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ARTICLE

Synthesis of dibenzoarsole derivatives from biarylborates via the twofold formation of C–As bonds using arsenium dication equivalents

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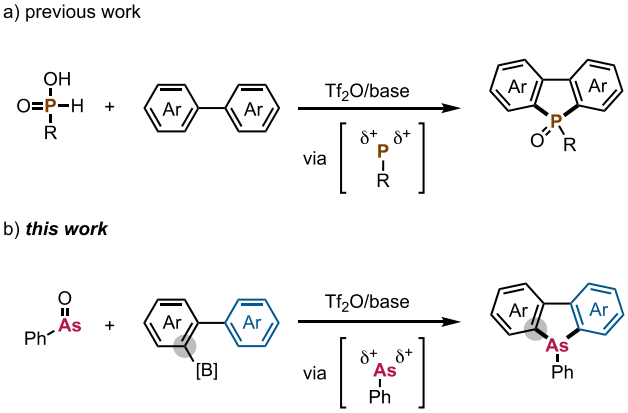
A strategy for the generation of arsenium dication equivalents from readily available and easy-to-handle phenylarsine oxide and Tf_2O has been developed. The *in-situ*-generated dication equivalent can react with biarylborates to directly produce the corresponding dibenzoarsoles, which are difficult to prepare by other means, via the successive formation of inter- and intramolecular C-As bonds. Furthermore, the unique oxygen atom insertion into the C–As bond in the dibenzoarsole is developed to form the corresponding [1,2]oxarsinine derivative.

Introduction

The design and synthesis of π-conjugated molecules are of significant interest for their applications in organic electronics, photovoltaics, and light-emitting diodes.[1] Enhancing the properties of these systems is often achieved by incorporating heteroatoms such as nitrogen, sulfur, and oxygen into the π-conjugated structure, which significantly alters their electronic distribution, optical properties, and molecular stability. [2]

Although a variety of heterocyclic compounds have already been synthesized, the development of arsenic-containing heterocyclic compounds still remains relatively limited. Compared to the traditional strategies with highly toxic and volatile arsenic chlorides or *H*-arsines,[3] their synthesis has witnessed remarkable progress as a result of appearance and design of reagents, catalysis, and conditions for the C–As bond forming reaction.[4] However, the electrophilic C–As bond forming reaction is particularly restricted in scope and generality. As one of the breakthroughs, Naka and Imoto have recently proposed a transformation that is based on a non-volatile intermediate that is generated *in situ* from $PhAsI_2$, which in turn can be obtained from the non-toxic and solid $(PhAs)_6$.[5] While this protocol eliminates the use of hazardous arsenic precursors, the lower electrophilicity of $PhAsI_2$ still requires highly reactive organometallic reagents, such as Grignard or lithium reagents for the formation of C-As bonds. Therefore, the development of efficient and concise reactions that produce C–As bonds, particularly for the synthesis of As-containing aromatic compounds, from stable and less toxic starting materials with high functional-group compatibility would be highly desirable.

In one of our previous reports, we have already used phosphenium dication equivalents to efficiently synthesize dibenzophospholes from simple biaryls and phosphinic acids (Scheme 1a).[6] Inspired by this success, we anticipated that this strategy could potentially be expanded to the generation and use of arsenium dication equivalents,[7] which can be obtained from solid and non-volatile Ph-As=O[8] and Tf_2O. Here, we report a straightforward synthetic route to dibenzoarsole derivatives from biarylborates via arsenium dication equivalents, which mediate the twofold formation of C–As bonds (Scheme 1b). This newly developed protocol enables the concise synthesis of dibenzoarsoles without the need to employ highly reactive organometallic reagents and/or dangerous arsenic precursors. The biarylborate can be readily and modularly prepared by the Suzuki-Miyaura coupling/Miyaura boration sequence from the readily available starting substrates.[9] Moreover, this protocol



Scheme 1 (a) Direct synthesis of dibenzophospholes from simple biaryls via P dication equivalents and (b) synthesis of dibenzoarsoles from biarylborates via the twofold formation of C–As bonds formation using arsenium dication equivalents.

