Supporting Information

Direct C4-H Phosphonation of 8-Hydroxyquinoline Derivatives
Employing Photoredox Catalysis and Silver Catalysis

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1. General Information

$^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker DPX-400 spectrometer using CDCl$_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. High resolution mass spectra were ensured on a MALDI-FTMS. All solvents were used directly without further purification. Petroleum ether, ethyl acetate and hexane were used for column chromatography. Chemical shift multiplicities are represented as follows: (s = singlet, d = doublet, t = triplet, m = multiplet, dd = double doublet, td = triplet doublet). Unless otherwise mentioned, all materials were commercially obtained and used without further purification.

2. Preparation of Substrates

All of the esters substrates were prepared from the corresponding acids and 8-hydroxyquinoline according to the reported procedure.$^1$

3. Optimization of Reaction Conditions

A 20 mL Schlenk tube was equipped with a magnetic stir bar and charged with 8-hydroxyquinoline ester 1a (24.9 mg, 0.1 mmol), diphenylphosphine oxide 2a (0.2 mmol, 2.0 equiv), photocatalyst (0.003 mmol, 3 mol%), AgX (0.01 mmol, 10 mol%), oxidant (0.2 mmol, 2 equiv), and solvent (1.0 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 6 h. Upon completion, the mixture was added into H$_2$O (20 mL) and extracted with CH$_2$Cl$_2$ (20 mL) three times. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100–200 mesh) using CH$_2$Cl$_2$/ethyl acetate as an eluent (2:1, V/V) to afford the pure product 3aa.

Table S1 Screening of Reaction Conditions$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>AgX</th>
<th>Oxidant</th>
<th>Solvent</th>
<th>Addition</th>
<th>yield (%)$^b$</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>acid red 94</td>
<td>Ag$_2$O</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>50%</td>
</tr>
<tr>
<td>2</td>
<td>acid red 94</td>
<td>AgOAc</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>acid red 94</td>
<td>AgI</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>4</td>
<td>acid red 94</td>
<td>AgNO$_2$</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>37%</td>
</tr>
<tr>
<td>5</td>
<td>acid red 94</td>
<td>Ag$_3$PO$_4$</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>acid red 94</td>
<td>AgNO$_3$</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>44%</td>
</tr>
<tr>
<td>7</td>
<td>acid red 94</td>
<td>Ag$_2$CO$_3$</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>48%</td>
</tr>
<tr>
<td>8</td>
<td>acid red 94</td>
<td>Ag$_2$SO$_4$</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>9</td>
<td>acid red 94</td>
<td>AgOTf</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>eosin Y</td>
<td>Ag$_2$O</td>
<td>K$_2$S$_2$O$_8$</td>
<td>CH$_3$CN/H$_2$O(3:2)</td>
<td>-</td>
<td>74%</td>
</tr>
</tbody>
</table>
Reaction conditions: 1a (0.1 mmol), 2a (0.2 mmol), AgX (10 mol%), photocatalyst (3 mol%, 26 W household light), oxidant (0.2 mmol, 2 equiv), additive (1.0 equiv), solvent (1.0 mL) under nitrogen for 8 h. \(^4\)Isolated yield. \(^5\)Under green LED. \(^6\)Under red LED. \(^7\)Under blue LED. \(^8\)Under dark. \(^9\)For Ag\(_2\)O (1.0 equiv). \(^{10}\)For Ag\(_2\)O (2.0 equiv). \(^{11}\)For no cosin Y. \(^{12}\)For 6 h, \(^{13}\)For 10 h, \(^{14}\)Under air, \(^{15}\)Under O\(_2\).
4. Typical Procedure for the Products

(a) Procedure for the synthesis of 3:

A 20 mL Schlenk tube was equipped with a magnetic stir bar and charged with 8-hydroxylquinoline ester 1 (0.1 mmol), diarylphosphine oxide 2 (0.2 mmol), eosin Y (2.1 mg, 0.003 mmol, 3 mol%), K$_2$S$_2$O$_8$ (0.2 mmol, 2 equiv), Ag$_2$O (2.3 mg, 0.01 mmol, 10 mol%) in CH$_3$CN/H$_2$O (3:2) (1.5 mL). The resulting mixture was stirred under the irradiation of 26 W household light under nitrogen at room temperature for 6 h. Upon completion, the mixture was added into H$_2$O (20 mL) and extracted with CH$_2$Cl$_2$ (20 mL) three times. The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100‒200 mesh) using CH$_2$Cl$_2$/ethyl acetate as an eluent (2:1, V/V) to afford the pure product 3.

(b) Procedure for the hydrolysis of 4a:

To a solution of 3aa (0.2 mmol) in ethyl alcohol (3 mL), NaOH (0.22 mmol, 1.1 equiv) was added, and the resulting mixture was stirred at 80 °C for 12 h. The solvent was removed by vacuum, and then 3 mL H$_2$O was added to the residue. The mixture was extracted with CH$_2$Cl$_2$ (3 × 5 mL). The combined organic layer was dried over anhydrous Na$_2$SO$_4$ and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (100‒200 mesh) using CH$_2$Cl$_2$/ethyl acetate (2:1, V/V) as an eluent to afford the pure product 4a.

5. Characterization Data of the Products

4-(diphenylphosphoryl)quinolin-8-yl benzoate (3aa):

Light yellow solid (78% yield); mp 88–89 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ: 8.85 (t, $J$= 4.0 Hz, 1H), 8.53–8.51 (m, 1H), 8.34–8.32 (m, 2H), 7.72–7.49 (m, 15H), 7.15 (dd, $J$= 15.1, 4.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 165.5, 149.1 (d, $J_{C-P}$ = 11.5 Hz), 148.2 (d, $J_{C-P}$ = 2.8 Hz), 141.9 (d, $J_{C-P}$ = 7.1 Hz), 138.8 (d, $J_{C-P}$ = 94.3 Hz), 133.7, 132.6 (d, $J_{C-P}$ = 2.8 Hz), 132.0 (d, $J_{C-P}$ = 10.0 Hz), 131.1 (d, $J_{C-P}$ = 106.3 Hz), 130.6, 129.4, 128.9 (d, $J_{C-P}$ = 12.5 Hz), 128.9, 128.6, 127.7, 126.7 (d, $J_{C-P}$ = 9.3 Hz), 125.7 (d, $J_{C-P}$ = 5.6 Hz), 122.2; $^{31}$P NMR (163 MHz, CDCl$_3$) δ: 30.7; HRMS (ESI-TOF): Calcd for C$_{28}$H$_{21}$NO$_3$P [M+H]$^+$: 450.1254, Found: 450.1255.

