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Visible-Light-Induced Decarboxylative Cyclization/Hydrogenation Cascade Reaction to Access Phenanthridin-6-yl(aryl)methanol by an Electron Donor−Acceptor Complex

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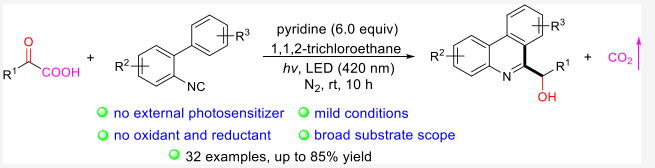
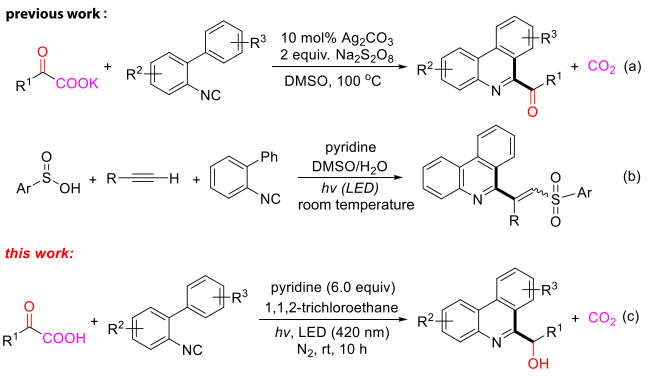
ABSTRACT: A novel and efficient visible-light-induced decarboxylative cyclization/hydrogenation cascade reaction of α-oxocarboxylic acids and 2-isocyanobiaryls has been developed. Without the need of any external photosensitizer, oxidant, and reductant, this method offers a mild and green approach for the synthesis of diverse alcohols in moderate to good yields. A mechanism indicated that an electron donor−acceptor complex-driven decarboxylation, radical addition/cyclization, and *in situ* photochemical reduction of ketones to alcohols could be involved in the reaction.



INTRODUCTION

α-Oxocarboxylic acids are stable and readily available, and the carboxyl group is a latent activating group, which can be easily removed in organic synthesis. Therefore, α-oxocarboxylic acids have often been employed as acyl synthons by decarboxylative transformations in recent decades.[1] For example, Pd-, Cu-, and Rh-catalyzed decarboxylative cross-couplings, in which metal-mediated decarboxylation affords acyl anion equivalents, are an attractive and useful strategy for the synthesis of diaryl ketones with aryl halides, arylboronic acids, and C−H moieties.[2] In 2014, the Lei group demonstrated a novel approach of the silver-catalyzed radical decarboxylation for the synthesis of 6-acyl phenanthridines from α-oxocarboxylates and isocyanides (Scheme 1a).[3] Recently, with the rise of visible-light photoredox catalysis, photocatalytic decarboxylation of α-oxocarboxylic acids has provided an effective and environmentally benign avenue to generate acyl radicals for the preparation of carbonyl compounds.[4] Despite these significant advances, synthetic challenges still remain because these methods need to employ expensive metal catalysts, strong oxidants, or additives. Furthermore, compared to extensive research on preparation of various aryl ketones *via* acyl anions or radicals, α-oxocarboxylic acids have not been utilized in the synthesis of functionalized alcohols, especially by *in situ* reduction of aryl ketones. Generally, reduction of carbonyl compounds serves as an efficient and direct synthetic pathway to their corresponding alcohols and is typically performed using complex hydrides as reducing agents or with molecular hydrogen in combination with precious metal catalysts.[5] However, most of these protocols require either a stoichiometric amount of hydride reagents or high catalyst loadings and elevated temperatures, which limit their synthetic application and functional group compatibilities. Therefore, developing a green, sustainable, and metal-free decarboxylation/hydrogenation cascade reaction for the synthesis of

Scheme 1. (a) Ag-Catalyzed Oxidative Radical Decarboxylation/Cyclization of α-Oxocarboxylates and Isocyanides for the Synthesis of 6-Acyl Phenanthridines; (b) Electron Donor−Acceptor (EDA) Driven Three-Component Reactions of Isocyanides, Alkynes, and Sulfinic Acids; (c) Decarboxylation/Hydrogenation Cascade Reaction for the Synthesis of Phenanthridin-6-yl(aryl)methanol



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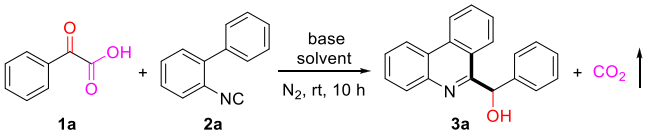
diverse alcohols from α-oxocarboxylic acids would be highly desirable.

EDA complexes resulting from the association of an electron donor molecule (D) with an electron acceptor molecule (A) can be excited by visible light to generate radical species for the synthetically valuable transformations without the need of any external photocatalyst.[6] During the past decades, the search for more environmentally friendly processes has led chemists toward the investigation of photochemical reactions driven by EDA complexes, and great achievements including catalytic asymmetric alkylation,[7] perfluoroalkylation,[8] and intramolecular cyclization[9] have been achieved. These promising results imply that EDA complexes may find more applications in organic synthesis. Inspired by these recent works and in continuation of our interest on radical transformation driven by EDA complexes (Scheme 1a,b),[10] herein, we disclose a visible-light-induced decarboxylative cyclization/hydrogenation cascade for the synthesis of phenanthridin-6-yl(aryl)-methanol from α-oxocarboxylic acids at room temperature without any external photosensitizer, oxidant, and reductant (Scheme 1c).

RESULTS AND DISCUSSION

In our initial investigation, we chose phenylglyoxylic acid (**1a**) and 2-isocyanobiphenyl (**2a**) as the model substrates to identify the optimal reaction conditions, and the results are summarized in Table 1. At first, we were delighted to find that visible-light irradiation of **1a** and **2a** in CH_2Cl_2 for 10 h under a N_2 atmosphere furnished the corresponding product **3a** in 41% yield, and the structure of **3a** was confirmed by the single-crystal X-ray diffraction (Table 1, entry 1). Further survey of solvents showed that 1,1,2-trichloroethane shows the best efficiency as a 78% yield of **3a** was provided (Table 1, entry 2). Other solvents including $CHCl_3$, THF, EtOAc, acetone, and cyclohexane were less effective and gave the inferior results (Table 1, entries 3−7). *N*,*N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were not suitable solvents and completely inhibited the reaction (Table 1, entries 8 and 9). Furthermore, pyridine was an essential parameter in the formation of **3a**, and other bases such as Et_3N, 4-dimethylaminopyridine (DMAP), and K_2CO_3 instead of pyridine were to be ineffective in the reaction. Therefore, the basicity of the base plays a vital role in visible-light-induced tandem transformation (Table 1, entries 10−12). When the model reaction was conducted under an air atmosphere, product **3a** was obtained in 45% yield (Table 1, entry 13). In addition, decreased yields were observed when the amount of pyridine and phenylglyoxylic acid was reduced (Table 1, entries 14 and 15). It should be noted that the reaction did not proceed in the absence of light even when the reaction mixture was heated to 60 °C for 10 h (Table 1, entries 16 and 17). Similarly, no product was detected under the irradiation with a blue LED (450 ± 5 nm) or a green LED (530 ± 5 nm) (Table 1, entries 18 and 19). All these results indicated that this tandem reaction is a photoinduced process.

