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Aminoboranes via Tandem Iodination/Dehydroiodination for One-Pot Borylation

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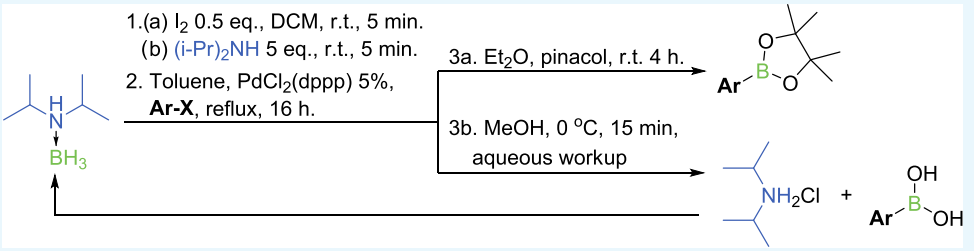

ABSTRACT: A rapid synthesis of aminoboranes from amine-boranes utilizing an iodination/dehydroiodination sequence is described. Monomeric aminoboranes are generated exclusively from several substrate adducts, following an E2-type elimination, with the added base playing a critical role in monomer vs dimer formation. Diisopropylaminoborane formed using this methodology has been applied to a one-pot palladium-catalyzed conversion of iodo- and bromoarenes to the corresponding boronates. Additionally, modification of the workup allows for isolation of the boronic acid and recovery of the utilized amine.

INTRODUCTION

Aminoboranes of the type $R_2N\text{-}BH_2$,[1] commonly obtained from amine-boranes ($R_2NH\text{-}BH_3$), have received considerable attention as valuable precursors for organic and material chemistry applications.[2−13] Borylations employing a variety of metal catalysts[2] and leaving groups[2a,b,3] have been developed, including for C−H borylation.[2d] Suitable aryl,[2a−d,3,4] alkenyl,[4a,5] and alkynyl[2e,f] substrates can be converted to boronate esters,[2b−d,3b,6] their complexes,[7] and boronic and borinic acids.[3a,7,8] They have been used for the preparation of polyaminoboranes[9] and boron nitride ceramics,[10] with recent uses in the production of molecular sensors,[11] mechanochromic materials,[12] and metal thin films.[13]

Despite all of these developments, there is still a need for a convenient synthesis of aminoboranes. One of the earliest routes involved the reduction of aminodihaloboranes with lithium aluminum hydride [Scheme 1. (i)].[14] Large-scale synthesis of aminoboranes using this protocol is limited by the highly reactive nature of the hydride and boron halide reagents. This method has since been supplanted by the thermal dehydrogenation of amine-boranes [Scheme 1. (ii)][2a] and reaction of lithium aminoborohydrides with suitable organohalides [Scheme 1. (iii)].[15] These routes, however, require elevated temperatures (160−220 °C) or the use of highly sensitive reagents (*n*-BuLi). Recently, Pucheault and coworkers reported the dehydrohalogenation of monochloroborane−amine complexes (which have been reported elsewhere[16]) for the preparation of aminoboranes [Scheme 1. (iv)].[6b] The dry, ethereal HCl utilized in this preparation is cumbersome to prepare,[17] and although it is commercially available, it is expensive relative to other halogen sources. Ethereal HCl is typically prepared at concentrations of 1−2 M, as more concentrated solutions tend to expel the highly corrosive HCl gas. Release of the solute gas and the low boiling point of the solvent necessitate frequent titration, as precise stoichiometry is critical for the preparation of monochloroborane-amines. Treatment of amine-boranes with *N*-halosuccinimides[18] or molecular halogens[16a,19] and the disproportionation reaction of BH_3- and BX_3-amines (X = halogen)[16a] are some of the other procedures that exist for the conversion of amine-boranes to haloborane−amine complexes.

As part of our ongoing projects on amine-boranes,[20] we were interested in developing a simple protocol for the preparation of aminoboranes. It occurred to us that the halogenation of amine-boranes with molecular halogens might provide a more convenient protocol. Although known for several decades,[16a] the potential utility of this protocol has not been exploited fully in organic synthesis. Described herein are the details of a simple route to aminoboranes via dehydrohalogenation of appropriate monoiodoborane−amine complexes [Scheme 1. (v)], avoiding the limitations of the previous protocols. This

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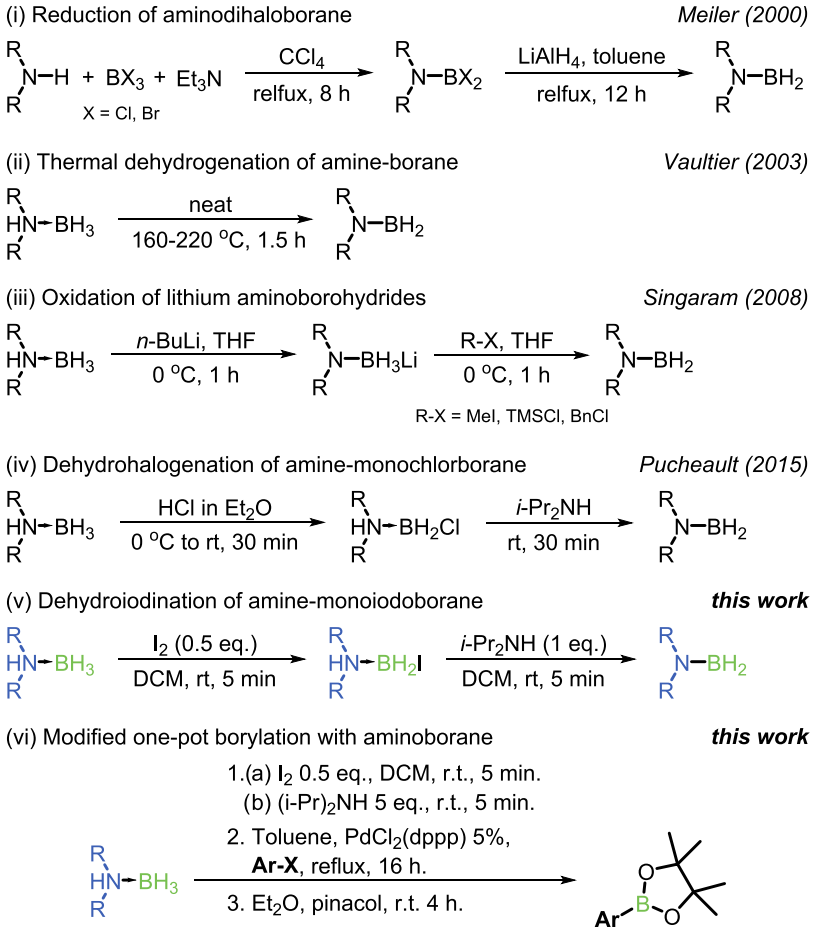
Scheme 1. Preparation of Aminoboranes and One-Pot Borylation



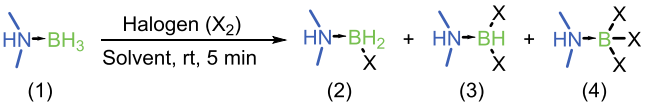
methodology has been extended to a modified Pd-catalyzed *one-pot* borylation of aryl halides [Scheme 1. (vi)].

RESULTS AND DISCUSSION

Halogenation. Over 60 years ago, Nöth described the monoiodination of trimethylamine-borane with molecular iodine in benzene.[16a] A similar procedure to prepare alkylhaloboranes from alkylboranes has also been reported.[21] Our initial attempts sought to optimize the conditions for the halogenation of a dialkylamine-borane by reacting dimethylamine-borane (**1c**) with 0.5 and 1.0 equiv of either bromine or iodine in CH_2Cl_2 or toluene and following the reaction by ^{11}B NMR spectroscopy.

With bromine, the nearly instantaneous halogenation readily went past the monohaloborane (Table 1 (2)) stage, providing appreciable quantities of the di- (Table 1 (3)) and trihalogenated boranes (Table 1 (4)), as detected in the ^{11}B NMR spectrum. Using 0.5 equiv of Br_2 also led to the formation of a mixture of di- and monobromoborane-amine in a 3:1 ratio. On the other hand, when 0.5 equiv of iodine was utilized, the amine-monohaloborane could be reliably produced in either solvent. Even a stoichiometric equivalent of iodine provided the monoiodoborane predominantly (80%). Halogenation of diisopropylamine-borane (**1f**) using *N*-chlorosuccinimide (NCS) and *N*-bromosuccinimide (NBS) was also examined as a potential route to the amine monohaloborane complexes. A full equivalent of NCS provided the desired monochloroborane, whereas NBS gave a mixture of mono- and dihalogenated products (Table 1).

