Photocatalytic Synthesis of 6 Phosphorylated Phenanthridines from 2 Isocyanobiphenyls via Radical C–P and C–C Bond Formation

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Article

Photocatalytic Synthesis of 6-Phosphorylated Phenanthridines from 2-Isocyanobiphenyls via Radical C–P and C–C Bond Formation

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Abstract: A mild, efficient, and photocatalytic synthesis of 6-phosphorylated phenanthridines via tandem radical addition/cyclization/aromatization of 2-isocyanobiphenyls with diarylphosphine oxides is reported. The method features operational simplicity, metal-free conditions, using low-cost rose Bengal as catalyst and sustainable air as terminal oxidant at room temperature, and providing the desired products in moderate to good yields.

Keywords: phenanthridine; 2-isocyanobiphenyls; diarylphosphine oxides; radical cyclization; metal-free

1. Introduction

Phenanthridine is a significant fused *N*-heterocycle, which is ubiquitous in many bioactive alkaloids, pharmaceuticals, natural products, and functional material molecules.[1-3] For example, Nitidine chloride (Figure 1) is an anti-cancer active natural product with phenanthridine motif that has been found to inhibit topoisomerase I and topoisomerase II.[4] NK109 (Figure 1) has been found to exhibit anti-tumor effects against a number of human cancer cell lines.[5] Fagaronine (Figure 1) is a antileukaemic and antimalarial active alkaloid.[6] In addition, trispheridine,[7] *N*-methylcrinasiadine,[8] and lycobetaine[9] are natural alkaloids with excellent bioactivities (Figure 1).

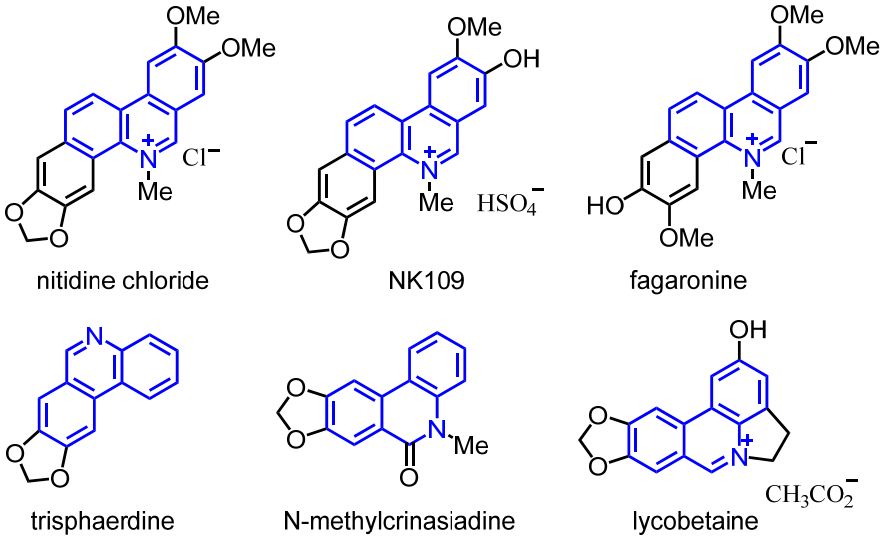

Figure 1. Representative bioactive phenanthridine derivatives.

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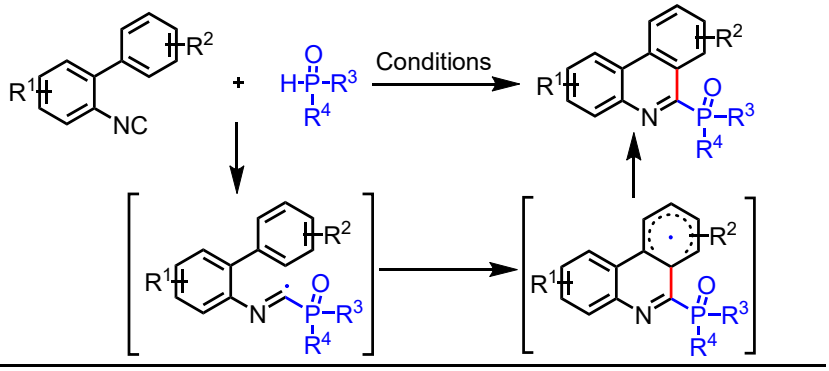
Extensive study and improvement on the synthesis of highly functionalized phenanthridine derivatives have been done due to their important biological activities. Great progress and developments have been made in the synthetic strategies of phenanthridine derivatives via C-H bond activation, radical addition cyclization, photochemical catalysis, isocyanide chemistry, etc.[10-12] The transformation proceeded in the absence or presence of various transition-metal catalysts, such as Pd, Mn, Cu, Ru, Ir, Rh, Fe, Ni and so on. The functionalization mainly focused on the 6-position of phenanthridine, including trifluoromethylation, difluoromethylation, arylation, alkylation, alkynylation, acylation, sulfonylation, phosphorylation, difluoromethylphosphonation, benzylation, trichooromethylation, thiolation, etc.

C-P bond construction has shown dramatic attention due to the potential applications of organophosphorous compounds in pharmaceutical chemistry and materials science.[13,14] In 2014, several methods for the synthesis of 6-phosphorylated phenanthridines initiated by Ag(I) or Mn(III) salts were reported via radical cascade cyclization [Scheme 1, eq(a-e)].[15-19] In 2016, Lakhdar and co-workers described the 6-phosphorylation of phenanthridines in the presence of diphenyliodonium salt and triethylamine under metal-free conditions [Scheme 1, eq(f)].[20] Subsequently, several photocatalytic methods were reported in the presence of photocatalyst $[Ir(ppy)_2(dtbpy)]PF_6$[21]/2D-COF-1[22]/4CzIPN-^{t}Bu[23] using $K_2S_2O_8$ or TBHP as oxidant [Scheme 1, eq(g-i)].

Recently, we have described the synthesis of 6-aroyl[24] and 6-benzylated[25] phenanthridines via iron-catalyzed cascade radical addition/cyclization of 2-biphenyl isocyanides. In 2019, we reported a visible-light-induced $Mn(acac)_3$-catalyzed method for the synthesis of 6-β-keto alkyl phenanthridines in the absence of extend oxidant.[26] In addition, we also described a Mn(III)-catalyzed radical process of 2-isocyanobiphenyls for the synthesis of 6-phosphorylated phenanthridines.[16] Herein, we report another alternative method for the preparation of 6-phosphorylated phenanthridines using low-cost Rose Bengal as catalyst and sustainable air as terminal oxidant under metal-free conditions at room temperature.



