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Cyclic Diaryl λ^3-Bromanes as Original Aryne Precursors.

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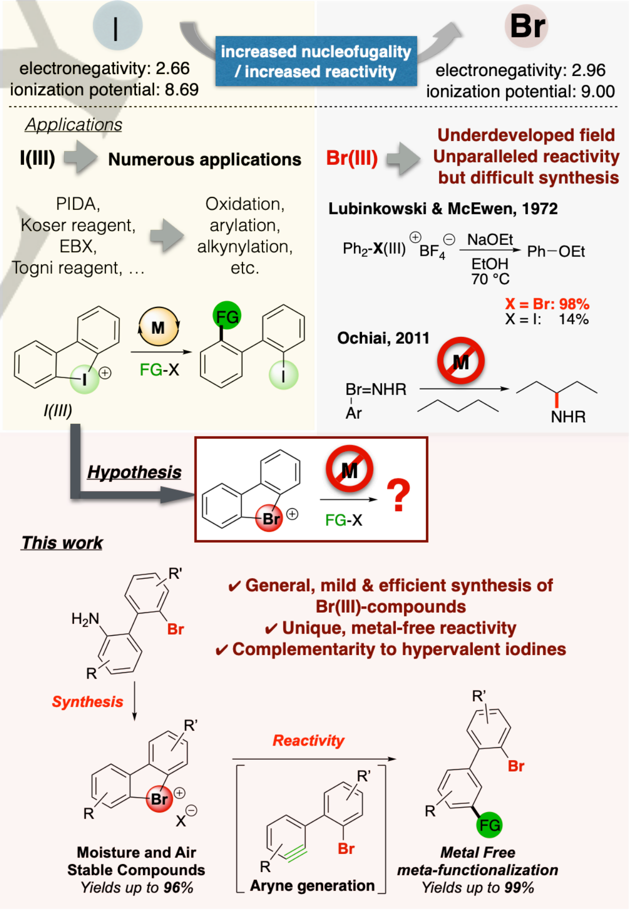
Abstract: Despite the widespread application of hypervalent iodines, the corresponding λ^3-bromanes are less explored. Herein we report a general, safe, and high-yielding strategy to access cyclic diaryl λ^3-bromanes. These unique compounds feature appealing and complementary reactivity to λ^3-iodanes, generating arynes under mild reaction conditions and in a presence of a weak base. Accordingly, formal *meta*-selective transition metal-free C-O and C-N couplings may be achieved. The mechanistic studies unambiguously support the aryne generation mechanism.

The chemistry of hypervalent compounds occupies a central role in modern organic synthesis.[1] In particular, the iodine atom has become the most established and widely applied within the λ^3- and λ^5- hypervalent molecules, serving as oxidants, electrophiles, catalysts, or radical initiators.[2] Among others, the commercially available diaryliodonium salts[3] and diacetoxy-iodobenzene[4] are key modern tools in arylation and oxidation reactions.

In marked contrast, the chemistry of hypervalent bromine compounds has attracted considerably less attention,[5] although their greater electronegativity and higher ionization potential[6] might confer increased and/or complementary reactivity (**Scheme 1**). [7] Accordingly, superior nucleofugality of λ^3-bromanes was witnessed in the arylation [8] reactions while sulfonylimino-λ^3-bromanes turned out to be potent aminating agents, mediating transition metal-free C(sp^3)-H activation of simple alkanes. [9] Very recently, cyclic hypervalent λ^3-bromide has been also engaged as Lewis-acid organo-catalyst for Michael reactions. [10] Despite the unique intrinsic properties of λ^3-bromanes, the lack of efficient protocols to prepare them has limited the development of this research field. While thermal decomposition of diazonium salts in presence of aryl bromide furnished λ^3-bromane as early as 1952,[11] harsh reaction conditions and low yields hampered further progress. More recently, a strategy based on ligand-exchange reactions using BrF_3 [12] as the key Br(III)-precursor has been designed but the extreme corrosivity and toxicity of this gaseous and poorly available reagent render this pathway unsuitable for general applications.