Table 1. Optimization of Halogen and Solvent Study[a]



entry	halogen (equiv)	amine-borane	solvent	^{11}B NMR peak ratio (1:2:3:4)[b]
1	I_2 (0.5)	**1c**	DCM	0:1:0:0
2	I_2 (1.0)	**1c**	DCM	0:4:1:0
3	Br_2 (0.5)	**1c**	DCM	1.25:1:3:0
4	Br_2 (1.0)	**1c**	DCM	0:1:1:0.75
5	I_2 (0.5)	**1c**	$CHCl_3$	indeterminate
6	I_2 (0.5)	**1c**	Et_2O	indeterminate
7	I_2 (0.5)	**1c**	PhMe	0:1:0:0
8	I_2 (0.5)	**1c**	Pentane	**1c** insoluble
9	NCS (1.0)	**1f**	DCM	0:1:0:0
10	NBS (1.0)	**1f**	DCM	1:1.6:2.1:0

[a]Reactions were performed at a 2 mmol scale with respect to the amine-borane. [b]Ratio determined by ^{11}B NMR (96 MHz) spectroscopy.

The scope of the iodination was demonstrated with a series of amine-boranes (**1a**−**1q**), prepared from sodium borohydride via a bicarbonate-promoted reaction of the desired amine (**1b**−**1q**)[20c] or by salt metathesis of the corresponding ammonium hydrochloride (**1a**).[22] As detailed in Table 2, all

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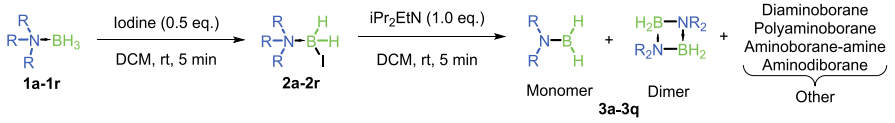
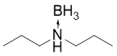
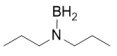
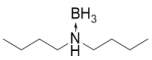
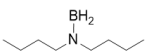
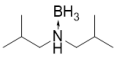
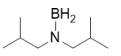
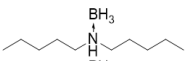
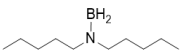
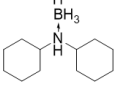
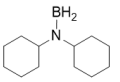
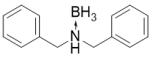
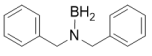
ACS Omega 2022, 7, 14377−14389

Table 2. Amine-Boranes Subjected to the Iodination/Dehydroiodination Sequence and Resulting Aminoboranes[a,b,c]



Entry	Amine-Borane #	Amine-Borane Structure	Amine-BH_2I[b] #	Aminoborane[c] #	Aminoborane[c] Structure	Monomer (%)	Dimer (%)	Other (%)
1	**1a**		**2a**	**3a**		11	14	76
2	**1b**		**2b**	**3b**		0	0	≥ 99
3	**1c**		**2c**	**3c**		22	58	20
4	**1d**		**2d**	**3d**		77	5	18
5	**1e**		**2e**	**3e**		78	0	22
6	**1f**		**2f**	**3f**		**≥ 99**	0	0
7	**1g**		**2g**	**3g**		80	0	20
8	**1h**		**2h**	**3h**		97	0	3
9	**1i**		**2i**	**3i**		86	0	14
10	**1j**		**2j**	**3j**		**≥ 99**	0	0
11	**1k**		**2k**	**3k**		23	70	7
12	**1l**		**2l**	**3l**		**≥ 99**	0	0
13	**1m**		**2m**	**3m**		21	0	79
14	**1n**		**2n**	**3n**		7	36	58
15	**1o**		**2o**	**3o**		59	30	11
16	**1p**		**2p**	**3p**		5	37	58
17	**1q**		**2q**	**3q**		**≥ 99**	0	0
18	**1r**		**2r**	**N/A**	-	-	-	-

[a]Reactions were performed at a 2 mmol scale with respect to the amine-borane. [b]Conversions were >99% by ^{11}B NMR (96 MHz) spectroscopy. [c]Composition determined by ^{11}B NMR (96 MHz) spectroscopy.

of the primary and secondary amine-borane complexes underwent quantitative iodination without any difficulty.[23]

Dehydrohalogenation. The dehydrohalogenation of these monoiodoborane−amine complexes was readily accomplished by the addition of a sufficiently bulky amine [*i*-Pr_2NEt (Hünig's base) or *i*-Pr_2NH] to the reaction mixture.[6b,16b] Quantitative conversion to the elimination products was observed in the ^{11}B NMR spectra. The monomeric or dimeric aminoborane species were typically produced, along with an equivalent of the corresponding ammonium iodide during the E2-type reaction (Table 2). Several groups[2a,14,15,24] previously used NMR spectroscopy, mass spectrometry, and X-ray crystallography to fully characterize both the aminoborane monomer[14,24a] and dimer[24,25] products. The assignment of ^{11}B NMR peaks to either monomer or dimer products in the present reaction was based on the similarity of ^{11}B NMR values observed from the fully characterized prior products. Similar complete characterizations have previously been made of the other proposed species detected in the present reaction including diaminoborane,[26] aminodiborane,[27] polyaminobor-

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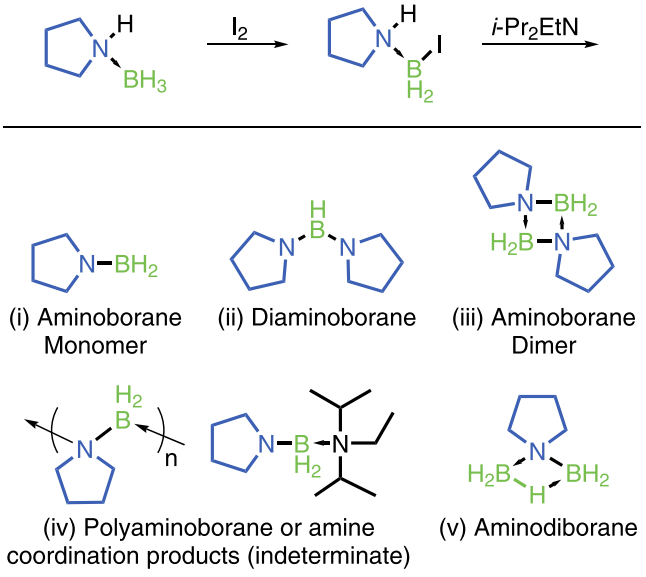
ACS Omega 2022, 7, 14377−14389

ane and amine-exchange products.[9,28] The proposed identities of these species are based on agreement between the ^{11}B NMR chemical shifts observed and those previously reported for similar fully characterized products. The iodination of pyrrolidine-borane and subsequent dehydroiodination using *N,N*-diisopropylethylamine (Scheme 2) followed by analysis using ^{11}B NMR spectroscopy revealed the formation of each of these products.

Scheme 2. Products of the Dehydrohalogenation Step



The spectrum obtained from the above reaction (Scheme 2) and the proposed identities of the chemical species represented by the peaks present in the spectrum are shown in Figure 1.

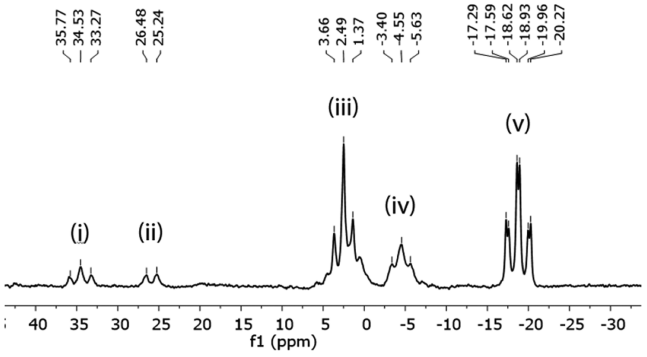
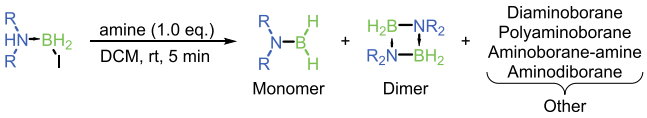


Figure 1. ^{11}B NMR (96 MHz) spectrum showing peaks that correspond to each of the dehydrohalogenation products.

