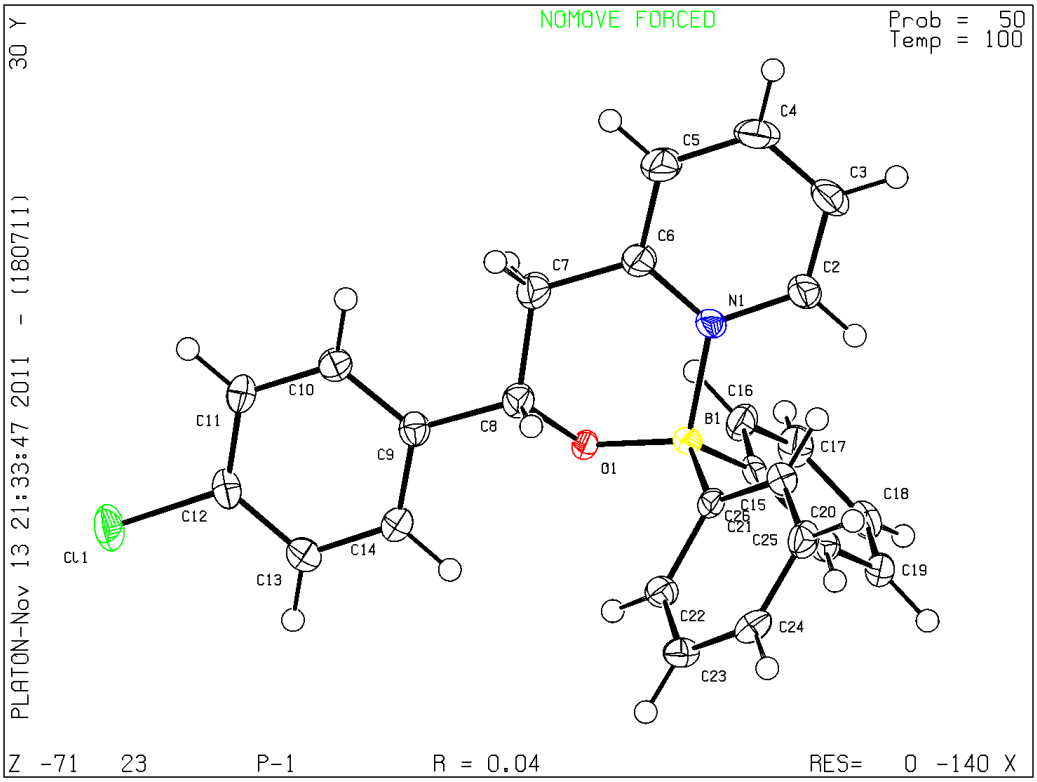
3 + Benzonitrile (22)

268 mg (0.52 mmol) of **3** was mixed with 10 mL toluene. 113 mg (1.10 mmol) of benzonitrile was added and heated at 100°C for 3 hours. After cooling, the solvent was removed in vacuo. The product was recrystallized from dichloromethane. Yield: 135 mg (72%). Mp: 180-182°C. δ_H (200 MHz; $CDCl_3$; $CHCl_3$): 5.14 (1 H, br s, N*H*), 5.44 (1 H, d, J 2.4, C*H*, *H*7), 6.62 (1 H, dt, J 6.7 and 1.5, *H*3), 6.90 (1 H, dd, J 9.4 and 1.2, *H*5), 7.10-7.29 (10 H, m, Ph-o, Ph-m and Ph-p), 7.32-7.41 (4 H, m, *H*4, PhCN-m and PhCN-p), 7.60-7.64 (2 H, m, PhCN-o), 8.18 (1 H, dd, J 8.0 and 1.8, *H*2). δ_C (50 MHz; $CDCl_3$; $CHCl_3$) 90.1 (*C*7), 115.5 (*C*3), 121.3 (*C*5), 126.2 (Ph-p), 126.6 (PhCN-o), 127.2 (Ph-m), 128.0 (PhCN-p), 128.7 (PhCN-m), 130.2 (*C*4), 133.3 (Ph-o), 135.6 (*C*2). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 0.84. HRMS (ESI) m/z calcd for $C_{25}H_{22}BN_2$ (**22**+H^+): 361.187603, found: 361.19393.



