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# Solution-state $^{15}N$ NMR and solid-state single-crystal XRD study of heterosubstituted diazaboroles and borinines prepared *via* an effective and simple microwave-assisted solvent-free synthesis

Cathryn A. Slabber, Craig D. Grimmer, Ross S. Robinson*

*School of Chemistry, University of KwaZulu-Natal, Private Bag X01, Scottsville, Pietermaritzburg 3209, South Africa*

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ABSTRACT

A quick and simple, solvent-free synthesis of nitrogen-basedboroles and borinines derived from 1,2-diaminobenzene and 1,8-diaminonaphthalene is reported and compared with the traditional synthetic method. Characterization by $^{15}N$ NMR spectroscopy of 12 compounds and single crystal X-Ray diffraction of 4 compounds provides supporting evidence for donation of electron density, from the N-atom to the vacant $p_z$ orbital of the B-atom. Furthermore comparison of the hitherto unreported crystal structure of 2-(4-Methylphenyl)-naptho[1,8-de][1,3,2]diazaborinine with similar compounds made in these laboratories reveals that solid-state packing and the dihedral angle between naphthyl and phenyl rings is determined by competing inter- and intra-molecular forces.



## 1. Introduction

While the use of boron-containing compounds is popular for such reactions as the Suzuki–Miyaura reaction and the Petasis reaction, the vast majority of the literature deals with the use of boronic acids or alkylated dioxoboroles, most of which have been based upon unstable boranes, such as catecholborane (HBCat) and pinacolborane (HBPin). These reagents have been reported to undergo disproportionation reactions (Scheme 1), resulting in lower reaction yields, and are air- and moisture-sensitive [1,2].

In order to avoid the problems encountered when working with reagents based on HBCat and HBPin, other heterosubstitutedboranes such as 2-phenyl-1,3,2-benzodiazaborole (HBPda) (Fig. 1) have been investigated [3]. These reagents are more stable with regards to storage and handling, but are also less reactive towards olefins, requiring the use of rhodium(I)-based catalysts, such as Wilkinson's Catalyst ($Rh(PPh_3)_3Cl$), to form the alkylated borole reagents needed for further reactions (Scheme 2), and these reactions are at present limited to the formation of terminal boron-carbon bonds [2,4]. Diazaborole reagents have been successfully used as reagents in Suzuki–Miyaura reactions, but their use is limited when compared with that of the dioxoborole-based reagents [5].

Consequently, an alternative method of creating these reagents was sought in order to make the reaction more cost-effective and to expand the scope of the reaction. Literature had presented a possible method which makes use of commercially available boronic acids and simple 1,2-diols or diamines to create a wide range of dioxo- or diazaboroles and borinines (Scheme 3) [6,7]. However, these reactions make use of hazardous solvents such as benzene and toluene, and therefore, in an attempt to find a "greener" method, a solventless approach was desired. This is possible, as these compounds have previously been made in a solvent less method using a ball mill [8]. Our thoughts then turned to the use of microwave irradiation instead of ball-milling, as this could potentially reduce the reaction time dramatically. Should this methodology prove successful, this could provide a rapid and easy method of creating similar heterosubstituted boroles and borinines as a large variety of boronic acids are commercially available, and others can be created using Grignard-type procedures [9,10]. These reagents could then be utilized further in Suzuki–Miyaura or Petasis-type reactions [11].

In this article we present the successful implementation of microwave irradiation in the creation of a number of diazaboroles and diazaborinines using a simple and effective solvent-free reaction methodology. We also present the first X-ray crystal structure

* Corresponding author.
*E-mail address:* robinsonr@ukzn.ac.za (R.S. Robinson).

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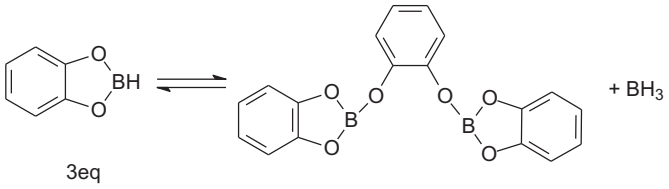
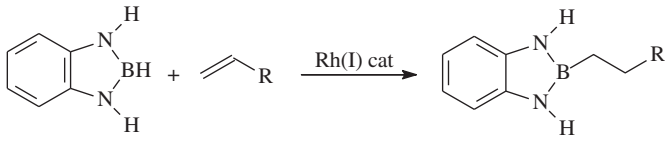



**Scheme 1.** The disproportionation reaction of HBCat.




**Scheme 2.** Rh(I)-catalysed alkylation of HBPda.

of 2-(4-Methylphenyl)-naphtho[1,8-de][1,3,2]diazaborinine and compare it with the structures of other similar compounds determined in these laboratories.

## 2. Results and discussion

In order to test the possibility of creating diazaboroles using this methodology, *o*-phenylenediamine **1** was combined with a number of commercially available boronic acids **2a**–**f** with both electron-donating and electron-withdrawing substituents (Scheme 4). Two different methods were evaluated in order to determine whether any advantage is gained by using microwave irradiation over the standard synthesis conditions of refluxing toluene.

To our delight, the desired products **3a**–**f** were obtained in very good yields in all cases (Table 1) [12]. While the yields are not as high as those reported by Kaupp et al. [8], access to a microwave oven in a synthetic laboratory is far more common than a ball-mill and the microwave procedure reported here requires a far shorter reaction time. Further purification of the products was not required as the products of the solution reactions precipitated out of solution on cooling to room temperature, and the NMR analyses of the products from the microwave reactions showed no side products. The use of a Dean and Stark trap in the solution reactions allowed for the removal of the water produced in the reaction, while the products from the microwave reactions were allowed to air dry.