It was noted that the reaction of Hünig's base with each of the amine-iodoborane complexes, other than isopropylamine-monoiodoborane, provided at least some amount of the aminoborane monomer. However, the primary iodoborane-amines (**1a**, **1b**) yielded very little of either the monomeric or dimeric aminoborane, but primarily a mixture of other boron species arising from the exchange of the amines present. The iodoborane complexes of secondary amines provided primarily aminoborane products, in either the monomeric or dimeric form, with the ratio dependent on the sterics of the amine in the borane complex. Compact or rigidly constrained amines, such as dimethylamine or piperidine, resulted in a higher proportion of dimeric aminoboranes (58 and 70%, respectively). Many of the iodoborane complexes of cyclic and acyclic secondary amines gave primarily the aminoborane monomer (**3d**−**3q**), with minimal formation of dimers or other products. Diisopropylaminoborane (**3f**), dicyclohexylaminoborane (**3j**), 2,6-dimethylpiperidinoborane (**3l**), and dibenzylaminoborane (**3q**) (entries 6, 10, 12, and 17 in Table 2) were each detected exclusively as the monomer (by ^{11}B NMR). The monochloroborane example produced from **1f** and NCS provided minimal monomer formation (~1%) with 1 or 2 equiv of *i*-Pr_2NEt, likely due to interference of the still present succinimide.

Influence of the Amines on Dehydrohalogenation. To assess the influence of the amine added as a base for the elimination, another series of dehydrohalogenation reactions was performed (Table 3). Iodoborane-amines with varying steric environments were reacted with amine bases with a range of substitutions (0° (NH_3), 1, 2, 3°) and sterics. The iodoboranes were prepared from diisopropylamine- (**1f**), dimethylamine- (**1c**), and piperidine-borane (**1k**), and their reactions with the added amines allowed for the identification of several trends in reactivity. The highly bulky iodoborane complex with diisopropylamine (**2f**) reacted with bulky amines, including diisopropyl-, dicyclohexyl-, diisobutyl-, and *N,N*-diisopropylethylamines to produce the diisopropylaminoborane monomer **3f** with 98−99% conversion. Slightly less hindered triethylamine and dibenzylamine provided 80−90% conversion to **3f**. The remainder of the 1° and less hindered 2° amines tested with **2f** gave what are presumed to be polyaminoborane or amine coordination products based on

Table 3. Aminoboranes Formed Using Various Amines[a,b]



entry	amine-borane	added amine	monomer (%)	dimer (%)	other (%)
1	**1f**	*i*-Pr_2NH	≥99	0	0
2	**1f**	Et_2NH	0	0	≥99
3	**1f**	Propylamine	0	0	≥99
4	**1f**	*t*-$BuNH_2$	0	0	≥99
5	**1f**	$BnNH_2$	0	0	≥99
6	**1f**	Bn_2NH	90	0	10
7	**1f**	Chx_2NH	≥99	0	0
8	**1f**	*i*-Bu_2NH	98	0	2
9	**1f**	Azepane	0	0	≥99
10	**1f**	Piperidine	0	0	≥99
11	**1f**	Morpholine	0	0	≥99
12	**1f**	Ammonia	0	0	≥99
13	**1f**	Et_3N	80	0	20
14	**1f**	*i*-Pr_2EtN	≥99	0	0
15	**1f**	Pyridine	0	0	≥99
16	**1c**	Piperidine	0	0	≥99
17	**1c**	Et_3N	1	40	59
18	**1c**	*i*-Pr_2EtN	7	77	16
19	**1k**	Piperidine	0	0	≥99
20	**1k**	*i*-Pr_2EtN	2	89	9

[a]Reactions were performed at the 2 mmol scale with respect to the amine-borane. [b]Ratio determined by ^{11}B NMR (96 MHz) spectroscopy.

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ACS Omega 2022, 7, 14377−14389

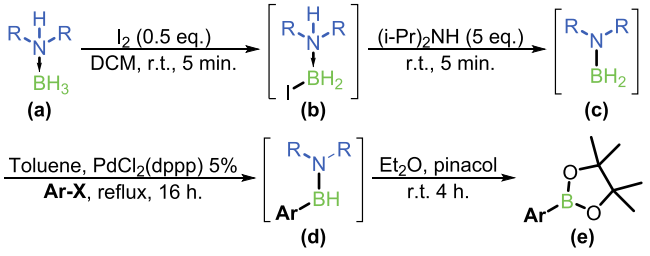
prior reports of these compounds made from diisopropylaminoborane.[9,28] A similar species was observed when unhindered **2c** was reacted with piperidine.

In the reactions of **2c**, increasing the bulk of the added amine (triethylamine and *N,N*-diisopropylethylamine) led to the partial formation of the dimeric dimethylaminoborane, 40% and 77%, respectively. A small amount of monomeric aminoborane was additionally detected in each case, 1% and 7%, respectively. The reaction of **2k** with piperidine gave the polyaminoborane exclusively, while *N,N*-diisopropylethylamine gave mainly (89%) dimeric aminoborane, with traces (2%) of the monomer present.

One-Pot Borylation. Arylboronates and boronic acids have traditionally been prepared by the reaction of trialkoxyboranes with aryl lithium[29] or Grignard reagents.[30] However, these organometallic reagents are highly reactive, making them incompatible with many functional groups. More recently, Miyaura and co-workers have reported the palladium-catalyzed cross-coupling reaction between aryl halides and bis(pinacolato)diboron (B_2pin_2).[31] This was later extended by Masuda to utilize pinacolborane (HBpin).[32] Although both B_2pin_2 and HBpin are commercially available, these reagents are costly and half of the B_2pin_2 reagent goes unused in the cross-coupling reaction. The preparation of B_2pin_2[33] is lengthy and uses highly reactive reagents (BBr_3, Na) and HBpin[34] uses unpleasant borane-dimethylsulfide. In 2003, Alcaraz and Vaultier utilized diisopropylaminoborane as an efficient source of boron for palladium catalyst borylation.[2a] Although the aminoborane precursor amine-boranes were expensive in 2003, there are now several simple procedures for their preparation from the corresponding amines using sodium borohydride and benign activators such as $NaHCO_3$[20c] and CO_2.[35]

As a further confirmation of the formation of aminoboranes from the iodination/dehydroiodination sequence, the presumed aminoboranes were subjected to palladium-catalyzed borylation of aryl halides, as described by Pucheault and Vaultier.[6b] To simplify the protocol, and further persuade organic chemists to embrace this process for Suzuki coupling,[36] we made two modifications to the above borylation protocol. (i) Separation of the ammonium salt formed during the dehydrohalogenation reaction was excluded since the salt from the borylation catalytic cycle does not interfere in the reaction.[6a,37,21] Reactions were performed with and without filtration of the salt, and identical overall yields (95%) were observed for the borylation of 4-iodoanisole with **3f**. This change makes the process one-pot. Also, (ii) "quenching" of the arylaminoborane intermediate with methanol, followed by transesterification with pinacol, was replaced with a direct pinacol "quench" without any loss in yield of the pinacol boronate (Scheme 3).

Scheme 3. Proposed Pathway for the One-Pot Synthesis of Pinacol Arylboronates from Amine-Boranes



The progress of the borylation of 4-iodoanisole was monitored, and the proposed intermediates, shown in Scheme 3, were confirmed by ^{11}B NMR spectroscopy. Starting from diisopropylamine-borane (δ −21.80 (q): Figure 2a), iodine

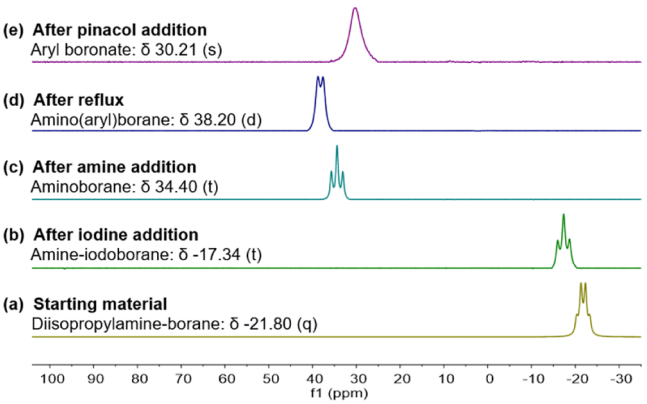


Figure 2. ^{11}B NMR (96 MHz) spectra depicting the progress of the one-pot conversion of amine-borane to arylboronates.

and amine addition leads to the peaks at δ −17.34 (t) and δ 34.40 (t) (Figure 2b,c, respectively). After reflux, the amino(aryl)borane intermediate was detected at δ 38.20 (Figure 2d). Addition of pinacol results in a slight upfield shift to δ 30.21 (s) (Figure 2e), representative of the pinacol boronate.