Conditions:

a) AgOAc (3.0 equiv), DMF, Ar, 100 °C (Studer et al);

b) $Mn(OAc)_3$ (3.0 equiv), toluene, N_2, 40 °C (Our previous work);

c) $Mn(OAc)_3 \cdot 2H_2O$ (3.0 equiv), NMP, N_2, 80 °C (Tang et al);

d) AgOAc (0.2 equiv), $PhI(OAc)_2$ (3.0 equiv), DMF, Ar, 100 °C (Wang, Ji et al);

e) $AgNO_3$ (2.0 equiv), MeCN, Ar, 60 °C (Yang et al);

f) Ph_2IOTf (1.3 equiv), Et_3N (2.0 equiv), CH_2Cl_2, 40 °C (Lakhdar et al);

g) Ir-PC, hv, $K_2S_2O_8$ (3.0 equiv), CsF (2.0 equiv), DMF, rt (Yan, Lu et al);

h) 2D-COF-1, $K_2S_2O_8$ (1.5 equiv), CsF (1.0 equiv), EA, N_2, 34 W Blue LED (Yu, Xu, Yang, et al);

i) 4CzIPN-^{t}Bu (5 mol%), TBHP (2.0 equiv), $NaHCO_3$ (2.0 equiv), MeCN, N_2, Blue LED (Chen, Yu et al);

j) Rose Bengal (5 mol%), DBU (3.0 equiv), $MeCN/H_2O$ (1.0/0.18,v/v), air, rt, 30 W Blue LED (Metal-free conditions, *this work*).

Scheme 1. Synthesis of 6-phosphorylated phenanthridines from 2-isocyanobiphenyls.

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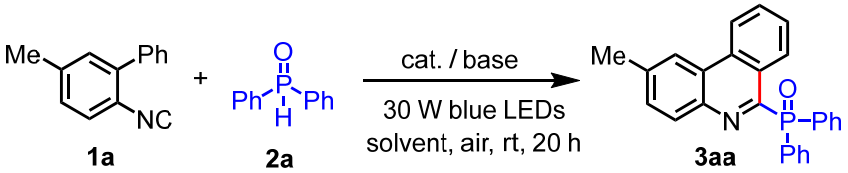
2. Results and Discussion

Initially, 2-isocyano-5-methyl-1,1'-biphenyl **1a** and diphenylphosphine oxide **2a** were chosen as model reaction substrates for optimization conditions. The desired product **3aa** was isolated in 15% yield using Rose Bengal (2 mol%) as catalyst and DBU as base in co-solvent MeCN/H_2O at room temperature under air atmosphere (Table 1, entry 1). Increasing the loading of catalyst to 5-10 mol% could improve the yields of **3aa** (Table 1, entries 2 and 3). An increase in the diphenylphosphine oxide **2a** amount from 1.5 equiv to 3.5-4.5 equiv, the results shown that the yields of target product **3aa** raised obviously (Table 1, entries 4 and 5). Then, we screened several organic photocatalysts, and the results shown that Eosin Y could promote the reaction smoothly and provide **3aa** in 61% yield, while only trace amount of desired product **3aa** was observed when Fluorescein and Rhodamine B were used as photocatalysts (Table 1, entries 6-8). In addition, a series of bases, involving Et_3N, DABCO, Na_2CO_3, and K_2CO_3 were surveyed, but no better yield was obtained (Table 1, entries 9-12). Then we attempted to change the amount of base, and the best result (84%) was obtained in the presence of 3.0 equiv of DBU (Table 1, entries 13-15). The examination of reaction medium shown that the effect of solvent is obvious. The reaction couldn't offer better yield in pure acetonitrile or other co-solvents, such as MeOH/H_2O, EtOH/H_2O, and THF/H_2O (Table 1, entries 16-19). The control experiment indicated that the irradiation of blue LED lights is important because no reaction was carried out in the dark (Table 1, entry 20).

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



Entry	**1a/2a**	Catalyst	Base	Solvent	Yield (%)[b]
1	1/1.5	Rose Bengal (2 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	15
2	1/1.5	Rose Bengal (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	36
3	1/1.5	Rose Bengal (10 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	32
4	1/3.5	Rose Bengal (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	78
5	1/4.5	Rose Bengal (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	77
6	1/3.5	Eosin Y (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	61
7	1/3.5	Fluorescein (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	trace
8	1/3.5	Rhodamine B (5 mol%)	DBU	MeCN/H_2O (1.0/0.18 mL)	trace
9	1/3.5	Rose Bengal (5 mol%)	NEt_3	MeCN/H_2O (1.0/0.18 mL)	69
10	1/3.5	Rose Bengal (5 mol%)	DABCO	MeCN/H_2O (1.0/0.18 mL)	trace
11	1/3.5	Rose Bengal (5 mol%)	Na_2CO_3	MeCN/H_2O (1.0/0.18 mL)	trace
12	1/3.5	Rose Bengal (5 mol%)	K_2CO_3	MeCN/H_2O (1.0/0.18 mL)	trace
13	1/3.5	Rose Bengal (5 mol%)	DBU[c]	MeCN/H_2O (1.0/0.18 mL)	38
14	**1/3.5**	**Rose Bengal (5 mol%)**	**DBU[d]**	**MeCN/H_2O (1.0/0.18 mL)**	**84**
15	1/3.5	Rose Bengal (5 mol%)	DBU[e]	MeCN/H_2O (1.0/0.18 mL)	80
16	1/3.5	Rose Bengal (5 mol%)	DBU[d]	MeCN	50
17	1/3.5	Rose Bengal (5 mol%)	DBU[d]	EtOH/H_2O (1.0/0.18 mL)	43
18	1/3.5	Rose Bengal (5 mol%)	DBU[d]	MeOH/H_2O (1.0/0.18 mL)	56
19	1/3.5	Rose Bengal (5 mol%)	DBU[d]	THF/H_2O (1.0/0.18 mL)	61
20[f]	1/3.5	Rose Bengal (5 mol%)	DBU	THF/H_2O (1.0/0.18 mL)	NR

[a] Reaction conditions: **1a** (0.2 mmol), base (2.0 equiv) and reaction were irradiated by 30 W blue LEDs at room temperature, stirring for 20 h under air atmosphere. [b] Isolated yields of **3aa**. [c] DBU (1.0 equiv). [d] DBU (3.0 equiv). [e] DBU (4.0 equiv). [f] The reaction was carried out in the dark.

