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Preparation of 3-Iodoquinolines from *N*-Tosyl-2-propynylamines with Diaryliodonium Triflate and *N*-Iodosuccinimide

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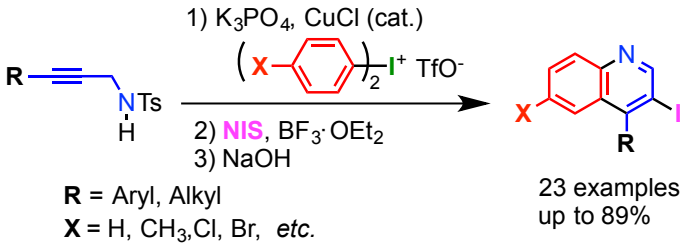
ABSTRACT:



4-Aryl- and 4-alkyl substituted 3-iodoquinolines could be smoothly obtained in one pot by treating *N*-tosyl-2-propynylamines with diaryliodonium triflate in the presence of K_3PO_4 and a catalytic amount of CuCl at room temperature, followed by treatment with *N*-iodosuccinimide and BF_3•OEt_2 at 0 °C, and then NaOH in methanol solution. The product, 3-iodo-4-phenylquinoline was smoothly transformed into 4-phenylquinoline with zinc; 4-phenyl-3-toluenesulfenylquinoline with toluenethiol, K_2CO_3, and CuI; 4-phenyl-3-phenylethynylquinoline with the Sonogashira coupling reaction; 4-phenyl-3-styrylquinoline with the Heck coupling reaction; 3,4-diphenylquinoline with the Suzuki-Miyaura coupling reaction; 2-cyclohexyl-3-iodo-4-phenylquinoline with cyclohexanecarboxylic acid, Ag_2CO_3, and $K_2S_2O_8$; and 3-iodo-2-(2',5'-dioxan-1'-yl)-4-phenylquinoline with benzoyl peroxide in dioxane.

INTRODUCTION

Quinoline derivatives, such as quinine, chloroquine, amodiaquine, primaquine, and mefloquine, are one of the most well-known antimalarial drugs, as shown in Fig. 1.[1a~1e] Other quinoline derivatives possessing anticancer,[1f,1g] antiasthmatic,[1h] and antibacterial[1i] activities are also known. In addition, it is known that such quinoline derivatives as 2-alkylquinolines and 2-arylquinolines exhibit a variety of biological activities, including antiprotozoal activity, potent inhibitory activity toward human immunodeficiency virus type-1 (HIV-1) integrase,[1j] and anti-inflammatory activity.[1k,1l] Therefore, synthetic studies of quinoline skeleton have been actively carried out.[2]

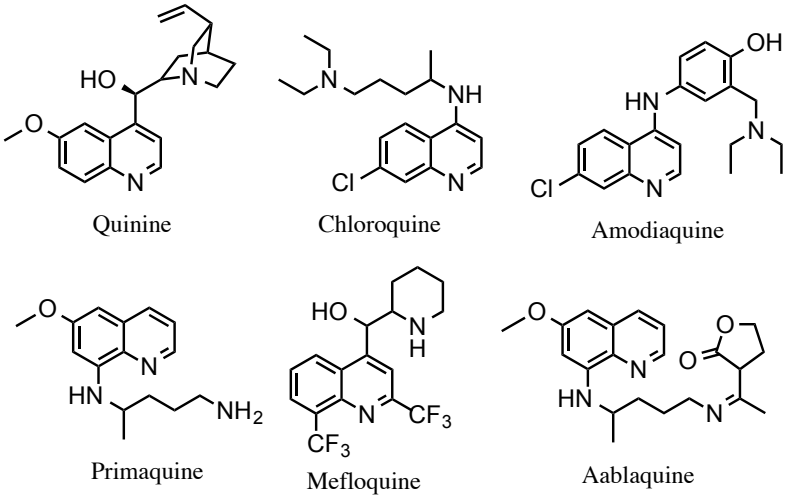


Fig. 1. Biologically Active Quinolines

For the construction of the quinoline skeleton with transition metals, the preparation of 3-substituted 2-amino-4-chloroquinolines with *o*-alkynylanilines and isocyanides in the presence of $PdCl_2$ and LiCl at 120 °C,[3a] the preparation of 2,3,4-trisubstituted quinolines with *o*-acylanilines and alkenyliodides in the presence of CuI and glycine at 130 °C,[3b] the preparation of 4-arylquinolines with β-arylacrolein and *O*-(4-cyanobenzoyl)hydroxylamine in the presence of *fac*-$Ir(ppy)_3$ and *p*-chlorobenzenesulfonic acid under LED irradiation conditions,[3c] and others[3d~3e] are reported recently. On the other hand, for the construction of the quinoline skeleton under transition-metal-free conditions, the preparation of 2,4-disubstituted 3-iodoquinolines with 1-(*o*-tosylamino)phenyl-2-propyn-1-ols with molecular iodine at 60 °C,[4a] the preparation of 3,4-disubstituted 2-thioalkoxyquinolines with

arylisothiocyanate, alkyl triflate, and alkynes at 130 °C,[4b] the preparation of 2-aroyl-4-arylquinolines with anilines, aryl methyl ketones, and styrene in the presence of molecular iodine at 80 °C,[4c] and others[4d~4g] are reported recently.

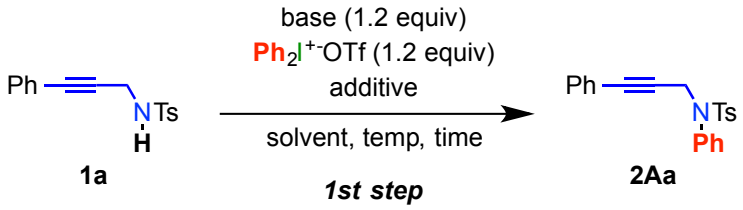
Diaryliodonium salts are very useful for the *C*-arylation of active C-H groups, the *O*-arylation of O-H groups, and the *N*-arylation of N-H groups.[5] In particular, the *N*-arylation of anilines, amides, phthalimides, morpholines, sulfonamides, *O*-protected hydroxylamines, and nitrogen-containing heterocycles with diaryliodonium salts have been actively studied recently.[6] For the preparation of quinoline skeleton with diaryliodoniym salts, the [2+2+2] cascade annulations with nitriles, alkynes, and diaryliodonium salt in the presence of $Cu(OTf)_2$ in 1,2-dichloroethane at 120 °C[7a] and with nitriles, 1-iodoalkynes, and diaryliodonium salt in the presence of $Cu(OTf)_2$ in 1,2-dichloroethane at 100 °C[7b] were recently reported to provide 2,3,4-trisubstituted quinolines and 2,4-diaryl-3-iodoquinolines, respectively.

Here, as part of our ongoing investigation of the synthetic use of diaryliodonium salts for heterocyclic compounds,[8] we would like to report an efficient one-pot preparation ([4+2] annulation) of various 4-aryl-3-iodoquinolines and 4-alkyl-3-iodoquinolines by treatment of *N*-tosyl 3-aryl-2-propynylamines and *N*-tosyl 3-alkyl-2-propynylamines, respectively, with diaryliodonium triflate in the presence of a base, followed by the reaction with *N*-iodosuccinimide (NIS) and then NaOH in methanol solution.

RESULTS AND DISCUSSION

First, the optimum conditions for the *N*-phenylation of *N*-tosyl 3-phenyl-2-propynylamine **1a** with diphenyliodonium triflate **A** (1.2 equiv.) in the presence of a base (1.2 equiv.), such as *t*-BuOK, NaH, K_2CO_3, or K_3PO_4, in toluene (3 mL) at 60 °C were examined and *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** was obtained in 37%, 14%, 45%, and 41% yields, respectively, as shown in Table 1 (entries 1-4). When the same reaction was carried out in the presence of K_3PO_4 in dichloromethane (3 mL) at 40 °C, *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** was obtained in 5% (entry 5).

Table 1. *N*-Phenylation of *N*-Tosyl 3-Phenyl-2-propynylamine 1a with Diphenyliodonium Triflate A.

