Supplementary Information

Copper-catalyzed aerobic oxidative coupling of ketones with P(O)-H compounds leading to β-ketophosphine oxides

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1. General information

All solvents were distilled before used by standard methods. $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR were recorded in CDCl$_3$ on bruker advance III 400 M NMR with TMS as internal standard at room temperature and chemical shifts were quoted in parts per million (ppm) downfield from tetramethylsilane. HRMS and LC-MS analyses were obtained on Bruker microTOF Q II mass spectrometer and Waters UPLC-Xevo TQ MS (PDA Detector) / Quattro Premier XE triquadrupole mass spectrometer by ESI method respectively. Flash column chromatography was carried out on silica gel (100-200 mesh). IR spectra were obtained with a PerkinElmer Spectrum One FTIR Spectrometer. Melting points were obtained with a X - 6 melting point apparatus. Commercial reagents from TCI (Shanghai) Development Co., Ltd., Alfa Aesar and Sigma Aldrich were without further purification.

2. Screening with different parameters

Table S1 Optimization of reaction conditions$^a$

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*a Reaction conditions: 1a (0.5 mmol), 2a (1 mmol), base (0.5 mmol), catalyst (5 mol%), solvent (5 mL), O₂ (balloon), 1h. TEA: Et₃N; DIPEA: Ethyldiisopropylamine; DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene; DCE: 1,2-dichloroethane; MTBE: methyl tert-butyl ether.

*b Yields of isolated products based on 1a.  
*c CuI (2 mol%).  
*d Air balloon, 8h.  
*e Under N₂.

3. Typical experimental procedure

**General method for oxidative coupling of ketones with P(O)-H compounds**

\[
\begin{align*}
\text{R}^1\text{R}^2\text{O} & + \text{H}^3\text{P}^3\text{Ph}^3 \to \text{Cul (5 mol%)} / \text{Et₃N (2.2equiv)} / \text{TBSOTf, O₂, MeCN, rt, 2h} \to \text{R}^1\text{R}^2\text{O}^P\text{R}^3^3
\end{align*}
\]

Ketone 1 (0.5 mmol), Et₃N (1.1 mmol), TBSOTf (0.6 mmol), P(O)-H compound 2 (1.0 mmol) and CuI (5 mg, 5 mol%) were added to MeCN (5 mL) in a dried flask, the reaction mixture was allowed to stir under dioxygen balloon at room temperature for 2h. After completion of the reaction, the reaction mixture was concentrated in vacuum. The residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate, or dichloromethane / methanol) to afford the corresponding product 3.

4. Preliminary mechanistic studies

(1) Radical trapping experiment

Acetophenone 1a (0.5 mmol), Et₃N (1.1 mmol), TBSOTf (0.6 mmol), diphenylphosphine oxide 2a (1.0 mmol), TEMPO (1 mmol) and CuI (5 mg, 5 mol%) were added to a dried flask with MeCN (5 mL), then the reaction mixture was stirred under dioxygen at room temperature for 3h. Ph₂P(O)-TEMPO was detected by LC-MS and none of the desired product 3aa was detected in the reaction mixture.
(2) $^{18}$O$_2$-labeling experiment using $^{18}$O$_2$

![Chemical structure](image)

Acetophenone (1a) (0.5 mmol), Et$_3$N (1.1 mmol), TBSOTf (0.6 mmol), diphenylphosphine oxide (1.0 mmol) and CuI (5mg, 5 mol%) were added to a dried flask with MeCN (5 mL), the reaction mixture was allowed to stir under $^{18}$O-labeled dioxygen (balloon) at room temperature for 2h. After completion of the reaction, the reaction mixture was concentrated in vaccum. The residue was purified by flash
chromatography on silica gel (petroleum ether / ethyl acetate = 1:1) to afford the β-ketophosphine oxide product $^{18}$O-3aa in 83% yield. Moreover, the side-product TBSOH was detected by HRMS.

