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One-Pot Synthesis of Multisubstituted 2-Aminoquinolines from Annulation of 1-Aryl Tetrazoles with Internal Alkynes via Double C−H Activation and Denitrogenation

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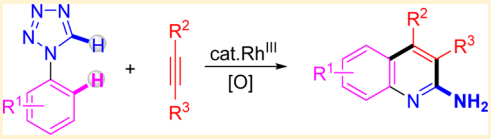
Supporting Information

ABSTRACT: An efficient, one-pot synthesis of multisubstituted 2-aminoquinolines from 1-aryl tetrazoles and internal alkynes has been developed. The reaction involves cyclization of 1-aryl tetrazoles with internal alkynes via rhodium(III)-catalyzed double C−H activation and copper(II)-mediated denitrogenation.



INTRODUCTION

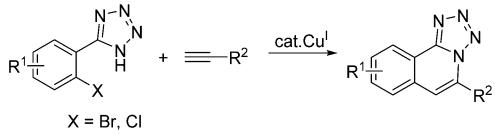
Quinolines are one of the most important classes of nitrogen-containing heterocycles, which are ubiquitous in natural products with biological activities.[1] They have also served as privileged scaffolds in medicinal chemistry.[2] Among them, 2-aminoquinolines are particularly of interest due to their pharmacological properties and have received much attention in drug discovery.[3] For example, C-3-substituted 2-aminoquinoline derivatives can be served as an efficient BACE1 (beta-site amyloid precursor protein cleaving enzyme 1) inhibitor for the remedy of Alzheimer's disease.[4] Nowadays, the most common approach to 2-aminoquinolines is based on the direct amination of 2-chloroquinoline through aromatic nucleophilic substitution.[5] However, this method needs preactivated substrates and the use of strong bases, which limit its scope. Therefore, methods for modular assembly of multisubstituted 2-aminoquinolines from readily available substrates are still needed to be developed.

Transition-metal-catalyzed C−H bond activation and functionalization has contributed greatly to the synthesis of heterocycles.[6] In particular, rhodium-catalyzed C−H activation has emerged as a versatile tool in generating diverse heterocyclic compounds through intermolecular cyclization with alkynes, and among these works, heteroatom-containing groups are widely used as directing groups for the C−H bond cleavage and functionalization at their ortho position.[7] More recently, the direct C−H activation without the coordination assistance coming from the directing group has received much attention in the construction of various heterocycles through dehydrogenation and cyclization with internal alkynes.[8] For example, Miura[8b,f] and Chen[8c,d] have developed Cp*Rh(III)-catalyzed aza-fused polycyclic quinolines syntheses via double C−H activation; however, the aza-fused rings cannot undergo further transformation.

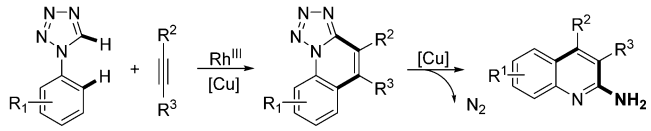
Tetrazoles are multinitrogen-containing compounds which are widely used in synthetic organic chemistry.[9−11] For example, they can be served as a nitrogen source through denitrogenation process[10] and directing groups for chelating-assisted C−H activation.[11] However, the tetrazole moiety for C−H activation is only used as directing group without further transformation. Thus, we are specifically interested in integrating the tetrazole group involved in C−H activation with its further transformation. Recently, Fu and co-workers[12] reported copper-catalyzed cyclization reaction for the synthesis of tetrazoloisoquinolines using substituted 5-(2-halophenyl)-1*H*-tetrazoles and terminal alkynes through carbon−halogen and nitrogen−hydrogen bond activation but also with halogenous waste generation (Scheme 1a).

Scheme 1. Synthesis of Nitrogen-Containing Heterocycle via Tetrazole and Alkyne

a) Fu, et al.: Copper-catalyzed domino synthesis of tetrazoloisoquinolines



b) This work: Rhodium-catalyzed double C-H activation, alkyne annulation, and denitrogenation for the synthesis of 2-aminoquinolines in one-pot



Inspired by these above attractive works and our continuing efforts in Rh-catalyzed C−H activation and alkyne annulation,[13] we envisioned that 1-aryl tetrazoles could couple with internal alkynes via rhodium-catalyzed C−H activation to prepare multisubstituted tetrazolo[1,5-*a*]quinolines or 2-aminoquinolins. To our delight, 1-phenyl-*1H*-tetrazole reacted with 1,2-diphenylacetylene smoothly and afforded 3,4-diphenyl-2-

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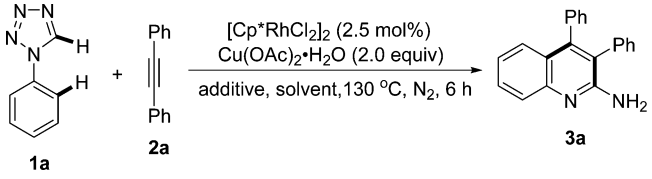
aminoquinolin as a sole product. Herein, we wish to report this efficient rhodium-catalyzed double C−H bond activation for the synthesis of substituted aminoquinolines via the process of denitrogenation (Scheme 1b).

RESULTS AND DISCUSSION

We initiated our investigation by employing 1-phenyl-1*H*-tetrazole (**1a**, 0.5 mmol) and 1,2-diphenylacetylene (**2a**, 0.2 mmol) as model substrates in the presence of 2.5 mol % of $[Cp^*RhCl_2]_2$, $Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv, 0.4 mmol) in 1,2-dichloroethane (DCE) at 130 °C for 6 h. Unfortunately, no product was detected (Table 1, entry 1). A variety of solvents

Table 1. Optimization of the Reaction Conditions[a]



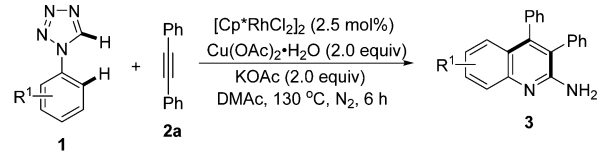
entry	additive (equiv)	solvent	yield (%)[b]
1	—	DCE	NR
2	—	dioxane	NR
3	—	THF	NR
4	—	CH_3CN	NR
5	—	DMSO	NR
6	—	toluene	NR
7	—	CH_3OH	trace
8	—	*o*-xylene	21
9	—	DMF	43
10	—	DMAc	55
11	KOAc (2.0)	DMAc	68
12	NaOAc (2.0)	DMAc	60
13	K_2CO_3 (2.0)	DMAc	37
14	Na_2CO_3 (2.0)	DMAc	29
15	AgOAc (2.0)	DMAc	trace
16	HOAc (2.0)	DMAc	trace
17	PivOH (2.0)	DMAc	trace
18	KOAc (3.0)	DMAc	67
19	KOAc (1.0)	DMAc	59
20[c]	KOAc (2.0)	DMAc	trace
21[d]	KOAc (2.0)	DMAc	69