4-(di-p-tolylphosphoryl)quinolin-8-yl benzoate (3ab):

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Light yellow solid (66% yield); mp 194–195 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.84 (t, \(J=3.8\) Hz, 1H), 8.53 (d, \(J=7.9\) Hz, 1H), 8.33 (d, \(J=7.6\) Hz, 2H), 7.67–7.63 (m, 1H), 7.59–7.51 (m, 8H), 7.31–7.29 (m, 4H), 7.15 (dd, \(J=14.8, 4.2\) Hz, 1H), 2.42 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 165.5, 149.1 (d, \(J_{C-P}=11.5\) Hz), 148.1 (d, \(J_{C-P}=2.6\) Hz), 143.2 (d, \(J_{C-P}=2.8\) Hz), 141.9 (d, \(J_{C-P}=7.0\) Hz), 139.2 (d, \(J_{C-P}=93.9\) Hz), 133.7, 132.0 (d, \(J_{C-P}=10.4\) Hz), 130.6, 129.7 (d, \(J_{C-P}=12.7\) Hz), 129.3 (d, \(J_{C-P}=8.0\) Hz), 129.0 (d, \(J_{C-P}=6.8\) Hz), 128.6, 127.9 (d, \(J_{C-P}=107.8\) Hz), 127.6, 126.7 (d, \(J_{C-P}=9.4\) Hz), 125.8 (d, \(J_{C-P}=5.5\) Hz), 122.2, 21.7; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 31.1; HRMS (ESI-TOF): Calcd for C\(_{30}\)H\(_{25}\)NO\(_3\)P [M+H]\(^+\): 478.1567, Found: 478.1569.

4-(bis(3,5-dimethylphenyl)phosphoryl)quinolin-8-yl benzoate (3ac):

Light yellow solid (53% yield); mp 109–110 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.85 (t, \(J=3.9\) Hz, 1H), 8.56–8.54 (m, 1H), 8.35–8.32 (m, 2H), 7.68–7.64 (m, 1H), 7.58–7.53 (m, 4H), 7.29 (d, \(J=12.6\) Hz, 4H), 7.21 (s, 2H), 7.16 (dd, \(J=14.8, 4.2\) Hz, 1H), 2.33 (s, 12H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 165.5, 149.1 (d, \(J_{C-P}=11.3\) Hz), 148.1 (d, \(J_{C-P}=2.5\) Hz), 141.9 (d, \(J_{C-P}=7.1\) Hz), 139.3 (d, \(J_{C-P}=92.7\) Hz), 138.6 (d, \(J_{C-P}=13.0\) Hz), 134.4 (d, \(J_{C-P}=2.8\) Hz), 133.7, 130.9 (d, \(J_{C-P}=104.1\) Hz), 130.7, 129.5 (d, \(J_{C-P}=10.0\) Hz), 129.4, 129.1 (d, \(J_{C-P}=6.6\) Hz), 128.6, 127.5, 126.8 (d, \(J_{C-P}=9.5\) Hz), 125.9 (d, \(J_{C-P}=5.4\) Hz), 122.1, 21.4; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 31.3; HRMS (ESI-TOF): Calcd for C\(_{32}\)H\(_{29}\)NO\(_3\)P [M+H]\(^+\): 506.1880, Found: 506.1881.

4-(di-p-tolylphosphoryl)quinolin-8-yl 3-methylbenzoate (3ad):

Light yellow solid (48% yield); mp 106–107 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.84 (t, \(J=3.8\) Hz, 1H), 8.54–8.52 (m, 1H), 8.15–8.12 (m, 2H), 7.59–7.53 (m, 6H), 7.48–7.40 (m, 2H), 7.31–7.29 (m, 4H), 7.14 (dd, \(J=14.8, 4.2\) Hz, 1H), 2.45 (s, 3H), 2.42 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 165.6, 149.1 (d, \(J_{C-P}=11.3\) Hz), 148.2 (d, \(J_{C-P}=2.7\) Hz), 143.1 (d, \(J_{C-P}=2.7\) Hz), 141.9 (d, \(J_{C-P}=7.0\) Hz), 139.3 (d, \(J_{C-P}=93.7\) Hz), 138.4, 134.5, 132.0 (d, \(J_{C-P}=10.3\) Hz), 131.0, 129.6 (d, \(J_{C-P}=12.8\) Hz), 129.3, 129.0 (d, \(J_{C-P}=6.6\) Hz), 128.5, 127.7, 127.5, 127.5, 126.6 (d, \(J_{C-P}=9.3\) Hz), 125.8

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(d, $J_{C,P} = 5.4$ Hz), 122.1, 21.7, 21.4; $^{31}$P NMR (163 MHz, CDCl$_3$) $\delta$: 31.0; HRMS (ESI-TOF): Calcd for C$_{31}$H$_{27}$NO$_3$P $[M+H]^+$: 492.1723, Found: 492.1724.

4-(diphenylphosphoryl)quinolin-8-yl 2-methylbenzoate (3ba):

![3ba](image)

Light yellow solid (67% yield); mp 95–97 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.87 (t, $J = 4.0$ Hz, 1H), 8.51–8.48 (m, 1H), 8.38–8.36 (m, 1H), 7.72–7.49 (m, 13H), 7.38-7.33 (m, 2H), 7.16 (dd, $J = 14.9$, 4.2 Hz, 1H), 2.71 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 166.2, 149.0 (d, $J_{C,P} = 11.3$ Hz), 148.3 (d, $J_{C,P} = 7.2$ Hz), 141.5, 138.8 (d, $J_{C,P} = 93.7$ Hz), 132.8, 132.6 (d, $J_{C,P} = 2.6$ Hz), 132.0 (d, $J_{C,P} = 10.0$ Hz), 131.9, 131.7, 131.2 (d, $J_{C,P} = 105.0$ Hz), 128.9 (d, $J_{C,P} = 12.5$ Hz), 128.9, 128.6, 127.7, 126.7 (d, $J_{C,P} = 9.4$ Hz), 126.0, 125.6 (d, $J_{C,P} = 5.6$ Hz), 122.3, 21.9; $^{31}$P NMR (163 MHz, CDCl$_3$) $\delta$: 30.6; HRMS (ESI-TOF) Calcd for C$_{29}$H$_{23}$NO$_3$P $[M+H]^+$: 464.1410, Found: 464.1413.

