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Synthesis of 6-Phosphorylated Phenanthridines by Mn(II)-Promoted Tandem Reactions of 2-Biaryl Isothiocyanates with Phosphine Oxides

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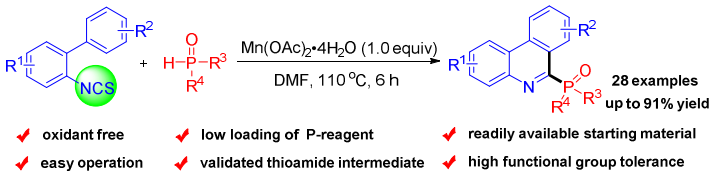
A novel Mn(II)-promoted tandem phosphorylation/cyclization reaction of 2-biaryl isothiocyanates with phosphine oxides was described. This is the first general method to synthesize 6-phosporylated phenanthridines from 2-biaryl isothiocyanates. The approach is featured by oxidant-free, low loading of P-reagent, easy operation, and high functional group tolerance.

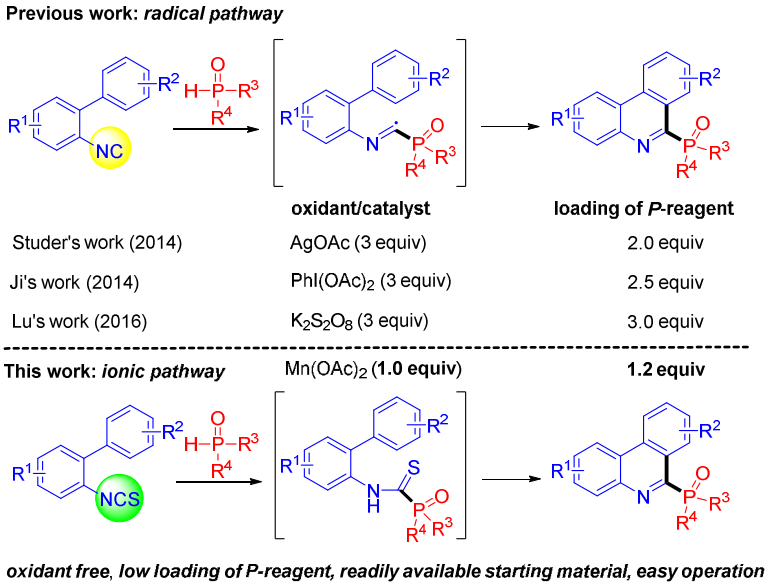
TOC Graphic



Organic phosphorus compounds are broadly applied in organic synthesis,[1] medicinal chemistry,[2] materials science,[3] and as phosphorus ligands.[4] Many P-substituted heterocycles show excellent biologic activities.[5] Therefore, the development of new and efficient methods to synthesize heterocycles containing P-substituents are always highly desirable.[6] Among them, the phenanthridine nucleus is a representative scaffold.[7] The established synthetic methods for 6-phosphorylated

phenanthridines involve 2-isocyanobiaryls-initiated radical cascade reactions (Scheme 1).[8,9] In 2014, Studer reported a pioneering work using 3 equiv of AgOAc as the oxidant and 2 equiv of P-reagent.[9a] In the same year, Ji described a similar radical process with excess of $PhI(OAc)_2$ as the oxidant (3 equiv).[9b] Very recently, Lu reported an efficient photoredox-mediated reaction,[9c] however, this method also required 3 equiv of $K_2S_2O_8$ as the oxidant and 3 equiv of P-reagent as the starting materials. Despite the robustness of these methods, all of them are using excess amount of oxidants and P-reagents. Therefore, from a sustainable perspective, developing a more environmentally friendly and convenient procedure for the synthesis of 6-phosphorylated phenanthridines has remained a great challenge.

Scheme 1. Synthetic Strategies toward 6-Phosporylated Phenanthridine Derivatives



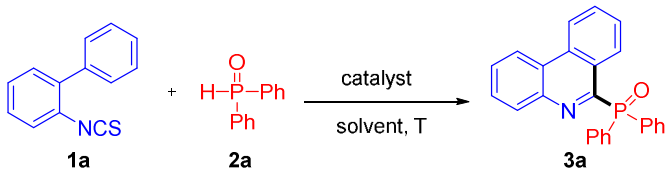
Isothiocyanates are easily-prepared synthetic intermediates with versatile chemical reactivity,[10] they could be used as electrophiles,[11] nucleophiles,[12] and radical receptors.[13] Recently, we have developed a tandem arylation/cyclization process for

the synthesis of 6-arylthio phenanthridines from 2-biaryl isothiocyanates.[14] As part of our ongoing endeavors to develop new protocols for the construction of phenanthridine derivatives, we describe herein a novel Mn(II)-promoted tandem reaction to synthesize 6-phosphorylated phenanthridines from 2-biaryl isothiocyanates and phosphine oxides under oxidant-free conditions is described. There are a number of advantages of this present method: (1) the reactions are promoted by stoichiometric low-cost Lewis acid. (2) The amount of P-reagents is decreased to 1.2 equiv, which make the reactions more environmentally benign. (3) In contrast to the 2-isocyanobiaryls-initiated radical reactions, our approach starts from more readily prepared 2-biaryl isothiocyanates. (4) The reactions are performed in air atmosphere and do not need anhydrous conditions, water brought into the system by $Mn(OAc)_2{\cdot}4H_2O$ exhibits no impact on the yields.

Initially, easily accessible 2-biphenyl isothiocyanate **1a** and diphenylphosphine oxide **2a** were selected as model substrates for reaction conditions optimization. Product **3a** was obtained in 27% yield in the presence of $Cu(OAc)_2{\cdot}H_2O$ as Lewis acid in DMF at 110 ℃ (Table 1, entry 1). This finding encouraged us to examine other low-cost Lewis acids, the results revealed that $Mn(OAc)_2{\cdot}4H_2O$ was the best choice, and the yield of **3a** increased to 76%, others such as $Fe(OAc)_2$, $Co(OAc)_2{\cdot}4H_2O$, $Ni(OAc)_2{\cdot}4H_2O$, $MnCO_3$, and $MnSO_4$ were all less effective (entries 2-7). It is noteworthy that the Lewis acid was indispensable in this transformation (entry 8). Solvent screening indicated that DMF was the most efficient one, and DMSO also gave a comparable yield (70%, entry 9), while other solvents

such as 1,4-dioxane, toluene, and CH_3NO_2 were all inferior (entries 10-12). The yield of **3a** dropped with decreasing the temperature to 100 °C or elevating to 120 °C (entries 13 and 14). Increasing the Lewis acid loading to 1.5 equiv did not affect the yield of the reaction (entry 15), however, reducing the loading from 1.0 to 0.5 equiv had a detrimental effect on the yield (entry 16). Finally, an optimized procedure involved stirring a 0.2 M solution of **1a** and **2a** (1.2 equiv) in DMF in the presence of 1.0 equiv $Mn(OAc)_2 \cdot 4H_2O$ at 110 °C for 6 h.

