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# Protecting Group-Free Synthesis of 1,2-Azaborines: A Simple Approach to the Construction of BN-Benzenoids

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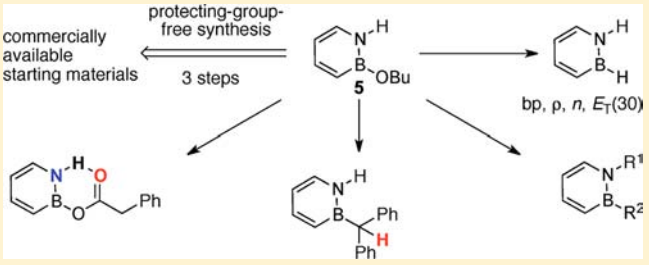
Supporting Information

**ABSTRACT:** The protecting group-free synthesis of a versatile 1,2-azaborine synthon **5** is described. Previously inaccessible 1,2-azaborine derivatives, including the BN isostere of phenyl phenylacetate and BN1 triphenylmethane were prepared from **5** and characterized. The structural investigation of BN phenyl phenylacetate revealed the presence of a unique *N*H-carbonyl hydrogen bond that is not present in the corresponding carbonaceous analogue. The methyne *C*H in BN triphenylmethane was found to be less acidic than the corresponding proton in triphenylmethane. The gram-quantity synthesis of the parent 1,2-azaborine **4** was demonstrated, which enabled the characterization of its boiling point, density, refractive index, and its polarity on the $E_T(30)$ scale.




## 1. INTRODUCTION

BN/CC isosterism, which is the replacement of a carbon−carbon bond unit with the isosteric boron−nitrogen bond unit, has recently emerged as a viable strategy to create structural diversity in molecular space.[1] In particular, the chemistry of 1,2-dihydro-1,2-azaborines (abbreviated as 1,2-azaborines), which are BN isosteres of the ubiquitous family of arenes, has attracted attention as novel aromatic compounds relevant to biomedical research and materials science applications.[2] From a basic science point of view, the close structural relationship between 1,2-azaborines and the quintessential aromatic compound benzene allows the examination of the consequences of BN/CC isosterism on electronic structure and aromaticity of delocalized $\pi$ electron systems.[3]

Dewar was the early pioneer of 1,2-azaborine chemistry,[4] creating the first examples in the 1960s. After a period of relative inactivity, the availability of new powerful synthetic tools at the turn of the millennium reinvigorated the interest in these BN heterocycles. Ashe and co-workers developed two complementary syntheses toward monocyclic 1,2-azaborines: (1) Katz-type ring-expansion rearrangement of five-membered lithium azaborolides[5] and (2) ring-closing metathesis/dehydrogenation sequence.[6,7] Piers developed methods for the preparation of new conjugated polycyclic BN-containing heterocycles such as derivatives of triphenylene, pyrene, and phenanthrene.[8] Perepichka,[9] Yamaguchi,[10] Nakamura,[11] Pei,[12] and Wang[13] each developed unique syntheses for extended conjugated BN heterocyclic systems for potential utility in organic electronics.

Late-stage functionaliztion strategies are arguably the most efficient and versatile approach to generate a vast array of derivatives from an assembled BN heterocyclic core. For monocyclic systems, chemists up to until recently had to choose between 1,2-azaborine synthons containing labile groups on either nitrogen, such as Ashe's *N*-TMS 1,2-azaborine **1**,[14] or on boron, such as the *B*−Cl 1,2-azaborine **2**[15] developed by our group (Figure 1). In both cases, the syntheses required

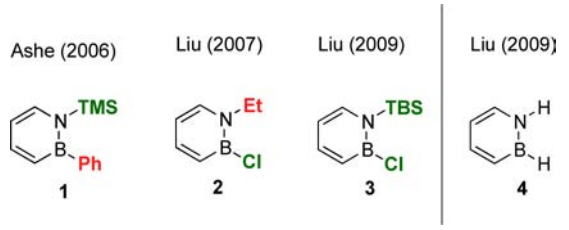



**Figure 1.** 1,2-azaborine synthons **1**−**3**. Nonremovable groups are labeled red. Removable and functionalizable groups are labeled green.

that a nonremovable group be attached to boron or nitrogen atoms, respectively, which was a significant synthetic limitation. In 2009 we prepared *N*-TBS *B*−Cl-1,2-azaborine **3**,[16] which is the first example of a 1,2-azaborine synthon that can be functionalized at both nitrogen and boron positions at late stage. The availability of **3** set the stage for the isolation and characterization of the long-sought parent 1,2-azaborine, **4**.[16]

