# Chelation-Assisted C–N Cross-Coupling of Phosphinamides and Aryl

# Bronic Acids with Copper Powder at Room Temperature

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### 1. General information

The reactions were carried out in 25-mL Schlenk tubes under O2. Unless noted otherwise, the materials obtained from commercial suppliers were used without further purification, and solvents were purified according to standard operating procedures. Flash column chromatography was performed using Silica Gel 60 (300-400 mesh). Analytical thin layer chromatography (TLC) was performed on Haiyang TLC silica gel GF254 (0.25 mm) plates. The <sup>1</sup>H, <sup>13</sup>C NMR, <sup>31</sup>P NMR and <sup>19</sup>F NMR spectra were recorded on a Brucker ADVANCE III spectrometer operating at 400 MHz, 100 MHz, 162 MHz and 376 MHz, respectively; and chemicals shifts are reported in ppm ( $\delta$ ) relative to internal tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet), and coupling constants (J) were reported in hertz. The NMR yields were determined by <sup>31</sup>P NMR spectra with triphenylphosphine oxide (at 29.0 ppm) as internal standard. The reactions were monitored by GC and GC-MS; GC-MS results were recorded on a GC-MS QP2010 while GC analyses on a GC 2014 plus equipment. The electron ionization (EI) approach was used as ionization method for HRMS measurements, and TOF was the mass analyzer type for EI.

Starting phosphinamide, e.g., P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (1a), N-(quinolin-8-yl)-P,P-di-p-tolylphosphinamide (1b) , N-(quinolin-8-yl)-P,P-di-mtolylphosphinamide (1c), P,P-bis(4-fluorophenyl)-N-(quinolin-8-yl)phosphinamide (1d) , P,P-bis(3-fluorophenyl)-N-(quinolin-8-yl)phosphinamide (1e) , P,P-bis(4chlorophenyl)-N-(quinolin-8-yl)phosphinamide (1f) , P,P-bis(4-methoxyphenyl)-N-(quinolin-8-yl)phosphinamide (1g)N-(2-(1H-pyrazol-1-yl)phenyl)-P,Pdiphenylphosphinamide N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-(1h)diphenylphosphinamide (1i), N,P,P-triphenyl-phosphinamide, N-(naphthalen-1-yl)-P,P-diphenylphosphinamide, N-(perfluorophenyl)-P,P-diphenylphosphinamide, P,P-(pyridin-3-yl)phosphinamide P.P-diphenyl-N-(pyridin-2diphenyl-Nand yl)phosphinamide were prepared according to literature procedures. Spectral data obtained for the starting phosphinamides are in good agreement with the reported data.1-2

### 2. Synthesis and characterization of starting materials



General procedure for the synthesis of phosphinamides

To a solution of arylmagnesium bromide (0.1 mol) in THF (100 mL), diethyl phosphate (4.1 g, 0.03 mol) in THF (20 mL) was added dropwise with vigorous stirring under the cooling of ice-water bath. Then the mixture thus obtained was heated under reflux for 1 h. After the reflux, the resulting reaction mixture was cooled to 0 °C, and hydrochloric acid (6 N, 50 mL) was added slowly upon stirring. The solution was then evaporated under reduced pressure. The residue was extracted with EtOAc (150 mL). The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo to give crude product A1 which was used directly for the next step without further purification.

Hydrogen peroxide (30%, 16 mL) was added dropwise to a suspension of A1 in aqueous NaOH (5 N, 16 mL) at 95 °C, and the mixture was stirred for 1 h at 100 °C. After the solution was cooled to 0 °C, concentrated hydrochloric acid (12 N) was added dropwise until no white solid was precipitated out. The precipitate was collected by filtration and washed with  $Et_2O$ , then dried in vacuo to give crude phosphinic acid A2 which was used directly without purification.

A suspension of A2 and thionyl chloride (20 mL) in anhydrous toluene (60 mL) was heated to 80  $^{\circ}$ C for 3 hours. After thionyl chloride and toluene were removed

under reduced pressure, the residue was re-dissolved in anhydrous toluene (50 mL) and evaporated to give phosphinic chloride A3.

To a solution of 8-aminoquinoline (4.6 g, 32 mmol), triethylamine (5 mL, 35 mmol), and *N*,*N*-dimethyl-4-aminopyridine (120 mg, 0.98 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL), a suspension of **A3** was added dropwise under N<sub>2</sub> atmosphere with vigorous stirring at 0 °C. Then the resulting mixture was warm to room temperature. After strring overnight, the reaction system was quenched with water (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×50 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel to afford the corresponding *P*,*P*-diaryl-*N*-(quinolin-8-yl)phosphinamide.

#### Analytical data for new starting phosphinamides

#### *P*,*P*-di-*m*-tolyl-*N*-(quinolin-8-yl)phosphinamide (1c)



1c was synthesized in 45% yield in 4 steps as a brown soild.  $R_f = 0.43$  (petroleum ether/ethyl acetate = 2:1), mp 165–166 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (d, *J* = 3.7 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 7.96 (d, *J* = 12.8 Hz, 1H), 7.82 (d, *J* = 12.8 Hz, 2H), 7.72–7.67 (m, 2H), 7.43–7.25 (m, 8H), 2.38 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.9, 138.7 (d, *J* = 12.9 Hz), 137.8, 136.3, 133.0 (d, *J* = 3.0 Hz), 132.6, 132.4 (d, *J* =

10.0 Hz), 131.3, 128.7 (d, J = 23.5 Hz), 128.7, 128.4, 127.1, 121.6, 119.2, 113.8 (d, J = 3.9 Hz), 21.4; <sup>31</sup>P NMR (162 Hz, CDCl<sub>3</sub>)  $\delta$  19.6. HRMS (ESI) calcd. for C<sub>23</sub>H<sub>22</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 372.1391; found: 372.1388.

#### P,P-bis(3-fluorophenyl)-N-(quinolin-8-yl)phosphinamide (1e)



1e was synthesized in 21% yield in 4 steps as a brown soild.  $R_f = 0.52$  (petroleum ether/ethyl acetate = 2:1), mp 145–146 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.77 (d, J = 4.0 Hz, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 13.5 Hz, 1H), 7.74 (dd, J = 12.1, 7.6 Hz, 2H), 7.66 (t, J = 10.9 Hz, 2H), 7.50–7.42 (m, 3H), 7.39–7.34 (m, 2H), 7.30–7.22 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7 (dd, J = 249.0, 18.4 Hz), 148.2, 138.6

(d, J = 7.2 Hz), 137.0, 136.3, 134.2 (dd, J = 128.7, 5.6 Hz), 130.9 (dd, J = 15.2, 7.4 Hz), 128.4, 127.5 (dd, J = 9.5, 3.2 Hz), 127.0, 121.8, 119.9, 119.6 (dd, J = 21.1, 2.6 Hz), 118.7 (q, J = 11.0 Hz), 113.8 (d, J = 3.8 Hz); <sup>31</sup>P NMR (162 Hz, CDCl<sub>3</sub>)  $\delta$  16.0 (t, J = 6.7 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>):  $\delta$  -110.43–110.51 (m). HRMS (ESI) calcd. for C<sub>21</sub>H<sub>16</sub>F<sub>2</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 381.0963; found: 381.0952.