As standard procedure, complete NMR analyses were carried out on compounds **3a**–**f**, including measurement of $^{15}$N NMR chemical shifts *via* either $^{15}$N–$^{1}$H HSQC or HMBC experiments. In all cases, it is interesting to note that the $^{15}$N chemical shifts of compounds **3a**–**f** (Table 2) are in the region between that typical of sp$^3$-hybridized nitrogen atoms (0–90 ppm) and the region corresponding to sp$^2$-hybridized nitrogen atoms (from 220 ppm) [13] (Fig. 2). This could corroborate the prevailing thought that electron donation occurs from the lone pair of electrons present on nitrogen atoms to the vacant $p_z$ orbital situated on the boron atoms (Fig. 3) [2,14,15]. This theory is further supported by DFT calculations carried out by Weber et al. [16], which show orbital overlap between the nitrogen atoms and the boron atoms in the HOMO calculations for structurally similar compounds.

Due to the success of the coupling reactions with **1**, the same methodology was used in reactions with 1,8-diaminonaphthalene **4.** As with the reactions with **1**, very good results were obtained (Table 3). Again, the same comment on the yield and reaction time of the microwave procedure *vs* the ball-milling procedure applies (*vide supra*). Further purification of the products was not required for these reactions either as the NMR analyses of the products from both the solution and the microwave reactions showed no evidence of side products. As in the previous reactions with **1**, a Dean and Stark trap was employed for the solution reactions, while the microwave synthesis reaction products were allowed to air dry.

As with compounds **3a**–**f**, the $^{15}$N chemical shifts of compounds **5a**–**f** (Table 4) show a significant downfield shift relative to the starting amine (Fig. 4), again indicating the probability of electron back-donation occurring between the nitrogen and boron.

On removal of the solution reaction of **4** and **2d** from heat, crystals were observed to be forming as the solution cooled. This prompted the growth of single crystals of **5d** suitable for X-ray diffraction analysis, as very little solid state structural information has been reported for any compound containing such a nitrogen–boron bond [16]. A perspective view of the molecule is given in Fig. 5.

To date, crystal structures have been determined for compounds **5a** [17], **5b** [18], **5d** [this work], and **5e** [19]. Selected structural data for these compounds are given in Table 5.

We first note that there are no significant differences between the B–C bond lengths. The value of 1.568Å measured for compound **5b** appears longer, but with a relatively high standard deviation of 0.004Å (that takes no account of systematic errors) it cannot be described as significantly different from the other B–C distances. However, the average B–N distance of 1.441(1)Å determined for compound **5d** is significantly longer than the (very similar) values measured for the other three compounds. Differences in the B–N distances in diazaboroles can be explained in terms of the back donation of electron density hypothesis, a hypothesis which is underpinned by ELF calculations of the type carried out by Berski, *et al.* [20]. These calculations show that a partial double bond exists between the boron and nitrogen atoms, and that two or more resonance hybrids need to be considered; B–N distances in the range 1.413Å to 1.442Å are predicted, the exact value depending on the extent of back donation of the nitrogen lone pair into the vacant *pz* orbital on the boron atom. Compound **5d** is distinguished from compounds **5a**, **5b** and **5e** by the attachment to the boron atom of an electron donating tolyl group. For this reason, the electron density on the boron atom in **5d** will be higher than that on the boron atom in the other three compounds; back donation will be correspondingly less, the B–N bond will have less double bond character and so the bond lengthens. In fact, the B–N bond lengths determined for compounds **5a**, **5b** and **5e** (average = 1.413Å) are significantly shorter than those of ~1.437Å reported by Weber, *et al.* [16], consistent with a high degree of back donation when electron withdrawing groups are attached to the boron atom. We now examine the dihedral angles shown for compounds **5a**, **5b**, **5d** and **5e** in Table 5. These angles provide a measure of the twist of the phenyl group out of the plane defined by the atoms of the

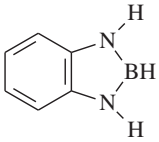
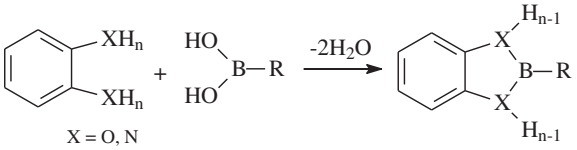
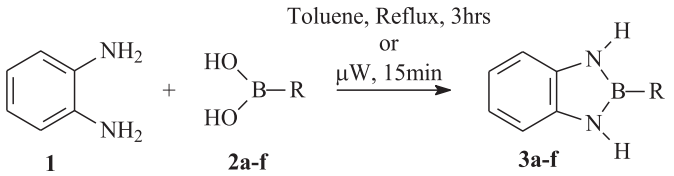


**Fig. 1.** 2-Phenyl-1,3,2-benzodiazaborole (HBPda).



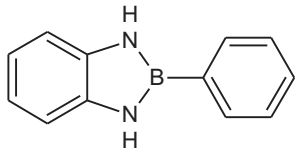
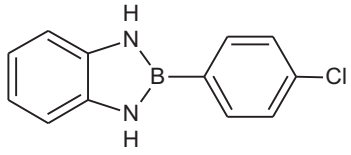
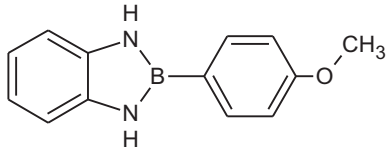
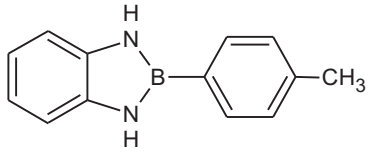
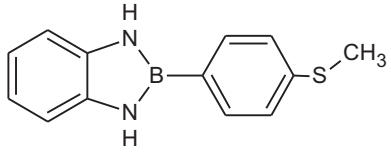
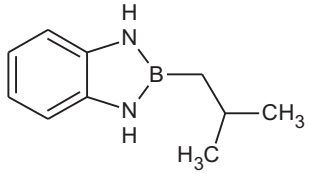

