Organic Synthesis

Synthesis and Reactivity of Six-Membered Cyclic Diaryl λ^3-Bromanes and λ^3-Chloranes

Dhananjay Bhattacherjee, Benson M. Kariuki, Bruno A. Piscelli, Rodrigo A. Cormanich, and Thomas Wirth*

Abstract: Despite the remarkable advancements in hypervalent iodine chemistry, exploration of bromine and chlorine analogues remains in its infancy due to their difficult synthesis. Herein, we introduce six-membered cyclic λ^3-bromanes and λ^3-chloranes. Through single-crystal X-ray structural analyses and conformational studies, we delineate the crucial bonding patterns pivotal for the thermodynamic stability of these compounds. Notably, these investigations reveal pronounced π–π stacking phenomena within the crystal lattice of hypercoordinated bromine(III) and chlorine(III) species. Their reactivity profile is explored as they are radical precursors or electrophilic reagents in metal-free intermolecular biaryl couplings, *O*- and *S*-arylations, and Cu(I)-promoted intramolecular biaryl couplings which is complementary to the known reactivity of five-membered bromanes and chloranes. Mechanistic insights are provided, elucidating the pathways governing their reactivity and underscoring the potential in organic synthesis.

Introduction

Hypervalent halogen compounds have long fascinated chemist for their captivating reactivity and applications in organic synthesis.[1] Amongst them, hypervalent iodine reagents have been extensively studied and employed due to their abundance, stability, minimal toxicity and intriguing reactivity.[2] However, their chlorine and bromine congeners are still in their infancy due to a lack of practical and efficient synthesis methods. Recent advancements in the conventional and electrochemical synthesis of hypervalent bromine(III) reagents have overcome some of these hurdles, unveiling their unique reactivity patterns and expanding the scope of hypervalent bromine chemistry.[3] Furthermore, theoretical insights and DFT calculations provide a deeper understanding of their structures and bond energies.[4]

Despite facing challenges stemming from their higher electronegativity and ionisation potential, chloranyl and bromanyl units have emerged as promising motifs, exhibiting enhanced nucleofugality and facilitating novel transformations.[5] The initial synthesis of cyclic bromine(III) and chlorine(III) compounds dates back to 1952 when Sandin and Hay used the thermal decomposition of diazonium salts for their preparation.[6] Subsequent improvement in reaction methods by Less and Heaney led to higher yields of those compounds.[7] The direct oxidation of biaryl derivatives with strong oxidants has also been used in the synthesis of five-membered bromine(III) salts.[8] In recent studies, Wencel-Delord et al. explored the thermal decomposition of diazonium salts leading to a wide array of five-membered cyclic diaryl λ^3-bromane and λ^3-chlorane reagents.[9] Yoshida and colleagues synthesised chiral versions of five-membered halonium salts with higher molecular complexity.[10] Despite these synthetic advancements in cyclic hypervalent bromine and chlorine chemistry, research remains constrained to five-membered rings, and the six-membered analogs are uncharted territory. Over the past decade, significant progress has been made in generating aryl radicals using aryl triflates, aryl carboxylic acids, aryl boronic acids, and iodine(III) reagents.[11] These advancements have facilitated a diverse array of reactions, leading to the formation of carbon-carbon and carbon-heteroatom bonds. Due to the remarkable reactivity of aryl radicals, there is still the need to devise more efficient precursors for their generation.

Herein, we report the use of chalcogen-tethered diaryl compounds for the synthesis of six-membered bromine(III) reagents. Attempts to achieve this via the thermal decomposition of diazonium salts was unsuccessful from diaryl ether, thioether and sulfone derivatives. However, the synthesis of six-membered diaryl bromonium and chloronium salts containing the sulfoxide moiety were successful. The X-ray structures of these bromonium and chloronium salts closely resemble the bis-halogen(III) structures reported by the Cuenca and Shafir research groups.[12] While the five-membered bromine(III) and chlorine(III) compounds serve as aryne precursors,[3] we report here the six-membered

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bromonium and chloronium species as being efficient aryl radical precursors as well as electrophilic reagents (Scheme 1).
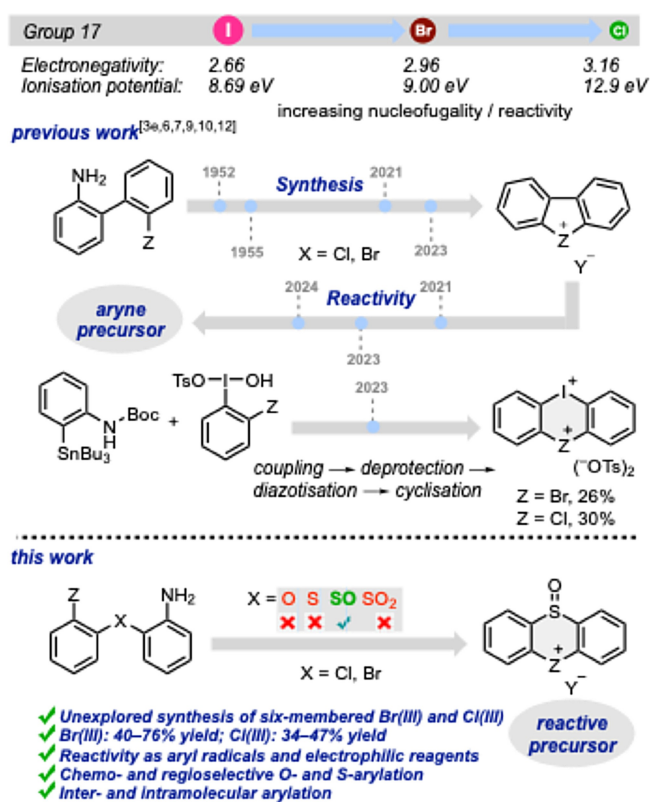
Results and Discussion

