



Boron coordination compounds derived from 2-phenyl-benzimidazole and 2-phenyl-benzotriazole bidentate ligands

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ABSTRACT

The syntheses and structural analyses of a series of boron heterocycles derived from 2-(1H-benzimidazol-2-yl)-phenylamine (**1**), 2-(1H-benzimidazol-2-yl)-phenol (**2**), 2-(1H-benzimidazol-2-yl)-benzenedisulfide (**3**), 2-[3-(1,1,1,3-tetramethyl-butyl)-phenyl]-2H-benzotriazole (**4**), 2-[3,5-bis-(1-methyl-1-phenylethyl)-phenyl]-2H-benzotriazole (**5**) and (C₆H₅)₂BOH or BF₃·OEt₂ are reported. The new boron compounds: diphenyl-[2-(1H-benzimidazol-2-yl-κN)-phenylamide-κN]-boron (**6**), diphenyl-[2-(1H-benzimidazol-2-yl-κN)-phenolate-κO]-boron (**7**), diphenyl-[2-(1H-benzimidazol-2-yl-κN)-benzenethiolate-κS]-boron (**8**), diphenyl-[2-(2H-benzotriazol-2-yl-κN)-4-(1,1,3,3-tetramethyl-butyl)-phenolate-κO]-boron (**9**), diphenyl-[2-(2H-benzotriazol-2-yl-κN)-4,6-(1-methyl-1-phenylethyl)-phenolate-κO]-boron (**10**), difluoro-[2-(1H-benzimidazol-2-yl-κN)-phenolate-κO]-boron (**11**), difluoro-[2-(2H-benzotriazol-2-yl-κN)-4-(1,1,3,3-tetramethylbutyl)-phenolate-κO]-boron (**12**) and difluoro-[2-(2H-benzotriazol-2-yl-κN)-4,6-(1-methyl-1-phenylethyl)-phenolate-κO]-boron (**13**) have four fused rings, with boron included in a six-membered ring and bound to N, O or S atoms and strongly coordinated by a nitrogen atom from the imidazole or triazole rings. Their structures are zwitterionic, with a negative charge on the boron and a delocalized positive charge on the ligand. Compounds **6–12** were studied by NMR, IR, mass spectrometry, and **6–10** and **12** by X-ray diffraction analyses.

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1. Introduction

There is considerable structural and biological interest in the study of aromatic six-membered ring compounds containing boron [1–4]. We have studied this kind of boron heterocycles derived from guanidinobenzimidazole [5], uroylbenzimidazole [6] and imidazole [7]. Herein, we report the syntheses and structural analyses of heterocyclic compounds derived from [BPh₂]⁺ or [BF₂]⁺ groups and 2-phenyl-benzimidazole and 2-phenyl-benzotriazole derivatives. The high Lewis acidity of these boron groups make them excellent models for transition metal coordination, with the advantage that they form diamagnetic molecules easily analyzed by NMR techniques. The chosen bidentate ligands were compounds **1–5**, Scheme 1. Comparison of benzimidazole and benzotriazole derivatives as coordinating molecules is interesting because the presence of a third nitrogen in the triazole, rather than a carbon in the imidazole, affects the resonance contributors and has an impact in the stability of the new heterocycles.

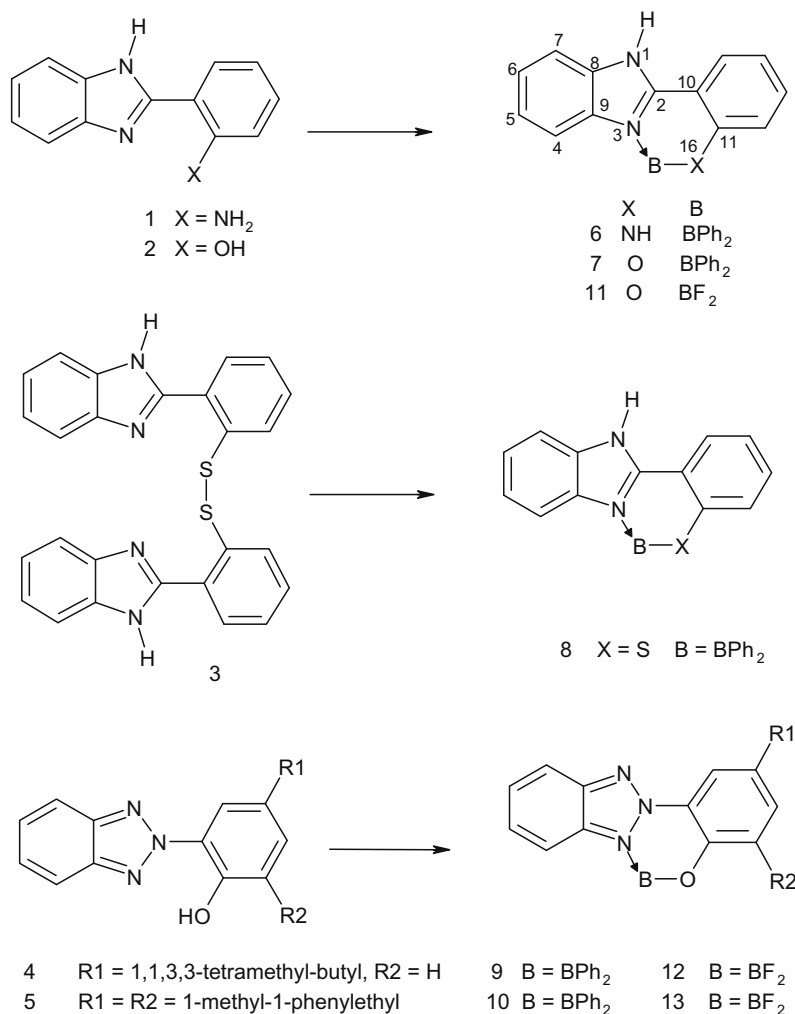
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Some of the starting ligands have been used before to prepare coordination compounds. Ligand **1** has been widely used for the preparation of a series of transition metal coordination compounds [8,9], whereas, compound **2** has been employed as a ligand for transition [10–13] and lanthanides metals [14]. The structural analysis of disulfide **3** has been recently reported [15]. Compound **4** has been used in the synthesis of Re(I) compounds [16]. Derivatives of compound **5** and elements of group 4 have been employed as catalysing agents [17]. Compounds **1** and **2** have been used to prepare phosphorus heterocycles [18,19]. Haloboron heterocycles derived from compound **2** are known. It was proposed that two benzimidazole ligands were coordinated to a BB₂⁺, through the imidazole nitrogen atom, however their structural characterization was not completed [20]. Planar diaminoboranes from ligand **1** have been prepared [21].