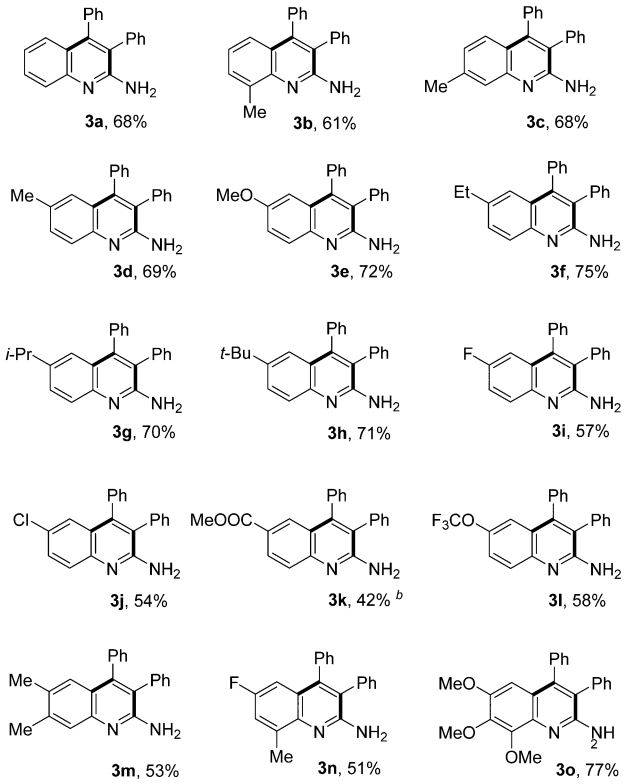
[a]Unless otherwise noted, reactions were carried out using **1a** (0.50 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol), additive (0.4 mmol) in 1.0 mL of DMAc at 130 °C under N_2 in a sealed tube for 6 h. [b]Isolated yields based on the amount of **2a** used. [c]At 100 °C. [d]At 150 °C.

were then examined, and the significant solvent effects were observed. No desired product **3a** was formed when the reaction was performed in dioxane, THF, CH_3CN, DMSO, toluene (Table 1, entries 2−6). CH_3OH was found to be ineffective for this reaction (Table 1, entry 7). By using *o*-xylene, DMF, or DMAc as solvents, **3a** was formed in moderate yield (Table 1, entries 8−10). For further optimization of the reaction system, various additives were also screened. Improved yield (68%) was obtained by using KOAc as additive (Table 1, entry 11). Other bases, such as NaOAc, K_2CO_3, and Na_2CO_3 were less effective and afforded inferior yields of **3a** (Table 1, entries 12−14). AgOAc and acids restrained the reaction and only a trace of the product was detected (Table 1, entries 15−17). The yield could not be improved by further variation of the amount of KOAc and reaction temperature (Table 1, entries 18−21).

Under the optimized reaction condition (indicated in entry 11 of Table 1), we next examined the scope of the reaction. As shown in Table 2, 1-aryl-1*H*-tetrazoles (**1**) with various

Table 2. Substrate Scope of Aryltetrazoles[a]





[a]Unless otherwise noted, reactions were carried out using **1** (0.50 mmol), **2a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol), and KOAc (0.4 mmol) in 1.0 mL of DMAc at 130 °C under N_2 in a sealed tube for 6 h. [b]For 8 h.

substitutes were employed to react with 1,2-diphenylacetylene (**2a**). No significant steric effect was observed by using 1-aryl-1*H*-tetrazoles with ortho-, meta-, or para-methyl on the phenyl ring as substrates, and corresponding products **3b**, **3c**, and **3d** were obtained in similar yields. 1-Aryl-1*H*-tetrazoles with electron-donating groups on the para-position of the phenyl ring showed higher reactivity than those with electron-withdrawing groups. Specifically, 1-aryl-1*H*-tetrazoles with electron-donating groups, such as Me, OMe, Et, *i*-Pr, and *t*-Bu on the para position of the phenyl ring reacted smoothly with 1,2-diphenylacetylene (**2a**) to afford corresponding products **3e**−**3h** in improved yields (70−75%). Meanwhile, 1-aryl-1*H*-tetrazoles with an electron-withdrawing group, such as F, Cl, CO_2Me, and CF_3O on the para position of the phenyl ring gave corresponding products **3i**−**3l** in declined yields (42−58%). It should be noted that multisubstituted 1-aryl-1*H*-

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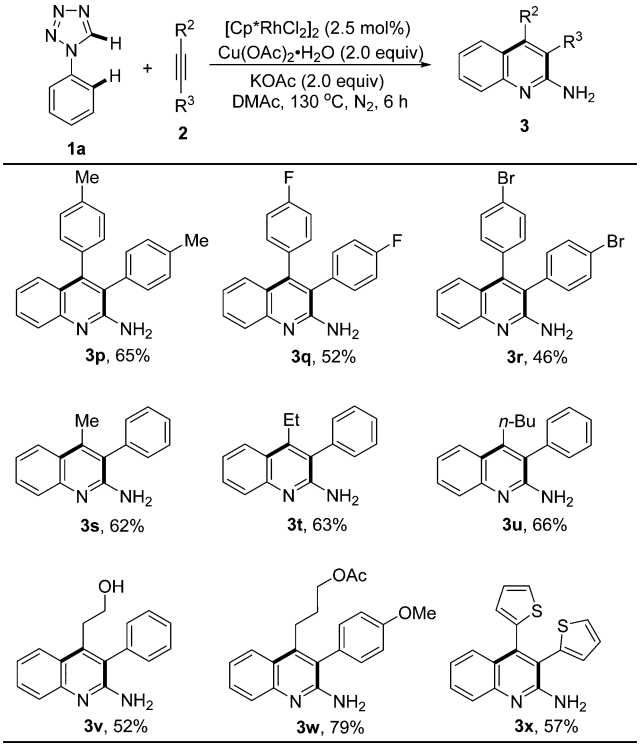
tetrazoles also reacted smoothly with **2a**, giving the corresponding products **3m**–**3o**.

