

# Synthesis and Lewis Acidic Behavior of a Cationic 9-Thia-10-boraanthracene<sup>†</sup>

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As part of our efforts in the chemistry of Lewis acidic organoboron compounds, we have synthesized a cationic borane ([1]<sup>+</sup>) featuring a 9-thia-10-boraanthracene moiety substituted at boron by the cationic anilium group [4-(Me<sub>3</sub>N)-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>]<sup>+</sup>. This new cationic borane has been fully characterized. Its UV–vis spectrum features a low-energy band at  $\lambda_{max} = 392$  nm which, as confirmed by computational studies, arises from a  $\pi - \pi^*$  transition of the 9-thia-10-boraanthracene chromophore. As a result of the low steric bulk present around the boron center and the inductive effects imparted by the anilium group, [1]<sup>+</sup> possesses unusual Lewis acidic properties and reacts with DMAP to form the corresponding adduct. This derivative also binds both fluoride and cyanide anions in THF to afford 1-F and 1-CN whose stability constants exceed 10<sup>7</sup> M<sup>-1</sup>. Although [1]<sup>+</sup> is unstable in pure water, it can be used to selectively extract cyanide under biphasic conditions in nitromethane/water.

## Introduction

The chemistry of Lewis acidic triarylboranes has experienced a resurgence of activity fueled by the discovery of numerous applications in the domains of catalysis<sup>1</sup> and small molecule activation<sup>2</sup> as well as optoelectronics.<sup>3,4</sup> Such organoboranes have also been extensively studied as receptors for small anions including fluoride and cyanide.<sup>3,5</sup> Research carried out in the past decade indicates that simple triarylboranes such as  $Mes_2PhB$ ,<sup>6</sup>  $Mes_3B$ ,<sup>7</sup> and  $Ant_3B^8$  (Ant = 9-anthryl) form stable fluoride complexes in organic solvents but not in water where the high hydration energy of the fluoride anion prevents complex formation. In an effort to overcome these limitations, we and others have investigated the synthesis and anion binding properties of triarylboranes decorated by peripheral cationic

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functionalities (Chart 1).<sup>9–14</sup> Because of favorable Coulombic effects, these boranes display a higher anion affinity and can sometimes be used for the complexation of fluoride and cyanide ions in aqueous environments. A common feature uniting these cationic boranes concerns the use of sterically encumbered ligands whose role is to protect the boron center from nucleophilic attack by water molecules. This steric protection can, for

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**Figure 1.** Top left: Electronic absorption (—) and emission (---) spectra of [1]OTf in THF. Top right: Cyclic voltammogram of [1]OTf at a scan rate of 100 mV s<sup>-1</sup> with *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. Bottom: Optimized structure of [1]<sup>+</sup> with an overlay of the HOMO and LUMO (isodensity value = 0.03).





example, be achieved by the use of a single 2,4,6-triisopropylphenyl (Tip) group as in  $\mathbf{D}^{12}$  or two bulky mesityl groups as in  $\mathbf{A}$ ,<sup>13</sup>  $\mathbf{B}$ ,<sup>11</sup> and  $\mathbf{C}$ .<sup>9</sup> Inspired by the work of Kobayashi and Kawashima who have investigated less sterically hindered cationic boranes such as  $\mathbf{E}$ ,<sup>14</sup> we have now synthesized and studied a cationic 9-thia-10-boraanthracene ([1]<sup>+</sup>) featuring a sterically accessible boron atom. In addition to reporting on the anion binding properties of this new compound, we also show that [1]<sup>+</sup> can form adducts with neutral Lewis bases such as DMAP.