2. Results and discussion

The reactions of compounds **1–5** with BPh₂OH and BF₃·OEt₂ afforded the new boron compounds **6–13**, which were analyzed by NMR, IR, mass spectrometry, and **6–10** and **12** by X-ray diffraction. The reactions of **1** and **3** with BF₃·OEt₂ gave a mixture of compounds that were not isolated neither properly assigned, Scheme 1.



Scheme 1. Synthesis of boron esters **6–13** from benzimidazole **1–3** and benzotriazole ligands **4–5**.

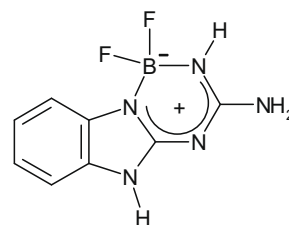
The ¹¹B NMR analysis of compounds **6–13** indicated that (a) the [BPh₂]⁺ or [BF₂]⁺ groups have substituted the labile O–H protons of **1**, **4** and **5** and the anilinic N–H of **2** and (b) that in compound **3** the S–S bond was cleaved in order to form an RS–B bond and probably an RS–F derivative which was not identified, Table 1. ¹¹B resonances of compounds **6–10** appear at lower frequencies with respect to ROBPh₂ (+45 ppm), RNBPh₂ (+41 ppm) or RSBPh₂ (+66–67 ppm) characteristic signals [22] indicating strong N → B bonds. A triplet was expected in the ¹¹B spectra of compounds **11–13** due to the ¹⁹F coupling, however only **11** showed this coupling (δ = +0.8 ppm, ¹J(¹¹B, ¹⁹F) = 14.0 Hz), due to a stronger N → B coordination bonding in benzimidazole than in benzotriazole. The ¹⁹F spectra of compounds **11–13** showed

two broad signals, in a 80–20 ratio, which corresponds to the ¹¹BF₂ and ¹⁰BF₂ isotopic groups respectively. The ¹⁹F chemical shifts of the benzimidazole compounds are similar to those found for a BF₂ derivative of 2-aminoguanidine benzimidazole (–135.2 ppm), Scheme 2 [5]. The benzotriazole compounds **12–13** present a shift in the ¹⁹F signals to lower frequencies (–142.0 to –144.5 ppm) with respect to the benzimidazole derivative (–136.4 ppm) which denotes that ¹⁹F is sensitive to the nature of the azole ring, Table 1.

¹H and ¹³C spectra of compounds **6–9**, **11–13** showed that all atoms have different resonances indicating that the N → B coordination bond partially stopped the tautomeric N–H or conformational equilibria characteristic of free benzimidazole or

Table 1
¹¹B and ¹⁹F NMR data of compounds **6–13**.

Compd, solvent	δ ¹¹ B/ ¹ J(¹¹ B, ¹⁹ F)	δ(¹¹ B)- ¹⁹ F δ(¹⁰ B)- ¹⁹ F [isotopic effect, Hz]
6 , CDCl ₃	–0.8	
7 , DMSO-d ₆	+3.5	
8 , DMSO-d ₆	–1.6	
9 , CDCl ₃	+6.7	
10 , CDCl ₃	+5.5	
11 , DMSO-d ₆	+0.8 triplet [14.0 Hz]	–136.4 and –136.5 [16.9]
12 , CDCl ₃	+1.0 broad	–142.0 and –141.9 [25.3]
13 , CDCl ₃	+0.6 broad	–144.5 and –144.4 [19.8]



Scheme 2. BF₂ heterocycle derived from 2-aminoguanidine benzimidazole, δ¹⁹F = –135.2 ppm [5].

Table 2
Selected ^{13}C data for **6–9, 11**.

Compounds	C8	C9	C11
6	132.6	135.7	151.6
7	133.5	135.3	160.8
8	134.9	136.1	145.5
9 (-20°C)	143.2	136.8	150.0
11	132.3	135.0	156.6
12	143.0	135.2	145.0
13			146.6

benzotriazole. These equilibria in free ligands make the N1–N3, CH8–CH9, CH4–CH7, and CH5–CH6 pairs equivalent, Table 2. C11 signals are shifted to higher frequencies due to the boron bonding, ($\Delta\delta$ from +2.7 to +9.1 ppm in **6–8**). In compounds **12** and **13**, the C11 resonance is a triplet by the fluorine atoms coupling [$^3J(^{13}\text{C},^{19}\text{F}) = 2.5$ (**12**) and 2.0 Hz (**13**)]. In **11** the triplet was not completely resolved due to a small value of the coupling constant. In the benzotriazole compounds **9**, and **13**, N \rightarrow B coordination bond shifted to lower frequencies the C9 signal, whereas the C8 resonance remains characteristic of a C–N–lone pair group, (~ 143 ppm) [23,24]. ^1H and ^{13}C spectra of **10–12** were complex and difficult to assign.

In order to study the dynamic behavior of **9** induced by a weak N \rightarrow B bond, (Scheme 3) ^1H , ^{13}C and ^{11}B NMR spectra in CDCl_3 were recorded at different temperatures between +20 and -60°C . The N \rightarrow B bond energy was calculated as being 55.3 kJ mol^{-1} [25].

Mass spectra of compounds **6–13** showed in all cases the molecular ion. The fragmentation is interesting because each compound lost a phenyl group or a fluorine atom to give, in almost all cases, the base peak. The trigonal boron atom contributes to the planarity of the fused tetracyclic planar framework. The calculated minimum energy structure for the sp^2 boron heterocycle in **7** is in Fig. 1.

Of interest in the reported heterocycles is the analysis of the electronic delocalization of the fused tetracyclic system. A resonance structure [coordination bond \leftrightarrow covalent bond] could average the B–N and B–Y (Y = NH, O or S) bond lengths, Scheme 4. The resonance contributors for the benzimidazole derivatives suggest a zwitterionic structure with the borate bearing the negative charge and a positive charge delocalized in the boron and the phenyl rings, whereas the benzotriazole compounds delocalize the positive charge in the benzotriazole rings. The structural data from X-ray diffraction analyses are of interest as they may be related to the electronic delocalization in the ligands and the nature of the boron coordination.