4-(diphenylphosphoryl)quinolin-8-yl 3-methylbenzoate (3ca):

![3ca](image)

Light yellow solid (68% yield); mp 116–118 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.85 (t, $J = 4.0$ Hz, 1H), 8.53–8.50 (m, 1H), 8.15–8.12 (m, 2H), 7.72–7.41 (m, 15H), 7.15 (dd, $J = 14.9$, 4.2 Hz, 1H), 2.46 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.6, 149.1 (d, $J_{C,P} = 11.4$ Hz), 148.2 (d, $J_{C,P} = 2.7$ Hz), 142.0 (d, $J_{C,P} = 7.3$ Hz), 138.8 (d, $J_{C,P} = 94.0$ Hz), 138.5, 134.5, 132.6 (d, $J_{C,P} = 2.7$ Hz), 132.0 (d, $J_{C,P} = 10.0$ Hz), 131.2 (d, $J_{C,P} = 105.1$ Hz), 131.0, 129.3, 128.9 (d, $J_{C,P} = 12.5$ Hz), 128.9, 128.5, 127.7, 126.6 (d, $J_{C,P} = 9.5$ Hz), 125.6 (d, $J_{C,P} = 5.5$ Hz), 122.2, 21.3; $^{31}$P NMR (163 MHz, CDCl$_3$) $\delta$: 30.6; HRMS (ESI-TOF) Calcd for C$_{29}$H$_{23}$NO$_3$P $[M+H]^+$: 464.1410, Found: 464.1412.

4-(diphenylphosphoryl)quinolin-8-yl 4-methylbenzoate (3da):

![3da](image)

Light yellow solid (66% yield); mp 107–109 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.85 (t, $J = 4.0$ Hz, 1H), 8.52–8.49 (m, 1H), 8.23–8.21 (m, 1H), 7.72–7.49 (m, 13H), 7.35–7.33 (m, 2H), 7.14 (dd, $J = 14.9$, 4.2 Hz, 1H), 2.47 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.5, 149.1 (d, $J_{C,P} = 11.4$ Hz), 148.3 (d, $J_{C,P} = 3.2$ Hz), 144.5, 142.0 (d, $J_{C,P} = 7.0$ Hz), 138.7 (d, $J_{C,P} = 94.1$ Hz), 132.6 (d, $J_{C,P} = 94.2$, 1H), 122.1, 21.7, 21.4; $^{31}$P NMR (163 MHz, CDCl$_3$) $\delta$: 31.0; HRMS (ESI-TOF) Calcd for C$_{31}$H$_{27}$NO$_3$P $[M+H]^+$: 492.1723, Found: 492.1724.
2.3 Hz), 132.0 (d, \( J_{CP} = 10.0 \) Hz), 131.2 (d, \( J_{CP} = 108.4 \) Hz), 129.4, 128.9 (d, \( J_{CP} = 12.4 \) Hz), 127.7, 126.7, 126.6, 126.6 (d, \( J_{CP} = 5.4 \) Hz), 122.3, 21.8; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.6; HRMS (ESI-TOF) Calcd for C\(_{29}\)H\(_{23}\)NO\(_3\)P [M+H]+: 464.1410, Found: 464.1413.

4-(diphenylphosphoryl)quinolin-8-yl 2-methoxybenzoate (3ea):

![Structure 3ea](image)

Light yellow solid (58% yield); mp 86−87 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.87 (t, \( J = 4.0 \) Hz, 1H), 8.48 (d, \( J = 8.2 \) Hz, 1H), 8.32−8.29 (m, 1H), 7.71−7.48 (m, 13H), 7.15 (dd, \( J = 15.0, 4.2 \) Hz, 1H), 7.10-7.04 (m, 2H), 3.93 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 164.2, 160.3, 149.0 (d, \( J_{CP} = 11.4 \) Hz), 148.2 (d, \( J_{CP} = 2.8 \) Hz), 142.1 (d, \( J_{CP} = 7.2 \) Hz), 139.1, 138.1, 134.85, 132.9, 132.6 (d, \( J_{CP} = 2.6 \) Hz), 132.0 (d, \( J_{CP} = 10.1 \) Hz), 132.0, 131.2 (d, \( J_{CP} = 105.1 \) Hz), 128.9 (d, \( J_{CP} = 12.3 \) Hz), 128.8, 127.6, 126.6 (d, \( J_{CP} = 9.4 \) Hz), 125.4 (d, \( J_{CP} = 5.4 \) Hz), 124.4, 119.5 (d, \( J_{CP} = 161.4 \) Hz), 112.3, 56.1; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.7; HRMS (ESI-TOF) Calcd for C\(_{29}\)H\(_{23}\)NO\(_4\)P [M+H]+: 480.1359, Found: 480.1362.

4-(diphenylphosphoryl)quinolin-8-yl 4-methoxybenzoate (3fa):

![Structure 3fa](image)

Light yellow solid (61% yield); mp 208−209 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.85 (t, \( J = 4.0 \) Hz, 1H), 8.51-8.49 (m, 1H), 8.29−8.27 (m, 2H), 7.71−7.66 (m, 4H), 7.62-7.48 (m, 8H), 7.14 (dd, \( J = 15.0, 4.2 \) Hz, 1H), 7.03-7.00 (m, 2H), 3.90 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 165.2, 164.0, 148.7 (d, \( J_{CP} = 11.5 \) Hz), 148.3 (d, \( J_{CP} = 2.9 \) Hz), 142.1 (d, \( J_{CP} = 7.2 \) Hz), 139.2, 138.3, 132.7, 132.6 (d, \( J_{CP} = 2.7 \) Hz), 132.0 (d, \( J_{CP} = 10.0 \) Hz), 131.9 (d, \( J_{CP} = 105.2 \) Hz), 128.9 (d, \( J_{CP} = 12.4 \) Hz), 127.7, 126.6 (d, \( J_{CP} = 9.4 \) Hz), 125.5 (d, \( J_{CP} = 5.4 \) Hz), 122.0 (d, \( J_{CP} = 63.4 \) Hz), 55.6; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.6; HRMS (ESI-TOF) Calcd for C\(_{29}\)H\(_{23}\)NO\(_4\)P [M+H]+: 480.1359, Found: 480.1361.

