NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

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Cite this: *New J. Chem.*, 2021, **45**, 6367

Catalyst-free synthesis of phenanthridines *via* electrochemical coupling of 2-isocyanobiphenyls and amines†

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Received 15th January 2021,
Accepted 19th February 2021

DOI: 10.1039/d1nj00250c

rsc.li/njc

Catalyst free synthesis of 6-aryl phenanthridines and amides through an electrochemical reaction is reported in this study. The coupling reaction proceeds by the cathodic reduction of *in situ* formed diazonium ions, which are formed from anilines and an alkyl nitrite. The generated aryl radical diazonium ions coupled from isocyanides furnished the desired products in good yields. This cascade reaction was conducted in an undivided cell equipped with an RVC as the anode and Pt as the cathode using nBu$_4$NBF$_4$ as the electrolyte at room temperature. A series of detailed mechanistic studies have also been performed, including a radical clock experiment and cyclic voltammetry analysis.

Introduction

Phenanthridines are privileged structural motifs due to the substantial interest in the fields of pharmaceuticals and medicinally relevant natural products.[1] The 6-aryl phenanthridine nucleus based structural motifs (such as ethidium bromide) were associated with a unique property related to the intercalation with DNA and RNA and/or a fluorescent marker for ds-DNA and ds-RNA (Fig. 1).[2]

Consequently, the development of novel strategies for synthesizing phenanthridines is highly desirable.[3,4] Conventionally, the Bischler–Napieralski reaction has been used for the preparation of phenanthridine derivatives in the presence of $POCl_3$ or PCl_5 at elevated temperatures. In a pioneering work, Chatani and co-workers demonstrated phenyl radical insertion, generated by phenyl boronic acid using a Mn(III) catalyst, into 2-isocyanobiphenyls for the phenanthridine synthesis.[5] In 2014, Zhu's group synthesized phenanthridine derivatives by arylative cyclization of 2-isocyanobiphenyls using oxidative insertion of anilines as the arylating source (Scheme 1a).[6] Recently, Mao and Zhou's group developed a visible light promoted synthesis of 6-substituted phenanthridines by the trapping of aryl radicals generated by hydrazine and 2-isocyanobiphenyls.[7] Despite these significant advances, the intrinsic shortcomings associated with transition metals/oxidants, harsh reaction conditions and the low substrate scope (phenyl hydrazines as the coupling partner) are some significant issues and reasons for developing the improved methods.

Over the years, prosperous development of sustainable and environment friendly processes for chemical transformation has led to remarkable progress and organic electrochemistry has efficiently contributed in this direction.[8] Organic electrochemistry is a broad term that defines chemical synthesis where activation is induced by electrons commonly consisting of anodic oxidations and cathodic reductions, replacing costly and toxic metal catalysts. Nonetheless, precise and regulated generation of reactive radicals to achieve predictable and tunable chemo-selectivity is still an enormous challenge. Recently, Studer and co-workers demonstrated a very important trifluoromethyl radical insertion, generated by the Togni reagent, into 2-isocyanobiphenyls for the phenanthridine synthesis (Scheme 1b).[9] This electrochemical synthesis requires no catalysts or oxidizing agents and provides efficient and scalable access to a range of phenanthridine and alike molecules.[10] Nevertheless, electrochemical aryl radical generation directly by amine *via* the reduction of *in situ* generated diazonium salts is relatively mild in nature but scarce in the literature.[11–16] Inspired by the above works, and from our recent experience in isocyanide chemistry,[17] here we have utilized isocyanides for electrochemical oxidative cross-coupling with amines for

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† Electronic supplementary information (ESI) available: Copy of ^{1}H NMR and ^{13}C NMR of all the synthesized compounds and CV studies. See DOI: 10.1039/d1nj00250c

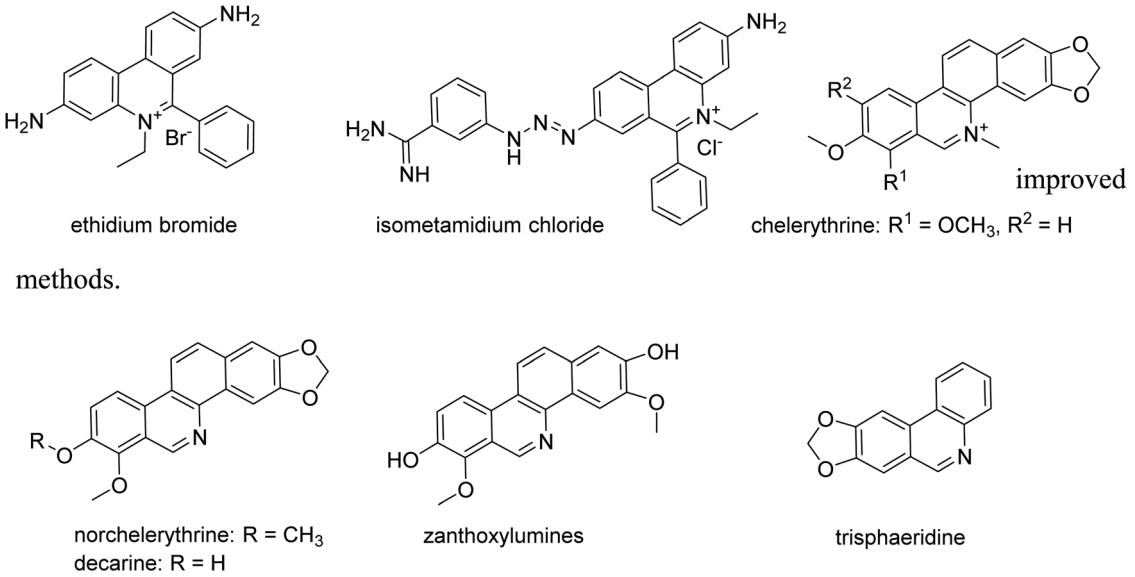


Fig. 1 Some representative alkaloids and bioactive phenanthridines.

carbodiimide synthesis.[18] We surmised whether the electrochemically generated aryl radicals could be trapped by isocyanides. Herein, we report the first electrochemical synthesis of 6-aryl phenanthridines and amides under mild conditions without the involvement of catalysts, metals and oxidants.

