Electronic Supplementary Information for:

Formation of N-heterocyclic, donor-stabilised borenium ions†

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General Considerations

All experiments and manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk techniques or in an MBraun inert atmosphere glovebox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and freshly distilled prior to use. The ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on a Bruker Spectrometer AM200, AM400 and referenced to solvent resonances. The starting material, β-diketiminato ligand L[1] was prepared according to the literature. Abbreviations: L = $\{HC[CMeN(Ar)]_2\}^-$, L' = $\{HC[C(Me)(C=CH_2)N(Ar)_2]\}$, Ar = 2,6-diisopropylphenyl, OTf = OSO_2CF_3, s = singlet; d = doublet; t = triplet; sept = septet; mult = multiplet; br = broad.

Single-Crystal X-ray Structure Determinations: Crystals were each mounted on a glass capillary in perfluorinated oil and measured in a cold N2 flow. The data of compounds **2** and **4** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo- Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on *F*2 with the SHELX-97 software package.[2] The positions of the H atoms were calculated and considered isotropically according to a riding model.

Experimental selections

Synthesis of $[LBBr]^+[BBr_4]^-$ 1

To a solution of LH (5.0 g, 12.0 mmol) in toluene (20 mL) at -78 °C was slowly added *n*-BuLi (7.5 mL, 1.6 M in n-hexane, 12.0 mmol). The solution was slowly warmed to room temperature and stirred for 5 hours. BBr_3 (1.2ml, 12.0 mmol) was added to this solution at -78 °C. After stirring overnight, the precipitate was filtered off and extracted by dichloromethane. The filtrate was concentrated and stored at −12 °C overnight to give pale yellow crystals of **1** (3.6 g, 36%).

^{1}H NMR (400.13 MHz, $CDCl_3$, 298K): δ = 1.11 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 1.05 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 2.47 (s, 6 H, NC*Me*), 2.16 (sept, ^{3}*J*HH = 6.7 Hz, 4 H, C*H*Me$_2$), 7.21 - 7.47 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 9.07 (s, 1 H, γ-C*H*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 298K): δ = 23.08 (NC*Me*$_2$), 23.8, 24.05 (CH*Me*$_2$), 29.04 (*C*HMe$_2$), 116.42 (γ-*C*H), 125.58, 131.12, 134.98, 142, 25 (2,6-*i*Pr$_2$*C*$_6$H$_3$), 173.13 (N-*C*); ^{11}B NMR (128.27 MHz, $CDCl_3$, 298K): δ = -24.6 (*B*Br$_4$), 29.9 (*B*-Br); Mp: 251-252 °C (decomposed); ESI-MS m/z (%): 508.25 $[LBBr]^+$.

Synthesis of L'BBr 2

A THF solution of lithium napthalenide (20 ml, 6.0 mmol) was added to compound **1** (1.2 g, 1.4 mmol) in THF (20 mL) at −78 °C, and then the reaction mixture was stirred for 2 h. After removal of solvent in vacuo, the residue was extracted with pentane. The resulting solution was concentrated and stored at −12 °C to give yellow crystals of **2** (0.2 g, 28 %).

^{1}H NMR (400.13 MHz, $CDCl_3$, 298K): δ = 1,22 (d, ^{3}*J*HH = 6.9 Hz, 6 H, CH*Me*$_2$), 1.23 (d, ^{3}*J*HH = 6.9 Hz, 6 H, CH*Me*$_2$), 1.26 (d, ^{3}*J*HH = 6.9 Hz, 6 H, CH*Me*$_2$), 1.27 (d, ^{3}*J*HH = 6.9 Hz, 6 H, CH*Me*$_2$), 1.59 (s, 3 H, NC*Me*), 3.19 (sept, ^{3}*J*HH = 6.5 Hz, 4 H, C*H*Me$_2$), 3.00 (s, 1 H, NCC*H*$_2$), 3.76 (s, 1 H, NCC*H*$_2$), 5.58 (s, 1 H, γ-C*H*), 7.17-7.26 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 298K): δ = 20.72 (NC*Me*), 24.09, 24.24, 24.4, 25.24 (CH*Me*$_2$), 28.56, 28.6 (*C*HMe$_2$), 83.93 (NC*C*H$_2$), 106.62 (γ-*C*H), 123.97, 124.38, 127.96, 128.3, 138.0, 138.16, 140.48, 145.8 (2,6-*i*Pr$_2$*C*$_6$H$_3$), 146.42 (N*C*=CH$_2$), 146.64 (N*C*Me); ^{11}B NMR (128.27 MHz, $CDCl_3$, 298K): δ = 27.2 ppm; M.p. 198-199 °C (decomposed).

HRMS calc. for $C_{29}H_{40}BBrN_2$: 506.4679, found: 506.4548.