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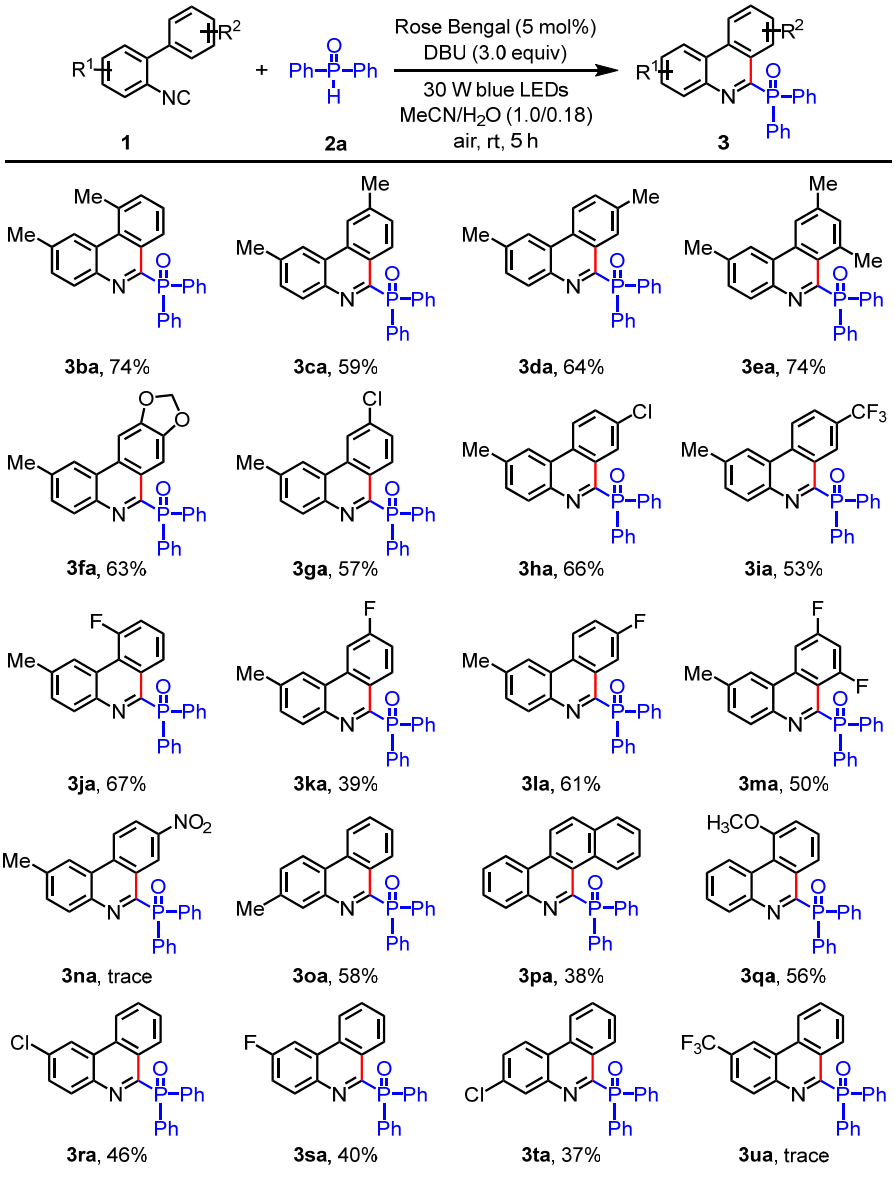
We next examined the generality and the substrate scope of 2-isocyanobiphenyls under the optimized reaction conditions (Scheme 2). Initially, the electronic effect of substituents R^2 was investigated. The reaction could tolerate both electron-donating groups and electron-withdrawing groups, such as methyl, methoxy, halogen (F, Cl), and trifluoromethyl on the *ortho-*, *meta-*, or *para-*position of the phenyl ring, providing the corresponding products in moderate to good yields. For instance, *ortho-* or *meta*-methyl substituted substrates **1b** and **1c** gave the target products **3ba** and **3ca** in 74% and 59% yields, respectively. *Para*-trifluoromethyl substituted substrate **1i** provided the product **3ia** in 53% yield under standard conditions. Unfortunately, when substrate **1n** bearing nitro group was used, only trace amount of desired product was observed under the same conditions. Then, 2-(2-isocyanophenyl)naphthalene was applied to the reaction with **2a**, the product **3pa** was obtained in low yield (38%). The electronic effect of substituent R^1 was significant, and the substrates with electron-withdrawing groups halogen (F, Cl) provided the corresponding products in **3ra-3ta** moderate yields 37-46%. The reaction didn't work when substate **1u** bears a strong electron-withdrawing group (-CF_3).



Scheme 2. Substrate scope of 2-isocyanobiphenyls.

