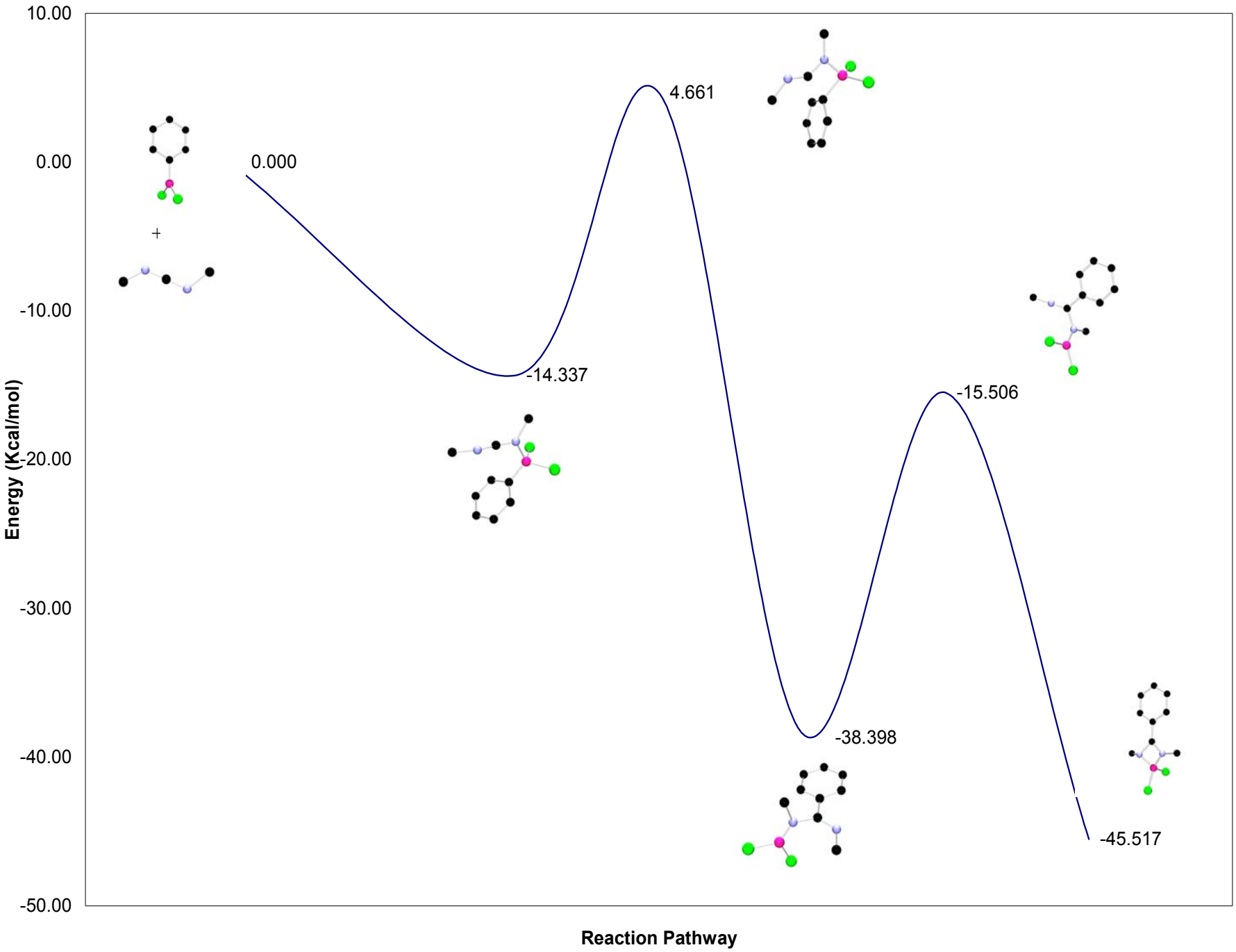
Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Isolation of an intermediate in the insertion of a carbodiimide into a boron-aryl bond

Nicholas J. Hill, Jennifer A. Moore, Michael Findlater and Alan H. Cowley*
Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, Texas 78712, USA. E-mail: cowley@mail.utexas.edu; FAX: (+1)512-471-6822; Tel: (+1)512-471-7484.


10.00
0.00
-10.00
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-50.00
Energy (Kcal/mol)
Reaction Pathway
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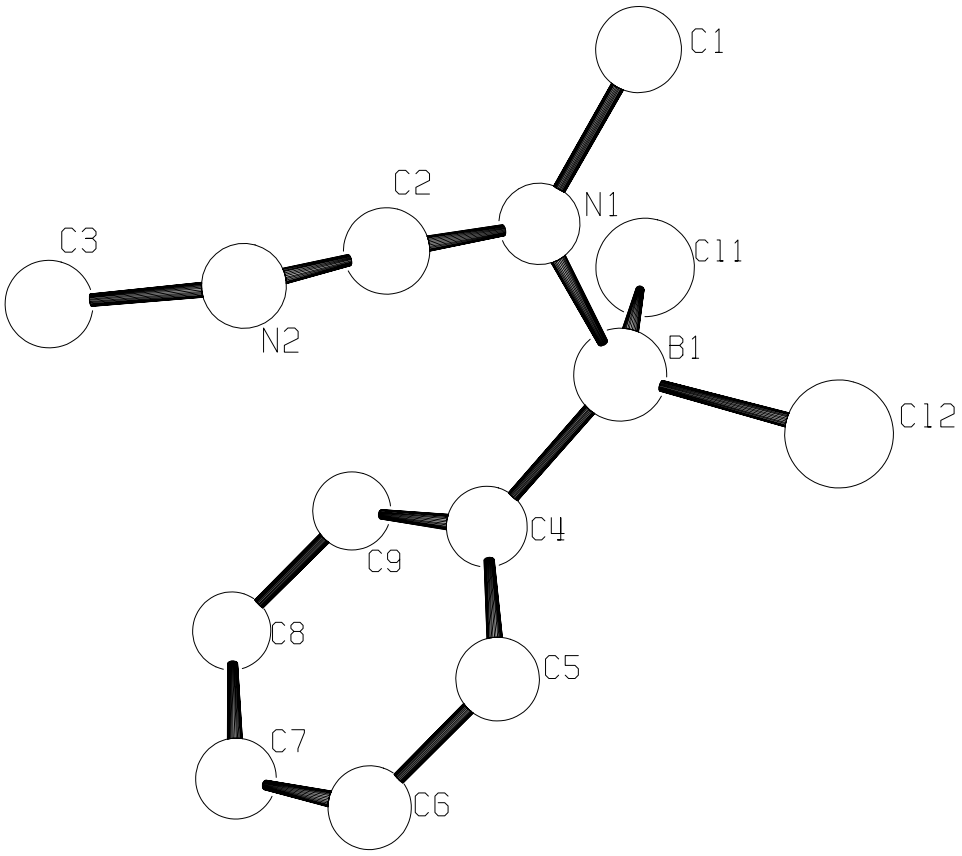
-14.337
4.661
-38.398
-15.506
-45.517
+