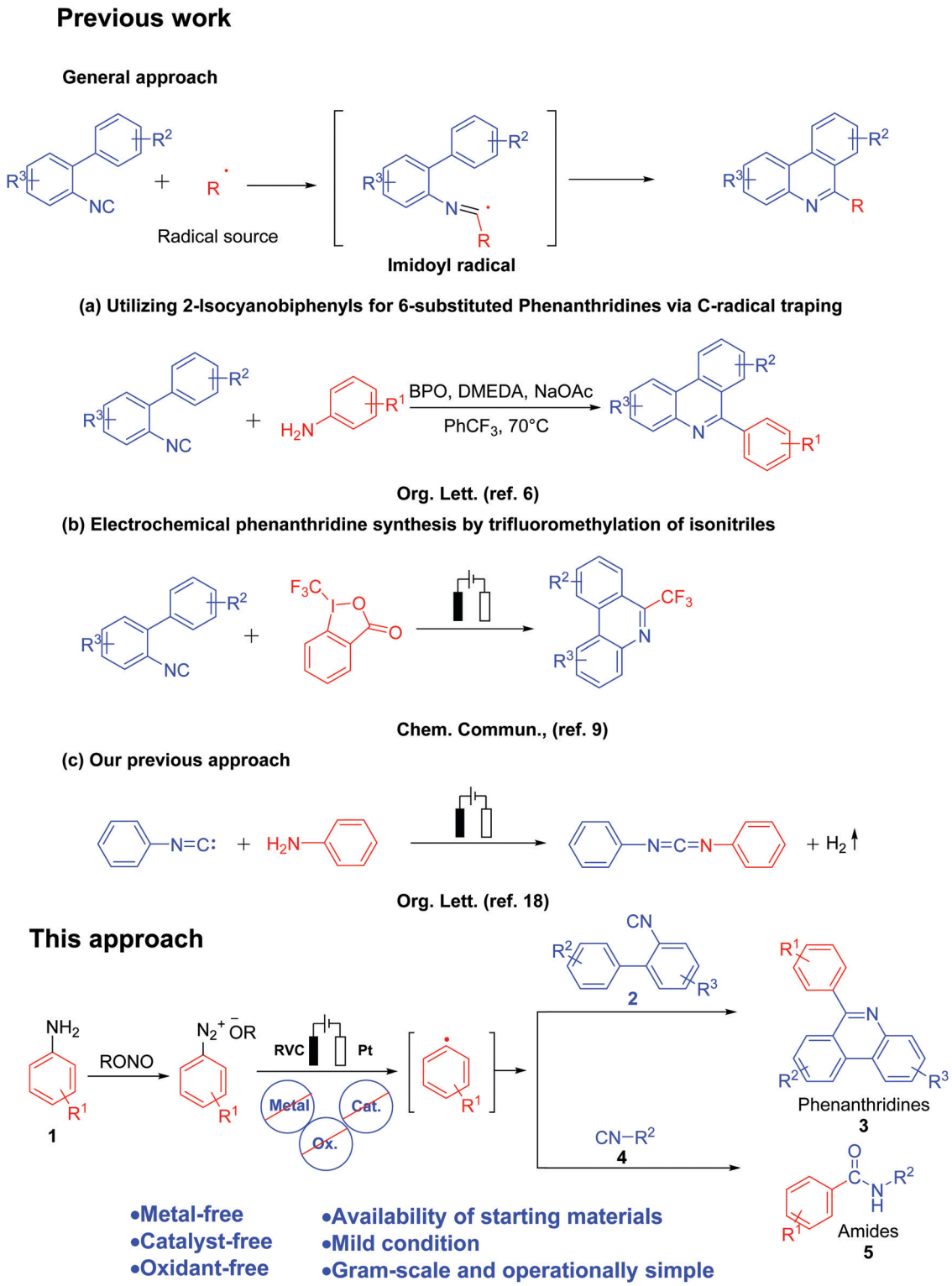
Results and discussion

Building upon previous works, our early efforts demonstrated that electrochemically generated phenyl radicals from *in situ* generated phenyl diazonium salt from aniline **1a** could be trapped by biphenylisocyanide **2a** for the synthesis of 6-arylated phenanthridine **3a** (Table 1). The electrochemical intramolecular cyclization cascade reaction was conducted at a constant current in an undivided cell equipped with an oxidatively robust reticulated vitreous carbon (RVC) as the anode (working electrode), and platinum (Pt), as the cathode (counter electrode). After screening a wide range of reaction systems, the desired 6-arylated phenanthridines **3a** were prepared in 81% yield using CH_3CN/HFIP (10 : 1) as solvent and nBu$_4$NBF$_4$ (0.1 M) as electrolyte under a constant current of 5 mA for 16 h (Table 1, entry 2). However, to our surprise, 84% yield of **3a** was obtained when 10 mA current was applied in 0.05 M electrolyte for 16 h (Table 1, entry 1). It is important to note that we could reduce the costly electrolyte amount to half just by changing the applied current.

Among the series of supporting electrolytes that were screened, no product **3a** was detected when nBu$_4$NBF$_4$ was replaced with NH_4I whereas in the presence of $LiClO_4$ and nBu$_4$NPF$_6$ it was isolated in lower yields (Table 1, entries 1 and 3–5). HFIP was found to be the best co-solvent with CH_3CN, possibly due to its low nucleophilic and protic nature, which could enhance the stability of radical or cationic intermediates. The use of other solvents, such as THF, MeOH and DMF produced inferior results compared with acetonitrile (Table 1, entries 6–8). Due to the potential effect of electrode materials to achieve the desired product **3a** in excellent yield, the RVC as the anode and Pt as the cathode were established as the best electrode for this electrolysis reaction, although comparable results were obtained when Pt was used as the anode in place of RVC (Table 1, entry 9). Other metal electrodes such as Cu and Ni were relatively less effective when used as cathodes (Table 1, entries 10–11). Extending the reaction time does not affect the reaction yield much but reducing the reaction time to 6 h reduced the yield of **3a** drastically (Table 1, entries 12 and 13).

Similarly, conducting the electrolysis using higher density (20 mA) also considerably reduced the yield of **3a** (Table 1, entry 14) and biphenyl **6** was the major product isolated (yield 49%). Moreover, when the reaction was performed under an air atmosphere, a decrease in the product yield was observed (Table 1, entry 18). Among the nitrite sources used such as *t*-BuONO and *n*-BuONO, isoamyl nitrite (i-AmONO) was the best (entries 19 and 20).

With the optimized conditions in hand, we next studied the substrate scope and generality of the present methodology for the synthesis of phenanthridines **3a–w** by varying the aryl amines **1** and 2-isocyanobiphenyls **2** (Table 2). A variety of different functional groups at aryl amines **1**, that bear both electron-donating groups (CH_3, OCH_3) and electron-withdrawing groups (F, Cl, Br, CN), showed great compatibility to give the corresponding products **3a–u** in moderate to excellent yields (Table 2). Different aryl amine bearing electron-donating CH_3 and OCH_3 at the *para*-position provided the corresponding products **3b**, **3c**, **3h**, and **3n** in 54–72% yields, whereas the electron-withdrawing groups on aryl amines **3d–f**, **3i–l**, and **3p–q** furnished good isolated yields of up to 81%, possibly due to alteration in radical activity due to the presence of an electron withdrawing group. It is to be noted that the unsubstituted aryl amines and 2-isocyanobiphenyl

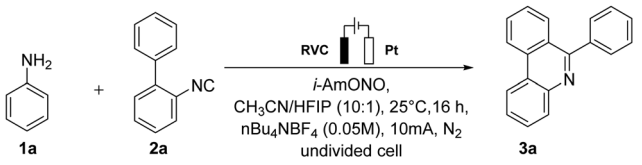


Scheme 1 Some previous reports showing conventional pathways towards utilizing C-centred radical trapping.

furnished phenanthridine **3a** in excellent yield (Table 2, entry 1, 84%). The reaction was very amenable, when different substituted 2-isocyanobiphenyls were used (**3f–3q**), whereas, few phenanthridine fused heteroaromatic polycyclic compounds were also well amenable to the standard reaction conditions (**3s–t**) in moderate yields of up to 62% yield. However, chloro substituted biphenyl isocyanide and heteroaromatic amine did not couple under standard conditions (**3v, 3w, 3x**).

At this juncture, we inquired whether this mode of phenyl radical generation could be extended to other related

Table 1 Optimization study[a]



Entry	Variation from standard conditions[a]	Yield[b] [%]
1	None	84
2	5 mA instead of 10 mA, 16 h and nBu$_4$NBF$_4$ (0.1 M)	81
3	NH_4I instead of nBu$_4$NBF$_4$	0
4	$LiClO_4$ instead of nBu$_4$NBF$_4$	67
5	nBu$_4$NPF$_6$ instead of nBu$_4$NBF$_4$	63
6	THF instead of CH_3CN	27
7	MeOH instead of HFIP	22
8	DMF instead of CH_3CN	47
9	Pt (+)/Pt (−) instead of RVC (+)/Pt (−)	77
10	RVC (+)/Cu (−) instead of RVC (+)/Pt (−)	56
11	RVC (+)/Ni (−) instead of RVC (+)/Pt (−)	67
12	24 h instead of 16 h	80
13	10 h instead of 16 h	36
14	20 mA instead of 10 mA	32
15	No electric current	0
16	50 °C instead of RT	16
17	5 mA instead of 10 mA and nBu$_4$NBF$_4$ (0.05 M)	49
18	Under air	13
19	t-BuONO instead of i-AmONO	62
20	n-BuONO instead of i-AmONO	51
21	No electric current and 80 °C	0

