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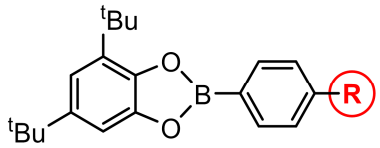

Impact of Substituents on Lewis Acidity

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Substituent Effects on the Lewis Acidity of 4,6-Di-*tert*-butylchatechol Boronate Esters

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ABSTRACT

In studying the factors which contribute to the Lewis acidity of organoboron compounds we investigated approaches to the design of robust, novel Lewis acids purposed for metal-free catalysis. Based on a sterically encumbered catechol motif, a series of boronate esters are shown to demonstrate modest Lewis acidities for the conventional Gutmann-Beckett test as an inquisitive investigation.

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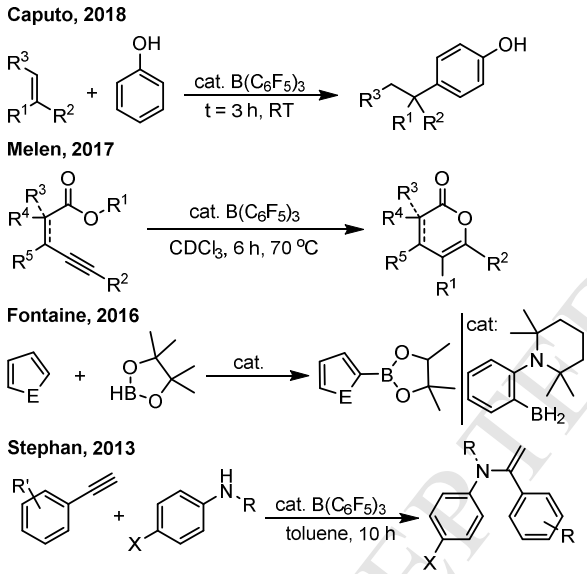
1. Introduction

Main-group Lewis acids are widely applied in modern synthetic chemistry to facilitate organic transformations.[1] Cheap, commercially-available group 13 trihalides such as BF_3 and $AlCl_3$, as well as simple organoboranes are widely utilized as activators and catalysts. These species typically serve to enhance electrophilicity of reactive sites on the substrate by drawing electron density from Lewis basic moieties or unsaturation. Recently, more complex main group Lewis acid species have drawn attention for their ability to mediate a wider range of transformations. Credited to relatively recent advancements in frustrated Lewis pair (FLP) chemistry,[2] low-valent main-group,[3] and hypervalent species such as phosphonium and stibonium cations,[4,5] p-block Lewis acid development has seen exponential growth in the 21st century. These new compounds demonstrate unprecedented reactivities, primarily owed to the Lewis acidity of the active center, and have found significant application in metal-free transformations. Our group and many others have investigated the application of borane Lewis acids in catalysis and a select few are highlighted in Scheme 1.[5-9]



Scheme 1 – A selection of Lewis acid catalyzed transformations.

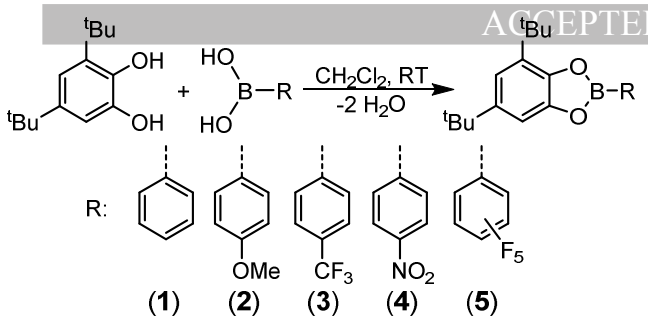
Strong Lewis acids are more widely applicable in catalysis and are generally achieved by the introduction of electron withdrawing pentafluorophenyl substituents. However, excessively strong Lewis acids can lead to issues of chemoselectivity or diminish turnover numbers. Chemoselectivity issues often result from indiscriminate interactions with donor atoms on the substrate, while an irreversibly strong association of the Lewis acid center to the substrate can have deleterious effects on catalytic turnover. The latter issue can be mitigated to an extent by using sterically hindered substrates (as in FLP catalysis). Furthermore, Lewis acids inherently bear empty, low-lying acceptor orbitals, making them often susceptible to detrimental association with water or coordinating solvents, which limits their practical application. Therefore, there is significant interest in synthesizing Lewis acids that are stable towards ambient conditions, yet acidic enough to promote chemical reactivity.