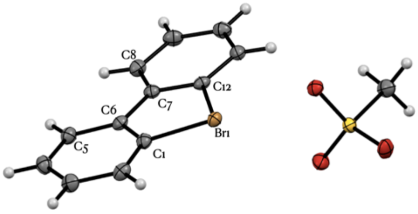
Expanding our interest in hypervalent compounds,[13] and considering the potential of biaryl λ^3-iodanes[14] as prominent substrates in transition metal-catalyzed cross coupling reactions, we have embarked on the exploration of the synthesis and chemical behavior of rare yet fascinating cyclic biaryl λ^3-bromanes. We hypothesized that their increased reactivity might render them appealing in transition metal-free transformations, thus paving the way towards complementary reactivity to the λ^3-iodane congeners. Here, we report the efficient, versatile and safe synthesis, isolation, and characterization of a large panel of cyclic diaryl λ^3-bromanes. Furthermore, these bromanes feature an original reactivity, undergoing metal-free C-O and C-N couplings. At room temperature and in the presence of a weak base, these diaryl λ^3-bromanes act as aryne-synthons, providing reactivity not attainable with the corresponding diaryl λ^3-iodanes,[15] thus illustrating disparity between these hypervalent compounds. This reactivity, implying formal C-H functionalization, occurring under mild reaction conditions and obviating need of fluorinating agents, is arguably amongst the most appealing and general routes furnishing arynes.[16]

Scheme 1. Hypervalent iodines and bromines reactivities



While the rare literature known protocols to access diaryl λ^3-bromanes are low-yielding, require several steps and harsh reaction conditions,[10,11] we surmised that **2a** might be afforded efficiently from **1a** *via* a single oxidation step while using finely selected oxidant and Brønsted acid (**Figure 2**). Rewardingly, while reacting, under mild conditions, **1a** with *t*BuONO and $MeSO_3H$, the desired compound **2a**-OMs was isolated in 93% yield. In marked contrast to the literature, the use of organic oxidant and solvent, together with only a small excess of the acid, turned out to be essential for the high-yielding reaction outcome. The gram-scale synthesis furnished **2a**-OMs in 74% yield *via* simple precipitation from diethyl ether. [17] Moreover, air and moisture stability of **2a**-OMs was further confirmed, as the storage of this compound over several months in the refrigerator altered neither its purity nor its reactivity. The X-ray analysis of **2a**-OMs reveals a tricyclic planar structure with a dihedral angle of -1.04(4)°.

Figure 1. X-ray structure of **2a**-OMs

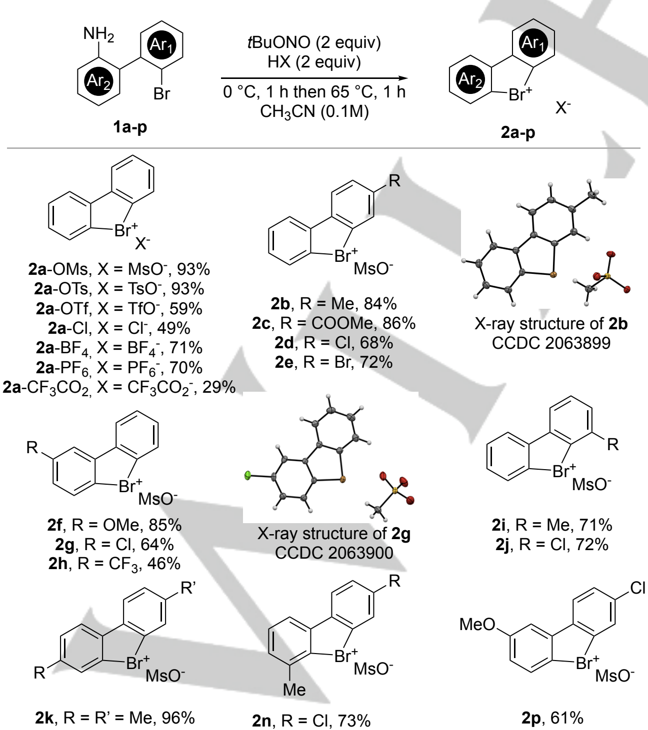


Bond lengths (Å)	
C1-Br1	1.928(2)
C12-Br1	1.932(2)
C1-Br1-C12	86.93(9)
Bond angles (°)	
C5-C6-C7-C8	-1.0(4)
C6-C1-Br1	111.31(5)
C7-C12-Br1	110.81(14)

The carbon-bromine bonds (C1-Br1 and C12-Br1) are slightly longer, (1.928(2) Å and 1.932(2) Å respectively) with respect to the bromobenzene (1.850 Å) consistently with a weak and therefore more reactive bond. Moreover, the angle between C1-Br1-C12 is 86.93(9)° reflects a T-shape structure typical for three-centered–four-electron (3c-4e) bonding.[10,16,18]

The generality of this protocol delivering diaryl λ^3-bromanes was further surveyed (**Figure 2**).

