Supplementary Information

Base-promoted direct oxyphosphorylation of alkynes with H-phosphine oxides in the presence of H₂O

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1. General Information

All reagents and solvents were used without further purification. ¹H and ¹³C NMR spectra were recorded in CDCl₃ or DMSO-d₆ with tetramethylsilane (TMS) as the internal standard, and ³¹P NMR spectra were obtained in CDCl₃ or DMSO-d₆ with H₃PO₄ as the internal standard. High resolution mass spectra (HRMS) were carried out on a Q-TOF mass spectrometer. Column chromatography was conducted on columns of silica gel (300-400 mesh).

2. General Procedure

Alkynes (1, 0.25 mmol), H-phosphine oxides (2, 0.5 mmol), LiOH (0.05 mmol), and DMF (2 mL) + H₂O (0.25 mL) were dissolved in round-bottomed flask and stirring at 60 °C for 3 h in an O₂ atmosphere. The reaction mixture was quenched with sodium bicarbonate (20 mL), extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated brine twice, and dried over anhydrous MgSO₄. After filtration, the solvent was evaporated in vacuum. The crude product was purified by silica gel chromatography (dichloromethane: methyl alcohol =30:1~50:1) to give the desired compounds.

3. Preliminary mechanistic studies

3.1 Labeling experiment with ¹⁸O₂
Phenylacetylene (1a, 0.25 mmol), diphenylphosphine oxide (2a, 0.5 mmol), LiOH (0.05 mmol), and DMF (2 mL) + H₂O (0.25 mL) were dissolved in round-bottomed flask and stirring at 60 °C for 3 h in an ¹⁸O₂ atmosphere. The reaction mixture was quenched with sodium bicarbonate (20 mL), extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated brine twice, and dried over anhydrous MgSO₄. After filtration, the solvent was evaporated in vacuum. The crude product was purified by silica gel chromatography (dichloromethane: methyl alcohol =30:1–50:1) to give the desired compounds 3a and 3a'. The product 3a' (yield: 60%), which was examined by HRMS in Fig. S1.

**3.2 H₂¹⁸O Isotope labeling experiment**
Phenylacetylene (1a, 0.25 mmol), diphenylphosphine oxide (2a, 0.5 mmol), LiOH (0.05 mmol), and DMF (2 mL) + H$_2$O (0.25 mL) were dissolved in round-bottomed flask and stirring at 60 °C for 3 h in an O$_2$ atmosphere. The reaction mixture was quenched with sodium bicarbonate (20 mL), extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated brine twice, and dried over anhydrous MgSO$_4$. After filtration, the solvent was evaporated in vacuum. The crude product was examined by MS in Fig. S2. The $^{18}$O isotope-labeled diphenylphosphine acid as by-product was found.

![Fig. S2. The MS analysis of H$_2$O Isotope labeling experiment](image)

3.3 Radical capture experiments with TEMPO

Phenylacetylene (1a, 0.25 mmol), diphenylphosphine oxide (2a, 0.5 mmol), TEMPO (0.5 mmol), LiOH (0.05 mmol), and DMF (2 mL) + H$_2$O (0.25 mL) were dissolved in round-bottomed flask and stirring at 60 °C for 3 h in an O$_2$ atmosphere. The reaction mixture was quenched with sodium bicarbonate (20 mL), extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with saturated brine twice, and dried over anhydrous MgSO$_4$. However, the desired product 3a was not detected by TCL analysis.

