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Substrate-Tuned Domino Annulation for Selective Synthesis of Poly-substituted Benzo[*f*]imidazo[2,1-*a*][2,7]naphthyridines and 3-Azaheterocyclic Substituted 2-Arylquinolines

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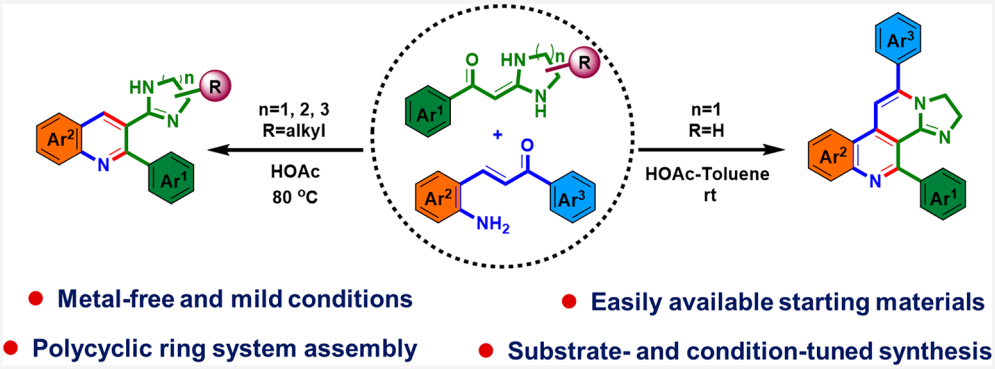

ABSTRACT: A domino annulation/oxidation of heterocyclic ketene aminals (HKAs) and 2-aminochalcones has been developed for the selective synthesis of poly-substituted benzo[*f*]imidazo[2,1-*a*][2,7]naphthyridines and 3-azaheterocyclic substituted 2-arylquinolines. These reactions proceed well under mild conditions without any additives. Plausible mechanisms for such a polycyclic ring system assembly were also proposed. Moreover, benzo[*f*]imidazo[2,1-*a*][2,7]naphthyridine **3g** displayed a fluorescence effect, demonstrating the potential applications in organic optical materials.

INTRODUCTION

The benzo[*c*][2,7]naphthyridine motif is fundamentally crucial because of its wide presence in natural alkaloids[1−3] and numerous pharmaceuticals with diverse biological activities.[4−7] Especially, those polycyclic fused aryl substituted benzo[*c*]-[2,7]naphthyridines are good organic optical and electronic materials because of their high rigidity as well as outstanding electrochemical and photo-physical properties (Figure 1).[8−10] Consequently, the development of efficient synthetic routes to benzo[*c*][2,7]naphthyridines with structural diversity and a polycyclic ring system is of great importance and interest to organic and medicinal chemists. So far, methods for poly-substituted benzo[*c*][2,7]naphthyridines included multi-step nucleophilic displacement of aromatic fluorine (Scheme 1, a)[11] and one-step direct coupling of pyridine methylstannanes and *ortho*-bromoacetanilides dual-catalyzed by $PdCl_2$(dppb)/CuO (Scheme 1, b).[12] Although the aforementioned strategies enable the construction of poly-substituted benzo[*c*][2,7]-naphthyridines, they are limited in complex starting materials, transition-metal catalysis, harsh reaction conditions, or low transformation efficiency (~8%). Moreover, the challenging polycyclic system assembly on benzo[*c*][2,7]naphthyridines also remains a great space worthy of further exploration.

Heterocyclic ketene aminals (HKAs) have been attractive building blocks for the synthesis of heterocyclic and fused heterocyclic compounds. Because of the conjugation of electron-donating amino groups and the electron-withdrawing carbonyl group with a highly polarized double bond (C=C),[13] the electron density of the α-carbon (C3) in HKAs is higher than that of the secondary amino groups (N1 and N5). As such, C3 and N1 of HKAs can serve as bis-nucleophiles to react with bis-electrophiles for the construction of heterocyclic fused compounds.[14] Previously, we and others have discovered the incorporation of two nucleophilic sites N1 and C3 and one electrophile site C4 (C=O) through a one-pot cascade reaction to construct polycyclic heterocycles.[15] In continuation of our ongoing efforts to develop one-pot multi-bond forming reactions for the assembly of polycyclic heterocycles, herein we

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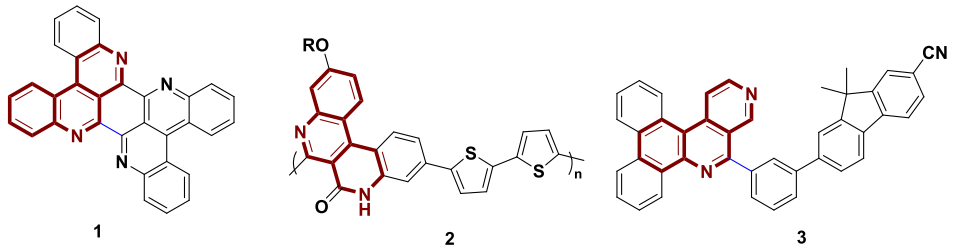
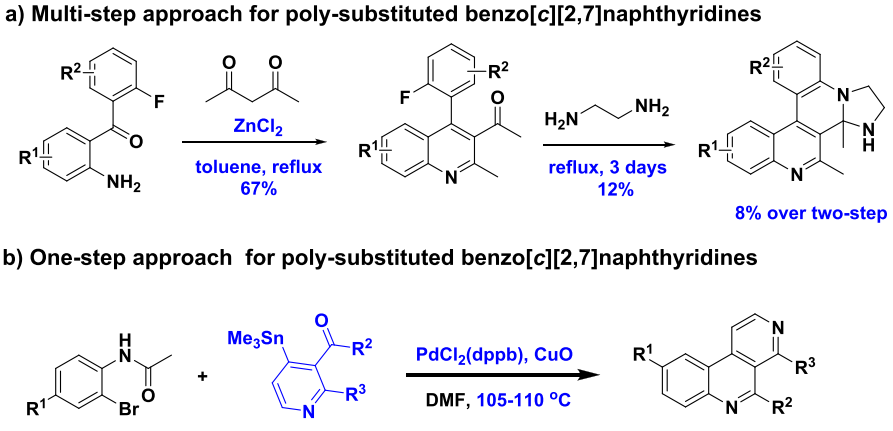
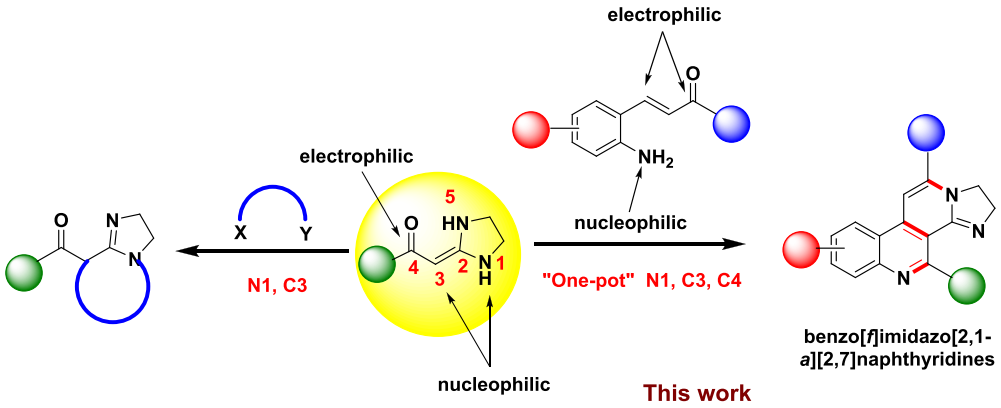