4-(diphenylphosphoryl)quinolin-8-yl 3,5-dimethoxybenzoate (3ga):

![Structure 3ga](image)

Light yellow solid (60% yield); mp 154−155 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.86 (t, \( J = 4.0 \) Hz,
1H), 8.54-8.51 (m, 1H), 7.72-7.67 (m, 4H), 7.48 (s, 1H), 7.47 (s, 1H), 7.15 (dd, J = 14.9, 4.2 Hz, 1H), 6.75 (t, J = 2.4 Hz, 1H), 3.90 (s, 6H); 13C NMR (100 MHz, CDCl3) δ: 165.2, 160.8, 149.1 (d, J_{C-P} = 11.4 Hz), 148.2 (d, J_{C-P} = 2.8 Hz), 141.9 (d, J_{C-P} = 7.2 Hz), 139.2, 138.3, 132.6 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 10.0 Hz), 131.1 (d, J_{C-P} = 105.1 Hz), 131.1, 128.9 (d, J_{C-P} = 12.4 Hz), 127.7, 126.6 (d, J_{C-P} = 9.4 Hz), 125.7 (d, J_{C-P} = 5.4 Hz), 122.2, 108.0, 106.7, 55.7; 31P NMR (163 MHz, CDCl3) δ: 30.6; HRMS (ESI-TOF) Calcd for C_{30}H_{25}NO_{3}P [M+H]^+: 510.1465, Found: 510.1469.

4-(diphenylphosphoryl)quinolin-8-yl 2-fluorobenzoate (3ha):

Light yellow solid (63% yield); mp 96–97 °C; 1H NMR (400 MHz, CDCl3) δ: 8.89 (t, J = 3.9 Hz, 1H), 8.54 (d, J = 8.2, 1H), 8.32-8.28 (m, 1H), 7.73-7.68 (m, 4H), 7.65-7.58 (m, 4H), 7.56-7.51 (m, 5H), 7.35–7.31 (m, 1H), 7.26–7.23 (m, 1H), 7.18 (dd, J = 14.9, 4.2 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ: 163.9, 162.8 (d, J_{C-F} = 3.9 Hz), 161.3, 149.1 (d, J_{C-P} = 11.4 Hz), 147.8 (d, J_{C-P} = 2.7 Hz), 141.7 (d, J_{C-P} = 9.4 Hz), 125.8 (d, J_{C-P} = 5.4 Hz), 124.2 (d, J_{C-P} = 4.0 Hz), 122.2, 117.9 (d, J_{C-P} = 9.2 Hz), 117.2 (d, J_{C-P} = 21.9 Hz); 31P NMR (163 MHz, CDCl3) δ: -111.912; HRMS (ESI-TOF): Calcd for C_{28}H_{20}FNO_{3}P [M+H]^+: 468.1159, Found: 468.1159.

4-(diphenylphosphoryl)quinolin-8-yl 3-fluorobenzoate (3ia):

Light yellow solid (66% yield); mp 169–170 °C; 1H NMR (400 MHz, CDCl3) δ: 8.85 (t, J = 3.8 Hz, 1H), 8.53 (d, J = 8.0, 1H), 8.11 (d, J = 7.7, 1H), 8.00 (d, J = 8.9, 1H), 7.72–7.67 (m, 4H), 7.62-7.55 (m, 3H), 7.53–7.50 (m, 6H), 7.37–7.33 (m, 1H), 7.16 (dd, J = 15.0, 4.1 Hz, 1H); 13C NMR (100 MHz, CDCl3) δ: 164.4 (d, J_{C-F} = 2.9 Hz), 162.6 (d, J_{C-F} = 245.8 Hz), 157.2, 149.2 (d, J_{C-P} = 11.5 Hz), 147.9 (d, J_{C-P} = 3.0 Hz), 141.7 (d, J_{C-F} = 7.2 Hz), 138.7 (d, J_{C-P} = 94.1 Hz), 132.7 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 10.1 Hz), 130.9 (d, J_{C-P} = 105.3 Hz), 130.3 (d, J_{C-P} = 7.7 Hz), 129.0 (d, J_{C-P} = 12.4 Hz), 127.7, 126.8 (d, J_{C-P} = 9.4 Hz), 126.3 (d, J_{C-P} = 3.0 Hz), 125.9 (d, J_{C-P} = 5.5 Hz), 122.2, 120.8 (d, J_{C-P} = 21.1 Hz), 117.4 (d, J_{C-P} = 23.0 Hz), 115.6; 31P NMR (163 MHz, CDCl3) δ: -108.038; HRMS (ESI-TOF): Calcd for C_{28}H_{20}FNO_{3}P [M+H]^+: 468.1159, Found: 468.1163.
4-(diphenylphosphoryl)quinolin-8-yl 4-fluorobenzoate (3ja):

Light yellow solid (65% yield); mp 86–87 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.87 (t, \(J= 3.9\) Hz, 1H), 8.54 (d, \(J= 7.3\) Hz, 1H), 8.38–8.34 (m, 2H), 7.74–7.69 (m, 4H), 7.64–7.58 (m, 4H), 7.56–7.51 (m, 5H), 7.28–7.25 (m, 1H), 7.17 (dd, \(J= 14.9, 4.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 167.5, 165.0, 164.5, 149.1 (d, \(J_{C-P}= 11.3\) Hz), 148.0 (d, \(J_{C-F}= 2.5\) Hz), 141.8 (d, \(J_{C-F}= 7.1\) Hz), 138.8 (d, \(J_{C-P}= 93.8\) Hz), 133.2 (d, \(J_{C-P}= 9.4\) Hz), 132.6 (d, \(J_{C-P}= 2.4\) Hz), 132.0 (d, \(J_{C-P}= 9.9\) Hz), 131.1 (d, \(J_{C-P}= 105.2\) Hz), 129.0 (d, \(J_{C-P}= 12.3\) Hz), 127.7, 126.7 (d, \(J_{C-P}= 9.4\) Hz), 125.8 (d, \(J_{C-P}= 5.4\) Hz), 125.6 (d, \(J_{C-P}= 2.8\) Hz), 122.2, 115.9 (d, \(J_{C-P}= 21.9\) Hz); \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): -30.7; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -104.355; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)FNO\(_3\)P [M+H]\(^+\): 468.1159, Found: 468.1161.

