Supporting Information

Efficient Nickel-catalyzed Phosphinylation of C-S Bonds Forming C-P Bonds

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1. General information

All reactions were carried out in oven-dried Schlenk tubes under N\textsubscript{2} atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. Column chromatography was performed using Silica Gel 60 (particle size 37–54 μm). The pure products were obtained by means of column chromatography. \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and \textsuperscript{31}P NMR data were acquired on a 400MHz spectrometer (400 MHz for \textsuperscript{1}H, 100 MHz for \textsuperscript{13}C, and 162 MHz for \textsuperscript{31}P NMR spectroscopy). Chemical shifts for \textsuperscript{1}H NMR are referred to internal Me\textsubscript{4}Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Data for \textsuperscript{31}P NMR were relative to H\textsubscript{3}PO\textsubscript{4} (85% solution in D\textsubscript{2}O, 0 ppm). HRMS were conducted in the Analytical Center at Hunan University, China.

2. Procedure for the Efficient Nickel-catalyzed Phosphinylation of C-S Bonds Forming C-P Bonds

Typical procedure: In a glove box (O\textsubscript{2} < 0.5 ppm, H\textsubscript{2}O < 0.5 ppm), 0.4 mmol diphenylphosphine oxide 2a, 1.25 mol% Ni(cod)$_2$, 0.6 mmol t-BuONa and 1.0 mL dry dioxane were charged into a 10 mL schlenk tube. After the schlenk tube was taken out, 0.4 mmol methyl(phenyl)sulfane 1a was added under N\textsubscript{2} atmosphere. Then the mixture was stirred at 100 °C for 18 h. After removal of the volatile, the residues were passed through a short silica chromatography (particle size 37–54 μm, pether/ethyl acetate as eluent) to afford analytically pure organophosphorus compounds 3a.

Procedure at 10 mmol scale: In a glove box (O\textsubscript{2} < 0.5 ppm, H\textsubscript{2}O < 0.5 ppm), 10 mmol (2.021 g) diphenylphosphine oxide 2a, 0.1 mol% (0.003 g) Ni(cod)$_2$, 15 mmol (1.442 g) t-BuONa and 20 mL dry dioxane were charged into a 100 mL schlenk tube. After the tube was taken out, 10 mmol (1.242 g) methyl(phenyl)sulfane 1a was added under N\textsubscript{2} atmosphere. Then the mixture was heated at 120 °C for 30 h. The mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2}. The crude product after removing the
volatiles under a reduced pressure was passed through a short SiO$_2$ column using EtOAc as an eluent to give the spectroscopically pure 3a in 92% yield (2.560 g).

3. $^{31}$P NMR data of the reaction mixture

**Procedure:** In a glove box (O$_2$ < 0.5 ppm, H$_2$O < 0.5 ppm), 1 mmol 2, 1.25 mol% Ni(cod)$_2$, 1.5 mmol t-BuONa (For n-Bu$_2$POH, t-BuOK was used as a base) and 3.0 mL dry dioxane (due to the multiple sampling for one reaction, the solvent was enlarged) were charged into a 10 mL schlenk tube. After the schlenk tube was taken out, 1 mmol 1 (if solid, 1 was added in the glove box; for sulfones: 1.1 mmol was loaded) was added under N$_2$ atmosphere. Samples for $^{31}$P NMR detection were acquired in a glove box.

**Copies of $^{31}$P NMR spectra**
Note: the $^{31}$P signal of $n$-Bu$_2$P(O)K is at 94.6 ppm, the $^{31}$P signal of $n$-Bu$_2$P(O)Ph is at 37.6 ppm.
4. Characterization and analytical data of products 3

**Triphenylphosphine oxide (3a).** White solid; \(^1^H\) NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.70–7.65 (m, 6H), 7.57–7.53 (m, 3H), 7.48–7.44 (m, 6H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 132.6 (d, \(J_{C,P} = 103.3\) Hz), 132.1 (d, \(J_{C,P} = 9.8\) Hz), 132.0 (d, \(J_{C,P} = 2.7\) Hz), 128.5 (d, \(J_{C,P} = 12.0\) Hz). \(^{31}\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.16. MS (EI): 277.