#### N-(2-(1H-pyrazol-1-yl)phenyl)-P,P-diphenylphosphinamide (1h)<sup>1,4</sup>



**1h** was synthesized in 90% yield as a white solid.  $R_f = 0.34$  (petroleum ether/ethyl acetate = 5:1), mp 124–126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (d, J = 11.8 Hz, 1H), 7.85–7.80 (m, 5H), 7.66 (s, 1H), 7.48–7.43 (m, 3H), 7.40 (d, J = 7.0 Hz, 4H), 7.25 (d, J = 7.8 Hz, 1H), 7.04–7.01 (m, 1H), 6.91–6.87 (m, 1H), 6.46 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.3, 134.2, 132.8,

131.8 (d, J = 2.5 Hz), 131.4 (d, J = 10.1 Hz), 129.5, 128.5 (d, J = 12.9 Hz), 128.2 (d, J = 7.6 Hz), 127.7, 122.0, 121.4, 120.3 (d, J = 4.5 Hz), 106.8. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  18.3. HRMS (ESI) calcd. for C<sub>21</sub>H<sub>18</sub>N<sub>3</sub>OP [M]<sup>+</sup>: 359.1387; found: 359.1382.

#### N-(2-(4,5-dihydrooxazol-2-yl)phenyl)-P,P-diphenylphosphinamide (1i)<sup>3</sup>



**1i** was synthesized in 40% yield as a yellow solid.  $R_f = 0.55$  (petroleum ether/ethyl acetate = 2:1), mp 122–125 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  11.00 (d, J = 13.0 Hz, 1H), 7.93–7.88 (m, 4H), 7.78 (d, J = 7.7 Hz, 1H), 7.46–7.35 (m, 7H), 7.15–7.11 (m, 1H), 6.84–6.81 (m, 1H), 4.29 (t, J = 9.3 Hz, 2H), 3.98 (t, J = 9.3 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.8 (d, J = 0.8 Hz),

142.8, 133.0, 131.9, 131.7 (d, J = 2.7 Hz), 131.4 (d, J = 10.1 Hz), 129.2, 128.4 (d, J = 12.9 Hz), 119.6, 117.9 (d, J = 5.0 Hz), 112.4 (d, J = 7.7 Hz), 65.8, 54.2. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  18.3. HRMS (ESI) calcd. for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 362.1184; found: 362.1180.

# General experimental procedure for the synthesis of *N*-aryl phosphinamide

An oven-dried 25-mL Schlenk tube, equipped with a magnetic stir bar and charged with phosphinamide (0.1 mmol), copper powder (6.4 mg, 1.0 equiv), and boronic acids (0.2 mmol, 2.0 equiv), was evacuated and backfilled with  $O_2$  three times. Then, acetonitrile (1.0 mL) was added under  $O_2$  atmosphere and the reaction mixture was stirred at 25–100 °C for 12–24 h and monitored by TLC or GC-MS analysis. Upon completion, the mixture was made to pass through a short pad of celite with CH<sub>2</sub>Cl<sub>2</sub> and the solution was concentrated in vacuo. The residue was purified by silica gel flash chromatography column to give the corresponding products.

# 3. <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>19</sup>F NMR spectra data of the products

#### *N,P,P*-triphenyl-*N*-(quinolin-8-yl)phosphinamide (3a)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.37$  (petroleum ether/ethyl acetate = 1:1), mp 210–212 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04 (d, J = 1.4 Hz, 1H), 8.05–7.97 (m, 6H), 7.57 (d, J = 8.1 Hz, 1H), 7.38–7.34 (m, 4H), 7.22–7.18 (m, 2H), 7.13 (d, J = 7.4 Hz, 4H), 7.03 (t, J = 7.4 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.2, 146.3 (d, J

= 3.1 Hz), 145.7 (d, J = 3.9 Hz), 140.7 (d, J = 2.6 Hz), 135.8, 132.9 (d, J = 9.6 Hz), 132.5 (d, J = 3.2 Hz), 131.5 (d, J = 130.5 Hz), 131.1 (d, J = 2.8 Hz), 129.0, 128.4, 128.0, 127.4 (d, J = 13.0 Hz), 126.5 (d, J = 1.2 Hz), 123.1 (d, J = 4.7 Hz), 122.9, 121.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.0. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 420.1391; found: 420.1386.

#### *N*-(4-ethylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3b)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.45$  (petroleum ether/ethyl acetate = 2:1), mp 130–132 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.90 (d, J = 2.1 Hz, 1H), 7.96– 7.87 (m, 5H), 7.75 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 7.9 Hz, 2H), 7.17–7.13 (t, J = 8.2 Hz, 2H), 7.00– 6.95 (m, 6H), 6.73 (d, J = 8.1 Hz, 2H), 2.29–2.23 (m, 2H), 0.91–0.87 (t, J = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 149.9, 146.0 (d, J = 3.3 Hz), 143.0 (d, J = 3.6 Hz), 140.8 (d, J = 3.6 Hz)

2.5 Hz), 138.7, 135.6, 132.6 (d, J = 9.7 Hz), 132.1 (d, J = 4.4 Hz), 130.9 (d, J = 2.6 Hz), 130.8, 128.7, 127.7, 127.5, 127.2 (d, J = 13.0 Hz), 126.2, 123.5 (d, J = 4.7 Hz), 121.0, 27.6, 15.0; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.7. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>25</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 448.1704; found: 448.1699.

#### *N*-(4-isopropylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3c)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.33$  (petroleum ether /ethyl acetate = 2/1), mp 191–193 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (d, J = 1.8 Hz, 1H), 7.96–7.87 (m, 6H), 7.46 (d, J = 8.1 Hz, 1H), 7.28–7.19 (m, 4H), 7.13–7.04 (m, 6H), 6.81 (d, J = 8.0 Hz, 2H), 2.66–2.58 (m, 1H), 1.00 (d, J = 6.8 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 146.3 (d, J = 3.1 Hz), 143.5, 143.1 (d, J = 3.6 Hz), 140.9 (d, J = 2.4Hz), 135.8, 132.8 (d, J = 9.7 Hz), 132.4 (d, J = 3.3 Hz),

131.6 (d, J = 130.9 Hz), 131.1 (d, J = 2.6Hz), 129.0, 127.8, 127.4 (d, J = 13.0Hz), 126.5 (d, J = 1.1Hz), 126.3, 123.4 (d, J = 4.7 Hz), 121.2, 33.1, 23.7; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.9. HRMS (ESI) calcd. for C<sub>30</sub>H<sub>27</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 462.1861; found: 462.1856.

