

One-Pot Synthesis of Heteroatom-Bridged Cyclic Diaryliodonium Salts

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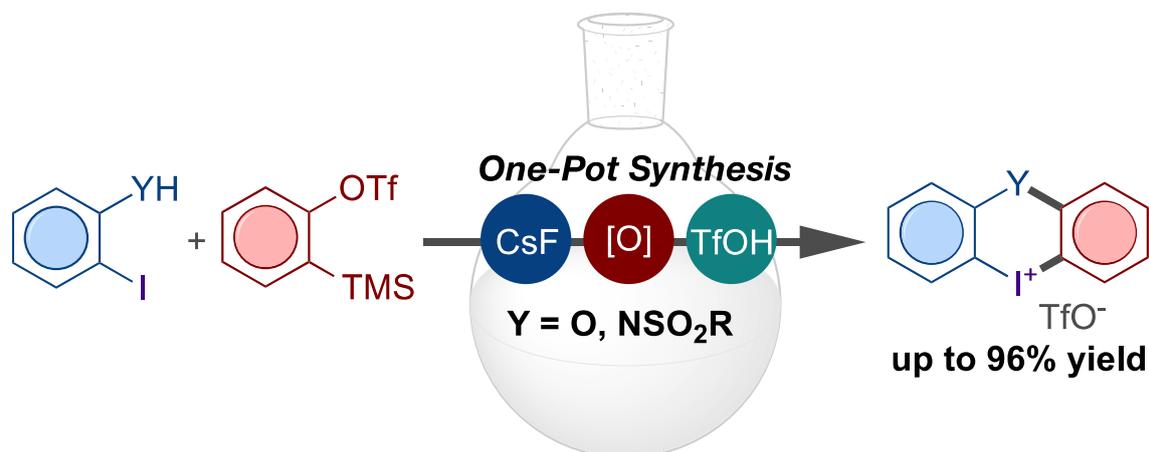
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Abstract

Two one-pot procedures for the construction of *O*- and *N*-bridged diaryliodonium triflates are described. An effective aryne-mediated arylation of *o*-iodophenols and -sulfonamides provides diarylether and diarylamine intermediates, which are subsequently oxidized and cyclized to the corresponding diaryliodoxonium and -iodazinium salts. Different derivatizations were applied to demonstrate their capacity as useful building blocks and gain a deeper understanding towards the general reactivity of these underdeveloped but potentially highly useful compounds.



Keywords

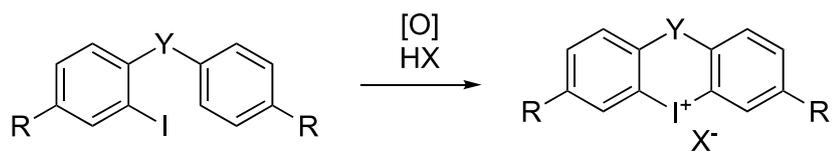
hypervalent iodine • iodonium salts • one-pot synthesis • heterocycles • arynes • arylation

Introduction

Hypervalent iodine compounds (iodanes) have found widespread applications as electrophilic group transfer reagents,^[1] as mild oxidants for the synthesis of natural products^[2] and in organo- and photocatalysis.^[3] Diaryliodonium salts are an important subclass among iodanes, which are commonly applied as electrophilic arylation reagents for transition-metal-catalyzed and metal-free arylations.^[4] In this regard, cyclic diaryliodonium salts which are characterized by two aryl moieties directly connected or bridged with carbon or heteroatoms have been utilized for the effective synthesis of mono- and double-functionalized diaryl-based molecules through regioselective ring opening with a wide range of nucleophiles.^[5] They can also be applied as starting materials for the synthesis of annulated hetero- and carbocycles. While carbon-based iodonium salts have been well studied, their heteroatom-bridged counterparts are underrepresented due to the low availability of efficient synthetic protocols. The first synthesis of *O*- and *N*-bridged cyclic iodonium salts was developed by Behringer *et al.* (Scheme 1, **a**), starting from diphenylether or -amine scaffolds. In a two-step procedure, the corresponding oxidized iodane was isolated and subsequent cyclization of the oxidized intermediate with sulfuric acid gave the desired cyclic iodonium salts.^[6] Modern approaches towards iodoxinium salts based on preexisting iodinated diarylethers have been described by Wen and Huber.^[7-8] Due to the growing interest of these reactive compounds, efficient and reliable procedures for their efficient synthesis are highly desirable.

Our group is interested in the synthesis and reactivity of novel cyclic iodonium salts as well as their use in catalysis. We developed two one-pot procedures for the synthesis of carbon-bridged cyclic iodonium salts.^[9] Based on these recent findings, we now want to report a unique one-pot synthesis of *O*- and *N*-bridged iodonium triflates **1** and **2** by treating substituted phenols and anilines with *in situ* generated arynes (Scheme 1, **b**).

a) Known approaches

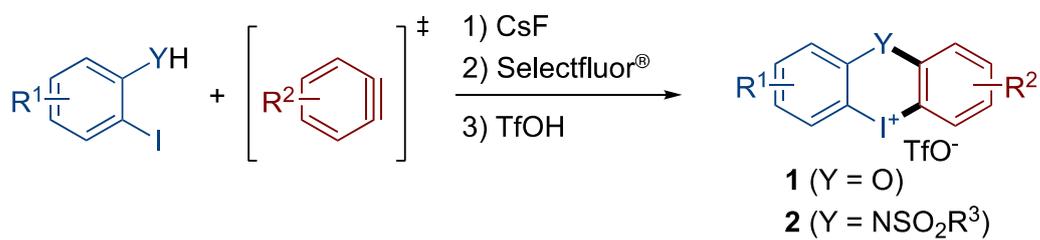


Y = O, NAc; X = HSO₄; R = H, NO₂ (Behringer, 1965)

Y = O; X = HSO₄; R = Me, CO₂Me, NO₂ (Wen, 2016)

