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# Synthesis of 3-Iodoquinolines by Copper-Catalyzed Tandem Annulation from Diaryliodoniums, Nitriles, and 1-Iodoalkynes

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**Abstract:** A novel method for the synthesis of 3-iodoquinolines was developed by copper-catalyzed tandem annulation from diaryliodoniums, nitriles, and 1-iodoalkynes. It is a method that is characterized by the most convenient operation and wide molecular diversity.

**Keywords:** annulation; copper catalysts; 1-iodoalkynes; iodoniums; synthesis of quinolones; tandem reactions

## Introduction

Quinolines are important heterocycles found in natural products and synthetic compounds. Their novel structures and properties have made them widely applicable in drug discovery[1] and material science.[2] Therefore, the synthesis of quinolines has continuously been an important research project. In recent years, numerous novel synthetic methods have been developed for this purpose[3] even though many well-known name reactions[4] had been established before, such as Combes synthesis, Conrad–Limpach–Knorr synthesis, Friedländer reaction, and Skraup–Doebner–Von Miller reaction (Figure 1). Among these methods, the introduction of a C-3 substituent on the quinoline ring usually is much more difficult than that of C-2 and C-4 substituents, thus significantly limiting the molecular diversity of quinolines.

In the past decade, metal-catalyzed cross-couplings of aryl halides have been played a crucial role in organic synthesis, such as Buchwald–Hartwig, Heck, Sonogashira, Suzuki, and Ullmann couplings. Recently, these couplings have been employed to efficiently synthesize C-3 subtituted quinolines starting from 3-iodoquinolines **1**. As shown in Figure 2, compound **1** has been recognized as a versatile precursor to successfully achieve the corresponding arylation,[5] alkenylation,[6] alkynylation[7] as well as the formations of C–N,[8] C–O,[9] and C–S[10] bonds. Since the iodine atom could not be replaced by other halogen atoms (such as Br and Cl)[8a,c,10b,c] in these couplings, the importance of the synthesis of 3-iodoquinolines **1** has been enhanced significantly.[11]

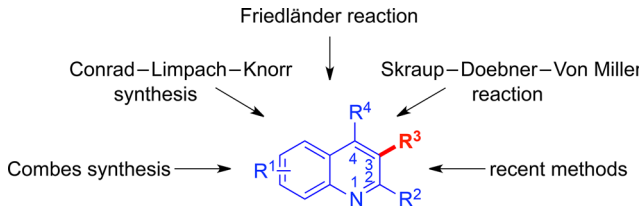



**Figure 1.** Some synthetic methods for quinolines.

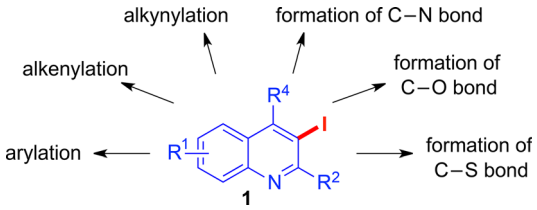
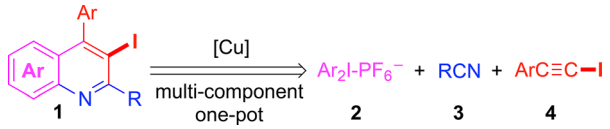



**Figure 2.** Some metal-catalyzed cross-couplings of **1**.

Herein, we would like to report a novel method for the easy synthesis of 3-iodoquinolines **1** by a copper-catalyzed tandem annulation from diaryliodoniums **2**, nitriles **3**, and 1-iodoalkynes **4** (Scheme 1).




**Scheme 1.** Retrosynthetic analysis of 3-iodoquinolines **1**.

## Results and Discussion

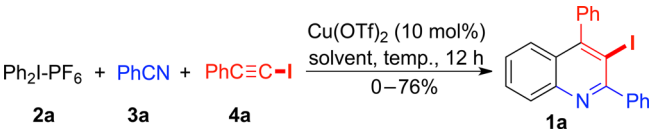
Literature reviews have shown that a few methods have been specifically developed for the synthesis of 3-iodoquinolines **1**.[11] Although they have different advantages, they all went through the linear synthesis strategy and the iodine atom was introduced into the target product in the last step. Due to this, a multi-step synthesis was required for each target product. Clearly, a multi-component, one-pot synthesis strategy is one of the best ways to solve this problem.

In 2009, 1-iodoalkyne **4** was first used for the synthesis of 5-iodo-1,2,3-triazoles.[12] In this method, the cycloaddition of the triple bond was accompanied by a highly regioselective introduction of an iodine atom on the 1,2,3-triazole ring.[13] However, 1-iodoalkyne **4** was rarely applied in the synthesis of the other heterocycles during the past years.[14,15] This phenomenon may arise from two reasons: (i) 1-iodoalkyne **4** structurally is an internal alkyne, but its behavior is more like that of a terminal alkyne in copper-catalyzed cycloadditions. It can be used as an alternative for a terminal alkyne but not for an internal alkyne; (ii) 1-iodoalkyne **4** usually goes through a copper-catalyzed and ligand-mediated mechanism.[12,13c,d] No reaction or inefficient reaction was observed under copper-free,[15] ligand-free[16] or non-copper catalytic conditions.[17] Therefore, we hypothesized that the terminal alkyne in copper-catalyzed cycloadditions can be replaced by 1-iodoalkyne **4** to directly generate iodo-substituted cycloadducts. This hypothesis has been supported by our recent two works.[13a,14a]