To test the applicability of our reaction, we also employed various substituted alkynes under the standard reaction conditions (Table 3). The substitution effect in the alkynes

Table 3. Substrate Scope of Alkynes[a]

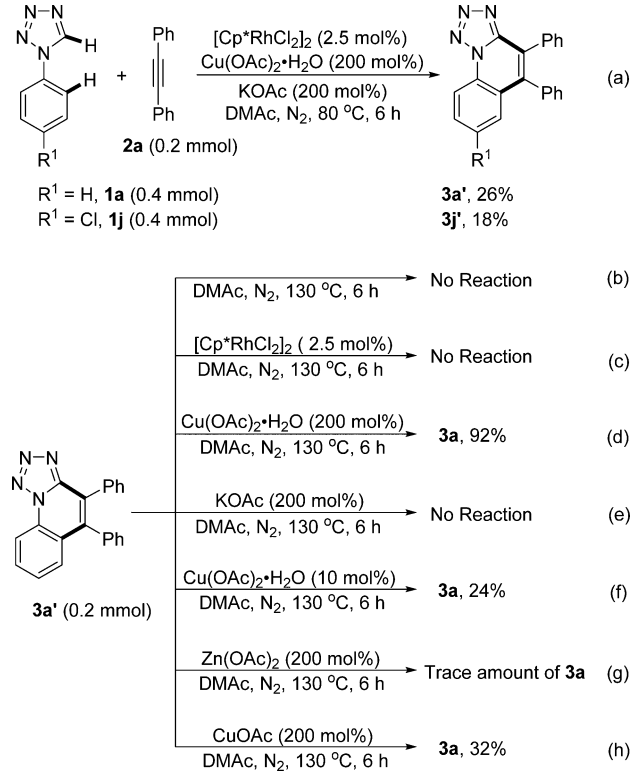


[a]Unless otherwise noted, reactions were carried out using **1a** (0.50 mmol), **2** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.4 mmol), and KOAc (0.4 mmol) in 1.0 mL of DMAc at 130 °C under N_2 in a sealed tube for 6 h.

moiety also exists. Symmetrical diarylacetylenes containing electron-donating group (Me) on the para position of the phenyl ring reacted smoothly to afford the corresponding product **3p** in 65% yield, while diphenylacetylenes containing electron-withdrawing groups (F and Br) gave corresponding products **3q** and **3r** in declined yields. For asymmetrically substituted alkynes, the desired products **3s**–**3w** were obtained with high regioselectivity. The structure of **3s** was unambiguously identified by single-crystal X-ray diffraction (see the Supporting Information). Notably, alkyne with a free hydroxyl group was also applicable for the reaction to afford the desired product **3v** in 52% yield. When 1-(5-chloropent-1-yn-1-yl)-4-methoxybenzene was used, the chlorine group was substituted by the acetate group in situ in the reaction system and afforded **3w** with complete regioselectivity in 79% yield. Di(2-thienyl)-acetylene also react smoothly to afford **3x** in 57% yield.

In the process of experimental condition optimization, 1-phenyl-1*H*-tetrazole reacted with 1,2-diphenylacetylene generated another single product 4,5-diphenyltetrazolo[1,5-*a*]-quinoline (**3a′**) in very low yield when the reaction temperature was decreased to 80 °C (Scheme 2a). The structure of **3j′** (a similar structure of **3a′**) was identified by single-crystal X-ray diffraction (see the Supporting Information). These results implied that the temperature was vital for the denitrogenative transannulation of the tetrazolo group. In addition, 4,5-

Scheme 2. Control Experiments

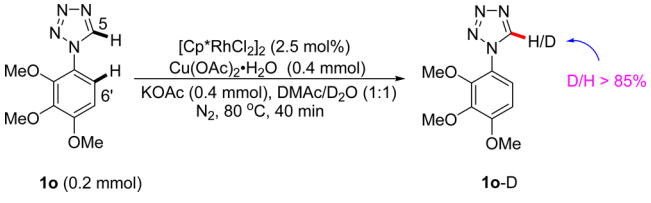


diphenyltetrazolo[1,5-*a*]quinoline (**3a′**) could be converted into 3,4-diphenyl-2-aminoquinolin (**3a**) with 92% yield in the presence of $Cu(OAc)_2{\cdot}H_2O$ (Scheme 2d), while other conditions were proved to be invalid (Scheme 2, panels b, c, and e). These results suggested that $Cu(OAc)_2$ is involved in the denitrogenative transannulation.

In addition, as shown in Scheme 2, we repeated the denitrogenation reaction of **3a′** in the presence of $Cu(OAc)_2$ (10 mol %) (f), $Zn(OAc)_2$ (2.0 equiv) (g), or CuOAc (2.0 equiv) (h) to further understand the role of $Cu(OAc)_2$. It was found that the use of catalytic amount of $Cu(OAc)_2$ resulted in low yield of **3a** (24%), $Zn(OAc)_2$ showed no catalytic activity, and the use of CuOAc gave **3a** in low yield (32%). These results indicate that the oxidative capability of $Cu(OAc)_2$ may be more relevant than its property as a Lewis acid to prompt the denitrogenation of **3a′**.

To further probe the reaction mechanism, we continued our investigation by using 1-(2,3,4-trimethoxyphenyl)-1*H*-tetrazole (**1o**) for the H/D exchange experiment, which was carried out in the mixture of DMAc/D_2O (1:1, 1.0 mL) at 80 °C under a N_2 atmosphere for 40 min (Scheme 3). A significant D/H exchange (>85%) at C(5) position indicated that the Rh(III) insertion process occurred initially and a reversible C–H bond rhodium process may be incorporated.

Scheme 3. Rhodium-Catalyzed H/D Exchange in DMA/D_2O



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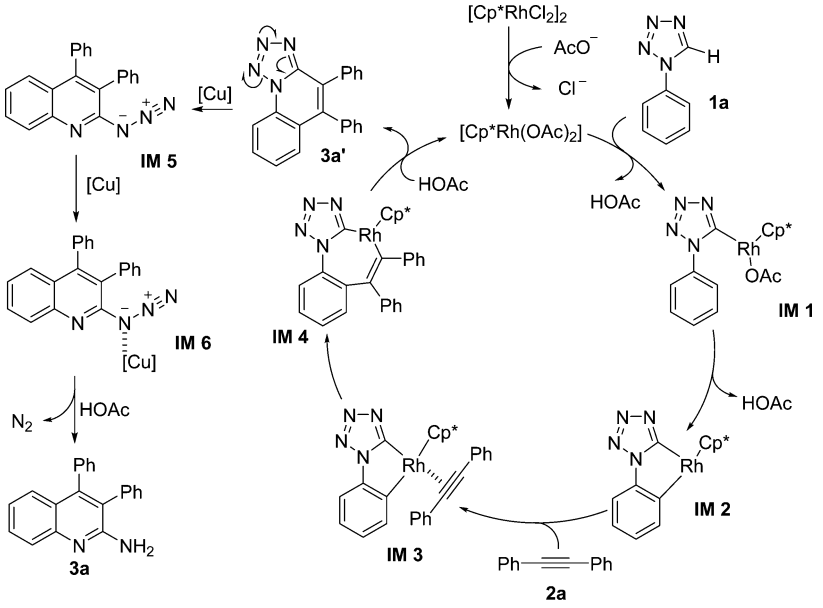
Scheme 4. Proposed Reaction Mechanism



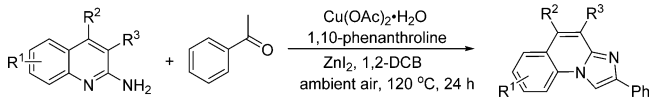
On the basis of the above experiment results and known rhodium-catalyzed C−H bond activation,[8,9] a plausible reaction mechanism is shown in Scheme 4. First, C(5)−H of 1-phenyl-*1H*-tetrazole undergoes reversible C−H activation and Rh(III) insertion to afford intermediate **IM 1**; the following C−H activation occurs on the ortho position of tetrazole to afford the five-membered ring rhodacycle intermediate **IM 2**. Diphenylacetylene coordinates to Rh(III) to form intermediate **IM 3**. Subsequently, Alkyne insertion of **IM 3** affords a seven-membered ring rhodacycle intermediate **IM4**. The reduction elimination of **IM 4** gives the isolated intermediate **3a′** and regenerated the rhodium catalyst. After that, the tautomerization of **3a′** occurs to give **IM 5** in the presence of copper salt. Finally, the reduction of **IM 6** affords the final product **3a** through denitrogenative transannulation[10] in the presence of copper from intermediate **IM 5**.

