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Note

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Single-Step Synthesis of Iodinated Oxazoles from *N*-Propargyl Amides Mediated by I_2/Iodosylbenzene/TMSOTf Systems

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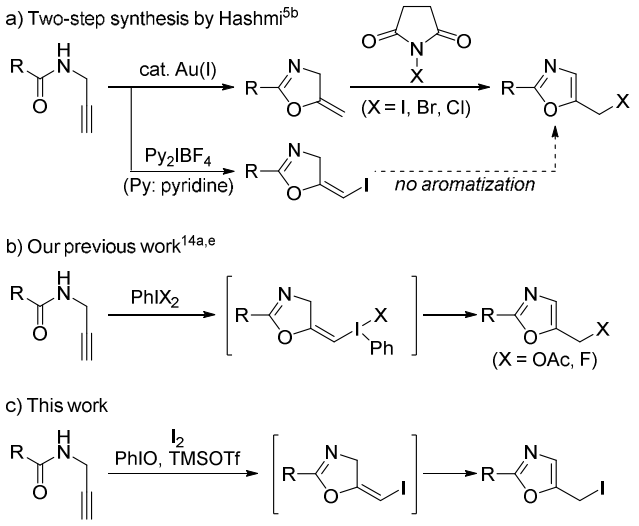
ABSTRACT: A combination of I_2, iodosylbenzene and TMSOTf is effective on a single-step synthesis of iodinated oxazoles from *N*-propargyl amides via the aromatization of the iodocyclized intermediates, which is difficult to proceed by the conventional iodocyclization methods. Compared to the former method consisting of the metal-catalyzed cyclization of *N*-propargyl amides followed by halogenation of alkylideneoxazolines, the present reaction provides facile and metal-free procedure.

Iodocyclization of unsaturated compounds bearing heteroatom nucleophiles provides a facile formation of heterocycles concomitant with the introduction of further functionalizable iodo components.[1] For the synthesis of the iodinated aromatic heterocycles, the iodocyclizations of various alkynes via *endo-dig* modes have been reported.[1,2] On the other hand, *exo*-iodocyclizations of alkynes generally give rise to *exo*-alkylidene products[3,4] and such products derived from *N*-propargyl amides hardly aromatize to the corresponding iodinated oxazoles (Scheme 1a).[5] The aromatization of these products has been achieved by further oxidation, which cannot remain iodo components.[6] Thus, there is room for the improvement in the *exo*-iodocyclizations of alkynes for the formation of iodinated aromatic heterocycles.

Scheme 1. Synthetic methods of halogenated oxazoles



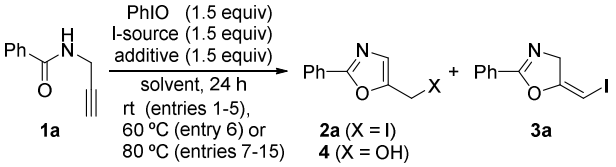
The *exo*-cycloisomerization of *N*-propargyl amides have been widely employed for the effective and versatile synthesis of 2,5-disubstituted oxazoles,[7] which are prevalent in many natural products and pharmaceutically active compounds.[8] Palladium-catalyzed cycloisomerization–coupling reactions can lead to oxazoles having carbon functional groups such as aryl and allyl groups in a single operation.[9] Also, since Hashmi *et al.* reported the gold-catalyzed formation of alkylideneoxazolines,[10,11] the authors and other groups have developed oxazole synthesis methods with the introduction of heteroatomic or carbon functional groups via the functionalization of the alkylideneoxazolines.[12] However, although such methods can be applied to the two-step synthesis of halogenated oxazoles (Scheme 1a),[5b,c,13] the direct synthesis of the halogenated oxazoles from *N*-propargyl amides has been unknown.

We have researched on the metal-free synthesis of aromatic heterocycles through the activation of alkynes by hypervalent iodine(III) reagents[14] to find the cycloisomerization–acetoxylation[14a] or –fluorination[14e] sequence of *N*-propargyl amides (Scheme 1b). Further studies on the I(III)-mediated cycloisomerization–functionalization reaction led to single-step synthesis of iodinated oxazoles from *N*-propargyl amides (Scheme 1c), which is described herein.

