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FULL PAPER

Transition-Metal-Free Synthesis of Phenanthridinones through Visible-Light-Driven Oxidative C–H Amidation

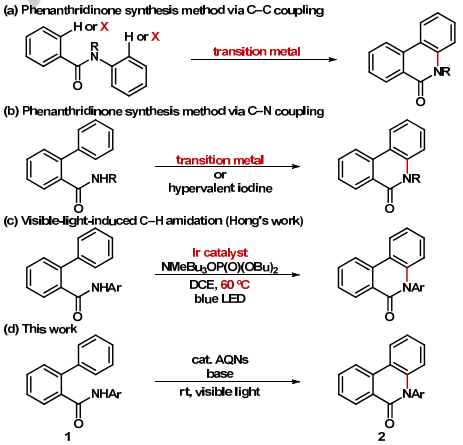
Kaoru Usami, [a] Dr. Eiji Yamaguchi, [a] Dr. Norihiro Tada[a] and Prof. Dr. Akichika Itoh *[a]

Abstract: The treatment of *N*-aryl biphenylcarboxamide, 1-chloroanthraquinone (1-Cl-AQN) catalyst, and K_2CO_3 in $CHCl_3$ under visible light irradiation affords phenanthridinone via radical cyclization. This reaction proceeds under transition-metal-free condition, room temperature, and direct C–H amidation. Mechanistic studies indicate that amidyl radical generation proceeds by visible light induced proton coupled electron transfer (PCET) from N–H bond of the amide.

Introduction

Phenanthridinones are important structural motifs in organic chemistry as they are present in many natural products and bioactive compounds.[1] Additionally, they can be converted into structures possessing functional groups at the ortho position of the biphenyl by hydrolysis of the lactam moiety. Generally, the lactam backbone is constructed via intramolecular amidation. To perform this, it is necessary to introduce an amino and a carboxyl group into the molecule. Notably, no ortho-position-selective intermolecular amination has been reported. Thus, to introduce an amino group into biphenyl, it is necessary to employ a stepwise approach that introduces a leaving group such as a halogen followed by coupling reactions, e.g., Buchwald–Hartwig amination,[2] Chan–Lam–Evans coupling,[3] and aromatic nucleophilic substitution.[4] For synthesizing phenanthridinone, many methods involving C–C coupling from *N*-phenylbenzamide have been reported, but this requires introducing a leaving group and using expensive transition metals (Scheme 1(a)).[5] However, phenanthridinone formation involving C–H amidation was recently reported, allowing direct skeleton formation from carboxamide (Scheme 1(b)). C–H amidation is economical because it is unnecessary to introduce a leaving group such as a halogen to the substrate.[6] In 2013, Yu's group reported a phenanthridinone synthetic method using copper iodide catalyst.[7] Additionally, Shiiya's group in 2013 and Xue's group in 2017 reported phenanthridinone synthesis by transition metal-free C–H amidation using a hypervalent iodine reagent, but the substrates were limited to *N*-alkoxy and *N*-phthaloyl compounds.[8] In 2018, Hong's group reported the intramolecular C–H amidation of biphenyl using a photocatalyst (Scheme 1(c)).[9] Although this is the first report of phenanthridinone formation using visible-light-photocatalyzed C–H amidation, the process required an expensive iridium photocatalyst at 60°C. Moreover, this reaction was not attempted with an electron-deficient aromatic ring as the substituent on the nitrogen atom of the amide.

From this perspective, we reported AQNs[10] catalyzed radical imidation of a heteroaromatic ring, which proceeded by generating an imidyl radical using oxidative PCET.[11] We therefore assumed that a transition-metal-free phenanthridinone synthesis could be developed using an AQN photocatalyst possessing a high oxidation potential rather than the iridium catalyst (Scheme 1(d)).[12] Herein, we have developed a mild and transition-metal-free oxidative phenanthridinone synthesis using an inexpensive commercial organophotocatalyst and a base under visible light irradiation. Moreover, in this reaction, we successfully used nitrogen atoms substituted with electron-deficient aromatic rings and heterocycles as substrates for the first time in a phenanthridinone synthesis under photoredox conditions.



Scheme 1. Various Methods for Constructing Phenanthridinones

Results and Discussion

We demonstrated intramolecular C–H amidation using *N*-phenyl biphenylcarboxamide (**1a**) as a model substrate (Table 1). We initially attempted cyclization reaction using the conditions for imidyl radical generation that we reported previously. *N*-phenyl biphenylcarboxamide (**1a**) provided the corresponding phenanthridinone (**2a**) in 35% yield in the presence of 2-^{t}Bu-AQN as a photocatalyst and K_2CO_3 as an additive in DMF under visible light irradiation (entry 1). We

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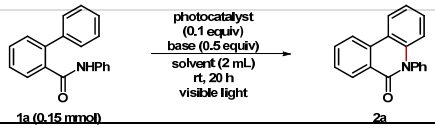
then tuned the reaction conditions to improve the yield. When this reaction was performed in polar solvents, a moderate yield was achieved, and using chloroform as the reaction solvent afforded a good yield (entries 2–4). These results indicated that the solubility of the substrate and catalyst significantly influenced the reactivity. As photocatalysts, AQNs generally showed good reactivity (entries 5–7). Moreover, the catalyst loading could be reduced to 1 mol% (entry 7). When the reaction was conducted without the base, the substrate was not completely consumed (entry 8). Although various inorganic bases accelerated the cyclization reaction, adding triethylamine did not affect the yield (entries 9–10). After finely tuning the reaction conditions, a 96% yield of phenanthridinone was obtained with 0.01 equiv of 1-Cl–AQN as the photosensitizer, 0.1 equiv of K_2CO_3 as the additive, and 2 mL of chloroform as the solvent under visible light irradiation (entry 11).

Table 1. Optimization of the Reaction Conditions[a,b]

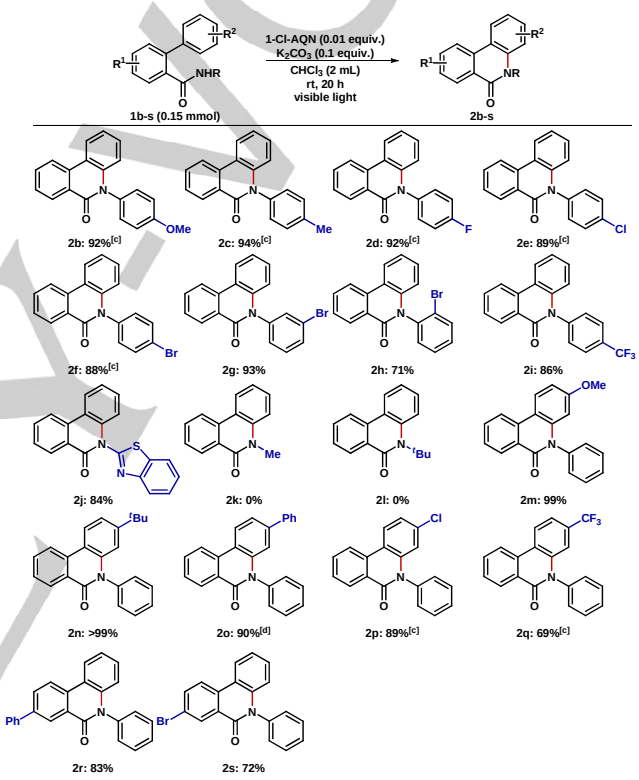


1a (0.15 mmol) 2a

entry	photocatalyst	base	solvent	yield (%)
1	2-^{t}Bu-AQN	K_2CO_3	DMF	35
2	2-^{t}Bu-AQN	K_2CO_3	MeCN	71
3	2-^{t}Bu-AQN	K_2CO_3	MeOH	63
4	2-^{t}Bu-AQN	K_2CO_3	$CHCl_3$	91
5	AQN	K_2CO_3	$CHCl_3$	85
6	1-Cl-AQN	K_2CO_3	$CHCl_3$	94
7[c]	1-Cl-AQN	K_2CO_3	$CHCl_3$	97
8[c]	1-Cl-AQN	-	$CHCl_3$	54
9[c]	1-Cl-AQN	NaOAc	$CHCl_3$	92
10[c]	1-Cl-AQN	Et_3N	$CHCl_3$	58
11[c,d]	1-Cl-AQN	K_2CO_3	$CHCl_3$	(96)

[a] Reaction conditions: A solution of **1a** (0.15 mmol), photocatalyst (0.1 equiv.), and base (0.5 equiv.) in solvent (2 mL) was irradiated with fluorescent lamp (23 W × 4) under air atmosphere and stirred for 20 h. [b] Yield was determined by ^{1}H NMR analysis of the crude reaction mixture. The number in parentheses is the isolated.

Having optimized the reaction conditions, we studied the scope and limitations of the reaction (Scheme 2). We initially performed experiments using substrates with different substituents on the nitrogen atom of the carboxamide. Those possessing an electron-rich aryl group provided excellent yields (**2b**, **2c**). Phenanthridinones with halogen substituents were produced in good yields (**2d–2h**). These products enabled further functionalization at these positions. Surprisingly, changes in bulkiness according to the substitution position did not significantly influence the yield (**2g**, **2h**). Moreover, a substituent with a carboxamide-substituted trifluoromethylphenyl group afforded 86% yield (**2i**). This reaction can also be applied to a substrate with a heterocyclic ring such as benzothiazole (**2j**). In a previous report by Hong, no cyclization reaction was reported of substrates with electron-deficient aromatic rings or heterocycles. However, no product was obtained with a substrate substituted with an alkyl group (**2k, 2l**). Subsequently, studies were conducted on substrates with a substituent on the biphenyl skeleton. In substrates with a substituent at the 4′ position, the yield of the target substance was not significantly affected by the electronic and steric actions of the substituents (**2m–2q**). Conversely, substrates with substituents at the 4-position afforded the corresponding phenanthridinones in good yields (**2r, 2s**).