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

entry	solvent	base	yield (%)[b]
1	CH_2Cl_2	pyridine	41
2	**1,1,2-trichloroethane**	**pyridine**	**78**
3	$CHCl_3$	pyridine	50
4	THF	pyridine	46
5	EtOAc	pyridine	65
6	acetone	pyridine	48
7	cyclohexane	pyridine	21
8	DMF	pyridine	0
9	DMSO	pyridine	0
10	1,1,2-trichloroethane	Et_3N	0
11	1,1,2-trichloroethane	DMAP	0
12	1,1,2-trichloroethane	K_2CO_3	0
13	1,1,2-trichloroethane	pyridine	45[c]
14	1,1,2-trichloroethane	pyridine	60[d]
15	1,1,2-trichloroethane	pyridine	55[e]
16	1,1,2-trichloroethane	pyridine	0[f]
17	1,1,2-trichloroethane	pyridine	0[g]
18	1,1,2-trichloroethane	pyridine	0[h]
19	1,1,2-trichloroethane	pyridine	0[i]

[a]Reaction conditions: phenylglyoxylic acid (**1a**, 0.75 mmol), 2-isocyanobiphenyl (**2a**, 0.25 mmol), the base (6.0 equiv), and the solvent (2 mL) at room temperature under a 3 W LED (420 ± 5 nm) irradiation for 10 h. [b]Isolated yield based on **2a**. [c]Under an air atmosphere. [d]Phenylglyoxylic acid (**1a**, 0.50 mmol). [e]Pyridine (4.0 equiv). [f]In the darkness. [g]Under an oil bath to 60 °C in the darkness. [h]Under a 3 W blue LED (450 ± 5 nm) irradiation. [i]Under a 3 W green LED (530 ± 5 nm) irradiation.

With optimized conditions in hand, we next examined the scope of the α-oxocarboxylic acid component in this decarboxylative cyclization/hydrogenation cascade reaction. As described in Scheme 2, a wide range of 2-oxo-2-phenylacetic acids with different substituents on the phenyl ring could be applied to react with **2a**, providing the desired products **3a**−**3n** in moderate-to-good yields. The reactions of substituted 2-oxo-2-phenylacetic acids with an electron-donating group, such as methyl, ethyl, *tert*-butyl, methoxy, or methylthio group, gave the products (**3b**−**3h**) in 70−78% yields. On the other hand, substituted 2-oxo-2-phenylacetic acids with an electron-withdrawing group including fluoro, chloro, bromo, or iodo were also good reaction partners and generated the corresponding products **3i**−**3m** in 50−73% yields. It was worth mentioning that the reaction showed good tolerance toward the halogen groups, which provide useful handles for further transformations through transition-metal-catalyzed classic cross-coupling reactions. In the case of disubstituted 2-oxo-2-phenylacetic acid, the reaction underwent smoothly, affording product **3n** in 65% yield. Heterocyclic α-oxocarboxylic acids, such as 2-oxo-2-(thien-2-yl)acetic acid, were also investigated, providing the corresponding product **3o** in 34% yield.

Subsequently, the substitution effect on both aromatic rings of biphenyl isocyanide **3** was investigated, and the results are summarized in Scheme 3. Once again, the reaction was not sensitive to the electronic nature of the substituents, as evidenced by the moderate-to-good yields of **3p**−**3ag**. Me-, F-, and Cl-substituted 2-isocyanobiphenyls on the para position of the isocyano moiety reacted efficiently with **1**, affording the corresponding products in yields ranging from 61 to 85% (**3p**−**3s**). Furthermore, 2-isocyanobiphenyls containing substituents, such as Me, OMe, *t*-Bu, F, Cl, CF_3, and SMe on the para position of the non-isocyanide phenyl ring, are all suitable substrates for this transformation, and the corresponding

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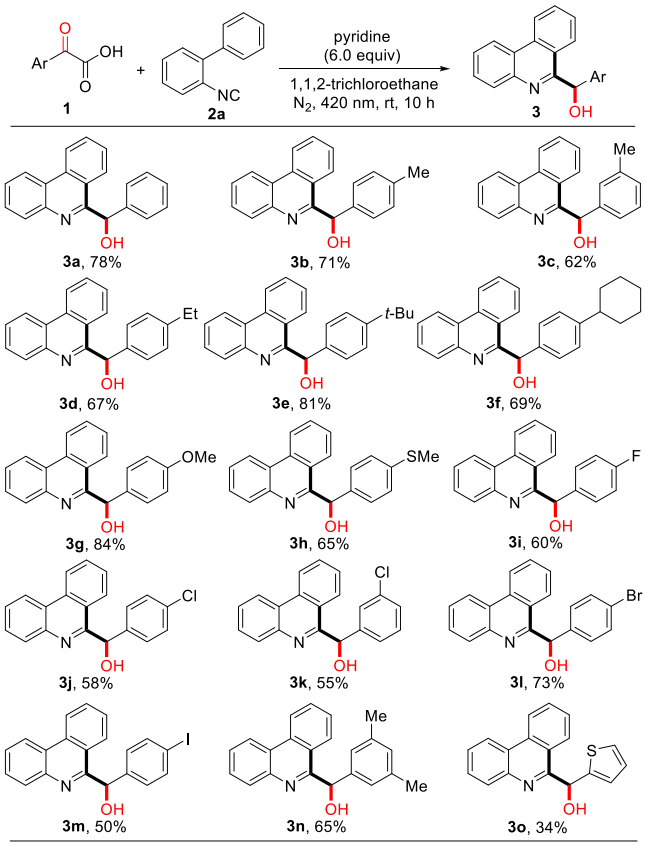
Scheme 2. Scope of α-Oxocarboxylic Acids[a]



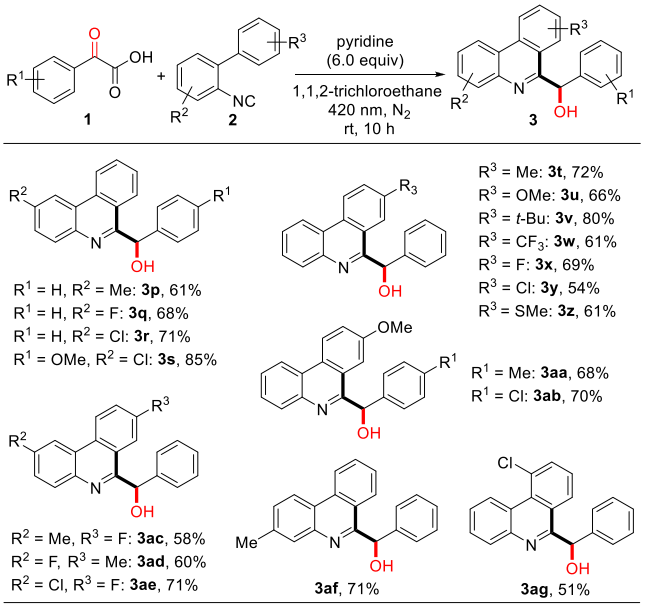
[a][Reaction conditions: α-oxocarboxylic acid (**1**, 0.75 mmol), 2-isocyanobiphenyl (**2a**, 0.25 mmol), pyridine (6.0 equiv), and 1,1,2-trichloroethane (2.0 mL) at room temperature under a 3 W LED (420 ± 5 nm) irradiation for 10 h; isolated yield based on **2a**].

products (**3t**−**3ab**) were obtained in moderate-to-good yields. In the other case, biphenyl isocyanides with two substituted groups on both aromatic rings were also effective to give the corresponding **3ac**−**3ae** in 58−71% yields. When the position of substituents on 2-isocyanobiphenyls was changed, **2** reacted smoothly with **1a**, affording the expected products **3af** and **3ag** in 71 and 51% yield, respectively.