Synthesis of $[LBBr]^+[OTf]^-$ 3

Trifluoromethanesulfonic acid (0.35 g, 2.4 mmol) was dropwise added with stirring to a cooled (-60°C) solution of **2** (1.0 g, 2.0 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo and the residue was extracted with toluene (30 mL). Filtration and subsequent concentration afforded crystals of **3** (0.2 g, 0.3 mmol, 18%).

^{1}H NMR (400.13 MHz, $CDCl_3$, 298K): δ = 1.18 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 1.24 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 2.37 (sept, ^{3}*J*HH = 6.8 Hz, 4 H, C*H*Me$_2$), 2.50 (s, 6 H, NC*Me*), 7.37 (d, ^{2}*J*HH = 7.8 Hz, 4 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 7.83 (t, ^{2}*J*HH = 7.8 Hz, 2 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 7.95 (s, 1 H, γ-C*H*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 298K): δ = 23.25 (NC*Me*$_2$), 24.1, 24.33 (CH*Me*$_2$), 29.15 (*C*HMe$_2$), 116.3 (γ-*C*H), 125.8, 131.23, 135.52, 142.96 (2,6-*i*Pr$_2$*C*$_6$H$_3$), 173.32 (N*C*Me); ^{11}B NMR (128.27 MHz, $CDCl_3$, 298K): δ = 29.8 ppm; M.p. 231-232 °C; ESI-MS m/z (%): 508.25 $[LBBr]^+$.

Synthesis of $[LB\text{-}L'BBr]^+[Br]^-$ 4

When a mixture of **2** (0.1 g, 0.2 mmol) and $CHCl_3$ (0.5 ml) in a sealed NMR tube was kept at 110°C for 4 days in the dark, the yellow solution turned gradually to violet. The quantitative formation of 4 was confirmed by NMR spectroscopy. The volatiles were removed in vacuo and the residue was extracted with toluene (5 mL). Filtration and subsequent concentration afforded crystals of **4** (89.1 mg, 89 %).

^{1}H NMR (400.13 MHz, $CDCl_3$, 298K): δ = 1.09 (d, ^{3}*J*HH = 6.8 Hz, 6 H, CH*Me*$_2$), 1.10 (d, ^{3}*J*HH = 6.8 Hz, 6 H, CH*Me*$_2$), 1.13 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 1.15 (d, ^{3}*J*HH = 6.8 Hz, 6 H, CH*Me*$_2$), 1.20 (d, ^{3}*J*HH = 6.8 Hz, 6 H, CH*Me*$_2$), 1.22 (d, ^{3}*J*HH = 6.8 Hz, 12 H, CH*Me*$_2$), 2.18 (NC*Me*), 2.27 (sept, ^{3}*J*HH = 6.8 Hz, 4 H, C*H*Me$_2$), 2.57 (s, 6 H, NC*Me*), 2.66 (sept, ^{3}*J*HH = 6.8 Hz, 4 H, C*H*Me$_2$), 4.84 (s, 1 H, γ-C*H*), 7.20-7.54 (m, 6 H, 2,6-*i*Pr$_2$C$_6$*H*$_3$), 9.33 (s, 1 H, γ-C*H*); ^{13}C{^{1}H}NMR (100.61 MHz, $CDCl_3$, 298K): δ = 21.39 (NC*Me*), 23.04 (NC*Me*$_2$), 23.97, 24.05, 24.11, 24.15, 24.18, 24.29 (CH*Me*$_2$), 28.7, 28.73, 29.2 (*C*HMe$_2$), 46.31 (NC=*C*HBr), 106.00 (γ-*C*H), 116.41 (γ-*C*H), 124.59, 124.80, 125.71, 128.28, 129.09, 131.27, 133.83, 135.18, 135.28, 142.6, 142.75, 144.46 (2,6-*i*Pr$_2$*C*$_6$H$_3$), 144.47 (N*C*=CHBr), 144.57 (N*C*Me), 173.74 (N*C*Me); ^{11}B NMR (128.27 MHz, $CDCl_3$, 298K): δ = 27.3, 29.6.
M.p.281-282 °C; ESI-MS m/z (%): 934.57 $[LB\text{-}L'BBr]^+$.

Crystallographic data for compound **2**

Empirical formula	C29 H40 B Br N2	
Formula weight	507.35	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.5324(9) Å	α= 90°
	b = 16.4444(11) Å	β= 103.889(9)°
	c = 13.7137(13) Å	γ = 90°
Volume	2743.6(4) $Å^3$	
Z	4	
Density (calculated)	1.228 Mg/m^3	
Absorption coefficient	1.517 mm^{-1}	
F(000)	1072	
Crystal size	0.38 x 0.32 x 0.17 mm^3	
Theta range for data collection	3.06 to 25.00°.	
Index ranges	-14<=h<=11, -19<=k<=19, -16<=l<=16	
Reflections collected	14104	
Independent reflections	4825 [R(int) = 0.1044]	
Completeness to theta = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7825 and 0.5964	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4825 / 288 / 306	
Goodness-of-fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0788, wR2 = 0.1681	
R indices (all data)	R1 = 0.1572, wR2 = 0.1905	
Largest diff. peak and hole	0.725 and -0.596 $e.Å^{-3}$	

Table 1. Bond lengths [Å] and angles [°] for **4**.

