Supporting Information

Visible-Light-Induced Tandem Phosphorylation Cyclization of Vinyl Azides under Mild Conditions

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1. General information

$^{1}$H NMR (400 MHz) and $^{13}$CNMR (100 MHz) spectra were recorded on a Bruker advance III 400 spectrometer in CDCl$_3$ with TMS as internal standard. $^{31}$P NMR (162 MHz) spectra and $^{19}$F NMR (376 MHz) were recorded on the same instrument. Mass spectra were measured using Thermo Scientific DSQ II. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. The safety issues for handling of azido compounds$^{[1,2]}$

2.1. Sodium azide (NaN$_3$)

Sodium azide is toxic (LD$_{50}$ oral = 27 mg/kg for rats) and can be absorbed through skin. Appropriate gloves are necessary when using it. It decomposes explosively upon heating to above 275 °C. Sodium azide is relatively safe especially in aqueous solution, unless acidified to form HN$_3$, which is volatile and highly toxic.

2.2. Organic azides

Organic azides are potentially explosive substances that can decompose with the slight input of energy from external sources (heat, light, pressure, etc). When designing the organic azides used for the project, we keep in mind the following equation. It is noted that this equation takes into account all nitrogen atoms in the organic azide, not just those in the azido group. All organic azides prepared in this work are satisfied with the equation above and they are enough stable to be stored under –20 ºC at least for 6 months. We have never experienced a safety problem with these materials.

$$\frac{N_C + N_O}{N_N} > 3 \quad (N_C: \text{number of the carbon atom, } N_O: \text{number of the oxygen atom, } N_N: \text{number of the carbon atom})$$

3. Synthesis of biaryl vinyl azides

3.1. Synthesis of biaryl alkenes

Biaryl alkenes were prepared by a two-step sequences including Suzuki-Miyaura coupling and Wittig reaction. The preparation of biaryl alkenes was described in previous reports, and the NMR spectroscopy was consisted with those data.$^{[1]}$

A general procedure for synthesis of biaryl alkene S1(R$_1$ =H, R$_2$ = Me):  

To a solution of 2-bromobenzaldehyde (9.41 g, 50.9 mmol) and p-tolylboronic acid (8.31 g, 61.1 mmol) in ethanol (60 mL) and 1,2-dimethoxyethane (DME) (80 mL) was added an aqueous solution of Na$_2$CO$_3$ 2M (100 mL, 200 mmol), followed by Pd(PPh$_3$)$_4$ (4.62 g, 4.0 mmol). The reaction was stirred at 90 °C under nitrogen atmosphere for 6 h. After completion, the reaction mixture was filtered through a short pad of celite and washed with Et$_2$O. The aqueousphase was extracted with Et$_2$O three times. The organic fractions were washed with brine, dried over MgSO$_4$, and concentrated under reduced pressure. The crude product was purified by column...
chromatography (hexane : EtOAc = 95 : 5) to biphenyl-2-carbaldehyde.

To a suspension of MePPh₃Br (27.29 g, 76.4 mmol) in THF (120 mL), t-BuOK (8.57 g, 76.4 mmol) was added portionwise. The reaction was allowed to stir at room temperature for 30 min. It was then cooled to -78°C and a solution of the intermediate aldehyde (8.81 g, 48.3 mmol) in THF (50 mL) was added dropwise. The mixture was stirred at -78°C for 1 h and then warmed to room temperature for 1 h. The reaction was quenched with water. The aqueous phase was extracted with Et₂O three times. The organic fractions were washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane : EtOAc = 97 : 3) to afford 2-vinylbiphenyl from 2-bromobenzaldehyde S₁.

All biaryl alkenes S were prepared through the same synthetic route as that of S₁.

3.2. Synthesis of biaryl vinyl azides (Hassner’s method)

A general procedure of method A (R₁ = H, R₂ = Me): this procedure was slightly modified from Hassner’s method.[3]

To a suspension of NaN₃ (2.119 g, 32.4 mmol) in acetonitrile (8.0 mL) was added dropwise a solution of iodine monochloride (3.175 g, 19.6 mmol) in CH₂Cl₂ (30 mL) at 0 °C. The mixture was stirred at the same temperature for 30 min and then cooled to -50 °C. A solution of 4’-methyl-2-vinylbiphenyl (2.520 g, 13.0 mmol) in CH₂Cl₂ (15 mL) was added slowly over 30 min. After that, the mixture was further kept at the same temperature for 15 min, and then was quenched with saturated aqueous Na₂S₂O₃. The aqueous layer was extracted two times with EtOAc. The combined extracts were washed with brine and dried over MgSO₄. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification. This step only led to a single regioisomer.

To a solution of the obtained compounds above in Et₂O (30 mL) was added t-BuOK (1.602 g, 14.3 mmol) at 0 °C, and the mixture was stirred for 2 h at the same temperature. The reaction was quenched with water, and the organic materials were extracted with Et₂O. The Et₂O solution was washed with brine, and dried over MgSO₄. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography silica gel (hexane :EtOAc = 99 : 1) to give vinyl azide 2-vinyl-1,1’-biphenyl S₂ as a pale yellow liquid.

All biarylvinyl azides were prepared through the same synthetic route as that of S₂.