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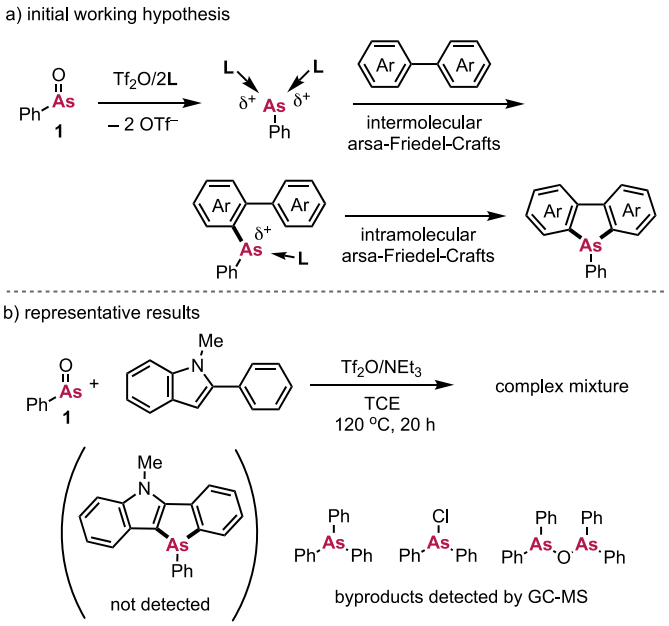
can also be applied to the synthesis of six-membered arsacycles and a largely π-extended dibenzoarsole derivative. Furthermore, we observed that dibenzoarsole oxides undergo ring-expansion reactions when treated with *m*CPBA or arynes, which leads to a diverse range of arsenic-containing heterocycles. We also note that during the course of this study Szewczyk, Sobolewski, Gryko and coworkers reported a related intramolecular electrophilic C–As bond forming reaction of triarylarsine oxide under Tf_2O-promoted conditions, delivering the π-extended arsolium salt, but the synthesis of neutral arsine derivatives still remains a challenge.[10]

Results and discussion

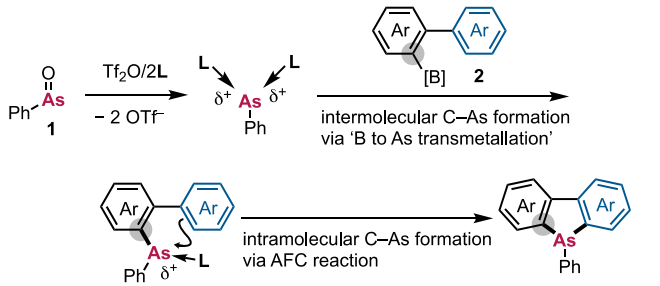
Based on our previously reported synthesis of dibenzophospholes mediated by phosphenium dication equivalents, we initially tried the reaction of some simple biaryls such as *N*-methyl-2-phenylindole with PhAs=O (**1**) and Tf_2O. Initially, our working hypothesis consisted of (1) the generation of highly electrophilic, coordinatively unsaturated arsenic dication equivalents upon treatment of **1** with Tf_2O,[11] whereby the two OTf ligands are displaced by external neutral Lewis bases (**L**), (2) an intermolecular arsa-Friedel-Crafts (AFC)-type reaction, and (3) a ring-closing reaction via an intramolecular AFC reaction (Scheme 2a).[7c] However, as far as we tested, this approach did not yield the desired dibenzoarsole product (Scheme 2b). Instead, Ph_3As, Ph_2AsCl,[12] and $(Ph_2As)_2O$ were detected by GC-MS analysis, which suggests that the cationic arsenic species is generated *in situ*, and that ligand scrambling on the cationic As moiety[13] is faster than the desired intermolecular formation of the C–As bond with the simple biaryl. Consequently, we hypothesized that more nucleophilic substrates, such as biarylboronic acids (**2**) could potentially be more effective to promote the formation of the first, intermolecular C–As bond, which would render the formation of the second, intramolecular C–As bond feasible. This modified working hypothesis is illustrated in Scheme 3.

