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A General Solution for Unstable Boronic Acids: Slow-Release Cross-Coupling from Air-Stable MIDA Boronates

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Boronic acids can serve as excellent building blocks for the synthesis of a wide range of natural products, pharmaceuticals, and materials.[1] However, some of the potentially most useful boronic acids, including 2-heterocyclic,[2−4] vinyl,[5] and cyclopropyl[6] derivatives, are inherently unstable, which can significantly limit their benchtop storage and/or efficient cross-coupling. Many important surrogates have been developed, including trifluoroborate salts,[7−10] trialkoxy or trihydroxyborate salts,[11,12] diethanolamine adducts,[13] sterically bulky boronic esters,[14] and boroxines.[15] However, none of these can provide air-stable and highly effective substitutes for all three of these challenging boronic acid classes. We herein report that *N*-methyliminodiacetic acid (MIDA) boronates[16,17] represent the first general solution to this problem by virtue of their uniform benchtop stability and remarkable capacity for in situ *slow release* of unstable boronic acids (Figure 1).

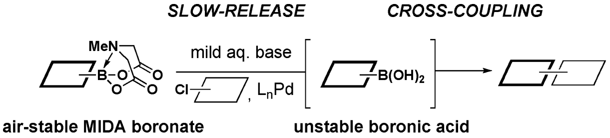


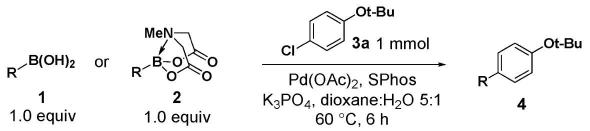
Figure 1

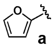
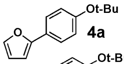
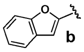
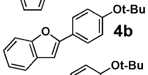
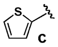
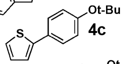
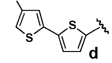
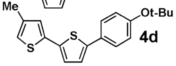
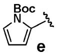
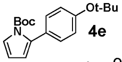
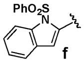
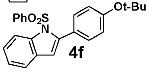
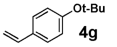
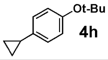
2-Heterocyclic, vinyl, and cyclopropyl boronic acids are known to decompose on the benchtop under air via protodeboronation, oxidation, and/or polymerization.[2−6] In addition, these processes are thought to be accelerated in the presence of heat, base, and/or a Pd catalyst, causing the in situ decomposition of unstable boronic acids to compete with their cross-coupling.[2] This latter challenge is exacerbated in couplings with slower-reacting halides, such as unactivated aryl chlorides.[2] We hypothesized that both of these problems might be solved if we could achieve rate-controlled in situ hydrolysis of air-stable MIDA boronates, thereby promoting "slow release" of the corresponding unstable boronic acids from bench-stable building blocks.

The hydrolysis of MIDA boronates with aqueous NaOH is fast, typically requiring <10 min at 23 °C.[17] In contrast, we discovered that K_3PO_4 in 5:1 dioxane/H_2O at 60 °C promotes the continuous release of boronic acids over ∼3 h.[18] Remarkably, aryl, heteroaryl, alkenyl, and alkyl MIDA boronates all behave similarly. Moreover, this release rate can be adjusted from 24 h to 30 min by varying the temperature from 23 to 100 °C.[18]

Having verified this capacity for slow release, we systematically compared the benchtop stability and cross-coupling efficiency of freshly prepared boronic acids **1a**−**h**[18,19] and the corresponding MIDA boronates **2a**−**h**[18] (Table 1). The benchtop instability of 2-heterocyclic, vinyl, and cyclopropyl boronic acids has frequently been discussed anecdotally,[2−15] yet there is very little quantitative data available. As shown in Table 1, we determined that boronic acids **1a**−**h** all decompose significantly on the benchtop under air over the course of just 15 days (entries 1−8).[18] In fact, with 2-furan, 2-pyrrole, 2-indole, vinyl, and cyclopropyl boronic acids, very little of the original material remains after this time. Alternatively, all of the MIDA boronates **2a**−**h** are indefinitely air-stable, with no decomposition detectable by ^{1}H NMR even after ≥60 days on the benchtop under air.[18]