A general goal is not to necessarily synthesize the strongest Lewis acid, rather it is to determine the appropriate Lewis acid that is most selective for a specific substrate or chemical transformation. Contrary to Brønsted acids (which have a well-defined, universal pKa scale), a discreet and direct method to quantify Lewis acidity remains a topic of discussion. One such method is the Childs Method, which indicates the strength of a Lewis acid by measuring the change in chemical shift of the β-proton of crotonaldehyde in the ^{1}H NMR spectrum before and after binding a Lewis acid.[10] The Gutmann-Beckett method is another spectroscopic technique, which uses Et_3PO as a probe molecule and investigates the chemical shift change in the ^{31}P NMR spectrum upon coordination to a Lewis acid; reported as unitless scalar values defined as an acceptor number (AN).[11,12] Finally, a measure of fluoride ion affinity (FIA) can be performed *in silico* or by comparing the isodesmic product of a fluoride adduct with the Lewis acid in question to provide a relative measure of affinity.[13]

The most commonly employed Lewis acids in main-group catalysis are from the family of sterically hindered, perhalogenated boranes, such as $B(C_6F_5)_3$. Strides have been made to improve the ambient stability of these Lewis acids. Work from the Ashley lab has shown that combination of dioxane and $B(C_6F_5)_3$ can tolerate water in hydrogenation catalysis.[14] Soos and co-workers also discovered that a water-tolerant borane, $B(p\text{-}C_6F_4H)_2(o\text{-}C_6Cl_2H_3)$, could be synthesized and applied as a catalyst by altering the halogen substitution pattern on the aromatic rings.[15] Nevertheless, most Lewis acid catalysts are still notoriously sensitive towards air and moisture, requiring handling under inert atmospheres. Substitution of an aryl-group with a heteroatom substituent (such as O or N) will diminish the Lewis acidity of the boron center through lone-pair donation, but can increase the relative stability. To that end, the use of catechol substituents on main-group Lewis acids has recently garnered interest. Derivatives of catechol boronate esters have been extensively utilized in Suzuki-Miyaura cross-coupling reactions due to their advantageous cost, stability and ease of preparation.[16] Greb and co-workers have shown that perchlorinated catechol substituents on a silicon center generate the neutral Lewis super acid $Si(O_2C_6Cl_4)_2$, capable of activating Sb–F bonds in the SbF_6 anion.[17] We were inspired by the bulky 3,5-di-*tert*-butylcatechol ligands used by Westcott and co-workers in their investigations into the synthesis and applications of arylspiroborates.[18,19] Therefore, to modulate the Lewis acid strength, while keeping a sterically bulky ligand, we endeavoured to explore the use of 3,5-di-*tert*-butylcatechol as a ligand for the synthesis of a series of boronate esters (Scheme 2). Herein we describe the impact that the third substituent has on the Lewis acidity of these boronate esters.

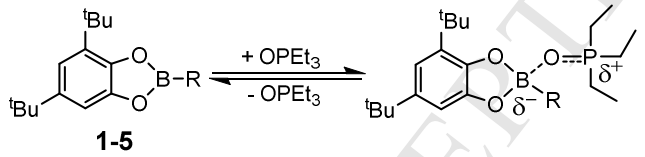
2. Results and Discussion

To explore the effects of an aryl substituent on the Lewis acidity of bulky boronate esters, we synthesized a series of 4,6-di-*tert*-butylcatechol boronate esters using standard procedures via a dehydration reaction from the corresponding boronic acid and diol.[20] The aryl substituents chosen for this study were phenyl, 4-methoxyphenyl, 4-(trifluoromethyl)phenyl, 4-nitrophenyl, and pentafluorophenyl groups. These represent a variety of substituents containing both electron-donating and electron-withdrawing functionalities. Starting from the corresponding arylboronic acid, a condensation reaction was performed with 3,5-di-*tert*-butylcatechol to produce the corresponding boronate esters (**1-5**) in excellent yields (60-99%) (Scheme 2).