**Figure S2.** Copy of HRMS spectra of product $^{18}$O-3aa
(3) Isotope-labeling experiment using $^{18}$O-labeled acetophenone

$^{18}$O-labeled acetophenone (prepared according the reference$^1$) ($^{18}$O-1a) (0.5 mmol), Et$_3$N (1.1 mmol), TBSOTf (0.6 mmol), diphenylphosphine oxide 2a (1.0 mmol) and CuI (5mg, 5 mol%) were added to a dried flask with MeCN (5 mL), the reaction mixture was allowed to stir under dioxygen (balloon) at room temperature for 2h. After completion of the reaction, the reaction mixture was concentrated in vacum. The residue was purified by flash chromatography on silica gel (petroleum ether / ethyl acetate =1:1) to afford the β-ketophosphine oxide product $^{16}$O-3aa in 88% yield.
(4) LC-MS analysis of the reaction mixture of model reaction

The model reaction was conducted at room temperature for 6 minutes. Then, the reaction mixture (1 mL) was taken to centrifuged tube and was analyzed by LC-MS using the following method: HPLC: UPLC: ACQUITY BEH C18 column, 2.1×100 mm, 1.7 μm; PDA detector: 254 nm; 25 °C. flow rate: 0.3 mL/min; The mobile phase consisted of A (water(0.1% formic acid)) and B (acetonitrile), gradient elution: B(acetonitrile): 5%-95%; run time: 10 min. MS: Capillary +2.5 kV; Cone 30 V; Source temperature 150 °C; Desolvation temperature 500 °C; Cone gas flow OFF; Desolvation gas flow 500 L/h. Scan 100-700 m/z.

Copies of LC-MS spectra
Figure S5. The analysis of LC-MS spectra for the reaction

Figure S6. The MS spectrum corresponding to the peak in LC spectrum at the retention time of 1.69 min.

Figure S7. The MS spectrum corresponding to the peak in LC spectrum at the retention time of 4.41 min.
5. Characterization data of products

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

\[ 
\text{H} \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 8.03 – 7.96 (m, 2H), 7.85 – 7.77 (m, 4H), 7.56 – 7.49 (m, 3H), 7.49 – 7.36 (m, 6H), 4.15 (d, \( J = 15.3 \) Hz, 2H). \[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 192.84 (d, \( J = 5.6 \) Hz), 136.96, 133.63, 132.19 (d, \( J = 2.8 \) Hz), 131.97 (d, \( J = 103.3 \) Hz), 131.12 (d, \( J = 9.8 \) Hz), 129.26, 128.66 (d, \( J = 12.3 \) Hz), 128.56, 43.27 (d, \( J = 58.0 \) Hz). \[ ^{31}\text{P} \text{NMR (162 MHz, CDCl}_3 \] \( \delta \) 26.92. HRMS (ESI) calcd for C\(_{20}\)H\(_{17}\)NaO\(_2\)P [M+Na]^+: 343.0858; found: 343.0860.

2-(diphenylphosphoryl)-1-(o-toly)ethanone (3ba)

\[ 
\text{H} \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.88 (dd, \( J = 7.7, 0.8 \) Hz, 1H), 7.85 – 7.76 (m, 4H), 7.57 – 7.50 (m, 2H), 7.50 – 7.42 (m, 4H), 7.35 (td, \( J = 7.5, 1.2 \) Hz, 1H), 7.25 (t, \( J = 7.4 \) Hz, 1H), 7.16 (d, \( J = 7.5 \) Hz, 1H), 4.15 (d, \( J = 15.1 \) Hz, 2H), 2.32 (s, 3H). \[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 192.99 (d, \( J = 5.6 \) Hz), 138.28, 137.00, 134.41, 132.14 (d, \( J = 2.8 \) Hz), 132.05 (d, \( J = 103.3 \) Hz), 131.14 (d, \( J = 9.8 \) Hz), 129.55, 128.61 (d, \( J = 12.3 \) Hz), 128.44, 126.59, 43.21 (d, \( J = 58.4 \) Hz), 21.32. \[ ^{31}\text{P} \text{NMR (162 MHz, CDCl}_3 \] \( \delta \) 26.98. HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)NaO\(_2\)P [M+Na]^+: 357.1015; found: 357.1019.

2-(diphenylphosphoryl)-1-(m-toly)ethanone (3ca)

\[ 
\text{H} \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.87 – 7.76 (m, 5H), 7.73 (s, 1H), 7.55 – 7.41 (m, 6H), 7.37 – 7.24 (m, 2H), 4.14 (d, \( J = 15.4 \) Hz, 2H), 2.34 (s, 3H). \[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 192.99 (d, \( J = 5.6 \) Hz), 138.28, 137.00, 134.41, 132.14 (d, \( J = 2.8 \) Hz), 132.05 (d, \( J = 103.3 \) Hz), 131.14 (d, \( J = 9.8 \) Hz), 129.55, 128.61 (d, \( J = 12.3 \) Hz), 128.44, 126.59, 43.21 (d, \( J = 58.4 \) Hz), 21.32. \[ ^{31}\text{P} \text{NMR (162 MHz, CDCl}_3 \] \( \delta \) 26.98. HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)NaO\(_2\)P [M+Na]^+: 357.1015; found: 357.1008.

