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Photochemistry | *Very Important Paper* |

Photochemical Transformation of *O*-(β-Arylethyl) Arylimidates into 2,4-Diaryl-5-iodoxazoles with 1,3-Diiodo-5,5-dimethylhydantoin

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Abstract: Treatment of *O*-(β-arylethyl) arylimidates with 1,3-diiodo-5,5-dimethylhydantoin (DIH) under irradiation with a tungsten lamp in 1,2-dichloroethane gave the corresponding 2,4-diaryl-5-iodoxazoles and 2,4-diaryloxazoles in good to moderate yields, respectively, depending on the aryl group. It was proposed that the reactions proceeded through the formation of *N*-iodoimidates by the reaction of *O*-(β-arylethyl) arylimidates with DIH, followed by the formation of iminyl radicals via homolytic N–I bond cleavage, the 1,5-H shift by the iminyl radicals, the C–I bond formation of the formed carbon-centered radicals with iodine, the nucleophilic cyclization by the imino groups to form 2,4-diaryloxazolines, the oxidation of the formed 2,4-diaryloxazolines to 2,4-diaryloxazoles, and the iodination of the formed 2,4-diaryloxazoles to 2,4-diaryl-5-iodoxazoles with DIH.

Introduction

Oxazoles are one of the most important heteroaromatics because an oxazole unit is contained in many natural products, such as plants and marine products, and some of those natural products show potent biological activities.[1] In particular, 2-aryloxazoles have attracted much attention due to their potent biological activities, such as antibacterial and antifungal activities, as shown in Figure 1.[1a,1b]

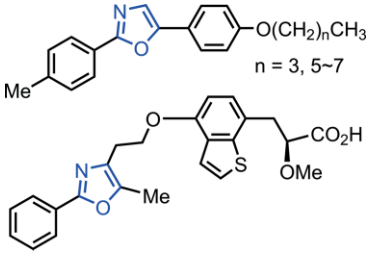

Figure 1. Biologically active 2-aryloxazoles.

Synthetic studies of the oxazole unit have been carried out extensively.[2] As typical conventional methods for the preparation of oxazoles, the Robinson-Gabriel synthesis with α-(acylamino)ketones and the Van Leusen reaction with aldehydes and α-(tosyl)methyl isocyanide for the formation of 2-unsubstituted oxazoles, the Fisher oxazole synthesis with cyanohydrins and aldehydes, and the Bredereck reaction with α-haloketones and amides for the formation of 2-substituted oxazoles are known. Recent reports for the preparation of oxazoles with transition metals are as follows:[3] the preparation of 2,4,5-triaryloxazoles with *O*-aroyl cyanohydrins in the presence of $Pd(TFA)_2$ and bpy;[3a] the preparation of 4,5-disubstituted 2-(trifluoromethyl)-oxazoles with oximes, arenethiol, trifluoroacetic anhydride, NIS, and $K_2S_2O_8$ in the presence of $Cu(OTf)_2$;[3b] the preparation of 4-substituted 2,5-diaryloxazoles with *trans*-2-aryl-3-nitrocyclopropane-1,1-dicarboxylates and aromatic nitriles in the presence of $SnCl_4$;[3c] the preparation of 2,5-diaryloxazoles with *N*-aroyl enamines in the presence of $CuCl_2$ and *N*-methylimidazole;[3d] the preparation of 2-aryl-5-methyloxazoles with aroyl chlorides and propargylamines via propargyl amides in the presence of $FeCl_3$;[3e] the preparation of 2-aryloxazole-4-carboxylates with aromatic amides and α-bromoketones in the presence of $AgSbF_6$;[3f] and others.[3g,3h] Moreover, recent reports for the preparation of oxazoles under transition-metal-free conditions are as follow:[4] the preparation of 2,5-diaryloxazoles with α-bromoacetophenones and benzylamines in the presence of Eosin Y under blue LED irradiation;[4a] the preparation of 4,5-disubstituted 2-methyloxazoles with *N*-acetyl enamines, fluorobenziodoxole, and BF_3•Et_2O;[4b] the electrochemical preparation of 2-aryl-5-(fluoromethyl)oxazoles with *N*-propargylamides in the presence of *p*-iodotoluene;[4c] the preparation of 2,4,5-triaryloxazoles with 2*H*-azirines and aromatic aldehydes in the presence of 9-mesityl-10-methylacridinium perchlorate under blue LED irradiation;[4d] the preparation of 2,4-disubstituted 5-aryloxazoles with alkyl aryl ketones, I_2, Oxone®, and CF_3SO_3H in nitriles;[4e] the preparation of 2,5-diaryloxazoles with α-bromoacetophenones, benzylamines, I_2, and K_2CO_3;[4f] the preparation of 2,4,5-trisubstituted oxazoles with *N*-acyl enamines, $PhI(OAc)_2$, and BF_3•Et_2O;[4g] the preparation of 4-substituted 2,5-diaryloxazoles with vinyliminophosphoranes and aroyl chlorides;[4h] and others.[4i,4j]

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On the other hand, the synthetic uses of imino-nitrogen-centered radical (iminyl radicals) for the preparation of nitrogen-containing heterocycles, such as dihydropyrroles and phenanthridines, have attracted much attention recently.[5] Recent synthetic studies of iminyl radicals for the preparation of nitrogen-containing heterocycles are as follows:[6] the preparation of pyrrolines (dihydropyrroles) from *O*-methyl oximes of aryl 3-butenyl ketones and SmI_2;[6a] the preparation of pyrrolines from *O*-benzoyl oximes of aryl 3-butenyl ketones and diethyl phosphite in the presence of $AgNO_3$;[6b] the preparation of cyclopenta[b]quinoxalines from *O*-aroyl oximes of cyclobutanones and aromatic isocyanides in the presence of *fac*-Ir(ppy)$_3$ under irradiation with LED lamp;[6c] the preparation of dihydronaphthalenones from *O*-benzoyl oximes of aryl isopentyl ketones in the presence of Fe(acac)$_3$;[6d] the preparation of spiropyrrolines from *O*-aroyl oximes of alkyl *o*-biaryl ketones in the presence of DBU under irradiation with a visible light;[6e] the preparation of 5-alkoxy-2-aryl-4-iodopyrrolines from *O*-alkyl imidates, NaI, and PhI(OAc)$_2$ under blue LED irradiation;[6f] and the preparation of quinazolinones from *N*-(3-butenyl),*N*-cyanobenzamides, arenesulfinic acids, and *t*BuOOH in the presence of Na_2Eosin Y under green LED irradiation, or *N*-(3-butenyl),*N*-cyanobenzamides and arenesulfonyl chlorides in the presence of Ru(bpy)$_3$Cl$_2$ under blue LED irradiation.[6g] Those reactions proceed through the formation of iminyl radicals at first, followed by the cyclization onto olefinic groups by iminyl radicals, the cyclization onto aromatic rings by iminyl radicals, or the 1,5-H shift by iminyl radicals and then cyclization. As regards synthetic studies of iminyl radicals for the preparation of nitrogen-containing heteroaromatics, we also reported the preparation of 6-aryl- or 6-alkylphenanthridines from the reactions of *o*-cyanobiaryls and aryllithiums or alkyllithiums, followed by the reaction with water and then with I_2 at 60 °C;[7a] the preparation of 6-arylphenanthridines from the reaction of aryl *o*-biaryl ketones, TMS_2NH, and Sc(OTf)$_3$, followed by the reaction with I_2 at 60 °C;[7b] and the preparation of 2-arylquinolines from the reactions of β-arylpropionitriles and aryllithiums, followed by the reaction with water and then with NIS (*N*-iodosuccinimide) under irradiation with a tungsten lamp.[7c] All those reactions proceed through the formation of *N*-iodoimines, their homolytic N–I bond cleavage to form iminyl radicals, and their cyclization on the aromatic rings.

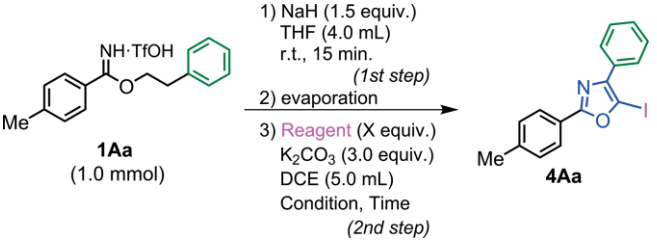
Recently, Nagib et al. reported interesting methods for the preparation of β-amino alcohols through the reactions of (trichloromethyl)imidates prepared from alcohols and trichloroacetonitrile, with NaI and PhI(OAc)$_2$ under visible-light irradiation, *via* the formation of iminyl radicals, their 1,5-H shift, their cyclization to form oxazolines, and their hydrolysis,[8a] and the preparation of γ-functionalized β-amino alcohols from alcohols through the reactions of (trichloromethyl)imidates with NaI and PhI(OAc)$_2$ under visible light irradiation via the formation of amidyl radicals, their 1,5-H shift, formation of olefinic group, iodocyclization, and their hydrolysis.[8b] He et al. also reported the preparation of β-amino alcohols from (trichloromethyl)-imidates, and 2-aryloxazolines from arylimidates with NIS or with NIS and Ag_2O at 110 °C.[8c]

As part of our synthetic studies of nitrogen-containing heteroaromatics using iminyl radicals,[7] we would like to report herein the preparation of 2,4-diaryl-5-iodoxazoles from *O*-(β-arylethyl) arylimidates with DIH (1,3-diiodo-5,5-dimethylhydantoin) under irradiation with a tungsten lamp.

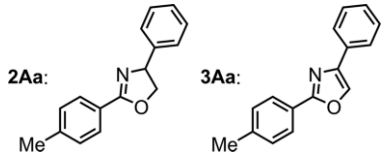
Results and Discussion

First, treatment of triflate salt **1Aa** (1.0 mmol) with NaH (1.5 equiv.) in THF (4.0 mL) gave free *O*-(β-phenylethyl) *p*-tolylimidate (1st step). After removal of the solvent, treatment of generated *O*-(β-phenylethyl) *p*-tolylimidate with NIS (4.0 equiv., 5.0 equiv., and 6.0 equiv.) in the presence of K_2CO_3 (3.0 equiv.) in 1,2-dichloroethane (DCE, 5.0 mL) under irradiation with a 300 W tungsten lamp for 6 h in the range of 35–38 °C (2nd step) gave 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** in 68 %, 54 %, and 65 % yields, together with 4-phenyl-2-*p*-tolyloxazoline **2Aa** in 15 %, 35 %, and 27 % yields, and 4-phenyl-2-*p*-tolyloxazole **3Aa** in 10 %, 11 %, and 0 % yields, respectively, as shown in Table 1 (entries 1–3). Under the same procedure and conditions, treatment of *O*-(β-phenylethyl) *p*-tolylimidate with 1,3-diiodo-5,5-dimethylhydantoin (DIH, 2.0 equiv., 2.5 equiv., and 3.0 equiv.), which has two N–I groups, gave **4Aa** in 42 %, 61 %, and 79 %

Table 1. Optimization for reaction conditions of 5-iodo-2-*p*-tolyl-4-phenyloxazole **4Aa**.



Entry	Reagent [equiv.]	Condition	Time [h]	Yield [%]
1	NIS (4.0)	300 W W-*hν*	6	68 (15)[a] (10)[b]
2	NIS (5.0)	300 W W-*hν*	6	54 (35)[a] (11)[b]
3	NIS (6.0)	300 W W-*hν*	6	65 (27)[a]
4	DIH (2.0)	300 W W-*hν*	6	42 (34)[a] (14)[b]
5	DIH (2.5)	300 W W-*hν*	6	61 (17)[a]
6	DIH (3.0)	300 W W-*hν*	6	79 (17)[a]
7	**DIH (3.0)**	**300 W W-*hν***	**8**	**87 (8)**[a]
8[c]	DIH (3.0)	300 W W-*hν*	8	19 (16)[a]
9[d]	DIH (3.0)	300 W W-*hν*	8	0 (74)[a] (20)[b]
10	DIH (3.0)	40 W W-*hν*	8	20 (56)[a]
11	DIH (3.0)	White LED	8	0 (14)[a]
12	DIH (3.0)	70 °C	8	0
13	I_2 (3.0)	300 W W-*hν*	6	6 (26)[a] (54)[e]
14[f]	DIH (3.0)	300 W W-*hν*	8	0
15[g]	DIH (3.0)	300 W W-*hν*	8	0



[a] Yield of compound **2Aa**. [b] Yield of compound **3Aa**. [c] Reaction was carried out without K_2CO_3. [d] In 2nd step, THF was used instead of DCE. [e] Yield of recovered *O*-(β-phenylethyl) *p*-tolylimidate. [f] In 2nd step, BHT (1.5 equiv.) was added. [g] In 2nd step, TEMPO (1.5 equiv.) was added.