Figure 1. Representative organic optical and electronic materials with polycyclic fused benzo[*c*][2,7]naphthyridines.

Scheme 1. Established Approaches to Poly-substituted Benzo[*c*][2,7]naphthyridines



Scheme 2. Reactivity of HKAs for the Assembly of Polycyclic Heterocycles



explore the domino annulation of HKAs and 2-aminochalcones through N1, C3, and C4. It is envisioned that the one-pot cascade coupling of HKAs and 2-aminochalcones would lead to the formation of poly-substituted benzo[*f*]-imidazo[2,1-*a*][2,7]naphthyridines (Scheme 2). One main challenge to overcome in this transformation is the competitive reactions between multiple electrophilic and nucleophilic sites in HKAs and 2-aminochalcones.

RESULTS AND DISCUSSION

For a proof-of-concept for the proposed ring-closing reaction, initial studies began with the examination of 2-(imidazolidin-2-ylidene)-1-phenylethan-1-one (**1a**) and (*E*)-3-(2-aminophenyl)-1-phenylprop-2-en-1-one (**2a**) as the model substrates. As shown in Table 1, when the substrates were treated with H_2SO_4 or TFA in MeCN, product **3a** was not obtained as expected, while (*E*)-3-(2-aminophenyl)-1-phenylprop-2-en-1-one **2a** itself was unexpectedly cyclized to the 2-phenylquinoline **5a** as the major product (entries 1 and 2). Instead, HOAc and CH_3CH_2COOH displayed moderate efficiency for this reaction under otherwise identical reaction conditions (entries 3 and 4). And the reactivity between **1a** and **2a** switched drastically, and around 17% HPLC yield of **3a** was observed (entry 3). Then the solvent effect was tested to optimize the conditions for the synthesis of **3a**. AcOH was found to promote the reactions in various solvents. Treatment of **1a** and **2a** in the presence of AcOH in 1,4-dioxane or toluene at 25 °C achieved the desired **3a** in higher conversions (56% for 1,4-dioxane and 63% for toluene, entries 5 and 6). Then, **3a** was isolated and characterized by HRMS and NMR. Compared with the established method (~8%), the yield of **3a** was quite satisfactory due to the numerous annulations and multi-bond formations that occurred in the "one-pot" transformation. But somewhat serendipitously, a side product **4a** was generated with an HPLC yield of 17% when the reaction was performed in pure HOAc (entry 7). Further structural analysis showed that **4a** was 3-(4,5-dihydro-1*H*-imidazol-2-yl)-2-phenylquino-

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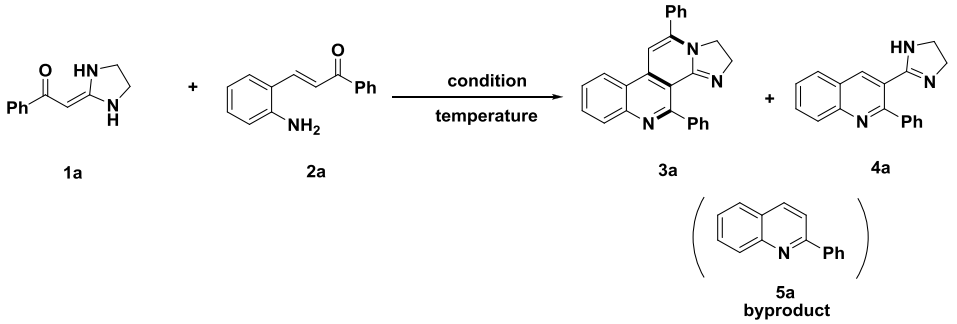
Table 1. Optimization of the Reaction Conditions[a]



no.	conditions	T/°C	conversion/%[b] 3a	4a
1	H_2SO_4/MeCN (v/v = 0.3:1)	25	ND	ND
2	TFA/MeCN (v/v = 0.3:1)	25	ND	ND
3	HOAc/MeCN (v/v = 0.3:1)	25	17	ND
4	CH_3CH_2COOH/MeCN (v/v = 0.3:1)	25	15	ND
5	HOAc/1,4-dioxane (v/v = 0.3:1)	25	56	1
6	HOAc/toluene (v/v = 0.3:1)	25	63(45)[c]	4
7	HOAc	25	67	17
8	HOAc	50	38	49
9	HOAc	80	20	70(63)[c]

[a]Unless otherwise noted, the reactions were conducted on a scale of 0.3 mmol of **1a** and 0.45 mmol of **2a** in 0.65 mL of solvent under an air atmosphere. [b]Conversions were determined by the completion of **1a** and calculated by HPLC analysis. [c]Isolated yields via silica gel chromatography. ND = no detected.

line. It is well-known that the quinoline ring ranks 22nd among the 351 ring systems found in marketed drugs.[16] Among the various quinolones developed, 3-azaheterocyclic substituted 2-arylquinolines are important, associated with a wide application in electroluminescent materials.[17] However, only a few approaches reported to construct this heterocyclic core on established quinoline-3-aldehydes.[16b,c] In this work, elevating the reaction temperatures from 25 to 80 °C, the yields of **4a** could be increased to 70% (63% for isolated yield, entry 9), while those of **3a** were suppressed to less than 20% (entries 8 and 9). On the basis of the reaction described above, the optimized reaction conditions were achieved by conducting the reaction at 25 °C in HOAc-toluene for benzo[*f*]-imidazo[2,1-*a*][2,7]naphthyridines **3** and 80 °C in HOAc for 3-azaheterocyclic substituted 2-arylquinolines **4**.