The optimized conditions shown in Scheme 3 were tested with several amine-boranes, such as monomer-forming dicyclohexylamine- (**1j**) and dibenzylamine-borane (**1q**), as well as the primarily dimer-forming dimethylamine-borane (**1c**) for the reaction. These complexes gave 90%, 91%, and 58% yields, respectively, as compared to the 95% yield with **1f** (Table 4).

Table 4. Study of Amine-Boranes as Boron Sources for One-Pot Borylation of Aryl Halides[a]

entry	amine-borane	monomer (%)	product obtained	yield[b] (%)
1	**1c**	7−22	**4a**	58
2	**1f**	≥99	**4a**	95
3	**1j**	≥99	**4a**	90
4	**1q**	≥99	**4a**	91

[a]Reactions were performed using 4-iodoanisole at the 1 mmol scale with respect to the aryl halide. [b]Isolated yields after flash chromatography are shown.

With the 58% product recovery when using dimeric aminoborane **3c**, we have demonstrated that dimers also participate in the borylation, *albeit* at a slower rate. Attempts are under way to improve the yields. Examination of bromine- and chlorine-containing arenes was also carried out with 4-bromo- and 4-chloroanisole. While the former provided 95% of the borylated product, the latter was unreactive, indicating that chlorine is not a suitable leaving group under the current reaction conditions (Table 5).[37,38]

Following confirmation of the reaction pathway, a series of aryl iodides or bromides were subjected to the above-described reaction conditions where 4-iodoanisole provided the boronate **4a** in 95% yield. Other ether-containing 4-ethoxy- (**4b**), 4-methoxy-2-methyl- (**4c**), 6-methoxynaphthyl- (**4d**), and 2,3-dihydrobenzofuryl- (**4e**) aryl halides gave equally high yields

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Table 5. Leaving Groups Studied for One-Pot Borylation[a]

entry	amine-borane	starting material	product obtained	yield[b] (%)
1	**1f**	$MeOC_6H_4$-Cl	none	
2	**1f**	$MeOC_6H_4$-Br	**9a**	95
3	**1f**	$MeOC_6H_4$-I	**9a**	95

[a]Reactions were performed at the 1 mmol scale with respect to the aryl halide. [b]Isolated yields after flash chromatography are shown.

(96%, 94%, 97%, and 98%, respectively). Unadorned bromobenzene (**4f**), as well as its counterparts with systems of extended conjugation, 2-naphthyl- (**4g**), 1-naphthyl- (**4h**), and 9-phenanthyl- (**4i**) halides, and hydrocarbon substituents, 4-methyl- (**4j**), 4-phenyl- (**4k**), and 3,5-di-t-butyl- (**4l**) aryl halides, all gave the corresponding boronates in excellent yields (97−99%). However, the 2,4,6-substituted bromomesitylene proved to be too sterically encumbered to undergo the reaction, and no product was isolated.

Boronates of functionalized aryl halides with methylthio- (**4m**), nitrile- (**4n**), and dimethylamino- (**4o**) groups were obtained in 96, 65, and 70%, respectively. However, substrates with reducible functionalities (keto-, formyl-, amido-, and nitro) provided mixtures of other products along with small quantities of the expected borylated products. Borylation of aryl halides with other ring halogens (chlorine or fluorine) was also shown to be feasible. 4-Chloro- (**4p**), 3,5-dichloro- (**4q**), 4-fluoro- (**4r**), and 4-trifluoromethyl- (**4s**) iodobenzenes gave the corresponding boronates in 89−99% yields. Attempted borylation of pentafluoroiodobenzene, however, gave none of the boronate ester. The results from the study of the substrate scope are summarized in Figure 3.

Amine Recycling. The reaction sequences in Scheme 3 suggested that the ammonium salt byproduct from both the borylation cycle and aminoborane synthesis could be recovered and recycled to regenerate the amine-borane. Applying an alteration in the workup procedure (Scheme 4) for the borylation of 4-iodoanisole provided 83% of 4-methoxyphenylboronic acid (**5a**) along with 86% of diisopropylammonium chloride. The recovered ammonium salt can be converted to the starting amine-borane via the salt metathesis protocol.[19] Though diisopropylamine is relatively inexpensive, the demonstrated recovery of the amine can be useful when a more valuable amine is utilized.

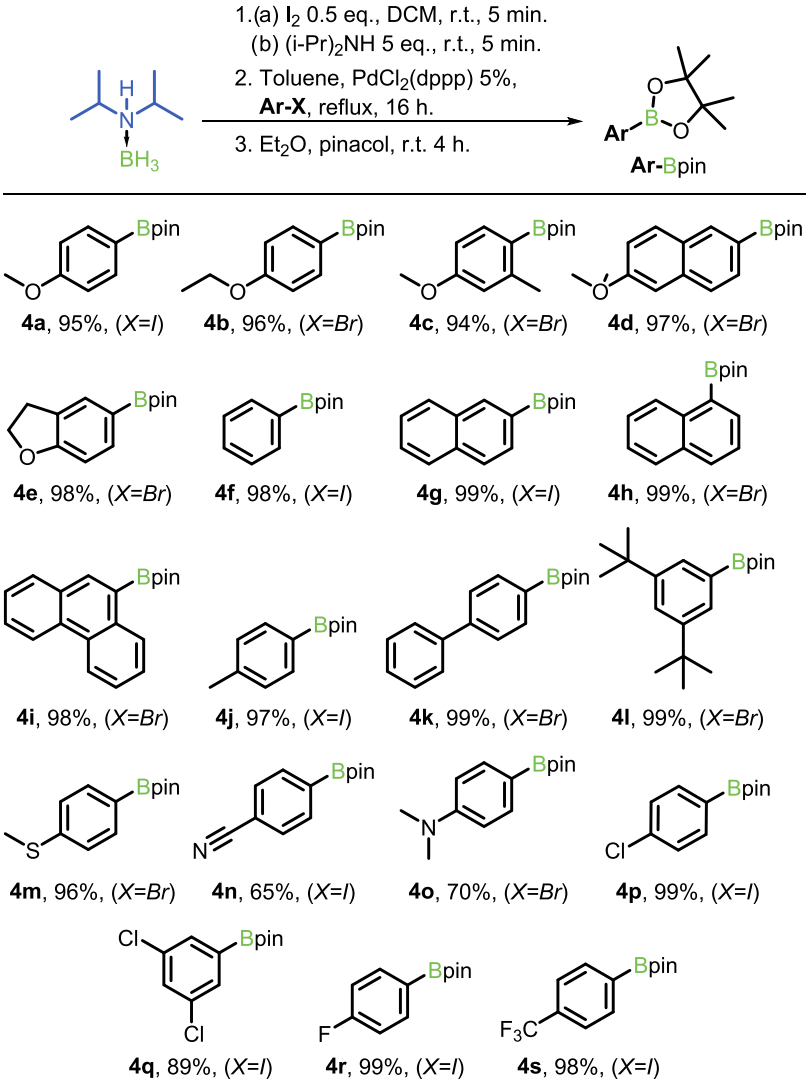

Figure 3. Scope of the one-pot borylation from amine-boranes.[a,b] [a]Reactions were performed at the 1 mmol scale with respect to the aryl halide. [b]Isolated yields after flash chromatography are shown.