Figure 2. Scope of Cyclic Diaryl λ^3-bromanes



2a-OMs, X = MsO⁻, 93%
2a-OTs, X = TsO⁻, 93%
2a-OTf, X = TfO⁻, 59%
2a-Cl, X = Cl⁻, 49%
2a-BF_4, X = BF_4^-, 71%
2a-PF_6, X = PF_6^-, 70%
2a-CF_3CO_2, X = $CF_3CO_2^-$, 29%

2b, R = Me, 84%
2c, R = COOMe, 86%
2d, R = Cl, 68%
2e, R = Br, 72%

2f, R = OMe, 85%
2g, R = Cl, 64%
2h, R = CF_3, 46%

2i, R = Me, 71%
2j, R = Cl, 72%

2k, R = R' = Me, 96%
2l, R = R' = Cl, 65%
2m, R = Me, R' = Cl, 61%

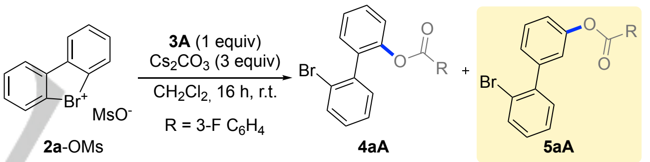
2n, R = Cl, 73%
2o, R = COOMe, 82%

2p, 61%

First, compatibility of this reaction with various acids was confirmed, thus delivering **2a** with different counter anions in excellent to moderate yields (93% to 29%). Subsequently, the reaction was extended towards an array of differently substituted 1,1'-bromo(amino)biphenyl **1b-p**, providing a collection of cyclic diaryl λ^3-bromanes. Electron-donating groups, such as methyl (**2b**, **2i, 2k**) and methoxy (**2f**), were well tolerated at different positions affording the products in excellent to quantitative yields (71 – 96%). Halogen-substituted starting materials were efficiently converted into the corresponding bromanes (**2d**, **2e**, **2g, 2j**, and **2l**) in high yields (64 – 72%). The presence of electron-withdrawing group such as methyl ester (**2c**, 86%) did not alter the reaction outcome while the CF_3 group (**2h**, 46%) significantly reduced the yield. The reaction protocol is also amenable to assemble dissymmetric cyclic diaryl λ^3-bromanes (**2m**, **2n**, **2o** and **2p**).

To compare the reactivity of this new class of hypervalent compounds with their iodinated congeners and drawing inspiration from Gu and Zhao works on metal-catalyzed functionalization of hypervalent λ^3-iodanes, [19] **2a**-OMs was reacted with a carboxylic acid **3A**, in a presence of Cu-catalyst and Cs_2CO_3 base (**Table 1**). The C-O bond formation occurred smoothly, but instead of the expected, as in the case of λ^3-iodanes, *ortho*-substituted product **4aA**, *meta*-functionalization took place selectively, furnishing **5aA** in 96% yield. This observation clearly shows a divergent reactivity between the λ^3-iodanes and λ^3-bromanes compounds.

Table 1. Selected optimization reactions.



