

## Supporting Information

### **Merging photoredox catalysis with transition metal catalysis: site-selective C4 or C5-H phosphonation of 8-aminoquinoline amides**

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## 1. General Information

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker DPX-400 spectrometer with  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used directly without further purification. Dichloromethane (analytical grade), ethyl acetate (analytical grade), and hexane (analytical grade) were used for column chromatography. Alizarin red S (analytical grade), eosin Y (analytical grade), eosin B (analytical grade), acid red 94 (analytical grade),  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  (analytical grade),  $\text{K}_2\text{S}_2\text{O}_8$  (analytical grade),  $\text{Ag}_2\text{O}$  (analytical grade), phosphine oxides (analytical grade), and PivONa (analytical grade) were obtained from commercial sources and used as-received without further purification unless otherwise noted.

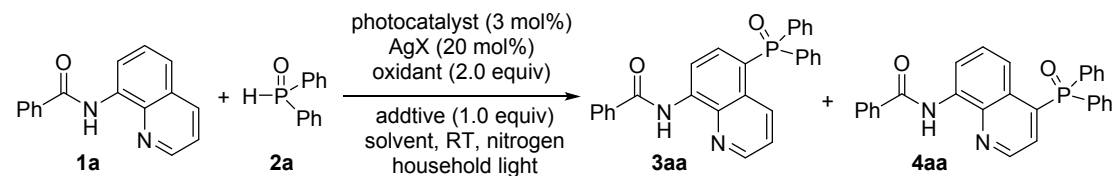
## 2. Preparation of Substrates

All amides were prepared from the corresponding acids and 8-aminoquinoline according to the reported procedure.<sup>1</sup>

## 3. Optimization of Reaction Conditions

A 10 mL reaction tube was equipped with a magnetic stir bar and charged with N-(quinolin-8-yl)benzamide **1a** (24.8 mg, 0.1 mmol), diarylphosphine oxide **2a** (41 mg, 0.2 mmol, 2 equiv), photocatalyst (0.003 mmol, 3 mol %), oxidant (0.2 mmol, 2 equiv), AgX (0.02 mmol, 20 mol %), additive (0.1 mmol, 1 equiv), and  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (1.5 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 8 h. Upon completion,  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to the reaction system, which was extracted with  $\text{H}_2\text{O}$  (20 mL), and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using hexane-EtOAc as an eluent to afford the pure product **3aa** and **4aa**.

**Table S1** Screening of reaction conditions of the C5 position<sup>a</sup>



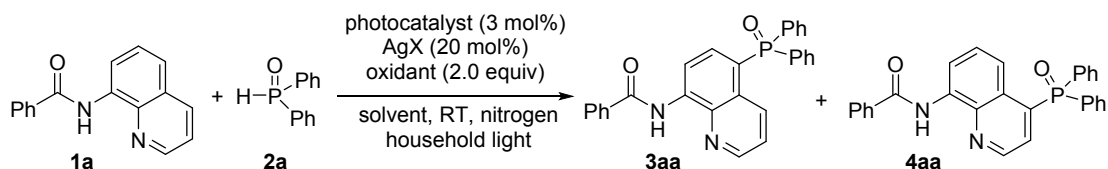
Entry	AgX	Oxidant	Solvent	Photocatalyst	Additive	<b>3aa</b> <sup>b</sup> (%)	<b>4aa</b> <sup>b</sup> (%)
1	$\text{Ag}_2\text{O}$	$\text{K}_2\text{S}_2\text{O}_8$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1)	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	-	76	15
2	$\text{Ag}_2\text{SO}_4$	$\text{K}_2\text{S}_2\text{O}_8$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:1)	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	-	63	12
3	$\text{Ag}_3\text{PO}_4$	$\text{K}_2\text{S}_2\text{O}_8$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}$	$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$	-	61	11

			(1:1)				
4	AgNO <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	47	21
5	AgOAc	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	66	19
6	AgOTf	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	60	15
7	Ag <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	59	12
8	-	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
9	Ag <sub>2</sub> O	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	70	15
10	Ag <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	48	19
11	Ag <sub>2</sub> O	Oxone	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
12	Ag <sub>2</sub> O	Mg(NO <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
13	Ag <sub>2</sub> O	BQ	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
14	Ag <sub>2</sub> O	TBHP	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
15	Ag <sub>2</sub> O	-	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
16	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Acetone/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	67	21
17	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
18	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Toluene/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
19	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Dioxane/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
20	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	EtOH/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	47	42
21	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (10:0)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	34	18
22	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (9:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	52	27
23	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (7:3)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	70	17
24	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:7)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	68	18

25	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:9)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	43	25
26	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (0:10)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	-	Trace	Trace
27	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub>	-	61	24
28	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Eosin Y	-	38	59
29	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Eosin B	-	30	50
30	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	-	32	63
31	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Alizarin red S	-	27	61
32	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	-	-	Trace	Trace
<b>33</b>	<b>Ag<sub>2</sub>O</b>	<b>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub></b>	<b>CH<sub>3</sub>CN/H<sub>2</sub>O (1:1)</b>	<b>[Ru(bpy)<sub>3</sub>]Cl<sub>2</sub></b>	<b>PivONa</b>	<b>93</b>	<b>Trace</b>
34	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivOH	75	22
35	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	AcONa	88	Trace
36	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	60	8
37	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	NaHCO <sub>3</sub>	85	Trace
38 <sup>c</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	74	Trace
39 <sup>d</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	78	Trace
40 <sup>e</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	Trace	Trace
41 <sup>f</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	Trace	Trace
42 <sup>g</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	92	Trace
43 <sup>h</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub>	PivONa	89	Trace

<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), photocatalyst (3 mol %), AgX (20 mol %), oxidant (0.2 mmol), additive (0.1 mmol), solvent (1.5 ml) at room temperature under nitrogen for 8 h. <sup>b</sup> Isolated yield. <sup>c</sup> blue LED. <sup>d</sup> green LED. <sup>e</sup> red LED. <sup>f</sup> dark. <sup>g</sup> For 9 h. <sup>h</sup> For 7 h.

**Table S2** Screening of reaction conditions of the C4 position<sup>a</sup>



Entry	AgX	Oxidant	Solvent	Photocatalyst	<b>3aa</b> <sup>b</sup> (%)	<b>4aa</b> <sup>b</sup> (%)
1	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	32	63
2	Ag <sub>2</sub> SO <sub>4</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	33	45
3	Ag <sub>3</sub> PO <sub>4</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	38	42
4	AgNO <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	27	55
5	AgOAc	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	32	44
6	AgOTf	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	29	51
7	Ag <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	37	47
8	-	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	Trace	Trace
9	Ag <sub>2</sub> O	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	30	56
10	Ag <sub>2</sub> O	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	19	42
11	Ag <sub>2</sub> O	-	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	Acid red 94	Trace	Trace
12	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Acetone/H <sub>2</sub> O (1:1)	Acid red 94	30	45
13	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	EtOH/H <sub>2</sub> O (1:1)	Acid red 94	27	32
14	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (10:0)	Acid red 94	20	39
15	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (9:1)	Acid red 94	22	49
16	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (4:1)	Acid red 94	25	63
17	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (7:3)	Acid red 94	23	65
<b>18</b>	<b>Ag<sub>2</sub>O</b>	<b>K<sub>2</sub>S<sub>2</sub>O<sub>8</sub></b>	<b>CH<sub>3</sub>CN/H<sub>2</sub>O (3:2)</b>	<b>Acid red 94</b>	<b>20</b>	<b>70</b>
19	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (2:3)	Acid red 94	24	60
20	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:7)	Acid red 94	21	55
21	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (0:10)	Acid red 94	Trace	Trace
22	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:2)	-	Trace	Trace
23 <sup>c</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:2)	Acid red 94	Trace	Trace
24 <sup>d</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:2)	Acid red 94	25	51
25 <sup>e</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:2)	Acid red 94	Trace	Trace
26 <sup>f</sup>	Ag <sub>2</sub> O	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	CH <sub>3</sub> CN/H <sub>2</sub> O (3:2)	Acid red 94	Trace	Trace

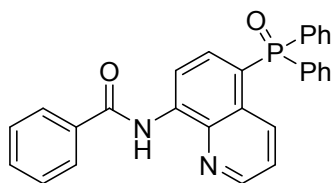
<sup>a</sup> Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), photocatalyst (3 mol %), AgX (20 mol %), oxidant (0.2 mmol), solvent (1.5 ml) at room temperature under nitrogen for 8 h. <sup>b</sup> Isolated yield. <sup>c</sup> blue LED. <sup>d</sup> green LED. <sup>e</sup> red LED. <sup>f</sup> dark.

#### 4. Typical Procedure for the Products

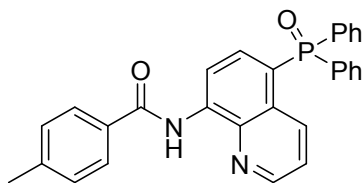
a) For the C5 position reaction: A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **1** (0.1 mmol), **2** (0.2 mmol, 2 equiv), [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub> (1.9 mg, 0.003 mmol, 3 mol %), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (54 mg, 0.2 mmol, 2 equiv), Ag<sub>2</sub>O (2.3 mg, 0.01 mmol, 10 mol %), PivONa (14.2 mg, 0.1 mmol, 1 equiv), and CH<sub>3</sub>CN/H<sub>2</sub>O = 1:1 (1.5 mL). The resulting mixture was stirred under the

irradiation of 26 W household light under nitrogen at room temperature for 8 h. Upon completion, CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added to the reaction system, which was extracted with H<sub>2</sub>O (20 mL), and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using CH<sub>2</sub>Cl<sub>2</sub>-EtOAc as an eluent to afford the pure product **3**.

b) For the C4 position reaction: A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **1** (0.1 mmol), **2** (0.2 mmol, 2 equiv), Acid red 94 (3.1 mg, 0.003 mmol, 3 mol %), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (54 mg, 0.2 mmol, 2 equiv), Ag<sub>2</sub>O (2.3 mg, 0.01 mmol, 10 mol %), and CH<sub>3</sub>CN/H<sub>2</sub>O = 2:3 (1.5 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 8 h. Upon completion, CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added to the reaction system, which was extracted with H<sub>2</sub>O (20 mL), and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using CH<sub>2</sub>Cl<sub>2</sub>-EtOAc as an eluent to afford the pure product **4**.

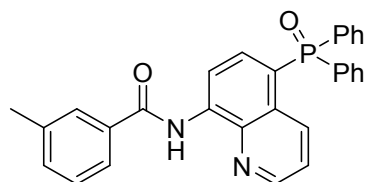


**N-(5-(diphenylphosphoryl)quinolin-8-yl)benzamide (3aa)**: Light yellow solid (93%); mp 214–216 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.98 (s, 1H), 9.10 (d, *J* = 8.1 Hz, 1H), 8.86 (d, *J* = 3.2 Hz, 1H), 8.82 (dd, *J* = 8.0 Hz, 1.9 Hz, 1H), 8.08 (d, *J* = 7.1 Hz, 2H), 7.71–7.66 (m, 4H), 7.60–7.54 (m, 5H), 7.50–7.43 (m, 5H), 7.36 (dd, *J*<sub>H-P</sub> = 15.0 Hz, 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.7, 148.6, 138.9 (d, *J*<sub>C-P</sub> = 9.3 Hz), 138.4 (d, *J*<sub>C-P</sub> = 2.7 Hz), 136.4 (d, *J*<sub>C-P</sub> = 4.9 Hz), 135.4 (d, *J*<sub>C-P</sub> = 11.7 Hz), 134.6, 132.3 (d, *J*<sub>C-P</sub> = 105.1 Hz), 132.2, 132.1 (d, *J*<sub>C-P</sub> = 2.7 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.1 Hz), 129.2 (d, *J*<sub>C-P</sub> = 8.5 Hz), 128.9, 128.7 (d, *J*<sub>C-P</sub> = 11.3 Hz), 127.3, 122.6 (d, *J*<sub>C-P</sub> = 105.7 Hz), 122.6, 114.2 (d, *J*<sub>C-P</sub> = 14.2 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.5; HRMS (ESI+): calcd for C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 449.1413, Found: 449.1414.

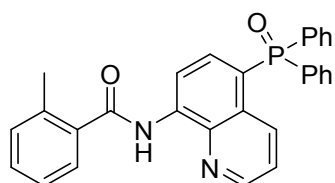


**N-(5-(diphenylphosphoryl)quinolin-8-yl)-4-methylbenzamide (3ba)**: Light yellow solid (80%); mp 228–230 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.94 (s, 1H), 9.09 (d, *J* = 8.5 Hz, 1H), 8.85 (d, *J* = 2.9 Hz, 1H), 8.80 (dd, *J* = 7.6 Hz, 2.1 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.70–7.66 (m, 4H), 7.58–7.55 (m, 2H), 7.49–7.42 (m, 5H), 7.37–7.32 (m, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ

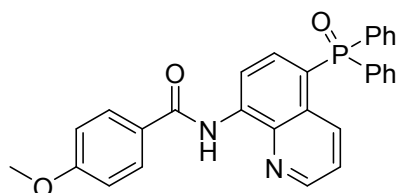
165.6, 148.5, 142.8, 138.9 (d,  $J_{C-P} = 9.5$  Hz), 138.6 (d,  $J_{C-P} = 2.6$  Hz), 136.3 (d,  $J_{C-P} = 5.0$  Hz), 135.5 (d,  $J_{C-P} = 11.9$  Hz), 132.3 (d,  $J_{C-P} = 105.0$  Hz), 132.1 (d,  $J_{C-P} = 2.7$  Hz), 132.0 (d,  $J_{C-P} = 10.0$  Hz), 131.8, 129.5, 129.2 (d,  $J_{C-P} = 8.6$  Hz), 128.7 (d,  $J_{C-P} = 12.3$  Hz), 127.4, 122.5, 122.3 (d,  $J_{C-P} = 104.9$  Hz), 114.1 (d,  $J_{C-P} = 14.5$  Hz), 21.5;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1573.



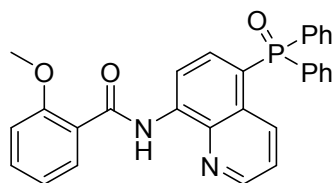
**N-(5-(diphenylphosphoryl)quinolin-8-yl)-3-methylbenzamide (3ca)**: Light yellow solid (82%); mp 205-207 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.93 (s, 1H), 9.09 (d,  $J = 8.4$  Hz, 1H), 8.85 (d,  $J = 2.9$  Hz, 1H), 8.81 (dd,  $J = 8.0$  Hz, 2.1 Hz, 1H), 7.87-7.84 (m, 2H), 7.71-7.66 (m, 4H), 7.59-7.55 (m, 2H), 7.50-7.39 (m, 7H), 7.35 (dd,  $J_{H-P} = 15.1$  Hz, 8.1 Hz, 1H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 148.6, 138.9 (d,  $J_{C-P} = 9.1$  Hz), 138.8, 138.5 (d,  $J_{C-P} = 2.5$  Hz), 136.3 (d,  $J_{C-P} = 5.1$  Hz), 135.5 (d,  $J_{C-P} = 12.0$  Hz), 134.6, 133.0, 132.3 (d,  $J_{C-P} = 105.2$  Hz), 132.1 (d,  $J_{C-P} = 2.5$  Hz), 132.0 (d,  $J_{C-P} = 10.0$  Hz), 129.2 (d,  $J_{C-P} = 8.5$  Hz), 128.7, 128.7 (d,  $J_{C-P} = 12.3$  Hz), 128.1, 124.2, 122.6, 122.4 (d,  $J_{C-P} = 106.5$  Hz), 114.2 (d,  $J_{C-P} = 14.4$  Hz), 21.4;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1571.



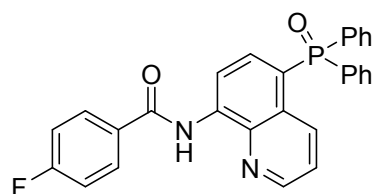
**N-(5-(diphenylphosphoryl)quinolin-8-yl)-2-methylbenzamide (3da)**: Light yellow solid (84%); mp 181-182 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.44 (s, 1H), 9.08 (d,  $J = 8.4$  Hz, 1H), 8.81 (dd,  $J = 7.8$  Hz, 1.8 Hz, 1H), 8.77 (d,  $J = 2.8$  Hz, 1H), 7.71-7.66 (m, 5H), 7.59-7.55 (m, 2H), 7.50-7.47 (m, 4H), 7.43-7.30 (m, 5H), 2.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.4, 148.5, 138.7 (d,  $J_{C-P} = 9.3$  Hz), 138.5 (d,  $J_{C-P} = 2.6$  Hz), 136.8, 136.3 (d,  $J_{C-P} = 4.9$  Hz), 136.0, 135.4 (d,  $J_{C-P} = 11.7$  Hz), 132.3 (d,  $J_{C-P} = 105.4$  Hz), 132.1 (d,  $J_{C-P} = 2.7$  Hz), 132.0 (d,  $J_{C-P} = 9.9$  Hz), 131.5, 130.6, 129.2 (d,  $J_{C-P} = 8.5$  Hz), 128.7 (d,  $J_{C-P} = 12.3$  Hz), 127.2, 126.1, 122.7 (d,  $J_{C-P} = 105.2$  Hz), 122.6, 114.2 (d,  $J_{C-P} = 14.5$  Hz), 20.2;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1572.



**N-(5-(diphenylphosphoryl)quinolin-8-yl)-4-methoxybenzamide (3ea):** Light yellow solid (81%); mp 198-200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.90 (s, 1H), 9.07 (d, *J* = 8.4 Hz, 1H), 8.84 (d, *J* = 2.8 Hz, 1H), 8.78 (dd, *J* = 8.0 Hz, 2.1 Hz, 1H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.70-7.65 (m, 4H), 7.58-7.54 (m, 2H), 7.49-7.41 (m, 5H), 7.35 (dd, *J*<sub>H-P</sub> = 15.0 Hz, 8.0 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 3.88 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.2, 162.8, 148.5, 138.8 (d, *J*<sub>C-P</sub> = 9.4 Hz), 138.6 (d, *J*<sub>C-P</sub> = 2.6 Hz), 136.3 (d, *J*<sub>C-P</sub> = 5.0 Hz), 135.5 (d, *J*<sub>C-P</sub> = 11.9 Hz), 132.3 (d, *J*<sub>C-P</sub> = 105.5 Hz), 132.1 (d, *J*<sub>C-P</sub> = 2.8 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.0 Hz), 129.3, 129.2 (d, *J*<sub>C-P</sub> = 8.7 Hz), 128.7 (d, *J*<sub>C-P</sub> = 12.3 Hz), 126.8, 122.5, 122.0 (d, *J*<sub>C-P</sub> = 105.6 Hz), 114.0, 114.0 (d, *J*<sub>C-P</sub> = 14.1 Hz), 55.4; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.7; HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 479.1519, Found: 479.1519.

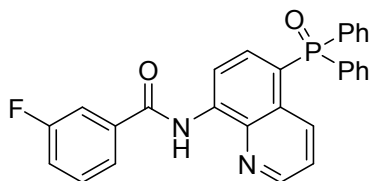


**N-(5-(diphenylphosphoryl)quinolin-8-yl)-2-methoxybenzamide (3fa):** Light yellow solid (92%); mp 237-238 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.56 (s, 1H), 9.06 (d, *J* = 8.4 Hz, 1H), 8.90 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 8.85 (d, *J* = 2.9 Hz, 1H), 8.30 (d, *J* = 7.5 Hz, 1H), 7.70-7.65 (m, 4H), 7.56-7.44 (m, 7H), 8.40 (dd, *J* = 8.4 Hz, 4.2 Hz, 1H), 7.33 (dd, *J*<sub>H-P</sub> = 15.4 Hz, 8.1 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 4.17 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.9, 157.7, 148.4, 139.7 (d, *J*<sub>C-P</sub> = 2.8 Hz), 139.3 (d, *J*<sub>C-P</sub> = 9.3 Hz), 136.1 (d, *J*<sub>C-P</sub> = 5.3 Hz), 135.6 (d, *J*<sub>C-P</sub> = 11.6 Hz), 133.5, 132.4 (d, *J*<sub>C-P</sub> = 104.8 Hz), 132.4, 132.0, 131.9, 129.2 (d, *J*<sub>C-P</sub> = 8.5 Hz), 128.6 (d, *J*<sub>C-P</sub> = 12.1 Hz), 122.3, 121.9 (d, *J*<sub>C-P</sub> = 105.6 Hz), 121.8, 121.3, 114.9 (d, *J*<sub>C-P</sub> = 14.4 Hz), 111.6, 56.1; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.6; HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>P [M+H]<sup>+</sup>: 479.1519, Found: 479.1521.