The thermal decomposition of diazonium salts has historically been used for synthesising bromonium and chloronium salts.[5,6,7,8] Initially, diaryl ethers were targeted as starting materials. Their reaction did not yield the desired six-membered aryl bromonium salts, only the precursor diazonium salts were isolated and all cyclisation attempts were unsuccessful. Similarly, diaryl thioethers and diaryl sulfones as precursors were unreactive (see Supporting Information). Only substituted diaryl sulfoxides proved to be suitable starting materials for six-membered μ-sulfoxo diaryl chloronium and bromonium salts.

Optimisation experiments revealed that the substrate **1** in a small excess of 0.1 M Brønsted acid solution in acetonitrile, along with 2 equivalents of *t*BuONO, was necessary to achieve the desired transformation at 75°C. Higher acid concentrations lead to decreased yields of the bromonium salts. Acetonitrile is the optimal solvent for achieving good yields of the bromonium salts (see Supporting Information). With these reaction conditions, we explored the feasibility of accessing μ-sulfoxo diaryl bromonium salts. Different Brønsted acids were used in the
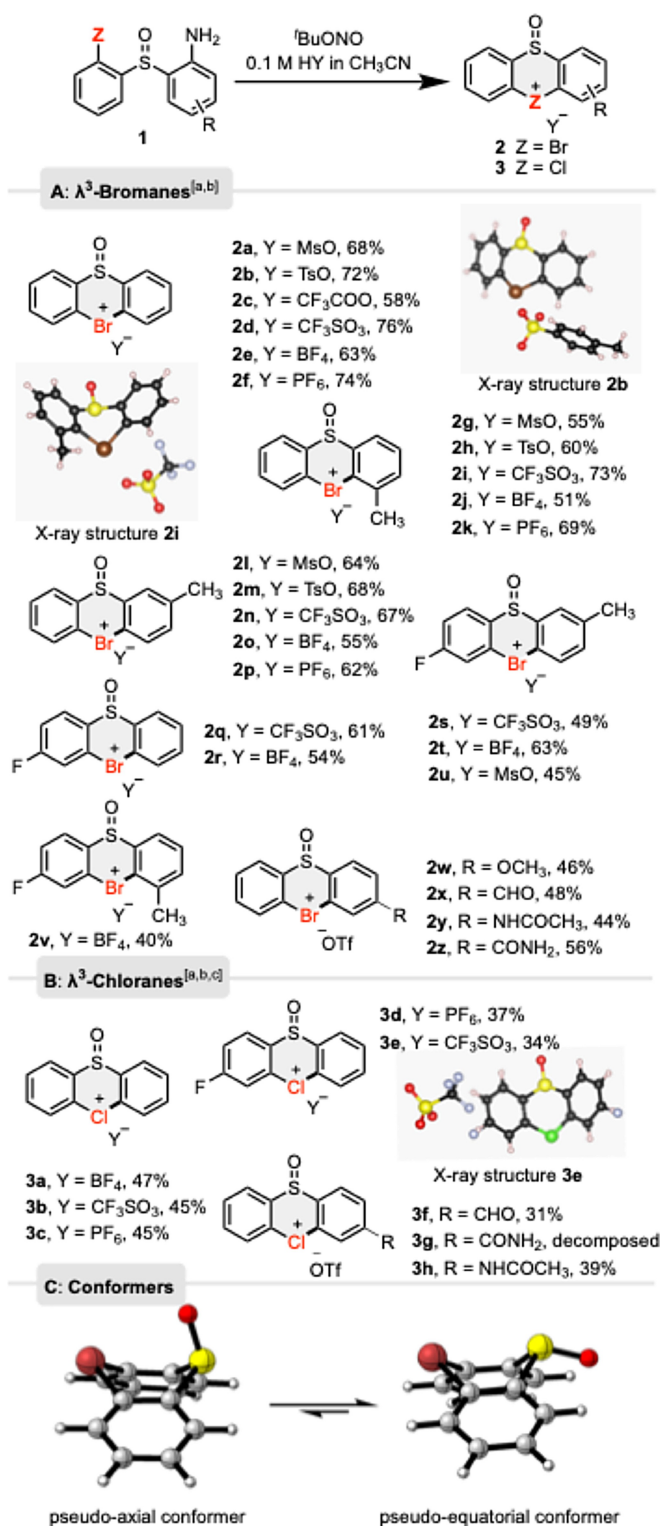
reaction of 2-((2-bromophenyl)sulfinyl)aniline **1** (Z=Br, R=H) leading to reaction products **2a**–**2f** in 58% to 76% yield. The bromonium salts **2** are easily isolated through precipitation from diethyl ether and remain stable at room temperature for several months. The X-ray structure of **2b** is shown in Scheme 2. Acetic acid and hydrochloric acid led to decomposition during bromonium salt synthesis. Subsequently, electron-rich unsymmetrical diaryl sulfoxides with methyl groups at various positions were investigated. Methyl groups were well tolerated at *ortho*- and *para*-positions and no significant variance in reactivity was observed, resulting in moderate to good yields of the corresponding bromanes **2g**–**2p**. Stronger Brønsted acids such as triflic acid and hexafluorophosphoric acid produce higher yields of the desired bromanes. Electron-deficient unsymmetrical bromanes from the corresponding diaryl sulfoxides are, however, formed in lower yields. Triflic acid provided 61% yield of **2q**, whereas tetrafluoroborate-derived Brønsted acid produced bromane **2r** in 54% yield. Of particular interest were the "push-pull" bromine(III) reagents (**2s**–**2v**), featuring an electron-donating methyl group at one aryl ring and an electron-withdrawing fluorine substituent at the other aryl ring, which were obtained in moderate to good yields. Functional groups such as ether, aldehyde, anilide, and amides were well tolerated under the reaction conditions, leading to the successful formation of compounds **2w**–**2z**. The electron-withdrawing cyano group failed to produce the expected bromane. Although the amide functionality successfully yielded **2z**, the starting material encountered solubility challenges. This issue was efficiently resolved by utilising a 0.05 M acidic solution, which allowed the reaction to proceed to completion.

