

Electrochemistry

Electrochemical Generation of Hypervalent Bromine(III) Compounds

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Abstract: In sharp contrast to hypervalent iodine(III) compounds, the isoelectronic bromine(III) counterparts have been little studied to date. This knowledge gap is mainly attributed to the difficult-to-control reactivity of λ^3 -bromanes as well as to their challenging preparation from the highly toxic and corrosive BrF_3 precursor. In this context, we present a straightforward and scalable approach to chelation-stabilized λ^3 -bromanes by anodic oxidation of parent aryl bromides possessing two coordinating hexafluoro-2-hydroxypropanyl substituents. A series of *para*-substituted λ^3 -bromanes with remarkably high redox potentials spanning a range from 1.86 V to 2.60 V vs. Ag/AgNO_3 was synthesized by the electrochemical method. We demonstrate that the intrinsic reactivity of the bench-stable bromine(III) species can be unlocked by addition of a Lewis or a Brønsted acid. The synthetic utility of the λ^3 -bromane activation is exemplified by oxidative C–C, C–N, and C–O bond forming reactions.

The chemistry of hypervalent halogen species has experienced tremendous development in the last decades, and hypervalent iodine(III) compounds have become mainstream reagents in contemporary organic synthesis.^[1] Recent selected applications of hypervalent iodine(III) compounds involve oxidative heterocycle formation,^[2] atom transfer reactions^[3] such as alkynylation^[4] and trifluoromethylation,^[5] oxidative rearrangements,^[6] and C–H functionalization.^[7] Additionally, electrochemically generated iodine(III) derivatives have been frequently utilized as ex-cell mediators (electro-generated reagents) in organic electrosynthesis.^[8] The corresponding

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isoelectronic hypervalent bromine(III) species feature superior reactivity to that of iodine(III) counterparts owing to the higher oxidizing ability, stronger electrophilicity and better nucleofugality of the bromanyl unit.^[9] Not surprisingly, the unique properties of bromine(III) reagents have allowed for the development of unprecedented synthetic transformations such as Hofmann rearrangement of sulfonamides to the corresponding *N*-arylsulfamoyl fluorides,^[10] unusual Bayer–Villiger-type oxidation of open-chain aliphatic aldehydes,^[9a] oxidative coupling of alkynes and primary alcohols to form conjugated enones^[11] as well as transition metal-free regioselective C–H amination of non-activated alkanes.^[12] Although these notable accomplishments highlight the remarkable synthetic potential of bromine(III) species,^[13a] the hypervalent bromine chemistry appears to be significantly less developed as compared to that of iodine(III) compounds. This striking bias apparently is to be attributed to the relatively poor stability and the high oxidizing power of bromine(III) reagents,^[13b] properties that have created a common perception of difficult-to-control reactivity and poor functional group compatibility. Furthermore, there is an apparent lack of convenient methods for the synthesis of bromine(III) species.

The synthesis of Br^{III} reagents is typically accomplished by a ligand exchange reaction between bromine trifluoride (BrF_3) and nucleophilic arene derivatives such as arylsilanes and arylstannanes.^[13] For example, BrF_3 reacts with phenyl trifluorosilane to form a relatively unstable phenyl- λ^3 -bromane **1**^[14] that is suitable both as reagent and as entry point for the synthesis of other derivatives via ligand exchange (Figure 1, top).^[15,16]

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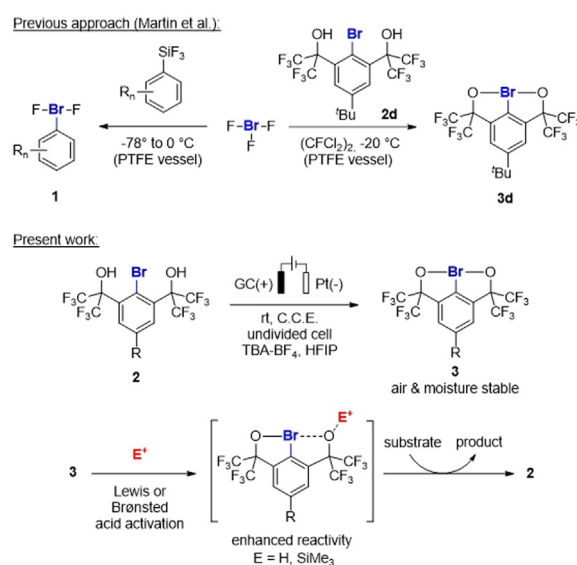
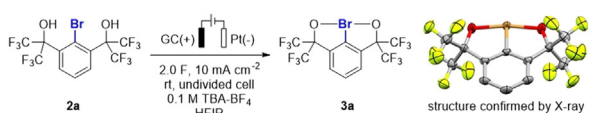