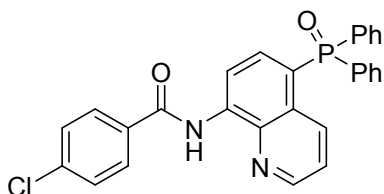


**N-(5-(diphenylphosphoryl)quinolin-8-yl)-4-fluorobenzamide (3ga):** Light yellow solid (73%); mp 211-212 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.95 (s, 1H), 9.12 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 2.8 Hz, 1H), 8.81 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 8.14-8.10 (m, 2H), 7.74-7.69 (m, 4H), 7.63-7.59 (m, 2H), 7.53-7.47 (m, 5H), 7.38 (dd, *J*<sub>H-P</sub> = 15.0 Hz, 7.9 Hz, 1H), 7.30-7.24 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.2 (d, *J*<sub>C-F</sub> = 253.0 Hz), 164.5, 148.6, 138.8 (d, *J*<sub>C-P</sub> = 9.3 Hz), 138.3 (d, *J*<sub>C-P</sub> = 2.8 Hz), 136.4 (d, *J*<sub>C-P</sub> = 4.8 Hz), 135.4 (d, *J*<sub>C-P</sub> = 11.8 Hz), 132.2 (d, *J*<sub>C-P</sub> = 105.2 Hz), 132.2 (d, *J*<sub>C-P</sub> = 2.5 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.1 Hz), 130.8 (d, *J*<sub>C-P</sub> = 3.0 Hz), 129.8 (d, *J*<sub>C-F</sub> = 9.2 Hz), 129.2 (d, *J*<sub>C-P</sub> = 8.5 Hz), 128.7 (d, *J*<sub>C-P</sub> = 12.2 Hz), 122.7, 122.6 (d, *J*<sub>C-P</sub> = 105.8 Hz), 116.0 (d, *J*<sub>C-F</sub> = 22.3 Hz), 114.2 (d, *J*<sub>C-P</sub> = 14.2 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.7; HRMS (ESI<sup>+</sup>): calcd for C<sub>28</sub>H<sub>20</sub>FN<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 467.1319, Found: 467.1323.

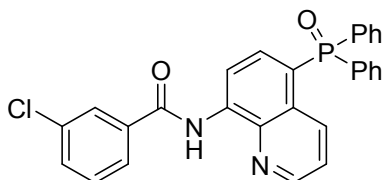




**N-(5-(diphenylphosphoryl)quinolin-8-yl)-3-fluorobenzamide (3ha):** Light yellow solid (77%); mp 202-203 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.95 (s, 1H), 9.09 (d,  $J = 8.5$  Hz, 1H), 8.85 (d,  $J = 2.9$  Hz, 1H), 8.78 (dd,  $J = 8.0$  Hz, 2.0 Hz, 1H), 7.84 (d,  $J = 7.7$  Hz, 1H), 7.77 (d,  $J = 9.0$  Hz, 1H), 7.70-7.65 (m, 4H), 7.59-7.44 (m, 8H), 7.38-7.27 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3 (d,  $J_{\text{C-F}} = 2.3$  Hz), 163.0 (d,  $J_{\text{C-F}} = 247.9$  Hz), 148.7, 138.8 (d,  $J_{\text{C-P}} = 9.4$  Hz), 138.1 (d,  $J_{\text{C-P}} = 2.9$  Hz), 136.8 (d,  $J_{\text{C-F}} = 6.6$  Hz), 136.4 (d,  $J_{\text{C-P}} = 5.2$  Hz), 135.4 (d,  $J_{\text{C-P}} = 11.8$  Hz), 132.2 (d,  $J_{\text{C-P}} = 105.1$  Hz), 132.2 (d,  $J_{\text{C-P}} = 2.5$  Hz), 132.0 (d,  $J_{\text{C-P}} = 9.9$  Hz), 130.5 (d,  $J_{\text{C-F}} = 7.9$  Hz), 129.2 (d,  $J_{\text{C-P}} = 8.4$  Hz), 128.7 (d,  $J_{\text{C-P}} = 12.2$  Hz), 123.0 (d,  $J_{\text{C-P}} = 105.3$  Hz), 122.7 (d,  $J_{\text{C-F}} = 2.9$  Hz), 122.7, 119.2 (d,  $J_{\text{C-F}} = 21.3$  Hz), 114.8 (d,  $J_{\text{C-F}} = 22.9$  Hz), 114.4 (d,  $J_{\text{C-P}} = 14.4$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{FN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 467.1319, Found: 467.1323.

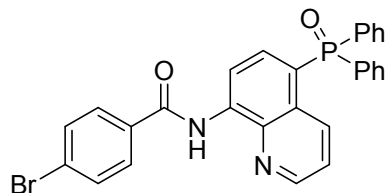


**4-chloro-N-(5-(diphenylphosphoryl)quinolin-8-yl)benzamide (3ia):** Light yellow solid (72%); mp 248-249 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.92 (s, 1H), 9.08 (d,  $J = 8.5$  Hz, 1H), 8.83 (d,  $J = 2.9$  Hz, 1H), 8.77 (dd,  $J = 8.0$  Hz, 1.9 Hz, 1H), 7.99 (d,  $J = 8.4$  Hz, 2H), 7.70-7.65 (m, 4H), 7.58-7.54 (m, 2H), 7.51-7.42 (m, 7H), 7.34 (dd,  $J_{\text{H-P}} = 15.4$  Hz, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.5, 148.6, 138.8 (d,  $J_{\text{C-P}} = 9.5$  Hz), 138.5, 138.2 (d,  $J_{\text{C-P}} = 2.5$  Hz), 136.4 (d,  $J_{\text{C-P}} = 4.9$  Hz), 135.4 (d,  $J_{\text{C-P}} = 11.8$  Hz), 132.9, 132.2 (d,  $J_{\text{C-P}} = 2.5$  Hz), 132.1 (d,  $J_{\text{C-P}} = 105.3$  Hz), 132.1, 132.0 (d,  $J_{\text{C-P}} = 10.0$  Hz), 129.1 (d,  $J_{\text{C-P}} = 7.2$  Hz), 129.1, 128.7 (d,  $J_{\text{C-P}} = 11.0$  Hz), 122.7 (d,  $J_{\text{C-P}} = 105.4$  Hz), 122.6, 114.3 (d,  $J_{\text{C-P}} = 14.5$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.8; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{ClN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 483.1024, Found: 483.1026.

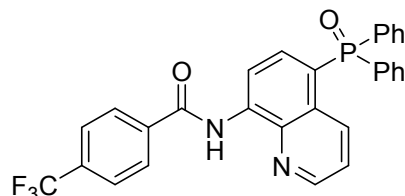


**3-chloro-N-(5-(diphenylphosphoryl)quinolin-8-yl)benzamide (3ja):** Light yellow solid (79%); mp 195-197 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.92 (s, 1H), 9.08 (d,  $J = 8.5$  Hz, 1H), 8.85 (d,  $J = 3.1$  Hz, 1H), 8.81 (dd,  $J = 7.9$  Hz, 1.8 Hz, 1H), 8.04 (s, 1H), 7.92 (d,  $J = 7.6$  Hz, 1H), 7.70-7.65 (m, 4H), 7.59-7.55 (m, 3H), 7.50-7.43 (m, 6H), 7.35 (dd,  $J_{\text{H-P}} = 15.0$  Hz, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 148.7, 138.8 (d,  $J_{\text{C-P}} = 9.6$  Hz), 138.1 (d,  $J_{\text{C-P}} = 2.7$  Hz), 136.4 (d,  $J_{\text{C-P}} = 5.1$

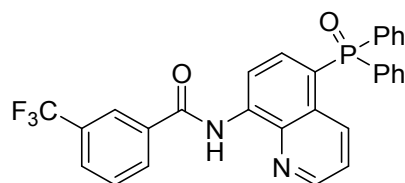
Hz), 136.3, 135.3 (d,  $J_{C-P}$  = 11.9 Hz), 135.1, 132.2, 132.2 (d,  $J_{C-P}$  = 2.6 Hz), 132.1 (d,  $J_{C-P}$  = 105.5 Hz), 132.0 (d,  $J_{C-P}$  = 10.0 Hz), 130.1, 129.2 (d,  $J_{C-P}$  = 8.4 Hz), 128.7 (d,  $J_{C-P}$  = 12.4 Hz), 127.8, 125.2, 122.9 (d,  $J_{C-P}$  = 105.2 Hz), 122.7, 114.4 (d,  $J_{C-P}$  = 14.5 Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.7; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{ClN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 483.1024, Found: 483.1024.



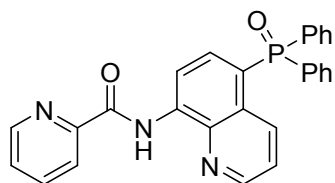
**4-bromo-N-(5-(diphenylphosphoryl)quinolin-8-yl)benzamide (3ka)**: Light yellow solid (62%); mp 247-249 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.93 (s, 1H), 9.09 (d,  $J$  = 8.5 Hz, 1H), 8.85 (d,  $J$  = 3.9 Hz, 1H), 8.77 (dd,  $J$  = 8.1 Hz, 1.9 Hz, 1H), 7.93 (d,  $J$  = 8.4 Hz, 2H), 7.70-7.65 (m, 6H), 7.59-7.56 (m, 2H), 7.50-7.43 (m, 5H), 7.35 (dd,  $J_{\text{H-P}}$  = 15.2 Hz, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.7, 148.7, 138.8 (d,  $J_{C-P}$  = 9.4 Hz), 138.2 (d,  $J_{C-P}$  = 2.5 Hz), 136.4 (d,  $J_{C-P}$  = 4.9 Hz), 135.4 (d,  $J_{C-P}$  = 11.8 Hz), 133.4, 132.2 (d,  $J_{C-P}$  = 2.7 Hz), 132.1 (d,  $J_{C-P}$  = 104.4 Hz), 132.1, 132.0 (d,  $J_{C-P}$  = 10.0 Hz), 129.2 (d,  $J_{C-P}$  = 8.2 Hz), 128.9, 128.7 (d,  $J_{C-P}$  = 12.5 Hz), 127.1, 122.8 (d,  $J_{C-P}$  = 105.2 Hz), 122.7, 114.3 (d,  $J_{C-P}$  = 14.6 Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.7; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{BrN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 527.0519, Found: 527.0519.



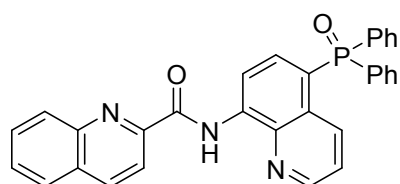
**N-(5-(diphenylphosphoryl)quinolin-8-yl)-4-(trifluoromethyl)benzamide (3la)**: Light yellow solid (68%); mp 226-227 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.00 (s, 1H), 9.09 (d,  $J$  = 8.5 Hz, 1H), 8.85 (d,  $J$  = 3.0 Hz, 1H), 8.79 (dd,  $J$  = 8.0 Hz, 1.9 Hz, 1H), 8.18 (d,  $J$  = 8.0 Hz, 2H), 7.82 (d,  $J$  = 8.0 Hz, 2H), 7.70-7.66 (m, 4H), 7.60-7.56 (m, 2H), 7.50-7.44 (m, 5H), 7.36 (dd,  $J_{\text{H-P}}$  = 15.1 Hz, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 148.8, 138.8 (d,  $J_{C-P}$  = 9.3 Hz), 138.0 (d,  $J_{C-P}$  = 2.8 Hz), 137.8, 136.5 (d,  $J_{C-P}$  = 5.0 Hz), 135.3 (d,  $J_{C-P}$  = 11.9 Hz), 133.8 (q,  $J_{C-F}$  = 33.2 Hz), 132.2 (d,  $J_{C-P}$  = 2.4 Hz), 132.2 (d,  $J_{C-P}$  = 105.5 Hz), 132.0 (d,  $J_{C-P}$  = 10.0 Hz), 129.2 (d,  $J_{C-P}$  = 8.5 Hz), 128.7 (d,  $J_{C-P}$  = 12.3 Hz), 127.8, 126.0 (q,  $J_{C-F}$  = 3.6 Hz), 123.7 (q,  $J_{C-F}$  = 272.9 Hz), 123.2 (d,  $J_{C-P}$  = 105.2 Hz), 122.8, 114.5 (d,  $J_{C-P}$  = 14.5 Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.7; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 517.1287, Found: 517.1288.



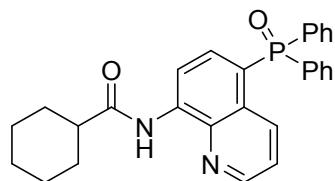
**N-(5-(diphenylphosphoryl)quinolin-8-yl)-3-(trifluoromethyl)benzamide (3ma)**: Light yellow solid (73%); mp 210-211 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 11.00 (s, 1H), 9.09 (d, *J* = 8.4 Hz, 1H), 8.87 (d, *J* = 3.1 Hz, 1H), 8.79 (dd, *J* = 7.9 Hz, 2.0 Hz, 1H), 8.33 (s, 1H), 8.23 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.77-7.66 (m, 5H), 7.60-7.56 (m, 2H), 7.50-7.45 (m, 5H), 7.35 (dd, *J*<sub>H-P</sub> = 15.3 Hz, 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.1, 148.8, 138.8 (d, *J*<sub>C-P</sub> = 9.5 Hz), 138.0 (d, *J*<sub>C-P</sub> = 2.8 Hz), 136.4 (d, *J*<sub>C-P</sub> = 5.2 Hz), 135.4, 135.3 (d, *J*<sub>C-P</sub> = 11.8 Hz), 132.2 (d, *J*<sub>C-P</sub> = 2.6 Hz), 132.1 (d, *J*<sub>C-P</sub> = 105.4 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.0 Hz), 131.5 (q, *J*<sub>C-F</sub> = 32.7 Hz), 130.2, 129.5, 129.2 (d, *J*<sub>C-P</sub> = 8.5 Hz), 128.7 (d, *J*<sub>C-P</sub> = 12.3 Hz), 128.7, 124.8 (q, *J*<sub>C-F</sub> = 3.8 Hz), 123.8 (q, *J*<sub>C-F</sub> = 272.4 Hz), 123.1 (d, *J*<sub>C-P</sub> = 105.0 Hz), 122.7, 114.4 (d, *J*<sub>C-P</sub> = 14.4 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.7; HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 517.1287, Found: 517.1294.



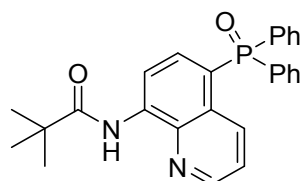
**N-(5-(diphenylphosphoryl)quinolin-8-yl)picolinamide (3na)**: Light yellow solid (55%); mp 213-214 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.47 (s, 1H), 9.05 (d, *J* = 8.4 Hz, 1H), 8.96 (d, *J* = 2.9 Hz, 1H), 8.87 (dd, *J* = 7.9 Hz, 2.0 Hz, 1H), 8.78 (d, *J* = 4.2 Hz, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.71-7.66 (m, 4H), 7.59-7.55 (m, 2H), 7.53-7.43 (m, 6H), 7.35 (dd, *J*<sub>H-P</sub> = 15.5 Hz, 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.1, 150.0, 149.0, 148.6, 139.4 (d, *J*<sub>C-P</sub> = 9.3 Hz), 138.4 (d, *J*<sub>C-P</sub> = 2.5 Hz), 137.5, 136.1 (d, *J*<sub>C-P</sub> = 5.2 Hz), 135.3 (d, *J*<sub>C-P</sub> = 11.7 Hz), 132.3 (d, *J*<sub>C-P</sub> = 105.1 Hz), 132.1 (d, *J*<sub>C-P</sub> = 2.8 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.0 Hz), 129.3 (d, *J*<sub>C-P</sub> = 8.5 Hz), 128.7 (d, *J*<sub>C-P</sub> = 12.4 Hz), 126.6, 122.7 (d, *J*<sub>C-P</sub> = 105.6 Hz), 122.6, 122.5, 114.4 (d, *J*<sub>C-P</sub> = 14.6 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.7; HRMS (ESI<sup>+</sup>): calcd for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 450.1366, Found: 450.1370.



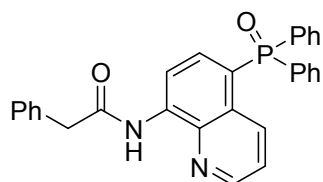
**N-(5-(diphenylphosphoryl)quinolin-8-yl)quinoline-2-carboxamide (3oa)**: Light yellow solid (36%); mp 287-288 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.70 (s, 1H), 9.08 (d, *J* = 8.4 Hz, 1H), 9.01 (d, *J* = 2.9 Hz, 1H), 8.91 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 8.42-8.36 (m, 3H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.83 (t, *J* = 7.3 Hz, 1H), 7.72-7.64 (m, 5H), 7.59-7.56 (m, 2H), 7.50-7.47 (m, 5H), 7.38 (dd, *J*<sub>H-P</sub> = 15.1 Hz, 8.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.3, 149.8, 149.0, 146.6, 139.5 (d, *J*<sub>C-P</sub> = 9.2 Hz), 138.5 (d, *J*<sub>C-P</sub> = 2.8 Hz), 137.7, 136.1 (d, *J*<sub>C-P</sub> = 5.2 Hz), 135.3 (d, *J*<sub>C-P</sub> = 11.8 Hz), 132.4 (d, *J*<sub>C-P</sub> = 105.4 Hz), 132.1 (d, *J*<sub>C-P</sub> = 3.7 Hz), 132.0 (d, *J*<sub>C-P</sub> = 10.2 Hz), 130.3, 130.2, 129.5, 129.4 (d, *J*<sub>C-P</sub> = 8.6 Hz), 128.7 (d, *J*<sub>C-P</sub> = 12.3 Hz), 128.3, 127.7, 122.7 (d, *J*<sub>C-P</sub> = 105.3 Hz), 122.6, 118.8, 114.4 (d, *J*<sub>C-P</sub> = 14.7 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.7; HRMS (ESI<sup>+</sup>): calcd for C<sub>31</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 500.1522, Found: 500.1527.



**N-(5-(diphenylphosphoryl)quinolin-8-yl)cyclohexanecarboxamide (3pa):** Light yellow solid (73%); mp 198-201 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 9.04 (d,  $J = 8.4$  Hz, 1H), 8.80 (d,  $J = 3.1$  Hz, 1H), 8.65 (dd,  $J = 8.0$  Hz, 2.1 Hz, 1H), 7.67-7.62 (m, 4H), 7.56-7.53 (m, 2H), 7.47-7.39 (m, 5H), 7.27 (dd,  $J_{\text{H-P}} = 15.8$  Hz, 8.1 Hz, 1H) 2.51-2.45 (m, 1H), 2.06 (d,  $J = 12.0$  Hz, 2H), 1.86 (d,  $J = 12.7$  Hz, 2H), 1.72 (d,  $J = 11.5$  Hz, 1H), 1.65-1.56 (m, 2H), 1.42-1.26 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 148.4, 138.6 (d,  $J_{\text{C-P}} = 10.0$  Hz), 138.5 (d,  $J_{\text{C-P}} = 2.9$  Hz), 136.3 (d,  $J_{\text{C-P}} = 5.0$  Hz), 135.5 (d,  $J_{\text{C-P}} = 11.7$  Hz), 132.3 (d,  $J_{\text{C-P}} = 105.1$  Hz), 132.1 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.0 (d,  $J_{\text{C-P}} = 10.0$  Hz), 129.1 (d,  $J_{\text{C-P}} = 8.4$  Hz), 128.3 (d,  $J_{\text{C-P}} = 12.3$  Hz), 122.4, 121.9 (d,  $J_{\text{C-P}} = 107.3$  Hz), 114.1 (d,  $J_{\text{C-P}} = 14.5$  Hz), 46.9, 29.6, 25.6, 25.6;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.7; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 455.1883, Found: 455.1886.