Computational analysis shows that μ-sulfoxo-λ^3-bromanes are present in both pseudo-axial and pseudo-equatorial conformations (Scheme 2, C). However, the pseudo-equatorial form is more stable and predominates, constituting 90% of the population at room temperature (see Supporting Information).

Calculations also suggest why sulfoxide diazo compound **R1** leads to the desired product, while sulfone diazo compound **R2** is unreactive (Figure 1). The transition state Gibbs free energy ($\Delta G^{\neq}$) for the sulfoxide reaction **TS1** is 32.9 kcal mol^{-1}, whereas for the sulfone derivative **TS2** it is 38.5 kcal mol^{-1}. The difference of 5.4 kcal mol^{-1} in the reaction barriers translates to the sulfoxide reaction being about 2 orders of magnitude faster than that of the sulfone. Moreover, the bromonium product from sulfoxide **P1** is 3.3 kcal mol^{-1} more stable than the product from the sulfone **P2**, making the formation of bromonium salts both kinetically and thermodynamically more favorable from sulfoxide than from sulfone derivatives (see Supporting Information for details). Subsequently, we have synthesised six-membered hypervalent chlorine(III) compounds using a similar procedure. The temperature during the reaction significantly influences the generation of chlorine(III) species. The optimisation of the temperatures has revealed that the maximum yield (47%) of **3a** can be achieved at 70°C. At lower temperatures a mixture of unreacted diazonium salt and hypervalent chlorine(III) compound is obtained. Chang-

Scheme 1. Synthesis of six-membered bromine(III) and chlorine(III) reagents.

A: λ³-Bromanes[a,b]

2a, Y = MsO, 68%
2b, Y = TsO, 72%
2c, Y = CF₃COO, 58%
2d, Y = CF₃SO₃, 76%
2e, Y = BF₄, 63%
2f, Y = PF₆, 74%

X-ray structure **2b**

X-ray structure **2i**

2g, Y = MsO, 55%
2h, Y = TsO, 60%
2i, Y = CF₃SO₃, 73%
2j, Y = BF₄, 51%
2k, Y = PF₆, 69%

2l, Y = MsO, 64%
2m, Y = TsO, 68%
2n, Y = CF₃SO₃, 67%
2o, Y = BF₄, 55%
2p, Y = PF₆, 62%

2q, Y = CF₃SO₃, 61%
2r, Y = BF₄, 54%

2s, Y = CF₃SO₃, 49%
2t, Y = BF₄, 63%
2u, Y = MsO, 45%

2v, Y = BF₄, 40%

2w, R = OCH₃, 46%
2x, R = CHO, 48%
2y, R = NHCOCH₃, 44%
2z, R = CONH₂, 56%

B: λ³-Chloranes[a,b,c]

3d, Y = PF₆, 37%
3e, Y = CF₃SO₃, 34%

X-ray structure **3e**

3a, Y = BF₄, 47%
3b, Y = CF₃SO₃, 45%
3c, Y = PF₆, 45%

3f, R = CHO, 31%
3g, R = CONH₂, decomposed
3h, R = NHCOCH₃, 39%

C: Conformers

pseudo-axial conformer ⇌ pseudo-equatorial conformer

Scheme 2. Synthesis of μ-sulfoxo diaryl cyclic λ³-bromane and λ³-chloranes. [a] Reaction conditions: ^{t}BuONO (2 eq.), 0.1 M HY (1.2 eq.), 75 °C. [b] Isolated yields. [c] 70 °C.