Table 1. Benchtop Stability and Cross-Coupling Efficiency of Boronic Acids and the Corresponding MIDA Boronates



		% remaining after benchtop storage under air[a]			% isolated yield from cross-coupling[c]	
entry	R	**1** (15 days)	**2** (60 days)	**4**	**1**	**2**
1	 **a**	7	>95[b]	 **4a**	68	**94**
2	 **b**	88	>95	 **4b**	50	**92**
3	 **c**	80	>95	 **4c**	37	**94**
4	 **d**	80	>95[b]	 **4d**	45	**96**
5	 **e**	<5	>95	 **4e**	61	**90**
6	 **f**	<5	>95	 **4f**	14	**93**
7[d]	 **g**	5	>95[b]	 **4g**	79	**98**
8[d]	 **h**	31	>95	 **4h**	95	**96**

[a] Freshly prepared boronic acids **1** and MIDA boronates **2** were stored as solids on the benchtop under air for 15 and 60 days, respectively.[18] [b] Stored for 107 days. [c] Reaction conditions: 1.0 equiv of **3a** (1 mmol), 1.0 equiv of **1** (freshly prepared, >95% pure) or **2**, 5 mol % $Pd(OAc)_2$, 10 mol % SPhos, 7.5 equiv of K_3PO_4, 0.07 M in 5:1 dioxane/H_2O, 60 °C, 6 h. [d] Cross-couplings were run at 100 °C.

We next tested the cross-coupling efficiency of freshly prepared boronic acids **1a**−**h**[19] with aryl chloride **3a** using $Pd(OAc)_2$/SPhos[2,20] as the catalyst and K_3PO_4 as the base. Only very low to moderate yields (14−68%) were observed for the 2-heterocyclic derivatives **1a**−**f** (entries 1−6), consistent with our observations that boronic acid decomposition kinetically competes with cross-coupling.[2,18] In stark contrast, all of the corresponding MIDA boronates **2a**−**f** coupled under identical conditions with aryl chloride **3a** in uniformly excellent yields (90−96%) *using in each case only 1 equiv of MIDA boronate*.[21] In many cases, the improvement in yield using **2** versus **1** is striking [e.g., 92 vs 50% with 2-benzofuran (entry 2), 94 vs 37% with 2-thiophene (entry 3), and 93 vs 14% with 2-indole (entry 6)]. In addition, vinyl MIDA boronate (**2g**) was significantly more effective than freshly prepared **1g** (entry 7).[5c,8]

Consistent with our hypothesis that these increases in yield are attributable to in situ slow release of the corresponding boronic acids, no significant differences in yields were observed for **1a** (64%) vs **2a**

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(59%) under *fast-release* conditions, i.e., using aqueous NaOH as base.[18] Moreover, the high yield observed for **2a** under slow-release conditions was replicated via syringe-pump-mediated addition of freshly prepared **1a** over the course of 3 h.[18] It is noteworthy that cyclopropyl boronic acid (**1h**) prepared immediately prior to the reaction can be as effective as MIDA boronate **2h** (entry 8), suggesting that benchtop decomposition of **1h** may be in large part responsible for the challenges frequently encountered with this boronic acid.[6a]

Encouraged by these results, we explored the scope of this slow-release method and found that even some of the most challenging aryl and heteroaryl chlorides can be efficiently coupled with MIDA boronates **2a**−**h** (Table 2). For example, the highly deactivated (electron-rich and sterically hindered) compound 2,4-dimethoxychlorobenzene (**3b**) represents an exceptionally difficult cross-coupling partner for unstable 2-heterocyclic boronic acids. Nonetheless, just 1.2 equiv of the corresponding MIDA boronates promoted this coupling in generally excellent to outstanding yields (entries 1, 5, 9, 12, and 14). Because of the great importance of polyheterocyclic scaffolds in pharmaceuticals, similar cross-couplings with inexpensive and readily available heteroaryl chlorides would also be highly valuable. We explored this possibility with **3d**−**i** and found that the 2-heterocyclic MIDA boronates are highly effective in such couplings (entries 3, 4, 6−8, 10, 11, 13, and 15). Even electronically deactivated heteroaryl chlorides such as **3f**−**h** were coupled to **2b** in good to excellent yields (entries 6−8).