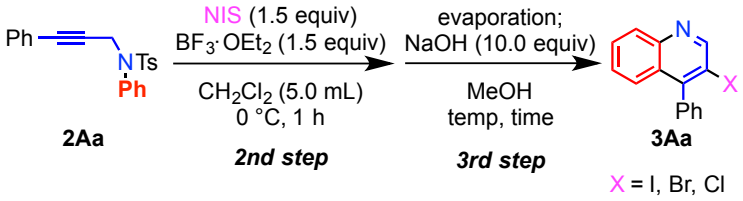


Entry	Base	Additive (mol%)	Solvent (mL)	Temp. (ºC)	Time (h)	Yield (%)
1	*t*-BuOK	-	toluene (3.0)	60	5	37
2	NaH	-	toluene (3.0)	60	5	14
3	K_2CO_3	-	toluene (3.0)	60	5	45
4	K_3PO_4	-	toluene (3.0)	60	5	41
5	K_3PO_4	-	CH_2Cl_2 (3.0)	40	5	5
6	K_3PO_4	CuBr (20)	CH_2Cl_2 (7.5)	rt	3	92
7	K_3PO_4	CuI (20)	CH_2Cl_2 (7.5)	rt	3	91
8	K_3PO_4	CuCl (20)	CH_2Cl_2 (7.5)	rt	3	88
9	K_3PO_4	CuCl (5)	CH_2Cl_2 (7.5)	rt	3	99
10	K_3PO_4	CuCl (5)	CH_2Cl_2 (3.0)	rt	3	90
11	K_3PO_4	-	CH_2Cl_2 (7.5)	rt	3	1

Then, based on a report for the effective *N*-phenylation of *N*-aryl arenesulfonamides with diaryliodonium triflate,[6b] the present *N*-phenylation of *N*-tosyl 3-phenyl-2-propynylamine **1a** with diphenyliodonium triflate **A** in the presence of K_3PO_4 and a catalyst (0.20 equiv.), such as CuBr, CuI, or CuCl, in dichloromethane (7.5 mL) at r.t. was carried out to form *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** in 92%, 91%, and 88% yields, respectively (entries 6-8). Finally, it was found that treatment of *N*-tosyl 3-phenyl-2-propynylamine **1a** with diphenyliodonium triflate **A**

(1.2 equiv.) in the presence of K_3PO_4 (1.2 equiv.) and CuCl (0.05 equiv.) in dichloromethane at room temperature for 3 h gave *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** in 99% yield (entry 9). The yield of *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** was slightly decreased by reduction of the amount of dichloromethane (3 mL) under same conditions (entry 10). Under the same reaction conditions but without CuCl, *N*-phenylation did not proceed at all (entry 11).

Table 2. Halocylization of *N*-Phenyl-*N*-Tosyl 3-Phenyl-2-propynylamine 2Aa to 3-Halo-4-phenylquinoline 3Aa.



Entry	MeOH (mL)	Temp. (ºC)	Time (h)	Yield (%)
1[a,b]	5.0	60	19	72
2[a]	5.0	60	19	85
3	5.0	60	19	87
4	10.0	60	19	95
5	5.0	50	19	90
6[d]	10.0	60	19	73
7[e]	10.0	60	19	15

[a] Under O_2 (in a sealed tube). [b] Without evaporation. [c] Without BF_3•OEt_2.

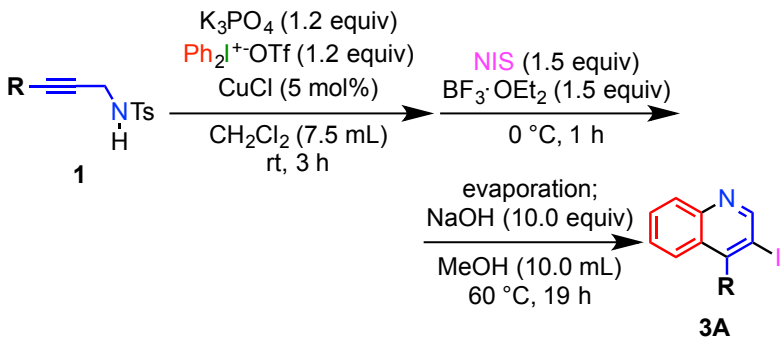
[d] NBS (1.5 equiv) was used instead of NIS. [e] NCS (1.5 equiv) was used instead of NIS.

Then, the preparation of the quinoline skeleton from *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** with NIS, followed by the reaction with NaOH was carried out, as shown in Table 2. Treatment of *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** with NIS and BF_3•OEt_2 in dichloromethane at 0 °C, the evaporation of the solvent, and treatment of the residue with NaOH in methanol solution provided 3-iodo-4-phenylquinoline **3Aa** in good yields, as shown in Table 2.

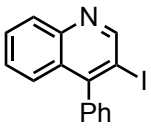
Finally, it was found that the treatment of *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** with NIS (1.5 equiv.) and BF_3•OEt_2 (1.5 equiv.) in dichloromethane at 0 °C for 1 h, the evaporation of the solvent, followed by the treatment of the residue with NaOH in methanol (10 mL) solution at 60 °C for 19 h provided 3-iodo-4-phenylquinoline **3Aa** in 95% yield (entry 4). Under the same procedure and conditions, the treatment of *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** with NIS alone did not generate iodocyclization product. The same treatment of *N*-phenyl-*N*-tosyl 3-phenyl-2-propynylamine **2Aa** with *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) instead of NIS under the same procedure and conditions generated 3-bromo-4-phenylquinoline and 3-chloro-4-phenylquinoline in 73% and 15% yields, respectively (entries 6 and 7).

Based on these results, a one-pot construction of the quinoline skeleton from *N*-tosyl 3-aryl-2-propynylamines **1** was carried out. Various *N*-tosyl 3-aryl-2-propynylamines **1** bearing phenyl (**a**), *o*-methylphenyl (**b**), *m*-methylphenyl (**c**), *p*-methylphenyl (**d**), *p*-fluorophenyl (**e**), *p*-bromophenyl (**f**), *p*-chlorophenyl (**g**), *o*-chlorophenyl (**h**), *m*-chlorophenyl (**i**), *p*-biphenyl (**j**), *p*-(methoxycarbonyl)phenyl (**k**), *p*-cyanophenyl (**l**), 2-naphthyl (**m**), 1-naphthyl (**n**), benzofuran-2-yl (**o**), and benzothiophen-2-yl (**p**) groups, were treated with diphenyliodonium triflate **A** (1.2 equiv.) in the presence of K_3PO_4 (1.2 equiv. or 1.5 equiv.) and a catalytic amount of CuCl (5 mol%) in dichloromethane at room temperature for 3 h, followed by the reaction with NIS (1.5 equiv. or 2.0 equiv.) and BF_3•OEt_2 (1.5 equiv., 2.0 equiv., or 3.0 equiv.) at 0 °C for one hour. After the reaction, the solvent was removed and the residue was treated with NaOH (10.0 equiv.)

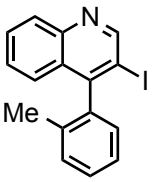
Table 3. One-Pot Transformation of *N*-Tosyl 2-Propynylamines 1 into 3-Iodoquinolines 3 with Diphenyliodonium Triflate A



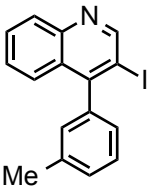
product, yield



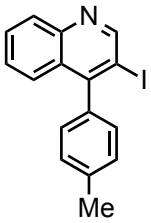
3Aa (89%) (87%)[a]



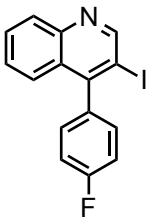
3Ab (85%)[b]



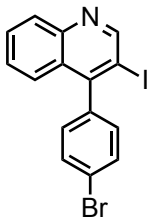
3Ac (87%)[b]



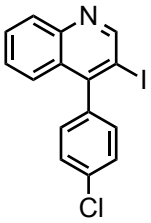
3Ad (84%)[b]



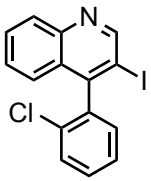
3Ae (73%)



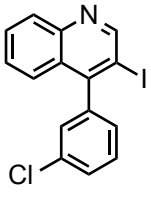
3Af (84%)



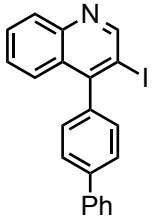
3Ag (80%)[c,d]



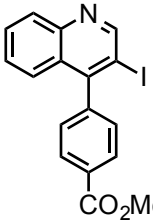
3Ah (82%)[c]