3.3. Characterization data of new biarylvinylazides
2-(1-azidovinyl)-4’-(trifluoromethyl)biphenyl(1e): yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.66 (2H, d, \(J = 9.0\) Hz), 7.32-7.47 (4H, m), 7.56 (2H, d, \(J = 9.0\) Hz), 4.94 (1H, s), 4.81 (1H, s); \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) 63.38; \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.22, 144.23, 138.98, 133.82, 130.30, 130.10, 129.69, 129.53, 129.25, 129.06, 128.17, 125.11, 125.16, 103.96.

\[
\begin{array}{c}
\text{MeO} \\
N_3 \\
\end{array}
\]

2-(1-azidovinyl)-2’-methylbiphenyl(1f): yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.47 (1H, m), 7.31-7.39 (2H, m), 7.15-7.25 (5H, m), 4.81 (1H, d, \(J = 3.0\) Hz), 4.63 (1H, d, \(J = 3.0\) Hz), 2.11 (3H, s); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.80, 140.46, 140.41, 135.52, 134.24, 130.58, 129.89, 129.43, 128.82, 128.70, 127.42, 127.22, 125.38, 103.24, 20.05.

\[
\begin{array}{c}
\text{MeO} \\
N_3 \\
\end{array}
\]

2-(1-azidovinyl)-2’-methoxybiphenyl(1g): yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.28-7.42 (5H, m), 7.22 (1H, d, \(J = 9.0\) Hz), 6.98 (1H, d, \(J = 9.0\) Hz), 6.90 (1H, d, \(J = 9.0\) Hz), 4.73 (1H, s), 4.42 (1H, s), 3.72 (3H, s); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.08, 144.63, 137.47, 134.76, 131.05, 130.69, 129.73, 128.84, 128.77, 128.19, 127.23, 120.45, 110.54, 102.78, 55.01.

\[
\begin{array}{c}
\text{MeO} \\
N_3 \\
\end{array}
\]

2’-(1-azidovinyl)-2,4-dimethylbiphenyl(1k): yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.46 (1H, m), 7.30-7.37 (2H, m), 7.17-7.20 (1H, m), 7.10 (1H, d, \(J = 9.0\) Hz), 7.05 (1H, d, \(J = 9.0\) Hz), 7.00 (1H, s), 4.80 (1H, s), 4.62 (1H, s), 2.31 (3H, s), 2.06 (3H, s); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 144.76, 140.59, 140.33, 134.68, 134.16, 132.33, 130.69, 130.07, 129.76, 128.72, 128.65, 128.12, 127.11, 103.20, 20.87, 19.51.

\[
\begin{array}{c}
\text{MeO} \\
N_3 \\
\end{array}
\]

2’-(1-azidovinyl)-3,5-dimethylbiphenyl(1l): yellow liquid, \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.29-7.40 (4H, m), 7.06 (2H, s), 6.97 (1H, s), 4.90 (1H, s), 4.77 (1H, s), 2.33 (6H, s); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.78, 140.70, 140.47, 137.47, 133.61, 130.37, 129.82, 129.18, 128.94, 127.11, 126.54, 103.45, 21.28.
2-(1-azidovinyl)-3-chloro-4'-methylbiphenyl(1n): yellow liquid, $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.40 (1H, d, $J = 3.0$ Hz), 7.29-7.36 (3H, m), 7.24 (1H, d, $J = 9.0$ Hz), 7.18 (2H, d, $J = 7.5$ Hz), 4.92 (1H, s), 4.79 (1H, s), 2.36 (3H, s); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.60, 138.79, 137.41, 136.29, 135.02, 132.85, 131.65, 129.77, 129.25, 128.97, 128.39, 104.05, 21.14.

2-(1-azidoprop-1-eny1)biphenyl(1o): yellow liquid. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.44-7.48 (2H, m), 7.32-7.39 (7H, m), 5.01 (1H, q, $J = 12.0$ Hz), 1.65 (3H, d, $J = 9.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.63, 140.28, 137.03, 133.92, 130.60, 130.36, 129.20, 128.82, 128.10, 127.53, 127.47, 115.89, 12.53.

4. General Procedures.

4.1. Optimization of Reaction Conditions

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<th>solvent</th>
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</tr>
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<td>10 mol % CuCl$_2$</td>
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<td>azirine</td>
<td></td>
</tr>
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<td>n.d.</td>
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1.4 10 mol % CuCl₂ 1.5 eq. K₂S₂O₃ CH₂CN n.d.
1.4 2 mol % Rhodamine B air CH₂CN trace
1.4 2 mol % Eosin Y air CH₂CN trace
1.4 2 mol % Rose bengal air CH₂CN trace
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O air CH₂CN 13%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. BPO CH₂CN n.d.
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. DICP CH₂CN 21%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. DTBP CH₂CN trace
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBHP CH₂CN trace
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP CH₂CN 43%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP THF n.d.
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP DCE 23%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP DMF trace
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP Tol n.d.
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. Na₂CO₃ CH₂CN 81%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. K₂CO₃ CH₂CN 63%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. K₂PO₄ CH₂CN 59%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. Li₂CO₃ CH₂CN 57%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. Na₂Ac CH₂CN 70%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. K₂HPO₄ CH₂CN 75%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. DABCO CH₂CN 64%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.5 eq. Na₂CO₃ CH₂CN 80%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.5 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN 90%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 2.0 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN 90%
1.4 1 mol % Ru(bpy)₂Cl₂·6H₂O 1.8 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN 66%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.8 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN n.d.
1.4 1.8 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN n.d.
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.2 eq. Na₂CO₃ CH₂CN n.d.
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.8 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN 71%
1.4 2 mol % Ru(bpy)₂Cl₂·6H₂O 1.8 eq. TBPP 1.2 eq. Na₂CO₃ CH₂CN n.d.

^ Reaction conditions: a solution of 1a, 2a, oxidant and photocatalyst (1equiv.=0.2 mmol) in the indicated solvent (0.1 M) was irradiated by 3W blue LED lamp at rt for 12 h under Ar. b Isolated yield. c at 80 °C. d No irradiation. e Irradiated by 3W green LED lamp. f Irradiated by 9W white LED lamp.