Table 1. Optimization of the reaction conditions[a]



1a **2a** **3a**

Entry	Catalyst (equiv)	Solvent	*T* [°C]	Yield [%][b]
1	$Cu(OAc)_2 \cdot H_2O$ (1.0)	DMF	110	27
2	$Fe(OAc)_2$ (1.0)	DMF	110	56
3	$Co(OAc)_2 \cdot 4H_2O$ (1.0)	DMF	110	51
4	$Ni(OAc)_2 \cdot 4H_2O$ (1.0)	DMF	110	44
5	**$Mn(OAc)_2 \cdot 4H_2O$ (1.0)**	**DMF**	**110**	**76**
6	$MnSO_4$ (1.0)	DMF	110	49
7	$MnCO_3$ (1.0)	DMF	110	26
8		DMF	110	8
9	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	DMSO	110	70
10	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	1,4-dioxane	110	26
11	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	toluene	110	47
12	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	CH_3NO_2	110	54
13	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	DMF	100	48
14	$Mn(OAc)_2 \cdot 4H_2O$ (1.0)	DMF	120	70

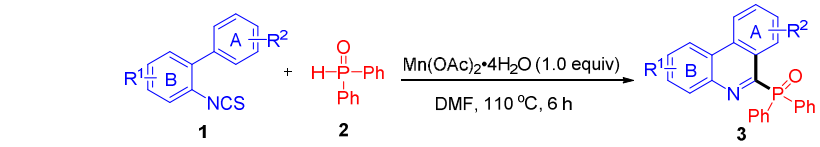
15	$Mn(OAc)_2{\cdot}4H_2O$ (1.5)	DMF	110	78
16	$Mn(OAc)_2{\cdot}4H_2O$ (0.5)	DMF	110	35

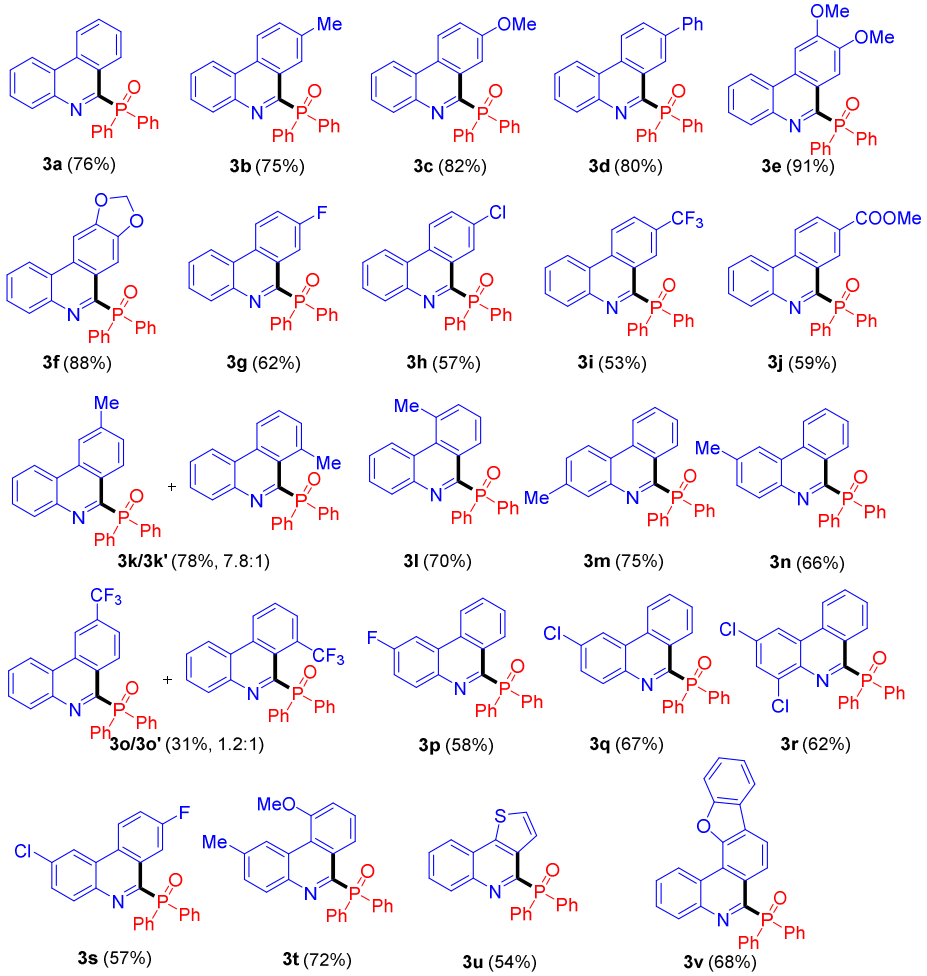
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), solvent (1.0 mL), 6 h. [b]Isolated yield based on **1a**.

By following the optimized conditions, the scope of 2-biaryl isothiocyanates was explored first (Table 2). Isothiocyanates bearing electron-donating substituents (-Me, -OMe, -Ph) on the *para* position of phenyl ring A performed the reaction smoothly to provide the corresponding products **3b-d** in good yields. Excellent yields were obtained with very electron rich dimethoxy, methylenedioxy substrates used for the synthesis of compounds **3e** and **3f**, whereas when substrates bearing electron-withdrawing groups (-F, -Cl, -CF_3, -COOMe) were used, moderate yields (53-62%) were observed for products **3g-j**. Compounds **3k-n** were obtained in moderate to good yields regardless of positions of the methyl group on the phenyl ring. It is worth mentioning that two unseparated regioisomers **3k** and **3k′** (7.8:1) were provided in 78% total yield with the reaction of 3-methylsubstituted isothiocyanate **1k** and **2a**. Similarly, unseparated isomers **3o** and **3o′** (1.2:1) were isolated in 31% total yield when electron-withdrawing 3-trifluoromethyl substituted isothiocyanate **1o** was reacted with **2a**. Notably, product **3p** with an electron-withdrawing fluoro group on the *meta* position of phenyl ring B, which could not obtain in the previous report,[9c] was generated in 58% yield under our conditions. Subsequently, isothiocyanates with two substituents were assessed and found that these substrates were compatible for the transformation, compounds **3r-t** were afforded in moderate yields. Heterocycles such as thiophene and dibenzofuran were also tolerated for the reactions, products **3u** and

3v were isolated in 54% and 68% yields, respectively. The structures of **3** were undoubtedly confirmed by X-ray crystallographic analysis of **3a** (See Figure S1).