To gain insights into this photoinduced decarboxylative/hydrogenation transformation, a series of optical absorption spectra of phenylglyoxylic acid (**1a**), 4′-chloro-2-isocyano-1,1′-biphenyl (**2b**), pyridine, and a combination of these components were recorded in 1,1,2-trichloroethane solution. As depicted in Figure 1, after mixing **1a** with **2b**, the solution developed a yellowish color, while its optical absorption spectrum showed a bathochromic displacement in the visible-light region, which is diagnostic of an EDA complex (Figure 1). Following Job's plot method, the stoichiometry of the EDA complex between **1a** and **2b** in solution was found to be 1:1 (for details, see Figure S1 in the Supporting Information). Meanwhile, the association constant K_{EDA} was calculated to be 5.02 M^{-1} in 1,1,2-trichloroethane using the Benesi−Hildebrand equation (Figure S2).[11] These results indicate that the EDA complex is formed between **1a** and **2b**, and visible-light irradiation of the transiently generated EDA complex is critical to afford radical species for reaction development.

More experiments were conducted to understand the mechanism of this reaction better. When 6-benzoyl phenanthridine (**4a**) was added to the reaction mixture of **1a** and **2c** under optimized reaction conditions, the corresponding hydrogenated product **3a** was obtained in 44% yield, along with **3x** and **4b** (Scheme 4a). Moreover, under 3 W LED (420 ± 5 nm) irradiation for 10 h, 6-benzoyl phenanthridine (**4a**) can also be hydrogenated to generate **3a** in 52% yield in the presence of 3.0 equiv **1a** (Scheme 4b). UV−visible (UV−vis) measurements revealed that **4a** can be excited with light at a wavelength of 420 nm because of its obvious absorption band in the wavelength below 480 nm (for details, see Figure S3 in the Supporting Information). Then, two radical-trapping experiments were performed. It is found that the formation of product **3a** was completely suppressed in the presence of TEMPO as a radical scavenger under optimized reaction conditions, and instead, TEMPO adducts **I** and **II** from benzoyl and hydrogen radicals were detected by electrospray ionization mass spectrometry (ESI-MS), providing evidence for the free-radical mechanism (Scheme 4c). On the other

Scheme 3. Scope of Biphenyl Isocyanides and α-Oxocarboxylic Acids[a]



[a][Reaction conditions: α-keto acid (**1**, 0.75 mmol), biphenyl isocyanide (**2**, 0.25 mmol), pyridine (6.0 equiv), and 1,1,2-trichloroethane (2.0 mL) at room temperature under a 3 W LED (420 ± 5 nm) irradiation for 10 h; isolated yield based on **2**].

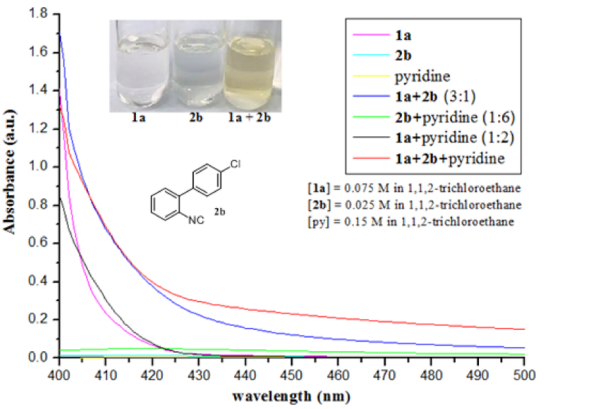


Figure 1. Optical absorption spectra of the reaction components.

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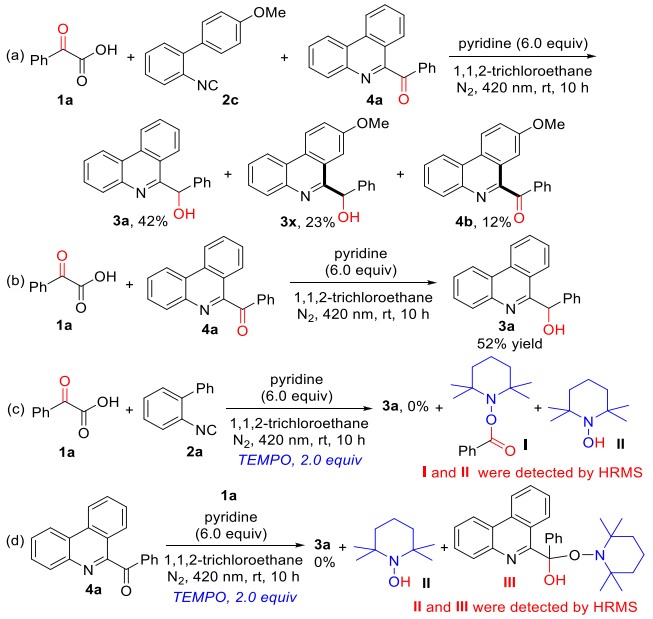
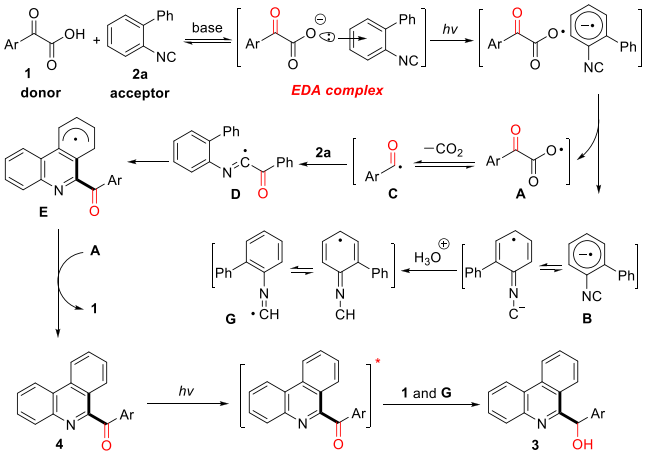
Scheme 4. Investigation of the Reaction Mechanism



hand, to further confirm the existence of intermediates for the hydrogenation process, the reaction of **4a** and **1a** with TEMPO was also carried out under optimized conditions. The ESI-MS analysis of the reaction mixture showed the existence of hydrogen and important carbon radical addition intermediates **II** and **III** (Scheme 4d). These results suggest that photoexcitation of **4a** could trigger the hydrogen radical abstraction to form carbon radicals in the hydrogenation step. Deuterium experiments indicated that H_2O and acids are the sources of hydrogen by using D-**1a** and D_2O (for details, see Figure S7a−c in the Supporting Information). Furthermore, the intermolecular kinetic isotopic effect (KIE) experiment confirmed that K_H/K_D for the arene C−H bond was 1.0, indicating that the cleavage of the arene C−H bond was not the rate-determining step, and free-radical cyclization was involved in this transformation (for details, see Figure S7d). A further control experiment suggested that the photochemical reduction of ketones to alcohols could be involved in the rate-determining step, with the starting material in one pot under optimized conditions (for details, see Figure S7e).