2-(diphenylphosphoryl)-1-(p-toly)ethanone (3da)

\[ 
\text{H} \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.89 (d, \( J = 8.2 \) Hz, 2H), 7.85 – 7.75 (m, 4H), 7.56 – 7.38 (m, 6H), 7.20 (d, \( J = 8.1 \) Hz, 2H), 4.12 (d, \( J = 15.3 \) Hz, 2H), 2.36 (s, 3H). \[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 192.34 (d, \( J = 5.6 \) Hz), 144.62, 134.55, 132.13 (d, \( J = 2.8 \) Hz), 132.06 (d, \( J = 103.2 \) Hz), 131.12 (d, \( J = 9.8 \) Hz), 129.43, 129.25, 128.62 (d, \( J = 12.3 \) Hz), 43.15 (d, \( J = 58.3 \) Hz), 21.72. \[ ^{31}\text{P} \text{NMR (162 MHz, CDCl}_3 \] \( \delta \) 27.01. HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)NaO\(_2\)P [M+Na]^+: 357.1015; found: 357.1011.

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

\[ 
\text{H} \text{NMR (400 MHz, CDCl}_3 \] \( \delta \) 7.85 – 7.75 (m, 4H), 7.58 (d, \( J = 7.8 \) Hz, 1H), 7.53 – 7.39 (m, 7H), 7.30 (t, \( J = 8.0 \) Hz, 1H), 7.06 (dd, \( J = 8.0, 2.3 \) Hz, 1H), 4.13 (d, \( J = 15.2 \) Hz, 2H), 3.77 (s, 3H). \[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \] \( \delta \) 192.67 (d, \( J = 5.7 \) Hz), 159.66, 138.29, 132.19 (d, \( J = 2.8 \) Hz), 131.95 (d, \( J = 103.3 \) Hz), 131.11 (d, \( J = 9.8 \) Hz), 129.58, 128.66 (d, \( J = 12.3 \) Hz), 122.22, 120.54, 112.75, 55.42, 43.30 (d, \( J = 58.4 \) Hz). \[ ^{31}\text{P} \text{NMR (162 MHz, CDCl}_3 \] \( \delta \) 27.02. HRMS (ESI) calcd for C\(_{21}\)H\(_{19}\)O\(_3\)P [M+H]^+: 351.1145; found: 351.1151.

Reference

2-(diphenylphosphoryl)-1-(4-methoxyphenyl)ethanone (3fa)

\[ \text{C}_2\text{H}_{10}\text{NaO}_2\text{P} [\text{M}+\text{Na}]^+ : 373.0964; \text{found} : 373.0969. \]

2-(diphenylphosphoryl)-1-(2-fluorophenyl)ethanone (3ga)

White solid; mp: 89.5-91.4 °C; \(^1\text{H} \text{NMR} \ (400 \text{ MHz, CDCl}_3) \delta 7.85 - 7.74 \ (m, 4H), 7.71 \ (m, 1H), 7.55 - 7.41 \ (m, 7H), 7.19 - 7.07 \ (m, 1H), 7.02 \ (dd, J = 11.1, 8.4 \ Hz, 1H), 4.25 \ (d, J = 14.7 \ Hz, 2H). \(^{13}\text{C} \text{NMR} \ (101 \text{ MHz, CDCl}_3) \delta 190.84 \ (dd, J = 6.0, 2.8 \ Hz), 161.61 \ (d, J = 254.8 \ Hz), 135.18 \ (d, J = 9.3 \ Hz), 132.13, 132.13 \ (d, J = 2.8 \ Hz), 131.08 \ (d, J = 9.8 \ Hz), 130.95 \ (d, J = 1.7 \ Hz), 128.62 \ (d, J = 12.3 \ Hz), 126.09 \ (d, J = 11.5 \ Hz), 124.50 \ (d, J = 3.4 \ Hz), 116.61 \ (d, J = 23.7 \ Hz), 46.69 \ (dd, J = 59.3, 7.1 \ Hz). \(^{31}\text{P} \text{NMR} \ (162 \text{ MHz, CDCl}_3) \delta 26.75. \ 19\text{F} \text{NMR} \ (376 \text{ MHz, CDCl}_3) \delta -109.27 \ (d, J = 1.2 \ Hz). \text{IR} \ (\text{cm}^{-1}), \text{KBr}: 1676 \ (\text{C}=\text{O}), 1183 \ (\text{P}=\text{O}). \text{HRMS (ESI) calcd for } C_{20}H_{16}NaFOP [\text{M}+\text{Na}]^+ : 339.0945; \text{found} : 339.0943. \]