Based on our examples for the I(III)-mediated cycloisomerization–functionalization reaction (Scheme 1b),[14a,b,e] the formation of the iodinated oxazole **2a** from *N*-propargyl amide **1a** using PhIO (1.5 equiv) and the source of iodine (I-source, 1.5 equiv) was attempted (Table 1, entries 1-12). Since PhI(OTBA)I derived from PhIO and TBAI (tetra-*n*-butylammonium iodide)[15] has been reported to promote the *exo*-iodocyclization of alkynes by Fan *et al.*,[4c] we envisaged that such reagents would work in the cycloisomerization–iodination reaction of **1a** as well as $PhIX_2$. Unfortunately, PhI(OTBA)I in CH_2Cl_2 or MeCN at room temperature did not give **2a** but hydroxylated oxazole **4** as a main product (20% or 17%, entry 1 or 2). On the other hand, by the use of acidic solvent such as HFIP (hexafluoro-2-propanol, pka = 9.3, bp: 59 ºC) and the addition of TMSOTf (trimethylsilyl trifluoromethanesulfonate, 1.5 equiv) as a Lewis acid in CH_2Cl_2, the iodocyclized product **3a** were formed in 42% and 29% yields, respectively (entries 3 and 4). Furthermore, under the similar condition to entry 4, the use of I_2 instead of TBAI brought about the improved yield of **3a** up to 62% (entry 5). To our delight, when the PhIO/I_2/TMSOTf system was employed in DCE (1,2-dichloroethane) at 80 ºC, the desired product **2a** was obtained in 52% yield (entry 7). Among the tested acid addi-

tives in the PhIO/I_2/acid systems (entries 7-11), TMSOTf was the best additive (entry 7). Moreover, each amount of PhIO, I_2, and TMSOTf was reduced to 1 equiv to improve the yield of **2a** up to 71% (entry 12). It should be mentioned that, in the absence of PhIO, the use of iodine reagents such as I_2 and NIS (*N*-iodosuccinimide) with TMSOTf or HOTf did not show good results (entries 13-15).

Table 1. Optimization of the reaction conditions[a]



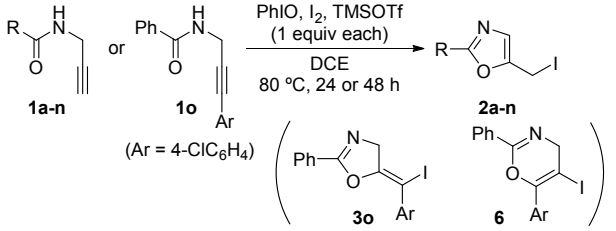
entry	I-source	additive	**2a** (%)[b]	**3a** (%)[b]
1	TBAI	-	0[c]	0
2	TBAI	-	0[d]	0
3	TBAI	-	0	42
4	TBAI	TMSOTf	0[e]	29
5	I_2	TMSOTf	0	62
6	I_2	TMSOTf	0	79
7	I_2	TMSOTf	52[e]	0
8	I_2	HOTf	34[e]	0
9	I_2	$HNTf_2$	21[e]	10
10	I_2	HBF_4	9[e]	17
11	I_2	$BF_3{\cdot}OEt_2$	7[e]	26
12[f]	I_2	TMSOTf	71	0
13[g]	I_2	TMSOTf	16	0
14[g]	NIS	TMSOTf	25	3
15[g]	NIS	HOTf	32	12

[a] Solvent: CH_2Cl_2 (entries 1, 4, 5), MeCN (entry 2), hexafluoro-2-propanol (HFIP, entries 3, 6), or 1,2-dichloroethane (DCE, entries 7-15). [b] Except for entry 12, yields were determined by ^1H NMR analysis. [c] **4**: 20%. [d] **4**: 17%. [e] 2-Phenyloxazole-5-carbaldehyde (**5**) was detected (3-10% yield). [f] Each amount of PhIO, I_2 and TMSOTf was reduced to 1 equiv. [g] PhIO was not added.