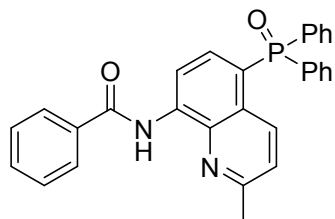


**N-(5-(diphenylphosphoryl)quinolin-8-yl)pivalamide (3qa):** Light yellow solid (76%); mp 184-186 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.49 (s, 1H), 9.04 (d,  $J = 8.4$  Hz, 1H), 8.80 (d,  $J = 2.9$  Hz, 1H), 8.65 (dd,  $J = 8.0$  Hz, 2.0 Hz, 1H), 7.67-7.62 (m, 4H), 7.57-7.53 (m, 2H), 7.47-7.39 (m, 5H), 7.28 (dd,  $J_{\text{H-P}} = 15.0$  Hz, 8.1 Hz, 1H), 1.41 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.6, 148.5, 138.9 (d,  $J_{\text{C-P}} = 9.5$  Hz), 138.5 (d,  $J_{\text{C-P}} = 2.6$  Hz), 136.3 (d,  $J_{\text{C-P}} = 5.1$  Hz), 135.5 (d,  $J_{\text{C-P}} = 11.8$  Hz), 132.3 (d,  $J_{\text{C-P}} = 105.4$  Hz), 132.1 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.0 (d,  $J_{\text{C-P}} = 9.9$  Hz), 129.1 (d,  $J_{\text{C-P}} = 8.5$  Hz), 128.6 (d,  $J_{\text{C-P}} = 12.3$  Hz), 122.4, 121.8 (d,  $J_{\text{C-P}} = 105.9$  Hz), 113.9 (d,  $J_{\text{C-P}} = 14.5$  Hz), 40.5, 27.6;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.8; HRMS (ESI+): calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 429.1726, Found: 429.1729.

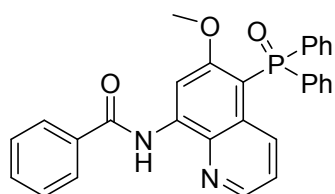


**N-(5-(diphenylphosphoryl)quinolin-8-yl)-2-phenylacetamide (3ra):** Light yellow solid (78%); mp 203-204 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.12 (s, 1H), 9.00 (d,  $J = 8.4$  Hz, 1H), 8.66 (d,  $J = 3.0$  Hz, 1H), 8.65 (dd,  $J = 8.0$  Hz, 1.8 Hz, 1H), 7.65-7.60 (m, 4H), 7.56-7.53 (m, 2H), 7.47-7.40 (m, 8H), 7.37-7.32 (m, 2H), 7.26 (dd,  $J_{\text{H-P}} = 15.0$  Hz, 8.4 Hz, 1H), 3.89 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 148.4, 138.5 (d,  $J_{\text{C-P}} = 9.6$  Hz), 138.2 (d,  $J_{\text{C-P}} = 2.7$  Hz), 136.1 (d,  $J_{\text{C-P}} = 5.0$

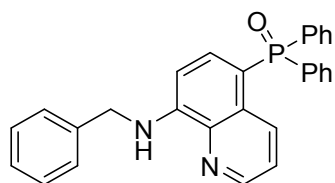
(Hz), 135.3 (d,  $J_{C-P} = 11.7$  Hz), 134.2, 132.2 (d,  $J_{C-P} = 105.3$  Hz), 132.1 (d,  $J_{C-P} = 2.6$  Hz), 132.0 (d,  $J_{C-P} = 9.8$  Hz), 129.5, 129.0, 129.0 (d,  $J_{C-P} = 7.8$  Hz), 128.6 (d,  $J_{C-P} = 12.2$  Hz), 127.5, 122.4 (d,  $J_{C-P} = 105.5$  Hz), 122.4, 114.0 (d,  $J_{C-P} = 14.5$  Hz), 45.4;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1572.



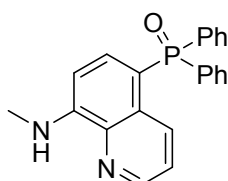
**N-(5-(diphenylphosphoryl)-2-methylquinolin-8-yl)benzamide (3sa):** Light yellow solid (82%); mp 213-214 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.05 (s, 1H), 8.95 (d,  $J = 8.7$  Hz, 1H), 8.78 (dd,  $J = 8.0$  Hz, 2.0 Hz, 1H), 8.08 (d,  $J = 6.9$  Hz, 2H), 7.71-7.66 (m, 4H), 7.62-7.55 (m, 5H), 7.50-7.47 (m, 4H), 7.33-7.27 (m, 2H), 2.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 157.7, 138.3 (d,  $J_{C-P} = 9.6$  Hz), 137.8 (d,  $J_{C-P} = 2.7$  Hz), 136.2 (d,  $J_{C-P} = 4.8$  Hz), 134.7, 134.4 (d,  $J_{C-P} = 11.8$  Hz), 132.4 (d,  $J_{C-P} = 104.7$  Hz), 132.1 (d,  $J_{C-P} = 5.1$  Hz), 132.1, 132.0 (d,  $J_{C-P} = 9.8$  Hz), 128.9, 128.6 (d,  $J_{C-P} = 12.3$  Hz), 127.3 (d,  $J_{C-P} = 10.7$  Hz), 127.3, 123.4, 122.2 (d,  $J_{C-P} = 105.6$  Hz), 114.2 (d,  $J_{C-P} = 14.4$  Hz), 25.3;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.6; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1573.



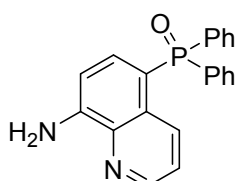
**N-(5-(diphenylphosphoryl)-6-methoxyquinolin-8-yl)benzamide (3ta):** Light yellow solid (95%); mp 226-228 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.13 (s, 1H), 10.07 (d,  $J = 8.6$  Hz, 1H), 8.77 (d,  $J = 5.0$  Hz, 1H), 8.73 (d,  $J = 2.8$  Hz, 1H), 8.08 (d,  $J = 6.9$  Hz, 2H), 7.78-7.73 (m, 4H), 7.61-7.55 (m, 3H), 7.52-7.43 (m, 7H), 3.42 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.9, 160.8 (d,  $J_{C-P} = 3.1$  Hz), 146.2, 140.4 (d,  $J_{C-P} = 2.7$  Hz), 134.0 (d,  $J_{C-P} = 108.7$  Hz), 135.4 (d,  $J_{C-P} = 3.1$  Hz), 134.9 (d,  $J_{C-P} = 9.3$  Hz), 134.4, 132.3, 132.1 (d,  $J_{C-P} = 6.3$  Hz), 131.3 (d,  $J_{C-P} = 8.1$  Hz), 131.2, 128.9, 128.1 (d,  $J_{C-P} = 12.7$  Hz), 127.3, 123.0, 104.6 (d,  $J_{C-P} = 105.9$  Hz), 103.3 (d,  $J_{C-P} = 7.1$  Hz), 55.6;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  32.2; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_3\text{P}$   $[\text{M}+\text{H}]^+$ : 479.1519, Found: 479.1524.



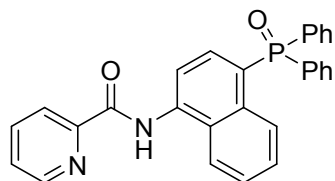
**(8-(benzylamino)quinolin-5-yl)diphenylphosphine oxide (3va)**: Light yellow solid (81%); mp 42-43 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 8.3 Hz, 1H), 8.68 (d, *J* = 2.9 Hz, 1H), 7.67-7.63 (m, 4H), 7.53-7.50 (m, 2H), 7.44-7.28 (m, 10H), 8.19 (d, *J* = 5.1 Hz, 1H), 7.05 (dd, *J*<sub>H-P</sub> = 15.2 Hz, 8.1 Hz, 1H), 6.43 (dd, *J* = 8.1 Hz, 1.7 Hz, 1H), 4.55 (d, *J* = 5.7 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.9 (d, *J*<sub>C-P</sub> = 1.7 Hz), 147.1, 138.2 (d, *J*<sub>C-P</sub> = 9.8 Hz), 138.1, 136.5 (d, *J*<sub>C-P</sub> = 12.5 Hz), 135.8 (d, *J*<sub>C-P</sub> = 5.4 Hz), 133.1 (d, *J*<sub>C-P</sub> = 104.8 Hz), 132.0 (d, *J*<sub>C-P</sub> = 9.8 Hz), 131.7 (d, *J*<sub>C-P</sub> = 2.4 Hz), 129.7 (d, *J*<sub>C-P</sub> = 9.0 Hz), 128.7, 128.4 (d, *J*<sub>C-P</sub> = 12.2 Hz), 127.4, 127.2, 122.4, 112.5 (d, *J*<sub>C-P</sub> = 113.1 Hz), 102.7 (d, *J*<sub>C-P</sub> = 15.5 Hz), 47.1; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 32.4; HRMS (ESI+): calcd for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>OP [M+H]<sup>+</sup>: 435.1621, Found: 435.1627.



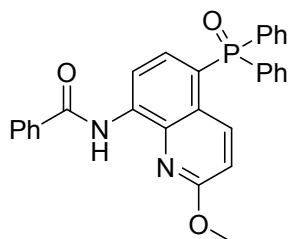
**(8-(methylamino)quinolin-5-yl)diphenylphosphine oxide (3wa)**: Light yellow solid (52%); mp 215-216 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.83 (d, *J* = 8.5 Hz, 1H), 8.66 (d, *J* = 4.0 Hz, 1H), 7.69-7.64 (m, 4H), 7.54-7.50 (m, 2H), 7.46-7.42 (m, 4H), 7.30 (dd, *J* = 8.6 Hz, 4.2 Hz, 1H), 7.14 (dd, *J*<sub>H-P</sub> = 15.1 Hz, 8.1 Hz, 1H), 6.73 (s, 1H), 6.44 (dd, *J* = 8.1 Hz, 2.4 Hz, 1H), 3.03 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.1 (d, *J*<sub>C-P</sub> = 2.0 Hz), 147.0, 138.2 (d, *J*<sub>C-P</sub> = 9.8 Hz), 136.6 (d, *J*<sub>C-P</sub> = 12.5 Hz), 135.8 (d, *J*<sub>C-P</sub> = 5.3 Hz), 133.4 (d, *J*<sub>C-P</sub> = 105.0 Hz), 132.1 (d, *J*<sub>C-P</sub> = 10.0 Hz), 131.6 (d, *J*<sub>C-P</sub> = 2.7 Hz), 129.7 (d, *J*<sub>C-P</sub> = 8.9 Hz), 128.4 (d, *J*<sub>C-P</sub> = 12.2 Hz), 122.4, 111.9 (d, *J*<sub>C-P</sub> = 113.5 Hz), 101.6 (d, *J*<sub>C-P</sub> = 15.5 Hz), 29.5; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 32.0; HRMS (ESI+): calcd for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>OP [M+H]<sup>+</sup>: 359.1308, Found: 359.1310.



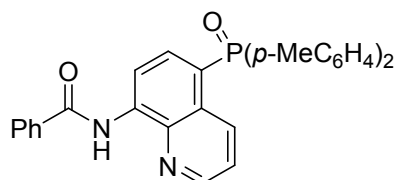
**(8-aminoquinolin-5-yl)diphenylphosphine oxide (3xa)**: Light yellow solid (34%); mp 240-242 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.82 (d, *J* = 8.4 Hz, 1H), 8.69 (d, *J* = 2.9 Hz, 1H), 7.67-7.62 (m, 4H), 7.53-7.49 (m, 2H), 7.44-7.41 (m, 4H), 7.28 (dd, *J* = 8.5 Hz, 4.0 Hz, 1H), 7.04 (dd, *J*<sub>H-P</sub> = 15.0 Hz, 7.9 Hz, 1H), 6.68 (dd, *J* = 7.9 Hz, 2.1 Hz, 1H), 5.54 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.3 (d, *J*<sub>C-P</sub> = 2.2 Hz), 147.5, 138.2 (d, *J*<sub>C-P</sub> = 9.9 Hz), 135.9 (d, *J*<sub>C-P</sub> = 12.5 Hz), 135.6 (d, *J*<sub>C-P</sub> = 5.4 Hz), 133.1 (d, *J*<sub>C-P</sub> = 104.9 Hz), 132.0 (d, *J*<sub>C-P</sub> = 9.8 Hz), 131.7 (d, *J*<sub>C-P</sub> = 2.5 Hz), 130.1 (d, *J*<sub>C-P</sub> = 8.8 Hz), 128.5 (d, *J*<sub>C-P</sub> = 12.2 Hz), 122.3, 114.2 (d, *J*<sub>C-P</sub> = 111.7 Hz), 107.0 (d, *J*<sub>C-P</sub> = 15.4 Hz); <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 31.8; HRMS (ESI+): calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>OP [M+H]<sup>+</sup>: 344.1151, Found: 344.1158.



**N-(4-(diphenylphosphoryl)naphthalen-1-yl)picolinamide (3ya)**: Light yellow solid (86%); mp 252-253 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.06 (s, 1H), 8.74-8.70 (m, 2H), 8.44 (dd,  $J = 8.0$  Hz, 1.9 Hz, 1H), 8.33 (d,  $J = 7.8$  Hz, 1H), 8.16 (d,  $J = 8.5$  Hz, 1H), 7.96-7.92 (m, 1H), 7.72-7.67 (m, 4H), 7.61 (t,  $J = 7.5$  Hz, 1H), 7.56-7.51 (m, 3H), 7.48-7.44 (m, 5H), 7.34 (dd,  $J_{\text{H-P}} = 15.6$  Hz, 8.0 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.2, 149.5, 148.2, 137.8, 136.7 (d,  $J_{\text{C-P}} = 3.0$  Hz), 134.6, 134.6 (d,  $J_{\text{C-P}} = 12.6$  Hz), 132.7 (d,  $J_{\text{C-P}} = 105.4$  Hz), 132.1 (d,  $J_{\text{C-P}} = 9.8$  Hz), 131.9 (d,  $J_{\text{C-P}} = 2.7$  Hz), 128.6, 128.5 (d,  $J_{\text{C-P}} = 12.0$  Hz), 127.4, 126.8 (d,  $J_{\text{C-P}} = 6.7$  Hz), 126.0 (d,  $J_{\text{C-P}} = 9.4$  Hz), 124.6 (d,  $J_{\text{C-P}} = 105.5$  Hz), 122.6, 120.5, 115.3 (d,  $J_{\text{C-P}} = 14.3$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  32.5; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 449.1413, Found: 449.1415.

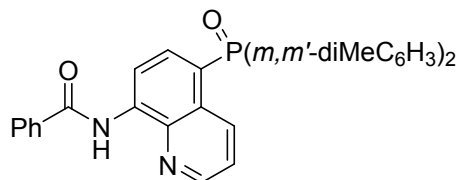


**N-(5-(diphenylphosphoryl)-2-methoxyquinolin-8-yl)benzamide (3za)**: Light yellow solid; mp 288-290 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.58 (s, 1H), 8.96 (d,  $J = 9.2$  Hz, 1H), 8.76 (dd,  $J = 8.2$  Hz, 2.6 Hz, 1H), 8.05-8.03 (m, 2H), 7.69-7.64 (m, 4H), 7.61-7.52 (m, 5H), 7.49-7.45 (m, 4H), 7.18 (dd,  $J = 15.2$  Hz, 8.1 Hz, 1H), 6.94 (d,  $J = 9.2$  Hz, 1H), 4.12 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.3, 161.4, 139.1 (d,  $J_{\text{C-P}} = 5.0$  Hz), 136.9 (d,  $J_{\text{C-P}} = 10.3$  Hz), 136.8 (d,  $J_{\text{C-P}} = 2.9$  Hz), 134.8, 132.5 (d,  $J_{\text{C-P}} = 98.7$  Hz), 132.3 (d,  $J_{\text{C-P}} = 11.8$  Hz), 132.1 (d,  $J_{\text{C-P}} = 10.3$  Hz), 132.0 (d,  $J_{\text{C-P}} = 9.7$  Hz), 129.0, 128.6 (d,  $J_{\text{C-P}} = 12.1$  Hz), 127.0, 125.9, 125.8, 122.6 (d,  $J_{\text{C-P}} = 105.1$  Hz), 115.0 (d,  $J_{\text{C-P}} = 14.6$  Hz), 114.3, 53.3;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  31.7; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_3\text{P}$   $[\text{M}+\text{H}]^+$ : 479.1519, Found: 479.1523.

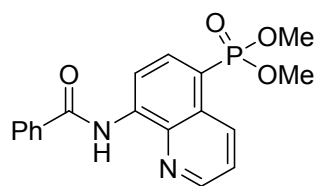


**N-(5-(di-p-tolylphosphoryl)quinolin-8-yl)benzamide (3ab)**: Light yellow solid (79%); mp 242-243 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.97 (s, 1H), 9.10 (d,  $J = 8.5$  Hz, 1H), 8.85-8.80 (m, 2H), 8.08 (d,  $J = 7.3$  Hz, 2H), 7.60-7.53 (m, 7H), 7.44 (dd,  $J = 8.5$  Hz, 4.1 Hz, 1H), 7.36 (dd,  $J_{\text{H-P}} = 15.3$  Hz, 8.0 Hz, 1H), 7.28 (d,  $J = 7.5$  Hz, 4H), 2.42 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.5, 142.6 (d,  $J_{\text{C-P}} = 2.7$  Hz), 138.8 (d,  $J_{\text{C-P}} = 9.3$  Hz), 138.2 (d,  $J_{\text{C-P}} = 2.7$  Hz), 136.5 (d,  $J_{\text{C-P}} =$

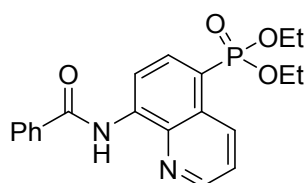
5.0 Hz), 135.3 (d,  $J_{C-P}$  = 11.7 Hz), 134.6, 132.2, 132.0 (d,  $J_{C-P}$  = 10.2 Hz), 129.4 (d,  $J_{C-P}$  = 12.8 Hz), 129.2 (d,  $J_{C-P}$  = 8.5 Hz), 129.2 (d,  $J_{C-P}$  = 107.9 Hz), 128.8, 127.3, 123.1 (d,  $J_{C-P}$  = 105.2 Hz), 122.5, 114.2 (d,  $J_{C-P}$  = 14.6 Hz), 21.6;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  32.0; HRMS (ESI+): calcd for  $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 477.1726, Found: 477.1732.



**N-(5-(bis(3,5-dimethylphenyl)phosphoryl)quinolin-8-yl)benzamide (3ac):** Light yellow solid (60%); mp 167-168 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.97 (s, 1H), 9.08 (d,  $J$  = 8.5 Hz, 1H), 8.85-8.80 (m, 2H), 8.08 (d,  $J$  = 6.9 Hz, 2H), 7.62-7.54 (m, 3H), 7.45 (dd,  $J$  = 8.5 Hz, 4.2 Hz, 1H), 7.37 (dd,  $J_{H-P}$  = 15.5 Hz, 8.0 Hz, 1H), 7.28 (d,  $J$  = 12.1 Hz, 4H), 7.18 (s, 2H), 2.31 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.5, 138.8 (d,  $J_{C-P}$  = 9.4 Hz), 138.3 (d,  $J_{C-P}$  = 12.9 Hz), 138.2 (d,  $J_{C-P}$  = 2.8 Hz), 136.5 (d,  $J_{C-P}$  = 5.0 Hz), 135.4 (d,  $J_{C-P}$  = 11.9 Hz), 134.6, 133.9 (d,  $J_{C-P}$  = 2.6 Hz), 132.2, 132.0 (d,  $J_{C-P}$  = 104.5 Hz), 129.5 (d,  $J_{C-P}$  = 9.9 Hz), 129.2 (d,  $J_{C-P}$  = 8.4 Hz), 128.9, 127.3, 123.0 (d,  $J_{C-P}$  = 103.2 Hz), 122.5, 114.3 (d,  $J_{C-P}$  = 14.5 Hz), 21.3;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  32.3; HRMS (ESI+): calcd for  $\text{C}_{32}\text{H}_{29}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 505.2039, Found: 505.2047.



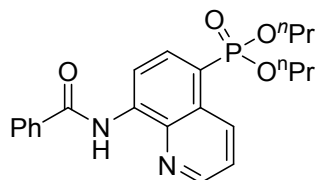
**dimethyl (8-benzamidoquinolin-5-yl)phosphonate (3ae):** Light yellow solid (45%); mp 150-151 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.99 (s, 1H), 8.97-8.87 (m, 3H), 8.26 (dd,  $J_{H-P}$  = 15.9 Hz, 8.1 Hz, 1H), 8.08 (d,  $J$  = 7.0 Hz, 2H), 7.62-7.54 (m, 4H), 3.81 (s, 3H), 3.78 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.5, 139.0 (d,  $J_{C-P}$  = 3.5 Hz), 138.5 (d,  $J_{C-P}$  = 13.7 Hz), 136.5 (d,  $J_{C-P}$  = 8.8 Hz), 135.5 (d,  $J_{C-P}$  = 3.6 Hz), 134.5, 132.2, 128.9, 128.1 (d,  $J_{C-P}$  = 11.7 Hz), 127.3, 122.9, 116.5 (d,  $J_{C-P}$  = 190.4 Hz), 114.6 (d,  $J_{C-P}$  = 16.6 Hz), 52.8 (d,  $J_{C-P}$  = 5.4 Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  20.7; HRMS (ESI+): calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_4\text{P}$   $[\text{M}+\text{H}]^+$ : 357.0999, Found: 385.1009.