# **Results and Discussion**

**Synthesis of Cationic Borane [1]OTf.** The reaction of 2,6dimethyl-4-dimethylaminophenyllithium<sup>15</sup> with 10-bromo-9thia-10-boraanthracene<sup>7</sup> was carried out in Et<sub>2</sub>O. The product

# Scheme 1. Synthesis of [1]OTf<sup>a</sup>



<sup>a</sup> Conditions: (i) Et<sub>2</sub>O, rt, 24 h; (ii) MeOTf (excess), CH<sub>2</sub>Cl<sub>2</sub>, rt, 1 h.

of this reaction, which was not isolated, was treated with MeOTf in CH<sub>2</sub>Cl<sub>2</sub> to afford the anilium borane  $[1]^+$  as a triflate salt (Scheme 1). This salt, which can be stored in air for extended periods of time, has been fully characterized. The <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> shows a series of aromatic CH resonances consistent with a perpendicular arrangement of the anilium and 9-thia-10-boraanthracene moieties. Accordingly, a single resonance is detected at 2.06 ppm for the two orthomethyl groups. The proton resonance of the trimethylammonium appears at 3.69 ppm, confirming the formation of an anilium species.<sup>15</sup> The broad <sup>11</sup>B NMR signal observed at 57.3 ppm agrees with the presence of a base-free, trigonal-planar boron center. While efforts to grow single crystals of this compound were unsuccessful, the structure of [1]OTf has been studied computationally using density functional theory (DFT) methods (B3LYP/6-31G(d) for S, C, and H atoms and 6-31+ G(d') for B and N atoms). The optimized structure of the cation is shown in Figure 1. The anilium and 9-thia-10-boraanthracene moieties adopt a perpendicular arrangement consistent with the <sup>1</sup>H NMR spectrum. This structure is also

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Scheme 2. Complexation Reaction of [1]OTf with DMAP



analogous to that reported for 10-mesityl-9-thia-10-boraanthracene, <sup>16</sup> a neutral analogue of  $[1]^+$ . The cyclic voltammogram of [1]OTf recorded in THF at room temperature shows a quasi-reversible reduction wave at  $E_{1/2}^{\text{red}} = -2.32 \text{ V} (\text{vs Fc/Fc}^+)$ (Figure 1), corresponding to the formation of a radical species. This reduction potential, which may be compared to that of Mes<sub>3</sub>B (-2.9 V vs Fc/Fc<sup>+</sup>) or [4-(Me<sub>3</sub>N)-2,6-Me<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>- $BMes_2$ <sup>+</sup> (-2.55 V vs Fc/Fc<sup>+</sup>),<sup>15</sup> suggests that the anilium substituent of  $[1]^+$  increases its electrophilicity.<sup>17</sup> The UV-vis spectrum of [1]OTf in THF features a distinct absorption band centered at 392 nm reminiscent of that observed in the case of 10-mesityl-9-thia-10-boraanthracene ( $\lambda_{max} = 387$  nm, cyclohexane) (Figure 1).<sup>16</sup> Time-dependent DFT calculations indicate that this low-energy band arises from a HOMO-LUMO excitation. This assignment is reinforced by the good match obtained between the computed energy of this band (367 nm) and that experimentally observed (392 nm). Inspection of the frontier molecular orbitals indicates that this band is a  $\pi - \pi^*$ transition centered on the 9-thia-10-boraanthracene moiety (Figure 1). The emission spectrum of [1]OTf mirrors the lowenergy band of the absorption spectrum, indicating that it originates from the  $\pi - \pi^*$  singlet excited state (Figure 1).

In order to probe the Lewis acidity of [1]OTf, we decided to investigate its reactivity toward p-dimethylaminopyridine (DM-AP) in chloroform at room temperature. This reaction produces the triflate salt [1-DMAP]OTf, which has been isolated in 77% yield (Scheme 2). Formation of [1-DMAP]OTf was confirmed by integration of the <sup>1</sup>H NMR spectrum, which indicates the presence of one coordinated DMAP molecule, as well as by detection of a <sup>11</sup>B NMR signal at 3.46 ppm corresponding to the four-coordinate boron center. The structure of [1-DMAP]OTf has been studied by single-crystal X-ray diffraction (Figure 2). The  $B-N_{DMAP}$  bond (B(1)-N(2)) of 1.642(5) Å is almost identical to that measured in the adduct Ph3B-DMAP (1.636(2) Å).<sup>18</sup> Coordination of the DMAP molecule to the boron center leads to a distinct pyramidalization of the latter, as indicated by the sum of the Carvl-B-Carvl angles  $(\sum)$  of 337°. Formation of DMAP adducts with cationic boranes such as **A** and **B** has not been observed.<sup>11,13</sup> Hence, the contrasting behavior of  $[1]^+$  may be assigned to the low steric protection of the boron center.