On the basis of the proposed mechanism, it is found that when the use of aryl-tetrazoles having an electron-rich group may form a more stable five-membered rhodacycle intermediate (**IM 2**), the use of diarylacetylenes bearing electron-donating group in phenyl ring should lead to the easier formation of alkyne-coordinated intermediate (**IM 3**). Therefore, we can understand the reason why in most cases, the use of aryl-tetrazoles or diarylacetylenes bearing electron-donating group(s) resulted in the formation of **3** in relatively higher yields as concluded in Tables 2 and 3.

Moreover, the further transformation of the 2-aminoquinolines into imidazo[1,2-*a*]quinolines was conducted (Scheme 5). By following Hajra's conditions[14] with slight modification, imidazo[1,2-*a*]quinolines (**4a**, **4c**, **4e**, **4h**, **4p**, and **4t**) were obtained by copper-catalyzed tandem oxidative cyclization of **3** in 52−72% yields.

In summary, we have developed a one-pot synthesis of multisubstituted 2-aminoquinolines by the cyclization of 1-aryl tetrazoles with internal alkynes through rhodium(III)-catalyzed double C−H bond activation and Cu(II)-mediated denitrogenation in moderate to good yields. Further applications and transformations of tetrazoles through Rh(III)-catalyzed C−H activation are in progress in our lab.

Scheme 5. Derivatization of 2-Aminoquinolines[a]



3 4

R^1 = H, R^2 = Ph, R^3 = Ph, **4a** (52%)
R^1 = 8-Me, R^2 = Ph, R^3 = Ph, **4c** (63%)
R^1 = 7-OMe, R^2 = Ph, R^3 = Ph, **4e** (58%)
R^1 = 7-Bu^t, R^2 = Ph, R^3 = Ph, **4h** (60%)
R^1 = H, R^2 = R^3 = 4-Me-C_6H_4, **4p** (77%)
R^1 = H, R^2 = Et, R^3 = Ph, **4t** (72%)

[a]Reaction conditions: substituted aminouquinolines (**3** 0.3 mmol), acetophenone (0.2 mmol). $Cu(OAc)_2·H_2O$ (10%), 1, 10-phenanthroline (20%), ZnI_2 (20%), 1,2-DCB (1.0 mL), air, 120 °C, 24 h, isolated yields.

EXPERIMENTAL SECTION

General Methods. All organic starting materials are analytically pure and used without further purification. All reactions were carried out without any particular precautions to extrude moisture or oxygen. Nuclear magnetic resonance (NMR) spectra were recorded using $CDCl_3$ as solvent at 298 K. ^{1}H NMR (400 MHz) chemical shifts (δ) were referenced to internal standard TMS (for ^{1}H, δ = 0.00 ppm). ^{13}C NMR (100 MHz) chemical shifts were referenced to internal solvent $CDCl_3$ (for ^{13}C, δ = 77.16 ppm). HRMS spectra were obtained on a high-resolution magnetic sector mass spectrometer with an electron spray ionization (ESI) source. The melting points are uncorrected. Rhodium catalyst $[Cp^*RhCl_2]^2$ was prepared following a literature procedure.[15] 1,2-Bis(4-methylphenyl)ethyne, 1,2-bis(4-fluorophenyl)-ethyne, 1,2-bis(4-bromophenyl)ethyne, and 1,2-di(thiophen-2-yl)-ethyne were prepared following a literature procedure[16] with our improvement.[13a] 4-Phenylbut-3-yn-1-ol and 1-(5-chloropent-1-yn-1-yl)-4-methoxybenzene were prepared following a literature procedure,[17] and 1-aryl tetrazoles were prepared according to the literature procedure.[10a]

Typical Procedure for the Synthesis of Substituted Quinoline. 1-Aryltetrazole (**1**, 0.5 mmol), internal alkyne (**2**, 0.2 mmol), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), $Cu(OAc)_2·H_2O$ (80 mg, 0.4 mmol), KOAc (39.3 mg, 0.4 mmol) were added to a thick-walled screw-capped Pyrex tube equipped with a magnetic stirrer. DMAc (1.0 mL) was added sequentially under N_2 atmosphere. Then the tube was sealed and stirred at 130 °C for 6 h. After the reaction was completed, it was cooled to room temperature and extracted with ethyl acetate for 3 times. The organic phase was dried over $MgSO_4$, filtered, and

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concentrated under reduced pressure, further purification by flash column chromatography on silica gel with petroleum ether/ethyl acetate/triethylamine (3:1:0.05−1:1:0.05) to provide the corresponding product (**3**).

Rhodium-Catalyzed H/D Exchange in DMAc/D_2O. $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol), 1-(2,3,4-trimethoxyphenyl)-1H-tetrazole (**1o**, 0.2 mmol), $Cu(OAc)_2{\cdot}H_2O$ (80 mg, 0.4 mmol), KOAc (39.4 mg, 0.4 mmol) were added to a thick-walled screw-called Pyrex tube equipped with a magnetic stirrer. DMAc (0.5 mL) and D_2O (0.50 mL) were added sequentially under a N_2 atmosphere. The reaction was performed at 80 °C in an oil bath for 40 min. Then it was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure, and further purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) to aford the product **1o**-D. The deuterium incorporation was estimated by ^1H NMR spectroscopy (see the Supporting Information).

Characterization Data. *4,5-Diphenyltetrazolo[1,5-a]quinoline (**3a′**).* White solid (16.7 mg, 26%), mp 246−248 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (1H, d, J = 8.0 Hz), 7.78−7.74 (1H, m), 7.61−7.59 (1H, m), 7.53−7.49 (1H, m), 7.31−7.24 (5H, m), 7.21−7.13 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 142.2, 135.1, 133.3, 130.6 (overlapped), 129.9, 128.6, 128.7, 128.4, 128.3, 128.2, 128.0, 127.8, 125.2, 125.0, 116.6; IR (KBr, cm^{-1}): 3080, 3056, 2926, 2853, 1592, 1554, 1517, 1491, 1441, 1091, 773, 755, 704; HRMS (ESI) calcd for $C_{21}H_{15}N_4$ ([M + H]$^+$): 323.1291. Found: 323.1294.