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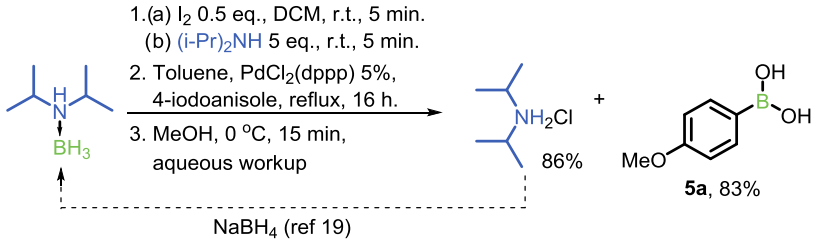
Scheme 4. Recovery of Diisopropylammonium Salt/Boronic Acid, and Regeneration of Amine-Borane[a,b]



[a]Reaction was performed at the 1 mmol scale with respect to the aryl halide. [b]Isolated yields after aqueous workup are shown.

CONCLUSIONS

In summary, we have described the preparation of aminoboranes, within minutes, at room temperature, in reagent-grade solvents from amine-boranes via an iodination-dehydroiodination sequence. Monomeric or dimeric aminoboranes can be produced by alteration of the coordinated amine, and the amine used for dehydrohalogenation, with the monomers being formed exclusively in several cases. Application of these monomeric aminoboranes has been demonstrated for a one-pot palladium-catalyzed conversion of aryl iodides and bromides containing substituents with varying steric and electronic environments to the corresponding boronate esters and boronic acids.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all manipulations were carried out under open air conditions. ^{11}B,^{19}F,^{13}C, and ^{1}H NMR spectra were recorded at room temperature, on a Varian INOVA 300 MHz NMR spectrophotometer. Chemical shifts (δ values) are reported in parts per million relative to $BF_3{\cdot}Et_2O$ for ^{11}B NMR. Data are reported as: δ value, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; h, hextet; hept, heptet; m, multiplet; br, broad) and integration. All solvents for routine isolation of products were reagent-grade. Sodium borohydride (powder, purity >99% by hydride estimation 1) was purchased from Oakwood Chemical. Tetrahydrofuran (THF, ACS reagent >99.0% containing 0.004% water and 0.025% BHT), toluene (anhydrous, ≥99.8%), iodine (ACS reagent, ≥99.8%), bromine (reagent grade), *N*-chlorosuccinimide (ReagentPlus, 99%), and *N*-bromosuccinimide (ReagentPlus, 99%) were purchased from Sigma-Aldrich. All amines, aryl halides, and pinacol were purchased from commercial sources and used without further purification. Flash chromatography was performed using silica gel 40−63 um, 60 Å with diethyl ether as the eluent.

Preparation of Amine Boranes via Sodium Bicarbonate (AB Procedure 1). Sodium borohydride (1.51 g, 2 equiv, 40 mmol) and powdered sodium bicarbonate (6.72 g, 4 equiv, 80 mmol) were transferred to a 100 mL dry round-bottom flask, charged with a magnetic stir-bar. The corresponding amine (1 equiv, 20 mmol) was charged into the reaction flask followed by addition of reagent-grade tetrahydrofuran (20 mL) at rt. Under vigorous stirring, water (0.36 mL, 4 equiv, 80 mmol) was added dropwise to prevent excessive frothing. Reaction progress was monitored by ^{11}B NMR spectroscopy. (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment to solubilize $NaBH_4$.) Upon completion of the reaction (4−48 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue was washed with THF. Removal of the solvent in vacuo from the filtrate yielded the corresponding amine-borane (**1b**, **1d**−**1r**). The residual solvent was removed by placing under a high vacuum for ∼12 h.

*Isopropylamine-borane (**1b**).* **1b** was synthesized using AB Procedure 1, obtained as a white solid (91%, 1.327 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.75 (s, 2H), 2.98 (dp, J = 12.9, 6.4 Hz, 1H), 1.22 (d, J = 6.5 Hz, 6H); ^{13}C NMR (75 MHz, chloroform-*d*) δ 50.2, 21.8; ^{11}B NMR (96 MHz, chloroform-*d*) δ −20.99 (q, J = 95.3 Hz).

*Diethylamine-borane (**1d**).* **1d** was synthesized using AB Procedure 1, obtained as a colorless liquid (95%, 1.652 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.58 (s, 1H), 2.72 (qd, J = 7.3, 5.6 Hz, 4H), 1.16 (t, J = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 48.8, 11.6.^{11}B NMR (96 MHz, chloroform-*d*) δ −17.44 (q, J = 95.9, 95.4 Hz).

*Dipropylamine-borane (**1e**).* **1e** was synthesized using AB Procedure 1, obtained as a colorless oil (92%, 2.116 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.56 (s, 1H), 2.67−2.52 (m, 4H), 1.69−1.54 (m, 4H), 0.82 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 56.8, 19.5, 11.3. ^{11}B NMR (96 MHz, chloroform-*d*) δ −16.67 (q, J = 96.4, 95.4 Hz).

*Diisopropylamine-borane (**1f**).* **1f** was synthesized using AB Procedure 1, obtained as a colorless oil (89%, 2.315 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.10 (hd, J = 6.6, 3.4 Hz, 3H), 1.15 (t, J = 6.3 Hz, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 52.0, 20.9, 18.9. ^{11}B NMR (96 MHz, chloroform-*d*) δ -21.80 (q, J = 96.4 Hz).

*Dibutylamine-borane (**1g**).* **1g** was synthesized using AB Procedure 1, obtained as a colorless oil (90%, 2.575 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.54 (s, 1H), 2.73−2.58 (m, 4H), 1.65−1.53 (m, 4H), 1.32−1.19 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 54.9, 28.3, 20.2, 13.8. ^{11}B NMR (96 MHz, chloroform-*d*) δ −16.58 (q, J = 99.9, 98.6 Hz).

*Diisobutylamine-borane (**1h**).* **1h** was synthesized using AB Procedure 1, obtained as a colorless oil (87%, 2.489 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.11 (s, 1H), 2.60 (dt, J = 12.3, 6.9 Hz, 2H), 2.40 (ddd, J = 12.6, 8.0, 5.2 Hz, 2H), 2.19 (dh, J = 7.8, 6.6 Hz, 2H), 0.90 (dd, J = 6.6, 2.1 Hz, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 63.6, 24.6, 20.2, 19.8. ^{11}B NMR (96 MHz, chloroform-*d*) δ -16.20 (q, J = 96.5, 95.9 Hz).

*Dipentylamine-borane (**1i**).* **1i** was synthesized using AB Procedure 1, obtained as a white solid (90%, 3.080 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.25 (s, 1H), 2.72 (dddd, J = 15.7, 13.9, 12.4, 6.9 Hz, 4H), 1.66 (dddd, J = 16.2, 9.3, 6.3, 2.6 Hz, 4H), 1.38−1.19 (m, 8H), 0.89 (t, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 55.3, 29.1, 26.1, 22.4, 14.0. ^{11}B NMR (96 MHz, chloroform-*d*) δ −16.44 (q, J = 98.9 Hz).

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*Dicyclohexylamine-borane (**1j**).* **1j** was synthesized using AB Procedure 1, obtained as a white solid (88%, 3.434 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.08−2.75 (m, 3H), 1.94−1.76 (m, 8H), 1.64 (tdd, J = 12.3, 8.9, 3.7 Hz, 6H), 1.22 (ddddd, J = 28.0, 21.8, 15.7, 8.7, 3.8 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 60.7, 31.0, 29.7, 25.8, 25.5, 25.3. ^{11}B NMR (96 MHz, chloroform-*d*) δ −20.69 (q, J = 97.8, 97.3 Hz).

*Piperidine-borane (**1k**).* **1k** was synthesized using AB Procedure 1, obtained as a white solid (99%, 1.959 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.75 (s, 1H), 3.39−3.10 (m, 2H), 2.47 (tdd, J = 13.5, 11.3, 2.7 Hz, 2H), 1.81−1.73 (m, 3H), 1.51 (tdd, J = 13.3, 10.8, 3.7 Hz, 2H), 1.31 (dddd, J = 16.1, 12.4, 8.6, 4.2 Hz, 1H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 53.4, 25.4, 22.6. ^{11}B NMR (96 MHz, chloroform-*d*) δ -15.55 (q, J = 95.9, 95.2 Hz).

