Heterogeneous & Homogeneous & Bio- & Nano-

CHEMCATCHEM

CATALYSIS

# Accepted Article

**Title:** Merging Visible-Light-Photoredox and LewisAcid-Catalysis for the Intramolecular Aza-Diels-Alder Reaction: Synthesis of Substituted Chromeno[4,3-b]quinolines and [1,6]Naphthyridines

**Authors:** Wuheng Dong, Yao Yuan, Xiaoshuang Gao, Bei Hu, Xiaomin Xie, and Zhao-Guo Zhang



**To be cited as:** *ChemCatChem* 10.1002/cctc.201800192

**Link to VoR:** http://dx.doi.org/10.1002/cctc.201800192

A Journal of

ChemPubSoc Europe

WILEY-VCH

www.chemcatchem.org

# Merging Visible-Light-Photoredox and Lewis-Acid-Catalysis for the Intramolecular Aza-Diels-Alder Reaction: Synthesis of Substituted Chromeno[4,3-*b*]quinolines and [1,6]Naphthyridines

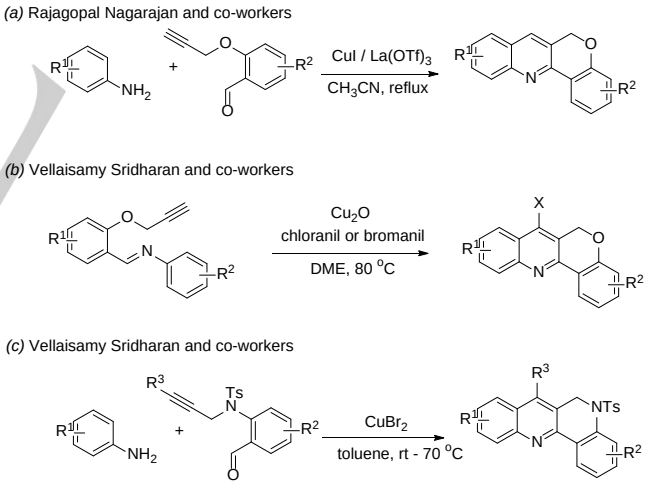
Wuheng Dong[a], Yao Yuan[a], Xiaoshuang Gao[a], Bei Hu[a], Xiaomin Xie[a], and Zhaoguo Zhang* [a], [b]

Dedication ((optional))

**Abstract:** Substituted chromeno[4,3-*b*]quinolines and [1,6]naphthyridines was achieved by tandem intramolecular aza-Diels-Alder reaction using a strategy of combination of visible-light-photoredox and Lewis-acid-catalysis. This intramolecular aza-Diels-Alder cycloaddition took place between the in situ generated benzylidene anilines derived from arylamines and salicylaldehyde or 2-aminoaryl aldehydes bearing a tethered alkene partner, followed by oxidative aromatization to give the target products. The study on the oxidative aromatization step reaveled that it is much faster than the cyclization step; both the combination of imine and Lewis acid, and the combination of photocatalyst and Lewis acid under aerobic condition with the irridation of visible light are efficient to achieve the transformation. This method provided a new access to the synthesis of important heterocycles under mild reaction conditions.

## Introduction

Substituted chromenoquinolines and 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines are biologically significant compounds, which widely occur in natural products, pharmaceuticals and bioactive materials.[1] For examples, 6*H*-chromeno[4,3-*b*]quinolines have been used as estrogen receptor β-selective ligands[1b] and as bioimaging reagents,[1e,1f] the spiro analogues of benzothiazolylchromeno derivatives have shown cytotoxic activity against breast cancer cells,[2] and dibenzo[*b*,*h*][1,6]naphthyridines have found applications in fluorescent DNA labelling due to their fluorescent properties.[3] Because of their biological importance, the development of methods for the preparation of them has attracted much attention from organic chemists.[1b,1e,3-4] One of the most efficient methods for their preparation was the aza-Diels-Alder reaction of *N*-aryl imines derived from aldehydes and anilines with electron-rich olefins or alkynes.[5] To furnish the quinolone structure, further oxidation of the corresponding tetrahydro / dihydroquinoline was usually conducted under harsh reaction conditions and toxic oxidants were often used.[6] Recently, chromenoquinoline skeleton have been synthesized, involving the copper-catalyzed aza-Diels-Alder reaction / aromatization cascade (**Scheme 1a,**[7] **1b**[8]), and the reaction of diaryliodonium triflates and arylpropynyloxy-benzonitriles.[9] In addition, the 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines have also been synthesized by the copper-catalyzed aza-Diels-Alder reaction / aromatization cascade reaction (**Scheme 1c**).[10] It is noteworthy that the above-mentioned reactions involve an alkyne group as dienophile. Given the importance of chromenoquinolines and 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines, developing a simple and efficient protocol for the acquisition of them from readily available starting materials under mild conditions is highly desirable.



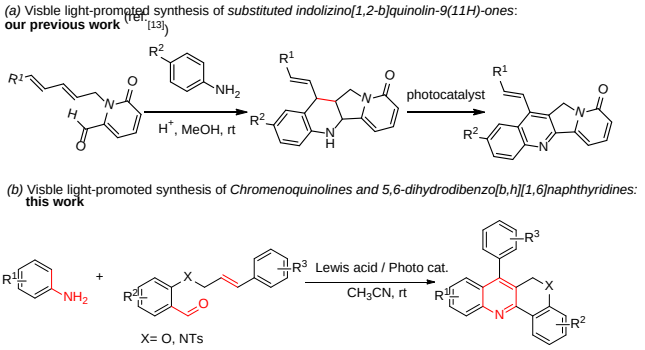

**Scheme 1.** One-pot access to chromenoquinolines and dibenzo[*b*,*h*][1,6]naphthyridines

Visible light photoredox reaction has revealed its power in organic synthesis,[11] especially in the oxidation reaction of amines to iminium ions followed by further functionalization.[12] Recently, we have reported the synthesis of substituted indolizino[1,2-*b*]quinolin-9(11*H*)-ones by merging visible-light-photoredox and Lewis acid catalysis.[13] In this work, the intramolecular aza-Diels-Alder cycloaddition between the in situ generated benzylidene anilines derived from arylamines and 6-oxo-1,6-dihydropyridine-2-carbaldehyde bearing a tethered

[a] Wuheng Dong, Yao Yuan, Bei Hu, Xiaoshuang Gao, Xiaomin Xie, and Zhaoguo Zhang * [a]
Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering
Shanghai Jiao Tong University
800 Dongchuan Road, Shanghai 200240, China
E-mail: zhaoguo@sjtu.edu.cn
[b] Shanghai Institute of Organic Chemistry
Chinese Academy of Sciences
345 Lingling Road, Shanghai 200032, China

Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate))

alkene partner, followed by a visible-light-induced photocatalytic aerobic oxidative aromatization to give the target products (**Scheme 2a**). Base on this work, we speculated that salicylaldehyde or 2-aminoaryl aldehydes could replace the 6-oxo-1,6-dihydropyridine-2-carbaldehyde to give the substituted chromeno[4,3-*b*]quinolines and [1,6]naphthyridines (**Scheme 2b**). Herein, we disclose the preparation of substituted chromeno[4,3-*b*]quinolines and [1,6]naphthyridines from readily available starting materials by merging visible-light-photoredox and Lewis acid catalysis.

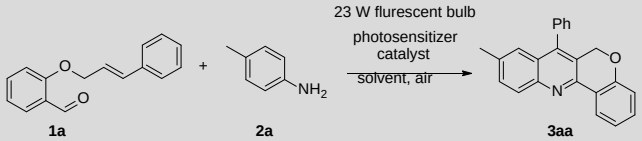



**Scheme 2.** Visible light-promoted synthesis of *N*-containing heterocycles skeleton.

## Results and Discussion

Initially, we tested the reaction of 2-(cinnamyloxy)benzaldehyde (**1a**) and *p*-toluidine (**2a**) using $Ru(bpy)_3(PF_6)_2$ (2 mol %) as photosensitizer and $CH_3CN$ as solvent under the irradiation of a 23 W household compact fluorescent lamp (CFL) at room temperature. Unfortunately, no desired compound was detected (**Table 1,** entry 1). We believe that the Lewis acid might play an important role in the formation of an imine intermediate and aza-Diels-Alder cycloaddition. [5a, 5h, 12d] When $Zn(OTf)_2$ (10 mol %) was employed as a catalyst to trigger this transformation, the reaction occurred in 72% yield (**Table 1,** entry 2). Other acid, such as $FeCl_3$, TsOH, and $BF_3.Et_2O$, were also tested for this transformation, to our delight, $BF_3.Et_2O$ was the most effective and an 85% isolated yield was obtained (**Table 1,** entries 3-5). Next, some commonly-used photosensitizer were investigated, and $Ru(bpy)_3(PF_6)_2$ was proved superior to others (**Table 1,** entries 6-10). Besides, we tested the solvents in this reaction, and acetonitrile was found to be the best solvent (**Table 1,** entries 11-13). Control experiments showed that both oxygen and visible light were essential for this reaction, only 24% of desired product was obtained when oxygen was absent, and only 30% yield was obtained when the reaction was conducted in the dark (**Table 1,** entries 14 and 15). Interestingly, the product **3aa** was obtained in 62% yield, even if the photosensitizer was absent (**Table 1,** entry 17).

