Preparation and synthetic applicability of novel imidazole-containing cyclic iodonium salts.

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Abstract

The novel approach to the preparation of imidazole-substituted cyclic iodonium salts has been developed via oxidative cyclization of 1-phenyl-5-iodoimidazole using cheap and available Oxone®/H_2SO_4 oxidative system. The structure of newly prepared compounds has been proved by X-ray monocrystal diffractometry revealing the characteristic surface features for cyclic iodonium salts. The prepared compounds demonstrated the high reactivity in the heterocyclization reactions with elemental sulfur affording benzo[5,1-*b*]imidazothiazoles with good yields.

Keywords: *iodonium salts; heterocyclization; benzoimidazothiazoles; arylheteroaryliodonium; reactivity; crystal structure*

Introduction

Nowadays, the chemistry of hypervalent compounds can be considered as the one of the fastest growing field of organic chemistry.[1] The λ^3-iodanes are widely applied as oxidants[1c,2] and group-transfer reagents[3]. Indeed, one of the most applicable class of iodine(III) derivatives is the diaryliodonium salts bearing two carbon-centered aryl ligands finding utilization as a convenient sources 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 has allowed for their direct transformation into various carbo- and heterocycles via innovative synthetic sequences. Thus, very recently a range of useful synthetic methods has been developed including the transformation of CIS into the 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]. Nowadays, such hetero- and carbocyclization have become a powerful tool for the preparation of fused cyclic building-blocks. Last two years, cyclic iodonium salts become a novel family of halogen-bonding catalysts.[9]

Despite the promising synthetic applicability CIS, their potentially wider usage is a still contingent upon resolving a series of issues and challenges. For example, the evaluation of CIS structure and properties mainly has been dedicated to the carbocyclic salts,[5] leaving heterocycle-containing iodonium salts have been evaluated poorly. The first example of pyridine and quinolone substituted iodonium salts ***2*** (Fig. 1, a) were reported by Detert.[10] Shortly after, Wen and co-workers prepared a wide range of heterocyclic CISs containing chromone and thiochromone moieties ***3*** (Fig. 1, a) and explored their synthetic potential as entry points to polycyclic cores.[6a,11] Indeed, the oxidation of iodoarenes bearing 6-membered heterocyclic moieties appears to proceed more readily than that of 5-membered electron-rich heterocycles. For this reason, the CISs based on thiophene and furan have been implemented as their benzo-conjugated derivatives ***4*** (Fig. 1, a).[6f,6g,12] Indeed, the only several examples of five-membered electron-rich heterocycles connected with low availability of starting materials and complexity of iodine oxidation.[12,13] Only recently, Nachtsheim developed a facile approach to the preparation of iodine-containing heterocycles bearing pyrazole moieties ***5*** (Fig. 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 preparation of cyclic iodonium salts containing imidazolyl moiety and demonstrated the synthetic applicability of such salts in the synthesis of conjugated thienoimidazoles.