**Scheme 3.** Synthesis of boroles from boronic acids.




a: R = Ph
b: R = *p*-PhCl
c: R = *p*-PhOMe
d: R =*p*-PhMe
e: R= *p*-PhSMe
f: R = $CH_2CH(CH_3)CH_3$

**Scheme 4.** Synthesis of compounds **3a**–**f** from *o*-phenylenediamine**1** and boronic acids **2a**–**f**.

**Table 1**
Synthesis of 1,3,2-benzodiazaboroles **3a**–**f**.

| Entry | Boronic acid | Product | Yield[a] | Yield[b] |
|---|---|---|---|---|
| 1 | **2a** |  **3a** | 95 | 95 |
| 2 | **2b** |  **3b** | 97 | 92 |
| 3 | **2c** |  **3c** | 94 | 88 |
| 4 | **2d** |  **3d** | 89 | 82 |
| 5 | **2e** |  **3e** | 95 | 87 |
| 6 | **2f** |  **3f** | 90 | 73 |

[a] Reaction conditions: **1** (2 mmol), **2** (2 mmol) Toluene (50 ml), 110 °C, 3 h.
[b] Reaction conditions: **1** (0.4 mmol), **2** (0.4 mmol) 150 °C, 150 W, 15 min.

**Table 2**
$^{15}N$ NMR shifts for compounds **3a**–**f**.

| Compound | $^{15}N$ NMR signal (ppm) |
|---|---|
| **3a** | 104 |
| **3b** | 111 |
| **3c** | 107 |
| **3d** | 110 |
| **3e** | 109 |
| **3f** | 113 |

napthodiazaborinine grouping. For compounds **5a** and **5b** the dihedral angle is small (6–8°) and so these two molecules are essentially planar. In contrast, the dihedral angles of 23° and 19° measured for compounds **5d** and **5e** respectively are large, rendering these two molecules non-planar. This would not be expected from a consideration of intramolecular non-bonded repulsions, in particular between the *ortho* protons of the phenyl group and the N–H protons; these are expected to be much the same for all four molecules in view of the close similarity in the B–C distances (*vide supra*). More likely is that differences in the dihedral angle are due to crystal packing forces. Consistent with this interpretation is that the packing motifs for compounds **5a** and **5b** are quite different from those of compounds **5d** and **5e**. For the former, the planar molecules stack parallel to each other along one of the unit cell axes with the stacks stabilised by attractive σ–π interactions [21]. For compound **5e**, the molecules stack in a staircase motif with successive molecules (steps) bound alternately by σ–π interactions between naptho groups, and C–H(methyl)···π(naptho) interactions. In fact, the latter interaction is facilitated by the out-of-plane bending of the phenyl group (see Fig. A.1). For compound **5d** there is no stacking discernable in the crystal structure: rather the moelcules adopt a zig-zag motif through the crystal (see Fig. A.2). We do not believe that this is because of any intermolecular steric effect due to the methyl group; after all, the van der Waals radii for the chlorine atom (in **5b**) is very similar to that of a methyl group [22], and compound **5b** is nearly planar. More likely is that it can be ascribed to the electron richness of the tolyl group, which has a result that π–π repulsions between parallel stacked molecules would be strong – too strong to be compensated for by attractive σ–π interactions [21].

## 3. Conclusions

We have successfully synthesised a range of diazaboroles in very good to excellent yields with no evidence of any side products, using microwave irradiation under solvent-free conditions. This simple methodology allows the rapid synthesis of boron reagents, which could be used in other popular applications, such as the Suzuki–Miyaura and the Petasis reactions. $^{15}N$ NMR spectroscopic analysis of these twelve compounds showed a significant