**Table 1.** Optimization of the reaction conditions[a]



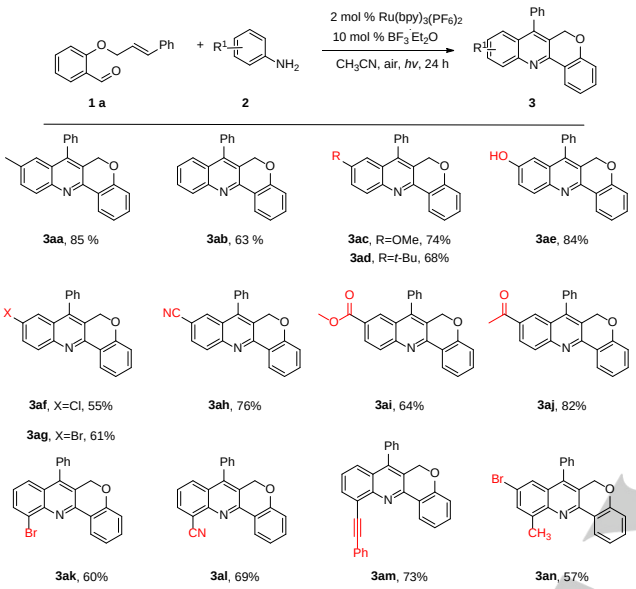

| Entry | Photosensitizer | Catalyst | Solvent | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $Ru(bpy)_3(PF_6)_2$ | | $CH_3CN$ | 0 |
| 2 | $Ru(bpy)_3(PF_6)_2$ | $Zn(OTf)_2$ | $CH_3CN$ | 72 |
| 3 | $Ru(bpy)_3(PF_6)_2$ | $FeCl_3$ | $CH_3CN$ | 41 |
| 4 | $Ru(bpy)_3(PF_6)_2$ | $TsOH.H_2O$ | $CH_3CN$ | 41 |
| 5 | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | $CH_3CN$ | 87 (85[c]) |
| 6 | $Ru(bpy)_3Cl_2 6H_2O$ | $BF_3.Et_2O$ | $CH_3CN$ | 58 |
| 7 | $[Ir(ppy)_2bpy]PF_6$ | $BF_3.Et_2O$ | $CH_3CN$ | 78 |
| 8 | $[Ir(ppy)_2dtb\text{-}bpy]PF_6$ | $BF_3.Et_2O$ | $CH_3CN$ | 72 |
| 9 | EosinY | $BF_3.Et_2O$ | $CH_3CN$ | 71 |
| 10 | EosinY Na | $BF_3.Et_2O$ | $CH_3CN$ | 67 |
| 11 | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | MeOH | 70 |
| 12 | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | DMSO | 47 |
| 13 | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | DCM | 45 |
| 14[d] | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | $CH_3CN$ | 24 |
| 15[e] | $Ru(bpy)_3(PF_6)_2$ | $BF_3.Et_2O$ | $CH_3CN$ | 30 |
| 16[e] | ------ | $BF_3.Et_2O$ | $CH_3CN$ | 33 |
| 17[f] | ------ | $BF_3.Et_2O$ | $CH_3CN$ | 62 |

[a] Conditions: **1a** (71.6 mg, 0.3 mmol), **2a** (33.6 mg, 0.3 mmol), photosensitizer (2 mol %), acid catalyst (10 mol %), solvent (3 mL), irradiation with a 23 W household light bulb at rt for 24 h. [b] $^1$HNMR yield was reported using 4,4'-ditertbutylbiphenyl as an internal standard. [c] Isolated yield. [d] Reaction mixture was degassed and carried out under $N_2$ atmosphere. [e] Reaction was carried out in the dark. [f] Without photosensitizer.

Under the optimized reaction conditions, we explored the substrate scope. As shown in **Scheme 3,** a variety of arylamines efficiently coupled with 2-(cinnamyloxy)benzaldehyde (**1a**) under standard reaction conditions to produce the corresponding chromenoquinolines **3** in good yields. Anilines with an electron-donating or weak electron-withdrawing group on the para-position of the benzene ring afforded the desired products in moderate to good yields (**Scheme 3**, **3ab-3ag**). Interestingly, hydroxyl, chloro, and bromo groups on the phenyl ring were well tolerated, which enable potential applications in further functionalization (**Scheme 3**, **3ae-3ag**). It is noteworthy that substrate with strong electron-withdrawing group such as cyano,

alkoxycarbonyl, and carbonyl group could also work well, and the corresponding products were isolated in good yields (**3ah-3aj**). However, no products were obtained when pyridine-2-amine and pyridine-3-amine were used as substrates. It seemed that steric hindrance did not play any significant role in the reaction, **3ak-3an** were obtained in moderate yields.

**Scheme 3.** Substrate scope-I[a]

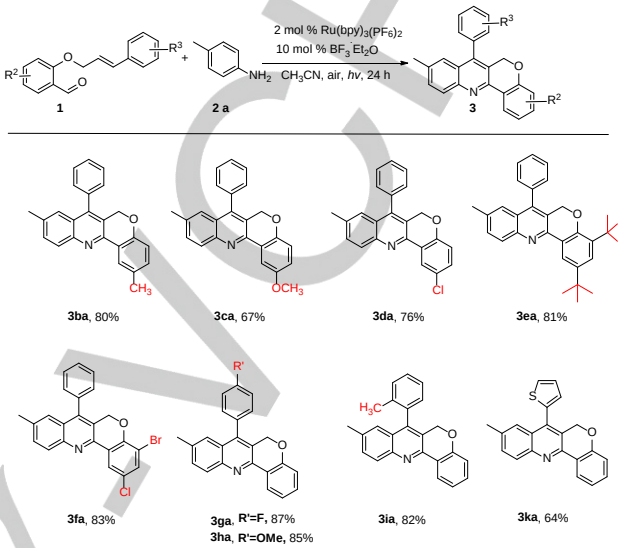



[a] Conditions: **1a** (71.6 mg, 0.3 mmol), **2** (0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (5.3 mg, 2 mol %), $BF_3{\cdot}Et_2O$ (10 mol %), MeCN (3 mL), irradiation with 23 W household light bulb at rt for 24 h.

Next, we extended this cyclization of 2-(cinnamyloxy)-benzaldehyde with substituents on the benzene ring and allyl counterpart (**Scheme 4)**. The substrates bearing alkyl, methoxyl, and halo groups on the salicylaldehyde moiety afforded the corresponding products **3ba**, **3ea**, **3ca**, and **3da** in moderate to good yields. In addition, various $R^3$-substituted aryl groups, such as *p*-fluoro-, *p*-methoxy-, and *o*-methylphenyls showed that the electronic nature of the substituents has hardly any effect on chemical yields, affording the products (**3ga**, **3ha**, and **3ia**) in good yields. Finally, the product **3ka** could be obtained in 64% yield when the heterocyclic substrate **1k** was introduced.

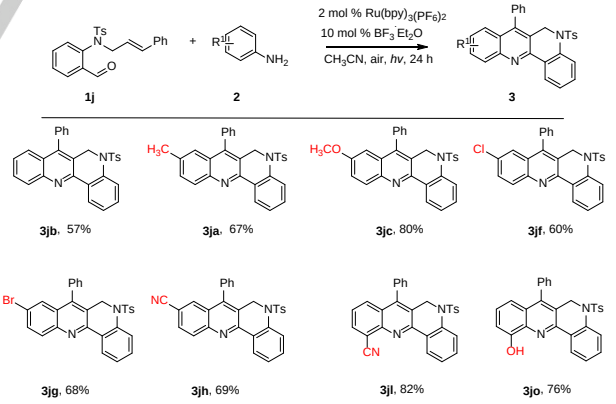
When 2-(cinnamyloxy)benzaldehyde (**1a**) was replaced by *N*-cinnamyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide (**1j**), the corresponding 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines products could be obtained (**Scheme 5)**. Compound **1j** react with **2b** to afford the desired product **3jb** in 57% yield under the same reaction conditions. Anilines bearing an electron-donating or electron-withdrawing substituent also afforded the target products in good to excellent yields (**3ja-3jo**). It is noteworthy that the 2-aminophenol could react with **1j** smoothly to give the corresponding product **3jo** in good yield, which may have a potential application as a biologically significant molecule.[14]

**Scheme 4.** Substrate scope-II[a]




[a] Conditions: **1** (0.3 mmol), **2a** (33.6 mg, 0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (5.3 mg, 2 mol %), $BF_3{\cdot}Et_2O$ (10 mol %), MeCN (3 mL), irradiation with 23 W household light bulb at rt for 24 h.

**Scheme 5.** Substrate scope-III[a]




[a] Conditions: **1j** (117.5 mg, 0.3 mmol), **2** (0.3 mmol), $Ru(bpy)_3(PF_6)_2$ (5.3 mg, 2 mol %), $BF_3{\cdot}Et_2O$ (10 mol %), MeCN (3 mL), irradiation with a 23 W household light bulb at rt for 24 h.