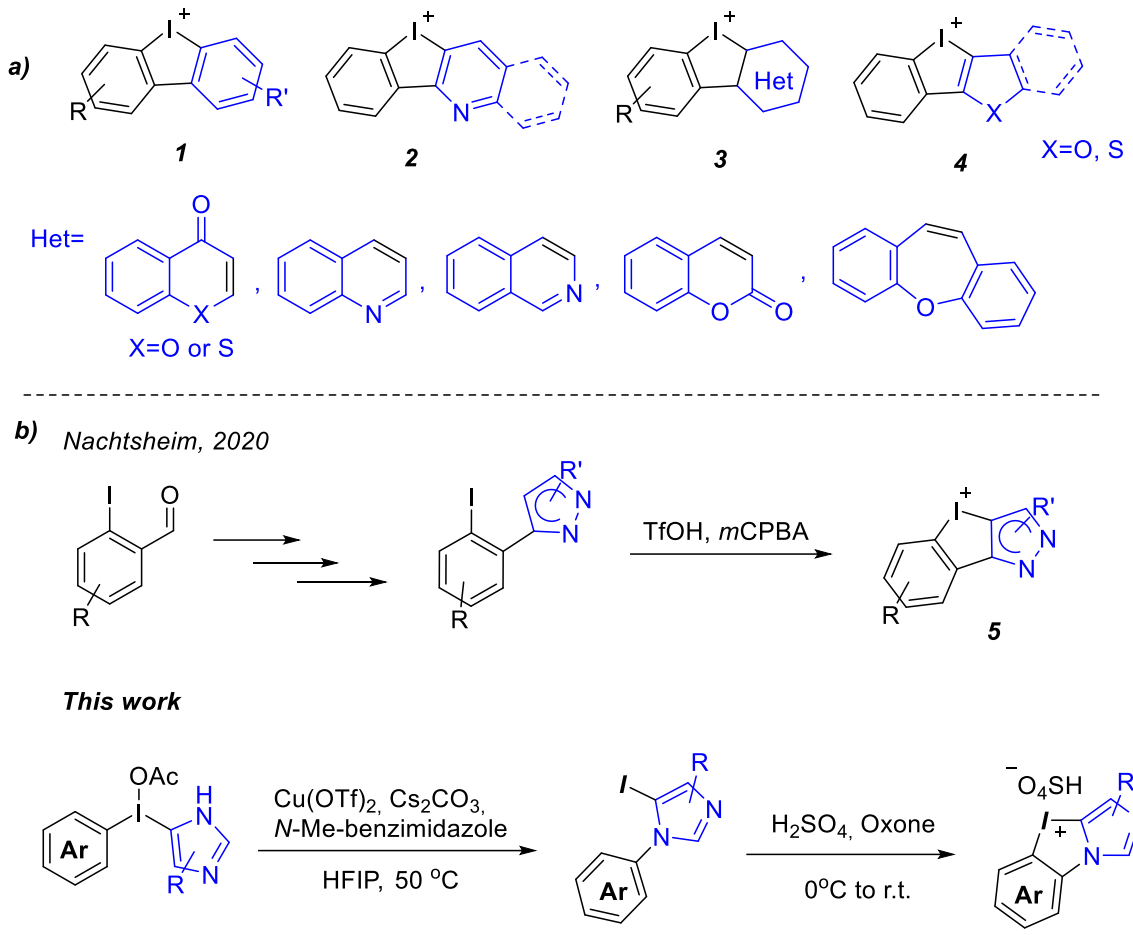


Figure 1. Examples of known cyclic iodonium salts.

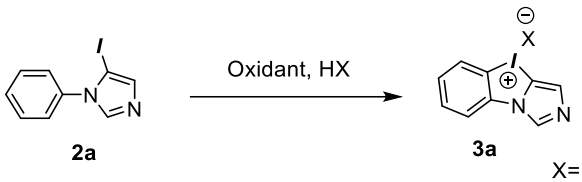
Results and discussion

The proposed synthetic pathway towards imidazole-substituted CISs is presented in Figure 1. Firstly, we proceeded to explore possible approaches for the oxidation of the iodine atom in 1-phenyl-5-iodoimidazole ***2a*** as the model substrate (Table 1). Surprisingly, 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 corresponding protonated imidazolium salts were obtained even at elevated temperature[14] (entries 1-3). This result highlight the challenge of achieving the oxidative cyclization in this system, given thatthe protonation of the imidazole nitrogen is expected to deactivate the iodine towards oxidation process. With that in mind, we tested the oxidative systems based on weaker acids such as AcOH in the presence of *m*CPBA, $NaBO_3$, $NaIO_4$ and bleach (entries 4-7). Unfortunately, we did not observe the formation of desired iodonium salt ***3a***.

These poor initial results led us to consider a peroxysulafe-based oxidant systems, in particularly the well-behaved Oxone® reagent. Indeed, the Oxone®/H_2SO_4 system is known to be efficient in the preparation of cyclic or non-cyclic iodonium salts[16]. In our case, a portionwise addition of finely grounded Oxone® to the solution of the iodoimidazole ***2a*** in H_2SO_4 under vigorous stirring led to the full consumption of starting material after 2 hours. A subsequent addition of water led to the precipitation of the desired product ***3a*** in 50% yield as a hydrogen sulfate salt Suspecting incomplete precipitation due to the solubility of iodonium hydrogen sulfates in water, we repeated

the experiment with the addition of Na_2CO_3 at the isolation stage, which led to the formation of the corresponding hydroxide form in 89% yield. Unfortunately, the extremely low solubility of this –OH form did not allow to use the common NMR spectroscopy technique for the structural characterization. Through a final round of optimization, the target ***3a***-HSO_4 was isolated in 84% via addition of a 9M solution of NaOH until only a pH of 4-5 is reached. The product is readily soluble in DMSO, and, to a lesser extent, in water and MeOH, and was used as a substrate for the further transformations.

Table 1. Optimization of the condition



2a **3a**

X= OTf, OAc, HSO_4

Entry	Oxidant	Additive / medium	Temp.	Time [h]	Yield [%][a]
1	*m*CPBA	*p*-TsOH, TFE	r.t.	24	0[b]
2	*m*CPBA	TfOH, TFE	r.t.	24	0[b]
3	*m*CPBA	TfOH, DCE	50 °C	65	0[b]
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[c]
7	$NaBO_3$	AcOH	50°C	24	0
8	Oxone®	H_2SO_4	0°C to r.t.	2	50[d,e]
9	Oxone®	H_2SO_4	0°C to r.t.	2	84[f,e]

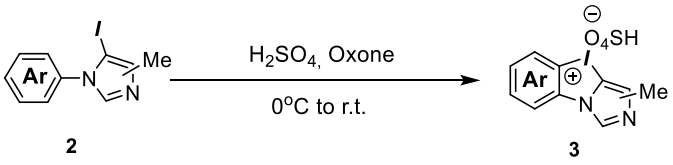
[a] Isolated yield; [b] Protonated ***2a*** was isolated; [c] Deiodination process occurred; [d] Isolation by precipitation with water, product as $^-HSO_4$ salt; [e] Reaction conditions:1-phenyl-5-iodoimidazole ***2a*** (0.5 mmol), Oxone® (0.325 mmol) in H_2SO_4 (0.8 ml) from 0° C to r.t. over 2h. [f]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