4-(diphenylphosphoryl)quinolin-8-yl 2-chlorobenzoate (3ka):

Light yellow (66% yield); mp 99–100 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.88 (t, \(J= 4.0\) Hz, 1H), 8.52 (d, \(J= 8.4\) Hz, 1H), 8.37–8.34 (m, 1H), 7.72–7.67 (m, 4H), 7.62–7.58 (m, 3H), 7.56–7.48 (m, 7H), 7.18 (dd, \(J= 14.9, 4.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 163.6, 149.1 (d, \(J_{C-P}= 11.5\) Hz), 147.8 (d, \(J_{C-P}= 2.8\) Hz), 141.7 (d, \(J_{C-P}= 7.2\) Hz), 138.8 (d, \(J_{C-P}= 93.9\) Hz), 134.8, 133.3, 132.7 (d, \(J_{C-P}= 2.0\) Hz), 132.6, 132.0 (d, \(J_{C-P}= 9.9\) Hz), 131.4, 131.1 (d, \(J_{C-P}= 105.1\) Hz), 129.0 (d, \(J_{C-P}= 12.4\) Hz), 128.9, 127.6, 126.8, 126.7 (d, \(J_{C-P}= 21.9\) Hz), 125.8 (d, \(J_{C-P}= 5.4\) Hz), 122.2; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.6; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)ClNO\(_3\)P [M+H]\(^+\): 484.0864, Found: 484.0867.

4-(diphenylphosphoryl)quinolin-8-yl 3-chlorobenzoate (3la):

Light yellow solid (65% yield); mp 108–110 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.85 (t, \(J= 4.0\) Hz, 1H), 8.55–8.52 (m, 1H), 8.32–8.31 (m, 1H), 8.2 2–8.19 (m, 1H), 7.72–7.67 (m, 4H), 7.65–7.58 (m, 3H), 7.56–7.47 (m, 7H), 7.15 (dd, \(J= 14.9, 4.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 164.2,
149.2 (d, \( J_{C,P} = 11.3 \) Hz), 147.9 (d, \( J_{C,P} = 2.9 \) Hz), 141.7 (d, \( J_{C,P} = 7.0 \) Hz), 139.0 (d, \( J_{C,P} = 93.7 \) Hz), 133.7, 132.6 (d, \( J_{C,P} = 2.6 \) Hz), 132.0 (d, \( J_{C,P} = 10.0 \) Hz), 131.5, 131.2, 131.1 (d, \( J_{C,P} = 105.1 \) Hz), 129.3, 129.0 (d, \( J_{C,P} = 12.3 \) Hz), 127.7, 127.5 (d, \( J_{C,P} = 3.9 \) Hz), 126.7 (d, \( J_{C,P} = 9.4 \) Hz), 126.0 (d, \( J_{C,P} = 5.5 \) Hz), 122.1; \( ^{31}P \) NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.5; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)ClNO\(_3\)P [M+H]+: 484.0864, Found: 484.0866.

4-(diphenylphosphoryl)quinolin-8-yl 4-chlorobenzoate (3ma):

\[ \text{3ma} \]

Light yellow solid (63% yield); mp 106–107 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.84 (t, \( J = 3.9 \) Hz, 1H), 8.54–8.52 (m, 1H), 8.28–8.25 (m, 2H), 7.72–7.67 (m, 4H), 7.54–7.49 (m, 7H), 7.15 (dd, \( J = 14.9, 4.2 \) Hz, 1H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 164.6, 149.1 (d, \( J_{C,P} = 11.5 \) Hz), 148.0 (d, \( J_{C,P} = 2.9 \) Hz), 141.8 (d, \( J_{C,P} = 7.1 \) Hz), 140.2, 138.9 (d, \( J_{C,P} = 93.6 \) Hz), 132.6 (d, \( J_{C,P} = 2.8 \) Hz), 132.1, 132.0 (d, \( J_{C,P} = 1.8 \) Hz), 131.1 (d, \( J_{C,P} = 105.1 \) Hz), 129.0, 128.9, 127.9, 127.6, 126.7 (d, \( J_{C,P} = 9.5 \) Hz), 125.8 (d, \( J_{C,P} = 5.5 \) Hz), 122.2; \( ^{31}P \) NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.6; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)ClNO\(_3\)P [M+H]+: 484.0864, Found: 484.0865.

4-(diphenylphosphoryl)quinolin-8-yl 3-bromobenzoate (3na):

\[ \text{3na} \]

Light yellow solid (49% yield); mp 108–109 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.84 (t, \( J = 4.0 \) Hz, 1H), 8.55–8.53 (m, 1H), 8.47–8.46 (m, 1H), 8.26–8.23 (m, 1H), 7.79–7.76 (m, 1H), 7.72–7.67 (m, 4H), 7.62–7.58 (m, 2H), 7.56 (m, 1H), 7.54–7.49 (m, 5H), 7.42 (t, \( J = 7.9 \) Hz, 1H), 7.16 (dd, \( J = 14.9, 4.2 \) Hz, 1H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \( \delta \): 164.1, 149.1 (d, \( J_{C,P} = 11.5 \) Hz), 147.9 (d, \( J_{C,P} = 2.8 \) Hz), 141.7 (d, \( J_{C,P} = 7.2 \) Hz), 138.9 (d, \( J_{C,P} = 93.8 \) Hz), 136.6, 133.5, 132.6 (d, \( J_{C,P} = 2.6 \) Hz), 132.0 (d, \( J_{C,P} = 9.9 \) Hz), 131.3, 131.1 (d, \( J_{C,P} = 105.1 \) Hz), 130.2, 129.1, 129.0 (d, \( J_{C,P} = 12.3 \) Hz), 129.0, 127.6, 126.7 (d, \( J_{C,P} = 9.4 \) Hz), 125.9 (d, \( J_{C,P} = 5.5 \) Hz), 122.7, 122.1; \( ^{31}P \) NMR (163 MHz, CDCl\(_3\)) \( \delta \): 30.6; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)BrNO\(_3\)P [M+H]+: 528.0359, Found: 528.0360.

4-(diphenylphosphoryl)quinolin-8-yl 4-bromobenzoate (3oa):

\[ \text{3oa} \]
Light yellow solid (54% yield); mp 101-102 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.84 (t, \(J = 3.9\) Hz, 1H), 8.54–8.52 (m, 1H), 8.19–8.17 (m, 2H), 7.72–7.67 (m, 7H), 7.63–7.58 (m, 2H), 7.56 (m, 1H), 7.54–7.49 (m, 5H), 7.15 (dd, \(J = 14.9, 4.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 164.8 149.1 (d, \(J_{C,P} = 11.3\) Hz), 148.0 (d, \(J_{C,P} = 2.7\) Hz), 141.7 (d, \(J_{C,P} = 7.2\) Hz), 138.8 (d, \(J_{C,P} = 93.9\) Hz), 132.6 (d, \(J_{C,P} = 2.8\) Hz), 132.1, 132.0, 132.0, 131.0 (d, \(J_{C,P} = 105.1\) Hz), 129.0, 129.0, 128.9, 128.3, 127.7, 126.7 (d, \(J_{C,P} = 9.4\) Hz), 125.8 (d, \(J_{C,P} = 5.6\) Hz), 122.1; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.7; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)BrNO\(_3\)P \([M+H]^+\): 528.0359, Found: 528.0359.