The molecular structures of compounds **6–10** and **12** were determined by X-ray diffraction analyses, Figs. 2–5. Selected bond lengths and angles are given in Table 3.

The study showed that the boron coordination forms a six-membered ring in a fused planar tetracycle. For compounds **6, 7, 9, 10** and **12**, the boron is out of a plane formed by the other five atoms and has one substituent in axial position. In compound **8**, there are four atoms in a plane [B–N3–C–C] with the sulfur atom

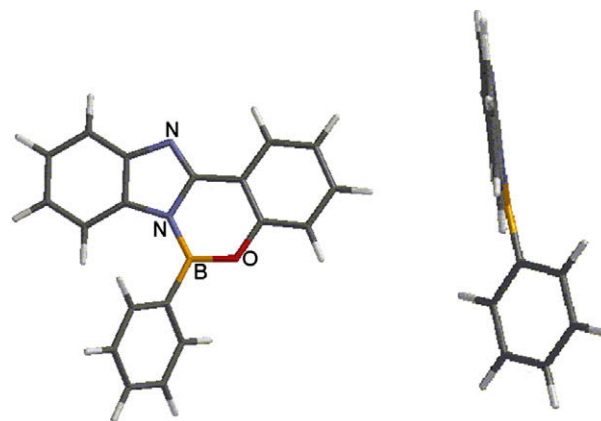


Fig. 1. The calculated minimum energy structure for the $[\text{M-Ph}]^+$ fragment of compound **7**.

out of it. Fig. 6 shows the six-membered ring conformation for compounds **6** and **8**.

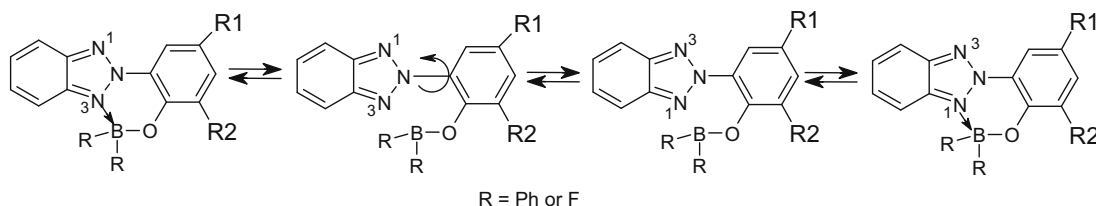
Analysis of the bond lengths in compounds **6–10** and **12** shows that the B–N3 bonds are in the range: 1.597(4)–1.641(3) Å, shorter than the N–B coordination bond (1.685 Å) found in a six-membered BPh₂ heterocycle, Scheme 5 [26]. The B–N16 bond length in **6** (1.535(4) Å) is shorter than a B–N covalent bond (1.61 Å) and the B–O16 bond length in compounds **7, 9, 10–12** varies from 1.436(4) to 1.506(3) Å whereas a reported B–O covalent bond is 1.452 Å, Scheme 5 [26] or 1.367 Å [27]. B–S bond lengths (1.947(5) and 1.958(5) Å) in compound **8** are slightly longer than the bond length for a tetracoordinated B–S (~ 1.896 Å) [27]. Therefore we can conclude that the coordination bonds are shorter than expected and covalent bonds are longer (with exception of **6**), indicating an electronic resonance in the six-membered ring, shown in Scheme 4.

On the other hand, the lengths of C(N)2–N3, C11–Y16, with exception of sulfur compound, and C(N)2–C10 and C10–C11 indicate the positive charge delocalization in the six-membered ring, Table 3.

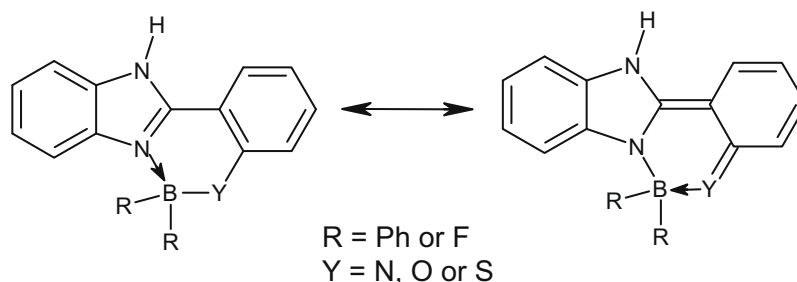
The diphenylboron molecules **6–10** showed cooperative intramolecular interactions of C–H with π electrons and lone pairs that contribute to a rigid molecular framework. These interactions are shown for compound **6**, Fig. 7.

Intermolecular interactions such as N–H \cdots O, H \cdots S, C–H \cdots O hydrogen bonds and π -stacking were found. In compound **6** which cocrystallized with DMSO, a water molecule is bound to the N–H (1.87 Å) and in turn two DMSO are linked to it, Fig. 8 (left). Compound **7** which crystallized from DMSO, presents an intermolecular hydrogen bond with the solvent, Fig. 8 (right).

One of the two molecules found in the asymmetric unit of **8** has a hydrogen bond between the sulfur atom and a CHCl_3 molecule (2.52 Å), which gives more sp^3 character to the sulfur (C–S–B angle $103.8(3)^\circ$), Fig. 9 (left). Compound **8** presented π -stacking interactions, Fig. 9 (right) and **12** F \cdots H–C and C–H \cdots N interactions, Fig. 10.



Scheme 3. Conformational equilibrium in compound **9**, produced by the opening of the N3 \rightarrow B bond, followed by N2–C10 bond rotation and N1 \rightarrow B bond formation.



Scheme 4. [Coordination bond ↔ covalent bond] resonance in benzimidazole derivatives.