3.4 LC-MS analysis experiment of the model reaction
Experimental conditions: HPLC: Waters C18 column, 2.0×150 mm, 3 µm; PDA detector: 254 nm; 25 °C. Flow rate: 0.2 ml/min. The mobile phase consisted of A (water) and B (methanol), gradient elution: 0-10 min, 85% B (methanol), 10-25 min, 90% B (methanol); Run time: 15 min. MS: Capillary 3.0 kv; Cone 40 v; Extraction cone 3 v; Source temperature 100 °C; Desolvation temperature 250 °C; Cone gas flow 40 L/h; Desolvation gas flow 600 L/h. Scan 100–800 m/z

Phenylacetylene (1a, 0.25 mmol), diphenylphosphine oxide (2a, 0.5 mmol), TEMPO (0.5 mmol), LiOH (0.05 mmol), and DMF (2 mL) + H2O (0.25 mL) were dissolved in round-bottomed flask and stirring at 60 °C for 30 min in an O2 atmosphere. And then, the reaction mixture was diluted with CH3CN (10 ml) and filtered. The filtrate was analysed by LC-MS, and the desired product 3a, vinylperoxyl intermediate 8, and diphenylphosphinic acid 9 were detected by LC-MS Fig. S3.
4. Characterization data of products

2-(diphenylphosphoryl)-1-phenylethanone (3a)

White solid; Yield = 85%, 68 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.14 (d, $J$=15.4 Hz, 2H), 7.38-7.53 (m, 9H), 7.78-7.83 (m, 4H), 7.96-7.98 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 133.03 (d, $J$ = 5.7 Hz), 137.13, 133.83, 132.52 (d, $J$ = 2.8 Hz), 131.67 (d, $J$ = 103.9 Hz), 131.32 (d, $J$ = 9.7 Hz), 129.45, 128.85 (d, $J$ = 12.3 Hz), 128.75, 43.52 (d, $J$ = 58.2 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.16. HRMS (ESI) calcd for C$_{20}$H$_{17}$NaO$_2$P [M+Na]$^+$: 343.0858; found: 343.0861.

2-(diphenylphosphoryl)-1-(4-fluorophenyl)ethanone (3b)

White solid; Yield = 73%, 62 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.14 (d, $J$ = 15.2 Hz, 2H), 7.04-7.07 (t, 2H), 7.42-7.46 (m, 4H), 7.49-7.52 (m, 2H), 7.76-7.79 (m, 4H), 8.01-8.04 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.34 (d, $J$ = 5.7 Hz), 166.15 (d, $J$ = 256.1 Hz), 133.57 (d, $J$ = 2.8 Hz), 132.38 (d, $J$ = 2.7 Hz), 132.28 (d, $J$ = 9.6 Hz), 131.36 (d, $J$ = 101.3 Hz), 131.14 (d, $J$ = 9.8 Hz), 128.81 (d, $J$ = 12.4 Hz), 115.78 (d, $J$ = 22.0 Hz), 43.64 (d, $J$ = 56.9 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.58. HRMS (ESI) calcd for C$_{20}$H$_{16}$FO$_2$P [M+Na]$^+$:
1-(4-chlorophenyl)-2-(diphenylphosphoryl)ethanone (3c)

White solid; Yield = 77%, 68 mg; $^1$H NMR (400 MHz, DMSO-d6) $\delta$ 4.56 (d, $J = 15.2$ Hz, 2H), 7.50-7.57 (m, 8H), 7.81-7.7386 (m, 4H), 7.99-8.02 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-d6) $\delta$ 192.93 (d, $J = 5.7$ Hz), 139.07, 136.21, 133.71 (d, $J = 103.5$ Hz), 132.32 (d, $J = 2.8$ Hz), 131.36 (d, $J = 9.8$ Hz), 131.12, 129.13, 129.04 (d, $J = 12.3$ Hz), 42.42 (d, $J = 56.7$ Hz). $^{31}$P NMR (162 MHz, DMSO-d6) $\delta$ 25.68. HRMS (ESI) calcd for C$_{20}$H$_{16}$ClNaO$_2$P [M+Na]$^+$: 377.0453; found: 377.0450.