**Diphenyl(p-tolyl)phosphine oxide (3b).** White solid; \(^1^H\) NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.66 (dd, \(J = 8.0\) Hz, \(J = 12.0\) Hz, 4H), 7.58–7.50 (m, 4H), 7.46–7.43 (m, 4H), 7.26 (dd, \(J = 1.6\) Hz, \(J = 8.0\) Hz, 2H), 2.39 (s, 3H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 142.5 (d, \(J_{C,P} = 2.6\) Hz), 132.8 (d, \(J_{C,P} = 103.4\) Hz), 132.1 (d, \(J_{C,P} = 10.1\) Hz), 132.1 (d, \(J_{C,P} = 9.8\) Hz), 131.8 (d, \(J_{C,P} = 2.7\) Hz), 129.3 (d, \(J_{C,P} = 12.5\) Hz), 129.1 (d, \(J_{C,P} = 106.0\) Hz), 128.5 (d, \(J_{C,P} = 12.0\) Hz), 21.6 (d, \(J_{C,P} = 0.9\) Hz). \(^{31}\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.23. MS (EI): 291.

**(4-Methoxyphenyl)diphenylphosphine oxide (3c).** White solid; \(^1^H\) NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.66 (dd, \(J = 8.0\) Hz, \(J = 12.0\) Hz, 4H), 7.61–7.51 (m, 4H), 7.46–7.43 (m, 4H), 6.97 (dd, \(J = 2.0\) Hz, \(J = 8.8\) Hz, 2H), 3.84 (s, 3H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 162.5 (d, \(J_{C,P} = 2.8\) Hz), 134.0 (d, \(J_{C,P} = 11.2\) Hz), 133.0 (d, \(J_{C,P} = 103.8\) Hz), 132.0 (d, \(J_{C,P} = 9.8\) Hz), 131.8 (d, \(J_{C,P} = 2.7\) Hz), 128.5 (d, \(J_{C,P} = 12.0\) Hz), 123.6 (d, \(J_{C,P} = 109.8\) Hz), 114.1 (d, \(J_{C,P} = 13.1\) Hz), 55.4. \(^{31}\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.08. MS (EI): 307.
(3-Methoxyphenyl)diphenylphosphine oxide (3d).\(^2\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.66 (dd, \(J = 8.0\) Hz, \(J = 12.0\) Hz, 4H), 7.54 (t, \(J = 7.6\) Hz, 2H), 7.48–7.44 (m, 4H), 7.38–7.33 (m, 1H), 7.39 (d, \(J = 13.2\) Hz, 1H), 7.14 (dd, \(J = 7.6\) Hz, \(J = 12.0\) Hz, 1H), 7.07 (dd, \(J = 1.6\) Hz, \(J = 8.0\) Hz, 1H), 3.79 (s, 3H).

\(^1\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 159.6 (d, \(J_{C-P} = 14.7\) Hz), 133.8 (d, \(J_{C-P} = 102.6\) Hz), 132.4 (d, \(J_{C-P} = 103.7\) Hz), 132.1 (d, \(J_{C-P} = 9.8\) Hz), 132.0 (d, \(J_{C-P} = 2.7\) Hz), 129.7 (d, \(J_{C-P} = 14.2\) Hz), 128.5 (d, \(J_{C-P} = 12.1\) Hz), 124.4 (d, \(J_{C-P} = 10.0\) Hz), 118.2 (d, \(J_{C-P} = 2.7\) Hz), 116.8 (d, \(J_{C-P} = 10.7\) Hz), 55.4. \(^3\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.31. MS (EI): 307.