**Reactions of [1]OTf with Fluoride and Cyanide.** Fluoride and cyanide anion capture by [1]OTf in organic solvent was also examined. Reaction of [1]OTf with *n*-tetrabutylammonium fluoride (TBAF) in CHCl<sub>3</sub> at room temperature results in the rapid formation of the corresponding zwitterionic fluoroborate 1-F, which could be isolated as a colorless crystalline power (Scheme 3). Similarly, [1]OTf reacts with KCN in MeOH at





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Figure 2. ORTEP drawing of [1-DMAP]OTf with thermal ellipsoid plots (50% probability). Solvent molecule, triflate counteranion, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): S(1)-C(6) 1.766(4), S(1)-C(7) 1.766(4), B(1)-C(1) 1.629(6), B(1)-C(12) 1.615(6), B(1)-C(13) 1.637(5); C(1)-B(1)-C(12) 110.5(3), C(1)-B(1)-C(13) 113.8(3), C(12)-B(1)-C(13) 112.7(3), C(1)-B(1)-N(2) 100.6(3), C(12)-B(1)-N(2) 105.4(3), C(13)-B(1)-N(2) 112.9(3).

### Scheme 3. Reactions of [1]OTf with TBAF and KCN



room temperature to afford a crystalline precipitate of the zwitterionic cyanoborate 1-CN (Scheme 3). Both 1-F and 1-CN have been fully characterized. The <sup>1</sup>H NMR spectra of these derivatives suggest that they adopt  $C_s$  symmetry in solution. The <sup>11</sup>B NMR signals detected at 2.7 ppm for **1**-F and –16.6 ppm for 1-CN are in the expected range for four-coordinate boron species.<sup>11,13</sup> The crystal structures of these two compounds have been determined (Figure 3). Compound 1-F crystallizes in the space group  $P2_1/n$  with two independent molecules in the asymmetric unit. These two molecules, denoted as molecules A and B, have very similar structures. The B-F bond lengths (1.480(7) Å for molecule A and 1.479(8) Å for molecule B) are comparable to those found in other triarvlfluoroborate species  $(1.47 \text{ Å})^{.11,13}$  Similarly, the B-C<sub>CN</sub> bond (B(1)-C(24)) of 1.626(5) Å observed in 1-CN is comparable to those of other triarylcyanoborate anions such as  $[Ph_3BCN]^-$  (1.65 Å).<sup>19</sup> As in [1-DMAP]OTf, the boron center of these derivatives is distinctly pyramidalized ( $\sum = 338.7^{\circ}$  for molecule A of 1-F, 338.4° for molecule B of 1-F, 333.5° for 1-CN), implying a loss of aromaticity of the 9-thia-10-boraanthracene unit.

In agreement with this loss of aromaticity, anion binding induces a quenching of the  $\pi - \pi^*$  transition detected at 392 nm in THF.<sup>16</sup> Titration experiments carried out by monitoring the progressive quenching of this band upon incremental addition of anions indicate that the fluoride and cyanide