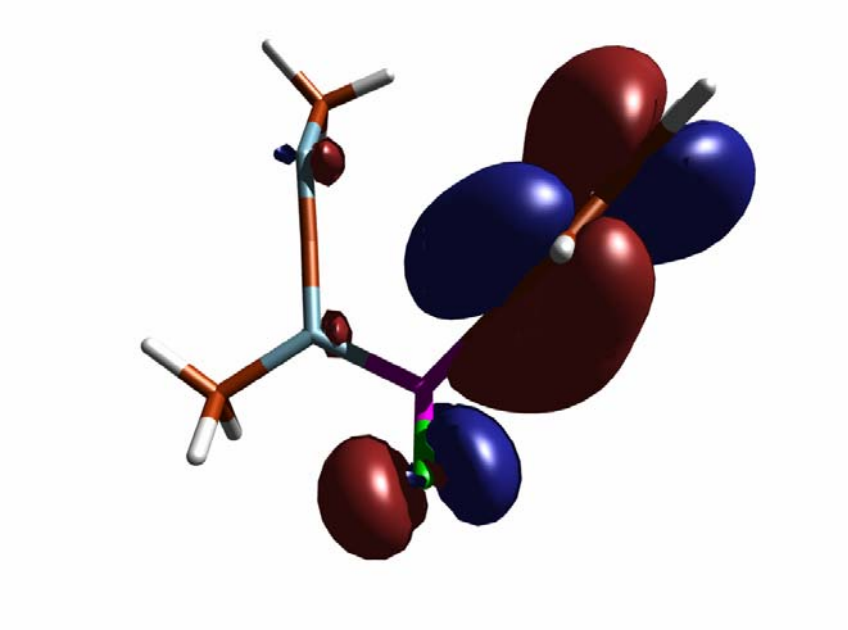
IM1



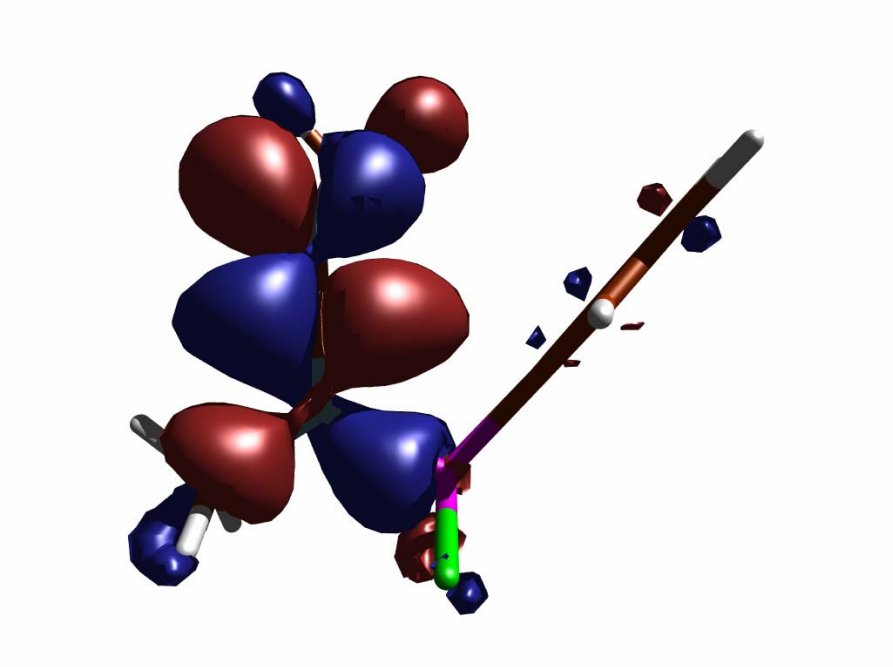
IM1

Bond	(Å)	Angle	Degrees	Dihedral	Degrees
B(1)-Cl(1)	1.88485	Cl(1)- B(1)-Cl(2)	110.876	Cl(2)-B(1)-N(1)-C(3)	0.721
B(1)-Cl(2)	1.87425	Cl(1)- B(1)-N(1)	104.316	C(2)-N(2)-C(3)-N(1)	152.219
B(1)-N(1)	1.64181	Cl(2)- B(1)-N(1)	105.025		
N(1)-C(1)	1.50502	B(1)-N(1)-C(3)	118.355		
N(1)-C(3)	1.26819	B(1)-N(1)-C(1)	119.619		
N(2)-C(3)	1.18587	N(1)-C(3)-N(2)	174.860		
B(1)-C(4)	1.60005	C(2)-N(2)-C(3)	143.645		
N(2)-C(2)	1.46217	C(4)-B(1)-N(1)	107.486		
C(4)-C(5)	1.40746				
C(5)-C(6)	1.39700				
C(6)-C(7)	1.39675				
C(7)-C(8)	1.39856				
C(8)-C(9)	1.39744				
C(9)-C(4)	1.41105				
Orbital energies	Kcal/mole				
HOMO	LUMO	HOMO-LUMO GAP			
-156.24	-31.0371	-125.203			