ing the Brønsted acid did not improve the yield of the chlorine(III) products; **3b** and **3c** were both obtained in 45% yield. The chloronium salts are stable at room temperature for several months. However, the electron deficient
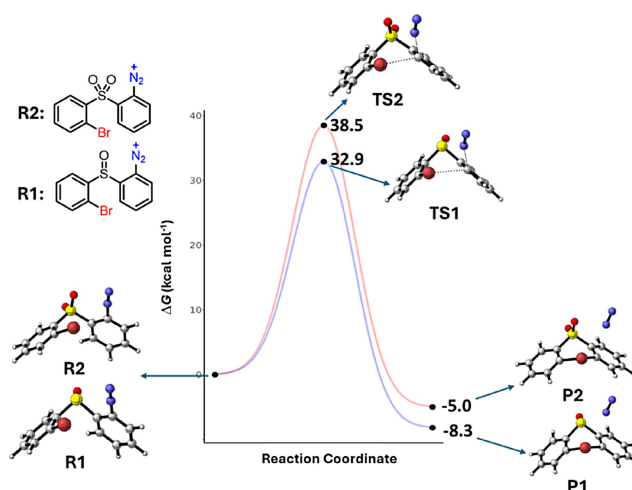

Figure 1. Reaction barriers calculated at the BHandH/aug-cc-pVTZ level.

unsymmetrical chloronium salts **3d** and **3e** were obtained in 37% and 34% yield, respectively, but electron-rich unsymmetrical chloronium salts could not be obtained under the reaction conditions as the products decomposed (see Supporting Information). Additionally, unsymmetrical chloronium salts with electron-withdrawing groups were synthesised and found to exhibit varying stability under ambient conditions. The synthesised compounds demonstrate reasonable stability and only compound **3g** decomposed rapidly after formation (see Supporting Information). In contrast, compounds **3f** and **3h** were successfully synthesised with yields of 31% and 39%, respectively. Notably, compound **3h** exhibited significant solubility issues and was unstable in DMSO-d_6 and DMF-d_7, posing challenges for its characterisation.

An interesting bonding pattern was observed in the X-ray structures of some bromine(III) compounds (Figure 2).[13] The crystal structure of **2b** is triclinic (space group P1̄) with cations and 4-methylbenzenesulfonate anions. The cation features a 115.9(1)° angle between aromatic ring planes. Anions interact through edge-to-face (C—H/π, 2.81 Å) and π–π interactions (3.72 Å) (Figure 2), with additional π–π interactions (3.60 Å) along the a-axis. Cations pair via C6–H6···O1 interactions and interact with sulfonate anions through C–H···O contacts (see Supporting Information, Figure S8). Anions have π–π and close O···Br contacts (2.74 Å and 2.68 Å). The crystal structure of **2i** is monoclinic (space group P2₁/c) with cations and trifluoromethanesulfonate anions. The cation has a 113.3(1)° angle between aromatic ring planes. Anions exhibit edge-to-face (4.91 Å) and π–π interactions (3.62 Å) (Figure 2), with additional π–π interactions (3.73 Å) along the b-axis, forming columns. Cations link through C–H···O contacts and trifluoromethane-sulfonate anions. There is an O···Br contact (2.86 Å) between anion and cation (see Supporting Information, Figure S9). The crystal structure of **3e** is triclinic (space group P1̄) with cations and trifluoromethanesulfonate anions. The cation has a 112.9(1)° angle between aromatic
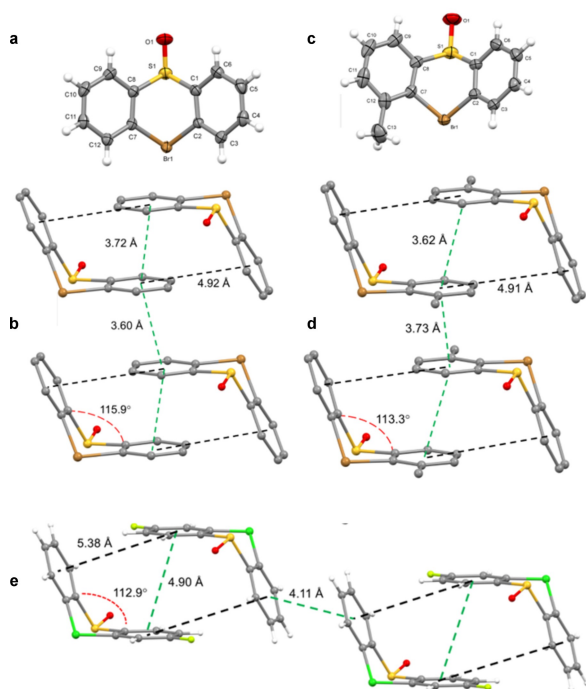
Figure 2. (a) X-ray structure **2b** with atom numbering; (b) Segment of the X-ray structure showing ring centroid-to-centroid contacts (green = π–π, black = edge-to-face); (c) X-ray structure **2i** with atom numbering; (d) Segment of the crystal structure showing ring centroid-to-centroid contacts (green = π–π, black = edge-to-face); (e) Segment of the crystal structure **3e** showing ring centroid-to-centroid contacts (green = π–π, black = edge-to-face). Hydrogens atoms have been omitted for clarity.