[1,1’-Biphenyl]-4-yldiphenylphosphine oxide (3e).\(^1\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.79–7.68 (m, 8H), 7.61–7.54 (m, 4H), 7.50–7.37 (m, 7H). \(^1\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 144.8 (d, \(J_{C-P} = 2.6\) Hz), 139.9, 132.6 (d, \(J_{C-P} = 10.2\) Hz), 132.5 (d, \(J_{C-P} = 103.8\) Hz), 132.1 (d, \(J_{C-P} = 9.9\) Hz), 132.0 (d, \(J_{C-P} = 4.5\) Hz), 131.0 (d, \(J_{C-P} = 104.7\) Hz), 130.0, 128.6 (d, \(J_{C-P} = 12.1\) Hz), 128.2, 127.3, 127.2. \(^3\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.32. MS (EI): 353.

diphenyl(4-(trifluoromethyl)phenyl)phosphine oxide (3f).\(^1\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 7.75 (dd, \(J = 8.0\) Hz, \(J = 11.2\) Hz, 2H), 7.64 (d, \(J = 7.6\) Hz, 2H), 7.58 (dd, \(J = 7.6\) Hz, \(J = 12.0\) Hz, 4H), 7.50 (t, \(J = 7.2\) Hz, 2H), 7.42–7.39 (m, 4H). \(^1\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 137.1 (d, \(J_{C-P} = 99.3\) Hz), 133.7 (dq, \(J_{C-P} = 2.9\) Hz, \(J_{C-F} = 32.6\) Hz), 132.6 (d, \(J_{C-P} = 10.1\) Hz), 132.4 (d, \(J_{C-P} = 2.7\) Hz), 132.0 (d, \(J_{C-P} = 10.0\) Hz), 131.6 (d, \(J_{C-P} = 102.2\) Hz), 128.8 (d, \(J_{C-P} = 12.2\) Hz), 125.4 (dq, \(J_{C-P} = 12.1\) Hz, \(J_{C-F} = 3.5\) Hz), 122.2 (q, \(J_{C-P} = 271.2\) Hz). \(^3\)P NMR (162 MHz CDCl\(_3\)):
δ 28.15. MS (EI): 345.

Naphthalen-2-yldiphenylphosphine oxide (3g).\(^1\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 8.29 (d, \(J = 13.6\) Hz, 1H), 7.91–7.86 (m, 3H), 7.72 (dd, \(J = 7.6\) Hz, \(J = 12.0\) Hz, 4H), 7.67–7.54 (m, 5H), 7.47 (dd, \(J = 7.6\) Hz, \(J = 7.2\) Hz, 4H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 134.7 (d, \(J_{C\text{-}P} = 2.3\) Hz), 134.1 (d, \(J_{C\text{-}P} = 9.3\) Hz), 132.5 (d, \(J_{C\text{-}P} = 103.8\) Hz), 132.4 (d, \(J_{C\text{-}P} = 13.1\) Hz), 132.2 (d, \(J_{C\text{-}P} = 9.9\) Hz), 132.1 (d, \(J_{C\text{-}P} = 2.6\) Hz), 129.5 (d, \(J_{C\text{-}P} = 102.0\) Hz), 129.0, 128.6 (d, \(J_{C\text{-}P} = 12.1\) Hz), 128.3 (d, \(J_{C\text{-}P} = 11.6\) Hz), 128.3, 127.9, 127.0, 126.9 (d, \(J_{C\text{-}P} = 10.6\) Hz). \(^{31}\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 29.42. MS (EI): 327.