3-((1,1'-biphenyl]-2-yl)-2H-azirine: Colorless liquid, ¹H NMR (300 MHz, CDCl₃) δ 8.04-8.01 (1H, m), 7.33-7.63 (8H, m), 1.50 (2H, s); ¹³C NMR (75 MHz, CDCl₃) δ 166.02, 143.74, 138.50, 132.34, 130.61, 130.23, 129.62, 127.80, 127.65, 123.15, 21.72.
4.2. General procedure for Phosphoryl radical onto vinyl azides

\[
\text{Ph}_3\text{P} + \text{HP(O)}\text{Ph}_2 \xrightarrow{\text{2 mol \% Ru(bpy)_3Cl}_2\cdot6\text{H}_2\text{O}} \xrightarrow{1.8 \text{ equiv. BzOO}^\text{Bu}} \xrightarrow{1.2 \text{ equiv. Na}_2\text{CO}_3} \xrightarrow{3 \text{ W blue LED lamp}} \text{PhCONPh}
\]
A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with vinyl azides (0.42 mmol, 1.4 equiv.), Ru(bpy)$_3$Cl$_2$6H$_2$O (0.006 mmol, 0.02 equiv.), HP(O)R$_4$R$_5$ (0.3 mmol, 1.0 equiv.), Na$_2$CO$_3$ (0.36 mmol, 1.2 equiv.). The flask was evacuated and backfilled with Ar for 3 times. tert-butylbenzoperoxoate (0.54 mmol, 1.8 equiv.) and CH$_3$CN (3.0 mL, 0.1 M) were added with syringe under N$_2$. The mixture was then irradiated by a 3 W blue LED lamp (away from tube 5-10 cm) at room temperature for 12 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product.

A 10 mL round bottom flask equipped with a rubber septum and magnetic stir bar was charged with nitriles and isocyanides (0.2 mmol, 1.0 equiv.), Ru(bpy)$_3$Cl$_2$.6H$_2$O (0.004 mmol, 0.02 equiv.), HP(O)R$_4$R$_5$ (0.24 mmol, 1.2 equiv.), Na$_2$CO$_3$ (0.24 mmol, 1.2 equiv.). The flask was evacuated and backfilled with Ar for 3 times. tert-butylbenzoperoxoate (0.3 mmol, 1.5 equiv.) and CH$_3$CN (2.0 mL, 0.1 M) were added with syringe under N$_2$. The mixture was then irradiated by a 3 W blue LED lamp (away from tube 5-10 cm) at room temperature for 12 h (monitored by TLC). After substrate was consumed and the solvent was removed under vacuum, the residue was purified by column chromatography to give the product.

4.3. Characterization data of new phenanthridine

6-([diphenylphosphoryl)methyl]-3-methylphenanthridine(3a), 110 mg, Yield: 90 %, white solid (M.P. = 189-190 °C), $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.40 (2H, d, $J$ = 8.9 Hz), 8.27 (1H, d, $J$ = 8.4 Hz), 7.84-7.90 (4H, m), 7.67-7.70 (2H, m), 7.57 (1H, t, $J$ = 8.1 Hz), 7.32-7.42 (7H, m), 4.49 (2H, d, $J$ = 15.2 Hz), 2.50 (3H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 29.83; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.74(d, $J$ = 7.9 Hz), 143.27(d, $J$ = 2.2 Hz), 132.69, 132.20 (d, $J$ = 100.8 Hz), 131.54, 131.52 (d, $J$ = 2.7 Hz), 131.20 (d, $J$ = 9.5 Hz), 130.36, 128.69, 128.34, 128.12 (d, $J$ = 12.1 Hz), 127.54, 126.76, 125.61 (d, $J$ = 2.1 Hz), 121.56, 121.15, 39.76 (d, $J$ = 62.9 Hz), 21.38. HRMS calcd for C$_{27}$H$_{22}$NOP: [M+H]$^+$ 408.1512, found 408.1516.
6-((diphenylphosphoryl)methyl)phenanthridine(3b), 111 mg, Yield: 94 %, white solid (M.P. = 202-203 °C), 1H NMR (400 MHz, CDCl3) δ 8.54 (1H, d, J = 8.3 Hz), 8.45-8.48 (2H, m), 7.84-7.89 (4H, m), 7.78 (1H, t, J = 8.1 Hz), 7.56-7.68 (3H, m), 7.35-7.45 (6H, m), 4.54 (2H, d, J = 15.1 Hz); 31P NMR (162 MHz, CDCl3) δ 29.96; 13C NMR (100 MHz, CDCl3) δ 153.86 (d, J = 8.0 Hz), 143.38, 138.37, 132.69, 132.46 (d, J = 101.1 Hz), 132.31(d, J = 8.2 Hz), 131.60 (d, J = 2.6 Hz), 131.26 (d, J = 9.5 Hz), 130.53, 129.22, 128.35, 128.18 (d, J = 12.1 Hz), 127.66, 127.34, 126.64, 125.99 (d, J = 2.1 Hz), 123.53, 121.83, 39.78 (d, J = 62.9 Hz). HRMS calcd for C20H19NOP: [M+H]+ 394.1355, found 394.1358.

6-((diphenylphosphoryl)methyl)-3-methoxyphenanthridine(3c), 115 mg, Yield: 91 %, white solid (M.P. = 196-197 °C), 1H NMR (400 MHz, CDCl3) δ 8.32-8.42 (3H, m), 7.82-7.88 (4H, m), 7.72 (1H, t, J = 9.0 Hz), 7.56 (1H, t, J = 9.0 Hz), 7.37-7.46 (6H, m), 7.27 (1H, s), 7.21 (1H, dd, J = 9.0 Hz, J = 3.0 Hz), 4.52 (2H, d, J = 15.2 Hz), 3.93 (3H, s); 31P NMR (162 MHz, CDCl3) δ 29.70; 13C NMR (100 MHz, CDCl3) δ 159.85, 154.39 (d, J = 7.9 Hz), 144.85, 133.00, 132.55 (d, J = 100.8 Hz), 131.63 (d, J = 2.8 Hz), 131.29 (d, J = 9.5 Hz), 130.67, 128.23 (d, J = 12.1 Hz), 127.73, 126.30, 125.14, 123.11, 121.38, 117.70, 117.57, 109.15, 55.46, 39.89 (d, J = 62.8 Hz); HRMS calcd for C27H22NO2P: [M+H]+ 424.1461, found 424.1464.