On the bases of these experimental results and previous reports,[6−10] a plausible mechanism is proposed in Scheme 5. First, an EDA complex was formed between α-oxocarboxylic acid **1** and **2a** in the presence of pyridine. Upon visible-light irradiation, this EDA complex generates a radical-ion pair by single-electron transfer from the donor to the acceptor. Second, the fragmentation of the radical-ion pair produces carboxylic radical **A** and radical anion **B**. After the release of CO_2 from carboxylic radical **A**, the resultant acyl radical **C** added to isonitrile produces another radical intermediate **D**, which undergoes the intramolecular radical cyclization to form radical intermediate **E**. Then, 6-acyl phenanthridine **4** is formed with the assistance of carboxylic radical **A**, along with 1 equiv of α-oxocarboxylic acid. Meanwhile, radical anion **B** formed in the previous process can abstract a hydrogen cation to generate imidoyl radical **G** through a resonance, which stores a hydrogen radical. Finally, 6-acyl phenanthridine **4** is excited under an irradiation of 3 W LED (420 ± 5 nm) and is reduced by **1** and **G** to yield the corresponding alcohol **3**.

Scheme 5. Proposed Mechanism for the Formation of 3



CONCLUSIONS

In summary, we have developed a visible-light-induced decarboxylative cyclization/hydrogenation cascade reaction of α-oxocarboxylic acids and 2-isocyanobiphenyls under external photosensitizer-, oxidant-, and reductant-free conditions. This reaction provides a green and facile method for direct synthesis of diverse alcohols with good functional group compatibility under mild reaction conditions. Mechanistic investigation revealed that the decarboxylative cyclizations driven by key photoactive species of the EDA complex and the subsequent photochemical reduction of 6-acyl phenanthridine could be involved in the reaction. Further exploration and applications of new EDA complexes generated from α-oxocarboxylic acids and other organic molecules in organic synthesis are still ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. The reactions were carried out with magnetic stirring under a nitrogen atmosphere. All ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 or 600 MHz Bruker FT-NMR spectrometer (400:600 and 100:150 MHz, respectively) in $CDCl_3$ as a solvent and recorded in parts per million relative to the internal standard tetramethylsilane. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (J are given in hertz, Hz); and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High-resolution mass spectroscopy (HRMS) data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS using ESI.

The chemicals and solvents were purchased from commercial suppliers without further purification unless otherwise specified. Products were purified by flash chromatography on 100−200 mesh silica gels, SiO_2. All manipulations that require heating for starting materials were conducted with an oil bath. The light source was purchased from Philips Electronics Ltd. The material of the irradiation vessel is borosilicate glass, and the solution was placed at a distance of ∼1.5 cm from the 3 W LED (420 ± 5 nm).

General Experimental Procedure. *General Procedure for the Synthesis of α-Oxocarboxylic Acids 1.* A representative procedure for the preparation of 2-(4-(methylthio)phenyl)-2-oxoacetic acid is described as follows:[12] 1-(*p*-tolyl)ethan-1-one (0.66 g, 4.0 mmol), selenium dioxide (SeO_2, 0.67 g, 6.0 mmol), and pyridine (4.0 mL) were added to a Schlenk flask and under a N_2 atmosphere. The mixture was stirred at 110 °C for 6 h. After the reaction, the solution was filtered and washed with EtOAc (10 mL). The combined organic layer and volatile materials were evaporated under reduced pressure. NaOH (2 M, 8.0 mL) was added after the concentrate. The solution

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was extracted with EtOAc twice, and the organic layer was separated. The combined aqueous layer was treated with HCl (12 M, 5.0 mL). The mixture was extracted with EtOAc thrice, the combined organic layer was dried over magnesium sulfate, and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography (eluent: AcOEt/hexane = 10:1), and 2-oxo-2-(*p*-tolyl)acetic acid (0.64 g, 81% yield) was obtained as a white solid. ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 8.27 (d, J = 8.4 Hz, 2H), 8.96 (br, 1H), 7.30 (d, J = 8.4 Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ 182.8, 161.5, 150.4, 131.7, 127.8, 124.9, 14.5. HRMS (ESI) $[M + H]^+$ calcd for $C_9H_9O_3S$, 197.0267; found, 197.0271.

Following the general procedure for the synthesis of **1**, the crude product was purified by silica gel column chromatography (eluent: AcOEt/hexane = 10:1) to afford 2-(4-cyclohexylphenyl)-2-oxoacetic acid as a yellow solid (0.79 g, 85% yield). ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 8.62 (br, 1H), 8.18 (d, J = 7.8 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.56−2.59 (m, 1H), 1.87 (d, J = 7.2 Hz, 4H), 1.77 (d, J = 13.2 Hz, 1H), 1.36−1.46 (m, 4H), 1.24−1.30 (m, 1H); ^{13}C NMR (150 MHz, $(CD_3)_2SO$): δ 184.8, 163.4, 156.7, 131.4, 129.7, 127.5, 44.9, 33.9, 26.6, 25.9. HRMS (ESI) $[M + H]^+$ calcd for $C_{14}H_{17}O_3$, 233.1172; found, 233.1168.

General Procedure for the Synthesis of 2-Arylisocyanides 2. All 2-arylisocyanides were prepared according to a reported method.[13] A representative procedure for the preparation of 4′-chloro-2-isocyano-1,1′-biphenyl (**2b**) is described as follows: 2-iodoaniline (1.10 g, 5.0 mmol), (4-chlorophenyl)boronic acid (0.94 g, 6.0 mmol, 1.2 equiv), $Pd(PPh_3)_2Cl_2$ (70.2 mg, 0.10 mmol, 0.02 equiv), and K_2CO_3 (2 M, 10 mL) were added to a Schlenk flask and dissolved in 1,2-dimethoxyethane (5 mL) under a N_2 atmosphere. The mixture was stirred at 80 °C for 16 h. After the reaction, water was added and extracted with EtOAc twice. The combined organic layer was dried over magnesium sulfate, and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1), and 4′-chloro-[1,1′-biphenyl]-2-amine (0.86 g, 84%) was obtained as a white solid.

In a 50 mL two-necked flask, acetic formic anhydride, which was prepared from the reaction of acetic anhydride (0.50 mL) with formic acid (0.60 mL) at room temperature for 10 min, was added dropwise to a stirred a solution of 4′-chloro-[1,1′-biphenyl]-2-amine (4.0 mmol, 0.81 g) in CH_2Cl_2 (10.0 mL), and the mixture was stirred at room temperature for 2 h. After the reaction, volatile materials were evaporated under reduced pressure. *N*-(4′-Chloro-[1,1′-biphenyl]-2-yl)-formamide (0.83 g, 90%) was obtained as a white solid. This compound was used for the subsequent dehydration without further purification.

N-(4′-Chloro-[1,1′-biphenyl]-2-yl)formamide (0.70 g, 3.0 mmol) was dissolved in $CHCl_3$ (10.0 mL) and Et_3N (2.4 mL, 16 mmol) under a N_2 atmosphere and cooled to 0 °C in an ice bath. Then, phosphoryl chloride (0.72 mL, 7.2 mmol, 3.0 mL of $CHCl_3$ solution) was added dropwise slowly to this mixture. After stirring for 1 h, the reaction temperature was down to room temperature and the mixture was stirred for another 1 h. After the reaction, the resulting mixture was cooled to 0 °C in an ice bath. Then, the mixture was quenched and neutralized by a saturated aqueous solution of Na_2CO_3. After vigorous stirring for 1 h, water (10.0 mL) was added and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (10.0 mL) twice. The combined organic layer was dried over sodium sulfate, and the solvent was removed by evaporation. The residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 20:1). 4′-Chloro-2-isocyano-1,1′-biphenyl (**2b**, 0.45 g, 70%) was obtained as a white solid.