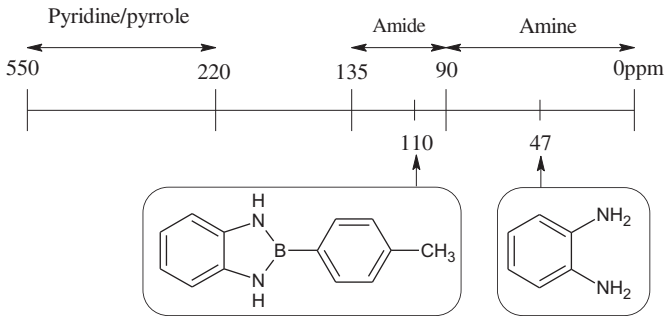



**Fig. 2.** Diagrammatic representation of the relative $^{15}N$ NMR chemical shifts (not to scale).

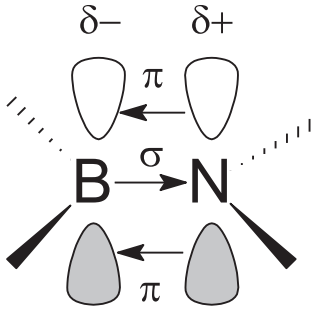
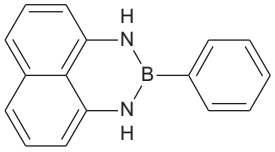
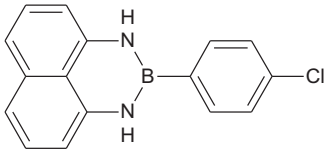
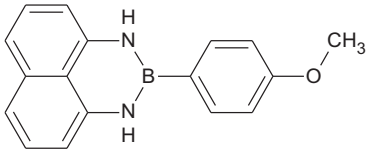
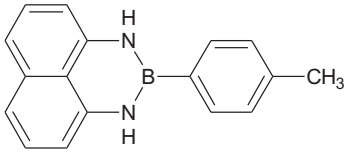
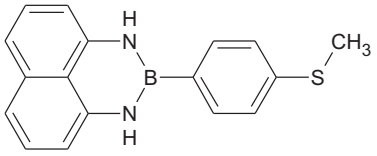
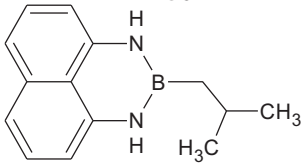



**Fig. 3.** Back-donation of the nitrogen lone pair into the vacant $p_z$ boron orbital.

**Table 3**
Synthesis of naphtho[1,8-*de*][1,3,2]diazaborinines **5a**–**f**.

| Entry | Boronic acid | Product | Yield[a] | Yield[b] |
|---|---|---|---|---|
| 1 | **2a** |  **5a** | 85 | 90 |
| 2 | **2b** |  **5b** | 75 | 88 |
| 3 | **2c** |  **5c** | 80 | 95 |
| 4 | **2d** |  **5d** | 80 | 75 |
| 5 | **2e** |  **5e** | 76 | 80 |
| 6 | **2f** |  **5f** | 84 | 75 |

[a] Reaction conditions: **4** (2 mmol), **2** (2 mmol) Toluene (50 ml), 110 °C, 3 h.
[b] Reaction conditions: **4** (0.4 mmol), **2** (0.4 mmol) 150 °C, 150 W, 15 min.

**Table 4**
$^{15}$N NMR shifts for compounds **5a**–**f**.

| Compound | $^{15}$N NMR signal (ppm) |
|---|---|
| **5a** | 101 |
| **5b** | 101 |
| **5c** | 101 |
| **5d** | 101 |
| **5e** | 101 |
| **5f** | 100 |

downfield shift in the position of the signal, away from the region of typical $sp^3$-hybridized amines and towards the region typical of $sp^2$-hybridized amines. These observations support the theory of electron back-donation from the nitrogen lone pair to the vacant $p_z$-orbital on the boron atom. Also supportive of the idea of back donation is an analysis of the B–N bond lengths, measured by means of X-Ray diffraction analysis of four diaminonaphthalene-based borinines. The X-ray analysis also shows (unexpectedly) that not all four molecules are planar, an observation that is explained in terms of crystal packing effects – very different packing motifs are obtained for the near planar molecules on one hand, and the non-planar molecules on the other.

## 4. Experimental

### 4.1. General procedures for the synthesis of compounds ***3a–f***

#### 4.1.1. Method A

To a solution of *o*-phenylenediamine in toluene (2 mmol in 50 ml) was added the boronic acid (2 mmol) in one portion. The round-bottomed flask was equipped with a Dean and Stark trap, and the solution was stirred and heated to reflux at 110 °C for 3 h. The precipitate was isolated by filtration and washed with minimal solvent (toluene).

#### 4.1.2. Method B

Theo-phenylenediamine (0.4 mmol) and boronic acid (0.4 mmol) were added to a microwave tube and sealed with a microwave septum. The tube was shaken to mix and subjected to microwave irradiation at 150 °C for 15 min (150 W) under a closed system. $^1$H, $^{11}$B and $^{13}$C NMR spectra in DMSO-*d6* were used to confirm the product obtained by this method was identical to that obtained for Method A.

### 4.2. General procedures for the synthesis of compounds ***5a–f***

#### 4.2.1. Method C

To a solution of 1,8-diaminonaphthalene in toluene (2 mmol in 50 ml) was added the boronic acid (2 mmol) in one portion. The round-bottomed flask was equipped with a Dean and Stark trap,

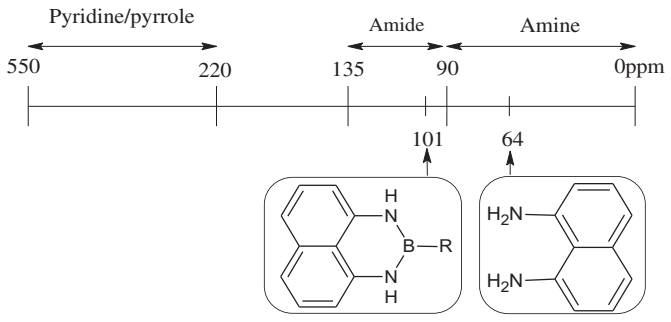



**Fig. 4.** Diagrammatic representation of the relative $^{15}$N chemical shifts of compounds **5a**–**f** (not to scale).

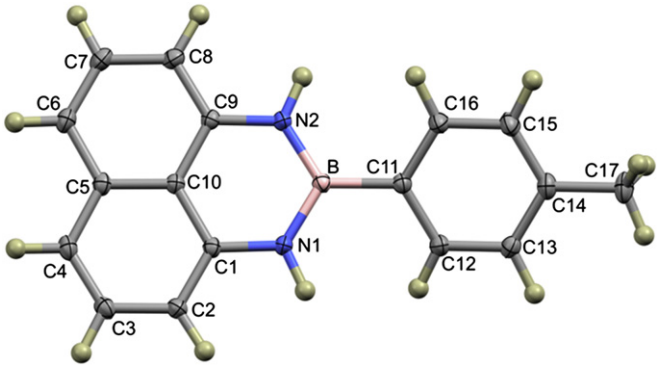



**Fig. 5.** ORTEP plot (50% ellipsoids) of **5d**.

and the solution was stirred and heated to reflux at 110 °C for 3 h. The solvent was removed in vacuo.