3-chloro-6-((diphenylphosphoryl)methyl)phenanthridine(3d): 70 mg, Yield: 55 %, white solid (M.P. = 203-204 °C), 1H NMR (400 MHz, CDCl3) δ 8.49 (2H, d, J = 4.5 Hz), 8.47 (1H, d, J = 4.5 Hz), 8.38 (1H, d, J = 8.8 Hz), 7.84-7.89 (4H, m), 7.80 (1H, t, J = 8.2 Hz), 7.69 (1H, t, J = 8.0 Hz), 7.53 (1H, dd, J = 8.8 Hz, J = 2.0 Hz), 7.38-7.48 (6H, m), 4.52 (2H, d, J = 15.0 Hz); 31P NMR (162 MHz, CDCl3) δ 29.84; 13C NMR (100 MHz, CDCl3) δ 155.44 (d, J = 7.9 Hz), 143.96, 133.98, 132.36 (d, J = 101.1 Hz), 132.34, 131.79 (d, J = 2.6 Hz), 131.27 (d, J = 9.5 Hz), 131.03, 128.42, 128.32 (d, J = 11.9 Hz), 127.96, 127.74, 127.23, 126.00, 123.32, 122.11, 121.82, 39.83 (d, J = 62.5 Hz); HRMS calcd for C26H19ClNOP: [M+H]+ 428.0966, found 428.0969.
6-(((diphenylphosphoryl)methyl)-3-(trifluoromethyl)phenanthridine (3e): 119 mg, Yield: 86 %, white solid (M.P. = 205-207 °C), ¹H NMR (400 MHz, CDCl₃) δ 8.49-8.54 (3H, m), 8.13 (1H, s), 7.84-7.90 (4H, m), 7.82 (1H, t, J = 8.2 Hz), 7.74 (2H, t, J = 7.3 Hz), 7.38-7.49 (6H, m), 4.53 (2H, d, J = 14.9 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 29.84; ¹³F NMR (376 MHz, CDCl₃) δ -62.2; ¹³C NMR (100 MHz, CDCl₃) δ 155.74 (d, J = 8.0 Hz), 142.58 (d, J = 2.3 Hz), 132.32 (d, J = 101.4 Hz), 131.92, 131.83 (d, J = 2.3 Hz), 131.22 (d, J = 9.5 Hz), 131.14, 130.14 (q, J = 65.6 Hz), 128.58, 128.35 (d, J = 12.2 Hz), 128.03, 126.70 (d, J = 4.3 Hz), 126.63 (d, J = 1.6 Hz), 125.87, 122.96, 122.49 (d, J = 2.9 Hz), 122.24, 39.89 (d, J = 62.2 Hz). HRMS calcd for C₂₇H₁₉F₃NOP: [M + H]⁺ 462.1629, found 462.1236.

6-(((diphenylphosphoryl)methyl)-1-methylphenanthridine (3f): 93 mg, Yield: 76 %, white solid (M.P. = 147-149 °C), ¹H NMR (400 MHz, CDCl₃) δ 8.79 (1H, d, J = 8.5 Hz), 8.51 (1H, d, J = 8.0 Hz), 7.85-7.90 (4H, m), 7.75-7.79 (2H, m), 7.68 (1H, t, J = 7.4 Hz), 7.52 (1H, t, J = 7.8 Hz), 7.34-7.43 (7H, m), 4.53 (2H, d, J = 15.1 Hz), 3.04 (3H, s); ³¹P NMR (162 MHz, CDCl₃) δ 30.06; ¹³C NMR (100 MHz, CDCl₃) δ 153.51 (d, J = 7.9 Hz), 144.83, 134.85, 134.07, 132.61 (d, J = 100.8 Hz), 131.62 (d, J = 2.7 Hz), 131.32 (d, J = 9.5 Hz), 130.97, 129.75, 128.22 (d, J = 11.8 Hz), 127.73, 127.53, 126.98 (d, J = 2.2 Hz), 126.66, 126.39, 123.38, 39.77 (d, J = 63.1 Hz), 26.66. HRMS calcd for C₂₇H₂₂NOP: [M + H]⁺ 408.1512, found 408.1514.

6-(((diphenylphosphoryl)methyl)-1-methoxyphenanthridine (3g): 50 mg, Yield: 40 %, white solid (M.P. = 151-153 °C), ¹H NMR (400 MHz, CDCl₃) δ 9.50 (1H, d, J = 8.6 Hz), 8.45 (1H, d, J = 8.0 Hz), 7.84-7.89 (4H, m), 7.76 (1H, t, J = 8.2 Hz), 7.64 (1H, t, J = 7.3 Hz), 7.50-7.56 (2H, m), 7.33-7.43 (6H, m), 7.21 (1H, dd, J = 7.1 Hz, J = 2.0 Hz), 4.53 (2H, d, J = 15.2 Hz), 4.07 (3H, s); ³¹P NMR (162 MHz, CDCl₃) δ 29.98; ¹³C NMR (100 MHz, CDCl₃) δ 157.91, 154.44 (d, J = 7.6 Hz), 145.38, 132.79, 132.60 (d, J = 100.8 Hz), 131.59 (d, J = 2.7 Hz), 131.33 (d, J = 9.5 Hz), 130.41, 128.19 (d, J = 11.9 Hz), 127.84, 127.72, 127.12, 126.69, 126.34 (d, J = 2.2 Hz), 122.13, 114.33, 107.85, 55.77, 39.87 (d, J = 63.0 Hz). HRMS calcd for C₂₇H₂₃NO₂P: [M + H]⁺ 424.1461, found 424.1463.
6-((diphenylphosphoryl)methyl)-1-phenylenanthridine(3h): 104 mg, Yield: 74 %, white solid (M.P. = 183-185 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.40 (1H, d, J = 8.2 Hz), 7.87-7.93 (5H, m), 7.61 (1H, t, J = 7.5 Hz), 7.58 (1H, d, J = 8.6 Hz), 7.50 (1H, t, J = 7.7 Hz), 7.33-7.45 (12H, m), 7.50 (1H, t, J = 7.5 Hz), 4.54 (2H, d, J = 15.1 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 30.00; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.12(d, J = 7.8 Hz), 144.48, 144.07, 139.80, 132.90, 132.64 (d, J = 101.1 Hz), 131.66 (d, J = 2.6 Hz), 131.34 (d, J = 9.5 Hz), 130.46, 129.02, 128.98, 128.89, 128.25 (d, J = 11.9 Hz), 127.27 (d, J = 2.3 Hz), 127.06 (d, J = 2.0 Hz), 127.02, 126.85, 121.95, 39.70 (d, J = 63.1 Hz). HRMS calcd for C$_{32}$H$_{28}$NOP: [M+H]$^+$ 470.1668, found 470.1671.