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Figure 3. ORTEP drawings of 1-F (left) and 1-CN (right) with thermal ellipsoid plots (50% probability). Solvent molecules and hydrogen atoms are omitted for clarity in each case. In the case of 1-F, only molecule A is shown. Selected bond lengths (Å) and angles (deg) for 1-F (the metrical parameters of molecule B are provided in brackets): S(1)-C(6) 1.765(5) [1.760(6)], S(1)-C(7) 1.768(5) [1.764(5)], B(1)-F(1) 1.485(6) [1.481(6)], B(1)-C(1) 1.630(7) [1.613(7)], B(1)-C(12) 1.617(7) [1.616(7)], B(1)-C(13) 1.640(7) [1.657(7)]; C(1)-B(1)-C(12) 111.1(4) [114.0(4)], C(1)-B(1)-C(13) 114.5(4) [111.3(4)], C(12)-B(1)-C(13) 113.1(4) [113.1(4)], F(1)-B(1)-C(1) 102.4(4) [104.5(4)], F(1)-B(1)-C(12) 105.2(4) [104.3(4)], F(1)-B(1)-C(13) 109.6(4) [109.0(4)]. Selected bond length (Å) and angles (deg) for 1-CN: S(1)-C(7) 1.770(3), S(1)-C(6) 1.771(2), B(1)-C(1) 1.627(4), B(1)-C(12) 1.625(4), B(1)-C(13) 1.647(4), B(1)-C(24) 1.627(4), N(2)-C(24) 1.155(3); C(1)-B(1)-C(12) 112.7(2), C(1)-B(1)-C(13) 111.7(2), C(12)-B(1)-C(13) 109.1(2), C(24)-B(1)-C(13) 103.8(2), C(24)-B(1)-C(12) 102.1(2), C(24)-B(1)-C(13) 117.2(2).



**Figure 4.** Top: UV–vis titration obtained upon addition of KF (left) and KCN (right) to a  $4.8 \times 10^{-5}$  M THF solution of [1]OTf. Bottom: <sup>1</sup>H NMR spectrum of [1]OTf in nitromethane- $d_3$  before and after layering/shaking with KCN/D<sub>2</sub>O solution (right).

binding constants of  $[1]^+$  in THF exceed  $10^7 \text{ M}^{-1}$  (Figure 4). Encouraged by these elevated values, which may be assigned to the cationic nature of the borane and the accessibility of the boron center, we decided to determine if anion binding could also be observed in protic media. To this end, the ability of  $[1]^+$  to capture fluoride and cyanide from water under biphasic conditions was investigated. Shaking a biphasic mixture consisting of KCN in  $D_2O$  (6.1 × 10<sup>-2</sup> M, 0.5 mL) and [1]OTf in nitromethane- $d_3$  (1.6  $\times$  10<sup>-2</sup> M, 0.5 mL) resulted in a 75% conversion of [1]OTf into 1-CN after 30 min based on <sup>1</sup>H NMR (Figure 3). An analogous experiment carried out with fluoride showed no formation of 1-F, indicating that  $[1]^+$  can selectively extract cyanide anions under these conditions. Attempts to use  $[1]^+$  in pure water were complicated by its slow decomposition. This lack of stability contrasts with the behavior of compounds such as A and **B** (Chart 1) and provides additional evidence for the increased reactivity of this exposed boron derivative. This

behavior is reminiscent of that observed for species such as E, which also decomposes in water.<sup>14</sup>

#### Conclusion

In conclusion, we report the synthesis of an aromatic boracycle ([1]<sup>+</sup>) whose boron atom is substituted by a cationic anilium substituent. This new derivative features a sterically accessible boron center and reacts with DMAP to form the corresponding adduct. This derivative also reacts with fluoride and cyanide anions in THF to afford the corresponding zwitterionic fluoroborate and cyanoborate species. Titration experiments indicate that the stability constants of these zwitterions exceed  $10^7 M^{-1}$ , thus reflecting the accessibility of the boron atom as well as the favorable inductive and Coulombic effects imparted by the anilium substituent. The unusual anion affinity of [1]<sup>+</sup> is also illustrated by its ability to selectively complex cyanide and not

Table 1. Crystal Data, I	Data Collection, and Structure Refin	nement for 1-F-0.5(Acetone), 1-C	N-Acetone, and [1-DMAP]OTf-Acetone
	,		