Br(1)-B(1)	1.932(8)	C(2)-N(1)-C(6)	117.6(5)
N(1)-C(2)	1.411(8)	B(1)-N(1)-C(6)	122.8(6)
N(1)-B(1)	1.412(9)	C(4)-N(2)-B(1)	118.9(5)
N(1)-C(6)	1.462(8)	C(4)-N(2)-C(18)	117.2(5)
N(2)-C(4)	1.413(8)	B(1)-N(2)-C(18)	123.8(6)
N(2)-B(1)	1.417(9)	N(1)-B(1)-N(2)	121.8(6)
N(2)-C(18)	1.458(8)	N(1)-B(1)-Br(1)	119.0(5)
C(1)-C(2)	1.401(9)	N(2)-B(1)-Br(1)	119.2(5)
C(2)-C(3)	1.417(9)	C(1)-C(2)-N(1)	121.6(6)
C(3)-C(4)	1.379(9)	C(1)-C(2)-C(3)	121.8(6)
C(4)-C(5)	1.444(9)	N(1)-C(2)-C(3)	116.6(6)
C(6)-C(7)	1.384(9)	C(4)-C(3)-C(2)	125.2(6)
C(6)-C(11)	1.405(9)	C(3)-C(4)-N(2)	117.8(6)
C(7)-C(8)	1.399(9)	C(3)-C(4)-C(5)	121.9(6)
C(7)-C(12)	1.515(9)	N(2)-C(4)-C(5)	120.2(6)
C(8)-C(9)	1.364(9)	C(7)-C(6)-C(11)	122.1(6)
C(9)-C(10)	1.365(9)	C(7)-C(6)-N(1)	119.6(6)
C(10)-C(11)	1.393(9)	C(11)-C(6)-N(1)	118.4(6)
C(11)-C(15)	1.518(9)	C(6)-C(7)-C(8)	117.9(6)
C(12)-C(14)	1.520(10)	C(6)-C(7)-C(12)	122.3(6)
C(12)-C(13)	1.523(10)	C(8)-C(7)-C(12)	119.8(6)
C(15)-C(16)	1.518(9)	C(9)-C(8)-C(7)	121.2(6)
C(15)-C(17)	1.528(10)	C(8)-C(9)-C(10)	119.9(6)
C(18)-C(19)	1.378(9)	C(9)-C(10)-C(11)	122.1(6)
C(18)-C(23)	1.382(9)	C(10)-C(11)-C(6)	116.8(6)
C(19)-C(20)	1.405(9)	C(10)-C(11)-C(15)	120.7(6)
C(19)-C(24)	1.518(9)	C(6)-C(11)-C(15)	122.5(6)
C(20)-C(21)	1.359(9)	C(7)-C(12)-C(14)	113.0(6)
C(21)-C(22)	1.380(9)	C(7)-C(12)-C(13)	111.8(6)
C(22)-C(23)	1.411(9)	C(14)-C(12)-C(13)	108.6(6)
C(23)-C(27)	1.515(9)	C(11)-C(15)-C(16)	111.3(6)
C(24)-C(25)	1.516(9)	C(11)-C(15)-C(17)	111.9(6)
C(24)-C(26)	1.520(10)	C(16)-C(15)-C(17)	110.5(6)
C(27)-C(29)	1.503(9)	C(19)-C(18)-C(23)	123.0(6)
C(27)-C(28)	1.545(9)	C(19)-C(18)-N(2)	119.2(6)
		C(23)-C(18)-N(2)	117.8(6)
C(2)-N(1)-B(1)	119.6(5)	C(18)-C(19)-C(20)	117.6(6)

C(18)-C(19)-C(24)	123.3(6)	C(22)-C(23)-C(27)	118.6(6)
C(20)-C(19)-C(24)	119.0(6)	C(25)-C(24)-C(19)	112.9(6)
C(21)-C(20)-C(19)	121.1(7)	C(25)-C(24)-C(26)	109.6(6)
C(20)-C(21)-C(22)	120.4(6)	C(19)-C(24)-C(26)	110.4(6)
C(21)-C(22)-C(23)	120.4(6)	C(29)-C(27)-C(23)	114.1(5)
C(18)-C(23)-C(22)	117.4(6)	C(29)-C(27)-C(28)	109.1(6)
C(18)-C(23)-C(27)	124.0(6)	C(23)-C(27)-C(28)	110.8(6)