*4.2.2. Method D*

The1,8-diaminonaphthalene (0.4 mmol) and boronic acid (0.4 mmol) were added to a microwave tube and sealed with a microwave septum. The tube was shaken to mix and subjected to microwave irradiation at 150 °C for 15 min (150 W) under a closed system. $^{1}$H, $^{11}$B and $^{13}$C NMR spectra in DMSO-*d6* were used to confirm the product obtained by this method was identical to that obtained for Method C.

*4.3. 2-Phenyl-1,3,2-benzodiazaborole (**3a**) [24]*

*4.3.1. Method A*

367 mg, 95%. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.80–6.84 ppm (m, $J$ = 5.2 Hz, $J$ = 3.2 Hz, 2H, 2x C**H**–CH–$C_q$–N) 7.04–7.07 ppm (m, $J$ = 5.2 Hz, $J$ = 3.2, 2H,2x CH–C**H**–$C_q$–N) 7.38–7.43 ppm (m, 3H, C**H**–C**H**–C**H**) 7.88–7.91 ppm (m, 2H, 2x CH–C**H**–$C_q$–B) 9.08 ppm (s, 2H, 2x N**H**); $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.8 ppm (s); $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 111.2 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 119.4 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 128.0 ppm (2x d, 2C, **C**H–CH–**C**H) 129.7 ppm (d, 1C,CH–**C**H–CH) 132.9 ppm (d, 2C, **C**H–$C_q$–B) 136.3 (s, 2C, 2x **$C_q$**–N); $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 104 ppm (s); HRMS calcd for $C_{12}H_{10}BN_2$: 193.0937; found 193.0938.

*4.3.2. Method B*

75 mg, 95%.

*4.4. 2-(4-Chlorophenyl)-1,3,2-benzodiazaborole(**3b**) [25]*

*4.4.1. Method A*

440 mg, 97%.$^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 6.80–6.84 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H, 2x C**H**–CH–$C_q$–N) 7.03–7.07 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H,2x CH–C**H**–$C_q$–N) 7.49 ppm (d, $J$ = 8.2 Hz, 2H, 2x C**H**–$C_q$–B) 7.90 ppm (d, $J$ = 8.2 Hz, 2H, 2x C**H**–$C_q$–Cl) 9.16 ppm (s, 2H, 2x N**H**); $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.4 ppm (s); $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 111.3 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 118.9 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 128.5 ppm (d, 2C, 2x **C**H–$C_q$–B) 134.7 ppm (s, 1C,CH–**$C_q$**–Cl) 135.6 ppm (d, 2C, 2x **C**H–$C_q$–Cl) 137.5 ppm (s, 2C, 2x **$C_q$**–N); $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 111 ppm (s); HRMS calcd for $C_{12}H_9BN_2Cl$: 227.0547; found 227.0551.

*4.4.2. Method B*

84 mg, 92%.

*4.5. 2-(4-Methoxyphenyl)-1,3,2-benzodiazaborole (**3c**) [26]*

*4.5.1. Method A*

419 mg, 94%.$^{1}$H NMR (500 MHz, DMSO-d6) $\delta$3.81 (s, 3H, C**H$_3$**) 6.76–6.80 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H, 2x C**H**–CH–$C_q$–N) 6.98 ppm (d, $J$ = 8.7 Hz, 2H,2x C**H**–$C_q$–O) 6.99–7.03 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H,2x C**H**–$C_q$–N) 7.82 ppm (d, $J$ = 8.6 Hz, 2H, 2x C**H**-$C_q$-B) 8.94 ppm (s, 2H, 2x N**H**); $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.9 ppm (s); $^{13}$C NMR (125 MHz, DMSO-d6)$\delta$ 55.4 (q, 1C, **C**H$_3$) 111.0 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 114.1 ppm (d, 2C, 2x C**H**–$C_q$–O) 118.9 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 135.4 (d, 2C, 2x **C**H–$C_q$–B) 138.1 ppm (s, 2C, 2x **$C_q$**–N) 160.7 ppm (s, 1C, **$C_q$**–$OCH_3$) $^{15}$NMR (50 MHz, DMSO-d6) $\delta$ 107 ppm; HRMS calcd for $C_{13}H_{12}BN_2O$: 223.1043; found 223.1041.

*4.5.2. Method B*

79 mg, 62%.

*4.6. 2-(4-methylphenyl)-1,3,2-benzodiazaborole (**3d**) [27]*

*4.6.1. Method A*

369 mg, 89%.$^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 2.33 ppm (s, 3H, C**H$_3$**) 6.77–6.81 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H, 2x C**H**–CH–$C_q$–N) 7.01–7.05 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H, 2x CH–C**H**–$C_q$–N) 7.23 ppm (d, $J$ = 8.2 Hz, 2H, 2x C**H**–$C_q$–B) 7.78 ppm (d, $J$ = 7.9 Hz, 2H, 2x C**H**–$C_q$–$CH_3$) 9.01 ppm (s, 2H, 2x N**H**); $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 29.5 ppm (s); $^{13}$C NMR (125 MHz, DMSO-d6) 21.6 ppm (q, 1C, **C**H$_3$) 111.2 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 118.6 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 129.0 ppm (d, 2C, 2x **C**H–$C_q$–B) 133.9 ppm (d, 2C, 2x **C**H–$C_q$–$CH_3$) 137.7 ppm (s, 2C, 2x **$C_q$**–N) 139.1 ppm (s, 1C, **$C_q$**–$CH_3$); $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 110 ppm; HRMS calcd for $C_{13}H_{12}BN_2$: 207.1094; found 207.1098.