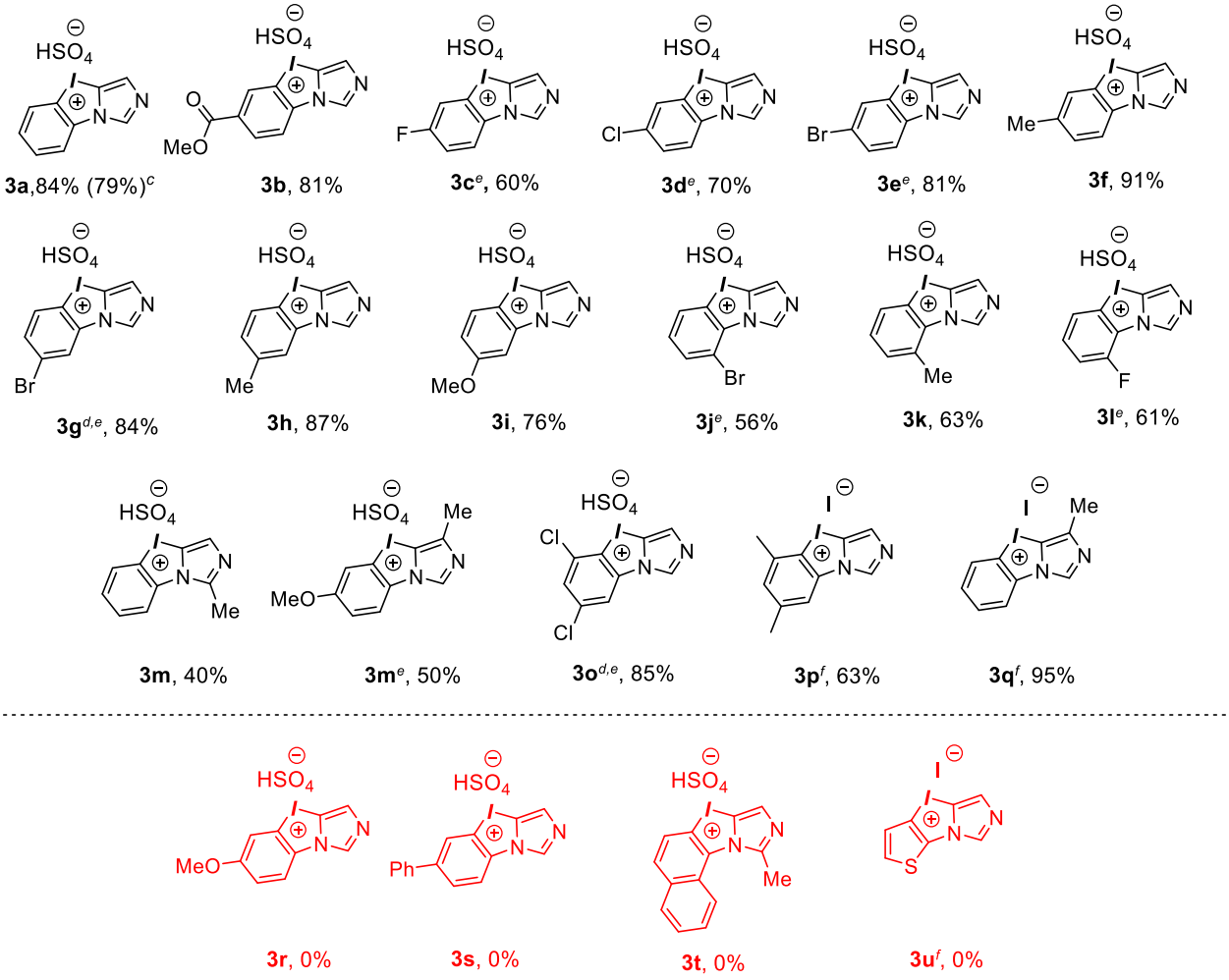
With the optimal conditions in hand, we sought to demonstrate the synthetic applicability of this approach in a broader range of 1-aryl-5-iodoimidazoles (Scheme 1). The series of substituted 1-aryl-5-iodoimidazole have been prepared by previously reported procedure[17], which can be considered as a highly straightforward method for accessing of substituted imidazoles bearing iodine in 5-position. The oxidation of 1-aryl-5-iodoimidazoles containing electron-donating groups in aryl ring proceeded smoothly with the formation of corresponding iodonium salts ***3f***, ***3h***, and ***3i*** with high yields. Under these conditions, halogen-substituted precursors (***2c-2e***, ***2g***, ***2j***, ***2l, 2o***) also underwent the oxidative cyclization, although in the initial runs the desired iodonium salts were obtained in somewhat lower yields due to incomplete conversion of starting material. Nevertheless, the addition of another portion of Oxone® and sulfuric acid to the reaction mixture allowed to achieve the full consumption of starting iodide ***2***, leading to synthetically meaningful yields of the target products (***3c-3e***, ***3g***, ***3j***, ***3l, 3o***). The oxidation of iodine was found to be sensitive to the steric hindrance both at the imidazole and the *N*-aryl ring. Thus, the 1-aryl-5-iodoimidazoles ***2j-2l*** containing substituent in *o*-position in the phenyl ring gave an ~60% yield of 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 ***3g-3i*** with the new C-I *para* to the *N*-Ar substituent group (the NMR of crude reaction mixture demonstrated less than 2% of isomer). This selectivity is likely favored by steric reasons, and is 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 the attainment of the necessary co-planarity on route the final cyclic structure. Indeed, the application of 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 naphtyl, the 4-methoxyphenyl or the 2-thienyl group. In all such cases, we observed complete consumption of starting material with the formation of a rather intractable mixture of what appears to be the over-oxidation products.

In some cases, the solubility of the prepared hydrogen sulfates salts was a critical factor for isolation and further characterization. For instance, the iodonium species ***3q*** had to be isolated as its iodide salt due to the high solubility of 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 characterization challenge.