Y = O; X = TfO; R = F (Huber, 2021)

b) This work: New one-pot approach



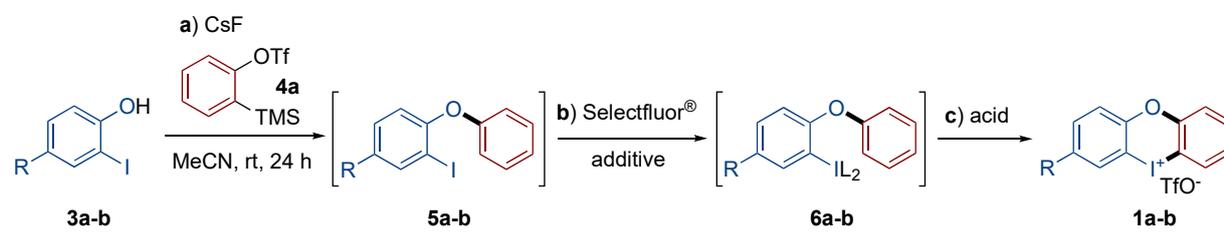
Scheme 1. Synthesis of heteroatom-bridged diaryliodonium salts.

Results and Discussion

To accomplish the proposed one-pot reaction we intended to utilize reactive aryne intermediates as arene electrophiles for achieving a metal-free C(sp²)-O and -N-coupling.^[10]

For the initial aryne-mediated arylation of *o*-iodophenols **3**, preliminary investigations revealed a procedure using CsF in MeCN as the most effective coupling strategy with (trimethylsilyl)aryl triflates **4** as aryne precursors to obtain diphenylether scaffolds **5** (Table 1, **a**).^[11] For the second step of this one-pot reaction, the oxidation (**b**) and cyclization (**c**) sequence with the most prominent oxidants (see Table S1, Supporting Information (SI)) were screened. We were able to establish Selectfluor[®] as the most effective oxidant. It was the only oxidant that resulted in quantitative oxidation of the intermediate **5a** to **6a**. A quantitative transformation was necessary since an incomplete oxidation resulted in the undesired formation of acyclic iodonium salts due to the electron-donating character of diphenylether motifs.

Table 1. Optimization of the One-Pot Procedure with Selectfluor[®] as Oxidant.



entry ^[a]	R	t _b ^[b] / h	acid (eq.)	T _c ^[c] / °C	T _c ^[c] / h	additive	yield of 1 (%) ^[d]
1	H (3a)	24	BF ₃ •OEt ₂ (4.0)	RT	1	-	35 ^[e]
2	H	24	BF ₃ •OEt ₂ (4.0)	0	2	-	42
3	H	24	BF ₃ •OEt ₂ (4.0)	-40	4	-	52
4	H	24	BF ₃ •OEt ₂ (4.0)	-40 – 80	5	AcOH	62
5	H	24	BF₃•OEt₂ (4.0) TfOH (1.5)	-40 – 80	2	AcOH	78
6	H	24	BF ₃ •OEt ₂ (4.0) TfOH (1.5)	0 – 80	2	AcOH	74
7	H	24	TfOH (4.0)	0 – 80	2	AcOH	81
8	Br (3b)	48	BF ₃ •OEt ₂ (4.0)	-40 – 80	5	AcOH	24

9^[f] Br 24+24 TfOH (4.0) 0 – 80 2 AcOH 74

^[a] General reaction conditions: Step a): **3** (0.100 mmol), **4a** (1.5 eq.), CsF (3.0 eq.), MeCN (1.6 mL), rt. Step b): Addition of Selectfluor[®] (4.0 eq.). Step c): Addition of acid. ^[b] Time for oxidation step. ^[c] Temperature and time for cyclization step. ^[d] Purity >97%. ^[e] Purity around 85% to 90%. ^[f] Addition of Selectfluor[®] (2.0 eq.) after 24 h in Step 2.

Using exclusively Selectfluor[®] throughout the following experiments we started further optimizations with *o*-iodophenol (**3a**, R = H, Table 1) as the model substrate. Coupling with the aryne precursor **4a**, subsequent oxidation for 24 h and cyclization with 4.0 equiv. BF₃•OEt₂ at room temperature yielded the desired iodoxinium salt **1a** in 35% yield (entry 1) as the triflate salt. When the cyclization step was performed at 0 °C the yield increased to 42% (entry 2). At -40 °C the desired product was obtained in 52% yield (entry 3). The use of AcOH as additive for the oxidation step resulted in a significantly diminished side product formation, most likely due to the formation of the more stable bisacetoxo I(III) derivate **6a** (L = OAc). This finally resulted in an improved formation of **1a** (62% yield, entry 4). A further significant improvement was achieved through addition of TfOH during the cyclization step which increased the yield of **1a** to 78% (entry 5). Performing the cyclization at 0 °C resulted in a diminished yield (entry 6). Further replacement of BF₃•OEt₂ with TfOH further increased the yield of **1a** to satisfying 81% (entry 7).