IM1

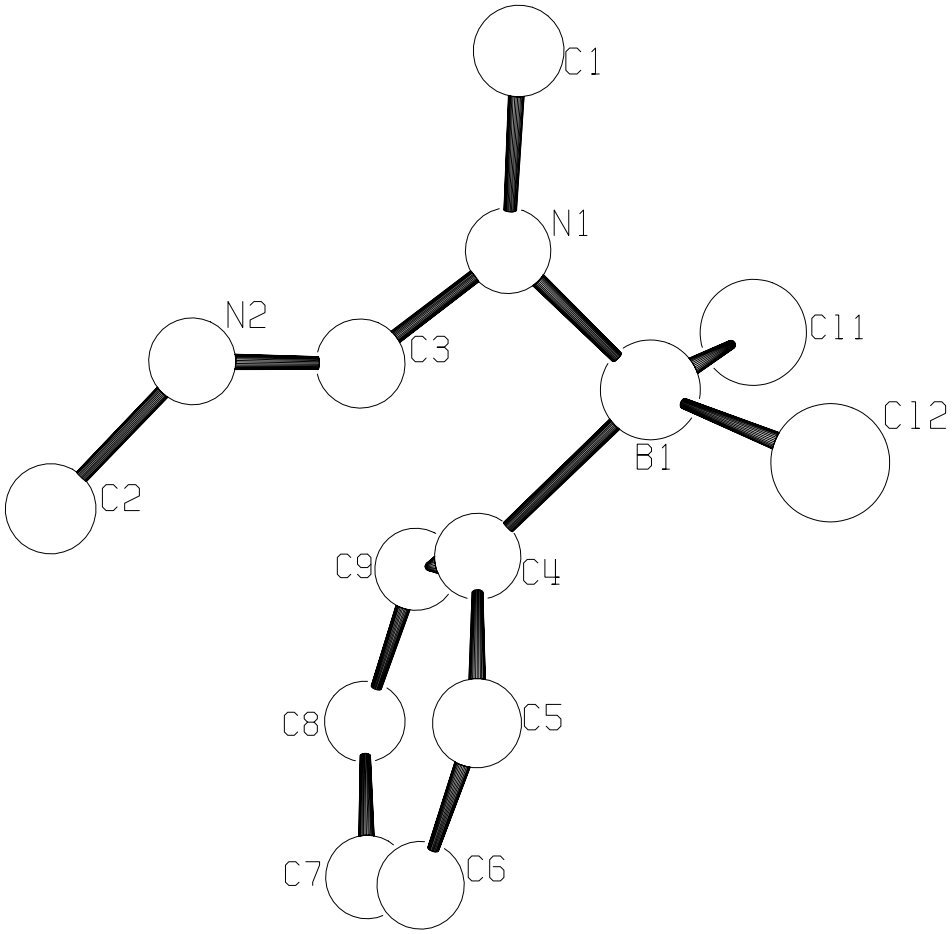


HOMO



LUMO

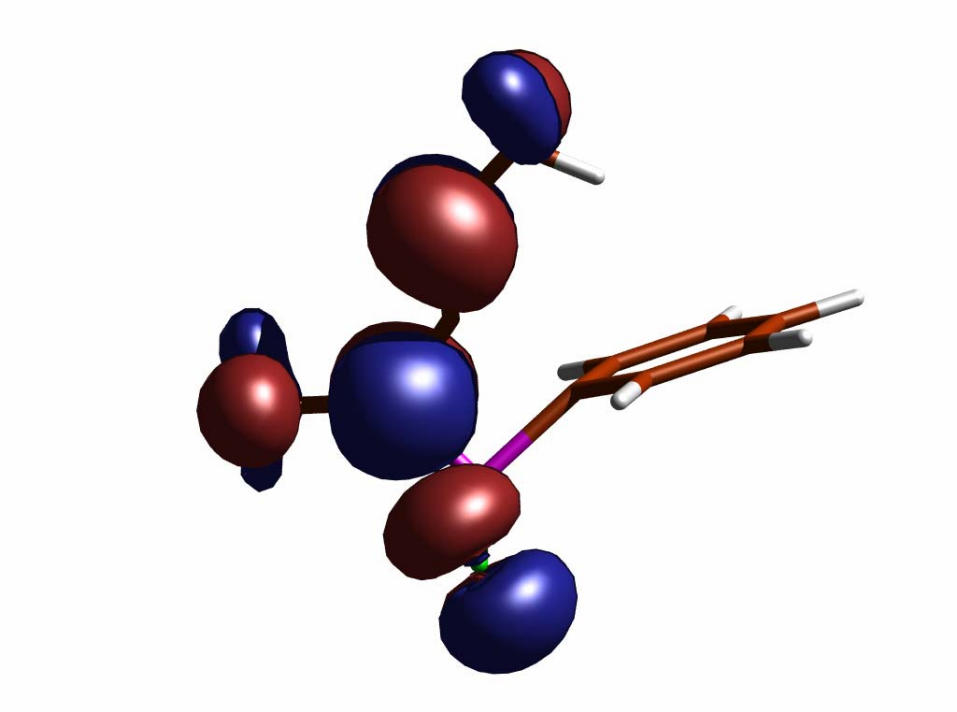
TS1



TS1

Bond	(Å)	Angle	Degrees	Dihedral	Degrees
B(1)-Cl(1)	1.86145	Cl(1)- B(1)-Cl(2)	111.57	Cl(2)-B(1)-N(1)-C(3)	-105.16
B(1)-Cl(2)	1.84707	Cl(1)- B(1)-N(1)	115.007	C(2)-N(2)-C(3)-N(1)	3.434
B(1)-N(1)	1.51956	Cl(2)- B(1)-N(1)	113.692		
N(1)-C(1)	1.47046	B(1)-N(1)-C(3)	99.365		
N(1)-C(3)	1.33753	B(1)-N(1)-C(1)	133.479		
N(2)-C(3)	1.23627	N(1)-C(3)-N(2)	140.070		
C(3)-C(4)	1.87103	C(2)-N(2)-C(3)	130.893		
N(2)-C(2)	1.45212	N(2)-C(3)-C(4)	125.025		
C(4)-C(5)	1.42746	N(1)-C(3)-C(4)	94.883		
C(5)-C(6)	1.39115				
C(6)-C(7)	1.39996				
C(7)-C(8)	1.40198				
C(8)-C(9)	1.38733				
C(9)-C(4)	1.43040				
Orbital energies	Kcal/mole				
HOMO	LUMO	HOMO-LUMO GAP			
-156.918	-71.3678	85.5498			