Crystallographic data for compound 4

Empirical formula	C72 H96 B2 Br2 N4	
Formula weight	1198.97	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.5298(6) Å	α= 91.285(3)°.
	b = 15.1978(6) Å	β= 96.864(4)°.
	c = 17.1182(8) Å	γ = 105.226(4)°.
Volume	3366.7(3) $Å^3$	
Z	2	
Density (calculated)	1.183 Mg/m^3	
Absorption coefficient	1.246 mm^{-1}	
F(000)	1272	
Crystal size	0.30 x 0.26 x 0.20 mm^3	
Theta range for data collection	2.90 to 25.00°.	
Index ranges	-16<=h<=16, -18<=k<=18, -20<=l<=20	
Reflections collected	35317	
Independent reflections	11828 [R(int) = 0.0789]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7887 and 0.7062	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11828 / 175 / 743	
Goodness-of-fit on F^2	0.845	
Final R indices [I>2sigma(I)]	R1 = 0.0494, wR2 = 0.1019	
R indices (all data)	R1 = 0.1206, wR2 = 0.1150	
Largest diff. peak and hole	0.765 and -0.419 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **4**.

Br(1)-B(1)	1.945(5)	C(23)-C(27)	1.524(7)
N(1)-B(1)	1.399(6)	C(24)-C(25)	1.513(6)
N(1)-C(2)	1.408(5)	C(24)-C(26)	1.534(6)
N(1)-C(6)	1.452(5)	C(27)-C(29)	1.521(7)
N(2)-B(1)	1.421(6)	C(27)-C(28)	1.541(6)
N(2)-C(4)	1.428(5)	C(30)-C(31)	1.509(6)
N(2)-C(18)	1.444(5)	C(31)-C(32)	1.375(6)
N(3)-C(31)	1.357(5)	C(32)-C(33)	1.359(6)
N(3)-B(2)	1.450(6)	C(33)-C(34)	1.505(6)
N(3)-C(35)	1.475(5)	C(35)-C(40)	1.396(6)
N(4)-C(33)	1.363(5)	C(35)-C(36)	1.398(6)
N(4)-B(2)	1.467(6)	C(36)-C(37)	1.384(6)
N(4)-C(47)	1.470(5)	C(36)-C(41)	1.523(7)
B(2)-C(5)	1.538(6)	C(37)-C(38)	1.366(7)
C(1)-C(2)	1.495(6)	C(38)-C(39)	1.377(7)
C(2)-C(3)	1.348(6)	C(39)-C(40)	1.399(6)
C(3)-C(4)	1.430(6)	C(40)-C(44)	1.519(7)
C(4)-C(5)	1.349(5)	C(41)-C(43)	1.525(7)
C(6)-C(11)	1.394(6)	C(41)-C(42)	1.529(7)
C(6)-C(7)	1.401(6)	C(44)-C(46)	1.487(13)
C(7)-C(8)	1.398(6)	C(44)-C(45)	1.530(8)
C(7)-C(12)	1.513(7)	C(47)-C(48)	1.405(6)
C(8)-C(9)	1.375(7)	C(47)-C(52)	1.408(6)
C(9)-C(10)	1.365(7)	C(48)-C(49)	1.387(6)
C(10)-C(11)	1.395(6)	C(48)-C(53)	1.505(7)
C(11)-C(15)	1.522(6)	C(49)-C(50)	1.362(7)
C(12)-C(13)	1.529(8)	C(50)-C(51)	1.380(6)
C(12)-C(14)	1.532(7)	C(51)-C(52)	1.368(6)
C(15)-C(16)	1.513(6)	C(52)-C(56)	1.516(6)
C(15)-C(17)	1.525(6)	C(53)-C(54)	1.532(6)
C(18)-C(19)	1.402(6)	C(53)-C(55)	1.533(6)
C(18)-C(23)	1.402(6)	C(56)-C(58)	1.522(6)
C(19)-C(20)	1.386(6)	C(56)-C(57)	1.534(7)
C(19)-C(24)	1.531(6)		
C(20)-C(21)	1.379(6)	B(1)-N(1)-C(2)	117.6(4)
C(21)-C(22)	1.368(7)	B(1)-N(1)-C(6)	123.8(4)
C(22)-C(23)	1.391(7)	C(2)-N(1)-C(6)	118.6(4)