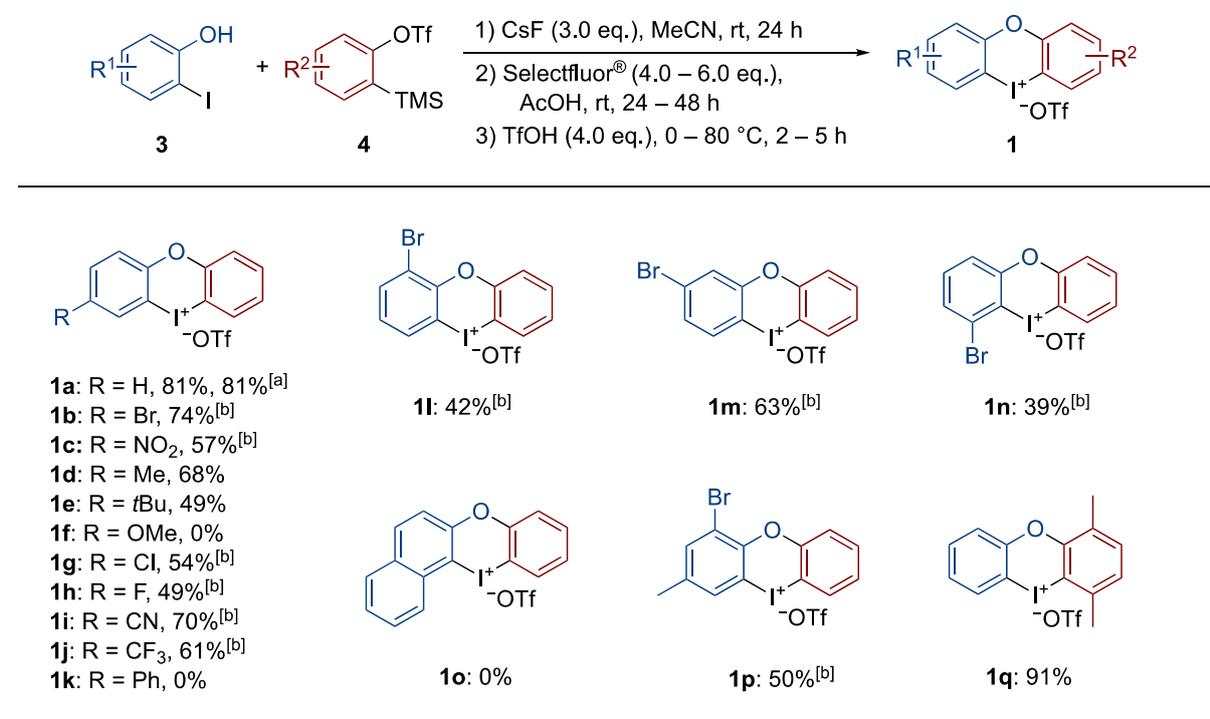
We then explored the addressable substrate scope under these optimized conditions. Performing the reaction on a 5 mmol scale gave **1a** in 81% yield (Scheme 2). With the electron-poor bromo-substituted substrate **3b**, we observed a significant drop in yield (entry 8), possibly due to a diminished stability of the I(III) intermediate. To circumvent this issue, addition of two equivalents of the oxidant after an initial oxidation period was necessary to increase the yield of **1b** to 74% (entry 9). These slightly modified conditions were then consequently applied for all electron poor substrates. The strong electron-poor 4-NO₂ derivate **1c** was isolated in a moderate yield of 57%.

Slightly activated derivates bearing 4-Me- and 4-*t*Bu-substituents **1d** and **1e** were obtained in up to 68% yield. The more electron-rich 4-OMe-substituted derivate gave an inseparable product mixture of **1f** after the cyclization step. The Cl- and F-substituted derivates **1g** and **1h** were yielded under the slightly optimized conditions

for electron-poor derivatives in 54% and 49% yield. CN- and CF₃-Substitutions were viable as well and subsequently **1i** and **1j** were obtained in up to 70% yield. Here, the cyclization step resulted in a decomposition of the oxidized intermediate. A 4-phenyl-substituted derivative **1k** did not react at all. A variation of the substitution pattern was feasible as 2-Br, 3-Br and 5-Br derivatives **1l-n** were isolated in 39% to 63% yield. This indicated that electronic or steric effects from substituents close to the bridge atoms may be relevant in the oxidation step. Also limitations of the method were visible for extended π -systems, as already observed for **1k**, but also for the naphthyl-derivative **1o**.

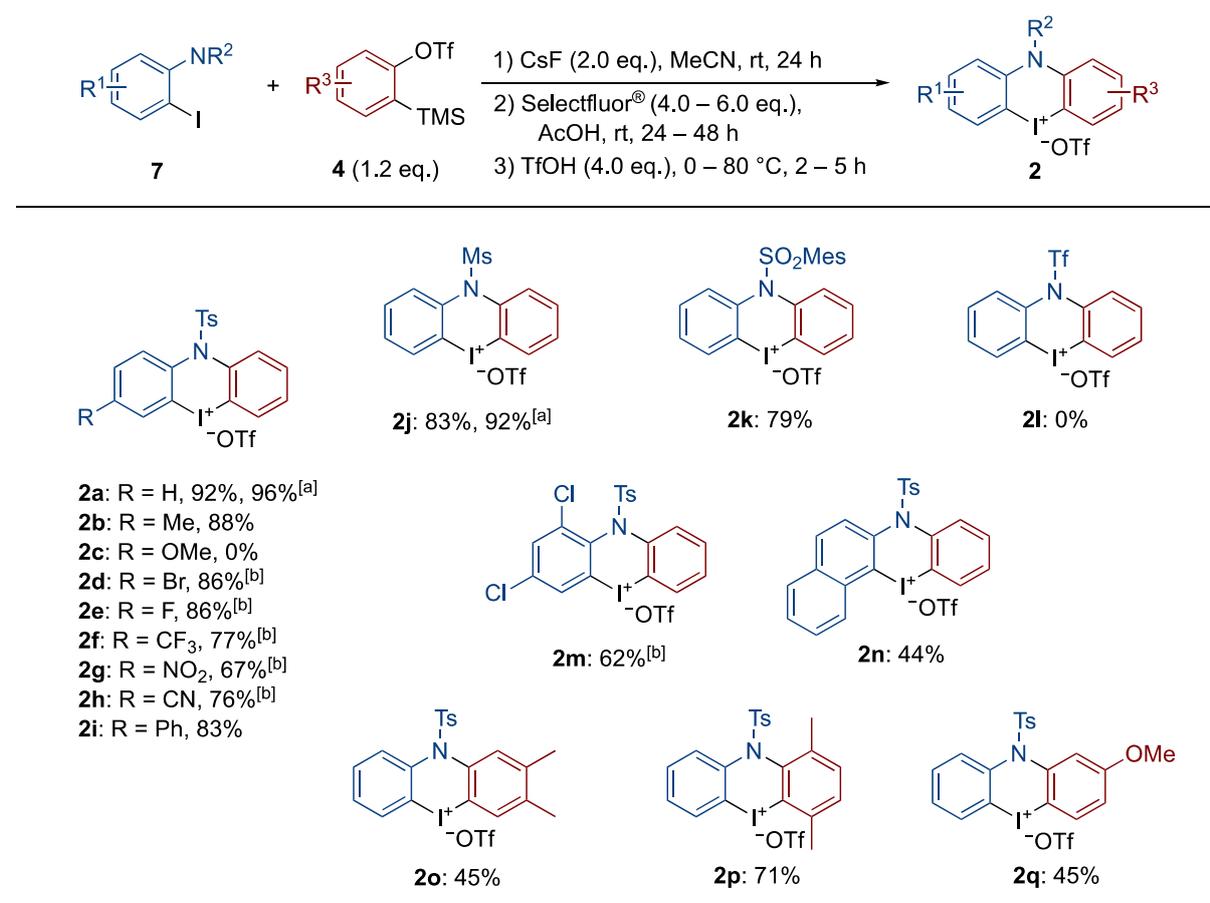
The lowered yield of the 2-Br-4-methyl derivative **1p** (50%) in comparison to **1d** verified the effects of substituents next to the iodacycle. The reaction of **3a** with a dimethyl-substituted (trimethylsilyl)aryl triflate **4b** yielded **1q** in 91%.