[a] Reaction conditions: all reactions were performed with an RVC anode, Pt cathode, constant current = 10 mA, **1a** (1.5 mmol), **2a** (0.50 mmol), i-AmONO (1.5 equiv.), nBu$_4$NBF$_4$ (0.05 M), CH_3CN/HFIP (10 : 1), (1F mol^{-1}), 25 °C, 16 h. [b] The yield of **3a** was isolated.

transformations by isocyanide trapping. Therefore, the electrochemical oxidative cyclization was further extended to similar optimization reaction condition for the synthesis of amides **5a–n**. After a series of screening of reaction conditions, we found that the direct electrolysis of aryl amines in an electrolyte solution of nBu$_4$NBF$_4$ in CH_3CN/H_2O (10 : 1) furnished amides in good to excellent yields. As shown in Table 3, a variety of aryl amines having both electron-donating groups (CH_3, OCH_3) and electron-withdrawing groups (NO_2, Br, F) were tested with t-butyl isocyanides and smoothly furnished the desired amides **5a–g** in good yields (Table 3). Different isocyanides were also examined under our optimized reaction conditions and furnished the desired products **5h–m** in moderate to good yields. Electron-withdrawing groups present on the benzene ring of phenyl amines such as NO_2 and Br led to very good yields (up to 81%) of amides **5e–g** (Table 3). By using different aliphatic isocyanides with substituents like cyclohexyl, benzyl and indolylethyl, a series of amides **5h–n** were successfully synthesized. Notably, the aromatic isocyanides containing an electron-donating group at the para position exhibited good reactivity, as product **5j** was obtained in 84% yield. In addition, 2,6-dimethyl substituted phenylisocyanide performed with lesser reactivity and furnished the amide **5k** in 54% yield whereas 4-bromophenyl isocyanide was well tolerated (**5l**, 78%). In addition, one heteroaromatic containing amine was also utilized for the synthesis of amide **5n** in moderate yield.

Next, we evaluated the scalability of this isocyanide insertion by performing reactions on a 5 mmol scale. The reaction with amine **1a** with biphenylisocyanide **2a** smoothly furnished the desired product **3a** (1.00 g) in 79% yield (Scheme 2). This result shows the potential of this insertion reaction in practical synthesis.

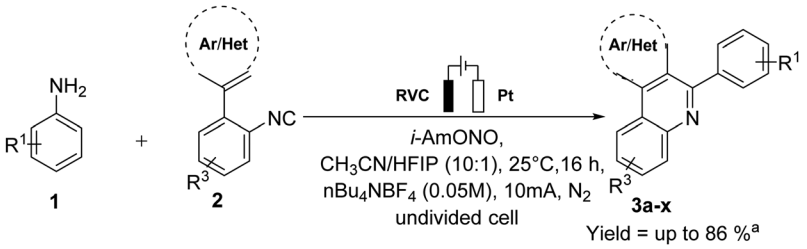
To gain insight into the mechanism of this method, we conducted control experiments, as shown in Scheme 3, to explore the existence of putative radical intermediates. In a control experiment, in the absence of isocyanides, biphenyl **6** was observed as the sole product during electrolysis (Scheme 3, eqn (a)). Thus, radical intermediates are possibly involved under the electrolysis conditions. We have also investigated the reaction mechanism under our optimized reaction conditions with a radical clock substrate, 2-(allyoxy)phenylamine **7**. This radical clock experiment gave the bicyclic phenanthridine **8** detected by HRMS (Scheme 3, eqn (b)), which again confirmed unambiguously to a radical mechanism. Similarly, the reaction of benzenediazonium tetrafluoroborate **9** under standard reaction conditions gave the corresponding product **3a** in good yields, again indicating the possible radical mechanism followed in the reaction.

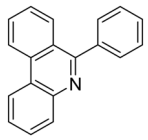
Furthermore, we also carried out cyclic voltammetry (CV) experiments to study the redox potential of the substrates (Fig. 2). Two reduction peaks were observed at −0.34 V and −1.92 V in nBu$_4$NBF$_4$ (0.05 M) as an electrolyte in CH_3CN, two reduction peaks, corresponding to the *in situ* reduction of aryl diazonium to aryl radicals and possibly further to aryl anion, respectively (for detailed analysis of CV please see the ESI† and Fig. S1–S5). On the basis of the control experimental results and literature reports[13] a plausible mechanism for the electrochemical oxidative cyclization reaction is proposed, as shown in Scheme 4. Initially, aryldiazonium ion **A** was formed from anilines and i-AmONO. Then, the aryl radical **B** was generated by single-electron-transfer (SET) reduction of the aryl diazonium salt **A** on the cathode. Phenanthridine synthesis was achieved by the formation of intermediate **C** by the coupling of **B** and **2**. Intramolecular cyclization of **C** and subsequent oxidative aromatization at the anode led to the corresponding carbocation **E**. Finally, removal of a proton from **E** afforded the targeted heterocycle **3**. Similarly, the generated aryl radical intermediate undergoes direct coupling with the isocyanide **4** to afford an imidoyl intermediate **G**. Finally, the hydration of imidoyl cation **G** leads to the formation of the amides **5**.

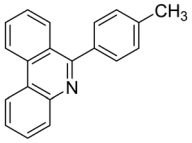
Conclusions

In summary, we have devised a highly atom-economical synthesis of 6-aryl substituted phenanthridines **3** by means of a radical-triggered pathway that involves a phenyl radical generated from aryl amines and 2-arylisocynides. Moreover, the electrochemical technology is also suitable for amides **5** using a similar strategy. Under undivided electrolytic conditions, a series of phenanthridines **3** and amides **5** can be obtained in good to excellent yields. Significantly, this reaction can be conducted on

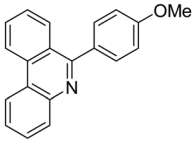
Table 2 Substrate scope for the synthesis of phenanthridines[a]



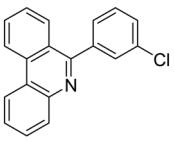

3a (84%)



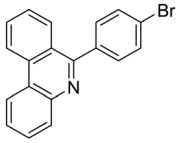
3b (72%)



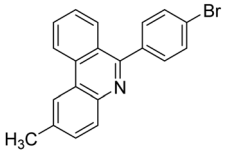
3c (56%)



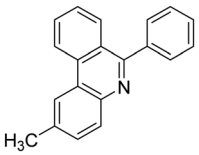
3d (82%)



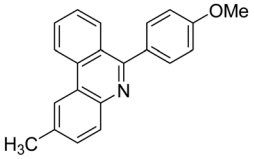
3e (70%)



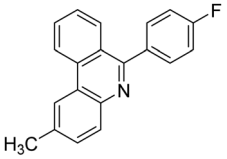
3f (68%)



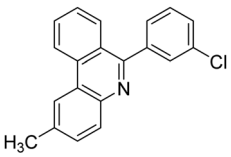
3g (84%)



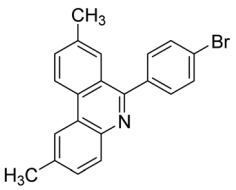
3h (66%)



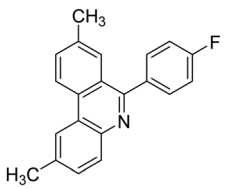
3i (76%)



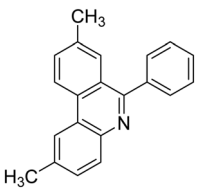
3j (66%)



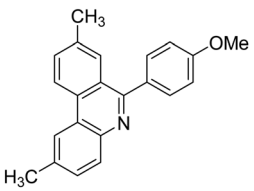
3k (75%)



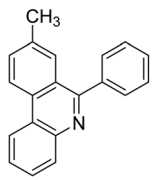
3l (86%)