Despite the advances that have been made in azaborine chemistry, significant synthetic challenges must still be overcome in order to unleash the full potential of azaborine heterocycles. The reported synthesis of the parent 1,2-azaborine **4**, illustrated in Scheme 1, makes the case in point; the synthesis is seven steps long with an overall isolated yield of 0.9%.[16] The use of high-molecular-weight reagents (e.g.,

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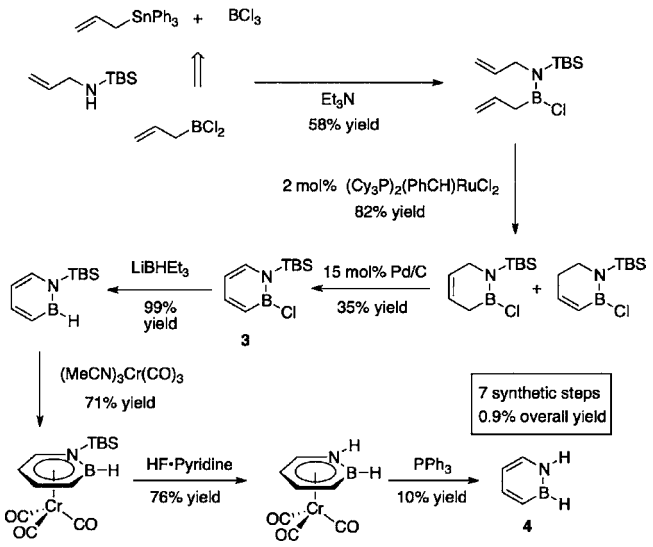
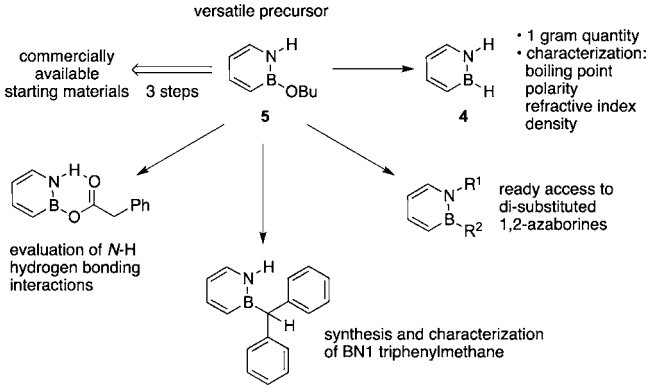
**Scheme 1. Reported Synthesis of the Parent 1,2-Dihydro-1,2-azaborine 4**




allyltriphenyltin) and the multiple protecting group manipulations (e.g., the purpose of the last three steps is simply to remove the *N*-TBS group) are certainly not compatible with the principles of an atom-economic and green process.[17] While a significant milestone, the costly synthesis of the parent 1,2-azaborine **4** prevented access to sufficient quantities of material needed for further characterization studies.

This article describes an efficient synthetic route toward 1,2-azaborine heterocycles. The key strategic advance is the removal of protecting-group manipulations on nitrogen, resulting in a simple three-step synthesis of a versatile 1,2-azaborine synthon **5**, which can subsequently be readily functionalized at both the nitrogen and boron positions (Scheme 2). We demonstrate that the parent 1,2-azaborine **4**

**Scheme 2. Summary of this Work**

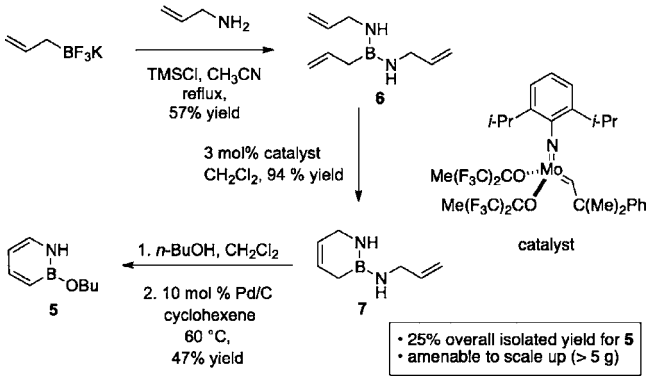



can be accessed in gram quantities using this new synthetic route, allowing previously unfeasible experimental characterization of its properties such as boiling point, density, polarity, and refractive index. Furthermore, precursor **5** allows access to new BN heterocycles that reveal intriguing bonding features as a result of BN/CC isosterism.

