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Very Important Publication

Dehydrogenative Cycloisomerization/Arylation Sequence of *N*-Propargyl Carboxamides with Arenes by Iodine(III)-Catalysis

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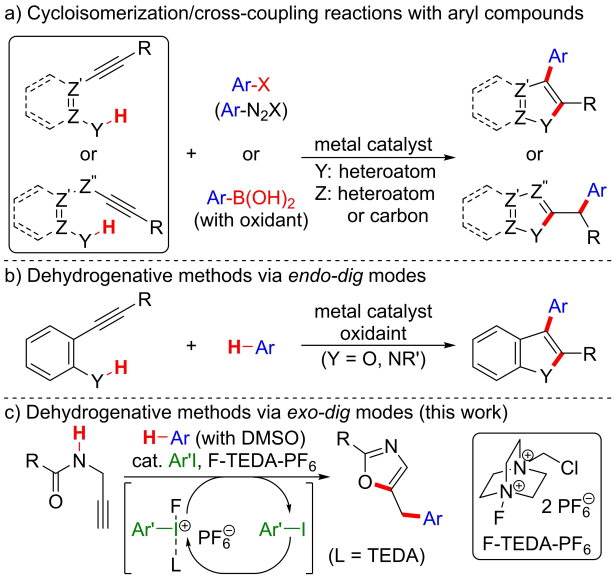
Abstract: Dehydrogenative cycloisomerization/arylation sequence of heteroatom nucleophile-tethered unactivated alkynes provides a facile and powerful approach to C–C bond formation between the generated heterocycles and unfunctionalized arenes. Here, we describe a hypervalent iodine(III)-catalyzed synthesis of oxazoles concomitant with the introduction of aryl groups into side chain from *N*-propargyl carboxamides and arenes, representing first C(sp^3)–C(sp^2) bond formation by the catalytic dehydrogenative cycloisomerization/arylation reaction in *exo-dig* modes.

Keywords: arylation; catalysis; cyclization; iodine; metal-free

Cycloisomerization and its tandem reactions of heteroatom nucleophile-tethered unactivated alkynes provides a facile and powerful approach to construction of heterocycles accompanying structural complexity.[1] Among them, the transition-metal-catalyzed tandem cycloisomerization/cross-coupling reactions with coupling partners such as aryl halides[2] and aryl diazonium salts[3] or nucleophiles such as arylboronic acids[4] allow C(sp^2)–C(sp^2) or C(sp^3)–C(sp^2) bond formation between the generated heterocycles and arenes (Scheme 1a). In addition, the reactions of cyclization precursors having leaving groups such as alkynyl azides[5a,b] and others[5c] with arenes have been reported for the facile synthesis of arylated heterocycles. However, these reactions require prefunctionalizations of alkyne substrates and/or coupling partners as tedious synthetic steps.

In consideration of reducing the number of synthetic steps and the production of waste, dehydrogenative C–H activation methods[6] have been developed for cycloisomerization/cross-coupling reactions of the unfunctionalized substrates with arenes[7] or other coupling partners.[8] Although the dehydrogenative cycloisomerization/arylation sequence in *endo-dig* modes have been achieved (Scheme 1b),[7,8] the *exo-dig* version[7d,e] leading to C(sp^3)–C(sp^2) bond formation have been unknown. Herein, we report a hypervalent iodine(III)-catalyzed dehydrogenative *exo*-cycloisomerization/cross-coupling reaction of *N*-propargyl carboxamides with unfunctionalized arenes (Scheme 1c).