In our updated working hypothesis, the highly electrophilic arsenium dication equivalent is generated from PhAs=O (**1**), Tf_2O, and **L**. The formation of the first C–As bond is considered to occur between the cationic As moiety and the arylboronic acid (B-to-As transmetallation), followed by an intramolecular AFC reaction that forms the second C-As bond.

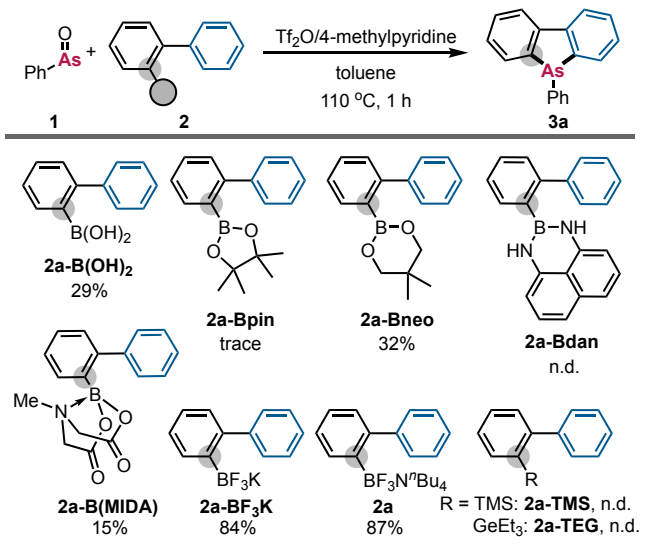
When we treated PhAs=O (**1**; 0.24 mmol) with biphenylboronic acid (**2a-B(OH)$_2$**; 0.1 mmol), Tf_2O (0.24 mmol), and 4-methylpyridine (0.36 mmol) in toluene at 110 ˚C for 1 hour, we observed the formation of the corresponding dibenzoarsole (**3a**)[5a] in 29% NMR yield (Scheme 4). These preliminary intriguing results prompted us to explore other biphenylboron derivatives. However, none of our attempts to use biphenylboronic acid pinacol ester (**2a-Bpin**), biphenylboronic acid neopentylglycol ester (**2a-Bneo**), biphenyl(naphthalene-1,8-diamino)boron (**2a-Bdan**), and biphenyl MIDA boronate (**2a-B(MIDA)**) improved the reaction efficiency. On the other hand, we found that biaryl trifluoroborates (**2a-BF$_3$K** and **2a**) gave better results. In particular, ammonium borate **2a** afforded



Scheme 2 (a) Our initial working hypothesis for the direct synthesis of dibenzoarsoles from simple biaryls using arsenium dication equivalents and (b) representative unsuccessful results; **L** = Lewis base.



Scheme 3 Revised working hypothesis for the synthesis of dibenzoarsole derivatives from biarylborates **2** via the twofold formation of C–As bonds using arsenium dication equivalents.



Scheme 4 Scope of biphenylboron derivatives. The NMR yields of the desired target (**3a**) are shown. Reaction conditions: **1** (0.24 mmol), **2** (0.10 mmol), Tf_2O (0.24 mmol), 4-methylpyridine (0.36 mmol), toluene (1.5 mL), 110 ˚C, 1 h, N_2. n.d. = not detected.