*4.6.2. Method B*

68 mg, 78%.

*4.7. 2-[4-(methylsulfanyl)phenyl]-1,3,2-benzodiazaborole (**3e**)*

*4.7.1. Method A*

454 mg, 95%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 2.50 ppm (s, 3H, SC**H$_3$**) 6.78–6.81 ppm (m, $J$ = 5.7 Hz, $J$ = 3.2 Hz, 2H, 2x C**H**–CH–$C_q$–N) 7.00–7.05 ppm (m, $J$ = 5.6 Hz, $J$ = 3.2 Hz, 2H, 2x CH–C**H**–$C_q$–N) 7.30 ppm (d, $J$ = 8.3 Hz, 2H, 2x C**H**–$C_q$–S) 7.82 ppm (d, $J$ = 8.3 Hz, 2H, 2x C**H**–$C_q$–B) 9.08 ppm (2, 2H, 2x-N**H**); $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.0 ppm (s);$^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 14.7 ppm (q, 1C, S**C**H$_3$) 111.1 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 118.7 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 125.6 ppm (d, 2C, 2x **C**H–$C_q$–S) 134.3 ppm (d, 2C, 2x **C**H–$C_q$–B) 137.7 ppm (s, 2C, 2x **$C_q$**–N) 140.1 ppm (s, 1C, **$C_q$**–$CH_3$); $^{15}$NMR (50 MHz, DMSO-d6) $\delta$ 109 ppm; HRMS calcd for $C_{13}H_{12}BN_2S$: 239.0814; found 239.0812.

*4.7.2. Method B*

83 mg, 87%.

**Table 5**
Selected X-Ray data for compounds **5a**, **5b**, **5d**, and **5e**.

| Compound | B–C bond distance (Å) | B–N bond distance (Å)[a] | Dihedral angle (°)[b] |
|---|---|---|---|
| **5a** | 1.562(2) | 1.414(2) | 8(1) |
| **5b** | 1.568(4) | 1.411(2) | 6(1) |
| **5d** | 1.559(1) | 1.441(1) | 23(1) |
| **5e** | 1.559(3) | 1.414(2) | 19(1) |

[a] Averaged value.
[b] Angle between mean planes through phenyl group carbon atoms and the non-hydrogen atoms of the napthodiazaborinane grouping.

### 4.8. 2-(2-Methylpropyl)-1,3,2-benzodiazaborole (**3f**)

#### 4.8.1. Method A

313 mg, 90%.$^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 0.96 ppm (d, $J$ = 6.5 Hz, 6H, 2x $CH_3$) 1.07 ppm (d, $J$ = 7.1 Hz, 2H, CH–C**H**$_2$–B), 1.91–1.99 ppm (m, $J$ = 6.7 Hz, 1H, $(CH_3)_2$–C**H**–$CH_2$) 6.70–6.73 ppm (m, $J$ = 5.6 Hz, $J$ = 3.2 Hz, 2H, C**H**–CH–$C_q$–N) 6.91–6.94 ppm (m, $J$ = 5.6 Hz, $J$ = 3.2 Hz, 2H, 2x CH–C**H**–$C_q$–N) 8.33 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 31.7 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 23.0 ppm (t, 1C, **C**H$_2$) 25.9 ppm (q, 2C, 2x $CH_3$) 26.2 ppm (d, 1C, CH) 110.6 ppm (d, 2C, 2x CH–**C**H–$C_q$–N) 118.0 ppm (d, 2C, 2x **C**H–CH–$C_q$–N) 137.4 ppm (s, 2C, 2x **C$_q$**–N) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 113 ppm; HRMS calcd for $C_{10}H_{15}BN_2$: 174.0516; found 174.0521.

#### 4.8.2. Method B

49 mg, 70%.

### 4.9. 2-Phenyl–naphtho[1,8-de][1,3,2]diazaborine (**5a**) [17]

#### 4.9.1. Method C

413 mg, 85%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 6.60 ppm (dd, $J$ = 7.5 Hz, $J$ = 0.75 Hz, 2H, 2x C**H**–$C_q$–N) 6.91 ppm (dd, $J$ = 8.3 Hz, $J$ = 0.72 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.09 ppm (dd, $J$ = 7.8 Hz, 2H, 2x CH–C**H**–CH) 7.42–7.48 ppm (m, 3H, C**H**–C**H**–C**H**) 7.92–7.94 ppm (m, $J$ = 7.7 Hz, $J$ = 1.7 Hz, 2H, C**H**–$C_q$–B) 8.24 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 30.0 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 106.1 ppm (d, 2C, 2x **C**H–$C_q$–N) 116.7 ppm (d, 2C, 2x **C**H–$C_q$–$C_q$) 120.1 ppm (s, 2C, 2x **C$_q$**–N) 127.9 ppm (d, 4C, **C**H–CH–**C**H and 2x **C**H–CH–$C_q$–$C_q$) 130.4 ppm (d, 1C, CH–**C**H–CH) 133.1 ppm (d, 2C, 2x **C**H–$C_q$–B) 136.4 ppm (s, 1C, CH–**C$_q$**–$C_q$) 142.8 ppm (s, 1C, $C_q$–**C$_q$**–$C_q$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 101 ppm; HRMS calcd for $C_{16}H_{12}BN_2$: 243.1094; found 243.1092.