	1-F-0.5(acetone)	1-CN-acetone	[1-DMAP]OTf-acetone
	Crystal	l Data	
formula $M_r$ cryst size (mm <sup>3</sup> ) cryst syst space group a (Å) b (Å) c (Å) $\beta$ (deg) V (Å <sup>3</sup> ) Z z (a cm <sup>-3</sup> )	$\begin{array}{c} C_{24.5}H_{28}BFNO_{0.5}S\\ 406.35\\ 0.17\times0.15\times0.12\\ monoclinic\\ P2_1/n\\ 8.9480(3)\\ 35.296(11)\\ 13.556(3)\\ 96.815(5)\\ 4251(2)\\ 8\\ 1,270\end{array}$	$\begin{array}{c} C_{27}H_{31}BN_{2}OS\\ 442.41\\ 0.24\times0.19\times0.13\\ orthorhombic\\ Pbca\\ 16.585(4)\\ 13.446(3)\\ 21.832(5)\\ \\ 4869(2)\\ 8\\ 1.207\end{array}$	$\begin{array}{c} C_{34}H_{41}BF_{3}N_{3}O_{4}S_{2}\\ 687.63\\ 0.30\times0.20\times0.20\\ monoclinic\\ P2_{1}/n\\ 12.900(6)\\ 17.592(8)\\ 16.313(7)\\ 111.056(5)\\ 3455(3)\\ 4\\ 1.222\end{array}$
$\rho_{\rm calc} (g {\rm cm}^{-1}) \ \mu ({\rm mm}^{-1}) \ F(000)$	0.174 1728	0.154 1888	0.212 1448
	Data Co	llection	
T (K) scan mode <i>hkl</i> range measd reflns unique reflns [ $R_{int}$ ] reflns used for refinement	$ \begin{array}{c} 110(2) \\ \omega \\ -10 \rightarrow +10 \\ -40 \rightarrow +40 \\ -15 \rightarrow +15 \\ 37 245 \\ 6684 [0.0936] \\ 6684 \end{array} $	$ \begin{array}{c} 110(2) \\ \omega \\ -18 \rightarrow +18 \\ -15 \rightarrow +15 \\ -22 \rightarrow +24 \\ 21 295 \\ 3817 \ [0.0929] \\ 3817 \end{array} $	$ \begin{array}{c} 110(2) \\ \omega \\ -14 \rightarrow +14 \\ -20 \rightarrow +20 \\ -18 \rightarrow +18 \\ 29970 \\ 5421 \ [0.0611] \\ 5421 \end{array} $
	Refine	ement	
refined params GOF on $F^2$ R1, <sup><i>a</i></sup> wR2, <sup><i>b</i></sup> all data $\rho_{\text{fin}}(\max/\min)$ (e Å <sup>-3</sup> )	523 1.008 0.0658, 0.1764 0.699, -0.655	289 1.008 0.0531, 0.1279 0.319, -0.270	424 1.008 0.0560, 0.1451 0.577, -0.563

<sup>*a*</sup> R1 = 
$$\sum ||F_{o}| - ||F_{c}|| / \sum |F_{o}|$$
. <sup>*b*</sup> wR2 = {[ $\sum w(F_{o}^{2} - F_{c}^{2})^{2}$ ]/[ $\sum w(F_{o}^{2})^{2}$ ]}<sup>1/2</sup>.

fluoride under biphasic conditions in nitromethane/water. The Lewis acidic properties of  $[1]^+$  suggest that this cationic borane could be used in sensors as a molecular recognition unit for cyanide anions. Its ability to complex neutral Lewis bases such as DMAP suggests that such cationic boranes may also find a use as Lewis acid catalysts for organic transformations.