2-(diphenylphosphoryl)-1-(3-fluorophenyl)ethanone (3ha)

\[ \text{C}_2\text{H}_{16}\text{NaFO}_2\text{P} [\text{M}+\text{Na}]^+ : 361.0764; \text{found} : 361.0750. \]

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

\[ \text{C}_2\text{H}_{16}\text{NaFOP} [\text{M}+\text{Na}]^+ : 361.0764; \text{found} : 361.0762. \]

1-(2-chlorophenyl)-2-(diphenylphosphoryl)ethanone (3ja)

\[ \text{C}_2\text{H}_{16}\text{ClNaFOP} [\text{M}+\text{Na}]^+ : 377.0469; \text{found} : 377.0459. \]

1-(3-chlorophenyl)-2-(diphenylphosphoryl)ethanone (3ka)

\[ \text{C}_2\text{H}_{16}\text{ClNaFOP} [\text{M}+\text{Na}]^+ : 377.0469; \text{found} : 377.0459. \]
138.44, 134.82, 133.48, 132.32 (d, J = 2.8 Hz), 131.70 (d, J = 103.5 Hz), 131.07 (d, J = 9.8 Hz), 129.91, 128.96, 128.72 (d, J = 12.3 Hz), 127.67, 43.49 (d, J = 57.0 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.63. HRMS (ESI) calcd for C$_{20}$H$_{16}$ClNaO$_2$P [M+Na]$^+$: 377.0469; found: 377.0474.

1-(4-chlorophenyl)-2-(diphenylphosphoryl)ethanone (3la)

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.6 Hz, 2H), 7.87 – 7.73 (m, 4H), 7.60 – 7.43 (m, 6H), 7.39 (d, J = 8.6 Hz, 2H), 4.12 (d, J = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 191.68 (d, J = 5.7 Hz), 140.24, 135.28, 132.32 (d, J = 2.8 Hz), 131.73 (d, J = 103.5 Hz), 131.07 (d, J = 9.8 Hz), 130.80, 128.86, 128.73 (d, J = 12.3 Hz), 43.57 (d, J = 56.7 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.71. HRMS (ESI) calcd for C$_{20}$H$_{16}$O$_2$P [M+Na]$^+$: 377.0453.

1-(2,4-dichlorophenyl)-2-(diphenylphosphoryl)ethanone (3ma)

![Chemical Structure](image)

White solid; mp: 87.8-88.2 °C; $^1$H NMR (400 MHz, CDCl₃) δ 7.83 – 7.70 (m, 4H), 7.51 (m, 7H), 7.31 (d, J = 1.8 Hz, 1H), 7.22 (d, J = 8.1 Hz, 1H), 4.21 (d, J = 14.6 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 193.76 (d, J = 6.0 Hz), 137.92, 137.12, 132.31 (d, J = 2.6 Hz), 132.06, 131.66 (d, J = 103.8 Hz), 131.27, 130.99 (d, J = 9.8 Hz), 130.19, 128.75 (d, J = 12.3 Hz), 127.43, 46.74 (d, J = 56.8 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.95. IR (cm$^{-1}$, KBr): 1670 (C=O), 1186 (P=O). HRMS (ESI) calcd for C$_{20}$H$_{16}$ClNaO$_2$P [M+Na]$^+$: 411.0079; found: 411.0081.

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

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl₃) δ 7.88 (d, J = 8.5 Hz, 2H), 7.80 (dd, J = 12.1, 7.4 Hz, 4H), 7.54 (m, 4H), 7.47 (m, 4H), 4.11 (d, J = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 191.89 (d, J = 5.6 Hz), 135.67, 132.32 (d, J = 2.9 Hz), 131.86, 131.71 (d, J = 103.5 Hz), 131.06 (d, J = 9.8 Hz), 130.88, 129.13, 128.74 (d, J = 12.3 Hz), 43.55 (d, J = 56.7 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.68. HRMS (ESI) calcd for C$_{20}$H$_{16}$BrNaO$_2$P [M+Na]$^+$: 420.9963; found: 420.9973.