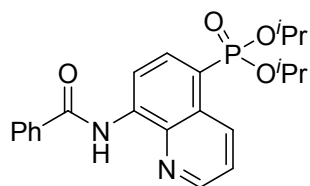
**dimethyl (8-benzamidoquinolin-5-yl)phosphonate (3af):** Light yellow solid (47%); mp 82-84 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.99 (s, 1H), 8.99-8.90 (m, 3H), 8.28 (dd,  $J_{H-P}$  = 15.9 Hz, 8.0 Hz, 1H), 8.09 (d,  $J$  = 7.0 Hz, 2H), 7.62-7.55 (m, 4H), 4.26-4.06 (m, 4H), 1.31 (d,  $J$  = 7.0 Hz, 6H);



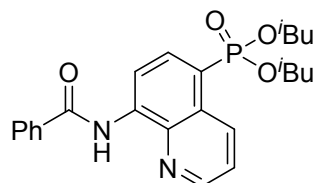
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.4, 138.8 (d,  $J_{\text{C-P}} = 3.4$  Hz), 138.5 (d,  $J_{\text{C-P}} = 13.4$  Hz), 136.2 (d,  $J_{\text{C-P}} = 9.1$  Hz), 135.7 (d,  $J_{\text{C-P}} = 3.6$  Hz), 134.6, 132.2, 128.9, 128.1 (d,  $J_{\text{C-P}} = 11.6$  Hz), 127.4, 122.7, 118.1 (d,  $J_{\text{C-P}} = 188.6$  Hz), 114.7 (d,  $J_{\text{C-P}} = 16.5$  Hz), 62.3 (d,  $J_{\text{C-P}} = 5.3$  Hz), 16.3 (d,  $J_{\text{C-P}} = 6.5$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  17.6; HRMS (ESI+): calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}_4\text{P}$   $[\text{M}+\text{H}]^+$ : 385.1312, Found: 385.1318.



**dipropyl (8-benzamidoquinolin-5-yl)phosphonate (3ag)**: Light yellow solid (40%); mp 141-142 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.98 (s, 1H), 8.98-8.89 (m, 3H), 8.28 (dd,  $J_{\text{H-P}} = 15.9$  Hz, 8.0 Hz, 1H), 8.08 (d,  $J = 6.9$  Hz, 2H), 7.61-7.54 (m, 4H), 4.13-4.05 (m, 2H), 4.02-3.94 (m, 2H), 1.72-1.64 (m, 4H), 0.91 (t,  $J = 7.4$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.4, 138.7 (d,  $J_{\text{C-P}} = 3.6$  Hz), 138.5 (d,  $J_{\text{C-P}} = 13.4$  Hz), 136.2 (d,  $J_{\text{C-P}} = 8.8$  Hz), 135.7 (d,  $J_{\text{C-P}} = 3.6$  Hz), 134.6, 132.2, 128.9, 128.1 (d,  $J_{\text{C-P}} = 11.7$  Hz), 127.3, 122.7, 118.1 (d,  $J_{\text{C-P}} = 189.5$  Hz), 114.7 (d,  $J_{\text{C-P}} = 16.5$  Hz), 67.8 (d,  $J_{\text{C-P}} = 5.6$  Hz), 23.7 (d,  $J_{\text{C-P}} = 6.7$  Hz), 10.1;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  17.8; HRMS (ESI+): calcd for  $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_4\text{P}$   $[\text{M}+\text{H}]^+$ : 413.1625, Found: 413.1621.

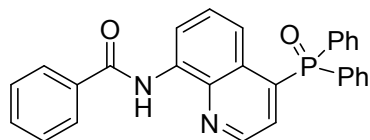


**diisopropyl (8-benzamidoquinolin-5-yl)phosphonate (3ah)**: Light yellow solid (44%); mp 76-77 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.98 (s, 1H), 8.98-8.89 (m, 3H), 8.31 (dd,  $J_{\text{H-P}} = 15.7$  Hz, 8.0 Hz, 1H), 8.09 (d,  $J = 6.9$  Hz, 2H), 7.61-7.55 (m, 4H), 4.78-4.69 (m, 2H), 1.40 (d,  $J = 6.1$  Hz, 6H), 1.17 (d,  $J = 6.2$  Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.4, 138.6 (d,  $J_{\text{C-P}} = 13.2$  Hz), 138.5 (d,  $J_{\text{C-P}} = 3.6$  Hz), 136.1 (d,  $J_{\text{C-P}} = 9.2$  Hz), 135.9 (d,  $J_{\text{C-P}} = 3.6$  Hz), 134.7, 132.2, 128.9, 128.0 (d,  $J_{\text{C-P}} = 11.5$  Hz), 127.4, 122.5, 119.7 (d,  $J_{\text{C-P}} = 189.1$  Hz), 114.7 (d,  $J_{\text{C-P}} = 16.6$  Hz), 71.6 (d,  $J_{\text{C-P}} = 5.5$  Hz), 24.1 (d,  $J_{\text{C-P}} = 3.9$  Hz), 23.8 (d,  $J_{\text{C-P}} = 4.9$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  15.2; HRMS (ESI+): calcd for  $\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_4\text{P}$   $[\text{M}+\text{H}]^+$ : 413.1625, Found: 413.1629.

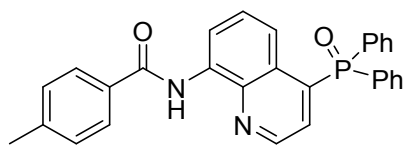


**diisobutyl (8-benzamidoquinolin-5-yl)phosphonate (3ai)**: Light yellow solid (42%); mp 39-40 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.98 (s, 1H), 8.98-8.89 (m, 3H), 8.28 (dd,  $J_{\text{H-P}} = 15.8$  Hz, 8.1

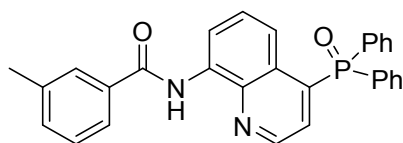
Hz, 1H), 8.08 (d,  $J = 7.0$  Hz, 2H), 7.60-7.54 (m, 4H), 3.93-3.88 (m, 2H), 3.81-3.75 (m, 2H), 1.98-1.89 (m, 2H), 0.91 (s, 6H), 0.89 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.7, 148.4, 138.7 (d,  $J_{\text{C-P}} = 3.7$  Hz), 138.5 (d,  $J_{\text{C-P}} = 13.4$  Hz), 136.1 (d,  $J_{\text{C-P}} = 9.7$  Hz), 135.7 (d,  $J_{\text{C-P}} = 3.6$  Hz), 134.6, 132.2, 128.9, 128.1 (d,  $J_{\text{C-P}} = 11.5$  Hz), 127.3, 122.6, 118.1 (d,  $J_{\text{C-P}} = 189.8$  Hz), 114.7 (d,  $J_{\text{C-P}} = 16.8$  Hz), 72.2 (d,  $J_{\text{C-P}} = 5.9$  Hz), 29.1 (d,  $J_{\text{C-P}} = 6.9$  Hz), 18.7;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  17.7; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_4\text{P}$  [M+H]<sup>+</sup>: 441.1938, Found: 441.1944.



**N-(4-(diphenylphosphoryl)quinolin-8-yl)benzamide (4aa)**: Light yellow solid (70%); mp 196-198 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.75 (s, 1H), 8.95 (d,  $J = 7.7$  Hz, 1H), 8.83 (t,  $J = 3.8$  Hz, 1H), 8.18 (d,  $J = 8.5$  Hz, 1H), 8.06 (d,  $J = 6.9$  Hz, 2H), 7.71-7.66 (m, 4H), 7.62-7.49 (m, 10H), 7.25 (dd,  $J_{\text{H-P}} = 14.1$  Hz, 4.4 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 146.8 (d,  $J_{\text{C-P}} = 11.8$  Hz), 144.6 (d,  $J_{\text{C-P}} = 2.2$  Hz), 139.2 (d,  $J_{\text{C-P}} = 94.3$  Hz), 139.0 (d,  $J_{\text{C-P}} = 7.7$  Hz), 135.2 (d,  $J_{\text{C-P}} = 2.3$  Hz), 135.0, 132.5 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.0$  Hz), 131.9, 131.1 (d,  $J_{\text{C-P}} = 105.4$  Hz), 128.9, 128.9 (d,  $J_{\text{C-P}} = 13.7$  Hz), 127.6 (d,  $J_{\text{C-P}} = 7.0$  Hz), 127.2, 126.6 (d,  $J_{\text{C-P}} = 9.4$  Hz), 121.4 (d,  $J_{\text{C-P}} = 5.5$  Hz), 117.2;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.2; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$  [M+H]<sup>+</sup>: 449.1413, Found: 449.1416.

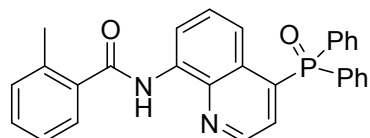


**N-(4-(diphenylphosphoryl)quinolin-8-yl)-4-methylbenzamide (4ba)**: Light yellow solid (62%); mp 187-189 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.71 (s, 1H), 8.93 (d,  $J = 7.7$  Hz, 1H), 8.83 (t,  $J = 3.9$  Hz, 1H), 8.16 (d,  $J = 8.4$  Hz, 1H), 7.95 (d,  $J = 7.9$  Hz, 2H), 7.71-7.66 (m, 4H), 7.61-7.58 (m, 2H), 7.54-7.48 (m, 5H), 7.33 (d,  $J = 7.9$  Hz, 2H), 7.25 (dd,  $J_{\text{H-P}} = 14.0$  Hz, 4.7 Hz, 1H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 146.7 (d,  $J_{\text{C-P}} = 11.7$  Hz), 142.4, 139.1 (d,  $J_{\text{C-P}} = 94.5$  Hz), 139.0 (d,  $J_{\text{C-P}} = 7.8$  Hz), 135.3 (d,  $J_{\text{C-P}} = 2.2$  Hz), 132.5 (d,  $J_{\text{C-P}} = 2.7$  Hz), 132.1, 131.9 (d,  $J_{\text{C-P}} = 10.0$  Hz), 131.1 (d,  $J_{\text{C-P}} = 105.5$  Hz), 129.4, 128.9, 128.8 (d,  $J_{\text{C-P}} = 12.3$  Hz), 127.6 (d,  $J_{\text{C-P}} = 7.2$  Hz), 127.2, 126.6 (d,  $J_{\text{C-P}} = 9.5$  Hz), 121.2 (d,  $J_{\text{C-P}} = 5.5$  Hz), 117.1, 21.5;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$  [M+H]<sup>+</sup>: 463.1570, Found: 463.1576.

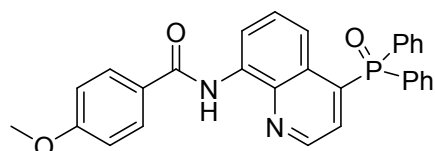


**N-(4-(diphenylphosphoryl)quinolin-8-yl)-3-methylbenzamide (4ca)**: Light yellow solid (60%); mp 153-155 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.70 (s, 1H), 8.94 (d,  $J = 7.7$  Hz, 1H), 8.84 (t,  $J =$

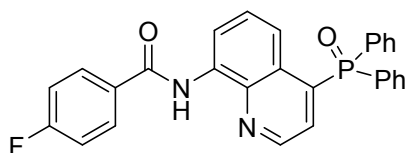
3.8 Hz, 1H), 8.17 (d,  $J = 8.3$  Hz, 1H), 7.87-7.83 (m, 2H), 7.71-7.66 (m, 4H), 7.62-7.58 (m, 2H), 7.55-7.49 (m, 5H), 7.44-7.37 (m, 2H), 7.25 (dd,  $J_{\text{H-P}} = 14.6$  Hz, 4.2 Hz, 1H), 2.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.6, 146.7 (d,  $J_{\text{C-P}} = 11.8$  Hz), 139.1 (d,  $J_{\text{C-P}} = 94.7$  Hz), 139.0 (d,  $J_{\text{C-P}} = 7.8$  Hz), 138.7, 135.2 (d,  $J_{\text{C-P}} = 2.0$  Hz), 135.0, 132.7, 132.6 (d,  $J_{\text{C-P}} = 2.5$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.1 (d,  $J_{\text{C-P}} = 105.8$  Hz), 128.9 (d,  $J_{\text{C-P}} = 12.6$  Hz), 128.6, 128.0, 127.6 (d,  $J_{\text{C-P}} = 7.1$  Hz), 127.2, 126.6 (d,  $J_{\text{C-P}} = 9.5$  Hz), 124.1, 121.3 (d,  $J_{\text{C-P}} = 5.6$  Hz), 117.2, 21.4;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1571.



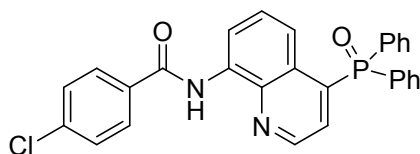
**N-(4-(diphenylphosphoryl)quinolin-8-yl)-2-methylbenzamide (4da)**: Light yellow solid (67%); mp 193-196 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.21 (s, 1H), 8.94 (d,  $J = 7.6$  Hz, 1H), 8.76 (t,  $J = 3.8$  Hz, 1H), 8.19 (d,  $J = 8.6$  Hz, 1H), 7.70-7.66 (m, 5H), 7.62-7.58 (m, 2H), 7.56-7.48 (m, 5H), 7.40 (t,  $J = 6.4$  Hz, 1H), 7.31 (t,  $J = 6.8$  Hz, 2H), 7.23 (dd,  $J_{\text{H-P}} = 14.7$  Hz, 4.4 Hz, 1H), 2.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.1, 146.7 (d,  $J_{\text{C-P}} = 11.7$  Hz), 139.1 (d,  $J_{\text{C-P}} = 94.6$  Hz), 138.8 (d,  $J_{\text{C-P}} = 7.6$  Hz), 136.7, 136.4, 135.3 (d,  $J_{\text{C-P}} = 2.3$  Hz), 132.5 (d,  $J_{\text{C-P}} = 2.6$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.4, 131.1 (d,  $J_{\text{C-P}} = 105.6$  Hz), 130.4, 128.9 (d,  $J_{\text{C-P}} = 12.5$  Hz), 128.8, 127.6 (d,  $J_{\text{C-P}} = 7.2$  Hz), 127.2, 126.6 (d,  $J_{\text{C-P}} = 9.8$  Hz), 126.0, 121.4 (d,  $J_{\text{C-P}} = 5.6$  Hz), 117.1, 20.2;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1572.



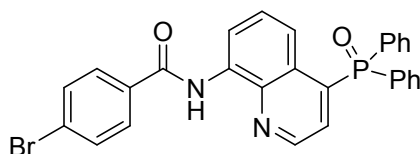
**N-(4-(diphenylphosphoryl)quinolin-8-yl)-4-methoxybenzamide (4ea)**: Light yellow solid (65%); mp 167-168 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.67 (s, 1H), 8.92 (d,  $J = 7.6$  Hz, 1H), 8.83 (t,  $J = 3.8$  Hz, 1H), 8.15 (d,  $J = 8.4$  Hz, 1H), 8.03 (d,  $J = 8.6$  Hz, 2H), 7.71-7.66 (m, 4H), 7.62-7.58 (m, 2H), 7.54-7.48 (m, 5H), 7.25 (dd,  $J_{\text{H-P}} = 14.6$  Hz, 4.4 Hz, 1H), 7.02 (d,  $J = 8.7$  Hz, 2H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.9, 162.6, 146.6 (d,  $J_{\text{C-P}} = 11.9$  Hz), 142.4, 139.1 (d,  $J_{\text{C-P}} = 94.6$  Hz), 139.0 (d,  $J_{\text{C-P}} = 7.8$  Hz), 135.4 (d,  $J_{\text{C-P}} = 2.2$  Hz), 132.5 (d,  $J_{\text{C-P}} = 2.5$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.0$  Hz), 131.1 (d,  $J_{\text{C-P}} = 105.7$  Hz), 129.1, 128.9 (d,  $J_{\text{C-P}} = 12.6$  Hz), 127.6 (d,  $J_{\text{C-P}} = 7.1$  Hz), 127.3, 126.6 (d,  $J_{\text{C-P}} = 9.5$  Hz), 121.1 (d,  $J_{\text{C-P}} = 5.6$  Hz), 117.0, 114.0, 55.4;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.4; HRMS (ESI+): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_3\text{P}$   $[\text{M}+\text{H}]^+$ : 479.1519, Found: 479.1524.



**N-(4-(diphenylphosphoryl)quinolin-8-yl)-4-fluorobenzamide (4fa):** Light yellow solid (60%); mp 228-230 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.69 (s, 1H), 8.91 (d,  $J = 7.6$  Hz, 1H), 8.83 (t,  $J = 3.9$  Hz, 1H), 8.19 (d,  $J = 8.5$  Hz, 1H), 8.09-8.06 (m, 2H), 7.71-7.66 (m, 4H), 7.62-7.59 (m, 2H), 7.54-7.49 (m, 5H), 7.28-7.19 (m, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1 (d,  $J_{\text{C-F}} = 253.0$  Hz), 164.3, 146.8 (d,  $J_{\text{C-P}} = 11.8$  Hz), 139.3 (d,  $J_{\text{C-P}} = 94.0$  Hz), 138.9 (d,  $J_{\text{C-P}} = 7.7$  Hz), 135.0 (d,  $J_{\text{C-P}} = 2.1$  Hz), 132.6 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.0$  Hz), 131.2 (d,  $J_{\text{C-P}} = 3.0$  Hz), 131.1 (d,  $J_{\text{C-P}} = 105.8$  Hz), 129.6 (d,  $J_{\text{C-F}} = 9.0$  Hz), 128.9, 128.9 (d,  $J_{\text{C-P}} = 12.3$  Hz), 127.6 (d,  $J_{\text{C-P}} = 7.0$  Hz), 126.7 (d,  $J_{\text{C-P}} = 9.6$  Hz), 121.5 (d,  $J_{\text{C-P}} = 5.4$  Hz), 117.2, 115.9 (d,  $J_{\text{C-F}} = 21.9$  Hz);  $^{31}\text{P NMR}$  (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.2; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{FN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 467.1319, Found: 467.1324.

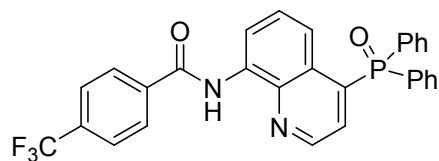


**4-chloro-N-(4-(diphenylphosphoryl)quinolin-8-yl)benzamide (4ga):** Light yellow solid (63%); mp 238-240 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.70 (s, 1H), 8.91 (d,  $J = 7.7$  Hz, 1H), 8.83 (t,  $J = 3.8$  Hz, 1H), 8.19 (d,  $J = 8.6$  Hz, 1H), 8.00 (d,  $J = 8.4$  Hz, 2H), 7.71-7.66 (m, 4H), 7.62-7.59 (m, 2H), 7.55-7.50 (m, 7H), 7.25 (dd,  $J_{\text{H-P}} = 14.7$  Hz, 4.3 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.3, 146.8 (d,  $J_{\text{C-P}} = 11.9$  Hz), 139.3 (d,  $J_{\text{C-P}} = 94.0$  Hz), 138.9 (d,  $J_{\text{C-P}} = 7.7$  Hz), 138.2, 134.9 (d,  $J_{\text{C-P}} = 2.1$  Hz), 133.4, 132.6 (d,  $J_{\text{C-P}} = 2.7$  Hz), 131.9 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.0 (d,  $J_{\text{C-P}} = 105.7$  Hz), 129.0 (d,  $J_{\text{C-P}} = 11.2$  Hz), 128.9 (d,  $J_{\text{C-P}} = 4.8$  Hz), 128.8, 128.7, 127.6 (d,  $J_{\text{C-P}} = 7.1$  Hz), 126.7 (d,  $J_{\text{C-P}} = 9.7$  Hz), 121.6 (d,  $J_{\text{C-P}} = 5.7$  Hz), 117.2;  $^{31}\text{P NMR}$  (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{ClN}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 483.1024, Found: 483.1024.