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





[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] Isolated yields; [c] Yield for 2 mmol scale; [d] Amount of reagents was scaled down (see Experimental section); [e] Increased amount of Oxone®; [f] Isolation by addition of KI.

The crystals suitable for X-Ray study have been grown from the water solution of salts ***3c*** and ***3j*** via slow evaporation as sulfates. The crystal structures of ***3c*** and ***3j*** are demonstrated in Fig. 1 and 2. The prepared compounds exhibited the similar structural features with cyclic iodonium salts reported earlier.[16a,18] According to these X-Ray structures, the iodonium salt ***3c*** formed the dimers coordinated by two sulfate anions. Compound ***3j*** forms as a co-crystal containing a molecule of water between two such dimeric units.

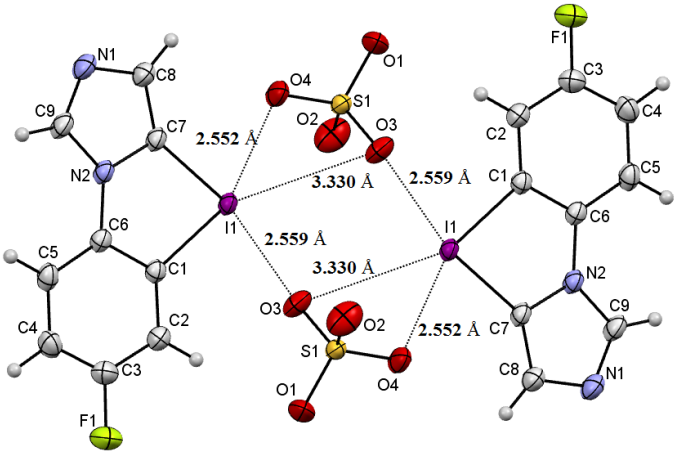


Figure 1. Crystal structure of ***3c*** showing the dimeric nature of the cyclic iodonium salt. Selective distances and angles: C1− I1 = 2.122(2) Å, C7− I1 = 2.077(2) Å, C1− C6 = 1.394(2) Å, C6 − N2 =1.408(3) Å, C7− N2= 1.388(2) Å, ∠C1−I1−C7 = 80.25(8)°, ∠I1−C7 –C8–H8 = -5.0°

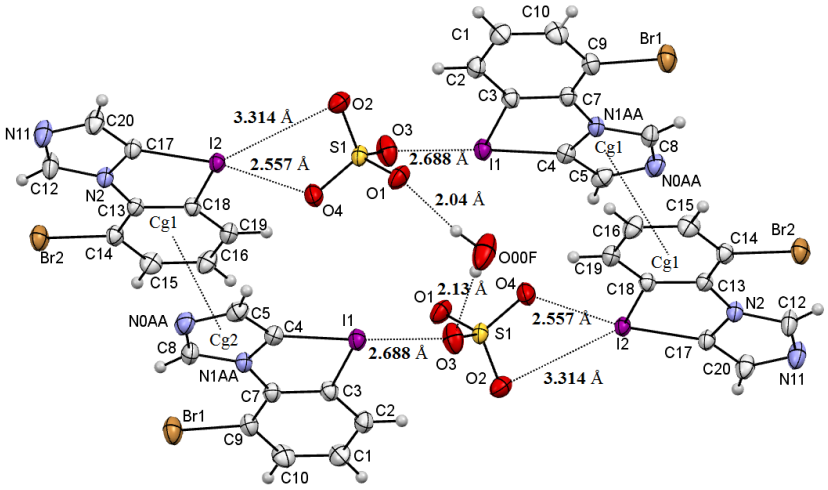
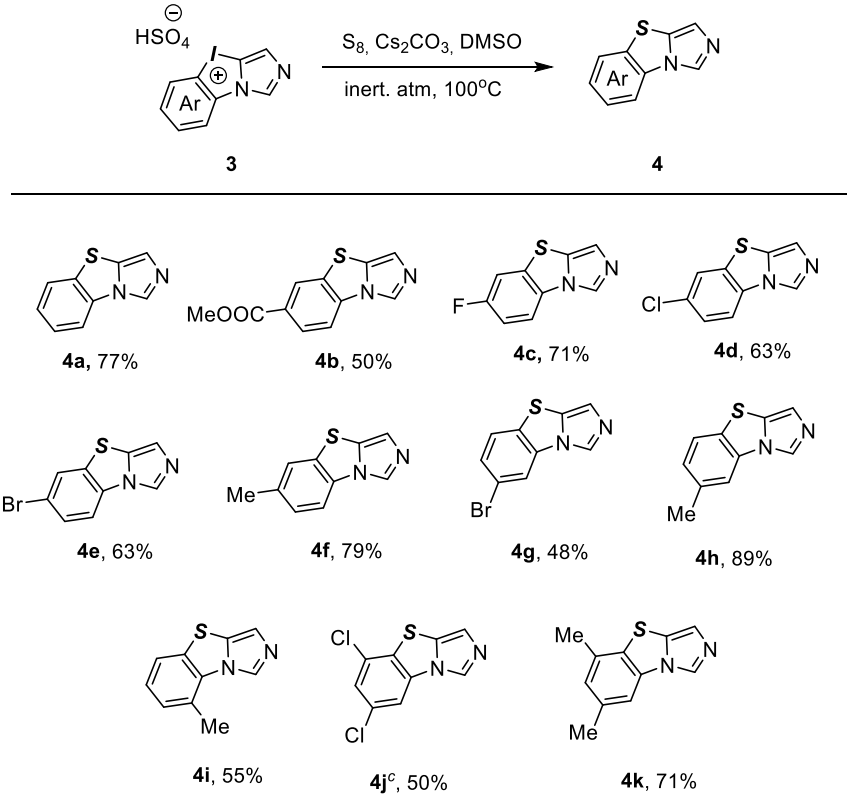