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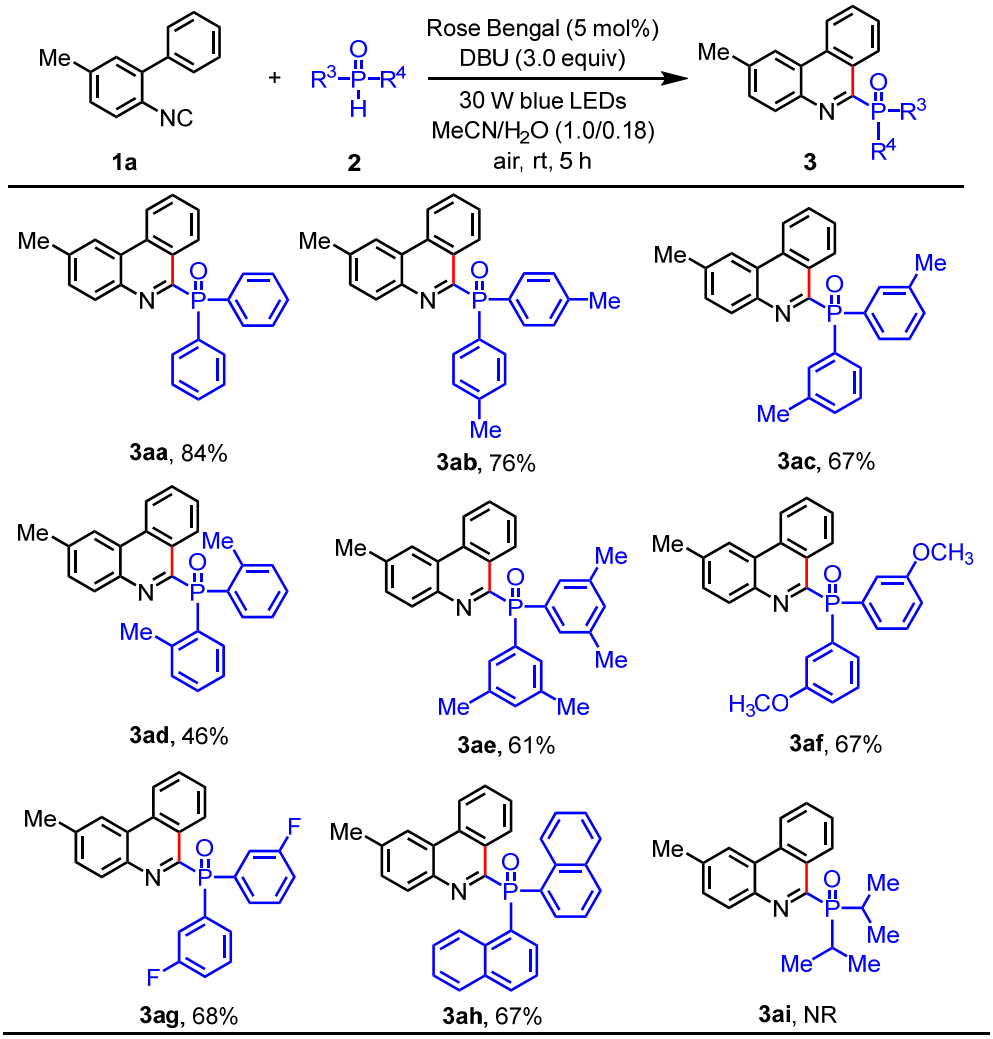
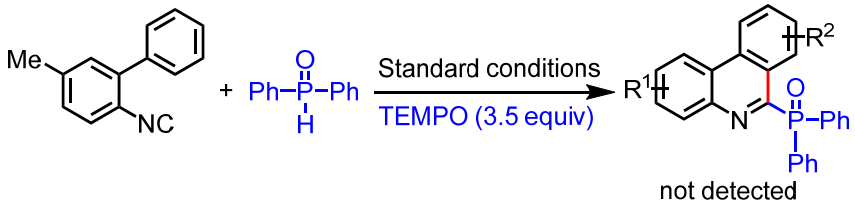
In addition, the substrate scope of diphenylphosphine oxides **2** was also examined under the optimal conditions (Scheme 3). The results shown that the electronic effect wasn't obviously, diaryl substituted phosphine oxides **2** with both electron-donating groups and electron-withdrawing groups were proceeded smoothly, providing the corresponding phosphorylation phenanthridines in good yields. Product **3ad** was isolated only in moderate yield (46%) due to the steric effect. However, no target product was observed in the case of diisopropyl phosphine oxide **2i**.



Scheme 3. Substrate scope of diphenylphosphine oxides.

A control experiment was executed to investigate the possible reaction mechanism (Scheme 4). The reaction was totally inhibited in the presence of radical scavenger of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 3.5 equiv) under standard reaction conditions. The results indicated that the transformation probably undergo cascade radical addition/cyclization processes.



Scheme 4. Control experiment in the presence of TEMPO.

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3. Materials and Methods

3.1. General Information

Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II instrument.

3.2. General Procedure for the photocatalytic synthesis of 6-phosphorylated phenanthridines from 2-isocyanobiphenyls

To a 25 mL quartz test tube containing a magnetic stir bar, was added 2-biphenyl isocyanides **1** (0.2 mmol), Rose Bengal (0.01 mmol, 5 mol%), DBU (3.0 equiv) under air, added diphenylphosphine oxides **2** (0.6 mmol, 3.0 equiv) and MeCN/H_2O (1.0/0.18 mL). The resulting mixture was stirred at room temperature under 30 W blue LEDs irradiation for 5 h. After completion, monitored by TLC, evaporation of the solvent under reduced pressure followed purification by silica gel chromatography using ethyl acetate – petroleum ether (1:3) as eluent to provide the desired products **3**.

3.3. Characterization Data for Products 3

*(2-Methylphenanthridin-6-yl)diphenylphosphine oxide (**3aa**):* Isolated (R_f = 0.6, EtOAc – petroleum ether = 1:3) as a white solid (66.1 mg, 84% yield), mp: 222 – 223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, *J* = 8.4 Hz, 1H), 8.57 (d, *J* = 8.4 Hz, 1H), 8.31 (s, 1H), 8.05 – 7.84 (m, 5H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.37 (m, 7H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6 (d, J_{C-P} = 128.7 Hz), 141.3 (d, J_{C-P} = 23.3 Hz), 139.1, 133.1 (d, J_{C-P} = 104.0 Hz), 132.4, 132.3 (d, J_{C-P} = 9.1 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 130.9, 130.8, 130.5, 128.5, 128.2 (d, J_{C-P} = 12.1 Hz), 127.9, 127.7, 124.2 (d, J_{C-P} = 2.4 Hz), 122.1, 121.7, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{26}H_{21}NOP$: 394.1355, found: 394.1358.

*(2-Methylphenanthridin-6-yl)di-p-tolylphosphine oxide (**3ab**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (64.1 mg, 76% yield), mp: 249 – 251 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.37 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.87 – 7.73 (m, 5H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.52 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.26 – 7.21 (m, 4H), 2.63 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (d, J_{C-P} = 128.4 Hz), 141.9 (d, J_{C-P} = 2.7 Hz), 141.2 (d, J_{C-P} = 23.4 Hz), 138.9, 132.3 (d, J_{C-P} = 9.5 Hz), 130.9, 130.4, 130.0 (d, J_{C-P} = 106.4 Hz), 128.9 (d, J_{C-P} = 12.5 Hz), 128.6, 127.9 (d, J_{C-P} = 23.0 Hz), 127.7, 124.2, 122.0, 121.6, 22.2, 21.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{25}NOP$: 422.1668, found: 422.1670.

