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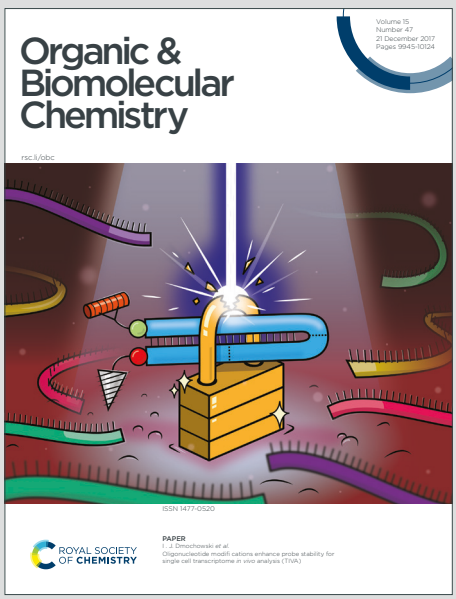

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PAPER

Transition Metal-Free α-Methylation of 1,8-Naphthyridine Derivatives Using DMSO as Methylation Reagent

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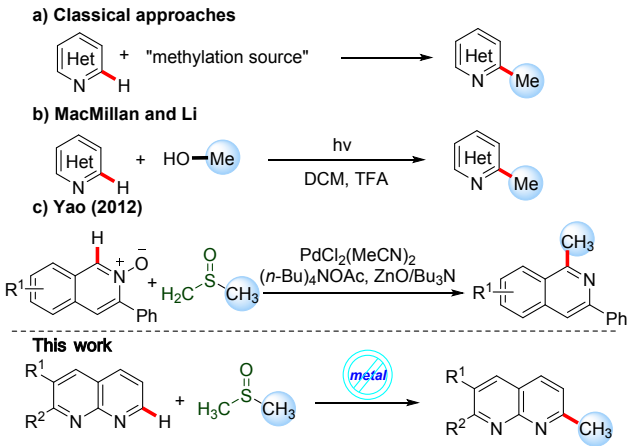
A practical approach to the direct *α*-methylation of 1,8-naphthyridines under mild reaction conditions has been developed using simple and readily available DMSO as a convenient and environmentally friendly carbon source. This method is transition metal-free and highly chemoselective, shows good functional group tolerance, and uses DMSO as a methyl source, providing efficient and rapid access to an important compound class, 2-methyl-1,8-naphthyridines.

Introduction

The methyl group is among the most important inert functional groups in organic chemistry.[1] The introduction of a methyl group into an aromatic molecule (namely methylation) is an important methodology in organic synthesis. In recent years, chemists have devoted much attention to the development of new methylation reagents that have successfully been applied to the methylation of heteroarenes.[2] Usually, the classic tool for aromatic methylation is directed orthometalation, which requires transition metals, stoichiometric amounts of oxidants, or sensitive methylation reagents (Scheme 1a).[3] Recently, MacMillan[4] and Li[5] developed some simple and mild protocols for the photoinduced methylation of heteroarenes using MeOH as the methylation reagent under an ambient atmosphere (Scheme 1b). In 2014, Gui et al. presented a two-step C–H functionalization method for the methylation of heteroarenes.[6] Despite significant progress in this field, the development of new synthetic methods for the *ortho*-methylation of *N*-heterocycles in a green, efficient, and metal-free manner remains highly desirable.



Scheme 1 Classical and developed synthetic methods for the ortho-methylation of N-heterocycles

In recent years, dimethyl sulfoxide (DMSO) has been used as solvent or substrate in organic synthesis owing to its low cost and low toxicity. [7] DMSO has been widely used in organic synthesis as a source of -Me,[8] -SMe,[9] -SOMe,[10] -SO_2Me,[11] -CH_2SMe,[12] and -CHO[13] groups in recent years. Although using DMSO as a carbon source has been well studied, to our knowledge, using DMSO as a methyl source has been less successful. For example, Yao et al. reported an excellent palladium-catalyzed alkylation of isoquinoline *N*-oxides using DMSO as a methyl surrogate (Scheme 1c), and Russell presented the methylation of aromatic hydrocarbons by dimethyl sulfoxide.[14] However, using palladium salt reduced the practicality of this method, and 1,8-naphthyridine substrates could not be accessed in this transformation. The 1,8-naphthyridine ring system is an attractive structural motif owing to its wide distribution in bioactive molecules and pharmaceuticals,[2a,15] which include a potent $\alpha_v\beta_3$ receptor antagonist **A**,[16] antibacterial agents **B**,[17] and CETP inhibitor **C**.[18] As part of our continuing research interest in the *ortho*-functionalization of *N*-heterocycles,[19] we aimed to design a mild *ortho*-methylation method for the laboratory methylation

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of 1,8-naphthyridines using a cheap and safe methylation source.

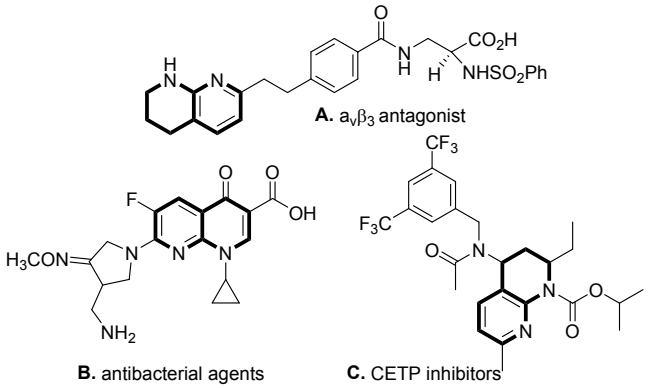
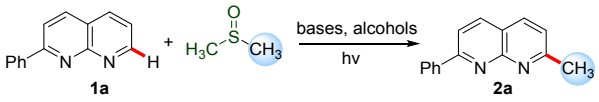


Figure 1 Representative biologically active compounds.

