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Preparation and Synthetic Applicability of Imidazole-Containing Cyclic Iodonium Salts

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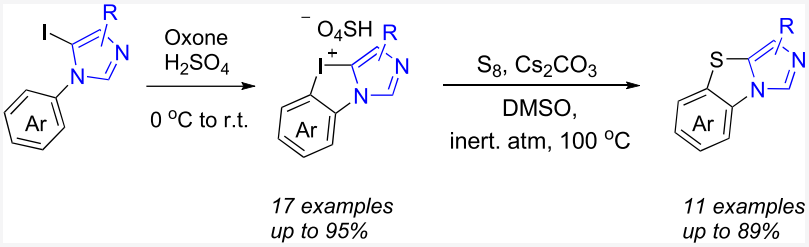

ABSTRACT: A novel approach to the preparation of imidazole-substituted cyclic iodonium salts has been developed via the oxidative cyclization of 1-phenyl-5-iodoimidazole using a cheap and available Oxone/H_2SO_4 oxidative system. The structure of the new polycyclic heteroarenes has been confirmed by single-crystal X-ray diffractometry, revealing the characteristic structure features for cyclic iodonium salts. The newly produced imidazole-flanked cyclic iodonium compounds were found to readily engage in a heterocyclization reaction with elemental sulfur, affording benzo[5,1-*b*]imidazothiazoles in good yields.

INTRODUCTION

Currently, the chemistry of hypervalent compounds has proven to be one of the fast-growing fields of organic chemistry.[1] Indeed, the λ^3-iodanes have found widespread applications in a variety of organic transformations, most commonly as oxidants[1,2] and group-transfer reagents.[3] Among these, one of the most applicable classes of iodine(III) derivatives are the so-called diaryliodonium salts, whose structure bears two carbon-centered aryl ligands bound to a central iodine atom. This latter compound class is often used as a convenient type of electrophilic synthons.[4]

In the last 10 years, there has been a particular resurgence of interest in cyclic iodonium salts (CIS), which are characterized by the presence of two electrophilic carbon centers in a rigid, normally tricyclic structure (Figure 1).[5] This structure and the unique reactivity of such substances have allowed for their direct transformation into various carbo- and heterocycles via innovative synthetic sequences. Thus, very recently, a range of useful synthetic methods have been developed including the transformation of CIS into sulfur- and nitrogen-containing heterocycles,[6] carbocyclization,[7] as well as processes for the selective ring-opening via the C−I bond cleavage, including an interesting enantioselective variant.[8] In fact, such hetero- and carbocyclizations processes are gaining prominence as powerful tools for accessing fused cyclic building blocks. In addition, a very recent development in this area involves the ability of cyclic iodonium salts also to act as a new class of halogen-bonding catalysts.[9]

Despite the promising synthetic applicability of CISs, their potentially wider usage is still contingent upon the chemical community resolving a series of issues and challenges. For example, the evaluation of the structure and properties of such cyclic salts has been centered on the simpler carbocyclic scaffold ***A***,[5] with its heterocycle-flanked congeners still relatively unexplored. The first examples of pyridine and quinolone substituted iodonium salts ***B*** (Figure 1, a) were reported by the Detert laboratory.[10] Shortly after, Wen and co-workers prepared a wide range of heterocyclic CISs containing chromone and thiochromone moieties ***C*** (Figure 1, a) and explored their synthetic potential as entry points to polycyclic cores.[6a,11] Indeed, the oxidation of iodoarenes bearing six-membered heterocyclic moieties appears to proceed more readily than that of those bearing five-membered electron-rich heterocycles. For this reason, the CISs based on thiophene and furan have been implemented as their benzo-conjugated derivatives ***D*** (Figure 1, a).[6f,g,12] Only a few examples exist of CIS' embedding five-membered electron-rich heterocycles, probably as a result of non-straightforward methods for the preparation of the necessary precursors, and the sensitivity of such heterocyclic

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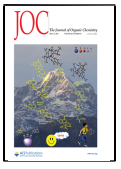

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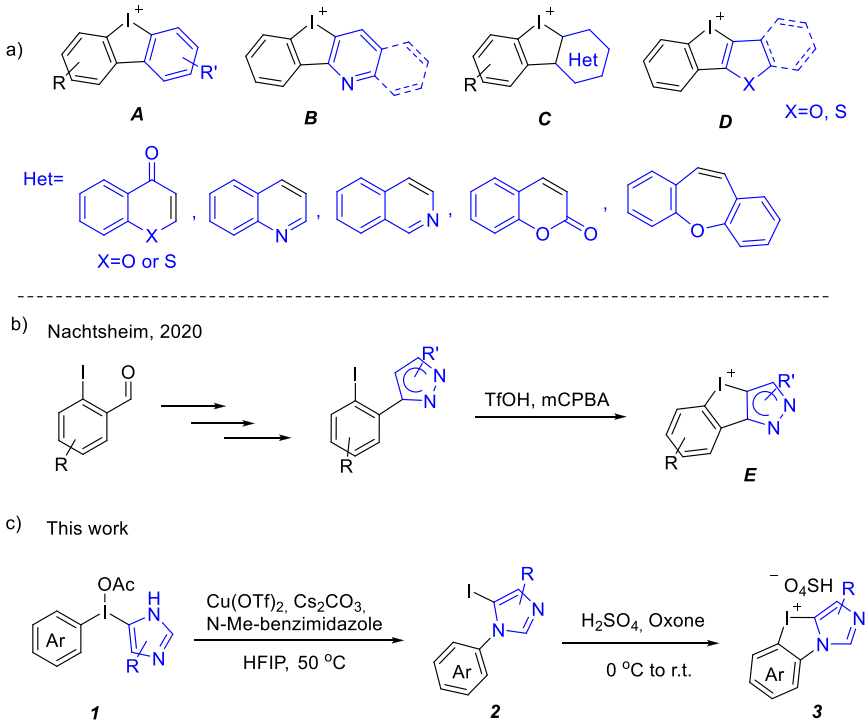


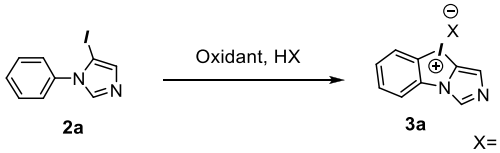
Figure 1. Examples of known cyclic iodonium salts.

cores to the conditions commonly employed in C-I oxidation.[12,13] Only recently, the Nachtsheim group developed a facile approach to the preparation of iodine-containing heterocycles flanked by a pyrazole moieties ***E*** (Figure 1, b).[14] In this context, we recently proposed a novel method for the synthesis of 1-aryl-5-iodoimidazoles, which may be construed as a promising substrate class for the formation of heterocycle-flanked cyclic iodonium salts. In order to explore the synthetic potential of such reagents, in this contribution, we have developed a method for the preparation of cyclic iodonium salts containing the imidazolyl moiety. We also go on to showcase the synthetic applicability of such salts in the synthesis of conjugated thienoimidazoles.

RESULTS AND DISCUSSION

As mentioned above, we envisioned accessing the imidazole-flanked cyclic iodonium salt family **3** via a two-step sequence involving an initial evolution of the iodonium salt **1** via Cu-catalyzed internal *N*-arylation, followed by an oxidative cyclization of the resulting 5-iodo-*N*-aryl imidazole **2** (Figure 1, c). Given that the initial Cu-catalyzed aryl transfer step had been studied in our prior study, we initially focused on identifying conditions for efficient oxidation of the iodine atom in the model 1-phenyl-5-iodoimidazole **2a** (Table 1). The early experiments revealed that the facile protonation of the ring nitrogen atoms under the acidic conditions, commonly employed in organo-iodine oxidation processes, strongly influenced the reactivity of **2**. Indeed, the previously reported methods involving *m*-CPBA as oxidant in the presence of strong acids did not result in the formation of desired hypervalent iodine species (entries 1−3, Table 1).[10,15] Thus, in the case of *p*-toluenesulfonic or trifluoromethanesulfonic acid, only the corresponding protonated imidazolium salts were obtained, even at elevated temperature[14] (entries 1−3). This result highlights the challenge of achieving the oxidative cyclization in this system, given that the protonation of the imidazole nitrogen is expected to deactivate the iodine toward oxidation. With that in mind, we tested the oxidative systems based on weaker acids, such as AcOH in the presence of *m*-CPBA, $NaBO_3$, $NaIO_4$ as well as bleach (entries 4−7). Unfortunately, we did not observe the formation of desired iodonium salt **3a**.

Table 1. Optimization of the Conditions



entry	oxidant	additive/medium	temp	time [h]	yield [%]
1	*m*CPBA	*p*-TsOH, TFE	r.t.	24	0[a]
2	*m*CPBA	TfOH, TFE	r.t.	24	0[a]
3	*m*CPBA	TfOH, DCE	50 °C	65	0[a]
4	*m*CPBA	AcOH	r.t.	24	0
5	Bleach	AcOH	r.t.	24	0
6	$NaIO_4$	NaOAc, Ac_2O, AcOH	125 °C	2	0[b]
7	$NaBO_3$	AcOH	50 °C	24	0
8	Oxone	H_2SO_4	0 °C to r.t.	2	50[c,d]
9	Oxone	H_2SO_4	0 °C to r.t.	2	84[d,e]

[a]Protonated **2a** was isolated. [b]Deiodination process occurred. [c]Isolation by precipitation with water, product was isolated as $^-HSO_4$ salt. [d]Reaction conditions:1-phenyl-5-iodoimidazole **2a** (0.5 mmol), Oxone (0.325 mmol) in H_2SO_4 (0.8 mL) from 0 °C to r.t. over 2 h. [e]Isolation by precipitation with 9 M NaOH solution.