Based on the above analyses, the synthetic methods for quinolines were investigated. We interestingly found that many methods have been reported to synthesize 3*H*-quinolines by using terminal alkynes as substrates, but only a few were catalyzed by copper catalysts.[18] Among them, the method reported by Chen et al. in 2013[18b] attracted our attention for its readily accessible substrates and three-component, one-pot procedure. Thus, following Chen's procedure, the mixture of diphenyliodonium hexafluorophosphate (**2a**), benzonitrile (**3a**), and 1-iodo-2-phenylethyne (**4a**) in $ClCH_2CH_2Cl$ was heated at 120 °C for 12 h in the presence of $Cu(OTf)_2$. As shown in Table 1, the desired product **1a** was obtained in 64% yield (entry 1). However, **1a** was obtained in 76% yield when the same reaction was run at 100 °C (entry 2). These results may stem from the fact that 1-iodoalkyne has lower thermal stability and higher reactivity than the corresponding terminal alkyne. But the yield of **1a** was reduced significantly when the reaction was run at 90 °C (entry 3). It was essential that the reaction needed to be protected by a nitrogen atmosphere (entry 4). The results in entries 5–9 indicated that $ClCH_2CH_2Cl$ was the best solvent for the reaction.

As shown in Table 2, the anions in diphenyliodonium and copper salt have significant effects on the re-

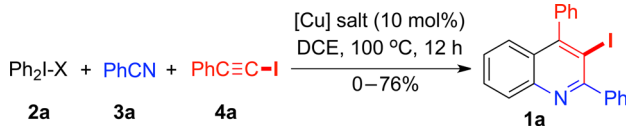
**Table 1.** Effects of the solvents and temperature.[a]




| Entry | Solvent | Temp. [°C] | Reaction under $N_2$ | Yield of **1a** [%][b] |
|---|---|---|---|---|
| 1 | DCE | 120 | yes | 64 |
| 2 | DCE | 100 | yes | 76 |
| 3 | DCE | 90 | yes | 46 |
| 4 | DCE | 100 | no | 45 |
| 5 | toluene | 100 | yes | 61 |
| 6 | dioxane | 100 | yes | 42 |
| 7 | DMSO | 100 | yes | 0 |
| 8 | DMF | 100 | yes | 0 |
| 9 | NMP | 100 | yes | 0 |

[a] The mixture of **2a** (0.5 mmol), **3a** (0.6 mmol), **4a** (0.6 mmol) and $Cu(OTf)_2$ (10 mol%) in solvent (2 mL) was heated for 12 h.
[b] Isolated yields.

**Table 2.** Effects of the anion part of the salts.[a]



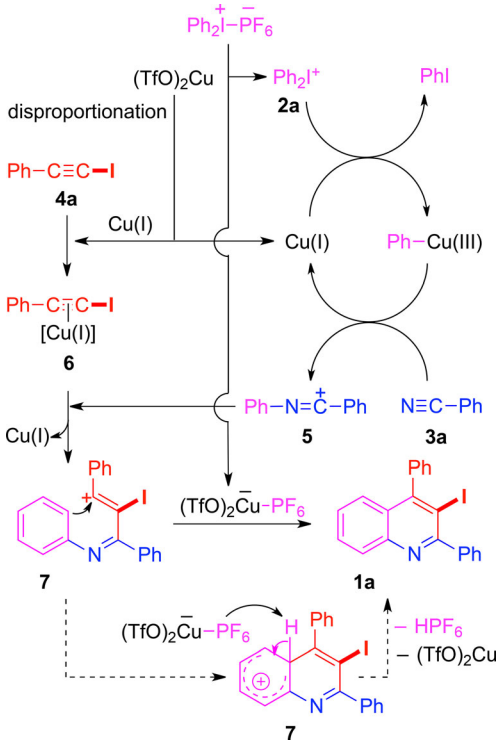

| Entry | $Ph_2I$-X (X=) | [Cu] salt | Yield of **1a** [%][b] |
|---|---|---|---|
| 1 | $PF_6$ (**2a**) | $Cu(OTf)_2$ | 76 |
| 2 | I (**2b**) | $Cu(OTf)_2$ | 50 |
| 3 | OTf (**2c**) | $Cu(OTf)_2$ | 20 |
| 4 | Cl (**2d**) | $Cu(OTf)_2$ | 5 |
| 5 | $PF_6$ (**2a**) | $CuBr_2$ | 55 |
| 6 | $PF_6$ (**2a**) | $CuCl_2$ | 46 |
| 7 | $PF_6$ (**2a**) | CuI | 34 |
| 8 | $PF_6$ (**2a**) | CuBr | 32 |
| 9 | $PF_6$ (**2a**) | CuCN | 30 |
| 10 | $PF_6$ (**2a**) | CuCl | 28 |
| 11 | $PF_6$ (**2a**) | $Cu(acac)_2$ | 5 |
| 12 | $PF_6$ (**2a**) | $Cu(OAc)_2$ | 0 |

[a] The mixture of diphenyliodonium salt **2** (0.5 mmol), **3a** (0.6 mmol), **4a** (0.6 mmol) and [Cu] salt (10 mol%) in DCE (2 mL) was heated for 12 h.
[b] Isolated yield.

action and the anions with the weakest nucleophilicity gave the best results. For example, the results in entries 1–4 indicated that $Ph_2I$-$PF_6$ (**1a**) had the highest reactivity. Similarly, the results in entries 5–12 showed that $Cu(OTf)_2$ had the most catalytic activity.