ring planes. Anions show less optimal edge-to-face (5.38 Å) and π–π interactions (4.90 Å) due to lateral offset, with significant π–π contact along the c-axis (4.11 Å). Cations and anions are linked by C–H···O interactions (see Supporting Information, Figure S10). The six-membered bromine(III) rings in **2b** and **2i** have similar bond lengths and angles (see Supporting Information, Table S6). In **3e**, Cl incorporation results in a six-membered chlorine(III) ring with larger angles: C1–C2–Cl1 [118.5(1)°], C7–Cl1–C2 [97.9(1)°], and C8–C7–Cl1 [118.3(1)°], compared to bromine(III) in **2b** and **2i**.

Initially, the chemo- and regioselective *O*- and *S*-arylation of the λ³-bromane and λ³-chlorane compounds were investigated (Scheme 3). After optimisation of reaction conditions, 2 equivalents of phenol or thiophenol derivatives and caesium carbonate in acetonitrile resulted in good to excellent yields of the desired *ortho*-selective hetero-aryl products (**4a–4k** and **5a–5e**). Remarkably, the reaction exhibited exclusive *ortho*-selectivity, underscoring the efficiency of the reaction. The reaction of **2d** and 2-bromophenol under the optimised conditions yielded the *O*-arylated product **4a** in excellent yield (89%). The X-ray structure of **4a** confirmed the desired *ortho*-selective arylation. Surprisingly, the corresponding iodine(III) compound (see Supporting Information) remains unreacted under the reaction conditions demonstrating the extraordinary reactivity of the
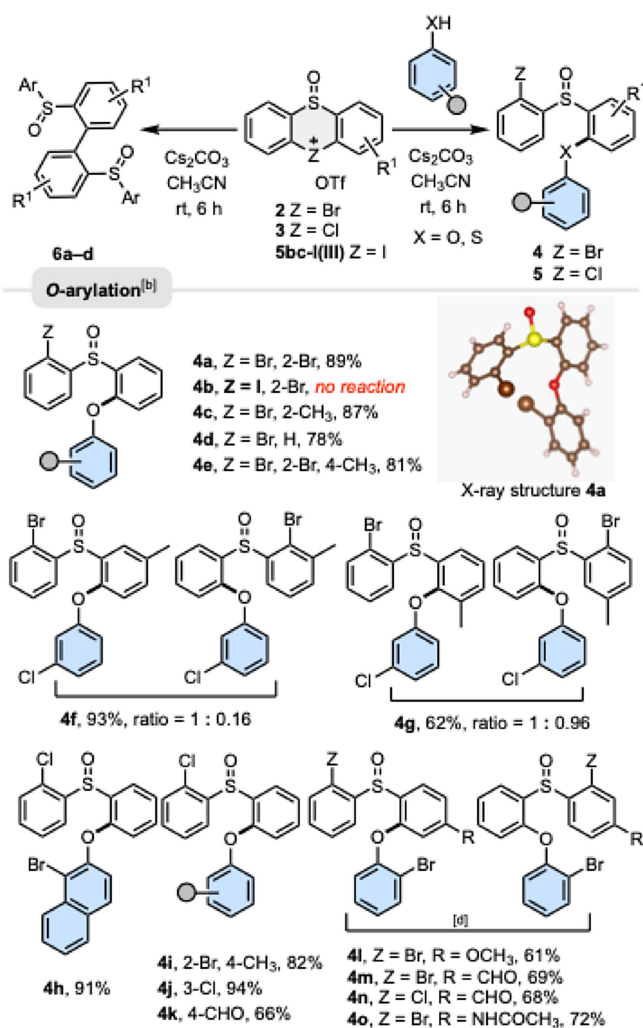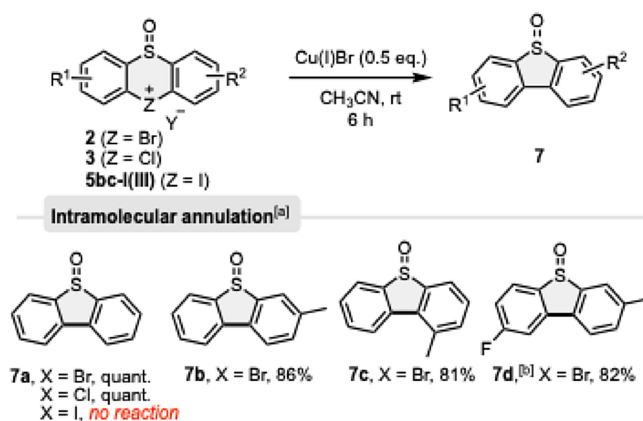