TS1



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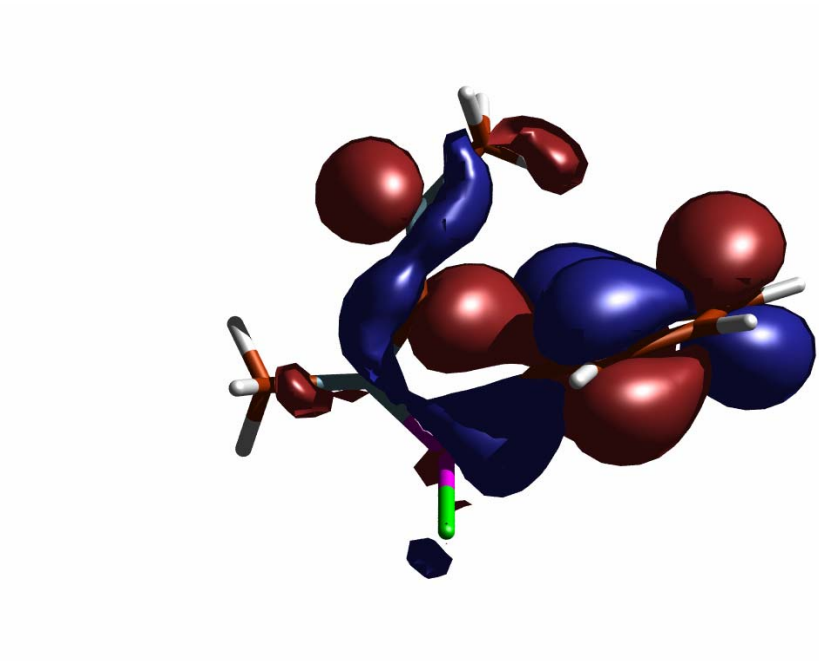
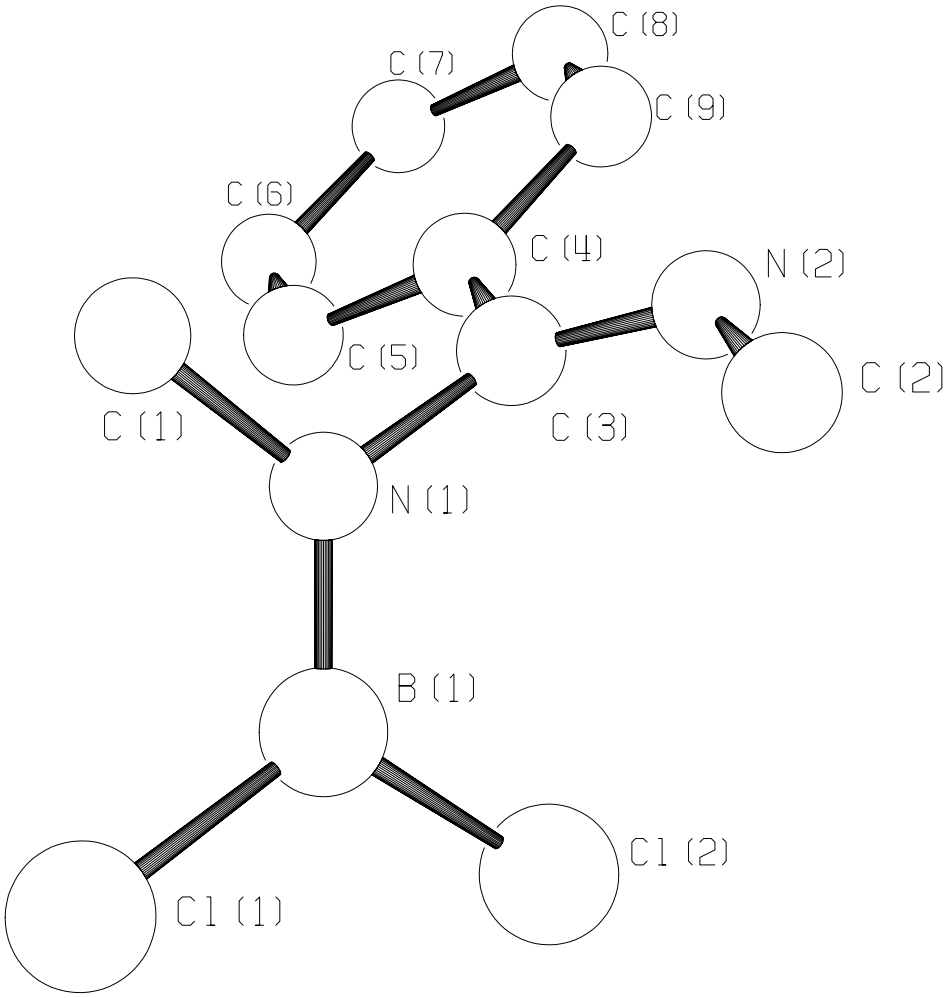