The ligands were then tested to improve the reaction efficiency, but all attempts failed. For example, $Et_3N$ has been recognized as an excellent ligand for copper-catalyzed cycloadditions of 1-iodoalkyne **4**.[12,13a,d,f] Unfortunately, when $Et_3N$ (20 mol%) was added into the reaction system (in entry 1, Table 2), **1a** was obtained in only 46% yield. When DIPEA, 1,10-phenanthroline, pyridine, 2,2′-dipyridine and triphenylphosphine were used as ligands, complicated mixtures were obtained. These results indicated that certain roles of the copper ions in the reaction may be weakened by those ligands.

In the literature, the mechanisms for copper-catalyzed reactions of diphenyliodoniums and alkynes have been well studied.[18b,19] Although $Cu(OTf)_2$ usually was used as an initial catalyst, Cu(I) and Cu(III) species were hypothesized to be formed *in situ* by the disproportionation of Cu(II) during the reaction and played different roles.[20] Thus, a pathway for our method was proposed and the functions for three different copper ions were assigned. As shown in Scheme 2, Cu(I) may be a dual catalyst to convert **2a** into phenylcopper [PhCu(III)] and to activate **4a** by forming the π-complex **6**. PhCu(III) may function as an equivalent of benzenium ion to attack **3a** to give *N*-phenylnitrilium salt **5**. Cu(II) may play two catalytic roles as both a Lewis acid and a Lewis base. (i) In the first step, $Ph_2I$-$PF_6$ is activated by Lewis acid $(TfO)_2Cu$ to generate $Ph_2I^+$ (**2a**) by forming Lewis base $(TfO)_2Cu^-$-$PF_6$. (ii) In the last step, the electrophilic annulation of the intermediate **7** is catalyzed by Lewis base $(TfO)_2Cu^-$-$PF_6$ to regenerate Lewis acid $(TfO)_2Cu$. Based on the above analyses, we believed that the function of Cu(II) as a Lewis acid may be seriously weakened by addition of a ligand (as a Lewis base). Since the substrate **3a** and the product **1a** may serve as weak ligands, our method proceeded under ligand-free-like conditions rather than real ligand-free conditions.