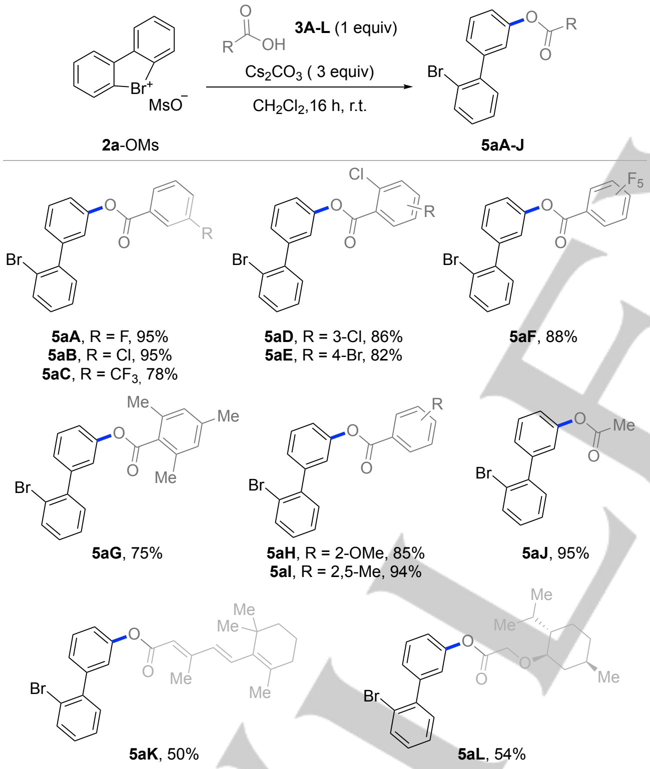
Deviation from the standard conditions[a]	Yield of 5aA[b]
10 mol% $Cu(OTf)_2$	96%
None/with Cs_2CO_3 99.994% Pure	95%
No Cs_2CO_3	-
I-OTf or **I**-OMs instead of **2a**-OMs	-

[a] Conditions: 0.1 mmol of hypervalent reagents (**2a**-OMs, **I**-OTf, **I**-OMs), 0.083 mmol of **3A** and 0.3 mmol of Cs_2CO_3 in 1 mL of CH_2Cl_2 at r.t. for 16 h. [b] Isolated yields.

To validate our hypothesis that **2a** might be an amenable substrate for metal-free transformations, coupling of **2a**-OMs and **3A** was performed in absence of the Cu-catalyst and at room temperature, delivering **5aA** in almost quantitative yield. The use of Cs_2CO_3 is essential to trigger the reaction, while high purity base (99.994%) confirmed the metal-free conditions. Remarkably, hypervalent iodines **I**-OTf and **I**-OMs are totally unreactive under such metal-free protocol.[15] Following these preliminary results, the generality of this transformation was explored (**Figure 3**). The mildness of the reaction conditions warrants its compatibility with a diversity of carboxylic acid coupling partners, including 3-halogenated benzoic acids, delivering **5aA** and **5aB** in high yields (95%). The strong electron-withdrawing CF_3 group slightly impacted the yield of **5aC** (78%) while halogenated and perfluorinated benzoic acids performed well furnishing **5aD-E**. Sterically hindered substrates were also found amenable providing **5aG**, **5aH** and **5aI** in good yields (up to 94%). In addition, the simple acetic acid **3J** successfully delivered **5aJ** in almost quantitative yield (95%). Our protocol also allows functionalization of complex substrates including *trans*-β-ionylidene acetic acid **3K** and menthyloxy acetic acid **3L** furnishing decorated products **5aK** and **5aL**.

Encouraged by the potential of the cyclic diaryl λ^3-bromanes in metal-free C-O couplings, we then focused on extending this reactivity towards amination reaction (**Figure 4**). Rewardingly, **2a**-OMs reacted smoothly with sterically hindered mesitylaniline **6A**, delivering the expected products **8aA** and **7aA** in excellent total yield (89%). The use of amines as nucleophiles seems to be less selective; although the *meta*-product is still favored, a considerable amount of *ortho*-functionalization was also formed.[20] However, both regioisomers were isolated separately, providing pure **8a** and **7a** in respectively 69 and 20% yield.