Results and discussion

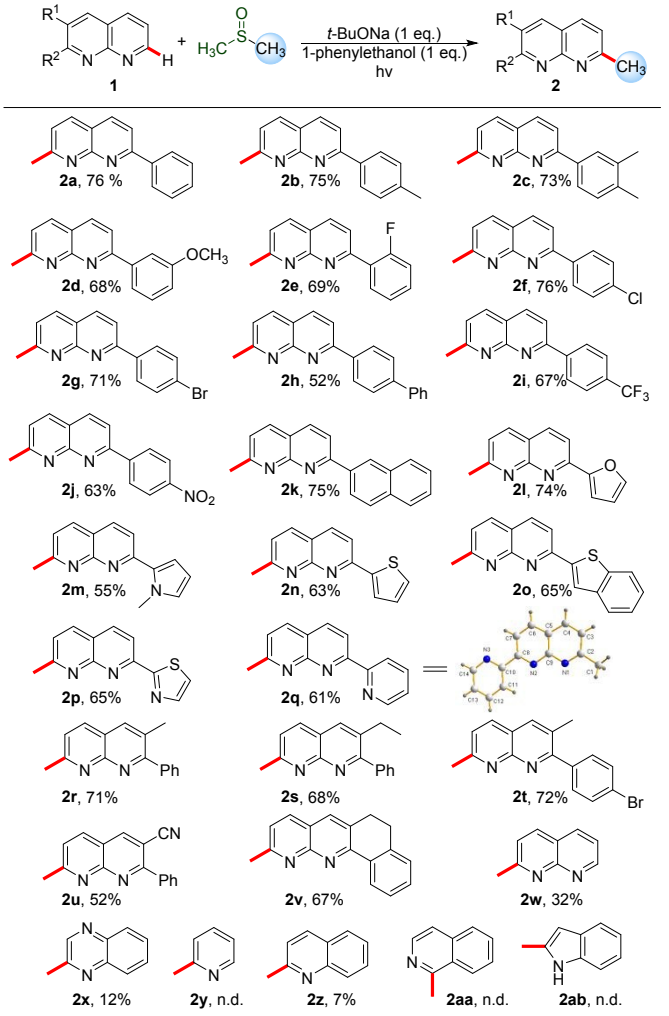
Initially, 2-phenyl-1,8-naphthyridine **1a** was selected as the model substrate and DMSO as solvent to investigate different reaction conditions, and a range of conventional bases and hydrogen donors (HDs) were evaluated, with the results summarized in Table 1. First, desired product **2a** was detected in 33% yield when using *t*-BuOK as base and isopropanol as HD in DMSO at 120 °C for 8h (entry 1). Conventional bases, such as NaOMe, HCO_2Na, NaOH, KOH, and *t*-BuONa were tested in the reaction, with *t*-BuONa found to be the most effective, affording product **2a** in 38% yield (Table 1, entries 2-6). The control experiment demonstrated that base and HD were indispensable, because no product was detected in their absence (Table 1, entries 7 and 8). Performing the reaction under visible light irradiation (blue LEDs, 3W) led to an increased yield (entry 9). Several HDs were screened (entries 10-12), with 1-phenylethanol found to be more effective than other alcohols. Finally, the reaction temperature was investigated, showing that 100 °C was optimal for this transformation, affording the desired product in 73% yield (entry 13).

Table 1 Optimization of Reaction Conditions [a]



Entry	Base	Alcohol	Yield (%)[b]
1	*t*-BuOK	isopropanol	38
2	NaOMe	isopropanol	19
3	HCO_2Na	isopropanol	17
4	NaOH	isopropanol	11
5	*t*-BuONa	isopropanol	41
6	KOH	isopropanol	12
7	*t*-BuONa	-	-
8	-	isopropanol	-
9[c]	*t*-BuONa	isopropanol	59
10	*t*-BuONa	methanol	28
11	*t*-BuONa	ethanol	36
12	*t*-BuONa	1-phenylethanol	68
13[d]	*t*-BuONa	1-phenylethanol	(64, 73, 71)

[a] Reaction conditions: Unless otherwise stated, all reactions were performed with **1a** (0.2 mmol), base (0.4 mmol), alcohol (0.2 mmol), and DMSO (1.5 mL) at 120 °C under N_2 protection for 8 h. [b] Isolated yield. [c] Under visible light irradiation (blue LEDs, 3W). [d] Yields from reaction temperatures of 90, 100, and 110 °C, respectively.



Scheme 2 Substrate scope of 1,8-naphthyridines.[a] Standard conditions: **1a** (0.2 mmol), *t*-BuONa (0.4 mmol), 1-phenylethanol (0.2 mmol), and DMSO (1.5 mL) at 100 °C under visible light irradiation. Isolated yields.

With optimized conditions in hand, the 1,8-naphthyridine substrate scope was explored. Various 1,8-naphthyridines bearing electron-withdrawing and/or electron-donating groups were effective for the transformation, with the results summarized in Scheme 2. Generally, the reactions proceeded smoothly to afford the desired 2-methylated products in reasonable to good isolated yields (**2a**-**2w**), and the electronic

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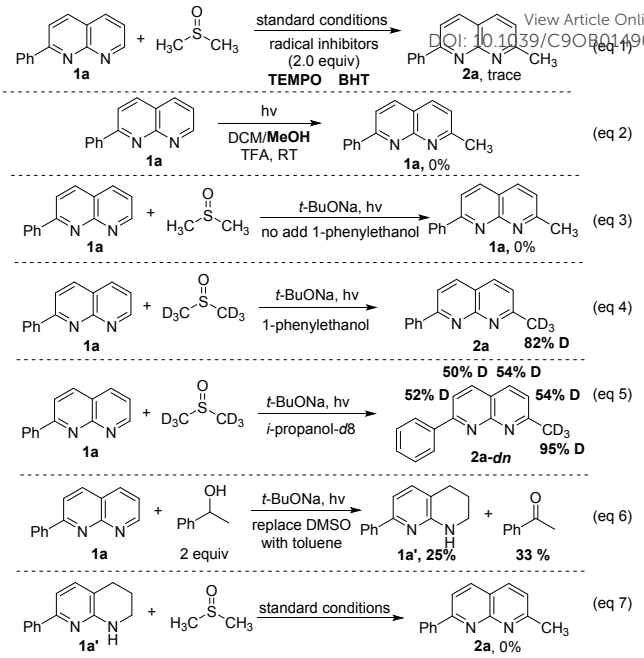
properties of the aryl ring substituents in the reactants had little effect on product formation. First, different 2-aryl-1,8-naphthyridines were employed in the transformation, affording the desired product in good yields of 52%-76% (**2a**-**2k**). Pleasingly, heteroaryl-substituted 1,8-naphthyridines also efficiently afforded the corresponding products (**2l**-**2q**), which are potential multidentate ligands for organometallic chemistry and catalysis applications.[20] The structure of **2q** was confirmed by X-ray diffraction analysis. Similarly, 2,3-disubstituted 1,8-naphthyridines (**1r**-**1v**) underwent effective reaction to generate 2-methylated products (**2r**-**2v**). Interestingly, when 1,8-naphthyridine **1w**, bearing two reactive α-sites, was used as substrate, the coupling reaction afforded one methyl substituent product (**2w**). Other N-heterocycles such as pyridine, isoquinoline and indole have been employed for the coupling reaction with DMSO under standard reaction conditions, however the formation of the desired coupling product was not observed, only quinoxaline and quinoline were able to afford the desired product in 12% and 7%, respectively.