To gain insight into the reaction, a time-concentration profile of the reaction of 2-(cinnamyloxy)benzaldehyde (**1a**) and p-toluidine (**2a**) under the optimized conditions was recorded by $^1H$ NMR spectroscopy. As shown in **Figure 1**, reaction of **1a** and **2a** afforded imine **4aa** in 45% yields within 15 min, along with the

desired product **3aa** and a secondary amine **5aa** in 15% and 33% yields, respectively. It is evident that the rates of formation of imine **4aa** and the oxidation of **I** by **4aa** to give **3aa** are fast. The consumption of **4aa** and **5aa** was fast at the first 4 hours and then was slow. To our surprise, the Diels-Alder adduct **I** was not observed, indicating that the oxidation rate of cycloadduct **I** by the imine **4aa** or the photocatalytic oxidation was much faster than the rate of its formation by Diels-Alder cycloaddition.

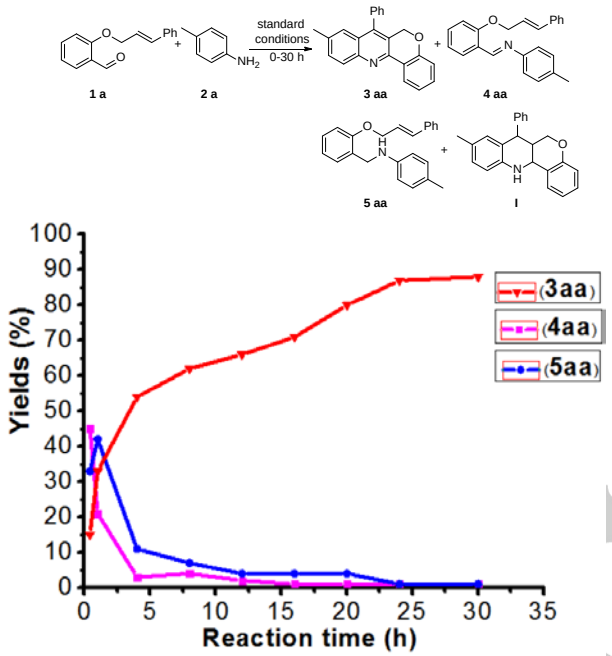
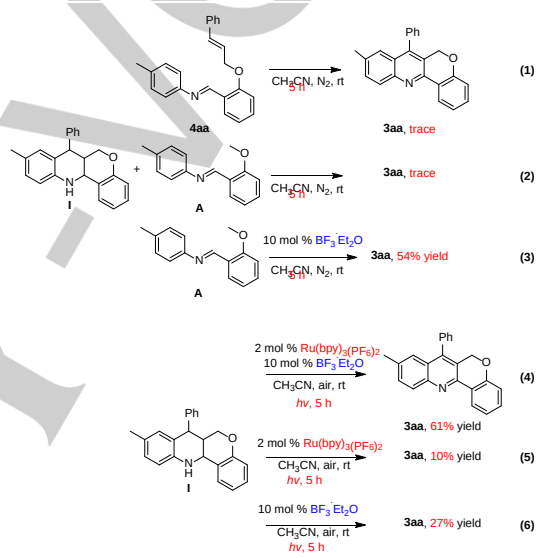


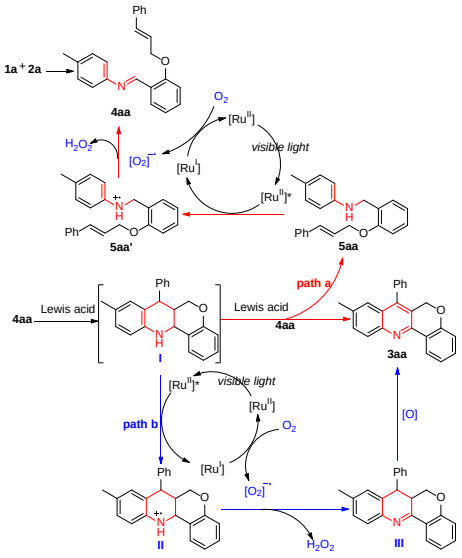

**Figure 1.** The time-concentration profile of the model reaction

To further clarify the product-forming profile, a series of verification experiments were performed as shown in Scheme 2. When Diels-Alder adduct product I and the imine (**4aa** or **A**, 2.5 equiv.) were treated in $CH_3CN$ at room temperature for 5 h under $N_2$ atmosphere, trace of the corresponding quinoline 3aa was observed (**Scheme 6**, **eq. 1** and **2**). However, in the presence of 10 mol % $BF_3.Et_2O$, under albeit the same reaction conditions as shown in **eq. 2**, the target product **3aa** could be obtained in 54% yield (**Scheme 6**, **eq. 3**), revealing that $BF_3.Et_2O$ plays the key role in accelerating the oxidation. Then, the reaction of the Diels-Alder adduct **I** under standard conditions to yield product **3aa** (61%) for 5 h (**Scheme 6**, **eq. 4**). It is noteworthy that only 10% of desired product was obtained when $BF_3.Et_2O$ was absent, and 27% yield was obtained when $Ru(bpy)_3(PF_6)_2$ was absent (**Scheme 5**, **eq. 5** and **6**). These results indicated that the adduct product **I** could also be efficiently oxidized in the presence of both photocatalyst and Lewis acid.

On the basis of the above experiments and previous reports, [12d] a plausible mechanism for the reaction is proposed in **Scheme 7**. The imine **4aa** is formed via condensation of **1a** and **2a**, followed by aza-Diels-Alder reaction to give the intermediate **I**. Then, the intermediate **I** was oxidized by the imine **4aa** in the presence of a Lewis acid to give the target product **3aa** and the amine **5aa** (**path a**). Subsequent the amine **5aa** was oxidized by the excited $Ru^{II}$* to give the radical amine cation **5aa'** and the reduced species $Ru^{I}$, which could be oxidized by oxygen to regenerate the $Ru^{II}$ catalyst. The intermediate **5aa'** was converted to the imine **4aa** by the $O_2$ or $O_2^{\bullet-}$ under the influence of the Lewis acid catalyst. Notably the peroxide was could be detected by the starch / KI test paper. It is also possible that the intermediate **I** was oxidized by the photocatalyst and Lewis acid under the irradiation of visible light to give the target product **3aa** (**path b**).




**Scheme 6.** Verification experiments




**Scheme 7.** Proposed mechanism

## Conclusions

In conclusion, we have developed a photocatalytic aerobic aza-Diels-Alder cycloaddition strategy under visible light to construct chromenoquinolines and 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines, which are important skeletons of biologically active molecules. The applicability of readily available starting materials and the use of air as the sole oxidant under the mild reaction conditions make this process very attractive. Further applications of this transformation toward other heterocyclic product are underway.

## Experimental Section

**General Procedures.** Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and were used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz or 500 MHz spectrometer. The chemical shifts for $^1$H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for $^{13}$C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.16 ppm) or dimethyl sulfoxide-d (39.52 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel (300-400 mesh).

**General procedure for the synthesis of substrate (1a-1j)**

The synthetic experimental procedures were based on the literature.[5h,15]

A 250 mL round-bottom flask was charged with cinnamyl bromide (9.47 g, 48 mmol), $K_2CO_3$ (7.19 g, 52 mmol), 2-hydroxybenzaldehyde (4.89 g, 40 mmol), and acetone (60 mL). The mixture was stirred at room temperature under a nitrogen atmosphere for 14 h. After completion, the mixture was filtered and washed with acetone (20 mL× 3). The solvent was removed under reduced pressure, the crude product was purified by silica-gel column chromatography (PE/EA = 20:1) to give 2-(cinnamyloxy)benzaldehyde as a white solid (8.90 g, 93% yield).

**2-(Cinnamyloxy)benzaldehyde**[5h] **(1a):** $R_f$=0.6 (PE/EA 10:1); white solid, 8.90 g, yield: 93%, m.p. 51.1–52.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.58 (d, *J* = 0.8 Hz, 1H), 7.87 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.6, 2.0 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.37 – 7.33 (m, 2H), 7.31 – 7.26 (m, 1H), 7.07 – 7.03 (m, 2H), 6.77 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.44 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.83 (dd, *J* = 5.6, 1.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.9, 161.2, 136.4, 136.2, 133.7, 129.0, 128.8, 128.7, 128.4, 126.9, 125.4, 123.7, 121.2, 113.2, 69.4.

**2-(Cinnamyloxy)-5-methylbenzaldehyde**[15b] **(1b):** $R_f$=0.5 (PE/EA 10:1); yellow solid, 1.10 g, yield: 84%, m.p. 59.5–61.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.54 (s, 1H), 7.66 – 7.65 (m, 1H), 7.44 – 7.41 (m, 2H), 7.37 – 7.32 (m, 3H), 7.30 – 7.26 (m, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.76 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.42 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.80 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.32 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.8, 159.0, 136.5, 136.1, 133.2, 130.2, 128.6, 128.3, 128.1, 126.6, 124.7, 123.6, 113.0, 69.1, 20.2.

**2-(Cinnamyloxy)-5-methoxybenzaldehyde**[15b] **(1c):** $R_f$=0.5 (PE/EA 10:1); white solid, 1.20 g, yield: 87%, m.p. 105.3–107.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.43 – 7.40 (m, 2H), 7.37 – 7.32 (m, 3H), 7.30 – 7.27 (m, 1H), 7.13 (dd, *J* = 9.2, 3.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.75 (dt, *J* = 15.6, 1.6 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.79 (dd, *J* = 6.0, 1.6 Hz, 2H), 3.81 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.8, 156.0, 154.0, 136.4, 133.7, 128.9, 128.4, 126.8, 125.6, 123.9, 123.7, 115.2, 110.5, 70.1, 56.0.

