Supporting Information

for

Ni-catalyzed construction of C–P bond from electron-deficient phenols via the in situ aryl C–O activation by PyBroP

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1. General Information

All reactions were carried out under N₂ atmosphere. The solvents were dried over Zeolite or distilled according to the standard method. Anhydrous NiCl₂ and ligands were purchased from J&K Chemical Ltd and Alfa Aesar, respectively. ¹H NMR and ¹³C NMR were recorded in CDCl₃ or in DMSO-D₆ using tetramethylsilane (TMS) as the internal standard. 85% H₃PO₄ was used as external standard for ³¹P NMR. All shifts were given in ppm. All coupling constants (J values) were reported in Hertz (Hz). High resolution mass was measured by using IonSpec 7.0T MALDI-FTICRMs. Column chromatography was performed on silica gel 200-300 mesh.

2. Experimental Procedures

General procedure for the cross-coupling of phenols with H-phosphine oxide (or H-phosphite) through in situ phenol activation mediated by PyBroP.

Phenol (0.5 mmol), PyBroP (1.1 equiv), and anhydrous K₂CO₃ (2.0 mmol) were charged in an oven-dried Schlenk tube equipped with a magnetic bar. The tube was then evacuated (3 × 5 min) under vacuum and backfilled with N₂. Dried MeCN (3 mL) were injected via syringe. The reaction mixture was stirred at 100 ºC for 3 h until phenol had disappeared as monitored by TLC. The reaction vessel was cooled down and recharged with NiCl₂(dppp) (0.05 mmol, 10 mol%) and diphenylphosphine oxide (0.75 mmol). The reaction mixture was then stirred at 100–120 ºC for additional hours. After cooling down, the reaction mixture was poured into water (30 mL) and extracted with CH₂Cl₂ (20 mL × 3). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to dryness. The crude material was purified by flash chromatography on silica gel using a mixture of hexane and acetone as eluents to give the desired cross-coupled products.


1-Naphthalenylidiphenylphosphine oxide (3a)¹

![1-Naphthalenylidiphenylphosphine oxide (3a)](image)

¹H NMR (600 MHz, CDCl₃) δ = 8.59 (d, J = 8.5 Hz, 1H), 8.02 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.72–7.66 (m, 4H), 7.58–7.52 (m, 2H), 7.52–7.41 (m, 6H), 7.41–7.36 (m, 1H), 7.34–7.28 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ = 133.89 (d, J = 7.5 Hz), 133.73 (d, J = 10.5 Hz), 133.24, 133.19, 132.49, 132.06 (d, J = 9.0 Hz), 131.85, 129.27, 128.73, 128.56 (d, J = 12.0 Hz), 127.60 (d, J = 4.5 Hz), 127.32, 126.47, 124.11 (d, J = 15.0 Hz). ³¹P NMR (162 MHz, CDCl₃) δ = 32.12.

Naphthalen-2-yldiphenylphosphine oxide (3b)²

![Naphthalen-2-yldiphenylphosphine oxide (3b)](image)

² Electronic Supplementary Material (ESI) for Chemical Communications

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1H NMR (600 MHz, CDCl3) δ = 8.29 (d, J = 13.8 Hz, 1H), 7.92–7.87 (m, 3H), 7.74–7.70 (m, 4H), 7.66–7.53 (m, 5H), 7.49–7.46 (m, 4H). 13C NMR (150 MHz, CDCl3) δ = 134.54, 133.83 (d, J = 9.0 Hz), 132.73, 132.25 (d, J = 13.5 Hz), 131.96 (d, J = 9.0 Hz), 131.85, 129.43 (d, J = 103.5 Hz), 128.77, 128.39 (d, J = 12.0 Hz), 128.20, 128.11, 127.66, 126.81, 126.66 (d, J = 10.5 Hz). 31P NMR (162 MHz, CDCl3) δ = 28.96.