Aryne precursors with other substitution patterns or more electron-donating or electron-withdrawing groups were challenging due to an inseparable isomer formation and decomposition in the cyclization step. A complete list of all substrates that could not be successfully synthesized are found in the SI (Figure S2).



Scheme 2. Substrate scope using the optimized conditions of Table 1. General reaction conditions: Step 1: **3** (0.100 mmol), **4** (1.5 eq.), CsF (3.0 eq.), MeCN (1.6 mL), rt. Step 2: Selectfluor[®] (4.0 eq.), AcOH (0.5 mL), rt. Step 3: TfOH (4.0 eq.), 0 – 80 °C. ^[a] Reaction was performed on a 5.00 mmol scale. ^[b] Addition of Selectfluor[®] (2.0 eq.) after 24 h in Step 2.

As we were also interested in the synthesis of *N*-bridged diaryliodonium salts, we additionally investigated *N*-tosylsulfonamide **7a** with **4a** as aryne source under slightly different conditions for the arylation step (Scheme 3). The desired product **2a** was obtained in a high yield of 92% without any further optimizations. Therefore, we started to investigate the scope and the scalability of this reaction. Performing the reaction on a 5 mmol scale gave **2a** in a slightly improved yield of 96%.



Scheme 3. Substrate scope. General reaction conditions: Step 1: **7** (0.100 mmol), **4** (1.2 eq.), CsF (2.0 eq.), MeCN (1.6 mL), rt. Step 2: Selectfluor[®] (4.0 eq.), AcOH (0.5 mL), rt. Step 3: TfOH (4.0 eq.), 0 – 80 °C. ^[a] Reaction was performed on a 5.00 mmol scale. ^[b] Addition of Selectfluor[®] (2.0 eq.) after 24 h in Step 2.

We then investigated a variety of substituents at the aryl moiety of the sulfonamide. While the 4-Me-substituted derivative **2b** could be obtained with a yield of 88%, OMe substitution resulted in a decomposition of **2c** as already observed for the *O*-bridged diaryliodonium triflate **1f**. For deactivated substrates it was again necessary to apply further amounts of oxidant after an initial oxidation time. Under these modified conditions, Br- and F-substituted derivatives **2d** and **2e** were obtained in up to 86% yield.

Electron-poor substrates such as NO₂-, CF₃- and CN-substituted salts **2f-h** were isolated in yields of up to 77%. In comparison to their oxygen analogs, the synthesis of the phenyl-substituted diaryliodonium triflate was successful yielding **2i** in 83%. Using methyl sulfonamide, the product **2j** was obtained in 83% yield on a small scale and 92% yield on a 5.0 mmol scale. Mesityl sulfonamide-substituted triflate **2k** was isolated in 79%. With R² = Tf, a complex mixture was obtained during the cyclization step and **2l** could not be further purified. Substrates with two electron-withdrawing substituents such as bis-Cl-disubstituted diphenylamines were viable for a selective cyclization yielding **2m** in 63% yield. Finally, the naphthalene-substituted diaryliodonium triflate **2n** was isolated in 44% yield.

The modified heteroatom bridge allowed the coupling with different trimethylsilyl(aryl) triflates **4**. The reaction of **7a** with various dimethyl-substituted aryne precursors **4b** and **4c** successfully provided **2o** and **2p** in 71% and 45% yield. The reaction with **4d** yielded the methoxy-substituted triflate **2q** in 45% yield, indicating that a strong electron-donating group may be relevant during the oxidation/cyclization sequence. However, the developed method offers a fast alternative for the syntheses of a broad range of diaryliodonium and -azinium triflates. Although there are still intrinsic issues for the selective synthesis of some diarylether or -amine scaffolds through aryne-mediated arylation, our effective oxidation/cyclization sequence can be used to achieve further heteroatom-bridged derivatives.

Single crystals for the oxygen-bridged iodonium triflates **1a** and **1b** as well as the nitrogen-bridged derivative **2a** to verify their solid-state structures were obtained (Figure 1). All structures show the typical, slightly distorted T-shaped structure which is commonly observed for I(III) derivatives with a C-I-O angle close to 170° and a C-I-C angle close to 90°. An intramolecular interaction of the internal heteroatom to the iodine center could not be identified since the I-O distance is for all structures approximately 0.3 Å higher than to the corresponding external oxygen of the triflate.

Furthermore, it should be emphasized that in case of diaryliodonium triflate **2a** a significant π -coordination of the tosyl arene ring to the I(III) center was observed (3.6 Å).