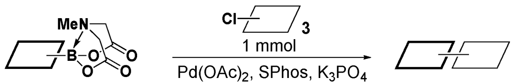
Vinylation of aryl and heteroaryl halides can provide styrene-like building blocks for a wide range of small molecules and materials.[5c] Thus, the development of a highly effective, nontoxic, environmentally friendly, and air-stable vinyl metal species has long been an important goal.[5c] Remarkably, vinyl MIDA boronate **2g** embodies all of these favorable properties and efficiently coupled even with the highly deactivated aryl chloride **3c** (entry 16) as well as a variety of heteroaryl chlorides (entries 17−19). Finally, **2h** coupled with highly deactivated aryl chlorides **3c** and **3b** (entries 20−21).

As a final example, the 2-pyridyl subunit appears with remarkable frequency in biologically active small molecules. However, the corresponding boronic acid is notoriously unstable[4,22] and difficult to cross-couple,[4,7,11a,23] particularly with aryl chlorides.[11a] Currently available surrogates either are not air-stable[11a,b,12] or cannot be isolated in chemically pure form.[13]

In contrast, 2-pyridyl MIDA boronate (**2i**) is isolable as a chemically pure and air-stable solid (X-ray structure shown in Table 3, ^{1}H NMR spectra showed no decomposition after 60 days on the benchtop under air). Consistent with a relatively lower rate of transmetalation for 2-pyridylboranes,[11a] conditions like those used in Tables 1 and 2 were not generally effective for couplings with **2i**. However, driven by the hypothesis that in-situ-generated 2-pyridyl boronic esters would be more stable than their boronic acid counterparts, we explored a variety of alcohol-containing solvent mixtures and found that DMF/IPA was advantageous. Moreover, it has been demonstrated that the addition of CuI[13,11b] or CuCl[14c] can promote cross-couplings with other 2-pyridylboranes. We therefore surveyed a series of copper salts and found that the inexpensive and nontoxic Cu(OAc)$_2$ was especially beneficial. As shown in Table 3, under these modified slow-release conditions, air-stable 2-pyridyl MIDA boronate (**2i**) can be cross-coupled with a variety of aryl and heteroaryl chlorides (entries 1−5). The capacity to effectively cross-couple two different 2-substituted heterocycles is a notable advantage of this methodology (Table 3, entries 3−5; also see Table 2, entries 4 and 11).

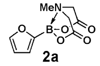
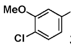
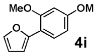
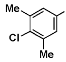
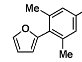
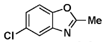
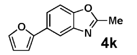
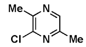
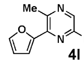
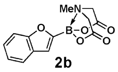
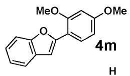
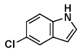
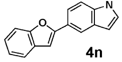
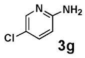
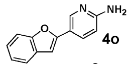
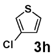
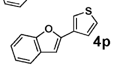
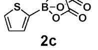
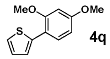
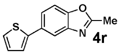
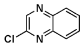
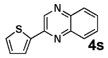
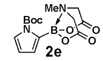
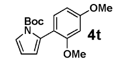
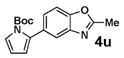
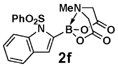
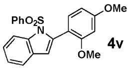
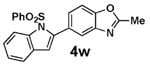
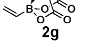
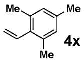
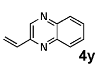
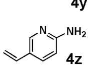
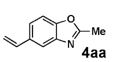
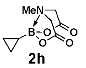
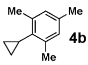
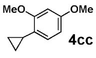
In summary, several highly advantageous features collectively make MIDA boronates an outstanding platform for the preparation and utilization of organoboranes in organic synthesis.[17] These include reversibly attenuated reactivity toward anhydrous cross-coupling conditions, compatibility with a wide range of synthetic reagents, air

Table 2. Slow-Release Cross-Coupling of Air-Stable 2-Heterocyclic, Vinyl, and Cyclopropyl MIDA Boronates with Aryl and Heteroaryl Chlorides[a]