Scheme 2 – Synthesis of boronate ester series.

Multinuclear NMR spectroscopy was used to characterize the products. The ^{1}H NMR spectrum of compound **1** showed two distinct *t*-butyl resonances at 1.55 ppm and 1.40 ppm in addition to the phenyl-resonances from the boronic acid. The ^{11}B NMR spectrum of **1** exhibited a broad resonance at 32.8 ppm, characteristic of tricoordinate boronate esters. Similarly, compounds **2-5** also displayed inequivalent *t*-butyl resonances in the corresponding ^{1}H NMR spectra between 1.30 – 1.57 ppm. Evidence of the condensation products was apparent for compounds **2-5** in the ^{11}B NMR with broad resonances observed between 29 – 31 ppm. These results show the aryl substituent on the boronate ester does not have a significant impact on the ^{11}B NMR resonance. Compounds **2-4** all indicated that a *para*-substituted aromatic ring was present in the products with two apparent doublets observed in the aromatic region in the ^{1}H NMR spectra. Finally, the ^{19}F NMR spectrum for compound **5** showed three resonances for the *ortho*-, *para*-, and *meta*-fluorine atoms of the pentafluorophenyl ring at -128.15, -146.85, and -160.81 ppm, respectively. The large $\Delta\ \delta_{para\text{-}meta}$ indicates that a three-coordinate boron center is present and implies that there could be a high Lewis acidity. Further evidence for the formation of **1-5** was provided by elemental analyses consistent with the expected products in each case. All five compounds were found to be relatively air and moisture stable in the solid state; even over a period of months. This was encouraging, and we sought to explore how Lewis acidic these compounds were.



Scheme 3 – Gutmann-Beckett method with **1-5**.

We initially investigated the Lewis acidity of these species by using the Gutmann-Beckett method. Free Et_3PO has a chemical shift of 41.0 ppm in the ^{31}P NMR spectrum in $CDCl_3$, and upon reaction with **1-5** we see a significant change in the ^{31}P NMR resonance for the Et_3PO probe (Figure 1). We utilized an excess of the phosphine oxide (1.5 eq.) to favour adduct formation as depicted in Scheme 3. The Et_3PO adduct with **1** resulted in a ^{31}P NMR resonance at 51.1 ppm which correlates to an acceptor number (AN) of 22.2. The acceptor number is calculated using a scale where Et_3PO has an AN=0 and $SbCl_5$ has an AN=100 (δ ^{31}P: 86.1).[21] The addition of donor substituents (-OMe) to the aryl substituent in **2** appears to decrease the Lewis acidity, as the corresponding ^{31}P NMR chemical shift of the adduct was found to be 47.3 ppm (AN=13.9). The introduction of electron withdrawing substituents in the *para*-position of the third substituent (-CF_3, **3**; -NO_2, **4)** resulted in an increase in Lewis acidity according to the Gutmann-Beckett method. The ^{31}P NMR chemical shift of the Et_3PO adduct of **3** was 61.9 ppm (AN=46.2) and **4** was 60.3 ppm (AN=42.6). These results imply that a trifluoromethyl substituent has a greater impact on the Lewis acidity than a nitro substituent. Finally, **5** was found to be the strongest Lewis acid of the series as it bears a pentafluorophenyl substituent. The ^{31}P NMR chemical shift of the Et_3PO adduct was 66.7 ppm (AN=56.7). In this case, the bulkier C_6F_5 substituent hinders the free rotation of the Et_3PO adduct, thus resulting in a slightly broader resonance. These data are compiled in Table 1.