## 2. RESULTS AND DISCUSSION

**Synthesis of Precursor 5.** Scheme 3 illustrates the synthesis of 1,2-azaborine synthon **5**. By generating allylboron

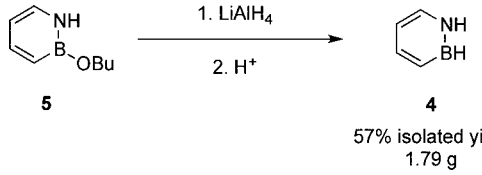
**Scheme 3. Synthesis of Synthon 5**




dichloride in situ from the commercially available potassium allyltrifluoroborate,[18] we eliminate the need for the use of the high-molecular-weight allyltin reagent employed in our previous synthesis. Instead of keeping one of the *B*−Cl bonds intact (previous synthesis), we substitute both *B*−Cl bonds at once with allylamine to afford the much less reactive **6**.[19] By eliminating the reactive *B*−Cl bond, we negate the need for an *N*-protecting group. Ring-closing metathesis with Schrock's Mo catalyst allows access to heterocycle **7** in 94% yield with the *N*−H bond intact. Substitution of the *B*-allylamino fragment with *n*-butanol followed by oxidation in the presence of catalytic amounts of Pd/C affords **5** in 47% yield.[20] This route produces gram quantities of compound **5** in an overall isolated yield of 25%.

**Gram-Scale Synthesis and Characterization of the Parent 1,2-Azaborine.** The parent 1,2-azaborine **4** can be generated from precursor **5** in a single step. Thus, our new protocol achieves the preparation of **4** in just four steps from commercially available starting materials instead of the seven steps used in the original synthesis. Scheme 4 shows that treatment of neat **5** with $LiAlH_4$ followed by quenching with decanoic acid results in the isolation of clean parent **4** in 57% isolated yield.

**Scheme 4. Gram-Scale Synthesis of Parent 1,2-Azaborine 4**




This newfound synthetic efficiency enables further characterization of the parent 1,2-azaborine **4** that was previously considered impractical due to lack of available material. The boiling point of **4**, measured to be 117 °C, was found by heating the material to reflux in a distillation apparatus and recording the temperature when the reflux had reached a steady state on the apparatus thermometer. The density of **4** was measured to be 0.904 g/mL by recording the mass of 800 $\mu$L of material, and the refractive index ($n_D$) was measured to be 1.528. We used Reichardt's betaine dye (2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate) as a solvatochromic indicator to evaluate the polarity of **4**. The $E_T(30)$ polarity scale is based on the $\lambda_{max}$ of absorptions of Reichardt's dye in various solvents. The $E_T(30)$ scale is defined by eq 1,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$$E_T(30)(\text{kcal mol}^{-1}) = \frac{28591}{\lambda_{max}^{abs}(\text{nm})} \quad (1)$$

where $\lambda_{max}$ is the wavelength at the maximum of the longest-wavelength intramolecular charge-transfer $\pi-\pi^*$ absorption band of Reichardt's dye.[21] Charge-transfer absorption wavelengths range from $\lambda_{max}$ = 453 nm in water (polar solvent) to $\lambda_{max}$ = 925 nm in hexane (nonpolar solvent). Figure 2 shows

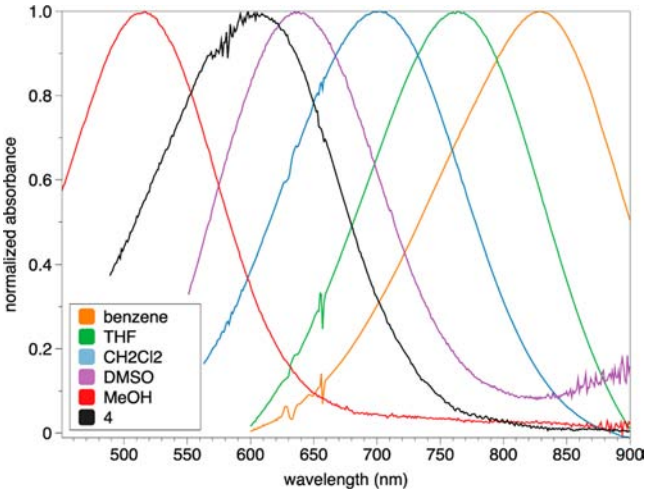
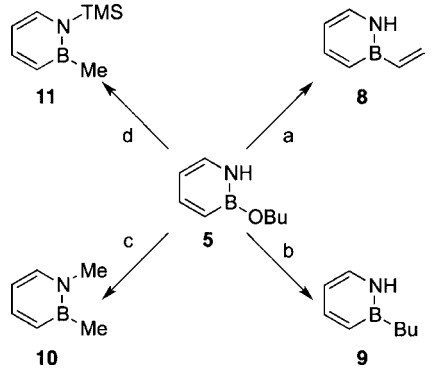