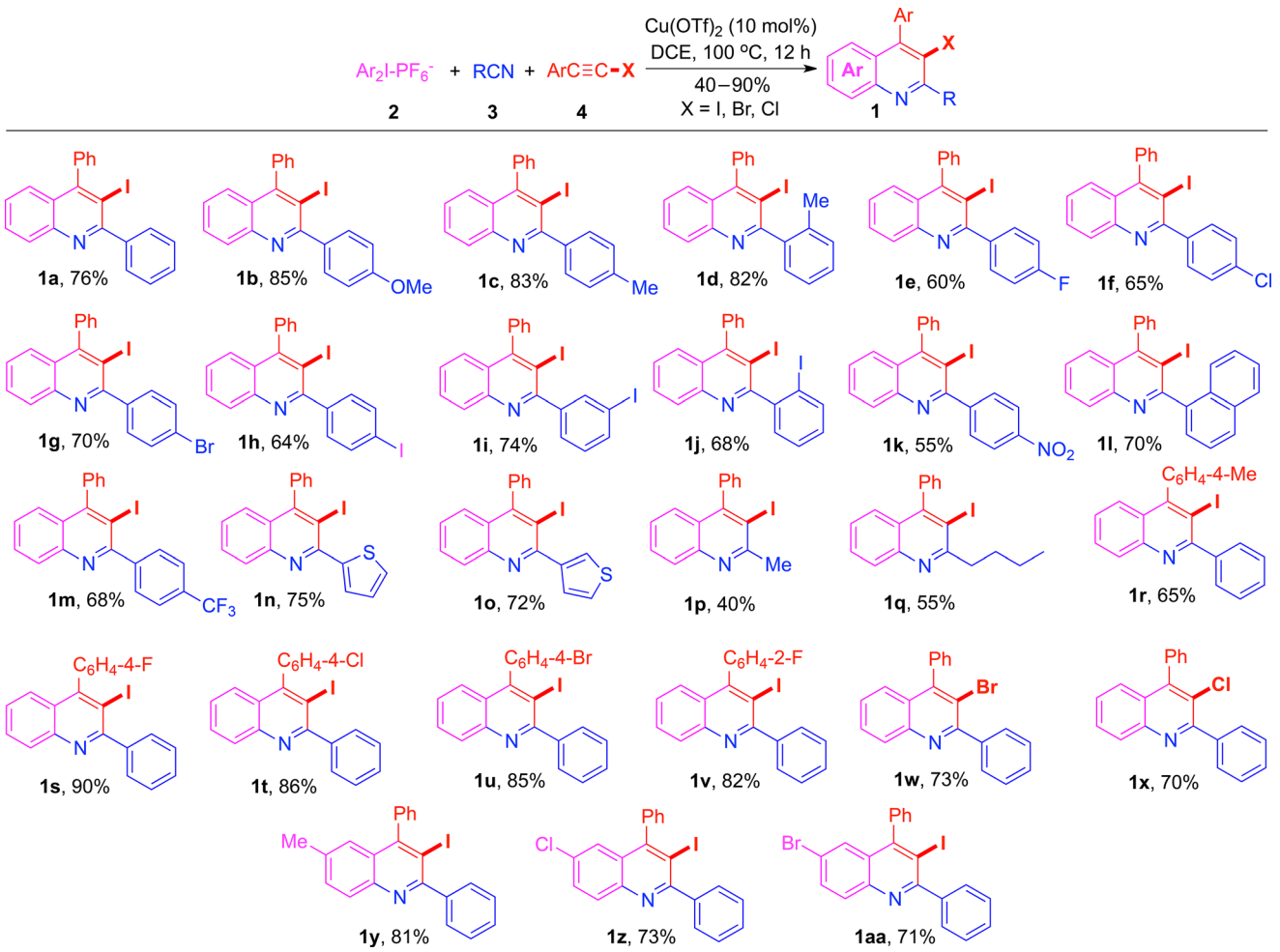

**Scheme 2.** A proposed pathway for the synthesis of **1a**.

Finally, the standard conditions for our method were assigned as shown in Scheme 3 and the scope of the method was examined. To fixed 1-iodo-2-phenylethyne (**4a**), all the tested aryl nitriles gave satisfactory results (**1a–1q**). Substrates with aryl rings substituted by EDGs gave higher yields of products (**1b–1d**) compared to those substituted by EWGs (**1e**, **1k**, **1m**). But, alkyl nitriles gave the desired products (**1p–1q**) in moderate yields, which may be caused by their α-active hydrogens. Thus, $PhCH_2CN$ and $NCCH_2CN$ (with α-active hydrogens) as well as $EtO_2CCN$ and $(OEt)_2(O)PCN$ (with EDGs) were unsuitable substrates for this method. To fixed benzonitrile (**3a**), all tested 1-iodo-2-arylethynes gave satisfactory results (**1r–1v**) and **1s** even was obtained in 90% yield. To our delight, **1w** and **1x** were obtained in 73% and 70% yields, respectively, from the corresponding 1-bromo-2-phenylethyne (PhC≡CBr, **4g**) and 1-chloro-2-phenylethyne (PhC≡CCl, **4h**) under similar conditions. Finally, three substituted diaryliodonium hexafluorophosphates were tested to give the corresponding products **1y**, **1z** and **1aa** in very similar results.

As shown in Figure 3, the structure of product **1u** was confirmed further by a single crystal X-ray diffraction analysis.[21]

## Conclusions

In summary, three items have been disclosed in this article. First, a novel strategy was proposed that the terminal alkyne in copper-catalyzed cycloadditions can be replaced by 1-iodoalkyne to directly generate iodo-substituted cycloadducts. Second, this novel strategy was proved and the reaction conditions were optimized by using the synthesis of 3-iodoquinoline as a model reaction. Finally, a novel method for the synthesis of 3-iodoquinolines was developed by a copper-catalyzed tandem annulation from diaryliodoniums, nitriles, and 1-iodoalkynes, by which a series of structurally novel 3-iodoquinolines was synthesized.




**Scheme 3.** Scope of the method.

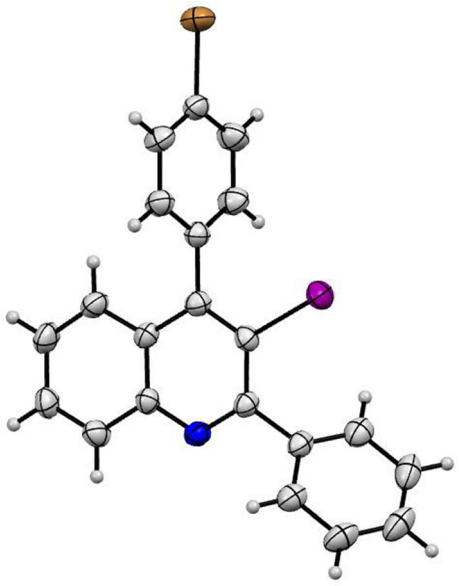


**Figure 3.** The structure of the product **1u**.

## Experimental Section

### General

All melting points were determined on a Yanaco melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Nicolet FT-IR 5DX spectrometer. All $^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded in $CDCl_3$. TMS was used as an internal reference and *J* values are given in Hz. HR-MS were obtained on a Bruker micrOTOF-Q II spectrometer. PE is petroleum ether (60–90 °C).

### Typical Procedure for the Synthesis of 2,4-Diphenyl-3-iodoquinoline (1a)

A suspension of $Ph_2I$-$PF_6$ (**2a**, 213 mg, 0.5 mmol), PhCN (**3a**, 62 mg, 0.6 mmol), PhC≡C–I (**4a**, 137 mg, 0.6 mmol) and $Cu(OTf)_2$ (18 mg, 0.05 mmol) in $ClCH_2CH_2Cl$ (2 mL) in a Schlenk tube was degassed. After the resultant mixture was stirred at 100 °C for 12 h under $N_2$, it was cooled down to room temperature and saturated aqueous $NaHCO_3$ (15 mL) was added. The mixture was stirred for 10 min and

then was extracted by $CH_2Cl_2$ (3×15 mL). The combined organic layers were dried over $Na_2SO_4$. Removal of the solvent gave a residue, which was purified by a column chromatography (silica gel, PE/EtOAc/$Et_3N$=100/5/1) to afford **1a** as white solid; yield: 154.8 mg (76%); mp 118–120 °C (lit.[11b] 118–122 °C). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.16 (d, $J$=8.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.66–7.63 (m, 2H), 7.56–7.43 (m, 6H), 7.42–7.40 (m, 2H), 7.31–7.29 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=161.8, 154.6, 146.8, 143.6, 142.1, 130.0, 129.3, 129.2 (3C), 129.0, 128.6 (2C), 128.5, 128.4, 127.9 (2C), 127.3, 127.2, 126.8, 98.5.

