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# Synthesis and structure of potential Lewis acid–Lewis base bifunctional catalysts: 1-*N*,*N*-dimethylamino-8-bororononaphthalene derivatives

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**Abstract**

A new series of boronate-amine substituted potential bifunctional catalysts have been prepared by directed lithiation of 1-*N*,*N*-dimethylnaphthalene, followed by reaction borate esters. Both diisopropyl and pincacol ester derivatives of the resulting boronates were prepared, together with a novel boroxine which shows novel N–B interactions in the crystal structure. The corresponding dimethyl-[8-(difluoroborolyl)-naphthalen-1-yl]-amine was directly accessed from the boroxine by reaction with potassium hydrogen fluoride.


*Keywords:* Metallation; Arylamine; Arylboronate; Boronic acid; Aryldifluoroborane; NMR; X-ray

## 1. Introduction

In recent years, there has been increased recognition of the advantages of bifunctional catalysts systems for a wide range of synthetic processes [1]. In particular, the cooperative interaction of both a Lewis acid and Lewis base function can be used to catalyse asymmetric aldol [2], cyanosilylation [3], Strecker [4], allylation [5], epoxide ring opening [6] reactions, and β-lactam construction [7]. As long ago as the 1960s, Letsinger had demonstrated [8] the beneficial, cooperative effect of both an amino and boronic acid function in the same molecule for effecting the ring opening of chlorohydrins. However, amino-boronate containing compounds have not been studied in detail as potential bifunctional catalysts, even though amino–boronic acid systems have attracted interest, for example in carbohydrate recognition [9]. In this paper, we report our first endeavours into the preparation bifunctional Lewis acid–Lewis base derivatives, based upon aryldifluoroborane and arylamine functions, respectively and in this case, using 1,8-naphthalene functionalisation.

Aryl and alkyl difluoroboranes have attracted relatively little interest as Lewis acids, however, aryldifluoroboranes are convenient Lewis acids which can be used as alternatives to boron trifluoride [10]. In addition, this class of Lewis acids shows different selectivity to boron trifluoride in Diels–Alder reactions, has the advantage of tunability through aryl-substitution and does not leave transition metal residues in the products. For these reasons, we decided to develop general routes for the synthesis of different classes of amino-difluoroborane derivatives in order to study the relative compatibility of these two functional groups, and later to examine their potential as bifunctional catalysts for different reactions. Our first target was structure **1** in which there is clearly potential for N–B intramolecular chelation. Hence, we wished to determine whether such compounds could be made conveniently and whether N–B chelation could prevent the boron function from interacting with

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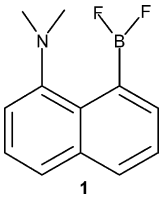
external Lewis bases.

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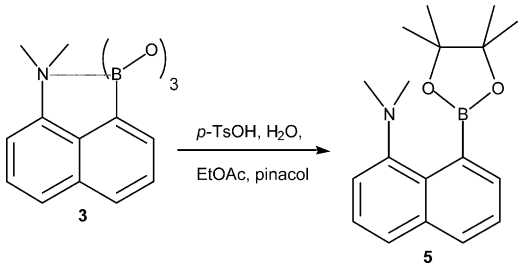
## 2. Results and discussion

### 2.1. Directed metallation route to 1-dimethylamino-8-bononaphthalene derivatives

In order to prepare compound **1**, introduction of the boron was achieved by directed metallation of 1-*N*,*N*-dimethylnaphthalene (**2**), by either of the reactions shown in Scheme 1, both of which rely upon a common lithiation reaction over several days with *n*-butyllithium, using the method reported by van Koten and coworkers 11a and Corriu and coworkers [11b], followed by quenching with either trimethylborate or triisopropylborate. In the former case, the corresponding boroxine trimer **3** was isolated in 69% yield, as a crystalline product, whereas in the latter case, the corresponding diisopropyl ester **4** was obtained in 48% yield after distillation. The diisopropyl ester was sensitive to hydrolysis and readily hydrolysed to form the boroxine trimer **3**. Indeed, this was used as a method for generating crystals of boroxine **3** suitable for single crystal X-ray structure analysis (vide infra) and the material produced was identical in all aspects to that produced directly using trimethylborate as electrophile in the metallation reaction (Scheme 1).