#### *N*-(4-butylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3d)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.28$  (petroleum ether /ethyl acetate = 2/1), mp 143–145 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.03 (d, J = 4.0 Hz, 1H), 8.05–8.00 (m, 5H), 7.94 (d, J = 8.2 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.34–7.3 (m, 4H), 7.19–7.11 (m, 6H), 6.84 (d, J = 8.0 Hz, 2H), 2.39 (t, J = 7.7 Hz, 2H), 1.45–1.38 (m,2H), 1.25–1.16 (m,2H), 0.82 (t, J = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 146.2 (d, J = 3.4 Hz), 143.1 (d, J = 3.6 Hz), 140.9 (d, J = 2.6

Hz), 137.8, 135.8, 132.87 (d, J = 9.7 Hz), 132.3 (d, J = 3.3 Hz), 131.4 (d, J = 131.0 Hz), 131.1 (d, J = 2.7 Hz), 129.0, 128.3, 127.8 (d, J = 0.7 Hz), 127.4 (d, J = 13.1 Hz), 126.4 (d, J = 1.3 Hz), 123.8 (d, J = 4.7 Hz), 121.1, 34.7, 33.2, 22.1, 13.7; <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.0. HRMS (ESI) calcd. for C<sub>31</sub>H<sub>29</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 476.2018; found: 476.2033.

#### *N*-(4-(tert-butyl)phenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3e)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.35$  (petroleum ether /ethyl acetate = 2/1), mp 200–202 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97–8.96 (m, 1H), 7.96–7.87 (m, 6H), 7.46 (d, J = 8.1 Hz, 1H), 7.27–7.23 (m, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.12–7.08 (m, 2H), 7.05–7.02 (m, 4H), 6.96 (d, J = 7.6 Hz, 2H), 1.07 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 150.16 (s), 145.6, 142.8 (d, J = 3.3 Hz), 140.8 (d, J = 1.6 Hz), 135.9, 132.8 (d, J = 9.6 Hz), 132.5 (d, J = 1.3 Hz), 132.2–132.1

(m), 131.1 (d, J = 2.2 Hz), 130.9, 129.0, 127.9, 127.4 (d, J = 12.9 Hz), 126.5, 125.2, 122.8 (d, J = 4.5 Hz), 121.2, 33.9, 31.1. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.94. HRMS (ESI) calcd. for C<sub>31</sub>H<sub>29</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 476.2018; found: 476.2025.

#### P,P-diphenyl-N-(quinolin-8-yl)-N-(p-tolyl)phosphinamide (3f)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.40$  (petroleum ether/ethyl acetate = 1/1). mp 195–197 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.92–8.91 (m, 1H), 7.96–7.89 (m, 5H), 7.79 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 8.1 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.21–7.14 (m, 2H), 7.06–6.98 (m, 6H), 6.71 (d, J = 8.0 Hz, 2H), 1.97 (s, 3H). <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>)  $\delta$ 150.0, 146.1 (d, J = 3.2 Hz), 143.0 (d, J = 3.7 Hz), 140.9 (d, J =

2.5 Hz), 135.7, 132.7 (d, J = 9.7 Hz), 132.6, 132.2 132.1 (d, J = 1.6 Hz), 130.9 (d, J = 2.6 Hz), 130.8, 128.9, 127.7, 127.3 (d, J = 12.9 Hz), 126.3 (d, J = 1.0 Hz), 123.8 (d, J = 4.6 Hz), 121.1, 20.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.8. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 434.1548; found: 434.1545.

#### P,P-diphenyl-N-(quinolin-8-yl)-N-(m-tolyl)phosphinamide (3g)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.4$  (petroleum ether /ethyl acetate = 1/1), mp 177–179 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95–8.94 (m, 1H), 7.95–7.86 (m, 6H), 7.46 (d, J = 8.1 Hz, 1H), 7.28–7.23 (m, 2H), 7.12–7.08 (m, 4H), 7.05–7.03 (m, 4H), 6.82 (t, J = 7.6 Hz, 1H), 6.5 (d, J = 7.4 Hz, 1H), 2.0 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1,

146.3 (d, J = 3.2 Hz), 145.6 (d, J = 3.7 Hz), 140.8 (d, J = 2.7 Hz), 138.1, 135.8, 132.8 (d, J = 9.7 Hz), 132.5 (d, J = 3.3 Hz), 132.1, 131.1 (d, J = 2.7 Hz), 130.8, 129.0, 128.1, 127.9, 127.4 (d, J = 13.1 Hz), 126.4 (d, J = 1.4 Hz), 124.0 (d, J = 6.4 Hz), 121.2, 120.6 (d, J = 4.8 Hz), 21.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.0. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 434.1548; found: 434.1543.

#### *P*,*P*-diphenyl-*N*-(quinolin-8-yl)-*N*-(*o*-tolyl)phosphinamide (3h)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.42$  (petroleum ether /ethyl acetate = 1/1), mp 207–208 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.72–8.70 (m, 1H), 8.33 (d, J =7.5 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.83–7.81 (m, 1H), 7.77– 7.72 (m, 4H), 7.43 (d, J = 8.1 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 7.23–7.14 (m, 3H), 7.12–7.08 (m, 4H), 6.87–6.84 (m, 3H), 2.30

(s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  148.7, 144.7 (d, J = 5.3 Hz), 141.9, 141.5 (d, J = 2.8 Hz), 139.0 (d, J = 3.4 Hz), 135.7, 133.8 (d, J = 2.8 Hz), 132.7 (d, J = 9.5 Hz), 132.2, 131.2 (d, J = 2.7 Hz), 130.9, 130.7, 130.0 (d, J = 4.0 Hz), 129.2, 127.6 (d, J = 12.9 Hz), 126.5, 126.1 (d, J = 14.9 Hz), 125.2, 120.8, 19.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  27.8.HRMS (ESI) calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 434.1548; found: 434.1560.