A similar procedure was used for the preparation of products **1b–1x** and **1aa**.

**2-(4-Methoxyphenyl)-4-phenyl-3-iodoquinoline (1b):** White solid; mp 192–194 °C (lit.[11b] 191–195 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.15 (d, $J$=11.4 Hz, 1H), 7.74–7.68 (m, 1H), 7.64 (d, $J$=11.9 Hz, 2H), 7.56–7.51 (m, 3H), 7.38 (d, $J$=5.5 Hz, 2H), 7.30–7.27 (m, 2H), 7.03–6.99 (m, 2H), 3.87 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=161.4, 159.8, 154.6, 146.9, 143.2, 136.2, 130.8 (2C), 130.0, 129.3, 129.1 (2C), 128.6 (2C), 128.4, 127.2, 127.0, 126.8, 113.3 (2C), 98.9, 55.3.

**2-(*p*-Tolyl)-4-phenyl-3-iodoquinoline (1c):** White solid; mp 182–184 °C (lit.[11b] 184–186 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.15 (d, $J$=8.7 Hz, 1H), 7.72–7.68 (m, 1H), 7.56–7.50 (m, 5H), 7.41–7.38 (m, 2H), 7.30–7.27 (m, 4H), 2.43 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=161.8, 154.5, 146.9, 142.1, 140.8, 138.4, 129.9, 129.3, 129.1 (2C), 129.0 (2C), 128.5 (4C), 128.4, 127.2, 127.0, 126.7, 98.7, 21.4.

**2-(*o*-Tolyl)-4-phenyl-3-iodoquinoline (1d):** White solid; mp 142–144 °C (lit.[11b] 140–146 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.17 (d, $J$=8.7 Hz, 1H) 7.74–7.70 (m, 1H), 7.56–7.50 (m, 3H), 7.44–7.41 (m, 2H), 7.34–7.30 (m, 6H), 2.19 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=162.8, 154.1, 146.9, 143.6, 141.6, 135.3, 130.0, 129.9, 129.3, 129.1, 129.0, 128.5 (3C), 128.4, 128.3, 127.2, 127.1, 126.7, 125.7, 99.9, 19.7.

**2-(4-Fluorophenyl)-4-phenyl-3-iodoquinoline (1e):** White solid; mp 174–176 °C; IR: $\nu$=3058, 2929, 1598, 1338 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.14 (d, $J$=8.7 Hz, 1H), 7.74–7.70 (m, 1H), 7.66–7.63 (m, 2H), 7.58–7.52 (m, 3H), 7.41–7.40 (m, 2H), 7.29–7.27(m, 2H), 7.19–7.15 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=162.8 (d, $J$=247.3 Hz), 160.7, 154.8, 146.8, 142.0, 139.6, 131.3 (d, $J$=8.4 Hz, 2C), 130.2, 129.3, 129.0 (2C), 128.6 (2C), 128.5, 127.3 (d, $J$=5.4 Hz, 2C), 126.8, 114.9 (d, $J$=21.4 Hz, 2C), 98.3; HR-MS (ESI-TOF): $m/z$=426.0147, calcd. for $C_{21}H_{14}FIN$ $[M+H]^+$: 426.0149.

**2-(4-Chlorophenyl)-4-phenyl-3-iodoquinoline (1f):** White solid; mp 180–182 °C (lit.[11b] 180–186 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.14 (d, $J$=8.3 Hz, 1H), 7.76–7.72 (m, 1H), 7.62–7.41 (m, 9H), 7.30–7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=160.6, 154.9, 146.8, 142.0, 141.9, 134.6, 130.8 (2C), 130.2, 129.3, 129.0 (2C), 128.6 (2C), 128.5, 128.2 (2C), 127.4, 127.3, 126.9, 98.0.

**2-(4-Bromophenyl)-4-phenyl-3-iodoquinoline (1g):** White solid; mp 200–202 °C (lit.[11b] 201–204 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.14 (d, $J$=8.7 Hz, 1H), 7.76–7.72 (m, 1H,), 7.64–7.53 (m, 7H), 7.43–7.41 (m, 2H), 7.29–7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=160.6, 154.9, 146.9, 142.4, 141.9, 131.1 (2C), 131.0 (2C), 130.2, 129.3, 129.0 (2C), 128.6 (2C), 128.5, 127.5, 127.4, 126.7, 122.9, 97.9.

**2-(4-Iodophenyl)-4-phenyl-3-iodoquinoline (1h):** White solid; mp 192–194 °C; IR: $\nu$=3052, 2929, 1583, 1382 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.14 (d, $J$=8.2 Hz, 1H), 7.85–7.82 (m, 2H), 7.76–7.71 (m, 1H), 7.59–7.53 (m, 3H), 7.43–7.41 (m, 4H), 7.29–7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=160.7, 154.9, 146.9, 143.0, 141.9, 137.1 (2C), 131.2 (2C), 130.2, 129.3, 129.0 (2C), 128.6 (2C), 128.5, 127.5, 127.4, 126.7, 97.8, 94.8; HR-MS (ESI-TOF): $m/z$=533.9208, calcd. for $C_{21}H_{14}I_2N$ $[M+H]^+$: 533.9210.