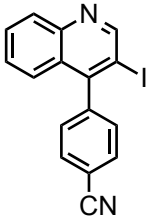
3Ai (83%)[c]



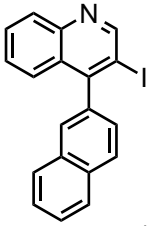
3Aj (53%)[c]



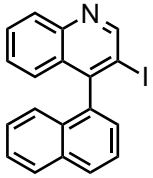
3Ak (65%)[e,f]



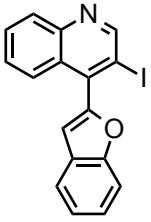
3Al (43%)[c,g]



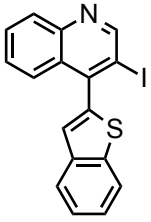
3Am (57%)[b,c]



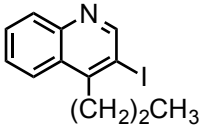
3An (81%)



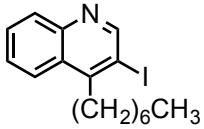
3Ao (45%)[b,c]



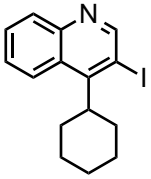
3Ap (53%)[b,c]



3Aq (60%)[b,e]



3Ar (56%)[b,e]

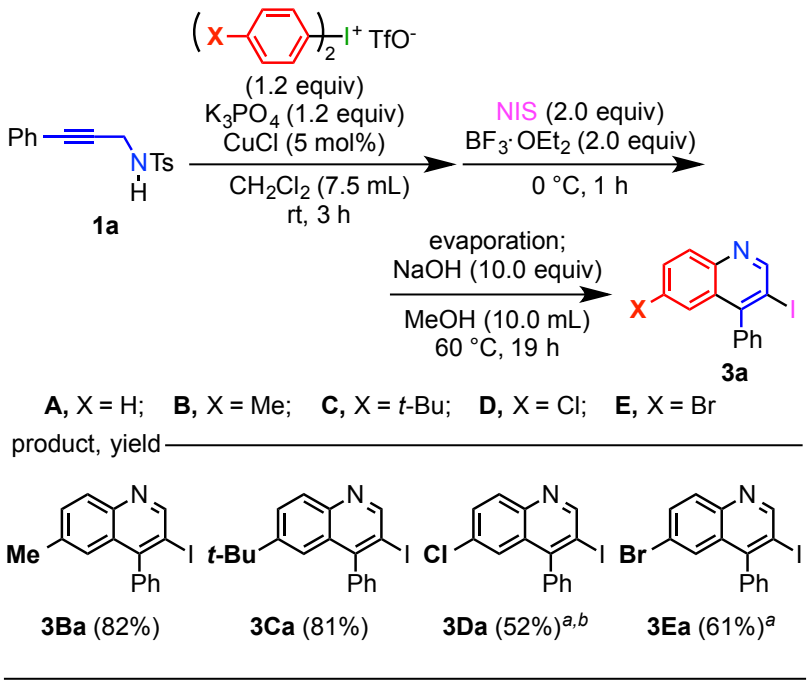


3As (57%)[b,e]

[a] **1a** (6.0 mmol) was used. [b] K_3PO_4 (1.5 equiv.) was used. [c] NIS (2.0 equiv.) and $BF_3{\cdot}OEt_2$ (2.0 equiv.) were used. [d] The 3rd reaction step was carried out at 50 °C. [e] NIS (2.0 equiv.) and $BF_3{\cdot}OEt_2$ (3.0 equiv.) were used. [f] TMSCl (10.0 equiv.) was added and the mixture was stirred for 24 h at 60 °C after 3rd step. [g] DIH (2.0 equiv.) was used instead of NIS.

in methanol at 60 °C (50 °C for **3Ag**) for 19 h to give the corresponding 4-aryl-3-iodoquinolines **3Aa**~**3Ap** in one pot in good to moderate yields, respectively, as shown in Table 3. For 3-iodoquinoline **3ak**, the methyl ester group was hydrolyzed by the treatment with NaOH in methanol at 3rd step reaction. Therefore, the formed carboxylate group was converted into methyl ester again by the treatment with TMSCl in methanol after 3rd step reaction. A gram-scale experiment with 6.0 mmol of *N*-tosyl 3-phenyl-2-propynylamine **1a** under the same procedure and conditions furnished 3-iodo-4-phenylquinoline **3Aa** in 87% yield. The structure of 4-(*p*-biphenyl)-3-iodoquinoline **3Aj** was supported by X-ray crystallographic analysis (see Supporting Information). *N*-Tosyl 3-alkyl-2-propynylamines **1** bearing propyl (**q**), heptyl (**r**), and cyclohexyl (**s**) groups were also treated under the same procedure and conditions to provide 4-alkyl-3-iodoquinolines **3Aq**~**3As** in moderate yields, respectively (Table 3).

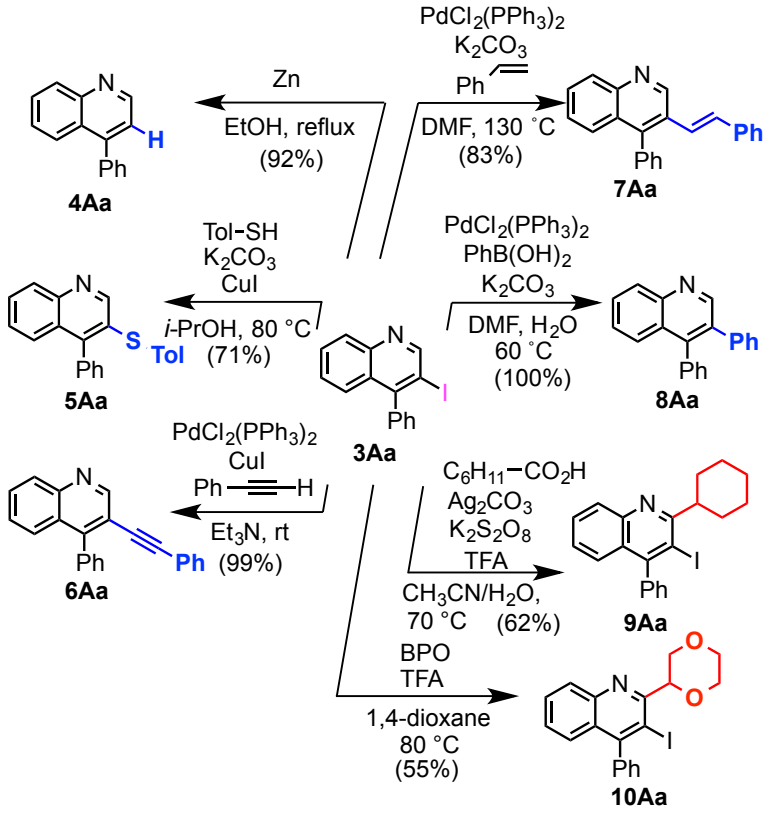
Table 4. One-Pot Transformation of *N*-Tosyl 3-Phenyl-2-propynylamine 1a into 6-Substituted 3-Iodo-4-phenylquinolines 3a with Diaryliodonium Triflates B-E



[a] K_3PO_4 (1.5 equiv.) was used. [b] NIS (2.0 equiv.) and $BF_3{\cdot}OEt_2$ (3.0 equiv.) were used.