Scheme 3. Application of μ-sulfoxo diaryl cyclic λ³-bromane and λ³-chloranes.[a] Reaction conditions: phenol or thiophenol (2 eq.), Cs₂CO₃ (2 eq.).[b] Isolated yield.[c] Reactions performed without phenol or thiophenol.

bromine(III) and chlorine(III) species over iodine(III). Electron-rich phenols, including *ortho*-cresol and phenol, were subjected to the reaction conditions. Also naphthols and disubstituted phenols were used as coupling partners. Products **4c–4k** were obtained in 62–94% yield (Scheme 3). Controlling regioselectivity was challenging with hypervalent bromane **2i**, resulting in a mixture of regioisomers **4g** in moderate yields. Unsymmetrical hypervalent bromine-(III) and chlorine(III) were well tolerated under the *O*-arylation conditions and delivered **4l–4o** in moderate to good yields. The regioselective formation of *O*-arylated products is controlled by the electron withdrawing ability of the substituents. In the case of ether functionalisation, the regioisomers **4l** were formed in a 2:1 ratio. With the electron-withdrawing aldehyde functionality in Br(III) and Cl(III) precursors, the regioisomeric ratio was around 1:0.2. However, *O*-arylation with anilides afforded the product in good yield, but in a 1:1 ratio of the isomers. Unfortunately, alkyl and benzyl alcohols were not suitable coupling partners for *O*-arylations under standard conditions (see supporting information). Thiophenols produced compounds **5a–5e** in moderate yields (Scheme 3). The reduced yields of the O- and S-arylation products can be attributed to the concurrent occurrence of the dimerisation reaction alongside the S_NAr reaction. In the absence of O- or S-nucleophiles, a dimerisation to biphenyls **6** was observed (Scheme 3). Recently, Baidya and co-authors reported five-membered diaryl λ^3-chloranes in highly *ortho*-selective ligand coupling reactions.[3i] Under the reaction conditions reported, the more facile benzyne formation is suppressed.

Optimising the reaction parameters revealed that 2 equivalents Cs_2CO_3 in acetonitrile at room temperature provided the best conditions for the biaryl coupling. The highly substituted biphenyls exist as mixtures of atropisomers. Under the optimised conditions, 92% yield of compound **6a** was obtained. The corresponding chlorane precursor formed **6b** in 78% yield. The six-membered λ^3-bromane and λ^3-chlorane demonstrated significantly higher reactivity compared to the six-membered λ^3-iodane, which produced only traces of the biaryl **6c**.

In the presence of copper(I)bromide, the μ-sulfoxodiaryl cyclic-λ^3-bromanes and chloranes efficiently undergo selective intramolecular biaryl coupling at ambient temperature. The resulting cyclic sulfoxides **7** were obtained in high yield. In Scheme 4, the reactivity of intramolecular annulation is shown for iodanes, bromanes, and chloranes. The λ^3-bromane and λ^3-chloranes yielded **7a** in quantitative yield, whereas λ^3-iodane **5bc-I(III)** is unreactive. The unsymmetric bromanes **2i** and **2o** resulted in 81% and 86% of the annulated products **7b** and **7c**, respectively. Only single isomers of the products were observed in each case. In addition, push-pull bromine(III) **2u** generated **7d** in 82% yield.

To get an insight into the reaction mechanism, several control experiments were performed (see Supporting Information). The reaction of bromane **2d** in the presence of enophiles such as furan or TsN_3 under basic conditions resulted in the formation of **6a** ruling out the formation of aryne intermediates (Table 1, entries 1+2). Conversely, *O*-

Scheme 4. Intramolecular annulation of μ-sulfoxo diaryl cyclic λ^3-bromane and λ^3-chloranes.[a] Isolated yield.[b] 60 °C.

Table 1: Mechanistic investigations.[a]

Entry	Reaction conditions	Product	Yield [%]
1	furan, Cs_2CO_3 (2 eq.)	**6a**	92
2	TsN_3, Cs_2CO_3 (2 eq.)	**6a**	92
3	Cs_2CO_3 (2 eq.)	**6a**	92
4	PhOH (2 eq.)	**4d**	traces
5	sodium phenoxide (2 eq.)	**4d**	86
6	PhOH (2 eq.), Cs_2CO_3 (2 eq.), exclusion of light	**4d**	78
7	BHT (2 eq.), Cs_2CO_3 (2 eq.)	**8**	68
		6a	18
8	PhOH (2 eq.), BHT (2 eq.), Cs_2CO_3 (2 eq.)	**8**	76
		4d	traces
9	**2o**, Cs_2CO_3 (2 eq.)	**6a**+**6d**+**9**	mixture

arylations produced only trace amounts of the desired product **6c** if Cs_2CO_3 is excluded from reaction (Table 1, entry 4). The *O*-arylation took place even in the dark prompting the introduction of radical traps into the reaction system. Addition of BHT (2,6-di-*tert*-butyl-4-methylphenol) to a solution of **2d** in acetonitrile and Cs_2CO_3 significantly reduced biaryl formation, and the resulting BHT adduct **8** was identified and confirmed by ESI-HRMS analysis (Table 1, entry 6). Similar experiments conducted with phenol led to a reduction in *O*-arylated product formation (see Supporting Information). The treatment of a mixture of two different λ^3-bromanes **2d** and **2o** under basic conditions resulted in the synthesis of cross-coupling product **9**, indicating the formation of radical intermediates.