#### **Experimental Section**

General Procedures. Methyl triflate (MeOTf) was purchased from TCI America and used without purification. TBAF (n-Bu<sub>4</sub>NF·3H<sub>2</sub>O), KF, and KCN were purchased from Alfa Aesar and used as received. Et<sub>2</sub>O was dried by reflux over Na/K. Hexane was dried by reflux over potassium metal. CH<sub>2</sub>Cl<sub>2</sub> was dried by passing through a column charged with activated alumina, then dried over CaH<sub>2</sub> under N<sub>2</sub> atmosphere and distilled prior to use. 4-Dimethylamino-2,6-dimethylphenyllithium was synthesized by following a published procedure.<sup>15</sup> 10-bromo-9-thia-10-boraanthracene was synthesized by following a published procedure.<sup>7</sup> Air-sensitive compounds were handled under N<sub>2</sub> atmosphere, using standard Schlenk and glovebox techniques. Electronic absorption spectra were recorded using an Ocean Optics USB4000 spectrometer with an Ocean Optics ISS light source. Emission spectra were collected at room temperature in THF solution using a PTI QuantaMaster 4 fluorescence spectrophotometer equipped with a model 810 PMT detector. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). NMR spectra were recorded on a Varian Unity Inova 400 FT NMR spectrometer (399.59 MHz for <sup>1</sup>H, 375.95 MHz for <sup>19</sup>F, 128.2 MHz for <sup>11</sup>B, 100.5 MHz for <sup>13</sup>C) by using an internal deuterium lock. Chemical shifts  $\delta$  are given in ppm and are referenced against external Me<sub>4</sub>Si (H,  $^{13}C, \delta = 0$  ppm), BF<sub>3</sub>·Et<sub>2</sub>O  $(^{11}\text{B}, \delta = 0 \text{ ppm})$ , and CFCl<sub>3</sub>  $(^{19}\text{F}, \delta = 0 \text{ ppm})$ .

**Theoretical Calculations.** Density functional theory calculations (full geometry optimization) were carried out with Gaussian03 using the gradient-corrected Becke exchange functional (B3LYP) and the Lee-Yang-Parr correlation functional. A 6-31G(d) basis set was used for S, C, and H atoms and a 6-31+G(d') basis set for B and N atoms. Frequency calculations were carried out on the optimized structure of each compound to confirm the absence of negative frequencies.

**Electrochemistry.** Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (model 610 A) with a glassy carbon working electrode and a platinum auxiliary electrode. The reference electrode was built from a silver wire inserted into a small glass tube fitted with a porous Vycor frit at the tip and filled with a THF solution containing (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> (0.1 M) and AgNO<sub>3</sub> (0.005 M). All three electrodes were immersed in a THF solution (5 mL) containing (*n*-Bu)<sub>4</sub>NPF<sub>6</sub> (0.1 M) as a support electrolye and the analyte (2.0 mM for [1]OTf). The electrolyte was dried under vacuum prior to use. In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the  $E_{1/2}^{\text{Red}}$  of the Fc/Fc<sup>+</sup> redox couple.

**Crystallography.** The crystallographic measurements were performed by using a Bruker APEX2 diffractometer with graphite - monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71069$  Å). Specimens of suitable size and quality were selected and mounted onto glass fibers with apiezon grease. The structures were solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on  $F^2$  with use of the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms.