*3,4-Diphenylquinolin-2-amine (**3a**).* White solid (40.1 mg, 68%), mp 241−243 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, d, J = 8.4 Hz), 7.56−7.52 (1H, m), 7.34 (1H, d, J = 8.0 Hz), 7.25−7.10 (11H, m), 4.93 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 147.7, 147.2, 136.7, 136.1, 130.3, 130.0, 129.4, 128.6, 127.7, 127.5, 127.2, 126.7, 125.8, 123.7, 123.3, 122.4. IR (KBr, cm^{-1}): 3481, 3281, 3121, 2924, 2851, 2742, 1634, 1608, 1565, 1490, 1464, 1442, 1249, 762, 704; HRMS (ESI) calcd for $C_{21}H_{17}N_2$ ([M + H]$^+$): 297.1386. Found: 297.1386.

*8-Methyl-3,4-diphenylquinolin-2-amine (**3b**).* White solid (37.9 mg, 61%), mp 161−163 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (1H, d, J = 6.8 Hz), 7.26−7.02 (12H, m), 4.74 (2H, br), 2.72 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 147.9, 146.2, 137.2, 136.4, 133.7, 130.3, 130.0, 129.6, 128.5, 127.6, 127.3, 127.0, 124.7, 123.5, 122.9, 122.0, 18.2. IR (KBr, cm^{-1}): 3477, 3290, 3170, 2915, 1617, 1565, 1467, 1424, 1243, 1071, 1029, 746, 700. HRMS (ESI) calcd for $C_{22}H_{19}N_2$ ([M + H]$^+$): 311.1543. Found: 311.1545.

*7-Methyl-3,4-diphenylquinolin-2-amine (**3c**).* White solid (42.2 mg, 68%), mp 220−222 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (1H, s), 7.23−7.08 (11H, m), 6.97 (1H, J = 8.4 Hz), 4.94 (2H, br), 2.48 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 147.4, 147.3, 139.5, 136.9, 136.2, 130.4, 129.9, 128.5, 127.6, 127.3, 127.0, 126.4, 125.2, 124.4, 122.3, 121.6. 21.7. IR (KBr, cm^{-1}): 3480, 3464, 3285, 3119, 3054, 2921, 1633, 1616, 1563, 1490, 1429, 1240, 869, 749, 699. HRMS (ESI) calcd for $C_{22}H_{19}N_2$ ([M + H]$^+$): 311.1543. Found: 311.1546.

*6-Methyl-3,4-diphenylquinolin-2-amine (**3d**).* White solid (42.8 mg, 69%), mp 222−224 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (1H, d, J = 8.8 Hz), 7.31 (1H, dd, J_1= 8.4 Hz, J_2= 1.6 Hz), 7.18−7.00 (11H, m), 4.70 (2H, br), 2.25 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 147.1, 145.5, 136.9, 136.3, 131.9, 131.4, 130.3, 130.0, 128.5, 127.6, 127.4, 127.1, 125.7, 125.6, 123.6, 123.3, 21.4. IR (KBr, cm^{-1}): 3480, 3467, 3284, 3134, 3056, 2696, 1631, 1565, 1492, 1432, 1419, 826, 786, 759, 699; HRMS (ESI) calcd for $C_{22}H_{19}N_2$ ([M + H]$^+$): 311.1543. Found: 311.1547.

*6-Methoxy-3,4-diphenylquinolin-2-amine (**3e**).* White solid (47.1 mg, 72%), mp 189−191 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (1H, d, J = 8.8 Hz), 7.25−7.09 (11H, m), 6.70 (1H, d, J = 2.8 Hz), 4.73 (2H, br), 3.65 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 154.1, 146.8, 142.7, 136.9, 136.3, 130.3, 129.9, 128.5, 127.7, 127.4, 127.2, 127.1, 124.1, 123.5, 120.5, 106.2, 55.3. IR (KBr, cm^{-1}): 3481, 3291, 3141, 3062, 2952, 2826, 1636, 1566, 1507, 1490, 1434, 1419, 1404, 1225, 1038, 828, 699; HRMS (ESI) calcd for $C_{22}H_{19}N_2O$ ([M + H]$^+$): 327.1492. Found: 327.1496.

*6-Ethyl-3,4-diphenylquinolin-2-amine (**3f**).* White solid (48.8 mg, 75%), mp 194−196 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (1H, d, J = 8.4 Hz), 7.37 (1H, d, J = 8.0 Hz), 7.16−7.06 (11H, m), 5.30 (2H, br), 2.57 (2H, q, J = 7.6 Hz), 1.13 (3H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 147.0, 145.6, 138.0, 136.8, 136.2, 130.2, 129.9, 129.8, 128.3, 127.4, 127.1, 126.9, 125.5, 124.4, 123.3, 123.2, 28.6, 15.7. IR (KBr, cm^{-1}): 3477, 3281, 3120, 3054, 2960, 2871, 1632, 1565, 1491, 1437, 1419, 830, 697. HRMS (ESI) calcd for $C_{23}H_{21}N_2$ ([M + H]$^+$): 325.1699. Found: 325.1698.

*6-Isopropyl-3,4-diphenylquinolin-2-amine (**3g**).* White solid (47.3 mg, 70%), mp 199−201 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (1H, d, J = 8.8 Hz), 7.46 (1H, dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.24−7.09 (11H, m), 5.0 (2H, br), 2.57 (1H, m), 1.17 (6H, d, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.2, 147.3, 145.8, 142.7, 136.8, 136.3, 130.3, 129.9, 128.4, 128.3, 127.6, 127.3, 127.0, 125.7, 123.3, 123.2, 33.9, 23.9. IR (KBr, cm^{-1}): 3478, 3460, 3284, 3124, 3056, 2955, 2870, 1635, 1565, 1494, 1437, 1420, 827, 698. HRMS (ESI) calcd for $C_{24}H_{23}N_2$ ([M + H]$^+$): 339.1856. Found: 339.1853.

*6-(Tert-butyl)-3,4-diphenylquinolin-2-amine (**3h**).* White solid (49.8 mg, 71%), mp 215−217 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.71−7.64 (2H, m), 7.30 (1H, d, J = 2.0 Hz), 7.26−7.10 (10H, m), 4.75 (2H, br), 1.24 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 147.8, 145.4, 145.1, 136.8, 136.3, 130.4, 130.0, 128.6, 128.0, 127.6, 127.4, 127.1, 125.4, 123.2, 123.1, 121.9, 34.6, 31.2. IR (KBr, cm^{-1}): 3482, 3285, 3145, 2955, 2867, 1631, 1565, 1492,1434, 1418, 1364, 1250, 890, 764, 698; HRMS (ESI) dalcd for $C_{25}H_{25}N_2$ ([M + H]$^+$): 353.2012. Found: 353.2013.