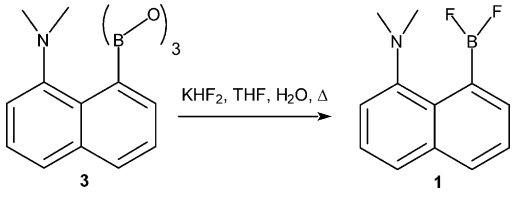
Due to the moisture sensitivity of the diisopropyl ester **4**, a more stable pinacol ester was prepared in order to aid structural studies of this class of amino–boronic acids. Boroxine trimer **3** was resistant to esterification under standard conditions (room temperature + diol) and forcing conditions had to be used to promote the esterification to the stable, crystalline (vide infra) pinacol ester **5**. Esterification was achieved in 60% yield, by refluxing boroxine **3** in a mixed solvent system with *para*-toluenesulfonic acid catalysis (Eq. (1)).




3 5 (1)

### 2.2. Synthesis of 1-dimethylamino-8-difluoroborylnaphthalene

In order to prepare the corresponding difluoroborane compound **1** from boroxine **3**, it is usually necessary to make the corresponding potassium trifluoroborate salt (i.e. of type $ArBF_3K$), which may then be converted to difluoroborane ($ArBF_2$) by treatment with chlorotrimethylsilane or boron trifluoride [10,12]. However, in the case of boroxine **3**, upon treatment with $KHF_2$ in water/THF in order to provide complete dissolution of the substrate, the difluoroborane system **1** was produced directly.

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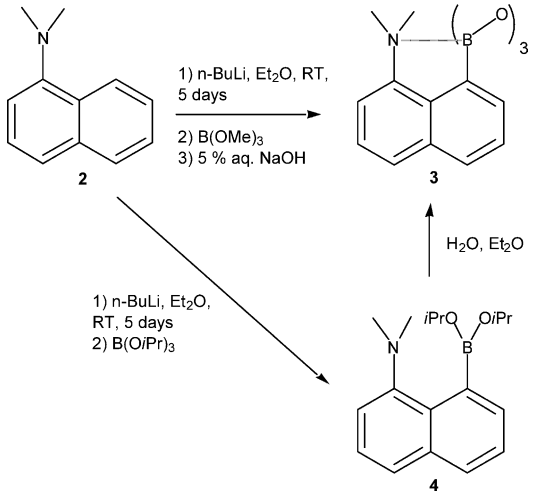
### 2.3. Spectroscopic properties and X-ray crystallography

Having isolated the boroxine **3**, the boronate ester derivatives **4** and **5** and the difluoroborane **1**, it is interesting to note the all structures show clear evidence for formation of an intramolecular 'ate'-complex by $^{11}$B-NMR, as shown by chemical shifts of 19, 18, 22 and 10 ppm, respectively. In each case, the proximal 1,8-relationship of the dimethylamino function to the boron centre ensures approximate tetrahedral geometry at boron. This is further reinforced by X-ray structure analysis (Table 1) of single crystals of boroxine **3** (Figs. 1 and 2) and pinacol ester **5** (Fig. 3). In each case, the effect of the N–B interaction can be seen, despite: (1) the




Scheme 1.