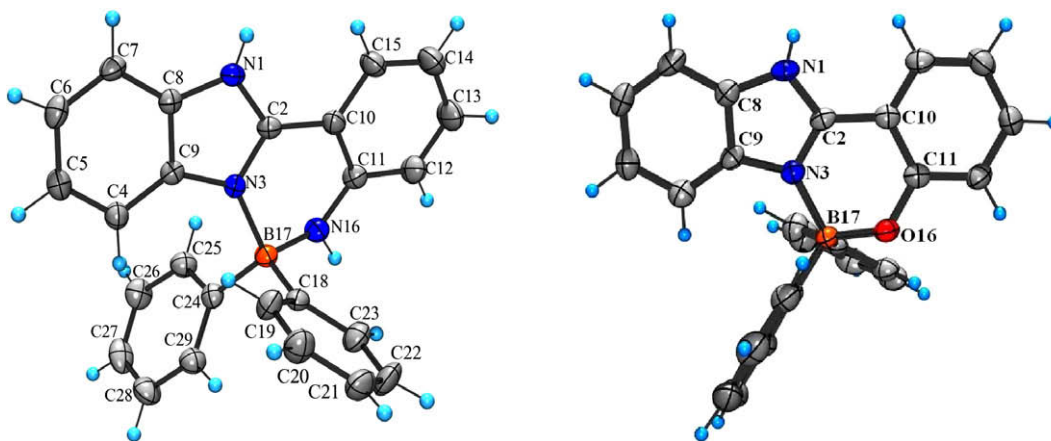


Fig. 2. ORTEP diagrams for **6** (left) and **7** (right).

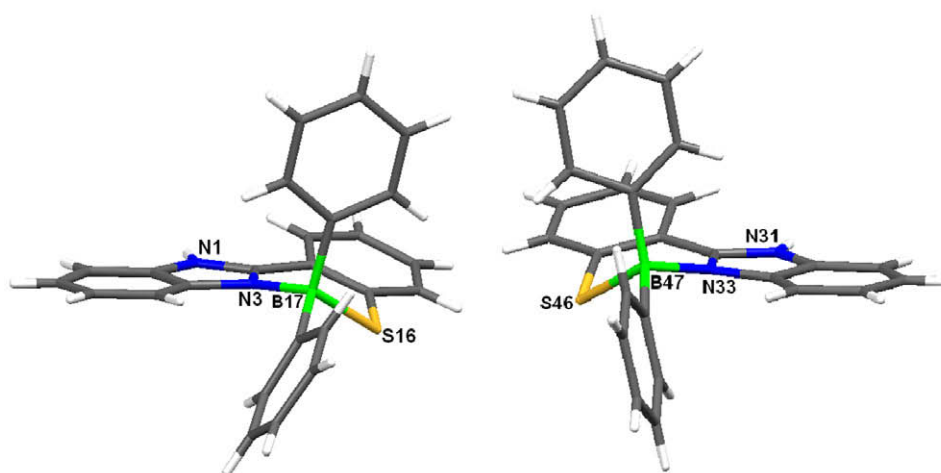


Fig. 3. The crystal of **8** presented two enantiomeric conformations, **8a** and **8b**, in the asymmetric unit.

3. Conclusion

Compounds **1–5** act as bidentate ligands when they react with $(C_6H_5)_2BOH$ or BF_3 . Their boron derivatives **6–13** are stable to air and moisture due to the BPh_2 and BF_2 groups strong coordination. NMR in solution and X-ray diffraction in the solid state allowed a structural analysis of the boron heterocycles. The resulting compounds are zwitterions. The boron atoms have a borate nature, whereas the positive charge is delocalized in part of the molecule. The benzimidazole has the strongest coordination bonds due to a more basic nitrogen atom. The benzotriazole has a weaker nitrogen atom due to the electronegativity of the nitrogen in position 2. The

boron in BF_2 being more acidic than in BPh_2 , produces the shortest $B \rightarrow N$ and $B-O$ bonds. Mass spectra have shown that the molecules lost a boron substituent in order to give a planar tetracyclic system where the boron can obtain a sp^2 hybridisation.

4. Experimental

4.1. General comments

Vacuum line techniques were employed for all manipulations of air and moisture sensitive compounds. THF was dried by distillation from sodium-benzophenone under a nitrogen

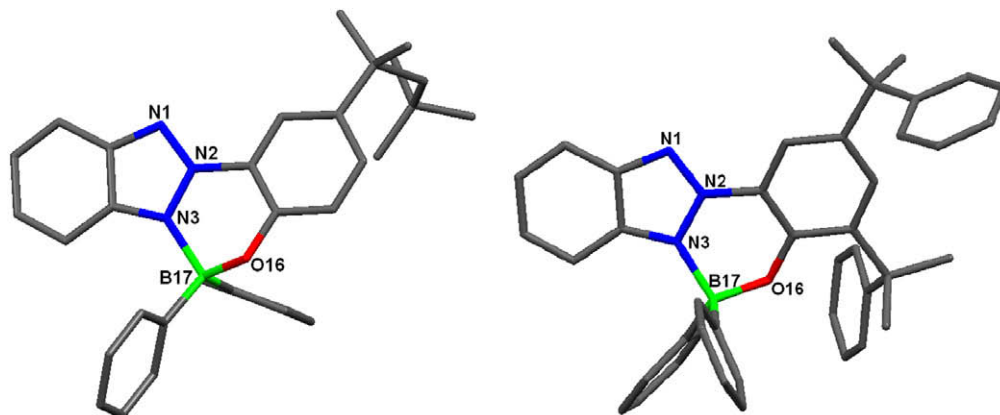


Fig. 4. Molecular structure of **9** (left) and **10** (right). For the clarity, hydrogen atoms are not shown.

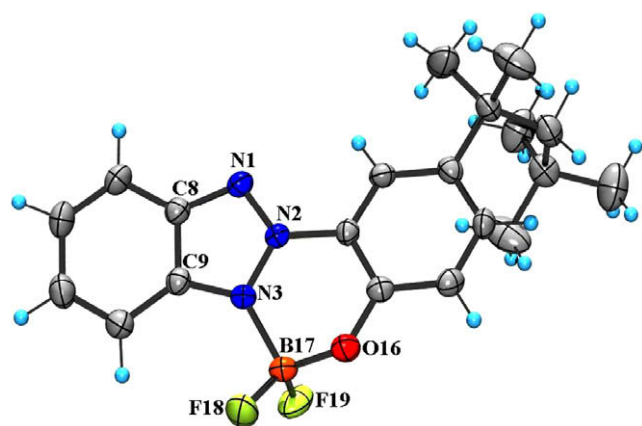


Fig. 5. ORTEP diagram for compound **12**.

atmosphere prior to use. Dry CDCl_3 , DMSO-d_6 , THF-d_8 , and boron compounds were purchased from Aldrich and used without further purification. The melting points were obtained on a Mel-Temp II apparatus and are uncorrected. IR spectra were taken in KBr disc using a FT Spectrum GX Perkin Elmer spectrometer. Mass spectra in the EI mode were recorded at 20 eV on a Hewlett-Packard HP 5989 spectrometer. Elemental analyses were performed on Flash 1112 Thermo Finnigan. ^1H , ^{13}C , ^{11}B , and ^{19}F NMR spectra were obtained on a Jeol GSX-270, Jeol Eclipse 400 MHz and Bruker Advance 300 MHz. ^1H and ^{13}C chemical shifts assignments were based on 2D experiment $^1\text{H}/^1\text{H}$ COSY, $^1\text{H}/^{13}\text{C}$ HETCOR and COLOC.