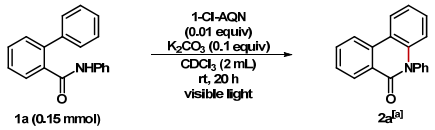
[a] Reaction conditions: A solution of **1** (0.15 mmol), 1-Cl-AQN (0.01 equiv), and K_2CO_3 (0.1 equiv) in $CHCl_3$ (2 mL) was irradiated with fluorescent lamp (23 W × 4) under air atmosphere and stirred for 20 h. [b] Yields refer to the isolated yield. [c] K_2CO_3 (0.3 equiv). [d] K_2CO_3 (0.5 equiv).

Scheme 2. Synthesis of Various Phenanthridinones[a,b]

When using a photocatalyst with a high oxidation potential, multiple routes are conceivable as potential reaction mechanisms. To further investigate the primary reaction mechanism, several control experiments were performed. When this reaction was conducted with a radical scavenger, such as 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), it did not proceed (Table 2, entry 1). This indicates that the reaction proceeds via a radical pathway. Moreover, we confirmed the role of the photocatalyst. When no 1-Cl–AQN was used in this cyclization, a large quantity of starting material remained unreacted (Table 2, entry 2). Furthermore, the desired phenanthridinone product was not

detected in the dark (Table 2, entry 3). Based on these results, it was suggested that the visible-light-excited photocatalyst was involved in forming reactive species. Besides nitrogen atoms, aromatic rings of biphenyl are also potential sites for oxidation by the photocatalyst. In 2015, Nicewicz reported arene C–H amination using an acridinium salt as an organophotoredox catalyst, which proceeded via single-electron oxidation of the arene.[13,14] This reaction did not proceed with a substrate possessing an alkyl group on the nitrogen atom, indicating that the pathway of nucleophilic addition following single-electron oxidation to arenes did not progress (Scheme 5, path b).

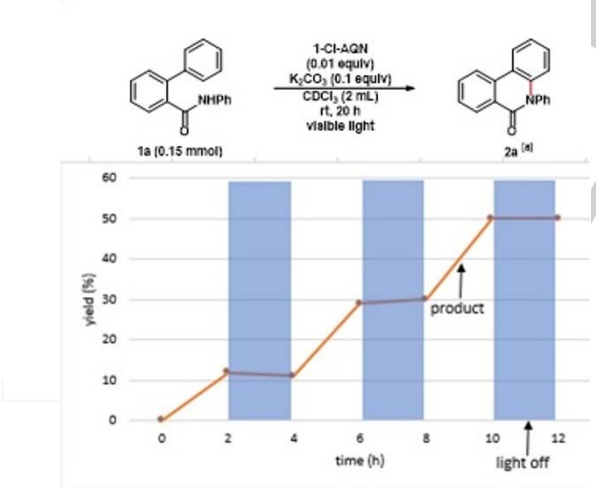
Table 2. Control Experiments[a]



entry	altered reaction conditions	yield (%)[a]
1	added TEMPO (1.0 equiv)	0
2	1-Cl-AQN (0 equiv)	0
3	under dark	0
4	under argon atmosphere	5

[a] Yield was determined by ^{1}H NMR analysis of the crude reaction mixture.

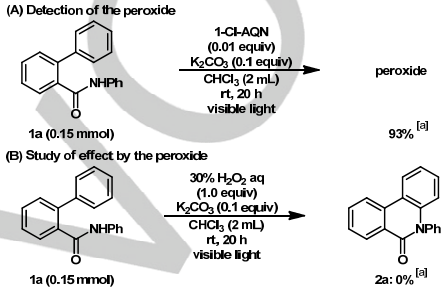
We also performed a time-course experiment with intermittent light intervals (Scheme 3). This indicated that the reaction rate did not change and that the product was only generated during light irradiation with a fluorescent lamp. Thus, it was suggested that the generated phenanthridinone or photoexcited substance did not affect the progress of the reaction.



[a] Yield was determined by ^{1}H NMR analysis of the crude reaction mixture.

Scheme 3. Time-Course Experiment[a]

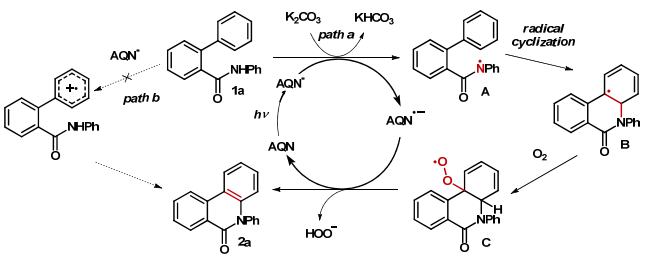
When this reaction was performed under an argon atmosphere, significant decreases in the yield and unreacted starting materials were confirmed (Table 2, entry 4), indicating that oxygen was involved in the reaction. However, since no new oxygen atoms were present in the product structure, it was believed that the oxygen promoted rearomatization in this reaction and was converted to hydrogen peroxide. Thus, we conducted iodometry to detect peroxide generated by the reaction (Scheme 4 (A)). As the result, approximately one equivalent of peroxide was detected. Furthermore, we confirmed that the peroxide was not related to the N–H bond activation (Scheme 4 (B)).



[a] Yield was determined by iodometry (A) or ^{1}H NMR analysis (B) of the crude reaction mixture.

Scheme 4. Study of Involvement of the Peroxide[a]

Based on the above results, we proposed a plausible pathway (Scheme 5). The AQN photocatalyst is initially excited by visible light irradiation. The excited photocatalyst promotes homolytic N–H bond activation of biphenylcarboxamide (**1a**) with base to afford the corresponding amidyl radical (**A**) via a PCET event. The resultant amidyl radical (**A**) yields the radical intermediate (**B**) via intramolecular radical cyclization. Subsequently, the radical intermediate (**B**) captures oxygen, inducing single-electron transfer with the AQN anion radical, whereby the corresponding phenanthridinone (**2a**) is formed, and simultaneously, the hydroperoxide anion is generated.



Scheme 5. Plausible Reaction Mechanism

Conclusions

In conclusion, we have reported a transition-metal-free phenanthridinone synthesis using an organophotocatalyst. This is the first method of phenanthridinone synthesis that

progresses direct C–H amidation without using a transition metal under visible light irradiation, and the reaction proceeds under mild conditions at low cost. Moreover, this has expanded the applicability of the substrates to a greater extent than previous photooxidative methods.

Experimental Section

General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 mm). Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F_{254}). The developed chromatogram was analyzed by UV lamp (254 nm). ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL ECA 500 (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR and 470 MHz for ^{19}F NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for ^{1}H NMR and 77.0 ppm ($CDCl_3$) for ^{13}C NMR. Infrared spectra were taken on a Perkin Elmer Spectrum 100 FTIR and are reported in reciprocal centimeters (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and JEOL JMS-T100GC and are reported as m/z (relative intensity). Melting points were measured on a Yanaco Micro Melting Point Apparatus and are uncorrected.

Substrate Preparation

General procedure for the synthesis of methyl 2-iodobenzoate

To the solution of 2-iodobenzoic acid (6.2 g, 25.0 mmol, 1.0 equiv) in DMF (1 M) was added K_2CO_3 (4.15 g, 30.0 mmol, 1.2 equiv). After gas evolution ceased, methyl iodide (1.71 mL, 27.5 mmol, 1.1 equiv) was added dropwise and the reaction mixture was stirred at room temperature overnight. H_2O was added to the reaction mixture and the aqueous phase was extracted with Et_2O. The combined organic layers were washed with H_2O, brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Without any purification to afford methyl 2-iodobenzoate (90%, 5.9 g).

Methyl 2-iodobenzoate (3m): The product was afforded as a pale yellow oil. R_f = 0.56 (9% EtOAc in *n*-Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4 Hz, 1 H), 7.76 (d, *J* = 7.4 Hz, 1 H), 7.37-7.34 (m, 1 H), 7.12-7.09 (m, 1 H), 3.89 (s, 3 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.0, 141.4, 135.1, 132.8, 131.0, 128.0, 94.2, 52.6. Data in accordance with the literature.[15]

General procedure for the synthesis of methyl 2-iodobenzoate

2-iodobenzoic acid (6.2 g, 25.0 mmol, 1.0 equiv) was taken up in concentrated H_2SO_4 (50 mL), and heated to 60 °C (oil bath). The solid NBS (5.34 g, 30.0 mmol, 1.2 equiv) was added a small amount to the reaction mixture during 15 minutes and stirred for 2 hours. The reaction was monitored by TLC. After the reaction was completed, a crushed ice was poured into the reaction mixture to precipitate the solid. The precipitated solid was filtered and washed with cold water. The solid was dissolved in EtOAc and the organic layer was washed with water and brine, dried with Na_2SO_4. The organic layer was filtered and concentrated in vacuo. The solid residue was used in the next step without any purification. To the solid residue in DMF (25 mL) at room temperature was added K_2CO_3 (4.15 g, 30.0 mmol 1.2 equiv). After gas evolution ceased, CH_3I (1.71 mL, 27.5 mmol, 1.1 equiv) was added dropwise and the reaction mixture was stirred at room temperature overnight. H_2O was added to the reaction mixture and the aqueous phase was extracted with Et_2O. The organic layers were combined, washed with H_2O, brine, and dried with $MgSO_4$. The organic layer was filtered and concentrated in vacuo. The residue was purified by column chromatography to afford methyl 5-bromo-2-iodobenzoate (79%, 6.7 g, 2 steps).