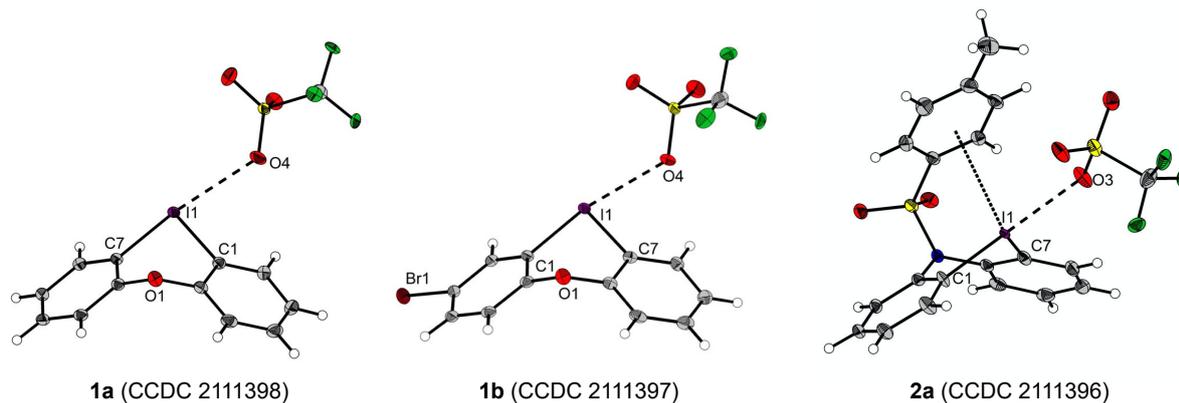
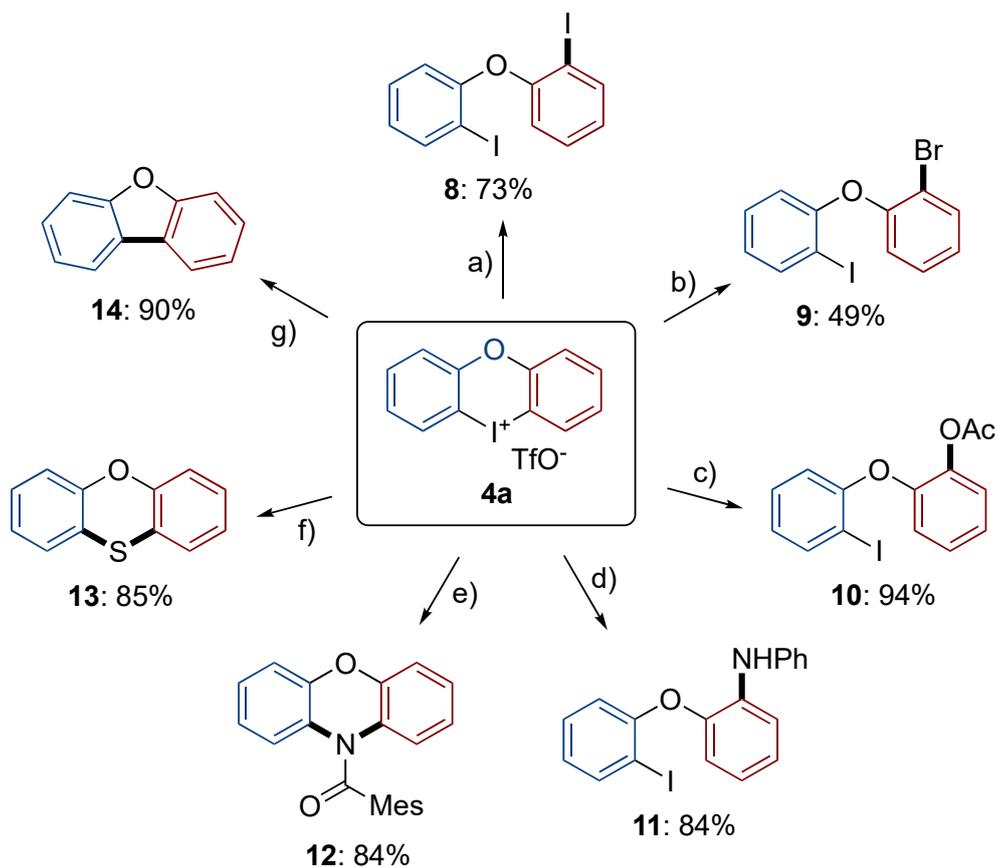


Figure 1. X-Ray structures (ORTEP drawing) for cyclic iodonium triflates **1a**, **1b** and **2a** with thermal ellipsoids displayed with 50% probability. Selected bond length and angles for **1a** (CCDC 2111398): I1-C7: 2.0913 Å, I1-C1: 2.0888 Å, I1-O4 2.8175 Å, I1-O1 3.1016 Å, C1-I1-C7 88.24°, C7-I1-O4 167.051°. Selected bond length and angles for **1b** (CCDC 2111397): I1-C1: 2.0897 Å, I1-C7: 2.0943 Å, I1-O4 2.7370 Å, I1-O1 3.1321 Å, C1-I1-C7 89.11°, C1-I1-O4 170.034°. Selected bond length and angles for **2a** (CCDC 2111396): C1-I1: 2.1204 Å, C7-I1: 2.0992 Å, I1-O3: 2.7316 Å I1-N1 3.1447 Å, I1-Tosyl: 3.6480 Å, C1-I1-C7: 89.73°, C7-I1-O3: 77.497°, C1-I1-O3 165.167°.