Under the optimized reaction conditions, the scope for the formation of **2** from various *N*-propargyl amides **1** is summarized in Table 2. Similar to benzamide **1a** (entry 1), nitro-substituted **1b-d**, cyano-substituted **1e** and chloro-substituted **1f-h** were smoothly converted to the corresponding iodinated oxazoles **2b-h** within 24 h in good yields (61-78%, entries 2-8). In cases of methyl-substituted **1i** and methoxy-substituted **1j**, although the reaction times were prolonged to 48 h, the desired **2i** and **2j** were obtained in 65% and 45% yields, respectively (entries 9 and 10). Furthermore, the PhIO/I_2/TMSOTf systems could be applied not only to heteroaromatic amide **1k** but also aliphatic amides **1l-n** (entries 11-14). Unfortunately, internal alkyne **1o** gave iodocyclized product **3o** in 42% yield along with iodinated oxazine **6** (24%) even under the similar conditions (entry 15). This result may be due to harder isomerization of more substituted alkenes **3o** to oxazole nucleus.[14g] Also, the iodocyclization of **1o** have been known to proceed via both 5-*exo* and 6-*endo* modes.[5e]

The obtained oxazole **2a** was treated with mesitylene in $MeNO_2$ to give the arylated product **7** in 67% yield (Scheme 2). Although Pd-catalyzed cycloisomerization–coupling reactions of propargyl amides has been reported for the direct formation of arylated oxazoles, the introduction of bulky aryl groups such as mesityl group has not been achieved.[9a] Also, the displacement of the iodine atoms to cyano, amino and azido groups was successful to form various functionalized oxazoles **8**, **9** and **10** in good yields (72-86%). Since the direct synthesis of these functionalized oxazoles from *N*-propargyl amides has not been developed, the present procedure would be alternative to the previous two-step methods.[16]

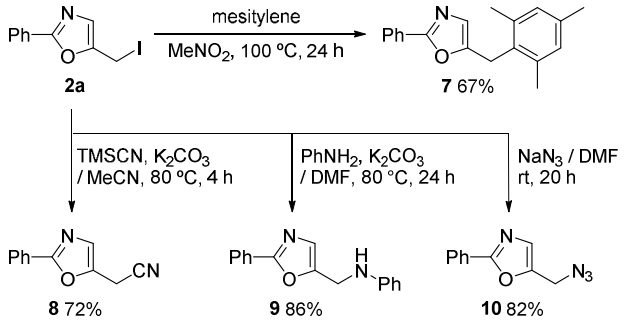
Table 2. Scope for the formation of 2



entry	**1**	R	time (h)	**2** yield (%)	
1	**1a**	Ph	24	**2a**	71
2	**1b**	*o*-$NO_2C_6H_4$	24	**2b**	75
3	**1c**	*m*-$NO_2C_6H_4$	24	**2c**	78
4	**1d**	*p*-$NO_2C_6H_4$	24	**2d**	71
5	**1e**	*m*-CNC_6H_4	24	**2e**	61
6	**1f**	*o*-ClC_6H_4	24	**2f**	77
7	**1g**	*m*-ClC_6H_4	24	**2g**	72
8	**1h**	*p*-ClC_6H_4	24	**2h**	61
9	**1i**	*p*-MeC_6H_4	48	**2i**	65
10	**1j**	*p*-$MeOC_6H_4$	48	**2j**	45
11	**1k**	2-thienyl	24	**2k**	69
12	**1l**	$PhCH_2CH_2$	24	**2l**	42
13	**1m**	^{i}Pr	24	**2m**	38
14	**1n**	^{t}Bu	24	**2n**	38
15	**1o**	–	24	**3o**	42[a]

[a] In addition to **3o**, **6** was obtained in 24% yield.