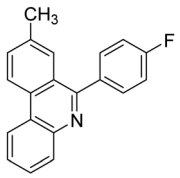
3m (57%)



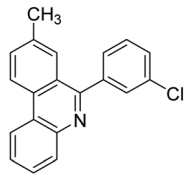
3n (54%)



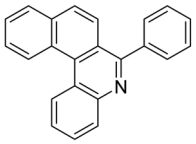
3o (68%)

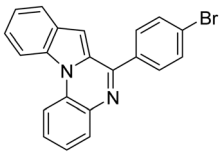


3p (78%)

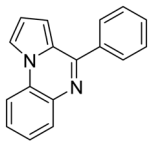


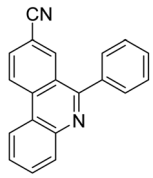
3q (68%)


3r (58%)



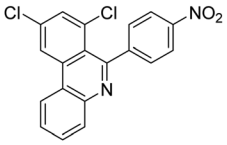
3s (48%)


3t (62%)

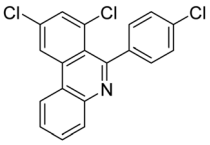


3u (67%)

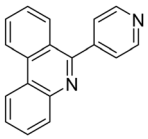
Table 2 (*continued*)



3v (0%)



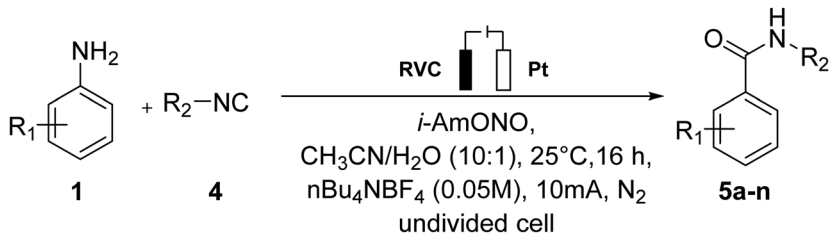
3w (0%)



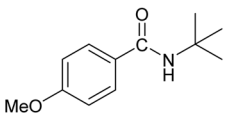
3x (0%)

[a] Isolated yields.

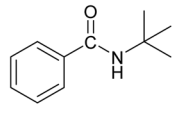
Table 3 Substrate scope of the electrochemical synthesis of amides[a]



1 **4** **5a-n**



5a (81%)



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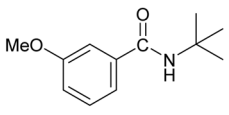

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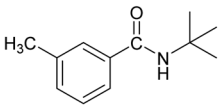

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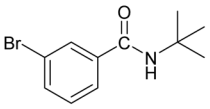
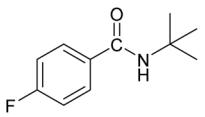
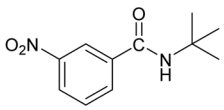


5e (78%)



5f (63%)



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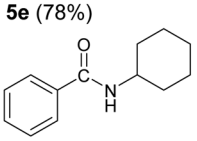
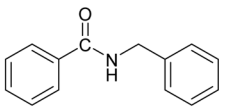
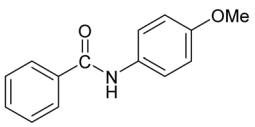


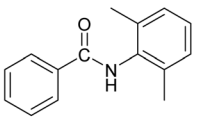
5h (46%)



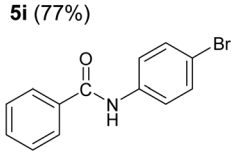
5i (77%)



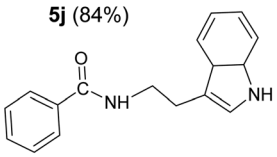
5j (84%)



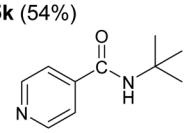
5k (54%)



5l (78%)



5m (42%)



5n (32%)

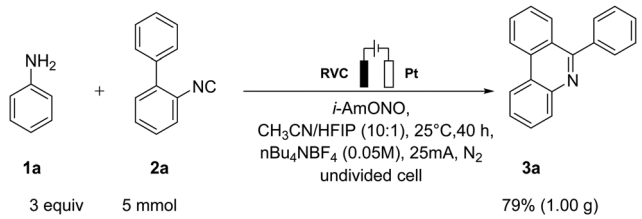
[a] Isolated yields.

a gram scale under atmospheric conditions. Furthermore, the control experiments, to prove the reaction mechanism, and cyclic voltammetry (CV) experiments, to study the redox potential of the substrates, were well studied. Further application of electrochemical isocyanide cross-coupling for other challenging phenanthridine nuclei is currently underway in our laboratory.

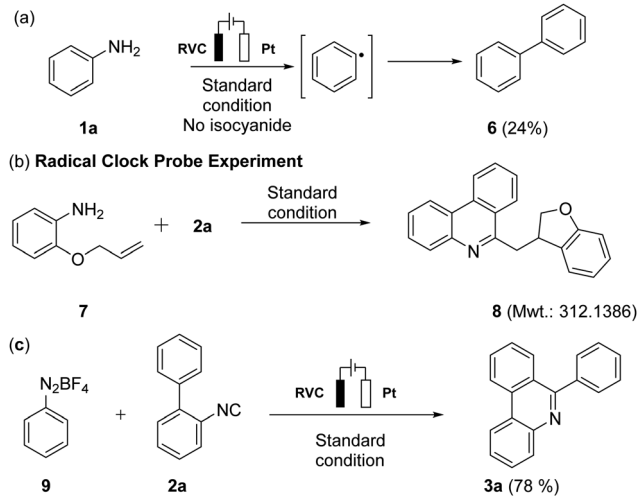
Experimental section

General information

All reactions involving moisture sensitive reagents or intermediates were carried out in pre-heated glassware under a nitrogen atmosphere. All solvents and chemicals were used as



Scheme 2 Gram-scale synthesis.



Scheme 3 Control experiments.

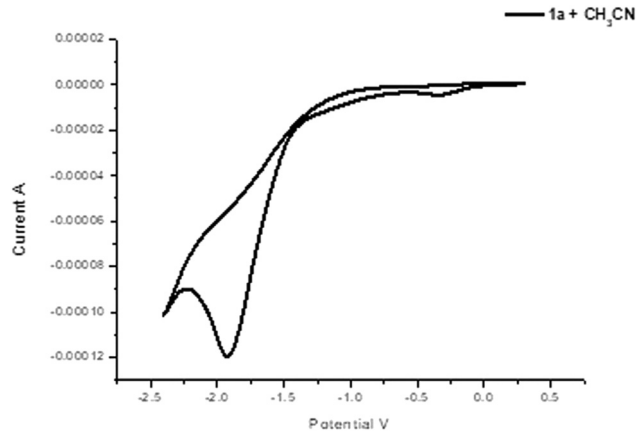


Fig. 2 Cyclic voltammograms of **1a** in CH_3CN, using a glassy carbon electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl as the reference electrode, at a scan rate of 0.1 V s^{-1}: **1a** (0.01 M) + i-AmONO (0.01 M) + nBu$_4$NBF$_4$ (0.05 M).

received from the suppliers (Alfa, Sigma Aldrich, Avra). Reactions were monitored using thin-layer chromatography (TLC) on commercial silica gel plates. Solvents for crystallization and extractions have been distilled once. Column chromatography was performed on silica gel (100–200 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz and 500 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal TMS standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.03) and relative to the signal of DMSO-d$_6$ (δ 2.50 ppm for ^{1}H NMR and δ 39.52 ppm for ^{13}C NMR). The following abbreviations were used to describe peak splitting patterns when appropriate: br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, J, were reported in Hertz (Hz). Mass spectra were recorded on a Bruker MicroTOF Q II mass spectrometer. The instrument used for electrolysis was IKA ElectraSyn 2.0 pro constant current DC power supply with three electrode cyclic voltammetry attachments and on our inhouse design electrolysis experiments. An oil bath was used for the heating conditions.