Figure 1. New approach to aryl- λ^3 -bromanes.

Bromine trifluoride has been also used by Martin et al. for the preparation of chelation-stabilized aryl- λ^3 -bromane **3a**.^[17] However, an important limitation of these approaches is the use of BrF_3 , a highly toxic and extremely reactive liquid that requires dedicated equipment (such as PTFE vessels etc.) and specific experimental techniques for its safe handling. Notably, high oxidation potentials of aryl bromides (e.g. 2.0 V vs. $\text{Ag}/0.01 \text{ M AgNO}_3$ for PhBr in CH_3CN)^[18] and poor stability of the resulting bromine(III) species complicates the direct two-electron oxidation by chemical oxidants, a method that is routinely employed for the synthesis of hypervalent iodine(III) counterparts from iodoarenes.^[19] Clearly, the development of a convenient synthetic approach to λ^3 -bromanes would open the door for the rapid development of hypervalent Br^{III} chemistry. Herein we report a straightforward and high yielding synthesis of Martin's hypervalent bromine(III) species **3** by anodic oxidation of the parent aryl bromide **2** (Figure 1, bottom). The extremely high reactivity of arylbromonium species^[13a] is tamed by the two coordinating *ortho* substituents, allowing **3** to be stored as a bench-stable reagent for extended periods of time. However, the reactivity of the electrochemically generated Br^{III} species can be unlocked by a Lewis acid (such as TMSOTf and $\text{BF}_3\cdot\text{OEt}_2$) or a Brønsted acid (TfOH) additive as described below.

Recently we reported on electrosynthesis of hypervalent iodine(III) species by anodic oxidation of aryl iodides in an undivided cell using HFIP as solvent.^[20] We hypothesized that the electrochemical oxidation would be suitable also for the synthesis of aryl- λ^3 -bromanes provided that they are compatible with anodic oxidation conditions. Hence, the air- and moisture-stable^[17b] aryl- λ^3 -bromane **3a** was chosen as the target substrate to verify the feasibility of its electrochemical synthesis. The published conditions for anodic oxidation of iodoarenes into λ^3 -iodanes were used as the starting point for the preparation of λ^3 -bromane **3a** (Table 1).

Table 1: Optimization of the electrochemical synthesis of **3a**.



Entry	Deviations from standard conditions	2a [%] ^[a]	3a [%] ^[a]	Mass balance [%] ^[a]
1	none	43	55	98
2	TFE	40	52	92
3	CH_3CN	93	6	99
4	BDD(+)	54	46	100
5	RVC(+)	60	40	100
6	0.1 $\text{TBA}\cdot\text{ClO}_4$	50	44	94
7	0.1 $\text{TBA}\cdot\text{PF}_6$	44	55	99
8	$j = 5 \text{ mA cm}^{-2}$	51	47	98
9	$j = 15 \text{ mA cm}^{-2}$	38	56	94
10	$j = 20 \text{ mA cm}^{-2}$	37	60	97
11	$q/\text{mol} = 3.0\text{F}$	30	67	97
12	$q/\text{mol} = 4.0\text{F}$	17	75 (63) ^[b]	92
13	$q/\text{mol} = 5.0\text{F}$	18	71	89

[a] Yields and mass balances determined by ^1H NMR spectroscopy of the post-electrolysis solution using 1,2,3,4-tetrafluorobenzene as the internal standard (0.3 mmol scale). [b] Isolated yield.