**5-Chloro-2-(cinnamyloxy)benzaldehyde**[15b] **(1d):** $R_f$=0.5 (PE/EA 10:1); white solid, 1.20 g, yield: 90%, m.p. 95.3–97.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.81 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.00 (d, *J* = 9.2 Hz, 1H), 6.75 (dd, *J* = 16.0, 1.6 Hz, 1H), 6.41 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.82 (dd, *J* = 5.6, 1.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.6, 159.6, 136.2, 135.6, 134.2, 129.0, 128.6, 128.1, 126.9, 126.7, 126.1, 123.1, 114.9, 69.8.

**3,5-Di-tert-butyl-2-(cinnamyloxy)benzaldehyde (1e):** $R_f$=0.4 (PE/EA 5:1); white solid, 1.60 g, yield: 89%, m.p. 124.8–125.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.73 (dd, *J* = 2.4, 0.4 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 1H), 6.84 – 6.80 (m, 1H), 6.48 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.65 (dd, *J* = 5.6, 1.6 Hz, 2H), 1.46 (s, 9H), 1.34 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 191.0, 160.0, 146.8, 143.3, 136.6, 133.2, 131.1, 129.7, 128.9, 128.3, 126.9, 124.3, 124.3, 79.5, 35.7, 35.0, 31.6, 31.2. HRMS (ESI-TOF) (m/z): $(M + Na)^+$ Calcd. for $C_{24}H_{30}O_2Na$ 373.2143; Found 373.2155.

**3-Bromo-5-chloro-2-(cinnamyloxy)benzaldehyde (1f):** $R_f$=0.5 (PE/EA 10:1); white solid, 1.60 g, yield: 90%, m.p. 85.2–86.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.82 (d, *J* = 2.8 Hz, 1H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.41 – 7.38 (m, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.27 (m, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 16.0, 6.4 Hz, 1H), 4.77 (dd, *J* = 6.4, 1.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 188.2, 157.5, 138.8, 136.0, 131.9, 131.2, 128.9, 128.7, 127.7, 127.0, 122.6, 119.6, 77.2. HRMS (ESI-TOF) (m/z): $(M + Na)^+$ Calcd. for $C_{16}H_{12}BrClO_2Na$ 372.9607; Found 372.9607.

**(*E*)-2-((3-(4-Fluorophenyl)allyl)oxy)benzaldehyde**[15b] **(1g):** $R_f$=0.2 (PE/EA 10:1); white solid, 1.10 g, yield: 88%, m.p. 57.3–59.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.56 (d, *J* = 0.8 Hz, 1H), 7.86 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 7.07 – 7.01 (m, 4H), 6.73 (dt, *J* = 16.0, 1.6 Hz, 1H), 6.35 (ddd, *J* = 11.6, 6.4, 5.6 Hz, 1H), 4.82 (dd, *J* = 6.0, 1.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.9, 162.8 (d, $J_{C-F}$ = 245.9 Hz), 161.1, 136.2, 132.5, 128.7, 128.4 (d, $J_{C-F}$ = 8.1 Hz), 125.3, 123.4, 121.2, 115.8 (d, $J_{C-F}$ = 21.6 Hz), 113.1, 69.2; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -35.7 (s, 1F).

**(*E*)-2-((3-(4-Methoxyphenyl)allyl)oxy)benzaldehyde**[15b] **(1h):** $R_f$=0.2 (PE/EA 10:1); white solid, 1.10 g, yield: 84%, m.p. 75.0–78.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.56 (d, *J* = 0.8 Hz, 1H), 7.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.2, 1.6 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.06 – 7.02 (m, 2H), 6.90 – 6.86 (m, 2H), 6.73 – 6.68 (m, 1H), 6.29 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.80 (dd, *J* = 6.0, 1.6 Hz, 2H), 3.82 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.1, 161.3, 159.9, 136.1, 133.5, 129.1, 128.6, 128.1, 125.3, 121.3, 121.0, 114.3, 113.2, 69.6, 55.5.

**(*E*)-2-((3-(*o*-Tolyl)allyl)oxy)benzaldehyde (1i):** $R_f$=0.5 (PE/EA 10:1); white solid, 1.00 g, yield: 82%, m.p. 69.6–70.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.57 (d, *J* = 0.8 Hz, 1H), 7.86 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.49 – 7.46 (m, 1H), 7.21 – 7.15 (m, 3H), 7.07 – 6.97 (m, 3H), 6.31 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.85 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.0, 161.2, 136.1, 135.9, 135.5, 131.7, 130.6, 128.7, 128.3, 126.5, 126.0, 125.4, 124.9, 121.1, 113.2,

69.5, 20.0. HRMS (ESI-TOF) (m/z): $(M + Na)^+$ Calcd. for $C_{17}H_{16}O_2Na$ 275.1048; Found 275.1048.

***N*-Cinnamyl-*N*-(2-formylphenyl)-4-methylbenzenesulfonamide**[15a] **(1j):** $R_f$=0.4 (PE/EA 10:1); white solid, 3.60 g, yield: 70%, m.p. 115.8–118 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.41 (d, *J* = 0.8 Hz, 1H), 7.97 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.31 – 7.18 (m, 9H), 6.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.09 (dt, *J* = 15.6, 6.8 Hz, 1H), 4.69 (s, 1H), 4.08 (s, 1H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.3, 144.5, 141.7, 136.2, 136.0, 135.6, 134.8, 134.4, 130.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.2, 126.7, 122.7, 54.4, 21.9.

(*E*)-2-((3-(Thiophen-2-yl)allyl)oxy)benzaldehyde **(1k):** $R_f$=0.4 (PE/EA 20:1); light yellow solid, 1.82 g, yield: 60%, m.p. 77.0–78.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 10.56 (s, 1H), 7.86 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.57 – 7.52 (m, 1H), 7.21 (d, *J* = 4.8 Hz, 1H), 7.07 – 6.97 (m, 4H), 6.89 (d, *J* = 16.0 Hz, 1H), 6.26 (dt, *J* = 16.0, 6.0 Hz, 1H), 4.79 (dd, *J* = 5.6, 1.6 Hz, 2H).; $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.0, 161.1, 141.3, 136.2, 128.7, 127.8, 126.9, 125.3, 123.0, 121.2, 113.1, 69.0. HRMS (ESI-TOF) (m/z): $(M + Na)^+$ Calcd. for $C_{14}H_{12}O_2SNa$ 267.0456; Found 267.0465.

**Typical Procedure: Preparation of 9-Methyl-7-phenyl-6*H*-chromeno [4,3-*b*]quinoline (3aa)**

*Caution!* The reaction is run in a sealed vessel under $O_2$. Though no incidents have been encountered in the submitters' laboratory, it is nonetheless recommended that a blast shield be used as a precaution.

A solution of 2-(cinnamyloxy)benzaldehyde (**1a**, 0.3 mmol, 71.5 mg), *p*-toluidine (**2a**, 0.3 mmol, 33.6 mg), $Ru(bpy)_3(PF_6)_2$ (0.006 mol, 5.3 mg) in $CH_3CN$ (3 mL) was mixed and then $BF_3{\cdot}Et_2O$ (0.03 mol, 9.0 mg) was added. The reaction solution was irradiated with a 23 W fluorescent light (distance app. 5 cm) under air atmosphere at room temperature for 24 h. After the completion of the reaction, the mixture was concentrated in vacuum and the pure product was obtained by flash column chromatography on silica gel (PE/EA = 50:1) to give the product **3aa**.

**9-Methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline**[9] **(3aa):** $R_f$=0.63 (PE/EA 10:1); yellow solid, 82.0 mg, yield: 85%, m.p. 192.0–194.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.38 – 7.29 (m, 3H), 7.22 – 7.16 (m, 2H), 6.98 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.09 (s, 2H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.9, 147.6, 146.4, 142.8, 135.9, 134.8, 131.3, 129.1, 129.0, 128.5, 128.2, 126.7, 125.4, 124.7, 123.4, 122.6, 122.2, 116.9, 66.6, 21.6.

**7-Phenyl-6*H*-chromeno[4,3-*b*]quinoline**[9] **(3ab):** $R_f$=0.79 (PE/EA 10:1); white solid, 58.8 mg, yield: 63%, m.p. 155.0–157.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.18 (ddd, *J* = 8.4, 1.2, 0.8 Hz, 1H), 7.71 – 7.67 (m, 1H), 7.59 – 7.48 (m, 4H), 7.42 – 7.36 (m, 2H), 7.33 – 7.31 (m, 2H), 7.21 – 7.17 (m, 1H), 6.99 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.12 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4, 148.8, 148.2, 143.8, 135.0, 132.0, 129.7, 129.4, 129.3, 128.9, 128.7, 127.2, 126.3, 126.2, 125.9, 123.7, 122.9, 122.6, 117.3, 66.9.

**9-Methoxy-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ac):** $R_f$=0.41 (PE/EA 10:1); yellow solid, 75.6 mg, yield: 74%, m.p. 163.5–165.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.37 – 7.31 (m, 4H), 7.20 – 7.15 (m, 1H), 6.97 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.75 (d, *J* = 2.8 Hz, 1H), 5.09 (s, 2H), 3.72 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7, 156.9, 146.5, 144.2, 142.4, 135.2, 131.3, 131.2, 129.2, 128.9, 128.6, 128.0, 125.4, 123.8, 123.1, 122.5, 121.5, 117.1, 104.5, 66.9, 55.4. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{18}NO_2$ 340.1338; Found 340.1338.