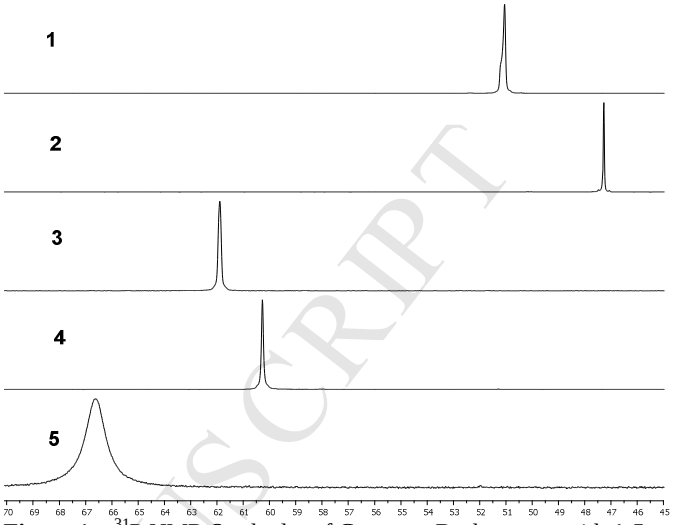


Figure 1 – ^{31}P NMR Stack plot of Gutmann-Beckett tests with **1-5**.

The Gutmann-Beckett acceptor numbers align well with other reported values in the literature.[21] According to this method, these Lewis acids are weaker than those which have been used in Lewis acid catalysis. For example, $B(C_6F_5)_3$ has an AN of 78.1, which is significantly higher than any of those in the reported series. Interestingly, **2**, as having a *p*-OMe substituent on the aromatic ring, shows similar Lewis acidity to trivalent alkyl borates ($B(OR)_3$).[21] The remaining boronate esters show similar Lewis acidity to those of other reported aryl boronate esters.[21] The effects of the two *t*-butyl substituents are clear, the Gutmann-Beckett AN has been reported for the catechol analogue, $C_6F_5B(O_2C_6H_4)$ and was found to be 65.2, which is significantly more acidic than the 56.7 we found for **5**.[22] Thus, the electron donating abilities of the two *t*-butyl groups clearly have an impact on the resultant Lewis acidity of the boron center.

	GB ^{31}P NMR δ (ppm)(AN)	TBAF ^{19}F NMR δ (ppm)
1	51.1 (22.2)	-133.6
2	47.3 (13.9)	-132.8
3	61.9 (46.2)	-134.5
4	60.3 (42.6)	-135.6
5	66.7 (56.7)	-123.9

Table 1 – Lewis acidity measurements of **1-5**.

In order to further investigate the Lewis acidity of these boronate esters, we treated **1-5** with one equivalent of tetrabutylammonium fluoride (TBAF) to observe if the boronate esters were Lewis acidic enough to bind a fluoride anion. Analyzing the reactions by ^{19}F NMR spectroscopy indicated that in all cases fluoride binding was occurring, forming the corresponding ammonium fluoroborate salts (See Supporting Information). Free TBAF appears at -112 ppm in the ^{19}F NMR spectrum and in all cases an upfield shift is observed upon reaction with **1-5** (Table 1). We were able to isolate the fluoride adduct of the most Lewis acidic species (**5**), as the tetrabutylammonium fluoroborate salt, **6**. The product was evident through multinuclear NMR analysis, with an observed

doublet resonance in the ^{11}B NMR spectrum at 9.11 ppm ($^{1}J_{BF}$ = 52.6 Hz), indicative of the formation of a tetracoordinate fluoroborate anion. Furthermore, the ^{19}F NMR spectrum shows that the *meta-para* fluorine gap decreases, indicating the formation of a 4-coordinate species (Δ13.96 ppm to Δ4.46 ppm). Also observed in the ^{19}F NMR spectrum is the B–F resonance at -123.86 ppm. Finally, **6** was unambiguously identified by X-ray crystallography as the tetrabutylammonium fluoroborate salt (Figure 2). In the solid state the B–F bond length was found to be 1.416(2) Å, which is typical for a fluoroborate salt.[23] The bond angles around the boron atom sum to 328.3°, indicating a near perfect tetrahedral geometry around the boron center.