Gratifyingly, electrochemical oxidation using glassy carbon (GC) as the working electrode and platinum foil as the counter electrode in a $\text{TBA}\cdot\text{BF}_4/\text{HFIP}$ electrolyte at 10 mA cm^{-2} afforded the desired **3a** in 55% yield (entry 1) after passing 2F per mole of starting material. The molecular structure of **3a** was confirmed by single crystal X-ray analysis (Table 1, graphics). Although the use of 2,2,2-trifluoroethanol (TFE) as a solvent gave similar results (entry 2), we refrained from using it in further experiments because of its high toxicity. In contrast, acetonitrile turned out to be unsuitable due to anodic degradation (Supporting Information, p. S47), resulting in poor conversion to **3a** (entry 3). The replacement of working electrode material to BDD or RVC (entry 4 and 5) gave no increase in product yield. $\text{TBA}\cdot\text{PF}_6$ can be used as an alternative to $\text{TBA}\cdot\text{BF}_4$ (entry 7 vs. 1), whereas $\text{TBA}\cdot\text{ClO}_4$ turned out to be inferior in terms of yield (entry 6). Lower current density (5 mA cm^{-2}) resulted in two-fold increase of the reaction time and slightly reduced product yield (entry 8 vs. entry 1). Higher current densities (15 and 20 mA cm^{-2} , entries 9 and 10, respectively) led to increased conversion at the expense of selectivity. Thus, a current density of 10 mA cm^{-2} was used in further optimization experiments. The increase of passed charge equivalents from 2.0F up to 3.0F resulted in the increase of λ^3 -bromane **3a** yield from 55% to 67% (entry 11 vs. 1). Higher yields of **3a** and improved conversion was observed after passing 4.0F. Nevertheless, further increase of the passed charge amount did not result in significant improvements, and a concomitant formation of degradation products was observed (entry 13 vs. 12).

With the optimized conditions in hand (entry 12), the scalability of the developed electrochemical synthesis of λ^3 -bromane **3a** was examined. We were pleased to find that the galvanostatic electrolysis in an undivided electrochemical cell could be readily performed on a 10 mmol scale to afford 3.50 g of **3a** in a single-batch (72% yield). Notably, λ^3 -bromane **3a** was isolated from the electrolysis mixture as > 95% pure (^1H -NMR assay) pale-yellow solid by simple filtration through a short silica plug followed by extractive workup (see Figure 2, bottom right).

After elaboration of the electrochemical protocol for synthesis of λ^3 -bromane **3a**, we intended to vary the substitution in *para* position to create a reagent platform with tunable reactivity and electrochemical properties. To establish access to compounds **3a-f**, the synthetic routes depicted in Figure 4 were developed. Introduction of 2-hydroxy-1,1,1,3,3,3-hexafluoropropanyl group in positions 2 and 5 of an aryl bromide was readily accomplished in two steps from 2-bromoisophthalic acids **5a-f**. The first step involved elaboration of acids **5a-f** into the corresponding acid chlorides, followed by the reaction with 2,2,2-trifluoroethanol to afford *bis*-trifluoroethyl esters **6a-f**. Subsequent treatment of esters **6a,d,e** with TMSCF_3 (7 equiv) in the presence of catalytic TBAF (10 mol %)^[21] afforded the desired alcohols **2a,d,e** in 57–72% yields. The synthesis of **2b,c,f** required the addition of excess (4 equiv) of TBAF ^[22] and TMSCF_3 (6 equiv)^[23] to furnish products in 62–69% yields. The nitration of **2a** afforded bromide **2f**. The starting 2-bromoisophthalic acids **5a-e** were obtained by the oxidation of the