4-(diphenylphosphoryl)quinolin-8-yl 2-iodobenzoate (3pa):

\[
\begin{align*}
\text{O} & \text{O} & \text{P} & \text{Ph} & \text{Ph} \\
\text{O} & \text{NC} & \text{Ph} & \text{Ph}
\end{align*}
\]

Light yellow solid (45% yield); mp 80–81 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.90 (t, \(J = 3.9\) Hz, 1H), 8.52 (d, \(J = 2.1\), 1H), 8.42–8.39 (m, 1H), 8.12 (d, \(J = 7.8\), 1H), 7.74–7.69 (m, 4H), 7.65–7.61 (m, 3H), 7.58–7.52 (m, 6H), 7.27–7.25 (m, 1H), 7.19 (dd, \(J = 14.9, 4.2\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 164.8, 149.1 (d, \(J_{C,P} = 11.3\) Hz), 147.8 (d, \(J_{C,P} = 2.8\) Hz), 141.7 (d, \(J_{C,P} = 9.3\) Hz), 133.5, 133.4, 132.6 (d, \(J_{C,P} = 2.6\) Hz), 132.4, 132.0 (d, \(J_{C,P} = 9.9\) Hz), 131.1 (d, \(J_{C,P} = 105.2\) Hz), 129.0 (d, \(J_{C,P} = 12.3\) Hz), 128.9, 128.6, 128.2, 127.6, 126.7 (d, \(J_{C,P} = 9.4\) Hz), 125.8 (d, \(J_{C,P} = 5.4\) Hz), 122.2, 95.3; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.6; HRMS (ESI-TOF): Calcd for C\(_{28}\)H\(_{20}\)INO\(_3\)P \([M+H]^+\): 476.0220, Found: 476.0218.

4-(diphenylphosphoryl)quinolin-8-yl 4-cyanobenzoate (3qa):

\[
\begin{align*}
\text{O} & \text{O} & \text{P} & \text{Ph} & \text{Ph} \\
\text{NC} & \text{Ph} & \text{Ph}
\end{align*}
\]

Light yellow solid (58% yield); mp 106–107 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.84 (t, \(J = 4.0\) Hz, 1H), 8.54–8.52 (m, 1H), 8.44–8.42 (m, 2H), 7.86–7.84 (m, 2H), 7.72–7.67 (m, 4H), 7.62–7.58 (m, 3H), 7.56–7.50 (m, 5H), 7.16 (dd, \(J = 14.9, 4.3\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 163.9, 149.2 (d, \(J_{C,P} = 11.5\) Hz), 147.7 (d, \(J_{C,P} = 2.8\) Hz), 141.5 (d, \(J_{C,P} = 7.2\) Hz), 139.0 (d, \(J_{C,P} = 93.5\) Hz), 133.3, 132.7 (d, \(J_{C,P} = 2.7\) Hz), 132.5, 132.0 (d, \(J_{C,P} = 10.0\) Hz), 131.0, 130.9 (d, \(J_{C,P} = 105.3\) Hz), 129.0, 129.0 (d, \(J_{C,P} = 12.5\) Hz), 127.7, 126.8 (d, \(J_{C,P} = 9.4\) Hz), 126.1 (d, \(J_{C,P} = 5.6\) Hz), 122.0, 117.5 (d, \(J_{C,P} = 96.4\) Hz); \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.7; HRMS (ESI-TOF): Calcd for C\(_{29}\)H\(_{20}\)N\(_2\)O\(_3\)P \([M+H]^+\): 475.1206, Found: 475.1209.

4 diphenylphosphoryl)quinolin-8-yl 3-(trifluoromethyl)benzoate (3ra):
4-(diphenylphosphoryl)quinolin-8-yl 4-(trifluoromethyl)benzoate (3sa):  

Light yellow solid (67% yield); mp 99–102 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.85 (t, \(J= 4.0 \) Hz, 1H), 8.60 (s, 1H), 8.57–8.54 (m, 1H), 8.52–8.50 (m, 1H), 7.93–7.91 (m, 1H), 7.72–7.67 (m, 5H), 7.63–7.56 (m, 4H), 7.54–7.50 (m, 4H), 7.16 (dd, \(J= 14.9, 4.3 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 164.2, 149.2 \((d, \ J_{C-P} = 11.5 \) Hz), 147.9 \((d, \ J_{C-P} = 2.9 \) Hz), 141.7 \((d, \ J_{C-P} = 7.0 \) Hz), 139.0 \((d, \ J_{C-P} = 93.8 \) Hz), 133.7, 132.6 \((d, \ J_{C-P} = 2.7 \) Hz), 132.0 \((d, \ J_{C-P} = 10.0 \) Hz), 131.3 \((d, \ J_{C-F} = 32.9 \) Hz), 131.1 \((d, \ J_{C-F} = 105.1 \) Hz), 130.3, 130.2 \((d, \ J_{C-P} = 3.6 \) Hz), 129.3, 129.0 \((d, \ J_{C-P} = 12.3 \) Hz), 128.9, 127.7, 127.5 \((d, \ J_{C-P} = 3.8 \) Hz), 126.7 \((d, \ J_{C-P} = 9.5 \) Hz), 126.0 \((q, \ J_{C-F} = 5.4 \) Hz), 123.7 \((q, \ J_{C-F} = 270.7 \) Hz), 122.1; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -62.704; HRMS (ESI-TOF): Calcd for C\(_{29}\)H\(_{20}\)F\(_3\)NO\(_3\)P \([M+H]^+\): 518.1127, Found: 518.1132.