**9-(Tert-butyl)-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ad):** $R_f$=0.71 (PE/EA 10:1); white solid, 73.6 mg, yield: 68%, m.p. 186.7–189.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.11 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.78 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.59 – 7.50 (m, 3H), 7.41 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 7.18 (ddd, *J* = 7.6, 7.2, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.11 (s, 2H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4, 149.2, 148.3, 146.8, 143.8, 135.3, 131.8, 129.5, 129.4, 128.9, 128.7, 128.4, 126.8, 125.9, 124.0, 123.0, 122.7, 121.3, 117.3, 67.1, 35.2, 31.3. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{26}H_{25}NO$ 366.1858; Found 366.1858.

**7-Phenyl-6*H*-chromeno[4,3-*b*]quinolin-9-ol (3ae):** $R_f$=0.13 (PE/EA 10:1); gray solid, 82.3 mg, yield: 84%, m.p. 246.0–248.0 °C; $^1$H NMR (400 MHz, DMSO) δ 9.98 (s, 1H), 8.35 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.40 – 7.36 (m, 3H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.17 (td, *J* = 7.2, 1.2 Hz, 1H), 7.00 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 5.06 (s, 2H); $^{13}$C NMR (100 MHz, DMSO) δ 156.9, 156.5, 145.3, 143.1, 141.9, 135.1, 131.9, 131.4, 129.7, 129.4, 129.1, 128.5, 125.4, 123.8, 123.0, 122.8, 122.6, 117.6, 107.4, 66.8. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{22}H_{16}NO_2$ 326.1181; Found 326.1181.

**9-Chloro-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline**[9] **(3af):** $R_f$=0.74 (PE/EA 10:1); yellow solid, 56.7 mg, yield: 55%, m.p. 174.5–175.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (ddd, *J* = 8.0, 2.0, 0.4 Hz, 1H), 8.11 (dd, *J* = 9.2, 0.8 Hz, 1H), 7.63 – 7.55 (m, 4H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.38 (ddd, *J* = 9.2, 7.2, 1.6 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.18 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.00 – 6.97 (m, 1H), 5.10 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.2, 146.6, 143.1, 134.4, 132.3, 132.2, 131.4, 130.4, 129.3, 129.2, 129.1, 128.0, 125.9, 125.1, 123.9, 123.4, 122.8, 117.4, 66.8.

**9-Bromo-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline**[9] **(3ag):** $R_f$=0.72 (PE/EA 10:1); yellow solid, 70.3 mg, yield: 61%, m.p. 196.5–198.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.03 (d, *J* = 9.2 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.61 – 7.55 (m, 4H), 7.39 (ddd, *J* = 9.2, 7.6, 2.0 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.20 – 7.16 (m, 2H), 6.98 (dd, *J* = 8.4, 1.2 Hz, 1H), 5.10 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.3, 146.8, 143.1, 134.3, 133.0, 132.4, 131.5, 129.4, 129.2, 129.1, 128.5, 126.0, 123.9, 123.4, 122.8, 120.5, 117.5, 66.8.

**7-Phenyl-6*H*-chromeno[4,3-*b*]quinoline-9-carbonitrile (3ah):** $R_f$=0.61 (PE/EA 10:1); yellow solid, 75.8 mg, yield: 76%, m.p. 190.0–191.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.0, 5.6 Hz, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.87 – 7.80 (m, 2H), 7.64 – 7.59 (m, 3H), 7.45 – 7.41 (m, 1H), 7.30 – 7.28 (m, 2H), 7.20 (td, *J* = 8.0, 1.2 Hz, 1H), 7.01 – 6.99 (m, 1H), 5.14 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7, 151.6, 149.1, 144.2, 133.4, 133.0, 132.6, 131.0, 130.1, 129.4, 129.3, 129.1, 126.7, 126.2, 124.5, 122.8, 119.0, 117.5, 109.5, 66.5. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{15}N_2O$ 335.1184; Found 335.1164.

**Methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline-9-carboxylate (3ai):** $R_f$=0.62 (PE/EA 10:1); yellow solid, 70.8 mg, yield: 64%, m.p. 198.0–200.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.55 – 8.52 (m, 1H), 8.28 – 8.19 (m, 3H), 7.62 – 7.56 (m, 3H), 7.43 – 7.38 (m, 1H), 7.33 – 7.31 (m, 2H), 7.21 – 7.17 (m, 1H), 7.00 – 6.98 (m, 1H), 5.12 (s, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.0, 157.8, 150.9, 150.2, 145.2, 134.3, 132.7, 130.1, 129.4, 129.21, 129.15, 129.1, 127.7, 126.5, 126.3, 123.8, 123.3, 122.8, 117.5, 66.9, 52.5. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{24}H_{18}NO_3$ 368.1287; Found 368.1281.

**1-(7-Phenyl-6*H*-chromeno[4,3-*b*]quinolin-9-yl)ethan-1-one (3aj):** $R_f$=0.52 (PE/EA 10:1); yellow solid, 86.5 mg, yield: 82%, m.p. 223.7–225.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.25 – 8.20 (m, 2H), 8.11 – 8.10 (m, 1H), 7.63 – 7.57 (m, 3H), 7.43 – 7.39 (m, 1H), 7.34 – 7.32 (m, 2H), 7.22 – 7.18 (m, 1H), 7.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.14 (s, 2H), 2.55 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 197.6, 157.7, 151.0, 150.1, 145.3, 134.5, 134.2, 132.7, 130.2, 129.3, 129.1, 128.3, 127.8, 126.4, 126.2, 123.8, 123.2, 122.8, 117.4, 66.7, 26.8. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{24}H_{18}NO_2$ 352.1338; Found 352.1351.

**11-Bromo-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ak):** $R_f$=0.73 (PE/EA 10:1); yellow solid, 72.0 mg, yield: 60%, m.p. 184.8–186.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.01 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.59 – 7.53 (m, 3H), 7.45 – 7.37 (m, 2H), 7.31 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 6.97 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.12 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.6, 149.6, 145.1, 144.4, 134.8, 133.3, 132.5, 129.5, 129.4, 129.1, 129.0, 128.7, 126.6, 126.5, 126.3, 125.8, 123.8, 123.5, 122.9, 117.3, 66.8. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{22}H_{15}BrNO$ 388.0337; Found 388.0337.

**7-Phenyl-6*H*-chromeno[4,3-*b*]quinoline-11-carbonitrile (3al):** $R_f$=0.6 (PE/EA 10:1); yellow solid, 69.3 mg, yield: 69%, m.p. 215.6–217.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.68 (ddd, *J* = 7.6, 1.6, 0.4 Hz, 1H), 8.07 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.62 – 7.56 (m, 3H), 7.44 – 7.40 (m, 2H), 7.31 – 7.28 (m, 2H), 7.22 – 7.18 (m, 1H), 6.99 – 6.97 (m, 1H), 5.14 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.7, 150.8, 147.5, 144.4, 135.5, 133.9, 133.1, 131.4, 129.4, 129.3, 129.2, 127.3, 126.8, 125.4, 124.5, 122.9, 122.7, 117.7, 117.3, 113.1, 66.6. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{15}N_2O$ 335.1184; Found 335.1184.

**7-Phenyl-11-(phenylethynyl)-6*H*-chromeno[4,3-*b*]quinoline (3am):** $R_f$=0.71 (PE/EA 10:1); yellow solid, 89.6 mg, yield: 73%, m.p. 175.4–177.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.94 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.59 – 7.53 (m, 3H), 7.47 – 7.44 (m, 2H), 7.43 – 7.36 (m, 4H), 7.33 – 7.30 (m, 2H), 7.20 (td, *J* = 7.6, 1.2 Hz, 1H), 6.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.13 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.6, 149.1, 148.1, 144.3, 134.9, 133.7, 132.3, 132.1, 129.5, 129.1, 128.9, 128.7, 128.6, 127.4, 126.9, 126.4, 125.9, 124.2, 123.8, 123.6, 123.4, 122.8, 117.4, 95.8, 88.1, 66.9. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{30}H_{20}NO$ 410.1545; Found 410.1545.

**9-Bromo-11-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3an):** $R_f$=0.85 (PE/EA 10:1); yellow solid, 68.3 mg, yield: 57%, m.p. 175.4–177.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 (dd, *J* = 2.4, 1.2 Hz, 1H), 7.60 – 7.53 (m, 3H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.28 – 7.26 (m, 2H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 6.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.09 (s, 2H), 2.89 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4, 147.7, 145.8, 143.1, 140.1, 134.8, 132.8, 132.1, 129.4, 129.1, 128.9, 128.3, 126.3, 125.9, 123.7, 123.4, 122.6, 120.2, 117.4, 66.9, 18.1. HRMS (ESI-TOF) (m/z): $(M + Na)^+$ Calcd. for $C_{23}H_{16}BrNONa$ 424.0313; Found 424.0313.

**2,9-Dimethyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ba):** $R_f$=0.62 (PE/EA 10:1); yellow solid, 79.8 mg, yield: 80%, m.p. 177.0–179.4 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.31 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.22 (s, 1H), 7.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 5.05 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H);$^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 148.3, 146.8, 143.2, 136.3, 135.4, 132.6, 132.0, 131.8, 129.5, 129.0, 128.7, 127.2, 125.8, 125.2, 123.5, 123.3, 117.1, 67.0, 22.0, 21.1. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{24}H_{21}NO$ 338.1545; Found 338.1545.