These poor initial results led us to consider persulfate-based oxidant systems, in particular, the well-behaved Oxone reagent. Indeed, the Oxone/H_2SO_4 combination is known to be efficient in the preparation of cyclic or noncyclic iodonium salts.[16] In our case, an addition of the finely ground Oxone (i.e., the triple salt $KHSO_5{\cdot}0.5KHSO_4{\cdot}0.5K_2SO_4$) to the solution of the iodoimi-

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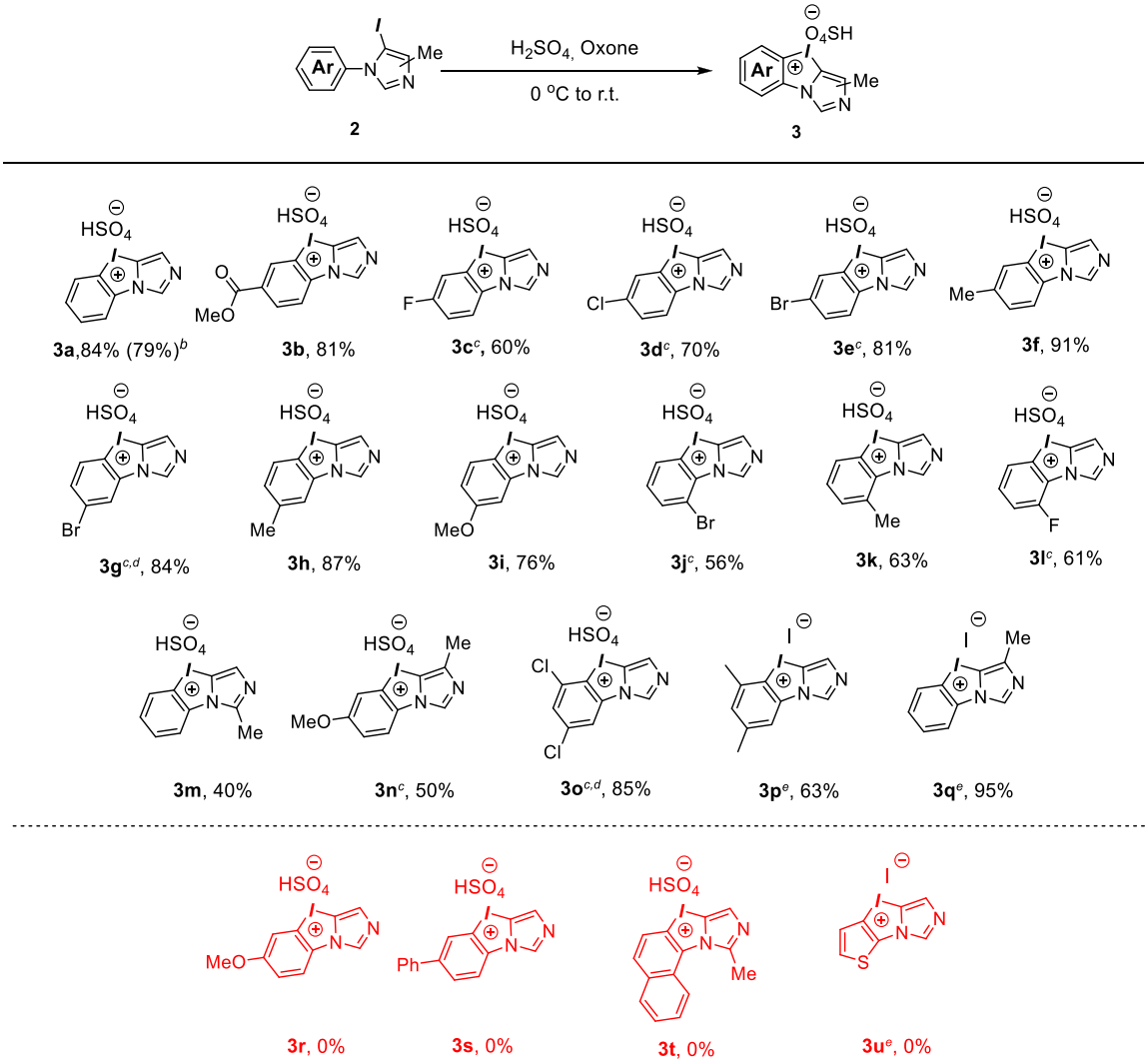
Scheme 1. Synthesis of Benzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium Derivatives 3a−3q[a]



[a]Reaction conditions: 1-aryl-5-iodoimidazole **2** (0.5 mmol), Oxone (0.325 mmol) in H_2SO_4 (0.8 mL) from 0 °C to r.t. [b]Yield for 2 mmol scale. [c]Increased amount of Oxone. [d]Amount of reagents was scaled down (see Experimental Section). [e]Isolation by addition of KI.

dazole **2a** in H_2SO_4 under vigorous stirring led to the full consumption of starting material after 2 h. A subsequent addition of water led to the precipitation of the desired product **3a** in 50% yield as a hydrogen sulfate salt. Suspecting incomplete product precipitation due to a partial solubility of iodonium hydrogen sulfates in water, we repeated the experiment with the addition of Na_2CO_3 at the isolation stage. This modification led to the isolation of the corresponding hydroxide form in 89% yield. Unfortunately, the extremely low solubility of this −OH species did not allow us to use common NMR spectroscopy for its structural characterization. Through a final round of optimization, the target **3a**-HSO_4 was isolated in 84% via the addition of a 9 M solution of NaOH so as to reach a pH value of 4−5. This form of the product is now readily soluble in DMSO and, to a lesser extent, in water and MeOH, and was used as a substrate for the further transformations.

With the optimal conditions in hand, we sought to demonstrate the synthetic applicability of this approach in a broader range of 1-aryl-5-iodoimidazoles (Scheme 1). As mentioned earlier, a series of substituted 1-aryl-5-iodoimidazoles have been prepared previously via a Cu-catalyzed intramolecular *N*-arylation,[17] with the method representing a straightforward method for accessing N-substituted imidazoles bearing iodine in the 5-position. In the context of the current study, the oxidation of 1-aryl-5-iodoimidazoles containing electron-donating groups on the aromatic ring, via the previously optimized procedure, proceeded smoothly to give corresponding iodonium salts **3f**, **3h**, and **3i** in high yields. Under these conditions, halogen-substituted precursors (**2c**−**2e**, **2g**, **2j**, **2l**, **2o**) also underwent the oxidative cyclization. For the latter substrate class, the initial runs led to the desired iodonium salts being obtained in somewhat lower yields due to incomplete conversion of starting material. Nevertheless, the addition of a second portion of Oxone and sulfuric acid led to the full consumption of starting iodide **2** with the formation of target products with meaningful yields (see products **3c**−**3e**, **3g**, **3j**, **3l**, **3o**). The oxidation of the C-I unit was found to be sensitive to the steric hindrance at both the imidazole and the *N*-aryl rings. Thus, the 1-aryl-5-iodoimidazoles **2j**−**2l** containing a substituent in the *o*-position of the phenyl ring gave an ∼60% yield of the target iodonium salts **3j**−**3l** independently of the electronic effects. It should be noted that, although two isomeric products are possible for the *meta*-substituted *N*-aryl precursors **2g**−**2i**, the process provided for a selective formation of species

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3g−**3i** with the new C-I *para* to the *N*-Ar substituent group, with the NMR of the crude reaction mixture revealing less than 2% of the isomer. This selectivity is likely governed by steric factors and is also in line with the Electrophilic Aromatic Substitution preferences (S_EAr) of the iodination step. It will be interesting to establish whether this lower efficiency stems from the steric hindrance of the 2-Me substituent hindering attainment of the necessary co-planarity en route the final cyclic structure. Indeed, application of a strong oxidative system did not allow for the preparation of the cyclic iodonium salts from 1-aryl-5-iodoimidazoles containing electron-rich *N*-(hetero)aryl substituents, such as the naphthyl, the 4-methoxyphenyl, or the 2-thienyl group. In all such cases, a complete consumption of starting material was accompanied by the formation of a rather intractable mixture, likely the result of an over-oxidation.

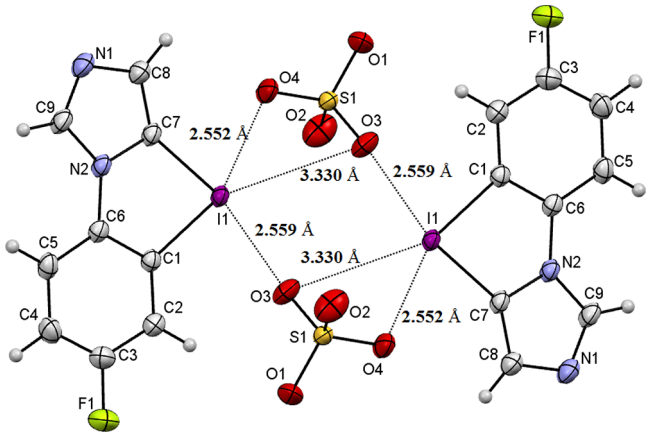

Figure 2. X-ray crystal structure of **3c** showing the dimeric nature of the cyclic iodonium salt. Selective distances and angles: C1−I1 = 2.122(2) Å, C7−I1 = 2.077(2) Å, C1−C6 = 1.394(2) Å, C6−N2 = 1.408(3) Å, C7−N2 = 1.388(2) Å, ∠C1−I1−C7 = 80.25(8)°, ∠I1−C7−C8−H8 = −5.0°. The molecular structure is represented by thermal vibration ellipsoids of 50% probability.

In some cases, the solubility of the final $^{-}HSO_4$ iodonium salts was a critical factor in their isolation and characterization. For instance, the iodonium species **3q** had to be isolated as its iodide salt due to the high solubility of the corresponding hydrogen sulfate form in water. In contrast, for product **3p**, the hydrogen sulfate form had a very low solubility in DMSO and other common solvents, to the point of making its characterization by NMR a challenge.