**Figure 2.** Solvatochromic studies using Reichardt's betaine dye.

that on the basis of $E_T(30)$ analysis, the polarity of the parent 1,2-azaborine **4** ($E_T(30)$ = 47.8 kcal/mol) is significantly higher than that of its carbonaceous counterpart, benzene ($E_T(30)$ = 34.3 kcal/mol), and similar to that of DMSO ($E_T(30)$ = 45.1 kcal/mol).

**Functionalization of Precursor 5.** Synthon **5** provides access to free-*N*H-containing BN isosteres of corresponding phenyl-based molecules. Addition of vinylmagnesium bromide to **5** followed by acidic workup affords BN styrene analogue **8**[22] in 62% yield (Scheme 5, path a). Similarly, treatment of **5** with *n*-BuLi followed by acidic workup furnishes the *B*-*n*-Bu derivative **9** in 83% yield. Synthon **5** also serves as a precursor to disubstituted (both at boron and nitrogen) 1,2-azaborines. The addition of MeLi to **5** installs a methyl group on boron, which can then be treated with electrophiles such as methyl

**Scheme 5. Functionalization of Synthon 5**[a]

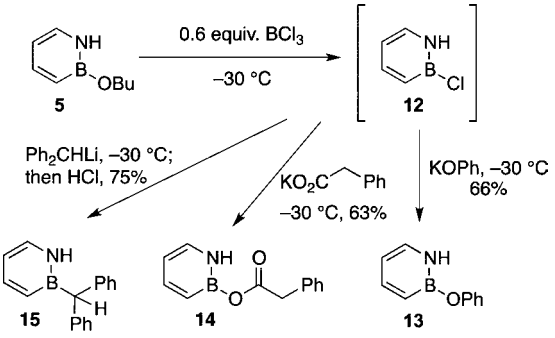



[a]Conditions: a) vinylMgBr, −30 °C $Et_2O$; HCl, 62%; b) *n*-BuLi, −30 °C $Et_2O$; HCl, 83%; c) MeLi, −30 °C $Et_2O$; MeI, 49%; d) MeLi, −30 °C $Et_2O$; TMSCl, 63%.

iodide (path c) or trimethylsilyl chloride (path d) to afford the BN *o*-xylene analogue **10** and the *B*-Me *N*-TMS 1,2-azaborine **11** in 49% and 63% yield, respectively.

Intermediate **5** can be activated toward nucleophilic attack by weaker nucleophiles that are incapable of displacing the strong B−O bond in **5**. Scheme 6 shows that treatment of **5** with $BCl_3$

**Scheme 6. Reactions of in Situ-Generated *B*-Cl Intermediate 12**




generates in situ the more reactive *B*−Cl *N*−H azaborine **12** at −30 °C. Subsequent reaction of intermediate **12** with the potassium phenoxide readily creates the diphenyl ether mimic **13**. The potassium salt of phenylacetic acid also readily adds to form the crystalline product **14**. Finally, treatment of **12** with diphenylmethyllithium followed by acidic workup affords the BN1 triphenylmethane analogue **15** in 75% yield.[23]

**Structure of Compound 14.** Crystals suitable for single-crystal X-ray diffraction analysis of compound **14** were grown from a concentrated solution of **14** in pentane. All H atoms were found on the residual density map and refined without restrictions. The intraring bond distances of the BN heterocycle are consistent with an azaborine bearing an electron-withdrawing *B*-substituent (Figure 3). In particular, the relatively