1-(4-bromophenyl)-2-(diphenylphosphoryl)ethanone (3d)

White solid; Yield = 79%, 79 mg; $^1$H NMR (400 MHz, DMSO-d6) $\delta$ 4.55 (d, $J = 15.2$ Hz, 2H), 7.50-7.58 (m, 6H), 7.70-7.72 (m, 2H), 7.80-7.86 (m, 4H), 7.91-7.93 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-d6) $\delta$ 193.10 (d, $J = 5.6$ Hz), 136.46, 134.15, 132.72 (d, $J = 2.9$ Hz), 132.29, 132.17 (d, $J = 103.5$ Hz), 131.34 (d, $J = 9.8$ Hz), 131.06, 129.08, 128.63 (d, $J = 12.3$ Hz), 41.82 (d, $J = 56.7$ Hz). $^{31}$P NMR (162 MHz, DMSO-d6) $\delta$ 25.69. HRMS (ESI) calcd for C$_{20}$H$_{16}$BrNaO$_2$P [M+Na]$^+$: 420.9963; found : 420.9966.

2-(diphenylphosphoryl)-1-(p-tolyl)ethanone (3e)

White solid; Yield = 84%, 70 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.36 (s, 3H), 4.16 (d, $J = 15.3$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.43-7.53 (m, 6H), 7.78-7.83 (m, 4H), 7.87-7.89 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.43, 144.82, 134.69, 132.37 (d, $J = 2.8$ Hz), 131.45 (d, $J = 103.2$ Hz), 131.38 (d, $J = 9.8$ Hz), 129.60, 129.44, 128.82 (d, $J = 12.3$ Hz), 43.42 (d, $J = 58.3$ Hz), 21.88. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.35. HRMS (ESI) calcd for C$_{21}$H$_{19}$NaO$_2$P [M+Na]$^+$: 357.1015; found: 357.1017.
2-(diphenylphosphoryl)-1-(4-methoxyphenyl)ethanone (3f)

White solid; Yield = 88%, 77 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.82 (s, 3H), 4.09 (d, $J = 15.3$ Hz, 2H), 6.87 (d, $J = 9.4$ Hz, 2H), 7.42-7.52 (m, 6H), 7.78-7.83 (m, 4H), 7.97 (d, $J = 9.5$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 191.24 (d, $J = 5.5$ Hz), 164.14, 132.24 (d, $J = 2.8$ Hz), 132.15 (d, $J = 103.3$ Hz), 131.93, 131.51 (d, $J = 9.8$ Hz), 130.26, 128.77 (d, $J = 12.3$ Hz), 113.88, 55.68, 43.20 (d, $J = 58.0$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.64. HRMS (ESI) calcd for C$_{21}$H$_{19}$NaO$_3$P [M+Na]$^+$: 373.0964; found: 373.0968.

2-(diphenylphosphoryl)-1-(4-(trifluoromethoxy)phenyl)ethan-1-one (3g)

White solid; Yield = 76%, 77 mg; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.11 (d, $J = 15.1$ Hz, 2H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.43-7.47 (m, 4H), 7.50-7.54 (m, 2H), 7.76-7.79 (m, 4H), 7.94 (d, $J = 7.5$ Hz, 2H), 8.05 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 191.49 (d, $J = 5.7$ Hz), 153.12 (q, $J = 1.4$ Hz), 135.32, 132.47 (d, $J = 2.7$ Hz), 131.78 (d, $J = 103.3$ Hz), 131.62, 131.25 (d, $J = 9.8$ Hz), 128.91 (d, $J = 12.6$ Hz), 120.43 (q, $J = 258.9$ Hz), 120.30, 43.75 (d, $J = 56.7$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 26.78. HRMS (ESI) calcd for C$_{21}$H$_{17}$F$_3$NaO$_3$P [M+Na]$^+$: 427.0687; found: 427.0684.