Crystals suitable for X-ray study were grown from the water solution of salts **3c** and **3j** in their sulfate form via slow evaporation. The **3c** was found to crystallize in a dimeric structural motif formed by short contacts between the hypervalent iodine centers and the and oxygen atoms of the sulfate anions (I1−O3 (2.559 and 3.330 Å)) (Figure 2). Additionally, the iodine atoms form close contacts with neighboring O4 atoms of sulfates (I1−O4 (2.552 Å)), which can be considered as yet another example of bifurcated two-centered halogen bonds.[18] The first coordination sphere of hypervalent iodine centers in **3c** is close to square planar geometry, as attested to by the CCOO torsion angle, i.e., O(3)−O(4)−C(1)−C(7), of 4.35°. Generally, the crystal structure of **3c** is in a good agreement with those published previously, such as carbocyclic iodonium salts.[16a,18,19]

The iodonium salt **3j** formed a more complicated structural motif due to the incorporation of water (Figure 3) and the appearance of additional π-stacking interactions between the aryl and the heteroaryl rings, with the distance between centroids Cg2 (imidazole ring) and Cg1 (benzene ring) of 3.550 Å. Thus, the iodonium cations formed the infinite chains connected by sulfate anions via short contacts of iodine atoms and oxygen atoms (I1−O3 (2.668 Å); I1−O2 (3.314 Å); I2−O4 (2.557 Å)). Surprisingly, for the iodine I1, we observed a contact with water molecule (2.95 Å), which replaces the interaction

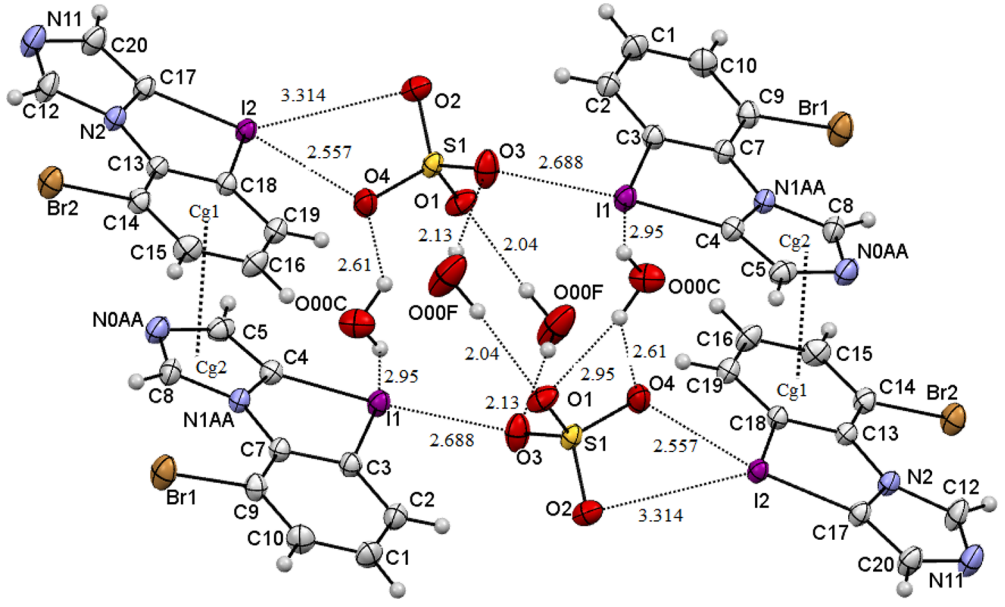

Figure 3. Crystal structure of **3j** showing the dimeric nature of the cyclic iodonium salt. Selective distances and angles: I1−C3 = 2.105(2) Å, I1−C4 = 2.058(2) Å, C3−C7 = 1.400(3) Å, C4−N1AA = 1.389(3) Å, C7−N1AA = 1.418(3) Å, ∠C3−I1−C4 = 80.23(8)°, ∠I1−C4 −C5−H5 = 4.5°, I2−C17 = 2.078(2) Å, I2−C18 = 2.118(2) Å. Inter-stacking interactions between iodonium salts: distance between centroids Cg1−Cg2 = 3.550 Å. The molecular structure is represented by thermal vibration ellipsoids of 50% probability.

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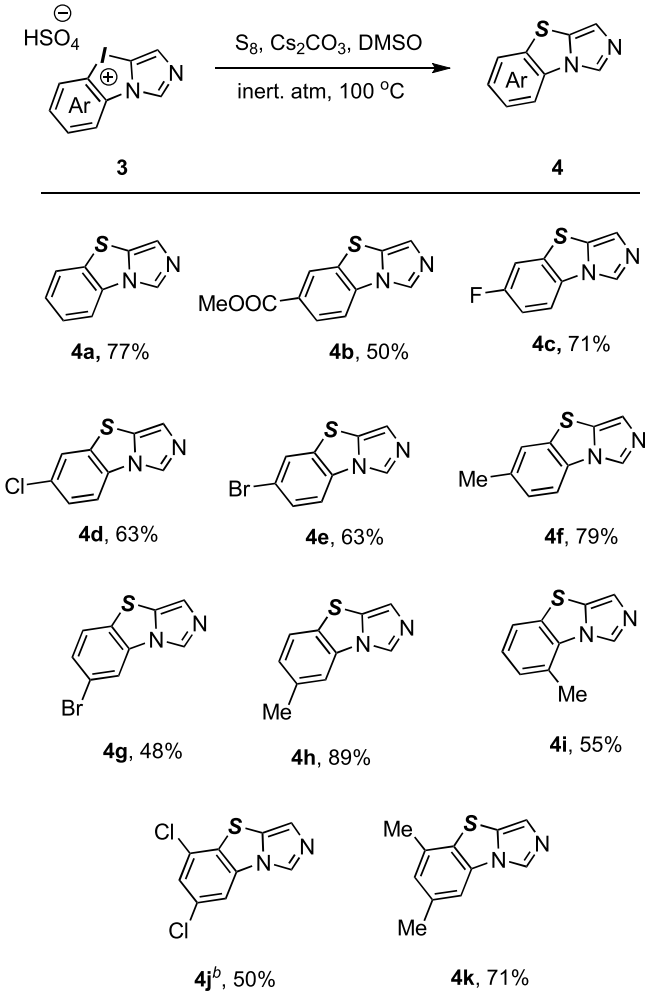
with the sulfate anion observed for **3c**. The other water molecules formed the hydrogen bonds with sulfate anions (2.04 and 2.13 Å).

In the next step, we sought to demonstrate the synthetic applicability of newly formed iodonium salts in a heterocycle-forming process, specifically through the use of elemental sulfur under basic conditions.[12] Such heterocyclizations ought to provide a novel method for the synthesis of benzo[5,1-*b*]imidazothiazoles (Scheme 2), which have wide application in drug and materials design.[20] The approach, we envisioned, would circumvent the use of metal-based catalysts[20,21] and appears to open an interesting path toward heteroatom-doped polycyclic aromatics.

Scheme 2. Synthesis of Benzo[5,1-*b*]imidazothiazoles 4a–4k[a]



[a]Reaction conditions: iodonium salt **3** (0,25 mmol), S_8 (0,125 mmol), Cs_2CO_3 (1 mmol) in DMSO (2.5 mL) at 100 °C for 4 h. [b]Amount of reagents was scaled down (see Experimental Section).

The reaction was tested under the previously published conditions, which involve a DMSO medium and using elemental sulfur as a radical source in the presence of Cs_2CO_3.[12] Heating of the reaction mixture led to the formation of a blue solution, consistent with the formation of a trisulfide radical.[12] The full conversion of starting materials was achieved after 4 h, and with the analysis of the reaction mixture confirming the formation of the target poly-aromatic heterocyclic core **4**. In general, the yield of the target product **4** did not show a clear dependence on the electronic nature of the *N*-aryl moiety. A slight decrease in yield was observed for the *ortho*-substituted iodonium salts, presumably due to steric hindrance.

Surprisingly, the iodonium salts **3m**, **3n**, **3q** bearing a substituent on the imidazolyl moiety were reluctant to undergo the heterocyclization under such conditions, with only the reduction products, i.e., the corresponding 1-aryl-5-iodoimidazoles, isolated from such attempts. A related behavior was also observed for salts **3j** and **3l**. For these, the desired benzo[5,1-*b*]imidazothiazoles were indeed detected by GC–MS chromatography, but the presence of the reduced iodonium salts impurities hampered their isolation in a pure form.

CONCLUSION

In conclusion, we have described a method for the preparation of a novel series of heterocycle-fused benzo[*d*]imidazo[5,1-*b*]-[1,3]iodazol-4-ium salts. The synthetic procedure includes the oxidation of 1-aryl-5-iodoimidazoles by a cheap and readily available Oxone in sulfuric acid medium, followed by a straightforward precipitation of the desired compounds by NaOH. The crystal structures of two representative compounds, in their sulfate form, revealed the typical dimeric structure for cyclic iodonium cations coordinated by two sulfate anions. The newly formed cyclic iodonium salts were well-suited as a platform core for a subsequent heterocyclization with elemental sulfur, with the formation of benzo[5,1-*b*]imidazothiazoles taking place with with good to high yields. We believe that this study, in addition to expanding our understanding of the formation and reactivity of heterocycle-containing cyclic iodonium species, also opens the door to further methods development, especially in the utilization of λ^3-iodane for the synthesis of heteroatom-doped polyarenes. This work also serves as an illustration of how the recently developed iodine-retentive coupling manifolds enabled by hypervalent iodine serve as a versatile platform for downstream complexity buildup.

EXPERIMENTAL SECTION

General Comments. All reagents and solvents were from commercial sources and used without further purification from freshly opened containers. Anhydrous DMSO was supplied by Sigma-Aldrich and used without additional purification. ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz, and ^{19}F NMR spectra were recorded at 376 MHz. Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the residual solvent signal. High resolution mass spectra were recorded on a maXis spectrometer and MicroTOF-Q, both from Bruker Daltronics with electrospray ionization (ESI) in positive mode and an Agilent 7200 Accurate Mass Q-TOF GC/MS with electron impact ionization (EI). X-ray data were collected on a BRUKER D8 VENTURE PHOTON 100 CMOS diffractometer with Mo Kα radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved and refined by direct methods using the SHELX.[22] Data were corrected for absorption effects using the multiscan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELX.[22] The coordinates of the hydrogen atoms were calculated by mixed methods. Crystal data and experimental details are given in the Supporting Information (Table S1). Supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk (2058419 and 2058420). All starting materials (diaryliodonium salt and 1-aryl-5-iodoimidazoles) were prepared according to slightly modified published procedures.[17,23]

Synthesis of Aryl Imidazolium Iodoacetates 1a–1q. Diaryliodonium salts **1a–1n**, **1p**, **1q** were prepared according to a slightly

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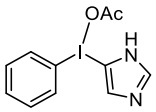
modified published procedure.[17] *All reactions were conducted in an argon atmosphere.*

General Procedure A (Described for 5 mmol Scale). A reaction vessel was charged with $NaIO_4$ (1.05 equiv, 5.25 mmol, 1.12 g), NaOAc (2.2 equiv, 11 mmol, 0.902 g), and aryl iodide (for solid substrates). The flask was evacuated and backfilled with argon (repeated 3 times). Then a mixture of AcOH (7.5 mL) and Ac_2O (0.75 mL) (and aryl iodide if it is a liquid) was added through a reflux condenser. The mixture was stirred at 115−125 °C on the oil bath for 4 h. It should be noted that the full conversion of starting material was not achieved and prolongation of reaction time did not lead to the better yield. After 4 h, the reaction mass was cooled to room temperature, 30 mL of water was added, and the aqueous layer was extracted with DCM 4 × 30 mL. The combined organic layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The oily residue was re-suspended in appropriate solvent (5 mL) and imidazole was added (10 mmol). The reaction mixture was stirred for 16−17 h at room temperature in air. Then, the solvent was evaporated under reduced pressure and the target product was isolated by precipitation with a MeCN/Et_2O mixture. The solid was filtered and washed with MeCN (2 mL) and Et_2O (3 × 10 mL).