Table 2. Substrate Scope of 2-Biary Isothiolyanates 1[a,b]



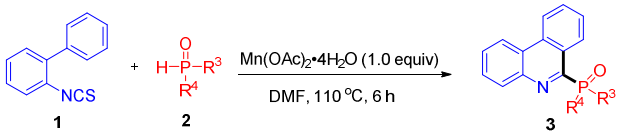


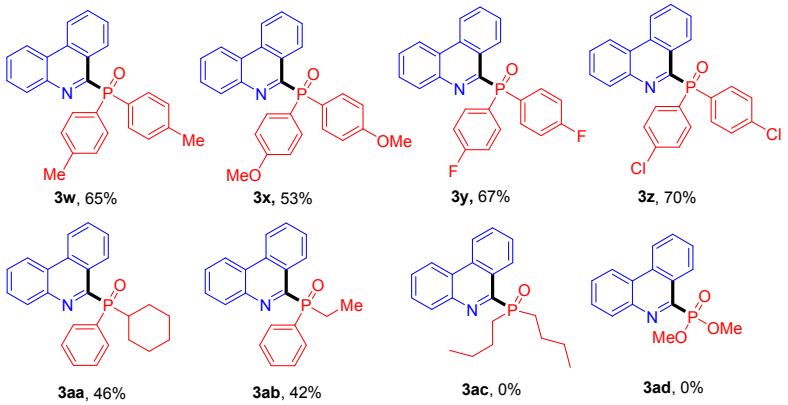
[a]Reaction conditions: **1** (0.4 mmol), **2** (0.48 mmol), DMF (2.0 mL). [b]Isolated yield.

Having established the scope of isothiocyanates **1**, we moved on to examine the P-reagents under the optimal conditions (Table 3). The electronic effect was not an important factor for the reactions. Both electron-donating groups (-Me, OMe) and

electron-withdrawing groups (-F, -Cl) on the phenyl ring were tolerated, the desired products **3w-z** were generated in moderate yields. The reaction also proceeded smoothly with cyclohexyl phenylphosphine oxide, providing the phenanthridine **3aa** in 46% yield. In addition, ethyl phenylphosphine oxide was a suitable P-reagent for the reaction and product **3ab** was isolated in 42% yield. However, no desired products **3ac** or **3ad** were generated for the reaction of dibutylphosphine oxide or dimethyl phosphonate with **1a**.

Table 3. Substrate Scope of P-reagents **2**[a,b]



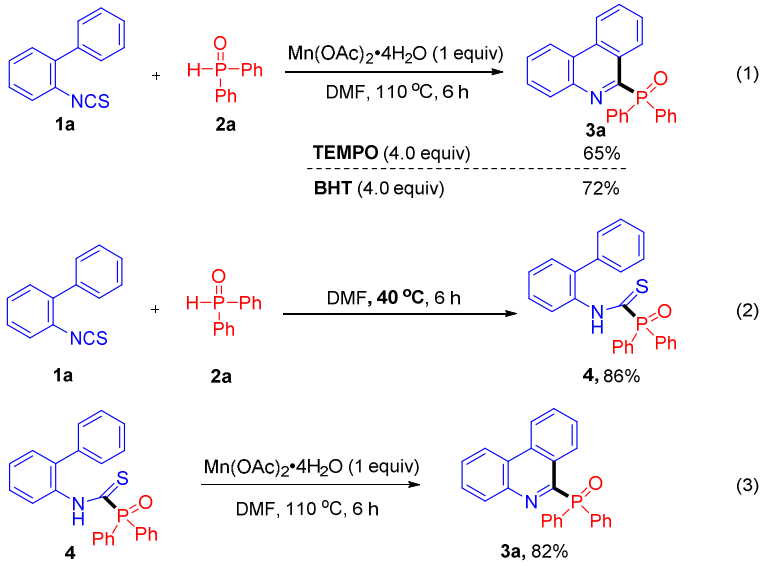


[a]Reaction conditions: **1** (0.4 mmol), **2** (0.48 mmol), DMF (2.0 mL). [b]Isolated yield.

Control experiments were performed to obtain some mechanism insight into the reaction. Initially, 4 equiv 2,2,6,6 tetramethylpiperidine *N*-oxide (TEMPO) was added in the reaction of **1a** with **2a**, product **3a** could be isolated in 65% yield (Scheme 2, eq 1). Similarly, the reaction was not influenced with the addition of 4 equiv 2,6-di-*tert*-butyl-4-methylphenol (BHT). These results indicated that the reaction

might not proceed in a radical pathway. When the reaction of **1a** and **2a** was performed in DMF at 40 °C, the thioamide **4** was obtained in 86% yield (eq 2). The structure of **4** was confirmed by X-ray crystallographic analysis (See Figure S2). Considering **4** was probably an intermediate in the transformation, the reaction of **4** under the standard conditions was evaluated. To our delight, the desired product **3a** was isolated in 82% yield, which confirmed our hypothesis (eq 3).

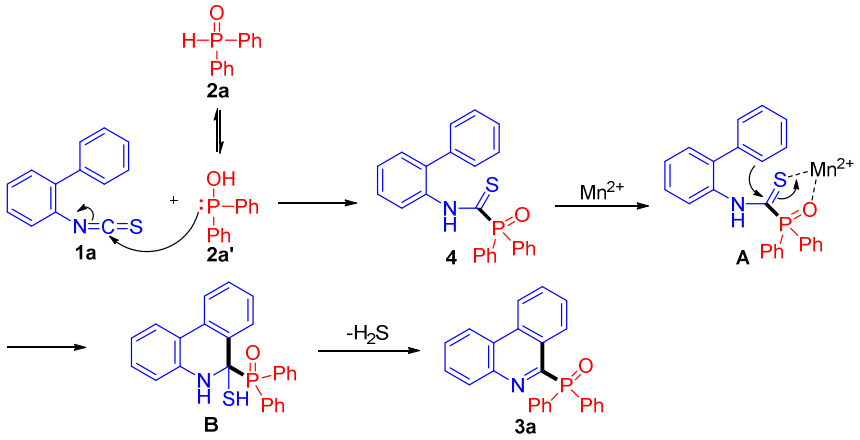
Scheme 2. Control Experiments for Mechanism



Based on the above results and previous reports,[15] a general mechanism is proposed for this reaction (Scheme 3). Initially, the diphenylphosphine oxide **2a** can tautomerize to the P-OH form **2a′**.[16] Next, the NCS group in **1a** would be attacked by **2a′** to give thioamide **4**. The unusual intramolecular cyclization of intermediate **4** in the presence of Mn(II) is the key process for this synthesis,[17] affording the intermediate **B**, which rapidly eliminates H_2S to provide the final product **3a**. The reason that cyclization could take place probably due to the high electron-negative

property of the P-substituted thioamide.

Scheme 3. Proposed Reaction Mechanism



CONCLUSION

In summary, we have developed an efficient tandem phosphorylation/cyclization process to synthesize 6-phosphorylated phenanthridines from 2-biaryl isothiocyanates with diarylphosphine oxide. Remarkably, the reaction was proceeded only in the presence of inexpensive Lewis acid $Mn(OAc)_2 \cdot 4H_2O$. Most attractively, compared to classical radical isocyanide insertion reactions, this approach not only avoids the use of excess expensive oxidants and P-reagents, but also uses readily available isothiocyanates as starting materials instead of isocyanides. This environmentally benign strategy is expected to become a useful alternative for the synthesis of 6-phosphorylated phenanthridine derivatives.