6-(diphenylphosphoryl)-2-naphthonitrile (3c)

1H NMR (600 MHz, CDCl3) δ = 8.37 (d, J = 13.4 Hz, 1H), 8.27 (s, 1H), 8.00–7.94 (m, 2H), 7.79–7.74 (m, 1H), 7.74–7.67 (m, 5H), 7.61–7.56 (m, 2H), 7.52–7.47 (m, 4H). 13C NMR (150 MHz, CDCl3) δ = 134.07, 133.80, 133.69 (d, J = 9.1 Hz), 133.54 (d, J = 12.1 Hz), 133.40, 132.26, 132.02 (d, J = 10.6 Hz), 131.8 (d, J = 105.7 Hz), 130.18, 128.66 (d, J = 12.1 Hz), 128.65, 128.58, 127.40, 118.54, 111.63. 31P NMR (162 MHz, CDCl3) δ = 28.02. HRMS: [M+H]+ m/z calcd for C23H17NOP: 354.1048, found: 354.1014.

2-(diphenylphosphoryl)-1-naphthonitrile (3d)

1H NMR (600 MHz, CDCl3) δ = 8.35 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 8.02–7.96 (m, 2H), 7.86–7.79 (m, 4H), 7.77–7.70 (m, 2H), 7.64–7.59 (m, 2H), 7.55–7.50 (m, 4H). 13C NMR (150 MHz, CDCl3) δ = 136.63 (d, J = 93.6 Hz), 134.00, 133.22 (d, J = 9.1 Hz), 132.57, 132.47, 132.28 (d, J = 10.6 Hz), 130.87 (d, J = 107.2 Hz), 129.43, 129.28, 128.71 (d, J = 12.1 Hz), 128.59, 128.11 (d, J = 7.6 Hz), 125.9, 115.38 (d, J = 6.0 Hz), 114.02 (d, J = 6.0 Hz). 31P NMR (162 MHz, CDCl3) δ = 27.14. HRMS: [M+H]+ m/z calcd for C23H17NOP: 354.1048, found: 354.1019.

Methyl 6-(diphenylphosphoryl)-2-naphthoate (3e)

1H NMR (600 MHz, CDCl3) δ = 8.63 (s, 1H), 8.33 (d, J = 13.6 Hz, 1H), 8.13 (dd, J = 8.6, 1.2 Hz, 1H), 8.01 (dd, J = 8.4, 2.1 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.75–7.68 (m, 5H), 7.60–7.55 (m, 2H), 7.52–7.46 (m, 4H), 3.99 (s, 3H). 13C NMR (150 MHz, CDCl3) δ = 166.74, 134.40 (d, J = 13.5 Hz), 133.80, 133.62 (d, J = 9.0 Hz), 132.81, 132.17 (d, J = 103.5 Hz), 132.15, 132.08, 130.71, 129.63, 129.54, 129.22, 128.63 (d, J = 12.0 Hz), 127.65 (d, J = 10.5 Hz), 126.32, 52.41. 31P NMR (162 MHz, CDCl3) δ = 28.56. HRMS: [M+H]+ m/z calcd for C24H20O3P: 387.1150, found: 387.1179.

Diphenyl(6-phenylnaphthalen-2-yl)phosphine oxide (3f)
\( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 8.31 \text{ (d, } J = 13.7 \text{ Hz, 1H), 8.07 \text{ (s, 1H), 7.98–7.93 (m, 2H), 7.83–7.80 (m, 1H), 7.76–7.69 (m, 6H), 7.69–7.64 (m, 1H), 7.59–7.54 (m, 2H), 7.53–7.45 (m, 6H), 7.43–7.39 (m, 1H).} \( ^{13} \)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 140.75, 140.17, 134.78, 133.50 \text{ (d, } J = 9.1 \text{ Hz), 132.77, 132.08, 131.92 \text{ (d, } J = 10.6 \text{ Hz), 131.79, 131.34 \text{ (d, } J = 13.6 \text{ Hz), 129.44 \text{ (d, } J = 104.2 \text{ Hz), 129.24, 128.74, 128.35 \text{ (d, } J = 12.1 \text{ Hz), 127.63, 127.22, 127.10 \text{ (d, } J = 10.6 \text{ Hz), 126.49, 125.37.} \) 

\( ^{31} \)P NMR (162 MHz, CDCl\(_3\)) \( \delta = 28.82. \) HRMS: [M+H]\(^+\) m/z calcld for C\(_{28}\)H\(_{22}\)OP: 405.1408, found: 405.1392.