General Procedure B (Described for 5 mmol Scale). A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with $NaIO_4$ (1.05 equiv, 5.25 mmol, 1.12 g), NaOAc (2.2 equiv, 11 mmol, 0.902 g), and aryl iodide (for solid substrates). The flask was evacuated and backfilled with argon (repeated 3 times). Then a mixture of AcOH (7.5 mL) and Ac_2O (0.75 mL) (and aryl iodide if it is a liquid) was added through a reflux condenser. This mixture was allowed to stir at 115−125 °C on the oil bath for 4 h. Usually full conversion of starting material was not achieved. After 4 h, the reaction was cooled to room temperature, 30 mL of water was added, and the aqueous layer was extracted with DCM 4 × 30 mL. The combined organic layer was dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. Pentane was added to the residue, and the precipitate was filtered and washed several times with pentane. Then solvent as indicated has been added to the obtained solid, and the suspension was allowed to stir for 5−10 min. Imidazole was added (neat, 2 equiv), and the mixture was allowed to stir for 16−17 h at room temperature in the air. Then the solvent was evaporated under reduced pressure and MeCN was added. The mixture was allowed to stir until a precipitate appeared and 1−2 h after that. The solid was filtered and washed with MeCN (2 mL) and Et_2O (3 × 10 mL) to obtain the desired product.

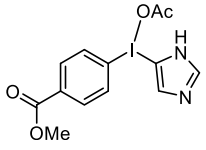
1a.



The reaction of (diacetoxyiodo)benzene (5 mmol, 1.611 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure B*** afforded (1*H*-imidazol-5-yl)(phenyl)iodonium acetate **1a** as a white solid, 1.35 g, yield 82%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 7.93−7.90 (m, 2H), 7.69 (d, J = 0.8 Hz, 1H), 7.56−7.52 (m, 1H), 7.50 (d, J = 0.8 Hz, 1H), 7.46−7.42 (m, 2H), 1.77 (s, 3H). ^{13}C (100 MHz, DMSO-d_6) δ 173.3, 144.8, 133.3, 132.6, 131.2, 130.8, 118.1, 101.6, 23.1.

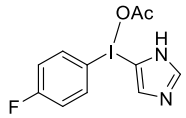
1b.



The reaction of methyl 4-iodobenzoate (5 mmol, 1.31 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(4-(methoxycarbonyl)phenyl)iodonium acetate **1b** as a white solid, 892 mg, yield 46%. mp = 135−136 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.18−8.14 (m, 2H), 8.09−8.06 (m, 3H), 7.85 (d, J = 1.2 Hz, 1H), 3.92 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 179.8, 166.8, 142.1, 135.5, 134.7, 133.3, 129.8, 121.8, 104.2, 53.2, 23.9. HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_{11}H_{10}IN_2O_2$ 328.9781; Found 328.9784.

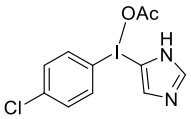
1c.



The reaction of 4-fluoroiodobenzene (5 mmol, 1.11 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene as white crystals (1.425 g, 84%). The reaction of (diacetoxyiodo)arene (3.82 mmol, 1.3 g) and imidazole (2 equiv, 7.64 mmol, 0.52 g) in MeOH (4 mL) afforded (4-fluorophenyl)(1*H*-imidazol-5-yl)iodonium acetate **1c** as a white solid, 957 mg, yield 72%. mp = 118−122 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94−7.91 (m, 2H), 7.59 (d, J = 0.8 Hz, 1H), 7.43 (d, J = 0.4 Hz, 1H), 7.34−7.30 (m, 2H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.9, 163.3 (d, J = 247 Hz), 145.3, 135.7 (d, J = 8 Hz), 133.0, 118.3 (d, J = 23 Hz), 112.2, 101.4, 22.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ −110.2 to −109.0 (m). HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_9H_7FIN_2$ 288.9632; Found 288.9651.

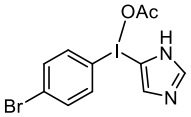
1d.



The reaction of 4-chloroiodobenzene (5 mmol, 1.61 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** gave (1*H*-imidazol-5-yl)(3-chlorophenyl)iodonium acetate **1d** as a white solid, 980 mg, yield 54%. mp = 135−137 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.06−8.02 (m, 3H), 7.85 (d, J = 0.8 Hz, 1H), 7.54−7.50 (m, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.2, 143.1, 139.7, 136.9, 132.9, 130.8, 114.9, 103.4, 24.2. HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_9H_7ClIN_2$ 304.9337; Found 304.9328.

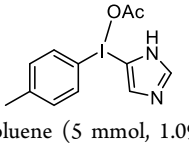
1e.



The reaction of 4-bromoiodobenzene (5 mmol, 1.42 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene (1.263 g, 63%). The reaction of (diacetoxyiodo)-arene (2.5 mmol, 1.003 g) and imidazole (2 equiv, 5 mmol, 0.34 g) in MeOH (2.5 mL) afforded (4-bromophenyl)(1*H*-imidazol-5-yl)-iodonium acetate **1e** as a white solid, 940 mg, yield 92%. mp = 134−136 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.04 (d, J = 1.2 Hz, 1H), 7.98−7.94 (m, 2H), 7.84 (d, J = 1.2 Hz, 1H), 7.69−7.65 (m, 2H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.1, 142.2, 137.1, 135.9, 129.8, 128.0, 115.7, 104.2, 24.1. HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_9H_7BrIN_2$ 348.8832; Found 348.8822.

1f.



The reaction of 4-iodotoluene (5 mmol, 1.09 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(4-methylphenyl)iodonium acetate **1f** as a white solid, 866 mg, yield 50%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond to the previously published[17]) δ 7.79 (d, J = 8.4 Hz, 2H), 7.67 (s, 1H), 7.50 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.2, 144.6, 141.0, 133.3, 132.2, 131.7, 114.4, 101.8, 23.0, 20.7.

https://doi.org/10.1021/acs.joc.1c00483
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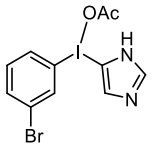
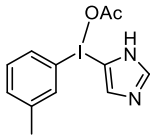
1g.



The reaction of 3-bromoiodobenzene (5 mmol, 1,42 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene (1.335 g, 67%). The reaction of (diacetoxyiodo)-arene (2.5 mmol, 1.003 g) and imidazole (2 equiv, 5 mmol, 0.34 g) in MeOH (2.5 mL) afforded (3-bromophenyl)(1*H*-imidazol-5-yl)-iodonium acetate **1g** as a white solid, 736 mg, yield 72%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 8.29 (s, 1H), 8.05−8.03 (m, 2H), 7.85(s, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 179.9, 142.1, 137.6, 136.4, 134.2, 134.1, 129.7, 125.1, 117.6, 104.5, 23.9.

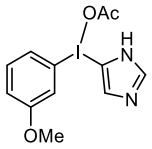
1h.



The reaction of 3-iodotoluene (5 mmol, 1.09 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(3-methylphenyl)iodonium acetate **1h** as a white solid, 807 mg, yield 47%. mp = 145−146 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.03 (d, J = 1.2 Hz, 1H), 7.92 (s, 1H), 7.86−7.84 (m, 2H), 7.47 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 2.39 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.0, 143.8, 141.6, 135.7, 134.0, 132.5, 132.5, 129.1, 117.2, 104.3, 24.0, 21.3. HRMS (ESI) m/z: $[M - OAc]^+$ Calcd for $C_{10}H_{10}IN_2$ 284.9883, found: 284.9866.

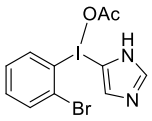
1i.



The reaction of 3-methoxyiodobenzene (5 mmol, 1.17 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(3-methoxyphenyl)iodonium acetate **1i** as a white solid, 828 mg, yield 46%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 7.70 (d, J = 0.8 Hz, 1H), 7.54−7.52 (m, 2H), 7.43 (ddd, J = 8.0, 1.6, 0.8 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.10 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 3.75 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.3, 160.2, 144.7, 132.7, 131.8, 125.1, 118.8, 118.2, 116.5, 101.6, 55.7, 23.1.

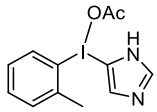
1j.



The reaction of 2-bromoiodobenzene (5 mmol, 1,415 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene (1.051 g, 52%). The reaction of (diacetoxyiodo)-arene (2.52 mmol, 1.011 mg) and imidazole (2 equiv, 5.04 mmol, 0.343 g) in MeOH (2,5 mL) afforded (2-bromophenyl)(1*H*-imidazol-5-yl)iodonium acetate **1j** as a white solid, 742 mg, yield 72%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 8.26 (dd, J = 8.0, 1.6 Hz, 1H), 8.07 (d, J = 0.8 Hz, 1H), 7.91 (dd, J = 8.0, 1.6 Hz, 1H), 7.83 (d, J = 1.2 Hz, 1H), 7.56 (td, J = 7.6, 1.6 Hz, 1H), 7.46 (td, J = 7.6, 1.6 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 179.9, 141.7, 139.4, 135.4, 134.9, 131.5, 129.5, 127.8, 123.2, 105.1, 23.9.

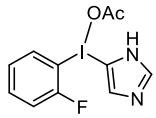
1k.



The reaction of 2-iodotoluene (5 mmol, 1.09 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(2-methylphenyl)iodonium acetate **1k** as a white solid, 985 mg, yield 57%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 8.21 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 0.4 Hz, 1H), 7.81 (d, J = 0.4 Hz, 1H), 7.58−7.53 (m, 2H), 7.29−7.25 (m, 1H), 2.73 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.0, 142.1, 141.4, 138.0, 134.2, 132.7, 130.4, 128.7, 122.4, 104.0, 25.5, 24.0.

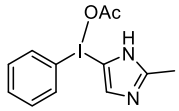
1l.