**2-Methoxy-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ca):** $R_f$=0.43 (PE/EA 10:1); yellow solid, 70.5 mg, yield: 67%, m.p. 224.6–227.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.59 – 7.51 (m, 4H), 7.32 – 7.28 (m, 2H), 7.22 (s, 1H), 6.96 – 6.90 (m, 2H), 5.04 (s, 2H), 3.96 (s, 3H), 2.41 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.3, 151.6, 148.1, 146.7, 143.3, 136.4, 135.3, 131.8, 129.5, 129.0, 128.7, 127.3, 125.2, 124.2, 123.3, 119.5, 118.4, 108.3, 67.1, 56.2, 22.0. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{24}H_{21}NO_2$ 354.1494; Found 354.1494.

**2-Chloro-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3da):** $R_f$=0.68 (PE/EA 10:1); yellow solid, 81.6 mg, yield: 76%, m.p. 247.1–249.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.31 – 7.27 (m, 3H), 7.23 – 7.22 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.08 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 155.8, 146.8, 143.5, 136.8, 135.1, 132.0, 131.5, 129.6, 129.4, 129.0, 128.8, 127.9, 127.4, 125.4, 125.2, 122.6, 118.8, 67.1, 22.0. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{18}ClNO$ 358.0999; Found 358.0999.

**2,4-Di-tert-butyl-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3ea):** $R_f$=0.76 (PE/EA 10:1); yellow solid, 105.9 mg, yield: 81%, m.p. 278.1–280.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.4 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.25 – 7.23 (m, 1H), 5.03 (s, 2H), 2.41 (s, 3H), 1.43 (s, 9H), 1.39 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.2, 146.9, 144.5, 142.7, 138.1, 136.0, 135.6, 131.5, 129.8, 129.7, 129.0, 128.6, 126.9, 126.5, 125.1, 124.2, 123.7, 120.3, 66.3, 35.1, 31.9, 30.2, 22.0. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{31}H_{34}NO$ 436.2640; Found 436.2650.

**4-Bromo-2-chloro-9-methyl-7-phenyl-6*H*-chromeno[4,3-*b*]quinoline (3fa):** $R_f$=0.81 (PE/EA 10:1); yellow solid, 108.7 mg, yield: 83%, m.p. 231.1–234.0 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.8 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.53 (m, 5H), 7.30 – 7.28 (m, 2H), 7.25 – 7.24 (m, 1H), 5.19 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.5, 146.8, 146.0, 143.8, 137.3, 134.8, 134.2, 132.3, 129.6, 129.3, 129.1, 128.9, 128.1, 127.5, 126.0, 125.2, 124.8, 122.0, 111.8, 67.7, 22.1. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{16}BrClNO$ 436.0104; Found 436.0104.

**7-(4-Fluorophenyl)-9-methyl-6*H*-chromeno[4,3-*b*]quinoline (3ga):** $R_f$=0.52 (PE/EA 10:1); yellow solid, 89.5 mg, yield: 87%, m.p. 131.4–133.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.53 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.31 – 7.27 (m, 4H), 7.20 – 7.16 (m, 2H), 7.00 – 6.97 (m, 1H), 5.08 (s, 2H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 246.7 Hz), 157.3, 148.1, 146.8, 142.2, 136.6, 131.9, 131.3 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.1, 129.7, 127.2, 125.8, 124.9, 123.8, 123.2, 122.8, 117.3, 116.2 (d, $J_{C\text{-}F}$ = 21.4 Hz), 66.9, 22.0; $^{19}$F NMR (376 MHz, $CDCl_3$) δ = -35.1 (s, 1F). HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{17}FNO$ 342.1294; Found 342.1295.

**7-(4-Methoxyphenyl)-9-methyl-6*H*-chromeno[4,3-*b*]quinoline (3ha):** $R_f$=0.42 (PE/EA 10:1); white solid, 90.1 mg, yield: 85%, m.p. 198.3–199.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.36 (ddd, *J* = 9.2, 7.2, 1.6 Hz, 1H), 7.27 (s, 1H), 7.24 – 7.21 (m, 2H), 7.17 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 – 7.07 (m, 2H), 6.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 5.12 (s, 2H), 3.93 (s, 3H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.8, 157.3, 148.1, 146.9, 143.1, 136.3, 131.75, 131.71, 130.8, 129.6, 127.6, 127.2, 125.8, 125.3, 124.0, 123.3, 122.7, 117.3, 114.4, 67.1, 55.6, 22.1. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{24}H_{20}NO_2$ 354.1494; Found 354.1494.

**9-Methyl-7-(*o*-tolyl)-6*H*-chromeno[4,3-*b*]quinoline (3ia):** $R_f$=0.64 (PE/EA 10:1); yellow solid, 83.1 mg, yield: 82%, m.p. 176.0–178.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.46 – 7.34 (m, 4H), 7.20 – 7.12 (m, 2H), 7.03 – 7.02 (m, 1H), 6.97 (dd, *J* = 8.0, 0.8 Hz, 1H), 5.04 – 4.91 (m, 2H), 2.40 (s, 3H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.4, 148.2, 146.9, 142.9, 136.6, 136.3, 134.8, 131.9, 131.8, 130.7, 129.7, 129.3, 128.9, 127.1, 126.5, 125.8, 124.8, 123.9, 123.2, 122.7, 117.4, 66.9, 22.0, 19.9. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{24}H_{20}NO$ 338.1545; Found 338.1545.

9-Methyl-7-(thiophen-2-yl)-6*H*-chromeno[4,3-*b*]quinoline (**3ka**): $R_f$=0.70 (PE/EA 10:1); yellow solid, 63.4 mg, yield: 64%, m.p. 197.0–198.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 5.2 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.44 (s, 1H), 7.38 – 7.34 (m, 1H), 7.28 – 7.26 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 3.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 2H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 157.3, 148.0, 146.8, 136.8, 136.0, 134.7, 132.0, 131.9, 129.6, 129.0, 128.0, 127.8, 127.6, 125.8, 125.0, 124.9, 123.7, 122.7, 117.3, 67.1, 22.1. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{21}H_{16}NOS$ 330.0953; Found 330.0947.

**7-Phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine (3jb):** $R_f$=0.51 (PE/EA 10:1); yellow solid, 78.8 mg, yield: 57%, m.p. 201.0–202.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.6, 2.0 Hz, 1H), 8.04 – 8.02 (m, 1H), 7.80 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.66 – 7.47 (m, 7H), 7.41 – 7.37 (m, 1H), 7.31 – 7.28 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 2H), 1.92 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.4, 147.7, 144.4, 143.9, 138.3, 134.8, 134.6, 131.4, 130.8, 129.6, 129.4, 129.2, 129.1, 128.9, 128.0, 127.9, 127.2, 126.7, 126.5, 126.1, 122.9, 48.1, 21.2. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{29}H_{23}N_2O_2S$ 463.1480; Found 463.1472.

**9-Methyl-7-phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine (3ja):** $R_f$=0.52 (PE/EA 10:1); white solid, 95.3 mg, yield: 67%, m.p. 244.6–245.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.55 – 7.45 (m, 3H), 7.30 – 7.27 (m, 2H), 7.20 (s, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.81 (s, 2H), 2.42 (s, 3H), 1.94 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 148.5, 146.4, 143.8, 138.2, 136.7, 135.1, 134.6, 131.7, 131.5, 130.5, 129.6, 129.3, 129.2, 129.0, 128.9, 127.9, 127.8, 127.2, 126.6, 126.3, 124.8, 122.9, 48.1, 22.1, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{30}H_{25}N_2O_2S$ 477.1637; Found 477.1637.

**9-Methoxy-7-phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine (3jc):** $R_f$=0.41 (PE/EA 10:1); yellow solid, 117.5 mg, yield: 80%, m.p. 208.4–210.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.78 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.65 – 7.55 (m, 3H), 7.53 – 7.44 (m, 2H), 7.31 – 7.28 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.74 – 6.68 (m, 3H), 4.81 (s, 2H), 3.73 (s, 3H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.0, 147.1, 143.8, 143.1, 137.9, 135.1, 134.6, 131.6, 131.1, 130.2, 129.4, 129.3, 129.1, 128.8, 127.9, 127.8, 127.7, 127.1, 126.1, 123.2, 121.6, 104.2, 55.6, 48.1, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{30}H_{25}N_2O_3S$ 493.1586; Found 493.1586.

**9-Chloro-7-phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine (3jf):** $R_f$=0.53 (PE/EA 10:1); white solid, 88.7 mg, yield: 60%, m.p. 229.7–231.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.80 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.67 – 7.53 (m, 5H), 7.49 (td, *J* = 7.6, 1.6 Hz, 1H), 7.43 (d, *J* = 2.4 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 4.82 (s, 2H), 1.96 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.7, 146.1, 143.9, 143.7, 138.3, 134.5, 134.2, 132.6, 131.2, 131.0, 130.3, 129.4, 128.9, 128.0, 127.9, 127.4, 127.2, 126.5, 124.9, 123.9, 48.0, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{29}H_{22}ClN_2O_2S$ 497.1091; Found 497.1091.

