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Gold-Catalyzed Proto- and Deuterodeboronation

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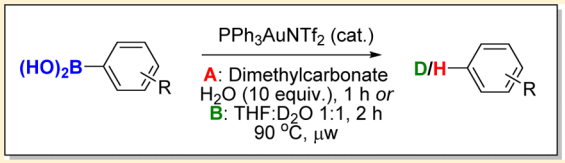
Supporting Information



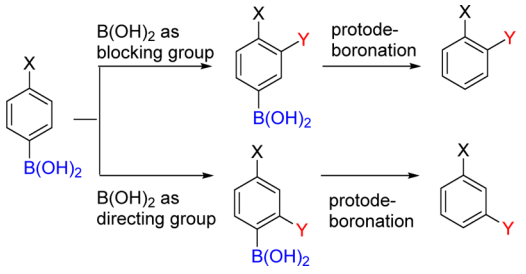
- *No acid or base additives*
- *Up to quant. yield*
- *Up to 100% deuteration*
- *Green solvents can be used*
- *Mechanistic Investigations*

ABSTRACT: A mild gold-catalyzed protodeboronation reaction, which does not require acid or base additives and can be carried out in "green" solvents, is described. As a result, the reaction is very functional-group-tolerant, even to acid- and base-sensitive functional groups, and should allow for the boronic acid group to be used as an effective traceless directing or blocking group. The reaction has also been extended to deuterodeboronations for regiospecific *ipso*-deuterations of aryls and heteroaryls from the corresponding organoboronic acid. Based on density functional theory calculations, a mechanism is proposed that involves nucleophilic attack of water at boron followed by rate-limiting B−C bond cleavage and facile protonolysis of a Au−σ-phenyl intermediate.

INTRODUCTION

Arylboronic acids are readily available and widely used substrates in organic chemistry.[1] Traditionally, protodeboronation of arylboronic acids is usually considered an unwanted side product,[2] especially in Pd-catalyzed couplings (along with homocoupling and oxidation).[3] Recently, however, the application of protodeboronation to organic synthesis has been elegantly demonstrated by several groups.[4] In particular, Cheon and co-workers have demonstrated the utility of protodeboronations as a means of easily removing boronic acid groups after it has been used as a blocking or directing group (Scheme 1).[5] Overall, this renders the boronic acid moiety a

Scheme 1. Use of Boronic Acid Moiety as a Traceless Blocking or Directing Group[5]



traceless blocking/directing group, whereby the latter allows access to the difficult overall "meta-direction" with electron-donating X groups.

Unfortunately, there are current limitations as protodeboronation of arylboronic acids usually require harsh conditions such as strong bases or acids and are strongly substituent-dependent.[6] While Cheon's metal-free protodeboronation is a welcome exception,[5] the additive-free procedure is limited to electron-rich arylboronic acids only. Furthermore, unless the aryl has an *ortho*- and *para*-OH group or very electron-donating NR_2 groups, the addition of acid (AcOH) or base (K_2CO_3) is required for other electron-rich arylboronic acids, which precludes the use of acid- and base-sensitive functional groups. In terms of transition-metal-catalyzed protodeboronations, previously reported Cu-,[7] Ag-,[8] or Pd-catalyzed[9] methods typically require the addition of a stoichiometric base and can suffer from selectivity issues, such as coupling or dehalogenation products observed with the Pd-catalyzed method.[9] Therefore, a mild and more general procedure, which is tolerant of both electron-donating and electron-withdrawing as well as various sensitive functional groups, is required in order to fully harness the potential of boronic acids as traceless blocking and directing groups.

In this article, we present a mild gold-catalyzed protodeboronation method, which not only is tolerant of various acid- and base-sensitive groups but also can be carried out in "green", environmentally benign, industrial-friendly solvents such as dimethylcarbonate.[10] Furthermore, the procedure can be adapted to effect *deutero*deboronations, which constitutes a practical and regiospecific *ipso*-deuteration technique. Synthetic procedures capable of incorporating deuterium (D) into organic molecules are highly sought after for wide ranging applications,[11] including mechanistic investigations,[12] analytical standards in stable-isotope tracer studies,[13] neutron scattering,[14] and drug targets with enhanced metabolic stability.[15] Synthetic methods toward deuterated compounds are also regularly applied toward the tritium analogues, which are often used as radiotracers in the pharmaceutical industry.[11]

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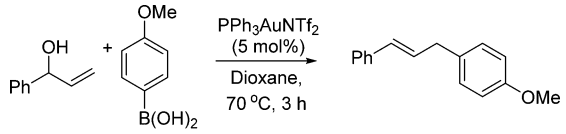
RESULTS AND DISCUSSION

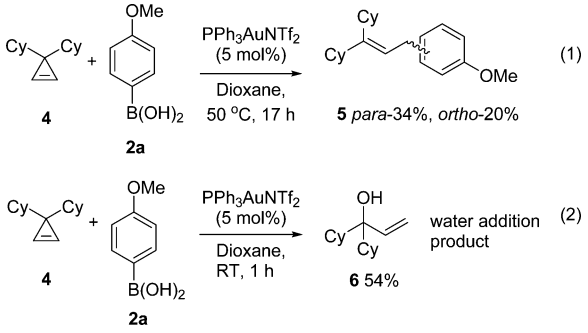
We originally discovered the gold-catalyzed protodeboronation reaction through a rather roundabout route. Our group has investigated many gold-catalyzed reactions using cyclopropenes[16] and allylic alcohols[17] as substrates. As part of these investigations, we explored the use of arylboronic acids as nucleophiles[18] in the gold(I)-catalyzed reaction with allylic[19] alcohols (Scheme 2) and cyclopropenes (Scheme 3). We were initially excited to find that arylations occurred under catalytic conditions to produce **3** and **5**, respectively (Schemes 2 and 3).[20,21]

Scheme 2. Preliminary Results on Gold-Catalyzed Arylations with Allylic Alcohols



1 **2a** **3** 67%

Scheme 3. Preliminary Results on Gold-Catalyzed Arylations with Cyclopropenes



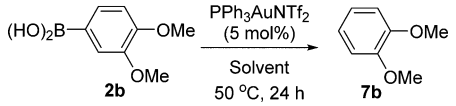
4 **2a** **5** *para*-34%, *ortho*-20%

4 **2a** **6** 54%

With the cyclopropene reaction, it soon became apparent (upon repeating the reaction at a lower temperature and monitoring over time) that the actual electrophile was not the cyclopropene **4** itself but was the allylic alcohol **6** that is formed upon addition of adventitious water to the gold intermediate[16a,c] (Scheme 3, eq 2). The reaction with allylic alcohol (Scheme 2) was only ever successful with *p*-MeO-C_6H_4 boronic acid **2a**, and further control experiments suggest that the reaction in Scheme 2 simply works by gold(I)-catalyzed protodeboronation of the arylboronic acid **2a**, followed by gold(I)-catalyzed Friedel–Crafts-type allylation[22] of the resulting aryl to form the observed product **3**.[23] Despite this disappointment, we discovered that gold(I) can readily catalyze the protodeboronation of arylboronic acids without the need for acid or base additives.[24] Since this coincided with a growing interest in protodeboronations as a tool in synthesis (vide ante), we set out to explore this reaction further.