Table 1
Crystal and structure refinement data for **3** and **5**

| Molecular compound | Boroxine trimer **3** | Pinacol ester **5** |
|---|---|---|
| *(a) Crystal data* | | |
| Chemical formula | $C_{36}H_{36}B_3N_3O_3$ | $C_{18}H_{24}BNO_2$ |
| Formula weight | 591.11 | 297.19 |
| Crystal system | hexagonal | triclinic |
| Space group | $P\bar{3}$ | $P\bar{1}$ |
| Unit cell dimensions | | |
| $a$ (Å) | 21.1451(7) | 10.3180(14) |
| $b$ (Å) | 21.1451(7) | 12.0316(16) |
| $c$ (Å) | 12.0020(7) | 14.5300(19) |
| $\alpha$ (°) | | 66.262(5) |
| $\beta$ (°) | | 86.552(5) |
| $\gamma$ (°) | | 86.573(6) |
| $V$ (Å$^3$) | 4647.3(3) | 1649.9(4) |
| $Z$ | 6 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.267 | 1.199 |
| $\mu$ (mm$^{-1}$) | 0.079 (Mo–$K_\alpha$) | 0.076 (Mo–$K_\alpha$) |
| *(b) Data collection, processing and refinement* | | |
| $2\theta$ max (°) | 58.54 | 61.14 |
| Data collected ($h$, $k$, $l$) | (−28, −25, −16) to (28, 26,16) | (−12, −12, −20) to (12, 17, 20) |
| Total reflections | 44 234 | 5059 |
| Unique reflections [$R_{int}$] (%) | 7645 (8.76) | 3438 (12.73) |
| Observed reflections | 4750 [$I > 4\sigma(I)$] | 1112 [$I > 4\sigma(I)$] |
| Absorption corrections | multi scan | none |
| Transmission factors | 0.90686–1.0000 | |
| Number of parameters | 406 | 397 |
| $R$ | 0.070 | 0.0696 |
| $R_w$ | 0.132 | 0.1388 |

geometric compression required for N–B interaction; and (2) the relatively low basicity of the aryl amine group. Indeed, the fact that the boroxine trimer **3** shows any sign of N–B interaction is particularly interesting since boroxine trimer systems, being aromatic, are planar. In addition, this system is crystallographically unique as far as we are aware, despite several reports of intramolecular boroxine–benzylamine systems [13], since it clearly shows deformation of the boroxine ring

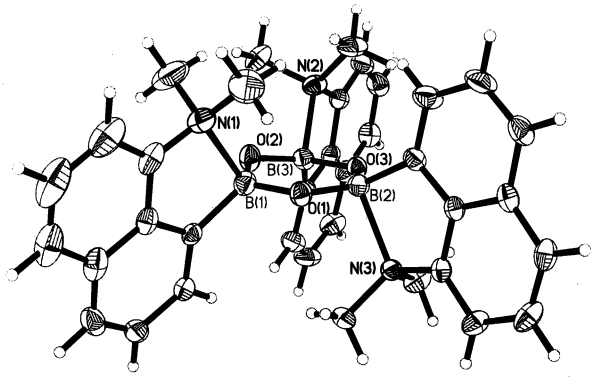



Fig. 1. ORTEP X-ray crystal structure of boroxime trimer **3**, showing 50% probability ellipsoids.

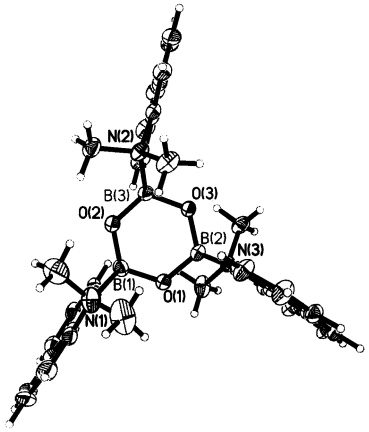



Fig. 2. ORTEP X-ray crystal structure of boroxime trimer **3**, projected onto the boroxine ring, showing 50% probability ellipsoids.

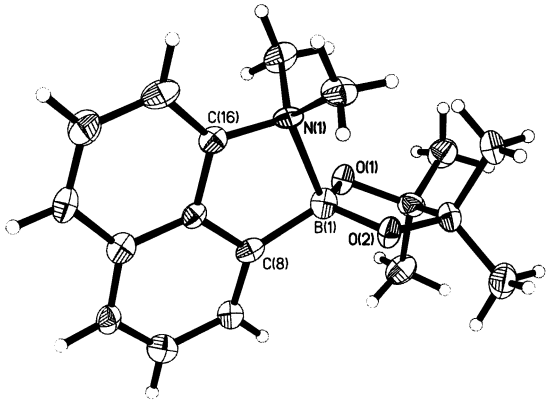



Fig. 3. ORTEP X-ray crystal structure of pinacol ester **5**, showing 50% probability ellipsoids.