General Procedure for Synthesis of 3. A typical experimental procedure for the synthesis of **3a** is described as follows: phenylglyoxylic acid (**1a**, 0.75 mmol), 2-isocyanobiphenyl (**2a**, 0.25 mmol), and pyridine (6.0 equiv) were added into an air-tight reaction tube (10 mL) with 2.0 mL of 1,1,2-trichloroethane. The tube containing the reactants and solvent was evacuated using a pump and back-filled with high-purified nitrogen (>99.99%). The reaction mixture was stirred at room temperature under irradiation with a 3 W LED (420 ± 5 nm) for 10 h. After the reaction, 1,1,2-trichloroethane was evaporated under reduced pressure. The resulting crude mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 5:1) to provide the desired product **3a** (55.6 mg) in 78% yield.

*Phenanthridin-6-yl(phenyl)methanol (**3a**).* White solid (55.6 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 8.0, 0.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.79−7.66 (m, 3H), 7.51 (td, J = 8.4, 1.2 Hz, 1H), 7.39−7.37 (m, 2H), 7.29−7.22 (m, 3H), 6.55 (s, 1H), 6.39 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.0, 143.0, 141.8, 133.4, 130.8, 129.6, 128.9, 128.8, 128.0, 127.8, 127.3, 127.2, 126.0, 124.4, 123.4, 122.5, 122.1, 72.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{16}NO$, 286.1226; found, 286.1222.

*Phenanthridin-6-yl(p-tolyl)methanol (**3b**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (53.1 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.24 (dd, J = 8.2, 1.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.78−7.71 (m, 2H), 7.67 (td, J = 8.4, 1.2 Hz, 1H), 7.51 (td, J = 8.0, 0.8 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.51 (s, 1H), 6.36 (s, 1H), 2.25 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 141.8, 140.1, 137.6, 133.3, 130.7, 129.6, 129.4, 128.9, 127.7, 127.3, 127.2, 126.0, 124.4, 123.4, 122.5, 122.1, 72.5, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1387.

*Phenanthridin-6-yl(m-tolyl)methanol (**3c**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (46.4 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 8.0 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.24 (dd, J = 8.2, 0.6 Hz, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.78−7.69 (m, 2H), 7.66 (td, J = 8.0, 1.2 Hz, 1H), 7.49 (td, J = 8.0, 1.2 Hz, 1H), 7.18−7.13 (m, 3H), 7.04−7.03 (m, 1H), 6.53 (s, 1H), 6.34 (s, 1H), 2.24 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.1, 142.9, 141.8, 138.4, 133.3, 130.7, 129.6, 128.9, 128.8, 128.6, 128.4, 127.3, 127.2, 126.0, 124.9, 124.4, 123.4, 122.4, 122.1, 72.8, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1383.

*(4-Ethylphenyl)(phenanthridin-6-yl)methanol (**3d**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (52.5 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.4 Hz, 1H), 8.24 (dd, J = 8.0, 1.2 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.79−7.72 (m, 2H), 7.69 (td, J = 8.4, 1.2 Hz, 1H), 7.51 (td, J = 8.4, 1.2 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H), 6.37 (s, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 144.0, 141.8, 140.3, 133.3, 130.7, 129.6, 128.9, 128.3, 127.8, 127.3, 127.2, 126.0, 124.4, 123.5, 122.5, 122.1, 72.5, 28.5, 15.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}NO$, 314.1539; found, 314.1543.

*(4-(tert-Butyl)phenyl)(phenanthridin-6-yl)methanol (**3e**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (69.1 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.23 (dd, J = 8.0, 0.8 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.77−7.69 (m, 2H), 7.65 (td, J = 8.0, 0.8 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.31−7.27 (m, 4H), 6.49 (s, 1H), 6.38 (s, 1H), 1.23 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.2, 150.8, 141.8, 139.9, 133.3, 130.7, 129.6, 128.8, 127.4, 127.3, 127.1, 126.0, 125.7, 124.4, 123.5, 122.4, 122.1, 72.3, 34.4, 31.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{24}NO$, 342.1852; found, 342.1854.

*(4-Cyclohexylphenyl)(phenanthridin-6-yl)methanol (**3f**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (63.4 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.77−7.69 (m, 2H), 7.66 (td, J = 8.4, 1.2 Hz, 1H), 7.49 (td, J = 8.0, 0.8 Hz, 1H), 7.28

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(d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.50 (br, 1H), 6.36 (s, 1H), 2.40 (br, 1H), 1.77−1.67 (m, 5H), 1.42−1.22 (m, 5H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 147.7, 141.8, 140.3, 133.3, 130.7, 129.5, 128.8, 127.6, 127.1, 126.0, 124.4, 123.4, 122.4, 122.1, 72.4, 44.2, 26.8, 26.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{26}H_{26}NO$, 368.2009; found, 368.2009.

(4-Methoxyphenyl)(phenanthridin-6-yl)methanol ***(3g)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (66.2 mg, 84% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.77−7.70 (m, 2H), 7.66 (td, J = 8.0, 1.2 Hz, 1H), 7.49 (td, J = 8.0, 0.8 Hz, 1H), 7.28 (d, J = 8.8 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H), 6.35 (s, 1H), 3.69 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.23, 159.22, 141.7, 135.4, 133.3, 130.7, 129.5, 129.0, 128.9, 127.3, 127.1, 126.0, 124.4, 123.4, 122.4, 122.1, 114.1, 72.2, 55.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO_2$, 316.1332; found, 316.1330.

(4-(Methylthio)phenyl)(phenanthridin-6-yl)methanol ***(3h)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (53.9 mg, 65% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 8.4 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.21 (dd, J = 8.0, 0.8 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.76−7.68 (m, 2H), 7.64 (td, J = 8.0, 0.8 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 6.33 (s, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.8, 141.6, 139.8, 138.2, 133.2, 130.7, 129.5, 128.9, 128.2, 127.3, 127.2, 126.7, 125.8, 124.3, 123.2, 122.4, 122.0, 72.2, 15.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NOS$, 332.1104; found, 332.1103.

(4-Fluorophenyl)(phenanthridin-6-yl)methanol ***(3i)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (45.5 mg, 60% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 7.2 Hz, 1H), 8.23 (dd, J = 8.0, 1.2 Hz, 1H), 7.94 (d, J = 8.4 Hz, 1H), 7.79−7.73 (m, 2H), 7.68 (td, J = 8.0, 1.2 Hz, 1H), 7.52 (td, J = 8.0, 0.8 Hz, 1H), 7.35−7.32 (m, 2H), 6.95 (t, J = 8.8 Hz, 2H), 6.53 (s, 1H), 6.37 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.4 (C−F, $1J_{C-F}$ = 246.0 Hz), 158.8, 141.7, 138.9 (C−F, $3J_{C-F}$ = 3.0 Hz), 133.4, 130.8, 129.6 (C−F, $3J_{C-F}$ = 2.0 Hz), 129.5, 129.0, 127.4, 127.3, 125.8, 124.4, 123.2, 122.6, 122.1, 115.6 (C−F, $2J_{C-F}$ = 21.3 Hz), 71.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}FNO$, 304.1132; found, 304.1127.