With the optimized reaction conditions in hand, we first investigated subsequent reactivity of HKAs **1** with 2-aminochalcones **2** (Table 2). A series of aryl-derived HKAs **1** were examined, and the tetracyclic products **3** were obtained in acceptable yields (Table 2, **3a**−**3j**). Methyl, chloro, and trifluomethyl groups were all tolerated under the reaction conditions. Also, the chemical structure of representative product **3b** was elucidated by single-crystal X-ray crystallography with an ellipsoid contour probability level of 30% (CCDC: 2041905; details in the Supporting Information). Also, the aryl ring was not limited to benzene, and the naphthyl, pyridinyl, thienyl, and furyl rings work well, giving the desired products **3e**−**3i** in 43−47%. Then, we further explored the generality of the present method by examining the electronic effects on 2-aminochalcones **2**. It was found that both the electron-withdrawing (Cl, Br, CF_3) and electron-donating (MeO) groups proceeded well to give the corresponding products (**3k**−**3p**, **3r**−**3s**, and **3q**). Moreover, during the substrate scope investigation of this reaction, benzo[*f*]imidazo[2,1-*a*][2,7]naphthyridine **3g** exhibited a fluorescence effect in DCM, possibly due to the rigid and planar structures as well as electronic effect (relevant photophysical data in the Supporting Information). These results suggested the potential utility of this protocol in the synthesis of organic optical materials.

However, products **3t** and **3u** were not obtained as expected when **2a** was reacted with six- or seven-membered rings bearing HKAs **1** under the standard conditions (Table 2). Instead, 3-azaheterocyclic substituted 2-arylquinolines **4** were detected, and the transformation efficiency could be improved when the reaction was conducted at 80 °C in HOAc. Except for the reaction conditions, the ring size can also influence the reaction reactivity between HKAs **1** and 2-aminochalcones **2**.

Motivated by the successful construction of the 3-azaheterocyclic substituted 2-arylquinolines by tuning the ring sizes of HKAs and the reaction conditions, we sought to extend the ring-closing reaction to HKAs **1** with various ring sizes in HOAc at 80 °C (Table 3). As expected, when using HKAs **1** bearing a five-membered ring with a two-methylene tether, the desired products **4a** and **4b** were obtained with yields of 67% and 60%, respectively. Moreover, the ring sizes of HKAs **1** affected the efficiency of the domino reaction. In general, the six- and seven-membered rings bearing HKAs **1** are generally more favorable for the transformation of **4** than those of five-membered ring bearing HKAs **1** (Table 3, **4c**−**4e** vs **4a**−**4b**). And the aliphatic substituents on the six-membered ring of HKAs **1** did not have an effect on the reaction, giving the corresponding product **4e** with a yield of 78%. The electronic effect on 2-aminochalcones **2** as the substituent R^2 slightly influences the transformation, delivering the desired products **4f** and **4g** with lower isolated yields of 69% and 55%, respectively. However, when the aromatic ring was substituted on the six-membered ring of HKAs **1**, the desired product **4h** failed to be obtained.

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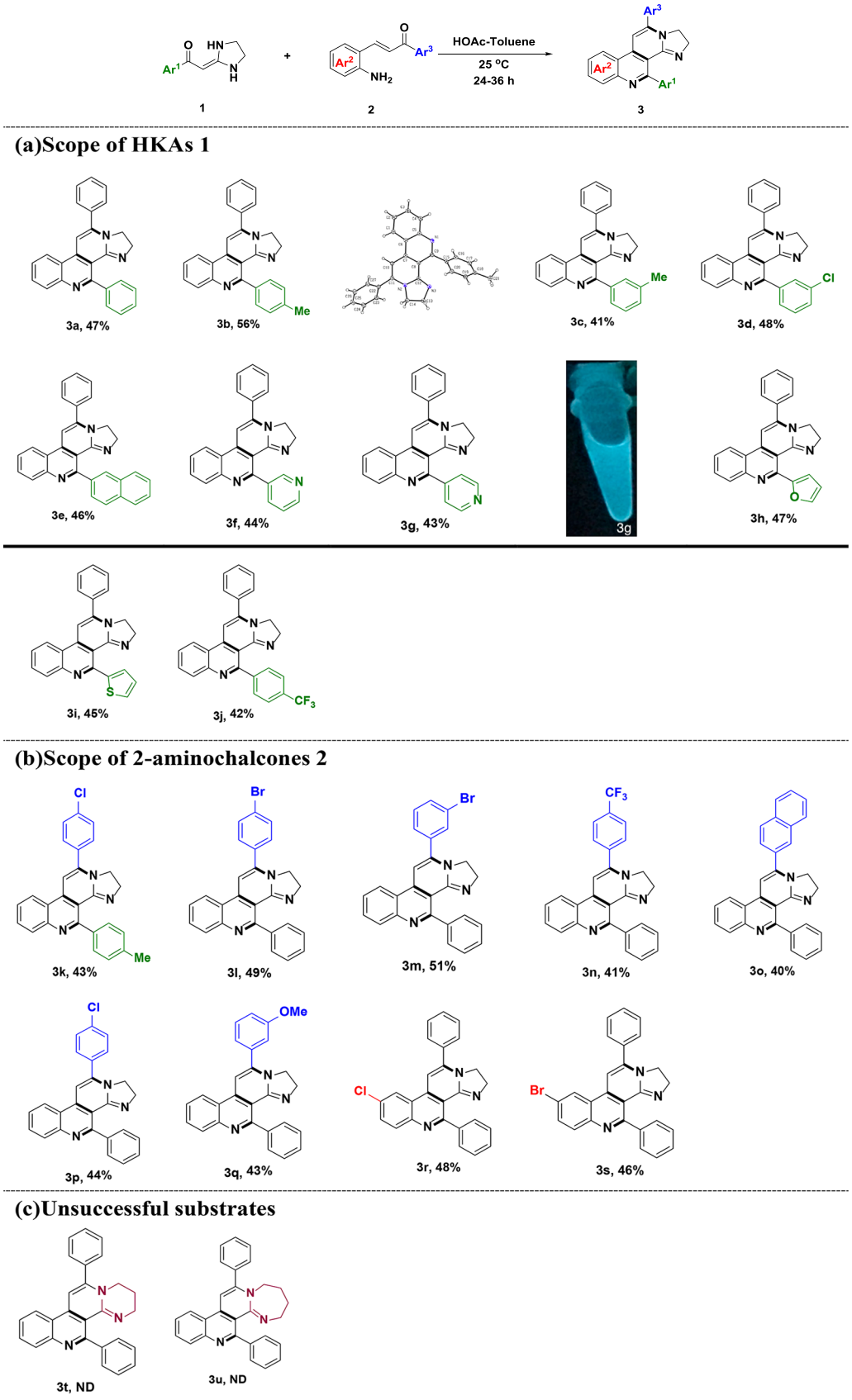
Table 2. Substrate Scope Investigation of HKAs and 2-Aminochalcones[a,b]



[a]Unless otherwise noted, the reactions were conducted on a scale of 1.0 mmol of **1** and 1.5 mmol of **2** in HOAc-toluene (0.6 mL/2.0 mL) at 25 °C under an air atmosphere. Isolated yields were determined by the completion of **1**. [b]Photographic image was taken in DCM (c = 10 μM) excited at 365 nm under a UV lamp.