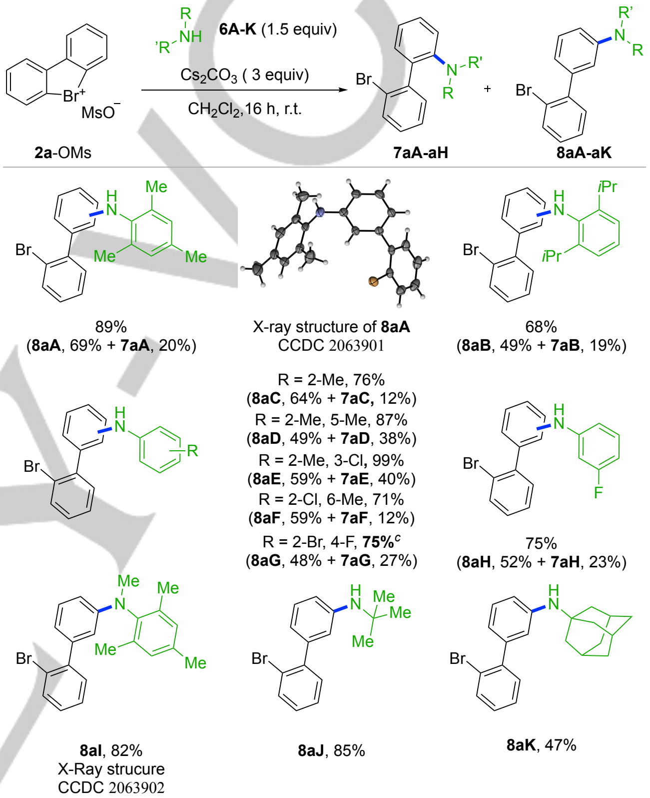
Figure 3. Scope of C-O bond formation



In analogy to the previous coupling, no reaction was observed while using λ^3-iodanes. Cs_2CO_3 and DCM remained the optimal base and solvent. Although C-N bond couplings are generally sensitive to steric hindrance, under this mild protocol encumbered anilines such as 2,4,6-trimethylaniline **6A** and 2,6-diisopropylaniline **6B** were found suitable, supplying the desired products (**8aA** + **7aA** and **8aB** + **7aB)** in good yields (89%, 69% respectively). Moreover, *o*-toluidine derivatives as **6C** and **6D** reacted smoothly and the presence of Cl-substituents (**6E**, **6F**) does not influence the efficiency of the reaction. The fluoro-substituted anilines were successfully converted to the desired products providing densely decorated anilines. This C-N coupling is also suitable for the synthesis of trisubstituted anilines and alkyl-anilines. Notably, the increased steric hindrance of the coupling partners allows superior regiocontrol. The 2,4,6-trimethyl-*N*-methyl aniline **6I** afforded **8aI** as a single regioisomer in 82% yield, while *tert*-butylamine **6J** and adamantylamine **6K** furnished selectively **8aJ** and **8aK** in 85% and 47% yields.

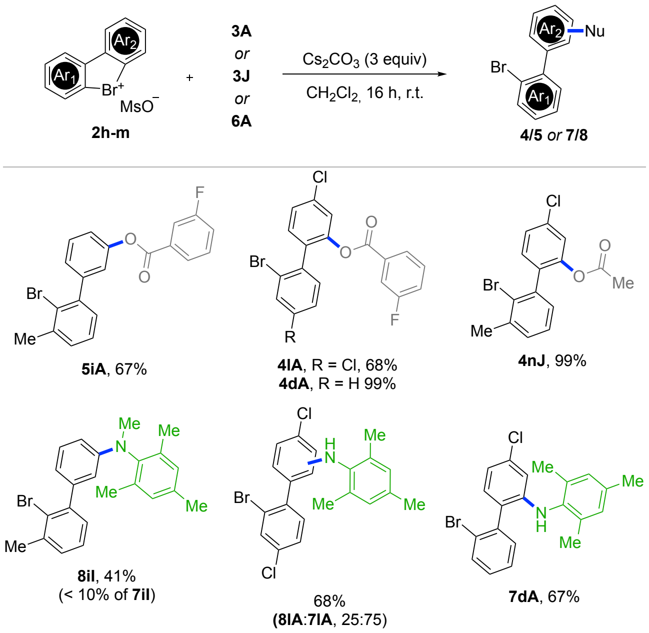
The unexpected *meta*-selectivity observed for these C-O and C-N couplings, combined with their metal-free character, clearly suggests a reaction pathway implying aryne intermediates.

Figure 4. Scope of C-N bond formation



In accordance with multiple experimental[21] and DFT[22] models, steric and electronic effects induce the *meta*- nucleophilic attack with respect to the more sterically congested and less stabilized *ortho*- functionalization. This selectivity trend is clearly reflected in our coupling reactions, with the generation of the major *meta*-substituted compounds. Accordingly, interesting reactivity patterns might be expected while exploring the reactivity of the dissymmetrical cyclic diaryl λ^3-bromanes (**Figure 5**). Not surprisingly, the substrate **2i** undergoes highly selective functionalization on one aromatic unit, delivering the *meta*-substituted products **5iA** and **8iI** in good to moderate yields (67% and 41% respectively). In clear contrast, the presence of chloro-substituents at 4-position of the symmetric substrates **2l** completely alters the selectivity pattern and the *ortho*-functionalized products **4lA** and **7lA** are afforded in high yields (68%). Herein, the electronic withdrawing inductive effect of the Cl-substituent outweighs the steric hindrance. The presence of Cl-atom on the aromatic ring of **2d** improved its reactivity, the aryne formation occurs selectively on the Cl-substituted aromatic ring thus delivering a single product **4da** and **7dA** out of four possible regioisomers. Finally, the reaction between **2n** and glacial acetic acid **3J** provided quantitatively **4nJ**.