2-(diphenylphosphoryl)-1-(3-(trifluoromethyl)phenyl)ethanone (3oa)

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 7.9 Hz, 1H), 8.18 (s, 1H), 7.87 – 7.75 (m, 5H), 7.62 – 7.45 (m, 7H), 4.18 (d, J = 15.2 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 191.74 (d, J = 5.7 Hz), 137.40, 132.80, 132.38 (d, J = 2.8 Hz), 131.61 (d, J = 102.1 Hz), 131.07 (q, J = 33.0 Hz), 131.06 (d, J = 9.8 Hz), 129.89 (q, J = 3.5 Hz), 129.29, 128.75 (d, J = 12.4 Hz), 125.77 (q, J = 3.8 Hz), 123.57 (q, J = 272.7 Hz), 43.63 (d, J = 56.3 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.65. $^{19}$F NMR (376 MHz, CDCl₃) δ -62.79. HRMS (ESI) calcd for C$_{21}$H$_{16}$F$_3$NaO$_2$P [M+H]$^+$: 389.0913; found: 389.0921.

4-(2-(diphenylphosphoryl)acetyl)benzonitrile (3pa)

![Chemical Structure](image)

$^1$H NMR (400 MHz, CDCl₃) δ 8.15 (d, J = 8.1 Hz, 2H), 7.80 (m, 4H), 7.74 (d, J = 8.1 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.54 – 7.43 (m, 4H), 4.16 (d, J = 15.1 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl₃) δ 191.81 (d, J = 5.2 Hz), 139.77, 132.51 (d, J = 2.4 Hz), 132.37, 131.40 (d, J = 104.1 Hz), 131.02 (d, J = 9.9 Hz), 129.78, 128.83 (d, J = 12.4 Hz), 117.94, 116.70, 44.06 (d, J = 55.2 Hz). $^{31}$P NMR (162 MHz, CDCl₃) δ 26.62. HRMS (ESI) calcd for C$_{21}$H$_{16}$NNaO$_2$P [M+Na]$^+$: 368.0811; found: 368.0813.

2-(diphenylphosphoryl)-1-(4-nitrophenyl)ethanone (3qa)

S10
methyl 4-(2-(diphenylphosphoryl)acetyl)benzoate (3ra)

\[
\begin{align*}
\text{O}_2\text{N} & \quad \text{O} \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.24 (m, 4H), 7.86 – 7.77 (m, 4H), 7.62 – 7.55 (m, 2H), 7.54 – 7.45 (m, 4H), 4.20 (d, \( J = 15.0 \text{ Hz} \), 2H). \( ^{13}\text{C NMR (101 MHz, CDCl}_3 \) \( \delta \) 191.69 (d, \( J = 5.5 \text{ Hz} \), 150.43 , 141.19, 132.54 (d, \( J = 2.4 \text{ Hz} \), 131.30 (d, \( J = 103.9 \text{ Hz} \), 131.02 (d, \( J = 9.8 \text{ Hz} \), 130.43, 128.85 (d, \( J = 12.4 \text{ Hz} \), 123.68 , 44.21 (d, \( J = 55.7 \text{ Hz} \). \( ^{31}\text{P NMR (162 MHz, CDCl}_3 \) \( \delta \) 26.75. HRMS (ESI) calcd for \( \text{C}_{20}\text{H}_{13}\text{NaO}_3\text{P} [\text{M}+\text{H}]^+ \): 366.0980; found: 366.0905.

2-(diphenylphosphoryl)-1-(naphthalen-2-yl)ethanone (3sa)

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\begin{align*}
\text{O} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 8.58 (s, 1H), 8.02 – 7.93 (m, 2H), 7.91 – 7.80 (m, 6H), 7.63 – 7.42 (m, 8H), 4.29 (d, \( J = 15.3 \text{ Hz} \), 2H). \( ^{13}\text{C NMR (101 MHz, CDCl}_3 \) \( \delta \) 192.69 (d, \( J = 5.6 \text{ Hz} \), 135.72, 134.29, 132.33, 132.22 (d, \( J = 2.8 \text{ Hz} \), 131.99, 131.93 (d, \( J = 103.4 \text{ Hz} \), 131.16 (d, \( J = 9.8 \text{ Hz} \), 129.99, 128.90, 128.68 (d, \( J = 12.3 \text{ Hz} \), 128.38, 127.68, 126.79, 124.12, 43.33 (d, \( J = 58.1 \text{ Hz} \). \( ^{31}\text{P NMR (162 MHz, CDCl}_3 \) \( \delta \) 27.31. HRMS (ESI) calcd for \( \text{C}_{26}\text{H}_{19}\text{NaO}_3\text{P} [\text{M}+\text{Na}]^+ \): 393.1015; found: 393.1005.