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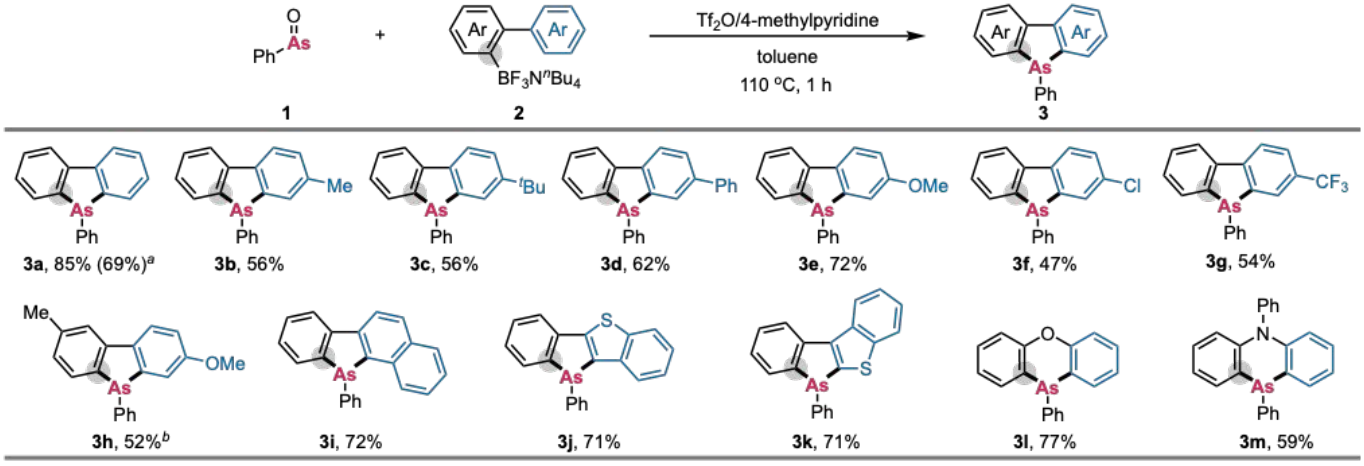
Much better results owing to its high solubility. In contrast, the desired product (**3a**) was not obtained when TMS- and Et_3Ge-substituted biphenyls (**2a-TMS** and **2a-TEG**) were used. Several observations that we made during our optimization studies should be noted here. We also examined several bases other than 4-methylpyridine, but no improvement was observed. Any other dehydrating agents such as $(CF_3CO)_2O$, Ts_2O, Ac_2O, and $PhNTf_2$, did not promote the reaction. The much better leaving ability of TfO^- is believed to be critical for successful sequential C–As bond formation while $PhNTf_2$ cannot form the arsenic dication equivalent because of its lower electrophilicity than that of Tf_2O. PhAs=O (**1**) is an indispensable arsenic source in this reaction, and **3a** and/or its oxide (**4a**) was formed only in <10% yield from Ph_3As or $PhAs(O)(OH)_2$ instead of **1** under otherwise identical conditions (for details, see the ESI†).

With the optimal conditions established, we investigated the scope of ammonium borates (**2**) with versatile biaryl skeletons (Scheme 5). The standard reaction conditions proved equally compatible with electron-neutral (Me, *t*-Bu, Ph), -donating (OMe), and -withdrawing (Cl and CF_3) groups, resulting in the formation of the corresponding dibenzoarsoles (**3b–g**) in good yield (47–72%). The substituent on the BF_3-substituted left ring was also tolerated (**3h**), where the electron-donating Me group facilitated the reaction even at lower temperature (60 ˚C). This reactivity trend is consistent with the intermolecular transmetallation mechanism in the first C–As formation (Scheme 3). Additionally, substrates with a higher π-conjugated system (**3i**) and heterocyclic benzothiophenes (**3j**[5g] and **3k**) also underwent the reaction smoothly. This strategy was further extended to the synthesis of six-membered arsacycles. Borates containing diaryl ether and triarylamine moieties were directly converted to the corresponding six-membered phenoxarsine **3l**[5h] and phenoarsazine **3m**[14] in acceptable yield. The reaction could also be performed on a 10-fold increased scale (**3a**), which showcases the practical utility and good reproducibility of the process. As a general trend, the more electron-rich aromatic rings (**3a–e**) showed higher reactivity than the electron-deficient ones (**3f** and **g**). In addition, the naphthalene ring selectively reacted at the more congested but more electron-rich α position (**3i**). These features are consistent with the aromatic electrophilic substitution mechanism, that is, AFC-type reaction in the second C–As bond formation process as proposed in Scheme 3.

