### **Supporting Information**

## Visible Light-Induced Cascade Reaction of Isocyanides and N-Arylacrylamides with Diphenylphosphine Oxide via Radical C-P and C-C Bond Formation

Chun-Xiao Li, De Shuang Tu, Rui Yao, Hong Yan\* and Chang-Sheng Lu\*

State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.

### **Table of Contents**

1.	General Information	S2
2.	Optimization of the Reaction Conditions of Radical Annulation	S3
3.	Synthesis and Characterization of Compounds	S4
4.	Gram-Scale Preparation of 3aa	<b>S18</b>
5.	Preliminary Mechanistic Studies	<b>S19</b>
6.	X-ray Crystallographic Data of Compound 3na	<b>S20</b>
7.	NMR Spectra for All Compounds	<b>S23</b>

#### **1. General Information**

Unless otherwise stated, all the reactions were performed under argon atmosphere. Solvents and reagents were used as received from suppliers unless otherwise stated. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR data were obtained on Bruker Advance III 400 MHz or 600MHz nuclear resonance spectrometers with CDCl<sub>3</sub> as solvents at ambient temperature. Chemical shifts were reported in units (ppm) by using TMS as an internal reference. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet and m = multiplet), coupling constant (J values) in Hz and integration. Chemical shifts for <sup>13</sup>C NMR spectra were recorded in ppm from chloroform using the central peak of CDCl<sub>3</sub> (77.0 ppm) as the internal standard. Biphenyl isocyanides<sup>1</sup> **1a-1n**, Vinyl isocyanides<sup>2</sup> **4a-4f** and *N*-arylacrylamides<sup>3</sup> **6a-6k** were prepared according to corresponding literature. Flash column chromatography was performed using 200-300 mesh silica with the indicated solvent system according to standard techniques. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). High resolution mass spectra were obtained using an Agilent 6210 Series TOF LC-MS or G6520B Accurate-Mass Q-TOF LC/MS equipped with electrospray ionization (ESI) probe operating in positive ion mode. The 23 W fluorescent light bulb was purchased from supermarket (daylight, energy saving, 220 V, 50 Hz).

2. Optimization of the Reaction Conditions of Radical Annulation Table S1. Visible-Light-Induced Phosphorylation/Cyclization of 1a with 2a<sup>a</sup>



	Ir-I	ir-li	FIrpic	Ru-l	
Entry	Photocatalyst	Base	Oxidant	Solvent	$\operatorname{Yield}^{b}(\%)$
1	Ir-I	K <sub>2</sub> CO <sub>3</sub>	Air (1atm)	DMF	N. D.
2	Ir-I	$K_2CO_3$	$O_2$ (1atm)	DMF	N. D.
3	Ir-I	$K_2CO_3$	$K_2S_2O_8$	DMF	56
4	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	DMF	82
5	Ir-II	$Cs_2CO_3$	$K_2S_2O_8$	DMF	71
6	FIrpic	$Cs_2CO_3$	$K_2S_2O_8$	DMF	64
$7^d$	Ru-I	$Cs_2CO_3$	$K_2S_2O_8$	DMF	trace
8	Ir-I	$Cs_2CO_3$	$Na_2S_2O_8$	DMF	73
9	Ir-I	$Cs_2CO_3$	$(NH_4)_2S_2O_8$	DMF	57
10	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	DMSO	42
11	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	NMP	28
$12^{c}$	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	DMF	18
13	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	DCM	21
14	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	MeOH	33
15	Ir-I	$Cs_2CO_3$	$K_2S_2O_8$	MeCN	38
16	Ir-I	CsF	$K_2S_2O_8$	DMF	<b>89(85)</b> <sup>f</sup>
17	Ir-I	DBU	$K_2S_2O_8$	DMF	57
18	Ir-I	Proton sponge	$K_2S_2O_8$	DMF	43
19	Ir-I	$K_2HPO_4$	$K_2S_2O_8$	DMF	38
20	Ir-I	K <sub>3</sub> PO <sub>4</sub>	$K_2S_2O_8$	DMF	46
21	Ir-I	KOAc	$K_2S_2O_8$	DMF	50
22	Ir-I	—	$K_2S_2O_8$	DMF	28
23		CsF	$K_2S_2O_8$	DMF	N. D.
$24^{e}$	Ir-I	CsF	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	DMF	N. D.

<sup>*a*</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), oxidant (entries 3-22, 0.9 mmol), base (0.6 mmol), and photocatalyst (0.003 mmol, 1 mol%) in solvent (3 mL) was irradiated by 23 W compact fluorescent light (CFL) under Ar for 12h at room temperature. <sup>*b* 31</sup>P NMR yield using methyldiphenylphosphine oxide as an internal standard. Values in parentheses indicate a yield after purification. <sup>*c*</sup> 30  $\mu$ L water was added into dried DMF. <sup>*d*</sup> Ru-I (5 mol%) <sup>*e*</sup> Reaction was performed in the dark. <sup>*f*</sup> Isolated yield.

#### 3. Synthesis and Characterization of Compounds

# General procedure for the preparation of 6-phosphorylated phenanthridines (Compounds 3aa-3qa, 3ab, 3ac, 3nd):

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, biphenyl isocyanides **1a-1q** (0.3 mmol),  $[Ir(ppy)_2(dtbpy)]PF_6$  (1 mol %, 0.003 mmol), phosphoryl species **2a-2e** (3.0 equiv, 0.9 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 equiv, 0.9 mmol), CsF (2.0 equiv. 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. 3 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 12 hours, the mixture was then diluted with 20 mL water and extract by ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, then the solvent was removed in vacuo and the residue was purified by chromatography on silica gel to afford **3aa-3qa**, **3ab**, **3ac** and **3nd**.

## *Physical data of the compounds*: (2,8-dimethylphenanthridin-6-yl)diphenylphosphine oxide (3aa)<sup>4</sup>:



White solid, PE/EA = 2/1, 103.8 mg, 85% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 9.30 (s, 1H), 8.52 (dd, J = 8.5, 1.6 Hz, 1H), 8.33 (s, 1H), 7.96-7.91 (m, 5H), 7.65 (dd, J = 8.49, 1.55 Hz, 1H), 7.52–7.42 (m, 7H), 2.61 (s, 3H), 2.55 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.9 (d, J = 129.8 Hz), 140.8 (d, J = 23.5 Hz), 138.9, 137.8, 133.3 (d, J = 104.6 Hz), 132.6, 132.3 (d, J = 9.2 Hz), 131.5 (d, J = 2.7 Hz), 130.7 (d, J = 1.3 Hz), 130.2 (d, J = 7.0 Hz), 129.9, 128.4, 128.0 (d, J = 12.0 Hz), 127.6, 124.3 (d, J = 2.5 Hz), 121.9 (d, J = 1.6 Hz), 121.4 (d, J = 1.0 Hz), 22.1, 21.9; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 28.07; HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOPNa [M+Na]<sup>+</sup> m/z 430.1331, found 430.1320.

(2-methylphenanthridin-6-yl)diphenylphosphine oxide (3ba)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/2$ , 88.4 mg, 75% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.48 (d, J = 8.3, 1H), 8.63 (d, J = 8.4, 1H), 8.37 (s, 1H), 7.96-7.91 (m, 5H), 7.82 (t, J = 7.8, 1H), 7.67 (t, J = 7.8, 1H), 7.54-7.42 (m, 7H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  155.5 (d, J = 129.6 Hz), 141.1 (d, J = 23.6 Hz), 139.0, 133.0 (d, J = 104.6 Hz), 132.3 (d, J = 9.1 Hz), 131.6, 130.8, 130.7,

130.4, 128.4, 128.1 (d, J = 12.0 Hz), 128.0, 127.8, 127.6, 124.2, 122.0, 121.6, 22.1; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  28.43; HRMS (ESI) calculated for C<sub>26</sub>H<sub>20</sub>NOPNa [M+Na]<sup>+</sup> m/z 416.1180, found 416.1173.