The reaction of 2-fluoroiodobenzene (5 mmol, 1.11 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene (0.903 g, 53%). The reaction of (diacetoxyiodo)-arene (2.4 mmol, 822 mg) and imidazole (2 equiv, 4.8 mmol, 0.326 g) in MeOH (2.5 mL) afforded (2-fluorophenyl)(1*H*-imidazol-5-yl)-iodonium acetate **1l** as a white solid, 652 mg, yield 78%. mp = 152−152 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (ddd, J = 7.6, 6.0, 1.6 Hz, 1H), 7.64 (d, J = 0.8 Hz, 1H), 7.63−7.57 (m, 1H), 7.45 (td, J = 8.0, 1.2 Hz, 2H), 7.24 (td, J = 7.6, 1.2 Hz, 1H), 1,74 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.5, 159.3 (d, J = 246 Hz), 143.3, 136.6, 134.1 (d, J = 7 Hz), 130.8, 126.9 (d, J = 3 Hz), 116.3 (d, J = 23 Hz), 106.9 (d, J = 24 Hz), 103.9, 23.1. ^{19}F NMR (376 MHz, DMSO-d_6) δ −99.1 to −99.0 (m). HRMS (ESI) m/z: $[M - OAc]^+$ Calcd for $C_9H_7FIN_2$ 288.9632; Found 288.9640.

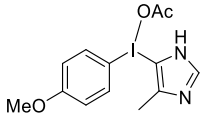
1m.



The reaction of (diacetoxyiodo)benzene (5 mmol, 1.61 g) and 2-methylimidazole (10 mmol, 0.82 g) in MeOH according to ***general procedure B*** afforded (2-methyl-1*H*-imidazol-5-yl)(phenyl)iodonium acetate **1m** as a white solid, 999 mg, yield 58%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 8.08−8.05 (m, 2H), 7.93 (s, 1H), 7.68−7.63 (m, 1H), 7.54−7.48 (m, 2H), 2.42 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.1, 140.8, 138.5, 135.3, 133.2, 132.9, 117.2, 104.3, 24.1, 10.8.

1n.



The reaction of 2-methoxyiodobenzene (5 mmol, 1,17 g) and $NaIO_4$ (5.25 mmol, 1.12 g) according to ***general procedure B*** afforded (diacetoxyiodo)arene (1,128 g, 64%). The reaction of (diacetoxyiodo)-arene (3,16 mmol, 1,111 mg) and 4-methylimidazole (2 equiv, 6.32 mmol, 0.518 g) in MeOH (3 mL) afforded (4-methoxyphenyl)(4-methyl-1*H*-imidazol-5-yl)iodonium acetate **1n** as a white solid, 447 mg, yield 38%. mp = 134−135 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 7.96 (d, J = 9.2 Hz, 2H), 7.77 (s, 1H), 7.03 (d, J = 9.2 Hz, 2H), 3.83 (s, 3H), 2.49 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.0, 164.2, 140.4, 137.7, 137.5, 118.5, 105.9, 105.0, 56.3, 24.1, 10.8. HRMS (ESI) m/z: $[M - OAc]^+$ Calcd for $C_{11}H_{12}IN_2O$ 314.9989; Found 314.9989.

https://doi.org/10.1021/acs.joc.1c00483
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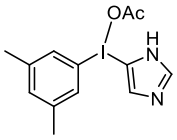
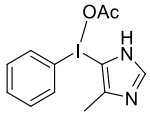
1p.



The reaction of 3,5-dimethyliodobenzene (5 mmol, 1.16 g) and imidazole (10 mmol, 0.681 g) in MeOH according to ***general procedure A*** afforded (1*H*-imidazol-5-yl)(3,5-dimethylphenyl)iodonium acetate **1p** as a white solid, 1.026 g, yield 57%. mp = 135−136 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.02 (d, J = 0.8 Hz, 1H), 7.83 (d, J = 0.8 Hz, 1H), 7.70 (s, 2H), 7.29 (s, 1H), 2.34 (s, 6H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.1, 143.4, 141.7, 134.8, 132.8, 129.2, 117.0, 104.0, 24.1, 21.2. HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_{11}H_{12}IN_2$ 299.0040; Found 299.0040.

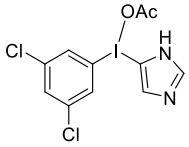
1q.



The reaction of (diacetoxyiodo)benzene (5 mmol, 1.61 g) and 4-methylimidazole (10 mmol, 0,82 g) in MeOH according to ***general procedure B*** afforded (1*H*-4-methylimidazol-5-yl)(phenyl)iodonium acetate **1q** as a white solid, 1.007 g, yield 59%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 8.05−8.02 (m, 2H), 7.79 (s, 1H), 7.67−7.63 (m, 1H), 7.53−7.48 (m, 2H), 2.50 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 180.1, 151.4, 135.5, 133.2, 132.9, 128.9, 117.4, 103.0, 24.1, 13.7.

Synthesis of (3,5-Dichlorophenyl)(1*H*-imidazol-5-yl)-iodonium Acetate 1o.[23] *1o*.



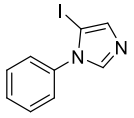
3,5-Dichloroiodobenzene (2 mmol, 0.546 g) was dissolved in a mixture of AcOH (18 mL) and TfOH (12 mmol, 1.1 mL), followed by portionwise addition of $Na_3BO_3{\cdot}4H_2O$ (20 mmol, 3.077 g) over 30 min under an argon atmosphere. The flask was capped, and the mixture was heated on the oil bath to 50 °C during 6 h. Then 40 mL of water was added. The water layer was extracted with DCM (4 × 25 mL). The combined organic layer was dried over $MgSO_4$, and the solvent was evaporated. The 3,5-dichloro(diacetoxyiodo)benzene (57%, 1.14 mmol, 0.445 g) was precipitated by addition of pentane. The prepared 3,5-dichloro(diacetoxyiodo)benzene was dissolved in MeOH (1.5 mL), and imidazole (2.3 mmol, 0.156 g) was added. The mixture was stirred for 16 h, and the solvent was removed in vacuo. MeCN (2 mL) was added to the oily residue, and the precipitated solid was filtered and washed with Et_2O several times to give (3,5-dichlorophenyl)(1*H*-imidazol-5-yl)iodonium acetate **1o** as a white solid, 355 mg, yield 78%. mp = 140−142 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.11 (d, J = 1.6 Hz, 2H), 8.06 (s, 1H), 7.87 (s, 1H), 7.75 (t, J = 1.6 Hz, 1H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 179.9, 142.0, 138.0, 133.5, 133.3, 129.7, 117.8, 105.3, 23.9. HRMS (ESI) m/z: [M − OAc]$^+$ Calcd for $C_9H_6Cl_2IN_2$ 338.8947; Found 338.8931.

Synthesis of 1-Aryl-5-Iodoimidazoles 2a−2q. General Procedure (Described for 2 mmol Scale). 1-Aryl-5-iodoimidazoles **2a−2q** were prepared according to a published procedure[17]

$Cu(OTf)_2$ (5 mol %, 0.1 mmol, 0.036 g), Cs_2CO_3 (1.5 equiv, 3 mmol, 0.978 g), and *N*-methylbenzimidazole (if not stated otherwise) (20 mol %, 0.4 mmol, 0.053 g) were charged in a 50 mL round-bottom flask equipped with a magnetic stir bar. 10 mL of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) had been added, and the mixture was allowed to stir for 30 min. Then aryl(imidazolyl)iodonium acetate **1** (2 mmol) was added (neat), the flask was capped, and reaction mass was heated to 50 °C on the oil bath for 16 h. After that, the solvent was removed by rotary evaporator under reduced pressure, and 1-aryl-5-iodoimidazole was isolated by column chromatography (hexane:EtOAc (10:1 → 3:2).

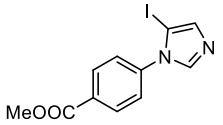
2a.



The reaction of acetate **1a** (2 mmol, 0.66 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-phenyl-5-iodoimidazole **2a** as off-white solid, 0.352 g, yield: 65%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 8.05 (s, 1H), 7.59−7.51 (m, 3H), 7.44−7.42 (m, 2H), 7.19 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.5, 136.9, 136.7, 129.4, 128.9, 126.7, 74.1.

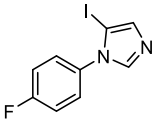
2b.



The reaction of acetate **1b** (2 mmol, 0.776 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded methyl 4-(5-iodoimidazol-1-yl)benzoate **2b** as a white solid, 0.459 g, yield: 70%. mp = 125−127 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.14−8.12 (m, 3H), 7.63 (d, J = 7.6 Hz, 2H), 7.24 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.5, 140.6, 140.4, 137.6, 130.3, 129.7, 126.8, 73.4, 52.5. HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_{11}H_9IN_2O_2$ 327.9703; Found 327.9703.

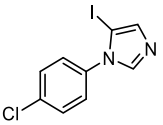
2c.



The reaction of acetate **1c** (2 mmol, 0.696 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(4-fluorophenyl)-5-iodoimidazole **2c** as a white solid, 0.271 g, yield: 47%. mp = 93−95 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 7.99 (d, J = 0.8 Hz, 1H), 7.46−7.43 (m, 2H), 7.33−7.29 (m, 2H), 7.20 (d, J = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 164.3 (d, J = 249.5 Hz), 141.6, 137.6, 134.3(d, J = 3 Hz), 130.3(d, J = 9.1 Hz), 117.3 (d, J = 24.2 Hz), 74.2. ^{19}F NMR (376 MHz, MeOD-d_4) δ −113.7 to −113.6 (m). HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_9H_6FIN_2$287.9554; Found 287.9553.

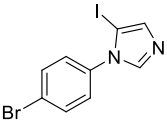
2d.



The reaction of acetate **1d** (2 mmol, 0.729 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(4-chlorophenyl)-5-iodoimidazole **2d** as an off-white solid, 0.377 g, yield: 62%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 8.06 (d, J = 0.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 0.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.6, 137.1, 135.5, 133.6, 129.4, 128.6, 74.1.

2e.



The reaction of acetate **1e** (2 mmol, 0.818 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(4-bromophenyl)-5-

https://doi.org/10.1021/acs.joc.1c00483
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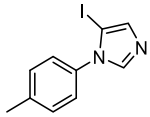
iodoimidazole **2e** as a pale brown solid, 0.401 g, yield: 58%. mp = 119−120 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.01 (d, J = 1.2 Hz, 1H), 7.75−7.72 (m, 2H), 7.37−7.35 (m, 2H), 7.21 (d, J = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 141.5, 137.9, 137.3, 133.8, 129.9, 124.4, 73.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_7BrIN_2$ 348.8832; Found 348.8860.

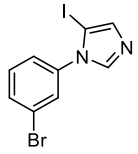
2f.



The reaction of acetate **1f** (2 mmol, 0.688 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(4-methylphenyl)-5-iodoimidazole **2f** as an off-white solid, 0.392 g, yield: 69%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 8.00 (d, J = 0.8 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 0.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.5, 138.6, 136.8, 134.2, 129.8, 126.5, 74.3, 20.7.

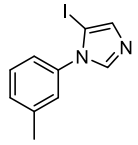
2g.