LUMO

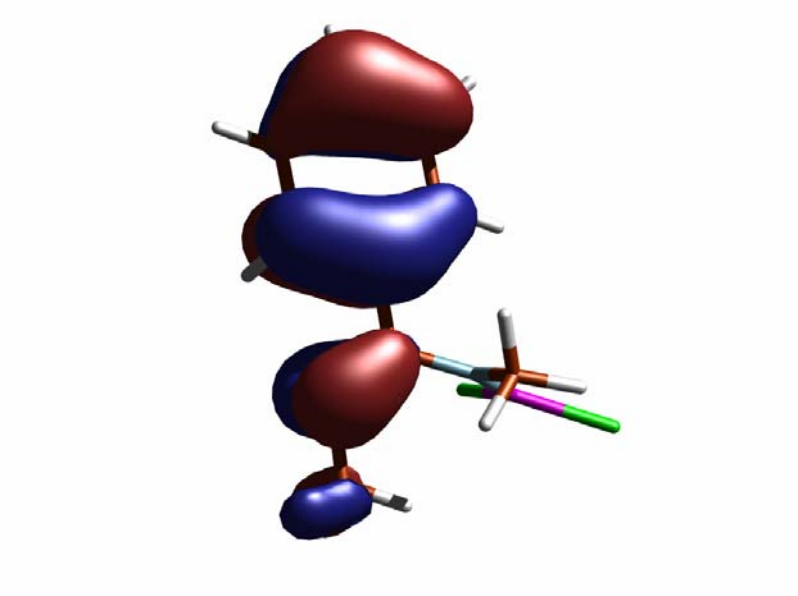
IM2



IM2

Bond	(Å)	Angle	Degrees	Dihedral	Degrees
B(1)-Cl(1)	1.78458	Cl(1)- B(1)-Cl(2)	117.386	Cl(2)-B(1)-N(1)-C(3)	-2.142
B(1)-Cl(2)	1.77938	Cl(1)- B(1)-N(1)	121.700	C(2)-N(2)-C(3)-N(1)	2.232
B(1)-N(1)	1.39817	Cl(2)- B(1)-N(1)	120.912		
N(1)-C(1)	1.47038	B(1)-N(1)-C(3)	122.142		
N(1)-C(3)	1.45857	B(1)-N(1)-C(1)	125.157		
N(2)-C(3)	1.27197	N(1)-C(3)-N(2)	123.604		
C(3)-C(4)	1.49127	C(2)-N(2)-C(3)	122.794		
N(2)-C(2)	1.44714	N(2)-C(3)-C(4)	120.267		
C(4)-C(5)	1.40373	N(1)-C(3)-C(4)	116.083		
C(5)-C(6)	1.39723				
C(6)-C(7)	1.39604				
C(7)-C(8)	1.40022				
C(8)-C(9)	1.39265				
C(9)-C(4)	1.40680				
Orbital energies	Kcal/mole				
HOMO	LUMO	HOMO-LUMO GAP			
-159.516	-38.2411	121.277			

IM2



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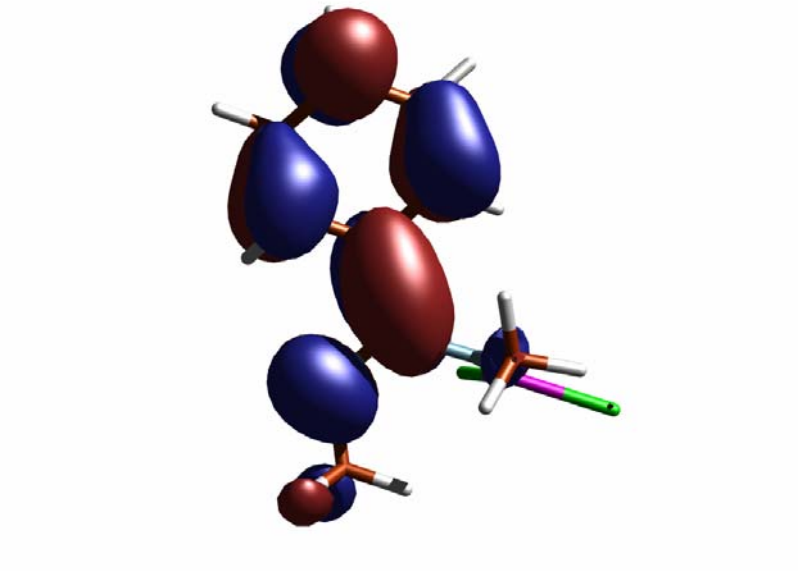
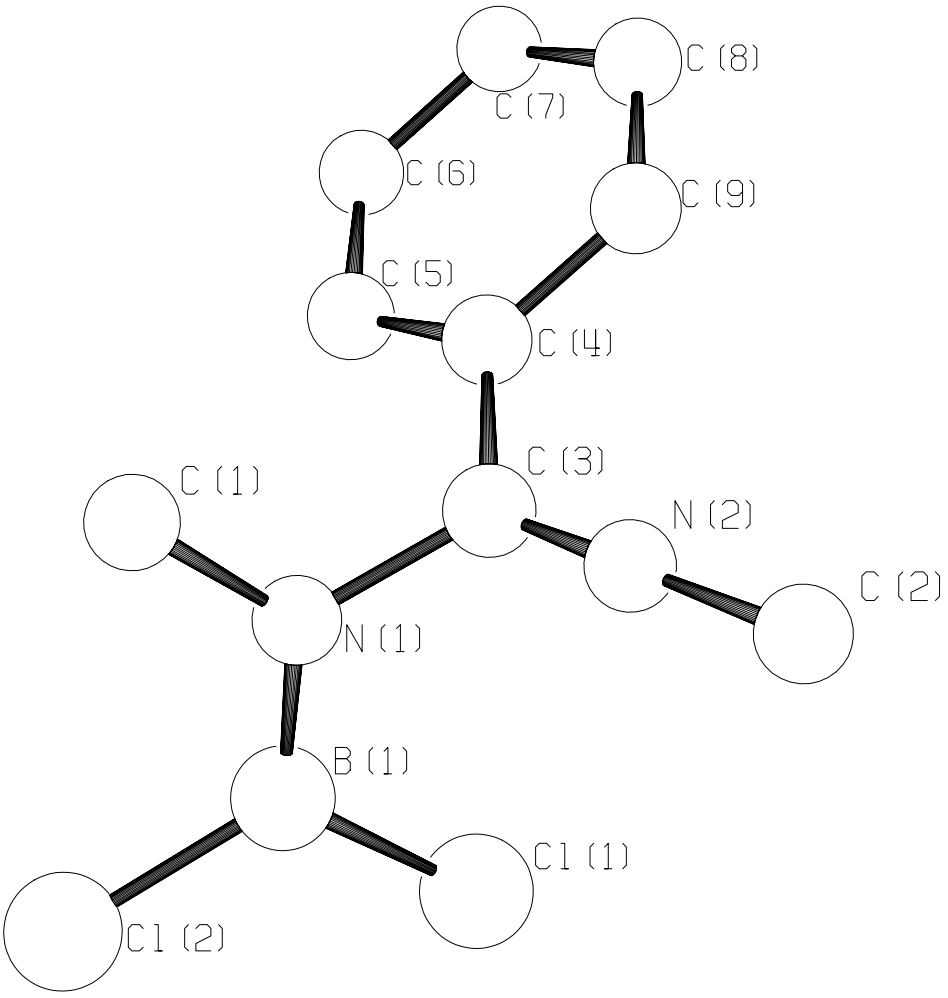