Figure 2. Crystal structure of ***3j*** showing the dimeric nature of the cyclic iodonium salt. Selective distances and angles: I1− C3 = 2.105(2) Å, I1− C4 = 2.058(2) Å, C3− C7 = 1.400(3) Å, C 4− N1AA = 1.389(3) Å, C7− N1AA= 1.418(3) Å, ∠C3−I1−C4 = 80.23(8)°, ∠I1−C4 –C5–H5= 4.5°. I2− C17= 2.078(2) Å, I2− C18 = 2.118(2) Å, Inter-stacking interactions between iodonium salts: distance between centroids Cg1− Cg2 = 3.663 Å.

In the next step, we sought to demonstrate the synthetic applicability of prepared iodonium salts in reactions of cyclization with elemental sulfur in basic conditions.[12] Such heterocyclization provides a novel way for the synthesis of benzo[5,1-b]imidazothiazoles, which have a wide application in the drug design.[19] The described methods of benzo[5,1-b]imidazothiazoles avoids the use of metal-based catalysts,[19,20] and appears open an interesting path towards heteroatom-doped polycyclic aromatics.

The reaction has been conducted in previously published conditions in DMSO using elemental sulfur as a radical source in the presence of Cs_2CO_3. The heating of reaction mixture led to the formation of blue solution indicating the formation of trisulfide radical.[12] The full conversion of starting materials has been achieved after 4 hours. In general, the yield of target product ***4*** did not show a clear dependence on the electronic nature of the N-aryl moiety. Slight decrease in yield has been observed for the *ortho*-substituted iodonium salts due to steric hindrance.

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



[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] Isolated yields; [c] Amount of reagents was scaled down (see Experimental section).

Surprisingly, the iodonium salts ***3m***, ***3n***, ***3q*** bearing substituent in the imidazolyl moiety were not prone to heterocyclization under such conditions. We isolated only reduction products – appropriate 1-aryl-5-iodoimidazoles. Salts ***3j*** and ***3l*** demonstrated the similar behavior: the formation of desired benzo[5,1-b]imidazothiazoles has been detected by GC-MS chromatography, but the presence of reduced ISs hampered isolation procedure. Thus, such benzothiazoles have not been isolated in 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 available and cheap Oxone® in sulfuric acid followed by a traightforward precipitation of the desired compounds by NaOH solution. The crystal structure of isolated compounds revealed the typical dimeric structure for cyclic iodonium cations coordinated by two sulfate anions. The prepared salts demonstrated the considerable reactivity in

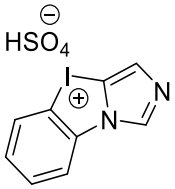
the heterocyclization with elemental sulfur with the formation of benzo[5,1-b]imidazothiazoles with good and high yields. We believe that our study will shed light on the reactivity of cyclic iodonium salts and will be interesting for the wide range of chemists.

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 residual solvent signal. High resolution mass spectra were recorded on maXis spectrometer and MicroTOF-Q both from Bruker Daltronics with electrospray ionization (ESI) in positive mode and 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 MoK_{α} radiation (λ = 0.71073 Å) using the φ and ω scans technique. The structures were solved and refined by direct methods using the SHELX[21]. Data were corrected for absorption effects using the multi-scan method (SADABS)[22]. All non-hydrogen atoms were refined anisotropically using SHELX[21]. The coordinates of the hydrogen atoms were calculated by mixed methods. Crystal data and experimental details are given in 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 (2058419-2058420). All starting materials (diaryliodonium salt and 1-aryl-5-iodoimidazoles) were prepared according to slightly modified published procedure[17].

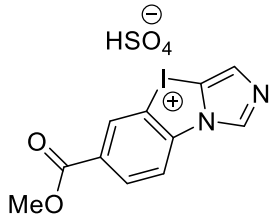
Synthesis of cyclic iodonium salts 3a-3q

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 ^{o}C. Then, finely grounded 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^{o}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) 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 9M NaOH solution was added dropwise with cooling by ice-water bath until the appearance of the precipitate (approx. 2-2.5 ml for 0.8 ml of H_2SO_4); the resulting suspension was allowed to stir for 1 hour 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.



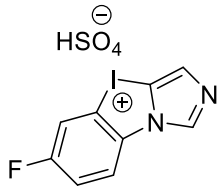
3a*:** The reaction of 1-phenyl-5-iodoimidazole ***2a (0.5 mmol, 135 mg) with one portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded benzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3a*** as white solid, 154 mg, yield: 84%. mp = 201-203^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6) 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/Q-TOF, positive ionization): calcd for $C_9H_6IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 268.9570, found: 268.9580.