Moreover, *N*-tosyl 3-phenyl-2-propynylamine **1a** was treated with diaryliodonium triflate (1. 2 equiv.), such as bis(*p*-methylphenyl)iodonium triflate **B**, bis(*t*-butylphenyl)iodonium triflate **C**, bis(*p*-chlorophenyl)iodonium triflate **D**, and bis(*p*-bromophenyl)iodonium triflate **E**, instead of diphenyliodonium triflate **A**, in the presence of K_3PO_4 (1.2 equiv.) and a catalytic amount of CuCl (5 mol%) in dichloromethane at room temperature for 3 h, followed by the reaction with NIS (2.0 equiv.) and BF_3•OEt_2 (2.0 equiv.) at 0 °C for one hour. After the reaction, the solvent was removed and the residue was treated with NaOH (10.0 equiv.) in methanol at 60 °C for 19 h to give the corresponding 6-substituted 4-phenyl-3-iodoquinolines **3Ba-3Ea** in 82%, 81%, 52%, and 61% yields, respectively, as shown in Table 4. Additionally, when *N*-tosyl 3-phenyl-2-propynylamine **1a** was treated with phenyl(mesityl)iodonium triflate instead of diphenyliodonium triflate **A** under the same procedure and conditions, 3-iodo-4-phenylquinoline was obtained in only 9% yield. Thus, phenyl(mesityl)iodonium triflate instead of diphenyliodonium triflate **A** is not effective

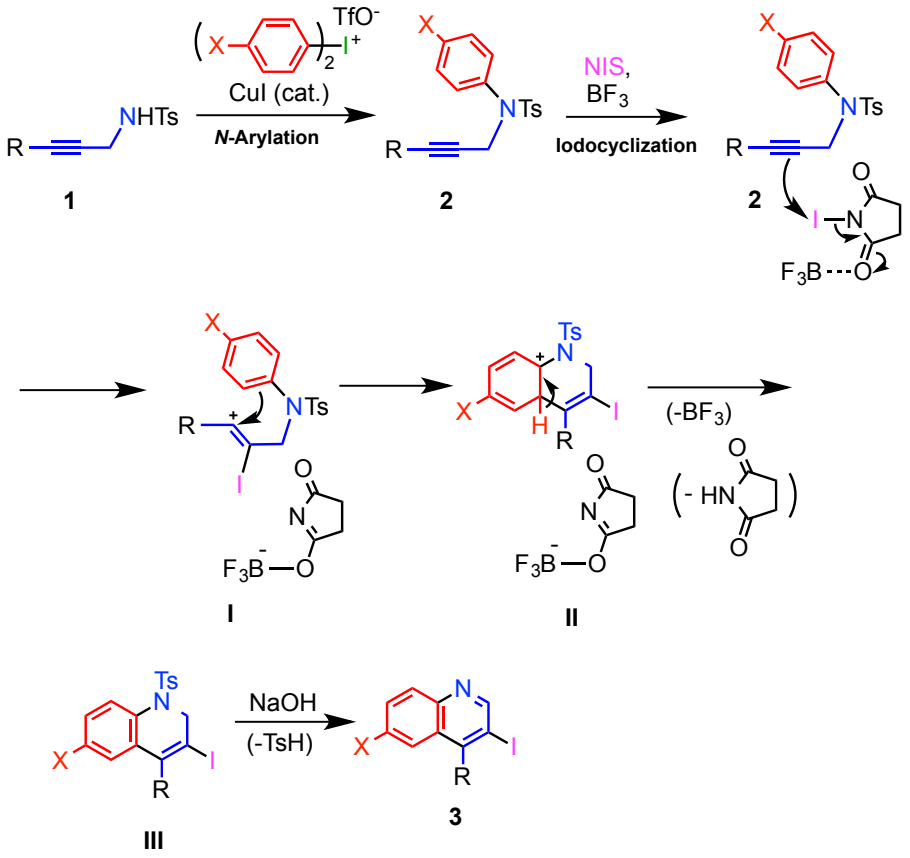
Scheme 1. Functionalization of 3-Iodo-4-Phenylquinoline



for the present reaction, although phenyl(mesityl)iodonium triflate is an excellent regioselective arylation reagent. This may be due to the steric hindrance of phenyl(mesityl)iodonium triflate in the reaction with *N*-tosyl 3-phenyl-2-propynylamine **1a**.

The obtained 4-substituted 3-iodoquinolines could be transformed into various quinoline derivatives, as shown in Scheme 1. For example, 3-iodo-4-phenylquinoline **3Aa** was smoothly reduced to 4-phenylquinoline **4Aa** in 92% yield with zinc in ethanol. Treatment of 3-iodo-4-phenylquinoline **3Aa** with toluenethiol and K_2CO_3 in the presence of CuI gave 4-phenyl-3-toluenesulfenylquinoline **5Aa** in 71% yield. The Sonogashira coupling reaction, the Heck coupling reaction, and the Suzuki-Miyaura coupling reaction of 3-iodo-4-phenylquinoline **3Aa** with phenylacetylene, styrene, and phenylboronic acid in the presence of $PdCl_2(Ph_3P)_2$ gave the coupling products, 4-phenyl-3-phenylethynylquinoline **6Aa**, 4-phenyl-3-styrylquinoline **7Aa**, and 3,4-diphenylquinoline **8Aa** in 99%, 83%, and 100% yields, respectively. The radical decarboxylative alkylation reaction[9] of 3-iodo-4-phenylquinoline **3Aa** with cyclohexanecarboxylic acid, Ag_2CO_3, and $K_2S_2O_8$ in the presence of CF_3CO_2H gave 2-cyclohexyl-3-iodo-4-phenylquinoline **9Aa** in 62% yield. Treatment of 3-iodo-4-phenylquinoline **3Aa** with benzoyl peroxide (BPO) in 1,4-dioxane generated 2-(2',5'-dioxan-1'-yl)-3-iodo-5-phenylquinoline **10Aa** in 55% yield via radical pathway.[10]

The possible reaction pathway form *N*-tosyl 2-propynylamines **1** into 3-iodoquinolines **3** with diaryliodonium triflates **A**~**E** through iodocyclization of the formed *N*-aryl-*N*-tosyl 2-propynylamines **2** onto the aromatic ring[11] is proposed in Scheme 2. Here, compound **III**, a precursor for qunoline **3**, can be isolated before the treatment with NaOH in methanol. Additionally, the present reaction with *N*-tosyl 3-phenyl-2-propynylamine **1a** with diphenyliodonium triflate **A** in the presence of TEMPO (0.5 equiv.) under the same procedure and conditions proceeded smoothly to give 3-iodo-4-phenylquinoline **3Aa** in 90% yield. Therefore, the present reaction does not contain any radical pathway.



Scheme 2. Possible Reaction Pathway

In conclusion, 4-aryl- and 4-alkyl-3-iodoquinolines were smoothly obtained in one pot by the treatment of *N*-tosyl 3-aryl-2-propynylamines and *N*-tosyl 3-alkyl-2-propynylamines with diaryliodonium triflate in the presence of K_3PO_4 and CuCl, followed by the reaction with NIS and BF_3•OEt_2, and then with NaOH in methanol solution. The obtained 3-iodoquinolines were easily transformed into various functionalized quinoline derivatives bearing a C-C bond at 2- or 3-position using Pd-catalyzed coupling reactions and radical coupling reactions.

EXPERIMENTAL SECTION

General: ^{1}H NMR spectra were measured on 500 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; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were

measured on 125 MHz spectrometers. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.0 ppm). Characteristic peaks in the infrared (IR) spectra were recorded in wave numbers, cm^{-1}. High-resolution mass spectra 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 (60F-254). The products were purified by column chromatography on silica gel 60 (63–200 mesh).

Diaryliodonium triflates: Diaryliodonium triflates A~E were prepared by the literature method in 51~84% yields.[12)]

Diphenyliodonium triflate (A): white solid; Mp: 178-179 °C (lit.[12a)] Mp 177-178 °C); IR (neat) 1566, 1472, 1444 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.49 (dd, 4H, *J* = 7.9, 7.5 Hz), 7.64 (dd, 2H, *J* = 7.9, 7.5 Hz), 7.98 (d, 4H, *J* = 7.5 Hz); ^{13}C{^{1}H}NMR (100 MHz, DMSO-d_6): δ = 116.6, 121.8 (q, $J_{C\text{-}F}$ = 315.9 Hz), 131.8, 132.1, 135.2.

Bis(4-methylphenyl)iodonium triflate (B): gray solid; Mp: 131 °C (decomposition) (lit.[12a)] Mp 182-184 °C); IR (neat) 3061, 1581, 1480, 1397 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 6H), 7.27 (d, 4H, *J* = 8.4 Hz) , 7.81 (d, 4H, *J* = 8.4 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.4, 109.8, 121.6 (q, $J_{C\text{-}F}$ = 367.8 Hz), 132.9, 135.0, 143.5; HRMS (ESI) Calcd for $C_{14}H_{14}I$ $[M]^+$ = 309.0135, Found = 309.0128; HRMS (ESI) Calcd for CO_3F_3S $[M]^+$ = 148.9515, Found = 148.9515.

Bis(4-*tert*-butylphenyl)iodonium triflate (C): white solid; Mp: 162-163 °C (lit.[12a)] Mp 164-165 °C); IR (neat) 2960, 1580, 1481, 1396 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 18H), 7.47 (d, 4H, *J* = 8.8 Hz) , 7.89 (d, 4H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 30.9, 35.2, 109.4, 121.8 (q, $J_{C\text{-}F}$ = 316.5 Hz), 129.5, 134.85, 156.47.