**2-(3-Iodophenyl)-4-phenyl-3-iodoquinoline (1i):** White solid; mp 140–142 °C; IR: $\nu$=3053, 2946, 1557, 1476, 1333 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.15 (d, $J$=8.7 Hz, 1H), 8.00 (t, $J$=1.4 Hz, 1H), 7.80–7.72 (m, 2H), 7.64–7.52 (m, 4H), 7.43–7.41 (m, 2H), 7.29–7.22 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=160.0, 154.9, 146.7, 145.5, 141.8, 138.0, 137.5, 130.3, 129.5, 129.3, 129.0 (2C), 128.6 (3C), 128.5, 127.5, 127.4, 126.8, 97.8, 93.7; HR-MS (ESI-TOF): $m/z$=533.9207, calcd. for $C_{21}H_{14}I_2N$ $[M+H]^+$: 533.9210.

**2-(2-Iodophenyl)-4-phenyl-3-iodoquinoline (1j):** White solid; mp 142–144 °C; IR: $\nu$=3058, 2945, 1632, 1560, 1532, 1472, 1336 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.18 (d, $J$=8.7 Hz, 1H), 7.95 (d, $J$=7.4 Hz, 1H), 7.77–7.73 (m, 1H), 7.58–7.41 (m, 7H), 7.36–7.34 (m, 1H), 7.30–7.27 (m, 1H), 7.15–7.11 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=163.3, 154.3, 148.2, 146.7, 141.4, 138.8, 130.1, 129.8, 129.4, 129.3, 129.2, 128.9, 128.7, 128.5 (2C), 128.2, 127.6, 127.5, 126.7, 99.2, 97.8; HR-MS (ESI-TOF): $m/z$=533.9206, calcd. for $C_{21}H_{14}I_2N$ $[M+H]^+$: 533.9210.

**2-(4-Nitrophenyl)-4-phenyl-3-iodoquinoline (1k):** White solid; mp 206–208 °C; IR: $\nu$=3066, 2850, 1600, 1511, 1342 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.36 (d, $J$=9.2 Hz, 2H), 8.14 (d, $J$=8.7 Hz, 1H), 7.85 (d, $J$=8.7 Hz, 2H), 7.79–7.75 (m, 1H), 7.60–7.55 (m, 3H), 7.49–7.43 (m, 2H), 7.30–7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=159.4, 155.2, 149.6, 147.8, 146.8, 141.6, 130.6 (2C), 130.5, 129.4, 129.0 (2C), 128.7 (3C), 127.9, 127.6, 126.9, 123.3 (2C), 96.8; HR-MS (ESI-TOF): $m/z$=453.0092, calcd. for $C_{21}H_{14}IN_2O_2$ $[M+H]^+$: 453.0094.

**2-(Naphthalene-1-yl)-4-phenyl-3-iodoquinoline (1l):** White solid; mp 160–162 °C; IR: $\nu$=3054, 2946, 1640, 1556, 1381 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.19 (d, $J$=8.7 Hz, 1H), 7.97–7.92 (m, 2H), 7.79–7.75 (m, 1H), 7.63–7.47 (m, 9H), 7.44–7.32 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=161.8, 154.3, 147.0, 141.6, 141.5, 133.5, 131.2, 130.1, 129.5, 129.2, 129.0, 128.7, 128.6 (2C), 128.5, 128.3, 127.4, 127.3, 126.8, 126.6, 126.3, 125.9, 125.5, 125.2, 100.4; HR-MS (ESI-TOF): $m/z$=458.0401, calcd. for $C_{25}H_{17}IN$ $[M+H]^+$: 458.0400.

**2-[4-(Trifluoromethyl)phenyl]-4-phenyl-3-iodoquinoline (1m):** White solid; mp 220–222 °C; IR: $\nu$=3060, 3029, 2924, 1611, 1482 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.14 (d, $J$=8.24 Hz, 1H), 7.79–7.72 (m, 5H), 7.59–7.53 (m, 3H), 7.43 (d, $J$=3.6 Hz, 2H), 7.30–7.28 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$=160.4, 155.0, 147.0, 146.9, 141.7, 130.6 (q, $J$=32.4 Hz),, 130.3, 129.8 (2C), 129.4, 129.0 (2C), 128.7 (2C), 128.6, 127.6, 127.5, 126.9, 125.0 (q, $J$=3.8 Hz, 2C), 124.1 (q, $J$=270.8 Hz), 97.4; HR-MS (ESI-TOF): $m/z$=476.0115, calcd. for $C_{21}H_{14}F_3IN$ $[M+H]^+$: 476.0118.

**2-(Thiophen-2-yl)-4-phenyl-3-iodoquinoline (1n):** White solid; mp 92–94 °C; IR: $\nu$=3064, 2960, 1637, 1559, 1432 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$=8.13 (d, $J$=

8.7 Hz, 1H), 7.89–7.88 (m, 1H), 7.73–7.69 (m, 1H), 7.59–7.50 (m, 4H), 7.40–7.33 (m, 2H), 7.28–7.25 (m, 2H), 7.16–7.13 (m, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 155.3, 154.4, 146.7, 145.2, 142.4, 130.2, 129.9, 129.2, 129.0 (2C), 128.6 (2C), 128.4, 128.0, 127.3, 127.2, 126.8, 126.7, 97.2; HR-MS (ESI-TOF): $m/z$ = 413.9810, calcd. for $C_{19}H_{13}INS$, $[M+H]^+$: 413.9808.