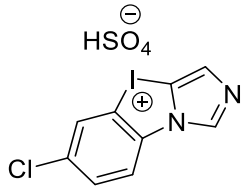
3b*:** The reaction of methyl 4-(5-iodo-imidazol-1-yl)benzoate ***2b (0.5 mmol, 164 mg) with additional portion of Oxone® *(0.2 g and 0.3 g respectively for the first and the second batch of the oxidant*) in H_2SO_4 *(0.8 ml for both portions*) according to ***general procedure*** afforded 6-(methoxycarbonyl)benzo[d]imidazo[5,1-b][1,3]iodazol-4-ium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

^{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/Q-TOF, positive ionization): calcd for $C_{11}H_8IN_2O_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 326.9625, found: 326.9625.



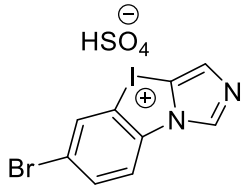
3c*:** The reaction of 1-(4-fluorophenyl)-5-iodoimidazole ***2c (0.5 mmol, 144 mg) with additional portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 6-fluorobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3c*** as off-white solid, 115 mg, yield: 60%. mp = 224-227ºC.

^{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/Q-TOF, positive ionization): calcd for $C_9H_5FIN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 286.9476, found: 286.9462.



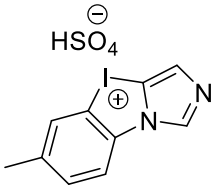
3d*:** The reaction of 1-(4-chlorophenyl)-5-iodoimidazole ***2d (0.5 mmol, 153 mg) with additional portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 6-chlorobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3d*** as off-white solid, 140 mg, yield: 70%. mp = 243-245ºC.

^{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/Q-TOF, positive ionization): calcd for $C_9H_5ClIN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 302.9180, found: 302,9165.

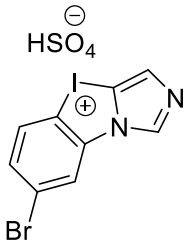


3e*:** The reaction of 1-(4-bromophenyl)-5-iodoimidazole ***2e (0.5 mmol, 175 mg) with additional portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 6-bromobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3e*** as pale brown solid, 180 mg, yield: 81%. mp = 255-258ºC.

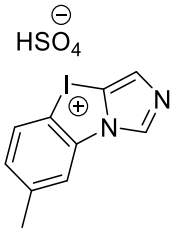
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 2,0 Hz, 1H), 8.06 (dd, J = 8.8, 2.0 Hz, 1H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.0, 134.8, 134.6, 133.1, 131.6, 119.4, 118.7, 113.8, 98.5. HRMS (ESI/Q-TOF, positive ionization): calcd for $C_9H_5BrIN_2^+$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



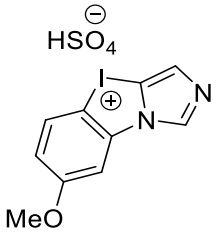
3f*:** The reaction of 1-(4-methylphenyl)-5-iodoimidazole ***2f (0.5 mmol, 142 mg) with one portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 6-methylbenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3f*** as off-white solid, 173 mg, yield: 91%. mp = 231-233ºC.
^{1}H 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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 282.9727, found: 282.9713.



3g*:** The reaction of 1-(3-bromophenyl)-5-iodoimidazole ***2g (0.39 mmol, 137 mg) with additional portion of Oxone® in H_2SO_4 (*scaled down to 0.39 mmol of* ***2g***) according to ***general procedure*** afforded 7-bromobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3g*** as off-white solid, 145 mg, yield: 84%. mp = 244-247ºC.
^{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/Q-TOF, positive ionization): calcd for $C_9H_5BrIN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 346.8675, found: 346.8678.

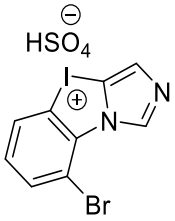


3h*:** The reaction of 1-(3-methylphenyl)-5-iodoimidazole ***2h (0.5 mmol, 142 mg) with one portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 7-methylbenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3h*** as white solid, 165 mg, yield: 87%. mp = 245-246ºC.
^{1}H NMR (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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 282.9727, found: 282.9726.

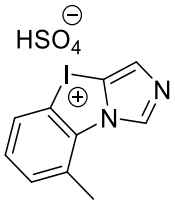


3i*:** The reaction of 1-(3-methoxyphenyl)-5-iodoimidazole ***2i (0.5 mmol, 150 mg) with one portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 7-

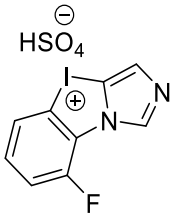
methoxybenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3i*** as off-white solid, 150 mg, yield: 76%. mp = 251-253ºC.
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 7.98 (d, *J* = 2.8 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.38 (s, 1H), 7.12 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.91 (s, 3H). ^{13}C 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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2O^+$ (m/z: $[M\text{-}HSO_4]^+$): 298.9676, found: 298.9665.



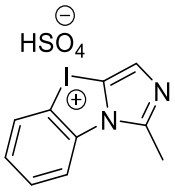
3j**:** The reaction of 1-(2-bromophenyl)-5-iodoimidazole ***2j*** (0.5 mmol, 175 mg) with additional portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 8-bromobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3j*** as off-white solid, 125 mg, yield: 56%. mp = 179-181ºC.
^{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/Q-TOF, positive ionization): calcd for $C_9H_5BrIN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 346.8675, found: 346.8676.