Initially, a solvent screen was carried out on arylboronic acid **2b** using PPh_3AuNTf_2 as the catalyst[25] (Table 1). Unlike previously reported Cu-,[7] Ag-,[8] or Pd-catalyzed[9] methods which typically require the addition of a stoichiometric base, the gold(I)-catalyzed reaction proceeds well in the absence of any additives. Furthermore, the reaction does not require dry solvents[26] or an inert atmosphere and can be carried out easily in air. The solvent screen shows THF, 2-methyl THF, and dimethylcarbonate to all be suitable solvents for fully protodeboronating **2b** to **7b** at 50 °C for 24 h (entries 7–9).

Table 1. Solvent Screen

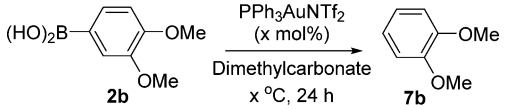


2b **7b**

entry	solvent[a]	yield (%)[b]
1	chloroform	54
2	acetonitrile	20
3	toluene	24
4	acetone	49
5[c]	water	8
6	dioxane	84
7	THF	97
8	**2-methyl THF**	**quant.**
9	**dimethylcarbonate**	**quant.**

[a]Nonanhydrous solvents used. [b]Determined using ^{1}H NMR analysis of the crude reaction mixture using dimethylsulfone as an internal standard. [c]Poor solubility.

Table 2. Varying Catalyst Loading and Temperatures

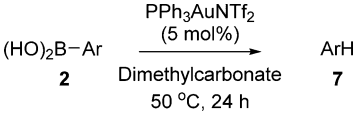


2b **7b**

entry	temp (°C)	mol % of catalyst	yield (%)[a]
1	50	1	16
2	50	3	62
3	30	5	34
4	40	5	47
5	50	5	quant.

[a]Determined using ^{1}H NMR analysis of the crude reaction mixture using dimethylsulfone as an internal standard.

Table 3. Electron-Poor Arylboronic Acids Are Not Fully Converted Using Initial Conditions



2 **7**

entry	aryl	yield (%)[a]
1	*m,p*-$(OMe)_2C_6H_3$	quant.
2	*p*-OHC_6H_4	quant.
3[b]	*p*-$CO_2EtC_6H_4$	48
4	*m*-$CO_2MeC_6H_4$	41

[a]Determined using ^{1}H NMR analysis of the crude reaction mixture using dimethylsulfone as an internal standard. [b]Increasing catalyst loading to 10 mol % or time to 48 h increases the yield to 57%.

Since dimethylcarbonate has the most "green credentials" as a solvent,[10] we opted to adopt it as our solvent of choice for further optimization.

Next, we ascertained that lowering the catalyst loading or temperature from 5 mol % and 50 °C, respectively, produced incomplete conversions (Table 2), so the initial optimal conditions remained as shown in entry 5, Table 2. Under these conditions, however, it was soon evident that only electron-rich arylboronic acids could be fully protodeboronated (entries 1 and 2, Table 3); electron-poor arylboronic acids resulted in incomplete protodeboronation and would require slightly harsher conditions for good conversions (entries 3 and 4, Table 3).

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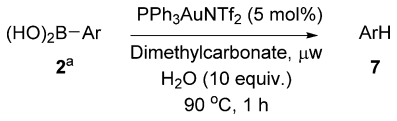
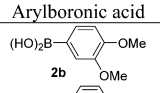
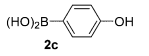
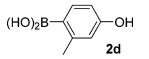
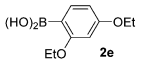
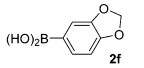
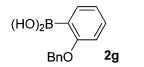
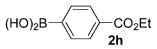
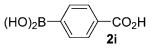
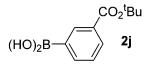
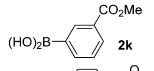
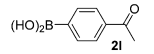
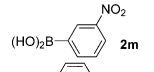
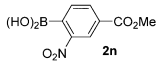
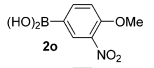
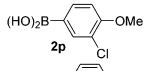
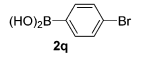
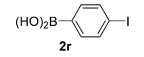
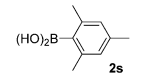
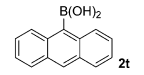
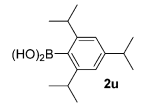
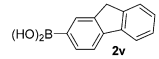
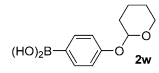
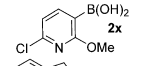
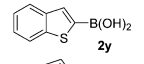
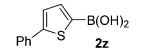
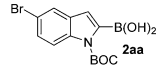
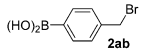
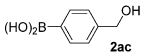
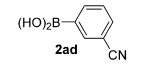
Table 4. Arylboronic Acid Scope under Microwave Conditions



Entry	Arylboronic acid	Product	Yield (%)
1[b]		**7b**	90
2		**7c**	65[c]
3		**7d**	92
4		**7e**	90
5		**7f**	62[c]
6		**7g**	93
7		**7h**	84
8		-	No conv.
9		**7j**,[d]	96[d]
10		**7k**	89
11[e]		**7l**	65
12		**7m**	92
13		**7n**	70
14		**7o**	97
15		**7p**	47[c]
16		**7q**	47[c]

Entry	Arylboronic acid	Product	Yield (%)
17		-	No conv.
18[f]		**7s**	95[c,f]
19[g]		**7t**	99
20[h]		**7u**	99
21		**7v**	74
22[i,j]		**7w**	83
23[h]		**7x**	72
24		**7y**	100
25		**7z**	85
26[j]		**7aa**	73
27		-	No conv.
28		-	No conv.
29		-	No conv.

[a]Commercial arylboronic acid; 10 equiv of H_2O added to ensure any arylboroxine is hydrated to the arylboronic acid, except entries 1,2, 7, and 11. [b]70 °C, 1.5 h. [c]Volatile product. [d]Carboxylic acid product. [e]2 × 5 mol % of catalyst over 4 h. [f]Reaction was done in THF-d_8, and yield was determined by ^{1}H NMR analysis using DMS as an internal standard. [g]2 h. [h]3 h. [i]4 h. [j]Unactivated 4 Å MS were added.

Pleasingly, slightly higher temperatures of 70−90 °C and utilizing microwave heating[27] allow for full conversion of both electron-donating and electron-withdrawing arylboronic acids in a much shorter reaction time (1−1.5 h, Table 4). For a more general procedure, 90 °C at 1 h was thus adopted. The *ortho*-, *meta*-, and *para*-substituted electron-rich arylboronic acids protodeboronated smoothly in excellent yields (entries 1−6; note that the lower yields of **7c** and **7f** reflect the slight volatility of the products). The *ortho*-, *meta*-, and *para*-substituted electron-poor arylboronic acids also protodeboronate smoothly under these conditions (entries 7 and 9−13). A carboxylic acid moiety, however, was found to inhibit protodeboronation (entry 8), but carboxylic acid products can nevertheless be readily obtained from protodeboronation and concurrent saponification of *tert*-butyl esters (entry 9). Unprotected base-sensitive ketone (entry 10) and ester functional groups (entries 7, 10, and 13) are tolerated, as are chloro- and bromoarylboronic acids (entries 15 and 16) but not aryl iodides (entry 17). Sterically bulky *ortho*-substituted substrates were also protodeboronated in high yields (entries 18−20), although longer reaction times of 2−3 h were necessary for full conversion of the bulkier substrates **2t** and **2u** (entries 19 and 20). Fluorene-2-boronic acid **2v**, with a readily oxidizable benzylic position, is also a competent substrate (entry 21).