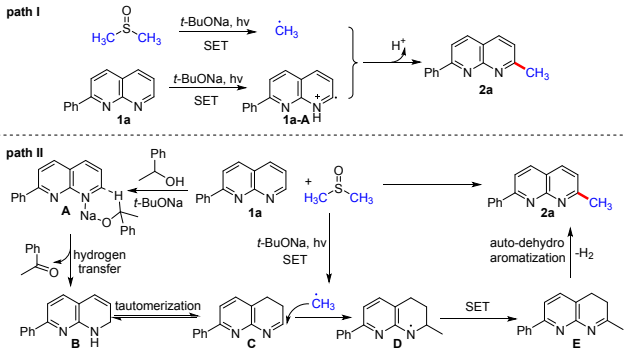
To gain insight into the reaction pathway, we conducted several verification experiments (Scheme 3). First, the reaction was conducted in the presence of radical inhibitors 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-ditert-butyl-4-methylphenol (BHT), with only a trace amount of **2a** detected by NMR analysis, showing that radical generation was involved in this transformation (eq. 1). However, when the reaction was run under conditions reported by the Li group (CH_3OH, hv, CH_2Cl_2 and TFA),[5] no product was detected, indicating that the reaction pathway was different to that reported in the literature. The absence of 1-phenylethanol resulted in no product generation (eq. 3), indicating that 1-phenylethanol played a crucial role in product formation, perhaps by acting as a hydrogen donor. An isotope-labeling experiment confirmed that the methyl group was obtained from DMSO, while different deuterium ratios were observed on the newly formed naphthyridyl unit when isopropanol-d_8 was used instead of 1-phenylethanol. This observation indicates that hydrogen was transferred from isopropanol-d_8 to 1,8-naphthyridine **1a** (eq. 4-5).

When the reaction between 2-phenyl-1,8-naphthyridine and 1-phenylethanol was performed with toluene instead of DMSO, product **1a'** (25% yield) and acetophenone (33% yield) were formed. The subsequent reaction of **1a'** with DMSO under standard conditions failed to give product **2a** (eq. 7), further supporting the effective suppression of over-hydrogenated tetrahydronaphthyridine formation.



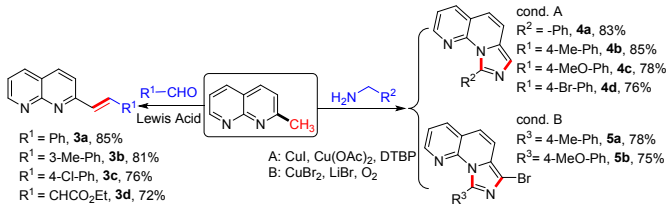
Scheme 3 Control experiments

On the basis of recent literature reports,[13] a plausible mechanistic pathway is depicted in path I. The reaction starts from a single electron transfer (SET) give radical intermediate **1a-A** and methyl radical, respectively from **1a** and DMSO. And then product **2a** is formed via radical coupling of radical intermediate **1a-A** and methyl radical (path I). However, on the basis of above control experiments and recent literature reports,[21] we believe that the reaction plausible mechanism is path II. The MPV-O reduction of **1a** by 1-phenylethanol under basic conditions, which gives a sodium alkoxide that interacts with the imine unit in **1a** to form transition state **A**, was the key reaction initiation step, and is known in the literature.[21b] Through a reversible MPV-O-type hydrogen transfer,[22] the subsequent protonation of **A** followed by thermodynamically favorable tautomerization of **B** liberates acetophenone, allylic amine **B**, and tautomer imine **C**. The reaction is initiated by a single-electron-transfer caused by *t*-BuONa and light, which causes dimethyl sulfoxide to decompose, forming a methyl radical. Addition of the generated methyl radical to imine C gives corresponding adduct **D**, which then interconverts to imine intermediate **E**. The dehydroaromatization of **E** then affords product **2a**.



Scheme 4 Plausible reaction pathways

Finally, we were interested in demonstrating the application of obtained compound **2w**. The 2-methyl group of *N*-heterocycles is a good active site, and acts as a one-carbon bridge. Under Lewis acid conditions,[23] various aldehydes reacted well to afford a variety of (*E*)-2-alkenylazaarenes in moderate to good yields. Using 2-methyl-1,8-naphthyridines bearing different benzylamine derivatives under different conditions (A and B) [24] gave imidazo-fused *N*-heterocycles in good yields (Scheme 5).



Scheme 4 Functionalization of methyl substituent in **2w**

Conclusions

In conclusion, we have described a direct α-methylenation of 1,8-naphthyridines using DMSO as the methyl source that is achieved under radical reaction conditions. DMSO acts as both solvent and a one-carbon source in this reaction, providing a highly atom-economical and environmentally benign approach to the synthesis of 2-methyl-1,8-naphthyridines. Based on control experiments, a plausible hydrogen transfer reaction path was proposed.

Experimental

General Information

All experiments were carried out under the standard conditions. Flash column chromatography was performed over silica gel (200–300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a BrukerAV500/400 instrument internally referenced to TMS, chloroform and DMSO signals. MS analyses were performed on an Agilent 5975 GC–MS instrument (EI). High resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) and time-of-flight (TOF) mass analysis. Melting points were uncorrected. The new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS.

Substrates preparation

1,8-Naphthyridines 1a-1g, 1i-1n, 1q-1s and 1u-1v were known compounds and prepared via the literature procedures.[19a, 25] Other substrates (1h, 1o, 1t, 1w) were commercially available, and purchased at J&K Chemic and Energy Chemical. 2-Amino-3-pyridinecarboxaldehyde (5 mmol), ketones (6 mmol), *t*-BuOK (20 mol %), and ethanol (10 mL) were introduced in a flask (50 mL). Then, it was stirred at 50 °C under atmosphere for 5 hours. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography to give the substrates 1.