LUMO

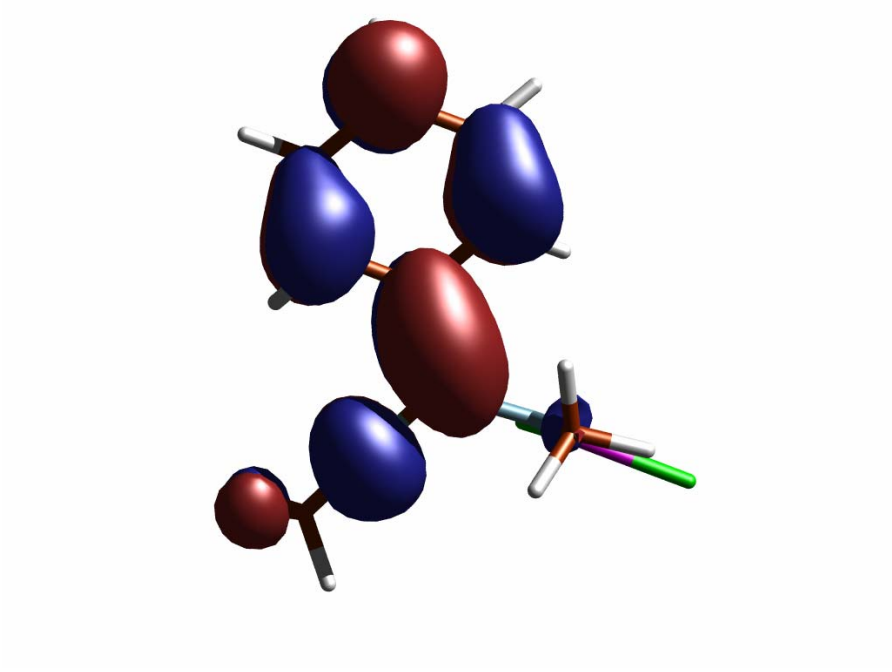
TS2



Bond	(Å)	Angle	Degrees	Dihedral	Degrees
B(1)-Cl(1)	1.79033	Cl(1)- B(1)-Cl(2)	117.387	Cl(2)-B(1)-N(1)-C(3)	112.201
B(1)-Cl(2)	1.78326	Cl(1)- B(1)-N(1)	121.429	C(2)-N(2)-C(3)-N(1)	115.693
B(1)-N(1)	1.40003	Cl(2)- B(1)-N(1)	121.178		
N(1)-C(1)	1.49151	B(1)-N(1)-C(3)	122.217		
N(1)-C(3)	1.51668	B(1)-N(1)-C(1)	124.954		
N(2)-C(3)	1.23026	N(1)-C(3)-N(2)	121.526		
C(3)-C(4)	1.50150	C(2)-N(2)-C(3)	179.968		
N(2)-C(2)	1.41915	N(2)-C(3)-C(4)	126.261		
C(4)-C(5)	1.40188	N(1)-C(3)-C(4)	112.201		
C(5)-C(6)	1.39585				
C(6)-C(7)	1.39632				
C(7)-C(8)	1.39889				
C(8)-C(9)	1.39190				
C(9)-C(4)	1.40281				
Orbital energies	Kcal/mole				
HOMO	LUMO	HOMO-LUMO GAP			
-140.401	-37.3751	103.026			