To our delight, even acid-sensitive THP acetal is tolerated (**2x**), as long as molecular sieves are added to the reaction (entry 22).[28,29] Similarly, heteroarylboronic acids protodeboronate well (entries 23−26), including one with an acid-sensitive Boc group (**2aa**). There were, however, several arylboronic acids that failed to react under these conditions (entries 27−29). It is unclear why these arylboronic acids do not react, though inhibition of gold catalyst by the functional groups is a possibility. Nevertheless, the results presented in Table 4 demonstrate a wide substrate scope (electron-rich, electron-poor, sterically hindered, base- and acid-sensitive) for the protodeboronation reaction.

As part of our investigations, a small screen of commercially available gold catalysts was also carried out (Table 5). While cationic gold(I) phosphines promote good conversion (Gagosz' catalyst[25] and Echavarren's catalysts,[30] entries 1 and 2), both gold(I) and gold(III) chlorides gave no conversion to

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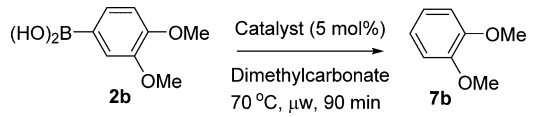
Table 5. Catalyst Screen



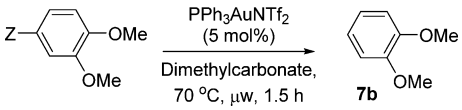
entry	catalyst	yield (%)[a]
1	$Ph_3PAuNTf_2$	quant.
2	*t*-Bu_2(*o*-biphenyl)$PAuSbF_6$·MeCN	92
3	Ph_3PAuCl	no conv.
4	Me_2SAuCl	no conv.
5	$AuCl_3$	no conv.
6	$NaAuCl_4·2H_2O$	no conv.
7	$Pd(OAc)_2$	52
8	$Pd_2(dba)_3$	no conv.
9	$Pd(PPh_3)_4$	no conv.

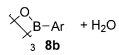
[a]Determined using ^{1}H NMR analysis of the crude reaction mixture using dimethylsulfone as an internal standard.

protodeboronated products (entries 3–6). For comparison with gold, a range of common palladium sources were also screened; no conversion was observed with $Pd_2(dba)_3$ or $Pd(PPh_3)_4$ (entries 8 and 9), with only modest conversion with $Pd(OAc)_2$ (entry 7).

Next, arylboroxine **8b**,[31] arylboronic ester **9b**,[31] potassium aryltrifluoroborate **10b**,[32] and MIDA-boronate **11b**[33] were evaluated in the gold-catalyzed protodeboronation reaction in order to ascertain their reactivity relative to arylboronic acids **2** (Table 6). **8b**–**11b** do not react under these conditions (entries

Table 6. Effect of Other Boronic Acid Derivatives



Entry	Z	Yield (%)[a]
1[b]	$(HO)_2B–Ar$ **2b**	Quant.
2[c]	 **8b**	No conv.
3[d]	 **8b**	Quant.
4	 **9b**	No conv.
5	$KF_3B–Ar$ **10b**	No conv.
6	 **11b**	No conv.

[a]Determined using ^{1}H NMR analysis of the crude reaction mixture using dimethylsulfone as an internal standard. [b]Arylboronic acid freshly recrystallized from water. [c]Arylboroxine formed from dehydrating arylboronic acid **2b** via heating under vacuum. [d]10 equiv of H_2O added to the reaction mixture.

2 and 4–6). However, since arylboroxine **8** is the dehydrated form of arylboronic acid **2**,[31] addition of 10 equiv of H_2O to the reacting mixture allows quantitative protodeboronation, presumably via preliminary in situ hydrolysis to the boronic acid **2b** (entry 3). Since commercially available arylboronic acids are typically a mixture of boronic acid and the corresponding boroxine,[1] addition of 10 equiv of H_2O was therefore adopted as the standard procedure in Table 4, to ensure reproducible results. In addition, the results in Table 6 show that orthogonal reactivity exists between arylboronic acids and the "protected" counterparts, arylboronic esters **9**, aryltrifluoroborates **10**, and MIDA-boronates **11**, which can potentially be exploited in synthesis.

To probe the mechanism of these protodeboronation reactions, we carried out DFT calculations (BP86-D3 level, correcting for THF solvent)[34] to model the reaction of $PhB(OH)_2$ with water at the $\{Au(PPh_3)\}^+$ fragment. The computed profile (Figure 1) starts from the $(Ph_3P)Au(PhB(OH)_2)·2H_2O$ adduct, **I·2H$_2$O**, in which the boronic acid binds to Au in an η^1-fashion via the *ipso*-carbon ($Au–C^1$ = 2.26 Å, $C^1–B$ = 1.61 Å; see Figure 2 for atom labeling).[35] No stable η^2-adducts were located. Two additional waters were included in the calculations because pathways based on a single water were found to have prohibitively high barriers, while tests with three water molecules exhibited a mechanism and energetics similar to those seen with two waters (see Supporting Information). Excess water is always present in the most efficient synthetic protocols. In **I·2H$_2$O** (G = 0.0 kcal/mol), the two water molecules form a square H-bonded array with the OH groups of the boronic acid. The reaction then starts from a higher energy conformer of this species, **Ia·2H$_2$O** (G = +4.1 kcal/mol), in which the added waters are located between the Au and B centers. From this position, one water can attack boron to form a weakly bound adduct, **II·2H$_2$O** (G = +8.4 kcal/mol, $B–O^1$ = 1.79 Å, $B–C^1$ = 1.64 Å). $B–C^1$ bond cleavage then proceeds via **TS(II–III)·2H$_2$O** at +18.4 kcal/mol with further shortening of the $B–O^1$ distance to 1.54 Å and elongation of $B–C^1$ to 2.08 Å (see Figure 2). This leads to **III·2H$_2$O**, which features a σ-Ph ligand ($Au–C^1$ = 2.06 Å) and a protonated boric acid–water cluster situated above the phenyl ring with one short Au···H contact (2.28 Å). The presence of a second water molecule facilitates this step by stabilizing the proton released upon nucleophilic attack. Protodeboronation is then completed by rotation of the $B(OH)_2(H_2O)^+·H_2O$ moiety to a perpendicular position and delivery of a proton onto the *ipso*-C via **TS(III–IV)·2H$_2$O** (G = +1.9 kcal/mol; $O^1–H^1$ = 1.15 Å, $C^1···H^1$ = 1.54 Å, $Au–C^1$ = 2.11 Å). This proton transfer is facilitated by H-bonding to the external water molecule and leads to **IV·B(OH)$_3$·H$_2$O** (G = −15.5 kcal/mol) in which a linear $(Ph_3P)Au(\eta^2\text{-}C_6H_6)$ complex interacts weakly with the $B(OH)_3·H_2O$ cluster. Protodeboronation therefore proceeds with an overall barrier of 18.4 kcal/mol, with the rate-limiting transition

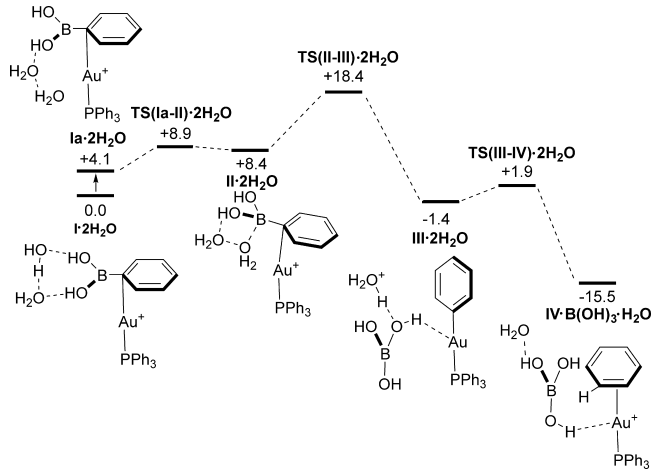


Figure 1. Computed free energy reaction profile (BP86-D3(THF), kcal/mol) for the protodeboronation of $PhB(OH)_2$ at $\{Au(PPh_3)\}^+$ with two water molecules.