(4-methoxynaphthalen-1-yl)diphenylphosphine oxide (3g)

\[
\begin{array}{c}
\text{O}\text{Me} \\
\end{array}
\]

\( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 8.49 \text{ (d, } J = 8.4 \text{ Hz, 1H), 8.32 \text{ (d, } J = 8.3 \text{ Hz, 1H), 7.72–7.65 (m, 4H), 7.57–7.50 (m, 2H), 7.50–7.41 (m, 6H), 7.25–7.21 (m, 1H), 6.73–6.69 (m, 1H), 4.02 (s, 3H).} \( ^{13} \)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 159.10, 135.20 \text{ (d, } J = 13.6 \text{ Hz), 134.81 \text{ (d, } J = 9.1 \text{ Hz), 133.23 \text{ (d, } J = 105.7 \text{ Hz), 132.04 \text{ (d, } J = 9.1 \text{ Hz), 131.62, 128.42 \text{ (d, } J = 12.1 \text{ Hz), 127.70, 127.30 \text{ (d, } J = 4.5 \text{ Hz), 126.05 \text{ (d, } J = 10.6 \text{ Hz), 125.74, 122.46, 120.06 \text{ (d, } J = 108.7 \text{ Hz), 102.13 \text{ (d, } J = 15.1 \text{ Hz), 55.59.} \) 

\( ^{31} \)P NMR (162 MHz, CDCl\(_3\)) \( \delta = 31.84. \) HRMS: [M+H]\(^+\) m/z calcld for C\(_{23}\)H\(_{20}\)O\(_2\)P: 359.1201, found: 359.1209.

(4-Biphenylyl)diphenylphosphine oxide (3h)

\[
\begin{array}{c}
\text{P(O)Ph}_2 \\
\end{array}
\]

\( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 7.77–7.66 \text{ (m, 8H), 7.62–7.58 \text{ (m, 2H), 7.58–7.53 \text{ (m, 2H), 7.51–7.44 \text{ (m, 6H), 7.41–7.37 \text{ (m, 1H).} } \) 

\( ^{13} \)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 144.69, 139.83, 132.82, 132.56 \text{ (d, } J = 10.6 \text{ Hz), 132.09, 132.02, 131.93, 130.99 \text{ (d, } J = 104.2 \text{ Hz), 128.90, 128.49 \text{ (d, } J = 12.1 \text{ Hz), 127.50 \text{ (d, } J = 105.0 \text{ Hz), 127.09.} \) 

\( ^{31} \)P NMR (162 MHz, CDCl\(_3\)) \( \delta = 29.02. \) 

(4-Acetylphenyl)diphenylphosphine oxide (3i)

\[
\begin{array}{c}
\text{O} \\
\end{array}
\]

\( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 8.05–7.99 \text{ (m, 2H), 7.83–7.77 \text{ (m, 2H), 7.70–7.63 \text{ (m, 4H), 7.60–7.55 \text{ (m, 2H), 7.52–7.45 \text{ (m, 4H), 2.63 (s, 3H).} } \) 

\( ^{13} \)C NMR (100 MHz, CDCl\(_3\)) \( \delta = 197.38, 139.37, 137.61 \text{ (d, } J = 100.0 \text{ Hz), 132.29 \text{ (d, } J = 11.0 \text{ Hz), 132.17, 131.89 \text{ (d, } J = 9.0 \text{ Hz), 131.13, 128.56 \text{ (d, } J = 12.0 \text{ Hz), 127.92 \text{ (d, } J = 12.0 \text{ Hz), 26.69.} \) 