6-(diphenylphosphoryl)-8-methoxy-2-methylphenanthridine (3ca)<sup>4</sup>:



White solid,  $PE/Et_2O = 2/3$ , 76.1 mg, 60% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 9.00 (d, J = 2.6, 1H), 8.52 (dd, J = 9.2, 1.7 Hz, 1H), 8.28 (s, 1H), 8.00-7.90 (m, 5H), 7.53-7.42 (m, 8H), 3.93 (s, 3H), 2.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.7, 154.1 (d, J = 130.5 Hz), 140.5 (d, J = 23.3 Hz), 139.0, 133.2 (d, J = 104.4 Hz), 132.3 (d, J = 9.2Hz), 131.5 (d, J = 2.7 Hz), 130.8 (d, J = 1.1 Hz), 129.5 (d, J = 23.1 Hz), 129.4, 128.1 (d, J = 12.1 Hz), 126.7 (d, J = 6.9 Hz), 124.4 (d, J = 2.5 Hz), 123.6 (d, J = 1.6 Hz), 122.3, 121.1 (d, J = 1.0 Hz), 107.4, 55.6, 22.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 29.53; HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 446.1286, found 446.1278.

6-(diphenylphosphoryl)-8-fluoro-2-methylphenanthridine (3da)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/1$ , 93.7 mg, 76% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.29 (dd, J = 10.2, 2.7 Hz, 1H), 8.62 (ddd, J = 9.1, 5.3, 1.6 Hz, 1H), 8.31 (s, 1H), 7.97-7.92 (m, 5H), 7.59-7.43 (m, 8H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 161.1 (d, J = 248.9 Hz), 154.58 (dd, J = 129.8, 4.4 Hz), 140.85 (dd, J = 23.0, 1.0 Hz), 139.6, 133.2, 132.3 (d, J = 9.3 Hz), 132.2, 131.7 (d, J = 2.8 Hz), 130.9, 130.3, 129.0, 128.2 (d, J = 12.2 Hz), 124.5 (dd, J = 8.6, 1.4 Hz), 123.8 (dd, J = 2.2, 1.0 Hz), 121.4, 120.2 (d, J = 24.4 Hz), 113.0 (d, J = 23.1 Hz), 22.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 27.40; HRMS (ESI) calculated for C<sub>26</sub>H<sub>19</sub>FNOPNa [M+Na]<sup>+</sup> m/z 434.1086, found 434.1078.

(8-chloro-2-methylphenanthridin-6-yl)diphenylphosphine oxide (3ea)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/1$ , 82.0 mg, 64% yield.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 9.63 (d, J = 2.1 Hz, 1H), 8.54 (dd, J = 8.9, 1.6 Hz, 1H), 8.30 (s, 1H), 7.97-7.92 (m, 5H), 7.75 (dd, J = 8.9, 2.2 Hz, 1H), 7.54-7.44 (m, 7H), 2.62 (s, 3H); <sup>13</sup>**C NMR (150 MHz, CDCl<sub>3</sub>)**: δ 154.5 (d, J = 129.2 Hz), 141.1 (d, J = 22.9 Hz), 139.6, 133.8, 133.2, 132.4, 132.3 (d, J = 9.1 Hz), 131.7 (d, J = 2.4 Hz), 131.5, 130.9, 130.8, 128.8 (d, J = 23.0 Hz), 128.2 (d, J = 12.3 Hz), 127.5, 123.7, 123.6, 121.5, 22.2; <sup>31</sup>**P NMR (162 MHz, CDCl<sub>3</sub>)**: δ 27.25; **HRMS** (ESI) calculated for C<sub>26</sub>H<sub>19</sub>CINOPNa [M+Na]<sup>+</sup> *m/z* 450.0790, found 450.0782.

(8-(tert-butyl)-2-methylphenanthridin-6-yl)diphenylphosphine oxide (3fa)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/1$ , 78.2 mg, 61% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.36 (d, J = 1.8 Hz, 1H), 8.55 (dd, J = 8.8, 1.5 Hz, 1H), 8.34 (s, 1H), 7.99-7.95 (m, 5H), 7.89 (dd, J = 8.7, 1.9 Hz, 1H), 7.53-7.42 (m, 7H), 2.62 (s, 3H), 1.37 (s, 9H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 155.8 (d, J = 129.8 Hz), 150.6, 141.0 (d, J = 23.4 Hz), 138.8, 133.2 (d, J = 104.2 Hz), 132.2 (d, J = 9.2 Hz), 131.4(d, J = 2.7 Hz), 130.8 (d, J = 1.1 Hz), 130.1 (d, J = 6.8 Hz), 130.0, 129.0, 128.1 (d, J = 12.1 Hz), 127.7 (d, J = 23.2 Hz), 124.3, 124.2 (d, J = 2.5 Hz), 121.8 (d, J = 1.6 Hz), 35.1, 31.1, 22.1; <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>): δ 27.63; **HRMS** (ESI) calculated for C<sub>30</sub>H<sub>28</sub>NOPNa [M+H]<sup>+</sup> *m/z* 450.1981, found 450.1984.

(2-methyl-8-(trifluoromethyl)phenanthridin-6-yl)diphenylphosphine oxide (3ga):



White solid, PE/EA = 2/1, 88.5 mg, 64% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 10.00 (s, 1H), 8.70 (d, J = 8.8 Hz, 1H), 8.35 (s, 1H), 8.02-7.96 (m, 6H), 7.61 (dd, J = 8.4, 1.5 Hz, 1H), 7.54-7.50 (m, 2H), 7.48-7.43 (m, 4H), 2.64 (s, 3H); <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>): δ 155.6 (d, J = 128.4 Hz), 141.7 (d, J = 22.7 Hz), 139.8, 134.3 (d, J = 6.4 Hz), 132.6 (d, J = 105.1 Hz), 132.2 (d, J = 9.2Hz), 131.8 (d, J = 2.8 Hz), 131.6, 130.9 (d, J = 0.8 Hz), 129.3 (q, J = 32.8 Hz), 128.2 (d, J = 12.2 Hz), 127.2 (d, J = 23.1 Hz), 126.6 (q, J = 3.1 Hz), 126.1 (q, J = 4.3 Hz), 125.2, 123.2 (d, J = 2.4 Hz), 123.1 (d, J = 1.4 Hz), 122.3, 121.9 (d, J = 0.6 Hz), 22.1; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 26.91; HRMS (ESI) calculated for C<sub>27</sub>H<sub>19</sub>F<sub>3</sub>NOPNa [M+Na]<sup>+</sup> m/z 484.1054, found 484.1048.

(10-methoxy-2-methylphenanthridin-6-yl)diphenylphosphine oxide (3ha):



White solid, PE/EA = 3/1, 68.5 mg, 54% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.31 (s, 1H), 9.10 (d, J = 8.2 Hz, 1H), 7.93-7.87 (m, 5H), 7.61 (t, J = 8.1 Hz, 1H), 7.53-7.48 (m, 3H), 7.45-7.41 (m, 4H), 7.29 (d, J = 7.9 Hz, 1H), 4.12 (s, 3H), 2.63 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 158.0 (d, J = 2.9 Hz), 155.0 (d, J = 130.8 Hz), 141.7 (d, J = 23.6 Hz), 138.8, 133.0 (d, J = 105.2 Hz), 132.3 (d, J = 9.2 Hz), 131.5 (d, J = 2.8 Hz), 130.6 (d, J = 1.1 Hz), 129.8 (d, J = 24.2 Hz), 129.6, 128.0 (d, J = 12.1 Hz), 127.9, 127.5 (d, J = 0.7 Hz), 124.0 (d, J = 2.6 Hz), 122.8 (d, J = 7.1 Hz), 120.6 (d, J = 0.8 Hz), 111.8, 55.7, 22.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 29.34; HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> *m/z* 446.1286, found 446.1281.