4-(diphenylphosphoryl)-2-methylquinolin-8-yl benzoate (3ta):  

Light yellow solid (52% yield); mp 99–101 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.84 (t, \(J= 3.8 \) Hz, 1H), 8.56–8.54 (m, 1H), 8.45 \((d, \ J_{C-P} = 8.3 \) Hz, 2H), 7.82 \((d, \ J= 8.3 \) Hz, 2H), 7.72–7.67 (m, 4H), 7.64–7.56 (m, 4H), 7.54–7.50 (m, 4H), 7.12–7.08 (d, \(J= 15.4 \) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 164.3, 149.1 \((d, \ J_{C-P} = 11.4 \) Hz), 147.9 \((d, \ J_{C-P} = 2.8 \) Hz), 141.6 \((d, \ J_{C-P} = 7.1 \) Hz), 139.0 \((d, \ J_{C-P} = 93.8 \) Hz), 135.3, 134.9, 132.6 \((d, \ J_{C-P} = 2.7 \) Hz), 132.0 \((d, \ J_{C-P} = 10.0 \) Hz), 131.1 \((d, \ J_{C-P} = 105.1 \) Hz), 130.9, 129.0 \((d, \ J_{C-P} = 12.4 \) Hz), 127.7, 126.7 \((d, \ J_{C-F} = 9.3 \) Hz), 126.0 \((d, \ J_{C-F} = 5.4 \) Hz), 125.7 \((d, \ J_{C-F} = 3.7 \) Hz), 122.1; \(^{31}\)P NMR (163 MHz, CDCl\(_3\)) \(\delta\): 30.6; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\): -63.100; HRMS (ESI-TOF): Calcd for C\(_{29}\)H\(_{20}\)F\(_3\)NO\(_3\)P \([M+H]^+\): 518.1127, Found: 518.1133.

4-(diphenylphosphoryl)-2-methylquinolin-8-yl benzoate (3ta):  

Light yellow solid (69% yield); mp 200–201 °C; \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.37–8.31 (m, 3H), 7.12–7.08 (d, \(J= 15.4 \) Hz, 1H), 2.55 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 165.7, 158.1 \((d, \ J_{C-P} = 11.4 \) Hz), 147.8 \((d, \ J_{C-P} = 3.0 \) Hz), 141.5 \((d, \ J_{C-P} = 7.7 \) Hz), 138.6 \((d, \ J_{C-P} = 94.0 \) Hz), 133.5, 132.6 \((d, \ J_{C-P} = 2.6 \) Hz), 132.0 \((d, \ J_{C-P} = 9.9 \) Hz), ...
131.3 (d, \(J_{C,P} = 104.9 \text{ Hz})\), 130.5, 129.7, 128.9 (d, \(J_{C,P} = 12.4 \text{ Hz})\), 128.6, 127.8 (d, \(J_{C,P} = 9.0 \text{ Hz})\), 127.0 (d, \(J_{C,P} = 7.0 \text{ Hz})\), 126.5, 125.3 (d, \(J_{C,P} = 5.3 \text{ Hz})\), 122.0, 25.8; \(^{31}\text{P} \text{ NMR (163 MHz, CDCl}_3) \delta: 30.4\); HRMS (ESI-TOF): Calcd for C\(_{29}\)H\(_{23}\)NO\(_3\)P \([\text{M+H}]^+\): 464.1410, Found: 464.1414.

4-(diphenylphosphoryl)-2-methylquinolin-8-yl 4-methylbenzoate (3ua):

![3ua]

Light yellow solid (67% yield); mp 157−158 °C; \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta: 8.35 (d, J= 8.4 \text{ Hz, 1H}), 8.21 (d, J= 8.1 \text{ Hz, 2H}), 7.71−7.67 (m, 4H), 7.60−7.57 (m, 2H), 7.52-7.48 (m, 5H), 7.44-7.40 (m, 1H), 7.34 (d, J= 8.0 \text{ Hz, 2H}), 7.10 (d, J= 15.3 \text{ Hz, 1H}), 2.54 (s, 3H), 2.47 (s, 3H); \(^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3) \delta: 165.7, 158.0 (d, J_{C,P} = 11.3 \text{ Hz}), 147.8 (d, J_{C,P} = 2.9 \text{ Hz}), 144.3, 141.6 (d, J_{C,P} = 7.5 \text{ Hz}), 138.6 (d, J_{C,P} = 93.9 \text{ Hz}), 132.5 (d, J_{C,P} = 2.4 \text{ Hz}), 132.0 (d, J_{C,P} = 9.9 \text{ Hz}), 131.3 (d, J_{C,P} = 104.8 \text{ Hz}), 130.5, 129.3, 128.9 (d, J_{C,P} = 12.3 \text{ Hz}), 127.8 (d, J_{C,P} = 9.0 \text{ Hz}), 127.0 (d, J_{C,P} = 6.7 \text{ Hz}), 126.9, 126.5, 125.2 (d, J_{C,P} = 5.2 \text{ Hz}), 122.1, 25.8, 21.8; \(^{31}\text{P} \text{ NMR (163 MHz, CDCl}_3) \delta: 30.3\); HRMS (ESI-TOF): Calcd for C\(_{30}\)H\(_{25}\)NO\(_3\)P \([\text{M+H}]^+\): 478.1567, Found: 478.1567.

4-(diphenylphosphoryl)-2-methylquinolin-8-yl 2-methylbenzoate (3va):

![3va]

Light yellow solid (64% yield); mp 96−97 °C; \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta: 8.34-8.32 (m, 2H), 8.72-8.67 (m, 4H), 7.62−7.58 (m, 2H), 7.52-7.48 (m, 6H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 2H), 7.12 (d, J= 15.3 \text{ Hz, 1H}), 2.72 (s, 3H), 2.59 (s, 3H); \(^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3) \delta: 166.6, 158.0 (d, J_{C,P} = 11.3 \text{ Hz}), 147.8 (d, J_{C,P} = 2.8 \text{ Hz}), 141.4 (d, J_{C,P} = 7.4 \text{ Hz}), 140.9, 138.6 (d, J_{C,P} = 93.9 \text{ Hz}), 132.5 (d, J_{C,P} = 2.4 \text{ Hz}), 132.5, 132.0 (d, J_{C,P} = 10.0 \text{ Hz}), 131.7, 131.4, 131.3 (d, J_{C,P} = 104.9 \text{ Hz}), 129.2, 128.9 (d, J_{C,P} = 12.2 \text{ Hz}), 127.8 (d, J_{C,P} = 9.1 \text{ Hz}), 127.0 (d, J_{C,P} = 7.0 \text{ Hz}), 126.5, 125.9, 125.2 (d, J_{C,P} = 5.2 \text{ Hz}), 122.1, 25.7, 21.6; \(^{31}\text{P} \text{ NMR (163 MHz, CDCl}_3) \delta: 30.3\); HRMS (ESI-TOF): Calcd for C\(_{30}\)H\(_{25}\)NO\(_3\)P \([\text{M+H}]^+\): 478.1567, Found: 478.1567.