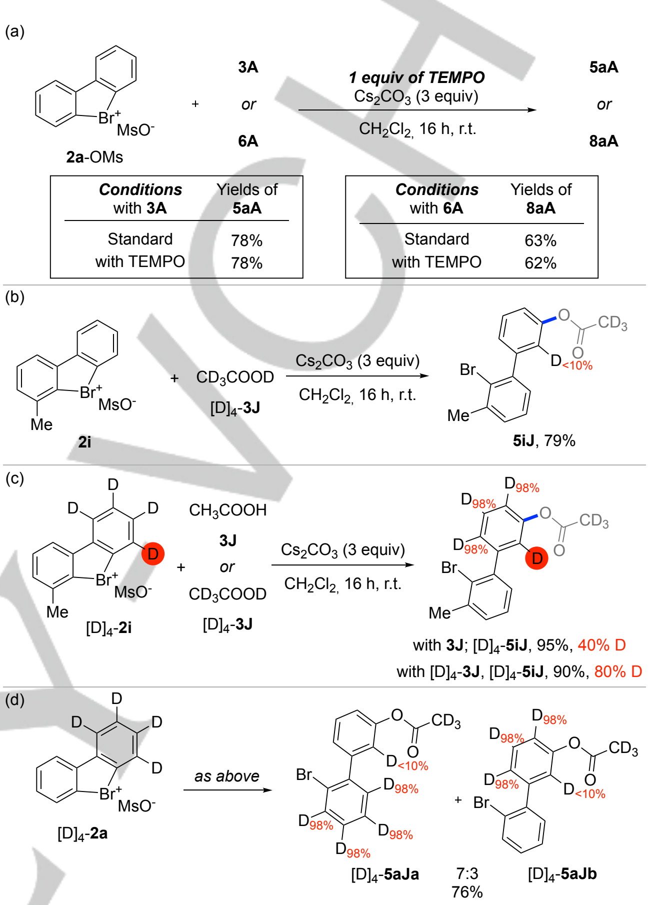
Figure 5. Selectivity with substituted Cyclic Diaryl λ^3-Bromanes



To complete this study, experimental mechanistic investigations were undertaken. The radical-type mechanistic scenario was ruled out as the addition of one equivalent of a radical scavenger, namely TEMPO, did not alter the reaction outcome either in presence of aniline **6A** or carboxylic acid **3A** (**Figure 6a**). Subsequently, studies involving deuterated substrates have been conducted. The reaction between the λ^3-bromane **2i** and the [D]$_4$-**3J** provided the *meta-* functionalized product **5iJ** in good yield with a low deuterium incorporation at the *ortho-* position (**Figure 6b**). Even such a small D-incorporation supports the generation of a carbanion intermediate during the reaction, which is either protonated or trapped by deuterated carboxylic acid. The reactivity of the partially deuterated [D]$_4$-**2i** was surveyed and the product [D]$_4$-**5iJ** was obtained by the reaction with **3J** and [D]$_4$-**3J** (**Figure 6c**). The formation of aryne and subsequent reaction with the carboxylic acid provided significant deuterium incorporation at the *ortho*-position (up to 80%). The reaction with **3J** indicates that this deuteration arises from the D-transfer between the substrate [D]$_4$-**2i** and the product [D]$_4$-**5iJ**, while not surprising even higher deuteration ratio was observed while omitting any proton source in the reaction mixture (reaction with [D]$_4$-**3J**). This observation suggests a possible "autocatalytic aryne generation" (**Scheme 2**). Moreover, when [D]$_4$-**2a**, the substrate bearing two reactive sites, potential to undergo aryne formation either *via* C-H or C-D cleavage, was reacted with CD_3CO_2D, two compounds [D]$_4$-**5aJa** and [D]$_4$-**5aJb** (corresponding to the functionalization of the protonated or deuterated aromatic unit) were afforded (**Figure 6d**). The products ratio of 7:3 suggest favored functionalization of the H$_4$-aromatic unit and therefore this aryne generation features KIE of 2.3.