**2-(Thiophen-3-yl)-4-phenyl-3-iodoquinoline (1o):** White solid; mp 116–118 °C; IR: $\nu$ = 3103, 3054, 2950, 1641, 1561, 1439 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.14 (d, $J$ = 8.3 Hz, 1H), 7.76–7.69 (m, 2H), 7.58–7.50 (m, 4H), 7.41–7.37 (m, 3H), 7.28–7.26 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.3, 154.7, 146.8, 144.0, 142.2, 130.0, 129.3, 129.2, 129.0 (2C), 128.6 (2C), 128.4, 127.3, 127.2, 126.8, 126.4, 124.8, 98.4; HR-MS (ESI-TOF): $m/z$ = 413.9811, calcd. for $C_{19}H_{13}INS$ $[M+H]^+$: 413.9808.

**2-Methyl-4-phenyl-3-iodoquinoline (1p):** White solid; mp 126–128 °C; IR: $\nu$ = 3055, 2999, 2923, 1636, 1558, 1368 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.04 (d, $J$ = 8.2 Hz, 1H), 7.71–7.67 (m, 1H), 7.57–7.51 (m, 3H), 7.34–7.32 (m, 2H), 7.22–7.19 (m, 2H), 3.05 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 159.8, 153.7, 146.8, 141.9, 129.8, 129.0 (2C), 128.6 (2C), 128.5, 128.4, 126.8, 126.7, 126.4, 100.4, 31.6; HR-MS (ESI-TOF): $m/z$ = 346.0085, calcd. for $C_{16}H_{13}IN$ $[M+H]^+$: 346.0087.

**2-Butyl-4-phenyl-3-iodoquinoline (1q):** White solid; mp 60–62 °C; IR: $\nu$ = 3058, 2959, 1637, 1553, 1378 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.06 (d, $J$ = 8.7 Hz, 1H), 7.70–7.65 (m, 1H), 7.57–7.51 (m, 3H), 7.32–7.31 (m, 2H), 7.22–7.19 (m, 2H), 3.30–3.22 (m, 2H), 1.89–1.82 (m, 2H), 1.59–1.49 (m, 2H), 1.01 (t, $J$ = 7.3, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 162.8, 153.9, 146.9, 142.2, 129.7, 129.0 (2C), 128.6, 128.5 (2C), 128.3, 126.9, 126.8, 126.4, 100.2, 43.0, 31.3, 22.8, 14.0; HR-MS (ESI-TOF): $m/z$ = 388.0554, calcd. for $C_{19}H_{19}IN$ $[M+H]^+$: 388.0557.

**2-Phenyl-4-(*p*-tolyl)-3-iodoquinoline (1r):** White solid; mp 150–152 °C (lit.[11b] 150–153 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16 (d, $J$ = 8.2 Hz, 1H), 7.73–7.69 (m, 1H), 7.65–7.63 (m, 2H), 7.51–7.36 (m, 7H), 7.18 (d, $J$ = 7.8 Hz, 2H), 2.48 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.8, 154.8, 146.8, 143.7, 139.1, 138.3, 130.0, 129.3, 129.3 (2C), 129.2 (2C), 128.9 (2C), 128.5, 127.9 (2C), 127.4, 127.1, 126.9, 98.8, 21.5.

**2-Phenyl-4-(4-fluorophenyl)-3-iodoquinoline (1s):** White solid; mp 178–180 °C; IR: $\nu$ = 3056, 2929, 1649, 1598, 1378 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16 (d, $J$ = 8.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.65–7.62 (m, 2H), 7.52–7.39 (m, 5H), 7.28–7.24 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 162.7 (d, $J$ = 247.0 Hz), 161.9, 153.6, 146.7, 143.6, 137.9, 131.0 (d, $J$ = 7.6 Hz, 2C), 130.1, 129.5, 129.2 (2C), 128.6, 127.9 (2C), 127.4 (2C), 126.5, 115.8 (d, $J$ = 21.9 Hz, 2C), 98.8. HR-MS (ESI-TOF): $m/z$ = 426.0145, calcd. for $C_{21}H_{14}FIN$ $[M+H]^+$: 426.0149.

**2-Phenyl-4-(4-chlorophenyl)-3-iodoquinoline (1t):** White solid; mp 192–194 °C; IR: $\nu$ = 3072, 2952, 1558, 1381 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16 (d, $J$ = 8.3 Hz, 1H), 7.75–7.71 (m, 1H), 7.65–7.63 (m, 2H), 7.56–7.37 (m, 7H), 7.24 (d, $J$ = 8.3 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.8, 153.4, 146.8, 143.5, 140.3, 134.6, 130.6 (2C), 130.2, 129.5, 129.2 (2C), 129.0 (2C), 128.6, 128.0 (2C), 127.4, 127.1, 126.4, 98.4; HR-MS (ESI-TOF): $m/z$ = 441.9861, calcd for $C_{21}H_{14}ClIN$ $[M+H]^+$: 441.9854.