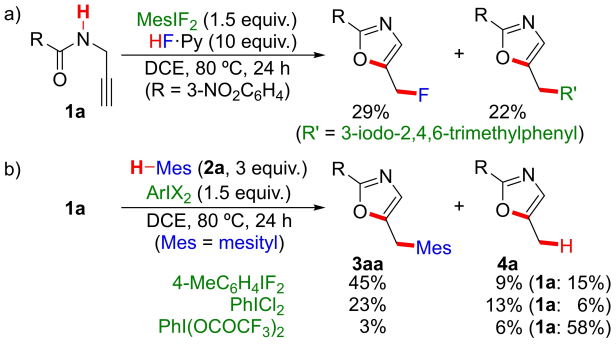
Hypervalent iodine(III) compounds have been emerged as an efficient reagent in the dehydrogenative C–C bond formations[9] such as cross-coupling reactions of arenes with different kinds of arenes,[10] aldehydes,[11a] active methines[11b] or simple alkanes,[11c] arylation of alkenes[12a,b] or alkynes,[12c,d] and iodonio-Claisen rearrangement.[13] Some of these dehydrogenative reactions have been extended to the iodine(III)-catalysis.[14] Nevertheless, the catalytic intermolecular arylation process has been limited to the cross-coupling reactions between the arenes.[14a–c] Furthermore, the *exo*-cycloisomerization/carbon-functionalization reactions of *N*-propargyl carboxamides have been developed for the effective and versatile synthesis of 2,5-disubstituted oxazoles[15a–c,e] or 5-alkylideneoxazolines,[15d–g] which are prevalent in many natural products and pharmaceutically active compounds.[1c,d] Unfortunately, except for the synthesis of dimeric ketones,[15e] only the tandem reaction via



Scheme 1. Catalytic cycloisomerization/arylation reactions.

carbonylation step has been known as the dehydrogenative method for the formation of oxazolines.[15d] Therefore, the development of the dehydrogenative cycloisomerization/arylation sequence of *N*-propargyl carboxamides (Scheme 1c) seemed challenging, but could be achieved by further research based on the findings of previous studies.[16]

In the previous study on the fluorocyclization of *N*-propargyl carboxamides using fluoro-λ^3-iodanes,[16b] we noticed the introduction of iodoarenes derived from difluoro(mesityl)-λ^3-iodane into oxazole products as a side reaction (Scheme 2a). In addition, in the preliminary experiments aiming at the comparison with other iodanes having chlorine or acyloxy ligands, it was found out that fluoroiodane was relatively effective on the dehydrogenative cycloisomerization/arylation reaction of *N*-propargyl amide **1a** with mesitylene (**2a**, 3 equiv.) in DCE (1,2-dichloroethane) under refluxing conditions (Scheme 2b, see also Scheme S1 in Supporting Information (SI)). Thus, we envisioned that a

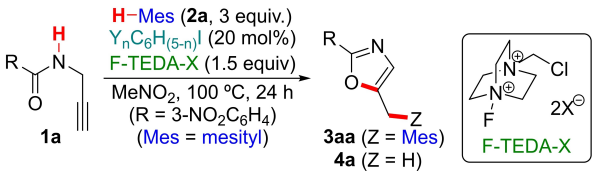


Scheme 2. Reactions of **1a** with **2a** using $ArIX_2$.

fluoroiodane-amine complex, which is catalytically generated from an iodoarene precatalyst and Selectfluor® (F-TEDA-BF_4) or its analogues (F-TEDA-X),[16a,b] would show its efficiency in the cycloisomerization/arylation reaction of *N*-propargyl amides. In addition, since the cyclized products **4a** were assumed to be formed by the produced acids,[17] amines derived from F-TEDA-X were expected to scavenge the acids.

Based on the above-mentioned results and working hypothesis, we initially evaluated iodoarenes (20 mol%) and F-TEDA-X (1.5 equiv.) for the cycloisomerization/arylation reaction of **1a** with **2a** (Table 1). The use of 4-iodotoluene with F-TEDA-BF_4 in $MeNO_2$ gave the desired product **3aa** in 18% yield at 100 °C for 24 h (entry 1), albeit **3aa** was obtained in lower yield or was not obtained in DCE or other solvents (MeCN, HFIP, THF, acetone, DMF, DMSO, see Table S1 in SI). When highly Me-substituted and

Table 1. Optimization of the reaction conditions.