4.2. Crystallographic study

Data were measured on a Nonius Kappa CCD instrument with a CCD area detector using graphite-monochromated $\text{MoK}\alpha$ radiation. Intensities were measured using $\phi + \omega$ scans. Crystals were obtained from DMSO (**6** and **7**) and CHCl_3 (**8–10** and **12**). All structures were solved using direct methods, using *SHELX-97* [28] and the refinement (based on F^2 of all data) was performed by full matrix least-squares techniques with *Crystals 12.84* [29]. In the asymmetric unit of compound **6**, there are two DMSO and one H_2O molecules. Compound **7** cocrystallized with DMSO . The cell of **8** has two molecules of the compound and one of CHCl_3 . The asymmetric unit of **10** has two molecules of CDCl_3 . All non-hydrogen atoms were refined anisotropically. In compounds **6** and **7** the DMSO hydrogen atoms were geometrically

placed. In compound **6** the other hydrogen atoms were refined, in **7** the hydrogen atoms were found but not refined with exception of the N–H. In compounds **8**, **9** and **12** the hydrogen atoms were found but not refined, with exception of the aromatic hydrogen atoms that were refined. Selected bond lengths and angles are presented in Table 3.

4.3. Syntheses

4.3.1. Diphenyl-[2-(1H-benzimidazol-2-yl-N)-phenolamide-N]-boron (**6**): general procedure for compounds (**6–10**)

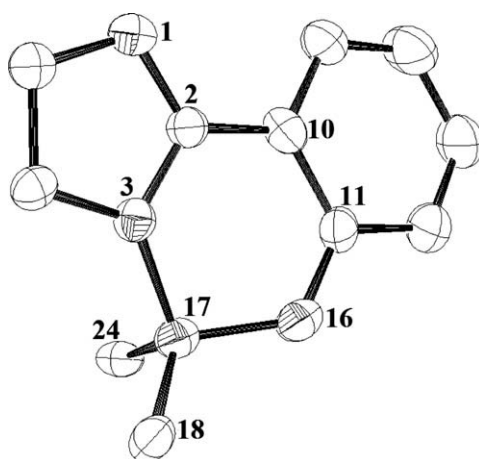
Using a Dean Stark trap, in a dry nitrogen atmosphere, compound **1** (392 mg, 1.9 mmol) was reacted with $(\text{C}_6\text{H}_5)_2\text{BOH}$ (341 mg, 1.9 mmol) in toluene (30 mL) and *p*-toluenesulfonic acid (30 mg). The reaction mixture was refluxed for 6 h, and then cooled and filtered. The solvent was evaporated in vacuum. The reaction product is a green crystalline solid (419 mg, 60%). Mp 210 °C. IR (KBr), ν (cm^{-1}): 1626 (C=N), 1554 (C=C), 1397 (B–N). MS m/z (%): 373(1) $[\text{M}]^+$, 296(100) $[\text{M}-\text{C}_6\text{H}_5]^+$, 218(5) $[\text{M}-2\text{C}_6\text{H}_5]^+$. NMR (CDCl_3), δ (ppm): ^1H 12.16 (NH), 7.03 (H4), 7.01 (H5), 7.17 (H6), 7.34 (H7), 6.60 (H12), 7.10 (H13), 6.35 (H14), 7.46 (H15). ^{13}C 152.0 (C2), 117.1 (C4), 123.4 (C5), 123.7 (C6), 111.4 (C7), 132.6 (C8), 135.7 (C9), 114.7 (C10), 151.6 (C11), 113.3 (C12), 133.9 (C13), 117.1 (C14), 125.8 (C15). Anal. Calc. for $\text{C}_{25}\text{H}_{20}\text{BN}_3\cdot 2(\text{CH}_3)_2\text{SO}\cdot \text{H}_2\text{O}$: C, 63.61; H, 6.26; N, 7.67. Exp.: C, 63.60; H, 5.99; N, 7.61%.

4.3.2. Diphenyl-[2-(1H-benzimidazol-2-yl-N)-phenolate-O]-boron (**7**)

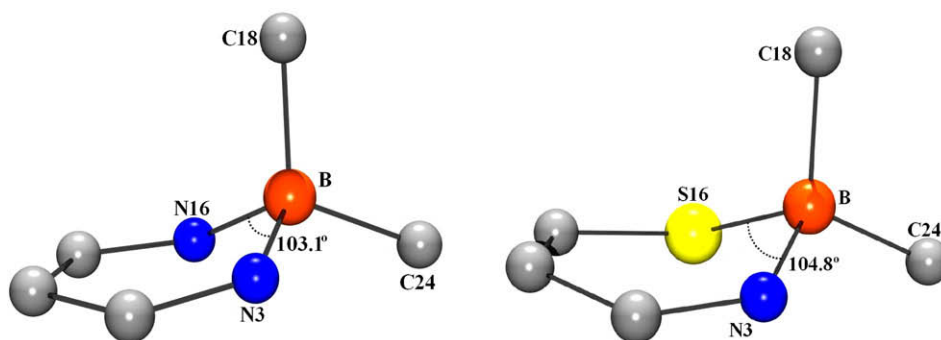
Ligand **2** (284 mg, 1.35 mmol) was reacted with $(\text{C}_6\text{H}_5)_2\text{BOH}$ (246 mg, 1.35 mmol). Compound **7** is a grey solid (350 mg, 69%). Mp. 260 °C. IR (KBr), ν (cm^{-1}): 1629, 1610 (C=N), 1574, 1554 (C=C), 1388 (B–O), 1196, 919 (B–N). MS: m/z (%): 374(2) $[\text{M}]^+$, 297(100) $[\text{M}-\text{C}_6\text{H}_5]^+$, 220(2) $[\text{M}-2(\text{C}_6\text{H}_5)]^+$. NMR (DMSO-d_6), δ (ppm): ^1H 14.35 (NH), 6.79 (H4), 7.13 (H5), 7.34 (H6), 7.70 (H7), 7.05 (H12), 7.42 (H13), 6.91 (H14), 7.93 (H15). ^{13}C 147.7 (C2), 116.3 (C4), 124.5 (C5), 125.0 (C6), 133.3 (C7), 133.5 (C8), 135.3 (C9), 111.2 (C10), 160.8 (C11), 118.9 (C12), 135.2 (C13), 120.5 (C14), 126.1 (C15). Anal. Calc. for $\text{C}_{25}\text{H}_{19}\text{BN}_2\text{O}\cdot 1/3(\text{CH}_3)_2\text{SO}$: C, 77.01; H, 5.29; N, 7.00. Exp.: C, 77.12; H, 5.57; N, 7.15%.