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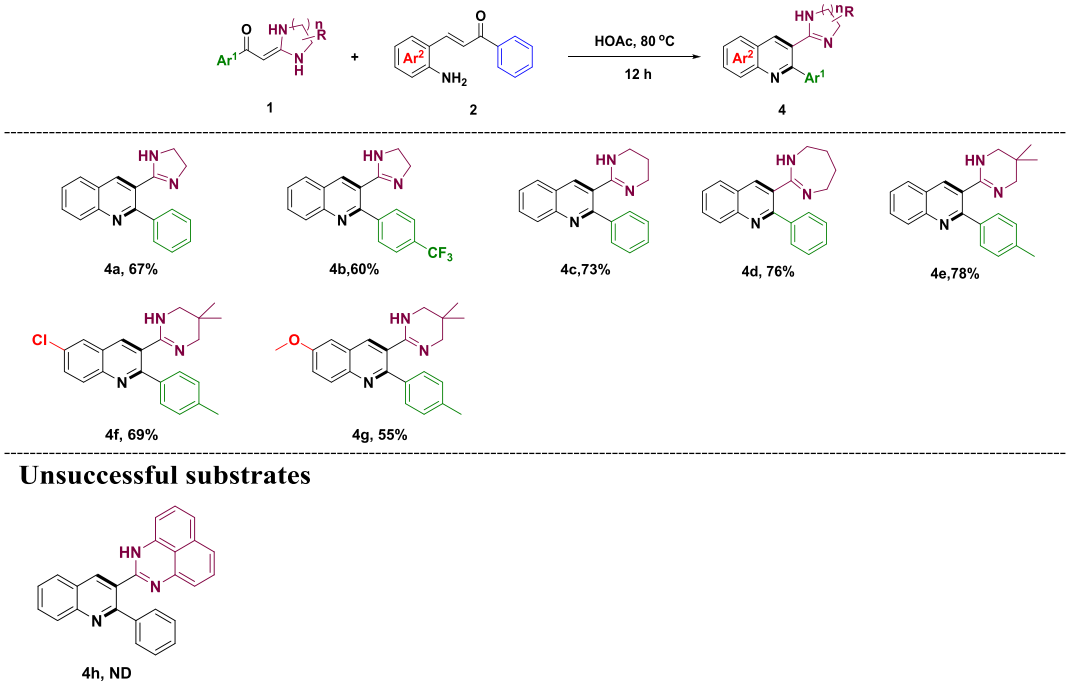
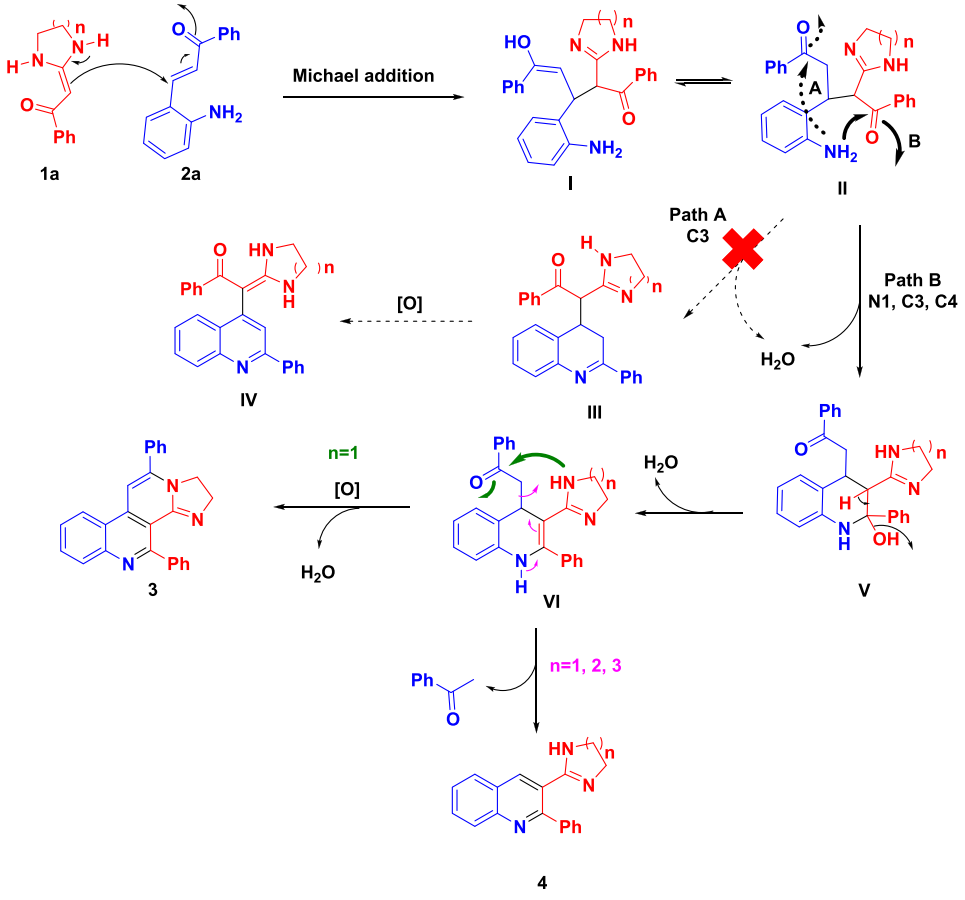
Table 3. Synthesis of 3-Azaheterocyclic Substituted 2-Arylquinolines 4[a]



[a]Unless otherwise noted, the reactions were conducted on a scale of 1.0 mmol of **1** and 1.5 mmol of **2** in 3.0 mL of HOAc at 80 °C under an air atmosphere. Isolated yields were determined by the completion of **1**.