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2-phenyl-1,8-naphthyridine (1a). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.27 (s, 1H), 8.75 (s, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.13 (s, 2H), 7.68 – 7.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 156.9, 155.9, 145.6, 137.0, 136.8, 130.8, 129.5, 128.7, 123.5, 119.9, 117.3, 106.7.

2-(p-tolyl)-1,8-naphthyridine (1b). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 – 9.07 (m, 1H), 8.27 – 8.14 (m, 4H), 7.99 (d, *J* = 8.5 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.3, 156.2, 153.7, 140.4, 137.6, 136.7, 135.7, 129.6, 127.8, 121.6, 121.6, 119.5, 21.4.

2-(3,4-dimethylphenyl)-1,8-naphthyridine (1c). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 1.5 Hz, 1H), 8.16 (dd, *J* = 14.5, 8.3 Hz, 3H), 7.98 (t, *J* = 6.7 Hz, 2H), 7.42 (dd, *J* = 7.7, 4.1 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 156.2, 153.6, 139.1, 137.5, 137.2, 136.7, 136.0, 130.1, 129.1, 125.2, 121.5, 119.6, 19.8, 19.7.

2-(3-methoxyphenyl)-1,8-naphthyridine (1d). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 – 8.95 (m, 1H), 8.06 (dd, *J* = 16.0, 8.3 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.39 – 7.25 (m, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.2, 160.0, 155.9, 153.7, 139.9, 137.7, 136.8, 129.7, 121.8, 120.2, 119.8, 116.7, 112.5, 55.5.

2-(2-fluorophenyl)-1,8-naphthyridine (1e). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.3 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 7.4 Hz, 1H), 8.14 – 8.01 (m, 2H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.58 – 7.39 (m, 2H), 7.18 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (d, *J* = 245.8 Hz), 158.9, 155.9, 154.0, 140.8 (d, *J* = 7.4 Hz), 138.1, 136.9, 130.3 (d, *J* = 8.1 Hz), 123.4, 122.1, 121.9, 119.5, 116.9 (d, *J* = 21.4 Hz), 114.8 (d, *J* = 23.1 Hz).

2-(4-chlorophenyl)-1,8-naphthyridine (1f). [25e] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (d, *J* = 2.4 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 3H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 156.0, 154.0, 138.0, 136.9, 136.8, 136.4, 129.2, 129.0, 121.9, 121.8, 119.4.

2-(4-bromophenyl)-1,8-naphthyridine (1g). [25e] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.5 Hz, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 3H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.47 (dd, *J* = 8.0, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 156.2, 154.1, 138.0, 137.4, 136.8, 132.0, 129.4, 124.9, 121.9, 121.8, 119.3.

2-(4-(trifluoromethyl)phenyl)-1,8-naphthyridine (1i). [25e] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (dd, *J* = 4.0, 1.7 Hz, 1H), 8.39 (d, *J* = 8.2 Hz, 2H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.48 (dd, *J* = 8.1, 4.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 155.9, 154.2, 141.7, 138.2, 136.8, 131.7 (d, *J* = 32.6 Hz), 128.1, 125.7 (q, *J* = 3.8 Hz), 122.7, 122.2, 122.0, 119.6.

2-(4-nitrophenyl)-1,8-naphthyridine (1j). [25e] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 3.4 Hz, 1H), 8.50 (d, *J* = 8.5 Hz, 2H), 8.44 – 8.34 (m, 3H), 8.28 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.57 (dd, *J* = 7.9, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 155.9, 154.6 148.8, 144.3, 138.5, 136.9, 128.8, 124.0, 122.7, 122.3, 119.7.

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2-(naphthalen-2-yl)-1,8-naphthyridine (1k). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.79 (s, 1H), 8.47 (d, *J* = 7.9 Hz, 1H), 8.28 – 8.07 (m, 3H), 7.98 (d, *J* = 6.4 Hz, 2H), 7.89 (s, 1H), 7.48 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 156.2, 153.8, 137.7, 136.7, 135.7, 134.3, 133.4, 130.8, 129.0, 128.5, 127.9, 127.7, 127.1, 126.4, 125.0, 121.8, 119.8.

2-(furan-2-yl)-1,8-naphthyridine (1l). [25e] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.58 (s, 1H), 7.48 (d, *J* = 3.3 Hz, 1H), 7.36 (dd, *J* = 8.0, 4.2 Hz, 1H), 6.63 – 6.52 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 153.8, 153.4, 152.1, 144.4, 137.7, 136.7, 121.6, 121.5, 118.2, 112.7, 111.8.

2-(1-methyl-1H-pyrrol-2-yl)-1,8-naphthyridine (1m). [25b] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.96 (m, 2H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.27 (dd, *J* = 7.3, 4.2 Hz, 1H), 6.78 (m, 2H), 6.15 (s, 1H), 4.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.9, 155.3, 153.2, 136.7, 136.5, 131.2, 129.0, 120.9, 120.5, 113.9, 108.1, 38.5.

2-(thiophen-2-yl)-1,8-naphthyridine (1n). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (d, *J* = 2.5 Hz, 1H), 8.11 (t, *J* = 8.1 Hz, 2H), 7.83 (t, *J* = 6.3 Hz, 2H), 7.51 (d, *J* = 4.8 Hz, 1H), 7.39 (dd, *J* = 7.9, 4.2 Hz, 1H), 7.15 (t, *J* = 4.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.0, 155.5, 153.8, 144.6, 137.6, 136.7, 130.0, 128.2, 127.1, 121.7, 121.5, 118.7.

2-(pyridin-2-yl)-1,8-naphthyridine (1q). [25b] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10-9.20 (m, 1H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.68-8.78 (m, 2H), 8.28 (d, J = 8.4 Hz, 1H), 8.19 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 7.80-7.90 (m, 1H), 7.46 (dd, *J* = 8.0 Hz, 4.0 Hz, 1H), 7.32-7.41 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 155.8, 155.4, 153.8, 149.1, 137.8, 137.0, 136.9, 124.6, 122.9, 122.5, 122.1, 120.0.