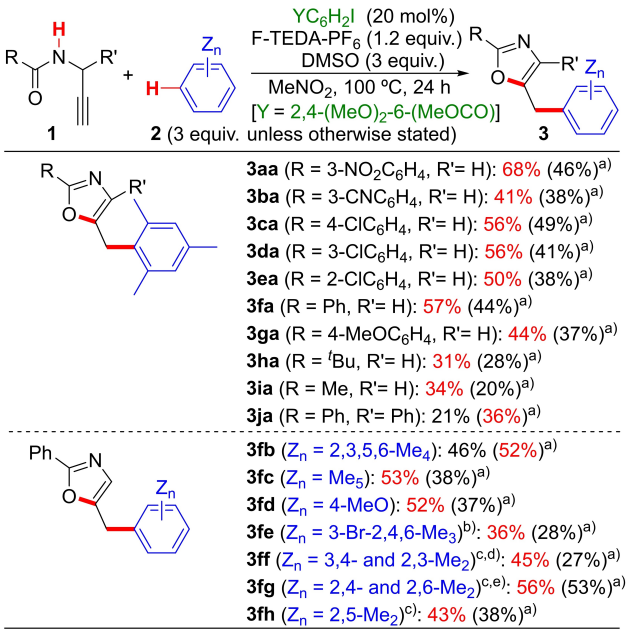
entry	Y_n	X	Yield[a] [%] 3aa	4a	1a[a] [%]
1	4-Me	BF_4	18	5	11
2	2,4,6-Me_3	BF_4	19	0	19
3	Me_5	BF_4	28	2	14
4	4-MeO	BF_4	25	0	25
5	2,4,6-$(MeO)_3$	BF_4	35	9	0
6	2,3,4,6-$(MeO)_4$	BF_4	13	0	55
7	2,4,6-$(MeO)_3$	PF_6	40	10	0
8	2,4-$(MeO)_2$-6-E	PF_6	45[b]	17[b]	0
9[c]	2,4-$(MeO)_2$-6-E	PF_6	46[b]	26[b]	0
10	2,4-$(MeO)_2$-6-E	BF_4	31	6	0
11	2,4-$(MeO)_2$-6-E	OTf	29	3	29
12	2,4-$(MeO)_2$-6-E	NTf_2	46	5	0
13[d]	2,4-$(MeO)_2$-6-E	–	0	3	80
14[c,e]	2,4-$(MeO)_2$-6-E	PF_6	57[b]	11[b]	0
15[f]	2,4-$(MeO)_2$-6-E	PF_6	68[b]	16[b]	0
16[g]	2,4-$(MeO)_2$-6-E	PF_6	60	12	0
17	2,4-$(MeO)_2$-6-E	–	0	0	quant.
18[f]	–	PF_6	<1	29	58

E = MeOCO.
[a] Values were determined by ^{1}H NMR analysis using AcOMe as an internal standard.
[b] Isolated yields.
[c] F-TEDA-X: 1.2 equiv.
[d] *m*CPBA (1.5 equiv.) was used instead of F-TEDA-X.
[e] Additive: DMSO (3 equiv.).
[f] DMSO (3 equiv.) was pretreated with F-TEDA-PF_6 (1.2 equiv.) at 100 °C for 1 h in $MeNO_2$.
[g] Ph_2SO instead of DMSO (footnote f).

MeO-substituted iodoarenes were employed as a precatalyst, the yields of **3aa** were improved (entries 2–7). In particular, 2,4,6-$(MeO)_3C_6H_2I$ in the presence of F-TEDA-BF_4 and F-TEDA-PF_6 afforded **3aa** in 35% and 40% yields, respectively (entries 5 and 7). Since it was concerned that the generated MeO-substituted fluoroiodane-amine catalyst was gradually decomposed due to its instability,[16a] we checked iodoarenes with the introduction of coordinating substituents at their *ortho*-positions[18] (Table S2 in SI for details). Consequently, by using 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ in the presence of F-TEDA-PF_6 (1.2 equiv.), **3aa** was obtained in 46% yield, albeit along with **4a** in 26% yield (entry 9). Among other F-TEDA-X (entries 10–12), F-TEDA-NTf_2 (1.5 equiv.) led to the similar yield of **3aa** but exhibited poor mass balance (entry 12). Also, the use of *m*CPBA (1.5 equiv.), which has been commonly employed for the iodine(III) catalysis,[10a,b,14a,c–g] instead of F-TEDA-X brought about the reduced yield of **3aa** because of the homo-coupling of **2a** (entry 13).