Scheme 3. Plausible Mechanistic Pathway



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On the basis of the above results, a tentative mechanism for the domino reaction of HKAs **1** and 2-aminochalcones **2** is depicted in Scheme 3. First, the α-C3 of HKAs **1a** reacts with the 2-aminochalcone **2a** via Michael addition to form the intermediate **I**. The intermediate **I** undergoes ketone-enol tautomerization to form intermediate **II**.[14g] Next, the amino group of 2-aminochalcones **2** could attack the intramolecular carbonyl group by either pathway A or pathway B. On the basis of the key intermediates captured by HRMS (details in the Supporting Information), the pathway B is more favorable under the optimized conditions to form intermediate **V**. The intermediate **VI** is formed by a subsequent dehydration of **V**. When a five-membered ring (n = 1) is involved in HKAs **1**, the intermediate **VI** undergoes an intramolecular nucleophilic attack through losing H_2O and auto-oxidation in the air to produce benzo[*f*]imidazo[2,1-*a*][2,7]naphthyridines **3** at 25 °C. On the other hand, the treatment of HKAs **1** bearing various heterocyclic rings (n = 1, 2, 3) with 2-aminochalcones **2** at 80 °C converted to 3-azaheterocyclic substituted 2-arylquinolines **4** via proceeding an elimination of acetophenone.

CONCLUSIONS

In conclusion, a tandem annulation/oxidation of heterocyclic ketene aminals (HKAs) and 2-aminochalcones was developed. The reaction was carried out under mild conditions without any additive in generally moderate to good yields. Importantly, this ring-closing reaction could be fined controlled for selective synthesis of various polycyclic systems. Moreover, benzo[*f*]-imidazo[2,1-*a*][2,7]naphthyridine **3g** displayed fluorescence when excited under 365 nm, demonstrating the potential applications in organic optical materials.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used without purification. Purifications of reaction products were carried out by chromatography using silica gel (200−300 mesh). Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were recorded for ^{1}H NMR at 500 MHz and for ^{13}C NMR at 125 MHz. For ^{1}H NMR, tetramethylsilane (TMS) served as internal standard (δ = 0) and data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant(s) in Hz. For ^{13}C NMR, TMS (δ = 0) or $CDCl_3$ (δ = 77.26) was used as internal standard and spectra were obtained with complete proton decoupling. HPLC analysis and the HRMS of all final products were confirmed on a Agilent 1290 HPLC-6224 Time of Fight Mass Spectrometer using PhenomenexLuna 5 μ C18, 100 Å, 150 × 4.60 mm 5 μm column at a flow rate of 0.5 mL/min using liner gradients buffer B in A (B: CH_3OH containing 0.1% formic acid, A: H_2O containing 0.1% formic acid). Mobile phase B was increased linearly from 5% to 95% over 7 min and 95% over the next 2 min, after which the column was equilibrated to 5% for 1 min. Heterocyclic ketene aminals (HKAs) **1** were prepared from the corresponding ketene dithioacetals with diamines.[18] 2-Aminochalcones **2** were readily prepared from reduction of the corresponding 2-nitrochalcone with Fe/HOAc/HCl.[19]

Typical Procedure for the Synthesis of Benzo[*f*]imidazo-[2,1-*a*][2,7]naphthyridines 3. A mixture of heterocyclic ketene aminals (HKAs) **1** (1.0 mmol) and 2-aminochalcones **2** (1.5 mmol, 1.5 equiv) was dissolved in HOAc (0.6 mL)-toluene (2.0 mL), and the reaction mixture was stirred at 25 °C in air for 24−36 h. Upon the completion *via* TLC detection, the reaction was quenched with aqueous $NaHCO_3$ (5 mL) and then extracted three times with DCM. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by silica-gel chromatography using DCM/MeOH affords benzo[*f*]imidazo-[2,1-*a*][2,7]naphthyridines **3**.

*4,11-Diphenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]-naphthyridine (**3a**).* Yellow solid (dichloromethane/methanol = 20:1) (175 mg, 47%), mp > 250 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.5 Hz, 1H), 7.98−7.93 (m, 1H), 7.80−7.72 (m, 5H), 7.65−7.59 (m, 7H), 4.61 (t, J = 10.5 Hz, 2H), 4.22 (t, J = 10.5 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.3, 156.3, 149.4, 147.3, 142.9, 142.3, 135.5, 130.9, 130.3, 129.9, 129.2, 129.0, 128.7,128.1, 127.9, 126.6, 123.3, 121. 8, 111.5, 98.3, 53.0, 49.1. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{26}H_{20}N_3$: 374.1657; found: 374.1660.

*11-Phenyl-4-(p-tolyl)-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]-naphthyridine (**3b**).* Yellow solid (dichloromethane/methanol = 20:1) (216 mg, 56%), mp 234.1−235 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 7.74−7.71 (m, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.56−7.54 (m, 2H), 7.53−7.50 (m, 4H), 7.24 (d, J = 7.5 Hz, 2H), 6.62 (s, 1H), 3.87−3.76 (m, 4H), 2.42 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6) δ 158.6, 154.9, 149.7, 146.6, 142.4, 139.6, 136. 5, 135.1, 130.9, 129.7, 129.3, 129. 0, 128.7, 128.0, 127.6, 126.6, 124.3, 121.3, 110.8, 96.8, 52.9, 48.2, 21.0. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{27}H_{22}N_3$: 388.1814; found: 388.1822.

*11-Phenyl-4-(m-tolyl)-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]-naphthyridine (**3c**).* Yellow solid (dichloromethane/methanol = 20:1) (158 mg, 41%), mp > 250 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.85 (t, J = 8.0 Hz, 1H), 7.68−7.59 (m, 3H), 7.56−7.53 (m, 3H), 7.44−7.36 (m, 3H), 7.35−7.32 (m, 1H), 7.04 (s, 1H), 4.19−4.11 (m, 2H), 3.96−3.92 (m, 2H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.7, 156.1, 149.5, 147.7, 142.7, 135.9, 135.6, 131.2, 130.6, 130.2, 130.1, 129.2, 128.4, 128.2, 127.7, 127.1, 126.7, 126.1, 123.7, 122.1, 112.6, 98.9, 53.2, 49.3, 20.2. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{27}H_{22}N_3$: 388.1814; found: 388.1805.

*4-(3-Chlorophenyl)-11-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3d**).* Yellow solid (dichloromethane/methanol = 20:1) (195 mg, 48%), mp 169.8−170.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.5 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 7.5 Hz, 1H), 7.66 (s, 1H), 7.60−7.50 (m, 7H), 7.37−7.36 (m, 2H), 6.63 (s, 1H), 3.83 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.9, 156.1, 149.7, 147.4, 144.0, 143.0, 135.7, 133.5, 130.9, 130.4, 129.9, 129.5, 129.1, 129.0, 128.2, 127.9, 127.5, 126.9, 123.4, 121.9, 111.5, 98.1, 53.3, 49.1. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{26}H_{19}ClN_3$: 408.1268; found: 408.1276.

