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Cyclic Diaryl λ^3 -Bromanes as Original Aryne Precursors

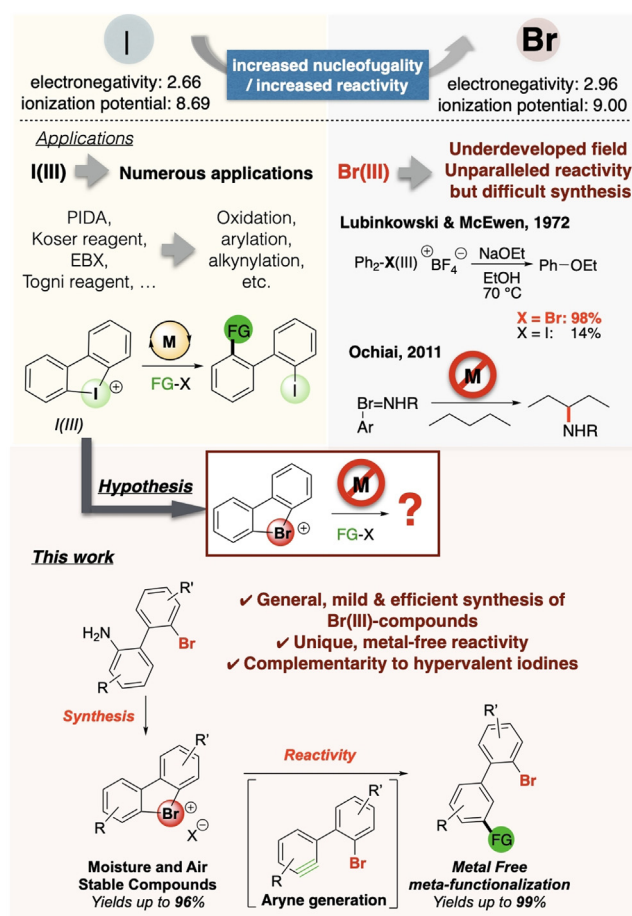
Matteo Lanzi, Quentin Dherbassy, and Joanna Wencel-Delord*

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 reactivity that is appealing and complementary to that of λ^3 -iodanes, generating arynes under mild reaction conditions and in the presence of a weak base. Accordingly, formal meta-selective transition-metal-free C–O and C–N couplings may be achieved. 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 diacetoxyiodobenzene^[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(sp³)-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 BrF₃^[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 reac-



Scheme 1. Reactivity of hypervalent iodines and bromines.

tions, 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]

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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 MeSO₃H, 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 $-1.04(4)^\circ$ (Figure 1). 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 $86.93(9)^\circ$ 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). 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 CF₃ group (**2h**, 46%) significantly reduced the yield. The reaction protocol is also amenable to

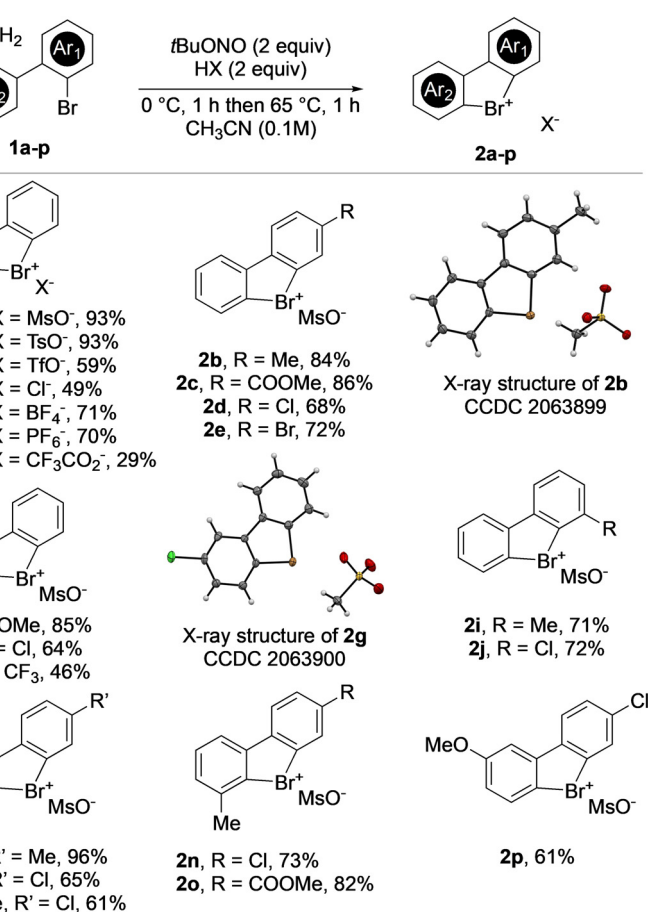
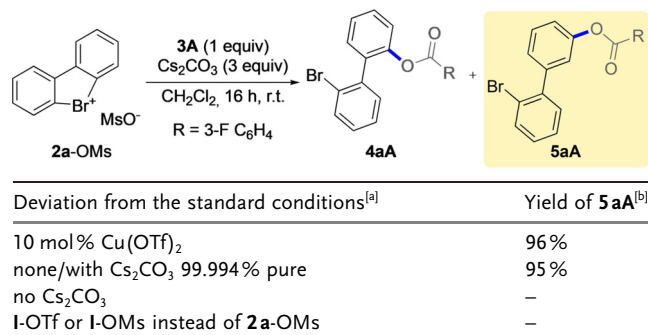