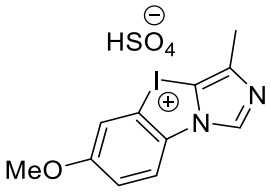
3k**:** The reaction of 1-(2-methylphenyl)-5-iodoimidazole ***2k*** (0.5 mmol, 142 mg) with one portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 8-methylbenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3k*** as off-white solid, 119 mg, yield: 63%. mp = 215-217ºC.
^{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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 282.9727, found: 282.9731.



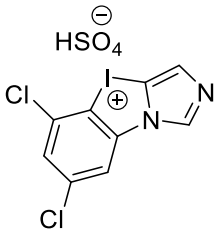
3l**:** The reaction of 1-(2-fluorophenyl)-5-iodoimidazole ***2l*** (0.5 mmol, 145 mg) with additional portion of Oxone® in H_2SO_4 according to ***general procedure*** afforded 8-fluorobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3l*** as off-white solid, 118 mg, yield: 61%. mp = 244-247ºC.
^{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 - -120.1 (m). HRMS (ESI/Q-TOF, positive ionization): calcd for $C_9H_5FIN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 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 ***general procedure*** afforded 1-methylbenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3m*** as off-white solid, 154 mg, yield: 40%. mp = 203-206ºC.
^{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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 282.9727, found: 282.9751.

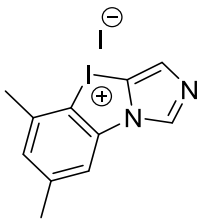


3n*:** The reaction of 1-(4-methoxyphenyl)-4-methyl-5-iodoimidazole ***2n (0.5 mmol, 157 mg) with additional portion of Oxone® *(0.2 g and 0.3 g respectively for the first and second batch of the oxidant*) in H_2SO_4 *(0,8 ml for both portions*) according to ***general procedure*** afforded 6-methoxy-3-methylbenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3n*** as pale brown solid, 103 mg, yield: 50%. mp = 225-227ºC.
^{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/Q-TOF, positive ionization): calcd for $C_{11}H_{10}IN_2O^+$ (m/z: $[M\text{-}HSO_4]^+$): 312.9832, found: 312.9838.



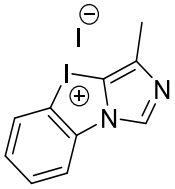
3o*:** The reaction of 1-(3,5-dichlorophenyl)-5-iodoimidazole ***2o (0.3 mmol, 102 mg) with additional portion of Oxone® in H_2SO_4 (*scaled down to 0.3 mmol*) according to ***general procedure*** afforded 5,7-dichlorobenzo[d]imidazo[5,1-b][1,3]iodazol-4-ium hydrogen sulfate ***3o*** as off-white solid, 110 mg, yield: 85%. mp = 205-208ºC.
^{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/Q-TOF, positive ionization): calcd for $C_9H_4Cl_2IN_2^+$ (m/z: $[M\text{-}HSO_4]^+$): 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 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 9M NaOH was added. Then reaction mass was diluted with water to the volume of 50 ml and KI (1.5 eq., 124 mg) in 2 ml of water was added. 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 yellow solid, 134 mg, yield: 63%. mp = 164-167ºC.

^{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/Q-TOF, positive ionization): calcd for $C_{11}H_{10}IN_2^+$ (m/z: $[M-I]^+$): 296.9883, found: 296.9883.

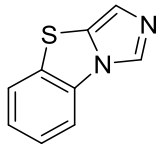


3q*:** Oxone® (0.325 mmol, 200 mg) was added under cooling with ice-water bath to the stirring solution of 4-methyl-1-phenyl-imidazole ***2q (0.5 mmol. 142 mg) in H_2SO_4 (0.8 ml). After the full conversion of the starting material the reaction mass was diluted with ice and water and only 1-1.5 ml of 9M NaOH was added. Then reaction mass was diluted with water to the volume of 50 ml and KI (1.5 eq., 124 mg) in 2 ml of water was added. 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 yellow solid, 195 mg, yield: 95%. mp = 126-129ºC.

^{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/Q-TOF, positive ionization): calcd for $C_{10}H_8IN_2^+$ (m/z: $[M-I]^+$): 282.9727, found: 282.9731.

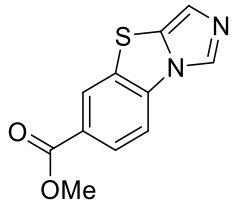
Synthesis of benz[d]imidazo[5,1-b]thiazoles 4a-4k.

General procedure (described for 0.25 mmol scale): *Reactions proceeded under argon atmosphere.* Schlenk tube equipped with 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 stream of argon and the mixture was allowed to react at 100ºC for 4 hours. The reaction mass was cooled to room temperature and diluted with water. Aqueous layer was extracted with EtOAc. Combined organic layer was dried over $MgSO_4$ and solvent was removed. Crude product was purified by column chromatography (hexane:ethylacetate – 10:1 to hexane:ethylacetate – 2:1).



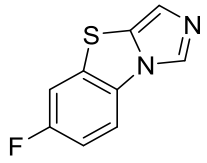
4a*:** The reaction of iodonium salt ***3a (0.25 mmol, 91.5 mg) according to ***general procedure*** afforded benzo[d]imidazo[5,1-b]thiazole ***4a*** as pale yellow solid, 33.5 mg, yield: 77%. mp = 99-101°C.

^{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/Q-TOF, positive ionization): calcd for $C_9H_6N_2SNa^+$ (m/z: $[M+Na]^+$): 197.0149, found: 197.0145.