EXPERIMENTAL SECTION

General information. All air- or moisture-sensitive reactions were conducted under a nitrogen atmosphere. Unless noted, all commercial reagents were used without further purification. Melting points were recorded on a microscopic melting

apparatus and uncorrected. ^{1}H NMR spectra were recorded at 500 MHz, and ^{13}C NMR spectra were recorded at 125 MHz in $CDCl_3$ or DMSO-d_6. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane (TMS). HRMS was obtained on a spectrometer with an ESI source. The X-ray single-crystal diffraction was performed on a CCD area detector. Silica gel (200−300 mesh) was used for column chromatography and silica GF254 for TLC.

Preparation of starting materials. 2-Isothiocyanato-1,1'-biaryl[14] and phosphine oxides[18] were prepared according to the literatures.

General procedure for the synthesis of 6-phosphorylated phenanthridines 3 (3a for example). To a 15 mL sealed tube was charged with a mixture of 2-isothiocyanato-1,1'-biphenyl **1a** (84.5 mg, 0.4 mmol), diphenylphosphine oxide **2a** (97 mg, 0.48 mmol), $Mn(OAc)_2{\cdot}4H_2O$ (98 mg, 0.4 mmol) and DMF (2.0 mL). The reaction mixture was allowed to stir at 110 ^{o}C for 6 h. After completion, the mixture was cooled to room temperature, diluted with EtOAc (20 mL), and washed by saturated NaCl (5 x 5.0 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel to afford the product **3a** as a white solid (115 mg, 76%).

Phenanthridin-6-yldiphenylphosphine oxide (3a)[9e]. White solid; mp 194−196 °C; R_f = 0.42 (PE/EA = 2:1 v/v); 115 mg, 76% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43−7.47 (m, 4H), 7.50−7.54 (m, 2H), 7.68−7.76 (m, 3H), 7.86 (t, J = 7.6 Hz, 1H), 7.92−7.96 (m, 4H), 8.06 (t, J = 4.6 Hz, 1H), 8.61 (t, J = 4.6 Hz, 1H), 8.67 (d, J = 8.2 Hz, 1H), 9.51 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 122.2, 124.4, 128.0, 128.2 (d, J = 10.9 Hz), 128.6, 128.7, 128.8, 131.2 (d, J

= 14.2 Hz), 131.7, 132.4 (d, J = 6.5 Hz), 133.4, 142.8 (d, J = 21.9 Hz), 156.9 (d, J = 128.3 Hz).

(8-Methylphenanthridin-6-yl)diphenylphosphine oxide (3b)[9e]. White solid; mp 205−207 °C; R_f = 0.58 (PE/EA = 2:1 v/v); 118 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.56 (s, 3H), 7.42−7.45 (m, 4H), 7.51 (t, J = 7.3 Hz, 2H), 7.65−7.72 (m, 3H), 7.94 (q, J = 6.3 Hz, 4H), 8.03 (d, J = 7.9 Hz, 1H), 8.54 (d, J = 3.7 Hz, 2H), 9.33 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.9, 121.9, 124.4, 127.7, 128.1 (d, J = 12.0 Hz), 128.7, 130.5, 131.0, 131.6, 132.3 (d, J = 8.0 Hz), 132.8 (d, J = 16.4 Hz), 133.6, 138.1, 142.4 (d, J = 23.9 Hz), 156.3 (d, J = 128.7 Hz).

8-Methoxyphenanthridin-6-yl)diphenylphosphine oxide (3c)[9e]. White solid; mp 182−184 °C; R_f = 0.36 (PE/EA = 2:1 v/v); 134 mg, 82% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.94 (s, 3H), 7.43−7.48 (m, 5H), 7.64 (t, J = 7.4 Hz, 2H), 7.69 (t, J = 7.6 Hz, 2H), 7.97 (q, J = 6.3 Hz, 4H), 8.04 (d, J = 8.1 Hz, 1H), 8.50 (d, J = 7.9 Hz, 1H), 8.54 (d, J = 9.1 Hz, 1H), 9.03 (d, J = 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.6, 107.5, 121.6, 122.6, 123.6, 124.5, 127.1, 127.6, 128.1 (d, J = 11.4 Hz), 128.8, 129.4 (d, J = 22.9 Hz), 131.1, 131.6, 132.3 (d, J = 7.9 Hz), 132.6, 133.5, 142.1 (d, J = 22.8 Hz), 155.5 (d, J = 129.6 Hz), 158.8.

Diphenyl(8-phenylphenanthridin-6-yl)phosphine oxide (3d)[9f]. White solid; mp 221−223 °C; R_f = 0.46 (PE/EA = 2:1 v/v); 146 mg, 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38 (t, J = 7.3 Hz, 1H), 7.44−7.48 (m, 6H), 7.52 (t, J = 7.2 Hz, 2H), 7.71 (t, J = 9.5 Hz, 4H), 7.98−8.02 (m, 4H), 8.07−8.11 (m, 2H), 8.58 (d, J = 6.4 Hz, 1H), 8.68 (d, J = 8.7 Hz, 1H), 9.84 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 122.1, 122.7, 124.2, 126.4, 127.5, 127.8, 128.2 (d, J = 12.1 Hz), 128.4, 128.6, 128.9, 129.0, 130.0, 131.1, 131.6, 132.2 (d, J = 9.0 Hz), 133.5, 140.1 (d, J = 55.2 Hz), 142.7 (d, J = 22.9 Hz), 157.0 (d, J = 128.7 Hz).

(8,9-Dimethoxyphenanthridin-6-yl)diphenylphosphine oxide (3e)[9b]. White solid; mp

215−217 °C; R_f = 0.16 (PE/EA = 2:1 v/v); 160 mg, 91% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.03 (s, 3H), 4.13 (s, 3H), 7.43−7.46 (m, 4H), 7.51 (t, J = 7.2 Hz, 2H), 7.64−7.70 (m, 2H), 7.92 (s, 1H), 7.98 (q, J = 6.3 Hz, 4H), 8.05 (d, J = 8.2 Hz, 1H), 8.46 (d, J = 7.9 Hz, 1H), 9.11(s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 56.0, 56.2, 101.7, 107.8, 121.6, 124.0 (d, J = 22.9 Hz), 127.7, 128.1 (d, J = 12.1 Hz), 128.8 (d, J = 6.5 Hz), 131.1, 131.6, 132.3 (d, J = 9.0 Hz), 132.8, 133.6, 142.5 (d, J = 22.9 Hz), 149.7, 152.6, 154.3 (d, J = 129.6 Hz).