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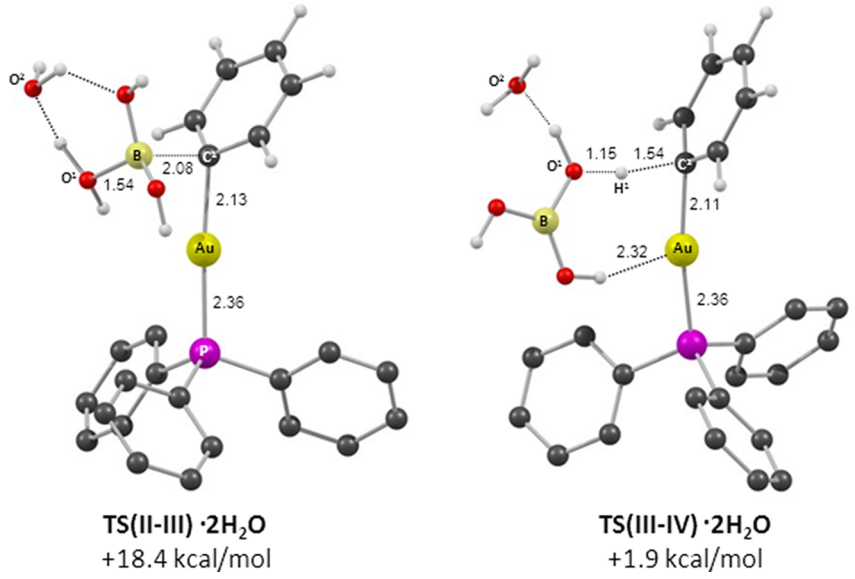
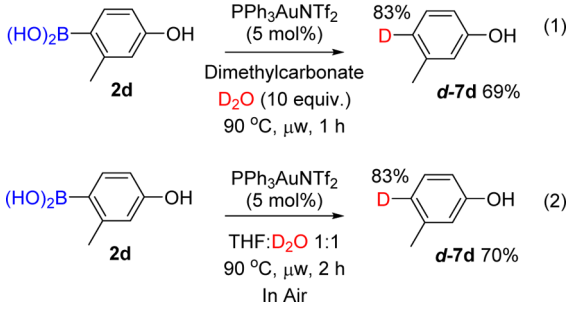


Figure 2. Computed structures of **TS(II–III)·2H$_2$O** (B–C bond cleavage) and **TS(III–IV)·2H$_2$O** (protonolysis) with key distances in Å. Phosphine H atoms are deleted for clarity.

state corresponding to cleavage of the B–C[1] bond. Once this is achieved, the subsequent protonolysis[36] has a minimal barrier. An analogous study on the parent MIDA-boronate (**11b**, Table 6, Ar = Ph) provided a computed barrier of 39.5 kcal/mol, consistent with the fact that this species does not undergo protodeboronation. This reflects the presence of a saturated boron center in this species, which must undergo B–N bond cleavage (ΔG = +17.9 kcal/mol) before nucleophilic attack can occur (see Supporting Information).

In order to provide evidence (or otherwise) for the *ipso*-selective protodeauration, the reaction was carried out in dried dimethylcarbonate with 10 equiv of added D$_2$O under strictly anhydrous conditions (eq 1, Scheme 4). Indeed, deuteration occurs only at the *ipso*-position (***d*-7d**, 83%), proving a regiospecific protodeauration step.

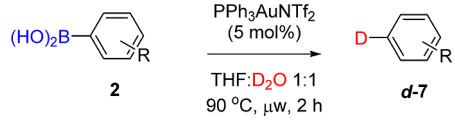
Scheme 4. Deuteration Studies To Prove *ipso*-Selective Proto(deutero)deauration

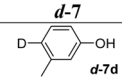
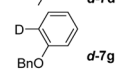
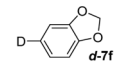
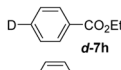
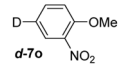
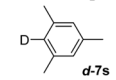
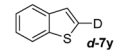
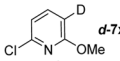
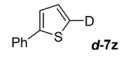


This *ipso*-deuteration result also shows that the gold(I)-catalyzed method can potentially be used as a regiospecific deuteration technique. The example shown in Scheme 4 is completely selective for the C bearing the boronic acid, and no deuteration is observed at any other position; therefore, it has potential as a selective deuterium-labeling technique for biochemical or mechanistic investigations. The reaction shown in Scheme 4 eq 1 was carried out under strictly anhydrous conditions (apart from the added D$_2$O) in order to maximize the amount of D incorporation. In order to improve the practicality of the method, we decided to increase the amount of D$_2$O in the reaction by using 1:1 THF/D$_2$O as solvent (solubility is poor in D$_2$O alone; see Table 1) (eq 2, Scheme 4). This practical deuteration method can be carried out readily in air and should be a mild, acid- and base-free deuteration method. Thus, a small substrate scope study was carried out (Table 7).

To our delight, electron-rich substrates deuterated regiospecifically in good yields (entries 1–3). The slightly lower 83% deuteration of ***d*-7d** compared to the full deuteration of ***d*-7g** and

Table 7. Regiospecific Deuterodeboronations



Entry	*d*-7	% Deuteration[a]	Yield (%)
1	 *d*-7d	83	70
2	 *d*-7g	100	88
3	 *d*-7f	100	98
4	 *d*-7h	100	<10%[b]
5	 *d*-7o	ND[c]	<15%[b]
6[d]	 *d*-7s	100	Quant.[b]
7	 *d*-7y	96	93
8[e]	 *d*-7x	95	58
9	 *d*-7z	98	98

[a]Determined by ^{1}H NMR analysis. [b]Determined by ^{1}H NMR analysis of the crude with dimethylsulfone as an internal standard. [c]Not determined. [d]Reaction done in THF-d_8. [e]4 h.

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d-**7f** is likely the result of the exchangeable phenolic proton present in the molecule. Unfortunately, arylboronic acids with electron-withdrawing groups reacted very sluggishly under these conditions and appear not to be good substrates for this method (entries 4 and 5). Nevertheless, this deuterodeboronation method is therefore complementary to the deuterodecarboxylation methods described previously, which were mainly suitable for electron-withdrawing aryls.[37] The sterically hindered position in **2s** is tolerated well (entry 6). Pleasingly, selective deuteration of heterocycles also proceeds well (entries 7−9). Therefore, from the substrate scope study shown in Table 7, it appears that the percent deuteration is generally excellent (>95%), except in cases where an exchanging proton is present in the substrate (entry 1, 83% D). In terms of conversions, the procedure works best with electron-rich aryl- or heteroarylboronic acid substrates.