Scheme 2. Conversion to other functionalized oxazoles

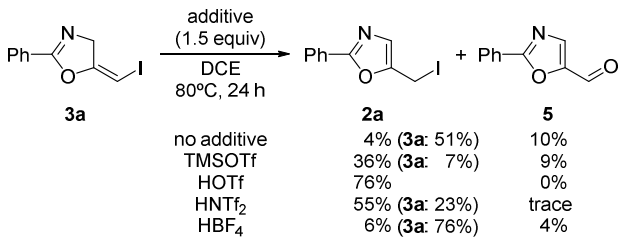


As shown in Table 1, from the results at room temperature in CH_2Cl_2 (entry 5) and at 80 ºC in DCE (entries 7 and 12) by PhIO/I_2/TMSOTf system, the iodocyclized product **3** was expected to be involved as an intermediate in the synthesis of the iodinated oxazole **2a**. Therefore, the control experiments using the isolated **3a** were carried out at 80 ºC in DCE (Scheme 3). As with the Caristi's report,[5a] in the absence of any additives, **3a** was scarcely aromatized to **2a** (4%) along with recovery of **3a** (50%). On the other hand, the addition of acid additives led

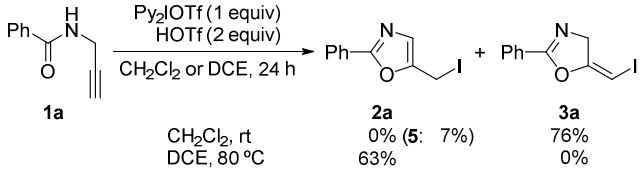
to the formation of **2a** and particularly the use of HOTf afforded **2a** in 76% yield. Thus, these results indicate that thermal and acidic conditions would promote the aromatization of initially formed **3a** to **2a**.

Since I_2 or NIS with TMSOTf or HOTf promoted the formation of **2a** from **1a** in DCE at 80 ºC albeit lower yields of **2a** (Table 1, entries 13-15), iodonium species such as IOTf would be generated from PhIO/I_2/TMSOTf system possibly. This would be supported by trap experiments of iodonium species using pyridine (Py), in which Py_2IOTf was detected from I_2 and TMSOTf with PhIO but slightly detected from I_2 and TMSOTf without PhIO (see, Supporting Information). Actually, **1a** was exposed with iodonium species generated from Py_2IOTf (1 equiv) and HOTf (2 equiv)[17] to give the iodocyclized product **3a** in 76% yield at room temperature or to give the iodinated oxazole **2a** in 63% yield at 80 ºC (Scheme 4). These results accord with those using PhIO/I_2/TMSOTf systems (Table 1, entries 5 and 12).

Scheme 3. Aromatization of iodocyclized product 3a

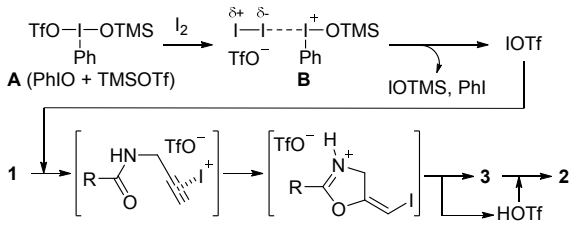


Scheme 4. Reactions of 1a with "IOTf" equivalent



On the basis of the above results, we propose that the formation of iodinated oxazoles **2** would proceed through the IOTf-mediated iodocyclization of propargyl amides **1** and then the aromatization of the iodocyclized intermediates **3** promoted by the generated HOTf under thermal conditions (Scheme 5). Compared with TMSOTf having harder acidity, iodine(III) species **A**[19] generated from PhIO and TMSOTf might be more effective on the activation of I_2. Therefore, IOTf would be more efficiently formed from the activated iodine **B** by the halogen-bonding interaction[20] with species **A**.

Scheme 5. Proprosed Reaction Mechanism



In conclusion, we have developed a single-step synthesis of iodinated oxazoles from *N*-propargyl amides using I_2, iodosylbenzene and TMSOTf. In these reactions, the iodinated oxazoles would be formed by the aromatization of iodocyclized intermediates under the thermal and acidic conditions. Furthermore, the trap experiments of iodonium species using pyridine and the control experiments using Py_2IOTf and HOTf suggested the possibility of the generation of "IOTf" from PhIO/I_2/TMSOTf systems. Since the direct synthesis of the halogenated oxazoles from *N*-propargyl amides has not been achieved, our findings provide an attractive procedure for the access to the halogenated oxazoles.