*(2-Methylphenanthridin-6-yl)di-m-tolylphosphine oxide (**3ac**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (56.5 mg, 67% yield), mp: 237 – 239 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 8.4 Hz, 1H), 8.50 (d, *J* = 8.4 Hz, 1H), 8.24 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.64 (m, 3H), 7.62 – 7.51 (m, 3H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.23 – 7.17 (m, 4H), 2.50 (s, 3H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (d, J_{C-P} = 128.1 Hz), 141.3 (d, J_{C-P} = 23.2 Hz), 139.0, 138.0 (d, J_{C-P} = 11.9 Hz), 133.0 (d, J_{C-P} = 104.4 Hz), 132.6 (d, J_{C-P} = 8.9 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 132.3 (d, J_{C-P} = 6.8 Hz), 130.9, 130.7, 130.4, 129.5 (d, J_{C-P} = 9.3 Hz), 128.6, 128.1, 128.0 (d, J_{C-P} = 12.8 Hz), 127.7, 124.2 (d, J_{C-P} = 2.4 Hz), 122.1, 121.7, 22.2, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{25}NOP$: 422.1668, found: 422.1671.

*(2-Methylphenanthridin-6-yl)di-o-tolylphosphine oxide (**3ad**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (38.8 mg, 46% yield), mp: 228 – 230 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 8.4 Hz, 1H), 8.58 (d, *J* = 8.4 Hz, 1H), 8.31 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.24 – 7.18 (m, 2H), 7.07 (t, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1 (d, J_{C-P} = 128.3 Hz), 143.4 (d, J_{C-P} = 7.8 Hz), 141.3 (d, J_{C-P} = 23.5 Hz), 139.1, 133.1 (d, J_{C-P} = 11.9 Hz), 132.4 (d, J_{C-P} = 6.5 Hz), 131.8 (d, J_{C-P} = 2.5 Hz), 131.6, 131.5, 131.1,

 doi:10.20944/preprints202305.1063.v1

130.7, 130.5, 130.4, 128.8, 127.7, 127.6 (d, J_{C-P} = 23.0 Hz), 125.3 (d, J_{C-P} = 12.8 Hz), 124.3, 122.2, 121.6, 22.2, 22.0, 22.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.2. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{25}NOP$: 422.1668, found: 422.1673.

*Bis(3,5-dimethylphenyl)(2-methylphenanthridin-6-yl)phosphine oxide (**3ae**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a white solid (54.8 mg, 61% yield). mp: 265 – 268 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.36 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.80 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.55-7.50 (m, 5H), 7.12 (s, 2H), 2.62 (s, 3H), 2.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0 (d, J_{C-P} = 127.6 Hz), 141.2 (d, J_{C-P} = 23.2 Hz), 138.9, 137.7 (d, J_{C-P} = 12.6 Hz), 133.4 (d, J_{C-P} = 2.8 Hz), 132.9 (d, J_{C-P} = 104.5 Hz), 132.3 (d, J_{C-P} = 6.8 Hz), 131.0, 130.5 (d, J_{C-P} = 30.6 Hz), 129.9 (d, J_{C-P} = 9.2 Hz), 128.2 (d, J_{C-P} = 100.6 Hz), 128.0 (d, J_{C-P} = 23.0 Hz), 124.2 (d, J_{C-P} = 2.4 Hz), 122.0, 121.6, 22.2, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{30}H_{29}NOP$: 450.1981, found: 450.1986.

*Bis(3-methoxyphenyl)(2-methylphenanthridin-6-yl)phosphine oxide (**3af**):* Isolated (R_f = 0.6, EtOAc – petroleum ether = 1:3) as a yellow solid (60.7 mg, 67% yield), mp: 241 – 243 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (d, *J* = 8.0 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.25 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.49 – 7.40 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.18 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 3.68 (s, 6H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, J_{C-P} = 15.0 Hz), 155.4 (d, J_{C-P} = 129.3 Hz), 141.2 (d, J_{C-P} = 23.5 Hz), 139.1, 134.2 (d, J_{C-P} = 103.4 Hz), 132.3 (d, J_{C-P} = 6.8 Hz), 130.9, 130.8, 130.5, 129.3 (d, J_{C-P} = 14.3 Hz), 128.4, 127.9 (d, J_{C-P} = 23.5 Hz), 127.7, 124.7 (d, J_{C-P} = 9.2 Hz), 124.3, 122.1, 121.7, 118.0 (d, J_{C-P} = 2.5 Hz), 117.0 (d, J_{C-P} = 10.1 Hz), 55.4, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.2. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{28}H_{25}NO_3P$: 454.1567, found: 454.1568.

*Bis(3-fluorophenyl)(2-methylphenanthridin-6-yl)phosphine oxide (**3ag**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a yellow solid (58.4 mg, 68% yield), mp: 257 – 259 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 8.4 Hz, 1H), 8.67 (d, *J* = 8.4 Hz, 1H), 8.40 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.77 – 7.62 (m, 5H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.22 (td, *J* = 8.4, 2.0 Hz, 2H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (dd, J_{C-F} = 247.9, J_{C-P} = 17.0 Hz Hz), 160.0, 153.4 (d, J_{C-P} = 131.6 Hz), 140.1 (d, J_{C-F} = 23.9 Hz), 138.5, 134.4 (dd, J_{C-P} = 103.5, J_{C-F} = 5.6 Hz Hz), 131.4 (d, J_{C-P} = 7.1 Hz), 130.0, 129.8, 129.7, 129.2 (d, J_{C-F} = 7.3 Hz), 129.1 (d, J_{C-F} = 7.3 Hz), 128.3, 128.1, 127.1, 127.0 (d, J_{C-P} = 3.0 Hz), 126.9, 126.8, 123.3, 121.2, 120.7, 118.3 (d, J_{C-F} = 9.9 Hz), 118.1, 118.0 (d, J_{C-F} = 9.1 Hz), 117. 9 (d, J_{C-P} = 2.6 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.9. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{26}H_{19}F_2NOP$: 430.1167, found: 430.1169.

*(2-Methylphenanthridin-6-yl)di(naphthalen-1-yl)phosphine oxide (**3ah**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a yellow solid (66.1 mg, 67% yield), mp: 293 – 296°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (dd, *J* = 8.2, 2.0 Hz, 1H), 8.49-8.44 (m, 3H), 8.20 (s, 1H), 7.88 – 7.79 (m, 3H), 7.75-7.72 (m, 4H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.31 (m, 5H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 (d, J_{C-P} = 129.5 Hz), 141.3 (d, J_{C-P} = 23.4 Hz), 139.2, 134.7 (d, J_{C-P} = 2.3 Hz), 134.0 (d, J_{C-P} = 8.9 Hz), 132.5 (d, J_{C-P} = 7.3 Hz), 132.4 (d, J_{C-P} = 6.9 Hz), 130.9, 130.8, 130.5, 130.4 (d, J_{C-P} = 103.8 Hz), 129.1, 128.5, 128.1, 127.9, 127.8 (2C), 127.7, 127.6, 126.7, 124.3, 122.2, 121.7, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{34}H_{25}NOP$: 494.1668, found: 494.1672.