Methyl 5-bromo-2-iodobenzoate (3r): The product was afforded as a colorless oil. R_f = 0.34 (7% EtOAc in *n*-Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 2.3 Hz, 1 H), 7.89-7.77 (m, 1 H), 7.27-7.23 (m, 1 H), 3.90 (s, 3 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.5, 142.7, 136.5, 135.8, 134.0, 122.3, 92.4, 52.9. Data in accordance with the literature.[15]

General procedure for the Suzuki-Miyaura cross-coupling

A flask was refilled with argon. The boronic acids (1.1 equiv), palladium acetate (0.01 equiv) and sodium carbonate (3.5 equiv) were added. Then the solution of methyl 2-iodobenzoate (2.0 mmol) in MeCN (4.8 mL) and H_2O (2.4 mL) was added in the flask. The reaction mixture was warmed up to 60 ºC (oil bath) and stirred overnight. After the reaction was completed, the reaction mixture was cooled dawn to room temperature. Then the mixture was concentrated in *vacuo* until MeCN was removed. The residue was diluted with CH_2Cl_2 and H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over $MgSO_4$, filtered and concentrated in *vacuo*. Purification of the crude product by column chromatography on silica gel provided methyl biphenyl-2-carboxylates.

Methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate (4m): Methyl 2-iodobenzoate (299.5 µL, 2.0 mmol) gave Methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate (quant., 507.9 mg) as a pale yellow oil. R_f = 0.10 (5% EtOAc in *n*-Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1 H), 7.50 (td, *J* = 1.1, 7.5 Hz, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.6 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 3.84 (s, 3 H), 3.66 (s, 3 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.5, 159.1, 142.1, 133.7, 131.3, 130.9, 130.8, 129.8, 129.5, 126.9, 113.6, 55.3, 52.1. Data in accordance with the literature.[2]

Methyl 4'-(*tert* butyl)-[1,1'-biphenyl]-2-carboxylate (4n): Methyl 2-iodobenzoate (299.5 µL, 2.0 mmol) gave Methyl 4'-(*tert* butyl)-[1,1'-biphenyl]-2-carboxylate (90%, 482.7 mg) as a white solid. R_f = 0.24 (5% EtOAc in *n*-Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 1 H), 7.52 (td, *J* = 1.1, 8.0 Hz, 1 H), 7.44-7.37 (m, 4 H), 7.37-7.25 (m, 2 H), 3.65 (s, 3 H), 1.37 (s, 9 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.5, 150.2, 142.4, 138.3, 131.3, 131.0, 130.9, 129.8,

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128.1, 127.0, 125.1, 52.0, 34.7, 31.5. Data in accordance with the literature.[16]

Methyl 4'-phenyl-[1,1'-biphenyl]-2-carboxylate (4o): Methyl 2-iodobenzoate (299.5 µL, 2.0 mmol) gave Methyl 4'-phenyl-[1,1'-biphenyl]-2-carboxylate (91%, 524.2 mg) as a white solid. m.p. = 106-107 ºC. R_f = 0.15 (5% EtOAc in *n*-Hexane) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.67-7.64 (m, 4 H), 7.55 (td, *J* = 1.2, 7.4 Hz, 1 H), 7.48-7.38 (m, 6 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 3.68 (s, 3 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.3, 142.2, 140.8, 140.4, 140.1, 131.4, 130.9, 130.9, 130.0, 128.9, 127.5, 127.3, 127.2, 126.9, 52.1. IR (ATR) 3032, 1724, 1572, 1086 cm^{-1}. HRMS (DART) Found 289.1232, Calcd. for $C_{20}H_{17}O_2$, $[M + H]^+$ 289.1229.

Methyl 4'-chloro-[1,1'-biphenyl]-2-carboxylate (4p): Methyl 2-iodobenzoate (299.5 µL, 2.0 mmol) gave Methyl 4'-chloro-[1,1'-biphenyl]-2-carboxylate (79%, 391.5 mg) as a colorless oil. R_f = 0.24 (5% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 1.1, 7.4 Hz, 1 H), 7.53 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.42 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.37 (d, *J* = 8.6 Hz, 2 H), 7.35-7.32 (m, 1 H), 7.24 (d, *J* = 8.6 Hz, 2 H), 3.67 (s, 3 H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.8, 141.5, 139.9, 133.5, 131.6, 130.8, 130.6, 130.2, 129.8, 128.3, 127.6, 52.1. Data in accordance with the literature.[17]

Methyl 4-phenyl-[1,1'-biphenyl]-2-carboxylate (4r): Methyl 5-bromo-2-iodobenzoate (681.5 mg, 2.0 mmol) gave Methyl 4-phenyl-[1,1'-biphenyl]-2-carboxylate (87%, 503.4 mg) as a white solid. R_f = 0.17 (5% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (t, *J* = 2.3 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.66 (dd, *J* = 1.7, 8.0 Hz, 2 H), 7.50-7.46 (m, 3 H), 7.43-7.36 (m, 6 H), 3.67 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.3, 141.4, 141.0, 140.3, 139.8, 131.4, 131.3, 129.9, 129.0, 128.6, 128.4, 128.2, 127.9, 127.4, 52.1. Data in accordance with the literature.[16]

General procedure for the saponification of methyl biphenyl-2-carboxylates

Methyl biphenyl-2-carboxylates was dissolved in MeOH (0.25 M) and aq. NaOH (1 M, 4.0 equiv) was added. The mixture was warmed up to 50 °C (oil bath) and stirred overnight. After the reaction was completed, the reaction mixture was cooled dawn to room temperature. Then the mixture was concentrated in *vacuo* until MeOH was removed. Aq. HCl (2 M) and Et_2O were added in the residue and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered and concentrated in *vacuo* to give biphenyl-2-carboxylic acids.

4'-Methoxy-[1,1'-biphenyl]-2-carboxylic acid (5m): Methyl 4'-methoxy-[1,1'-biphenyl]-2-carboxylate (460.3 mg, 1.9 mmol) gave 4'-methoxy-[1,1'-biphenyl]-2-carboxylic acid (83%, 358.3 mg) as a white solid. R_f = 0.49 (10% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 1 H), 7.54 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 7.36 (d, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 8.6 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 3.84 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.0, 159.2, 143.0, 133.4, 132.2, 131.3, 130.8, 129.7, 129.4, 126.9, 113.7, 55.4. Data in accordance with the literature.[16]

4'-(*tert* Butyl)-[1,1'-biphenyl]-2-carboxylic acid (5n): Methyl 4'-(*tert* butyl)-[1,1'-biphenyl]-2-carboxylate (456.2 mg, 1.7 mmol) gave 4'-(*tert* butyl)-[1,1'-biphenyl]-2-carboxylic acid (85%, 366.8 mg) as a white solid. R_f = 0.56 (10% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 1.1, 8.0 Hz, 1 H), 7.56 (td, *J* = 1.7, 6.3 Hz, 1 H), 7.44-7.38 (m, 4 H), 7.31-7.29 (m, 2 H), 1.38 (s, 9 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.1, 150.3, 143.3, 138.0, 132.2, 131.5, 130.8, 129.4, 128.3, 127.1, 125.2, 34.7, 31.5. Data in accordance with the literature.[16]

4'-Phenyl-[1,1'-biphenyl]-2-carboxylic acid (5o): Methyl 4'-phenyl-[1,1'-biphenyl]-2-carboxylate (490.2 mg, 1.7 mmol) gave 4'-phenyl-[1,1'-biphenyl]-2-carboxylic acid (86%, 402.6 mg) as a white solid. R_f = 0.49 (10% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1 H), 7.64-7.62 (m, 4 H), 7.58 (td, *J* = 1.7, 8.0 Hz, 1 H), 7.46-7.41 (m, 6 H), 7.35 (t, *J* = 7.5 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.8, 143.1, 140.8, 140.3, 140.1, 132.3, 131.3, 130.9, 129.2, 129.0, 128.9, 127.4, 127.4, 127.2, 126.9. Data in accordance with the literature.[18]

4'-Chloro-[1,1'-biphenyl]-2-carboxylic acid (5p): Methyl 4'-chloro-[1,1'-biphenyl]-2-carboxylate (370.0 mg, 1.5 mmol) gave 4'-chloro-[1,1'-biphenyl]-2-carboxylic acid (83%, 290.7 mg) as a white solid. R_f = 0.50 (10% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 1 H), 7.56 (t, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.36 (d, *J* = 8.6 Hz, 2 H), 7.32 (d, *J* = 8.6 Hz, 2 H), 7.26-7.24 (m, 2 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.1, 142.4, 139.6, 133.6, 132.4, 131.3, 131.1, 129.9, 129.0, 128.3, 127.7. Data in accordance with the literature.[19]

4'-Trifluoromethyl-[1,1'-biphenyl]-2-carboxylic acid (5q): Methyl 2-iodobenzoate (299.5 µL, 2.0 mmol) gave 4'-trifluoromethyl-[1,1'-biphenyl]-2-carboxylic acid (85%, 451.1 mg, 2 steps) as a white solid. R_f = 0.44 (10% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 1.1, 8.0 Hz, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.60 (td, *J* = 1.1, 7.5 Hz, 1 H), 7.48 (td, *J* = 1.1, 6.8 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 6.9 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.0, 144.9, 142.4, 132.6, 131.3, 129.9, 129.7, 129.4, 129.2, 128.9, 128.9, 128.7, 128.1, 127.6, 125.4, 125.0, 125.0, 123.3, 121.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.3. Data in accordance with the literature.[16]

General procedure for the synthesis of N-arylamides from carbonic acids

General procedure for the preparation of acyl chlorides from carbonic acids

A dry flask was refilled with argon. The solution of the carbonic acid and DMF (1 drop) in CH_2Cl_2 (1.25 M) was added. Then thionyl chloride (1.2 equiv) was added in the solution at 0 ºC. The reaction mixture was stirred for 30 min at 0 ºC and then stirred at room temperature for 3 h. After the reaction was completed, the solvent was removed under reduced pressure to give acyl chlorides.