Representative procedure for the preparation of biphenyl isocyanides (2)[19]

All biphenyl isocyanides were prepared according to the reported method. A typical procedure for the synthesis of **2** is shown below.

Synthesis of [1,1′-biphenyl]-2-amine

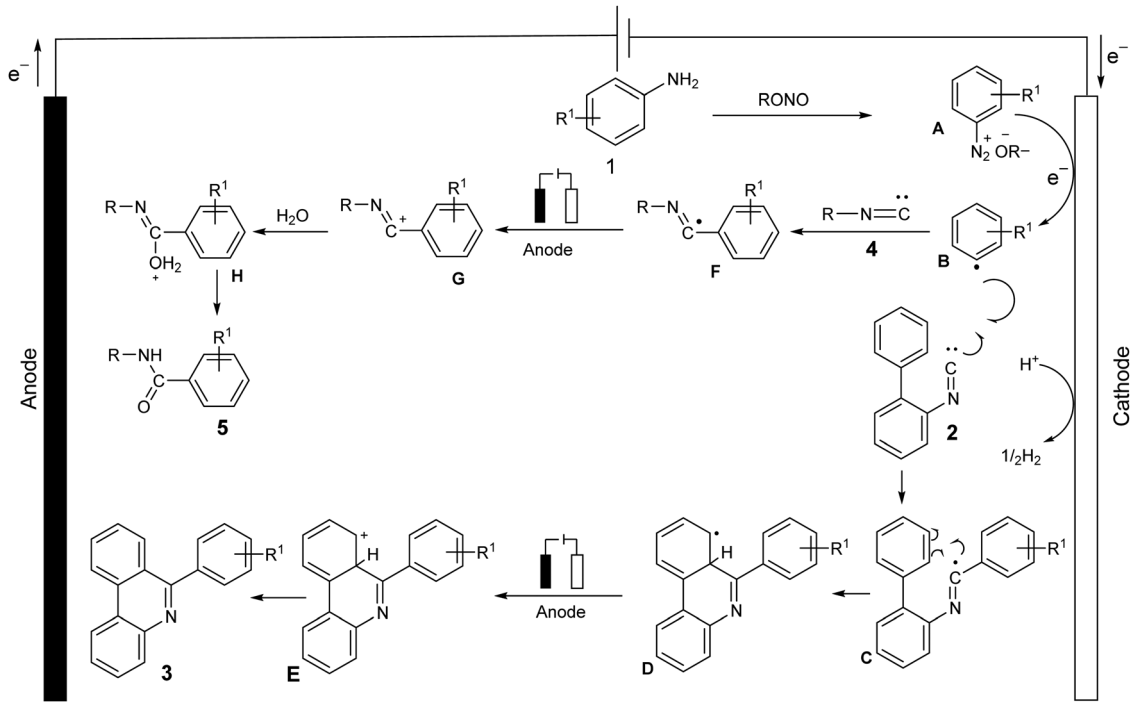
To an oven-dried three necked flask, 2-bromoaniline (860 mg, 5 mmol), phenylboronic acid (725 mg, 6 mmol), an aqueous solution of K_2CO_3 (2 M, 5 mL) and DMF (10 mL) were added under a stream of N_2. The mixture was stirred for 30 min at room temperature under an N_2 atmosphere. To the stirred mixture, $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol) was added at room temperature, and the mixture was stirred overnight at 80 °C. The reaction mixture was then cooled to room temperature and diluted with EtOAc. The organic layer was washed with water and dried over Na_2SO_4. After removing the volatiles *in vacuo*, the residue was subjected to column chromatography on silica gel (petroleum ether/EtOAc) to afford 2-phenylaniline (750 mg, 82%).

Synthesis of *N*-([1,1′-biphenyl]-2-yl)formamide

Acetic formic anhydride (0.89 mL) was added dropwise to a solution of [1,1′-biphenyl]-2-amine (727 mg, 4.30 mmol) at 0 °C in THF (10 mL) under stirring. The mixture was stirred for 2 h at room temperature. Then, the mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL) and extracted with EtOAc (30 mL) three times. The extract was dried over Na_2SO_4 and concentrated under reduced pressure to give formamide (717 mg, 3.63 mmol) as a pale yellow oil. This material was used for the subsequent dehydration without further purification.

Synthesis of 2-isocyano-1,1′-biphenyl

THF (8 mL), and NEt_3 (4.3 mL) were added to the flask containing *N*-([1,1′-biphenyl]-2-yl)formamide, and $POCl_3$ (0.5 mL, 1.5 eq.) in 2 mL of THF was added slowly *via* syringe for a period of 1 h at 0 °C, and the mixture was stirred for another 2 h at 0 °C. To the reaction mixture was added 15 mL of EtOAc at 0 °C. The mixture was slowly quenched with saturated aqueous solution of $NaHCO_3$ (20 mL) and stirred for 30 min at 0 °C. Then, the mixture was extracted with EtOAc (30) three times, dried over Na_2SO_4 and evaporated under reduced pressure. The compound was purified



Scheme 4 Plausible mechanism.

by column chromatography (petroleum ether/EtOAc 19 : 1, 5%) to give **2** as a pale yellow solid (650 mg, 3.63 mmol).

General procedure for the synthesis of 3

An undivided cell was equipped with a RVC plate (15 mm × 15 mm × 5 mm) anode and a platinum plate (15 mm × 15 mm × 0.3 mm) cathode. The compound aromatic amines **1** (1.5 mmol), i-AmONO (1.5 equiv.), biphenylisocynide **2** (0.5 mmol) and supporting electrolyte nBu$_4$NBF$_4$ (0.05 M) in CH$_3$CN/HFIP (10 : 1, 6 mL) was first stirred for 10 min, and after the complete consumption of amine on TLC, the reaction was electrolyzed under constant current conditions (10 mA at 25 °C) under nitrogen atmosphere for 16 h. Electrodes were washed with ethyl acetate (10 mL), and when the reaction was finished, the solution was extracted with ethyl acetate (40 mL). The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel (ethyl acetate/petroleum ether 1 : 9 = 10%).

Larger-scale synthesis of 3a

An undivided cell (50 mL) was equipped with RVC electrodes (20 × 35 × 5 mm) as the anode, platinum electrodes (20 × 35 × 0.5 mm) as the cathode. Using a stir bar, aniline **1a** (1.395 g, 15 mmol), i-AmONO (1.757 g, 15 mmol), 2-isocyano-1,1′-biphenyl **2a** (0.896 g, 5.0 mmol), CH$_3$CN/HFIP (10 : 1, 20 mL) and supporting electrolyte nBu$_4$NBF$_4$ (0.329 g, 0.05 M) were first stirred for 10 min, after the complete consumption of amine on TLC reaction was electrolyzed under constant current conditions (25 mA at 25 °C) under nitrogen conditions for 40 h. Electrodes were washed with ethyl acetate (10 mL), when the reaction was finished, the solution was extracted with ethyl acetate (80 mL). The combined organic layer was dried with Na_2SO_4, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel (ethyl acetate/petroleum ether 1 : 9 = 10%) yield (1.00 g, 79%).

Characterization of the products

6-Phenylphenanthridine (3a)[19a,b]. White solid, isolated yield (107 mg, 84%) (for 0.5 mmol),^{1}H NMR (400 MHz, CDCl$_3$): δ 7.53–7.59 (m, 3H), 7.60 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.68 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.73–7.79 (m, 3H), 7.85 (td, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 8.10 (dd, J_1 = 8 Hz, J_2 = 0.4 Hz, 1H), 8.24 (td, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 8.62 (td, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 122.9, 122.2, 123.7, 125.2, 126.9, 127.1, 128.4, 128.7, 128.8, 128.9, 129.7, 130.3, 130.6, 133.4, 139.8, 143.8, 161.3.