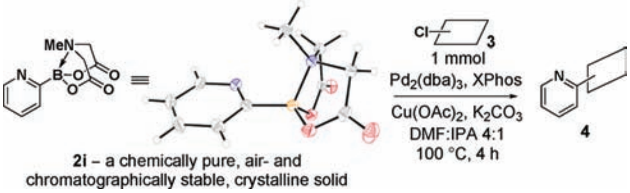
air-stable
MIDA boronates **2**

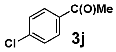
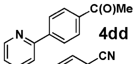
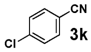
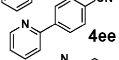
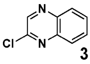
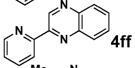
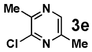
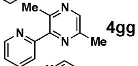
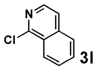
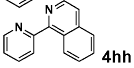
1 mmol
Pd(OAc)$_2$, SPhos, K$_3$PO$_4$
dioxane:H$_2$O 5:1
60 °C, 6 h

entry	2	3	4	% isolated yield
1	 **2a**	 **3b**	 **4i**	99
2	**2a**	 **3c**	 **4j**	97
3	**2a**	 **3d**	 **4k**	99
4	**2a**	 **3e**	 **4l**	91
5	 **2b**	**3b**	 **4m**	94
6	**2b**	 **3f**	 **4n**	94
7[b]	**2b**	 **3g**	 **4o**	85
8[b]	**2b**	 **3h**	 **4p**	85
9	 **2c**	**3b**	 **4q**	98
10	**2c**	**3d**	 **4r**	99
11	**2c**	 **3i**	 **4s**	97
12[c]	 **2e**	**3b**	 **4t**	81
13[c]	**2e**	**3d**	 **4u**	98
14	 **2f**	**3b**	 **4v**	97
15	**2f**	**3d**	 **4w**	93
16[d,e]	 **2g**	**3c**	 **4x**	91
17[d,e]	**2g**	**3i**	 **4y**	87
18[d,e]	**2g**	**3g**	 **4z**	76
19[d,e]	**2g**	**3d**	 **4aa**	96
20[b,d,f]	 **2h**	**3c**	 **4bb**	79
21[d]	**2h**	**3b**	 **4cc**	97

[a] General reaction conditions: 1 equiv of aryl halide (1 mmol), 1.2 equiv of MIDA boronate, 5 mol % Pd(OAc)$_2$, 10 mol % SPhos, 7.5 equiv of K$_3$PO$_4$, 0.07 M in 5:1 dioxane/H$_2$O, 60 °C, 6 h. [b] Using 1.5 equiv of MIDA boronate. [c] Using 0.5 mmol of aryl halide, 0.6 mmol of MIDA boronate (1.2 equiv) [d] At 100 °C. [e] Reaction time 2 h. [f] Reaction time 24 h.

Table 3. Slow-Release Cross-Coupling of Air-Stable 2-Pyridyl MIDA Boronate **2i** with Aryl and Heteroaryl Chlorides[a]



entry	3	4	% isolated yield
1	 **3j**	 **4dd**	72
2	 **3k**	 **4ee**	60
3	 **3i**	 **4ff**	79
4	 **3e**	 **4gg**	52
5	 **3l**	 **4hh**	74

[a] Reaction conditions: 1.0 equiv of aryl halide **3** (1 mmol), 1.5 equiv of MIDA boronate **2i**, 1.5 mol % Pd$_2$(dba)$_3$, 6 mol % XPhos, 50 mol % Cu(OAc)$_2$, 5 equiv of K$_2$CO$_3$, 0.1 M in 4:1 DMF/IPA, 100 °C, 4 h.

stability, solubility in many common organic solvents, monomeric constitution, and compatibility with silica gel chromatography.[17] We now report that MIDA boronates also possess the highly enabling capacity for in situ slow release of the corresponding unstable boronic acids. This remarkably general solution has transformed a wide range of unstable boronic acids into air-stable and highly effective cross-coupling partners, many of which are now commercially available.[24]

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Supporting Information Available: Procedures, spectral data, and spectra for all new compounds and crystallographic data for **2i** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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