**9-Bromo-7-phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine (3jg):** $R_f$=0.61 (PE/EA 10:1); white solid, 110.4 mg, yield: 68%, m.p. 217.5–218.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.67 – 7.60 (m, 4H), 7.56 (td, *J* = 7.6, 1.6 Hz, 1H), 7.49 (td, *J* = 7.6, 1.2 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.72 – 6.69 (m, 2H), 4.82 (s, 2H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.8, 146.3, 144.0, 143.6, 138.3, 134.5, 134.1, 132.9, 131.3, 131.1, 129.5, 129.4, 128.9, 128.2, 128.0, 127.9, 127.2, 126.5, 123.9, 120.8, 47.9, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{29}H_{22}BrN_2O_2S$ 541.0585; Found 541.0585.

**7-Phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine-9-carbonitrile (3jh):** $R_f$=0.55 (PE/EA 10:1); yellow solid, 100.4 mg, yield: 69%, m.p. 253.8–254.6 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.70 – 7.64 (m, 3H), 7.62 – 7.58 (m, 3H), 7.51 (td, *J* = 8.0, 1.6 Hz, 1H), 7.28 – 7.25 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 4.85 (s, 2H), 1.95 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.2, 148.6, 145.0, 144.1, 138.8, 134.4, 133.4, 132.6, 131.8, 130.9, 130.6, 130.1, 129.9, 129.7, 129.4, 129.0, 128.1, 128.0, 127.2, 126.9, 126.2, 124.8, 119.0, 110.0, 47.8, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{30}H_{22}N_3O_2S$ 488.1433; Found 488.1425.

**7-Phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridin-11-ol (3jo):** $R_f$=0.12 (PE/EA 10:1); white solid, 108.5 mg, yield: 76%, m.p. 196.9–198.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.21 (s, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64 – 7.48 (m, 5H), 7.34 – 7.29 (m, 3H), 7.12 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.99 – 6.92 (m, 3H), 6.63 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 2H), 1.97 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 152.3, 147.3, 145.0, 144.1, 138.4, 137.4, 134.7, 134.2, 131.0, 130.9, 129.4, 129.2, 128.8, 128.1, 128.0, 127.8, 127.2, 127.1, 126.2, 123.6, 116.5, 109.8, 48.1, 21.2. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{29}H_{23}N_2O_3S$ 479.1429; Found 479.1429.

**7-Phenyl-5-tosyl-5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridine-11-carbonitrile (3jl):** $R_f$=0.52 (PE/EA 10:1); yellow solid, 121.0 mg, yield: 82%, m.p. 229.8–231.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.05 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.72 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.67 – 7.57 (m, 4H), 7.52 (td, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.27 (dd, *J* = 8.0, 2.8 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 4.85 (s, 2H), 2.00 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 151.2, 146.9, 144.9, 144.2, 138.6, 135.4, 134.2, 133.7, 131.7, 131.2, 130.6, 129.7, 129.5, 129.4, 128.9, 128.2, 127.6, 127.4, 127.2, 126.7, 125.7, 124.6, 117.5, 113.1, 47.9, 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{30}H_{22}N_3O_2S$ 488.1433; Found 488.1433.

**(*E*)-1-(2-(cinnamyloxy)phenyl)-*N*-(*p*-tolyl)methanimine** (**4aa**): $R_f$=0.66 (PE/EA 10:1); yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.16 (d, *J* = 6.8 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.24 (m, 1H), 7.17 (q, *J* = 8.0 Hz, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.42 (dt, *J* = 16.0, 5.6 Hz, 1H), 4.79 (d, *J* = 5.6 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 158.8, 156.0, 150.4, 136.5, 135.8, 133.5, 132.7, 130.0, 128.9, 128.3, 127.9, 126.9, 125.5, 124.3, 121.4, 121.3, 69.5 21.3. HRMS (ESI-TOF) (m/z): (M + H)$^+$ Calcd. for $C_{23}H_{22}NO$ 328.1701; Found 328.1701.

**(*E*)-*N*-(2-(cinnamyloxy)benzyl)-4-methylaniline** (**5aa**): $R_f$=0.51 (PE/EA 10:1); white solid; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 2H), 7.27 – 7.20 (m, 2H), 6.97 – 6.90 (m, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 6.41 (dt, *J* = 16.0, 5.2 Hz, 1H), 4.75 – 4.74 (m, 2H), 4.37 (s, 2H), 4.05 (s, 1H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 156.8, 146.6, 136.8, 132.9, 130.0, 129.4, 128.9, 128.5, 128.4, 128.2, 126.9, 126.8, 124.8, 121.2, 113.6, 112.1, 68.9, 44.3, 20.8. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{24}NO$ 330.1858; Found 330.1858.

**(6a*RS*,7*SR*,12a*RS*)-9-Methyl-7-phenyl-6a,7,12,12a-tetrahydro-6*H*-chromeno[4,3-*b*]quinoline** (**I**): The procedure was adopted from the literature: [16] A 100 mL round-bottom flask was charged with 2-(cinnamyloxy)benzaldehyde (**1a**, 0.95 g, 4 mmol), 4-nitrotoluene (0.55 g, 4 mmol), iron powder (0.89 g, 16 mmol), citric acid monohydrate (3.07 g, 16 mmol), montmorillonite K10 (600 mg), and water (30 mL). The mixture was stirred at 80 °C under a nitrogen atmosphere for 4 h. After completion, the mixture was filtered with suction and washed with water (20 mL× 3) and then extracted with hot acetone (30 mL× 3). The solvent was removed under reduced pressure, the crude product was purified by silica-gel column chromatography (PE/DCM = 1:1) to give **I** as a white solid (0.92 g, 70% yield). $R_f$=0.51 (PE/EA 10:1); white solid, m.p. 206.1–207.8 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 3H), 7.28 (t, *J* = 7.0 Hz, 1H), 7.22 – 7.17 (m, 3H), 6.99 (ddd, *J* = 7.5, 7.5, 1.5 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.44 (s, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.24 (s, 1H), 4.03 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.85 (t, *J* = 11.5 Hz, 1H), 3.80 (d, *J* = 12.0 Hz, 1H), 2.45 (dddd, *J* = 11.0, 11.0, 11.0, 3.5 Hz, 1H), 2.09 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ 154.2, 143.1, 142.1, 130.8, 129.2, 128.8, 128.7, 128.4, 128.2, 127.1, 125.6, 125.0, 122.9, 120.8, 117.1, 116.4, 67.7, 52.4, 47.1, 41.5, 20.7. HRMS (ESI-TOF) (m/z): $(M + H)^+$ Calcd. for $C_{23}H_{22}NO$ 328.1701; Found 328.1707.

## Acknowledgements

The authors acknowledge the financial support provided by the National Natural Science Foundation of China (No. 21232003).

**Keywords:** chromeno[4,3-*b*]quinolines•[1,6]naphthyridines•aza-Diels-Alder reaction•Lewis-acid-catalysis•visible-light-photoredox

[1] a) M. Anzini, A. Cappelli, S. Vomero, G. Giorgi, T. Langer, M. Hamon, N. Merahi, B. M. Emerit, A. Cagnotto, M. Skorupska, T. Mennini, J. C. Pinto, *J. Med. Chem.* **1995**, *38*, 2692-2704; b) A. T. Vu, A. N. Campbell, H. A. Harris, R. J. Unwalla, E. S. Manas, R. E. Mewshaw, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 4053-4056; c) R. A. Heald, M. F. G. Stevens, *Org. Biomol. Chem.* **2003**, *1*, 3377-3389; d) E. Kiselev, T. S. Dexheimer, Y. Pommier, M. Cushman, *J. Med. Chem.* **2010**, *53*, 8716-8726; e) W. Huang, W. Lin, X. Guan, *Tetrahedron Lett.* **2014**, *55*, 116-119; f) D. Kand, A. M. Kalle, S. J. Varma, P. Talukdar, *Chem. Commun.* **2012**, *48*, 2722-2724; g) N. Mulakayala, D. Rambabu, M. R. Raja, C. M, C. S. Kumar, A. M. Kalle, G. Rama Krishna, C. Malla Reddy, M. V. Basaveswara Rao, M. Pal, *Bioorg. Med. Chem.* **2012**, *20*, 759-768.

[2] A. Anand Kumar, R. Kulbhushan, K. Mahendra, *Lett. Drug. Des. Discov.* **2014**, *11*, 594-600.

[3] Okuma, T. Koga, S. Ozaki, Y. Suzuki, K. Horigami, N. Nagahora, K. Shioji, M. Fukuda, M. Deshimaru, *Chem. Commun.* **2014**, *50*, 15525-15528.

[4] a) M. M. Tomashevskaya, O. A. Tomashenko, A. A. Tomashevskii, V. V. Sokolov, A. A. Potekhin, Russ. *J. Org. Chem.* **2007**, *43*, 77-82; b) G. Sabitha, R. S. Babu, B. V. Subba Reddy, J. S. Yadav, *Synth. Commun.* **1999**, *29*, 4403-4408; c) M. Jida, B. Deprez, *New J. Chem.* **2012**, *36*, 869; d) M. Shiri, M. Fathollahi-Lahroud, Z. Yasaei, *Tetrahedron* **2017**, *73*, 2501-2503; e) J. B. Singh, K. Chandra Bharadwaj, T. Gupta, R. M. Singh, *RSC Adv.* **2016**, *6*, 26993-26999.