#### N-(4-fluorophenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3i)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.35$  (petroleum ether /ethyl acetate = 1/1), mp 211–213 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (d, J = 1.8 Hz, 1H), 7.95– 7.89 (m, 6H), 7.48 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 4.2 Hz 2H), 7.29–7.26 (m, 2H), 7.18–7.12 (m, 2H), 7.06 (s, 4H), 6.65 (t, J =8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  160.5, 158.1, 150.2, 146.0 (d, J = 3.6 Hz), 141.4 (t, J = 3.2 Hz), 141.0 (d, J = 2.3 Hz),

135.9, 132.8 (d, J = 9.7 Hz), 132.0 (d, J = 3.3 Hz), 131.0 (d, J = 131.1 Hz), 131.3 (d, J = 2.7 Hz), 129.1, 128.0, 127.5 (d, J = 13.1 Hz), 126.4–126.23 (m), 121.3, 115.0 (d, J = 22.3 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.6. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  - 119.1. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>FN<sub>2</sub>OP [M]<sup>+</sup>: 438.1297; found: 438.1295.

#### N-(4-chlorophenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3j)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.55$  (petroleum ether/ethyl acetate = 1:1), mp 184–186 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (d, J = 4.0 Hz, 1H), 7.94–7.87 (m, 6H), 7.50 (d, J = 8.1 Hz, 1H), 7.30–7.26 (m, 2H), 7.23 (d, J = 8.5 Hz, 2H), 7.18–7.12 (m, 2H), 7.08–7.04 (m, 4H), 6.90 (d, J = 8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 146.1 (d, J = 3.1 Hz), 144.3 (d, J = 4.1 Hz), 140.5 (d, J = 2.4 Hz), 136.0, 132.8 (d, J = 9.8 Hz), 132.4 (d, J = 3.1 Hz), 131.7, 131.3 (d, J = 5.4 Hz)

2.8 Hz), 130.4, 129.0, 128.3 (d, J = 7.3 Hz), 128.2 (d, J = 1.1 Hz), 127.5 (d, J = 13.1 Hz), 126.5 (d, J = 1.4 Hz), 124.5 (d, J = 4.8 Hz), 121.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.5. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>ClN<sub>2</sub>OP [M]<sup>+</sup>: 454.1002; found: 454.0996.

#### N-(4-bromophenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3k)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.41$ (petroleum ether /ethyl acetate = 1/1), mp 201–203 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96–8.95 (m, 1H), 7.94–7.85 (m, 6H), 7.51 (d, J = 8.1 Hz, 1H), 7.30–7.26 (m, 2H), 7.18–7.13 (m, 4H), 7.08–7.03 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 146.1 (d, J = 2.9 Hz), 144.9 (d, J = 4.1 Hz), 140.3 (d, J = 2.4 Hz), 136.0, 132.8 (d, J = 9.8 Hz), 132.4 (d, J = 3.1 Hz), 131.7, 131.47–131.27 (m), 130.4, 129.0, 128.3 (d, J = 1.0 Hz), 127.5

(d, J = 13.1 Hz), 126.5 (d, J = 1.4 Hz), 124.6 (d, J = 4.8 Hz), 121.4, 115.9. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.5. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>BrN<sub>2</sub>OP [M]<sup>+</sup>: 498.0497; found: 498.0491.

#### *N*-(4-iodophenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (31)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.50$  (petroleum ether /ethyl acetate = 1/1). mp 306–308 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95–8.93 (m, 1H), 7.94–7.87 (m, 5H), 7.86–7.82 (m, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.28–7.25 (m, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.13 (t, J = 7.3 Hz, 2H), 7.06– 7.04 (m, 4H), 6.98 (d, J = 8.5 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 146.0 (d, J = 2.9 Hz), 145.5 (d, J = 4.2 Hz), 140.0 (d, J = 2.3 Hz), 137.2, 135.9, 132.7 (d, J = 9.8 Hz), 132.4

(d, J = 3.1 Hz),131.4–131.3 (m), 130.0, 128.9, 128.3 (d, J = 0.9 Hz), 127.5 (d, J = 13.1 Hz), 126.51 (d, J = 1.3 Hz), 124.6 (d, J = 4.8 Hz), 121.4, 86.5. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.8. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>IN<sub>2</sub>OP [M]<sup>+</sup>: 546.0358; found: 546.0352.

#### N-(3-fluorophenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3m)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.37$  (petroleum ether /ethyl acetate = 1/1). mp 104–105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04–9.03 (m, 1H), 8.03–7.98 (m, 4H), 7.96–7.92 (m, 2H), 7.57 (d, J = 8.1 Hz, 1H), 7.37–7.33 (m, 2H), 7.21–7.18 (m, 3H), 7.14–7.10 (m, 4H), 6.98–6.92 (m, 2H), 6.55–6.51 (t, J = 8.2 Hz 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 

163.7, 161.3, 150.4, 147.3 (dd, J = 10.0, 4.5 Hz), 146.1 (d, J = 2.7 Hz), 140.0 (d, J = 1.9 Hz), 135.9, 132.7 (d, J = 9.8 Hz), 132.5 (d, J = 3.0 Hz), 131.6, 131.3 (d, J = 2.7 Hz), 129.6 (d, J = 139.4 Hz ), 129.2 (d, J = 9.4 Hz), 128.4, 127.5 (d, J = 13.1 Hz), 126.4 (d, J = 1.3 Hz), 121.4, 118.0–117.9 (m), 109.7–109.2 (m). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.0. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.2. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>FN<sub>2</sub>OP [M]<sup>+</sup>: 438.1297; found: 438.1292.

#### *N*-(4-methoxyphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3n)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.27$  (petroleum ether /ethyl acetate = 1/1), mp 173–174 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04 (d, J = 2.1 Hz, 1H), 8.09– 8.02 (m, 5H), 7.91 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.31–7.26 (m, 2H), 7.18–7.14 (m, 6H), 6.58 (d, J = 8.6 Hz, 2H), 3.56–3.54 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 149.9, 145.9 (d, J = 3.8 Hz), 141.5 (d, J = 3.0 Hz), 138.3 (d, J = 3.2 Hz), 135.7, 132.7 (d, J = 9.5 Hz),

131.7 (d, J = 3.5 Hz), 132.5 (d, J = 131.0 Hz), 131.0 (d, J = 2.6 Hz), 128.2(d, J = 153.2 Hz) 127.3 (d, J = 12.9 Hz), 127.1 (d, J = 4.4 Hz), 127.1 (d, J = 4.4 Hz), 126.3, 121.0, 113.5, 54.9. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.8. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 450.1497; found: 450.1492.

#### P,P-diphenyl-N-(quinolin-8-yl)-N-(4-vinylphenyl)phosphinamide (30)



The phosphinamide compound was obtained as a yellow solid. Rf = 0.42 (petroleum ether /ethyl acetate = 1/1), mp 114–116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95–8.89 (m, 1H), 7.96–7.89 (m,5H), 7.79 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 2H). 7.21–7.14 (m, 2H), 7.05–6.98 (m, 6H), 1.97 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ 150.0, 146.1 (d, *J* = 3.2 Hz), 143.0 (d, *J* = 3.6 Hz), 140.9 (d, *J* = 2.5 Hz), 135.7, 132.7 (d, *J* = 9.7 Hz), 132.6, 132.1, 132.1 (d, *J* =

1.6 Hz), 130.9 (d, J = 2.6 Hz), 130.8, 127.7, 127.3 (d, J = 13.0 Hz), 126.2 (d, J = 1 Hz), 123.8 (d, J = 4.6 Hz), 121.1, 20.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  24.8. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>23</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 446.1548; found: 446.1543.