*2,6-Dimethylpiperidine-borane (**1l**).* **1l** was synthesized using AB Procedure 1, obtained as a white solid (87%, 2.210 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.79 (s, 1H), 3.07−2.85 (m, 2H), 2.71 (dddd, J = 21.0, 12.3, 6.2, 2.8 Hz, 2H), 2.49 (s, 1H), 2.35 (s, 1H), 1.97 (tdd, J = 14.3, 10.7, 3.1 Hz, 2H), 1.84 (s, 0H), 1.86−1.67 (m, 5H), 1.68−1.56 (m, 1H), 1.57−1.41 (m, 3H), 1.39 (d, J = 6.3 Hz, 6H), 1.34 (td, J = 6.1, 4.0 Hz, 3H), 1.29 (d, J = 6.6 Hz, 6H), 1.27−1.16 (m, 2H), 1.16−0.65 (m, 2H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 59.4, 59.4, 34.7, 25.8, 24.1, 23.1, 22.3, 20.7. ^{11}B NMR (96 MHz, chloroform-*d*) δ −17.62 (q, J = 96.5, 95.8 Hz), −25.85 (q, J = 96.3 Hz).

*2,2,6,6-Tetramethylpiperidine-borane (**1m**).* **1m** was synthesized using AB Procedure 1, obtained as a white solid (85%, 2.636 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 2.82 (s, 1H), 1.86−1.63 (m, 4H), 1.58−1.43 (m, 2H), 1.38 (s, 6H), 1.33 (s, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 58.6, 41.0, 34.0, 20.7, 16.7. ^{11}B NMR (96 MHz, chloroform-*d*) δ −22.00 (q, J = 97.8 Hz).

*Morpholine-borane (**1n**).* **1n** was synthesized using AB Procedure 1, obtained as a white solid (97%, 1.958 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 4.40 (s, 1H), 3.91 (dd, J = 12.7, 3.6 Hz, 2H), 3.55 (td, J = 12.3, 2.3 Hz, 2H), 3.13−2.97 (m, 2H), 2.75 (dtd, J = 13.9, 11.5, 3.6 Hz, 2H), 2.31−0.65 (m, 3H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 65.8, 52.0. ^{11}B NMR (96 MHz, chloroform-*d*) δ −15.47 (q, J = 95.9 Hz).

*Azepane-borane (**1o**).* **1o** was synthesized using AB Procedure 1, obtained as a white solid (93%, 2.102 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 4.06 (s, 1H), 3.21 (ddt, J = 13.8, 6.8, 3.1 Hz, 2H), 2.74 (tdd, J = 12.1, 10.1, 5.3 Hz, 2H), 1.81 (ddq, J = 12.8, 6.0, 3.0 Hz, 2H), 1.64 (dddd, J = 17.1, 11.3, 9.4, 5.6 Hz, 6H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 55.1, 27.2, 26.7. ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.56 (q, J = 95.9 Hz).

*Pyrrolidine-borane (**1p**).* **1p** was synthesized using AB Procedure 1, obtained as a white solid (88%, 1.495 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 4.64 (s, 1H), 3.32−3.02 (m, 2H), 2.60 (ttd, J = 10.7, 7.4, 6.4, 3.0 Hz, 2H), 1.96−1.82 (m, 2H), 1.76 (dqd, J = 8.0, 4.6, 2.3 Hz, 2H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 54.2, 24.7. ^{11}B NMR (96 MHz, chloroform-*d*) δ −17.25 (q, J = 94.7 Hz).

*Dibenzylamine-borane (**1q**).* **1q** was synthesized using AB Procedure 1, obtained as a white solid (92%, 3.884 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.41−7.29 (m, 6H), 7.27−7.16 (m, 4H), 4.19 (s, 1H), 4.00 (dd, J = 13.1, 5.2 Hz, 2H), 3.87−3.69 (m, 2H), 2.31−1.24 (m, 3H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 134.2, 129.7, 128.8, 128.6, 58.4. ^{11}B NMR (96 MHz, chloroform-*d*) δ −15.15.

*Triethylamine-borane (**1r**).* **1r** was synthesized using AB Procedure 1, obtained as a colorless liquid (97%, 2.232 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 2.61 (q, J = 7.3 Hz, 6H), 1.02 (t, J = 7.3 Hz, 9H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 52.3, 8.6. ^{11}B NMR (96 MHz, chloroform-*d*) δ −13.81 (q, J = 97.2, 96.8 Hz).

Preparation of Amine Boranes via Salt Metathesis (AB Procedure 2). Sodium borohydride (0.76 g, 20 mmol) and the appropriate ammonium salt (20 mmol) were transferred to a 100 mL dry round-bottom flask, charged with a magnetic stir-bar. This was followed by addition of reagent-grade tetrahydrofuran (20.0 mL) at rt. Reaction progress was monitored by ^{11}B NMR spectroscopy. (Note: A drop of anhydrous DMSO is added to the reaction aliquot before running the ^{11}B NMR experiment to solubilize $NaBH_4$.) Upon completion of the reaction (1−24 h, as determined by ^{11}B NMR), the reaction contents were filtered through sodium sulfate and celite and the solid residue was washed with THF. Removal of the solvent in vacuo from the filtrate yielded the corresponding amine-borane. No further purification was necessary in the examples (**1a**, **1c**) presented here.

*Ethylamine-borane (**1a**).* **1a** was synthesized using AB Procedure 2, obtained as a white solid (79%, 0.930 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 3.83 (s, 2H), 3.00−2.69 (m, 2H), 1.23 (t, J = 7.3 Hz, 3H), 1.45 (q, J = 86.1 Hz, 3H); ^{13}C NMR (75 MHz, chloroform-*d*) δ 43.6, 14.5; ^{11}B NMR (96 MHz, chloroform-*d*) δ −20.09 (q, J = 95.2 Hz).

*Dimethylamine-borane (**1c**).* **1c** was synthesized using AB Procedure 2, obtained as a white solid (93%, 1.096 g). ^{1}H NMR (300 MHz, chloroform-*d*) δ 4.30 (s, 1H), 2.46 (d, J = 5.8 Hz, 6H), 1.42 (dd, J = 188.2, 91.9 Hz, 3H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 44.4. ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.76 (q, J = 95.5 Hz).

General Amine-Iodoborane Synthesis Procedure. In a 25 mL round-bottom flask, containing a stir-bar, the amine-borane (2 mmol, 1 equiv) was weighed. This was followed by addition of dichloromethane (4 mL). After dissolution of the amine-borane, iodine (1 mmol, 0.5 equiv) was added portionwise at rt. After stirring for 5 min at rt, the reaction mixture was analyzed using ^{11}B NMR spectroscopy. (All iodoboranes are unisolated intermediates identified by ^{11}B NMR spectroscopy.)

*Ethylamine-iodoborane (**2a**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −18.10 (t, J = 129.8 Hz).

*Isopropylamine-iodoborane (**2b**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −18.41 (t, J = 131.2 Hz).

*Dimethylamine-iodoborane (**2c**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −13.53 (t, J = 130.0 Hz).

*Diethylamine-iodoborane (**2d**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −15.14 (t, J = 129.8 Hz).

*Dipropylamine-iodoborane (**2e**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.63 (t, J = 130.5 Hz).

*Diisopropylamine-iodoborane (**2f**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −17.34 (t, J = 131.7 Hz).

*Diisopropylamine-chloroborane (**2f-Cl**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −7.64 (t, J = 123.5 Hz).

*Dibutylamine-iodoborane (**2g**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.59 (t, J = 134.5 Hz).

*Diisobutylamine-iodoborane (**2h**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.38 (t, J = 131.4 Hz).

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*Dipentylamine-iodoborane (**2i**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −13.92 (d, J = 136.2 Hz).

*Dicyclohexylamine-iodoborane (**2j**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −17.36 (d, J = 140.9 Hz).

*Piperidine-iodoborane (**2k**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.16 (t, J = 131.0 Hz).

*2,6-Dimethylpiperidine-iodoborane (**2l**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −15.89 (t, J = 132.6 Hz), −20.18 (t, J = 131.9 Hz).

*2,2,6,6-Tetramethylpiperidine-iodoborane (**2m**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −17.68 (t, J = 132.6 Hz).

*Morpholine-iodoborane (**2n**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.57 (t, J = 130.5 Hz).

*Azepane-iodoborane (**2o**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −13.59 (t, J = 127.8 Hz).