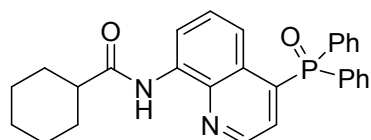


**4-bromo-N-(4-(diphenylphosphoryl)quinolin-8-yl)benzamide (4ha):** Light yellow solid (57%); mp 244-245 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.71 (s, 1H), 8.91 (d,  $J = 7.7$  Hz, 1H), 8.83 (t,  $J = 3.8$  Hz, 1H), 8.20 (d,  $J = 8.5$  Hz, 1H), 7.93 (d,  $J = 8.4$  Hz, 2H), 7.71-7.66 (m, 6H), 7.62-7.59 (m, 2H), 7.56-7.49 (m, 5H), 7.26 (dd,  $J_{\text{H-P}} = 14.8$  Hz, 4.3 Hz, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 146.9 (d,  $J_{\text{C-P}} = 11.8$  Hz), 139.4 (d,  $J_{\text{C-P}} = 93.5$  Hz), 138.9 (d,  $J_{\text{C-P}} = 8.5$  Hz), 135.0 (d,  $J_{\text{C-P}} = 2.1$  Hz), 133.9, 132.6 (d,  $J_{\text{C-P}} = 2.6$  Hz), 132.1, 132.0 (d,  $J_{\text{C-P}} = 10.1$  Hz), 131.1 (d,  $J_{\text{C-P}} = 105.8$  Hz), 128.9 (d,  $J_{\text{C-P}} = 11.2$  Hz), 128.9 (d,  $J_{\text{C-P}} = 4.1$  Hz), 128.9, 127.6 (d,  $J_{\text{C-P}} = 7.1$  Hz), 126.8, 126.7 (d,  $J_{\text{C-P}} = 9.8$  Hz), 121.7 (d,  $J_{\text{C-P}} = 5.7$  Hz), 117.3;  $^{31}\text{P NMR}$  (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.2;

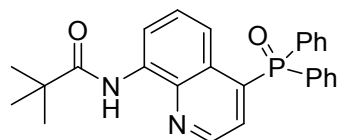
HRMS (ESI<sup>+</sup>): calcd for C<sub>28</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 527.0519, Found: 527.0518.



**N-(4-(diphenylphosphoryl)quinolin-8-yl)-4-(trifluoromethyl)benzamide (4ia)**: Light yellow solid (61%); mp 220-221 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.78 (s, 1H), 8.92 (d, *J* = 7.6 Hz, 1H), 8.84 (t, *J* = 3.8 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.71-7.66 (m, 4H), 7.62-7.59 (m, 2H), 7.57-7.49 (m, 5H), 7.26 (dd, *J*<sub>H-P</sub> = 14.8 Hz, 4.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.0, 146.9 (d, *J*<sub>C-P</sub> = 11.8 Hz), 139.4 (d, *J*<sub>C-P</sub> = 94.4 Hz), 138.9 (d, *J*<sub>C-P</sub> = 7.8 Hz), 138.3, 134.7 (d, *J*<sub>C-P</sub> = 2.1 Hz), 133.5 (q, *J*<sub>C-F</sub> = 32.6 Hz), 132.6 (d, *J*<sub>C-P</sub> = 2.7 Hz), 131.9 (d, *J*<sub>C-P</sub> = 10.0 Hz), 131.1 (d, *J*<sub>C-P</sub> = 105.9 Hz), 128.9 (d, *J*<sub>C-P</sub> = 12.3 Hz), 128.8, 127.7, 127.6 (d, *J*<sub>C-P</sub> = 7.6 Hz), 126.7 (d, *J*<sub>C-P</sub> = 9.7 Hz), 125.8 (q, *J*<sub>C-F</sub> = 3.8 Hz), 123.6 (q, *J*<sub>C-F</sub> = 273.3 Hz), 121.9 (d, *J*<sub>C-P</sub> = 5.5 Hz), 117.4; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 30.2; HRMS (ESI<sup>+</sup>): calcd for C<sub>29</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 517.1287, Found: 517.1290.

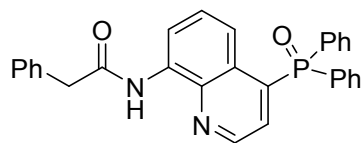


**N-(4-(diphenylphosphoryl)quinolin-8-yl)cyclohexanecarboxamide (4ja)**: Light yellow solid (72%); mp 244-246 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.91 (s, 1H), 8.82-8.80 (m, 2H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.71-7.66 (m, 4H), 7.63-7.59 (m, 2H), 7.52-7.46 (m, 5H), 7.25 (dd, *J*<sub>H-P</sub> = 19.5 Hz, 5.3 Hz, 1H), 2.51-2.45 (m, 1H), 2.09 (d, *J* = 12.0 Hz, 2H), 1.88 (d, *J* = 12.3 Hz, 2H), 1.75 (d, *J* = 11.1 Hz, 1H), 1.68-1.60 (s, 2H), 1.44-1.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.7, 146.5 (d, *J*<sub>C-P</sub> = 11.8 Hz), 139.0 (d, *J*<sub>C-P</sub> = 94.5 Hz), 138.7 (d, *J*<sub>C-P</sub> = 7.8 Hz), 135.2 (d, *J*<sub>C-P</sub> = 2.2 Hz), 132.5 (d, *J*<sub>C-P</sub> = 2.6 Hz), 131.9 (d, *J*<sub>C-P</sub> = 10.0 Hz), 131.2 (d, *J*<sub>C-P</sub> = 105.7 Hz), 128.9, 128.8 (d, *J*<sub>C-P</sub> = 12.3 Hz), 127.5 (d, *J*<sub>C-P</sub> = 7.1 Hz), 126.5 (d, *J*<sub>C-P</sub> = 9.6 Hz), 120.9 (d, *J*<sub>C-P</sub> = 5.6 Hz), 117.0, 46.9, 29.7, 29.6, 25.7; <sup>31</sup>P NMR (163 MHz, CDCl<sub>3</sub>) δ 30.2; HRMS (ESI<sup>+</sup>): calcd for C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sub>2</sub>P [M+H]<sup>+</sup>: 455.1883, Found: 455.1885.

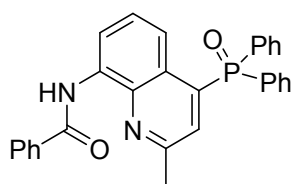


**N-(4-(diphenylphosphoryl)quinolin-8-yl)pivalamide (4ka)**: Light yellow solid (61%); mp 190-191 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.26 (s, 1H), 8.81-8.79 (m, 2H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.69-7.64 (m, 4H), 7.61-7.57 (m, 2H), 7.50-7.45 (m, 5H), 7.23 (dd, *J*<sub>H-P</sub> = 15.5 Hz, 5.5 Hz, 1H), 1.41 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.2, 146.6 (d, *J*<sub>C-P</sub> = 11.6 Hz), 139.0 (d, *J*<sub>C-P</sub> = 7.7 Hz), 138.9 (d, *J*<sub>C-P</sub> = 94.6 Hz), 135.3 (d, *J*<sub>C-P</sub> = 2.3 Hz), 132.5 (d, *J*<sub>C-P</sub> = 2.6 Hz), 131.9 (d, *J*<sub>C-P</sub> =

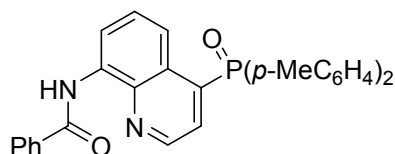
10.0 Hz), 131.2 (d,  $J_{C-P} = 106.4$  Hz), 128.9, 128.8 (d,  $J_{C-P} = 11.1$  Hz), 127.5 (d,  $J_{C-P} = 7.4$  Hz), 126.5 (d,  $J_{C-P} = 9.6$  Hz), 120.9 (d,  $J_{C-P} = 5.5$  Hz), 116.9, 40.4, 27.7;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 429.1726, Found: 429.1727.



**N-(4-(diphenylphosphoryl)quinolin-8-yl)-2-phenylacetamide (41a)**: Light yellow solid (73%); mp 195-196 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (s, 1H), 8.75 (d,  $J = 7.6$  Hz, 1H), 8.66 (t,  $J = 3.9$  Hz, 1H), 8.10 (d,  $J = 8.5$  Hz, 1H), 7.67-7.56 (m, 6H), 7.49-7.37 (m, 9H), 7.34-7.30 (m, 1H), 7.25 (dd,  $J_{H-P} = 15.0$  Hz, 4.2 Hz, 1H), 3.87 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.4, 146.6 (d,  $J_{C-P} = 12.0$  Hz), 138.9 (d,  $J_{C-P} = 94.3$  Hz), 138.6 (d,  $J_{C-P} = 7.7$  Hz), 134.9 (d,  $J_{C-P} = 2.5$  Hz), 134.5, 132.5 (d,  $J_{C-P} = 2.5$  Hz), 131.9 (d,  $J_{C-P} = 10.1$  Hz), 131.1 (d,  $J_{C-P} = 105.9$  Hz), 129.5, 129.0, 128.8 (d,  $J_{C-P} = 12.5$  Hz), 128.7, 127.4 (d,  $J_{C-P} = 7.2$  Hz), 127.3, 126.5 (d,  $J_{C-P} = 9.5$  Hz), 121.2 (d,  $J_{C-P} = 5.5$  Hz), 116.9, 45.3;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.3; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1569.



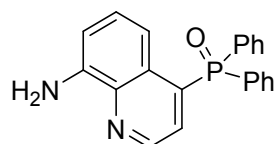
**N-(4-(diphenylphosphoryl)-2-methylquinolin-8-yl)benzamide (4ma)**: Light yellow solid (60%); mp 259-260 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.81 (s, 1H), 8.90 (d,  $J = 7.7$  Hz, 1H), 8.07-8.02 (m, 3H), 7.71-7.66 (m, 4H), 7.61-7.42 (m, 10H), 7.23 (d,  $J_{H-P} = 15.2$  Hz, 1H), 2.72 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 155.8 (d,  $J_{C-P} = 11.7$  Hz), 139.3 (d,  $J_{C-P} = 94.1$  Hz), 138.5 (d,  $J_{C-P} = 8.1$  Hz), 135.2, 134.5 (d,  $J_{C-P} = 2.4$  Hz), 132.5 (d,  $J_{C-P} = 2.5$  Hz), 131.9 (d,  $J_{C-P} = 10.1$  Hz), 131.8, 131.3 (d,  $J_{C-P} = 105.7$  Hz), 128.8 (d,  $J_{C-P} = 12.4$  Hz), 128.8, 127.7, 127.6 (d,  $J_{C-P} = 7.6$  Hz), 127.2, 125.6 (d,  $J_{C-P} = 7.4$  Hz), 121.1 (d,  $J_{C-P} = 5.4$  Hz), 117.1, 25.5;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  29.8; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_2\text{P}$   $[\text{M}+\text{H}]^+$ : 463.1570, Found: 463.1572.



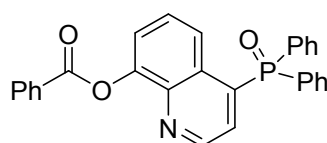
**N-(4-(di-p-tolylphosphoryl)quinolin-8-yl)benzamide (4ab)**: Light yellow solid (45%); mp 186-187 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.76 (s, 1H), 8.94 (d,  $J = 7.5$  Hz, 1H), 8.83 (t,  $J = 3.8$  Hz, 1H), 8.19 (d,  $J = 8.5$  Hz, 1H), 8.07 (d,  $J = 6.8$  Hz, 2H), 7.58-7.52 (m, 8H), 7.31-7.24 (m, 5H), 2.42 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 146.8 (d,  $J_{C-P} = 11.7$  Hz), 143.1 (d,  $J_{C-P} = 2.6$  Hz), 139.6 (d,  $J_{C-P} = 94.1$  Hz), 138.9 (d,  $J_{C-P} = 7.6$  Hz), 135.1 (d,  $J_{C-P} = 2.5$  Hz), 135.0, 131.9 (d,  $J_{C-P} =$

10.2 Hz), 131.9, 129.6 (d,  $J_{C-P}$  = 12.6 Hz), 128.8, 128.0 (d,  $J_{C-P}$  = 108.4 Hz), 127.6 (d,  $J_{C-P}$  = 7.0 Hz), 127.2, 126.6 (d,  $J_{C-P}$  = 9.6 Hz), 121.5 (d,  $J_{C-P}$  = 5.5 Hz), 117.1, 21.6;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.6; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{30}\text{H}_{25}\text{N}_2\text{O}_2\text{P}$  [M+H]<sup>+</sup>: 477.1726, Found: 477.1733.

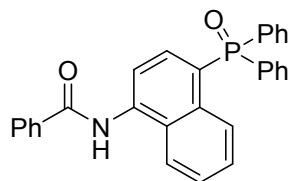
c) A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **3aa** or **4aa** (44.8 mg, 0.1 mmol), NOH (20 mg, 0.5 mmol, 5 equiv), and  $\text{CH}_3\text{CH}_2\text{OH}$  (2.0 mL). The resulting mixture was heated at 80 °C for 12 h, and cooled to room temperature. Upon completion,  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to the reaction system, and the resulting mixture was filtered through a pad of Celite. The filtrate was extracted with  $\text{H}_2\text{O}$  (20 mL), and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (2 × 10 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using  $\text{CH}_2\text{Cl}_2$ -EtOAc as an eluent to afford the pure product **3xa** or **4pa**.



**(8-aminoquinolin-4-yl)diphenylphosphine oxide (4pa)**: Light yellow solid (92%); mp 257-258 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (t,  $J$  = 4.0 Hz, 1H), 7.73-7.63 (m, 5H), 7.56-7.53 (m, 2H), 7.47-7.44 (m, 4H), 7.22 (t,  $J$  = 8.0 Hz, 1H), 7.04 (dd,  $J_{\text{H-P}}$  = 15.2 Hz, 7.2 Hz, 1H), 6.88 (dd,  $J$  = 7.4, 1H), 5.08 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.5 (d,  $J_{C-P}$  = 12.1 Hz), 144.6 (d,  $J_{C-P}$  = 2.2 Hz), 138.4 (d,  $J_{C-P}$  = 7.7 Hz), 137.8 (d,  $J_{C-P}$  = 95.7 Hz), 132.2 (d,  $J_{C-P}$  = 2.8 Hz), 131.9 (d,  $J_{C-P}$  = 9.9 Hz), 131.4 (d,  $J_{C-P}$  = 105.2 Hz), 128.8, 128.7 (d,  $J_{C-P}$  = 12.4 Hz), 128.1 (d,  $J_{C-P}$  = 7.0 Hz), 126.5 (d,  $J_{C-P}$  = 9.9 Hz), 115.5 (d,  $J_{C-P}$  = 5.9 Hz), 110.4;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.6; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{21}\text{H}_{17}\text{N}_2\text{OP}$  [M+H]<sup>+</sup>: 344.1151, Found: 344.1153.



**4-(diphenylphosphoryl)quinolin-8-yl benzoate (7)**: Light yellow solid; mp 88-89 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.85 (t,  $J$  = 3.9 Hz, 1H), 8.51 (d,  $J$  = 8.0 Hz, 1H), 8.32 (d,  $J$  = 7.5 Hz, 2H), 7.72-7.49 (m, 15H), 7.15 (dd,  $J_{\text{H-P}}$  = 14.9 Hz, 4.2 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  165.4, 149.0 (d,  $J_{C-P}$  = 11.6 Hz), 148.1 (d,  $J_{C-P}$  = 2.8 Hz), 141.8 (d,  $J_{C-P}$  = 7.1 Hz), 138.6 (d,  $J_{C-P}$  = 94.5 Hz), 133.6, 132.5 (d,  $J_{C-P}$  = 2.7 Hz), 131.9 (d,  $J_{C-P}$  = 10.0 Hz), 131.0 (d,  $J_{C-P}$  = 105.7 Hz), 130.5, 129.3, 128.9 (d,  $J_{C-P}$  = 12.5 Hz), 128.8, 128.6, 127.6, 126.6 (d,  $J_{C-P}$  = 9.5 Hz), 121.5 (d,  $J_{C-P}$  = 5.5 Hz), 122.2;  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  30.8; HRMS (ESI<sup>+</sup>): calcd for  $\text{C}_{29}\text{H}_{22}\text{NO}_2\text{P}$  [M+H]<sup>+</sup>: 450.1254, Found: 450.1260.

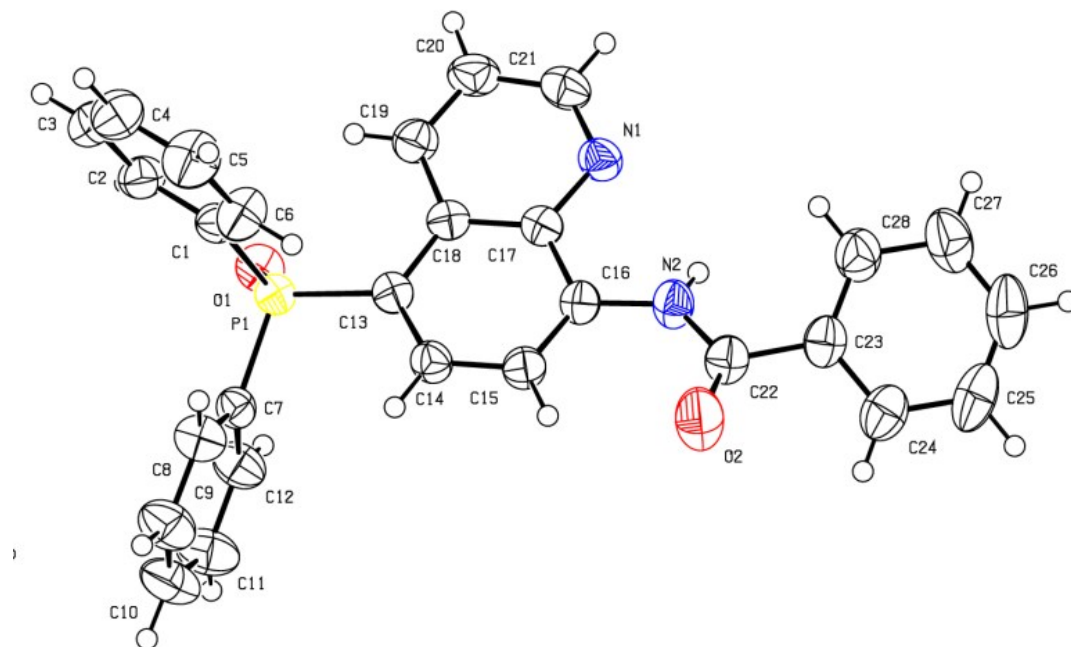


**N-(4-(diphenylphosphoryl)naphthalen-1-yl)benzamide (9)**: Light yellow solid; mp 287-288 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.38 (s, 1H), 8.36 (d,  $J = 7.0$  Hz, 2H), 8.23 (d,  $J = 8.4$  Hz, 1H), 8.00 (d,  $J = 8.2$  Hz, 1H), 7.65-7.51 (m, 9H), 7.44-7.36 (m, 5H), 7.26-7.23 (m, 1H), 7.15 (t,  $J = 7.7$  Hz, 1H), 6.82 (dd,  $J_{\text{H-P}} = 15.8$  Hz, 7.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 137.8 (d,  $J_{\text{C-P}} = 3.2$  Hz), 134.4, 133.7 (d,  $J_{\text{C-P}} = 14.8$  Hz), 133.7, 132.4 (d,  $J_{\text{C-P}} = 104.2$  Hz), 131.9 (d,  $J_{\text{C-P}} = 3.3$  Hz), 131.9, 128.6 (d,  $J_{\text{C-P}} = 11.9$  Hz), 128.6, 128.3 (d,  $J_{\text{C-P}} = 9.2$  Hz), 128.0, 127.5 (d,  $J_{\text{C-P}} = 5.9$  Hz), 126.8, 126.2, 124.8 (d,  $J_{\text{C-P}} = 105.1$  Hz), 122.9, 120.5 (d,  $J_{\text{C-P}} = 14.5$  Hz);  $^{31}\text{P}$  NMR (163 MHz,  $\text{CDCl}_3$ )  $\delta$  32.3; HRMS (ESI+): calcd for  $\text{C}_{28}\text{H}_{20}\text{NO}_3\text{P}$   $[\text{M}+\text{H}]^+$ : 448.1461, Found: 448.1467.