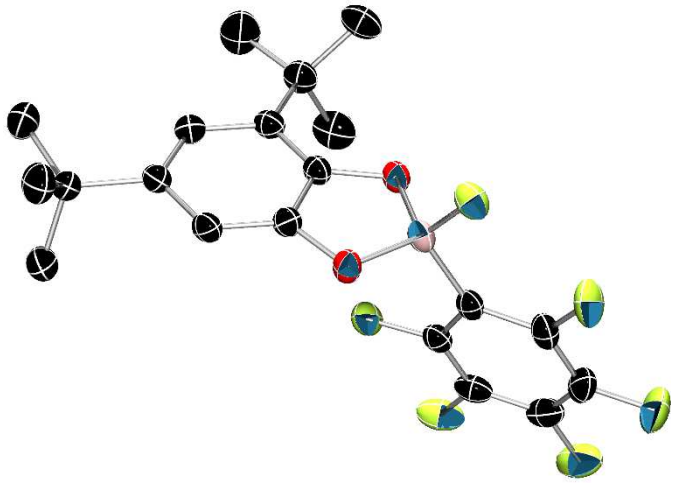


Figure 2 – Molecular structure of **6** (the tetrabutylammonium cation and hydrogens are excluded for clarity). C: Black, O: Red, B: Pink, F: Yellow/Green. Thermal ellipsoids at 50% probability.

Empirical Formula	$C_{36}H_{56}BF_6NO_2$
Formula wt. (g mol^{-1})	659.62
Crystal System	Monoclinic
Space Group	$P2_{1/n}$
a (Å)	14.1568(6)
b (Å)	15.1202(6)
c (Å)	17.6289(7)
α (°)	90
β (°)	99.166(2)
γ (°)	90
V (Å^3)	3725.3
Z	4
d (mg m^{-3})	1.176
μ (*mm*$^{-1}$)	0.761
Total Data	67834
Unique Data	6632
I > 2σ (I^2)	5785
Variables	425
R_1	0.0462
wR_2	0.1133
GOF	1.017

Table 2 – Crystallographic data for **6**.

In conclusion, we have synthesized a series of boronate esters using 3,5-di-*tert*-butylcatechol as a substituent and analyzed how various functional groups on the second aromatic ring influence the relative Lewis acidity. The trend shows that substituting electron donating or withdrawing groups in the *para* position of the aromatic ring has a significant influence on the relative Lewis acidity, and through the Gutmann-Beckett method, found that the Lewis acidity trend follows **5** > **3** > **4** > **1** > **2**. We were able to isolate and crystalize the fluoride adduct of the most Lewis acidic species, bearing a pentafluorophenyl substituent (**6**). Research is underway in our laboratory to explore the ability of these air stable Lewis acids to act as catalysts.

3. Experimental section

All manipulations were performed using either an MBraun LABstar Glove Box Workstation under N_2 atmosphere or in a fume hood. All glassware was dried in an oven at 110 °C before being transferred into the glovebox. Solvents were prepared from an MBraun MB-SPS 800 solvent drying system under N_2 atmosphere using oven-heated glassware. Commercially available reagents were purchased from either Sigma-Aldrich, TCI Chemicals or Oakwood Chemicals and employed without further purification; unless otherwise stated. Chloroform-*d* and benzene-d_6 were transferred to Strauss flasks and dried over activated molecular sieves, then degassed with cycles of freeze-pump-thawing, following transfer to the glovebox. Adduct formation reactions were done in 20 mL scintillation vials with appropriately sized, oven dried, Teflon stir bars. Experiments monitored by NMR spectroscopy over time, were conducted in NMR tubes (8" x 5 mm) sealed with standard plastic caps and wrapped with parafilm or J-Young NMR tubes (8" x 5 mm). ^{1}H, ^{11}B{^{1}H}, ^{13}C{^{1}H}, and ^{19}F NMR spectra were acquired at 25 °C on either a Bruker 700 MHz Spectrometer, Bruker DRX 600 MHz Spectrometer, Bruker ARX 400 MHz Spectrometer equipped with a variable temperature probe, or Bruker ARX 300 MHz Spectrometer. Chemical shifts are given relative to SiMe4 and referenced to the residual solvent signal (^{1}H, ^{13}C{^{1}H}) either to $CDCl_3$ (δ 7.26, 77.16 ppm) respectively. ^{11}B{^{1}H} and ^{19}F{^{1}H} NMR spectra were referenced relative to either 15% BF_3-Et_2O or an internal reference such as starting material. NMR spectra were analyzed using either TopSpin 3.2 or MestReNova 6.0.2-5475 software. Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. The conventional abbreviations were used as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), br (broad). Elemental Analysis was carried out on an ElementarVarioELcube using VarioELcube software (V4.0.13), samples were run in triplicate. Crystallographic data for the structure **6** has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 1872813. Copies of the data can be obtained free of charge on application to CCSC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk)