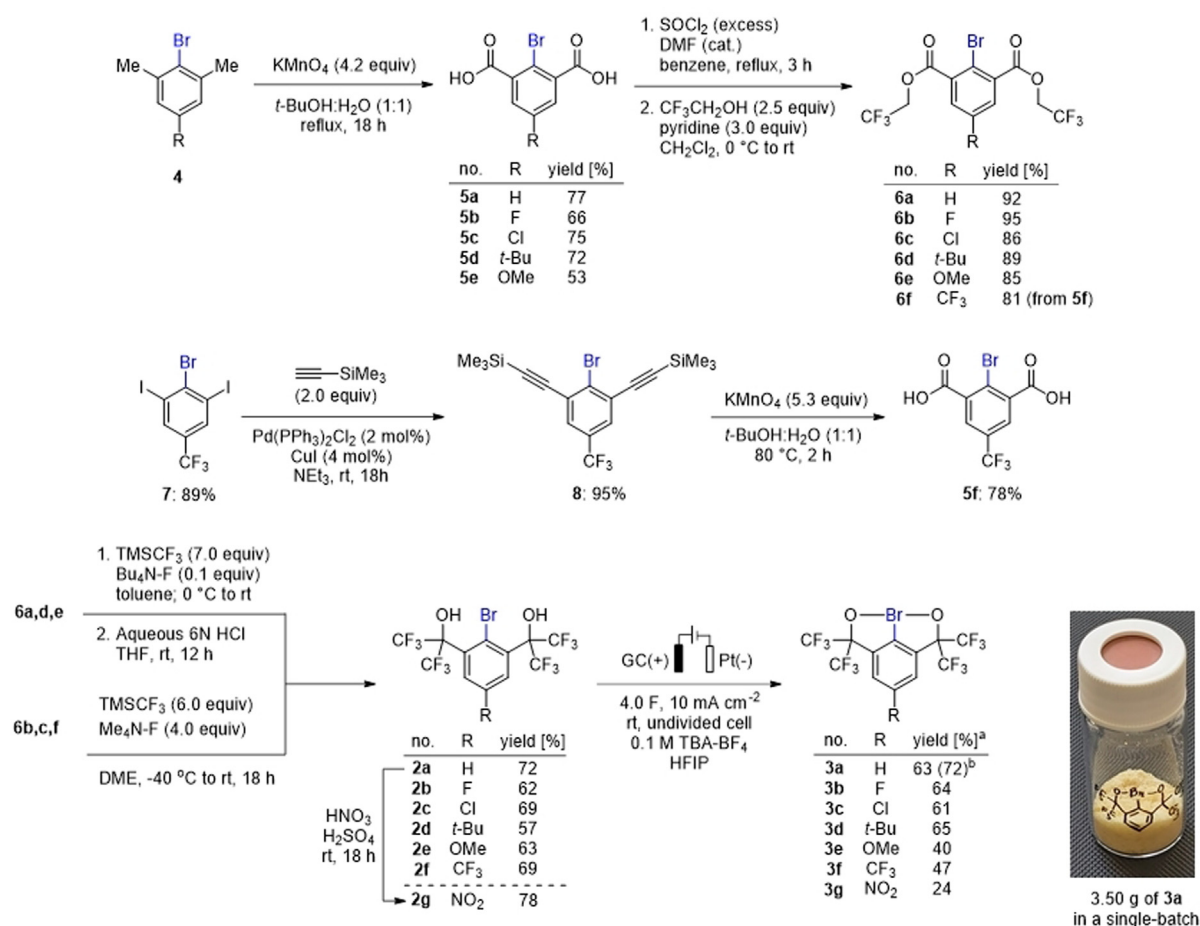


Figure 2. Synthesis of bromides **2a–g**. [a] Average yield of two runs on 0.3 mmol scale. [b] Yield on 10.0 mmol scale.

corresponding commercially available 2-bromo-*m*-xylenes **4a–e** with KMnO_4 .^[24] Acid **5f** was synthesized by chemoselective cross-coupling of the two iodo-moieties in **7** (prepared by iodination of 4-bromobenzotrifluoride)^[25] with ethynyltrimethylsilane under Sonogashira cross-coupling conditions,^[26] followed by oxidative cleavage of the acetylene subunit in **8** with KMnO_4 (Figure 2). Finally, application of the optimized electrolysis conditions (Table 1, entry 12) to the oxidation of **2b–g** rendered λ^3 -bromanes **3b–g** in 24–66% yields. It should also be noted that attempts toward oxidation of **5a** and bromoarene related to **2a** carrying one chelating moiety remained unsuccessful (for details see the Supporting Information, p. S21).