The reaction of acetate **1g** (2 mmol, 0.818 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(3-bromophenyl)-5-iodoimidazole **2g** as an off-white solid, 0.377 g, yield: 54%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 8.10 (s, 1H), 7.76−7.73 (m, 2H), 7.55−7.47 (m, 2H), 7.20 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.7, 138.0, 137.1, 131.8, 131.2, 129.4, 126.0, 121.8, 74.0.

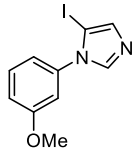
2h.



The reaction of acetate **1h** (2 mmol, 0.688 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(3-methylphenyl)-5-iodoimidazole **2h** as an off-white solid, 0.426 g, yield: 75%. mp = 61−62 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 7.95 (s, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 7.22 (s, 1H), 7.19−7.17 (m, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 141.4, 141.1, 138.0, 137.6, 131.2, 130.3, 128.5, 125.0, 73.7, 21.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{10}H_{10}IN_2$ 284.9883; Found 284.9874.

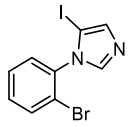
2i.



The reaction of acetate **1i** (2 mmol, 0.72 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(3-methoxyphenyl)-5-iodoimidazole **2i** as an off-white solid, 0.452 g, yield: 75%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 8.04 (s, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.18 (s, 1H), 7.10 (dd, J = 8.4, 2.4 Hz, 1H), 7.01−6.98 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 140.5, 137.6, 136.9, 130.2, 118.6, 114.6, 112.3, 73.8, 55.5.

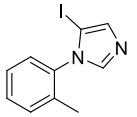
2j.



The reaction of acetate **1j** (2 mmol, 0.818 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(2-bromophenyl)-5-iodoimidazole **2j** as a white solid, 0.420 g, yield: 60%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 7.95 (d, J = 1.2 Hz, 1H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.57 (td, J = 7.6, 1.6 Hz, 1H), 7.53−7.48 (m, 1H), 7.44 (dd, J = 7.6, 1.6 Hz, 1H), 7.22 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 141.6, 137.5, 137.0, 134.7, 132.9, 131.6, 129.8, 123.9, 74.9.

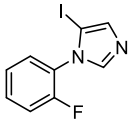
2k.



The reaction of acetate **1k** (2 mmol, 0.688 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(2-methylphenyl)-5-iodoimidazole **2k** as a pale yellow oil, 0.318 g, yield: 56%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 7.96 (d, J = 0.8 Hz, 1H), 7.49−7.44 (m, 2H), 7.40−7.36 (m, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.21 (d, J = 0.8 Hz, 1H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.5, 136.1, 136.1, 135.6, 130.9, 129.8, 128.5, 127.0, 75.2, 17.2.

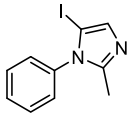
2l.



The reaction of acetate **1l** (2 mmol, 0.696 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(2-fluorophenyl)-5-iodoimidazole **2l** as a white solid, 0.288 g, yield: 50%. mp = 60−62 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 7.99 (s, 1H), 7.64−7.58 (m, 1H), 7.45−7.36 (m, 3H), 7.23 (s, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 158.7 (d, J = 250 Hz), 142.2, 137.4, 133.1 (d, J = 8 Hz), 131.0, 126.2 (d, J = 4 Hz), 125.9 (d, J = 13 Hz), 117.8 (d, J = 20 Hz), 74.8. ^{19}F NMR (376 MHz, MeOD-d_4) δ −123.2 to −123.1 (m). HRMS (EI) m/z: $[M]^{+\cdot}$ Calcd for $C_9H_6FIN_2$ 287.9554; Found 287.9554.

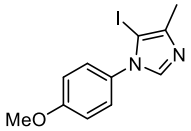
2m.



The reaction of acetate **1m** (2 mmol, 0.688 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-phenyl-2-methyl-5-iodoimidazole **2m** as an off-white solid, 0.230 g, yield: 40%.

^{1}H NMR (400 MHz, DMSO-d_6) (the NMR spectra correspond with the previously published[17]) δ 7.60−7.52 (m, 3H), 7.34−7.32 (m, 2H), 7.04 (s, 1H), 2.19 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.2, 137.1, 134.4, 129.5, 129.3, 128.2, 73.5, 14.5.

2n.



The reaction of acetate **1n** (2 mmol, 0.748 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(4-methoxyphenyl)-4-

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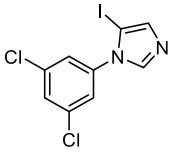
methyl-5-iodoimidazole **2n** as a yellowish solid, 0.289 g, yield: 46%. mp = 83−85 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (s, 1H), 7.32−7.28 (m, 2H), 7.10−7.06 (m, 2H), 3.82 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.3, 142.2, 140.1, 130.1, 128.1, 114.4, 74.3, 55.6, 14.6. HRMS (EI) m/z: $[M]^{+\cdot}$ Calcd for $C_{11}H_{11}IN_2O$ 313.9911; Found 313.9911.

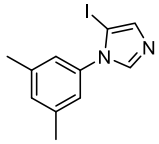
2o.



The reaction of acetate **1o** (0.875 mmol, 0.349 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(3,5-dichlorophenyl)-5-iodoimidazole **2o** as an off-white solid, 0.171 g, yield: 58%. mp = 127−131 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.06 (d, J = 0.8 Hz, 1H), 7.69−7.68 (m, 1H), 7.51 (d, J = 2 Hz, 2H), 7.23 (d, J = 0.8 Hz, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 141.7, 140.0, 138.3, 136.8, 130.5, 127.1, 73.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_9H_6Cl_2IN_2$ 338.8947; Found 338.8966.

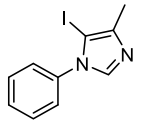
2p.



The reaction of acetate **1p** (2 mmol, 0.716 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 1-(3,5-dimethylphenyl)-5-iodoimidazole **2p** as an off-white solid, 0.375 g, yield: 63%. mp = 132−134 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 1H), 7.17 (s, 2H), 7.03 (s, 2H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 140.4, 138.8, 136.8, 136.5, 130.2, 124.2, 74.0, 20.7. HRMS (EI) m/z: $[M]^{+\cdot}$ Calcd for $C_{11}H_{11}IN_2$ 297.9961; Found 297.9961.

2q.

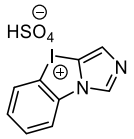


The reaction of acetate **1q** (2 mmol, 0.688 g) in HFIP solution according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 3:2)) afforded 4-methyl-1-phenyl-5-iodoimidazole **2q** as an off-white solid, 0.484 g, yield: 87%.

^{1}H NMR (400 MHz, MeOD-d_4) (the NMR spectra correspond with the previously published[17]) δ 7.95 (s, 1H), 7.58−7.53 (m, 3H), 7.39−7.37 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 144.0, 140.9, 138.6, 130.5, 130.4, 128.0, 73.0, 14.4.

Synthesis of Cyclic Iodonium Salts 3a−3q. *General Procedure.* A 10 mL reaction tube equipped with a stir bar was charged with 96% H_2SO_4 (0.8 mL) and cooled to between 0 and 5 °C. Then, finely ground 1-aryl-5-iodoimidazole **2** (0.5 mmol) was added, and the resulting mixture was stirred for 20 min, followed by the addition of finely ground Oxone (1.3 equiv, 0.325 mmol, 0.2 g) in one portion. The stirring was continued for 1 h between 0 and 5 °C. Next, the ice−water bath was removed and stirring was continued for 1 h at room temperature. For some substrates, an additional portion of Oxone (0.325 mmol, 0.2 g) and H_2SO_4 (0.8 mL) was required after 2 h of reaction (addition under cooling with ice−water bath). After full consumption of the initial material, as gauged by TLC (hexane:EtOAc = 2:1), ice was added to the reaction mixture (1−2 g). Then, the mixture was diluted with cold water to the total volume of 7 mL. A 9 M NaOH solution was added dropwise with cooling by ice−water bath until the appearance of the precipitate (approximately 2−2.5 mL for 0.8 mL of H_2SO_4); the resulting suspension was allowed to stir for 1 h at room temperature. The final solid was filtered and washed with cold water (2 × 3 mL), Et_2O (3 × 5 mL) and dried under vacuum.

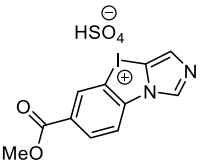
3a.



The reaction of 1-phenyl-5-iodoimidazole **2a** (0.5 mmol, 135 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded benzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3a** as a white solid, 154 mg, yield: 84%. mp = 201−203 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.81 (t, J = 7.6 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.7, 134.8, 131.9, 131.50, 131.3, 128.6, 117.3, 112.2, 97.9. HRMS (ESI) m/z: $[M - HSO_4]^+$ Calcd for $C_9H_6IN_2$ 268.9570; Found 268.9580.

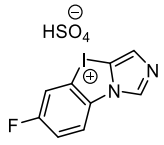
3b.



The reaction of methyl 4-(5-iodo-imidazol-1-yl)benzoate **2b** (0.5 mmol, 164 mg) with an additional portion of Oxone (*0.2 and 0.3 g, respectively, for the first and the second batch of the oxidant*) in H_2SO_4 (*0.8 mL for both portions*) according to the ***general procedure*** afforded 6-(methoxycarbonyl)benzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3b** as an off-white solid, 212 mg, yield: 81%. mp = 248−249 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.28 (s, 1H), 8.67 (d, J = 1.6 Hz, 1H), 8.43 (d, J = 8.4 Hz, 1H), 8.35 (dd, J = 8.4, 2 Hz, 1H), 7.45 (s, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.4, 138.3, 136.4, 132.9, 132.3, 131.9, 129.1, 117.2, 113.1, 98.9, 52.9. HRMS (ESI) m/z: $[M - HSO_4]^+$ Calcd for $C_{11}H_8IN_2O_2$ 326.9625; Found 326.9625.

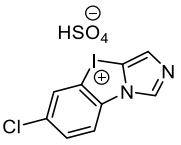
3c.



The reaction of 1-(4-fluorophenyl)-5-iodoimidazole **2c** (0.5 mmol, 144 mg) with an additional portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 6-fluorobenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium hydrogen sulfate **3c** as an off-white solid, 115 mg, yield: 60%. mp = 224−227 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H), 8.38 (dd, J = 9.2, 4.4 Hz, 1H), 7.91 (dd, J = 7.6, 2,8 Hz, 1H), 7.78 (td, J = 8.8, 2.8 Hz, 1H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.9 (d, J = 247 Hz), 135.7, 132.1 (d, J = 2 Hz), 131.6, 119.4 (d, J = 24 Hz), 118.3 (d, J = 18 Hz), 118.1, 113.1 (d, J = 10 Hz), 98.6. ^{19}F NMR (376 MHz, DMSO-d_6) δ 111.8−111.7 (m). HRMS (ESI) m/z: $[M - HSO_4]^+$ Calcd for $C_9H_5FIN_2$ 286.9476; Found 286.9462.