**2-Phenyl-4-(4-bromophenyl)-3-iodoquinoline (1u):** White solid; mp 212–214 °C (lit.[11b] 212–214 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.16 (d, $J$ = 8.3 Hz, 1H), 7.76–7.69 (m, 3H), 7.64–7.61 (m, 2H), 7.51–7.37 (m, 5H), 7.20–7.17 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.8, 153.4, 146.8, 143.5, 140.8, 131.9 (2C), 130.8 (2C), 130.2, 129.5, 129.2 (2C), 128.6, 128.0 (2C), 127.5, 127.0, 126.4, 122.8, 98.3.

**2-Phenyl-4-(2-fluorophenyl)-3-iodoquinoline (1v):** White solid; mp 106–108 °C; IR: $\nu$ = 3060, 2929, 1617, 1567, 1378 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.19 (d, $J$ = 8.3 Hz, 1H), 7.75 (t, $J$ = 8.2 Hz, 1H), 7.68–7.66 (m, 2H), 7.56–7.34 (m, 7H), 7.30–7.26 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 161.8, 159.0 (d, $J$ = 246.0 Hz), 149.4, 146.8, 143.4, 131.1 (d, $J$ = 2.9 Hz), 130.9 (d, $J$ = 7.6 Hz), 130.2, 129.6, 129.4, 129.2 (2C), 128.6, 128.0 (2C), 127.6, 127.2, 126.1, 124.5 (d, $J$ = 2.9 Hz), 116.2 (d, $J$ = 21.0 Hz), 99.0; HR-MS (ESI-TOF): $m/z$ = 426.0146, calcd. for $C_{21}H_{14}FIN$ $[M+H]^+$: 426.0149.

**2,4-Diphenyl-3-bromoquinoline (1w):**[11j] White solid; mp 92–94 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.18 (d, $J$ = 8.7 Hz, 1H), 7.75–7.71 (m, 3H), 7.59–7.46 (m, 6H), 7.44 (m, 2H), 7.37–7.35 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 158.9, 149.6, 146.4, 140.9, 138.0, 129.8, 129.6, 129.4 (2C), 129.2 (2C), 128.7, 128.5 (2C), 128.4, 128.0 (2C), 127.9, 127.3, 126.4, 118.5.

**2,4-Diphenyl-3-chloroquinoline (1x):**[11j] White solid; mp 106–108 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.18 (d, $J$ = 8.2 Hz, 1H), 7.82–7.79 (m, 2H), 7.72–7.68 (m, 1H), 7.58–7.43 (m, 8H), 7.40–7.38 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 157.5, 146.9, 146.1, 139.4, 135.8, 129.7, 129.6, 129.5 (2C), 129.4 (2C), 128.8, 128.5 (2C), 128.4, 128.1 (2C), 127.7, 127.2, 126.4, 126.1.

**2,4-Diphenyl-6-methyl-3-iodoquinoline (1y):**[11j] White solid; mp 152–156 °C; $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.05 (d, $J$ = 8.72 Hz, 1H), 7.64–7.61 (m, 2H), 7.58–7.51 (m, 4H), 7.50–7.41 (m, 3H), 7.29–7.26 (m, 2H), 7.14 (s, 1H), 2.40 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 160.8, 153.8, 145.4, 143.7, 142.3, 137.3, 132.3, 129.2 (3C), 129.1 (2C), 128.6 (2C), 128.4, 128.3, 127.9 (2C), 127.3, 125.5, 98.6, 21.7.

**2,4-Diphenyl-6-chloro-3-iodoquinoline (1z):** White solid; mp 172–174 °C (lit.[11b] 169–174 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.09 (d, $J$ = 8.72 Hz, 1H), 7.67–7.62 (m, 3H), 7.59–7.54 (m, 3H), 7.52–7.46 (m, 3H), 7.37 (d, $J$ = 2.28 Hz, 1H), 7.29–7.26 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 162.1, 153.9, 145.3, 143.3, 141.4, 133.1, 131.0 (2C), 129.1 (2C), 128.9 (2C), 128.8 (2C), 128.7, 128.7, 128.0 (2C), 127.8, 125.5, 99.8.

**2,4-Diphenyl-6-bromo-3-iodoquinoline (1aa):** White solid; mp 184–186 °C (lit.[11b] 146–152 °C); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 8.02 (d, $J$ = 8.72 Hz, 1H), 7.77 (m, 1H), 7.65–7.62 (m, 2H), 7.60–7.54 (m, 4H), 7.51–7.45 (m, 3H), 7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ = 162.3, 153.8, 145.4, 143.3, 141.3, 133.6, 131.1, 129.1 (2C), 128.9 (2C), 128.8 (2C), 128.8 (2C), 128.7, 128.2, 128.0 (2C), 121.4, 99.8.

## Supporting Information

Copies of the $^1$H NMR and $^{13}$C NMR spectra for all compounds and **1a–1z** and **1aa** and the CIF file for the single crystal X-ray diffraction analysis of **1u** are available in the Supporting Information.

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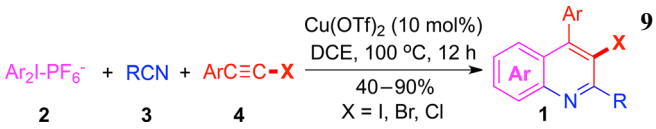
[21] CCDC 1447247 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 3-Iodoquinolines by Copper-Catalyzed Tandem Annulation from Diaryliodoniums, Nitriles, and 1-Iodoalkynes

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