6-(m-Tolyl)phenanthridine (3b)[20a]. Brown solid, isolated yield (97 mg, 72%) (for 0.5 mmol),^{1}H NMR (400 MHz, CDCl$_3$): δ 2.48 (s, 3H), 7.35 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H), 7.62 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.69 (td, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 7.76 (td, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.87 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.12 (d, J = 8 Hz, 1H), 8.37 (d, J = 7.6 Hz, 1H), 8.62 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.5, 121.9, 122.2, 123.8, 125.1, 126.9, 127.2, 127.3, 128.2, 129.1, 129.3, 129.7, 129.8, 130.4, 131.1, 133.6, 138.3, 161.4.

6-(4-Methoxyphenyl)phenanthridine (3c)[20a]. White solid, isolated yield (80 mg, 56%) (for 0.5 mmol),^{1}H NMR (400 MHz, CDCl$_3$): δ 3.92 (s, 3H), 7.08 (tt, J_1 = 8.8 Hz, J_2 = 2, 2H), 7.60 (td, J_1 = 7.6 Hz, J_2 = 0.8, 1H), 7.65 (td, J_1 = 7.2 Hz, J_2 = 1.2, 1H), 7.70 (dd, J_1 = 8.4 Hz, J_2 = 2, 2H), 7.73 (td, J_1 = 8 Hz, J_2 =

1.2, 1H), 7.83 (td, J_1 = 8 Hz, J_2 = 0.8, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.23 (dd, J_1 = 8.4 Hz, J_2 = 0.8, 1H), 8.60 (d, J = 7.6 Hz, 1H), 8.69 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 113.9, 121.9, 122.2, 123.6, 125.4, 126.7, 127.1, 128.8, 128.9, 130.2, 130.5, 131.2, 132.3, 133.5, 143.7, 160.1, 160.9.

6-(3-Chlorophenyl)phenanthridine (3d)[20a]. Brown solid, isolated yield (118 mg, 82%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.54 (m, 2H), 7.61–7.66 (m, 2H), 7.69 (td, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.75 (t, J = 2 Hz, 1H), 7.76 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.86 (td, J_1 = 7.6 Hz, J_2 = 1.2, 1H), 8.05 (dd, J_1 = 8 Hz, J_2 = 0.4 Hz, 1H), 8.25 (dd, J_1 = 8 Hz, J_2 = 0.8 Hz, 1H), 8.61 (dd, J_1 = 8 Hz, J_2 = 1.2, 1H), 8.69 (d, J = 8.4, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ 121.9, 122.3, 123.8, 124.9, 127.3, 127.4, 127.9, 128.5, 128.9, 129.0, 129.7, 129.8, 130.2, 130.9, 133.5, 134.5, 141.2, 143.4, 159.6.

6-(4-Bromophenyl)phenanthridine (3e)[20a]. White solid, isolated yield (117 mg, 70%) (for 0.5 mmol), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.65 (m, 3H), 7.68–7.72 (m, 3H), 7.75 (td, J_1 = 7.6 Hz, J_2 = 1.6, 1H), 7.85 (td, J_1 = 7.2 Hz, J_2 = 1.2, 1H), 8.05 (dd, J_1 = 8 Hz, J_2 = 0.8, 1H), 8.22 (dd, J_1 = 8 Hz, J_2 = 0.8, 1H), 8.61 (dd, J_1 = 8 Hz, J_2 = 1.6, 1H), 8.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.0, 122.3, 123.1, 123.7, 124.9, 127.1, 127.5, 128.4, 128.9, 130.3, 130.7, 131.4, 131.6, 133.5, 138.6, 143.7, 159.9.

6-(4-Bromophenyl)-2-methylphenanthridine (3f)[20b]. Brown solid, isolated yield (118 mg, 68%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H), 7.59–7.65 (m, 4H), 7.69 (s, 1H), 7.71 (s, 1H), 7.86 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 8.04 (dd, J_1 = 8.4 Hz, J_2 = 0.4 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 8.39 (s, 1H), 8.68 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 121.6, 122.4, 123.7, 124.7, 127.4, 128.8, 129.1, 129.5, 131.1, 131.2, 131.6, 131.7, 133.5, 137.6, 158.7.

2-Methyl-6-phenylphenanthridine (3g)[20b]. Pale yellow solid, isolated yield (113 mg, 84%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.62 (s, 3H), 7.52 (d, J = 10.8 Hz, 5H), 7.71 (d, J = 6 Hz, 2H), 7.76 (t, J = 8.4 Hz, 1H), 8.05 (d, J = 8 Hz, 1H), 8.12 (d, J = 8 Hz, 1H), 8.35 (s, 1H), 8.62 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 121.5, 122.1, 123.5, 125.2, 126.9, 128.3, 128.5, 128.7, 129.7, 129.9, 130.3, 130.5, 133.1, 136.7, 139.8, 141.9, 160.2.

6-(4-Methoxyphenyl)-2-methylphenanthridine (3h)[19b]. White solid, isolated yield (99 mg, 66%) (for 0.5 mmol), ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.65 (s, 3H), 3.91 (s, 3H), 7.07 (dt, J_1 = 8.8 Hz, J_2 = 2 Hz, 2H), 7.56 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.58 (td, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.68 (dt, J_1 = 8.8 Hz, J_2 = 2 Hz, 2H), 7.81 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 8.10 (d, J = 8.4 Hz, 2H), 8.13 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.39 (s, 1H), 8.67 (d, J = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 55.4, 113.9, 121.5, 122.2, 123.4, 125.4, 126.9, 128.7, 130.0, 130.2, 130.5, 131.2, 132.4, 133.2, 136.6, 142.2, 159.9, 160.0.

6-(4-Fluorophenyl)-2-methylphenanthridine (3i)[20c]. Pale yellow solid, isolated yield (109 mg, 76%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$ + DMSO): δ 2.68 (s, 3H), 7.25 (tt, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 2H), 7.60 (dd, J_1 = 8 Hz, J_2 = 2 Hz, 1H), 7.62 (td, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.73–7.78 (m, 2H), 7.86 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 8.07 (dd, J_1 = 8.4 Hz, J_2 = 0.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 8.42 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO): δ 22.0, 115.3, 115.5, 121.6, 122.3, 123.6, 125.2, 127.1, 128.6, 129.9, 130.5, 130.7, 131.6, 131.7, 133.3, 135.7, 137.1, 141.8, 159.2, 161.9, 164.4.

6-(3-Chlorophenyl)-2-methylphenanthridine (3j)[20b]. Brown solid, isolated yield (100 mg, 66%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.66 (s, 3H), 7.46–7.52 (m, 2H), 7.59–7.64 (m, 3H), 7.75 (s, 1H), 7.83 (t, J = 7.2 Hz, 1H), 8.03 (d, J = 8 Hz, 1H), 8.11 (d, J = 8 Hz, 1H), 8.40 (s, 1H), 8.68 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 121.6, 122.3, 123.6, 125.0, 127.2, 128.0, 128.4, 128.8, 129.7, 129.9, 130.1, 130.5, 130.7, 133.2, 134.5, 137.2, 141.6, 142.0, 158.7.

6-(4-Bromophenyl)-2,8-dimethylphenanthridine (3k). Light yellow solid, isolated yield (136 mg, 75%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$ + DMSO): δ 2.51 (s, 3H), 2.64 (s, 3H), 7.55 (d, J = 8.4 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8 Hz, 3H), 7.79 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 8.36 (s, 1H), 8.57 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO): δ 21.4, 21.7, 121.2, 122.0, 122.8, 123.4, 124.5, 127.5, 128.9, 130.1, 130.8, 131.2, 131.2, 132.4, 137.0, 137.1, 158.1; HRMS (ESI-TOF) m/z [M + H]$^+$calcd for $C_{21}H_{17}BrN$ 362.0539; found 362.0534.