*Pyrrolidine-iodoborane (**2p**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −15.07 (t, J = 129.5 Hz).

*Dibenzylamine-iodoborane (**2q**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ −14.51.

*Triethylamine-iodoborane (**2r**).* ^{11}B NMR (96 MHz,) δ −14.31 (t, J = 100.5 Hz).

General Aminoborane Synthesis Procedure. In a 25 mL round-bottom flask containing a stir-bar, the amine-borane (2 mmol, 1 equiv) was weighed. This was followed by addition of dichloromethane (4 mL). After dissolution of the amine-borane, iodine (1 mmol, 0.5 equiv) was added portionwise at rt. After complete formation of the amine-iodoborane complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylethylamine (2 mmol, 1 equiv) was added dropwise to the stirred reaction mixture at rt. After stirring for 5 min at rt, the reactions were complete. (All aminoboranes are unisolated intermediates identified by ^{11}B NMR spectroscopy.)

*Ethylaminoborane (**3a**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 34.96−28.30 (m), 20.83, 4.78 to −1.67 (m), −8.19 (dd, J = 244.6, 98.1 Hz), −19.94 (dd, J = 181.8, 88.0 Hz), −21.84 to −27.21 (m).

*Isopropylaminoborane (**3b**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 34.08−23.60 (m), 20.60, −10.73, −18.75 to −31.65 (m).

*Dimethylaminoborane (**3c**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 37.07 (t, J = 128.4 Hz, aminoborane monomer), 4.71 (t, J = 112.1 Hz, aminoborane dimer), −0.53 to −4.43 (m).

*Diethylaminoborane (**3d**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.16 (t, J = 128.0 Hz, aminoborane monomer), 1.63 (t, J = 112.8 Hz, aminoborane dimer), −4.27 (t, J = 107.2 Hz).

*Dipropylaminoborane (**3e**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.59 (t, J = 127.9 Hz, aminoborane monomer), −3.45.

*Diisopropylaminoborane (**3f**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 34.40 (t, J = 126.8 Hz, aminoborane monomer).

*Dibutylaminoborane (**3g**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.56 (t, J = 125.4 Hz, aminoborane monomer), −3.42.

*Diisobutylaminoborane (**3h**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.99 (t, J = 128.9 Hz, aminoborane monomer), −2.99.

*Dipentylaminoborane (**3i**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.53 (t, J = 129.2 Hz, aminoborane monomer), −3.56.

*Dicyclohexylaminoborane (**3j**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 34.60 (t, J = 126.2 Hz, aminoborane monomer).

*Piperidinoborane (**3k**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 35.26 (t, J = 126.4 Hz, aminoborane monomer), 1.52 (t, J = 111.0 Hz, aminoborane dimer), −1.87.

*2,6-Dimethylpiperidinoborane (**3l**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 31.21 (t, J = 126.9 Hz, aminoborane monomer).

*2,2,6,6-Tetramethylpiperidinoborane (**3m**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 36.05 (t, J = 129.1 Hz, aminoborane monomer), −17.70 (t, J = 132.4 Hz), −20.62 to −24.28 (m).

*Morpholinoborane (**3n**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 35.94 (t, J = 132.3 Hz, aminoborane monomer), 1.53 (t, J = 112.7 Hz, aminoborane dimer), −2.08, −15.23 (d, J = 96.8 Hz).

*Azepanoborane (**3o**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 37.34 (t, J = 127.3 Hz, aminoborane monomer), 2.80 (t, J = 113.4 Hz, aminoborane dimer), −1.92, −14.19 (d, J = 98.3 Hz), −18.39.

*Pyrrolidinoborane (**3p**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 34.55 (t, J = 128.5 Hz, aminoborane monomer), 25.91 (d, J = 126.1 Hz, diaminoborane), 2.52 (t, J = 109.6 Hz, aminoborane dimer), −4.55 (t, J = 110.4 Hz, exchange/coordination compound), −18.77 (td, J = 128.6, 32.3 Hz, aminodiborane).

*Dibenzylaminoborane (**3q**).* ^{11}B NMR (96 MHz, chloroform-*d*) δ 39.22 (t, J = 149.2 Hz, aminoborane monomer).

General Procedure for Boronate Ester Synthesis (General Procedure 1). In a 25 mL round-bottom flask containing a stir-bar, the amine-borane (2 mmol, 2 equiv) was weighed. This was followed by addition of dichloromethane (5 mL). After dissolution of the amine-borane, iodine (1 mmol, 1 equiv) was added portionwise at rt. After complete formation of the iodoborane−amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylamine (5 mmol, 5 equiv) was added to the stirred reaction mixture at rt. After stirring for 5 min at rt, the reaction was complete. Then, by stirring toluene (5 mL), the aryl halide substrate (1 mmol, 1 equiv) and $PdCl_2$(dppp) (0.05 mmol, 0.05 equiv) were added to the reaction mixture at rt. A reflux condenser was affixed to the flask, and the mix was brought to reflux. After completion (∼12−16 h), the reaction mixture was cooled to rt and then brought to 0 °C using an ice-water bath. At 0 °C, diethyl ether (3 mL) was added to the mixture, followed by pinacol (1.1 mmol, 1.1 equiv). The mixture was stirred for 4 h while being allowed to warm to rt. After completion, the reaction mixture was diluted with diethyl ether (10 mL) and the crude mixture was passed through a pad of silica gel contained in a fritted glass Büchner funnel and eluted with diethyl ether as necessary. The resulting filtrate was condensed by rotary evaporation followed by drying in vacuo for 12 h.

*2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4a**).* **4a** was synthesized using General Procedure 1, obtained as a yellow oil (95%, 222 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.78 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.82 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 162.00, 136.43, 113.26, 83.55, 55.12, 24.98. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.46. Compound characterization is in accordance with previous reports.[6b]

*2-(4-Ethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4b**).* **4b** was synthesized using General Procedure 1, obtained as a yellow oil (96%, 238 mg). ^{1}H NMR (300 MHz,

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ACS Omega 2022, 7, 14377−14389

chloroform-*d*) δ 7.76 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.42 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 11H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 161.38, 136.41, 113.76, 83.54, 63.24, 24.97, 14.91. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.40. Compound characterization is in accordance with previous reports.[39]

*2-(4-Methoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4c**).* **4c** was synthesized using General Procedure 1, obtained as a yellow oil (94%, 233 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.78 (d, *J* = 8.9 Hz, 1H), 6.76 (s, 2H), 3.83 (s, 3H), 2.58 (s, 3H), 1.37 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 161.59, 147.14, 137.81, 115.47, 110.09, 83.13, 55.03, 25.03, 22.61. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.71. Compound characterization is in accordance with previous reports.[40]

*2-(6-Methoxynaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4d**).* **4d** was synthesized using General Procedure 1, obtained as a yellow oil (97%, 275 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.32 (s, 1H), 7.85−7.71 (m, 3H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.93 (s, 3H), 1.40 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 158.39, 136.34, 135.91, 131.03, 130.17, 128.29, 125.86, 118.65, 105.56, 83.83, 55.34, 25.04.^{11}B NMR (96 MHz, chloroform-*d*) δ 30.96. Compound characterization is in accordance with previous reports.[41]

*2-(2,3-Dihydrobenzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4e**).* **4e** was synthesized using General Procedure 1, obtained as a yellow oil (98%, 241 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.67 (s, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 4.58 (t, *J* = 8.7 Hz, 2H), 3.19 (t, *J* = 8.7 Hz, 2H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 162.70, 135.46, 126.44, 108.94, 83.50, 71.37, 29.30, 24.97. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.39. Compound characterization is in accordance with previous reports.[42]

*4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**4f**).* **4f** was synthesized using General Procedure 1, obtained as a yellow oil (98%, 200 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.89−7.80 (m, 2H), 7.52−7.44 (m, 1H), 7.43−7.35 (m, 2H), 1.37 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 134.66, 131.19, 127.64, 83.78, 25.00. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.67. Compound characterization is in accordance with previous reports.[39]

*4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**4g**).* **4g** was synthesized using General Procedure 1, obtained as a yellow oil (99%, 251 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.44 (d, *J* = 1.1 Hz, 1H), 7.97−7.81 (m, 4H), 7.52 (dqd, *J* = 8.4, 6.8, 1.6 Hz, 2H), 1.43 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 136.21, 134.97, 132.75, 130.35, 128.61, 127.67, 126.95, 125.76, 83.96, 25.08. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.75. Compound characterization is in accordance with previous reports.[41]