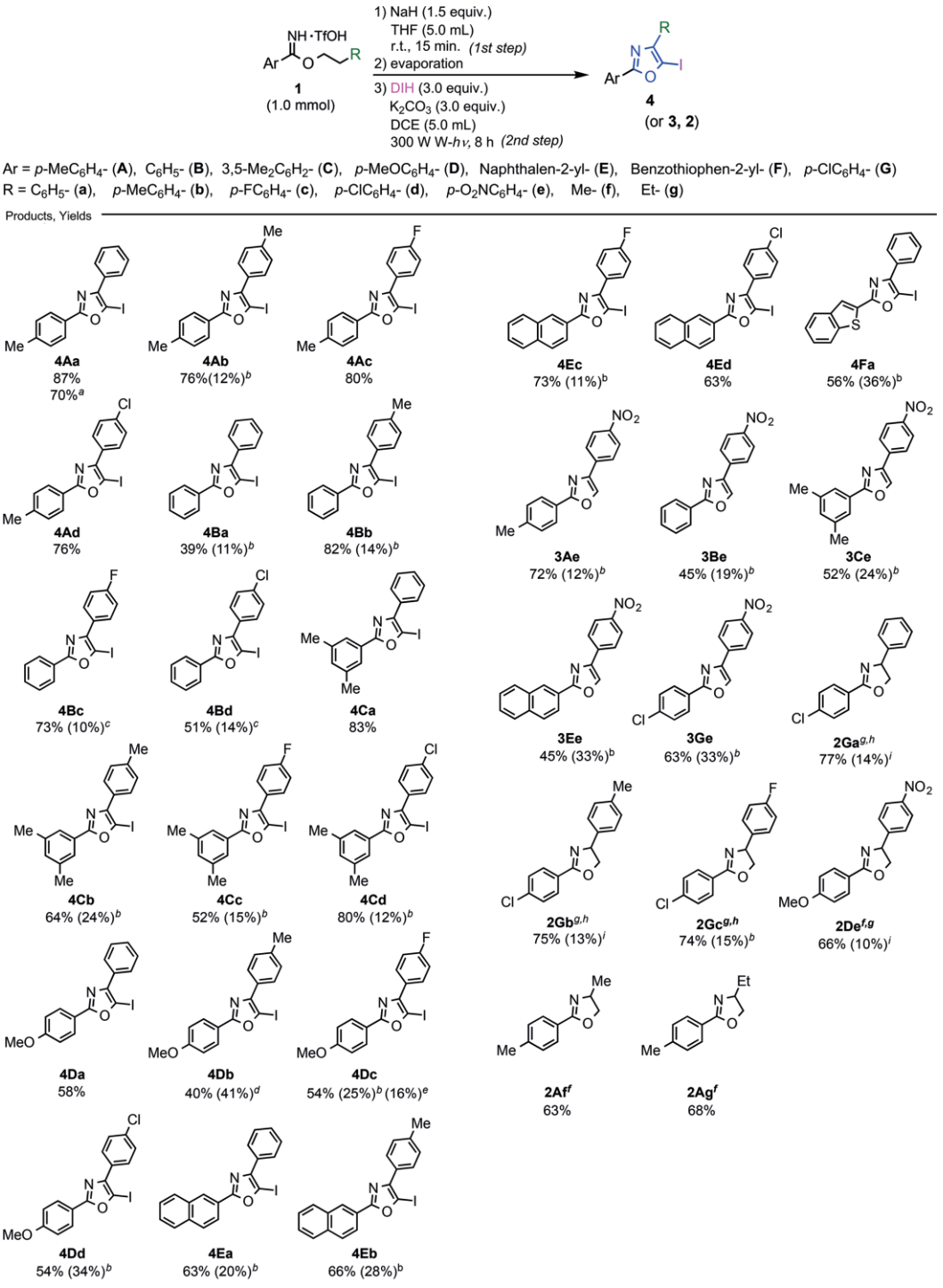
yields, together with **2Aa** in 34 %, 17 %, and 17 % yields, and **3Aa** in 14 %, 0 %, and 0 % yields, respectively (entries 4–6). Thus, DIH was a better choice than NIS for the formation of 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** in 79 % yield (entry 6). Moreover, when the reaction time in the 2nd step was prolonged to 8 h under the same conditions, the yield of 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** was improved to 87 % (entry 7). On the other hand, when the reaction was carried out without K_2CO_3 under the same conditions in the 2nd step, the yield of **4Aa** was dramatically decreased to 19 %, and **2Aa** was formed as well in 16 % yield (entry 8). When THF was used instead of DCE in the 2nd reaction step, **4Aa** was not obtained at all, and **2A**a and **3Aa** were generated in 74 % and 20 % yields, respectively (entry 9).

Instead of a 300 W tungsten lamp, when the reaction of *O*-(β-phenylethyl) *p*-tolylimidate with DIH was carried out under irradiation with a 40 W tungsten lamp and a white LED lamp (13.6 W) in the 2nd step, the yields of **4Aa** were 20 % and 0 %, and those of **2Aa** were in 56 % and 14 %, respectively (entries 10, 11). Furthermore, when the 2nd reaction step was conducted under warming conditions at 70 °C instead of irradiation with a 300 W tungsten lamp, 5-iodooxazole **4Aa** was not formed at all (entry 12). When molecular iodine (3.0 equiv.) instead of DIH was used in the 2nd reaction step, 5-iodoxazole **4Aa** was obtained in only 6 % yield, together with oxazoline **2Aa** and starting *O*-(β-phenylethyl) *p*-tolylimidate in 26 % and 54 % yields, respectively (entry 13).

From those results, treatment of *O*-(β-phenylethyl) *p*-tolylimidate (1.0 mmol) with DIH (3.0 equiv.) and K_2CO_3 (3.0 equiv.) in DCE (5.0 mL) under irradiation with a 300 W tungsten lamp for 8 h in the 2nd reaction step gave 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** in the best yield (entry 7). As a gram-sale experiment, treatment of salt **1Aa** (5.0 mmol) under the same procedure and conditions as those of entry 7 gave 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** in 70 % yield, as shown in Scheme 1. To understand the reaction mechanism, the reactions of *O*-(β-phenylethyl) *p*-tolylimidate with DIH and K_2CO_3 in DCE in the 2nd step were carried out in the presence of 2,6-di-*tert*-butyl-*p*-cresol (BHT, 1.5 equiv.) and 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 1.5 equiv.) under the same conditions as those of entry 7. However, 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** and related compounds **2Aa** and **3Aa** were not formed at all in both reactions (entries 14, 15). Thus, the results suggest that the 2nd step is a radical-mediated reaction.

Based on those results, triflate salts **1Ab**–**1Ad**, **1Ba**–**1Bd**, and **1Ca**–**1Cd** of *O*-(β-arylethyl) *p*-tolylimidates, *O*-(β-arylethyl) phenylimidates, and *O*-(β-arylethyl) 3,5-dimethylphenylimidates (1.0 mmol) bearing phenyl (**a**), *p*-tolyl (**b**), *p*-fluorophenyl (**c**), and *p*-chlorophenyl (**d**) groups were treated with NaH (1.5 equiv.) in THF (5.0 mL) at room temperature for 15 min. (1st step), followed by removal of the solvent and subsequent treatment with DIH (3.0 equiv.) and K_2CO_3 (3.0 equiv.) in DCE (5.0 mL) under irradiation with a 300 W tungsten lamp for 8 h (2nd step) to give 4-aryl-5-iodo-2-*p*-tolyloxazoles **4Ab**–**4Ad**, 4-aryl-5-iodo-2-phenyloxazoles **4Ba**–**4Bd**, and 4-aryl-2-(3′,5′-dimethylphenyl)-5-iodoxazoles **4Ca**–**4Cd** in good to moderate yields, respectively, except **4Ba**, together with small amounts of oxazolines **2** and oxazoles **3** depending on the substituent, as shown in Scheme 1. Treatment of triflate salts **1Da**–**1Dd** and **1Ea**–**1Ed** of *O*-(β-arylethyl) *p*-methoxyphenylimidates and *O*-(β-arylethyl) naphthalen-2-ylimidates bearing phenyl (**a**), *p*-tolyl (**b**), *p*-fluorophenyl (**c**), and *p*-chlorophenyl (**d**) groups under the same procedure and conditions gave also 4-aryl-5-iodo-2-*p*-methoxyphenyloxazoles **4Da**–**4Dd** and 4-aryl-5-iodo-2-(naphthalen-2′-yl)oxazoles **4Ea**–**4Ed** in moderate to good yields, respectively, together with oxazolines **2** depending on the substituent of the aromatics.

Here, 5-iodo-2-*p*-methoxyphenyl-4-*p*-tolyloxazole **4Db** was formed in 40 % yield together with *p*-iodoanisole in 41 % yield, which would be generated through the electrophilic *ipso*-substitution of the *p*-methoxyphenylimidate group by an iodonium species in the reaction of *O*-β-(*p*-tolyl)ethyl *p*-methoxyphenylimidate with DIH. In addition, 4-*p*-fluorophenyl-5-iodo-2-*p*-methoxyphenyloxazole **4Dc** was produced in 54 % yield together with *p*-methoxybenzonitrile in 16 % yield, the latter of which would be formed via a radical β-cleavage reaction of the formed iminyl radical. Treatment of triflate salt **1Fa** of *O*-(β-phenylethyl) benzothiophen-2-ylimidate under the same procedure and conditions gave 2-(benzothiophen-2′-yl)-5-iodo-4-phenyloxazole **4Fa** in 56 % yield, together with oxazoline **2Fa** in 36 % yield, whereas the same treatment of triflate salt of *O*-(β-phenylethyl) benzofuran-2-ylimidate under the same procedure and conditions gave 2-(benzofuran-2′-yl)-5-iodo-4-phenyloxazole in low yield (ca. 10 %). The same treatment of *O*-(β-*p*-nitrophenylethyl) arylimidate salts **1Ae**, **1Be**, **1Ce**, **1Ee**, and **1Ge** gave 2-aryl-4-*p*-nitrophenyloxazoles **3Ae**, **3Be**, **3Ce**, **3Ee**, and **3Ge** in good to moderate yields, together with their oxazolines **2** in 12 %, 19 %, 24 %, 33 %, and 33 % yields, respectively. Thus, the results suggest that the iodination of formed 2-aryl-4-*p*-nitrophenyloxazoles at 5-position does not proceed smoothly because of the electron-withdrawing *p*-nitrophenyl group at 4-position. On the other hand, when *O*-(β-arylethyl) *p*-chlorophenylimidates derived from **1Ga**, **1Gb**, and **1Gc** bearing an electron-withdrawing group, i.e., a *p*-chlorophenyl group, at 2-position were treated with DIH under the same irradiation conditions in the range of 35–38 °C, *p*-chlorobenzonitrile was obtained in 64 %, 72 %, and 74 % yields, respectively, probably via the radical β-elimination of the formed iminyl radicals, without the formation of oxazolines and oxazoles. However, when the same irradiation reactions of *O*-(β-arylethyl) *p*-chlorophenylimidates were carried out at 10 °C, corresponding oxazolines **2Ga**, **2Gb**, and **2Gc** were obtained in 77 %, 75 %, and 74 % yields, together with their 5-iodoxazoles in low yields, respectively, although the reaction mixtures were further warmed at 40 °C for 5 h after the irradiation. Treatment of *O*-β-(*p*-nitrophenyl)ethyl *p*-methoxyphenylimidate salt **1De** that has an electron-withdrawing group, i.e., a *p*-nitrophenyl group, under the same procedure and conditions gave also oxazolines **2De** in 66 % yield, together with 5-iodooxazole **4De** in low yield. Moreover, treatment of *O*-propyl *p*-tolylimidate salt **1Af** and *O*-butyl *p*-tolylimidate salt **1Ag** under the same procedure and conditions also gave 4-methyl-2-*p*-tolyloxazoline **2Af** and 4-ethyl-2-*p*-tolyloxazoline **2Ag** in 63 % and 68 % yields, respectively, although the reaction mixtures were further warmed at



Scheme 1. Transformation of arylimidates **1** to 5-iodooxazoles **4**.

40 °C for 24 h after the irradiation. Thus, oxidation of formed oxazolines **2** bearing electron-withdrawing groups, such as a *p*-nitrophenyl group, and an alkyl group at 4-position to the corresponding oxazoles **3** did not proceed smoothly under the present reaction conditions. Moreover, when the triflate salt of *O*-(β-phenylethyl) *p*-(trifluoromethyl)phenylimidate was treated