6-(4-Fluorophenyl)-2,8-dimethylphenanthridine (3l). White solid, isolated yield (130 mg, 86%) (for 0.5 mmol), ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.50 (s, 3H), 2.63 (s, 3H), 7.51 (t, J = 8.8 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.87–7.91 (m, 2H), 7.99 (d, J = 8.4 Hz, 1H), 8.26 (d, J = 8.4 Hz, 1H), 8.75 (s, 1H), 8.92 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.2, 21.6, 115.7, 115.9, 122.6, 123.3, 124.1, 124.4, 129.0, 130.0, 131.8, 131.9, 132.9, 133.8, 136.1, 139.2, 157.7, 162.3, 164.7; HRMS (ESI-TOF) m/z [M + H]$^+$calcd for $C_{21}H_{17}FN$ 302.1340; found 302.1332.

2,8-Dimethyl-6-phenylphenanthridine (3m)[20d]. Pale yellow solid, isolated yield (80 mg, 57%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 2.62 (s, 3H), 7.51–7.57 (m, 4H), 7.63 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.83 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.53 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 22.0, 121.3, 122.1, 123.6, 125.3, 128.2, 128.4, 128.6, 129.7, 129.7, 130.2, 131.1, 132.3, 136.8, 137.0, 139.6, 141.4, 159.9.

6-(4-Methoxyphenyl)-2,8-dimethylphenanthridine (3n). Pale yellow solid, isolated yield (84 mg, 54%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 2.57 (s, 3H), 3.87 (s, 3H), 7.13 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 8.54 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 21.9, 55.8, 114.2, 122.4, 123.2, 123.6, 124.9, 128.2, 128.4, 130.9, 131.3, 131.8, 133.6, 137.5, 137.9, 159.0, 160.4; HRMS (ESI-TOF) m/z [M + H]$^+$calcd for $C_{22}H_{20}NO$ 314.1539; found 314.1542.

8-Methyl-6-phenylphenanthridine (3o)[20e]. White solid, isolated yield (91 mg, 68%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.52–7.59 (m, 3H), 7.63 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 2H), 7.70 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 3H), 7.85 (s, 1H), 8.26 (d, J = 8 Hz, 1H), 8.54 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 121.7, 122.1, 123.8, 125.3, 126.9, 128.3, 128.4, 128.7, 129.7, 130.0, 131.3, 132.5, 137.2, 139.5, 143.1, 160.9.

6-(4-Fluorophenyl)-8-methylphenanthridine (3p). Pale yellow solid, isolated yield (112 mg, 78%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$ + DMSO): δ 2.55 (s, 3H), 7.31 (t, J = 7.2 Hz, 2H), 7.74–7.83 (m, 5H), 7.88 (s, 1H), 8.47 (s, 1H), 8.63–8.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO): δ 20.9, 114.8, 115.0, 121.4, 121.8, 123.2, 123.7, 126.8, 127.3, 127.8, 128.5, 131.2, 131.3, 131.4, 133.7, 137.6, 139.2, 158.4, 161.5, 164.0; HRMS (ESI-TOF) m/z $[M + H]^+$calcd for $C_{20}H_{15}FN$ 288.1183; found 288.1188.

6-(3-Chlorophenyl)-8-methylphenanthridine (3q). Pale yellow solid, isolated yield (103 mg, 68%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H), 7.52 (s, 2H), 7.60 (d, J = 4.8 Hz, 1H), 7.67–7.76 (m, 4H), 7.80 (s, 1H), 8.28 (d, J = 7.6 Hz, 1H), 8.56 (t, J = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 121.8, 122.3, 123.9, 125.0, 127.4, 127.9, 128.0, 128.7, 129.0, 129.7, 129.8, 131.5, 132.9, 134.5, 137.6, 159.3; HRMS (ESI-TOF) m/z $[M + H]^+$calcd for $C_{20}H_{15}ClN$ 304.0888; found 304.0888.

6-Phenylbenzo[k]phenanthridine (3r)[20f]. White solid, isolated yield (88 mg, 58%) (for 0.5 mmol),^{1}H NMR (500 MHz, DMSO-d_6): δ 7.57–7.62 (m, 3H), 7.70 (dd, J_1 = 6 Hz, J_2 = 1 Hz, 2H), 7.80 (td, J_1 = 6 Hz, J_2 = 1 Hz, 1H), 7.84 (td, J_1 = 5.5 Hz, J_2 = 0.5 Hz, 2H) 7.87 (t, J = 6.5 Hz, 2H), 8.06 (d, J = 7.5 Hz, 1H), 8.17 (dd, J_1 = 6 Hz, J_2 = 1.5 Hz, 1H), 8.24 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 1H), 9.05 (d, J = 7 Hz, 1H), 9.16 (d, J = 6.5 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 123.0, 123.2, 124.2, 126.8, 127.1, 127.4, 128.2, 128.2, 128.3, 128.3, 128.3, 128.7, 128.7, 129.8, 129.9, 131.5, 134.2, 139.5, 145.1, 159.6.

6-(4-Bromophenyl)indolo[1,2-*a*]quinoxaline (3s)[20f]. White solid, isolated yield (89 mg, 48%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (s, 1H), 7.48 (t, J = 6 Hz, 2H), 7.60 (t, J = 6.5 Hz, 1H), 7.66 (t, J = 6 Hz, 1H) 7.74 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 7 Hz, 2H), 7.97 (d, J = 7 Hz, 1H), 8.09 (d, J = 6.5 Hz, 1H), 8.54 (d, J = 7.5 Hz, 1H), 8.57 (d, J = 7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.3, 114.6, 114.7, 122.8, 122.9, 124.3, 124.4, 124.6, 128.6, 128.8, 129.2, 130.3, 130.6, 131.9, 133.2, 136.2, 137.2, 155.1.

4-Phenylpyrrolo[1,2-*a*]quinoxaline (3t)[20g]. White solid, isolated yield (76 mg, 62%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (t, J = 3.5 Hz, 1H), 6.99 (d, J = 3.5 Hz, 1H), 7.45 (td, J_1 = 6.5 Hz, J_2 = 0.5 Hz, 1H), 7.51–7.56 (m, 4H), 7.88 (d, J = 7 Hz, 1H), 7.99–8.01 (m, 3H), 8.04 (dd, J_1 = 7 Hz, J_2 = 1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 108.7, 113.6, 113.9, 114.6, 125.3, 125.4, 127.2, 127.5, 128.6, 128.6, 129.8, 130.3, 136.3, 138.5, 154.4.

6-Phenylphenanthridine-8-carbonitrile (3u). White solid, isolated yield (94 mg, 67%) (for 0.5 mmol), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.64 (m, 3H), 7.69–7.72 (m, 2H), 7.74 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.84 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 8.01 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 8.27 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 8.46 (d, J = 1.6 Hz, 1H), 8.60 (d, J = 8 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.6, 122.4, 122.5, 123.6, 124.7, 127.8, 128.8, 129.4, 129.7, 130.7, 130.7, 131.7, 134.3, 136.0, 144.7, 160.4; HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{20}H_{13}N_2$ 281.1073; found 281.1080.

General procedure for the synthesis of 5

An undivided cell was equipped with a RVC plate (15 mm × 15 mm × 5 mm) anode and a platinum plate (15 mm × 15 mm × 0.3 mm) cathode. The compound of amine **1** (1.5 mmol), i-AmONO (1.5 equiv.), isocyanide **4** (0.5 mmol) and supporting electrolyte nBu$_4$NBF$_4$ (0.05 M) in CH_3CN : H_2O (10 : 1, 7 mL) was first stirred for 10 min, after the complete consumption of amine in the TLC reaction it was electrolyzed under constant current conditions (10 mA at 25 °C) under nitrogen conditions for 16 h. Electrodes were washed with ethyl acetate (10 mL), when the reaction was finished, the solution was extracted with ethyl acetate (40 mL). The combined organic layer was dried with $MgSO_4$, filtered. The solvent was removed with a rotary evaporator. The pure product was obtained by column chromatography on silica gel (ethyl acetate/petroleum ether 1 : 4 = 20%).