General procedure for the synthesis of *N*-arylamides from acyl chlorides

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A dry flask was refilled with argon. The solution of the anilines (1.0 equiv) and triethylamine in CH_2Cl_2 (0.625 M) was added. Then the acyl chlorides in CH_2Cl_2 (0.5 M) was added dropwise in the solution at 0 ºC. The reaction mixture was stirred for 30 min at 0 ºC and then stirred at room temperature overnight. After the reaction was completed, aqueous NH_4Cl was added to the reaction mixture. The mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. Purification of the crude product by column chromatography on silica gel provided the *N*-arylamides.

***N*-Phenyl biphenyl-2-carboxamide (1a):** 2-Phenyl-benzoic acid (1.0 g, 5.0 mmol) gave *N*-phenyl biphenyl-2-carboxamide (81%, 1.1 g) as a white solid. R_f = 0.41 (25% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.4 Hz, 1 H), 7.54 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.49-7.38 (m, 7 H), 7.22 (t, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 7.05 (t, *J* = 7.4 Hz, 1 H), 6.94 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 140.0, 139.7, 137.6, 135.4, 130.8, 130.5, 129.7, 129.1, 128.9, 128.2, 128.0, 124.5, 120.0. Data in accordance with the literature.[20]

***N*-4-Methoxyphenyl biphenyl-2-carboxamide (1b):** 2-Phenyl-benzoic acid (396.4 mg, 2.0 mmol) gave *N*-4-methoxyphenyl biphenyl-2-carboxamide (32%, 191.2 mg) as a pale yellow solid. m.p. = 159-160 ºC. R_f = 0.31 (25% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.8 Hz, 1 H), 7.53 (t, *J* = 6.8 Hz, 1 H), 7.48-7.40 (m, 7 H), 7.00 (d, *J* = 8.6 Hz, 2 H), 6.81 (brs, 1 H), 6.75 (d, *J* = 8.0 Hz, 2 H), 3.74 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 156.6, 140.1, 139.6, 135.5, 130.7, 130.4, 129.6, 129.0, 128.9, 128.1, 128.0, 122.0, 114.1, 55.5. IR (ATR) 3213, 3028, 1640, 1509, 1028 cm^{-1}. HRMS (DART) Found 304.1322, Calcd. for $C_{20}H_{18}NO_2$, $[M + H]^+$ 304.1338.

***N*-4-Methylphenyl biphenyl-2-carboxamide (1c):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-4-methylphenyl biphenyl-2-carboxamide (45%, 260.2 mg) as a white solid. m.p. = 146-148 ºC. R_f = 0.36 (25% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1 H), 7.55-7.52 (m, 1 H), 7.49-7.39 (m, 7 H), 7.02 (d, *J* = 8.6 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 6.83 (brs, 1 H), 2.26 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.1, 140.1, 139.6, 135.0, 134.2, 130.7, 130.4, 129.7, 129.4, 129.0, 128.9, 128.2, 128.0, 120.1, 21.0. IR (ATR) 3233, 3054, 1600, 1511 cm^{-1}. HRMS (DART) Found 288.1382, Calcd. for $C_{20}H_{18}NO$, $[M + H]^+$ 288.1388.

***N*-4-Fluorophenyl biphenyl-2-carboxamide (1d):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-4-fluorophenyl biphenyl-2-carboxamide (46%, 266.8 mg) as a white solid. m.p. = 145-147 ºC. R_f = 0.32 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 1 H), 7.54 (td, *J* = 1.1, 7.5 Hz, 1 H), 7.49-7.39 (m, 7 H), 7.05-7.02 (m, 2 H), 6.90 (t, *J* = 8.6 Hz, 2 H), 6.85 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 160.5, 158.6, 140.1, 139.6, 135.1, 133.6, 130.9, 130.4, 129.7, 129.1, 128.9, 128.2, 128.0, 121.9, 121.8, 115.7, 115.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -117.7. IR (ATR) 3249, 3059, 1652, 1504, 1206 cm^{-1}. HRMS (DART) Found 292.1136, Calcd. for $C_{19}H_{15}FNO$, $[M + H]^+$ 292.1138.

***N*-4-Chlorophenyl biphenyl-2-carboxamide (1e):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-4-chlorophenyl biphenyl-2-carboxamide (22%, 136.6 mg) as a pale yellow solid. m.p. = 166-168 ºC. R_f = 0.43 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 1 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.49-7.39 (m, 7 H), 7.17 (d, *J* = 8.5 Hz, 2 H), 7.03 (d, *J* = 8.6 Hz, 2 H), 6.89 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 140.0, 139.7, 136.2, 135.0, 131.0, 130.5, 129.8, 129.5, 129.1, 128.9, 128.9, 128.3, 128.1, 121.1. IR (ATR) 3273, 3020, 1653, 1536, 1091 cm^{-1}. HRMS (DART) Found 308.0832, Calcd. for $C_{19}H_{15}ClNO$, $[M + H]^+$ 308.0842.

***N*-4-Bromophenyl biphenyl-2-carboxamide (1f):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-4-bromophenyl biphenyl-2-carboxamide (45%, 314.6 mg) as a pale yellow solid. m.p. = 172-173 ºC. R_f = 0.43 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 1 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.49-7.40 (m, 7 H), 7.31 (d, *J* = 8.6 Hz, 2 H), 6.98 (d, *J* = 8.6 Hz, 2 H), 6.88 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 140.0, 139.7, 136.7, 134.9, 131.9, 131.0, 130.5, 129.8, 129.1, 128.9, 128.3, 128.1, 121.5, 117.1. IR (ATR) 3279, 3105, 1653, 1537, 1072 cm^{-1}. HRMS (DART) Found 352.0340, Calcd. for $C_{19}H_{15}BrNO$, $[M + H]^+$ 352.0337.

***N*-3-Bromophenyl biphenyl-2-carboxamide (1g):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-3-bromophenyl biphenyl-2-carboxamide (81%, 573.0 mg) as a white solid. m.p. = 141-142 ºC. R_f = 0.45 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (t, *J* = 7.5 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.49-7.42 (m, 8 H), 7.16 (d, *J* = 8.0 Hz, 1 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 6.99 (brs, 1 H), 6.91 (d, *J* = 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.3, 139.9, 139.7, 138.9, 134.9, 131.0, 130.5, 130.2, 129.7, 129.2, 128.9, 128.3, 128.1, 127.4, 122.9, 122.6, 118.4. IR (ATR) 3216, 3056, 1656, 1596, 1046 cm^{-1}. HRMS (DART) Found 352.0344, Calcd. for $C_{19}H_{15}BrNO$, $[M + H]^+$ 352.0337.

***N*-2-Bromophenyl biphenyl-2-carboxamide (1h):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-2-bromophenyl biphenyl-2-carboxamide (33%, 229.7 mg) as a white solid. m.p. = 88-89 ºC. R_f = 0.58 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 7.5 Hz, 1 H), 7.55 (dd, *J* = 1.2, 7.5 Hz, 2 H), 7.50-7.45 (m, 4 H), 7.40-7.36 (m, 3 H), 7.35-7.33 (m, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 6.91 (td, *J* = 1.1, 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.8, 139.8, 139.7, 135.8, 135.6, 132.3, 131.0, 130.8, 129.5, 129.1, 129.0, 128.7, 128.3, 127.9, 125.1, 121.5, 113.0. IR (ATR) 3209, 3026, 1656, 1522, 1028 cm^{-1}. HRMS (DART) Found 352.0348, Calcd. for $C_{19}H_{15}BrNO$, $[M + H]^+$ 352.0337.

***N*-4-Trifluoromethylphenyl biphenyl-2-carboxamide (1i):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-4-trifluoromethylphenyl biphenyl-2-carboxamide (61%, 413.1 mg) as a white solid. m.p. = 138-140 ºC. R_f = 0.29 ($CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.47-7.40 (m, 9 H), 7.26 (d, *J* = 7.5 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.5, 140.7, 140.1, 139.9, 139.8, 134.7, 131.7, 131.2, 130.5, 129.7, 129.1, 128.9, 128.5, 128.4, 128.2, 128.1, 127.4, 126.3, 126.2, 126.2, 126.1, 126.0, 125.2, 123.1, 119.9, 119.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.0. IR (ATR) 3250, 3065, 1666, 1543,

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1320 cm^{-1}. HRMS (DART) Found 342.1117, Calcd. for $C_{20}H_{15}F_3NO$, [M + H]$^+$ 342.1106.