3-methyl-2-phenyl-1,8-naphthyridine (1r). [25b] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.00 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 2H), 7.53 – 7.37 (m, 4H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 154.8, 152.9, 140.1, 137.7, 135.9, 130.6, 129.3, 128.6, 128.1, 121.9, 121.8, 20.6.

3-ethyl-2-phenyl-1,8-naphthyridine (1s). [25b] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98-9.10 (m, 1H), 7.95-8.25 (m, 2H), 7.49-7.68 (m, 2H), 7.32-7.53 (m, 4H), 2.73-2.85 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 154.5, 152.9, 140.2, 136.6, 136.2, 135.9, 129.0, 128.4, 128.0, 121.9, 121.9, 25.9, 14.6.

2-phenyl-1,8-naphthyridine-3-carbonitrile (1u). [25c] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.27 (s, 1H), 8.75 (s, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.13 (s, 2H), 7.68 – 7.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) : δ 161.3, 157.0, 155.9, 145.6, 137.0, 136.8, 130.8, 129.5, 128.7, 123.5, 119.9, 117.3, 106.7.

5,6-dihydronaphtho[1,2-b][1,8]naphthyridine (1v). [19a] Known compound, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95-9.12 (m, 1H), 8.74 (d, *J* = 7.6 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.28-7.48 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 1H), 3.02 (t, *J* = 6.8 Hz, 2H), 2.92 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 155.6, 152.6, 139.5, 136.1, 134.5, 133.9, 131.7, 130.4, 127.8, 127.2, 126.9, 122.2, 121.4, 28.4, 28.0.

Typical procedure for the synthesis of 2.

In a Schlenk tube of 25mL, 1,8-naphthyridines 1 (0.2 mmol), *t*-BuONa (0.4 mmol, 2.0 equiv), and 1-phenylethanol (0.2 mmol, 1 equiv) were dissolved in DMSO (2 mL) under visible light irradiation (blue LEDs, 3W) and stirred at 100 °C for 8 h, irradiation was conducted in a photochemical reactor equipped with visible light irradiation (420 nm<λ<780 nm). After completion of the reaction, the resulting solution was cooled to room temperature; the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3×5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC on silica gel to give the desired product (2).

Spectral data of compounds

2-methyl-7-phenyl-1,8-naphthyridine (2a). Known compound [2a]; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.30 (m, 2H), 8.17 (dd, J = 8.4, 3.0 Hz, 1H), 8.05 (dd, J = 8.2, 2.9 Hz, 1H), 7.93 (dd, J = 8.4, 2.9 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.33 (dd, J = 8.2, 2.5 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ163.3, 160.0, 155.9, 138.7, 137.4, 136.6, 129.9, 128.7, 127.9, 122.6, 119.7, 118.8, 25.7. HRMS (ESI): Calcd. for $C_{15}H_{13}N_2$ $[M+H]^+$: 221.1073; found: 221.1064.

2-methyl-7-(p-tolyl)-1,8-naphthyridine (2b). Yellow solid (52.7 mg, 75% yield), known compound[2a] ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 2H), 8.16 – 8.08 (m, 1H), 8.01 (dd, *J* = 11.8, 5.6 Hz, 1H), 7.89 (dd, *J* = 11.7, 5.9 Hz, 1H), 7.30 (t, *J* = 9.0 Hz, 3H), 2.81 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 159.9, 155.9, 140.1, 137.2, 136.5, 135.9, 129.5, 127.8, 122.4, 119.5, 118.6, 25.7, 21.4. HRMS (ESI): Calcd. for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230; found: 235.1222.

2-(3,4-dimethylphenyl)-7-methyl-1,8-naphthyridine (2c). Yellow oil (54.4 mg, 73% yield); R_f = 0.4 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 2.71 (s, 3H), 2.24 (d, *J* = 16.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.0, 155.9, 138.9, 137.1, 137.0, 136.5, 136.1, 130.0, 129.1, 125.1, 122.3, 119.5, 118.6, 25.7, 19.8, 19.7. HRMS (ESI): Calcd. for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; found: 249.1377.

2-(3-methoxyphenyl)-7-methyl-1,8-naphthyridine (2d). White solid (51.0 mg, 68% yield), m.p: 136.2-137.9 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) *δ*8.13 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.91 (m, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.6 Hz, 1H), 3.91 (s, 3H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ*163.3, 160.1, 159.8, 155.7, 140.1, 137.4, 136.7, 129.6, 122.7, 120.3, 119.8, 119.1, 116.5, 112.6, 55.6, 25.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{15}N_2O$ 251.1179; found: 251.1169.

2-(2-fluorophenyl)-7-methyl-1,8-naphthyridine (2e). Yellow solid (52.5 mg, 69% yield), m.p: 99.9-101.1 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 10.3 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.44 (td, *J* = 8.0, 5.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.09 (m, 1H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 164.3, 163.6, 162.3, 157.1 (d, *J* = 356.1 Hz), 140.9 (d, *J* = 7.5 Hz), 137.7, 136.6 (s), 130.2 (d, *J* = 7.8 Hz), 123.3 (d, *J* = 2.7 Hz), 122.9, 119.9, 118.7, 116.8 (d, *J* = 21.2 Hz), 114.8 (d, *J* = 23.0 Hz), 25.7.^{19}F NMR (471 MHz, $CDCl_3$) δ -112.9. HRMS (ESI): Calcd. for $C_{15}H_{12}FN_2$ $[M+H]^+$: 239.0979; found: 239.0968.

2-(4-chlorophenyl)-7-methyl-1,8-naphthyridine (2f). White solid (57.9 mg, 76% yield), m.p: 189.0-191.1 °C ; R_f = 0.3 (petroleum

ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.24 (m, 2H), 8.20 (dd, *J* = 8.3, 3.1 Hz, 1H), 8.07 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.90 (dd, *J* = 8.3, 3.5 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.37 (d, *J* = 8.2 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 158.7, 155.8, 137.7, 137.0, 136.6, 136.2, 129.2, 128.9, 122.9, 119.8, 118.5, 25.8. HRMS (ESI): Calcd. for $C_{15}H_{12}ClN_2$ $[M+H]^+$: 255.0684; found: 255.0672.