## 5. References

1 T. Truong, K. Klimovica and O. Daugulis, *J. Am. Chem. Soc.*, 2013, **135**, 9342.

## 6. The Single Crystal X-ray Diffraction Study of 3aa, 4aa and 3ya.

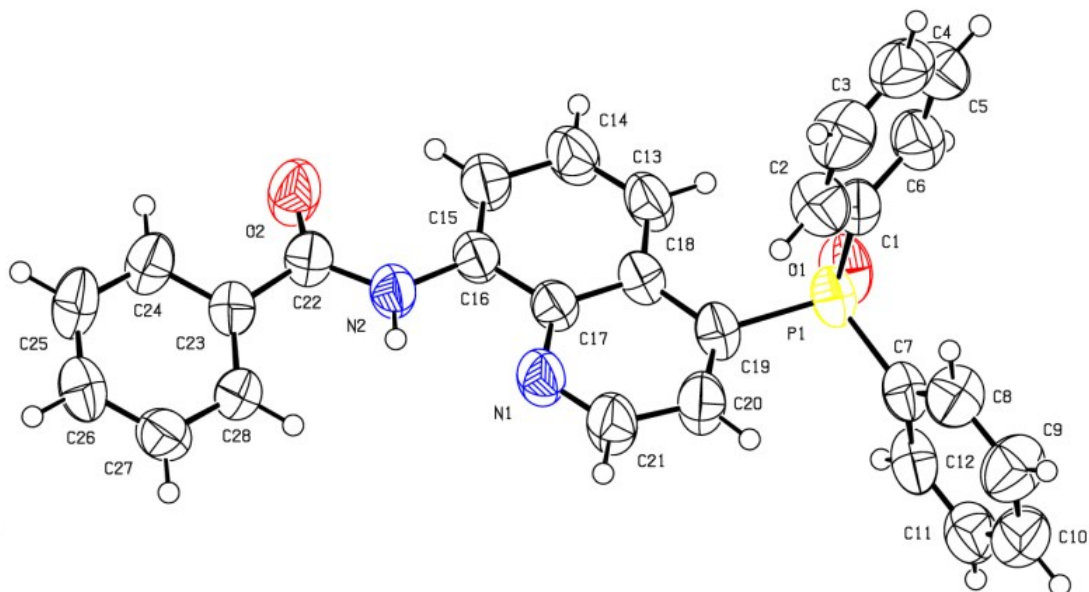


CCDC 1527635 (**3aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S3** Crystal data and structure refinement for **3aa**.



Identification code	201608113
Empirical formula	C <sub>28</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> P
Formula weight	448.44
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	12.9056(3)
b/Å	8.9810(2)
c/Å	20.4045(5)
α/°	90
β/°	106.848(3)
γ/°	90
Volume/Å <sup>3</sup>	2263.47(10)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.316
μ/mm <sup>-1</sup>	1.302
F(000)	936.0
Crystal size/mm <sup>3</sup>	0.22 × 0.2 × 0.15
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.156 to 134.15
Index ranges	-15 ≤ h ≤ 13, -10 ≤ k ≤ 9, -24 ≤ l ≤ 24
Reflections collected	8616
Independent reflections	4050 [R <sub>int</sub> = 0.0364, R <sub>sigma</sub> = 0.0361]
Data/restraints/parameters	4050/0/303
Goodness-of-fit on F <sup>2</sup>	1.041
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0412, wR <sub>2</sub> = 0.1062
Final R indexes [all data]	R <sub>1</sub> = 0.0506, wR <sub>2</sub> = 0.1138
Largest diff. peak/hole / e Å <sup>-3</sup>	0.34/-0.31

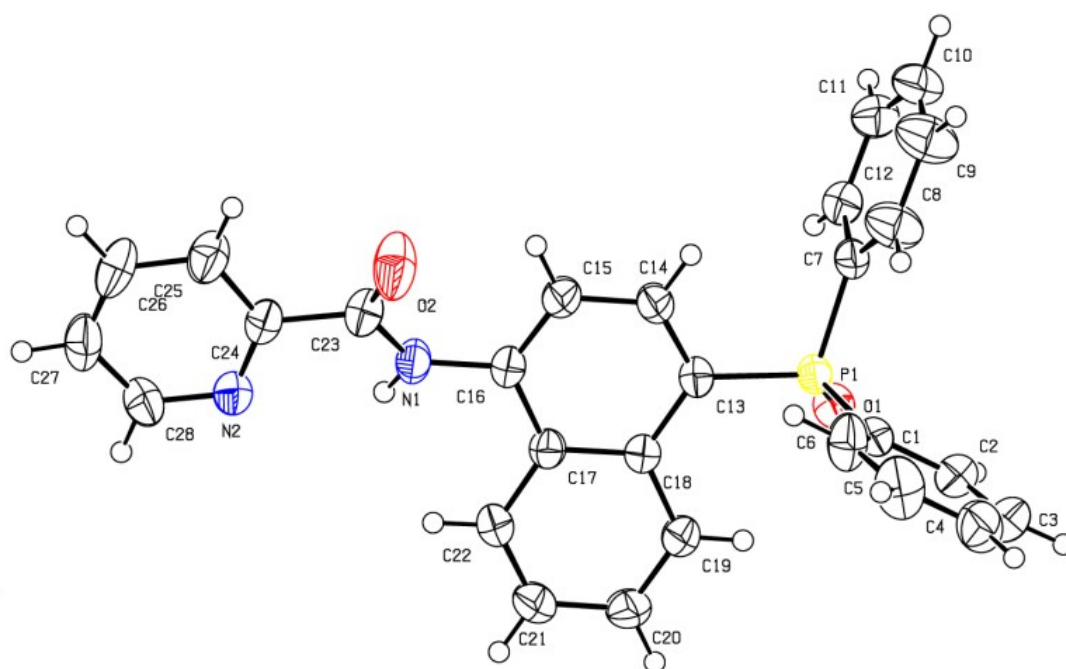


CCDC 1527636 (**4aa**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S4** Crystal data and structure refinement for **4aa**.

Identification code	201608114
Empirical formula	C <sub>28</sub> H <sub>21</sub> N <sub>2</sub> O <sub>2</sub> P
Formula weight	448.44
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	14.3374(5)
b/Å	9.7100(4)
c/Å	18.7718(7)
α/°	90
β/°	105.341(4)
γ/°	90
Volume/Å <sup>3</sup>	2520.23(16)
Z	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.182
μ/mm <sup>-1</sup>	1.169
F(000)	936.0
Crystal size/mm <sup>3</sup>	0.21 × 0.18 × 0.16
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	6.942 to 134.16
Index ranges	-16 ≤ h ≤ 17, -7 ≤ k ≤ 11, -22 ≤ l ≤ 13
Reflections collected	9535

Independent reflections	4509 [ $R_{\text{int}} = 0.0261$ , $R_{\text{sigma}} = 0.0291$ ]
Data/restraints/parameters	4509/0/299
Goodness-of-fit on $F^2$	1.049
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0467$ , $wR_2 = 0.1343$
Final R indexes [all data]	$R_1 = 0.0561$ , $wR_2 = 0.1436$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.28/-0.20

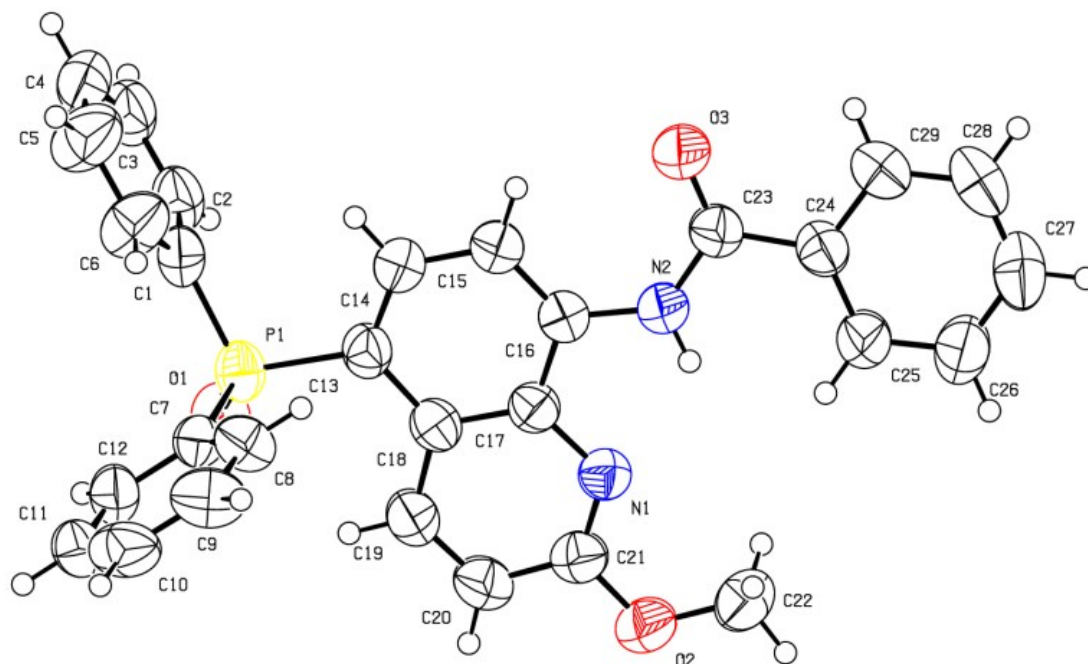


CCDC 1543497 (**3ya**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table S5** Crystal data and structure refinement for **3ya**.

Identification code	20170442
Empirical formula	$C_{28}H_{21}N_2O_2P$
Formula weight	448.44
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.9961(5)
$b/\text{\AA}$	8.6310(3)
$c/\text{\AA}$	21.6563(7)
$\alpha/^\circ$	90
$\beta/^\circ$	95.014(4)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2233.68(15)
Z	4

$\rho_{\text{calc}}/\text{cm}^3$	1.333
$\mu/\text{mm}^{-1}$	1.319
F(000)	936.0
Crystal size/ $\text{mm}^3$	$0.18 \times 0.15 \times 0.1$
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.54184$ )
$2\theta$ range for data collection/ $^\circ$	7.398 to 134.174
Index ranges	$-14 \leq h \leq 11, -10 \leq k \leq 6, -25 \leq l \leq 22$
Reflections collected	8345
Independent reflections	3994 [ $R_{\text{int}} = 0.0279, R_{\text{sigma}} = 0.0348$ ]
Data/restraints/parameters	3994/0/299
Goodness-of-fit on $F^2$	1.058
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0406, wR_2 = 0.1051$
Final R indexes [all data]	$R_1 = 0.0494, wR_2 = 0.1133$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.29/-0.29



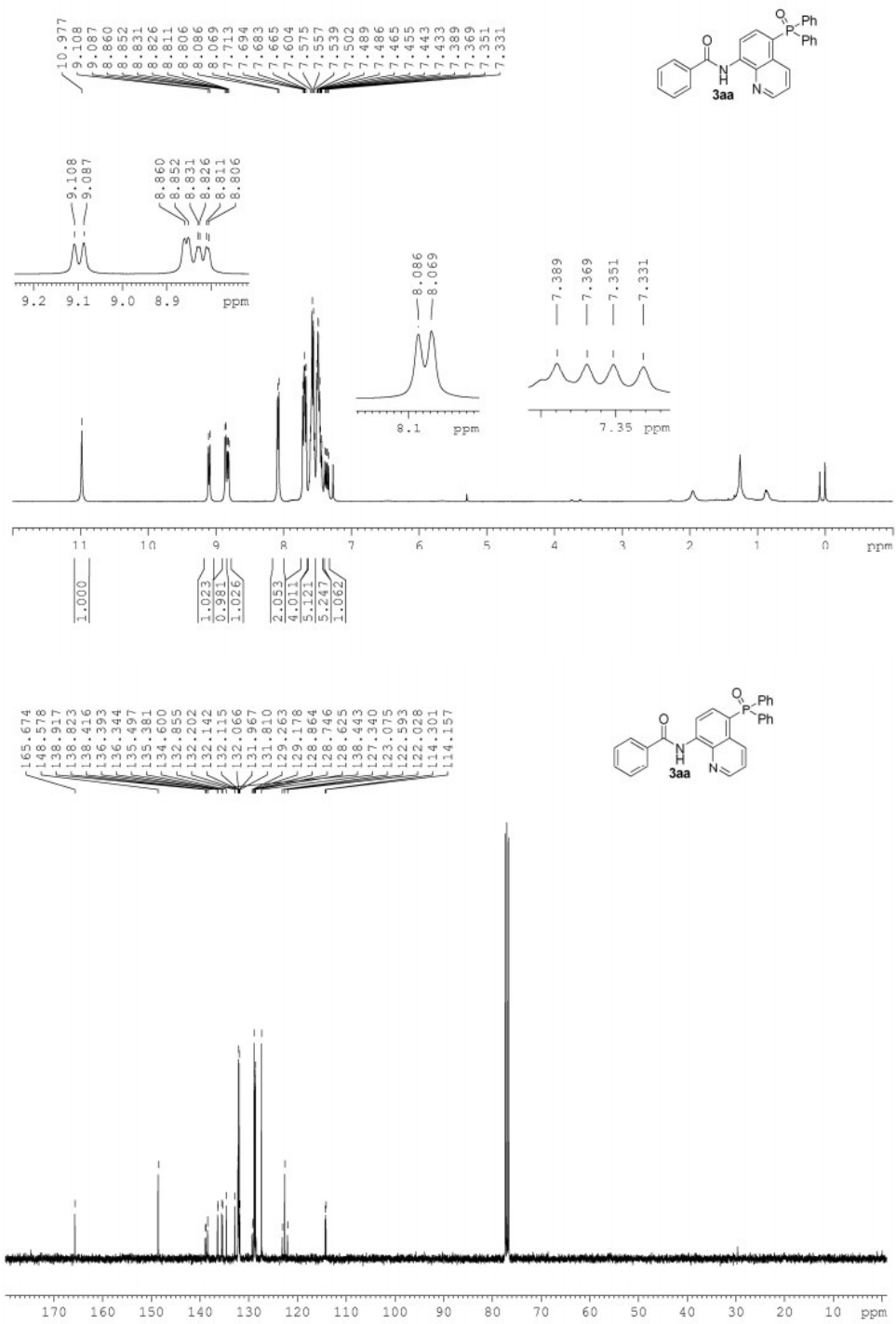
CCDC 1554232 (**3za**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

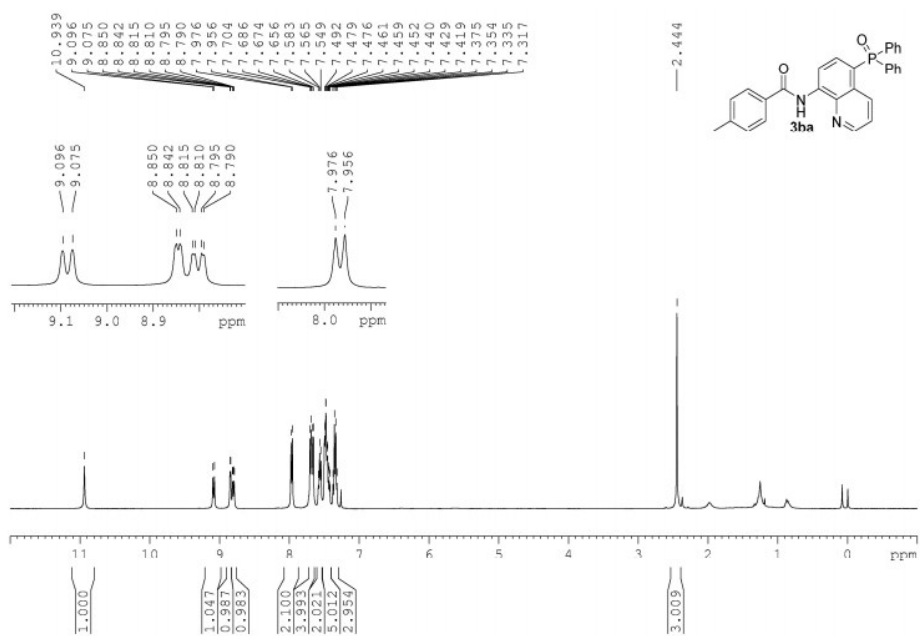
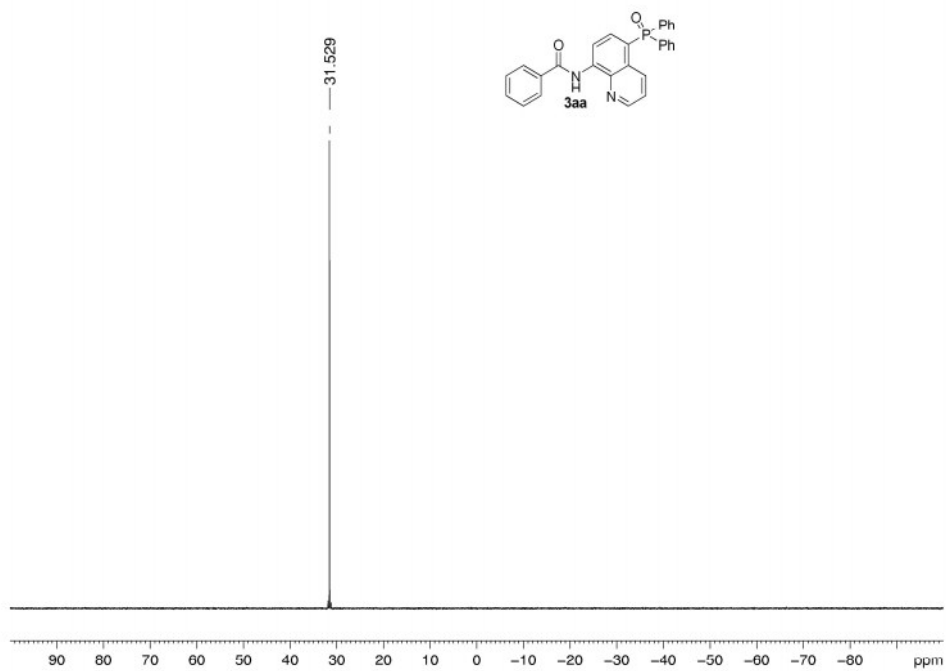
**Table S6** Crystal data and structure refinement for **3za**.