Subsequently, we expected the improved yield of **3aa** by suppressing the formation of **4a** in the catalytic system using F-TEDA-PF_6 (entry 9) and thus attempted the addition of amines or other additives (Table S3 in SI for details). As a result, the addition of sulfoxide (3 equiv.) such as DMSO and Ph_2SO improved the yield of **3aa**, although the formation of **4a** could not be completely suppressed (entries 14–16). Particularly, when DMSO was treated with F-TEDA-PF_6 at 100 °C for 1 h in $MeNO_2$ before the addition of substrates and precatalyst, **3aa** was obtained in good yield (68%, entry 15). It should be mentioned that the removal of F-TEDA-PF_6 (entry 17) and iodoarene precatalyst (entry 18) from the optimized conditions (entry 15) did not produce **3aa**.

With the optimized conditions in hand, we next investigated the scope of the reaction using various *N*-propargyl amides **1a–i** and arenes **2a–h** (Scheme 3). Similar to **1a**, aromatic amides **1c-f** smoothly reacted with mesitylene (**2a**, 3 equiv.) to give the corresponding arylated oxazoles **3ca–3fa** in 50–57% yields. Also, the cyano-substituted **1b**, the MeO-substituted **1g**, aliphatic amides **1h** and **1i** were converted to the desired oxazoles **3ga–3ia**, albeit in relatively lower yields (31-44%). These lower yields may be due to the reduced efficiency for the activation of alkynes by fluoroiodane species through the coordination of cyano group of **1b** and aminocarbonyl groups of **1g–1i** having relatively high Lewis basicity. Similar results were observed in our previous study on the fluorocyclization of *N*-propargyl amides.[16a,b] Furthermore, the present catalytic systems could be applied to the reaction of **1j** having Ph-substituent at the propargyl position with mesitylene (**2a**) and the reaction of **1f** with various arenes **2b–h**. Although the increased amount of 2-bromomesitylene (**2e**, 5 equiv.) and

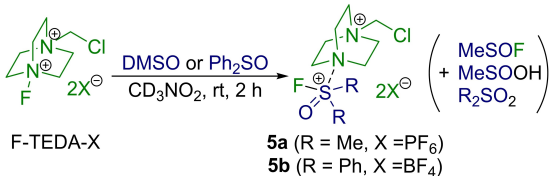


a) Values in parenthesis show yields in the absence of DMSO.
b) **2e**: 5 equiv. c) **2f-h**: 20 equiv. d) 3,4-Me_2:2,3-Me_2 = 2:1.
e) 2,4-Me_2:2,6-Me_2 = 6:1.

Scheme 3. Scope of substrates **1** and coupling partners **2**.

xylenes **2f–h** (20 equiv.) was required, the arylated oxazoles **3fb–3fh** were obtained in 36–56%. Notably, in all cases except for the formation of **3ja** and **3fb** (see yields in parenthesis), the addition of DMSO was found out to be effective on the present catalysis.

To obtain insights into the additive effects of DMSO, we checked an active species generated from sulfoxide and F-TEDA-X (Scheme 4). When DMSO was exposed to F-TEDA-PF_6 in CD_3NO_2 at rt for 2 h, F-TEDA-PF_6 was consumed completely and the corresponding peaks of fluoro-λ^6-sulfane **5a** and MeSOF[19] were appeared in ^1H and ^{19}F NMR spectra (Figure S1 and S2 in SI for details). However, the molecular ion peak of **5a** was not detected in ESI-Mass spectrum likely because of its instability. On the other hand, Ph_2SO was treated with F-TEDA-BF_4 or F-TEDA-PF_6 in CD_3NO_2 or CH_3NO_2 under the similar conditions to give the corresponding peaks of fluoro-λ^6-sulfane **5b**[20] in ^1H and ^{19}F NMR spectra (Figure S3 and S4) as well as the molecular ion peak of **5b** in