4.3.3. Diphenyl-[2-(1H-benzimidazol-2-yl-N)-benzenethiolate-S]-boron (**8**)

Compound **3** (440 mg, 1 mmol) was reacted with $(\text{C}_6\text{H}_5)_2\text{BOH}$ (355 mg, 2 mmol). Compound **8** is a green crystalline solid (286 mg, 75%). Mp 166 °C. IR (KBr), ν (cm^{-1}): 1601 (C=N), 1559 (C=C), 1345 (B–S). MS: m/z (%): 390(2) $[\text{M}]^+$, 313(100) $[\text{M}-\text{C}_6\text{H}_5]^+$. NMR (DMSO-d_6), δ (ppm): ^1H 11.34 (NH), 6.58 (H4), 6.44 (H5), 6.86

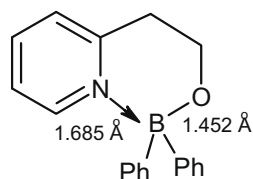
Table 3
Selected geometric parameters

	6	7	8a	8b	9	10	12
<i>Bond lengths (Å)</i>							
B–C(F)18	1.634(5)	1.624(4)	1.623(6)	1.605(7)	1.606(4)	1.619(6)	1.365(4)
B–C24(F)19	1.625(4)	1.606(4)	1.601(7)	1.606(8)	1.607(4)	1.612(5)	1.372(4)
B–N3	1.597(4)	1.606(3)	1.605(6)	1.602(5)	1.641(3)	1.636(4)	1.605(4)
B–Y16	1.535(4)	1.506(3)	1.947(5)	1.958(5)	1.480(3)	1.481(4)	1.436(4)
C11–Y16	1.355(4)	1.339(3)	1.754(5)	1.772(5)	1.353(3)	1.332(4)	1.358(3)
C(N)2–N3	1.339(4)	1.331(3)	1.331(5)	1.343(5)	1.345(3)	1.341(4)	1.346(3)
C(N)2–N1	1.349(4)	1.348(3)	1.360(5)	1.340(5)	1.318(3)	1.323(4)	1.314(3)
C(N)2–C10	1.438(4)	1.445(3)	1.457(6)	1.449(6)	1.426(3)	1.422(4)	1.416(4)
C10–C11	1.431(4)	1.407(4)	1.404(6)	1.396(6)	1.386(3)	1.392(5)	1.403(4)
<i>Bond angles (°)</i>							
C18–B–C24(F)19	113.7(2)	115.5(2)	114.7(4)	116.7(4)	118.4(2)	115.3(3)	112.1(3)
C18–B–N3	108.5(2)	108.9(2)	108.2(3)	112.2(4)	108.4(2)	107.6(3)	107.7(3)
C24–B–N3	108.8(2)	110.5(2)	111.3(3)	107.6(3)	106.4(2)	108.9(3)	106.1(3)
C18–B–Y16	111.8(3)	107.1(2)	112.7(3)	104.7(3)	108.1(2)	112.3(3)	111.2(3)
C24(F)19–BY16	110.4(2)	109.8(2)	104.9(3)	111.3(3)	111.7(2)	108.3(3)	112.3(3)
N3–B–Y16	103.1(2)	104.5(2)	104.8(3)	103.6(3)	102.7(2)	103.7(3)	107.1(2)

**Fig. 6.** Conformation of six-membered heterocycles in compounds **6** (left) and **8** (right).

(H6), 7.55 (H7), 7.25 (H12), 7.46 (H13), 6.96 (H14), 8.21 (H15). ¹³C 149.2 (C2), 120.8 (C4), 125.6 (C5), 126.5 (C6), 112.2 (C7), 134.9

(C8), 136.1 (C9), 121.8 (C10), 145.5 (C11), 131.5 (C12), 136.0 (C13), 135.7 (C14), 132.6 (C15). Anal. Calc. for C₂₅H₁₉BN₂S·1/2CHCl₃: C, 68.06; H, 4.37; N, 6.23. Exp.: C, 67.69; H, 4.62; N, 6.68%.

**Scheme 5.** Bond lengths in diphenyl[2-(2-pyridyl)-ethoxy]-borane [26].

4.3.4. Diphenyl-[2-(2H-benzotriazol-2-yl)-N-(1,1,3,3-tetramethylbutyl)-phenolate-O]-boron (**9**)

Compound **4** (1.83 g, 5.65 mmol) was reacted with (C₆H₅)₂BOH (1.03 g, 5.65 mmol). Compound **9** is a yellow crystalline solid. (2.01 g, 73%). Mp 230 °C. IR (KBr), ν (cm⁻¹): 1624 (C=N), 1571 (C=C), 1364 (B–O). MS: *m/z* (%): 487(0.3) [M]⁺, 410(100) [M–C₆H₅]⁺. NMR (CDCl₃), δ (ppm): ¹H 6.88 (H4), 7.55 (H5), 7.43