(2-methylbenzofuro[3,2-k]phenanthridin-6-yl)diphenylphosphine oxide (3ia)<sup>4</sup>:



White solid,  $PE/Et_2O = 2/3$ , 69.6 mg, 48% yield.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**: δ 9.56 (d, J = 8.6 Hz, 1H), 9.41 (s, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.08 (d, J = 7.6 Hz, 1H), 8.00-7.94 (m, 5H), 7.83 (d, J = 8.3 Hz, 1H), 7.62-7.42 (m, 9H), 2.75 (s, 3H); <sup>13</sup>**C NMR (100 MHz, CDCl<sub>3</sub>)**: δ 156.6, 155.1 (d, J = 130.1 Hz), 151.9 (d, J = 3.1 Hz), 141.6 (d, J = 23.5 Hz), 139.6, 133.0 (d, J = 105.2 Hz), 132.4 (d, J = 9.2 Hz), 131.6 (d, J = 2.6 Hz), 130.6, 130.5, 128.1 (d, J = 12.2 Hz), 127.9, 127.6 (d, J = 24.1 Hz), 126.6, 125.4, 123.5, 123.36, 123.33, 122.3 (d, J = 2.4 Hz), 121.1, 120.2, 120.1, 112.0, 22.5; <sup>31</sup>**P NMR (162 MHz, CDCl<sub>3</sub>**): δ 28.95; **HRMS** (ESI) calculated for C<sub>33</sub>H<sub>22</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 506.1286, found 506.1282.

(9-methylbenzo[c][2,7]naphthyridin-5-yl)diphenylphosphine oxide (3ja)<sup>4</sup>:



White solid, EA only, 79.2 mg, 67% yield.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)**:  $\delta$  10.76 (s, 1H), 8.91 (d, J = 5.8 Hz, 1H), 8.38 (d, J = 5.6 Hz, 1H), 8.35 (s, 1H), 8.02-7.92 (m, 5H), 7.67 (dd, J = 8.4, 1.6 Hz, 1H), 7.53-7.44

(m, 6H), 2.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  156.2 (d, J = 127.8 Hz), 152.2, 148.2, 142.3 (d, J = 22.4 Hz), 140.0, 137.1 (d, J = 6.6 Hz), 132.8, 132.3 (d, J = 105.3 Hz), 132.2 (d, J = 9.4 Hz), 131.9 (d, J = 2.8 Hz), 131.0 (d, J = 1.2 Hz), 128.3 (d, J = 12.3 Hz), 123.1 (d, J = 23.0 Hz), 122.1 (d, J = 0.6 Hz), 122.0 (d, J = 2.3 Hz), 115.4, 22.1; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  27.36; HRMS (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOPNa [M+Na]<sup>+</sup> m/z 417.1133, found 417.1128.

(2-methyl-[1,3]dioxolo[4,5-j]phenanthridin-6-yl)diphenylphosphine oxide (3ka)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/2$ , 61.6 mg, 47% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.98 (s, 1H), 8.14 (s, 1H), 7.95-7.89 (m, 6H), 7.52-7.41 (m, 7H), 6.11 (s, 2H), 2.60 (s, 3H); <sup>13</sup>C **NMR** (100 MHz, CDCl<sub>3</sub>): δ 153.3 (d, J = 130.7 Hz), 151.1, 148.2, 140.9 (d, J = 23.4 Hz), 138.5, 133.1 (d, J = 104.8 Hz), 132.3 (d, J = 9.2 Hz), 131.6 (d, J = 2.6 Hz), 130.7 (d, J = 1.1 Hz), 130.5 (d, J = 7.3Hz), 129.9, 128.1 (d, J = 12.2Hz), 125.1 (d, J = 23.8 Hz), 124.4 (d, J = 2.4 Hz), 121.3, 105.5, 102.0, 99.8 (d, J = 1.6 Hz), 22.1; <sup>31</sup>P **NMR** (162 MHz, CDCl<sub>3</sub>): δ 28.21; **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOPNa [M+Na]<sup>+</sup> m/z 460.1078, found 460.1071.

Phenanthridin-6-yldiphenylphosphine oxide (3la)<sup>4</sup>:



White solid, PE/EA = 2/1, 96.9 mg, 85% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.52 (d, J = 8.3 Hz, 1H), 8.66 (d, J = 8.3 Hz, 1H), 8.61-8.59 (m, 1H), 8.07-8.05 (m, 1H), 7.97-7.92 (m, 4H), 7.85 (t, J = 7.5 Hz, 1H), 7.75-7.68 (m, 3H), 7.54-7.73 (m, 6H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 156.8 (d, J = 128.6 Hz), 142.7 (d, J = 23.3 Hz), 133.3, 132.6 (d, J = 6.8 Hz), 132.293 (d, J = 9.2 Hz), 132.28, 131.7 (d, J = 2.6 Hz), 131.1, 130.0, 128.8, 128.66, 128.55, 128.2 (d, J = 12.2 Hz), 127.9, 127.8 (d, J = 23.2 Hz), 124.3 (d, J = 2.2 Hz), 122.1; <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>): δ 28.19; **HRMS** (ESI) calculated for C<sub>25</sub>H<sub>18</sub>NOPNa [M+Na]<sup>+</sup> m/z 402.1024, found 402.1015.

(2,4-dimethylphenanthridin-6-yl)diphenylphosphine oxide (3ma)<sup>4</sup>:



White solid,  $PE/Et_2O = 1/2$ , 72.0 mg, 59% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.39 (d, J = 8.2 Hz, 1H), 8.63 (d, J = 8.4 Hz, 1H), 8.22 (s, 1H), 7.92-7.87 (m, 4H), 7.80 (td, J = 7.7, 1.0, 1H), 7.65(td, J = 7.7, 0.8, 1H), 7.53-7.40 (m, 7H), 2.58 (s, 3H), 2.45 (s, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 153.9 (d, J = 131.3 Hz), 140.0 (d, J = 22.8 Hz), 138.8 (d, J = 1.3 Hz), 138.7, 133.1 (d, J =99.7 Hz), 132.6 (d, J = 1.6 Hz), 132.3 (d, J = 9.2 Hz), 131.5 (d, J = 2.7 Hz), 131.3, 130.5, 128.3, 128.1 (d, J = 12.1 Hz), 127.58 (d, J = 23.9 Hz), 127.54, 124.2 (d, J = 2.5Hz), 122.3 (d, J = 1.5 Hz), 119.4 (d, J = 1.0 Hz), 22.1, 17.9; <sup>31</sup>**P NMR** (162 MHz, **CDCl**<sub>3</sub>): δ 29.72; **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>22</sub>NOPNa [M+Na]<sup>+</sup> *m/z* 430.1337, found 430.1328.