*4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (**4h**).* **4h** was synthesized using General Procedure 1, obtained as a yellow oil (99%, 250 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.85 (dd, *J* = 8.4, 1.3 Hz, 1H), 8.16 (dd, *J* = 6.8, 1.4 Hz, 1H), 8.03−7.94 (m, 1H), 7.90−7.86 (m, 1H), 7.60 (ddd, *J* = 8.4, 6.8, 1.6 Hz, 1H), 7.55−7.50 (m, 2H), 1.48 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 136.88, 135.63, 133.17, 131.60, 128.38, 128.32, 126.32, 125.81, 125.47, 124.95, 83.79, 25.13. ^{11}B NMR (96 MHz, chloroform-*d*) δ 31.23. Compound characterization is in accordance with previous reports.[41]

*4,4,5,5-Tetramethyl-2-(phenanthren-9-yl)-1,3,2-dioxaborolane (**4i**).* **4i** was synthesized using General Procedure 1, obtained as a yellow oil (98%, 298 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 9.02 (d, *J* = 8.0 Hz, 1H), 8.80−8.71 (m, 2H), 8.58 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 3H), 7.69 (d, *J* = 7.8 Hz, 1H), 1.55 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 138.25, 134.54, 131.95, 131.04, 129.98, 129.37, 129.18, 127.84, 126.79, 126.59, 126.51, 126.23, 122.71, 122.55, 83.97, 25.20. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.73. Compound characterization is in accordance with previous reports.[43]

*4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (**4j**).* **4j** was synthesized using General Procedure 1, obtained as a yellow oil (97%, 211 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.37 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 141.30, 134.75, 128.46, 83.64, 25.00. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.65. Compound characterization is in accordance with previous reports.[6b]

*2-([1,1′-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4k**).* **4k** was synthesized using General Procedure 1, obtained as a yellow oil (99%, 277 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.71−7.64 (m, 4H), 7.48 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.41 (d, *J* = 7.1 Hz, 1H), 1.42 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 143.83, 140.92, 135.23, 128.73, 127.53, 127.19, 127.12, 126.44, 83.88, 25.05. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.47. Compound characterization is in accordance with previous reports.[39]

*2-(3,5-Di-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4l**).* **4l** was synthesized using General Procedure 1, obtained as a pale-yellow solid (99%, 313 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.71 (d, *J* = 2.1 Hz, 2H), 7.65−7.54 (m, 1H), 1.39 (s, 18H), 1.38 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 149.71, 128.73, 125.51, 83.56, 34.93, 31.65, 25.01. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.58. Compound characterization is in accordance with previous reports.[44]

*4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (**4m**).* **4m** was synthesized using General Procedure 1, obtained as a yellow oil (96%, 240 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.79−7.67 (m, 2H), 7.27−7.18 (m, 2H), 2.48 (s, 3H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 142.50, 134.99, 124.88, 83.74, 24.98, 15.15. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.48. Compound characterization is in accordance with previous reports.[39]

*4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-benzonitrile (**4n**).* **4n** was synthesized using General Procedure 1, obtained as an orange solid (65%, 149 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 1.42−1.24 (m, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 134.99, 130.99, 118.75, 114.43, 84.46, 24.96. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.10. Compound characterization is in accordance with previous reports.[39]

*N,N-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**4o**).* **4o** was synthesized using General Procedure 1, obtained as a yellow oil (70%, 173 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.70 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 2.99 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 152.40, 136.04, 111.18, 83.16, 40.21, 24.97. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.38. Compound characterization is in accordance with previous reports.[43]

*2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4p**).* **4p** was synthesized using General Procedure 1,

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ACS Omega 2022, 7, 14377−14389

obtained as an orange oil (99%, 236 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.75 (dd, J = 8.3, 1.6 Hz, 2H), 7.35 (dd, J = 8.4, 1.6 Hz, 2H), 1.41−1.29 (m, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 137.45, 136.05, 127.93, 84.03, 24.97. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.30. Compound characterization is in accordance with previous reports.[41]

*2-(3,5-Dichlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4q**).* **4q** was synthesized using General Procedure 1, obtained as an orange oil (89%, 243 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.65 (d, J = 2.0 Hz, 2H), 7.42 (t, J = 2.0 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 134.61, 132.61, 130.98, 84.51, 24.94. ^{11}B NMR (96 MHz, chloroform-*d*) δ 29.74. Compound characterization is in accordance with previous reports.[45]

*2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4r**).* **4r** was synthesized using General Procedure 1, obtained as an orange oil (99%, 220 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.91−7.72 (m, 2H), 7.13−6.98 (m, 2H), 1.35 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 164.93 (d, J = 250.3 Hz), 136.88 (d, J = 8.1 Hz), 114.78 (d, J = 20.1 Hz), 83.91, 24.96. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.19. ^{19}F NMR (282 MHz, chloroform-*d*) δ −109.90 (p, J = 7.8 Hz). Compound characterization is in accordance with previous reports.[39]

*4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**4s**).* **4s** was synthesized using General Procedure 1, obtained as a pale-orange solid (98%, 266 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 7.94 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 1.36 (s, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 134.92, 132.71 (q, J = 32.0 Hz), 124.18 (q, J = 4.1 Hz), 84.22, 24.87. ^{11}B NMR (96 MHz, chloroform-*d*) δ 30.27. ^{19}F NMR (282 MHz, chloroform-*d*) δ −64.57. Compound characterization is in accordance with previous reports.[6b]

Procedure for Synthesis of Boronic Acid and Amine Recovery (General Procedure 2). In a 25 mL round-bottom flask containing a stir-bar, the amine-borane (2 mmol, 2 equiv) was weighed. This was followed by addition of dichloromethane (5 mL). After dissolution of the amine-borane, iodine (1 mmol, 1 equiv) was added portionwise at rt. After complete formation of the iodoborane−amine complex, as evidenced by a return to colorlessness of the reaction mixture, diisopropylamine (5 mmol, 5 equiv) was added to the stirred reaction mixture at rt. After stirring for 5 min at rt, the reaction was complete. Then, by stirring toluene (5 mL), the aryl halide substrate (1 mmol, 1 equiv) and $PdCl_2$(dppp) (0.05 mmol, 0.05 equiv) were added to the reaction mixture at rt. A reflux condenser was affixed to the flask, and the mix was brought to reflux. After completion (∼12−16 h), the reaction mixture was cooled to rt and then brought to 0 °C using an ice-water bath. At 0 °C, methanol (8 mL) was added to the mixture, and the solvent was removed by rotary evaporation. The residue was then dissolved with sodium hydroxide (3 M, 8 mL). The aqueous layer was washed with hexanes (3 × 10 mL), and the hexane layers were set aside. The aqueous layer was then acidified with 3 M HCl until reaching a pH of 1. The slurry was extracted with diethyl ether (4 × 15 mL). The combined organic portions were dried over sodium sulfate, filtered through cotton, and condensed via rotary evaporation followed by drying in vacuo for 12 h to retrieve the boronic acid. To the earlier separated hexane fractions was added 2 M ethereal HCl (5 mL) precipitating the ammonium salt. The salt was collected on a filter paper in a Hirsch funnel and washed with hexanes (2 × 10 mL). The solid was transferred to a preweighed flask and dried in vacuo for 12 h.

*(4-Methoxyphenyl)boronic Acid (**5a**).* **5a** was synthesized using General Procedure 2, obtained as an off-white solid (83%, 126 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 8.15 (d, J = 8.3 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 162.98, 137.38, 113.42, 55.19. ^{11}B NMR (96 MHz, chloroform-*d*) δ 29.25. Compound characterization is in accordance with previous reports.[3a]

Diisopropylammonium Chloride. Diisopropylammonium chloride was recovered using General Procedure 2, obtained as a white solid (86%, 828 mg). ^{1}H NMR (300 MHz, chloroform-*d*) δ 9.17 (s, 2H), 3.38 (hept, J = 6.4 Hz, 2H), 1.48 (d, J = 6.5 Hz, 12H). ^{13}C NMR (75 MHz, chloroform-*d*) δ 47.42, 19.24.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01461.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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