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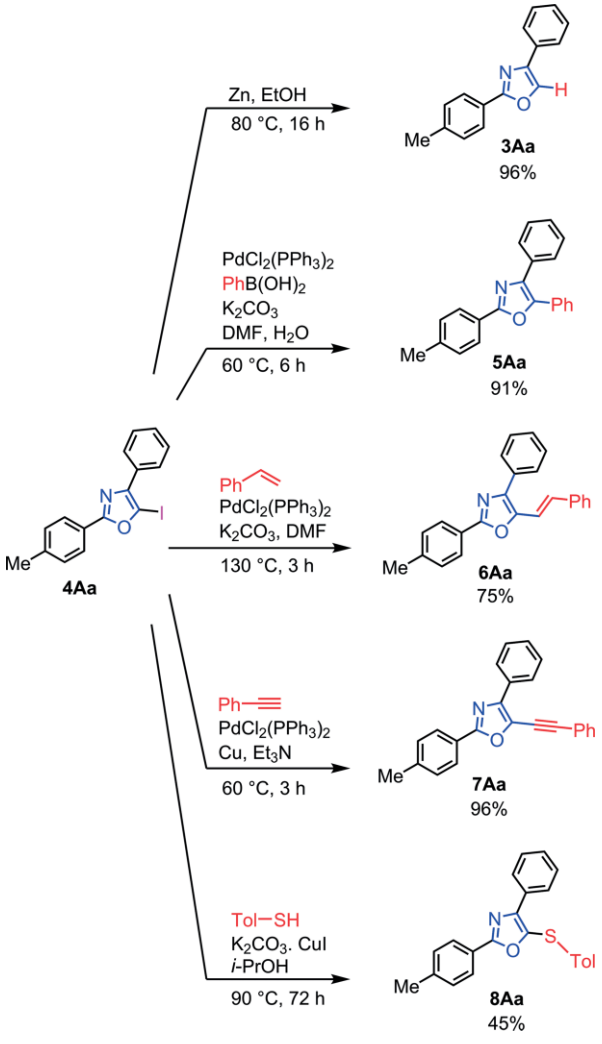
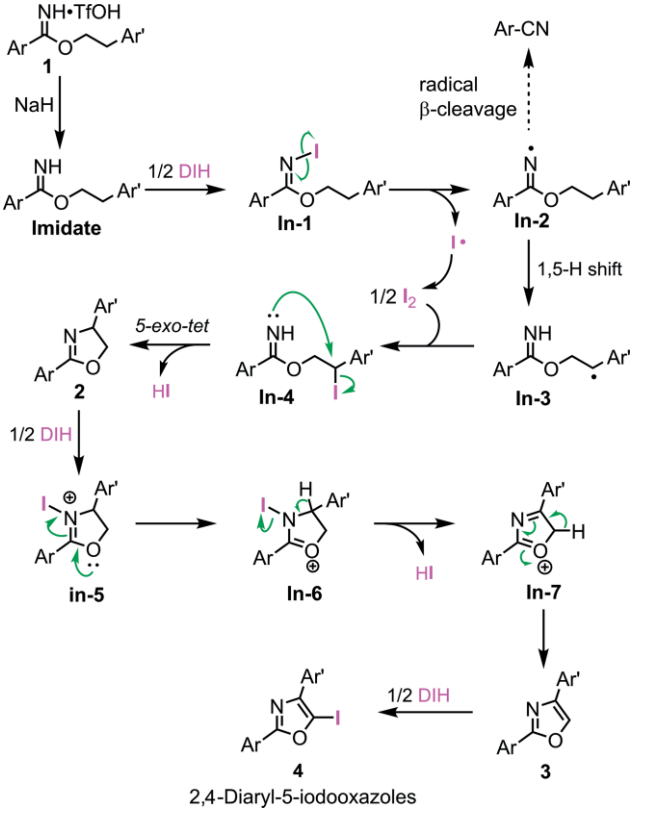
under the same procedure and conditions, the reaction did not proceed at all, i.e., *N*-iodonation did not occur due to the presence of a powerful electron-withdrawing group, such as a *p*-(trifluoromethyl)phenyl group. Taken together, treatment of *O*-(β-arylethyl) arylimidates bearing *p*-tolyl (**A**), phenyl (**B**), 3,5-dimethylphenyl (**C**), *p*-methoxyphenyl (**D**), naphthalen-2-yl (**E**), and benzothiophen-2-yl (**F**) groups in the arylimidate part, and bearing phenyl (**a**), *p*-tolyl (**b**), *p*-fluorophenyl (**c**), and *p*-chlorophenyl (**d**) groups in the β-arylethyl part, gave mainly the corresponding 2,4-diaryl-5-iodoxazoles. On the other hand, treatment of *O*-(β-arylethyl) arylimidates bearing a *p*-chlorophenyl group in the arylimidate part, and bearing an alkyl group instead of a β-arylethyl group gave oxazolines **2**. Thus, the oxidation of formed oxazolines **2** to oxazoles **3** and the iodination of oxazoles **3** to 5-iodoxazoles **4** bearing electron-withdrawing aryl groups or alkyl groups with DIH did not proceed smoothly.

Once 2,4-diaryl-5-iodoxazoles were obtained, they could be smoothly converted into various 2,4-diaryloxazole derivatives. Warming treatment of 5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** with Zn in ethanol gave 4-phenyl-2-*p*-tolyloxazole **3Aa** in 96 % yield, as shown in Scheme 2. Treatment of **4Aa** with $PhB(OH)_2$ and K_2CO_3 in a mixture of DMF and water, with styrene and K_2CO_3 in DMF, and with ethynylbenzene and Cu in Et_3N in the presence of $PdCl_2(Ph_3P)_2$ under warming conditions gave 4,5-diphenyl-2-*p*-tolyloxazole **5Aa**, 4-phenyl-5-styryl-2-*p*-tolyloxazole **6Aa**, and 4-phenyl-5-phenylethynyl-2-*p*-tolyloxazole **7Aa** in good yields, respectively. 4-Phenyl-5-*p*-toluenesulfenyl-2-*p*-tolyloxazole **8Aa** could be also obtained by the treatment of **4Aa** with *p*-toluenethiol and K_2CO_3 in the presence of CuI in *i*PrOH in moderate yield.

A plausible reaction mechanism is shown in Scheme 3. *O*-(β-Arylethyl) arylimidate generated from the reaction of triflate salt **1** and NaH reacts with DIH to form *N*-iodoimidate **In-1**. Once *N*-iodoimidate **In-1** is formed, homolytic bond cleavage of its N–I bond occurs to produce iminyl radical **In-2** and an iodine atom. The 1,5-hydrogen atom shift (1,5-H shift)[9] from benzylic hydrogen atom via a six-membered transition state by iminyl radical **In-2** occurs to form benzylic carbon-centred radical **In-3**, which smoothly reacts with molecular iodine to form β-iodoethyl arylimidate **In-4**. Intramolecular nucleophilic cyclization of **In-4** occurs in the *5-exo-tet* mode to give 2,4-diaryloxazoline **2**. 2,4-Diaryloxazoline **2** further reacts with DIH to generate 2,4-diaryloxazole **3** through intermediates **In-5**, **In-6**, and **In-7**. Iodination of oxazole **3** finally occurs to form 2,4-diaryl-5-iodooxazole **4**, without electron-withdrawing groups, such as *p*-chlorophenyl and *p*-nitrophenyl groups at 2- or 4-position, or bearing an alkyl group at 4-position. Practically, the treatment of 4-phenyl-2-*p*-tolyloxazoline **2Aa** and 4-phenyl-2-*p*-tolyloxazole **3Aa** with DIH (2.0 equiv.) and K_2CO_3 (1.5 equiv.) in DCE (5.0 mL) for 8 h under irradiation with a tungsten lamp gave



Scheme 2. Derivatization of **2Aa**.



Scheme 3. Plausible reaction mechanism.

5-iodo-4-phenyl-2-*p*-tolyloxazole **4Aa** in 53 % and 55 % yields, respectively.

Finally, quite recently, Nagib et al. reported the preparation of 2,4-diaryloxazoles from *O*-(β-arylethyl) arylimidates with CsI and $PhI(OAc)_2$ in toluene under 23 W fluorescent lighting, that was exceedingly related to the present study.[10]

Conclusions

O-(β-Arylethyl) arylimidates, which can be prepared easily as solids of triflate salts by the reaction of aromatic nitriles and β-arylethyl alclohols in the presence of TfOH, react with DIH under irradiation with a tungsten lamp to form the corresponding 2,4-diaryl-5-iodoxazoles in good to moderate yields, through the formation of *N*-iodoimidates, the homolytic bond cleavage of their N–I bonds, the 1,5-H shift by iminyl radicals, the nucleophilic cyclization in the *5-exo-tet* mode to form oxazolines, the oxidation of the oxazolines to oxazoles, and the iodination of the oxazoles at 5-position. Thus, the present method is a multi-step one-pot transition-metal-free reaction for the preparation of 2,4-diaryl-5-iodoxazoles and 2.4-diaryloxazoles from *O*-(β-arylethyl) arylimidates. It should be note that electron-withdrawing aryl groups, such as the *p*-nitrophenyl group, in the imidates retarded the reaction. We believe the present method would be useful because it provides a straightforward procedure for the preparation of 2,4-diaryloxazoles from *O*-(β-arylethyl) arylimidates under transition-metal-free conditions.

Experimental Section

General. ^{1}H NMR spectra were measured on 400 MHz spectrometers. Chemical shifts were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sext = sextet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on 100 MHz spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$ at 77.0 ppm, or $[D_6]$DMSO at 39.5 ppm). Characteristic peaks in the infrared (IR) spectra were recorded in wave number, cm^{-1} on a JASCO FT/IR-4100 spectrometer. Melting points were determined using a Yamato Melting Point Apparatus Model MP-21. High-resolution mass spectra (HRMS) were recorded by Thermo Fisher Scientific Exactive Orbitrap mass spectrometers. Melting points were uncorrected. Thin-layer chromatography (TLC) was performed using 0.25 mm silica gel plates (60F254). The products were purified by column chromatography on neutral silica gel 60N (63–200 mesh).

Typical Procedure for Preparation of *O*-(β-arylethyl) Arylimidate·TfOH Salts 1: Triflate salts **1** were prepared based on the literature[8a] with aromatic nitriles and β-arylethanols with TfOH. To a solution of 2-phenylethyl alcohol (20.0 mmol, 2443.0 mg) and *p*-tolunitrile (24.0 mmol, 2812.0 mg) in CH_2Cl_2 (40.0 mL) was added TfOH (24.0 mmol, 2.1 mL) at room temperature. The obtained mixture was stirred for 24 h at 60 °C under argon atmosphere, and then evaporated under reduced pressure. Diethyl ether was added to the mixture at 0 °C until precipitation occurred. The salt was filtered, and washed with diethyl ether to give *O*-(β-phenylethyl) *p*-tolylimidate·TfOH salt (**1Aa**, 444.8 mg, 57 %).

***O*-(β-Phenylethyl) *p*-tolylimidate·TfOH salt (1Aa)**: white solid; mp: 172–173 °C; IR (neat): $\tilde{\nu}$ = 3065, 1610, 1449, 1238, 1026, 736, 630 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 3.26 (t, 2H, *J* = 5.9 Hz), 4.88 (t, 2H, *J* = 6.1 Hz), 7.27–7.37 (m, 7H), 7.87 (d, 2H, *J* = 8.3 Hz), 10.1 (s, 1H), 10.6 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 21.8, 39.5, 73.6, 121.2 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.4, 127.4, 129.1 (2C), 129.4 (2C), 129.6 (2C), 130.4 (2C), 137.1, 147.2, 171.7; HRMS (ESI): Calcd for $C_{16}H_{18}ON$ $[M]^+$ = 240.1383, Found = 240.1378.

***O*-[β-(*p*-Toyl)ethyl] *p*-tolylimidate·TfOH salt (1Ab)**: white solid; mp: 164–166 °C; IR (neat): $\tilde{\nu}$ = 3073, 1609, 1449, 1224, 1024, 742, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 2.44 (s, 3H), 3.21 (t, 2H, *J* = 5.9 Hz), 4.86 (t, 2H, *J* = 6.1 Hz), 7.14 (d, 2H, *J* = 7.9 Hz), 7.19 (d, 2H, *J* = 8.2 Hz), 7.33 (d, 2H, *J* = 7.9 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 10.1 (s, 1H), 10.6 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 20.7, 21.4, 33.3, 73.4, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.0, 129.0 (2C), 129.1 (2C), 129.3 (2C), 130.0 (2C), 133.6, 136.1, 146.8, 171.3; HRMS (ESI): Calcd for $C_{17}H_{20}ON$ $[M]^+$ = 254.1539, Found = 254.1532.

***O*-[β-(*p*-Fluorophenyl)ethyl] *p*-tolylimidate·TfOH salt (1Ac)**: white solid; mp: 167–169 °C; IR (neat): $\tilde{\nu}$ = 3056, 1610, 1467, 1223, 1024, 828, 630 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 3.24 (t, 2H, *J* = 5.9 Hz), 4.86 (t, 2H, *J* = 6.1 Hz), 7.04 (t, 2H, *J* = 8.6 Hz), 7.25–7.29 (m, 2H), 7.34 (d, 2H, *J* = 8.2 Hz), 7.87 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.3, 39.1, 73.1, 115.3 (d, 2C, $J_{C\text{-}F}$ = 20.7 Hz), 120.8 (q, $J_{C\text{-}F}$ = 321.3 Hz), 123.0, 129.0 (2C), 130.0 (2C), 131.1 (d, 2C, $J_{C\text{-}F}$ = 7.5 Hz), 132.9, 146.7, 161.4 (d, $J_{C\text{-}F}$ = 242.4 Hz), 171.2; HRMS (ESI): Calcd for $C_{16}H_{17}ONF$ $[M]^+$ = 258.1289, Found = 258.1280.

***O*-[β-(*p*-Chlorophenyl)ethyl] *p*-tolylimidate·TfOH salt (1Ad)**: white solid; mp: 166–168 °C; IR (neat): $\tilde{\nu}$ = 3071, 1609, 1449, 1224, 1024, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 3.23(t, 2H, *J* = 5.9 Hz), 4.86 (t, 2H, *J* = 6.1 Hz), 7.24 (d, 2H, *J* = 8.4 Hz), 7.31–7.35 (m, 4H), 7.86 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 21.4, 39.1, 72.9, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.0, 128.6 (2C), 129.0 (2C), 130.0 (2C), 131.1 (2C), 131.8, 135.9, 146.8, 171.3; HRMS (ESI): Calcd for $C_{16}H_{17}ON^{35}Cl$ $[M]^+$ = 274.0993, Found = 274.0984.

***O*-[β-(*p*-Nitrophenyl)ethyl] *p*-tolylimidate·TfOH salt (1Ae)**: white solid; mp: 164–165 °C; IR (neat): $\tilde{\nu}$ = 3054, 1607, 1520, 1235, 1023, 630 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 3.39 (t, 2H, *J* = 5.9 Hz), 4.94 (t, 2H, *J* = 6.1 Hz), 7.35 (d, 2H, *J* = 8.2 Hz), 7.50 (d, 2H, *J* = 8.6 Hz), 7.86 (d, 2H, *J* = 8.6 Hz), 8.22 (d, 2H, *J* = 8.8 Hz), 10.1 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 21.3, 39.1, 72.4, 120.8 (q, $J_{C\text{-}F}$ = 322.3 Hz), 122.9, 123.6 (2C), 129.0 (2C), 130.0 (2C), 130.6 (2C), 145.3, 146.6, 146.8, 171.2; HRMS (ESI): Calcd for $C_{16}H_{17}O_3N_2$ $[M]^+$ = 285.1234, Found = 285.1230.