Bis(4-chlorophenyl)iodonium triflate (D): white solid; Mp: 177-178 °C (lit.[12a)] Mp 175-176 °C); IR (neat) 1557, 1471, 1390 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, 4H, *J* = 8.8 Hz) , 7.93 (d, 4H, *J* = 8.8 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ =111.1, 121.8 (q, $J_{C\text{-}F}$ = 316.4 Hz), 132.3, 136.7, 139.6.

Bis(4-bromophenyl)iodonium triflate (E): white solid; Mp: 201-202 °C (lit.[12b] Mp 198 °C); IR (neat) 1555, 1471, 1384 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, 4H, *J* = 8.8 Hz) , 7.87 (d, 4H, *J* = 8.8 Hz); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ = 115.4, 121.8 (q, J_{C-F} = 316.5 Hz), 126.4, 134.7, 137.1.

Typical procedure for one-pot conversion of *N*-tosyl-2-propynylamines 1 into 3-iodo-4-phenylquinolines 3

To a mixture of *N*-tosyl-3-phenyl-2-propynylamine **1a** (0.5 mmol, 142.7 mg), CuCl (5 mol%, 2.6 mg), and $K_3PO_4 \cdot nH_2O$ (0.6 mmol, 172.1 mg) in CH_2Cl_2 (7.5 mL) was added diphenyliodonium trifluoromethanesulfonate (0.6 mmol, 258.1 mg). The obtained mixture was stirred for 3 h at room temperature, and the flask was flushed by argon gas. Then, NIS (0.75 mmol, 172.2 mg) and $BF_3 \cdot OEt_2$ (0.75 mmol, 94 μL) were added at 0 °C, and the obtained mixture was stirred for 1 h at 0 °C. Then, the solvent was removed, and NaOH (5.0 mmol, 206.1 mg) and MeOH (10 mL) were added to the residue, and the obtained mixture was stirred for 19 h at 60 °C. Saturated Na_2SO_3 aqueous solution (10 mL) was added to the reaction mixture, and the product was extracted with $CHCl_3$ (15 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 8:1) to give 3-iodo-4-phenylquinolin (**3Aa**) (147.7 mg, 89% yield).

3-Iodo-4-phenylquinolin (**3Aa**): Yield: 147.7 mg (89%); white solid; Mp: 131-132 °C; IR (neat) 3062, 1499, 1485 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (d, 2H, *J* = 7.5 Hz), 7.41-7.49 (m, 2H), 7.51-7.59 (m, 3H), 7.73 (t, 1H, *J* = 7.5 Hz), 8.12 (d, 1H, *J* = 8.6 Hz), 9.25 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.3, 126.7, 127.3, 128.6 (2C), 128.9, 129.0, 129.4, 129.6, 140.3, 147.1, 152.3, 156.5; HRMS (ESI) Calcd for $C_{15}H_{11}NI$ $[M+H]^+$ = 331.9931, Found = 331.9927.

3-Iodo-4-(2'-methylphenyl)quinoline (**3Ab**): Yield: 146.2 mg (85%); white solid; Mp: 83-84 °C; IR (neat) 3017, 1499, 1482 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96 (s, 3H), 7.07 (d, 1H, *J* = 7.6 Hz), 7.31-7.47 (m, 5H), 7.73 (t, 1H, *J* = 7.6 Hz), 8.13 (d, 1H, *J* = 8.3 Hz), 9.25 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 19.5, 96.7, 126.2, 126.3, 127.5, 128.6 (2C), 128.8, 129.5, 129.7, 130.3, 135.4, 139.9, 147.0, 152.4, 156.5; HRMS

(ESI) Calcd for $C_{16}H_{13}NI$ $[M+H]^+$ = 346.0087, Found = 346.0082.

3-Iodo-4-(3'-methylphenyl)quinoline (**3Ac**): Yield: 150.3 mg (87%); pale yellow solid; Mp: 83-84 °C; IR (neat) 3060, 1498, 1482 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3H), 7.06 (d, 1H, *J* = 6.8 Hz), 7.07 (s, 1H), 7.34 (d, 1H, *J* = 7.5 Hz), 7.40-7.52 (m, 3H), 7.72 (t, 1H, *J* = 7.5 Hz), 8.11 (d, 1H, *J* = 8.4 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 21.5, 96.2, 126.0, 126.7, 127.2, 128.4, 128.8, 129.2, 129.3, 129.4, 129.5, 138.2, 140.1, 147.0, 152.4, 156.4; HRMS (ESI) Calcd for $C_{16}H_{13}NI$ $[M+H]^+$ = 346.0087, Found = 346.0084.

3-Iodo-4-(4'-methylphenyl)quinoline (**3Ad**): Yield: 145.2 mg (84%); white solid; Mp: 155-156 °C; IR (neat) 2959, 1491, 1375 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3H), 7.16 (d, 2H, *J* = 7.7 Hz) , 7.37 (d, 2H, *J* = 7.7 Hz) , 7.42 (t, 1H, *J* = 7.6 Hz), 7.50 (d, 1H, *J* = 7.6 Hz), 7.71 (t, 1H, *J* = 7.6 Hz), 8.11 (d, 1H, *J* = 8.4 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ =21.4, 96.5, 126.7, 127.2, 128.8, 129.0, 129.2, 129.3, 129.5, 137.2, 138.4, 147.1, 152.4, 156.5; HRMS (ESI) Calcd for $C_{16}H_{13}NI$ $[M+H]^+$ = 346.0087, Found = 346.0084.

4-(4'-Fluorophenyl)-3-iodoquinoline (**3Ae**): Yield: 128.2 mg (73%); white solid; Mp: 105-106 °C; IR (neat) 3063, 1509, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.25-7.27 (m, 4H), 7.45 (d, 2H, *J* = 8.3 Hz), 7.71-7.78 (m, 1H), 8.13 (d, 1H, *J* = 8.3 Hz), 9.25 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.6, 115.7 (d, $J_{C\text{-}F}$ = 21.6 Hz), 126.3, 127.4, 128.8, 129.5, 129.7, 130.9 (d, $J_{C\text{-}F}$ = 8.5 Hz), 136.0 (d, $J_{C\text{-}F}$ = 3.8 Hz), 147.0, 151.2, 156.4, 162.7 (d, $J_{C\text{-}F}$ = 249.0 Hz); HRMS (ESI) Calcd for $C_{15}H_{10}NFI$ $[M+H]^+$ = 349.9836, Found = 349.9832.

4-(4'-Bromophenyl)-3-iodoquinoline (**3Af**): Yield: 172.0 mg (84%); pale yellow solid; Mp: 162-163 °C; IR (neat) 3064, 1500, 1483 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, 2H, *J* = 8.3 Hz), 7.43-7.48 (m, 2H), 7.70-7.78 (m, 3H), 8.13 (d, 1H, *J* = 8.3 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.1, 113.0, 126.2, 127.6, 128.5, 129.5, 129.8, 130.7, 131.9, 139.0, 147.0, 151.0, 156.5; HRMS (ESI) Calcd for $C_{15}H_{10}NBrI$ $[M+H]^+$ = 409.9036, Found = 409.9034.

4-(4'-Chlorophenyl)-3-iodoquinoline (**3Ag**): Yield: 145.4 mg (80%); white solid; Mp: 146-147 °C; IR (neat) 2924, 1500, 1484 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23 (d, 2H, *J* = 8.5 Hz), 7.43-7.47 (m, 2H), 7.55 (d, 2H, *J* = 8.5 Hz), 7.71-7.78 (m, 1H), 8.13 (d, 1H, *J* = 8.3 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.2, 126.2, 127.5, 128.6, 128.9, 129.5, 129.7, 130.4, 134.7, 138.4, 147.0, 150.9, 156.4; HRMS (ESI) Calcd for $C_{15}H_{10}NClI$ $[M+H]^+$ = 365.9541, Found = 365.9541.