1-(4-acetylphenyl)-2-(diphenylphosphoryl)ethan-1-one (3h)

White solid; Yield = 83%, 75 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.58 (s, 3H), 4.14 (d, $J = 15.2$ Hz, 2H), 7.43-7.46 (m, 4H), 7.51 (t, $J = 7.3$ Hz, 2H), 7.75-7.79 (m, 4H), 7.94 (d, $J = 7.5$ Hz, 2H), 8.05 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.52, 192.52, 140.45, 140.10, 132.33 (d, $J = 2.6$ Hz), 131.31 (d, $J = 103.5$ Hz), 131.20 (d, $J = 9.8$ Hz), 131.12, 129.60, 128.87, 128.8 (d, $J = 12.1$ Hz), 128.4, 43.91 (d, $J = 58.2$ Hz), 26.99. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 26.78. HRMS (ESI) calcd for C$_{22}$H$_{19}$NaO$_3$P [M+Na]$^+$: 385.1108; found: 385.1112.
4-(2-(diphenylphosphoryl)acetyl)benzonitrile (3i)

White solid; Yield = 73%, 63 mg; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.14 (d, $J$ = 15.1 Hz, 2H), 7.45-7.48 (m, 4H), 7.52-7.55 (m, 2H), 7.72 (d, $J$ = 8.1 Hz, 2H), 7.76-7.78 (m, 4H), 8.15 (d, $J$ = 8.1 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.91 (d, $J$ = 5.2 Hz), 139.90, 132.62 (d, $J$ = 2.4 Hz), 132.47, 131.450 (d, $J$ = 104.1 Hz), 131.05 (d, $J$ = 9.9 Hz), 129.87, 128.95 (d, $J$ = 12.4 Hz), 118.03, 116.79, 44.09 (d, $J$ = 55.2 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 26.59. HRMS (ESI) calcd for C$_{21}$H$_{16}$NNaO$_2$P [M+Na]$^+$: 368.0811; found: 368.0815.

2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3j)

White solid; Yield = 76%, 74 mg; $^1$H NMR (400 MHz, DMSO-d$_6$): δ 4.64 (d, $J$ = 15.1 Hz, 2H), 7.50-7.58 (m, 6H), 7.81-7.87 (m, 6H), 8.17-8.28 (m, 2H). $^{13}$C NMR (101 MHz, DMSO-d$_6$): δ 193.52 (d, $J$ = 5.7 Hz), 140.53, 133.68 (q, $J$ = 32.6 Hz), 132.69 (d, $J$ = 2.7 Hz), 131.74 (d, $J$ = 103.3 Hz), 131.05 (d, $J$ = 9.9 Hz), 129.11, 128.99 (d, $J$ = 12.4 Hz), 125.90 (q, $J$ = 272.9 Hz), 123.73 (q, $J$ = 3.7 Hz), 43.55 (d, $J$ = 56.3 Hz); $^{31}$P NMR (162 MHz, DMSO-d$_6$): δ 25.69. HRMS (ESI) calcd for C$_{21}$H$_{17}$F$_3$NaO$_2$P [M+Na]$^+$: 411.0738; found: 411.0736.

1-([1,1'-biphenyl]-4-yl)-2-(diphenylphosphoryl)ethan-1-one (3k)

White solid; Yield = 71%, 70 mg; $^1$H NMR (400 MHz, CDCl$_3$): δ 4.16 (d, $J$ = 15.3 Hz, 2H), 7.36-7.38 (m, 1H), 7.43-7.47 (m, 6H), 7.49-7.53 (m, 2H), 7.57-7.63 (m, 4H), 7.80-7.85 (m, 4H), 8.08-8.10 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 192.40 (d, $J$ = 5.5 Hz), 146.28, 139.82, 135.78, 132.38 (d, $J$ = 2.7 Hz), 131.19 (d, $J$ = 103.0 Hz), 131.02 (d, $J$ = 9.9 Hz), 129.14, 129.01, 128.82 (d, $J$ = 12.3 Hz), 128.42, 127.41, 127.25, 43.52 (d, $J$ = 57.7 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): δ 26.99. HRMS (ESI) calcd for C$_{26}$H$_{22}$NaO$_2$P [M+Na]$^+$: 419.1177; found:
2-(diphenylphosphoryl)-1-(m-tolyl)ethanone (3l)