3-(4-bromophenyl)-7-methyl-1,8-naphthyridine (2g). Grey solid (63.5 mg, 71% yield), known compound [2a]; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 8.5, 1.1 Hz, 3H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.68 – 7.58 (m, 2H), 7.36 (d, *J* = 8.2 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 158.8, 155.7, 137.7, 137.4, 136.7, 131.9, 129.4, 124.7, 122.9, 119.8, 118.5, 25.7. HRMS (ESI): Calcd. for $C_{15}H_{12}BrN_2$ $[M+H]^+$: 299.0178; found: 299.0168.

3-([1,1'-biphenyl]-4-yl)-7-methyl-1,8-naphthyridine (2h). Yellow solid (46.2 mg, 52% yield), m.p: 208.0-210.1 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.4 Hz, 2H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.1 Hz, 2H), 7.39 (dd, *J* = 20.6, 7.6 Hz, 2H), 2.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 159.5, 155.9, 142.7, 140.4, 137.4, 136.7, 128.9, 128.3, 127.7, 127.4, 127.2, 122.7, 119.7, 118.8, 25.7. HRMS (ESI): Calcd. for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386; found: 297.1374.

2-methyl-7-(4-(trifluoromethyl)phenyl)-1,8-naphthyridine (2i). Grey solid (57.9 mg, 67% yield), known compound [2a]; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 2H), 8.21 (dd, *J* = 8.2, 3.8 Hz, 1H), 8.08 (dd, *J* = 8.1, 3.5 Hz, 1H), 7.93 (dd, *J* = 8.2, 3.9 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.37 (dd, *J* = 8.2, 3.0 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8, 158.3, 155.6, 141.8, 137.9, 136.7, 131.52 (d, *J* = 32.4 Hz), 128.1, 125.63 (q, *J* = 3.1 Hz), 125.2, 123.2, 120.1, 118.8, 25.7.^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6. HRMS (ESI): Calcd. for $C_{16}H_{12}F_3N_2$ $[M+H]^+$: 289.0947; found: 289.0935.

2-methyl-7-(4-nitrophenyl)-1,8-naphthyridine (2j). Brown solid (50.1 mg, 63% yield), m.p: 224.0-225.1 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 7.1 Hz, 2H), 8.38 – 8.26 (m, 3H), 8.12 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 2.86 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 157.3, 155.7, 148.6, 144.5, 138.2, 136.7, 128.7, 123.9, 123.7, 120.3, 118.9, 25.8. HRMS (ESI): Calcd. for $C_{15}H_{12}N_3O_2$ $[M+H]^+$: 266.0924; found: 266.0914.

2-methyl-7-(naphthalen-2-yl)-1,8-naphthyridine (2k). Yellow solid (60.8 mg, 75% yield), m.p: 194.4-196.0 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.49 (d, *J* = 8.6 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.08 (dd, *J* = 11.1, 8.4 Hz, 2H), 7.99 (t, *J* = 8.0 Hz, 2H), 7.93 – 7.84 (m, 1H), 7.62 – 7.49 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 1H), 2.87 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 159.8, 155.8, 137.4, 136.8, 135.8, 134.2, 133.4, 129.0, 128.4, 127.9, 127.7, 127.0, 126.4, 125.1, 122.7, 119.8, 119.0, 25.7. HRMS (ESI): Calcd. for $C_{19}H_{15}N_2$ $[M+H]^+$: 271.1230; found: 271.1219.

2-(furan-2-yl)-7-methyl-1,8-naphthyridine (2l). Yellow solid (46.6 mg, 74% yield), m.p: 123.4-125.1 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.3, 6.1 Hz, 1H), 7.98 (dd, *J* = 8.1, 6.0 Hz, 1H), 7.88 (dd, *J* = 8.3, 6.1 Hz, 1H), 7.69 – 7.57 (m, 1H), 7.51 (dd, *J* = 3.1, 2.6 Hz, 1H), 7.27 (dd, *J* = 7.5, 4.7 Hz, 1H), 6.59 (td, *J* = 3.3, 1.7 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 155.7, 153.6, 151.9, 144.2, 137.4, 136.6, 122.4, 119.6, 117.3, 112.8, 111.5, 25.6. HRMS (ESI): Calcd. for $C_{13}H_{11}N_2O$ $[M+H]^+$: 211.0866; found: 211.0859.

2-methyl-7-(1-methyl-1H-pyrrol-2-yl)-1,8-naphthyridine (2m). Yellow oil (36.8 mg, 55 % yield); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 15.2, 8.3 Hz, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 6.87 (dd, *J* = 11.1, 2.1 Hz, 2H), 6.31 – 6.18 (m, 1H), 4.33 (s, 3H), 2.82 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 155.6, 155.2, 136.7, 136.3, 131.5, 128.6, 121.8, 120.3, 118.5, 113.6, 108.1, 38.3, 25.7. HRMS (ESI): Calcd. for $C_{14}H_{14}N_3$ $[M+H]^+$: 224.1182; found: 224.1173.

2-methyl-7-(thiophen-2-yl)-1,8-naphthyridine (2n). White solid (42.7 mg, 63% yield), known compound[2a]; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.77 (d, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.47 (dd, *J* = 5.0, 0.5 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.15 – 7.07 (m, 1H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4, 155.6, 155.2, 144.7, 137.3, 136.6, 129.7, 128.1, 126.9, 122.4, 119.6, 117.8, 25.6. HRMS (ESI): Calcd. for $C_{13}H_{11}N_2S$ $[M+H]^+$: 227.0637; found: 227.0630.

2-(benzo[b]thiophen-2-yl)-7-methyl-1,8-naphthyridine (2o). Yellow solid (53.8 mg, 65% yield), m.p: 210.6-212.7 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.06 (s, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (t, *J* = 7.4 Hz, 2H), 7.86 – 7.78 (m, 1H), 7.40 – 7.34 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.7, 155.7, 155.3, 144.7, 141.6, 140.3, 137.3, 136.6, 125.6, 124.5, 124.5, 123.7, 122.8, 122.8, 120.1, 118.2, 77.3, 77.1, 76.8, 25.7. HRMS (ESI): Calcd. for $C_{17}H_{13}N_2S$ $[M+H]^+$: 277.0794; found: 277.0788.