B(1)-N(2)-C(4)	121.5(4)	C(16)-C(15)-C(17)	110.3(4)
B(1)-N(2)-C(18)	121.1(4)	C(11)-C(15)-C(17)	112.0(4)
C(4)-N(2)-C(18)	117.2(3)	C(19)-C(18)-C(23)	121.6(4)
C(31)-N(3)-B(2)	122.4(4)	C(19)-C(18)-N(2)	120.1(4)
C(31)-N(3)-C(35)	115.5(4)	C(23)-C(18)-N(2)	118.3(4)
B(2)-N(3)-C(35)	121.9(4)	C(20)-C(19)-C(18)	118.1(4)
C(33)-N(4)-B(2)	121.3(4)	C(20)-C(19)-C(24)	121.0(5)
C(33)-N(4)-C(47)	116.2(4)	C(18)-C(19)-C(24)	120.9(4)
B(2)-N(4)-C(47)	121.6(4)	C(21)-C(20)-C(19)	120.8(5)
N(1)-B(1)-N(2)	121.5(4)	C(22)-C(21)-C(20)	120.5(5)
N(1)-B(1)-Br(1)	118.8(4)	C(21)-C(22)-C(23)	121.2(5)
N(2)-B(1)-Br(1)	119.7(4)	C(22)-C(23)-C(18)	117.7(5)
N(3)-B(2)-N(4)	113.7(4)	C(22)-C(23)-C(27)	119.8(4)
N(3)-B(2)-C(5)	123.5(4)	C(18)-C(23)-C(27)	122.5(4)
N(4)-B(2)-C(5)	122.6(4)	C(25)-C(24)-C(19)	113.2(4)
C(3)-C(2)-N(1)	120.3(4)	C(25)-C(24)-C(26)	107.1(4)
C(3)-C(2)-C(1)	121.5(4)	C(19)-C(24)-C(26)	112.7(4)
N(1)-C(2)-C(1)	118.1(4)	C(29)-C(27)-C(23)	109.3(4)
C(2)-C(3)-C(4)	125.9(4)	C(29)-C(27)-C(28)	110.3(4)
C(5)-C(4)-N(2)	123.7(4)	C(23)-C(27)-C(28)	113.8(5)
C(5)-C(4)-C(3)	123.1(4)	N(3)-C(31)-C(32)	119.9(4)
N(2)-C(4)-C(3)	113.2(4)	N(3)-C(31)-C(30)	120.3(4)
C(4)-C(5)-B(2)	124.4(4)	C(32)-C(31)-C(30)	119.8(4)
C(11)-C(6)-C(7)	122.3(4)	C(33)-C(32)-C(31)	121.6(5)
C(11)-C(6)-N(1)	118.6(4)	C(32)-C(33)-N(4)	120.5(4)
C(7)-C(6)-N(1)	119.1(4)	C(32)-C(33)-C(34)	118.6(4)
C(8)-C(7)-C(6)	117.0(4)	N(4)-C(33)-C(34)	120.8(4)
C(8)-C(7)-C(12)	120.1(5)	C(40)-C(35)-C(36)	122.2(4)
C(6)-C(7)-C(12)	122.9(4)	C(40)-C(35)-N(3)	118.3(4)
C(9)-C(8)-C(7)	121.4(5)	C(36)-C(35)-N(3)	119.2(4)
C(10)-C(9)-C(8)	120.3(5)	C(37)-C(36)-C(35)	117.7(5)
C(9)-C(10)-C(11)	121.2(5)	C(37)-C(36)-C(41)	118.6(5)
C(6)-C(11)-C(10)	117.8(5)	C(35)-C(36)-C(41)	123.6(4)
C(6)-C(11)-C(15)	123.1(4)	C(38)-C(37)-C(36)	121.6(5)
C(10)-C(11)-C(15)	119.1(4)	C(37)-C(38)-C(39)	119.8(5)
C(7)-C(12)-C(13)	114.0(5)	C(38)-C(39)-C(40)	121.5(5)
C(7)-C(12)-C(14)	110.6(5)	C(35)-C(40)-C(39)	116.9(5)
C(13)-C(12)-C(14)	109.4(5)	C(35)-C(40)-C(44)	123.8(4)
C(16)-C(15)-C(11)	112.1(4)	C(39)-C(40)-C(44)	119.3(5)

C(36)-C(41)-C(43)	114.0(4)	C(50)-C(49)-C(48)	121.8(5)
C(36)-C(41)-C(42)	109.5(4)	C(49)-C(50)-C(51)	119.8(5)
C(43)-C(41)-C(42)	109.8(5)	C(52)-C(51)-C(50)	121.9(5)
C(46)-C(44)-C(40)	115.8(7)	C(51)-C(52)-C(47)	117.5(4)
C(46)-C(44)-C(45)	98.3(9)	C(51)-C(52)-C(56)	119.3(5)
C(40)-C(44)-C(45)	112.0(5)	C(47)-C(52)-C(56)	123.1(5)
C(48)-C(47)-C(52)	121.7(4)	C(48)-C(53)-C(54)	110.4(5)
C(48)-C(47)-N(4)	121.3(4)	C(48)-C(53)-C(55)	112.7(4)
C(52)-C(47)-N(4)	116.7(4)	C(54)-C(53)-C(55)	108.0(4)
C(49)-C(48)-C(47)	117.2(5)	C(52)-C(56)-C(58)	112.2(4)
C(49)-C(48)-C(53)	119.2(4)	C(52)-C(56)-C(57)	111.0(4)
C(47)-C(48)-C(53)	123.6(5)	C(58)-C(56)-C(57)	110.2(4)

Computational Methods

DFT calculations of the compounds **2-4** were performed at the B3LYP level using 6-31G(d) basis set with the GAUSSIAN-03 program package.[3] The structure obtained by X-ray analysis was used as the input for these calculation of compounds **2**-**4**. Cartesian coordinates of optimized structures are shown in Table 3-5.