(4-Chlorophenyl)(phenanthridin-6-yl)methanol ***(3j)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (46.4 mg, 58% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 7.2 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 7.6 Hz, 2H), 7.71 (td, J = 8.0, 1.2 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 6.36 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.5, 141.7, 141.5, 133.8, 133.5, 130.9, 129.6, 129.2, 129.1, 129.0, 127.5, 127.4, 125.8, 124.5, 123.2, 122.7, 122.2, 72.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}ClNO$, 320.0837; found, 320.0833.

(3-Chlorophenyl)(phenanthridin-6-yl)methanol ***(3k)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (44.0 mg, 55% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.25 (dd, J = 8.4, 0.8 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.2 Hz, 2H), 7.71 (td, J = 8.4, 1.2 Hz, 1H), 7.57 (td, J = 8.0, 0.8 Hz, 1H), 7.36 (s, 1H), 7.29−7.27 (m, 1H), 7.22−7.20 (m, 2H), 6.54 (s, 1H), 6.35 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 144.9, 141.7, 134.6, 133.5, 131.0, 130.1, 129.6, 129.1, 128.2, 128.0, 127.51, 127.46, 126.1, 125.7, 124.5, 123.2, 122.7, 122.2, 72.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}ClNO$, 320.0837; found, 320.0834.

(4-Bromophenyl)(phenanthridin-6-yl)methanol ***(3l)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (66.5 mg, 73% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.62 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 7.2 Hz, 1H), 8.24 (dd, J = 8.0, 1.2 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.79 (t, J = 8.0 Hz, 2H), 7.71 (td, J = 8.4, 1.2 Hz, 1H), 7.55 (td, J = 8.4, 1.2 Hz, 1H), 7.40 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.54 (s, 1H), 6.35 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 142.0, 141.7, 133.5, 131.9, 130.9, 129.60, 129.55, 129.1, 127.5, 127.4, 125.7, 124.5, 123.2, 122.7, 122.2, 122.0, 72.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}BrNO$, 364.0332; found, 364.0334.

(4-Iodophenyl)(phenanthridin-6-yl)methanol ***(3m)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (51.4 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, J = 8.4 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.78 (t, J = 7.6 Hz, 2H), 7.70 (t, J = 8.4 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 2H), 6.53 (s, 1H), 6.33 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 142.6, 141.7, 137.9, 133.4, 130.9, 129.8, 129.6, 129.0, 127.5, 127.4, 125.7, 124.5, 123.2, 122.7, 122.2, 93.7, 72.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}INO$, 412.0193; found, 412.0194.

(3,5-Dimethylphenyl)(phenanthridin-6-yl)methanol ***(3n)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (50.9 mg, 65% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, J = 8.4 Hz, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.25 (dd, J = 8.0, 0.8 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.78−7.70 (m, 2H), 7.66 (td, J = 8.0, 1.2 Hz, 1H), 7.50 (td, J = 8.0, 0.8 Hz, 1H), 6.97 (br, 2H), 6.85 (s, 1H), 6.52 (s, 1H), 6.30 (s, 1H), 2.20 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.1, 142.8, 141.7, 138.3, 133.3, 130.6, 129.7, 129.6, 128.8, 127.3, 127.1, 126.0, 125.6, 124.4, 123.5, 122.4, 122.1, 72.8, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{20}NO$, 314.1539; found, 314.1539.

Phenanthridin-6-yl(thiophen-2-yl)methanol ***(3o)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a yellow solid (24.6 mg, 34% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 8.64 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 7.8 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 7.82 (td, J = 8.4 Hz, 1H), 7.78 (td, J = 7.2 Hz, 1H), 7.70 (t, J = 7.8 Hz, 1H), 7.60 (t, J = 8.4 Hz, 1H), 7.20 (d, J = 5.4 Hz, 1H), 6.96 (d, J = 3.6 Hz, 1H), 6.89−6.87 (m, 1H), 6.68 (s, 1H), 6.46 (s, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 158.4, 147.0, 141.9, 133.5, 131.0, 129.7, 129.0, 127.5, 127.4, 126.7, 125.9, 125.8, 124.5, 123.4, 122.6, 122.1, 67.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}NOS$, 292.0791; found, 292.0789.

(2-Methylphenanthridin-6-yl)(phenyl)methanol ***(3p)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (45.7 mg, 61% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, J = 8.0 Hz, 1H), 8.26 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.66 (td, J = 8.0, 0.8 Hz, 1H), 7.55 (dd, J = 8.2, 1.4 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.36 (d, J = 6.8 Hz, 2H), 7.27−7.20 (m, 3H), 6.57 (s, 1H), 6.35 (s, 1H), 2.59 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.9, 143.1, 140.0, 137.1, 133.0, 130.5, 130.4, 129.2, 128.7, 127.9, 127.8, 127.1, 125.8, 124.2, 123.4, 122.4, 121.7, 72.6, 21.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1383.

(2-Fluorophenanthridin-6-yl)(phenyl)methanol ***(3q)***. Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (51.6 mg, 68% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.4 Hz, 1H), 8.20−8.17 (m, 1H), 8.06 (dd, J = 10.0, 2.8 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.70 (td, J = 8.4, 0.8 Hz, 1H), 7.53−7.44 (m, 2H), 7.36 (d, J = 6.8 Hz, 2H), 7.29−7.22 (m, 3H), 6.39 (s, 1H), 6.36 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.4 (C−F, $1J_{C-F}$ = 245.9 Hz), 158.3, 142.8, 138.5, 132.7

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(C−F, $4J_{C-F}$ = 4.3 Hz), 131.7 (C−F, $3J_{C-F}$ = 9.0 Hz), 130.7, 128.8, 128.0, 127.9, 127.7, 125.9, 125.7 (C−F, $3J_{C-F}$ = 9.0 Hz), 123.3, 122.6, 117.7 (C−F, $2J_{C-F}$ = 24.2 Hz), 107.1 (C−F, $2J_{C-F}$ = 23.4 Hz), 72.7. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{15}FNO$, 304.1132; found, 304.1128.

(2-Chlorophenanthridin-6-yl)(phenyl)methanol (**3r**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (56.8 mg, 71% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.41−8.38 (m, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.72−7.66 (m, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.29−7.22 (m, 3H), 6.36 (br, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.4, 142.7, 140.1, 133.1, 132.2, 131.0, 130.9, 129.4, 128.8, 128.03, 127.95, 127.7, 126.0, 125.4, 123.4, 122.4, 121.7, 72.7. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{15}ClNO$, 320.0837; found, 320.0835.

(2-Chlorophenanthridin-6-yl)(4-methoxyphenyl)methanol (**3s**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (74.3 mg, 85% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.43−8.41 (m, 2H), 8.12 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.72 (td, *J* = 8.4, 1.2 Hz, 1H), 7.68 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.53 (td, *J* = 8.0, 0.8 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.33−6.29 (m, 2H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.6, 159.3, 140.1, 135.1, 133.1, 132.2, 130.9, 129.3, 129.0, 127.9, 126.1, 125.4, 123.4, 122.5, 121.7, 114.2, 72.2, 55.1. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}ClNO_2$, 350.0942; found, 350.0943.

(8-Methylphenanthridin-6-yl)(phenyl)methanol (**3t**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (53.9 mg, 72% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.20 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.74−7.69 (m, 2H), 7.63 (td, *J* = 8.4, 1.6 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 6.8 Hz, 2H), 7.23−7.19 (m, 1H), 6.57 (s, 1H), 6.35 (s, 1H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.6, 143.0, 141.4, 137.3, 132.5, 131.2, 129.4, 128.7, 128.4, 127.9, 127.8, 127.1, 125.3, 124.5, 123.5, 122.3, 121.9, 72.6, 21.7. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1384.