General Procedure for the synthesis of 4,6-di-*tert*-butylcatechol boronate esters (1-5)

To a 250 mL round-bottom flask, 3,5-di-*tert*-butylcatechol (1.6 mmol) and corresponding boronic acid (1.6 mmol) in CH_2Cl_2 (100 mL), were stirred under ambient conditions for 12-16 hrs. The reaction mixture was dried over $MgSO_4$ and filtered. Solvent was removed *in vacuo* yielding a crude oil. The crude material was dissolved in minimal acetonitrile and crystallized in a freezer (-25 °C). The precipitate was vacuum filtered to yield the corresponding boronate ester. NMR spectra were obtained

from samples which have been stored on the bench for extended periods of time.

(**1**) 4,6-di-*tert*-butyl-2-phenylbenzo[d][1,3,2]dioxaborole**:**

Following the general procedures, 3,5-di-*tert*-butylcatechol (0.3604 g, 1.6 mmol) and phenylboronic acid (0.1954 g, 1.6 mmol) was stirred for 12 hrs and the product isolated in 84.9 % (0.4186 g) yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.13 (d, $^{3}J_{HH}$ = 7.3 Hz, 2H), 7.59 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H), 7.52 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H), 7.28 (s, 1H), 7.13 (s, 1H), 1.55 (s, 9H), 1.40 (s, 9H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.79; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.60, 145.88, 144.26, 135.12, 135.04, 132.24, 128.32, 116.66, 107.78, 35.15, 34.62, 31.96, 29.96. EA for $C_{20}H_{25}O_2B$: Expected 77.94% C, 8.18% H, 0% N. Found 80.11% C, 8.05% H, 0.16% N.

(**2**):4,6-di-*tert*-butyl-2-(4-methoxyphenyl)benzo[d][1,3,2]-dioxaborole:

Following the general procedures, 3,5-di-*tert*-butylcatechol (0.3604 g, 1.6 mmol) and 4-methoxyphenylboronic acid (0.2434 g, 1.6 mmol) was stirred for 12 hrs and the product isolated in 95.0 % (0.5141 g) yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.10 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 7.28 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H), 7.13 (d, $^{4}J_{HH}$ = 1.7 Hz, 1H), 7.05 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 3.90 (s, 3H), 1.57 (s, 9H), 1.41 (s, 9H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.33; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.95, 148.69, 145.65, 144.34, 136.87, 134.93, 116.47, 113.96, 107.69, 107.61, 55.26, 35.11, 34.74, 31.98, 29.97. EA for $C_{21}H_{27}O_3B$: Expected 74.57% C, 8.05% H, 0% N. Found 76.97% C, 7.89% H, 0.24% N.

(**3**):4,6-di-*tert*-butyl-2-(4-(trifluoromethyl)phenyl)benzo[d][1,3,2] dioxaborole:

Following the general procedures, 3,5-di-*tert*-butylcatechol (0.3604 g, 1.6 mmol) and 4-trifluoromethylphenylboronic acid (0.3041 g, 1.6 mmol) was stirred for 12 hrs and the product isolated in 90.9 % (0.5472 g) yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.27 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H), 7.79 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H), 7.34 (s, 1H), 7.22 (s, 1H), 1.60 (s, 9H), 1.45 (s, 9H);z ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.03; ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.05; ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.54, 146.41, 144.19, 135.44, 135.32, 133.84 (q, $^{2}J_{CF}$ = 32.6 Hz), 130.54 (m), 125.05, 124.21 (q, $^{1}J_{CF}$ = 270.8 Hz), 120.15, 117.10, 108.00, 35.22, 34.70, 31.96, 30.03. EA for $C_{21}H_{24}O_2BF_3$: Expected 67.04% C, 6.43% H. Found 68.93% C, 6.01% H, 0.16% N.