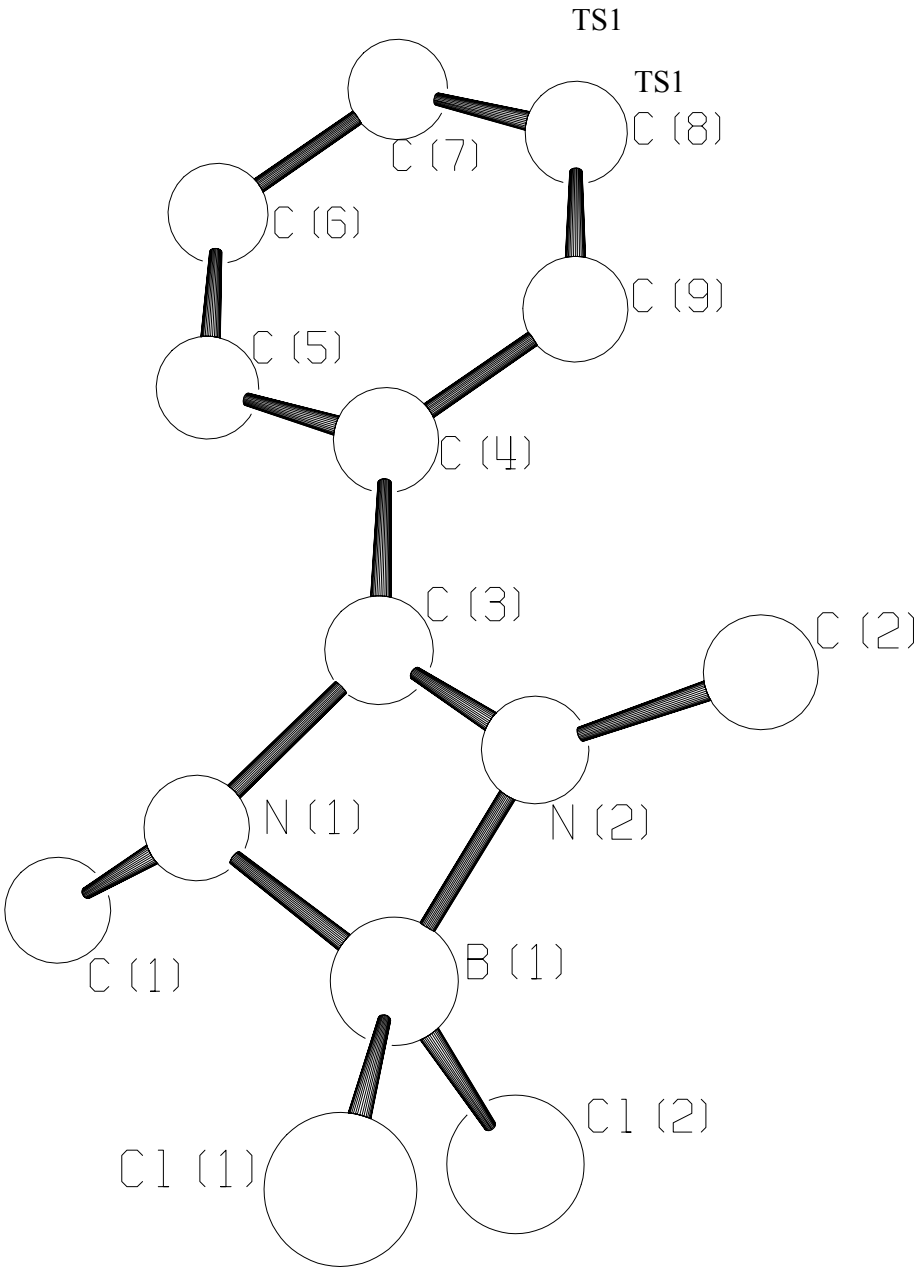
TS2

HOMO



LUMO

3



3

Bond	(Å)	Angle	Degrees	Dihedral	Degrees
B(1)-Cl(1)	1.87000	Cl(1)- B(1)-Cl(2)	105.863	Cl(2)-B(1)-N(1)-C(3)	138.635
B(1)-Cl(2)	1.87000	Cl(1)- B(1)-N(1)	118.857	C(2)-N(2)-C(3)-N(1)	-163.444
B(1)-N(1)	1.54054	Cl(2)- B(1)-N(1)	113.456		
N(1)-C(1)	1.74000	B(1)-N(1)-C(3)	84.720		
N(1)-C(3)	1.50419	B(1)-N(1)-C(1)	120.395		
N(2)-C(3)	1.33736	N(1)-C(3)-N(2)	94.960		
C(3)-C(4)	1.54000	C(2)-N(2)-C(3)	134.838		
N(2)-C(2)	1.47000	N(2)-C(3)-C(4)	132.537		
C(4)-C(5)	1.40140	N(1)-C(3)-C(4)	132.502		
C(5)-C(6)	1.40140	B(1)- N(2)-C(3)	90.321		
C(6)-C(7)	1.40140				
C(7)-C(8)	1.40140				
C(8)-C(9)	1.40140				
C(9)-C(4)	1.40140				
B(1)-N(2)	1.54834				
B(1)-C(3)	2.05161				
Orbital energies	Kcal/mole				
HOMO	LUMO	HOMO-LUMO GAP			
-155.248	-47.4342	107.814			

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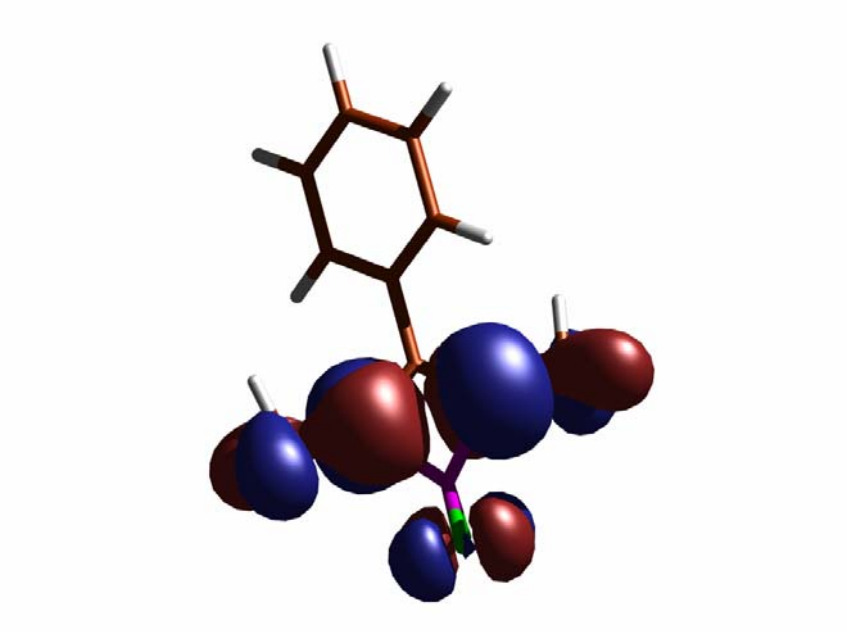
3