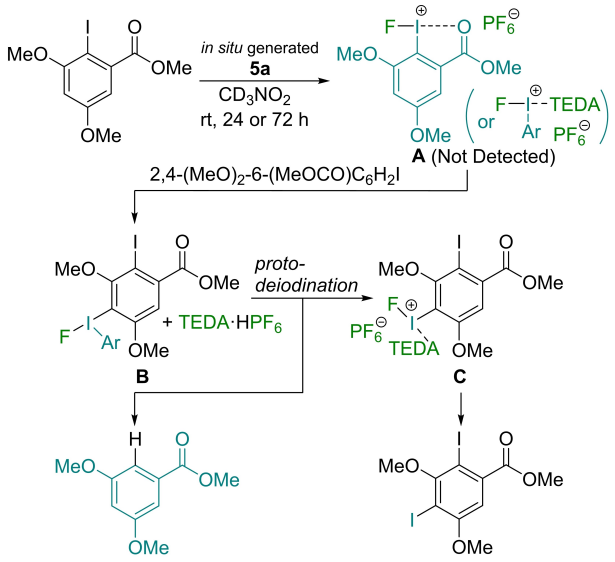


Scheme 4. Formation of fluoro-λ^6-sulfane **5**.

ESI-Mass spectrum (Figure S5). Hence, these results indicate that fluoro-λ^6-sulfane **5a** would be the active species (Scheme 4).

In order to confirm fluoro-λ^6-sulfane **5** works as an oxidant, we next attempted the isolation of iodine(III) species **A** derived from 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ and **5a**. However, when the iodoarene was exposed to **5a** *in situ* generated from DMSO and F-TEDA-PF_6, the iodoarene was consumed at 100 °C giving rise to a complex mixture. Therefore, the time-course ^1H NMR analysis was carried out using a mixture of *in situ* generated **5a** and 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ in CD_3NO_2 at room temperature (Scheme 5, see also Figure S6 and S7 in SI for details). In the spectrum 24 h after the sample preparation, the peaks of λ^3-iodane like hydrolysis derivative of **A** clearly appeared along with those of methyl 3,5-dimethoxybenzoate and 1,3-I_2-2,4-$(MeO)_2$-6-$(MeOCO)C_6H$. In 72 h, **5a** was consumed completely and the intensity of peaks of 3,5-dimethoxybenzoate were increased by a factor of about two, although the intensity of the above-mentioned λ^3-iodane and 1,3-I_2-2,4-$(MeO)_2$-6-$(MeOCO)C_6H$ was unchanged. Hence, these results suggest that **5a** would works as the oxidant of the iodoarene.

As for the formation of 3,5-dimethoxybenzoate and 1,3-I_2-2,4-$(MeO)_2$-6-$(MeOCO)C_6H$, it would be probably due to the decomposition of iodine(III) species **A**. As shown in Scheme 5, in the absence of *N*-propargyl amide **1**, **A** reacts with 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ to form diaryliodane **B**, which is converted into 3,5-dimethoxybenzoate and iodine(III) intermediate **C** via proto-deiodination by the generated acid. Furthermore, the reduction of **C** afford 1,3-I_2-2,4-$(MeO)_2$-6-$(MeOCO)C_6H$. Notably, in the reaction of **1a** with **2a**, the use of 1,3-I_2-2,4-$(MeO)_2$-6-$(MeOCO)C_6H$ as the precatalyst did not give good result (Table S1 in SI). Additionally, although the use of F-TEDA-PF_6 without DMSO mostly completed the oxidation of 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ at rt for 10 min in CD_3NO_2, a more complicated mixture was obtained likely because of the reaction of F-TEDA-PF_6 and/or TEDA with the generated iodine(III) species besides the above decomposition process. This result shows the importance of slow generation of this unstable iodine species.