*6-Fluoro-3,4-diphenylquinolin-2-amine (**3i**).* White solid (35.8 mg, 57%), mp 217−219 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.70−7.66 (1H, m), 7.32−7.16 (7H, m), 7.13 (2H, J = 6.8 Hz), 7.08−7.06 (2H, m), 6.96 (1H, dd, J_1 = 10.4 Hz, J_2 = 2.8 Hz), 4.89 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2 (d, J = 240.1 Hz), 155.2, 147.1 (d, J = 4.6 Hz), 144.1, 136.3, 135.8, 130.2, 129.8, 128.6, 127.9, 127.7, 127.6, 127.4, 124.1, 124.0, 118.8 (d, J = 25.1 Hz), 110.4 (d, J = 22.9 Hz); IR (KBr, cm^{-1}): 3476, 3300, 3163, 3074, 3024, 1628, 1564, 1507, 1493, 1452, 1420, 1201, 834, 760. HRMS (ESI) calcd for $C_{21}H_{16}FN_2$ ([M + H]$^+$): 315.1292. Found: 315.1296.

*6-Chloro-3,4-diphenylquinolin-2-amine (**3j**).* White solid (35.5 mg, 54%), mp 226−228 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (1H, d, J = 8.8 Hz), 7.50−7.47 (1H, m), 7.30 (1H, d, J = 2.4 Hz), 7.28−7.20 (6H, m), 7.14−7.07 (4H, m), 4.90 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 147.0, 145.7, 136.0, 135.7, 130.2, 130.0, 129.9, 128.7, 127.9, 127.8, 127.7, 127.5, 127.4, 125.5, 124.5, 124.1. IR (KBr, cm^{-1}): 3475, 3284, 3140, 2850, 2812, 1630, 1583, 1565, 1484, 1436, 1420, 824, 699. HRMS (ESI) calcd for $C_{21}H_{16}ClN_2$ ([M + H]$^+$): 331.0997. Found: 331.0997.

*Methyl-2-amino-3,4-diphenylquinoline-6-carboxylate (**3k**).* White solid (29.8 mg, 42%), mp 244−246 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.17−8.11 (2H, m), 7.71 (1H, d, J = 8.8 Hz), 7.29−7.20 (6H, m), 7.15−7.09 (4H, m), 5.13 (2H, br), 3.84 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 155.6, 147.7, 147.2, 136.7, 136.1, 130.3, 130.0, 129.4, 128.6, 127.7, 127.5, 127.2, 126.7, 125.8, 123.7, 123.3, 122.4, 52.0. IR (KBr, cm^{-1}): 3483, 3408, 3292, 3151, 2946, 2738, 1707, 1610, 1424, 1273, 1238, 1110, 1020, 757, 700. HRMS (ESI) calcd for $C_{23}H_{19}N_2O_2$ ([M + H]$^+$): 355.1441. Found: 355.1446.

*3,4-Diphenyl-6-(trifluoromethoxy)quinolin-2-amine (**3l**).* White solid (44.0 mg, 58%), mp 179−181 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (1H, d, J = 9.2 Hz), 7.42−7.39 (1H, m), 7.27−7.07 (11H, m), 5.15 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 147.4, 145.7, 143.9, 135.9, 135.6, 130.1, 129.8, 128.7, 127.9, 127.7, 127.6, 127.4, 124.3, 123.8, 123.2, 120.5 (q, J = 255.2 Hz), 118.2. IR (KBr, cm^{-1}): 3483, 3290, 3124, 2737, 1636, 1566, 1491, 1427, 1241, 1198, 1072, 1022, 832, 700. HRMS (ESI) calcd for $C_{22}H_{16}F_3N_2O$ ([M + H]$^+$): 381.1209. Found: 381.1211.

*6,7-Dimethyl-3,4-diphenylquinolin-2-amine (**3m**).* White solid (34.3 mg, 53%), mp 203−205 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (1H, s), 7.25−7.17 (6H, m), 7.15−7.06 (5H, m), 4.73 (2H, br), 2.40 (3H, s), 2.23 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.0, 146.9, 146.1, 139.3, 137.0, 136.4, 131.8, 130.4, 130.0, 128.5, 127.6, 127.3, 127.0, 126.0, 125.8, 122.4, 122.1, 20.3, 19.8. IR (KBr, cm^{-1}):

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3482, 3469, 3283, 3147, 3053, 2917, 1629, 1620, 1559, 1490, 1429, 1405, 1245, 1018, 699. HRMS (ESI) calcd for $C_{23}H_{21}N_2$ ([M + H]$^+$): 325.1699. Found: 325.1700.

*6-Fluoro-8-methyl-3,4-diphenylquinolin-2-amine (**3n**).* White solid (33.4 mg, 51%), mp 212−214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.19 (7H, m), 7.14−7.12 (2H, m), 7.08−7.06 (2H, m), 6.82 (1H, dd, J_1 = 10.4 Hz, J_2 = 2.8 Hz), 4.72 (2H, br), 2.72 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6 (d, J = 239.3 Hz), 154.1, 147.4 (d, J = 5.7 Hz), 143.1, 136.7 (d, J = 8.6 Hz), 136.5, 136.2, 130.2, 129.9, 128.6, 127.8, 127.5, 127.3, 123.8 (d, J = 9.5 Hz), 123.7, 118.9 (d, J = 24.8 Hz), 107.9 (d, J = 21.9 Hz), 18.2. IR (KBr, cm^{-1}): 3511, 3399, 3062, 3034, 2959, 2920, 1607, 1598, 1487, 1420, 1194, 1137, 875, 721, 701. HRMS (ESI) calcd for $C_{22}H_{18}FN_2$ ([M + H]$^+$): 329.1449. Found: 329.1449.

*6,7,8-Trimethoxy-3,4-diphenylquinolin-2-amine (**3o**).* White solid (59.6 mg, 77%), mp 208−210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19−7.15 (2H, m), 7.19−7.15 (3H, m), 7.05−7.03 (5H, m), 7.00 (1H, s), 4.65 (2H, br), 3.97 (3H, s), 3.81 (3H, s), 3.20 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 154.9, 149.7, 145.8, 145.4, 140.1, 139.2, 136.0, 130.4, 128.5, 128.1, 126.9, 126.3, 125.6, 122.4, 112.8, 102.1, 60.7, 60.4, 55.7. IR (KBr, cm^{-1}): 3504, 3394, 3381, 3051, 3025, 2939, 2825, 1590, 1557, 1485, 1458, 1437, 1396, 1337, 1244, 1153, 1111, 1103, 1068, 993, 948, 834, 730, 705. HRMS (ESI) calcd for $C_{24}H_{23}N_2O_3$ ([M + H]$^+$): 387.1703. Found: 387.1701.

*3,4-Di-p-tolylquinolin-2-amine (**3p**).* White solid (42.2 mg, 65%), mp 252−254 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (1H, d, J = 8.4 Hz), 7.53−7.50 (1H, m), 7.33 (1H, d, J = 8.4 Hz), 7.13−6.97 (9H, m), 4.91 (2H, br), 2.29 (3H, s), 2.27 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 147.7, 147.2, 137.0, 136.6, 133.8, 133.1, 130.1, 129.8, 129.3, 129.2, 128.4, 126.7, 125.7, 124.0, 123.3, 122.2, 21.2, 21.1. IR (KBr, cm^{-1}): 3467, 3284, 3116, 3060, 2917, 2859, 1636, 1606, 1565, 1496, 1430, 1339, 763. HRMS (ESI) calcd for $C_{23}H_{21}N_2$ ([M + H]$^+$): 325.1699. Found: 325.1703.