*(2,10-Dimethylphenanthridin-6-yl)diphenylphosphine oxide (**3ba**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a white solid (60.3 mg, 74% yield), mp: 222 – 225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 8.0 Hz, 1H), 8.52 (s, 1H), 7.89 – 7.73 (m, 5H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.37-7.30 (m, 4H), 3.01 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156. 1 (d, J_{C-P} = 129.0 Hz), 142.3 (d, J_{C-P} = 23.8 Hz), 138.0, 135.3, 135.0, 133.2 (d, J_{C-P} = 104.3 Hz), 132.3 (d, J_{C-P} = 9.1 Hz), 131.9 (d, J_{C-P} = 6.7 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 131.2, 129.5, 129.3 (d, J_{C-P} = 23.4 Hz), 128.1 (d, J_{C-P} = 12.1 Hz), 127.2, 127.0, 126.4, 125.7 (d, J_{C-P}= 2.4 Hz), 27.1, 22.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4. HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{27}H_{23}NOP$: 408.1512, found: 408.1515.

*(2,8-Dimethylphenanthridin-6-yl)diphenylphosphine oxide (**3da**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a white solid (48.1 mg, 64% yield), mp: 231 – 233 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.29 (s, 1H), 7.97 – 7.87 (m, 5H), 7.61 (dd, *J* = 8.4, 1.2

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Hz, 1H), 7.53 – 7.36 (m, 7H), 2.58 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0 (d, J_{C-P} = 129.0 Hz), 140.9 (d, J_{C-P} = 23.4 Hz), 139.0, 137.9, 133.6 (d, J_{C-P} = 104.0 Hz), 132.7, 132.4 (d, J_{C-P} = 9.1 Hz), 131.5 (d, J_{C-P} = 2.6 Hz), 130.8, 130.2 (d, J_{C-P} = 6.9 Hz), 130.0, 128.4, 128.1 (d, J_{C-P} = 12.0 Hz), 127.6, 124.3 (d, J_{C-P} = 2.5 Hz), 122.0, 121.5, 22.2, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{27}H_{23}NOP$: 408.1512, found: 408.1516.

*Diphenyl(2,7,9-trimethylphenanthridin-6-yl)phosphine oxide (**3ea**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a white solid (62.3 mg, 74% yield), mp: 255 – 257 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.72 – 7.65 (m, 4H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.40-7.35 (m, 2H), 7.34 – 7.27 (m, 5H), 7.17 (s, 1H), 2.84 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4 (d, J_{C-P} = 129.9 Hz), 140.5, 139.8 (d, J_{C-P} = 24.1 Hz), 138.9, 137.4, 135.1 (d, J_{C-P} = 106.9 Hz), 134.2 (d, J_{C-P} = 6.7 Hz), 133.3, 132.0 (d, J_{C-P} = 8.9 Hz), 131.1 (d, J_{C-P} = 2.5 Hz), 130.3, 130.2, 128.0 (d, J_{C-P} = 12.1 Hz), 125.7 (d, J_{C-P} = 23.7 Hz), 124.1 (d, J_{C-P} = 2.6 Hz), 121.8, 120.0, 25.0, 22.2, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.2. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{28}H_{25}NOP$: 422.1668, found: 422.1672.

*(2-Methyl-[1,3]dioxolo[4,5-j]phenanthridin-6-yl)diphenylphosphine oxide (**3fa**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:1) as a white solid (53.3 mg, 63% yield), mp: 262 – 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.11 (s, 1H), 7.98 – 7.84 (m, 6H), 7.54 – 7.38 (m, 7H), 6.08 (s, 2H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4 (d, J_{C-P} = 131.3 Hz), 151.1, 148.2, 141.0 (d, J_{C-P} = 23.2 Hz), 138.5, 133.8, 132.2 (d, J_{C-P} = 103.9 Hz), 132.3 (d, J_{C-P} = 9.1 Hz), 131.6, 130.7 130.5 (d, J_{C-P} = 7.4 Hz), 129.9, 128.1 (d, J_{C-P} = 12.0 Hz), 125.2 (d, J_{C-P} = 23.4 Hz), 124.4, 121.4, 105.6, 102.0, 99.8, 22.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{27}H_{21}NO_3P$: 4038.1254, found: 438.1257.

*(9-Chloro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3ga**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (48.8 mg, 57% yield), mp: 211 – 214 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 8.8 Hz, 1H), 8.57 (s, 1H), 8.27 (s, 1H), 7.97 – 7.86 (m, 5H), 7.60 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.47-7.41 (m, 4H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (d, J_{C-P} = 130.1 Hz), 141.5 (d, J_{C-P} = 22.9 Hz), 139.5, 137.4, 133.8 (d, J_{C-P} = 6.7 Hz), 132.8 (d, J_{C-P} = 104.4 Hz), 132.3 (d, J_{C-P} = 9.2 Hz), 131.8, 131.2, 130.9, 130.2, 128.4, 128.2 (d, J_{C-P} = 12.0 Hz), 126.3 (d, J_{C-P} = 23.4 Hz), 123.2, 121.7 (d, J_{C-P} = 12.1 Hz), 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{20}ClNOP$: 428.0966, found: 428.0972.

*(8-Chloro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3ha**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a white solid (56.5 mg, 66% yield), mp: 229 – 231 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 2.0 Hz, 1H), 8.46 (dd, *J* = 8.8, 1.2 Hz, 1H), 8.23 (s, 1H), 8.06 – 7.90 (m, 5H), 7.69 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.46 – 7.39 (m, 4H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154. 5 (d, J_{C-P} = 128.6 Hz), 141.1 (d, J_{C-P} = 22.7 Hz), 139.7, 133.8, 132.9 (d, J_{C-P} = 104.6 Hz), 132. 3 (d, J_{C-P} = 9.1 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.5, 130.9, 130.8, 130.7 (d, J_{C-P} = 6.8 Hz), 128.8 (d, J_{C-P} = 23.1Hz), 128.2 (d, J_{C-P} = 12.1 Hz), 127.5, 123.7, 123.6 (d, J_{C-P} = 2.4 Hz), 121.5, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.2. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{20}ClNOP$: 428.0966, found: 428.0969.