Diphenyl(pyridin-2-yl)phosphine oxide (3h).\(^3\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 8.77 (d, \(J = 4.0\) Hz, 1H), 8.30 (t, \(J = 6.8\) Hz, 1H), 7.91–7.81 (m, 5H), 7.52–7.37 (m, 7H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 156.4 (d, \(J_{C\text{-}P} = 130.9\) Hz), 150.2 (d, \(J_{C\text{-}P} = 19.0\) Hz), 136.2 (d, \(J_{C\text{-}P} = 9.3\) Hz), 132.2 (d, \(J_{C\text{-}P} = 103.4\) Hz), 132.1 (d, \(J_{C\text{-}P} = 9.4\) Hz), 131.9 (d, \(J_{C\text{-}P} = 2.8\) Hz), 128.349 (d, \(J_{C\text{-}P} = 12.1\) Hz), 128.346 (d, \(J_{C\text{-}P} = 19.8\) Hz), 125.3 (d, \(J_{C\text{-}P} = 3.2\) Hz). \(^{31}\)P NMR (162 MHz CDCl\(_3\)): \(\delta\) 20.80. MS (EI): 278.

Diphenyl(quinolin-3-yl)phosphine oxide (3i).\(^4\) White solid; \(^1\)H NMR (400 MHz CDCl\(_3\)): \(\delta\) 9.02–9.00 (m, 1H), 8.64 (d, \(J = 13.2\) Hz, 1H), 8.16 (d, \(J = 8.4\) Hz, 1H), 7.89–7.82 (m, 2H), 7.73 (dd, \(J = 8.0\) Hz, \(J = 12.0\) Hz, 4H), 7.63–7.58 (m, 3H), 7.52–7.49 (dd, \(J = 7.2\) Hz, \(J = 7.2\) Hz, 4H). \(^{13}\)C NMR (100 MHz CDCl\(_3\)): \(\delta\) 150.8 (d, \(J_{C\text{-}P} = 12.4\) Hz), 149.1 (d, \(J_{C\text{-}P} = 1.3\) Hz), 142.1 (d, \(J_{C\text{-}P} = 7.4\) Hz), 132.5 (d, \(J_{C\text{-}P} = 2.8\) Hz), 132.1 (d, \(J_{C\text{-}P} = 10.1\) Hz), 131.9, 131.8 (d, \(J_{C\text{-}P} = 104.7\) Hz), 129.5,
128.8 (d, $J_{C,P} = 12.3$ Hz), 128.8, 127.7, 126.8 (d, $J_{C,P} = 10.4$ Hz), 126.0 (d, $J_{C,P} = 100.5$ Hz). $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 26.37. MS (EI): 328.

Phenyldi-$p$-tolylphosphine oxide (3j).$^1$ White solid; $^1$H NMR (400 MHz CDCl$_3$): $\delta$ 7.65 (dd, $J = 7.6$ Hz, $J = 12.0$ Hz, 2H), 7.57–7.52 (m, 5H), 7.46–7.42 (m, 2H), 7.26 (d, $J = 6.8$ Hz, 4H), 2.39 (s, 6H). $^{13}$C NMR (100 MHz CDCl$_3$): $\delta$ 142.4 (d, $J_{C,P} = 2.8$ Hz), 132.9 (d, $J_{C,P} = 103.3$ Hz), 132.1 (d, $J_{C,P} = 10.2$ Hz), 132.1 (d, $J_{C,P} = 9.8$ Hz), 131.8 (d, $J_{C,P} = 2.7$ Hz), 129.3 (d, $J_{C,P} = 12.5$ Hz), 129.2 (d, $J_{C,P} = 106.5$ Hz), 128.4 (d, $J_{C,P} = 12.1$ Hz), 21.6 (d, $J_{C,P} = 1.0$ Hz). $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 29.64. MS (EI): 305.

Dibutyl(phenyl)phosphine oxide (3k).$^1$ White solid; $^1$H NMR (400 MHz CDCl$_3$): $\delta$ 7.70 (dd, $J = 8.4$ Hz, $J = 8.4$ Hz, 2H), 7.51 (b, 3H), 2.02–1.81 (m, 4H), 1.60 (br, 2H), 1.38 (br, 6H), 0.87 (t, $J = 6.8$ Hz, 6H). $^{13}$C NMR (100 MHz CDCl$_3$): $\delta$ 132.7 (d, $J_{C,P} = 91.9$ Hz), 131.4 (d, $J_{C,P} = 2.6$ Hz), 130.4 (d, $J_{C,P} = 8.7$ Hz), 128.6 (d, $J_{C,P} = 11.0$ Hz), 29.7 (d, $J_{C,P} = 68.1$ Hz), 24.1 (d, $J_{C,P} = 14.5$ Hz), 23.5 (d, $J_{C,P} = 4.0$ Hz), 13.56. $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 40.71. MS (EI): 238.