Figure 2. Scope of cyclic diaryl λ^3 -bromanes.

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 Cs₂CO₃ base (Table 1). The C–O bond formation occurred smoothly, but instead of the expected, as in the

Table 1: Selected optimization reactions.



[a] Conditions: 0.1 mmol of hypervalent reagent (**2a-OMs**, I-OTf, I-OMs), 0.083 mmol of **3A**, nd 0.3 mmol of Cs₂CO₃ in 1 mL of CH₂Cl₂ at room temperature for 16 h. [b] Isolated yields.

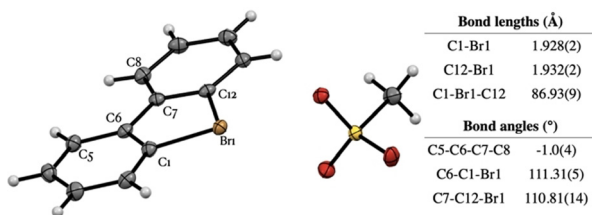


Figure 1. X-ray structure of **2a-OMs**.

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.

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–F**. 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 menthylloxy 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

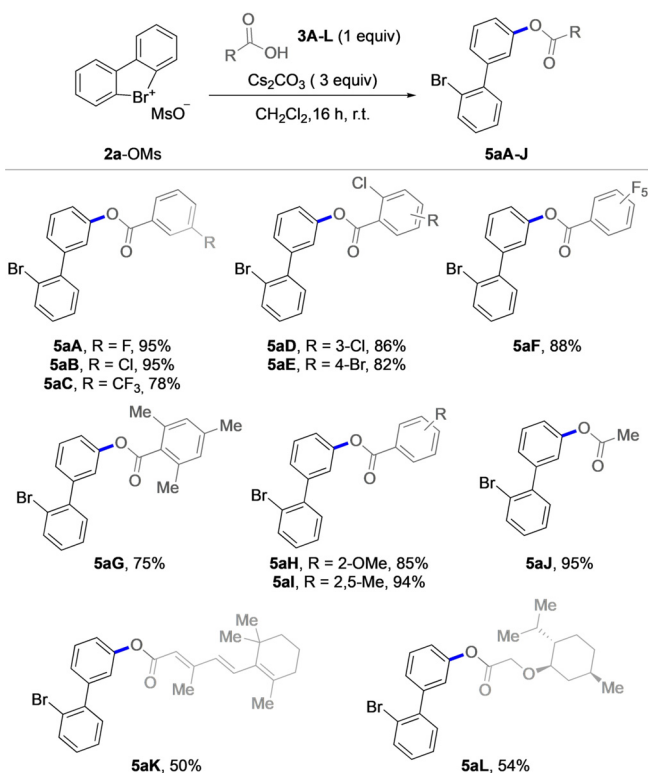


Figure 3. Scope of products generated by C–O bond formation.

(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 **8aA** and **7aA** in, respectively 69 and 20% yield.

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%, 68% 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.

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 **2I** completely alters the selectivity pattern and the *ortho*-functionalized products **4IA** and **7IA** 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**.