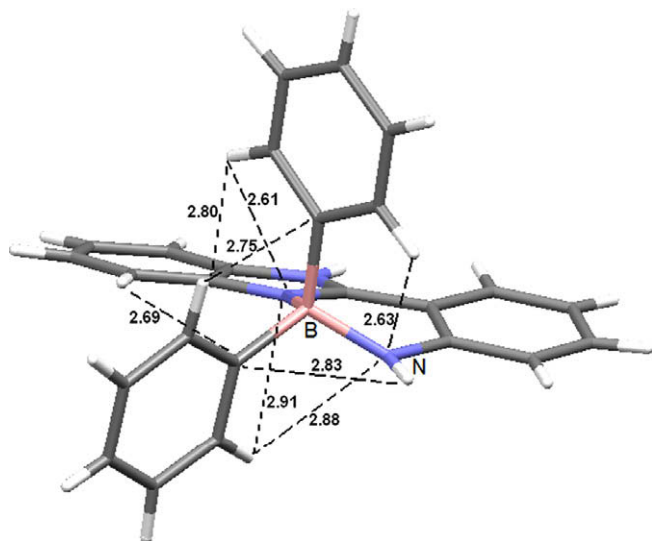


Fig. 7. Cooperative intramolecular interactions of C–H with π electrons and lone pairs contribute to a rigid molecular framework, shown here for compound **6** (distances in Å).

(H6), 8.08 (H7), 7.32 (H12), 7.51 (H13), 8.12 (H15). ^{13}C 115.3 (C4), 128.3 (C5), 131.0 (C6), 118.9 (C7), 143.2 (C8), 136.8 (C9), 124.3 (C10), 150.0 (C11), 121.0 (C12), 131.3 (C13), 142.2 (C14), 116.5 (C15). Anal. Calc. for $\text{C}_{32}\text{H}_{34}\text{BN}_3\text{O}$: C, 78.85; H, 7.03; N, 8.62. Exp.: C, 78.90; H, 7.43; N, 8.61%.

4.3.5. Diphenyl-[2-(2H-benzotriazol-2-yl-N)-4,6-(1-methyl-1-phenylethyl)-phenolate-O]-boron (**10**)

Compound **5** (800 mg, 1.8 mmol) was reacted with $(\text{C}_6\text{H}_5)_2\text{BOH}$ (325 mg, 1.78 mmol). Compound **10** is a yellow solid (820 mg, 75%). Mp 150 °C. IR (KBr), ν (cm^{-1}): 1600 (C=N), 1572 (C=C), 1311 (B–O). MS: m/z (%): 611(0.3) $[\text{M}]^+$, 534(100) $[\text{M}-\text{C}_6\text{H}_5]^+$. Anal. Calc. for $\text{C}_{42}\text{H}_{38}\text{BN}_3\text{O}$: C, 82.48; H, 6.26; N, 6.87. Exp.: C, 82.45; H, 6.35; N, 6.91%.

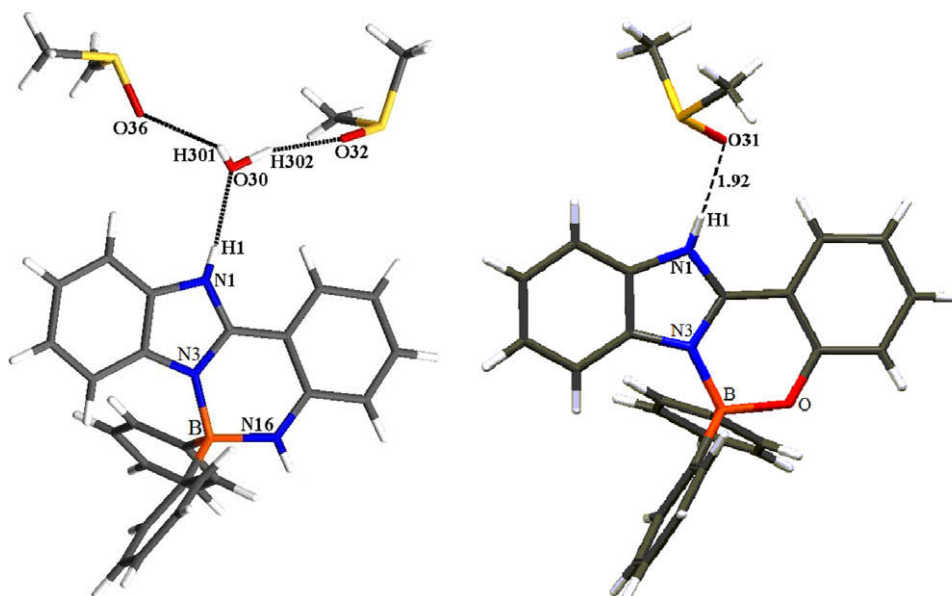


Fig. 8. Intermolecular H-bonds in compounds **6** (left) and **7** (right).

4.3.6. Difluoro-[2-(1H-benzimidazol-2-yl-N)-phenolate-O]-boron (**11**): general procedure for compounds **11–13**

Compound **2** (200 mg, 1 mmol) was dissolved in dried toluene (15 mL). The solution was cooled to -78°C in a dry nitrogen atmosphere and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.12 mL, 1 mmol) was added dropwise. The solution was refluxed for 6 h and then cooled and evaporated under vacuum. Compound **11** is a dark green solid (350 mg, 69%). Dec. at 310 °C. IR (KBr), ν (cm^{-1}): 1631 (C=N), 1569 (C=C), 1380 (B–O), 1181 (B–F), 930 (B–N). MS: m/z (%): 258(10) $[\text{M}]^+$, 238 (100) $[\text{M}-\text{HF}]^+$. NMR ($\text{DMSO}-d_6$), δ (ppm): ^1H 14.2 (NH), 7.80 (H4), 7.50 (H5), 7.53 (H6), 7.79 (H7), 7.12 (H12), 7.59 (H13), 7.17 (H14), 8.11 (H15). ^{13}C 147.3 (C2), 115.0 (C4), 125.0 (C5), 125.5 (C6), 113.2 (C7), 132.3 (C8), 135.0 (C9), 108.6 (C10), 156.6 (C11), 119.2 (C12), 132.1 (C13), 119.9 (C14), 125.6 (C15). Anal. Calc. for $\text{C}_{13}\text{H}_9\text{BF}_2\text{N}_2\text{O}\cdot 1/3(\text{CH}_3)_2\text{SO}$: C, 57.78; H, 3.90; N, 9.86. Exp.: C, 57.38; H, 3.71; N, 9.78%.