We next attempted the synthesis of a largely π-extended dibenzoarsole derivative. 2,6-Bis(3-benzothienylborate)naphthalene **2n** was transformed, via the fourfold formation of C–As bonds, to the corresponding highly condensed, bent-type S,As-acene **3n** in 49% yield (Scheme 6). The solid-state structure of **3n** was unambiguously confirmed by single-crystal X-ray diffraction analysis (CCDC 2329867).† The single crystal of **3n** showed face-to-face slipped columnar structure, where the stacking distance was relatively long (ca. 3.839 Å). This result indicates the weak π- π stacking because of the intermolecular steric repulsions arising from the two Ph rings on arsenic atoms. It is also noteworthy that no any special interactions including arsenic and sulfur atoms were observed while there were some CH/CH and CH/π interactions between the Ph ring on arsenic and the edge of benzothiophene moiety. The preliminary photoluminescent properties of **3a**, **3j**, **3k**, and **3n** were investigated. The compounds **3a**[5a] and **3j**[5g] were reported in the literature, but their properties were also surveyed again to compare those of regioisomeric **3k** and more π-extended benzothiophene-fused derivative **2n**. Their UV/vis absorption and fluorescence spectra in $CHCl_3$ (1.0×10^{-5} M) are summarized in Figure 1 and Table 1. All compounds exhibited little to no fluorescence, compared to the N-, O-, and S-analogues (carbazole, dibenzofuran, and dibenzothiophene, respectively). This is most likely due to the presence of arsenic, a heavy atom, which promotes intersystem crossing to the triplet state, thus quenching fluorescence emission. This is a kind of typical heavy atom effects owing to the spin-orbital interaction, suggesting the possibility for applications as unique phosphorescence materials. The higher-fused bisbenzothiophene derivative **3n** showed absorption peaks in the visible region.



Scheme 5 Synthesis of dibenzoarsoles **3** by via the twofold formation of C–As bonds between biarylborates **2** and phenylarsine oxide (**1**). Reaction conditions: **1** (0.24 mmol), **2** (0.10 mmol), Tf_2O (0.24 mmol), 4-methylpyridine (0.36 mmol), toluene (1.5 mL), 110 ˚C, 1 h, N_2. Isolated yields are shown. [a] On the 1.0 mmol scale. [b] With Et_3N instead of 4-methylpyridine at 60 ˚C.

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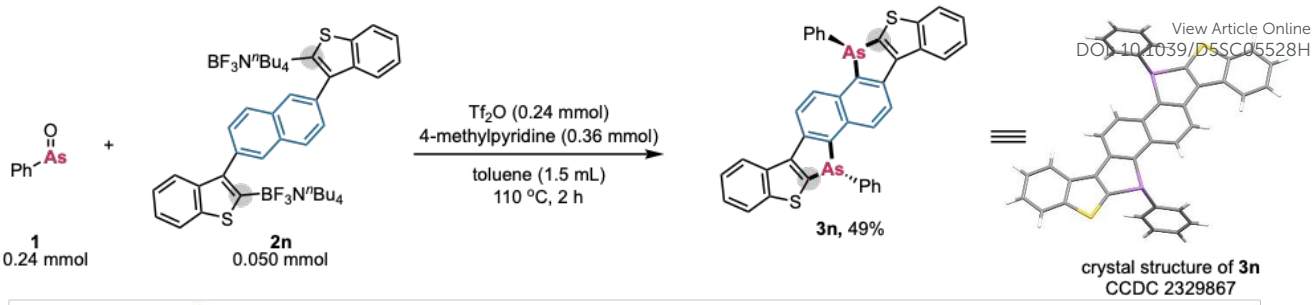

Scheme 6 Synthesis of S,As-acene (**3n**) via the fourfold formation of C–As bonds and its crystal structure.