away from planarity, as shown by a small O–B–O–B torsion of 0.6° and much larger B–O–B–O torsion of 10.3°. Hence, in this case, the proximal placement of the nitrogen function forces intramolecular N–B interaction to occur, providing partial quaternisation at the boron centre. Clearly, despite the boron atoms being in a boroxine ring, they are still sufficiently Lewis acidic to interact with the neighbouring nitrogen atom. The weak nature of the N–B interaction in the boroxine system **3** is evidenced by a C–B–N bond angle of 92°, a C–N–B bond angle of 103° and a relatively long N–B bond length of 1.97 Å. There is also bending of the amino and boron groups towards each other, causing angle compression from the usual 120°, to 114 and 112° for the C(Ar)–C(Ar)–N and C(Ar)–C(Ar)–B angles, respectively. In contrast, the pinacol ester **5** is capable of greater N–B chelation, with a C–B–N bond angle of 95°, a C–N–B bond angle of 113°, a shorter N–B bond length of 1.89 Å and slightly more severe angle compression from the usual 120°, to 113 for both the C(Ar)–C(Ar)–N and C(Ar)–C(Ar)–B angles. The fact that the $^{11}$B shift is 22 ppm for pinacol ester **5**, versus 18

ppm in the diisopropyl ester **4** can be explained by the reported [14] effect of ring strain imposed by the pinacol ester versus acylic ester.

Although the difluoroborane system **1** has yet to be crystallised to produce crystals which are suitable for single crystal structure analysis, this compound also shows clear signs of B–N chelation, as evidenced by a $^{11}$B-NMR shift of approximately 10 ppm and $^{11}$B–$^{19}$F coupling of 58 Hz, producing a broad triplet (Fig. 4). As anticipated [15], the $^{19}$F-NMR spectrum is diagnostic of fluorine attached to an asymmetric (boron) quadrupole, resulting in a broad, asymmetric multiplet signal, as shown in Fig. 5. Thus, the effect of the two fluorine atoms on boron, is to enhance the Lewis acidic nature of the boron centre, resulting in a strong N–B interaction. producing an approximately tetrahedral boron and thus, an entirely predictable $^{11}$B-NMR chemical shift, in complete agreement with such a structural analysis [12b].

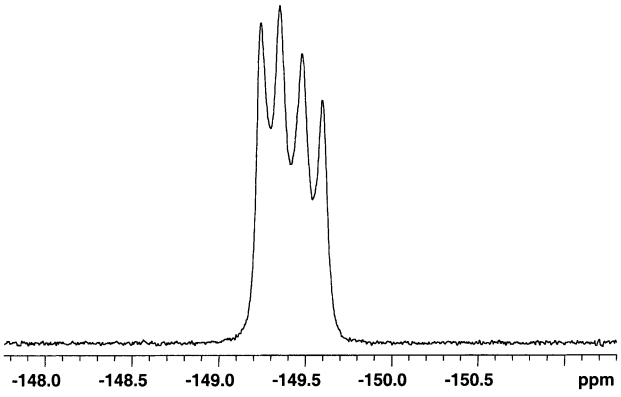



Fig. 5. $^{19}$F-NMR spectrum of difluoroborane **1**, showing the effect of the asymmetric boron quadrupole.

### 2.4. Conclusions

We have prepared novel examples of potential bifunctional catalysts in which both Lewis acidic boron and Lewis basic nitrogen functions can be handled conveniently, despite their proximal position, in a 1,8-naphthalene system. It is clear that the nitrogen and boron functions interact, even in the novel boroxine system **3** and despite the relatively low nitrogen basicity. The examination of compounds such as **1** as potential catalysts in different reactions is currently underway and will be reported in due course.

## 3. Experimental

All $^{1}$H-NMR spectra were obtained using either a 250 MHz Varian Oxford, or 300 MHz Varian, or 400 MHz Varian Mercury, or 500 MHz Varian spectrometer, using partially deuterated solvent signals as the internal standards. $^{13}$C-NMR spectra were recorded at 100 MHz on a Varian Oxford spectrometer, or 125.5 MHz on a Varian Inova AS500 NMR spectrometer. $^{11}$B-NMR spectra were recorded at 96 MHz on a Varian Mercury spectrometer or 128.4 MHz on a Bruker 400 spectrometer. $^{19}$F-NMR were recorded at 188.18 MHz on a Varian 200 spectrometer or 470.26 MHz on a 500 MHz Varian spectrometer. Mass spectra were recorded on a Micromass Autospec. High resolution mass spectra were obtained from a Micromass Autospec spectrometers. Elemental analyses were carried out on an Exeter Analytical CE-440 elemental analyser. Infra red spectra were obtained using a Perkin–Elmer 1615 FTIR operating from a Grams Analyst1600. UV spectra were recorded on an ATI Unicam UV2 UV–vis spectrometer. Melting points were determined using an Electrothermal melting point apparatus.