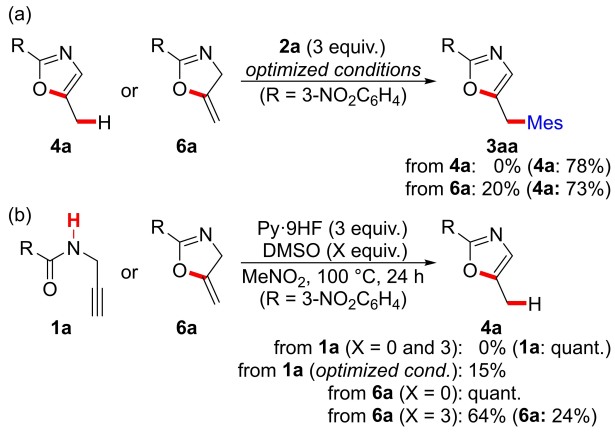


Scheme 5. Proposed decomposition mechanism of **A**.

Since the cyclized products **4** were observed as a byproduct in most of the reaction of **1** with **2**, there was a possibility that the byproducts **4** and/or methyleneoxazolines **6** would be involved as an intermediate of the arylated oxazoles **3**. Therefore, the control experiments using **4a** and **6a** were conducted (Scheme 6a). In the presence of **2a**, **6a** was exposed to the optimized conditions to give **4a** in 73% yield along with **3aa** in 20% yield. Whereas, **4a** was not converted into **3aa** under the similar conditions. Thus, **6** would be mainly involved in the formation of **4**, albeit partially involved in the formation of **3**.

Alternatively, there was a possibility that the cyclized products **4** would be formed through the cycloisomerization of *N*-propargyl amides **1** by the generated acid,[17] which would be HF in the present case. However, regardless of the presence or the absence of DMSO, Py·9HF (Py = pyridine, 1 equiv.) did not promote the cycloisomerization of **1a** even at 90 °C for 24 h, although the optimized conditions in the absence of aromatics **2** led to conversion of **1a** to **4a** (Scheme 6b). On the other hand, **6a** was smoothly converted into **4a** by Py·9HF, especially in the absence of DMSO. These results support the involvement of **6** as the intermediate of the cyclized products **4**, whose formation would be suppressed to a certain degree by DMSO as a Lewis base.

On the basis of the above-mentioned results and our previous report on iodine(III)-mediated/catalyzed oxidative cycloisomerization of *N*-propargyl amides,[16]



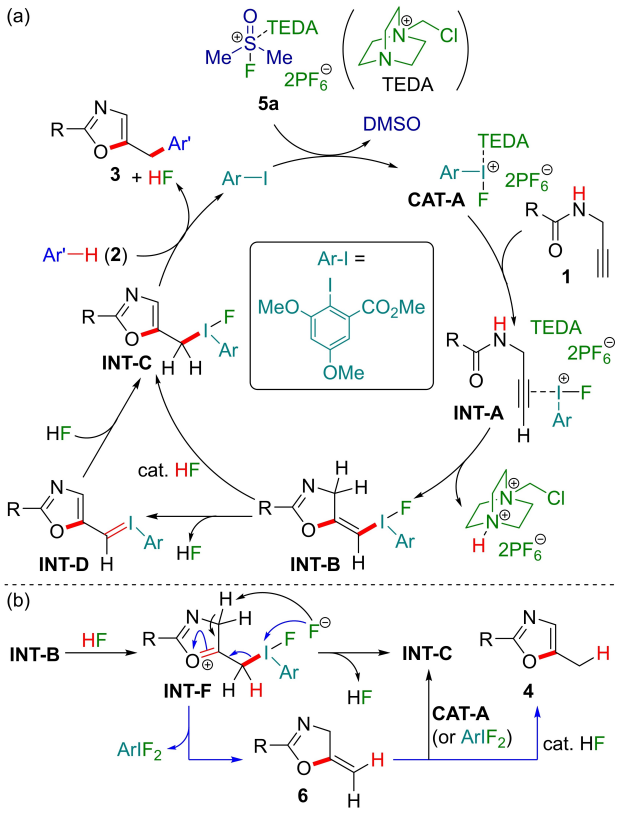
Scheme 6. Control experiments using **1a**, **4a** and **6**.