[1,3]Dioxolo[4,5-*j*]phenanthridin-6-yldiphenylphosphine oxide (3f)[9e]. White solid; mp 231−233 °C; R_f = 0.23 (PE/EA = 2:1 v/v); 149 mg, 88% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (s, 2H), 7.42−7.46 (m, 4H), 7.51 (q, J = 4.9 Hz, 2H), 7.63−7.68 (m, 2H), 7.92−7.96 (m, 5H), 8.00 (t, J = 4.6 Hz, 1H), 8.39 (t, J = 4.6 Hz, 1H), 9.04 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 99.8, 102.0, 105.7, 121.9, 124.5, 125.0 (d, J = 23.4 Hz), 128.1 (d, J = 11.8 Hz), 128.3, 131.0, 131.6, 132.3 (d, J = 8.0 Hz), 132.6, 133.5, 142.5 (d, J = 22.9 Hz), 148.3, 151.3, 154.6 (d, J = 130.6 Hz).

(8-Fluorophenanthridin-6-yl)diphenylphosphine oxide (3g)[9e]. White solid; mp 218−220 °C; R_f = 0.37 (PE/EA = 2:1 v/v); 99 mg, 62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46−7.54 (m, 6H), 7.60 (t, J = 7.0 Hz, 1H), 7.73 (q, J = 6.8 Hz, 2H), 7.96 (q, J = 6.3 Hz, 4H), 8.08 (d, J = 7.6 Hz, 1H), 8.54 (d, J = 7.3 Hz, 1H), 8.64 (d, J = 5.1 Hz, 1H), 9.33 (dd, J = 1.9, 9.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 113.2 (d, J = 23.3 Hz), 120.5 (d, J = 23.9 Hz), 121.9, 124.0, 124.5 (d, J = 8.0 Hz), 128.2 (d, J = 12.2 Hz), 128.6, 129.0 (d, J = 9.2 Hz), 129.2, 129.3 (d, J = 6.4 Hz), 131.2, 131.8, 132.3 (d, J = 9.0 Hz), 133.2, 142.4 (d, J = 21.9 Hz), 156.0 (dd, J = 3.8, 128.3 Hz), 161.3 (d, J = 249.3 Hz).

(8-Chlorophenanthridin-6-yl)diphenylphosphine oxide (3h)[9e]. White solid; mp 226−228 °C;

R_f = 0.46 (PE/EA = 2:1 v/v); 94 mg, 57% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45−7.54 (m, 6H), 7.73 (s, 2H), 7.79 (t, J = 8.0 Hz, 1H), 7.95 (q, J = 6.3 Hz, 4H), 8.06 (s, 1H), 8.56 (q, J = 8.9 Hz, 2H), 9.67 (d, J = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 122.0, 123.7, 127.7, 128.2 (d, J = 11.8 Hz), 128.7, 129.1 (d, J = 25.5 Hz), 131.1 (d, J = 19.0 Hz), 131.8, 132.3 (d, J = 7.8 Hz), 133.2, 134.0, 142.6 (d, J = 22.9 Hz), 155.9 (d, J = 128.7 Hz).

Diphenyl(8-(trifluoromethyl)phenanthridin-6-yl)phosphine oxide (3i)[9e]. White solid; mp 176−178 °C; R_f = 0.58 (PE/EA = 2:1 v/v); 95 mg, 53% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (q, J = 3.8 Hz, 4H), 7.53 (t, J = 7.2 Hz, 2H), 7.79 (t, J = 3.7 Hz, 2H), 7.96−8.04 (m, 5H), 8.13 (d, J = 6.6 Hz, 1H), 8.61 (d, J = 7.9 Hz, 1H), 8.76 (d, J = 8.1 Hz, 1H), 10.04 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 122.4, 122.7, 123.2, 123.3, 123.8 (d, J = 272.1 Hz), 126.2, 126.9, 127.2 (d, J = 23.5 Hz), 128.2 (d, J = 11.5 Hz), 129.3, 129.7, 129.9, 131.2, 131.8, 132.3 (d, J = 8.0 Hz), 133.0, 134.7, 143.3 (d, J = 22.9 Hz), 157.1 (d, J = 127.6 Hz).

Methyl 6-(diphenylphosphoryl)phenanthridine-8-carboxylate (3j). White solid; mp 207−209 °C; R_f = 0.35 (PE/EA = 2:1 v/v); 103 mg, 59% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.98 (s, 3H), 7.44−7.46 (m, 4H), 7.52 (t, J = 7.0 Hz, 2H), 7.78 (t, J = 3.8 Hz, 2H), 7.98 (q, J = 6.3 Hz, 4H), 8.10 (t, J = 4.6 Hz, 1H), 8.47 (d, J = 8.5 Hz, 1H), 8.62 (d, J = 7.6 Hz, 1H), 8.70 (d, J = 8.6 Hz, 1H), 10.31 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 52.5, 122.5 (d, J = 23.1 Hz), 123.6, 127.4 (d, J = 21.9 Hz), 128.2 (d, J = 11.4 Hz), 129.1, 120.3, 129.8, 130.7, 131.0 (d, J = 24.3 Hz), 131.8, 132.4, 133.2, 135.5, 143.4 (d, J = 21.9 Hz), 157.5 (d, J = 127.6 Hz), 166.5. HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{27}H_{21}NO_3P$, 438.1253, found 438.1255.

(9-Methylphenanthridin-6-yl)diphenylphosphine oxide and (7-Methylphenanthridin-6-yl) diphenylphosphine oxide (3k/3k')[9b]. White solid; R_f = 0.49 (PE/EA = 2:1 v/v); 123 mg, 78%

yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.62 (s, 3H), 2.99 (s, 0.38H), 7.42−7.45 (m, 4.5H), 7.50 (t, J = 7.3 Hz, 3.25H), 7.62 (t, J = 7.5 Hz, 0.21H), 7.68−7.74 (m, 2.32H), 7.76−7.82 (m, 0.58H), 7.91−7.95 (m, 4H), 8.03 (t, J = 4.6 Hz, 1H), 8.43 (s, 1H), 8.56 (t, J = 9.5 Hz, 1.28H), 9.40 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.4, 25.0, 120.2, 121.7, 122.1, 122.2, 124.2, 126.1 (d, J = 23.3 Hz), 128.1 (d, J = 12.1 Hz), 128.4, 128.5, 128.9, 129.6, 130.5 (d, J = 8.2 Hz), 131.1, 131.2, 132.0 (d, J = 8.7 Hz), 132.6, 132.8 (d, J = 6.2 Hz), 133.5, 134.1,134.4, 137.9, 141.6, 142.9 (d, J = 22.9 Hz), 156.5 (d, J = 128.7 Hz).