(2-chlorophenanthridin-6-yl)diphenylphosphine oxide (3na):



White solid, PE/EA = 2/1, 101.6 mg, 82% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.50 (d, J = 8.3 Hz, 1H), 8.57-8.54 (m, 2H), 7.99-7.84 (m, 6H), 7.72 (t, J = 7.4 Hz, 1H), 7.65 (dd, J = 8.7, 2.2 Hz, 1H), 7.53-7.26 (m, 6H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 157.2 (d, J = 127.8 Hz), 141.1 (d, J = 23.5 Hz), 134.9, 132.61 (d, J = 105.2 Hz), 132.56, 132.2 (d, J = 9.3 Hz), 131.8 (d, J = 2.5 Hz), 131.6 (d, J = 6.6 Hz), 131.3, 129.3, 128.6 (d, J = 14.7 Hz), 128.2 (d, J = 12.2 Hz), 127.9 (d, J = 22.8 Hz), 125.4 (d, J = 2.2 Hz), 122.1, 121.8; <sup>31</sup>**P NMR** (162 MHz, **CDCl<sub>3</sub>**): δ 28.42; **HRMS** (ESI) calculated for C<sub>25</sub>H<sub>17</sub>ClNOPNa [M+Na]<sup>+</sup> *m/z* 436.0634, found 436.0624.

(3-fluorophenanthridin-6-yl)diphenylphosphine oxide (3qa)



White solid, PE/EA = 2/1, 60.7 mg, 51% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.50 (d, J = 8.3 Hz, 1H), 8.67-8.47 (m, 2H), 8.01-7.79 (m, 5H), 7.68 (t, J = 7.3 Hz, 2H), 7.56-7.36 (m, 7H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ 162.4 (d, J = 249.3 Hz), 158.4 (d, J = 126.8 Hz), 143. 8 (dd, J = 23.6, 11.7 Hz), 133.1, 132.4 (d, J = 6.9 Hz), 132.23 (d, J = 9.3 Hz), 132.0, 131.8 (d, J = 2.8 Hz), 131.4, 128.21 (d, J = 99.8 Hz), 128.20 (d, J = 12.2 Hz), 127.4 (d, J = 22.8 Hz), 124.10

(dd, J = 9.3, 0.9 Hz), 121.9, 121.03 (t, J = 2.2 Hz), 117.94 (d, J = 24.0 Hz), 115.31 (dd, J = 20.2, 0.9 Hz) <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  28.49; HRMS (ESI) calculated for C<sub>25</sub>H<sub>17</sub>FNOPNa [M+Na]<sup>+</sup> *m/z* 420.0929, found 420.0930.

(2,8-dimethylphenanthridin-6-yl)di-p-tolylphosphine oxide (3ab):



White solid, PE/EA = 2/1, 108.3 mg, 83% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 9.29 (s, 1H), 8.47 (d, J = 8.3 Hz, 1H), 8.29 (s, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.80 (dd, J = 11.2, 8.1 Hz, 4H), 7.60 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.23 (d, J = 6.2 Hz, 4H), 2.58 (s, 3H), 2.53 (s, 3H), 2.35 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ155.3 (d, J = 129.5 Hz), 141.8 (d, J = 2.8 Hz), 140.8 (d, J = 23.4 Hz), 138.2 (d, J = 104.0 Hz), 132.5, 132.2 (d, J = 9.5 Hz), 130.7 (d, J = 0.8 Hz), 130.6, 130.1 (d, J = 6.9 Hz), 129.8, 129.5, 128.8 (d, J = 12.5 Hz), 128.2 (d, J = 23.1 Hz), 127.6, 124.2 (d, J = 2.5 Hz), 121.8 (d, J = 1.3 Hz), 121.3 (d, J = 0.7Hz), 22.12, 21.8, 22.51, 22.50; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 28.67; HRMS (ESI) calculated for C<sub>29</sub>H<sub>16</sub>NOPNa [M+Na]<sup>+</sup> m/z 458.1650, found 458.1652.

*tert*-butyl(2,8-dimethylphenanthridin-6-yl)(phenyl)phosphine oxide (3ac):



White solid, PE/EA = 2/1, 74.3 mg, 64% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.25 (s, 1H), 8.48 (dd, J = 8.4, 1.0 Hz, 1H), 8.34 (s, 1H), 8.17 (d, J = 8.3 Hz, 1H), 8.13 – 8.06 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.49 – 7.36 (m, 3H), 2.64 (s, 3H), 2.49 (s, 3H), 1.44 (d, J = 15.0 Hz, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ155.7 (d, J = 116.5 Hz), 140.35 (d, J = 21.8 Hz), 138.17 (d, J = 116.4 Hz), 132.78 (d, J = 7.8 Hz), 132.4, 131.6, 131.2 (d, J = 2.7 Hz), 130.8, 130.3 (d, J = 1.0 Hz), 130.04, 129.98, 128.6 (d, J = 20.2 Hz), 127.8, 127.7, 124.22 (d, J = 2.4 Hz), 121.68 (d, J = 1.2 Hz), 121.5, 35.8 (d, J = 70.8 Hz), 25.3, 22.1, 21.8; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 38.83; HRMS (ESI) calculated for C<sub>25</sub>H<sub>26</sub>NOPNa [M+Na]<sup>+</sup> *m/z* 410.1650, found 410.1652

ethyl (2-chlorophenanthridin-6-yl)(phenyl)phosphinate (3nd):



White solid, PE/EA = 3/1, 27.9 mg, 23% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 9.32 (d, J = 8.1 Hz, 1H), 8.57-8.54 (m, 2H), 8.13 (d, J = 8.7 Hz, 1H), 8.06-8.01 (m, 2H), 7.88 (td, J = 7.8, 1.2Hz, 1H), 7.77 (td, J = 7.8, 1.0Hz, 1H), 7.68 (dd, J = 8.7, 2.2 Hz, 1H), 7.56-7.45 (m, 3H), 4.48-4.27 (m, 2H), 1.47 (t, J = 7.0 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 156.1 (d, J = 161.1 Hz), 141.3 (d, J = 21.2 Hz), 134.9, 132.7, 132.4, 131.8 (d, J = 169.3 Hz), 131.6 (d, J = 8.0 Hz), 130.9, 130.0, 129.4, 128.5 (d, J = 13.1 Hz), 128.3 (d, J = 13.4 Hz), 127.0 (d, J = 26.5 Hz), 125.6 (d, J = 1.4 Hz), 122.2, 121.7, 62.4 (d, J = 6.5 Hz), 16.6 (d, J = 6.4 Hz); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 28.58; HRMS (ESI) calculated for C<sub>21</sub>H<sub>17</sub>ClNO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 404.0583, found 404.0575.

# General procedure for the preparation of 1-(diphenylphosphoryl) isoquinolines (Compounds 5aa-5fa):

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **4a-4f** (0.3 mmol),  $[Ir(ppy)_2(dtbpy)]PF_6$  (1 mol%, 0.003 mmol), diphenylphosphine oxide **2a** (3.0 equiv, 0.9mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 equiv, 0.9mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv. 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. 3 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 20 hours, the mixture was then diluted with 20mL water and extract by ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, and then the solvent concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the **5aa-5fa**.

#### Methyl 1-(diphenylphosphoryl)-4-phenylisoquinoline-3-carboxylate (5aa):



White solid, PE/EA = 2/1, 86.1 mg, 62% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.68 (d, J = 8.4 Hz, 1H), 8.08 (dd, J = 11.6, 7.0 Hz, 4H), 7.74-7.67 (m, 3H), 7.51-7.45 (m, 9H), 7.34-7.32 (m, 2H), 3.65 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.8, 155.1 (d, J = 128.6 Hz), 140.1 (d, J = 21.5 Hz), 136.0 (d, J = 3.0 Hz), 135.9 (d, J = 7.1 Hz), 135.4 (d, J = 1.0 Hz), 132.8 (d, J = 105.1 Hz), 132.4 (d, J = 9.2 Hz), 131.695 (d, J = 2.7 Hz), 131.705 (d, J = 22.0 Hz), 131.0,

129.40, 129.38, 128.2, 128.0, 127.1 (d, J = 23.0 Hz), 52.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  24.75; HRMS (ESI) calculated for C<sub>29</sub>H<sub>22</sub>NO<sub>3</sub>PNa [M+Na]<sup>+</sup> *m/z* 486.1235, found 486.1229.