***O*-Propyl *p*-tolylimidate·TfOH salt (1Af)**: white solid; mp: 108–110 °C; IR (neat): $\tilde{\nu}$ = 3079, 1611, 1461, 1222, 1163, 1024, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, 3H, *J* = 7.4 Hz), 2.00 (sext, 2H, *J* = 7.4 Hz), 2.46 (s, 3H), 4.61 (t, 2H, *J* = 6.3 Hz), 7.37 (d, 2H, *J* = 8.1 Hz), 8.00 (d, 2H, *J* = 8.5 Hz); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 10.0, 21.2, 21.4, 74.5, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.2, 129.1 (2C), 130.0 (2C), 146.7, 171.5; HRMS (ESI): Calcd for $C_{11}H_{16}ON$ $[M]^+$ = 178.1226, Found = 178.1225.

***O*-Butyl *p*-tolylimidate·TfOH salt (1Ag)**: white solid; mp: 114–115 °C; IR (neat): $\tilde{\nu}$ = 3032, 1608, 1454, 1224, 1160, 1028, 631 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.02 (t, 3H, *J* = 7.5 Hz), 1.56 (sext, 2H, *J* = 7.7 Hz), 1.95 (quin, 2H, *J* = 7.0 Hz), 2.46 (s, 3H), 4.65 (t, 2H, *J* = 6.1 Hz), 7.37 (d, 2H, *J* = 8.4 Hz), 7.99 (d, 2H, *J* = 8.4 Hz), 10.1 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 13.5, 18.5, 21.4, 29.5, 72.9, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.2, 129.0 (2C), 130.0 (2C), 146.7, 171.5; HRMS (ESI): Calcd for $C_{12}H_{18}ON$ $[M]^+$ = 192.1383, Found = 192.1378.

***O*-(β-Phenylethyl) phenylimidate·TfOH salt (1Ba)**: white solid; mp: 124–126 °C; IR (neat): $\tilde{\nu}$ = 3081, 1602, 1456, 1238, 1023, 698 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.27 (t, 2H, *J* = 5.9 Hz), 4.92 (t, 2H, *J* = 6.1 Hz), 7.28–7.38 (m, 5H), 7.54 (t, 2H, *J* = 8.2 Hz), 7.72 (t, 1H, *J* = 7.7 Hz), 7.97 (dd, 2H, *J* = 8.6, 1.1 Hz); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 33.7, 73.5, 121.0 (q, $J_{C\text{-}F}$ = 322.3 Hz), 126.1, 127.1, 128.8 (2C), 129.1 (2C), 129.3 (2C), 129.4 (2C), 135.6, 136.8, 171.6; HRMS (ESI): Calcd for $C_{15}H_{16}ON$ $[M]^+$ = 226.1226, Found = 226.1223.

***O*-[β-(*p*-Tolyl)ethyl] phenylimidate·TfOH salt (1Bb)**: white solid; mp: 125–127 °C; IR (neat): $\tilde{\nu}$ = 3102, 1602, 1381, 1243, 1025, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.23 (t, 2H, *J* = 6.1 Hz), 4.88 (t, 2H, *J* = 6.1 Hz), 7.16 (d, 2H, *J* = 7.9 Hz), 7.20 (d, 2H, *J* = 8.3 Hz), 7.55 (t, 2H, *J* = 7.9 Hz), 7.73 (t, 1H, *J* = 7.6 Hz), 7.98 (dd, 2H, *J* = 8.6, 1.4 Hz), 10.3 (s, 1H), 10.8 (s, 1H); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 20.7, 33.2, 73.5, 120.8 (q, $J_{C\text{-}F}$ = 322.3 Hz), 126.0, 129.0 (2C), 129.1 (2C), 129.2 (2C), 129.4 (2C), 133.5, 135.6, 136.0, 171.5; HRMS (ESI): Calcd for $C_{16}H_{18}ON$ $[M]^+$ = 240.1383, Found = 240.1378.

***O*-[β-(*p*-Fluorophenyl)ethyl] phenylimidate·TfOH salt (1Bc)**: white solid; mp: 100–102 °C; IR (neat): $\tilde{\nu}$ = 3080, 1601, 1511, 1223, 1024, 626 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.25 (t, 2H, *J* = 6.1 Hz), 4.88 (t, 2H, *J* = 6.1 Hz), 7.04 (t, 2H, *J* = 8.6 Hz), 7.28–7.30 (m, 2H), 7.55 (t, 2H, *J* = 7.7 Hz), 7.74 (t, 1H, *J* = 7.5 Hz), 7.97 (d, 2H, *J* = 7.5 Hz); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 32.8, 73.4, 115.4 (d, $J_{C\text{-}F}$ = 20.7 Hz), 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 126.0, 129.1 (2C), 129.4 (2C), 131.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 132.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 135.6, 161.5 (d, $J_{C\text{-}F}$ = 246.4 Hz), 171.6; HRMS (ESI): Calcd for $C_{15}H_{15}ONF$ $[M]^+$ = 244.1132, Found = 244.1127.

***O*-[β-(*p*-Chlorophenyl)ethyl] phenylimidate·TfOH salt (1Bd)**: white solid; mp: 130–132 °C; IR (neat): $\tilde{\nu}$ = 3091, 1602, 1382, 1242, 1025, 627 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3. 25 (t, 2H, *J* = 5.9 Hz), 4.89 (t, 2H, 5.9 Hz), 7.24–7.28 (m, 2H), 7.33 (d, 2H, *J* = 8.6 Hz), 7.56 (t, 2H, *J* = 7.7 Hz), 7.74 (t, 1H, *J* = 7.5 Hz), 7.97 (dd, 2H, *J* = 8.6, 1.4 Hz); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 32.9, 73.1, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 126.0, 128.6 (2C), 129.0 (2C), 129.4 (2C), 131.1 (2C), 131.8, 135.6, 135.8, 171.5; HRMS (ESI): Calcd for $C_{15}H_{15}ON^{35}Cl$ $[M]^+$ = 260.0837, Found = 260.0833.

***O*-[β-(*p*-Nitrophenyl)ethyl] phenylimidate·TfOH salt (1Be)**: white solid; mp: 134–136 °C; IR (neat): $\tilde{\nu}$ = 3064, 1600, 1523, 1240, 1023, 697 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.41 (t, 2H, *J* = 6.1 Hz), 4.97 (t, 2H, *J* = 6.3 Hz), 7.52 (d, 2H, *J* = 8.4 Hz), 7.58 (t, 2H, *J* = 7.9 Hz), 7.77 (t, 1H, *J* = 7.9 Hz), 7.97 (d, 2H, *J* = 7.9 Hz), 8.24 (d, 2H, *J* = 8.4 Hz), 10.4 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, [D_6]DMSO: δ = 33.3, 72.6, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.7 (2C), 125.9, 129.0 (2C), 129.4 (2C), 130.6 (2C), 135.6, 145.3, 146.6, 171.5; HRMS (ESI): Calcd for $C_{15}H_{15}O_3N_2$ $[M]^+$ = 285.1234, Found = 285.1230.

***O*-(β-Phenylethyl) 3,5-dimethylphenylimidate·TfOH salt (1Ca)**: white solid; mp: 127–129 °C; IR (neat): $\tilde{\nu}$ = 3049, 1600, 1241, 1026, 630 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6H), 3.26 (t, 2H, *J* = 5.9 Hz), 4.88 (t, 2H, *J* = 5.9 Hz), 7.27–7.37 (m, 6H), 7.54 (s, 2H), 10.1 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.9 (2C), 34.2, 73.9, 120.1 (q, $J_{C\text{-}F}$ = 319.5 Hz), 124.6, 126.7 (2C), 127.1, 128.7 (2C), 128.9 (2C), 136.1, 137.8, 139.4 (2C), 172.7; HRMS (ESI): Calcd for $C_{17}H_{20}ON$ $[M]^+$ = 254.1539, Found = 254.1538.

***O*-[β-(*p*-Tolyl)ethyl] 3,5-dimethylphenylimidate·TfOH salt (1Cb)**: white solid; mp: 151–153 °C; IR (neat): $\tilde{\nu}$ = 3039, 1601, 1226, 1158, 1025, 631 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 2.36 (s, 6H), 3.22 (t, 2H, *J* = 6.1 Hz), 4.85 (t, 2H, *J* = 6.1 Hz), 7.16 (d, 2H, *J* = 7.9 Hz), 7.20 (d, 2H, *J* = 8.2 Hz), 7.33 (s, 1H), 7.54 (s, 2H), 10.1 (s, 1H), 10.6 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.9 (2C), 21.0, 33.9, 74.2, 120.1 (q, $J_{C\text{-}F}$ = 318.5 Hz), 124.6, 126.8 (2C), 128.8 (2C), 129.4 (2C), 133.0, 136.8, 137.8, 139.4 (2C), 172.8; HRMS (ESI): Calcd for $C_{18}H_{22}ON$ $[M]^+$ = 268.1696, Found = 268.1692.

***O*-[β-(*p*-Fluorophenyl)ethyl] 3,5-dimethylphenylimidate·TfOH salt (1Cc)**: white solid; mp: 128–130 °C; IR (neat): $\tilde{\nu}$ = 3048, 1602, 1508, 1223, 1027, 835, 631 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6H), 3.24 (t, 2H, *J* = 6.1 Hz), 4.85 (t, 2H, *J* = 6.1 Hz), 7.04 (t, 2H, *J* = 8.8 Hz), 7.27–7.30 (m, 2H), 7.34 (s, 1H), 7.55 (s, 2H), 10.1 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.9 (2C), 33.4, 73.8, 115.6 (d, $J_{C\text{-}F}$ = 20.1 Hz), 120.1 (q, $J_{C\text{-}F}$ = 318.5 Hz), 124.5, 126.7 (2C), 130.5 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.7 (d, $J_{C\text{-}F}$ = 3.8 Hz), 137.8, 139.4 (2C), 162.0 (d, $J_{C\text{-}F}$ = 245.2 Hz), 172.7; HRMS (ESI): Calcd for $C_{17}H_{19}ONF$ $[M]^+$ = 272.1445, Found = 272.1441.

***O*-[β-(*p*-Chlorophenyl)ethyl] 3,5-dimethylphenylimidate·TfOH salt (1Cd)**: white solid; mp: 140–141 °C; IR (neat): $\tilde{\nu}$ = 3039, 1600, 1226, 1024, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6H), 3.24 (t, 2H, *J* = 6.1 Hz), 4.86 (t, 2H, *J* = 6.1 Hz), 7.25 (d, 2H, *J* = 6.3 Hz), 7.33 (d, 2H, *J* = 8.6 Hz), 7.34 (s, 1H), 7.54 (s, 2H), 10.1 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 20.9 (2C), 33.5, 73.6, 120.1 (q, $J_{C\text{-}F}$ = 319.5 Hz), 124.5, 126.7 (2C), 128.8 (2C), 130.3 (2C), 133.0, 134.5, 137.9, 139.5 (2C), 172.7; HRMS (ESI): Calcd for $C_{17}H_{19}ONCl$ $[M]^+$ = 288.1150, Found = 288.1146.

***O*-[β-(*p*-Nitrophenyl)ethyl] 3,5-dimethylphenylimidate·TfOH salt (1Ce)**: white solid; mp: 169–170 °C; IR (neat): $\tilde{\nu}$ = 3078, 1606, 1517, 1246, 1028, 634 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6H), 3.39 (t, 2H, *J* = 6.1 Hz), 4.93 (t, 2H, *J* = 6.1 Hz), 7.36 (s, 1H), 7.51 (d, 2H, *J* = 8.8 Hz), 7.55 (s, 2H), 8.23 (d, 2H, *J* = 8.8 Hz), 10.2 (s, 1H), 10.7 (s, 1H); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 20.7 (2C), 39.1, 72.5, 120.8 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.6 (2C), 125.8, 126.5 (2C), 130.6 (2C), 137.0, 138.9 (2C), 145.2, 146.6, 171.6; HRMS (ESI): Calcd for $C_{17}H_{19}O_3N_2$ $[M]^+$ = 299.1390, Found = 299.1385.

***O*-(β-Phenylethyl) *p*-methoxyphenylimidate·TfOH salt (1Da)**: yellow solid; mp: 155–157 °C; IR (neat): $\tilde{\nu}$ = 3067, 1601, 1456, 1241, 1225, 1021, 750 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.25 (t, 2H, *J* = 6.1 Hz), 3.89 (s, 3H), 4.86 (t, 2H, *J* = 6.1 Hz), 6.99 (d, 2H, *J* = 9.0 Hz), 7.27–7.37 (m, 5H), 7.96 (d, 2H, *J* = 9.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 34.3, 55.8, 73.7, 114.8 (2C), 116.3, 120.2 (q, $J_{C\text{-}F}$ = 318.5 Hz), 127.1, 128.8 (2C), 128.9 (2C), 131.7 (2C), 136.2, 165.9, 171.5; HRMS (ESI): Calcd for $C_{16}H_{18}O_2N$ $[M]^+$ = 256.1332, Found = 256.1330.

***O*-[β-(*p*-Tolyl)ethyl] *p*-methoxyphenylimidate·TfOH salt (1Db)**: yellow solid; mp: 135–137 °C; IR (neat): $\tilde{\nu}$ = 2987, 1605, 1463, 1233, 1160, 1020, 632 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.21 (t, 2H, *J* = 5.9 Hz), 3.90 (s, 3H), 4.83 (t, 2H, *J* = 5.9 Hz), 7.00 (d, 2H, *J* = 9.1 Hz), 7.12–7.20 (m, 4H), 7.97 (d, 2H, *J* = 9.1 Hz), 9.91 (s, 1H), 10.4 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.0, 33.9, 55.8, 73.9, 114.8 (2C), 116.4, 120.2 (q, $J_{C\text{-}F}$ = 318.5 Hz), 128.7 (2C), 129.4 (2C), 131.7 (2C), 133.1, 136.7, 165.9, 171.5; HRMS (ESI): Calcd for $C_{17}H_{20}O_2N$ $[M]^+$ = 270.1489, Found = 270.1486.