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

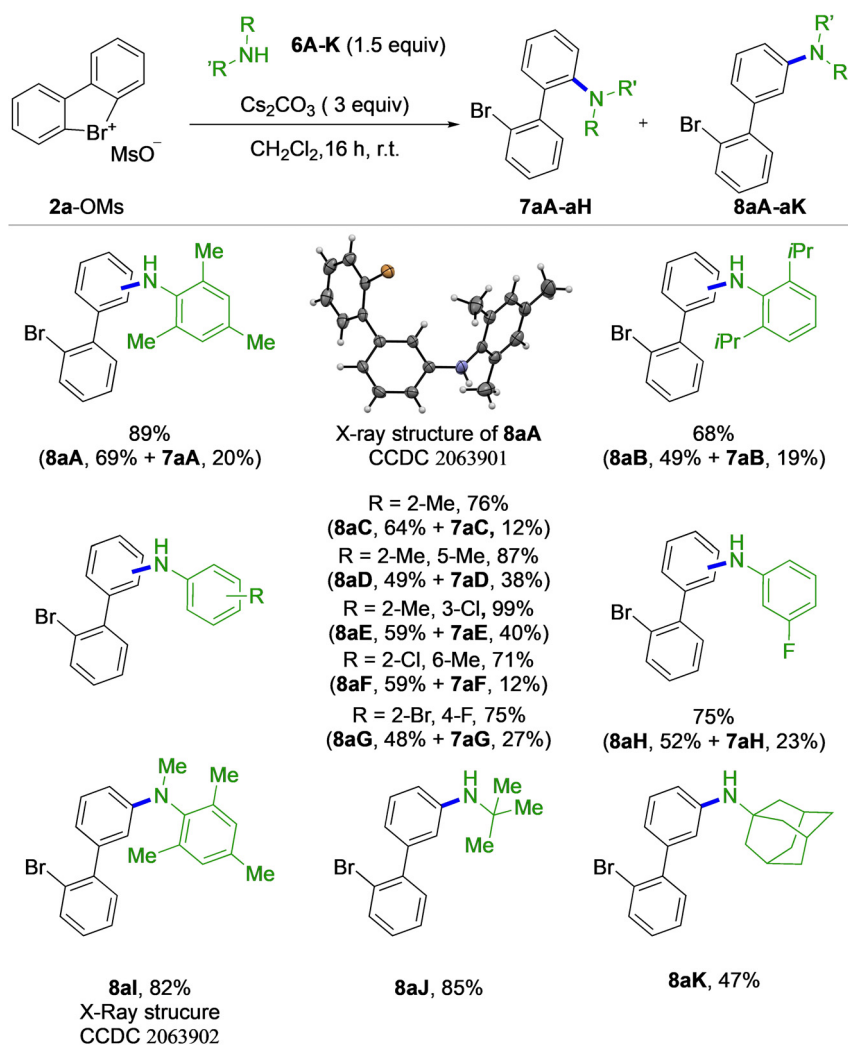


Figure 4. Scope of products generated by C–N bond formation. ok

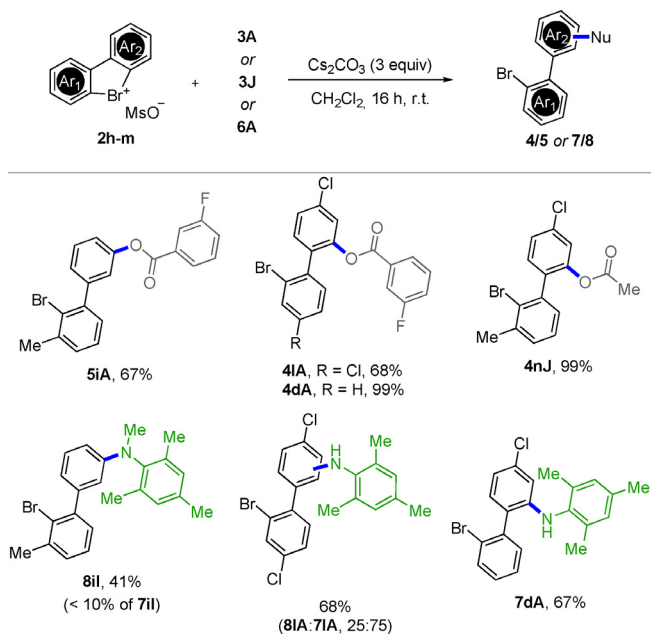


Figure 5. Selectivity of reactions with substituted cyclic diaryl λ^3 -bromanes.