#### *N*-(4-formylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3p)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.34$  (petroleum ether /ethyl acetate = 2/1), mp 134–136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.65 (s, 1H), 8.94–8.93 (m, 1H), 7.94–7.87 (m, 5H), 7.77 (d, J = 7.2 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.32–7.28 (m, 2H), 7.16–7.11 (m, 3H), 7.09–7.05 (m, 5H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.8, 151.3 (d, J = 4.6 Hz), 150.5, 145.9 (d, J = 2.3 Hz), 139.0 (d, J = 3.1 Hz)

2.2 Hz), 136.0, 132.6 (d, J = 10.1 Hz), 132.5 (d, J = 2.8 Hz), 131.6 (d, J = 2.7 Hz), 131.1, 130.4, 130.1, 129.8, 128.9 (d, J = 7.3 Hz), 127.6 (d, J = 13.3 Hz), 126.5 (d, J = 1.5 Hz), 121.6, 120.4 (d, J = 5.0 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.9. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 448.1341; found: 448.1335.

#### *N*-(3-formylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3q)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.28$  (petroleum ether /ethyl acetate = 1/1), mp 128–130 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.71 (s, 1H), 9.04 (d, J =1.4 Hz, 1H), 8.03–7.95 (m, 6H), 7.68 (d, J = 8.0 Hz, 1H), 7.64 (s, 1H), 7.60 (d, J = 8.1 Hz, 1H), 7.39–7.35 (m, 3H), 7.23– 7.20 (m, 2H), 7.18–7.12 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 192.1, 150.4, 146.5 (d, J = 4.2 Hz), 146.0 (d, J = 2.8 Hz), 139.8 (d, J = 2.2 Hz), 136.6, 136.0, 132.7 (d, J = 9.8 Hz), 132.3 (d, J = 3.0 Hz), 131.4 (d, J = 2.7 Hz), 130.1, 129.0, 128.9, 128.5, 128.4 (d, J = 4.7 Hz), 127.5 (d, J = 13.1 Hz), 126.4 (d, J = 0.9Hz), 123.9 (d, J = 4.9 Hz), 123.3, 121.5. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 26.0. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>21</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 448.1341; found: 448.1332.

#### *N*-(4-acetylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3r)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.23$  (petroleum ether/ethyl acette = 1/1). mp 205–207 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.03 (s, 1H), 8.02–7.97 (m, 5H), 7.86 (d, J = 6.9 Hz, 1H), 7.64–7.60 (m, 3H), 7.40–7.35 (m, 2H), 7.24–7.20 (m, 2H), 7.15 (d, J = 8.0 Hz, 6H), 2.40 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  196.7, 150.4, 150.1 (d, J = 4.5 Hz), 145.9 (d, J = 2.2 Hz), 139.1 (d, J = 1.7 Hz), 136.0, 132.6 (d, J =10.0 Hz), 132.4 (d, J = 2.8 Hz), 131.4–131.3 (m), 130.5, 130.0,

128.9, 128.8 128.7, 127.5 (d, J = 13.2 Hz), 126.4 (d, J = 0.5 Hz), 121.5, 119.9 (d, J = 4.8 Hz), 26.0. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.3. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 462.1497; found: 462.1492.

#### *N*-(3-acetylphenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3s)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.26$  (petroleum ether /ethyl acetate = 1/1), mp 156–158 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (d, J = 3.9 Hz, 1H), 7.96– 7.90 (m, 6H), 7.83 (s, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.30–7.26 (m, 2H), 7.18– 7.11 (m, 2H), 7.07–6.99 (m, 5H), 2.25 (s, 3H). <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>)  $\delta$  197.8, 150.3, 145.9 (d, J = 2.8 Hz), 145.7 (d, J = 4.0 Hz), 139.8 (d, J = 1.8 Hz), 137.0, 135.9, 132.6 (d, J = 9.8 Hz), 132.2 (d, J = 3.0 Hz), 131.4–131.3 (m), 130.0, 128.9, 128.5, 128.3, 127.5 (d, J = 13.1 Hz), 127.3 (d, J = 4.4 Hz), 126.4, 122.9 (d, J = 4.6 Hz), 122.4, 121.4, 26.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.8. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 462.1497; found: 462.1495.

#### N-(4-(methylsulfonyl)phenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3t)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.08$  (petroleum ether /ethyl acetate = 1/1), mp 250–251 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (d, J = 3.8 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.94–7.86 (m, 4H), 7.77 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.37–7.30 (m, 2H), 7.19–7.16 (m, 2H), 7.13–7.08 (m, 6H), 2.85 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.7 (d, J = 1.2 Hz), 150.6 (d, J =4.6 Hz), 146.0 (d, J = 2.6 Hz), 139.0–138.9 (m), 136.1 (d, J =

0.9 Hz), 132.7 (d, J = 10.0 Hz), 132.5 (d, J = 3.2 Hz), 131.7, 131.1 (d, J = 3.3 Hz), 129.8 (d, J = 3.3 Hz), 129.0, 128.0 (d, J = 0.8 Hz), 127.7 (d, J = 13.2 Hz), 126.6, 121.8 (d, J = 1.0 Hz), 120.5, 120.4 (d, J = 5.0 Hz), 44.6. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  27.0. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>PS [M]<sup>+</sup>: 498.1167; found: 498.1162.

#### *N*-(3-((diphenylphosphoryl)(quinolin-8-yl)amino)phenyl)acetamide (3u)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.51$  (petroleum ether/ethyl acetate = 1/1), mp 123–125 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.90 (s, 1H), 8.46 (d, *J* = 56.0 Hz, 1H), 7.90 (s, 4H), 7.79 (d, *J* = 17.0 Hz, 2H), 7.42 (d, *J* = 23.4 Hz, 2H), 7.29 (s, 1H), 7.14 (d, *J* = 37.8 Hz, 4H), 7.01 (s, 5H) , 6.83 (s, 1H), 1.78 (s, 3H). <sup>13</sup>C NMR

(100 MHz, DMSO)  $\delta$  168.5, 151.2, 146.6 (d, J = 4.1 Hz), 146.2 (d, J = 2.7 Hz), 140.52 (d, J = 2.1 Hz), 140.1, 136.8, 132.9, 132.8 (d, J = 9.4 Hz), 132.5 (d, J = 2.8 Hz), 131.95 (d, J = 1.2 Hz), 131.6, 129.4, 128.9 (d, J = 14.6 Hz), 128.2 (d, J = 12.5 Hz), 126.9, 122.3, 117.91 (d, J = 4.4 Hz), 114.2, 113.7 (d, J = 5.0 Hz), 24.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.2. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>24</sub>N<sub>3</sub>O<sub>2</sub>P [M]<sup>+</sup>: 477.1606; found: 477.1600.