*3,4-Bis(4-fluorophenyl)quinolin-2-amine (**3q**).* White solid (33.8 mg, 52%), mp 269−271 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, d, J = 8.4 Hz), 7.59−7.55 (1H, m), 7.30 (1H, d, J = 8.4 Hz), 7.19−6.95 (9H, m), 4.79 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (d, J = 246.6 Hz), 161.9 (d, J = 245.9 Hz), 155.3, 147.3, 147.1, 132.5 (d, J = 3.4 Hz), 132.1 (d, J = 8.1 Hz), 131.8 (d, J = 3.1 Hz), 131.6 (d, J = 8.0 Hz), 129.7, 126.5, 126.0, 123.7, 122.8, 122.5, 115.9 (d, J = 21.4 Hz), 115.0 (d, J = 21.4 Hz). IR (KBr, cm^{-1}): 3500, 3480, 3310, 3160, 3066, 2748, 1890, 1646, 1605, 1565, 1495, 1432, 1218, 1157, 1095, 1015, 828, 767, 741. HRMS (ESI) calcd for $C_{21}H_{15}F_2N_2$ ([M + H]$^+$): 333.1198. Found: 333.1201.

*3,4-Bis(4-bromophenyl)quinolin-2-amine (**3r**).* White solid (41.5 mg, 46%), mp 280−282 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, d, J = 8.4 Hz), 7.60−7.56 (1H, m), 7.44−7.41 (4H, m), 7.29−7.26 (1H, m), 7.19−7.16 (1H, m), 7.03−6.96 (4H, m), 4.71 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 147.4, 146.6, 135.4, 134.7, 132.2, 132.0, 131.5, 131.3, 129.9, 126.4, 126.1, 123.3, 122.9, 122.1, 122.0, 121.8. IR (KBr, cm^{-1}): 3475, 3291, 3118, 3056, 2740, 1637, 1607, 1568, 1486, 1430, 1387, 1068, 1012, 806, 757, 736. HRMS (ESI) calcd for $C_{21}H_{15}Br_2N_2$ ([M + H]$^+$): 452.9597. Found: 452.9598.

*4-Methyl-3-phenylquinolin-2-amine (**3s**).* White solid (29.0 mg, 62%), mp 136−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84−7.82 (1H, m), 7.68−7.66 (1H, m), 7.57−7.48 (3H, m), 7.44−7.40 (1H, m), 7.30−7.25 (3H, m), 4.78 (2H, br), 2.32 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 146.8, 142.1, 136.8, 129.8, 129.3, 129.1, 128.0, 126.2, 124.1, 124.0, 123.9, 122.3, 15.8. IR (KBr, cm^{-1}): 3462, 3288, 3106, 1636, 1607, 1559, 1424, 1226, 1020, 1002, 857, 756, 707. HRMS (ESI) calcd for $C_{16}H_{15}N_2$ ([M + H]$^+$): 235.1230. Found: 235.1233.

*4-Ethyl-3-phenylquinolin-2-amine (**3t**).* White solid (31.1 mg, 63%), mp 157−159 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (1H, d, J = 8.4 Hz), 7.67 (1H, d, J = 8.0 Hz), 7.53−7.39 (4H, m), 7.29−7.23 (3H, m), 4.96 (2H, br), 2.72 (2H, q, J = 7.6 Hz), 1.12 (3H, t, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 147.8, 147.3, 136.5, 129.6, 129.2, 128.9, 127.9, 126.3, 124.0, 123.2, 122.5, 122.1, 22.4, 14.8; IR (KBr, cm^{-1}): 3468, 3289, 3144, 2971, 2872, 1632, 1583, 1570, 1505, 1424, 1218, 1133, 1006, 848, 757, 705. HRMS (ESI) calcd for $C_{17}H_{17}N_2$ ([M + H]$^+$): 249.1386. Found: 249.1388.

*4-Butyl-3-phenylquinolin-2-amine (**3u**).* White solid (36.5 mg, 66%), mp 128−130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86−7.83 (1H, m), 7.69−7.66 (1H, m), 7.56−7.42 (4H, m), 7.31−7.27 (3H, m), 4.80 (2H, br), 2.73−2.67 (2H, m), 1.53−1.50 (2H, m), 1.30−1.23 (2H, m), 0.81−0.76 (3H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 147.3, 146.8, 136.6, 129.7, 129.2, 129.0, 128.0, 126.4, 124.1, 123.4, 122.9, 122.2, 32.6, 29.0, 22.9, 13.6. IR (KBr, cm^{-1}): 3479, 3291, 3147, 3064, 2963, 2860, 1632, 1580, 1565, 1503, 1462, 1430, 1224, 1010, 757, 702. HRMS (ESI) calcd for $C_{19}H_{21}N_2$ ([M + H]$^+$): 277.1699. Found: 277.1697.

*2-(2-Amino-3-phenylquinolin-4-yl)ethanol (**3v**).* White solid (27.4 mg, 52%), mp 165−167 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (1H, d, J = 8.0 Hz), 7.61 (1H, d, J = 8.4 Hz), 7.53−7.37 (4H, m), 7.26−7.22 (3H, m), 4.60 (2H, br), 3.77 (2H, t, J = 7.6 Hz), 3.05 (2H, t, J = 7.2 Hz), 2.95 (1H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 147.0, 142.5, 136.1, 129.7, 129.4, 129.3, 128.2, 126.2, 124.7, 124.2, 123.1, 122.6, 62.0, 32.8. IR (KBr, cm^{-1}): 3469, 3369, 3181, 3050, 2981, 2870, 1623, 1607, 1569, 1506, 1430, 1319, 1050, 763, 707. HRMS (ESI) calcd for $C_{17}H_{17}N_2O$ ([M + H]$^+$): 265.1335. Found: 265.1334.

*3-(2-Amino-3-(4-methoxyphenyl)quinolin-4-yl)propyl acetate (**3w**).* White solid (55.4 mg, 79%), mp 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (1H, d, J = 8.4 Hz), 7.68 (1H, d, J = 8.0 Hz), 7.57−7.53 (1H, m), 7.31−7.27 (1H, m), 7.20 (2H, d, J = 8.8 Hz), 7.05 (2H, d, J = 8.4 Hz), 4.66 (2H, br), 3.98 (2H, t, J = 6.4 Hz), 3.88 (3H, s), 2.83−2.79 (2H, m), 1.95 (3H, s), 1.90−1.83 (2H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 159.3, 156.1, 147.2, 145.6, 130.8, 129.0, 128.1, 126.4, 123.7, 123.5, 122.7, 122.3, 114.7, 63.8, 55.2, 29.2, 25.6, 20.7. IR (KBr, cm^{-1}): 3466, 3312, 3170, 2961, 1735, 1605, 1429, 1247, 1034, 761. HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3$ ([M + H]$^+$): 351.1703. Found: 351.1706.