White solid; Yield = 80%, 67 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.34 (s, 3H), 4.12 (d, $J = 15.4$ Hz, 2H), 7.27-7.33 (m, 2H), 7.42-7.46 (m, 4H), 7.49-7.52 (m, 2H), 7.71 (s, 1H), 7.77-7.81 (m, 5H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 193.08, 138.39, 137.12, 134.50, 132.35 (d, $J = 2.8$ Hz), 131.25 (d, $J = 103.5$ Hz), 131.08 (d, $J = 9.9$ Hz), 128.70 (d, $J = 12.3$ Hz), 128.53, 126.67, 43.34 (d, $J = 56.3$ Hz), 21.38.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.20.

HRMS (ESI) calcd for C$_{21}$H$_{19}$NaO$_2$P [M+Na]$^+$: 357.1015; found: 357.1010.

2-(diphenylphosphoryl)-1-(o-tolyl)ethanone (3m)

White solid; Yield = 74%, 62 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.28 (s, 3H), 4.11 (d, $J = 15.1$ Hz, 2H), 7.12 (d, $J = 7.5$ Hz, 1H), 7.19-7.22 (m, 1H), 7.25-7.30 (m, 1H), 7.42 (m, 4H), 7.46-7.53 (m, 2H), 7.68 - 7.81 (m, 4H), 7.83 (d, $J = 7.8$ Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 195.80, 139.04, 137.58, 132.44 (d, $J = 2.8$ Hz), 132.05 (d, $J = 103.2$ Hz), 131.94, 131.11 (d, $J = 9.8$ Hz), 130.38, 128.75 (d, $J = 12.3$ Hz), 125.88, 45.73 (d, $J = 58.7$ Hz), 21.36. $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.29. HRMS (ESI) calcd for C$_{21}$H$_{19}$NaO$_2$P [M+Na]$^+$: 357.1015; found: 357.1019.

2-(diphenylphosphoryl)-1-(3-methoxyphenyl)ethanone (3n)

White solid; Yield = 85%, 70 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.80 (s, 3H), 4.14 (d, $J = 15.6$ Hz, 2H), 7.04-7.12 (m, 1H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.42-7.55 (m, 7H), 7.59 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.75-7.83 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.85 (d, $J = 5.7$ Hz), 159.87, 138.49, 132.44 (d, $J = 2.8$ Hz), 132.14 (d, $J = 103.7$ Hz), 131.32 (d, $J = 9.8$ Hz), 129.75, 128.76 (d, $J = 12.3$ Hz), 122.41, 120.77, 112.94, 55.64, 43.63 (d, $J = 58.5$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 27.07. HRMS (ESI) calcd for C$_{21}$H$_{19}$O$_3$P [M+H]$^+$: 351.1145; found:
2-(diphenylphosphoryl)-1-(2-methoxyphenyl)ethan-1-one (3o)

White solid; Yield = 75%, 62 mg; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 3.74 (s, 3H), 4.47 (d, \(J = 14.0\) Hz, 2H), 6.96-7.01 (m, 1H), 7.02 (d, \(J = 8.4\) Hz, 1H), 7.42 (dd, \(J = 7.6\) Hz, 2.0 Hz, 1H), 7.44-7.55 (m, 7H), 7.74-7.79 (m, 4H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 194.69 (d, \(J = 6.5\) Hz), 158.54, 134.72, 134.21 (d, \(J = 101.2\) Hz), 132.13 (d, \(J = 2.7\) Hz), 130.98 (d, \(J = 9.8\) Hz), 130.24, 129.03 (d, \(J = 11.9\) Hz), 128.56, 120.79, 112.71, 56.13, 46.34 (d, \(J = 60.9\) Hz). \(^{31}\)P NMR (162 MHz, DMSO-\(d_6\)) \(\delta\) 25.11. HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)O\(_3\)P [M+H]\(^+\): 351.1145; found: 351.1139.