(10-Methylphenanthridin-6-yl)diphenylphosphine oxide (3l)[9e]. White solid; mp 211−213 °C; R_f = 0.44 (PE/EA = 2:1 v/v); 110 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.14 (s, 3H), 7.44 (q, J = 4.0 Hz, 4H), 7.51 (t, J = 6.8 Hz, 2H), 7.60 (t, J = 7.7 Hz, 1H), 7.70 (q, J = 5.4 Hz, 3H), 7.89−7.92 (m, 4H), 8.06 (t, J = 4.7 Hz, 1H), 8.86 (d, J = 9.2 Hz, 1H), 9.45 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 26.9, 122.0, 125.7, 126.6, 127.2 (d, J = 22.4 Hz), 127.9, 128.1 (d, J = 11.3 Hz), 128.6, 129.2 (d, J = 22.9 Hz), 131.5, 132.3 (d, J = 8.0 Hz), 132.7, 133.5, 135.2, 143.9 (d, J = 22.9 Hz), 157.3 (d, J = 128.7 Hz).

(3-Methylphenanthridin-6-yl)diphenylphosphine oxide (3m). White solid; mp 193−195 °C; R_f = 0.46 (PE/EA = 2:1 v/v); 118 mg, 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.55 (s, 3H), 7.43−9.46 (m, 4H), 7.49−7.55 (m, 3H), 7.64 (t, J = 7.6 Hz, 1H), 7.82 (t, J = 10.2 Hz, 2H), 7.94 (q, J = 6.4 Hz, 4H), 8.47 (d, J = 7.9 Hz, 1H), 8.60 (d, J = 7.1 Hz, 1H), 9.49 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.3, 121.8, 122.0, 127.3, 127.3, 127.6, 127.8, 128.1 (d, J = 11.1 Hz), 128.5, 130.5 (d, J = 8.0 Hz), 130.8, 131.5, 132.3 (d, J = 7.0 Hz), 132.7 (d, J = 9.8 Hz), 133.6, 138.9, 142.8 (d, J = 22.9 Hz), 156.8 (d, J = 128.6 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{26}H_{21}NOP$, 394.1355, found 394.1356.

(2-Methylphenanthridin-6-yl)diphenylphosphine oxide (3n)[9e]. White solid; mp 210−212 °C; R_f = 0.54 (PE/EA = 2:1 v/v); 104 mg, 66% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.63 (s, 3H), 7.72−7.45 (m, 4H), 7.49−7.54 (m, 3H), 7.67 (t, J = 7.6 Hz, 1H), 7.82 (t, J = 7.6 Hz, 1H), 7.93 (q, J = 6.6 Hz, 5H), 8.37 (s, 1H), 8.63 (d, J = 7.93 Hz, 1H), 9.48 (d, J = 8.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.1, 121.6, 122.0, 124.2, 127.7, 128.1 (d, J = 11.0 Hz), 128.5, 130.4, 130.8 (d, J = 18.9 Hz), 131.6, 132.3 (d, J = 7.1 Hz), 132.8, 133.6, 139.0, 141.2 (d, J = 23.4 Hz), 155.6 (d, J = 129.4 Hz).

Diphenyl(9-(trifluoromethyl)phenanthridin-6-yl)phosphine oxide and Diphenyl(7-(trifluoromethyl)phenanthridin-6-yl)phosphine oxide (3o/3o'). Colorless oil; R_f = 0.62 (PE/EA = 2:1 v/v); 56 mg, 31% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10−7.22 (m, 5.78H), 7.32−7.40 (m, 6.19H), 7.44−7.60 (m, 7.66H), 7.69−7.74 (m, 2.44H), 7.79−7.86 (m, 5.18H), 8.02 (t, J = 4.5 Hz, 0.94H), 8.20 (d, J = 8.2 Hz, 1.42H), 8.54 (d, J = 9.6 Hz, 1.99H), 8.84 (s, 1.20H), 9.62 (d, J = 8.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 118.3, 118.7 (d, J = 4.2 Hz), 120.1 (d, J = 3.3 Hz), 121.0, 121.5, 121.9 (d, J = 3.0 Hz), 122.7 (d, J = 2.6 Hz), 123.7 (d, J = 2.0 Hz), 123.8, 123.9 (d, J = 3.4 Hz), 124.0 (d, J = 3.7 Hz), 124.2, 124.7, 125.0, 125.1 (d, J = 2.4 Hz), 125.2 (d, J = 3.7 Hz), 125.5, 127.3 (d, J = 12.3 Hz), 127.9, 128.1, 128.2, 128.4, 128.5, 128.7 (d, J = 12.4 Hz), 129.2, 130.1 (d, J = 6.6 Hz), 130.2, 130.3, 130.5 (d, J = 14.4 Hz), 130.7 (d, J = 14.0 Hz), 130.8, 130.9 (d, J = 2.7 Hz), 131.2 (d, J = 9.4 Hz), 131.4 (t, J = 3.4 Hz), 131.5, 131.6, 131.7 (d, J = 3.6 Hz), 132.7 (d, J = 19.0 Hz), 137.5 (d, J = 70.4 Hz), 142.0 (d, J = 22.0 Hz), 155.7 (d, J = 127.6 Hz), 158.1, 161.1. HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{26}H_{18}F_3NOP$, 448.1078, found 448.1079.

(2-Fluorophenanthridin-6-yl)diphenylphosphine oxide (3p)[9e]. White solid; mp 233−235 °C; R_f = 0.33 (PE/EA = 2:1 v/v); 92 mg, 58% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.45 (q, J = 5.1

Hz, 5H), 7.53 (t, *J* = 7.1 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.91 (q, *J* = 6.3 Hz, 4H), 8.05 (q, *J* = 4.9 Hz, 1H), 8.19 (dd, *J* = 9.7, 2.0 Hz, 1H), 8.53 (d, *J* = 7.9 Hz, 1H), 9.50 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 107.1 (d, *J* = 23.1 Hz), 117.8 (d, *J* = 24.9 Hz), 122.3, 126.0, 127.8 (d, *J* = 22.9 Hz), 128.2 (d, *J* = 11.6 Hz), 128.6 (d, *J* = 18.9 Hz), 131.1, 131.7, 132.2 (d, *J* = 8.0 Hz), 133.2, 133.6, 139.6 (d, *J* = 24.0 Hz), 156.1 (d, *J* = 128.6 Hz), 162.4 (d, *J* = 250.2 Hz).

(2-Chlorophenanthridin-6-yl)diphenylphosphine oxide (3q)[9b]. White solid; mp 237−239 °C; R_f = 0.48 (PE/EA = 2:1 v/v); 111 mg, 67% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43−7.46 (m, 4H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.64 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.85−7.93 (m, 5H), 7.98 (d, *J* = 8.7 Hz, 1H), 8.55 (d, *J* = 2.1 Hz, 1H), 8.6 (s, 1H), 9.50 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 121.8, 122.1, 125.5, 128.2 (d, *J* = 11.0 Hz), 128.7 (d, *J* = 26.3 Hz), 129.3, 131.3, 131.8, 132.3 (d, *J* = 7.4 Hz), 132.6, 133.2, 134.9, 141.1 (d, *J* = 22.9 Hz), 157.4 (d, *J* = 127.7 Hz).