Methyl 1-(diphenylphosphoryl)-7-methyl-4-(p-tolyl)isoquinoline-3-carboxylate (5ba):



White solid, PE/EA = 2/1, 63.4 mg, 43% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.45 (s, 1H), 8.10-8.04 (m, 4H), 7.59 (dd, J = 8.7, 1.7 Hz, 1H), 7.53-7.43 (m, 7H), 7.31 (s, 1H), 7.29 (s, 1H), 7.21 (s, 1H), 7.19 (s, 1H), 3.68 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.9, 153.6 (d, J = 129.8 Hz), 140.0, 139.3 (d, J = 23.6 Hz), 137.8, 136.3 (d, J = 3.0 Hz), 134.3 (d, J = 7.0 Hz), 133.2, 133.1 (d, J = 104.9 Hz), 132.5 (d, J = 1.2 Hz), 132.4 (d, J = 9.1 Hz), 132.1 (d, J = 22.1 Hz), 131.6 (d, J = 2.7 Hz), 129.2, 128.9, 128.1 (d, J = 12.2 Hz), 126.9 (d, J = 0.6 Hz), 125.8, 52.1, 22.1, 21.3; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  24.59; HRMS (ESI) calculated for C<sub>31</sub>H<sub>26</sub>NO<sub>3</sub>PNa [M+Na]<sup>+</sup> m/z 514.1548, found 514.1540.

#### Methyl

7-chloro-4-(4-chlorophenyl)-1-(diphenylphosphoryl)isoquinoline-3-carboxylate (5ca):



Pale yellow solid, PE/EA = 2/1, 111.5 mg, 70% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.84 (d, J = 1.8 Hz, 1H), 8.11-8.06 (m, 4H), 7.63-7.46 (m, 10H), 7.24 (d, J = 8.4 Hz, 2H), 3.71 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  166.2, 154.8 (d, J = 127.4 Hz), 140.0 (d, J = 20.8 Hz), 136.1, 134.9 (d, J = 2.8 Hz), 134.7, 134.2 (d, J = 6.8 Hz), 133.4 (d, J = 0.9 Hz), 133.0, 132.5, 132.4, 132.3, 132.2, 131.9 (d, J = 2.9 Hz), 130.7, 128.7, 128.3, 128.2, 126.2, 52.4; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  23.81; HRMS (ESI) calculated for C<sub>29</sub>H<sub>20</sub>Cl<sub>2</sub>NO<sub>3</sub>PNa [M+Na]<sup>+</sup> *m/z* 554.0456, found 554.0451.

(1-(diphenylphosphoryl)-4-phenylisoquinolin-3-yl)(pyrrolidin-1-yl)methanone (5da):



White solid, PE/EA = 2/1, 91.9 mg, 61% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.49 (dd, J = 6.7, 2.6 Hz, 1H), 7.92-7.88 (m, 4H), 7.74-7.61 (m, 3H), 7.52-7.36 (m, 11H), 3.33 (t, J = 7.0 Hz, 2H), 2.71 (t, J = 6.8 Hz, 2H), 1.67 (p, J = 6.8 Hz, 2H), 1.52 (p, J = 6.8 Hz, 2H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 166.4, 154.4 (d, J = 132.1 Hz), 146.1 (d, J = 21.5 Hz), 135.8 (d, J = 7.2 Hz), 134.6, 132.7 (d, J = 3.0 Hz), 132.5 (d, J = 105.6 Hz), 132.3 (d, J = 9.4 Hz), 131.7 (d, J = 2.5 Hz), 131.1, 130.90, 130.87, 129.9, 128.4 (d, J = 7.1 Hz), 128.3, 128.1 (d, J = 12.2 Hz), 126.7 (d, J = 88.9 Hz), 47.2, 45.2, 25.7, 24.2; <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>): δ 28.57; **HRMS** (ESI) calculated for C<sub>32</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 525.1708, found 525.1704.

(1-(diphenylphosphoryl)-4-phenylisoquinolin-3-yl)(piperidin-1-yl)methanone (5ea):



White solid, PE/EA = 2/1, 102.2 mg, 66% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 9.46 (m, 1H), 7.94-7.89 (m, 4H), 7.72-7.62 (m, 3H), 7.49-7.40 (m, 11H), 3.44-3.34 (m, 2H), 2.83-2.72 (m, 2H), 1.45-1.30 (m, 4H), 0.92-0.80 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.6, 154.7 (d, J = 128.4 Hz), 145.7 (d, J = 21.5 Hz), 135.7 (d, J = 7.2 Hz), 133.6 (d, J = 128.8 Hz), 132.3 (d, J =9.3 Hz), 132.1 (d, J = 3.0 Hz), 131.9, 131.6 (d, J = 2.7 Hz), 130.9, 130.7, 130.0, 128.4 (d, J = 11.7 Hz), 128.3, 128.1 (d, J = 12.3 Hz), 126.6 (d, J = 101.7 Hz), 47.5, 42.2, 25.3, 25.2, 24.2; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 28.04; HRMS (ESI) calculated for C<sub>33</sub>H<sub>29</sub>N<sub>2</sub>O<sub>2</sub>PNa [M+Na]<sup>+</sup> *m*/z 539.1864, found 539.1858.

(1-(diphenylphosphoryl)-4-phenylisoquinolin-3-yl)(morpholino)methanone (5fa):



White solid, PE/EA = 2/1, 90.1 mg, 58% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.74-9.19 (m, 1H), 8.01-7.81 (m, 4H), 7.79-7.59 (m, 3H), 7.55-7.32 (m, 11H), 3.52-3.40 (m, 4H), 2.91 (dt, J = 9.3, 4.4 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 166.8, 155.0 (d, J = 127.3 Hz), 144.6 (d, J = 21.5 Hz), 135.6 (d, J = 7.0 Hz), 134.1 (d, J = 0.6 Hz), 132.8 (d, J = 2.9 Hz), 132.4 (d, J = 105.6 Hz), 132.2 (d, J = 9.3 Hz), 131.8 (d, J = 2.5 Hz), 131.1, 130.9 (d, J = 21.5 Hz), 129.3 (d, J = 126.3 Hz), 128.4, 128.2 (d, J = 12.2 Hz), 126.7 (d, J = 112.5 Hz), 66.4, 66.1, 46.7, 41.6; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 28.20; HRMS (ESI) calculated for  $C_{32}H_{27}N_2O_3PNa$  [M+Na]<sup>+</sup> *m/z* 541.1657, found 541.1649.

# General procedure for the preparation of oxindole derevatives (Compounds 7aa-7ka):

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **6a-6k** (0.3 mmol),  $[Ir(ppy)_2(dtbpy)]PF_6$  (1 mol%, 0.003 mmol), diphenylphosphine oxide **2a** (3.0 equiv, 0.9 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 equiv, 0.9 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv. 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. 3 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 20 hours, the mixture was then diluted with 20mL water and extract by ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, and then the solvent concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the **7aa-7ka**.