(8-Methoxyphenanthridin-6-yl)(phenyl)methanol (**3u**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (52.0 mg, 66% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.42−8.39 (m, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.32−7.23 (m, 5H), 6.68 (s, 1H), 6.26 (s, 1H), 3.71 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.2, 157.9, 142.9, 140.8, 129.4, 128.8, 128.0, 127.8, 127.6, 127.2, 124.50, 124.47, 124.0, 121.5, 121.4, 106.0, 73.0, 55.2. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{18}NO_2$, 316.1332; found, 316.1333.

(8-(tert-Butyl)phenanthridin-6-yl)(phenyl)methanol (**3v**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (68.3 mg, 80% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, *J* = 3.6 Hz, 1H), 8.41 (d, *J* = 4.4 Hz, 1H), 8.19 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.96 (d, *J* = 2.0 Hz, 1H), 7.75 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.67 (td, *J* = 7.2, 1.2 Hz, 1H), 7.58 (td, *J* = 8.4, 1.2 Hz, 1H), 7.42−7.40 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 2H), 7.20−7.16 (m, 1H), 6.74 (s, 1H), 6.36 (s, 1H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.0, 150.1, 143.1, 141.4, 131.1, 129.3, 128.9, 128.6, 128.3, 127.82, 127.78, 127.0, 124.3, 123.1, 122.2, 121.9, 73.0, 34.9, 31.0. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{24}NO$, 342.1852; found, 342.1854.

Phenyl(8-(trifluoromethyl)phenanthridin-6-yl)methanol (**3w**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (53.9 mg, 61% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (d, *J* = 8.8 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.34 (s, 1H), 8.29 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.94 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.86 (td, *J* = 8.4, 1.2 Hz, 1H), 7.75 (td, *J* = 8.0, 1.2 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.32−7.22 (m, 3H), 6.40 (br, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.2, 142.5, 142.4, 135.6, 130.2, 129.9, 129.1 (C−F, $2J_{C-F}$ = 32.8 Hz), 129.0, 128.3, 127.9, 127.7, 126.7 (C−F, $3J_{C-F}$ = 3.0 Hz), 123.65(C−F, $1J_{C-F}$ = 271.0 Hz), 123.66, 123.5(C−F, $4J_{C-F}$ = 4.3 Hz), 122.7, 122.5, 72.9. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{15}F_3NO$, 354.1100; found, 354.1102.

(8-Fluorophenanthridin-6-yl)(phenyl)methanol (**3x**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (52.3 mg, 69% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.50−8.47 (m, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.43 (td, *J* = 8.8, 2.4 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 2H), 7.30−7.22 (m, 3H), 6.44 (s, 1H), 6.26 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.9 (C−F, $1J_{C-F}$ = 247.6 Hz), 158.2 (C−F, $4J_{C-F}$ = 4.0 Hz), 142.3, 141.3, 129.9 (C−F, $4J_{C-F}$ = 1.8 Hz), 129.6, 128.9, 128.8, 128.2, 127.7, 127.6, 125.0 (C−F, $3J_{C-F}$ = 8.5 Hz), 124.5(d, *J* = 8.1 Hz), 123.9, 121.8, 120.0 (C−F, $2J_{C-F}$ = 23.8 Hz), 110.6 (C−F, $2J_{C-F}$ = 21.7 Hz), 72.8. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{15}FNO$, 304.1132; found, 304.1134.

(8-Chlorophenanthridin-6-yl)(phenyl)methanol (**3y**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (43.2 mg, 54% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.48 (t, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 2.0 Hz, 1H), 7.79 (td, *J* = 8.0, 0.8 Hz, 1H), 7.72−7.67 (m, 2H), 7.38 (d, *J* = 7.2 Hz, 2H), 7.32−7.23 (m, 3H), 6.39 (s, 1H), 6.31 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.1, 142.4, 141.7, 133.3, 131.7, 131.4, 129.7, 129.3, 128.9, 128.2, 127.74, 127.69, 125.3, 124.33, 124.27, 123.8, 122.0, 72.7. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{15}ClNO$, 320.0837; found, 320.0837.

(8-(Methylthio)phenanthridin-6-yl)(phenyl)methanol (**3z**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (50.5 mg, 61% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 8.0 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 7.75 (td, *J* = 8.4, 1.2 Hz, 1H), 7.69−7.58 (m, 3H), 7.36 (d, *J* = 6.8 Hz, 2H), 7.31−7.24 (m, 3H), 6.61 (s, 1H), 6.29 (s, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.9, 142.9, 141.3, 138.8, 130.6, 129.6, 128.9, 128.6, 128.1, 127.9, 127.4, 124.3, 123.9, 122.7, 121.8, 121.1, 73.0, 15.3. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{18}NOS$, 332.1104; found, 332.1104.

(8-Methoxyphenanthridin-6-yl)(p-tolyl)methanol (**3aa**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a yellow solid (56.0 mg, 68% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (t, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.70 (td, *J* = 8.0, 0.8 Hz, 1H), 7.64 (td, *J* = 8.0, 1.2 Hz, 1H), 7.33 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.28−7.26 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 6.24 (s, 1H), 3.74 (s, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 158.1, 140.9, 140.0, 137.7, 129.5, 127.8, 127.7, 127.6, 127.2, 124.6, 124.5, 124.0, 121.6, 121.4, 106.1, 72.8, 55.3, 21.1. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{20}NO_2$, 330.1489; found, 330.1484.

(4-Chlorophenyl)(8-methoxyphenanthridin-6-yl)methanol (**3ab**). Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (61.2 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, *J* = 9.2 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.21 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.72 (td, *J* = 7.2, 1.6 Hz, 1H), 7.70 (td, *J* = 8.0, 1.2 Hz, 1H), 7.38 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 2.4 Hz, 1H), 6.64 (s, 1H), 6.25 (s, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.4, 157.5, 141.5, 140.8, 133.9, 129.5, 129.2, 129.0, 128.0, 127.8, 127.4, 124.6, 124.4, 124.3, 121.6, 121.5, 106.0, 72.2, 55.4. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{17}ClNO_2$, 350.0942; found, 350.0941.

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*(8-Fluoro-2-methylphenanthridin-6-yl)(phenyl)methanol (**3ac**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (46.0 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (dd, J = 9.2, 5.6 Hz, 1H), 8.24 (s, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.58 (td, J = 9.2, 1.8 Hz, 2H), 7.46 (td, J = 9.2, 2.8 Hz, 1H), 7.36 (d, J = 7.2 Hz, 2H), 7.31−7.24 (m, 3H), 6.46 (s, 1H), 6.26 (s, 1H), 2.63 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.9 (C−F, $1J_{C-F}$ = 247.4 Hz), 157.1, 142.5, 139.7, 137.7, 130.5, 129.8, 129.4, 129.0, 128.2, 127.8, 125.1 (C−F, $3J_{C-F}$ = 8.5 Hz), 124.6 (C−F, $3J_{C-F}$ = 8.1 Hz), 123.9, 121.5, 119.8 (C−F, $2J_{C-F}$ = 23.8 Hz), 110.5 (C−F, $2J_{C-F}$ = 21.7 Hz), 72.8, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}FNO$, 318.1289; found, 318.1288.