7-chloro-6-((diphenylphosphoryl)methyl)-3-methylphenylenanthridine(3i): 113 mg, Yield: 85 %, white solid (M.P. = 202-204 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.34 (1H, d, J = 8.9 Hz), 8.26 (1H, d, J = 1.9 Hz), 8.24 (1H, d, J = 8.4 Hz), 7.83-7.89 (4H, m), 7.68 (1H, s), 7.62 (1H, dd, J = 8.8 Hz, J = 2.0 Hz), 7.36-7.45 (7H, m), 4.45 (2H, d, J = 15.2 Hz), 2.53 (3H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.56; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.75 (d, J = 7.9 Hz), 143.39 (d, J = 2.1 Hz), 138.93, 132.68, 132.47 (d, J = 101.0 Hz), 131.73 (d, J = 2.7 Hz), 131.29 (d, J = 9.5 Hz), 131.16, 130.93, 128.95, 128.88, 128.27 (d, J = 12.1 Hz), 126.75, 126.50 (d, J = 2.2 Hz), 123.41, 121.50, 120.59, 39.57 (d, J = 62.8 Hz), 21.46. HRMS calcd for C$_{27}$H$_{25}$ClNOP: [M+H]$^+$ 442.1122, found 442.1126.

6-((diphenylphosphoryl)methyl)-1,3-dimethylphenylenanthridine(3j): 95 mg, Yield: 75 %, white solid (M.P. = 171-173 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.77 (1H, d, J = 8.5 Hz), 8.45 (1H, d, J = 8.1 Hz), 7.86-7.91 (4H, m), 7.73 (1H, t, J = 7.2 Hz), 7.65 (1H, t, J = 7.4 Hz), 7.35-7.45 (7H, m), 7.29 (1H, d, J = 15.0 Hz), 4.53(2H, d, J = 15.0 Hz), 2.99 (3H, s), 2.54 (3H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 30.00; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.69 (d, J = 8.0 Hz), 143.20 (d, J = 2.2 Hz), 135.50, 134.38, 132.89 (d, J = 100.9 Hz), 132.25, 131.53 (d, J = 2.7 Hz), 131.29 (d, J = 9.5 Hz), 130.40, 129.32, 128.32, 128.23 (d, J = 12.0 Hz), 127.28, 126.83 (d, J = 2.3 Hz), 126.57, 126.48, 123.28 (d, J= 1.4 Hz), 39.24 (d, J= 64.3 Hz), 26.59, 18.65. HRMS calcd for C$_{32}$H$_{30}$NOP: [M+H]$^+$ 422.1668, found 422.1670.
6-((diphenylphosphoryl)methyl)-2,4-dimethylphenanthidine (3k): 116 mg, Yield: 92%, white solid (M.P. = 174-176 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.49 (1H, d, J = 8.3 Hz), 8.34 (1H, d, J = 8.2 Hz), 8.08 (1H, s), 7.85-7.91 (4H, m), 7.70 (1H, t, J = 8.0 Hz), 7.59 (1H, t, J = 7.2 Hz), 7.33-7.44 (6H, m), 7.30 (1H, s), 4.50 (2H, d, J = 15.1 Hz), 2.55 (3H, s), 2.50 (3H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 30.20; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 151.02 (d, J = 8.1 Hz), 140.34 (d, J = 2.2 Hz), 136.97, 135.93, 132.84 (d, J = 100.6 Hz), 132.81, 131.50 (d, J = 2.7 Hz), 131.31 (d, J = 9.4 Hz), 130.81, 129.99, 128.16 (d, J = 12.0 Hz), 127.17, 126.98, 125.88 (d, J = 2.3 Hz), 123.26, 122.11, 119.22, 39.08 (d, J = 64.3 Hz), 21.85, 18.04. HRMS calcd for C$_{39}$H$_{39}$NOP: [M+H]$^+$ at 422.1668, found 422.1670.

6-((diphenylphosphoryl)methyl)benzo[c]phenanthidine (3l): 70 mg, Yield: 53%, white solid (M.P. = 186-188 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.88-8.91 (1H, m), 8.59 (1H, d, J = 8.3 Hz), 8.45 (2H, t, J = 10.3 Hz), 7.89-7.96 (6H, m), 7.80 (1H, t, J = 7.4 Hz), 7.61-7.69 (3H, m), 7.36-7.45 (6H, m), 4.66 (2H, d, J = 15.0 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 30.14; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.33 (d, J = 8.2 Hz), 140.01 (d, J = 2.2 Hz), 133.15, 133.10, 132.74 (d, J = 100.9 Hz), 131.65 (d, J = 2.7 Hz), 131.35 (d, J = 9.4 Hz), 130.44, 128.32 (d, J = 12.0 Hz), 127.44, 127.30, 127.16, 126.51, 126.48, 124.80, 122.38, 120.44, 119.75, 39.21 (d, J = 64.2 Hz). HRMS calcd for C$_{39}$H$_{39}$NOP: [M+H]$^+$ at 444.1512, found 444.1515.