To demonstrate the utilization of these novel iodonium salts as reactive synthetic building blocks and to get further insights into their reactivity, a variety of derivatizations were investigated (Scheme 4). Copper-catalyzed ring opening of the diphenyliodonium triflate **1a** with TBAI yielded the desired diiodo derivate **8** in 73% yield.^[12] Counterion exchange^[13] was achieved by treating a hot solution of the triflate derivate with an aqueous solution of KBr. Subsequent thermolysis^[14] of the resulting bromide salt resulted in the formation of **9** in 49% yield. The copper-catalyzed acidic ring opening of **1a** with acetate^[15] yielded the monofunctionalized derivate **10** in 94%. With nitrogen nucleophiles, such as aniline, the ring opening^[16] afforded **11** in 84% yield. A common additional copper-catalyzed ring closure to phenoxazine derivatives could not be conducted under literature known conditions.^[16] Copper-catalyzed treatment with mesitylamide yielded pure phenoxazine **12** in 84%. Additional bifunctionalizations were achieved by a sulfur-iodine exchange^[17] or by a palladium-catalyzed carbon-carbon coupling^[18] to obtain phenoxathiine **13** in 85% yield and dibenzofuran **14** in 90% yield.



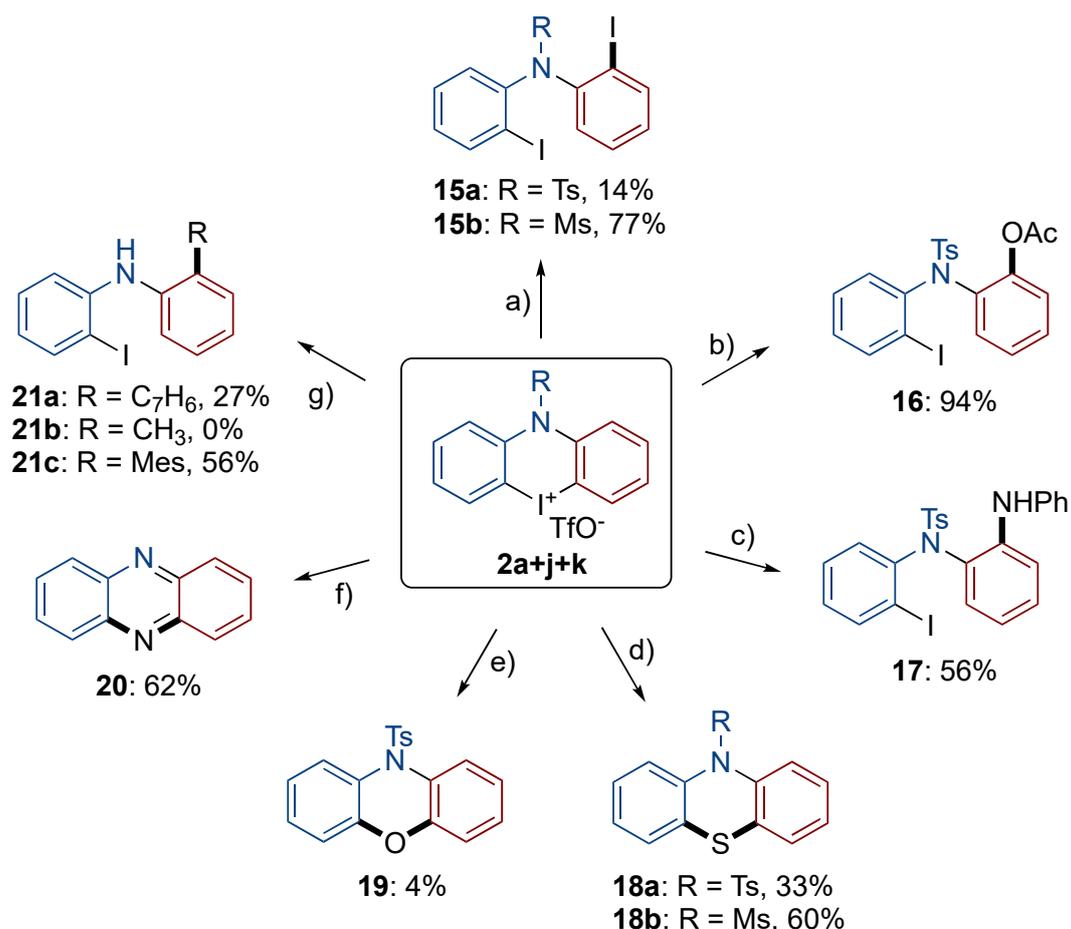
Scheme 4. Representative derivatizations of diaryliodoquinonium triflate **1a**.^a

^a Reaction conditions: a) CuI, DMEDA, TBAI, dioxane, rt – 60 °C, 48 h; b) (i) KBr, H₂O, EtOH, 80 °C, 5 min, (ii) 200 °C, 5 min; c) NaOAc, CuSO₄•5 H₂O, Ac₂O, AcOH, 120 °C, 24 h; d) PhNH₂, Cu(OAc)₂•H₂O, Na₂CO₃, *i*PrOH, 40 °C, 22 h; e) MesCONH₂, CuI, diglyme, K₂CO₃, *p*-xylene, 120 °C, 18 h; f) KSAc, Cu(OTf)₂, DMSO, 100 °C, 24 h; g) Pd/C, NaOAc, DMA, 140 °C, 24 h.

Finally, the novel iodoquinonium triflates were also derivatized with similar procedures (Scheme 5). A copper(I)iodide-mediated ring opening of **2a** yielded the diiododiphenylamine **15a** in a low yield of 14%. A change of the sulfonamide from *N*-tosyl to *N*-mesyl yielded the desired product **15b** in a good yield of 77%. The copper-catalyzed ring opening of **2a** with acetate furnished monofunctionalized **16** in 94% yield. While the yield for the derivatization with aniline significantly dropped compared to the oxygen derivative, the *o*-diphenylamine **17** could still be obtained in 56% yield. An additional ring closure to the phenazine could not be observed due to major decomposition at elevated temperatures. Sulfur-iodine exchange reactions^[19] of **2a** and **2j** afforded the phenothiazines **18a** and **18b** in 33% and 60% yield, respectively. The insertion of oxygen to **2a** only provided traces (4%) of the desired phenoxazine **19**. In contrast, the copper-catalyzed nitrogen functionalization^[20] of **2j** with sodium

azide gave the *N*-deprotected and aromatic phenazine (**20**) in 62% yield through azide induced ring opening followed by rearomatization under loss of the mesylate.