2-(diphenylphosphoryl)-1-(pyridin-3-yl)ethanone (3ta)

White solid; mp: 125.3-128.3 °C; \( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 9.11 (s, 1H), 8.70 (d, \( J = 3.8 \text{ Hz} \), 1H), 8.30 (m, 1H), 7.83 – 7.73 (m, 4H), 7.55 – 7.39 (m, 6H), 7.34 (m, 1H), 4.14 (d, \( J = 15.1 \text{ Hz} \), 2H). \( ^{13}\text{C NMR (101 MHz, CDCl}_3 \) \( \delta \) 191.98 (d, \( J = 5.8 \text{ Hz} \), 153.70, 150.39, 136.69, 132.39 (d, \( J = 2.9 \text{ Hz} \), 132.21, 131.56 (d, \( J = 102.5 \text{ Hz} \), 131.00 (d, \( J = 9.9 \text{ Hz} \), 128.76 (d, \( J = 12.4 \text{ Hz} \), 123.41, 43.65 (d, \( J = 56.4 \text{ Hz} \). \( ^{31}\text{P NMR (162 MHz, CDCl}_3 \) \( \delta \) 26.62. IR (cm\(^{-1}\), KBr):1682 (C=O), 1181 (P=O). HRMS (ESI) calcd for \( \text{C}_{30}\text{H}_{17}\text{NO}_3\text{P} [\text{M}+\text{H}]^+ \): 322.0991; found: 322.0998.

2-(diphenylphosphoryl)-1-(furan-2-yl)ethanone (3ua)

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\begin{align*}
\text{O} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.86 – 7.75 (m, 4H), 7.56 – 7.41 (m, 7H), 7.28 (d, \( J = 3.6 \text{ Hz} \), 1H), 6.47 (dd, \( J = 3.6, 1.7 \text{ Hz} \), 1H), 4.01 (d, \( J = 15.5 \text{ Hz} \), 2H). \( ^{13}\text{C NMR (101 MHz, CDCl}_3 \) \( \delta \) 180.50 (d, \( J = 5.4 \text{ Hz} \), 152.49, 147.29, 132.16 (d, \( J = 2.8 \text{ Hz} \), 131.84 (d, \( J = 103.4 \text{ Hz} \), 131.07 (d, \( J = 9.9 \text{ Hz} \), 128.59 (d, \( J = 12.3 \text{ Hz} \), 119.64, 112.77, 43.04 (d, \( J = 57.7 \text{ Hz} \). \( ^{31}\text{P NMR (162 MHz, CDCl}_3 \) \( \delta \) 26.92. HRMS (ESI) calcd for \( \text{C}_{19}\text{H}_{13}\text{NaO}_3\text{P} [\text{M}+\text{Na}]^+ \): 333.0651; found: 333.0642.

2-(diphenylphosphoryl)-1-(thiophen-2-yl)ethanone (3va)

\[
\begin{align*}
\text{S} & \quad \text{O} \\
\text{Ph} & \quad \text{Ph} \\
\end{align*}
\]

\( ^1\text{H NMR (400 MHz, CDCl}_3 \) \( \delta \) 7.90 (dd, \( J = 3.8, 0.9 \text{ Hz} \), 1H), 7.87 – 7.76 (m, 4H), 7.64 (dd, \( J = 4.9, 0.9 \text{ Hz} \), 1H), 7.59 – 7.52 (m, 2H), 7.52 – 7.43 (m, 4H), 7.10 (dd, \( J = 4.8, 4.0 \text{ Hz} \), 1H), 4.07 (d, \( J = 15.3 \text{ Hz} \), 2H). \( ^{13}\text{C NMR (101 MHz, CDCl}_3 \) \( \delta \) 184.99 (d, \( J = 5.3 \text{ Hz} \), 144.44, 135.29, 135.09, 132.26 (d, \( J = 2.8 \text{ Hz} \), 131.73 (d, \( J = 103.7 \text{ Hz} \), 131.15 (d, \( J = 9.9 \text{ Hz} \), 128.67 (d, \( J = 12.4 \text{ Hz} \), 128.51, 44.28 (d, \( J = 57.3 \text{ Hz} \). \( ^{31}\text{P NMR (162 MHz, CDCl}_3 \) \( \delta \) 26.76. HRMS (ESI) calcd for \( \text{C}_{19}\text{H}_{13}\text{NaO}_3\text{PS} [\text{M}+\text{Na}]^+ \): 349.0423; found: 349.0409.