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 $[\text{D}]_4$ -**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 $[\text{D}]_4$ -**2i** was surveyed and the product $[\text{D}]_4$ -**5iJ** was obtained by the reaction with **3J** and $[\text{D}]_4$ -**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 $[\text{D}]_4$ -**2i** and the product $[\text{D}]_4$ -**5iJ**, while not surprising even higher deuteration ratio was observed while omitting any proton source in the reaction mixture (reaction with $[\text{D}]_4$ -**3J**). This observation suggests a possible “autocatalytic aryne generation” (Scheme 2). Moreover, when $[\text{D}]_4$ -**2a**, the substrate bearing two reactive sites, potential to undergo aryne formation either via C–H or C–D cleavage, was reacted with $\text{CD}_3\text{CO}_2\text{D}$, two compounds $[\text{D}]_4$ -**5aJa** and $[\text{D}]_4$ -**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 $[\text{H}]_4$ -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 (Hammett constant $\sigma_{\text{I}} = 1.63$ for $-\text{Br}(\text{Ph})\text{BF}_4$) account for the β -elimination in a presence of a weak base.^[23]

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

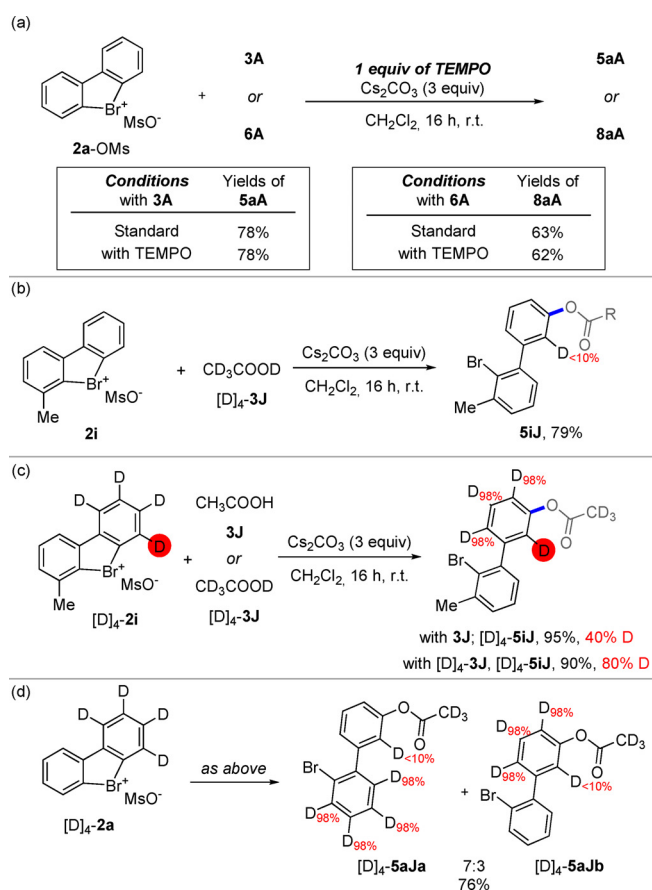
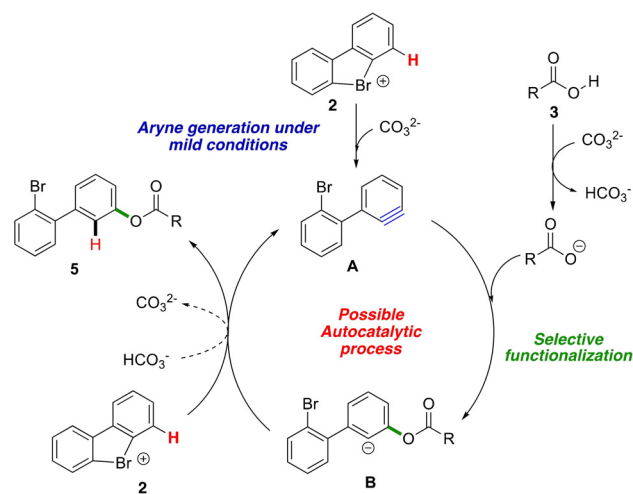


Figure 6. Mechanistic investigations.



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

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.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: arynes · hypervalent bromine · hypervalent iodine · metal-free coupling · λ^3 -bromanes

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