1-(3,5-dimethylphenyl)-2-(diphenylphosphoryl)ethan-1-one (3p)

White solid; Yield = 81%, 70 mg; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 2.29 (s, 6H), 4.10 (d, \(J = 15.5\) Hz, 2H), 7.13 (s, 1H), 7.38-7.46 (m, 4H), 7.47-7.51 (m, 4H), 7.76-7.81 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 193.26 (d, \(J = 5.5\) Hz), 138.25, 137.21, 135.43, 132.42 (d, \(J = 103.0\) Hz), 132.23 (d, \(J = 2.6\) Hz), 131.32 (d, \(J = 9.8\) Hz), 128.74 (d, \(J = 12.5\) Hz), 127.07, 43.26 (d, \(J = 58.8\) Hz), 21.29. \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) 27.12. HRMS (ESI) calcd for C\(_{22}\)H\(_{22}\)FNaO\(_2\)P [M+Na]\(^+\): 371.1177; found: 371.1175.

2-(diphenylphosphoryl)-1-(naphthalen-2-yl)ethan-1-one (3q)

White solid; Yield = 68%, 59 mg; \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 4.70 (d, \(J = 15.4\) Hz, 2H), 7.52-7.55 (m, 8H), 7.88-7.93 (m, 7H), 7.95-7.96 (m, 1H), 8.78 (s, 1H). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 193.57 (d, \(J = 6.5\) Hz), 135.58, 134.77, 134.45, 133.44, 132.47 (d, \(J = 1.9\) Hz), 132.23 (d, \(J = 2.6\) Hz), 131.18 (d, \(J = 9.7\) Hz), 130.16, 129.36, 128.94 (d, \(J = 11.9\) Hz), 128.51, 128.09, 127.38, 124.24, 41.73 (d, \(J = 61.2\) Hz). \(^{31}\)P NMR (162 MHz, DMSO-\(d_6\)): \(\delta\) 25.87. HRMS (ESI) calcd for C\(_{24}\)H\(_{19}\)O\(_3\)P [M+H]\(^+\): 371.1195; found: 371.1189.
2-(diphenylphosphoryl)-1-(thiophen-2-yl)ethan-1-one (3r)

White solid; Yield = 65%, 49 mg; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.04 (d, $J$ = 15.3 Hz, 2H), 7.07 (t, 1H), 7.43-7.46 (m, 4H), 7.49-7.52 (m, 2H), 7.61 (d, $J$ = 4.9 Hz, 1H), 7.77-7.81 (m, 4H), 7.85 (d, $J$ = 3.8 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 185.1, 144.58, 135.40, 135.18, 132.42 (d, $J$ = 2.8 Hz), 131.83 (d, $J$ = 103.6 Hz), 131.32 (d, $J$ = 9.7 Hz), 128.81 (d, $J$ = 12.5 Hz), 128.62, 44.48 (d, $J$ = 57.4 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 26.89.

HRMS (ESI) calcd for C$_{18}$H$_{15}$SO$_2$P [M+H]$^+$: 327.1195; found: 327.1193.

ethyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3s)

White solid; Yield = 69%, 50 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.26 (t, $J$ = 7.0 Hz, 3H), 3.59-3.79 (m, 2H), 4.20-3.80 (m, 2H), 7.39-7.45 (m, 4H), 7.52-7.54 (m, 2H), 7.74-7.78 (m, 2H), 7.92-7.94 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.35 (d, $J$ = 5.5 Hz), 136.94, 133.69, 132.89 (d, $J$ = 2.9 Hz), 131.97 (d, $J$ = 10.3 Hz), 130.72 (d, $J$ = 132.9 Hz), 129.66, 128.83 (d, $J$ = 13.3 Hz), 128.67, 61.65 (d, $J$ = 6.2 Hz), 43.16 (d, $J$ = 86.4 Hz), 16.44 (d, $J$ = 6.7 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 34.50. HRMS (ESI) calcd for C$_{16}$H$_{17}$NaO$_3$P [M+Na]$^+$: 311.0808; found: 311.0810.