CONCLUSION

In conclusion, we have developed a mild gold(I)-catalyzed protodeboronation method that can be used in "green" solvents, is tolerant of a variety of functional groups (including acid- and base-sensitive groups), and is general to a wide range of arylboronic acids. It is hoped that this simple, mild, and general protodeboronation method will enable the more widespread use of boronic acids as blocking/directing groups. DFT calculations propose a mechanism that involves sequential nucleophilic attack of water at boron, rate-limiting B−C bond cleavage, and facile protonolysis of a Au−σ-phenyl intermediate.

In the presence of D_2O, it can also be utilized as a mild, base- and acid-free regiospecific *ipso*-deuteration technique. The deuterodeboronation works smoothly for heteroaryl and electron-rich arylboronic acid substrates, which makes it complementary to deuterodecarboxylation methods which are limited to electron-withdrawing aryls. We envisage that this method should see applications in selective deuterium labeling of compounds for biochemical or mechanistic investigations.

EXPERIMENTAL SECTION

1,2-Dimethoxybenzene (7b).[38] Boronic acid (0.14 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 5.4 mg, 5 mol %), and dimethylcarbonate (0.75 mL, 0.20 M) were added to the microwave tube and heated at 70 °C for 1.5 h in the microwave. The resulting mixture was passed through a silica plug, washed with 49:1 hexane/ether, and then concentrated. The product was purified by column chromatography (9:1 hexane/ether) to yield product **7b** as a colorless oil (90%, 16.8 mg, 0.120 mmol): ν_{max}/cm^{-1} 3000, 2944, 2834 (C−H), 1592, 1503, 1460, 1440 (Ar C−C), 1052 (C−O); ^1H NMR (300 MHz, $CDCl_3$) δ 6.95−6.86 (m, 4H), 3.86 (s, 6H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 149.2 (C), 121.0 (CH), 111.5 (CH), 55.9 (CH_3).

Phenol (7c).[39] Boronic acid (0.18 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), and dimethylcarbonate (0.75 mL, 0.25 M) were added to the microwave tube and heated at 70 °C for 1.5 h in the microwave. The resulting mixture was passed through a silica plug and washed with ether. The product was then purified by column chromatography (4:1 pentane/ether) to yield product **7c** as a colorless oil (65%, 11.3 mg, 0.12 mmol): ν_{max}/cm^{-1} 3372 (O−H), 3025, 2921, 2852 (C−H), 1595, 1499, 1471, 1451 (Ar C−C); ^1H NMR (300 MHz, acetone-d_6) δ 8.24 (br s, 1H), 7.14−7.21 (m, 2H), 6.77−6.84 (m, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, acetone-d_6) δ 158.3 (C), 130.2 (CH), 120.1 (CH), 116.1 (CH).

***m*-Cresol (7d).**[39] Boronic acid (0.33 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 13 mg, 5 mol %), dimethylcarbonate (1.3 mL, 0.25 M), and H_2O (59 μL, 3.3 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was then passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (9:1 then 4:1 pentane/ether) to yield product **7d** as a yellow oil (92%, 33 mg, 0.31 mmol): R_f 0.1 (9:1 pentane/ether); ν_{max} (cm^{-1}) 3307 (O−H), 2921 (C−H), 1489, 1461 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, 1H, J = 7.8 Hz), 6.74−6.78 (m, 1H), 6.62−6.68 (m, 2H), 4.83 (s, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 155.6 (C), 140.0 (C), 129.6 (CH), 121.7 (CH), 116.2 (CH), 112.4 (CH), 21.5 (CH_3).

1,3-Diethoxybenzene (7e).[40] Boronic acid (0.24 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 9 mg, 5 mol %), dimethylcarbonate (0.96 mL, 0.25 M), and H_2O (43 μL, 2.4 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (49:1 then 9:1 pentane/ether) to yield product **7e** as a colorless oil (90%, 36 mg, 0.22 mmol): R_f 0.6 (9:1 pentane/ether); ν_{max} (cm^{-1}) 2979, 2930 (C−H), 1492, 1474 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.13−7.20 (m, 1H), 6.45−6.52 (m, 3H), 4.02 (q, 4H, J = 7.0 Hz), 1.40 (t, 6H, J = 7.0 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.3 (C), 129.9 (CH), 106.8 (CH), 101.5 (CH), 63.5 (CH_2), 15.0 (CH_3).

1,3-Benzodioxole (7f).[41] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (10:1 pentane/ether) to yield product **7f** as a colorless oil (62%, 15.7 mg, 0.103 mmol): R_f 0.76 (5:1 pentane/ether); ν_{max} (cm^{-1}) 2924 (C−H), 2358, 2339 (O−CH_2−O), 1478, 1360 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 6.83 (m, 4H), 5.95 (s, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 147.5 (C), 121.8 (CH), 108.8 (CH), 100.7 (CH_2).

Benzyl Phenyl Ether (7g).[42] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (15:1 pentane/ether) to yield product **7g** as a white solid (93%, 34.7 mg, 0.189 mmol): R_f 0.75 (5:1 pentane/ether); mp 42−43 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.12−7.30 (m, 7H), 7.83−7.91 (m, 3H), 4.97 (s, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 158.9 (C), 137.2 (C), 129.6 (CH), 128.7 (CH), 128.1 (CH), 127.6 (CH), 121.1 (CH), 115.0 (CH), 70.0 (CH_2); found (FTMS + pAPCI) $[M + H]^+$ 185.0960, $C_{13}H_{13}O$ requires 185.0961.

Ethyl Benzoate (7h).[43] Boronic acid (0.13 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 5.1 mg, 5 mol %), and dimethylcarbonate (0.75 mL, 0.20 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with 9:1 hexane/ether, and then concentrated. The product was purified by column chromatography (9:1 pentane/ether) to yield product **7h** as a colorless oil (84%, 16.2 mg, 0.107 mmol): ν_{max}/cm^{-1} 2983 (C−H), 1712 (C═O), 1602, 1451, 1367 (Ar C−C), 1274 (C−O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, 2H, J = 7.54 Hz), 7.58 (t, 1H, J = 7.54 Hz), 7.47 (m, 2H), 4.38 (q, 2H, J = 7.2 Hz), 1.40 (t, 3H, J = 7.2 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 166.8 (C), 132.9 (CH), 130.7 (C), 129.7 (CH), 128.5 (CH), 61.1 (CH_2), 14.5 (CH_3).

Benzoic Acid (7j′).[44] Boronic acid (0.22 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 9 mg, 5 mol %), dimethylcarbonate (0.88 mL, 0.25 M), and H_2O (40 μL, 2.2 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (49:1 then 9:1 pentane/ether) to yield product **7j′** as a white solid (96%, 26 mg, 0.22 mmol): R_f 0.1 (9:1 pentane/ether); mp 121−122 °C; ν_{max}/cm^{-1} 3071, 2830 (O−H), 2554 (C−H), 1679 (C═O), 1601, 1582, 1452, 1420 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 9.12−12.0 (br s, 1H), 8.12−8.16 (m, 2H), 7.60−7.65 (m, 1H), 7.46−

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7.52 (m, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 172.4 (C), 134.0 (CH), 130.4 (CH), 129.5 (C), 128.6 (CH).