EXPERIMENTAL SECTION

General information. Iodosylbenzene, molecular iodine and trimethylsilyl trifluoromethanesulfonate (TMSOTf) are commercially available. According to procedures reported in the literatures, *N*-propargyl carboxamides **1a**,[10a] **1b**,[14e] **1c**,[14e] **1d**,[9f] **1e**,[14e] **1f**,[14e] **1g**,[14e] **1h**,[18a] **1i**,[18a] **1j**,[18b] **1k**,[9f] **1l**,[18c] **1m**,[18d] **1n**[18e] and **1o**[5e] were prepared. Products **3a**,[5b] **4**[12a] and **5**[6a] are known compounds. ^{1}H and ^{13}C NMR spectra were measured at 300 and 75 MHz in $CDCl_3$, and the chemical shifts are given in ppm using $CHCl_3$ (7.26 ppm) in $CDCl_3$ for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR as an internal standard, respectively. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broadened). Mass spectra and HRMS were recorded on double-focusing magnetic sector by FAB methods. All reactions were carried out under an argon atmosphere.

*General procedure for synthesis of iodinated oxazoles **2***. In an aluminum foil-covered test tube, iodosylbenzene (88.0 mg, 0.40 mmol) was treated with trimethylsilyl trifluoromethanesulfonate (72.4 μL, 0.40 mmol) in 1,2-dichloroethane (4 mL) at room temperature for 5 min. And then, to the reaction mixture was added molecular iodine (101.5 mg, 0.40 mmol) and **1a-o** (0.40 mmol) in turn. After being stirred at 80 ºC for 24 h (48 h in cases of **1i** and **1j**), the reaction mixture was quenched with sat. $NaHCO_3$ and sat. $Na_2S_2O_3$, and then extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by preparative thin layer chromatography (PTLC, hexane:AcOEt = 5:1, 3:1 or 2:1) to give **2a-n**, or **3o** and **6**.

*5-(Iodomethyl)-2-phenyloxazole (**2a**)*. R_f = 0.68 (hexane:AcOEt = 3:1). Brown solid (82.2 mg, 71%). The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5b]

*5-(Iodomethyl)-2-(2-nitrophenyl)oxazole (**2b**)*. R_f = 0.37 (hexane:AcOEt = 2:1). Brown solid (99.9 mg, 75%). Mp 105-106 ºC. IR (KBr) ν cm^{-1}; 1532, 1358, 535. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.45 (s, 2H), 7.21 (s, 1H), 7.59-7.54 (m, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -11.4, 120.8, 124.0, 126.1, 130.4, 131.3, 132.2, 150.5, 157.2 (Note that two carbon peaks overlap with each other). FAB-LM *m/z*: 331 (M^++H^+). FAB-HM Calcd for $C_{10}H_8IN_2O_3$ (M^++H^+): 330.9580; found: 330.9556.

*5-(Iodomethyl)-2-(3-nitrophenyl)oxazole (**2c**)*. R_f = 0.43 (hexane:AcOEt = 3:1). Pale yellow solid (103.8 mg, 78%). Mp 102-104 ºC. IR (KBr) ν cm^{-1}; 1520, 1348, 523. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.51 (s, 2H), 7.23 (s, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 8.30-8.35 (m, 1H), 8.38 (dt, *J* = 8.0, 1.9 Hz, 1H), 8.88 (t, *J* = 1.9 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -11.3, 121.4, 125.0, 126.4, 128.8, 130.2, 132.0, 148.8, 150.2, 159.6. FAB-LM *m/z*: 331 (M^++H^+). FAB-HM Calcd for $C_{10}H_8IN_2O_3$ (M^++H^+): 330.9580; found: 330.9607.

*5-(Iodomethyl)-2-(4-nitrophenyl)oxazole (**2d**)*. R_f = 0.54 (hexane:AcOEt = 3:1). Pale yellow solid (94.6 mg, 71%). Mp 133-135 ºC. IR (KBr) ν cm^{-1}; 1519, 1338, 526. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.51 (s, 2H), 7.26 (s, 1H), 8.22 (d, *J* = 9.0 Hz, 2H),

8.34 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -11.2, 124.3, 126.7, 127.1, 132.5, 148.8, 150.6, 159.7. FAB-LM *m/z*: 331 (M^++H^+). FAB-HM Calcd for $C_{10}H_8IN_2O_3$ (M^++H^+): 330.9580; found: 330.9556.