***N*-2-benzothiazolyl biphenyl-2-carboxamide (1j):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N*-2-benzothiazolyl biphenyl-2-carboxamide (40%, 266 mg) as a pale brown solid. m.p. = 207-209 ºC. R_f = 0.28 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1 H), 7.46 (d, *J* = 7.4 Hz, 1 H), 7.39 (td, *J* = 1.5, 7.4 Hz, 1 H), 7.34-7.15 (m, 8 H), 7.01 (t, *J* = 7.4 Hz, 1 H), 6.53 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.4, 160.1, 147.3, 141.0, 139.6, 133.4, 131.5, 131.3, 130.8, 129.1, 128.7, 128.6, 127.9, 127.5, 126.1, 123.8, 121.2, 119.7. IR (ATR) 3123, 3058, 1683, 1599, 1544 cm^{-1}. HRMS (DART) Found 331.0902, Calcd. for $C_{20}H_{15}N_2OS$, [M + H]$^+$ 331.0905.

***N*-Methyl biphenyl-2-carboxamide (1k):** 2-Phenyl-benzoic acid (500 mg, 2.5 mmol) gave *N*-methyl biphenyl-2-carboxamide (63%, 331.4 mg) as a white solid. R_f = 0.38 (67% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.4 Hz, 1 H), 7.47 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.41-7.31 (m, 7 H), 5.23 (brs, 1 H), 2.66 (d, *J* = 5.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.4, 140.2, 139.4, 135.7, 130.2, 128.9, 128.7, 128.7, 128.6, 127.9, 127.7, 26.8. Data in accordance with the literature.[20]

***N-tert* Butyl biphenyl-2-carboxamide (1l):** 2-Phenyl-benzoic acid (396.2 mg, 2.0 mmol) gave *N-tert* butyl biphenyl-2-carboxamide (53%, 270.2 mg) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 1.2, 7.5 Hz, 1 H), 7.46-7.37 (m, 7 H), 7.33 (dd, *J* = 1.2, 7.5 Hz, 1 H), 4.98 (brs, 1 H), 1.10 (s, 9 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.4, 140.6, 139.4, 136.9, 130.1, 129.9, 129.1, 129.0, 128.7, 127.8, 127.7, 51.4, 28.3. Data in accordance with the literature.[20]

***N*-Phenyl 4'-methoxy-biphenyl-2-carboxamide (1m):** 4'-Methoxy-[1,1'-biphenyl]-2-carboxylic acid (342.4 mg, 2.0 mmol) gave *N*-phenyl 4'-methoxy-biphenyl-2-carboxamide (92%, 416.4 mg) as a white solid. m.p. = 130-132 ºC. R_f = 0.30 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 1 H), 7.52 (td, *J* = 1.2, 7.5 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.42-7.39 (m, 3 H), 7.24 (t, *J* = 7.4 Hz, 2 H), 7.16 (d, *J* = 7.5 Hz, 2 H), 7.06 (t, *J* = 7.4 Hz, 1 H), 6.96 (d, *J* = 8.6 Hz, 3 H), 3.82 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.7, 139.2, 137.7, 135.2, 132.2, 130.8, 130.5, 130.2, 129.7, 129.0, 127.6, 124.5, 120.0, 114.5, 55.5. IR (ATR) 3238, 3003, 1653, 1531, 1178 cm^{-1}. HRMS (DART) Found 304.1333, Calcd. for $C_{20}H_{18}NO_2$, [M + H]$^+$ 304.1338.

***N*-Phenyl 4'-*tert* butyl-biphenyl-2-carboxamide (1n):** 4'-*tert* Butyl-[1,1'-biphenyl]-2-carboxylic acid (330.6 mg, 1.3 mmol) gave *N*-phenyl 4'-*tert* butyl-biphenyl-2-carboxamide (80%, 342.7 mg) as a white solid. m.p. = 136-138 ºC. R_f = 0.32 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.5 Hz, 1 H), 7.53 (td, *J* = 1.1, 7.5 Hz, 1 H), 7.48-7.39 (m, 6 H), 7.20 (t, *J* = 8.0 Hz, 2 H), 7.04 (t, *J* = 8.0 Hz, 4 H), 1.37 (s, 9 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 151.3, 139.7, 137.8, 137.2, 135.3, 130.8, 130.3, 129.9, 128.8, 128.8, 127.9, 126.1, 124.4, 120.2, 34.8, 31.4. IR (ATR) 3241, 3029, 1656, 1526 cm^{-1}. HRMS (DART) Found 330.1873, Calcd. for $C_{23}H_{24}NO$, [M + H]$^+$ 330.1858.

***N*-Phenyl 4'-phenyl-biphenyl-2-carboxamide (1o):** 4'-Phenyl-[1,1'-biphenyl]-2-carboxylic acid (384.1 mg, 1.4 mmol) gave *N*-phenyl 4'-phenyl-biphenyl-2-carboxamide (36%, 177.6 mg) as a white solid. m.p. = 236-238 ºC. R_f = 0.34 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.60 (dd, *J* = 1.2, 7.4 Hz, 2 H), 7.56 (d, *J* = 8.1 Hz, 3 H), 7.51-7.45 (m, 4 H), 7.39-7.36 (m, 1 H), 7.21 (t, *J* = 7.5 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.04 (t, *J* = 7.4 Hz, 1 H), 6.93 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.3, 141.1, 140.5, 139.2, 138.9, 137.6, 135.5, 130.9, 130.4, 129.7, 129.4, 129.0, 128.1, 127.8, 127.7, 127.2, 124.6, 120.0. IR (ATR) 3294, 3024, 1659, 1543 cm^{-1}. HRMS (DART) Found 350.1559, Calcd. for $C_{25}H_{20}NO$, [M + H]$^+$ 350.1545.

***N*-Phenyl 4'-chloro-biphenyl-2-carboxamide (1p):** 4'-Chloro-[1,1'-biphenyl]-2-carboxylic acid (279.2 mg, 1.2 mmol) gave *N*-phenyl 4'-chloro-biphenyl-2-carboxamide (20%, 75.2 mg) as a white solid. m.p. = 199-201 ºC. R_f = 0.26 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1 H), 7.53 (td, *J* = 1.2, 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.43-7.38 (m, 5 H), 7.29-7.25 (m, 1 H), 7.21 (d, *J* = 7.4 Hz, 2 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.94 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.3, 138.4, 137.5, 135.7, 134.3, 130.8, 130.4, 130.1, 129.3, 129.2, 129.1, 128.3, 124.8, 120.0. IR (ATR) 3225, 3026, 1649, 1592, 1087 cm^{-1}. HRMS (DART) Found 308.0835, Calcd. for $C_{19}H_{15}ClNO$, [M + H]$^+$ 308.0842.

***N*-Phenyl 4'-trifluoromethyl-biphenyl-2-carboxamide (1q):** 4'-trifluromethyl-[1,1'-biphenyl]-2-carboxylic acid (452.6 mg, 1.7 mmol) gave *N*-phenyl 4'-trifluoromethyl-biphenyl-2-carboxamide (58%, 337.7 mg) as a white solid. m.p. = 198-200 ºC. R_f = 0.29 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.4 Hz, 1 H), 7.67 (d, *J* = 8.6 Hz, 2 H), 7.60-7.56 (m, 3 H), 7.51 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.43 (d, *J* = 8.1 Hz, 1 H), 7.27-7.24 (m, 2 H), 7.18 (d, *J* = 8.1 Hz, 2 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.97 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.1, 143.7, 140.2, 138.4, 137.4, 135.9, 131.6, 130.9, 130.4, 130.3, 129.3, 129.2, 129.1, 128.6, 128.5, 125.9, 125.8, 125.0, 124.9, 120.2, 120.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.5. IR (ATR) 3229, 3063, 1648, 1548, 1323 cm^{-1}. HRMS (DART) Found 342.1103, Calcd. for $C_{20}H_{15}F_3NO$, [M + H]$^+$ 342.1106.

***N*-Phenyl 4-phenyl-biphenyl-2-carboxamide (1r):** 4-Phenyl-[1,1'-biphenyl]-2-carboxylic acid (384.4 mg, 1.1 mmol) gave *N*-phenyl 4-phenyl-biphenyl-2-carboxamide (17%, 65.3 mg) as a white solid. m.p. = 183-185 ºC. R_f = 0.50 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 1.7 Hz, 1 H), 7.77 (dd, *J* = 1.7, 8.0 Hz, 1 H), 7.68 (d, *J* = 7.5 Hz, 2 H), 7.52-7.38 (m, 9 H), 7.24 (t, *J* = 7.5 Hz, 2 H), 7.14 (d, *J* = 7.5 Hz, 2 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 7.00 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 167.2, 140.9, 139.7, 139.7, 138.4, 137.6, 135.8, 131.0, 129.3, 129.1, 129.1, 129.0, 128.3, 128.0, 127.2, 124.6, 120.1. IR (ATR) 3186, 3028, 1644, 1544 cm^{-1}. HRMS (DART) Found 350.1545, Calcd. for $C_{25}H_{20}NO$, [M + H]$^+$ 350.1545.

***N*-Phenyl 4-bromo-biphenyl-2-carboxamide (1s):** 4-bromo-[1,1'-biphenyl]-2-carboxylic acid (332.5 mg, 1.2 mmol) gave *N*-phenyl 4-

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bromo-biphenyl-2-carboxamide (18%, 78.1 mg) as a white solid. m.p. = 131-133 ºC. R_f = 0.53 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.2 Hz, 1 H), 7.64 (dd, *J* = 1.2, 8.1 Hz, 1 H), 7.43-7.41 (m, 4 H), 7.28 (d, *J* = 8.0 Hz, 1 H), 7.22 (t, *J* = 8.0 Hz, 3 H), 7.09-7.05 (m, 3 H), 7.00 (brs, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.7, 138.9, 138.5, 137.3, 136.9, 133.8, 132.5, 132.0, 129.2, 129.0, 128.8, 128.6, 124.8, 122.1, 120.2. IR (ATR) 3292, 3060, 1652, 1522, 1078 cm^{-1}. HRMS (DART) Found 352.0328, Calcd. for $C_{19}H_{15}BrNO$, $[M + H]^+$ 352.0337.