\( ^{31} \)P NMR (162 MHz, CDCl\(_3\)) \( \delta = 27.97. \) 

(4-Cyanophenyl)diphenylphosphane oxide (3j)

\[
\begin{array}{c}
\text{NC} \\
\end{array}
\]

\( ^1 \)H NMR (600 MHz, CDCl\(_3\)) \( \delta = 7.83–7.78 \text{ (m, 2H), 7.77–7.73 \text{ (m, 2H), 7.68–7.63 \text{ (m, 4H), 7.62–7.57 \text{ (m, 2H), 7.53–7.48 \text{ (m, 4H).} } \) 

\( ^{13} \)C NMR (150 MHz, CDCl\(_3\)) \( \delta = 138.17 \text{ (d, } J = 96.0 \)
(4-Methoxyphenyl)diphenylphosphine oxide (3k)\(^1,4\)

\[\text{Ph} = \text{Ph} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{Ph} \quad \text{Ph}\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.72-7.63\) (m, 4H), 7.63–7.51 (m, 4H), 7.51–7.43 (m, 4H), 7.01–6.95 (m, 2H), 3.85 (s, 3H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 162.49, 133.95\) (d, \(J = 10.5\) Hz), 132.92 (d, \(J = 103.5\) Hz), 132.04 (d, \(J = 10.5\) Hz), 131.77, 128.42 (d, \(J = 12.0\) Hz), 123.50 (d, \(J = 109.5\) Hz), 114.08 (d, \(J = 13.5\) Hz), 55.31. \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 27.57\).

Diphenyl(quinolin-2-yl)phosphine oxide (3l)

\[\text{Ph} = \text{Ph} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{Ph} \quad \text{Ph}\]

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.38–8.30\) (m, 2H), 8.17 (d, \(J = 8.5\) Hz, 1H), 8.03–7.96 (m, 4H), 7.87 (d, \(J = 8.1\), 1H), 7.78–7.73 (m, 1H), 7.64–7.60 (m, 1H), 7.54–7.48 (m, 2H), 7.48–7.42 (m, 4H). \(^13\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 157.12\) (d, \(J = 131.4\) Hz), 148.10 (d, \(J = 22.7\) Hz), 136.08 (d, \(J = 9.1\) Hz), 132.83, 132.19, 132.13, 131.74, 130.29, 129.97, 128.23 (d, \(J = 12.1\) Hz), 128.10, 127.83, 123.32 (d, \(J = 22.7\) Hz). \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 20.18\). HRMS: [M+H]\(^+\) \(m/z\) calcd for C\(_{21}\)H\(_{17}\)NOP: 330.1048, found: 330.1034.

Phenanthridin-6-yldiphenylphosphine oxide (3m)

\[\text{Ph} = \text{Ph} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{Ph} \quad \text{Ph}\]

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 9.52\) (d, \(J = 8.3\) Hz, 1H), 8.67 (d, \(J = 8.3\) Hz, 1H), 8.63–8.59 (m, 1H), 8.09–8.04 (m, 1H), 7.98–7.90 (m, 4H), 7.89–7.83 (m, 1H), 7.76–7.67 (m, 3H), 7.55–7.49 (m, 2H), 7.48–7.42 (m, 4H). \(^13\)C NMR (150 MHz, DMSO) \(\delta = 156.65\) (d, \(J = 126.84\) Hz), 142.97 (d, \(J = 22.7\) Hz), 132.77 (d, \(J = 102.7\) Hz), 132.19 (d, \(J = 7.6\) Hz), 131.87, 131.68, 131.62, 130.41, 129.35 (d, \(J = 3.0\) Hz), 128.45 (d, \(J = 12.1\) Hz), 127.93, 127.55, 126.91, 126.76, 123.77, 123.05, 122.88. \(^31\)P NMR (162 MHz, DMSO) \(\delta = 25.41\). HRMS: [M+H]\(^+\) \(m/z\) calcd for C\(_{25}\)H\(_{19}\)NOP: 380.1204, found: 380.1187.