For characterization of the electrochemical properties of the bromoarene/ λ^3 -bromane redox couples, all synthesized bromides **2a–g** were studied by cyclic voltammetry, using a 0.1 M NBu_4BF_4 /HFIP electrolyte, a glassy carbon working electrode and a $\text{Ag}/0.01 \text{ M AgNO}_3$ reference ($E_0 = -87 \text{ mV}$ vs. Fc/Fc^+ couple;^[27] for more details, see p. S43). In the range between 0 and 2.7 V, each of the bromoarenes exhibits a single irreversible feature associated with the oxidation of Br^{I} to Br^{III} . The corresponding half-peak potentials ($E_{\text{P}/2}$) are situated in the range between 1.86 V (**2e**, R = OMe) and 2.60 V (**2g**, R = NO_2 ; see table in Figure 3). It follows that i) the anodically generated bromanes can be considered as

strong oxidants due to the high $E_{\text{P}/2}$ values and ii) that with the compounds synthesized thus far, the potential of **2** is flexibly tunable within a range of 0.66 V. A Hammett treatment (Figure 3, bottom right) using σ_{p^+} substituent coefficients^[28] shows that $E_{\text{P}/2}$ is dependent on the electron donating or withdrawing ability of the substituent R and follows a linear trend according to Equation (1),

$$E_{\text{P}/2}(\mathbf{2}) = 2.25 \text{ V} + 0.47 \text{ V } \sigma_{\text{p}^+} \quad (1)$$

wherein the slope provides a measure of the influence of the substituents upon the observed potential, while the intercept refers to the $E_{\text{P}/2}$ of the unsubstituted compound of the series.^[29]

The stabilization of the characteristic pseudo-trigonal bipyramidal geometry of λ^3 -bromanes **3** by 2-benzobromaoxole rings (for X-ray structure of **3a**, see Table 1 graphics)^[30] endows Martin's bromine(III) species with remarkable stability. Given the high oxidizing power and strong electrophilicity of λ^3 -bromanes,^[13a] the observed stability is striking. Not only it allowed for the electrosynthesis, isolation and purification of λ^3 -bromanes **3a–g**, but also made possible their convenient handling and storage for extended periods of time. In the meantime, the synthetic application of λ^3 -bromanes **3a–g** would require activation to unlock their intrinsic