Intramolecular C–H amidation of *N*-aryl biphenyl-2-carboxamide

A solution of *N*-aryl biphenyl-2-carboxamide (0.15 mmol), 1-Cl-AQN (0.4 mg, 0.0015 mmol) and K_2CO_3 (2.1 mg, 0.015 mmol) in $CHCl_3$ (2 mL) was irradiated with fluorescent lamp (23W x 4) at approximately 6 cm away from the light source and stirred for 20 h. The reaction mixture was concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel provided desired product.

1 mmol scale procedure

The reaction was conducted in round-bottom-flask (30 ml). A solution of *N*-3-bromophenyl biphenyl-2-carboxamide (**1g**) (352.2 mg, 1 mmol), 1-Cl-AQN (2.4 mg, 0.01 mmol) and K_2CO_3 (41.5 mg, 0.3 mmol) in $CHCl_3$ (13 mL) was irradiated with fluorescent lamp (23W x 4) at approximately 6 cm away from the light source and stirred for 20 h. The reaction mixture was concentrated in *vacuo*. Purification of the crude product by flash chromatography on silica gel provided desired product (**2g**) (93%, 326.4 mg).

5-Phenylphenanthridin-6(5H)-one (2a): *N*-Phenyl biphenyl-2-carboxamide (41.0 mg, 0.15 mmol) gave 5-phenylphenanthridin-6(5H)-one (96%, 38.9 mg) as a pale yellow solid. R_f = 0.28 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 1.2, 8.1 Hz, 1 H), 8.33 (d, *J* = 8.1 Hz, 1 H), 8.30 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.81 (td, *J* = 1.1, 8.0 Hz, 1 H), 7.61 (t, *J* = 8.0 Hz, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 7.5 Hz, 2 H), 7.32-7.26 (m, 2 H), 7.24 (d, *J* = 8.6 Hz, 2 H), 6.70 (dd, *J* = 1.7, 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.8, 139.3, 138.4, 134.1, 132.9, 130.3, 129.2, 129.1, 128.9, 128.3, 126.0, 123.1, 122.7, 121.9, 119.1, 117.1. Data in accordance with the literature.[9]

5-(4-Methoxyphenyl)phenanthridin-6(5H)-one (2b): *N*-(4-Methoxyphenyl) biphenyl-2-carboxamide (45.5 mg, 0.15 mmol) gave 5-(4-methoxyphenyl)phenanthridin-6(5H)-one (92%, 41.5 mg) as an orange solid. R_f = 0.29 (1% MeOH in $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 1.2, 8.1 Hz, 1 H), 8.33 (d, *J* = 8.1 Hz, 1 H), 8.30 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.81 (td, *J* = 1.1, 8.0 Hz, 1 H), 7.61 (t, *J* = 8.0 Hz, 1 H), 7.33-7.26 (m, 2 H), 7.24 (d, *J* = 8.6 Hz, 2 H), 7.12 (d, *J* = 9.1 Hz, 2 H), 6.76 (dd, *J* = 1.7, 8.0 Hz, 1 H), 3.90 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.1, 159.7, 139.6, 134.1, 132.9, 130.9, 130.1, 129.2, 128.2, 126.0, 123.1, 122.7, 121.9, 119.2, 117.2, 115.6, 55.7. Data in accordance with the literature.[9]

5-(4-Methylphenyl)phenanthridin-6(5H)-one (2c): *N*-(4-Methylphenyl) biphenyl-2-carboxamide (43.1 mg, 0.15 mmol) gave 5-(4-methylphenyl)phenanthridin-6(5H)-one (94%, 40.2 mg) as a pale yellow solid. R_f = 0.24 (16% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.0 Hz, 1 H), 8.33 (d, *J* = 8.6 Hz, 1 H), 8.30 (dd, *J* = 1.8, 8.6 Hz, 1 H), 7.80 (t, *J* = 7.5 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.41 (d, *J* = 8.0 Hz, 2 H), 7.29 (td, *J* = 1.7, 8.0 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 6.74 (d, *J* = 8.5 Hz, 1 H), 2.48 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.9, 139.4, 138.8, 135.7, 134.1, 132.9, 131.0, 129.2, 128.8, 128.2, 126.0, 123.1, 122.7, 121.9, 119.1, 117.2, 21.4. Data in accordance with the literature.[9]

5-(4-Fluorophenyl)phenanthridin-6(5H)-one (2d): *N*-(4-Fluorophenyl) biphenyl-2-carboxamide (43.7 mg, 0.15 mmol) gave 5-(4-fluorophenyl)phenanthridin-6(5H)-one (92%, 40.0 mg) as a white solid. R_f = 0.33 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 1.2, 8.0 Hz, 1 H), 8.34 (d, *J* = 8.0 Hz, 1 H), 8.31 (dd, *J* = 1.7, 7.4 Hz, 1 H), 7.82 (td, *J* = 1.2, 8.0 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.34-7.28 (m, 6 H), 6.69 (dd, *J* = 1.7, 7.4 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.6, 161.9, 161.6, 139.2, 134.2, 134.1, 133.1, 131.0, 129.3, 129.1, 128.3, 125.8, 123.2, 122.9, 121.9, 119.2, 117.4, 117.3, 116.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -112.5. Data in accordance with the literature.[9]

5-(4-Chlorophenyl)phenanthridin-6(5H)-one (2e): *N*-(4-Chlorophenyl) biphenyl-2-carboxamide (46.2 mg, 0.15 mmol) gave 5-(4-chlorophenyl)phenanthridin-6(5H)-one (89%, 40.6 mg) as a white solid. R_f = 0.25 ($CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 1.2, 8.0 Hz, 1 H), 8.34 (d, *J* = 8.6 Hz, 1 H), 8.31 (dd, *J* = 1.7, 7.5 Hz, 1 H), 7.82 (td, *J* = 1.2, 8.0 Hz, 1 H), 7.64-7.58 (m, 3 H), 7.34-7.27 (m, 4 H), 6.69 (dd, *J* = 1.2, 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.8, 139.0, 136.8, 134.9, 134.1, 133.1, 130.7, 130.6, 129.3, 129.1, 128.4, 125.8, 123.2, 123.0, 121.9, 119.2, 116.9. Data in accordance with the literature.[9]

5-(4-Bromophenyl)phenanthridin-6(5H)-one (2f): *N*-(4-Bromophenyl) biphenyl-2-carboxamide (52.8 mg, 0.15 mmol) gave 5-(4-bromophenyl)phenanthridin-6(5H)-one (88%, 46.2 mg) as a white solid. R_f = 0.27 (20% EtOAc in *n*-Hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.0 Hz, 1 H), 8.34 (d, *J* = 8.6 Hz, 1 H), 8.31 (dd, *J* = 1.7, 7.5 Hz, 1 H), 7.82 (t, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.6 Hz, 2 H), 7.62 (t, *J* = 8.1 Hz, 1 H), 7.34-7.25 (m, 2 H), 7.22 (d, *J* = 8.6 Hz, 2 H), 6.69 (dd, *J* = 1.7, 7.4 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.7, 138.9, 137.4, 134.1, 133.6, 133.1, 131.0, 129.3, 129.1, 128.4, 125.8, 123.3, 123.0, 123.0, 122.0, 119.2, 116.9. Data in accordance with the literature.[9]

5-(3-Bromophenyl)phenanthridin-6(5H)-one (2g): *N*-(3-Bromophenyl) biphenyl-2-carboxamide (52.8 mg, 0.15 mmol) gave 5-(3-bromophenyl)phenanthridin-6(5H)-one (93%, 48.8 mg) as a pale yellow solid. R_f = 0.28 ($CHCl_3$). m.p. = 192-194 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.1 Hz, 1 H), 8.34-8.28 (m, 2 H), 7.84-7.80 (m, 1 H), 7.68 (dd, *J* = 1.1, 8.1 Hz, 1 H), 7.52 (t, *J* = 1.7 Hz, 1 H), 7.50 (t, *J* = 8.1 Hz, 1 H), 7.35-7.28 (m, 3 H), 6.68 (dd, *J* = 1.2, 8.0 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.7, 139.6, 138.8, 134.1, 133.2, 132.5, 132.2, 131.5, 129.4, 129.1, 128.4, 128.2, 125.7, 123.6, 123.3, 123.1, 122.0, 119.1, 116.9. IR (ATR) 3061, 1649, 1575, 1061 cm^{-1}. HRMS (DART) Found 350.0177, Calcd. for $C_{19}H_{13}BrNO$, $[M + H]^+$ 350.0181.

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5-(2-Bromophenyl)phenanthridin-6(5H)-one (2h): *N*-(2-Bromophenyl) biphenyl-2-carboxamide (52.8 mg, 0.15 mmol) gave 5-(2-bromophenyl)phenanthridin-6(5H)-one (71%, 37.1 mg) as a yellow viscous oil. R_f = 0.28 ($CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 1.1, 8.0 Hz, 1 H), 8.35 (d, *J* = 8.6 Hz, 1 H), 8.33 (dd, *J* = 1.7, 8.1 Hz, 1 H), 7.86-7.81 (m, 2 H), 7.62 (td, *J* = 1.1, 8.0 Hz, 2 H), 7.56 (td, *J* = 1.1, 8.0 Hz, 2 H), 7.44-7.39 (m, 2 H), 7.35-7.29 (m, 2 H), 6.57 (dd, *J* = 1.7, 8.0 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.1, 138.1, 137.6, 134.3, 134.3, 133.2, 131.1, 130.6, 129.5, 129.4, 129.3, 128.3, 125.8, 123.8, 123.3, 123.1, 122.0, 119.2, 116.3. IR (ATR) 3074, 1655, 1590, 1041 cm^{-1}. HRMS (DART) Found 350.0196, Calcd. for $C_{19}H_{13}BrNO$, $[M + H]^+$ 350.0181.