*(2-Methyl-8-(trifluoromethyl)phenanthridin-6-yl)diphenylphosphine oxide (**3ia**):* Isolated (R_f = 0.6, EtOAc – petroleum ether = 1:3) as a yellow solid (48.9 mg, 53% yield), mp: 199 – 201 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.70 (d, *J* = 8.8 Hz, 1H), 8.35 (s, 1H), 8.05 – 7.95 (m, 6H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.47 – 7.41 (m, 4H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8 (d, J_{C-P} = 127.7 Hz), 141.8 (d, J_{C-P} = 12.5 Hz), 139.9, 134.4 (d, J_{C-P} = 6.2 Hz), 132.8 (d, J_{C-P} = 105.4 Hz), 132.3 (d, J_{C-P} = 9.1 Hz), 131.8 (d, J_{C-P} = 2.6 Hz), 131.7, 131.0, 129.4 (q, J_{C-F} = 32.6 Hz), 128.3 (d, J_{C-P} = 12.1 Hz), 127.3 (d, J_{C-P} = 22.9 Hz), 126.6 (q, $^1J_{C-F}$ = 3.1 Hz), 126.2 (d, J_{C-P} = 4.3 Hz), 123.9 (q, J_{C-F} = 270.8 Hz), 123.2 (d, J_{C-P} = 2.2 Hz), 123.1, 122.0, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.8. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{27}H_{20}F_3NOP$: 462.1229, found: 462.1232.

*(10-Fluoro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3ja**):* Isolated (R_f = 0.3, EtOAc – petroleum ether = 1:3) as a white solid (55.1 mg, 67% yield), mp: 192 – 194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, *J* = 8.2 Hz, 1H), 8.78 (s, 1H), 7.96 – 7.86 (m, 5H), 7.65 – 7.58 (m, 1H), 7.57 – 7.48 (m, 4H), 7.47 – 7.42 (m, 4H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, $^1J_{C-F}$ = 253.5 Hz), 155.0 (d, J_{C-P} = 129.1 Hz), 141.5 (d, J_{C-P} = 23.0 Hz), 139.8, 132.8 (d, J_{C-P} = 104.8 Hz), 132.3 (d, J_{C-P} = 9.1 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 130.7 (d, J_{C-F} = 17.7 Hz), 129. 9 (d, J_{C-F} = 24.3), 128.2 (d, J_{C-P} = 12.1 Hz), 128.1 (d, J_{C-P} = 8.9

Hz), 126.6 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 124.6 (d, $J_{C\text{-}P}$ = 4.0 Hz), 121.8 (m), 117.3 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 22.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.6. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{20}FNOP$: 412.1261, found: 412.1267.

*(9-Fluoro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3ka**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (32.1 mg, 39% yield), mp: 205 – 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (dd, *J* = 9.2, 6.0 Hz, 1H), 8.23 (s, 1H), 8.21 (d, *J* = 9.2 Hz, 1H), 7.98 – 7.89 (m, 5H), 7.57 – 7.49 (m, 3H), 7.47 – 7.36 (m, 5H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, $^{1}J_{C\text{-}F}$ = 251.6 Hz), 155.1 (d, $^{2}J_{C\text{-}P}$ = 128.9 Hz), 141.3 (d, $^{2}J_{C\text{-}F}$ = 23.2 Hz), 139.2, 135.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 134.9 (d, $J_{C\text{-}P}$ = 9.3 Hz), 132.9 (d, $J_{C\text{-}P}$ = 104.4 Hz), 132.4, 132.3, 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.6, 131.2, 130.9, 128.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 125.1 (d, $^{2}J_{C\text{-}P}$ = 24.3 Hz), 123.8, 121.8, 116.9 (d, $J_{C\text{-}F}$ = 23.3 Hz), 107.2 (d, $J_{C\text{-}F}$ = 22.2 Hz), 22.1.^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{20}FNOP$: 412.1261, found: 412.1265.

*(8-Fluoro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3la**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:3) as a yellow solid (50.2 mg, 61% yield), mp: 216 – 219 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (dd, *J* = 10.2, 2.6 Hz, 1H), 8.61 – 8.54 (m, 1H), 8.27 (s, 1H), 7.98 – 7.90 (m, 5H), 7.56 – 7.47 (m, 4H), 7.46 – 7.40 (m, 4H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, $^{1}J_{C\text{-}F}$ = 247.4 Hz), 154.6 (d, $J_{C\text{-}P}$ = 129.2 Hz), 140.9 (d, $^{2}J_{C\text{-}F}$ = 23.5 Hz), 132.8 (d, $J_{C\text{-}P}$ = 104.3 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.9, 130.4, 129.3 (d, $^{3}J_{C\text{-}F}$ = 9.3 Hz), 129.0 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 124.6 (d, $J_{C\text{-}P}$ = 8.5 Hz), 123.9, 121.4 120.3 (d, $J_{C\text{-}F}$ = 24.2 Hz), 113.1 (d, $^{2}J_{C\text{-}F}$ = 23.1 Hz), 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.4. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{20}FNOP$: 412.1261, found: 412.1263.

*(7,9-Difluoro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (**3ma**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:1) as a white solid (42.9 mg, 50% yield), mp: 245 – 247 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.08 (d, *J* = 9.6 Hz, 1H), 7.80 – 7.70 (m, 5H), 7.56-7.51 (m, 3H), 7.48 – 7.43 (m, 4H), 7.04 (t, *J* = 9.6 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $^{1}J_{C\text{-}F}$ = 252.5 Hz), 160.2 (d, $^{1}J_{C\text{-}F}$ = 246.6 Hz), 141.2, 140.1, 136.1, 133.1 (d, $J_{C\text{-}P}$ = 109.2 Hz), 131.9, 131.8, 131.4, 131.3, 130.9, 128.8, 128.0 (d, $J_{C\text{-}P}$ = 12.2 Hz), 122.5, 121.9, 104.3 (d, $J_{C\text{-}F}$ = 27.2 Hz), 103.9, 22.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.8 (d, *J* = 4.1 Hz). HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{19}F_2NOP$: 430.1167, found: 430.1171.