***O*-[β-(*p*-Fluorophenyl)ethyl] *p*-methoxyphenylimidate·TfOH salt (1Dc)**: yellow solid; mp: 149–150 °C; IR (neat): $\tilde{\nu}$ = 2988, 1602, 1466, 1235, 1024, 629 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.23 (t, 2H, *J* = 5.9 Hz), 3.90 (s, 3H), 4.84 (t, 2H, *J* = 5.9 Hz), 7.00 (d, 2H, *J* = 9.3 Hz), 7.04 (t 2H, *J* = 8.6 Hz), 7.25–7.29 (m, 2H), 7.97 (d, 2H, *J* = 9.1 Hz), 9.91 (s, 1H), 10.5 (s, 1H); ^{13}C-NMR (100 MHz, [D_6]DMSO): δ = 32.8, 56.0, 72.9, 114.9 (2C), 115.4 (d, $J_{C\text{-}F}$ = 20.7 Hz), 117.3, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 131.1 (d, 2C, $J_{C\text{-}F}$ = 8.5 Hz), 131.5 (2C), 133.0, 161.4 (d, $J_{C\text{-}F}$ = 242.4 Hz), 165.2, 170.6; HRMS (ESI): Calcd for $C_{16}H_{17}O_2NF$ $[M]^+$ = 274.1238, Found = 274.1234.

***O*-[β-(*p*-Chlorophenyl)ethyl] *p*-methoxyphenylimidate·TfOH salt (1Dd)**: yellow solid; mp: 150–152 °C; IR (neat): $\tilde{\nu}$ = 3086, 1601, 1441, 1240, 1023, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.23 (t, 2H, *J* =

5.9 Hz), 3.90 (s, 3H), 4.84 (t, 2H, *J* = 6.1 Hz), 7.00 (d, 2H, *J* = 8.8 Hz), 7.24 (d, 2H, *J* = 8.6 Hz), 7.32 (d, 2H, *J* = 8.4 Hz), 7.96 (d, 2H, *J* = 9.1 Hz), 9.92 (s, 1H), 10.5 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 33.6, 55.8, 73.3, 114.8 (2C), 116.2, 120.1 (q, $J_{C\text{-}F}$ = 318.5 Hz), 128.9 (2C), 130.2 (2C), 131.6 (2C), 133.0, 134.6, 166.0, 171.5; HRMS (ESI): Calcd for $C_{16}H_{17}O_2N^{35}Cl$ $[M]^+$ = 290.0942, Found = 290.0939.

***O*-[β-(*p*-Nitrophenyl)ethyl] *p*-methoxyphenylimidate·TfOH salt (1De)**: yellow solid; mp: 149–151 °C; IR (neat): $\tilde{\nu}$ = 3057, 1602, 1520, 1230, 1023, 631 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.38 (t, 2H, *J* = 5.9 Hz), 3.91 (s, 3H), 4.93 (t, 2H, *J* = 5.9 Hz), 7.01 (d, 2H, *J* = 8.8 Hz), 7.50 (d, 2H, *J* = 8.4 Hz), 7.96 (d, 2H, *J* = 8.8 Hz), 8.23 (d, 2H, *J* = 8.4 Hz), 9.96 (s, 1H), 10.5 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 33.5, 56.1, 72.3, 115.0 (2C), 117.3, 120.9 (q, $J_{C\text{-}F}$ = 321.3 Hz), 123.7 (2C), 130.6 (2C), 131.6 (2C), 145.4, 146.7, 165.3, 170.7; HRMS (ESI): Calcd for $C_{16}H_{17}O_4N_2$ $[M]^+$ = 301.1183, Found = 301.1180.

***O*-(β-Phenylethyl) naphthalen-2-ylimidate·TfOH salt (1Ea)**: yellow solid; mp: 163–165 °C; IR (neat): $\tilde{\nu}$ = 3061, 1487, 1237, 1166, 1027, 633 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.33 (t, 2H, *J* = 6.1 Hz), 4.97 (t, 2H, *J* = 6.1 Hz), 7.28–7.40 (m, 5H), 7.61 (t, 1H, *J* = 7.0 Hz), 7.69 (dd, 1H, *J* = 8.3, 1.4 Hz), 7.86–7.90 (m, 2H), 7.94 (d, 1H, *J* = 8.8 Hz), 8.03 (d, 1H, *J* = 8.1 Hz), 8.65 (s, 1H), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 33.7, 73.5, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.1, 123.4, 127.0, 128.0, 128.0, 128.7 (2C), 129.1, 129.3 (2C), 129.7, 130.1, 131.5, 131.6, 135.8, 136.7, 171.4; HRMS (ESI): Calcd for $C_{19}H_{18}ON$ $[M]^+$ = 276.1383, Found = 267.1379.

***O*-[β-(*p*-Tolyl)ethyl] naphthalen-2-ylimidate·TfOH salt (1Eb)**: yellow solid; mp: 159–160 °C; IR (neat): $\tilde{\nu}$ = 3092, 1486, 1240, 1167, 1028, 634 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 3.28 (t, 2H, *J* = 5.8 Hz), 4.94 (t, 2H, *J* = 5.8 Hz), 7.18 (d, 2H, *J* = 7.6 Hz), 7.24 (d, 2H, *J* = 8.3 Hz), 7.61 (t, 1H, *J* = 6.8 Hz), 7.69 (t, 1H, *J* = 6.8 Hz), 7.88–7.90 (m, 2H), 7.95 (d, 1H, *J* = 8.8 Hz), 8.04 (d, 1H, *J* = 7.9 Hz), 8.67 (s, 1H), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 20.7, 39.1, 73.6, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.1, 123.4, 128.0, 128.0, 129.2 (2C), 129.3 (2C), 129.7 (2C), 130.1, 131.5, 131.7, 133.6, 135.8, 136.1, 171.4; HRMS (ESI): Calcd for $C_{20}H_{20}ON$ $[M]^+$ = 290.1539, Found = 290.1537.

***O*-[β-(*p*-Fluorophenyl)ethyl] naphthalen-2-ylimidate·TfOH salt (1Ec)**: yellow solid; mp: 167–169 °C; IR (neat): $\tilde{\nu}$ = 3062, 1487, 1238, 1166, 1026, 634 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.30 (t, 2H, *J* = 5.9 Hz), 4.94 (t, 2H, *J* = 6.1 Hz), 7.07 (t, 2H, *J* = 8.6 Hz), 7.31–7.34 (m, 2H), 7.63 (t, 1H, *J* = 7.9 Hz), 7.70 (t, 1H, *J* = 7.3 Hz), 7.86 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.90 (d, 1H, *J* = 8.2 Hz), 7.96 (d, 1H, *J* = 8.8 Hz), 8.03 (d, 1H, *J* = 7.9 Hz), 8.66 (s, 1H), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 32.8, 73.4, 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 120.8 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.1, 123.4, 128.0, 128.0, 129.2, 129.7, 130.1, 131.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.5, 131.6, 132.9, 135.8, 161.4 (d, $J_{C\text{-}F}$ = 242.4 Hz), 171.4; HRMS (ESI): Calcd for $C_{19}H_{17}ONF$ $[M]^+$ = 294.1289, Found = 294.1285.

***O*-[β-(*p*-Chlorophenyl)ethyl] naphthalen-2-ylimidate·TfOH salt (1Ed)**: yellow solid; mp: 167–169 °C; IR (neat): $\tilde{\nu}$ = 3088, 1488, 1239, 1028, 632 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.29 (t, 2H, *J* = 6.1 Hz), 4.94 (t, 2H, *J* = 6.1 Hz), 7.29 (d, 2H, *J* = 8.6 Hz), 7.35 (d, 2H, *J* = 8.6 Hz), 7.61 (t, 1H, *J* = 7.0 Hz), 7.69 (t, 1H, *J* = 8.2 Hz), 7.85 (dd, 1H, *J* = 8.7, 1.8 Hz), 7.88 (d, 1H, *J* = 8.2 Hz), 7.94 (d, 1H, *J* = 8.6 Hz), 8.02 (d, 1H, *J* = 8.2 Hz), 8.64 (d, 1H, *J* = 1.6 Hz), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 33.0, 73.2, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.1, 123.4, 127.9, 128.0, 128.6 (2C), 129.2, 129.7, 130.1, 131.2 (2C), 131.5, 131.6, 131.7, 135.8, 135.9, 171.4; HRMS (ESI): Calcd for $C_{19}H_{17}ON^{35}Cl$ $[M]^+$ = 310.0993, Found = 310.0991.

***O*-[β-(*p*-Nitrophenyl)ethyl] naphthalen-2-ylimidate·TfOH salt (1Ee)**: yellow solid; mp: 152–154 °C; IR (neat): $\tilde{\nu}$ = 3058, 1515, 1247, 1165, 1028, 634 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.45 (t, 2H, *J* = 5.9 Hz), 5.02 (t, 2H, *J* = 5.9 Hz), 7.55 (d, 2H, *J* = 8.6 Hz), 7.64 (t, 1H, *J* = 7.7 Hz), 7.72 (t, 1H, *J* = 7.7 Hz), 7.84 (dd, 1H, *J* = 8.8, 2.0 Hz), 7.90 (d, 1H, *J* = 8.6 Hz), 7.97 (d, 1H, *J* = 8.8 Hz), 8.03 (d, 1H, *J* = 8.2 Hz), 8.25 (d, 2H, *J* = 8.6 Hz), 8.66 (s, 1H), 10.4 (s, 1H), 11.0 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 33.4, 72.7, 120.9 (q, $J_{C\text{-}F}$ = 321.3 Hz), 123.1, 123.4, 123.7 (2C), 128.0, 128.0, 129.2, 129.7, 130.1, 130.6 (2C), 131.5, 131.7, 135.9, 145.3, 146.7, 171.5; HRMS (ESI): Calcd for $C_{19}H_{17}O_3N_2$ $[M]^+$ = 321.1234, Found = 321.1231.

***O*-(β-Phenylethyl) benzothiophen-2-ylimidate·TfOH salt (1Fa)**: yellow solid; mp: 163–165 °C; IR (neat): $\tilde{\nu}$ = 3003, 1525, 1365, 1239, 1164, 1025, 632 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.26 (t, 2H, *J* = 5.8 Hz), 4.90 (t, 2H, *J* = 5.8 Hz), 7.28–7.39 (m, 5H), 7.47 (td, 1H, *J* = 7.5, 1.1 Hz), 7.56 (td, 1H, *J* = 8.3, 1.1 Hz), 7.88 (dd, 1H, *J* = 8.3, 0.9 Hz), 8.00 (d, 1H, *J* = 7.9 Hz), 8.72 (s, 1H), 10.2 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $[D_6]$DMSO): δ = 33.8, 73.9, 121.0 (q, $J_{C\text{-}F}$ = 322.3 Hz), 123.3, 126.1, 126.7, 127.1, 127.9, 128.8 (2C), 129.0, 129.4 (2C), 133.6, 136.7, 138.1, 142.3, 166.7; HRMS (ESI): Calcd for $C_{17}H_{16}ONS$ $[M]^+$ = 282.0947, Found = 282.0947.

***O*-(β-Phenylethyl) *p*-chlorophenylimidate·TfOH salt (1Ga)**: white solid; mp: 129–131 °C; IR (neat): $\tilde{\nu}$ = 3033, 1595, 1447, 1227, 1024, 633 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.26 (t, 2H, *J* = 5.9 Hz), 4.90 (t, 2H, *J* = 6.1 Hz),7.27–7.30 (m, 3H), 7.35 (t, 2H, *J* = 8.2 Hz), 7.50 (d, 2H, *J* = 8.6 Hz), 7.91(d, 2H, *J* = 8.8 Hz), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 34.2, 74.5, 120.0 (q, $J_{C\text{-}F}$ = 318.5 Hz), 123.1, 127.3 (2C), 128.8 (3C), 129.8 (2C), 130.5 (2C), 135.8, 143.0, 171.6; HRMS (ESI): Calcd for $C_{15}H_{15}ON^{35}Cl$ $[M]^+$ = 260.0837, Found = 260.0838.

***O*-[β-(*p*-Tolyl)ethyl] *p*-chlorophenylimidate·TfOH salt (1Gb)**: white solid; mp: 145–147 °C; IR (neat): $\tilde{\nu}$ = 3033, 1591, 1447, 1227, 1023, 649 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 3.22 (t, 2H, *J* = 5.9 Hz), 4.87 (t, 2H, *J* = 5.9 Hz), 7.11–7.19 (m, 4H), 7.51 (d, 2H, *J* = 8.8 Hz), 7.93 (d, 2H, *J* = 8.8 Hz), 10.3 (s, 1H), 10.9 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.0, 33.8, 74.7, 120.0 (q, $J_{C\text{-}F}$ = 319.5 Hz), 123.2, 128.7 (2C), 129.5 (2C), 129.8 (2C), 130.5 (2C), 132.7, 136.9, 143.1, 171.7; HRMS (ESI): Calcd for $C_{16}H_{17}ON^{35}Cl$ $[M]^+$ = 274.0993, Found = 274.0995.