Table 3. Cartesian coordination (x, y, z) of optimized structure for **2**

Br	0.027059	0.000123	-1.839219	H	-3.122127	-0.879076	2.71677
N	1.251562	-0.0001	0.807046	H	-3.122246	0.877982	2.717102
C	2.427351	0.000026	2.955392	H	4.900553	2.140231	-1.034328
B	0.015979	-0.000081	0.105586	H	6.010311	-0.000135	-1.574807
N	-1.237762	-0.000204	0.797517	H	4.900698	-2.140475	-1.033914
C	1.282962	-0.000102	2.235872	H	1.565711	-2.380526	0.672857
C	-0.025424	-0.000283	2.869927	H	1.507651	-2.63425	-1.809902
C	-1.207195	-0.000335	2.215422	H	1.560106	-4.208819	-0.982024
C	-2.514158	-0.000553	2.96006	H	3.016479	-3.562435	-1.757414
C	2.533708	-0.000087	0.131945	H	4.311209	-3.737771	0.55035
C	3.154404	1.231118	-0.165199	H	2.836206	-4.398922	1.267529
C	4.409	1.203413	-0.786344	H	3.596355	-2.96072	1.976314
C	5.035523	-0.000121	-1.093782	H	1.565385	2.380403	0.672064
C	4.409084	-1.203643	-0.786104	H	3.59544	2.960242	1.976481
C	3.154492	-1.231307	-0.164961	H	2.83601	4.398665	1.267362
C	2.494909	-2.574565	0.12968	H	4.311203	3.737135	0.550889
C	2.122145	-3.288978	-1.184688	H	3.017216	3.562418	-1.757524
C	3.36484	-3.467011	1.033369	H	1.56073	4.208977	-0.982512
C	2.494823	2.574414	0.129287	H	1.508243	2.634518	-1.810606
C	3.364523	3.466625	1.033441	H	-4.893903	2.139781	-1.042535
C	2.122657	3.289054	-1.185114	H	-6.010453	0.000707	-1.568796
C	-2.524088	0.000038	0.126624	H	-4.894529	-2.138791	-1.042946
C	-3.144382	1.231477	-0.179179	H	-1.564809	-2.395422	0.662247
C	-4.402757	1.203422	-0.7928	H	-2.93052	-3.490425	-1.85481
C	-5.032776	0.000521	-1.093875	H	-1.485989	-4.151263	-1.066611
C	-4.403108	-1.202627	-0.79303	H	-1.432963	-2.543349	-1.826506
C	-3.144736	-1.231165	-0.179438	H	-3.654845	-3.081547	1.86767
C	-2.47595	-2.577764	0.084475	H	-2.809212	-4.45475	1.132879
C	-2.054842	-3.231404	-1.247549	H	-4.27108	-3.811364	0.377542
C	-3.356942	-3.530791	0.913441	H	-1.564041	2.395104	0.662608
C	-2.475263	2.577842	0.08509	H	-4.270175	3.811525	0.379062
C	-3.355916	3.530694	0.914621	H	-2.808031	4.454522	1.134221
C	-2.054261	3.231921	-1.246746	H	-3.653593	3.081154	1.868778
H	2.370787	0.000004	4.038002	H	-1.432629	2.543955	-1.826083
H	3.409626	0.000125	2.503648	H	-1.485153	4.151568	-1.065533
H	-0.034718	-0.000404	3.953948	H	-2.929969	3.491412	-1.853762
H	-2.324225	-0.000744	4.03607				