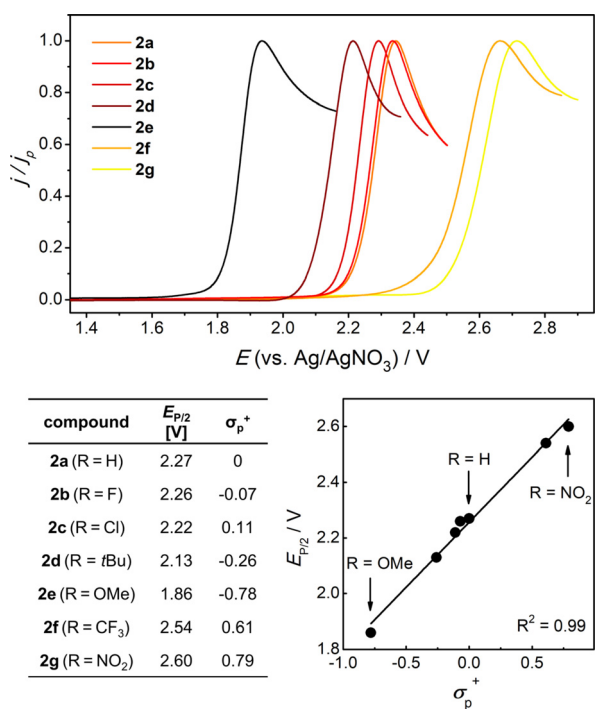
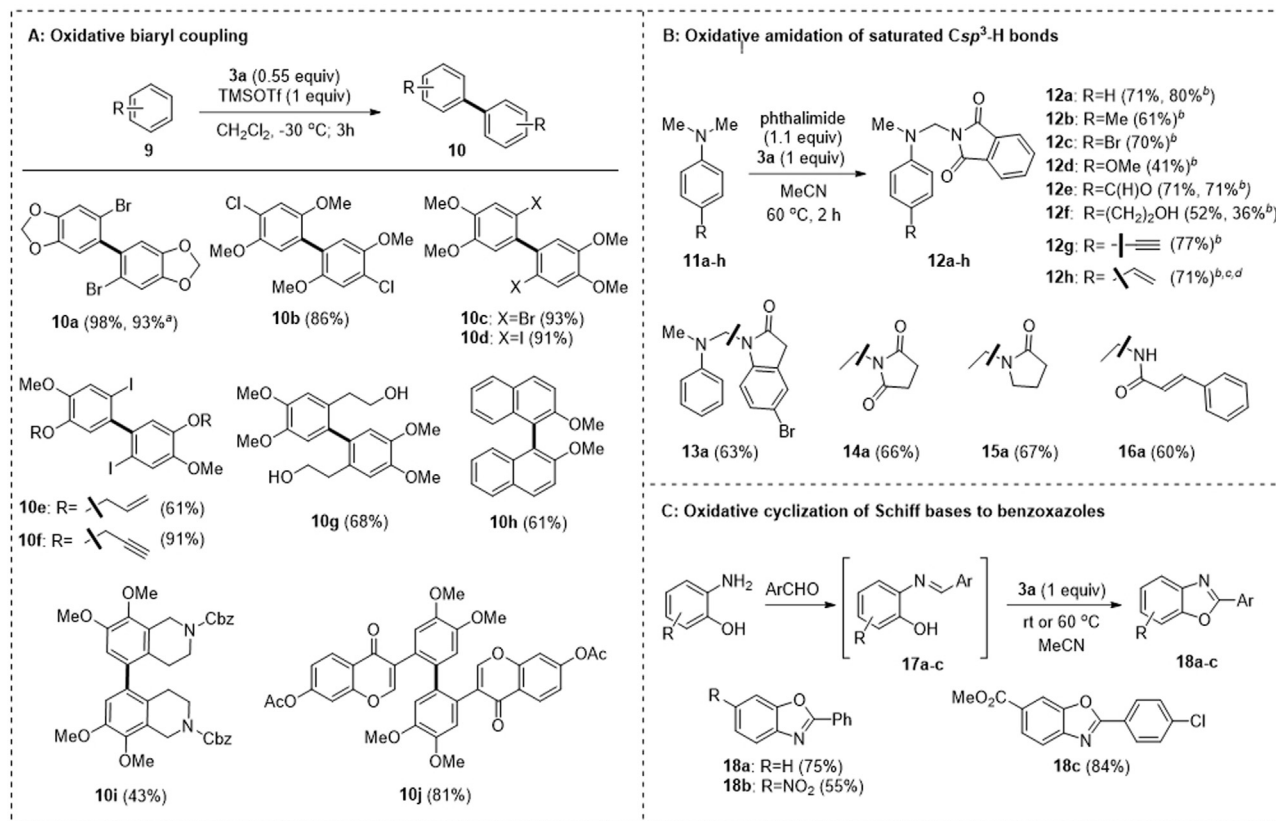


Figure 3. Top: Background and *iR* drop corrected linear sweep voltammograms (LSV) of aryl bromides **2a–g** ($c = 5$ mM) recorded at 10 mV s⁻¹. Bottom: Plot of the half-peak potentials $E_{p/2}$ (extracted from the LSVs) vs. the σ_p^+ substituent constants.