#### N-(4-cyanophenyl)-P,P-diphenyl-N-(quinolin-8-yl)phosphinamide (3v)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.39$  (petroleum ether/ethyl acetate = 1/1), mp 158–160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (d, J = 4.0 Hz, 1H), 7.94 (d, J = 8.3 Hz, 1H), 7.91–7.86 (m, 3H), 7.75 (d, J = 7.1 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.34–7.27 (m, 2H), 7.20–7.18 (m, 3H), 7.15 (d, J = 7.2 Hz, 2H) 7.05 (d, J = 8.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.6, 149.6 (d, J = 4.8 Hz), 145.8 (d, J = 2.3 Hz), 138.7 (d, J = 2.2 Hz), 136.1, 132.6 (d, J = 10.1 Hz), 132.4,

132.4, 131.7 (d, J = 2.8 Hz), 130.9, 129.6, 129.0–128.8 (m), 127.6 (d, J = 13.3 Hz), 126.5 (d, J = 1.5 Hz), 121.7, 120.6 (d, J = 5.0 Hz), 119.1, 104.4. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  27.0. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>20</sub>N<sub>3</sub>OP [M]<sup>+</sup>: 445.1344; found: 445.1339.

#### P,P-diphenyl-N-(quinolin-8-yl)-N-(4-(trifluoromethyl)phenyl)phosphinamide (3w)



The phosphinamide compound was obtained as a white solid.  $R_f$ = 0.53 (petroleum ether/ethyl acetate = 1/1), mp 98–100 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (d, *J* = 4.0 Hz, 1H), 7.94–7.87 (m, 6H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.30–7.26 (m, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 7.18–7.12 (m, 2H), 7.08–7.04 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.5, 148.7 (d, *J* = 5.2 Hz), 146.0 (d, *J* = 2.4 Hz), 139.4, 136.0, 132.6 (d, *J* = 9.9 Hz), 132.4 (d, *J* = 2.7 Hz), 131.5–131.4 (m), 130.1, 128.8 (d, *J* 

= 25.5 Hz), 127.5 (d, J = 13.2 Hz), 126.4, 125.5–125.4 (m), 123.7, 123.4, 122.8, 121.5, 120.8 (d, J = 4.9 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 26.2. 19F NMR (376 MHz, CDCl<sub>3</sub>) δ -61.7 (d, J = 3.4 Hz). HRMS (ESI) calcd. for C<sub>28</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 488.1265; found: 488.1260.

#### P,P-diphenyl-N-(quinolin-8-yl)-N-(3-(trifluoromethyl)phenyl)phosphinamide (3x)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.59$  (petroleum ether/ethyl acetate = 1/1), mp 162–164 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (d, J = 2.4 Hz, 1H), 7.95–7.90 (m, 6H), 7.52–7.47 (m, 2H), 7.39 (s, 1H), 7.31–7.27 (m, 2H), 7.18–7.12 (m, 2H), 7.08–7.00 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.4, 146.1–146.0 (m), 139.9 (d, J = 2.3 Hz), 136.0,

132.8 (d, J = 9.8 Hz), 132.3 (d, J = 3.1 Hz), 131.5–131.4 (m), 130.7, 130.4, 129.6 (d, J = 115.0 Hz), 128.7, 128.5, 127.6 (d, J = 13.1 Hz), 126.5 (d, J = 1.2 Hz), 126.0 (d, J = 3.7 Hz), 125.1, 122.4, 121.5–121.4 (m), 119.8–119.6 (m), 119.4–119.3 (m). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 25.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.7. HRMS (ESI) calcd. for C<sub>28</sub>H<sub>20</sub>F<sub>3</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 488.1265; found: 488.1268.

## N-(3,5-bis(trifluoromethyl)phenyl)-P,P-diphenyl-N-(quinolin-8yl)phosphinamide (3y)



The phosphinamide compound was obtained as a yellow solid.  $R_f 0.71$  (petroleum ether/ethyl acetate = 1/1), mp 118–120 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.95 (d, *J* = 1.9 Hz, 1H), 7.97–7.89 (m, 6H) , 7.57 (s, 3H), 7.35–7.31 (m, 2H), 7.26 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.09 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>; list of

signals, C–P and C–F coupling not resolved)  $\delta$  168.7, 150.6, 148.1, 146.9, 146.9, 145.8, 145.8, 139.1, 139.1, 138.3, 138.2, 134.5, 132.8, 132.7, 132.2, 132.2, 131.8, 131.8, 131.5, 131.2, 130.9, 129.6, 129.2, 129.0, 127.9, 127.9, 127.7, 127.4, 126.6, 126.6, 124.4, 122.5, 122.4, 122.4, 121.8, 121.6, 121.4, 116.4, 116.1, 116.1, 116.0, 116.0, 116.0. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.8. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  - 63.0. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>19</sub>F<sub>6</sub>N<sub>2</sub>O<sub>1</sub>P [M]<sup>+</sup>: 556.1139; found: 556.1134.

#### *N*-(4-nitrophenyl)-*P*,*P*-diphenyl-*N*-(quinolin-8-yl)phosphinamide (3z)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.31$  (petroleum ether/ethyl acetate = 1/1), mp 143–145 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.98 (s, 3H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.45–7.39 (m, 2H), 7.26 (d, *J* = 5.8 Hz, 3H), 7.16–7.10 (m, 6H). <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  151.6 (d, *J* = 4.8 Hz), 150.7, 145.7 (d, *J* = 2.2 Hz), 141.7, 138.7 (d, *J* = 2.1

Hz), 136.2, 132.6 (d, J = 10.1Hz), 132.5(d, J = 2.7Hz), 131.9(d, J = 2.7 Hz), 130.7 (d, J = 4.9Hz), 129.3(d, J = 45.0 Hz), 129.1 (d, J = 1.2 Hz), 127. 8 (d, J = 13.3Hz), 126.6 (d, J = 1.3Hz), 124.3, 121.8, 119.9–119.8 (m). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  27.6. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>20</sub>N<sub>3</sub>O<sub>3</sub>P [M]<sup>+</sup>: 465.1242; found: 465.1237.