S11
2-(diphenylphosphoryl)-1-phenylpropan-1-one (3wa)

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 7.95 - 7.87 (m, 2H), 7.87 - 7.82 (m, 2H), 7.80 - 7.73 (m, 2H), 7.53 - 7.31 (m, 9H), 4.62 (dq, \ J = 14.3, 7.1 Hz, 1H), 1.58 (dd, \ J = 16.1, 7.1 Hz, 3H). \\
\mathrm{C} & \text{ NMR (101 MHz, CDCl}_3\mathrm{)} = 198.12 (d, \ J = 2.9 Hz), 137.03 (d, \ J = 1.3 Hz), 133.18, 132.08 (d, \ J = 2.9 Hz), 132.02 (d, \ J = 2.8 Hz), 131.81 (d, \ J = 9.3 Hz), 131.50 (d, \ J = 9.1 Hz), 131.04 (d, \ J = 101.8 Hz), 130.60 (d, \ J = 99.9 Hz), 128.62 (d, \ J = 11.2 Hz), 128.45, 128.44, 45.68 (d, \ J = 59.7 Hz), 12.98 (d, \ J = 3.4 Hz). \\
\mathrm{P} & \text{ NMR (162 MHz, CDCl}_3\mathrm{)} = 31.15. \text{ HRMS (ESI) calcd for } C_{32}H_{29}NaO_3P [M+Na]^+: 357.1015; \text{ found: } 357.1016.
\end{align*}
\]

1-(diphenylphosphoryl)propan-2-one (3xa)

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 7.81 - 7.69 (m, 4H), 7.57 - 7.51 (m, 2H), 7.51 - 7.44 (m, 4H), 3.60 (d, \ J = 14.8 Hz, 2H), 2.31 (s, 3H). \\
\mathrm{C} & \text{ NMR (101 MHz, CDCl}_3\mathrm{)} = 200.98 (d, \ J = 5.2 Hz), 132.32 (d, \ J = 2.8 Hz), 131.82 (d, \ J = 103.4 Hz), 130.85 (d, \ J = 9.9 Hz), 128.81 (d, \ J = 12.3 Hz), 47.94 (d, \ J = 56.4 Hz), 32.71. \\
\mathrm{P} & \text{ NMR (162 MHz, CDCl}_3\mathrm{)} = 26.33. \text{ HRMS (ESI) calcd for } C_{18}H_{15}NaO_3P [M+H]^+: 259.0882; \text{ found: } 259.0881.
\end{align*}
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2-(di-p-tolylphosphoryl)-1-phenylethanone (3ab)

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 8.05 - 7.96 (m, 2H), 7.68 (dd, \ J = 11.9, 8.1 Hz, 4H), 7.52 (t, \ J = 7.4 Hz, 1H), 7.40 (t, \ J = 7.7 Hz, 2H), 7.25 (dd, \ J = 8.0, 2.5 Hz, 4H), 4.11 (d, \ J = 15.3 Hz, 2H), 2.37 (s, 6H). \\
\mathrm{C} & \text{ NMR (101 MHz, CDCl}_3\mathrm{)} = 193.04 (d, \ J = 5.6 Hz), 142.60 (d, \ J = 2.9 Hz), 137.04, 133.50, 131.10 (d, \ J = 10.2 Hz), 129.35 (d, \ J = 12.6 Hz), 129.30, 128.87 (d, \ J = 107.7 Hz), 128.49, 43.56 (d, \ J = 57.7 Hz), 21.63. \\
\mathrm{P} & \text{ NMR (162 MHz, CDCl}_3\mathrm{)} = 27.28. \text{ HRMS (ESI) calcd for } C_{22}H_{21}NaO_3P [M+Na]^+: 371.1171; \text{ found: } 371.1159.
\end{align*}
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2-(bis(4-methoxyphenyl)phosphoryl)-1-phenylethanone (3ac)

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 8.02 - 7.94 (m, 2H), 7.76 - 7.65 (m, 4H), 7.52 (t, \ J = 7.4 Hz, 1H), 7.40 (t, \ J = 7.7 Hz, 2H), 6.94 (dd, \ J = 8.9, 2.3 Hz, 4H), 4.09 (d, \ J = 15.5 Hz, 2H), 3.81 (s, 6H). \\
\mathrm{C} & \text{ NMR (101 MHz, CDCl}_3\mathrm{)} = 193.24 (d, \ J = 5.5 Hz), 162.51 (d, \ J = 2.9 Hz), 137.03, 133.50, 133.00 (d, \ J = 11.2 Hz), 129.26, 128.50, 123.33 (d, \ J = 110.3 Hz), 114.13 (d, \ J = 13.4 Hz), 55.34, 43.83 (d, \ J = 58.1 Hz), 31.38. \\
\mathrm{P} & \text{ NMR (162 MHz, CDCl}_3\mathrm{)} = 27.07. \text{ HRMS (ESI) calcd for } C_{22}H_{21}NaO_3P [M+Na]^+: 403.1070; \text{ found: } 403.1070.
\end{align*}
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2-(bis(4-fluorophenyl)phosphoryl)-1-phenylethanone (3ad)