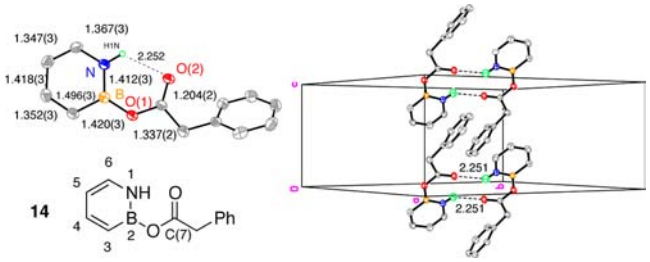



**Figure 3.** (Left) ORTEP illustrations, with thermal ellipsoids drawn at the 35% probability level. (Right) Packing diagram of compound **14**.

short boron−nitrogen (1.412(3) Å) and boron−carbon distances (1.496(3) Å) are shorter than those in a typical *B*-alkoxide substituted 1,2-azaborine (B−*N* = 1.436(2) Å, B−*C* = 1.518(2) Å)[15] and on par with those exhibited by 1,2-azaborine borenium cations (e.g., for $Ph_3P{=}O$ adduct: B−*N* = 1.420(3) Å, B−*C* = 1.496(3) Å).[24] The exocyclic oxygen atom O(1) of **14** is mostly $sp^2$-hybridized, with B−O(1)−C(7) = 127.4(1)°. The C(7)−O(1)−B−N torsion angle of 7.7(3)° and the B−O(1) bond distance of 1.420(3) Å suggest some double-bond character between oxygen and boron (sum of single-bond covalent radii = 1.48 Å).[25] However, compared to a typical *B*-alkoxide substituted 1,2-azaborine (B−*O* = 1.389(2) Å),[15] the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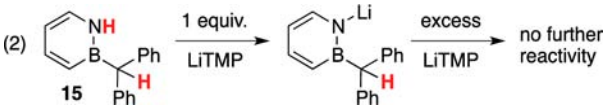
observed B−O distance in **14** is significantly longer, indicating weakening of the B−O $\pi$ bonding in compound **14**.

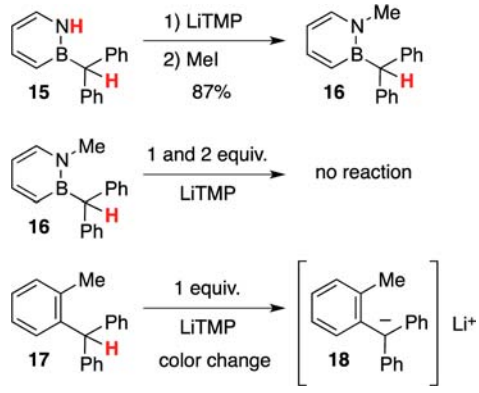
The most unique feature of the structure of **14** is the coplanar orientation between the BN heterocycle and the ester group (B−O(1)−C(7)−O(2) torsion angle = 3.1(3)°). A survey of structures of phenyl carboxylic esters (compound **14** is the BN isostere of phenyl phenylacetate) shows that the preferred orientation between the ester group and the carbonaceous phenyl ring is a perpendicular one, not a coplanar arrangement.[26] The coplanar conformation observed in **14** may be a result of hydrogen bonding between H1N and O(2) (distance = 2.252 Å).[27] It is also worth noting that intermolecular hydrogen bonding (distance = 2.251 Å) between two molecules of **14** is observed in the solid state (see packing diagram in Figure 3). The elongated C(7)═O(2) bond (1.204 (2) Å vs ∼1.195 Å[26] for a typical C═O ester bond) and the shortened C(7)−O(1) bond (1.337 (2) Å vs ∼1.356 Å[26] for a typical C−O ester bond) are consistent with O(2) serving as a hydrogen-bond acceptor. The observed C═O stretching frequency of 1703 $cm^{-1}$ for compound **14** is significantly lower than that of phenyl phenylacetate (1749 $cm^{-1}$),[28] which is also consistent with hydrogen bonding. Overall, we conclude that compound **14** exhibits unique bonding features that are very distinct from its carbonaceous counterpart, highlighting the potential of diversity that can be created by BN/CC isosterism.