Methyl Benzoate (7k).[45] Boronic acid (0.28 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 11 mg, 5 mol %), dimethylcarbonate (1.1 mL, 0.25 M), and H_2O (50 μL, 2.8 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (49:1 then 9:1 pentane/ether) to yield product **7k** as a colorless oil (89%, 34 mg, 0.25 mmol): R_f 0.7 (20:1 pentane/ether); ν_{max}/cm^{-1} 3026, 2916, 2852 (C−H), 1725 (C═O), 1492, 1451 (Ar C−C), 1262 (C−O); ^1H NMR (300 MHz, CD_2Cl_2) δ 7.99−8.04 (m, 2H), 7.56 (tt, 1H, J = 1.4, 6.5 Hz), 7.41−7.48 (m, 2H), 3.88 (s, 3H); $^{13}C\{^1H\}$ NMR: (75.5 MHz, CD_2Cl_2) δ 167.4 (C), 133.4 (CH), 130.9 (C), 130.0 (CH), 128.9 (CH), 52.5 (CH_3).

Acetophenone (7l).[46] Boronic acid (0.22 mmol, 1 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 9 mg, 5 mol %), and dimethyl carbonate (0.8 mL) were added to the microwave tube and placed in the microwave and heated at 90 °C for 2 h. A second portion of PPh_3AuNTf_2 (5 mol %) was then added to the reaction mixture, which was then heated in the microwave for a further 2 h at 90 °C. The resulting mixture was then passed through a silica plug and washed with ether. The product was purified by column chromatography (7:1 pentane/ether) to yield product **7l** as a colorless oil (65%, 17.2 mg, 0.14 mmol): R_f 0.52 (5:1 pentane/ether); ν_{max} (cm^{-1}) 3062 (C−H), 1682 (C═O), 1598, 1582, 1448 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.94−7.98 (m, 2H), 7.57 (tt, 1H, J = 1.3, 6.3 Hz), 7.43−7.50 (m, 2H), 2.61 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 198.3 (C), 137.3 (C), 133.2 (CH), 128.7 (CH), 128.4 (CH), 26.7 (CH_3).

Nitrobenzene (7m).[47] Boronic acid (0.30 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 12 mg, 5 mol %), dimethylcarbonate (1.2 mL, 0.25 M), and H_2O (54 μL, 3.0 mmol, 10 equiv) were added to the microwave tube and placed in the microwave at 90 °C for 1 h. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (49:1 then 9:1 pentane/ether) to yield product **7m** as a colorless oil (92%, 34 mg, 0.28 mmol): R_f 0.5 (9:1 pentane/ether); ν_{max} (cm^{-1}) 3076, 2859 (C−H), 1518 (NO_2), 1477 (Ar C−C), 1343 (NO_2); ^1H NMR (300 MHz, $CDCl_3$) δ 8.22−8.26 (m, 2H), 7.70 (tt, 1H, J = 1.2, 6.7 Hz), 7.52−7.59 (m, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 148.4 (C), 134.7 (CH), 129.4 (CH), 123.6 (CH).

Methyl 3-Nitrobenzoate (7n).[48] Boronic acid (0.22 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 9 mg, 5 mol %), dimethylcarbonate (0.88 mL, 0.25 M), and H_2O (40 μL, 3.0 mmol, 10 equiv) were added to the microwave tube and placed in the microwave at 90 °C for 1 h. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (49:1 then 9:1 pentane/ether) to yield product **7n** as a white solid (70%, 28 mg, 0.15 mmol): R_f 0.2 (9:1 pentane/ether); mp 77−78 °C; ν_{max} (cm^{-1}) 2955 (C−H), 1726 (C═O), 1531 (NO_2), 1480, 1442 (Ar C−C), 1349 (NO_2), 1263 (C−O−C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.87−8.89 (m, 1H), 8.42 (ddd, 1H, J = 1.1, 2.3, 8.2 Hz), 8.37 (dt, 1H, J = 1.7, 7.7 Hz), 7.63−7.69 (m, 1H), 3.99 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 165.1 (C), 148.5 (C), 136.4 (CH), 132.0 (C), 129.8 (CH), 127.6 (CH), 124.8 (CH), 53.0 (CH_3).

2-Nitroanisole (7o).[49] Boronic acid (0.25 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 10 mg, 5 mol %), dimethylcarbonate (1.5 mL, 0.16 M), and H_2O (42 μL, 2.5 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was then passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (3:1 pentane/ether) to yield product **7o** as an oil (97%, 37.7 mg, 0.246 mmol): R_f 0.30 (3:1 pentane/ether); ν_{max} (cm^{-1}) 2946, 2923, 2916, 2844 (C−H), 1582 (NO_2), 1492, 1463, 1451, 1438 (Ar C−C), 1347 (NO_2), 1276 (C−O−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, 1H, J = 1.7, 8.1 Hz), 7.53 (ddd, 1H, J = 1.7, 7.4, 8.5 Hz), 7.09 (dd, 1H, J = 1.1, 8.5 Hz), 7.02 (ddd, 1H, J = 1.1, 7.4, 8.1 Hz), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 153.1 (C), 139.8 (C), 134.3 (CH), 125.8 (CH), 120.4 (CH), 113.6 (CH), 56.6 (CH_3).

2-Chloroanisole (7p).[50] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (7:1 pentane/ether) to yield product **7p** as a colorless oil (47%, 13.6 mg, 0.097 mmol): R_f 0.57 (5:1 pentane/ether); ν_{max} (cm^{-1}) 2940, 2838 (C−H), 1588, 1485, 1462, 1449 (Ar C−C), 1274 (C−O−C); ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (dd, 1H, J = 1.6, 7.8 Hz), 7.20−7.25 (m, 1H), 6.87−6.95 (m, 2H), 3.90 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 155.1 (C), 130.4 (CH), 127.9 (CH), 122.6 (C), 121.4 (CH), 112.2 (CH), 56.2 (CH_3).

Bromobenzene (7q).[51] Boronic acid (0.25 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 9.8 mg, 5 mol %), dimethylcarbonate (1.5 mL, 0.17 M), and H_2O (45 μL, 2.5 mmol, 10 equiv) were added to the microwave tube and heated in the microwave at 90 °C for 1 h. The resulting mixture was then passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (20:1 pentane/ether) to yield product **7q** as a colorless liquid (47%, 18.3 mg, 0.102 mmol): R_f 0.65 (20:1 pentane/ether); ν_{max} (cm^{-1}) 3064 (C−H), 1577, 1473, 1442 (Ar C−C), 730 (C−Br); ^1H NMR (300 MHz, $CDCl_3$) δ 7.54−7.59 (m, 2H), 7.26−7.39 (m, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 131.6 (CH), 130.1 (CH), 127.0 (CH), 122.6 (C).

1,3,5-Trimethylbenzene (7s).[52] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 10 equiv), and THF-d_8 (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. Internal standard dimethylsulfone (9.4 mg, 0.5 equiv) was added to the mixture. ^1H NMR yield of 95% was obtained. Due to the volatile nature of the product, an isolated yield was not obtained: ^1H NMR (300 MHz, THF-d_8) δ 6.24 (s, 3H), 1.72 (s, 9H).