Synthesis of Cationic Borane [1]OTf. A solution of 2,6dimethyl-4-dimethylaminophenyllithium (120.8 mg, 0.78 mmol) in Et<sub>2</sub>O (20 mL) was slowly added to a solution of 10-bromo-9thia-10-boraanthracene (321.6 mg, 1.17 mmol) in Et<sub>2</sub>O (20 mL) at room temperature. After stirring for 24 h, the solvent was removed *in vacuo*. The resulting residue was extracted with hexanes (20 mL) and filtered. Evaporation of solvent from the filtrate afforded a yellow powder, which was used without further purification. MeOTf (500.0 mg, 3.05 mmol) was added to a solution of the crude product in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). After stirring for 1 h, hexane was added to the reaction mixture to afford a precipitate of [1]OTf (231 mg, 0.46 mmol, 59%). [1]OTf: colorless powder, mp 335 °C (dec); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>)  $\delta$  2.06 (s, 6H), 3.82 (s, 9H), 7.33 (dd, <sup>3</sup>J<sub>H-H</sub> = 8.0 Hz, 2H), 7.38 (s, 2H), 7.69–7.71 (m, 4H), 7.83 (d, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, 2H); <sup>13</sup>C NMR (100.5 Hz, CDCl<sub>3</sub>)  $\delta$  23.18, 57.28, 116.42, 120.67 (CF<sub>3</sub>), 124.96, 125.53, 132.46, 132.71, 138.90, 142.11, 144.78, 146.27, 147.56; <sup>11</sup>B NMR (128.2 Hz, CDCl<sub>3</sub>)  $\delta$  57.3. Anal. Calcd for C<sub>24</sub>H<sub>27</sub>BF<sub>3</sub>NO<sub>4</sub>S<sub>2</sub> ([1]OTf-H<sub>2</sub>O): C, 54.86; H, 5.18, Found: C, 55.09; H, 5.01.

**Reaction of [1]OTf with DMAP.** Addition of a solution of DMAP (14.6 mg, 0.12 mmol) in CHCl<sub>3</sub> (2 mL) to a CHCl<sub>3</sub> (3 mL) solution of **[1]**OTf (55.0 mg, 0.11 mmol) resulted in the formation of a colorless precipitate. After stirring for 30 min, the mixture was filtered and the solid was washed with Et<sub>2</sub>O (5 mL) and dried under vacuum. Recrystallization from acetone/Et<sub>2</sub>O vapor diffusion afforded **[1-DMAP]**OTf as colorless crystals (53.3 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf: colorless crystals (53.3 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf: colorless crystals (53.4 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf: colorless crystals (53.3 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf: colorless crystals (53.4 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf: colorless crystals (53.3 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf. colorless crystals (53.3 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf. colorless crystals (53.4 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf. colorless crystals (53.4 mg, 0.08 mmol, 77%). **[1-DMAP]**OTf. (100.5 Hz, acetone-d<sub>6</sub>)  $\delta$  24.53, 38.57, 56.58, 106. 48, 118.60, 121.32, 125.00, 125.45, 126.23, 134.30, 137.69, 144.50, 144.80, 146.13, 147.02, 153.53, 155.24; <sup>11</sup>B NMR (128.2 Hz, acetone-d<sub>6</sub>)  $\delta$  3.46. Anal. Calcd for C<sub>31</sub>H<sub>35</sub>BF<sub>3</sub>N<sub>3</sub>O<sub>3</sub>S<sub>2</sub> (**[1-DMAP]**OTf-(acetone)): C, 59.39; H, 6.01. Found: C, 59.19; H, 6.08.

**Reaction of [1]OTf with TBAF.** Addition of a solution of TBAF (31.6 mg, 0.10 mmol) in CHCl<sub>3</sub> (5 mL) to a CHCl<sub>3</sub> solution of **1** (52.8 mg, 0.10 mmol) resulted in the formation of a colorless precipitate. After stirring for 30 min, the mixture was filtered and the solid was washed with Et<sub>2</sub>O (5 mL) and dried under vacuum. Colorless crystals of **1**-F (35.6 mg, 0.09 mmol, 94%) were obtained by recrystallization using acetone/Et<sub>2</sub>O vapor diffusion. **1**-F: colorless crystal, mp 372 °C (dec); <sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>)  $\delta$  2.22 (s, 3H), 2.23 (s, 3H), 3.72 (s, 9H), 6.79 (dd, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 2H), 6.91 (dd, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 2H), 7.05 (dd, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 2H), 7.13 (d, <sup>3</sup>J<sub>H-H</sub> = 8.4 Hz, 2H), 7.15 (s, 2H); <sup>13</sup>C NMR (100.5 Hz, acetonitrile-d<sub>3</sub>)  $\delta$  24.89, 24.96, 57.55, 116.98, 123.19, 123.84, 124.97, 134.57, 136.87, 136.90, 143.44, 144.42 (two signals corresponding to the *ipso*-carbons of the boron atom could not be observed due to broadening by a quadrupole moment of <sup>11</sup>B nuclei); <sup>11</sup>B NMR (128.2 Hz, acetone-d<sub>6</sub>)  $\delta$  2.68; <sup>19</sup>F NMR (375.9 Hz, acetone-d<sub>6</sub>)  $\delta$  -159.7.