We were also intended to performed a literature-known rearrangement of *N*-sulfonamide-based acyclic iodonium salts.^[21] Here, in case of cyclic diaryliodonium species, the rearrangement product **21a** was obtained in only 27% yield, while the Ms-substituted derivate **21b** could not be observed. To verify the reactivity, the mesityl sulfonamide **2k** gave a significant increase in product formation due to the prevention of side reactions yielding **21c** in 56%.



Scheme 5. Derivatizations of Diaryliodonium Triflates **2a+j+k**.^a

^a Reaction conditions: a) CuI, DMEDA, TBAI, dioxane, rt, 18 h; b) NaOAc, CuSO₄•5 H₂O, Ac₂O, AcOH, 120 °C, 20 h; c) PhNH₂, Cu(OAc)₂•H₂O, Na₂CO₃, *i*PrOH, 40 °C, 24 h; d) S₈, Cs₂CO₃, DMSO, 100 °C, 3 h; e) Cu(OAc)₂•H₂O, ethylene glycol, Na₂CO₃, DMF, H₂O, 100 °C, 48 h; f) CuTc, NaN₃, PPh₃, Cs₂CO₃, H₂O, DMA, 120 °C, 48 h; g) NEt₃, MeCN, 80 °C, 18 h.

Summary

In conclusion, we developed an aryne-based one-pot procedure for the synthesis of iodoxinium and iodazinium triflates. Initiated by an aryne-mediated metal-free O- or N-arylation followed by an oxidative cyclization, a variety of o-iodophenols and sulfonamides were successfully transformed into diaryliodoxinium and diaryliodazinium triflates in high yields. With further derivatizations, a wide range of applications of these mostly unknown iodonium salts was demonstrated. Further derivatizations should be developed for heteroatom-bridged iodonium salts, since they have an altered, albeit interesting reactivity compared to their pure carbon analogs. Deeper investigations towards the reactivity and novel derivatizations using heteroatom-bridged iodonium salts are under current investigation in our laboratories.

Experimental Section

Detailed optimization studies, experimental procedures, analytical data (^1H -, ^{13}C - and ^{19}F -NMR-chemical shifts, IR-bands, melting points) including the corresponding NMR-spectra as well as the X-ray data can be found in the supporting information.

References

1. (a) Caspers, L. D.; Nachtsheim, B. J., Directing-Group-mediated C–H-Alkynylations. *Chem. Asian J.* **2018**, *13* (10), 1231-1247; (b) Charpentier, J.; Früh, N.; Togni, A., Electrophilic Trifluoromethylation by Use of Hypervalent Iodine Reagents. *Chem. Rev.* **2015**, *115* (2), 650-682; (c) Li, Y.; Hari, D. P.; Vita, M. V.; Waser, J., Cyclic Hypervalent Iodine Reagents for Atom-Transfer Reactions: Beyond Trifluoromethylation. *Angew. Chem. Int. Ed. Engl.* **2016**, *55* (14), 4436-54; (d) Yoshimura, A.; Zhdankin, V. V., Advances in Synthetic Applications of Hypervalent Iodine Compounds. *Chem. Rev.* **2016**, *116* (5), 3328-435.
2. (a) Maertens, G.; L'Homme, C.; Canesi, S., Total synthesis of natural products using hypervalent iodine reagents. *Front. Chem.* **2015**, *2* (115); (b) Silva, J. L. F.;

Olofsson, B., Hypervalent iodine reagents in the total synthesis of natural products. *Nat. Prod. Rep.* **2011**, *28* (10), 1722-1754.

3. (a) Abazid, A. H.; Nachtsheim, B. J., A Triazole-Substituted Aryl Iodide with Omnipotent Reactivity in Enantioselective Oxidations. *Angew. Chem. Int. Ed.* **2020**, *59* (4), 1479-1484; (b) Abazid, A. H.; Clamor, N.; Nachtsheim, B. J., An Enantioconvergent Benzylic Hydroxylation Using a Chiral Aryl Iodide in a Dual Activation Mode. *ACS Catalysis* **2020**, *10* (15), 8042-8048; (c) Boelke, A.; Nachtsheim, B. J., Evolution of N-Heterocycle-Substituted Iodoarenes (NHIAs) to Efficient Organocatalysts in Iodine(I/III)-Mediated Oxidative Transformations. *Adv. Synth. Catal.* **2020**, *362* (1), 184-191; (d) Parra, A., Chiral Hypervalent Iodines: Active Players in Asymmetric Synthesis. *Chem. Rev.* **2019**, *119* (24), 12033-12088; (e) Massignan, L.; Tan, X.; Meyer, T. H.; Kuniyil, R.; Messinis, A. M.; Ackermann, L., C-H Oxygenation Reactions Enabled by Dual Catalysis with Electrogenerated Hypervalent Iodine Species and Ruthenium Complexes. *Angew. Chem. Int. Ed.* **2020**, *59* (8), 3184-3189; (f) Vaillant, F. L.; Waser, J., Decarboxylative Alkynylation and Cyanation of Carboxylic Acids using Photoredox Catalysis and Hypervalent Iodine Reagents. *Chimia* **2017**, *71* (4), 226-230; (g) Mukherjee, S.; Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Glorius, F., Alkynylation of C(O)-H Bonds Enabled by Photoredox-Mediated Hydrogen-Atom Transfer. *Angew. Chem. Int. Ed.* **2017**, *56* (46), 14723-14726; (h) Baralle, A.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C., Aryl Radical Formation by Copper(I) Photocatalyzed Reduction of Diaryliodonium Salts: NMR Evidence for a Cull/Cul Mechanism. *Chem. Eur. J.* **2013**, *19* (33), 10809-10813; (i) Heinen, F.; Engelage, E.; Dreger, A.; Weiss, R.; Huber, S. M., Iodine(III) Derivatives as Halogen Bonding Organocatalysts. *Angew. Chem. Int. Ed.* **2018**, *57* (14), 3830-3833.