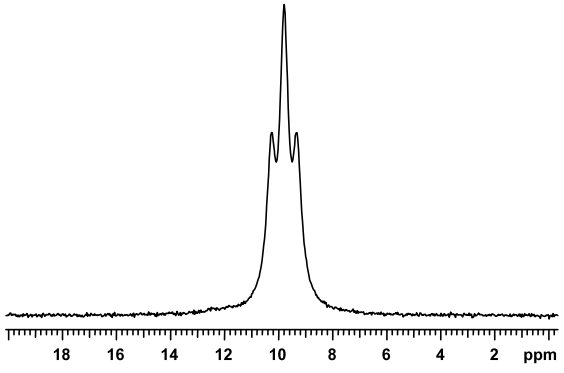



Fig. 4. $^{11}$B-NMR spectrum of difluoroborane **1**, showing $^{19}$F coupling.

All starting materials were obtained commercially from Aldrich or Lancaster and used as received, unless otherwise stated. Solvents were also used as received, unless otherwise stated. Tetrahydrofuran and ether were distilled from sodium benzophenone ketyl. Dichloromethane and toluene were distilled from calcium hydride. *N*,*N*-dimethyl-1-naphthylamine and TMEDA were distilled from calcium hydride. Alkyl lithiums were acquired from Aldrich and were titrated immediately prior to each use [16]. Air and moisture sensitive reactions were performed under argon and all glassware for use in sensitive reactions was heated for at least 12 h at 160 °C, or flame dried immediately prior to use. Air and moisture sensitive reagents were stored under argon and introduced by syringe or cannula through rubber septa. Evaporations were carried out at 20 mmHg using a Buchi rotary evaporator and water bath, followed by evaporation to dryness ($< 2$ mmHg).

### 3.1. Preparation of 1,3,5-tris-(1-N,N-dimethylamino)-8-naphthylboroxine (3)

*N,N*-dimethylnapthyl-1-amine (**2**) (24.5 ml, 0.149 mol) was added to diethyl ether (450 ml) at room temperature (r.t.). A 2.5 M solution of *n*-butyllithium in hexanes (59.6 ml, 0.149 mol) was added and the reaction was left to stir for 125 h. The reaction mixture was cooled to −78 °C and trimethylborate (50 ml, 0.48 mol) was added as rapidly as possible without raising the temperature of the reaction above −70 °C with vigorous stirring. The reaction was allowed to proceed at −78 °C for 1 h, then allowed to warm to r.t. over 3 h. A 5% (w/v) solution of NaOH was added to the reaction (400 ml), the mixture was stirred vigorously for 30 min and the white precipitate was collected by filtration, then washed with diethyl ether (2 × 100 ml) and 5% (w/v) NaOH (2 × 50 ml). Residual solvent was evaporated to yield boroxine **3** as a white powder (20.14 g, 69%); m.p. > 280 °C; IR (film) (inter alia) 665, 760, 780 (s), 828, 1056, 1116, 1204, 1254, 1452 $cm^{-1}$; UV (MeCN) 220 ($\varepsilon$ 12 050), 288 ($\varepsilon$ 1580), 320 ($\varepsilon$ 590) nm; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 2.91 (s, 6H), 7.25 (dd, $J = 7.5$ and 0.9 Hz, 1H), 7.37 (t, $J = 8.1$ Hz, 1H), 7.58 (dd, $J = 6.3$ and 8.1 Hz, 1H), 7.62 (dd, $J = 8.1$ and 0.9 Hz, 1H), 7.68 (dd, $J = 8.1$ and 0.9 Hz, 1H), 7.81 (d, $J = 6.3$ Hz, 1H); $^3$C-NMR (100 MHz, $CD_3CN$) $\delta$ 45.3, 115.2, 124.15, 124.24, 125.1, 126.4, 126.6, 131.8, 133.6, 149.9; $^{11}$B (96 MHz, $CDCl_3$) $\delta$ 19 (br); ESMS (+ve ion, acetonitrile/0.1% TFA) *m/z* 592.3 (100%, $MH^+$); Accurate MS (ES) $C_{36}H_{37}B_3N_3O_3$ requires *m/z* 592.3114, found *m/z* 592.3101.