Anal. Calcd for  $C_{24.5}H_{28}BFNO_{0.5}S$  (1-F-0.5(acetone), two molecules of 1-F and one acetone molecule were in the unit cell): C, 72.41; H, 6.95. Found: C, 72.33; H, 6.85.

Reaction of [1]OTf with KCN. Addition of a solution of KCN (13.5 mg, 0.21 mmol) in MeOH (10 mL) to a MeOH (10 mL) solution of [1]OTf (104.9 mg, 0.21 mmol) resulted in the formation of a colorless precipitate. After stirring for 30 min, the mixture was filtered and the solid was washed with methanol and dried under vacuum. Colorless crystals of 1-CN (68.4 mg, 0.18 mmol, 86%) were isolated by recrystallization using acetone/hexane vapor diffusion. 1-CN: colorless crystal, mp. 350 °C (dec); <sup>1</sup>H NMR (400 Hz, acetone- $d_6$ )  $\delta$  2.23 (s, 6H), 3.79 (s, 9H), (dcc), 11 NiNK (400 Hz, actione  $a_6$ ) 0 2.25 (s, 6H), 5.77 (s, 5H), 6.81 (ddd,  ${}^{3}J_{H-H}$ =7.2 Hz,  ${}^{3}J_{H-H}$ =7.2 Hz,  ${}^{4}J_{H-H}$ =1.2 Hz, 2H), 6.92 (m, 4H), 7.11 (dd,  ${}^{3}J_{H-H}$ =8.0 Hz,  ${}^{4}J_{H-H}$ =1.2 Hz, 2H), 7.30 (s, 2H);  ${}^{13}C$  NMR (100.5 Hz, acetonitrile- $d_3$ )  $\delta$  25.52, 57.01, 117.52, 117.60, 124.41, 124.80, 125.04, 133.47, 136.48, 136.51, 145.56 (two signals corresponding to the *ipso*-carbons of the boron atom could not be observed due to broadening by a quadrupole moment of <sup>11</sup>B nuclei); <sup>11</sup>B NMR (128.2 Hz, acetone- $d_6$ )  $\delta$  -16.58. Anal. Calcd for C<sub>25,2</sub>H<sub>27,4</sub>BN<sub>2</sub>O<sub>0,4</sub>S (1-CN-0.4(acetone), approximately 60% of acetone molecules in the crystalline product were lost upon drying in vacuo): C, 74.26; H, 6.78. Found: C, 74.21; H, 6.53.

**Biphasic Cyanide Capture.** A solution of [1]OTf in nitromethane- $d_3$  (0.5 mL, 1.6 × 10<sup>-2</sup> M) was layered with a solution of KCN in D<sub>2</sub>O (0.5 mL, 6.1 × 10<sup>-2</sup> M), and the sample was shaken for 30 min. After separation of the layers, the <sup>1</sup>H NMR spectrum of the nitromethane- $d_3$  layer showed 75% conversion of [1]<sup>+</sup> into 1-CN.

Titration of [1]OTf with Fluoride and Cyanide in THF. Solutions of [1]OTf (3.0 mL,  $4.8 \times 10^{-5}$  M, THF) were titrated with incremental (5  $\mu$ L) amounts of fluoride or cyanide anions by addition of a  $3.0 \times 10^{-3}$  M solution of KF in MeOH or a  $3.8 \times 10^{-3}$  M solution of KCN in MeOH.

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**Supporting Information Available:** Crystallographic data for **1-**F, **1-**CN, and **[1-**DMAP]OTf in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.