(2,4-Dichlorophenanthridin-6-yl)diphenylphosphine oxide (3r). White solid; mp 252−254 °C; R_f = 0.42 (PE/EA = 2:1 v/v); 111 mg, 62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.47 (t, *J* = 3.8 Hz, 4H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.77−7.82 (m, 2H), 7.90 (t, *J* = 7.6 Hz, 1H), 8.08 (q, *J* = 6.3 Hz, 4H), 8.47 (d, *J* = 1.8 Hz, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 9.69 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 120.6, 122.4, 126.6, 128.2 (d, *J* = 12.2 Hz), 128.9, 129.3 (d, *J* = 34.8 Hz), 131.4, 131.8, 132.0, 132.4 (d, *J* = 8.0 Hz), 132.9, 134.3, 136.9, 137.7 (d, *J* = 22.9 Hz), 158.1 (d, *J* = 126.6 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{17}Cl_2NOP$, 448.0419, found 448.0419.

(2-Chloro-8-fluorophenanthridin-6-yl)diphenylphosphine oxide (3s). White solid; mp

241−243 °C; R_f = 0.52 (PE/EA = 2:1 v/v); 98 mg, 57% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44−7.48 (m, 4H), 7.53 (q, J = 4.9 Hz, 2H), 7.59−7.65 (m, 2H), 7.91−7.95 (m, 4H), 7.99 (d, J = 8.5 Hz, 1H), 8.48 (s, 1H), 8.55 (q, J = 4.6 Hz, 1H), 9.33 (dd, J = 2.4, 10.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 113.4 (d, J = 23.3 Hz), 120.8 (d, J = 24.9 Hz), 121.6, 124.7 (d, J = 8.0 Hz), 125.0, 128.3 (d, J = 11.9 Hz), 129.2, 131.9, 132.2 (d, J = 9.2 Hz), 132.6, 132.8, 135.4, 140.8 (d, J = 21.9 Hz), 156.4 (d, J = 127.7 Hz), 161.6 (d, J = 250.3 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{17}ClFNOP$, 432.0714, found 432.0711.

(10-Methoxy-2-methylphenanthridin-6-yl)diphenylphosphine oxide (3t)[9c]. White solid; mp 223−225 °C; R_f = 0.32 (PE/EA = 2:1 v/v); 122 mg, 72% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.62 (s, 3H), 4.12 (s, 3H), 7.29 (d, J = 8.0 Hz, 1H), 7.41−7.44 (m, 4H), 7.50 (t, J = 9.4 Hz, 3H), 7.61 (t, J = 8.2 Hz, 1H), 7.89 (d, J = 6.5 Hz, 5H), 9.11 (d, J = 7.9 Hz, 1H), 9.31 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 22.6, 55.8, 111.8, 120.7, 124.0, 127.5, 128.1 (d, J = 13.3Hz), 129.6, 130.6, 131.5, 132.3 (d, J = 7.6 Hz), 132.8, 133.6, 138.8, 141.7, 155.6, 158.1.

Diphenyl(thieno[3,2-*c*]quinolin-4-yl)phosphine oxide (3u)[9f]. Light yellow solid; mp 240−242 °C; R_f = 0.36 (PE/EA = 2:1 v/v); 83 mg, 54% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43−7.47 (m, 4H), 7.50−7.53 (m, 2H), 7.60 (d, J = 5.4 Hz,1H), 7.65−7.72 (m, 2H), 7.78−8.02 (m, 4H), 8.14−8.18 (m, 2H), 8.67 (d, J = 5.5 Hz,1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 123.4, 124.4, 125.3, 126.6, 128.2 (d, J = 11.8 Hz), 128.6, 131.1, 131.8, 132.3 (d, J = 8.9 Hz), 133.1, 135.4 (d, J = 23.9 Hz), 142.8 (d, J = 21.9 Hz), 146.4 (d, J = 8.9 Hz), 152.3 (d, J = 130.6 Hz).

Benzofuro[3,2-*k*]phenanthridin-6-yldiphenylphosphine oxide (3v). White solid; mp 271−273 °C; R_f = 0.21 (PE/EA = 2:1 v/v); 128 mg, 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46 (s, 5H), 7.53 (t, J = 7.1 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.81 (q, J = 8.9 Hz, 2H), 7.90 (t, J =

7.5 Hz, 1H), 7.97 (q, *J* = 6.4 Hz, 4H), 8.11 (t, *J* = 9.2 Hz, 2H), 8.26 (d, *J* = 8.5 Hz, 1H), 9.60 (d, *J* = 8.5 Hz, 1H), 9.67 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 112.1, 120.8 (d, *J* = 114.7 Hz), 122.4, 123.5 (d, *J* = 13.9 Hz), 125.6, 127.2, 127.5 (d, *J* = 24.3 Hz), 128.1 (d, *J* = 11.2 Hz), 129.0 (d, *J* = 39.0 Hz), 130.8, 131.7, 132.4 (d, *J* = 8.0 Hz), 133.4, 143.2 (d, *J* = 22.9 Hz), 151.8, 156.5 (d, *J* = 129.1 Hz), 156.7. HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{31}H_{21}NO_2P$, 470.1304, found 470.1303.

Phenanthridin-6-yldi-*p*-tolylphosphine oxide (3w)[9e]. White solid; mp 204−206 °C; R_f = 0.28 (PE/EA = 2:1 v/v); 106 mg, 65% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.38 (s, 6H), 7.24 (s, 4H), 7.66−7.71 (m, 3H), 7.81 (t, *J* = 9.6 Hz, 5H), 8.06 (t, *J* = 4.6 Hz, 1H), 8.59 (d, *J* = 7.7 Hz, 1H), 8.64 (d, *J* = 7.7 Hz, 1H), 9.52 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.6, 122.0, 124.3, 127.8, 128.6, 128.7 (d, *J* = 5.4 Hz), 128.9 (d, *J* = 11.8 Hz), 129.4, 130.3, 130.9, 131.2, 132.3 (d, *J* = 8.0 Hz), 132.5, 142.0, 142.8 (d, *J* = 22.9 Hz), 157.4 (d, *J* = 125.7 Hz).

Bis(4-methoxyphenyl)(phenanthridin-6-yl)phosphine oxide (3x). White solid; mp 89−91 °C; R_f = 0.17 (PE/EA = 2:1 v/v); 93 mg, 53% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.82 (s, 6H), 6.95 (q, *J* = 3.5 Hz, 4H), 7.67−7.73 (m, 3H), 7.84 (q, *J* = 6.64 Hz, 5H), 8.07 (t, *J* = 4.6 Hz, 1H), 8.59 (t, *J* = 4.58 Hz, 1H), 8.65 (d, *J* = 8.06 Hz, 1H), 9.53 (d, *J* = 8.54 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 55.2, 113.7 (d, *J* = 12.0 Hz), 122.0, 124.1 (d, *J* = 34.9 Hz), 124.9, 127.8, 128.6 (d, *J* = 13.9 Hz), 131.0 (d, *J* = 28.2 Hz), 132.5, 134.1 (d, *J* = 8.0 Hz), 142.7 (d, *J* = 22.9 Hz), 157.6 (d, *J* = 127.7 Hz), 162.2. HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{27}H_{23}NO_3P$, 440.1410, found 440.1410.