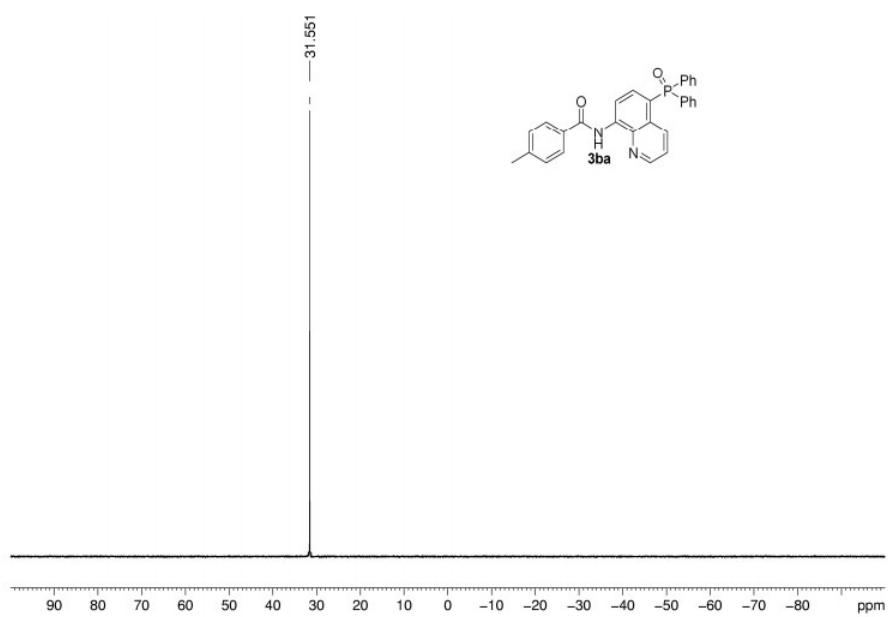
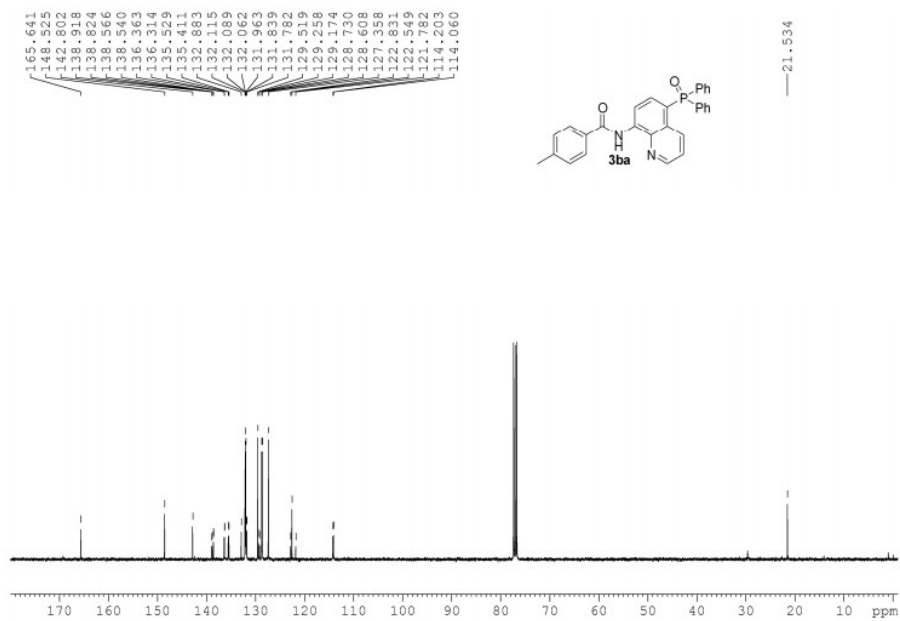
Identification code	20170698
Empirical formula	$\text{C}_{29}\text{H}_{23}\text{N}_2\text{O}_3\text{P}$
Formula weight	478.46
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1

a/Å	9.5853(9)
b/Å	9.8739(8)
c/Å	14.7007(14)
$\alpha$ /°	103.110(8)
$\beta$ /°	94.035(8)
$\gamma$ /°	114.371(8)
Volume/Å <sup>3</sup>	1213.1(2)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.310
$\mu/\text{mm}^{-1}$	1.279
F(000)	500.0
Crystal size/mm <sup>3</sup>	0.15 × 0.11 × 0.1
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54184)
2 $\Theta$ range for data collection/°	10.25 to 134.006
Index ranges	-11 ≤ h ≤ 8, -11 ≤ k ≤ 11, -16 ≤ l ≤ 17
Reflections collected	8680
Independent reflections	4325 [R <sub>int</sub> = 0.0222, R <sub>sigma</sub> = 0.0318]
Data/restraints/parameters	4325/0/322
Goodness-of-fit on F <sup>2</sup>	1.021
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0467, wR <sub>2</sub> = 0.1246
Final R indexes [all data]	R <sub>1</sub> = 0.0583, wR <sub>2</sub> = 0.1360
Largest diff. peak/hole / e Å <sup>-3</sup>	0.25/-0.25

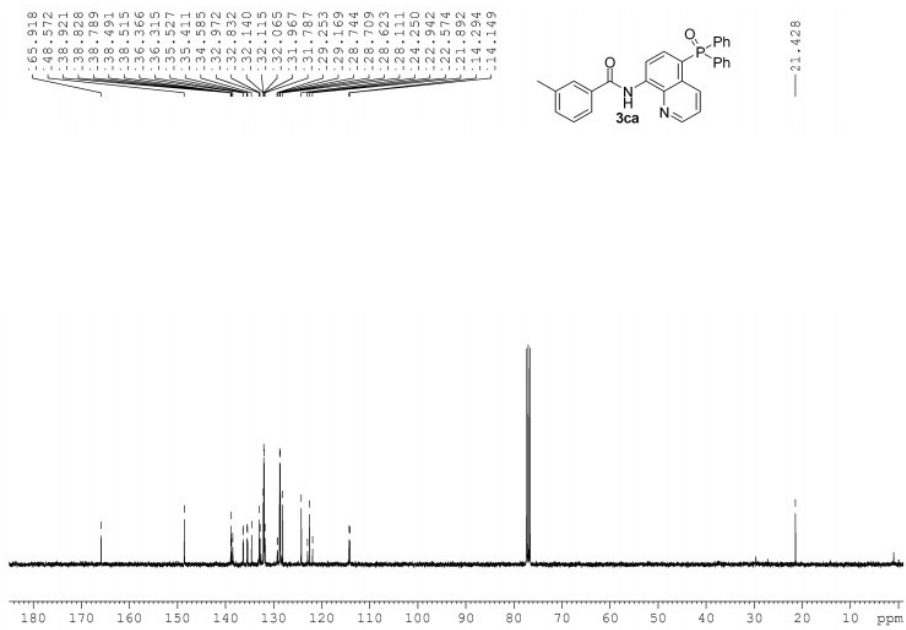
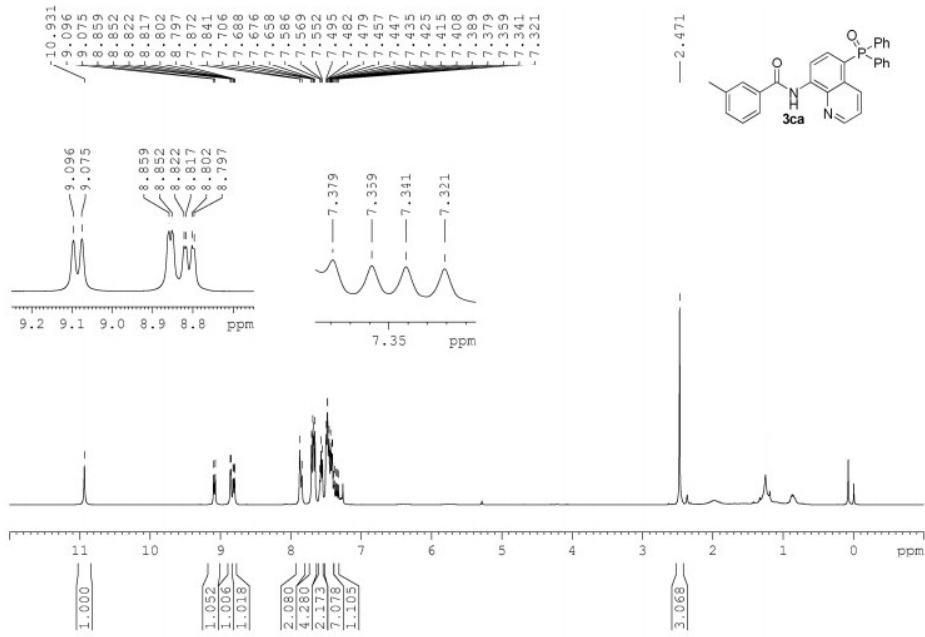
## 7. Copies of $^1\text{H}$ , $^{13}\text{C}$ and $^{31}\text{P}$ NMR Spectra for the Products

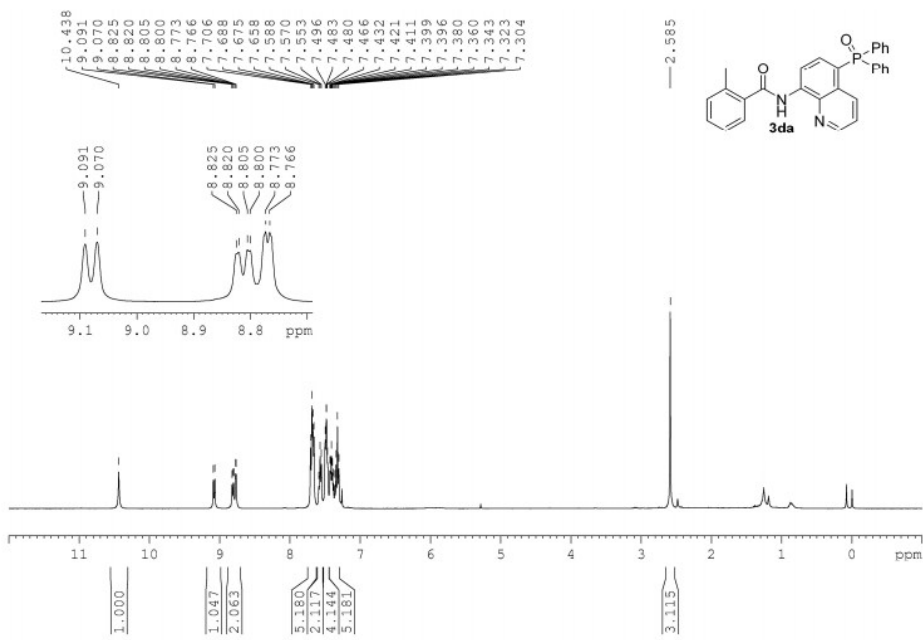
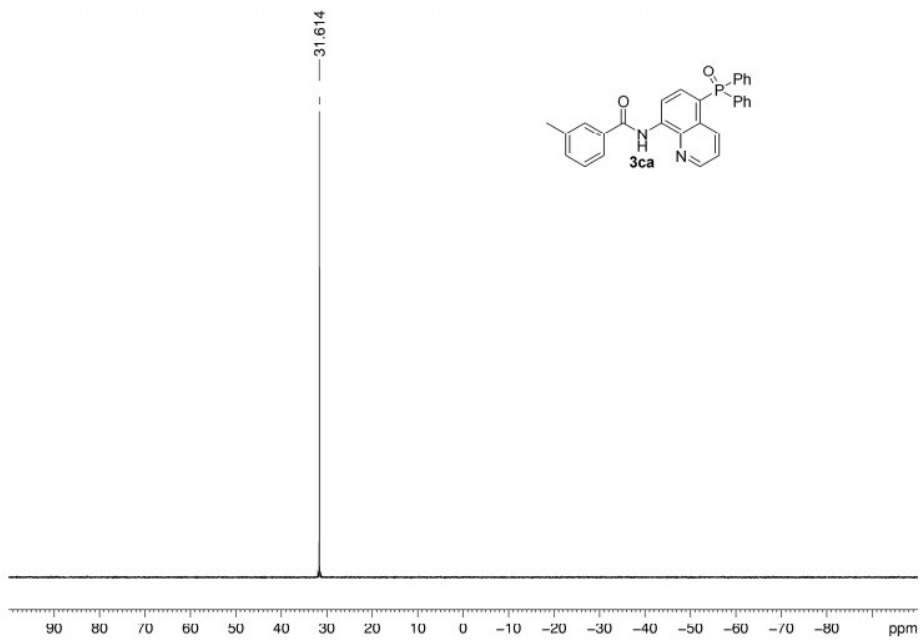


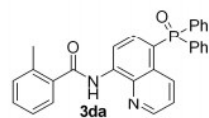
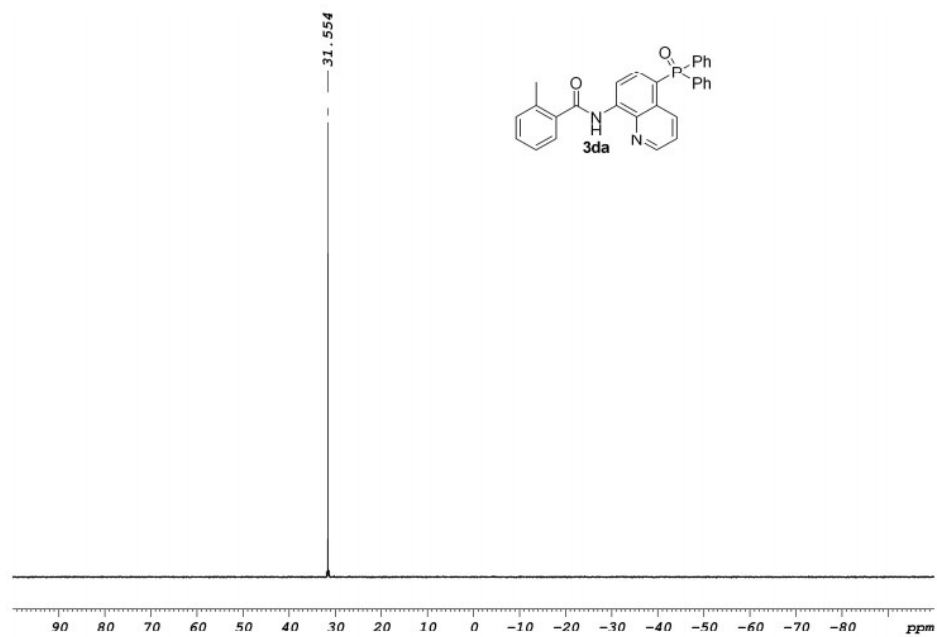
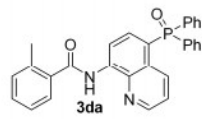
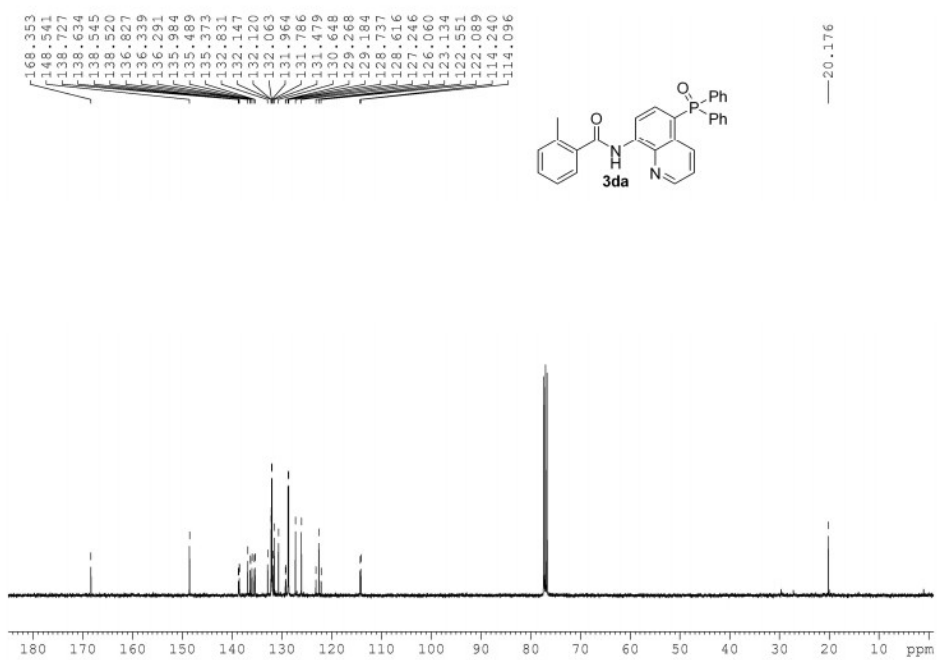


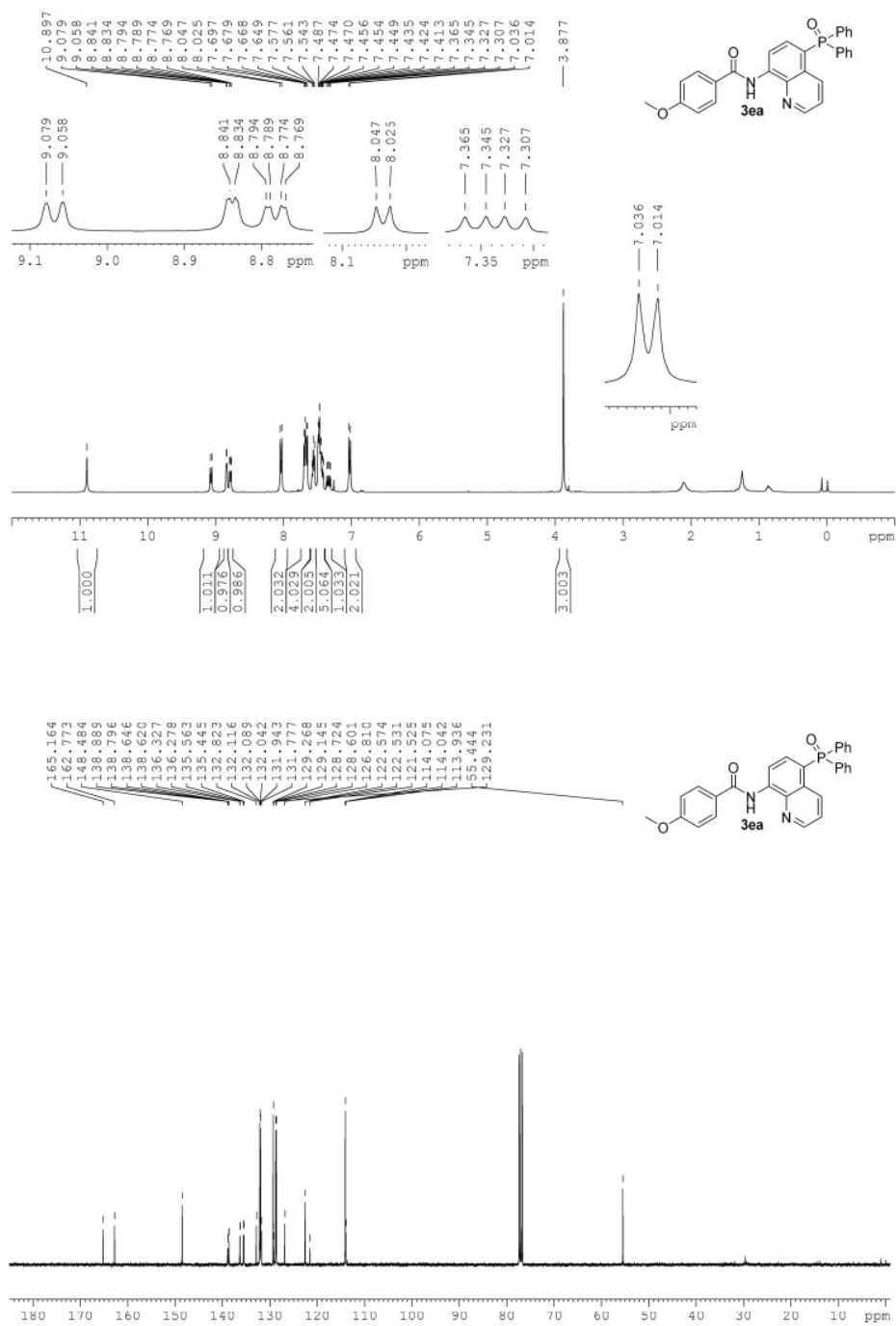


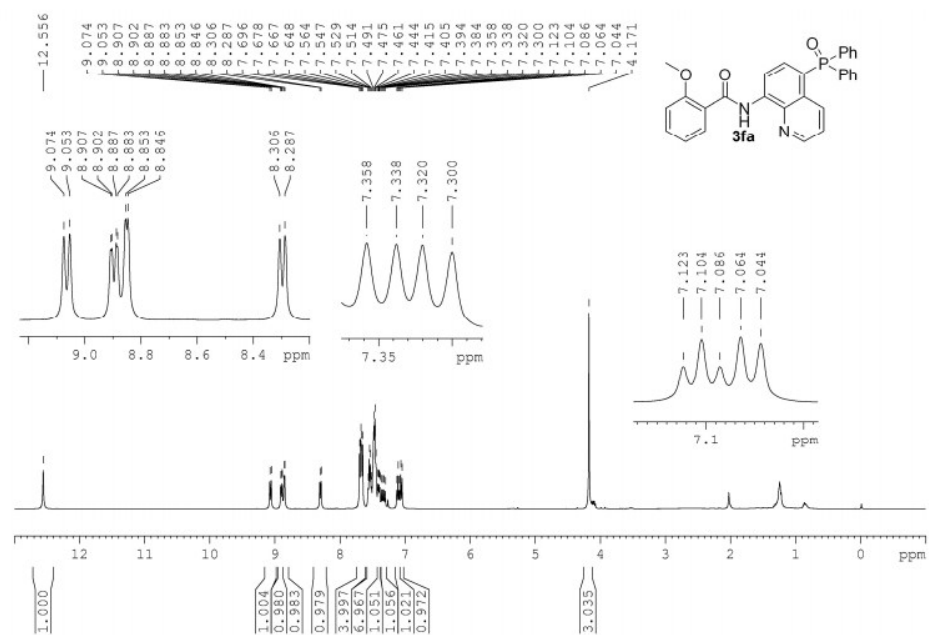
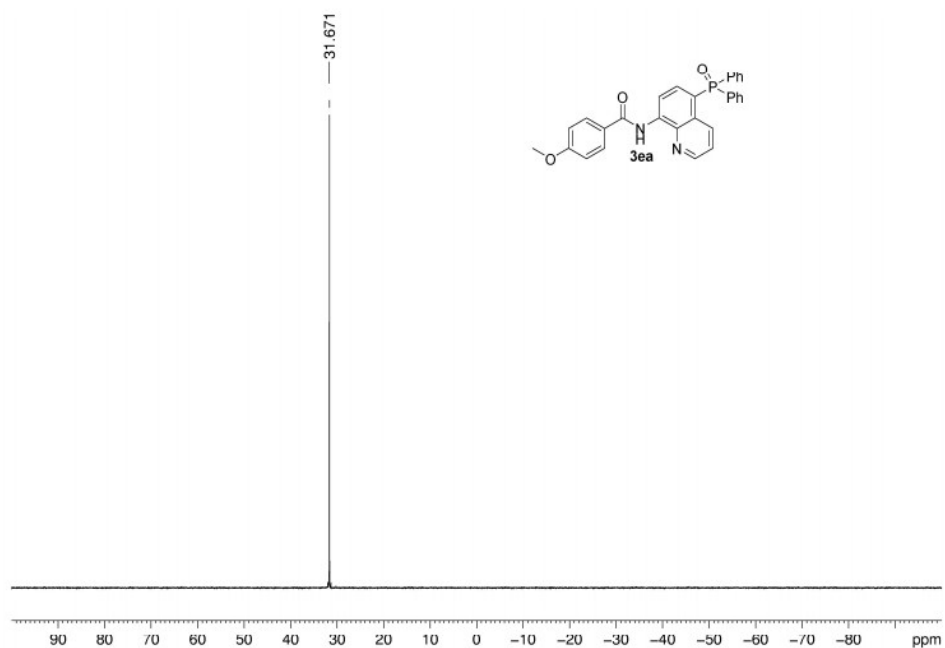