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 8.01 - 7.92 (m, 2H), 7.87 - 7.74 (m, 4H), 7.54 (t, \ J = 7.4 Hz, 1H), 7.41 (t, \ J = 7.7 Hz, 2H), 7.21 - 7.09 (m, 4H), 4.14 (d, \ J = 15.6 Hz, 2H). \\
\mathrm{C} & \text{ NMR (101 MHz, CDCl}_3\mathrm{)} = 192.71 (d, \ J = 5.6 Hz), 165.18 (dd, \ J = 254.3, 3.4 Hz), 136.75, 133.87, 133.71 (dd, \ J = 11.4, 8.9 Hz), 129.19, 128.65, 127.71 (dd, \ J = 106.9, 3.4 Hz), 116.15 (dd, \ J = 21.5, 13.6 Hz), 43.30 (d, \ J = 59.7 Hz). \\
\mathrm{F} & \text{ NMR (376 MHz, CDCl}_3\mathrm{)} = -105.77 (d, \ J = 1.5 Hz). \text{ HRMS (ESI) calcd for } C_{20}H_{12}F_2NaO_2P [M+Na]^+: 379.0670; \text{ found: } 379.0679.
\end{align*}
\]

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

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\begin{align*}
\mathrm{H} & \text{ NMR (400 MHz, CDCl}_3\mathrm{)} = 7.97 (d, \ J = 7.5 Hz, 2H), 7.79 (dd, \ J = 12.4, 7.1 Hz, 2H), 7.55 (dd, \ J = 11.7, 4.3 Hz, 2H), 7.46 (m, 4H), 4.20 -
\end{align*}
\]

3.89 (m, 2H), 3.87 – 3.73 (m, 2H), 1.26 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.20 (d, $J = 5.5$ Hz), 136.79, 133.53, 132.73 (d, $J = 2.9$ Hz), 131.85 (d, $J = 10.3$ Hz), 130.08 (d, $J = 132.9$ Hz), 129.09, 128.63 (d, $J = 13.3$ Hz), 128.52, 61.47 (d, $J = 6.2$ Hz), 43.02 (d, $J = 86.4$ Hz), 16.32 (d, $J = 6.7$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 34.39. HRMS (ESI) calcd for C$_{16}$H$_{17}$NaO$_3$P $[M+Na]^+$: 311.0808; found: 311.0822.

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

1H NMR (400 MHz, CDCl$_3$) δ 8.10 – 7.96 (m, 2H), 7.61 (t, $J = 7.4$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 4.15 (p, $J = 7.2$ Hz, 4H), 3.65 (d, $J = 22.7$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 192.00 (d, $J = 6.6$ Hz), 136.53 (d, $J = 1.8$ Hz), 133.70, 129.07, 128.63, 62.67 (d, $J = 6.5$ Hz), 38.49 (d, $J = 129.9$ Hz), 16.26 (d, $J = 6.4$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.91. HRMS (ESI) calcd for C$_{12}$H$_{17}$NaO$_4$P $[M+Na]^+$: 279.0757; found: 279.0770.

dibutyl (2-oxo-2-phenylethyl)phosphonate (3ag)

1H NMR (400 MHz, CDCl$_3$) δ 8.07 – 7.97 (m, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.7$ Hz, 2H), 4.13 – 4.01 (m, 4H), 3.64 (d, $J = 22.8$ Hz, 2H), 1.64 – 1.54 (m, 4H), 1.33 (dq, $J = 14.7$, 7.4 Hz, 4H), 0.89 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.93 (d, $J = 6.5$ Hz), 136.53 (d, $J = 1.8$ Hz), 133.62, 66.32 (d, $J = 6.8$ Hz), 38.33 (d, $J = 129.5$ Hz), 32.36 (d, $J = 6.4$ Hz), 18.62, 13.56. $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.86. HRMS (ESI) calcd for C$_{16}$H$_{25}$NaO$_4$P $[M+Na]^+$: 335.1383; found: 335.1391.

tert-butyldimethyl((1-phenylvinyl)oxy)silane(1a')

1H NMR (400 MHz, CDCl$_3$) δ 7.66 (m, 2H), 7.41 – 7.30 (m, 3H), 4.94 (d, $J = 1.7$ Hz, 1H), 4.47 (d, $J = 1.7$ Hz, 1H), 1.06 (s, 9H), 0.26 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.95, 137.78, 128.17, 128.07, 125.28, 90.91, 25.89, 18.37, -4.59.
6. Copies of NMR spectra for products