2-(7-methyl-1,8-naphthyridin-2-yl) thiazole (2p). Brown solid (44.3 mg, 65% yield), m.p: 123.4-125.1 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 – 8.33 (m, 1H), 8.21 (dd, *J* = 9.6, 5.5 Hz, 1H), 8.10 – 8.03 (m, 1H), 7.97 (d, *J* = 1.8 Hz, 1H), 7.53 (dd, *J* = 3.6, 2.6 Hz, 1H), 7.38 – 7.29 (m, 1H), 2.81 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 163.9, 155.4, 154.0, 144.2, 137.9, 136.8, 123.4, 123.2, 121.4, 118.1, 25.7. HRMS (ESI): Calcd. for $C_{12}H_{10}N_3S$ $[M+H]^+$: 228.0590; found: 228.0582.

2-methyl-7-(pyridin-2-yl)-1,8-naphthyridine (2q). Yellow solid (30.0 mg, 61% yield), m.p: 115.2-117.5 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (d, *J* = 7.6 Hz, 1H), 8.76 (dd, *J* = 3.3, 1.4 Hz, 1H), 8.71 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.30 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.14 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.50 – 7.39 (m, 2H), 2.88 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.40, 159.04, 155.59, 155.56, 149.04, 137.54, 137.03, 136.81, 124.58, 123.12, 122.61, 120.92, 119.22, 25.75. HRMS (ESI): Calcd. for $C_{14}H_{12}N_3$ $[M+H]^+$: 222.1026; found: 222.1018.

3,7-dimethyl-2-phenyl-1,8-naphthyridine (2r). Black solid (49.9 mg, 71% yield), m.p: 118.1-119.8 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 1H), 2.80 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.03, 162.31, 154.45, 140.25, 137.49, 135.82, 129.61, 129.32, 128.43, 127.96, 122.81, 119.74, 25.56, 20.54. HRMS (ESI): Calcd. for $C_{16}H_{15}N_2$ $[M+H]^+$: 235.1230; found: 235.1221.

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2-ethyl-7-methyl-2-phenyl-1,8-naphthyridine (2s). Yellow solid (50.6 mg, 68% yield), m.p: 117.4-119.6 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 3.1 Hz, 1H), 8.02 (d, *J* = 2.2 Hz, 1H), 7.71 – 7.59 (m, 2H), 7.51 – 7.41 (m, 3H), 7.34 (dd, *J* = 8.2, 2.9 Hz, 1H), 2.86 (q, *J* = 7.3 Hz, 2H), 2.79 (s, 3H), 1.21 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 162.3, 154.0, 140.3, 136.2, 135.7, 135.6, 129.1, 128.3, 127.9, 122.8, 119.9, 25.8, 25.5, 14.8. HRMS (ESI): Calcd. for $C_{17}H_{17}N_2$ $[M+H]^+$: 249.1386; found: 249.1376.

2-(4-bromophenyl)-3,7-dimethyl-1,8-naphthyridine (2t). Grey solid (67.4 mg, 72% yield), m.p: 158.0-160.7 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 3.4 Hz, 1H), 7.57 (d, *J* = 2.9 Hz, 4H), 7.31 (d, *J* = 8.2 Hz, 1H), 2.77 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 161.6, 154.3, 139.0, 137.8, 135.9, 131.2, 131.1, 129.4, 123.1, 122.9, 119.9, 25.6, 20.5. HRMS (ESI): Calcd. for $C_{16}H_{14}BrN_2$ $[M+H]^+$: 313.0335; found: 313.0335.

7-methyl-2-phenyl-1,8-naphthyridine-3-carbonitrile (2u). White solid (38.2 mg, 52% yield), m.p: 150.4-152.1 °C ; R_f = 0.2 (petroleum ether/ethyl acetate = 3/1, v/v);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 – 8.62 (m, 1H), 8.18 – 8.09 (m, 3H), 7.55 (dd, *J* = 3.4, 2.4 Hz, 3H), 7.48 (d, *J* = 8.2 Hz, 1H), 2.90 – 2.85 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 161.2, 155.7, 145.1, 136.9, 136.7, 130.6, 129.5, 128.6, 124.5, 118.0, 117.6, 105.6, 26.1. HRMS (ESI): Calcd. for $C_{16}H_{12}N_3$ $[M+H]^+$: 246.1026; found: 246.1016.

10-methyl-5,6-dihydronaphtho[1,2-b][1,8]naphthyridine (2v). Brown solid (49.5 mg, 67% yield), m.p: 140.4-141.7 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.5 Hz, 1H), 7.94 (s, 1H), 7.84 (d, *J* = 9.2 Hz, 1H), 7.38 (dd, *J* = 14.0, 6.7 Hz, 2H), 7.30 – 7.24 (m, 2H), 3.09 (d, *J* = 5.3 Hz, 2H), 2.98 (d, *J* = 5.5 Hz, 2H), 2.80 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 156.1, 155.3, 139.4, 136.1, 134.4, 134.2, 130.9, 130.3, 127.9, 127.3, 127.1, 122.4, 120.2, 28.4, 28.2), 25.6. HRMS (ESI): Calcd. for $C_{17}H_{15}N_2$ $[M+H]^+$: 247.1230; found: 247.1219.

2-methyl-1,8-naphthyridine (2w). White solid (13.8 mg, 32% yield), m.p: 95.9-97.7 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.06 – 8.95 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.02, 155.79, 153.25, 136.94, 136.75, 123.06, 121.39, 120.75, 25.67. HRMS (ESI): Calcd. for $C_9H_9N_2$ $[M+H]^+$: 145.0760; found: 145.0769.

2-methylquinoxaline (2x). Grey oid (12% yield), known compound [26]; R_f = 0.3 (petroleum ether/ethyl acetate = 6/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.04 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.01 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.76-7.68 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 148.3, 144.3, 143.3, 132.4, 131.5, 131.3, 131.0, 25.0.

2-methylquinoline (2z). Yellow oil (7% yield); known compound [26]; R_f = 0.4 (petroleum ether/ethyl acetate = 6/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (t, *J* = 8.3 Hz, 2H), 7.79 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.54 – 7.48 (m, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 147.7, 136.3, 129.5, 128.5, 127.5, 126.5, 125.8, 122.1, 25.3.

(E)-2-styryl-1,8-naphthyridine (3a). Yellow oil (39.5 mg, 85% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 3/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.18 – 8.05 (m, 2H), 7.96 (d, *J* = 16.2 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 3H), 7.45 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 156.0, 153.8, 137.4, 136.8, 136.4, 136.2, 129.1, 128.9, 127.8, 127.6, 121.9, 121.5, 121.2. HRMS (ESI): Calcd. for $C_{16}H_{13}N_2$ $[M+H]^+$: 233.1073; found: 233.1065.