Table 4. Cartesian coordination (x, y, z) of optimized structure for **3**

Br	0.000016	0.000463	-1.825519	H	-4.274961	3.800782	0.424843
N	-1.242194	-0.000073	0.819842	H	1.548871	2.419715	0.646853
C	-2.54353	0.000373	0.132734	H	-6.006057	0.001652	-1.557846
N	1.242196	-0.000471	0.819836	H	0	-0.001215	3.93074
C	-1.222998	-0.000509	2.182418	H	-4.89472	-2.137682	-1.036738
B	-0.000004	-0.000042	0.076758	H	1.547615	-2.420615	0.643958
C	-2.477983	-2.588715	0.087911	H	4.277188	3.799747	0.425081
C	4.401394	-1.205229	-0.785226	H	3.625079	3.078134	1.901511
C	-3.347321	3.53044	0.940038	H	2.808299	4.458348	1.14936
C	2.47718	2.588689	0.08839	H	-1.546734	2.420182	0.644168
C	-5.029227	0.00129	-1.083302	H	4.894098	2.138602	-1.036216
C	-0.000001	-0.000908	2.848768	H	-4.892536	2.140148	-1.037974
C	-4.402211	-1.203838	-0.784391	H	3.111851	-0.878777	2.707463
C	2.476183	-2.589455	0.085891	H	2.303194	-0.002022	4.02791
C	3.350053	3.529366	0.94116	H	3.111764	0.876424	2.708559
C	1.222997	-0.000919	2.182417	H	3.622991	-3.080323	1.899328
C	-3.143067	1.239635	-0.170829	H	4.275769	-3.801061	0.422766
C	-2.475488	2.589433	0.086539	H	2.806373	-4.459899	1.145828
C	-3.144379	-1.238451	-0.170026	H	-3.627886	-3.078906	1.899573
C	3.143478	-1.239427	-0.171011	H	-2.809856	-4.458722	1.14802
C	4.401872	1.204554	-0.784069	H	-4.278073	-3.800338	0.422219
C	-4.400967	1.205946	-0.785112	H	-2.980452	3.5127	-1.834567
C	3.143977	1.238656	-0.169806	H	-1.477248	2.578792	-1.854506
C	2.50625	-0.001367	2.955817	H	-1.526011	4.177127	-1.074808
C	3.348403	-3.530876	0.93853	H	1.527341	4.176858	-1.072098
C	-3.351611	-3.52983	0.939434	H	1.47715	2.578538	-1.851771
C	-2.089973	3.254502	-1.251333	H	2.980805	3.511706	-1.833143
C	2.090705	3.253962	-1.249121	H	-2.980321	-3.510476	-1.834526
C	-2.090592	-3.253232	-1.249719	H	-1.527477	-4.176313	-1.072858
C	2.090263	-3.253765	-1.252244	H	-1.476537	-2.577512	-1.851532
C	2.543522	-0.000413	0.132743	H	1.477336	-2.577721	-1.854843
C	-2.506268	-0.000874	2.95579	H	1.526407	-4.176527	-1.0761
C	5.029299	-0.000318	-1.083144	H	2.980588	-3.511543	-1.835898
H	-1.550081	-2.420198	0.647189	H	-3.110395	-0.879936	2.709542
H	4.893268	-2.139228	-1.038252	H	-3.113237	0.875259	2.706393
H	-2.805234	4.4594	1.147471	H	-2.303241	0.001209	4.027887
H	-3.621391	3.079453	1.900777	H	6.006164	-0.000288	-1.557615