### 3.2. Preparation of dimethyl-[8-(diisopropyloxyborolyl)-naphthalen-1-yl]-amine (4)

*N,N*-dimethylnapthyl-1-amine (**2**) (10.5 ml, 0.064 mol) was added to diethyl ether (180 ml) at r.t. A 1.2 M solution of *n*-butyllithium in hexanes (50.25 ml, 0.064 mol) was added and the reaction was left to stir for 125 h. The reaction mixture was cooled to −78 °C and triisopropyl borate (10.18 ml, 0.071 mol) was added as rapidly as possible without raising the temperature of the reaction above −70 °C with vigorous stirring. The reaction was allowed to proceed at −78 °C for 1 h, then allowed to warm to r.t. over 3 h. The mixture was then filtered and rinsed with diethyl ether (2 × 50 ml). The solvent was evaporated to yield the crude borate. This was then distilled on Kugelrohr to produce boronate **4** as a colourless liquid (b.p. 135 °C, 0.7 mmHg) (12.8 g, 48%); IR (film) (inter alia) 750, 890, 971, 1050, 1120, 1150, 1170 (s), 1455 $cm^{-1}$; UV (MeCN) 192 ($\varepsilon$ 1750), 220 ($\varepsilon$ 4590), 292 ($\varepsilon$ 510) nm; $^1$H-NMR (300 MHz, $CDCl_3$) $\delta$ 1.14 (d, $J = 6$ Hz, 6H), 1.21 (d, $J = 6$ Hz, 6H), 2.73 (s, 6H), 4.07 (sept, $J = 6$ Hz, 2H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.40–7.58 (m, 3H), 7.67 (d, $J = 8.1$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H); $^{13}$C-NMR (75 MHz, $CDCl_3$) $\delta$ 133.8, 129.8, 126.9, 126.8, 125.8, 125.7, 116.5, 65.2, 47.8, 25.4, 25.2; $^{11}$B-NMR (128.4 MHz, MeCN) $\delta$ 17.7 (br); ESMS (+ve ion, MeCN) *m/z* 299.2 (100%, $M^+$); Accurate MS (ES) $C_{18}H_{28}BNO_2$ requires *m/z* 301.1988, found *m/z* 301.1986.

### 3.3. Preparation of single crystals for 1,3,5-tris-(1-N,N-dimethylamino)-8-naphthylboroxine (3)

To a solution of *N,N*-dimethylnaphthyl-1-aminediisopropylborate (**4**) (1.0 g, 3.34 mmol) in diethylether (9 ml) was added water (10 ml). The mixture was left to stand for 48 h and colourless crystals were formed at the biphasic interface, which were identical to boroxine **3** (0.59 g, 90%) and were suitable for X-ray analysis.