we proposed the catalytic cycle for the present synthesis of the arylated oxazoles **3** from **1** and **2** (Scheme 7a). At first, ArI precatalyst is oxidized with fluoro-λ^6-sulfane **5a**, which is derived from DMSO and F-TEDA-PF_6, to fluoroiodane-amine complex **CAT-A**. The generated **CAT-A** activates the triple bond of **1** (**INT-A**) to form a cyclized intermediate **INT-B**. And then, **INT-B** is aromatized to **INT-C** via 1,4-elimination of HF in **INT-B** followed by the addition of HF to iodonium ylide **INT-D** and/or via isomerization of **INT-B** by the generated HF. Finally, nucleophilic substitution of **INT-C** by aromatics **2** (Ar'-H) affords the arylated oxazoles **3** along with the regeneration of ArI precatalyst. Since **CAT-A** is very unstable iodine(III) species as shown in Scheme 5, the generation of **CAT-A** at low concentration by the relatively weak oxidation ability of fluoro-λ^6-sulfane **5a** would effect on the catalysis.

The formation of the byproduct **4** is proposed as shown in Scheme 7b. The isomerization of **INT-B** into **INT-C** by HF proceeds via protonation of enol moiety of **INT-B** and subsequent deprotonation of cyclic moiety of **INT-F** by fluoride ion. In the latter process, the fluoride ion gives rise to deiodination of **INT-F** along blue arrows to form **6**, which is converted into **4** by HF. The proto-deiodination of β-iodinated enols like **INT-B** by acid has been known.[21] Instead of HF, **CAT-A** and/or $ArIF_2$ (generated by the proto-deiodination of **INT-B**) reacts with **6** to give **INT-C** and this process would be partially involved in the formation of **3**. In addition to the generation of fluoro-λ^6-sulfane **5a**, DMSO would inhibit the proto-deiodination of **INT-B** and the HF-mediated conversion of **6** into **4** as the Lewis base. Thus, the mechanism in Scheme 7a would be a main route of accessing to the arylated oxazoles **3**.

Note that we do not consider the involvement of diaryliodonium salts[22] generated from **CAT-A** and arenes **2** in the formation of the arylated oxazoles **3**. It is because no products introducing aromatic rings derived from ArI precatalysts instead of **2** were identified under the conditions using other ArI precatalysts (Table 1 and S1-S3) as well as the optimized conditions (Scheme 3) and the corresponding diaryliodonium salt was not detected when 2,4-$(MeO)_2$-6-$(MeOCO)C_6H_2I$ was treated with F-TEDA-PF6 in the present of mesitylene (**2a**).[23]

In summary, we have developed a novel method of synthesis oxazoles with the introduction of aryl groups via the iodine(III)-catalyzed reaction of *N*-propargyl carboxamides and arenes. The present work is the first report of C(sp^3)–C(sp^2) bond formation by the catalytic dehydrogenative cycloisomerization/arylation reaction in *exo-dig* modes. Based on the results of the control experiments, we proposed that dialkyl(fluoro)-λ^6-sulfane would work as the terminal oxidant in the present iodine(III)-catalysis. Since the use of dialkyl-λ^6-sulfanes has been unknown for the generation of hypervalent iodine compounds, this report provides useful findings in the field of λ^3-iodane catalysis as well as the powerful method of oxazole synthesis.



Scheme 7. Proposed reaction mechanism.

Experimental Section

Representative procedure for the reaction of 1a with 2b. After DMSO (85.2 μL, 1.2 mmol) was treated with F-TEDA-PF_6 (226 mg, 0.48 mmol) in $MeNO_2$ (4.0 mL) at 100 °C for 1 h, methyl 2-iodo-3,5-dimethoxybenzoate (25.8 mg, 0.08 mmol), **1a** (81.7 mg, 0.4 mmol) and **2a** (167 μL, 1.2 mmol) were added in turn at the ambient temperature. After being stirred at 100 °C for 24 h, the reaction mixture was diluted with ether and filtered through a pad of silica gel. The filtrate was concentrated in vacuo to dryness and then the residue was purified by preparative thin layer chromatography (PTLC, hexane:AcOEt = 2:1) to give **3aa** (R_f = 0.44, 87.1 mg, 68%).

Acknowledgements

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