4.3.7. Difluoro-[2-(2H-benzotriazol-2-yl-N)-4-(1,1,3,3-tetramethylbutyl)-phenolate-O]-boron (**12**)

Compound **4** (200 mg, 0.6 mmol) was reacted with $\text{BF}_3\cdot\text{Et}_2\text{O}$ (87 mg, 0.6 mmol, 78 μL). Compound **12** was crystallized from CHCl_3 and is a yellow solid (184 mg, 80%). Mp 166 °C. IR (KBr), ν (cm^{-1}): 1618 (C=N), 1576 (C=C), 1364 (B–O), 1175 (B–F), 888 (B–N). MS: m/z (%): 371(6.0) $[\text{M}]^+$, 323(2.0) $[\text{M}-\text{BF}_2]^+$, 300(100) $[\text{M}-\text{C}_5\text{H}_{11}]^+$. NMR (CDCl_3), δ (ppm): ^1H 8.12 (H4), 7.67 (H5), 7.74 (H6), 8.09 (H7), 7.27 (H12), 7.57 (H13), 8.27 (H15). ^{13}C 114.7 (C4), 129.3 (C5), 132.1 (C6), 119.0 (C7), 143.0 (C8), 135.2 (C9), 122.3 (C10), 146.0 (C11) [$^3J(^{13}\text{C}, ^{19}\text{F}) = 2.5$ Hz], 120.7 (C12), 131.7 (C13), 144.0 (C14), 116.0 (C15). Anal. Calc. for $\text{C}_{32}\text{H}_{34}\text{BN}_3\text{O}$: C, 64.71; H, 6.52; N, 11.32. Exp.: C, 64.91; H, 6.70; N, 11.30%.

4.3.8. Difluoro-[2-(2H-benzotriazol-2-yl-N)-4,6-(1-methyl-1-phenylethyl)-phenolate-O]-boron (**13**)

Compound **5** (200 mg, 0.45 mmol) was reacted with $\text{BF}_3\cdot\text{Et}_2\text{O}$ (63 mg, 0.45 mmol, 56 μL). Compound **13** is a yellow solid that was purified by sublimation (197 mg, 89%). Mp. 227 °C. E.M: m/z (%): 495(65) $[\text{M}]^+$, 480(91) $[\text{M}-\text{CH}_3]^+$, 460(100) $[\text{M}-\text{HFCH}_3]^+$. NMR (CDCl_3), δ (ppm): ^{13}C 145.0 (C11) [$^3J(^{13}\text{C}, ^{19}\text{F}) = 2.0$ Hz]. Anal.

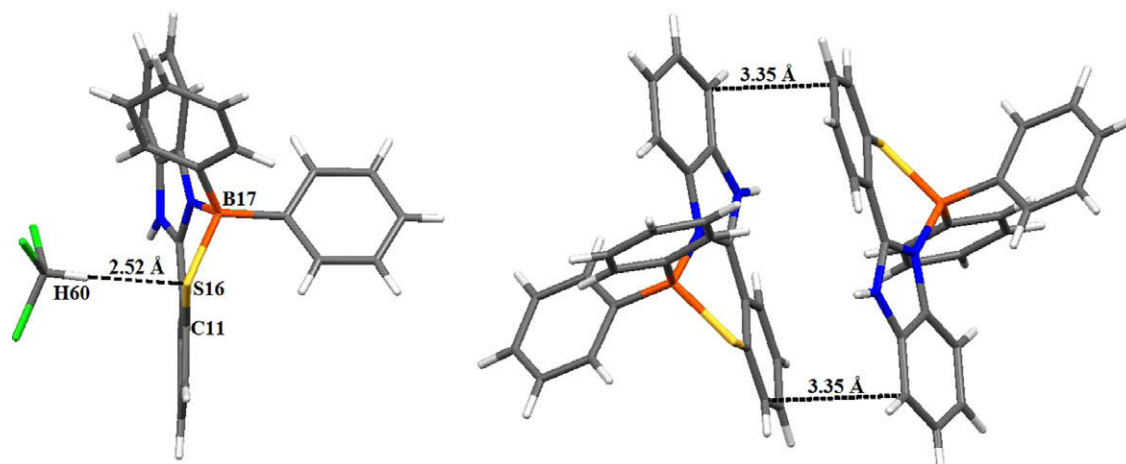


Fig. 9. Solid state structure of compound **8**, showing the S...H bond (left). π -Stacking in **8** [C7–C12 distance = 3.35 Å] (right).

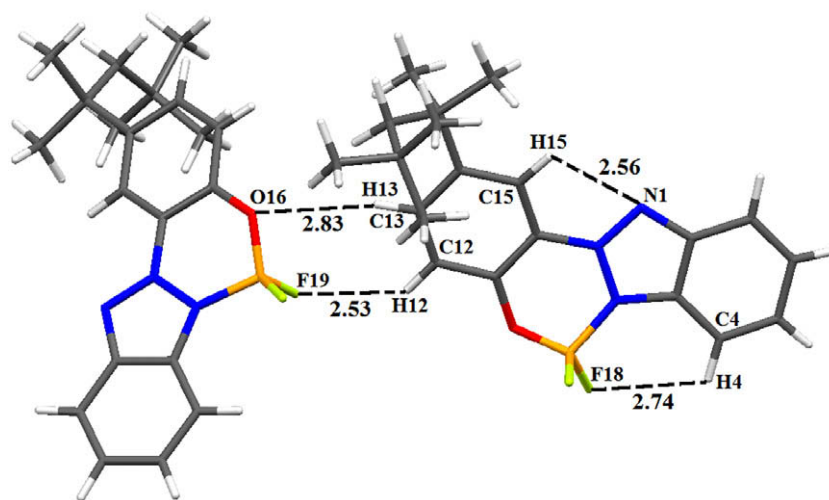


Fig. 10. Weak Interactions in difluoro compound **12**.

Calc. for $C_{32}H_{34}BN_3O$: C, 72.74; H, 5.70; N, 8.48. Exp.: C, 73.08; H, 5.33; N, 8.32%. IR (KBr), ν (cm^{-1}): 1601 (C=N), 1577 (C=C), 1360 (B–O), 1160 (B–F), 889 (B–N).

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Appendix A. Supplementary material

CCDC 735744, 735745, 735746, 735747, 735748 and 735749 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.029](https://doi.org/10.1016/j.jorganchem.2009.07.029).

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