#### 3-((diphenylphosphoryl)methyl)-1,3-dimethylindolin-2-one (7aa)<sup>5</sup>:



White solid, PE/isopropanol = 10/1, 90.0 mg, 80% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60-7.53 (m, 2H), 7.53-7.45 (m, 2H), 7.45-7.27 (m,

H NMR (400 MHz, CDCl<sub>3</sub>). δ 7.60-7.33 (m, 2H), 7.35-7.43 (m, 2H), 7.45-7.27 (m, 6H), 7.19-7.13(m, 2H), 6.78 (td, J = 7.6, 0.8 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 3.09 (dd, J = 15.2, 10.3 Hz, 1H), 3.01 (s, 3H), 2.86 (dd, J = 15.2, 10.7 Hz, 1H), 1.43 (d, J = 1.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 179.4 (d, J = 4.2 Hz), 142.8, 133.6 (d, J = 1.7 Hz, 3H);

= 99.4 Hz), 131.3 (d, J = 2.6 Hz), 131.1 (d, J = 2.7 Hz), 130.6 (d, J = 9.4 Hz), 130.4 (d, J = 9.2 Hz), 128.3 (d, J = 11.8 Hz), 128.1 (d, J = 11.8 Hz), 127.9, 124.7, 122.0, 107.7, 45.4 (d, J = 3.8 Hz), 37.4 (d, J = 71.4 Hz), 26.8 (d, J = 12.0 Hz), 26.2; <sup>31</sup>P **NMR (162 MHz, CDCl<sub>3</sub>)**: δ 28.04; **HRMS** (ESI) calculated for C<sub>23</sub>H<sub>22</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 398.1286, found 398.1288.

3-((diphenylphosphoryl)methyl)-1,3,5-trimethylindolin-2-one (7ba)<sup>5</sup>:



Yellow solid, PE/isopropanol = 10/1, 85.2 mg, 73% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55-7.45 (m, 4H), 7.42-7.35 (m, 2H), 7.35-7.27 (m, 4H), 6.92 (d, J = 7.9 Hz, 1H), 6.78 (s, 1H), 6.58 (d, J = 7.9 Hz, 1H), 3.12-3.01 (m, 4H), 2.80 (dd, J = 15.1, 9.7 Hz, 1H), 2.06 (s, 3H), 1.41 (d, J = 1.6 Hz, 3H); <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>): δ 179.4 (d, J = 4.2 Hz), 140.8, 133.7 (d, J = 99.2 Hz), 133.4 (d, J = 98.8 Hz), 131.33 (d, J = 2.7 Hz), 131.28, 131.2 (d, J = 2.7 Hz), 131.0 (d, J = 2.8 Hz), 131.6 (d, J = 9.4 Hz), 131.4 (d, J = 9.2 Hz), 128.21 (d, J = 1.6 Hz), 128.18, 128.1 (d, J = 4.2 Hz), 107.5, 45.4 (d, J = 3.8 Hz), 37.5 (d, J = 71.7 Hz), 26.7 (d, J = 12.1 Hz), 26.4, 20.8; <sup>31</sup>**P** NMR (162 MHz, CDCl<sub>3</sub>): δ 25.75; HRMS (ESI) calculated for  $C_{24}H_{24}NO_2PNa [M+Na]^+ m/z 412.1442$ , found 412.1440.

3-((diphenylphosphoryl)methyl)-5-methoxy-1,3-dimethylindolin-2-one (7ca)<sup>5</sup>:



White solid, PE/isopropanol = 10/1, 83.8 mg, 69% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 7.55-7.46 (m, 4H), 7.41-7.26 (m, 6H), 6.72 (d, J = 2.5 Hz, 1H), 6.66 (dd, J = 8.4, 2.5 Hz, 1H), 6.56 (d, J = 8.4 Hz, 1H), 3.59 (s, 3H), 3.09-2.99 (m, 4H), 2.80 (dd, J = 15.1, 9.8 Hz, 1H), 1.40 (d, J = 1.5 Hz, 3H); <sup>13</sup>**C** NMR (100 MHz, CDCl<sub>3</sub>): δ 179.0 (d, J = 4.5 Hz), 155.4, 136.5, 133.7 (d, J = 99.1 Hz), 133.2 (d, J = 98.9 Hz), 132.5 (d, J = 2.7 Hz), 131.3 (d, J = 2.7 Hz), 131.0 (d, J = 2.7 Hz), 130.5 (d, J = 9.4 Hz), 130.4 (d, J = 9.2 Hz), 128.2 (d, J = 5.8 Hz), 128.1 (d, J = 5.8 Hz), 113.1, 111.3, 108.1, 55.4, 45.8 (d, J = 3.9 Hz), 37.4 (d, J = 71.4 Hz), 26.6 (d, J = 11.7 Hz), 26.4; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 25.75; HRMS (ESI) calculated for C<sub>24</sub>H<sub>24</sub>NO<sub>3</sub>PNa [M+Na]<sup>+</sup> *m/z* 428.1391, found 428.1394.

3-((diphenylphosphoryl)methyl)-1,3-dimethyl-5-phenylindolin-2-one (7da)<sup>6</sup>:



White solid, PE/isopropanol = 10/1, 82.5 mg, 61% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.54-7.45 (m, 4H), 7.41-7.21 (m, 13H), 6.74 (d, J = 8.1 Hz, 1H), 3.16 (dd, J = 15.2, 10.8 Hz, 1H), 3.11 (s, 3H), 2.89 (dd, J = 15.2, 9.9 Hz, 1H), 1.47 (d, J = 1.7 Hz, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 166.4, 154.4 (d, J = 128.6 Hz), 146.1 (d, J = 21.5 Hz), 135.8 (d, J = 7.2 Hz), 134.6, 132.7 (d, J = 3.0 Hz), 132.5 (d, J = 105.6 Hz), 132.3 (d, J = 9.4 Hz), 131.7 (d, J = 2.5 Hz), 131.0 (d, J = 21.6 Hz), 129.9, 128.4 (d, J = 7.1 Hz), 128.3, 128.1 (d, J = 12.2 Hz), 127.2, 126.3, 47.2, 45.2, 25.7, 24.2; <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>): δ 26.18; **HRMS** (ESI) calculated for C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 474.1599, found 474.1599.

#### 3-((diphenylphosphoryl)methyl)-5-fluoro-1,3-dimethylindolin-2-one (7ea)<sup>5</sup>:



Yellow solid, PE/isopropanol = 10/1, 96.7 mg, 82% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.59-7.46 (m, 4H), 7.46-7.28 (m, 6H), 6.87-6.74 (m, 2H), 6.59 (dd, J = 8.4, 4.1 Hz, 1H), 3.10-2.99 (m, 4H), 2.81 (dd, J = 15.2, 9.4 Hz, 1H), 1.39 (d, J = 1.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  179.0 (d, J = 4.3 Hz), 158.7 (d, J = 240.3 Hz), 139.0 (d, J = 1.7 Hz), 133.3 (d, J = 99.4 Hz), 133.04 (d, J = 99.2 Hz), 132.9 (dd, J = 8.2, 2.6 Hz), 131.5 (d, J = 2.7 Hz), 131.4 (d, J = 2.8 Hz), 130.5 (d, J = 9.4 Hz), 130.4 (d, J = 9.2 Hz), 128.3 (d, J = 8.3 Hz), 128.2 (d, J = 8.3 Hz), 114.2 (d, J = 23.5 Hz), 112.8 (d, J = 25.2 Hz), 108.1 (d, J = 8.1 Hz), 45.8 (dd, J = 3.9, 1.7 Hz), 37.4 (d, J = 71.4 Hz), 26.5, 26.4; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  25.75; HRMS (ESI) calculated for C<sub>23</sub>H<sub>21</sub>FNO<sub>2</sub>PNa [M+Na]<sup>+</sup> *m/z* 416.1192, found 416.1187.