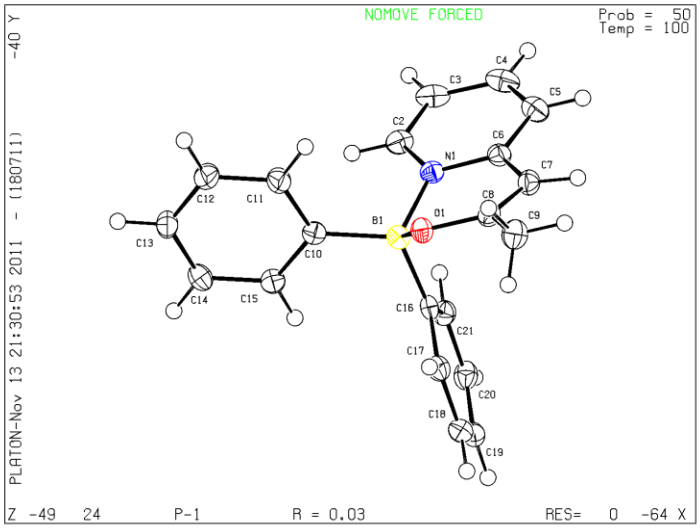
3 + 4-chlorobenzaldehyde (23)

127 mg (0.25 mmol) of **3** was mixed with 10 mL of toluene. 70 mg (0.50 mmol) of 4-chlorobenzaldehyde was added and heated at 100°C for 2 h. After cooling, the solvent was removed in vacuo. Pale yellow crystalline product was obtained, and was purified by washing with 2 mL of acetonitrile. Crystals suitable for X-ray diffraction were obtained by slow evaporation from acetone. Yield: 177 mg (89%). Mp: 179-181°C. δ_H (200 MHz; C_6D_6; C_6H_6): 2.22 (1 H, dd, J 17.2 and 4.2, C*H*$_2$), 2.37 (1 H, dd, J 17.0 and 9.4, C*H*$_2$), 4.75 (1 H, dd, J 9.1 and 4.3, C*H*), 5.77 (1 H, t, J 6.7, *H*3), 5.84 (1 H, d, J 7.8, *H*5), 6.29 (1 H, dt, J 7.8 and 1.4, *H*4), 6.86-7.12 (10 H, m, Ph-Cl, Ph-o and Ph-m), 7.57(2 H, dd, J 8.0 and 1.4, Ph-p), 7.72 (1 H, dd, J 5.9 and 1.1, *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 39.8 (*C*7), 68.1 (C8), 121.5 (*C*3), 126.5 (Ph-Cl), 127.1 (*C*5), 127.7 (Ph-o), 128.5 (Ph-Cl), 132.7 (Ph-m), 134.6 (Ph-p), 139.0 (*C*4), 133.3 (Ph-o), 144.5 (*C*-ipso), 145.3 (*C*2), 156.6 (*C*6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 7.5. HRMS (ESI) m/z calcd for $C_{25}H_{22}BClNO$ (**23**+H^+): 398.148296, found: 398.14317.



3 + *N*,*N*-dimethylacetamide (24)

126 mg (0.25 mmol) of **3** was mixed with 10 mL of toluene. 58 mg (0.67 mmol) of *N*,*N*-dimethylacetamide was added and heated 100°C for 3 h. The contents were cooled to room temperature, and the solvent was removed in vacuo. The product was recrystallized from dichloromethane. The product was recrystallized a second time from acetonitrile, which give rise to crystals suitable for X-ray diffraction. Yield: 105 mg (70%). Mp: 164-166°C. δ_H (200 MHz; C_6D_6; C_6H_6): 1.83 (3 H, s, C*H*$_3$), 5.00 (1 H, s, *H*7), 6.48 (1 H, dt, J 6.6 and 1.3, *H*3), 6.03 (1 H, dd, J 8.0 and 0.8, *H*5), 6.57 (1 H, dt, J 7.9 and 1.4, *H*4), 7.20-7.38 (6 H, m, Ph-p and Ph-m), 7.53-7.62 (5 H, m, Ph-o and *H*2). δ_C (50 MHz; C_6D_6; C_6H_6) 22.9 (*C*9), 97.0 (*C*7), 118.0 (*C*3), 120.0 (*C*5), 126.9 (Ph-p), 127.6 (Ph-m), 133.6 (Ph-o), 139.1 (*C*4), 142.4 (C2), 153.3(C8), 158.0 (C6). δ_B (64 MHz; $CDCl_3$; BF_3OEt_2) 5.5. HRMS (ESI) m/z calcd for $C_{20}H_{19}BNO$ (**24**+H^+): 300.155969, found: 300.15460.