4-(Diphenylphosphoryl)benzonitrile (3m).$^3$ White solid; $^1$H NMR (400 MHz CDCl$_3$): $\delta$ 7.84–7.75 (m, 4H), 7.68–7.58 (m, 6H), 7.52–7.49 (m, 4H). $^{13}$C NMR (100 MHz CDCl$_3$): $\delta$ 138.3 (d, $J_{C,P} = 99.0$ Hz), 132.7 (d, $J_{C,P} = 5.3$ Hz), 132.6 (d, $J_{C,P} = 1.6$ Hz), 132.0 (d, $J_{C,P} = 11.9$ Hz), 132.0 (d, $J_{C,P} = 10.0$ Hz), 131.0 (d, $J_{C,P} = 105.0$ Hz), 128.9 (d, $J_{C,P} = 12.3$ Hz), 117.9 (d, $J_{C,P} = 1.3$ Hz),
115.7 (d, $J_{C,P} = 3.1$ Hz). $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 28.20. MS (EI): 302.

(4-(2-Methylprop-1-en-1-yl)phenyl)diphenylphosphine oxide (3n). White solid, m.p. 125–126 °C; $^1$H NMR (400 MHz CDCl$_3$): $\delta$ 7.71–7.66 (dd, $J = 8.0$ Hz, $J = 12.0$ Hz, 4H), 7.62–7.52 (m, 4H), 7.46 (dd, $J = 7.2$ Hz, $J = 7.2$ Hz, 4H), 7.31 (d, $J = 6.8$ Hz, 2H), 6.27 (s, 1H), 1.92 (s, 3H), 1.87 (s, 3H). $^{13}$C NMR (100 MHz CDCl$_3$): $\delta$ 142.5 (d, $J_{C,P} = 2.8$ Hz), 138.2, 132.6 (d, $J_{C,P} = 103.6$ Hz), 132.1 (d, $J_{C,P} = 9.9$ Hz), 131.9 (d, $J_{C,P} = 5.5$ Hz), 131.9 (d, $J_{C,P} = 1.8$ Hz), 129.1 (d, $J_{C,P} = 106.0$ Hz), 128.7 (d, $J_{C,P} = 12.4$ Hz), 128.5 (d, $J_{C,P} = 12.1$ Hz), 124.3 (d, $J_{C,P} = 1.1$ Hz), 27.1, 19.6. $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 29.50. HRMS: Cal. for C$_{22}$H$_{21}$O$_1$P$_1$ 332.1330. Found [M] 332.1316. IR: 3056, 2929, 2912, 1653, 1183, 1119, 871, 721 cm$^{-1}$.

Diphenyl(4-(thiophen-2-yl)phenyl)phosphine oxide (3o). Pale yellow oil; $^1$H NMR (400 MHz CDCl$_3$): $\delta$ 7.72–7.64 (m, 8H), 7.55 (t, $J = 7.6$ Hz, 2H), 7.49–7.45 (m, 4H), 7.39 (d, $J = 3.6$ Hz, 1H), 7.33 (d, $J = 4.8$ Hz, 1H), 7.09 (dd, $J = 4.4$ Hz, $J = 4.0$ Hz, 1H). $^{13}$C NMR (100 MHz CDCl$_3$): $\delta$ 142.9 (d, $J_{C,P} = 1.2$ Hz), 137.8 (d, $J_{C,P} = 2.9$ Hz), 132.8 (d, $J = 10.2$ Hz), 132.3 (d, $J_{C,P} = 104.4$ Hz), 132.1 (d, $J_{C,P} = 9.9$ Hz), 132.1 (d, $J_{C,P} = 2.9$ Hz), 130.9 (d, $J_{C,P} = 105.1$ Hz), 128.6 (d, $J_{C,P} = 12.1$ Hz), 128.4, 126.3, 125.7 (d, $J_{C,P} = 12.4$ Hz), 124.5. $^{31}$P NMR (162 MHz CDCl$_3$): $\delta$ 29.30. HRMS: Cal. for C$_{22}$H$_{17}$O$_1$P$_1$S$_1$ 360.0738. Found 360.0723. IR: 3055, 1433, 1181, 1117, 733, 697 cm$^{-1}$.