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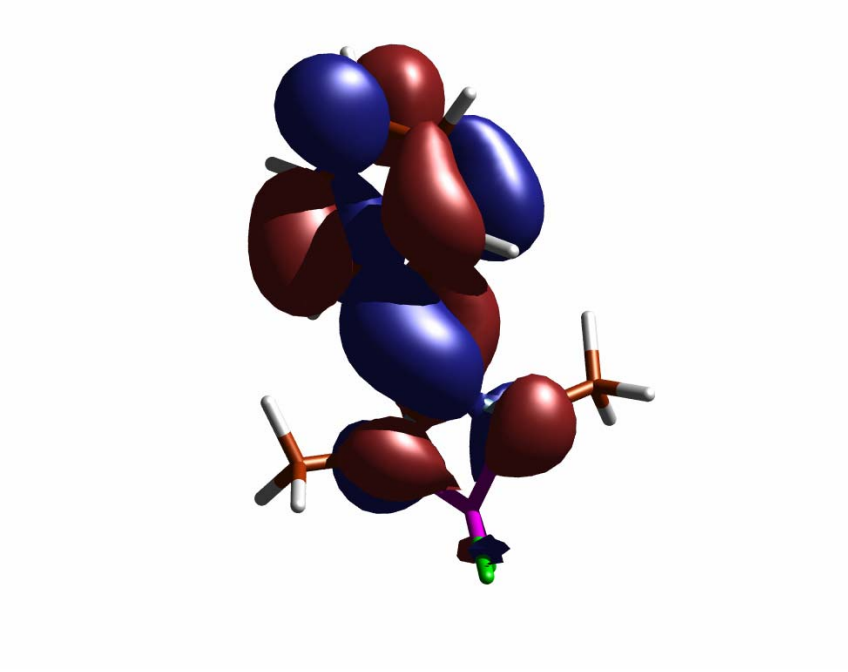

LUMO

Experimental

General procedures

All manipulations and reactions were performed under a dry, oxygen-free, catalyst-scrubbed argon atmosphere using a combination of standard Schlenk techniques or in an M-Braun or Vacuum Atmospheres drybox. All glassware was oven-dried and vacuum- and argon flow-degassed before use. All solvents were distilled over sodium benzophenone ketyl and degassed prior to use. 1,3-dicyclohexylcarbodiimide and dichlorophenylborane were obtained commercially and used without further purification.

Physical measurements

Low-resolution CI mass spectra were obtained on a Finnigan MAT TSQ-700 mass spectrometer and high-resolution CI mass spectra recorded on a VG Analytical ZAB-VE sector instrument. All MS analyses were performed on samples that had been sealed in glass capillaries under an argon atmosphere. ^{1}H, $^{13}C\{^{1}H\}$, and ^{11}B NMR spectra were recorded at 295 K in C_6D_6 solutions on a GE QE-300 instrument (^{1}H, 300 MHz; ^{13}C, 75 MHz, ^{11}B, 96 MHz) immediately following removal of the sample from the drybox. ^{1}H and $^{13}C\{^{1}H\}$ chemical shift values are reported in parts per million (ppm) relative to $SiMe_4$ (δ 0.00), using residual solvent resonances as internal standards. ^{11}B NMR data are referenced to BF_3:OEt_2 (δ 0.00). Melting points (uncorrected) were obtained on a Fisher-Johns apparatus after flame-sealing the samples in glass capillaries under argon.

X-ray crystallography

For compounds **1** and **2**, a crystal of suitable quality was removed from a Schlenk flask under positive argon pressure, covered immediately with degassed hydrocarbon oil and mounted on a glass fiber. The X-ray diffraction data were collected at 153 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream low-temperature device and a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods and refined by full-matrix least-squares cycles on F^2. All non-hydrogen atoms were allowed anisotropic thermal motion, and hydrogen atoms were placed in fixed, calculated positions using a riding model (C-H 0.96 Å).

Preparations

1. A solution of $PhBCl_2$ (0.77 g, 4.85 mmol) in 5 mL of hexanes was added to a cold (-78 ^oC) stirred solution of CyN=C=NCy (1.00 g, 4.85 mmol) in 15 mL of hexane. The reaction mixture was warmed to room temperature, stirred for 2 h and the solvent was removed *in vacuo* to give a white powder. Recrystallization of this powder from toluene solution afforded colourless crystals of **1** (1.71 g, 96% yield, mp 110-112 ^oC).

^1H NMR (C_6D_6): δ 7.39-7.19 (s, 5H); 3.13 (br s, 2H); 2.17 (br s, 4H); 1.68-0.95 (br m, 16H); ^{13}C NMR (C_6D_6): δ 154.34; 136.28; 133.93; 133.11; 58.52; 55.68; 33.95; 32.57; 31.26; 26.51; 26.37; 25.38; 25.04; 24.40; ^{11}B NMR (C_6D_6): δ 8.17 (s). MS (CI^+, CH_4): *m/z* 364 (M^+), 207 (100%, CyN=C=NCy + H^+); HRMS (CI, CH_4) calcd. for $C_{19}H_{27}N_2BCl_2$, 364.1644; found 364.1671.

2. ^{n}BuLi (3.2 mmol, 2.0 mL 1.6 M solution in hexanes) was added to a cold (-78 ^{o}C) stirred solution of PhBr (0.5 g, 3.2 mmol) in 15 mL of hexane. The reaction mixture was warmed to room temperature, stirred for 2 h and then re-cooled to -78 ^{o}C, whereupon a solution of CyN=C=NCy (0.66 g, 3.2 mmol) in 10 mL hexane was added dropwise. The mixture was again warmed to room temperature, stirred for 2 h and then re-cooled to -78 ^{o}C, followed by dropwise addition of BCl_3 (3.2 mmol, 3.2 mL 1.0 M solution in hexanes). After stirred reaction mixture had warmed to room temperature overnight, it was filtered through Celite® and the solvent stripped from the filtrate to afford a white powder. Recrystallization of this powder from toluene solution afforded a crop of colourless crystals of **2** (1.03 g, 88% yield, mp 90-92 ^{o}C).

^{1}H NMR (C_6D_6): δ 3.49 (s, 2H); 2.09 (s, 4H); 1.67-1.45 (m, 10H); 1.14-1.05 (m, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ 176.17; 132.55; 129.79; 127.99; 54.95; 33.70; 27.23; 25.94: ^{11}B NMR (C_6D_6): δ 6.25 (s). MS (CI^+, CH_4): *m/z* 364 (M^+), 329 (100%, M – Cl); HRMS (CI, CH_4) calcd. for $C_{19}H_{27}N_2BCl_2$, 364.1644; found 364.1642.