diethyl (2-oxo-2-phenylethyl)phosphonate (3t)

Colorless oil; Yield = 52%, 33 mg; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.24 (t, $J$ = 7.1 Hz, 6H), 3.63 (d, $J$ = 22.7 Hz, 2H), 4.12 (p, $J$ = 7.2 Hz, 4H), 7.45 (t, 2H), 7.54-7.58 (m, 1H), 7.98-8.00 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.00 (d, $J$ = 6.6 Hz), 136.52 (d, $J$ = 1.8 Hz), 133.63, 129.01, 128.57, 62.68 (d, $J$ = 6.5 Hz), 38.49 (d, $J$ = 129.9 Hz), 16.19 (d, $J$ = 6.4 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 21.35. HRMS (ESI) calcd for C$_{12}$H$_{17}$NaO$_4$P [M+Na]$^+$: 279.0757; found: 279.0751.

diisopropyl (2-oxo-2-phenylethyl)phosphonate (3u)
Colorless oil; Yield = 43%, 31 mg; $^1$H NMR (400 MHz, CDCl$_3$) δ 1.27-1.29 (m, 12H), 3.61 (d, $J = 22.8$ Hz, 2H), 4.70-4.78 (m, 2H), 7.46-7.50 (m, 2H), 7.57-7.60 (m, 1H), 8.02-8.04 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.06 (d, $J = 6.6$ Hz), 136.71, 133.45, 129.12, 128.47, 71.48 (d, $J = 6.6$ Hz), 39.27 (d, $J = 129.5$ Hz), 23.81 (dd, $J = 5.1$ Hz, $J = 21.1$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.71; HRMS (ESI) calcd for C$_{12}$H$_{17}$O$_4$P $[\text{M+Na}^+]$: 307.1070; found 307.1073.

2-(bis(4-chlorophenyl)phosphoryl)-1-phenylethanone (3v)

White solid; Yield = 75%, 73 mg; $^1$H NMR (400 MHz, CDCl$_3$) δ 4.11 (d, $J = 15.6$ Hz, 2H), 7.41-7.47 (m, 6H), 7.54-7.58 (m, 1H), 7.69-7.75 (m, 4H), 7.94-7.95 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.66 (d, $J = 5.8$ Hz), 139.27 (d, $J = 3.5$ Hz), 136.88, 134.09, 132.68 (d, $J = 10.8$ Hz), 130.37 (d, $J = 104.8$ Hz), 129.36, 129.26 (d, $J = 12.9$ Hz), 128.84, 43.23 (d, $J = 59.9$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 25.94. HRMS (ESI) calcd for C$_{20}$H$_{16}$Cl$_2$NaO$_3$P $[\text{M+Na}^+]$: 411.0084, found: 411.0087.

2-(di-p-tolylphosphoryl)-1-phenylethanone (3w)

White solid; Yield = 79%, 69 mg; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.35 (s, 6H), 4.08 (d, $J = 15.3$ Hz, 2H), 7.22-7.26 (m, 4H), 7.39 (m, 2H), 7.51 (m, 1H), 7.63-7.69 (m, 4H), 7.97-8.00 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 193.16 (d, $J = 5.7$ Hz), 142.71 (d, $J = 2.7$ Hz), 137.21, 133.59, 131.24 (d, $J = 10.2$ Hz), 129.47 (d, $J = 12.5$ Hz), 129.39, 128.98 (d, $J = 105.7$ Hz), 128.60, 43.71 (d, $J = 57.7$ Hz) 21.70. $^{31}$P NMR (162 MHz, CDCl$_3$): δ 27.26. HRMS (ESI) calcd for C$_{22}$H$_{21}$NaO$_3$P $[\text{M+Na}^+]$: 371.2124, found: 371.2119.