Diphenyl(4-(pyrimidin-2-yl)phenyl)phosphine oxide (3p). White solid; m.p.: 181–182 °C, $^1$H
NMR (400 MHz CDCl$_3$): δ 8.83 (d, $J = 4.8$ Hz, 2H), 8.54 (d, $J = 7.2$ Hz, 2H), 7.82 (dd, $J = 8.4$ Hz, $J = 11.4$ Hz, 2H), 7.71 (dd, $J = 7.6$ Hz, $J = 12.0$ Hz, 4H), 7.56 (t, $J = 7.6$ Hz, 2H), 7.48 (dd, $J = 6.4$ Hz, $J = 6.4$ Hz, 4H), 7.24 (d, $J_{C-P} = 4.8$ Hz, 1H). $^{13}$C NMR (100 MHz CDCl$_3$): δ 163.8, 157.4, 140.9 (d, $J_{C-P} = 2.8$ Hz), 134.8 (d, $J_{C-P} = 102.4$ Hz), 132.4 (d, $J_{C-P} = 10.0$ Hz), 132.4 (d, $J_{C-P} = 103.8$ Hz), 132.1 (d, $J_{C-P} = 9.8$ Hz), 132.1, 128.6 (d, $J_{C-P} = 12.1$ Hz), 128.1 (d, $J_{C-P} = 12.2$ Hz), 119.8. $^{31}$P NMR (162 MHz CDCl$_3$): δ 28.96. HRMS: Cal. for C$_{22}$H$_{17}$O$_1$N$_2$P$_1$: 356.1078. Found [M-H] 355.0987. IR: 3030, 1559, 1419, 1183, 1116, 708 cm$^{-1}$.

![Tert-butyldiphenylphosphine oxide (3q)](image)

Tert-butyldiphenylphosphine oxide (3q). White solid; $^1$H NMR (400 MHz CDCl$_3$): δ 7.96 (dd, $J = 8.8$ Hz, $J = 8.8$ Hz, 4H), 7.54–7.46 (m, 6H), 1.25 (d, $J = 15.2$ Hz, 9H). $^{13}$C NMR (100 MHz CDCl$_3$): δ 132.2 (d, $J_{C-P} = 8.1$ Hz), 131.5 (d, $J_{C-P} = 2.6$ Hz), 131.2 (d, $J_{C-P} = 89.8$ Hz), 128.3 (d, $J_{C-P} = 10.8$ Hz), 34.0 (d, $J_{C-P} = 70.5$ Hz), 25.2. $^{31}$P NMR (162 MHz CDCl$_3$): δ 38.73. MS (EI): 258.

![Dicyclohexyl(phenyl)phosphine oxide (3r)](image)

Dicyclohexyl(phenyl)phosphine oxide (3r). White solid; $^1$H NMR (400 MHz CDCl$_3$): δ 7.59 (t, $J = 7.6$ Hz, 2H), 7.45–7.40 (m, 3H), 1.98 (br, 4H), 1.75–1.53 (m, 8H), 1.24–1.05 (m, 10H). $^{13}$C NMR (100 MHz CDCl$_3$): δ 131.5 (d, $J_{C-P} = 7.6$ Hz), 131.2 (d, $J_{C-P} = 1.8$ Hz), 129.9 (d, $J_{C-P} = 84.3$ Hz), 128.3 (d, $J_{C-P} = 10.3$ Hz), 35.1 (d, $J_{C-P} = 66.9$ Hz), 26.5 (d, $J_{C-P} = 11.6$ Hz), 26.4 (d, $J_{C-P} = 11.8$ Hz), 25.8, 25.5, 24.6 (d, $J_{C-P} = 2.9$ Hz). $^{31}$P NMR (162 MHz CDCl$_3$): δ 45.40. MS (EI): 289.