Bis(4-fluorophenyl)(phenanthridin-6-yl)phosphine oxide (3y). Light yellow solid; mp 135−137 °C; R_f = 0.36 (PE/EA = 2:1 v/v); 111 mg, 67% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.13−7.17 (m, 4H), 7.70−7.77 (m, 3H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.90−7.96 (m, 4H), 8.06 (t, *J* =

4.8 Hz, 1H), 8.62 (t, J = 4.6 Hz, 1H), 8.68 (d, J = 8.2 Hz, 1H), 9.48 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 115.6 (dd, J = 13.6, 20.7 Hz), 122.2, 124.4, 127.7 (d, J = 23.9 Hz), 128.2 (d, J = 43.9 Hz), 128.2, 128.9 (d, J = 21.6 Hz), 131.1 (d, J = 25.9 Hz), 132.6 (d, J = 5.6 Hz), 134.7 (t, J = 8.8 Hz), 142.6 (d, J = 23.9 Hz), 156.3 (d, J = 130.6 Hz), 165.1 (d, J = 252.3 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{17}F_2NOP$, 416.1010, found 416.1010.

Bis(4-chlorophenyl)(phenanthridin-6-yl)phosphine oxide (3z). White solid; mp 211−213 °C; R_f = 0.48 (PE/EA = 2:1 v/v); 125 mg, 70% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.44 (t, J = 4.0 Hz, 4H), 7.70−7.78 (m, 3H), 7.84−7.90 (m, 5H), 8.07 (t, J = 4.3 Hz, 1H), 8.62 (d, J = 7.3 Hz, 1H), 8.68 (d, J = 8.3 Hz, 1H), 9.45 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 122.2, 124.4, 127.7 (d, J = 23.8 Hz), 128.1 (d, J = 33.0), 128.6 (d, J = 11.6 Hz), 128.9 (d, J = 25.1 Hz), 130.8, 131.1 (d, J = 31.1 Hz), 131.6, 132.6, 133.6 (d, J = 7.0 Hz), 138.5, 142.6 (d, J = 23.9 Hz), 155.9 (d, J = 130.6 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{17}Cl_2NOP$, 448.0419, found 448.0420.

Cyclohexyl(phenanthridin-6-yl)(phenyl)phosphine oxide (3aa). White solid; mp 189−191 °C; R_f = 0.32 (PE/EA = 2:1 v/v); 71 mg, 46% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.26−1.42 (m, 3H), 1.61 (s, 2H), 1.72−1.81 (m, 4H), 2.04 (d, J = 8.2 Hz, 1H), 3.12 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 8.1 Hz, 3H), 7.66 (t, J = 7.6 Hz, 1H), 7.74 (t, J = 7.4 Hz, 1H), 7.78−7.82 (m, 2H), 7.99 (t, J = 8.8 Hz, 2H), 8.29 (d, J = 7.9 Hz, 1H), 8.60 (t, J = 9.2 Hz, 2H), 9.50 (d, J = 7.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.2, 24.9, 26.0, 26.4 (q, J = 6.6 Hz), 37.2 (d, J = 75.8 Hz), 122.0 (d, J = 32.9 Hz), 124.4, 127.8, 128.1, 128.3 (d, J = 11.2 Hz), 128.5 (d, J = 2.3 Hz), 128.7, 130.9 (d, J = 6.0 Hz), 131.3, 131.5 (d, J = 8.0 Hz), 131.8, 132.4 (d, J = 7.0 Hz), 132.5, 142.9 (d, J = 21.9 Hz), 157.5 (d, J = 115.7 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{25}NOP$, 386.1668, found 386.1667.

Ethyl(phenanthridin-6-yl)(phenyl)phosphine oxide (3ab). White solid; mp 170−172 °C; R_f =

0.30 (PE/EA = 2:1 v/v); 56 mg, 42% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.29-1.36 (m, 3H), 2.55-2.65 (m, 1H), 2.90-2.99 (m, 1H), 7.38-7.46 (m, 3H), 7.65 (t, J = 7.6 Hz, 1H), 7.76 (t, J = 7.1 Hz, 1H), 7.81 (q, J = 7.0 Hz, 2H), 7.91 (q, J = 6.1 Hz, 2H), 8.28 (d, J = 7.9 Hz, 1H), 8.61 (q, J = 7.1 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 5.5, 23.1 (d, J = 78.6 Hz), 122.1 (d, J = 15.0 Hz), 124.5, 127.3 (d, J = 20.9 Hz), 127.8, 128.4 (t, J = 9.9 Hz), 128.7 (d, J = 14.4 Hz), 130.9, 131.6, 132.5 (d, J = 26.9 Hz), 133.4, 142.9 (d, J = 22.9 Hz), 157.6 (d, J = 120.7 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{21}H_{19}NOP$, 332.1199, found 332.1197.

Procedure for the synthesis of compound 4. To a 15 mL sealed tube was charged with a mixture of **1a** (84.5 mg, 0.4 mmol), **2a** (97 mg, 0.48 mmol), and DMF (2.0 mL). The reaction mixture was allowed to stir at 40 ^{o}C for 6 h monitored by TLC. After that, the mixture was cooled to room temperature, diluted with EtOAc (20 mL), and washed by saturated NaCl (5 x 5.0 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel to afford the product **4** as a yellow solid (142 mg, 86%).

N-([1,1'-biphenyl]-2-yl)-1-(diphenylphosphoryl)methanethioamide (4). Yellow solid; mp 136−138 °C; R_f = 0.45 (PE/EA = 2:1 v/v). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.32−7.38 (m, 5H), 7.39−7.48 (m, 7H), 7.57 (t, J = 7.2 Hz, 2H), 7.89 (q, J = 6.5 Hz, 4H), 8.28 (d, J = 7.3 Hz, 1H), 10.99 (br s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 124.7, 128.0 (d, J = 15.7 Hz), 128.3 (d, J = 12.5 Hz), 128.6, 128.9 (d, J = 41.2 Hz), 129.5, 130.8, 132.5, 132.8 (d, J = 8.0 Hz), 134.9 (d, J = 10.0 Hz), 137.1 (d, J = 14.0 Hz), 196.0 (d, J = 88.9 Hz). HRMS (ESI-TOF, $[M + H]^+$): calcd for $C_{25}H_{21}NOPS$, 414.1076, found 414.1076.

Supporting Information Available: X-ray data for **3a** and **4** CIF format; ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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