2-(3-Cyanophenyl)-5-(iodomethyl)oxazole (***2e***). R_f = 0.47 (hexane:AcOEt = 2:1). Brown solid (76.0 mg, 61%). Mp 99-100 ºC. IR (KBr) ν cm^{-1}; 2228, 533. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.49 (s, 2H), 7.24 (s, 1H), 7.59 (t, J = 7.9 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 8.27 (d, J = 7.9 Hz, 1H), 8.32 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -11.0, 113.4, 118.0, 126.2, 128.4, 129.8, 129.9, 130.3, 133.7, 150.0, 159.6. FAB-LM *m/z*: 311 (M^++H^+). FAB-HM Calcd for $C_{11}H_8IN_2O$ (M^++H^+): 310.9681; found: 310.9673.

2-(2-Chlorophenyl)-5-(iodomethyl) oxazole (***2f***). R_f = 0.64 (hexane:AcOEt = 3:1). Brown solid (98.5 mg, 77%). Mp 59-61 ºC. IR (KBr) ν cm^{-1}; 738, 510. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.49 (s, 2H), 7.20 (s, 1H), 7.31-7.44 (m, 2H), 7.51 (dd, J = 7.2, 1.9 Hz, 1H), 7.99 (dd, J = 6.9, 1.9 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -10.6, 125.8, 125.9, 126.9, 130.8, 131.3, 131.4, 132.5, 149.3, 159.6. FAB-LM *m/z*: 320 (M^++H^+). FAB-HM Calcd for $C_{10}H_8ClINO$ (M^++H^+): 319.9339; found: 319.9362.

2-(3-Chlorophenyl)-5-(iodomethyl) oxazole (***2g***). R_f = 0.70 (hexane:AcOEt = 3:1). Brown solid (92.3 mg, 72%). Mp 75-77 ºC. IR (KBr) ν cm^{-1}; 738, 510. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.48 (s, 2H), 7.17 (s, 1H), 7.34-7.47 (m, 2H), 7.92 (d, J = 7.1 Hz, 1H), 8.02 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -10.5, 124.5, 126.1, 126.4, 128.7, 130.2, 130.7, 135.0, 149.4, 160.6. FAB-LM *m/z*: 320 (M^++H^+). FAB-HM Calcd for $C_{10}H_8ClINO$ (M^++H^+): 319.9339; found: 319.9341.

2-(4-Chlorophenyl)-5-(iodomethyl) oxazole (***2h***). R_f = 0.68 (hexane:AcOEt = 3:1). Brown solid (77.7 mg, 61%). Mp 95-96 ºC. IR (KBrt) ν cm^{-1}; 733, 521. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.49 (s, 2H), 7.17 (s, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.99 (d, J = 8.5 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -10.3, 125.6, 126.1, 127.7, 129.2, 136.8, 149.1, 161.0. FAB-LM *m/z*: 320 (M^++H^+). FAB-HM Calcd for $C_{10}H_8ClINO$ (M^++H^+): 319.9339; found: 319.9341.

5-(Iodomethyl)-2-(4-methylphenyl)oxazole (***2i***). R_f = 0.69 (hexane:AcOEt = 3:1). Pale yellow solid (78.3 mg, 65%). Mp 72-73 ºC. IR (KBr) ν cm^{-1}; 3033, 523. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.40 (s, 3H), 4.49 (s, 2H), 7.14 (s, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.93 (d, J = 8.0 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -9.7, 21.5, 124.5, 126.0, 126.4, 129.6, 141.1, 148.5, 162.3. FAB-LM *m/z*: 300 (M^++H^+). FAB-HM Calcd for $C_{11}H_{11}INO$ (M^++H^+): 299.9885; found: 299.9898.

5-(Iodomethyl)-2-(4-methoxyphenyl)oxazole (***2j***). R_f = 0.53 (hexane:AcOEt = 3:1). Brown solid (56.9 mg, 45%). Mp 82-84 ºC. IR (KBr) ν cm^{-1}; 1256, 1024, 528. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 3.86 (s, 3H), 4.49 (s, 2H), 6.97 (d, J = 8.9 Hz, 2H), 7.12 (s, 1H), 7.99 (d, J = 8.9 Hz, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -9.6, 55.3, 114.3, 119.9, 125.9, 128.1, 148.2, 161.6, 162.1. FAB-LM *m/z*: 316 (M^++H^+). FAB-HM Calcd for $C_{11}H_{11}INO_2$ (M^++H^+): 315.9834; found: 315.9847.