(9H-carbazol-4-yl)diphenylphosphine oxide (3n)

\[\text{Ph} = \text{Ph} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{Ph} \quad \text{Ph}\]

\(^1\)H NMR (600 MHz, DMSO) \(\delta = 11.69\) (s, 1H), 8.51 (d, \(J = 8.1\) Hz, 1H), 7.78 (d, \(J = 8.1\) Hz, 1H), 7.63–7.55 (m, 6H), 7.55–7.49 (m, 4H), 7.49–7.45 (m, 1H), 7.45–7.39 (m, 1H), 7.32 (t, \(J = 7.6\) Hz, 1H), 6.92 (t, \(J = 7.5\) Hz, 1H), 6.76 (dd, \(J = 14.8, 7.2\) Hz, 1H). \(^13\)C NMR (150 MHz, DMSO) \(\delta = 140.09\) (d, \(J = 12.1\) Hz), 140.00, 132.75 (d, \(J = 102.7\) Hz), 131.86, 131.56 (d, \(J = 12.1\) Hz), 132.42, 132.36, 131.84, 131.79, 131.73, 130.9 (d, \(J = 105.0\) Hz), 128.63 (d, \(J = 12.0\) Hz), 116.53 (d, \(J = 334.5\) Hz). \(^31\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 27.57\).
9.1 Hz), 128.65 (d, J = 12.1 Hz), 125.98, 125.38 (d, J = 102.7 Hz), 125.35, 124.35 (d, J = 4.5 Hz), 124.34 (d, J = 30.2 Hz), 123.15 (d, J = 9.1 Hz), 120.87, 118.23, 115.49, 110.74. $^{31}$P NMR (162 MHz, DMSO) δ = 29.50. HRMS: [M+H]$^+$ m/z calcld for C$_{23}$H$_{19}$NOP: 368.1204, found: 368.1203.

Diphenyl(quinolin-8-yl)phosphine oxide (3o)$^5$

$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.80–8.73 (m, 1H), 8.37 (dd, J = 14.1, 7.1 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.06 (d, J = 7.8 Hz, 1H), 7.88–7.80 (m, 4H), 7.71–7.65 (m, 1H), 7.51–7.46 (m, 2H), 7.44–7.37 (m, 5H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 149.81, 148.00 (d, J = 4.5 Hz), 137.30 (d, J = 7.6 Hz), 136.1, 133.62 (d, J = 108.7 Hz), 132.80, 132.18 (d, J = 10.6 Hz), 131.24, 131.23 (d, J = 101.2 Hz), 128.24 (d, J = 6.0 Hz), 127.91 (d, J = 12.1 Hz), 126.96 (d, J = 13.6 Hz), 121.47. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 28.84.

2-Pyridyldiphenylphosphine Oxide (3p)$^6$

$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.80–8.76 (m, 1H), 8.34–8.29 (m, 1H), 7.92–7.83 (m, 5H), 7.54–7.49 (m, 2H), 7.47–7.42 (m, 4H), 7.41–7.36 (m, 1H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 156.37 (d, J = 130.5 Hz), 150.08 (d, J = 19.5 Hz), 136.11 (d, J = 9.0 Hz), 132.50, 132.05 (d, J = 9.0 Hz), 131.82, 128.32, 128.24, 125.20. $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 20.60.

3-Pyridyldiphenylphosphine Oxide (3q)

$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.80 (m, 2H), 8.11–8.05 (m, 1H), 7.72–7.65 (m, 4H), 7.62–7.57 (m, 2H), 7.54–7.48 (m, 4H), 7.48–7.43 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 152.53, 152.41, 139.73 (d, J = 7.0 Hz), 132.36, 131.94 (d, J = 10.0 Hz), 131.00, 129.64, 128.73 (d, J = 13.0 Hz), 123.45 (d, J = 9.0 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 26.09. HRMS: [M+H]$^+$ m/z calcld for C$_{17}$H$_{15}$NOP: 280.0891, found: 280.0875.