#### 4.9.2. Method D

98 mg, 90%.

### 4.10. 2-(4-Chlorophenyl)–naphtho[1,8-de][1,3,2]diazaborine (**5b**) [18]

#### 4.10.1. Method C

415 mg, 75%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 6.58 ppm (dd, $J$ = 7.3 Hz, $J$ = 0.85 Hz, 2H, 2x C**H**–$C_q$–N) 6.91 ppm (dd, $J$ = 8.3 Hz, $J$ = 0.84 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.08 ppm (dd, $J$ = 7.8 Hz, 2H, 2x CH–C**H**–CH) 7.49–7.53 ppm (m, 2H, C**H**–$C_q$–C**H**) 7.94–7.97 ppm (m, 2H, 2x C**H**–$C_q$–B) 8.30 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.8 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 106.2 ppm (d, 2C, 2x **C**H–$C_q$–N) 116.8 ppm (d, 2C, 2x C**H**–$C_q$–$C_q$) 120.2 ppm (s, 2C, 2x **C$_q$**–N) 128.1 ppm (d, 2x CH–**C**H–CH or **C**H–$C_q$–Cl) 128.2 ppm (d, 2x CH–**C**H–CH or **C**H–$C_q$–Cl) 135.0 ppm (d, 2C, 2x **C**H–$C_q$–B) 135.5 ppm (s, 1C, CH–**C$_q$**–Cl or CH–**C$_q$**–$C_q$) 136.4 ppm (s, 1C, CH–**C$_q$**–Cl or CH–**C$_q$**–$C_q$) 142.3 ppm (s, 1C, $C_q$–**C$_q$**–$C_q$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 101 ppm; HRMS calcd for $C_{16}H_{11}BN_2Cl$: 277.0704; found 277.0701.

#### 4.10.2. Method D

88 mg, 88%.

### 4.11. 2-(4-Methoxyphenyl)–naphtho[1,8-de][1,3,2]diazaborine (**5c**) [28]

#### 4.11.1. Method C

437 mg, 80%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 3.81 ppm (s, 3H, $CH_3$) 6.58 ppm (dd, $J$ = 7.4 Hz, $J$ = 0.95 Hz, 2H, 2x C**H**–$C_q$–N) 6.88 ppm (dd, $J$ = 8.2 Hz, $J$ = 0.76 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.00 ppm (d, $J$ = 8.7 Hz, 2H, 2x C**H**–$C_q$–O) 7.07 ppm (t, $J$ = 8.0 Hz, 2H, 2x CH–C**H**–CH) 7.89 ppm (d, $J$ = 8.7 Hz, 2H, 2x C**H**–$C_q$–B) 8.19 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.7 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 55.5 ppm (q, 1C, **C**$H_3$) 105.9 ppm (d, 2C, 2x **C**H–$C_q$–N) 113.7 ppm (d, 2C, 2x **C**H–$C_q$–O) 116.5 ppm (d, 2C, 2x **C**H–$C_q$–$C_q$) 119.9 ppm (s, 2C, 2x $C_q$–N) 128.1 ppm (d, 2C, 2x CH–**C**H–CH) 134.8 ppm (d, 2C, 2x **C**H–$C_q$–B) 136.4 ppm (s, 1C, CH–**C$_q$**–$C_q$) 142.9 ppm (s, 1C, $C_q$–**C$_q$**–$C_q$) 161.5 ppm (s, 1C, **C$_q$**–O–$CH_3$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 101 ppm; HRMS calcd for $C_{17}H_{14}BN_2O$: 273.1199; found 273.1201.

#### 4.11.2. Method D

103 mg, 95%.

### 4.12. 2-(4-Methylphenyl)-naphtho[1,8-de][1,3,2]diazaborine (**5d**) [28]

#### 4.12.1. Method C

411 mg, 80%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 2.35 ppm (s, 3H, C**H**$_3$) 6.58 ppm (dd, $J$ = 7.4 Hz, $J$ = 0.85 Hz, 2H 2x C**H**–$C_q$–N) 6.89 ppm (dd, $J$ = 8.2 Hz, $J$ = 0.90 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.09 ppm (dd, $J$ = 7.8 Hz, 2H, 2x CH–C**H**–CH) 7.25 ppm (dd, $J$ = 8.0 Hz, $J$ = 0.60 Hz, 2H, 2x C**H**–$C_q$–$CH_3$) 7.82 ppm (d, $J$ = 7.9 Hz, 2H, 2x C**H**–$C_q$–B) 8.19 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 29.2 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 21.6 ppm (q, 1C, **C**$H_3$) 106.0 ppm (d, 2C, 2x **C**H–$C_q$–N) 116.6 ppm (d, 2C, 2x **C**H–$C_q$–$C_q$) 120.0 ppm (s, 2C, 2x **C$_q$**–N) 128.1 ppm (d, 2C, 2x CH–**C**H–CH) 128.7 ppm (d, 2C, 2x **C**H–$C_q$–$CH_3$) 133.2 ppm (d, 2C, 2x **C**H–$C_q$–B) 136.4 ppm (s, 2C, 2x CH–**C$_q$**–$C_q$) 139.9 ppm (s,1C, **C$_q$**–$CH_3$) 142.9 ppm (s, 2C, 2x $C_q$–**C$_q$**–$C_q$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 101 ppm; HRMS calcd for $C_{17}H_{14}BN_2$ : 257.1250; found 257.1248.