4-(2'-Chlorophenyl)-3-iodoquinoline (**3Ah**): Yield: 150.4 mg (82%); white solid; Mp: 136-137 °C; IR (neat) 3010, 1501, 1472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.21 (d, 1H, *J* = 7.6 Hz), 7.32 (d, 1H, *J* = 7.6 Hz), 7.44-7.53 (m, 3H), 7.61 (d, 1H, *J* = 7.7 Hz), 7.75 (t, 1H, *J* = 7.6 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 9.26 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.4, 125.9, 127.1, 127.6, 128.4, 129.6, 129.8, 129.9, 130.2, 130.5, 132.8, 138.9, 146.9, 149.9, 156.4; HRMS (ESI) Calcd for $C_{15}H_{10}NClI$ $[M+H]^+$ = 365.9541, Found = 365.9541.

4-(3'-Chlorophenyl)-3-iodoquinoline (**3Ai**): Yield: 152.2 mg (83%); white solid; Mp: 115-116 °C; IR (neat) 3045, 1500, 1473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.14-7.20 (m, 1H), 7.27-7.29 (m, 1H), 7.43-7.53 (m, 4H), 7.74 (t, 1H, *J* = 7.3 Hz) , 8.13 (d, 1H, *J* = 8.4 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.0, 126.3, 127.3, 127.6, 128.5, 128.9, 129.1, 129.6, 129.9, 130.0, 134.6, 141.8, 147.0, 150.7, 156.5; HRMS (ESI) Calcd for $C_{15}H_{10}NClI$ $[M+H]^+$ = 365.9541, Found = 365.9539.

4-(Biphenyl-4'-yl)-3-iodoquinoline (**3Aj**): Yield: 108.2 mg (53%); white solid; Mp: 165-166 °C; IR (neat) 3033, 1565, 1483 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, 2H, *J* = 8.4 Hz), 7.39-7.57 (m, 5H), 7.72-7.76 (m, 3H), 7.78 (d, 2H, *J* = 8.4 Hz), 8.13 (d, 1H, *J* = 8.6 Hz), 9.27 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.4, 126.7, 127.1, 127.2, 127.4, 127.7, 128.9 (2C), 129.5, 129.6, 129.7, 139.1, 140.3, 141.4, 147.2, 152.1, 156.6; HRMS (ESI) Calcd for $C_{21}H_{15}NI$ $[M+H]^+$ = 408.0244, Found = 408.0244.

3-Iodo-4-(4'-methoxycarbonylphenyl)quinoline (**3Ak**): Yield: 126.9 mg (65%); white solid; Mp: 133-134 °C; IR (neat) 2956, 1717, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 3H), 7.36-7.40 (m, 3H), 7.45 (t, 1H, *J* = 7.6 Hz), 7.75 (t, 1H, *J* = 7.6 Hz), 8.14 (d, 1H, *J* = 8.5 Hz), 8.25 (d, 2H, *J* = 8.5 Hz), 9.25 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz,

$CDCl_3$): δ = 52.3, 95.5, 126.2, 127.6, 128.4, 129.2, 129.5, 129.9, 129.9, 130.4, 144.7, 147.0, 151.2, 156.4, 166.5; HRMS (ESI) Calcd for $C_{17}H_{13}O_2NI$ $[M+H]^+$ = 389.9985, Found = 389.9985.

4-(4'-Cyanophenyl)-3-iodoquinoline (**3Al**): Yield: 78.5 mg (43%); white solid; Mp: 139-140 °C; IR (neat) 3033, 2228, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, 1H, *J* = 8.0 Hz), 7.42 (d, 2H, *J* = 8.4 Hz), 7.47 (t, 1H, *J* = 7.8 Hz), 7.77 (t, 1H, *J* = 7.7 Hz), 7.88 (d, 2H, *J* = 8.4 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 9.23 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 95.2, 124.1, 125.7, 128.0 (2C), 129.8, 130.1 (2C), 130.4, 146.6, 147.0, 148.0, 149.9, 156.5; HRMS (ESI) Calcd for $C_{16}H_{10}N_2I$ $[M+H]^+$ = 356.9883, Found = 356.9879.

3-Iodo-4-(naphthalen-2'-yl)quinoline (**3Am**): Yield: 109.3 mg (57%); white solid; Mp: 163-164 °C; IR (neat) 3057, 1565, 1496 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36-7.43 (m, 2H), 7.49 (d, 1H, *J* = 7.9 Hz), 7.57-7.63 (m, 2H), 7.73 (t, 1H, *J* = 7.6 Hz), 7.77 (s, 1H), 7.89-8.00 (m, 2H) ,8.04 (d, 1H, *J* = 8.4 Hz), 8.15 (d, 1H, *J* = 8.4 Hz), 9.29 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 96.4, 126.66, 126.69, 126.7, 126.8, 127.4, 127.9, 128.3, 128.39, 128.42, 129.0, 129.5, 129.7, 133.0, 133.1, 137.6, 147.1, 152.2, 156.6; HRMS (ESI) Calcd for $C_{19}H_{13}NI$ $[M+H]^+$ = 382.0087, Found = 382.0088.

3-Iodo-4-(naphthalen-1'-yl)quinoline (**3An**): Yield: 154.9 mg (81%); pale yellow solid; Mp: 162-163 °C; IR (neat) 3048, 1565, 1496 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.15 (d, 1H, *J* = 8.4 Hz), 7.23 (d, 1H, *J* = 8.4 Hz), 7.31-7.37 (m, 3H), 7.53 (t, 1H, *J* = 7.0 Hz), 7.66 (t, 1H, *J* = 7.6 Hz), 7.77 (t, 1H, *J* = 7.6 Hz) , 7.99 (d, 1H, *J* = 8.2 Hz), 8.05 (d, 1H, *J* = 8.2 Hz), 8.18 (d, 1H, *J* = 8.4 Hz), 9.32 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 97.6, 125.2, 125.4, 126.3, 126.7, 126.8, 127.0, 127.5, 128.5, 129.0, 129.5 (2C), 129.8, 130.6, 133.5, 137.9, 147.0, 151.2, 156.6; HRMS (ESI) Calcd for $C_{19}H_{13}NI$ $[M+H]^+$ = 382.0087, Found = 382.0086.

4-(Benzofuran-2'-yl)-3-iodoquinoline (**3Ao**): Yield: 83.6 mg (45%); white solid; Mp: 133-134 °C; IR (neat) 3062, 1558, 1493 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (s, 1H), 7.37 (t, 1H, *J* = 7.7 Hz), 7.43 (t, 1H, *J* = 8.2 Hz), 7.53 (t, 1H, *J* = 7.9 Hz), 7.63 (d, 1H, *J* = 8.2 Hz), 7.74-7.82 (m, 3H), 8.15 (d, 1H, *J* = 8.4 Hz), 9.30(s, 1H); $^{13}C\{^1H\}$NMR

(100 MHz, $CDCl_3$): δ = 96.3, 109.2, 111.7, 121.6, 123.4, 125.3, 125.8, 127.9, 128.0, 128.7, 129.7, 130.1, 141.6, 147.1, 152.5, 155.1, 156.9; HRMS (ESI) Calcd for $C_{17}H_{11}ONI$ $[M+H]^+$ =371.9880, Found = 371.9876.

4-(Benzo[*b*]thiophen-2'-yl)-3-iodoquinoline (**3Ap**): Yield: 103.2 mg (53%); white solid; Mp: 191-192 °C; IR (neat) 3052, 1490, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 1H), 8.14 (d, 1H, *J* = 8.2 Hz), 7.43-4.50 (m, 3H), 7.75 (d, 1H, *J* = 7.9 Hz), 7.77 (d, 1H, *J* = 7.5 Hz), 7.90-7.96 (m, 2H), 9.27 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 98.0, 122.4, 124.2, 124.8, 125.0, 125.5, 126.4, 127.8, 129.5 (2C), 130.0, 139.5, 140.6, 140.7, 145.7, 147.0, 156.5; HRMS (ESI) Calcd for $C_{17}H_{11}NIS$ $[M+H]^+$ =387.9651, Found = 387.9648.

3-Iodo-4-propylquinoline (**3Aq**): Yield: 89.7 mg (60%); colorless oil; IR (neat) 3068, 2958, 1501 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.13 (t, 3H, *J* = 7.4 Hz), 5.03 (s, 2H), 1.66-1.76 (m, 2H), 3.22 (t, 2H, *J* = 8.3 Hz), 7.57 (t, 1H, *J* = 8.8 Hz), 7.72 (t, 1H, *J* = 8.8 Hz), 8.04 (d, 1H, *J* = 9.4 Hz), 8.07 (d, 1H, *J* = 8.8 Hz), 9.10 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ =14.4, 22.8, 38.8, 97.4, 124.0, 127.2, 128.4, 129.4, 130.1, 147.3, 151.0, 157.0; HRMS (ESI) Calcd for $C_{12}H_{13}NI$ $[M+H]^+$ =298.0087, Found = 298.0085.