*(2-Fluoro-8-methylphenanthridin-6-yl)(phenyl)methanol (**3ad**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (47.6 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 8.17 (dd, J = 8.8, 5.6 Hz, 1H), 8.01 (dd, J = 10.0, 2.4 Hz, 1H), 7.74 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.44 (td, J = 8.4, 2.4 Hz, 1H), 7.38 (d, J = 7.2 Hz, 2H), 7.30−7.22 (m, 3H), 6.43 (d, J = 4.8 Hz, 1H), 6.33 (d, J = 4.8 Hz, 1H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4 (C−F, $1J_{C-F}$ = 245.7 Hz), 158.0 (C−F, $4J_{C-F}$ = 2.3 Hz), 142.9, 138.2, 138.1, 132.5, 131.6 (C−F, $3J_{C-F}$ = 9.0 Hz), 130.6 (C−F, $4J_{C-F}$ = 4.1 Hz), 128.7, 127.9, 127.7, 125.8 (C−F, $3J_{C-F}$ = 9.2 Hz), 125.4, 123.5, 122.5, 117.2 (C−F, $2J_{C-F}$ = 24.2 Hz), 106.9 (C−F, $2J_{C-F}$ = 23.3 Hz), 72.5, 21.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{17}FNO$, 318.1289; found, 318.1289.

*(2-Chloro-8-fluorophenanthridin-6-yl)(phenyl)methanol (**3ae**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (60.0 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43 (dd, J = 9.2, 5.2 Hz, 1H), 8.38 (d, J = 2.0 Hz, 1H), 8.15 (d, J = 8.8 Hz, 1H), 7.69 (dd, J = 8.8, 2.4 Hz, 1H), 7.61 (dd, J = 9.6, 2.4 Hz, 1H), 7.48 (td, J = 9.2, 2.4 Hz, 1H), 7.36 (d, J = 6.8 Hz, 2H), 7.32−7.25 (m, 3H), 6.26 (s, 1H), 6.23 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4 (C−F, $1J_{C-F}$ = 249.0 Hz), 158.7, 142.1, 139.8, 133.7, 131.1, 129.4, 129.0, 128.3, 127.7, 125.2 (C−F, $3J_{C-F}$ = 8.7 Hz), 125.0, 124.9 (C−F, $3J_{C-F}$ = 8.0 Hz), 121.6, 120.3 (C−F, $2J_{C-F}$ = 25.0 Hz), 110.9 (C−F, $2J_{C-F}$ = 21.9 Hz), 72.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}ClFNO$, 338.0742; found, 338.0741.

*(3-Methylphenanthridin-6-yl)(phenyl)methanol (**3af**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (53.1 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.53 (d, J = 8.4 Hz, 1H), 8.41 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.2 Hz, 1H), 7.52−7.45 (m, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.28−7.21 (m, 3H), 6.59 (s, 1H), 6.37 (s, 1H), 2.61 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9, 143.0, 141.9, 139.2, 133.4, 130.7, 129.1, 129.0, 128.7, 127.9, 127.8, 126.9, 125.9, 123.1, 122.3, 122.1, 121.9, 72.7, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}NO$, 300.1383; found, 300.1381.

*(10-Chlorophenanthridin-6-yl)(phenyl)methanol (**3ag**).* Following the general procedure for the synthesis of **3**, the crude product was purified by silica gel column chromatography (eluent: hexane/AcOEt = 5:1) to afford a white solid (40.8 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (d, J = 8.4 Hz, 1H), 8.27 (dd, J = 8.0, 1.2 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.83−7.79 (m, 2H), 7.69 (td, J = 8.8, 1.2 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 6.8 Hz, 2H), 7.29−7.22 (m, 3H), 6.46 (d, J = 5.2 Hz, 1H), 6.35 (d, J = 4.8 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.6, 142.7, 134.5, 131.8, 130.4, 129.8, 129.3, 128.8, 128.1, 127.7, 127.1, 126.8, 126.4, 125.9, 125.3, 123.6, 72.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{15}ClNO$, 320.0837; found, 320.0835.

*Phenanthridin-6-yl(phenyl)methanone (**4a**).* White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.70 (d, J = 8.4 Hz, 1H), 8.64 (dd, J = 5.2, 1.2 Hz, 1H), 8.21 (dd, J = 5.2, 1.2 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.04 (dd, J = 8.0, 0.9 Hz, 2H), 7.89−7.86 (m, 1H), 7.79−7.73 (m, 2H), 7.65 (td, J = 8.4, 1.2 Hz, 1H), 7.63−7.60 (m, 1H), 7.47 (t, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 194.8, 157.5, 142.6, 136.2, 133.9, 133.3, 131.2, 130.8, 130.6, 129.1, 128.5, 128.2, 127.8, 127.3, 124.4, 123.8, 122.3, 122.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{14}NO$, 284.1070; found, 284.1071.

*General Procedure for the Synthesis of **3a** from **1a** and **4a**.* Phenylglyoxylic acid (**1a**, 0.75 mmol), phenanthridin-6-yl(phenyl)-methanone (**4a**, 0.25 mmol), and pyridine (6.0 equiv) were added into an air-tight reaction tube (10 mL) with 2.0 mL of 1,1,2-trichloroethane. The tube containing the reactants and solvent was evacuated using a pump and back-filled with high-purified nitrogen (>99.99%). The reaction mixture was stirred at room temperature under irradiation with a 3 W LED (420 ± 5 nm) for 10 h. After the reaction, 1,1,2-trichloroethane was evaporated under reduced pressure. The resulting crude mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 7:1) to provide the desired product **3a** (38.5 mg) in 52% yield.

*General Procedure for the Reaction of **1a**, **2c**, and **4a**.* Phenylglyoxylic acid (**1a**, 0.75 mmol), 2-isocyano-4′-methoxy-1,1′-biphenyl (**2c**, 0.25 mmol), phenanthridin-6-yl(phenyl)methanone (**4a**, 0.25 mmol), and pyridine (6.0 equiv) were added into an air-tight reaction tube (10 mL) with 2.0 mL of 1,1,2-trichloroethane. The tube containing the reactants and solvent was evacuated using a pump and back-filled with high-purified nitrogen (>99.99%). The reaction mixture was stirred at room temperature under photoirradiation with a 3 W LED (420 ± 5 nm) for 10 h. After the reaction, volatile materials were evaporated under reduced pressure. The resulting crude mixture was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 9:1) to provide the hydrogenated product **3a** (30 mg) and **3x** (18 mg) in 42 and 23% yield, respectively, and produce **4b** in 12% yield (9.4 mg).

*(8-Methoxyphenanthridin-6-yl)(phenyl)methanone (**4b**).* White solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.61 (d, J = 9.0 Hz, 1H), 8.56−8.54 (m, 1H), 8.18−8.17 (m, 1H), 8.05 (d, J = 7.8 Hz, 2H), 7.74−7.70 (m, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.53−7.47 (m, 4H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 194.9, 159.0, 156.1, 141.8, 136.3, 133.9, 130.9, 130.6, 128.5, 128.3, 128.0, 127.8, 125.2, 124.7, 123.9, 122.5, 121.7, 106.6, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}NO_2$, 314.1176; found, 314.1175.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01916.

Characterization of EDA complexes, mechanism investigation, and copies of ^{1}H and ^{13}C NMR spectra of all new compounds (PDF)

Crystallographic data of 3a (CIF)

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