***O*-[β-(*p*-Fluorophenyl)ethyl] *p*-chlorophenylimidate·TfOH salt (1Gc)**: white solid; mp: 129–130 °C; IR (neat): $\tilde{\nu}$ = 3033, 1594, 1448, 1225, 1021, 628 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.24 (t, 2H, *J* = 6.1 Hz), 4.87 (t, 2H, *J* = 6.1 Hz), 7.04 (tt, 2H, *J* = 8.6, 2.0 Hz), 7.24–7.29 (m, 2H), 7.53 (d, 2H, *J* = 8.6 Hz), 7.92 (d, 2H, *J* = 8.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 33.4, 74.4, 115.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 120.0 (q, $J_{C\text{-}F}$ = 318.5 Hz), 123.1, 129.8 (2C), 130.4 (d, $J_{C\text{-}F}$ = 7.5 Hz), 130.5 (2C), 131.4 (d, $J_{C\text{-}F}$ = 2.8 Hz), 143.2, 162.0 (d, $J_{C\text{-}F}$ = 245.2 Hz), 171.6; HRMS (ESI): Calcd for $C_{15}H_{14}ON^{35}ClF$ $[M]^+$ = 278.0742, Found = 278.0742.

***O*-[β-(*p*-Nitrophenyl)ethyl] *p*-chlorophenylimidate·TfOH salt (1Ge)**: white solid; mp: 151–153 °C; IR (neat): $\tilde{\nu}$ = 3032, 1592, 1524, 1227, 1021, 630 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.39 (t, 2H, *J* = 5.9 Hz), 4.96 (t, 2H, *J* = 6.1 Hz), 7.94 (d, 2H, *J* = 8.6 Hz), 7.54 (d, 2H, *J* = 8.6 Hz), 7.92 (d, 2H, *J* = 8.6 Hz), 8.23 (d, 2H, *J* = 8.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 33.6, 73.6, 120.9 (q, $J_{C\text{-}F}$ = 322.3 Hz), 125.0, 127.0, 128.7 (2C), 129.2 (2C), 129.6 (2C), 130.9 (2C), 136.6, 140.7, 170.6; HRMS (ESI): Calcd for $C_{15}H_{14}O_3N_2{}^{35}Cl$ $[M]^+$ = 305.0687, Found = 305.0688.

Typical Procedure for Transformation of *O*-(β-Arylethyl) Arylimidate·TfOH Salts 1 into 2,4-Diaryl-5-iodoxazoles 4: To a solution of *O*-(β-phenylethyl) *p*-tolylimidate·TfOH salt **(1Aa**, 1.0 mmol, 389.4 mg) in THF (4.0 mL) was added NaH (1.5 mmol, 65.0 mg) at room temperature. The obtained mixture was stirred for 15 min. at

room temperature under argon atmosphere. After removal of the solvent, 1,2-dichloroethane (5.0 mL), K_2CO_3 (3.0 mmol, 414.6 mg), and DIH (3.0 mmol, 1140.0 mg) were added to the residue. The obtained mixture was stirred for 8 h in the range of 35–38 °C under irradiation with a 300 W tungsten lamp. Sat. Na_2SO_3 aq. solution (15.0 mL) was added to the reaction mixture and the product was extracted with $CHCl_3$ (15.0 mL × 3). The organic layer was dried with Na_2SO_4 and filtered. After removal of the solvent, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 314.8 mg, 87 %).

5-Iodo-4-phenyl-2-*p*-tolyloxazole (4Aa): Yield: 314.8 mg (87 %); white solid; mp: 90–92 °C; IR (neat): $\tilde{\nu}$ = 2915, 1558, 1500, 1093, 725, 689 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.28 (d, 2H, *J* = 8.1 Hz), 7.38 (t, 1H, *J* = 7.4 Hz), 7.47 (t, 2H, *J* = 7.4 Hz), 7.98 (d, 2H, *J* = 8.3 Hz), 8.04 (d, 2H, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.9, 34.3, 74.0, 121.8, 127.2, 128.8 (2C), 128.9 (2C), 129.2 (2C), 130.2 (2C), 136.1, 147.8, 172.3; HRMS (ESI): Calcd for $C_{16}H_{13}ONI$ $[M + H]^+$ = 362.0036, Found = 362.0031.

5-Iodo-2,4-di-*p*-tolyloxazole (4Ab): Yield: 283.8 mg (76 %); white solid; mp: 125–126 °C; IR (neat): $\tilde{\nu}$ = 2973, 1501, 1086, 960, 826, 728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.41 (s, 3H), 7.26–7.28 (m, 4H), 7.93 (d, 2H, *J* = 8.2 Hz), 7.97 (d, 2H, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.6, 81.9, 124.1, 126.3 (2C), 126.8 (2C), 127.7, 129.1 (2C), 129.4 (2C), 138.3, 141.1, 145.0, 166.0; HRMS (ESI): Calcd for $C_{17}H_{15}ONI$ $[M + H]^+$ = 376.0193, Found = 376.0188.

4-*p*-Fluorophenyl-5-iodo-2-*p*-tolyloxazole (4Ac): Yield: 304.2 mg (80 %); white solid; mp: 122–124 °C; IR (neat): $\tilde{\nu}$ = 2987, 1500, 1222, 1087, 962, 827, 730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.15 (t, 2H, *J* = 8.6 Hz), 7.29 (d, 2H, *J* = 7.9 Hz), 7.97 (d, 2H, *J* = 8.4 Hz), 8.00–8.05 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 82.1, 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 123.9, 126.3 (2C), 126.7, 128.8 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.5 (2C), 141.3, 144.2, 162.8 (d, $J_{C\text{-}F}$ = 248.1 Hz), 166.1; HRMS (ESI): Calcd for $C_{16}H_{12}ONFI$ $[M + H]^+$ = 379.9942, Found = 379.9938.

4-*p*-Chlorophenyl-5-iodo-2-*p*-tolyloxazole (4Ad): Yield: 300.0 mg (76 %); white solid; mp: 136–138 °C; IR (neat): $\tilde{\nu}$ = 2987, 1498, 1089, 961, 827, 729 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.28 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.6 Hz), 7.96 (d, 2H, *J* = 8.1 Hz), 8.00 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 82.6, 123.9, 126.3 (2C), 128.1 (2C), 128.6 (2C), 129.1, 129.5 (2C), 134.3, 141.3, 144.0, 166.2; HRMS (ESI): Calcd for $C_{16}H_{12}ONClI$ $[M + H]^+$ = 395.9647, Found = 395.9643.

2,4-Diphenyl-5-iodoxazole (4Ba): Yield: 134.7 mg (39 %); white solid; mp: 92–93 °C; IR (neat): $\tilde{\nu}$ = 3054, 1557, 1447, 1287, 1090, 704cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.39 (tt, 1H, *J* = 7.3, 1.4 Hz), 7.45–7.50 (m, 5H), 8.05 (d, 2H, *J* = 7.0 Hz), 8.08–8.11 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 82.9, 126.4 (2C), 126.7, 126.9 (2C), 128.4 (2C), 128.5, 128.8 (2C), 130.5, 130.8, 145.1, 165.9; HRMS (ESI): Calcd for $C_{15}H_{11}ONI$ $[M + H]^+$ = 347.9880, Found = 347.9875.

5-Iodo-2-phenyl-4-*p*-tolyloxazole (4Bb): Yield: 295.9 mg (82 %); white solid; mp: 101–103 °C; IR (neat): $\tilde{\nu}$ = 2987, 1495, 1086, 960, 818, 687 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.28 (d, 2H, *J* = 8.4 Hz), 7.46–7.49 (m, 3H), 7.94 (d, 2H, *J* = 8.2 Hz), 8.07–8.10 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 82.4, 126.3 (2C), 126.8 (3C), 127.6, 128.8 (2C), 129.2 (2C), 130.7, 138.4, 145.2, 165.8; HRMS (ESI): Calcd for $C_{16}H_{13}ONI$ $[M + H]^+$ = 362.0036, Found = 362.0031.

4-*p*-Fluorophenyl-5-iodo-2-phenyloxazole (4Bc): Yield: 266.0 mg (73 %); white solid; mp: 118–119 °C; IR (neat): $\tilde{\nu}$ = 2987, 1494, 1231, 1093, 836, 684 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.16 (t, 2H, *J* = 8.7 Hz), 7.47–7.49 (m, 3H), 8.01–8.11 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 82.6, 115.5 (d, 2C, $J_{C\text{-}F}$ = 21.6 Hz), 126.3 (2C), 126.5, 126.6, 128.8 (2C), 128.8 (d, 2C, $J_{C\text{-}F}$ = 8.5 Hz), 130.9, 144.3, 162.8 (d, $J_{C\text{-}F}$ = 248.1 Hz), 165.9; HRMS (ESI): Calcd for $C_{15}H_{10}ONFI$ $[M + H]^+$ = 365.9786, Found = 365.9780.

4-*p*-Chlorophenyl-5-iodo-2-phenyloxazole (4Bd): Yield: 194.0 mg (51 %); white solid; mp: 123–124 °C; IR (neat): $\tilde{\nu}$ = 2987, 1477, 1092, 961, 830 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.44 (d, 2H, *J* = 8.6 Hz), 7.47–7.50 (m, 3H), 8.01 (d, 2H, *J* = 8.6 Hz), 8.07–8.09 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.0, 126.4 (2C), 126.5, 128.1 (2C), 128.7 (2C), 128.8 (2C), 129.0, 130.9, 134.3, 144.1, 166.0; HRMS (ESI): Calcd for $C_{15}H_{10}ON^{35}ClI$ $[M + H]^+$ = 381.9490, Found = 381.9486.

2-(3′,5′-Dimethylphenyl)-5-iodo-4-phenyloxazole (4Ca): Yield: 310.7 mg (83 %); white solid; mp: 151–153 °C; IR (neat): $\tilde{\nu}$ = 2969, 1540, 1442, 1229, 1097, 694 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 6H), 7.11 (s, 1H), 7.38 (t, 1H, *J* = 7.5 Hz), 7.47 (t, 2H, *J* = 7.5 Hz), 7.71 (s, 2H), 8.04 (d, 2H, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (2C), 82.6, 124.1 (2C), 126.4, 126.9 (2C), 128.4 (2C), 130.5, 132.5 (2C), 138.4 (2C), 144.9, 166.2; HRMS (ESI): Calcd for $C_{17}H_{15}ONI$ $[M + H]^+$ = 376.0193, Found = 376.0194.

2-(3′,5′-Dimethylphenyl)-5-iodo-4-*p*-tolyloxazole (4Cb): Yield: 248.7 mg (64 %); white solid; mp: 111–113 °C; IR (neat): $\tilde{\nu}$ = 2915, 1557, 1495, 1224, 1087, 957, 732 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 6H), 2.40 (s, 3H), 7.10 (s, 1H), 7.27 (d, 2H, *J* = 8.2 Hz), 7.71 (s, 2H), 7.93 (d, 2H, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (2C), 21.4, 82.1, 124.1 (2C), 126.5, 126.8 (2C), 127.7, 129.1 (2C), 132.5, 138.3, 138.4 (2C), 145.0, 166.1; HRMS (ESI): Calcd for $C_{18}H_{17}ONI$ $[M + H]^+$ = 390.0349, Found = 390.0348.

4-*p*-Fluorophenyl-2-(3′,5′-dimethylphenyl)-5-iodoxazole (4Cc): Yield: 203.3 mg (52 %); white solid; mp: 142–143 °C; IR (neat): $\tilde{\nu}$ = 2971, 1558, 1491, 1293, 1102, 835 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 6H), 7.11 (s, 1H), 7.15 (tt, 2H, *J* = 8.8, 1.8 Hz), 7.70 (s, 2H), 8.01–8.04 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (2C), 82.3, 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 124.0 (2C), 126.3, 126.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 128.7 (d, $J_{C\text{-}F}$ = 8.5 Hz), 132.6 (2C), 138.4 (2C), 144.1, 162.7 (d, $J_{C\text{-}F}$ = 248.1 Hz), 166.2; HRMS (ESI): Calcd for $C_{17}H_{14}ONFI$ $[M + H]^+$ = 394.0099, Found = 394.0099.

4-*p*-Chlorophenyl-2-(3′,5′-dimethylphenyl)-5-iodoxazole (4Cd): Yield: 329.4 mg (80 %); white solid; mp: 131–133 °C; IR (neat): $\tilde{\nu}$ = 2910, 1557, 1479, 1227, 1085, 733 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 6H), 7.11 (s, 1H), 7.44 (d, 2H, *J* = 8.2 Hz), 7.70 (s, 2H), 8.00 (d, 2H, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (2C), 82.8, 124.1 (2C), 126.3, 128.1 (2C), 128.6 (2C), 129.1, 132.7, 134.3, 138.5 (2C), 144.0, 166.3; HRMS (ESI): Calcd for $C_{17}H_{14}ON^{35}ClI$ $[M + H]^+$ = 409.9803, Found = 409.9804.

5-Iodo-2-*p*-methoxyphenyl-4-phenyloxazole (4Da): Yield: 217.5 mg (58 %); yellow solid; mp: 92–93 °C; IR (neat): $\tilde{\nu}$ = 2973, 1615, 1498, 1246, 1021, 826 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 6.98 (t, 2H, *J* = 9.0 Hz), 7.38 (t, 1H, *J* = 7.6 Hz), 7.47 (t, 2H, *J* = 7.6 Hz), 8.01–8.05 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.4, 81.9, 114.1 (2C), 119.5, 126.8 (2C), 128.0 (2C), 128.4, 128.4 (2C), 130.6, 144.8, 161.6, 165.9; HRMS (ESI): Calcd for $C_{16}H_{13}O_2NI$ $[M + H]^+$ = 377.9985, Found = 377.9980.