4-Heptyl-3-iodoquinoline (**3Ar**): Yield: 94.9 mg (56%); colorless oil; IR (neat) 3069, 1505, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, 3H, *J* = 6.9 Hz), 1.30-1.42 (m, 6H), 1.50-1.58 (m, 2H), 1.62-1.70 (m, 2H), 3.22 (t, 2H, *J* = 7.9 Hz), 7.57 (t, 1H, *J* = 7.8 Hz), 7.72 (t, 1H, *J* = 7.6 Hz), 8.06 (t, 2H, *J* = 8.8 Hz), 9.09 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 14.1, 22.6, 29.0, 29.3, 29.9, 31.8, 37.1, 97.4, 124.0, 127.2, 128.3, 129.4, 130.1, 147.3, 151.2, 157.0; HRMS (ESI) Calcd for $C_{16}H_{21}NI$ $[M+H]^+$ =354.0713, Found = 354.0711.

4-Cyclohexyl-3-iodoquinoline (**3As**): Yield: 96.5 mg (57%); colorless oil; IR (neat) 3064, 1495, 1473 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.40-1.59 (m, 3H), 1.92 (d, 5H, *J* = 12.9 Hz), 2.23 (q, 2H, *J* = 12.7 Hz), 3.55 (t, 1H, *J* = 12.7 Hz), 6.96 (d, 1H, *J* = 8.3 Hz), 7.52 (t, 1H, *J* = 7.7 Hz), 7.69 (t, 1H, *J* = 7.5 Hz), 8.39 (d, 1H, *J* = 8.6 Hz), 9.15 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 26.0, 27.1, 30.8, 52.9, 99.3, 125.3, 125.7, 128.2, 129.0, 130.6, 148.6, 153.6, 157.6; HRMS (ESI) Calcd for $C_{15}H_{17}NI$ $[M+H]^+$

=338.0400, Found = 338.0398.

3-Iodo-6-methyl-4-phenylquinoline (3Ba): Yield: 141.7 mg (82%); white solid; Mp: 136-137 °C; IR (neat) 3044, 1563, 1488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.19 (s, 1H), 7.23-7.28 (m, 2H), 7.52-7.60 (m, 4H), 8.01 (d, 1H, *J* = 8.6 Hz), 9.17 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ =21.7, 96.4, 125.3, 128.5, 128.6, 128.9, 129.0, 129.1, 131.9, 137.7, 140.5, 145.7, 151.5, 155.6; HRMS (ESI) Calcd for $C_{16}H_{13}NI$ $[M+H]^+$ = 346.0087, Found = 346.0085.

6-(*tert*-Butyl)-3-iodo-4-phenylquinoline (3Ca): Yield: 157.0 mg (81%); pale yellow solid; Mp: 115-116 °C; IR (neat) 2958, 2362, 1990 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 9H), 7.28 (d, 2H, *J* = 7.9 Hz), 7.37 (d, 1H, *J* = 2.0 Hz), 7.53-7.58 (m, 3H), 7.81 (d, 1H, *J* = 8.9 Hz), 8.05 (d, 1H, *J* = 8.8 Hz), 9.18 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 30.9, 35.0, 96.2, 121.6, 128.5 (2C), 128.5, 128.6, 128.9, 129.0, 140.4, 145.6, 150.3, 152.1, 155.9; HRMS (ESI) Calcd for $C_{19}H_{19}NI$ $[M+H]^+$ = 388.0557, Found = 388.0557.

6-Chloro-3-iodo-4-phenylquinoline (3Da): Yield: 95.6 mg (52%); pale yellow solid; Mp: 169-170 °C; IR (neat) 3045, 1601, 1480 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.23-7.29 (m, 2H), 7.43 (d, 1H, *J* = 2.5 Hz), 7.52-7.61 (m, 3H), 7.65 (dd, 1H, *J* = 9.1, 2.5 Hz) , 8.05 (d, 1H, *J* = 8.8 Hz), 9.23 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 97.5, 125.4, 128.8, 128.9, 129.0, 129.4, 130.7, 131.1, 133.3, 139.6, 145.5, 151.5, 156.8; HRMS (ESI) Calcd for $C_{15}H_{10}NClI$ $[M+H]^+$ = 365.9541, Found = 365.9539.

6-Bromo-3-iodo-4-phenylquinoline (3Ea): Yield: 125.2 mg (61%); white solid; Mp: 183-184 °C; IR (neat) 3045, 1597, 1474 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.29 (m, 2H), 7.55-7.61 (m, 4H), 7.78 (d, 1H, *J* = 9.0 Hz), 7.98 (d, 1H, *J* = 9.1 Hz), 9.24 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 97.5, 121.6, 128.7, 128.8, 128.9, 129.0, 129.8, 131.2, 133.2, 139.6, 145.7, 151.4, 157.0; HRMS (ESI) Calcd for $C_{15}H_{10}NBrI$ $[M+H]^+$ = 409.9036, Found = 409.9034.

***N*-Tosyl-1,2-dihydro-3-iodo-4-phenylquinoline (IIIAa)**: Without treatment with NaOH in methanol: pale yellow solid; Mp: 181-182 °C; IR (neat) 1595, 1491, 1449

cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 4.88 (s, 2H), 6.42 (d, 2H, *J* = 6.3 Hz), 6.53 (dd, 1H, *J* = 7.9, 1.4 Hz), 7.07 (td, 1H, *J* = 7.7, 1.4, Hz), 7.18 (d, 2H, *J* = 8.2 Hz), 7.25-7.36 (m, 4H) , 7.43 (d, 2H, *J* = 8.2 Hz) , 7.77 (dd, 1H, *J* = 8.0, 1.1, Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 21.4, 56.8, 92.6, 126.6, 126.9, 127.3, 127.5, 128.0, 128.2, 128.4, 129.1, 129.4, 130.9, 134.1, 135.6, 140.0, 143.0, 143.8; HRMS (APCI) Calcd for $C_{22}H_{19}INO_2S$ $[M+H]^+$ = 488.0174, Found = 488.0176.

Preparation of 4-phenylquinoline (4Aa)

To a mixture of 3-iodo-4-phenylquinoline **(3Aa**) (0.5 mmol, 165.6 mg) in EtOH (7.5 mL) was added Zn powder (5 mmol, 363.3 mg). Under the 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 = 5:1) to afford 4-phenylquinoline (**4Aa**) (94.4 mg, 92% yield).

4-Phenylquinoline (4Aa): Yield: 94.4 mg (92%); pale yellow oil; IR (neat) 3059, 1508, 1490 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, 1H, *J* = 4.3 Hz), 7.47-7.55(m, 6H), 7.73 (t, 1H, *J* = 7.7 Hz), 7.92 (d, 1H, *J* = 8.4 Hz), 8.18 (d, 1H, *J* = 8.4 Hz) , 8.95 (d, 1H, *J* = 4.3 Hz); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ = 121.2, 125.7, 126.5, 126.6, 128.3, 128.4, 129.2, 129.4, 129.7, 137.8, 148.3, 148.5, 149.8; HRMS (ESI) Calcd for $C_{15}H_{12}N$ $[M+H]^+$ = 206.0964, Found = 206.0965.

Preparation of 4-phenyl-3-*p*-toluenesulfenylquinoline (5Aa)

To a mixture of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 165.7 mg), CuI (0.025 mmol, 4.8 mg), K_2CO_3 (0.1 mmol, 138.2 mg), and *p*-Tol-SH (0.55 mmol, 68.4 mg) in ^{i}PrOH (5.0 mL) was added ethylene glycol (1.0 mmol, 56 μL). Under the argon atmosphere, the obtained mixture was stirred for 48 h at 80°C. H_2O (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 8:1) to give 4-phenyl-3-*p*-toluenesulfenylquinoline **(5Aa)** (116.6 mg, 71% yield).