6-(1-(diphenylphosphoryl)ethyl)phenanthridine (3m): 67 mg, Yield: 55%, white solid (M.P. = 194-197 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (1H, d, J = 8.2 Hz), 8.49 (1H, d, J = 8.0 Hz), 8.39 (1H, d, J = 7.3 Hz), 8.01-8.05 (3H, m), 7.67-7.77 (4H, m), 7.57-7.64 (2H, m), 7.25-7.41 (6H, m), 4.45 (2H, td, J = 22.9 Hz, J = 7.4 Hz), 1.88 (3H, dd, J = 16.0 Hz, J = 7.2 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 34.25; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.85 (d, J = 4.1 Hz), 143.12, 132.92, 132.28 (d, J = 97.2 Hz), 131.78 (dd, J = 62.3 Hz, J = 9.0 Hz), 131.34 (dd, J = 11.3 Hz, J = 2.6 Hz), 131.11, 130.22, 129.50, 128.48, 127.99 (dd, J = 11.45 Hz, J = 3.7 Hz), 127.19, 126.78, 125.18 (d, J = 3.5 Hz), 123.35, 122.23, 121.51, 42.44 (d, J = 68.2 Hz), 15.12 (d, J = 2.3 Hz). HRMS calcd for C$_{27}$H$_{29}$NOP: [M+H]$^+$ at 408.1512, found 408.1515.
6-((bis(4-methoxyphenyl)phosphoryl)methyl)-3-methylphenanthridine(3n): 98 mg. Yield: 70 %, white solid (M.P. = 142-144 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.46 (1H, d, $J = 8.2$ Hz), 8.41 (1H, d, $J = 8.2$ Hz), 8.33 (1H, d, $J = 8.4$ Hz), 7.70-7.79 (6H, m), 7.60 (1H, t, $J = 7.4$ Hz), 7.39 (1H, d, $J = 8.1$ Hz), 6.86 (4H, dd, $J = 8.8$ Hz, $J = 2.1$ Hz), 4.45 (2H, d, $J = 15.4$ Hz), 3.76 (6H, s), 2.54 (3H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 29.96; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.70 (d, $J = 2.8$ Hz), 154.28 (d, $J = 7.8$ Hz), 143.51, 138.42, 133.11 (d, $J = 10.9$ Hz), 132.75, 130.38, 128.79, 128.33, 128.28 (d, $J = 101.6$ Hz), 126.81, 125.74 (d, $J = 2.0$ Hz), 124.64, 123.57, 121.61 (d, $J = 5.0$ Hz), 121.24, 113.70 (d, $J = 13.9$ Hz), 55.17, 40.38 (d, $J = 62.9$ Hz), 21.44. HRMS calcd for C$_{29}$H$_{26}$NO$_3$P: [M+H]$^+$ 468.1723, found 468.1724.

![Chemical structure of 6-((bis(4-methoxyphenyl)phosphoryl)methyl)-3-methylphenanthridine(3n)](image)

6-((dip-tolylphosphoryl)methyl)-3-methylphenanthridine(3o): 82 mg. Yield: 63 %, white solid (M.P. = 158-160 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 2.32 (6H, s), 2.54 (3H, s), 4.48 (2H, d, $J = 15.2$ Hz), 7.15-7.18 (4H, m), 7.40 (1H, d, $J = 8.4$ Hz), 7.61 (1H, d, $J = 7.8$ Hz), 7.70-7.77 (6H, m), 8.34 (1H, d, $J = 8.4$ Hz), 7.43-7.48 (2H, m); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 30.19; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.47, 22.61, 40.16 (d, $J = 62.8$ Hz), 121.31, 121.60, 121.66, 125.80, 126.86, 127.86, 128.36, 128.82, 128.94 (d, $J = 12.3$ Hz), 129.63 (d, $J = 103.2$ Hz), 130.42, 131.30 (d, $J = 9.9$ Hz), 132.82, 138.43, 141.93 (d, $J = 2.6$ Hz), 143.53, 154.19 (d, $J = 7.8$ Hz). HRMS calcd for C$_{29}$H$_{25}$NOP: [M+H]$^+$ 436.1825, found 436.1824.

![Chemical structure of 6-((dip-tolylphosphoryl)methyl)-3-methylphenanthridine(3o)](image)

6-((dio-tolylphosphoryl)methyl)-3-methylphenanthridine(3p): 70 mg. Yield: 54 %, white solid (M.P. = 168-170 °C). $^1$H NMR (400 MHz, CDCl$_3$) δ 8.53 (1H, t, $J = 8.2$ Hz), 8.47 (1H, t, $J = 8.2$ Hz), 8.37 (1H, t, $J = 8.4$ Hz), 8.03 (1H, t, $J = 7.5$ Hz), 8.00 (1H, t, $J = 7.7$ Hz), 7.77 (1H, t, $J = 7.4$ Hz), 7.62 (1H, t, $J = 7.6$ Hz), 7.62 (1H, s), 7.42 (1H, d, $J = 8.2$ Hz), 7.35 (2H, t, $J = 7.5$ Hz), 7.24
(3H, t, J = 7.6 Hz), 7.12 (4H, d, J = 4.5 Hz), 7.10 (1H, d, J = 4.6 Hz), 4.61 (2H, d, J = 14.7 Hz), 2.54 (3H, s), 2.24 (6H, s); $^{31}$P NMR (162 MHz CDCl$_3$) δ 32.71; $^{13}$C NMR (100 MHz CDCl$_3$) δ 154.12, 141.92 (d, J = 2.0 Hz), 138.38, 132.80, 132.22, 132.12, 131.94, 131.62, 131.59, 131.48, 130.97, 130.40, 128.78, 128.38, 128.03, 126.68, 126.00 (d, J = 2.0 Hz), 125.46, 125.34, 121.62, 121.55, 121.24 (d, J = 6.5 Hz), 39.06 (d, J = 62.5 Hz), 21.45, 21.17 (d, J = 4.2 Hz). HRMS calcd for C$_{29}$H$_{26}$NOP: [M+H]$^+$ 436.1825, found 436.1823.