The mechanistic study of *O*- and *S*-arylation in 6-membered bromanes reveals a strong preference for con-

certed S$_N$Ar pathways over benzyne or single-electron transfer (SET) mechanisms due to the electron-deficient nature of the ring, enhanced by the S=O spacer (Figure 3). For *O*-arylation, S$_N$Ar through **TS−SNAr−O** is kinetically and thermodynamically favored with a barrier of 21.2 kcal mol^{-1} (Figure 3, brown pathway), producing **4d** with an energy release of −127.0 kcal mol^{-1}, while the benzyne pathway is excluded as experimentally and energetically unfavorable (Figure 3, blue pathway). The energetics are in agreement with previous calculations by Wencel-Delord et al. on their study of 5-membered bromanes.[9b] The higher electrophilicity of *ipso*- and *ortho*-carbons, confirmed by molecular electrostatic potential (MEP) maps, enhances nucleophilic susceptibility (Figure 4). In biaryl coupling, a radical mechanism involving aryl radical dimerisation (**TS-rad-C**) is supported by radical trapping experiments and a low energy barrier of 9.8 kcal mol^{-1} (Figure 3, green pathway). *S*-Arylation similarly proceeds via an S$_N$Ar pathway (**TS-SNAr-S**), favored by 26.8 kcal mol^{-1} over its radical counterpart, yielding **5a** with an energy release of −133.5 kcal mol^{-1} (Figure S7, see Supporting Information).

These findings underscore the role of electron deficiency in dictating pathway selectivity. Based on the theoretical and experimental evidences and previous literature, the most plausible mechanism is depicted in Scheme 5.[11,12,14] Initially, hypervalent compound **2a** undergoes a anion exchange reaction with carbonate to **I**. We have observed that the stability of the hypervalent compounds is influenced by the nature of the anions, with anions from strong acids significantly stabilising hypervalent bromine(III) and chlorine(III) species (see above). An NMR experiment was performed to track the intermediate **I** but rapid formation of
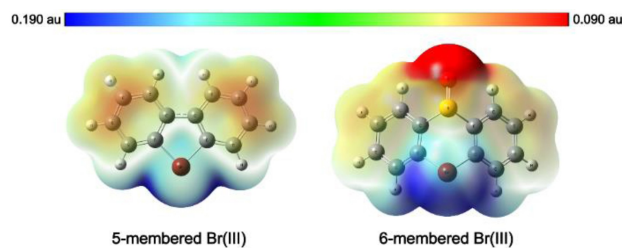

Figure 4. Mapped molecular electrostatic potential (MEP) for 5- and 6-membered bromanes, calculated at the PCM-BHandH−D3BJ/6-31+G** theoretical level.