5-Iodo-2-*p*-methoxyphenyl-4-*p*-tolyloxazole (4Db): Yield: 154.9 mg (40 %); white solid; mp: 125–127 °C; IR (neat): $\tilde{\nu}$ = 2968, 1501, 1251, 1023, 825 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 3.88 (s, 3H), 6.98 (d, 2H, *J* = 8.8 Hz), 7.27 (d, 2H, *J* = 8.2 Hz), 7.92 (d, 2H, *J* = 8.2 Hz), 8.02 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.3, 55.4, 81.3, 114.1 (2C), 119.6, 126.8 (2C), 127.8, 128.0 (2C), 129.1 (2C), 138.3, 144.9, 161.6, 165.8; HRMS (ESI): Calcd for $C_{17}H_{15}O_2NI$ $[M + H]^+$ = 392.0142, Found = 392.0138.

4-*p*-Fluorophenyl-5-iodo-2-*p*-methoxyphenyloxazole (4Dc): Yield: 214.4 mg (54 %); yellow solid; mp: 136–138 °C; IR (neat): $\tilde{\nu}$ = 1613, 1499, 1245, 1023, 827 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 6.98 (d, 2H, *J* = 9.1 Hz), 7.15 (t, 2H, *J* = 8.6 Hz), 7.99–8.04 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.4, 81.5, 114.2 (2C), 115.4 (d, $J_{C\text{-}F}$ = 21.6 Hz), 119.4, 126.8, 128.1 (2C), 128.7 (d, $J_{C\text{-}F}$ = 8.5 Hz), 144.1, 161.4, 162.7 (d, $J_{C\text{-}F}$ = 249.0 Hz), 165.9; HRMS (ESI): Calcd for $C_{16}H_{12}O_2NFI$ $[M + H]^+$ = 395.9891, Found = 395.9886.

4-*p*-Chlorophenyl-5-iodo-2-*p*-methoxyphenyloxazole (4Dd): Yield: 221.9 mg (54 %); white solid; mp: 136–137 °C; IR (neat): $\tilde{\nu}$ = 1503, 1251, 1023, 834 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 6.99 (d, 2H, *J* = 9.1 Hz), 7.43 (d, 2H, *J* = 8.8 Hz), 7.98–8.03 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.4, 82.0, 114.2 (2C), 119.3, 128.1 (4C), 128.6 (2C), 129.1, 134.2, 143.9, 161.7, 166.0; HRMS (ESI): Calcd for $C_{16}H_{12}O_2NClI$ $[M + H]^+$ = 411.9596, Found = 411.9591.

5-Iodo-2-(naphthalen-2′-yl)-4-phenyloxazole (4Ea): Yield: 249.2 mg (63 %); white solid; mp: 111–113 °C; IR (neat): $\tilde{\nu}$ = 1549, 1444, 1291, 1093, 822, 753 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (tt, 1H, *J* = 7.4, 2.0 Hz), 7.50 (t, 2H, *J* = 7.4 Hz), 7.53–7.58 (m, 2H), 7.87–7.90 (m, 1H), 7.93–7.98 (m, 2H), 8.09 (d, 2H, *J* = 7.0 Hz), 8.19 (dd, 1H, *J* = 8.5, 1.8 Hz), 8.60 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.1, 123.1, 123.9, 126.4, 126.8, 126.9 (2C), 127.4, 127.8, 128.5 (2C), 128.5, 128.6, 128.8, 130.5, 132.9, 134.3, 145.2, 166.0; HRMS (ESI): Calcd for $C_{19}H_{13}ONI$ $[M + H]^+$ = 398.0036, Found = 398.0032.

5-Iodo-2-(naphthalen-2′-yl)-4-*p*-tolyloxazole (4Eb): Yield: 271.3 mg (66 %); white solid; mp: 130–131 °C; IR (neat): $\tilde{\nu}$ = 1547, 1493, 1290, 1086, 818, 751 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.30 (d, 2H, *J* = 7.6 Hz), 7.53–7.57 (m, 2H), 7.86–7.89 (m, 1H), 7.92–7.98 (m, 4H), 8.18 (dd, 1H, *J* = 8.6, 1.8 Hz), 8.58 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 82.6, 123.1, 124.0, 126.4, 126.8, 126.8 (2C), 127.4, 127.6, 127.8, 128.6, 128.8, 129.2 (2C), 132.9, 134.3, 138.4, 145.3, 165.9; HRMS (ESI): Calcd for $C_{20}H_{15}ONI$ $[M + H]^+$ = 412.0193, Found = 412.0187.

4-*p*-Fluorophenyl-5-iodo-2-(naphthalen-2′-yl)oxazole (4Ec): Yield: 303.7 mg (73 %); white solid; mp: 144–146 °C; IR (neat): $\tilde{\nu}$ = 1547, 1491, 1214, 1095, 835, 753 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.18 (t, 2H, *J* = 8.8 Hz), 7.54–7.59 (m, 2H), 7.87–7.90 (m, 1H), 7.93–7.97 (m, 2H), 8.05–8.10 (m, 2H), 8.17 (dd, 1H, *J* = 8.6, 1.8 Hz), 8.58 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 82.8, 115.5 (d, 2C, $J_{C\text{-}F}$ = 21.6 Hz), 123.0, 123.8, 126.4, 126.6 (2C), 126.8, 127.5, 127.9, 128.7, 128.8 (d, 2C, $J_{C\text{-}F}$ = 8.5 Hz), 132.9, 134.3, 144.5, 162.8 (d, $J_{C\text{-}F}$ = 249.0 Hz), 166.0; HRMS (ESI): Calcd for $C_{19}H_{12}ONFI$ $[M + H]^+$ = 415.9942, Found = 415.9938.

4-*p*-Chlorophenyl-5-iodo-2-(naphthalen-2′-yl)oxazole (4Ed): Yield: 273.0 mg (63 %); white solid; mp: 140–142 °C; IR (neat): $\tilde{\nu}$ = 1549, 1479, 1282, 1090, 828, 751 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, 2H, *J* = 8.8, Hz), 7.53–7.59 (m, 2H), 7.86–7.90 (m, 1H), 7.92–7.97 (m, 2H), 8.04 (d, 2H, *J* = 8.8 Hz), 8.16 (dd, 1H, *J* = 8.6, 1.8 Hz), 8.56 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.3, 123.0, 123.7, 126.5, 126.8, 127.5, 127.8, 128.1 (2C), 128.7 (2C), 128.8, 129.0 (2C), 132.9, 134.3 (2C), 144.2, 166.0; HRMS (ESI): Calcd for $C_{19}H_{12}ON^{35}ClI$ $[M + H]^+$ = 431.9647, Found = 431.9642.

2-(Benzothiophen-2′-yl)-5-iodo-4-phenyloxazole (4Fa): Yield: 203.7 mg (56 %); yellow solid; mp: 162–164 °C; IR (neat): $\tilde{\nu}$ = 1600, 1445, 1293, 1074, 962, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38–7.45 (m, 3H), 7.46–7.50 (m, 2H), 7.84–7.90 (m, 2H), 7.97 (s, 1H), 8.03–8.06 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 83.2, 122.5, 124.7, 125.0, 125.0, 126.1, 127.0 (2C), 128.5 (2C), 128.6, 128.7, 130.1, 139.3, 140.7, 145.4, 161.9; HRMS (ESI): Calcd for $C_{17}H_{11}ONIS$ $[M + H]^+$ = 403.9601, Found = 403.9601.

4-*p*-Nitrophenyl-2-*p*-tolyloxazole (3Ae): Yield: 202.2 mg (72 %); yellow solid; mp: 194–197 °C; IR (neat): $\tilde{\nu}$ = 1605, 1504, 1330, 1105, 852, 728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 7.31 (d, 2H, *J* = 8.2 Hz), 7.97–8.02 (m, 4H), 8.10 (s, 1H), 8.30 (d, 2H, *J* = 9.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 124.2 (2C), 126.0 (2C), 126.6 (2C), 129.6 (2C), 135.1, 137.5, 140.0 (2C), 141.3, 147.2, 162.8; HRMS (ESI): Calcd for $C_{16}H_{13}O_3N_2$ $[M + H]^+$ = 281.0921, Found = 281.0923.

4-*p*-Nitrophenyl-2-phenyloxazole (3Be): Yield: 120.2 mg (45 %); yellow solid; mp: 176–178 °C; IR (neat): $\tilde{\nu}$ = 1603, 1515, 1330, 1107, 856, 714 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49–7.53 (m, 3H), 8.00 (d, 2H, *J* = 9.0 Hz), 8.11–8.16 (m, 3H), 8.30 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 124.2 (2C), 126.1 (2C), 126.6 (2C), 126.9, 128.9 (2C), 130.9, 135.4, 137.4, 140.1, 147.2, 162.6; HRMS (ESI): Calcd for $C_{15}H_{11}O_3N_2$ $[M + H]^+$ = 267.0764, Found = 267.0767.

4-*p*-Nitrophenyl-2-(3′,5′-dimethylphenyl)oxazole (3Ce): Yield: 154.3 mg (52 %); yellow solid; mp: 174–176 °C; IR (neat): $\tilde{\nu}$ = 1608, 1513, 1333, 1112, 851, 733 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 6H), 7.14 (s, 1H), 7.75 (s, 2H), 7.99 (d, 2H, *J* = 9.0 Hz), 8.11 (s, 1H), 8.30 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.2 (2C), 124.1 (2C), 124.3 (2C), 126.0 (2C), 126.6, 132.6, 135.2, 137.5, 138.5 (2C), 140.0, 147.1, 162.9; HRMS (ESI): Calcd for $C_{17}H_{15}O_3N_2$ $[M + H]^+$ = 295.1077, Found = 295.1077.

2-(Naphthalen-2′-yl)-4-*p*-nitrophenyloxazole (3Ee): Yield: 316.3 mg (45 %); yellow solid; mp: 196–198 °C; IR (neat): $\tilde{\nu}$ = 1598, 1507, 1305, 1105, 829, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55–7.60 (m, 2H), 7.88–7.91 (m, 1H), 7.96–7.98 (m, 2H), 8.03 (d, 2H, *J* = 8.8 Hz), 8.17 (s, 1H), 8.21 (dd, 1H, *J* = 8.6, 1.6 Hz), 8.31 (d, 2H, *J* = 8.6 Hz), 8.62 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 123.3, 124.1, 124.2 (2C), 126.1 (2C), 126.8, 126.9, 127.6, 127.9, 128.8 (2C), 132.9, 134.4, 135.6, 137.4, 140.3, 147.3, 162.8; HRMS (ESI): Calcd for $C_{19}H_{13}O_3N_2$ $[M + H]^+$ = 317.0921, Found = 317.0918.

2-*p*-Chlorophenyl-4-*p*-nitrophenyloxazole (3Ge): Yield: 190.2 mg (63 %); yellow solid; mp: 184–186 °C; IR (neat): $\tilde{\nu}$ = 1607, 1513, 1342, 1088, 851, 732 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (td, 2H, *J* = 8.8, 2.0 Hz), 7.99 (td, 2H, *J* = 9.0, 2.0 Hz), 8.07 (td, 2H, *J* = 8.8, 2.0 Hz), 8.13 (s, 1H), 8.31 (td, 2H, *J* = 9.0, 2.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 124.2 (2C), 125.3, 126.1 (2C), 127.9 (2C), 129.2 (2C), 135.6, 137.1, 137.2, 140.3, 147.3, 161.6; HRMS (ESI): Calcd for $C_{15}H_{10}O_3N_2Cl$ $[M + H]^+$ = 303.0347, Found = 303.0347.

2-*p*-Chlorophenyl-4-phenyloxazoline (2Ga): Yield: 197.9 mg (77 %); white solid; mp: 86–87 °C; IR (neat): $\tilde{\nu}$ = 1641, 1488, 1258, 1069, 696 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.28 (t, 1H, *J* = 8.3 Hz), 4.80 (dd, 1H, *J* = 10.1, 8.5 Hz), 5.38 (dd, 1H, *J* = 10.1, 8.1 Hz), 7.27–7.31 (m, 3H), 7.35–7.38 (m, 2H), 7.42 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 8.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 70.2, 75.0, 126.0, 126.7 (2C), 127.7, 128.7 (2C), 128.8 (2C), 129.8 (2C), 137.7, 142.1, 163.8; HRMS (ESI): Calcd for $C_{15}H_{13}ON^{35}Cl$ $[M + H]^+$ = 258.0680, Found = 258.0684.

2-*p*-Chlorophenyl-4-*p*-tolyloxazoline (2Gb): Yield: 203.6 mg (75 %); white solid; mp: 100–101 °C; IR (neat): $\tilde{\nu}$ = 1643, 1489, 1269, 1074, 954, 810 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 4.27 (t, 1H, *J* = 8.3 Hz), 4.78 (dd, 1H, *J* = 10.2, 8.3 Hz), 5.35 (dd, 1H, *J* = 10.1, 8.3Hz), 7.15–7.20 (m, 4H), 7.41 (d, 2H, *J* = 8.8 Hz), 7.97 (d, 2H, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.1, 69.9, 75.0, 126.1, 126.6 (2C), 128.6 (2C), 129.4 (2C), 129.8 (2C), 137.4, 137.6, 139.1, 163.6; HRMS (ESI): Calcd for $C_{16}H_{15}ON^{35}Cl$ $[M + H]^+$ = 272.0837, Found = 272.0840.