*4-(Naphthalen-2-yl)-11-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3e**).* Yellow solid (dichloromethane/methanol = 20:1) (194 mg, 46%), mp 231.6−232.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 7.5 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.92−7.71 (m, 6H), 7.61−7.56 (m, 3H), 7.60−7.52 (m, 3H), 7.48−7.41 (m, 2H), 6.71 (s, 1H), 3.82−3.69 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.2, 156.2, 149.5, 147.6, 143.0, 140.0, 135.7, 133.6, 133.5, 130.9, 130.5, 129.9, 129.0, 128.9, 128.1, 127.9, 127.9, 127.7, 126.8, 126.7, 126.1, 125.6, 123.4, 121.9, 98.3, 53.1, 49.1. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{30}H_{22}N_3$: 424.1814; found: 424.1814.

*11-Phenyl-4-(pyridin-3-yl)-1,2-dihydrobenzo[f]imidazo[2,1-a]-[2,7]naphthyridine (**3f**).* Yellow solid (dichloromethane/methanol = 20:1) (164 mg, 44%), mp 139.2−143.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 7.76 (t, J = 7.0 Hz, 1H), 7.66 (s, 1H), 7.61−7.54 (m, 4H), 7.55−7.49 (m, 3H), 7.40−7.35 (m, 2H), 6.65 (s, 1H), 3.84 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.7, 156.0, 149.6, 147.2, 143.9, 142.9, 135.5, 133.5, 130.9, 130.3, 129.9, 129.4, 128.9, 128.2, 127.8, 127.4, 126.8, 123. 3, 121.9, 111.4, 98.1, 53.2, 49.0. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{25}H_{19}N_4$: 375.1610; found: 375.1618.

*11-Phenyl-4-(pyridin-4-yl)-1,2-dihydrobenzo[f]imidazo[2,1-a]-[2,7]naphthyridine (**3g**).* Yellow solid (dichloromethane/methanol = 20:1) (160 mg, 43%), mp 243.4−244.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (s, 2H), 8.19 (d, J = 7.5 Hz, 1H), 8.11 (d, J = 8.0 Hz,

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1H), 7.81−7.73 (m, 1H), 7.61−7.51 (m, 8H), 6.64 (s, 1H), 3.81 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.9, 155.8, 150.3, 149.9, 149.3, 147.4, 143.0, 135.5, 131.1, 130.5, 129. 9, 129.0, 127.9, 127.2, 123.9, 123.4, 122.2, 111.4, 97.9, 53.3, 49.1. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{25}H_{19}N_4$: 375.1610; found: 375.1618.

*4-(Furan-2-yl)-11-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a]-[2,7]naphthyridine (**3h**).* Yellow solid (dichloromethane/methanol = 20:1) (170 mg, 47%), mp 169.3−170.9 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.76 (t, J = 7.5 Hz, 1H), 7.60 (s, 1H), 7.58−7.50 (m, 6H), 7.08 (d, J = 3.0 Hz, 1H), 6.68 (s, 1H), 6.59 (s, 1H), 4.03−3.99 (m, 2H), 3.94−3.90 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8, 153.6, 149.5, 148.5, 147.5, 143.1, 143.0, 135.4, 131.1, 130.5, 130.0, 129.1, 127.9, 127.1, 123.4, 122.0, 111.7, 111.6, 111.3, 98.7, 52.9, 49.3. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}N_3O$: 364.1444; found: 364.1440.

*11-Phenyl-4-(thiophen-2-yl)-1,2-dihydrobenzo[f]imidazo[2,1-a]-[2,7]naphthyridine (**3i**).* Yellow solid (dichloromethane/methanol = 20:1) (170 mg, 45%), mp 181.5−183.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 3.5 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.58−7.55 (m, 2H), 7.54−7.49 (m, 4H), 7.43 (d, J = 5.0 Hz, 1H), 7.12−7.09 (m, 1H), 6.62 (s, 1H), 3.97−3.93 (m, 2H), 3.87−3.84 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 154.8, 151.0, 149.5, 146.3, 143.4, 143.0, 134.5, 131.5, 130.2, 130.0, 129.3, 129.0, 128.8, 128.1, 128.0, 127.0, 127.0, 124.5, 121.0, 98.5, 51.3, 48.6. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{24}H_{18}N_3S$: 380.1221; found: 380.1225.

*11-Phenyl-4-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzo[f]-imidazo[2,1-a][2,7]naphthyridine (**3j**).* Yellow solid (dichloromethane/methanol = 20:1) (185 mg, 42%), mp 230.7−231.3 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 8.53 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.84−7.80 (m, 1H), 7.76−7.69 (m, 6H), 7.64−7.61 (m, 1H), 7.59−7.54 (m, 3H), 6.88 (s, 1H), 3.86−3.82 (m, 2H), 3.65−3.61 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 157.1, 154.7, 149.8, 146.5, 142.6, 134.9, 131.2, 129.8, 129.7, 129.4, 128.8, 128.7, 128.0, 127.1, 124.6 (q, J = 270 Hz), 124.4, 124.0 (q, J = 3.75 Hz), 121.5, 119.8, 110.4, 97.3, 52.6, 48.2. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{19}F_3N_3$: 442.1526; found: 442.1520.

*11-(4-Chlorophenyl)-4-(p-tolyl)-1,2-dihydrobenzo[f]imidazo-[2,1-a][2,7]naphthyridine (**3k**).* Yellow solid (dichloromethane/methanol = 20:1) (181 mg, 43%), mp > 250 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.76−7.71 (m, 1H), 7.63 (d, J = 8.0 Hz, 2H), 7.57−7.52 (m, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.60 (s, 1H), 3.82 (m, 4H), 2.45 (s, 3H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2, 156.2, 149.8, 147.3, 142.9, 140.9, 140.1, 133.9, 132.8, 130.8, 130.7, 130.3, 129.6, 127.9, 127.7, 126.7, 123.3, 121.9, 111.5, 97.6, 53.4, 49.0, 21.5. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{21}ClN_3$: 422.1424; found: 422.1432.

*11-(4-Bromophenyl)-4-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3l**).* Yellow solid (dichloromethane/methanol = 20:1) (220 mg, 49%), mp 129.4−132.3 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 8.86 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.05−7.99 (m, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.82−7.79 (m, 1H), 7.77−7.73 (m, 4H), 7.58−7.57 (m, 3H), 4.40−4.36 (m, 2H), 3.78−3.74 (m, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 157.3, 155.4, 146.7, 146.3, 143.5, 138.9, 133.1, 132.0, 131.8, 130.9, 129.7, 129.4, 128.5, 128.2, 127.2, 125.1, 124.4, 120.5, 106.5, 99.5, 49.6, 46.1. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{19}BrN_3$: 452.0762; found: 452.0760.