3d.



The reaction of 1-(4-chlorophenyl)-5-iodoimidazole **2d** (0.5 mmol, 153 mg) with an additional portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 6-chlorobenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium hydrogen sulfate **3d** as an off-white solid, 140 mg, yield: 70%. mp = 243−245 °C.

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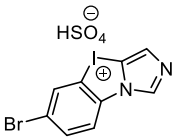
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.06 (s, 1H), 8.38 (s, 1H), 8.24 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.32 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.9, 134.3, 132.0, 131.6, 131.5, 130.4, 118.2, 113.5, 98.6. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_5ClIN_2$ 302.9180; Found 302.9165.

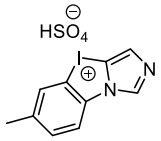
3e.



The reaction of 1-(4-bromophenyl)-5-iodoimidazole **2e** (0.5 mmol, 175 mg) with an additional portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 6-bromobenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium hydrogen sulfate **3e** as a pale brown solid, 180 mg, yield: 81%. mp = 255−258 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 2,0 Hz, 1H), 8.06 (dd, J = 8.8, 2.0 Hz, 1H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.0, 134.8, 134.6, 133.1, 131.6, 119.4, 118.7, 113.8, 98.5. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_5BrIN_2$ 346.8675; Found 346.8701.

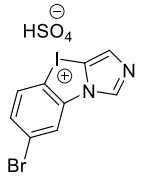
3f.



The reaction of 1-(4-methylphenyl)-5-iodoimidazole **2f** (0.5 mmol, 142 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 6-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3f** as an off-white solid, 173 mg, yield: 91%. mp = 231−233 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.14 (s, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.89 (s, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.39 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.7, 135.4, 132.6, 132.5, 131.4, 130.8, 116.8, 112.0, 97.6, 20.8. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{10}H_8IN_2$ 282.9727; Found 282.9713.

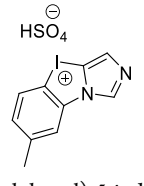
3g.



The reaction of 1-(3-bromophenyl)-5-iodoimidazole **2g** (0.39 mmol, 137 mg) with an additional portion of Oxone in H_2SO_4 (*scaled down to 0.39 mmol of* ***2g***) according to the ***general procedure*** afforded 7-bromobenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3g** as an off-white solid, 145 mg, yield: 84%. mp = 244−247 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.69 (d, J = 2.0 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.71 (dd, J = 8.8, 2.0 Hz, 1H), 7.40 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.3, 136.0, 132.8, 131.6, 131.1, 125.1, 120.1, 111.5, 98.6. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_5BrIN_2$ 346.8675; Found 346.8678.

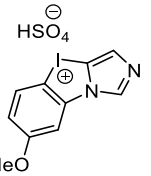
3h.



The reaction of 1-(3-methylphenyl)-5-iodoimidazole **2h** (0.5 mmol, 142 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 7-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3h** as a white solid, 165 mg, yield: 87%. mp = 245−246 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (s, 1H), 8.18 (d, J = 0.8 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.2−7.30 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.3, 135.3, 134.8, 131.5, 131.1, 129.2, 117.4, 108.8, 99.0, 20.8. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{10}H_8IN_2$ 282.9727; Found 282.9726.

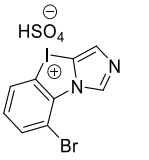
3i.



The reaction of 1-(3-methoxyphenyl)-5-iodoimidazole **2i** (0.5 mmol, 150 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 7-methoxybenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3i** as an off-white solid, 150 mg, yield: 76%. mp = 251−253 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.98 (d, J = 2.8 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 7.38 (s, 1H), 7.12 (dd, J = 9.2, 2.8 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.4, 135.9, 135.7, 131.8, 131.6, 115.2, 102.9, 100.8, 98.1, 56.4. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{10}H_8IN_2O$ 298.9676; Found 298.9665.

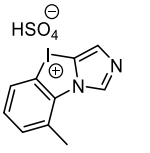
3j.



The reaction of 1-(2-bromophenyl)-5-iodoimidazole **2j** (0.5 mmol, 175 mg) with an additional portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 8-bromobenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium hydrogen sulfate **3j** as an off-white solid, 125 mg, yield: 56%. mp = 179−181 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.52 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.6, 137.1, 133.7, 131.4, 130.8, 128.9, 114.5, 110.1, 99.0. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_5BrIN_2$ 346.8675; Found 346.8676.

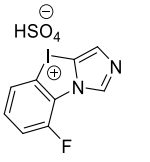
3k.



The reaction of 1-(2-methylphenyl)-5-iodoimidazole **2k** (0.5 mmol, 142 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 8-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3k** as an off-white solid, 119 mg, yield: 63%. mp = 215−217 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.49 (s, 1H), 7.44 (t, J = 8.0 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.1, 134.8, 134.1, 131.2, 129.0, 128.9, 127.8, 112.3, 97.7, 21.4. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{10}H_8IN_2$ 282.9727; Found 282.9731.

3l.



The reaction of 1-(2-fluorophenyl)-5-iodoimidazole **2l** (0.5 mmol, 145 mg) with an additional portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 8-fluorobenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium hydrogen sulfate **3l** as an off-white solid, 118 mg, yield: 61%. mp = 244−247 °C.

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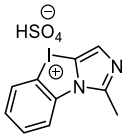
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.84 (d, J = 2.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.83 (dd, J = 10.8, 8.4 Hz, 1H), 7.56 (td, J = 8.4, 5.2 Hz, 1H), 7.46 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.3 (d, J = 252 Hz), 137.4 (d, J = 13 Hz), 131.3, 128.7 (d, J = 6 Hz), 127.1 (d, J = 3 Hz), 124.3 (d, J = 14 Hz), 119.1 (d, J = 18 Hz), 113.8, 98.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ −120.2 to −120.1 (m). HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_5FIN_2$ 286.9476; Found 286.9473.

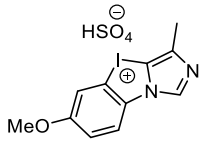
3m.



The reaction of 2-methyl-1-phenyl-5-iodoimidazole **2m** (0.5 mmol, 142 mg) with one portion of Oxone in H_2SO_4 according to the ***general procedure*** afforded 1-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3m** as an off-white solid, 154 mg, yield: 40%. mp = 203−206 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7,6 Hz, 1H), 7.26 (s, 1H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 145.7, 135.6, 131.9, 131.4, 130.3, 128.0, 118.3, 111.7, 96.4, 16.9. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{10}H_8IN_2$ 282.9727; Found 282.9751.

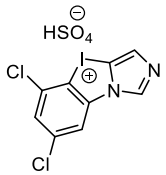
3n.



The reaction of 1-(4-methoxyphenyl)-4-methyl-5-iodoimidazole **2n** (0.5 mmol, 157 mg) with an additional portion of Oxone (*0.2 and 0.3 g, respectively, for the first and second batch of the oxidant*) in H_2SO_4 (*0.8 mL for both portions*) according to the ***general procedure*** afforded 6-methoxy-3-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3n** as a pale brown solid, 103 mg, yield: 50%. mp = 225−227 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.11 (s, 1H), 7.82 (dd, J = 8.8, 2.8 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 4.02 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.6, 148.9, 143.4, 138.4, 133.9, 128.2, 113.9, 106.6, 95.0, 57.9, 14.3. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_{11}H_{10}IN_2O$ 312.9832; Found 312.9838.

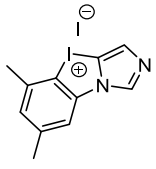
3o.



The reaction of 1-(3,5-dichlorophenyl)-5-iodoimidazole **2o** (0.3 mmol, 102 mg) with an additional portion of Oxone in H_2SO_4 (*scaled down to 0.3 mmol*) according to the ***general procedure*** afforded 5,7-dichlorobenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium hydrogen sulfate **3o** as an off-white solid, 110 mg, yield: 85%. mp = 205−208 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.18 (s, 1H), 8.45 (s, 1H), 7.80 (s, 1H), 7.56 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 137.3, 137.1, 136.7, 133.9, 133.3, 126.8, 115.8, 99.5, 95.8. HRMS (ESI) m/z: [M − HSO_4]$^+$ Calcd for $C_9H_4Cl_2IN_2$ 336.8791; Found 336.8817.

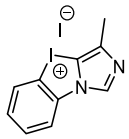
Synthesis of 5,7-Dimethylbenzo[*d*]imidazo[5,1-*b*][1,3]-iodazol-4-ium Iodide 3p and 3-Methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium Iodide 3q. *3p*.



Oxone (0.325 mmol, 200 mg) was added under cooling with an ice−water bath to the stirring solution of 1-(3,5-dimethylphenyl)-5-iodoimidazole **2p** (0.5 mmol. 149 mg) in H_2SO_4 (0.8 mL). After the full conversion of the starting material, the reaction mass was diluted with ice and water and only 1−1.5 mL of 9 M NaOH was added. Then the reaction mass was diluted with water to the volume of 50 mL and KI (1.5 equiv, 124 mg) in 2 mL of water was added. The precipitate was filtered and washed with water and acetone to give 5,7-dimethylbenzo-[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium iodide **3p** as a yellow solid, 134 mg, yield: 63%. mp = 164−167 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.15 (s, 1H), 7.95 (s, 1H), 7.55 (s, 1H), 7.14 (s, 1H), 2.51 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.9 139.3, 136.1, 134.4, 132.7, 129.9, 115.9, 114.6, 93.5, 22.9, 20.7. HRMS (ESI) m/z: [M − I]$^+$ Calcd for $C_{11}H_{10}IN_2$ 296.9883; Found 296.9883.

3q.