Anthracene (7t).[53] Boronic acid (0.23 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 8.8 mg, 5 mol %), dimethylcarbonate (1.5 mL, 0.15 M), and H_2O (41 μL, 2.3 mmol, 10 equiv) were added to the microwave tube and heated at 90 °C for 2 h in the microwave. The resulting mixture was the passed through a silica plug and washed with ether. The product was purified by column chromatography (40:1 pentane/ether) to yield product **7t** as a yellow solid (99%, 40.2 mg, 0.226 mmol): R_f 0.62 (40:1 pentane/ether); mp 194−196 °C; ν_{max} (cm^{-1}) 3049, 3024, 2921 (C−H), 1590, 1533, 1450 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.44 (s, 2H), 8.00−8.06 (m, 4H), 7.46−7.52 (m, 4H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 131.8 (C), 128.3 (CH), 126.3 (CH), 125.5 (CH).

1,3,5-Trisopropylbenzene (7u).[54] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 3 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (pentane) to yield product **7u** as a colorless oil (99%, 37.8 mg, 0.18 mmol): R_f 0.86 (5:1 pentane/ether); ν_{max} (cm^{-1}) 2957 (C−H), 1599, 1465, 1381 (Ar C−C); ^1H NMR (300 MHz, $CDCl_3$) δ 6.96 (s, 3H), 2.92 (sept, 3H, J = 6.9 Hz), (d, 18H, J = 6.9 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 148.8 (C), 122.2 (CH), 34.4 (CH), 24.3 (CH_3).

Fluorocene (7v).[55] Boronic acid (0.12 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 4.7 mg, 5 mol %), dimethylcarbonate (0.75 mL, 0.15 M), and H_2O (21 μL, 1.2 mmol, 10 equiv) were added to the microwave tube and heated in the microwave at 90 °C for 1 h. The resulting mixture was then passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (40:1 pentane/ether) to yield product **7v** as a yellow solid (74%, 14.6 mg, 0.088 mmol): mp 116−118 °C; ν_{max} (cm^{-1}) 3024, 2917 (C−H), 1574, 1490, 1477, 1447 (Ar C−C) ;^1H NMR (300 MHz, $CDCl_3$) δ 7.81 (dt, 2H, J = 0.9, 7.3 Hz), 7.55−7.58 (m, 2H), 7.37−7.42 (m, 2H), 7.32 (td, 2H, J = 1.2, 7.3 Hz), 3.92 (s, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 143.3 (C), 141.8 (C), 126.9 (CH), 126.8 (CH) 125.2 (CH), 120.0 (CH), 37.1 (CH_3).

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2-Phenoxytetrahydro-2*H*-pyran (7w).[56] Boronic acid (0.20 mmol), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), unactivated powdered 4 Å molecular sieves (20 mg), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL) were added to a microwave tube and heated in the microwave at 90 °C for 4 h. The resulting mixture was passed through an alumina plug and washed with ether. The product was purified by column chromatography (alumina used, 25:1 pentane/ether) to yield product **7w** as a colorless oil (83%, 29.2 mg, 0.164 mmol): R_f 0.88 (5:1 pentane/ether, alumina TLC plate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25−7.31 (m, 2H), 7.04−7.09 (m, 2H), 6.96−7.01 (m, 1H), 5.43 (t, 1H, *J* = 3.3 Hz), 3.87−3.97 (m, 1H), 3.57−3.65 (m, 1H), 1.97−2.07 (m, 1H), 1.84−1.90 (m, 2H), 1.57−1.73 (m, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 157.2 (C), 129.5 (CH), 121.7 (CH), 116.6 (CH), 96.5 (CH), 62.2 (CH_2), 30.6 (CH_2), 25.4 (CH_2), 19.0 (CH_2); found (GC/MS EI+) $[M]^+$ 178.0993, $C_{11}H_{14}O_2$ requires 178.0994.

2-Chloro-6-methoxypyridine (7x).[57] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 3 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (15:1 pentane/ether) to yield product **7x** as a colorless oil (72%, 16.9 mg, 0.118 mmol): R_f 0.70 (5:1 pentane/ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, 1H, *J* = 7.5, 8.2 Hz), 6.90 (dd, 1H, *J* = 0.7, 7.5 Hz), 6.65 (dd, 1H, *J* = 0.7, 8.2 Hz), 3.94 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 164.0 (C), 148.5 (C), 140.6 (CH), 116.4 (CH), 109.2 (CH), 54.1 (CH_3); found (FTMS + pNSI) $[M + H]^+$ 144.0207, C_6H_7ClNO requires 144.0211.

1-Benzothiophene (7y).[58] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), and dimethylcarbonate (0.8 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with pentane, and then concentrated to yield product **7y** as a colorless oil (100%, 27.5 mg, 0.2 mmol). Note: the product begins to decompose if left on silica for too long: ^{1}H (300 MHz, $CDCl_3$) δ 7.77−7.82 (m, 1H), 7.71−7.76 (m, 1H), 7.33 (d, 1H, *J* = 5.4 Hz), 7.21−7.29 (m, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 139.8 (C), 139.7 (C), 126.4 (CH), 124.31 (CH), 124.26 (CH), 124.0 (CH), 123.7 (CH), 122.6 (CH); found (FTMS + pAPCI) $[M + H]^+$ 135.0262, C_8H_7S requires 135.0263.

2-Phenylthiophene (7z).[59] Boronic acid (0.10 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 3.7 mg, 5 mol %), H_2O (20 μL, 1.0 mmol, 10 equiv), and dimethylcarbonate (0.4 mL, 0.25 M) were added to the microwave tube and heated at 90 °C for 1 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (pentane) to yield product **7z** as a colorless oil (85%, 13.7 mg, 0.09 mmol): R_f 0.78 (5:1 pentane/ether); ^{1}H (300 MHz, $CDCl_3$, referenced to TMS) δ 7.51−7.55 (m, 2H), 7.26−7.33 (m, 2H), 7.16−7.24 (m, 3H), 7.00 (1H, dd, *J* = 3.6, 5.1 Hz); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 144.6 (C), 134.6 (C), 129.0 (CH), 128.1 (CH), 127.6 (CH), 126.1 (CH), 124.9 (CH), 123.2 (CH); found (FTMS + pAPCI) $[M + H]^+$ 161.0414, $C_{10}H_9S$ requires 161.0419.

***N*-Boc-5-Bromoindole (7aa).**[60] Boronic acid (0.20 mmol, 1.0 equiv), PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %), H_2O (40 μL, 2.0 mmol, 10 equiv), dimethylcarbonate (0.8 mL, 0.25 M), and 1 bead of unactivated 4 Å molecular sieves were added to the microwave tube and heated at 90 °C for 3 h in the microwave. The resulting mixture was passed through a silica plug, washed with ether, and then concentrated. The product was purified by column chromatography (15:1 pentane/ether) to yield product **7aa** as colorless oil (73%, 42.1 mg, 0.142 mmol): R_f 0.67 (5:1 pentane/ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, 1H, *J* = 8.8 Hz), 7.69 (d, 1H, *J* = 2.3 Hz), 7.59 (d, 1H, *J* = 3.7 Hz), 7.40 (dd, 1H, *J* = 2.3, 8.8 Hz), 6.50 (d, 1H, *J* = 3.7 Hz), 1.67 (s, 9H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 149.5 (C), 134.1 (C), 132.4 (C), 127.1 (CH × 2), 123.6 (CH), 116.7 (CH), 116.1 (C), 106.6 (CH), 84.2 (C), 28.3 (CH_3); found (FTMS + pAPCI) $[M + H]^+$ 296.0275, $C_{13}H_{15}BrNO_2$ requires 296.0281.