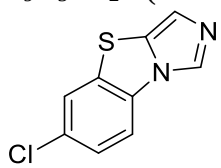
4b*:** The reaction of iodonium salt ***3b (0.25 mmol, 96 mg) according to ***general procedure*** afforded methyl benzo[d]imidazo[5,1-b]thiazole-6-carboxylate ***4b*** as waxy pale brown solid, 29 mg, yield: 50%.

^{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/Q-TOF): calcd for $C_{11}H_8N_2O_2S$ (m/z: $[M]^+$): 232.0301, found: 232.0301.



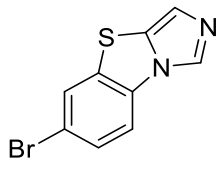
4c*:** The reaction of iodonium salt ***3c (0.25 mmol, 96 mg) according to ***general procedure*** afforded 6-fluorobenzo[d]imidazo[5,1-b]thiazole ***4c*** as waxy yellow solid, 34 mg, yield: 71%.

^{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 – -115.9 (m). HRMS (EI/Q-TOF): calcd for $C_9H_5FN_2S$ (m/z: $[M]^+$): 193.0230, found: 193.0230.



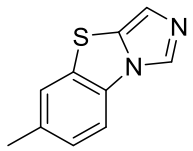
4d*:** The reaction of iodonium salt ***3d (0.25 mmol, 100 mg) according to ***general procedure*** afforded 6-chlorobenzo[d]imidazo[5,1-b]thiazole ***4d*** as pale yellow solid, 39 mg, yield: 63%. mp = 165-168°C (recrystallized sample).

^{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/Q-TOF, positive ionization): calcd for $C_9H_5ClN_2S^+$ (m/z: $[M+H]^+$): 208.9935, found: 208.9936.



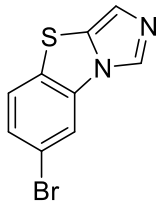
4e*:** The reaction of iodonium salt ***3e (0.25 mmol, 111 mg) according to ***general procedure*** afforded 6-bromobenzo[d]imidazo[5,1-b]thiazole ***4e*** as yellowish solid, 40 mg, yield: 63%. mp = 186-188°C.

^{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/Q-TOF, positive ionization): calcd for $C_9H_4BrN_2SNa^+$ (m/z: $[M+Na]^+$): 274.9249, found: 274.9248.



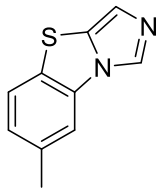
4f*:** The reaction of iodonium salt ***3f (0.25 mmol, 95 mg) according to ***general procedure*** afforded 6-methylbenzo[d]imidazo[5,1-b]thiazole ***4f*** as waxy pale yellow solid, 37 mg, yield: 79%.

^{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/Q-TOF): calcd for $C_{10}H_8N_2S^+$ (m/z: $[M]^+$): 188.0403, found: 188.0403.



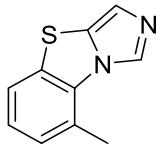
4g*:** The reaction of iodonium salt ***3g (0.25 mmol, 111 mg) according to ***general procedure*** afforded 7-bromobenzo[d]imidazo[5,1-b]thiazole ***4g*** as waxy solid, 30 mg, yield: 48%.

^{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/Q-TOF): calcd for $C_9H_5BrN_2S^+$ (m/z: $[M]^+$): 251.9357, 253.9336, found: 251.9351, 253.9331.



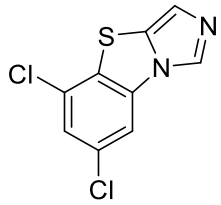
4h*:** The reaction of iodonium salt ***3h (0.25 mmol, 95 mg) according to ***general procedure*** afforded 7-methylbenzo[d]imidazo[5,1-b]thiazole ***4h*** as waxy solid, 42 mg, yield: 89%. mp = 128-130°C.

^{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/Q-TOF): calcd for $C_{10}H_8N_2S^+$ (m/z: $[M]^+$): 188.0403, found: 188.0403.



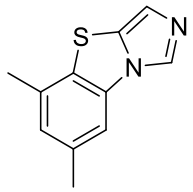
4i*:** The reaction of iodonium salt ***3k (0.25 mmol, 95 mg) according to **general procedure** afforded 8-methylbenzo[d]imidazo[5,1-b]thiazole ***4i*** as waxy pale yellow solid, 26 mg, yield: 55%.

^{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, 117.7, 19.5. HRMS (EI/Q-TOF): calcd for $C_{10}H_8N_2S^+$ (m/z: $[M]^+$): 188.0403, found: 188.0403.



4j*:** The reaction of iodonium salt ***3o (0.2 mmol, 87 mg) according to ***general procedure*** *(scaled down to 0.2 mmol)* afforded 5,7-dichlorobenzo[d]imidazo[5,1-b]thiazole ***4j*** as 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/Q-TOF, positive ionization): calcd for $C_9H_5Cl_2N_2S^+$ (m/z: $[M+H]^+$): 242.9539, found: 242.9545.



4k*:** The reaction of iodonium salt ***3p (0.25 mmol, 106 mg) according to ***general procedure*** afforded 5,7-dimethylbenzo[d]imidazo[5,1-b]thiazole ***4k*** as 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/Q-TOF, positive ionization): calcd for $C_{11}H_{10}N_2S^+$ (m/z: $[M+H]^+$): 203.0637, found: 203.0637.

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