X-ray table.

	1	**1a**	**2**	**2a**	**2b**	**3**	**4**
Empirical formula	$C_{10}H_{16}BN$	$C_{17}H_{35}BLiN_3O$	$C_{28}H_{40}B_2N_2$	$C_{21}H_{39}BLiN_3O$	$C_{23}H_{39}BLiNO_3$	$C_{36}H_{32}B_2N_2$	$C_{38}H_{26}B_2N_3$
Formula weight	161.05	315.23	426.24	367.30	395.30	514.26	546.24
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	$Pna2_1$	P-1	$P2_1/n$	P-1	C2/c	$P2_1/c$
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
T (K)	100(2)	100(2)	247(2)	100(2)	101(2)	100(2)	100(2)
a (Å)	30.181(3)	10.166(4)	8.6278(7)	9.537(2)	9.1997(5)	20.0937(16)	19.7442(8)
b (Å)	9.9266(8)	13.303(6)	11.1348(8)	19.523(5)	10.0620(5)	9.9331(8)	8.9337(4)
c (Å)	14.6281(12)	15.011(6)	13.2544(10)	11.571(3)	13.7746(7)	15.1773(12)	16.7141(7)
α	90	90	71.123(1)	90	75.513(1)	90	90
β	118.99	90	89.295(1)	91.102(3)	85.615(1)	112.871(1)	103.467(1)
γ	90	90	87.433(1)	90	66.257(1)	90	90
V ($Å^3$)	3833.4(5)	2030.2(15)	1203.64(16)	2153.9(9)	1129.62(10)	2791.1(4)	2867.1(2)
Z	16	4	2	4	2	4	4
ρ_{calcd} (g cm^{-3})	1.116	1.031	1.176	1.133	1.162	1.224	1.265
μ (mm^{-1})	0.063	0.063	0.066	0.068	0.073	0.070	0.073
F(000) (e)	1408	696	464	808	432	1088	1140
Crystal size (mm)	0.64 × 0.55 × 0.26	0.86 × 0.46 × 0.39	0.35 × 0.32 × 0.30	0.40 × 0.33 × 0.32	0.66 × 0.46 × 0.44	0.52 × 0.28 × 0.18	0.48 × 0.26 × 0.20
θ range (deg)	2.19 to 25.42	2.05 to 18.16	1.62 - 25.40	2.05 – 18.53	2.28 to 25.52	2.20 to 25.46	2.12 to 25.31
hkl range	-36 → 36 -11 → 11 -17 → 17	-8 → 8 -11 → 11 -13 → 13	-10 → 10 -13 → 13 -15 → 15	-8 → 8 -17 → 17 -10 → 10	-11 → 11 -12 → 12 -16 → 16	-24 → 24 -12 → 12 -18 → 18	-23 → 23 -10 → 10 -20 → 20
Reflections collected / unique	18815/3529	8205/1421	12312/4432	10308/1602	11471/4176	13754/2591	27952/5218
Data / restraints / parameters	3529/0/221	1421/1/215	4432/0/289	1602/0/249	4176/0/263	2591/0/181	5218/0/389
GOF on F^2	1.053	1.105	1.028	1.292	1.051	1.033	1.044
R1/wR2 [I > 2sigma(I)]	0.0380/0.1010	0.0410/0.1014	0.0511/0.1161	0. 0915/ 0.2621	0.0585/0.1394	0.0363/0.0827	0.0531/0.1483
R1/wR2 (all data)	0.0432/0.1051	0.0446/0.1044	0.1029/0.1372	0.0974/0.2649	0.0708/0.1486	0.0501/0.0907	0.0656/0.1596
Largest diff. peak and hole ($e.Å^{-3}$)	0.299 and -0.197	0.153 and -0.172	0.240 and -0.229	0.379 and -0.285	1.038 and -0.645	0.270 and -0.211	0.850 and -0.208

CIF files in separate attachment.