#### N-phenyl-N-(quinolin-8-yl)-P,P-di-p-tolylphosphinamide (3ba)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.33$  (petroleum ether/ethyl acetate = 1/1), mp 97–99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.93 (d, J = 2.0 Hz, 1H), 7.89–7.86 (m, 2H), 7.82–7.77 (m,4H), 7.46–7.42 (m, 1H), 7.28–7.23 (m, 4H), 6.92 (t, J = 7.5 Hz, 2H), 6.83 (d, J = 5.7 Hz, 4H), 6.76–6.72 (m, 1H), 2.06 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.1, 146.3 (d, J = 2.9 Hz), 145.8 (d, J = 3.7 Hz), 141.3 (d, J = 2.8 Hz), 140.9 (d, J = 5.8

1.8 Hz), 135.8, 132.7 (d, J = 10.0 Hz), 132.4 (d, J = 3.2 Hz), 131.9 (d, J = 10.1 Hz), 129.1 (d, J = 6.4 Hz), 128.9, 128.2 (d, J = 13.6 Hz), 127.8, 126.4 (d, J = 1.0 Hz), 123.2 (d, J = 4.7 Hz), 122.7, 121.1, 21.3. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.2. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>25</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 448.1704; found: 448.1697.

#### *N*-phenyl-*N*-(quinolin-8-yl)-*P*,*P*-di-*m*-tolylphosphinamide (3ca)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.51$  (petroleum ether /ethyl acetate = 1/1), mp 145–147 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (d, J = 2.2 Hz, 1H), 7.89–7.86 (m, 2H), 7.80–7.76 (m, J = 11.7, 2H), 7.71 (d, J = 12.6 Hz, 2H), 7.50–7.43 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 3.6 Hz, 2H), 6.94–6.88 (m, 6H), 6.76–6.72 (m, 1H), 2.03 (s, 6H). <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>)  $\delta$  149.9, 146.3 (d, J = 3.2 Hz), 145.7 (d, J = 3.7 Hz), 140.8 (d, J = 2.5 Hz), 137.0 (d, J = 12.9 Hz), 135.8, 133.3 (d, J = 9.8 Hz), 132.6–132.2 (m), 131.9 (d, J = 2.9 Hz ), 131.3 (d, J = 129.8 Hz) 129.8 (d, J = 9.7 Hz), 129.1–128.9 (m), 128.2, 128.1 (d, J = 12.8 Hz), 127.9 , 127.2 (d, J = 13.7 Hz), 126.3 (d, J = 1.3 Hz), 123.2 (d, J = 4.7 Hz), 121.9 (d, J = 170.0 Hz), 21.0. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  26.0. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>25</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 448.1704; found: 448.1699.

#### P,P-bis(4-fluorophenyl)-N-phenyl-N-(quinolin-8-yl)phosphinamide (3da)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.62$  (petroleum ether/ethyl acetate = 1/1). mp 97–99 °C <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.04 (d, J = 1.6 Hz, 1H), 8.06–7.96 (m, 6H), 7.67–7.60 (m, 1H), 7.41–7.35 (m, 4H), 7.04 (t, J = 7.4 Hz, 2H), 6.89–6.87 (m, 1H), 6.82 (t, J = 8.5 Hz, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.5 (dd, J = 251.2 Hz, 3.4 Hz), 150.3, 146.2 (d, J = 3.1 Hz), 145.5 (d, J = 4.0 Hz), 140.6 (d, J = 2.5 Hz), 136.2,

135.4 (dd, J = 11.1 Hz, 8.8 Hz), 132.6 (d, J = 3.1 Hz), 129.1, 128.6, 128.3, 127.2 (dd, J = 135.2 Hz, 3.3 Hz), 126.6 (d, J = 1.5 Hz), 123.4, 123.3 (d, J = 4.9 Hz), 121.5, 114.9 (dd, J = 21.1, 14.3 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  23.1. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -107.4. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>19</sub>F<sub>2</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 456.1203; found: 456.1200.

#### P,P-bis(3-fluorophenyl)-N-phenyl-N-(quinolin-8-yl)phosphinamide (3ea)



The phosphinamide compound was obtained as a yellow solid.  $R_f = 0.56$  (petroleum ether /ethyl acetate = 1/1), mp 125–127 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.98 (d, J = 2.2 Hz, 1H), 7.90 (t, J = 8.9 Hz, 2H), 7.76–7.69 (m, 4H), 7.50 (d, J = 8.1 Hz, 1H), 7.36–7.25 (m, 4H), 7.02–6.93 (m, 4H), 6.79 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.8 (dd, J = 247.1 Hz, 18.6 Hz), 150.4, 145.6 (dd, J = 89.3 Hz, 3.1 Hz), 140.2 (d, J = 2.5 Hz), 136.1,

133.6 (dd, J = 131.5Hz, 6.0 Hz), 132.4 (d, J = 3.2 Hz), 129.4 (q, J = 7.3 Hz), 129.0, 128.7 (d, J = 3.1 Hz), 128.6, 128.6, 126.4, 126.5 (d, J = 1.1 Hz), 123.7, 123.5 (d, J = 4.9 Hz), 121.5, 119.6 (q, J = 10.7 Hz), 118.6 (dd, J = 21.1, 2.5 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  22.0 (t, J = 6.8 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -112.3 (d, J = 6.8 Hz). HRMS (ESI) calcd. for C<sub>27</sub>H<sub>19</sub> F<sub>2</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 456.1203; found: 456.1198.

#### P,P-bis(4-chlorophenyl)-N-phenyl-N-(quinolin-8-yl)phosphinamide (3fa)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.77$  (petroleum ether/ethyl acetate = 1/1), mp 225–227 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 (s, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92–7.85 (m, 5H), 7.56 (d, J = 8.1 Hz, 1H), 7.34–7.29 (m, 4H), 7.04 (d, J = 8.1 Hz, 4H), 6.98 (t, J = 7.4 Hz, 2H), 6.83 (t, J = 7.3 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  150.3, 146.1 (d, J = 3.2 Hz), 145.2 (d, J = 4.0 Hz), 140.3 (d, J = 2.6 Hz), 138.0 (d, J = 5.2 Hz)

3.5 Hz), 136.2, 134.3 (d, J = 10.6 Hz), 132.5 (d, J = 3.2 Hz), 129.6 (d, J = 133.7 Hz),129.1, 128.6, 128.4, 127.9 (d, J = 13.7 Hz), 126.6 (d, J = 1.2 Hz), 123.6, 123.5 (d, J = 4.9 Hz), 121.5. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  23.2. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>19</sub>Cl<sub>2</sub>N<sub>2</sub>OP [M]<sup>+</sup>: 488.0612; found: 488.0607.