### 3.4. Dimethyl-[8-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-naphthalen-1-yl]-amine (5)

A mixture of boroxine **3** (1.01 g, 1.69 mmol), pinacol (0.66 g, 5.07 mmol), *para*-toluenesulfonic acid (0.66 g, 3.4 mmol), diethyl ether (100 ml) and water (100 ml) was vigorously stirred for 3 days. The organic layer was separated, the water layer was re-extracted with diethyl ether (4 × 100 ml), the combined organic extracts were partially evaporated, the resulting solution was absorbed on to silica gel and the remaining solvent evaporated. The resulting solid was added to a silica gel column and the product was eluted (hexane–ethyl acetate, 4:1 as eluant) to yield white crystals of pinacol ester **5** (0.908 g, 60%) (m.p. 77.4–78.2 °C); IR $cm^{-1}$ (film) (inter alia) 773 (s), 821, 884, 971, 1051, 1122, 1149, 1181 (s), 1460 $cm^{-1}$; UV (MeCN) 192 ($\varepsilon$ 1340), 224 ($\varepsilon$ 5940), 284 ($\varepsilon$ 660) nm; $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$ 1.43 (s, 12H), 2.86 (s, 6H), 7.33 (d, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 8.5$ Hz, 1H), 7.56 (t, $J = 7.0$ Hz, 1H), 7.65 (d, $J = 6.5$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.5$ Hz, 1H); $^{13}$C-NMR (125.7 MHz, $CDCl_3$) $\delta$ 26.6, 47.8, 81.7, 115.0, 125.75, 125.77, 125.95, 128.3, 129.1, 132.7, 134.7, 150.4; $^{11}$B-NMR (96 MHz, $CDCl_3$) $\delta$ 22 (br); ESMS (+ve ion, MeCN) 297.3 (100%, $M^+$); Anal. Calc.: $C_{18}H_{24}BNO_2$ requires C, 72.74; H, 8.14; N, 4.71. Found: C, 72.93; H, 8.24; N, 4.53%.

### 3.5. Preparation of dimethyl-[8-(difluoroborolyl)-naphthalen-1-yl]-amine (1)

1,3,5-Tris-(1-*N*,*N*-dimethylamino)-8-naphthylboroxine (**3**) (1.0 g, 1.69 mmol) was dissolved in THF (450 ml) with stirring under reflux, potassium hydrogen difluoride (1.58 g, 20.2 mmol) dissolved in water (50 ml) was added, the reaction was stirred under reflux for 5 h. The solvent was removed in vacuo, the product was extracted with chloroform (2 × 50 ml), followed by filtration through a fine glass sinter. Evaporation gave naphthylborondifluoride **1** as light red-brown solid (0.58 g, 52%); IR (nujol) (inter alia) 699, 780, 1080, 1126, 2922 (s) $cm^{-1}$; UV (MeCN) 224 ($\varepsilon$ 3290), 280 ($\varepsilon$ 300); $^1$H-NMR (400 MHz,

$CDCl_3$) $\delta$ 2.95 (s, 6H), 7.36 (dd, $J = 7.6$ and 1.6 Hz, 1H), 7.53 (dt, $J = 7.6$ and 0.6 Hz, 1H), 7.67 (dt, $J = 8.4$ and 1.6 Hz, 1H), 7.76–7.85 (m, 3H); $^{13}$C-NMR (125.7 MHz, $CDCl_3$) $\delta$ 48.1, 112.8, 125.2, 125.8, 126.5, 127.5, 129.3, 131.7, 134.2, 148.4; $^{11}$B-NMR (128 MHz; $CDCl_3$) $\delta$ 9.82 (br t, $J = 58$ Hz); $^{19}$F-NMR (470.26 MHz, $CDCl_3$) $\delta$ −148.3 (unsymmetric q, $J = 58$ Hz); ESMS (inter alia) (+ve ion, MeCN) 243.1 (100%, $MHNa^+$); Anal. Calc.: $C_{12}H_{12}BF_2N$ requires C, 65.80; H, 5.52; N, 6.39. Found: C, 65.55; H, 5.59; N, 6.23%.

### 3.6. X-ray crystallography

Both crystals were mounted using hair fibres onto a Bruker SMART 1K diffractometer and data were recorded at 120 K using Mo–$K_\alpha$ ($\lambda = 0.71073$ Å) X-radiation by use of omega-phi scans. Hydrogen atoms placed geometrically were not refined. The maximum and minimum peaks in the final difference Fourier map were: 0.383 and −0.306 e Å$^{-3}$, respectively for compound **3** and 0.132 and −0.142 e Å$^{-3}$, respectively for compound **5**. Calculations were performed using the crystallographic packages SMART [17], SAINT [18] and SHELXTL [19], absorption correction was applied by the use of SADABS [18]. The neutral atom scattering factors were taken from The International Tables for Crystallography [20]. Compound **5** provided a twinned dataset. Final refinement was performed using one twin component for non-overlapping reflections. Reflections were deconvoluted using the twinning program GEMINI [21], see Section 4 for further details.

## 4. Supplementary material

Crystallographic data for the structure determinations of compounds **3** and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 204262 and 204906, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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