**BN1 Triphenylmethane 15.** Triphenylmethane is a molecule of fundamental importance in understanding resonance stabilization of organic anions, cations, and radicals. The central carbon on triphenylmethane is significantly more acidic ($pK_a$ = 30.6 in DMSO)[29] than most hydrocarbons, due to resonance stabilization of the resulting anion by the conjugated $\pi$-system. We sought to investigate the consequence of BN/CC isosterism on the acidity of the methyne proton of triphenylene by evaluating the acid−base chemistry of BN1 triphenylmethane **15**, which we prepared according to Scheme 6. Compound **15** has the potential to be deprotonated at multiple sites (*N*H and *C*H). Treatment of BN1 triphenylmethane **15** with 1 equiv of lithium tetramethylpiperidine (LiTMP; $pK_a$ of TMP = 37.3)[30] deprotonated only the *N*H of the 1,2-azaborine ring ($pK_a \approx 26$),[14] leaving the methyne *C*H untouched (eq 2). Subsequent addition of excess LiTMP (up to 5 equiv total) also did not remove the methyne *C*H.




It appeared that the *N*H group in **15** is interfering with the investigation of the acid−base chemistry of the methyne *C*H in **15**. Thus, we replaced the protic *N*H of **15** with an *N*-methyl group. Treatment of **15** with LiTMP followed by addition of methyl iodide yielded *N*-protected compound **16** as a crystalline solid in 87% yield (Scheme 7, top). Compound **16** was subjected to 1 and 2 equiv of LiTMP, however, no deprotonation of the methyne *C*H was observed (Scheme 7, middle). The use of PhLi ($pK_a$ of bezene = 43) resulted in nucleophilic addition to boron, not in the desired deprotonation.[31] On the other hand, the all-carbon *o*-tolyldiphenylmethane **17** readily underwent deprotonation when treated with 1 equiv of LiTMP, producing the red-colored deprotonated species **18** (Scheme 7, bottom).[32]

**Scheme 7. Synthesis and Acid−Base Chemistry of 16**




Unfortunately, the electrophilicity of boron prevented definitive $pK_a$ determination of the central methylene *C*H on our BN-triphenylmethane system using bracketing experiments. Nevertheless, one conclusion that we can draw from our experiments is that the methyne *C*H in **16** is significantly less acidic than its carbonaceous counterpart. This is consistent with the increase in $pK_a$ value of the *N*H proton in BN indole when compared to the natural indole.[33] The boron atom appears to exert a substantial inductive effect on its neighboring atoms that reduces their ability to stabilize negative charge.

Slow evaporation of an etheric solution of **16** yielded crystals suitable for single-crystal X-ray diffraction analysis. Both triphenylmethane and **16** display propeller-like geometry in the solid state, with edge-to-face orientation between the rings of neighboring molecules. The CC bond lengths within the rings of triphenylmethane and **16** are very similar, but significant differences associated with BN/CC isosterism are seen between the intraring bond distances of the BN heterocyclic portion of **16** and the corresponding CC distances in triphenylmethane (Figure 4). These differences are due to the relatively large covalent radius of boron and the relatively short covalent radius of nitrogen in comparison to carbon.[25a]

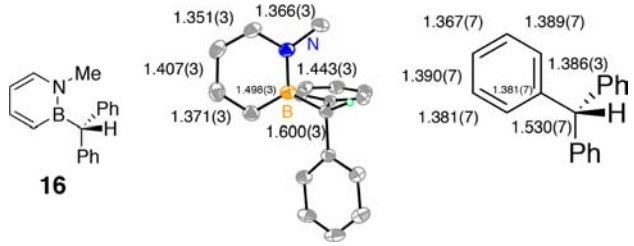



**Figure 4.** ORTEP illustration of *N*-Me-BN1-triphenylmethane **16** with thermal ellipsoids drawn at the 35% level.

## 3. CONCLUSION

We have demonstrated the utility of our new 1,2-azaborine synthon **5** in the rapid construction of *BN* analogs of fundamentally interesting benzenoids that were previously inaccessible. Synthesis of the BN isostere of phenyl phenylacetate **14** revealed the presence of *N*H-carbonyl hydrogen bonding that is not present in the corresponding carbonaceous analogue. Synthesis of BN1 triphenylmethane derivatives **15** and **16** allowed us to determine that the methyne *C*H proton of BN1 triphenylmethane is much less acidic than that of triphenylmethane itself. The synthetic economy gained by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circumventing protection/deprotection protocols enables access to diverse 1,2-azaborine structures in four synthetic steps. This is exemplified in the gram-quantity synthesis of the parent 1,2-azaborine **4**, enabling the characterization of its boiling point, density, refractive index, and its polarity on the $E_T(30)$ scale. With less time and resources required for the synthesis of 1,2-azaborine structures, efforts can be redirected toward studying the properties of these heterocycles and exploring possible applications derived thereof.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures, spectroscopic data, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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