(E)-2-(3-methylstyryl)-1,8-naphthyridine (3b). Yellow oil (39.9 mg, 81% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09 (dd, *J* = 4.1, 1.9 Hz, 1H), 8.13 – 8.08 (m, 2H), 7.95 (d, *J* = 14.2 Hz, 1H), 7.64 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.30 (dd, *J* = 11.7, 4.4 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 156.1, 153.8, 138.4, 137.3, 136.7, 136.5, 136.2, 129.9, 128.8, 128.2, 127.7, 124.8, 121.9, 121.5, 121.2, 21.5. HRMS (ESI): Calcd. for $C_{17}H_{15}N_2$ $[M+H]^+$: 247.1230; found: 247.1224.

(E)-2-(4-chlorostyryl)-1,8-naphthyridine (3c). Yellow oil (40.4 mg, 76% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 1/1, v/v); ^{1}H NMR (500 MHz,) δ 9.10 (dd, *J* = 4.2, 1.9 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 16.1 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.43 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.39 – 7.31 (m, 3H). ^{13}C NMR (126 MHz,) δ 158.6, 156.0, 153.9, 137.5, 136.8, 135.0, 134.7, 134.7, 129.1, 128.7, 128.2, 122.0, 121.6, 121.4. HRMS (ESI): Calcd. for $C_{16}H_{12}ClN_2$ $[M+H]^+$: 267.0684; found: 267.0675.

Ethyl (E)-3-(1,8-naphthyridin-2-yl)acrylate (3d). White solid (32.8 mg, 72% yield), m.p: 87.4-90.1°C ; R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.26 (dd, *J* = 14.2, 5.5 Hz, 2H), 7.92 (d, *J* = 15.8 Hz, 1H), 7.71 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.55 (dd, *J* = 7.9, 4.1 Hz, 1H), 7.21 (d, *J* = 14.2 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 156.6, 154.3, 142.9, 138.1, 137.2, 125.7, 122.9, 122.6, 122.1, 61.0, 14.3. HRMS (ESI): Calcd. for $C_{13}H_{13}N_2O_2$ $[M+H]^+$: 229.0972; found: 229.0960.

9-phenylimidazo[1,5-a][1,8]naphthyridine (4a). Brown solid (40.7 mg, 83% yield), m.p: 89.0-90.4 °C ; R_f = 0.3 (petroleum ether/ethyl acetate = 5/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.25 (m, 1H), 7.90 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.83 – 7.79 (m, 2H), 7.61 (s, 1H), 7.50 – 7.44 (m, 3H), 7.37 (dd, *J* = 11.1, 5.1 Hz, 1H), 7.31 – 7.28 (m, 1H), 6.95 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 144.3, 143.9, 136.0, 133.7, 131.4, 130.3, 128.4, 127.3, 123.6, 121.4, 120.2, 119.6, 118.6. HRMS (ESI): Calcd. for $C_{16}H_{12}N_3$ $[M+H]^+$: 246.1026; found: 246.1035.

9-(p-tolyl)imidazo[1,5-a][1,8]naphthyridine (4b). Brown oil (43.5 mg, 85% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.93 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.61 (s, 1H), 7.39 (d, *J* = 9.3 Hz, 1H), 7.32 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.28 (d, *J* = 9.3 Hz, 2H), 6.96 (d, *J* = 9.3 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.28, 144.42, 144.09, 138.28, 135.95, 131.30, 130.69, 130.15, 128.02, 123.49, 121.36, 120.27, 119.39, 118.65, 21.56. HRMS (ESI): Calcd. for $C_{17}H_{14}N_3$ $[M+H]^+$: 260.1182; found: 260.1176.

9-(4-methoxyphenyl)imidazo[1,5-a][1,8]naphthyridine (4c). Yellow oil (42.9 mg, 78% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.4 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.59 (s, 1H), 7.37 (d, *J* = 9.2 Hz, 1H), 7.32 (dd, *J* = 7.7, 4.6 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 9.3 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.77, 146.24, 144.47, 143.88, 135.96, 131.70, 131.22, 126.06, 123.37, 121.36, 120.32, 119.31, 118.68, 112.68, 55.32. HRMS (ESI): Calcd. for $C_{17}H_{14}N_3O$ $[M+H]^+$: 276.1131; found: 276.1124.

9-(4-bromophenyl)imidazo[1,5-a][1,8]naphthyridine (4d). Yellow solid (49.1 mg, 76% yield), m.p: 117.0-119.1 °C; R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.6, 1.8 Hz, 1H), 7.97 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.57 (m, 3H), 7.41 (d, *J* = 9.3 Hz, 1H), 7.36 (dd, *J* = 7.7, 4.6 Hz, 1H), 7.00 (d, *J* = 9.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 144.2, 142.7, 136.2, 132.5, 132.0, 131.5, 130.4, 123.8, 122.7, 121.6, 120.2, 119.7, 118.6. HRMS (ESI): Calcd. for $C_{16}H_{11}BrN_3$ $[M+H]^+$: 324.0131; found: 324.0125.

7-bromo-9-(p-tolyl)imidazo[1,5-a][1,8]naphthyridine (5a). Yellow oil (52.6 mg, 78% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 2/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 9.3 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 144.1, 143.4, 138.8, 136.3, 130.2, 129.5, 128.6, 128.1, 121.9, 120.3, 120.2, 117.5, 110.6, 21.6. HRMS (ESI): Calcd. for $C_{17}H_{13}BrN_3$ $[M+H]^+$: 338.0287; found: 338.0276.

7-bromo-9-(4-methoxyphenyl)imidazo[1,5-a][1,8]-naphthyridine (5b). Yellow oil (52.9 mg, 75% yield); R_f = 0.3 (petroleum ether/ethyl acetate = 1/1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.01 (d, *J* = 9.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 146.5, 144.2, 143.2, 136.3, 131.8, 128.5, 124.9, 121.9, 120.3, 120.1, 117.6, 112.7, 110.5, 55.4. HRMS (ESI): Calcd. for $C_{17}H_{13}BrN_3O$ $[M+H]^+$: 354.0237; found: 354.0228.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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