[5] a) S. Laschat, J. Lauterwein, *J. Org. Chem.* **1993**, *58*, 2856-2861; b) J. Muhuhi, M. R. Spaller, *J. Org. Chem.* **2006**, *71*, 5515-5526; c) G. Sabitha, E. Venkata Reddy, C. Maruthi, J. S. Yadav, *Tetrahedron Lett.* **2002**, *43*, 1573-1575; d) R. G. Jacob, G. Perin, G. V. Botteselle, E. J. Lenardão, *Tetrahedron Lett.* **2003**, *44*, 6809-6812; e) R. D. R. S. Manian, J. Jayashankaran, R. Ramesh, R. Raghunathan, *Tetrahedron Lett.* **2006**, *47*, 7571-7574; f) S. Maiti, S. K. Panja, K. Sadhukhan, J. Ghosh, C. Bandyopadhyay, *Tetrahedron Lett.* **2012**, *53*, 694-696; g) X. Zhang, B. Liu, X. Shu, Y. Gao, H. Lv, J. Zhu, *J. Org. Chem.* **2012**, *77*, 501-510; h) H. Twin, R. A. Batey, *Org. Lett.* **2004**, *6*, 4913-4916; i) A. A. Kudale, D. O. Miller, L. N. Dawe, G. J. Bodwell, *Org. Biomol. Chem.* **2011**, *9*, 7196-7206; j) K. C. Majumdar, S. Ponra, S. Ganai, *Synlett* **2010**, 2575-2578; k) R. Suresh, S. Muthusubramanian, R. Senthilkumaran, G. Manickam, *J. Org. Chem.* **2012**, *77*, 1468-1476.

[6] a) R. Rohlmann, T. Stopka, H. Richter, O. Garcia Mancheno, *J. Org. Chem.* **2013**, *78*, 6050-6064; b) R. K. Kawade, D. B. Huple, R. J. Lin, R. S. Liu, *Chem. Commun.* **2015**, *51*, 6625-6628; c) H. Richter, O. García Mancheño, *Org. Lett.* **2011**, *13*, 6066-6069; d) S. Desrat, P. van de Weghe, *J. Org. Chem.* **2009**, *74*, 6728-6734.

[7] R. Nagarajan, S. Ramesh, V. Gaddam, *Synlett* **2010**, 757-760.

[8] X. Yu, J. Wang, Z. Xu, Y. Yamamoto, M. Bao, *Org. Lett.* **2016**, *18*, 2491-2494.

[9] K. Aradi, P. Bombicz, Z. Novak, *J. Org. Chem* **2016**, *81*, 920-931.

[10] I. Muthukrishnan, P. Vinoth, T. Vivekanand, S. Nagarajan, C. U. Maheswari, J. C. Menendez, V. Sridharan, *J. Org. Chem.* **2016**, *81*, 1116-1124.

[11] a) C. K. Prier, D. A. Rankic, D. W. MacMillan, *Chem. Rev.* **2013**, *113*, 5322-5363; b) L. Shi, W. Xia, *Chem. Soc. Rev.* **2012**, *41*, 7687-7697; c) J. M. Narayanam, C. R. Stephenson, *Chem. Soc. Rev.* **2011**, *40*, 102-113; d) J. R. Chen, X. Q. Hu, L. Q. Lu, W. J. Xiao, *Chem. Soc. Rev.* **2016**, *45*, 2044-2056.

[12] a) A. G. Condie, J. C. González-Gómez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464-1465; b) M. Rueping, D. Leonori, T. Poisson, *Chem. Commun.* **2011**, *47*, 9615-9617; c) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny, D. C. Fabry, *Chem. Commun.* **2011**, *47*, 2360-2362; d) M. Rueping, S. Q. Zhu, R. M. Koenigs, *Chem. Commun.* **2011**, *47*, 8679-8681; e) G. Q. Xu, C. G. Li, M. Q. Liu, J. Cao, Y. C. Luo, P. F. Xu, *Chem. Commun.* **2016**, *52*, 1190-1193; f) Z. Q. Wang, M. Hu, X. C. Huang, L. B. Gong, Y. X. Xie, J. H. Li, *J. Org. Chem.* **2012**, *77*, 8705-8711; g) S. Q. Zhu, M. Rueping, *Chem. Commun.* **2012**, *48*, 11960-11962; h) X.-W. Gao, Q.-Y. Meng, M. Xiang, B. Chen, K. Feng, C.-H. Tung, L.-Z. Wu, *Adv. Synth. Catal.* **2013**, *355*, 2158-2164; i) X.-W. Gao, Q.-Y. Meng, J.-X. Li, J.-J. Zhong, T. Lei, X.-B. Li, C.-H. Tung, L.-Z. Wu, *ACS Catalysis* **2015**, 5, 2391-2396; j) Q. H. Deng, Y. Q. Zou, L. Q. Lu, Z. L. Tang, J. R. Chen, W. J. Xiao, *Chem. Asian. J.* **2014**, *9*, 2432-2435; k) S. Chen, Q. Wan, A. K. Badu-Tawiah, *Angew. Chem.* **2016**, *128*, 9491-9495; *Angew. Chem. Int. Ed.* **2016**, *55*, 9345-9349; l) K. H. He, F. F. Tan, C. Z. Zhou, G. J. Zhou, X. L. Yang, Y. Li, *Angew. Chem.* **2017**, *129*, 3126-3130; *Angew. Chem. Int. Ed.* **2017**, *56*, 3080-3084; m) M. K. Sahoo, G. Jaiswal, J. Rana, E. Balaraman, *Chem. Eur. J.* **2017**, *23*, 14167-14172; n) C. Lin, L. Zhen, Y. Cheng, H. J. Du, H. Zhao, X. Wen, L. Y. Kong, Q. L. Xu, H. Sun, *Org Lett* **2015**, *17*, 2684-2687; o) W. Dong, B. Hu, X. Gao, Y. Li, X. Xie, Z. Zhang, *J. Org. Chem.* **2016**, *81*, 8770-8776; p) X. Yang, L. Li, Y. Li, Y. Zhang, *J. Org. Chem.* **2016**, *81*, 12433-12442.

[13] W. Dong, Y. Yuan, B. Hu, X. Gao, H. Gao, X. Xie, Z. Zhang, *Org. Lett.* **2018**, *20*, 80-83.

[14] a) M. I. Fernández-Bachiller, C. Pérez, G. C. González-Muñoz, S. Conde, M. G. López, M. Villarroya, A. G. García, M. I. Rodríguez-Franco, *J. Med. Chem.* **2010**, *53*, 4927-4937; b) S. Tardito, A. Barilli, I. Bassanetti, M. Tegoni, O. Bussolati, R. Franchi-Gazzola, C. Mucchino,

L. Marchiò, *J. Med. Chem.* **2012**, *55*, 10448-10459; c) E. Serrao, B. Debnath, H. Otake, Y. Kuang, F. Christ, Z. Debyser, N. Neamati, *J. Med. Chem.* **2013**, *56*, 2311-2322.

[15] a) S.-i. Nakano, K. Kakugawa, T. Nemoto, Y. Hamada, *Adv. Synth. Catal.* **2014**, *356*, 2088-2096; b) C. Min, C.-T. Lin, D. Seidel, *Angew. Chem.* **2015**, *127*, 6708-6712; *Angew. Chem. Int. Ed.* **2015**, *54*, 6608-6612; c) K. Watanabe, T. Mino, E. Ishikawa, M. Okano, T. Ikematsu, Y. Yoshida, M. Sakamoto, K. Sato, K. Yoshida, *Eur. J. Org. Chem.* **2017**, 2359-2368; d) T. Yokosaka, H. Nakayama, T. Nemoto, Y. Hamada, *Org. Lett.* **2013**, *15*, 2978-2981.

[16] H.-G. Imrich, J. Conrad, U. Beifuss, *Eur. J. Org. Chem.* **2016**, 5706-5715.

**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

## FULL PAPER

Text for Table of Contents

((Insert TOC Graphic here: max. width: 5.5 cm; max. height: 5.0 cm))

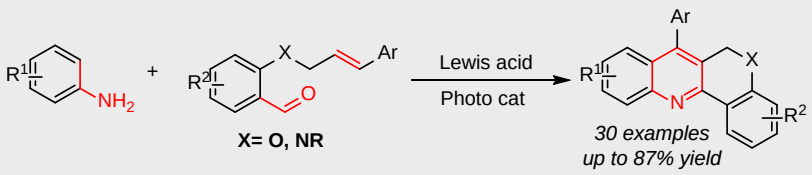
*Author(s), Corresponding Author(s)**

***Page No. – Page No.***

**Title**

Layout 2:

## FULL PAPER




*Wuheng Dong, Yao Yuan, Xiaoshuang Gao, Bei Hu, Xiaomin Xie, and Zhaoguo Zhang **

***Page No. – Page No.***

**Merging Visible-Light-Photoredox and Lewis-Acid-Catalysis for the Intramolecular Aza-Diels-Alder Reaction: Synthesis of Substituted Chromeno[4,3-*b*]quinolines and [1,6]Naphthyridines**

A photocatalytic aerobic aza-Diels-Alder cycloaddition strategy under visible light to construct chromenoquinolines and 5,6-dihydrodibenzo[*b*,*h*][1,6]naphthyridines, which are important skeletons of biologically active molecules.
The applicability of readily available starting materials and the use of air as the sole oxidant under the mild reaction conditions make this process very attractive.