5-(4-Trifluoromethylphenyl)phenanthridin-6(5H)-one (2i): *N*-(4-Trifluoromethylphenyl) biphenyl-2-carboxamide (51.2 mg, 0.15 mmol) gave 5-(4-trifluoromethylphenyl)phenanthridin-6(5H)-one (86%, 43.9 mg) as a white solid. R_f = 0.31 ($CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 1.2, 7.5 Hz, 1 H), 8.35 (d, *J* = 8.6 Hz, 1 H), 8.34-8.32 (m, 1 H), 7.89 (d, *J* = 8.6 Hz, 2 H), 7.85-7.82 (m, 1 H), 7.63 (t, *J* = 7.5 Hz, 1 H), 7.49 (d, *J* = 8.6 Hz, 2 H), 7.34-7.30 (m, 2 H), 6.64-6.62 (m, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.7, 147.7, 141.7, 138.7, 134.1, 133.3, 131.3, 131.0, 130.1, 129.4, 129.1, 128.4, 127.5, 127.5, 127.2, 127.2, 125.7, 125.0, 123.3, 123.1, 122.8, 122.0, 119.2, 116.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.4. Data in accordance with the literature.[9]

5-(2-benzothiazolyl)phenanthridin-6(5H)-one (2j): *N*-(2-Benzothiazolyl) biphenyl-2-carboxamide (49.6 mg, 0.15 mmol) gave 5-(2-benzothuazolyl)phenanthridin-6(5H)-one (84%, 41.6 mg) as a white solid. R_f = 0.28 ($CHCl_3$). m.p. = 196-198 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 1.2, 8.0 Hz, 1 H), 8.33 (d, *J* = 8.0 Hz, 1 H), 8.30 (dd, *J* = 1.7, 8.0 Hz, 1 H), 8.15 (d, *J* = 8.6 Hz, 1 H), 7.99 (d, *J* = 8.0 Hz, 1 H), 7.85 (td, *J* = 1.2, 8.0 Hz, 1 H), 7.64-7.57 (m, 2 H), 7.55-7.52 (m, 1 H), 7.38-7.33 (m, 2 H), 6.92 (dd, *J* = 1.7, 8.0 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.9, 158.6, 150.5, 137.9, 136.8, 134.3, 133.8, 129.7, 129.2, 128.5, 126.6, 126.5, 125.2, 124.4, 123.9, 123.3, 122.2, 122.2, 119.2, 116.5. IR (ATR) 3060, 1664, 1591 cm^{-1}. HRMS (DART) Found 329.0759, Calcd. for $C_{20}H_{13}N_2OS$, $[M + H]^+$ 329.0749.

3-Methoxy-5-phenylphenanthridin-6(5H)-one (2m): *N*-Phenyl 4'-methoxy-biphenyl-2-carboxamide (45.5 mg, 0.15 mmol) gave 3-methoxy-5-phenyl phenanthridin-6(5H)-one (99%, 44.7 mg) as a yellow solid. R_f = 0.16 ($CHCl_3$). m.p. = 161-163 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 1 H), 8.20 (dd, *J* = 6.3, 8.0 Hz, 2 H), 7.77 (td, *J* = 1.2, 8.0 Hz, 1 H), 7.61 (t, *J* = 7.5 Hz, 2 H), 7.55-7.51 (m, 2 H), 7.33 (dd, *J* = 1.7, 9.2 Hz, 2 H), 6.86 (dd, *J* = 2.3, 9.2 Hz, 1 H), 6.17 (d, *J* = 2.8 Hz, 1 H), 3.68 (s, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.2, 160.4, 140.7, 138.4, 134.3, 132.9, 130.3, 129.1, 128.9, 127.1, 124.8, 124.5, 121.3, 112.8, 109.4, 102.1, 55.4. IR (ATR) 3054, 1651, 1583, 1046 cm^{-1}. HRMS (DART) Found 302.1177, Calcd. for $C_{20}H_{16}NO_2$, $[M + H]^+$ 302.1181.

3-*tert* Butyl-5-phenylphenanthridin-6(5H)-one (2n): *N*-Phenyl 4'-*tert* butyl-biphenyl-2-carboxamide (49.4 mg, 0.15 mmol) gave 3-*tert* butyl-5-phenyl phenanthridin-6(5H)-one (>99%, 49.1 mg) as a white solid. R_f = 0.13 ($CHCl_3$). m.p. = 216-218 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.0 Hz, 1 H), 8.31 (d, *J* = 8.6 Hz, 1 H), 8.22 (d, *J* = 8.6 Hz, 1 H), 7.79 (td, *J* = 1.1, 8.1 Hz, 1 H), 7.65-7.62 (m, 2 H), 7.60-7.53 (m, 2 H), 7.37-7.33 (m, 3 H), 6.69 (d, *J* = 1.8 Hz, 1 H), 1.19 (s, 9 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.0, 152.8, 139.1, 138.5, 134.1, 132.9, 130.2, 129.2, 129.1, 128.9, 127.8, 125.7, 122.8, 121.7, 120.4, 116.7, 113.9, 35.0, 31.1. IR (ATR) 3071, 1652, 1597 cm^{-1}. HRMS (DART) Found 328.1714, Calcd. for $C_{23}H_{22}NO$, $[M + H]^+$ 328.1701.

3,5-Diphenylphenanthridin-6(5H)-one (2o): *N*-Phenyl 4'-phenyl-biphenyl-2-carboxamide (52.4 mg, 0.15 mmol) gave 3,5-diphenyl phenanthridin-6(5H)-one (90%, 47.1 mg) as a yellow solid. R_f = 0.20 ($CHCl_3$). m.p. = 223-225 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.4 Hz, 1 H), 8.36 (d, *J* = 8.0 Hz, 2 H), 7.83 (td, *J* = 1.7, 7.4 Hz, 1 H), 7.65-7.61 (m, 3 H), 7.56-7.52 (m, 2 H), 7.44-7.37 (m, 4 H), 7.35-7.31 (m, 1 H), 6.90 (d, *J* = 1.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.0, 142.1, 140.2, 139.7, 138.3, 133.9, 133.0, 130.4, 129.2, 129.0, 129.0, 128.2, 128.0, 127.2, 125.9, 123.6, 121.9, 121.8, 118.2, 115.4. IR (ATR) 3053, 1660, 1587 cm^{-1}. HRMS (DART) Found 348.1387, Calcd. for $C_{25}H_{18}NO$, $[M + H]^+$ 348.1388.

3-Chloro-5-phenylphenanthridin-6(5H)-one (2p): *N*-Phenyl 4'-chloro-biphenyl-2-carboxamide (46.2 mg, 0.15 mmol) gave 3-chloro-5-phenyl phenanthridin-6(5H)-one (89%, 40.8 mg) as a white solid. R_f = 0.17 ($CHCl_3$). m.p. = 200-201 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 1.2, 8.0 Hz, 1 H), 8.26 (d, *J* = 8.0 Hz, 1 H), 8.20 (d, *J* = 8.6 Hz, 1 H), 7.81 (td, *J* = 1.1, 8.0 Hz, 1 H), 7.65-7.61 (m, 3 H), 7.58-7.55 (m, 1 H), 7.33-7.31 (m, 2 H), 7.24 (dd, *J* = 2.3, 8.6 Hz, 1 H), 6.68 (d, *J* = 2.3 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.7, 140.1, 137.8, 135.1, 133.4, 133.2, 130.5, 129.3, 129.2, 129.0, 128.5, 125.7, 124.4, 123.0, 121.9, 117.7, 116.9. IR (ATR) 3061, 1659, 1582, 1104 cm^{-1}. HRMS (DART) Found 306.0673, Calcd. for $C_{19}H_{13}ClNO$, $[M + H]^+$ 306.0686.

5-Phenyl-3-trifluoromethyl-phenanthridin-6(5H)-one (2q): *N*-Phenyl 4'-trifluoromethyl-biphenyl-2-carboxamide (51.2 mg, 0.15 mmol) gave 5-phenyl-3-trifluoromethyl-phenanthridin-6(5H)-one (69%, 35.2 mg) as a white solid. R_f = 0.25 ($CHCl_3$). m.p. = 157-159 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 1.1, 8.0 Hz, 1 H), 8.40 (d, *J* = 8.6 Hz, 1 H), 8.36 (d, *J* = 8.0 Hz, 1 H), 7.86 (td, *J* = 1.1, 8.0 Hz, 1 H), 7.71-7.63 (m, 3 H), 7.59-7.56 (m, 1 H), 7.51 (dd, *J* = 1.2, 8.6 Hz, 1 H), 7.34-7.32 (m, 2 H), 6.93 (s, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.6, 140.1, 139.3, 137.5, 133.3, 132.9, 131.1, 130.8, 130.6, 129.4, 129.3, 129.2, 129.0, 128.6, 128.3, 126.5, 124.9, 124.8, 123.9, 122.6, 122.4, 121.8, 120.2, 119.1, 119.1, 114.0, 114.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.6. IR (ATR) 3062, 1665, 1519, 1330 cm^{-1}. HRMS (DART) Found 340.0958, Calcd. for $C_{20}H_{13}F_3NO$, $[M + H]^+$ 340.0949.