Diphenyl(pyridin-4-yl)phosphine oxide (3r)

$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.80–8.73 (m, 2H), 7.70–7.64 (m, 4H), 7.64–7.58 (m, 4H), 7.54–7.48 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 149.82 (d, J = 9.1 Hz), 142.06 (d, J = 96.6 Hz), 132.44, 131.88 (d, J = 9.1 Hz), 130.84 (d, J = 105.7 Hz), 128.70 (d, J = 12.1 Hz), 125.66 (d, J = 4.5 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 26.65. HRMS: [M+H]$^+$ m/z calcld for C$_{17}$H$_{15}$NOP: 280.0891, found: 280.0886.
Diethyl naphthalen-1-ylphosphonate (5a)\(^{7-12}\)

![Diethyl naphthalen-1-ylphosphonate](image)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.53 (d, J = 8.5 \text{ Hz}, 1H), 8.25 (ddd, J = 16.3, 7.0, 1.0 \text{ Hz}, 1H), 8.04 (d, J = 8.2 \text{ Hz}, 1H), 7.90 (d, J = 8.1 \text{ Hz}, 1H), 7.64–7.58 (m, 1H), 7.58–7.50 (m, 2H), 4.15 (m, 4H), 1.31 (t, J = 7.1 Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 134.47 (d, J = 9.1 \text{ Hz}), 133.48 (d, J = 3.0 \text{ Hz}), 133.47 (d, J = 12.0 \text{ Hz}), 128.62, 127.26, 126.53 (d, J = 19.6 Hz), 126.21, 124.53 (d, J = 182.7 Hz), 124.38 (d, J = 16.6 Hz), 62.01 (d, J = 6.0 Hz), 16.19 (d, J = 6.0 Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 18.88.\)

Dimethyl naphthalen-1-ylphosphonate (5b)

![Dimethyl naphthalen-1-ylphosphonate](image)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.47 (d, J = 8.4 \text{ Hz}, 1H), 8.24 (dd, J = 7.2, 16.8 \text{ Hz}, 1H), 8.06 (d, J = 7.6 \text{ Hz}, 1H), 7.61 (t, J = 6.6 Hz, 1H), 7.57–7.53 (m, 2H), 3.80 (m, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 134.87 (d, J = 9.0 \text{ Hz}), 133.85 (d, J = 1.5 \text{ Hz}), 133.53 (d, J = 12.0 \text{ Hz}), 128.76, 127.61, 126.49, 126.37, 124.47 (d, J = 16.5 Hz), 123.15, 133.81 (d, J = 10.6 Hz), 128.70, 128.17 (d, J = 13.6 Hz), 128.04, 127.60, 126.67, 126.24 (d, J = 10.6 Hz), 125.26 (d, J = 188.8 Hz), 61.97 (d, J = 4.5 Hz), 16.15 (d, J = 6.0 Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 22.04.\)

Diethyl naphthalen-2-ylphosphonate (5c)\(^{7,8,10,11,12}\)

![Diethyl naphthalen-2-ylphosphonate](image)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.44 (d, J = 15.5 \text{ Hz}, 1H), 7.96–7.90 (m, 2H), 7.88 (d, J = 8.1 \text{ Hz}, 1H), 7.79–7.74 (m, 1H), 7.54–7.62 (m, 2H), 4.15 (m, 4H), 1.34 (t, J = 7.0 Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 134.79, 133.81 (d, J = 10.6 \text{ Hz}), 132.15 (d, J = 16.6 \text{ Hz}), 128.70, 128.17 (d, J = 13.6 Hz), 128.04, 127.60, 126.67, 126.24 (d, J = 10.6 Hz), 125.26 (d, J = 188.8 Hz), 61.97 (d, J = 4.5 Hz), 16.15 (d, J = 6.0 Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 18.80.\)

Diethyl (6-cyanonaphthalen-2-yl)phosphonate (5d)