reactivity. To this end, oxidative biaryl coupling^[31] was chosen as a model reaction to develop the in situ bromane activation (Figure 4). As anticipated, the non-activated **3a** did not effect the homocoupling of benzodioxole **9a** in DCM at room temperature after 18 h. We envisioned that the reactivity of λ^3 -bromane **3a** could be enhanced by weakening the stabilizing effect of the two chelating *ortho*-substituents using a suitable Lewis acid.^[32] Indeed, a nearly quantitative formation of biaryl **10a** (98% yield) was observed after 3 h at -30°C (Figure 4) when **3a** was used together with TMSOTf^[33] (1:2 ratio, respectively). Alternatively, BF₃·OEt₂ could be employed for the activation of bromane **2a** in HFIP as the solvent (35% yield of **10a**). Finally, TfOH as additive (1.05 equiv) also effected the **3a**-mediated biaryl formation in DCM (93% yield of **10a**). Hence, both Lewis and Brønsted acids are suitable for the enhancement of λ^3 -bromane reactivity possibly by increase of cationic character of **3a** upon interactions with the Lewis basic oxygen atom.^[32,34] Noteworthy, CV studies showed that an in-cell mediated biaryl coupling is not possible, since the substrates are easier to oxidize than the bromoarenes (for details see the Supporting Information, p. S46).

The scope of substrates for the λ^3 -bromane-mediated biaryl formation was briefly explored using TMSOTf as the activator (Figure 4A). The reaction features remarkable functional group compatibility. Not only halides are tolerated (biaryls **10a–d**) but also allylic and propargylic subunits as



^a Activation with 1.05 equiv. TfOH; ^b with K-phthalimide (1.1 equiv); ^c ¹H-NMR yields (mesitylene as an internal standard); ^d 51% isolated yield.

Figure 4. Synthetic applications of electrogenerated bromane reagent **3a**.

well as primary alcohols (**10 e,f,g**, respectively) are compatible with the **3 a**-mediated biaryl formation. Biaryls **10 h** and **10 i** as well as bi-isoflavone derivative **10 j** can be also obtained using TMS-OTf activation of λ^3 -bromane **3 a** (Figure 4 A).

We were pleased to find that λ^3 -bromane **3 a** also effected the oxidative amidation of *N,N*-dimethylanilines **11 a–h** with imides (phthalimide and succinimide) as well as with various amides such as pyrrolidin-2-one, oxindole and cinnamamide (Figure 4 B).^[35] Relatively electron-rich anilines **11 a,b,d** are suitable as substrates. Notably, the oxidative amination with λ^3 -bromane **3 a** is compatible with the presence of vinylic, propargylic and primary alcohol moieties in anilines (**11 f–h**) as well as with bromine and aldehyde substituents (**11 c,e**). Finally, λ^3 -bromane **3 a** was also found to be suitable for the oxidative cyclization of Schiff bases **17 a–c** to benzoxazoles (**18 a–c**; Figure 4 C). Further studies to expand the application scope of λ^3 -bromane **3 a** are ongoing in our laboratories.

In summary, an efficient, reliable, and inexpensive approach to Martin's hypervalent bromine (III) species is reported. The key step of the synthesis is anodic oxidation of the parent aryl bromides in an undivided cell using a glassy carbon as the working electrode, platinum as the counter electrode, TBA-BF₄ as the supporting electrolyte and HFIP as the solvent. The use of an undivided cell under constant current conditions allowed for easy scale-up of the electrolysis as demonstrated by the preparation of the bench-stable λ^3 -bromane in multi-gram quantities. A series of aryl bromides with oxidation half-peak potentials spanning the range from 1.86 V to 2.60 V were converted into the corresponding λ^3 -bromanes. Cyclic voltammetry studies showed good correlation between the half-peak potentials and Hammett substituent coefficients for aryl bromides. The aryl bromides could be readily obtained from 2-bromoisophthalic acids in three steps. The reactivity of Martin's λ^3 -bromane is sufficient for oxidative amidation and benzoxazole formation and could be further enhanced by Lewis or Brønsted acid additives as demonstrated by the successful application of the reagent in the biaryl coupling. The developed electrochemical approach to λ^3 -bromanes offers considerable advantages as compared to the existing methods that rely on highly toxic, hazardous, and difficult-to-handle BrF₃ as the key reagent. Therefore, we believe that our approach may open the door to the development of unprecedented synthetic transformations that would benefit from the unique properties of hypervalent bromine-(III) species.

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Conflict of interest

The authors declare no conflict of interest.

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