*3,4-Di(thiophen-2-yl)quinolin-2-amine (**3x**).* White solid (35.2 mg, 57%), mp 209−211 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (1H, d, J = 8.0 Hz), 7.62−7.56 (2H, m), 7.36−7.32 (2H, m), 7.22−7.18 (1H, m), 7.03−6.97 (4H, m), 5.10 (2H, br). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 147.5, 143.0, 136.5, 136.4, 130.2, 129.5, 129.1, 127.5, 127.1, 127.0, 126.7, 126.5, 125.9, 123.9, 122.9, 117.4. IR (KBr, cm^{-1}): 3447, 3283, 3161, 3095, 2923, 1623, 1605, 1559, 1490, 1409, 1228, 844, 762, 711. HRMS (ESI) calcd for $C_{17}H_{13}N_2S_2$ ([M + H]$^+$): 309.0515. Found: 309.0516.

*2,4,5-Triphenylimidazo[1,2-a]quinoline (**4a**).* Yellow solid (40.9 mg, 52%), mp 152−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (1H, s), 7.92 (2H, d, J = 7.5 Hz), 7.83 (1H, d, J = 8.2 Hz), 7.50−7.46 (2H, m), 7.37−7.29 (4H, m), 7.24−7.13 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 143.9, 136.9, 135.5, 135.3, 133.9, 131.7, 131.2, 131.1, 128.7, 128.5, 128.4, 128.2, 127.9, 127.4, 127.3, 127.1, 127.0, 125.9, 124.3, 124.1, 114.9, 106.9. IR (KBr, cm^{-1}): 3361, 3059, 3023, 2923, 2854, 1595, 1518, 1454, 1421, 1319, 1249, 1163, 1073, 943, 751, 718, 707. HRMS (ESI) calcd for $C_{29}H_{21}N_2$ ([M + H]$^+$): 397.1699. Found: 397.1699.

*8-Methyl-2,4,5-triphenylimidazo[1,2-a]quinoline (**4c**).* Yellow solid (51.8 mg, 63%), mp 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (1H, s), 7.96 (2H, d, J = 8.0 Hz), 7.80 (1H, s), 7.43−7.36 (5H, m), 7.30−7.13 (10H, m), 2.57 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.3, 139.1, 137.2, 135.6, 135.4, 134.1, 131.9, 131.3, 131.1, 128.53, 128.49, 127.9 (overlapped), 127.5, 127.4, 127.1, 126.0, 125.9, 122.0, 115.0, 106.7, 21.8. IR (KBr, cm^{-1}): 3057, 3026, 2920, 2851, 1685, 1654, 1591, 1559, 1448, 1319, 1071, 1027, 909, 818, 741, 695. HRMS (ESI) calcd for $C_{30}H_{23}N_2$ ([M + H]$^+$): 411.1856. Found: 411.1855.

*7-Methoxy-2,4,5-triphenylimidazo[1,2-a]quinoline (**4e**).* Yellow solid (49.3 mg, 58%), mp 195−197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (1H, s), 7.96−7.91 (3H, m), 7.40−7.36 (4H, m), 7.32−7.18 (10H, m), 6.96 (1H, d, J = 2.4 Hz), 3.71 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 145.0, 143.6, 137.0, 135.6, 135.0, 134.1, 131.3, 131.1, 129.3, 128.5, 128.0, 127.5, 127.4, 127.3, 127.1, 126.6, 126.0, 125.4, 116.9, 116.2, 110.6, 106.8, 21.8. IR (KBr, cm^{-1}): 3122, 3056, 2960, 2853, 1614, 1539, 1514, 1479, 1377, 1293, 1237, 1159, 820, 737, 694. HRMS (ESI) calcd for $C_{30}H_{23}N_2O$ ([M + H]$^+$): 427.1805. Found: 427.1807.

*7-(Tert-butyl)-2,4,5-triphenylimidazo[1,2-a]quinoline (**4h**).* Yellow solid (53.9 mg, 60%), mp 204−206 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (1H, s), 7.98−7.93 (3H, m), 7.69 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.55 (1H, s), 7.40−7.36 (4H, m), 7.32−7.19 (9H, m), 1.27 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 145.1, 144.1, 137.1, 135.7 (overlapped), 134.1, 131.3, 131.2, 130.0, 128.7, 128.5, 127.9, 127.5, 127.4, 127.2, 127.1, 126.3, 126.0, 124.8, 123.9, 114.7, 106.7, 34.7, 31.3. IR (KBr, cm^{-1}): 3060, 3032, 2955, 2868, 1594, 1558, 1423, 1364, 1314, 1072, 1021, 977, 816, 775, 703. HRMS (ESI) calcd for $C_{33}H_{29}N_2$ ([M + H]$^+$): 453.2325. Found: 453.2326.

*2-Phenyl-4,5-di-p-tolylimidazo[1,2-a]quinoline (**4p**).* Yellow solid (65.1 mg, 77%), mp 251−253 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (1H, s), 7.99−7.94 (3H, m), 7.59−7.54 (2H, m), 7.40−7.25 (6H, m), 7.13−7.04 (6H, m), 2.36 (3H, s), 2.31 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 144.2, 136.7, 136.6, 135.2, 134.1, 132.6, 131.8, 131.2, 131.0, 128.8, 128.7 (overlapped), 128.4, 128.1 (overlapped), 127.4, 126.0, 124.5, 124.3, 114.9, 106.8, 21.30, 21.26. IR (KBr, cm^{-1}): 3152, 3075, 3031, 2918, 1992, 1903, 1596, 1515, 1453, 1420, 1320, 1158, 1111, 1022, 858, 804, 769, 719. HRMS (ESI) calcd for $C_{31}H_{25}N_2$ ([M + H]$^+$): 425.2012. Found: 425.2009.

*5-Ethyl-2,4-diphenylimidazo[1,2-a]quinoline (**4t**).* Yellow solid (52.1 mg, 72%), mp 100−102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (1H, s), 7.98 (1H, d, J = 8.0 Hz), 7.92−7.87 (3H, m), 7.60−7.56 (1H, m), 7.52−7.43 (6H, m), 7.34−7.30 (2H, m), 7.23−7.20 (1H, m), 2.85 (2H, q, J = 7.2 Hz), 1.21 (3H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 144.5, 136.4, 135.4, 134.0, 132.2, 130.1, 128.7, 128.4, 128.1, 128.0, 127.6, 127.3, 126.2, 125.9, 124.5, 122.9, 115.4, 106.4, 22.1, 15.3. IR (KBr, cm^{-1}): 3147, 3056, 2966, 2926, 2869, 1603, 1521, 1451, 1235, 1177, 1068, 1033, 904, 759, 732, 695. HRMS (ESI) calcd for $C_{25}H_{21}N_2$ ([M + H]$^+$): 349.1699. Found: 349.1703.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of all the products and X-ray structural details of **3s** and **3j′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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