![ethyl](image1)

**ethyl (3-methylphenanthridin-6-yl)methyl(phenyl)phosphinate (3q):** 27 mg. Yield: 24 %, colorless oil, $^1$H NMR (400 MHz, CDCl$_3$) δ 8.52 (1H, d, J = 8.2 Hz), 8.38 (1H, d, J = 8.4 Hz), 8.24 (1H, d, J = 8.2 Hz), 7.67-7.78 (4H, m), 7.58 (1H, t, J = 8.1 Hz), 7.42-7.47 (2H, m), 7.26-7.36 (2H, m), 3.86-4.16 (2H, m), 4.15 (2H, d, J = 18.5 Hz), 2.55 (3H, s), 1.20 (3H, t, J = 7.0 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 38.34; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.54 (d, J = 8.1 Hz), 143.64 (d, J = 2.7 Hz), 138.57, 132.85, 131.13 (d, J = 2.8 Hz), 131.88 (d, J = 9.9 Hz), 130.48 (d, J = 129.8 Hz), 130.38, 16.30 (d, J = 6.5 Hz), 129.03, 128.41, 128.19 (d, J = 13.0 Hz), 127.27, 126.65, 125.36 (d, J = 2.8 Hz), 121.80, 121.61, 121.27 (d, J = 1.5 Hz), 61.10 (d, J = 6.4 Hz), 39.32 (d, J = 91.6 Hz), 21.45. HRMS calcd for C$_{29}$H$_{26}$NOP: [M+H]$^+$ 375.1388, found 375.1386.

![2-isopropyl-5-methylcyclohexyl](image2)

**2-isopropyl-5-methylcyclohexyl(3-methylphenanthridin-6-yl)methyl(phenyl)phosphinate (3r):** 41 mg, Yield: 28 %, white solid (M.P. = 127-129 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.55 (1H, d, J = 8.2 Hz), 8.41 (2H, d, J = 8.3 Hz), 7.83-7.89 (3H, m), 7.39 (1H, t, J = 7.3 Hz), 7.66 (1H, t, J = 7.2 Hz), 7.38-7.51 (4H, m), 4.16-4.25 (1H, m), 4.10 (2H, dd, J = 17.4 Hz, J = 4.5 Hz), 2.57 (3H, s), 1.66-1.70 (2H, m), 1.45-1.51 (2H, m), 1.18-1.22 (2H, m), 0.70-0.92 (3H, m), 0.67 (3H, d, J = 6.5 Hz), 0.52 (3H, d, J = 7.0 Hz), 0.24 (3H, d, J = 6.9 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 35.46; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.84 (d, J = 9.2 Hz), 143.77, 138.48, 133.40 (d, J = 128.5 Hz), 131.92 (d, J = 2.8 Hz), 132.91, 131.67 (d, J = 10.1 Hz), 130.45, 129.16, 128.35, 128.14 (d, J = 13.0 Hz), 127.93, 126.75, 125.58 (d, J = 2.2 Hz), 121.67, 121.62, 121.41 (d, J = 1.4 Hz), 48.45 (d, J = 6.0 Hz), 42.90, 41.15, 40.23, 32.93, 31.34, 24.84, 22.42, 21.83, 21.49, 20.72, 14.63. HRMS calcd for C$_{31}$H$_{36}$NO$_2$P: [M+H]$^+$ 485.2484, found 485.2487.
6-((di-tert-butylphosphoryl)methyl)-3-methylphenanthridine (3s): 78 mg, Yield: 71 %, white solid (M.P. = 166-168 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.80 (1H, d, J = 8.1 Hz), 8.52 (1H, d, J = 8.2 Hz), 8.41 (1H, d, J = 8.4 Hz), 7.84 (1H, s), 7.79 (1H, t, J = 7.7 Hz), 7.71 (1H, t, J = 7.2 Hz), 7.45 (1H, d, J = 8.3 Hz), 3.97 (2H, d, J = 12.2 Hz), 2.58 (3H, s), 1.31 (9H, s), 1.27 (9H, s); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 60.00; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.21 (d, J = 7.0 Hz), 143.53, 138.55, 132.71, 130.67, 129.31, 128.40, 126.92, 126.09, 121.82, 121.48, 121.28, 36.82 (d, J = 44.5 Hz), 34.68 (d, J = 58.4 Hz), 26.92, 21.47. HRMS calcd for C$_{32}$H$_{36}$NOP: [M+H]$^+$ 368.2138, found 368.2139.

![Image of 6-((di-tert-butylphosphoryl)methyl)-3-methylphenanthridine (3s)]

6-((diphenylphosphoryl)methyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (5a): 68 mg, Yield: 71 %, white solid (M.P. = 233-235 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.36-8.33 (1H, m), 8.12 (1H, dd, J = 8.3 Hz, J = 4.7 Hz), 7.67-7.79 (3H, m), 7.49-7.54 (3H, m), 7.34-7.41 (3H, m), 7.10-7.22 (3H, m), 6.91-6.96 (1H, m), 6.82-6.87 (2H, m), 3.72 (2H, ddd, J = 40.8 Hz, J = 14.2 Hz, J = 14.2 Hz), 3.61 (3H, s), 1.88 (3H, d, J = 2.3 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 28.08; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.22, 158.06 (d, J = 1.9 Hz), 143.84, 139.05, 134.82 (d, J = 98.9 Hz), 133.08 (d, J = 98.9 Hz), 133.00, 131.66, 131.20 (d, J = 2.6 Hz), 130.48 (d, J = 9.5 Hz), 130.05 (d, J = 9.5 Hz), 129.95 (d, J = 2.6 Hz), 129.12, 128.22, 128.21 (d, J = 11.7 Hz), 127.19 (d, J = 11.7 Hz), 126.19, 122.77, 122.13, 115.45, 111.88, 110.75, 48.43 (d, J = 4.2 Hz), 40.94 (d, J = 70.2 Hz), 32.03 (d, J = 14.3 Hz), 29.95. HRMS calcd for C$_{33}$H$_{47}$N$_2$O$_3$P: [M+H]$^+$ 477.1726, found 477.1728.