*(3-Methylphenanthridin-6-yl)diphenylphosphine oxide (**3oa**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (45.6 mg, 58% yield), mp: 197 – 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.4 Hz, 1H), 8.32 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.88-7.80 (m, 4H), 7.72 (s, 1H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.37 (m, 3H), 7.36 – 7.30 (m, 4H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, $J_{C\text{-}P}$ = 128.2 Hz), 142.9 (d, $J_{C\text{-}P}$ = 23.1 Hz), 139.0, 133.1 (d, $J_{C\text{-}P}$ = 104.1 Hz), 132.7 (d, $J_{C\text{-}P}$ = 6.9 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.9, 130.6, 130.5, 128.5, 128.2 (d, $J_{C\text{-}P}$ = 12.1 Hz), 127.5 (d, $J_{C\text{-}P}$ = 12.6 Hz), 127.4, 122.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 121.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{21}NOP$: 394.1355, found: 394.1358.

*Benzo[i]phenanthridin-5-yldiphenylphosphine oxide (**3pa**):* Isolated (R_f = 0.5, EtOAc – petroleum ether = 1:1) as a white solid (32.6 mg, 38% yield), mp: 221 – 223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (d, *J* = 8.8 Hz, 1H), 9.09-9.06 (m, 1H), 9.05 – 9.00 (m, 1H), 8.16 – 8.12 (m, 1H), 8.04-8.00 (m, 1H), 7.98 – 7.90 (m, 5H), 7.77– 7.66 (m, 4H), 7.54 – 7.40 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (d, $J_{C\text{-}P}$ = 128.2 Hz), 144.8 (d, $J_{C\text{-}P}$ = 23.3 Hz), 133.1 (d, $J_{C\text{-}P}$ = 104.6 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.9 (d, $J_{C\text{-}P}$ = 6.8 Hz), 131.7, 131.6, 130.9, 128.9, 128.8, 128.7, 128.5, 128.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.1, 127.4 (d, $J_{C\text{-}P}$ = 22.6 Hz), 127.2, 126.7, 124.6, 124.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.1. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{29}H_{21}NOP$: 430.1355, found: 430.1359.

*(10-Methoxyphenanthridin-6-yl)diphenylphosphine oxide (**3qa**):* Isolated (R_f = 0.3, EtOAc – petroleum ether = 1:1) as a white solid (45.9 mg, 56% yield), mp: 244 – 246 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 – 9.45 (m, 1H), 9.14 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.98 (m, 1H), 7.93-7.86 (m, 4H), 7.72 – 7.64 (m, 2H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.46-7.40 (m, 4H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 156.4 (d, $J_{C\text{-}P}$ = 129.1 Hz), 143.3 (d, $J_{C\text{-}P}$ = 23.2 Hz), 133.1 (d, $J_{C\text{-}P}$ = 104.5 Hz), 132.3 (d, $J_{C\text{-}P}$ = 104.5 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.4 Hz), 130.9, 129.7 (d, $J_{C\text{-}P}$ = 23.8 Hz), 128.7, 128.2, 128.1 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 124.2, 123.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 120.8, 112.1, 55.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.2. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{26}H_{21}NO_2P$: 410.1304, found: 410.1309.

*(2-Chlorophenanthridin-6-yl)diphenylphosphine oxide (**3ra**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (38.1 mg, 46% yield), mp: 241 – 243 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.47 (s), 7.89 (d, *J* = 8.8 Hz, 1H), 7.86 – 7.80 (m, 4H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.56 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.47-7.42 (m, 2H), 7.40-7.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3 (d, J_{C-P} = 128.2 Hz), 140.1 (d, J_{C-P} = 23.4 Hz), 138.2, 133.9, 131.6 (d, J_{C-P} = 104.7 Hz), 131.5, 131.3, 131.2, 130.8 (d, J_{C-P} = 2.6 Hz), 130.3, 128.3, 127.7, 127.5, 127.2 (d, J_{C-P} = 12.2 Hz), 124.4, 121.1, 120.7, 113.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{18}ClNOP$: 414.0809, found: 414.0813.

*(2-Fluorophenanthridin-6-yl)diphenylphosphine oxide (**3sa**):* Isolated (R_f = 0.3, EtOAc – petroleum ether = 1:3) as a yellow solid (31.8 mg, 40% yield), mp: 235 – 237 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 8.4 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.13 – 8.09 (m, 1H), 7.99 – 7.93 (m, 1H), 7.86 – 7.76 (m, 5H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.33 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J_{C-F} = 248.9 Hz), 155.1 (d, J_{C-P} = 131.7 Hz), 138.6 (d, J_{C-P} = 23.1 Hz), 132.5 (d, J_{C-P} = 9.3 Hz), 131.7 (d, J_{C-P} = 104.3 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.7, 130.1, 127.6 (d, J_{C-F} = 16.3 Hz), 127.2 (d, J_{C-P} = 12.1 Hz), 126.6, 124.9, 121.3, 116.8 (d, J_{C-F} = 24.5 Hz), 106.1 (d, J_{C-F} = 23.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{18}FNOP$: 398.1105, found: 398.1112.

*(3-Chlorophenanthridin-6-yl)diphenylphosphine oxide (**3ta**):* Isolated (R_f = 0.4, EtOAc – petroleum ether = 1:3) as a white solid (30.6 mg, 37% yield), mp: 194 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 1.6 Hz, 1H), 7.87-7.80 (m, 4H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.47 – 7.41 (m, 2H), 7.41 – 7.32 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5 (d, J_{C-P} = 125.7 Hz), 143.2 (d, J_{C-P} = 23.4 Hz), 134.5, 132.6 (d, J_{C-P} = 104.5 Hz), 132.2 (d, J_{C-P} = 9.1 Hz), 131.9, 131.5, 130.1, 129.3, 128.8, 128.3 (d, J_{C-P} = 12.3 Hz), 127.8 (d, J_{C-P} = 22.7 Hz), 123.6, 122.9 (d, J_{C-P} = 2.4 Hz), 122.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3. HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{25}H_{18}ClNOP$: 414.0809, found: 414.0816.

4. Conclusions

Rose Bengal was found to be an available photocatalyst for the cascade phosphorylation cyclization of 2-isocyanobiphenyls. A wide range of 6-phosphorylated phenanthridines have been synthesized efficiently via visible-light-induced radical addition cyclization under metal-free conditions. Biological screening of these P-containing compounds is in progress in our laboratory.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org. The experimental procedures and characterization (^{1}H- and ^{13}C-NMR and ^{31}P-NMR) for all of the products are provided in the supporting information.

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