4-(diphenylphosphoryl)quinolin-8-yl pivalate (3wa):

![3wa]

Light yellow solid (34% yield); mp 185−186 °C; \(^1\text{H} \text{ NMR (400 MHz, CDCl}_3) \delta: 8.85 (t, J= 4.0 \text{ Hz, 1H}), 8.72-8.67 (m, 4H), 7.62−7.58 (m, 2H), 7.52-7.48 (m, 6H), 7.45-7.41 (m, 1H), 7.38-7.33 (m, 2H), 7.12 (d, J= 15.3 \text{ Hz, 1H}), 2.72 (s, 3H), 2.59 (s, 3H); \(^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3) \delta: 166.6, 158.0 (d, J_{C,P} = 11.3 \text{ Hz}), 147.8 (d, J_{C,P} = 2.8 \text{ Hz}), 141.4 (d, J_{C,P} = 7.4 \text{ Hz}), 140.9, 138.6 (d, J_{C,P} = 93.9 \text{ Hz}), 132.5 (d, J_{C,P} = 2.4 \text{ Hz}), 132.5, 132.0 (d, J_{C,P} = 10.0 \text{ Hz}), 131.7, 131.4, 131.3 (d, J_{C,P} = 104.9 \text{ Hz}), 129.2, 128.9 (d, J_{C,P} = 12.2 \text{ Hz}), 127.8 (d, J_{C,P} = 9.1 \text{ Hz}), 127.0 (d, J_{C,P} = 7.0 \text{ Hz}), 126.5, 125.9, 125.2 (d, J_{C,P} = 5.2 \text{ Hz}), 122.1, 25.7, 21.6; \(^{31}\text{P} \text{ NMR (163 MHz, CDCl}_3) \delta: 30.3\); HRMS (ESI-TOF): Calcd for C\(_{30}\)H\(_{25}\)NO\(_3\)P \([\text{M+H}]^+\): 478.1567, Found: 478.1567.
1H), 8.44 (d, J= 8.4 Hz, 1H), 7.70−7.64 (m, 4H), 7.62−7.59 (m, 2H), 7.52−7.46 (m, 5H), 7.42−7.40 (m, 1H), 7.13 (dd, J= 15.0, 4.2 Hz, 1H), 1.49 (s, 1H); 13C NMR (100 MHz, CDCl3) δ: 177.5, 148.9 (d, J_{C-P} = 11.6 Hz), 148.4 (d, J_{C-P} = 3.0 Hz), 142.0 (d, J_{C-P} = 9.2 Hz), 138.5 (d, J_{C-P} = 93.6 Hz), 132.6 (d, J_{C-P} = 2.8 Hz), 132.0 (d, J_{C-P} = 10.1 Hz), 131.2 (d, J_{C-P} = 104.8 Hz), 128.9 (d, J_{C-P} = 12.4 Hz), 128.7, 127.6, 126.5 (d, J_{C-P} = 9.4 Hz), 125.3 (d, J_{C-P} = 5.6 Hz), 121.9, 39.3, 27.4; 31P NMR (163 MHz, CDCl3) δ: 30.7; HRMS (ESI-TOF): Calcd for C_{26}H_{25}NO_{3}P [M+H]^+: 430.1567, Found: 430.1569.

4-(diphenylphosphoryl)quinolin-8-yl 2-phenylbutanoate (3xa):

Light yellow solid (37% yield); mp 79−80 °C; 1H NMR (400 MHz, CDCl3) δ: 8.81 (t, J= 3.9 Hz, 1H), 8.42 (d, J= 8.5 Hz, 1H), 7.68−7.58 (m, 6H), 7.50−7.48 (m, 6H), 7.45−7.36 (m, 3H), 7.32−7.28 (m, 2H), 7.13 (dd, J= 14.9, 4.2 Hz, 1H), 3.97 (t, J= 7.6 Hz, 1H), 2.40−2.33 (m, 1H) 2.02−2.00 (m, 1H), 1.08 (t, J= 7.4 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ: 173.0, 148.8 (d, J_{C-P} = 11.5 Hz), 148.0 (d, J_{C-P} = 2.7 Hz), 141.8 (d, J_{C-P} = 7.2 Hz), 138.7, 138.6 (d, J_{C-P} = 94.0 Hz), 132.6 (d, J_{C-P} = 2.2 Hz), 132.0 (d, J_{C-P} = 18.2 Hz), 132.0, 131.6 (d, J_{C-P} = 7.2 Hz), 130.5 (d, J_{C-P} = 7.6 Hz), 129.0, 128.9, 128.6, 128.4, 127.6, 127.4, 126.6 (d, J_{C-P} = 9.4 Hz), 125.5 (d, J_{C-P} = 5.4 Hz), 121.9, 53.2, 29.7, 27.0; 31P NMR (163 MHz, CDCl3) δ: 30.7; HRMS (ESI-TOF): Calcd for C_{31}H_{27}NO_{3}P [M+H]^+: 492.1723, Found: 492.1727.

6. References


CCDC 1580532 (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.

**Table S2 Crystal Data and Structure Refinement for 3aa**

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<td>F(000)</td>
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<tr>
<td>Crystal size/mm³</td>
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Radiation: MoKα (λ = 0.71073)
2θ range for data collection/°: 6.956 to 52.732
Index ranges: -15 ≤ h ≤ 14, -27 ≤ k ≤ 26, -6 ≤ l ≤ 11
Reflections collected: 10630
Independent reflections: 4823 [R(int) = 0.0316, R(sigma) = 0.0539]
Data/restraints/parameters: 4823/0/307
Goodness-of-fit on F²: 1.021
Final R indexes [I>2σ (I)]: R₁ = 0.0537, wR₂ = 0.1154
Final R indexes [all data]: R₁ = 0.0895, wR₂ = 0.1371
Largest diff. peak/hole / e Å⁻³: 0.25/-0.29

8. The Experiment of Trapping the Phosphonyl Radical

\[
\text{HP}^\text{O}^\text{Ph} + \text{OH} \rightarrow \text{standard conditions} \rightarrow 2 \text{h} \rightarrow \text{BHT} \rightarrow 7 \text{a}
\]

HRMS (ESI+) m/z: [M+Na]+
Calcd for C_{27}H_{33}O_{2}P
421.2291; found: 421.2290

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