![Image of 6-((diphenylphosphoryl)methyl)-4,6-dimethyl-4H-pyrido[4,3,2-gh]phenanthridin-5(6H)-one (5a)]

6-((diphenylphosphoryl)methyl)-4,6-dimethyl-4H-benzo[a]pyrido[4,3,2-gh]phenanthridin-5(6H)-one (5b): 62 mg, Yield: 57 %, white solid (M.P. = 199-200 °C), $^1$H NMR (400 MHz, CDCl$_3$) δ 8.96 (1H, d, J = 8.4 Hz), 8.61 (1H, d, J = 8.7 Hz), 7.97 (1H, d, J = 7.6 Hz), 7.83 (1H, d, J = 8.8 Hz), 7.80 (1H, t, J = 8.3 Hz), 7.66-7.72 (3H, m), 7.62 (1H, d, J = 7.0 Hz), 7.43 (1H, d, J = 8.8 Hz), 7.34-7.42 (3H, m), 7.24 (1H, d, J = 7.9 Hz), 7.06-7.12 (2H, m), 6.65-6.74 (3H, m), 3.70-3.78 (2H, m), 3.67 (3H, s), 1.88 (3H, d, J = 2.3 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.82; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.23 (d, J = 1.6 Hz), 157.22, 143.89, 138.93, 134.86 (d, J = 99.0 Hz), 132.98, 132.93, 132.68 (d, J = 98.8 Hz), 131.36, 131.31 (d, J = 2.5 Hz), 130.48 (d, J = 9.5 Hz), 130.03 (d, J = 9.6 Hz), 129.87 (d, J = 2.8 Hz), 129.70, 129.22, 128.50, 128.31 (d, J = 11.7 Hz), 127.75, 127.48, 127.25 (d, J = 11.8 Hz), 126.31, 126.00, 120.30, 119.41, 113.32, 110.03, 48.43 (d, J = 4.2 Hz), 40.94 (d, J = 70.2 Hz), 32.06 (d, J = 14.4 Hz), 30.15; HRMS calcd for C$_{34}$H$_{42}$N$_2$O$_3$P: [M+H]$^+$ 527.1883, found 527.1884.
6-(diphenylphosphoryl)-8-fluorophenanthridine (7a): 57 mg, Yield: 72 %, white solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 9.33 (dd, 1H, $J = 2.6$ Hz, $J = 10.2$ Hz), 8.62-8.59 (m, 1H), 8.50-8.48 (m, 1H), 8.07-8.05 (m, 1H), 7.98-7.93 (m, 4H), 7.73-7.66 (m, 2H), 7.59-7.43 (m, 7H); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.44; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -109.58; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 161.2 (d, $J = 247.8$ Hz), 155.8 (dd, $J = 4.3$ Hz, $J = 127.7$ Hz), 142.3 (d, $J = 22.6$ Hz), 132.6 (d, $J = 104.3$ Hz), 132.2 (d, $J = 9.0$ Hz), 131.1, 128.8 (d, $J = 62.7$ Hz), 128.2 (d, $J = 12.2$ Hz), 124.5 (d, $J = 8.7$ Hz), 123.8, 121.8, 120.4 (d, $J = 24.3$ Hz), 113.1 (d, $J = 23.1$ Hz); HRMS calcd for C$_{25}$H$_{17}$FNOP [M+H]$^+$ 398.1105, found 398.1103.

ethyl 6-(diphenylphosphoryl)phenanthridine-8-carboxylate (7b): 46 mg, Yield: 51 %, white solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 10.20 (d, 1H, $J = 1.2$ Hz), 8.67-8.65 (m, 1H), 8.59-8.57 (m, 1H), 8.45-8.42 (m, 1H), 8.09-8.07 (m, 1H), 8.02-7.97 (m, 2H), 7.77-7.72 (m, 2H), 7.55-7.44 (m, 2H), 4.43 (q, 2H, $J = 7.1$ Hz), 1.43 (t, 3H, $J = 7.1$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 27.12; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.9, 157.6 (d, $J = 126.5$ Hz), 143.3 (d, $J = 22.6$ Hz), 135.3 (d, $J = 6.6$ Hz), 132.6 (d, $J = 104.3$ Hz), 132.2 (d, $J = 9.2$ Hz), 131.7 (d, $J = 2.6$ Hz), 131.1, 130.8, 130.5, 129.7, 129.5, 129.1, 128.2 (d, $J = 12.0$ Hz), 127.0 (d, $J = 22.8$ Hz), 123.6 (d, $J = 2.2$ Hz), 122.5 (d, $J = 19.3$ Hz), 61.3, 14.3; HRMS calcd for C$_{28}$H$_{22}$NO$_3$P [M+H]$^+$ 452.1410, found 452.1409.

6-(diphenylphosphoryl)-8-methoxyphenanthridine (7c): 50 mg, Yield: 61 %, white solid, $^1$H NMR (400 MHz, CDCl$_3$) δ 9.02 (d, 1H, $J = 2.6$ Hz), 8.55-8.48 (m, 2H), 8.05-8.03 (m, 1H), 7.99-7.94 (m, 4H), 7.70-7.62 (m, 2H), 7.54-7.43 (m, 7H), 3.94 (s, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 158.7, 155.4 (d, $J = 128.4$ Hz), 142.0 (d, $J = 23.1$ Hz), 132.9 (d, $J = 104.0$ Hz), 132.2 (d, $J = 9.2$ Hz), 131.6 (d, $J = 2.7$ Hz), 131.0, 129.4 (d, $J = 23.0$ Hz), 128.8, 128.1 (d, $J = 12.1$ Hz), 127.6, 127.0 (d, $J = 6.7$ Hz), 124.5 (d, $J = 2.3$ Hz), 123.6, 122.6, 121.6, 107.4, 55.6; HRMS calcd for C$_{28}$H$_{20}$NO$_3$P [M+H]$^+$ 410.1304, found 410.1299.
5. References


6. Spectra