*11-(3-Bromophenyl)-4-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3m**).* Yellow solid (dichloromethane/methanol = 20:1) (230 mg, 51%), mp 221.4−222.1 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.5 Hz, 1H), 7.77 (t, J = 7.5 Hz, 1H), 7.73 (s, 1H), 7.69−7.63 (m, 3H), 7.57 (t, J = 7.5 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.46−7.38 (m, 4H), 6.66 (s, 1H), 3.83 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.3, 156.0, 147.8, 147.4, 142.6, 142.2, 137.5, 132.9, 131.0, 130.9, 130.5, 130.4, 129.1, 128.2, 127.9, 126.8, 126.5, 123.3, 123.0, 121.7, 111.8, 98.7, 53.2, 49.1. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{19}BrN_3$: 452.0762; found: 452.0763.

*4-Phenyl-11-(4-(trifluoromethyl)phenyl)-1,2-dihydrobenzo[f]-imidazo[2,1-a][2,7]naphthyridine (**3n**).* Yellow solid (dichloromethane/methanol = 20:1) (180 mg, 41%), mp 136.8−139.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.5 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.84−7.75 (m, 3H), 7.73−7.71 (m, 2H), 7.68−7.67 (m, 2H), 7.59−7.56 (m, 1H), 7.49−7.39 (m, 3H), 6.71 (s, 1H), 3.84 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.5, 156.2, 147.3, 147.0, 143.1, 140.6, 137.6, 132.5 (q, J = 32.5 Hz), 132.2, 130.6, 129.9, 129.2, 128.9, 128.7, 127.7, 126.3 (q, J = 3.75 Hz), 123.7 (q, J = 265 Hz), 123.4, 121.2, 109.8, 102.8, 49.7. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{19}F_3N_3$: 442.1531; found: 442.1533.

*11-(Naphthalen-2-yl)-4-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3o**).* Yellow solid (dichloromethane/methanol = 20:1) (169 mg, 40%), mp 227.9−229.9 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, J = 8.0 Hz, 1H), 8.16−8.15 (m, 2H), 8.04−7.92 (m, 3H), 7.82 (t, J = 7.5 Hz, 1H), 7.76−7.68 (m, 3H), 7.66−7.59 (m, 3H), 7.53−7.46 (m, 3H), 7.09 (s, 1H), 4.14 (t, J = 10.0 Hz, 2H), 3.94 (t, J = 10. 0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.2, 156.4, 149.4, 147.4, 143.0, 142.0, 133.7, 133.1, 132.6, 131.2, 130.4, 129.2, 128.9, 128.6, 128.4, 128.1, 128.0, 127.7, 127.6, 127.4, 127.3, 126.9, 125.0, 123.4, 121.7, 99.6, 52.4, 49.4. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{30}H_{22}N_3$: 424.1808; found: 424.1803.

*11-(4-Chlorophenyl)-4-phenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]naphthyridine (**3p**).* Yellow solid (dichloromethane/methanol = 20:1) (179 mg, 44%), mp 164.7−167.3 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 7.78−7.74 (m, 1H), 7.68−7.66 (m, 2H), 7.59−7.55 (m, 1H), 7.54−7.49 (m, 4H), 7.48−7.41 (m, 3H), 6.66 (s, 1H), 3.85−3.79 (m, 4H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.3, 156.1, 148.2, 147.4, 142.7, 142.2, 136.1, 133.9, 131.0, 130.4, 129.3, 129.2, 129.1, 128.2, 128.0, 126.8, 123.3, 121.7, 111.7, 98.7, 53.1, 48. 9. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{19}ClN_3$: 408.1268; found: 408.1258.

*11-(3-Methoxyphenyl)-4-phenyl-1,2-dihydrobenzo[f]imidazo-[2,1-a][2,7]naphthyridine (**3q**).* Yellow solid (dichloromethane/methanol = 20:1) (173 mg, 43%), mp 244.8−245.6 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 8.67 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.88 (t, J = 7.0 Hz, 1H), 7.68 (t, J = 7.0 Hz, 1H), 7.62−7.59 (m, 2H), 7.51 (t, J = 8.5 Hz, 1H), 7.47−7.43 (m, 3H), 7.37 (s, 1H), 7.32−7.28 (m, 2H), 7.15 (dd, J = 8.0, 1.5 Hz, 1H), 4.08 (t, J = 10.0 Hz, 2H), 3.86 (s, 3H), 3.67 (t, J = 10.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 159. 8, 158. 5, 155.5, 149.1, 146.9, 143.4, 141.3, 135.7, 132.3, 130.5, 129.9, 129.6, 128.8, 128.1, 127.8, 125.2, 121.4, 120.9, 116.4, 114.2, 109.3, 101.4, 55.9, 50.2, 49.3. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{27}H_{22}N_3O$: 404.1757; found: 404.1763.

*8-Chloro-4,11-diphenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]-naphthyridine (**3r**).* Yellow solid (dichloromethane/methanol = 20:1) (195 mg, 48%), mp 218.9−220.2 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 2.0 Hz, 1H), 8.06 (d, J = 9.0 Hz, 1H), 7.74 (dd, J = 9.0, 2.0 Hz, 1H), 7.69−7.68 (m, 2H), 7.64−7.62 (m, 2H), 7.56−7.54 (m, 3H), 7.50−7.45 (m, 3H), 6.93 (s, 1H), 4.14 (t, J = 10.0 Hz, 2H), 3.93 (t, J = 10.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.9, 156.2, 149.3, 145.7, 142.5, 140.5, 134.0, 133.3, 132.5, 132.0, 130.6, 129.3, 129.2, 128.6, 128.2, 128.1, 122.9, 122.2, 110.1, 101.5, 50.1, 49.7. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{19}ClN_3$: 408.1262; found: 408.1254.

*8-Chloro-4,11-diphenyl-1,2-dihydrobenzo[f]imidazo[2,1-a][2,7]-naphthyridine (**3s**).* Yellow solid (dichloromethane/methanol = 20:1) (207 mg, 46%), mp 233.9−234.7 °C. ^1H NMR (500 MHz, DMSO-d_6) δ 8.77 (d, J = 2.0 Hz, 1H), 7.88−7.86 (m, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.72−7.68 (m, 2H), 7.56−7.52 (m, 3H), 7.52−7.49 (m, 2H), 7.37−7.35 (m, 3H), 6.90 (s, 1H), 3.82 (t, J = 10.0 Hz, 2H), 3.61 (t, J = 10.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, DMSO-d_6) δ 159.5, 155.1, 150.6, 145.7, 142.5, 142.3, 135.2, 134.4, 131.8, 130.2, 129.4, 129.1, 128.5, 128.0, 127.5, 127.2, 123.3, 120.4, 111.6, 97.5, 53.2, 48.7. HRMS (ESI-TOF): m/z $[M + H]^+$ calcd for $C_{26}H_{19}BrN_3$: 452.0757; found: 452.0760.