# **3-((diphenylphosphoryl)methyl)-1,3-dimethyl-5-(trifluoromethyl)indolin-2-one** (7fa)<sup>5</sup>:



Yellow solid, PE/isopropanol = 10/1, 115.6 mg, 87% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.57-7.52 (m, 2H), 7.41-7.31 (m, 7H), 7.28-7.24 (m, 2H), 7.05 (d, J = 1.1 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 3.17 (s, 3H), 3.13 (dd, J = 15.1, 12.0 Hz, 1H), 2.84 (dd, J = 15.1, 7.8 Hz, 1H), 1.43 (d, J = 1.9 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  179.4 (d, J = 3.2 Hz), 146.4 (d, J = 0.8 Hz), 133.4 (d, J = 99.6

Hz), 132.6 (d, J = 99.4 Hz), 131.6, 131.5 (d, J = 2.7 Hz), 131.4 (d, J = 2.7 Hz), 130.3 (d, J = 9.4 Hz), 130.0 (d, J = 9.4 Hz), 128.4 (d, J = 7.3 Hz), 128.2 (d, J = 7.4 Hz), 125.8 (q, J = 3.8 Hz), 124.0 (q, J = 271.6 Hz), 123.8 (q, J = 32.5 Hz), 121.1 (q, J = 3.7 Hz), 107.7, 45.2 (d, J = 3.9 Hz), 37.6 (d, J = 71.2 Hz), 26.6, 26.5; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>):  $\delta$  25.38; HRMS (ESI) calculated for C<sub>24</sub>H<sub>21</sub>FNO<sub>2</sub>PNa [M+Na]<sup>+</sup> *m/z* 466.1160, found 466.1157.

1-((diphenylphosphoryl)methyl)-1-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinol in-2(1H)-one (7ga)<sup>5</sup>:



Yellow oil, PE/EA = 2:1, 52.9 mg, 44% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 7.64-7.55 (m, 2H), 7.52-7.47 (m, 2H), 7.45-7.29 (m, 6H), 7.05 (d, J = 7.4 Hz, 1H), 6.90 (d, J = 7.6 Hz, 1H), 6.71 (t, J = 7.5 Hz, 1H), 3.61 (m, 1H), 3.35 (m, 1H), 3.07 (m, 1H), 2.87 (m, 1H), 2.66 (dd, J = 10.5, 5.2 Hz, 1H), 1.93-1.81 (m, 2H), 1.42 (d, J = 1.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 179.6 (d, J = 4.8 Hz), 138.6, 133.7 (d, J = 99.0 Hz), 133.1 (d, J = 98.0 Hz), 131.3(d, J = 2.6 Hz), 131.1 (d, J = 2.7 Hz), 131.0 (d, J = 9.7 Hz), 130.5 (d, J = 9.1 Hz), 130.2 (d, J = 2.6 Hz), 128.4 (d, J = 11.7 Hz), 128.1 (d, J = 11.8 Hz), 126.6, 122.8, 121.7, 119.8, 46.7 (d, J = 3.7 Hz), 38.8, 37.4 (d, J = 71.4 Hz), 26.6 (d, J = 11.8 Hz), 24.4, 20.9; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 27.55; HRMS (ESI) calculated for C<sub>25</sub>H<sub>24</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> *m/z* 424.1442, found 424.1443.

1-benzyl-3-((diphenylphosphoryl)methyl)-3-methylindolin-2-one (7ia)<sup>5</sup>:



Wax solid, PE/EA = 2/1, 96.1 mg, 71% yield.

<sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60-7.52 (m, 4H), 7.42-7.38 (m, 2H), 7.34-7.30 (m, 4H), 7.27-7.25 (m, 4H), 7.23-7.18 (m, 1H), 7.16 (d, J = 7.3 Hz, 1H), 7.00 (td, J = 7.8, 0.9 Hz, 1H), 6.69 (td, J = 7.7, 0.9 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 5.03 (d, J = 15.8 Hz, 1H), 4.40 (d, J = 15.8 Hz, 1H), 3.07 (dd, J = 15.2, 11.0 Hz, 1H), 2.91 (dd, J = 15.2, 9.8 Hz, 1H), 1.47 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 179.6 (d, J = 4.8 Hz), 142.0, 136.0, 133.5 (d, J = 99.2 Hz), 133.2 (d, J = 98.9 Hz), 131.45 (d, J = 2.1 Hz), 131.37 (d, J = 2.6 Hz), 131.2 (d, J = 2.6 Hz), 130.6 (d, J = 9.3 Hz), 130.5 (d, J = 9.2 Hz), 128.6, 128.3 (d, J = 11.8 Hz), 128.2 (d, J = 11.8 Hz), 127.7, 127.3, 127.1, 124.8, 122.1, 108.8, 45.5 (d, J = 4.0 Hz), 43.9, 37.2 (d, J = 71.6 Hz), 26.8 (d, J = 11.6 Hz) ; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>): δ 26.10; HRMS (ESI) calculated for C<sub>29</sub>H<sub>26</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 474.1599, found 474.1600.

3-((diphenylphosphoryl)methyl)-1,3-dimethyl-1,3-dihydro-2H-benzo[g]indol-2-o ne (7ja)<sup>5</sup>:



White solid, PE/EA = 2:1, 65.0 mg, 51% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ7.56 (d, J = 8.0 Hz, 1H), 7.51-7.27 (m, 10H), 7.26-7.20 (m, 2H), 7.09 (td, J = 7.6, 2.9 Hz, 2H), 6.79 (d, J = 7.5 Hz, 1H), 3.84 (dd, J = 15.0, 9.7 Hz, 1H), 3.34 (s, 3H), 3.00 (dd, J = 15.0, 11.4 Hz, 1H), 1.74 (d, J = 2.4 Hz, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 172.3 (d, J = 2.1 Hz), 136.5, 135.3 (d, J = 2.5 Hz), 133.4 (d, J = 99.1 Hz), 133.0, 132.8 (d, J = 98.1 Hz), 131.1 (d, J = 2.7 Hz), 131.02 (d, J = 2.6 Hz), 130.96, 130.9, 130.6 (d, J = 9.4 Hz), 128.1 (d, J = 11.8 Hz), 127.7 (d, J = 11.7 Hz), 126.4 (d, J = 3.8 Hz), 126.2, 124.2, 122.2, 119.1, 108.4, 45.2 (d, J = 3.5 Hz), 42.3 (d, J = 69.9 Hz), 35.0 (d, J = 13.8 Hz), 29.8; <sup>31</sup>**P NMR** (162 **MHz, CDCl<sub>3</sub>**): δ 27.55; **HRMS** (ESI) calculated for C<sub>27</sub>H<sub>24</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 448.1442, found 448.1439.

3-((diphenylphosphoryl)methyl)-1,3,4,6-tetramethylindolin-2-one (7ka)<sup>5</sup>:



White solid, PE/isopropanol = 10/1, 77.4 mg, 64% yield.

<sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.47-7.37 (m, 6H), 7.32-7.27 (m, 4H), 6.40 (s, 1H), 6.34 (s, 1H), 3.26 (dd, J = 15.1, 10.1 Hz, 1H), 2.96-2.82 (m, 4H), 2.31 (s, 3H), 2.07 (s, 3H), 1.46 (d, J = 2.3 Hz, 3H); <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>): δ 179.3, 143.5, 138.0, 135.2, 133.4 (d, J = 98.9 Hz), 132.4 (d, J = 97.5 Hz), 131.3(d, J = 2.6 Hz), 131.1 (d, J = 2.7 Hz), 131.0 (d, J = 9.7 Hz), 130.5 (d, J = 9.1 Hz), 128.0 (d, J = 12.3 Hz), 127.9 (d, J = 12.3 Hz), 125.6 (d, J = 2.9 Hz), 125.3, 106.6, 45.2 (d, J = 3.6 Hz), 36.8 (d, J = 70.9 Hz), 26.2, 25.3 (d, J = 14.3 Hz), 21.5, 18.3; <sup>31</sup>**P NMR** (162 MHz, CDCl<sub>3</sub>): δ 27.55; **HRMS** (ESI) calculated for C<sub>25</sub>H<sub>26</sub>NO<sub>2</sub>PNa [M+Na]<sup>+</sup> m/z 426.1599, found 426.1604.

#### 4. Gram-Scale Preparation of 3aa

An oven-dried Schlenk tube (100 mL) was equipped with a magnetic stir bar, **1a** (3 mmol, 0.76g),  $[Ir(ppy)_2(dtbpy)]PF_6$  (0.03 mmol, 30mg), diphenylphosphine oxide **2a** (9 mmol, 1.82g), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (9 mmol, 2.43g) and CsF (6 mmol, 0.91g). The flask was evacuated and backfilled with Ar for 3 times. 30 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light

bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 24 hours, the mixture was then diluted with 200 mL water and extract by ethyl acetate ( $3 \times 40$  mL). The combined organic layers were dried over sodium sulfate, then the solvent was removed in vacuo and the residue was purified by chromatography on silica gel to afford **3aa** (0.99g, 81% yield).

#### 5. Preliminary Mechanistic Studies:

#### 5.1 Free radical capture experiments

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **6a** (0.3 mmol),  $[Ir(ppy)_2(dtbpy)]PF_6$  (1 mol%, 0.003 mmol), diphenylphosphine oxide (3.0 equiv, 0.9 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 equiv, 0.9 mmol), CsF (2.0 equiv. 0.6 mmol) and TEMPO (2.0 equiv, 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. 3 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 20 hours, the mixture was then diluted with 20mL water and extract by ethyl acetate (3×10 mL). Compound **7aa** was not detected.

#### 5.2 Intermolecular KIE experiment:

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **6a** (0.15 mmol) **d**<sub>5</sub>-**6a** (0.15 mmol),  $[Ir(ppy)_2(dtbpy)]PF_6$  (1 mol%, 0.003 mmol), diphenylphosphine oxide **2a** (3.0 equiv, 0.9 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3.0 equiv, 0.9 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.0 equiv. 0.6 mmol). The flask was evacuated and backfilled with Ar for 3 times. 3 mL dry DMF was added with syringe under Ar. The tube was placed at a distance (app.5 cm) from 23 W fluorescent light bulb, and the resulting solution was stirred at ambient temperature under visible-light irradiation. After 4 hours, the mixture was then diluted with 20mL water and extract by ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, and then the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the product **7aa** and *d*<sub>4</sub>-**7aa**. The products were under <sup>1</sup>H-NMR analysis.



4h, 27% yield,  $k_{\rm H}/k_{\rm D}$ =1.0.



Figure S1. <sup>1</sup>H NMR spectrum of the mixture of compounds 7aa and  $d_4$ -7aa.

#### 6. X-ray Crystallographic Data of Compound 3na

**X-Ray diffraction:** X-ray diffraction data were collected on a Bruker SMART Apex II CCD diffractometer by means of graphitemonochromated Mo K $\alpha$  ( $\lambda = 0.71073$ ) radiation at 291 K. During collection of the intensity data, no significant decay was observed. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and *w*R<sub>2</sub>values are given for all reflections.

Empirical formula	C25 H17 Cl N O P
Molecular weight	413.82
Crystal size (mm <sup>3</sup> )	$0.30 \times 0.26 \times 0.24$
Temperature(K)	296(2)
Radiation	Mo-Kα(0.7103Å)
Crystal system	Monoclinic
Space group	'P2(1)/c
a (Å)	13.831(7)
b (Å)	16.046(8)

X-rav	crystal	structure	analysis	of 3na:
				· · · · · · · · · · · · · · · · · · ·

c (Å)	9.430(5)
α (°)	90.00
β(°)	105.784(8)
$\gamma(^{\circ})$	90.00
$V(\text{\AA}^3)$	2014.0(18)
Ζ	4
$D_c$ (g cm <sup>-3</sup> )	1.365
$\mu$ (mm <sup>-1</sup> ) absort.coeff	0.286
F (000)	856
$\theta$ rang (deg)	2.54 /26.37
Reflections collected	14710 ( $R_{int} = 0.0475$ )
Indep. reflns	3540
Refns obs. $[I > 2\sigma(I)]$	2851
Data/restr./paras	3540 /175 /262
Goodness-of-fit on $F^2$	1.088
$R_1$ , $wR_2$ (all data)	0.0539 /0.1280
$R_1, wR_2[I > 2\sigma(I)]$	0.0419 /0.1111
Larg.peak/hole(e. Å)	0.276 /-0.323



Crystal structure of compound **3na**. (Thermals ellipsoids are shown with 30% probability.)

#### **References:**

- 1. J. Liu; C. Fan; H. Yin; C. Qin; G. Zhang; X. Zhang; H. Yi and A. Lei, *Chem. Commun.* **2014**, *50*, 2145.
- 2. H. Jiang; Y. Cheng; R. Wang; Y. Zhang and S. Yu, Chem. Commun. 2014, 50, 6164.
- 3. X. Liu; X. Ma; Y. Huang and Z. Gu, Org. Lett. 2013, 15, 4814.
- 4. Zhang, B.; Daniliuc C. G.; Studer, A. Org. Lett. 2014, 16, 250.
- 5. Li, Y. M.; Sun, M.; Wang, H. L.; Tian Q. P.; Yang, S. D. Angew. Chem. Int. Ed. **2013**, *52*, 3972.
- 6. Li, Y.-M.; Shen, Y.; Chang, K.-J.; Yang, S.-D. Tetrahedron, 2014, 70, 1991.

### 7. NMR Spectra for All Compounds 3aa- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



3aa-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



3ba-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



## 3ba- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3ba-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)





### 3ca-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)





3da-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)





130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 fl (ppm)

3ea-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



## 3ea-<sup>13</sup>C-NMR (150M, CDCl<sub>3</sub>)







3fa- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



## 3fa-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3fa- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)













3ha- <sup>1</sup>H-NMR ( 400M, CDCl<sub>3</sub>)





3ha-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



### 3ia-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



## 3ia- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3ia- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



3ja-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)


3ja-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3ja- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)















3la- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)







## 3ma-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



3ma- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3ma-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



3na-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)





3na-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)





3qa-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



3qa-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



3ab- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)





3ab- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)















3nd-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)





3nd-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)











5ba-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)





5ba- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)





5ca-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)









5da-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



5da-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



# 5ea-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



# 5ea- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



5ea-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



5fa- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)











7aa- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)





7ba- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



7ba- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



7ba-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)









7ca-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)



7da-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)











7ea-<sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



7ea- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)

7fa-<sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)







## 7fa-<sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)

-25.375







7ga- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)









7ia- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)



# 7ja- <sup>1</sup>H-NMR (400M, CDCl<sub>3</sub>)



# 7ja- <sup>13</sup>C-NMR (100M, CDCl<sub>3</sub>)








## 7ka- <sup>31</sup>P-NMR (162M, CDCl<sub>3</sub>)

-25.253





130 110 90 60 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (rom)