4. (a) Merritt, E. A.; Olofsson, B., Diaryliodonium salts: a journey from obscurity to fame. *Angew. Chem. Int. Ed.* **2009**, *48* (48), 9052-70; (b) Novák, Z.; Aradi, K.; Tóth, B.; Tolnai, G., Diaryliodonium Salts in Organic Syntheses: A Useful Compound Class for Novel Arylation Strategies. *Synlett* **2016**, *27* (10), 1456-1485.

5. (a) Chatterjee, N.; Goswami, A., Synthesis and Application of Cyclic Diaryliodonium Salts: A Platform for Bifunctionalization in a Single Step. *Eur. J. Org. Chem.* **2017**, *2017* (21), 3023-3032; (b) Grushin, V. V., Cyclic diaryliodonium ions: old mysteries solved and new applications envisaged. *Chem. Soc. Rev.* **2000**, *29* (5), 315-324.

6. Beringer, F. M.; Kravetz, L.; Topliss, G. B., Iodonium Salts Containing Heterocyclic Iodine¹⁻³. *J. Org. Chem.* **1965**, *30* (4), 1141-1148.
7. Luo, B.; Cui, Q.; Luo, H.; Hu, Y.; Huang, P.; Wen, S., N-Benzyldithiocarbamate Salts as Sulfur Sources to Access Tricyclic Thioheterocycles Mediated by Copper Species. *Adv. Synth. Catal.* **2016**, *358* (17), 2733-2738.
8. Reinhard, D. L.; Heinen, F.; Stoesser, J.; Engelage, E.; Huber, S. M., Tuning the Halogen Bonding Strength of Cyclic Diaryliodonium Salts. *Helv. Chim. Acta* **2021**, *104* (2), e2000221.
9. Caspers, L. D.; Spils, J.; Damrath, M.; Lork, E.; Nachtsheim, B. J., One-Pot Synthesis and Conformational Analysis of Six-Membered Cyclic Iodonium Salts. *J. Org. Chem.* **2020**, *85* (14), 9161-9178.
10. (a) Shi, J.; Li, L.; Li, Y., o-Silylaryl Triflates: A Journey of Kobayashi Aryne Precursors. *Chemical Reviews* **2021**, *121* (7), 3892-4044; (b) Sanz, R., RECENT APPLICATIONS OF ARYNE CHEMISTRY TO ORGANIC SYNTHESIS. A REVIEW. *Org. Prep. Proced. Int.* **2008**, *40* (3), 215-291; (c) Wenk, H. H.; Winkler, M.; Sander, W., One Century of Aryne Chemistry. *Angew. Chem. Int. Ed.* **2003**, *42* (5), 502-528.
11. Liu, Z.; Larock, R. C., Facile N-Arylation of Amines and Sulfonamides and O-Arylation of Phenols and Arenecarboxylic Acids. *J. Org. Chem.* **2006**, *71* (8), 3198-3209.
12. Wu, B.; Yoshikai, N., Conversion of 2-Iodobiaryls into 2,2'-Diiodobiaryls via Oxidation-Iodination Sequences: A Versatile Route to Ladder-Type Heterofluorenes. *Angew. Chem. Int. Ed.* **2015**, *127* (30), 8860-8863.
13. Karele, B. Y.; Kalnin, S. V.; Grinberga, I. P.; Neiland, O. Y., Iodonium derivatives of heterocyclic compounds. *Chem. Heterocycl. Compd.* **1973**, *9* (2), 226-229.
14. Tolstaya, T. P.; Egorova, L. D.; Lisichkina, I. N., Oxidative cyclization of halobenzophenone oximes to 4,2'-iodonia-3-phenyl-1,2-benzisoxazole salts. *Chem. Heterocycl. Compd.* **1985**, *21* (4), 392-396.
15. Hu, Z.; Tang, Y.; Yu, B., Glycosylation with 3,5-Dimethyl-4-(2'-phenylethynylphenyl)phenyl (EPP) Glycosides via a Dearomative Activation Mechanism. *J. Am. Chem. Soc.* **2019**, *141* (12), 4806-4810.
16. Zhu, D.; Liu, Q.; Luo, B.; Chen, M.; Pi, R.; Huang, P.; Wen, S., Synthesis of Carbazoles via One-Pot Copper-Catalyzed Amine Insertion into Cyclic

Diphenyleneiodoniums as a Strategy to Generate a Drug-Like Chemical Library. *Adv. Synth. Catal.* **2013**, 355 (11-12), 2172-2178.

17. Shimizu, M.; Ogawa, M.; Tamagawa, T.; Shigitani, R.; Nakatani, M.; Nakano, Y., Copper-Catalyzed Double S-Arylation of Potassium Thioacetate with Dibenziodolium Triflates: Facile Synthesis of Unsymmetrical Dibenzothiophenes. *Eur. J. Org. Chem.* **2016**, 2016 (16), 2785-2788.

18. Panda, N.; Mattan, I.; Nayak, D. K., Synthesis of Dibenzofurans via C–H Activation of o-Iodo Diaryl Ethers. *J. Org. Chem.* **2015**, 80 (13), 6590-6597.

19. Wang, M.; Fan, Q.; Jiang, X., Transition-Metal-Free Diarylannulated Sulfide and Selenide Construction via Radical/Anion-Mediated Sulfur-Iodine and Selenium-Iodine Exchange. *Org. Lett.* **2016**, 18 (21), 5756-5759.

20. Wang, M.; Fan, Q.; Jiang, X., Nitrogen-Iodine Exchange of Diaryliodonium Salts: Access to Acridine and Carbazole. *Org. Lett.* **2018**, 20 (1), 216-219.

21. Chen, H.; Wang, L.; Han, J., Aryl radical-induced desulfonylative ipso-substitution of diaryliodonium salts: an efficient route to sterically hindered biaryl amines. *Chem. Commun.* **2020**, 56 (42), 5697-5700.