2-*p*-Chlorophenyl-4-*p*-fluorophenyloxazoline (2Gc): Yield: 205.0 mg (74 %); white solid; mp: 98–100 °C; IR (neat): $\tilde{\nu}$ = 1637, 1507, 1223, 1094, 832 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 4.24 (t,

1H, *J* = 8.3 Hz), 4.80 (dd, 1H, *J* = 10.1, 8.5 Hz), 5.37 (dd, 1H, 10.1, 8.1 Hz), 7.05 (tt, 2H, *J* = 8.5, 2.0 Hz), 7.24–7.29 (m, 2H), 7.42 (d, 2H, *J* = 8.8 Hz), 7.97 (d, 2H, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 69.4, 74.9, 115.6 (d, $J_{C\text{-}F}$ = 21.6 Hz), 125.8, 128.3 (d, $J_{C\text{-}F}$ = 8.5 Hz), 128.7 (2C), 129.8 (2C), 137.8, 137.9 (d, $J_{C\text{-}F}$ = 2.8 Hz), 162.2 (d, $J_{C\text{-}F}$ = 245.2 Hz), 163.9; HRMS (ESI): Calcd for $C_{15}H_{12}ON^{35}ClF$ $[M + H]^+$ = 276.0586, Found = 276.0588.

2-*p*-Methoxyphenyl-4-*p*-nitrophenyloxazoline (2De): Yield: 197.9 mg (66 %); yellow solid; mp: 100–102 °C; IR (neat): $\tilde{\nu}$ = 2955, 1650, 1421, 1337, 1247, 1074, 739 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3H), 4.21 (t, 1H, *J* = 8.3 Hz), 4.84 (dd, 1H, *J* = 10.1, 8.5 Hz), 5.48 (dd, 1H, *J* = 10.1, 8.1 Hz), 6.97 (d, 2H, *J* = 8.8 Hz), 7.49 (d, 2H, *J* = 8.5 Hz), 7.98 (d, 2H, *J* = 9.0 Hz), 8.22 (d, 2H, *J* = 9.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 55.4, 69.3, 74.2, 113.8 (2C), 119.3, 123.9 (2C), 127.6 (2C), 130.3 (2C), 147.3, 149.9, 162.5, 165.5; HRMS (ESI): Calcd $C_{16}H_{15}O_4N_2$ for $[M + H]^+$ = 299.1026, Found = 299.1024.

4-Methyl-2-*p*-tolyloxazoline (2Af): Yield: 110.1 mg (63 %); yellow oil; IR (neat): $\tilde{\nu}$ = 2966, 1644, 1512, 1259, 1059, 727 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.36 (d, 3H, *J* = 6.6 Hz), 2.39 (s, 3H), 3.94 (t, 2H, *J* = 7.9 Hz), 4.32–4.41 (m, 1H), 4.51 (dd, 1H, *J* = 9.3, 7.9 Hz), 7.21 (d, 2H, *J* = 7.9 Hz), 7.83 (d, 2H, *J* = 8.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.4, 21.5, 61.8, 73.9, 125.0, 128.1 (2C), 129.0 (2C), 141.5, 163.5; HRMS (ESI): Calcd for $C_{11}H_{14}ON$ $[M + H]^+$ = 176.1070, Found = 176.1071.

4-Ethyl-2-*p*-tolyloxazoline (2Ag): Yield: 128.1 mg (68 %); yellow oil; IR (neat): $\tilde{\nu}$ = 2963, 1646, 1352, 1064, 827, 727 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, 3H, *J* = 7.4 Hz), 1.55–1.66 (m, 1H), 1.72–1.83 (m, 1H), 2.39 (s, 3H), 4.04 (t, 1H, *J* = 7.9 Hz), 4.19–4.27 (m, 1H), 4.46 (dd, 1H, *J* = 9.3, 8.3 Hz), 7.21 (d, 2H, *J* = 8.5 Hz), 7.83 (d, 2H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 9.92, 21.5, 28.6, 67.8, 72.0, 125.0, 128.1 (2C), 128.9 (2C), 141.5, 163.5; HRMS (ESI): Calcd for $C_{12}H_{16}ON$ $[M + H]^+$ = 190.1226, Found = 190.1223.

Transformation of 5-Iodo-4-phenyl-2-*p*-tolyloxazole 4Aa into 4-Phenyl-2-*p*-tolyloxazole 3Aa: To a mixture of 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 0.5 mmol, 180.6 mg) in EtOH (7.5 mL) was added Zn powder (5.0 mmol, 363.3 mg) under argon atmosphere. The obtained mixture was stirred for 16 h at refluxing temperature. The cooled mixture was filtered through celite, and then the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: *n*-hexane/AcOEt = 9:1) to afford 4-phenyl-2-*p*-tolyloxazole (**3Aa**, 113.4 mg, 96 %).

4-Phenyl-2-*p*-tolyloxazole (3Aa): Yield: 113.4 mg (96 %); white solid; mp: 109–110 °C; IR (neat): $\tilde{\nu}$ = 1498, 1117, 1075, 929, 732 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.27–7.35 (m, 3H), 7.43 (t, 2H, *J* = 7.9 Hz), 7.82 (d, 2H, *J* = 8.1 Hz), 7.94 (s, 1H), 8.01 (d, 2H, *J* = 7.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.5, 124.8, 125.6 (2C), 126.4 (2C), 128.0, 128.7 (2C), 129.4 (2C), 131.2, 133.1, 140.6, 141.8, 162.1; HRMS (ESI): Calcd for $C_{16}H_{14}ON$ $[M + H]^+$ = 236.1070, Found = 236.1067.

Transformation of 5-Iodo-4-phenyl-2-*p*-tolyloxazole 4Aa into 4,5-Diphenyl-2-*p*-tolyloxazole 5Aa: To a mixture of 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 0.5 mmol, 180.6 mg) and $PhB(OH)_2$ (1.0 mmol, 121.9 mg) in DMF (10.0 mL) was added $PdCl_2(PPh_3)_2$ (0.025 mmol, 17.5 mg) under argon atmosphere. The obtained mixture was stirred for 30 min at room temperature. Then, K_2CO_3 (1.0 mmol, 138.2 mg) in H_2O (2.0 mL) was added to the mixture, and the obtained mixture was stirred for 6 h at 60 °C. Water (5.0 mL) was added to the reaction mixture, and the product was extracted with CH_2Cl_2 (15.0 mL × 3) and washed with brine (15.0 mL × 2). The organic layer was dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 4,5-diphenyl-2-*p*-tolyloxazole (**5Aa**, 141.1 mg, 91 %).

4,5-Diphenyl-2-*p*-tolyloxazole (5Aa): Yield: 141.1 mg (91 %); white solid; mp: 126–128 °C; IR (neat): $\tilde{\nu}$ = 2987, 1496, 1021, 964, 762, 685 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.29 (d, 2H, *J* = 7.9 Hz), 7.34 –7.43 (m, 6H), 7.68 (d, 2H, *J* = 6.7 Hz), 7.73 (d, 2H, *J* = 6.7 Hz), 8.05 (d, 2H, *J* = 8.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.5, 124.6, 126.4 (2C), 126.4 (2C), 128.1 (3C), 128.4, 128.5 (2C), 128.6 (2C), 129.0, 129.4 (2C), 132.6, 136.6, 140.6, 145.2, 160.3; HRMS (ESI): Calcd for $C_{22}H_{18}ON$ $[M + H]^+$ = 312.1383, Found = 312.1384.

Transformation of 5-Iodo-4-phenyl-2-*p*-tolyloxazole 4Aa into 4-Phenyl-(*E*)-5-styryl-2-*p*-tolyloxazole 6Aa: To a mixture of 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 0.5 mmol, 180.6 mg), K_2CO_3 (1.0 mmol, 138.2 mg), and $PdCl_2(PPh_3)_2$ (0.010 mmol, 7.0 mg) in DMF (5.0 mL) was added styrene (1.0 mmol, 57 μL) under argon atmosphere. The obtained mixture was stirred for 3 h at 60 °C. Sat. $NaHCO_3$ aq. solution (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15.0 mL × 3) and washed with brine (15.0 mL). The organic layer was dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 4-phenyl-(*E*)-5-styryl-2-*p*-tolyloxazole (**6Aa**, 126.9 mg, 75 %).

4-Phenyl-(*E*)-5-styryl-2-*p*-tolyloxazole (6Aa): Yield: 126.9 mg (75 %); yellow solid; mp: 136–138 °C; IR (neat): $\tilde{\nu}$ = 1652, 1498, 1080, 953, 705 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 7.21 (d, 1H, *J* = 16.1 Hz), 7.27–7.32 (m, 4H), 7.37–7.42 (m, 3H), 7.50 (t, 2H, *J* = 7.7 Hz), 7.53 (d, 2H, *J* = 7.3 Hz), 7.80 (d, 2H, *J* = 7.0 Hz), 8.08 (d, 2H, *J* = 8.4 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 113.4, 124.5, 126.6 (3C), 127.7 (2C), 128.0 (3C), 128.8 (3C), 129.5 (2C), 129.7 (2C), 132.2, 136.7, 138.6, 140.8, 144.9, 160.3; HRMS (ESI): Calcd for $C_{24}H_{20}ON$ $[M + H]^+$ = 338.1539, Found = 338.1541.

Transformation of 5-Iodo-4-phenyl-2-*p*-tolyloxazole 4Aa into 4-Phenyl-5-phenylethynyl-2-*p*-tolyloxazole 7Aa: To a mixture of 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 0.5 mmol, 180.6 mg), CuI (0.010 mmol, 1.9 mg), and $PdCl_2(PPh_3)_2$ (0.010 mmol, 7.0 mg) in Et_3N (2.5 mL) was added ethynylbenzene (0.6 mmol, 66 μL) under argon atmosphere. The obtained mixture was stirred for 3 h at 60 °C. H_2O (2.5 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15.0 mL × 3) and washed with brine (15.0 mL). The organic layer was dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 4-phenyl-5-phenylethynyl-2-*p*-tolyloxazole (**7Aa**, 161.3 mg, 96 %).

4-Phenyl-5-phenylethynyl-2-*p*-tolyloxazole (7Aa): Yield: 161.3 mg (96 %); yellow solid; mp: 112–114 °C; IR (neat): $\tilde{\nu}$ = 2987, 2198, 1499, 1248, 1078 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.30 (d, 2H, *J* = 8.1 Hz), 7.38 (tt, 1H, *J* = 7.4, 2.0 Hz), 7.41–7.43 (m, 3H), 7.48 (t, 2H, *J* = 7.4 Hz), 7.60–7.63 (m, 2H), 8.06 (d, 2H, *J* = 8.1 Hz), 8.23 (d, 2H, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.6, 78.4, 100.1, 122.0, 124.2, 126.4 (2C), 126.8 (2C), 128.6 (4C), 129.0, 129.1, 129.5 (2C), 131.0 (2C), 131.4 (2C), 141.2, 143.6, 161.1; HRMS (ESI): Calcd for $C_{24}H_{18}ON$ $[M + H]^+$ = 336.1383, Found = 336.1383.

Transformation of 5-Iodo-4-phenyl-2-*p*-tolyloxazole 4Aa into 4-Phenyl-5-*p*-toluenesulfenyl-2-*p*-tolyloxazole 8Aa: To a mixture of 5-iodo-4-phenyl-2-*p*-tolyloxazole (**4Aa**, 0.5 mmol, 180.6 mg), CuI (0.025 mmol, 4.8 mg), K_2CO_3 (0.1 mmol, 138.2 mg), and *p*-toluenethiol (0.55 mmol, 68.4 mg) in *i*PrOH (5.0 mL) was added ethylene glycol (1.0 mmol, 56 μL) under argon atmosphere. The obtained mixture was stirred for 72 h at 90 °C. H_2O (5.0 mL) was added to

the reaction mixture, and the product was extracted with EtOAc (15.0 mL × 3) and washed with brine (15 mL). The organic layer was dried with Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane/EtOAc = 9:1) to give 4-phenyl-5-*p*-toluenesulfenyl-2-*p*-tolyloxazole (**8Aa**, 161.5 mg, 45 %).

4-Phenyl-5-*p*-toluenesulfenyl-2-*p*-tolyloxazole (8Aa): Yield: 161.5 mg (45 %); white solid; mp: 101–103 °C; IR (neat): $\tilde{\nu}$ = 2971, 1498, 1180, 1073, 803, 731 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 3H), 2.41 (s, 3H), 7.09 (d, 2H, *J* = 8.3 Hz), 7.20 (d, 2H, *J* = 8.1 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 7.36 (tt, 1H, *J* = 7.2, 2.0 Hz), 7.44 (t, 2H, *J* = 7.2 Hz), 8.02 (d, 2H, *J* = 8.3 Hz), 8.18 (d, 2H, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 21.0, 21.6, 124.3, 126.7 (2C), 127.3 (2C), 128.0 (2C), 128.4 (2C), 128.6, 129.5 (2C), 130.1 (2C), 130.9, 131.2, 136.0, 136.9, 141.3, 145.9, 163.6; HRMS (ESI): Calcd for $C_{23}H_{20}ONS$ $[M + H]^+$ = 358.1260, Found = 358.1262.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra of all *O*-(2-arylethyl) arylimidate•TfOH salts **1**, all 2,5-diaryl-5-iodooxazoles **4**, and derivatives **3Aa**–**8Aa**, including 2,5-diaryloxazolines **2Ga**, **2Gb**, **2Gc**, **2De**, **2Af**, and **2Ag** and 2,5-diaryloxazoles **3Ae**, **3Be**, **3Ce**, **3Ee**, and **3Ge**.

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Keywords: Oxazole · Iminyl Radical · Imidate · DIH · 1,5-H shift

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Photochemistry

2,4-Diaryl-5-iodoxazoles could be obtained by the treatment of *O*-(β-arylethyl) arylimidates with 1,3-diiodo-5,5-dimethylhydantoin (DIH) under irradiation with a tungsten lamp. This reaction proceeds through multiple stets, i.e., formation of *N*-iodoimidate, iminyl radical, 1,5-H shift, *5-exo-tet* cyclization to oxazoline, oxidation to oxazole, and iodination to 5-iodoxazole.

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