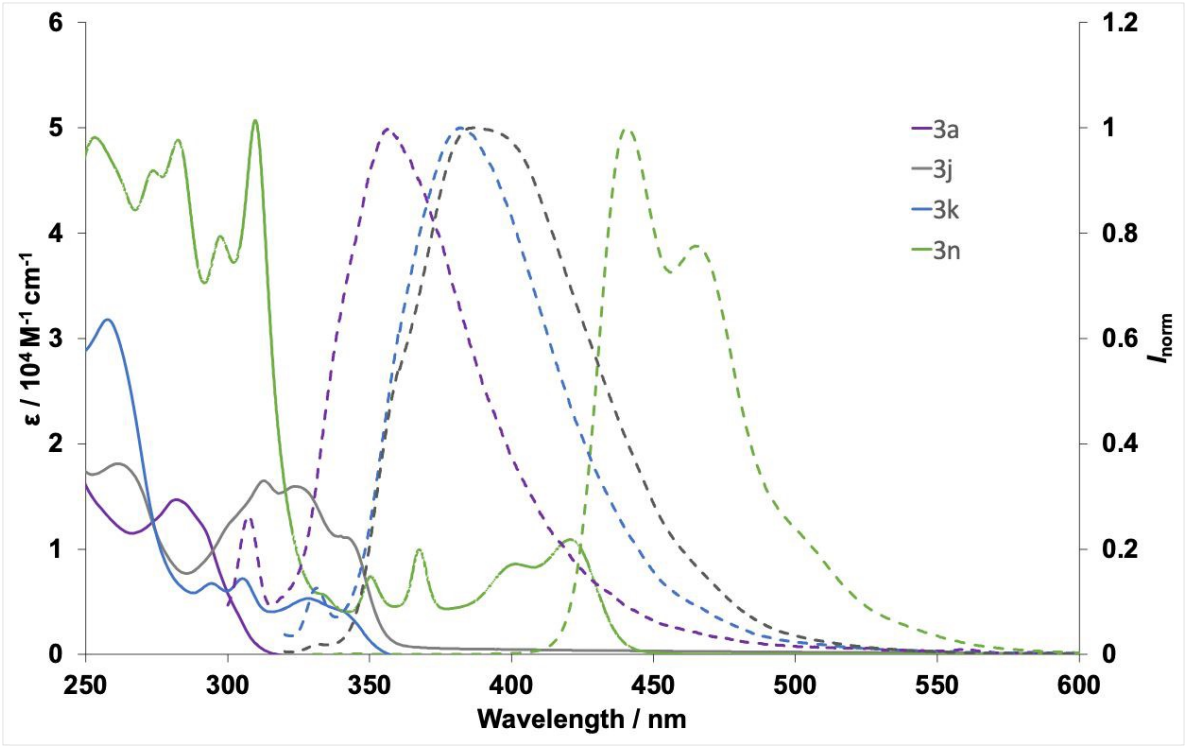

Figure 1 UV/vis absorption (solid lines) and fluorescence spectra (dashed lines) of **3a, 3j, 3k,** and **3n** in $CHCl_3$ (1.0×10^{-5} M)

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Table 1 Optical properties of **3a**, **3j**, **3k**, and **3n**[a]

3	λ_{abs} (nm) (ε (10^4 M^{-1} cm^{-1}))	λ_{FI} (nm)[b]	Φ (%)
3a	282 (1.5)	307, 357	1
3j	262 (1.8), 313 (1.6), 324 (1.6)	387	1
3k	258 (3.2), 294 (0.67), 305 (0.72), 328 (0.53)	331, 382	1
3n	253 (4.9), 274 (4.6), 282 (4.9), 297 (4.0), 310 (5.0), 350 (0.74), 367 (1.0), 402 (0.86), 421 (1.1)	441, 465	3

[a]Measured in $CHCl_3$ (1.0×10^{-5} M). [b] Excited at 280 (**3a**), 300 (**3j**), 300 (**3k**), and 310 nm (**3n**), respectively.