***N*-(*tert*-Butyl)-4-methoxybenzamide (5a)[21a].** White solid, isolated yield (84 mg, 81%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 9H), 3.84 (s, 3H), 5.91 (s, 1H), 6.89 (d, J = 7.6 Hz, 2H), 7.68 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.9, 51.4, 55.4, 113.5, 128.0, 128.4, 161.8, 166.4.

***N*-(*tert*-Butyl)benzamide (5b)[21a,b].** White solid, isolated yield (66 mg, 74%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 9H), 6.02 (s, 1H), 7.38 (t, J = 6.4 Hz, 2H), 7.44 (t, J = 6.4 Hz, 1H), 7.71 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 51.5, 126.7, 128.4, 131.0, 135.8, 166.9.

***N*-(*tert*-Butyl)-3-methoxybenzamide (5c)[21a].** White solid, isolated yield (71 mg, 69%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.46 (s, 9H), 3.83 (s, 3H), 5.95 (s, 1H), 6.98 (dd, J_1 = 8 Hz, J_2 = 2.4 Hz, 1H), 7.20 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.27 (t, J = 8 Hz, 1H), 7.32 (t, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 51.6, 55.4, 112.1, 117.3, 118.4, 129.4, 137.4, 159.8, 166.7.

***N*-(*tert*-Butyl)-3-methylbenzamide (5d)[21a].** White solid, isolated yield (70 mg, 73%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 9H), 2.38 (s, 3H), 5.97 (s, 1H), 7.27–7.30 (m, 2H), 7.47–7.50 (m, 1H), 7.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 28.8, 51.5, 123.6, 127.4, 128.3, 131.7, 135.8, 138.2, 167.1.

3-Bromo-*N*-(*tert*-butyl)benzamide (5e)[21a]. White solid, isolated yield (100 mg, 78%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.47 (s, 9H), 5.93 (s, 1H), 7.27 (t, J = 8 Hz, 1H), 7.58 (dt, J_1 = 8 Hz, J_2 = 1.2 Hz, 1H), 7.63 (d, J = 8 Hz, 1H), 7.84 (t, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.7, 51.9, 122.6, 125.3, 129.9, 130.1, 134.0, 137.9, 165.4.

***N*-(*tert*-Butyl)-4-fluorobenzamide (5f)[21a].** White solid, isolated yield (61 mg, 63%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 9H), 5.91 (s, 1H), 7.04 (t, J = 8.8 Hz, 2H), 7.69–7.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 45.8, 51.7, 115.3, 115.5, 128.9, 129.0, 132.0, 132.1, 163.2, 165.7, 165.8.

***N*-(*tert*-Butyl)-3-nitrobenzamide (5g)[21c].** Pale yellow solid, isolated yield (90 mg, 81%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.49 (s, 9H), 6.09 (s, 1H), 7.59 (t, J = 8 Hz, 1H), 8.08 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.29–8.32 (m, 1H), 8.50 (t, J = 2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.8, 52.3, 121.5, 125.7, 129.7, 133.1, 137.5, 148.1, 164.4.

***N*-Cyclohexylbenzamide (5h)[21c].** White solid, isolated yield (47 mg, 46%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19–1.28 (m, 3H), 1.39–1.47 (m, 2H), 1.64 (t, J = 4.8 Hz, 1H), 1.73 (dd, J_1 = 6.2 Hz, J_2 = 3.2 Hz, 2H), 2.01 (t, J = 3.6 Hz, 2H), 3.95–4.03

(m, 1H), 6.03–6.14 (m, 1H), 7.38–7.50 (m, 3H), 7.74–7.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.9, 25.5, 33.2, 48.7, 126.5, 128.5, 128.5, 131.2, 135.0, 166.7.

***N*-Benzylbenzamide (5i)[21a].** Brown solid, isolated yield (81 mg, 77%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 4.62 (dd, J_1 = 5.4 Hz, J_2 = 2.4 Hz, 2H), 6.58 (s, 1H), 7.27–7.31 (m, 1H), 7.34 (d, J = 4.4 Hz, 4H), 7.39 (td, J_1 = 7 Hz, J_2 = 1.2 Hz, 2H), 7.47 (tt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.78–7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.1, 126.9, 127.6, 127.9, 128.6, 128.8, 131.5, 134.3, 138.2, 167.4.

***N*-(4-Methoxyphenyl)benzamide (5j)[21d].** Pale yellow solid, isolated yield (95 mg, 84%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 6.88 (dt, J_1 = 9.2 Hz, J_2 = 2.8 Hz, 2H), 7.45 (t, J = 6.8 Hz, 2H), 7.52 (t, J = 1.2 Hz, 1H), 7.53 (d, J = 2.8 Hz, 1H), 7.55 (s, 1H), 7.82 (s, 1H), 7.85 (d, J = 1.6 Hz, 1H), 7.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.2, 122.1, 126.9, 128.7, 130.9, 131.7, 135.0, 156.6, 165.6.

***N*-(2,6-Dimethylphenyl)benzamide (5k)[21c].** White solid, isolated yield (61 mg, 54%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 6H), 7.08–7.16 (m, 3H), 7.44 (d, J = 7.2 Hz, 2H), 7.53 (tt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.58 (s, 1H), 7.88 (t, J = 1.2 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 127.2, 127.4, 128.2, 128.7, 131.7, 133.9, 134.4, 135.6, 165.9.

***N*-(4-Bromophenyl)benzamide (5l)[21e].** White solid, isolated yield (108 mg, 78%) (for 0.5 mmol),^{1}H NMR (100 MHz, $CDCl_3$ + DMSO): δ 7.30–7.40 (m, 5H), 7.57 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 7.2 Hz, 2H), 9.16 (s, 1H); ^{13}C NMR (400MHz, $CDCl_3$ + DMSO): δ 116.5, 122.1, 127.6, 128.6, 131.8, 135.1, 138.2, 166.2, 207.1.

***N*-(2-(3*a*,7*a*-Dihydro-1*H*-indol-3-yl)ethyl)benzamide (5m)[21f].** Yellow solid, isolated yield (56 mg, 42%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 3.05 (t, J = 6.8 Hz, 2H), 3.76 (d, J = 5.6 Hz, 2H), 6.43 (s, 1H), 7.00 (s, 1H), 7.08 (t, J = 7.2 Hz, 1H), 7.17 (t, J = 8 Hz, 1H), 7.33 (t, J = 8 Hz, 3H), 7.42 (t, J = 7.2 Hz, 1H), 7.61 (d, J = 8 Hz, 1H), 7.65 (d, J = 7.2 Hz, 2H), 8.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.2, 40.3, 111.4, 112.7, 118.7, 119.4, 122.1, 122.2, 126.9, 127.2, 128.5, 131.4, 134.4, 136.4, 167.7.

***N*-(*tert*-Butyl)isonicotinamide (5n)[21g].** White solid, isolated yield (28 mg, 32%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 9H), 6.19 (s, 1H), 7.51 (d, J = 6 Hz, 2H), 8.63 (d, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.6, 52.0, 120.7, 142.8, 150.3, 164.8.

1,1′-Biphenyl (6)[22]. Pale yellow solid, isolated yield (19 mg, 24%) (for 0.5 mmol),^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (tt, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 7.28 (tt, J_1 = 7.6 Hz, J_2 = 2.4 Hz, 4H), 7.48–7.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.1, 127.5, 129.0, 136.9.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

This work was supported by the grant from the SERB-India, grant no. SRG/2020/000721. SS sincerely thanks Dr Prabhat Kumar Baroliya, Department of Chemistry, MLSU for providing access to instrument for CV studies.

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