Typical Procedure for the Synthesis of 3-Azaheterocyclic Substituted 2-Arylquinolines 4. A mixture of heterocyclic ketene aminals (HKAs) **1** (1.0 mmol) and 2-aminochalcones **2** (1.5 mmol,

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1.5 equiv) was dissolved in HOAc (3.0 mL), and the reaction mixture was stirred at 80 °C in an oil bath in air for 12−24 h. Upon the completion *via* TLC detection, the reaction was quenched with aqueous $NaHCO_3$ (5 mL) and then extracted three times with DCM. The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by silica-gel chromatography using DCM/MeOH affords **4**.

*3-(4,5-Dihydro-1H-imidazol-2-yl)-2-phenylquinoline (**4a**).* Yellow oil (dichloromethane/methanol = 5:1) (182 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.80−7.75 (m, 3H), 7.59−7.56 (m, 1H), 7.53−7.46 (m, 3H), 3.63 (s, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.9, 156.6, 148.3, 139.8, 138.7, 130.93, 129.4, 129.3, 128.7, 128.6, 128.1, 127.2, 126.4, 124.2, 50.6. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{18}H_{16}N_3$: 274.1339; found: 274.1344.

*3-(4,5-Dihydro-1H-imidazol-2-yl)-2-(4-(trifluoromethyl)phenyl)-quinoline (**4b**).* Brown oil (dichloromethane/methanol = 5:1) (204 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.79−7.76 (m, 3H), 7.66 (d, J = 8.5 Hz, 2H), 7.61−7.60−7.57 (m, 2H), 3.59 (s, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.9, 154.8, 148.3, 142.7, 138.9, 131.7, 131.0 (q, J = 32.5 Hz), 129.4, 129.3, 128.1, 127.9, 126.0, 125.3, 124.0 (q, J = 270 Hz), 121.6, 48.6, 48.5. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{19}H_{15}F_3N_3$: 342.1213; found: 342.1222.

*2-Phenyl-3-(1,4,5,6-tetrahydropyrimidin-2-yl)quinoline (**4c**).* Yellow oil (dichloromethane/methanol = 5:1) (209 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14−8.08 (m, 1H), 8.01−7.96 (m, 1H), 7.77−7.72 (m, 2H), 7.71−7.65 (m, 1H), 7.62−7.59 (m, 1H), 7.47−7.41 (m, 1H), 7.38−7.32 (m, 3H), 3.04 (s, 4H), 1.59 (s, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.2, 155.7, 147.8, 139.7, 137.5, 130.3, 130.2, 129.1, 128.8, 128.7, 128.2, 127.8, 126.8, 126.4, 41.9, 19.9. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{19}H_{18}N_3$: 288.1495; found: 288.1489.

*2-Phenyl-3-(4,5,6,7-tetrahydro-1H-1,3-diazepin-2-yl)quinoline (**4d**).* Green oil (dichloromethane/methanol = 5:1) (228 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.09 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.77−7.76 (m, 2H), 7.72−7.68 (m, 1H), 7.53−7.50 (m, 1H), 7.47−7.44 (m, 2H), 7.42−7.38 (m, 1H), 3.07 (s, 4H), 1.63−1.62 (m, 4H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.0, 156.1, 146.9, 139.2, 137.2, 131.2, 129.4, 128.2, 127.8, 127.7, 127.5, 126.9, 125.9, 125.5, 56.9, 52.4, 47.5, 27.6. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{20}H_{20}N_3$: 302.1652; found: 302.1657.

*3-(5,5-Dimethyl-1,4,5,6-tetrahydropyrimidin-2-yl)-2-(p-tolyl)-quinoline (**4e**).* Yellow soild (dichloromethane/methanol = 5:1) (256 mg, 78%), mp 187.1−187.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 8.01 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 6.5 Hz, 3H), 7.48 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 2H), 2.81 (s, 4H), 2.36 (s, 3H), 0.86 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.5, 154.5, 147.9, 138.7, 137.7, 137.1, 130.2, 130.2, 129.2, 129.1, 128.8, 127.8, 126.7, 126.5, 54.1, 26.3, 25.3, 21.4. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{22}H_{24}N_3$: 330.1965; found: 330.1975.

*6-Chloro-3-(5,5-dimethyl-1,4,5,6-tetrahydropyrimidin-2-yl)-2-(p-tolyl)quinoline (**4f**).* Brown solid (dichloromethane/methanol = 5:1) (250 mg, 69%), mp 122.9−123.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.65 (d, J = 2.0 Hz, 1H), 7.59 (dd, J = 9.0, 2.5 Hz, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 2.67 (s, 4H), 2.31 (s, 3H), 0.78 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 177.0, 158.0, 156.7, 146.7, 139.3, 137.7, 135.9, 132.9, 132.3, 130.9, 129.2, 128.9, 126.8, 126.1, 124.7, 51.0, 25.5, 24.6, 23.7, 21.4. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{22}H_{23}ClN_3$: 364.1575; found: 364.1569.

*3-(5,5-Dimethyl-1,4,5,6-tetrahydropyrimidin-2-yl)-6-methoxy-2-(p-tolyl)quinoline (**4g**).* Brown oil (dichloromethane/methanol = 5:1) (197 mg, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.33 (dd, J = 9.5, 3.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 3.0 Hz, 1H), 3.88 (s, 3H), 2.83 (s, 4H), 2.35 (s, 3H), 0.88 (s, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 158.3, 157.2, 153.8, 144.7, 138.9, 137.5, 136.7, 130.8, 129.4, 129.0, 127.3, 124.3, 105.5, 55.9, 52.5, 26.1, 25.1, 24.2, 21.5. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{23}H_{26}N_3O$: 360.2070; found: 360.2075.

*2-Phenylquinoline (**5a**).* Colorless liquid (dichloromethane/methanol = 100:1) (88 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24−8.16 (m, 4H), 7.88 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.75−7.72 (m, 1H), 7.57−7.51 (m, 3H), 7.52−7.46 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.5, 148.4, 139.8, 136.9, 129.9, 129.8, 129.4, 129.0, 127.7, 127.6, 127.3, 126.4, 119.1. HRMS (ESI-TOF): m/z [M + H]$^+$ calcd for $C_{15}H_{12}N$: 206.0964; found: 206.0958.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00112.

HRMS spectra for the key intermediates in the proposed mechanism, X-ray crystallography data for **3b** as well as photophysical data of **3g**, and copies of NMR spectra of final products (PDF)

Accession Codes

CCDC 2041905 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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