Oxone (0.325 mmol, 200 mg) was added under cooling with an ice−water bath to the stirring solution of 4-methyl-1-phenyl-imidazole **2q** (0.5 mmol. 142 mg) in H_2SO_4 (0.8 mL). After the full conversion of the starting material, the reaction mass was diluted with ice and water and only 1−1.5 mL of 9 M NaOH was added. Then the reaction mass was diluted with water to the volume of 50 mL and KI (1.5 equiv, 124 mg) in 2 mL of water was added. The yellow precipitate was filtered and washed with water and acetone to give 3-methylbenzo[*d*]imidazo[5,1-*b*][1,3]iodazol-4-ium iodide **3q** as a yellow solid, 195 mg, yield: 95%. mp = 126−129 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.02 (s, 1H), 8.49 (dd, J = 8.4, 0.8 Hz, 1H), 8.20 (dd, J = 8.0, 1.6 Hz, 1H), 7.81−7.77 (m, 1H), 7.50 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 138.0, 134.7, 133.6, 132.2, 131.4, 128.1, 116.8, 110.0, 97.0, 13.9. HRMS (ESI) m/z: [M − I]$^+$ Calcd for $C_{10}H_8IN_2$ 282.9727; Found 282.9731.

Synthesis of Iodonium Salt 3a on 2 mmol Scale. A 50 mL round-bottom flask equipped with a stir bar was charged with 96% H_2SO_4 (2.4 mL) and cooled to between 0 and 5 °C. Then, finely ground 1-phenyl-5-iodoimidazole **2a** (2 mmol) was added, and the resulting mixture was stirred for 20 min, followed by portionwise addition of finely ground Oxone (1.3 equiv, 2.6 mmol, 0.8 g) over 5 min. The stirring was continued for 1 h between 0 and 5 °C. Next, the ice−water bath was removed and stirring was continued for 1 h at room temperature. After full consumption of the initial material, as gauged by TLC (hexane:EtOAc = 2:1), ice was added to the reaction mixture (5 g). Then, the mixture was diluted with cold water to the total volume of 25 mL. A 9 M NaOH solution was added dropwise with cooling by an ice−water bath until the appearance of the precipitate (approximately 9 mL); the resulting suspension was allowed to stir for 1 h at room temperature. The final solid was filtered and washed with cold water (2 × 10 mL) and Et_2O (3 × 10 mL) and dried under vacuum to give iodonium salt **3a** as an off-white solid, 579 mg, yield: 79%.

Synthesis of Benz[*d*]imidazo[5,1-*b*]thiazoles 4a−4k. *General Procedure (Described for 0.25 mmol Scale). Reactions proceeded under an argon atmosphere.* A Schlenk tube equipped with a magnetic stir bar was charged with cyclic iodonium salt **3**, S_8 (0.125 mmol, 32 mg), and Cs_2CO_3 (1 mmol, 326 mg). After 3 cycles of vacuum/refill, anhydrous DMSO (2.5 mL) had been added under a stream of argon, and the mixture was allowed to react at 100 °C on the oil bath for 4 h. The reaction mass was cooled to room temperature and diluted with water. The aqueous layer was extracted with EtOAc. The combined organic layer was dried over $MgSO_4$, and the solvent was removed. The crude product was purified by column chromatography, eluting with hexane:EtOAc (10:1 → 2:1).

https://doi.org/10.1021/acs.joc.1c00483
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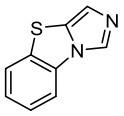
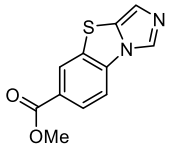
4a.



The reaction of iodonium salt **3a** (0.25 mmol, 91.5 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded benzo[*d*]imidazo[5,1-*b*]thiazole **4a** as a pale yellow solid, 33.5 mg, yield: 77%. mp = 99−101 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.42−7.38 (m, 1H), 7.14 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 132.6, 130.9, 128.2, 127.5, 126.3, 125.8, 124.9, 118.3, 113.8. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_9H_6N_2SNa$ 197.0144; Found 197.0145.

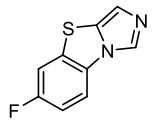
4b.



The reaction of iodonium salt **3b** (0.25 mmol, 96 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded methyl benzo[*d*]imidazo[5,1-*b*]thiazole-6-carboxylate **4b** as a waxy pale brown solid, 29 mg, yield: 50%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (br.s, 1H), 8.55 (s, 1H), 8.22 (d, J = 8.4 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.22 (br.s, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.4, 134.1, 133.6, 127.6, 127.0, 126.4, 113.8, 52.5. HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_{11}H_8N_2O_2S$ 232.0301; Found 232.0301.

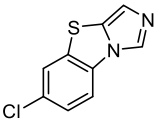
4c.



The reaction of iodonium salt **3c** (0.25 mmol, 96 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 6-fluorobenzo[*d*]imidazo[5,1-*b*]thiazole **4c** as a waxy yellow solid, 34 mg, yield: 71%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.75 (s, 1H), 8.13 (dd, J = 8.8, 4.8 Hz, 1H), 7.88 (dd, J = 9.2, 2.4 Hz, 1H), 7.41−7.36 (m, 1H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.5(d, J = 240 Hz), 134.5 (d, J = 10 Hz), 127.9, 118.7, 114.8 (d, J = 10 Hz), 113.6 (d, J = 24 Hz), 111.9 (d, J = 27 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ −116.0 to −115.9 (m). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_9H_6FN_2S$ 193.0230; Found 193.0230.

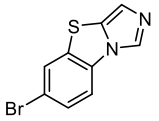
4d.



The reaction of iodonium salt **3d** (0.25 mmol, 100 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 6-chlorobenzo[*d*]imidazo[5,1-*b*]thiazole **4d** as a pale yellow solid, 39 mg, yield: 63%. mp = 165−168 °C (recrystallized sample).

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.61 (s, 1H), 7.89 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 2.0 Hz, 1H), 7.42 (dd, J = 8.8, 2.0 Hz, 1H), 7.09 (s, 1H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 136.3, 132.6, 131.3, 130.1, 129.0, 127.5, 125.3, 118.8, 115.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_9H_6ClN_2S$ 208.9935; Found 208.9936.

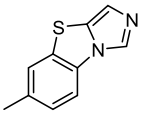
4e.



The reaction of iodonium salt **3e** (0.25 mmol, 111 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 6-bromobenzo[*d*]imidazo[5,1-*b*]thiazole **4e** as a yellowish solid, 40 mg, yield: 63%. mp = 186−188 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.78 (s, 1H), 8.21 (d, J = 1.6 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.69 (dd, J = 8.4, 2.0 Hz, 1H), 7.14 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 135.0, 130.3, 129.1, 128.5, 127.7, 127.3, 118.5, 117.5, 115.3. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_9H_5BrN_2SNa$ 274.9249; Found 274.9248.

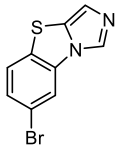
4f.



The reaction of iodonium salt **3f** (0.25 mmol, 95 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 6-methylbenzo[*d*]imidazo[5,1-*b*]thiazole **4f** as a waxy pale yellow solid, 37 mg, yield: 79%.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.54 (s, 1H), 7.75 (d, J = 8.4 Hz, 1H), 7.47 (s, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.05 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 137.8, 134.4, 130.4, 130.0, 128.5, 128.2, 125.4, 118.3, 114.2, 21.3. HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_{10}H_8N_2S$ 188.0403; Found 188.0403.

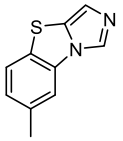
4g.



The reaction of iodonium salt **3g** (0.25 mmol, 111 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 7-bromobenzo[*d*]imidazo[5,1-*b*]thiazole **4g** as a waxy solid, 30 mg, yield: 48%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.79 (s, 1H), 8.47 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.57 (dd, J = 8.4, J = 2.0 Hz, 1H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 132.2, 132.1, 128.6, 128.4, 128.1, 126.6, 118.5, 118.5, 116.9. HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_9H_5BrN_2S$ 251.9351; Found 251.9357.

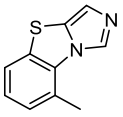
4h.



The reaction of iodonium salt **3h** (0.25 mmol, 95 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 7-methylbenzo[*d*]imidazo[5,1-*b*]thiazole **4h** as a waxy solid, 42 mg, yield: 89%. mp = 128−130 °C.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.57 (s, 1H), 7.74 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.06 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 138.1, 132.5, 131.1, 130.4, 128.4, 125.1, 118.3, 118.2, 115.1, 21.3. HRMS (EI) m/z: [M]$^{+\cdot}$ Calcd for $C_{10}H_8N_2S$ 188.0403; Found 188.0403.

4i.



The reaction of iodonium salt **3k** (0.25 mmol, 95 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 8-methylbenzo[*d*]imidazo[5,1-*b*]thiazole **4i** as a waxy pale yellow solid, 26 mg, yield: 55%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 7.74−7.69 (m, 1H), 7.31−7.29 (m, 2H), 7.18 (s, 1H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 132.7, 130.6, 129.9, 128.2, 127.8, 125.5, 125.1, 122.2,

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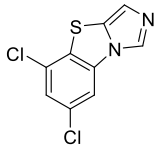
117.7, 19.5. HRMS (EI) m/z: $[M]^{+\cdot}$ Calcd for $C_{10}H_8N_2S$ 188.0403; Found 188.0403.

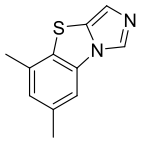
4j.



The reaction of iodonium salt **3o** (0.2 mmol, 87 mg) according to the ***general procedure*** (*scaled down to 0.2 mmol*) after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 5,7-dichlorobenzo[*d*]imidazo[5,1-*b*]thiazole **4j** as a waxy yellow solid, 24.5 mg, yield: 50%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 1H), 8.38 (d, J = 2.0 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.20 (d, J = 1.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 132.6, 131.5, 131.3, 129.2, 128.0, 126.9, 125.0, 119.3, 113.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_9H_5Cl_2N_2S$ 242.9545; Found 242.9539.

4k.



The reaction of iodonium salt **3p** (0.25 mmol, 106 mg) according to the ***general procedure*** after column chromatography (hexane:EtOAc (10:1 → 2:1)) afforded 5,7-dimethylbenzo[*d*]imidazo[5,1-*b*]thiazole **4k** as a waxy pale yellow solid, 36 mg, yield: 71%.

^{1}H NMR (400 MHz, MeOD-d_4) δ 8.51 (s, 1H), 7.52 (s, 1H), 7.05 (s, 1H), 6.99 (s, 1H), 2.41 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, MeOD-d_4) δ 138.2, 134.8, 132.2, 130.7, 130.2, 128.8, 128.6, 118.3, 112.5, 21.3, 19.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{11}N_2S$ 203.0637; Found 203.0648.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00483.

Single-crystal X-ray diffraction data for compounds **3c** and **3j** and NMR spectra for all compounds (PDF)

Accession Codes

CCDC 2058419 and 2058420 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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