![Diethyl (6-cyanonaphthalen-2-yl)phosphonate](image)

\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta = 8.47 (d, J = 15.3 \text{ Hz}, 1H), 8.28 (s, 1H), 8.05–8.01 (m, 1H), 8.01–7.97 (m, 1H), 7.93–7.87 (m, 1H), 7.72–7.69 (m, 1H), 4.18 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H). \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta = 133.77, 133.60, 133.53, 133.40, 130.11, 130.00, 128.69 (d, J = 15.1 Hz), 128.23 (d, J = 9.1 Hz), 127.28, 118.52, 111.61, 62.40 (d, J = 6.0 Hz), 16.27 (d, J = 6.0 Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta = 16.77.\) HRMS: [M+Na]\(^+\) m/z calcd for C\(_{15}\)H\(_{16}\)NO\(_3\)PNa: 312.0765, found: 312.0762.

Diethyl (1-cyanonaphthalen-2-yl)phosphonate (5e)

S7
1H NMR (600 MHz, CDCl₃) δ = 8.43 (d, J = 8.4 Hz, 1H), 8.19–8.09 (m, 2H), 7.98 (d, J = 7.1 Hz, 6H). 13C NMR (150 MHz, CDCl₃) δ = 134.18, 132.85, 132.76, 132.40 (d, J = 13.6 Hz), 132.07 (d, J = 185.7 Hz), 129.24 (d, J = 15.1 Hz), 128.49, 128.18 (d, J = 7.6 Hz), 125.96, 115.56 (d, J = 7.6 Hz), 113.46 (d, J = 4.5 Hz), 63.22 (d, J = 6.0 Hz), 16.13 (d, J = 6.0 Hz). 31P NMR (162 MHz, CDCl₃) δ = 12.84. HRMS: [M+Na]+ m/z calcld for C₁₅H₁₆NO₃PNa: 312.0765, found: 312.0749.

Methyl 6-(diethoxyphosphoryl)-2-naphthoate (5f)

1H NMR (600 MHz, CDCl₃) δ = 8.64 (s, 1H), 8.46 (d, J = 15.4 Hz, 1H), 8.16–8.11 (m, 1H), 8.06–8.01 (m, 1H), 7.86–7.80 (m, 1H), 4.17 (m, 4H), 4.00 (s, 3H), 1.35 (t, J = 7.0 Hz, 6H). 13C NMR (150 MHz, CDCl₃) δ = 166.55, 134.19 (d, J = 18.1 Hz), 133.92, 133.39 (d, J = 9.1 Hz), 130.53, 129.53 (d, J = 15.1 Hz), 129.38, 129.02, 128.09 (d, J = 187.2 Hz), 127.12 (d, J = 10.6 Hz), 126.08, 62.19 (d, J = 4.5 Hz), 52.23, 16.21 (d, J = 6.0 Hz). 31P NMR (162 MHz, CDCl₃) δ = 17.65. HRMS: [M+H]+ m/z calcld for C₁₆H₂₀O₅P: 323.1048, found: 323.1046.

Diethyl (6-phenylnaphthalen-2-yl)phosphonate (5g)

1H NMR (600 MHz, CDCl₃) δ = 8.46 (d, J = 15.4 Hz, 1H), 8.07 (s, 1H), 8.03–7.99 (m, 1H), 7.99–7.95 (m, 1H), 7.85–7.81 (m, 1H), 7.81–7.76 (m, 1H), 7.74–7.71 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.39 (m, 1H), 4.17 (m, 4H), 1.35 (t, J = 7.0 Hz, 6H). 13C NMR (150 MHz, CDCl₃) δ = 140.92, 140.41, 135.23, 133.71 (d, J = 10.6 Hz), 131.43 (d, J = 16.6 Hz), 129.37, 128.89, 128.53 (d, J = 15.1 Hz), 127.77, 127.40, 126.86 (d, J = 10.6 Hz), 126.56, 125.53, 125.36 (d, J = 187.2 Hz), 62.12 (d, J = 4.5 Hz), 16.30 (d, J = 6.0 Hz). 31P NMR (162 MHz, CDCl₃) δ = 18.81. HRMS: [M+H]+ m/z calcld for C₂₀H₂₂O₃P: 341.1306, found: 341.1316.