![Diisopropyl (4-cyanophenyl)phosphonate (3s)](image)

Diisopropyl (4-cyanophenyl)phosphonate (3s). Colorless oil; $^1$H NMR (400 MHz CDCl$_3$): δ
7.95–7.90 (m, 2H), 7.76–7.73 (m, 2H), 4.78–4.70 (m, 2H), 1.39 (d, J = 6.0 Hz, 6H), 1.24 (d, J = 6.0 Hz, 6H). $^{13}$C NMR (100 MHz CDCl$_3$): δ 135.5 (d, $J_{C,P} = 187.3$ Hz), 132.2 (d, $J_{C,P} = 9.7$ Hz), 131.9 (d, $J_{C,P} = 14.9$ Hz), 118.0 (d, $J_{C,P} = 1.3$ Hz), 115.7 (d, $J_{C,P} = 3.4$ Hz), 71.7 (d, $J_{C,P} = 5.8$ Hz), 24.0 (d, $J_{C,P} = 4.1$ Hz), 23.9 (d, $J_{C,P} = 4.7$ Hz). $^{31}$P NMR (162 MHz CDCl$_3$): δ 13.11. MS (EI): 267.

(10-[(1-Methylpiperidin-2-yl)ethyl]-10H-phenothiazin-2-yl)diphenylphosphine oxide (3t).

Colorless oil; $^1$H NMR (400 MHz CDCl$_3$): δ 7.66 (dd, J = 7.6 Hz, J = 10.8 Hz, 4H), 7.63–7.46 (m, 6H), 7.28–7.11 (m, 4H), 7.05–7.00 (m, 1H), 7.96–7.86 (m, 2H), 3.93–3.75 (m, 2H), 2.84 (d, J = 11.6 Hz, 1H), 2.14–2.05 (m, 6H), 1.80–1.59 (m, 5H), 1.38–1.28 (m, 2H). $^{13}$C NMR (100 MHz CDCl$_3$): δ 145.4 (d, $J_{C,P} = 14.0$ Hz), 144.6, 132.9 (d, $J_{C,P} = 6.8$ Hz), 132.1, 132.0 (d, $J_{C,P} = 10.0$ Hz), 132.0, 131.9 (d, $J_{C,P} = 3.4$ Hz), 131.3 (d, $J_{C,P} = 100.9$ Hz), 130.9 (d, $J_{C,P} = 2.9$ Hz), 128.6 (d, $J_{C,P} = 12.1$ Hz), 128.1 (d, $J_{C,P} = 105.7$ Hz), 127.7 (d, $J_{C,P} = 15.3$ Hz), 127.3 (d, $J_{C,P} = 14.2$ Hz), 127.3 (d, $J_{C,P} = 8.8$ Hz), 126.1 (d, $J_{C,P} = 10.8$ Hz), 124.2, 123.1, 118.3 (d, $J_{C,P} = 11.1$ Hz), 116.0, 62.0, 57.0, 43.9, 42.5, 30.2, 29.2, 25.1, 23.7. $^{31}$P NMR (162 MHz CDCl$_3$): δ 29.50. HRMS: Cal. for C$_{32}$H$_{33}$O$_1$N$_2$P$_1$S$_1$ 524.2051. Found 524.2044. IR: 3055, 2931, 2852, 1458, 1402, 1180, 1118, 751, 697 cm$^{-1}$. 

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5. References


6. Copies of $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra
7. Copies of IR spectra

[Images of IR spectra with chemical structures and wavenumbers]