5,8-Diphenylphenanthridin-6(5H)-one (2r): *N*-Phenyl 4-phenyl-biphenyl-2-carboxamide (52.4 mg, 0.15 mmol) gave 5,8-diphenyl phenanthridin-6(5H)-one (83%, 43.0 mg) as a white solid. R_f = 0.28 ($CHCl_3$). m.p. = 205-207 ºC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.80 (d, *J* = 1.8 Hz, 1 H), 8.41 (d, *J* = 8.1 Hz, 1 H), 8.33 (dd, *J* = 1.7, 6.3 Hz, 1 H), 8.07 (dd, *J* = 1.7, 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.64 (t,

J = 8.6 Hz, 2 H), 7.56 (dd, *J* = 1.1, 7.4 Hz, 1 H), 7.50 (t, *J* = 8.6 Hz, 2 H), 7.40 (td, *J* = 1.1, 7.4 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.33-7.28 (m, 2 H), 6.71 (dd, *J* = 1.7, 7.5 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 161.9, 140.9, 139.8, 139.3, 138.4, 133.0, 131.7, 130.3, 129.2, 129.2, 129.1, 128.9, 128.0, 127.3, 127.1, 126.3, 123.1, 122.8, 122.6, 119.0, 117.2. IR (ATR) 3057, 1648, 1588 cm^{-1}. HRMS (DART) Found 348.1395, Calcd. for $C_{25}H_{18}NO$, $[M + H]^+$ 348.1388.

8-Bromo-5-phenylphenanthridin-6(5H)-one (2s): *N*-Phenyl 4-bromo-biphenyl-2-carboxamide (52.8 mg, 0.15 mmol) gave 8-bromo-5-phenylphenanthridin-6(5H)-one (72%, 37.6 mg) as a pale yellow solid. R_f = 0.26 ($CHCl_3$). m.p. = 239-241 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 2.2 Hz, 1 H), 8.24 (dd, *J* = 1.1, 7.4 Hz, 1 H), 8.20 (d, *J* = 9.1 Hz, 1 H), 7.89 (dd, *J* = 2.3, 8.6 Hz, 1 H), 7.62 (t, *J* = 7.4 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.34-7.27 (m, 4 H), 6.68 (dd, *J* = 1.1, 8.0 Hz, 1 H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 160.6, 139.2, 138.1, 136.0, 133.0, 131.8, 130.4, 129.6, 129.1, 127.4, 123.8, 123.1, 123.0, 122.4, 118.5, 117.3. HRMS (DART) Found 350.0181, Calcd. for $C_{19}H_{13}BrNO$, $[M + H]^+$ 350.0181.

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Keywords: C-H amidation • visible-light • transition-metal-free • organophotocatalyst • phenanthridinones

[1] a) S. Patil, S. Kamath, T. Sanchez, N. Neamati, R. F. Schinazic, J. K. Buolamwini, *Bioorg. Med. Chem*., **2007**, *15*, 1212-1228; b) L. Lehtiö, A. Jemth, R. Collins, O. Loseva, A. Johansson, N. Markova, M. Hammarström, A. Flores, L. Holmberg-Schiavone, J. Weigelt, T. Helleday, H. Schüler, T. Karlberg, *J. Med. Chem*., **2009**, *52*, 3108-3111; c) S. Pegoraro, M. Lang, T. Dreker, J. Kraus, S. Hamm, C. Meere, J. Feurle, S. Tasler, S. Prütting, Z. Kuras, V. Visan, S. Grissmer, *Bioorg. Med. Chem. Lett.,* **2009**, *19*, 2299-2304; d) Z. Jin, *Nat. Prod. Rep*., **2011**, *28*, 1126-1142.

[2] a) J. P. Wolfe, S. Wagaw, J. Marcoux, S. L. Buchwald, *Acc. Chem. Res*., **1998**, *31*, 805-818; b) J. F. Hartwig, *Acc. Chem. Res*., **1998**, *31*, 852-860.

[3] a) P. Y. S. Lam, G. Vincent, C. G. Clark, S. Deudon, P. K. Jadhav, *Tetrahedron Lett.*, **2001**, *42*, 3415-3418; b) K. S. Rao, T. Wu, *Tetrahedron*, **2012**, *68*, 7735-7754.

[4] a) H. C. Van der Plas, H. C. *Acc. Chem. Res*., **1978**, *11*, 462-468; b) M. Makosza, J. Winiarski, *Acc. Chem. Res*., **1987**, *20*, 282-289; c) A. Kaga, H. Hayashi, H. Hakamata, M. Oi, M. Uchiyama, R. Takita, S. Chiba, *Angew. Chem. Int. Ed*., **2017**, *56*, 11807-11811; d) N. E. S. Tay, D. A. Nicewicz, *J. Am. Chem. Soc*., **2017**, *139*, 16100-16104.

[5] a) D. E. Ames, A. Opalko, *Tetrahedron*, **1984**, *40*, 1919-1925; b) M. A. Siddiqui, V. Snieckus, *Tetrahedron Lett.*, **1988**, *29*, 5463-5466; c) T. Furuta, Y. Kitamura, A. Hashimoto, S. Fujii, K. Tanaka, T. Kan, *Org. Lett.*, **2007**, *9*, 183-186; d) J. Karthikeyan, C. -H. Cheng, *Angew. Chem. Int. Ed.*, **2011**, *50*, 9880-9883; e) N. Ishida, Y. Nakanishi, T. Moriya, M. Murakami, *Chem. Lett.*, **2011**, *40*, 1047-1049.

[6] H. -Y. Thu, W. -Y. Yu, C. -M. Che, *J. Am. Chem. Soc*., **2006**, *128*, 9048-9049.

[7] Q. Gui, Z. Zhiyong Yang, X. Chen, J. Liu, Z. Tan, R. Guo, W. Yu, *Synlett*, **2013**, *24*, 1016-1020.

[8] a) Shiiya's report: Y. Kikugawa, A. Nagashima, T. Sakamoto, E. Miyazawa, M. Shiiya, *J. Org. Chem*., **2003**, *68*, 6739-6744; b) Xue's report: D. Liang, W. Yu, N. Nguyen, J. R. Deschamps, G. H. Imler, Y. Li, A. D. MacKerell Jr., C. Jiang, F. Xue, *J. Org. Chem*., **2017**, *82*, 3589-3596.

[9] Y. Moon, E. Jang, S. Choi, S. Hong, *Org. Lett*., **2018**, *20*, 240-243.

[10] N. A. Romero, D. A. Nicewicz, *Chem. Rev*., **2016**, *116*, 10075-10166.

[11] T. Yamaguchi, E. Yamaguchi, A. Itoh, *Org. Lett*., **2017**, *19*, 1282-1285.

[12] 1-Cl-AQN (+1.9 V) shows higher oxidation potential than the iridium photocatalyst (Ir(III)*/Ir(II) = +1.21 V).

[13] a) N. A. Romero, K. A. Margrey, N. E. Tay, D. A. Nicewicz, D. A. *Science*, **2015**, *349*, 1326-1330; b) K. A. Margrey, J. B. McManus, S. Bonazzi, F. Zecri, D. A. Nicewicz, *J. Am. Chem. Soc.*, **2017**, *139*, 11288-11299.

[14] Acridinium salt possesses high oxidation potential (+2.15 V).

[15] M. Yudasaka, T. Maruyama, E. Yamaguchi, N. Tada, A. Itoh, *Eur. J. Org. Chem.*, **2018**, 550-556.

[16] T. Morack, J. B. Metternich, R. Gilmour, *Org. Lett.*, **2018**, *20*, 1316-1319.

[17] P. C. Meltzer, B. Blundell, Y. F. Yong, Z. Chen, C. George, M. D. Gonzalez, B. K. Madras, *J. Med. Chem.*, **2000**, *43*, 2982-2991.

[18] J. -J. Dai, W. -T. Xu, Y. -D. Wu, W. -M. Zhang, Y. Gong, X. -P. He, X. -Q. Zhang, H. -J. Xu, *J. Org. Chem.*, **2015**, *80*, 911-919.

[19] Y. Li, Y. -J. Ding, J. Y. Wang, Y. -M. Su, X. -S. Wang, *Org.*, *Lett.* **2013**, *15*, 2574-2577.

[20] A. Kehl, V. M. Breising, D. Schollmeyer, S. R. Waldvogel, *Chem. Eur. J.*, **2018**, *24*, 17230-17233.

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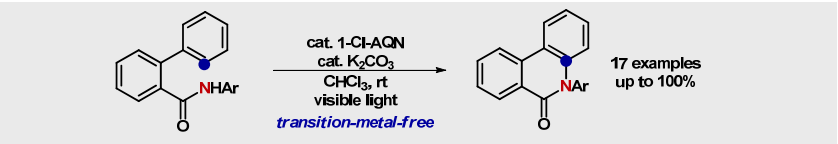

We have developed a method to construct a phenanthridinone skeleton frequently found in bioactive substances without using transition metals. This reaction proceeds photooxidative C–H amidation with the visible light irradiation and the commercially available organophotocatalyst. Phenanthridinones are afforded under mild conditions at low cost in this synthetic method.

C–H amidation, organophotocatalyst

*Kaoru Usami, Eiji Yamaguchi, Norihiro Tada and Akichika Itoh **

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Transition-Metal-Free Synthesis of Phenanthridinones through Visible-Light-Driven Oxidative C–H Amidation