Table 5. Cartesian coordination (x, y, z) of optimized structure for **4**

Br	3.81389	-0.015813	2.065608	C	2.045068	-3.168429	3.213137
N	1.094114	-0.00657	0.984991	C	2.061879	3.134458	3.244834
N	2.934399	-0.000316	-0.703355	C	-4.061846	1.937098	2.617124
N	-3.060549	-1.232014	-1.313121	C	-4.5251	-2.050678	1.133262
N	-3.050994	1.249249	-1.309983	C	0.473692	-3.353405	-2.202675
C	1.956707	0.006733	-1.707462	C	-5.977817	2.512065	1.06699
C	4.34307	-0.001123	-1.082096	C	-0.302266	-3.595971	2.360722
C	-1.251262	-0.002091	0.217618	C	-1.362108	-3.741115	-3.883821
C	-4.485203	0.015785	-2.75402	C	4.942196	-3.251351	0.229788
C	0.639028	0.007243	-1.381282	C	4.422775	-3.524469	-2.241123
C	0.651661	-0.010894	2.372187	C	-4.087153	-1.934392	2.607715
C	-4.041955	1.229681	-2.24613	C	-6.000504	-2.492182	1.048133
C	-2.797372	-2.565589	-0.739992	H	-1.548626	-0.012912	1.265463
C	0.097544	0.000103	-0.035252	H	-5.262153	0.019722	-3.50674
B	2.487984	-0.00685	0.65852	H	-0.074877	0.011561	-2.196304
C	-2.780017	2.579021	-0.731355	H	-0.239685	2.120765	4.864732
C	0.447135	1.219436	3.035733	H	6.877525	-2.14093	-1.817506
B	-2.408446	0.005344	-0.814851	H	3.285531	2.409331	-0.800669
C	-0.077651	1.186779	4.334334	H	-5.32252	2.915254	-1.89486
C	5.003824	-1.233895	-1.275329	H	-5.384143	2.268806	-3.544954
C	0.438131	-1.244917	3.02595	H	-4.011259	3.261135	-3.00121
C	-3.568634	2.989379	0.368343	H	-1.192109	5.493824	-1.431462
C	5.008457	1.230845	-1.263767	H	1.213965	2.390244	1.421578
C	6.347207	-1.204873	-1.669314	H	3.018306	0.890668	-3.36826
C	-3.591239	-2.977694	0.355292	H	1.534792	0.018031	-3.807093
C	4.348315	2.581833	-0.999775	H	3.015674	-0.863612	-3.37727
C	-1.895902	3.463468	-1.387357	H	6.885837	2.135726	-1.796818
C	-4.722135	2.489189	-2.705418	H	-0.254881	-2.155666	4.847977
C	-1.854692	4.790024	-0.937508	H	-1.220129	-5.483943	-1.449065
C	0.871337	2.561829	2.447177	H	-4.077394	4.668659	1.610846
C	2.402954	0.013252	-3.143597	H	-0.774064	-0.020007	5.975369
C	-4.049831	-1.202813	-2.250733	H	6.009073	3.485107	0.10827
C	6.351859	1.200368	-1.657766	H	4.887406	2.552041	1.111833
C	-0.08626	-1.218738	4.324869	H	4.421801	4.160544	0.510524
C	-1.881332	-4.779631	-0.953959	H	-4.449658	1.063186	0.703335
C	-3.479464	4.328009	0.77111	H	-2.644826	-6.258748	0.409194
C	-0.366357	-0.017481	4.968131	H	8.060077	-0.003098	-2.172066
C	4.953014	3.234544	0.260358	H	1.18887	-2.409649	1.399663
C	-4.504279	2.063004	1.144836	H	-1.073008	1.986311	-2.702614
C	-2.679685	-5.219606	0.095281	H	-4.112071	-4.660826	1.587549
C	7.017676	-0.002548	-1.865944	H	3.276684	-2.409894	-0.821506
C	0.852144	-2.585682	2.426471	H	-4.02456	-3.225258	-3.026765
C	-1.914986	-3.45068	-1.397275	H	-5.400892	-2.227795	-3.551518
C	-0.984814	3.066193	-2.548807	H	-5.329233	-2.892396	-1.908719
C	-3.509714	-4.318747	0.751567	H	5.474653	3.798501	-2.44114
C	4.338526	-2.584659	-1.023555	H	3.901327	4.464689	-1.996321
C	-4.734229	-2.45697	-2.718077	H	4.000856	3.088704	-3.110588
C	4.43773	3.532645	-2.208463	H	-2.606677	6.265671	0.435791
C	-2.647395	5.228321	0.116699	H	-1.083312	-1.970768	-2.704352
C	-0.996923	-3.051132	-2.552342	H	-1.106515	3.197931	1.777374
C	-0.278191	3.577584	2.379748	H	0.06949	4.513124	1.927156
C	-1.357362	3.759464	-3.876603	H	-0.66392	3.820619	3.376693
C	0.48824	3.366736	-2.207943	H	-2.356593	3.487512	-4.231253

H	-0.645634	3.474452	-4.659437	H	-6.344056	2.556145	0.035311
H	-1.322642	4.850134	-3.780046	H	-0.680012	-3.846157	3.358935
H	0.667055	4.444625	-2.129868	H	0.037532	-4.52896	1.89706
H	1.143236	2.983211	-2.997347	H	-1.134426	-3.208007	1.769023
H	0.780925	2.902356	-1.262861	H	-1.324952	-4.831988	-3.790785
H	1.754279	-3.43029	4.236938	H	-0.648016	-3.451679	-4.662855
H	2.860759	-2.443761	3.267032	H	-2.360764	-3.470778	-4.241428
H	2.417156	-4.078365	2.727809	H	5.997118	-3.504444	0.074041
H	1.765845	3.392455	4.268095	H	4.40779	-4.177566	0.472264
H	2.441649	4.045067	2.76677	H	4.880225	-2.576301	1.087435
H	2.87377	2.405583	3.300167	H	3.986594	-3.070426	-3.138576
H	-3.030811	1.58087	2.704186	H	3.882896	-4.456298	-2.037006
H	-4.713403	1.23465	3.148168	H	5.458345	-3.792301	-2.477555
H	-4.12677	2.900274	3.134872	H	-4.158816	-2.899779	3.120456
H	-4.464173	-1.048933	0.696948	H	-4.736984	-1.231243	3.139973
H	0.761032	-2.888938	-1.255961	H	-3.054566	-1.584008	2.700494
H	1.134077	-2.971111	-2.98819	H	-6.149386	-3.483934	1.488427
H	0.650374	-4.431517	-2.122771	H	-6.362998	-2.530403	0.014899
H	-6.120167	3.502823	1.511639	H	-6.636869	-1.789347	1.597278
H	-6.615557	1.810244	1.615828				

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