Deuterodeboronation. *General Procedure A.* Boroxine (0.20 mmol), dry THF (0.4 mL), and D_2O (0.4 mL) were added to the microwave tube followed by PPh_3AuNTf_2 (2:1 toluene adduct, 7.4 mg, 5 mol %) and heated in the microwave at 90 °C for 2 h. The resulting mixture was passed through a plug of silica and washed with ether. The products were purified by column chromatography (pentane/ether).

3-Methyl-(4-*d*)phenol (*d*-7d). General procedure A was followed to yield product ***d*-7d** (83% deuteration) as a colorless oil (70%, 15.3 mg, 0.139 mmol). Purified by column chromatography (5:1 pentane/ether); R_f 0.26 (5:1 pentane/ether); ν_{max} (cm^{-1}) 3311 (O−H), 2921 (C−H), 2250 (C−D), 1584, 1473, 1448 (Ar C−C), 1240 (C−O−C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10−7.16 (m, 1H), 6.62−6.67 (m, 2H), 4.76 (s, 1H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 155.5 (C), 139.9 (C), 129.4 (CH), 121.8 (C, t, *J* = 24.4 Hz), 116.1 (CH), 112.3 (CH), 21.4 (CH_3); found (FTMS + pAPCI) $[M + H]^+$ 110.0708, C_7H_8DO requires 110.0711.

1-(Benzyloxy)benzene-2-*d* (*d*-7g). General procedure A was followed to yield product ***d*-7g** (100% deuteration) as a white solid (88%, 33.4 mg, 0.183 mmol). Purified by column chromatography (15:1 pentane/ether): R_f 0.80 (5:1 pentane/ether); mp 38−39 °C; ν_{max} (cm^{-1}) 3064, 3030 (C−H), 2869 (C−D), 1589, 1474, 1462, 1452, 1444 (Ar C−C), 1230 (C−O−C); ^{1}H NMR (300 MHz, $CDCl_3$, referenced using TMS) δ 7.14−7.40 (m, 7H), 6.84−6.93 (m, 2H), 4.97 (s, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 158.9 (C), 137.2 (C), 129.6 (CH), 129.5 (CH), 128.7 (CH), 128.1 (CH), 127.6 (CH), 121.1 (CH), 115.0 (CH), 114.7 (C, t, *J* = 24.4 Hz) 70.0 (CH_2); found (GC/MS EI) $[M]^+$ 185.0951, $C_{13}H_{11}DO$ requires 185.0955.

Benzo[*d*][1,3]dioxole-5-*d* (*d*-7f). General procedure A was followed with the exception that the silica plug was washed with pentane and then 10:1 pentane ether to yield product ***d*-7f** (100% deuteration) as a colorless oil (98%, 23.7 mg, 0.193 mmol): ν_{max} (cm^{-1}) 2891 (C−H), 1500, 1474, 1442 (Ar C−C), 1229 (C−O−C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.83 (m, 3H), 5.95 (s, 2H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 147.5 (2 × C), 121.6 (CH), 121.5 (C, t, *J* = 24.8 Hz), 108.8 (CH), 108.7 (CH), 100.7 (CH_2); found (FTMS + pAPCI) $[M - H]^+$ 122.0344, $C_7H_4DO_2$ requires 122.0347.

1,3,5-Trimethyl(2-*d*)benzene (*d*-7s). General procedure A was followed, but THF-d_8 was used instead of THF, and no silica plug was used. Instead, an internal standard dimethylsulfone (9.4 mg, 0.5 equiv) was added to the reaction mixture, which was then dried with $MgSO_4$. ^{1}H NMR analysis indicated quantitative yield, and the product ***d*-7s** was 100% deuterated. The product was not isolated due to its volatility: ^{1}H NMR (300 MHz, THF-d_8) δ 6.24 (s, 3H), 1.72 (s, 9H).

Benzo[*b*]thiophene-2-*d* (*d*-7y).[37b] General procedure A was followed with the exception that the silica plug was washed with pentane instead of ether to yield product ***d*-7y** (96% deuteration) as a colorless oil (93%, 25.6 mg, 0.190 mmol). Note: the product begins to decompose if left on silica for too long: ν_{max} (cm^{-1}) 3053 (C−H), 2313 (C−D), 1454, 1414 (C−C Ar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89−7.94 (m, 1H), 7.83−7.87 (m, 1H), 7.33−7.42 (m, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 139.8 (C), 139.7 (C), 126.2 (C, t, *J* = 28.2 Hz), 124.31 (CH), 124.28 (CH), 123.8 (CH), 123.7 (CH), 122.6 (CH); found (FTMS + pAPCI) $[M]^+$ 135.0246, C_8H_5DS requires 135.0247. Mass spectrometry calculated 95% deuteration, which is consistent with NMR data.

2-Chloro-6-methoxypyridine-5-*d* (*d*-7x). General procedure A was followed with the exception of reaction time, which was extended to 4 h rather than 2 h to yield product ***d*-7x** (95% deuteration) as a colorless oil (58%, 16.5 mg, 0.114 mmol). Purified by column chromatography (15:1 pentane/ether): R_f 0.78 (5:1 pentane/ether); ν_{max} (cm^{-1}) 2954 (C−H), 1587, 1574, 1552 (C−C Ar), 1259 (C−O−C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (dt, 1H, *J* = 1.0, 7.5 Hz), 6.89 (d, 1H, *J* = 7.5 Hz), 3.94 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 164.0 (C), 148.5 (C), 140.5 (CH), 116.3 (CH), 109.0 (C, t, *J* = 25.6 Hz), 54.1 (CH_3); found (FTMS + p NSI) $[M + H]^+$ 145.0271, C_6H_6DClNO requires 145.0273.

2-Phenylthiophene-5-*d* (*d*-7z). General procedure A was followed but on a smaller scale (0.10 mmol instead of 0.20 mmol), and a silica plug was washed with pentane to yield product ***d*-7z** (98% deuteration) as a colorless oil (98%, 16.0 mg, 0.099 mmol): ν_{max} (cm^{-1}) 3073 (C−H), 2324 (C−D) 1599, 1530, 1485, 1445, 1420 (C−C Ar); ^{1}H NMR (300 MHz, acetone-d_6) δ 7.64−7.69 (m, 2H), 7.37−7.46 (m, 3H), 7.30 (tt,

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1H, J = 1.3, 6.7 Hz), 7.12 (d, 1H, J = 3.6 Hz) ; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 144.5 (C), 134.6 (C), 129.0 (CH), 128.0 (CH), 127.6 (CH), 126.1 (CH), 124.9 (C, t, J = 14.7 Hz), 123.2 (CH); found (FTMS + pAPCI) $[M + H]^+$ 161.0400, $C_{10}H_8DS$ requires 161.0404.

Computational Details. Calculations were run with Gaussian 03, revision D.01,[61] with PCM solvent corrections run with Gaussian 09, revision A.02.[62] Geometry optimizations were performed using the BP86 functional[63] with Au and P centers described with the Stuttgart RECPs and associated basis sets[64] (with added d-orbital polarization on P (ζ = 0.387))[65] and 6-31G** basis sets for all other atoms.[66] All stationary points were fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). Frequency calculations also provided a free energy in the gas phase, computed at 298.15 K and 1 atm. For transition states, IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Energies reported in the text are based on the gas-phase free energies and incorporate a correction for dispersion effects using Grimme's D3 parameter set[67] (i.e., BP86-D3) as well as solvation (PCM approach) in THF.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra and computational data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01041.

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Notes

The authors declare no competing financial interest.

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