#### 4.12.2. Method D

77 mg, 75%.

### 4.13. 2-[4-(Methylsulfanyl)phenyl]–naphtho[1,8-de][1,3,2] diazaborine (**5e**) [19]

#### 4.13.1. Method C

441 mg, 76%. $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 2.52 ppm (s, 3H, SC**H**$_3$) 6.58 ppm (dd, $J$ = 7.4 Hz, $J$ = 0.85 Hz, 2H, 2x C**H**–$C_q$–N) 6.89 ppm (dd, $J$ = 8.1 Hz, $J$ = 0.82 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.07 ppm (m, $J$ = 7.7 Hz, 2H, 2x CH–C**H**–CH) 7.31 ppm (d, $J$ = 8.4 Hz, 2H, 2x C**H**–$C_q$–$SCH_3$) 7.87 ppm (d, $J$ = 8.3 Hz, 2H, 2x C**H**-$C_q$-B) 8.22 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 28.7 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 14.7 ppm (q, 1C, SC**H**$_3$) 106.1 ppm (d, 2C, 2x **C**H–$C_q$–N) 116.6 ppm (d, 2C, 2x **C**H–$C_q$–$C_q$) 120.1 ppm (s, 2C, 2x **C$_q$**–N) 125.2 ppm (d, 2C, 2x **C**H–$C_q$–$SCH_3$) 128.1 ppm (d, 2C, 2x CH–**C**H–CH) 133.6 ppm (d, 2C, 2x **C**H–$C_q$–B) 136.4 ppm (s, 2C, 2x CH–**C$_q$**–$C_q$) 141.0 ppm (s, 1C, **C$_q$**–S) 142.8 ppm (s, 2C, 2x $C_q$–**C$_q$**–$C_q$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 100 ppm HRMS calcd for $C_{17}H_{15}BN_2S$: 290.1049; found 290.1050.

#### 4.13.2. Method D

93 mg, 80%.

### 4.14. 2-(2-Methylpropyl)-naphtho[1,8-de][1,3,2]diazaborine (**5f**)

#### 4.14.1. Method C

376 mg, 84%; $^{1}$H NMR (500 MHz, DMSO-d6) $\delta$ 0.77 ppm (d, $J$ = 7.4 Hz, 2H, C**H**$_2$–B) 0.95 ppm (d, 6.6 Hz, 6H, 2x C**H**$_3$–CH–$CH_2$) 1.9–2.0 ppm (m, 1H, $CH_3$–C**H**–$CH_2$) 6.39 ppm (dd, $J$ = 7.5 Hz, $J$ = 0.95 Hz, 2H, 2x C**H**–$C_q$–N) 6.83 ppm (dd, $J$ = 8.4 Hz, $J$ = 0.83 Hz, 2H, 2x C**H**–$C_q$–$C_q$) 7.02 ppm (m, $J$ = 7.8 Hz, 2H, 2x CH–C**H**–CH) 7.70 ppm (s, 2H, 2x N**H**) $^{11}$B NMR (160 MHz, DMSO-d6) $\delta$ 32.6 ppm (s) $^{13}$C NMR (125 MHz, DMSO-d6) $\delta$ 24.8 ppm (d, 1C, $CH_3$–**C**H–$CH_2$) 25.4 ppm (q, 2C, 2x **C**$H_3$–CH–$CH_2$) 25.8 ppm (t, 1C, **C**H$_2$–B) 104.9 ppm (d, 2C, 2x **C**H–$C_q$–N)

115.6 ppm (d, 2C, 2x **C**H–$C_q$–$C_q$) 119.4 ppm (s, 2C, 2x **C**$_q$–N) 127.5 ppm (d, 2C, 2x CH–**C**H–CH) 135.9 ppm (s, 2x CH–**C**$_q$–$C_q$) 142.4 ppm (s, 2C, 2x $C_q$–**C**$_q$–$C_q$) $^{15}$N NMR (50 MHz, DMSO-d6) $\delta$ 100 ppm (s); HRMS calcd for $C_{14}H_{17}BN_2$: 224.1104; found 224.1109.

#### 4.14.2. Method D

67 mg, 75%.

### 4.15. X-ray crystallographic study

Single crystals of compound **5d** were grown by slow evaporation of a solution of the compound in dichloromethane following filtration through a silica plug. Crystal data: $C_{17}H_{15}BN_2$ (MW = 258.12 g mol$^{-1}$); 0.08 × 0.12 × 0.38 mm; monoclinic; space group $P2_1/n$ (No. 14); $a$ = 10.783(1), $b$ = 10.149(1), $c$ = 13.535(2) Å, $\beta$ = 113.0(1)°; $Z$ = 4, $V$ = 1363.6(2)Å$^3$; $D_{calcd}$ = 1.257 g cm$^{-3}$; $\mu$ = 0.074 mm$^{-1}$. Intensity data were collected on a Oxford Diffraction Xcalibur CCD diffractometer with monochromated MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å), at 22 °C, in the $\theta$ range 2–25°. The structure was solved by means of direct methods using SHELXS-97 [23], and refined on $F^2$ on all data by full matrix least-squares methods. A riding model with idealised geometry was used for all hydrogen atoms. Anisotropic refinement (241 parameters) of all non-hydrogen atoms converged at $R_1$ = 0.0494 [3953 unique reflections with $I > 2\sigma(I)$], w$R_2$ (all 5103 data) = 0.0631 and a max. residual electron density of 0.49 e.Å$^3$.

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## Appendix A. Supplementary material

Supplementary material related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2012.09.018.

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