biaryls was observed (see Supporting Information). This outcome may result from the homolytic cleavage of the C–Br bond, generating a transient aryl radical intermediate (**II**), which can dimerise to form biaryl **6**. The formation of radicals through a SET mechanism facilitated by Cs$_2$CO$_3$ has been well-documented in the literature.[15] On the other hand, phenols and thiophenols under basic conditions prefer S$_N$Ar type reaction which results in *ortho*-selective *O*- or *S*-coupled products. This is further supported by computational studies. Additionally, Cu(I)Br might participate in radical addition with **2a** to form intramolecular coupling product **7** via the formation of **III**.[16] XPS data are also provided and indicate a change in the oxidation state of the Cu metal after the reaction (Figure S12, see Supporting Information).
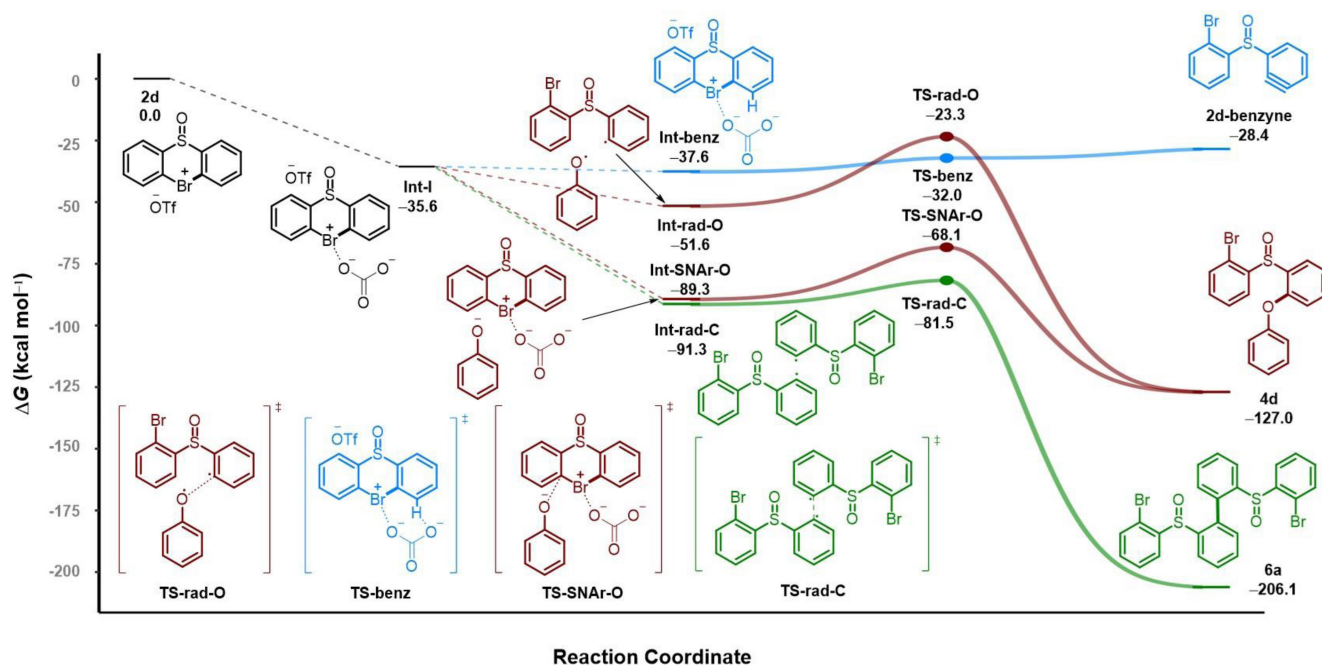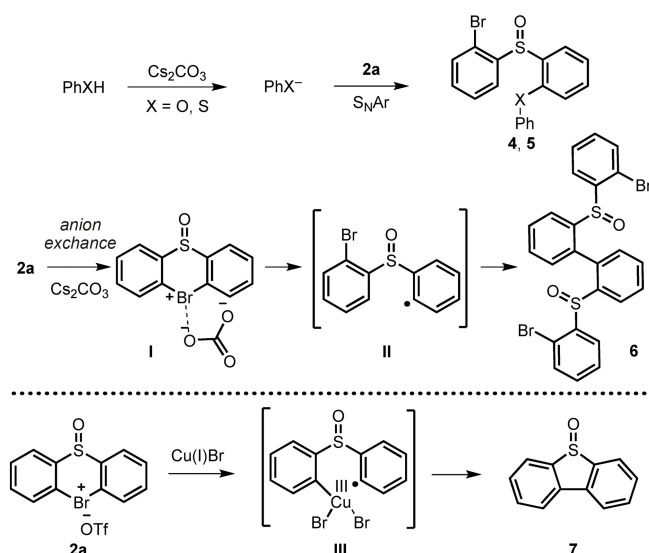

Figure 3. Reaction barriers for the derivatizations of **2d** at the DLPNO-CCSD(T)/cc-pVTZ//BHandH−D3BJ/6-31+G**+COSMO-RS (acetonitrile) theoretical level.

Scheme 5. Possible reaction mechanisms.

Conclusion

This study reveals the development of a novel library comprising six-membered cyclic diaryl λ^3-bromane and λ^3-chlorane reagents. Within the domain of six-membered hypervalent bromine(III) and chlorine(III) compounds, this likely stands as the primary account of their synthesis and crystal structures. The reactivity of the new reagents differs significantly from their five-membered homologs. This study demonstrates the synthetic utility of these novel reagents in *ortho*-selective *O*- and *S*-arylation reactions, metal-free intermolecular biaryl formation as well as in copper-mediated intramolecular annulations. Our research high-lights the potential of these novel reagents, offering versatile strategies for the construction of diverse molecular architec-tures.

Supporting Information

The authors have cited additional references within the Supporting Information.[17–23]

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Detailed experimental procedures and characterisation data are provided in the Supporting Information. Information about the data that underpins the results presented in this article can be found in the Cardiff University data catalogue at http://doi.org/10.17035/cardiff.28196231.

Keywords: arylation · aryl radicals · hypervalent bromine · hypervalent chlorine · S$_N$Ar reaction

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Research Article

Organic Synthesis

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Synthesis and Reactivity of Six-Membered
Cyclic Diaryl λ^3-Bromanes and λ^3-Chloranes

metal-free *O*- and *S*-arylation
metal-free biaryl coupling
intramolecular biaryl coupling
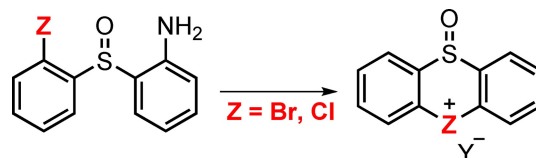
The synthesis of six-membered hyper-valent bromine(III) and chlorine(III) compounds through their diazonium salts is demonstrated. High yielding chemo- and regioselective *O*- and *S*- arylations are possible at ambient temperature, which can also be utilized for intermolecular or intramolecular biaryl synthesis by modifying the reaction conditions.