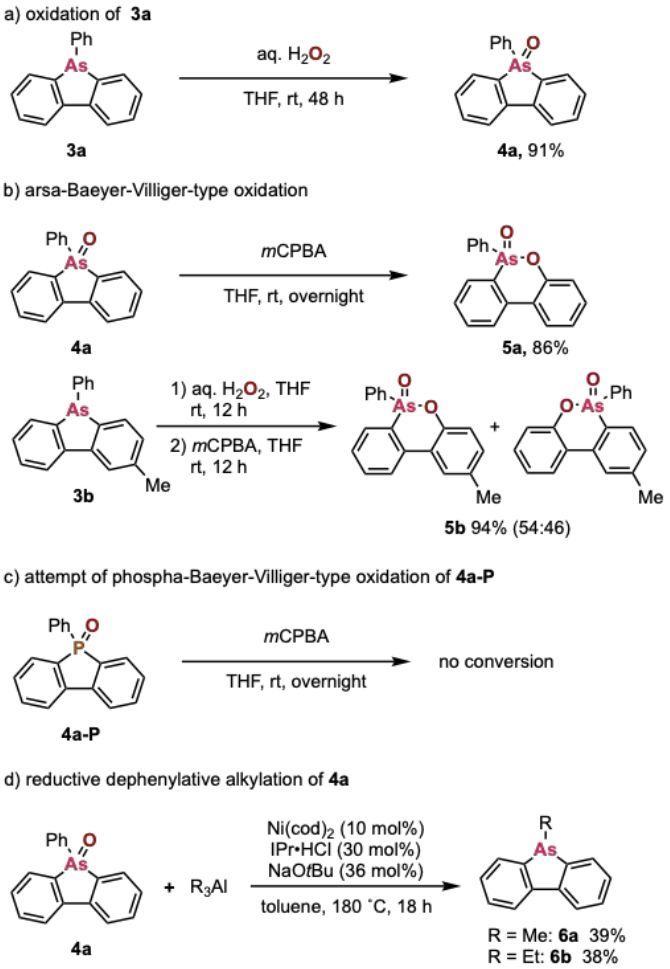
The electrochemical properties of the aforementioned compounds were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in *o*-dichlorobenzene/MeCN (10/1, v/v, for **3a, 3j,** and **3k**) or dichloromethane (for **3n**) with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte *versus* ferrocene/ferrocenium ion (Fc/Fc^+) (Figures S3–6†), and their HOMO and LUMO levels were estimated according to the first oxidation potentials and the optical band gaps (E_g^{opt}) (Table 2). The cyclic voltammograms of **3a, 3j**, **3k**, and **3n** showed irreversible oxidation waves, and the oxidation potential values $E^{1/2}_{ox}$ were thus determined by DPV. In comparison with the parent dibenzoarsole **3a**, the benzothiophene-fused dibenzoarsole derivatives (**3j**, **3k**, and **3n**) exhibited $E^{1/2}_{ox}$ values that were shifted in negative direction probably due to the presence of the electron-donating thiophene ring. Given its lower LUMO and higher HOMO levels, a larger intramolecular charge-transfer ability is suggested for **3n**. Almost all the aforementioned values are identical for **3j** and **3k**, which suggests that the orientation of the benzothiophene ring fusion does not significantly affect the optoelectronic properties.