5-(Iodomethyl)-2-(thiophen-2-yl)oxazole (***2k***). R_f = 0.66 (hexane:AcOEt = 3:1). Yellow solid (79.8 mg, 69%). The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5b]

5-(Iodomethyl)-2-phenethyloxazole (***2l***). R_f = 0.63 (hexane:AcOEt = 2:1). Brown oil (52.6 mg, 42%). IR (neat) ν cm^{-1}; 2933, 2866, 520. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.99-3.15 (m, 4H), 4.38 (s, 2H), 6.94 (s, 1H), 7.17-7.25 (m, 3H), 7.26-7.34 (m, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -10.2, 30.1, 32.9, 124.4, 126.5, 128.4, 128.6, 140.2, 148.5, 164.6. FAB-LM *m/z*: 314 (M^++H^+). FAB-HM Calcd for $C_{12}H_{13}INO$ (M^++H^+): 314.0042; found: 314.0030.

5-(Iodomethyl)-2-isopropyloxazole (***2m***). R_f = 0.59 (hexane:AcOEt = 3:1). Yellow oil (38.3 mg, 38%). IR (neat) ν cm^{-1}; 2973, 519. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.33 (d, J = 7.0 Hz, 3H), 3.03 (septet, J = 7.0 Hz, 1H), 4.38 (s, 2H), 6.92 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -9.8, 20.2, 28.4, 124.3, 148.1, 169.6. FAB-LM *m/z*: 251 (M^++H^+). FAB-HM Calcd for $C_7H_{11}INO$ (M^++H^+): 251.9885; found: 251.9889.

2-tert-Butyl-5-(iodomethyl)oxazole (***2n***). R_f = 0.67 (hexane:AcOEt = 3:1). Brown oil (40.1 mg, 38%). IR (neat) ν cm^{-1}; 2971, 521. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 1.37 (s, 9H), 4.39 (s, 2H), 6.92 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; -9.7, 28.4, 33.8, 124.0, 148.1, 171.8. FAB-LM *m/z*: 266 (M^++H^+). FAB-HM Calcd for $C_8H_{13}INO$ (M^++H^+): 266.0042; found: 266.0012.

(E)-5-[(4-Chlorophenyl)iodomethylene]-4,5-dihydro-2-phenyloxazole (***3o***). R_f = 0.56 (hexane:AcOEt = 5:1). White solid (65.7 mg, 42%). The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5e]

6-(4-Chlorophenyl)-5-iodo-2-phenyl-4H-1,3-oxazine (***6***). R_f = 0.71 (hexane:AcOEt = 5:1). White solid (37.4 mg, 24%). The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5e]

Synthesis of 2-phenyl-5-(2,4,6-trimethylbenzyl)oxazole (***7***). A solution of **2a** (114.0 mg, 0.4 mmol) and mesitylene (167 μL, 1.2 mmol) in nitromethane (4 mL) was stirred at 100 ºC for 24 h. And then, the reaction mixture was concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 8:1) to give **7** (R_f = 0.36, 74.2 mg, 67%) as a white solid: Mp 76-77 ºC. IR (KBr) ν cm^{-1}; 2919, 1488. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 2.30 (s, 3H), 2.38 (s, 6H), 4.05 (d, J = 1.1 Hz, 2H), 6.65 (t, J = 1.1 Hz, 1H), 6.92 (s, 2H), 7.38-7.50 (m, 3H), 7.96-8.06 (m, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; 19.8, 20.8, 25.9, 124.3, 126.0, 127.8, 128.8, 129.2, 130.0, 136.5, 136.9, 151.0, 161.0 (Note that two carbon peaks overlap with each other). FAB-LM *m/z*: 278 (M^++H^+). FAB-HM Calcd for $C_{19}H_{20}NO$ (M^++H^+): 278.1545; found: 278.1537.