Diethyl biphenyl-4-ylphosphonate (5h)

1H NMR (600 MHz, CDCl₃) δ = 7.88 (dd, J = 13.0, 8.1 Hz, 2H), 7.69 (dd, J = 8.1, 3.8 Hz, 2H), 7.63–7.59 (m, 2H), 7.49–7.44 (m, 2H), 7.42–7.38 (m, 1H), 4.15 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H). 13C NMR (150 MHz, CDCl₃) δ = 145.10, 139.86, 132.20 (d, J = 10.6 Hz), 128.84, 128.06, 127.16, 127.01, 126.81 (d, J = 190.3 Hz), 62.06 (d, J = 4.5 Hz), 16.26 (d, J = 7.6 Hz). 31P NMR (162 MHz, CDCl₃) δ = 18.71.

Diethyl 4-acetylphenylphosphonate (5i)

1H NMR (600 MHz, CDCl₃) δ = 8.10–8.01 (m, 1H), 7.85–7.81 (m, 1H), 7.81–7.76 (m, 1H), 7.74–7.71 (m, 2H), 7.53–7.48 (m, 2H), 7.44–7.39 (m, 1H), 1.35 (t, J = 7.0 Hz, 6H). 13C NMR (150 MHz, CDCl₃) δ = 140.92, 140.41, 135.23, 133.71 (d, J = 10.6 Hz), 131.43 (d, J = 16.6 Hz), 129.37, 128.89, 128.53 (d, J = 15.1 Hz), 127.77, 127.40, 126.86 (d, J = 10.6 Hz), 126.56, 125.53, 125.36 (d, J = 187.2 Hz), 62.12 (d, J = 4.5 Hz), 16.30 (d, J = 6.0 Hz). 31P NMR (162 MHz, CDCl₃) δ = 18.81. HRMS: [M+H]+ m/z calcld for C₂₀H₂₂O₃P: 341.1306, found: 341.1316.

Diethyl biphenyl-4-ylphosphonate (5h)
$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.05–8.01 (m, 2H), 7.95–7.89 (m, 2H), 4.15 (m, 4H), 2.64 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 197.41, 139.79, 133.34 (d, $J = 187.2$ Hz), 132.01 (d, $J = 9.1$ Hz), 127.98 (d, $J = 15.1$ Hz), 62.38 (d, $J = 6.0$ Hz), 26.73, 16.26 (d, $J = 6.0$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 16.58.

Diethyl quinolin-2-ylphosphonate (5j)

$^1$H NMR (600 MHz, CDCl$_3$) δ = 8.30–8.26 (m, 2H), 8.03–7.99 (m, 1H), 7.89–7.85 (m, 1H), 7.81–7.76 (m, 1H), 7.66–7.62 (m, 1H), 4.32 (m, 4H), 1.39 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (150 MHz, CDCl$_3$) δ = 152.57 (d, $J = 225.0$ Hz), 148.04 (d, $J = 27.2$ Hz), 136.00 (d, $J = 12.1$ Hz), 130.23, 129.98, 128.38 (d, $J = 3.0$ Hz), 128.16, 127.54, 123.13 (d, $J = 27.2$ Hz), 63.99 (d, $J = 6.0$ Hz), 16.20 (d, $J = 6.0$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 10.19. HRMS: [M+H]$^+$ m/z calcd for C$_{13}$H$_{17}$NO$_3$P: 266.0946, found: 266.0948.

References

Figure S1. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 3a
Figure S2. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 3b
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Figure S4. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 3d
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Figure S25. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 5g
Figure S26. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 5h
Figure S27. $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 5i
**Figure S28.** $^1$H-, $^{13}$C-, and $^{31}$P NMR of compound 5j