Table 2 Absorption wavelengths, HOMO-LUMO energy gaps, and DPV data of **3a**, **3j**, **3k**, and **3n**

3	λ_{onset}^{abs} (nm)[a]	E_g^{opt} (eV)[b]	$E^{1/2}_{ox}$ (V)[c]	E_{HOMO} (eV)[d]	E_{LUMO} (eV)[e]
3a	308	4.03	1.35	–6.15	–2.12
3j	357	3.47	0.96	–5.76	–2.29
3k	356	3.48	0.90	–5.70	–2.22
3n	441	2.81	0.67	–5.47	–2.66

[a] Measured in $CHCl_3$. [b] Determined from the onset of the normalized absorption spectra. [c] Performed in *o*-dichlorobenzene/MeCN (10:1, v/v for **3a**, **3j**, and **3k**) or CH_2Cl_2 (for **3n**) in the presence of Bu_4NPF_6. *v* = 0.10 V/s (**3a**), 0.050 V/s (**3j** and **3k**), and 0.030 V/s (**3n**), versus Fc/Fc^+. [d] The approximation for Fc/Fc^+ level is -4.8 eV versus vacuum: E_{HOMO} = -4.8 - $E^{1/2}_{ox}$. [e] Estimated from E_{HOMO} and E_g^{opt}: E_{LUMO} = E_{HOMO} + E_g^{opt}.

Finally, we explored the derivatization of the obtained dibenzoarsoles. Dibenzoarsole **3a** was successfully oxidized with aqueous hydrogen peroxide to furnish dibenzoarsole oxide **4a**[15] in 91% yield (Scheme 7a). The reaction of **4a** with *m*CPBA promoted an arsa-Baeyer-Villiger oxidation to produce a six-membered arsenic-containing cyclic compound (**5a**) via an oxygen-atom insertion into the C–As bond (Scheme 7b). The methyl-substituted **3b** could also be converted to the corresponding ring-expanded product **5b** by sequential treatment with hydrogen peroxide and *m*CPBA albeit with poor regioselectivity. It should be noted here that examples of oxygen-insertion reactions into aromatic heterocyclic compounds are scarce.[16] Indeed, the phosphorus analogue, i.e., benzophosphole oxide **4a-P**, was not converted under otherwise identical conditions (Scheme 7c), which highlights the unique reactivity of dibenzoarsole oxides. These ring-expansion reactions represent a kind of skeletal editing of heteroaromatics,[17] which enables access to novel arsenic-containing cyclic compounds. Furthermore, dibenzoarsole oxide **4a** reacted with trialkylaluminums under Ni catalysis[18] to produce the corresponding 5-alkyldibenzoarsoles **6a**[5a] and **6b** with the removal of Ph group and oxygen (Scheme 7d), which can complement inaccessibility to the toxic methyl- and ethylarsine oxide starting substrates with high volatility.



Scheme 7 (a) Oxidation of **3a**, (b) arsa-Baeyer-Villiger-type oxidation of **4a** and **3b,** (c) attempted phospha-Baeyer-Villiger-type oxidation of **4a-P**, and (d) reductive dephenylative alkylation of of **4a.** For detailed reaction conditions, see the ESI†.

Conclusions

We have developed a new strategy for generation of arsenium dication equivalents from stable, easy-to-handle, and relatively benign phenylarsine oxide and Tf_2O. The *in-situ*-generated dication equivalent can react with biarylborates to produce the corresponding dibenzoarsoles via the successive formation of inter- and intramolecular C–As bonds. This protocol enables the synthesis of oxygen- and nitrogen-containing arsenic six-membered-ring derivatives as well as a highly condensed benzothiophene-containing dibenzoarsole. Moreover, we have investigated the oxygen atom insertion into the As–C bond in the dibenzoarsole oxide to obtain the [1,2]oxarsinine heterocycle. The most salient feature of this method is that it is based on the non-volatile phenylarsine oxide and diarylboronic acids; both are stable and of mild reactivity. This protocol thus provides an avenue to a variety of arsenic-containing heterocycles that have previously been difficult to access, as exemplified by largely π-extended octacyclic system **3n** bearing two arsole and two thiophene rings in the molecular core.

Data Availability

All experimental procedures and spectroscopic data can be found in the ESI.†

Author Contributions

K. N. and K. H. conceived the idea. K. N. and H. I. performed all experiments. Y. N. assisted X-ray analysis. K. H. supervised the project. K. N. and K. H. wrote the manuscript. All the authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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All experimental procedures and spectroscopic data can be found in the ESI.