4-Phenyl-3-*p*-toluenesulfenylquinoline (5Aa): Yield: 116.6 mg (71%); white solid; Mp: 128-129 °C; IR(neat) 3060, 1563, 1486 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H), 7.10 (d, 2H, *J* = 8.1 Hz) , 7.21 (d, 2H, *J* = 8.1 Hz), 7.32-7.36 (m, 2H), 7.41-7.56 (m, 5H), 7.66 (t, 1H, *J* = 7.5 Hz) , 8.08 (d, 1H, *J* = 8.3 Hz), 8.67 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.0, 127.1, 127.5, 128.4, 128.5, 129.0, 129.4, 129.5, 129.6, 130.2, 130.6, 132.2, 136.0, 137.9, 146.5, 147.3, 151.7; HRMS (ESI) Calcd for $C_{22}H_{18}NS$ $[M+H]^+$ = 328.1154, Found = 328.1152.

Preparation of 4-phenyl-3-phenylethynylquinoline (6Aa)

To a mixture of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 165.7 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 the 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 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 5:1) to give 4-phenyl-3-phenylethynylquinoline (**6Aa**) (151.1 mg, 99% yield).

4-Phenyl-3-phenylethynylquinoline (6Aa): Yield: 151.1 mg (99%); pale yellow solid; Mp: 148-149 °C; IR (neat) 3050, 2199, 1488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.31 (m, 5H), 7.48-7.61 (m, 6H), 7.69-7.76 (m, 2H), 8.16 (d, 1H, *J* = 8.7 Hz), 9.08 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 86.8, 95.2, 116.4, 122.7, 126.2, 126.5, 127.1, 128.1, 128.2, 128.4, 128.5, 129.57, 129.61, 130.0, 131.4, 136.0, 147.1, 149.9, 152.0; HRMS (ESI) Calcd for $C_{23}H_{16}N$ $[M+H]^+$ = 306.1277, Found = 306.1273.

Preparation of (*E*)-4-phenyl-3-styrylquinoline (7Aa)

To a mixture of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 165.7 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 the argon atmosphere, the obtained mixture was stirred for 3 h at 60°C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the

solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 5:1) to give (*E*)-4-phenyl-3-styrylquinoline (**7Aa**) (126.9 mg, 83% yield).

(*E*)-4-Phenyl-3-styrylquinoline (7Aa): Yield: 126.9 mg (83%); white solid; Mp: 174-175 °C; IR (neat) 3057, 1631, 1489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.96 (d, 1H, *J* = 16.6 Hz), 7.21-7.39 (m, 8H), 7.44 (t, 1H, *J* = 7.6 Hz), 7.51-7.60 (m, 4H), 7.67 (t, 1H, *J* = 7.6 Hz), 8.14 (d, 1H, *J* = 8.3 Hz), 9.35 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 124.6, 126.5, 126.6, 126.8, 127.3, 127.8, 128.0, 128.2, 128.5, 128.7, 128.9, 129.4, 130.1, 131.0, 135.8, 136.9, 145.1, 147.2, 148.4; HRMS (ESI) Calcd for $C_{23}H_{18}N$ $[M+H]^+$ = 308.1434, Found = 308.1431.

Preparation of 3,4-diphenylquinoline (8Aa)

To a mixture of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 167.1 mg) and $PhB(OH)_2$ (1.0 mmol, 121.9 mg) in DMF (10 mL) was added $PdCl_2(PPh_3)_2$ (0.025 mmol, 17.5 mg). Under the 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 mL) was added to the mixture, and the obtained mixture was stirred for 1.5 h at 60°C. H_2O (5 mL) was added to the reaction mixture, and the product was extracted with CH_2Cl_2 (15 mL × 3), and washed with brine (15 mL × 2). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 5:1) to give 3,4-diphenylquinoline (**8Aa**) (140.1 mg, 100% yield).

3,4-Diphenylquinoline (8Aa): Yield: 140.1 mg (100%); white solid; Mp: 137-138 °C; IR (neat) 3061, 1566, 1484 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.16-7.29 (m, 7H), 7.33-7.39 (m, 3H), 7.49 (t, 1H, *J* = 7.7 Hz), 7.67-7.76 (m, 2H), 8.20 (d, 1H, *J* = 8.4 Hz), 9.01 (s, 1H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 126.4, 126.7, 126.9, 127.0, 127.6, 127.9, 128.0, 128.8, 129.4, 130.0, 130.3, 132.9, 136.1, 138.0, 145.3, 147.4, 151.7; HRMS (ESI) Calcd for $C_{21}H_{16}N$ $[M+H]^+$ = 282.1277, Found = 282.1277.

Preparation of 2-cyclohexyl-3-iodo-4-phenylquinoline (9Aa)

To a mixture of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 165.7 mg), cyclohexanecarboxylic acid (1.0 mmol, 124 μL), Ag_2CO_3 (0.1 mmol, 17.0 mg), and $K_2S_2O_8$ (1.0 mmol, 270.4 mg) in MeCN/H_2O (5:1, 12 mL) was added trifluoroacetic acid (0.65 mmol, 50 μL). Under the argon atmosphere, the obtained mixture was stirred for 6 h at 70°C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane : EtOAc = 30:1) to give 2-cyclohexyl-3-iodo-4-phenylquinoline **(9Aa)** (127.8 mg, 62% yield).

2-Cyclohexyl-3-iodo-4-phenylquinoline (9Aa): Yield: 127.8 mg (62%); white solid; Mp: 101-102 °C; IR (neat) 3056, 1499 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35-1.57 (m, 3H), 1.73-1.85 (m, 3H), 1.92 (d, 2H, *J* = 12.9 Hz), 2.05 (d, 2H, *J* = 11.8 Hz), 3.46 (t, 1H, *J* = 11.6 Hz), 7.22 (d, 2H, *J* = 7.7 Hz), 7.28-7.34 (m, 2H), 7.48-7.58 (m, 3H) 7.67 (t, 1H, *J* = 7.3 Hz), 8.07 (d, 1H, *J* = 8.38 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 26.1, 26.5, 32.1, 49.1, 101.5, 126.3, 126.7, 127.2, 128.2, 128.5, 129.0, 129.1, 129.5, 142.6, 147.0, 153.6, 165.3; HRMS (ESI) Calcd for $C_{21}H_{21}NI$ $[M+H]^+$ = 414.0713, Found = 414.0713.

Preparation of 2-(1',4'-dioxan-2'-yl)-3-iodo-4-phenylquinoline (10Aa)

To a solution of 3-iodo-4-phenylquinoline (**3Aa**) (0.5 mmol, 167.1 mg) and trifluoroacetic acid (0.65 mmol, 50 μL) in 1,4-dioxane (4.0 mL) was added benzoyl peroxide (1.0 mmol, 323.0 mg) at room temperature, and the flask was flushed by argon gas. Then, the mixture was stirred for 4 h at 80 °C. Saturated $NaHCO_3$ aqueous solution (5.0 mL) was added to the reaction mixture, and the product was extracted with EtOAc (15 mL × 3), and washed with brine (15 mL). The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed under reduced pressure, the residue was purified by silica-gel column chromatography (eluent: *n*-hexane:EtOAc = 5:1) to give 2-(1',4'-dioxan-2'-yl)-3-iodo-4-phenylquinoline **(10Aa)** (115.1 mg, 55% yield).

2-(1',4'-Dioxan-2'-yl)-3-iodo-4-phenylquinoline (10Aa): Yield: 115.1 mg (55%); white solid; Mp: 119-120 °C; IR (neat) 2956, 1502, 1180 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$): δ = 3.83-3.97 (m, 2H), 4.02-4.12 (m, 3H), 4.25 (dd, 1H, *J* = 11.6, 2.5 Hz), 5.39 (d, 1H, *J* = 9.6 Hz), 7.18-7.24 (m, 2H), 7.32-7.43 (m, 2H), 7.50-7.59 (m, 3H), 7.71 (t, 1H, *J* = 7.6 Hz), 8.21 (d, 1H, *J* = 8.4 Hz); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ = 66.3, 67.7, 69.9, 80.8, 98.6, 126.7, 127.6, 128.0, 128.51, 128.54, 128.7, 128.9, 129.1, 129.6, 129.9, 141.8, 146.7, 154.6, 156.1; HRMS (ESI) Calcd for $C_{19}H_{17}O_2NI$ $[M+H]^+$ = 418.0298, Found = 418.0299.

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: http://pubs.acs.org. NMR charts of all quinolines **3, IIIAa, 4Aa~10Aa**, and diaryliodonium triflates **A~E**, and X-ray analytical data of **3Aj**.

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