(**4**):4,6-di-*tert*-butyl-2-(4-nitrophenyl)benzo[d][1,3,2]dioxaborole:

Following the general procedures, 3,5-di-*tert*-butylcatechol (0.3604 g, 1.6 mmol) and 4-nitrophenylboronic acid (0.2673 g, 1.6 mmol) was stirred for 12 hrs and the product isolated in 59.5 % (0.5651 g) yield. ^{1}H NMR (400 MHz; $CDCl_3$): δ 8.31 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 8.26 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.28 (s, 1H), 7.17 (s, 1H), 1.55 (s, 9H), 1.40 (s, 9H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.38; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.34, 148.31, 146.58, 143.96, 135.85, 135.46, 123.04, 117.25, 107.97, 35.16, 34.62, 31.88, 29.95. EA for $C_{20}H_{24}O_4B$: Expected 68.01% C, 6.85% H, 3.97% N. Found 69.45% C, 6.58% H, 4.16% N.

(**5**):4,6-di-*tert*-butyl-2-(perfluorophenyl)benzo[d][1,3,2]-dioxaborole:

Following the general procedures, 3,5-di-*tert*-butylcatechol (0.3604 g, 1.6 mmol) and pentafluorophenylboronic acid (0.3392 g, 1.6 mmol) was stirred for 12 hrs and the product isolated in 98.7% (0.6288 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.16 (s, 1H), 1.49 (s, 9H), 1.37 (s, 9H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 29.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ -128.15, -146.85, -160.81; ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.27, 147.79, 146.89, 144.14, 143.42, 137.75, 135.72, 117.49, 108.18, 35.26, 34.59, 31.91, 29.83. EA for $C_{20}H_{20}O_2BF_5$: Expected 60.33% C, 5.06% H, 0% N. Found 62.69% C, 4.72% H, 0.11% N.

(**6**) Tetrabutylammonium 4,6-di-*tert*-butyl-2-fluoro-2-(perfluorophenyl)benzo[d][1,3,2]dioxaborol-2-uide

Compound **5** (47.8 mg, 0.12 mmol) was added to TBAF (31.4 mg, 0.12 mmol) in benzene (1 mL) and $CHCl_3$ (0.2 mL). After stirring for 1 hr, the solution was triturated with pentanes. The precipitated was vacuum filtered, yielding a pale-yellow powder in 34.4% (0.0272 g) yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 6.60 (s, 1H), 6.59 (m, 8H), 3.17 (m, 8H), 1.56 (m, 8H), 1.43 (s, 9H), 1.36 (m, 8H), 1.27 (s, 9H), 0.96 (m, 12H); ^{11}B NMR (128 MHz, $CDCl_3$) δ 9.11 (d, $^{1}J_{BF}$ = 52.6 Hz) ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.86, -133.75, -161.23, -165.69; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.61, 148.08, 147.67, 140.34, 138.89, 136.71, 129.90, 111.51, 104.25, 58.51, 34.42, 34.11, 32.09, 29.77, 23.86, 19.58, 13.59. EA for $C_{36}H_{56}O_2NBF_6$: Expected 65.55% C, 8.56% H, 2.12% N. Found 68.53% C, 8.86% H, 2.93% N.

General Procedure for the probing of the Lewis acidity of 1-5 using the Gutmann-Beckett method

Under N_2 atmosphere, Et_3PO (1.5 eq.) was added to the corresponding boronate ester **1-5** (0.2 mmol). The mixture was warmed, melting the Et_3PO, followed by the addition of C_6D_6 and sealed under N_2 in an NMR tube for NMR spectroscopy.

General Procedure for the probing of the Lewis acidity of 1-5 using Tetrabutylammonium fluoride

Under N_2 atmosphere, TBAF (1.5 eq.) was added to the corresponding boronate ester **1-5** (0.2 mmol) and dissolved in C_6D_6, and an internal standard of α,α,α-trifluoromethyltoluene was added. The mixture was then sealed under N_2 in an NMR tube for NMR spectroscopy.

X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. Data reduction was performed using the SAINT software package, and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least squares on F2 using XL as implemented in the SHELXTL suite of programs. All nonhydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

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Supplementary Material

All NMR spectra and X-Ray crystallographic data are provided in the Supplementary Materials documents.