#### P,P-bis(4-methoxyphenyl)-N-phenyl-N-(quinolin-8-yl)phosphinamide (3ga)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.19$  (petroleum ether /ethyl acetate = 1/1), mp 284–286 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.94 (d, J = 1.4 Hz, 1H), 7.87–7.82 (m, 6H), 7.47 (d, J = 8.1 Hz, 1H), 7.26 (t, J = 8.1 Hz, 4H), 6.93 (t, J = 7.4 Hz, 2H), 6.74 (t, J = 7.2 Hz, 1H), 6.54 (d, J = 8.0 Hz, 4H), 3.54 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  161.6 (d, J = 2.8 Hz), 150.1, 146.33 (d, J = 2.8 Hz), 145.8 (d, J = 3.8

Hz), 140.9 (d, J = 2.2 Hz), 135.9, 134.5 (d, J = 11.1 Hz), 132.4 (d, J = 2.9 Hz), 128.9, 128.2, 127.1 (d, J = 141.4 Hz), 123.8, 123.0 (d, J = 4.5 Hz), 122.6, 122.4, 121.2, 112.9 (d, J = 14.0 Hz), 54.9. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.5. HRMS (ESI) calcd. for C<sub>29</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>P [M]<sup>+</sup>: 480.1603; found: 480.1597.

#### *N*-(2-(4,5-dihydrooxazol-2-yl)phenyl)-*N*,*P*,*P*-triphenylphosphinamide (4)



The phosphinamide compound was obtained as a white solid.  $R_f = 0.25$  (petroleum ether /ethyl acetate = 2/1), mp 92–95 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73–7.68 (m, 4H), 7.54 (d, J =7.8 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.7 Hz, 4H), 7.18–7.14 (m, 4H), 7.03–6.99 (m, 1H), 6.95–6.91 (m, 2H), 6.78–6.75 (m, 1H), 4.15 (t, J = 9.5 Hz, 2H), 3.87 (t, J = 9.5 Hz,

2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  162.6, 145.3 (d, J = 2.5 Hz), 142.5 (d, J = 1.3 Hz), 132.8 (d, J = 2.9 Hz), 132.5 (d, J = 9.7 Hz), 131.7, 131.3 (d, J = 2.7 Hz), 131.2, 130.5 (d, J = 12.4 Hz), 128.3 (d, J = 4.1 Hz), 128.1, 127.6 (d, J = 12.9 Hz), 126.69, 124.6 (d, J = 5.2 Hz), 123.4, 66.6, 54.8. <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>)  $\delta$  25.4. HRMS (ESI) calcd. for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub>P [M]<sup>+</sup>: 438.1497; found: 438.1495.

# 4. References

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Copies of <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>19</sup>F NMR charts of the Compounds



 $^{13}\text{C}$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound 1c







<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectra of compound **1e** 







 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectra of compound 1h



 $^{13}\text{C}$  NMR (100MHz, CDCl\_3) spectra of compound 1i







<sup>130</sup> <sup>110</sup> <sup>90</sup> <sup>80</sup> <sup>70</sup> <sup>60</sup> <sup>50</sup> <sup>40</sup> <sup>30</sup> <sup>20</sup> <sup>10</sup> <sup>0</sup> <sup>-10</sup> <sup>-30</sup> <sup>-50</sup> <sup>-70</sup> <sup>-90</sup> <sup>-110</sup> <sup>-130</sup> <sup>-150</sup> <sup>-170</sup> <sup>-190</sup> <sup>-210</sup> <sup>-230</sup> <sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3a** 





<sup>13</sup>C NMR (100MHz, CDCl3) spectra of compound **3b** 







 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3c



<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3d** 





11.5

10.5

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 f1 (ppm)



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3e



 $^{13}C$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound 3f







 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3g

#### 



<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3h**


<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of compound **3i** 



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3i** 



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of compound **3**j





# A89645 A89645 B89593 B89593 B89593 B89535 A89555 A89555 A89555 A89555 A895455 A89545



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3k** 



 $^1\text{H}$  NMR (400MHz, CDCl<sub>3</sub>) spectra of compound **3**l



<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3**I

#### C90416 -90382 -90382 -90382 -90385 -800171 -80056 -800171 -779861 -779803 -775529 -771480 -771480 -771480 -771480 -771486 -771







<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3m** 



<sup>19</sup>F NMR (376MHz, CDCl<sub>3</sub>) spectrum of compound **3m** 

#### 



 $^{13}\text{C}$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound 3n









 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound  $\boldsymbol{3o}$ 

9,6544 9,942 8,93942 8,93942 8,93942 8,93942 8,93942 8,93942 1,73908 1,73908 1,75560 1,75569 1,7556





 $^{13}C$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound  $\boldsymbol{3p}$ 



 $^1\text{H}$  NMR (400MHz, CDCl\_3) spectra of compound 3q



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound  $\boldsymbol{3q}$ 



 $^{13}C$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound 3r



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of compound **3s** 



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3s



<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3t** 







 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3u

# 





 $^{13}\text{C}$  NMR (100MHz, CDCl<sub>3</sub>) spectra of compound 3v







<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3**w



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of compound 3x



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3x







<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3**y



 $^1\text{H}$  NMR (400MHz, CDCl<sub>3</sub>) spectra of compound 3z



 $^{31}P$  NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 3z



<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3ba** 









### 9.0442 9.0442 9.0442 9.0402 9.0402 9.0403 9.0403 9.0404



<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3da** 



<sup>19</sup>F NMR (376MHz, CDCl<sub>3</sub>) spectrum of compound **3da** 

## 









<sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>) spectra of compound **3ea**


<sup>19</sup>F NMR (376MHz, CDCl<sub>3</sub>) spectrum of compound **3ea** 

## -8.9685 -7.9989 -7.9989 -7.9998 -7.9998 -7.9920 -7.7992 -7.7373 -7.7373 -7.7373 -7.7345 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.7775 -7.77755 -7.7775 -7.77



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)





<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound **3fa** 



<sup>1</sup>H NMR (400MHz, CDCl<sub>3</sub>) spectra of compound **3ga** 



 $^{130} \text{ }^{110} \text{ }^{90} \text{ }^{80} \text{ }^{70} \text{ }^{60} \text{ }^{50} \text{ }^{40} \text{ }^{30} \text{ }^{20} \text{ }^{10} \text{ }^{-10} \text{ }^{-30} \text{ }^{-50} \text{ }^{-70} \text{ }^{-90} \text{ }^{-110} \text{ }^{-130} \text{ }^{-150} \text{ }^{-170} \text{ }^{-190} \text{ }^{-210} \text{ }^{-230}$   $^{31}\text{P NMR} (162\text{MHz, CDCl}_3) \text{ spectrum of compound 3ga}$ 

## 





<sup>31</sup>P NMR (162MHz, CDCl<sub>3</sub>) spectrum of compound 4