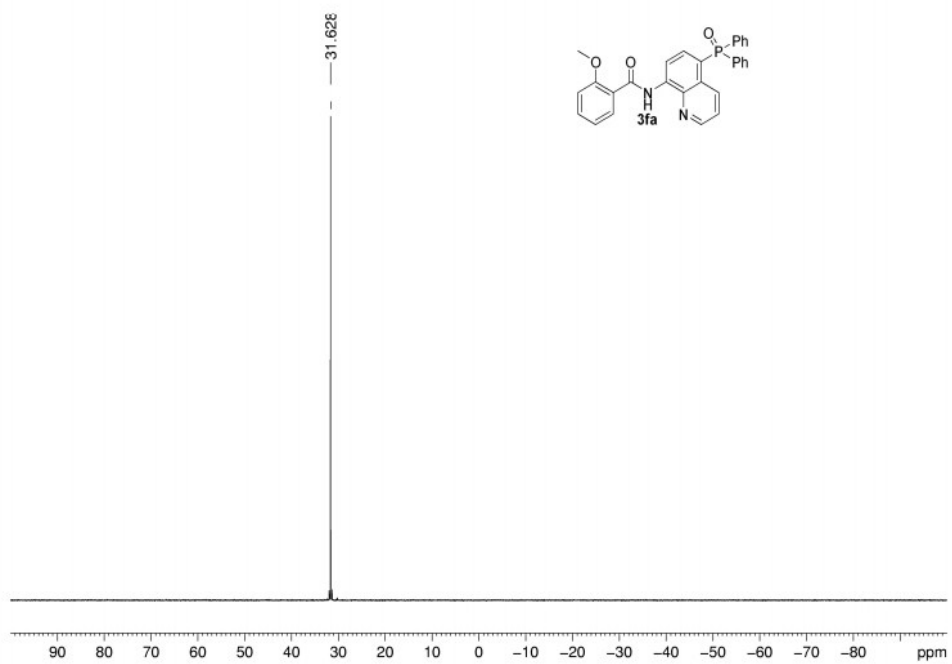
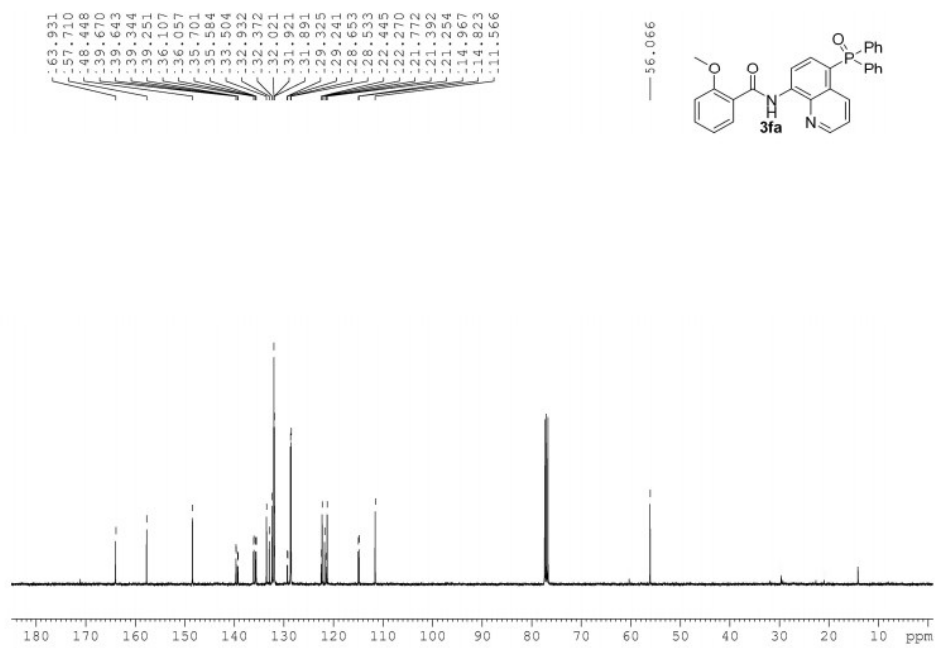




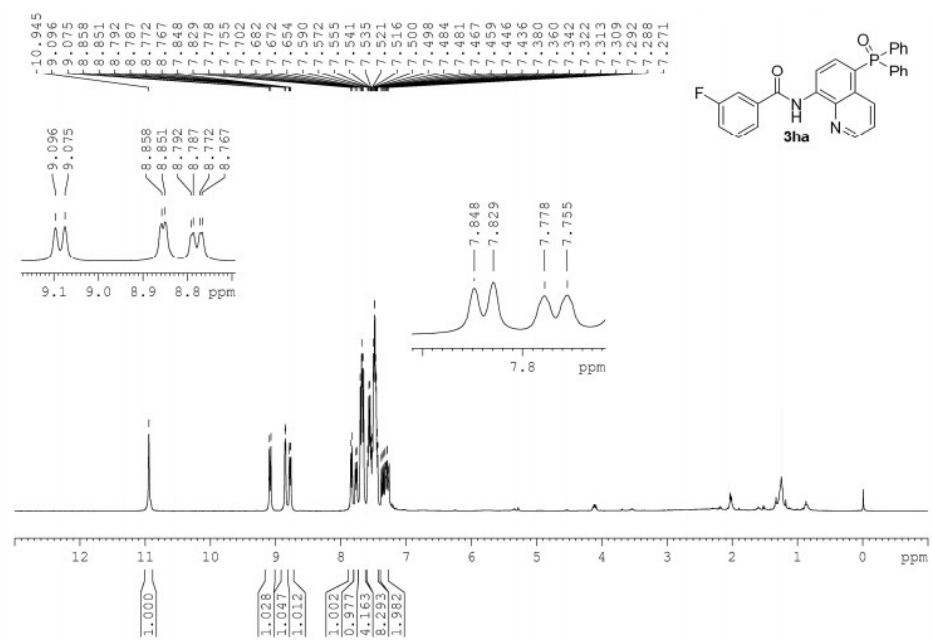
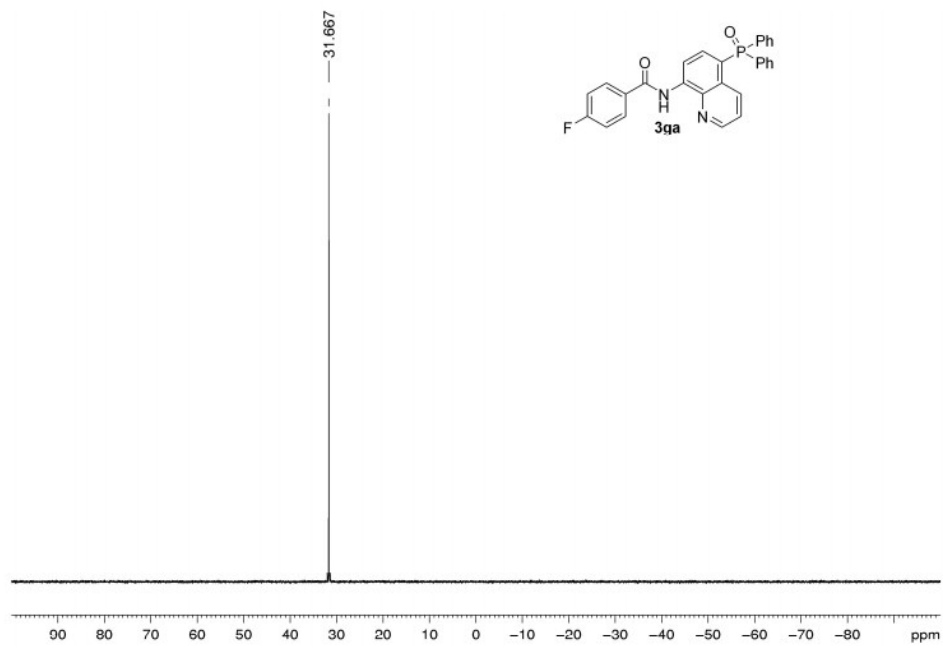




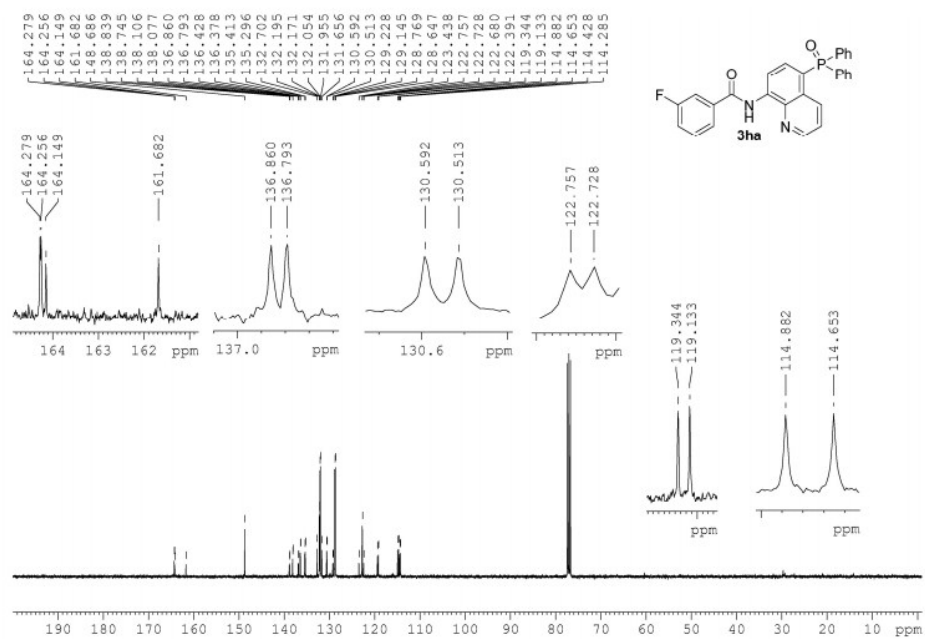


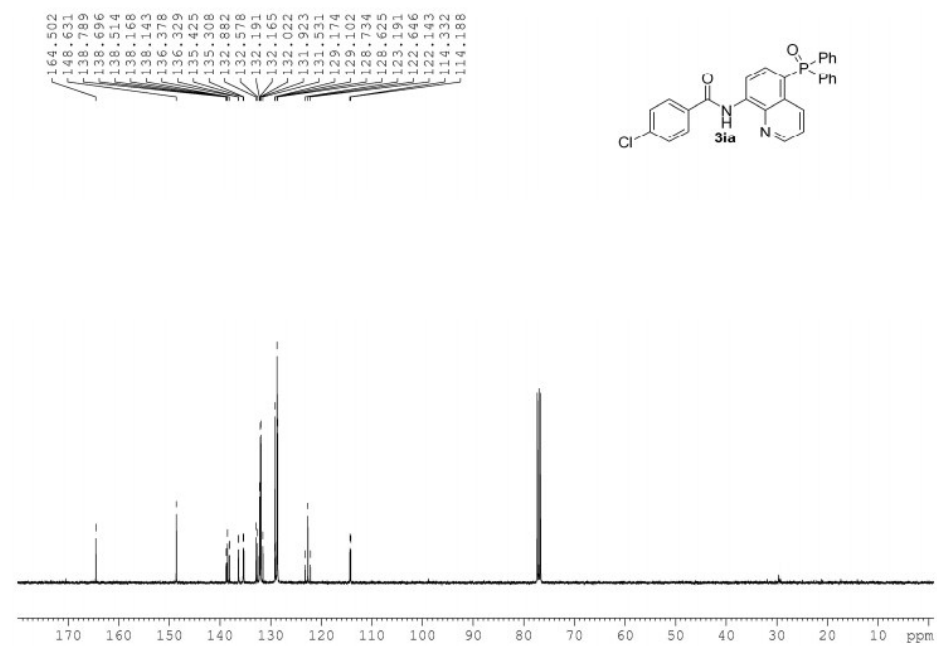
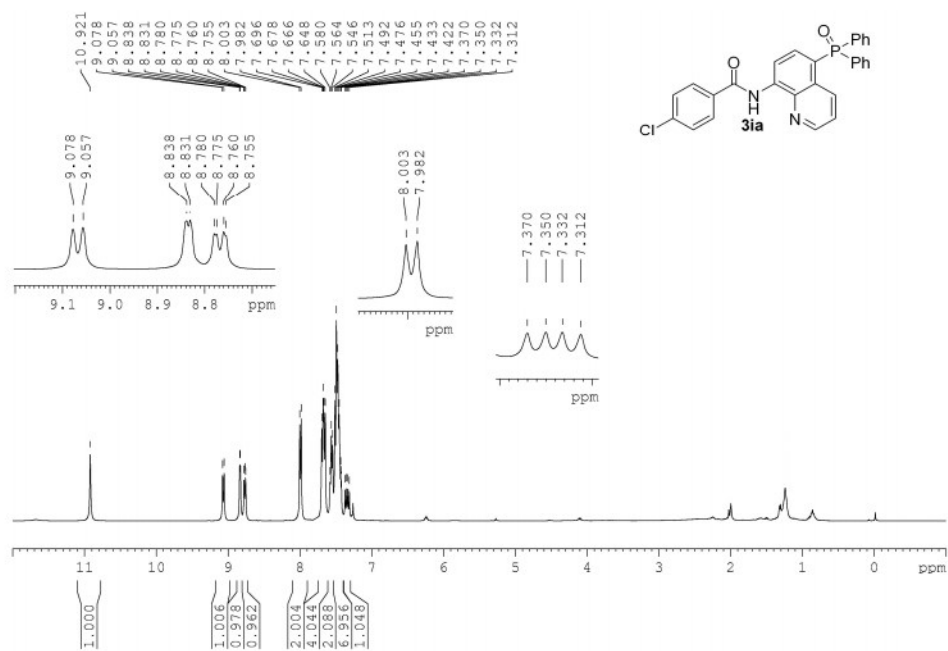


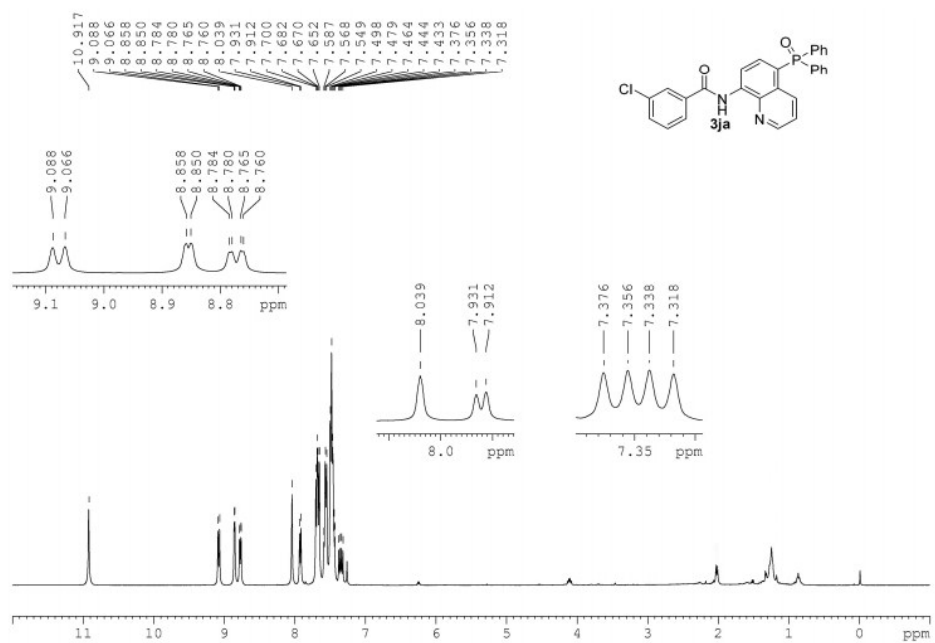
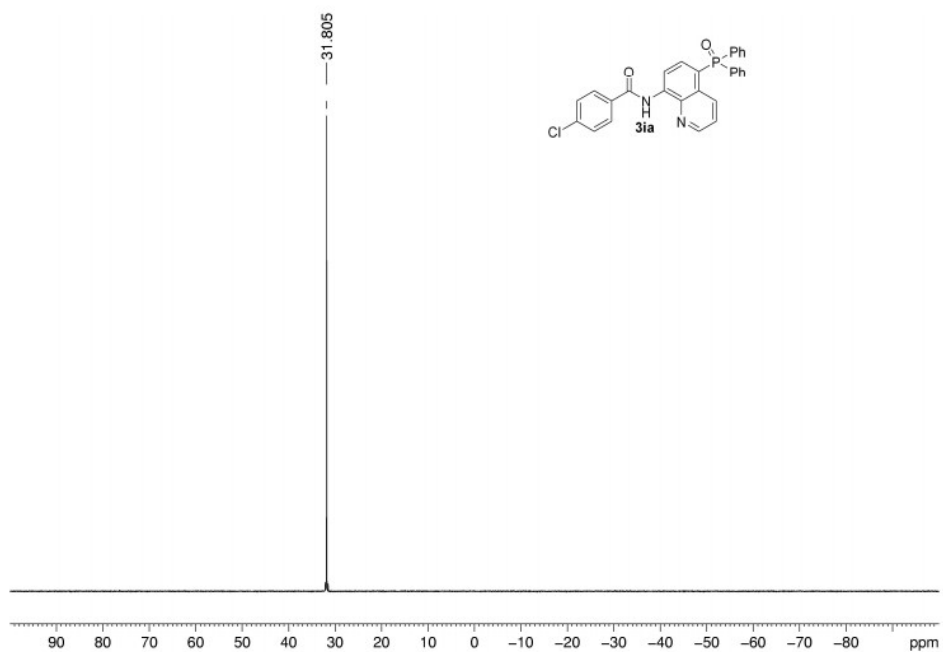




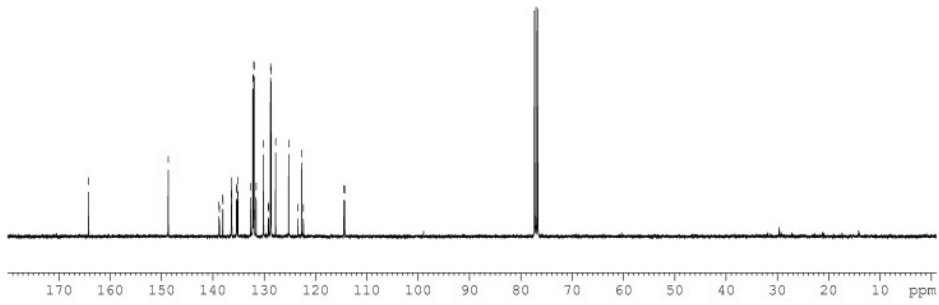
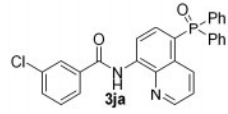








164.212  
 148.696  
 138.810  
 138.715  
 138.083  
 136.402  
 136.310  
 135.403  
 135.286  
 135.108  
 132.619  
 132.205  
 132.179  
 132.040  
 131.941  
 131.571  
 130.128  
 129.193  
 129.109  
 128.762  
 128.640  
 127.768  
 125.229  
 123.403  
 122.679  
 122.358  
 114.453  
 114.309



31.721