Synthesis of 2-(2-phenyloxazol-5-yl)acetonitrile (***8***). To a solution of **2a** (114.0 mg, 0.4 mmol) and trimethylsilyl cyanide (107 μL, 0.8 mmol) in acetonitrile (4 mL) was added K_2CO_3 (110.6 mg, 0.8 mmol). After being stirred at 80 ºC for 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 3:1) to give **8** (R_f = 0.26, 72.1 mg, 72%) as a pale yellow solid. The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[16a]

Synthesis of N-[(2-phenyloxazol-5-yl)methyl]benzenamine (***9***). To a solution of **2a** (114.0 mg, 0.4 mmol) and aniline (73 μL, 0.8 mmol) in *N*,*N*-dimethylformamide (4 mL) was added K_2CO_3 (110.6 mg, 0.8 mmol). After being stirred at 80 ºC for 24 h, the reaction mixture was quenched with H_2O and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hexane:AcOEt = 3:1) to give **9** (R_f = 0.39, 87.3 mg, 86%) as a pale yellow solid. Mp 86-87 ºC. IR (KBr) νcm^{-1}; 3322, 1604, 1322. ^{1}H NMR (300 MHz, $CDCl_3$) δ; 4.10 (br.s, 1H), 4.46 (s, 2H), 6.74 (d, J = 7.7 Hz, 2H), 6.80 (t, J = 7.7 Hz, 1H), 7.08 (s, 1H), 7.24 (t, J = 7.7 Hz, 2H), 7.40-7.53 (m, 3H), 7.98-8.13 (m, 2H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ; 39.3, 113.3, 118.5, 125.7, 126.3, 127.5, 128.8, 129.4, 130.4, 147.2, 149.8, 161.6. FAB-LM *m/z*: 251 (M^++H^+). FAB-HM Calcd for $C_{16}H_{15}N_2O$ (M^++H^+): 251.1184; found: 251.1170.

Synthesis of 5-(azidomethyl)-2-phenyloxazole (***10***). A solution of **2a** (114.0 mg, 0.4 mmol) and sodium azide (39.0 mg, 0.6 mmol) in *N*,*N*-dimethylformamide (4 mL) was stirred at room temperature for 24 h. And then, the reaction mixture was quenched with H_2O and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC (hex-

ane:AcOEt = 8:1) to give **10** (R_f = 0.23, 65.9 mg, 82%) as a pale yellow solid. The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[12d]

*Aromatization of iodocyclized product **3a** to **2a***. A solution of **3** (114.0 mg, 0.4 mmol) and trifluoromethanesulfonic acid (53 μL, 0.6 mmol) in 1,2-dichloroethane (4 mL) at 80 ºC for 24 h. And then, the reaction mixture was quenched with sat. $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by PTLC to give **2a** (86.6 mg, 76%) as a brown solid. The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5b]

*General procedure for reactions of **1a** with "IOTf" equivalent*. In an aluminum foil-covered test tube, bis(pyridine)iodonium trifluoromethanesulfonate[18f] (173.7 mg, 0.40 mmol) was treated with trifluoromethanesulfonic acid (71.0 μL, 0.80 mmol) in dichloromethane (or 1,2-dichloroethane, 4 mL) at room temperature for 5 min. And then, to the reaction mixture was added **1a** (63.7 mg, 0.40 mmol). After being stirred at room temperature (or 80 ºC) for 24 h, the reaction mixture was quenched with sat. $NaHCO_3$ and sat. $Na_2S_2O_3$, and then extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuo to dryness. The residue was purified by preparative thin layer chromatography (PTLC) to give **3** (86.6 mg, 76%) as a yellow solid [or **2** (71.8 mg, 63%) as a brown solid]. The ^{1}H and ^{13}C NMR spectra of the product was identical to those reported in the literature.[5b]

ASSOCIATED CONTENT

Supporting Information. Spectra for all new compounds. The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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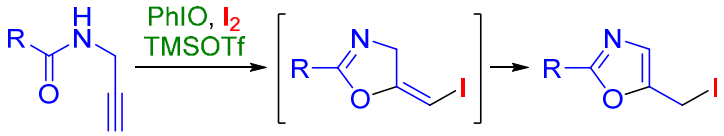
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