Based on these investigations, a plausible mechanism for the C-O coupling is proposed (**Scheme 2**). Initially, base-mediated deprotonation of **2** furnishes the first benzyne intermediate **A**. Remarkably, the unusual nucleofugality and the strong electron-withdrawing ability of trivalent bromide (Hammet constant σI = 1.63 for -Br(Ph)BF$_4$) account for the β-elimination in a presence of a weak base. [23]

Figure 6. Mechanistic Investigations



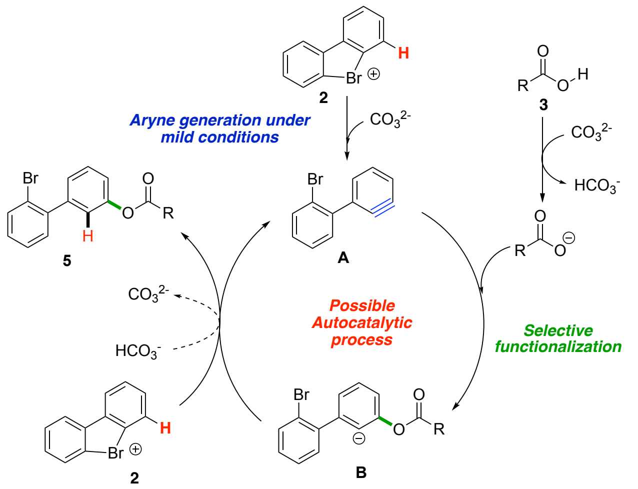
Conditions with 3A	Yields of 5aA
Standard	78%
with TEMPO	78%

Conditions with 6A	Yields of 8aA
Standard	63%
with TEMPO	62%

Notably, strong lithium bases are usually required to generate arynes via deprotonative C-H approach from the monofunctionalized precursors[24] and the nucleofugality of λ^3-iodanes seems inadequate as no reaction was observed while using these more common hypervalent compounds. The subsequent *meta-* selective nucleophilic attack onto the benzyne intermediate **A** forms the new C-O bond and generates the carbanion intermediate **B**. Considering the strong reactivity of **B** and based on the deuteration experiments (**Figure 6c**), the autocatalytic process may be expected, implying the attack of **B** on the new molecule of the hypervalent bromine resulting in the protonation of **B** and concomitant generation of the aryne intermediate **A**. However, a partial protonation of **B** either from the carboxylic acid and/or from the hydrogen carbonate conjugate Brønsted acid cannot be excluded.

In conclusion, we report herein the first simple, versatile, safe and scalable protocol for the synthesis of cyclic diaryl λ^3-bromanes. The study of the reactivity of these bromanes highlights their unique behavior and thus a set of mild reaction conditions for the generation of benzyne was established. A carbonate-mediated arylation of carboxylic acids and anilines was achieved delivering a family of decorated bromo-biaryl compounds. This study constitutes a key step toward the development of the chemistry of hypervalent bromines.

Scheme 2. A plausible reaction mechanism for the C-O bond formation



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Keywords: λ^3-bromanes • hypervalent bromine • aryne • metal-free coupling • hypervalent iodine

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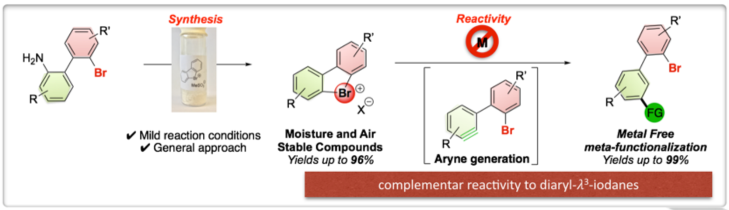

Diaryl λ^3-bromanes are rare and unexplored hypervalent compounds. Efficient and mild protocol affords now a large panel of these hypervalent compounds, featuring complimentary reactivity to the corresponding diaryl λ^3-iodanes. Due to their high reactivity, metal-free *meta*-selective C-O and C-N coupling occurs through the *in situ* aryne generation.